Supporting Information

Reversible metathesis of ammonia in an acyclic Germylene-Ni\(^0\) complex

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1. Experimental methods and data………………..S2
2. X-ray Crystallographic details…………………S48
3. Computational methods and details………..S55
1. Experimental methods and data

**General considerations.** All experiments and manipulations were carried out under a dry oxygen free argon atmosphere using standard Schlenk techniques, or in a MBraun inert atmosphere glovebox containing an atmosphere of high purity argon. THF and diethyl ether were dried by distillation over a sodium/benzophenone mixture and stored over activated 4Å mol sieves. C₆D₆ was dried and stored over a potassium mirror. All other solvents were dried over activated 4Å mol sieves and degassed prior to use. NiBr₂-DME,¹ NiCl₂-DME,² DipπN(H)Li,³ and PPh₂CH₂Li·TMEDA⁴ were synthesized according to known literature procedures. All other reagents were used as received. Commercial CyNH₂, when used as received, contained enough residual moisture to allow for the synthesis of 6a. NMR spectra were recorded on a Bruker AV 400 or 500 Spectrometer. The ¹H and ¹³C{¹H} NMR spectra were referenced to the residual solvent signals as internal standards.²⁹Si NMR spectra were externally calibrated with SiMe₄. ³¹P NMR spectra were externally calibrated with H₃PO₄. LIFDI MS spectra were measured at a Waters Micromass LCT TOF mass spectrometer equipped with an LIFDI ion source (LIFDI 700) from Linden CMS GmbH. The samples were dissolved in dry toluene and filtered using a syringe filter under an inert atmosphere. The TOF setup was externally calibrated using polystyrene. ESI-MS was performed on an exactive plus orbitrap spectrometer from Thermo Fischer Scientific. Infrared spectra were measured with the Alpha FT IR from Bruker containing a platinum diamond ATR device. The compounds were measured as solids under inert conditions in a glovebox. For the ammonia activation experiments water free ammonia 5.0 was used.

**Ph³PhDippNKH.** A yellow suspension of PPh₂CH₂Li·TMEDA (6.0 g, 18.6 mmol) in 100 mL hexane was cooled to -78 °C. The mixture was stirred vigorously and Ph₂SiCl₂ (3.9 mL, 18.6 mmol) was added. The mixture was allowed to warm to RT overnight. All volatiles were subsequently removed in vacuo, leaving a yellow oil. DipπN(H)Li (3.4 g, 18.6 mmol) was added to the residue, and the flask cooled to -78 °C, followed by the addition of 50 mL THF. The mixture was stirred until dissolution of all solids was observed. The cold bath was then removed and the reaction allowed to warm to RT, leading to an orange solution. All volatiles were removed in vacuo and the oily residue extracted with 50 mL hexane, and filtered. The solvent was removed in vacuo and KH (0.9 g, 28.3 mmol) was added. After addition of 50 mL THF, gas started to evolve, and the mixture was vigorously stirred for a further 16 h. The dark brown suspension was filtered, and all volatiles were removed in vacuo. To the resulting oil 50 mL hexane was added, and the mixture treated in an ultrasonic bath causing the precipitation of copious pale brown powder, which was filtered and washed multiple times with hexane, and subsequently
dried *in vacuo* to yield $^{\text{Ph}}^{\text{Ph}}$DippNK as an off-white powder (8.5 g, 14.3 mmol, 77%). Colourless crystals suitable for X-ray diffraction analysis were obtained after two days from a concentrated THF/TMEDA solution layered with hexane stored at -32°C. $^1$H NMR (THF-d$_8$, 400 MHz, 298 K): $\delta$ = 0.91 (d, 12H, $^3$J$_{HH}$ = 6.9 Hz, Dipp-Pr$i$-CH$_3$), 1.97 (d, 2H, $^2$J$_{HP}$ = 5.4 Hz, Ph$_2$P-CH$_2$), 3.94 (hept, 2H, $^3$J$_{HH}$ = 6.9 Hz, Dipp-Pr$i$-CH$_3$), 6.24 (t, 1H, $^3$J$_{HH}$ = 7.4 Hz, Ar-CH$_3$), 6.74 (d, 2H, $^3$J$_{HH}$ = 7.4 Hz, Ar-CH$_3$), 7.00 (m, 6H, Ar-CH$_3$), 7.10 (m, 6H, Ar-CH$_3$), 7.27 (m, 4H, Ar-CH$_3$), 7.48 (m, 4H, Ar-CH$_3$). $^{13}$C($^1$H) NMR (THF-d$_8$, 101 MHz, 298 K): $\delta$ = 19.7 (d, $^1$J$_{CP}$ = 29.2 Hz, Ph$_2$P-CH$_2$), 24.9 (Dipp-Pr$i$-CH$_3$), 28.1 (Dipp-Pr$i$-CH), 112.6, 123.00, 127.3, 127.5, 128.3, 128.7, 133.4, 133.6, 135.8, 141.4, 143.9, 144.0, 146.7, 146.7 and 156.2 (Ar-C). $^{31}$P($^1$H) NMR (THF-d$_8$, 162 MHz, 298 K): $\delta$ = -19.1 (s, CH$_2$-PPh$_2$). $^{29}$Si($^1$H) NMR (THF-d$_8$, 99 MHz, 298 K): $\delta$ = -47.4 (d, $^2$J$_{SiP}$ = 14.7 Hz, SiPh$_2$).

N.B. The extremely high reactivity of the potassium amide precluded the reproducible acquisition mass spectrometry data.

$^{\text{Ph}}^{\text{Ph}}$DippNK. The procedure for the synthesis of $^{\text{Ph}}^{\text{Ph}}$DippNK was followed, but using Ph$_2$SiCl$_2$, Pr$_2$SiCl$_2$ (5.6 mL, 31 mmol). The product $^{\text{Ph}}^{\text{Ph}}$DippNK was isolated as a pale-yellow powder (11.8 g, 72%). $^1$H NMR (THF-d$_8$, 400 MHz, 298 K): $\delta$ = 0.88 (m, 14H, Si-Pr$i$-CH$_3$/ Dipp-Pr$i$-CH$_3$), 1.02 (d, 12H, $^3$J$_{HH}$ = 6.9 Hz, Dipp-Pr$i$-CH$_3$), 1.50 (d, 2H, $^2$J$_{HP}$ = 6.6 Hz, Ph$_2$P-CH$_2$), 4.01 (hept, 2H, $^3$J$_{HH}$ = 6.8 Hz, Dipp-Pr$i$-CH$_3$), 6.14 (t, 1H, $^3$J$_{HH}$ = 7.4 Hz, Ar-CH$_3$), 6.69 (d, 2H, $^3$J$_{HH}$ = 7.4 Hz, Ar-CH$_3$), 7.23 (m, 6H, Ar-CH$_3$), 7.52 (m, 4H, Ar-CH$_3$). $^{13}$C($^1$H) NMR (THF-d$_8$, 101 MHz, 298 K): $\delta$ = 6.9 (Ph$_2$P-CH$_2$), 18.4 (Pr$i$-CH), 20.2 and 20.4 (Pr$i$-CH$_3$), 27.4 (Pr$i$-CH), 111.5, 122.9, 123.0, 128.6, 128.8, 133.5, 133.7, 140.8, 144.8, 145.0 and 157.0 (Ar-C). $^{31}$P($^1$H) NMR (THF-d$_8$, 162 MHz, 298 K): $\delta$ = -18.7 (s, CH$_2$-PPh$_2$). $^{29}$Si($^1$H) NMR (THF-d$_8$, 79 MHz, 298 K): $\delta$ = -29.3 (d, $^2$J$_{SiP}$ = 12.2 Hz, SiPr$_2$).

N.B. The extremely high reactivity of the potassium amide precluded the reproducible acquisition of mass spectrometry data.

$^{\text{Ph}}^{\text{Ph}}$DippGeCl, 1a. A pale brown solution of $^{\text{Ph}}^{\text{Ph}}$DippNK (7.0 g, 11.7mmol) in 20 mL THF was added dropwise to a stirring solution of GeCl$_2$-dioxane (2.7 g, 11.7 mmol) in 10 mL THF at -78°C, and subsequently allowed to warm to RT, resulting in the formation of an orange solution. All volatiles were removed *in vacuo*, the residue extracted in 20 mL DCM, and filtered. The solvent was removed *in vacuo* and the residue washed with hexane to yield 1a as an off-white powder (7.0 g, 10.5 mmol, 90%). Colourless crystals suitable for X-ray diffraction analysis were obtained from a concentrated diethyl ether
at RT. ¹H NMR (C₆D₆, 400 MHz, 298 K): δ = 0.09 (d, 3H, ³JHH = 6.4 Hz, Dipp-Pr⁻CH₃), 0.68 (d, 3H, ³JHH = 6.6 Hz, Dipp-Pr⁻CH₃), 0.86 (d, 3H, ³JHH = 6.5 Hz, Dipp-Pr⁻CH₃), 1.43 (d, 3H, ³JHH = 6.5 Hz, Dipp-Pr⁻CH₃), 2.54 (m, 3H, Ph₂P-CH₂/Dipp-Pr⁻CH₃), 4.28 (m, 1H, Dipp-Pr⁻CH₃), 7.02 (m, 14 H, Ar-CH₃), 7.21 (m, 3H, Ar-CH₃), 7.46 (m, 2H, Ar-CH₃), 7.65 (m, 2H, Ar-CH₃), 8.26 (d, 2H, ³JHH = 7.1 Hz, Ar-CH₃). ¹³C[¹H] NMR (C₆D₆, 101 MHz, 298 K): δ = 8.1 (Ph₂P-CH₂), 21.4, 22.6 and 28.0 (Dipp-Pr⁻CH₃), 28.2 and 28.6 (Dipp-Pr⁻CH₃), 28.8 (Dipp-Pr⁻CH₃), 123.9, 124.6, 125.6, 129.0, 129.1, 129.6, 129.7, 131.1, 131.5, 132.8, 132.9, 133.3, 133.4, 134.8, 135.4, 135.7, 137.3, 137.8, 140.8, 140.9, 147.8 and 149.7 (Ar-C). ³¹P[¹H] NMR (C₆D₆, 162 MHz, 298 K): δ = 4.0 (s, CH₂-PPh₂). ²⁹Si[¹H] NMR (C₆D₆, 79 MHz, 298 K): δ = -4.0 (d, ²JSSIP = 13.4 Hz, SiPh₂). MS/LIFDI-HRMS found (calcd) m/z: 665.1466 (665.1490) for [M⁺].

**PhIPDippGeCl, 1b.** The procedure for the synthesis of 1a was followed, but using PhIPDippNK (3 g, 5.7 mmol), and GeCl₂-dioxane (1.32 g, 5.7 mmol). Chloro-germylene 1b was isolated as a micro-crystalline pale-yellow powder (2.57 g, 76 %). Colourless crystals suitable for X-ray diffraction analysis were obtained from a concentrated benzene solution stored at RT. ¹H NMR (C₆D₆, 400 MHz, 298 K): δ = 0.56 (d, 3H, ³JHH = 7.4 Hz, Si-Pr⁻CH₃), 0.81 (m, 4H, Dipp-Pr⁻CH₃/Si-Pr⁻CH₃), 0.90 (d, 3H, ³JHH = 6.7 Hz, Dipp-Pr⁻CH₃), 1.05 (d, 3H, ³JHH = 7.6 Hz, Si-Pr⁻CH₃), 1.14 (m, 3H, Si-Pr⁻CH₃), 1.43 (d, 3H, ³JHH = 6.8 Hz, Dipp-Pr⁻CH₃), 1.47 (d, 3H, ³JHH = 6.8 Hz, Dipp-Pr⁻CH₃), 1.60 (m, 4H, Si-Pr⁻CH₃/Dipp-Pr⁻CH₃), 1.86 (m, 1H, Ph₂P-CH₂), 2.15 (m, 1H, Ph₂P-CH₂), 2.68 (hept, 1H, ³JHH = 6.6 Hz, Dipp-Pr⁻CH₃), 4.24 (hept, 1H, ³JHH = 6.8 Hz, Dipp-Pr⁻CH₃), 7.02 (m, 7 H, Ar-CH₃), 7.10 (t, 1H, ³JHH = 7.6 Hz, Ar-CH₃), 7.18 (m, 1H, Ar-CH₃), 7.42 (m, 2H, Ar-CH₃), 7.67 (m, 2H, Ar-CH₃). ¹³C[¹H] NMR (C₆D₆, 101 MHz, 298 K): δ = 3.2 (Ph₂P-CH₂), 15.3 and 16.1 (Si-Pr⁻CH₃), 17.8, 20.0, 20.2 and 20.4 (Si-Pr⁻CH₃), 22.9 and 22.9 (Dipp-Pr⁻CH₃), 27.8 and 28.0 (Dipp-Pr⁻CH₃), 29.0 and 29.1 (Dipp-Pr⁻CH₃), 123.9, 124.1, 125.2, 128.9, 129.0, 129.2, 129.3, 130.9, 131.5, 131.8, 132.1, 132.6, 132.7, 133.0, 133.1, 142.1, 142.2, 147.4 and 149.6 (Ar-C). ³¹P[¹H] NMR (C₆D₆, 162 MHz, 298 K): δ = 1.3 (s, CH₂-PPh₂). ²⁹Si[¹H] NMR (C₆D₆, 79 MHz, 298 K): δ = 16.0 (d, ²JSSIP = 10.8 Hz, SiPr₂). MS/LIFDI-HRMS found (calcd) m/z: 597.1794 (597.1803) for [M⁺].

[PhPPhDippGe(Br)₂NiBr₂]₃, 2. To a mixture of 1a (150 mg, 0.23 mmol) and NiBr₂-DME (690 mg, 2.3 mmol) was added 5 mL toluene, and the reaction mixture heated to 100°C with stirring for 30 min, leading to a deep red-brown solution over a pale orange solid. The reaction was filtered hot, and the solution allowed to slowly cool, whereupon red crystals of 2 formed over the course of a few hours. These allowed for the acquisition of the molecular structure of 2. This compound appeared to rapidly disproportionate to NiBr₂ and bromo-germylene 3a in solution, precluding the acquisition of any further data for this compound.
**Ph**PhDippGeBr, 3a. To a mixture of 1a (200 mg, 0.30 mmol) and NiBr₂·DME (540 mg, 1.8 mmol) was added 5 mL toluene and 1 mL THF, and the resulting mixture stirred for 1 h. All volatiles were removed in vacuo and the residue extracted with 5 mL toluene. The solution was concentrated and layered with hexane yielding colourless crystals of 3a suitable for X-ray diffraction analysis (127 mg, 0.18 mmol, 54%). ¹H NMR (CD₂D₆, 400 MHz, 298 K): δ = 0.06 (d, 3H, ³JHH = 6.6 Hz, Dipp-Pr⁻CH₃), 0.67 (d, 3H, ³JHH = 6.7 Hz, Dipp-Pr⁻CH₃), 0.93 (d, 3H, ³JHH = 6.6 Hz, Dipp-Pr⁻CH₃), 1.46 (d, 3H, ³JHH = 6.6 Hz, Dipp-Pr⁻CH₃), 2.55 (m, 3H, Ph₂P-CH₂/Dipp-Pr⁻CH₃), 4.26 (hept, 1H, ³JHH = 6.9 Hz, Dipp-Pr⁻CH₃), 6.99 (m, 14 H, Ar-CH), 7.21 (m, 3H, Ar-CH), 7.46 (m, 2H, Ar-CH), 7.60 (m, 2H, Ar-CH), 8.30 (d, 2H, ³JHH = 7.3 Hz, Ar-CH). ¹³C{¹H} NMR (CD₂D₆, 101 MHz, 298 K): δ = 8.4 (Ph₂P-CH₂), 21.4 and 22.6 (Dipp-Pr⁻CH₃), 28.1 and 28.2 (Dipp-Pr⁻CH), 28.5 and 29.0 (Dipp-Pr⁻CH₃), 123.1, 124.0, 124.8, 125.7, 128.9, 129.0, 129.1, 129.6, 129.8, 131.0, 131.6, 132.7, 132.8, 133.3, 133.4, 134.5, 135.4, 137.6, 140.5, 140.6, 147.8 and 149.9 (Ar-C). ³¹P{¹H} NMR (CD₂D₆, 162 MHz, 298 K): δ = 1.9 (s, CH₂-PPPh₂). ²⁹Si{¹H} NMR (CD₂D₆, 99 MHz, 298 K): δ = -3.9 (d, ²JSiP = 13.9 Hz, SiPh₂); MS/LIFDI-HRMS found (calcd) m/z: 709.1012 (709.0984) for [M]⁺.

