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Supporting Information for:

Synthesis, X-Ray Structure, and Ring-Opening Polymerization of Pentacoordinate Silicon-Bridged [1]Ferrocenophane

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General: All manipulation was carried out under nitrogen using Schlenk tube technique. ^{1}H (300 MHz), ^{13}C (75.5 MHz), and ^{29}Si (56.6 MHz) NMR were recorded on Brucker ARX-300 spectrometer. Chemical shifts were referred to C_6D_5H (7.16 ppm) for ^{1}H NMR, C_6D_6 (128 ppm) for ^{13}C NMR, and Me_4Si (0 ppm) for ^{29}Si NMR. Solvents were purified as follows: diethyl ether and hexane by distillation from benzophenone ketyl under nitrogen; dichloromethane by distillation from calcium hydride under nitrogen.

(Chloromethyl)trichlorosilane and ferrocene were purchased from Aldrich. *N*-Methyl-*N*-trimethylsilylacetamide was purchased from Tokyo Kasei and purified by distillation from calcium hyderide.

Synthesis of 4: *n*-Butyllithium (5.4 mL, 1.59 M) in *n*-hexane was added to 0.845 g (4.5 mmol) of ferrocene dissolved in 1.2 mL of hexane, followed by 1.3 mL (8.6 mmol) of TMEDA.[1] The reaction was allowed to proceed overnight, ca 17 h. Bulk of *n*-hexane was removed under reduced pressure and 30 mL of ether was added. A slurry of dilithioferrocene in ether was cooled to –78 °C and treated dropwise with 0.85 mL (1.25 g, 6.8 mmol) of (chloromethyl)trichlorosilane and slowly warmed to room temperature. After stirring for 19 h, ether was removed under reduced pressure and the crude product was redissolved in 50 mL of *n*-hexane. The resulting slurry was filtered to remove LiCl and the filtrate was concentrated under reduced pressure to give a red-orange residue. Recrystallization of this material from *n*-hexane at –20 °C afforded 573 mg (43%) of **4** as a

red-orange crystals suitable for single crystal X-ray diffraction. ^{1}H NMR (300 MHz, C_6D_6) δ 4.29 (s, 4 H, Cp H), 4.12 (s, 2 H, Cp H), 3.95 (s, 2 H, Cp H), 2.84 (s, 2 H, CH_2); $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6) δ 79.1 (Cp), 79.0 (Cp), 76.0 (Cp), 74.6(Cp), 31.4 (*ipso*-Cp), 28.2 (CH_2); ^{29}Si NMR (59.6 MHz, C_6D_6) δ -0.27. Anal. Calcd for $C_{11}H_{10}Cl_2FeSi$: C, 44.48; H, 3.39. Found: C, 44.39; H, 3.37.

Synthesis of 1: *N*-Methyl-*N*-trimethylsilylacetamide (1.13 g, 7.78 mmol) was added dropwise to a solution of **4** (460 mg, 1.55 mmol) in *n*-hexane (2 mL) at room temperature. After stirring for 2 h, the reaction mixture was concentrated under reduced pressure to give a red solid (460mg, 89%), which was recrystallized from dichloromethane at –40 °C to afford **1** as dark red crystals suitable for single crystal X-ray diffraction. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 4.49, 4.46, 4.42, 4.23 (4 x m, 4 x 2 H, Cp H), 3.19 (s, 3 H, NCH_3), 3.17 (s, 2H, CH_2), 2.29 (s, 3 H, $COCH_3$); $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2) δ 174.8 (CO), 81.8 (Cp), 79.2 (Cp), 78.5 (Cp), 77.0 (Cp), 47.5 (*ipso*-Cp), 44.0 (CH_2), 37.1 (NCH_3), 17.3 (CH_3); ^{29}Si NMR (59.6 MHz, CD_2Cl_2) δ -69.7; UV/vis (CH_2Cl_2) λ_1 = 320 nm (sh, ε_1 = 389 $cm^{-1}M^{-1}$), λ_2 = 420 nm (ε_2 = 233 $cm^{-1}M^{-1}$). Anal. Calcd for $C_{14}H_{16}ClFeNOSi$: C, 50.39; H, 4.83; N, 4.20. Found: C, 50.42; H, 4.84; N, 4.14.

Ring-opening polymerization of 1: A solution of **1** (100 mg, 0.30 mmol) and silylium salt, $[Me_2SiCH_2N(Me)(MeC{=}O)]^+[B(3,5\text{-}(CF_3)_2C_6H_3)_4]^-$ (**3**) (3.0 mg, 0.0030 mmol) in dichloromethane (8.3 mL) was stirred at room temperature for 14 days. The resulting solution was concentrated to 1 mL. This was added slowly, dropwise to a large excess of dried *n*-hexane (ca. 100 mL). The precipitated yellow powder was collected and dried in vacuo. The yield was 53 mg (53%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 3.7-4.9 (m, 8 H), 2.5-3.7 (m, 5 H), 1.5-2.5 (m, 3 H); ^{29}Si NMR (59.6 MHz, CD_2Cl_2) δ -57.31, -59.78; UV/vis (CH_2Cl_2) λ_1 = 330 nm (ε_1 = 1305 $cm^{-1}M^{-1}$), λ_2 = 420 nm (ε_2 = 195 $cm^{-1}M^{-1}$). Anal. Calcd for $C_{14}H_{16}ClFeNOSi$: C, 50.39; H, 4.83. Found: C, 50.48; H, 5.03.

