Nitrile Insertion into a Boryl-substituted Five-membered Zirconacycloallenoid: Unexpected formation of a Zwitterionic Boratirane Product

Juri Ugolotti, Gerald Kehr, Roland Fröhlich, Stefan Grimme and Gerhard Erker

Organisch-Chemisches Institut der Universität, Corrensstrasse 40, Münster,Germany. Fax:+49 251 8336503; Tel:+49 251 8333221; E-mail: erker@uni-muenster.de.

Supporting Information

General Procedures. Reactions with air- and moisture sensitive compounds were carried out under an argon atmosphere using Schlenk-type glassware or a glovebox. Solvents were dried with the procedure reported by *Grubbs* (Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics*, 1996, *15*, 1518-1520) or, particularly deuterated solvents, were distilled from appropriate drying agents and stored under an argon atmosphere. The following instruments were used for physical characterization of the compounds: NMR: Varian Inova 500 (^{1}H: 500 MHz; ^{11}B: 161 MHz; ^{13}C: 126 MHz; ^{19}F: 470 MHz; ^{29}Si: 99 MHz {using INEPT pulse sequence based on $J_{Si,H}$ = 7 Hz}). Most NMR assignments were supported by additional 2D experiments. The IR spectra were obtained with a Varian 3100 FT-IR (EXCALIBUR Series) spectrometer, the MS GC-EI with Triplequad TSQ (Thermo-Finnigan-MAT, Bremen). Elemental analyses were performed with a Foss-Heraeus CHN-O-Rapid instrument.
X-ray Crystal Structure Analyses. Data sets was collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, 1997, *276*, 307-326), absorption correction Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Cryst.* 2003, *A59*, 228-234), structure solution SHELXS-97 (G.M. Sheldrick, *Acta Cryst.* 1990, *A46*, 467-473), structure refinement SHELXL-97 (G.M. Sheldrick, *Acta Cryst.* 2008, *A64*, 112-122), graphics SCHAKAL (E. Keller, Univ. Freiburg, 1997).

Preparation of complex 5a.
Complex **3a** (400 mg, 0.507 mmol) and acetonitrile (25 mg, 0.609 mmol, 20% excess) were placed in two different Schlenk flasks of 100 mL and 50 mL volume each, and dissolved by 30 and 5 mL dry toluene, respectively. The acetonitrile solution was added by cannula under argon to the zirconacycloallenoid solution

with stirring. The dark-red clear solution was stirred at room temperature for 2 hours, after which the excess acetonitrile was removed and the volume reduced to 10 mL under vacuum. The solution was then stored at -30 °C over night, after which 100 mg of crystalline product were recovered. The volume was then reduced to 3 mL under vacuum and the solution stored at -30 °C over night again, allowing the recovery of other 105 mg of product. From NMR determination it appears that the product crystallised with one molecule of toluene per four molecule of **5a**. Isolated yield = 47%. Crystals of **5a** suitable for single-crystal X-ray diffraction were obtained in C_6D_6 at room temperature.
Crystal data for $C_{36}H_{36}BF_{10}NSi_2Zr$ * C_6H_6 (**5a**), M = 908.98, monoclinic, space group $P2_1/c$ (No. 14), a = 10.9479(2), b = 10.8207(2), c = 35.2290(5) Å, β = 91.172(1)°, V = 4172.49(12) Å^3, D_c = 1.447 g cm^{-3}, μ = 0.397 mm^{-1}, Z = 4, λ = 0.71073 Å, T = 223(2) K, 34244 reflections collected (±h, ±k, ±l), [($sin\theta$)/λ] = 0.66 Å^{-1}, 9312 independent (R_{int} = 0.050) and 6812 observed reflections [$I \geq 2\sigma(I)$], 523 refined parameters, R = 0.045, wR^2 = 0.128. The R values are given for the observed reflections [$I \geq 2\sigma(I)$] and wR^2 values are given for all reflections.