**Ph**P**DippGeBr**, 3b. The procedure for the synthesis of 3a was followed, using 1b (155 mg, 0.26 mmol) and NiBr₂·DME (480 mg, 1.56 mmol). Filtration of the reaction mixture, concentration, and layering with hexane led to the formation of large X-ray quality crystals (85 mg, 0.13 mmol, 51 %). ¹H NMR(CD₂D₆, 400 MHz, 298 K): δ = 0.55 (d, 3H, ³JHH = 7.3 Hz, Si-Pr⁻CH₃), 0.79 (m, 4H, Dipp-Pr⁻CH₃/Si-Pr⁻CH₃), 0.94 (d, 3H, ³JHH = 6.7 Hz, Dipp-Pr⁻CH₃), 1.02 (d, 3H, ³JHH = 7.6 Hz, Si-Pr⁻CH₃), 1.13 (d, 3H, ³JHH = 6.4 Hz, Si-Pr⁻CH₃), 1.44 (d, 3H, ³JHH = 6.9 Hz, Dipp-Pr⁻CH₃), 1.51 (d, 3H, ³JHH = 6.6 Hz, Dipp-Pr⁻CH₃), 1.63 (m, 4H, Si-Pr⁻CH₃/Dipp-Pr⁻CH), 1.90 (m, 1H, Ph₂P-CH₂), 2.27 (m, 1H, Ph₂P-CH₂), 2.68 (hept, 1H, ³JHH = 6.3 Hz, Dipp-Pr⁻CH), 4.23 (hept, 1H, ³JHH = 7.1 Hz, Dipp-Pr⁻CH), 7.00 (m, 6 H, Ar-CH), 7.10 (t, 2H, ³JHH = 7.6 Hz, Ar-CH), 7.19 (m, 1H, Ar-CH), 7.41 (m, 2H, Ar-CH), 7.64 (m, 2H, Ar-CH). ¹³C{¹H} NMR (CD₂D₆, 101 MHz, 298 K): δ = 3.6 (Ph₂P-CH₂), 15.5, 15.5, 16.3 and 16.3 (Si-Pr⁺-CH), 17.9, 20.1, 20.6 and 20.7 (Si-Pr⁻-CH₃), 22.8 and 22.9 (Dipp-Pr⁻-CH₃), 27.9 and 27.9 (Dipp-Pr⁺-CH), 29.2 and 29.7 (Dipp-Pr⁻-CH₃), 124.0, 124.2, 125.4, 128.8, 128.9, 129.1, 129.2, 130.9, 131.5, 131.8, 132.6, 132.7, 132.9, 133.0, 141.9, 142.0, 147.5, 149.8 and 149.9 (Ar-C). ³¹P{¹H} NMR (CD₂D₆, 162 MHz, 298 K): δ = -0.4 (s, CH₂-PPPh₂).

[Ph**Ph**DippGe(Cl)]Ni(PPh₃)₂, 4a. To a mixture of 1a (1.60 g, 2.4 mmol), NiCl₂·DME (0.53 g, 2.4 mmol), PPh₃ (1.26 g, 4.8 mmol), and Zn (0.94 g, 14.4 mmol) was added 10 mL THF, and the resulting mixture stirred for 24 h at RT resulting in a deep red reaction
mixture. All volatiles were removed in vacuo and the residue extracted with 20 mL diethyl ether. Dark red crystals of 4a, which were suitable for X-Ray diffraction analysis, were obtained after storing the solution at RT overnight (1.55g, 1.8 mmol, 52%). $^1$H NMR (C$_6$D$_6$, 400 MHz, 298 K): $\delta$ = 0.49 (d, 6H, $^3$J$_{HH}$ = 6.6 Hz, Dipp-Pr$i$-CH$_3$), 1.28 (bs, 6H, Dipp-Pr$i$-CH$_3$), 3.03 (s, 2H, Ph$_2$P-CH$_2$), 3.72 (hept, 2H, $^3$J$_{HH}$ = 6.6 Hz, Dipp-Pr$i$-CH$_3$), 6.63 (m, 3 H, Ar-CH$_3$), 6.94 (m, 36H, Ar-CH$_3$), 7.32 (d, 5H, $^3$J$_{HH}$ = 6.2 Hz, Ar-CH$_3$), 7.52 (s, 9H, Ar-CH$_3$). $^{13}$C($^1$H) NMR (C$_6$D$_6$, 101 MHz, 298 K): $\delta$ = 20.0 (Ph$_2$P-CH$_2$), 23.8 and 26.1 (Dipp-Pr$i$-CH$_3$), 29.2 (Dipp-Pr$i$-CH), 124.0, 125.6, 127.2, 128.8, 128.9, 129.1, 132.3, 134.5, 134.6, 135.3, 136.0, 138.6, 138.9, 142.3 and 145.5 (Ar-C). $^{31}$P($^1$H) NMR (C$_6$D$_6$, 81 MHz, 298 K): $\delta$ = 7.1 (t, $^2$J$_{PP}$ = 18.2 Hz, Ph$_2$P-Ni-(PPh$_3$)$_2$), 39.8 (bs, Ph$_2$P-Ni-(PPh$_3$)$_2$).

N.B. Conducting the reaction with NiBr$_2$-DME in place of the related chloride leads to the formation of a mixture of [$^{p}$PhDipp(Cl)Ge]Ni(PPh$_3$)$_2$ and [$^{p}$PhDipp(Br)Ge]Ni(PPh$_3$)$_2$, with considerably shorted reaction times. This mixture could be used in further chemistry with no issues.

[$^{p}$PhDippGe(Cl)Ni(PPh$_3$)$_2$, 4b. To a mixture of 1b (50 mg, 0.075 mmol), NiCl$_2$-DME(17 mg, 0.075 mmol), PPh$_3$ (40 mg, 0.150 mmol) and Zn (39 mg, 0.600 mmol) was added 2 mL THF, and the resulting mixture stirred for 72 h at RT, resulting in a deep red suspension. All volatiles were removed in vacuo and the residue extracted with 5 mL diethyl ether. Dark red crystals of 4b, which were suitable for X-Ray diffraction analysis, were obtained after storing the solution at RT overnight (46 mg, 0.039 mmol, 52%). $^1$H NMR (C$_6$D$_6$, 400 MHz, 298 K): $\delta$ = 0.64 (d, 6H, $^3$J$_{HH}$ = 7.3 Hz, Si-Pr$i$-CH$_3$), 0.86 (d, 6H, $^3$J$_{HH}$ = 7.4 Hz, Si-Pr$i$-CH$_3$), 1.30 (d, 6H, $^3$J$_{HH}$ = 6.5 Hz, Dipp-Pr$i$-CH$_3$), 1.43 (m, 8H, Dipp-Pr$i$-CH$_3$/Si-Pr$i$-CH), 2.41 (d, 2H, $^2$J$_{HP}$ = 8.8 Hz, Ph$_2$P-CH$_2$), 3.85 (hept, 2H, $^3$J$_{HH}$ = 6.3 Hz, Dipp-Pr$i$-CH$_3$), 6.82 (t, 4H, $^3$J$_{HH}$ = 7.3 Hz, Ar-CH$_3$), 6.96 (m, 22H, Ar-CH$_3$), 7.20 (m, 4H, Ar-CH$_3$), 7.43 (m, 13H, Ar-CH$_3$). $^{13}$C($^1$H) NMR (C$_6$D$_6$, 101 MHz, 298 K): $\delta$ = 14.1 (Si-Pr$i$-CH), 17.9 and 18.2 (Si-Pr$i$-CH$_3$), 19.3 (d, $^1$J$_{CP}$ = 6.3 Hz, Ph$_2$P-CH$_2$), 24.8 and 26.6 (Dipp-Pr$i$-CH$_3$), 28.6 (Dipp-Pr$i$-CH), 124.4, 125.5, 128.7, 133.4, 133.5, 134.5, 134.6, 138.8, 138.8, 139.1, 139.1, 143.1, 144.1, 144.3 and 145.3 (Ar-C). $^{31}$P($^1$H) NMR (C$_6$D$_6$, 81 MHz, 298 K): $\delta$ = 9.6 (t, $^2$J$_{PP}$ = 18.0 Hz, Ph$_2$P-Ni-(PPh$_3$)$_2$), 39.7 (d, $^2$J$_{PP}$ = 14.7 Hz, Ph$_2$P-Ni-(PPh$_3$)$_2$). $^{29}$Si($^1$H) NMR (C$_6$D$_6$, 99 MHz, 298 K): $\delta$ = 8.3 (d, $^2$J$_{SiP}$ = 1.8 Hz, SiPr$i$-2). $\lambda_{max}$, nm (c, Lcm$^{-1}$mol$^{-1}$): 473 (1685), 362 (9160). MS/LIFDI-HRMS found (calcd) m/z: 888.1679 (888.1671) for [M-PPh$_3$-2CH$_3$+1H]$^+$.
N.B. Conducting the reaction with NiBr₂·DME in place of the related chloride leads to the formation of a mixture of [Ph₃P(Dipp(Cl)Ge)]Ni(PPh₃)₂ and [Ph₃P(Dipp(Br)Ge)]Ni(PPh₃)₂, with considerably shorted reaction times. This mixture could be used in further chemistry with no issues.

Attempted synthesis of [Ph₃P(Dipp(Br)]Ni(PPh₃)₂, 4-Br. Compound 1a was stirred with an excess of NiBr₂·DME in THF, in order to generate 3a in situ, and the mixture canula transferred onto a mixture of Zn powder and 2 equivs. Ph₃P. The resulting mixture became dark brown over the course of 2 hrs. Analysis indicated a small amount of a new product presumed to be 4-Br, along with large amounts of free Ph₃P and free ligand. One or two crystals formed from a diethyl ether extract of the reaction mixture, allowing for X-ray diffraction analysis of 4-Br (see Figure S83). Due to the very low yield, no further data was collected.

[Ph₃P(Dipp(NH₂)]Ni(PPh₃)₂, 5a. Compound 4a (20 mg, 0.016 mmol) was dissolved in 0.4 mL C₆D₆ in an NMR tube. An excess of ammonia was added to the NMR tube, which was then closed and shaken leading to an immediate colour change from deep red to bright orange, with concomitant formation of a colourless solid (NH₄Cl). The solution was filtered, and volatiles removed in vacuo to yield 5a as an orange powder (15 mg, 0.013 mmol, 83%). Dark orange crystals suitable for X-ray diffraction analysis were obtained by storage of a concentrated toluene solution layered with hexane at -32°C.

1H NMR (C₆D₆, 400 MHz, 298 K): δ = 0.50 (d, 6H, 3Jₖₖ = 6.6 Hz, Dipp-Pr¹-CH₃), 1.14 (m, 6H, Dipp-Pr¹-CH₃), 2.97 (s, 2H, Ph₂P-CH₃), 3.14 (s, 2H, Ge-NH₂), 3.79 (hept, 2H, 13Jₖₖ = 7.3 Hz, Dipp-Pr¹-CH₃), 6.67 (m, 3 H, Ar-CH), 6.81 (m, 6H, Ar-CH), 7.00 (m, 31H, Ar-CH), 7.32 (d, 4H, 3Jₖₖ = 6.6 Hz, Ar-CH), 7.48 (s, 9H, Ar-CH). 13C{¹H} NMR (C₆D₆, 101 MHz, 298 K): δ = 20.1 (Ph₂P-CH₃), 23.6 and 26.1 (Dipp-Pr¹-CH₃), 28.8 (Dipp-Pr¹-CH), 124.4, 125.2, 127.1, 131.6, 132.3, 134.3, 134.5, 136.1, 136.3, 140.2, 141.1 and 146.3 (Ar-C).

31P{¹H} NMR (C₆D₆, 81 MHz, 298 K): δ = 9.3 (t, 2Jₚₚ = 15.6 Hz, Ph₂P-Ni-(PPh₃)₂), 39.8 (d, 2Jₚₚ = 14.2 Hz, Ph₂P-Ni-(PPh₃)₂). 29Si{¹H} NMR (C₆D₆, 99 MHz, 298 K): δ = - 14.8 (d, 2Jₛₛ = 3.2 Hz, SPh₂). λₘₚₚ, nm ((ε, Lcm⁻¹mol⁻¹): 358 (5845). IR, ν/cm⁻¹ (ATR): 3354 and 3461 (br, w, Ge-NH₂). MS/LIFDI-HRMS found (calcd) m/z: 966.2156 (966.2253) for [M-PPh₃]⁺.

[Ph₃P(Dipp(NH₂)]Ni(PPh₃)₂, 5b. Compound 4b (200 mg, 0.17 mmol) was dissolved in 2 mL toluene, and an excess of ammonia was added to the flask at -78°C, which was sealed and shaken leading to an immediate colour change from deep red to bright orange, with the formation of considerable colourless precipitate. The flask was open, and the reaction warmed to ambient temperature. The solution was filtered, and all volatile removed in vacuo. The crude
product was dissolved in pentane, filtered, and stored to -32°C to obtain fine orange crystalline needles. The solid was filtered and washed with pentane to yield 5b as an orange powder (130 mg, 0.11 mmol, 66%). 1H NMR(C6D6, 400 MHz, 298 K): δ = 0.66 (d, 6H, 3JHH = 7.3 Hz, Si-Pri-CH3), 0.87 (d, 6H, 3JHH = 7.5 Hz, Si-Pri-CH3), 1.12 (d, 6H, 3JHH = 6.6 Hz, Dipp-Pri-CH3), 1.33 (m, 2H, Si-Pri-CH), 1.43 (d, 6H, 3JHH = 6.7 Hz, Dipp-Pri-CH3), 2.31 (d, 2H, 3JHP = 9.0 Hz, Ph2P-CH3), 2.98 (s, 2H, Ge-NH2), 3.90 (hept, 2H, 3JHH = 6.2 Hz, Dipp-Pri-CH3), 6.85 (t, 4H, 3JHH = 7.3 Hz, Ar-CH), 6.96 (m, 23H, Ar-CH), 7.32 (t, 4H, 3JHH = 8.1 Hz, Ar-CH), 7.40 (m, 12H, Ar-CH). 13C{1H} NMR (C6D6, 101 MHz, 298 K): δ = 14.3 (Si-Pri-CH), 18.2 and 18.5 (Si-Pri-CH3), 19.5 (Ph2P-CH2), 24.7 and 26.5 (Dipp-Pri-CH3), 28.1 (Dipp-Pri-CH), 124.7, 125.0, 127.6, 127.6, 127.7, 128.9, 133.3, 134.3, 134.3, 134.4, 140.2, 140.3, 140.4, 140.4, 140.5, 140.6, 142.2, 145.4, 145.6 and 146.1 (Ar-C). 31P{1H} NMR (C6D6, 81 MHz, 298 K): δ = 10.9 (t, 2JPP = 15.7 Hz, Ph2P-Ni-(PPh3)2), 39.3 (d, 2JPP = 15.7 Hz, Ph2P-Ni-(PPh3)2). 29Si{1H} NMR (C6D6, 99 MHz, 298 K): δ = 6.3 (d, 2JSiP = 1.8 Hz, SiPr2), λmax, nm (ε, Lcm⁻¹mol⁻¹): 358 (9220). IR, ν/cm⁻¹ (ATR): 3354 and 3461 (br, w, Ge-NH2). MS/LIFDI-HRMS found (calcd) m/z: 898.2479 (998.2566) for [M-PPh3]+.

N.B. Attempts to isolate the ammonia adduct of 4b by addition of ammonia to toluene solutions of 4b kept a low temperature, followed by careful layering with heptane and storage at -40°C, led only to the isolation of ammonia activation product 5b.

