

Redox flexibility in a germanium hydride manifold: hydrogen shuttling via oxidative addition and reductive elimination

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Supplementary Information

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(i) General considerations

All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of dry argon or dinitrogen. Solvents were degassed by sparging with argon and dried by passing through a column of the appropriate drying agent using a commercially available Braun SPS and stored over potassium. Diethyl ether and THF were dried over and distilled from sodium and benzophenone/potassium (respectively) and stored over a potassium mirror or sodium mirror, respectively. NMR spectra were measured in benzene- d_6 which was dried over CaH_2 , with the solvent then being distilled under reduced pressure, degassed by three freeze-pump-thaw cycles and stored under argon in Teflon valve ampoules. NMR samples were prepared under argon in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. NMR spectra were measured on a Bruker Avance III HD Nanobay 400 MHz NMR spectrometer equipped with a 9.4 T magnet, Bruker Avance III 500 MHz NMR spectrometer equipped with a 11.75 T magnet or a Bruker Avance III NMR 500 MHz NMR spectrometer equipped with a 11.75 T magnet and a ^{13}C detect cryoprobe. 1H and ^{13}C NMR spectra were referenced internally to residual protio-solvent (1H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Infra-red spectra were measured on a Nicolet 500 FT-IR spectrometer. Samples were measured as a Nujol mull and were prepared inside a glovebox before being sealed in an airtight cell. Elemental analyses were carried out at London Metropolitan University or by Elemental Microanalysis Ltd., Okehampton, Devon. $K[HBEt_3]$ and $K[OC(O)H]$ were used as received (Aldrich); CO_2 was dried over P_2O_5 prior to use.

(ii) Starting materials

The synthesis of $[2,6-(iPr_2NCH_2)_2C_6H_3]GeCl$ was carried out as per literature precedent.^{s1} The preparation of $K[(O(C_{10}H_7-1))]$ is outlined below. All other reagents were used as received.

Preparation of $K[(O(C_{10}H_7-1))]$ ($K[ONaph]$): To a slurry of KH (0.33 g, 8.23 mmol) in tetrahydrofuran (THF) (7 mL) at room temperature was added a solution of 1-naphthol (1.00 g, 6.94 mmol), also in THF. Hydrogen evolution was observed and the resulting slurry was stirred overnight at room temperature and subsequently filtered. Volatiles were removed *in vacuo* and the resulting solid was washed with a portion of pentane (10 mL) and dried thoroughly *in vacuo* to yield a white powder.

(iii) Novel compounds

Synthesis of $[(2,6\text{-}i\text{PrN}_2\text{CH}_2)_2\text{C}_6\text{H}_3]\text{Ge}(\text{H})_3$ ($(\text{Ar}^{\text{NiPr}_2}\text{Ge}(\text{H}))_3$, **2):** Method A (from **1**): To a Schlenk tube containing $\text{Ar}^{\text{NiPr}_2}\text{GeCl}$ (**1**; 1.50 g, 3.64 mmol) and $\text{K}[\text{HBEt}_3]$ (0.60 g, 4.34 mmol) was added toluene (7 mL). The resulting pale yellow solution was stirred at room temperature for 3 h, during which time a fine precipitate was evolved. Volatiles were subsequently removed *in vacuo*, yielding a bright yellow powder, which was extracted with *n*-hexane (50 mL) and filtered. The solution was then concentrated until the incipient point of crystallisation and stored overnight at 6°C, producing small colourless crystals. More crystals were then produced by storing the solution overnight at -30°C; the crystals were then isolated and dried *in vacuo*. Yield: 0.49 g (36%). Crystals of **2** which were suitable for X-ray crystallography were obtained by storage of a concentration solution of **2** in toluene at -30°C for 3 d. Method B (from **3**): To a solution of $\text{Ar}^{\text{NiPr}_2}\text{Ge}(\text{ONaph})$ (**3**; 0.03 g, 0.06 mmol) in benzene- d_6 (0.5 mL) was added pinacolborane (HBpin) (15 μL , 0.10 mmol). The resulting solution was shaken vigorously and the reaction monitored by ^1H and $^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopy until the consumption of **3** (and formation of **2**) reached >95% completion (*ca.* 6 h). The ^1H NMR spectrum of the product is consistent with that of **2** when prepared by Method A. The identity of the co-product (Naph)OBpin was confirmed by removal of volatiles *in vacuo*, followed by redissolving the resulting solid in CDCl_3 and analysis of the resulting solution by ^1H and $^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopy; the data are consistent with those reported by Bertrand *et al.*^{s2} Method C (from **4**): To a solution of $\text{Ar}^{\text{NiPr}_2}\text{Ge}\{\text{OC}(\text{O})\text{H}\}$ (**4**; 0.03 g, 0.07 mmol) in benzene- d_6 (0.5 mL) was added pinacolborane (HBpin) (50 μL , 0.34 mmol). The resulting solution immediately evolved a pale yellow colour and was analysed (within 5 min) by ^1H and $^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopy. The spectra showed complete conversion of **4** to **2**; the ^1H NMR spectrum of the product is consistent with that of **2** when prepared by Method A. The data obtained for the co-product $\text{HC}(\text{O})\text{OBpin}$ are consistent with those reported in the literature.^{s3} **Spectroscopic data:** ^1H NMR (400 MHz, benzene- d_6 , 298 K): δ_{H} 0.86 (6H, d, $^3J_{\text{HH}} = 6.7$ Hz, CH_3 of $i\text{Pr}$), 0.93 (6H, d, $^3J_{\text{HH}} = 6.7$ Hz, CH_3 of $i\text{Pr}$), 0.96 (12H, d, $^3J_{\text{HH}} = 6.6$ Hz, CH_3 of $i\text{Pr}$), 1.00 (12H, d, $^3J_{\text{HH}} = 6.6$ Hz, CH_3 of $i\text{Pr}$), 1.14 (6H, d, $^3J_{\text{HH}} = 6.7$ Hz, CH_3 of $i\text{Pr}$), 1.18 (6H, d, $^3J_{\text{HH}} = 6.7$ Hz, CH_3 of $i\text{Pr}$), 1.21 – 1.62 (12H, m (br.), CH_3 of $i\text{Pr}$), 2.99 (4H, d, $^3J_{\text{HH}} = 6.7$ Hz, CH of $i\text{Pr}$), 3.13 (4H, d, $^3J_{\text{HH}} = 6.7$ Hz, CH of $i\text{Pr}$), 3.32 (4H, d, $^3J_{\text{HH}} = 6.7$ Hz, CH of $i\text{Pr}$), 3.47 and 3.80 (4H, AB system, $^2J_{\text{HH}} = 16.3$ Hz, CH_2N), 3.37 and 3.91 (2H, AB system, $^2J_{\text{HH}} = 14.7$ Hz, CH_2N), 4.08 and 4.26 (2H, AB system, $^2J_{\text{HH}} = 14.5$ Hz, CH_2N), 4.40 – 4.67 (2H, m (br.) CH_2N), 4.70 (1H, d, $^3J_{\text{HH}} = 7.1$ Hz, GeH), 4.88 (1H, d, $^3J_{\text{HH}} = 9.7$ Hz, GeH), 4.99 (1H, dd, $^3J_{\text{HH}} = 9.7, 7.1$ Hz, GeH), 5.01 – 5.16 (2H, m (br.) CH_2N), 7.15 – 7.18 (2H, m, CH of Ar), 7.23 – 7.29 (1H, m, CH of Ar), 7.34 – 7.40 (2H, m, CH of Ar), 7.88 (2H, d, $^3J_{\text{HH}} = 7.7$ Hz, CH of Ar), 7.92 – 8.01 (2H, m (br.), CH of Ar). Broad resonances for CH_3 of $i\text{Pr}$ (12H) and CH of $i\text{Pr}$ (4H) are obscured. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, benzene- d_6 , 298K): δ_{C} 20.2 (CH_3 of $i\text{Pr}$), 20.7 (CH_3 of $i\text{Pr}$), 20.9 (CH_3 of $i\text{Pr}$), 21.5 (CH_3 of $i\text{Pr}$), 22.0 (2 overlapping signals, (CH_3 of $i\text{Pr}$), 22.6 (CH_3 of $i\text{Pr}$), 48.3 (CH of $i\text{Pr}$), 48.4 (CH of $i\text{Pr}$), 50.4 (CH_2N), 51.9 (br., CH_2N), 52.7 (CH of $i\text{Pr}$), 53.6 (CH of $i\text{Pr}$), 56.9 (CH_2N), 57.0 (CH_2N), 123.3 (ArC), 123.7 (ArC), 125.9 (ArC), 127.1 (ArC), 128.5 (ArC), 134.7 (ArC), 137.7 (ArC), 145.5 (ArC), 145.7 (ArC), 148.0 (ArC), 148.4 (ArC), 161.4 (ArC). IR (nujol/ cm^{-1}): $\nu_{\text{Ge-H}}$ 1981, 2003, 2042 cm^{-1} **Elemental microanalysis:** calc. for $\text{C}_{60}\text{H}_{108}\text{N}_6\text{Ge}_3$ C 63.69%, H 9.62%, N 7.43%, meas. C 63.58%, H 9.65%, N 7.45%.

