A Unique Transition Metal-Stabilized Silicon Cation

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Supporting Information

Contents

1 Materials and Methods

1.1 Experimental Details

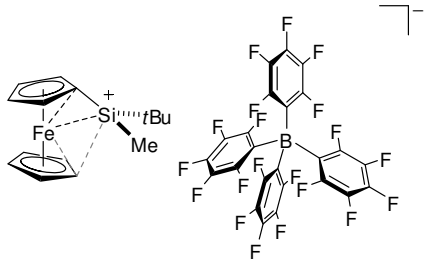
All reactions were performed in flame-dried glassware using an MBraun glove box (O_2 < 0.5 ppm, H_2O < 0.5 ppm) or Schlenk techniques under a static pressure of argon. 1,2-$Cl_2C_6H_4$ (purchased from Acros) and 1,2-$Cl_2C_6D_4$ (purchased from Armar Chemicals) were distilled from calcium hydride prior to use. $Ph_3C^+\cdot[B(C_6F_5)_4]^-$ (**2**$^+\cdot[B(C_6F_5)_4]^-$),[S1] $(Ph_3C^+)_2\cdot[B_{12}Cl_{12}]^{2-}$ {(**2**$^+)_2\cdot[B_{12}Cl_{12}]^{2-}$}[S2] and *tert*-butylferrocenylmethylsilane (**1**)[S3] were prepared according to reported procedures.

^{1}H, ^{13}C, ^{11}B, ^{19}F and ^{29}Si NMR spectra were recorded in 1,2-$Cl_2C_6D_4$ on Bruker AV 300 and Varian Inova 500 instruments. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) and referenced to the residual solvent resonance as the internal standard (1,2-$Cl_2C_6D_4$: δ = 6.94 and 7.20 ppm for ^{1}H NMR and 127.1, 130.1 and 132.5 ppm for ^{13}C NMR with TMS = 0.00 ppm). ^{11}B, ^{19}F, and ^{29}Si NMR spectra were calibrated according to the IUPAC recommendation using a unified chemical shift scale based on the proton resonance of TMS as primary reference.[S4] Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet), coupling constants (Hz) and integration.

1.2 General Procedure for the Generation of Ferrocene-Stabilized Silylium Ions

In a glove box, a solution of *tert*-butylferrocenylmethylsilane (**1**, 1.00 equiv or 2.00 equiv) in 1,2-$Cl_2C_6D_4$ (0.5 mL) was added to a suspension of the indicated trityl salt {**2**$^+\cdot[B(C_6F_5)_4]^-$ (1.00 equiv) or (**2**$^+)_2\cdot[B_{12}Cl_{12}]^{2-}$ (1.00 equiv)} in 1,2-$Cl_2C_6D_4$ (0.2 mL) in an 8 mL vial equipped with a magnetic stir bar. The resulting red-brown solution was stirred for 1 min and was then transferred to an NMR tube. The tube was evacuated using a Schlenk line and sealed.

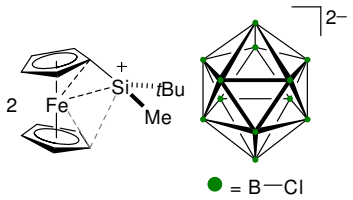
tert-Butylferrocenylmethylsilylium tetrakis(pentafluorophenyl)borate (**3**$^+\cdot[B(C_6F_5)_4]^-$)



3$^+\cdot[B(C_6F_5)_4]^-$
$C_{39}H_{21}BF_{20}FeSi$
964.29 g/mol

Prepared from *tert*-butylferrocenylmethylsilane (**1**, 23.3 mg, 81.5 µmol, 1.00 equiv) and **2**$^+\cdot[B(C_6F_5)_4]^-$ (75.1 mg, 81.5 µmol, 1.00 equiv) according to the general procedure. **^{1}H NMR** (300 MHz, 1,2-$Cl_2C_6D_4$): δ/ppm = 0.70 (s, 3H), 1.06 (s, 9H), 3.56 (br s, 1H), 3.91 (br s, 1H), 4.27 (s, 5H), 5.20 (br s, 2H). **^{13}C NMR** (125 MHz, 1,2-$Cl_2C_6D_4$): δ/ppm = –4.7, 24.3, 27.4, 64.8, 73.7, 81.0, 86.3, 124.1, 136.4 (d, $J_{C,F}$ = 242 Hz), 138.3 (d, $J_{C,F}$ = 242 Hz), 148.4 (d, $J_{C,F}$ = 242 Hz). **^{11}B NMR** (160 MHz, 1,2-$Cl_2C_6D_4$): δ/ppm = –16.4. **^{19}F NMR** (470 MHz, 1,2-$Cl_2C_6D_4$): δ/ppm = –166.1, –162.2, –132.0. **^{29}Si NMR** (60 MHz, 1,2-$Cl_2C_6D_4$): δ/ppm = 114.6.

Bis(*tert*-butylferrocenylmethylsilylium) *closo*-dodecachlorododecaborate {($\mathbf{3}^+$)$_2$·[$B_{12}Cl_{12}$]$^{2-}$}



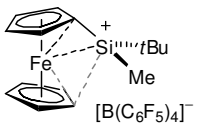
($\mathbf{3}^+$)$_2$·[$B_{12}Cl_{12}$]$^{2-}$
$C_{30}H_{42}B_{12}Cl_{12}Fe_2Si_2$
1121.69 g/mol

Prepared from *tert*-butylferrocenylmethylsilane (**1**, 24.0 mg, 83.9 µmol, 2.00 equiv) and ($\mathbf{2}^+$)$_2$·[$B_{12}Cl_{12}$]$^{2-}$ (43.7 mg, 41.9 µmol, 1.00 equiv) according to the general procedure. Yellow single crystals suitable for X-ray diffraction were obtained either from an NMR sample by standing over night at room temperature or from a solution in 1,2-$Cl_2C_6H_4$. **^{1}H NMR** (500 MHz, 1,2-$Cl_2C_6D_4$): δ/ppm = 0.74 (s, 3H), 1.06 (s, 9H),3.83 (br s, 2H), 4.43 (s, 5H), 5.46 (br s, 2H). **^{13}C NMR** (125 MHz, 1,2-$Cl_2C_6D_4$): δ/ppm = –4.0, 24.4, 27.8, 64.5, 74.0, 81.3, 87.3. **^{11}B NMR** (160 MHz, 1,2-$Cl_2C_6D_4$): δ/ppm = –11.8. **^{29}Si NMR** (99 MHz, 1,2-$Cl_2C_6D_4$): δ/ppm = 114.3.

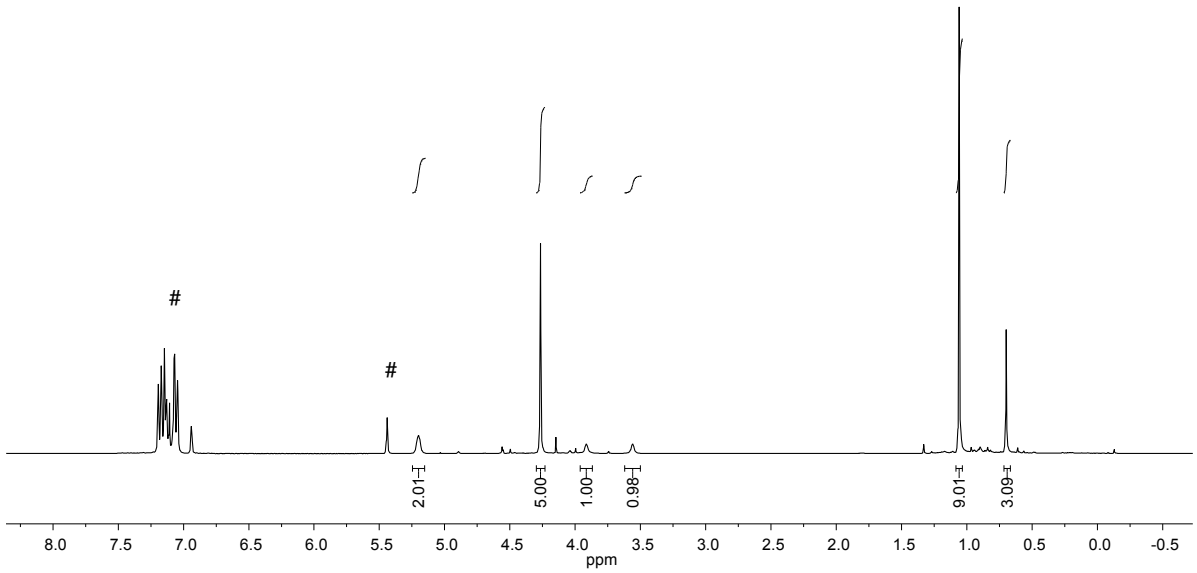
2 ^{1}H, ^{13}C, ^{11}B, ^{19}F and ^{29}Si NMR Spectra

tert-Butylferrocenylmethylsilylium tetrakis(pentafluorophenyl)borate (**3**$^{+}$·[B(C$_6$F$_5$)$_4$]$^{-}$):

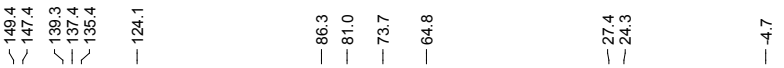
(^{1}H):



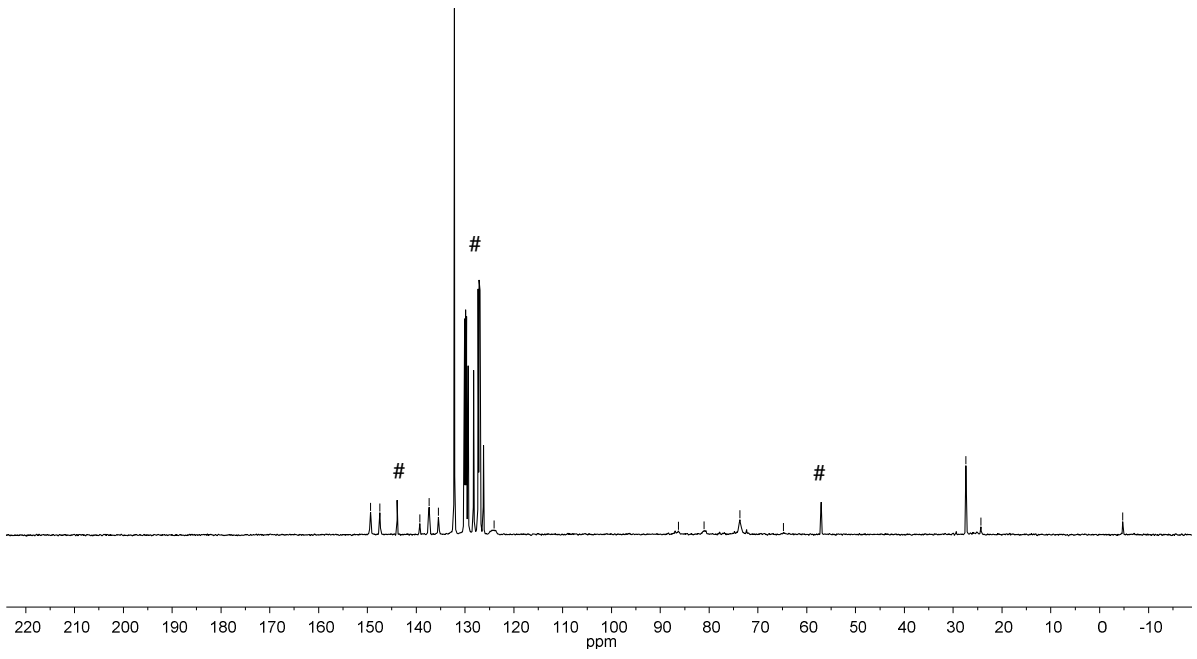
Ph$_3$CH: #



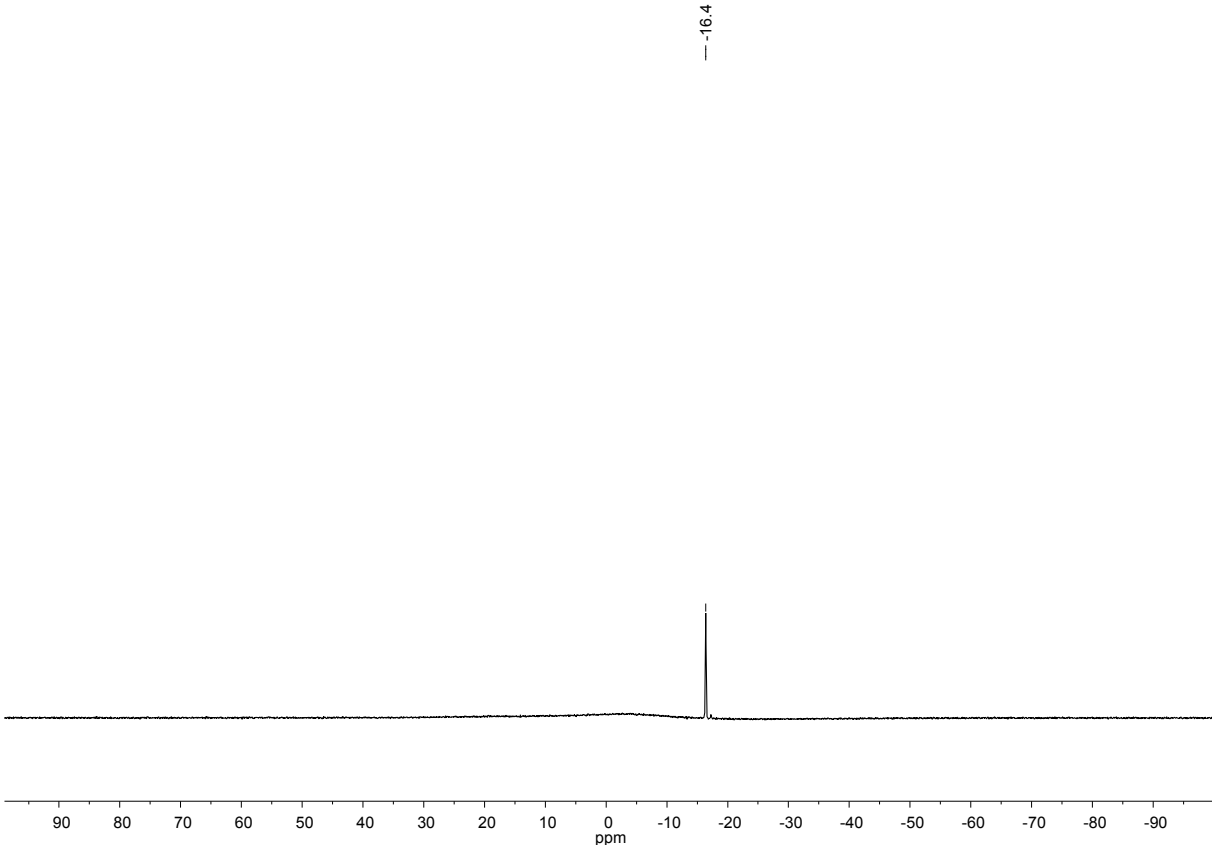
(^{13}C):