References

(1) Wrighton, M. S.; Palazzotto, M. C.; Bocarsly, A. B.; Bolts, J. M.; Fischer, A. B.; Nadjo, L. *J. Am. Chem. Soc.* **1978**, *100*, 7264.

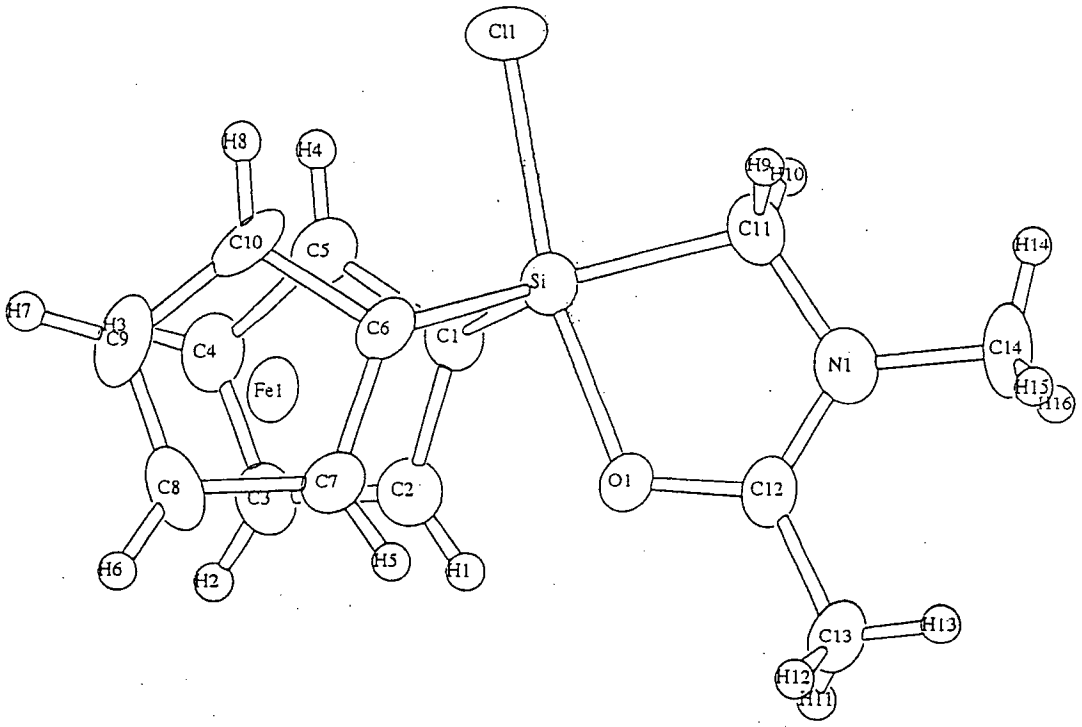

Figure S1. X-ray structure and atom-labeling scheme for **1**

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{14}H_{16}ClFeNOSi$
Formula Weight	333.67
Crystal Color, Habit	red, prismatic
Crystal Dimensions	0.10 X 0.10 X 0.05 mm
Crystal System	orthorhombic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	20 (25.4 - 29.6°)
Omega Scan Peak Width at Half-height	0.37°
Lattice Parameters	a = 12.493(3) Å b = 14.339(4) Å c = 7.544(3) Å V = 1351.5(7) Å^3
Space Group	$Pna2_1$ (#33)
Z value	4
D_{calc}	1.640 g/cm^3
F_{000}	688.00
μ(MoKα)	13.90 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku AFC7R
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Attenuator	Zr foil (factor = 7.26)

Take-off Angle	6.0°
Detector Aperture	3.0 mm horizontal 3.5 mm vertical
Crystal to Detector Distance	235 mm
Voltage, Current	50kV, 250mA
Temperature	-70.0°C
Scan Type	ω-2θ
Scan Rate	8.0°/min (in ω) (up to 5 scans)
Scan Width	$(1.15 + 0.30 \tan \theta)°$
$2\theta_{max}$	55.0°
No. of Reflections Measured	Total: 1672
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w(\|Fo\| - \|Fc\|)^2$
Least Squares Weights	$w = \frac{1}{\sigma^2(Fo)} = [\sigma_c^2(Fo) + \frac{p^2}{4}Fo^2]^{-1}$
p-factor	0.0240
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>2.00σ(I))	964
No. Variables	173
Reflection/Parameter Ratio	5.57
Residuals: R; Rw	0.040 ; 0.041
Residuals: R1	0.040
No. of Reflections to calc R1	964
Goodness of Fit Indicator	1.31

