Supporting information for

Four- and Three-coordinate Planar Iron(II) Complexes Supported by Bulky Organosilyl Ligands

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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 4Å prior to use. ^{1}H NMR spectrum was recorded using a JEOL Lambda 400 spectrometer and ECZ 600 spectrometer at ambient temperature. ^{1}H NMR chemical shifts (δ values) were given in ppm relative to the solvent signal. Elemental analyses (C, H, N) were carried out on externally at A Rabbit Science Co., Ltd. Starting materials, $Fe[Si(SiMe_3)_3]_2(THF)_2$[1],1,1,4,4-tetrakis(trimethylsilyl)octamethylcyclohexasilane[2], $MeIM^{Me}$ [3], $^{Me}CAAC$[4] were synthesized by the method reported in the literature. Other reagents were purchased from Tokyo Chemical Industries Co., Ltd. or FUJIFILM Wako Pure Chemical Co., Inc. or Kanto Chemical Co., Inc. or Sigma Aldrich, and were used without further purification.

Synthesis of *trans*-$Fe[Si(SiMe_3)_3]_2(MeIM^{Me})_2$ (2). In a 50 mL Schlenk tube, $Fe[Si(SiMe_3)_3]_2(THF)_2$ (**1**) (347 mg, 0.500 mmol) was dissolved in toluene (2 mL), then $MeIM^{Me}$ (126 mg, 1.01 mmol) in toluene (2 mL) was added to this solution. The solution was stirred at room temperature for 30 min. The color of the solution turned from dark green to dark brown. The reaction solution was evaporated *in vacuo*, and the obtained solid was dissolved in diethyl ether (10 mL), then the solution was centrifuged to remove the insoluble materials. The solvent was concentrated to ca. 2 mL, and the remaining solution was cooled at -30 °C, from which complex **2** was obtained as red crystals in 66% yield (263 mg). ^{1}H NMR (400 MHz, r.t., C_6D_6): δ = -46.24 (brs, 12H, CH_3), 5.00 (s, 54H, CH_3), 16.10 (s, 12H, CH_3). Magnetic susceptibility (Evans): μ_{eff} = 3.75 (C_6D_6, 20 °C). Anal calcd for $C_{32}H_{78}N_4Si_8Fe$; C 48.07, H 9.83, N 7.01; found: C 48.07, H 9.82, N 7.15.

Synthesis of *cis*-$Fe[Si_8Me_{14}](MeIM^{Me})_2$ (3). In a 50 mL Schlenk tube, 1,1,4,4-tetrakis(trimethylsilyl)octamethylcyclohexasilane (291 mg, 0.501 mmol) was dissolved in DME (4 mL), then KO^{t}Bu (114 mg, 1.02 mmol) was added to this solution. The solution was stirred at room temperature for 18 h. During the course of the reaction, the color of the solution turned to yellow. The solution was evaporated *in vacuo*, and the obtained yellow oil was dissolved in toluene (4 mL). In a 20 mL vial, $FeBr_2$ (108 mg, 0.502 mmol) was suspended in toluene (2 mL), then TMEDA (75 μL, 0.500 mmol) was added to this suspension. The suspension was stirred at room temperature for 30 min. To this suspension was added yellow solution of the potassium salt of silyl dianion prepared above. The reaction mixture was stirred at room temperature for 30 min. The pale-yellow suspension turned to dark brown solution, then the solution was centrifuged to remove the insoluble materials. To the solution was added $MeIM^{Me}$ (125 mg, 1.01 mmol) in toluene (2 mL), and stirred at room temperature for 30 min. The dark brown solution turned to dark red, then the solution was evaporated *in vacuo*, and the obtained solid was dissolved in diethyl ether (5 mL), then the solution was centrifuged to remove the insoluble materials. The solvent was concentrated to ca. 2 mL, and the remaining solution was cooled at -30 °C, from which complex **3** was obtained as red crystals in 52% yield (193 mg). ^{1}H NMR (400 MHz, r.t., C_6D_6): δ = -78.37 (brs, 12H, CH_3), -31.32 (s, 12H, CH_3), -1.40 (s, 18H, CH_3), 11.98 (s, 12H, CH_3), 15.87 (s, 12H, CH_3). Magnetic susceptibility (Evans): μ_{eff} = 4.13 (C_6D_6, 21 °C). Anal calcd for $C_{28}H_{66}N_4Si_8Fe$;

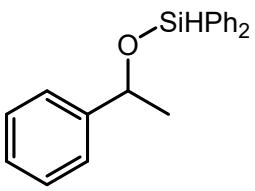
C 45.48, H 9.00, N 7.58; found: C 45.46, H 7.98, N 7.66. Even though a number of attempts have been made, we have been unable to obtain satisfactory elemental analysis values for **3**, presumably due to the high instability toward both air and moisture.

Synthesis of Fe[Si_8Me_{14}](^{Me}CAAC) (4). In a 50 mL Schlenk tube, 1,1,4,4-tetrakis(trimethylsilyl)octamethylcyclohexasilane (292 mg, 0.502 mmol) was dissolved in DME (4 mL), then KO^{t}Bu (114 mg, 1.02 mmol) was added to this solution. The solution was stirred at room temperature for 18 h. In the course of this reaction, the color of the solution turned to yellow. The solution was evaporated *in vacuo*, and the obtained yellow oil was dissolved in toluene (4 mL). In a 20 mL vial, $FeBr_2$ (108 mg, 0.502 mmol) was suspended in toluene (2 mL), then TMEDA (75 μL, 0.500 mmol) was added to this suspension. The suspension was stirred at room temperature for 30 min. To this suspension was added yellow solution of the potassium salt of silyl dianion prepared above. The reaction mixture was stirred at room temperature for 30 min. The pale-yellow suspension turned to dark brown solution, then the solution was centrifuged to remove the insoluble materials. The mother liquid was evaporated *in vacuo*, and the obtained solid was dissolved in pyridine (2 mL). The solution stirred for 15 min at room temperature, then solvent was removed *in vacuo*. The reaction mixture was dissolved in diethyl ether (4 mL), then solution of ^{Me}CAAC (143 mg, 0.501 mmol) in diethyl ether (2 mL) was added to this solution. The solution was stirred at room temperature for 10 min. The color of the solution turned from green-brown to dark red-purple. The mother liquid was evaporated *in vacuo*, and the obtained solid was dissolved in diethyl ether (4 mL). The solvent was concentrated to ca. 2 mL, and the remaining solution was cooled at -30 °C, from which complex **4** was obtained as dark purple crystals in 21% yield (82 mg). ^{1}H NMR (400 MHz, r.t., C_6D_6): δ = -40.07 (brs, 12H, CH_3), 0.29-2.11 (m, 12H, CH_3), 3.27 (brs, 2H, CH_2), 4.58 (brs, 2H, CH_2), 5.08 (brs, 6H, CH_3), 11.57 (brs, 1H, Ar-H), 12.71 (brs, 6H, CH_3), 17.43 (brs, 2H, Ar-H), 30.99 (brs, 12H, CH_3), 50.63 (brs, 18H, CH_3). Magnetic susceptibility (Evans): μ_{eff} = 5.83 (C_6D_6, 20 °C). Anal calcd for $C_{34}H_{73}N_1Si_8Fe$; C 52.59, H 9.48, N 1.80; found: C 52.57, H 9.52, N 1.95.

General Procedure for the hydrosilylation of acetophenone with Ph_2SiH_2 catalyzed by iron(II) complexes. Acetophenone (360 μL, 3.0 mmol) and Ph_2SiH_2 (1.21 mL, 6.6 mmol) were placed in a 4 mL vial, then an iron(II) complexes **2**, **3** or **4** (0.003 mmol, 0.1 mol%) was added to this mixture. The resulting mixture was stirred at r.t. for 1 h, then conversion of acetophenone was estimated by ^{1}H NMR spectrum.

General Procedure for the hydrosilylation of acetophenone with TMDS catalyzed by iron(II) complexes. Acetophenone (120 μL, 1.0 mmol) and 1,1,3,3-tetramethyldisiloxane (TMDS) (390 μL, 2.2 mmol) were placed in a 4 mL vial, then an iron(II) complexes **1**, **2**, **3** or **4** (0.005 mmol, 0.5 mol%) was added. The resulting mixture was stirred at r.t. for 24 h, then conversion was estimated by ^{1}H NMR spectrum.

Isolation of the silyl ether. In the hydrosilylation of acetophenone with Ph_2SiH_2, the silyl ether was isolated according to the following procedure. In a 20 mL vial, acetophenone (1.80 g, 15 mmol) and Ph_2SiH_2 (6.10 g, 33 mmol) were placed in a 20 mL vial, then an iron(II) complex **2** (6.1 mg, 0.0076 mmol, 0.05 mol%) was added to this mixture. The resulting mixture



was stirred at r.t. for 1 h. After the reaction, the reaction mixture was distilled under reduced pressure (170 °C, 3 Pa) to obtain the product as colorless oil. Isolated yield: 4.10 g (89 %). ^{1}H NMR (600 MHz, r.t., $CDCl_3$): δ = 1.51 (d, 3H, CH_3), 5.00 (q, 1H, CH), 5.41 (s, 1H, SiH), 7.24-7.64 (m, 15H, Ar-H). ^{13}C NMR (150MHz, r.t., $CDCl_3$): δ = 26.4 (CH_3), 72.8 (CH), 125.7 (C_6H_5), 127.3 (C_6H_5), 128.1 (C_6H_5), 128.4 (C_6H_5), 130.4 (C_6H_5), 134.1 (C_6H_5), 134.4 (C_6H_5), 134.8 (C_6H_5), 145.4 (C_6H_5). ^{29}Si NMR (119 MHz, r.t., $CDCl_3$): δ = -12.42. The actual NMR charts were shown in **Figures S4**-**S6**.

Figure S1. ^{1}H NMR spectrum of solution of **2** in C_6D_6 at room temperature.

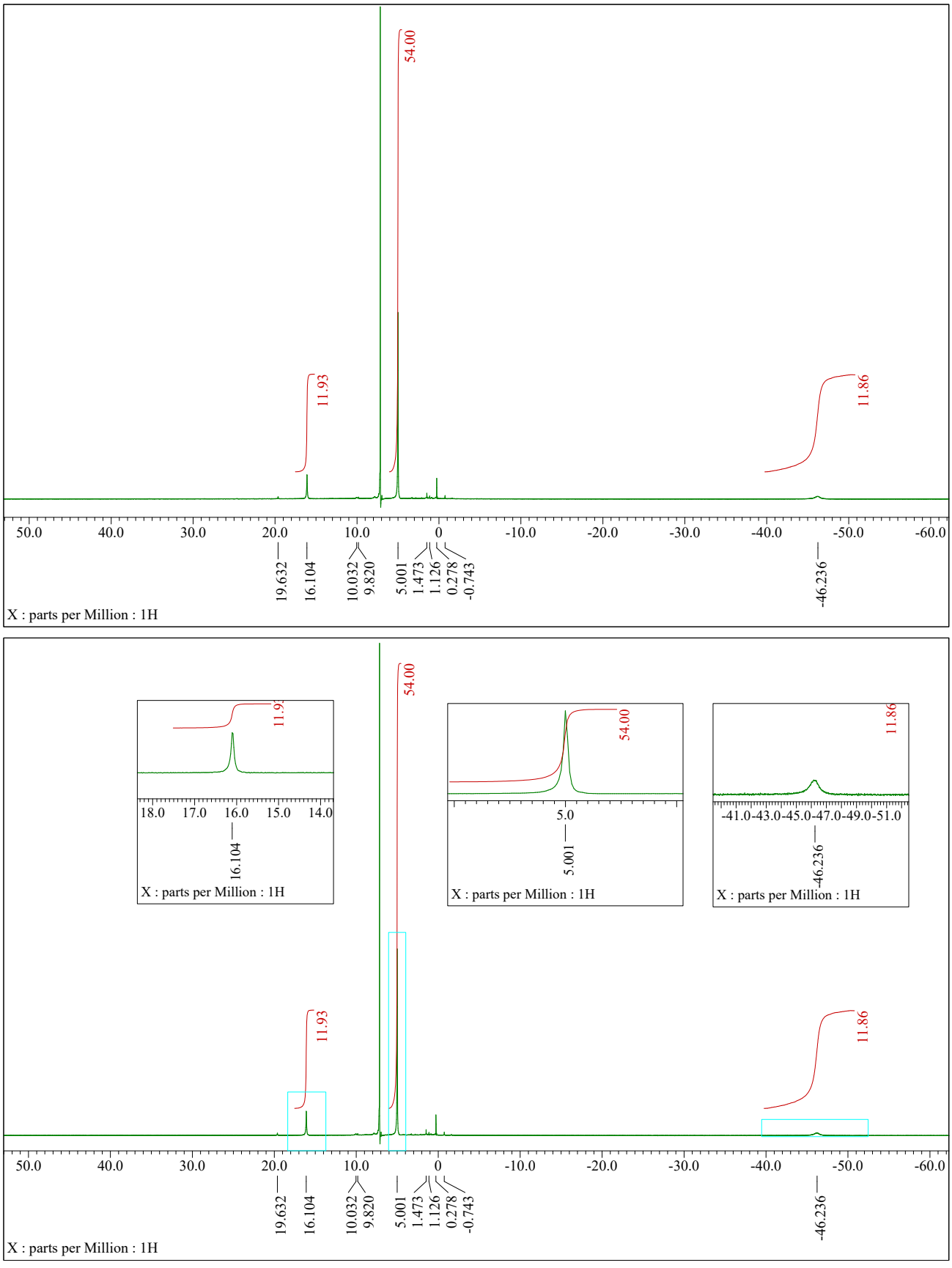


Figure S2. ^{1}H NMR spectrum of solution of **3** in C_6D_6 at room temperature.

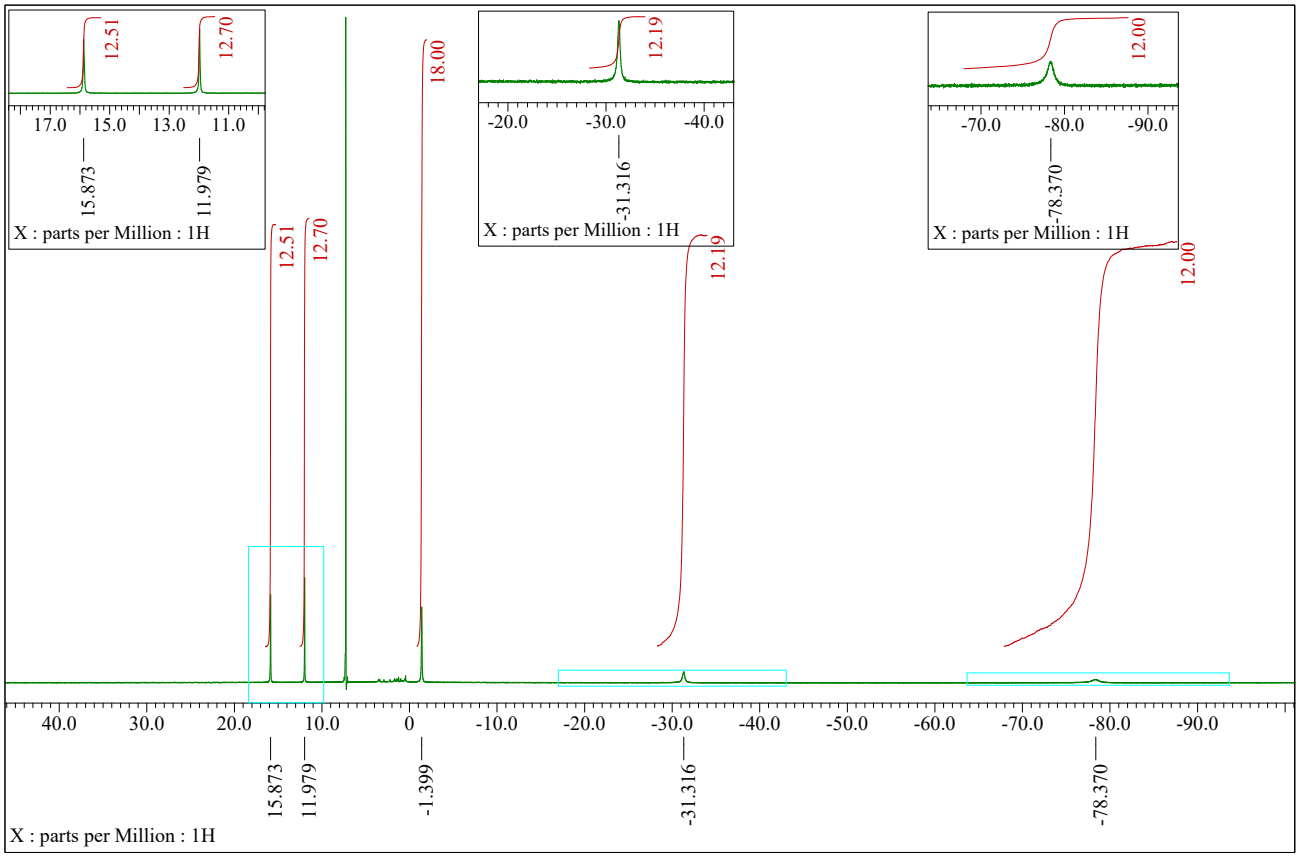


Figure S3. ^{1}H NMR spectrum of solution of **4** in C_6D_6 at room temperature.

