σ or π? Bonding interactions in a series of rhenium metallotetrylenes

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Experimental Procedures

General Considerations: Unless otherwise stated, all reactions were performed under an inert atmosphere of nitrogen or argon, either using standard Schlenk line techniques or in an MBraun inert atmosphere glove box. Glassware and Celite® were stored in an oven at ca. 150 ºC for at least 3 hours prior to use. Molecular sieves (4 Å) were activated by heating to 200 ºC overnight under vacuum prior to storage in a glovebox. NMR spectra were recorded on Bruker AV-700, AV-600, AV-500, and AVB-400 spectrometers. ^{1}H and ^{13}C{^{1}H} NMR chemical shifts (δ) were calibrated relative to residual solvent peaks and reported in parts per million (ppm). ^{29}Si NMR chemical shifts were referenced to an internal standard of tetramethylsilane (TMS). ^{1}H and ^{13}C NMR assignments were routinely confirmed by ^{1}H-^{13}C (HSQC) NMR experiments. FT-IR samples were prepared as Nujol mulls and data acquired between KBr disks using a Thermo Scientific Nicolet iS10 FT-IR spectrometer. Melting points were determined using sealed capillaries prepared under nitrogen on an OptiMelt automated melting point system. Elemental analyses were performed at the Microanalytical Facility at the College of Chemistry, University of California, Berkeley. Unless otherwise noted, "room temperature" or "ambient temperature" both refer to ca. 23 °C.

Materials: Diethyl ether, *n*-hexane, *n*-pentane, toluene, and THF were purified, dried, and degassed using a Phoenix solvent drying system commercially available from JC Meyer Solvent Systems. Deuterated solvents were obtained from Cambridge Isotope Laboratories and dried by stirring over sodium/benzophenone (C_6D_6 and toluene-d_8) or calcium hydride ($CDCl_3$ and pyridine-d_5), degassed with three freeze-pump-thaw cycles, and stored over molecular sieves. Reagents Na[Re(μ^5-Cp)(BDI)] (BDI = N,N′-bis(2,6-diisopropylphenyl)-3,5-dimethyl-β-diketiminate),[1] SiCl[PhC(N^{t}Bu)$_2$],[2] GeCl[PhC(N^{t}Bu)$_2$],[3] and SnCl[PhC(N^{t}Bu)$_2$][4] were prepared according to literature methods. All other chemicals were obtained from commercial sources and used as received.

Re(Si[PhC(N^{t}Bu)$_2$])(η^5-Cp)(BDI) (1a) and (BDI)Re(μ-η^5:η^1-C$_5$H$_4$)(SiH[PhC(N^{t}Bu)$_2$]) (1b)
In 20 mL glass scintillation vials, a solution of Na[Re(μ^5-Cp)(BDI)] (50 mg, 0.073 mmol) in 4 mL of THF was added, via pipette, to a stirring solution of SiCl[PhC(N^{t}Bu)$_2$] (21 mg, 0.071 mmol) in 2 mL of THF. The reaction mixture was stirred at ambient temperature for one hour before volatiles were removed *in vacuo*. The residue was triturated with pentane (2 x 2 mL), and 8 mg of crude solids were filtered and analyzed via ^{1}H NMR (600 MHz, 298 K, C_6D_6), which revealed a clean 1:0.55 ratio of **1a** to **1b** in solution. The remaining crude solids were then extracted and filtered through Celite in three fractions. The first fraction was carefully extracted with minimal pentane (5 mL), decanting a dark red solution of pentane away from green solids which remained in the reaction vial. The second fraction was extracted with a mixture of pentane (2 mL) and Et_2O (4 mL) and was a primarily dark red solution, again decanted away from green solids. The final fraction was extracted with Et_2O (5 mL) and was a dark green solution. All three fractions were concentrated under reduced pressure and stored at –40 °C overnight.

Fractions one and two: removal of a dark green supernatant and drying *in vacuo* led to the isolation of dark red crystals (18 mg, fraction one and 19 mg, fraction two). Fractions one and two were combined, and, after recrystallization from pentane, dark red crystals of **1a** (24 mg) were isolated. Total yield: 24 mg, 37 %. X-ray quality crystals of **1a** were obtained from pentane at –40 °C. M.p.: 176-181 °C. ^{1}H NMR (700 MHz, 298 K, C_6D_6) δ 0.77 (s, 9H, ^{t}Bu), 1.31 (d, 6H, BDI CH(*Me*)$_2$, J = 6.7 Hz), 1.36 (d, 6H, BDI CH(*Me*)$_2$, J = 6.7 Hz), 1.40 (s, 9H, ^{t}Bu), 1.42 (d, 6H, BDI CH(*Me*)$_2$, J = 6.9 Hz), 1.51 (d, 6H, BDI CH(*Me*)$_2$, J = 6.9 Hz),

1.78 (s, 6H, HC[*Me*C(NAr)]$_2$), 3.73 (m, 2H, BDI C*H*(Me)$_2$), 4.34 (s, 5H, Cp), 4.81 (s, 1H, *H*C[MeC(NAr)]$_2$), 4.86 (m, 2H, BDI C*H*(Me)$_2$), 6.91 (t, 2H, Ar, *J* = 7.5 Hz), 6.99 (t, 1H, Ar, *J* = 7.5 Hz), 7.04 (d, 4H, Ar, *J* = 4.7 Hz), 7.13 (m, 4H, Ar). ^{13}C NMR (151 MHz, 298 K, C_6D_6) δ 24.22 (HC[*Me*C(NAr)]$_2$), 24.89 (BDI CH(*Me*)$_2$), 25.35 (BDI CH(*Me*)$_2$), 25.37 (BDI CH(*Me*)$_2$), 25.54 (BDI CH(*Me*)$_2$), 26.40 (BDI *C*H(Me)$_2$), 28.27 (BDI *C*H(Me)$_2$), 32.42 (^{t}Bu), 33.10 (^{t}Bu), 53.15, 54.94, 79.77 (Cp), 106.49 (H*C*[MeC(NAr)]$_2$), 123.13 (Ar), 124.77 (Ar), 125.52 (Ar), 126.13 (Ar), 127.81 (Ar), 129.65 (Ar), 136.96, 142.74, 143.11, 153.90, 164.88, 177.68. ^{29}Si NMR (119 MHz, 298 K, C_6D_6): Despite numerous efforts across a range of 400 to –100 ppm, we were unable to observe any silicon signals for **1a**. Anal. calcd. for $C_{49}H_{69}N_4ReSi$ (**1a**): C, 63.39; H, 7.49; N, 6.04 %. Found: C, 62.99; H, 7.31; N, 5.85 %.

Fraction three: upon removal of the supernatant and drying *in vacuo*, dark green crystals of **1b** (10 mg) were isolated. Total yield: 10 mg, 15 %. X-ray quality crystals of **1b** were obtained from Et_2O at –40 °C. M.p.: ca. 209 °C (decomp.). ^{1}H NMR (600 MHz, 298 K, C_6D_6) δ 0.77 (s, 9H, ^{t}Bu), 1.04 (d, 3H, BDI CH(*Me*)$_2$, *J* = 6.7 Hz), 1.07 (d, 3H, BDI CH(*Me*)$_2$, *J* = 6.7 Hz), 1.09 (d, 3H, BDI CH(*Me*)$_2$, *J* = 6.8 Hz), 1.10 (d, 3H, BDI CH(*Me*)$_2$, *J* = 6.8 Hz), 1.20 (s, 9H, ^{t}Bu), 1.45 (d, 3H, BDI CH(*Me*)$_2$, *J* = 6.8 Hz), 1.51 (d, 3H, BDI CH(*Me*)$_2$, *J* = 6.8 Hz), 1.64 (d, 3H, BDI CH(*Me*)$_2$, *J* = 6.8 Hz), 1.70 (d, 3H, BDI CH(*Me*)$_2$, *J* = 6.6 Hz), 1.88 (m, 2H, BDI C*H*(Me)$_2$), 2.18 (s, 3H, HC[*Me*C(NAr)]$_2$), 2.22 (s, 3H, HC[*Me*C(NAr)]$_2$), 3.84 (d, 1H, Cp, *J* = 2.1 Hz), 4.44 (d, 1H, Cp, *J* = 2.1 Hz), 4.51 (m, 1H, BDI C*H*(Me)$_2$), 4.70 (q, 1H, Cp, *J* = 2.1 Hz), 4.85 (t, 1H, Cp, *J* = 2.0 Hz), 4.88 (m, 1H, BDI C*H*(Me)$_2$), 5.74 (d, 1H, Si-*H*, *J* = 2.3 Hz, $^1J_{Si,H}$ = 238.1 Hz), 6.04 (s, 1H, *H*C[MeC(NAr)]$_2$), 6.88 (m, 1H, Ar), 6.92-6.98 (m, 3H, Ar), 7.09–7 .15 (m, 4H, Ar), 7.36 (dd, 1H, Ar, *J* = 7.4, 1.8 Hz), 7.40 (dd, 1H, Ar, *J* = 7.5, 2.1 Hz), 7.42 (m, 1H, Ar). ^{13}C NMR (151 MHz, 298 K, C_6D_6) δ 24.67 (HC[*Me*C(NAr)]$_2$), 24.93 (HC[*Me*C(NAr)]$_2$), 25.24 (BDI CH(*Me*)$_2$), 25.42 (BDI CH(*Me*)$_2$), 25.45 (BDI CH(*Me*)$_2$), 25.49 (BDI CH(*Me*)$_2$), 25.64 (BDI CH(*Me*)$_2$), 25.68 (BDI CH(*Me*)$_2$), 27.30 (BDI CH(*Me*)$_2$), 27.76 (BDI CH(*Me*)$_2$), 28.17 (BDI *C*H(Me)$_2$), 28.90 (BDI *C*H(Me)$_2$ – this signal corresponds to two overlapped methine carbons despite their chemical inequivalence), 29.06 (BDI *C*H(Me)$_2$), 32.03 (^{t}Bu), 33.40 (^{t}Bu), 48.69, 52.90, 54.39, 66.27 (Cp), 70.78, 78.24, 78.73, 107.40 (H*C*[MeC(NAr)]$_2$), 123.12 (Ar), 123.27 (Ar), 124.16 (Ar), 124.28 (Ar), 125.05 (Ar), 125.33 (Ar), 127.64 (Ar), 127.72 (Ar), 129.22 (Ar), 129.32 (Ar), 134.71 (Ar), 139.59 (Ar), 140.17 (Ar), 140.59 (Ar), 140.86 (Ar), 154.80, 154.96, 161.70, 162.90, 169.99. *The 13C spectrum is missing one aromatic carbon bound to a hydrogen. Based on an HSQC experiment, we believe this peak likely lie underneath the benzene-d_6 signal. ^{29}Si NMR (119 MHz, 298 K, C_6D_6) δ -58.3. FT-IR (Nujol/KBr): 2128 cm^{-1} (*Si-H*). Anal. calcd. for $C_{49}H_{69}N_4ReSi$ (**1b**): C, 63.39; H, 7.49; N, 6.04 %. Found: C, 63.12; H, 7.29; N, 5.85 %.

(η^5-Cp)(BDI)Re(μ-N$_2$)Si[PhC(N^{t}Bu)$_2$] (1c)

In 20 mL glass scintillation vials inside a nitrogen filled glovebox, a solution of Na[Re(μ^5-Cp)(BDI)] (31 mg, 0.044 mmol) in 3 mL of Et_2O and a solution of SiCl[PhC(N^{t}Bu)$_2$] (13 mg, 0.044 mmol) in 2 mL of Et_2O were prepared and stirred while cooling to –78 °C in the cold well of the glovebox. The solution of Na[Re(μ^5-Cp)(BDI)] was then added, via pipette, to the stirring solution of SiCl[PhC(N^{t}Bu)$_2$]. The reaction mixture was stirred at –78 °C for thirty minutes before volatiles were removed *in vacuo* while the vial remained in the cold well. Again in the cold well, the residue was triturated with cold pentane (2 mL), extracted with cold pentane (5 mL), and the resulting solution was filtered through Celite, concentrated under reduced pressure, and stored at –40 ºC overnight. Upon removal of the supernatant and drying *in vacuo* for ten minutes in the cold well, dark red crystals (31 mg) were isolated. ^{1}H NMR (600 MHz, 298 K, C_6D_6) revealed a clean 1:3 ratio of **1a** to **1c** in solution. While **1a** continually crystallized under the same conditions as **1c**, under a microscope we were able to selectively choose a single crystal of **1c** suitable for X-ray diffraction which had been crystallized from pentane at –40 ºC. *The following characterization of **1c** was possible, despite the inability to separate **1c** from **1a**, because we have corresponding data for **1a** and were thus able to independently assign characteristic data for **1c**. ^{1}H NMR (700 MHz, 298 K, C_6D_6) δ

1.22 (s, 18H, ^{t}Bu), 1.23 (m, 6H, BDI CH(*Me*)$_2$), 1.31 (d, 6H, BDI CH(*Me*)$_2$, J = 6.9 Hz), 1.51 (d, 6H, BDI CH(*Me*)$_2$, J = 6.7 Hz), 1.57 (d, 6H, BDI CH(*Me*)$_2$, J = 6.9 Hz), 1.70 (s, 6H, HC[*Me*C(NAr)]$_2$), 3.32 (m, 2H, BDI C*H*(Me)$_2$), 4.19 (bm, 2H, BDI C*H*(Me)$_2$), 4.46 (s, 5H, Cp), 4.73 (s, 1H, *H*C[MeC(NAr)]$_2$), 6.91–7.14 (m, 10H, Ar), 7.28 (m, 2H, Ar), 7.41 (m, 1H, Ar). ^{29}Si NMR (119 MHz, 298 K, C_6D_6) δ –1.6. FT-IR (Nujol/KBr): 1682 cm^{-1} (Re*N*=*N*Si[PhC(N^{t}Bu)$_2$]).

Re(Ge[PhC(N^{t}Bu)$_2$])(η^5-Cp)(BDI) (2)

In 20 mL glass scintillation vials inside a nitrogen filled glovebox, a solution of Na[Re(μ^5-Cp)(BDI)] (112 mg, 0.162 mmol) in 5 mL of Et_2O and a suspension of GeCl[PhC(N^{t}Bu)$_2$] (55 mg, 0.163 mmol) in 4 mL of Et_2O were prepared and stirred while cooling to –78 °C in the cold well of the glovebox. The solution of Na[Re(μ^5-Cp)(BDI)] was then added, via pipette, to the stirring solution of GeCl[PhC(N^{t}Bu)$_2$]. The reaction mixture was stirred at –78 °C for one hour before volatiles were removed *in vacuo*. The residue was triturated with pentane at ambient temperature (3 mL), extracted with pentane (8 mL), and the resulting solution was filtered through Celite, concentrated under reduced pressure, and stored at –40 ºC overnight. Upon removal of the supernatant and drying *in vacuo*, red crystals of **2** (119 mg) were isolated. Total yield: 119 mg, 75 %. X-ray quality crystals of **2** were obtained from pentane at –40 ºC. M.p.: ca. 117 ºC (decomp.). ^{1}H NMR (500 MHz, 273 K, toluene-d_8) δ 0.81 (s, 9H, ^{t}Bu), 1.20 (s, 9H, ^{t}Bu), 1.28 (d, 6H, BDI CH(*Me*)$_2$, J = 6.7 Hz), 1.30 (d, 6H, BDI CH(*Me*)$_2$, J = 6.7 Hz), 1.37 (d, 6H, BDI CH(*Me*)$_2$, J = 6.9 Hz), 1.41 (d, 6H, BDI CH(*Me*)$_2$, J = 6.8 Hz), 1.89 (s, 6H, HC[*Me*C(NAr)]$_2$), 3.30 (m, 2H, BDI C*H*(Me)$_2$), 4.00 (s, 5H, Cp), 4.62 (m, 2H, BDI C*H*(Me)$_2$), 5.07 (s, 1H, *H*C[MeC(NAr)]$_2$), 6.92 (t, 2H, Ar, J = 8.0 Hz), 6.95–7.01 (m, 5H, Ar), 7.04 (dd, 2H, Ar, J = 6.8, 2.5 Hz), 7.14 (d, 2H, Ar, J = 6. Hz). ^{13}C NMR (151 MHz, 273 K, toluene-d_8) δ 24.02 (HC[*Me*C(NAr)]$_2$), 24.61 (BDI CH(*Me*)$_2$), 25.02 (BDI CH(*Me*)$_2$), 25.51 (BDI CH(*Me*)$_2$), 25.57 (BDI CH(*Me*)$_2$), 26.34 (BDI *C*H(Me)$_2$), 28.28 (BDI *C*H(Me)$_2$), 32.57 (^{t}Bu), 32.57 (^{t}Bu), 52.67 (^{t}Bu bound carbon), 55.03 (^{t}Bu bound carbon), 77.03 (Cp), 106.73 (H*C*[MeC(NAr)]$_2$), 122.83 (Ar), 124.84 (Ar), 125.44 (Ar), 125.46 (Ar), 127.45 (Ar), 127.65 (Ar), 128.28 (Ar), 129.21 (Ar), 138.05 (Ar), 142.30 (Ar), 142.48 (Ar), 153.46, 164.47, 172.11. Anal. calcd. for $C_{49}H_{69}N_4ReGe$ (**2**) C, 60.49; H, 7.15; N, 5.76 %. Found: C, 60.56; H, 6.98; N, 5.63 %.

Ge[Re(η^5-Cp)(BDI)]$_2$ (3)

In 20 mL glass scintillation vials, a solution of Na[Re(μ^5-Cp)(BDI)] (51 mg, 0.074 mmol) in 4 mL of THF and a solution of $GeCl_2$·dioxane (9 mg, 0.04 mmol) in 3 mL of THF were prepared and stirred while cooling to –78 °C in the cold well of the glovebox. The solution of Na[Re(μ^5-Cp)(BDI)] was then added, via pipette, to the stirring solution of $GeCl_2$·dioxane, leading to a rapid color change from dark red to dark purple. The reaction mixture was stirred at –78 °C for one hour before volatiles were removed *in vacuo*. The residue was triturated with hexane (2 x 2 mL), extracted with toluene (6 mL), and the resulting solution was filtered through Celite. Toluene and volatiles were removed *in vacuo*, leaving behind a waxy, dark purple residue. Pentane (0.5 mL) was added to this residue and allowed to sit for five minutes before being removed *in vacuo*. Pentane (1 mL) was again added to the residue, and the products were stored overnight at room temperature to crystallize. Upon removal of the supernatant and drying *in vacuo*, dark red crystals of **3** (32 mg) were isolated. Total yield: 32 mg, 61 %. X-ray quality crystals of **3** were obtained from pentane at room temperature. M.p.: 140–143 °C. ^{1}H NMR (600 MHz, 298 K, C_6D_6) δ 0.96 (d, 3H, BDI CH(*Me*)$_2$, J = 6.9 Hz), 1.02 (d, 3H, BDI CH(*Me*)$_2$, J = 6.6 Hz), 1.06 (d, 3H, BDI CH(*Me*)$_2$, J = 6.5 Hz), 1.07 (d, 3H, BDI CH(*Me*)$_2$, J = 6.7 Hz), 1.12 (d, 3H, BDI CH(*Me*)$_2$, J = 6.8 Hz), 1.21 (d, 3H, BDI CH(*Me*)$_2$, J = 6.7 Hz), 1.27 (d, 3H, BDI CH(*Me*)$_2$, J = 6.6 Hz), 1.53 (d, 3H, BDI CH(*Me*)$_2$, J = 6.8 Hz), 1.90 (m, 1H, BDI C*H*(Me)$_2$), 2.50 (s, 3H, HC[*Me*C(NAr)]$_2$), 2.61 (s, 3H, HC[*Me*C(NAr)]$_2$), 2.65 (m, 1H, BDI C*H*(Me)$_2$), 3.99 (m, 1H, BDI C*H*(Me)$_2$), 4.39 (m, 1H, BDI C*H*(Me)$_2$), 5.36 (s, 5H, Cp), 5.87 (s, 1H, *H*C[MeC(NAr)]$_2$), 6.93 (dd, 1H, BDI Ar, J = 7.6, 1.7 Hz), 6.99 (t, 1H, BDI Ar, J = 7.6 Hz), 7.06 (dd, 1H, BDI Ar, J = 7.7, 1.7 Hz).

^{13}C NMR (151 MHz, 298 K, C_6D_6) δ 22.43 (BDI CH(*Me*)$_2$), 22.92 (HC[*Me*C(NAr)]$_2$), 24.80 (BDI *C*H(Me)$_2$), 25.08 (BDI CH(*Me*)$_2$), 25.24 (HC[*Me*C(NAr)]$_2$), 25.42 (BDI CH(*Me*)$_2$), 25.54 (BDI CH(*Me*)$_2$), 25.99 (BDI CH(*Me*)$_2$), 26.49 (BDI CH(*Me*)$_2$), 26.75 (BDI CH(*Me*)$_2$), 26.86 (BDI CH(*Me*)$_2$), 28.17 (BDI *C*H(Me)$_2$), 28.33 (BDI *C*H(Me)$_2$), 28.68 (BDI *C*H(Me)$_2$), 77.72 (Cp), 112.56 (H*C*[MeC(NAr)]$_2$), 123.27 (BDI Ar), 125.10 (BDI Ar), 125.66 (BDI Ar), 126.21, 142.05, 142.84, 143.47, 145.99, 153.23, 153.77, 167.86, 175.67. Anal. calcd. for $C_{68}H_{92}N_4Re_2Ge$ (**3**): C, 57.90; H, 6.57; N, 3.97 %. Found: C, 58.09; H, 6.76; N, 3.72 %.

Re(Sn[PhC(N^{t}Bu)$_2$])(η^5-Cp)(BDI) (4)

In 20 mL glass scintillation vials inside a nitrogen filled glovebox, a solution of Na[Re(μ^5-Cp)(BDI)] (30 mg, 0.043 mmol) in 3 mL of Et_2O and a suspension of SnCl[PhC(N^{t}Bu)$_2$] (16 mg, 0.042 mmol) in 2 mL of Et_2O were prepared and stirred while cooling to –78 °C in the cold well of the glovebox. The solution of Na[Re(μ^5-Cp)(BDI)] was then added, via pipette, to the stirring solution of SnCl[PhC(N^{t}Bu)$_2$]. The reaction mixture was stirred at –78 °C for 1.5 hours before volatiles were removed *in vacuo* while the vial remained in the cold well. Again in the cold well, the residue was triturated with cold pentane (2 mL), extracted with cold pentane (5 mL), and the resulting solution was filtered through Celite, concentrated under reduced pressure, and allowed to start crystallizing at room temperature. After two hours, removal of the supernatant and drying *in vacuo* led to the isolation of dark purple crystals of **4** (33 mg). Total yield: 33 mg, 77 %. X-ray quality crystals of **4** were obtained from pentane at –40 ºC. M.p.: ca. 110 ºC (decomp.). ^{1}H NMR (400 MHz, 270 K, toluene-d_8) δ 0.91 (s, 18H, ^{t}Bu), 1.02 (d, 6H, BDI CH(*Me*)$_2$, *J* = 6.8 Hz), 1.09 (d, 6H, BDI CH(*Me*)$_2$, *J* = 6.6 Hz), 1.39 (d, 6H, BDI CH(*Me*)$_2$, *J* = 6.5 Hz), 1.44 (d, 6H, BDI CH(*Me*)$_2$, *J* = 6.6 Hz), 1.80 (m, 2H, BDI C*H*(Me)$_2$), 2.62 (s, 6H, HC[*Me*C(NAr)]$_2$), 4.30 (m, 2H, BDI C*H*(Me)$_2$), 4.82 (s, 5H, Cp), 6.31 (s, 1H, *H*C[MeC(NAr)]$_2$), 6.94 (m, 6H, Ar), 7.00 (m, 1H, Ar), 7.15 (dd, 2H, Ar, *J* = 6.8, 2.5 Hz), 7.21 (m, 2H, Ar). ^{13}C NMR (151 MHz, 298 K, C_6D_6) δ 23.64 (HC[*Me*C(NAr)]$_2$), 24.88 (BDI CH(*Me*)$_2$), 25.18 (BDI CH(*Me*)$_2$), 25.40 (BDI CH(*Me*)$_2$), 25.53 (BDI CH(*Me*)$_2$), 27.24 (BDI *C*H(Me)$_2$), 29.50 (BDI *C*H(Me)$_2$), 32.66 (^{t}Bu), 52.67 (tBu bound carbon), 75.05 (Cp), 108.10 (H*C*[MeC(NAr)]$_2$), 122.96 (Ar), 125.05 (Ar), 125.08 (Ar), 127.18 (Ar), 127.48 (Ar), 129.13 (Ar), 140.86, 141.04, 141.43, 156.73, 164.10, 167.17. Anal. calcd. for $C_{49}H_{69}N_4ReSi$ (**4**): C, 57.75; H, 6.83; N, 5.50 %. Found: C, 57.73; H, 6.77; N, 5.35 %.