Max Shift/Error in Final Cycle	0.08
Maximum peak in Final Diff. Map	0.41 $e^-/\AA^3$
Minimum peak in Final Diff. Map	-0.29 $e^-/\AA^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
Fe(1)	0.31053(8)	0.11965(8)	0.320(3)	2.28(2)
Cl(1)	0.2852(2)	0.3834(2)	0.256(3)	4.04(5)
Si	0.3838(2)	0.2678(1)	0.133(3)	2.38(5)
O(1)	0.4835(4)	0.1913(3)	0.005(3)	2.5(1)
N(1)	0.5121(5)	0.3208(4)	-0.148(3)	2.8(1)
C(1)	0.2709(6)	0.1840(5)	0.093(3)	2.3(1)
C(2)	0.2927(6)	0.0855(5)	0.062(3)	2.5(1)
C(3)	0.2229(6)	0.0298(5)	0.159(3)	2.8(2)
C(4)	0.1537(6)	0.0887(6)	0.255(3)	3.1(1)
C(5)	0.1792(6)	0.1819(5)	0.215(3)	2.7(1)
C(6)	0.4285(5)	0.2135(5)	0.349(3)	2.4(1)
C(7)	0.4719(5)	0.1192(5)	0.351(3)	2.4(1)
C(8)	0.4257(6)	0.0667(6)	0.491(3)	3.1(2)
C(9)	0.3560(7)	0.1263(7)	0.585(3)	3.7(2)
C(10)	0.3574(6)	0.2145(6)	0.502(3)	3.1(2)
C(11)	0.4344(6)	0.3613(5)	-0.026(3)	2.9(2)
C(12)	0.5341(6)	0.2319(5)	-0.120(3)	2.5(1)
C(13)	0.6134(6)	0.1808(6)	-0.221(3)	3.1(2)
C(14)	0.5599(7)	0.3807(7)	-0.283(3)	4.5(2)
H(1)	0.344	0.064	-0.008	2.967
H(2)	0.222	-0.033	0.164	3.370
H(3)	0.101	0.070	0.332	3.664
H(4)	0.145	0.233	0.260	3.173
H(5)	0.521	0.097	0.276	2.848

Table 1. Atomic coordinates and B_{iso}/B_{eq} (continued)

atom	x	y	z	B_{eq}
H(6)	0.439	0.006	0.518	3.690
H(7)	0.317	0.111	0.684	4.452
H(8)	0.319	0.264	0.542	3.708
H(9)	0.467	0.410	0.043	3.490
H(10)	0.376	0.386	-0.088	3.490
H(11)	0.580	0.129	-0.275	3.754
H(12)	0.668	0.159	-0.142	3.754
H(13)	0.644	0.221	-0.306	3.754
H(14)	0.530	0.441	-0.272	5.442
H(15)	0.635	0.384	-0.261	5.442
H(16)	0.546	0.356	-0.394	5.442

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

Table 2. Anisotropic Displacement Parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	0.0293(5)	0.0370(5)	0.0204(4)	-0.0019(6)	-0.0007(6)	0.0028(7)
Cl(1)	0.055(1)	0.033(1)	0.066(2)	0.0085(10)	0.018(1)	-0.010(1)
Si	0.031(1)	0.031(1)	0.028(1)	0.0001(9)	0.0012(10)	0.001(1)
O(1)	0.035(3)	0.032(3)	0.027(3)	0.001(2)	0.008(2)	0.001(2)
N(1)	0.032(3)	0.041(3)	0.034(4)	-0.008(3)	-0.008(3)	0.004(3)
C(1)	0.026(3)	0.038(3)	0.025(3)	0.003(2)	-0.007(3)	0.005(3)
C(2)	0.032(5)	0.038(3)	0.024(2)	-0.004(3)	-0.012(3)	-0.004(3)
C(3)	0.044(5)	0.034(4)	0.029(5)	-0.009(3)	-0.006(3)	0.001(3)
C(4)	0.030(2)	0.048(4)	0.038(5)	-0.010(3)	0.002(3)	0.004(4)
C(5)	0.026(3)	0.043(4)	0.031(4)	0.001(3)	-0.002(3)	-0.002(3)
C(6)	0.027(3)	0.039(3)	0.024(3)	-0.001(2)	0.003(3)	-0.005(3)
C(7)	0.030(1)	0.040(3)	0.021(4)	0.004(3)	-0.005(3)	-0.004(4)
C(8)	0.040(4)	0.044(5)	0.033(4)	-0.005(3)	-0.016(3)	0.019(3)
C(9)	0.047(5)	0.075(5)	0.019(2)	-0.005(4)	0.002(3)	0.006(4)
C(10)	0.037(5)	0.061(4)	0.020(4)	0.003(4)	0.005(3)	-0.020(3)
C(11)	0.042(5)	0.033(4)	0.036(5)	-0.005(3)	0.001(3)	0.007(3)
C(12)	0.026(4)	0.042(3)	0.026(4)	-0.004(3)	-0.002(3)	0.005(3)
C(13)	0.033(4)	0.047(5)	0.039(6)	-0.002(4)	0.013(4)	0.003(4)
C(14)	0.062(6)	0.061(6)	0.049(6)	-0.012(5)	0.020(5)	0.023(5)

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 3. Bond Lengths($\AA$)

atom	atom	distance	atom	atom	distance
Fe(1)	Si	2.708(3)	Fe(1)	C(1)	2.005(9)
Fe(1)	C(2)	2.02(1)	Fe(1)	C(3)	2.078(9)
Fe(1)	C(4)	2.068(9)	Fe(1)	C(5)	2.027(9)
Fe(1)	C(6)	2.008(8)	Fe(1)	C(7)	2.030(8)
Fe(1)	C(8)	2.078(9)	Fe(1)	C(9)	2.08(1)
Fe(1)	C(10)	2.02(1)	Cl(1)	Si	2.264(4)
Si	O(1)	1.920(6)	Si	C(1)	1.878(9)
Si	C(6)	1.891(9)	Si	C(11)	1.905(9)
O(1)	C(12)	1.281(9)	N(1)	C(11)	1.46(1)
N(1)	C(12)	1.32(1)	N(1)	C(14)	1.46(1)
C(1)	C(2)	1.46(1)	C(1)	C(5)	1.47(1)
C(2)	C(3)	1.39(1)	C(3)	C(4)	1.41(1)
C(4)	C(5)	1.41(1)	C(6)	C(7)	1.46(1)
C(6)	C(10)	1.46(1)	C(7)	C(8)	1.42(1)
C(8)	C(9)	1.41(1)	C(9)	C(10)	1.41(1)
C(12)	C(13)	1.45(1)			