[5bPΦDippGe(OH)]Ni(PPh3)2, 6a. ‘Wet’ cyclohexylylaniline (100 mg, 0.16 mmol) was added to a stirring solution of 4a (200 mg, 0.16 mmol) in 5 mL toluene leading to an immediate colour change from deep red to light red-orange. The mixture was stirred for 30 min. All volatiles were then removed in vacuo and the residue extracted with diethyl ether, and filtered. Orange-red crystals of 6a suitable for X-ray diffraction analysis formed over the course of two hours at ambient temperature (133 mg, 0.11 mmol, 68%). 1H NMR(C6D6, 400 MHz, 298 K): δ = 0.47 (d, 6H, 3JHH = 6.3 Hz, Dipp-Pri-CH3), 1.10 (m, 6H, Dipp-Pri-CH3), 2.99 (s, 2H, Ph2P-CH3), 3.77 (hept, 2H, 3JHH = 6.4 Hz, Dipp-Pri-CH3), 4.15 (s, 1H, Ge-OH), 6.67 (m, 3H, Ar-CH), 6.83 (m, 6H, Ar-CH), 7.01 (m, 30H, Ar-CH), 7.34 (d, 4H, 3JHH = 7.0 Hz, Ar-CH), 7.54 (s, H, Ar-CH). 13C{1H} NMR (C6D6, 101 MHz, 298 K): δ = 19.4 (Ph2P-CH2), 23.3 and 26.2 (Dipp-Pri-CH3), 28.9 (Dipp-Pri-CH), 124.5, 125.7, 127.2, 128.9, 132.3, 134.5, 134.5, 134.6, 135.7, 135.8, 136.0, 138.8, 139.7, 139.9, 140.0 and 146.6 (Ar-C). 31P{1H} NMR (C6D6, 81 MHz, 298 K): δ = 9.0 (t, 2JPP = 15.8 Hz, Ph2P-Ni-(PPh3)2), 40.6 (d, 2JPP = 15.8 Hz, Ph2P-Ni-(PPh3)2). 29Si{1H} NMR (C6D6, 99 MHz, 298 K): δ = -14.4 (d, 2JSiP = 4.6 Hz, SiPh2). λmax, nm (ε, Lcm⁻¹mol⁻¹): 354 (18570). IR, ν/cm⁻¹ (ATR): 3547 (m, Ge-OH); MS/LIFDI-HRMS found (calcd) m/z: 967.2057 (967.2093) for [M-PPh3]+.
[\text{[Ph}^\text{iiiDippGe(OH)]Ni(PPh}_3)_2, 6b. Wet’ cyclohexylaniline (100 mg, 1.00 mmol) and 0.05 mL degassed H\textsubscript{2}O were added to a solution of 4b (200 mg, 0.17 mmol) in 5 mL toluene leading to an immediate colour change from deep red to light orange-red. The mixture was stirred for 30 min. All volatiles were subsequently removed \textit{in vacuo}, the residue extracted with diethyl ether, and filtered. Orange-red crystals of 6b suitable for X-ray diffraction analysis formed over the course of four hours (116 mg, 0.10 mmol, 59%). \textsuperscript{1}H NMR(C\textsubscript{6}D\textsubscript{6}, 400 MHz, 298 K): \(\delta = 0.68\) (d, 6H, \(^3\text{J}_{\text{HH}} = 7.3\) Hz, Si-Pr\textsuperscript{i}-CH\textsubscript{3}), 0.87 (d, 6H, \(^4\text{J}_{\text{HH}} = 7.5\) Hz, Si-Pr\textsuperscript{i}-CH\textsubscript{3}), 1.10 (d, 6H, \(^5\text{J}_{\text{HH}} = 6.7\) Hz, Dipp-Pr\textsuperscript{i}-CH\textsubscript{3}), 1.31 (m, 2H, Si-Pr\textsuperscript{i}-CH\textsubscript{3}), 1.38 (d, 6H, \(^3\text{J}_{\text{HH}} = 6.7\) Hz, Dipp-Pr\textsuperscript{i}-CH\textsubscript{3}), 2.33 (d, 2H, \(^2\text{J}_{\text{HP}} = 8.8\) Hz, Ph\textsubscript{2}P-CH\textsubscript{3}), 3.89 (m, 2H, Dipp-Pr\textsuperscript{i}-CH\textsubscript{3}), 3.95 (d, 1H, \(^4\text{J}_{\text{HP}} = 2.8\) Hz, Ge-OH), 6.85 (t, 4H, \(^3\text{J}_{\text{HH}} = 7.4\) Hz, Ar-CH\textsubscript{3}), 6.97 (m, 19H, Ar-CH\textsubscript{3}), 7.09 (m, 4H, Ar-CH\textsubscript{3}), 7.22 (t, 4H, \(^3\text{J}_{\text{HH}} = 8.2\) Hz, Ar-CH\textsubscript{3}), 7.46 (m, 12H, Ar-CH\textsubscript{3}). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (C\textsubscript{6}D\textsubscript{6}, 101 MHz, 298 K): \(\delta = 14.5\) and 14.5 (Si-Pr\textsuperscript{i}-CH\textsubscript{3}), 18.2 and 18.3 (Si-Pr\textsuperscript{i}-CH\textsubscript{3}), 18.7 (Ph\textsubscript{2}P-CH\textsubscript{3}), 24.2 and 26.7 (Dipp-Pr\textsuperscript{i}-CH\textsubscript{3}), 28.3 (Dipp-Pr\textsuperscript{i}-CH\textsubscript{3}), 124.7, 125.6, 127.6, 127.7, 128.9, 133.2, 133.4, 134.4, 134.5, 134.6, 139.9, 139.9, 140.0, 140.1, 140.2, 140.3, 144.8, 145.0 and 146.4 (Ar-C). \textsuperscript{31}P\{\textsuperscript{1}H\} NMR (C\textsubscript{6}D\textsubscript{6}, 81 MHz, 298 K): \(\delta = 11.17\) (t, \(^2\text{J}_{\text{PP}} = 15.8\) Hz, Ph\textsubscript{2}P-Ni-(PPh\textsubscript{3})\textsubscript{2}), 40.32 (d, \(^2\text{J}_{\text{PP}} = 16.00\) Hz, Ph\textsubscript{2}P-Ni-(PPh\textsubscript{3})\textsubscript{2}). \textsuperscript{29}Si\{\textsuperscript{1}H\} NMR (C\textsubscript{6}D\textsubscript{6}, 99 MHz, 298 K): \(\delta = 6.52\) (s, SiPr\textsubscript{2}). \(\lambda_{\text{max}}\), nm (\(\varepsilon,\ \text{Lcm}^{-1}\text{mol}^{-1}\)): 354 (17142). IR, \(\nu/cm^{-1}\) (ATR): 3551 (s, m, Ge-OH); MS/LIFDI-HRMS found (calcd) m/z: 899.2415 (899.2406) for [M-PPh\textsubscript{3}]\textsuperscript{+}.

\textbf{Reversibility experiments:}

Compound 4b (20 mg, 0.17 mmol) was dissolved in 0.4 mL C\textsubscript{6}D\textsubscript{6} in an NMR tube and the tube charged with ammonia, closed and shaken. The \textsuperscript{31}P NMR spectrum was measured to confirm the sole presence of 5b. All volatiles were removed \textit{in vacuo} and the mixture was redissolved in 0.4 mL C\textsubscript{6}D\textsubscript{6} followed by ultrasonication for 30 min. This cycle was repeated two more times, resulting in restoration of the dark red colouration attributable to dissolved 4b. \textsuperscript{1}H (Figure S70) and \textsuperscript{31}P (Figure S68) NMR spectroscopic analysis of the crude reaction confirmed a mixture with 78% 4b and 22% 5b/6b confirming the reversibility of the reaction of 4b with ammonia.

N. B. Related experiment using 4a also show reversibility, but considerably greater formation of hydroxide compound 6a, due to extremely high moisture sensitivity of this compound when compared with 4b.
Figure S1. $^1$H NMR spectrum of PhPhDippNK as a solution in THF-$d_8$ at ambient temperature. *indicates small amounts of TMEDA; # indicates small amounts of PhDippNH, which forms upon dissolution.

Figure S2. $^{31}$P NMR spectrum of PhPhDippNK as a solution in THF-$d_8$ at ambient temperature.
Figure S3. $^{13}$C NMR spectrum of $^{\text{PhPh}}$DippNK as a solution in THF-$d_8$ at ambient temperature. *indicates small amounts of TMEDA; #indicates small amounts of $^{\text{PhPh}}$DippNH, which forms upon dissolution.

Figure S4. $^{29}$Si NMR spectrum of $^{\text{PhPh}}$DippNK as a solution in THF-$d_8$ at ambient temperature.
Figure S5. $^1$H NMR spectrum of PhIP$^{\text{DippNK}}$ as a solution in THF-d$_8$ at ambient temperature. *indicates small amounts of TMEDA; #indicates small amounts of PhIP$^{\text{DippNH}}$, which forms upon dissolution.

Figure S6. $^{31}$P NMR spectrum of PhIP$^{\text{DippNK}}$ as a solution in THF-d$_8$ at ambient temperature.
Figure S7. $^{13}$C NMR spectrum of $^{\text{PhIPDippNK}}$ as a solution in THF-d$_8$ at ambient temperature.

Figure S8. $^{29}$Si NMR spectrum of $^{\text{PhIPDippNK}}$ as a solution in THF-d$_8$ at ambient temperature.
Figure S9. $^1$H NMR spectrum of 1a as a solution in C$_6$D$_6$ at ambient temperature.

Figure S10. $^{31}$P NMR spectrum of 1a as a solution in C$_6$D$_6$ at ambient temperature.
Figure S11. $^{13}$C NMR spectrum of 1a as a solution in C$_6$D$_6$ at ambient temperature.

Figure S12. $^{29}$Si NMR spectrum of 1a as a solution in C$_6$D$_6$ at ambient temperature.
Figure S13. Top: Experimental LIFDI/MS of 1a; Bottom: Calculated MS spectrum of 1a.

Figure S14. ¹H NMR spectrum of 1b as a solution in C₆D₆ at ambient temperature.
Figure S15. $^{31}$P NMR spectrum of 1b as a solution in C$_6$D$_6$ at ambient temperature.

Figure S16. $^{13}$C NMR spectrum of 1b as a solution in C$_6$D$_6$ at ambient temperature.
Figure S17. $^{29}$Si NMR spectrum of $1b$ as a solution in C$_6$D$_6$ at ambient temperature.

Figure S18. Top: Experimental LIFDI/MS of $1b$; Bottom: Calculated MS spectrum of $1b$. 
Figure S19. $^1$H NMR spectrum of 3a as a solution in C$_6$D$_6$ at ambient temperature.

Figure S20. $^{31}$P NMR spectrum of 3a as a solution in C$_6$D$_6$ at ambient temperature.
Figure S21. $^{13}$C NMR spectrum of 3a as a solution in C$_6$D$_6$ at ambient temperature.

Figure S22. $^{29}$Si NMR spectrum of 3a as a solution in C$_6$D$_6$ at ambient temperature.
Figure S23. Top: Experimental LIFDI/MS of 3a; Bottom: Calculated MS spectrum of 3a.

Figure S24. Top: Crude $^{31}$P NMR reaction mixture of 1 eq. 1a and 2 eq. NiBr$_2$-DME in toluene/THF; Bottom: Crude $^{31}$P NMR reaction mixture of 1 eq. 1a and 6 eq. NiBr$_2$-DME in toluene/THF.
Figure S25. $^1$H NMR spectrum of 3b as a solution in C$_6$D$_6$ at ambient temperature.

Figure S26. $^{31}$P NMR spectrum of 3b as a solution in C$_6$D$_6$ at ambient temperature.
**Figure S27.** $^{13}$C NMR spectrum of 3b as a solution in C$_6$D$_6$ at ambient temperature.

**Figure S28.** Crude $^{31}$P NMR reaction mixture of 1eq. 1b and 1eq. NiBr$_2$-DME in toluene/THF.
Figure S29. $^1$H NMR spectrum of 4a as a solution in C$_6$D$_6$ at ambient temperature. *indicates small amounts of diethyl ether.

Figure S30. $^{31}$P NMR spectrum of 4a as a solution in C$_6$D$_6$ at ambient temperature. *indicates small amounts of 6a.
Figure S31. Crude $^{31}$P NMR of reaction mixture of $1a$ with Ni(COD)$_2$ and 2 eq. PPh$_3$ in toluene, showing the formation of $4a$.

Figure S32. $^{31}$P NMR of a typical mixture of $[\text{PhPhDipp(Cl)Ge}]\text{Ni}(\text{PPh}_3)_2$ and $[\text{PhPhDipp(Br)Ge}]\text{Ni}(\text{PPh}_3)_2$. 
**Figure S33.** $^{13}$C NMR spectrum of 4a as a solution in C$_6$D$_6$ at ambient temperature.

**Figure S34.** $^{29}$Si NMR spectrum of 4a as a solution in C$_6$D$_6$ at ambient temperature.
Figure S35. *Top:* Experimental LIFDI/MS of 4a; *Bottom:* Calculated MS spectrum of 4a.

Figure S36. ATR-IR spectrum of 4a.
Figure S37. UV/vis spectrum of a $1.9 \times 10^{-4}$ M solution of 4a in toluene at ambient temperature.

Figure S38. $^1$H NMR spectrum of 4b as a solution in C$_6$D$_6$ at ambient temperature.
Figure S39. $^{31}$P NMR spectrum of 4b as a solution in C$_6$D$_6$ at ambient temperature. *indicates small amount of an unknown impurity.

Figure S40. $^{31}$P NMR of a typical mixture of [Ph$_2$Dipp(Cl)Ge]Ni(PPh$_3$)$_2$ and [Ph$_2$Dipp(Br)Ge]Ni(PPh$_3$)$_2$. 
Figure S41. $^{13}$C NMR spectrum of 4b as a solution in C$_6$D$_6$ at ambient temperature.

Figure S42. $^{29}$Si NMR spectrum of 4b as a solution in C$_6$D$_6$ at ambient temperature.
Figure S43. Top: Experimental LIFDI/MS of 4b; Bottom: Calculated MS spectrum of 4b.

Figure S44. ATR-IR spectrum of 4b.
Figure S45. UV/vis spectrum of a 1.9x10^{-4} M solution of 4b in toluene at ambient temperature.

Figure S46. ^1H NMR spectrum of 5a as a solution in C\textsubscript{6}D\textsubscript{6} at ambient temperature. *indicates small amounts of diethyl ether; #indicates small amounts of 6a.
Figure S47. $^{31}$P NMR spectrum of 5a as a solution in C$_6$D$_6$ at ambient temperature. *indicates small amounts of 6a.
**Figure S48.** $^{13}$C NMR spectrum of 5a as a solution in C$_6$D$_6$ at ambient temperature.

**Figure S49.** $^{29}$Si NMR spectrum of 5a as a solution in C$_6$D$_6$ at ambient temperature.

**Figure S50.** *Top:* Experimental LIFDI/MS of 5a; *Bottom:* Calculated MS spectrum of 5a.
Figure S51. ATR-IR spectrum of 5a.

Figure S52. UV/vis spectrum of a 7.7x10^{-5} M solution of 5a in toluene at ambient temperature.
Figure S53. $^1$H NMR spectrum of $5b$ as a solution in $\text{C}_6\text{D}_6$ at ambient temperature.

Figure S54. $^{31}$P NMR spectrum of $5b$ as a solution in $\text{C}_6\text{D}_6$ at ambient temperature. *indicates small amounts of $6b$, *indicates small amounts of an unknown impurity.
Figure S55. $^{13}$C NMR spectrum of 5b as a solution in C$_6$D$_6$ at ambient temperature.

Figure S56. $^{29}$Si-NMR spectrum of 5b as a solution in C$_6$D$_6$ at ambient temperature.
Figure S57. *Top:* Experimental LIFDI/MS of 5b; *Bottom:* Calculated MS spectrum of 5b.

Figure S58. ATR-IR spectrum of 5b.
Figure S59. UV/vis spectrum of a $7.7 \times 10^5$ M solution of 5b in toluene at ambient temperature.

Figure S60. $^1$H NMR spectrum of 6a as a solution in C$_6$D$_6$ at ambient temperature.
Figure S61. $^{31}$P NMR spectrum of 6a as a solution in C$_6$D$_6$ at ambient temperature.

Figure S62. $^{13}$C NMR spectrum of 6a as a solution in C$_6$D$_6$ at ambient temperature.
Figure S63. $^{29}$Si NMR spectrum of 6a as a solution in $\text{C}_6\text{D}_6$ at ambient temperature.

Figure S64. Top: Experimental LIFDI/MS of 6a; Bottom: Calculated MS spectrum of 6a.
Figure S65. ATR-IR spectrum of 6a.

Figure S66. UV/vis spectrum of a 7.7x10⁻⁶ M solution of 6a in toluene at ambient temperature.
Figure S67. $^1$H NMR spectrum of 6b as a solution in C$_6$D$_6$ at ambient temperature.

Figure S68. $^{31}$P NMR spectrum of 6b as a solution in C$_6$D$_6$ at ambient temperature.
Figure S69. $^{13}$C NMR spectrum of 6b as a solution in $C_6D_6$ at ambient temperature.

Figure S70. $^{29}$Si NMR spectrum of 6b as a solution in $C_6D_6$ at ambient temperature.
Figure S71. Top: Experimental LIFDI/MS of 6b; Bottom: Calculated MS spectrum of 6b.

Figure S72. ATR-IR spectrum of 6b.
Figure S73. UV/vis spectrum of a $7.7 \times 10^{-5}$ M solution of 6b in toluene at ambient temperature.

Figure S74. Top: $^{31}$P NMR spectrum of 4b; Middle: $^{31}$P NMR spectrum of 5b; Bottom: Crude $^{31}$P-NMR reaction mixture of 4b with ammonia after three cycles of removing ammonia from the reaction mixture and ultrasonication.
Figure S75. Crude $^1$H NMR reaction mixture of 4b with ammonia after three cycles of removing ammonia from the reaction mixture and ultrasonication. Mixture of 78% 4b (22% 5b/6b) and presence of ammonia can be seen.

Figure S76. Top: Cutout from $^1$H NMR spectrum of 6b; Top/Middle: Cutout from $^1$H NMR spectrum of 4b; Bottom/Middle: Cutout from $^1$H NMR spectrum of 5b; Bottom: Cutout from crude $^1$H NMR reaction mixture of 4b with ammonia after three cycles of removing volatiles and ultrasonication.
2. X-Ray Crystallographic details

Single crystals of $^{\text{PhiDippNH}}$, $^{\text{PhPhDippNK}}$, 1a/b, 1a·Et$_2$O, 2, 2', 3a/b, 4a/b, 4-Br, 5a, and 6a/b suitable for X-ray structural analysis were mounted in perfluoroalkyl ether oil on a nylon loop and positioned in a 150 K cold N$_2$ gas stream. Data collection was performed with a STOE StadiVari diffractometer (MoK$\alpha$ radiation) equipped with a Dectris PILATUS 300K detector. Structures were solved by Direct Methods (SHELXS-97) and refined by full-matrix least-squares calculations against $F^2$ (SHELXL-2018). The positions of the hydrogen atoms were calculated and refined using a riding model, aside from protons on N2 (5a) and O1 (6a/b). All non-hydrogen atoms were treated with anisotropic displacement parameters. Crystal data, details of data collections, and refinements for all structures can be found in their CIF files, which are available free of charge via www.ccdc.cam.ac.uk/data_request/cif, and are summarized in Tables S1-S3. In compounds 2 and 4a' the electron density of highly disordered co-crystallized solvent molecules (details in respective CIFs) was removed using the PLATON SQUEEZE function.

![Figure S77](image_url) Molecular structure of $^{\text{PhiDippNH}}$, with thermal ellipsoids at 40% probability. Hydrogen atoms are omitted for clarity, aside from that at N1. Selected bond distances (Å) and angles (°): P1···N1 3.354(2); Si1-N1 1.753(2); Si1-C19 1.894(2); P1-C19 1.868(2); P1-C19-Si1 114.73(1); N1-Si1-C19 105.62(9).

![Figure S78](image_url) Molecular structure of $^{\text{PhPhDippNK·2(THF)(TMEDA)}}$, with thermal ellipsoids at 40% probability. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): N1-K001 3.270(2); N2-K001 2.275(5); P1-K001 3.510(2); N1-K001-P1 69.98(5); P1-K001-N2 81.16(1).
Figure S79. Molecular structure of 1a, with thermal ellipsoids at 40% probability. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ge1-Cl1 2.3404(9); Ge1-P1 2.4547(9); Ge1-N1 1.925(2); N1-Ge1-Cl1 101.45(5); Cl1-Ge1-P1 86.08(2); N1-Ge1-P1 85.38(5).

