Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION

p-tert-Butyltetrathiatetramercaptocalix[4]arene as a Sulfur-Rich Platform for Molybdenum, Tungsten and Nickel

Daniela Buccella and Gerard Parkin,*

Department of Chemistry,

Columbia University,

New York, New York 10027, USA.

EXPERIMENTAL SECTION

General Considerations

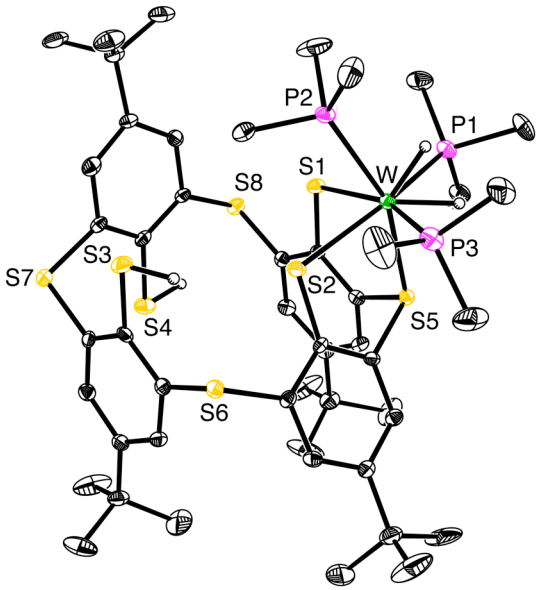
All manipulations were performed using a combination of dry glovebox, high vacuum, and Schlenk techniques under an argon atmosphere unless otherwise specified.[1] Solvents were purified and degassed by standard procedures. ^{1}H NMR spectra were measured on Bruker 300 DRX, Bruker 400 DRX, and Bruker Avance 500 DMX spectrometers. ^{1}H chemical shifts are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity (δ 7.16 for C_6D_5H).[2] ^{13}C NMR spectra are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the solvent (δ 128.06 for C_6D_6)[2]. ^{31}P chemical shifts are reported in ppm relative to 85% H_3PO_4 ($\delta = 0$) and were referenced using $P(OMe)_3$ ($\delta = 141.0$) as an external standard. Coupling constants are given in hertz. Infrared spectra were recorded on Nicolet Avatar 370 DTGS spectrometer and are reported in cm^{-1}. Mass spectra were obtained on a Micromass Quadrupole-Time-of-Flight mass spectrometer using fast atom bombardment (FAB). $Mo(PMe_3)_6$,[3] $W(PMe_3)_4(\eta^2\text{–}CH_2PMe_2)H$,[4] $Ni(PMe_3)_4$,[5] and [S_4Calix^{But}(SH)$_4$][6] were prepared by the literature methods or modifications thereof. [S_4Calix^{But}(SH)$_4$] was recrystallized from benzene prior use.

Synthesis of [S_4Calix^{But}(SH)$_2$(S)$_2$]W(PMe$_3$)$_3$H$_2$

A solution of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ (72 mg, 0.128 mmol) in benzene (5 mL) was added dropwise, over a period of 30 min, to a solution of [S_4Calix^{But}(SH)$_4$] (100 mg, 0.127 mmol) in benzene (10 mL). The resulting mixture was stirred for 30 min at room temperature. After this period, the solution was concentrated *in vacuo* (to *ca.* 2 mL) and then lyophilized. The solid obtained was dissolved in benzene (*ca*. 10 mL) and the solution was passed through a short column of silica gel (1″ diameter × 2″ height), washing with benzene until the eluate was colorless. The resulting solution was concentrated *in vacuo* (to *ca.* 2 mL) and then lyophilized to give [S_4Calix^{But}(SH)$_2$(S)$_2$]W(PMe$_3$)$_3$H$_2$ as a yellow powder (105 mg, 69 %). X-Ray quality

crystals of [S_4Calix^{But}(SH)$_2$(S)$_2$]W(PMe$_3$)$_3$H$_2$ were obtained by slow evaporation of a solution of the compound in benzene.

^{1}H NMR data (C_6D_6): 7.78 [s, 2 aromatic H of [S_4Calix^{But}(SH)$_2$(S)$_2$]], 7.68 [overlapping s, 2 aromatic H of [S_4Calix^{But}(SH)$_2$(S)$_2$]], 7.68 [d, $^4J_{HH}$ = 2, 2 aromatic H of [S_4Calix^{But}(SH)$_2$(S)$_2$]], 7.65 [d, $^4J_{HH}$ = 2, 2 aromatic H of [S_4Calix^{But}(SH)$_2$(S)$_2$]], 6.41 [s, 2 H of [S_4Calix^{But}(S<u>H</u>)$_2$(S)$_2$]], 1.44 [d, $^2J_{HP}$ = 8, 9 H of W(P<u>Me</u>$_3$)$_3$], 1.22 [m, 18 H of W(P<u>Me</u>$_3$)$_3$], 1.20 [s, 18 H of 2 Bu^t of [S_4Calix^{But}(SH)$_2$(S)$_2$]], 1.11 [s, 18 H of 2 Bu^t of [S_4Calix^{But}(SH)$_2$(S)$_2$]], -3.2 to -3.8 [m, 2 WH]. ^{31}P NMR (C_6D_6): -23.76 [broad m, 1 P of W(PMe$_3$)$_3$], -31.46 [d, $^2J_{PP}$= 17 $^1J_{PW}$= 146, 2 P of W(PMe$_3$)$_3$]. ^{13}C{^{1}H} NMR (C_6D_6): 146.5 [s, 2 aromatic C of [(S_4Calix^{But}(SH)$_2$(S)$_2$]], 145.4 [s, 2 aromatic C of [(S_4Calix^{But}(SH)$_2$(S)$_2$]], 136.3 [s, 2 aromatic C of [(S_4Calix^{But}(SH)$_2$(S)$_2$]], 135.7 [s, 2 aromatic C of [(S_4Calix^{But}(SH)$_2$(S)$_2$]], 133.8 [s, 2 aromatic C of [(S_4Calix^{But}(SH)$_2$(S)$_2$]], 133.2 [s, 2 aromatic C of [(S_4Calix^{But}(SH)$_2$(S)$_2$]], 132.5 [s, 2 aromatic C of [(S_4Calix^{But}(SH)$_2$(S)$_2$]], 132.1 [s, 2 aromatic C of [(S_4Calix^{But}(SH)$_2$(S)$_2$]], 129.0 [broad, overlapping solvent, remaining aromatic C of [(S_4Calix^{But}(SH)$_2$(S)$_2$]], 34.3 [s, 2 <u>C</u>(CH$_3$)$_3$ of [(S_4Calix^{But}(SH)$_2$(S)$_2$]], 34.2 [s, 2 <u>C</u>(CH$_3$)$_3$ of [(S_4Calix^{But}(SH)$_2$(S)$_2$]], 31.5 [s, 6 C(<u>C</u>H$_3$)$_3$ of [(S_4Calix^{But}(SH)$_2$(S)$_2$]], 31.3 [s, 6 C(<u>C</u>H$_3$)$_3$ of [(S_4Calix^{But}(SH)$_2$(S)$_2$]], 24.5 [m, 6 C of P(<u>C</u>H$_3$)$_3$], 24.5 [d, $^2J_{CP}$= 14, 3 C of P(<u>C</u>H$_3$)$_3$]. Mass Spectrum (FAB+): m/z = 1195.53 {M-1}. Anal. Calcd. For [S_4Calix^{But}(SH)$_2$(S)$_2$]W(PMe$_3$)$_3$H$_2$•0.5(C_6H_6): C, 50.5 %, H, 6.4 %. Found: C, 50.2 %, H, 6.1 %.



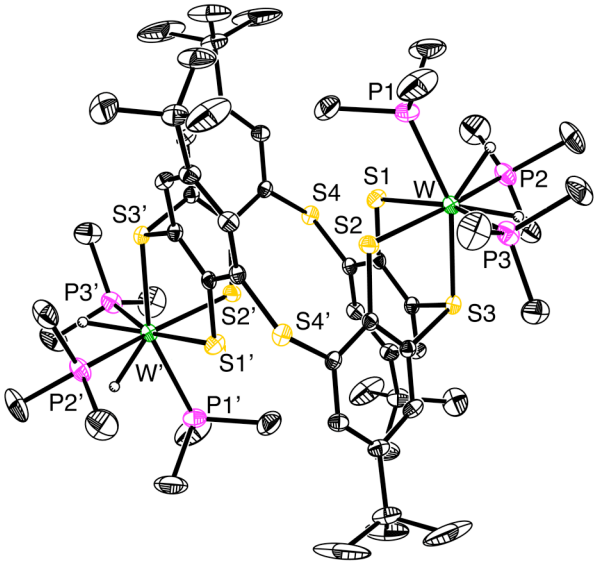
Molecular structure of [S_4Calix^{But}(SH)$_2$(S)$_2$]W(PMe$_3$)$_3$H$_2$

(20 % thermal parameters)

Synthesis of *syn*- and *anti*-{[S_4Calix^{But}(S)$_4$]}[W(PMe$_3$)$_3$H$_2$]$_2$

W(PMe$_3$)$_4$(η^2-CH$_2$PMe$_2$)H (44 mg, 0.078 mmol) was added to a solution of [S_4Calix^{But}(SH)$_4$] (30 mg, 0.038 mmol) in benzene (2 mL). The mixture was stirred for 20 min and then allowed to stand at room temperature for 18 h. After this period, yellow-orange crystals of pure *anti*-{[S_4Calix^{But}(S)$_4$]}[W(PMe$_3$)$_3$H$_2$]$_2$ (22 mg, 36 %) were collected from the reaction mixture by filtration. The filtrate was lyophilized and the residue obtained was washed with cold pentane (2 × 1 mL) and dried *in vacuo* to give *syn*-{[S_4Calix^{But}(S)$_4$]}[W(PMe$_3$)$_3$H$_2$]$_2$ as a yellow powder (24 mg, 39 %). X-ray quality crystals of *anti*-{[S_4Calix^{But}(S)$_4$]}[W(PMe$_3$)$_3$H$_2$]$_2$ were obtained directly from the reaction mixture, while X-ray quality crystals of *syn*-{[S_4Calix^{But}(S)$_4$]}[W(PMe$_3$)$_3$H$_2$]$_2$ were obtained by slow evaporation of a solution of the compound in benzene. Monitoring the reaction by ^{1}H NMR spectroscopy indicates that the *syn* and *anti* isomers of {[S$_4$Calix^{But}(S)$_4$]}[W(PMe$_3$)$_3$H$_2$]$_2$ are formed in a *ca.* 1:1 ratio.

