Supporting information for

A Four Coordinated Iron(II)-digermyl Complex as an Effective Precursor for the Catalytic Dehydrogenation of Ammonia Borane

Yoshinao Kobayashi and Yusuke Sunada

Contents

Table S1. Dehydrogenation of ammonia borane catalyzed by **1** in the presence of ^{t}BuOH as an additive. [a]

entry	additive	ligand	Time (h)	Conv. (%)[b]
1	^{t}BuOH	none	24	~ 0
2		phenanthroline	24	50
3[c]		phenanthroline	24	37
4		phenanthroline	72	70
5		bathophenanthroline	24	9
6		diimine[d]	24	24
7		$^{i}Pr_2IM^{Me}$[e]	24	32
8		TMEDA	24	~ 0
9		pyridine	24	5

[a] All reactions were carried out with ammonia borane (0.5 mmol), catalytic amount of **1** (5 mol%), ^{t}BuOH (5 mol%), and ligand (5 mol%) at 55 ºC in THF (5 mL). [b] Conversion of ammonia borane was determined by ^{11}B NMR. [c] reaction was performed with 10 mol% of ^{t}BuOH. [d] diimine = 2,3-bis(2,4,6-trimethylphenylimino)butane [e] $^{i}Pr_2IM^{Me}$ = 1,3-diisopropyl-4,5-dimethyl-imidazol-2-ylidene

Table S2. Dehydrogenation of ammonia borane catalyzed in the presence of various additives.[a]

entry	additive	Cat.	ligand	Time (h)	Conv. (%)[b]
1	none	**1**	phenanthroline	24	5
2	^{t}BuOH	**1**		24	50
3[c]	^{t}BuOH	**2**		24	72
4	$^{t}BuNH_2$	**1**		24	76
5	diethylamine	**1**		24	64
6	diphenyamine	**1**		24	61
7	2,4,6-trimethylaniline	**1**		24	64
8	2,6-diisopropylaniline	**1**		24	30
9	2-ethylhexanoic acid	**1**		24	39
10	none	**1**	none	24	~ 0
11	diphenyamine	**1**		24	~ 0
12	2,4,6-trimethylaniline	**1**		24	~ 0
13	2,6-diisopropylaniline	**1**		24	11
14	2-ethylhexanoic acid	**1**		24	19
15	diphenyamine	**1**	$^{i}Pr_2IM^{Me}$	24	19
16	2,4,6-trimethylaniline	**1**		24	14
17	2,6-diisopropylaniline	**1**		24	14
18	2-ethylhexanoic acid	**1**		24	~ 0

[a] All reactions were carried out with ammonia borane (0.5 mmol), catalytic amount of **1** (5 mol%), phenanthrolne (5 mol%), and additive (5 mol%) at 55 ºC in THF (5 mL) for 24h. [b] Conversion of ammonia borane was determined by ^{11}B NMR. [c] Complex **2** was used instead of **1**.

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

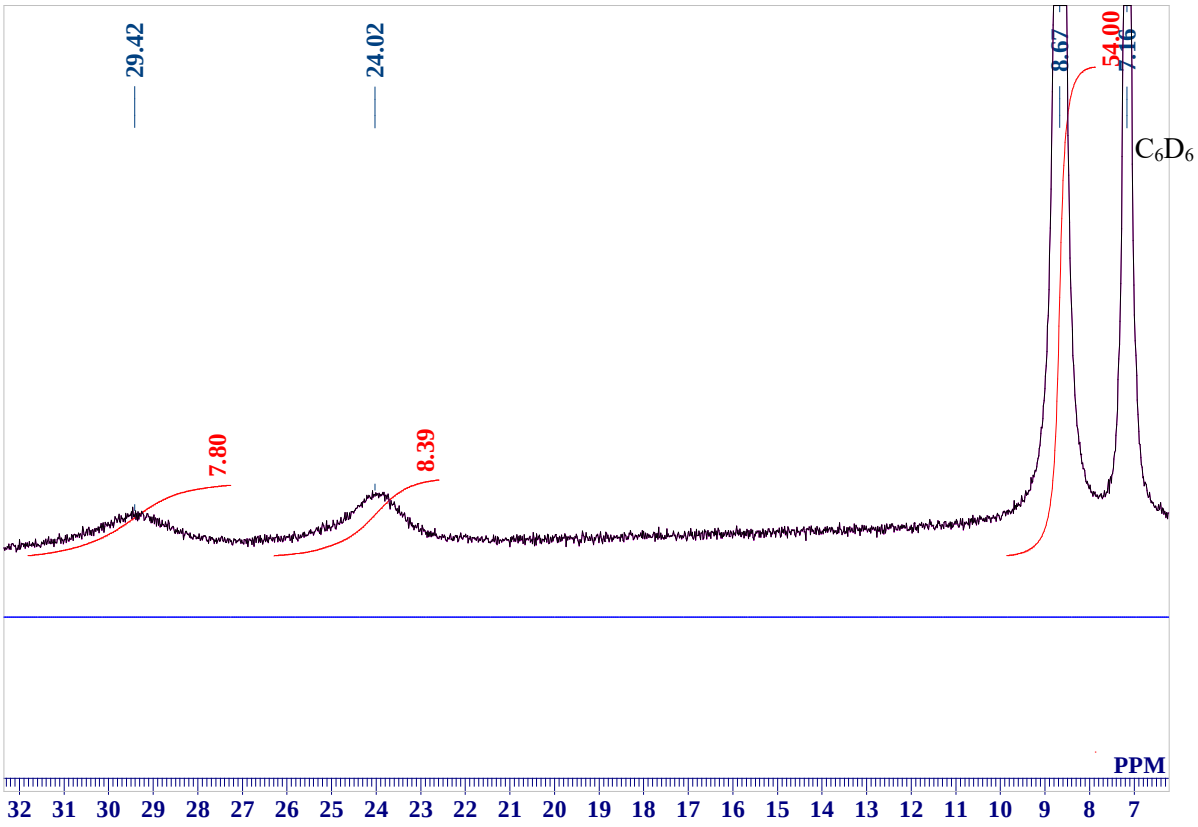


Figure S2-1. ^{1}H NMR spectrum (in THF-d_8 at room temperature) of the crude product obtained from the hydrogenation ammonia borane catalyzed by **1** in the presence of ^{t}BuOH and phenanthroline (Table 1 entry 2 in the main manuscript or Table S1 entry 2 in the supporting information).