NMR Spectroscopy

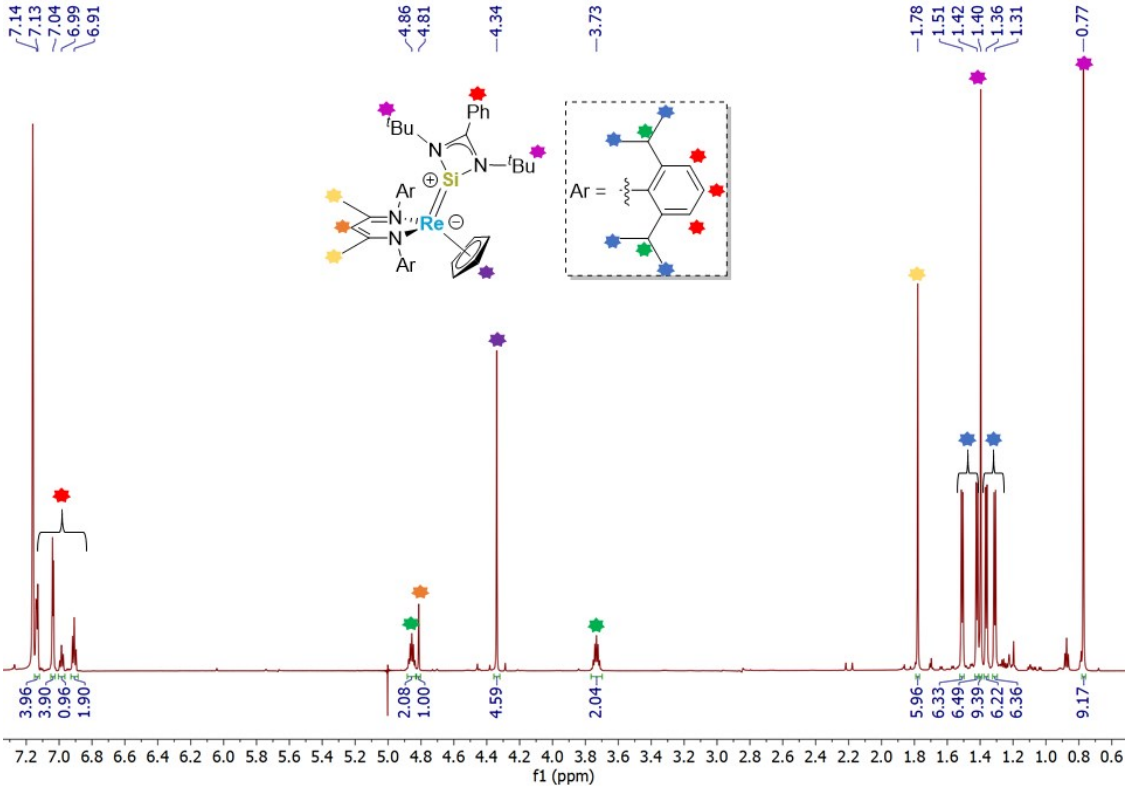

Figure S1. ^{1}H NMR spectrum of Re(Si[PhC(N^{t}Bu)$_2$])(η^5-Cp)(BDI) (**1a**) in C_6D_6 (700 MHz, 293 K).

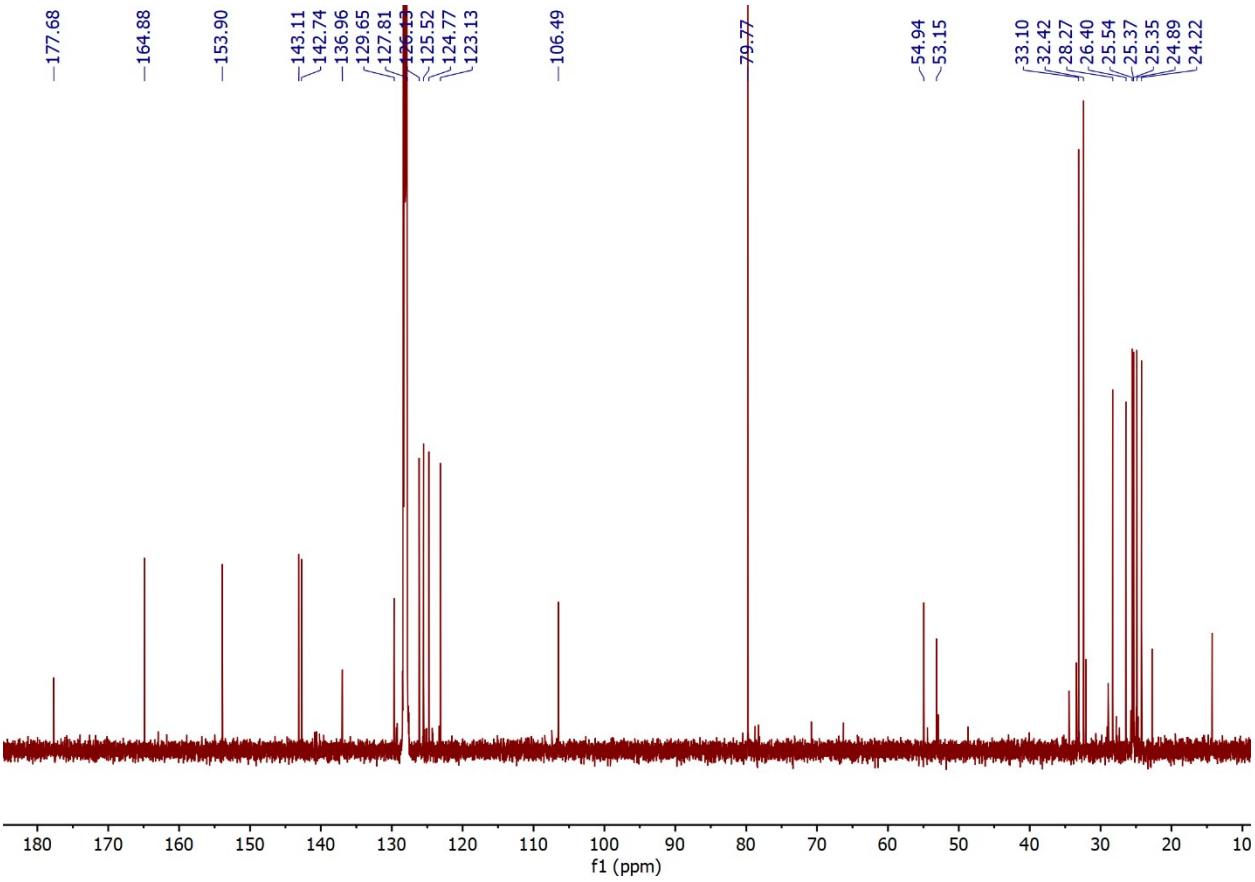

Figure S2. ^{13}C NMR spectrum of Re(Si[PhC(N^{t}Bu)$_2$])(η^5-Cp)(BDI) (**1a**) in C_6D_6 (151 MHz, 298 K).

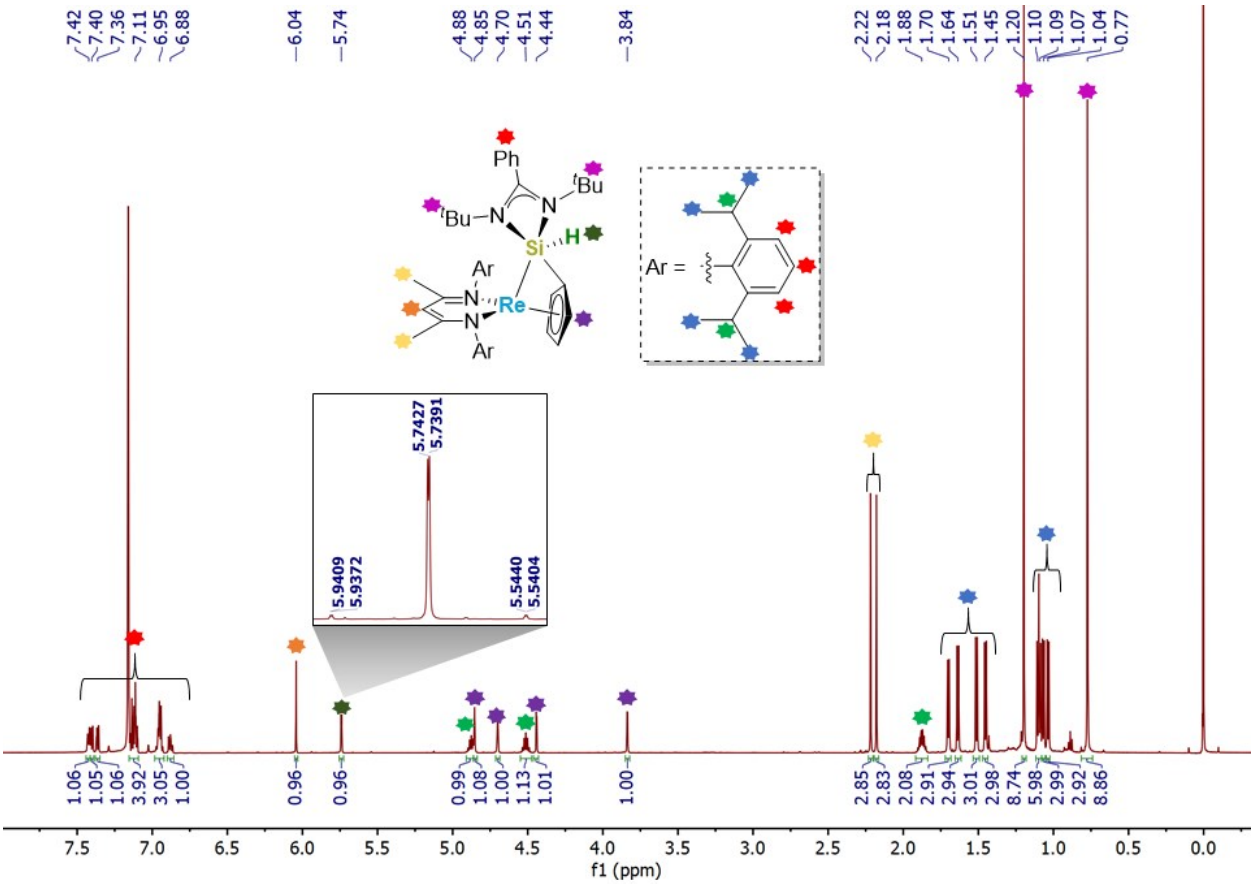

Figure S3. ^{1}H NMR spectrum of (BDI)Re(μ-η^{5}:η^{1}-Cp)(SiH[PhC(N^{t}Bu)$_2$]) (**1b**) in C_6D_6 (600 MHz, 298 K). Minor ^{29}Si satellites can be observed at 5.54 and 5.94 ppm corresponding to one-bond coupling of the silane proton with silicon (inset). An internal standard of $SiMe_4$ (0 ppm) is also present.

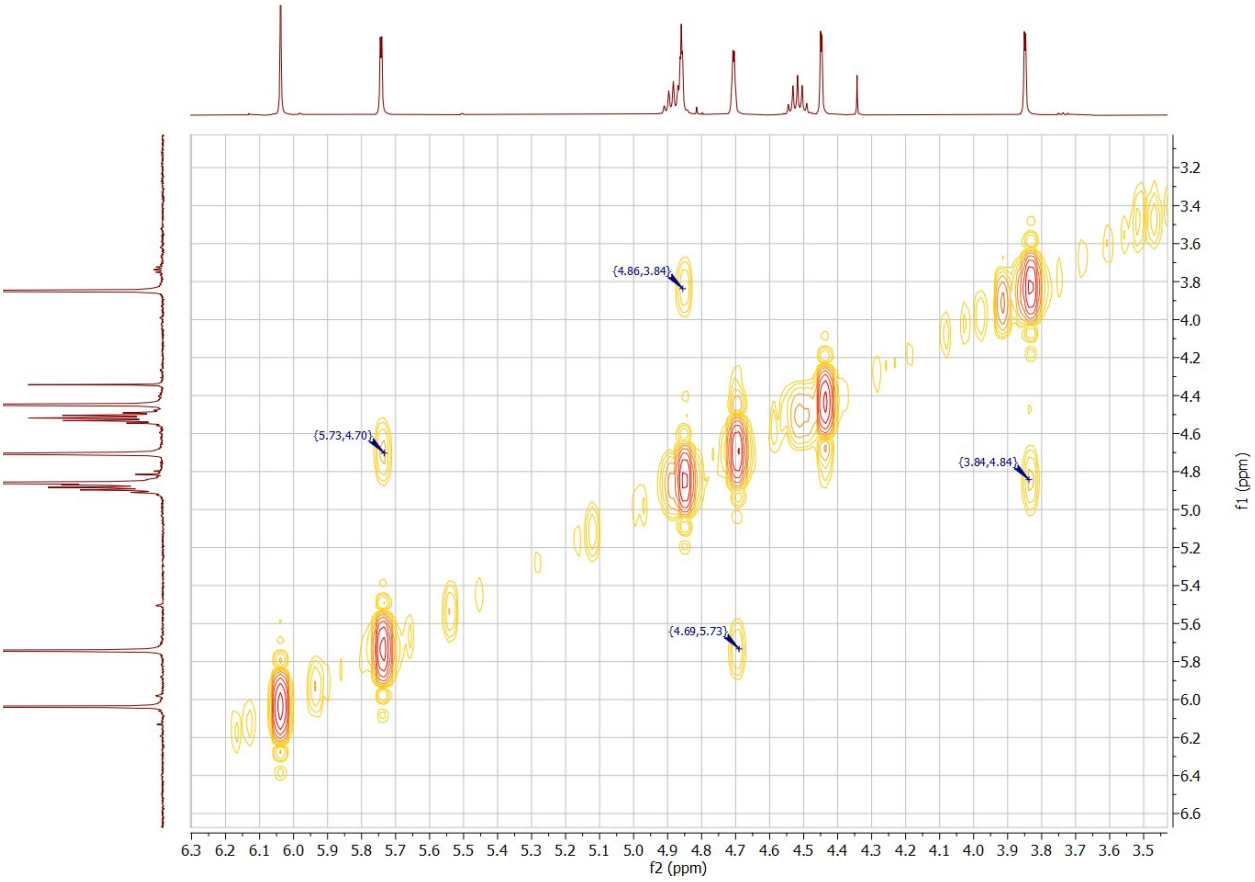

Figure S4. ^{1}H-^{1}H COSY NMR spectrum of (BDI)Re(μ-η^{5}:η^{1}-Cp)(SiH[PhC(N^{t}Bu)$_2$]) (**1b**) in C_6D_6 (600 MHz, 298 K), highlighting the region containing cross peaks attributable to long range coupling between Si–*H* and a Cp–*H*.

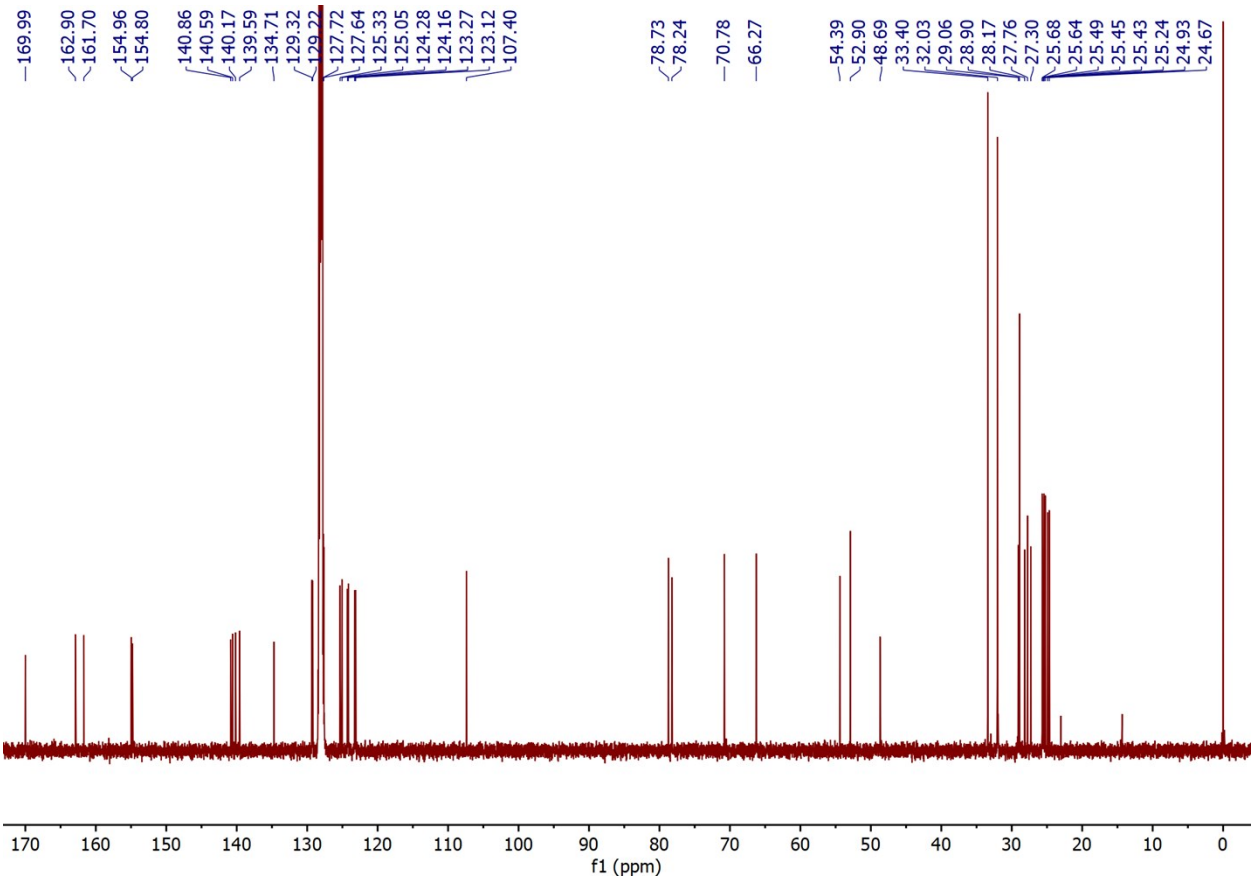

Figure S5. ^{13}C NMR spectrum of (BDI)Re(μ-η^5:η^1-Cp)(SiH[PhC(N^{t}Bu)$_2$]) (**1b**) in C_6D_6 (151 MHz, 298 K). Minor residual pentane present. Spectrum is missing one aromatic carbon bound to a hydrogen. Based on an HSQC experiment, we believe this peak may lie underneath the benzene-d_6 signal.

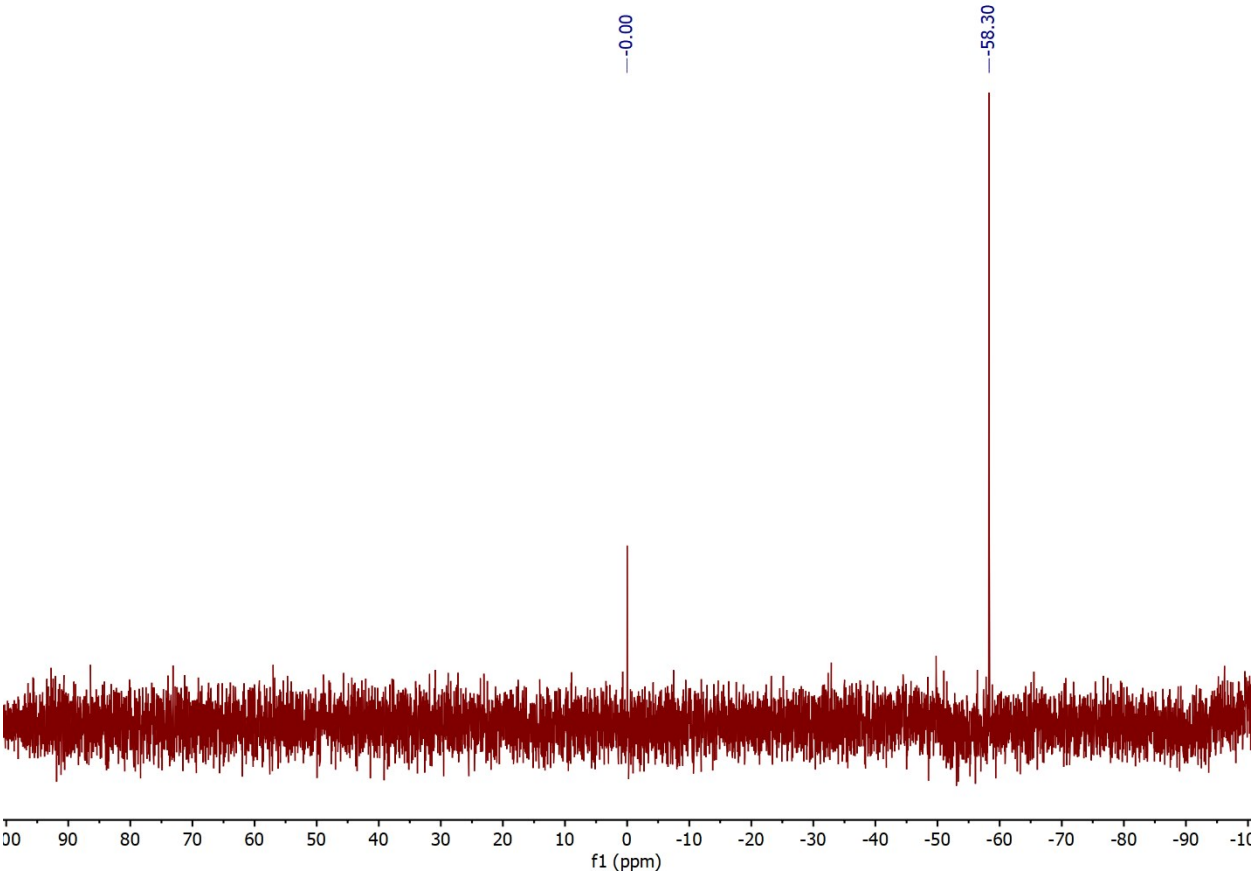

Figure S6. $^{29}Si\{^{1}H\}$ NMR spectrum of (BDI)Re(μ-η^5:η^1-Cp)(SiH[PhC(N^{t}Bu)$_2$]) (**1b**) in C_6D_6 (119 MHz, 298 K). Referenced to an internal standard of $SiMe_4$ (0 ppm).