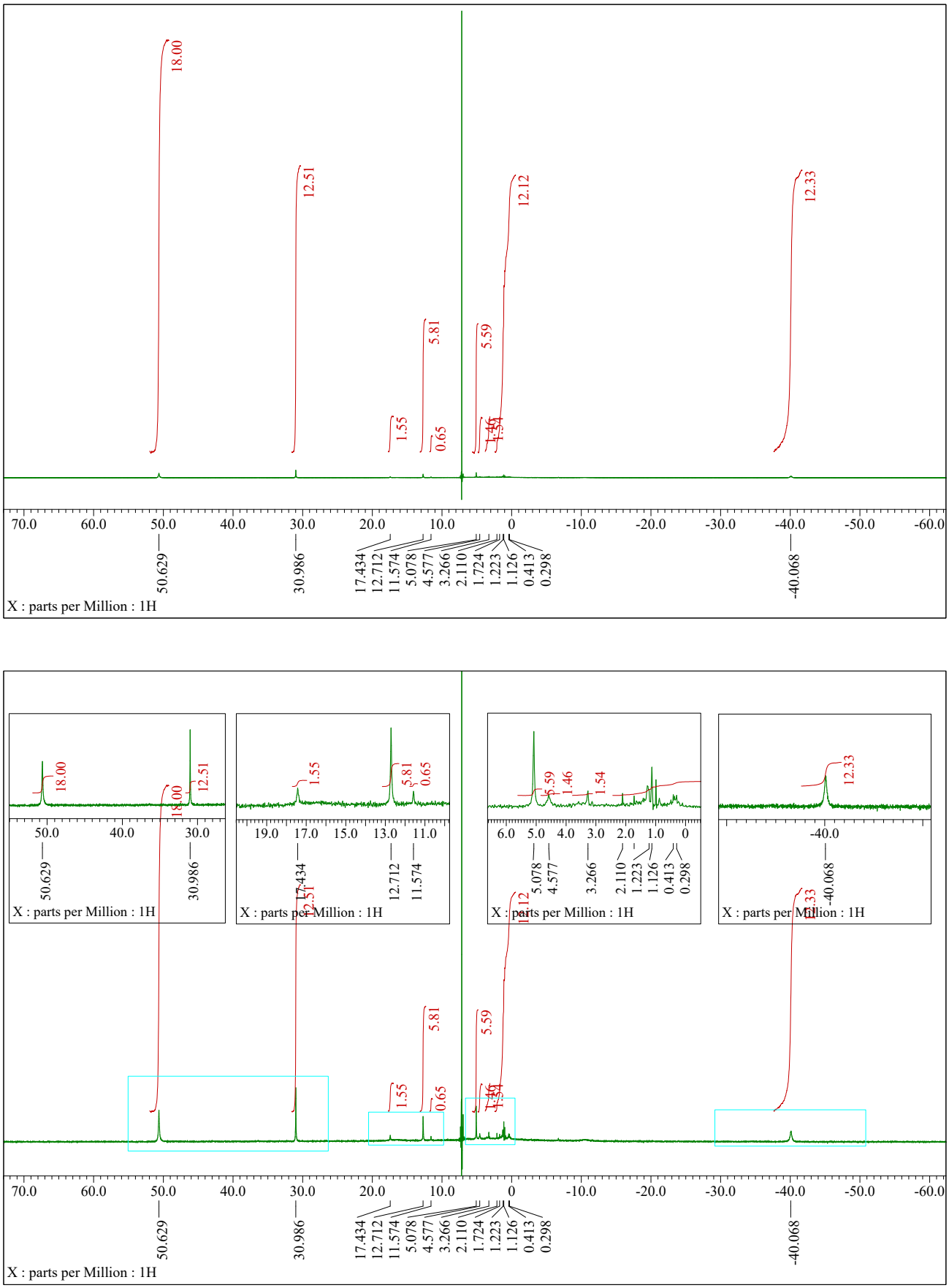


Figure S4. ^{1}H NMR spectrum of solution of silyl ether in $CDCl_3$ at room temperature.

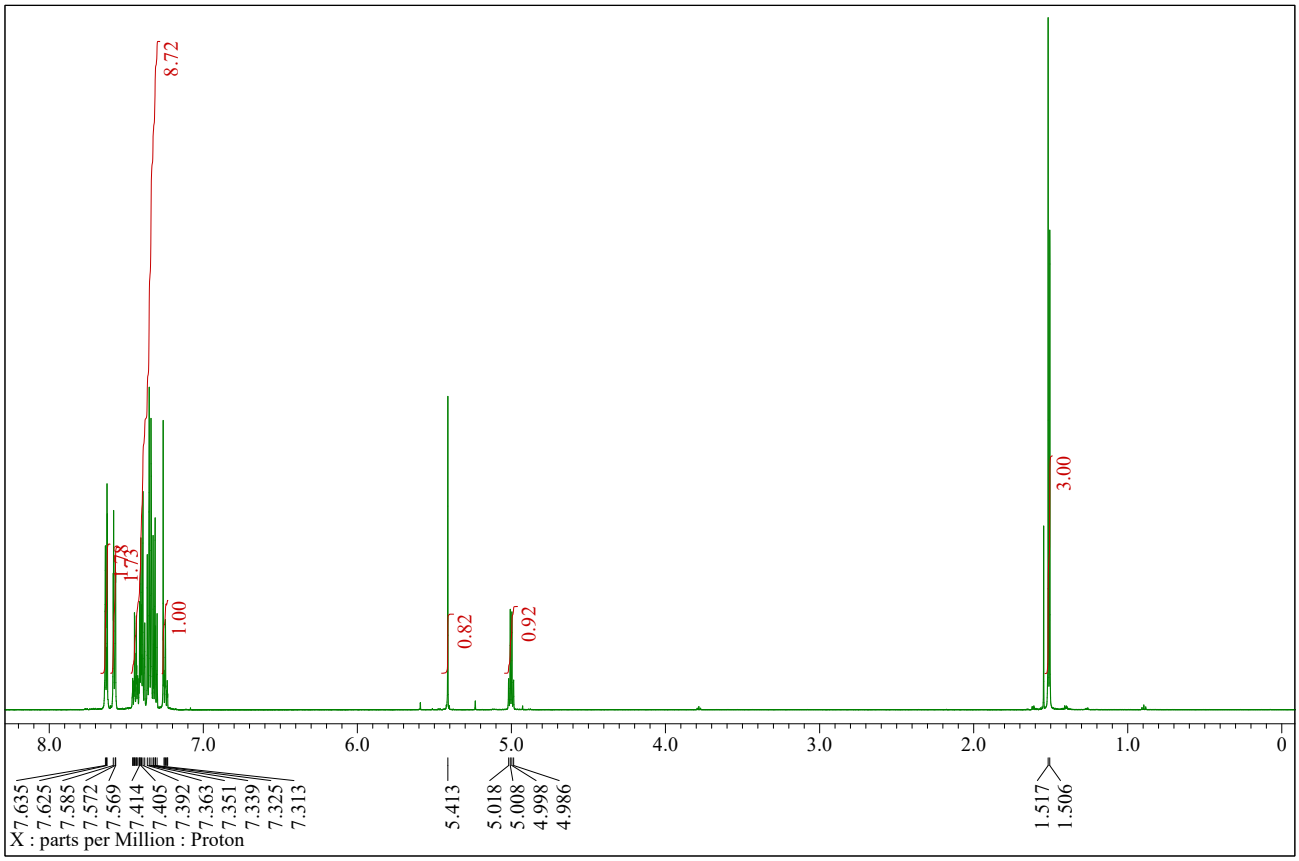


Figure S5. ^{13}C NMR spectrum of solution of silyl ether in $CDCl_3$ at room temperature.

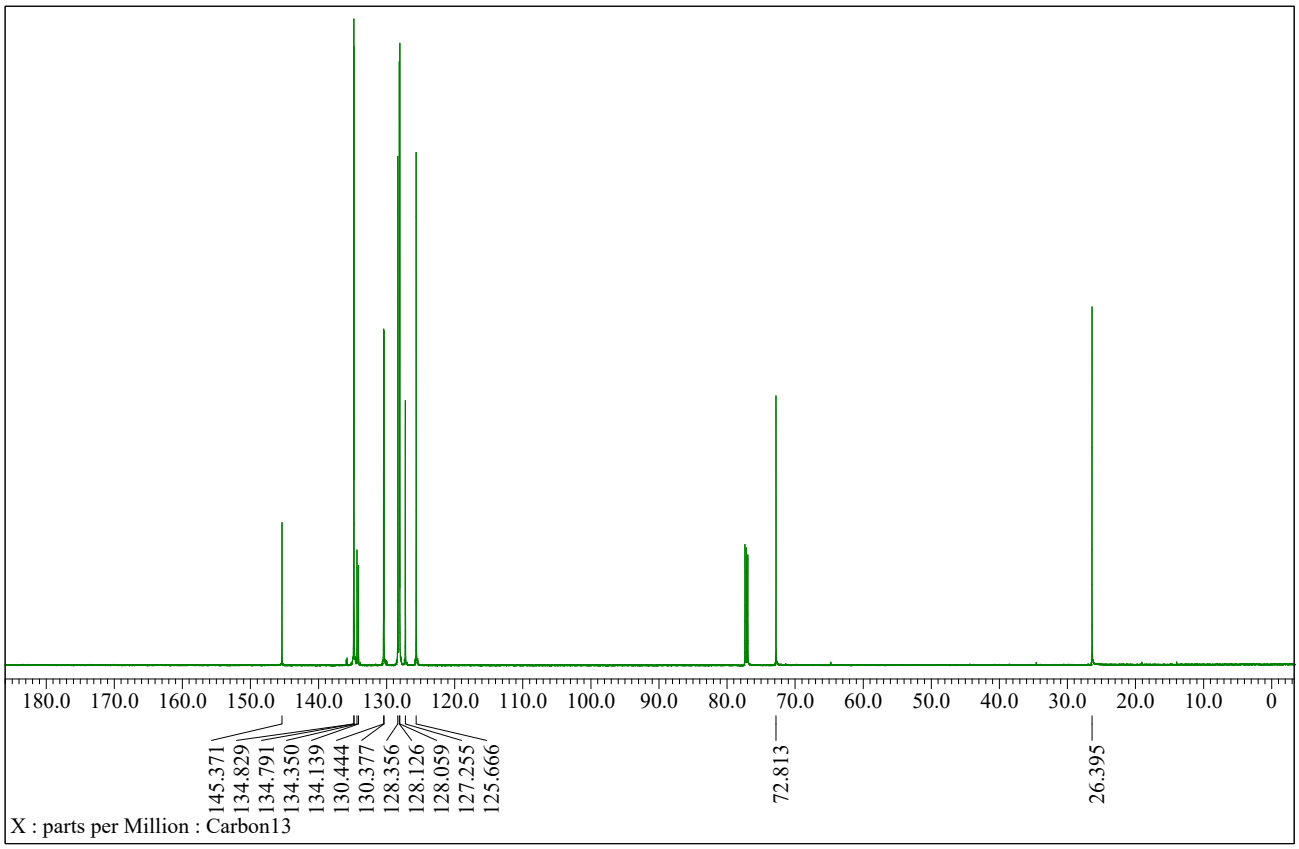
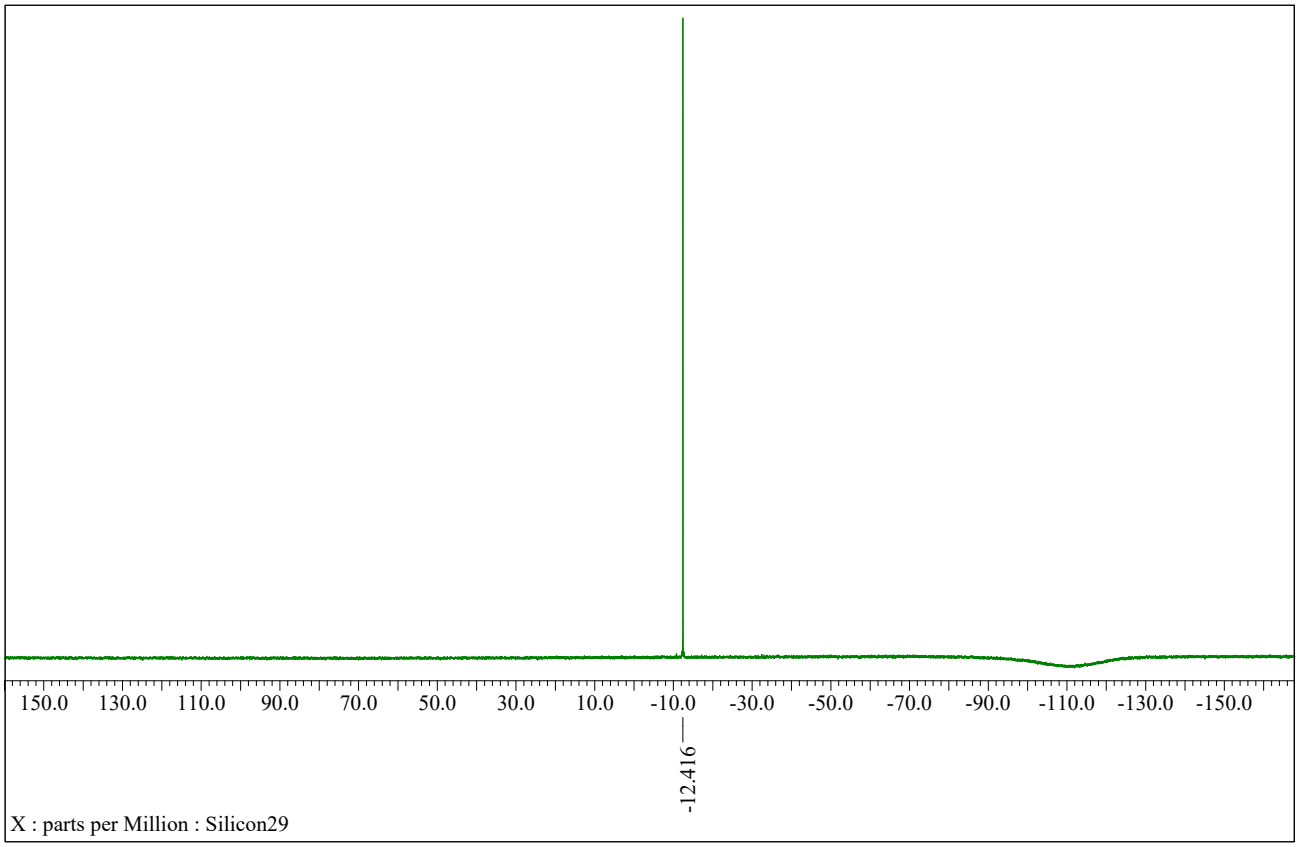


Figure S6. ^{29}Si NMR spectrum of solution of silyl ether in $CDCl_3$ at room temperature.



General procedure of theoretical calculation

All density functional theory (DFT) calculations were performed using Gaussian 16, Revision C.01. Tight convergence criterion was used for SCF cycles throughout the calculations (SCF = tight). B3PW91 functional was used with the 6-31G** basis set for H, C, N, and Si, and with the SDD basis set, which uses the Stuttgart-Dresden effective core potentials, for Fe. Unless otherwise specified, the default settings were used throughout the study. Geometry optimization for $(MeIM^{Me})_2Fe[Si(SiMe_3)_3]_2$ was performed using a single crystal XRD-determined solid-state structure as a starting geometry. For $S = 1$ spin configuration, $(MeIM^{Me})_2Fe[Si(SiMe_3)_3]_2$ resulted in a square planar geometry ($\mathbf{2}_{\mathbf{s\text{-}opt}}$). For the calculation of $S = 2$ spin configuration, initial structure was manually modified into quasi-tetrahedral structure, which was used for geometry optimization and resulted in a tetrahedral geometry ($\mathbf{2}_{\mathbf{t\text{-}opt}}$). These theoretical structural data were summarized in Figures S7 and Table S1 for $\mathbf{2}_{\mathbf{s\text{-}opt}}$ and Figure S8 and Table S3 for $\mathbf{2}_{\mathbf{t\text{-}opt}}$. For these optimized structures ($\mathbf{2}_{\mathbf{s\text{-}opt}}$ and $\mathbf{2}_{\mathbf{t\text{-}opt}}$), frequency analyses were also performed, and no-imaginary frequency was observed, confirming the local minima of these geometries. While the sum of electronic and thermal enthalpies of $\mathbf{2}_{\mathbf{s\text{-}opt}}$ = −3923.556384 Hartree, that of $\mathbf{2}_{\mathbf{t\text{-}opt}}$ = −3923.565107 Hartree, which is 0.008723 Hartree (≈ 5.47 kcal mol^{-1}) lower in energy.

Figure S7. Optimized geometry of $\mathbf{2}_{\mathbf{s\text{-}opt}}$. All hydrogen atoms are omitted for clarity.