^{1}H NMR (C_6D_6, 500 MHz, 298 K, TMS): δ 5.77(β), 5.47(α), 5.43(β'), 5.33(α') (each m, each 1H, Cp^A), 5.43(β'), 5.28(α), 5.14(β), 3.81(α') (each m, each 1H, Cp^B), 3.49 (s, 1H, 2-H), 2.11 (d J = 1.4 Hz, 3H, 1-CH_3), 1.69 (s, 3H, CH_3^A), 1.62 (s, 3H, CH_3^B), 0.27 (s, $^2J_{Si,H}$ = 6.2 Hz, 9H, 5-Si$(CH_3)_3$), 0.04 (s, $^2J_{Si,H}$ = 6.3 Hz, 9H, 3-Si$(CH_3)_3$). ^{13}C{^{1}H} NMR (C_6D_6, 126 MHz, 298 K, TMS): δ 183.1(C1), 149.2 ($^1J_{FC}$ = 247 Hz), 148.9 ($^1J_{FC}$ = 243 Hz) 140.1 ($^1J_{FC}$ = 247 Hz) 137.7 ($^1J_{FC}$ = 243 Hz) (each dm, C_6F_5), 148.6 (C4), 127.2(i), 112.9(α), 112.6(β), 107.9(α'), 107.5(β') (Cp^A), 126.7(i), 113.8(β'),111.9(α'), 108.6(α),106.8(β) (Cp^B), 97.3 (br, C5), 69.2 (br, C2), 20.7 (d J = 6.4 Hz, 1-CH_3), 17.7 (br, C3), 15.3 (CH_3^A), 15.2 (CH_3^B), 2.6 (d J = 2.5 Hz, 5-Si$(CH_3)_3$), -0.3 (3-Si$(CH_3)_3$), n.o. ($C_6F_5^i$). ^{13}C,^{1}H GHSQC (C_6D_6, 126 / 500 MHz, 298 K, TMS): δ ^{13}C / ^{1}H 113.8 / 5.43 ($Cp^{\beta,B}$), 112.9 / 5.47 ($Cp^{\alpha,A}$), 112.6 / 5.77 ($Cp^{\beta,A}$), 111.9 / 3.81 ($Cp^{\alpha,B}$), 108.6 / 5.28 ($Cp^{\alpha,B}$), 107.9 / 5.37 ($Cp^{\alpha,A}$), 107.5 / 5.43 ($Cp^{\beta,A}$), 106.8 / 5.14 ($Cp^{\beta,B}$), 69.2 / 3.49 (C2, $^1J_{CH}$ = 156 Hz), 20.7 / 2.11 (1-CH_3), 15.3 / 1.69 (CH_3^A), 15.2 / 1.62 (CH_3^B), 2.6 / 0.27 (5-Si$(CH_3)_3$), -0.3 / 0.04 (3-Si$(CH_3)_3$). ^{1}H,^{13}C GHMBC (C_6D_6, 500 / 126 MHz, 298 K, TMS): δ ^{1}H / ^{13}C 5.77 / 127.2, 107.9 ($Cp^{\beta,A}$ / $Cp^{i,A}$, $Cp^{\alpha,A}$), 5.43 / 126.7, 111.9, 108.6 ($Cp^{\beta,B}$ / $Cp^{i,B}$, $Cp^{\alpha,B}$, $Cp^{\alpha,B}$), 5.28 / 113.8, 111.9, 106.8 ($Cp^{\alpha,B}$ / $Cp^{\beta,B}$, $Cp^{\alpha,B}$, $Cp^{\beta,B}$), 5.14 / 126.7, 111.9 ($Cp^{\beta,B}$ / $Cp^{i,B}$, $Cp^{\alpha,B}$), 3.49 / 148.6, 20.7, 17.7 (2-H / C4, 1-CH_3, C3), 2.11 / 183.1, 69.2 (1-CH_3 / C1, C2), 1.69 / 127.2, 112.9, 107.9 (CH_3^A / $Cp^{i,A}$, $Cp^{\alpha,A}$, $Cp^{\alpha,A}$), 1.62 / 126.7, 111.9, 108.6 (CH_3^B / $Cp^{i,B}$, $Cp^{\alpha,B}$, $Cp^{\alpha,B}$), 0.27 / 97.3 (5-Si$(CH_3)_3$ / C5), 0.04 / 17.7 (3-Si$(CH_3)_3$ / C3). ^{29}Si{^{1}H} NMR (C_6D_6, 99 MHz, 298 K, TMS): δ 4.2 (3-Si), -8.0 (5-Si). ^{29}Si,^{1}H GHMQC (C_6D_6, 99 / 500 MHz, 298 K, TMS): δ ^{29}Si / ^{1}H 4.2 / 3.49, 0.04 (3-Si / 2-H, 3-Si$(CH_3)_3$), -8.0 / 0.27 (5-Si / 5-Si$(CH_3)_3$). ^{11}B{^{1}H} NMR (C_6D_6, 161 MHz, 298 K, $BF_3{\cdot}OEt_2$): δ -15.6 (s, $\nu_{1/2}$ ≈ 30 Hz). ^{19}F NMR (C_6D_6, 470 MHz, 298 K, $CFCl_3$): -124.0, -128.4 (each m, each 1F, *o*-F), -158.9 (m, 1F, *p*-F), -163.7, -164.5 (each m, each 1F, *m*-F) (C_6F_5), n.o. (*o*-F), -158.7 (m, 1F, *p*-F), -164.1 (br, 2F, *m*-F) (C_6F_5). [Cp^A is in a cis position to 3-$SiMe_3$].