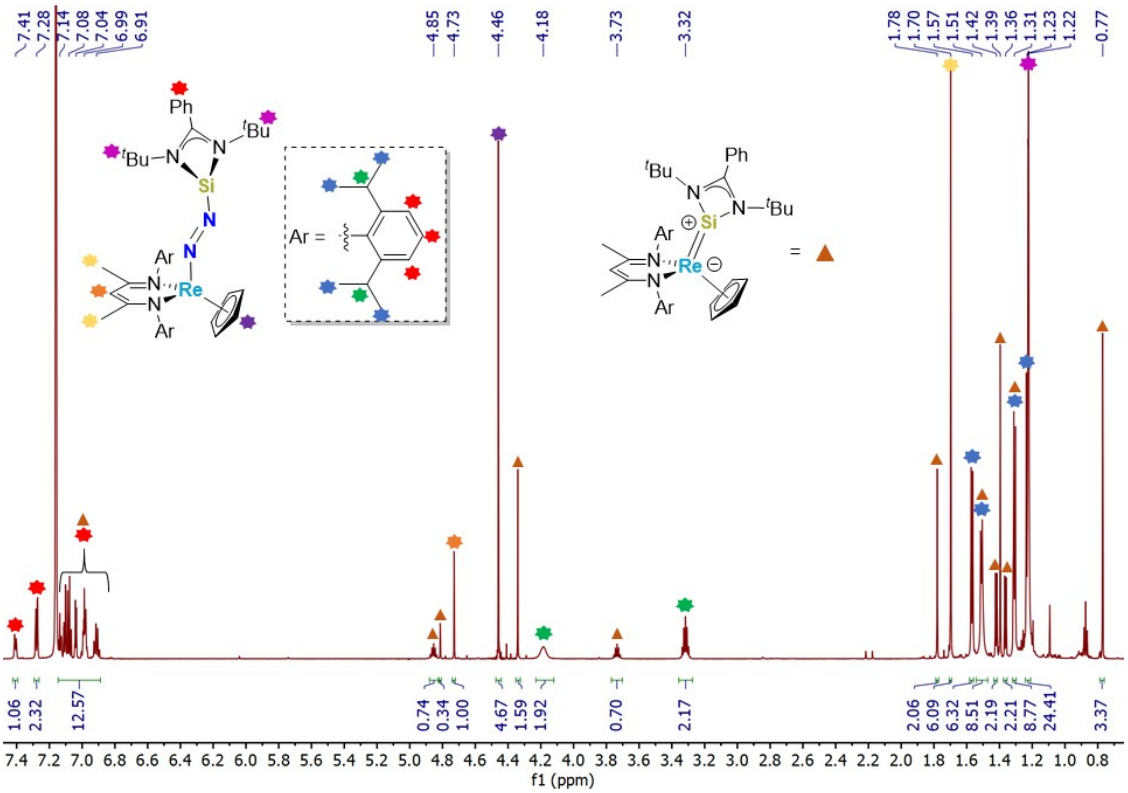

Figure S7. ^{1}H NMR spectrum of a 3:1 mixture of (η^5-Cp)(BDI)Re(μ-N_2)Si[PhC(N^{t}Bu)$_2$] (**1c**) to Re(Si[PhC(N^{t}Bu)$_2$])(η^5-Cp)(BDI) (**1a**) in C_6D_6 (700 MHz, 293 K).

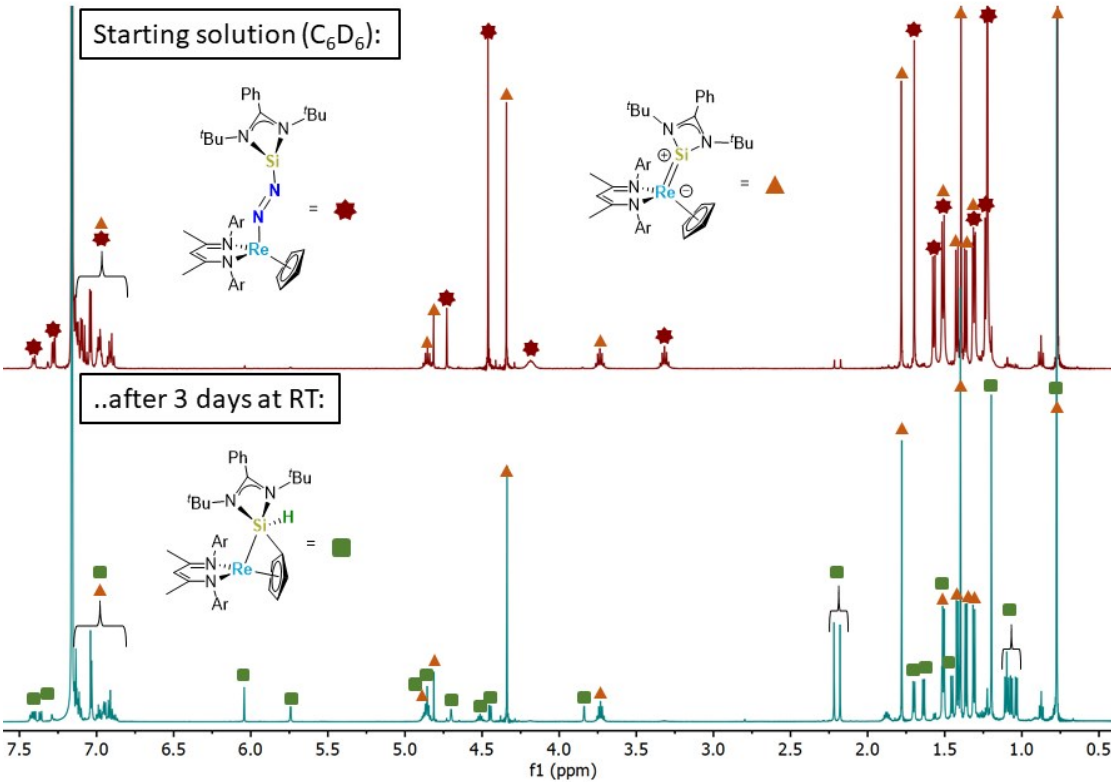

Figure S8. Stacked ^{1}H NMR spectrum showing conversion of **1c** to **1b** in C_6D_6 (700 MHz, 293 K).

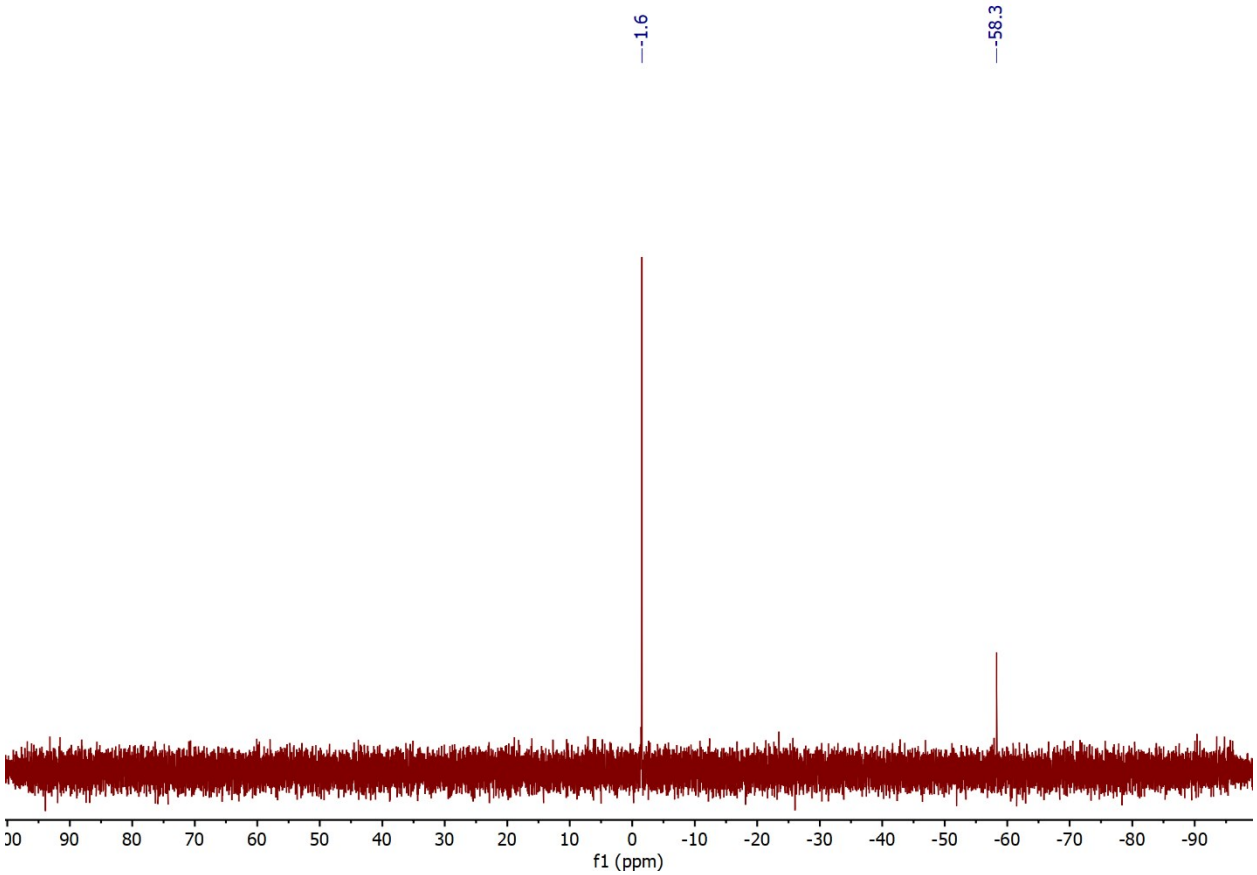

Figure S9. $^{29}Si\{^{1}H\}$ NMR spectrum of (η^5-Cp)(BDI)Re(μ-N_2)Si[PhC(N^{t}Bu)$_2$] (**1c**) in C_6D_6 (119 MHz, 298 K). Referenced to the minor product peak, (BDI)Re(μ-η^5:η^1-Cp)(SiH[PhC(N^{t}Bu)$_2$]), which resides at -58.3 ppm relative to an internal standard of $SiMe_4$ (see Figure S6).

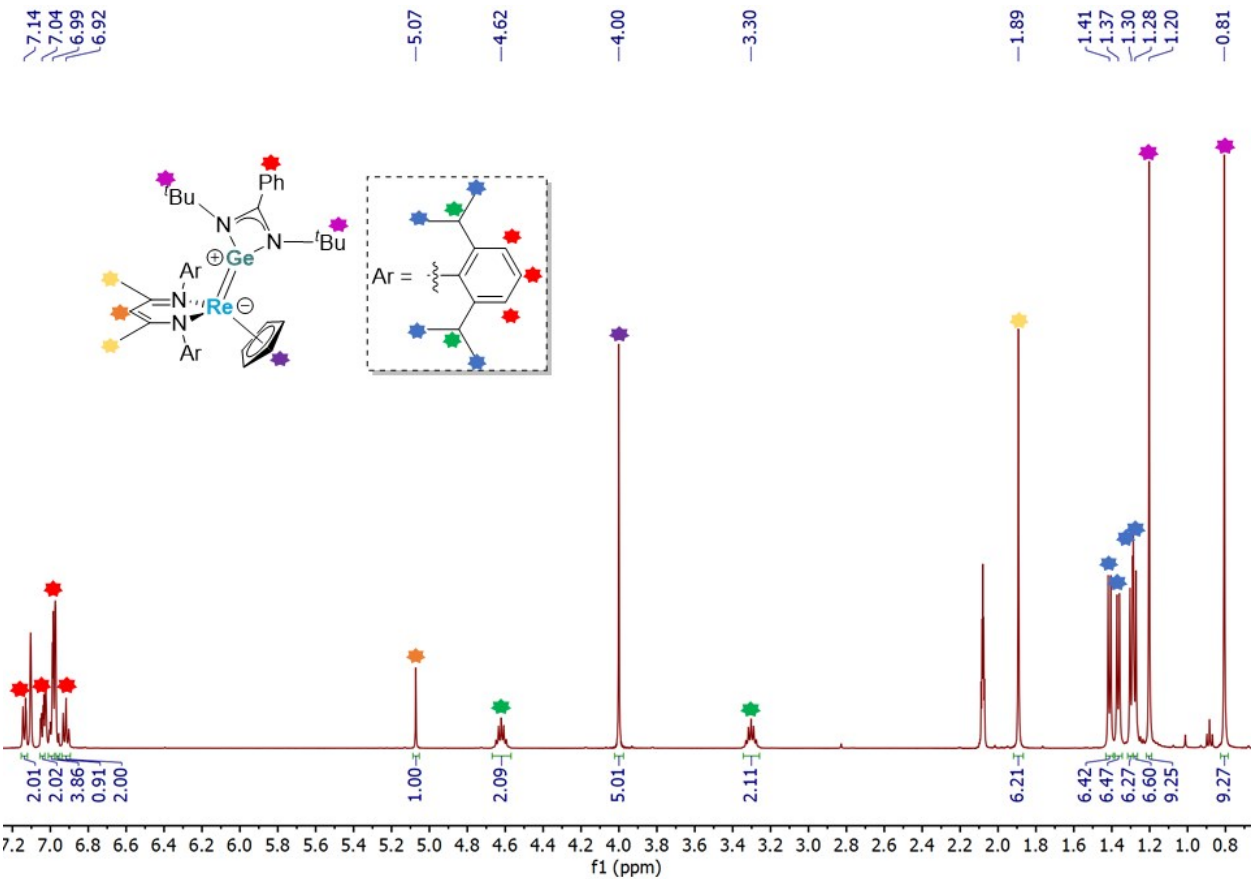

Figure S10. ^{1}H NMR spectrum of Re(Ge[PhC(N^{t}Bu)$_2$])(η^5-Cp)(BDI) (**2**) in toluene-d_8 (500 MHz, 273 K).

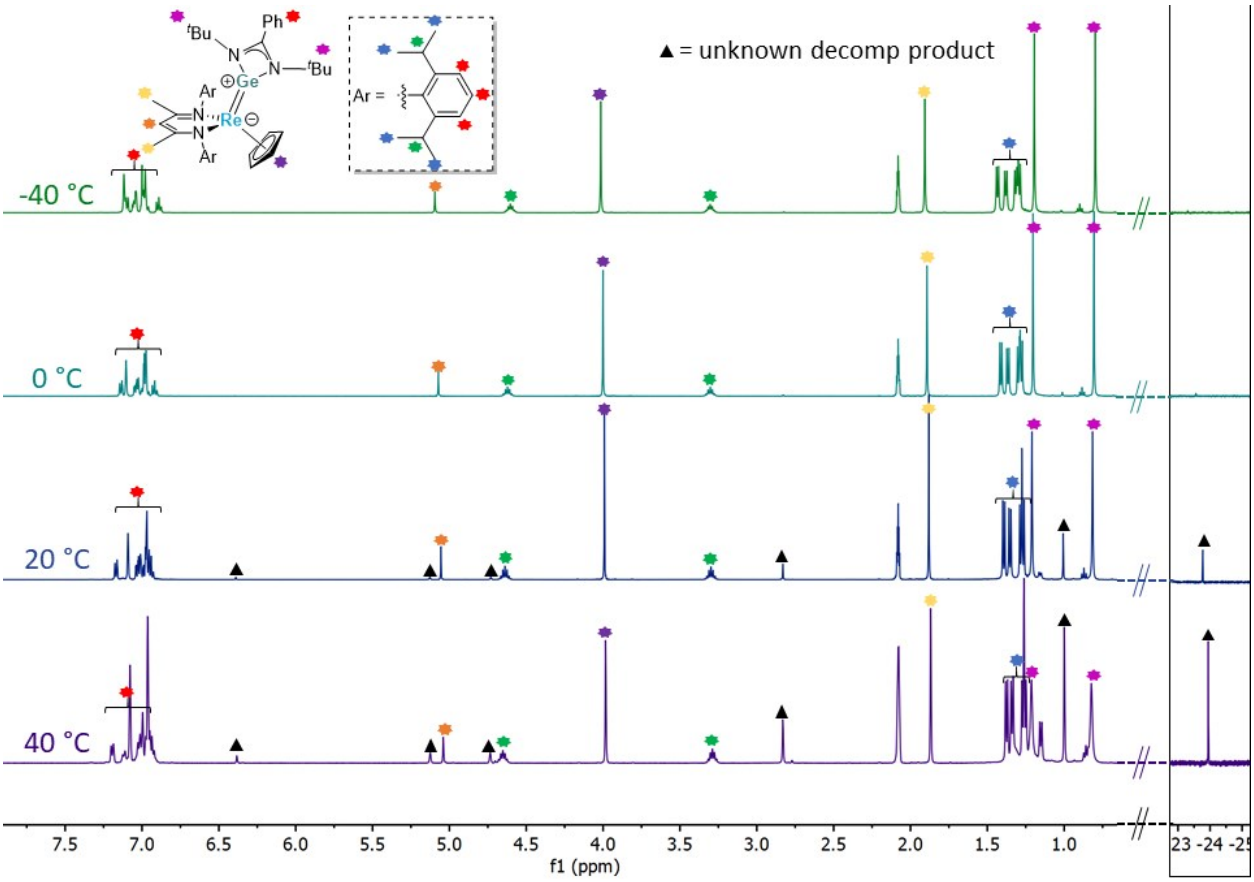

Figure S11. Variable temperature ^{1}H NMR spectrum of the diamagnetic region and upfield region (inset) of Re(Ge[PhC(N^{t}Bu)$_2$])(η^5-Cp)(BDI) (**2**) n toluene-d_8 (500 MHz, 233–313 K). Starting at ~273 K, the product **2** begins to decompose, possibly into a rhenium–hydride complex (resonances denoted by the black triangles); Re–*H* ^{1}H NMR peaks for this ligand system are typically observed in the –20 to –30 ppm region.

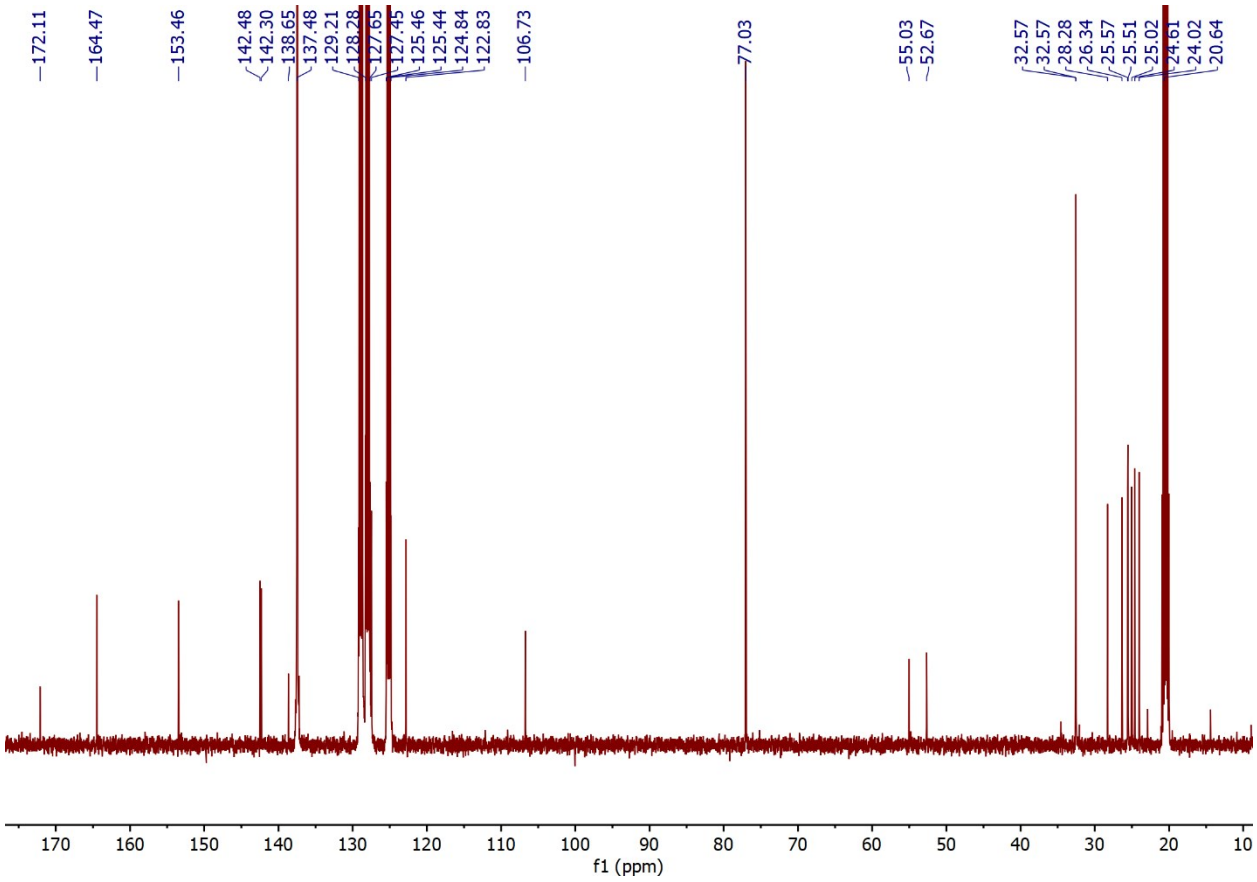

Figure S12. ^{13}C NMR spectrum of Re(Ge[PhC(N^{t}Bu)$_2$])(η^5-Cp)(BDI) (**2**) in toluene-d_8 (151 MHz, 273 K).

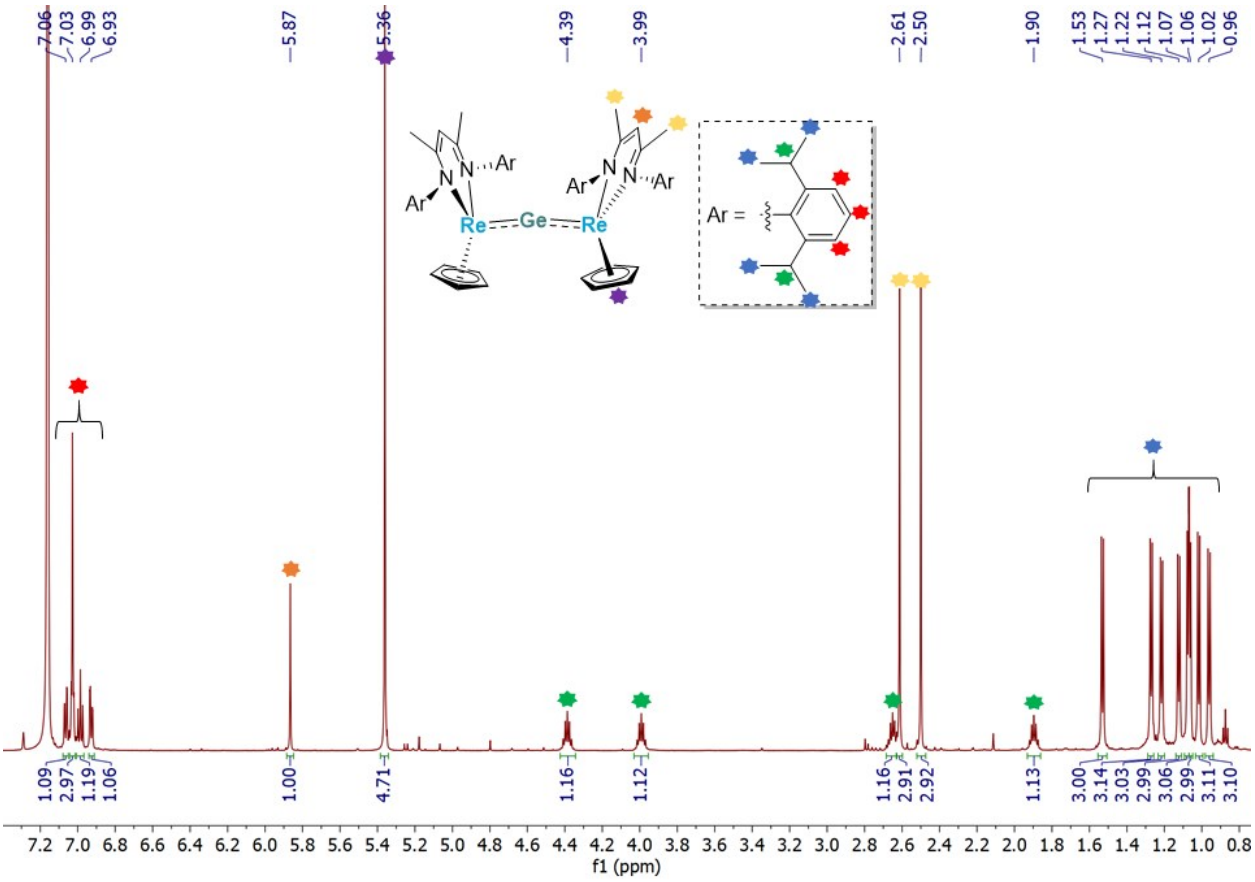

Figure S13. ^{1}H NMR spectrum of μ-Ge[Re(η^{5}-Cp)(BDI)]$_2$ (**3**) in C_6D_6 (600 MHz, 298 K). Minor residual pentane present.

