Electronic Supplementary Information

Docking of Tetra-methyl Zirconium to the Surface of Silica: A Well-Defined Pre-catalyst for Conversion of CO_2 to Cyclic Carbonates

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1- Experimental Section

Materials and Syntheses

All samples were handled with the exclusion of air and moisture by the use of standard Schlenk line and glovebox techniques. The syntheses and sample treatments were carried out using high-vacuum lines (pressure $<10^{-5}$ mbar). *n-Pentane*, tetrahydrofuran (THF) and d^8-THF were distilled from a Na alloy under argon. The solvents were degassed through freeze-pump-thaw cycles. $SiO_{2\text{-}700}$ was prepared from Aerosil silica supplied by Degussa (specific surface area 200 m^2/g), which was partially dehydroxylated at 700 °C under high vacuum ($<10^{-5}$ mbar) for 15 h to give a white solid having a specific surface area of 190 m^2/g

and containing 0.5-0.6 OH groups/nm^2. The Starting reagents $ZrCl_4$, BuLi, ^{13}MeI, propylene oxide and TBAB (Tetra-*n*-butylammonium bromide) were purchased from Aldrich. Before using, the propylene oxide was distilled from CaH_2 and TBAB was melted 150°C and stirred under vacuum in a Schlenk tube for 5 hours then stored under argon. Pure carbon dioxide (99.999%) was purchased from Abdullah Hashim Industrial gases & Equipment (AHG) and used as supplied.

Elemental Analyses

Elemental analyses were performed at the KAUST core laboratory. Analysis of gas-phase of release methane after the treatment of the zirconium complex with distilled water was performed with an Agilent 6850 gas chromatography with a split injector coupled with a flame ionization detector. An HP-PLOT Al_2O_3 KCl 30 m × 0.53 mm, 20.00 mm capillary column coated with a stationary phase of aluminum oxide deactivated with KCl was used with helium as the carrier gas at 32.1 kPa. Each analysis was carried out under the same conditions: a flow rate of 1.5 mL/min and isothermal operation at 80 °C.

GC and GC-MS

GC measurements were performed with an Agilent 7890A Series (FID detection). Method for GC analyses: Column HP-5; 30m length x 0.32mm ID x 0.25 µm film thickness; Flow rate: 1 mL/min (N_2); split ratio: 50/1; Inlet temperature: 250 °C, Detector temperature: 250 °C; Temperature program: 40 °C (3 min), 40-250 °C (12 °C/min), 250 °C (3 min), 250-300 °C (10 °C/min), 300 °C (3 min); propylene oxide retention time: t_R = 3.12 min, cyclic carbonate retention time: t_R = 9.54 min.

GC-MS measurements were performed with an Agilent 7890A Series coupled with Agilent 5975C Series. GC/MS equipped with a capillary column coated with none polar stationary phase HP-5MS was used for molecular weight determination and identification that allowed the separation of organic compounds according to their boiling points differences.

IR Spectroscopy

IR spectra of solid samples were recorded with a Nicolet 6700 FT-IR spectrometer by using a DRIFT cell equipped with CaF_2 windows. The samples were prepared in an argon-filled glovebox. Typically, 64 scans were accumulated for each spectrum (resolution 4 cm^{-1}).

Liquid-State Nuclear Magnetic Resonance Spectroscopy

All liquid-state NMR spectra were recorded on Bruker AVANCE 600 MHz spectrometers. Chemical shifts were measured relative to the residual ^{1}H or ^{13}C resonance in the deuterated solvent: d^{8}-THF.[1]

Solid-State Nuclear Magnetic Resonance

One-dimensional ^{1}H MAS and ^{13}C CP-MAS solid-state NMR spectra were recorded on a Bruker AVANCE III spectrometer operating at 400 and 100 MHz resonance frequencies for ^{1}H, ^{13}C respectively, with a conventional double resonance 4mm CPMAS probe. The samples were introduced under argon into zirconia rotors, which were then tightly closed. The spinning frequency was set to 14 and 10 KHz for 1H, ^{13}C spectra, respectively. NMR chemical shifts are reported with respect to TMS as an external reference. For CP/MAS ^{13}C and ^{29}Si NMR, the following sequence was used: 90 0 pulses on the proton (pulse length 2.4 s), then a cross-polarization step with a contact time typically 2 ms, and finally the acquisition of the ^{13}C signal under high-power proton decoupling. The delay between the scan was set to 5 s, to allow the complete relaxation of the ^{1}H nuclei and the number of scans was between 3,000-5,000 for carbon, and 32 for proton. An apodization function (exponential) corresponding to a line broadening of 80 Hz was applied prior to Fourier transformation.