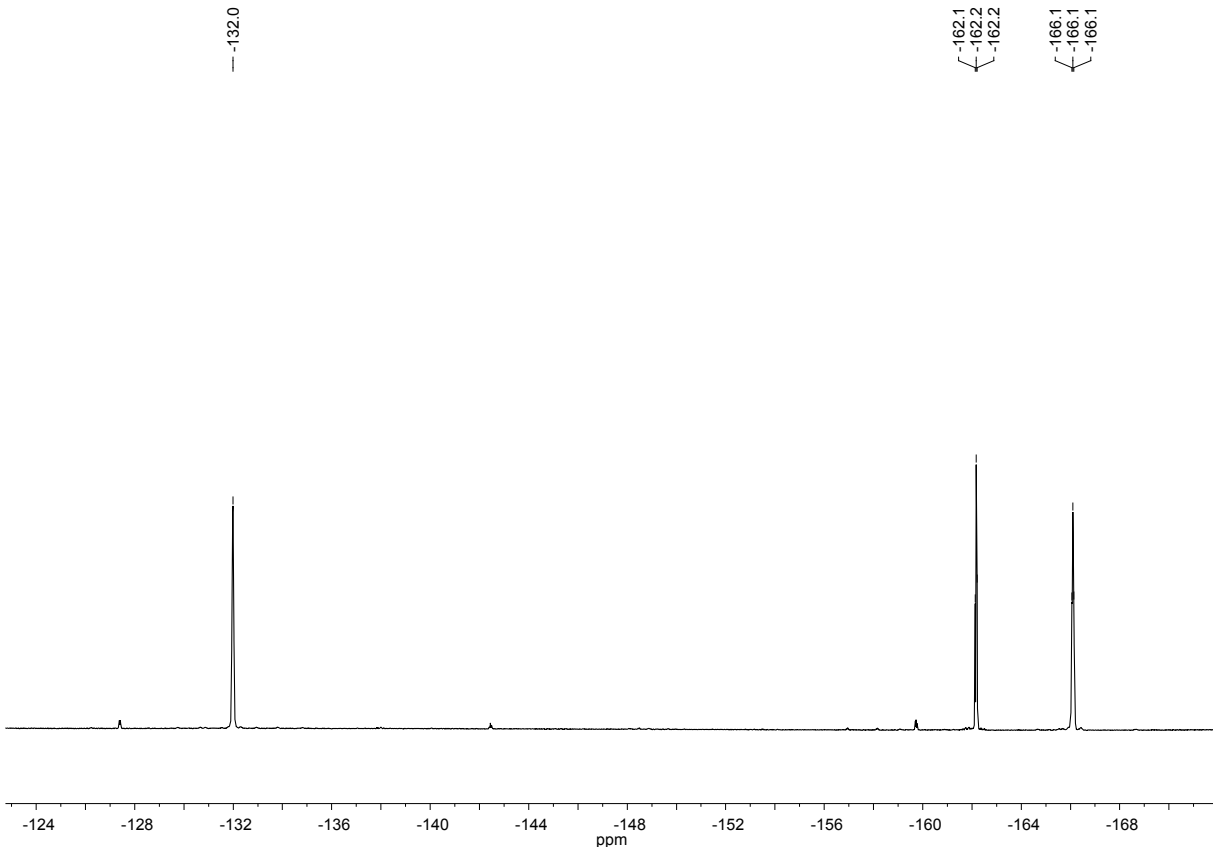
Ph$_3$CH: #



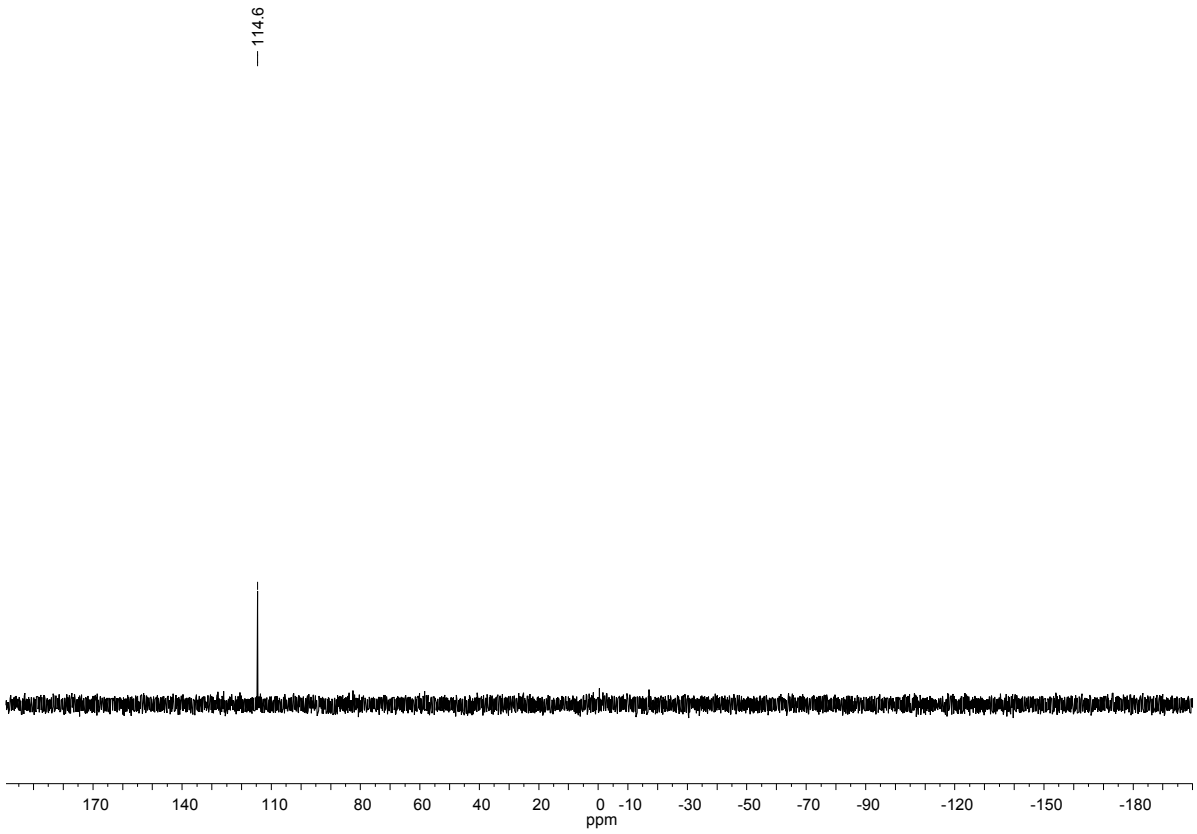
(^{11}B):


-16.4
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
ppm

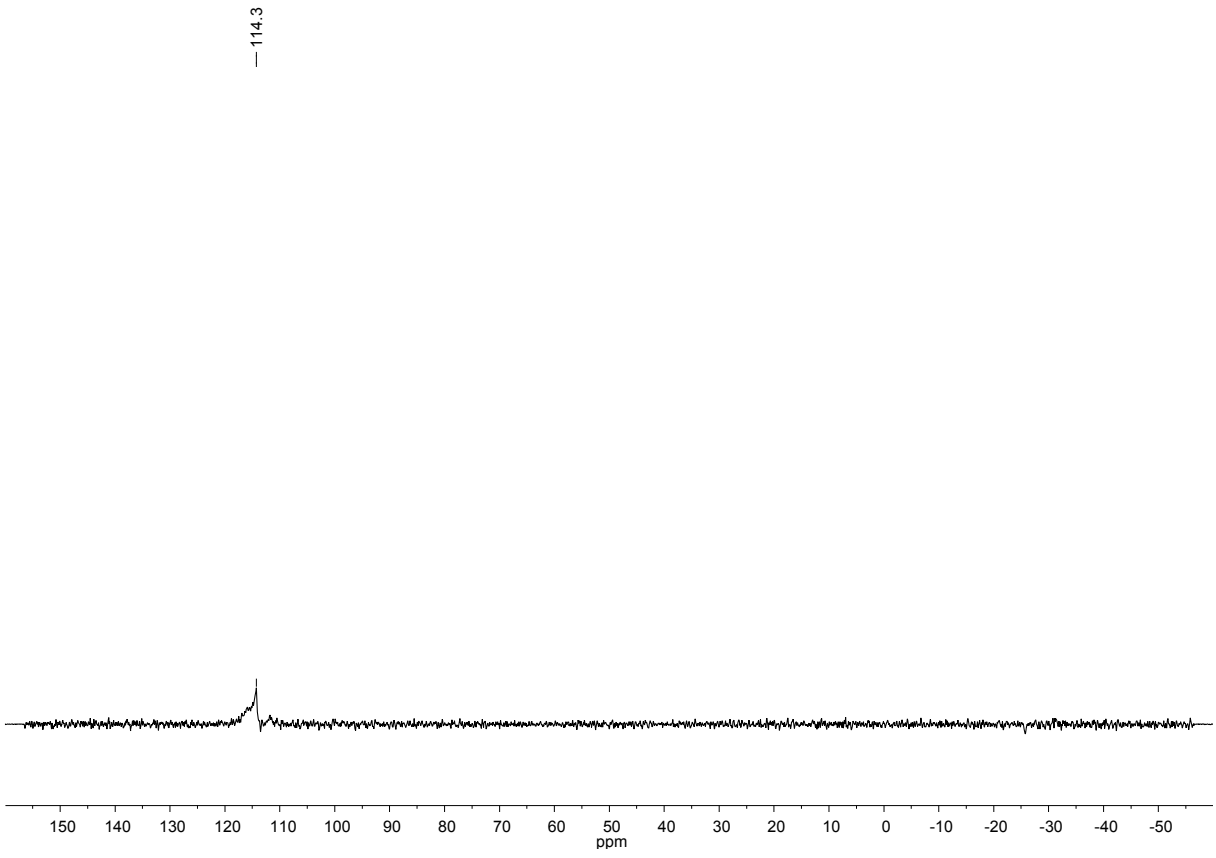
(^{19}F):


-132.0
-162.1
-162.2
-162.2
-166.1
-166.1
-166.1
-124
-128
-132
-136
-140
-144
-148
-152
-156
-160
-164
-168
ppm

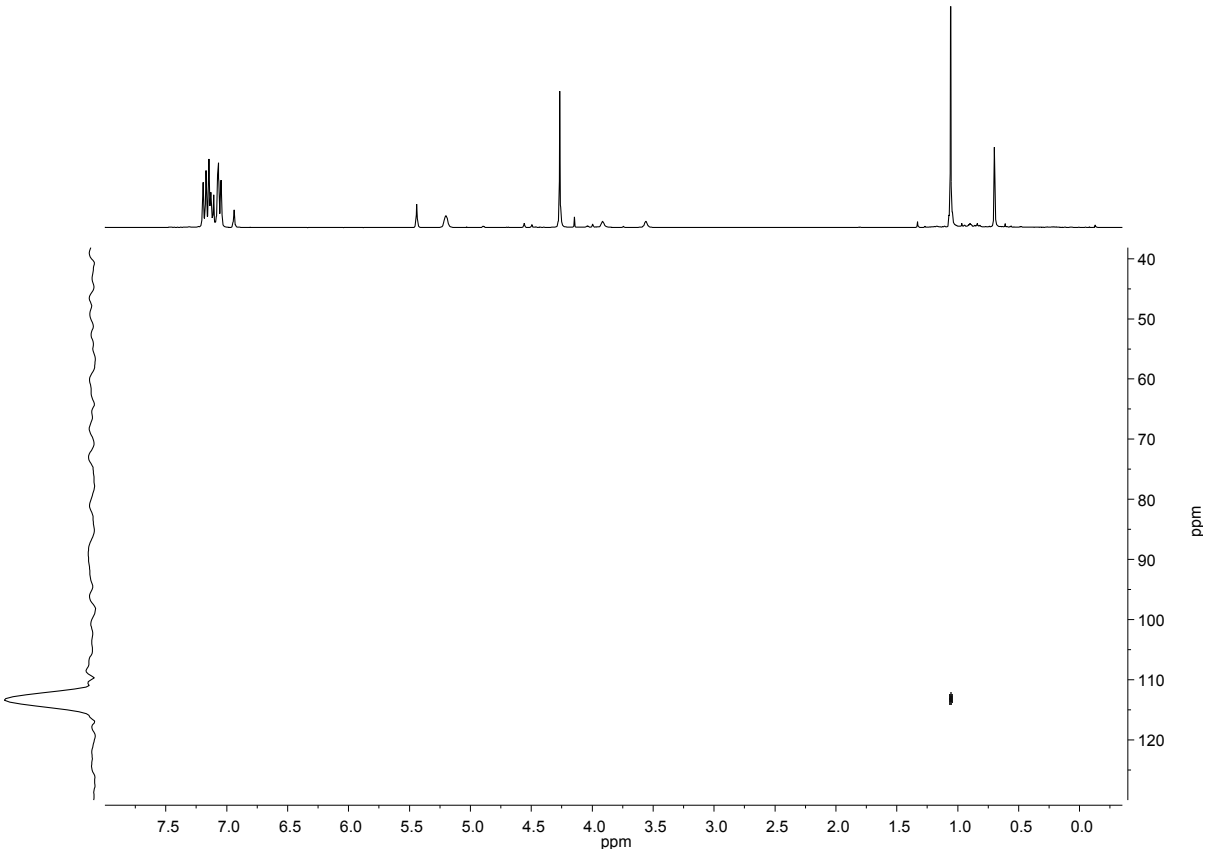
(^{29}Si DEPT):



(^{29}Si):

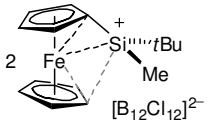


(^{1}H, ^{29}Si HMQC):