Synthesis of {2,6-(*i*-PrN₂CH₂)₂C₆H₃}Ge(O(C₁₀H₇-1)) (Ar^{NiPr₂}Ge(ONaph), **3):** To a Schlenk tube containing Ar^{NiPr₂}GeCl (0.50 g, 1.22 mmol) and K[O(C₁₀H₇-1)] (K[ONaph]) (0.29 g, 1.59 mmol) was added tetrahydrofuran (THF) (5 mL). The solution was stirred overnight at room temperature before volatiles were removed *in vacuo* and the resulting yellow powder treated with pentane (5 mL). Volatiles were again removed *in vacuo* and the product extracted into pentane (10 mL) and separated from the insoluble residue by filtration. The resulting solution was concentrated to the point of incipient crystallisation and stored at room temperature overnight, yielding colourless crystals of **3** which were suitable for X-ray crystallography. Yield: 0.44 g (70%). **Spectroscopic data:** ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_H 0.91 (12H, d, ³J_{HH} = 6.7 Hz, CH₃ of *i*Pr), 1.00 (12H, d, ³J_{HH} = 6.6 Hz, CH₃ of *i*Pr), 3.22 (4H, d, ³J_{HH} = 6.7 Hz, CH of *i*Pr), 3.77 and 4.04 (4H, AB system, ²J_{HH} = 15.0 Hz, CH₂N), 7.07 (2H, d, ³J_{HH} = 7.5 Hz, *m*-CH of Ar), 7.20 – 7.30 (3H, m, CH of Naph and *p*-CH of Ar), 7.36 (1H, d, ³J_{HH} = 8.2 Hz, CH of Naph), 7.51 (1H, t, ³J_{HH} = 7.9 Hz, CH of Naph), 7.73 (2H, apparent t, ³J_{HH} = 9.0 Hz, CH of Naph) and 8.52 (1H, d, ³J_{HH} = 8.2 Hz, CH of Naph). ¹³C{¹H} NMR (101 MHz, benzene-d₆, 298K): δ_C 20.1, 21.1 (CH₃ of *i*Pr), 51.4 (CH of *i*Pr), 53.7 (CH₂N), 109.6 (ArC of Naph), 117.5 (ArC of Naph), 123.5 (*m*-ArC of Ar^{NiPr₂}), 124.1 (2 overlapping resonances, ArC of Naph), 126.0 (ArC of Naph), 127.0 (ArC of Naph), 128.0 (ArC of Naph), 128.4 (*p*-ArC of Ar^{NiPr₂}), 129.6 (ArC of Naph), 136.2 (ArC of Naph), 148.8 (*o*-ArC of Ar^{NiPr₂}), 157.4 (*ipso*-ArC of Ar^{NiPr₂}) and 160.0 (ArC of Naph). **Elemental microanalysis:** calc. for C₃₀H₄₂N₂OGe C 69.39%, H 8.15%, N 5.39%, meas. C 69.18%, H 8.00%, N 5.55%.