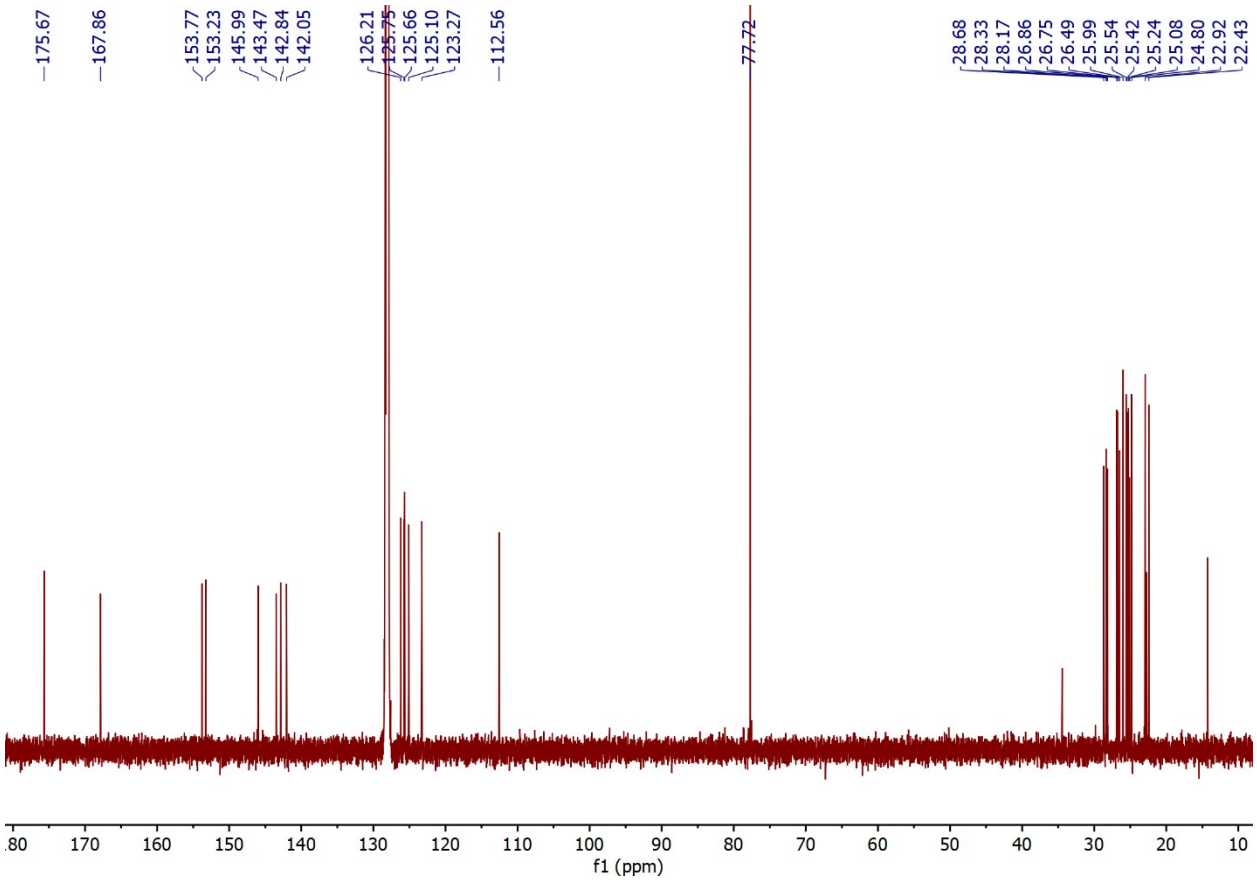

Figure S14. ^{13}C NMR spectrum of μ-Ge[Re(η^5-Cp)(BDI)]$_2$ (**3**) in C_6D_6 (151 MHz, 298 K). Minor residual pentane present.

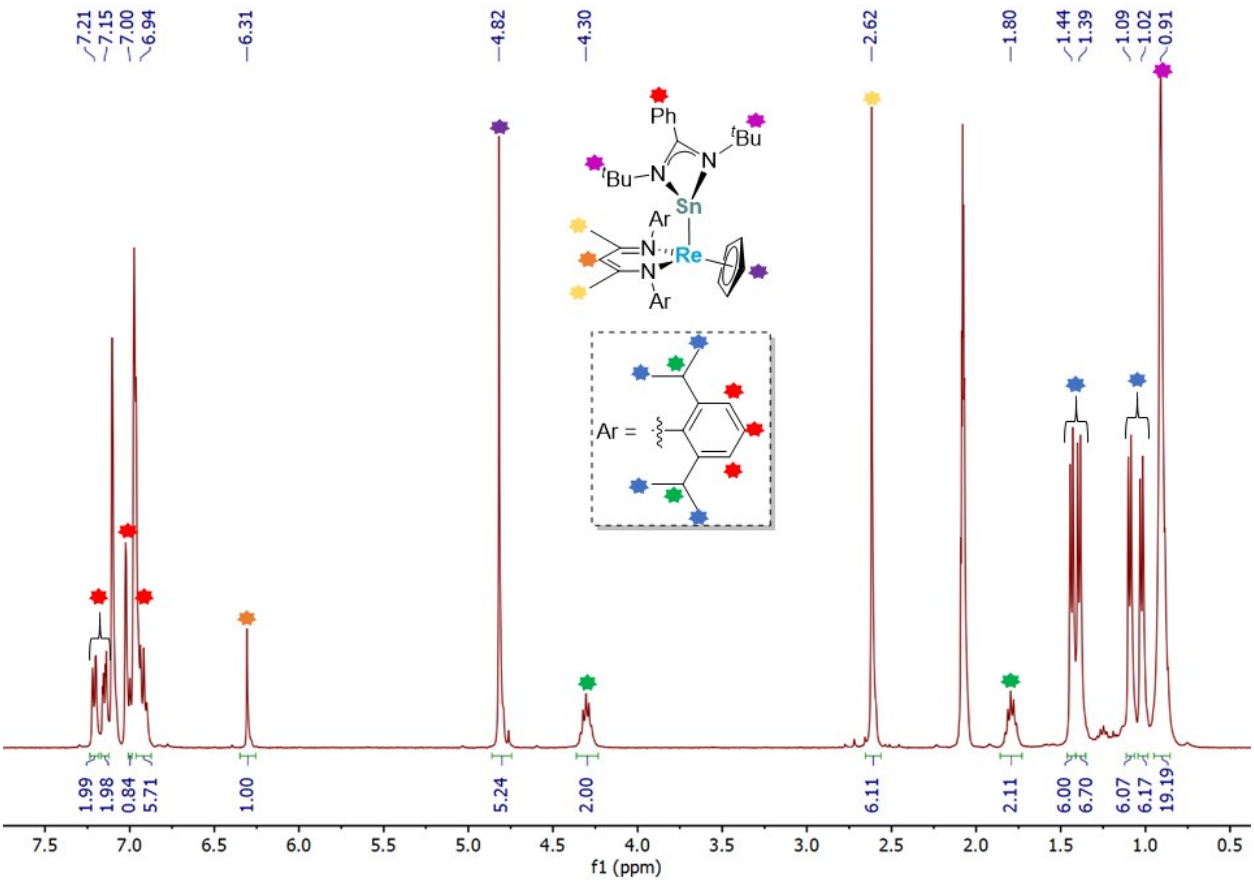

Figure S15. ^{1}H NMR of Re(Sn[PhC(N^{t}Bu)$_2$])(η^5-Cp)(BDI) (**4**) in toluene-d_8 (400 MHz, 270 K).

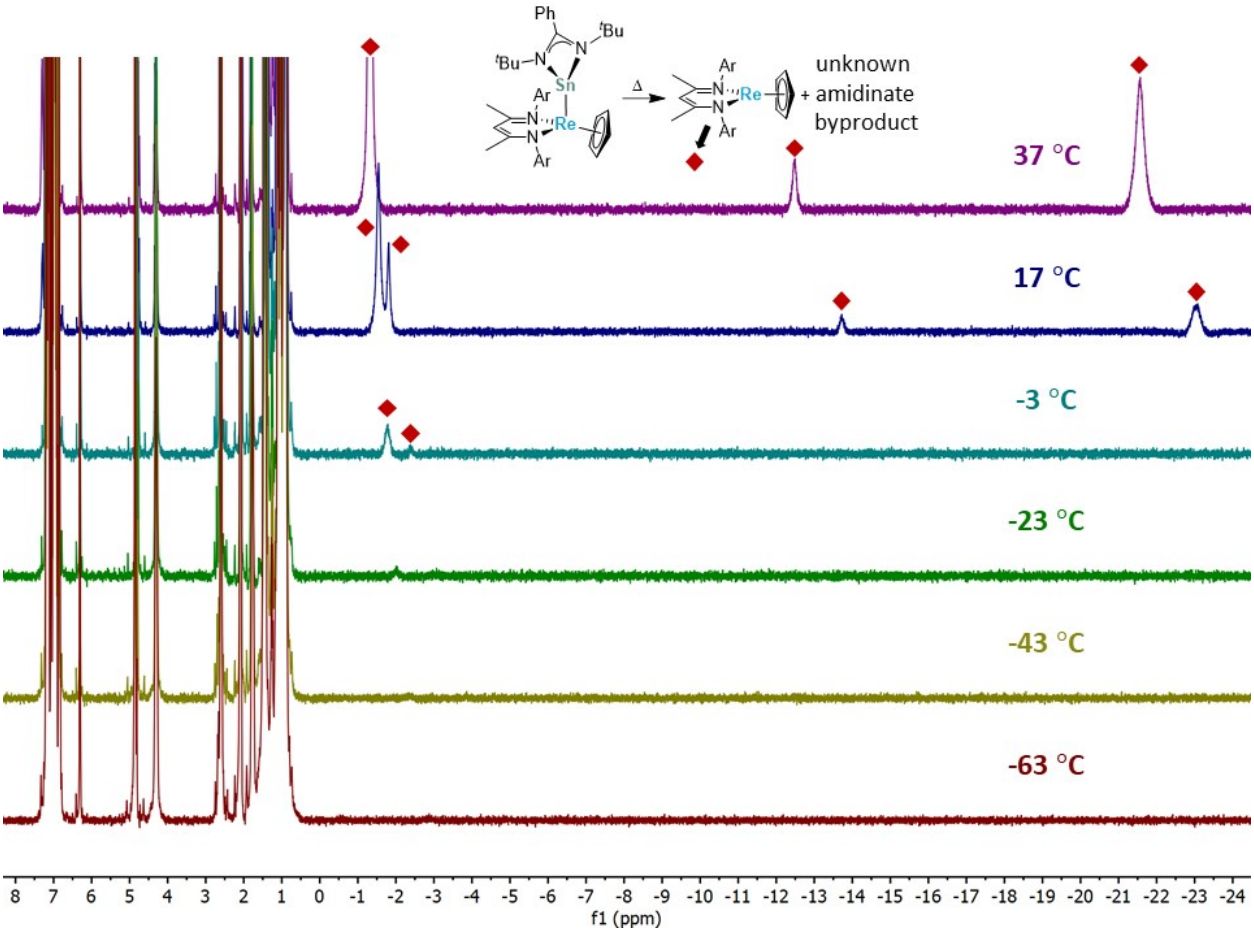

Figure S16. Variable temperature ^{1}H NMR spectrum of the upfield region of Re(Sn[PhC(N^{t}Bu)$_2$])(η^5-Cp)(BDI) (**4**) in toluene-d_8 (400 MHz, 210–310 K). Starting at ~270 K, the product **4** begins to decompose into paramagnetic Re(η^5-Cp)(BDI)[1] as well as an unknown amidinate byproduct.

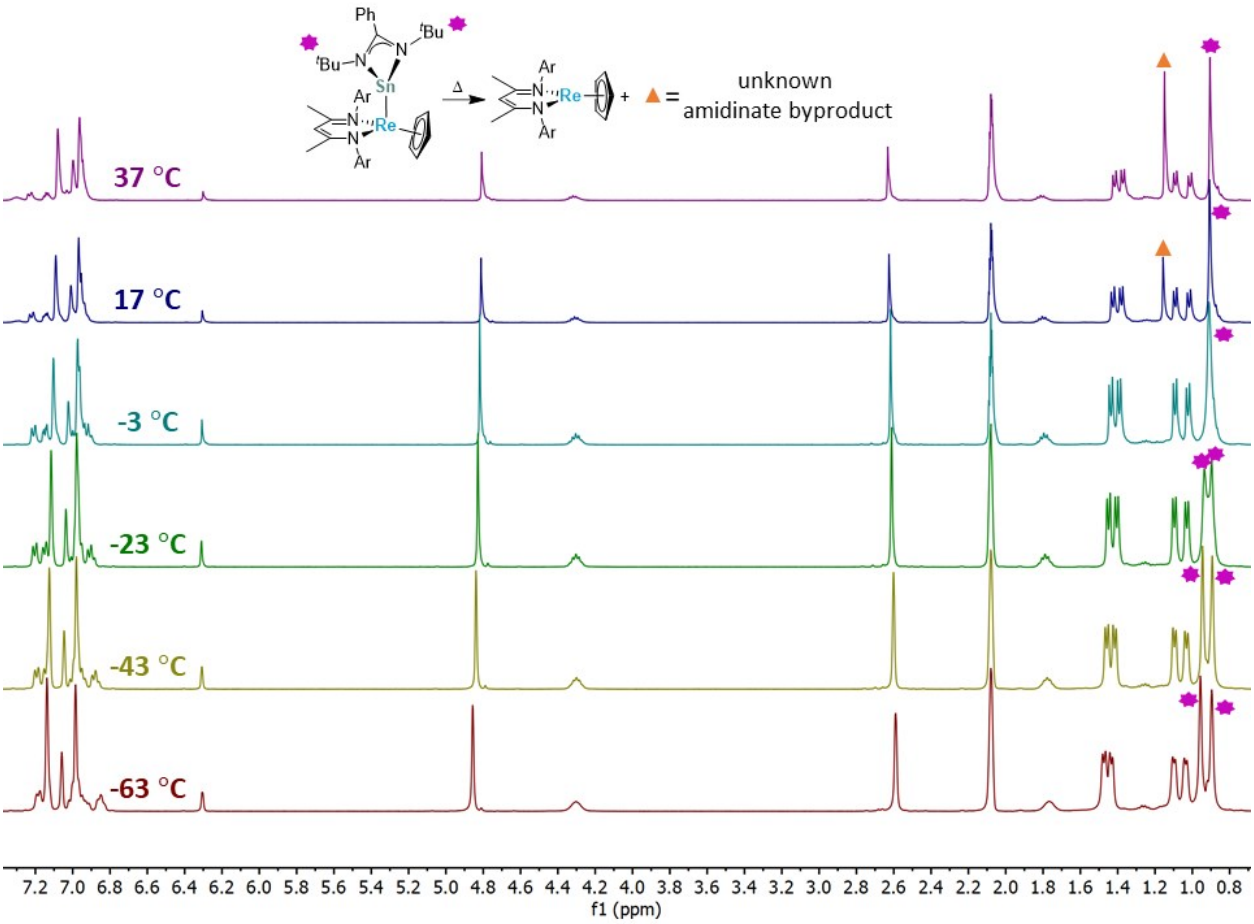

Figure S17. Variable temperature ^{1}H NMR spectrum of the diamagnetic region of Re(Sn[PhC(N^{t}Bu)$_2$])(η^5-Cp)(BDI) (**4**) in toluene-d_8 (400 MHz, 210–310 K). Starting at ~270 K, the product **4** begins to decompose into paramagnetic Re(η^5-Cp)(BDI)[1] as well as an unknown amidinate byproduct.

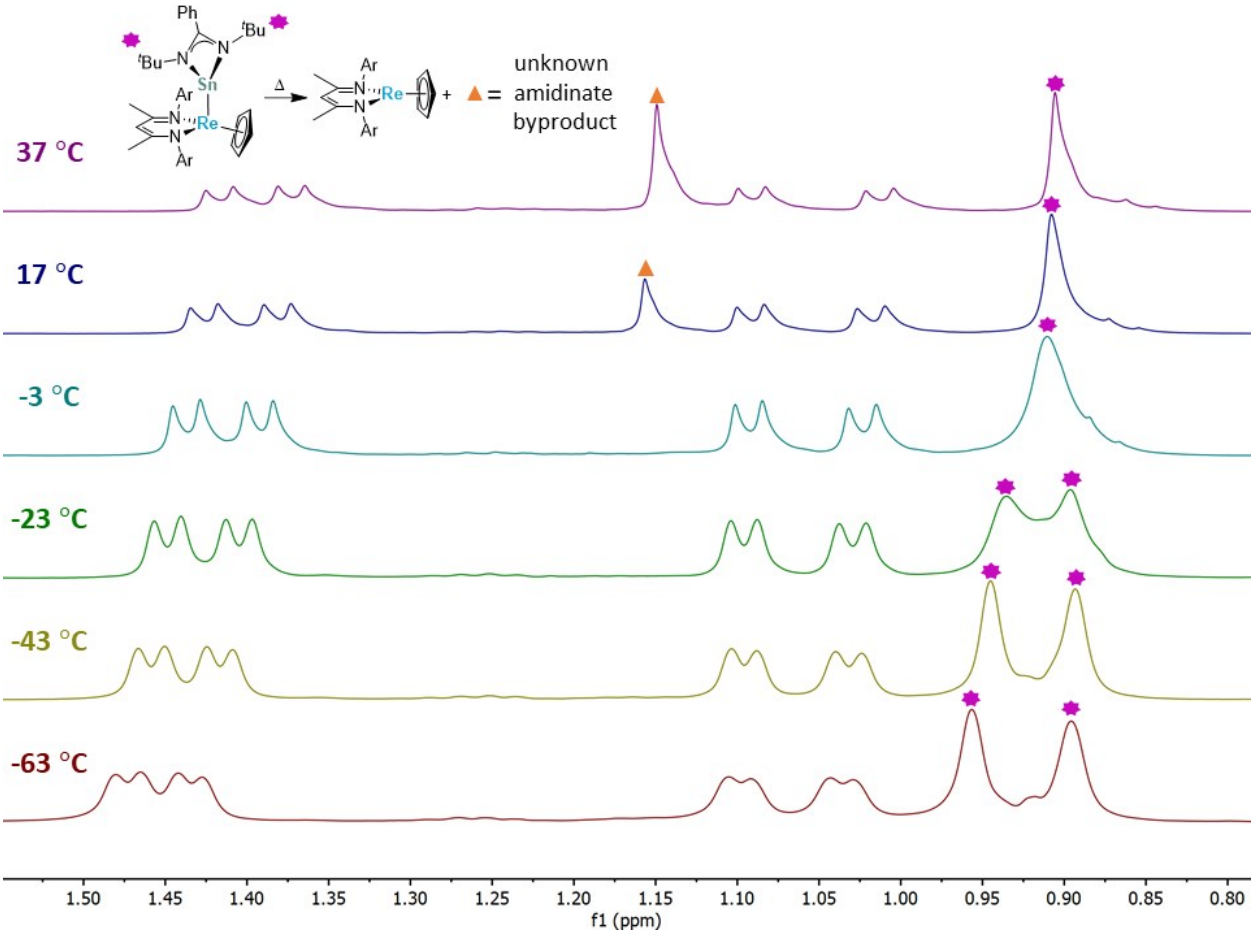

Figure S18. Variable temperature ^{1}H NMR spectrum of a zoomed in spectral region of Re(Sn[PhC(N^{t}Bu)$_2$])(η^5-Cp)(BDI) (**4**) in toluene-d_8 (400 MHz, 210–310 K). At 210 K, the *t*-butyl groups of **4** are distinguishable as two separate peaks due to restricted bond rotation, and these signals coalesce around 270 K. Also, starting at ~270 K, the product **4** begins to decompose into paramagnetic Re(η^5-Cp)(BDI)[1] as well as an unknown amidinate byproduct.

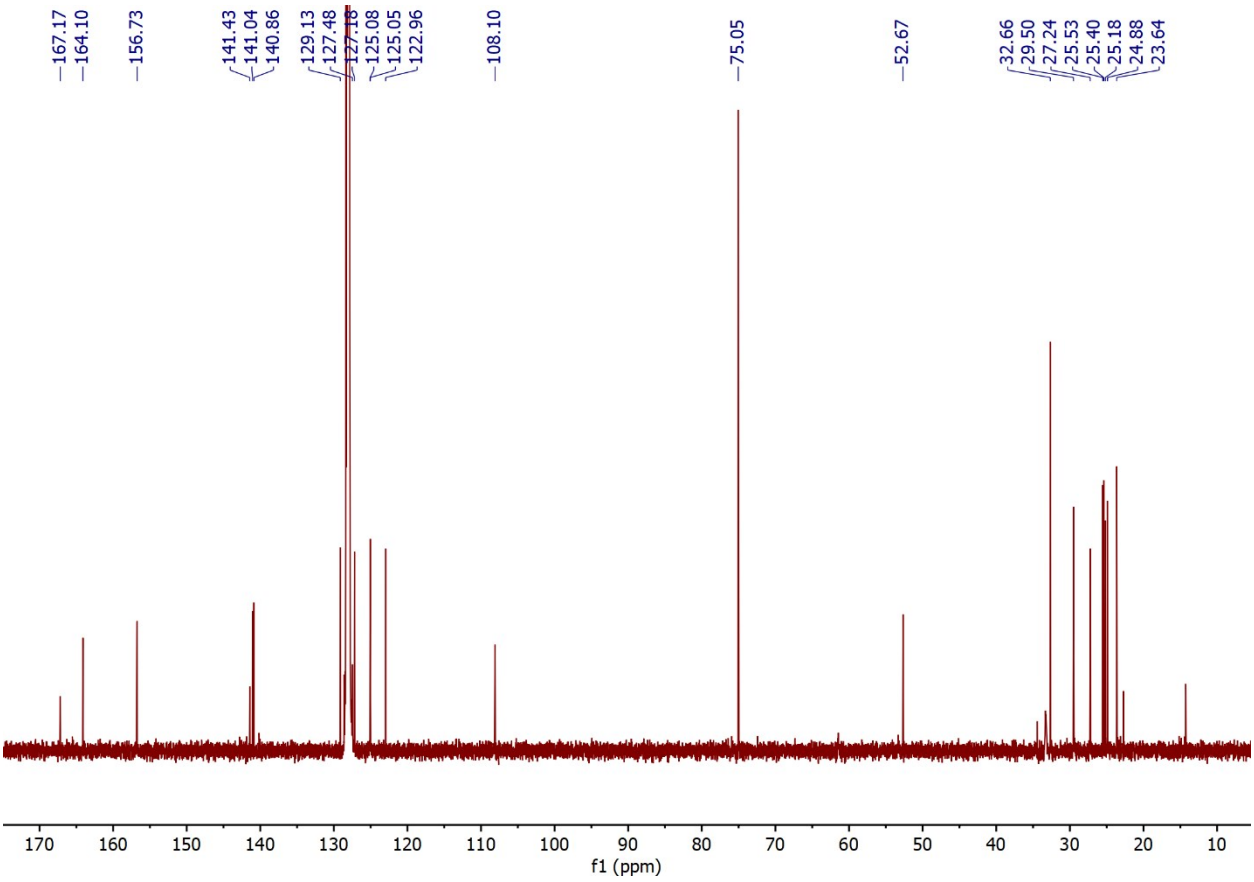

Figure S19. ^{13}C NMR of Re(Sn[PhC(N^{t}Bu)$_2$])(η^5-Cp)(BDI) (**4**) in C_6D_6 (151 MHz, 298 K). Minor residual pentane present.