^{1}H NMR (C_7D_8, 500 MHz, 243 K, TMS): δ 5.68(β), 5.38(α), 5.28(β'), 5.17(α') (each m, each 1H, Cp^A), 5.40(β'), 5.12(α), 5.00(β), 3.52(α') (each m, each 1H, Cp^B), 3.42 (s, 1H, 2-H), 2.03 (s, 3H, 1-CH_3), 1.58 (s, 3H, $CH_3{}^A$), 1.51 (s, 3H, $CH_3{}^B$), 0.18 (s, 9H, 5-$Si(CH_3)_3$), -0.02 (s, 9H, 3-$Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_7D_8, 126 MHz, 243 K, TMS): δ 182.9 (C1), 149.0 ($^1J_{FC}$ = 256 Hz), 148.8 ($^1J_{FC}$ = 244 Hz) 148.2 ($^1J_{FC}$ = 238 Hz) 139.8 ($^1J_{FC}$ = 244 Hz) 137.4 ($^1J_{FC}$ = 247 Hz) (each dm, C_6F_5), 146.9 (C4), 127.5(i), 112.9 ($^1J_{CH}$ = 175 Hz, α), 112.6 ($^1J_{CH}$ = 174 Hz, β),107.3 ($^1J_{CH}$ = 174 Hz, α'), 107.1 ($^1J_{CH}$ = 176 Hz, β') (Cp^A), 126.8(i), 114.0 ($^1J_{CH}$ = 177 Hz, β'),111.6 ($^1J_{CH}$ = 175 Hz, α'), 108.1 ($^1J_{CH}$ = 174 Hz, α), 106.4 ($^1J_{CH}$ = 175 Hz, β) (Cp^B), 97.4 (br., C5), 68.8 (br., $^1J_{CH}$ = 156 Hz, C2), 20.5 ($^1J_{CH}$ = 129 Hz, 1-CH_3), 17.2 (br., C3), 15.3 ($^1J_{CH}$ = 129 Hz, $CH_3{}^A$), 15.1 ($^1J_{CH}$ = 129 Hz, $CH_3{}^B$), 2.4 (d J = 2.4 Hz, $^1J_{CH}$ = 119 Hz, 5-$Si(CH_3)_3$), -0.3 ($^1J_{CH}$ = 118 Hz, 3-$Si(CH_3)_3$), n.o. ($C_6F_5{}^i$). ^{13}C,^{1}H GHSQC (C_6D_6, 126 / 500 MHz, 243 K, TMS): δ ^{13}C / ^{1}H 114.0 / 5.40 ($Cp^{\beta,B}$), 112.9 / 5.38 ($Cp^{\alpha,A}$), 112.6 / 5.68 ($Cp^{\beta,A}$), 111.6 / 3.52 ($Cp^{\alpha,B}$), 108.1 / 5.12 ($Cp^{\alpha,B}$), 107.3 / 5.17 ($Cp^{\alpha,A}$), 107.1 / 5.28 ($Cp^{\beta,A}$), 106.4 / 5.00 ($Cp^{\beta,B}$), 68.8 / 3.42 (C2), 20.5 / 2.03 (1-CH_3), 15.3 / 1.58 ($CH_3{}^A$), 15.1 / 1.51 ($CH_3{}^B$), 2.4 / 0.18 (5-$Si(CH_3)_3$), -0.3 / -0.02 (3-$Si(CH_3)_3$). ^{1}H,^{13}C GHMBC (C_6D_6, 500 / 126 MHz, 298 K, TMS): δ ^{1}H / ^{13}C 5.68 / 127.5, 112.9, 107.1 ($Cp^{\beta,A}$ / $Cp^{i,A}$, $Cp^{\alpha,A}$, $Cp^{\beta,A}$), 5.40 / 126.8, 111.6, 108.1 ($Cp^{\beta,B}$ / $Cp^{i,B}$, $Cp^{\alpha,B}$, $Cp^{\alpha,B}$), 5.38 / 127.5, 112.6, 107.1 ($Cp^{\alpha,A}$ / $Cp^{i,A}$, $Cp^{\beta,A}$, $Cp^{\beta,A}$), 5.28 / 127.5, 112.9, 107.3 ($Cp^{\beta,A}$ / $Cp^{i,A}$, $Cp^{\alpha,A}$, $Cp^{\alpha,A}$), 5.17 / 127.5, 112.6, 107.1 ($Cp^{\alpha,A}$ / $Cp^{i,A}$, $Cp^{\beta,A}$, $Cp^{\beta,A}$), 5.12 / 126.8, 114.0, 111.6, 106.4 ($Cp^{\alpha,B}$ / $Cp^{i,B}$, $Cp^{\beta,B}$, $Cp^{\alpha,B}$, $Cp^{\beta,B}$), 5.00 / 126.8, 114.0, 111.6 ($Cp^{\beta,B}$ / $Cp^{i,B}$, $Cp^{\beta,B}$, $Cp^{\alpha,B}$), 3.52 / 126.8, 108.1, 106.4 ($Cp^{\alpha,B}$ / $Cp^{i,B}$, $Cp^{\alpha,B}$, $Cp^{\beta,B}$), 3.42 / 146.9, 97.4, 20.5, 17.2 (2-H / C4, C5, 1-CH_3, C3), 2.03 / 182.9, 68.8 (1-CH_3 / C1, C2), 1.58 / 127.5, 112.9, 107.3 (Cp^A / $Cp^{i,A}$, $Cp^{\alpha,A}$, $Cp^{\alpha,A}$), 1.51 / 126.9, 111.6, 108.1 (Cp^B / $Cp^{i,B}$, $Cp^{\alpha,B}$, $Cp^{\alpha,B}$), 0.18 / 146.9, 97.4 (5-$Si(CH_3)_3$ / C5, C4), -0.02 / 17.2 (3-$Si(CH_3)_3$ / C3). $^{11}B\{^1H\}$ NMR (C_7D_8, 160 MHz, 298 K, $BF_3\cdot OEt_2$): δ -16.0 (s, $\nu_{1/2} \approx$ 70 Hz). $^{29}Si\{^1H\}$ NMR (C_7D_8, 99 MHz, 243 K, TMS): δ 4.2 (3-Si), -8.2 (5-Si). ^{29}Si,^{1}H GHMQC (C_7D_8, 99 / 500 MHz, 243 K, TMS): δ ^{29}Si / ^{1}H 4.2 / 3.42, -0.02 (3-Si / 2-H, 3-$Si(CH_3)_3$), -8.2 / 0.18 (5-Si / 5-$Si(CH_3)_3$). ^{19}F NMR (C_7D_8, 470 MHz, 243 K, $CFCl_3$): -124.3, -128.5 (each m, each 1F, *o*-F), -158.5 (m, 1F, *p*-F), -163.5, -164.1 (each m, each 1F, *m*-F) (C_6F_5), 126.9, -132.7 (each br, each 1F, *o*-F), -158.2(m, 1F, *p*-F), -163.5 (m), -163.8 (br) (each 1F, *m*-F) (C_6F_5). [Cp^A is in a cis position to 3-$SiMe_3$].

