Contents

General. Manipulation of air and moisture sensitive compounds was carried out under a dry nitrogen atmosphere using Schlenk tube techniques associated with a high-vacuum line or in the glove box which was filled with dry nitrogen. All solvents were purchased from Kanto Chemical Co. Inc., and was dried over activated molecular sieves. ^{1}H, ^{13}C{^{1}H}, ^{29}Si{^{1}H} NMR spectra were recorded on a JEOL Lambda 400 spectrometer at ambient temperature unless otherwise noted. ^{1}H, ^{13}C{^{1}H}, ^{29}Si{^{1}H} NMR chemical shifts (δ values) were given in ppm relative to the solvent signal (^{1}H, ^{13}C{^{1}H}) or standard resonances (^{29}Si{^{1}H}: external tetramethylsilane). Elemental analyses were performed by a Thermo Scientific FLASH 2000 Organic Elemental Analyzer. IR spectra were recorded on a PerkinElmer Spectrum Two spectrometer. The starting compounds, Pd(CN^{t}Bu)$_2$[1], and ClPh$_2$Si-SiPh$_2$Cl[2] were synthesized by the method reported in the literature. All reagents were purchased from Tokyo Chemical Industries Co., Ltd. or Sigma-Aldrich, and were used without further purification.

Synthesis of 1,3- dimethyl -4,5-diethylimidazol-2-thione. This compound was synthesized according to the slightly modified method reported in the literature.[3] In a 200 mL Schlenk tube equipped with a reflux condenser, 1,3-dimethylthiourea (4.26 g, 40.9 mmol), propioin (5.00 mL, 40.9 mmol), and hexan-1-ol (120 mL) were added. The reaction mixture was heated to reflux with an oil bath for overnight, then the solvent was removed *in vacuo* at 65 °C. The remaining residue was washed with water (1 mL), and was extracted with diethyl ether (40 mL). The organic solution was stored at -20 °C, then the formed colorless crystals was washed with cold diethyl ether (3 x 10 mL) to afford 1,3-dimethyl-4,5-diethylimidazol-2-thione in 57% yield (4.30 g, 23.3 mmol). ^{1}H NMR (400 MHz, r.t., C_6D_6): δ = 0.65 (t, 6H, -CH_2CH_3), 1.87 (q, 4H, -CH_2CH_3), 3.23 (s, 6H, N-CH_3). ^{13}C{^{1}H} NMR (100 MHz, r.t., C_6D_6): 14.43 (s, -CH_2CH_3), 16.78 (s, -CH_2CH_3), 31.50 (s, N-CH_3), 125.46 (s, C=C), 163.68 (s, C=S). Anal calcd for $C_9H_{16}N_2S$; C 58.65, H 8.75, N 15.20; found: C 58.25, H 8.73, N 15.03.

Synthesis of 1,3-dimethyl-4,5-diethylimidazol-2-ylidene (Me$_2$IM^{Et}). This compound was synthesized according to the slightly modified method reported in the literature.[3] In a 50 mL schlenk tube, sodium (0.390 g, 17.1 mmol) and potassium (1.34 g, 34.2 mmol) were sequentially added, then Na/K was formed by heating with a heat-gun under reduced pressure. Then 1,2-dimethoxyethane (45 mL) solution of 1,3-dimethyl-4,5-diethylimidazol-2-thione (3.15 g, 17.1 mmol) was cautiously added with vigorous stirring, and the reaction mixture was stirred under reflux for overnight. Then the solvent was removed *in vacuo*, and remaining crude product was extracted with pentane (45 mL). This solution was centrifuged to remove the insoluble materials. The mother liquid was cooled to -20 °C, then Me$_2$IM^{Et} was isolated as colorless crystals in 53% yield (1.39 g, 9.10 mmol). ^{1}H NMR (400 MHz, r.t., C_6D_6): δ = 0.83 (t, 6H, -CH_2CH_3), 2.07 (q, 4H, -CH_2CH_3), 3.44 (s, 6H, N-CH_3). ^{13}C{^{1}H} NMR (100 MHz, r.t., C_6D_6): 14.92 (-CH_2CH_3), 17.15 (-CH_2CH_3), 35.13 (N-CH_3), 128.59 (C=C), 214.55 (s, NCN). Anal calcd for $C_9H_{16}N_2$; C 71.01, H 10.59, N 18.40; found: C 71.51, H 11.01, N 18.21.

Synthesis of Ph$_2$Si(μ-Pz^{Me2})$_2$SiPh$_2$ (1). In a 50 mL schlenk tube, ClPh$_2$Si-SiPh$_2$Cl (1.00 g, 2.30 mmol) was dissolved in THF (15 mL), then THF solution of Li(Pz^{Me2}) (4.90 mmol) (prepared by the reaction of 3,5-dimethylpyrazole with 1 equiv. of ^{n}BuLi in THF) was added to this solution at room temperature. The solution

was stirred at 40 °C for overnight. The reaction mixture was centrifuged, and the insoluble materials was collected and dried *in vacuo* to afford **1** as white powder in 56% yield (720 mg, 1.30 mmol). Crystals suitable for X-ray diffraction analysis were obtained by recrystallization from toluene. ^{1}H NMR (400 MHz, r.t., C_6D_6): δ = 1.87 (s, 12H, CH_3), 5.69 (s, 2H, C-H in Pz^{Me2}), 7.15-7.18 (m, 12H, Ph), 7.87-7.90 (m, 8H, Ph). ^{13}C{^{1}H} NMR (100 MHz, r.t., C_6D_6): 12.88 (CH_3 in Pz^{Me2}), 109.39 (s, C-4 in Pz^{Me2}), 127.92 (s, Ph), 129.23 (s, Ph), 136.00 (s, Ph), 137.48 (s, Ph), 145.91 (s, C-3,5 in Pz^{Me2}). ^{29}Si{^{1}H} NMR (119 MHz, r.t., C_6D_6): no signals were observed due to the low solubility. Anal calcd for $C_{34}H_{34}N_4Si_2$; C 73.60, H 6.18, N 10.10; found: C 73.57, H 6.14, N 9.80.

Synthesis of 2. In a 50 mL schlenk tube, disilane **1** (100 mg, 0.180 mmol) was dissolved in toluene (4.5 mL), then toluene (3 mL) solution of $Pd(CN^tBu)_2$ (100 mg, 0.360 mmol) was added to this solution at room temperature. The solution was stirred at room temperature for 1 hr. The solvent was removed *in vacuo*, and the obtained solid was dissolved in diethyl ether (15 mL). This solution was centrifuged to remove the small amount of insoluble materials. The obtained solution was cooled to -20 °C, then **2** was isolated as yellow crystals in 88 % yield (148 mg, 0.159 mmol). ^{1}H NMR (400 MHz, r.t., C_6D_6): δ = 0.55 (s, 18H, $CNCMe_3$), 1.58 (s, 6H, CH_3 in Pz^{Me2}), 2.41 (s, 6H, CH_3 in Pz^{Me2}), 5.88 (s, 2H, C-H in Pz^{Me2}), 7.10-7.13 (m, 12H, Ph), 7.62-7.64 (m, 8H, Ph). ^{13}C{^{1}H} NMR (100 MHz, r.t., C_6D_6): 13.36 (s, CH_3 in Pz^{Me2}), 14.29 (s, -C(*C*H_3)$_3$), 14.77 (s, CH_3 in Pz^{Me2}), 29.31 (s, -*C*(CH_3)$_3$), 106.83 (s, 4-C in Pz^{Me2}), 126.86 (s, Ph), 127.52 (s, Ph), 128.59 (s, Ph), 135.11 (s, Ph), 147.21 (s, 3,5-C in Pz^{Me2}), 151.70 (s, 3,5-C in Pz^{Me2}) (one peak assignable to the <u>*C*</u>N^{t}Bu moiety was not detected). ^{29}Si{^{1}H} NMR (119 MHz, r.t., C_6D_6): 15.12 (s). IR (ATR): ν_{CN} = 2134 cm^{-1}. Anal calcd for $C_{44}H_{52}N_6Pd_2Si_2$; C 56.59, H 5.61, N 9.00; found: C 56.96, H 5.89, N 8.56.

Synthesis of 3. In a 50 mL schlenk tube, disilane **1** (226 mg, 0.407 mmol) was dissolved in toluene (6 mL), then the mixture of $Ni(cod)_2$ (112 mg, 0.407 mmol) and Me_2IM^{Et} (62.0 mg, 0.407 mmol) in toluene (6 mL) was added to this solution at room temperature. The solution was stirred at 75 °C for overnight. The solvent was removed *in vacuo*, and the obtained solid was dissolved in cyclopentyl methyl ether (12 mL). This solution was centrifuged to remove the small amount of insoluble materials. The obtained solution was cooled to -20 °C, then **3** was isolated as yellow crystals in 77 % yield (233 mg, 0.314 mmol). Monitoring this reaction by ^{1}H NMR indicateed that no detectable intermediary species was formed in the course of this reaction (Figure S9) ^{1}H NMR (400 MHz, r.t., C_6D_6): δ = 0.71 (t, 6H, -CH_2C*H*$_3$), 1.56 (s, 3H, CH_3 in Pz^{Me2}), 1.72 (s, 9H, CH_3 in Pz^{Me2}), 1.85 (dq, 4H, -C*H*$_2CH_3$), 2.94 (s, 6H, N-CH_3), 5.54 (s, 1H, C-H in Pz^{Me2}), 5.63 (s, 1H, C-H in Pz^{Me2}), 7.18-7.25 (m, 8H, Ph), 7.37-7.41 (m, 4H, Ph), 7.56-7.58 (m, 4H, Ph), 8.44-8.46 (m, 4H, Ph). ^{13}C{^{1}H} NMR (100 MHz, r.t., C_6D_6): 12.34 (s, CH_3 in Pz^{Me2}), 13.46 (s, CH_3 in Pz^{Me2}), 13.49 (s, CH_3 in Pz^{Me2}), 14.89 (s, -CH_2CH_3), 16.60 (s, -CH_2CH_3), 33.69 (s, N-CH_3), 104.39 (s, 4-C in Pz^{Me2}), 112.16 (s, 4-C in Pz^{Me2}), 126.93 (s, Ph), 127.39 (s, Ph), 127.45 (s, Ph), 127.75 (s, Ph), 130.21 (s, C=C in Me_2IM^{Et}), 134.58 (s, Ph), 135.54 (s, Ph), 144.02 (s, 3,5-C in Pz^{Me2}), 144.97 (s, 3,5-C in Pz^{Me2}), 145.45 (s, 3,5-C in Pz^{Me2}), 147.79(s, Ph), 148.76(s, Ph), 190.12(s, Ni-C). ^{29}Si{^{1}H} NMR (119 MHz, r.t., C_6D_6): 37.31 (s), -51.25 (s). Anal calcd for $C_{43}H_{50}N_6Si_2Ni$; C 67.44, H 6.58, N 10.97; found: C 67.46, H 6.58, N 10.69.

Synthesis of 4. In a 50 mL schlenk tube, disilane **1** (200 mg, 0.360 mmol) was dissolved in toluene (10 mL), then the mixture of $Ni(cod)_2$ (100 mg, 0.360 mmol) and Me_2IM^{Et} (110 mg, 0.72 mmol) in toluene (12 mL) was added to this solution at room temperature. The solution was stirred at 100 °C for overnight. The solvent was removed *in vacuo*, and the obtained solid was dissolved in pentane (10 mL). This solution was centrifuged to remove the small amount of insoluble materials. The obtained solution was cooled to -20 °C, then **4** was isolated as yellow crystals in 31 % yield (95.8 mg, 0.110 mmol). ^{1}H NMR (400 MHz, r.t., C_6D_6): δ = 0.64 (t, 12H, -CH_2CH_3), 1.53 (s, 6H, CH_3 in Pz^{Me2}), 1.71 (q, 8H, -CH_2CH_3), 2.58 (s, 6H, CH_3 in Pz^{Me2}), 3.54 (s, 12H, N-CH_3), 5.87 (s, 2H, C-H in Pz^{Me2}), 6.96-7.00 (m, 12H, Ph), 7.32-7.34 (m, 8H, Ph). ^{13}C{^{1}H} NMR (100 MHz, r.t., C_6D_6): 14.10 (s, CH_3 in Pz^{Me2}), 14.23 (s, CH_3 in Pz^{Me2}), 14.57 (s, -CH_2CH_3), 16.70 (s, -CH_2CH_3), 35.03 (s, N-CH_3), 106.72 (s, 4-C in Pz^{Me2}), 126.20 (s, Ph), 126.85 (s, Ph), 130.38 (s, C=C in Me_2IM^{Et}), 133.98 (s, Ph), 147.41 (s, 3,5-C in Pz^{Me2}), 147.79 (s, 3,5-C in Pz^{Me2}), 184.67 (s, Ni-C) (one peak assignable to the Ph group was not detected presumably due to the overlapping). ^{29}Si{^{1}H} NMR (119 MHz, r.t., C_6D_6): 10.14 (s). Anal calcd for $C_{52}H_{66}N_8Si_2Ni$; C 68.04, H 7.25, N 12.21; found: C 67.80, H7.56, N 11.98.

Reaction of disilane 1 with $Ni(cod)_2$ in the absence of Me_2IM^{Et}. In a J-Young NMR tube, disilane **1** (4 mg, 7.2 x 10^{-3} mmol) was dissolved in C_6D_6, then C_6D_6 solution of $Ni(cod)_2$ (2 mg, 7.2 x 10^{-3} mmol) was added at room temperature. The solution was kept at room temperature for 1h, then kept at 75 °C for overnight. ^{1}H NMR spectrum of this solution indicate that no reaction took place. The actual NMR charts are shown in Figure S10.

Reaction of disilane 1 with 2 equiv. of $Ni(cod)_2$ and 4 equiv. of Me_2IM^{Et}. In a 50 mL schlenk tube, disilane **1** (200 mg, 0.360 mmol) was dissolved in toluene (10 mL), then the mixture of $Ni(cod)_2$ (200 mg, 0.720 mmol) and Me_2IM^{Et} (220 mg, 1.44 mmol) in toluene (20 mL) was added to this solution at room temperature. The solution was stirred at 100 °C for overnight. The solvent was removed *in vacuo*, and the ^{1}H NMR spectrum of the crude product indicates the complex **4** was formed as the major product as shown in Figure S11.

Interconverstion from 3 to 4.

In a J-young NMR tube, complex **3** (17.0 mg, 0.0222 mmol) was dissolved in C_6D_6 (0.5 mL), then 1equiv. of Me_2IM^{Et} (3.38 mg, 0.0222 mmol) was added to this solution at room temperature. The solution was kept for several fours at 60 °C, then quantitative formation of **4** was confirmed by the ^{1}H NMR spectrum.

Interconversion from 4 to 3.

In a J-young NMR tube, complex **4** (3.30 mg, 0.0036 mmol) was dissolved in C_6D_6 (0.5 mL), then 1equiv. of $Ni(cod)_2$ (1.00 mg, 0.0036 mmol) and disilane **1** (2.00 mg, 0.0036 mmol) was added to this solution at room temperature. The solution was kept for 18 hrs at 100 °C, then quantitative formation of **3** was confirmed by the ^{1}H NMR spectrum.

Reaction of 1 with 1 equiv. of pyridine.

In a J-young NMR tube, disilane **1** (10 mg, 0.018 mmol) was dissolved in C_6D_6 (0.5 mL), then 1equiv. of pyridine (1.5 μL, 0.018 mmol) was added to this solution at room temperature. The solution was kept for 18

hrs at room temperature. ^{1}H NMR spectrum revealed that almost all the disilane was recovered, but the formation of trace amounts of a new species was detected (ca. 7% relative to **1**). Then this solution was heated for 18 hrs at 80 ^{o}C. It was found that the intensity of this new signal did not change in the ^{1}H NMR spectrum of the obtained solution.

Figure S1-1. ^{1}H NMR spectrum of solution of 1,3- dimethyl -4,5-diethylimidazol-2-thione in C_6D_6 at room temperature.

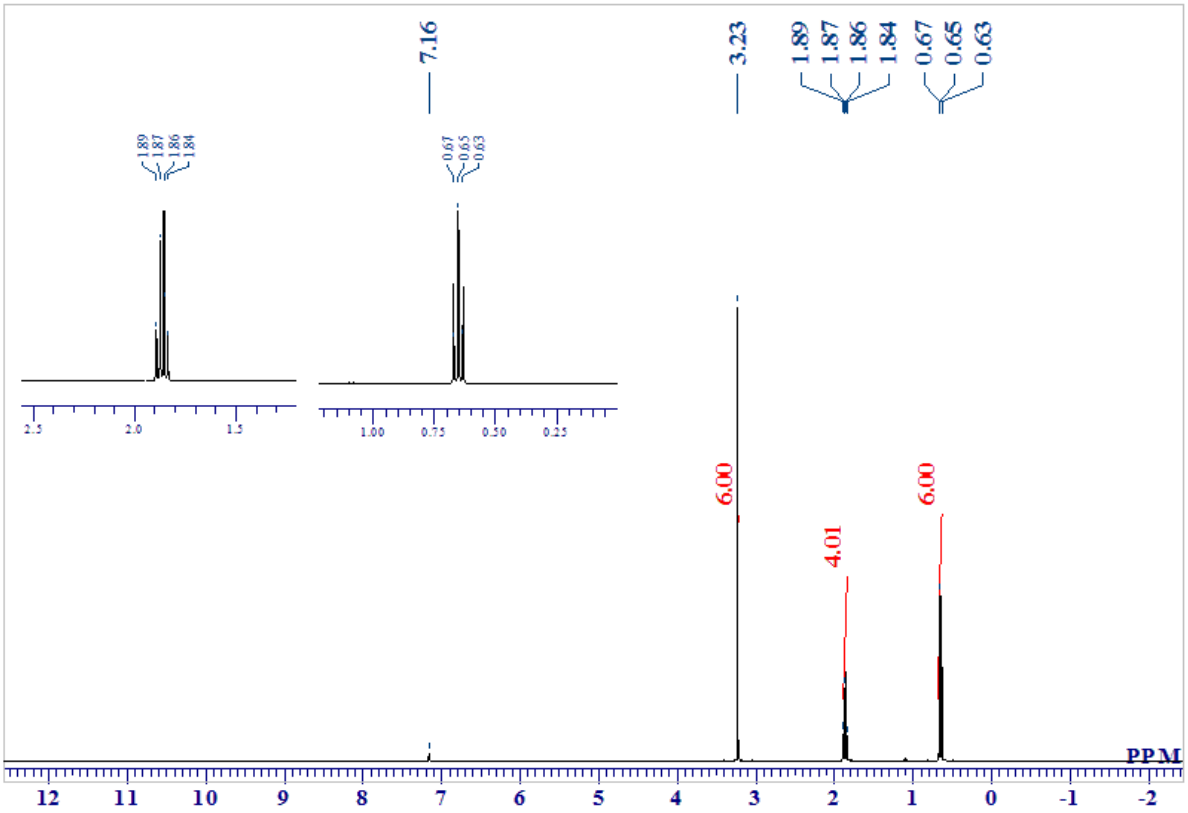


Figure S1-2. $^{13}C\{^{1}H\}$ NMR spectrum of solution of 1,3- dimethyl -4,5-diethylimidazol-2-thione in C_6D_6 at room temperature.

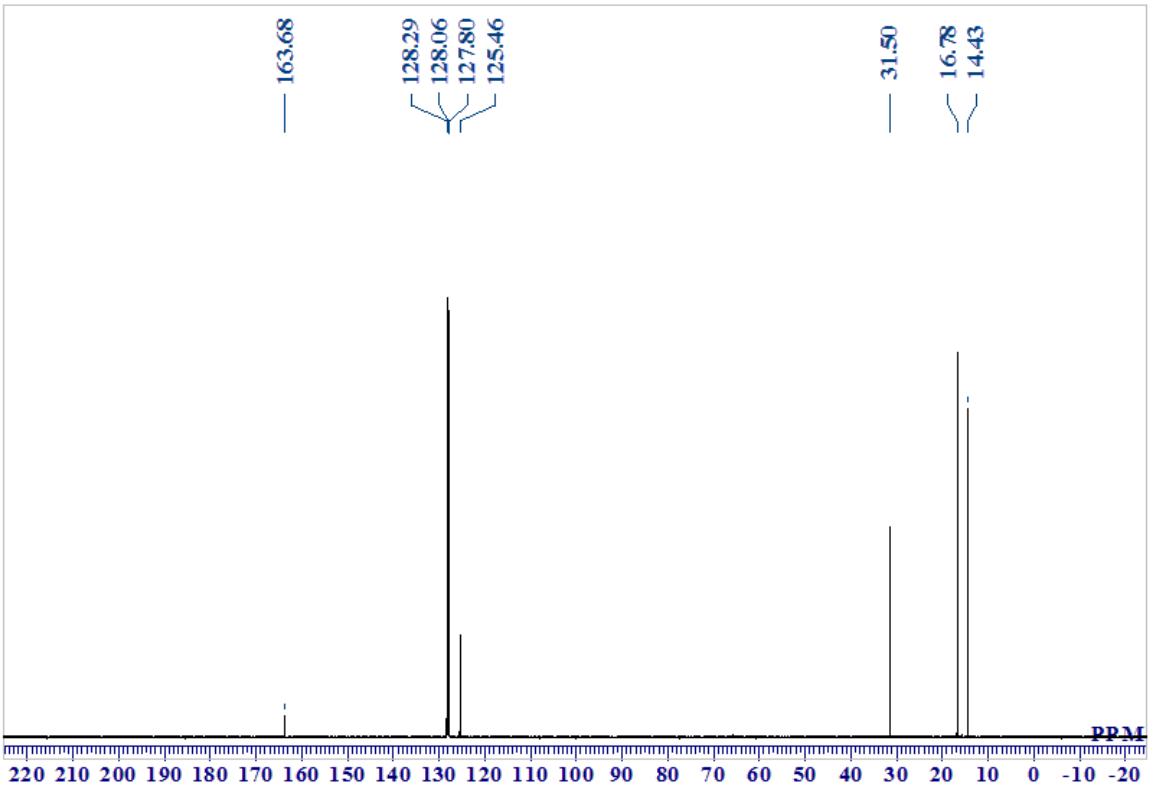


Figure S2-1. ^{1}H NMR spectrum of solution of 1,3-dimethyl-4,5-diethylimidazol-2-ylidene in C_6D_6 at room temperature.

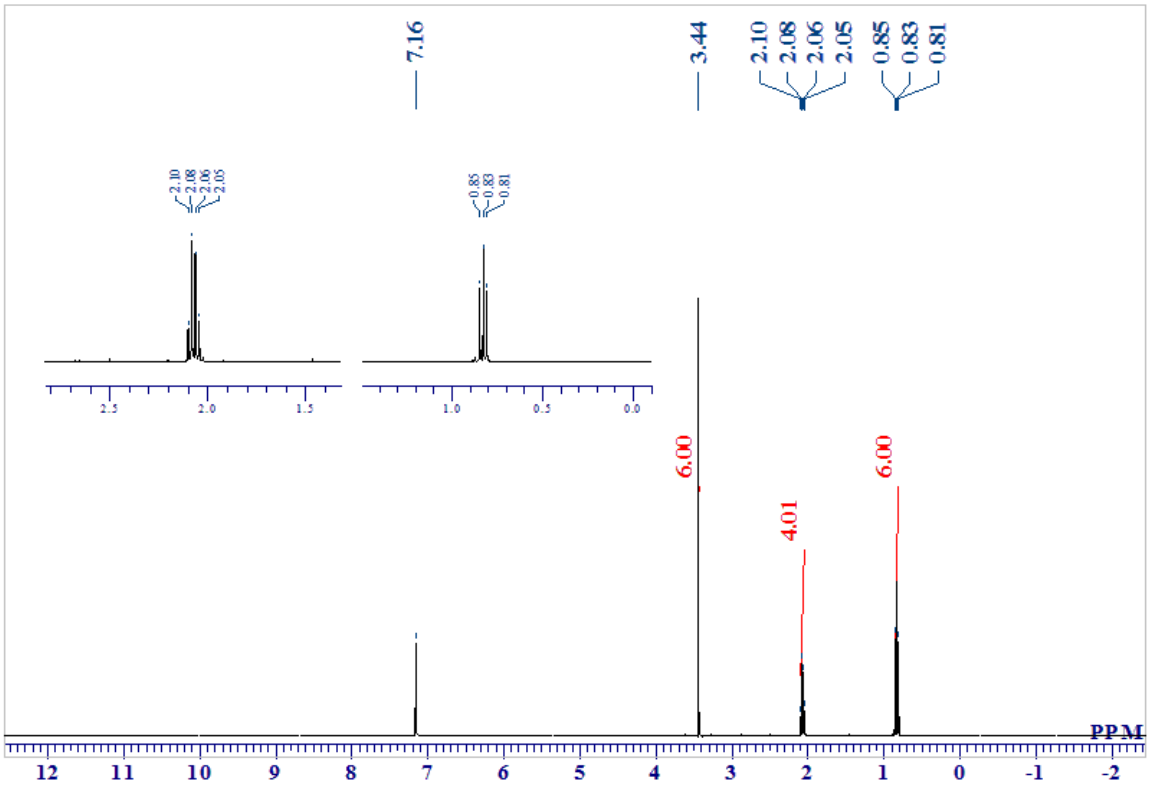


Figure S2-2. ^{13}C{^{1}H} NMR spectrum of solution of 1,3-dimethyl-4,5-diethylimidazol-2-ylidene in C_6D_6 at room temperature.

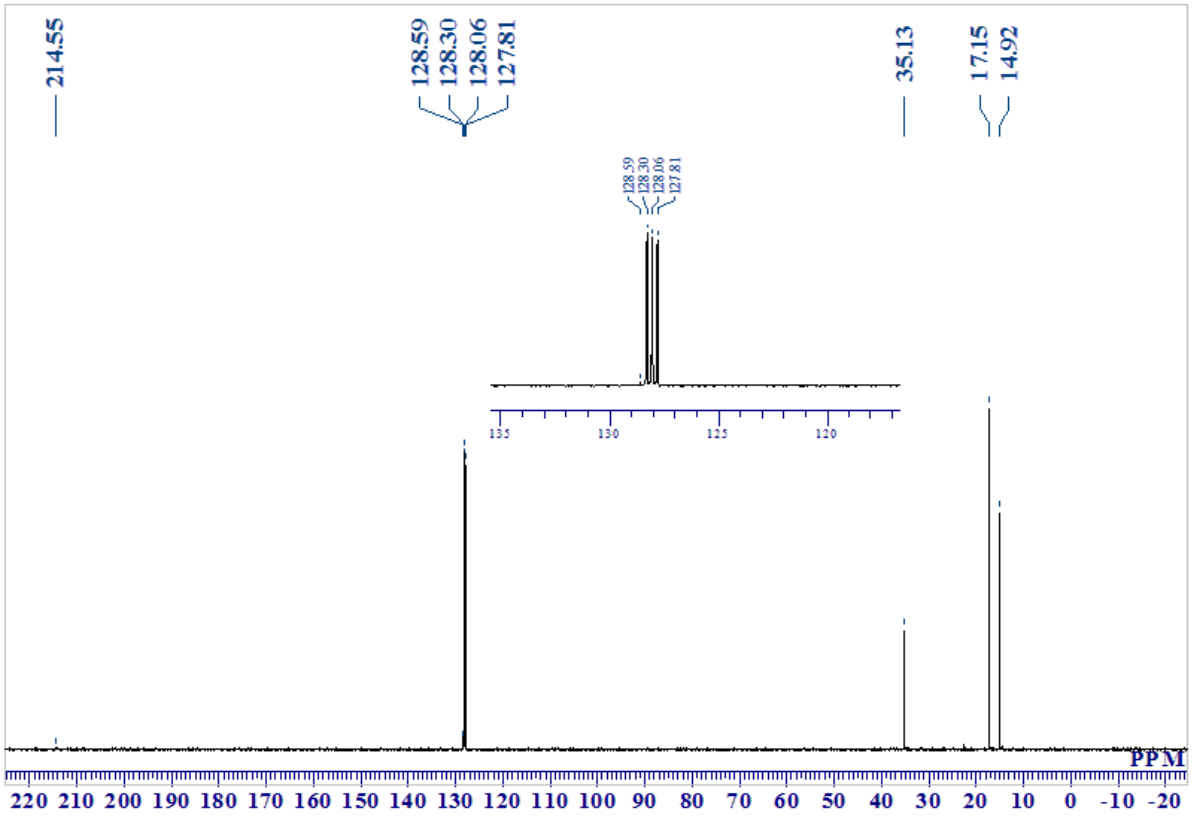


Figure S3-1. ^{1}H NMR spectrum of solution of **1** in C_6D_6 at room temperature.