Characterization of anti-{[$S_4Calix^{But}(S)_4$]}[$W(PMe_3)_3H_2$]$_2$: ^{1}H NMR data (C_6D_6): 7.82 [m, 8 aromatic H of [$S_4Calix^{But}(S)_4$]], 1.37 [s, 36 H of 4 Bu^t of [$S_4Calix^{But}(S)_4$]], 1.30 [m, 36 H of W(P<u>Me</u>$_3$)], 1.20 [d, $^2J_{HP}$ = 8 , 18 H of W(P<u>Me</u>$_3$)], -3.0 to -4.0 [m, 4 WH]. $^{31}P\{^1H\}$ NMR (C_6D_6): -20.60 [t, $^2J_{PP}$ = 20, $^1J_{PW}$ = 234, 2 P of $W(PMe_3)_3$], -33.26 [d, $^2J_{PP}$ = 20, $^1J_{PW}$ = 163, 4 P of $W(PMe_3)_3$]. IR (KBr disc, cm^{-1}): 2963 (s), 2903 (s), 2868 (m), 2804 (w), 1848 (m), 1572 (w), 1504 (w), 1477 (m), 1462 (w), 1421 (m), 1400 (s), 1375 (m), 1360 (w), 1295 (m), 1276 (s), 1260 (s), 1199 (w), 1184 (w), 1147 (m), 1040 (m), 960 (s), 943 (s), 884 (w), 873 (w), 856 (m), 790 (w), 783 (w), 714 (s), 677 (s), 666 (s), 626 (w), 609 (w). Anal. Calcd. For [$S_4Calix^{But}(S)_4$][$W(PMe_3)_3H_2$]$_2$: C, 43.3 %, H, 6.4 %. Found: C, 43.3 %, H, 6.3 %.

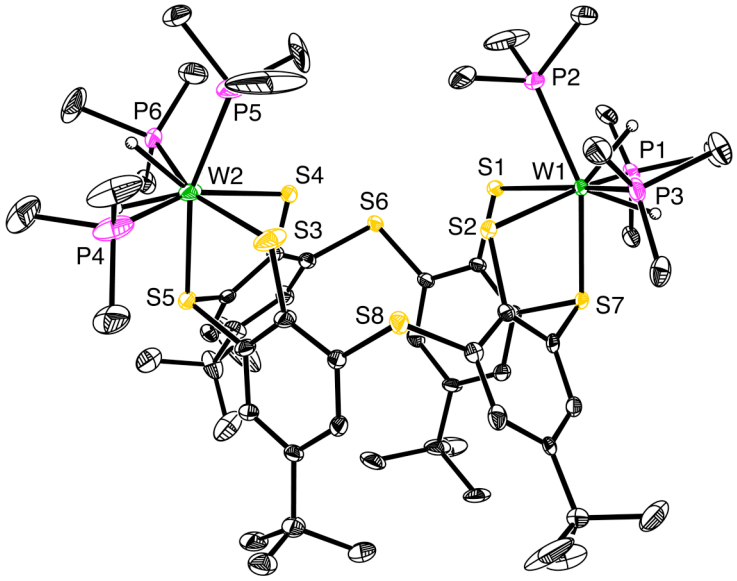


Molecular structure of anti-{[$S_4Calix^{But}(S)_4$]}[$W(PMe_3)_3H_2$]$_2$. The molecule exhibits crystallographic inversion symmetry.

(20 % thermal parameters)

Characterization of syn-{[$S_4Calix^{But}(S)_4$]}[$W(PMe_3)_3H_2$]$_2$: ^{1}H NMR data (C_6D_6): 7.54 [d, $^4J_{HH}$ = 2, 4 aromatic H of [$S_4Calix^{But}(S)_4$]], 7.45 [d, $^4J_{HH}$ = 2, 4 aromatic H of [$S_4Calix^{But}(S)_4$]], 1.73 [d, $^2J_{HP}$ = 8 , 18 H of $W(PMe_3)_3$], 1.29 [m, 36 H of $W(PMe_3)_3$], 1.22 [s, 36 H of 4 Bu^t of [$S_4Calix^{But}(S)_4$]], -3.1 to -3.9 [m, 4 WH]. $^{31}P\{^1H\}$ NMR (C_6D_6): -26.50 [t, $^2J_{PP}$= 14, $^1J_{PW}$= 235, 2 P of $W(PMe_3)_3$], -33.18 [d, $^2J_{PP}$= 14, $^1J_{PW}$= 148, 4 P of $W(PMe_3)_3$]. $^{13}C\{^1H\}$ NMR (C_6D_6):

157.2 [d, $^{3}J_{CP}$ = 10, 4 aromatic C of [S_4Calix^{But}(S)$_4$]], 143.4 [s, 4 aromatic C of [S_4Calix^{But}(S)$_4$]], 142.7 [s, 4 aromatic C of [S_4Calix^{But}(S)$_4$]], 138.9 [s, 4 aromatic C of [S_4Calix^{But}(S)$_4$]], 132.1 [s, 4 aromatic C of [S_4Calix^{But}(S)$_4$]], 34.1 [s, 4 $\underline{C}(CH_3)_3$ of [S_4Calix^{But}(S)$_4$]], 31.8 [s, 12 C($\underline{C}H_3)_3$ of [S_4Calix^{But}(S)$_4$]], 24.8 [m, 18 C of P($\underline{C}H_3)_3$], one aromatic signal obscured by solvent. IR (KBr disc, cm^{-1}): 2963 (s), 2904 (s), 2868 (m), 2801 (w), 1913 (w), 1856 (m), 1574 (w), 1477 (m), 1462 (w), 1421 (m), 1401 (m), 1374 (m), 1360 (w), 1295 (m), 1279 (m), 1259 (s), 1191 (w), 1148 (w), 1139 (w), 1042 (m), 962 (s), 942 (s), 880 (w), 853 (m), 782 (w), 712 (s), 667 (s).



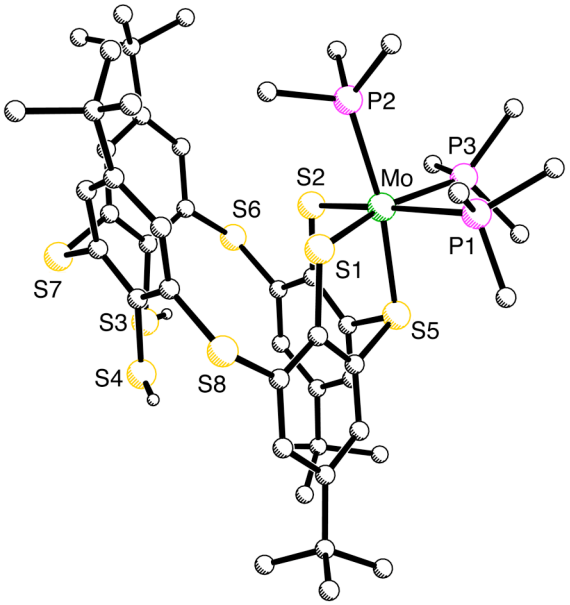
Molecular structure of syn-{[S_4Calix^{But}(S)$_4$]}[W(PMe$_3$)$_3$H$_2$]$_2$

(30 % thermal parameters)

Synthesis of [S_4Calix^{But}(SH)$_2$(S)$_2$]Mo(PMe$_3$)$_3$

A mixture of Mo(PMe$_3$)$_6$ (70 mg, 0.127 mmol) and [S_4Calix^{But}(SH)$_4$] (100 mg, 0.127 mmol) was treated with benzene (5 mL) and stirred at room temperature for 18 h. The solution was then degassed by a freeze-pump-thaw cycle, and stirring was continued at room temperature. The procedure was repeated periodically until no more hydrogen evolution was detected (after approx. 36 h). After this period, the volatile components were removed by lyophilization, and the resulting solid was washed with cold pentane

(2 × 1 mL) and dried *in vacuo* to give [S_4Calix^{But}(SH)$_2$(S)$_2$]Mo(PMe$_3$)$_3$ as a purple solid (103 mg, 73 %). Crystals of [S_4Calix^{But}(SH)$_2$(S)$_2$]Mo(PMe$_3$)$_3$ suitable for X-ray diffraction analysis were obtained from hexane at –20°C. ^{1}H NMR data (C_6D_6): 8.16 [s, 2 aromatic H of [S_4Calix^{But}(SH)$_2$(S)$_2$]], 7.90 [s, 4 aromatic H of [S_4Calix^{But}(SH)$_2$(S)$_2$]], 7.70 [s, 2 aromatic H of [S_4Calix^{But}(SH)$_2$(S)$_2$]], 1.36 [broad d, $^2J_{HP}$ = 5, 9 H of Mo(P<u>Me</u>$_3$)], 1.24 [s, 18 H of 2 Bu^t [S_4Calix^{But}(SH)$_2$(S)$_2$]], 1.14 [s, 18 H of 2 Bu^t [S_4Calix^{But}(SH)$_2$(S)$_2$]], 0.99 [m, 18 H of Mo(P<u>Me</u>$_3$)]. ^{31}P{^{1}H} NMR (C_6D_6): -24.7 [broad s, 3 P of Mo(PMe$_3$)$_3$]. ^{13}C{^{1}H} NMR (C_6D_6): 147.2 [s, 2 aromatic C of [(S_4Calix^{But}(SH)$_2$(S)$_2$]], 147.1 [s, 2 aromatic C of [(S_4Calix^{But}(SH)$_2$(S)$_2$]], 135.6 [s, 2 aromatic C of [(S_4Calix^{But}(SH)$_2$(S)$_2$]], 135.1 [s, 2 aromatic C of [(S_4Calix^{But}(SH)$_2$(S)$_2$]], 134.6 [s, 2 aromatic C of [(S_4Calix^{But}(SH)$_2$(S)$_2$]], 133.5 [s, 2 aromatic C of [(S_4Calix^{But}(SH)$_2$(S)$_2$]], 132.7 [s, 2 aromatic C of [(S_4Calix^{But}(SH)$_2$(S)$_2$]], 129.1 [s, 2 aromatic C of [(S_4Calix^{But}(SH)$_2$(S)$_2$]], 34.4 [s, 2 <u>C</u>(CH$_3$)$_3$ of [(S_4Calix^{But}(SH)$_2$(S)$_2$]], 34.3 [s, 2 <u>C</u>(CH$_3$)$_3$ of [(S_4Calix^{But}(SH)$_2$(S)$_2$]], 31.5 [overlapping m, 9 C of P(<u>C</u>H$_3$)$_3$], 31.5 [s, 6 C(<u>C</u>H$_3$)$_3$ of [(S_4Calix^{But}(SH)$_2$(S)$_2$]], 31.3 [s, 6 C(<u>C</u>H$_3$)$_3$ of [(S_4Calix^{But}(SH)$_2$(S)$_2$]], four aromatic signals not observed.