Elemental analysis: $C_{36}H_{36}NBF_{10}Si_2Zr\cdot{}^1/_4C_7H_8$, calc.: C = 53.10%, H = 4.49%, N = 1.64%; measured: C = 52.66%, H = 4.61%, N = 1.70%.

FT-IR (KBr, cm^{-1}, selected bands): 3688, 3477, 2956, 1909, 1647, 1517, 1472, 1392, 1304, 1287, 1248, 1127, 1094, 1037.

MS (GC-EI, *m/z*): 829.3 [M], 750.2 [M – $C_5H_4(CH_3)$], 248.1 [$Zr(C_5H_4(CH_3))_2$].

Generation of complex 5b.

Complex **3a** (50.7 mg, 0.064 mmol) and 2,2'-dimethylpropionitrile (5.3 mg, 0.064 mmol) were mixed in a small phial in an argon-filled glove-box, and dissolved by 0.8 mL C_6D_6. The dark-red clear solution was placed into a NMR tube, which was then sealed under vacuum and measured.

^{1}H NMR (C_6D_6, 500 MHz, 298 K, TMS): δ 5.70(β'), 5.67(α), 5.54(β), 5.48(α') (each m, each 1H, Cp^A), 5.31(α), 5.15(β), 5.02(β'), 4.71(α') (each m, each 1H, Cp^B), 3.51 (s, 1H, 2-H), 1.76 (s, 3H, CH_3^A), 1.63 (s, 3H, CH_3^B), 1.23 (s, 9H, $C(CH_3)_3$), 0.36 (s, 9H, 5-$Si(CH_3)_3$), 0.05 (s, 9H, 3-$Si(CH_3)_3$) ^{13}C{^{1}H} NMR (C_6D_6, 126 MHz, 298 K, TMS): δ 196.8 (C1), 149.0 ($^1J_{FC}$ = 245 Hz), 148.6 ($^1J_{CF}$ = 243 Hz), 140.0 ($^1J_{FC}$ = 250 Hz), 137.6 ($^1J_{FC}$ = 250 Hz) (each dm, C_6F_5), 147.4 (C4), 123.7(i), 114.0(β'), 113.9(α'), 111.1(α), 108.8(β) (Cp^B), 123.4(i), 113.7(β'), 112.5(α), 111.9(α'), 110.0(β) (Cp^A), 115.4 (C5), 63.5 (br., C2), 38.6 (*C*$(CH_3)_3$), 29.5 (d J = 2.0 Hz, $C(CH_3)_3$), 23.6 (br., C3), 15.1 (CH_3^A), 15.0 (CH_3^B), 3.0 (d J = 2.7 Hz, 5-$Si(CH_3)_3$), 0.5 (3-$Si(CH_3)_3$), n.o. ($C_6F_5^i$). ^{13}C,^{1}H GHSQC (C_6D_6, 126 / 500 MHz, 298 K, TMS): δ ^{13}C / ^{1}H 113.7 / 5.70 ($Cp^{\beta,A}$), 112.5 / 5.67 ($Cp^{\alpha,A}$), 110.0 / 5.54 ($Cp^{\beta,A}$), 111.9 / 5.48 ($Cp^{\alpha,A}$), 114.0 / 5.02 ($Cp^{\beta,B}$), 113.9 / 4.71 ($Cp^{\alpha,B}$), 111.1 / 5.31 ($Cp^{\alpha,B}$), 108.8 / 5.15 ($Cp^{\beta,B}$), 