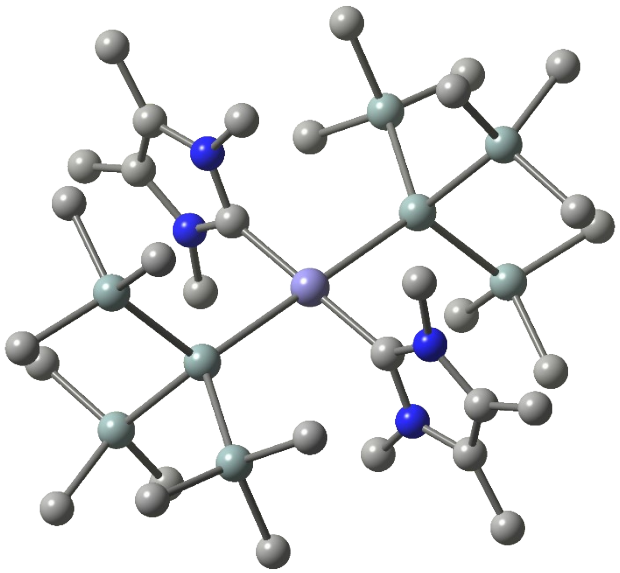


Table S1. Cartesian coordinates of optimized structures of $\mathbf{2}_{\mathbf{s\text{-}opt}}$.

Fe	-0.00000600	0.00001600	-0.00011800
Si	2.62786100	0.04044700	-0.04229000
Si	3.80040700	-1.22648600	-1.71336500
Si	3.82827100	2.12456600	-0.19471300
Si	3.63182600	-0.86237400	1.94049800

N	-0.09920900	2.84933900	-1.08564600
N	0.02411600	2.77668400	1.04963400
C	3.68145200	-0.35255700	-3.40483200
H	4.17986800	0.62222400	-3.38825700
H	4.15967800	-0.95648500	-4.18567400
H	2.64071300	-0.18424700	-3.70421700
C	3.18610400	-3.01062300	-1.99997600
H	2.98812100	-3.54114900	-1.06424900
H	2.28007200	-3.04564000	-2.60861100
H	3.96408100	-3.56286300	-2.54156600
C	5.65785100	-1.49569200	-1.37744200
H	5.80991200	-2.16904500	-0.52745500
H	6.10540300	-1.97655000	-2.25684200
H	6.21138600	-0.57629000	-1.18071100
C	3.25643600	3.28739000	-1.59275500
H	3.17785400	2.77050400	-2.55445300
H	2.29199800	3.74388500	-1.35968800
H	3.98834100	4.09610200	-1.70924600
C	3.68896000	3.15616500	1.40460100
H	4.04762400	2.61233200	2.28433300
H	4.29257300	4.06735800	1.31046500
H	2.65605600	3.46263100	1.59278500
C	5.70111900	1.98161100	-0.52717300
H	6.22822300	1.34020900	0.18231100
H	5.90285600	1.61152800	-1.53737700
H	6.13669800	2.98673700	-0.45687400
C	2.79577700	-0.27997000	3.55718400
H	2.99514600	0.78471700	3.72355900
H	1.71236200	-0.42105700	3.57481800
H	3.21904100	-0.82291000	4.41163200
C	5.45856400	-0.40355700	2.23208700
H	6.10476500	-0.71721400	1.40799400
H	5.59734300	0.67164800	2.38031300
H	5.80840100	-0.90886600	3.14155100
C	3.62906700	-2.77122300	1.92036500
H	4.41689300	-3.13507900	1.25202200
H	3.83794500	-3.17268300	2.91989600
H	2.68687500	-3.19442800	1.56314700

C	-0.01189800	1.97295200	-0.04842800
C	-0.05513100	2.45793300	-2.47728700
H	-1.00729900	2.65026700	-2.97744600
H	0.74316800	2.99369700	-2.99712400
H	0.16427400	1.39031900	-2.51388000
C	-0.13473900	4.17376800	-0.64565500
C	-0.24663500	5.32588300	-1.58131700
H	-1.15323200	5.26448200	-2.19448800
H	-0.28913900	6.26371300	-1.02346400
H	0.61114000	5.38662500	-2.26177400
C	-0.05119700	4.12735900	0.71405100
C	-0.04052600	5.22373700	1.71985800
H	0.88171500	5.22921600	2.31261400
H	-0.11051900	6.19149700	1.21861400
H	-0.88743900	5.14960000	2.41166000
C	0.19250700	2.22985800	2.37947300
H	0.11704800	3.02293300	3.12416800
H	-0.58812200	1.48919900	2.57650100
H	1.17067300	1.74994800	2.46544200
Si	-2.62787100	-0.04046000	0.04227600
Si	-3.80039600	1.22657100	1.71331700
Si	-3.82829800	-2.12456400	0.19488000
Si	-3.63185800	0.86228000	-1.94056400
N	0.09907600	-2.84924400	1.08557600
N	-0.02396800	-2.77675200	-1.04972100
C	-3.68152500	0.35258100	3.40476500
H	-4.18011500	-0.62211200	3.38815500
H	-4.15963300	0.95655300	4.18564400
H	-2.64081200	0.18406700	3.70412300
C	-3.18604700	3.01067700	2.00003000
H	-2.98818100	3.54130500	1.06433500
H	-2.27994800	3.04564200	2.60856800
H	-3.96397400	3.56284600	2.54176700
C	-5.65783100	1.49585100	1.37741200
H	-5.80992500	2.16910700	0.52735500
H	-6.10531400	1.97682600	2.25678400
H	-6.21140400	0.57644000	1.18083600
C	-3.25660000	-3.28731500	1.59303500

H	-3.17814800	-2.77039400	2.55472600
H	-2.29213400	-3.74381600	1.36011400
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C	-3.68888700	-3.15631000	-1.40433300
H	-4.04734600	-2.61251700	-2.28417400
H	-4.29261300	-4.06742900	-1.31021500
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H	-5.90285600	-1.61174900	1.53759400
H	-6.13682700	-2.98661100	0.45667700
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H	-1.71237100	0.42101100	-3.57484400
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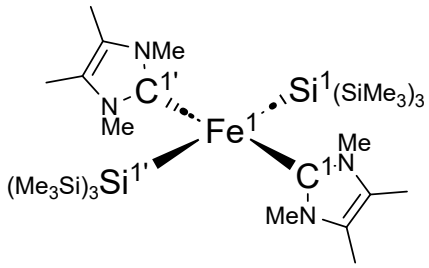
H	-6.10478800	0.71723100	-1.40810300
H	-5.59737700	-0.67180200	-2.38018500
H	-5.80842000	0.90858800	-3.14168900
C	-3.62912000	2.77112400	-1.92042300
H	-4.41697100	3.13496300	-1.25209800
H	-3.83796200	3.17261300	-2.91994900
H	-2.68694100	3.19431600	-1.56315900
C	0.01192900	-1.97293400	0.04828000
C	0.05496700	-2.45771400	2.47718200
H	1.00721100	-2.64974400	2.97731000
H	-0.74315500	-2.99364800	2.99711300
H	-0.16473300	-1.39015500	2.51368300
C	0.13469000	-4.17370700	0.64569200
C	0.24657300	-5.32575100	1.58144400
H	1.15312000	-5.26425800	2.19468100
H	0.28917100	-6.26361800	1.02366100
H	-0.61124900	-5.38649600	2.26184100
C	0.05130000	-4.12740200	-0.71402800
C	0.04077200	-5.22385000	-1.71975700
H	-0.88138400	-5.22937400	-2.31264500
H	0.11070600	-6.19157500	-1.21843600
H	0.88778100	-5.14976400	-2.41144800

C	-0.19229200	-2.23006700	-2.37962300
H	-0.11570000	-3.02305200	-3.12430200
H	0.58775200	-1.48868400	-2.57624100
H	-1.17085900	-1.75106800	-2.46609100

Table S2. Actual and calculated bond distances and angles for $\mathbf{2}_{\mathbf{s\text{-}opt}}$.



	Actual bond distances / angles	Calculated bond distances / angles
Si(1)-Fe(1)	2.5385 Å	2.6285 Å
C(1)-Fe(1)	1.956 Å	1.9736 Å
Si(1)-Fe(1)-C(1)	92.65 °	90.56 °
Si(1)-Fe(1)-C(1')	87.35 °	89.44 °

Figure S8. Optimized geometry of $\mathbf{2}_{\text{t-opt}}$. All hydrogen atoms are omitted for clarity.

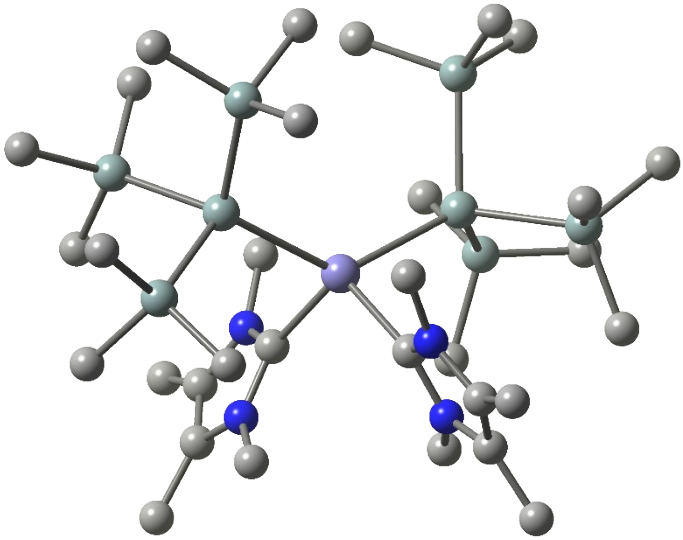


Table S3. Cartesian coordinates of optimized structures of $\mathbf{2}_{\text{t-opt}}$.

Fe	-0.00442800	-0.04675400	-0.28417700
Si	2.46251200	0.33785300	0.79858600
Si	3.95580300	-1.52291700	0.66932600
Si	3.80417200	2.09777700	-0.12349100
Si	2.58194200	0.81499600	3.13359400
N	-0.31026600	2.88718100	-1.47548400
N	-1.04671000	1.50612500	-2.92289300
C	4.59701900	-1.86579400	-1.09766000
C	3.12369100	-3.15063900	1.20687600
C	5.51897400	-1.38455600	1.75055400
C	3.45184600	2.36936700	-1.98154200
C	3.54673500	3.79794600	0.72864800
C	5.69112500	1.84136300	-0.03692100
C	1.16853800	1.97799800	3.64833500
C	4.18936400	1.65698600	3.71668100
C	2.45116900	-0.76590300	4.18926200
C	-0.46956200	1.55460400	-1.68957200
C	0.20946800	3.45292600	-0.24642000
C	-0.77224400	3.65504400	-2.53723400
C	-0.72300900	5.14196700	-2.54089600

C	-1.24316400	2.77136300	-3.46429800
C	-1.86370100	2.99382200	-4.79827000
C	-1.43609700	0.28443700	-3.59674800
Si	-2.48411600	-0.25766900	0.80376200
Si	-3.59472200	1.79799800	1.32285900
Si	-2.75598800	-1.46100900	2.85902800
Si	-4.13534600	-1.25283000	-0.61349900
N	1.24531600	-1.85479700	-2.63162700
N	0.25491400	-3.10100300	-1.21291600
C	-2.78531900	2.67216800	2.80774500
C	-3.58716400	3.05655800	-0.11027400
C	-5.44756700	1.64788700	1.74880400
C	-1.43725900	-0.95357900	4.12507300
C	-2.58149600	-3.35362800	2.65711500
C	-4.41461800	-1.21453000	3.76351800
C	-3.47872400	-2.71111700	-1.65939800
C	-5.65396600	-1.97497800	0.28298600
C	-4.85929300	-0.00304000	-1.86407300
C	0.50662300	-1.79440800	-1.48870100
C	1.81484200	-0.70036900	-3.29543300
C	1.45450300	-3.16191000	-3.05673100
C	2.23536200	-3.50067800	-4.27752000
C	0.82046500	-3.95883800	-2.14752900
C	0.69333700	-5.43912900	-2.06678500
C	-0.46586700	-3.55217400	-0.03958100
H	4.99473200	-0.96921200	-1.58388300
H	5.40053400	-2.61199300	-1.06770300
H	3.79516600	-2.27156600	-1.72253800
H	2.66073600	-3.06868400	2.19480300
H	2.34962100	-3.43672200	0.48909400
H	3.86129900	-3.96174300	1.24635000
H	5.27588400	-1.28473300	2.81240300
H	6.12101000	-2.29485600	1.63431400
H	6.14478000	-0.53332600	1.46995600
H	3.77770600	1.50368300	-2.56815000
H	2.38818900	2.52945700	-2.18526900
H	4.00509400	3.24167900	-2.35153400
H	4.34663900	3.96992000	1.45627200

H	3.60328600	4.61065400	-0.00639200
H	2.60023100	3.89329500	1.26667600
H	6.03548100	1.78232200	1.00017700
H	6.02300400	0.93577800	-0.55356300
H	6.19578400	2.69572300	-0.50607500
H	1.26901200	2.95794000	3.16807800
H	0.19668100	1.56305500	3.36725200
H	1.16759100	2.14128900	4.73294400
H	5.07845900	1.07879500	3.44824200
H	4.30071500	2.66046300	3.29632100
H	4.17341600	1.75679600	4.80944000
H	3.37204700	-1.35499700	4.12864500
H	2.29568100	-0.50356700	5.24286100
H	1.62492200	-1.41326400	3.88410700
H	-0.43168800	-1.04367100	3.70797500
H	-0.58359700	3.96377900	0.30748800
H	0.60721600	2.63785200	0.36077100
H	1.01333500	4.15834500	-0.46398300
H	-1.30093600	5.56673300	-1.71235700
H	0.30346100	5.51652500	-2.45613100
H	-1.14208700	5.53355500	-3.47007700
H	-2.88668000	2.60233500	-4.84199500
H	-1.91136100	4.06187200	-5.02000300
H	-1.29236600	2.51539800	-5.60249600
H	-0.88242100	0.16518200	-4.53331700
H	-1.21712900	-0.55217000	-2.93466000
H	-2.50559400	0.29064600	-3.81915600
H	-2.87329100	2.07421100	3.72080000
H	-3.27459700	3.63593800	2.99617200
H	-1.71962700	2.86009600	2.64410400
H	-2.58370100	3.26438500	-0.48593100
H	-4.02763400	4.00181700	0.23148700
H	-4.18462600	2.69967100	-0.95445200
H	-6.02784900	1.27164400	0.90022800
H	-5.83956200	2.64246500	1.99765500
H	-5.63908100	0.99064600	2.59974700
H	-1.56617700	0.08553800	4.44398500
H	-1.49369200	-1.58577100	5.01977400

H	-3.18284900	-3.75310900	1.83390400
H	-2.91560700	-3.84554100	3.57877200
H	-1.54044600	-3.64978300	2.49482900
H	-5.28299100	-1.45230700	3.14348900
H	-4.52401400	-0.18621800	4.12186700
H	-4.43879000	-1.87101000	4.64263500
H	-3.32129900	-3.59391000	-1.03081300
H	-2.53296800	-2.48494100	-2.16155600
H	-4.21473300	-2.98518200	-2.42535700
H	-6.19121400	-1.20975700	0.85087700
H	-5.37701800	-2.77302700	0.97929900
H	-6.35177900	-2.40061100	-0.44932900
H	-5.54458300	0.69162700	-1.36806200
H	-5.42840700	-0.52777800	-2.64160900
H	-4.08761000	0.59964300	-2.35142100
H	2.90604600	-0.75834900	-3.28977100
H	1.50952200	0.19193500	-2.75069400
H	1.46748000	-0.63814500	-4.33130100
H	1.79088400	-3.06928500	-5.18220300
H	2.27299500	-4.58338200	-4.41433500
H	3.26837700	-3.14024700	-4.21188300
H	-0.35184000	-5.76296000	-2.13167900
H	1.10304600	-5.82931700	-1.12833100
H	1.23745000	-5.91256000	-2.88660900
H	-1.23412500	-4.27526900	-0.31878800
H	-0.94410700	-2.68452600	0.41644500
H	0.21927000	-4.00992200	0.67980100

Figure S9. Optimized geometry of **3**. All hydrogen atoms are omitted for clarity.

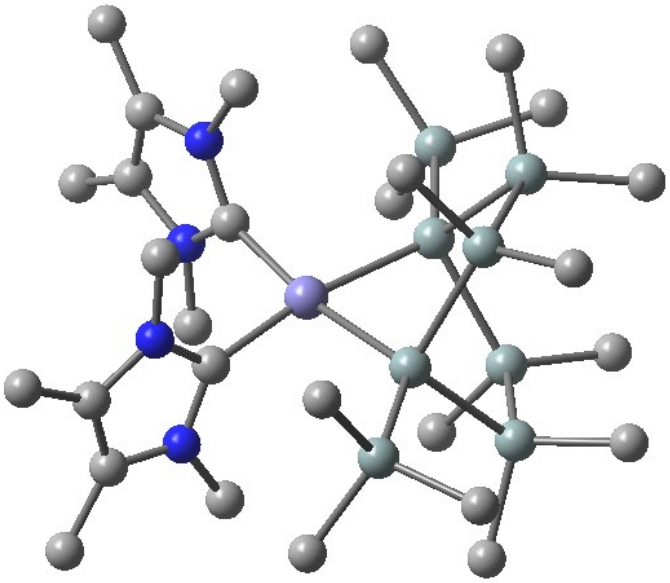


Table S4. Cartesian coordinates of optimized structures of **3**.