Synthesis of {2,6-(*i*-PrN₂CH₂)₂C₆H₃}Ge{OC(O)H} (Ar^{NiPr₂}Ge{OC(O)H}, **4):** Method A: To a Schlenk tube containing **1** (0.50 g, 1.21 mmol) and K[OC(O)H] (0.13 g, 1.55 mmol) was added THF (5 mL). After stirring the slurry overnight at room temperature, volatiles were removed *in vacuo* and the resulting oily residue treated with pentane (10 mL). Filtration of the resulting slurry, followed by concentration and storage of the pale yellow solution at room temperature overnight, yielded colourless crystals of **4** which were suitable for X-ray crystallography. Yield: 0.42 g (82%). Method B: A solution of **2** (0.02 g, 0.018 mmol) in benzene-d₆ (0.5 mL) in an NMR tube fitted with a J. Young's valve was degassed by three freeze-pump-thaw cycles, back-filled with carbon dioxide (*ca.* 1 bar) and shaken vigorously. The reaction was monitored by ¹H NMR spectroscopy until it reached completion; the ¹H NMR spectrum of the product is consistent with that of **4** prepared by Method A. **Spectroscopic data:** ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_H 1.00 (12H, d, ³J_{HH} = 6.7 Hz, CH₃ of *i*Pr), 1.05 (12H, d, ³J_{HH} = 6.7 Hz, CH₃ of *i*Pr), 3.23 (4H, sept, ³J_{HH} = 6.7 Hz, CH of *i*Pr), 3.69 and 3.88 (4H, AB system, ²J_{HH} = 15.1 Hz, CH₂N), 6.98 (2H, d, ³J_{HH} = 7.5 Hz, *m*-CH of Ar), 7.17 (1H, t, ³J_{HH} = 7.5 Hz, *p*-CH of Ar), 8.84 ppm (1H, s, OC(O)H). ¹³C{¹H} NMR (101 MHz, benzene-d₆, 298 K): δ_C 20.5, 20.8 (CH₃ of *i*Pr), 51.5 (CH of *i*Pr), 53.9 (CH₂N), 123.3 (*m*-ArC), 128.6 (*p*-ArC), 148.7 (*o*-ArC), 156.6 (*ipso*-ArC) and 166.0 (OC(O)H). **IR** (nujol/cm⁻¹): ν_{C=O} 1656. **Elemental microanalysis:** calc. for C₂₁H₃₆N₂O₂Ge C 59.89%, H 8.62%, N 6.65%, meas. C 59.97%, H 8.79%, N 6.67%.

Synthesis of [{2,6-(*i*-PrN₂CH₂)₂C₆H₃}Ge(H)₂][B(C₆F₅)₄] ([Ar^{NiPr₂}Ge(H)₂][B(C₆F₅)₄], **5):** A mixture of **2** (0.08 g, 0.07 mmol) and [Ph₃C][B(C₆F₅)₄] (0.11 g, 0.12 mmol, 1.8 equiv.) was dissolved in 1,2-difluorobenzene, resulting in a bright orange solution which was stirred at room temperature for 36 h. After filtration, bright yellow crystals of **5** (as the hexane hemi-solvate) suitable for X-ray crystallography

were obtained from a 1,2-difluorobenzene/hexane layering at room temperature. Yield: 40 mg (52%).

Spectroscopic data: $^1\text{H NMR}$ (400 MHz, bromobenzene- d_5 , 298 K): δ_{H} 0.76 (12H, d, $^3J_{\text{HH}} = 6.5$ Hz, CH_3 of $i\text{Pr}$), 0.77 (12H, d, $^3J_{\text{HH}} = 6.5$ Hz, CH_3 of $i\text{Pr}$), 2.87 (4H, sept, $^3J_{\text{HH}} = 6.5$ Hz, CH of $i\text{Pr}$), 3.45 (4H, s, CH_2N), 5.92 (2H, s, Ge-H), 6.88 (2H, d, $^3J_{\text{HH}} = 7.6$ Hz, $m\text{-CH}$ of Ar), 7.30 (1H, t, $^3J_{\text{HH}} = 7.6$ Hz, $p\text{-CH}$ of Ar). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, bromobenzene- d_5 , 298 K): δ_{C} 17.2, 19.1 (CH_3 of $i\text{Pr}$), 49.5 (CH_2N), 54.7 (CH of $i\text{Pr}$), 121.2 ($ipso\text{-ArC}$ of $\text{Ar}^{\text{NiPr}_2}$), 123.2 ($m\text{-ArC}$ of $\text{Ar}^{\text{NiPr}_2}$), 124.2 (br. m, $ipso\text{-C}$ of $\text{B}(\text{C}_6\text{F}_5)$), 133.5 ($p\text{-ArC}$ of $\text{Ar}^{\text{NiPr}_2}$), 136.4 (br. d, $^1J_{\text{CF}} = 250$ Hz, $m\text{-CF}$ of $\text{B}(\text{C}_6\text{F}_5)$), 138.3 (d of t, $^1J_{\text{CF}} = 248$ Hz, $p\text{-CF}$ of $\text{B}(\text{C}_6\text{F}_5)$), 143.8 ($o\text{-ArC}$ of $\text{Ar}^{\text{NiPr}_2}$), 148.5 (br. d, $^1J_{\text{CF}} = 242$ Hz, $o\text{-CF}$ of $\text{B}(\text{C}_6\text{F}_5)$). $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, bromobenzene- d_5 , 298 K): $\delta_{\text{C}} -15.9$. $^{19}\text{F}\{^1\text{H}\}$ NMR (377 MHz, bromobenzene- d_5 , 298 K): -131.4 (2F, br. d, $^3J_{\text{FF}} = 12.2$ Hz, $o\text{-CF}$), -161.8 (1F, t, $^3J_{\text{FF}} = 21.0$ Hz, $p\text{-CF}$), -165.7 (2F, br. m, $m\text{-CF}$). IR (nujol/ cm^{-1}): $\nu_{\text{Ge-H}}$ 2162, 2179.