Molecular structure of [S_4Calix^{But}(SH)$_2$(S)$_2$]Mo(PMe$_3$)$_3$

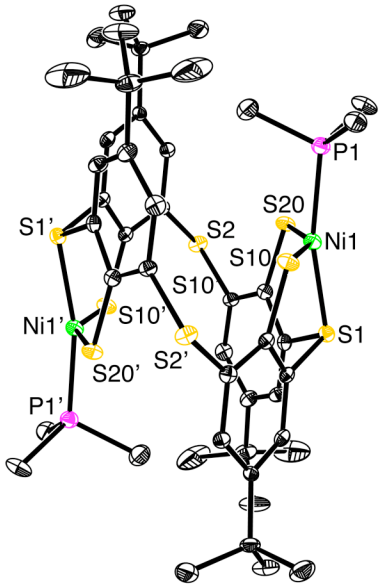
Determination of the equilibrium constant for oxidative addition of H_2 to $[S_4Calix^{But}(SH)_2(S)_2]Mo(PMe_3)_3$.

A solution of $[S_4Calix^{But}(SH)_2(S)_2]Mo(PMe_3)_3$ (10 mg, 0.009 mmol) in C_6D_6 (600 μL) in an NMR tube equipped with a J.Young valve was degassed and treated with H_2 (1 atm). The mixture was allowed to stand at room temperature and was monitored by ^1H NMR spectroscopy, thereby indicating that equilibration with $[S_4Calix^{But}(SH)_2(S)_2]Mo(PMe_3)_3H_2$ was attained over a period of 3 days. The ratio of the $[S_4Calix^{But}(SH)_2(S)_2]Mo(PMe_3)_3H_2$ and $[S_4Calix^{But}(SH)_2(S)_2]Mo(PMe_3)_3$ in solution was established by integration of the aromatic signals in the ^1H NMR spectrum. The equilibrium constant, 1.1×10^3 M^{-1} was calculated using a concentration of H_2 in benzene of 2.914×10^{-3} M.[7] ^1H NMR data for $[S_4Calix^{But}(SH)_2(S)_2]Mo(PMe_3)_3H_2$ (C_6D_6): 7.75 [s, 2 aromatic H of $[S_4Calix^{But}(SH)_2(S)_2]$], 7.68 [d, $^4J_{HH}$ = 2, 2 aromatic H of $[S_4Calix^{But}(SH)_2(S)_2]$], 7.65 [overlapping s, 2 aromatic H of $[S_4Calix^{But}(SH)_2(S)_2]$], 7.65 [d, $^4J_{HH}$ = 2, 2 aromatic H of $[S_4Calix^{But}(SH)_2(S)_2]$], 6.59 [s, 2 H of $[S_4Calix^{But}(\underline{S}H)_2(S)_2]$], 1.29 [d, $^2J_{HP}$ = 7, 9 H of Mo(P$\underline{Me}_3$)], 1.19 [s, 18 H of 2 Bu^t of $[S_4Calix^{But}(SH)_2(S)_2]$], 1.10 [s, 18 H of 2 Bu^t of $[S_4Calix^{But}(SH)_2(S)_2]$], 1.08 [m, 18 H of Mo(P$\underline{Me}_3$)], -3.7 to -6.2 [very broad m, 2 MoH]. ^{31}P NMR (C_6D_6): 3.56 [broad m, 1 P of $Mo(PMe_3)_3$], 1.42 [d, $^2J_{PP}$= 24, 2 P of $Mo(PMe_3)_3$].

Synthesis of $[S_4Calix^{But}(S)_4][Ni(PMe_3)]_2$

A solution of $Ni(PMe_3)_4$ (71 mg, 0.196 mmol) in benzene (3 mL) was added to a solution of $[S_4Calix^{But}(SH)_4]$ (75 mg, 0.096 mmol) in benzene (8 mL). The resulting solution was stirred for 20 min, and then allowed to stand at room temperature for 12 h. After this period the mixture was concentrated *in vacuo* to half the volume. The solid was collected by filtration, washed with pentane (2×3 mL) and dried *in vacuo,* to give $[S_4Calix^{But}(S)_4][Ni(PMe_3)]_2$ as red crystals (72 mg, 71 %). X-Ray quality crystals of $[S_4Calix^{But}(S)_4][Ni(PMe_3)]_2$ were obtained by slow cooling of a solution in hot benzene. ^1H NMR data (C_6D_6): 7.85 [d, $^4J_{HH}$ = 1.8, 2 aromatic H of $[S_4Calix^{But}(S)_4]$], 7.42 [broad s, 2

aromatic H of [$S_4Calix^{But}(S)_4$]], 1.17 [s, 36 H of 4 Bu^t of [$S_4Calix^{But}(S)_4$]], 0.70 [d, $^2J_{HP}$ = 11, 18 H of 2 of Ni(P<u>Me</u>$_3$)]. $^{31}P\{^1H\}$ NMR (C_6D_6): -6.95 [s, 2 P of Ni(PMe_3)]. Mass Spectrum (FAB+): m/z = 1050.4 {M}. IR (KBr disc, cm^{-1}): 2961 (s), 2904 (m), 2868 (m), 1572 (m), 1504 (w), 1477 (m), 1463 (m), 1401 (s), 1377 (m), 1361 (m), 1304 (w), 1284 (m), 1258 (s), 1190 (w), 1147 (m), 1059 (w), 1038 (m), 955 (s), 882 (m), 871 (m), 851 (w), 787 (w), 749 (w), 740 (w), 710 (m), 679 (m), 657 (w), 626 (w), 561 (m), 512 (w), 501 (m), 471 (w). Anal. Calcd. For [$S_4Calix^{But}(S)_4$][Ni(PMe_3)$_2$]•(C_6H_6): C, 55.32 %, H, 6.07 %. Found: C, 55.32 %, H, 6.14 %.



Molecular structure of [$S_4Calix^{Bu^t}(S)_2$][Ni(PMe_3)]$_2$. The molecule exhibits crystallographic inversion symmetry.

(20 % thermal parameters)

X-ray structure determinations

X-ray diffraction data were collected on either a Bruker Apex II diffractometer or a Bruker P4 diffractometer equipped with a SMART CCD detector. Crystal data, data collection and refinement parameters are summarized in Table 1. The structures were

solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 6.1).[8]

Table 1. Crystal, intensity collection and refinement data.

	[(S_4Calix$^{Bu^t}$(SH)$_2$(S)$_2$]–W(PMe$_3$)$_3$H$_2$·(C_6H_6)	***anti*–[(S_4Calix$^{Bu^t}$(S)$_4$]–[W(PMe$_3$)$_3$H$_2$]$_2$·2(C_6H_6)**
lattice	Triclinic	Triclinic
formula	$C_{55}H_{81}P_3S_8W$	$C_{70}H_{114}P_6S_8W_2$
formula weight	1275.44	1765.61
space group	*P–1*	*P–1*
a / Å	14.3750(6)	12.5194(9)
b / Å	14.9573(7)	12.5419(9)
c / Å	15.3607(8)	15.1273(10)
α / °	89.2720(10)	67.232(2)
β / °	75.8420(10)	77.1440(10)
γ / °	76.8000(10)	79.1250(10)
V / Å^3	3114.5(3)	2121.3(3)
Z	2	1
temperature (K)	243	243
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.360	1.382
μ (Mo Kα), mm^{-1}	2.233	3.054
θ max, deg.	28.28	28.27
no. of data	14001	9434
no. of parameters	636	412
R_1 [$I > 2\sigma(I)$]	0.0507	0.0432
wR_2 [$I > 2\sigma(I)$]	0.0650	0.0797
GOF	1.031	1.032

Table 1. Crystal, intensity collection and refinement data (continued)

	***syn*–[(S_4Calix^{But}(S)$_4$]–[W(PMe$_3$)$_3$H$_2$]$_2$·(C_6H_6)**	**[(S_4Calix^{But}(S)$_4$]–[Ni(PMe$_3$)]$_2$·2(C_6H_6)**
lattice	Monoclinic	Triclinic
formula	$C_{64}H_{108}P_6S_8W_2$	$C_{58}H_{74}Ni_2P_2S_8$
formula weight	1687.50	1207.01
space group	$P2_1/n$	$P\text{–}1$
a / Å	16.5666(18)	12.0009(7)
b / Å	19.595(2)	16.9077(11)
c / Å	23.604(3)	17.2253(12)
α / °	90.00	107.1050(10)
β / °	96.152(2)	103.4440(10)
γ / °	90.00	103.6220(10)
V / Å^3	7618.4(15)	3070.5(3)
Z	4	2
temperature (K)	125	243
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.471	1.306
μ (Mo Kα), mm^{-1}	3.398	0.972
θ max, deg.	26.37	25.03
no. of data	15575	10181
no. of parameters	733	632
R_1 [$I > 2\sigma(I)$]	0.0730	0.0650
wR_2 [$I > 2\sigma(I)$]	0.1667	0.1020
GOF	1.164	1.046

Computational Details

Calculations were carried out using DFT as implemented in the Jaguar 7.0 suite of *ab initio* quantum chemistry programs.[9] Geometry optimizations were performed with the B3LYP density functional[10] using the 6–31G** (C, H, P and S) and LACVP (Mo) basis sets.[11] The energies of the optimized structures were reevaluated by additional single point calculations on each optimized geometry using cc–pVTZ(–f) correlation consistent triple–ζ basis set for C, H, P, S and LACV3P for Mo (Table 2).