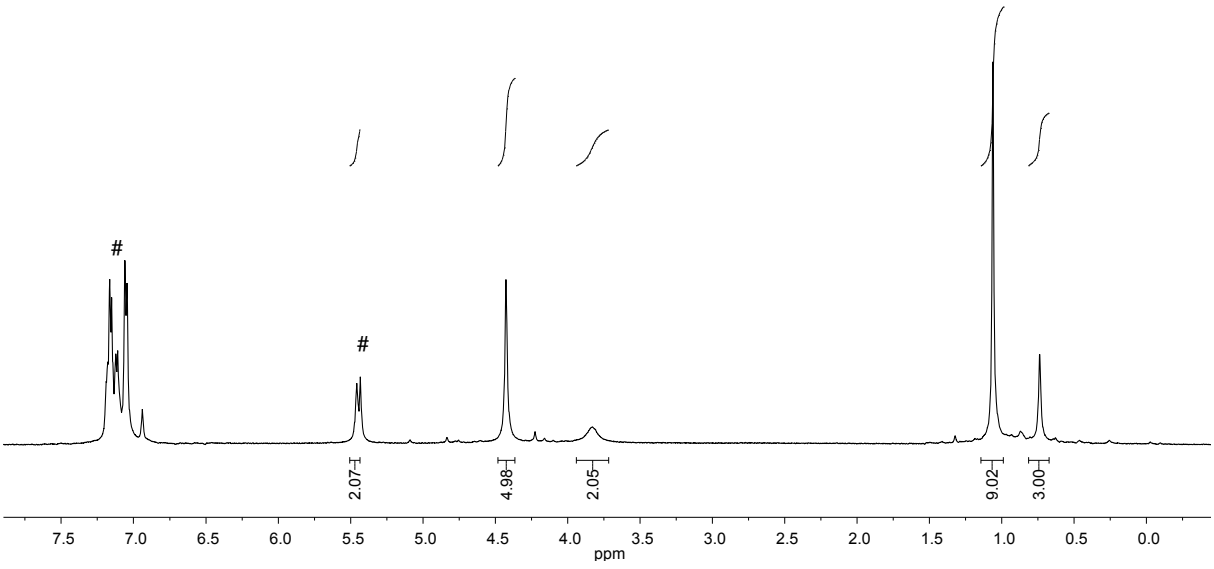

40
50
60
70
80
90
100
110
120
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

Bis(*tert*-butylferrocenylmethylsilylium) *closo*-dodecachlorododecaborate {($\mathbf{3}^{+}$)$_2$·[$B_{12}Cl_{12}$]$^{2-}$}:

(^{1}H):

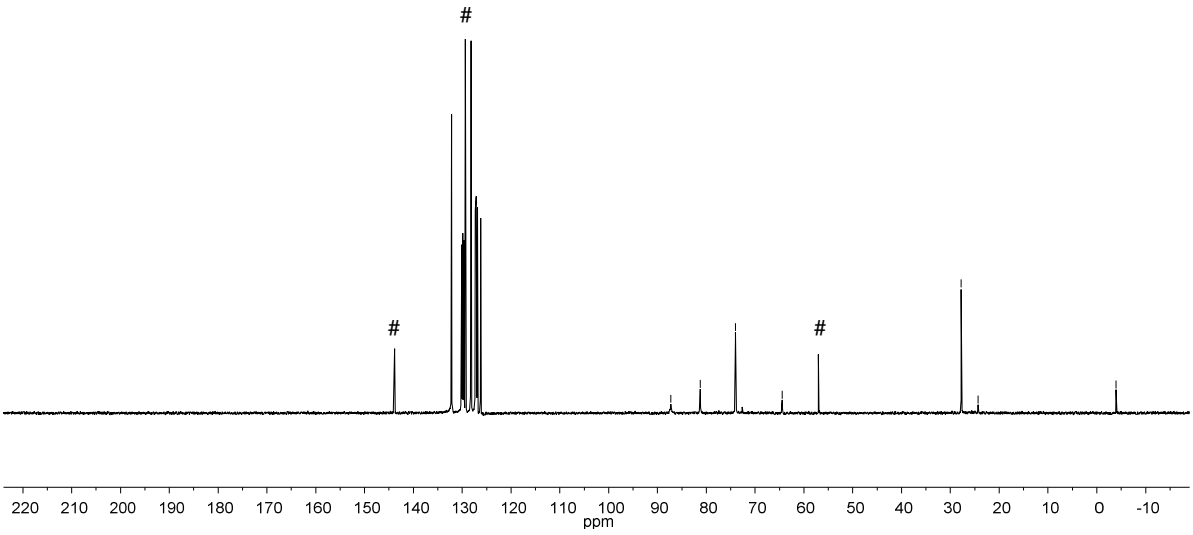


Ph$_3$CH: #

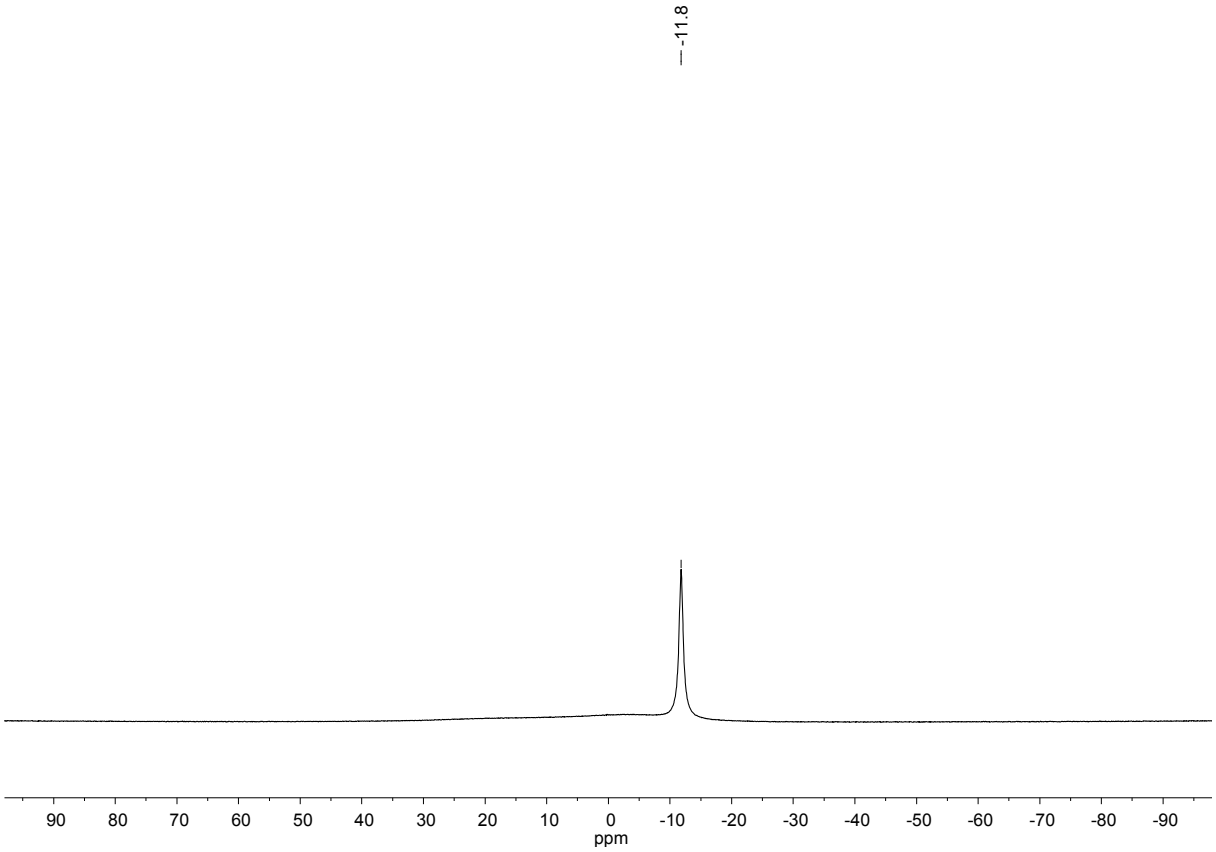


(^{13}C):

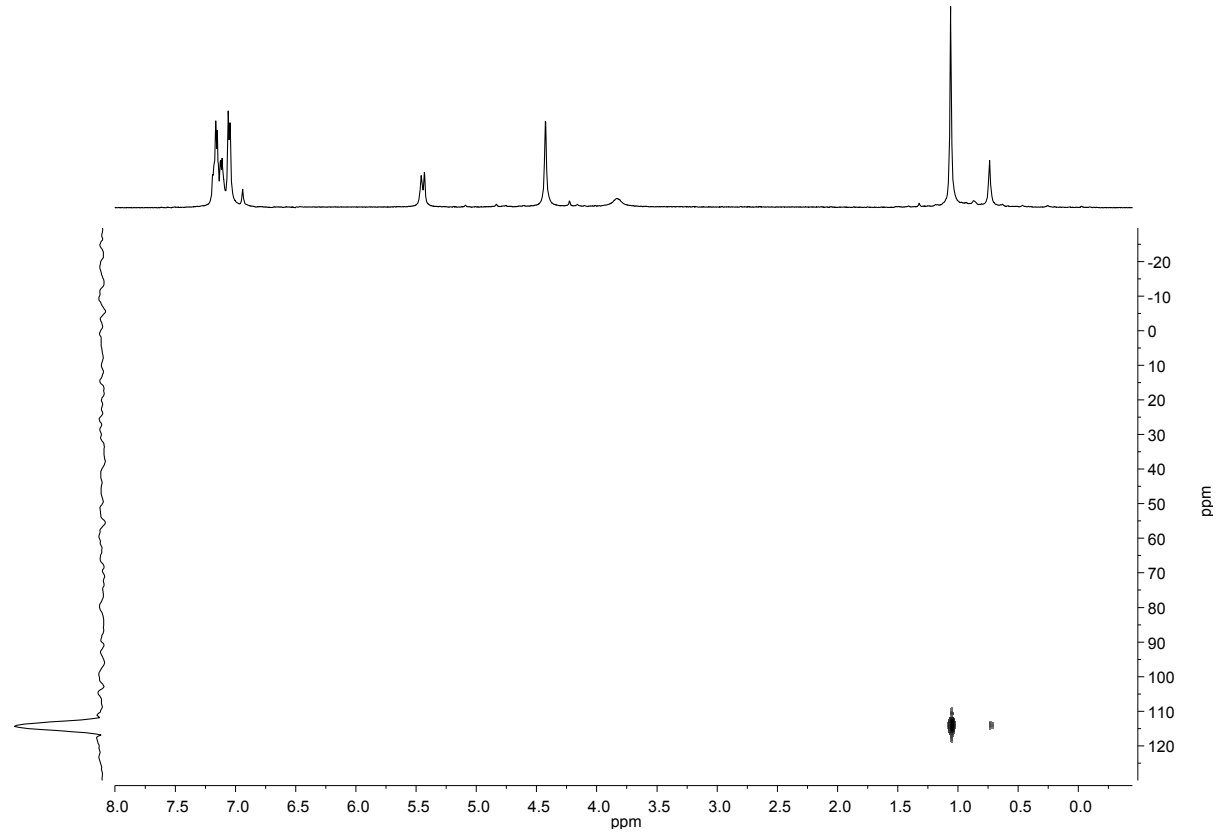
Ph$_3$CH: #



(^{11}B):



(^{1}H, ^{29}Si HMQC):



3 Crystal Data and Details of Data Collection

Formula: 2 ($C_{15}H_{21}FeSi$) $B_{12}Cl_{12}$ * 2 ($C_6H_4Cl_2$), M = 1419.62, yellow crystal 0.50 x 0.30 x 0.10 mm, a = 13.5158(3), b = 17.0228(3), c = 26.8741(5) Å, β = 95.909(1)°, V = 6150.3(2) Å^3, ρ_{calc} = 1.533 g cm^{-3}, μ = 1.238 mm^{-1}, empirical absorption correction ($0.5764 \leq T \leq 0.8862$), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 57595 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.66 Å^{-1}, 14376 independent (R_{int} = 0.057) and 10511 observed reflections [$I \geq 2\,\sigma(I)$], 822 refined parameters, R = 0.107, wR^2 = 0.331, max. (min.) residual electron density 3.09 (–1.69) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator. Programs used: data collection COLLECT[S5], data reduction Denzo-SMN[S6], absorption correction Denzo[S7], structure solution SHELXS-97[S8], structure refinement SHELXL-97[S9], graphics SCHAKAL[S10].

R-values are given for the observed reflections, wR^2-values are given for all reflections.

CCDC 824901 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk].

Comments on the quality of the analysis:

The accuracy of the analysis is limited due to the disorder of the solvent molecules. The highest remaining electron density is located close to the chlorine atoms of the solvents, even when the refinement was done with split positions. – There is also remaining electron density close to the silicon atoms, in both molecules the density is less than 1 Å away, in molecule "A" the density is 0.99 e Å^{-3}, in molecule "B" it is 2.53 e Å^{-3}, leading to slightly different geometries. Refinements with split positions gave no chemical meaningful model. We tried to improve the quality by measurements at different temperatures down to –150 °C, these data sets show more equal geometries around the silicon atoms, but "freezing" of the disorder of the solvent molecules led to even worse results. The remaining electron density and the behavior during refinements might indicate some ordering phenomena around the silicon atoms.

3.1 Comparison of the Diagnostic X-Ray Data of Molecule "A" and Molecule "B"

Table S1. Bond lengths, tilt angles, dip angles, and average angles.