X-ray Crystallography

In a dry nitrogen glovebox, samples of single crystals of **1a**, **1b**, **1c**, **2**, **3** and **4** were coated in Paratone-N oil for transport to diffraction facilities. Crystals were mounted on either a MiTeGen 10 μm aperture Dual-Thickness MicroMount (for **1b**, **1c**, **3**, and **4**) or on a Kaptan loop (for **1a** and **2**). X-ray diffraction data for **1b**, **1c**, **3**, and **4** were collected at the Advanced Light Source (ALS), Lawrence Berkeley National Lab, Berkeley, CA, station 12.2.1 using a silicon monochromated beam of 17 keV (λ = 0.7288 Å) synchrotron radiation. X-ray diffraction data **1a** and **2** were collected at CheXray, Berkeley, CA, using a Rigaku XtaLAB P200 instrument equipped with a MicroMax-007 HF microfocus rotating anode and a Pilatus 200K hybrid pixel array detector using monochromated Mo Kα radiation (λ = 0.71073 Å). All data collections were conducted at 100 K, with the crystals cooled by a stream of dry nitrogen. For **1b**, **1c**, **3**, and **4**, Bruker APEX 2 or APEX3 software was used for the data collections, Bruker SAINT V8.37A or V8.38A software was used to conduct the cell refinement and data reduction procedures,[5] and absorption corrections were carried out by a multi-scan method utilizing the SADABS program.[5] For **1a** and **2**, CrysAlisPro was used for the data collections and data processing, including a multi-scan absorption correction applied using the SCALE3 ABSPACK scaling algorithm within CrysAlisPro.[6] Initial structure solutions were found using direct methods (SHELXT),[7] and refinements were carried out using SHELXL-2014,[8] as implemented by WinGX (for **3**)[9] or Olex2(for **1a**, **1b**, **1c**, **2**, and **4**).[10] Thermal parameters for all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined isotropically, except for the silane hydrogen (H1) in **1b**, which was located explicitly in the difference map and refined isotropically. Thermal ellipsoid plots were made using Mercury.[11] All structures were deposited to the Cambridge Crystallographic Data Centre (CCDC), with deposition numbers 204928 (**1a**), 204929 (**1b**), 204930 (**1c**), 204931 (**2**), 204932 (**3**), and 204933 (**4**).

Table S1. Crystallographic details and refinement metrics for compounds **1a-c** and **2**.

	1a	**1b**	**1c**	**2**
Empirical formula	$C_{54}H_{81}N_4ReSi$	$C_{49}H_{69}N_4ReSi$	$C_{49}H_{69}N_6ReSi$	$C_{49}H_{69}N_4ReGe$
Formula weight	1000.51	928.37	956.39	972.87
Color, habit	Red, plate	Green, block	Orange, block	Dark orange, prism
Temperature/K	100(2)	100(2)	100(2)	100(2)
Crystal system	triclinic	monoclinic	monoclinic	triclinic
Space group	P-1	$P2_1/c$	$P2_1/n$	P-1
a/Å	9.3802(3)	22.1653(8)	13.5200(7)	9.3575(2)
b/Å	12.9055(4)	10.2310(4)	25.196(2)	13.0104(3)
c/Å	21.1791(5)	19.6887(7)	14.1374(7)	20.9269(4)
α/°	96.261(2)	90	90	94.783(2)
β/°	92.718(2)	96.153(1)	101.580(2)	92.965(2)
γ/°	102.594(3)	90	90	100.914(2)
Volume/Å^3	2480.5(2)	4439.1(3)	4718.0(4)	2487.33(9)
Z	2	4	4	2
ρ_{calc}g/cm^3	1.340	1.389	1.346	1.299
μ/mm^{-1}	2.512	2.966	2.794	3.069
F(000)	1044.0	1920.0	1976.0	996.0
Crystal size/mm^3	0.180 × 0.150 × 0.050	0.055 × 0.025 × 0.025	0.120 × 0.060 × 0.060	0.310 × 0.090 × 0.070
Radiation	MoKα (λ = 0.71073)	synchrotron (λ = 0.7288)	synchrotron (λ = 0.7288)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.088 to 52.744	4.268 to 54.194	3.562 to 55.702	5.718 to 52.744
Index ranges	$-11 \le h \le 11$, $-16 \le k \le 15$, $-26 \le l \le 26$	$-27 \le h \le 27$, $-12 \le k \le 12$, $-24 \le l \le 24$	$-17 \le h \le 17$, $-32 \le k \le 32$, $-18 \le l \le 18$	$-11 \le h \le 11$, $-16 \le k \le 16$, $-26 \le l \le 26$
Reflections collected	50669	61901	69801	46677
Independent reflections	10121	9088	10424	10142
R_{int}	0.0889	0.0422	0.0646	0.0853
Completeness to Θ = 25.93°	100.0	100.0	100.0	100.0
Data/restraints/parameters	10121/8/601	9088/0/516	10424/0/530	10142/0/512
Goodness-of-fit	1.023	1.065	1.150	0.990
R_1 / wR_2 [I≥2σ(I)]	0.0338 / 0.0784	0.0193 / 0.0409	0.0676 / 0.1424	0.0326 / 0.0749
R_1 / wR_2 [all data]	0.0398 / 0.0804	0.0227 / 0.0422	0.0743 / 0.1455	0.0402 / 0.0773
Largest diff. peak/hole / e Å^{-3}	2.02/–1.16	0.45/–0.62	10.12/–2.64	2.61/–1.54
CCDC	2048928	2048929	2048930	2048931

Table S2. Crystallographic details and refinement metrics for compounds **3** and **4**.

	3	**4**
Empirical formula	$C_{73}H_{104}N_4Re_2Ge$	$C_{211}H_{312}N_{16}Re_4Sn_4$
Formula weight	1482.59	4292.31
Color, habit	Brown, block	Maroon, rod
Temperature/K	100(2)	100(2)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	12.4047(5)	11.8518(5)
b/Å	16.4384(7)	19.5560(9)
c/Å	17.3177(8)	23.628(2)
α/°	103.050(2)	65.925(2)
β/°	102.812(2)	78.503(2)
γ/°	96.440(2)	88.700(2)
Volume/Å^3	3305.2(2)	4889.1(4)
Z	2	1
ρ_{calc}g/cm^3	1.490	1.458
μ/mm^{-1}	4.396	3.198
F(000)	1504.0	2190.0
Crystal size/mm^3	0.120 × 0.050 × 0.030	0.100 × 0.025 × 0.025
Radiation	synchrotron (λ = 0.7288)	synchrotron (λ = 0.7288)
2Θ range for data collection/°	4.132 to 56.63	3.958 to 54.192
Index ranges	-16 ≤ h ≤ 16, -21 ≤ k ≤ 21, -22 ≤ l ≤ 22	-14 ≤ h ≤ 14, -24 ≤ k ≤ 24, -29 ≤ l ≤ 29
Reflections collected	50181	66753
Independent reflections	15203	20001
R_{int}	0.0380	0.0790
Completeness to Θ = 25.93°	100.0	100.0
Data/restraints/parameters	15203/0/743	20001/21/1117
Goodness-of-fit	1.042	0.993
R_1 / wR_2 [I≥2σ(I)]	0.0263 / 0.0522	0.0446 / 0.1147
R_1 / wR_2 [all data]	0.0348 / 0.0563	0.0517 / 0.1209
Largest diff. peak/hole / e Å^{-3}	1.02/–1.08	1.93/–1.39
CCDC	2048932	2048933

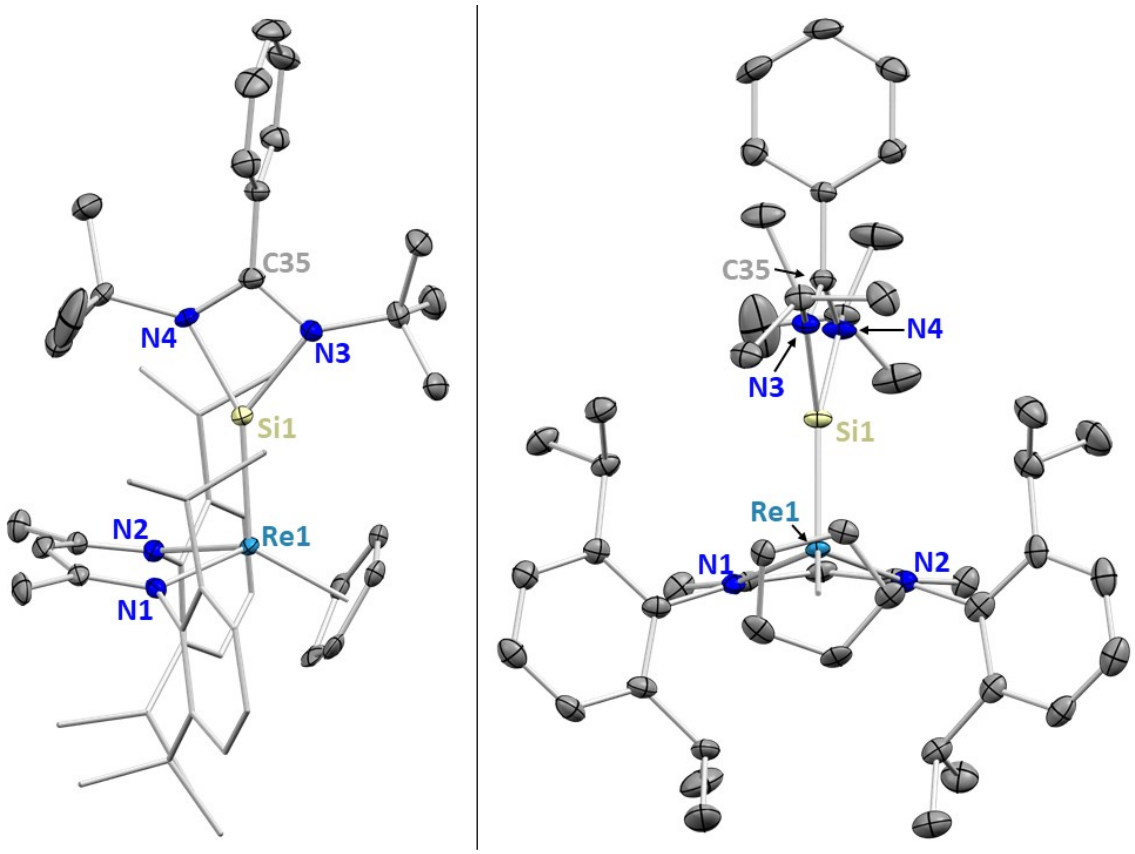

Figure S20. X-ray crystal structure of **1a** shown from the side (left) and front (right) with 50% probability ellipsoids. The BDI diisopropylphenyl groups in the side view are shown in wireframe, and hydrogen atoms are omitted for clarity. A pentane molecule, which can be found in the asymmetric unit, is also omitted.

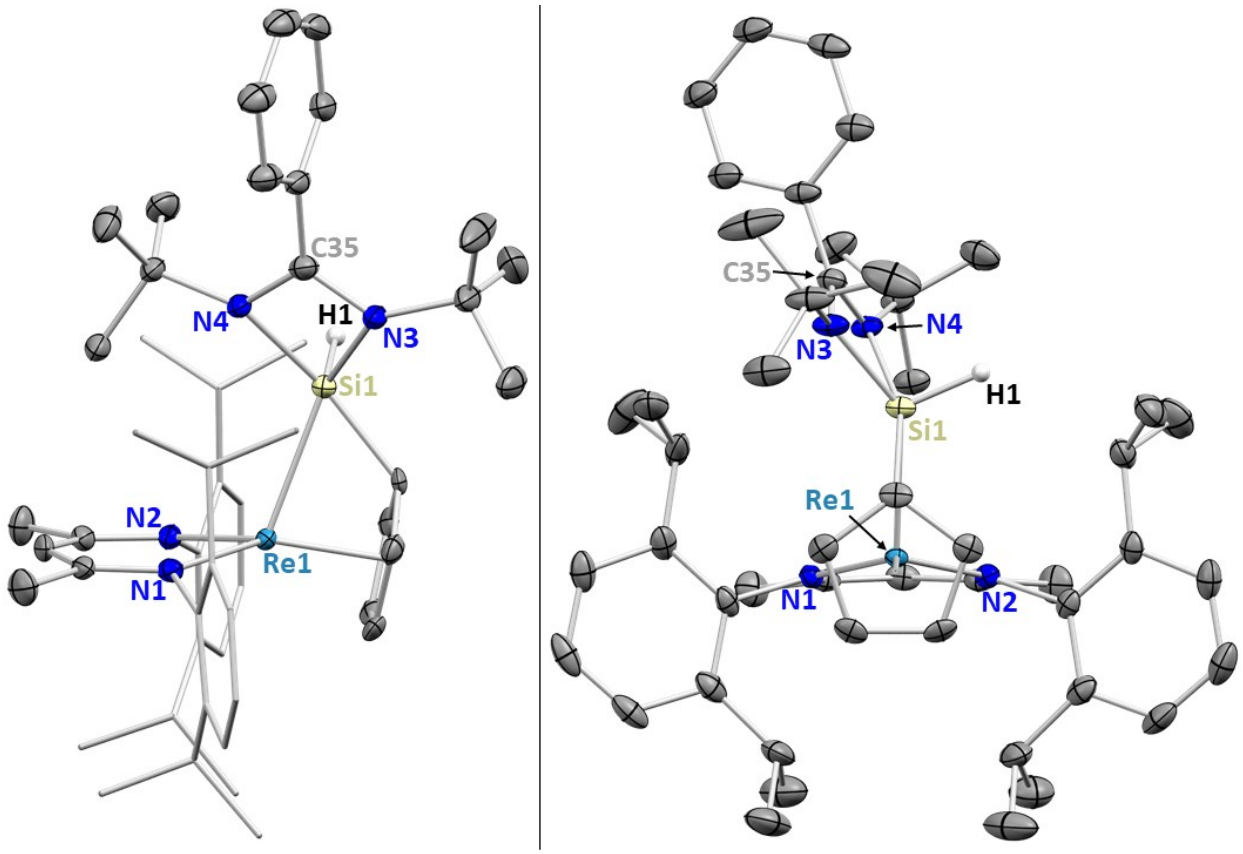

Figure S21. X-ray crystal structure of **1b** shown from the side (left) and front (right) with 50% probability ellipsoids. The BDI diisopropylphenyl groups in the side view are shown in wireframe, and hydrogen atoms (other than H1) are omitted for clarity. The silane hydrogen (H1) was located in the difference map and refined isotropically.

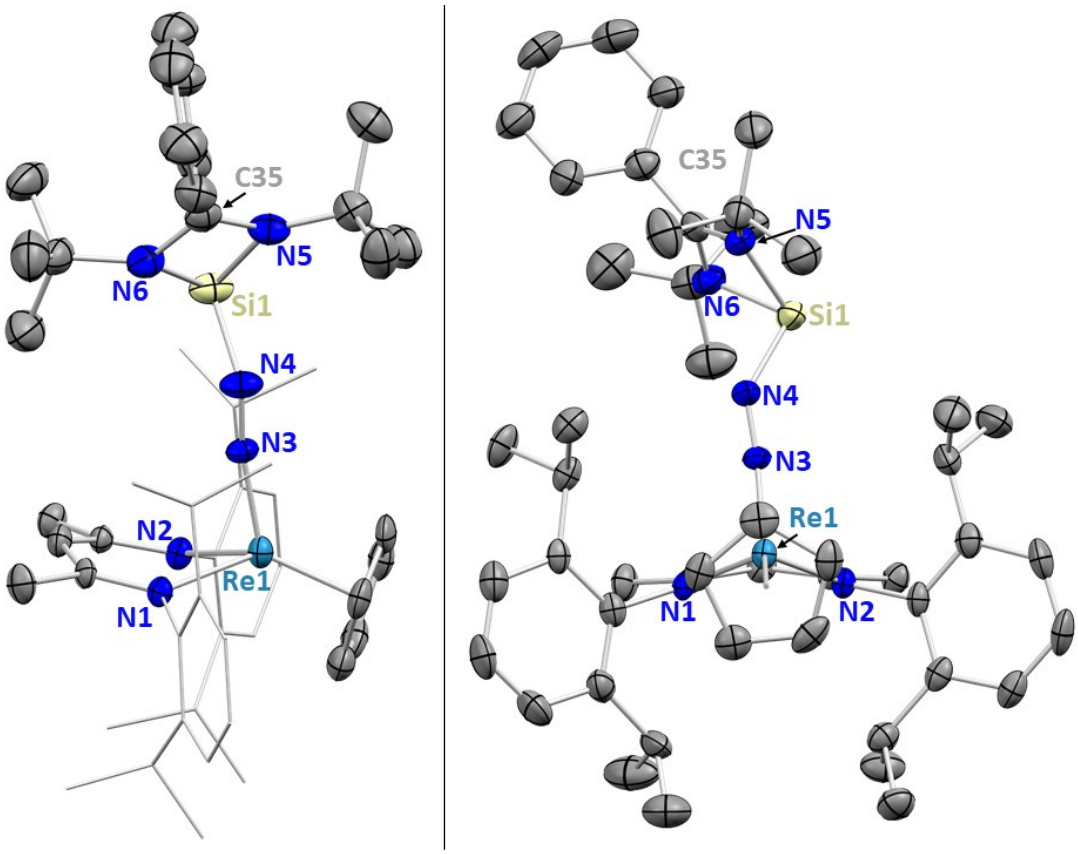

Figure S22. X-ray crystal structure of **1c** shown from the side (left) and front (right) with 50% probability ellipsoids. The BDI diisopropylphenyl groups in the side view are shown in wireframe, and hydrogen atoms are omitted for clarity.

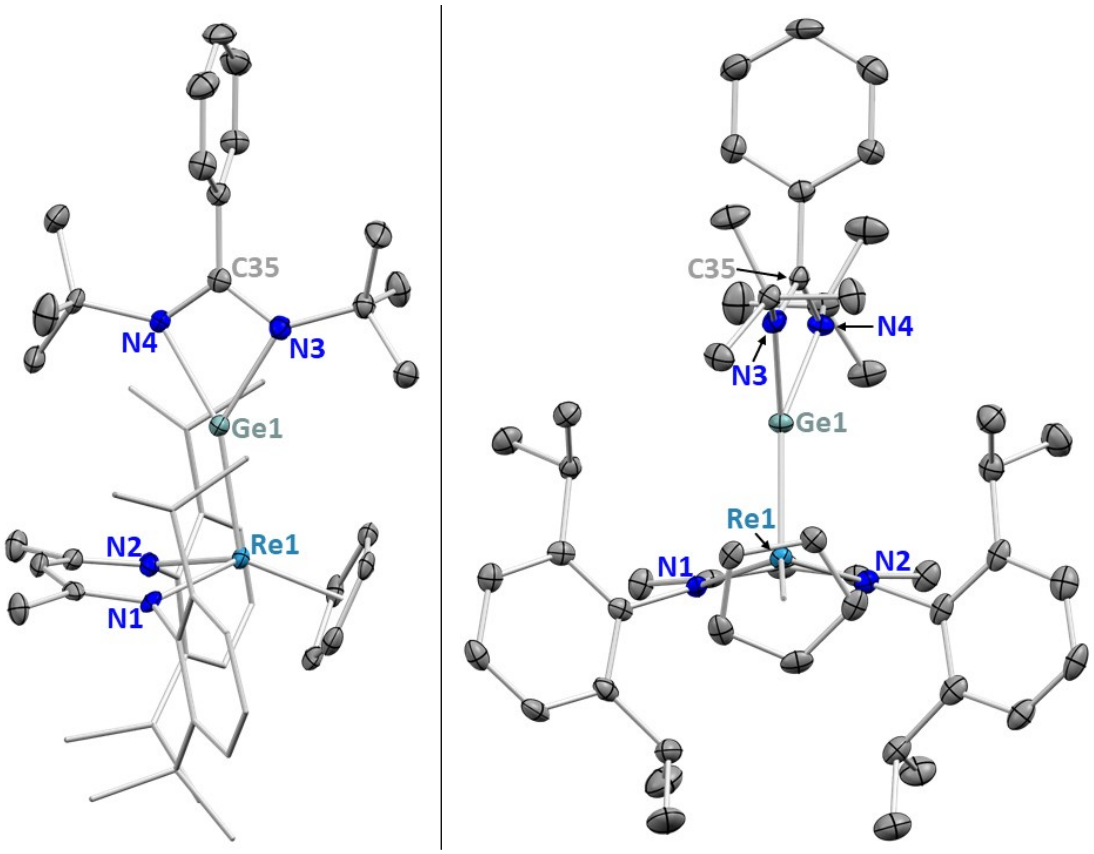

Figure S23. X-ray crystal structure of **2** shown from the side (left) and front (right) with 50% probability ellipsoids. The BDI diisopropylphenyl groups in the side view are shown in wireframe, and hydrogen atoms are omitted for clarity.

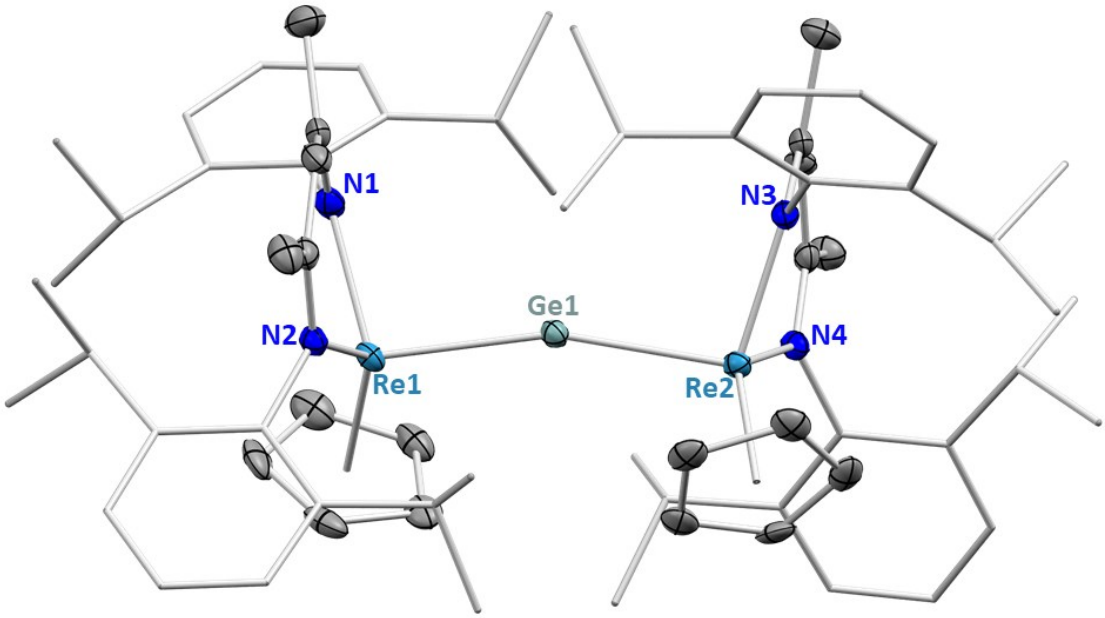

Figure S24. X-ray crystal structure of **3** with 50% probability ellipsoids. The BDI diisopropylphenyl groups are shown in wireframe, and hydrogen atoms are omitted for clarity. A pentane molecule, which can be found in the asymmetric unit, is also omitted.