63.5 / 3.51 (C2), 15.1 / 1.76 (CH_3^A), 15.0 / 1.63 (CH_3^B), 29.5 / 1.23 ($C(CH_3)_3$), 3.0 / 0.36 (5-$Si(CH_3)_3$), 0.5 / 0.05 (3-$Si(CH_3)_3$). ^{1}H,^{13}C GHMBC (C_6D_6, 500 / 126 MHz, 298 K, TMS): δ ^{1}H / ^{13}C 5.70 / 123.4, 112.5 ($Cp^{\beta,A}$ / $Cp^{i,A}$, $Cp^{\alpha,A}$), 5.67 / 113.7 , 111.9 ($Cp^{\beta,A}$ / $Cp^{\beta,A}$, $Cp^{\alpha,A}$), 5.54 / 123.4, 111.9 ($Cp^{\beta,A}$ / $Cp^{i,A}$, $Cp^{\alpha,A}$), 5.48 / 112.5, 110.0 ($Cp^{\alpha,A}$ / $Cp^{\alpha,A}$, $Cp^{\beta,A}$), 5.31 / 113.9, 108.8 ($Cp^{\alpha,B}$ / $Cp^{\alpha,B}$, $Cp^{\beta,B}$), 5.15 / 123.7, 114.0, 111.1 ($Cp^{\beta,B}$ / $Cp^{i,B}$, $Cp^{\beta,B}$, $Cp^{\alpha,B}$), 5.02 / 123.7, 113.9, 111.1 ($Cp^{\beta,B}$ / $Cp^{i,B}$, $Cp^{\alpha,B}$, $Cp^{\alpha,B}$), 4.71 / 114.0, 111.1, 108.8 ($Cp^{\alpha,B}$ / $Cp^{\beta,B}$, $Cp^{\alpha,B}$, $Cp^{\beta,B}$), 3.51 / 147.4, 115.4, 38.6, 23.6 (2-H / C4, C5, *C*$(CH_3)_3$, C3), 1.76 / 123.4, 112.5, 111.9 (CH_3^A / $Cp^{i,A}$, $Cp^{\alpha,A}$, $Cp^{\alpha,A}$), 1.63 / 123.7, 113.9, 111.1 (CH_3^B / $Cp^{i,B}$, $Cp^{\alpha,B}$, $Cp^{\alpha,B}$), 1.23 / 196.8, 38.6 ($C(CH_3)_3$ / C1, *C*$(CH_3)_3$), 0.36 / 147.4, 115.4 (5-$Si(CH_3)_3$ / C4, C5), 0.05 / 23.6 (3-$Si(CH_3)_3$ / C3). ^{11}B{^{1}H} NMR (C_6D_6, 160 MHz, 298 K, $BF_3{\cdot}OEt_2$): δ -13.0 (s, $\nu_{1/2} \approx$ 35 Hz). ^{29}Si{^{1}H} NMR (C_6D_6, 99 MHz, 298 K, TMS): δ 3.3 (3-Si), -8.5 (5-Si). ^{29}Si,^{1}H GHMQC (C_7D_8, 99 / 500 MHz, 243 K, TMS): δ ^{29}Si / ^{1}H 3.3 / 3.51, 0.05 (3-Si / 2-H, 3-$Si(CH_3)_3$), -8.5 / 0.36 (5-Si / 5-$Si(CH_3)_3$). ^{19}F NMR (C_6D_6, 470 MHz, 298 K, $CFCl_3$): -123.4, -126.5 (each m, each 1F, *o*-F), -158.9 (m, 1F, *p*-F), -163.2, -164.1 (each m, each 1F, *m*-F) (C_6F_5), -128.9 (br, 2F, *o*-F), -158.8 (m, 1F, *p*-F), -164.1 (m, 2F, *m*-F) (C_6F_5). [Cp^A is in a cis position to 3-$SiMe_3$].