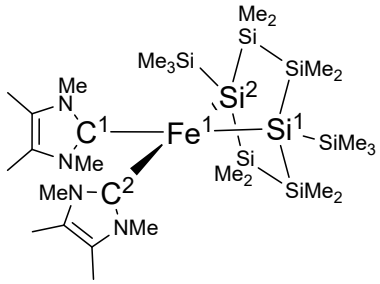
Fe	-0.0000030	0.7071580	-0.0000780
Si	1.6693940	-1.1127630	-0.1661760
Si	1.3386640	-2.6694410	1.5980310
Si	-0.9315980	-2.2590870	2.1073490
Si	-1.6695130	-1.1126230	0.1662060
Si	-1.3388720	-2.6692110	-1.5980930
Si	0.9314470	-2.2590700	-2.1073550
Si	4.0251180	-0.8771050	-0.3910600
Si	-4.0252650	-0.8769450	0.3909600
N	2.0948930	2.4938400	1.2935120
N	1.9941080	2.8482120	-0.8127500
N	-1.9938610	2.8481860	0.8129070
N	-2.0945840	2.4945040	-1.2934770
C	4.8408860	0.2064320	0.9519040
H	5.9330030	0.1768640	0.8506510
H	4.5906430	-0.1453020	1.9583490
H	4.5262710	1.2513620	0.8633890
C	4.5436690	-0.1048850	-2.0573770
H	4.2326950	-0.7293260	-2.9012890
H	5.6341290	0.0048790	-2.1087630

H	4.1013120	0.8873890	-2.1956130
C	4.9093020	-2.5616410	-0.2896840
H	5.9865650	-2.4427800	-0.4616380
H	4.5247510	-3.2669620	-1.0326660
H	4.7795050	-3.0197540	0.6964870
C	2.4358290	-2.2720040	3.1186210
H	2.2858910	-1.2495660	3.4794200
H	3.4986420	-2.3904230	2.8791560
H	2.2050750	-2.9527370	3.9465830
C	1.6949880	-4.5050530	1.2070520
H	1.0789500	-4.8741240	0.3825310
H	1.4910760	-5.1305390	2.0842730
H	2.7446750	-4.6480280	0.9282800
C	-0.9758420	-1.1010160	3.6372950
H	-0.6190510	-1.6296470	4.5289970
H	-1.9926370	-0.7474710	3.8405720
H	-0.3366810	-0.2225640	3.4990120
C	-1.9209920	-3.8020030	2.6514440
H	-1.4417190	-4.2809840	3.5137420
H	-1.9954950	-4.5437560	1.8516690
H	-2.9392120	-3.5272740	2.9499390
C	-4.8408630	0.2068790	-0.9518550
H	-4.5255570	1.2516240	-0.8636620
H	-5.9329580	0.1780000	-0.8501730
H	-4.5912280	-0.1451970	-1.9583440
C	-4.5440360	-0.1050830	2.0573730
H	-5.6345590	0.0040380	2.1088500
H	-4.1022780	0.8874600	2.1956340
H	-4.2326380	-0.7293640	2.9012460
C	-4.9094870	-2.5614390	0.2892900
H	-4.7788720	-3.0199760	-0.6965640
H	-5.9868830	-2.4424420	0.4603010
H	-4.5256130	-3.2664720	1.0329000
C	-2.4356550	-2.2712200	-3.1188360
H	-3.4985880	-2.3891030	-2.8796340
H	-2.2050480	-2.9520920	-3.9467310
H	-2.2851130	-1.2488690	-3.4796290
C	-1.6957300	-4.5048260	-1.2076390

H	-2.7453820	-4.6475330	-0.9286300
H	-1.0795890	-4.8744300	-0.3834310
H	-1.4922630	-5.1300530	-2.0851490
C	0.9756580	-1.1007520	-3.6371130
H	0.6185670	-1.6290780	-4.5288720
H	1.9925070	-0.7474070	-3.8404880
H	0.3367490	-0.2221670	-3.4984930
C	1.9208710	-3.8018500	-2.6517920
H	2.9387140	-3.5267440	-2.9512480
H	1.4410600	-4.2812430	-3.5135610
H	1.9963700	-4.5433590	-1.8518950
C	1.4692260	2.0547460	0.1638610
C	1.9302150	1.8745720	2.5905290
H	1.3941800	0.9351840	2.4408740
H	1.3678290	2.5159020	3.2774350
H	2.9052080	1.6500420	3.0303260
C	2.9851520	3.5360530	1.0307840
C	3.8093920	4.1766670	2.0912980
H	4.5230110	3.4722440	2.5351350
H	3.1921430	4.5772580	2.9039390
H	4.3850250	5.0061960	1.6748400
C	2.9197370	3.7623590	-0.3104650
C	3.6468130	4.7334020	-1.1722240
H	4.2747650	5.3847500	-0.5605220
H	2.9610310	5.3734480	-1.7396390
H	4.3027740	4.2306440	-1.8931280
C	1.6083700	2.7459800	-2.2023670
H	0.8536070	3.4953160	-2.4647870
H	1.2041670	1.7462500	-2.3721950
H	2.4783740	2.8767270	-2.8501050
C	-1.4690510	2.0549380	-0.1639310
C	-1.6084300	2.7452560	2.2025570
H	-2.4785760	2.8757130	2.8501650
H	-0.8537000	3.4944340	2.4655320
H	-1.2043160	1.7454190	2.3719760
C	-3.6462160	4.7335870	1.1728770
H	-4.2742040	5.3850760	0.5613640
H	-2.9602490	5.3734860	1.7402390

H	-4.3021050	4.2308340	1.8938480
C	-2.9193850	3.7625790	0.3108720
C	-2.9847390	3.5367300	-1.0304560
C	-3.8088640	4.1777700	-2.0907990
H	-4.3847130	5.0069870	-1.6740190
H	-4.5222940	3.4734620	-2.5351200
H	-3.1915350	4.5788760	-2.9031260
C	-1.9299530	1.8755890	-2.5906690
H	-1.3938980	0.9361730	-2.4412960
H	-1.3676150	2.5171150	-3.2774370
H	-2.9049600	1.6511440	-3.0304820

Table S5. Actual and calculated bond distances and angles for **3**.



	Actual bond distances / angles	Calculated bond distances / angles
Si(1)-Fe(1)	2.4091(6) Å	2.47518 Å
Si(2)-Fe(1)	2.4260(6) Å	2.47519 Å
C(1)-Fe(1)	1.987(1) Å	2.00038 Å
C(2)-Fe(1)	1.980(1) Å	2.00037 Å
Si(1)-Fe(1)-Si(2)	85.99(2) °	85.34539 °
C(1)-Fe(1)-C(2)	95.96(6) °	95.29077 °
Si(1)-Fe(1)-C(2)	89.74(4) °	90.31615 °
Si(2)-Fe(1)-C(1)	89.67(4) °	90.31252 °

X-ray data collection and reduction

X-ray crystallography for compounds **2** and **3** were performed on a Rigaku Saturn CCD area detector with graphite monochromated Mo-Kα radiation (λ=0.71075 Å), and single crystals of **4** suitable for X-ray crystallography were analyzed by synchrotron radiation at beam line BL02B1 (λ = 0.41440 Å) of Spring-8 (Hyogo, Japan) using PILATUS3 X CdTe 1M detector. The data were collected at 123 K for **2**, **3** and 133 K for **4** and using ω scan in the θ range of $2.31 \leq \theta \leq 31.27$ deg (**2**), $2.19 \leq \theta \leq 31.29$ deg (**3**), $0.76 \leq \theta \leq 15.57$ 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[5], 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 6744 observed reflections and 218 variable parameters for **2**, 12586 observed reflections and 392 variable parameters for **3**, 10,527 observed reflections and 444 variable parameters for **4**. Neutral atom scattering factors were taken from International Tables for Crystallography (IT), Vol. C, Table 6.1.1.4[6]. Anomalous dispersion effects were included in F_{calc}[7]; the values for Δf' and Δf'' were those of Creagh and McAuley[8]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[9]. All calculations were performed using the CrystalStructure[10] crystallographic software package except for refinement, which was performed using SHELXL Version 2017/1[11]. Details of final refinement as well as the bond lengths and angle are summarized in Tables S6, S7 and S8, and the numbering scheme employed is also shown in Figures S10, S11 and S12, which were drawn with ORTEP at 50% probability ellipsoids. CCDC 2258218 (**2**), 2258219 (**3**) and 2258220 (**4**) contain the supplementary crystallographic data for this paper.

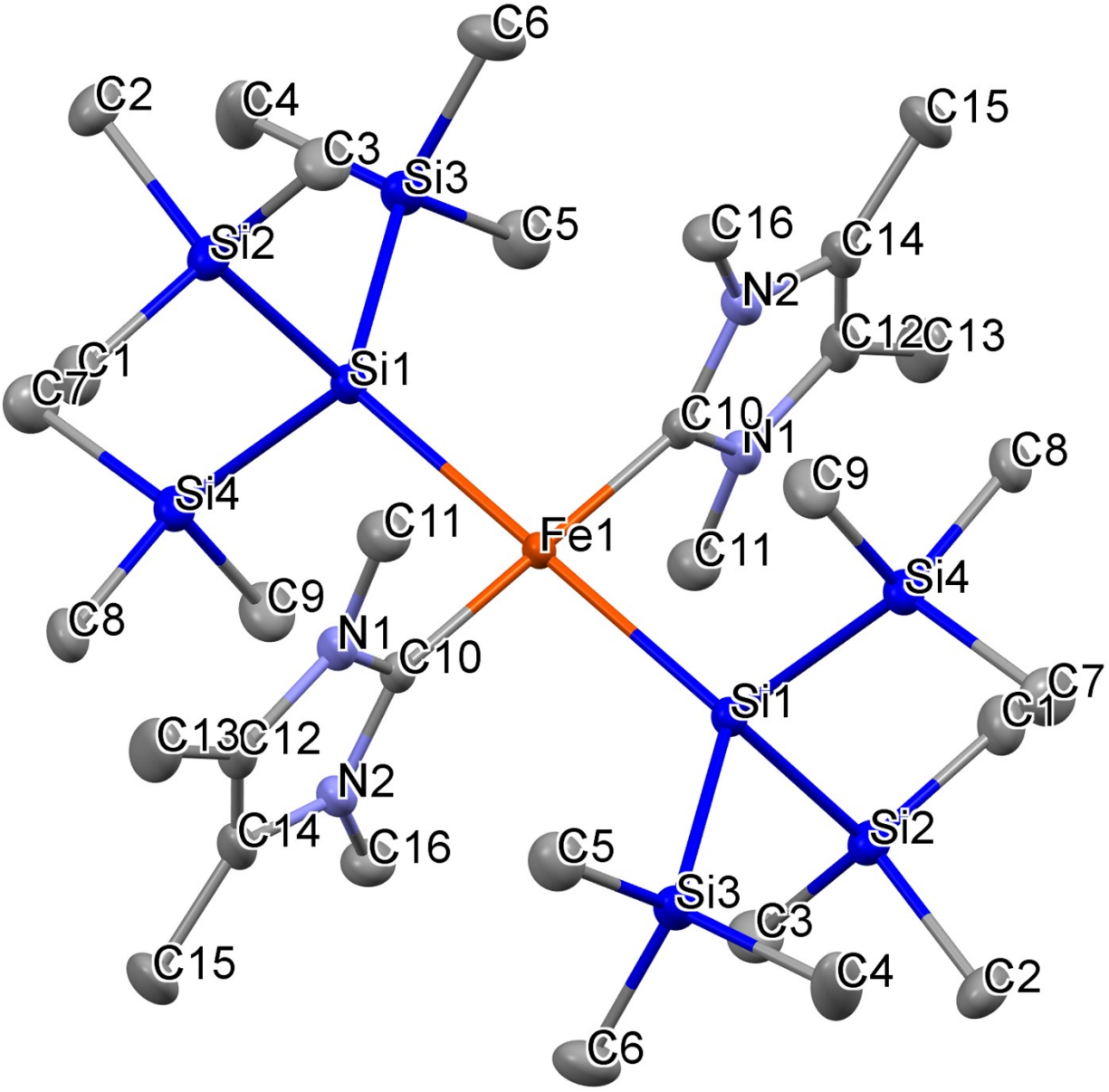


Figure S10. ORTEP drawing of **2** (50% probability of the thermal ellipsoids). Hydrogen atoms were omitted for clarity.

Table S6. Crystal data and structure refinement for **2**.

Empirical Formula	$C_{32}H_{78}FeN_4Si_8$
Formula Weight	799.53
Crystal Color, Habit	red, block
Crystal Dimensions	0.500 X 0.500 X 0.500 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 9.4550(3) Å
	b = 11.6117(3) Å
	c = 11.8561(3) Å
	α = 95.209(2) °
	β = 109.339(3) °
	γ = 105.223(2) °
	V = 1162.32(6) Å^3
Space Group	P-1 (#2)
Z value	1
D_{calc}	1.142 g/cm^3
F_{000}	436.00
μ(MoKα)	5.557 cm^{-1}
Diffractometer	Saturn724
Radiation	MoKα (λ = 0.71075 Å)
	graphite monochromated
Voltage, Current	50kV, 24mA
Temperature	-150.0°C
Detector Aperture	72.8 x 72.8 mm
Data Images	1440 exposures
ω oscillation Range (χ=45.0, ϕ=0.0)	-70.0 - 110.0°
Exposure Rate	2.0 sec./°
Detector Swing Angle	20.00°
ω oscillation Range (χ=45.0, ϕ=90.0)	-70.0 - 110.0°
Exposure Rate	2.0 sec./°
Detector Swing Angle	20.00°
ω oscillation Range (χ=45.0, ϕ=180.0)	-70.0 - 110.0°
Exposure Rate	2.0 sec./°
Detector Swing Angle	20.00°
ω oscillation Range (χ=45.0, ϕ=270.0)	-70.0 - 110.0°
Exposure Rate	2.0 sec./°
Detector Swing Angle	20.00°

Detector Position	45.00 mm
Pixel Size	0.035 mm
$2\theta_{max}$	62.4°
No. of Reflections Measured	Total: 19300
	Unique: 6744 (R_{int} = 0.0672)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.243 - 0.757)
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	$w = 1/ [\sigma^2(Fo^2) + (0.0748 \cdot P)^2 + 0.1103 \cdot P]$
	where $P = (Max(Fo^2,0) + 2Fc^2)/3$
$2\theta_{max}$ cutoff	62.4°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	6744
No. Variables	218
Reflection/Parameter Ratio	30.94
Residuals: R1(I>2.00σ(I))	0.0449
Residuals: R (All reflections)	0.0505
Residuals: wR2 (All reflections)	0.1233
Goodness of Fit Indicator	1.072
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.87 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.85 $e^-/Å^3$

Atomic coordinates and B_{iso}/B_{eq} and occupancy

atom	x	y	z	B_{eq}	occ
Fe1	0.50000	0.50000	0.50000	1.117(7)	1/2
Si1	0.33740(4)	0.32428(3)	0.32077(3)	1.244(8)	1
Si2	0.47500(5)	0.24754(4)	0.21330(4)	1.603(8)	1
Si3	0.17849(5)	0.13730(4)	0.34085(4)	1.641(9)	1
Si4	0.15066(5)	0.37940(4)	0.16587(3)	1.587(8)	1
N1	0.31575(15)	0.38747(11)	0.64332(11)	1.596(19)	1
N2	0.49671(15)	0.30680(11)	0.65394(11)	1.70(2)	1
C1	0.5440(2)	0.35322(16)	0.11718(15)	2.31(3)	1
C2	0.3602(2)	0.09863(15)	0.10213(15)	2.51(3)	1
C3	0.65052(19)	0.21297(16)	0.31907(15)	2.30(3)	1
C4	0.0333(2)	0.03752(17)	0.19130(16)	3.28(4)	1
C5	0.04849(19)	0.15062(16)	0.42789(16)	2.39(3)	1
C6	0.2957(2)	0.03955(15)	0.41750(17)	2.73(3)	1
C7	0.0062(2)	0.25906(16)	0.02984(15)	2.83(3)	1
C8	0.2449(2)	0.49878(15)	0.09351(14)	2.24(3)	1
C9	0.02369(19)	0.43857(16)	0.23444(16)	2.46(3)	1
C10	0.43598(17)	0.39206(12)	0.60381(12)	1.45(2)	1
C11	0.20449(19)	0.45299(15)	0.59966(15)	2.13(3)	1
C12	0.30400(19)	0.30291(13)	0.71884(13)	1.96(2)	1
C13	0.1815(2)	0.28198(17)	0.77413(17)	2.86(3)	1
C14	0.4178(2)	0.25258(13)	0.72576(13)	2.03(3)	1
C15	0.4644(3)	0.15809(16)	0.79323(17)	3.06(3)	1
C16	0.63081(19)	0.28079(15)	0.63799(15)	2.27(3)	1

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

Anisotropic displacement parameters

Atom	U11	U22	U33	U12	U13	U23
Fe1	0.01812(14)	0.01231(14)	0.01107(14)	0.00367(10)	0.00494(10)	0.00273(10)
Si1	0.01825(18)	0.01429(18)	0.01231(18)	0.00377(14)	0.00366(14)	0.00242(13)
Si2	0.0227(2)	0.0199(2)	0.01717(19)	0.00753(15)	0.00584(15)	0.00141(15)
Si3	0.0231(2)	0.01560(19)	0.01766(19)	0.00073(15)	0.00433(15)	0.00231(15)
Si4	0.0215(2)	0.0209(2)	0.01546(19)	0.00814(15)	0.00276(15)	0.00264(15)
N1	0.0281(6)	0.0165(5)	0.0167(6)	0.0034(5)	0.0114(5)	0.0048(4)
N2	0.0314(7)	0.0160(5)	0.0164(6)	0.0065(5)	0.0081(5)	0.0052(4)
C1	0.0329(8)	0.0340(9)	0.0230(7)	0.0099(7)	0.0130(6)	0.0065(6)
C2	0.0396(9)	0.0270(8)	0.0256(8)	0.0108(7)	0.0101(7)	-0.0030(6)