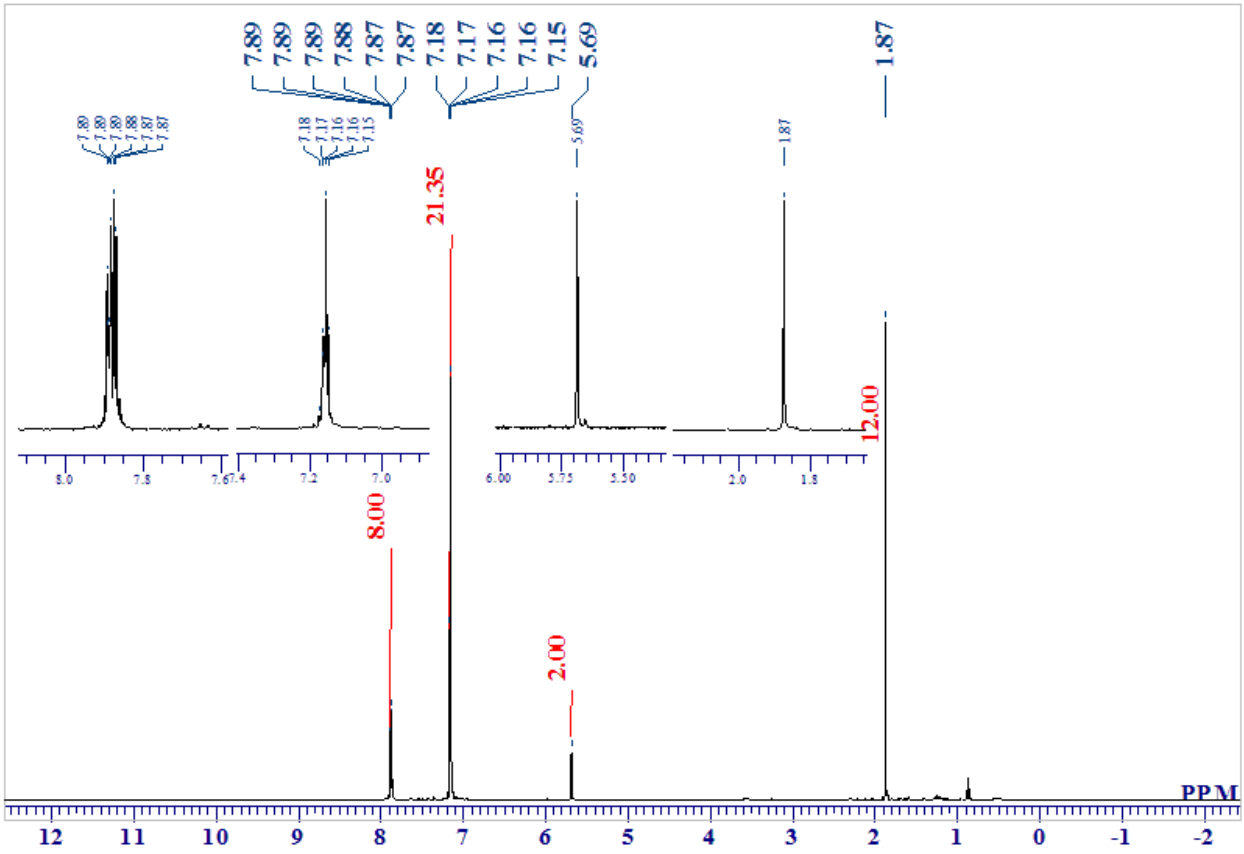


Figure S3-2. $^{13}C\{^{1}H\}$ NMR spectrum of solution of **1** in C_6D_6 at room temperature.

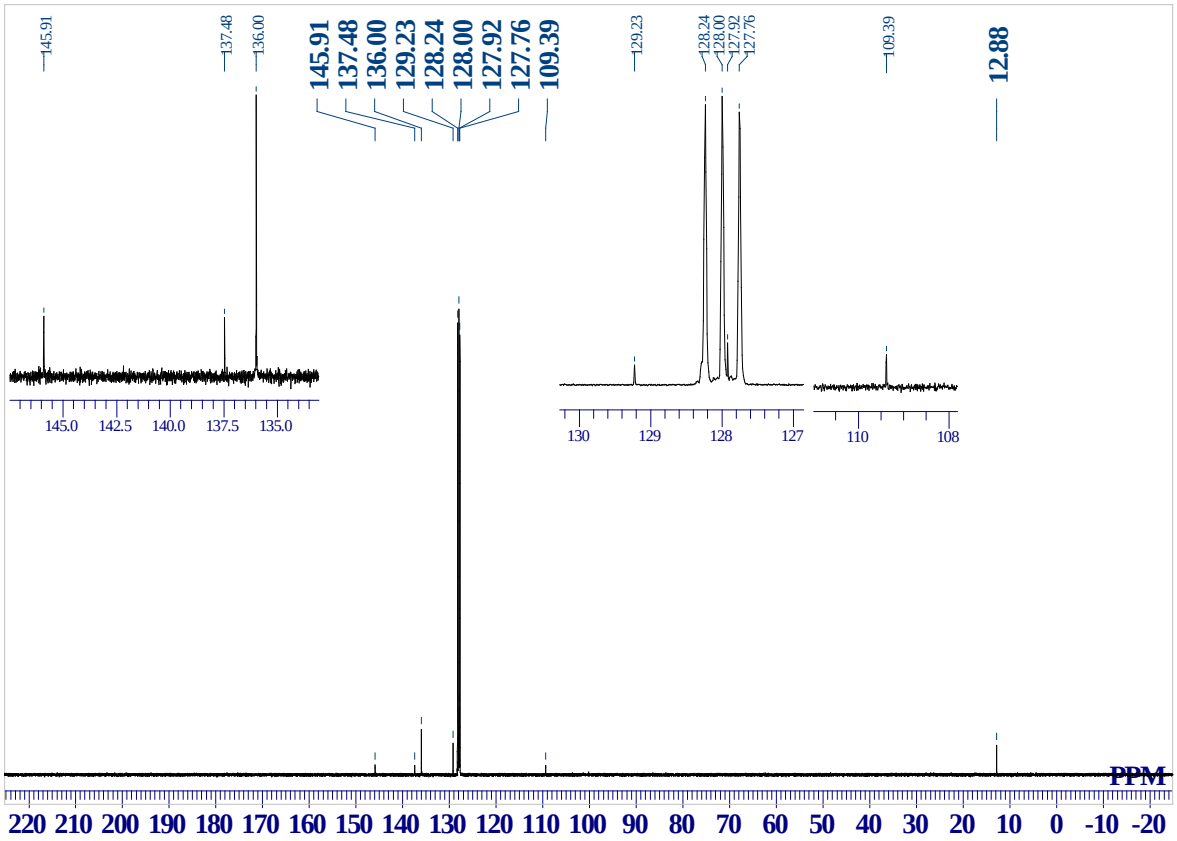


Figure S4-1. ^{1}H NMR spectrum of solution of **2** in C_6D_6 at room temperature.

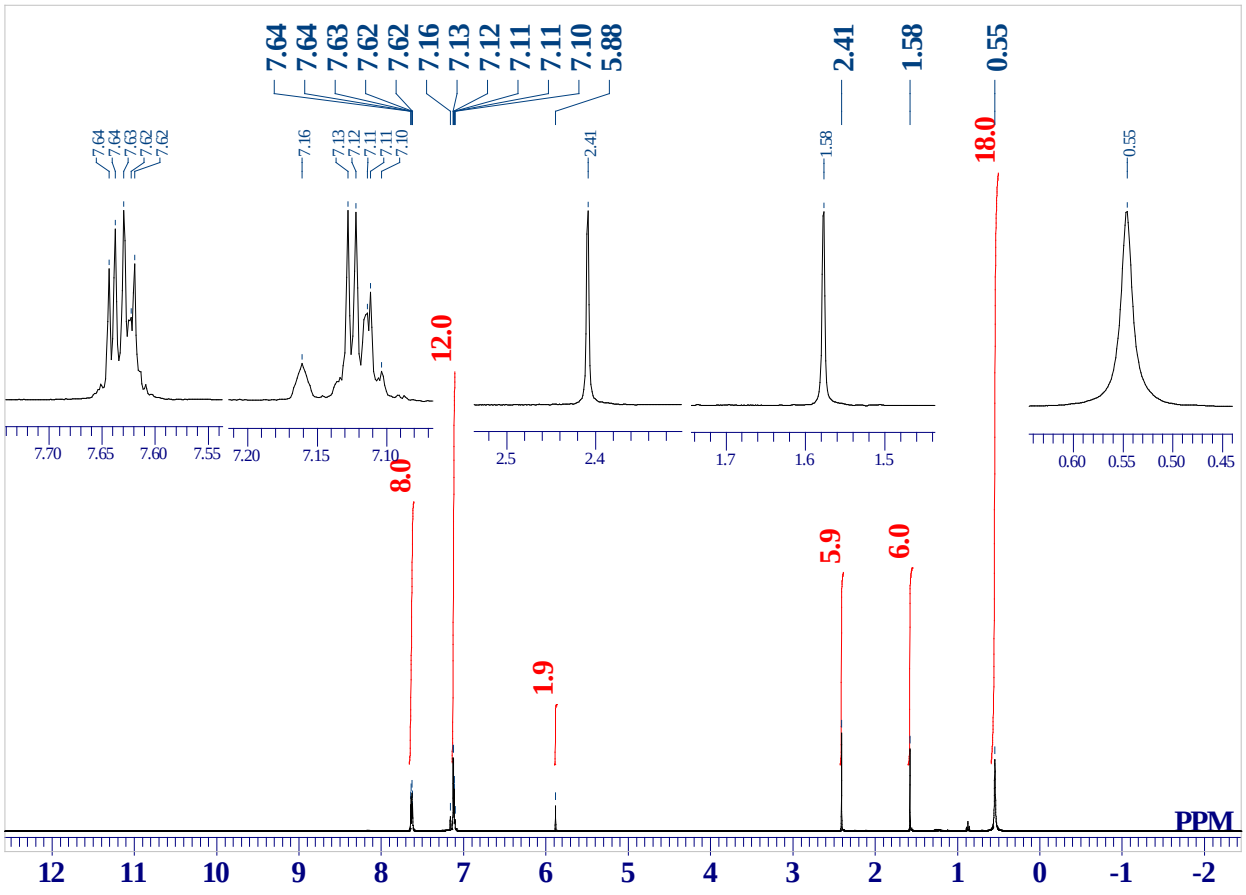


Figure S4-2. $^{13}C\{^{1}H\}$ NMR spectrum of solution of **2** in C_6D_6 at room temperature.

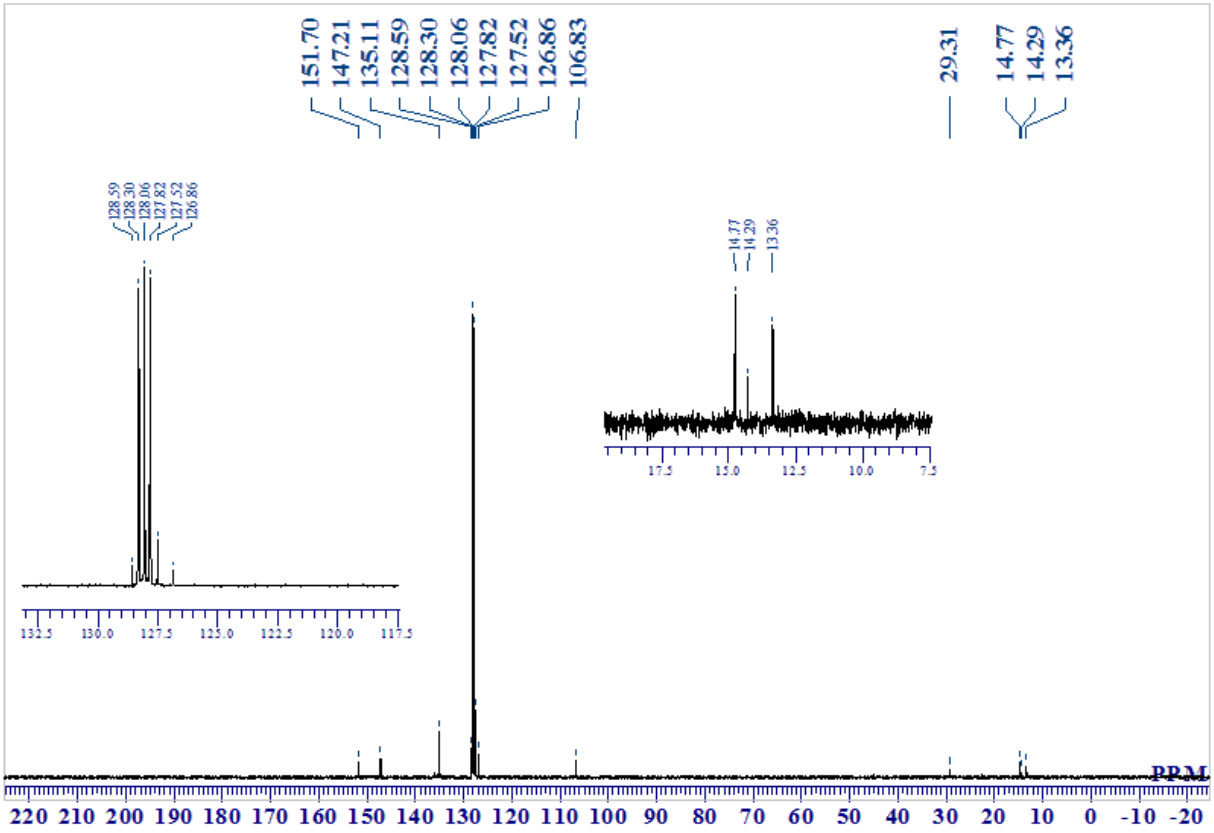


Figure S4-3. $^{29}Si\{^{1}H\}$ NMR spectrum of solution of **2** in C_6D_6 at room temperature.

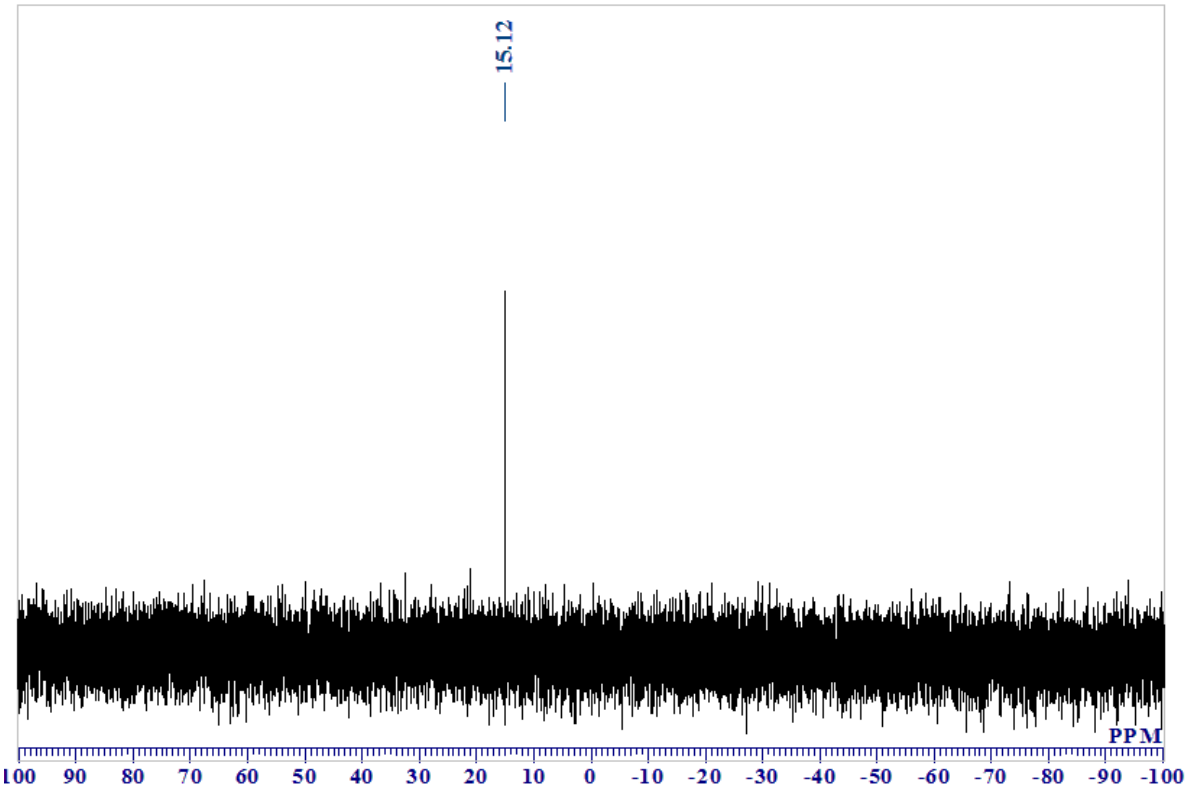


Figure S5-1. ^{1}H NMR spectrum of solution of **3** in C_6D_6 at room temperature.

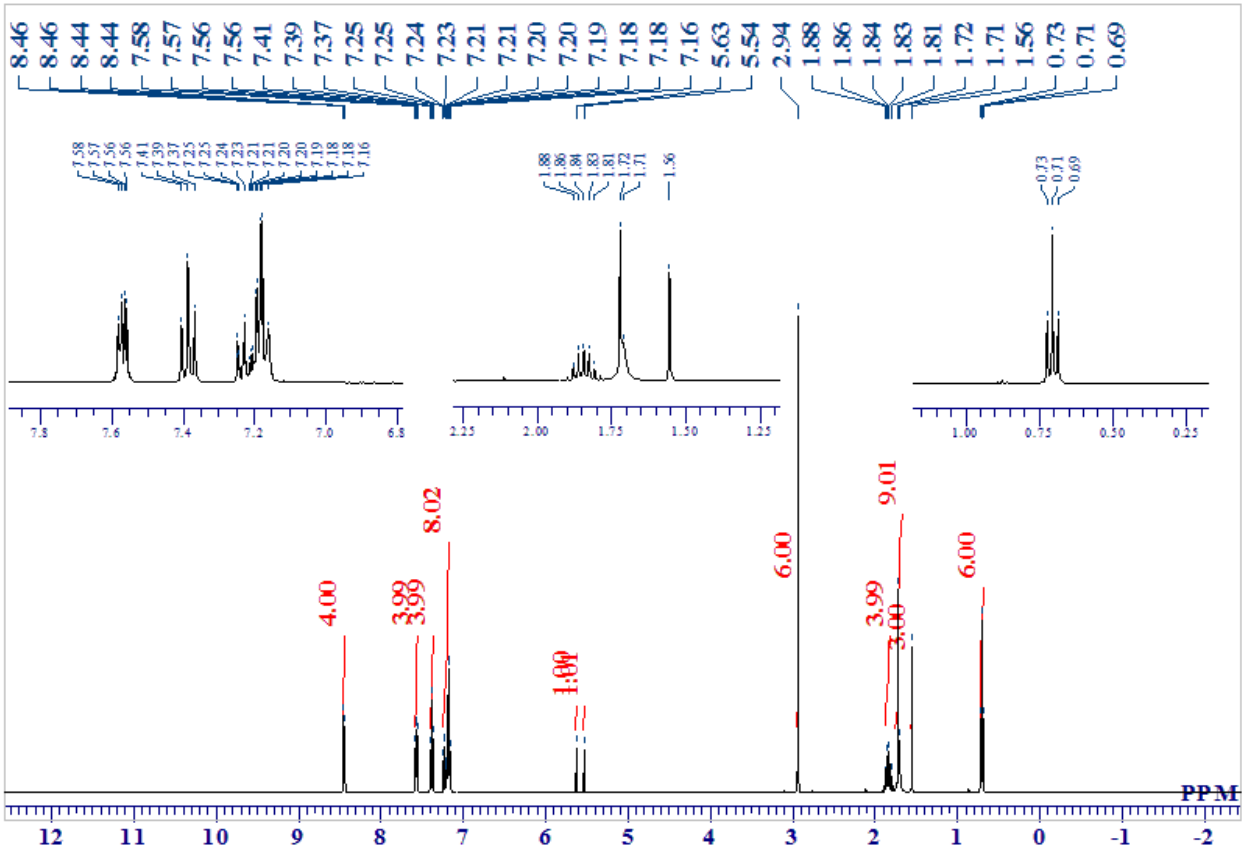


Figure S5-2. $^{13}C\{^{1}H\}$ NMR spectrum of solution of **3** in C_6D_6 at room temperature.

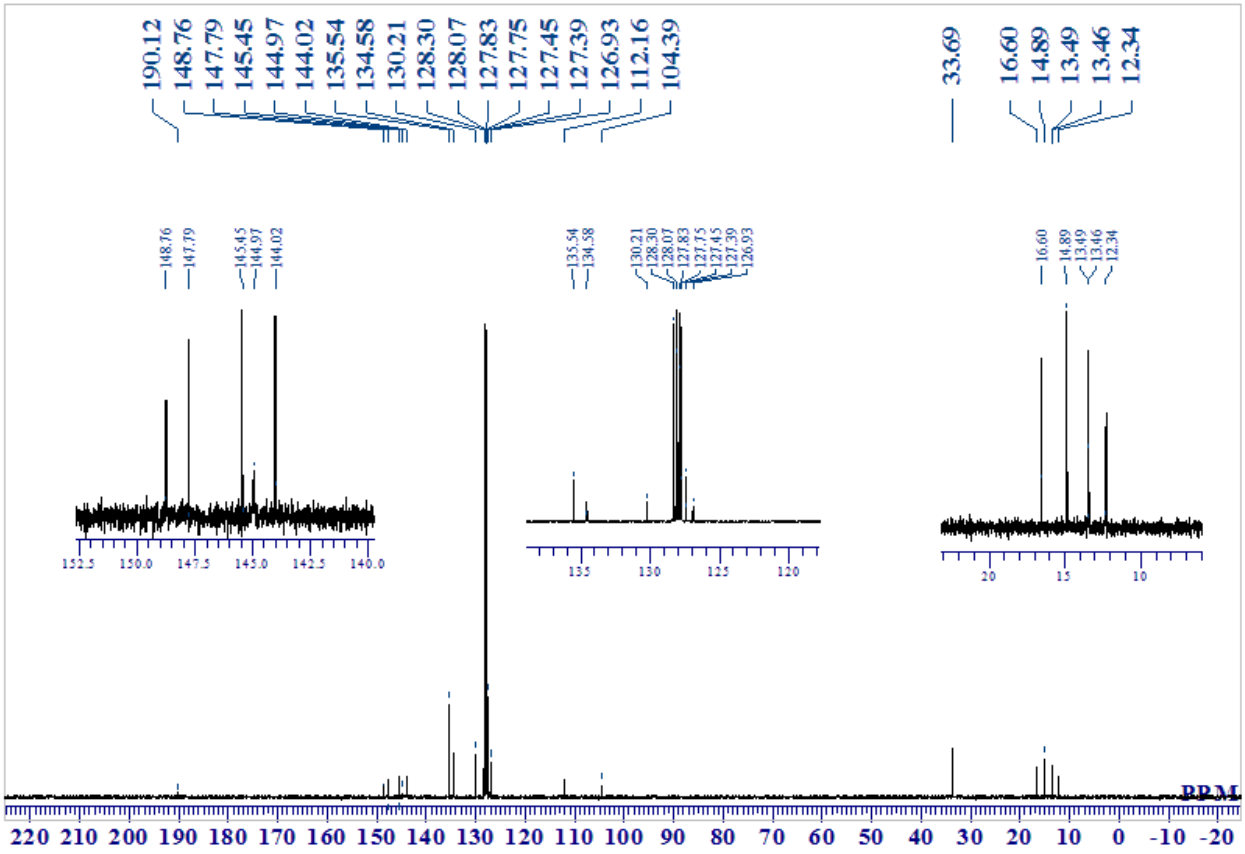


Figure S5-3. $^{29}Si\{^{1}H\}$ NMR spectrum of solution of **3** in C_6D_6 at room temperature.

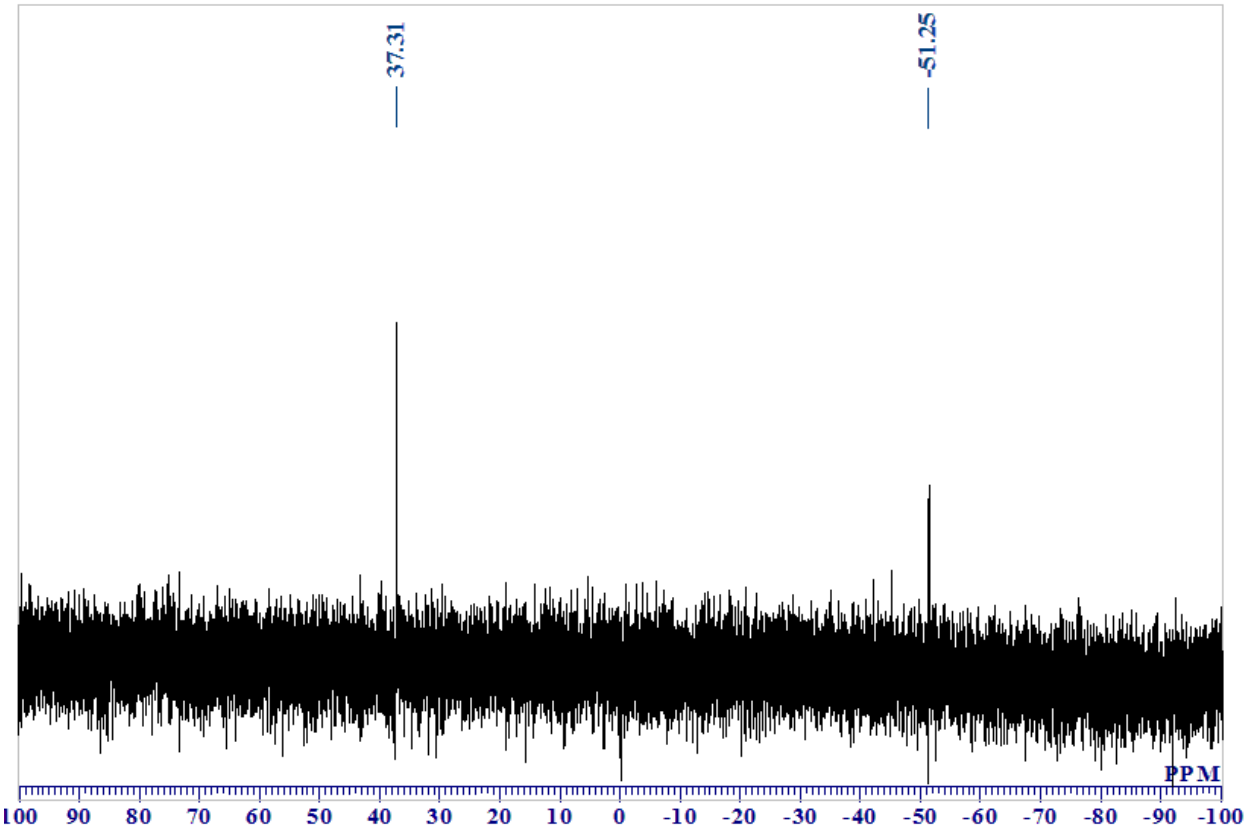


Figure S6-1. ^{1}H NMR spectrum of solution of **4** in C_6D_6 at room temperature.

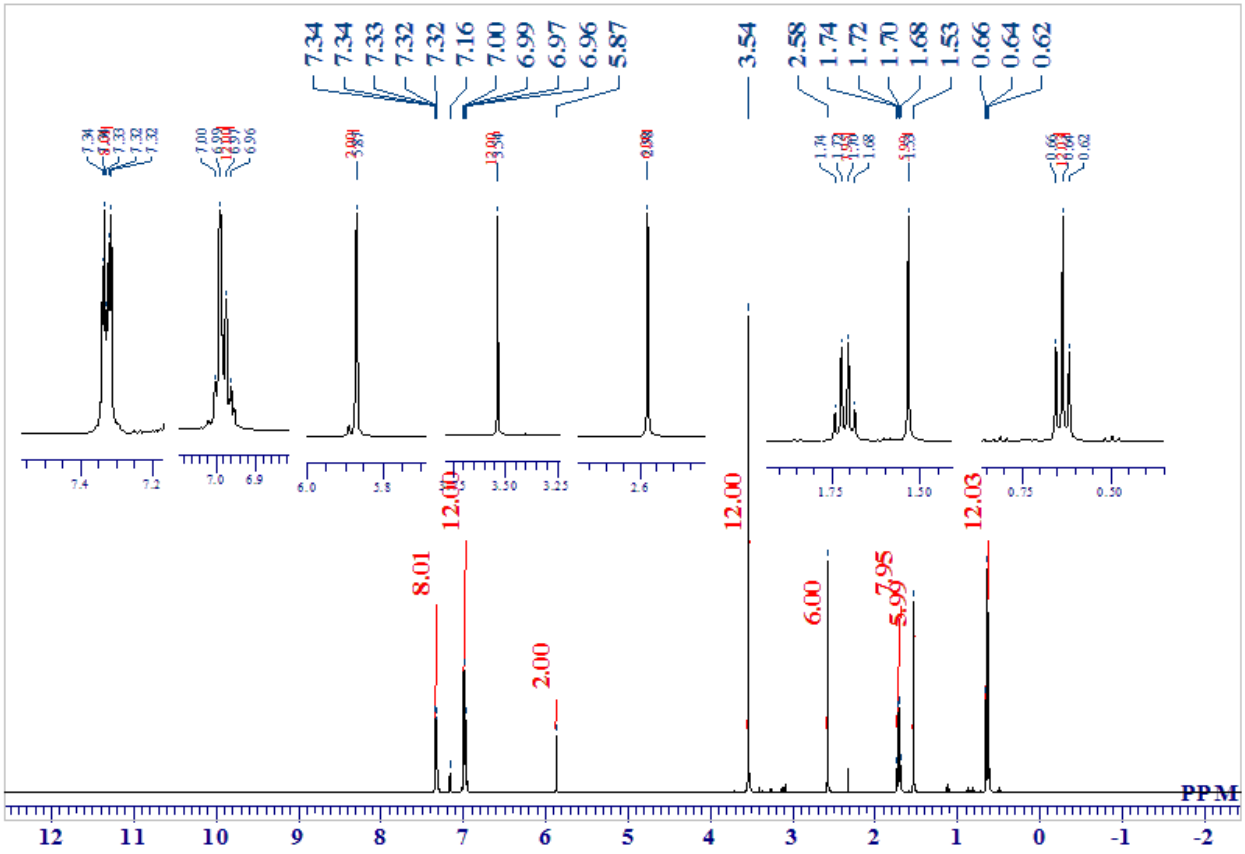


Figure S6-2. $^{13}C\{^{1}H\}$ NMR spectrum of solution of **4** in C_6D_6 at room temperature.