Figure S80. Molecular structure of 2', with thermal ellipsoids at 40% probability. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ni1-N2 1.898(3); N1-Br2 2.3276(6); P1-Ni1 2.175(1); Ni1-Ge1 2.2672(6); N1-Ge1 1.856(3); Ge1-Ni1-P1 88.54(3); N2-Ni1-Ge1 88.59(9); P1-Ni1-Br2 94.86(3); N2-Ni1-Br2 91.75(9).
Figure S81. Molecular structure of 3b, with thermal ellipsoids at 40% probability. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ge1-Br1 2.468(1); Ge1-P1 2.450(2); Ge1-N1 1.928(6); N1-Ge1-Br1 101.83(2); Br1-Ge1-P1 85.83(4); N1-Ge1-P1 85.92(2).

Figure S82. Molecular structure of 4a, with thermal ellipsoids at 40% probability. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ge1-Ni1 2.192(1); N1-Ge1 1.869(2); P1-Ni1 2.204(1); P2-Ni1 2.2054(9); P3-Ni1 2.2030(8); N1-Ge1-Cl1 98.62(8); Ni1-Ge1-N1 131.96(6); Ni1-Ge1-Cl1 129.03(6).
Figure S83. Molecular structure of 4-Br, with thermal ellipsoids at 40% probability. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ge1-Ni1 2.1995(7); N1-Ge1 1.876(3); P1-Ni1 2.208(1); P2-Ni1 2.203(1); P3-Ni1 2.215(1); N1-Ge1-Br1 98.86(9); Ni1-Ge1-N1 132.38(9); Ni1-Ge1-Br1 128.46(2).

Figure S84. Molecular structure of 6a, with thermal ellipsoids at 40% probability. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ge1-Ni1 2.1956(7); N1-Ge1 1.892(3); O1-Ge1 1.780(2); P1-Ni1 2.209(1); P2-Ni1 2.216(1); P3-Ni1 2.196(1); N1-Ge1-O1 100.67(1); Ni1-Ge1-O1 130.08(9); Ni1-Ge1-N1 129.24(8).
Table S1. Summary of X-ray crystallographic data for \( \text{PhiP}^{\text{DippNH}} \), \( \text{PhPh}^{\text{DippNK}-2(\text{THF})(\text{TMEDA})} \), and 1a/b.

|                  | \( \text{PhiP}^{\text{DippNH}} \) | \( \text{PhPh}^{\text{DippNK}-2(\text{THF})(\text{TMEDA})} \) | 1a                  | 1a-Et2O             | 1b                  |
|------------------|----------------------------------|----------------------------------|---------------------|---------------------|---------------------|
| empirical form.  | \( \text{C}_{31}\text{H}_{44}\text{NPSi} \) | \( \text{C}_{48}\text{H}_{63}\text{KN}_{2} \text{O}_{2}\text{PSi} \) | \( \text{C}_{37}\text{H}_{39}\text{ClGeNPSi} \) | \( \text{C}_{37}\text{H}_{39}\text{ClGeNPSi} \) | \( \text{C}_{37}\text{H}_{39}\text{ClGeNPSi} \) |
| formula wt       | 489.73                           | 798.16                           | 664.79              | 738.91              | 635.82              |
| crystal syst.    | monoclinic                       | triclinic                         | triclinic           | triclinic           | monoclinic           |
| space group      | \( \text{C}2/c \)                | \( \text{P}-1 \)                  | \( \text{P}-1 \)    | \( \text{P}-1 \)    | \( \text{P}2_1/c \) |
| \( a \) (Å)      | 35.733(7)                        | 11.280(2)                        | 11.000(2)           | 11.250(2)           | 15.550(3)           |
| \( b \) (Å)      | 9.740(19)                        | 13.730(3)                        | 12.100(2)           | 17.780(4)           | 19.910(4)           |
| \( c \) (Å)      | 17.970(4)                        | 15.610(3)                        | 13.500(3)           | 20.520(4)           | 21.820(4)           |
| \( \alpha \) (deg.) | 90                               | 84.30(3)                         | 96.00(3)            | 88.30(3)            | 90                  |
| \( \beta \) (deg.) | 107.22(3)                        | 83.70(3)                         | 93.00(3)            | 75.70(3)            | 95.60(3)            |
| \( \gamma \) (deg.) | 90                               | 72.90(3)                         | 109.00(3)           | 73.30(3)            | 90                  |
| vol (Å\(^3\))   | 5974(2)                          | 2291.0(9)                        | 1682.5(7)           | 3805.8(15)          | 6723(2)             |
| \( Z \)          | 8                                | 2                                | 2                   | 4                   | 8                   |
| \( \rho \text{(calc. (g.cm}^{-3}) \) | 1.089                           | 1.157                           | 1.312               | 1.290               | 1.256               |
| \( \mu \) (mm\(^{-1}\)) | 0.150                           | 0.215                           | 1.099               | 0.981               | 1.097               |
| \( F(000) \)     | 2128                             | 858                              | 692                 | 1552                | 2680                |
| \( T \) (K)      | 150(2)                           | 150(2)                           | 150(2)              | 150(2)              | 150(2)              |
| reflns collect. | 21921                            | 22863                            | 16730               | 38663               | 76019               |
| unique reflns    | 5840                             | 8979                             | 6600                | 14909               | 15430               |
| \( R \text{int.} \) | 0.0652                           | 0.0469                           | 0.0225              | 0.0734              | 0.1118              |
| \( R1 [b-2\sigma(b)] \) | 0.0489                           | 0.0641                           | 0.0318              | 0.0504              | 0.0570              |
| \( wR2 \text{[all data]} \) | 0.1441                           | 0.1979                           | 0.0855              | 0.1315              | 0.1237              |
| CCDC No.         | 2057308                          | 2057309                          | 2057295             | 2057296             | 2057297             |
**Table S2.** Summary of X-ray crystallographic data for 2, 2', 3a/b, and 4a.

|                | 2                  | 2'                 | 3a                  | 3b                  | 4a                  |
|----------------|--------------------|--------------------|---------------------|---------------------|---------------------|
| **empirical form.** | C_{74}H_{78}Br_{6}Ge_{2}N_{2}Ni_{2}P_{2}Si_{2} & C_{41}H_{44}Br_{2}ClGeN_{3}NiPSi & C_{31}H_{43}BrGeNPSi & C_{31}H_{43}BrGeNPSi & C_{43}H_{45}BrGeNPSi |
| formula wt     | 1855.56            | 964.42             | 787.36              | 641.22              | 1256.49             |
| crystal syst.  | monoclinic         | monoclinic         | triclinic           | triclinic           | triclinic           |
| space group    | C2/c               | P2_1/c             | P-1                 | P-1                 | P-1                 |
| a (Å)          | 40.613(8)          | 20.250(4)          | 11.330(2)           | 11.110(2)           | 12.160(2)           |
| b (Å)          | 9.870(2)           | 11.150(2)          | 13.510(3)           | 17.260(4)           | 13.520(3)           |
| c (Å)          | 23.160(5)          | 18.550(4)          | 13.610(3)           | 18.290(4)           | 20.800(4)           |
| α (deg.)       | 90                 | 90                 | 79.10(3)            | 65.10(3)            | 75.40(3)            |
| β (deg.)       | 101.59(3)          | 94.50(3)           | 86.70(3)            | 88.40(3)            | 89.00(3)            |
| γ (deg.)       | 90                 | 90                 | 69.60(3)            | 85.30(3)            | 70.90(3)            |
| vol (Å³)       | 9094(3)            | 4175.4(15)         | 1917.3(8)           | 3170.5(13)          | 3119.1(13)          |
| Z              | 4                  | 4                  | 2                   | 8                   | 2                   |
| ρ(calc) (g.cm⁻³) | 1.355              | 1.534              | 1.364               | 1.343               | 1.338               |
| μ (mm⁻¹)       | 3.795              | 3.248              | 1.945               | 2.334               | 1.080               |
| F(000)         | 3696               | 1948               | 812                 | 1328                | 1307                |
| T (K)          | 150(2)             | 150(2)             | 150(2)              | 150(2)              | 150(2)              |
| refns collect. | 8903               | 56139              | 16584               | 44725               | 31898               |
| unique refns   | 8903               | 8203               | 7387                | 12450               | 12162               |
| R int          | 0.0897             | 0.0421             | 0.0636              | 0.0291              | 0.0301              |
| R1 [I>2σ(I)]   | 0.0470             | 0.0352             | 0.0513              | 0.0609              | 0.0336              |
| wR2 (all data) | 0.1402             | 0.0907             | 0.1598              | 0.1968              | 0.0834              |
| CCDC No.       | 2057298            | 2057299            | 2057300             | 2057301             | 2057302             |
Table S3. Summary of X-ray crystallographic data for compounds 4-Br, 4b, 5a, and 6a/b.

|                | 4-Br  | 4b-Et₂O | 5a   | 6a-Et₂O | 6b-Et₂O |
|----------------|-------|---------|------|---------|---------|
| empirical form | C₇₃H₆₉BrGeNNiP₃Si | C₇₃H₆₃ClGeNNiO₃P₃Si | C₇₃H₇₁GeN₂NiP₃Si | C₇₃H₆₉GeNNiO₂P₃Si | C₇₃H₆₄GeNNiO₂P₃Si |
| formula wt     | 1292.50 | 1254.13 | 1228.61 | 1303.72 | 1235.69 |
| crystal syst.  | triclinic | monoclinic | triclinic | monoclinic | monoclinic |
| space group    | P-1 | P2₁/c | P-1 | P2₁/c | P2₁/c |
| a (Å)          | 12.680(3) | 17.370(4) | 12.180(2) | 17.680(4) | 17.430(4) |
| b (Å)          | 15.530(3) | 19.770(4) | 13.550(3) | 19.180(4) | 19.840(4) |
| c (Å)          | 19.470(4) | 19.410(4) | 20.860(4) | 19.180(4) | 19.410(4) |
| α (deg.)       | 98.60(3) | 90 | 75.10(3) | 90 | 90 |
| β (deg.)       | 92.00(3) | 102.70(3) | 88.30(3) | 108.80(3) | 103.40(3) |
| γ (deg.)       | 91.30(3) | 90 | 70.40(3) | 90 | 90 |
| vol (Å³)       | 3787.1(13) | 6502(2) | 3128.1(13) | 6629(3) | 6529(2) |
| Z              | 2 | 4 | 2 | 4 | 4 |
| ρ(calc) (g.cm⁻³) | 1.133 | 1.281 | 1.304 | 1.306 | 1.257 |
| μ (mm⁻¹)       | 1.288 | 0.928 | 0.922 | 0.876 | 0.885 |
| F(000)         | 1336 | 2640 | 1284 | 2736 | 2608 |
| T (K)          | 150(2) | 150(2) | 150(2) | 150(2) | 150(2) |
| reflns collect. | 56477 | 71318 | 32911 | 73271 | 73734 |
| unique reflns  | 15676 | 12767 | 12253 | 13006 | 12827 |
| R_{int}        | 0.0410 | 0.0524 | 0.0395 | 0.0868 | 0.0946 |
| R1 [I>2σ(I)]   | 0.0531 | 0.0380 | 0.0364 | 0.0426 | 0.0454 |
| wR2 (all data) | 0.1658 | 0.1021 | 0.0912 | 0.1056 | 0.1189 |
| CCDC No.       | 2057304 | 2057303 | 2057305 | 2057306 | 2057307 |
3. Computational methods and details

DFT calculations were performed at the ωB97X-D3(SMD=benzene)/def2-TZVPP//ωB97X-D3(SMD=benzene)/def2-SVP level of theory. Stationary points on the potential energy surface (PES) were characterized by harmonic vibrational frequency calculations. Transition states, which had one imaginary frequency, were analysed by intrinsic reaction coordinate (IRC) calculations to confirm the corresponding intermediates. Calculations were carried out using the GAUSSIAN 16 program suite.

**Table S4.** NBO analysis of the central GeNi moiety in 4'.

| Bond | Occupation | Atom | s-character | p-character | d-character |
|------|------------|------|-------------|-------------|-------------|
|      | 1.95       | Ge   | 76.43%      | 11.76%      | 0.01%       |
|      |            | Ni   | 23.57%      | 72.92%      | 1.19%       |

**Table S5.** NBO analysis of the central GeNi moiety in 5'.

| Bond | Occupation | Atom | s-character | p-character | d-character |
|------|------------|------|-------------|-------------|-------------|
|      | 1.93       | Ge   | 74.06%      | 17.97%      | 0.01%       |
|      |            | Ni   | 25.94%      | 71.34%      | 1.84%       |

**Table S6.** NBO analysis of the central GeNi moiety in 6'.

| Bond | Occupation | Atom | s-character | p-character | d-character |
|------|------------|------|-------------|-------------|-------------|
|      | 1.94       | Ge   | 74.22%      | 14.24%      | 0.01%       |
|      |            | Ni   | 25.78%      | 71.56%      | 1.57%       |

**Table S7.** Calculated bond lengths [Å], NPA charges of Ge and Ni atoms, Wiberg Bond Index (WBI) and Mayer Bond Order (MBO) in 4', 5', and 6'.

| Bond length [Å] | NPA charge | WBI//MBO             |
|-----------------|------------|----------------------|
| Ge-Ni           | Ge-Cl/Ge-NH₂/Ge-OH | Ge | Ni | Ge-Ni | Ge-Cl/Ge-NH₂/Ge-OH |
| 4'  | 2.161 | 2.263/-/- | +1.13 | -0.79 | 1.20/1.13 | 0.73/-/-/0.82/-/-|
| 5'  | 2.203 | -/1.816/- | +1.34 | -0.82 | 1.11/0.98 | -0.76/-/-/1.10/-/-|
| 6'  | 2.177 | -/-1.801 | +1.40 | -0.83 | 1.17/1.07 | -/-0.61/-/-/0.93|
Figure S85. HOMO (left, –6.60 eV) and LUMO (right, 0.62 eV) of 4'.

Figure S86. HOMO (left, –6.35 eV) and LUMO (right, 0.96 eV) of 5'.

Figure S87. HOMO (left, –6.50 eV) and LUMO (right, 0.90 eV) of 6'.
| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| N  | -5.007308 | -2.385914 | 2.062789 |
| H  | -4.703003 | -1.642495 | 2.691934 |
| H  | -5.799601 | -1.993127 | 1.553879 |
| H  | -5.411240 | -3.098894 | 2.670647 |