Table 2. Cartesian Coordinates for Geometry Optimized Structures

$[(S_4Calix^H(SH)_2(S)_2]Mo(PMe_3)_3H_2$
-5561.37570552486 Hartrees

atom	x	y	z
Mo1	-1.3593496667	1.4175339904	3.5579425472
P2	-2.9350699754	0.1948242293	5.1081176802
P3	-2.8789219908	3.3229216213	2.8298483716
P4	0.4766900169	2.9899083219	4.3191930078
S5	-2.8765743503	0.1089236182	1.9653939751
S6	-0.0494808056	1.9209236965	1.3525266954
S7	-0.5660108733	3.1396390790	-2.1668248103
S8	-2.1070780465	-1.7824669006	-2.8882039141
S9	0.0525993445	-0.6560125538	3.3024392764
S10	2.4099777940	2.2805528748	-0.8596611598
S11	-1.8878225079	1.1458283290	-4.3688231666
S12	-4.1646234848	-2.0238234831	-0.2345929464
C13	-2.0321026283	-1.3764441141	1.5483502242
C14	-2.5949645633	-2.2968088007	0.6163471608
C15	-2.0056489451	-3.5456843981	0.4032030885
C16	-0.8511568949	-3.9321963464	1.0833441865
C17	-0.2567906032	-3.0315917460	1.9606461305
C18	-0.8233860878	-1.7702767741	2.1651422885
C19	1.3419794497	0.8491355938	1.3422274774

C20	1.4577094713	-0.2257163802	2.2527823595
C21	2.6172106711	-0.9922717692	2.3640949258
C22	3.7049582972	-0.7400112989	1.5308867420
C23	3.5942835122	0.2618187390	0.5673464032
C24	2.4329052850	1.0313644716	0.4446567765
C25	0.3324347288	1.7035849873	-2.7011001751
C26	1.6177691467	1.3676040595	-2.2085687785
C27	2.3405811387	0.3232399787	-2.7964935222
C28	1.8082619023	-0.4259122120	-3.8404313010
C29	0.5139225196	-0.1554614872	-4.2755986614
C30	-0.2315404932	0.8808883003	-3.7066813318
C31	-3.0813753683	-0.4121858720	-2.3140192278
C32	-3.9755811154	-0.5270902766	-1.2206924511
C33	-4.8637197406	0.5153748123	-0.9329883704
C34	-4.8491076595	1.6955400091	-1.6708674109
C35	-3.8864272445	1.8632965877	-2.6627986974
C36	-3.0006993338	0.8306694508	-2.9870505122
C37	-2.7479089025	-1.6463101016	5.1748259152
C38	-2.7536070799	0.6057933577	6.9090728086
C39	-4.7728529196	0.3550238103	4.9292186247
C40	-4.6314102228	2.9515902159	2.3495832364
C41	-2.3738588203	4.2890852758	1.3314391706
C42	-3.1709239462	4.6768273089	4.0630450650
C43	2.2090563568	2.3354011564	4.3829748442
C44	0.7769711108	4.6078136204	3.4598533101
C45	0.2998823309	3.5804968201	6.0708169646
H46	-1.8975553638	2.3706265994	4.8470636029
H47	-0.6870908430	1.0790469711	5.0767721453
H48	0.2415857472	3.3747703275	-1.1092511368
H49	-2.8234459522	-2.6945738138	-2.1964113761
H50	-2.4694746765	-4.2272188670	-0.3040780074
H51	-0.4123010632	-4.9101652668	0.9126708443
H52	0.6574284063	-3.2980336265	2.4818523006
H53	2.6650044460	-1.7824376649	3.1078932739

H54	4.6182719421	-1.3200694043	1.6212927307
H55	4.4239215573	0.4666432091	-0.1026075243
H56	3.3355923014	0.1045137293	-2.4233546665
H57	2.3849104802	-1.2268077137	-4.2925920777
H58	0.0557297552	-0.7577226565	-5.0530891802
H59	-5.5574155129	0.3877437769	-0.1084854093
H60	-5.5485780493	2.4947201970	-1.4439643717
H61	-3.8079009696	2.8017000325	-3.2023750011
H62	-1.7231522269	-1.8991609252	5.4611811237
H63	-2.9512756988	-2.0730723196	4.1908450378
H64	-3.4382609310	-2.0797127066	5.9059618461
H65	-1.7290251462	0.3969413181	7.2278457384
H66	-3.4466953984	0.0216572863	7.5233738599
H67	-2.9473389133	1.6707649469	7.0632162112
H68	-5.0752432317	1.3815918488	5.1553881511
H69	-5.2863380069	-0.3199382684	5.6219270909
H70	-5.0599112506	0.1097278766	3.9050451803
H71	-5.1391165695	3.8730450543	2.0454790443
H72	-5.1743759157	2.5037773817	3.1832949756
H73	-4.6329802253	2.2475690861	1.5148511298
H74	-1.3765778448	4.7122332682	1.4637415122
H75	-3.0878716046	5.0975306077	1.1413405275
H76	-2.3464536788	3.6208764941	0.4663694659
H77	-2.2229673139	5.1182838641	4.3791245273
H78	-3.6613585109	4.2599619361	4.9471537288
H79	-3.8046283636	5.4630706865	3.6396568442
H80	2.8751058772	3.0688489694	4.8495333335
H81	2.5668750545	2.1185782493	3.3756697482
H82	2.2314912831	1.4104767999	4.9650761961
H83	1.6276065448	5.1282873151	3.9123249329
H84	-0.1038009326	5.2507316375	3.5362217299
H85	0.9844503142	4.4176725655	2.4052141235
H86	1.1302901945	4.2340900569	6.3575183895
H87	0.2744287167	2.7176529748	6.7413477756

H88	-0.6408319101	4.1254057408	6.1862208876

[(S_4Calix^H(SH)$_2$(S)$_2$]Mo(PMe$_3$)$_3$ singlet state
-5560.18421026200 Hartrees

atom	x	y	z
Mo1	-1.3382591748	1.4406334778	3.1589391848
P2	-2.7814882916	0.5770663199	5.1912633208
P3	-2.7939969379	3.3820885365	2.8261929661
P4	0.2769183167	2.7617265671	4.7467734867
S5	-2.8316407912	0.0584681141	1.9352341887
S6	0.1019225796	2.1701875523	1.4216361174
S7	-0.7280654995	3.0768535814	-2.2055450236
S8	-2.0471172466	-1.9031858627	-2.7725568032
S9	0.1146119165	-0.5468142443	3.1934113753
S10	2.3623671861	2.4088810608	-1.0036320553
S11	-2.0146195172	0.9823772071	-4.3149696077
S12	-4.1432503630	-2.2338584087	-0.1367658003
C13	-1.9929791080	-1.4881865360	1.5883868283
C14	-2.5715491373	-2.4527135708	0.7274273395
C15	-1.9642882396	-3.7048817432	0.5660997070
C16	-0.7807196204	-4.0221849005	1.2265530704
C17	-0.1650132682	-3.0580040566	2.0211024160
C18	-0.7499408384	-1.8006884124	2.1683263679
C19	1.4321174392	0.9786980050	1.2515683604
C20	1.5147315698	-0.1484336112	2.0866982473
C21	2.6458223184	-0.9644248710	2.1055446038
C22	3.7089962587	-0.7035798600	1.2418781257
C23	3.6033686924	0.3457854896	0.3317493791
C24	2.4660284604	1.1611707408	0.3036242173
C25	0.2344036482	1.6835345640	-2.7415526623
C26	1.5584213370	1.4319842046	-2.3016582613
C27	2.3067534852	0.4100529313	-2.8977911478
C28	1.7637454859	-0.4022329176	-3.8866314253
C29	0.4394446089	-0.2135724332	-4.2686682354

C30	-0.3305025658	0.8042486950	-3.6988093210
C31	-3.1043443165	-0.5902524521	-2.2187909951
C32	-3.9913204622	-0.7352115654	-1.1244566765
C33	-4.9170084083	0.2763043764	-0.8386171729
C34	-4.9491064405	1.4521174895	-1.5802968245
C35	-4.0049853412	1.6481459979	-2.5839178141
C36	-3.0840018382	0.6468950334	-2.9073469824
C37	-2.5745287041	-1.2427188192	5.5025666159
C38	-2.6938152229	1.1842628562	6.9490269438
C39	-4.6220368807	0.6651037790	4.9591566474
C40	-4.4788531083	3.0937333798	2.0919780863
C41	-2.2006147972	4.7070389122	1.6612352427
C42	-3.2785008115	4.4531783121	4.2767310811
C43	1.9452877827	1.9866900945	5.0019848657
C44	0.7809080865	4.4183438934	4.0808194511
C45	-0.0855468377	3.2697986897	6.4992821173
H46	0.1116647755	3.4053462564	-1.1987109624
H47	-2.7029047828	-2.8537877000	-2.0738493964
H48	-2.4325716205	-4.4351576991	-0.0875456872
H49	-0.3289529952	-5.0010390340	1.1004060970
H50	0.7726814113	-3.2814746783	2.5202985458
H51	2.6963018032	-1.7972253568	2.8008035316
H52	4.6000433892	-1.3231528233	1.2656226496
H53	4.4092175407	0.5451157632	-0.3671867688
H54	3.3308850982	0.2564146291	-2.5761007731
H55	2.3598035060	-1.1869479541	-4.3411710800
H56	-0.0197605432	-0.8626628617	-5.0064737872
H57	-5.5999282606	0.1313813111	-0.0090637710
H58	-5.6756350586	2.2251718231	-1.3521390677
H59	-3.9690916740	2.5829856437	-3.1331972187
H60	-1.5456845805	-1.4424425019	5.8156504919
H61	-2.7619209873	-1.7916796663	4.5768223928
H62	-3.2607954895	-1.5998949382	6.2783153846
H63	-1.7133126983	0.9684289644	7.3778013788