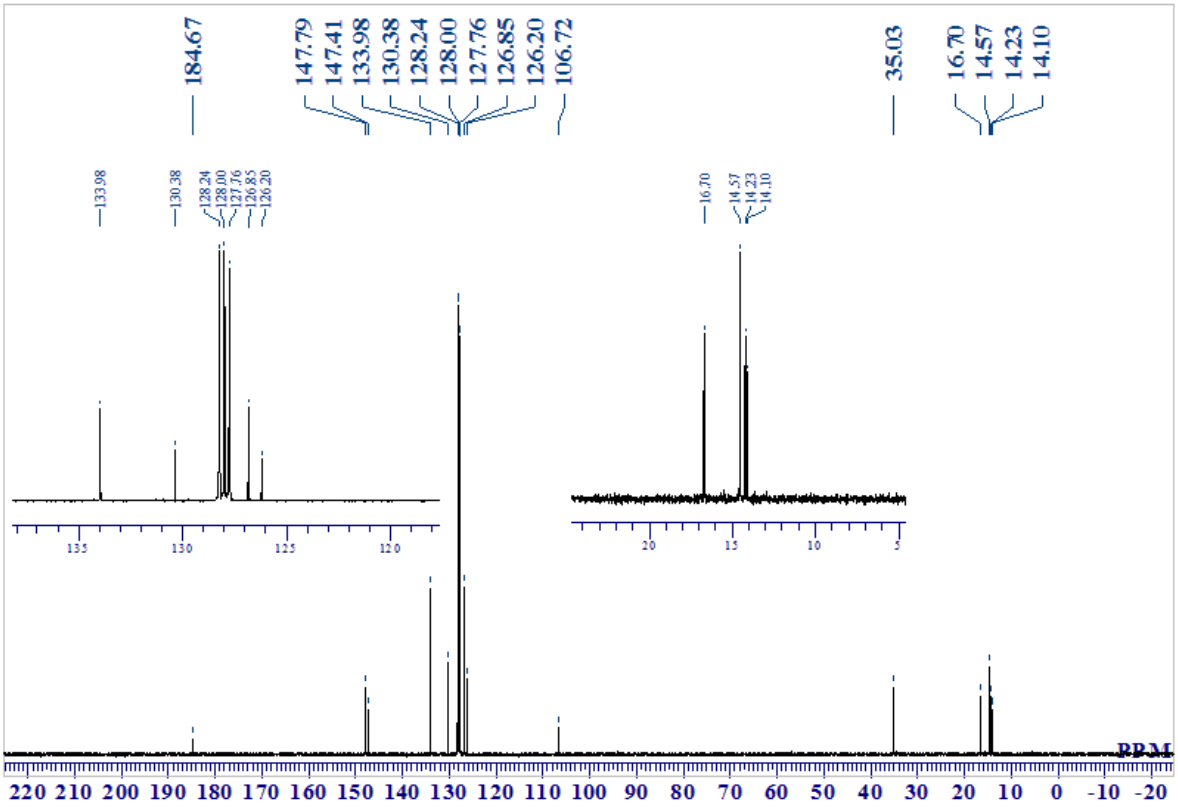


Figure S6-3. $^{29}Si\{^{1}H\}$ NMR spectrum of solution of **4** in C_6D_6 at room temperature.

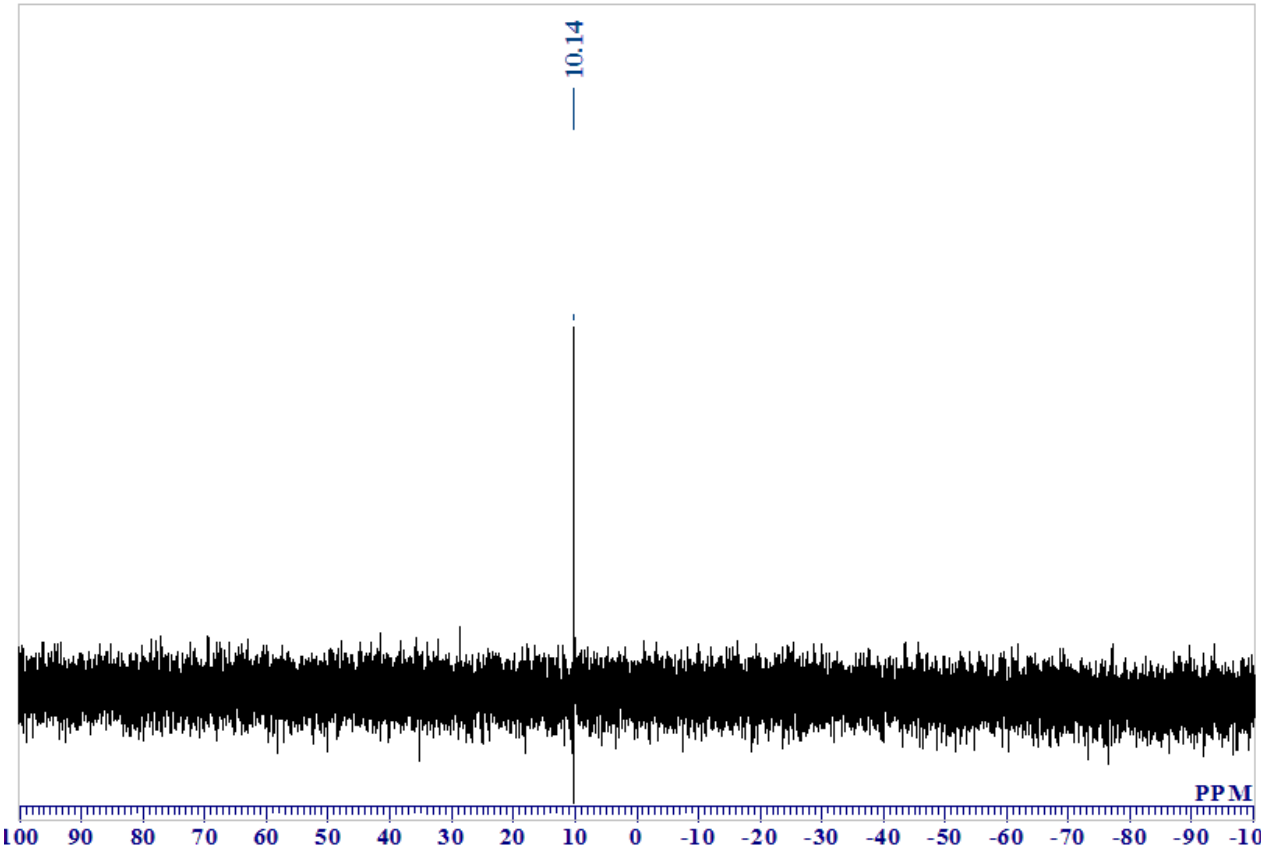


Figure S7-1. ^{1}H NMR spectrum of the crude product obtained from the reaction of **3** and Me_2IM^{Et} at 60 °C (upper) and the ^{1}H NMR spectrum of isolated complex **4** (lower).

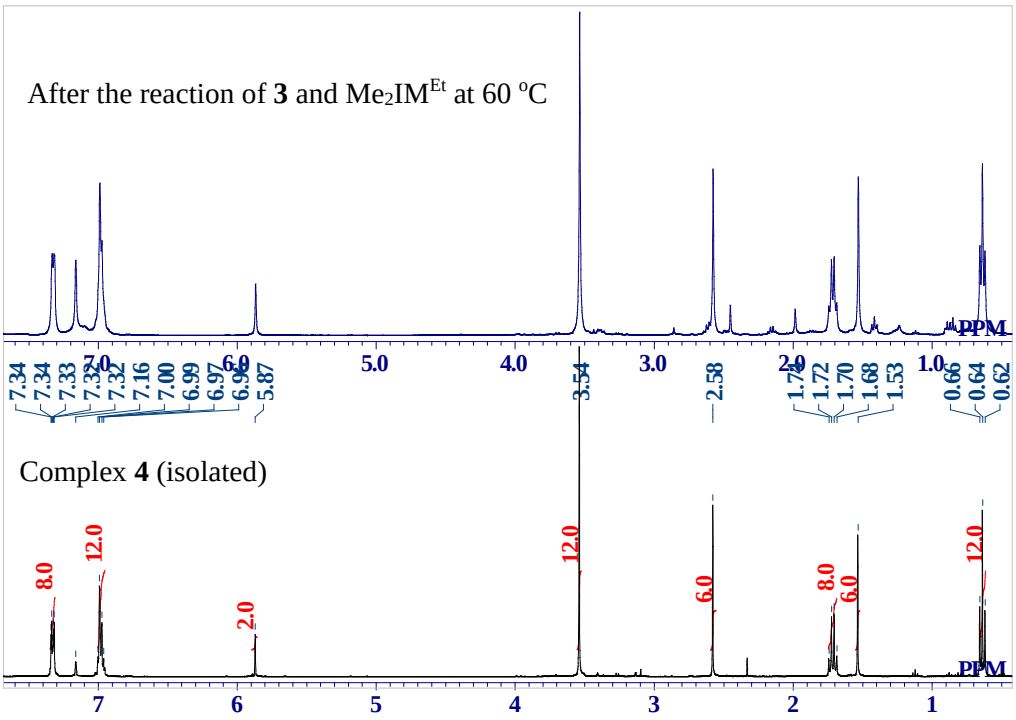


Figure S7-2. ^{1}H NMR spectrum of the crude product obtained from the reaction of **4** with Ni(cod)$_2$ and **1** (upper: after 30 min after the reaction at room temperature, middle: after 18 hrs at 100 ^{o}C) and the ^{1}H NMR spectrum of isolated complex **3** (lower).

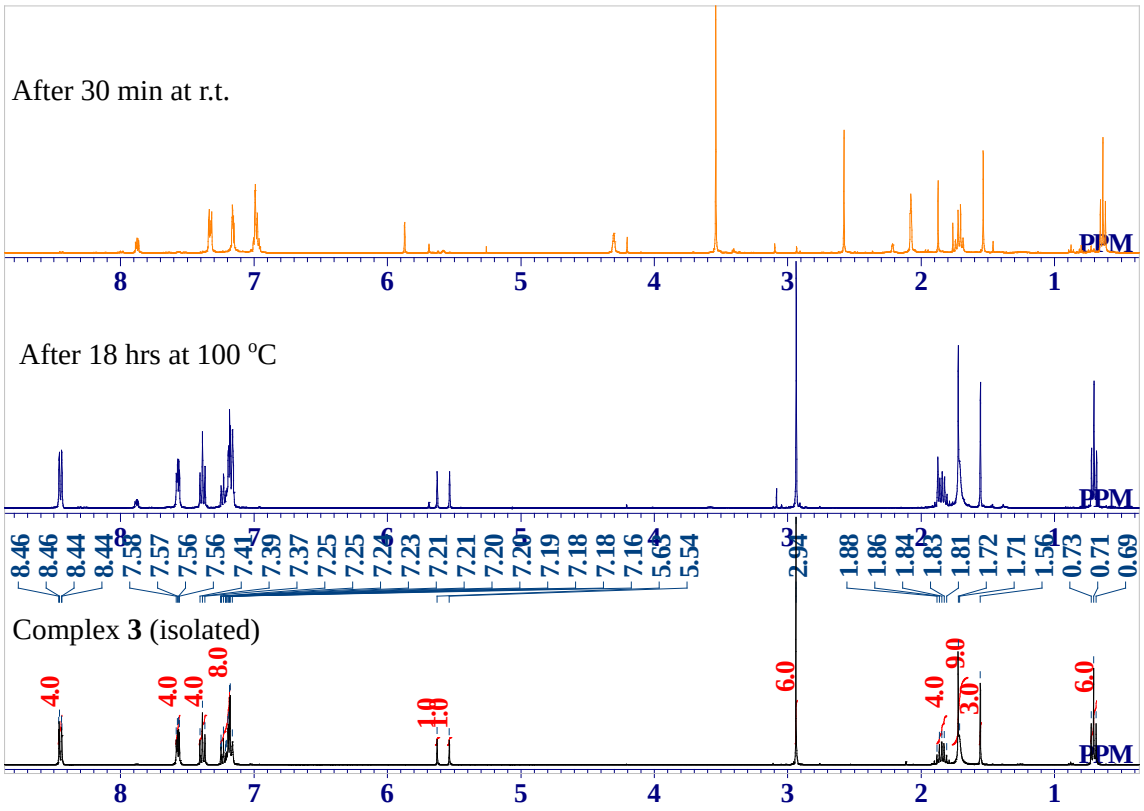


Figure S8. ^{1}H NMR spectrum obtained from the reaction of **1** with 1 equiv. pyridine in C_6D_6 at room temperature for 1h.

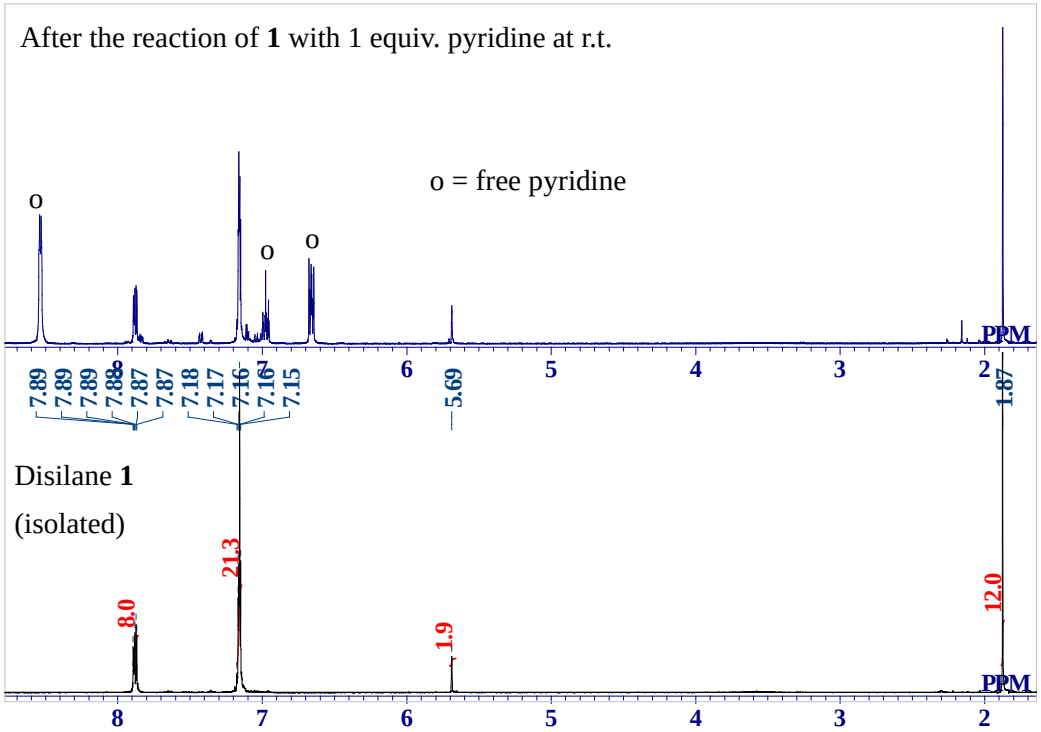


Figure S9. ^{1}H NMR spectra of the crude product obtained from the reaction of **1** with Ni(cod)$_2$ in the absence of Me$_2$IM^{Et} in C_6D_6.

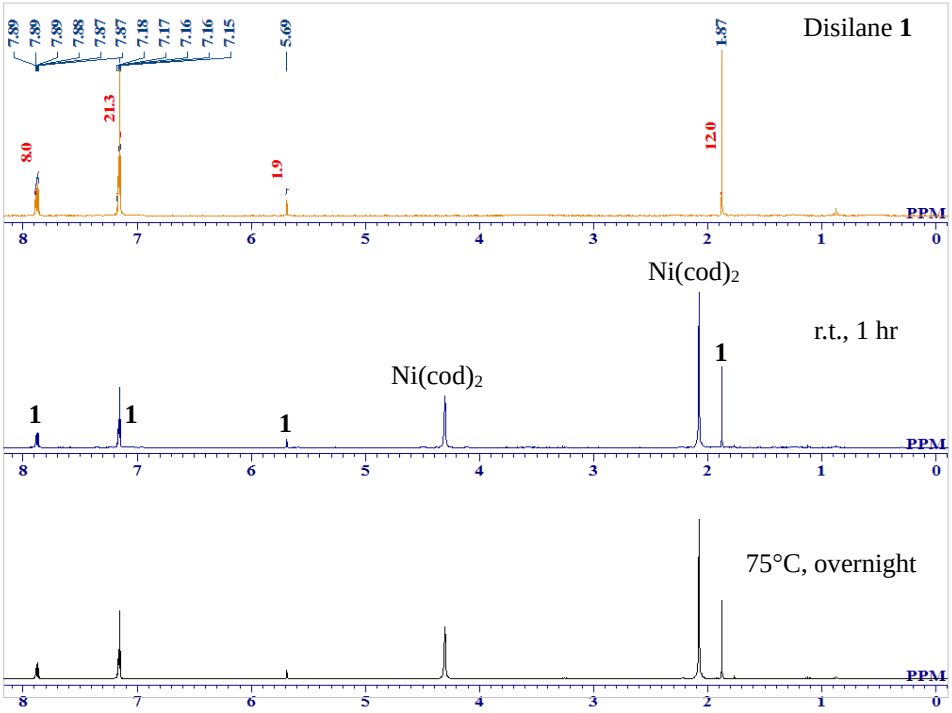


Figure S10. Monitoring the reaction of disilane **1** with 1 equiv. of Ni(cod)$_2$ and Me$_2$IM^{Et} by ^{1}H NMR spectrum in C_6D_6. (formation of unidentified product (marked as x) was confirmed as the minor product which may be the nickel(0) species bearing Me$_2$IM^{Et}.)

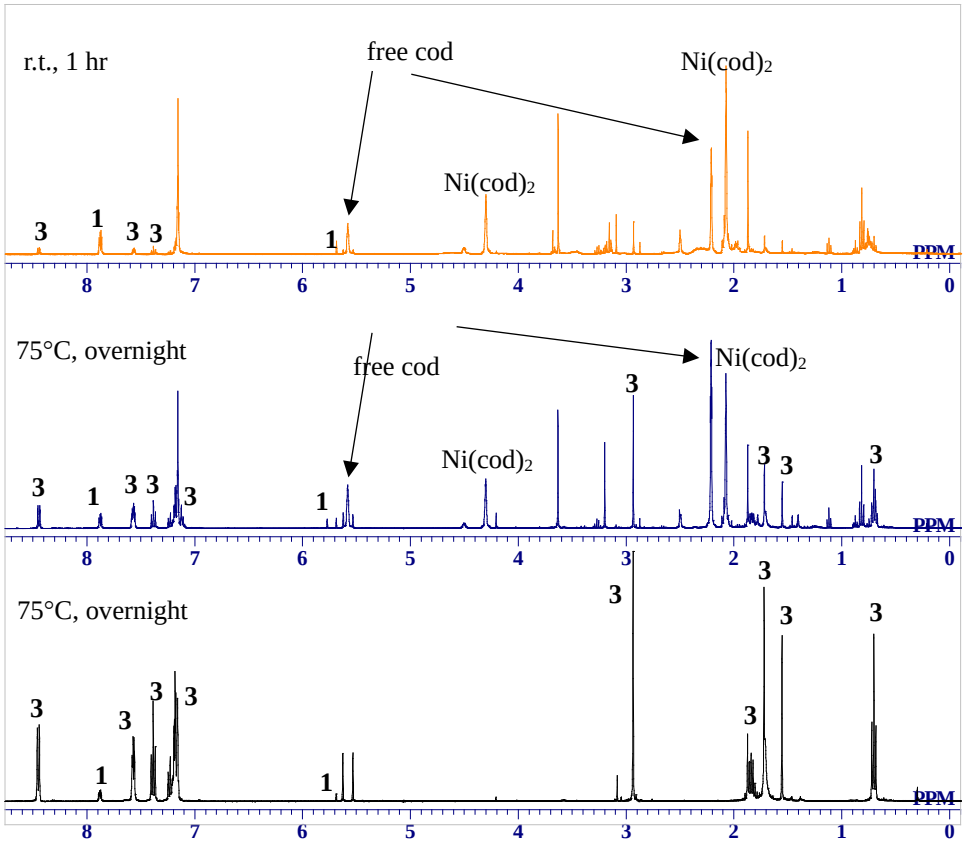


Figure S11. Monitoring the reaction of disilane **1** with 2 equiv. of $Ni(cod)_2$ and 4 equiv. of Me_2IM^{Et} by ^1H NMR spectrum in C_6D_6. (formation of unidentified product (marked as x) was confirmed as the minor product which may be the nickel(0) species bearing Me_2IM^{Et}.)

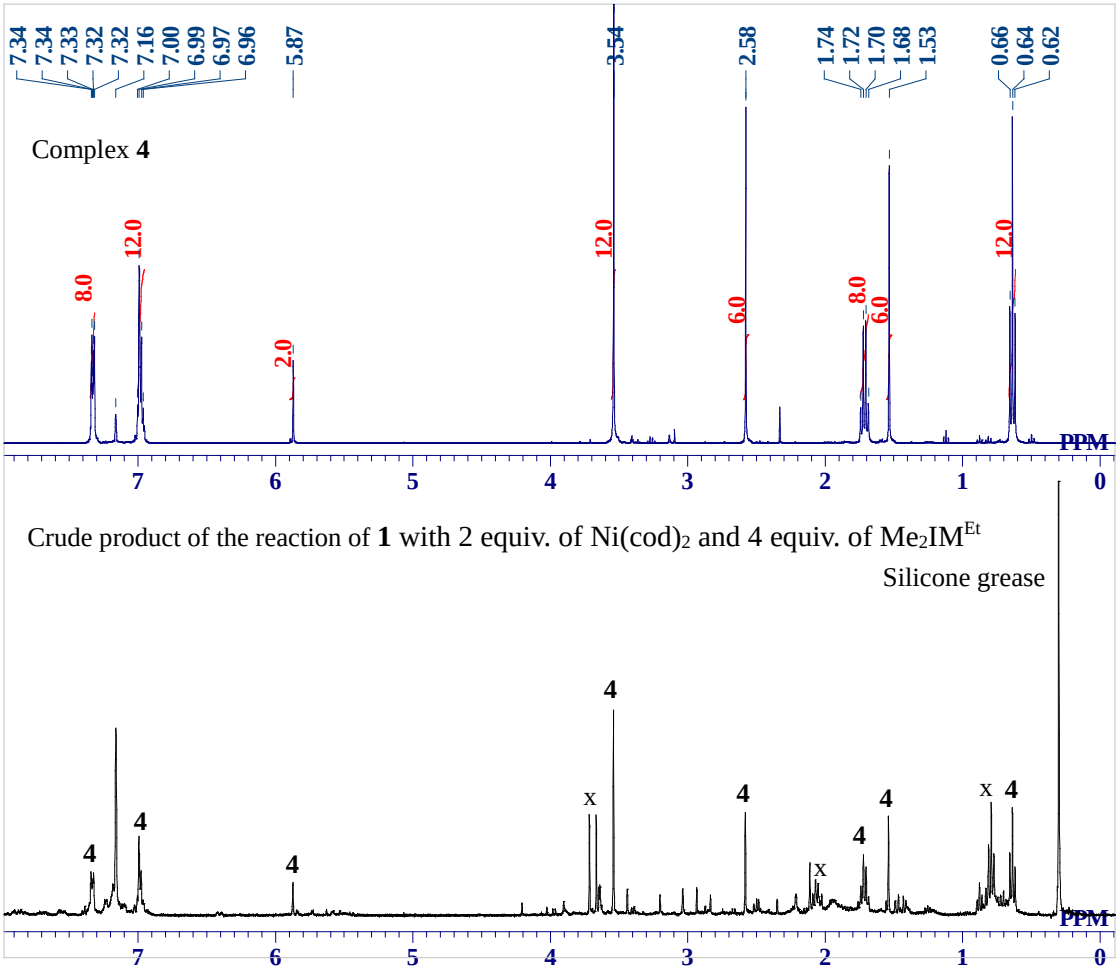
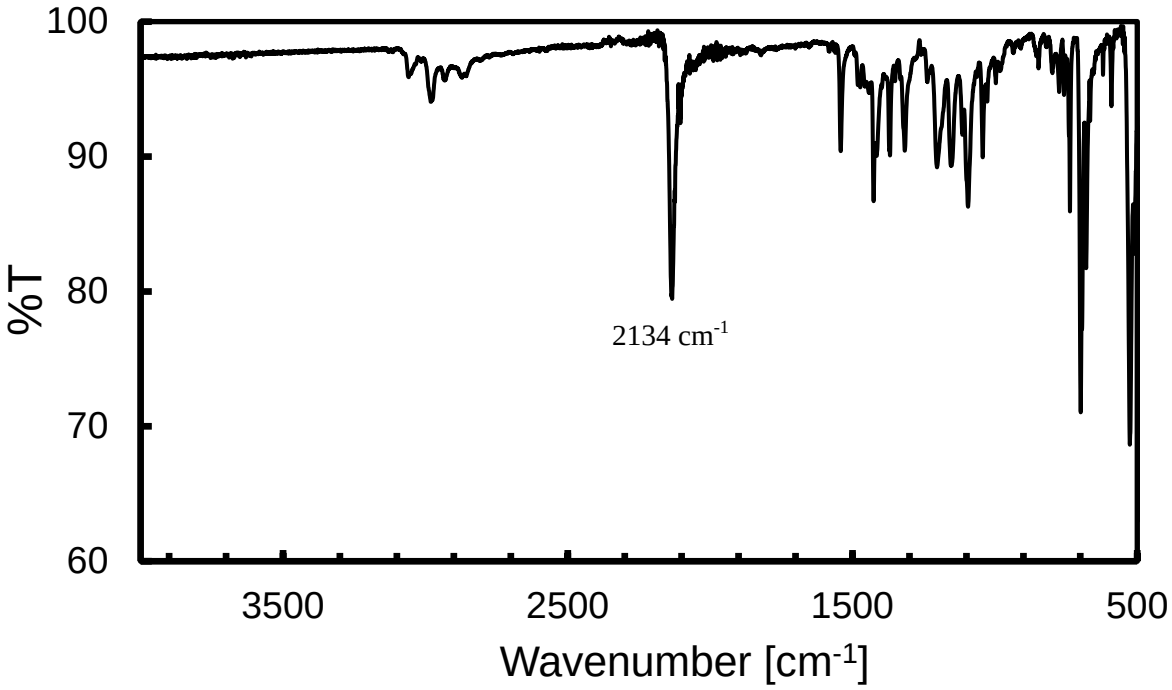


Figure S12. ATR-IR spectrum of **2** in the solid state.



Computational Details

All of the calculations were performed using the Gaussian 09 program.[4] Geometry optimization for compounds **1**, **2** and **3** was carried out by using the DFT method with the B3PW91[5] or M06[6] functional, and the selected bond distances for disilane **1** (actual disilane **1** and optimized $\mathbf{1}_{opt}$), complex **2** (actual complex **2** and optimized $\mathbf{2}_{opt}$) and **3** (actual complex **3** and optimized $\mathbf{3}_{opt}$) were summarized in Figure S13. The calculated values of Mayer bond index and Wiberg bond index are summarized in Table S-1, S-2, and S-3. Natural Bond Orbital (NBO) analyses were performed using the NBO 3.1 program implemented in Gaussian 09. The effective core potentials and the basis set by the Stuttgart–Dresden–Bonn group[7] and were used for Pd and Ni and the 6-31G** basis sets[8] were used for C, N, Si and hydrogen atoms.

Table S1. Calculated bond index (Mayer bond index and Wiberg bond index) for $\mathbf{1}_{opt}$.