**Table S9.** Cartesian geometry of 4’ in Angstrom [Å].

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| Ge | -1.870584 | -0.332556 | 0.541523 |
| Ni | 0.211344 | 0.003890 | 0.068217 |
| P  | -0.004884 | 0.794045 | -1.990583 |
| P  | 0.987306 | 1.324620 | 1.647434 |
| Si | -3.237799 | 0.601204 | -2.113317 |
| P  | 1.389603 | -1.852767 | 0.003324 |
| N  | -3.396657 | -0.130500 | -0.492323 |
| Cl | -2.857983 | -0.975142 | 2.473316 |
| C  | -4.687468 | -0.585130 | -0.079796 |
| C  | -0.127548 | 2.604796 | -2.365330 |
| C  | -3.523758 | 2.458552 | -2.095749 |
| C  | -1.384481 | 2.812171 | 1.952527 |
| H  | -1.565031 | 2.534998 | 0.910331 |
| C  | 1.304893  | 0.377478 | -3.231769 |
| C  | -1.529197 | 0.178117 | -2.826959 |
| H  | -1.467404 | -0.922533 | -2.833062 |
| H  | -1.547071 | 0.490936 | -3.885743 |
| C  | -2.307941 | 3.616412 | 2.616675 |
| H  | -3.197498 | 3.970632 | 2.089769 |
| C  | -2.101622 | 3.954450 | 3.952840 |
| H  | -2.831461 | 4.573068 | 4.481647 |
| C  | -0.315001 | 3.061356 | 3.678936 |
|   |       |       |       |
|---|-------|-------|-------|
| H | -0.372922 | 2.346581 | -4.505958 |
| C | 2.209800  | 2.603691  | 1.116025  |
| C | 1.235047  | -0.748040  | -4.060551  |
| H | 0.361693  | -1.404044  | -4.035694  |
| C | -5.560693 | 0.271465  | 0.619629  |
| C | 2.449524  | 1.186450  | -3.299419  |
| H | 2.525701  | 2.073184  | -2.663939  |
| C | 1.228944  | -3.167914  | 1.302717  |
| C | -0.319198 | 5.353310  | -2.913604  |
| H | -0.393463 | 6.422625  | -3.129025  |
| C | -0.413725 | 4.422046  | -3.951080  |
| H | -0.560230 | 4.761466  | -4.979903  |
| C | 3.205375  | -1.554783  | -0.041278  |
| C | 3.953602  | -1.513738  | 1.142767  |
| H | 3.491171  | -1.785116  | 2.095292  |
| C | 3.418059  | -0.252797  | -4.981168  |
| C | -0.023079 | 3.546102  | -1.343109  |
| H | 0.147851  | 3.205903  | -0.323202  |
| C | 3.494309  | 0.877712  | -4.165247  |
| H | 4.376782  | 1.522674  | -4.198076  |
| C | -0.964282 | 3.492001  | 4.612604  |
| H | -0.797702 | 3.747101  | 5.662325  |
| C | 1.889125  | 0.508715  | 3.034364  |
| C | -0.118940 | 4.913565  | -1.608819  |
| H | -0.029549 | 5.632132  | -0.789783  |
| C | -4.068542 | -2.886979  | -0.935933  |
| C | 3.174894  | -0.916970  | 5.079945  |
| H | 3.679324  | -1.476260  | 5.872368  |
| C | -5.105600 | 1.630903  | 1.077605  |
| C | 3.188335  | 0.845851  | 3.425300  |
| H | 3.717616  | 1.661349  | 2.927516  |
| C | -0.230746 | 2.349963  | 2.597955  |
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | 2.285196  | -1.062107 | -4.926020 |
| H       | 2.210911  | -1.949594 | -5.559996 |
| C       | 3.826583  | 0.137632  | 4.444335  |
| H       | 4.843913  | 0.411188  | 4.736226  |
| C       | 5.290312  | -1.119136 | 1.126779  |
| H       | 5.853308  | -1.094843 | 2.063338  |
| C       | 2.057521  | -3.690334 | -2.127695 |
| H       | 3.108498  | -3.601307 | -1.843813 |
| C       | 5.165482  | -0.782508 | -1.253713 |
| H       | 5.627995  | -0.490355 | -2.199969 |
| C       | 3.828814  | -1.174799 | -1.238005 |
| H       | 3.262811  | -1.174017 | -2.171440 |
| C       | -5.062120 | -1.917437 | -0.352820 |
| C       | -6.345372 | -2.346820 | -0.003832 |
| H       | -6.641931 | -3.376249 | -0.225297 |
| C       | 1.235639  | -0.542287 | 3.691548  |
| H       | 0.213664  | -0.803603 | 3.404816  |
| C       | 0.076054  | -3.216885 | 2.087689  |
| H       | -0.692524 | -2.449699 | 1.978786  |
| C       | 1.075476  | -2.961538 | -1.448611 |
| C       | -0.033899 | 2.700386  | 3.939627  |
| H       | 0.854234  | 2.350128  | 4.471850  |
| C       | -6.835851 | -0.195251 | 0.953898  |
| H       | -7.519613 | 0.469542  | 1.490064  |
| C       | 4.082732  | 4.443820  | 0.123394  |
| H       | 4.806431  | 5.162982  | -0.268852 |
| C       | 3.161229  | 2.212440  | 0.165272  |
| H       | 3.156586  | 1.183892  | -0.205726 |
| C       | 1.872293  | -1.251356 | 4.705890  |
| H       | 1.352024  | -2.076517 | 5.198814  |
| C       | 2.209375  | 3.929067  | 1.563990  |
| H       | 1.472662  | 4.262618  | 2.298717  |
|   | X         | Y         | Z        |
|---|-----------|-----------|----------|
| C | 1.712263  | -4.535771 | -3.182040|
| H | 2.496500  | -5.084593 | -3.710057|
| C | 4.098959  | 3.120875  | -0.318662|
| H | 4.837462  | 2.795120  | -1.055969|
| C | 3.135907  | 4.844895  | 1.063632 |
| H | 3.114569  | 5.880390  | 1.412896 |
| C | -7.237595 | -1.487715 | 0.630718 |
| H | -8.240067 | -1.833722 | 0.895054 |
| C | 5.902178  | -0.752252 | -0.070348|
| H | 6.950132  | -0.441817 | -0.081509|
| C | 2.186449  | -4.181303 | 1.456034 |
| H | 3.090824  | -4.182355 | 0.841174 |
| C | 2.002689  | -5.197383 | 2.389742 |
| H | 2.762819  | -5.975956 | 2.498399 |
| C | 0.378659  | -4.685114 | -3.559078|
| H | 0.110555  | -5.348558 | -4.385434|
| C | -0.261451 | -3.132133 | -1.827599|
| H | -1.039065 | -2.579007 | -1.294092|
| C | 0.851446  | -5.225853 | 3.179408 |
| H | 0.707966  | -6.023825 | 3.913352 |
| C | -0.115439 | -4.236965 | 3.020250 |
| H | -1.026623 | -4.248470 | 3.624239 |
| C | -0.612510 | -3.989815 | -2.867136|
| H | -1.664385 | -4.109556 | -3.140666|
| H | -5.936153 | 2.194974  | 1.525476 |
| H | -4.682698 | 2.231104  | 0.261262 |
| H | -4.319949 | 1.523739  | 1.843732 |
| H | -4.545563 | -3.845941 | -1.181343|
| H | -3.266427 | -3.097042 | -0.207106|
| H | -3.587057 | -2.501483 | -1.845907|
| C | -4.505613 | -0.121942 | -3.293060|
| H | 4.239577  | -0.500692 | -5.658438|
Table S10. Cartesian geometry of transition state (6.5 kcal/mol) in Figure S84 in Angstrom [Å].

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|----------|---------------|---------------|---------------|
| C        | 1.332813      | -4.301150     | 1.771785      |
| C        | 0.958085      | -2.952867     | 1.683386      |
| C        | 0.314052      | -2.362920     | 2.770756      |
| C        | 0.039661      | -3.097121     | 3.925200      |
| C        | 0.409218      | -4.437697     | 4.000901      |
| C        | 1.060614      | -5.038400     | 2.920636      |
| P        | 1.269145      | -1.938593     | 0.165791      |
| Ni       | 0.265581      | 0.012319      | 0.029870      |
| P        | 0.110246      | 0.613637      | -2.086590     |
| C        | 1.359262      | -0.076712     | -3.270381     |
| C        | 1.179555      | -1.320037     | -3.888563     |
| C        | 2.166487      | -1.855405     | -4.717361     |
| C        | 3.348378      | -1.153756     | -4.946905     |
| C        | 3.537145      | 0.088823      | -4.339959     |
| C        | 2.553368      | 0.619691      | -3.509564     |
| C        | 0.818833      | -3.215854     | -1.104327     |
| C        | 1.723618      | -4.074189     | -1.737868     |
| C        | 1.281061      | -5.018365     | -2.665519     |
| C        | -0.074765     | -5.132263     | -2.963018     |
| C        | -0.990682     | -4.297956     | -2.321101     |
| C        | -0.543281     | -3.345123     | -1.409331     |
| C        | 3.113845      | -1.954443     | 0.109460      |
| Element | X-coordinate | Y-coordinate | Z-coordinate |
|---------|--------------|--------------|--------------|
| C       | 3.877841     | -2.068876    | 1.276522     |
| C       | 5.265465     | -1.926382    | 1.238231     |
| C       | 5.913863     | -1.678688    | 0.030883     |
| C       | 5.163554     | -1.571823    | -1.140440    |
| C       | 3.777976     | -1.698860    | -1.099431    |
| P       | 1.118596     | 1.459405     | 1.455945     |
| C       | 1.663145     | 0.854959     | 3.116170     |
| C       | 2.992274     | 0.498404     | 3.364608     |
| C       | 3.368587     | -0.026132    | 4.602082     |
| C       | 2.422981     | -0.193423    | 5.610577     |
| C       | 1.092836     | 0.154974     | 5.370636     |
| C       | 0.714074     | 0.663656     | 4.131505     |
| Ge      | -1.860001    | -0.198421    | 0.567545     |
| N       | -2.664507    | -2.844587    | 1.373095     |
| C       | 0.079316     | 2.912754     | 1.959557     |
| C       | -0.978531    | 3.292452     | 1.129121     |
| C       | -1.773493    | 4.398109     | 1.426381     |
| C       | -1.528698    | 5.136562     | 2.581534     |
| C       | -0.488011    | 4.761558     | 3.431658     |
| C       | 0.309635     | 3.661963     | 3.122450     |
| C       | 2.678482     | 2.285250     | 0.878707     |
| C       | 3.409081     | 1.624463     | -0.114190    |
| C       | 4.599838     | 2.156799     | -0.605094    |
| C       | 5.066124     | 3.377295     | -0.121861    |
| C       | 4.339312     | 4.054127     | 0.858225     |
| C       | 3.157480     | 3.511142     | 1.359268     |
| Cl      | -2.788495    | 0.175160     | 2.613534     |
| N       | -3.356584    | 0.015186     | -0.545169    |
| Si      | -3.107341    | 0.704418     | -2.162717    |
| C       | -3.171900    | 2.584000     | -2.143995    |
| C       | -4.685195    | -0.330026    | -0.154190    |
| C       | -5.500138    | 0.583745     | 0.551858     |
| Element | X Coordinate | Y Coordinate | Z Coordinate |
|---------|--------------|--------------|--------------|
| C       | -6.783949    | 0.188000     | 0.944262     |
| C       | -7.274842    | -1.078548    | 0.648781     |
| C       | -6.478331    | -1.967945    | -0.064599    |
| C       | -5.192223    | -1.612807    | -0.481056    |
| C       | -5.046667    | 1.983379     | 0.881075     |
| C       | -4.404879    | -2.612026    | -1.295880    |
| C       | -1.465934    | 0.044633     | -2.854723    |
| C       | 0.186061     | 2.375846     | -2.663751    |
| C       | -0.201677    | 2.744812     | -3.960652    |
| C       | -0.116264    | 4.068878     | -4.381362    |
| C       | 0.370168     | 5.051276     | -3.515091    |
| C       | 0.776278     | 4.696455     | -2.232436    |
| C       | 0.683528     | 3.367211     | -1.816842    |
| C       | -4.449474    | 0.143951     | -3.351572    |
| H       | -1.173127    | 2.700957     | 0.231564     |
| H       | -1.506077    | -1.047548    | -2.704781    |
| H       | -1.467336    | 0.201946     | -3.946834    |
| H       | -2.589445    | 4.679128     | 0.754942     |
| H       | -2.151953    | 6.001049     | 2.824906     |
| H       | -0.572181    | 1.990341     | -4.660533    |
| H       | 0.265710     | -1.893829    | -3.718615    |
| H       | 2.717769     | 1.595045     | -3.043366    |
| H       | 0.436560     | 6.090687     | -3.847311    |
| H       | -0.427335    | 4.338202     | -5.394082    |
| H       | 3.387567     | -2.261738    | 2.233520     |
| H       | 1.014643     | 3.100321     | -0.815370    |
| H       | 4.457260     | 0.652963     | -4.515453    |
| H       | -0.295286    | 5.328148     | 4.346128     |
| H       | 1.168951     | 5.448675     | -1.543163    |
| H       | 2.721515     | -0.592906    | 6.583163     |
| H       | 3.748864     | 0.630395     | 2.587142     |
| H       | 2.004238     | -2.830089    | -5.184297    |
|     | X        | Y        | Z        |
|-----|----------|----------|----------|
| H   | 4.413669 | -0.294630| 4.777716 |
| H   | 5.840390 | -2.012478| 2.164140 |
| H   | 2.791366 | -4.012869| -1.517839|
| H   | 5.657647 | -1.377817| -2.096149|
| H   | 3.205514 | -1.592081| -2.023721|
| H   | -6.861699| -2.961527| -0.317549|
| H   | -0.337430| 0.906228 | 3.946170 |
| H   | 0.015229 | -1.316279| 2.706573 |
| H   | 1.114420 | 3.381437 | 3.806337 |
| H   | -7.408741| 0.897197 | 1.496859 |
| H   | 5.993525 | 3.805688 | -0.510707|
| H   | 3.023131 | 0.684229 | -0.511897|
| H   | 0.340573 | 0.023970 | 6.153830 |
| H   | 2.605549 | 4.060703 | 2.124869 |
| H   | 2.007202 | -5.671603| -3.156468|
| H   | 5.155043 | 1.617053 | -1.376994|
| H   | 4.695769 | 5.015600 | 1.236498 |
| H   | -8.279452| -1.370812| 0.965026 |
| H   | 7.001316 | -1.568116| 0.000324 |
| H   | 1.838762 | -4.786545| 0.932647 |
| H   | 1.355049 | -6.089817| 2.970765 |
| H   | -0.419960| -5.872934| -3.688960|
| H   | -1.261148| -2.689047| -0.911261|
| H   | 0.188601 | -5.018709| 4.900401 |
| H   | -0.468658| -2.611616| 4.762587 |
| H   | -2.059105| -4.386162| -2.536608|
| H   | -5.168567| 2.189914 | 1.954624 |
| H   | -5.647626| 2.725486 | 0.331223 |
| H   | -3.991314| 2.142873 | 0.633240 |
| H   | -4.892206| -2.794182| -2.266788|
| H   | -4.349902| -3.586887| -0.786085|
| H   | -3.383057| -2.268410| -1.489016|
Table S11. Cartesian geometry of intermediate (1.7 kcal/mol) in Figure S84 in Angstrom [Å].

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|----------|---------------|---------------|---------------|
| C        | -1.003009     | -4.245596     | -2.389768     |
| C        | -0.101948     | -5.156020     | -2.941220     |
| C        | 1.240763      | -5.100103     | -2.572885     |
| C        | 1.683486      | -4.145030     | -1.657661     |
| C        | 0.794081      | -3.215794     | -1.105540     |
| C        | -0.549077     | -3.281860     | -1.492209     |
| P        | 1.242371      | -1.921163     | 0.152694      |
| C        | 3.086869      | -1.960589     | 0.073001      |
| C        | 3.866822      | -2.032539     | 1.232541      |
| C        | 5.254210      | -1.897832     | 1.168772      |
| C        | 5.885554      | -1.699839     | -0.056888     |
| C        | 5.118806      | -1.637704     | -1.220897     |
| C        | 3.733678      | -1.758154     | -1.155004     |
| Ni       | 0.250124      | 0.015849      | 0.028750      |
| P        | 1.144241      | 1.454442      | 1.439938      |
| C        | 0.127707      | 2.921858      | 1.951314      |
| C        | -0.951943     | 3.288872      | 1.145097      |
| C        | -1.743257     | 4.394621      | 1.450502      |
| Element | X  | Y   | Z    |
|---------|----|-----|------|
| C       | -1.472401 | 5.145741 | 2.591479 |
| C       | -0.411037  | 4.781463  | 3.420502 |
| C       | 0.381230   | 3.680277  | 3.103302 |
| Ge      | -1.893655  | -0.244188 | 0.607590 |
| Cl      | -2.765889  | 0.481249  | 2.627578 |
| N       | -3.382334  | -0.027338 | -0.550921 |
| C       | -4.700421  | -0.427010 | -0.187362 |
| C       | -5.567610  | 0.454898  | 0.502206 |
| C       | -6.838109  | 0.007478  | 0.879893 |
| C       | -7.274735  | -1.279533 | 0.585759 |
| C       | -6.433643  | -2.139107 | -0.110395 |
| C       | -5.155749  | -1.732206 | -0.508986 |
| C       | -5.189481  | 1.880520  | 0.812512 |
| C       | -4.310049  | -2.704699 | -1.295887 |
| P       | 0.097589   | 0.647525  | -2.073769 |
| C       | -1.485818  | 0.111171  | -2.856077 |
| Si      | -3.124405  | 0.737591  | -2.125108 |
| C       | -4.474089  | 0.209101  | -3.322255 |
| C       | 0.189321   | 2.413596  | -2.646711 |
| C       | -0.184685  | 2.789871  | -3.945751 |
| C       | -0.083341  | 4.113668  | -4.363895 |
| C       | 0.405731   | 5.089862  | -3.492085 |
| C       | 0.797256   | 4.728496  | -2.206687 |
| C       | 0.687656   | 3.399468  | -1.794361 |
| C       | 1.338458   | -0.043589 | -3.270255 |
| C       | 1.145051   | -1.274774 | -3.909277 |
| C       | 2.130050   | -1.815771 | -4.736793 |
| C       | 3.325378   | -1.130891 | -4.946565 |
| C       | 3.527856   | 0.100172  | -4.321244 |
| C       | 2.545818   | 0.635787  | -3.491678 |
| C       | 2.722377   | 2.258808  | 0.874040 |
| C       | 3.462729   | 1.578914  | -0.098402 |
|     |      |      |      |
|-----|------|------|------|
| C   | 4.671383 | 2.089140 | -0.569825 |
| C   | 5.146694 | 3.306893 | -0.088704 |
| C   | 4.409985 | 4.003486 | 0.869627  |
| C   | 3.211497 | 3.481711 | 1.352401  |
| C   | 1.679028 | 0.855185 | 3.107784  |
| C   | 3.003875 | 0.491736 | 3.368595  |
| C   | 3.367929 | -0.031301 | 4.610475 |
| C   | 2.414244 | -0.189113 | 5.612923 |
| C   | 1.089047 | 0.171023 | 5.362878  |
| C   | 0.722671 | 0.678382 | 4.119353  |
| C   | -3.177099 | 2.617933 | -2.073302 |
| C   | 0.951326 | -2.933864 | 1.684041 |
| C   | 0.297837 | -2.336403 | 2.763309 |
| C   | 0.035148 | -3.050916 | 3.933150 |
| C   | 0.428434 | -4.382943 | 4.034682 |
| C   | 1.092401 | -4.990907 | 2.966394 |
| C   | 1.352163 | -4.272324 | 1.802444 |
| H   | -1.166968 | 2.681264 | 0.263800 |
| H   | -1.526817 | -0.986248 | -2.760712 |
| H   | -1.494614 | 0.317909 | -3.939770 |
| H   | -2.578870 | 4.663368 | 0.798905 |
| H   | -2.092378 | 6.010685 | 2.841368 |
| H   | -0.553419 | 2.039857 | -4.651638 |
| H   | 0.219888 | -1.834636 | -3.757589 |
| H   | 2.722506 | 1.602184 | -3.011921 |
| H   | 0.485526 | 6.129185 | -3.822002 |
| H   | -0.382762 | 4.387083 | -5.379038 |
| H   | 3.389802 | -2.185921 | 2.203558 |
| H   | 1.007185 | 3.128044 | -0.791225 |
| H   | 4.458099 | 0.651895 | -4.481022 |
| H   | -0.199060 | 5.357155 | 4.325080 |
| H   | 1.190978 | 5.475897 | -1.512421 |
H  2.702371  -0.588846  6.588902
H  3.766965   0.616648  2.596006
H  1.955622  -2.780344 -5.220596
H  4.410124  -0.306798  4.794451
H  5.842963  -1.949152  2.088655
H  2.741007  -4.125562 -1.385071
H  5.599065  -1.483212 -2.190832
H  3.146880  -1.687868  2.074203
H  -6.772162  -3.148877  -0.362879
H  -0.324337   0.933280  3.926558
H  -0.003895  -1.290704  2.680078
H   1.199233   3.405074  3.773807
H  -7.499444   0.694726  1.418049
H   6.088860   3.718017  -0.461817
H   3.070042   0.641897  -0.496300
H   0.330210   0.050610  6.141468
H   2.653551   4.046755  2.102641
H   1.956262  -5.807394  -3.000100
H   5.234438   1.533490 -1.324348
H   4.771911   4.963718  1.246146
H  -8.270676  -1.609096   0.891466
H   6.972655  -1.593609  -0.107279
H   1.872432  -4.765537   0.977182
H   1.409089  -6.034662   3.038378
H  -0.446576  -5.906069  -3.657723
H  -1.239137  -2.532218  -1.097135
H   0.220600  -4.950244   4.945788
H  -0.474411  -2.555770   4.764340
H  -2.058377  -4.276357  -2.672859
H  -5.380558   2.113630   1.870112
H  -5.793221   2.577089   0.207710
H  -4.130490   2.076936   0.616438
Table S12. Cartesian geometry of intermediate (4.9 kcal/mol) in Figure S84 in Angstrom [Å].