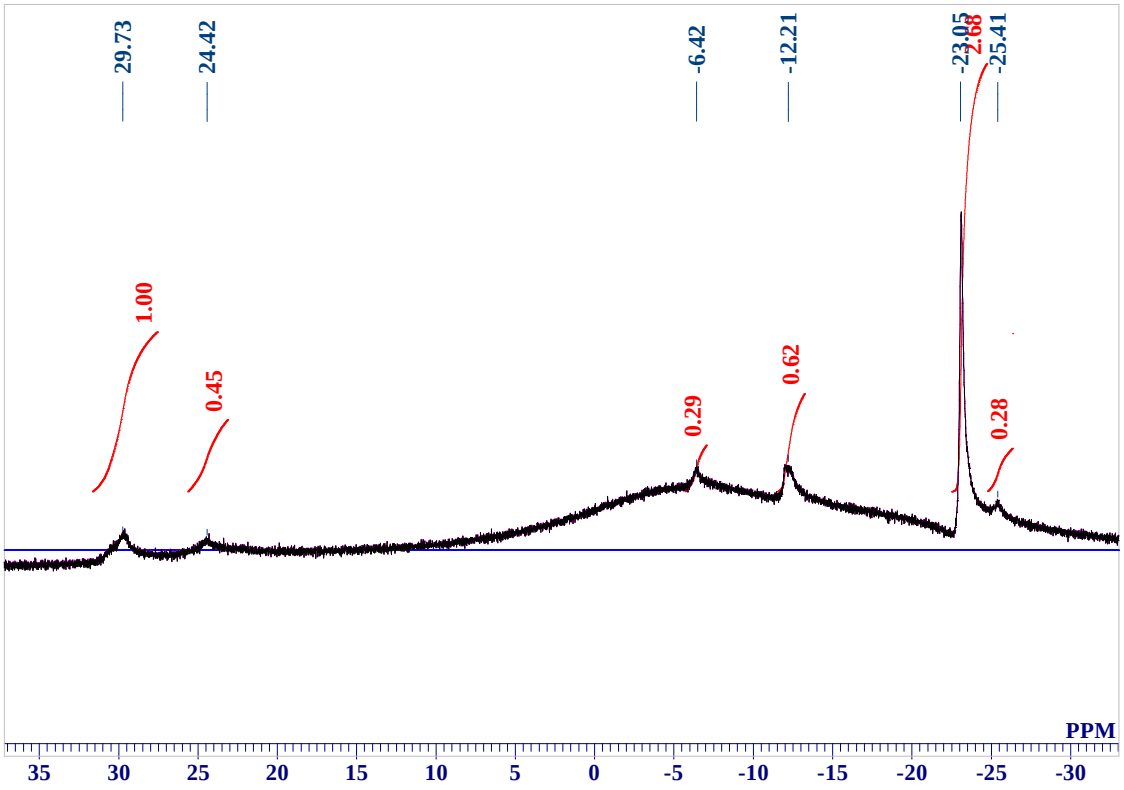


Figure S2-2. ^{1}H NMR spectrum (in THF-d_8 at room temperature) of the crude product obtained from the hydrogenation ammonia borane catalyzed by **1** in the presence of ^{t}BuNH$_2$ and phenanthroline (Table 2 entry 4 in the main manuscript or Table S2 entry 4 in the supporting information).

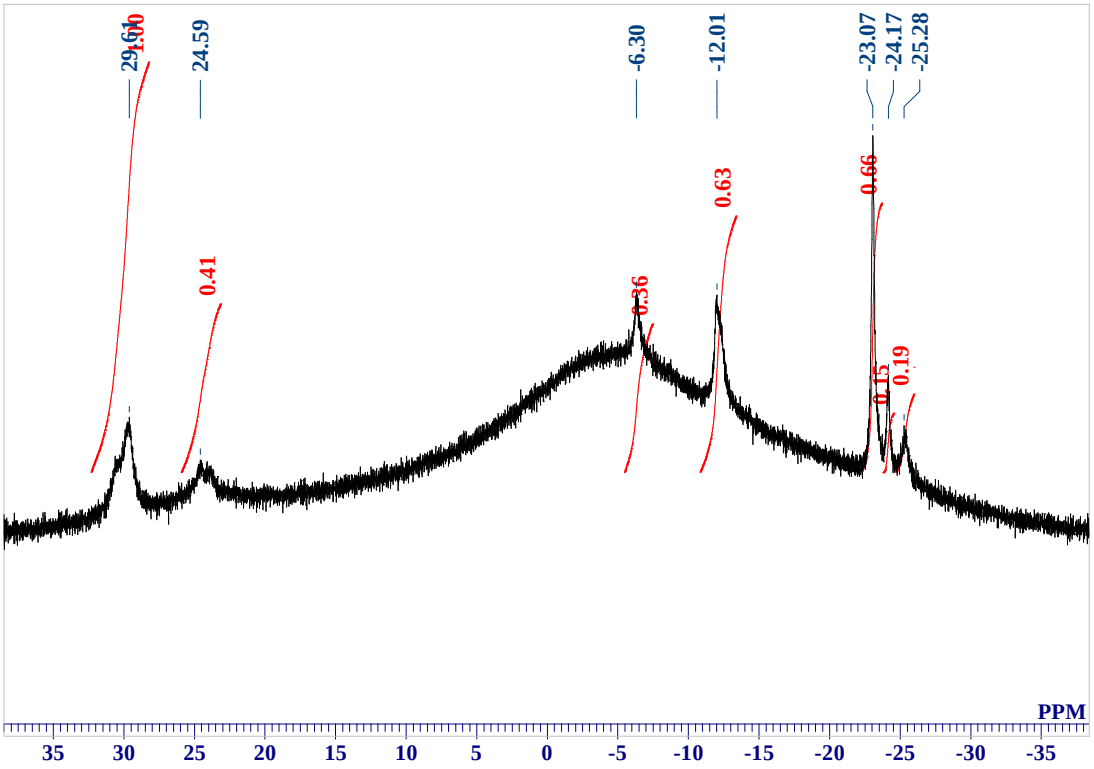
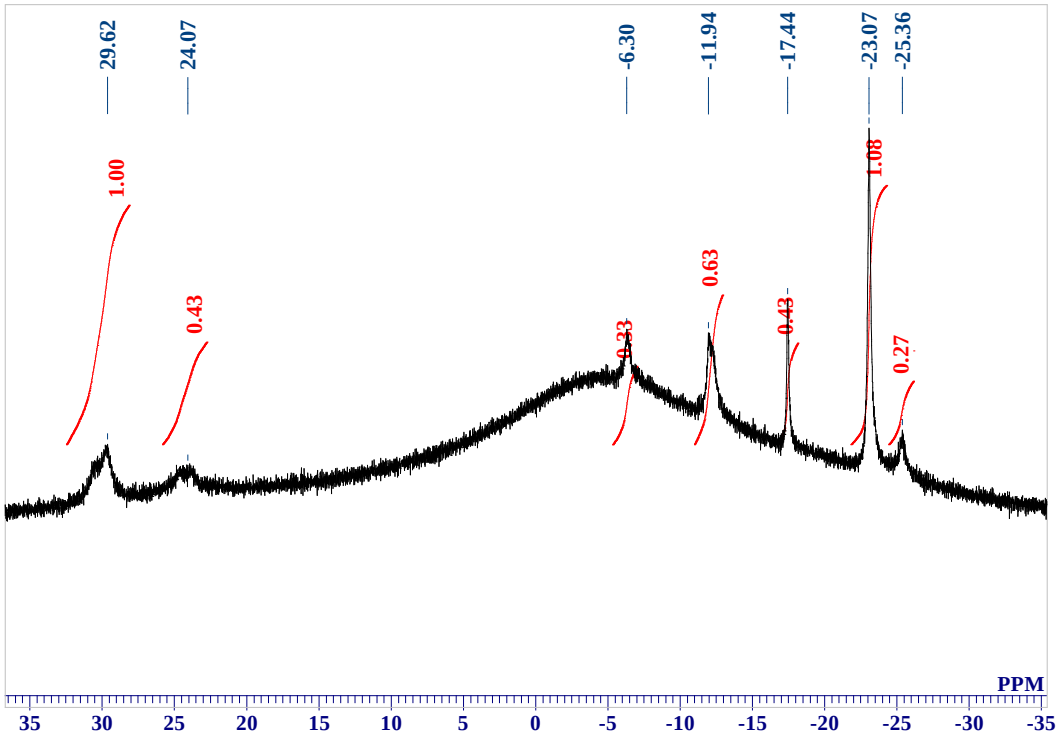


Figure S2-3. ^{1}H NMR spectrum (in THF-d_8 at room temperature) of the crude product obtained from the hydrogenation ammonia borane catalyzed by **1** in the presence of Et_2NH and phenanthroline (Table 2 entry 5 in the main manuscript or Table S2 entry 5 in the supporting information).