H64	-3.4539822515	0.6821069691	7.5559230290
H65	-2.8636874224	2.2619215103	6.9932517030
H66	-4.9511717073	1.7071742318	4.9941583277
H67	-5.1409384399	0.1068823979	5.7459439331
H68	-4.8794841343	0.2465940469	3.9842413840
H69	-5.0155502963	4.0368928729	1.9399990209
H70	-5.0710767068	2.4502419625	2.7464046211
H71	-4.3639664986	2.5842822300	1.1320166476
H72	-1.2391554202	5.1027736920	1.9959206397
H73	-2.9204699057	5.5293243372	1.5850238748
H74	-2.0555913436	4.2659649243	0.6713968945
H75	-2.3842353644	4.8912747541	4.7296487884
H76	-3.7748931825	3.8433469844	5.0373768987
H77	-3.9531184447	5.2650724152	3.9824838967
H78	2.6033090063	2.6290402154	5.5973809645
H79	2.4111139745	1.7980604275	4.0318984645
H80	1.8267177049	1.0262881884	5.5116521604
H81	1.5820566361	4.8534532988	4.6887017611
H82	-0.0754570658	5.0975156193	4.0923626485
H83	1.1184205924	4.3044931048	3.0491891015
H84	0.7018334421	3.9374056094	6.8636867384
H85	-0.1270066648	2.3972400161	7.1528551601
H86	-1.0437289460	3.7908716598	6.5544078211

[(S_4Calix^H(SH)$_2$(S)$_2$]Mo(PMe$_3$)$_3$ triplet state
-5560.18266395550 Hartrees

atom	x	y	z
Mo1	-1.3235149930	1.4905509839	3.3129279710
P2	-2.8463858876	0.4810474692	5.1574824949
P3	-2.8247078773	3.4638372724	2.8231370830
P4	0.3552737189	2.8786646147	4.7281186226
S5	-2.8012245261	0.1217628864	1.8579865456
S6	0.1788562382	2.2176942859	1.4512849695
S7	-0.7601666078	2.9259706466	-2.0924608534

S8	-1.9920939706	-1.9267894041	-2.7264997530
S9	0.1171331568	-0.5263624961	3.2245265670
S10	2.3786663056	2.3306330045	-1.0473599226
S11	-2.0131869728	0.9358428191	-4.3606327619
S12	-4.1260647944	-2.2275723163	-0.1225018489
C13	-1.9893282375	-1.4230389954	1.5937243152
C14	-2.5615956677	-2.4212231947	0.7557916943
C15	-1.9833454339	-3.6910679755	0.6587848993
C16	-0.8331597431	-4.0230722273	1.3729188436
C17	-0.2235571567	-3.0462480560	2.1555344411
C18	-0.7762834284	-1.7665245164	2.2353117211
C19	1.4173721590	0.9751935726	1.2496492950
C20	1.4927079807	-0.1501430563	2.1031008691
C21	2.5859307568	-1.0175741618	2.0957448408
C22	3.6253487956	-0.8278846125	1.1892741989
C23	3.5282423931	0.2106695609	0.2641898090
C24	2.4356940034	1.0819261064	0.2607772106
C25	0.2336924027	1.6157229856	-2.7625682307
C26	1.5805510913	1.3919077740	-2.3778012529
C27	2.3542867230	0.4479786635	-3.0621599642
C28	1.8176429449	-0.3211014717	-4.0905623659
C29	0.4745316007	-0.1668663574	-4.4202876070
C30	-0.3196329943	0.7804739381	-3.7649875730
C31	-3.0907170520	-0.6195875675	-2.2342028898
C32	-3.9970812850	-0.7568535335	-1.1537022245
C33	-4.9555902261	0.2339839199	-0.9148417474
C34	-5.0058554986	1.3849048685	-1.6941481716
C35	-4.0459365217	1.5791961482	-2.6826803035
C36	-3.0888254798	0.5975195725	-2.9572953819
C37	-2.6396508418	-1.3484597703	5.3618578505
C38	-2.7361471640	1.0194632774	6.9360125166
C39	-4.6801831754	0.5878976783	4.9033173983
C40	-4.4795463315	3.1389795478	2.0500372380
C41	-2.1914356655	4.7492536172	1.6465795341

C42	-3.3213245368	4.5165814712	4.2752025629
C43	2.0457840507	2.1309319810	4.8632687777
C44	0.7874375678	4.5719032261	4.1060003493
C45	0.0324229836	3.2743976396	6.5191075307
H46	0.0929493713	3.1985620087	-1.0800370898
H47	-2.6452783445	-2.8687015851	-2.0133327075
H48	-2.4536210003	-4.4303356637	0.0163113717
H49	-0.4070158845	-5.0186758037	1.2992080779
H50	0.6873720517	-3.2727256381	2.7001717755
H51	2.6218670654	-1.8389236028	2.8050811820
H52	4.4874032615	-1.4878606539	1.1898900758
H53	4.3132449665	0.3594326256	-0.4704870193
H54	3.3939313754	0.3238479652	-2.7785157954
H55	2.4329727712	-1.0468243274	-4.6132180980
H56	0.0175443876	-0.7861247985	-5.1851575665
H57	-5.6476155626	0.0946973080	-0.0911867206
H58	-5.7586158226	2.1444753017	-1.5039503445
H59	-4.0242890165	2.4997689190	-3.2571698513
H60	-1.6159679849	-1.5715356755	5.6754006952
H61	-2.8199084392	-1.8359845158	4.4013114290
H62	-3.3373328065	-1.7456436222	6.1065811273
H63	-1.7377844687	0.8059701644	7.3268883216
H64	-3.4711416148	0.4923586633	7.5533466920
H65	-2.9129881113	2.0953444449	7.0201976788
H66	-5.0119963205	1.6267162286	4.9873781277
H67	-5.2153789724	-0.0119163804	5.6472226797
H68	-4.9129588758	0.2208264536	3.9013145227
H69	-5.0162902470	4.0760750916	1.8656034625
H70	-5.0830828400	2.5006430530	2.6990101689
H71	-4.3317503047	2.6139202086	1.1026210104
H72	-1.2439586674	5.1592913296	2.0018241049
H73	-2.9152679522	5.5615194003	1.5209017140
H74	-2.0119657546	4.2752207553	0.6780461416
H75	-2.4352512802	4.9403865368	4.7555619044

H76	-3.8517277522	3.9082978330	5.0133791644
H77	-3.9758434347	5.3367491070	3.9609052769
H78	2.7259819691	2.7827206015	5.4218270106
H79	2.4446449313	1.9680093040	3.8596978173
H80	1.9819652175	1.1629674325	5.3683539072
H81	1.6121082692	5.0034400085	4.6832944437
H82	-0.0785450716	5.2350666084	4.1856699802
H83	1.0753112227	4.4937627188	3.0554679109
H84	0.8310886226	3.8983784759	6.9344973932
H85	-0.0262834717	2.3517832350	7.1019411080
H86	-0.9179543554	3.8054108615	6.6252757747

$[(S_4\text{Calix}^{H}(SH)_2(S)_2]W(PMe_3)_3H_2$
-5561.67550076989 Hartrees

atom	x	y	z
W1	-2.7871151579	0.4079086260	2.9575053005
P2	-4.7591408548	-1.1183535032	3.3377365646
P3	-4.0365876611	2.4796416695	2.1961918032
P4	-1.5317902158	1.6623915653	4.7602370362
S5	-3.4244762578	-0.3634834216	0.6104175727
S6	-0.7549208853	1.4311462389	1.6841524015
S7	0.0434914287	3.5845488942	-1.2788927032
S8	-0.5954875076	-0.7985522624	-3.8222348998
S9	-1.2424108090	-1.5572674712	2.7722390074
S10	2.3454675544	2.2735877245	0.7941926649
S11	-0.1216842887	2.4134025867	-4.2968431513
S12	-3.5121222767	-1.7468555836	-2.4210975741
C13	-2.3593637040	-1.7022469155	0.1898159741
C14	-2.4089070882	-2.2975210937	-1.1025458563
C15	-1.6814986279	-3.4583253583	-1.3794710473
C16	-0.8850916354	-4.0659341808	-0.4099213038
C17	-0.7835851890	-3.4716591475	0.8433942614
C18	-1.4856524135	-2.2979408778	1.1233213438
C19	0.6072654723	0.3445618840	1.9356829790