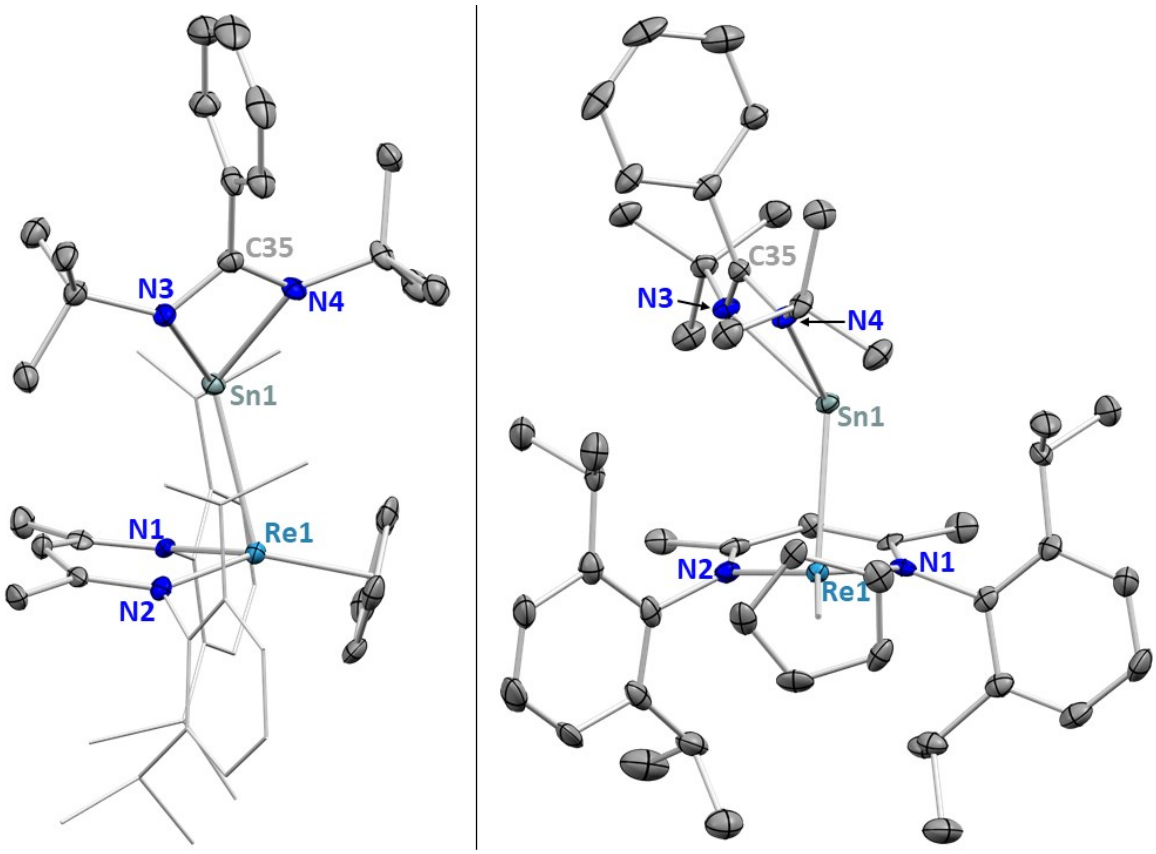

Figure S25. X-ray crystal structure of **4** shown from the side (left) and front (right) with 50% probability ellipsoids. The BDI diisopropylphenyl groups in the side view are shown in wireframe, and hydrogen atoms are omitted for clarity. A pentane molecule, which can be found in the unit cell, is also omitted.

Table S3. Selected distances (Å) and angles (deg) for **1a**, **1b**, **2**, **3**, and **4**.[a]

complex	Re–E[b]	Re–N1	Re–N2	Re–Cp(cent)	Re–E–C35	Re–E–N3[d]	Re–E–N4[d]
1a	2.2413(9)	2.188(3)	2.178(3)	1.900(2)	172.6(2)	138.80(9)	151.4(1)
1b	2.5299(8)	2.053(2)	2.060(2)	1.855(2)	138.66(6)	113.80(6)	140.38(6)
2	2.3322(4)	2.166(3)	2.153(3)	1.878(2)	168.39(8)	139.76(8)	151.49(8)
3	2.4395(5) 2.4367(5)	2.099(3) 2.092(2)	2.122(2) 2.124(3)	1.880(2) 1.880(2)	[c]	–	–
4	2.7562(5) 2.7532(5)	2.046(4) 2.057(4)	2.060(5) 2.058(4)	1.885(3) 1.881(2)	138.70(9) 137.21(9)	129.58(9) 128.6(1)	124.82(9) 124.35(9)

[a]There are two molecules of **4** in the asymmetric unit, leading to two reported values for these measurements.
[b]E = Si, Ge, Sn
[c]There is no amidinate-based C35 in this complex, but the Re1–Ge–Re2 angle was measured at 163.18(2)°.
[d]Measurements only apply to complexes containing amidinate based N3 and N4 atoms.

Table S4. Selected distances (Å) and angles (deg) for **1c**.

complex	Re–N3	Re–N1	Re–N2	Re–Cp(cent)	N3–N4	Si–N4	Re–N3–N4	N3–N4–Si
1c	1.778(6)	2.128(6)	2.136(5)	1.901(3)	1.19(2)	1.773(8)	168.9(6)	137.2(6)
							N4–Si–N5	N4–Si–N6
							96.8(3)	98.0(4)

FT-IR Spectroscopy

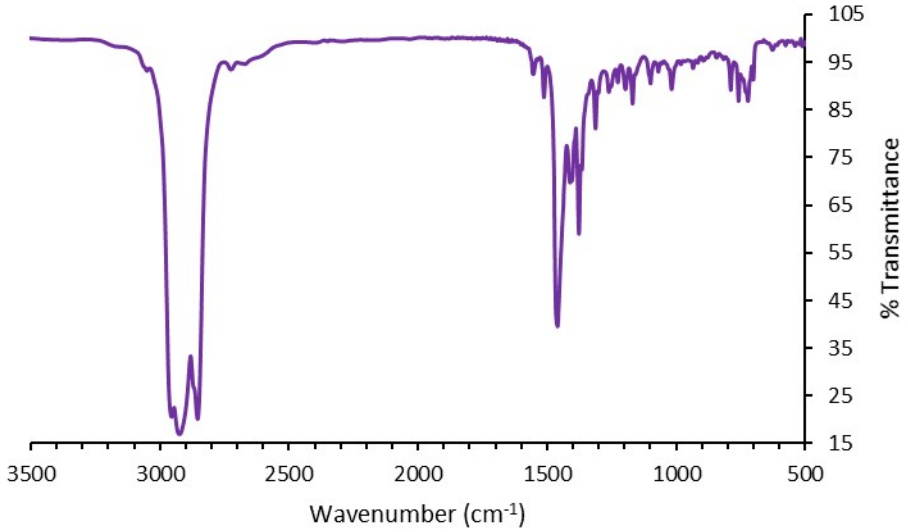

Figure S26. FT-IR spectrum (Nujol/KBr) of Re(Si[PhC(N^{t}Bu)$_2$])(η^5-Cp)(BDI) (**1a**).

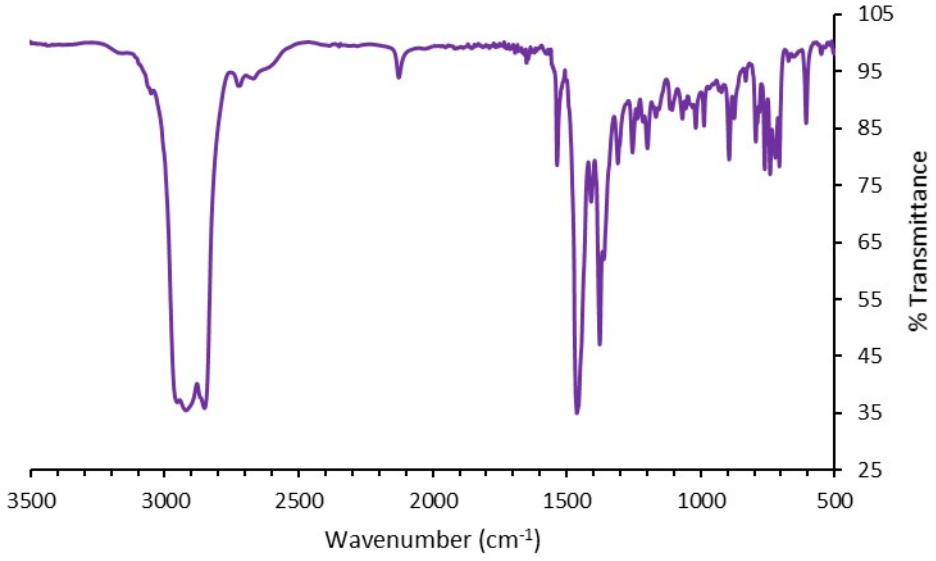

Figure S27. FT-IR spectrum (Nujol/KBr) of (BDI)Re(μ-η^5:η^1-Cp)(SiH[PhC(N^{t}Bu)$_2$]) (**1b**). $\nu_{Si\text{-}H}$ 2128 cm^{-1}.

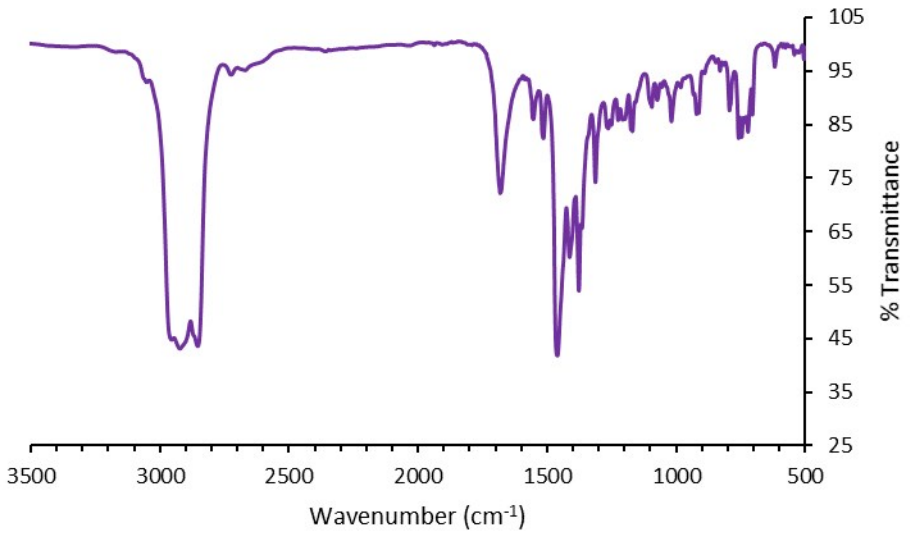

Figure S28. FT-IR spectrum (Nujol/KBr) of a mixture of (η^5-Cp)(BDI)Re(μ-N_2)Si[PhC(N^{t}Bu)$_2$] (**1c**) and Re(Si[PhC(N^{t}Bu)$_2$])(η^5-Cp)(BDI) (**1a**). ν_{NN}: 1682 cm^{-1}.

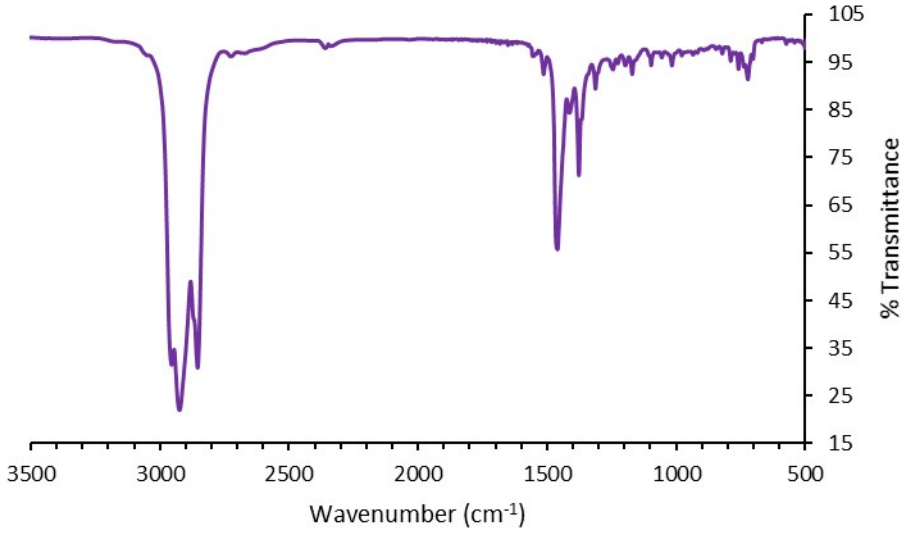

Figure S29. FT-IR spectrum (Nujol/KBr) of Re(Ge[PhC(N^{t}Bu)$_2$])(η^5-Cp)(BDI) (**2**).

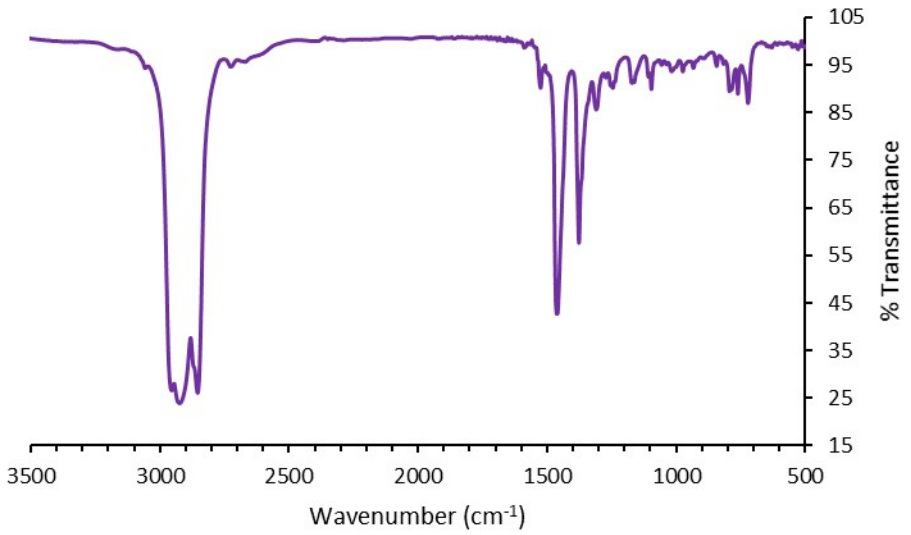

Figure S30. FT-IR spectrum (Nujol/KBr) of μ_2-Ge[Re(η^5-Cp)(BDI)]$_2$ (**3**).

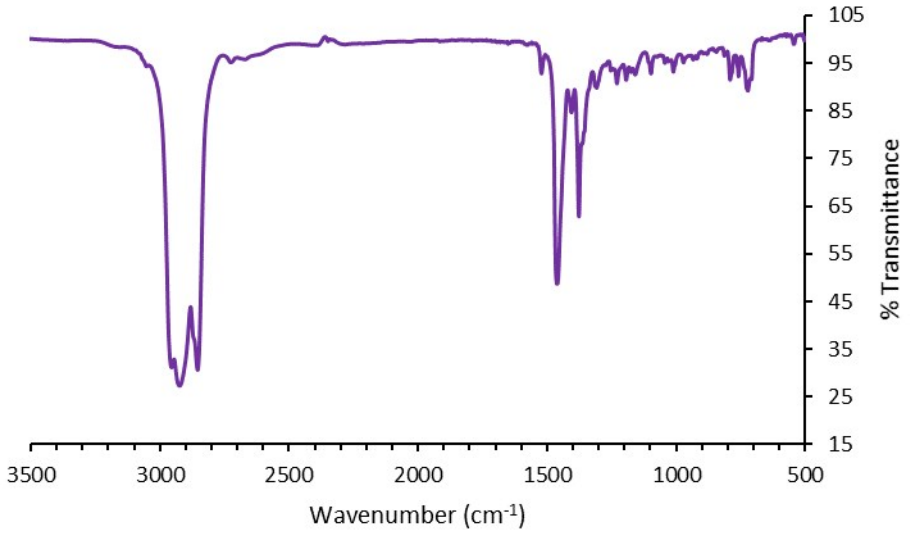

Figure S31. FT-IR spectrum (Nujol/KBr) of Re(Sn[PhC(N^{t}Bu)$_2$])(η^5-Cp)(BDI) (**4**).

Computational Details

All calculations were performed using Gaussian09 suite of programs[12] using Becke's 3-parameter hybrid functional[13] combined with the non-local correlation functional provided by Burke et al.[14] The Re, Ge and Si atoms were represented with a small-core Stuttgart-Dresden relativistic effective core potential associated with their adapted basis set.[15–17] Additionally, the Si basis set was augmented by a d-polarization function ($\alpha = 0.284$)[18] to represent the valence orbitals. All the other atoms C, N and H were described with a 6-31G (d,p), double –ζ quality basis set.[19,20] The electronic structures and bonding have been investigated using Natural Bond Orbital (NBO) analyses.[21,22] The enthalpy energy was computed at T=298 k in the gas phase.

Table S5. Select calculated natural charges, natural bonding orbital compositions, and Wiberg Bond Indices for **1a**, **1b**, **1c**, **2**, **3**, and **4**.

complex	Natural Charges		Natural Bonding Orbital Contributions						WBI	
			Bond		Total	s	p	d		
1a	Re1	-0.72	1	Re1	36.41%	22.27%	55.70%	22.02%	Re1–Si1	1.64
	Si1	1.36		Si1	63.59%	86.50%	13.50%	–	Re1	5.37
			2	Re1	65.78%	0.31%	14.09%	85.60%	Si1	3.00
				Si1	34.22%	0.61%	99.99%	–		
1b	Re1	-0.72	1	Re1	46.33%	45.01%	38.62%	16.37%	Re1–Si1	0.69
	Si1	1.48		Si1	53.67%	34.10%	65.90%	–	Re1	5.03
									Si1	3.29
1c	Re1	0.17	1	Re1	50%	3.22%	1.70%	95.08%	Re1–N3	1.6
	N3	0.05		N3	50%	1.70%	98.27%	–	Re1–N4	0.5
	N4	-0.62	2	Re1	50%	0.48%	1.57%	97.95%	N3–N4	1.8
	Si1	1.14		N3	50%	0.01%	99.96%	–	N4–Si1	0.59
			3	Re1	26%	22.29%	10.31%	67.40%	Re1	5.59
				N3	74%	59.18%	40.80%	–	N3	3.70
			4	N3	50%	38.76%	61.16%	–	N4	3.05
				N4	50%	37.39%	62.50%	–	Si1	1.75
			5	N4	88%	4.00%	95.93%	–		
				Si1	12%	21.04%	77.13%	1.83%		
2	Re1	-0.67	1	Re1	30%	19.29%	61.62%	19.09%	Re1–Ge1	1.5
	Ge1	1.32		Ge1	70%	92.19%	7.77%	–	Re1	5.32
			2	Re1	74%	0.06%	3.41%	96.54%	Ge1	2.76
				Ge1	26%	1.45%	98.38%	–		
3 (singlet)	Re1	-0.43	1	Re1	69.42%	6.62%	41.43%	51.94%	Re1–Ge1	1.08
	Ge1	1.01		Ge1	30.58%	7.67%	92.33%	–	Re2–Ge1	1.10
	Re2	-0.44	1	Re2	70.07%	5.85%	40.49%	53.66%	Re1	5.26
				Ge1	29.93%	7.52%	92.58%	–	Ge1	2.98
									Re2	5.27
3 (triplet)	Re1	-0.44	1	Re1	34.19%	28.29%	53.66%	18.04%	Re1–Ge1	1.16
	Ge1	1.06		Ge1	65.81%	76.92%	23.08%	–	Re2–Ge1	1.16
	Re2	-0.44	1	Re2	49.24%	34.12%	23.23%	42.65%	Re1–Re2	0.15
				Ge1	50.76%	50.06%	49.94%	–	Re1	4.86
									Ge1	2.99
									Re2	4.84

4	Re1	-0.43	1	Re1	70%	8.14%	44.23%	47.63%	Re1–Sn1	0.9
	Sn1	1.18		Sn1	30%	9.39%	90.54%	–	Re1	5.11
									Sn1	2.06

Table S6. Comparison of experimental and computational distances (Å) and angles (deg) for **3**, as well as calculated electronic energies.

complex	Re1–Ge	Re2-Ge	Re1–Ge–Re2	Electronic Energy (Hartrees)	ΔE (kcal/mol)
3 (experimental)	2.4395(5)	2.4367(5)	163.18(2)	–	–
3 (singlet)	2.525	2.534	151.99	–3023.784875	0
3 (triplet)	2.48	2.48	159.3	–3023.781629	+2.04
3 (quintet)	2.445	2.488	161.55	–3023.723192	+38.70

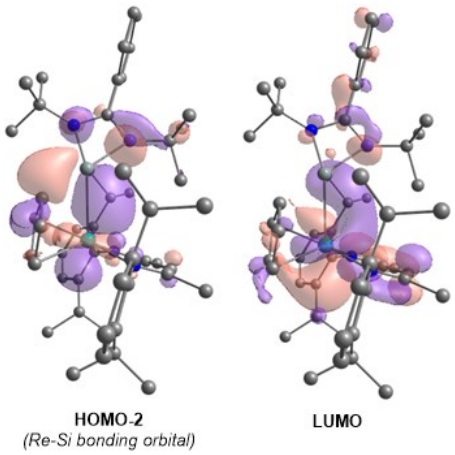

Figure S32. Renderings of select calculated molecular orbitals of **1b** including a rhenium-silicon bonding orbital (HOMO–2) and the LUMO.

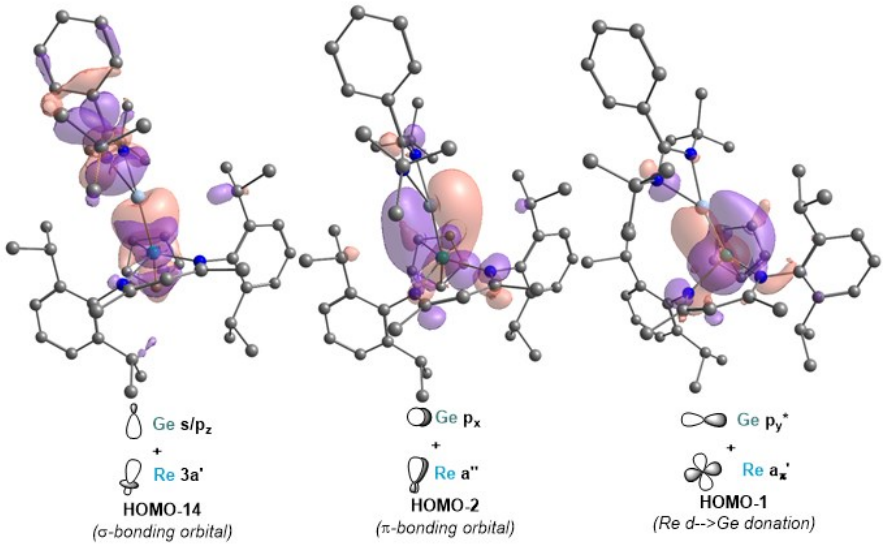

Figure S33. Renderings of select calculated molecular orbitals of **1c** including Re→N_2 π-backbonding orbitals (HOMO-1 and HOMO-2) and a pure Si non-bonding lone pair orbital (HOMO-4), along with qualitative relevant fragment orbitals shown below each rendering.

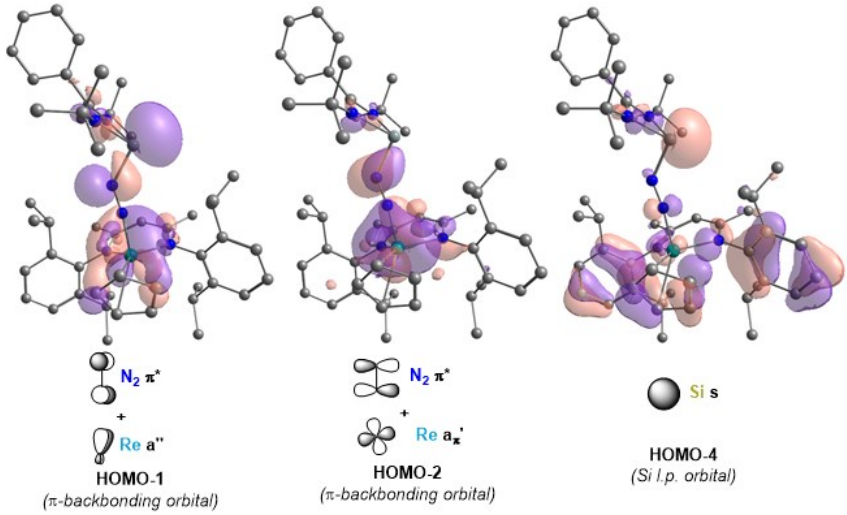

Figure S34. Renderings of select calculated molecular orbitals of **2** including a σ-bonding orbital (HOMO–14), π-bonding orbital (HOMO-2) and Re d-orbital donation towards Ge (HOMO-1), along with qualitative relevant fragment orbitals shown below each rendering.