	Mayer bond index		Wiberg bonx index	
	B3PW91	M06	B3PW91	M06
Si(1)-Si(2)	0.834	0.828	0.861	0.857
Si(1)-N(1)	0.443	0.443	0.379	0.351
Si(2)-N(2)	0.383	0.382	0.295	0.314
N(1)-N(2)	1.162	1.148	1.171	1.158

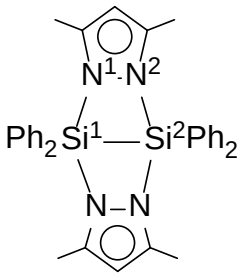


Table S2. Calculated bond index (Mayer bond index and Wiberg bond index) for $\mathbf{2}_{opt}$.

	Mayer bond index		Wiberg bonx index	
	B3PW91	M06	B3PW91	M06
Pd(1)-Pd(2)	0.350	0.250	0.356	0.328
Pd(1)-Si(1)	0.933	0.908	0.670	0.650
Pd(1)-N(4)	0.232	0.259	0.294	0.277
Pd(1)-C(1)	0.739	0.747	0.716	0.682
Si(1)-N(1)	0.583	0.600	0.473	0.474
N(1)-N(2)	1.145	1.123	1.170	1.166
Pd(1)-Si(2)	0.178	0.249	0.154	0.267

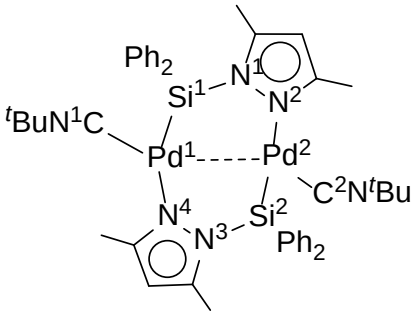


Table S3. Calculated bond index (Mayer bond index and Wiberg bond index) for $\mathbf{3}_{opt}$.

	Mayer bond index		Wiberg bonx index	
	B3PW91	M06	B3PW91	M06
Ni(1)-Si(1)	0.838	0.807	0.649	0.609
Ni(1)-Si(2)	0.978	0.937	0.703	0.661
Ni(1)-N(2)	0.536	0.566	0.372	0.346
Ni(1)-C(1)	0.833	0.831	0.541	0.520
Si(1)-N(1)	0.397	0.432	0.344	0.346
Si(1)-N(3)	0.268	0.286	0.262	0.229
Si(1)-C(2)	0.855	0.875	0.686	0.666
Si(1)-C(3)	0.846	0.877	0.674	0.665
N(1)-N(2)	1.181	1.162	1.194	1.179
N(3)-N(4)	1.163	1.151	1.160	1.152

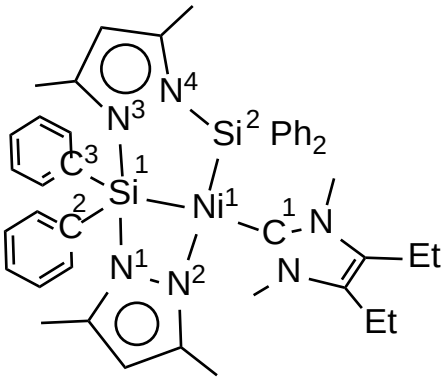


Figure S13-1. Selected bond distances (Å) in **1** from XRD (data with error) and the optimized structure $\mathbf{1}_{opt}$ (data in brackets) with B3PW91 (upper) and with M06 (lower). All hydrogen atoms were omitted for clarity. The blue balls are silicon atoms, the pale blue balls are nitrogen atoms, the grey ones are carbon atoms. The molecular structure of **1** was well reproduced by M06 functional. Calculation by B3PW91 also well reproduced the molecular structure of **1** except for the Si-N bond lengths.

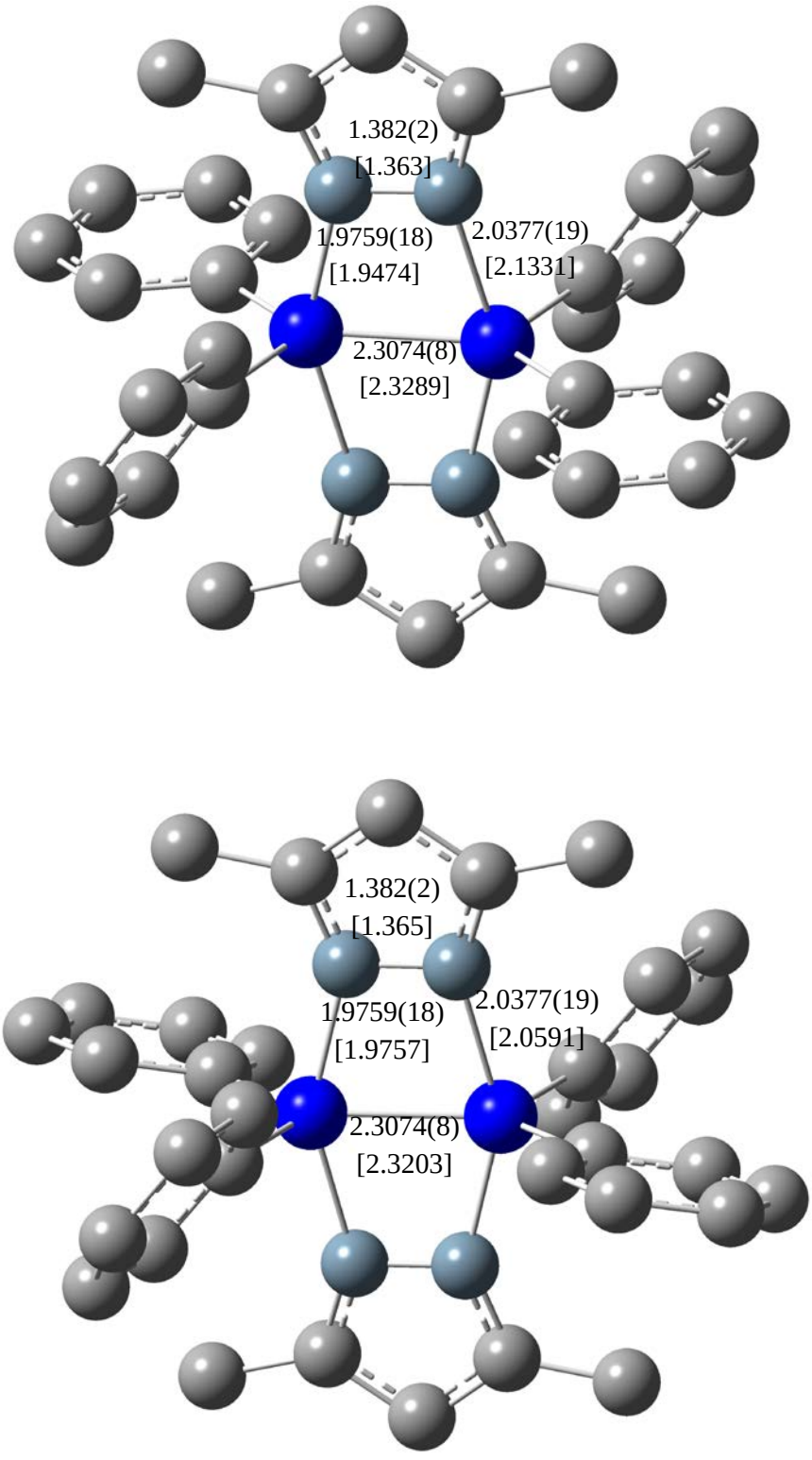


Figure S13-2. Selected bond distances (Å) in **2** from XRD (data with error) and the optimized structure $\mathbf{2}_{opt}$ (data in brackets) with B3PW91 (upper) and with M06 (lower). For clarity, only the *ipso*-carbon atoms of the Ph group are shown, and all hydrogen atoms were omitted. The orange balls palladium atoms, the blue balls are silicon atoms, the pale blue balls are nitrogen atoms, the grey ones are carbon atoms. The molecular structure of **2** was well reproduced by B3PW91 functional except for the Pd-C(isocyanide) bond length. In contrast, optimized structure obtained by the M06 functional slightly differs from the actual structure in terms of the angle between Pd-Pd axis and Pd-C axis.

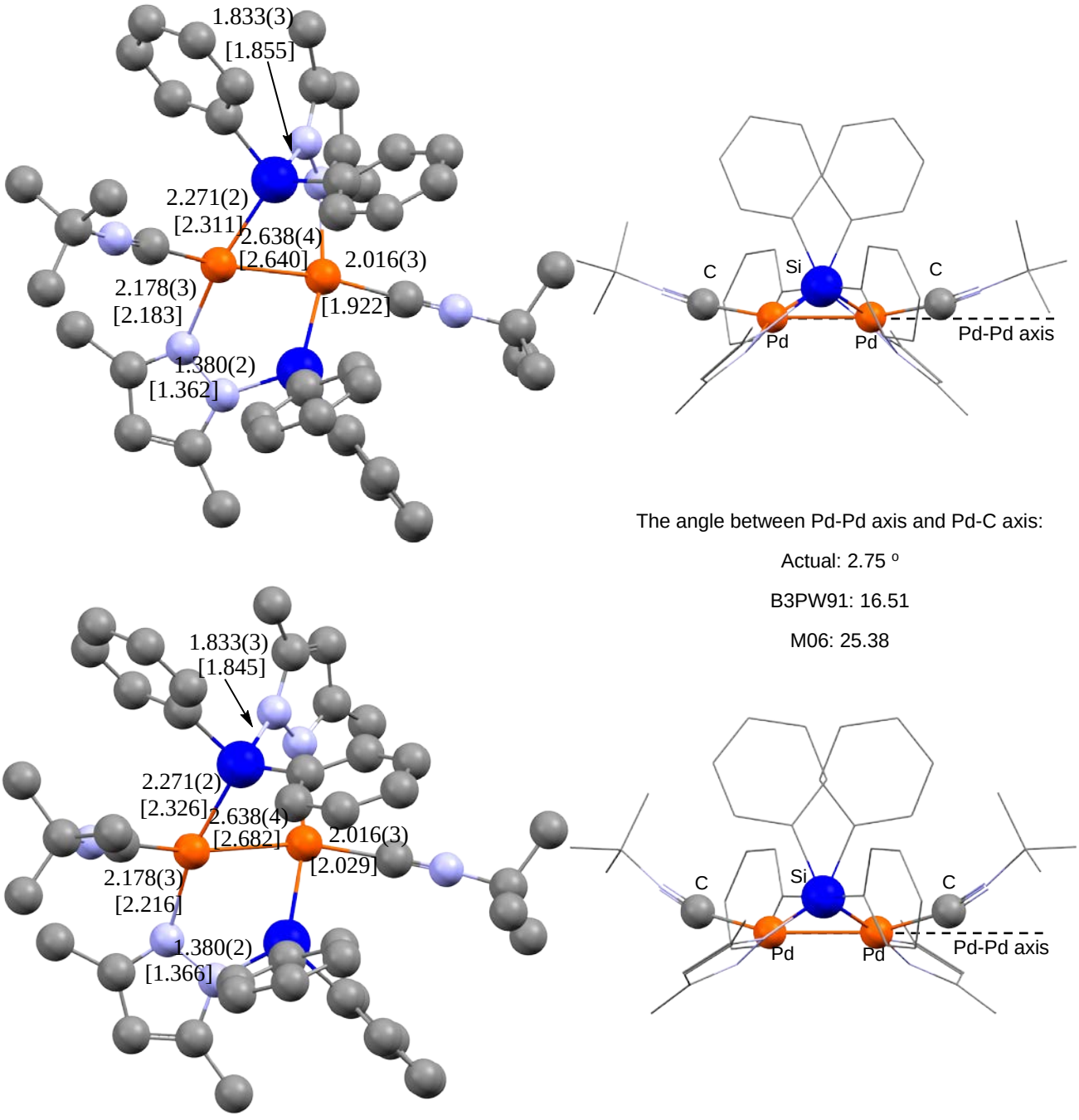


Figure S13-3. Selected bond distances (Å) in **3** from XRD (data with error) and the optimized structure $\mathbf{3}_{opt}$ (data in brackets) with B3PW91 (upper) and with M06 (lower). For clarity, only the *ipso*-carbon atoms of the Ph group are shown, and all hydrogen atoms were omitted. The orange ball is a nickel atom, the blue balls are silicon atoms, the pale blue balls are nitrogen atoms, the grey ones are carbon atoms.

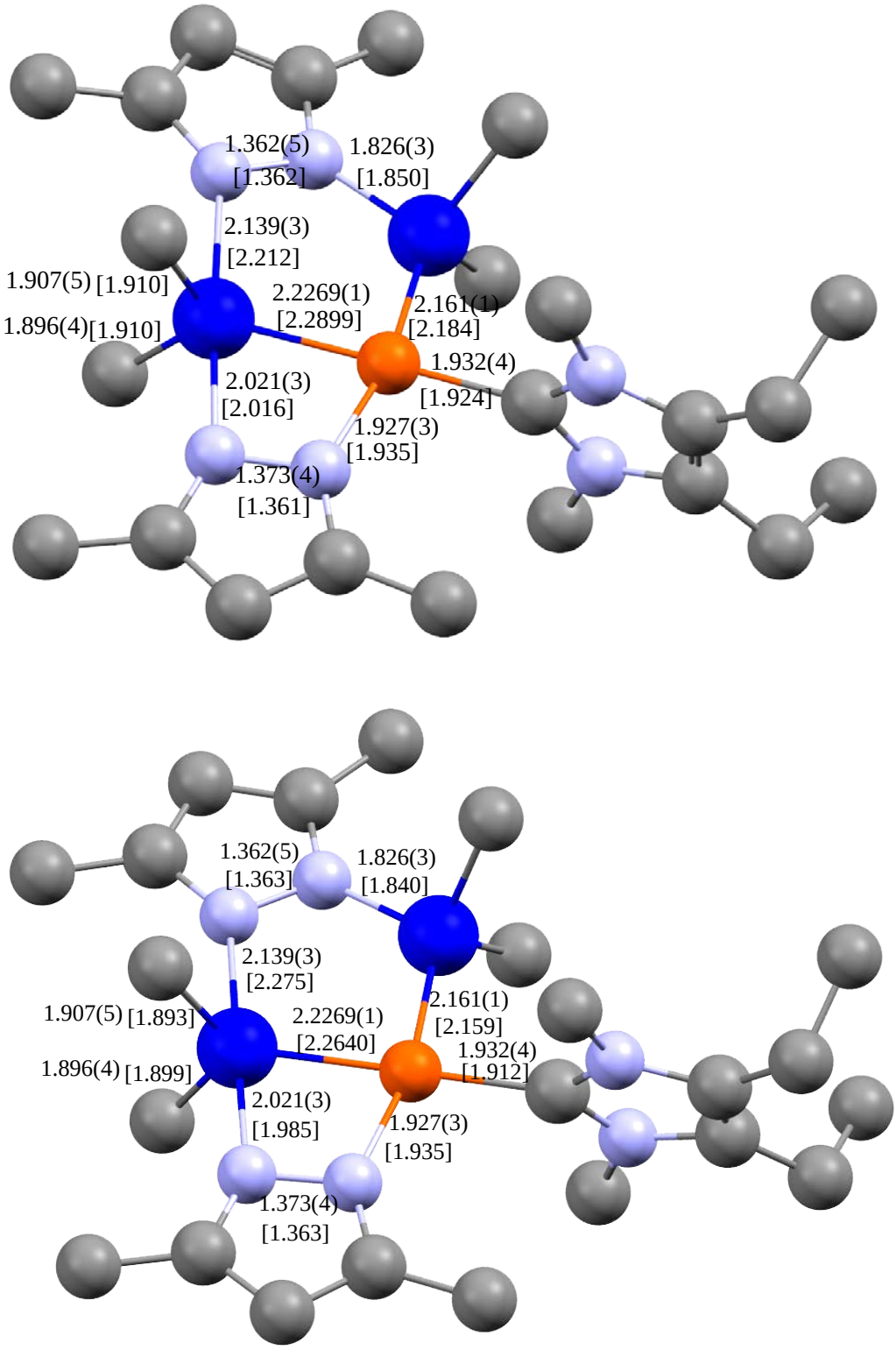
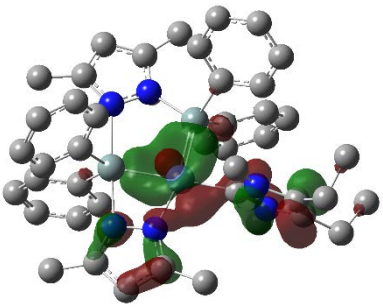
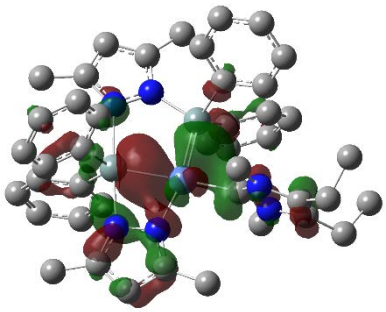


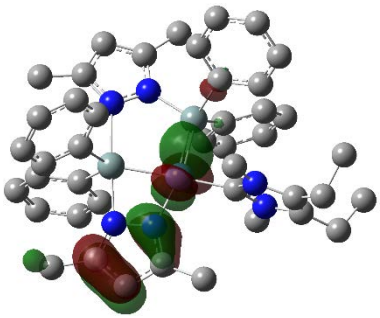
Figure S14-1. Selected orbital figures for $\mathbf{3}_{opt}$ depicted with the isovalue of 0.03 calculated by B3PW91 functionals.



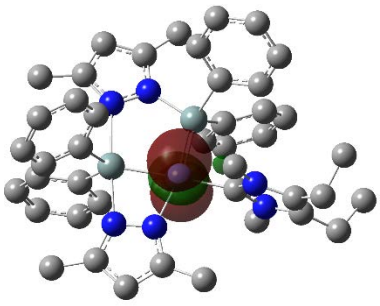
HOMO-3



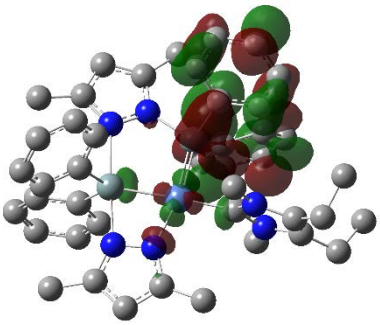
HOMO-2



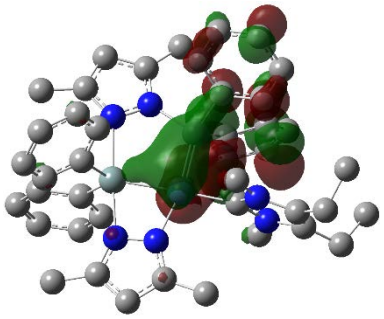
HOMO-1



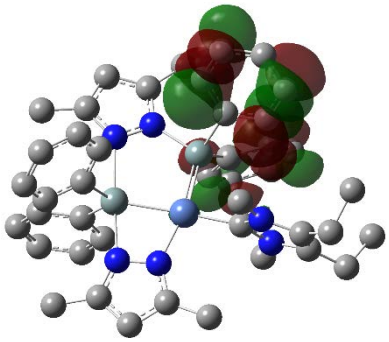
HOMO



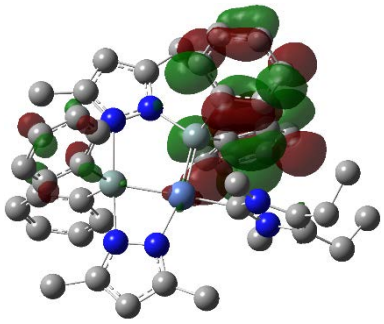
LUMO



LUMO+1

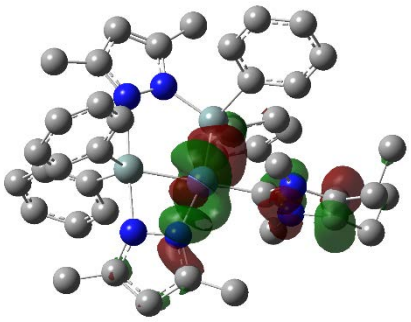


LUMO+2

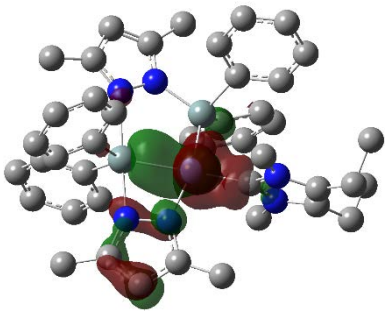


LUMO+3

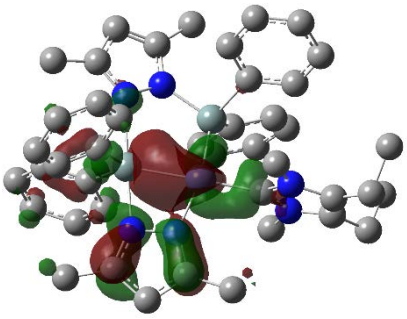
Figure S14-2. Selected orbital figures for $\mathbf{3}_{opt}$ depicted with the isovalue of 0.03 calculated by M06 functionals.



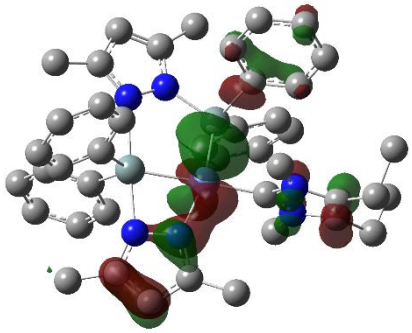
HOMO-3



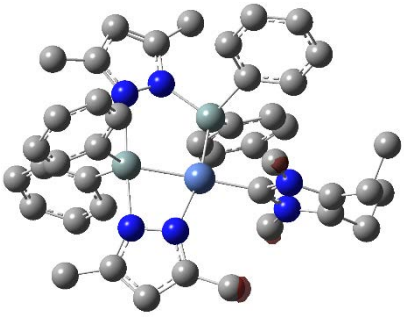
HOMO-2



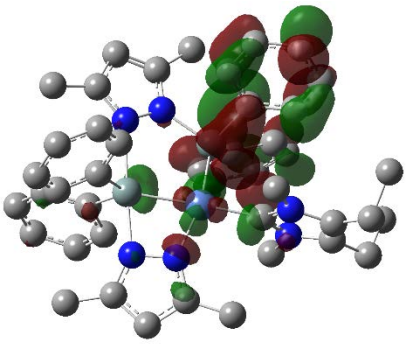
HOMO-1



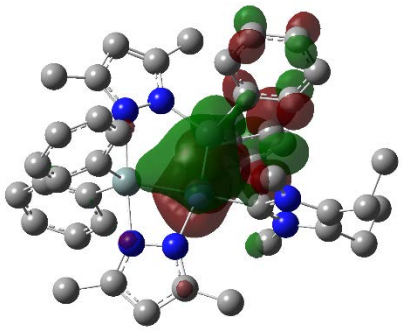
HOMO



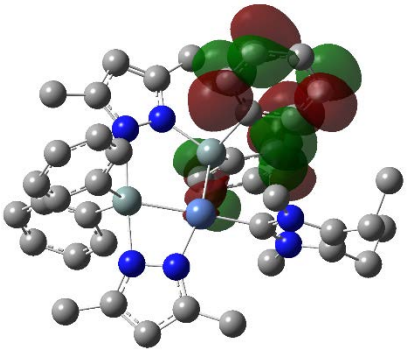
LUMO



LUMO+1



LUMO+2



LUMO+3

Table S3. The results of NBO analysis for Ni-Si(1) bond in $\mathbf{3}_{opt}$.

with B3PW91 functional

(38.75%) 0.6225*Ni 1 s(15.04%)p 3.47(52.16%)d 2.18(32.80%)
f 0.00(0.00%)
0.0004 0.3806 0.0745 0.0035 -0.0031
0.0002 0.0009 0.6442 0.0064 0.0097
-0.0002 -0.0005 -0.3234 -0.0143 0.0015
-0.0002 -0.0001 0.0397 -0.0005 0.0011
0.0000 -0.3065 -0.0496 -0.0108 0.0371
0.0018 0.0020 0.0314 -0.0113 0.0007
0.4718 0.0204 0.0105 0.0013 -0.0765
-0.0042 -0.0003 -0.0026 0.0009 0.0003
-0.0001 0.0030 -0.0020

(61.25%) 0.7826*Si 2 s(37.11%)p 1.69(62.78%)d 0.00(0.10%)
0.0000 0.0000 0.6084 -0.0316 -0.0001
-0.7896 0.0285 0.0001 -0.0173 0.0054
0.0000 -0.0563 -0.0015 -0.0083 0.0050
-0.0025 0.0236 -0.0196

with M06 functional

1. (1.66437) BD (1)Ni 1 -Si 2

(38.45%) 0.6201*Ni 1 s(14.50%)p 3.63(52.66%)d 2.27(32.84%)
f 0.00(0.00%)
0.0008 0.3718 0.0819 0.0028 -0.0015
0.0008 0.0009 0.6404 0.0055 0.0117
0.0000 -0.0004 -0.3403 -0.0161 0.0011
-0.0002 -0.0002 -0.0163 -0.0026 0.0015
-0.0001 -0.3208 -0.0462 -0.0107 -0.0152
-0.0095 -0.0009 -0.0609 0.0120 -0.0003
0.4626 0.0174 0.0079 -0.0028 -0.0683
-0.0045 0.0001 -0.0027 0.0010 0.0001
0.0000 0.0028 -0.0021

(61.55%) 0.7845*Si 2 s(36.67%)p 1.72(63.22%)d 0.00(0.12%)
0.0000 -0.0001 0.6045 -0.0346 0.0000
-0.7942 0.0253 0.0002 -0.0028 0.0031
0.0001 -0.0262 0.0019 -0.0104 -0.0001
-0.0022 0.0217 -0.0238