C20	0.4357007397	-0.9340993099	2.5103372447
C21	1.5076603708	-1.7550303741	2.8585831215
C22	2.8119758851	-1.3393379829	2.5991610072
C23	3.0140269517	-0.1161170746	1.9615004647
C24	1.9427707624	0.7112307317	1.6073446120
C25	1.2113526547	2.3540945663	-1.8030366935
C26	2.2249161612	1.8356616019	-0.9590891557
C27	3.2140437978	1.0000609356	-1.4904294008
C28	3.2085398267	0.6333187842	-2.8325940163
C29	2.1705687078	1.0712916822	-3.6501482321
C30	1.1677420936	1.9045912233	-3.1454441320
C31	-1.8572651451	0.3657528469	-3.3690008610
C32	-3.0919314229	-0.0373449007	-2.8019505226
C33	-4.1214271512	0.8959070956	-2.6376688538
C34	-3.9367091687	2.2332009631	-2.9740945377
C35	-2.6877529858	2.6576996967	-3.4184012797
C36	-1.6472198293	1.7441012386	-3.6122469693
C37	-4.4915668055	-2.9186963527	2.9913021758
C38	-5.3412429013	-1.2083498712	5.0974235578
C39	-6.3816631791	-0.8442633064	2.4816633007
C40	-5.3997386071	2.3301421920	0.9443405367
C41	-3.0643725420	3.8284912530	1.3756299829
C42	-4.9339164006	3.4179946059	3.5197946167
C43	0.0966163205	0.9860918038	5.3323459241
C44	-1.0774413488	3.4519782894	4.5606967036
C45	-2.4257306098	1.7350895426	6.3862376190
H46	-3.8660677739	1.0089593440	4.1325639899
H47	-2.7400553774	-0.3816798080	4.4717081579
H48	0.3643842537	3.4786247725	0.0292632883
H49	-1.4282319328	-1.8596366857	-3.7512747614
H50	-1.7529179289	-3.8939288746	-2.3719241595
H51	-0.3356220522	-4.9738108680	-0.6377156752
H52	-0.1460127476	-3.9095510830	1.6050876139
H53	1.3170764045	-2.7128110960	3.3339415187

H54	3.6569859705	-1.9607512385	2.8788414056
H55	4.0219045003	0.2212980481	1.7401909531
H56	3.9987195494	0.6408975209	-0.8328341770
H57	3.9894613762	-0.0071340023	-3.2303960479
H58	2.1117547265	0.7571242860	-4.6868784495
H59	-5.0661938762	0.5547601815	-2.2276465767
H60	-4.7454554344	2.9473088412	-2.8485824401
H61	-2.5016856977	3.7079366159	-3.6193843774
H62	-3.6517547365	-3.2840243477	3.5891976506
H63	-4.2548843774	-3.0571352431	1.9345927996
H64	-5.3848286698	-3.5011696936	3.2399517991
H65	-4.5176433677	-1.5368651956	5.7364648794
H66	-6.1781732943	-1.9062678093	5.2031334631
H67	-5.6565804142	-0.2164159491	5.4319734861
H68	-6.8205563780	0.0986954357	2.8204345417
H69	-7.0801504839	-1.6555388906	2.7117094502
H70	-6.2209902527	-0.8014160672	1.4028826233
H71	-5.8225227774	3.3180677383	0.7335113826
H72	-6.1912785181	1.6746997131	1.3103229980
H73	-4.9965731238	1.9075321210	0.0218643303
H74	-2.2534751441	4.1677875476	2.0221087898
H75	-3.7151698576	4.6759996012	1.1359429719
H76	-2.6242779001	3.4402204899	0.4530552729
H77	-4.2441823518	3.7224665146	4.3101980869
H78	-5.6958434614	2.7728785968	3.9656764835
H79	-5.4169363455	4.3094474458	3.1066033170
H80	0.4615666789	1.5495716935	6.1973944634
H81	0.8330826713	1.0479302338	4.5299221135
H82	-0.0227538847	-0.0635572544	5.6132599178
H83	-0.5162321417	3.8038326148	5.4326035646
H84	-1.9765475693	4.0649778982	4.4567501500
H85	-0.4650665643	3.5674255431	3.6642993361
H86	-1.8306932230	2.2569726428	7.1428195634
H87	-2.6325658640	0.7185140451	6.7302115481

H88	-3.3815807354	2.2509147865	6.2631929848

[(S_4Calix^H(SH)$_2$(S)$_2$]W(PMe$_3$)$_3$ singlet state
-5560.46977463939 Hartrees

atom	x	y	z
W1	-1.3150189460	1.4850352884	3.2083497954
P2	-2.7632117147	0.5465747614	5.1688670899
P3	-2.7707509653	3.4118447069	2.8572665667
P4	0.2592306807	2.7931690209	4.8136100281
S5	-2.7786886714	0.1321949285	1.9274909507
S6	0.1465559660	2.2237615717	1.4917358139
S7	-0.7913718531	2.9313154280	-2.1436123450
S8	-2.0048944995	-1.9413893092	-2.6580086605
S9	0.1198917942	-0.4868245944	3.2506414897
S10	2.3446686137	2.3587478986	-1.0424344859
S11	-2.0381021234	0.8814592169	-4.3217573452
S12	-4.1364875897	-2.2293272595	-0.0450837314
C13	-1.9697779280	-1.4525549573	1.6437251566
C14	-2.5601158981	-2.4339255566	0.8136824857
C15	-1.9728951115	-3.7004762753	0.6938334689
C16	-0.7996431187	-4.0167019555	1.3737691644
C17	-0.1769894939	-3.0369974726	2.1455423489
C18	-0.7434313110	-1.7680176379	2.2463836271
C19	1.4376347076	0.9809842905	1.2648315119
C20	1.5113698460	-0.1399591805	2.1041454939
C21	2.6085010914	-0.9991214740	2.0922429743
C22	3.6463072694	-0.7867336164	1.1859201154
C23	3.5435342679	0.2567202517	0.2694294024
C24	2.4379995517	1.1161349365	0.2745659891
C25	0.2102116465	1.6002566859	-2.7540037549
C26	1.5539146754	1.3865978179	-2.3540201409
C27	2.3286031534	0.4222280590	-3.0084707956
C28	1.7946985022	-0.3754648311	-4.0162210031
C29	0.4524382424	-0.2313328753	-4.3552748737

C30	-0.3419975690	0.7353172918	-3.7305041411
C31	-3.1037323288	-0.6349410253	-2.1668918737
C32	-4.0024691532	-0.7601187341	-1.0780519892
C33	-4.9531385879	0.2391996627	-0.8364236082
C34	-5.0027154991	1.3833318981	-1.6262620155
C35	-4.0539036702	1.5623656077	-2.6287561488
C36	-3.1041417494	0.5735681199	-2.9032168890
C37	-2.6216913077	-1.2957277603	5.3701651574
C38	-2.6108367030	1.0312201677	6.9591995819
C39	-4.6063734674	0.6948638076	4.9803154534
C40	-4.4287236186	3.1234492695	2.0543078874
C41	-2.1716307941	4.7608004752	1.7174452606
C42	-3.3280758009	4.4759345713	4.2934558790
C43	1.9207750244	2.0110363506	5.1026701767
C44	0.7922739564	4.4559704049	4.1797409199
C45	-0.1506097759	3.2798864844	6.5621894318
H46	0.0859524156	3.2883699303	-1.1799624423
H47	-2.6613908588	-2.8870140089	-1.9530749858
H48	-2.4515851805	-4.4433407664	0.0618764093
H49	-0.3626589902	-5.0065033763	1.2821973074
H50	0.7512662733	-3.2583906019	2.6631846108
H51	2.6537665507	-1.8265462358	2.7944306895
H52	4.5155432550	-1.4377051154	1.1812530113
H53	4.3295759962	0.4201186020	-0.4609416418
H54	3.3671018555	0.3043639176	-2.7181779175
H55	2.4120837549	-1.1156909992	-4.5154728061
H56	-0.0018944277	-0.8727497604	-5.1032114198
H57	-5.6388277135	0.1118945728	-0.0057860388
H58	-5.7468927152	2.1503212829	-1.4333857773
H59	-4.0354454142	2.4769978606	-3.2127000030
H60	-1.5982808435	-1.5553640267	5.6555265839
H61	-2.8465169097	-1.7831497455	4.4191668055
H62	-3.3120384453	-1.6669029750	6.1352746352
H63	-1.6214127428	0.7663818783	7.3391720922

H64	-3.3599273210	0.4964696154	7.5518398344
H65	-2.7615558744	2.1046322755	7.0887654218
H66	-4.9115507468	1.7413096647	5.0626219003
H67	-5.1244865462	0.1141215096	5.7512140116
H68	-4.8912131096	0.3218669582	3.9943797462
H69	-4.9656716232	4.0665420280	1.9047026062
H70	-5.0416076436	2.4607646251	2.6699035845
H71	-4.2751100427	2.6398458924	1.0862173350
H72	-1.2235557740	5.1723338752	2.0719316607
H73	-2.9046392053	5.5707614299	1.6353389430
H74	-2.0031773797	4.3306888350	0.7264711554
H75	-2.4590244430	4.9316536129	4.7776390424
H76	-3.8422560913	3.8589417445	5.0366066202
H77	-4.0059110309	5.2746142439	3.9714642958
H78	2.5756152090	2.6552624427	5.6997218813
H79	2.3966654233	1.8117588350	4.1391803391
H80	1.7893026360	1.0558192022	5.6196260016
H81	1.5854531645	4.8722212718	4.8103194342
H82	-0.0576292517	5.1436747758	4.1836401079
H83	1.1513733768	4.3529446705	3.1542584460
H84	0.6325790022	3.9357454919	6.9556412847
H85	-0.2168761027	2.4009264916	7.2045774870
H86	-1.1047537867	3.8106943761	6.5965759867

[(S_4Calix^H(SH)$_2$(S)$_2$]W(PMe$_3$)$_3$ triplet state
-5560.45972106575 Hartrees

atom	x	y	z
W1	-1.340407949	1.446323488	3.353035875
P2	-2.791142457	0.489623767	5.215290612
P3	-2.826517678	3.388159568	2.891849401
P4	0.332266406	2.822575306	4.675110386
S5	-2.855383714	0.079173882	1.953760414
S6	0.058849400	2.122679286	1.402608609
S7	-0.675755408	3.098589899	-2.253426226