Optimized structure (TPSS-D/def2-TZVP)
of **5a** in cartesian coordinates (Bohr):

5.02836109668281	3.77520389294929	-2.61474073501246	c
6.05320333695463	2.09740684128607	-4.43523762730218	c
8.20113080228110	0.92605537502291	-3.31926823898264	c
8.55218709002271	1.95794480658783	-0.85265724935881	c
6.58162438714389	3.71303320665889	-0.41970857620036	c
4.56455355195638	-0.59547930019604	-0.71033885108939	zr
3.46755320791492	-4.96385397743316	0.76058896199182	c
5.27814134257359	-5.29220201625862	-1.19893177720468	c
7.58627214652014	-4.23821634446912	-0.32307939818675	c
7.20903809009432	-3.29844912260445	2.17333039424027	c
4.65411940273846	-3.76180557334108	2.84126077171305	c
4.79160933582855	-6.53533997365291	-3.70147465102200	c
5.05400252661865	1.65429517725197	-7.04921615020480	c
0.06918003512398	1.18506789029199	0.78880674119626	c
1.90334690541940	1.37346439015664	2.29636291870449	c
2.99478445711557	2.56363795183303	5.38462880402690	si
2.81094119947683	6.12565705613310	5.31024432824268	c
1.71212869756157	-1.19063958158884	-3.11528672665650	n
-0.36497698729436	-0.96775458624725	-4.30079225486904	c
-0.71386151322497	-1.90247864796642	-6.98493455295625	c
-2.24855101925297	1.42145236784052	-0.50430091150146	c
-3.51884379259704	4.72640007193850	0.01894779503193	si
-6.45240609683593	5.25092041468410	-1.92742115608381	c
-2.57773938711964	0.20442351226671	-3.11810046913693	c
-4.06772839241972	-1.10870189422252	-0.81611089491833	b
-3.12292751834975	-3.71063480817123	0.41809992161859	c
-2.50227177031432	-3.99234417404422	2.96882169731734	c
-1.86311126923049	-6.30889080276086	4.05122273967884	c
-1.83408392415783	-8.47579423025137	2.55763760919197	c
-2.43689159490117	-8.29052308577914	-0.00092688972046	c
-3.06926930645436	-5.93638712550644	-0.99714672548696	c
-2.47721965731142	-1.97461167705643	4.52908050629398	f
-1.21535090863222	-6.46473798148806	6.51023319988116	f
-1.17601273578180	-10.71322151172077	3.55782808730535	f
-2.36946964339097	-10.36908650681990	-1.46855092610070	f
-3.65702087942645	-5.85700558343332	-3.49082563836806	f
-7.08730006103724	-0.75326487311492	-0.84783570811736	c
-8.47093515928836	-0.29674476783370	1.35182109520595	c
-11.05862492406628	0.17830676209519	1.38202711751823	c
-12.39151852580383	0.15432937450707	-0.89022691537661	c
-11.11312807505631	-0.36211873210111	-3.13273400820649	c
-8.51909311790735	-0.81818276700997	-3.06578864143932	c
-7.26533821244149	-0.25491032511991	3.60894702215324	f