	Molecule "A" (cf. Figure 2)			Molecule "B"		
Bond lengths	Si–C$_{ipso}$:	Si–Fe:	Si–C'$_{ipso}$:	Si–C$_{ipso}$:	Si–Fe:	Si–C'$_{ipso}$:
	1.829(9) Å	2.492(2) Å	2.784(9) Å	1.928(9) Å	2.458(3) Å	2.579(9) Å
Tilt angle	11.6°			10.5°		
Dip angle α*	44.8°			48.0°		
Average C–Si–C angle	117.8°			116.3°		

3.2 Supplementary Figure S1: Crystal Structure of $[C_{15}H_{21}FeSi]_2\ [B_{12}Cl_{12}] \cdot 2\ C_6H_4Cl_2$ $\{(3^+)_2 \cdot [B_{12}Cl_{12}]^{2-} \cdot 2\ C_6H_4Cl_2\}$

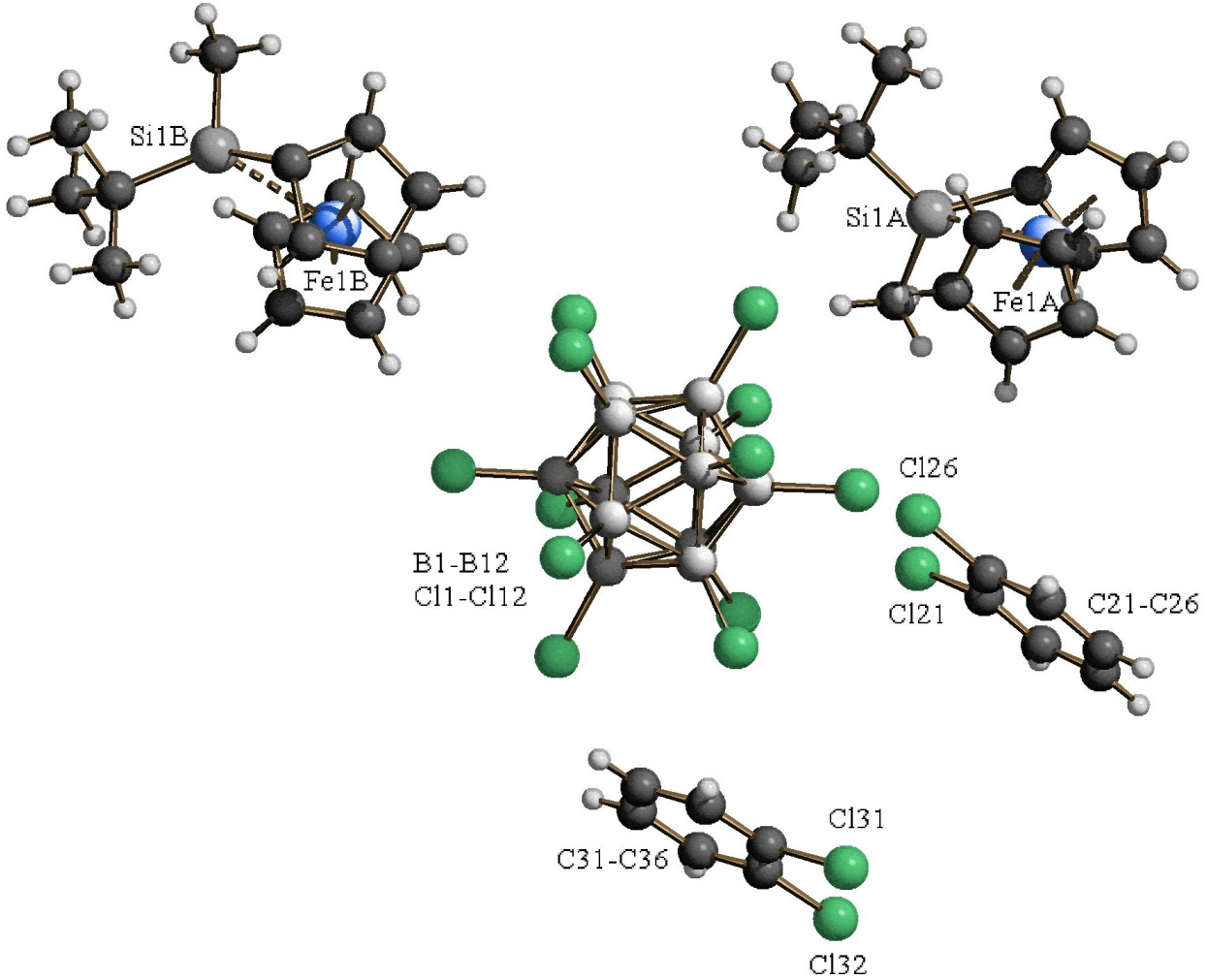


Figure S1. Crystal Structure of $[C_{15}H_{21}FeSi]_2\ [B_{12}Cl_{12}] \cdot 2\ C_6H_4Cl_2$.

3.3 Supplementary Tables S2–S6: Complete Crystal Data

Table S2. Crystal data and structure refinement.

Empirical formula	$C_{42}\ H_{50}\ B_{12}\ Cl_{16}\ Fe_2\ Si_2$
Formula weight	1419.62
Temperature	223(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/c$ (No. 14)
Unit cell dimensions	a = 13.5158(3) Å b = 17.0228(3) Å β = 95.909(1)° c = 26.8741(5) Å
Volume	6150.3(2) $Å^3$
Z, Calculated density	4, 1.533 Mg/m^3
Absorption coefficient	1.238 mm^{-1}
F(000)	2856
Crystal size	0.50 x 0.30 x 0.10 mm
Theta range for data collection	4.07 to 27.76°
Limiting indices	−17<=h<=17, −18<=k<=22, −34<=l<=34
Reflections collected / unique	57595 / 14376 [R(int) = 0.057]
Completeness to theta = 27.76	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8862 and 0.5764
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14376 / 822 / 773
Goodness-of-fit on F^2	1.046
Final R indices [I>2σ(I)]	R1 = 0.1067, wR^2 = 0.2951
R indices (all data)	R1 = 0.1344, wR^2 = 0.3307
Largest diff. peak and hole	3.089 and −1.690 e.$Å^{-3}$

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3).
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Fe(1A)	7925(1)	5221(1)	-1522(1)	54(1)
Si(1A)	7467(2)	5016(1)	-656(1)	60(1)
C(1A)	8466(6)	5644(5)	-840(3)	62(2)
C(2A)	9261(6)	5287(5)	-1084(3)	65(2)
C(3A)	9345(7)	5693(6)	-1540(4)	78(2)
C(4A)	8619(6)	6305(5)	-1580(4)	70(2)
C(5A)	8102(6)	6280(5)	-1161(3)	64(2)
C(6A)	7580(8)	4083(5)	-1730(3)	70(2)
C(7A)	7897(9)	4497(6)	-2131(3)	80(3)
C(8A)	7272(9)	5134(6)	-2237(4)	81(3)
C(9A)	6537(7)	5109(5)	-1903(4)	72(2)
C(10A)	6718(7)	4465(5)	-1595(3)	67(2)
C(11A)	6305(6)	5530(6)	-546(4)	72(2)
C(12A)	7733(7)	4070(5)	-298(3)	67(2)
C(13A)	7037(13)	3424(8)	-465(5)	125(5)
C(14A)	7668(11)	4240(7)	245(4)	100(3)
C(15A)	8782(13)	3775(11)	-357(7)	148(6)
Fe(1B)	3190(1)	592(1)	827(1)	51(1)
Si(1B)	3186(2)	-504(2)	1423(1)	78(1)
C(1B)	3530(7)	-565(5)	745(3)	66(2)
C(2B)	2767(8)	-329(6)	357(3)	74(2)
C(3B)	3139(8)	274(6)	82(3)	73(2)
C(4B)	4128(7)	435(6)	275(3)	72(2)
C(5B)	4372(6)	-87(5)	673(3)	64(2)
C(6B)	1992(6)	1123(6)	1092(4)	75(2)
C(7B)	2406(7)	1627(5)	759(4)	72(2)
C(8B)	3406(7)	1777(5)	946(3)	68(2)
C(9B)	3601(6)	1363(5)	1404(3)	64(2)
C(10B)	2742(6)	963(6)	1493(3)	67(2)
C(11B)	4262(6)	-537(5)	1899(3)	57(2)
C(12B)	2049(6)	-1016(5)	1606(4)	69(2)
C(13B)	1735(12)	-701(9)	2105(6)	129(5)
C(14B)	2398(9)	-1860(7)	1727(6)	102(3)
C(15B)	1194(10)	-1038(9)	1198(6)	124(4)
B(1)	1979(5)	3189(5)	-2008(3)	44(2)
B(2)	2996(6)	2511(5)	-1974(3)	47(2)
B(3)	2175(5)	3847(5)	-1495(3)	47(2)
B(4)	1339(5)	3036(4)	-1470(3)	43(1)
B(5)	3212(5)	3517(4)	-1805(3)	45(2)
B(6)	1840(5)	2216(4)	-1761(3)	41(1)
B(7)	1967(5)	2292(4)	-1094(3)	43(1)
B(8)	3185(5)	2618(5)	-898(3)	46(2)
B(9)	3818(5)	2753(4)	-1441(3)	44(2)
B(10)	2979(5)	1961(4)	-1410(3)	44(2)
B(11)	2165(5)	3287(5)	-930(3)	47(2)
B(12)	3316(5)	3583(4)	-1138(3)	43(1)
Cl(1)	1311(2)	3461(2)	-2591(1)	72(1)
Cl(2)	3447(2)	2125(1)	-2526(1)	68(1)
Cl(3)	1768(2)	4848(1)	-1534(1)	71(1)
Cl(4)	24(1)	3193(1)	-1492(1)	64(1)
Cl(5)	3876(2)	4166(1)	-2170(1)	63(1)
Cl(6)	1054(1)	1498(1)	-2085(1)	58(1)
Cl(7)	1309(1)	1644(1)	-713(1)	61(1)
Cl(8)	3842(2)	2338(2)	-311(1)	74(1)
Cl(9)	5138(1)	2611(1)	-1430(1)	63(1)
Cl(10)	3376(2)	955(1)	-1367(1)	67(1)
Cl(11)	1703(2)	3668(1)	-377(1)	71(1)
Cl(12)	4118(1)	4301(1)	-823(1)	62(1)
C(21A)	3757(6)	8073(6)	-1171(3)	114(3)

C(22A)	3631(8)	8822(5)	−1373(5)	109(3)
C(23A)	3729(10)	8946(6)	−1877(5)	79(3)
C(24A)	3954(10)	8321(8)	−2178(4)	99(4)
C(25A)	4081(9)	7572(7)	−1976(4)	105(4)
C(26A)	3983(6)	7448(5)	−1472(4)	119(3)
Cl(21)	3622(8)	8013(7)	−565(3)	160(3)
Cl(26)	4135(9)	6537(6)	−1231(5)	181(4)
C(21B)	3705(15)	8087(10)	−579(4)	125(4)
C(22B)	3564(15)	8761(8)	−870(6)	111(3)
C(23B)	3621(11)	8722(6)	−1383(6)	109(3)
C(24B)	3819(7)	8009(7)	−1605(4)	107(3)
C(25B)	3960(8)	7335(6)	−1314(4)	123(3)
C(26B)	3902(13)	7374(8)	−801(4)	121(4)
Cl(24)	3893(9)	7953(7)	−2221(4)	153(4)
Cl(25)	4195(9)	6479(6)	−1596(5)	157(4)
C(31A)	−708(8)	3088(7)	−4145(4)	149(4)
C(32A)	−957(8)	3709(6)	−3845(4)	143(3)
C(33A)	−1195(11)	3565(9)	−3363(5)	140(4)
C(34A)	−1184(14)	2801(10)	−3179(5)	134(4)
C(35A)	−934(14)	2181(8)	−3479(6)	137(4)
C(36A)	−696(11)	2325(7)	−3962(6)	138(4)
Cl(31)	−420(10)	3284(9)	−4725(4)	191(4)
Cl(32)	−978(9)	4629(6)	−4060(5)	196(4)
C(31B)	−1090(15)	3590(12)	−3284(5)	140(4)
C(32B)	−1119(15)	4391(11)	−3385(6)	122(4)
C(33B)	−860(12)	4668(8)	−3841(6)	146(4)
C(34B)	−573(8)	4143(8)	−4196(5)	151(4)
C(35B)	−544(9)	3342(8)	−4094(5)	152(4)
C(36B)	−803(13)	3066(9)	−3639(6)	142(3)
Cl(34)	−262(8)	4470(7)	−4740(4)	164(4)
Cl(35)	−186(12)	2727(9)	−4533(6)	209(5)

Table S4. Bond lengths [Å] and angles [°].

Fe(1A)-C(1A)	2.033(8)
Fe(1A)-C(8A)	2.037(9)
Fe(1A)-C(5A)	2.048(8)
Fe(1A)-C(7A)	2.048(9)
Fe(1A)-C(2A)	2.054(8)
Fe(1A)-C(6A)	2.057(8)
Fe(1A)-C(9A)	2.052(8)
Fe(1A)-C(10A)	2.070(9)
Fe(1A)-C(3A)	2.087(9)
Fe(1A)-C(4A)	2.083(9)
Fe(1A)-Si(1A)	2.492(2)
Si(1A)-C(1A)	1.829(9)
Si(1A)-C(11A)	1.848(8)
Si(1A)-C(12A)	1.891(9)
C(1A)-C(5A)	1.439(12)
C(1A)-C(2A)	1.450(11)
C(2A)-C(3A)	1.422(13)
C(2A)-H(2A)	0.9400
C(3A)-C(4A)	1.427(13)
C(3A)-H(3A)	0.9400
C(4A)-C(5A)	1.385(13)
C(4A)-H(4A)	0.9400
C(5A)-H(5A)	0.9400
C(6A)-C(7A)	1.392(14)
C(6A)-C(10A)	1.413(14)
C(6A)-H(6A)	0.9400
C(7A)-C(8A)	1.387(14)
C(7A)-H(7A)	0.9400
C(8A)-C(9A)	1.407(15)
C(8A)-H(8A)	0.9400
C(9A)-C(10A)	1.379(12)
C(9A)-H(9A)	0.9400
C(10A)-H(10A)	0.9400
C(11A)-H(11A)	0.9700
C(11A)-H(11B)	0.9700
C(11A)-H(11C)	0.9700
C(12A)-C(13A)	1.487(16)
C(12A)-C(14A)	1.498(13)
C(12A)-C(15A)	1.527(18)
C(13A)-H(13A)	0.9700
C(13A)-H(13B)	0.9700
C(13A)-H(13C)	0.9700
C(14A)-H(14A)	0.9700
C(14A)-H(14B)	0.9700
C(14A)-H(14C)	0.9700
C(15A)-H(15A)	0.9700
C(15A)-H(15B)	0.9700
C(15A)-H(15C)	0.9700
Fe(1B)-C(1B)	2.039(8)
Fe(1B)-C(5B)	2.047(7)
Fe(1B)-C(6B)	2.046(8)
Fe(1B)-C(10B)	2.049(8)
Fe(1B)-C(7B)	2.054(8)
Fe(1B)-C(2B)	2.056(9)
Fe(1B)-C(8B)	2.059(9)
Fe(1B)-C(9B)	2.064(8)
Fe(1B)-C(4B)	2.065(8)
Fe(1B)-C(3B)	2.067(8)
Fe(1B)-Si(1B)	2.458(3)
Si(1B)-C(11B)	1.836(8)
Si(1B)-C(12B)	1.877(8)
Si(1B)-C(1B)	1.928(9)
C(1B)-C(5B)	1.429(13)
C(1B)-C(2B)	1.445(12)
C(2B)-C(3B)	1.389(14)
C(2B)-H(2B)	0.9400
C(3B)-C(4B)	1.409(14)