C3	0.0286(8)	0.0301(8)	0.0299(8)	0.0149(6)	0.0078(6)	0.0058(6)
C4	0.0486(11)	0.0280(9)	0.0240(8)	-0.0145(8)	0.0053(8)	0.0005(7)
C5	0.0271(8)	0.0288(8)	0.0309(8)	0.0017(6)	0.0108(6)	0.0061(7)
C6	0.0388(9)	0.0214(8)	0.0440(10)	0.0103(7)	0.0137(8)	0.0120(7)
C7	0.0342(9)	0.0311(9)	0.0260(8)	0.0078(7)	-0.0059(7)	0.0004(7)
C8	0.0379(9)	0.0299(8)	0.0175(7)	0.0135(7)	0.0076(6)	0.0076(6)
C9	0.0307(8)	0.0388(9)	0.0304(8)	0.0187(7)	0.0124(7)	0.0104(7)
C10	0.0255(7)	0.0145(6)	0.0123(6)	0.0034(5)	0.0056(5)	0.0018(5)
C11	0.0296(8)	0.0253(7)	0.0280(8)	0.0083(6)	0.0131(6)	0.0063(6)
C12	0.0352(8)	0.0190(7)	0.0164(6)	-0.0006(6)	0.0118(6)	0.0035(5)
C13	0.0470(10)	0.0319(9)	0.0302(9)	0.0002(8)	0.0237(8)	0.0072(7)
C14	0.0397(9)	0.0172(7)	0.0158(6)	0.0025(6)	0.0089(6)	0.0054(5)
C15	0.0621(12)	0.0260(8)	0.0270(8)	0.0126(8)	0.0136(8)	0.0147(7)
C16	0.0344(8)	0.0241(7)	0.0285(8)	0.0129(6)	0.0096(7)	0.0054(6)

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

Bond lengths (Å)

Atom	atom	distance	atom	atom	distance
Fe1	Si1	2.5385(3)	Fe1	Si11	2.5385(3)
Fe1	C10	1.9563(15)	Fe1	C101	1.9563(15)
Si1	Si2	2.3687(7)	Si1	Si3	2.3761(6)
Si1	Si4	2.3578(5)	Si2	C1	1.886(2)
Si2	C2	1.8863(15)	Si2	C3	1.8843(18)
Si3	C4	1.8841(16)	Si3	C5	1.874(2)
Si3	C6	1.877(2)	Si4	C7	1.8838(14)
Si4	C8	1.8774(19)	Si4	C9	1.885(2)
N1	C10	1.356(2)	N1	C11	1.444(2)
N1	C12	1.395(2)	N2	C10	1.357(2)
N2	C14	1.396(2)	N2	C16	1.444(3)
C12	C13	1.488(3)	C12	C14	1.337(3)
C14	C15	1.489(3)			

Symmetry Operators:

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

Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
Si1	Fe1	Si11	180.000(18)	Si1	Fe1	C10	87.35(3)

Si1	Fe1	C101	92.65(3)	Si11	Fe1	C10	92.65(3)
Si11	Fe1	C101	87.35(3)	C10	Fe1	C101	180.00(9)
Fe1	Si1	Si2	116.914(16)	Fe1	Si1	Si3	122.511(19)
Fe1	Si1	Si4	111.867(18)	Si2	Si1	Si3	99.22(2)
Si2	Si1	Si4	102.28(2)	Si3	Si1	Si4	101.099(19)
Si1	Si2	C1	113.15(7)	Si1	Si2	C2	115.85(7)
Si1	Si2	C3	111.82(7)	C1	Si2	C2	103.64(8)
C1	Si2	C3	108.57(8)	C2	Si2	C3	102.96(8)
Si1	Si3	C4	113.95(7)	Si1	Si3	C5	115.65(6)
Si1	Si3	C6	113.35(6)	C4	Si3	C5	102.43(9)
C4	Si3	C6	104.95(9)	C5	Si3	C6	105.28(9)
Si1	Si4	C7	118.92(7)	Si1	Si4	C8	112.64(6)
Si1	Si4	C9	108.35(6)	C7	Si4	C8	102.48(7)
C7	Si4	C9	104.60(8)	C8	Si4	C9	109.27(9)
C10	N1	C11	122.72(14)	C10	N1	C12	111.83(14)
C11	N1	C12	125.08(16)	C10	N2	C14	111.59(15)
C10	N2	C16	123.29(15)	C14	N2	C16	125.07(14)
Fe1	C10	N1	126.15(12)	Fe1	C10	N2	130.36(13)
N1	C10	N2	103.49(13)	N1	C12	C13	121.81(17)
N1	C12	C14	106.41(16)	C13	C12	C14	131.78(16)
N2	C14	C12	106.65(14)	N2	C14	C15	122.10(18)
C12	C14	C15	131.24(19)				

Symmetry Operators:

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

Torsion Angles(°)

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

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
Si1	Fe1	C10	N1	-97.20(8)	Si1	Fe1	C10	N2	83.32(9)
C10	Fe1	Si1	Si2	-117.10(5)	C10	Fe1	Si1	Si3	5.35(5)
C10	Fe1	Si1	Si4	125.47(5)	Si1	Fe1	C101	N11	-82.80(8)
Si1	Fe1	C101	N21	96.68(9)	C101	Fe1	Si1	Si2	62.90(5)
C101	Fe1	Si1	Si3	-174.65(5)	C101	Fe1	Si1	Si4	-54.53(5)
Si11	Fe1	C10	N1	82.80(8)	Si11	Fe1	C10	N2	-96.68(9)
C10	Fe1	Si11	Si21	-62.90(5)	C10	Fe1	Si11	Si31	174.65(5)
C10	Fe1	Si11	Si41	54.53(5)	Si11	Fe1	C101	N11	97.20(8)
Si11	Fe1	C101	N21	-83.32(9)	C101	Fe1	Si11	Si21	117.10(5)
C101	Fe1	Si11	Si31	-5.35(5)	C101	Fe1	Si11	Si41	-125.47(5)

Fe1	Si1	Si2	C1	-72.39(2)	Fe1	Si1	Si2	C2	168.132(19)
Fe1	Si1	Si2	C3	50.59(3)	Fe1	Si1	Si3	C4	165.88(2)
Fe1	Si1	Si3	C5	47.55(3)	Fe1	Si1	Si3	C6	-74.16(3)
Fe1	Si1	Si4	C7	-175.10(2)	Fe1	Si1	Si4	C8	65.04(3)
Fe1	Si1	Si4	C9	-55.97(2)	Si2	Si1	Si3	C4	-63.78(3)
Si2	Si1	Si3	C5	177.89(2)	Si2	Si1	Si3	C6	56.17(3)
Si3	Si1	Si2	C1	153.742(18)	Si3	Si1	Si2	C2	34.26(3)
Si3	Si1	Si2	C3	-83.28(2)	Si2	Si1	Si4	C7	58.99(3)
Si2	Si1	Si4	C8	-60.87(3)	Si2	Si1	Si4	C9	178.121(18)
Si4	Si1	Si2	C1	50.16(2)	Si4	Si1	Si2	C2	-69.32(3)
Si4	Si1	Si2	C3	173.13(2)	Si3	Si1	Si4	C7	-43.11(3)
Si3	Si1	Si4	C8	-162.98(2)	Si3	Si1	Si4	C9	76.01(2)
Si4	Si1	Si3	C4	40.78(3)	Si4	Si1	Si3	C5	-77.55(3)
Si4	Si1	Si3	C6	160.73(2)	C11	N1	C10	Fe1	8.30(16)
C11	N1	C10	N2	-172.11(10)	C10	N1	C12	C13	179.64(9)
C10	N1	C12	C14	-0.68(13)	C12	N1	C10	Fe1	-178.28(8)
C12	N1	C10	N2	1.31(12)	C11	N1	C12	C13	-7.12(18)
C11	N1	C12	C14	172.56(10)	C10	N2	C14	C12	1.13(13)
C10	N2	C14	C15	-178.54(9)	C14	N2	C10	Fe1	178.08(9)
C14	N2	C10	N1	-1.48(12)	C16	N2	C10	Fe1	0.61(17)
C16	N2	C10	N1	-178.96(10)	C16	N2	C14	C12	178.55(10)
C16	N2	C14	C15	-1.11(17)	N1	C12	C14	N2	-0.26(12)
N1	C12	C14	C15	179.36(10)	C13	C12	C14	N2	179.37(12)
C13	C12	C14	C15	-1.0(2)					

Symmetry Operators:

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

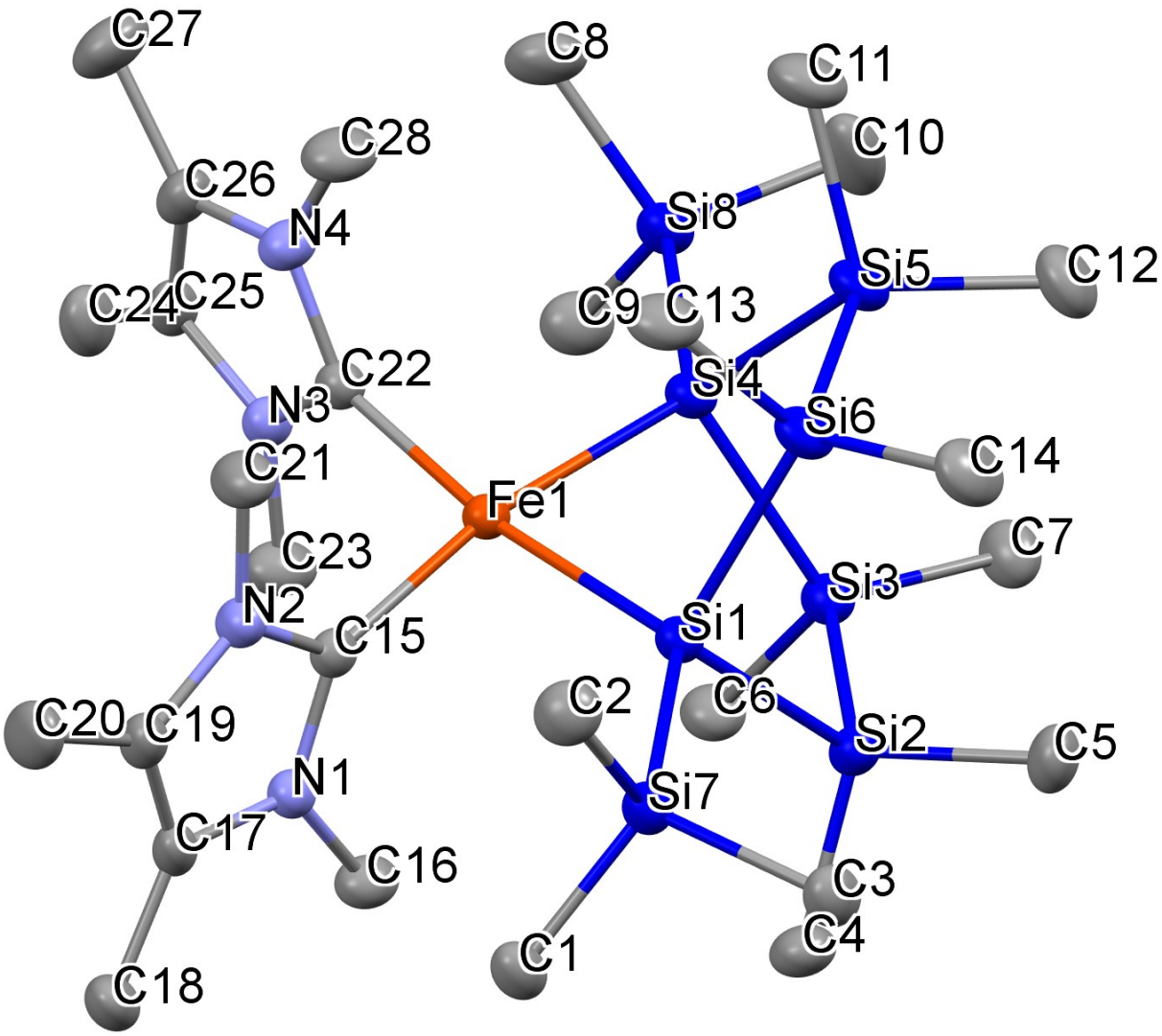


Figure S11. ORTEP drawing of **3** (50% probability of the thermal ellipsoids). Hydrogen atoms were omitted for clarity.

Table S7. Crystal data and structure refinement for **3**.

Empirical Formula	$C_{28}H_{66}FeN_4Si_8$
Formula Weight	739.39
Crystal Color, Habit	red, platelet
Crystal Dimensions	0.200 X 0.200 X 0.100 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 10.1857(2) Å
	b = 22.6499(6) Å
	c = 18.6628(5) Å
	β = 93.809(2) °
	V = 4296.09(18) Å^3
Space Group	$P2_1/n$ (#14)
Z value	4
D_{calc}	1.143 g/cm^3
F_{000}	1600.00
μ(MoKα)	5.964 cm^{-1}
Diffractometer	Saturn724
Radiation	MoKα (λ = 0.71075 Å)
	graphite monochromated
Voltage, Current	50kV, 24mA
Temperature	-150.0°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°
Exposure Rate	12.0 sec./°
Detector Swing Angle	20.00°
ω oscillation Range (χ=45.0, ϕ=90.0)	-70.0 - 110.0°
Exposure Rate	12.0 sec./°
Detector Swing Angle	20.00°
Detector Position	45.00 mm
Pixel Size	0.035 mm
$2\theta_{max}$	62.5°
No. of Reflections Measured	Total: 40854
	Unique: 12586 (R_{int} = 0.0292)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.674 - 0.942)

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	$w = 1/ [\sigma^2(Fo^2) + (0.0411 \cdot P)^2 + 0.6263 \cdot P]$
	where $P = (Max(Fo^2,0) + 2Fc^2)/3$
$2\theta_{max}$ cutoff	62.5^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	12586
No. Variables	392
Reflection/Parameter Ratio	32.11
Residuals: R1(I>2.00σ(I))	0.0338
Residuals: R (All reflections)	0.0499
Residuals: wR2 (All reflections)	0.0839
Goodness of Fit Indicator	1.031
Max Shift/Error in Final Cycle	0.002
Maximum peak in Final Diff. Map	0.41 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.24 $e^-/Å^3$

Atomic coordinates and B_{iso}/B_{eq}

Atom	x	y	z	B_{eq}
Fe1	0.46521(2)	0.69987(2)	0.27085(2)	1.408(4)
Si1	0.56887(4)	0.61794(2)	0.21470(2)	1.463(6)
Si2	0.47266(4)	0.60438(2)	0.09878(2)	1.809(7)
Si3	0.39581(4)	0.69964(2)	0.07205(2)	1.755(6)
Si4	0.50663(4)	0.75492(2)	0.16315(2)	1.572(6)
Si5	0.72831(4)	0.74545(2)	0.13786(2)	2.032(7)
Si6	0.77705(4)	0.65672(2)	0.19830(2)	1.974(7)
Si7	0.60882(4)	0.52321(2)	0.26189(2)	1.723(6)
Si8	0.44436(4)	0.85294(2)	0.13934(2)	1.933(7)
N1	0.29839(11)	0.61080(5)	0.34566(6)	1.724(19)
N2	0.46484(12)	0.63739(5)	0.41238(6)	1.91(2)
N3	0.28108(11)	0.79267(5)	0.31606(6)	1.737(19)
N4	0.47482(12)	0.81668(5)	0.35397(6)	1.99(2)
C1	0.46139(15)	0.48606(6)	0.29676(8)	2.26(2)
C2	0.73750(17)	0.52382(7)	0.33905(9)	2.66(3)
C3	0.66864(16)	0.47163(7)	0.19214(8)	2.39(3)
C4	0.32817(16)	0.55182(7)	0.09720(9)	2.61(3)
C5	0.58480(18)	0.57467(7)	0.03131(8)	2.78(3)
C6	0.21228(15)	0.69796(7)	0.08245(9)	2.43(3)
C7	0.41492(16)	0.72413(8)	-0.02354(8)	2.67(3)
C8	0.50752(18)	0.90808(7)	0.20811(10)	3.04(3)
C9	0.26097(16)	0.86163(7)	0.13356(10)	2.80(3)
C10	0.5041(2)	0.87881(8)	0.05175(10)	3.77(4)
C11	0.82995(16)	0.80818(7)	0.17996(10)	3.00(3)
C12	0.77221(17)	0.74358(8)	0.04124(9)	3.10(3)
C13	0.85638(16)	0.67757(7)	0.28937(9)	2.80(3)
C14	0.89868(16)	0.60738(8)	0.15538(10)	3.01(3)
C15	0.40622(13)	0.64603(6)	0.34587(7)	1.62(2)
C16	0.20826(15)	0.60117(7)	0.28337(8)	2.31(3)
C17	0.29032(15)	0.58100(6)	0.41087(8)	2.07(2)
C18	0.18354(17)	0.53863(7)	0.42319(9)	2.91(3)
C19	0.39554(16)	0.59796(6)	0.45269(8)	2.15(2)
C20	0.4423(2)	0.58045(8)	0.52681(8)	3.28(3)
C21	0.58398(16)	0.66789(7)	0.43779(8)	2.63(3)
C22	0.40706(13)	0.77386(6)	0.31641(7)	1.66(2)
C23	0.17142(15)	0.75836(7)	0.28604(9)	2.63(3)