Table 4. Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
C(2)	H(1)	0.89	C(3)	H(2)	0.90
C(4)	H(3)	0.91	C(5)	H(4)	0.91
C(7)	H(5)	0.89	C(8)	H(6)	0.91
C(9)	H(7)	0.92	C(10)	H(8)	0.91
C(11)	H(9)	0.96	C(11)	H(10)	0.94
C(13)	H(11)	0.94	C(13)	H(12)	0.96
C(13)	H(13)	0.94	C(14)	H(14)	0.95
C(14)	H(15)	0.95	C(14)	H(16)	0.93

Table 5. Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
Si	Fe(1)	C(1)	43.9(3)	Si	Fe(1)	C(2)	74.2(3)
Si	Fe(1)	C(3)	111.3(3)	Si	Fe(1)	C(4)	111.5(3)
Si	Fe(1)	C(5)	74.1(3)	Si	Fe(1)	C(6)	44.3(3)
Si	Fe(1)	C(7)	74.1(3)	Si	Fe(1)	C(8)	112.1(3)
Si	Fe(1)	C(9)	111.8(3)	Si	Fe(1)	C(10)	74.3(3)
C(1)	Fe(1)	C(2)	42.4(3)	C(1)	Fe(1)	C(3)	70.1(4)
C(1)	Fe(1)	C(4)	70.3(4)	C(1)	Fe(1)	C(5)	42.8(3)
C(1)	Fe(1)	C(6)	88.2(4)	C(1)	Fe(1)	C(7)	110.1(4)
C(1)	Fe(1)	C(8)	150.4(4)	C(1)	Fe(1)	C(9)	150.0(4)
C(1)	Fe(1)	C(10)	110.1(4)	C(2)	Fe(1)	C(3)	39.7(3)
C(2)	Fe(1)	C(4)	67.4(4)	C(2)	Fe(1)	C(5)	69.0(4)
C(2)	Fe(1)	C(6)	110.5(4)	C(2)	Fe(1)	C(7)	102.7(4)
C(2)	Fe(1)	C(8)	126.0(4)	C(2)	Fe(1)	C(9)	165.4(4)
C(2)	Fe(1)	C(10)	148.4(4)	C(3)	Fe(1)	C(4)	39.7(3)
C(3)	Fe(1)	C(5)	67.7(4)	C(3)	Fe(1)	C(6)	150.1(4)
C(3)	Fe(1)	C(7)	126.0(4)	C(3)	Fe(1)	C(8)	120.0(4)
C(3)	Fe(1)	C(9)	137.0(4)	C(3)	Fe(1)	C(10)	164.9(4)
C(4)	Fe(1)	C(5)	40.1(3)	C(4)	Fe(1)	C(6)	150.0(4)
C(4)	Fe(1)	C(7)	165.5(4)	C(4)	Fe(1)	C(8)	136.4(4)
C(4)	Fe(1)	C(9)	119.7(4)	C(4)	Fe(1)	C(10)	125.4(4)
C(5)	Fe(1)	C(6)	110.0(4)	C(5)	Fe(1)	C(7)	148.2(4)
C(5)	Fe(1)	C(8)	164.4(4)	C(5)	Fe(1)	C(9)	125.1(4)
C(5)	Fe(1)	C(10)	101.8(4)	C(6)	Fe(1)	C(7)	42.3(3)
C(6)	Fe(1)	C(8)	70.6(3)	C(6)	Fe(1)	C(9)	70.3(4)

Table 5. Bond Angles(°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
C(6)	Fe(1)	C(10)	42.4(3)	C(7)	Fe(1)	C(8)	40.5(3)
C(7)	Fe(1)	C(9)	67.6(4)	C(7)	Fe(1)	C(10)	68.7(4)
C(8)	Fe(1)	C(9)	39.6(4)	C(8)	Fe(1)	C(10)	67.7(4)
C(9)	Fe(1)	C(10)	40.1(4)	Fe(1)	Si	Cl(1)	100.2(1)
Fe(1)	Si	O(1)	91.8(2)	Fe(1)	Si	C(1)	47.7(3)
Fe(1)	Si	C(6)	47.8(3)	Fe(1)	Si	C(11)	172.2(3)
Cl(1)	Si	O(1)	167.9(2)	Cl(1)	Si	C(1)	97.2(3)
Cl(1)	Si	C(6)	96.2(3)	Cl(1)	Si	C(11)	85.7(3)
O(1)	Si	C(1)	92.3(3)	O(1)	Si	C(6)	90.3(3)
O(1)	Si	C(11)	82.6(4)	C(1)	Si	C(6)	95.6(4)
C(1)	Si	C(11)	126.7(4)	C(6)	Si	C(11)	137.2(4)
Si	O(1)	C(12)	115.6(5)	C(11)	N(1)	C(12)	114.9(8)
C(11)	N(1)	C(14)	118.6(7)	C(12)	N(1)	C(14)	126.5(8)
Fe(1)	C(1)	Si	88.4(4)	Fe(1)	C(1)	C(2)	69.3(5)
Fe(1)	C(1)	C(5)	69.4(5)	Si	C(1)	C(2)	120.5(6)
Si	C(1)	C(5)	119.8(6)	C(2)	C(1)	C(5)	103.1(7)
Fe(1)	C(2)	C(1)	68.3(5)	Fe(1)	C(2)	C(3)	72.4(5)
C(1)	C(2)	C(3)	110.7(8)	Fe(1)	C(3)	C(2)	67.9(5)
Fe(1)	C(3)	C(4)	69.8(5)	C(2)	C(3)	C(4)	108.1(8)
Fe(1)	C(4)	C(3)	70.5(5)	Fe(1)	C(4)	C(5)	68.4(5)
C(3)	C(4)	C(5)	108.7(8)	Fe(1)	C(5)	C(1)	67.8(5)
Fe(1)	C(5)	C(4)	71.5(5)	C(1)	C(5)	C(4)	109.3(7)
Fe(1)	C(6)	Si	87.9(4)	Fe(1)	C(6)	C(7)	69.6(4)
Fe(1)	C(6)	C(10)	69.3(5)	Si	C(6)	C(7)	119.9(6)