C(3B)-H(3B)	0.9400
C(4B)-C(5B)	1.402(12)
C(4B)-H(4B)	0.9400
C(5B)-H(5B)	0.9400
C(6B)-C(7B)	1.398(14)
C(6B)-C(10B)	1.428(13)
C(6B)-H(6B)	0.9400
C(7B)-C(8B)	1.416(13)
C(7B)-H(7B)	0.9400
C(8B)-C(9B)	1.418(12)
C(8B)-H(8B)	0.9400
C(9B)-C(10B)	1.388(12)
C(9B)-H(9B)	0.9400
C(10B)-H(10B)	0.9400
C(11B)-H(11D)	0.9700
C(11B)-H(11E)	0.9700
C(11B)-H(11F)	0.9700
C(12B)-C(15B)	1.510(16)
C(12B)-C(14B)	1.537(14)
C(12B)-C(13B)	1.542(16)
C(13B)-H(13D)	0.9700
C(13B)-H(13E)	0.9700
C(13B)-H(13F)	0.9700
C(14B)-H(14D)	0.9700
C(14B)-H(14E)	0.9700
C(14B)-H(14F)	0.9700
C(15B)-H(15D)	0.9700
C(15B)-H(15E)	0.9700
C(15B)-H(15F)	0.9700
B(1)-B(3)	1.775(11)
B(1)-B(4)	1.780(10)
B(1)-B(2)	1.790(11)
B(1)-Cl(1)	1.787(7)
B(1)-B(5)	1.789(10)
B(1)-B(6)	1.800(10)
B(2)-B(9)	1.770(11)
B(2)-B(10)	1.783(11)
B(2)-B(6)	1.790(10)
B(2)-Cl(2)	1.786(7)
B(2)-B(5)	1.789(11)
B(3)-Cl(3)	1.790(8)
B(3)-B(12)	1.787(10)
B(3)-B(4)	1.789(10)
B(3)-B(5)	1.794(10)
B(3)-B(11)	1.792(11)
B(4)-B(6)	1.768(10)
B(4)-B(7)	1.779(10)
B(4)-B(11)	1.787(11)
B(4)-Cl(4)	1.792(7)
B(5)-B(9)	1.776(11)
B(5)-Cl(5)	1.779(7)
B(5)-B(12)	1.786(10)
B(6)-B(10)	1.774(10)
B(6)-B(7)	1.788(10)
B(6)-Cl(6)	1.787(7)
B(7)-B(8)	1.766(10)
B(7)-B(11)	1.763(11)
B(7)-B(10)	1.774(10)
B(7)-Cl(7)	1.800(7)
B(8)-B(10)	1.772(11)
B(8)-B(12)	1.781(11)
B(8)-B(11)	1.784(11)
B(8)-B(9)	1.779(10)
B(8)-Cl(8)	1.793(8)
B(9)-B(10)	1.770(10)
B(9)-B(12)	1.796(10)
B(9)-Cl(9)	1.798(7)
B(10)-Cl(10)	1.796(7)
B(11)-B(12)	1.779(10)
B(11)-Cl(11)	1.793(8)

B(12)-Cl(12)	1.788(7)
C(21A)-C(22A)	1.3900
C(21A)-C(26A)	1.3900
C(21A)-Cl(21)	1.659(8)
C(22A)-C(23A)	1.3900
C(22A)-H(22A)	0.9400
C(23A)-C(24A)	1.3900
C(23A)-H(23A)	0.9400
C(24A)-C(25A)	1.3900
C(24A)-H(24A)	0.9400
C(25A)-C(26A)	1.3900
C(25A)-H(25A)	0.9400
C(26A)-Cl(26)	1.684(8)
C(21B)-C(22B)	1.3900
C(21B)-C(26B)	1.3900
C(21B)-H(21B)	0.9400
C(22B)-C(23B)	1.3900
C(22B)-H(22B)	0.9400
C(23B)-C(24B)	1.3900
C(23B)-H(23B)	0.9400
C(24B)-C(25B)	1.3900
C(24B)-Cl(24)	1.672(9)
C(25B)-C(26B)	1.3900
C(25B)-Cl(25)	1.689(9)
C(26B)-H(26B)	0.9400
C(31A)-C(32A)	1.3900
C(31A)-C(36A)	1.3900
C(31A)-Cl(31)	1.680(9)
C(32A)-C(33A)	1.3900
C(32A)-Cl(32)	1.669(9)
C(33A)-C(34A)	1.3900
C(33A)-H(33A)	0.9400
C(34A)-C(35A)	1.3900
C(34A)-H(34A)	0.9400
C(35A)-C(36A)	1.3900
C(35A)-H(35A)	0.9400
C(36A)-H(36A)	0.9400
C(31B)-C(32B)	1.3900
C(31B)-C(36B)	1.3900
C(31B)-H(31B)	0.9400
C(32B)-C(33B)	1.3900
C(32B)-H(32B)	0.9400
C(33B)-C(34B)	1.3900
C(33B)-H(33B)	0.9400
C(34B)-C(35B)	1.3900
C(34B)-Cl(34)	1.660(9)
C(35B)-C(36B)	1.3900
C(35B)-Cl(35)	1.685(9)
C(36B)-H(36B)	0.9400

C(1A)-Fe(1A)-C(8A)	163.1(4)
C(1A)-Fe(1A)-C(5A)	41.3(3)
C(8A)-Fe(1A)-C(5A)	121.9(4)
C(1A)-Fe(1A)-C(7A)	155.4(4)
C(8A)-Fe(1A)-C(7A)	39.7(4)
C(5A)-Fe(1A)-C(7A)	154.1(4)
C(1A)-Fe(1A)-C(2A)	41.6(3)
C(8A)-Fe(1A)-C(2A)	144.5(4)
C(5A)-Fe(1A)-C(2A)	68.2(3)
C(7A)-Fe(1A)-C(2A)	115.7(4)
C(1A)-Fe(1A)-C(6A)	129.0(4)
C(8A)-Fe(1A)-C(6A)	67.1(4)
C(5A)-Fe(1A)-C(6A)	165.9(4)
C(7A)-Fe(1A)-C(6A)	39.6(4)
C(2A)-Fe(1A)-C(6A)	111.6(4)
C(1A)-Fe(1A)-C(9A)	135.1(4)
C(8A)-Fe(1A)-C(9A)	40.2(4)
C(5A)-Fe(1A)-C(9A)	112.0(4)
C(7A)-Fe(1A)-C(9A)	66.6(4)
C(2A)-Fe(1A)-C(9A)	174.8(4)

C(6A)-Fe(1A)-C(9A)	66.8(4)
C(1A)-Fe(1A)-C(10A)	120.9(4)
C(8A)-Fe(1A)-C(10A)	66.7(4)
C(5A)-Fe(1A)-C(10A)	130.2(4)
C(7A)-Fe(1A)-C(10A)	66.4(4)
C(2A)-Fe(1A)-C(10A)	136.6(4)
C(6A)-Fe(1A)-C(10A)	40.1(4)
C(9A)-Fe(1A)-C(10A)	39.1(4)
C(1A)-Fe(1A)-C(3A)	68.8(4)
C(8A)-Fe(1A)-C(3A)	108.4(4)
C(5A)-Fe(1A)-C(3A)	67.0(4)
C(7A)-Fe(1A)-C(3A)	98.9(4)
C(2A)-Fe(1A)-C(3A)	40.2(4)
C(6A)-Fe(1A)-C(3A)	122.7(4)
C(9A)-Fe(1A)-C(3A)	145.0(4)
C(10A)-Fe(1A)-C(3A)	162.7(4)
C(1A)-Fe(1A)-C(4A)	68.4(4)
C(8A)-Fe(1A)-C(4A)	98.4(4)
C(5A)-Fe(1A)-C(4A)	39.2(4)
C(7A)-Fe(1A)-C(4A)	116.3(4)
C(2A)-Fe(1A)-C(4A)	67.6(4)
C(6A)-Fe(1A)-C(4A)	154.8(4)
C(9A)-Fe(1A)-C(4A)	116.1(4)
C(10A)-Fe(1A)-C(4A)	154.1(4)
C(3A)-Fe(1A)-C(4A)	40.0(4)
C(1A)-Fe(1A)-Si(1A)	46.3(3)
C(8A)-Fe(1A)-Si(1A)	138.3(3)
C(5A)-Fe(1A)-Si(1A)	73.2(3)
C(7A)-Fe(1A)-Si(1A)	132.6(3)
C(2A)-Fe(1A)-Si(1A)	76.2(2)
C(6A)-Fe(1A)-Si(1A)	93.0(3)
C(9A)-Fe(1A)-Si(1A)	98.7(3)
C(10A)-Fe(1A)-Si(1A)	74.6(2)
C(3A)-Fe(1A)-Si(1A)	113.2(3)
C(4A)-Fe(1A)-Si(1A)	110.6(3)
C(1A)-Si(1A)-C(11A)	115.4(4)
C(1A)-Si(1A)-C(12A)	121.9(4)
C(11A)-Si(1A)-C(12A)	116.2(4)
C(1A)-Si(1A)-Fe(1A)	53.5(3)
C(11A)-Si(1A)-Fe(1A)	112.3(3)
C(12A)-Si(1A)-Fe(1A)	122.8(3)
C(5A)-C(1A)-C(2A)	105.5(7)
C(5A)-C(1A)-Si(1A)	112.7(6)
C(2A)-C(1A)-Si(1A)	118.6(6)
C(5A)-C(1A)-Fe(1A)	69.9(5)
C(2A)-C(1A)-Fe(1A)	70.0(5)
Si(1A)-C(1A)-Fe(1A)	80.2(3)
C(3A)-C(2A)-C(1A)	108.4(8)
C(3A)-C(2A)-Fe(1A)	71.2(5)
C(1A)-C(2A)-Fe(1A)	68.5(4)
C(3A)-C(2A)-H(2A)	125.8
C(1A)-C(2A)-H(2A)	125.8
Fe(1A)-C(2A)-H(2A)	126.1
C(2A)-C(3A)-C(4A)	107.8(8)
C(2A)-C(3A)-Fe(1A)	68.7(5)
C(4A)-C(3A)-Fe(1A)	69.8(5)
C(2A)-C(3A)-H(3A)	126.1
C(4A)-C(3A)-H(3A)	126.1
Fe(1A)-C(3A)-H(3A)	126.9
C(5A)-C(4A)-C(3A)	108.5(8)
C(5A)-C(4A)-Fe(1A)	69.1(5)
C(3A)-C(4A)-Fe(1A)	70.1(5)
C(5A)-C(4A)-H(4A)	125.8
C(3A)-C(4A)-H(4A)	125.8
Fe(1A)-C(4A)-H(4A)	126.6
C(4A)-C(5A)-C(1A)	110.0(8)
C(4A)-C(5A)-Fe(1A)	71.8(5)
C(1A)-C(5A)-Fe(1A)	68.8(4)
C(4A)-C(5A)-H(5A)	125.0

C(1A)-C(5A)-H(5A)	125.0
Fe(1A)-C(5A)-H(5A)	126.0
C(7A)-C(6A)-C(10A)	107.0(8)
C(7A)-C(6A)-Fe(1A)	69.9(5)
C(10A)-C(6A)-Fe(1A)	70.5(5)
C(7A)-C(6A)-H(6A)	126.5
C(10A)-C(6A)-H(6A)	126.5
Fe(1A)-C(6A)-H(6A)	124.8
C(6A)-C(7A)-C(8A)	109.0(10)
C(6A)-C(7A)-Fe(1A)	70.5(5)
C(8A)-C(7A)-Fe(1A)	69.7(5)
C(6A)-C(7A)-H(7A)	125.5
C(8A)-C(7A)-H(7A)	125.5
Fe(1A)-C(7A)-H(7A)	125.8
C(7A)-C(8A)-C(9A)	107.5(9)
C(7A)-C(8A)-Fe(1A)	70.6(5)
C(9A)-C(8A)-Fe(1A)	70.4(5)
C(7A)-C(8A)-H(8A)	126.3
C(9A)-C(8A)-H(8A)	126.3
Fe(1A)-C(8A)-H(8A)	124.3
C(10A)-C(9A)-C(8A)	108.3(9)
C(10A)-C(9A)-Fe(1A)	71.2(5)
C(8A)-C(9A)-Fe(1A)	69.3(5)
C(10A)-C(9A)-H(9A)	125.9
C(8A)-C(9A)-H(9A)	125.9
Fe(1A)-C(9A)-H(9A)	125.2
C(9A)-C(10A)-C(6A)	108.2(8)
C(9A)-C(10A)-Fe(1A)	69.7(5)
C(6A)-C(10A)-Fe(1A)	69.5(5)
C(9A)-C(10A)-H(10A)	125.9
C(6A)-C(10A)-H(10A)	125.9
Fe(1A)-C(10A)-H(10A)	126.5
Si(1A)-C(11A)-H(11A)	109.5
Si(1A)-C(11A)-H(11B)	109.5
H(11A)-C(11A)-H(11B)	109.5
Si(1A)-C(11A)-H(11C)	109.5
H(11A)-C(11A)-H(11C)	109.5
H(11B)-C(11A)-H(11C)	109.5
C(13A)-C(12A)-C(14A)	109.7(10)
C(13A)-C(12A)-C(15A)	106.9(12)
C(14A)-C(12A)-C(15A)	108.2(11)
C(13A)-C(12A)-Si(1A)	113.3(8)
C(14A)-C(12A)-Si(1A)	107.7(7)
C(15A)-C(12A)-Si(1A)	110.9(8)
C(12A)-C(13A)-H(13A)	109.5
C(12A)-C(13A)-H(13B)	109.5
H(13A)-C(13A)-H(13B)	109.5
C(12A)-C(13A)-H(13C)	109.5
H(13A)-C(13A)-H(13C)	109.5
H(13B)-C(13A)-H(13C)	109.5
C(12A)-C(14A)-H(14A)	109.5
C(12A)-C(14A)-H(14B)	109.5
H(14A)-C(14A)-H(14B)	109.5
C(12A)-C(14A)-H(14C)	109.5
H(14A)-C(14A)-H(14C)	109.5
H(14B)-C(14A)-H(14C)	109.5
C(12A)-C(15A)-H(15A)	109.5
C(12A)-C(15A)-H(15B)	109.5
H(15A)-C(15A)-H(15B)	109.5
C(12A)-C(15A)-H(15C)	109.5
H(15A)-C(15A)-H(15C)	109.5
H(15B)-C(15A)-H(15C)	109.5
C(1B)-Fe(1B)-C(5B)	40.9(4)
C(1B)-Fe(1B)-C(6B)	131.3(4)
C(5B)-Fe(1B)-C(6B)	169.0(4)
C(1B)-Fe(1B)-C(10B)	118.8(4)
C(5B)-Fe(1B)-C(10B)	131.1(3)
C(6B)-Fe(1B)-C(10B)	40.8(4)
C(1B)-Fe(1B)-C(7B)	159.8(4)
C(5B)-Fe(1B)-C(7B)	150.6(4)