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|----------|---------------|---------------|---------------|
| C        | 0.682264      | -4.664902     | 0.586033      |
| C        | 0.718899      | -3.302016     | 0.909852      |
| C        | 0.315859      | -2.911755     | 2.191174      |
| C        | -0.113890     | -3.849018     | 3.130000      |
| C        | -0.158908     | -5.200391     | 2.791304      |
| C        | 0.242332      | -5.604425     | 1.517498      |
| P        | 1.227462      | -1.967574     | -0.281241     |
| Ni       | 0.377920      | 0.010153      | 0.015712      |
| P        | 0.351358      | 1.089513      | -1.901726     |
| C        | 1.643016      | 0.659610      | -3.167174     |
| C        | 1.463106      | -0.349380     | -4.120035     |
| C        | 2.491871      | -0.699697     | -4.996686     |
| C        | 3.719549      | -0.044037     | -4.939265     |
| C        | 3.907483      | 0.974503      | -4.003142     |
|  |  |  |  |
|---|---|---|---|
| C  | 2.880946 | 1.319949 | -3.128487 |
| C  | 0.802828 | -2.840428 | -1.866270 |
| C  | 1.682476 | -3.629041 | -2.616090 |
| C  | 1.261495 | -4.241487 | -3.797230 |
| C  | -0.050427 | -4.090757 | -4.242802 |
| C  | -0.944562 | -3.324203 | -3.495307 |
| C  | -0.512791 | -2.704922 | -2.325692 |
| C  | 3.064911 | -2.151485 | -0.234608 |
| C  | 3.731028 | -2.674139 | 0.879014 |
| C  | 5.125679 | -2.667004 | 0.942010 |
| C  | 5.874317 | -2.145615 | -0.110486 |
| C  | 5.220218 | -1.628608 | -1.230338 |
| C  | 3.829625 | -1.623472 | -1.286446 |
| P  | 1.255845 | 1.101981 | 1.709493 |
| C  | 1.729234 | 0.156503 | 3.231422 |
| C  | 3.027692 | -0.330466 | 3.418633 |
| C  | 3.334722 | -1.141159 | 4.512825 |
| C  | 2.351561 | -1.467879 | 5.443652 |
| C  | 1.053569 | -0.985058 | 5.268636 |
| C  | 0.742864 | -0.189283 | 4.168631 |
| Ge | -1.802533 | -0.303555 | 0.467707 |
| N  | -3.221557 | 0.237751 | -0.673295 |
| Si | -2.865118 | 1.271119 | -2.066166 |
| C  | -2.886078 | 3.114503 | -1.685857 |
| C  | 0.246664 | 2.462268 | 2.472548 |
| C  | -0.814055 | 2.985059 | 1.728412 |
| C  | -1.602748 | 4.023713 | 2.216255 |
| C  | -1.351724 | 4.547248 | 3.481814 |
| C  | -0.310594 | 4.024134 | 4.249642 |
| C  | 0.480836 | 2.991440 | 3.750190 |
| C  | 2.865628 | 1.966351 | 1.366441 |
| C  | 3.654367 | 1.435331 | 0.340625 |
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| C       | 4.897433| 1.983488| 0.028841|
| C       | 5.357643| 3.099628| 0.723953|
| C       | 4.570966| 3.653834| 1.734244|
| C       | 3.338816| 3.088720| 2.057956|
| Cl      | -2.672072| 0.161099| 2.589109|
| C       | -4.584099| -0.088272| -0.412427|
| C       | -5.388290| 0.747756| 0.402373|
| C       | -6.715123| 0.385703| 0.658151|
| C       | -7.271158| -0.768731| 0.116269|
| C       | -6.489618| -1.577195| -0.701961|
| C       | -5.157208| -1.254685| -0.979114|
| C       | -4.880485| 2.044274| 0.980109|
| C       | -4.379416| -2.173783| -1.889882|
| C       | -1.203783| 0.787476| -2.846506|
| C       | 0.504920 | 2.934600| -2.080950|
| C       | 0.274619 | 3.573670| -3.309048|
| C       | 0.414457 | 4.951967| -3.435683|
| C       | 0.799999 | 5.722006| -2.334968|
| C       | 1.054102 | 5.099049| -1.117584|
| C       | 0.909105 | 3.715587| -0.999411|
| C       | -4.161364| 0.991833| -3.402755|
| N       | -2.552552| -2.243223| 0.765789|
| H       | -1.023278| 2.553521| 0.747051|
| H       | -1.262039| -0.297373| -3.026358|
| H       | -1.169170| 1.257233| -3.844110|
| H       | -2.425103| 4.412975| 1.609680|
| H       | -1.972130| 5.356453| 3.876406|
| H       | -0.008875| 2.988625| -4.188391|
| H       | 0.513913 | -0.884923| -4.185312|
| H       | 3.046200 | 2.120361| -2.402009|
| H       | 0.910338 | 6.805374| -2.434124|
| H       | 0.225357 | 5.430093| -4.400571|
|   |        |        |          |        |        |        |
|---|--------|--------|----------|--------|--------|--------|
| H | 3.160658 | -3.084682 | 1.715678 |
| H | 1.126650  | 3.238221  | -0.046435 |
| H | 4.861468  | 1.506381  | -3.951570 |
| H | -0.114234 | 4.420393  | 5.249360 |
| H | 1.369412  | 5.683060  | -0.249172 |
| H | 2.595698  | -2.095745 | 6.304689 |
| H | 3.814421  | -0.080130 | 2.702849 |
| H | 2.325638  | -1.494571 | -5.729033 |
| H | 4.354840  | -1.514401 | 4.637968 |
| H | 5.626586  | -3.074531 | 1.824431 |
| H | 2.714069  | -3.768013 | -2.285584 |
| H | 5.793695  | -1.217369 | -2.065473 |
| H | 3.330971  | -1.194813 | -2.159798 |
| H | -6.919212 | -2.482999 | -1.141411 |
| H | -0.286741 | 0.152053  | 4.024532 |
| H | 0.322551  | -1.850480 | 2.442901 |
| H | 1.281453  | 2.587512  | 4.375603 |
| H | -7.325801 | 1.035867  | 1.292866 |
| H | 6.326539  | 3.541850  | 0.477526 |
| H | 3.272411  | 0.581671  | -0.222337 |
| H | 0.272066  | -1.234783 | 5.991690 |
| H | 2.743549  | 3.541921  | 2.852750 |
| H | 1.969804  | -4.842367 | -4.374055 |
| H | 5.500308  | 1.538322  | -0.767276 |
| H | 4.919538  | 4.535417  | 2.278862 |
| H | -8.311082 | -1.032843 | 0.326678 |
| H | 6.966470  | -2.142104 | -0.059818 |
| H | 0.985998  | -5.003497 | -0.407172 |
| H | 0.208573  | -6.662027 | 1.242285 |
| H | -0.376482 | -4.567051 | -5.170836 |
| H | -1.197084 | -2.066376 | -1.761171 |
| H | -0.510002 | -5.938810 | 3.516902 |
Table S13. Cartesian geometry of intermediate (10.5 kcal/mol) in Figure S84 in Angstrom [Å].

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|----------|---------------|---------------|---------------|
| C        | 0.844092      | 3.777872      | -0.995008     |
| C        | 0.550279      | 2.962633      | -2.085753     |
| C        | 0.419614      | 3.563885      | -3.347258     |
| C        | 0.552649      | 4.940197      | -3.499621     |
| C        | 0.832795      | 5.744648      | -2.391612     |
| C        | 0.985259      | 5.159126      | -1.139120     |
| Element | X | Y | Z |
|---------|---|---|---|
| P       | 0.362792 | 1.125078 | -1.867870 |
| C       | -1.214030 | 0.867871 | -2.788908 |
| Si      | -2.839586 | 1.397509 | -1.965955 |
| C       | -4.172767 | 1.158814 | -3.274040 |
| Ni      | 0.401463  | 0.073765  | 0.062539  |
| Ge      | -1.775486 | -0.240014 | 0.525912  |
| N       | -2.449649 | -2.228192 | 0.733500  |
| P       | 1.208109  | -1.925098 | -0.220848 |
| C       | 3.039676  | -2.168143 | -0.199974 |
| C       | 3.707391  | -2.623235 | 0.942745  |
| C       | 5.102065  | -2.653194 | 0.987297  |
| C       | 5.849989  | -2.242193 | -0.113621 |
| C       | 5.194257  | -1.793355 | -1.261550 |
| C       | 3.803340  | -1.747731 | -1.299891 |
| C       | 0.683468  | -3.213371 | 1.014866  |
| C       | 0.584010  | -4.581540 | 0.730845  |
| C       | 0.135486  | -5.477581 | 1.700824  |
| C       | -0.213636 | -5.023259 | 2.972851  |
| C       | -0.109122 | -3.665053 | 3.270626  |
| C       | 0.329923  | -2.772563 | 2.294214  |
| C       | 0.733400  | -2.826099 | -1.776982 |
| C       | 1.560992  | -3.707100 | -2.483369 |
| C       | 1.101533  | -4.352937 | -3.631386 |
| C       | -0.199503 | -4.145775 | -4.086669 |
| C       | -1.040560 | -3.281650 | -3.386738 |
| C       | -0.567911 | -2.626034 | -2.252753 |
| P       | 1.344936  | 1.197944  | 1.695216  |
| C       | 2.939327  | 2.042593  | 1.248039  |
| C       | 3.782624  | 1.337856  | 0.380168  |
| C       | 5.012157  | 1.859309  | -0.015499 |
| C       | 5.406997  | 3.120809  | 0.426341  |
| C       | 4.564003  | 3.847808  | 1.265451  |
|   |   |   |   |
|---|---|---|---|
| C | 3.344895 | 3.311498 | 1.680749 |
| C | 1.629450 | 0.631649 | -3.132220 |
| C | 1.403850 | -0.360705 | -4.092634 |
| C | 2.419153 | -0.757086 | -4.965619 |
| C | 3.677609 | -0.163558 | -4.896439 |
| C | 3.911785 | 0.836658 | -3.950525 |
| C | 2.899427 | 1.226247 | -3.078165 |
| C | 1.867654 | 0.290126 | 3.227353 |
| C | 3.173753 | -0.167444 | 3.428791 |
| C | 3.495938 | -0.933617 | 4.551180 |
| C | 2.520543 | -1.242884 | 5.495374 |
| C | 1.214640 | -0.785833 | 5.307826 |
| C | 0.889956 | -0.034867 | 4.181506 |
| C | 0.383309 | 2.566625 | 2.502330 |
| C | -0.791682 | 3.014721 | 1.895285 |
| C | -1.550859 | 4.040982 | 2.454981 |
| C | -1.148312 | 4.626542 | 3.652250 |
| C | 0.015230 | 4.180923 | 4.282074 |
| C | 0.771868 | 3.159197 | 3.713472 |
| N | -3.193363 | 0.376102 | -0.561588 |
| C | -4.568340 | 0.126253 | -0.279631 |
| C | -5.314716 | 1.012133 | 0.535304 |
| C | -6.670427 | 0.754020 | 0.765460 |
| C | -7.301907 | -0.354173 | 0.211584 |
| C | -6.569980 | -1.218218 | -0.594971 |
| C | -5.213774 | -0.996951 | -0.852897 |
| C | -4.708285 | 2.244470 | 1.155981 |
| C | -4.488144 | -1.970158 | -1.748522 |
| Cl | -2.649978 | 0.054225 | 2.672595 |
| C | -2.801843 | 3.240355 | -1.583241 |
| N | -4.971753 | -3.503008 | 1.354728 |
| H | -1.111233 | 2.538111 | 0.965183 |
H  -1.311099  -0.211295  -2.984419
H  -1.184335   1.355040  -3.778367
H  -2.465645   4.373346   1.956797
H  -1.742919   5.426345   4.101854
H   0.220296   2.949413  -4.230198
H   0.429172  -0.846872  -4.168343
H   3.100072   2.007690  -2.339711
H   0.939566   6.826287  -2.511590
H   0.440463   5.390071  -4.489773
H   3.138360  -2.947997   1.817327
H   0.970035   3.329040  -0.012600
H   4.892141   1.316738  -3.888033
H   0.334249   4.628066   5.227165
H   1.217316   5.771565  -0.264085
H   2.776387  -1.836111   6.377266
H   3.956313   0.071575   2.705086
H   2.217382  -1.537813  -5.704247
H   4.522841  -1.283878   4.687253
H   5.604034  -3.003146   1.893397
H   2.581515  -3.896512  -2.143240
H   5.767348  -1.467013  -2.133620
H   3.305592  -1.371635  -2.197478
H  -7.061783  -2.084825  -1.049229
H  -0.144523   0.289760   4.031189
H   0.379627  -1.705199   2.511643
H   1.672015   2.813336   4.229229
H  -7.239661   1.447444   1.393474
H   6.364758   3.542133   0.109970
H   3.457517   0.369486  -0.002427
H   0.439331  -1.019703   6.042772
H   2.702717   3.907383   2.332618
H   1.770334  -5.026912  -4.173545
|   |               |            |          |
|---|---------------|------------|----------|
| H | 5.653357      | 1.277716   | -0.683978|
| H | 4.856755      | 4.845291   | 1.603130 |
| H | -8.362619     | -0.539698  | 0.402628 |
| H | 6.942380      | -2.269922  | -0.078090|
| H | 0.845033      | -4.958974  | -0.260387|
| H | 0.054618      | -6.540416  | 1.457397 |
| H | -0.556898     | -4.653399  | -4.986167|
| H | -1.207939     | -1.907616  | -1.734273|
| H | -0.570428     | -5.72528   | 3.729031 |
| H | -0.380819     | -3.288594  | 4.260161 |
| H | -2.062019     | -3.102939  | -3.734430|
| H | -4.872165     | 2.251715   | 2.244224 |
| H | -5.168344     | 3.158033   | 0.745547 |
| H | -3.628135     | 2.293010   | 0.988086 |
| H | -5.035649     | -2.126325  | -2.690643|
| H | -4.399026     | -2.955197  | -1.262435|
| H | -3.479506     | -1.618888  | -1.994372|
| H | 4.472322      | -0.474423  | -5.579392|
| H | -3.969490     | 1.838077   | -4.118724|
| H | -5.176562     | 1.403784   | -2.892308|
| H | -4.202845     | 0.133980   | -3.674864|
| H | -2.114537     | 3.507602   | -0.766469|
| H | -3.806544     | 3.605332   | -1.318385|
| H | -2.474067     | 3.798025   | -2.476424|
| H | -3.455971     | -2.503385  | 0.862787 |
| H | -2.084360     | -2.815605  | -0.019742|
| H | -1.976859     | -2.556525  | 1.579567 |
| H | -5.333763     | -2.885206  | 2.101506 |
| H | -5.743332     | -3.643848  | 0.703335 |
| H | -4.786970     | -4.411011  | 1.781272 |
| N | -5.748748     | -1.386279  | 3.306478 |
| H | -4.897135     | -0.860152  | 3.091378 |
Table S14. Cartesian geometry of transition state (14.5 kcal/mol) Figure S84 in Angstrom [Å].