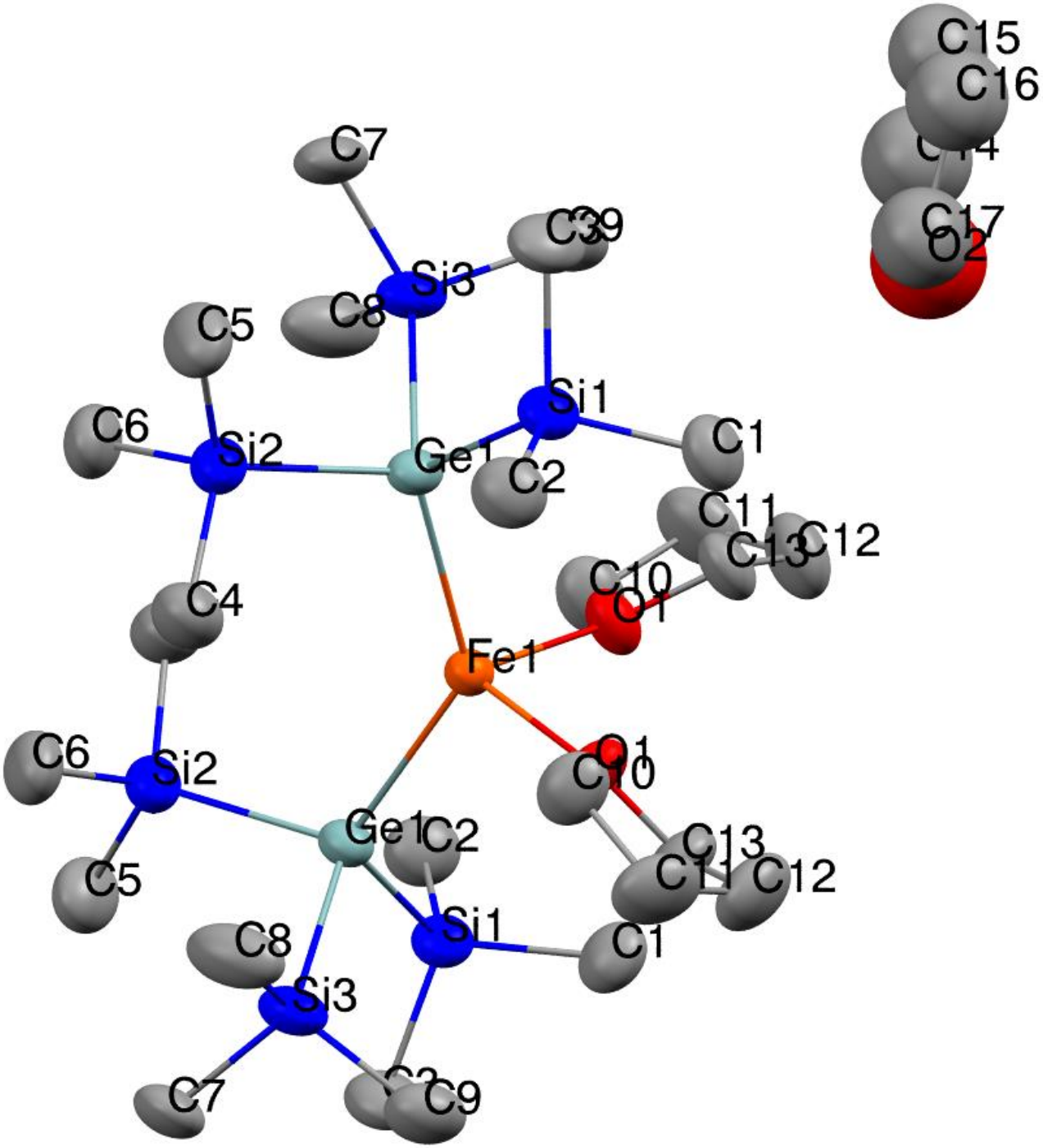


Figure S3. ORTEP drawing of **1** (50% probability of the thermal ellipsoids)

Table S3-1. Crystal data and structure refinement for **1**.

Empirical Formula	$C_{34}H_{70}FeGe_2O_4Si_6$
Formula Weight	912.46
Crystal Color, Habit	red, block
Crystal Dimensions	0.150 X 0.120 X 0.120 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 13.851(4) Å
	b = 10.450(3) Å
	c = 19.003(6) Å
	β = 110.932(4) º
	V = 2569.1(13) Å^3
Space Group	P2/c (#13)
Z value	2
D_{calc}	1.179 g/cm^3
F_{000}	960.00
μ(MoKα)	16.084 cm^{-1}
Diffractometer	Saturn724
Radiation	MoKα (λ = 0.71075 Å)
	multi-layer mirror monochromated
Voltage, Current	50kV, 24mA
Temperature	-89.8ºC
Detector Aperture	72.8 x 72.8 mm
Data Images	720 exposures
ω oscillation Range (χ=45.0, ϕ=0.0)	-70.0 - 110.0º
Exposure Rate	48.0 sec./º
Detector Swing Angle	19.95º
ω oscillation Range (χ=45.0, ϕ=90.0)	-70.0 - 110.0º
Exposure Rate	48.0 sec./º
Detector Swing Angle	19.95º
Detector Position	44.78 mm
Pixel Size	0.141 mm
$2\theta_{max}$	55.0º
No. of Reflections Measured	Total: 20941
	Unique: 5750 (R_{int} = 0.1206)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.694 - 0.824)

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	$w = 1/ [\sigma^2(Fo^2) + (0.0971 \cdot P)^2 + 0.0000 \cdot P]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$
$2\theta_{max}$ cutoff	55.0^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	5750
No. Variables	188
Reflection/Parameter Ratio	30.59
Residuals: R1 (I>2.00σ(I))	0.0604
Residuals: R (All reflections)	0.0838
Residuals: wR2 (All reflections)	0.1814
Goodness of Fit Indicator	1.055
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.81 $e^-/Å^3$
Minimum peak in Final Diff. Map	-1.02 $e^-/Å^3$