(iv) ^1H and ^{13}C NMR spectra of novel compounds

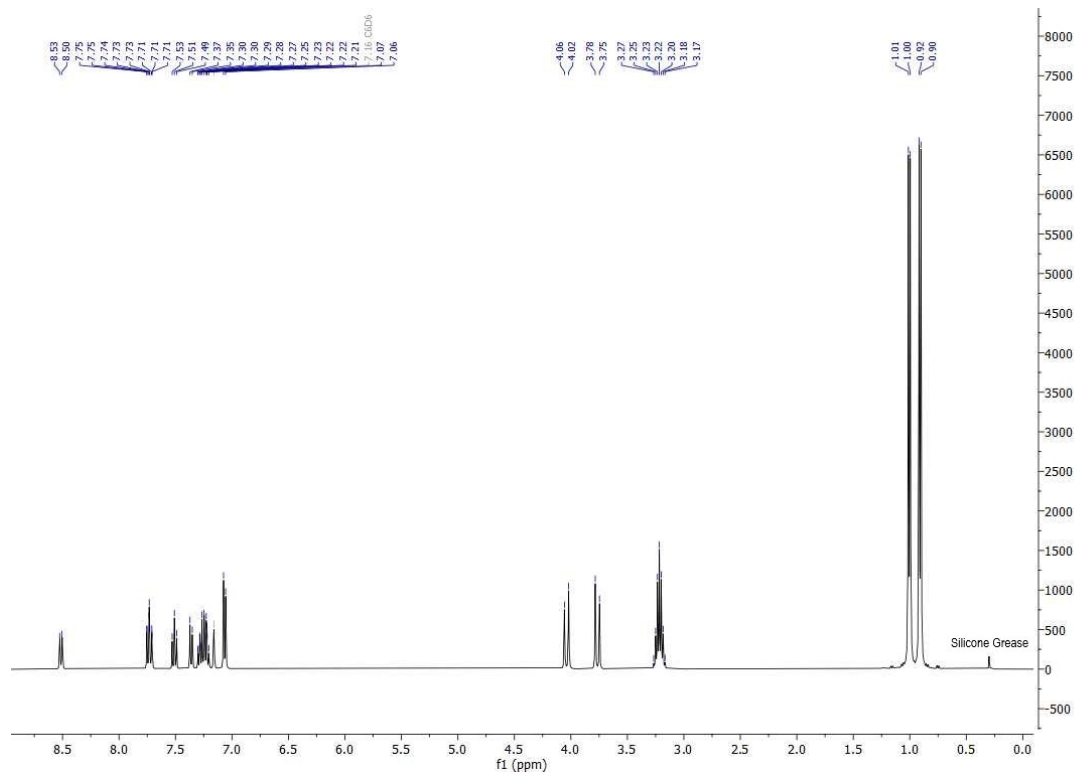


Figure s1. ^1H NMR spectrum of $\text{Ar}^{\text{NiPr}_2}\text{Ge}(\text{ONaph})$ measured in benzene- d_6 at 298 K. Silicone grease impurity has been labelled.

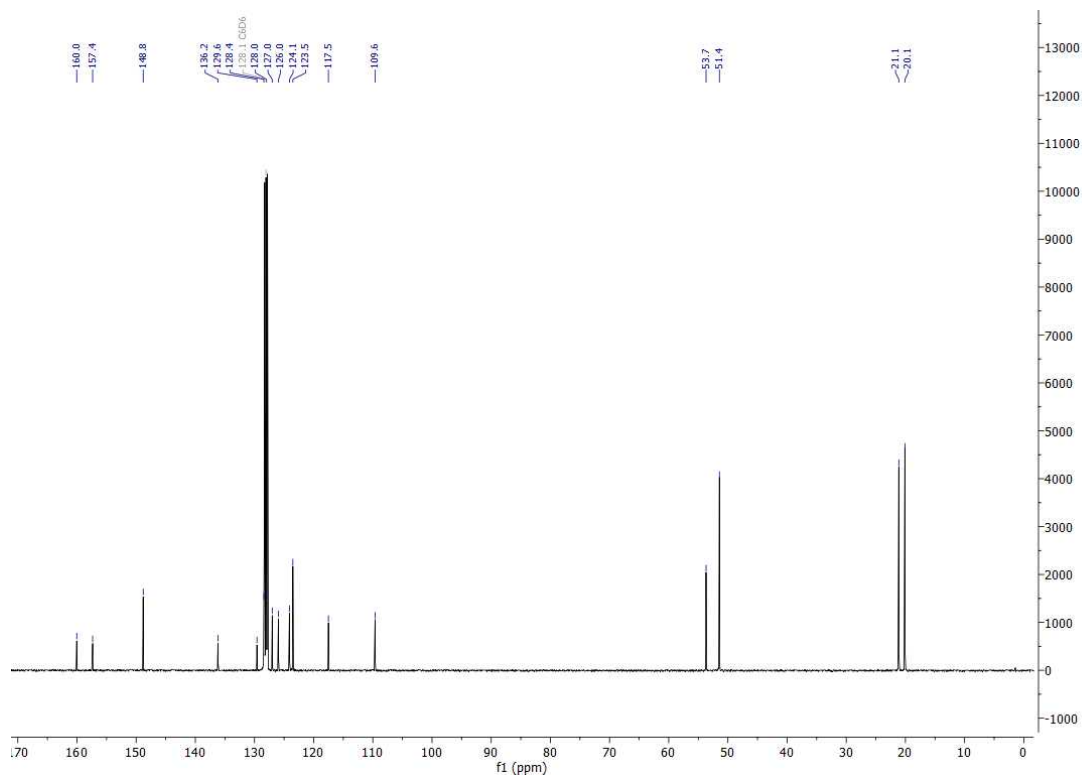


Figure s2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Ar}^{\text{NiPr}_2}\text{Ge}(\text{ONaph})$ measured in benzene- d_6 at 298 K.