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|----------|---------------|---------------|---------------|
| C        | 3.800489      | -1.710337     | -1.317724     |
| C        | 3.038661      | -2.157768     | -0.226892     |
| C        | 3.710253      | -2.584880     | 0.924283      |
| C        | 5.104493      | -2.563216     | 0.985737      |
| C        | 5.850098      | -2.124629     | -0.106194     |
| C        | 5.191525      | -1.702994     | -1.262676     |
| P        | 1.200202      | -1.965433     | -0.259742     |
| C        | 0.760991      | -2.860312     | -1.831103     |
| C        | 1.622082      | -3.686158     | -2.563225     |
| C        | 1.191345      | -4.308572     | -3.735313     |
| C        | -0.114206     | -4.132365     | -4.189988     |
| C        | -0.990715     | -3.329585     | -3.460327     |
| C        | -0.548142     | -2.699621     | -2.300222     |
| Ni       | 0.370998      | 0.016940      | 0.033271      |
| P        | 0.351591      | 1.086770      | -1.880188     |
| C        | 0.541622      | 2.928289      | -2.081266     |
| C        | 0.912529      | 3.719792      | -0.995871     |
| C        | 1.075593      | 5.100147      | -1.125771     |
| C        | 0.869005      | 5.710148      | -2.358766     |
| C        | 0.512457      | 4.929932      | -3.462167     |
| C        | 0.357310      | 3.554301      | -3.323875     |
| P        | 1.286439      | 1.109358      | 1.700644      |
| C        | 0.305923      | 2.473848      | 2.494808      |
| C        | -0.791790     | 2.980524      | 1.796529      |
| C        | -1.560525     | 4.023151      | 2.308473      |
| C        | -1.250489     | 4.564826      | 3.553326      |
| Element | x       | y       | z       |
|---------|---------|---------|---------|
| C       | -0.170945 | 4.055914 | 4.276844 |
| C       | 0.599226  | 3.019301 | 3.752913 |
| C       | 1.800392  | 0.185874 | 3.226197 |
| C       | 0.820389  | -0.177119 | 4.164058 |
| C       | 1.149445  | -0.945090 | 5.277771 |
| C       | 2.461720  | -1.381210 | 5.469532 |
| C       | 3.440144  | -1.032651 | 4.542144 |
| C       | 3.113454  | -0.250302 | 3.432396 |
| C       | 2.884458  | 1.979616  | 1.309858 |
| C       | 3.701722  | 1.374096  | 0.348524 |
| C       | 4.934365  | 1.922759  | -0.000424|
| C       | 5.354843  | 3.116002  | 0.583538 |
| C       | 4.537547  | 3.746099  | 1.521682 |
| C       | 3.317349  | 3.179560  | 1.888593 |
| Ge      | -1.824032 | -0.367306 | 0.489453 |
| Cl      | -2.580106 | 0.168564  | 2.693796 |
| C       | 0.704655  | -3.285542 | 0.955061 |
| C       | 0.702997  | -4.656684 | 0.666532 |
| C       | 0.280076  | -5.582325 | 1.619241 |
| C       | -0.139260 | -5.155123 | 2.880118 |
| C       | -0.132275 | -3.794715 | 3.182130 |
| C       | 0.279034  | -2.872482 | 2.220816 |
| N       | -2.610144 | -2.155159 | 0.772688 |
| N       | -3.232362 | 0.278448  | -0.642880|
| C       | -4.591500 | -0.066488 | -0.424275|
| C       | -5.161790 | -1.197278 | -1.063428|
| C       | -6.501447 | -1.528618 | -0.824073|
| C       | -7.289930 | -0.771952 | 0.037791 |
| C       | -6.735671 | 0.345769  | 0.654340 |
| C       | -5.407482 | 0.721912  | 0.427903 |
| C       | -4.368540 | -2.074722 | -2.000320|
| C       | -4.900249 | 1.992226  | 1.059194 |
| Element | X       | Y     | Z      |
|---------|---------|-------|--------|
| Si      | -2.84846| 1.349900 | -1.992639 |
| C       | -2.798142| 3.180526 | -1.554211 |
| C       | -4.169567| 1.174590 | -3.327401 |
| C       | -1.218949| 0.827364 | -2.813210 |
| C       | 1.619790 | 0.619942 | -3.157125 |
| C       | 1.400810 | -0.374832 | -4.116727 |
| C       | 2.411611 | -0.752788 | -5.002876 |
| C       | 3.660472 | -0.137903 | -4.949370 |
| C       | 3.888103 | 0.865691 | -4.005667 |
| C       | 2.879952 | 1.236768 | -3.120154 |
| N       | -4.916884| -2.440836 | 1.969777 |
| N       | -5.548205| -0.521900 | 4.017036 |
| H       | -1.043072| 2.527094 | 0.835171 |
| H       | -1.311177| -0.254992 | -2.995172 |
| H       | -1.183109| 1.302454 | -3.808243 |
| H       | -2.413733| 4.399946 | 1.738086 |
| H       | -1.853250| 5.378073 | 3.966684 |
| H       | 0.097975 | 2.960467 | -4.204772 |
| H       | 0.433939 | -0.877963 | -4.180355 |
| H       | 3.076283 | 2.022738 | -2.385601 |
| H       | 0.992878 | 6.791176 | -2.467858 |
| H       | 0.358275 | 5.397614 | -4.438151 |
| H       | 3.142594 | -2.927796 | 1.792835 |
| H       | 1.085184 | 3.252000 | -0.028997 |
| H       | 4.860082 | 1.363911 | -3.955230 |
| H       | 0.073030 | 4.467353 | 5.260011 |
| H       | 1.366953 | 5.692698 | -0.254344 |
| H       | 2.719845 | -1.988370 | 6.341359 |
| H       | 3.897461 | 0.017870 | 2.720171 |
| H       | 2.214033 | -1.536552 | -5.739559 |
| H       | 4.472550 | -1.365737 | 4.681715 |
| H       | 5.608131 | -2.893016 | 1.898555 |
|      |               |               |               |
|------|---------------|---------------|---------------|
| H    | 2.648744      | -3.847066     | -2.226853     |
| H    | 5.762182      | -1.355366     | -2.128141     |
| H    | 3.299881      | -1.352814     | -2.221382     |
| H    | -6.930751     | -2.402139     | -1.325917     |
| H    | -0.218378     | 0.130036      | 4.007026      |
| H    | 0.253181      | -1.804253     | 2.440178      |
| H    | 1.433717      | 2.627498      | 4.341279      |
| H    | -7.353641     | 0.961683      | 1.315839      |
| H    | 6.314385      | 3.559288      | 0.304192      |
| H    | 3.350958      | 0.462815      | -0.138989     |
| H    | 0.371626      | -1.210355     | 5.999169      |
| H    | 2.697141      | 3.695409      | 2.624098      |
| H    | 1.887058      | -4.937112     | -4.298128     |
| H    | 5.559596      | 1.417744      | -0.742171     |
| H    | 4.852289      | 4.689590      | 1.975341      |
| H    | -8.332510     | -1.045449     | 0.221388      |
| H    | 6.942173      | -2.108804     | -0.056751     |
| H    | 1.021122      | -5.013199     | -0.315696     |
| H    | 0.274783      | -6.647325     | 1.371693      |
| H    | -0.448350     | -4.616899     | -5.110962     |
| H    | -1.218322     | -2.036321     | -1.748473     |
| H    | -0.474377     | -5.883760     | 3.623394      |
| H    | -0.456748     | -3.439414     | 4.163831      |
| H    | -2.017162     | -3.179173     | -3.806187     |
| H    | -5.296021     | 2.111861      | 2.078597      |
| H    | -5.235554     | 2.868020      | 0.479107      |
| H    | -3.808102     | 2.010793      | 1.120031      |
| H    | -4.876104     | -2.181266     | -2.971949     |
| H    | -4.252349     | -3.093932     | -1.595951     |
| H    | -3.368251     | -1.663880     | -2.182238     |
| H    | 4.451775      | -0.434019     | -5.642826     |
| H    | -3.946770     | 1.877133      | -4.148069     |
Table S15. Cartesian geometry of intermediate (11.1 kcal/mol) in Figure S84 in Angstrom [Å].

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|----------|---------------|---------------|---------------|
| C        | -5.140250     | -1.246809     | -1.047894     |
| C        | -4.593183     | -0.097646     | -0.421474     |
| C        | -5.431577     | 0.692758      | 0.407782      |
| C        | -6.758661     | 0.304444      | 0.620809      |
| C        | -7.290198     | -0.830397     | 0.015028      |
| C        | -6.478869     | -1.592071     | -0.821310     |
| N        | -3.239037     | 0.265283      | -0.633260     |
| Ge       | -1.819616     | -0.370733     | 0.498462      |
| Cl       | -2.542114     | 0.244307      | 2.707705      |
| C        | -4.946372     | 1.978209      | 1.026089      |
| C        | -4.322637     | -2.126307     | -1.960893     |
| Ni       | 0.375339      | 0.029046      | 0.030307      |
| P        | 1.279152      | 1.113377      | 1.709636      |
| C        | 0.306751      | 2.500360      | 2.476252      |
| Element | x    | y    | z    |
|---------|------|------|------|
| C       | -0.755850 | 3.023147 | 1.736035 |
| C       | -1.517950 | 4.088369 | 2.208040 |
| C       | -1.240964 | 4.636263 | 3.458034 |
| C       | -0.202492 | 4.108184 | 4.226326 |
| C       | 0.563433  | 3.049574 | 3.740586 |
| P       | 0.343896  | 1.096609 | -1.884723 |
| C       | 1.602086  | 0.644281 | -3.178482 |
| C       | 1.391870  | -0.385821 | -4.102559 |
| C       | 2.391330  | -0.759588 | -5.002709 |
| C       | 3.621799  | -0.106580 | -4.999054 |
| C       | 3.840294  | 0.933079  | -4.093414 |
| C       | 2.842058  | 1.302070  | -3.195240 |
| C       | 0.517410  | 2.940263  | -2.083750 |
| C       | 0.938055  | 3.726529  | -1.012337 |
| C       | 1.091038  | 5.108166  | -1.141771 |
| C       | 0.830184  | 5.724537  | -2.361171 |
| C       | 0.429900  | 4.949165  | -3.452765 |
| C       | 0.281347  | 3.572731  | -3.314325 |
| C       | -1.229655 | 0.811836  | -2.805143 |
| Si      | -2.860758 | 1.333121  | -1.985447 |
| C       | -2.810761 | 3.166263  | -1.555454 |
| C       | -4.182743 | 1.148388  | -3.318191 |
| P       | 1.215427  | -1.949654 | -0.245180 |
| C       | 0.788078  | -2.852040 | -1.815851 |
| C       | 1.672614  | -3.634222 | -2.566887 |
| C       | 1.253608  | -4.259435 | -3.742155 |
| C       | -0.062265 | -4.127995 | -4.181737 |
| C       | -0.961891 | -3.369880 | -3.432033 |
| C       | -0.532385 | -2.738286 | -2.268152 |
| N       | -2.602103 | -2.131057 | 0.843225 |
| C       | 3.054495  | -2.137972 | -0.212649 |
| C       | 3.732628  | -2.670586 | 0.888750 |
| Atomic Number | X-C | Y-C | Z-C |
|---------------|-----|-----|-----|
| C             | 5.128161 | -2.669294 | 0.935171 |
| C             | 5.866300 | -2.144138 | -0.122637 |
| C             | 5.200361 | -1.616754 | -1.230816 |
| C             | 3.809562 | -1.605457 | -1.269414 |
| C             | 0.720267 | -3.269537 | 0.968807 |
| C             | 0.703333 | -4.638608 | 0.672334 |
| C             | 0.277401 | -5.566028 | 1.622101 |
| C             | -0.129365 | -5.142037 | 2.888003 |
| C             | -0.106235 | -3.783340 | 3.198203 |
| C             | 0.307714 | -2.859448 | 2.239967 |
| C             | 2.901619 | 1.953540 | 1.346521 |
| C             | 3.628267 | 1.460119 | 0.259327 |
| C             | 4.875247 | 1.985287 | -0.075927 |
| C             | 5.403605 | 3.042102 | 0.661450 |
| C             | 4.681307 | 3.558272 | 1.738225 |
| C             | 3.444988 | 3.015073 | 2.082058 |
| C             | 1.764904 | 0.181013 | 3.237052 |
| C             | 3.055254 | -0.336648 | 3.397673 |
| C             | 3.373236 | -1.134316 | 4.498306 |
| C             | 2.408785 | -1.418504 | 5.462287 |
| C             | 1.118355 | -0.908032 | 5.311873 |
| C             | 0.796469 | -0.124545 | 4.206221 |
| N             | -5.511780 | -0.428802 | 3.947116 |
| N             | -4.993520 | -2.421693 | 2.022290 |
| H             | -0.984814 | 2.564103 | 0.772207 |
| H             | -1.311224 | -0.275348 | -2.963923 |
| H             | -1.202137 | 1.266526 | -3.809731 |
| H             | -2.340186 | 4.479179 | 1.601962 |
| H             | -1.838920 | 5.468018 | 3.840682 |
| H             | -0.014765 | 2.982776 | -4.186194 |
| H             | 0.440437 | -0.920975 | -4.124858 |
| H             | 3.029996 | 2.121229 | -2.495796 |
H  0.946938  6.806459  -2.468908
H  0.235577  5.421700  -4.419484
H  3.170138 -3.084089  1.729268
H  1.159783  3.253974  -0.057907
H  4.795397  1.465525  -4.086988
H  0.012302  4.521384  5.215466
H  1.417134  5.696316  -0.280095
H  2.661007 -2.036093  6.328602
H  3.826902 -0.120828  2.654144
H  2.199656 -1.571182  -5.710050
H  4.386995 -1.530949  4.602277
H  5.637914 -3.084217  1.809166
H  2.708306 -3.757284  -2.243098
H  5.765179 -1.201014  -2.069802
H  3.301492 -1.167475  -2.133104
H  -6.889631 -2.478296  -1.315969
H  -0.228547  0.236562  4.079751
H  0.291301 -1.792580  2.466545
H  1.360463  2.641635  4.367819
H  -7.393746  0.923070  1.263504
H  6.375898  3.466753  0.397971
H  3.190540  0.651981  -0.329618
H  0.350593 -1.126890  6.059648
H  2.902644  3.436536  2.930315
H  1.967170 -4.853982  -4.319243
H  5.428217  1.567780  -0.921476
H  5.085014  4.392075  2.319087
H  -8.332530 -1.113202  0.185963
H  6.959008 -2.145224  -0.085286
H  1.013901 -4.991905  -0.313860
H  0.260263 -6.629554  1.368342
H  -0.387139 -4.613393  -5.105589
Table S16. Cartesian geometry of 5' in Angstrom [Å].

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|----------|--------------|--------------|--------------|
| Ge       | 1.870902     | -0.430238    | -0.718195    |
| Ni       | -0.191100    | 0.030820     | -0.095611    |
| Element | X  | Y  | Z  |
|---------|----|----|----|
| P       | 0.078105 | 0.575052 | 2.029073 |
| P       | -0.946169 | 1.577483 | -1.444014 |
| Si      | 3.301517 | 0.296027 | 2.005133 |
| P       | -1.331567 | -1.835548 | -0.217295 |
| N       | 3.407803 | -0.328493 | 0.350988 |
| N       | 2.649169 | -1.002262 | -2.256155 |
| C       | 4.675692 | -0.744049 | -0.145535 |
| C       | 0.189894 | 2.325932 | 2.637104 |
| C       | 3.606622 | 2.149378 | 2.127482 |
| C       | 1.311794 | 3.226304 | -1.135988 |
| H       | 1.501619 | 2.580279 | -0.275264 |
| C       | -1.194700 | -0.009097 | 3.247976 |
| C       | 1.612364 | -0.165525 | 2.737439 |
| H       | 1.521115 | -1.254734 | 2.591981 |
| H       | 1.670757 | -0.009841 | 3.828501 |
| C       | 2.177692 | 4.280253 | -1.430007 |
| H       | 3.044167 | 4.468421 | -0.790577 |
| C       | 1.937377 | 5.089362 | -2.537841 |
| H       | 2.615224 | 5.913589 | -2.774774 |
| C       | 0.658556 | 2.638977 | 3.921837 |
| H       | 0.999266 | 1.846112 | 4.593056 |
| C       | -2.455624 | 2.492626 | -0.861987 |
| C       | -1.108546 | -1.263711 | 3.863105 |
| H       | -0.250372 | -1.912845 | 3.675854 |
| C       | 5.505586 | 0.160307 | -0.844149 |
| C       | -2.323143 | 0.783127 | 3.511121 |
| H       | -2.416713 | 1.769231 | 3.048521 |
| C       | -1.145763 | -2.886666 | -1.733717 |
| C       | 0.245450 | 4.990678 | 3.543025 |
| H       | 0.270878 | 6.025030 | 3.896118 |
| C       | 0.692000 | 3.956530 | 4.369272 |
| H       | 1.065154 | 4.179287 | 5.372308 |
| C     | 3.172665 | -1.723492 | -0.117426 |
|-------|----------|-----------|-----------|
| C     | -3.972848| -1.796671 | -1.263570 |
| H     | -3.521382| -2.031243 | -2.230590 |
| C     | -3.238238| -0.923355 | 4.958782  |
| C     | -0.265421| 3.370167  | 1.830387  |
| H     | -0.662445| 3.148802  | 0.841027  |
| C     | -3.332893| 0.333191  | 4.357994  |
| H     | -4.200430| 0.970401  | 4.549774  |
| C     | 0.830693 | 4.836107  | -3.349006 |
| H     | 0.639809 | 5.456707  | -4.228315 |
| C     | -1.501412| 1.044357  | -3.125783 |
| C     | -0.239465| 4.693667  | 2.273182  |
| H     | -0.604473| 5.487743  | 1.616649  |
| C     | 4.134857 | -3.102559 | 0.602512  |
| C     | -2.276565| 0.046544  | -5.637854 |
| H     | -2.580549| -0.335195 | -6.615768 |
| C     | 5.016105 | 1.542481  | -1.188847 |
| C     | -2.840442| 0.742096  | -3.391034 |
| H     | -3.597868| 0.894859  | -2.617292 |
| C     | 0.186319 | 2.971421  | -1.925637 |
| C     | -2.121532| -1.717838 | 4.708914  |
| H     | -2.031544| -2.703856 | 5.171622  |
| C     | -3.224553| 0.243943  | -4.636968 |
| H     | -4.277496| 0.016661  | -4.825067 |
| C     | -5.346957| -1.563896 | -1.191325 |
| H     | -5.951196| -1.621138 | -2.100793 |
| C     | -1.894863| -3.920076 | 1.715349  |
| H     | -2.960378| -3.775175 | 1.525918  |
| C     | -5.159504| -1.196519 | 1.180745  |
| H     | -5.615067| -0.963068 | 2.146814  |
| C     | -3.786576| -1.413956 | 1.105224  |
| H     | -3.182748| -1.336985 | 2.012621  |
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| C       | 5.084056 | -2.085886 | 0.026497 |
| C       | 6.354445 | -2.474588 | -0.408076 |
| H       | 6.676522 | -3.509047 | -0.255247 |
| C       | -0.551842 | 0.825749 | -4.135633 |
| H       | 0.505528 | 1.034975 | -3.943085 |
| C       | -0.566307 | -2.325230 | -2.871233 |
| H       | -0.250656 | -1.282351 | -2.831248 |
| C       | -0.944875 | -3.140105 | 1.047418 |
| C       | -0.034595 | 3.787767 | -3.045663 |
| H       | -0.885987 | 3.596850 | -3.703714 |
| C       | 6.767547 | -0.268042 | -1.271129 |
| H       | 7.415337 | 0.436737 | -1.801204 |
| C       | -4.783177 | 3.693403 | 0.159902 |
| H       | -5.687544 | 4.163332 | 0.555291 |
| C       | -3.204477 | 1.870176 | 0.141858 |
| H       | -2.853392 | 0.914964 | 0.536464 |
| C       | -0.936122 | 0.341148 | -5.382868 |
| H       | -0.182051 | 0.187674 | -6.159913 |
| C       | -2.885021 | 3.738086 | -1.340138 |
| H       | -2.319385 | 4.262103 | -2.113117 |
| C       | -1.501608 | -4.889732 | 2.638918 |
| H       | -2.263357 | -5.477479 | 3.157920 |
| C       | -4.365562 | 2.455780 | 0.643308 |
| H       | -4.937139 | 1.942573 | 1.421153 |
| C       | -4.036398 | 4.334589 | -0.829316 |
| H       | -4.353655 | 5.309559 | -1.208233 |
| C       | 7.203455 | -1.569310 | -1.038391 |
| H       | 8.197075 | -1.884646 | -1.366471 |
| C       | -5.945793 | -1.264252 | 0.030135 |
| H       | -7.022571 | -1.083530 | 0.087673 |
| C       | -1.565057 | -4.223501 | -1.784000 |
| H       | -2.023409 | -4.688514 | -0.907237 |
| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|----------|---------------|---------------|---------------|
| C        | -1.400376     | -4.974396     | -2.944819     |
| H        | -1.727400     | -6.017177     | -2.964822     |
| C        | -0.151047     | -5.108858     | 2.899389      |
| H        | 0.156027      | -5.868353     | 3.623086      |
| C        | 0.409728      | -3.379780     | 1.312399      |
| H        | 1.167497      | -2.785040     | 0.796491      |
| C        | -0.818651     | -4.399125     | -4.076969     |
| H        | -0.687095     | -4.990558     | -4.986992     |
| C        | -0.406001     | -3.070018     | -4.039863     |
| H        | 0.042816      | -2.605549     | -4.922018     |
| C        | 0.808008      | -4.355634     | 2.221840      |
| H        | 1.872529      | -4.524696     | 2.406174      |
| H        | 5.813575      | 2.137945      | -1.655588     |
| H        | 4.650596      | 2.086048      | -0.308206     |
| H        | 4.176032      | 1.485729      | -1.901010     |
| H        | 4.638691      | -4.063302     | 0.778556      |
| H        | 3.305018      | -3.285653     | -0.101542     |
| H        | 3.688079      | -2.769193     | 1.549126      |
| C        | 4.602646      | -0.506723     | 3.100434      |
| H        | -4.030703     | -1.278576     | 5.622684      |
| H        | 4.587643      | -0.021018     | 4.090248      |
| H        | 5.615984      | -0.375767     | 2.687828      |
| H        | 4.438054      | -1.583426     | 3.260049      |
| H        | 2.939336      | 2.752860      | 1.493354      |
| H        | 4.649050      | 2.389263      | 1.861827      |
| H        | 3.453965      | 2.481728      | 3.167100      |
| H        | 3.625941      | -1.256572     | -2.366944     |
| H        | 2.075801      | -1.311241     | -3.032113     |