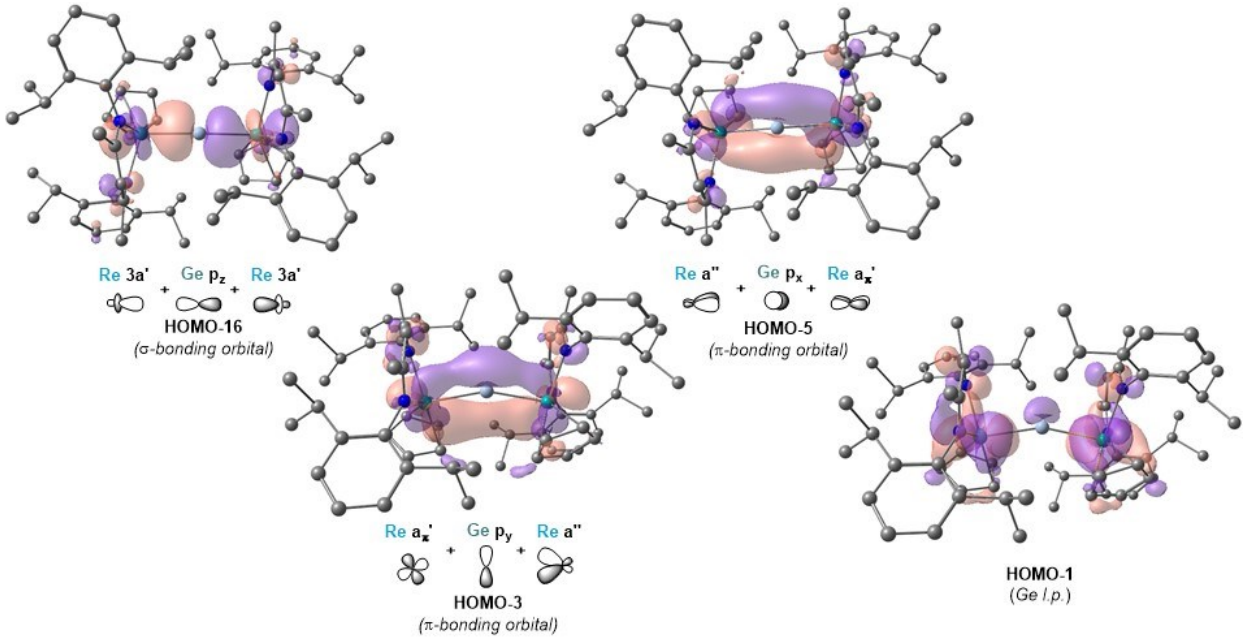

Figure S35. Renderings of select calculated molecular orbitals of **3** calculated as a triplet, along with qualitative relevant fragment orbitals shown below certain renderings.

Table S7. Cartesian coordinates of all optimized complexes.

Complex 1a

C	6.009439	1.101949	0.025511
C	5.279074	-0.076425	0.216680
C	5.949949	-1.252233	0.570910
C	7.333203	-1.247408	0.734601
C	8.057872	-0.072094	0.538743
C	7.393594	1.101060	0.181912
C	3.797929	-0.069266	0.058597
N	2.923599	0.254498	1.012160
C	3.109588	0.293727	2.476466
C	4.390821	1.020200	2.917176
Si	1.357763	-0.129828	-0.183407
N	3.125908	-0.388523	-1.054085
C	3.622539	-0.506511	-2.441136
C	2.639479	-1.407593	-3.191666
Re	-0.870469	-0.037061	-0.747471
C	-0.883075	-1.008660	-2.874201
C	-0.472275	0.365002	-2.933470
C	-1.533921	1.192767	-2.446373
C	-2.619033	0.304502	-2.073265
C	-2.185458	-1.038574	-2.328738
N	-1.639465	-1.431156	0.784041
C	-2.108864	-2.730264	0.381694
C	-3.494020	-2.924249	0.135696
C	-3.945029	-4.190258	-0.251917

C	-3.068817	-5.257156	-0.409478
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C	-4.509444	-1.801689	0.307023
C	-5.542003	-1.752753	-0.828204
C	0.268153	-3.708424	0.545614
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C	-3.113528	3.193282	-0.025790
C	0.728424	3.526170	0.182203
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C	-4.271360	2.282924	0.364132
C	-4.859808	2.666653	1.732264
C	-1.662613	-1.164866	2.090112
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C	-1.542406	2.547167	2.961470
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C	-5.406238	2.278312	-0.671824
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C	5.008718	-1.159701	-2.563865
C	3.659833	0.887955	-3.085293
C	3.103445	-1.140482	3.029919
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H	1.970097	1.065476	4.143652
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H	5.300399	0.456683	2.705175
H	4.343655	1.178314	3.999749
H	4.468089	2.000763	2.438135

Complex 1b

Re 1.032878 0.063238 -0.560781
Si -1.432414 -0.724837 -0.868688
N -3.231368 -0.121767 -1.292710
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N 1.952062 -1.243411 0.773604
N 1.244044 1.557314 0.852791
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C -4.052755 -1.393157 -3.228502
C -5.333050 0.637907 -2.484813
C -1.799090 4.013072 2.239388
C -2.415095 2.998956 0.031368
C 5.567868 -0.490775 -1.035240
C 4.536865 3.218126 -1.432336
C 0.440051 -4.647936 1.700563
C -3.107962 0.910752 -3.507649
C 4.505542 3.032801 1.060570
C -0.341474 -4.598735 -0.674268
C 0.489920 -3.857957 0.382101
C 3.951406 -4.553615 -1.031351
C 4.623495 -3.369585 -0.764360
C -1.306460 3.130179 1.080859
C -1.292579 -0.848880 2.683922
C 1.925885 -3.612735 -0.054706
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H 2.120887 2.371293 4.007796
H 1.971016 3.500033 2.648431
H 2.990064 -0.787513 -2.584839
H -0.975742 5.544559 0.019524
H -5.325910 -2.489172 -0.182073
H 0.754900 -2.259349 -2.468930
H 1.041121 6.588880 -0.956338
H 2.134916 0.201795 3.786453

Complex 1c

Re	9.461324000	11.834787000	2.338785000
Si	7.616699000	7.913824000	3.625795000
N	8.814225000	13.168569000	3.931493000
N	11.110692000	11.356671000	3.670536000
N	6.316302000	7.906843000	5.054252000
C	9.026551000	12.921677000	5.221374000
N	5.839879000	7.463220000	3.005275000
N	7.557361000	9.704029000	3.230674000
C	7.968777000	14.270969000	3.564496000
C	12.010891000	10.622170000	5.853623000
H	11.641256000	9.605275000	6.030175000
H	12.125957000	11.103156000	6.827702000
H	12.989161000	10.537400000	5.380437000
C	11.004922000	11.365297000	4.997336000
C	8.200225000	13.623677000	6.280435000
H	7.894372000	14.625987000	5.978722000
H	8.746516000	13.685898000	7.224127000
H	7.286378000	13.046464000	6.462510000
C	13.390769000	11.799237000	2.860888000
C	6.577595000	14.089454000	3.387153000
C	4.782382000	12.918012000	4.723633000
H	5.164778000	13.372024000	5.643003000
H	4.361132000	11.938734000	4.977051000
H	3.957185000	13.545627000	4.368135000
C	9.964245000	11.992469000	5.703198000
H	9.988961000	11.867702000	6.780030000
C	12.330553000	10.881468000	3.075888000

C	13.823529000	13.486955000	4.704999000
H	13.255432000	12.929024000	5.451594000
H	13.767330000	14.548716000	4.970755000
H	14.873004000	13.178263000	4.775639000
C	13.284795000	13.259443000	3.283118000
H	12.217796000	13.508759000	3.290043000
C	5.282160000	12.160669000	2.378741000
H	4.537269000	12.827554000	1.928379000
H	4.793490000	11.207328000	2.604162000
H	6.064627000	11.965095000	1.642546000
C	10.394722000	11.391494000	0.325542000
H	11.015893000	10.546566000	0.065645000
C	5.878047000	12.765987000	3.656144000
H	6.623243000	12.059387000	4.029163000
C	8.954353000	11.481132000	0.254145000
H	8.287573000	10.669185000	-0.009497000
C	4.077090000	6.792070000	4.687689000
C	5.804510000	15.181268000	2.976934000
H	4.735360000	15.044883000	2.833579000
C	8.551981000	12.840289000	0.528965000
H	7.559330000	13.261781000	0.458824000
C	5.373962000	7.393595000	4.256701000
C	14.570167000	11.339646000	2.265902000
H	15.389476000	12.033728000	2.102688000
C	14.716847000	10.013504000	1.877571000
H	15.640633000	9.676056000	1.415052000
C	8.551309000	15.548685000	3.361631000
C	13.993236000	14.223161000	2.320916000
H	15.083535000	14.140940000	2.391542000
H	13.736935000	15.257631000	2.571369000
H	13.718780000	14.051726000	1.275344000
C	3.984258000	5.424162000	4.972326000
H	4.867208000	4.797154000	4.889313000
C	10.863988000	12.719970000	0.609412000
H	11.899060000	12.987867000	0.766156000
C	12.475400000	9.528086000	2.694237000
C	13.672884000	9.124243000	2.093085000
H	13.789575000	8.083605000	1.800700000
C	6.365805000	16.433262000	2.764521000
H	5.745278000	17.268724000	2.451284000
C	10.318423000	16.262537000	5.033514000
H	9.775461000	17.188749000	5.255375000
H	11.387777000	16.459876000	5.169960000
H	10.024126000	15.512899000	5.770491000
C	11.405016000	8.478424000	2.946297000
H	10.554142000	8.975234000	3.422005000
C	10.036355000	15.799829000	3.594549000
H	10.546684000	14.841247000	3.449739000
C	6.396803000	8.057795000	6.513295000
C	9.764799000	13.582560000	0.733850000
H	9.808888000	14.628062000	1.002795000

C	5.314796000	6.955588000	1.730460000
C	2.936236000	7.595026000	4.806587000
H	3.001918000	8.655253000	4.580718000
C	11.905411000	7.375520000	3.892278000
H	12.691923000	6.773016000	3.423488000
H	11.080113000	6.703183000	4.151246000
H	12.317081000	7.786745000	4.818690000
C	10.896153000	7.850448000	1.642207000
H	10.438631000	8.604826000	0.997319000
H	10.138652000	7.091668000	1.865129000
H	11.706230000	7.365804000	1.084964000
C	5.305497000	9.014500000	7.016139000
H	5.366782000	9.971109000	6.489374000
H	5.436738000	9.201833000	8.087211000
H	4.305630000	8.597845000	6.870450000
C	7.771696000	8.675707000	6.799127000
H	8.573589000	8.004675000	6.472672000
H	7.890014000	8.846022000	7.873677000
H	7.893239000	9.632099000	6.281424000
C	7.729287000	16.609153000	2.967066000
H	8.165431000	17.592019000	2.814141000
C	6.299311000	6.706708000	7.239776000
H	5.313622000	6.250548000	7.120570000
H	6.475863000	6.845170000	8.311963000
H	7.054526000	6.011927000	6.858448000
C	1.635880000	5.674244000	5.483796000
H	0.688880000	5.240546000	5.792067000
C	6.253579000	7.499955000	0.645450000
H	6.265986000	8.593354000	0.661308000
H	5.923845000	7.166011000	-0.343026000
H	7.277765000	7.142534000	0.799264000
C	10.645168000	16.815677000	2.617697000
H	10.405606000	16.593517000	1.573072000
H	11.735238000	16.823622000	2.718300000
H	10.300404000	17.835175000	2.823246000
C	1.722345000	7.037076000	5.202982000
H	0.843252000	7.669157000	5.290448000
C	2.768625000	4.869596000	5.368115000
H	2.708258000	3.807358000	5.587408000
C	3.896498000	7.478641000	1.462149000
H	3.168750000	7.071226000	2.167266000
H	3.582270000	7.189748000	0.453641000
H	3.872812000	8.570680000	1.527163000
C	5.336399000	5.418986000	1.689151000
H	6.340123000	5.045879000	1.916292000
H	5.055572000	5.061470000	0.692473000
H	4.633470000	4.990297000	2.408318000
N	8.402697000	10.516716000	2.932552000

Complex 2

Re	3.184353000	4.465673000	14.931679000

Ge	4.442737000	6.395719000	14.322331000
N	3.510828000	4.710444000	17.081955000
N	4.902965000	3.119411000	15.000676000
N	4.372111000	8.026948000	13.016147000
N	5.621919000	8.157369000	14.833439000
C	4.676855000	4.547852000	17.695581000
C	0.974177000	4.605377000	15.143990000
H	0.454501000	5.039608000	15.986558000
C	5.803261000	3.958845000	17.088755000
H	6.695677000	3.930743000	17.705746000
C	1.964697000	3.073785000	13.684908000
H	2.355069000	2.163257000	13.251510000
C	5.859576000	3.169291000	15.929152000
C	1.283863000	5.263389000	13.922491000
H	1.066077000	6.300840000	13.707662000
C	2.367156000	5.030896000	17.897961000
C	1.883107000	4.321774000	13.019584000
H	2.206794000	4.510631000	12.006113000
C	5.267947000	8.754378000	13.703570000
C	1.396239000	3.225336000	15.006984000
H	1.214763000	2.432079000	15.716249000
C	1.652405000	3.982771000	18.535605000
C	5.043085000	2.143663000	13.950095000
C	2.101268000	2.528213000	18.474175000
H	2.750483000	2.426428000	17.598551000
C	5.751994000	2.453695000	12.766230000
C	2.872978000	7.229520000	11.294945000
H	3.656238000	6.623849000	10.830826000
H	2.150372000	7.511374000	10.523025000
H	2.358693000	6.620048000	12.036149000
C	1.940451000	6.369327000	18.065308000
C	4.472506000	0.854776000	14.108359000
C	3.466083000	8.483428000	11.939775000
C	2.705502000	7.556172000	17.505580000
H	3.579752000	7.162952000	16.978382000
C	7.147092000	2.380888000	15.769848000
H	7.041579000	1.521924000	15.107679000
H	7.510027000	2.036507000	16.741245000
H	7.920565000	3.032296000	15.346588000
C	4.888205000	5.042906000	19.113537000
H	5.272863000	6.069015000	19.080350000
H	5.630167000	4.433928000	19.635388000
H	3.968447000	5.058608000	19.698025000
C	5.815207000	10.069295000	13.247148000
C	4.167469000	9.274842000	10.821765000
H	4.477621000	10.272243000	11.132790000
H	3.467648000	9.391457000	9.987339000
H	5.043908000	8.734696000	10.451386000
C	5.865791000	4.546152000	11.365577000
H	6.026979000	4.008777000	10.423802000
H	6.329955000	5.534649000	11.268675000

H	4.790574000	4.686556000	11.501075000
C	5.836375000	1.492303000	11.753078000
H	6.377474000	1.733810000	10.841484000
C	6.851159000	8.332953000	15.630024000
C	3.768187000	0.439437000	15.391951000
H	3.491826000	1.359939000	15.915760000
C	5.263492000	0.235871000	11.891992000
H	5.345654000	-0.499276000	11.095856000
C	6.460009000	3.782030000	12.555336000
H	6.289874000	4.387936000	13.452378000
C	6.894937000	10.123421000	12.357838000
H	7.315490000	9.201541000	11.967274000
C	1.868845000	8.347690000	16.492591000
H	1.520926000	7.698921000	15.684270000
H	2.465895000	9.153798000	16.051680000
H	0.991377000	8.804208000	16.965316000
C	6.626119000	7.557306000	16.931727000
H	5.812425000	8.007971000	17.506676000
H	7.532401000	7.579974000	17.545938000
H	6.374763000	6.511127000	16.730097000
C	4.595724000	-0.074510000	13.070191000
H	4.163912000	-1.064275000	13.189402000
C	2.919790000	2.134297000	19.715271000
H	3.827648000	2.731717000	19.815713000
H	3.217463000	1.081095000	19.658508000
H	2.325866000	2.266374000	20.627342000
C	0.511758000	4.298319000	19.282531000
H	-0.037291000	3.500022000	19.773490000
C	0.931252000	1.544614000	18.322741000
H	0.341036000	1.470486000	19.242900000
H	1.311076000	0.539617000	18.111983000
H	0.246970000	1.828523000	17.517701000
C	5.267935000	11.262438000	13.732161000
H	4.442479000	11.226064000	14.437040000
C	2.332239000	9.331741000	12.538253000
H	1.807194000	8.778884000	13.322659000
H	1.606381000	9.606433000	11.765020000
H	2.721963000	10.256030000	12.974834000
C	0.783739000	6.626908000	18.809024000
H	0.452311000	7.655675000	18.927597000
C	6.864849000	12.538070000	12.443726000
H	7.272343000	13.495608000	12.132174000
C	7.419458000	11.351902000	11.963189000
H	8.259469000	11.382476000	11.274912000
C	5.786534000	12.490266000	13.326316000
H	5.351661000	13.410416000	13.706372000
C	7.973740000	3.603790000	12.361804000
H	8.428912000	3.041828000	13.181998000
H	8.469438000	4.579593000	12.302468000
H	8.197853000	3.066241000	11.433385000
C	0.063325000	5.605960000	19.413226000

H	-0.830178000	5.826987000	19.990953000
C	4.710518000	-0.356865000	16.309188000
H	5.053701000	-1.271896000	15.812479000
H	4.195522000	-0.648792000	17.231546000
H	5.592761000	0.224023000	16.588946000
C	3.194668000	8.487033000	18.625453000
H	2.355739000	8.938857000	19.166483000
H	3.793579000	9.305441000	18.209512000
H	3.807798000	7.954224000	19.358497000
C	7.158909000	9.794166000	15.998940000
H	7.506257000	10.384334000	15.149793000
H	7.948614000	9.805941000	16.757890000
H	6.276815000	10.281991000	16.424791000
C	8.046464000	7.718573000	14.882176000
H	7.846256000	6.670760000	14.636882000
H	8.948918000	7.758151000	15.502173000
H	8.254053000	8.259833000	13.954352000
C	2.487867000	-0.369097000	15.142516000
H	1.805759000	0.140676000	14.455825000
H	1.955969000	-0.532959000	16.085214000
H	2.703628000	-1.358593000	14.724947000

Complex 3-singlet

C	-5.380941000	-2.021310000	-1.512111000
C	-3.977582000	-2.170274000	-1.343320000
C	-3.253254000	-2.984490000	-2.248328000
C	-3.943041000	-3.613740000	-3.291748000
C	-5.310258000	-3.465963000	-3.467634000
C	-6.014250000	-2.672585000	-2.576312000
N	-3.343372000	-1.504935000	-0.214344000
Re	-2.426179000	0.390394000	-0.512859000
Ge	0.003076000	0.007581000	0.099224000
Re	2.421679000	-0.380584000	-0.513001000
N	3.347139000	1.509456000	-0.190673000
C	3.974601000	2.187763000	-1.315706000
C	5.372171000	2.015256000	-1.511968000
C	6.001738000	2.680399000	-2.569476000
C	5.299720000	3.511167000	-3.427872000
C	3.938433000	3.679409000	-3.227067000
C	3.251528000	3.035726000	-2.190001000
C	6.259717000	1.182728000	-0.593801000
C	7.144861000	2.078507000	0.289308000
C	1.771598000	3.353996000	-2.034030000
C	1.570142000	4.702690000	-1.323229000
C	-1.768009000	-3.285546000	-2.113640000
C	-1.545748000	-4.631536000	-1.403870000
C	-6.272379000	-1.227135000	-0.564272000
C	-7.155433000	-0.215656000	-1.309557000
C	7.159473000	0.210241000	-1.369789000
C	1.041497000	3.393619000	-3.385874000
C	-1.052907000	-3.315910000	-3.473438000

C	-7.173452000	-2.156449000	0.266693000
C	3.588990000	2.052856000	1.009565000
C	4.001921000	3.502642000	1.167800000
C	3.475083000	1.343212000	2.216853000
C	3.354803000	-0.034127000	2.416413000
N	3.035300000	-0.909069000	1.439885000
C	3.192139000	-2.307471000	1.801280000
C	4.426116000	-2.967837000	1.560830000
C	4.571840000	-4.298579000	1.967496000
C	3.546888000	-4.986453000	2.602460000
C	2.346543000	-4.333978000	2.833808000
C	2.147058000	-3.002643000	2.451229000
C	5.626138000	-2.280779000	0.922392000
C	6.558257000	-1.677941000	1.986615000
C	0.788489000	-2.390092000	2.737843000
C	0.388276000	-2.456360000	4.219732000
C	6.436091000	-3.214816000	0.010055000
C	-0.282776000	-3.087254000	1.892517000
C	3.608590000	-0.513445000	3.830469000
C	-3.573644000	-2.067688000	0.980404000
C	-3.976974000	-3.522291000	1.120348000
C	-3.454875000	-1.377057000	2.197900000
C	-3.338224000	-0.002302000	2.418501000
N	-3.031527000	0.886551000	1.452236000
C	-3.190463000	2.282869000	1.819283000
C	-2.139541000	2.980463000	2.455107000
C	-2.329538000	4.317844000	2.820788000
C	-3.528144000	4.972736000	2.586968000
C	-4.562585000	4.279511000	1.972778000
C	-4.425689000	2.942597000	1.583457000
C	-0.789135000	2.356232000	2.751496000
C	-0.405253000	2.423372000	4.237698000
C	-5.630694000	2.243768000	0.968283000
C	-6.477533000	3.171323000	0.084227000
C	0.299464000	3.036933000	1.916185000
C	-6.527489000	1.618842000	2.049939000
C	-3.575364000	0.454666000	3.842550000
C	1.261453000	-1.130634000	-2.332095000
C	2.360950000	-0.346431000	-2.789814000
C	3.545821000	-0.981978000	-2.288132000
C	3.158499000	-2.178701000	-1.572570000
C	1.744150000	-2.284486000	-1.619968000
C	-1.263382000	1.221527000	-2.294170000
C	-1.802838000	2.341672000	-1.571869000
C	-3.212743000	2.177497000	-1.554495000
C	-3.539914000	0.981198000	-2.300199000
C	-2.322580000	0.404328000	-2.791706000
H	0.220843000	-0.956167000	-2.564429000
H	2.322257000	0.529741000	-3.420191000
H	4.556523000	-0.648554000	-2.477313000
H	3.820944000	-2.900031000	-1.115867000

H	1.148282000	-3.088067000	-1.213309000
H	-0.212212000	1.090826000	-2.508560000
H	-1.245450000	3.160355000	-1.140935000
H	-3.912788000	2.858814000	-1.092678000
H	-4.533091000	0.612331000	-2.516167000
H	-2.237236000	-0.452407000	-3.443724000
H	7.005511000	-3.953803000	0.584139000
H	7.161556000	-2.637903000	-0.570237000
H	5.802084000	-3.763346000	-0.693755000
H	5.242805000	-1.459906000	0.307247000
H	6.070853000	-0.881412000	2.553456000
H	7.454140000	-1.252691000	1.520940000
H	6.885486000	-2.449304000	2.693285000
H	5.515663000	-4.804643000	1.790388000
H	3.685487000	-6.018385000	2.913489000
H	1.538354000	-4.864252000	3.330727000
H	-0.022090000	-3.064975000	0.831902000
H	-1.245965000	-2.584524000	2.014963000
H	-0.393578000	-4.136798000	2.190734000
H	0.817211000	-1.336141000	2.437363000
H	0.245098000	-3.490484000	4.552332000
H	-0.560550000	-1.930928000	4.371692000
H	1.133706000	-2.003646000	4.880189000
H	2.675244000	-0.836899000	4.299683000
H	4.030134000	0.290484000	4.436797000
H	4.287357000	-1.367895000	3.865431000
H	3.677211000	1.925674000	3.109472000
H	4.379371000	3.947671000	0.248588000
H	4.759015000	3.611518000	1.948457000
H	3.128714000	4.081722000	1.491947000
H	6.588028000	-0.470480000	-2.006723000
H	7.746330000	-0.394593000	-0.671715000
H	7.873717000	0.738467000	-2.009713000
H	5.611237000	0.595417000	0.062289000
H	7.835059000	2.668942000	-0.324064000
H	7.744592000	1.469135000	0.974218000
H	6.555551000	2.775767000	0.887359000
H	7.071431000	2.553391000	-2.709925000
H	5.806722000	4.027237000	-4.238572000
H	3.389373000	4.343146000	-3.887162000
H	1.361976000	4.246182000	-3.993542000
H	-0.035541000	3.502642000	-3.236852000
H	1.210589000	2.487914000	-3.976633000
H	1.330777000	2.562736000	-1.416165000
H	2.003767000	4.708859000	-0.321662000
H	0.503557000	4.936316000	-1.228166000
H	2.036866000	5.512702000	-1.895656000
H	0.053731000	3.003031000	0.852430000
H	1.255585000	2.525722000	2.056420000
H	0.415607000	4.088286000	2.205485000
H	-0.829208000	1.302808000	2.449261000