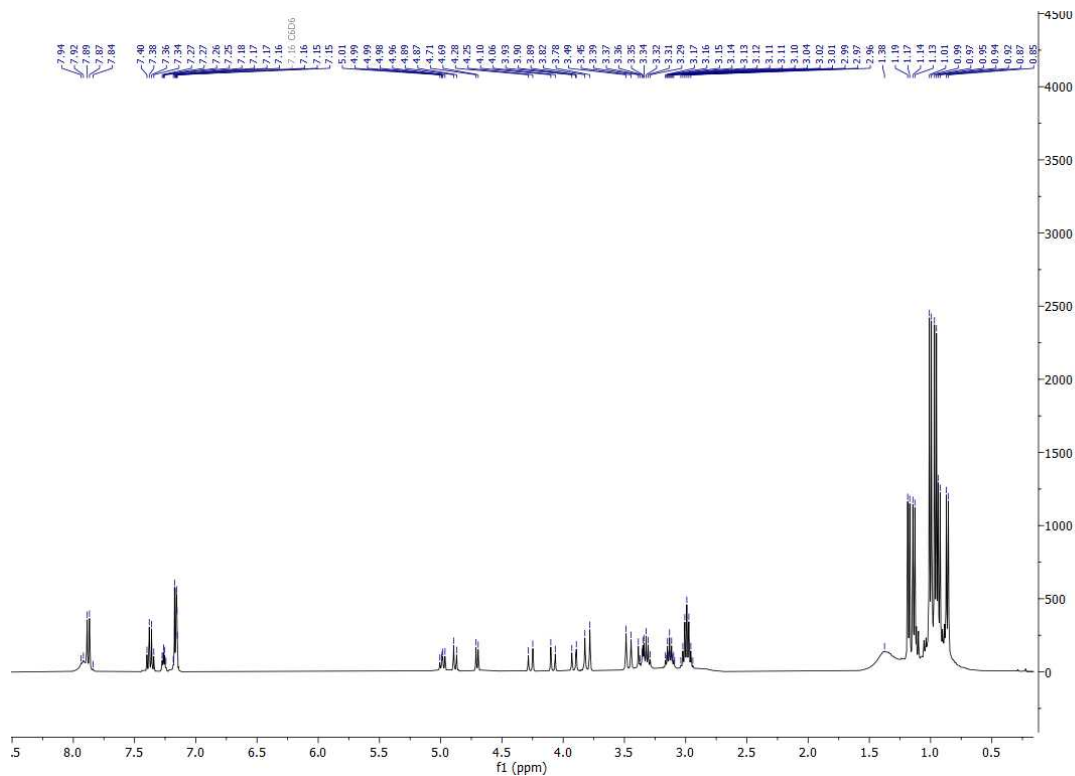


Figure s3. ^1H NMR spectrum of $(\text{Ar}^{\text{NiPr}_2})\text{GeGe}(\text{Ar}^{\text{NiPr}_2})(\text{H})\text{Ge}(\text{Ar}^{\text{NiPr}_2})(\text{H})_2$ measured in benzene- d_6 at 298 K.

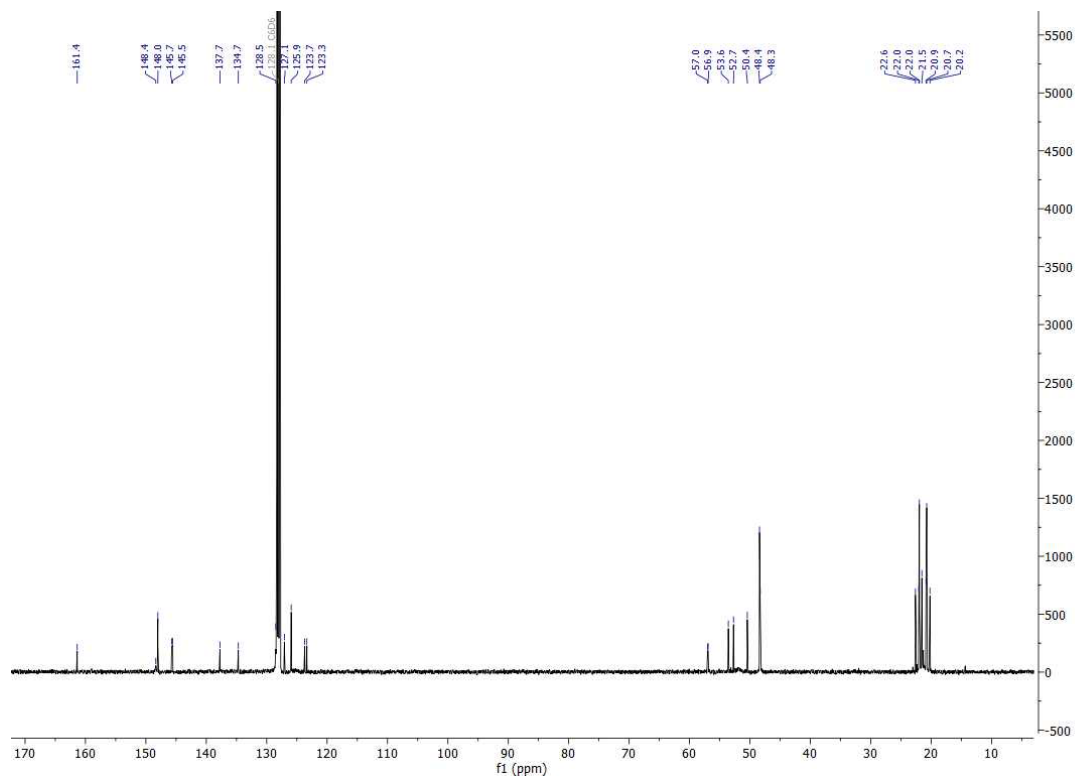


Figure s4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $(\text{Ar}^{\text{NiPr}_2})\text{GeGe}(\text{Ar}^{\text{NiPr}_2})(\text{H})\text{Ge}(\text{Ar}^{\text{NiPr}_2})(\text{H})_2$ measured in benzene- d_6 at 298 K.