C(6B)-Fe(1B)-C(7B)	39.9(4)
C(10B)-Fe(1B)-C(7B)	67.5(4)
C(1B)-Fe(1B)-C(2B)	41.3(3)
C(5B)-Fe(1B)-C(2B)	67.6(4)
C(6B)-Fe(1B)-C(2B)	111.8(4)
C(10B)-Fe(1B)-C(2B)	133.1(4)
C(7B)-Fe(1B)-C(2B)	119.4(4)
C(1B)-Fe(1B)-C(8B)	158.9(4)
C(5B)-Fe(1B)-C(8B)	118.9(4)
C(6B)-Fe(1B)-C(8B)	67.5(4)
C(10B)-Fe(1B)-C(8B)	67.1(4)
C(7B)-Fe(1B)-C(8B)	40.3(4)
C(2B)-Fe(1B)-C(8B)	150.3(4)
C(1B)-Fe(1B)-C(9B)	130.5(3)
C(5B)-Fe(1B)-C(9B)	110.9(4)
C(6B)-Fe(1B)-C(9B)	67.6(4)
C(10B)-Fe(1B)-C(9B)	39.4(3)
C(7B)-Fe(1B)-C(9B)	67.5(4)
C(2B)-Fe(1B)-C(9B)	169.3(4)
C(8B)-Fe(1B)-C(9B)	40.2(3)
C(1B)-Fe(1B)-C(4B)	68.7(4)
C(5B)-Fe(1B)-C(4B)	39.9(3)
C(6B)-Fe(1B)-C(4B)	150.9(4)
C(10B)-Fe(1B)-C(4B)	157.9(4)
C(7B)-Fe(1B)-C(4B)	113.3(4)
C(2B)-Fe(1B)-C(4B)	67.2(4)
C(8B)-Fe(1B)-C(4B)	98.7(4)
C(9B)-Fe(1B)-C(4B)	119.0(4)
C(1B)-Fe(1B)-C(3B)	68.2(3)
C(5B)-Fe(1B)-C(3B)	66.8(3)
C(6B)-Fe(1B)-C(3B)	120.3(4)
C(10B)-Fe(1B)-C(3B)	160.7(4)
C(7B)-Fe(1B)-C(3B)	99.9(4)
C(2B)-Fe(1B)-C(3B)	39.4(4)
C(8B)-Fe(1B)-C(3B)	113.4(4)
C(9B)-Fe(1B)-C(3B)	150.8(4)
C(4B)-Fe(1B)-C(3B)	39.9(4)
C(1B)-Fe(1B)-Si(1B)	49.7(3)
C(5B)-Fe(1B)-Si(1B)	76.0(2)
C(6B)-Fe(1B)-Si(1B)	93.1(3)
C(10B)-Fe(1B)-Si(1B)	69.1(3)
C(7B)-Fe(1B)-Si(1B)	132.3(3)
C(2B)-Fe(1B)-Si(1B)	78.6(3)
C(8B)-Fe(1B)-Si(1B)	130.7(3)
C(9B)-Fe(1B)-Si(1B)	90.7(3)
C(4B)-Fe(1B)-Si(1B)	114.3(3)
C(3B)-Fe(1B)-Si(1B)	115.5(3)
C(11B)-Si(1B)-C(12B)	114.4(4)
C(11B)-Si(1B)-C(1B)	114.0(4)
C(12B)-Si(1B)-C(1B)	120.4(4)
C(11B)-Si(1B)-Fe(1B)	115.0(3)
C(12B)-Si(1B)-Fe(1B)	125.5(3)
C(1B)-Si(1B)-Fe(1B)	53.8(2)
C(5B)-C(1B)-C(2B)	105.2(8)
C(5B)-C(1B)-Si(1B)	111.7(6)
C(2B)-C(1B)-Si(1B)	116.3(7)
C(5B)-C(1B)-Fe(1B)	69.9(5)
C(2B)-C(1B)-Fe(1B)	70.0(5)
Si(1B)-C(1B)-Fe(1B)	76.5(3)
C(3B)-C(2B)-C(1B)	108.6(9)
C(3B)-C(2B)-Fe(1B)	70.7(5)
C(1B)-C(2B)-Fe(1B)	68.7(5)
C(3B)-C(2B)-H(2B)	125.7
C(1B)-C(2B)-H(2B)	125.7
Fe(1B)-C(2B)-H(2B)	126.4
C(2B)-C(3B)-C(4B)	109.2(8)
C(2B)-C(3B)-Fe(1B)	69.9(5)
C(4B)-C(3B)-Fe(1B)	70.0(4)
C(2B)-C(3B)-H(3B)	125.4
C(4B)-C(3B)-H(3B)	125.4

Fe(1B)-C(3B)-H(3B)	126.3
C(5B)-C(4B)-C(3B)	107.3(9)
C(5B)-C(4B)-Fe(1B)	69.4(4)
C(3B)-C(4B)-Fe(1B)	70.1(5)
C(5B)-C(4B)-H(4B)	126.4
C(3B)-C(4B)-H(4B)	126.4
Fe(1B)-C(4B)-H(4B)	125.7
C(4B)-C(5B)-C(1B)	109.6(8)
C(4B)-C(5B)-Fe(1B)	70.7(4)
C(1B)-C(5B)-Fe(1B)	69.2(4)
C(4B)-C(5B)-H(5B)	125.2
C(1B)-C(5B)-H(5B)	125.2
Fe(1B)-C(5B)-H(5B)	126.5
C(7B)-C(6B)-C(10B)	107.5(8)
C(7B)-C(6B)-Fe(1B)	70.4(5)
C(10B)-C(6B)-Fe(1B)	69.7(5)
C(7B)-C(6B)-H(6B)	126.3
C(10B)-C(6B)-H(6B)	126.3
Fe(1B)-C(6B)-H(6B)	125.3
C(6B)-C(7B)-C(8B)	108.3(8)
C(6B)-C(7B)-Fe(1B)	69.7(5)
C(8B)-C(7B)-Fe(1B)	70.0(5)
C(6B)-C(7B)-H(7B)	125.9
C(8B)-C(7B)-H(7B)	125.9
Fe(1B)-C(7B)-H(7B)	125.9
C(7B)-C(8B)-C(9B)	107.7(8)
C(7B)-C(8B)-Fe(1B)	69.7(5)
C(9B)-C(8B)-Fe(1B)	70.1(5)
C(7B)-C(8B)-H(8B)	126.2
C(9B)-C(8B)-H(8B)	126.2
Fe(1B)-C(8B)-H(8B)	125.6
C(10B)-C(9B)-C(8B)	108.1(8)
C(10B)-C(9B)-Fe(1B)	69.7(5)
C(8B)-C(9B)-Fe(1B)	69.7(5)
C(10B)-C(9B)-H(9B)	126.0
C(8B)-C(9B)-H(9B)	126.0
Fe(1B)-C(9B)-H(9B)	126.3
C(9B)-C(10B)-C(6B)	108.5(8)
C(9B)-C(10B)-Fe(1B)	70.9(5)
C(6B)-C(10B)-Fe(1B)	69.5(5)
C(9B)-C(10B)-H(10B)	125.8
C(6B)-C(10B)-H(10B)	125.8
Fe(1B)-C(10B)-H(10B)	125.4
Si(1B)-C(11B)-H(11D)	109.5
Si(1B)-C(11B)-H(11E)	109.5
H(11D)-C(11B)-H(11E)	109.5
Si(1B)-C(11B)-H(11F)	109.5
H(11D)-C(11B)-H(11F)	109.5
H(11E)-C(11B)-H(11F)	109.5
C(15B)-C(12B)-C(14B)	109.0(9)
C(15B)-C(12B)-C(13B)	112.4(11)
C(14B)-C(12B)-C(13B)	104.3(10)
C(15B)-C(12B)-Si(1B)	114.0(8)
C(14B)-C(12B)-Si(1B)	104.3(6)
C(13B)-C(12B)-Si(1B)	111.9(7)
C(12B)-C(13B)-H(13D)	109.5
C(12B)-C(13B)-H(13E)	109.5
H(13D)-C(13B)-H(13E)	109.5
C(12B)-C(13B)-H(13F)	109.5
H(13D)-C(13B)-H(13F)	109.5
H(13E)-C(13B)-H(13F)	109.5
C(12B)-C(14B)-H(14D)	109.5
C(12B)-C(14B)-H(14E)	109.5
H(14D)-C(14B)-H(14E)	109.5
C(12B)-C(14B)-H(14F)	109.5
H(14D)-C(14B)-H(14F)	109.5
H(14E)-C(14B)-H(14F)	109.5
C(12B)-C(15B)-H(15D)	109.5
C(12B)-C(15B)-H(15E)	109.5
H(15D)-C(15B)-H(15E)	109.5

C(12B)-C(15B)-H(15F)	109.5
H(15D)-C(15B)-H(15F)	109.5
H(15E)-C(15B)-H(15F)	109.5
B(3)-B(1)-B(4)	60.4(4)
B(3)-B(1)-B(2)	108.4(5)
B(4)-B(1)-B(2)	107.4(5)
B(3)-B(1)-Cl(1)	122.6(5)
B(4)-B(1)-Cl(1)	120.4(5)
B(2)-B(1)-Cl(1)	121.9(5)
B(3)-B(1)-B(5)	60.4(4)
B(4)-B(1)-B(5)	108.3(5)
B(2)-B(1)-B(5)	60.0(4)
Cl(1)-B(1)-B(5)	123.9(5)
B(3)-B(1)-B(6)	107.9(5)
B(4)-B(1)-B(6)	59.2(4)
B(2)-B(1)-B(6)	59.8(4)
Cl(1)-B(1)-B(6)	119.9(5)
B(5)-B(1)-B(6)	107.8(5)
B(9)-B(2)-B(10)	59.7(4)
B(9)-B(2)-B(1)	107.8(5)
B(10)-B(2)-B(1)	107.7(5)
B(9)-B(2)-B(6)	107.6(5)
B(10)-B(2)-B(6)	59.6(4)
B(1)-B(2)-B(6)	60.4(4)
B(9)-B(2)-Cl(2)	121.3(5)
B(10)-B(2)-Cl(2)	123.3(5)
B(1)-B(2)-Cl(2)	121.4(5)
B(6)-B(2)-Cl(2)	123.1(5)
B(9)-B(2)-B(5)	59.9(4)
B(10)-B(2)-B(5)	107.6(5)
B(1)-B(2)-B(5)	60.0(4)
B(6)-B(2)-B(5)	108.2(5)
Cl(2)-B(2)-B(5)	120.1(5)
B(1)-B(3)-Cl(3)	122.3(5)
B(1)-B(3)-B(12)	108.0(5)
Cl(3)-B(3)-B(12)	120.9(5)
B(1)-B(3)-B(4)	59.9(4)
Cl(3)-B(3)-B(4)	123.1(5)
B(12)-B(3)-B(4)	107.4(5)
B(1)-B(3)-B(5)	60.2(4)
Cl(3)-B(3)-B(5)	121.4(5)
B(12)-B(3)-B(5)	59.8(4)
B(4)-B(3)-B(5)	107.7(5)
B(1)-B(3)-B(11)	108.0(5)
Cl(3)-B(3)-B(11)	121.8(5)
B(12)-B(3)-B(11)	59.6(4)
B(4)-B(3)-B(11)	59.9(4)
B(5)-B(3)-B(11)	107.6(5)
B(6)-B(4)-B(7)	60.5(4)
B(6)-B(4)-B(1)	61.0(4)
B(7)-B(4)-B(1)	108.8(5)
B(6)-B(4)-B(3)	108.7(5)
B(7)-B(4)-B(3)	107.7(5)
B(1)-B(4)-B(3)	59.7(4)
B(6)-B(4)-B(11)	108.2(5)
B(7)-B(4)-B(11)	59.3(4)
B(1)-B(4)-B(11)	108.0(5)
B(3)-B(4)-B(11)	60.2(4)
B(6)-B(4)-Cl(4)	121.8(5)
B(7)-B(4)-Cl(4)	122.6(5)
B(1)-B(4)-Cl(4)	121.0(5)
B(3)-B(4)-Cl(4)	120.8(5)
B(11)-B(4)-Cl(4)	121.7(5)
B(9)-B(5)-Cl(5)	121.9(5)
B(9)-B(5)-B(12)	60.6(4)
Cl(5)-B(5)-B(12)	121.5(5)
B(9)-B(5)-B(1)	107.5(5)
Cl(5)-B(5)-B(1)	122.2(5)
B(12)-B(5)-B(1)	107.4(5)
B(9)-B(5)-B(2)	59.5(4)