Table S3-2. Atomic coordinates and B_{iso}/B_{eq} and occupancy

atom	x	y	z	B_{eq}	occ
Ge1	0.31867(3)	0.47638(4)	0.71739(2)	2.746(13)	1
Fe1	0.50000	0.38223(7)	0.75000	2.393(16)	1/2
Si1	0.18075(9)	0.35443(13)	0.63096(7)	3.22(2)	1
Si2	0.29267(10)	0.68294(13)	0.66052(8)	3.72(3)	1
Si3	0.26420(10)	0.50633(14)	0.82240(7)	3.62(3)	1
O1	0.4947(2)	0.2385(3)	0.67141(15)	3.36(6)	1
O2	0.7655(8)	-0.0249(8)	0.5965(5)	13.6(2)	1
C1	0.2037(4)	0.1769(5)	0.6466(3)	4.51(10)	1
C2	0.1659(4)	0.3859(6)	0.5298(2)	4.63(11)	1
C3	0.0495(4)	0.3867(6)	0.6369(3)	4.94(11)	1
C4	0.3588(5)	0.6919(6)	0.5901(3)	5.48(12)	1
C5	0.1524(5)	0.7296(6)	0.6105(3)	5.78(13)	1
C6	0.3490(5)	0.8130(6)	0.7313(3)	5.54(12)	1
C7	0.1496(4)	0.6147(6)	0.8022(3)	4.78(11)	1
C8	0.3691(4)	0.5799(7)	0.9044(3)	6.26(16)	1
C9	0.2273(4)	0.3536(6)	0.8559(3)	5.16(12)	1
C10	0.4460(4)	0.2630(5)	0.5906(2)	4.37(10)	1
C11	0.4841(5)	0.1610(7)	0.5526(3)	5.81(14)	1
C12	0.5227(5)	0.0574(6)	0.6115(3)	5.71(13)	1
C13	0.5641(4)	0.1321(5)	0.6826(3)	4.11(9)	1
C14	0.7928(11)	0.0019(12)	0.5338(7)	12.3(4)	1
C15	0.9064(9)	0.0013(10)	0.5634(6)	9.9(3)	1
C16	0.9427(9)	-0.0219(10)	0.6486(6)	10.7(3)	1
C17	0.8414(10)	-0.0100(10)	0.6661(7)	10.4(3)	1

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

Table S3-3. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ge1	0.0260(2)	0.0410(3)	0.0371(3)	-0.00032(16)	0.01105(18)	-0.00454(17)
Fe1	0.0292(4)	0.0319(4)	0.0305(4)	0.00000	0.0115(3)	0.00000
Si1	0.0296(6)	0.0497(7)	0.0394(7)	-0.0038(5)	0.0080(5)	-0.0043(5)
Si2	0.0394(6)	0.0406(7)	0.0621(8)	0.0018(5)	0.0188(6)	0.0006(6)
Si3	0.0324(6)	0.0640(9)	0.0442(7)	-0.0031(5)	0.0176(5)	-0.0123(6)
O1	0.0498(17)	0.0446(18)	0.0305(14)	0.0139(14)	0.0112(13)	-0.0035(12)
C1	0.060(3)	0.054(3)	0.049(3)	-0.018(2)	0.010(2)	-0.007(2)
C2	0.054(3)	0.075(4)	0.039(3)	0.001(3)	0.007(2)	0.007(2)
C3	0.033(2)	0.080(4)	0.070(3)	-0.008(2)	0.014(2)	-0.013(3)
C4	0.070(4)	0.069(4)	0.080(4)	-0.003(3)	0.040(3)	0.004(3)
C5	0.060(3)	0.059(4)	0.095(4)	0.015(3)	0.021(3)	0.021(3)
C6	0.073(4)	0.044(3)	0.097(4)	-0.008(3)	0.034(3)	-0.012(3)
C7	0.049(3)	0.069(4)	0.076(3)	0.004(3)	0.038(3)	-0.013(3)
C8	0.053(3)	0.126(6)	0.062(3)	-0.016(4)	0.024(3)	-0.039(4)
C9	0.059(3)	0.087(5)	0.058(3)	0.001(3)	0.030(3)	0.003(3)

C10	0.068(3)	0.063(3)	0.028(2)	0.011(3)	0.008(2)	0.002(2)
C11	0.078(4)	0.097(5)	0.046(3)	0.009(3)	0.023(3)	-0.021(3)
C12	0.082(4)	0.063(4)	0.068(4)	0.013(3)	0.021(3)	-0.022(3)
C13	0.055(3)	0.050(3)	0.051(3)	0.019(2)	0.021(2)	-0.003(2)

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 S3-4. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
Ge1	Fe1	2.5589(8)	Ge1	Si1	2.3936(13)
Ge1	Si2	2.3831(15)	Ge1	Si3	2.3927(17)
Fe1	O1	2.101(3)	Fe1	O1[1]	2.101(3)
Si1	C1	1.888(5)	Si1	C2	1.887(5)
Si1	C3	1.891(6)	Si2	C4	1.874(7)
Si2	C5	1.897(6)	Si2	C6	1.875(6)
Si3	C7	1.874(6)	Si3	C8	1.874(5)
Si3	C9	1.856(7)	O1	C10	1.463(5)
O1	C13	1.435(6)	O2	C14	1.401(19)
O2	C17	1.374(13)	C10	C11	1.486(9)
C11	C12	1.511(9)	C12	C13	1.487(7)
C14	C15	1.470(18)	C15	C16	1.533(15)
C16	C17	1.56(2)			

Symmetry Operators:

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

Table S3-5. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
Fe1	Ge1	Si1	115.79(4)	Fe1	Ge1	Si2	115.74(4)
Fe1	Ge1	Si3	115.02(3)	Si1	Ge1	Si2	102.52(5)
Si1	Ge1	Si3	103.29(5)	Si2	Ge1	Si3	102.60(6)
Ge1	Fe1	Ge1[1]	134.77(4)	Ge1	Fe1	O1	108.70(8)
Ge1	Fe1	O1[1]	103.26(9)	Ge1[1]	Fe1	O1	103.26(9)
Ge1[1]	Fe1	O1[1]	108.70(8)	O1	Fe1	O1[1]	88.70(12)
Ge1	Si1	C1	111.53(14)	Ge1	Si1	C2	112.06(18)
Ge1	Si1	C3	114.36(18)	C1	Si1	C2	106.4(3)
C1	Si1	C3	106.1(3)	C2	Si1	C3	105.8(2)
Ge1	Si2	C4	109.6(2)	Ge1	Si2	C5	115.0(2)
Ge1	Si2	C6	112.00(19)	C4	Si2	C5	107.7(3)
C4	Si2	C6	106.9(3)	C5	Si2	C6	105.2(3)
Ge1	Si3	C7	113.84(19)	Ge1	Si3	C8	111.4(2)
Ge1	Si3	C9	112.4(2)	C7	Si3	C8	105.7(3)
C7	Si3	C9	105.9(3)	C8	Si3	C9	107.1(3)
Fe1	O1	C10	120.5(3)	Fe1	O1	C13	126.7(2)
C10	O1	C13	108.9(4)	C14	O2	C17	116.8(11)
O1	C10	C11	105.9(4)	C10	C11	C12	104.3(5)
C11	C12	C13	102.5(5)	O1	C13	C12	104.6(4)
O2	C14	C15	104.5(9)	C14	C15	C16	107.9(11)

C15	C16	C17	103.5(9)		O2	C17	C16	102.8(11)	

Symmetry Operators:

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

Table S3-6. Torsion Angles(°)