Table 5. Bond Angles(°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
Si	C(6)	C(10)	120.0(6)	C(7)	C(6)	C(10)	103.3(8)
Fe(1)	C(7)	C(6)	68.1(4)	Fe(1)	C(7)	C(8)	71.6(5)
C(6)	C(7)	C(8)	110.2(8)	Fe(1)	C(8)	C(7)	67.9(5)
Fe(1)	C(8)	C(9)	70.3(5)	C(7)	C(8)	C(9)	107.7(8)
Fe(1)	C(9)	C(8)	70.0(5)	Fe(1)	C(9)	C(10)	67.7(5)
C(8)	C(9)	C(10)	108.3(8)	Fe(1)	C(10)	C(6)	68.2(5)
Fe(1)	C(10)	C(9)	72.2(6)	C(6)	C(10)	C(9)	110.4(8)
Si	C(11)	N(1)	109.8(6)	O(1)	C(12)	N(1)	117.0(8)
O(1)	C(12)	C(13)	119.8(8)	N(1)	C(12)	C(13)	123.1(8)

Table 6. Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
Fe(1)	C(2)	H(1)	125.3	C(1)	C(2)	H(1)	125.0
C(3)	C(2)	H(1)	124.3	Fe(1)	C(3)	H(2)	126.9
C(2)	C(3)	H(2)	126.8	C(4)	C(3)	H(2)	125.1
Fe(1)	C(4)	H(3)	126.1	C(3)	C(4)	H(3)	125.8
C(5)	C(4)	H(3)	125.5	Fe(1)	C(5)	H(4)	126.1
C(1)	C(5)	H(4)	125.9	C(4)	C(5)	H(4)	124.8
Fe(1)	C(7)	H(5)	128.0	C(6)	C(7)	H(5)	125.5
C(8)	C(7)	H(5)	124.3	Fe(1)	C(8)	H(6)	127.9
C(7)	C(8)	H(6)	127.1	C(9)	C(8)	H(6)	125.2
Fe(1)	C(9)	H(7)	128.8	C(8)	C(9)	H(7)	126.3
C(10)	C(9)	H(7)	125.4	Fe(1)	C(10)	H(8)	126.9
C(6)	C(10)	H(8)	125.7	C(9)	C(10)	H(8)	123.9
Si	C(11)	H(9)	108.4	Si	C(11)	H(10)	108.7
N(1)	C(11)	H(9)	110.1	N(1)	C(11)	H(10)	110.4
H(9)	C(11)	H(10)	109.3	C(12)	C(13)	H(11)	109.2
C(12)	C(13)	H(12)	108.7	C(12)	C(13)	H(13)	109.2
H(11)	C(13)	H(12)	109.0	H(11)	C(13)	H(13)	111.3
H(12)	C(13)	H(13)	109.5	N(1)	C(14)	H(14)	108.6
N(1)	C(14)	H(15)	108.4	N(1)	C(14)	H(16)	109.0
H(14)	C(14)	H(15)	109.0	H(14)	C(14)	H(16)	111.1
H(15)	C(14)	H(16)	110.7				