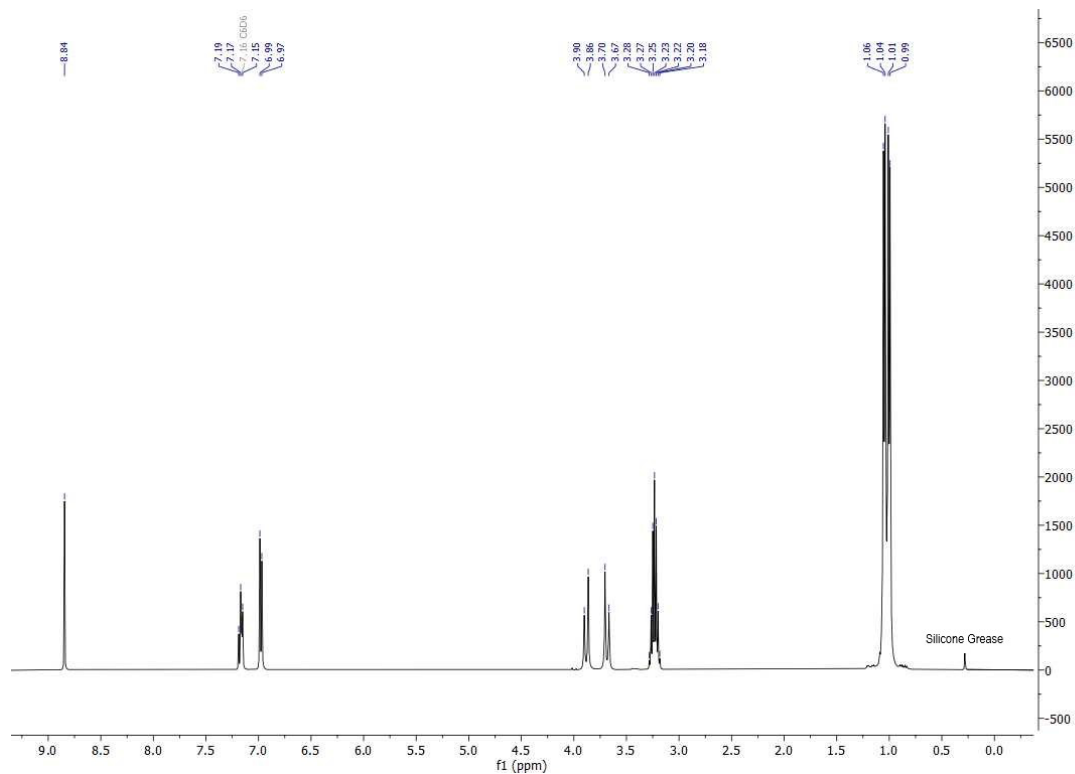


Figure s5. ^1H NMR spectrum of $\text{Ar}^{\text{NiPr}_2}\text{Ge}\{\text{OC}(\text{O})\text{H}\}$ measured in benzene- d_6 at 298 K. Silicone grease impurity has been labelled.

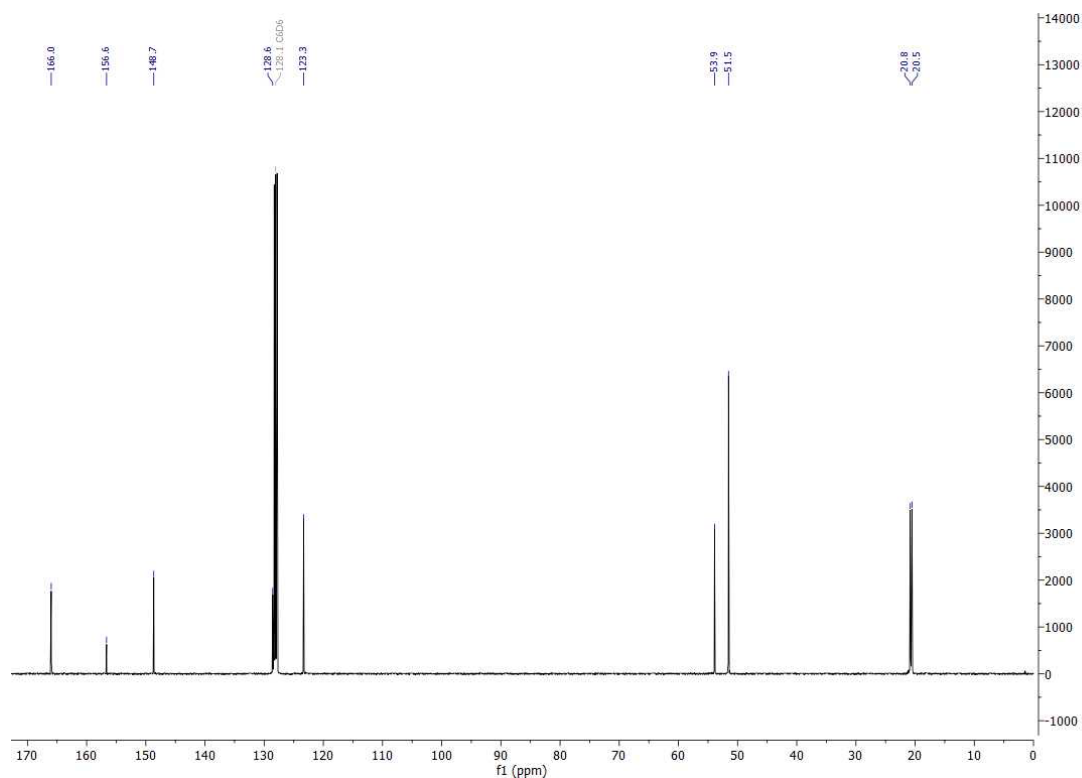


Figure s6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Ar}^{\text{NiPr}_2}\text{Ge}\{\text{OC}(\text{O})\text{H}\}$ measured in benzene- d_6 at 298 K.