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

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
Fe1	Ge1	Si1	C1	36.75(8)	Fe1	Ge1	Si1	C2	-82.46(6)
Fe1	Ge1	Si1	C3	157.15(5)	Si1	Ge1	Fe1	Ge1[1]	147.34(4)
Si1	Ge1	Fe1	O1	14.74(5)	Si1	Ge1	Fe1	O1[1]	-78.42(5)
Fe1	Ge1	Si2	C4	40.89(6)	Fe1	Ge1	Si2	C5	162.34(6)
Fe1	Ge1	Si2	C6	-77.65(8)	Si2	Ge1	Fe1	Ge1[1]	27.31(5)
Si2	Ge1	Fe1	O1	-105.28(5)	Si2	Ge1	Fe1	O1[1]	161.56(4)
Fe1	Ge1	Si3	C7	164.06(5)	Fe1	Ge1	Si3	C8	44.62(8)
Fe1	Ge1	Si3	C9	-75.60(6)	Si3	Ge1	Fe1	Ge1[1]	-92.18(4)
Si3	Ge1	Fe1	O1	135.22(4)	Si3	Ge1	Fe1	O1[1]	42.06(5)
Si1	Ge1	Si2	C4	-86.11(7)	Si1	Ge1	Si2	C5	35.33(9)
Si1	Ge1	Si2	C6	155.34(7)	Si2	Ge1	Si1	C1	163.73(7)
Si2	Ge1	Si1	C2	44.52(8)	Si2	Ge1	Si1	C3	-75.88(8)
Si1	Ge1	Si3	C7	-68.81(8)	Si1	Ge1	Si3	C8	171.75(6)
Si1	Ge1	Si3	C9	51.53(6)	Si3	Ge1	Si1	C1	-89.89(7)
Si3	Ge1	Si1	C2	150.90(6)	Si3	Ge1	Si1	C3	30.51(8)
Si2	Ge1	Si3	C7	37.51(7)	Si2	Ge1	Si3	C8	-81.93(7)
Si2	Ge1	Si3	C9	157.85(5)	Si3	Ge1	Si2	C4	166.98(5)
Si3	Ge1	Si2	C5	-71.58(8)	Si3	Ge1	Si2	C6	48.43(8)
Ge1	Fe1	O1	C10	49.7(2)	Ge1	Fe1	O1	C13	-155.3(2)
Ge1	Fe1	O1[1]	C10[1]	-97.9(2)	Ge1	Fe1	O1[1]	C13[1]	57.2(3)
Ge1[1]	Fe1	O1	C10	-97.9(2)	Ge1[1]	Fe1	O1	C13	57.2(3)
Ge1[1]	Fe1	O1[1]	C10[1]	49.7(2)	Ge1[1]	Fe1	O1[1]	C13[1]	-155.3(2)
O1	Fe1	O1[1]	C10[1]	153.2(2)	O1	Fe1	O1[1]	C13[1]	-51.7(3)
O1[1]	Fe1	O1	C10	153.2(2)	O1[1]	Fe1	O1	C13	-51.7(3)
Fe1	O1	C10	C11	162.6(2)	Fe1	O1	C13	C12	177.2(2)
C10	O1	C13	C12	-25.4(5)	C13	O1	C10	C11	3.5(5)
C14	O2	C17	C16	-22.7(11)	C17	O2	C14	C15	16.8(12)
O1	C10	C11	C12	19.3(5)	C10	C11	C12	C13	-34.2(6)
C11	C12	C13	O1	36.5(6)	O2	C14	C15	C16	-2.5(11)
C14	C15	C16	C17	-9.7(10)	C15	C16	C17	O2	18.2(10)

Symmetry Operators:

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

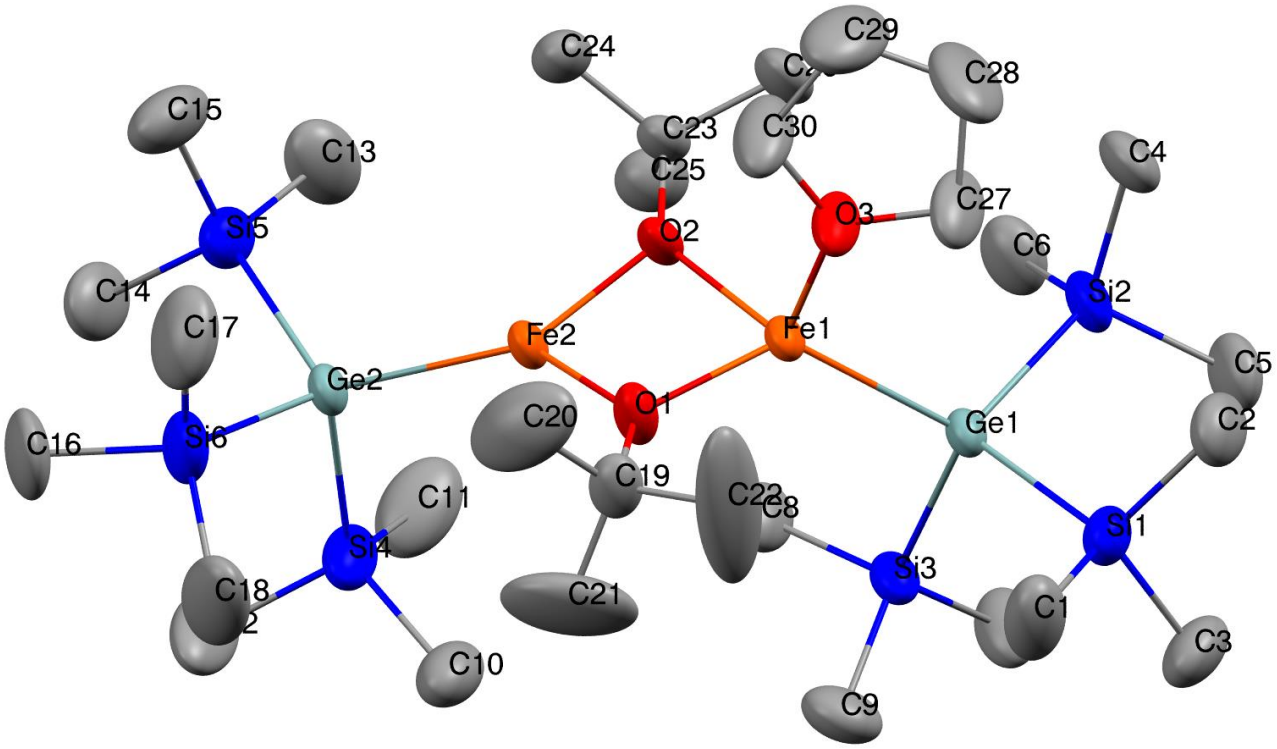


Figure S4. ORTEP drawing of **6** (50% probability of the thermal ellipsoids)

Table S4-1. Crystal data and structure refinement for **6**.