Table S-4. The DFT-optimized Geometry for complex $\mathbf{1}_{opt}$ (in XYZ format)

with B3PW91 functional

Si	-1.041200	0.420800	-0.307800	C	3.669000	2.067700	3.354500
N	-1.493200	-0.526700	1.332400	C	3.347800	2.593100	2.104600
N	-0.363400	-1.184000	1.720100	C	2.584100	1.847600	1.206200
C	-2.518600	-0.882600	2.133800	H	-2.598100	-2.300400	3.838600
C	-2.036200	-1.808300	3.055900	H	-4.549000	-0.686400	2.757300
C	-0.675800	-1.976200	2.756500	H	-3.895400	0.754200	1.953500
C	-3.897200	-0.339800	1.952100	H	-4.328900	-0.665900	0.999300
C	0.321100	-2.868700	3.421200	H	-0.145400	-3.817800	3.700700
C	-1.787100	2.110500	0.109400	H	1.158100	-3.087100	2.753300
C	-1.137700	2.977300	1.005400	H	0.717700	-2.419800	4.339600
C	-1.679000	4.219200	1.331400	H	-0.195100	2.681200	1.459700
C	-2.888100	4.626700	0.767900	H	-1.155900	4.870100	2.027400
C	-3.552400	3.781800	-0.118400	H	-3.310800	5.595600	1.021200
C	-3.006900	2.537500	-0.440700	H	-4.498300	4.087700	-0.558600
C	-2.112400	-0.563100	-1.531300	H	-3.545700	1.889000	-1.127800
C	-2.441500	-0.062000	-2.802000	H	-2.090000	0.920700	-3.098400
C	-3.213700	-0.796600	-3.700600	H	-3.456400	-0.377000	-4.673700
C	-3.669000	-2.067700	-3.354500	H	-4.267500	-2.644700	-4.054700
C	-3.347800	-2.593100	-2.104600	H	-3.693200	-3.585200	-1.825100
C	-2.584100	-1.847600	-1.206200	H	-2.348000	-2.277500	-0.236700
Si	1.041200	-0.420800	0.307800	H	2.598100	2.300400	-3.838600
N	1.493200	0.526700	-1.332400	H	4.549000	0.686400	-2.757300
N	0.363400	1.184000	-1.720100	H	3.895400	-0.754200	-1.953500
C	2.518600	0.882600	-2.133800	H	4.328900	0.665900	-0.999300
C	2.036200	1.808300	-3.055900	H	0.145400	3.817800	-3.700700
C	0.675800	1.976200	-2.756500	H	-1.158100	3.087100	-2.753300
C	3.897200	0.339800	-1.952100	H	-0.717700	2.419800	-4.339600
C	-0.321100	2.868700	-3.421200	H	0.195100	-2.681200	-1.459700
C	1.787100	-2.110500	-0.109400	H	1.155900	-4.870100	-2.027400
C	1.137700	-2.977300	-1.005400	H	3.310800	-5.595600	-1.021200
C	1.679000	-4.219200	-1.331400	H	4.498300	-4.087700	0.558600
C	2.888100	-4.626700	-0.767900	H	3.545700	-1.889000	1.127800
C	3.552400	-3.781800	0.118400	H	2.090000	-0.920700	3.098400
C	3.006900	-2.537500	0.440700	H	3.456400	0.377000	4.673700
C	2.112400	0.563100	1.531300	H	4.267500	2.644700	4.054700
C	2.441500	0.062000	2.802000	H	3.693200	3.585200	1.825100
C	3.213700	0.796600	3.700600	H	2.348000	2.277500	0.236700

with M06 functional

Si	-1.010600	0.456300	-0.341100	C	3.643800	2.030300	3.353800
N	-1.507000	-0.493400	1.318700	C	3.280200	2.575000	2.126600
N	-0.381300	-1.177700	1.676000	C	2.520100	1.828700	1.231000
C	-2.534900	-0.917300	2.073700	H	-2.638800	-2.461600	3.668200
C	-2.066200	-1.908400	2.932700	H	-4.564800	-0.696400	2.699100
C	-0.704100	-2.046100	2.644200	H	-3.897700	0.719000	1.852300
C	-3.907300	-0.376800	1.885800	H	-4.340600	-0.727500	0.939500
C	0.302200	-2.960500	3.249600	H	-0.178200	-3.871800	3.618700
C	-1.763900	2.139200	0.048100	H	1.064100	-3.245900	2.513700
C	-1.000400	3.136000	0.670500	H	0.812500	-2.492500	4.101400
C	-1.542500	4.383200	0.960300	H	0.038300	2.933800	0.937200
C	-2.866000	4.662400	0.630400	H	-0.930700	5.140900	1.445800
C	-3.643000	3.686900	0.014700	H	-3.290500	5.639200	0.852900
C	-3.094700	2.438500	-0.270700	H	-4.677900	3.898400	-0.247500
C	-2.092000	-0.528500	-1.540300	H	-3.713400	1.686000	-0.762400
C	-2.468200	-0.005000	-2.784500	H	-2.160200	1.003800	-3.060400
C	-3.238900	-0.739800	-3.679900	H	-3.522400	-0.304800	-4.636200
C	-3.643800	-2.030300	-3.353800	H	-4.242300	-2.609300	-4.053800
C	-3.280200	-2.575000	-2.126600	H	-3.593000	-3.583400	-1.862900
C	-2.520100	-1.828700	-1.231000	H	-2.256000	-2.269900	-0.268100
Si	1.010600	-0.456300	0.341100	H	2.638800	2.461600	-3.668200
N	1.507000	0.493400	-1.318700	H	4.564800	0.696400	-2.699100
N	0.381300	1.177700	-1.676000	H	3.897700	-0.719000	-1.852300
C	2.534900	0.917300	-2.073700	H	4.340600	0.727500	-0.939500
C	2.066200	1.908400	-2.932700	H	0.178200	3.871800	-3.618700
C	0.704100	2.046100	-2.644200	H	-1.064100	3.245900	-2.513700
C	3.907300	0.376800	-1.885800	H	-0.812500	2.492500	-4.101400
C	-0.302200	2.960500	-3.249600	H	-0.038300	-2.933800	-0.937200
C	1.763900	-2.139200	-0.048100	H	0.930700	-5.140900	-1.445800
C	1.000400	-3.136000	-0.670500	H	3.290500	-5.639200	-0.852900
C	1.542500	-4.383200	-0.960300	H	4.677900	-3.898400	0.247500
C	2.866000	-4.662400	-0.630400	H	3.713400	-1.686000	0.762400
C	3.643000	-3.686900	-0.014700	H	2.160200	-1.003800	3.060400
C	3.094700	-2.438500	0.270700	H	3.522400	0.304800	4.636200
C	2.092000	0.528500	1.540300	H	4.242300	2.609300	4.053800
C	2.468200	0.005000	2.784500	H	3.593000	3.583400	1.862900
C	3.238900	0.739800	3.679900	H	2.256000	2.269900	0.268100

Table S-5. The DFT-optimized Geometry for complex $\mathbf{2}_{\mathbf{opt}}$ (in XYZ format)

with B3PW91 functional

Pd	-1.104100	-0.723500	-0.767700	C	0.436300	3.459600	-2.457900
Si	1.689100	-1.368600	0.020500	C	-0.567700	4.443000	-2.388600
N	-0.099100	-2.437200	-1.671900	C	-1.527200	3.953400	-1.516500
N	1.104500	-2.724500	-1.102700	C	1.695500	3.452100	-3.258900
N	-3.867500	-2.086700	-0.073800	C	-2.793800	4.608400	-1.074200
C	-2.877800	-1.565000	-0.431900	C	-1.201200	1.984000	1.751300
C	-5.086900	-2.669300	0.412700	C	-0.694000	3.273900	1.981600
C	-4.829500	-4.158100	0.683300	C	-0.391100	3.716400	3.269400
C	-5.480800	-1.938900	1.704200	C	-0.593900	2.876100	4.363500
C	-6.165400	-2.486700	-0.664400	C	-1.088700	1.588400	4.158000
C	-0.436100	-3.459300	-2.458400	C	-1.379300	1.148400	2.867000
C	0.567600	-4.443000	-2.388500	C	-3.584800	1.641100	-0.082400
C	1.526900	-3.953400	-1.516200	C	-4.254400	1.410900	-1.298000
C	-1.694700	-3.451400	-3.260300	C	-5.630200	1.599700	-1.421900
C	2.793400	-4.608600	-1.073500	C	-6.381200	2.007000	-0.316600
C	1.201200	-1.984100	1.751200	C	-5.743100	2.224200	0.903200
C	0.693400	-3.273800	1.981300	C	-4.361300	2.046900	1.013600
C	0.390500	-3.716500	3.269100	H	-5.743900	-4.626100	1.060300
C	0.593700	-2.876500	4.363300	H	-4.527400	-4.673500	-0.232700
C	1.089000	-1.588900	4.158100	H	-4.039600	-4.284900	1.428800
C	1.379700	-1.148800	2.867100	H	-6.413900	-2.359300	2.092100
C	3.584700	-1.641100	-0.082500	H	-4.704100	-2.055500	2.465100
C	4.254200	-1.411000	-1.298200	H	-5.626000	-0.872300	1.514800
C	5.630000	-1.599900	-1.422200	H	-7.106900	-2.922900	-0.316800
C	6.381100	-2.007100	-0.317000	H	-6.324500	-1.425200	-0.870800
C	5.743100	-2.224200	0.902900	H	-5.874200	-2.985100	-1.593400
C	4.361400	-2.046800	1.013400	H	0.598700	-5.388900	-2.911500
Pd	1.104100	0.723600	-0.767400	H	-2.328400	-4.311200	-3.016900
Si	-1.689200	1.368600	0.020500	H	-2.258300	-2.536500	-3.064200
N	0.099300	2.437600	-1.671400	H	-1.476800	-3.498200	-4.333000
N	-1.104600	2.724700	-1.102500	H	2.784700	-5.656200	-1.385100
N	3.867600	2.086700	-0.073600	H	3.675800	-4.127800	-1.505900
C	2.877800	1.565000	-0.431500	H	2.910100	-4.574300	0.013300
C	5.087100	2.669200	0.412800	H	0.525700	-3.941800	1.139600
C	4.829600	4.157800	0.684400	H	-0.000400	-4.720400	3.418600
C	5.481800	1.938000	1.703600	H	0.364400	-3.221300	5.368600
C	6.165200	2.487400	-0.664900	H	1.240600	-0.921700	5.002900

H	1.739000	-0.132000	2.724700	H	2.331300	4.309100	-3.011200
H	3.684700	-1.079300	-2.165000	H	2.256600	2.534800	-3.066600
H	6.117900	-1.429700	-2.379300	H	1.478400	3.504400	-4.331500
H	7.454300	-2.155100	-0.408700	H	-2.785400	5.655900	-1.386400
H	6.318800	-2.543500	1.768700	H	-3.676100	4.127200	-1.506500
H	3.878600	-2.237600	1.969000	H	-2.910600	4.574700	0.012600
H	5.744000	4.625700	1.061200	H	-0.526700	3.942100	1.140000
H	4.527100	4.673700	-0.231200	H	-0.000700	4.720400	3.419100
H	4.040000	4.284000	1.430200	H	-0.364600	3.220800	5.368800
H	6.414900	2.358400	2.091400	H	-1.239900	0.920900	5.002700
H	4.705400	2.054100	2.464900	H	-1.738100	0.131500	2.724400
H	5.627100	0.871600	1.513500	H	-3.685100	1.079000	-2.164900
H	7.106700	2.923500	-0.317500	H	-6.118200	1.429400	-2.378900
H	6.324400	1.426000	-0.871900	H	-7.454400	2.155000	-0.408200
H	5.873400	2.986200	-1.593500	H	-6.318700	2.543600	1.769000
H	-0.598800	5.388800	-2.911800	H	-3.878400	2.237800	1.969000

with M06 functional

Pd	-1.083300	-0.790400	-1.068000	C	3.542500	-1.515500	-0.188800
Si	1.646900	-1.296400	-0.209600	C	4.250100	-1.357900	-1.390700
N	-0.047300	-2.596200	-1.827000	C	5.623300	-1.566600	-1.458100
N	1.168800	-2.758700	-1.227300	C	6.330300	-1.920600	-0.309200
N	-3.783500	-2.034200	0.044300	C	5.654000	-2.057300	0.899100
C	-2.867400	-1.613000	-0.559000	C	4.274500	-1.860100	0.953300
C	-4.844300	-2.420100	0.939500	Pd	1.083200	0.790400	-1.068000
C	-4.880800	-3.943700	0.994700	Si	-1.647000	1.296400	-0.209600
C	-4.519700	-1.829400	2.309500	N	0.047200	2.596100	-1.827100
C	-6.152900	-1.853900	0.399700	N	-1.169000	2.758600	-1.227500
C	-0.409800	-3.773400	-2.328000	N	3.783300	2.034200	0.044300
C	0.589400	-4.724600	-2.057100	C	2.867100	1.613100	-0.558800
C	1.569400	-4.054600	-1.347100	C	4.844400	2.420100	0.939300
C	-1.714100	-3.940900	-3.023200	C	4.881200	3.943600	0.994300
C	2.833500	-4.593400	-0.777400	C	4.520200	1.829500	2.309400
C	1.043300	-1.770900	1.519500	C	6.152800	1.853700	0.399100
C	0.210300	-2.875500	1.750800	C	0.409700	3.773400	-2.328000
C	-0.229200	-3.190400	3.033900	C	-0.589400	4.724500	-2.057000
C	0.166500	-2.412200	4.119100	C	-1.569500	4.054500	-1.347200
C	0.992400	-1.311300	3.910600	C	1.714100	3.940900	-3.023200
C	1.410100	-0.989900	2.623000	C	-2.833700	4.593300	-0.777500

C	-1.043300	1.771000	1.519400	H	2.028800	-0.101200	2.470100
C	-0.210200	2.875700	1.750400	H	3.705300	-1.073600	-2.293600
C	0.229500	3.190600	3.033400	H	6.145600	-1.453000	-2.406300
C	-0.166000	2.412600	4.118800	H	7.404700	-2.086100	-0.357700
C	-0.991900	1.311700	3.910600	H	6.199300	-2.333100	1.800100
C	-1.409900	0.990100	2.623100	H	3.754500	-2.004500	1.901500
C	-3.542600	1.515500	-0.188700	H	5.681700	4.269700	1.668500
C	-4.250200	1.357800	-1.390600	H	5.069800	4.364200	0.000100
C	-5.623400	1.566400	-1.457900	H	3.928400	4.339500	1.364900
C	-6.330400	1.920600	-0.309100	H	5.298600	2.114900	3.027000
C	-5.654100	2.057500	0.899200	H	3.552400	2.199100	2.671000
C	-4.274500	1.860300	0.953400	H	4.478900	0.734600	2.250600
H	-5.681000	-4.269800	1.669100	H	6.975800	2.140800	1.064200
H	-5.069600	-4.364300	0.000500	H	6.108300	0.759200	0.343600
H	-3.927800	-4.339300	1.365000	H	6.360800	2.246800	-0.602300
H	-5.297900	-2.114900	3.027400	H	-0.606100	5.767300	-2.350300
H	-3.551700	-2.198700	2.670800	H	1.627700	4.624700	-3.874000
H	-4.478700	-0.734500	2.250700	H	2.474200	4.348800	-2.343800
H	-6.975700	-2.141100	1.065000	H	2.077600	2.972700	-3.382500
H	-6.108500	-0.759400	0.344300	H	-2.896800	5.665800	-0.984800
H	-6.361100	-2.247000	-0.601700	H	-3.721500	4.107200	-1.199200
H	0.606100	-5.767300	-2.350400	H	-2.878800	4.455300	0.310000
H	-1.627700	-4.624800	-3.874100	H	0.100300	3.500400	0.910700
H	-2.474300	-4.348800	-2.343900	H	0.875400	4.053700	3.188600
H	-2.077600	-2.972800	-3.382500	H	0.166600	2.664800	5.123900
H	2.896600	-5.665900	-0.984600	H	-1.298200	0.690800	4.750900
H	3.721400	-4.107500	-1.199100	H	-2.028600	0.101400	2.470400
H	2.878600	-4.455400	0.310200	H	-3.705400	1.073300	-2.293400
H	-0.100400	-3.500400	0.911200	H	-6.145800	1.452800	-2.406100
H	-0.875000	-4.053500	3.189300	H	-7.404800	2.086200	-0.357600
H	-0.165800	-2.664500	5.124300	H	-6.199300	2.333400	1.800200
H	1.298800	-0.690400	4.750800	H	-3.754500	2.004900	1.901600

Table S-6. The DFT-optimized Geometry for complex $\mathbf{3}_{\mathbf{opt}}$ (in XYZ format)

with B3PW91 functional

Ni	-0.147000	0.806700	-0.102400	C	-2.604100	-3.021200	-3.938000
Si	2.101200	0.397000	0.043500	C	-1.273600	-2.601100	-3.921000
Si	-0.589500	-1.329200	0.008300	C	-0.702900	-2.135500	-2.737400
N	1.998300	2.372700	-0.344200	C	3.245300	0.099500	-1.457100
N	0.652200	2.561800	-0.268800	C	2.673900	0.124900	-2.740900
N	2.102100	-1.785500	0.405900	C	3.442200	-0.052700	-3.890600
N	0.920800	-2.393700	0.104500	C	4.818600	-0.250900	-3.787100
N	-2.892700	1.358200	-1.153300	C	5.413200	-0.264000	-2.527100
N	-2.725600	1.717900	0.951600	C	4.633600	-0.092100	-1.380900
C	2.595100	3.524000	-0.702400	C	2.984200	0.624800	1.721200
C	1.597700	4.492700	-0.847000	C	4.175800	1.349400	1.883400
C	0.390400	3.848600	-0.567100	C	4.759000	1.529600	3.138700
C	4.069600	3.670200	-0.887200	C	4.149200	1.001600	4.275100
C	-0.987400	4.425900	-0.573900	C	2.957000	0.290200	4.143500
C	1.074100	-3.746500	0.137800	C	2.390700	0.103000	2.883500
C	2.390700	-4.003800	0.477100	H	1.734900	5.530200	-1.120900
C	3.002200	-2.749500	0.637700	H	4.281900	4.462300	-1.610900
C	-0.023600	-4.715800	-0.150100	H	4.569700	3.940200	0.050500
C	4.426700	-2.490600	1.000400	H	4.516500	2.743700	-1.257300
C	-2.013100	1.276700	-0.119300	H	-0.954500	5.468300	-0.901200
C	-4.022300	2.085100	0.598500	H	-1.654400	3.880200	-1.248200
C	-4.129800	1.853900	-0.743900	H	-1.442000	4.403500	0.422400
C	-5.023600	2.622600	1.569000	H	2.853400	-4.974600	0.591800
C	-5.761500	1.555600	2.389700	H	0.314100	-5.727700	0.086400
C	-5.291400	2.025900	-1.667400	H	-0.918400	-4.505200	0.442500
C	-6.076100	0.733700	-1.935800	H	-0.315800	-4.687200	-1.204300
C	-2.524900	1.061100	-2.525100	H	4.797300	-3.296500	1.640500
C	-2.148100	1.832100	2.277600	H	5.059400	-2.456800	0.107200
C	-1.548700	-1.898800	1.564900	H	4.538700	-1.545700	1.534800
C	-0.907000	-2.576600	2.617200	H	-5.755700	3.215400	1.009600
C	-1.586200	-2.937100	3.781300	H	-4.528500	3.327200	2.248900
C	-2.938600	-2.635100	3.926200	H	-6.469600	2.023000	3.081400
C	-3.599600	-1.958700	2.901500	H	-6.321400	0.879800	1.736200
C	-2.909700	-1.587500	1.747100	H	-5.067900	0.948800	2.978800
C	-1.435200	-2.080200	-1.536500	H	-4.944900	2.447700	-2.619200
C	-2.766500	-2.524300	-1.576400	H	-5.965100	2.775500	-1.237600
C	-3.347800	-2.985400	-2.759400	H	-6.902200	0.919400	-2.629700

H	-5.439000	-0.042200	-2.370300	H	-4.379300	-3.330400	-2.756300
H	-6.494900	0.334500	-1.007200	H	-3.053000	-3.383700	-4.859300
H	-3.122300	0.239500	-2.927300	H	-0.678800	-2.638300	-4.830600
H	-2.644800	1.947700	-3.155800	H	0.337800	-1.817900	-2.744900
H	-1.476800	0.762500	-2.525500	H	1.604100	0.301400	-2.840000
H	-2.175900	2.869500	2.625100	H	2.967800	-0.029200	-4.869000
H	-2.673000	1.191000	2.990300	H	5.422700	-0.387000	-4.680400
H	-1.107500	1.509100	2.209900	H	6.487500	-0.406200	-2.433600
H	0.144800	-2.836500	2.525500	H	5.123700	-0.100300	-0.411300
H	-1.057300	-3.461200	4.573600	H	4.666000	1.782500	1.016400
H	-3.472900	-2.923500	4.827700	H	5.688400	2.087300	3.228600
H	-4.656600	-1.722300	2.999400	H	4.597900	1.144800	5.254900
H	-3.447600	-1.039600	0.976600	H	2.469200	-0.122800	5.023400
H	-3.359600	-2.534100	-0.666000	H	1.466200	-0.464000	2.798000

with M06 functional

Ni	-0.142600	0.842300	0.136600	C	-5.710300	0.806000	2.576600
Si	2.075100	0.387200	0.160100	C	-5.280700	2.026800	-1.347000
Si	-0.596400	-1.241000	-0.203600	C	-5.814200	0.691500	-1.866900
N	2.016200	2.367300	0.034800	C	-2.412800	1.570000	-2.251200
N	0.690500	2.583900	0.265200	C	-2.246000	1.299000	2.612800
N	2.024600	-1.882400	0.303800	C	-1.668200	-2.001000	1.173200
N	0.853800	-2.372800	-0.193200	C	-1.046900	-2.688200	2.228200
N	-2.851900	1.514100	-0.870600	C	-1.768000	-3.148000	3.326100
N	-2.768400	1.469100	1.271000	C	-3.143000	-2.944900	3.391900
C	2.602900	3.521100	-0.322300	C	-3.784200	-2.266000	2.359500
C	1.627000	4.520100	-0.306100	C	-3.051800	-1.784700	1.276800
C	0.438200	3.885400	0.061700	C	-1.326500	-1.617900	-1.918300
C	4.052200	3.612100	-0.646100	C	-2.657800	-1.970800	-2.172800
C	-0.930400	4.448200	0.227600	C	-3.132100	-2.125100	-3.474500
C	0.933400	-3.723000	-0.327700	C	-2.276400	-1.938000	-4.556000
C	2.188700	-4.108200	0.098900	C	-0.942400	-1.608900	-4.326800
C	2.840300	-2.924300	0.485200	C	-0.479000	-1.449500	-3.025200
C	-0.193200	-4.550300	-0.834400	C	3.142900	0.225800	-1.400500
C	4.229500	-2.798200	1.006300	C	2.605500	0.691200	-2.609300
C	-2.002900	1.284500	0.164000	C	3.338400	0.662100	-3.791400
C	-4.078100	1.819400	0.938000	C	4.642900	0.175300	-3.787700
C	-4.131200	1.844000	-0.421600	C	5.201500	-0.281800	-2.598500
C	-5.143100	2.074500	1.945500	C	4.455000	-0.259000	-1.422600

C	3.058700	0.365600	1.777800	H	-5.035100	0.130000	-2.398400
C	4.345900	0.906800	1.881400	H	-6.152600	0.065200	-1.032500
C	5.051700	0.874500	3.081700	H	-2.637700	2.552600	-2.682600
C	4.469400	0.315900	4.215200	H	-1.328700	1.421100	-2.259900
C	3.180500	-0.205900	4.140900	H	-2.880300	0.784500	-2.856900
C	2.488800	-0.182500	2.934000	H	-2.556300	2.130400	3.254800
H	1.769000	5.571700	-0.526600	H	-2.580600	0.348000	3.049000
H	4.269800	4.546700	-1.172200	H	-1.152500	1.289000	2.547000
H	4.669000	3.588900	0.261600	H	0.028100	-2.873600	2.185900
H	4.367800	2.775700	-1.283500	H	-1.255500	-3.674300	4.129100
H	-0.923200	5.533400	0.087300	H	-3.713000	-3.314900	4.241500
H	-1.635800	4.016200	-0.495800	H	-4.861100	-2.109400	2.398400
H	-1.329400	4.236200	1.227600	H	-3.578400	-1.219600	0.503300
H	2.588000	-5.115200	0.125800	H	-3.341800	-2.148700	-1.342900
H	0.080000	-5.609000	-0.805000	H	-4.171700	-2.402500	-3.643100
H	-1.099500	-4.412300	-0.230300	H	-2.644700	-2.059400	-5.572600
H	-0.451100	-4.287000	-1.867500	H	-0.260200	-1.475400	-5.164300
H	4.490300	-3.681000	1.599600	H	0.569800	-1.188900	-2.863600
H	4.954400	-2.733200	0.184900	H	1.592800	1.103000	-2.616900
H	4.347400	-1.909500	1.634500	H	2.896300	1.029800	-4.715900
H	-5.949700	2.634200	1.454200	H	5.223700	0.157900	-4.707700
H	-4.757600	2.740800	2.730700	H	6.224400	-0.653800	-2.584900
H	-6.488600	1.041500	3.310000	H	4.914200	-0.603300	-0.495800
H	-6.150100	0.157800	1.808400	H	4.819100	1.346300	1.001300
H	-4.929500	0.227600	3.084500	H	6.057700	1.287300	3.133000
H	-4.990900	2.668400	-2.191500	H	5.017100	0.289900	5.155100
H	-6.078600	2.565800	-0.819900	H	2.716800	-0.638100	5.026000
H	-6.655500	0.834600	-2.553100	H	1.487100	-0.614200	2.878200

X-ray data collection and reduction

X-ray crystallography for compounds **1**, **3** and **4** was performed on a Rigaku Saturn CCD area detector with graphite monochromated Mo-Kα radiation (λ=0.71075 Å), and single crystals of **2** suitable for X-ray crystallography were analyzed by synchrotron radiation at beam line BL02B1 (λ=0.41170 Å) of Spring-8 (Hyogo, Japan) using PILATUS3 X CdTe 1M detector. The data were collected at 183(2) K for **1**, **3** and **4** and 100(1) K for **2** using ω scan in the θ range of $3.01 \leq \theta \leq 27.48$ deg (**1**), $2.54 \leq \theta \leq 11.90$ deg (**2**), $3.01 \leq \theta \leq 27.45$ deg (**3**), $3.01 \leq \theta \leq 27.45$ deg (**4**). The data obtained were processed using Crystal-Clear (Rigaku) on a Pentium computer, and were corrected for Lorentz and polarization effects. The structures were solved by direct methods[9], and expanded using Fourier techniques. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 3,277 observed reflections and 181 variable parameters for **1**, 5,542 observed reflections and 244 variable parameters for **2**, 9,151 observed reflections and 469 variable parameters for **3**, 5,688 observed reflections and 286 variable parameters for **4**. Neutral atom scattering factors were taken from International Tables for Crystallography (IT), Vol. C, Table 6.1.1.4[10]. Anomalous dispersion effects were included in Fcalc[11]; the values for Δf' and Δf" were those of Creagh and McAuley[12]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[13]. All calculations were performed using the CrystalStructure[14] crystallographic software package except for refinement, which was performed using SHELXL Version 2017/1[15]. Details of final refinement as well as the bond lengths and angle are summarized in Tables S7, S8, S9 and S10, and the numbering scheme employed is also shown in Figures S15, 16, 17 and 18, which were drawn with ORTEP at 50% probability ellipsoids. CCDC 1990818 (**1**), 1990819 (**2**), 1990820 (**3**) and 1990821 (**4**) contain the supplementary crystallographic data for this paper.

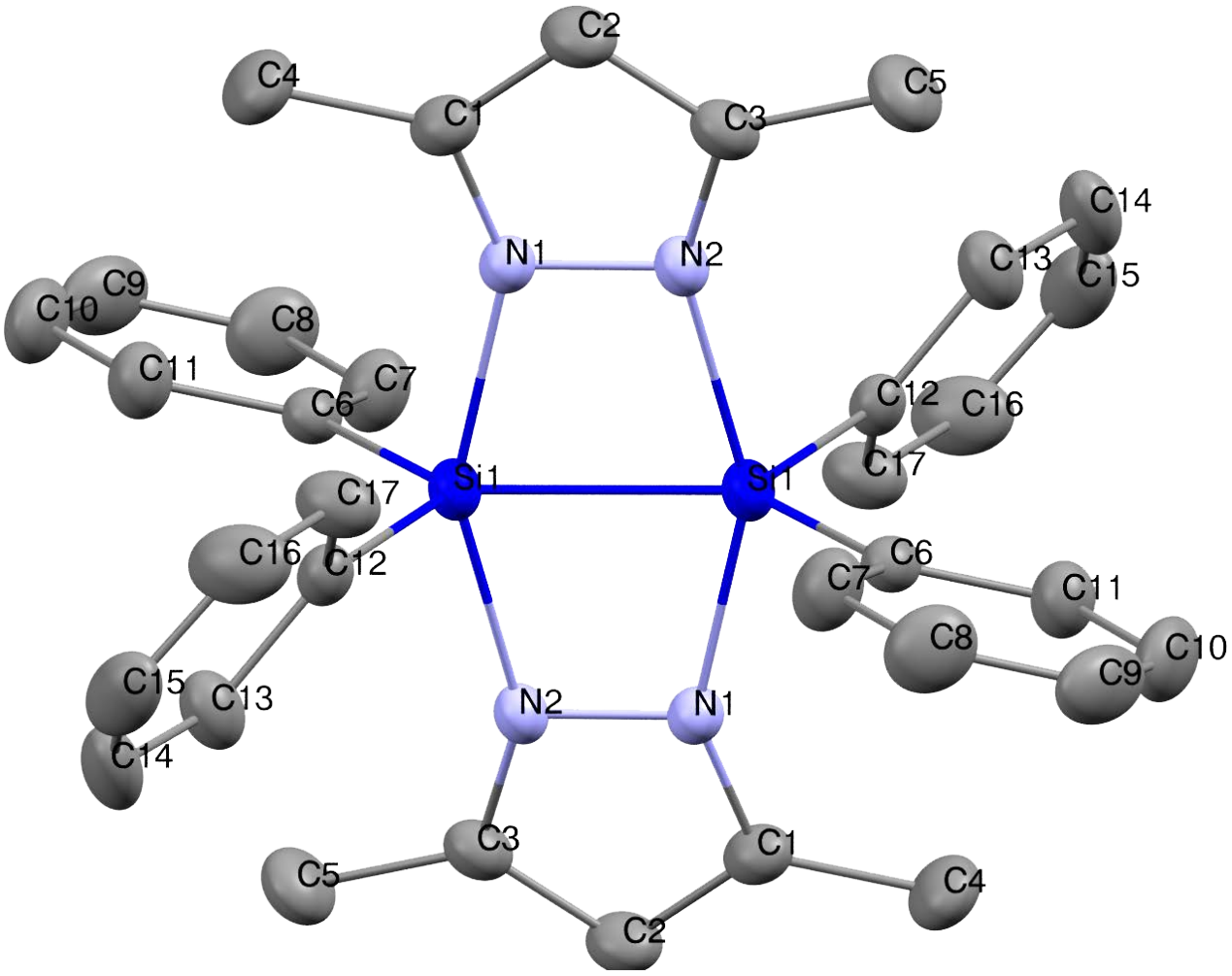


Figure S15. ORTEP drawing of **1** (50% probability of the thermal ellipsoids). Hydrogen atoms were omitted for clarity.

Table S7-1. Crystal data and structure refinement for **1**.