Cl(5)-B(5)-B(2)	122.2(5)
B(12)-B(5)-B(2)	108.0(5)
B(1)-B(5)-B(2)	60.0(4)
B(9)-B(5)-B(3)	108.1(5)
Cl(5)-B(5)-B(3)	121.6(5)
B(12)-B(5)-B(3)	59.9(4)
B(1)-B(5)-B(3)	59.4(4)
B(2)-B(5)-B(3)	107.6(5)
B(4)-B(6)-B(10)	107.9(5)
B(4)-B(6)-B(7)	60.0(4)
B(10)-B(6)-B(7)	59.7(4)
B(4)-B(6)-Cl(6)	121.4(4)
B(10)-B(6)-Cl(6)	122.1(5)
B(7)-B(6)-Cl(6)	121.9(4)
B(4)-B(6)-B(2)	107.9(5)
B(10)-B(6)-B(2)	60.0(4)
B(7)-B(6)-B(2)	107.7(5)
Cl(6)-B(6)-B(2)	122.1(4)
B(4)-B(6)-B(1)	59.8(4)
B(10)-B(6)-B(1)	107.6(5)
B(7)-B(6)-B(1)	107.5(5)
Cl(6)-B(6)-B(1)	122.0(5)
B(2)-B(6)-B(1)	59.8(4)
B(8)-B(7)-B(11)	60.7(4)
B(8)-B(7)-B(10)	60.1(4)
B(11)-B(7)-B(10)	108.6(5)
B(8)-B(7)-B(4)	108.8(5)
B(11)-B(7)-B(4)	60.6(4)
B(10)-B(7)-B(4)	107.5(5)
B(8)-B(7)-B(6)	108.2(5)
B(11)-B(7)-B(6)	108.4(5)
B(10)-B(7)-B(6)	59.7(4)
B(4)-B(7)-B(6)	59.4(4)
B(8)-B(7)-Cl(7)	121.5(5)
B(11)-B(7)-Cl(7)	121.2(5)
B(10)-B(7)-Cl(7)	121.8(5)
B(4)-B(7)-Cl(7)	121.6(5)
B(6)-B(7)-Cl(7)	121.6(5)
B(7)-B(8)-B(10)	60.2(4)
B(7)-B(8)-B(12)	107.8(5)
B(10)-B(8)-B(12)	108.3(5)
B(7)-B(8)-B(11)	59.6(4)
B(10)-B(8)-B(11)	107.8(5)
B(12)-B(8)-B(11)	59.9(4)
B(7)-B(8)-B(9)	108.0(5)
B(10)-B(8)-B(9)	59.8(4)
B(12)-B(8)-B(9)	60.6(4)
B(11)-B(8)-B(9)	108.2(5)
B(7)-B(8)-Cl(8)	122.8(5)
B(10)-B(8)-Cl(8)	122.7(5)
B(12)-B(8)-Cl(8)	120.3(5)
B(11)-B(8)-Cl(8)	121.5(5)
B(9)-B(8)-Cl(8)	121.2(5)
B(2)-B(9)-B(10)	60.5(4)
B(2)-B(9)-B(5)	60.6(4)
B(10)-B(9)-B(5)	108.8(5)
B(2)-B(9)-B(8)	108.6(5)
B(10)-B(9)-B(8)	59.9(4)
B(5)-B(9)-B(8)	108.3(5)
B(2)-B(9)-B(12)	108.3(5)
B(10)-B(9)-B(12)	107.7(5)
B(5)-B(9)-B(12)	60.0(4)
B(8)-B(9)-B(12)	59.7(4)
B(2)-B(9)-Cl(9)	121.3(5)
B(10)-B(9)-Cl(9)	122.4(5)
B(5)-B(9)-Cl(9)	120.5(5)
B(8)-B(9)-Cl(9)	122.0(5)
B(12)-B(9)-Cl(9)	121.3(5)
B(9)-B(10)-B(7)	108.0(5)
B(9)-B(10)-B(6)	108.3(5)

B(7)-B(10)-B(6)	60.5(4)
B(9)-B(10)-B(8)	60.3(4)
B(7)-B(10)-B(8)	59.7(4)
B(6)-B(10)-B(8)	108.5(5)
B(9)-B(10)-B(2)	59.8(4)
B(7)-B(10)-B(2)	108.6(5)
B(6)-B(10)-B(2)	60.4(4)
B(8)-B(10)-B(2)	108.3(5)
B(9)-B(10)-Cl(10)	122.7(5)
B(7)-B(10)-Cl(10)	120.8(5)
B(6)-B(10)-Cl(10)	120.3(5)
B(8)-B(10)-Cl(10)	121.9(5)
B(2)-B(10)-Cl(10)	121.7(5)
B(7)-B(11)-B(12)	108.0(5)
B(7)-B(11)-B(8)	59.7(4)
B(12)-B(11)-B(8)	60.0(4)
B(7)-B(11)-Cl(11)	119.9(5)
B(12)-B(11)-Cl(11)	123.3(5)
B(8)-B(11)-Cl(11)	121.6(5)
B(7)-B(11)-B(4)	60.1(4)
B(12)-B(11)-B(4)	107.8(5)
B(8)-B(11)-B(4)	107.6(5)
Cl(11)-B(11)-B(4)	121.2(5)
B(7)-B(11)-B(3)	108.3(5)
B(12)-B(11)-B(3)	60.0(4)
B(8)-B(11)-B(3)	107.9(5)
Cl(11)-B(11)-B(3)	122.9(5)
B(4)-B(11)-B(3)	60.0(4)
B(11)-B(12)-B(8)	60.1(4)
B(11)-B(12)-B(5)	108.5(5)
B(8)-B(12)-B(5)	107.8(5)
B(11)-B(12)-Cl(12)	123.5(5)
B(8)-B(12)-Cl(12)	122.5(5)
B(5)-B(12)-Cl(12)	119.9(5)
B(11)-B(12)-B(3)	60.3(4)
B(8)-B(12)-B(3)	108.3(5)
B(5)-B(12)-B(3)	60.3(4)
Cl(12)-B(12)-B(3)	122.0(5)
B(11)-B(12)-B(9)	107.6(5)
B(8)-B(12)-B(9)	59.7(4)
B(5)-B(12)-B(9)	59.5(4)
Cl(12)-B(12)-B(9)	120.8(5)
B(3)-B(12)-B(9)	107.5(5)
C(22A)-C(21A)-C(26A)	120.0
C(22A)-C(21A)-Cl(21)	114.7(6)
C(26A)-C(21A)-Cl(21)	125.3(6)
C(23A)-C(22A)-C(21A)	120.0
C(23A)-C(22A)-H(22A)	120.0
C(21A)-C(22A)-H(22A)	120.0
C(24A)-C(23A)-C(22A)	120.0
C(24A)-C(23A)-H(23A)	120.0
C(22A)-C(23A)-H(23A)	120.0
C(23A)-C(24A)-C(25A)	120.0
C(23A)-C(24A)-H(24A)	120.0
C(25A)-C(24A)-H(24A)	120.0
C(26A)-C(25A)-C(24A)	120.0
C(26A)-C(25A)-H(25A)	120.0
C(24A)-C(25A)-H(25A)	120.0
C(25A)-C(26A)-C(21A)	120.0
C(25A)-C(26A)-Cl(26)	119.6(6)
C(21A)-C(26A)-Cl(26)	120.4(6)
C(22B)-C(21B)-C(26B)	120.0
C(22B)-C(21B)-H(21B)	120.0
C(26B)-C(21B)-H(21B)	120.0
C(21B)-C(22B)-C(23B)	120.0
C(21B)-C(22B)-H(22B)	120.0
C(23B)-C(22B)-H(22B)	120.0
C(22B)-C(23B)-C(24B)	120.0
C(22B)-C(23B)-H(23B)	120.0
C(24B)-C(23B)-H(23B)	120.0

C(25B)-C(24B)-C(23B)	120.0
C(25B)-C(24B)-Cl(24)	119.4(6)
C(23B)-C(24B)-Cl(24)	120.6(6)
C(24B)-C(25B)-C(26B)	120.0
C(24B)-C(25B)-Cl(25)	118.7(6)
C(26B)-C(25B)-Cl(25)	121.3(6)
C(25B)-C(26B)-C(21B)	120.0
C(25B)-C(26B)-H(26B)	120.0
C(21B)-C(26B)-H(26B)	120.0
C(32A)-C(31A)-C(36A)	120.0
C(32A)-C(31A)-Cl(31)	118.7(6)
C(36A)-C(31A)-Cl(31)	121.3(6)
C(33A)-C(32A)-C(31A)	120.0
C(33A)-C(32A)-Cl(32)	119.4(6)
C(31A)-C(32A)-Cl(32)	120.6(6)
C(32A)-C(33A)-C(34A)	120.0
C(32A)-C(33A)-H(33A)	120.0
C(34A)-C(33A)-H(33A)	120.0
C(35A)-C(34A)-C(33A)	120.0
C(35A)-C(34A)-H(34A)	120.0
C(33A)-C(34A)-H(34A)	120.0
C(34A)-C(35A)-C(36A)	120.0
C(34A)-C(35A)-H(35A)	120.0
C(36A)-C(35A)-H(35A)	120.0
C(35A)-C(36A)-C(31A)	120.0
C(35A)-C(36A)-H(36A)	120.0
C(31A)-C(36A)-H(36A)	120.0
C(32B)-C(31B)-C(36B)	120.0
C(32B)-C(31B)-H(31B)	120.0
C(36B)-C(31B)-H(31B)	120.0
C(33B)-C(32B)-C(31B)	120.0
C(33B)-C(32B)-H(32B)	120.0
C(31B)-C(32B)-H(32B)	120.0
C(32B)-C(33B)-C(34B)	120.0
C(32B)-C(33B)-H(33B)	120.0
C(34B)-C(33B)-H(33B)	120.0
C(35B)-C(34B)-C(33B)	120.0
C(35B)-C(34B)-Cl(34)	119.8(7)
C(33B)-C(34B)-Cl(34)	120.2(7)
C(36B)-C(35B)-C(34B)	120.0
C(36B)-C(35B)-Cl(35)	121.5(7)
C(34B)-C(35B)-Cl(35)	118.5(7)
C(35B)-C(36B)-C(31B)	120.0
C(35B)-C(36B)-H(36B)	120.0
C(31B)-C(36B)-H(36B)	120.0

Table S5. Anisotropic displacement parameters ($Å^2$ x 10^3).
The anisotropic displacement factor exponent takes the form:
$-2\,\pi^2\,[\,h^2\,a^{*2}\,U_{11} + \ldots + 2\,h\,k\,a^*\,b^*\,U_{12}\,]$

	U11	U22	U33	U23	U13	U12
Fe(1A)	62(1)	51(1)	49(1)	-1(1)	3(1)	8(1)
Si(1A)	62(1)	61(1)	57(1)	-5(1)	9(1)	6(1)
C(1A)	66(5)	62(4)	57(4)	-12(3)	-1(3)	4(4)
C(2A)	51(4)	79(5)	63(5)	3(4)	0(3)	9(4)
C(3A)	58(5)	100(7)	79(6)	-2(5)	16(4)	-1(5)
C(4A)	64(5)	70(5)	77(5)	14(4)	7(4)	-4(4)
C(5A)	65(5)	54(4)	73(5)	-6(4)	4(4)	3(3)
C(6A)	98(6)	48(4)	63(5)	-4(3)	3(4)	2(4)
C(7A)	99(7)	81(6)	57(5)	-15(4)	2(5)	10(5)
C(8A)	105(7)	75(6)	59(5)	7(4)	-5(5)	2(5)
C(9A)	66(5)	68(5)	77(6)	-6(4)	-19(4)	8(4)
C(10A)	85(6)	61(5)	54(4)	-3(3)	-3(4)	-17(4)
C(11A)	51(4)	86(6)	79(6)	-18(5)	12(4)	2(4)
C(12A)	90(6)	66(5)	45(4)	3(3)	14(4)	9(4)
C(13A)	161(9)	106(7)	103(7)	10(6)	-15(7)	-17(7)
C(14A)	135(8)	100(6)	65(5)	-4(5)	17(5)	-1(6)
C(15A)	149(9)	150(9)	147(9)	47(8)	30(8)	35(8)
Fe(1B)	51(1)	60(1)	43(1)	-3(1)	5(1)	10(1)
Si(1B)	55(1)	82(2)	93(2)	26(1)	-11(1)	-14(1)
C(1B)	82(5)	56(4)	57(4)	-7(3)	-5(4)	12(4)
C(2B)	86(6)	73(5)	59(5)	-9(4)	-12(4)	7(5)
C(3B)	99(7)	80(6)	39(4)	-6(4)	-3(4)	29(5)
C(4B)	85(6)	84(6)	52(4)	0(4)	28(4)	29(5)
C(5B)	65(5)	74(5)	55(4)	4(4)	14(3)	26(4)
C(6B)	50(4)	94(6)	82(6)	-12(5)	15(4)	15(4)
C(7B)	83(6)	62(5)	70(5)	-1(4)	7(4)	27(4)
C(8B)	84(6)	57(4)	67(5)	-4(4)	18(4)	6(4)
C(9B)	65(5)	71(5)	56(4)	-17(4)	9(3)	-6(4)
C(10B)	58(4)	89(6)	56(4)	-8(4)	14(3)	5(4)
C(11B)	55(4)	60(4)	55(4)	-1(3)	-1(3)	5(3)
C(12B)	49(4)	50(4)	107(7)	-5(4)	10(4)	-6(3)
C(13B)	130(8)	123(8)	141(9)	-26(7)	57(7)	-28(7)
C(14B)	93(6)	79(6)	136(8)	3(6)	19(6)	-13(5)
C(15B)	94(7)	137(8)	135(8)	22(7)	-8(6)	-23(6)
B(1)	42(3)	51(4)	39(3)	4(3)	5(3)	-4(3)
B(2)	47(4)	51(4)	44(4)	-7(3)	14(3)	-5(3)
B(3)	39(3)	48(4)	56(4)	3(3)	8(3)	2(3)
B(4)	37(3)	48(4)	44(4)	-3(3)	10(3)	2(3)
B(5)	44(4)	46(4)	47(4)	2(3)	11(3)	-2(3)
B(6)	35(3)	49(4)	39(3)	-2(3)	8(2)	-3(3)
B(7)	39(3)	50(4)	41(3)	3(3)	6(3)	-6(3)
B(8)	42(3)	53(4)	43(4)	-1(3)	1(3)	-7(3)
B(9)	35(3)	47(4)	50(4)	-1(3)	9(3)	0(3)
B(10)	37(3)	40(3)	55(4)	5(3)	1(3)	1(3)
B(11)	41(3)	54(4)	46(4)	-4(3)	10(3)	-4(3)
B(12)	43(3)	51(4)	37(3)	-4(3)	7(3)	-6(3)
Cl(1)	66(1)	95(2)	53(1)	24(1)	-8(1)	-9(1)
Cl(2)	66(1)	84(1)	59(1)	-27(1)	28(1)	-16(1)
Cl(3)	67(1)	45(1)	101(2)	2(1)	13(1)	10(1)
Cl(4)	36(1)	71(1)	84(1)	-5(1)	11(1)	4(1)
Cl(5)	65(1)	68(1)	59(1)	12(1)	17(1)	-18(1)
Cl(6)	52(1)	66(1)	56(1)	-14(1)	6(1)	-16(1)
Cl(7)	60(1)	71(1)	51(1)	14(1)	9(1)	-19(1)
Cl(8)	72(1)	93(2)	53(1)	20(1)	-17(1)	-14(1)
Cl(9)	35(1)	64(1)	90(1)	-11(1)	7(1)	0(1)
Cl(10)	57(1)	44(1)	100(2)	4(1)	2(1)	7(1)
Cl(11)	72(1)	89(1)	57(1)	-28(1)	29(1)	-19(1)
Cl(12)	57(1)	64(1)	66(1)	-19(1)	10(1)	-19(1)
C(21A)	102(4)	122(4)	118(4)	-1(4)	10(4)	-10(4)
C(22A)	92(5)	110(5)	123(5)	-9(5)	4(5)	-6(5)