S8	-2.045573124	-1.880571074	-2.791838933
S9	0.093731387	-0.540687418	3.242502760
S10	2.363715554	2.366419551	-0.974326367
S11	-1.978890611	0.997860817	-4.346434568
S12	-4.136686103	-2.177185992	-0.155519080
C13	-2.008734541	-1.430973528	1.594179762
C14	-2.573041195	-2.400040895	0.718338568
C15	-1.973236479	-3.654823315	0.568208996
C16	-0.805097538	-3.988181533	1.251516860
C17	-0.198448425	-3.029959904	2.058701763
C18	-0.777176273	-1.768227630	2.200365598
C19	1.390384871	0.969847733	1.285880074
C20	1.495491527	-0.136051517	2.157588352
C21	2.639960953	-0.932226131	2.213740504
C22	3.709425172	-0.682245717	1.356821568
C23	3.592070157	0.339154131	0.414427703
C24	2.444873386	1.134638236	0.345553615
C25	0.261309850	1.674351498	-2.754021525
C26	1.568870471	1.396493562	-2.283134965
C27	2.306858857	0.353468207	-2.855165020
C28	1.768644890	-0.451363306	-3.852887454
C29	0.457203975	-0.236516514	-4.264632817
C30	-0.302961996	0.799609713	-3.715103978
C31	-3.086897763	-0.552867514	-2.244100089
C32	-3.974394253	-0.685174604	-1.149989727
C33	-4.890709299	0.335783807	-0.870521130
C34	-4.913334094	1.508129511	-1.618392815
C35	-3.966888975	1.691127946	-2.622504675
C36	-3.055210666	0.679794871	-2.940098603
C37	-2.580842172	-1.334801806	5.471380680
C38	-2.642044952	1.078563973	6.974138143
C39	-4.632924882	0.595168562	5.014445528
C40	-4.503960717	3.060973546	2.172638538
C41	-2.218100668	4.656307706	1.684172955

C42	-3.273245523	4.461711224	4.341761577
C43	1.999953789	2.049282672	4.929561195
C44	0.833625526	4.464442777	3.971588179
C45	-0.025692932	3.347100129	6.425155417
H46	0.139054741	3.399108022	-1.217407998
H47	-2.708774094	-2.817984590	-2.082042852
H48	-2.436411818	-4.379458825	-0.095205107
H49	-0.360514698	-4.970892237	1.133113897
H50	0.729582271	-3.260223332	2.572639805
H51	2.694848521	-1.743418930	2.934041238
H52	4.610805479	-1.284054116	1.410390774
H53	4.402900150	0.533260890	-0.280215187
H54	3.318344250	0.176516630	-2.506332438
H55	2.357203088	-1.251996045	-4.289020718
H56	-0.001087752	-0.881184698	-5.006738889
H57	-5.576454649	0.198978917	-0.041530060
H58	-5.633939632	2.288451853	-1.394806097
H59	-3.922116229	2.622722006	-3.176679525
H60	-1.547851050	-1.546642020	5.761173844
H61	-2.788926610	-1.852122318	4.531972853
H62	-3.255599492	-1.708611667	6.248879974
H63	-1.636649998	0.876683848	7.351343069
H64	-3.365481256	0.566646076	7.617445125
H65	-2.820813562	2.155164048	7.030719824
H66	-4.959098968	1.636083397	5.092894529
H67	-5.143743994	0.010184402	5.786608325
H68	-4.898777009	0.211571537	4.027204723
H69	-5.037786011	3.997583530	1.977517761
H70	-5.093805819	2.446335853	2.855532523
H71	-4.385014536	2.509013203	1.236840441
H72	-1.269709026	5.077016284	2.022895230
H73	-2.949277006	5.461374252	1.553738201
H74	-2.044528437	4.168342576	0.721515542
H75	-2.372919799	4.913560968	4.765783963

H76	-3.753930421	3.862302220	5.119631446
H77	-3.958029991	5.261314659	4.040159599
H78	2.661203397	2.707015968	5.503805176
H79	2.454789984	1.840121992	3.958965252
H80	1.886623930	1.102223870	5.464687330
H81	1.676569056	4.886738578	4.528980267
H82	-0.004713746	5.164571517	4.025652491
H83	1.110307485	4.330283117	2.924061873
H84	0.762941605	4.008786144	6.799050738
H85	-0.082313432	2.471926786	7.075645616
H86	-0.981442959	3.874757517	6.477297330

syn–[(S_4Calix^H(S)$_4$][W(PMe$_3$)$_3$H$_2$]$_2$
-7012.16521086407 Hartrees (B3YLP/6-31G and LACVP)**

atom	x	y	z
W1	1.6125730229	4.1905322212	0.8732416075
H2	3.2523699837	3.9641739147	1.2862898289
H3	2.6983881628	4.0440185150	-0.4450760891
W4	-4.8024827872	6.9831367943	5.4966579747
H5	-6.4128029567	7.1095982099	6.0550569324
H6	-5.0042965567	7.3839939185	7.1428410588
P7	2.3180049575	1.8035527523	0.5070230720
P8	2.0065810525	4.2565298761	3.3739338584
P9	2.9193717141	6.3243977568	0.4003908074
P10	-5.5191171700	9.3812152855	5.7809189146
P11	-2.6210659175	7.1245847871	6.7673440585
P12	-5.5812904048	4.9392523353	6.7849644907
S13	-0.3771519803	2.8033692219	1.6703842496
S14	-0.1127916627	6.1023041288	1.3088840831
S15	-3.4247626577	8.2546797621	3.7424513998
S16	-3.7604155676	4.9450147934	4.1975879687
S17	-6.3533104074	6.7296715035	3.5587317616
S18	-3.4326229087	2.1380081528	2.4133036339
S19	0.2577903362	4.2130006195	-1.2466275222

S20	-1.8685408608	8.8750171395	0.9261982601
C21	-1.6272207184	2.9862620753	0.4434236860
C22	-1.3476172701	3.4476864711	-0.8582797321
C23	-2.2968750694	3.4109617465	-1.8798753271
H24	-2.0352604043	3.7593829983	-2.8743690860
C25	-3.5834758466	2.9631061124	-1.6039674877
C26	-3.9117858881	2.5768636790	-0.3059575595
H27	-4.9261036681	2.2653401679	-0.0891740880
C28	-2.9677190867	2.6034413467	0.7216023463
C29	-0.6090765402	6.6666791942	-0.2807049664
C30	-1.2433742925	7.9255771397	-0.4759030499
C31	-1.3809284994	8.4484107676	-1.7682490942
H32	-1.7864098919	9.4501918023	-1.8779786136
C33	-1.0185680298	7.7136902091	-2.8992014224
C34	-0.5364597472	6.4148389591	-2.7289775056
H35	-0.2900806292	5.7979982392	-3.5890239405
C36	-0.3463622979	5.9094156948	-1.4445612804
C37	-4.2164471042	7.9531519635	2.1877442350
C38	-5.5231699486	7.4304373233	2.0998292406
C39	-6.2249242894	7.3570445640	0.8965077526
H40	-7.2354481438	6.9603851888	0.8848322981
C41	-5.6110970013	7.7598314544	-0.2823970882
C42	-4.2971058169	8.2170469760	-0.2408675365
H43	-3.8087083629	8.5038774715	-1.1641026127
C44	-3.5876363403	8.2996619483	0.9592320948
C45	-5.0669509446	4.2975575832	3.2064217607
C46	-4.9965450519	3.0217909778	2.5760983950
C47	-6.1573562723	2.4298972200	2.0626533739
H48	-6.0913090880	1.4143160918	1.6832954033
C49	-7.3746620171	3.1111645692	2.0214421340
C50	-7.4199839671	4.4286707685	2.4753173050
H51	-8.3351269753	5.0101380401	2.4063694860
C52	-6.2824824410	5.0000025979	3.0433360299
C53	2.1920609529	0.5331533761	1.8560169762

H54	2.4923671629	-0.4523947689	1.4844439856
H55	1.1624986516	0.4859624972	2.2150958676
H56	2.8503704416	0.8080674165	2.6855626119
C57	4.0952726134	1.5665819156	0.0281205918
H58	4.3177961475	0.5129776448	-0.1704337077
H59	4.7409059419	1.9236151883	0.8351546921
H60	4.3132318429	2.1558350001	-0.8661556049
C61	1.4709560233	0.9159949161	-0.8804198567
H62	1.8498983615	-0.1053974992	-0.9912842790
H63	1.6383810390	1.4634586507	-1.8124009578
H64	0.3970176043	0.8835332319	-0.6823570384
C65	3.7576743588	4.0119448241	3.9319162701
H66	3.8361180365	4.0759015544	5.0223584018
H67	4.4030128557	4.7708186220	3.4816562470
H68	4.1115123663	3.0301947509	3.6055267551
C69	1.1462750528	3.0270303405	4.4706668916
H70	1.4676999442	3.1691749627	5.5078975822
H71	1.3773771783	2.0062046982	4.1615191405
H72	0.0659139297	3.1646818541	4.3975655570
C73	1.5629646647	5.8020810000	4.3028747947
H74	1.6677471161	5.6454403104	5.3815886149
H75	0.5314043413	6.0786033766	4.0723313552
H76	2.2057838850	6.6292253132	3.9988260198
C77	4.7444843376	6.0574519211	0.1819175250
H78	5.2579930385	6.9992713717	-0.0382830175
H79	4.9111287408	5.3564578291	-0.6401252358
H80	5.1692428674	5.6209844869	1.0898640487
C81	2.5875550050	7.2691150740	-1.1644729545
H82	3.3581193050	8.0354363505	-1.3016919905
H83	1.6121534699	7.7522579443	-1.1239491960
H84	2.6031891967	6.5900549443	-2.0202548990
C85	2.9524104802	7.7416095850	1.6023244601
H86	3.4382080972	8.6123557460	1.1495516272
H87	3.5163868917	7.4593763408	2.4958102998