Empirical Formula	$C_{34}H_{34}N_4Si_2$
Formula Weight	554.84
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.200 X 0.150 X 0.100 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 10.379(3) Å
	b = 9.789(2) Å
	c = 14.974(4) Å
	β = 105.172(4) ^{o}
	V = 1468.3(6) Å^3
Space Group	$P2_1/c$ (#14)
Z value	2
D_{calc}	1.255 g/cm^3
F_{000}	588.00
μ(MoKα)	1.511 cm^{-1}
Diffractometer	Saturn724
Radiation	MoKα (λ = 0.71075 Å)
	multi-layer mirror monochromated
Voltage, Current	50kV, 24mA
Temperature	-69.8^{o}C
Detector Aperture	72.8 x 72.8 mm
Data Images	720 exposures
ω oscillation Range (χ=45.0, ϕ=0.0)	-70.0 - 110.0^o
Exposure Rate	10.0 sec./^{o}
Detector Swing Angle	19.90^o
ω oscillation Range (χ=45.0, ϕ=90.0)	-70.0 - 110.0^o
Exposure Rate	10.0 sec./^{o}
Detector Swing Angle	19.90^o
Detector Position	44.82 mm
Pixel Size	0.141 mm
$2\theta_{max}$	54.9^o
No. of Reflections Measured	Total: 11741
	Unique: 3277 (R_{int} = 0.0376)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.852 - 0.985)
Structure Solution	Direct Methods

Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w $(Fo^2 - Fc^2)^2$
Least Squares Weights	$w = 1/ [\sigma^2(Fo^2) + (0.0592 \cdot P)^2 + 1.0479 \cdot P]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$
$2\theta_{max}$ cutoff	54.9^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	3277
No. Variables	181
Reflection/Parameter Ratio	18.10
Residuals: R1 (I>2.00σ(I))	0.0510
Residuals: R (All reflections)	0.0632
Residuals: wR2 (All reflections)	0.1322
Goodness of Fit Indicator	1.058
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.40 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.40 $e^-/Å^3$

Table S7-2. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
Si1	0.39382(5)	0.04435(5)	-0.02634(4)	1.687(13)
N1	0.38438(15)	-0.05300(16)	0.08737(11)	1.77(3)
N2	0.50633(15)	-0.11808(16)	0.11655(11)	1.80(3)
C1	0.3046(2)	-0.0992(2)	0.13864(14)	2.17(3)
C2	0.3745(2)	-0.1952(2)	0.20081(14)	2.49(4)
C3	0.4999(2)	-0.2049(2)	0.18442(13)	2.19(3)
C4	0.1645(2)	-0.0493(3)	0.12352(17)	3.19(4)
C5	0.6142(2)	-0.2953(2)	0.23095(16)	3.11(4)
C6	0.33063(19)	0.21561(19)	0.00102(13)	1.82(3)
C7	0.4183(2)	0.3200(2)	0.04038(16)	2.86(4)
C8	0.3730(3)	0.4450(2)	0.06347(19)	3.53(5)
C9	0.2382(3)	0.4687(2)	0.04769(18)	3.49(5)
C10	0.1490(2)	0.3681(2)	0.00804(18)	3.30(4)
C11	0.1946(2)	0.2430(2)	-0.01508(15)	2.60(4)
C12	0.25779(19)	-0.05458(19)	-0.10988(13)	1.87(3)
C13	0.1931(2)	-0.0033(2)	-0.19669(15)	2.61(4)
C14	0.0893(2)	-0.0735(3)	-0.25646(16)	3.13(4)
C15	0.0487(2)	-0.1980(3)	-0.23148(17)	3.30(5)
C16	0.1146(3)	-0.2542(3)	-0.14750(18)	3.74(5)
C17	0.2166(2)	-0.1831(2)	-0.08706(15)	2.77(4)

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table S7-3. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Si1	0.0196(3)	0.0191(3)	0.0238(3)	0.00058(19)	0.0029(2)	-0.00074(19)
N1	0.0214(8)	0.0228(8)	0.0238(8)	0.0002(6)	0.0069(6)	0.0004(6)
N2	0.0221(8)	0.0214(8)	0.0238(8)	0.0020(6)	0.0042(6)	0.0019(6)
C1	0.0276(10)	0.0287(10)	0.0283(10)	-0.0064(8)	0.0112(8)	-0.0016(8)
C2	0.0357(11)	0.0320(11)	0.0284(10)	-0.0071(9)	0.0109(9)	0.0046(8)
C3	0.0333(11)	0.0252(9)	0.0236(9)	-0.0016(8)	0.0056(8)	0.0033(8)
C4	0.0295(11)	0.0505(14)	0.0458(13)	-0.0018(10)	0.0179(10)	0.0044(11)
C5	0.0429(13)	0.0349(12)	0.0380(12)	0.0048(10)	0.0063(10)	0.0136(10)
C6	0.0259(9)	0.0216(9)	0.0223(9)	0.0014(8)	0.0072(7)	0.0013(7)
C7	0.0317(11)	0.0299(11)	0.0476(13)	-0.0027(9)	0.0112(10)	-0.0076(10)
C8	0.0555(16)	0.0257(11)	0.0559(15)	-0.0076(10)	0.0197(13)	-0.0114(10)
C9	0.0633(17)	0.0247(11)	0.0514(15)	0.0122(11)	0.0272(13)	-0.0002(10)

C10	0.0377(12)	0.0371(12)	0.0535(14)	0.0153(10)	0.0169(11)	0.0033(11)
C11	0.0288(11)	0.0299(11)	0.0388(12)	0.0018(9)	0.0066(9)	-0.0021(9)
C12	0.0215(9)	0.0234(9)	0.0262(9)	0.0007(7)	0.0065(8)	-0.0040(7)
C13	0.0324(11)	0.0272(10)	0.0346(11)	0.0019(9)	-0.0005(9)	-0.0004(9)
C14	0.0326(11)	0.0434(13)	0.0350(12)	0.0093(10)	-0.0055(9)	-0.0084(10)
C15	0.0278(11)	0.0517(15)	0.0442(13)	-0.0111(10)	0.0065(10)	-0.0232(11)
C16	0.0543(15)	0.0453(14)	0.0443(14)	-0.0269(12)	0.0157(12)	-0.0118(11)
C17	0.0432(13)	0.0321(11)	0.0294(11)	-0.0113(9)	0.0084(10)	-0.0017(9)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S7-4. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
Si1	$Si1^1$	2.3074(8)	Si1	N1	1.9759(18)
Si1	$N2^1$	2.0377(19)	Si1	C6	1.884(2)
Si1	C12	1.8899(18)	N1	N2	1.382(2)
N1	C1	1.346(3)	N2	C3	1.340(3)
C1	C2	1.387(3)	C1	C4	1.494(3)
C2	C3	1.390(3)	C3	C5	1.497(3)
C6	C7	1.392(3)	C6	C11	1.394(3)
C7	C8	1.386(3)	C8	C9	1.376(4)
C9	C10	1.375(3)	C10	C11	1.389(3)
C12	C13	1.391(3)	C12	C17	1.400(3)
C13	C14	1.389(3)	C14	C15	1.373(4)
C15	C16	1.379(3)	C16	C17	1.386(3)

Symmetry Operators:

(1) -X+1,-Y,-Z

Table S7-5. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
$Si1^1$	Si1	N1	77.42(5)	$Si1^1$	Si1	$N2^1$	75.75(5)
$Si1^1$	Si1	C6	128.04(6)	$Si1^1$	Si1	C12	120.98(7)
N1	Si1	$N2^1$	152.95(7)	N1	Si1	C6	98.23(8)
N1	Si1	C12	97.26(8)	$N2^1$	Si1	C6	95.47(8)
$N2^1$	Si1	C12	99.45(8)	C6	Si1	C12	110.96(8)
Si1	N1	N2	104.30(13)	Si1	N1	C1	146.11(13)
N2	N1	C1	108.29(15)	$Si1^1$	N2	N1	102.11(11)
$Si1^1$	N2	C3	149.59(14)	N1	N2	C3	108.00(17)
N1	C1	C2	108.63(19)	N1	C1	C4	121.55(18)

C2	C1	C4	129.8(2)	C1	C2	C3	106.1(2)
N2	C3	C2	109.00(17)	N2	C3	C5	122.5(2)
C2	C3	C5	128.5(2)	Si1	C6	C7	121.29(16)
Si1	C6	C11	121.85(14)	C7	C6	C11	116.85(19)
C6	C7	C8	121.8(2)	C7	C8	C9	120.1(2)
C8	C9	C10	119.5(2)	C9	C10	C11	120.3(2)
C6	C11	C10	121.47(19)	Si1	C12	C13	121.87(15)
Si1	C12	C17	121.47(14)	C13	C12	C17	116.66(17)
C12	C13	C14	121.8(2)	C13	C14	C15	120.3(2)
C14	C15	C16	119.2(2)	C15	C16	C17	120.5(2)
C12	C17	C16	121.4(2)				

Symmetry Operators:

(1) -X+1,-Y,-Z

Table S7-6. Torsion Angles(°)

(Those having bond angles > 160 or < 20 degrees are excluded.)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
$Si1^{1}$	Si1	N1	N2	-5.25(7)	$Si1^{1}$	Si1	N1	C1	-169.1(2)
N1	Si1	$Si1^{1}$	$N1^{1}$	-180.00(5)	N1	Si1	$Si1^{1}$	N2	3.56(5)
N1	Si1	$Si1^{1}$	$C6^{1}$	89.33(6)	N1	Si1	$Si1^{1}$	$C12^{1}$	-89.02(6)
$Si1^{1}$	Si1	$N2^{1}$	$N1^{1}$	5.08(7)	$Si1^{1}$	Si1	$N2^{1}$	$C3^{1}$	-166.7(2)
$N2^{1}$	Si1	$Si1^{1}$	$N1^{1}$	-3.56(5)	$N2^{1}$	Si1	$Si1^{1}$	N2	180.00(5)
$N2^{1}$	Si1	$Si1^{1}$	$C6^{1}$	-94.23(6)	$N2^{1}$	Si1	$Si1^{1}$	$C12^{1}$	87.42(6)
$Si1^{1}$	Si1	C6	C7	15.61(19)	$Si1^{1}$	Si1	C6	C11	-162.91(9)
C6	Si1	$Si1^{1}$	$N1^{1}$	-89.33(9)	C6	Si1	$Si1^{1}$	N2	94.23(9)
C6	Si1	$Si1^{1}$	$C6^{1}$	-180.00(9)	C6	Si1	$Si1^{1}$	$C12^{1}$	1.65(10)
$Si1^{1}$	Si1	C12	C13	-120.32(13)	$Si1^{1}$	Si1	C12	C17	60.06(17)
C12	Si1	$Si1^{1}$	$N1^{1}$	89.02(8)	C12	Si1	$Si1^{1}$	N2	-87.42(8)
C12	Si1	$Si1^{1}$	$C6^{1}$	-1.65(10)	C12	Si1	$Si1^{1}$	$C12^{1}$	180.00(8)
N1	Si1	$N2^{1}$	$N1^{1}$	12.7(2)	N1	Si1	$N2^{1}$	$C3^{1}$	-159.08(16)
$N2^{1}$	Si1	N1	N2	-12.9(2)	$N2^{1}$	Si1	N1	C1	-176.68(14)
N1	Si1	C6	C7	96.05(14)	N1	Si1	C6	C11	-82.47(14)
C6	Si1	N1	N2	-132.54(9)	C6	Si1	N1	C1	63.6(2)
N1	Si1	C12	C13	160.02(14)	N1	Si1	C12	C17	-19.60(16)
C12	Si1	N1	N2	114.96(10)	C12	Si1	N1	C1	-48.9(2)
$N2^{1}$	Si1	C6	C7	-60.56(14)	$N2^{1}$	Si1	C6	C11	120.91(14)
C6	Si1	$N2^{1}$	$N1^{1}$	132.99(9)	C6	Si1	$N2^{1}$	$C3^{1}$	-38.8(2)
$N2^{1}$	Si1	C12	C13	-41.34(16)	$N2^{1}$	Si1	C12	C17	139.04(14)
C12	Si1	$N2^{1}$	$N1^{1}$	-114.66(9)	C12	Si1	$N2^{1}$	$C3^{1}$	73.5(2)

C6	Si1	C12	C13	58.29(18)	C6	Si1	C12	C17	-121.33(15)
C12	Si1	C6	C7	-162.88(13)	C12	Si1	C6	C11	18.60(18)
Si1	N1	N2	$Si1^{1}$	5.94(11)	Si1	N1	N2	C3	-169.71(9)
Si1	N1	C1	C2	163.03(17)	Si1	N1	C1	C4	-16.0(3)
N2	N1	C1	C2	-0.44(19)	N2	N1	C1	C4	-179.46(14)
C1	N1	N2	$Si1^{1}$	176.52(12)	C1	N1	N2	C3	0.87(18)
$Si1^{1}$	N2	C3	C2	-172.54(17)	$Si1^{1}$	N2	C3	C5	7.0(4)
N1	N2	C3	C2	-0.95(19)	N1	N2	C3	C5	178.59(14)
N1	C1	C2	C3	-0.1(2)	C4	C1	C2	C3	178.78(19)
C1	C2	C3	N2	0.7(2)	C1	C2	C3	C5	-178.83(16)
Si1	C6	C7	C8	-177.95(14)	Si1	C6	C11	C10	177.91(13)
C7	C6	C11	C10	-0.7(3)	C11	C6	C7	C8	0.6(3)
C6	C7	C8	C9	0.0(4)	C7	C8	C9	C10	-0.7(4)
C8	C9	C10	C11	0.6(4)	C9	C10	C11	C6	0.1(4)
Si1	C12	C13	C14	-177.21(14)	Si1	C12	C17	C16	178.43(15)
C13	C12	C17	C16	-1.2(3)	C17	C12	C13	C14	2.4(3)
C12	C13	C14	C15	-1.0(4)	C13	C14	C15	C16	-1.8(4)
C14	C15	C16	C17	3.0(4)	C15	C16	C17	C12	-1.5(4)

Symmetry Operators:

(1) -X+1,-Y,-Z

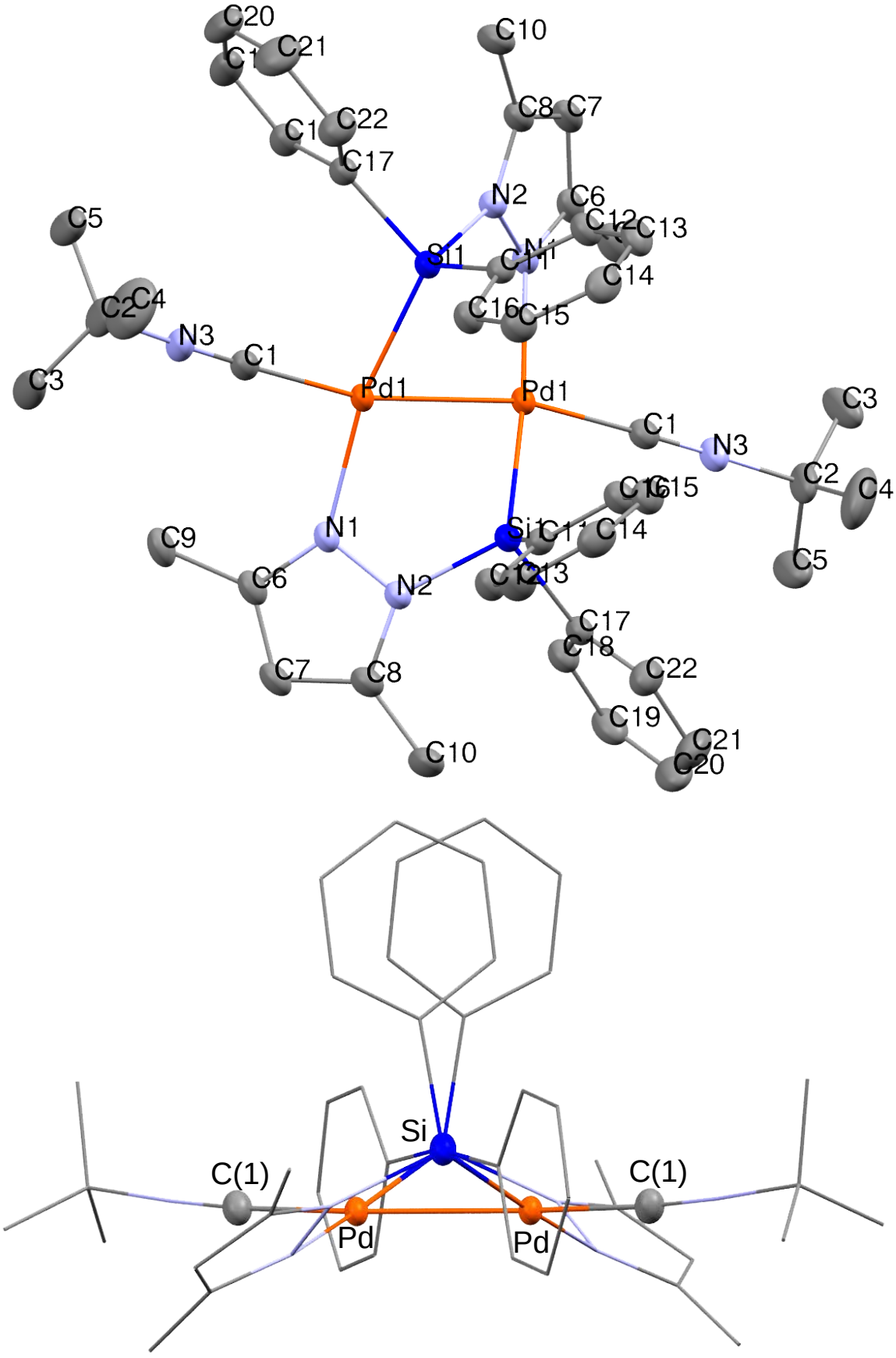


Figure S16. ORTEP drawing of **2** (50% probability of the thermal ellipsoids). Hydrogen atoms were omitted for clarity.

Table S8-1. Crystal data and structure refinement for **2**.

Empirical Formula	$C_{44}H_{52}N_6Pd_2Si_2$
Formula Weight	933.91
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.080 X 0.080 X 0.050 mm
Crystal System	monoclinic
Lattice Type	C-centered
Lattice Parameters	a = 20.04(3) Å
	b = 23.534(16) Å
	c = 12.734(17) Å
	β = 126.46(3) ^{o}
	V = 4830(10) $Å^3$
Space Group	C2/c (#15)
Z value	4
D_{calc}	1.284 g/cm^3
F_{000}	1912.00
μ(unknown radiation, λ = 0.41170Å)	0.000 cm^{-1}
Diffractometer	R-AXIS IV
unknown Radiation (λ = 0.41170Å)	
	monochromated
Voltage, Current	8kV, 100mA
Temperature	-173.0^{o}C
Detector Aperture	300.0 x 300.0 mm
Data Images	1080 exposures
ω oscillation Range (χ=45.0, ϕ=0.0)	0.0 - 180.0^o
Exposure Rate	600.0 sec./^{o}
Detector Swing Angle	0.00^o
ω oscillation Range (χ=45.0, ϕ=90.0)	0.0 - 180.0^o
Exposure Rate	600.0 sec./^{o}
Detector Swing Angle	0.00^o
ω oscillation Range (χ=45.0, ϕ=180.0)	0.0 - 180.0^o
Exposure Rate	600.0 sec./^{o}
Detector Swing Angle	0.00^o
Detector Position	130.00 mm
Pixel Size	0.172 mm
$2\theta_{max}$	31.0^o
No. of Reflections Measured	Total: 53730
	Unique: 5542 (R_{int} = 0.0565)

Corrections	Lorentz-polarization Absorption (trans. factors: 0.802 - 1.000)
Structure Solution	Direct Methods (SHELXT Version 2014/5)
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w $(Fo^2 - Fc^2)^2$
Least Squares Weights	$w = 1/ [\sigma^2(Fo^2) + (0.0271 \cdot P)^2 + 3.1482 \cdot P]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$
$2\theta_{max}$ cutoff	31.0^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	5542
No. Variables	244
Reflection/Parameter Ratio	22.71
Residuals: R1 (I>2.00σ(I))	0.0211
Residuals: R (All reflections)	0.0255
Residuals: wR2 (All reflections)	0.0538
Goodness of Fit Indicator	1.025
Max Shift/Error in Final Cycle	0.004
Maximum peak in Final Diff. Map	0.33 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.48 $e^-/Å^3$

Table S8-2. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
Pd1	0.44537(2)	0.65844(2)	0.62179(2)	1.264(3)
Si1	0.62292(3)	0.62148(2)	0.80187(4)	1.546(7)
N1	0.53195(8)	0.68308(6)	0.57955(13)	1.67(2)
N2	0.60625(8)	0.65427(6)	0.65743(13)	1.73(2)
N3	0.28418(9)	0.65171(7)	0.32966(14)	2.30(3)
C1	0.34325(11)	0.65600(7)	0.43500(17)	1.94(3)
C2	0.20844(12)	0.64348(10)	0.19781(18)	3.06(4)
C3	0.22363(14)	0.66799(13)	0.1028(2)	4.32(5)
C4	0.19180(16)	0.58017(13)	0.1792(3)	5.45(7)
C5	0.13904(13)	0.67623(13)	0.1878(2)	3.98(5)
C6	0.52904(11)	0.70472(7)	0.48005(16)	1.91(3)
C7	0.60148(11)	0.68997(8)	0.49270(17)	2.21(3)
C8	0.64887(11)	0.65803(8)	0.60459(17)	2.11(3)
C9	0.45728(12)	0.74012(8)	0.37634(17)	2.46(3)
C10	0.73150(12)	0.63094(10)	0.66276(19)	2.91(3)
C11	0.60868(9)	0.54284(7)	0.76928(16)	1.71(2)
C12	0.59331(11)	0.51668(8)	0.65833(17)	2.14(3)
C13	0.58226(12)	0.45829(8)	0.64038(18)	2.49(3)
C14	0.58733(11)	0.42491(8)	0.73363(19)	2.55(3)
C15	0.60335(11)	0.44949(8)	0.84516(18)	2.38(3)
C16	0.61354(11)	0.50761(7)	0.86238(17)	2.11(3)
C17	0.74039(10)	0.63063(7)	0.91818(15)	1.82(3)
C18	0.77417(11)	0.68556(8)	0.94911(17)	2.24(3)
C19	0.85914(12)	0.69487(9)	1.02659(18)	2.83(3)
C20	0.91295(12)	0.64921(10)	1.0758(2)	3.38(4)
C21	0.88203(12)	0.59470(10)	1.0502(2)	3.59(4)
C22	0.79612(11)	0.58539(9)	0.97223(19)	2.67(3)

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table S8-3. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd1	0.01725(6)	0.01768(6)	0.01213(6)	0.00081(4)	0.00820(5)	0.00057(4)
Si1	0.0204(2)	0.0215(2)	0.0169(2)	-0.00047(16)	0.01104(17)	-0.00003(16)
N1	0.0235(7)	0.0216(7)	0.0172(6)	-0.0009(5)	0.0115(5)	0.0008(5)
N2	0.0216(6)	0.0258(7)	0.0192(6)	-0.0000(5)	0.0124(6)	0.0011(5)
N3	0.0247(7)	0.0397(9)	0.0187(7)	0.0050(6)	0.0106(6)	0.0004(6)

C1	0.0250(8)	0.0285(8)	0.0215(8)	0.0035(6)	0.0144(7)	0.0017(6)
C2	0.0251(9)	0.0605(13)	0.0161(8)	0.0053(8)	0.0044(7)	-0.0035(8)
C3	0.0380(11)	0.103(2)	0.0199(9)	0.0235(12)	0.0153(9)	0.0078(11)
C4	0.0462(14)	0.0699(18)	0.0482(15)	-0.0097(13)	0.0048(12)	-0.0203(13)
C5	0.0268(10)	0.0913(18)	0.0254(10)	0.0136(11)	0.0113(8)	0.0032(11)
C6	0.0324(9)	0.0213(8)	0.0205(8)	-0.0042(6)	0.0165(7)	-0.0015(6)
C7	0.0346(9)	0.0325(9)	0.0227(8)	-0.0053(7)	0.0201(7)	-0.0013(7)
C8	0.0287(8)	0.0324(9)	0.0237(8)	-0.0035(7)	0.0181(7)	-0.0027(7)
C9	0.0406(10)	0.0301(9)	0.0243(8)	0.0024(7)	0.0200(8)	0.0062(7)
C10	0.0306(9)	0.0577(13)	0.0291(9)	0.0033(9)	0.0215(8)	0.0018(9)
C11	0.0195(7)	0.0236(8)	0.0215(8)	0.0012(6)	0.0121(6)	-0.0001(6)
C12	0.0296(8)	0.0300(9)	0.0233(8)	0.0024(7)	0.0166(7)	0.0006(7)
C13	0.0352(10)	0.0302(9)	0.0296(9)	0.0036(7)	0.0194(8)	-0.0059(7)
C14	0.0311(9)	0.0220(8)	0.0400(10)	0.0017(7)	0.0191(8)	-0.0029(7)
C15	0.0326(9)	0.0269(9)	0.0313(9)	0.0012(7)	0.0191(8)	0.0048(7)
C16	0.0301(8)	0.0281(9)	0.0238(8)	-0.0019(7)	0.0169(7)	-0.0020(7)
C17	0.0212(7)	0.0299(8)	0.0181(7)	-0.0008(6)	0.0116(6)	0.0006(6)
C18	0.0285(9)	0.0336(9)	0.0232(8)	-0.0045(7)	0.0155(7)	0.0001(7)
C19	0.0326(10)	0.0467(11)	0.0273(9)	-0.0145(8)	0.0173(8)	-0.0025(8)
C20	0.0219(9)	0.0669(15)	0.0320(10)	-0.0077(9)	0.0118(8)	0.0029(10)
C21	0.0262(10)	0.0546(13)	0.0442(12)	0.0091(9)	0.0147(9)	0.0129(10)
C22	0.0267(9)	0.0362(10)	0.0335(10)	0.0017(7)	0.0151(8)	0.0048(8)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S8-4. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
Pd1	$Pd1^1$	2.638(4)	Pd1	$Si1^1$	2.271(2)
Pd1	N1	2.178(3)	Pd1	C1	2.016(3)
Si1	N2	1.833(3)	Si1	C11	1.881(2)
Si1	C17	1.907(3)	N1	N2	1.380(2)
N1	C6	1.334(3)	N2	C8	1.369(4)
N3	C1	1.150(2)	N3	C2	1.460(3)
C2	C3	1.525(5)	C2	C4	1.514(4)
C2	C5	1.528(4)	C6	C7	1.406(4)
C6	C9	1.500(2)	C7	C8	1.374(3)
C8	C10	1.497(3)	C11	C12	1.397(3)
C11	C16	1.402(3)	C12	C13	1.389(3)
C13	C14	1.376(4)	C14	C15	1.383(4)

C15	C16	1.381(3)	C17	C18	1.403(3)
C17	C22	1.393(3)	C18	C19	1.387(3)
C19	C20	1.381(3)	C20	C21	1.377(3)
C21	C22	1.402(3)			

Symmetry Operators:

(1) -X+1,Y,-Z+1/2+1

Table S8-5. Bond angles (O)

atom	atom	atom	angle	atom	atom	atom	angle
Pd1[1]	Pd1	Si1[1]	74.82(11)	Pd1[1]	Pd1	N1	96.23(11)
Pd1[1]	Pd1	C1	167.01(8)	Si1[1]	Pd1	N1	168.19(4)
Si1[1]	Pd1	C1	92.67(14)	N1	Pd1	C1	96.63(14)
Pd1[1]	Si1	N2	118.13(8)	Pd1[1]	Si1	C11	114.86(9)
Pd1[1]	Si1	C17	113.84(12)	N2	Si1	C11	106.23(10)
N2	Si1	C17	97.84(11)	C11	Si1	C17	103.76(7)
Pd1	N1	N2	111.67(16)	Pd1	N1	C6	138.10(11)
N2	N1	C6	106.83(19)	Si1	N2	N1	113.78(16)
Si1	N2	C8	136.53(12)	N1	N2	C8	109.69(18)
C1	N3	C2	177.1(2)	Pd1	C1	N3	176.32(17)
N3	C2	C3	107.5(2)	N3	C2	C4	106.98(16)
N3	C2	C5	107.6(2)	C3	C2	C4	112.2(3)
C3	C2	C5	110.1(2)	C4	C2	C5	112.2(2)
N1	C6	C7	109.73(15)	N1	C6	C9	121.7(2)
C7	C6	C9	128.5(2)	C6	C7	C8	106.5(2)
N2	C8	C7	107.2(2)	N2	C8	C10	124.02(19)
C7	C8	C10	128.7(3)	Si1	C11	C12	124.75(16)
Si1	C11	C16	118.05(16)	C12	C11	C16	117.21(18)
C11	C12	C13	121.3(2)	C12	C13	C14	120.0(2)
C13	C14	C15	120.0(2)	C14	C15	C16	120.0(2)
C11	C16	C15	121.5(2)	Si1	C17	C18	119.28(12)
Si1	C17	C22	123.68(14)	C18	C17	C22	117.01(17)
C17	C18	C19	121.93(17)	C18	C19	C20	119.8(2)
C19	C20	C21	119.8(2)	C20	C21	C22	120.2(2)
C17	C22	C21	121.1(2)				

Symmetry Operators:

(1) -X+1,Y,-Z+1/2+1

Table S8-6. Torsion Angles(°)