Empirical Formula	$C_{30}H_{80}Fe_2Ge_2O_3Si_6$
Formula Weight	914.35
Crystal Color, Habit	brown, block
Crystal Dimensions	0.300 X 0.300 X 0.200 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 15.448(2) Å b = 16.956(2) Å c = 19.743(3) Å β = 102.5078(18) ° V = 5048.6(13) Å^3
Space Group	$P2_1/c$ (#14)
Z value	4
D_{calc}	1.203 g/cm^3
F_{000}	1936.00
μ(MoKα)	19.075 cm^{-1}
Diffractometer	Saturn724
Radiation	MoKα (λ = 0.71075 Å) multi-layer mirror monochromated
Voltage, Current	50kV, 24mA
Temperature	-74.8°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	10.0 sec./°
Detector Swing Angle	19.88°
ω oscillation Range (χ=45.0, ϕ=90.0)	-70.0 - 110.0°
Exposure Rate	10.0 sec./°
Detector Swing Angle	19.88°
Detector Position	44.83 mm
Pixel Size	0.141 mm
$2\theta_{max}$	55.0°
No. of Reflections Measured	Total: 40092 Unique: 11471 (R_{int} = 0.1003)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.399 - 0.683)
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	$w = 1/ [\sigma^2(Fo^2) + (0.0717 \cdot P)^2 + 1.6288 \cdot P]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$
$2\theta_{max}$ cutoff	55.0^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	11471
No. Variables	388
Reflection/Parameter Ratio	29.56
Residuals: R1 (I>2.00σ(I))	0.0483
Residuals: R (All reflections)	0.0535
Residuals: wR2 (All reflections)	0.1311
Goodness of Fit Indicator	1.047
Max Shift/Error in Final Cycle	0.002
Maximum peak in Final Diff. Map	1.37 $e^-/Å^3$
Minimum peak in Final Diff. Map	-1.23 $e^-/Å^3$

Table S4-2. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
Ge1	0.88697(2)	0.66999(2)	0.68285(2)	2.387(6)
Ge2	0.42575(2)	0.76161(2)	0.56987(2)	2.631(7)
Fe1	0.78005(2)	0.77415(2)	0.62523(2)	2.181(7)
Fe2	0.58729(2)	0.78758(2)	0.58687(2)	2.345(7)
Si1	1.00431(5)	0.70639(5)	0.77827(4)	3.459(14)
Si2	0.96150(5)	0.59841(5)	0.60805(4)	3.395(14)
Si3	0.80205(5)	0.57363(4)	0.72736(4)	3.093(13)
Si4	0.40775(6)	0.65090(6)	0.63997(5)	4.62(2)
Si5	0.34206(5)	0.73403(6)	0.45552(5)	3.907(17)
Si6	0.34741(6)	0.86775(7)	0.60824(5)	4.72(2)
O1	0.68146(11)	0.82983(11)	0.65811(9)	3.09(3)
O2	0.68126(11)	0.75813(12)	0.54174(9)	3.06(3)
O3	0.84822(12)	0.86795(12)	0.59436(12)	3.98(4)
C1	0.9711(3)	0.7845(3)	0.8352(2)	6.42(10)
C2	1.1027(2)	0.7460(2)	0.7476(2)	4.80(7)
C3	1.0454(3)	0.6212(3)	0.8373(2)	5.86(9)
C4	1.0144(2)	0.6658(2)	0.55304(19)	4.77(7)
C5	1.0538(2)	0.5345(2)	0.6573(2)	5.34(8)
C6	0.8846(2)	0.5303(2)	0.5482(2)	5.21(7)
C7	0.8580(3)	0.4758(2)	0.7484(2)	5.65(9)
C8	0.6959(2)	0.5547(2)	0.66289(19)	4.85(7)
C9	0.7710(3)	0.6114(3)	0.80817(19)	5.55(8)
C10	0.4849(3)	0.6574(3)	0.7277(2)	5.88(9)
C11	0.4338(3)	0.5579(2)	0.5968(3)	7.59(13)
C12	0.2924(3)	0.6410(4)	0.6554(3)	9.7(2)
C13	0.3942(3)	0.6591(3)	0.4069(2)	6.51(11)
C14	0.2294(2)	0.6928(3)	0.4576(2)	6.12(9)
C15	0.3262(3)	0.8269(3)	0.4027(2)	6.48(10)
C16	0.2232(2)	0.8572(3)	0.5810(3)	7.21(12)
C17	0.3763(3)	0.9633(3)	0.5713(3)	7.20(12)
C18	0.3710(3)	0.8756(4)	0.7050(2)	8.94(17)
C19	0.68186(19)	0.88576(18)	0.71259(14)	3.54(5)
C20	0.6332(4)	0.9574(3)	0.6820(3)	8.71(16)
C21	0.6336(6)	0.8487(4)	0.7626(3)	10.9(2)
C22	0.7729(3)	0.9029(5)	0.7486(4)	14.0(3)
C23	0.67580(18)	0.72688(18)	0.47354(13)	3.21(5)
C24	0.6143(2)	0.7797(2)	0.42266(15)	4.19(6)
C25	0.6415(3)	0.6436(2)	0.47181(18)	4.78(7)
C26	0.7691(2)	0.7280(2)	0.45904(17)	4.71(7)
C27	0.9433(2)	0.8748(2)	0.6093(2)	5.53(9)
C28	0.9633(3)	0.9153(4)	0.5488(3)	8.49(15)
C29	0.8830(3)	0.9552(3)	0.5134(3)	7.40(13)
C30	0.8125(2)	0.9311(2)	0.5484(3)	6.24(10)