C24	0.14141(17)	0.87638(7)	0.35511(9)	2.83(3)
C25	0.26985(15)	0.84604(6)	0.35181(8)	2.05(2)
C26	0.39181(16)	0.86115(6)	0.37631(8)	2.29(3)
C27	0.4423(2)	0.91336(8)	0.41806(10)	3.65(4)
C28	0.61643(16)	0.81748(7)	0.36531(10)	2.83(3)

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

Anisotropic displacement parameters

Atom	U11	U22	U33	U12	U13	U23
Fe1	0.01813(9)	0.01652(10)	0.01875(10)	0.00045(7)	0.00044(7)	0.00101(7)
Si1	0.01830(17)	0.01708(18)	0.02025(18)	0.00098(13)	0.00154(14)	0.00176(13)
Si2	0.0282(2)	0.02008(19)	0.02030(19)	0.00003(15)	0.00048(15)	-0.00005(14)
Si3	0.02260(19)	0.0227(2)	0.02101(19)	-0.00045(14)	-0.00161(15)	0.00304(15)
Si4	0.01954(18)	0.01789(18)	0.02220(19)	-0.00038(13)	0.00065(14)	0.00312(14)
Si5	0.02004(19)	0.0251(2)	0.0323(2)	-0.00230(15)	0.00332(16)	0.00656(16)
Si6	0.01724(18)	0.0244(2)	0.0336(2)	0.00051(14)	0.00304(16)	0.00477(16)
Si7	0.02394(19)	0.01872(18)	0.02299(19)	0.00341(14)	0.00285(15)	0.00309(14)
Si8	0.0272(2)	0.01902(19)	0.0273(2)	0.00067(15)	0.00246(16)	0.00545(15)
N1	0.0232(6)	0.0206(6)	0.0220(6)	-0.0010(4)	0.0039(5)	-0.0008(4)
N2	0.0291(6)	0.0233(6)	0.0198(6)	-0.0028(5)	0.0004(5)	0.0003(5)
N3	0.0235(6)	0.0193(6)	0.0234(6)	0.0017(4)	0.0027(5)	-0.0001(4)
N4	0.0269(6)	0.0222(6)	0.0261(6)	-0.0002(5)	-0.0024(5)	-0.0019(5)
C1	0.0324(8)	0.0228(7)	0.0315(8)	0.0020(6)	0.0086(6)	0.0044(6)
C2	0.0376(9)	0.0302(8)	0.0325(8)	0.0046(7)	-0.0042(7)	0.0055(7)
C3	0.0334(8)	0.0251(8)	0.0331(8)	0.0055(6)	0.0071(7)	0.0015(6)
C4	0.0386(9)	0.0264(8)	0.0336(9)	-0.0063(6)	-0.0020(7)	-0.0033(6)
C5	0.0479(10)	0.0336(9)	0.0250(8)	0.0031(7)	0.0083(7)	-0.0025(6)
C6	0.0259(8)	0.0328(8)	0.0331(8)	-0.0030(6)	-0.0032(6)	0.0006(6)
C7	0.0343(9)	0.0418(9)	0.0245(8)	-0.0002(7)	-0.0033(6)	0.0068(7)
C8	0.0451(10)	0.0219(8)	0.0472(10)	-0.0056(7)	-0.0083(8)	0.0039(7)
C9	0.0314(8)	0.0295(8)	0.0446(10)	0.0052(6)	-0.0036(7)	0.0028(7)
C10	0.0690(13)	0.0311(9)	0.0461(11)	0.0105(9)	0.0246(10)	0.0165(8)
C11	0.0278(8)	0.0349(9)	0.0504(11)	-0.0087(7)	-0.0024(7)	0.0083(8)
C12	0.0330(9)	0.0467(10)	0.0395(10)	0.0009(7)	0.0128(7)	0.0084(8)
C13	0.0253(8)	0.0336(9)	0.0464(10)	-0.0039(6)	-0.0065(7)	0.0040(7)
C14	0.0247(8)	0.0382(9)	0.0525(11)	0.0042(7)	0.0110(7)	0.0019(8)
C15	0.0220(7)	0.0186(6)	0.0210(7)	0.0019(5)	0.0027(5)	-0.0015(5)
C16	0.0256(7)	0.0277(8)	0.0341(8)	-0.0018(6)	-0.0020(6)	-0.0024(6)

C17	0.0358(8)	0.0204(7)	0.0236(7)	-0.0017(6)	0.0115(6)	-0.0024(5)
C18	0.0437(10)	0.0321(9)	0.0370(9)	-0.0101(7)	0.0175(7)	-0.0039(7)
C19	0.0391(9)	0.0227(7)	0.0205(7)	-0.0016(6)	0.0070(6)	0.0006(5)
C20	0.0627(12)	0.0395(10)	0.0227(8)	-0.0079(8)	0.0055(8)	0.0058(7)
C21	0.0357(9)	0.0370(9)	0.0260(8)	-0.0082(7)	-0.0061(7)	0.0019(6)
C22	0.0240(7)	0.0191(7)	0.0199(7)	-0.0005(5)	0.0007(5)	0.0018(5)
C23	0.0227(7)	0.0290(8)	0.0476(10)	-0.0000(6)	-0.0015(7)	-0.0024(7)
C24	0.0421(10)	0.0302(8)	0.0368(9)	0.0096(7)	0.0140(7)	0.0006(7)
C25	0.0360(8)	0.0181(7)	0.0245(7)	0.0035(6)	0.0073(6)	0.0019(5)
C26	0.0419(9)	0.0205(7)	0.0246(7)	0.0007(6)	0.0034(6)	-0.0026(6)
C27	0.0602(13)	0.0323(9)	0.0454(11)	-0.0006(8)	-0.0027(9)	-0.0157(8)
C28	0.0291(8)	0.0319(8)	0.0451(10)	-0.0034(6)	-0.0087(7)	-0.0033(7)

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

Bond lengths (Å)

atom	atom	distance	atom	atom	distance
Fe1	Si1	2.4091(6)	Fe1	Si4	2.4260(6)
Fe1	C15	1.9799(14)	Fe1	C22	1.9873(14)
Si1	Si2	2.3352(5)	Si1	Si6	2.3340(6)
Si1	Si7	2.3446(6)	Si2	Si3	2.3377(6)
Si2	C4	1.8916(17)	Si2	C5	1.8799(17)
Si3	Si4	2.3404(6)	Si3	C6	1.8926(16)
Si3	C7	1.8906(16)	Si4	Si5	2.3471(6)
Si4	Si8	2.3434(6)	Si5	Si6	2.3417(6)
Si5	C11	1.8973(17)	Si5	C12	1.8869(18)
Si6	C13	1.8927(17)	Si6	C14	1.8861(18)
Si7	C1	1.8752(16)	Si7	C2	1.8818(17)
Si7	C3	1.8804(16)	Si8	C8	1.8738(18)
Si8	C9	1.8743(17)	Si8	C10	1.876(2)
N1	C15	1.3574(17)	N1	C16	1.4491(18)
N1	C17	1.3988(19)	N2	C15	1.3554(17)
N2	C19	1.3901(19)	N2	C21	1.449(2)
N3	C22	1.3517(17)	N3	C23	1.4430(19)
N3	C25	1.3891(18)	N4	C22	1.3580(17)
N4	C26	1.3965(19)	N4	C28	1.444(2)
C17	C18	1.480(2)	C17	C19	1.339(2)
C19	C20	1.487(2)	C24	C25	1.483(2)

C25	C26	1.339(2)	C26	C27	1.489(2)	

Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
Si1	Fe1	Si4	85.994(18)	Si1	Fe1	C15	89.74(4)
Si1	Fe1	C22	170.90(4)	Si4	Fe1	C15	168.55(4)
Si4	Fe1	C22	89.67(4)	C15	Fe1	C22	95.96(6)
Fe1	Si1	Si2	109.59(2)	Fe1	Si1	Si6	101.27(2)
Fe1	Si1	Si7	127.71(2)	Si2	Si1	Si6	104.89(2)
Si2	Si1	Si7	106.22(2)	Si6	Si1	Si7	104.90(2)
Si1	Si2	Si3	100.97(2)	Si1	Si2	C4	112.05(5)
Si1	Si2	C5	115.55(5)	Si3	Si2	C4	109.17(5)
Si3	Si2	C5	113.40(5)	C4	Si2	C5	105.72(7)
Si2	Si3	Si4	101.55(2)	Si2	Si3	C6	106.17(5)
Si2	Si3	C7	114.72(6)	Si4	Si3	C6	111.61(5)
Si4	Si3	C7	116.97(6)	C6	Si3	C7	105.48(7)
Fe1	Si4	Si3	103.00(2)	Fe1	Si4	Si5	110.012(19)
Fe1	Si4	Si8	125.75(2)	Si3	Si4	Si5	103.24(2)
Si3	Si4	Si8	104.93(2)	Si5	Si4	Si8	107.48(2)
Si4	Si5	Si6	99.07(2)	Si4	Si5	C11	110.74(6)
Si4	Si5	C12	119.11(6)	Si6	Si5	C11	110.54(5)
Si6	Si5	C12	112.64(6)	C11	Si5	C12	104.78(8)
Si1	Si6	Si5	102.75(2)	Si1	Si6	C13	108.27(5)
Si1	Si6	C14	117.44(6)	Si5	Si6	C13	106.42(5)
Si5	Si6	C14	115.35(6)	C13	Si6	C14	106.02(7)
Si1	Si7	C1	114.71(5)	Si1	Si7	C2	112.05(5)
Si1	Si7	C3	111.39(5)	C1	Si7	C2	105.71(7)
C1	Si7	C3	105.38(7)	C2	Si7	C3	107.04(7)
Si4	Si8	C8	115.17(6)	Si4	Si8	C9	111.50(5)
Si4	Si8	C10	111.21(6)	C8	Si8	C9	105.36(8)
C8	Si8	C10	105.79(8)	C9	Si8	C10	107.28(9)
C15	N1	C16	124.07(12)	C15	N1	C17	112.05(11)
C16	N1	C17	123.68(12)	C15	N2	C19	112.32(12)
C15	N2	C21	122.65(12)	C19	N2	C21	125.01(12)
C22	N3	C23	122.84(12)	C22	N3	C25	112.36(11)
C23	N3	C25	124.67(12)	C22	N4	C26	111.85(12)
C22	N4	C28	123.58(12)	C26	N4	C28	124.47(12)
Fe1	C15	N1	130.06(10)	Fe1	C15	N2	126.91(10)

N1	C15	N2	103.00(11)	N1	C17	C18	122.30(13)
N1	C17	C19	106.12(13)	C18	C17	C19	131.55(14)
N2	C19	C17	106.52(13)	N2	C19	C20	122.16(14)
C17	C19	C20	131.30(15)	Fe1	C22	N3	125.00(10)
Fe1	C22	N4	131.87(10)	N3	C22	N4	103.13(11)
N3	C25	C24	121.62(13)	N3	C25	C26	106.39(13)
C24	C25	C26	131.94(14)	N4	C26	C25	106.26(12)
N4	C26	C27	122.29(14)	C25	C26	C27	131.44(15)

Torsion Angles(o)

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

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
Si1	Fe1	Si4	Si3	58.476(17)	Si1	Fe1	Si4	Si5	-51.049(19)
Si1	Fe1	Si4	Si8	177.95(2)	Si4	Fe1	Si1	Si2	-51.023(19)
Si4	Fe1	Si1	Si6	59.406(16)	Si4	Fe1	Si1	Si7	178.45(2)
Si1	Fe1	C15	N1	-84.51(11)	Si1	Fe1	C15	N2	97.96(10)
C15	Fe1	Si1	Si2	118.34(4)	C15	Fe1	Si1	Si6	-131.23(4)
C15	Fe1	Si1	Si7	-12.19(4)	Si4	Fe1	C22	N3	93.82(10)
Si4	Fe1	C22	N4	-86.46(11)	C22	Fe1	Si4	Si3	-129.53(4)
C22	Fe1	Si4	Si5	120.94(4)	C22	Fe1	Si4	Si8	-10.06(4)
C15	Fe1	C22	N3	-76.18(10)	C15	Fe1	C22	N4	103.53(12)
C22	Fe1	C15	N1	102.60(11)	C22	Fe1	C15	N2	-74.93(11)
Fe1	Si1	Si2	Si3	25.89(2)	Fe1	Si1	Si2	C4	-90.18(3)
Fe1	Si1	Si2	C5	148.64(2)	Fe1	Si1	Si6	Si5	-52.69(2)
Fe1	Si1	Si6	C13	59.63(2)	Fe1	Si1	Si6	C14	179.558(19)
Fe1	Si1	Si7	C1	51.72(3)	Fe1	Si1	Si7	C2	-68.81(3)
Fe1	Si1	Si7	C3	171.31(2)	Si2	Si1	Si6	Si5	61.30(2)
Si2	Si1	Si6	C13	173.63(2)	Si2	Si1	Si6	C14	-66.45(3)
Si6	Si1	Si2	Si3	-82.13(2)	Si6	Si1	Si2	C4	161.81(2)
Si6	Si1	Si2	C5	40.63(3)	Si2	Si1	Si7	C1	-80.05(3)
Si2	Si1	Si7	C2	159.42(2)	Si2	Si1	Si7	C3	39.54(3)
Si7	Si1	Si2	Si3	167.114(18)	Si7	Si1	Si2	C4	51.05(3)
Si7	Si1	Si2	C5	-70.13(3)	Si6	Si1	Si7	C1	169.195(19)
Si6	Si1	Si7	C2	48.66(3)	Si6	Si1	Si7	C3	-71.22(2)
Si7	Si1	Si6	Si5	173.007(17)	Si7	Si1	Si6	C13	-74.67(3)
Si7	Si1	Si6	C14	45.26(3)	Si1	Si2	Si3	Si4	13.84(2)
Si1	Si2	Si3	C6	-102.94(2)	Si1	Si2	Si3	C7	140.98(2)
C4	Si2	Si3	Si4	132.02(6)	C4	Si2	Si3	C6	15.23(6)

C4	Si2	Si3	C7	-100.84(6)	C5	Si2	Si3	Si4	-110.40(6)
C5	Si2	Si3	C6	132.82(6)	C5	Si2	Si3	C7	16.74(6)
Si2	Si3	Si4	Fe1	-49.34(2)	Si2	Si3	Si4	Si5	65.18(2)
Si2	Si3	Si4	Si8	177.647(18)	C6	Si3	Si4	Fe1	63.41(6)
C6	Si3	Si4	Si5	177.94(6)	C6	Si3	Si4	Si8	-69.60(6)
C7	Si3	Si4	Fe1	-175.00(6)	C7	Si3	Si4	Si5	-60.47(6)
C7	Si3	Si4	Si8	51.99(6)	Fe1	Si4	Si5	Si6	23.46(2)
Fe1	Si4	Si5	C11	-92.66(3)	Fe1	Si4	Si5	C12	145.81(2)
Fe1	Si4	Si8	C8	56.75(3)	Fe1	Si4	Si8	C9	-63.24(3)
Fe1	Si4	Si8	C10	177.077(19)	Si3	Si4	Si5	Si6	-85.90(2)
Si3	Si4	Si5	C11	157.98(2)	Si3	Si4	Si5	C12	36.44(3)
Si3	Si4	Si8	C8	175.36(2)	Si3	Si4	Si8	C9	55.37(3)
Si3	Si4	Si8	C10	-64.32(3)	Si5	Si4	Si8	C8	-75.22(3)
Si5	Si4	Si8	C9	164.792(19)	Si5	Si4	Si8	C10	45.10(3)
Si8	Si4	Si5	Si6	163.512(17)	Si8	Si4	Si5	C11	47.39(3)
Si8	Si4	Si5	C12	-74.14(3)	Si4	Si5	Si6	Si1	16.96(2)
Si4	Si5	Si6	C13	-96.74(2)	Si4	Si5	Si6	C14	146.01(2)
C11	Si5	Si6	Si1	133.23(6)	C11	Si5	Si6	C13	19.54(6)
C11	Si5	Si6	C14	-97.72(6)	C12	Si5	Si6	Si1	-109.94(6)
C12	Si5	Si6	C13	136.37(6)	C12	Si5	Si6	C14	19.12(6)
C16	N1	C15	Fe1	7.1(2)	C16	N1	C15	N2	-174.93(11)
C15	N1	C17	C18	-178.22(11)	C15	N1	C17	C19	-0.07(15)
C17	N1	C15	Fe1	-177.87(10)	C17	N1	C15	N2	0.11(14)
C16	N1	C17	C18	-3.2(2)	C16	N1	C17	C19	174.99(11)
C15	N2	C19	C17	0.07(15)	C15	N2	C19	C20	178.58(11)
C19	N2	C15	Fe1	177.96(10)	C19	N2	C15	N1	-0.11(14)
C21	N2	C15	Fe1	-0.23(19)	C21	N2	C15	N1	-178.30(11)
C21	N2	C19	C17	178.21(12)	C21	N2	C19	C20	-3.3(2)
C23	N3	C22	Fe1	4.38(19)	C23	N3	C22	N4	-175.40(11)
C22	N3	C25	C24	177.02(11)	C22	N3	C25	C26	-0.79(15)
C25	N3	C22	Fe1	-179.71(10)	C25	N3	C22	N4	0.51(14)
C23	N3	C25	C24	-7.2(2)	C23	N3	C25	C26	175.03(12)
C22	N4	C26	C25	-0.42(15)	C22	N4	C26	C27	-179.60(11)
C26	N4	C22	Fe1	-179.81(11)	C26	N4	C22	N3	-0.05(14)
C28	N4	C22	Fe1	3.7(2)	C28	N4	C22	N3	-176.53(12)
C28	N4	C26	C25	176.02(12)	C28	N4	C26	C27	-3.2(2)
N1	C17	C19	N2	-0.00(15)	N1	C17	C19	C20	-178.32(13)
C18	C17	C19	N2	177.91(14)	C18	C17	C19	C20	-0.4(3)