The 2D ^{1}H-^{13}C heteronuclear correlation (HETCOR): solid-state NMR spectroscopy experiments were conducted on a Bruker AVANCE III spectrometer using a 3.2 mm MAS probe. The experiments were performed according to the following scheme: 900 proton pulse, t1 evolution period, cross-polarization (CP) to carbon spins, and detection of carbon magnetization under TPPM decoupling1,2. For the cross-polarization step, a ramped radio frequency (RF) field centered at 75 KHz was applied to protons, while the carbon RF field was matched to obtain an optimal signal. A total of 32 t1 increments with 2000 scans were collected. The sample spinning frequency was 8.5 kHz. A 2D Fourier transformation gives through space between pairs of neighboring carbon (in F2) and proton (in F1) nuclei. Using a short contact time (0.5 ms) for the CP step, the polarization transfer in the dipolar correlation experiment is expected to be quite selective, which is to lead to correlation only between pairs of attached ^{1}H-^{13}C spins (C-H directly bonded). Using longer contact times (10 ms), we found that it is possible to observe extra correlation peaks, which arise from longer range dipolar thought-space interaction. These long-range spectra yield further information about the structure.

^{1}H-^{1}H multiple-Quantum Spectroscopy: Two-dimensional double-quantum (DQ) and triple-quantum (TQ) experiments were recorded a Bruker AVANCE III spectrometer operating at 600 MHz with a conventional double resonance 3.2 mm CPMAS probe, according to the following general scheme3: excitation of DQ coherences, t1 evolution, Z-filter, and detection. The spectra were recorded in a rotor synchronized

fashion in t1; that is the t1 increment was set equal to one rotor period (4.545 μs). One cycle of the standard back-to-back (BABA) recoupling sequence was used for the excitation and reconversion period. Quadrature detection in w1 was achieved using the States-TPPI method. A spinning frequency of 22 KHz was used. The 900 proton pulse length was 2.5 μs, while a recycle delay of 5 s was used. A total of 128 t1 increments with 32 scans each were recorded. Double (DQ)- and Triple (TQ)-quantum proton spectroscopies under fast MAS have recently shown to be powerful techniques to probe the structural information and dynamics inherent proton-proton dipolar couplings. The DQ frequency in the w1 dimension corresponds to the sum of two single quantum (SQ) frequencies of the two coupled protons and correlates in the w2 dimension with the two corresponding proton resonances. The TQ frequency in the w1 dimension corresponds to the sum of the three SQ frequencies of the three coupled protons and correlates in the w2 dimension with the three individual proton resonances. Conversely, groups of less than three equivalent spins will not give rise to diagonal signals in the spectrum. Two-dimensional DQ and TQ correlations experiments can thus apply to determine in a reliable way the number of the attached equivalent proton.

Preparation of the Silica Partially Dehydroxylated at 700 °C

Typically, 4.000 g of Degussa Aerosil 200 silica was treated in a quartz reactor fitting a tubular furnace under a high vacuum line (10^{-5} Torr) at 700 °C for 16 hours. FT-IR: 3747 cm^{-1} ($\nu_{(SiO-H)}$).

Preparation of labeled MeLi ($^{13}CH_3$)Li

In a 200 mL Schlenk, 15 mL of 1.6 M BuLi was taken under argon, and to that 3.4 g (24 mmol) of ^{13}MeI diluted in 25 mL of pentane was added dropwise at −20 °C with stirring. A white precipitate formed immediately, and the solution was stirred for another 30 min after the addition of ^{13}MeI. The precipitate was then filtered and dried under a vacuum to produce a white solid (^{13}MeLi). A small amount of ^{13}MeLi was taken and titrated with deoxygenated water to quantify the amount of methyl lithium present by quantifying the release of methane (around 55% ^{13}MeLi was found).

Preparation of $ZrMe_4$ on THF (1) and its characterization by liquid-state NMR

Under argon atmosphere, $ZrCl_4$ (120 mg, 0.5 mmol) was added into one compartment of a chilled (-80 ^{o}C) double-schlenk tube and dissolved with 25 ml of dry THF, 70 mg of *MeLi dissolved on 5 ml of THF (55% by gas calibration, ca. 5.5 equiv.) was added into the suspension. The reaction mixture was allowed to stir at -10 - 0 ^{o}C for 3 h; the suspension became red-brown. The solution was filtrated to the other side of the

double schlenk, which is a pure solution of $ZrMe_4$. A slurry of the solution was taken, then the THF was evaporated at -10 °C, and 0.4 ml of d^8-THF was added on the tube under an inert atmosphere and analyzed by solution NMR. ^{1}H NMR (d^8-THF at 0 °C): δ= 0.257 ppm and 0.07 ppm, ^{13}C NMR (d^8-THF at 0 °C): δ= 41 ppm. ^{1}H-^{13}C COSY, H at 0.186 ppm correlates with C at 41 ppm.

Grafting of prepared $(THF)_2Zr(CH_3)_4$ on $SiO_{2\text{-}700}$:[(≡Si−O−Zr)$(CH_3)_3(THF)_2$] and [(≡Si−O−Zr)$_2(CH_3)_2(THF)_2$] (2)

In a chilled (-10 °C) double-Schlenk tube, silica Aerosil(700) (1 g, Aerosil-200 was dehydroxylated at 700 °C for 18 h under high vacuum (10^{-5} mBar) to generate Aerosil (700)) was added into one compartment, following with chilled $ZrMe_4$ solution produced in the first step from 0.5 mmol $ZrCl_4$. The reaction mixture was allowed to stir at - 10 °C for 3 h, the silica took on a slight gray tinge. After filtration and washing with THF for three times and one time with pentane, the product was dried under vacuum for 1 h at -10 °C, then, it was dried on the high vacuum line for another 1 h to afford a grey powder product. Elemental analysis gives 3.9% Zr, 5.23% C, and 0.95% H.