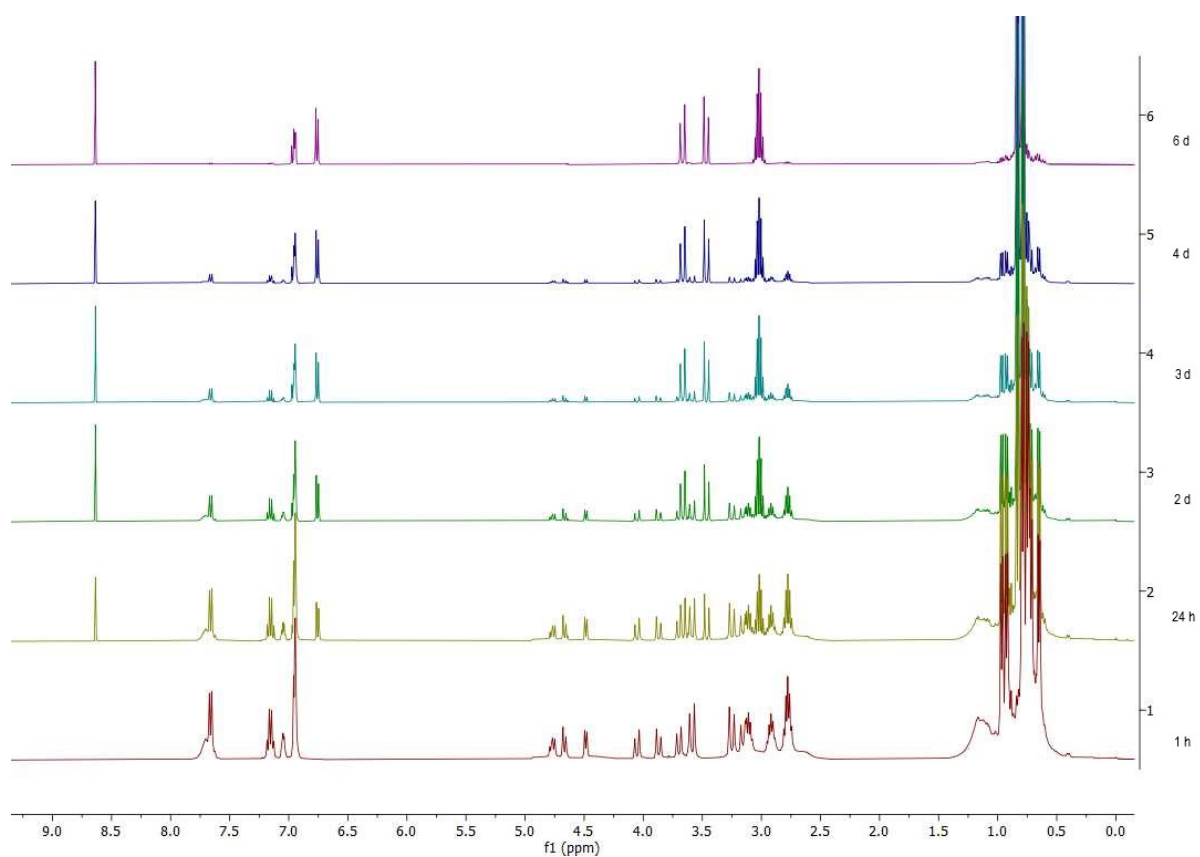


Figure s7. A stack plot of ¹H NMR spectra showing the progression of the reaction of $(\text{Ar}^{\text{NiPr}_2})\text{GeGe}(\text{Ar}^{\text{NiPr}_2})(\text{H})\text{Ge}(\text{Ar}^{\text{NiPr}_2})(\text{H})_2$ (**2**) with CO_2 to yield $\text{Ar}^{\text{NiPr}_2}\text{Ge}\{\text{OC}(\text{O})\text{H}\}$ (**4**).

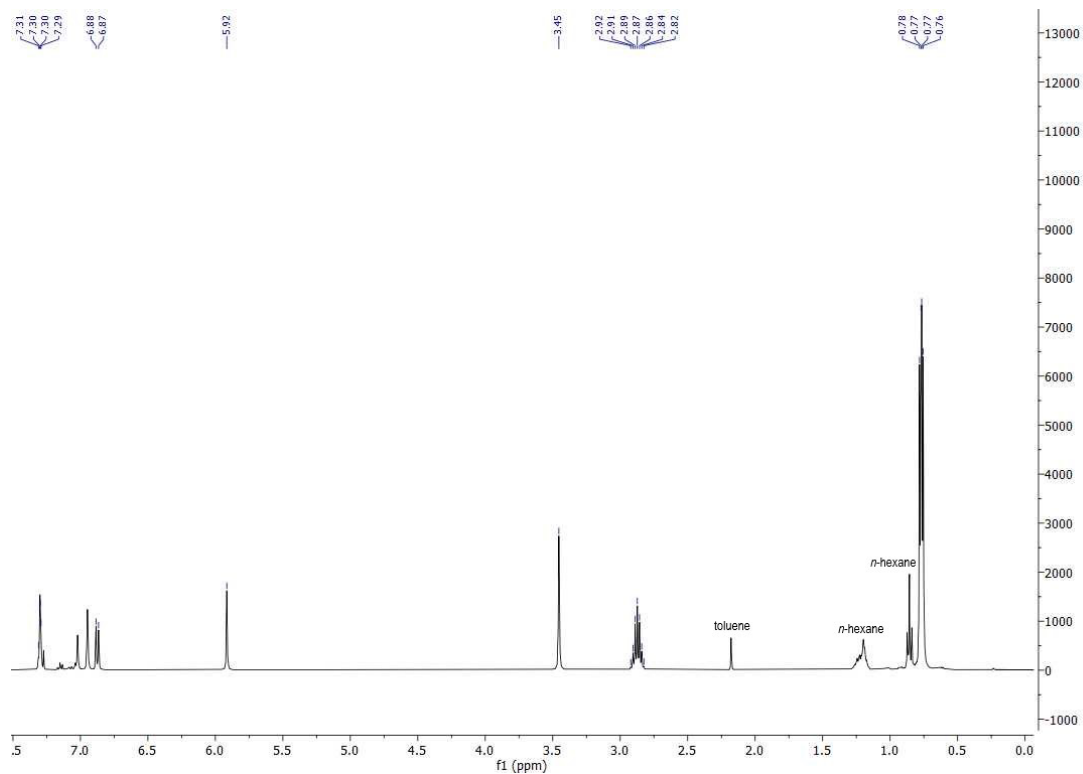


Figure s8. ^1H NMR spectrum of $[\text{Ar}^{\text{NiPr}_2}\text{Ge}(\text{H})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ measured in bromobenzene- d_5 at 298 K. *N*-hexane and toluene impurities have been labelled. The *n*-hexane solvent is included within crystals of the hemi-solvate.