N3	C25	C26	N4	0.70(15)	N3	C25	C26	C27	179.76(13)
C24	C25	C26	N4	-176.80(15)	C24	C25	C26	C27	2.3(3)

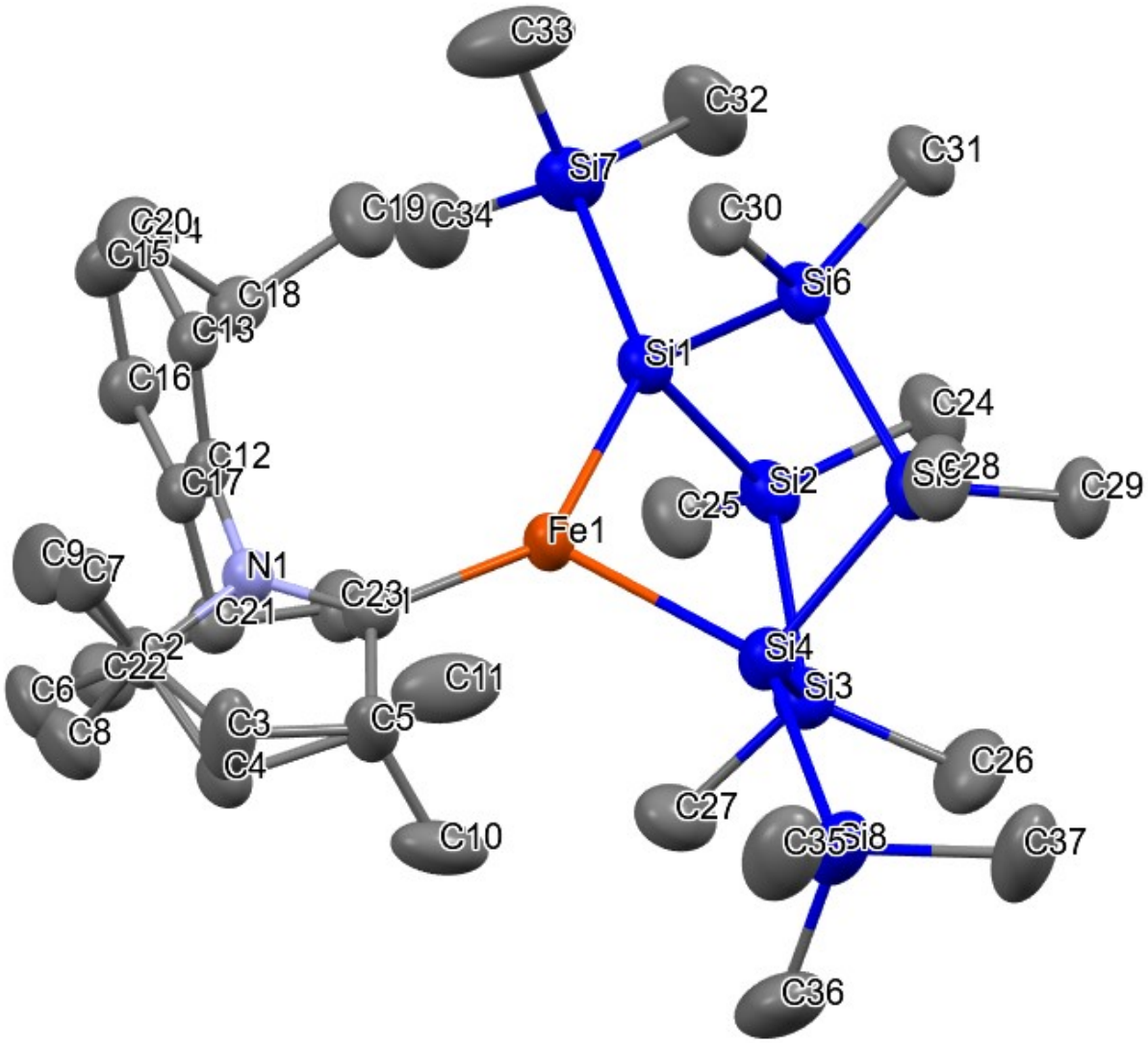


Figure S12. ORTEP drawing of **4** (50% probability of the thermal ellipsoids). Hydrogen atoms were omitted for clarity.

Table S8. Crystal data and structure refinement for **4**.

Empirical Formula	$C_{34}H_{65}FeNSi_8$
Formula Weight	768.43
Crystal Color, Habit	brown, platelet
Crystal Dimensions	0.100 X 0.100 X 0.100 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 9.4785(7) Å
	b = 23.6413(17) Å
	c = 21.2483(16) Å
	b = 102.331(7) ^{o}
	V = 4651.6(6) Å^3
Space Group	$P2_1/n$ (#14)
Z value	4
D_{calc}	1.097 g/cm^3
F_{000}	1656.00
Diffractometer	R-AXIS IV
unknown Radiation (λ = 0.41220Å)	
	monochromated
Voltage, Current	8kV, 100mA
Temperature	-173.0^{o}C
Detector Aperture	300.0 x 300.0 mm
Data Images	720 exposures
ω oscillation Range (χ=45.0, ϕ=0.0)	0.0 - 180.0^o
Exposure Rate	240.0 sec./^{o}
ω oscillation Range (χ=45.0, ϕ=90.0)	0.0 - 180.0^o
Exposure Rate	240.0 sec./^{o}
Detector Position	130.00 mm
Pixel Size	0.172 mm
$2\theta_{max}$	31.1^o
No. of Reflections Measured	Total: 68058
	Unique: 10527 (R_{int} = 0.0400)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.785 - 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	$\omega = 1/ [\sigma^2(Fo^2) + (0.0448 \cdot P)^2 + 1.2928 \cdot P]$ 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)	10527
No. Variables	444
Reflection/Parameter Ratio	23.71
Residuals: R1 (I>2.00σ(I))	0.0292
Residuals: R (All reflections)	0.0346
Residuals: wR2 (All reflections)	0.0795
Goodness of Fit Indicator	1.034
Max Shift/Error in Final Cycle	0.002
Maximum peak in Final Diff. Map	$0.56\ e^-/Å^3$
Minimum peak in Final Diff. Map	$-0.22\ e^-/Å^3$

Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}	occ
Fe1	0.56151(2)	0.73347(2)	0.35505(2)	1.397(4)	1
Si1	0.64413(4)	0.72167(2)	0.25225(2)	1.384(6)	1
Si2	0.84639(4)	0.78173(2)	0.27045(2)	1.535(6)	1
Si3	0.81792(4)	0.84419(2)	0.35239(2)	1.708(6)	1
Si4	0.57207(4)	0.83956(2)	0.35279(2)	1.596(6)	1
Si5	0.45870(4)	0.86165(2)	0.24674(2)	1.563(6)	1
Si6	0.46239(4)	0.77703(2)	0.18949(2)	1.463(6)	1
Si7	0.69629(5)	0.64724(2)	0.18840(2)	1.923(7)	1
Si8	0.52484(5)	0.91336(2)	0.41912(2)	2.305(8)	1
N1	0.51512(12)	0.63434(5)	0.44402(5)	1.281(17)	1
C1	0.50994(14)	0.68809(6)	0.43012(6)	1.384(19)	1
C2	0.46852(15)	0.61751(6)	0.50617(6)	1.59(2)	1
C3	0.3936(6)	0.67243(15)	0.5210(2)	2.65(6)	1/2
C4	0.4680(4)	0.67551(14)	0.53828(15)	1.56(5)	1/2
C5	0.45385(18)	0.71952(6)	0.48212(7)	1.90(2)	1
C6	0.5854(6)	0.57844(19)	0.5476(3)	2.02(7)	1/2
C7	0.3280(7)	0.5884(2)	0.4916(3)	2.04(8)	1/2
C8	0.5941(7)	0.6005(2)	0.5568(3)	2.39(8)	1/2
C9	0.3539(7)	0.5680(2)	0.4933(3)	2.40(9)	1/2
C10	0.56222(18)	0.76365(8)	0.51350(8)	2.67(3)	1
C11	0.31258(17)	0.74819(9)	0.45149(9)	2.96(3)	1
C12	0.56183(14)	0.59076(5)	0.40491(6)	1.289(19)	1
C13	0.45833(14)	0.56383(5)	0.35741(6)	1.396(19)	1
C14	0.50444(15)	0.51841(6)	0.32506(7)	1.72(2)	1
C15	0.64620(16)	0.50097(6)	0.33878(7)	1.81(2)	1
C16	0.74767(15)	0.52995(6)	0.38371(7)	1.70(2)	1
C17	0.70859(14)	0.57589(5)	0.41729(6)	1.385(19)	1
C18	0.30375(14)	0.58389(6)	0.33654(7)	1.61(2)	1
C19	0.28313(17)	0.61155(7)	0.27012(7)	2.23(2)	1
C20	0.19403(16)	0.53630(7)	0.33458(8)	2.12(2)	1
C21	0.82478(14)	0.60992(6)	0.46116(6)	1.54(2)	1
C22	0.93120(16)	0.57306(6)	0.50793(7)	2.05(2)	1
C23	0.90627(15)	0.64577(6)	0.42085(7)	1.93(2)	1
C24	0.87219(16)	0.82155(7)	0.19661(7)	2.19(2)	1
C25	1.01876(15)	0.74043(7)	0.29806(8)	2.14(2)	1

C26	0.89291(19)	0.91665(7)	0.34144(9)	2.81(3)	1
C27	0.92646(19)	0.81611(8)	0.43130(8)	2.67(3)	1
C28	0.26593(16)	0.88370(7)	0.24403(8)	2.32(3)	1
C29	0.54587(16)	0.92039(6)	0.20830(8)	2.08(2)	1
C30	0.28019(15)	0.74304(6)	0.18409(7)	1.97(2)	1
C31	0.47899(17)	0.78860(7)	0.10331(7)	2.17(2)	1
C32	0.7844(2)	0.67450(9)	0.12311(9)	3.45(4)	1
C33	0.5334(2)	0.60610(10)	0.14874(11)	4.25(5)	1
C34	0.8281(2)	0.59718(7)	0.23723(9)	2.87(3)	1
C35	0.3438(2)	0.90778(8)	0.44063(10)	3.26(3)	1
C36	0.6652(2)	0.91792(8)	0.49581(9)	3.56(4)	1
C37	0.5308(3)	0.98254(7)	0.37642(10)	3.61(4)	1

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

Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe1	0.02288(10)	0.01520(10)	0.01680(10)	0.00170(7)	0.00823(7)	0.00118(7)
Si1	0.01786(17)	0.01889(17)	0.01683(17)	0.00215(13)	0.00592(13)	0.00160(13)
Si2	0.01654(17)	0.02464(19)	0.01860(17)	0.00069(14)	0.00702(13)	0.00319(14)
Si3	0.02153(18)	0.02160(19)	0.02172(18)	-0.00106(14)	0.00452(14)	0.00028(14)
Si4	0.02430(19)	0.01725(18)	0.02138(18)	0.00063(14)	0.00997(14)	0.00029(13)
Si5	0.01801(17)	0.01784(18)	0.02484(19)	0.00108(13)	0.00750(14)	0.00411(14)
Si6	0.01799(17)	0.01989(18)	0.01786(17)	0.00052(13)	0.00417(13)	0.00414(13)
Si7	0.0282(2)	0.0260(2)	0.02122(18)	0.00363(16)	0.01052(15)	-0.00211(15)
Si8	0.0418(2)	0.01813(19)	0.0328(2)	-0.00004(17)	0.01949(19)	-0.00299(16)
N1	0.0189(5)	0.0155(5)	0.0159(5)	0.0009(4)	0.0072(4)	0.0006(4)
C1	0.0199(6)	0.0165(6)	0.0170(6)	0.0018(5)	0.0060(5)	-0.0010(5)
C2	0.0280(7)	0.0186(6)	0.0165(6)	0.0006(5)	0.0111(5)	0.0032(5)
C3	0.052(2)	0.0204(16)	0.038(2)	0.0075(18)	0.031(2)	0.0063(14)
C4	0.0229(15)	0.0211(14)	0.0165(14)	0.0004(13)	0.0069(12)	0.0022(10)
C5	0.0392(8)	0.0167(6)	0.0208(7)	0.0050(6)	0.0165(6)	0.0007(5)
C6	0.0316(19)	0.026(2)	0.020(2)	0.002(2)	0.0068(14)	0.0100(18)
C7	0.037(3)	0.021(2)	0.0240(18)	-0.010(2)	0.0155(17)	-0.002(2)
C8	0.038(2)	0.035(3)	0.0190(19)	-0.002(2)	0.0076(15)	0.007(2)
C9	0.033(3)	0.029(3)	0.032(2)	-0.013(2)	0.0128(17)	0.007(2)
C10	0.0325(8)	0.0444(10)	0.0215(7)	0.0080(7)	-0.0007(6)	-0.0127(7)
C11	0.0217(7)	0.0502(11)	0.0416(9)	0.0034(7)	0.0094(7)	-0.0209(8)
C12	0.0207(6)	0.0122(6)	0.0179(6)	0.0013(5)	0.0084(5)	0.0015(5)

C13	0.0200(6)	0.0150(6)	0.0188(6)	-0.0003(5)	0.0059(5)	0.0017(5)
C14	0.0259(7)	0.0178(6)	0.0228(6)	-0.0020(5)	0.0079(5)	-0.0025(5)
C15	0.0287(7)	0.0174(6)	0.0253(7)	0.0024(5)	0.0119(6)	-0.0047(5)
C16	0.0216(6)	0.0195(6)	0.0256(7)	0.0037(5)	0.0101(5)	0.0003(5)
C17	0.0203(6)	0.0156(6)	0.0180(6)	-0.0002(5)	0.0069(5)	0.0023(5)
C18	0.0196(6)	0.0189(6)	0.0220(6)	0.0004(5)	0.0031(5)	-0.0012(5)
C19	0.0270(7)	0.0296(8)	0.0271(7)	0.0012(6)	0.0030(6)	0.0059(6)
C20	0.0221(7)	0.0257(7)	0.0320(8)	-0.0025(6)	0.0043(6)	0.0006(6)
C21	0.0193(6)	0.0180(6)	0.0213(6)	0.0014(5)	0.0043(5)	0.0002(5)
C22	0.0252(7)	0.0255(7)	0.0251(7)	0.0032(6)	0.0008(6)	0.0027(6)
C23	0.0213(6)	0.0237(7)	0.0287(7)	-0.0027(5)	0.0061(5)	0.0034(6)
C24	0.0248(7)	0.0354(8)	0.0255(7)	0.0000(6)	0.0107(6)	0.0084(6)
C25	0.0189(6)	0.0340(8)	0.0303(8)	0.0028(6)	0.0094(6)	0.0067(6)
C26	0.0312(8)	0.0283(8)	0.0467(10)	-0.0089(6)	0.0072(7)	0.0004(7)
C27	0.0379(9)	0.0353(9)	0.0251(7)	0.0069(7)	-0.0006(6)	-0.0025(6)
C28	0.0221(7)	0.0277(8)	0.0403(9)	0.0044(6)	0.0109(6)	0.0056(6)
C29	0.0262(7)	0.0215(7)	0.0333(8)	0.0009(6)	0.0111(6)	0.0072(6)
C30	0.0203(6)	0.0262(7)	0.0270(7)	-0.0012(5)	0.0024(5)	0.0050(6)
C31	0.0291(7)	0.0340(8)	0.0195(7)	-0.0001(6)	0.0052(6)	0.0061(6)
C32	0.0625(12)	0.0467(11)	0.0307(9)	0.0104(9)	0.0299(8)	0.0037(8)
C33	0.0428(10)	0.0608(14)	0.0587(13)	-0.0073(9)	0.0127(9)	-0.0363(11)
C34	0.0478(10)	0.0287(8)	0.0358(9)	0.0153(7)	0.0163(7)	0.0022(7)
C35	0.0504(11)	0.0297(9)	0.0526(11)	0.0060(8)	0.0312(9)	-0.0037(8)
C36	0.0629(13)	0.0336(9)	0.0395(10)	-0.0092(9)	0.0123(9)	-0.0168(8)
C37	0.0736(14)	0.0200(8)	0.0529(11)	0.0024(8)	0.0344(10)	0.0017(7)

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

Bond lengths (Å)

atom	atom	distance	atom	atom	distance
Fe1	Si1	2.4886(6)	Fe1	Si4	2.5110(7)
Fe1	C1	2.0658(15)	Si1	Si2	2.3504(6)
Si1	Si6	2.3404(6)	Si1	Si7	2.3383(7)
Si2	Si3	2.3421(7)	Si2	C24	1.8899(17)
Si2	C25	1.8861(15)	Si3	Si4	2.3347(6)
Si3	C26	1.8880(18)	Si3	C27	1.8904(17)
Si4	Si5	2.3390(6)	Si4	Si8	2.3453(7)