Oxygen insertion reaction

50 mg of sample **2** was taken in a reactor tube inside the glovebox. The reactor tube was evacuated in high vacuum and to that, 1 atm of O_2 was passed at room temperature. After 10 minutes, it was open to the air, and solid-state NMR was carried out.

Catalytic test

In a typical reaction, a high-pressure stirred batch reactor (35 mL) was used whereby complex **2** (the catalyst), CO_2 and propylene oxide (the reactants) and TBAB (nucleophile) were introduced.

10 mg (3.3×10^{-3} mmol of Zr) of Complex **2** was mixed with three different amounts of propylene oxide; 1 mL (14.34 mmol), 2mL (28.68 mmol) and 3 mL (43.03 mmol), to these mixtures, 47 mg (0.14 mmol), 94 mg (0.28 mmol) and 141 mg (0.42 mmol) of TBAB were added respectively. Then, 100 psi of CO_2 were introduced for each mixture. Each vessel was heated to 60 °C and held for 16 h. Then the mixture was cooled, mixed with dichloromethane, and filtered. The products' composition was quantified by gas chromatography and qualified by GC-MS.

Computational Details

All the DFT geometry optimizations were performed at the hybrid GGA PBE0 level[(a)[2] of Perdew, Burke and Ernzerhof with the Gaussian09 package.[3] The electronic configuration of the systems as described with the split-valence Def2SVP basis set [4, 5] for the main group atoms, while for zirconium we adopted the quasi-relativistic SDD effective core potential, with the associated triple-ζ valence basis set.[6-8] The reported NMR values were built through single-point energy calculations on the PBE0/Def2SVP~sdd geometries including corrections due to dispersion through the Grimme's method with Becke–Johnson damping (GD3BJ keyword in Gaussian). [9, 10] However, the solvent effects were included with the Solvation Model Based on Density (SMD) model using the THF solvent.[11]

The silica models in Figure S1 were elaborated from the work of Sautet et al.[12] using structure 001-5 for model1 and structure 001-4 for model2. For models of monopodal species on $SiO_{2\text{-}700}$, the initial silica surface selected for NMR property computations was taken from the previously optimized structure of Emsley and co-workers.[13] The surface species were exchanged from that of the prior study with the species of interest here and truncated at the second coordination sphere for the NMR tensor computations. Further, where applicable, oxygen atoms at the silica surface were terminated with hydrogen atoms.

2- Supporting Section 1: FT-IR spectra of $SiO_{2\text{-}700}$ after grafting of $Zr(CH_3)_4$ complex in

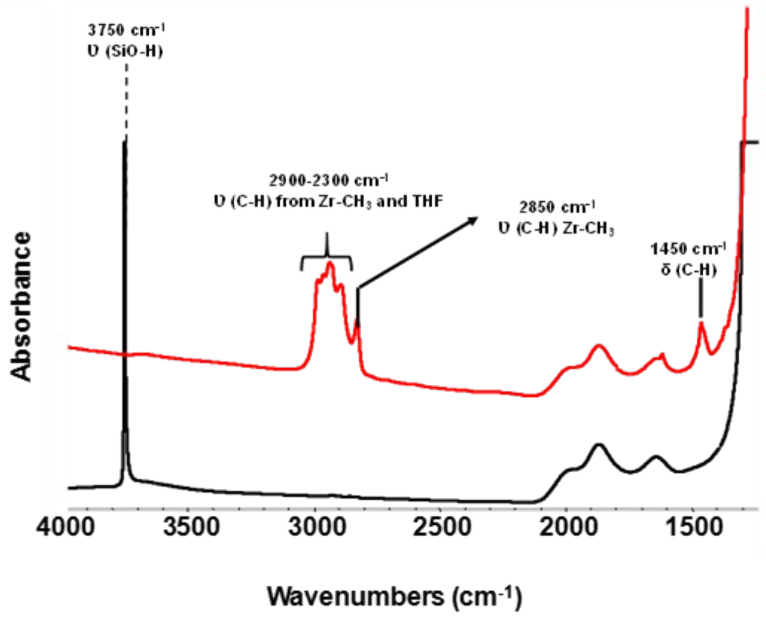


Figure S1: FT-IR spectra of SiO_{2-700} (black), after grafting of $Zr(CH_3)_4$ complex (red) in THF.