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

Table S4-3. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ge1	0.02321(13)	0.03178(14)	0.03761(14)	0.00174(9)	0.01078(10)	0.00454(10)
Ge2	0.02006(13)	0.04228(16)	0.03895(15)	0.00021(10)	0.00927(10)	0.00107(11)
Fe1	0.02088(16)	0.03066(18)	0.03294(18)	-0.00132(12)	0.00940(12)	0.00404(13)
Fe2	0.02026(16)	0.03791(19)	0.03255(17)	-0.00161(13)	0.00925(12)	-0.00359(13)
Si1	0.0315(4)	0.0512(4)	0.0457(4)	0.0023(3)	0.0018(3)	0.0040(3)
Si2	0.0325(4)	0.0441(4)	0.0578(5)	0.0078(3)	0.0217(3)	-0.0007(4)
Si3	0.0336(4)	0.0380(4)	0.0494(4)	0.0010(3)	0.0166(3)	0.0119(3)
Si4	0.0330(4)	0.0686(6)	0.0716(6)	-0.0116(4)	0.0063(4)	0.0271(5)
Si5	0.0339(4)	0.0639(5)	0.0469(4)	-0.0125(4)	0.0004(3)	-0.0013(4)
Si6	0.0385(4)	0.0775(7)	0.0629(5)	0.0251(4)	0.0099(4)	-0.0093(5)
O1	0.0269(8)	0.0470(10)	0.0433(10)	0.0027(7)	0.0067(7)	-0.0173(8)
O2	0.0261(8)	0.0636(12)	0.0288(8)	0.0003(8)	0.0104(7)	-0.0064(8)
O3	0.0270(9)	0.0504(11)	0.0730(13)	-0.0066(8)	0.0087(9)	0.0286(10)
C1	0.055(2)	0.113(3)	0.067(2)	0.015(2)	-0.0059(18)	-0.032(2)
C2	0.0361(16)	0.069(2)	0.074(2)	-0.0098(15)	0.0026(15)	0.0061(18)
C3	0.057(2)	0.086(3)	0.069(2)	0.000(2)	-0.0098(17)	0.029(2)
C4	0.0522(18)	0.072(2)	0.068(2)	0.0092(16)	0.0371(16)	0.0068(17)
C5	0.0525(19)	0.062(2)	0.093(3)	0.0258(17)	0.0262(18)	0.007(2)
C6	0.061(2)	0.059(2)	0.082(2)	0.0025(17)	0.0258(18)	-0.0227(18)
C7	0.060(2)	0.0472(18)	0.113(3)	0.0092(16)	0.032(2)	0.031(2)
C8	0.0415(16)	0.066(2)	0.076(2)	-0.0167(15)	0.0113(15)	0.0152(18)
C9	0.081(3)	0.080(2)	0.062(2)	-0.012(2)	0.0390(19)	0.0057(19)
C10	0.056(2)	0.094(3)	0.068(2)	-0.007(2)	0.0037(17)	0.031(2)
C11	0.098(3)	0.047(2)	0.126(4)	-0.019(2)	-0.017(3)	0.013(2)
C12	0.046(2)	0.178(6)	0.145(5)	-0.020(3)	0.020(3)	0.098(5)
C13	0.065(2)	0.104(3)	0.076(3)	-0.022(2)	0.010(2)	-0.041(2)
C14	0.0403(18)	0.104(3)	0.081(3)	-0.028(2)	-0.0026(17)	0.006(2)
C15	0.078(3)	0.098(3)	0.058(2)	-0.021(2)	-0.012(2)	0.021(2)
C16	0.0409(19)	0.125(4)	0.109(3)	0.038(2)	0.019(2)	-0.001(3)
C17	0.074(3)	0.060(2)	0.131(4)	0.023(2)	0.003(3)	-0.011(3)
C18	0.088(3)	0.176(6)	0.078(3)	0.063(4)	0.021(2)	-0.033(3)
C19	0.0413(14)	0.0478(15)	0.0429(14)	0.0050(12)	0.0037(11)	-0.0192(12)
C20	0.180(6)	0.060(2)	0.082(3)	0.042(3)	0.010(3)	-0.018(2)
C21	0.246(9)	0.126(5)	0.063(3)	-0.027(5)	0.081(4)	-0.030(3)
C22	0.057(3)	0.246(8)	0.202(7)	0.023(4)	-0.031(4)	-0.181(7)
C23	0.0380(14)	0.0573(16)	0.0293(12)	0.0014(12)	0.0132(10)	-0.0025(11)
C24	0.0507(17)	0.072(2)	0.0355(14)	0.0068(15)	0.0070(12)	0.0039(14)
C25	0.072(2)	0.0578(19)	0.0513(17)	-0.0046(17)	0.0124(16)	-0.0076(15)
C26	0.0465(17)	0.094(3)	0.0448(16)	0.0080(17)	0.0239(14)	-0.0034(16)
C27	0.0299(15)	0.073(2)	0.104(3)	-0.0144(15)	0.0076(16)	0.037(2)
C28	0.073(3)	0.123(4)	0.145(5)	0.005(3)	0.065(3)	0.062(4)
C29	0.089(3)	0.102(3)	0.086(3)	-0.035(3)	0.010(2)	0.047(3)

C30	0.0476(19)	0.065(2)	0.121(3)	-0.0028(17)	0.011(2)	0.056(2)

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 S4-4. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
Ge1	Fe1	2.5155(5)	Ge1	Si1	2.3951(8)
Ge1	Si2	2.3908(10)	Ge1	Si3	2.3795(9)
Ge2	Fe2	2.4841(6)	Ge2	Si4	2.3840(11)
Ge2	Si5	2.3922(10)	Ge2	Si6	2.3821(12)
Fe1	O1	2.0151(19)	Fe1	O2	2.0075(16)
Fe1	O3	2.071(2)	Fe2	O1	1.9291(16)
Fe2	O2	1.9263(19)	Si1	C1	1.879(5)
Si1	C2	1.878(4)	Si1	C3	1.878(4)
Si2	C4	1.881(4)	Si2	C5	1.884(4)
Si2	C6	1.880(4)	Si3	C7	1.876(4)
Si3	C8	1.873(3)	Si3	C9	1.875(4)
Si4	C10	1.881(4)	Si4	C11	1.878(5)
Si4	C12	1.880(5)	Si5	C13	1.875(5)
Si5	C14	1.885(4)	Si5	C15	1.875(5)
Si6	C16	1.886(4)	Si6	C17	1.870(5)
Si6	C18	1.870(5)	O1	C19	1.433(3)
O2	C23	1.432(3)	O3	C27	1.439(4)
O3	C30	1.434(5)	C19	C20	1.486(6)
C19	C21	1.498(8)	C19	C22	1.462(6)
C23	C24	1.517(4)	C23	C25	1.506(5)
C23	C26	1.529(5)	C27	C28	1.469(8)
C28	C29	1.453(7)	C29	C30	1.469(7)

Table S4-5. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
Fe1	Ge1	Si1	119.06(3)	Fe1	Ge1	Si2	115.72(3)
Fe1	Ge1	Si3	106.78(2)	Si1	Ge1	Si2	103.47(3)
Si1	Ge1	Si3	105.68(3)	Si2	Ge1	Si3	104.91(3)
Fe2	Ge2	Si4	107.53(3)	Fe2	Ge2	Si5	118.94(3)
Fe2	Ge2	Si6	112.82(3)	Si4	Ge2	Si5	106.67(4)
Si4	Ge2	Si6	106.21(4)	Si5	Ge2	Si6	103.88(3)
Ge1	Fe1	O1	130.64(5)	Ge1	Fe1	O2	125.75(6)
Ge1	Fe1	O3	110.27(5)	O1	Fe1	O2	80.49(7)
O1	Fe1	O3	101.71(8)	O2	Fe1	O3	101.94(8)
Ge2	Fe2	O1	137.83(6)	Ge2	Fe2	O2	136.65(5)
O1	Fe2	O2	84.76(8)	Ge1	Si1	C1	113.20(12)
Ge1	Si1	C2	111.48(12)	Ge1	Si1	C3	112.74(12)
C1	Si1	C2	106.61(19)	C1	Si1	C3	105.69(19)
C2	Si1	C3	106.63(17)	Ge1	Si2	C4	112.09(12)
Ge1	Si2	C5	112.60(14)	Ge1	Si2	C6	112.14(13)
C4	Si2	C5	105.81(17)	C4	Si2	C6	107.75(17)

C5	Si2	C6	106.01(16)	Ge1	Si3	C7	115.13(14)
Ge1	Si3	C8	109.78(12)	Ge1	Si3	C9	110.04(14)
C7	Si3	C8	107.01(16)	C7	Si3	C9	107.7(2)
C8	Si3	C9	106.80(17)	Ge2	Si4	C10	111.00(15)
Ge2	Si4	C11	109.52(17)	Ge2	Si4	C12	113.5(2)
C10	Si4	C11	108.2(2)	C10	Si4	C12	106.8(2)
C11	Si4	C12	107.6(3)	Ge2	Si5	C13	114.27(12)
Ge2	Si5	C14	111.41(14)	Ge2	Si5	C15	109.87(13)
C13	Si5	C14	105.1(2)	C13	Si5	C15	107.6(2)
C14	Si5	C15	108.3(2)	Ge2	Si6	C16	113.16(17)
Ge2	Si6	C17	110.48(17)	Ge2	Si6	C18	112.3(2)
C16	Si6	C17	106.6(2)	C16	Si6	C18	105.0(2)
C17	Si6	C18	109.0(3)	Fe1	O1	Fe2	95.41(8)
Fe1	O1	C19	132.16(15)	Fe2	O1	C19	132.30(16)
Fe1	O2	Fe2	95.75(8)	Fe1	O2	C23	134.54(16)
Fe2	O2	C23	129.33(15)	Fe1	O3	C27	124.3(2)
Fe1	O3	C30	127.54(18)	C27	O3	C30	107.8(3)
O1	C19	C20	108.4(3)	O1	C19	C21	107.2(3)
O1	C19	C22	110.1(4)	C20	C19	C21	109.4(4)
C20	C19	C22	112.6(4)	C21	C19	C22	109.0(4)
O2	C23	C24	107.7(2)	O2	C23	C25	108.5(2)
O2	C23	C26	107.8(2)	C24	C23	C25	111.8(2)
C24	C23	C26	110.5(3)	C25	C23	C26	110.4(3)
O3	C27	C28	104.8(3)	C27	C28	C29	107.5(4)
C28	C29	C30	106.7(4)	O3	C30	C29	106.4(3)