(Those having bond angles > 160 or < 20 degrees are excluded.)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
Pd1[1]	Pd1	Si1[1]	N2[1]	41.15(5)	Pd1[1]	Pd1	Si1[1]	C11[1]	-85.51(5)
Pd1[1]	Pd1	Si1[1]	C17[1]	155.07(4)	Si1[1]	Pd1	Pd1[1]	Si1	133.23(6)
Si1[1]	Pd1	Pd1[1]	N1[1]	-38.92(5)	Pd1[1]	Pd1	N1	N2	42.88(9)
Pd1[1]	Pd1	N1	C6	-161.70(14)	N1	Pd1	Pd1[1]	Si1	-38.92(6)
N1	Pd1	Pd1[1]	N1[1]	148.94(6)	C1	Pd1	Si1[1]	N2[1]	-135.27(7)
C1	Pd1	Si1[1]	C11[1]	98.07(7)	C1	Pd1	Si1[1]	C17[1]	-21.35(6)
C1	Pd1	N1	N2	-138.98(10)	C1	Pd1	N1	C6	16.44(16)
Pd1[1]	Si1	N2	N1	-23.86(10)	Pd1[1]	Si1	N2	C8	156.06(11)
Pd1[1]	Si1	C11	C12	135.88(12)	Pd1[1]	Si1	C11	C16	-43.96(12)
Pd1[1]	Si1	C17	C18	-63.35(17)	Pd1[1]	Si1	C17	C22	118.85(15)
N2	Si1	C11	C12	3.34(14)	N2	Si1	C11	C16	-176.50(10)
C11	Si1	N2	N1	106.84(11)	C11	Si1	N2	C8	-73.24(14)
N2	Si1	C17	C18	62.18(16)	N2	Si1	C17	C22	-115.61(17)
C17	Si1	N2	N1	-146.29(11)	C17	Si1	N2	C8	33.63(15)
C11	Si1	C17	C18	171.10(15)	C11	Si1	C17	C22	-6.69(19)
C17	Si1	C11	C12	-99.23(15)	C17	Si1	C11	C16	80.93(15)
Pd1	N1	N2	Si1	-17.33(13)	Pd1	N1	N2	C8	162.73(8)
Pd1	N1	C6	C7	-156.07(12)	Pd1	N1	C6	C9	25.2(3)
N2	N1	C6	C7	0.10(16)	N2	N1	C6	C9	-178.66(11)
C6	N1	N2	Si1	179.55(10)	C6	N1	N2	C8	-0.39(15)
Si1	N2	C8	C7	-179.39(11)	Si1	N2	C8	C10	1.0(3)
N1	N2	C8	C7	0.53(17)	N1	N2	C8	C10	-179.12(13)
N1	C6	C7	C8	0.22(18)	C9	C6	C7	C8	178.88(14)
C6	C7	C8	N2	-0.46(18)	C6	C7	C8	C10	179.18(14)
Si1	C11	C12	C13	-179.03(11)	Si1	C11	C16	C15	179.67(12)
C12	C11	C16	C15	-0.2(3)	C16	C11	C12	C13	0.8(3)
C11	C12	C13	C14	-0.8(3)	C12	C13	C14	C15	0.1(3)
C13	C14	C15	C16	0.6(3)	C14	C15	C16	C11	-0.5(3)
Si1	C17	C18	C19	-175.96(15)	Si1	C17	C22	C21	175.68(15)
C18	C17	C22	C21	-2.2(3)	C22	C17	C18	C19	2.0(3)
C17	C18	C19	C20	-0.2(4)	C18	C19	C20	C21	-1.5(4)
C19	C20	C21	C22	1.3(4)	C20	C21	C22	C17	0.6(4)

Symmetry Operators:

(1) -X+1,Y,-Z+1/2+1

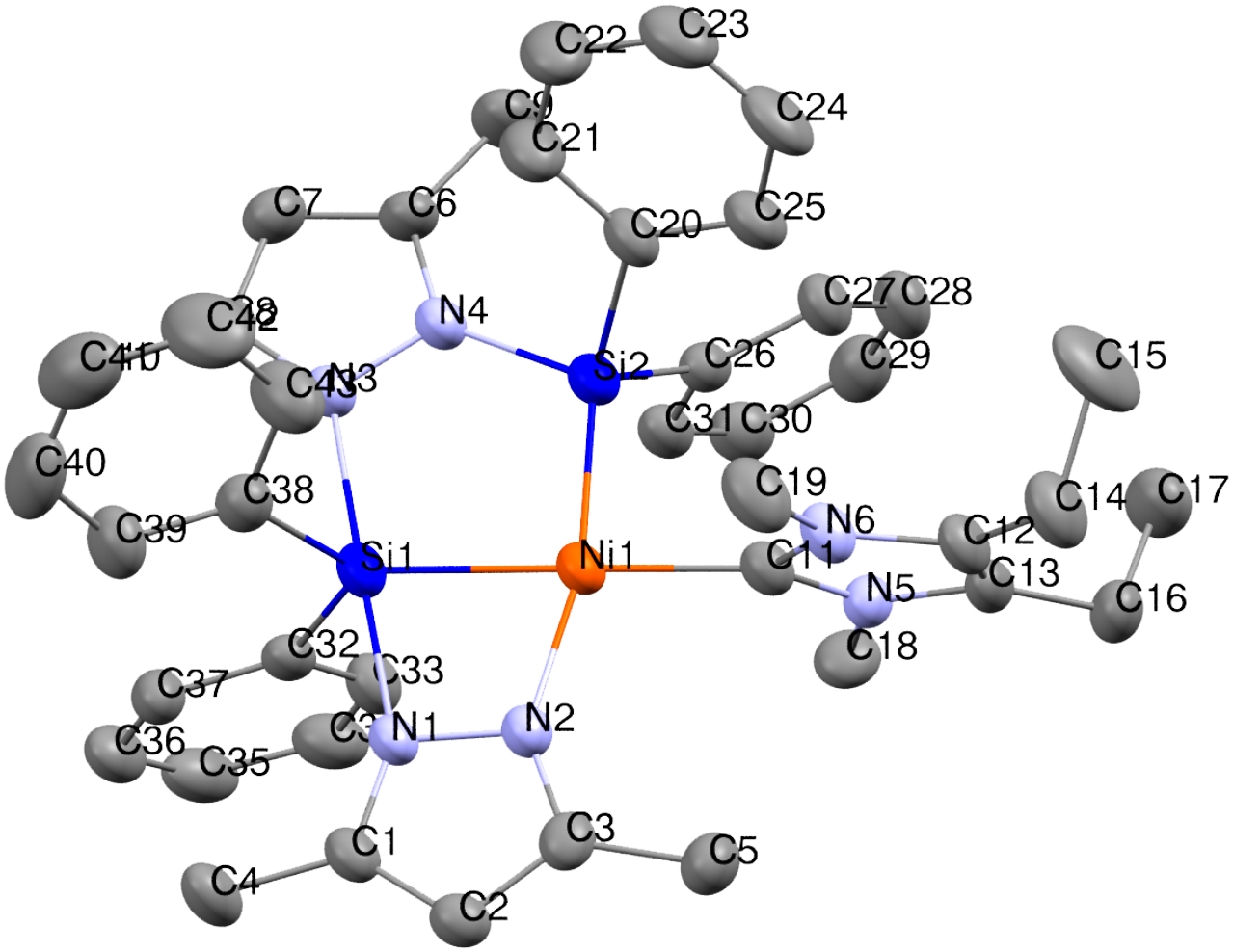


Figure S17. ORTEP drawing of **3** (50% probability of the thermal ellipsoids). Hydrogen atoms were omitted for clarity.

Table S9-1. Crystal data and structure refinement for **3**.

Empirical Formula	$C_{43}H_{50}N_6NiSi_2$
Formula Weight	765.78
Crystal Color, Habit	yellow, block
Crystal Dimensions	0.100 X 0.100 X 0.100 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 11.583(3) Å
	b = 14.712(4) Å
	c = 23.855(7) Å
	β = 98.977(4) ^{o}
	V = 4015.4(19) $Å^3$
Space Group	$P2_1/n$ (#14)
Z value	4
D_{calc}	1.267 g/cm^3
F_{000}	1624.00
μ(MoKα)	5.811 cm^{-1}
Diffractometer	Saturn724
Radiation	MoKα (λ = 0.71075 Å)
	multi-layer mirror monochromated
Voltage, Current	50kV, 24mA
Temperature	-74.8^{o}C
Detector Aperture	72.8 x 72.8 mm
Data Images	720 exposures
ω oscillation Range (χ=45.0, ϕ=0.0)	-70.0 - 110.0^o
Exposure Rate	10.0 sec./^{o}
Detector Swing Angle	19.86^o
ω oscillation Range (χ=45.0, ϕ=90.0)	-70.0 - 110.0^o
Exposure Rate	10.0 sec./^{o}
Detector Swing Angle	19.86^o
Detector Position	44.80 mm
Pixel Size	0.141 mm
$2\theta_{max}$	54.9^o
No. of Reflections Measured	Total: 32773
	Unique: 9151 (R_{int} = 0.1216)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.754 - 0.944)
Structure Solution	Direct Methods (SHELXT Version 2014/5)

Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w $(Fo^2 - Fc^2)^2$
Least Squares Weights	$w = 1/ [\sigma^2(Fo^2) + (0.0754 \cdot P)^2$ + 0.0000 · P] where $P = (Max(Fo^2,0) + 2Fc^2)/3$
$2\theta_{max}$ cutoff	54.9^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	9151
No. Variables	469
Reflection/Parameter Ratio	19.51
Residuals: R1 (I>2.00σ(I))	0.0755
Residuals: R (All reflections)	0.1274
Residuals: wR2 (All reflections)	0.1858
Goodness of Fit Indicator	1.052
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.54 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.59 $e^-/Å^3$

Table S9-2. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
Ni1	0.27009(4)	0.35394(3)	0.49305(2)	2.484(13)
Si1	0.30519(10)	0.26662(8)	0.57228(5)	2.71(2)
Si2	0.26911(10)	0.23395(8)	0.44073(5)	2.67(2)
N1	0.2949(3)	0.3933(2)	0.60383(13)	2.68(6)
N2	0.2742(3)	0.4409(2)	0.55374(13)	2.72(6)
N3	0.3185(3)	0.1335(2)	0.53776(14)	2.70(6)
N4	0.3114(3)	0.1298(2)	0.48028(14)	2.85(6)
N5	0.3101(3)	0.4644(2)	0.39270(13)	2.55(6)
N6	0.1301(3)	0.4612(2)	0.40252(14)	2.84(6)
C1	0.3023(3)	0.4521(3)	0.64744(17)	2.72(7)
C2	0.2848(3)	0.5388(3)	0.62533(18)	2.90(7)
C3	0.2681(3)	0.5295(3)	0.56702(18)	2.77(7)
C4	0.3271(4)	0.4210(3)	0.70773(17)	3.88(9)
C5	0.2477(4)	0.6013(3)	0.52129(19)	3.68(9)
C6	0.3272(4)	0.0425(3)	0.46397(18)	3.14(8)
C7	0.3423(4)	-0.0101(3)	0.51238(19)	3.48(8)
C8	0.3368(4)	0.0475(3)	0.55738(18)	3.07(8)
C9	0.3232(5)	0.0137(3)	0.4039(2)	4.62(11)
C10	0.3492(4)	0.0251(3)	0.61901(19)	3.93(9)
C11	0.2365(3)	0.4301(3)	0.42650(16)	2.56(7)
C12	0.1372(4)	0.5145(3)	0.35445(17)	3.00(8)
C13	0.2505(4)	0.5158(3)	0.34806(17)	2.81(7)
C14	0.0332(4)	0.5568(3)	0.3191(2)	4.30(10)
C15	-0.0271(5)	0.4966(4)	0.2727(2)	6.50(15)
C16	0.3104(4)	0.5586(3)	0.30342(18)	3.58(9)
C17	0.3407(5)	0.4923(3)	0.2586(2)	4.92(11)
C18	0.4366(3)	0.4557(3)	0.40623(19)	3.36(8)
C19	0.0245(4)	0.4442(3)	0.42662(19)	4.02(9)
C20	0.1194(4)	0.2004(3)	0.40126(17)	3.09(8)
C21	0.0571(4)	0.1280(3)	0.4202(2)	4.11(10)
C22	-0.0543(4)	0.1063(4)	0.3945(2)	4.65(11)
C23	-0.1091(4)	0.1562(4)	0.3488(2)	4.58(10)
C24	-0.0503(4)	0.2279(4)	0.3295(2)	4.45(10)
C25	0.0620(4)	0.2502(3)	0.35497(18)	3.60(9)
C26	0.3792(3)	0.2307(3)	0.38914(17)	2.64(7)
C27	0.3532(4)	0.2398(3)	0.33082(17)	3.25(8)
C28	0.4390(4)	0.2404(3)	0.29657(19)	3.87(9)

C29	0.5546(4)	0.2316(3)	0.3201(2)	3.72(9)
C30	0.5842(4)	0.2224(3)	0.37793(19)	3.42(8)
C31	0.4973(4)	0.2222(3)	0.41168(18)	3.00(8)
C32	0.4599(4)	0.2501(3)	0.61059(17)	2.68(7)
C33	0.5507(4)	0.2689(3)	0.57960(18)	3.32(8)
C34	0.6673(4)	0.2553(3)	0.6022(2)	3.86(9)
C35	0.6975(4)	0.2223(3)	0.6568(2)	4.14(10)
C36	0.6115(4)	0.2053(3)	0.6886(2)	3.91(9)
C37	0.4950(4)	0.2191(3)	0.66620(18)	3.27(8)
C38	0.1802(4)	0.2198(3)	0.60710(19)	3.16(8)
C39	0.1806(4)	0.2005(3)	0.6640(2)	4.05(9)
C40	0.0873(5)	0.1573(3)	0.6834(3)	4.95(12)
C41	-0.0094(5)	0.1340(4)	0.6468(3)	5.47(13)
C42	-0.0153(5)	0.1544(4)	0.5903(3)	6.09(14)
C43	0.0781(4)	0.1970(4)	0.5714(2)	4.76(11)

B_{eq} = 8/3 $\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table S9-3. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni1	0.0312(3)	0.0364(3)	0.0252(3)	-0.0015(2)	-0.0003(2)	0.0010(2)
Si1	0.0344(6)	0.0414(7)	0.0257(6)	-0.0027(5)	-0.0001(5)	0.0031(5)
Si2	0.0345(6)	0.0375(6)	0.0278(6)	-0.0030(5)	-0.0004(5)	-0.0004(5)
N1	0.0379(19)	0.0372(19)	0.0252(17)	-0.0051(15)	-0.0002(15)	-0.0000(14)
N2	0.0364(19)	0.0370(19)	0.0291(18)	-0.0040(14)	0.0018(15)	0.0015(15)
N3	0.0373(19)	0.0381(19)	0.0266(17)	-0.0034(14)	0.0035(15)	-0.0011(14)
N4	0.041(2)	0.038(2)	0.0274(18)	-0.0041(15)	0.0018(15)	-0.0007(15)
N5	0.0327(18)	0.0318(18)	0.0314(18)	-0.0003(14)	0.0019(15)	0.0035(14)
N6	0.0279(18)	0.049(2)	0.0302(18)	0.0029(15)	0.0032(15)	0.0001(15)
C1	0.029(2)	0.045(2)	0.029(2)	-0.0012(17)	0.0007(17)	-0.0025(18)
C2	0.032(2)	0.040(2)	0.037(2)	0.0004(17)	0.0032(18)	-0.0056(19)
C3	0.024(2)	0.039(2)	0.042(2)	-0.0010(17)	0.0043(18)	0.0050(19)
C4	0.060(3)	0.050(3)	0.033(2)	0.009(2)	-0.005(2)	-0.003(2)
C5	0.052(3)	0.040(3)	0.048(3)	-0.004(2)	0.006(2)	0.006(2)
C6	0.051(3)	0.031(2)	0.037(2)	-0.0035(19)	0.008(2)	-0.0066(18)
C7	0.049(3)	0.032(2)	0.050(3)	-0.0019(19)	0.006(2)	-0.001(2)
C8	0.048(3)	0.031(2)	0.036(2)	0.0008(18)	0.001(2)	0.0007(18)
C9	0.087(4)	0.041(3)	0.046(3)	-0.002(2)	0.007(3)	-0.009(2)
C10	0.067(3)	0.036(2)	0.043(3)	0.001(2)	0.002(2)	0.007(2)

C11	0.029(2)	0.040(2)	0.028(2)	0.0017(17)	0.0047(17)	-0.0030(17)
C12	0.040(2)	0.043(2)	0.028(2)	0.0081(18)	-0.0053(18)	0.0031(18)
C13	0.047(3)	0.028(2)	0.030(2)	0.0025(17)	-0.0007(19)	0.0032(17)
C14	0.050(3)	0.071(3)	0.039(3)	0.013(2)	-0.004(2)	0.006(2)
C15	0.072(4)	0.109(5)	0.053(3)	0.032(3)	-0.031(3)	-0.011(3)
C16	0.059(3)	0.039(2)	0.039(3)	-0.003(2)	0.011(2)	0.006(2)
C17	0.086(4)	0.058(3)	0.046(3)	-0.008(3)	0.021(3)	-0.005(2)
C18	0.027(2)	0.045(2)	0.054(3)	-0.0042(18)	0.001(2)	-0.000(2)
C19	0.033(2)	0.078(3)	0.042(3)	0.009(2)	0.004(2)	-0.003(2)
C20	0.036(2)	0.052(3)	0.027(2)	-0.0013(19)	0.0012(18)	-0.0018(19)
C21	0.044(3)	0.064(3)	0.045(3)	-0.015(2)	-0.003(2)	0.001(2)
C22	0.048(3)	0.067(3)	0.059(3)	-0.021(2)	-0.002(3)	0.001(3)
C23	0.042(3)	0.079(4)	0.051(3)	-0.011(3)	-0.001(2)	-0.015(3)
C24	0.044(3)	0.085(4)	0.035(3)	0.004(3)	-0.010(2)	-0.009(2)
C25	0.044(3)	0.056(3)	0.034(2)	-0.003(2)	-0.004(2)	-0.005(2)
C26	0.038(2)	0.029(2)	0.032(2)	-0.0002(16)	0.0001(18)	0.0001(16)
C27	0.045(3)	0.047(3)	0.030(2)	0.005(2)	0.001(2)	0.0021(19)
C28	0.062(3)	0.053(3)	0.033(2)	0.006(2)	0.010(2)	0.001(2)
C29	0.055(3)	0.042(3)	0.049(3)	0.004(2)	0.021(2)	0.000(2)
C30	0.043(3)	0.040(2)	0.047(3)	0.0066(19)	0.006(2)	-0.004(2)
C31	0.046(3)	0.033(2)	0.033(2)	0.0043(18)	-0.000(2)	-0.0020(17)
C32	0.042(2)	0.027(2)	0.032(2)	-0.0021(17)	0.0012(19)	-0.0036(17)
C33	0.046(3)	0.046(3)	0.033(2)	0.002(2)	0.000(2)	0.0018(19)
C34	0.040(3)	0.051(3)	0.054(3)	-0.003(2)	0.003(2)	-0.015(2)
C35	0.048(3)	0.041(3)	0.060(3)	0.008(2)	-0.018(3)	-0.010(2)
C36	0.057(3)	0.044(3)	0.041(3)	0.001(2)	-0.014(2)	0.001(2)
C37	0.048(3)	0.039(2)	0.036(2)	-0.0076(19)	0.000(2)	0.0036(19)
C38	0.045(3)	0.037(2)	0.038(2)	0.0001(19)	0.010(2)	-0.0010(18)
C39	0.056(3)	0.062(3)	0.038(3)	0.002(2)	0.015(2)	0.004(2)
C40	0.083(4)	0.055(3)	0.060(4)	0.011(3)	0.042(3)	0.012(3)
C41	0.070(4)	0.061(3)	0.087(5)	-0.009(3)	0.044(4)	-0.011(3)
C42	0.048(3)	0.103(5)	0.082(5)	-0.023(3)	0.016(3)	-0.017(4)
C43	0.048(3)	0.087(4)	0.048(3)	-0.012(3)	0.013(3)	-0.007(3)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S9-4. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
Ni1	Si1	2.2689(13)	Ni1	Si2	2.1609(13)

Ni1	N2	1.927(3)	Ni1	C11	1.932(4)
Si1	N1	2.021(3)	Si1	N3	2.139(3)
Si1	C32	1.896(4)	Si1	C38	1.907(5)
Si2	N4	1.826(3)	Si2	C20	1.904(4)
Si2	C26	1.906(4)	N1	N2	1.373(4)
N1	C1	1.345(5)	N2	C3	1.346(5)
N3	N4	1.362(5)	N3	C8	1.354(5)
N4	C6	1.362(5)	N5	C11	1.359(5)
N5	C13	1.398(5)	N5	C18	1.456(5)
N6	C11	1.354(5)	N6	C12	1.402(5)
N6	C19	1.452(6)	C1	C2	1.384(6)
C1	C4	1.494(6)	C2	C3	1.381(6)
C3	C5	1.510(6)	C6	C7	1.378(6)
C6	C9	1.488(6)	C7	C8	1.377(6)
C8	C10	1.492(6)	C12	C13	1.346(6)
C12	C14	1.493(6)	C13	C16	1.497(6)
C14	C15	1.503(7)	C16	C17	1.529(7)
C20	C21	1.401(6)	C20	C25	1.403(6)
C21	C22	1.377(6)	C22	C23	1.384(7)
C23	C24	1.373(7)	C24	C25	1.387(6)
C26	C27	1.383(6)	C26	C31	1.394(5)
C27	C28	1.382(7)	C28	C29	1.375(7)
C29	C30	1.376(7)	C30	C31	1.384(7)
C32	C33	1.404(6)	C32	C37	1.402(6)
C33	C34	1.389(6)	C34	C35	1.383(7)
C35	C36	1.366(7)	C36	C37	1.387(6)
C38	C39	1.386(7)	C38	C43	1.386(6)
C39	C40	1.394(8)	C40	C41	1.351(8)
C41	C42	1.372(10)	C42	C43	1.385(8)

Table S9-5. Bond angles (^{O})

atom	atom	atom	angle	atom	atom	atom	angle
Si1	Ni1	Si2	90.16(5)	Si1	Ni1	N2	76.70(10)
Si1	Ni1	C11	178.29(13)	Si2	Ni1	N2	166.79(10)
Si2	Ni1	C11	90.97(12)	N2	Ni1	C11	102.15(15)
Ni1	Si1	N1	76.98(10)	Ni1	Si1	N3	102.23(10)
Ni1	Si1	C32	120.47(14)	Ni1	Si1	C38	121.19(13)
N1	Si1	N3	178.81(15)	N1	Si1	C32	92.57(15)
N1	Si1	C38	94.48(17)	N3	Si1	C32	87.06(15)

N3	Si1	C38	86.70(16)	C32	Si1	C38	117.94(19)
Ni1	Si2	N4	114.23(12)	Ni1	Si2	C20	114.80(14)
Ni1	Si2	C26	116.72(13)	N4	Si2	C20	100.86(17)
N4	Si2	C26	99.21(17)	C20	Si2	C26	108.88(18)
Si1	N1	N2	99.1(2)	Si1	N1	C1	151.7(3)
N2	N1	C1	109.1(3)	Ni1	N2	N1	107.2(2)
Ni1	N2	C3	145.5(3)	N1	N2	C3	107.3(3)
Si1	N3	N4	115.4(2)	Si1	N3	C8	137.6(3)
N4	N3	C8	107.0(3)	Si2	N4	N3	117.1(2)
Si2	N4	C6	132.9(3)	N3	N4	C6	109.6(3)
C11	N5	C13	111.8(3)	C11	N5	C18	122.6(3)
C13	N5	C18	125.2(3)	C11	N6	C12	111.7(3)
C11	N6	C19	122.8(3)	C12	N6	C19	125.4(3)
N1	C1	C2	108.1(3)	N1	C1	C4	121.8(4)
C2	C1	C4	130.1(4)	C1	C2	C3	106.4(4)
N2	C3	C2	109.2(3)	N2	C3	C5	121.0(4)
C2	C3	C5	129.8(4)	N4	C6	C7	107.1(4)
N4	C6	C9	123.9(4)	C7	C6	C9	128.9(4)
C6	C7	C8	107.0(4)	N3	C8	C7	109.2(4)
N3	C8	C10	122.2(4)	C7	C8	C10	128.6(4)
Ni1	C11	N5	129.6(3)	Ni1	C11	N6	126.6(3)
N5	C11	N6	103.8(3)	N6	C12	C13	106.4(3)
N6	C12	C14	123.3(4)	C13	C12	C14	130.2(4)
N5	C13	C12	106.3(4)	N5	C13	C16	122.8(4)
C12	C13	C16	130.9(4)	C12	C14	C15	114.3(4)
C13	C16	C17	114.4(4)	Si2	C20	C21	120.9(3)
Si2	C20	C25	122.5(3)	C21	C20	C25	116.4(4)
C20	C21	C22	121.9(4)	C21	C22	C23	120.7(5)
C22	C23	C24	118.8(4)	C23	C24	C25	121.0(4)
C20	C25	C24	121.3(4)	Si2	C26	C27	125.7(3)
Si2	C26	C31	117.9(3)	C27	C26	C31	116.3(4)
C26	C27	C28	122.1(4)	C27	C28	C29	120.2(4)
C28	C29	C30	119.5(5)	C29	C30	C31	119.6(4)
C26	C31	C30	122.3(4)	Si1	C32	C33	116.8(3)
Si1	C32	C37	127.6(3)	C33	C32	C37	115.6(4)
C32	C33	C34	122.0(4)	C33	C34	C35	120.2(5)
C34	C35	C36	119.2(4)	C35	C36	C37	120.6(4)
C32	C37	C36	122.2(4)	Si1	C38	C39	127.8(3)
Si1	C38	C43	116.9(4)	C39	C38	C43	115.1(4)

C38	C39	C40	122.2(4)	C39	C40	C41	120.7(6)
C40	C41	C42	119.2(6)	C41	C42	C43	119.8(5)
C38	C43	C42	123.0(5)				

Table S9-6. Torsion Angles(°)

(Those having bond angles > 160 or < 20 degrees are excluded.)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
Si1	Ni1	Si2	N4	-6.84(7)	Si1	Ni1	Si2	C20	108.98(6)
Si1	Ni1	Si2	C26	-121.85(6)	Si2	Ni1	Si1	N1	-178.62(4)
Si2	Ni1	Si1	N3	2.29(5)	Si2	Ni1	Si1	C32	96.11(7)
Si2	Ni1	Si1	C38	-91.28(7)	Si1	Ni1	N2	N1	-0.17(15)
Si1	Ni1	N2	C3	177.1(4)	N2	Ni1	Si1	N1	0.11(10)
N2	Ni1	Si1	N3	-178.97(11)	N2	Ni1	Si1	C32	-85.15(11)
N2	Ni1	Si1	C38	87.45(11)	Si2	Ni1	C11	N5	-82.3(3)
Si2	Ni1	C11	N6	97.1(3)	C11	Ni1	Si2	N4	174.45(13)
C11	Ni1	Si2	C20	-69.74(13)	C11	Ni1	Si2	C26	59.43(13)
N2	Ni1	C11	N5	99.3(3)	N2	Ni1	C11	N6	-81.3(3)
C11	Ni1	N2	N1	178.54(19)	C11	Ni1	N2	C3	-4.2(4)
Ni1	Si1	N1	N2	-0.15(13)	Ni1	Si1	N1	C1	-175.7(5)
Ni1	Si1	N3	N4	3.8(2)	Ni1	Si1	N3	C8	-179.2(3)
Ni1	Si1	C32	C33	-19.2(3)	Ni1	Si1	C32	C37	162.5(2)
Ni1	Si1	C38	C39	-150.3(2)	Ni1	Si1	C38	C43	33.8(3)
N1	Si1	C32	C33	-95.6(2)	N1	Si1	C32	C37	86.1(3)
C32	Si1	N1	N2	120.5(2)	C32	Si1	N1	C1	-55.0(5)
N1	Si1	C38	C39	-72.8(3)	N1	Si1	C38	C43	111.3(3)
C38	Si1	N1	N2	-121.16(19)	C38	Si1	N1	C1	63.3(5)
N3	Si1	C32	C33	83.3(2)	N3	Si1	C32	C37	-95.1(3)
C32	Si1	N3	N4	-116.8(2)	C32	Si1	N3	C8	60.3(3)
N3	Si1	C38	C39	107.4(3)	N3	Si1	C38	C43	-68.5(3)
C38	Si1	N3	N4	125.0(2)	C38	Si1	N3	C8	-58.0(3)
C32	Si1	C38	C39	22.5(4)	C32	Si1	C38	C43	-153.4(2)
C38	Si1	C32	C33	167.9(2)	C38	Si1	C32	C37	-10.4(4)
Ni1	Si2	N4	N3	11.5(3)	Ni1	Si2	N4	C6	-176.5(2)
Ni1	Si2	C20	C21	-103.1(3)	Ni1	Si2	C20	C25	71.9(3)
Ni1	Si2	C26	C27	-107.7(3)	Ni1	Si2	C26	C31	69.5(3)
N4	Si2	C20	C21	20.2(3)	N4	Si2	C20	C25	-164.8(3)
C20	Si2	N4	N3	-112.2(2)	C20	Si2	N4	C6	59.9(3)
N4	Si2	C26	C27	129.2(3)	N4	Si2	C26	C31	-53.6(3)
C26	Si2	N4	N3	136.4(2)	C26	Si2	N4	C6	-51.5(3)