3- Supporting section 2: ^{1}H, ^{13}C and HETCOR of Sample 2 after reacting with O_2/air

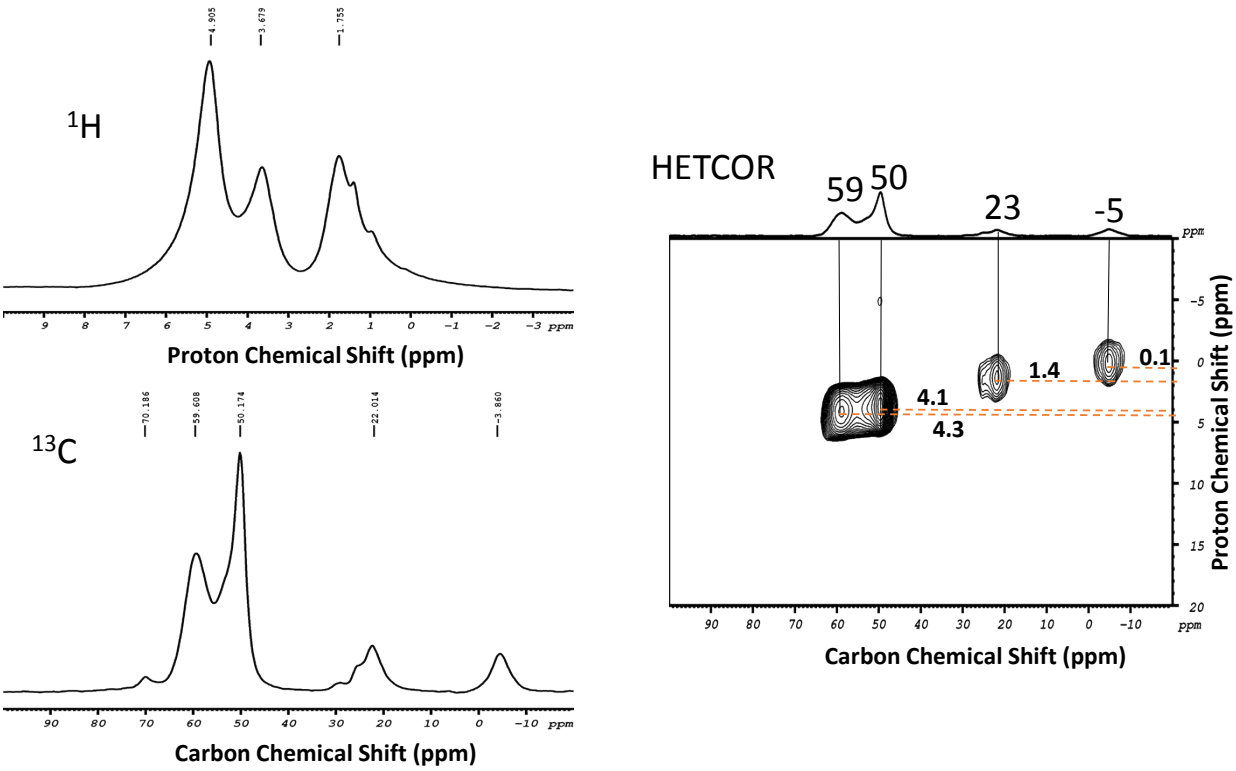
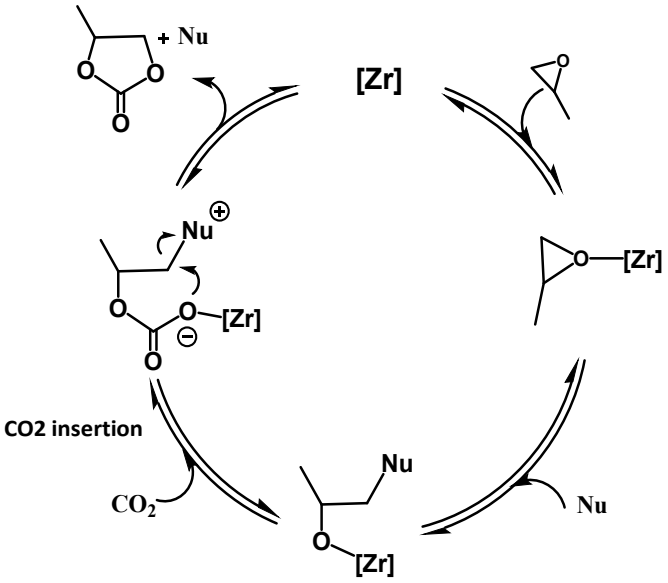


Figure S2: ^{1}H, ^{13}C and HETCOR of Sample **2** after reacting with O_2/air

4- Supporting Section 3: A catalytic pathway representing the cycloaddition of CO_2 to propylene oxide catalyzed by $[(\equiv Si{-}O{-})Zr(CH_3)_3(THF)_2]$



Scheme S1: A catalytic pathway representing the cycloaddition of CO_2 to propylene oxide catalyzed by $[(\equiv Si{-}O{-}Zr)(CH_3)_3(THF)_2]$ and $[(\equiv Si{-}O{-}Zr)_2(CH_3)_2(THF)_2]$

5- Supporting Section 4: Chemical shift parameters obtained from simulation of ^{1}H NMR and ^{13}C NMR spectra by DFT calculations.

Table S1. Chemical shift parameters (in ppm) obtained from simulations of ^{1}H NMR and ^{13}C NMR spectra by DFT calculations.