C(23A)	59(5)	73(5)	101(6)	29(5)	−10(5)	−5(5)
C(24A)	89(5)	102(6)	102(6)	19(5)	−7(5)	−9(5)
C(25A)	97(6)	108(6)	108(6)	7(5)	−2(5)	−4(5)
C(26A)	108(5)	118(5)	129(5)	10(5)	5(5)	−7(5)
Cl(21)	150(5)	219(6)	116(5)	−16(5)	38(4)	−37(5)
Cl(26)	181(6)	148(6)	211(7)	53(6)	10(6)	12(5)
C(21B)	115(6)	143(6)	118(6)	−8(6)	16(5)	−17(6)
C(22B)	100(5)	118(5)	116(5)	−14(5)	10(5)	−9(5)
C(23B)	93(5)	111(5)	120(5)	−8(5)	4(5)	−6(5)
C(24B)	96(4)	110(5)	114(5)	3(4)	3(4)	−7(4)
C(25B)	113(5)	123(5)	130(5)	7(5)	7(5)	−5(5)
C(26B)	110(6)	131(6)	122(6)	2(5)	16(5)	−12(5)
Cl(24)	153(6)	167(7)	135(6)	−3(5)	−2(5)	−12(5)
Cl(25)	160(6)	136(6)	175(7)	−34(6)	12(6)	25(5)
C(31A)	138(6)	155(6)	152(6)	−8(5)	3(5)	2(5)
C(32A)	130(5)	147(5)	150(5)	−5(4)	5(4)	4(4)
C(33A)	128(5)	146(6)	143(6)	−7(5)	8(5)	2(5)
C(34A)	123(6)	140(6)	139(6)	4(5)	8(5)	0(5)
C(35A)	127(6)	137(7)	145(7)	6(6)	5(6)	1(6)
C(36A)	127(6)	139(7)	144(7)	−5(6)	1(6)	2(6)
Cl(31)	192(7)	212(8)	164(7)	22(6)	2(6)	−17(7)
Cl(32)	166(6)	173(6)	242(8)	15(6)	−19(6)	−16(6)
C(31B)	128(5)	147(6)	144(6)	−7(5)	9(5)	3(5)
C(32B)	112(6)	129(6)	128(6)	−16(6)	17(6)	13(6)
C(33B)	133(6)	144(6)	159(6)	−5(6)	1(6)	3(6)
C(34B)	133(6)	158(6)	160(6)	−6(5)	2(5)	4(5)
C(35B)	139(6)	157(6)	156(6)	−10(5)	2(5)	3(5)
C(36B)	131(5)	146(5)	148(5)	−4(4)	5(4)	2(4)
Cl(34)	128(5)	202(7)	152(6)	−9(5)	−31(5)	−1(5)
Cl(35)	202(7)	208(8)	212(8)	−28(7)	−12(7)	−9(7)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3).

	x	y	z	U(eq)
H(2A)	9654	4859	-962	78
H(3A)	9798	5580	-1773	94
H(4A)	8509	6663	-1846	84
H(5A)	7589	6627	-1097	77
H(6A)	7882	3634	-1578	84
H(7A)	8446	4365	-2303	96
H(8A)	7329	5514	-2487	97
H(9A)	6012	5469	-1892	87
H(10A)	6335	4308	-1340	81
H(11A)	6460	5977	-328	107
H(11B)	5872	5172	-389	107
H(11C)	5973	5710	-862	107
H(13A)	7241	3187	-766	188
H(13B)	6369	3633	-534	188
H(13C)	7045	3030	-203	188
H(14A)	7995	3824	446	149
H(14B)	6975	4269	307	149
H(14C)	7992	4737	332	149
H(15A)	9264	4107	-165	222
H(15B)	8897	3792	-707	222
H(15C)	8852	3239	-236	222
H(2B)	2126	-547	301	89
H(3B)	2787	534	-189	88
H(4B)	4546	820	158	86
H(5B)	4994	-117	863	77
H(6B)	1339	926	1058	90
H(7B)	2078	1831	461	86
H(8B)	3860	2093	794	82
H(9B)	4206	1361	1611	76
H(10B)	2667	641	1771	80
H(11D)	4039	-466	2228	86
H(11E)	4724	-121	1836	86
H(11F)	4592	-1041	1884	86
H(13D)	1465	-176	2055	193
H(13E)	2309	-686	2353	193
H(13F)	1233	-1044	2220	193
H(14D)	1843	-2170	1818	153
H(14E)	2920	-1853	2003	153
H(14F)	2652	-2089	1435	153
H(15D)	747	-1463	1263	185
H(15E)	1448	-1121	878	185
H(15F)	837	-543	1192	185
H(22A)	3478	9245	-1169	131
H(23A)	3643	9453	-2014	95
H(24A)	4020	8405	-2519	118
H(25A)	4233	7149	-2180	126
H(21B)	3666	8113	-232	150
H(22B)	3430	9242	-720	133
H(23B)	3526	9177	-1580	130
H(26B)	3998	6918	-604	145
H(33A)	-1364	3984	-3160	168
H(34A)	-1345	2704	-2853	161
H(35A)	-926	1664	-3355	164
H(36A)	-527	1905	-4164	165
H(31B)	-1265	3404	-2976	168
H(32B)	-1313	4746	-3146	147
H(33B)	-880	5209	-3910	175
H(36B)	-783	2524	-3570	171

4 Density Functional Theory (DFT) Calculations

The Turbomole program was used for the DFT calculations (Version 6.3).[S11] Geometry optimisation of the silicon cation was performed using the meta-GGA density functional TPSS[S12] including an atom-pairwise correction for dispersion forces[S13] using the def2-TZVPP basis set[S14] without solvent or counterion effects. The structure remains essentially the same when a continuum solvation model[S15] is applied in the geometry optimization (1,2-$Cl_2C_6H_4$, ε = 9.84). – Orbital localization was performed with the Boys method[S16] as implemented in Turbomole. NMR chemical shift calculations (GIAO-DFT[S17]) of the silicon cation and tetramethylsilane with BP86[S18] using Turbomole[S19] resulted in isotropic shieldings of 312.06 ppm (TMS) and 195.66 ppm (silicon cation).

4.1 Absolute Energies and Cartesian Coordinates for Calculated Molecules

Carbenium ion (general structure **I** with R = *t*Bu and Me)
E (TPSS-D3/dev2-TZVPP) = -1886.36341705153 Eh

```
         38
   FE        -1.27604649     -1.01919116      0.24259439
   C         -2.91475135      0.00738320     -0.54112024
   C         -1.80979177      0.56097922      1.40831128
   C         -0.95431843      0.95645434      0.28483795
   C         -1.69120685      0.59358976     -0.93110572
   C         -2.98868650     -0.01230436      0.88543607
   C         -0.59501306     -2.53508336      1.47511140
   C         -1.80353751     -2.91030893      0.80934287
   C         -1.57045902     -2.85655906     -0.60345492
   C         -0.22312177     -2.43637078     -0.81439638
   C          0.37783718     -2.25514886      0.47421168
   C          0.45066118      0.97796111      0.43139942
   C          0.99677555      0.95058523      1.83843701
   C          1.46237132      1.30689238     -0.65453053
   C          2.04493594      2.69950752     -0.23898712
   C          2.62110802      0.28293831     -0.69238647
   C          0.92654912      1.44956363     -2.08597002
   H         -3.65583843     -0.39844593     -1.21522610
   H         -1.58240390      0.68368578      2.45586696
   H         -1.37092413      0.72710840     -1.94799348
   H         -3.79690948     -0.42989244      1.46886184
   H         -0.44895542     -2.47277929      2.54407534
   H         -2.73700603     -3.17015172      1.28777792
   H         -2.29926300     -3.06541761     -1.37363208
   H          0.25860752     -2.29548828     -1.77104259
   H          1.38945984     -1.92407121      0.65885133
   H          0.82835096      1.92857649      2.30707540
   H          0.49948168      0.20094386      2.45354256
   H          2.06834037      0.76041013      1.85513340
   H          2.57887116      2.65737267      0.71175182
   H          2.75082994      3.00701657     -1.01505652
   H          1.25549430      3.45327991     -0.17207536
   H          3.08419317      0.12077515      0.28314559
   H          2.27527202     -0.67674694     -1.08454821
   H          3.39477638      0.65981179     -1.36638285
   H          0.13690787      2.20140646     -2.16028423
   H          1.75087103      1.77551181     -2.72572453
   H          0.56653861      0.49620624     -2.48184692
```

Borane (general structure **II** with R = *t*Bu and Me)

E (TPSS-D3/dev2-TZVPP) = -1873.35731048670 Eh

38

FE	-1.48544985	-1.12351304	0.23081664
C	-3.00925659	0.01714592	-0.53236287
C	-1.85398227	0.48337634	1.40823064
C	-0.97758597	0.84422690	0.30538112
C	-1.73788399	0.54581363	-0.89624160
C	-3.08226707	-0.02049227	0.89546790
C	-0.68343074	-2.57036984	1.42818080
C	-1.88884102	-3.03237655	0.80870887
C	-1.71223898	-2.96303594	-0.61115206
C	-0.39879669	-2.45619216	-0.86976585
C	0.23805215	-2.22134951	0.39164774
B	0.54889062	1.03011099	0.48465634
C	1.09782475	0.98637954	1.97806646
C	1.59373952	1.37259843	-0.68177467
C	2.13114337	2.79040412	-0.33754851
C	2.79146911	0.39532039	-0.66851027
C	1.05009741	1.42060068	-2.11988667
H	-3.77245623	-0.32994736	-1.21568093
H	-1.59587471	0.54955500	2.45580271
H	-1.39035741	0.65856066	-1.91043217
H	-3.91090699	-0.39865668	1.47860313
H	-0.50627169	-2.48306958	2.49099479
H	-2.78435463	-3.35317191	1.32246337
H	-2.45183956	-3.22085661	-1.35639365
H	0.03212097	-2.26961099	-1.84344529
H	1.23357275	-1.82786562	0.53823114
H	0.74262017	1.87544324	2.52095164
H	0.71104371	0.12508522	2.53522494
H	2.18862378	0.97802772	2.06472230
H	2.61405113	2.81509168	0.64401395
H	2.87284849	3.09480223	-1.08807490
H	1.32724643	3.53555289	-0.34113266
H	3.24800592	0.31350316	0.32261321
H	2.48798651	-0.60772590	-0.98825261
H	3.56592836	0.74183921	-1.36591564
H	0.22889399	2.13768323	-2.21918947
H	1.84476445	1.72906185	-2.81264583
H	0.69287082	0.43805089	-2.44637204

Silylium ion (general structure **III** with R = *t*Bu and Me = compound **3**$^+$)
E (TPSS-D3/dev2-TZVPP) = -2137.80904344507 Eh

38

FE	-1.41024355	-0.89486184	0.24565249
C	-3.13664723	-0.07838764	-0.57132914
C	-2.19166401	0.58556817	1.43006815
C	-1.37656369	1.13498047	0.35762006
C	-2.00076552	0.71230760	-0.88594073
C	-3.25403976	-0.15730030	0.85143927
C	-0.50823839	-2.31162492	1.43902452
C	-1.66680982	-2.85177710	0.81520769
C	-1.49817378	-2.76443810	-0.60474086
C	-0.23374111	-2.17092333	-0.86937095
C	0.39260518	-1.89220871	0.39851874
SI	0.39613388	0.75077348	0.54021808
C	1.07206176	0.81587479	2.27750835
C	1.64289984	1.21308307	-0.80017095
C	2.14472975	2.61742880	-0.35974782
C	2.83938703	0.23926831	-0.82151246
C	1.03381286	1.31928990	-2.20878657
H	-3.78594216	-0.56564302	-1.28514044
H	-1.99668414	0.69038351	2.48769064
H	-1.63887084	0.92461756	-1.87974447
H	-4.00732815	-0.71247184	1.39251637
H	-0.33033434	-2.23465798	2.50180425
H	-2.53779247	-3.23587445	1.32642601
H	-2.22056700	-3.06985799	-1.34792036
H	0.18898910	-1.97357617	-1.84349246
H	1.42470538	-1.59363231	0.54068211
H	1.23821178	1.85767499	2.57260346
H	0.38407939	0.36573912	2.99695250
H	2.03268833	0.29646919	2.34974360
H	2.66431888	2.58691756	0.60249176
H	2.85659201	2.98357128	-1.10889364
H	1.32845912	3.34504737	-0.29426053
H	3.27614870	0.09025577	0.17223122
H	2.56549065	-0.73672272	-1.23384664
H	3.62641444	0.65390805	-1.46177657
H	0.25158501	2.08266583	-2.25470411
H	1.81801088	1.61133958	-2.91675874
H	0.61708202	0.36679407	-2.55026180

4.2 Calculated Dip Angles

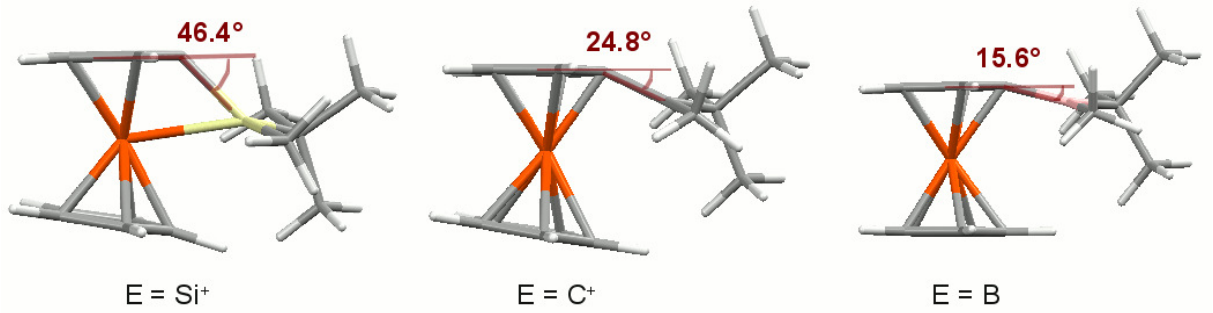


Figure S2. Comparison of the dip angle for ferrocenyl compounds *t*BuFcMeE (DFT optimized, TPSS-D3/def2-TZVPP). The extraordinary bending of the silicon atom towards the ferrocene substitutent is also reflected in the Fe–E distances: Fe–Si$^+$: 2.461 Å (left), Fe–C$^+$ (middle): 2.647 Å, Fe–B (right): 2.973 Å.

5 References and Notes

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