Si5	Si6	2.3455(7)	Si5	C28	1.8891(16)
Si5	C29	1.8885(17)	Si6	C30	1.8859(15)
Si6	C31	1.8910(16)	Si7	C32	1.879(2)
Si7	C33	1.866(2)	Si7	C34	1.8668(18)
Si8	C35	1.872(2)	Si8	C36	1.8737(19)
Si8	C37	1.8770(19)	N1	C1	1.3031(18)
N1	C2	1.5318(18)	N1	C12	1.4510(18)
C1	C5	1.519(2)	C2	C3	1.544(4)
C2	C4	1.532(4)	C2	C6	1.562(5)
C2	C7	1.472(6)	C2	C8	1.480(5)
C2	C9	1.580(6)	C3	C4	0.726(6)
C3	C5	1.564(5)	C4	C5	1.567(4)
C5	C10	1.515(2)	C5	C11	1.518(2)
C6	C8	0.558(7)	C7	C9	0.537(7)
C12	C13	1.4013(16)	C12	C17	1.4041(18)
C13	C14	1.395(2)	C13	C18	1.5135(18)
C14	C15	1.376(2)	C15	C16	1.3834(19)
C16	C17	1.392(2)	C17	C21	1.5135(17)
C18	C19	1.530(2)	C18	C20	1.527(2)
C21	C22	1.5285(18)	C21	C23	1.527(2)

Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
Si1	Fe1	Si4	94.24(2)	Si1	Fe1	C1	142.21(5)
Si4	Fe1	C1	123.40(4)	Fe1	Si1	Si2	100.74(2)
Fe1	Si1	Si6	96.09(2)	Fe1	Si1	Si7	137.63(3)
Si2	Si1	Si6	103.37(2)	Si2	Si1	Si7	106.50(2)
Si6	Si1	Si7	108.14(2)	Si1	Si2	Si3	106.49(2)
Si1	Si2	C24	114.20(5)	Si1	Si2	C25	111.12(5)
Si3	Si2	C24	111.04(6)	Si3	Si2	C25	108.95(5)
C24	Si2	C25	105.01(7)	Si2	Si3	Si4	104.28(2)
Si2	Si3	C26	111.98(7)	Si2	Si3	C27	108.10(6)
Si4	Si3	C26	116.44(6)	Si4	Si3	C27	109.56(6)
C26	Si3	C27	106.26(8)	Fe1	Si4	Si3	95.21(2)
Fe1	Si4	Si5	103.26(2)	Fe1	Si4	Si8	135.90(2)
Si3	Si4	Si5	103.86(2)	Si3	Si4	Si8	106.62(2)
Si5	Si4	Si8	107.79(2)	Si4	Si5	Si6	104.75(2)
Si4	Si5	C28	109.47(6)	Si4	Si5	C29	115.30(5)

Si6	Si5	C28	109.94(5)	Si6	Si5	C29	110.27(6)
C28	Si5	C29	107.07(7)	Si1	Si6	Si5	105.79(2)
Si1	Si6	C30	110.45(5)	Si1	Si6	C31	115.42(5)
Si5	Si6	C30	106.27(5)	Si5	Si6	C31	113.10(6)
C30	Si6	C31	105.50(7)	Si1	Si7	C32	110.64(7)
Si1	Si7	C33	113.40(8)	Si1	Si7	C34	110.73(6)
C32	Si7	C33	107.48(10)	C32	Si7	C34	106.12(10)
C33	Si7	C34	108.15(9)	Si4	Si8	C35	113.38(6)
Si4	Si8	C36	111.98(7)	Si4	Si8	C37	109.17(7)
C35	Si8	C36	108.01(10)	C35	Si8	C37	107.64(10)
C36	Si8	C37	106.33(9)	C1	N1	C2	116.41(12)
C1	N1	C12	124.33(12)	C2	N1	C12	119.26(11)
Fe1	C1	N1	132.67(11)	Fe1	C1	C5	119.01(10)
N1	C1	C5	108.32(12)	N1	C2	C3	100.8(2)
N1	C2	C4	100.40(16)	N1	C2	C6	109.9(2)
N1	C2	C7	110.8(3)	N1	C2	C8	111.2(3)
N1	C2	C9	110.9(3)	C3	C2	C4	27.3(2)
C3	C2	C6	133.2(3)	C3	C2	C7	90.1(3)
C3	C2	C8	114.4(3)	C3	C2	C9	109.2(3)
C4	C2	C6	110.3(2)	C4	C2	C7	115.0(3)
C4	C2	C8	89.9(2)	C4	C2	C9	132.2(3)
C6	C2	C7	110.0(3)	C6	C2	C8	20.9(3)
C6	C2	C9	92.2(3)	C7	C2	C8	125.2(3)
C7	C2	C9	19.9(3)	C8	C2	C9	110.0(3)
C2	C3	C4	75.4(4)	C2	C3	C5	104.8(3)
C4	C3	C5	76.8(5)	C2	C4	C3	77.3(4)
C2	C4	C5	105.2(2)	C3	C4	C5	76.4(4)
C1	C5	C3	105.04(19)	C1	C5	C4	104.06(16)
C1	C5	C10	110.32(14)	C1	C5	C11	108.68(12)
C3	C5	C4	26.8(2)	C3	C5	C10	123.19(19)
C3	C5	C11	99.0(2)	C4	C5	C10	100.51(16)
C4	C5	C11	123.2(2)	C10	C5	C11	109.53(13)
C2	C6	C8	71.2(7)	C2	C7	C9	91.5(10)
C2	C8	C6	87.9(8)	C2	C9	C7	68.7(9)
N1	C12	C13	118.87(11)	N1	C12	C17	118.80(10)
C13	C12	C17	122.30(12)	C12	C13	C14	117.38(12)
C12	C13	C18	123.62(12)	C14	C13	C18	118.85(11)
C13	C14	C15	121.40(12)	C14	C15	C16	120.09(14)

C15	C16	C17	121.21(13)	C12	C17	C16	117.43(11)
C12	C17	C21	122.94(11)	C16	C17	C21	119.47(12)
C13	C18	C19	109.22(12)	C13	C18	C20	112.85(11)
C19	C18	C20	109.74(11)	C17	C21	C22	112.94(11)
C17	C21	C23	109.77(11)	C22	C21	C23	109.79(11)

Torsion Angles(°)

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

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
Si1	Fe1	Si4	Si3	-59.365(16)	Si1	Fe1	Si4	Si5	46.220(17)
Si1	Fe1	Si4	Si8	-179.82(2)	Si4	Fe1	Si1	Si2	48.558(17)
Si4	Fe1	Si1	Si6	-56.327(16)	Si4	Fe1	Si1	Si7	178.11(2)
Si1	Fe1	C1	N1	3.61(15)	Si1	Fe1	C1	C5	-176.40(3)
C1	Fe1	Si1	Si2	-126.56(6)	C1	Fe1	Si1	Si6	128.56(6)
C1	Fe1	Si1	Si7	3.00(7)	Si4	Fe1	C1	N1	-170.55(8)
Si4	Fe1	C1	C5	9.43(9)	C1	Fe1	Si4	Si3	117.05(4)
C1	Fe1	Si4	Si5	-137.36(4)	C1	Fe1	Si4	Si8	-3.40(5)
Fe1	Si1	Si2	Si3	-20.25(2)	Fe1	Si1	Si2	C24	-143.17(2)
Fe1	Si1	Si2	C25	98.28(2)	Fe1	Si1	Si6	Si5	49.45(2)
Fe1	Si1	Si6	C30	-65.14(3)	Fe1	Si1	Si6	C31	175.32(2)
Fe1	Si1	Si7	C32	-170.35(2)	Fe1	Si1	Si7	C33	68.80(3)
Fe1	Si1	Si7	C34	-52.98(4)	Si2	Si1	Si6	Si5	-53.15(3)
Si2	Si1	Si6	C30	-167.73(2)	Si2	Si1	Si6	C31	72.73(3)
Si6	Si1	Si2	Si3	78.74(2)	Si6	Si1	Si2	C24	-44.18(3)
Si6	Si1	Si2	C25	-162.74(2)	Si2	Si1	Si7	C32	-42.54(3)
Si2	Si1	Si7	C33	-163.39(2)	Si2	Si1	Si7	C34	74.83(3)
Si7	Si1	Si2	Si3	-167.430(19)	Si7	Si1	Si2	C24	69.65(3)
Si7	Si1	Si2	C25	-48.91(3)	Si6	Si1	Si7	C32	67.99(3)
Si6	Si1	Si7	C33	-52.85(3)	Si6	Si1	Si7	C34	-174.64(2)
Si7	Si1	Si6	Si5	-165.79(2)	Si7	Si1	Si6	C30	79.62(3)
Si7	Si1	Si6	C31	-39.92(3)	Si1	Si2	Si3	Si4	-19.23(3)
Si1	Si2	Si3	C26	-145.98(2)	Si1	Si2	Si3	C27	97.31(2)
C24	Si2	Si3	Si4	105.65(5)	C24	Si2	Si3	C26	-21.09(5)
C24	Si2	Si3	C27	-137.81(5)	C25	Si2	Si3	Si4	-139.16(6)
C25	Si2	Si3	C26	94.09(6)	C25	Si2	Si3	C27	-22.63(6)
Si2	Si3	Si4	Fe1	49.52(2)	Si2	Si3	Si4	Si5	-55.54(3)
Si2	Si3	Si4	Si8	-169.247(19)	C26	Si3	Si4	Fe1	173.43(7)
C26	Si3	Si4	Si5	68.37(7)	C26	Si3	Si4	Si8	-45.33(7)

C27	Si3	Si4	Fe1	-65.99(6)	C27	Si3	Si4	Si5	-171.05(6)
C27	Si3	Si4	Si8	75.24(7)	Fe1	Si4	Si5	Si6	-17.96(2)
Fe1	Si4	Si5	C28	99.88(2)	Fe1	Si4	Si5	C29	-139.35(2)
Fe1	Si4	Si8	C35	-50.96(4)	Fe1	Si4	Si8	C36	71.56(4)
Fe1	Si4	Si8	C37	-170.96(2)	Si3	Si4	Si5	Si6	80.91(2)
Si3	Si4	Si5	C28	-161.24(2)	Si3	Si4	Si5	C29	-40.48(3)
Si3	Si4	Si8	C35	-167.34(2)	Si3	Si4	Si8	C36	-44.81(3)
Si3	Si4	Si8	C37	72.67(3)	Si5	Si4	Si8	C35	81.67(3)
Si5	Si4	Si8	C36	-155.81(2)	Si5	Si4	Si8	C37	-38.33(3)
Si8	Si4	Si5	Si6	-166.22(2)	Si8	Si4	Si5	C28	-48.38(3)
Si8	Si4	Si5	C29	72.39(3)	Si4	Si5	Si6	Si1	-20.10(3)
Si4	Si5	Si6	C30	97.33(2)	Si4	Si5	Si6	C31	-147.38(2)
C28	Si5	Si6	Si1	-137.63(6)	C28	Si5	Si6	C30	-20.19(6)
C28	Si5	Si6	C31	95.09(6)	C29	Si5	Si6	Si1	104.54(5)
C29	Si5	Si6	C30	-138.03(5)	C29	Si5	Si6	C31	-22.74(5)
C1	N1	C2	C3	14.01(13)	C1	N1	C2	C4	-13.76(13)
C1	N1	C2	C6	-129.98(11)	C1	N1	C2	C7	108.26(12)
C1	N1	C2	C8	-107.69(12)	C1	N1	C2	C9	129.55(11)
C2	N1	C1	Fe1	179.05(9)	C2	N1	C1	C5	-0.93(13)
C1	N1	C12	C13	-91.65(15)	C1	N1	C12	C17	90.22(14)
C12	N1	C1	Fe1	-0.76(19)	C12	N1	C1	C5	179.25(9)
C2	N1	C12	C13	88.54(12)	C2	N1	C12	C17	-89.59(13)
C12	N1	C2	C3	-166.16(9)	C12	N1	C2	C4	166.07(9)
C12	N1	C2	C6	49.85(13)	C12	N1	C2	C7	-71.91(13)
C12	N1	C2	C8	72.13(13)	C12	N1	C2	C9	-50.63(13)
Fe1	C1	C5	C3	167.39(7)	Fe1	C1	C5	C4	-164.92(7)
Fe1	C1	C5	C10	-57.86(12)	Fe1	C1	C5	C11	62.24(13)
N1	C1	C5	C3	-12.62(13)	N1	C1	C5	C4	15.07(13)
N1	C1	C5	C10	122.12(11)	N1	C1	C5	C11	-117.77(11)
N1	C2	C3	C4	-91.9(3)	N1	C2	C3	C5	-20.1(2)
N1	C2	C4	C3	93.3(3)	N1	C2	C4	C5	21.5(2)
N1	C2	C6	C8	97.6(6)	N1	C2	C7	C9	94.1(7)
N1	C2	C8	C6	-90.3(7)	N1	C2	C9	C7	-93.5(7)
C3	C2	C4	C3	0.0(4)	C3	C2	C4	C5	-71.8(4)
C4	C2	C3	C4	0.0(3)	C4	C2	C3	C5	71.8(5)
C3	C2	C6	C8	-30.0(8)	C6	C2	C3	C4	38.9(6)
C6	C2	C3	C5	110.7(4)	C3	C2	C7	C9	-164.3(7)
C7	C2	C3	C4	156.9(4)	C7	C2	C3	C5	-131.3(3)

C3	C2	C8	C6	156.4(6)	C8	C2	C3	C4	27.6(5)
C8	C2	C3	C5	99.4(3)	C3	C2	C9	C7	16.7(8)
C9	C2	C3	C4	151.3(4)	C9	C2	C3	C5	-136.9(3)
C4	C2	C6	C8	-12.2(7)	C6	C2	C4	C3	-150.8(3)
C6	C2	C4	C5	137.4(3)	C4	C2	C7	C9	-152.8(6)
C7	C2	C4	C3	-25.6(4)	C7	C2	C4	C5	-97.5(3)
C4	C2	C8	C6	168.6(7)	C8	C2	C4	C3	-155.1(4)
C8	C2	C4	C5	133.1(3)	C4	C2	C9	C7	33.9(9)
C9	C2	C4	C3	-37.7(5)	C9	C2	C4	C5	-109.6(4)
C6	C2	C7	C9	-27.5(8)	C7	C2	C6	C8	-140.1(6)
C6	C2	C8	C6	0.0(6)	C8	C2	C6	C8	0.0(7)
C6	C2	C9	C7	154.2(7)	C9	C2	C6	C8	-149.2(6)
C7	C2	C8	C6	47.5(8)	C8	C2	C7	C9	-43.8(9)
C8	C2	C9	C7	143.0(7)	C9	C2	C8	C6	33.0(8)
C2	C3	C4	C2	0.00(5)	C2	C3	C4	C5	109.4(2)
C2	C3	C5	C1	20.7(3)	C2	C3	C5	C4	-70.8(4)
C2	C3	C5	C10	-106.6(2)	C2	C3	C5	C11	132.9(2)
C4	C3	C5	C1	91.5(4)	C4	C3	C5	C4	-0.0(3)
C4	C3	C5	C10	-35.8(5)	C4	C3	C5	C11	-156.3(4)
C5	C3	C4	C2	-109.4(2)	C5	C3	C4	C5	0.00(6)
C2	C4	C5	C1	-23.1(2)	C2	C4	C5	C3	72.5(2)
C2	C4	C5	C10	-137.36(18)	C2	C4	C5	C11	100.8(2)
C3	C4	C5	C1	-95.6(4)	C3	C4	C5	C3	-0.0(4)
C3	C4	C5	C10	150.2(4)	C3	C4	C5	C11	28.3(5)
C2	C6	C8	C2	0.00(6)	C2	C7	C9	C2	-0.00(5)
N1	C12	C13	C14	-173.81(10)	N1	C12	C13	C18	10.62(18)
N1	C12	C17	C16	173.34(10)	N1	C12	C17	C21	-11.26(18)
C13	C12	C17	C16	-4.72(18)	C13	C12	C17	C21	170.68(11)
C17	C12	C13	C14	4.25(18)	C17	C12	C13	C18	-171.32(11)
C12	C13	C14	C15	-0.6(2)	C12	C13	C18	C19	106.24(14)
C12	C13	C18	C20	-131.41(12)	C14	C13	C18	C19	-69.27(15)
C14	C13	C18	C20	53.08(17)	C18	C13	C14	C15	175.24(11)
C13	C14	C15	C16	-2.5(2)	C14	C15	C16	C17	2.0(2)
C15	C16	C17	C12	1.5(2)	C15	C16	C17	C21	-174.06(12)
C12	C17	C21	C22	134.58(12)	C12	C17	C21	C23	-102.55(14)
C16	C17	C21	C22	-50.11(16)	C16	C17	C21	C23	72.76(14)

Reference

(1) Arata, S.; Sunada, Y. *Dalton Trans*. 2019, **48**, 2891-2895.

(2) Fischer, R.; Konopa, T.; Ully, S.; Baumgartner, J.; Marschner, C. *J. Organomet. Chem*. 2003, **685**, 79-92.

(3) Ansell, M. B.; Roberts, D. E.; Cloke, F. G. N.; Navarro, O.; Spencer, J. *Angew. Chem. Int. Ed.* 2015, **54,** 5578-5582.

(4) Xiao, Y.; Liu, Z.; Liang, J.; Yang, K.; Huang, W. *Dalton Trans.* 2022, **51**, 15873-15882.

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

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

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

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

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

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

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