C20	Si2	C26	C27	24.3(3)	C20	Si2	C26	C31	-158.5(2)
C26	Si2	C20	C21	124.0(3)	C26	Si2	C20	C25	-61.1(3)
Si1	N1	N2	Ni1	0.2(2)	Si1	N1	N2	C3	-178.20(18)
Si1	N1	C1	C2	176.1(4)	Si1	N1	C1	C4	-3.2(8)
N2	N1	C1	C2	0.7(4)	N2	N1	C1	C4	-178.6(3)
C1	N1	N2	Ni1	178.0(2)	C1	N1	N2	C3	-0.4(4)
Ni1	N2	C3	C2	-177.3(3)	Ni1	N2	C3	C5	1.8(7)
N1	N2	C3	C2	-0.0(4)	N1	N2	C3	C5	179.1(3)
Si1	N3	N4	Si2	-9.3(3)	Si1	N3	N4	C6	176.84(18)
Si1	N3	C8	C7	-176.7(2)	Si1	N3	C8	C10	2.9(6)
N4	N3	C8	C7	0.5(4)	N4	N3	C8	C10	-179.9(3)
C8	N3	N4	Si2	172.8(3)	C8	N3	N4	C6	-1.1(4)
Si2	N4	C6	C7	-171.3(3)	Si2	N4	C6	C9	6.7(6)
N3	N4	C6	C7	1.2(4)	N3	N4	C6	C9	179.2(3)
C11	N5	C13	C12	0.7(4)	C11	N5	C13	C16	-177.8(3)
C13	N5	C11	Ni1	179.2(3)	C13	N5	C11	N6	-0.3(4)
C18	N5	C11	Ni1	-7.1(5)	C18	N5	C11	N6	173.4(3)
C18	N5	C13	C12	-172.8(3)	C18	N5	C13	C16	8.7(5)
C11	N6	C12	C13	0.6(4)	C11	N6	C12	C14	179.3(3)
C12	N6	C11	Ni1	-179.7(3)	C12	N6	C11	N5	-0.2(4)
C19	N6	C11	Ni1	3.5(5)	C19	N6	C11	N5	-177.0(3)
C19	N6	C12	C13	177.4(3)	C19	N6	C12	C14	-4.0(6)
N1	C1	C2	C3	-0.7(4)	C4	C1	C2	C3	178.5(4)
C1	C2	C3	N2	0.4(4)	C1	C2	C3	C5	-178.6(3)
N4	C6	C7	C8	-0.8(4)	C9	C6	C7	C8	-178.7(4)
C6	C7	C8	N3	0.2(5)	C6	C7	C8	C10	-179.3(4)
N6	C12	C13	N5	-0.8(4)	N6	C12	C13	C16	177.6(3)
N6	C12	C14	C15	-87.6(5)	C13	C12	C14	C15	90.7(5)
C14	C12	C13	N5	-179.3(4)	C14	C12	C13	C16	-0.9(7)
N5	C13	C16	C17	76.8(4)	C12	C13	C16	C17	-101.3(5)
Si2	C20	C21	C22	175.8(3)	Si2	C20	C25	C24	-175.6(3)
C21	C20	C25	C24	-0.4(6)	C25	C20	C21	C22	0.5(7)
C20	C21	C22	C23	-0.4(8)	C21	C22	C23	C24	0.1(8)
C22	C23	C24	C25	0.0(8)	C23	C24	C25	C20	0.1(7)
Si2	C26	C27	C28	177.3(2)	Si2	C26	C31	C30	-177.7(2)
C27	C26	C31	C30	-0.2(5)	C31	C26	C27	C28	0.0(5)
C26	C27	C28	C29	0.1(6)	C27	C28	C29	C30	-0.1(6)
C28	C29	C30	C31	-0.1(6)	C29	C30	C31	C26	0.3(6)
Si1	C32	C33	C34	-176.9(2)	Si1	C32	C37	C36	176.6(2)

C33	C32	C37	C36	-1.7(5)	C37	C32	C33	C34	1.6(5)
C32	C33	C34	C35	0.0(6)	C33	C34	C35	C36	-1.6(6)
C34	C35	C36	C37	1.4(6)	C35	C36	C37	C32	0.3(6)
Si1	C38	C39	C40	-172.9(3)	Si1	C38	C43	C42	173.7(3)
C39	C38	C43	C42	-2.7(7)	C43	C38	C39	C40	3.1(6)
C38	C39	C40	C41	-1.4(7)	C39	C40	C41	C42	-0.8(8)
C40	C41	C42	C43	1.1(8)	C41	C42	C43	C38	0.7(8)

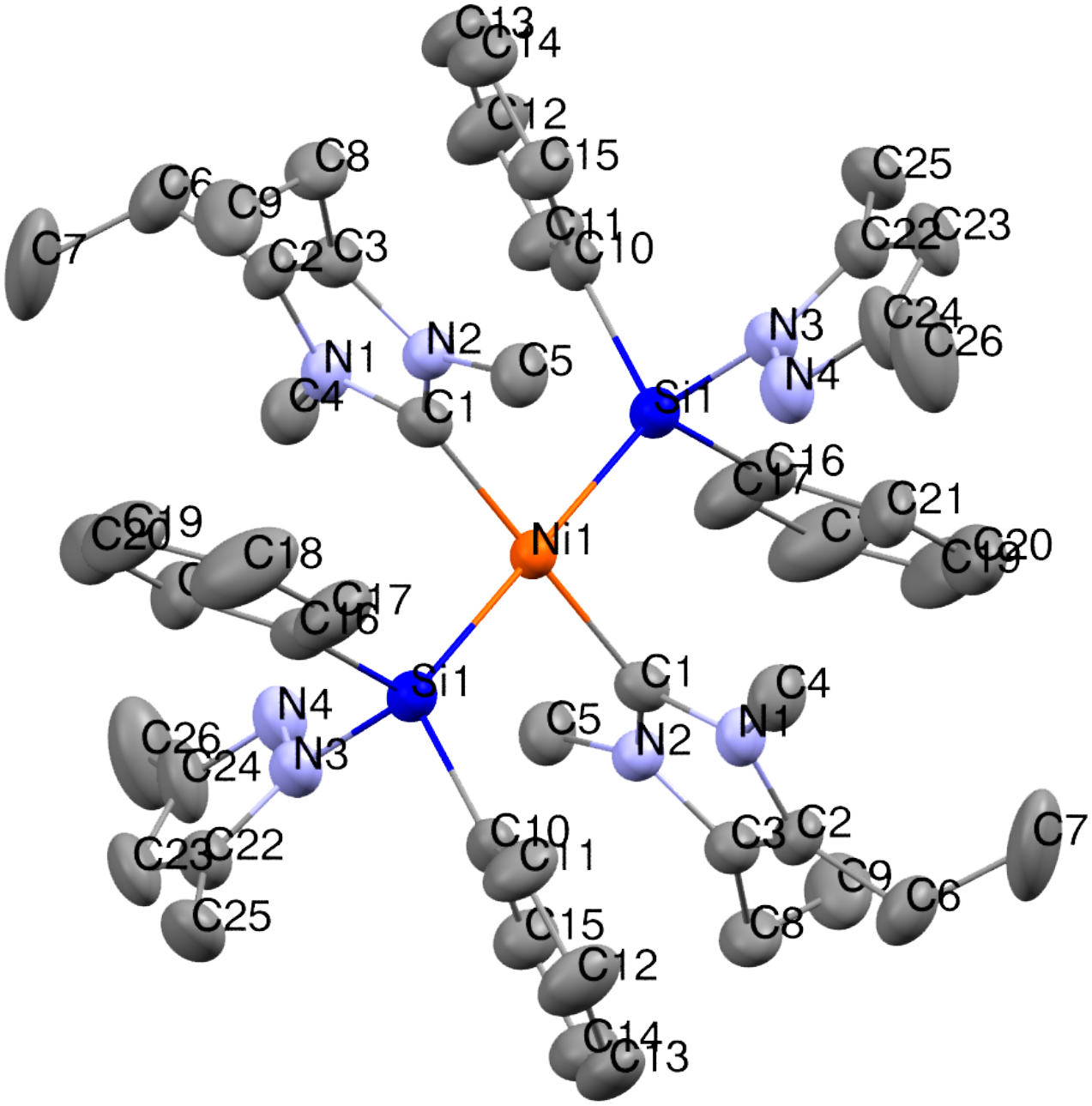


Figure S18. ORTEP drawing of **4** (50% probability of the thermal ellipsoids). Hydrogen atoms were omitted for clarity.

Table S10-1. Crystal data and structure refinement for **4**.

Empirical Formula	$C_{52}H_{66}N_8NiSi_2$
Formula Weight	918.02
Crystal Color, Habit	yellow, block
Crystal Dimensions	0.150 X 0.100 X 0.080 mm
Crystal System	orthorhombic
Lattice Type	Primitive
Lattice Parameters	a = 17.514(3) Å
	b = 11.9262(17) Å
	c = 23.970(4) Å
	V = 5006.7(12) $Å^3$
Space Group	Pbca (#61)
Z value	4
D_{calc}	1.218 g/cm^3
F_{000}	1960.00
μ(MoKα)	4.782 cm^{-1}
Diffractometer	Saturn724
Radiation	MoKα (λ = 0.71075 Å)
	multi-layer mirror monochromated
Voltage, Current	50kV, 24mA
Temperature	-69.8°C
Detector Aperture	72.8 x 72.8 mm
Data Images	246 exposures
ω oscillation Range (χ=0.0, ϕ=0.0)	-60.0 - 63.0°
Exposure Rate	10.0 sec./°
Detector Swing Angle	19.88°
Detector Position	44.76 mm
Pixel Size	0.141 mm
$2\theta_{max}$	55.0°
No. of Reflections Measured	Total: 13431
	Unique: 5688 (R_{int} = 0.0642)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.772 - 0.962)
Structure Solution	Direct Methods (SHELXT Version 2014/5)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma\ w\ (Fo^2 - Fc^2)^2$
Least Squares Weights	$w = 1/ [\ \sigma^2(Fo^2) + (0.0951 \cdot P)^2$
	$+ 0.0000 \cdot P\ ]$

	where P = (Max(Fo^2,0) + 2Fc^2)/3
$2\theta_{max}$ cutoff	55.0^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	5688
No. Variables	286
Reflection/Parameter Ratio	19.89
Residuals: R1 (I>2.00σ(I))	0.0629
Residuals: R (All reflections)	0.1080
Residuals: wR2 (All reflections)	0.1904
Goodness of Fit Indicator	0.999
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.39 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.47 $e^-/Å^3$

Table S10-2. Atomic coordinates and B_{iso}/B_{eq} and occupancy

atom	x	y	z	B_{eq}	occ
Ni1	0.50000	0.50000	0.50000	2.195(15)	1/2
Si1	0.59103(5)	0.48345(7)	0.43130(4)	2.57(2)	1
N1	0.58462(15)	0.3454(2)	0.39941(12)	2.98(5)	1
N2	0.52263(17)	0.2788(2)	0.41199(13)	3.38(6)	1
N3	0.62177(16)	0.4790(2)	0.58210(12)	2.75(5)	1
N4	0.56922(15)	0.3203(2)	0.56706(11)	2.56(5)	1
C1	0.56630(18)	0.4313(3)	0.55169(14)	2.54(6)	1
C2	0.66157(19)	0.4011(3)	0.61506(14)	2.91(6)	1
C3	0.62764(19)	0.3014(3)	0.60524(15)	2.91(6)	1
C4	0.6427(2)	0.5968(3)	0.57724(16)	3.41(7)	1
C5	0.5182(2)	0.2344(3)	0.54574(16)	3.42(7)	1
C6	0.7260(2)	0.4303(3)	0.65207(17)	4.08(8)	1
C7	0.7023(3)	0.4811(5)	0.7075(2)	7.24(15)	1
C8	0.6454(2)	0.1884(3)	0.62905(17)	3.68(7)	1
C9	0.6024(3)	0.1601(3)	0.68147(18)	4.84(9)	1
C10	0.69617(19)	0.4818(3)	0.45274(14)	2.78(6)	1
C11	0.7482(2)	0.5680(3)	0.44476(18)	4.21(8)	1
C12	0.8231(2)	0.5607(4)	0.4618(2)	5.02(10)	1
C13	0.8490(2)	0.4656(4)	0.48778(18)	4.34(9)	1
C14	0.7998(2)	0.3789(3)	0.49657(17)	4.15(8)	1
C15	0.7239(2)	0.3876(3)	0.47966(17)	3.62(7)	1
C16	0.58222(19)	0.5738(3)	0.36600(15)	3.19(7)	1
C17	0.6128(2)	0.6814(4)	0.3596(2)	4.84(10)	1
C18	0.6033(3)	0.7415(5)	0.3098(3)	7.06(15)	1
C19	0.5609(3)	0.6948(5)	0.2671(2)	6.32(13)	1
C20	0.5283(3)	0.5934(5)	0.2732(2)	5.54(10)	1
C21	0.5379(3)	0.5347(4)	0.32164(17)	4.35(8)	1
C22	0.6268(2)	0.2955(3)	0.35806(15)	3.32(7)	1
C23	0.5925(2)	0.1964(3)	0.34567(17)	4.30(8)	1
C24	0.5283(3)	0.1886(3)	0.37967(16)	4.21(8)	1
C25	0.6967(2)	0.3461(3)	0.33359(18)	4.44(8)	1
C26	0.4711(3)	0.0972(4)	0.3840(2)	6.90(13)	1

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha$

Table S10-3. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}

Ni1	0.0288(3)	0.0282(3)	0.0265(3)	-0.0012(2)	-0.0009(2)	0.0013(2)
Si1	0.0306(5)	0.0382(5)	0.0289(5)	0.0003(4)	0.0003(4)	0.0019(4)
N1	0.0352(16)	0.0443(15)	0.0336(16)	-0.0018(13)	0.0041(13)	-0.0004(14)
N2	0.0500(18)	0.0431(16)	0.0354(17)	-0.0087(15)	0.0050(14)	-0.0015(14)
N3	0.0388(16)	0.0330(14)	0.0328(15)	-0.0073(12)	-0.0010(13)	-0.0005(12)
N4	0.0331(15)	0.0308(13)	0.0333(16)	-0.0011(12)	-0.0016(12)	0.0029(12)
C1	0.0318(18)	0.0285(15)	0.0360(18)	-0.0010(14)	0.0050(14)	0.0018(14)
C2	0.0364(19)	0.0441(19)	0.0299(18)	0.0002(16)	-0.0030(14)	0.0053(16)
C3	0.0375(19)	0.0355(17)	0.0375(19)	0.0031(15)	-0.0010(15)	0.0013(16)
C4	0.048(2)	0.0383(18)	0.044(2)	-0.0109(17)	-0.0046(18)	0.0029(17)
C5	0.051(2)	0.0357(18)	0.043(2)	-0.0042(17)	-0.0048(18)	0.0004(17)
C6	0.049(2)	0.058(2)	0.048(2)	-0.0091(19)	-0.0142(19)	0.009(2)
C7	0.102(4)	0.128(4)	0.045(3)	-0.049(4)	-0.019(3)	-0.007(3)
C8	0.053(2)	0.0405(19)	0.046(2)	0.0091(18)	-0.0040(19)	0.0066(17)
C9	0.090(3)	0.046(2)	0.048(3)	0.007(2)	-0.002(2)	0.013(2)
C10	0.0337(18)	0.0434(18)	0.0285(17)	-0.0016(15)	0.0027(14)	0.0007(15)
C11	0.046(2)	0.050(2)	0.064(3)	-0.0018(19)	-0.013(2)	0.022(2)
C12	0.044(2)	0.064(3)	0.083(4)	-0.014(2)	-0.018(2)	0.019(3)
C13	0.034(2)	0.075(3)	0.056(3)	0.004(2)	-0.0092(19)	0.008(2)
C14	0.048(2)	0.056(2)	0.054(3)	0.009(2)	-0.0043(19)	0.012(2)
C15	0.044(2)	0.0417(19)	0.052(2)	-0.0014(17)	-0.0047(18)	0.0071(18)
C16	0.0319(19)	0.052(2)	0.037(2)	0.0044(16)	0.0060(16)	0.0088(17)
C17	0.049(2)	0.066(3)	0.070(3)	-0.006(2)	-0.018(2)	0.025(2)
C18	0.060(3)	0.099(4)	0.110(5)	-0.011(3)	-0.008(3)	0.069(4)
C19	0.069(3)	0.118(4)	0.053(3)	0.021(3)	0.001(3)	0.042(3)
C20	0.077(3)	0.093(3)	0.041(3)	0.023(3)	-0.003(2)	0.006(3)
C21	0.064(3)	0.066(2)	0.035(2)	0.009(2)	-0.006(2)	0.003(2)
C22	0.046(2)	0.046(2)	0.035(2)	0.0027(17)	0.0012(16)	-0.0021(17)
C23	0.079(3)	0.048(2)	0.036(2)	0.005(2)	0.007(2)	-0.0113(18)
C24	0.080(3)	0.048(2)	0.032(2)	-0.016(2)	0.008(2)	-0.0074(18)
C25	0.049(2)	0.071(3)	0.049(3)	0.007(2)	0.011(2)	-0.009(2)
C26	0.131(5)	0.071(3)	0.060(3)	-0.047(3)	0.020(3)	-0.014(3)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S10-4. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
Ni1	Si1	2.3005(9)	Ni1	$Si1^1$	2.3005(9)
Ni1	C1	1.886(3)	Ni1	$C1^1$	1.886(3)

Si1	N1	1.819(3)	Si1	C10	1.912(3)
Si1	C16	1.906(4)	N1	N2	1.378(4)
N1	C22	1.372(5)	N2	C24	1.330(5)
N3	C1	1.341(4)	N3	C2	1.404(4)
N3	C4	1.457(4)	N4	C1	1.375(4)
N4	C3	1.391(4)	N4	C5	1.452(4)
C2	C3	1.350(5)	C2	C6	1.477(5)
C3	C8	1.496(5)	C6	C7	1.518(7)
C8	C9	1.504(6)	C10	C11	1.387(5)
C10	C15	1.384(5)	C11	C12	1.377(6)
C12	C13	1.371(6)	C13	C14	1.362(6)
C14	C15	1.394(6)	C16	C17	1.399(6)
C16	C21	1.397(6)	C17	C18	1.401(8)
C18	C19	1.382(8)	C19	C20	1.347(8)
C20	C21	1.366(7)	C22	C23	1.359(5)
C22	C25	1.487(5)	C23	C24	1.391(6)
C24	C26	1.485(7)			

Symmetry Operators:

(1) -X+1,-Y+1,-Z+1

Table S10-5. Bond angles (^{O})

atom	atom	atom	angle	atom	atom	atom	angle
Si1	Ni1	$Si1^{1}$	180.00(4)	Si1	Ni1	C1	90.36(10)
Si1	Ni1	$C1^{1}$	89.64(10)	$Si1^{1}$	Ni1	C1	89.64(10)
$Si1^{1}$	Ni1	$C1^{1}$	90.36(10)	C1	Ni1	$C1^{1}$	180.00(19)
Ni1	Si1	N1	109.62(9)	Ni1	Si1	C10	118.42(11)
Ni1	Si1	C16	118.89(11)	N1	Si1	C10	99.39(13)
N1	Si1	C16	99.29(15)	C10	Si1	C16	107.72(15)
Si1	N1	N2	118.6(2)	Si1	N1	C22	131.6(2)
N2	N1	C22	109.4(3)	N1	N2	C24	106.2(3)
C1	N3	C2	112.6(3)	C1	N3	C4	123.2(3)
C2	N3	C4	123.9(3)	C1	N4	C3	111.1(3)
C1	N4	C5	124.2(3)	C3	N4	C5	124.7(3)
Ni1	C1	N3	128.2(2)	Ni1	C1	N4	128.1(2)
N3	C1	N4	103.6(3)	N3	C2	C3	105.4(3)
N3	C2	C6	124.1(3)	C3	C2	C6	130.4(3)
N4	C3	C2	107.2(3)	N4	C3	C8	123.4(3)
C2	C3	C8	129.4(3)	C2	C6	C7	114.3(4)
C3	C8	C9	114.7(3)	Si1	C10	C11	126.0(3)

Si1	C10	C15	118.2(3)	C11	C10	C15	115.8(3)
C10	C11	C12	122.6(4)	C11	C12	C13	120.1(4)
C12	C13	C14	119.3(4)	C13	C14	C15	120.1(4)
C10	C15	C14	122.1(3)	Si1	C16	C17	125.3(3)
Si1	C16	C21	118.8(3)	C17	C16	C21	115.8(4)
C16	C17	C18	121.2(4)	C17	C18	C19	119.2(5)
C18	C19	C20	120.6(5)	C19	C20	C21	120.0(5)
C16	C21	C20	123.0(4)	N1	C22	C23	107.3(3)
N1	C22	C25	123.5(3)	C23	C22	C25	129.1(4)
C22	C23	C24	106.6(3)	N2	C24	C23	110.4(4)
N2	C24	C26	120.2(4)	C23	C24	C26	129.4(4)

Symmetry Operators:

(1) -X+1,-Y+1,-Z+1

Table S10-6. Torsion Angles(O)

(Those having bond angles > 160 or < 20 degrees are excluded.)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
Si1	Ni1	C1	N3	84.1(3)	Si1	Ni1	C1	N4	-95.8(3)
C1	Ni1	Si1	N1	85.04(10)	C1	Ni1	Si1	C10	-27.91(10)
C1	Ni1	Si1	C16	-161.85(10)	Si1	Ni1	$C1^{1}$	$N3^{1}$	95.9(3)
Si1	Ni1	$C1^{1}$	$N4^{1}$	-84.2(3)	$C1^{1}$	Ni1	Si1	N1	-94.96(10)
$C1^{1}$	Ni1	Si1	C10	152.09(10)	$C1^{1}$	Ni1	Si1	C16	18.15(10)
$Si1^{1}$	Ni1	C1	N3	-95.9(3)	$Si1^{1}$	Ni1	C1	N4	84.2(3)
C1	Ni1	$Si1^{1}$	$N1^{1}$	94.96(10)	C1	Ni1	$Si1^{1}$	$C10^{1}$	-152.09(10)
C1	Ni1	$Si1^{1}$	$C16^{1}$	-18.15(10)	$Si1^{1}$	Ni1	$C1^{1}$	$N3^{1}$	-84.1(3)
$Si1^{1}$	Ni1	$C1^{1}$	$N4^{1}$	95.8(3)	$C1^{1}$	Ni1	$Si1^{1}$	$N1^{1}$	-85.04(10)
$C1^{1}$	Ni1	$Si1^{1}$	$C10^{1}$	27.91(10)	$C1^{1}$	Ni1	$Si1^{1}$	$C16^{1}$	161.85(10)
Ni1	Si1	N1	N2	10.5(2)	Ni1	Si1	N1	C22	-178.6(2)
Ni1	Si1	C10	C11	-107.2(2)	Ni1	Si1	C10	C15	71.6(2)
Ni1	Si1	C16	C17	88.9(3)	Ni1	Si1	C16	C21	-86.7(2)
N1	Si1	C10	C11	134.3(2)	N1	Si1	C10	C15	-46.9(2)
C10	Si1	N1	N2	135.3(2)	C10	Si1	N1	C22	-53.7(3)
N1	Si1	C16	C17	-152.5(2)	N1	Si1	C16	C21	31.9(3)
C16	Si1	N1	N2	-114.8(2)	C16	Si1	N1	C22	56.1(3)
C10	Si1	C16	C17	-49.5(3)	C10	Si1	C16	C21	135.0(2)
C16	Si1	C10	C11	31.4(3)	C16	Si1	C10	C15	-149.9(2)
Si1	N1	N2	C24	174.35(17)	Si1	N1	C22	C23	-173.2(2)
Si1	N1	C22	C25	7.0(5)	N2	N1	C22	C23	-1.6(4)
N2	N1	C22	C25	178.6(3)	C22	N1	N2	C24	1.5(3)

N1	N2	C24	C23	-0.9(4)	N1	N2	C24	C26	178.2(3)
C1	N3	C2	C3	-1.4(4)	C1	N3	C2	C6	179.2(3)
C2	N3	C1	Ni1	-178.0(2)	C2	N3	C1	N4	1.9(3)
C4	N3	C1	Ni1	-3.4(5)	C4	N3	C1	N4	176.5(3)
C4	N3	C2	C3	-175.9(3)	C4	N3	C2	C6	4.7(5)
C1	N4	C3	C2	1.0(4)	C1	N4	C3	C8	-179.2(3)
C3	N4	C1	Ni1	178.2(2)	C3	N4	C1	N3	-1.7(3)
C5	N4	C1	Ni1	-1.4(5)	C5	N4	C1	N3	178.7(3)
C5	N4	C3	C2	-179.5(3)	C5	N4	C3	C8	0.3(5)
N3	C2	C3	N4	0.2(3)	N3	C2	C3	C8	-179.6(3)
N3	C2	C6	C7	79.5(4)	C3	C2	C6	C7	-99.7(4)
C6	C2	C3	N4	179.5(3)	C6	C2	C3	C8	-0.3(6)
N4	C3	C8	C9	-89.1(4)	C2	C3	C8	C9	90.7(4)
Si1	C10	C11	C12	179.6(2)	Si1	C10	C15	C14	179.7(2)
C11	C10	C15	C14	-1.4(5)	C15	C10	C11	C12	0.8(5)
C10	C11	C12	C13	-0.1(7)	C11	C12	C13	C14	-0.0(7)
C12	C13	C14	C15	-0.6(6)	C13	C14	C15	C10	1.4(6)
Si1	C16	C17	C18	180.0(2)	Si1	C16	C21	C20	-179.9(3)
C17	C16	C21	C20	4.1(6)	C21	C16	C17	C18	-4.4(5)
C16	C17	C18	C19	2.2(7)	C17	C18	C19	C20	0.7(7)
C18	C19	C20	C21	-1.1(8)	C19	C20	C21	C16	-1.5(7)
N1	C22	C23	C24	1.0(4)	C25	C22	C23	C24	-179.2(3)
C22	C23	C24	N2	-0.1(4)	C22	C23	C24	C26	-179.0(3)

Symmetry Operators:

(1) -X+1,-Y+1,-Z+1

References

(1) M. Suginome, H. Oike, S. -S. Park and Y. Ito, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 289-299.

(2) R. Tacke, J. Heemann, M. Penka, I. Richter and B. Wagner, *Z. Naturforsch*., 2002, **57b**, 731-735.

(3) N. Kuhn and T. Kratz, *Synthesis*, 1993, 561-562.

(4) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09, Revision C.01;* Gaussian, Inc., Wallingford, CT, 2010.

(5) (a) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098–3100; (b) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372-1377; (c) A. D. Becke, *J. Chem. Phys*., 1993, **98**, 5648-5652; (d) J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev. B*, 1992, **46**, 6671-6687; (e) J. P. Perdew and Y. Wang, *Phys. Rev. B*, 1992, **45**, 13244-13249; (f) J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev. B*, 1993, **48,** 4978; (g) J. P. Perdew, K. Burke and Y. Wang, *Phys. Rev. B*, 1996, **54**, 16533-16539.

(6) (a) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098-3100; (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789; (c) A. D. Becke, *J. Chem. Phys*., 1993, **98**, 5648-5652.

(7) D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. Preuß, *Theor. Chim. Acta*, 1990, **77**, 123-14.

(8) (a) M. S. Gordon, *Chem. Phys. Lett.*, 1980, **76**, 163−168; (b) P. C. Hariharan and J. A. Pople, *Mol. Phys.*, 1974, **27**, 209−214; (c) P. C. Hariharan and J. A. Pople, *Theor. Chem. Acc.*, 1973, **28**, 213−222; (d) W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257−2261; (e) R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724−728.

(9) SIR2008: M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, D. Siliqi and R. Spagna, *J. Appl. Cryst.*, 2007, **40**, 609-613.

(10) International Tables for Crystallography, Vol. C; (Ed. A. J. C. Wilson) Kluwer Academic Publishers, Dordrecht, Netherlands, Table 6.1.1.4, 1992, pp. 572.

(11) J. A. Ibers and W. C. Hamilton, *Acta Cryst*., 1964, **17**, 781-782.

(12) D. C. Creagh, W. J. McAuley, in *International Tables for Crystallography, Vol C*; (Ed. A. J. C. Wilson), Kluwer Academic Publishers, Dordrecht, Netherlands, Table 4.2.6.8, 1992, pages 219-222.

(13) D. C. Creagh, J. H. Hubbell, in *International Tables for Crystallography*, *Vol C*; (Ed. A. J. C. Wilson), Kluwer Academic Publishers, Boston, Table 4.2.4.3, 1992, pages 200-206.

(14) CrystalStructure 4.2.5: Crystal Structure Analysis Package, Rigaku Corporation (2000-2017). Tokyo 196-8666, Japan.

(15) SHELXL Version 2017/1: G. M. Sheldrick, *Acta Cryst*., 2008, **A64**, 112-122.