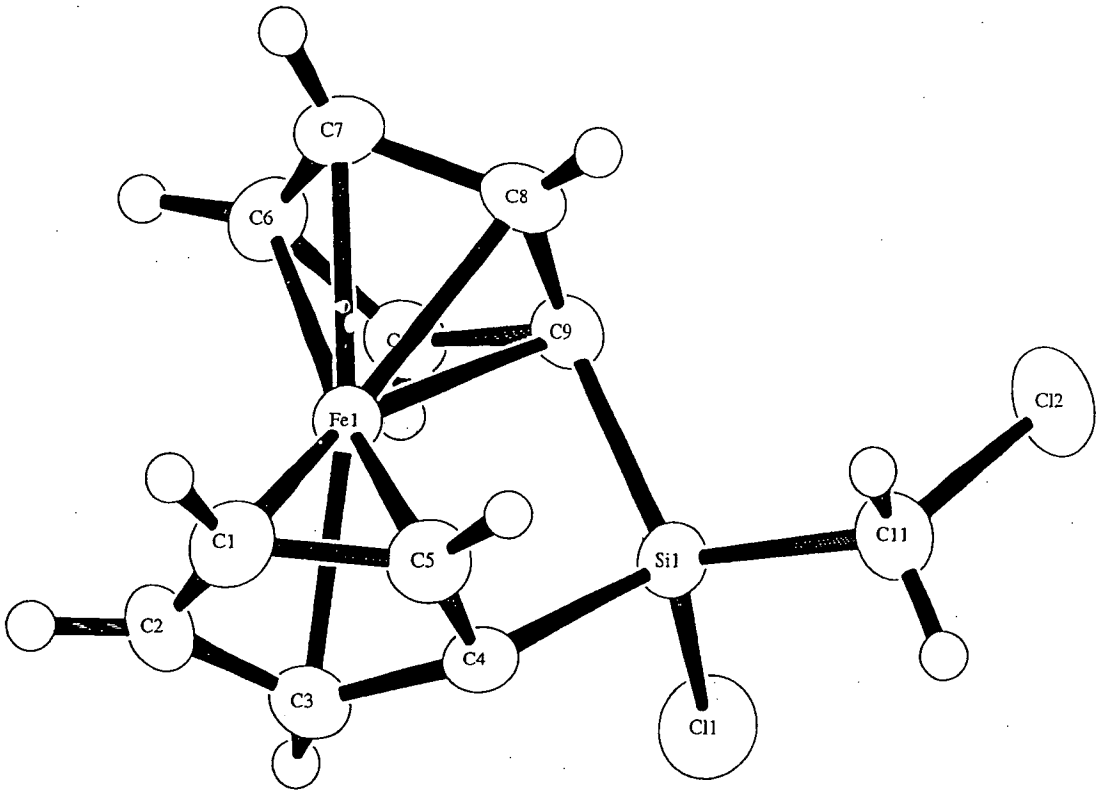

Figure S2. X-ray structure and atom-labeling scheme for **3**

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$FeSiC_{11}Cl_2H_{10}$
Formula Weight	297.04
Crystal Color, Habit	red, prismatic
Crystal Dimensions	0.20 X 0.20 X 0.40 mm
Crystal System	orthorhombic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	25 (29.5 - 30.0°)
Omega Scan Peak Width at Half-height	0.23°
Lattice Parameters	a = 9.625(5) Å b = 15.549(2) Å c = 7.753(3) Å
	V = 1160.2(6) $Å^3$
Space Group	$P2_12_12_1$ (#19)
Z value	4
D_{calc}	1.700 g/cm^3
F_{000}	600.00
μ(MoKα)	18.21 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku AFC7R
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Attenuator	Zr foil (factor = 7.26)

Take-off Angle	6.0°
Detector Aperture	3.0 mm horizontal 3.5 mm vertical
Crystal to Detector Distance	235 mm
Voltage, Current	50kV, 200mA
Temperature	-70.0°C
Scan Type	ω-2θ
Scan Rate	16.0°/min (in ω) (up to 5 scans)
Scan Width	$(1.57 + 0.30 \tan \theta)°$
$2\theta_{max}$	55.0°
No. of Reflections Measured	Total: 1550
Corrections	Lorentz-polarization Absorption (trans. factors: 0.8856 - 0.9940)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w(\|Fo\| - \|Fc\|)^2$
Least Squares Weights	$w = \frac{1}{\sigma^2(Fo)} = [\sigma_c^2(Fo) + \frac{p^2}{4}Fo^2]^{-1}$
p-factor	0.0400
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00σ(I))	1454
No. Variables	137
Reflection/Parameter Ratio	10.61
Residuals: R; Rw	0.023 ; 0.033
Residuals: R1	0.023
No. of Reflections to calc R1	1454

Goodness of Fit Indicator	1.17
Max Shift/Error in Final Cycle	0.04
Maximum peak in Final Diff. Map	0.18 $e^-/\AA^3$
Minimum peak in Final Diff. Map	-0.21 $e^-/\AA^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
Fe(1)	0.02070(4)	0.90889(2)	0.69956(5)	2.303(7)
Cl(1)	-0.24211(8)	0.74548(5)	0.9496(1)	4.00(2)
Cl(2)	-0.50595(8)	0.91203(6)	0.8246(1)	4.27(2)
Si(1)	-0.22306(7)	0.83989(4)	0.76630(9)	2.26(1)
C(1)	0.0944(3)	0.8740(2)	0.4554(4)	3.38(5)
C(2)	0.1547(3)	0.8216(2)	0.5866(4)	3.49(6)
C(3)	0.0460(3)	0.7797(2)	0.6782(4)	2.98(5)
C(4)	-0.0857(3)	0.8073(2)	0.6098(4)	2.45(4)
C(5)	-0.0533(3)	0.8658(2)	0.4696(4)	2.86(5)
C(6)	0.0920(3)	0.9824(2)	0.9057(4)	3.18(5)
C(7)	0.0329(3)	1.0363(2)	0.7772(4)	3.29(5)
C(8)	-0.1074(3)	1.0092(2)	0.7503(4)	2.78(5)
C(9)	-0.1364(3)	0.9359(2)	0.8617(3)	2.44(4)
C(10)	-0.0092(3)	0.9217(2)	0.9576(3)	2.76(4)
C(11)	-0.3954(3)	0.8632(2)	0.6682(4)	3.08(5)
H(1)	-0.384	0.902	0.572	3.719
H(2)	-0.437	0.812	0.626	3.719
H(3)	0.061	0.741	0.788	4.439
H(4)	0.250	0.823	0.575	4.439
H(5)	0.137	0.913	0.369	4.439
H(6)	-0.117	0.897	0.377	4.439
H(7)	0.189	0.986	0.952	4.439
H(8)	0.073	1.088	0.715	4.439
H(9)	-0.168	1.038	0.672	4.439