**Table S17.** Cartesian geometry of NH$_4$Cl+NH$_3$ in Angstrom [Å].
### Table S18. Cartesian geometry of NH₄Cl in Angstrom [Å].

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|----------|---------------|---------------|---------------|
| N        | -5.343639     | -1.589304     | 2.692828      |
| Cl       | -2.980936     | -0.473119     | 4.033093      |
| H        | -5.524564     | -1.103599     | 1.814448      |
| H        | -6.177253     | -1.494122     | 3.273081      |
| H        | -5.230159     | -2.579990     | 2.477857      |
| H        | -4.105342     | -1.011250     | 3.394985      |

### Table S19. Cartesian geometry of intermediate (19.5 kcal/mol) in Figure S84 in Angstrom [Å].

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|----------|---------------|---------------|---------------|
| C        | 2.269470      | -4.295252     | 1.227828      |
| C        | 1.395888      | -3.195721     | 1.281024      |
| C        | 0.510244      | -3.100833     | 2.354459      |
| C        | 0.496238      | -4.076033     | 3.355346      |
| C        | 1.372031      | -5.153396     | 3.297771      |
| C        | 2.262487      | -5.261716     | 2.226243      |
| P        | 1.398234      | -1.938468     | -0.083518     |
| Ni       | 0.104042      | -0.043996     | 0.162216      |
|  |  |  |  |
|---|---|---|---|
| P  | -0.080055 | 0.822463 | -1.903737 |
| C  | 1.149499 | 0.294605 | -3.187678 |
| C  | 0.939272 | -0.846360 | -3.970559 |
| C  | 1.868696 | -1.230621 | -4.937134 |
| C  | 3.019992 | -0.473513 | -5.143734 |
| C  | 3.236160 | 0.671055 | -4.375724 |
| C  | 2.311136 | 1.049315 | -3.405537 |
| C  | 0.939170 | -3.066798 | -1.478573 |
| C  | 1.842090 | -3.860993 | -2.195083 |
| C  | 1.392054 | -4.727184 | -3.190356 |
| C  | 0.031003 | -4.828711 | -3.474618 |
| C  | -0.880498 | -4.057190 | -2.756090 |
| C  | -0.424328 | -3.178347 | -1.775918 |
| C  | 3.210883 | -1.686556 | -0.297638 |
| C  | 4.039448 | -1.642968 | 0.832016 |
| C  | 5.390378 | -1.325243 | 0.713848 |
| C  | 5.938667 | -1.043767 | -0.536536 |
| C  | 5.123723 | -1.081274 | -1.666294 |
| C  | 3.770143 | -1.393720 | -1.547894 |
| P  | 1.164307 | 1.345632 | 1.610345 |
| C  | 1.773910 | 0.497407 | 3.126303 |
| C  | 3.131366 | 0.379973 | 3.438141 |
| C  | 3.536582 | -0.324185 | 4.574067 |
| C  | 2.590125 | -0.907430 | 5.412100 |
| C  | 1.231966 | -0.780548 | 5.115069 |
| C  | 0.826063 | -0.087209 | 3.979592 |
| Ge | -2.089882 | -0.517703 | 0.694072 |
| N  | -3.514533 | -0.013582 | -0.456884 |
| Si | -3.285460 | 0.944153 | -1.899949 |
| C  | -3.286698 | 2.807507 | -1.632917 |
| C  | 0.083377 | 2.646451 | 2.348421 |
| C  | -1.030831 | 3.068923 | 1.620141 |
| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| C    | -1.871 | 4.067  | 2.103  |
| C    | -1.619 | 4.642  | 3.346  |
| C    | -0.527 | 4.211  | 4.099  |
| C    | 0.319  | 3.219  | 3.606  |
| C    | 2.649  | 2.299  | 1.069  |
| C    | 3.349  | 1.811  | -0.038 |
| C    | 4.479  | 2.470  | -0.519 |
| C    | 4.916  | 3.640  | 0.098  |
| C    | 4.221  | 4.141  | 1.199  |
| C    | 3.095  | 3.477  | 1.683  |
| Cl   | -2.798 | 0.389  | 2.648  |
| C    | -4.813 | -0.519 | -0.153 |
| C    | -5.733 | 0.258  | 0.591  |
| C    | -6.984 | -0.279 | 0.911  |
| C    | -7.349 | -1.557 | 0.505  |
| C    | -6.459 | -2.309 | -0.254 |
| C    | -5.199 | -1.808 | -0.598 |
| C    | -5.436 | 1.676  | 1.009  |
| C    | -4.313 | -2.662 | -1.473 |
| C    | -1.661 | 0.361  | -2.704 |
| C    | 0.007  | 2.641  | -2.245 |
| C    | -0.341 | 3.132  | -3.514 |
| C    | -0.238 | 4.487  | -3.807 |
| C    | 0.228  | 5.382  | -2.840 |
| C    | 0.594  | 4.907  | -1.586 |
| C    | 0.484  | 3.545  | -1.297 |
| C    | -4.653 | 0.578  | -3.135 |
| N    | -2.447 | -2.264 | 1.180  |
| H    | -1.251 | 2.585  | 0.667  |
| H    | -1.716 | -0.739 | -2.687 |
| H    | -1.659 | 0.655  | -3.765 |
| H    | -2.738 | 4.379  | 1.515  |
|   |     |      |      |
|---|-----|------|------|
| H | -2.283310 | 5.417071 | 3.737187 |
| H | -0.688371  | 2.449291  | -4.293415 |
| H | 0.043024   | -1.454062 | -3.835086 |
| H | 2.492249   | 1.955571  | -2.822102 |
| H | 0.310802   | 6.447147  | -3.072495 |
| H | -0.519310  | 4.849608  | -4.799159 |
| H | 3.626404   | -1.859174 | 1.820020 |
| H | 0.786436   | 3.192345  | -0.316140 |
| H | 4.130726   | 1.278909  | -4.534169 |
| H | -0.335108  | 4.644856  | 5.083914 |
| H | 0.971578   | 5.589184  | -0.820359 |
| H | 2.908446   | -1.458322 | 6.300868 |
| H | 3.884524   | 0.836172  | 2.790722 |
| H | 1.681684   | -2.126921 | -5.533644 |
| H | 4.602210   | -0.411023 | 4.803454 |
| H | 6.017008   | -1.298898 | 1.609259 |
| H | 2.913488   | -3.805204 | -1.990565 |
| H | 5.538848   | -0.859646 | -2.653065 |
| H | 3.148011   | -1.406372 | -2.444536 |
| H | -6.746537  | -3.307553 | -0.597159 |
| H | -0.242397  | 0.006781  | 3.755510 |
| H | -0.203375  | -2.278832 | 2.411462 |
| H | 1.161118   | 2.882540  | 4.216887 |
| H | -7.685042  | 0.326967  | 1.493642 |
| H | 5.797069   | 4.165975  | -0.278936 |
| H | 2.991494   | 0.907765  | -0.534918 |
| H | 0.481218   | -1.230628 | 5.769459 |
| H | 2.560335   | 3.892554  | 2.539271 |
| H | 2.114620   | -5.329681 | -3.747009 |
| H | 5.011930   | 2.067601  | -1.384411 |
| H | 4.554157   | 5.061894  | 1.685946 |
| H | -8.329743  | -1.963017 | 0.768522 |
| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|----------|---------------|---------------|---------------|
| Ge       | 1.927219      | -0.480329     | -0.630370     |
| Ni       | -0.139100     | -0.029896     | -0.113074     |
| P        | 0.086117      | 0.652565      | 1.982576      |
| P        | -0.925469     | 1.407674      | -1.568966     |

Table S20. Cartesian geometry of 6' in Angstrom [Å].
| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| Si      | 3.311562 | 0.578612 | 1.986943 |
| P       | -1.350053 | -1.859755 | -0.185328 |
| N       | 3.461352 | -0.234016 | 0.418391 |
| O       | 2.688449 | -1.280249 | -2.053293 |
| C       | 4.725321 | -0.700872 | -0.039271 |
| C       | 0.150048 | 2.438141 | 2.487895 |
| C       | 3.466653 | 2.450088 | 1.860997 |
| C       | 1.436035 | 2.913392 | -1.709064 |
| H       | 1.603586 | 2.503571 | -0.710403 |
| C       | -1.166025 | 0.093859 | 3.231122 |
| C       | 1.655788 | 0.060940 | 2.757762 |
| H       | 1.645371 | -1.040727 | 2.718611 |
| H       | 1.688192 | 0.331497 | 3.827324 |
| C       | 2.360720 | 3.795655 | -2.262513 |
| H       | 3.242476 | 4.089885 | -1.686995 |
| C       | 2.163294 | 4.288777 | -3.551129 |
| H       | 2.890645 | 4.974077 | -3.994279 |
| C       | 0.342474 | 2.803494 | 3.829457 |
| H       | 0.433917 | 2.032058 | 4.600762 |
| C       | -2.167019 | 2.629580 | -0.941921 |
| C       | -1.030297 | -1.114764 | 3.923360 |
| H       | -0.147024 | -1.738506 | 3.776145 |
| C       | 5.537183 | 0.117782 | -0.855757 |
| C       | -2.321013 | 0.859234 | 3.450583 |
| H       | -2.450751 | 1.809986 | 2.926764 |
| C       | -1.296311 | -3.051088 | -1.613388 |
| C       | 0.264746 | 5.145479 | 3.239024 |
| H       | 0.305313 | 6.197502 | 3.533834 |
| C       | 0.402779 | 4.142599 | 4.202203 |
| H       | 0.552777 | 4.407800 | 5.252194 |
| C       | -3.152826 | -1.512400 | -0.026359 |
| C       | -3.923710 | -1.241444 | -1.165692 |
|  |  |  |  |
|---|---|---|---|
| H | -3.494499 | -1.373942 | -2.161489 |
| C | -3.165067 | -0.784070 | 5.010081 |
| C | 0.008789 | 3.450917 | 1.541223 |
| H | -0.156133 | 3.186720 | 0.498562 |
| C | -3.307203 | 0.428927 | 4.334532 |
| H | -4.195817 | 1.045519 | 4.493801 |
| C | 1.036309 | 3.898220 | -4.273426 |
| H | 0.879578 | 4.274373 | -5.287632 |
| C | -1.811267 | 0.727580 | -3.039365 |
| C | 0.064427 | 4.797149 | 1.907080 |
| H | -0.056114 | 5.570165 | 1.143115 |
| C | 4.214962 | -2.947481 | 1.013411 |
| C | -3.077664 | -0.509747 | -5.216666 |
| H | -3.576344 | -0.997619 | -6.058255 |
| C | 5.042294 | 1.462033 | -1.318715 |
| C | -3.082258 | 1.142862 | -3.451273 |
| H | -3.598938 | 1.943877 | -2.917489 |
| C | 0.288534 | 2.528933 | -2.411982 |
| C | -2.022924 | -1.554114 | 4.800100 |
| H | -1.895696 | -2.506517 | 5.321163 |
| C | -3.710998 | 0.527195 | -4.534391 |
| H | -4.706999 | 0.857862 | -4.840332 |
| C | -5.237238 | -0.792393 | -1.048592 |
| H | -5.816086 | -0.583563 | -1.951887 |
| C | -2.004229 | -4.004394 | 1.633162 |
| H | -3.042125 | -3.923270 | 1.301107 |
| C | -5.047768 | -0.862486 | 1.349792 |
| H | -5.476392 | -0.712490 | 2.344045 |
| C | -3.731644 | -1.306831 | 1.232922 |
| H | -3.147671 | -1.485159 | 2.138074 |
| C | 5.139831 | -2.014132 | 0.278525 |
| C | 6.395965 | -2.454044 | -0.149337 |
|   |   |   |   |
|---|---|---|---|
| H | 6.722050 | -3.465783 | 0.108249 |
| C | -1.178441 | -0.306843 | -3.741082 |
| H | -0.186571 | -0.641782 | -3.426882 |
| C | -0.113397 | -3.185588 | -2.348068 |
| H | 0.754226 | -2.555062 | -2.136821 |
| C | -1.030681 | -3.134996 | 1.126740 |
| C | 0.103358 | 3.028586 | -3.707662 |
| H | -0.777573 | 2.738170 | -4.286491 |
| C | 6.785602 | -0.359900 | -1.268287 |
| H | 7.419271 | 0.278967 | -1.890495 |
| C | -4.070108 | 4.367709 | 0.173772 |
| H | -4.806832 | 5.046872 | 0.611023 |
| C | -3.052348 | 2.180963 | 0.046270 |
| H | -2.979754 | 1.148786 | 0.399800 |
| C | -1.803835 | -0.921265 | -4.822227 |
| H | -1.299178 | -1.736377 | -5.347347 |
| C | -2.245199 | 3.963049 | -1.359944 |
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| C | -3.186490 | 4.827707 | 0.800701 |
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| C | 7.224239 | -1.629588 | -0.905143 |
| H | 8.205152 | -1.985875 | -1.229221 |
| C | -5.805929 | -0.601341 | 0.209810 |
| H | -6.835619 | -0.246198 | 0.301054 |
| C | -2.367513 | -3.904361 | -1.914144 |
| H | -3.297551 | -3.842123 | -1.343583 |
| C | -2.270242 | -4.841778 | -2.939406 |
| H | -3.122776 | -5.489196 | -3.161814 |
|  |  |  |  |
|---|---|---|---|
| C  | -0.346265 | -5.122895 | 2.995524 |
| H  | -0.082736 | -5.892999 | 3.725259 |
| C  | 0.290205  | -3.292573 | 1.558776 |
| H  | 1.055119  | -2.6168319 | 1.166160 |
| C  | -1.089470 | -4.958620 | -3.672604 |
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| H  | 1.676675  | -4.384343 | 2.79152 |
| H  | 3.645636  | -1.401329 | -1.999597 |
| H  | 5.808953  | 1.985758  | -1.906753 |
| H  | 4.753633  | 2.107099  | -0.477750 |
| H  | 4.149617  | 1.350268  | -1.956062 |
| H  | 4.701451  | -3.912324 | 1.211911 |
| H  | 3.314482  | -3.148987 | 0.409481 |
| H  | 3.874341  | -2.532335 | 1.972426 |
| C  | 4.670778  | 0.024214  | 3.158104 |
| H  | -3.940859 | -1.125819 | 5.700161 |
| H  | 4.627863  | 0.640442  | 4.071627 |
| H  | 5.668081  | 0.171953  | 2.712867 |
| H  | 4.588538  | -1.029760 | 3.464472 |
| H  | 2.816716  | 2.896877  | 1.094301 |
| H  | 4.507913  | 2.731498  | 1.633661 |
| H  | 3.204985  | 2.921494  | 2.822531 |

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