	Chemical group	^{1}H NMR	^{13}C NMR
THF	(O)-$\mathbf{CH_2}$-(CH_2)	3.5	66.2
	(CH_2)-$\mathbf{CH_2}$-(CH_2)	1.5	27.4
$ZrMe_4$	Zr-$\mathbf{CH_3}$	0.3	30.4
$Zr(Me)_4(THF)_1$	Zr-$\mathbf{CH_3}$	0.1	32.8
	(O)-$\mathbf{CH_2}$-(CH_2)	3.7	68.4
	(CH_2)-$\mathbf{CH_2}$-(CH_2)	1.7	27.0
$Zr(Me)_4(THF)_2$	Zr-$\mathbf{CH_3}$	0.2	33.0
	(O)-$\mathbf{CH_2}$-(CH_2)	3.6	68.1
	(CH_2)-$\mathbf{CH_2}$-(CH_2)	1.6	28.3
Model1-$Zr(Me)_3$	Zr-$\mathbf{CH_3}$	0.4	31.7
Model1-$Zr(Me)_3(THF)_1$	Zr-$\mathbf{CH_3}$	0.0	29.9
	(O)-$\mathbf{CH_2}$-(CH_2)	3.9	69.5
	(CH_2)-$\mathbf{CH_2}$-(CH_2)	1.7	23.8
Model1-$Zr(Me)_3(THF)_2$	Zr-$\mathbf{CH_3}$	-0.1	30.5
	Zr-$\mathbf{CH_3}$	0.0	35.2
	Zr-$\mathbf{CH_3}$	-0.2	24.6
	(O)-$\mathbf{CH_2}$-(CH_2)	3.8	68.9
	(CH_2)-$\mathbf{CH_2}$-(CH_2)	1.7	27.0
Model2-$Zr_2(Me)_4$	Zr-$\mathbf{CH_3}$	0.7	35.4
	Zr-$\mathbf{CH_3}$	0.6	33.0

Model2-$Zr_2(Me)_4(THF)_2$	Zr-**CH_3**	0.9	35.1
	Zr-**CH_3**	-0.1	21.2
	Zr-**CH_3**	0.0	31.3
	Zr-**CH_3**	0.2	34.1
	Zr-**CH_3**	0.1	27.6
	Zr-**CH_3**	0.0	27.2
	(O)-**CH_2**-(CH_2)	3.8	68.4
	(CH_2)-**CH_2**-(CH_2)	1.6	24.8
	(O)-**CH_2**-(CH_2)	4.1	68.7
	(CH_2)-**CH_2**-(CH_2)	1.8	26.8
	(O)-**CH_2**-(CH_2)	3.8	67.4
	(CH_2)-**CH_2**-(CH_2)	1.6	27.4
	(O)-**CH_2**-(CH_2)	4.1	70.8
	(CH_2)-**CH_2**-(CH_2)	1.8	24.1
Model3-$Zr(Me)_2$	Zr-**CH_3**	1.1	41.8
	Zr-**CH_3**	0.8	35.8
Model3-$Zr(Me)_2(THF)_1$	Zr-**CH_3**	0.5	37.0
	Zr-**CH_3**	0.7	33.7
	(O)-**CH_2**-(CH_2)	4.3	70.7
	(CH_2)-**CH_2**-(CH_2)	1.9	26.9
Model3-$Zr(Me)_2(THF)_2$	Zr-**CH_3**	0.6	30.9
	Zr-**CH_3**	-0.1	32.8
	Zr-**CH_3**	0.0	
	Zr-**CH_3**	0.1	

	Zr-**CH_3**	0.1	
	Zr-**CH_3**	0.3	
	(O)-**CH_2**-(CH_2)	4.2	70.7
	(CH_2)-**CH_2**-(CH_2)	1.9	26.9
Model3-Zr$(Me)_2(THF)_2$ methylated	Zr-**CH_3**	0.2	30.9
	(O)-**CH_2**-(CH_2)	4.1	70.7
	(CH_2)-**CH_2**-(CH_2)	1.9	26.9
	-Si-**CH_3**	0.4	-1.6

Table S2. The xyz coordinates for all the DFT optimized structures (absolute energies in a.u.).

Model1-Zr$(Me)_3$	
Zero-point correction= 0.259761 (Hartree/Particle) Thermal correction to Energy= 0.294545 Thermal correction to Enthalpy= 0.295489 Thermal correction to Gibbs Free Energy= 0.182655 Sum of electronic and zero-point Energies= -3314.148983 Sum of electronic and thermal Energies= -3314.114200 Sum of electronic and thermal Enthalpies= -3314.113256 Sum of electronic and thermal Free Energies= -3314.226089	43 a1-ZrCH34 SCF Done: -3314.40874462 A.U. Si -3.102112 2.466179 -1.635277 Si -3.539090 -3.242930 0.500508 Si -0.861917 -2.663594 -1.137836 Si -0.876610 3.782502 0.278435 Si -3.803475 -0.364529 1.854929 Si -1.067372 0.123134 -2.331789 Si -1.024320 1.146051 2.047993 O -0.927521 2.696998 1.526708 O -3.554977 -1.964116 1.544566 O -2.403919 1.019741 -2.036829 O -2.440961 0.504111 1.495850 O -2.093286 -3.329028 -0.293867 O -1.431886 -1.479835 -2.150470