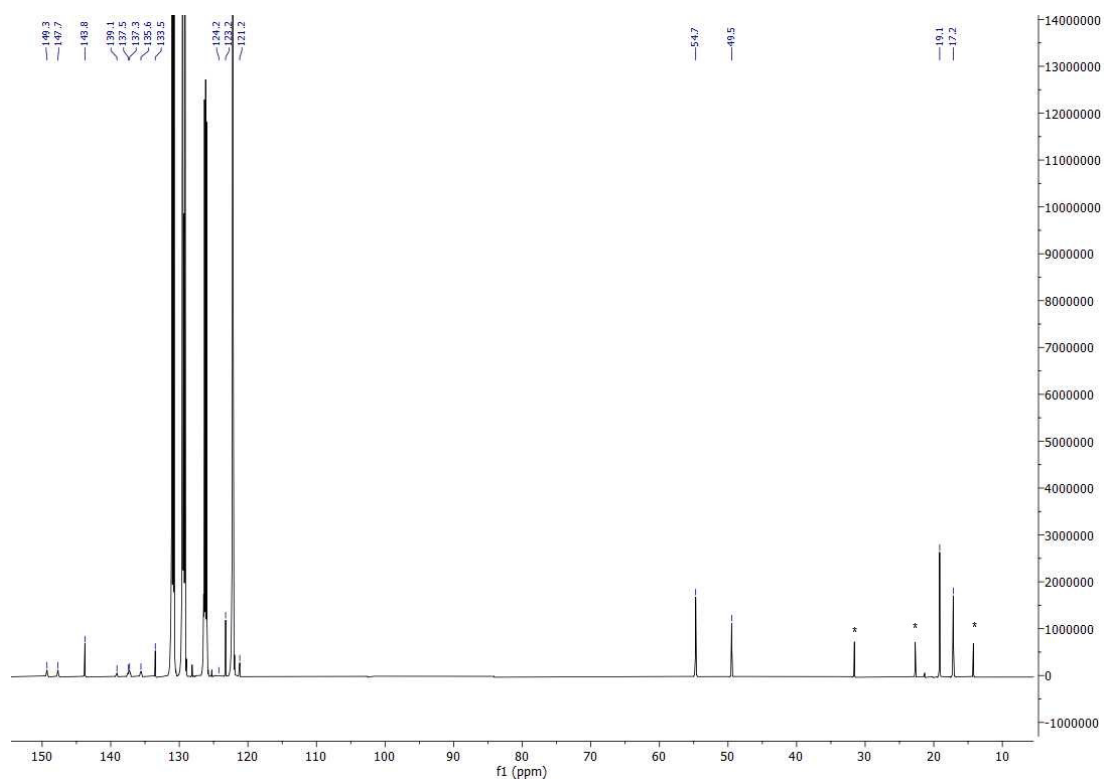


Figure s9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{Ar}^{\text{NiPr}_2}\text{Ge}(\text{H})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ measured in bromobenzene- d_5 at 298 K. Resonances marked with a * correspond to the resonances for the *n*-hexane solvent included within crystals of the hemi-solvate.

(v) X-ray crystallographic studies

Crystallographic details: 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 N₂ cooling device.^{s4} Data were collected at 150 K using mirror monochromated Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$; Oxford Diffraction Supernova). Data collected were processed using the CrysAlisPro package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro).^{s5} Equivalent reflections were merged and diffraction patterns processed with the CrysAlisPro suite. Structures were subsequently solved using SHELXT-2018 and refined on F² using the SHELXL 2019 package and the graphical interface Olex2.^{s6-s8}

Table s1. Selected X-ray data collection and refinement parameters for compounds **2** - **5**.

	(Ar ^{NiPr2})GeGe(Ar ^{NiPr2})(H)Ge(Ar ^{NiPr2})(H) ₂ 2	Ar ^{NiPr2} Ge(ONaph) 3	Ar ^{NiPr2} Ge{OC(O)H} 4
Formula	C ₆₀ H ₁₀₈ Ge ₃ N ₆	C ₃₀ H ₄₂ GeN ₂ O	C ₂₁ H ₃₆ GeN ₂ O ₂
Fw (g mol ⁻¹)	1131.29	519.24	421.11
Cell setting	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	15.4003(2)	8.2011(3)	14.3981(2)
<i>b</i> (Å)	14.5568(2)	10.5814(6)	11.37830(10)
<i>c</i> (Å)	29.3234(3)	16.5784(5)	14.8745(2)
α (°)	90	102.491(3)	90
β (°)	105.1050(10)	100.285(3)	118.729(2)
γ (°)	90	93.091(4)	90
<i>V</i> (Å ³)	6346.57(14)	1375.61(10)	2136.86(6)
<i>Z</i>	4	2	4
ρ_{calc} (g cm ⁻³)	1.184	1.254	1.309
Radiation, λ (Å)	Cu K α (1.54184)	Cu K α (1.54184)	Cu K α (1.54184)
μ (mm ⁻¹)	1.958	1.681	2.069
Reflns collected	51734	13167	21768
Independent reflns	13268	5678	4443
$R_{\text{(int)}}$	0.0306	0.0274	0.0330
Parameters	655	383	243
R_1 (all data/ $I > 2\sigma(I)$)	0.0316/0.0257	0.0299/0.0283	0.0310/0.0260
ωR_2 (all data/ $I > 2\sigma(I)$)	0.0658/0.0625	0.0744/0.0727	0.0695/0.0658
GooF	1.032	1.044	1.028
<i>T</i> /K	150.0(2)	150.0(2)	150.0(2)
CCDC ref.	2242325	2242326	2242237

Table S1 (cont). Selected X-ray data collection and refinement parameters for compounds **2 - 5**.

[(Ar ^{NiPr2} Ge(H) ₂][B(C ₆ F ₅) ₄] _{0.5} (C ₆ H ₁₄) 5	
Formula	[C ₂₀ H ₃₇ GeN ₂][BC ₂₄ F ₂₀] _{0.5} (C ₆ H ₁₄)
Fw (g mol ⁻¹)	1100.24
Cell setting	Orthorhombic
Space group	<i>P b c a</i>
<i>a</i> (Å)	18.1855(2)
<i>b</i> (Å)	22.2471(3)
<i>c</i> (Å)	22.8462(3)
α (°)	90
β (°)	90
γ (°)	90
<i>V</i> (Å ³)	9243.0(2)
<i>Z</i>	8
ρ_{calc} (g cm ⁻³)	1.581
Radiation, λ (Å)	Cu K α (1.54184)
μ (mm ⁻¹)	1.973
Refins collected	64509
Independent refins	9607
<i>R</i> _(int)	0.0469
Parameters	657
<i>R</i> ₁ (all data/ <i>I</i> > 2 σ (<i>I</i>))	0.0457/0.0308
ωR ₂ (all data/ <i>I</i> > 2 σ (<i>I</i>))	0.0815/0.0734
GooF	1.016
<i>T</i> /K	150.0(2)
CCDC Deposition No.	2242328

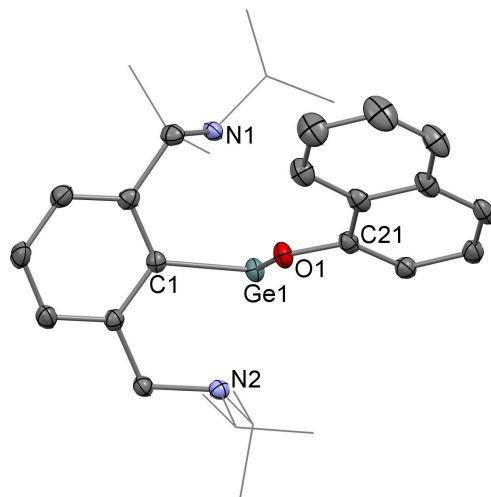


Figure s10. The molecular structures of $\text{Ar}^{\text{NiPr}_2}\text{Ge}(\text{ONaph})$ (**3**) in the solid state as determined by X-ray crystallography. Thermal ellipsoids set at the 40% probability level. Selected hydrogen atoms omitted and $i\text{Pr}$ substituents shown in wireframe format for clarity. Selected bond lengths (Å) and angles ($^\circ$): Ge1–O1 1.9049(10), Ge1–C1 1.9968(13), O1–C21 1.3478(16), Ge1–N1 2.836(3), Ge1–N2 2.426(1), O1–Ge1–C1 90.53(5), C21–O1–Ge1 123.80(9).

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