-12.28328981330029	0.65786403588586	3.56089557825828	f
-14.89041216444610	0.59932699958665	-0.91345549428143	f
-12.39703932577158	-0.41653990124502	-5.32939740565050	f
-7.40531889511415	-1.32012379067037	-5.32059382065753	f
-4.16784837922583	5.14051432841341	3.48700495249063	c
-0.98595304730373	7.02478994681582	-0.99381199047733	c
6.36771075089018	1.60171419354998	6.01172059405419	c
0.91896582538596	1.28805033038334	7.96863192877660	c
-3.79725909220741	1.21509115138156	-4.42879297582517	h
-0.96737922679029	-0.27237113660247	-8.24269113780366	h
-2.42843619823268	-3.05304635531382	-7.09746709268868	h
0.92825472968963	-2.99109441537315	-7.59989639238616	h
-2.56333925239536	4.44275237956017	4.59978449120849	h
-5.83953818280460	4.07317208667668	4.07825537493739	h
-4.46198144352557	7.13764051894752	3.97030603153455	h
-0.56350575173316	6.83676246071163	-3.01785262773807	h
0.76217294365996	6.67717279153289	0.06616823085898	h
-1.55981728873004	8.98958917884615	-0.65048816422787	h
-6.92773535218333	7.27269597383517	-1.93536241646706	h
-8.07759923191966	4.21049008099507	-1.17723838336311	h
-6.18121836645051	4.66596670449048	-3.89921869006047	h
6.51156960135060	-0.40410834376427	6.50892616480416	h
7.11155984498506	2.69846712512565	7.61020478106346	h
7.59709041540471	1.94417691997725	4.37849758228445	h
-1.05779905128283	1.84001081630067	7.68537452428607	h
1.54323158459665	2.01462976230215	9.81152719853698	h
0.97588962804553	-0.78253650726799	8.03374494264681	h
4.03965907105464	6.95291438983197	3.85900301044083	h
3.39369282524544	6.90399693659236	7.14558869550318	h
0.87662653938924	6.76173606808869	4.92918436337608	h
9.33715585921336	-4.16237572728029	-1.37800201473882	h
8.61146513273003	-2.37133683296601	3.33404241875295	h
3.74242979716068	-3.23177978027429	4.59137824291977	h
1.50342493961670	-5.48122334263463	0.61697636697597	h
6.04632717147740	-5.78641618953941	-5.16824502442697	h
2.83330088560682	-6.22530238257142	-4.28680612181751	h
5.11620811732216	-8.58077630882106	-3.56538328770118	h
9.39262023143263	-0.47012025236996	-4.22213450657233	h
10.02668477709620	1.44168400615199	0.46725963649690	h
6.26995283909066	4.77317915229249	1.29785936080752	h
3.31443164385859	4.86636893943861	-2.83474730987974	h
3.01108653804122	1.95876147557463	-7.10581442515812	h
5.43955730856558	-0.27816671967886	-7.67888050436424	h
5.94589792277630	2.96358011177187	-8.39030872253782	h