	O -2.023011 3.438163 -0.856736 O 0.219452 -1.934633 -0.117453 O 0.108692 0.484997 -1.217864 O 0.230415 0.258934 1.454325 H -4.265993 2.182437 -0.758303 H -4.632551 -3.079800 -0.496439 H -0.568291 0.383204 -3.694948 H -3.688401 -4.485793 1.294695 H -4.904445 0.147753 0.998495 H -3.512150 3.159653 -2.883515 H -1.172426 5.122368 0.844134 H -4.106389 -0.223926 3.303551 H 0.465429 3.738972 -0.358712 H -0.197682 -3.729998 -1.906823 H -0.964114 1.123086 3.520820 Si 0.757097 -0.381472 0.037279 O 2.380212 -0.331920 -0.002298 Zr 4.333674 -0.193180 0.139112 C 4.894775 1.598129 1.329314 H 4.032882 2.046433 1.855770 H 5.653162 1.342572 2.093944 H 5.331411 2.381968 0.681465 C 5.165989 -2.001205 1.126932 H 5.575503 -1.751478 2.124336 H 4.412010 -2.796297 1.268794 H 5.992953 -2.430946 0.529703 C 5.229072 -0.011533 -1.887772 H 5.732702 -0.951425 -2.183780 H 4.482206 0.223480 -2.667332 H 5.991744 0.790529 -1.908016

Model1-$Zr(Me)_3(THF)_1$	
Zero-point correction= 0.380251 (Hartree/Particle)	56
Thermal correction to Energy= 0.420809	a1-ZrCH34THF SCF Done: -3546.44322049 A.U.
Thermal correction to Enthalpy= 0.421754	Si 4.064393 -2.567386 -1.432469
Thermal correction to Gibbs Free Energy= 0.294529	Si 4.567867 3.102239 0.693924
Sum of electronic and zero-point Energies= -3546.062969	Si 2.000327 2.643606 -1.140318
Sum of electronic and thermal Energies= -3546.022411	Si 1.617173 -3.773475 0.266796
Sum of electronic and thermal Enthalpies= -3546.021467	Si 4.581441 0.239360 2.104713
Sum of electronic and thermal Free Energies= -3546.148692	Si 2.194832 -0.152547 -2.301710
	Si 1.732908 -1.148531 2.052024
	O 1.618256 -2.697228 1.522949
	O 4.439245 1.843975 1.755232
	O 3.473698 -1.093410 -1.897027
	O 3.223370 -0.575638 1.629031
	O 3.189175 3.260474 -0.199524
	O 2.606216 1.437745 -2.106032
	O 2.876258 -3.492388 -0.762376
	O 0.813095 1.965397 -0.212749
	O 0.925225 -0.464335 -1.284491
	O 0.576859 -0.208159 1.358762
	H 5.152636 -2.335258 -0.449076
	H 5.718412 2.859703 -0.219843
	H 1.802884 -0.407891 -3.700857
	H 4.737417 4.347921 1.480517
	H 5.736188 -0.333228 1.364540
	H 4.561909 -3.282889 -2.636332
	H 1.792388 -5.129041 0.847110
	H 4.742095 0.109447 3.577382
	H 0.340186 -3.661953 -0.484904

	H 1.452494 3.737632 -1.961192 H 1.552451 -1.124784 3.515528 Si 0.184705 0.438885 -0.102871 O -1.419659 0.452690 -0.287153 Zr -3.397080 0.356440 -0.245700 C -6.620366 -0.868460 -0.551223 H -7.213882 -0.543586 -1.424294 H -5.980965 -1.703846 -0.858021 C -6.599756 1.087367 0.627591 H -5.945499 1.744042 1.213578 H -7.194546 1.713535 -0.060901 C -7.505581 -1.154713 0.660781 H -8.518810 -1.446974 0.351141 H -7.092699 -1.980521 1.256909 C -7.481336 0.161992 1.462756 H -7.039863 0.002586 2.456427 H -8.481994 0.591806 1.610306 O -5.778697 0.214174 -0.150190 C -3.687584 -0.978153 -2.038542 H -3.875254 -2.034660 -1.764115 H -4.502669 -0.657100 -2.713466 H -2.752140 -0.972890 -2.627477 C -3.613598 -0.561687 1.795956 H -4.116839 -1.547026 1.749560 H -2.624174 -0.717168 2.260678 H -4.203093 0.074486 2.484300 C -3.834533 2.556746 -0.441193 H -4.695429 2.787670 -1.095394 H -4.019229 3.040542 0.537835 H -2.947611 3.056772 -0.871401