Table 1. Atomic coordinates and B_{iso}/B_{eq} (continued)

atom	x	y	z	B_{eq}
H(10)	-0.002	0.878	1.046	4.439

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

Table 2. Anisotropic Displacement Parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	0.0264(2)	0.0283(2)	0.0328(2)	-0.0008(1)	0.0015(1)	-0.0075(2)
Cl(1)	0.0552(5)	0.0489(4)	0.0480(4)	-0.0032(3)	0.0059(4)	0.0177(4)
Cl(2)	0.0386(4)	0.0698(5)	0.0540(4)	0.0105(4)	0.0072(3)	-0.0115(4)
Si(1)	0.0272(3)	0.0303(3)	0.0283(3)	-0.0020(3)	0.0007(3)	-0.0001(3)
C(1)	0.041(1)	0.046(1)	0.042(1)	-0.009(1)	0.016(1)	-0.014(1)
C(2)	0.027(1)	0.050(1)	0.056(2)	0.0053(10)	0.004(1)	-0.026(1)
C(3)	0.036(1)	0.0305(9)	0.046(2)	0.005(1)	-0.006(1)	-0.013(1)
C(4)	0.033(1)	0.025(1)	0.035(1)	-0.0025(8)	-0.0001(9)	-0.0092(8)
C(5)	0.039(1)	0.040(1)	0.029(1)	-0.002(1)	0.003(1)	-0.0078(9)
C(6)	0.034(1)	0.044(1)	0.043(1)	-0.006(1)	-0.005(1)	-0.018(1)
C(7)	0.045(1)	0.0300(10)	0.050(1)	-0.005(1)	0.004(1)	-0.012(1)
C(8)	0.041(1)	0.028(1)	0.036(1)	0.0072(9)	0.002(1)	-0.0069(9)
C(9)	0.031(1)	0.033(1)	0.030(1)	0.0023(9)	0.0033(9)	-0.0086(9)
C(10)	0.036(1)	0.037(1)	0.0314(10)	0.0034(10)	-0.004(1)	-0.010(1)
C(11)	0.034(1)	0.043(1)	0.040(1)	0.003(1)	-0.0046(10)	-0.006(1)

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 3. Bond Lengths($\AA$)

atom	atom	distance	atom	atom	distance
Fe(1)	Si(1)	2.631(1)	Fe(1)	C(1)	2.093(3)
Fe(1)	C(2)	2.067(3)	Fe(1)	C(3)	2.030(3)
Fe(1)	C(4)	2.008(3)	Fe(1)	C(5)	2.033(3)
Fe(1)	C(6)	2.081(3)	Fe(1)	C(7)	2.073(3)
Fe(1)	C(8)	2.026(3)	Fe(1)	C(9)	2.011(3)
Fe(1)	C(10)	2.031(3)	Cl(1)	Si(1)	2.052(1)
Cl(2)	C(11)	1.783(3)	Si(1)	C(4)	1.865(3)
Si(1)	C(9)	1.864(3)	Si(1)	C(11)	1.860(3)
C(1)	C(2)	1.426(5)	C(1)	C(5)	1.431(4)
C(2)	C(3)	1.422(4)	C(3)	C(4)	1.439(4)
C(4)	C(5)	1.452(4)	C(6)	C(7)	1.420(5)
C(6)	C(10)	1.415(4)	C(7)	C(8)	1.430(4)
C(8)	C(9)	1.456(4)	C(9)	C(10)	1.449(4)

Table 4. Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
C(1)	H(5)	0.99	C(2)	H(4)	0.92
C(3)	H(3)	1.06	C(5)	H(6)	1.07
C(6)	H(7)	1.00	C(7)	H(8)	1.01
C(8)	H(9)	0.96	C(10)	H(10)	0.97
C(11)	H(1)	0.97	C(11)	H(2)	0.95

Table 5. Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
Si(1)	Fe(1)	C(1)	111.99(9)	Si(1)	Fe(1)	C(2)	111.83(9)
Si(1)	Fe(1)	C(3)	73.70(9)	Si(1)	Fe(1)	C(4)	44.96(9)
Si(1)	Fe(1)	C(5)	74.09(9)	Si(1)	Fe(1)	C(6)	111.53(9)
Si(1)	Fe(1)	C(7)	112.53(9)	Si(1)	Fe(1)	C(8)	74.53(9)
Si(1)	Fe(1)	C(9)	44.93(8)	Si(1)	Fe(1)	C(10)	73.74(8)
C(1)	Fe(1)	C(2)	40.1(1)	C(1)	Fe(1)	C(3)	68.2(1)
C(1)	Fe(1)	C(4)	69.8(1)	C(1)	Fe(1)	C(5)	40.6(1)
C(1)	Fe(1)	C(6)	136.5(1)	C(1)	Fe(1)	C(7)	119.4(1)
C(1)	Fe(1)	C(8)	125.5(1)	C(1)	Fe(1)	C(9)	151.0(1)
C(1)	Fe(1)	C(10)	164.6(1)	C(2)	Fe(1)	C(3)	40.6(1)
C(2)	Fe(1)	C(4)	69.8(1)	C(2)	Fe(1)	C(5)	68.3(1)
C(2)	Fe(1)	C(6)	118.7(1)	C(2)	Fe(1)	C(7)	135.6(1)
C(2)	Fe(1)	C(8)	165.3(1)	C(2)	Fe(1)	C(9)	150.6(1)
C(2)	Fe(1)	C(10)	124.8(1)	C(3)	Fe(1)	C(4)	41.7(1)
C(3)	Fe(1)	C(5)	69.2(1)	C(3)	Fe(1)	C(6)	124.5(1)
C(3)	Fe(1)	C(7)	164.2(1)	C(3)	Fe(1)	C(8)	148.2(1)
C(3)	Fe(1)	C(9)	110.4(1)	C(3)	Fe(1)	C(10)	101.2(1)
C(4)	Fe(1)	C(5)	42.1(1)	C(4)	Fe(1)	C(6)	150.1(1)
C(4)	Fe(1)	C(7)	151.8(1)	C(4)	Fe(1)	C(8)	111.3(1)
C(4)	Fe(1)	C(9)	89.9(1)	C(4)	Fe(1)	C(10)	110.3(1)
C(5)	Fe(1)	C(6)	165.8(1)	C(5)	Fe(1)	C(7)	126.1(1)
C(5)	Fe(1)	C(8)	102.2(1)	C(5)	Fe(1)	C(9)	110.7(1)
C(5)	Fe(1)	C(10)	147.8(1)	C(6)	Fe(1)	C(7)	40.0(1)
C(6)	Fe(1)	C(8)	68.2(1)	C(6)	Fe(1)	C(9)	69.7(1)