H88	1.9310017311	7.9994590069	1.8872929833
C89	-4.2889481233	10.7311246122	6.1098791782
H90	-4.7819228337	11.7089001049	6.1230627666
H91	-3.5259984876	10.7224540060	5.3290900784
H92	-3.8143272383	10.5674595007	7.0818602907
C93	-6.7010235933	9.6833787005	7.1796760482
H94	-6.9998685123	10.7356371094	7.2284418342
H95	-6.2309392275	9.3990013978	8.1250374676
H96	-7.5904714052	9.0629770126	7.0430123796
C97	-6.4721590560	10.1266436687	4.3778479889
H98	-6.7668728721	11.1563483499	4.6062828257
H99	-7.3713406503	9.5323047654	4.1920946791
H100	-5.8545653843	10.1184000530	3.4774441393
C101	-2.7603341462	7.3201548413	8.6069698745
H102	-1.7710436660	7.3421616808	9.0762139784
H103	-3.3381310299	6.4958074155	9.0325472745
H104	-3.2845328053	8.2525153252	8.8336222418
C105	-1.4225347525	8.4946636563	6.3947350605
H106	-0.5241975432	8.3871663934	7.0116920203
H107	-1.8767346418	9.4660973911	6.5950279339
H108	-1.1456995086	8.4579100216	5.3387834373
C109	-1.4447678371	5.6936254303	6.6510398276
H110	-0.5126062742	5.9133678703	7.1827774032
H111	-1.2258503016	5.5000124843	5.5986663533
H112	-1.8923129599	4.7917611804	7.0698115209
C113	-6.7904003337	3.7563976792	6.0197070092
H114	-7.1355846312	3.0441840492	6.7768278582
H115	-6.3237464056	3.2061864741	5.2024338765
H116	-7.6501793781	4.3016801815	5.6245629673
C117	-6.5200213435	5.3435893937	8.3365138583
H118	-6.8349608883	4.4332395442	8.8573609069
H119	-7.4034471197	5.9336459422	8.0790720973
H120	-5.8967849874	5.9428367032	9.0053902298
C121	-4.3617940541	3.7120927068	7.4632669774

H122	-4.8863588892	2.8664984220	7.9202967683
H123	-3.7340330335	4.1816572085	8.2255976686
H124	-3.7306830432	3.3492774357	6.6496757683
H125	-4.3343427165	2.9315630599	-2.3881107888
H126	-8.2616434898	2.6320973068	1.6178340149
H127	-6.1425619809	7.7062979563	-1.2280813092
H128	-1.1324939791	8.1366986832	-3.8926059214

anti–[(S_4Calix^H(S)$_4$][W(PMe$_3$)$_3$H$_2$]$_2$
-7012.17714580913 Hartrees (B3YLP/6-31G and LACVP)**

atom	x	y	z
W1	-2.3849312860	2.9788863696	1.0221263284
H2	-3.2118466259	3.9477524182	2.1743692170
H3	-3.4159969410	4.1628695744	0.3292912766
S4	-2.3980681645	0.4392849392	0.8910625178
S5	0.1393476795	2.6813922833	0.8505273930
S6	-2.1676696763	2.6663231902	-1.4701335757
S7	-3.2998638515	-2.6357734545	0.0886556506
P8	-1.9172476959	2.3693519329	3.4154606334
P9	-4.8757043252	2.4291254731	0.9503139491
P10	-1.4644151529	5.3425117246	0.9816569835
C11	-2.6671122740	-0.0010777560	-0.7824028308
C12	-3.0230829814	-1.3344580461	-1.1215632512
C13	-3.3127048952	-1.6737322490	-2.4465330106
H14	-3.5766502552	-2.7027011756	-2.6738617194
C15	-3.2683813903	-0.7200495924	-3.4646651354
C16	-2.8991761408	0.5892564347	-3.1543181845
H17	-2.8600349585	1.3472532712	-3.9311518957
C18	-2.5844577573	0.9312412235	-1.8380926312
C19	0.5615627970	2.6640836228	-0.8527862419
C20	-0.3995442681	2.7083503753	-1.8846230795
C21	-0.0423115887	2.8541352326	-3.2270827643
H22	-0.8175539042	2.9278453241	-3.9840992224
C23	1.3030210627	2.9033062603	-3.5889225437

C24	2.2762645357	2.7827709590	-2.5957587796
H25	3.3292791909	2.7754861088	-2.8623333843
C26	1.9268238271	2.6599047346	-1.2484400412
C27	-1.3199986465	3.6926163178	4.5664259170
H28	-1.2422453609	3.3099001323	5.5894493799
H29	-2.0076352394	4.5424527654	4.5531251756
H30	-0.3338616296	4.0317400164	4.2425781322
C31	-3.3300246522	1.6892757882	4.4042167897
H32	-3.0229832579	1.4848256557	5.4355903731
H33	-3.6654300745	0.7581926774	3.9427500790
H34	-4.1597851325	2.4013630428	4.4133001460
C35	-0.6457402673	1.0620732122	3.7351496649
H36	-0.5567543712	0.8893265482	4.8136456927
H37	0.3215060249	1.3697054542	3.3338506854
H38	-0.9327785266	0.1323066752	3.2410168721
C39	-5.9676902762	3.7747782698	1.6156116613
H40	-7.0265656684	3.5381822815	1.4676721826
H41	-5.7338832484	4.7144710998	1.1092382236
H42	-5.7760616194	3.9088038828	2.6838792575
C43	-5.5880468170	2.2612664033	-0.7570162126
H44	-6.6801718939	2.1876743317	-0.7177411305
H45	-5.1896909763	1.3673810895	-1.2407917523
H46	-5.3082854375	3.1324856446	-1.3557046697
C47	-5.6633613321	0.9522260672	1.7546863759
H48	-6.7189807820	0.8932271097	1.4694166449
H49	-5.5998525023	1.0376495898	2.8414512709
H50	-5.1467278364	0.0424762937	1.4450506897
C51	-0.0411214339	5.9058665579	2.0345689408
H52	0.2831120434	6.9051593632	1.7258184020
H53	0.7889276093	5.2052139709	1.9287977544
H54	-0.3478059458	5.9478553762	3.0822546201
C55	-0.9045010895	5.9563732954	-0.6760413124
H56	-0.6386135464	7.0176853805	-0.6306508077
H57	-1.7086801583	5.8190806117	-1.4042909334

H58	-0.0360500312	5.3838821222	-1.0070558940
C59	-2.7033173803	6.6587989046	1.4105206903
H60	-2.2637173498	7.6589086068	1.3349342864
H61	-3.0652326880	6.5019037808	2.4303353768
H62	-3.5578381962	6.5903543840	0.7323319481
S63	2.3980681645	-0.4392849392	-0.8910625178
S64	-0.1393476795	-2.6813922833	-0.8505273930
S65	2.1676696763	-2.6663231902	1.4701335757
S66	3.2998638515	2.6357734545	-0.0886556506
C67	2.6671122740	0.0010777560	0.7824028308
C68	3.0230829814	1.3344580461	1.1215632512
C69	3.3127048952	1.6737322490	2.4465330106
H70	3.5766502552	2.7027011756	2.6738617194
C71	3.2683813903	0.7200495924	3.4646651354
C72	2.8991761408	-0.5892564347	3.1543181845
H73	2.8600349585	-1.3472532712	3.9311518957
C74	2.5844577573	-0.9312412235	1.8380926312
C75	-0.5615627970	-2.6640836228	0.8527862419
C76	0.3995442681	-2.7083503753	1.8846230795
C77	0.0423115887	-2.8541352326	3.2270827643
H78	0.8175539042	-2.9278453241	3.9840992224
C79	-1.3030210627	-2.9033062603	3.5889225437
C80	-2.2762645357	-2.7827709590	2.5957587796
H81	-3.3292791909	-2.7754861088	2.8623333843
C82	-1.9268238271	-2.6599047346	1.2484400412
W83	2.3849312860	-2.9788863696	-1.0221263284
H84	3.2118466259	-3.9477524182	-2.1743692170
H85	3.4159969410	-4.1628695744	-0.3292912766
P86	1.9172476959	-2.3693519329	-3.4154606334
P87	4.8757043252	-2.4291254731	-0.9503139491
P88	1.4644151529	-5.3425117246	-0.9816569835
C89	1.3199986465	-3.6926163178	-4.5664259170
H90	1.2422453609	-3.3099001323	-5.5894493799
H91	2.0076352394	-4.5424527654	-4.5531251756

H92	0.3338616296	-4.0317400164	-4.2425781322
C93	3.3300246522	-1.6892757882	-4.4042167897
H94	3.0229832579	-1.4848256557	-5.4355903731
H95	3.6654300745	-0.7581926774	-3.9427500790
H96	4.1597851325	-2.4013630428	-4.4133001460
C97	0.6457402673	-1.0620732122	-3.7351496649
H98	0.5567543712	-0.8893265482	-4.8136456927
H99	-0.3215060249	-1.3697054542	-3.3338506854
H100	0.9327785266	-0.1323066752	-3.2410168721
C101	5.9676902762	-3.7747782698	-1.6156116613
H102	7.0265656684	-3.5381822815	-1.4676721826
H103	5.7338832484	-4.7144710998	-1.1092382236
H104	5.7760616194	-3.9088038828	-2.6838792575
C105	5.5880468170	-2.2612664033	0.7570162126
H106	6.6801718939	-2.1876743317	0.7177411305
H107	5.1896909763	-1.3673810895	1.2407917523
H108	5.3082854375	-3.1324856446	1.3557046697
C109	5.6633613321	-0.9522260672	-1.7546863759
H110	6.7189807820	-0.8932271097	-1.4694166449
H111	5.5998525023	-1.0376495898	-2.8414512709
H112	5.1467278364	-0.0424762937	-1.4450506897
C113	0.0411214339	-5.9058665579	-2.0345689408
H114	-0.2831120434	-6.9051593632	-1.7258184020
H115	-0.7889276093	-5.2052139709	-1.9287977544
H116	0.3478059458	-5.9478553762	-3.0822546201
C117	0.9045010895	-5.9563732954	0.6760413124
H118	0.6386135464	-7.0176853805	0.6306508077
H119	1.7086801583	-5.8190806117	1.4042909334
H120	0.0360500312	-5.3838821222	1.0070558940
C121	2.7033173803	-6.6587989046	-1.4105206903
H122	2.2637173498	-7.6589086068	-1.3349342864
H123	3.0652326880	-6.5019037808	-2.4303353768
H124	3.5578381962	-6.5903543840	-0.7323319481
H125	-3.5155233917	-0.9949267081	-4.4858531642

H126	1.5900637437	3.0171715947	-4.6300206732
H127	3.5155233917	0.9949267081	4.4858531642
H128	-1.5900637437	-3.0171715947	4.6300206732

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