Model1-$Zr(Me)_3(THF)_2$	
Zero-point correction= 0.500005 (Hartree/Particle)	69
Thermal correction to Energy= 0.546318	a1-ZrCH34THF2 SCF Done: -3778.46931057 A.U.
Thermal correction to Enthalpy= 0.547262	Si -4.844424 -1.778394 -2.605424
Thermal correction to Gibbs Free Energy= 0.408946	Si -4.490205 -0.680328 2.673880
Sum of electronic and zero-point Energies= -3777.969306	Si -1.989266 -2.062996 1.230906
Sum of electronic and thermal Energies= -3777.922993	Si -5.183096 1.116192 -1.298870
Sum of electronic and thermal Enthalpies= -3777.922048	Si -2.632822 1.908527 3.166099
Sum of electronic and thermal Free Energies= -3778.060365	Si -1.834682 -2.246879 -1.790906
	Si -2.531417 2.352999 0.026621
	O -3.843303 1.451154 -0.395031
	O -3.720808 0.670636 3.220344
	O -3.209562 -2.014119 -2.657886
	O -2.554432 2.572110 1.651662
	O -3.438915 -1.686320 1.892130
	O -2.217439 -2.751355 -0.257870
	O -5.225802 -0.493979 -1.640221
	O -1.108055 -0.679246 1.005154
	O -1.005221 -0.826624 -1.646676
	O -1.162336 1.571775 -0.441566
	H -5.512163 -2.976599 -2.037298
	H -5.572979 -0.295261 1.732407
	H -1.018426 -3.259638 -2.482957
	H -5.031024 -1.403164 3.853679
	H -3.109632 2.971260 4.086968
	H -5.288636 -1.502611 -3.997366
	H -6.393954 1.447221 -0.506668
	H -1.289515 1.407945 3.557071
	H -5.127951 1.901386 -2.565725

	H -1.277178 -3.002614 2.115340 H -2.560753 3.672520 -0.633261 Si -0.491878 0.066363 -0.347578 O 1.110586 0.193646 -0.304708 Zr 3.049326 -0.203372 0.001985 C 5.794004 -2.125832 -0.448925 H 4.954864 -2.721848 -0.832617 H 6.307155 -1.653734 -1.301425 C 5.964827 -1.068907 1.652456 H 6.134824 -0.025552 1.944723 H 5.326899 -1.544818 2.416740 C 6.746488 -2.920977 0.427731 H 6.203925 -3.717531 0.961415 H 7.551596 -3.391821 -0.153853 C 7.233019 -1.863590 1.410173 H 8.005052 -1.227862 0.946917 H 7.648712 -2.279837 2.338747 O 5.271208 -1.079967 0.394236 C 3.891730 -0.256179 -2.114710 H 3.171758 0.257838 -2.777804 H 4.875848 0.225380 -2.262786 H 3.971080 -1.293070 -2.492119 C 3.599998 0.945919 1.882732 H 4.516265 1.562447 1.887130 H 2.750632 1.629541 2.071108 H 3.653402 0.260910 2.750649 C 2.513763 -2.325895 0.625100 H 2.319058 -2.953186 -0.267949 H 3.275333 -2.852833 1.229382 H 1.578124 -2.328791 1.213748

	C 4.270368 3.021920 -0.724588 O 3.087546 2.225231 -0.727873 C 2.066886 2.831026 -1.528905 C 2.542493 4.255140 -1.757767 C 4.055953 4.073644 -1.802305 H 4.391298 3.478975 0.273108 H 5.140075 2.373300 -0.915221 H 1.980972 2.275232 -2.479679 H 1.109415 2.747371 -0.998591 H 2.124236 4.696733 -2.673510 H 2.256178 4.898727 -0.910026 H 4.365386 3.684218 -2.785658 H 4.621206 4.996740 -1.609717

Model2-$Zr_2(Me)_4$	
	102 a2-ZrCH34 SCF Done: -8026.42830540 A.U. Si -2.404147 2.953151 0.258607 Si -1.032838 -2.912215 0.877118 Si 5.650312 -1.381466 -0.678335 Si -6.308259 0.697684 0.837866 Si 0.262043 1.550553 -0.147565 Si 1.721388 -4.197142 1.292734 Si -7.217256 -2.380499 0.504062 Si -1.483742 5.975017 0.516305 Si -0.477806 -1.112075 -1.605941 Si -4.709774 1.932610 -1.615775 Si -3.381440 -4.865267 0.232108 Si 5.825200 0.318844 -3.329913 Si 2.414707 3.363263 -1.564054

	Si 3.701956 -3.835208 -1.219721 Si -5.249593 -3.262309 -1.878383 Si -2.551100 0.418750 -3.457647 Si 0.154555 5.562128 -2.228224 Si 1.249023 -3.350276 -3.174955 Si 2.910034 1.316262 -4.032590 O -2.622372 1.962488 1.590806 O -0.692625 -2.179047 2.321142 O 5.488305 -0.779370 0.831678 O -5.091835 1.030215 1.947972 O 0.153539 1.185965 1.430817 O 2.037644 -3.004066 2.383276 O -1.109335 2.400561 -0.574779 O 0.251016 -3.876504 0.572789 H 6.902135 -2.168712 -0.786404 H -6.863952 -3.329362 1.591409 O -2.164599 4.479490 0.762096 O -1.229341 -1.811692 -0.321808 O 5.687041 -0.125383 -1.746583 O -3.760321 2.879122 -0.652577 O -2.424608 -3.761715 1.019796 O -5.730148 1.076410 -0.644310 H -4.384198 -5.341089 1.219388 H 3.586687 3.944044 -0.889914 O 4.373689 -2.346465 -1.076103 O -6.647959 -0.892712 0.972056 O 1.569338 2.471813 -0.464158 O 2.896006 -4.221538 0.156202 H -0.785738 6.361947 1.765673 O 0.320458 0.227221 -1.112992