H	-0.251657000	3.457732000	4.565069000
H	0.533806000	1.885409000	4.405557000
H	-1.166171000	1.987327000	4.891473000
H	-1.515234000	4.849664000	3.305808000
H	-3.659519000	6.010182000	2.882356000
H	-5.505476000	4.787945000	1.797022000
H	-6.009807000	0.836505000	2.609338000
H	-7.420728000	1.169956000	1.601558000
H	-6.860926000	2.382829000	2.761655000
H	-5.246461000	1.433175000	0.339152000
H	-7.044292000	3.895102000	0.679931000
H	-7.207919000	2.587610000	-0.482467000
H	-5.871467000	3.737042000	-0.630701000
H	-2.623338000	0.691472000	4.327050000
H	-4.059996000	-0.332572000	4.423217000
H	-4.188523000	1.355894000	3.895548000
H	-3.647470000	-1.974560000	3.082946000
H	-4.323970000	-3.967375000	0.189257000
H	-4.753885000	-3.643137000	1.879650000
H	-3.106526000	-4.093383000	1.465717000
H	-1.359276000	-4.179538000	-4.072856000
H	0.028094000	-3.397701000	-3.336499000
H	-1.250882000	-2.417904000	-4.066918000
H	-1.330775000	-2.488314000	-1.501551000
H	-1.963227000	-4.637516000	-0.395449000
H	-0.476558000	-4.859668000	-1.325406000
H	-2.016638000	-5.445633000	-1.967116000
H	-3.391640000	-4.249769000	-3.976492000
H	-5.820319000	-3.970654000	-4.283569000
H	-7.088667000	-2.564409000	-2.696038000
H	-7.868149000	-2.706189000	-0.378498000
H	-7.769405000	-1.575454000	0.979109000
H	-6.595883000	-2.891083000	0.830927000
H	-5.630784000	-0.674224000	0.127303000
H	-6.566831000	0.503925000	-1.884936000
H	-7.769866000	0.343999000	-0.597456000
H	-7.842399000	-0.710642000	-2.003356000

Complex 3-triplet

Re	-1.547589	1.796639	7.594031
Re	-2.039201	1.930948	2.742954
Ge	-2.176231	1.637959	5.199362
N	-4.009684	1.176065	2.270207
N	-3.085173	0.478248	8.358011
N	-2.755809	3.422451	8.265384
N	-1.277509	0.049478	2.077394
C	-0.309485	3.136022	1.894841
C	-1.442837	3.374179	1.054807
C	-2.459091	3.993875	1.847155
C	-1.953330	4.181936	3.161403
C	-0.615074	3.634927	3.195820

C 0.415241 0.774636 6.987556
C 0.168381 0.477492 8.353766
C 0.196963 1.699571 9.094751
C 0.418528 2.771222 8.173092
C 0.561713 2.208224 6.869548
C -5.747021 -0.578560 2.054001
C -5.055150 0.882827 -1.410212
C -5.507112 3.587586 5.112683
C -4.091106 3.204088 -1.488820
C -4.434257 2.015010 -0.576927
C -6.972979 1.545876 5.068042
C -5.787570 2.258880 4.402255
C -5.340859 2.426704 0.572212
C -6.469665 3.192167 0.258854
C -7.359372 3.617488 1.234551
C -7.104357 3.288685 2.556382
C -5.994377 2.519403 2.923434
C -5.106547 2.063271 1.923324
C -4.313388 -0.123401 2.237533
C -3.358163 -1.156833 2.340910
C -1.263447 -2.428549 1.990846
C -1.975095 -1.098818 2.141111
C -5.414234 -0.176039 8.894417
C -2.016615 -2.152909 5.552091
C -0.915701 -0.301179 11.960464
C -4.480573 -2.500451 5.909512
C -3.235485 -1.739625 6.385041
C -3.409092 -0.018903 12.133515
C -2.215927 -0.090450 11.167865
C -2.924919 -1.947139 7.853559
C -2.721507 -3.260586 8.291396
C -2.387471 -3.546621 9.605721
C -2.227942 -2.495737 10.497429
C -2.412910 -1.163888 10.109717
C -2.785510 -0.881551 8.770664
C -4.359459 0.842687 8.512430
C -4.822793 2.166625 8.362365
C -4.901263 4.634479 8.535752
C -4.095320 3.360819 8.376560
C -1.693888 -1.445327 -1.447916
C 2.289740 1.087610 3.988009
C -0.413015 5.916730 5.863702
C -1.406245 3.425378 12.258318
C -1.152215 0.923035 -2.045544
C -1.290963 -0.072361 -0.884050
C 1.887562 -1.389605 4.133831
C 1.359307 -0.060667 3.568418
C -2.793367 6.720143 5.935307
C -1.802927 5.672905 6.471180
C -3.812152 4.028026 11.930984
C -2.497122 3.688982 11.209447

C -1.739679 5.697241 7.988988
C -1.246624 6.866282 8.582800
C -1.172632 7.016998 9.957920
C -1.584487 5.966848 10.765192
C -2.075124 4.773394 10.226852
C -2.169156 4.632569 8.814965
C 1.187716 -0.307679 -0.730986
C 2.400154 -0.383289 -0.061352
C 2.403518 -0.281283 1.320330
C 1.222604 -0.121265 2.056424
C -0.012882 -0.053140 1.371502
C -0.020466 -0.137788 -0.047945
H -0.432983 0.573772 -2.793708
H -2.110323 1.041997 -2.560152
H -0.817105 1.907866 -1.707037
H -2.096569 0.270626 -0.229306
H -1.935233 -2.161325 -0.659482
H -2.578377 -1.348939 -2.086982
H -0.887442 -1.870388 -2.056591
H 1.174192 -0.389360 -1.814201
H 3.328417 -0.520175 -0.609248
H 3.348312 -0.344221 1.853283
H 2.886847 -1.614437 3.745131
H 1.967191 -1.347562 5.225853
H 1.238844 -2.231354 3.877117
H 0.362479 0.134434 3.979603
H 1.912110 2.053764 3.641079
H 2.391653 1.129296 5.075977
H 3.295912 0.959192 3.575666
H -0.582333 -2.582893 2.834070
H -1.978787 -3.253027 1.979149
H -0.655774 -2.481383 1.086094
H -3.771566 -2.157675 2.390695
H -6.178059 -0.200342 1.123490
H -5.804955 -1.668310 2.041126
H -6.385138 -0.206735 2.859765
H -3.712524 4.059069 -0.920949
H -3.328716 2.918594 -2.219678
H -4.962913 3.546738 -2.055967
H -3.502870 1.646367 -0.139080
H -6.030733 1.183456 -1.809246
H -4.414251 0.627942 -2.261392
H -5.198290 -0.026376 -0.820409
H -6.656834 3.452985 -0.778973
H -8.234148 4.204203 0.967575
H -7.784062 3.631086 3.332020
H -7.203945 0.587764 4.592419
H -6.742123 1.350071 6.119847
H -7.882811 2.155828 5.037007
H -4.900629 1.626607 4.517234
H -6.373436 4.257192 5.059025

H -5.276523 3.405146 6.162653
H -4.655956 4.100177 4.657336
H -2.494767 7.732654 6.228163
H -2.832301 6.698375 4.840534
H -3.807738 6.556604 6.309323
H -2.140650 4.673856 6.173687
H 0.303562 5.157560 6.190874
H -0.457258 5.901351 4.771186
H -0.014361 6.893782 6.155529
H -0.928510 7.685324 7.943604
H -0.799028 7.938869 10.395188
H -1.530742 6.075498 11.844815
H -4.656070 4.097130 11.241450
H -4.052023 3.253618 12.667655
H -3.730652 4.981998 12.464715
H -2.653810 2.770048 10.638067
H -1.281699 4.277068 12.935263
H -1.676440 2.565482 12.878537
H -0.432743 3.229560 11.799397
H -4.771861 5.271281 7.655226
H -5.964406 4.409616 8.640159
H -4.585823 5.227192 9.396395
H -5.897575 2.285266 8.438124
H -5.154970 -0.709489 9.812011
H -6.381481 0.307999 9.039357
H -5.522574 -0.937421 8.117011
H -5.376486 -2.229844 6.476767
H -4.670221 -2.275229 4.855375
H -4.351252 -3.584966 5.997853
H -3.405679 -0.669838 6.221027
H -1.832046 -3.230686 5.631338
H -2.184009 -1.906191 4.502806
H -1.117632 -1.632108 5.891929
H -2.833406 -4.073737 7.579151
H -2.245639 -4.573680 9.931002
H -1.958596 -2.711533 11.527422
H -3.575941 -0.987368 12.618673
H -3.227466 0.719699 12.922089
H -4.331810 0.264865 11.620622
H -2.142416 0.867915 10.647031
H -0.053285 -0.437820 11.301186
H -0.716498 0.559118 12.606400
H -0.973780 -1.179872 12.611464
H 0.626505 2.692552 1.583326
H -1.520154 3.121435 0.006950
H -3.440884 4.291683 1.504065
H -2.457707 4.696473 3.963678
H 0.069739 3.693492 4.027668
H 0.532845 0.049666 6.198173
H 0.004267 -0.510787 8.762140
H 0.074048 1.796642 10.163738

H 0.507282 3.818049 8.430539
H 0.838353 2.745779 5.975198

Complex 3-quintuplet

C	5.482920000	1.943755000	-1.468562000
C	4.067989000	2.068854000	-1.422628000
C	3.408435000	2.824028000	-2.419433000
C	4.167469000	3.425356000	-3.431358000
C	5.547719000	3.311498000	-3.479437000
C	6.191245000	2.572146000	-2.497382000
N	3.347601000	1.454878000	-0.321355000
Re	2.451995000	-0.461293000	-0.525561000
Ge	0.091087000	0.030344000	-0.122282000
Re	-2.343491000	0.387814000	-0.496236000
N	-3.324538000	-1.453563000	-0.385583000
C	-4.035608000	-2.060786000	-1.476565000
C	-5.460689000	-2.062242000	-1.467898000
C	-6.156295000	-2.695455000	-2.501301000
C	-5.499512000	-3.315498000	-3.555240000
C	-4.113703000	-3.317781000	-3.562273000
C	-3.364539000	-2.720848000	-2.540590000
C	-6.285584000	-1.406245000	-0.371182000
C	-6.955547000	-2.444699000	0.542154000
C	-1.855645000	-2.902076000	-2.602012000
C	-1.485025000	-4.373886000	-2.351748000
C	1.907158000	3.056078000	-2.452770000
C	1.559329000	4.542423000	-2.268323000
C	6.284661000	1.181534000	-0.423707000
C	7.323537000	0.248390000	-1.062234000
C	-7.355781000	-0.471507000	-0.952517000
C	-1.270561000	-2.451814000	-3.948801000
C	1.306283000	2.545831000	-3.770713000
C	6.994723000	2.126894000	0.559977000
C	-3.468600000	-2.133317000	0.834552000
C	-3.545465000	-3.638426000	0.820441000
C	-3.462792000	-1.469826000	2.060056000
C	-3.342851000	-0.113219000	2.383345000
N	-3.102754000	0.871906000	1.432603000
C	-3.315039000	2.222597000	1.882608000
C	-4.620032000	2.785137000	1.823765000
C	-4.839262000	4.073795000	2.321737000
C	-3.810367000	4.833960000	2.859811000
C	-2.535694000	4.291712000	2.903523000
C	-2.267597000	2.999040000	2.437485000
C	-5.812942000	2.035727000	1.255162000
C	-6.711047000	1.487692000	2.374869000
C	-0.836754000	2.508652000	2.551510000
C	-0.318137000	2.505745000	3.997222000
C	-6.636612000	2.909192000	0.295927000
C	0.084868000	3.371536000	1.681344000
C	-3.419645000	0.262473000	3.843459000

C	3.409064000	2.134094000	0.839892000
C	3.703197000	3.619427000	0.836182000
C	3.215020000	1.545402000	2.090512000
C	3.184199000	0.174871000	2.425976000
N	3.003333000	-0.801329000	1.536935000
C	3.175471000	-2.148566000	2.053162000
C	2.088409000	-2.813958000	2.662683000
C	2.288704000	-4.086957000	3.208334000
C	3.528290000	-4.706604000	3.177014000
C	4.590921000	-4.049927000	2.572397000
C	4.443636000	-2.780246000	2.002947000
C	0.685888000	-2.241181000	2.712674000
C	0.094586000	-2.185481000	4.127864000
C	5.674711000	-2.133129000	1.388200000
C	6.452026000	-3.104200000	0.485896000
C	-0.227760000	-3.060115000	1.794845000
C	6.608016000	-1.565657000	2.469453000
C	3.373791000	-0.135346000	3.896110000
C	-1.662008000	1.103885000	-2.572079000
C	-3.025460000	0.704693000	-2.673380000
C	-3.819889000	1.581713000	-1.873648000
C	-2.937144000	2.520350000	-1.260629000
C	-1.611009000	2.250028000	-1.688385000
C	1.827072000	-1.212372000	-2.583386000
C	1.736028000	-2.333920000	-1.680301000
C	3.036859000	-2.589494000	-1.178889000
C	3.943454000	-1.659846000	-1.780216000
C	3.190795000	-0.798023000	-2.641814000
H	-0.834997000	0.697820000	-3.132953000
H	-3.400856000	-0.130376000	-3.248107000
H	-4.890400000	1.527638000	-1.742290000
H	-3.224670000	3.289316000	-0.556890000
H	-0.737529000	2.839683000	-1.460213000
H	1.021308000	-0.824592000	-3.187873000
H	0.848527000	-2.907234000	-1.459496000
H	3.295269000	-3.362825000	-0.468168000
H	5.011216000	-1.619465000	-1.618964000
H	3.595439000	-0.011471000	-3.264268000
H	-7.154975000	3.717528000	0.822646000
H	-7.404995000	2.312157000	-0.203528000
H	-6.010456000	3.372052000	-0.474160000
H	-5.417315000	1.184367000	0.694452000
H	-6.174244000	0.772221000	3.002528000
H	-7.586009000	0.976812000	1.958083000
H	-7.073700000	2.299812000	3.015657000
H	-5.842573000	4.489428000	2.287981000
H	-4.001642000	5.833385000	3.241420000
H	-1.722439000	4.876423000	3.326268000
H	-0.264312000	3.403091000	0.646231000
H	1.098949000	2.966891000	1.691623000
H	0.122385000	4.402943000	2.050802000

H	-0.804713000	1.480951000	2.173918000
H	-0.270503000	3.520310000	4.408608000
H	0.694438000	2.089423000	4.029966000
H	-0.950558000	1.912197000	4.663085000
H	-2.454331000	0.606151000	4.235265000
H	-3.724965000	-0.604424000	4.435324000
H	-4.134516000	1.068528000	4.041117000
H	-3.570406000	-2.124225000	2.921568000
H	-4.311075000	-4.026584000	0.139460000
H	-3.768064000	-4.015375000	1.822743000
H	-2.592836000	-4.089273000	0.508460000
H	-6.924239000	0.274441000	-1.627400000
H	-7.877528000	0.054811000	-0.147478000
H	-8.115394000	-1.022176000	-1.517500000
H	-5.604941000	-0.813957000	0.245585000
H	-7.642023000	-3.084034000	-0.025564000
H	-7.535287000	-1.944854000	1.326196000
H	-6.218528000	-3.085704000	1.029949000
H	-7.242737000	-2.698613000	-2.479516000
H	-6.059318000	-3.798722000	-4.351345000
H	-3.591850000	-3.826680000	-4.368440000
H	-1.677883000	-3.034590000	-4.781218000
H	-0.185882000	-2.595038000	-3.965648000
H	-1.483050000	-1.398503000	-4.156035000
H	-1.418168000	-2.285561000	-1.808336000
H	-1.856232000	-4.725633000	-1.386153000
H	-0.398621000	-4.518569000	-2.374613000
H	-1.914938000	-5.019533000	-3.125507000
H	0.208523000	-3.159478000	0.797449000
H	-1.201932000	-2.574583000	1.697691000
H	-0.379818000	-4.068786000	2.196179000
H	0.719736000	-1.218017000	2.323098000
H	-0.029362000	-3.186823000	4.554653000
H	-0.894681000	-1.718892000	4.094462000
H	0.718654000	-1.610282000	4.819093000
H	1.448752000	-4.596907000	3.672106000
H	3.666060000	-5.690779000	3.616418000
H	5.565247000	-4.529169000	2.547492000
H	6.117768000	-0.791152000	3.065170000
H	7.503030000	-1.122359000	2.018777000
H	6.937469000	-2.357183000	3.152191000
H	5.329662000	-1.300425000	0.769351000
H	6.941376000	-3.894439000	1.064836000
H	7.240711000	-2.574370000	-0.056704000
H	5.802575000	-3.590195000	-0.248492000
H	2.424257000	-0.445189000	4.344166000
H	3.729052000	0.746350000	4.432203000
H	4.077500000	-0.953077000	4.060406000
H	3.278303000	2.222356000	2.934554000
H	4.570383000	3.875950000	0.225613000
H	3.867992000	3.986924000	1.850535000

H	2.848803000	4.160679000	0.416316000
H	1.743801000	3.058858000	-4.633411000
H	0.227668000	2.724902000	-3.803844000
H	1.484205000	1.474424000	-3.899809000
H	1.470299000	2.483532000	-1.627055000
H	1.968222000	4.949800000	-1.339956000
H	0.473459000	4.688868000	-2.251249000
H	1.953848000	5.146653000	-3.092419000
H	3.657837000	4.011659000	-4.191093000
H	6.115741000	3.796132000	-4.268693000
H	7.273807000	2.486323000	-2.521936000
H	7.672395000	2.805212000	0.028910000
H	7.590940000	1.552529000	1.277353000
H	6.288071000	2.734468000	1.129383000
H	5.580336000	0.571350000	0.148417000
H	6.880275000	-0.410415000	-1.814996000
H	7.795525000	-0.372648000	-0.294944000
H	8.126314000	0.809289000	-1.552027000

Complex 4

Re	9.500056000	12.369209000	3.374908000
Sn	9.757851000	14.144705000	1.223229000
N	7.553841000	13.105710000	3.527984000
N	10.095570000	13.739858000	4.818404000
N	11.461664000	15.700048000	0.804181000
N	11.352600000	13.866198000	-0.472138000
C	10.955334000	11.163089000	2.070100000
H	11.601348000	11.576248000	1.308706000
C	9.618197000	10.659773000	1.858288000
H	9.092856000	10.584846000	0.917591000
C	9.133418000	10.202997000	3.115233000
H	8.179023000	9.722347000	3.283515000
C	10.184931000	10.417896000	4.090661000
H	10.151263000	10.137745000	5.135443000
C	11.324686000	10.966458000	3.426040000
H	12.275912000	11.202480000	3.880373000
C	5.790230000	14.789224000	4.051868000
H	5.537404000	15.179772000	3.061325000
H	5.647429000	15.596470000	4.773093000
H	5.074359000	13.994689000	4.272617000
C	7.221304000	14.296266000	4.081913000
C	8.141649000	15.143945000	4.711826000
H	7.736532000	16.093443000	5.045617000
C	9.446921000	14.870226000	5.148841000
C	10.106538000	15.924934000	6.009815000
H	9.361716000	16.512880000	6.551418000
H	10.672581000	16.617097000	5.375306000
H	10.807824000	15.498821000	6.728145000
C	6.442056000	12.255536000	3.130217000
C	5.974325000	11.266616000	4.036927000
C	4.903456000	10.451094000	3.658536000

H	4.541413000	9.697261000	4.350721000
C	4.285201000	10.582413000	2.422135000
H	3.456379000	9.935273000	2.148267000
C	4.738192000	11.557841000	1.549112000
H	4.254085000	11.675309000	0.583138000
C	5.798623000	12.410334000	1.879925000
C	6.188181000	13.457892000	0.850413000
H	6.963841000	14.095936000	1.289097000
C	5.012560000	14.358311000	0.438378000
H	4.255733000	13.800619000	-0.123804000
H	5.368471000	15.167572000	-0.208583000
H	4.509927000	14.808925000	1.299002000
C	6.783867000	12.795814000	-0.398821000
H	7.626604000	12.150803000	-0.136250000
H	7.138427000	13.553505000	-1.106779000
H	6.037281000	12.177581000	-0.910525000
C	6.561612000	11.087926000	5.429579000
H	7.601579000	11.431545000	5.386981000
C	5.819467000	11.955472000	6.459270000
H	5.898521000	13.020264000	6.226931000
H	6.231097000	11.802628000	7.463110000
H	4.755669000	11.692422000	6.490818000
C	6.574253000	9.627057000	5.899433000
H	5.567747000	9.259447000	6.127426000
H	7.159453000	9.534585000	6.818488000
H	7.011947000	8.957195000	5.152801000
C	11.232813000	13.364908000	5.643452000
C	12.561549000	13.637101000	5.245464000
C	13.616053000	13.147550000	6.024971000
H	14.637158000	13.344790000	5.708991000
C	13.392341000	12.441345000	7.197572000
H	14.225784000	12.071998000	7.788896000
C	12.085137000	12.238297000	7.617214000
H	11.905039000	11.719623000	8.554448000
C	10.992356000	12.688249000	6.868449000
C	9.598025000	12.475415000	7.444555000
H	8.873964000	12.642107000	6.641915000
C	9.300863000	13.485870000	8.566045000
H	10.009037000	13.365104000	9.394008000
H	8.291253000	13.331646000	8.963251000
H	9.368091000	14.518861000	8.218124000
C	9.386057000	11.055073000	7.985564000
H	9.603086000	10.290181000	7.234856000
H	8.348374000	10.928141000	8.310313000
H	10.016544000	10.851433000	8.857491000
C	12.917611000	14.501836000	4.049406000
H	11.987715000	14.796006000	3.555699000
C	13.765234000	13.765120000	3.006429000
H	14.728975000	13.443245000	3.417482000
H	13.964557000	14.429347000	2.160043000
H	13.244608000	12.885169000	2.624411000

C	13.653135000	15.769087000	4.516827000
H	13.070762000	16.331919000	5.252766000
H	13.863496000	16.431047000	3.670459000
H	14.613109000	15.520127000	4.982566000
C	11.873036000	15.085567000	-0.309950000
C	12.864517000	15.710337000	-1.252347000
C	12.470599000	16.467062000	-2.362683000
H	11.415494000	16.569179000	-2.596405000
C	13.421011000	17.070350000	-3.183680000
H	13.097511000	17.655772000	-4.039951000
C	14.780605000	16.918312000	-2.913052000
H	15.521136000	17.388095000	-3.554210000
C	15.183271000	16.157670000	-1.816860000
H	16.240145000	16.031407000	-1.598665000
C	14.232081000	15.561651000	-0.990720000
H	14.549874000	14.983998000	-0.127710000
C	11.417904000	17.154478000	1.058726000
C	10.876686000	17.321270000	2.484827000
H	9.908993000	16.819004000	2.601736000
H	10.734469000	18.381854000	2.716065000
H	11.572774000	16.903225000	3.214104000
C	10.434801000	17.854537000	0.102004000
H	10.791328000	17.828009000	-0.929848000
H	10.311470000	18.906950000	0.382333000
H	9.452909000	17.371390000	0.143513000
C	12.790625000	17.847885000	0.990982000
H	13.532569000	17.295432000	1.574772000
H	12.710146000	18.855960000	1.413010000
H	13.163139000	17.945136000	-0.029782000
C	11.646968000	12.885952000	-1.537193000
C	10.547526000	11.819129000	-1.464475000
H	10.527640000	11.331533000	-0.489899000
H	10.718175000	11.044665000	-2.218818000
H	9.566035000	12.265886000	-1.651569000
C	11.594988000	13.461442000	-2.966210000
H	10.681631000	14.046950000	-3.112822000
H	11.581471000	12.634605000	-3.684685000
H	12.454157000	14.087750000	-3.204726000
C	13.014031000	12.218499000	-1.307553000
H	13.826258000	12.944909000	-1.393568000
H	13.185407000	11.433438000	-2.052523000
H	13.069133000	11.759618000	-0.315737000

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