Table 5. Bond Angles(°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
C(6)	Fe(1)	C(10)	40.2(1)	C(7)	Fe(1)	C(8)	40.8(1)
C(7)	Fe(1)	C(9)	70.2(1)	C(7)	Fe(1)	C(10)	68.2(1)
C(8)	Fe(1)	C(9)	42.3(1)	C(8)	Fe(1)	C(10)	69.3(1)
C(9)	Fe(1)	C(10)	42.0(1)	Fe(1)	Si(1)	Cl(1)	120.51(4)
Fe(1)	Si(1)	C(4)	49.53(8)	Fe(1)	Si(1)	C(9)	49.62(9)
Fe(1)	Si(1)	C(11)	129.4(1)	Cl(1)	Si(1)	C(4)	108.63(9)
Cl(1)	Si(1)	C(9)	109.8(1)	Cl(1)	Si(1)	C(11)	110.1(1)
C(4)	Si(1)	C(9)	99.1(1)	C(4)	Si(1)	C(11)	114.8(1)
C(9)	Si(1)	C(11)	113.9(1)	Fe(1)	C(1)	C(2)	69.0(2)
Fe(1)	C(1)	C(5)	67.5(2)	C(2)	C(1)	C(5)	107.3(3)
Fe(1)	C(2)	C(1)	70.9(2)	Fe(1)	C(2)	C(3)	68.3(2)
C(1)	C(2)	C(3)	108.6(3)	Fe(1)	C(3)	C(2)	71.1(2)
Fe(1)	C(3)	C(4)	68.3(1)	C(2)	C(3)	C(4)	109.1(3)
Fe(1)	C(4)	Si(1)	85.5(1)	Fe(1)	C(4)	C(3)	69.9(2)
Fe(1)	C(4)	C(5)	69.9(2)	Si(1)	C(4)	C(3)	117.7(2)
Si(1)	C(4)	C(5)	117.9(2)	C(3)	C(4)	C(5)	105.9(3)
Fe(1)	C(5)	C(1)	72.0(2)	Fe(1)	C(5)	C(4)	68.0(2)
C(1)	C(5)	C(4)	109.1(3)	Fe(1)	C(6)	C(7)	69.7(2)
Fe(1)	C(6)	C(10)	68.0(2)	C(7)	C(6)	C(10)	108.5(3)
Fe(1)	C(7)	C(6)	70.3(2)	Fe(1)	C(7)	C(8)	67.8(1)
C(6)	C(7)	C(8)	107.8(3)	Fe(1)	C(8)	C(7)	71.4(2)
Fe(1)	C(8)	C(9)	68.3(1)	C(7)	C(8)	C(9)	109.0(3)
Fe(1)	C(9)	Si(1)	85.5(1)	Fe(1)	C(9)	C(8)	69.4(2)
Fe(1)	C(9)	C(10)	69.7(2)	Si(1)	C(9)	C(8)	118.5(2)

Table 5. Bond Angles(°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
Si(1)	C(9)	C(10)	117.3(2)	C(8)	C(9)	C(10)	105.2(3)
Fe(1)	C(10)	C(6)	71.8(2)	Fe(1)	C(10)	C(9)	68.2(2)
C(6)	C(10)	C(9)	109.5(3)	Cl(2)	C(11)	Si(1)	109.7(2)

Table 6. Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
Fe(1)	C(1)	H(5)	126.5	C(2)	C(1)	H(5)	131.2
C(5)	C(1)	H(5)	121.4	Fe(1)	C(2)	H(4)	130.3
C(1)	C(2)	H(4)	108.8	C(3)	C(2)	H(4)	142.3
Fe(1)	C(3)	H(3)	121.2	C(2)	C(3)	H(3)	124.1
C(4)	C(3)	H(3)	126.3	Fe(1)	C(5)	H(6)	129.9
C(1)	C(5)	H(6)	118.8	C(4)	C(5)	H(6)	131.9
Fe(1)	C(6)	H(7)	127.9	C(7)	C(6)	H(7)	126.0
C(10)	C(6)	H(7)	125.5	Fe(1)	C(7)	H(8)	129.8
C(6)	C(7)	H(8)	130.4	C(8)	C(7)	H(8)	121.6
Fe(1)	C(8)	H(9)	127.8	C(7)	C(8)	H(9)	121.8
C(9)	C(8)	H(9)	129.2	Fe(1)	C(10)	H(10)	128.1
C(6)	C(10)	H(10)	128.5	C(9)	C(10)	H(10)	122.0
Cl(2)	C(11)	H(1)	109.2	Cl(2)	C(11)	H(2)	109.9
Si(1)	C(11)	H(1)	109.6	Si(1)	C(11)	H(2)	110.5
H(1)	C(11)	H(2)	107.9				