Table S4-6. Torsion Angles(°)

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

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
Fe1	Ge1	Si1	C1	35.58(5)	Fe1	Ge1	Si1	C2	-84.61(4)
Fe1	Ge1	Si1	C3	155.50(3)	Si1	Ge1	Fe1	O1	-72.95(4)
Si1	Ge1	Fe1	O2	176.59(3)	Si1	Ge1	Fe1	O3	54.07(4)
Fe1	Ge1	Si2	C4	50.96(4)	Fe1	Ge1	Si2	C5	170.14(3)
Fe1	Ge1	Si2	C6	-70.39(4)	Si2	Ge1	Fe1	O1	162.75(3)
Si2	Ge1	Fe1	O2	52.29(4)	Si2	Ge1	Fe1	O3	-70.23(3)
Fe1	Ge1	Si3	C7	162.08(3)	Fe1	Ge1	Si3	C8	41.27(4)
Fe1	Ge1	Si3	C9	-75.99(3)	Si3	Ge1	Fe1	O1	46.42(3)
Si3	Ge1	Fe1	O2	-64.04(3)	Si3	Ge1	Fe1	O3	173.44(2)
Si1	Ge1	Si2	C4	-81.09(4)	Si1	Ge1	Si2	C5	38.08(5)
Si1	Ge1	Si2	C6	157.55(4)	Si2	Ge1	Si1	C1	165.65(4)
Si2	Ge1	Si1	C2	45.46(5)	Si2	Ge1	Si1	C3	-74.44(5)
Si1	Ge1	Si3	C7	-70.22(4)	Si1	Ge1	Si3	C8	168.98(3)
Si1	Ge1	Si3	C9	51.71(4)	Si3	Ge1	Si1	C1	-84.35(4)
Si3	Ge1	Si1	C2	155.46(4)	Si3	Ge1	Si1	C3	35.57(5)
Si2	Ge1	Si3	C7	38.76(4)	Si2	Ge1	Si3	C8	-82.05(4)
Si2	Ge1	Si3	C9	160.69(3)	Si3	Ge1	Si2	C4	168.33(3)
Si3	Ge1	Si2	C5	-72.49(4)	Si3	Ge1	Si2	C6	46.98(4)

Fe2	Ge2	Si4	C10	42.17(5)	Fe2	Ge2	Si4	C11	-77.25(4)
Fe2	Ge2	Si4	C12	162.47(4)	Si4	Ge2	Fe2	O1	-72.76(4)
Si4	Ge2	Fe2	O2	93.48(4)	Fe2	Ge2	Si5	C13	47.43(6)
Fe2	Ge2	Si5	C14	166.37(3)	Fe2	Ge2	Si5	C15	-73.65(5)
Si5	Ge2	Fe2	O1	166.02(3)	Si5	Ge2	Fe2	O2	-27.74(4)
Fe2	Ge2	Si6	C16	169.44(4)	Fe2	Ge2	Si6	C17	50.06(5)
Fe2	Ge2	Si6	C18	-71.87(5)	Si6	Ge2	Fe2	O1	44.01(4)
Si6	Ge2	Fe2	O2	-149.75(3)	Si4	Ge2	Si5	C13	-74.23(5)
Si4	Ge2	Si5	C14	44.71(5)	Si4	Ge2	Si5	C15	164.70(4)
Si5	Ge2	Si4	C10	170.80(4)	Si5	Ge2	Si4	C11	51.38(5)
Si5	Ge2	Si4	C12	-68.90(5)	Si4	Ge2	Si6	C16	-73.00(5)
Si4	Ge2	Si6	C17	167.62(4)	Si4	Ge2	Si6	C18	45.68(6)
Si6	Ge2	Si4	C10	-78.85(5)	Si6	Ge2	Si4	C11	161.73(4)
Si6	Ge2	Si4	C12	41.45(5)	Si5	Ge2	Si6	C16	39.30(6)
Si5	Ge2	Si6	C17	-80.08(5)	Si5	Ge2	Si6	C18	157.98(5)
Si6	Ge2	Si5	C13	173.80(5)	Si6	Ge2	Si5	C14	-67.26(5)
Si6	Ge2	Si5	C15	52.73(5)	Ge1	Fe1	O1	Fe2	-115.49(6)
Ge1	Fe1	O1	C19	68.34(17)	Ge1	Fe1	O2	Fe2	119.78(6)
Ge1	Fe1	O2	C23	-53.4(2)	Ge1	Fe1	O3	C27	-4.89(18)
Ge1	Fe1	O3	C30	166.80(14)	O1	Fe1	O2	Fe2	-14.09(8)
O1	Fe1	O2	C23	172.76(19)	O2	Fe1	O1	Fe2	14.06(8)
O2	Fe1	O1	C19	-162.10(17)	O1	Fe1	O3	C27	136.89(15)
O1	Fe1	O3	C30	-51.43(18)	O3	Fe1	O1	Fe2	114.40(8)
O3	Fe1	O1	C19	-61.76(16)	O2	Fe1	O3	C27	-140.50(16)
O2	Fe1	O3	C30	31.18(19)	O3	Fe1	O2	Fe2	-114.17(9)
O3	Fe1	O2	C23	72.69(19)	Ge2	Fe2	O1	Fe1	156.03(4)
Ge2	Fe2	O1	C19	-27.8(2)	Ge2	Fe2	O2	Fe1	-156.18(3)
Ge2	Fe2	O2	C23	17.5(2)	O1	Fe2	O2	Fe1	14.59(8)
O1	Fe2	O2	C23	-171.73(17)	O2	Fe2	O1	Fe1	-14.53(8)
O2	Fe2	O1	C19	161.63(17)	Fe1	O1	C19	C20	123.74(18)
Fe1	O1	C19	C21	-118.33(19)	Fe1	O1	C19	C22	0.2(3)
Fe2	O1	C19	C20	-51.1(3)	Fe2	O1	C19	C21	66.8(3)
Fe2	O1	C19	C22	-174.69(13)	Fe1	O2	C23	C24	-138.16(17)
Fe1	O2	C23	C25	100.6(2)	Fe1	O2	C23	C26	-19.0(3)
Fe2	O2	C23	C24	50.7(3)	Fe2	O2	C23	C25	-70.6(3)
Fe2	O2	C23	C26	169.88(13)	Fe1	O3	C27	C28	146.34(18)
Fe1	O3	C30	C29	-149.59(17)	C27	O3	C30	C29	23.2(4)
C30	O3	C27	C28	-26.7(4)	O3	C27	C28	C29	20.0(5)
C27	C28	C29	C30	-6.2(5)	C28	C29	C30	O3	-10.2(5)