	H 1.661288 -5.538813 1.905486 H 6.550254 1.615962 -3.369531 O -6.525416 -2.849850 -0.907796 O -0.385670 5.914880 -0.705879 O 0.582062 -2.137102 -2.275230 O -3.799494 0.884560 -2.473550 H -2.536901 -5.965328 -0.298216 H 6.541553 -0.736097 -4.095951 O 2.902706 2.422083 -2.807108 H 4.736950 -4.857346 -1.465798 H -8.684146 -2.285837 0.295060 H -2.577652 6.919240 0.166977 O -1.625993 -0.713249 -2.701194 H -5.500186 2.802457 -2.503556 O -4.146741 -4.149055 -1.036222 O 4.337195 0.492609 -4.027692 O 1.447716 4.550979 -2.158776 O 2.667427 -3.833063 -2.495903 H -5.783206 -4.097061 -2.983581 H -0.941609 4.911167 -2.998052 H 0.307010 -4.500630 -3.206530 H -1.727732 1.610972 -3.794871 H 2.789077 2.044569 -5.323594 H -4.602127 -2.022246 -2.372124 H -3.137197 -0.216026 -4.663299 H 0.592356 6.828569 -2.867071 H 1.528232 -2.836472 -4.540065 H 1.796203 0.349825 -3.852424 H -3.559780 1.664401 1.733672 H -1.400267 -1.731844 2.810993

	H -4.996570 0.397713 2.673544 H -7.501356 1.512175 1.136365 Zr -0.899280 1.130406 3.121683 Zr 5.260725 0.089356 2.581587 H 1.248645 -2.524517 2.685062 C 0.458884 0.229542 4.656299 H 1.405640 0.802678 4.682913 H 0.030664 0.269119 5.675325 H 0.727776 -0.823024 4.456518 C -2.665823 -0.259020 3.625637 H -3.239875 -0.725837 2.804186 H -2.443822 -1.041993 4.374882 H -3.349937 0.439865 4.153005 C -1.111949 3.121673 4.086713 H -0.333007 3.268576 4.856165 H -1.054369 3.959925 3.371063 H -2.096734 3.187451 4.589022 C 3.901275 1.845284 2.483115 H 3.262430 1.884260 1.583562 H 3.228124 1.856527 3.362154 H 4.492986 2.781024 2.513791 C 4.575844 -1.324626 4.145717 H 3.969609 -0.798529 4.908950 H 3.935566 -2.113368 3.708038 H 5.419096 -1.812795 4.669323 C 7.246636 0.855299 3.240530 H 7.918254 0.033386 3.551164 H 7.767054 1.426420 2.450046 H 7.128615 1.529310 4.110858

Model2-$Zr_2(Me)_4(THF)_1$	
	128 a2-ZrCH34THF SCF Done: -8490.48442411 A.U. Si -3.740882 2.365382 2.194727 Si -1.104380 -2.407550 -1.510631 Si 5.352856 0.574537 -2.015103 Si -6.220821 -1.440227 1.962269 Si -1.014510 1.952067 0.594633 Si 1.578771 -3.617352 -2.443960 Si -6.246632 -4.166941 0.304222 Si -3.733557 5.450145 2.935672 Si -1.429717 0.695409 -2.228489 Si -5.865380 1.166575 0.150945 Si -3.484890 -3.499659 -3.157713 Si 4.814962 3.680261 -2.164600 Si 0.608274 4.590958 0.352101 Si 3.267405 -1.182139 -3.607029 Si -6.466269 -2.644742 -2.504674 Si -4.424894 1.473614 -2.689288 Si -2.267965 6.005389 0.118979 Si 0.560263 0.295416 -4.678182 Si 1.802930 4.458854 -2.630511 O -3.525706 1.198071 3.318837 O -0.614518 -2.789284 0.030390 O 5.995950 -0.134451 -0.699059 O -5.048664 -1.122628 3.097589 O -0.557709 0.544064 1.260005 O 1.772506 -4.208434 -0.916093 O -2.442767 2.472794 1.202882 O 0.124351 -2.804786 -2.509858

	H 6.321850 0.601009 -3.138772 H -5.014273 -4.988960 0.179474 O -3.939339 3.813674 2.920695 O -1.443445 -0.818147 -1.596136 O 4.922451 2.123700 -1.623260 O -5.075429 2.047570 1.283443 O -2.455140 -3.260824 -1.875520 O -6.195847 -0.334193 0.748321 H -3.803956 -4.951034 -3.202649 H 1.435788 5.193874 1.412724 O 3.986198 -0.216012 -2.496830 O -5.891746 -2.921965 1.334451 O 0.115542 3.108939 0.874186 O 2.758252 -2.561538 -2.871085 H -3.056911 5.827809 4.201715 O -1.196612 1.783656 -1.034363 H 1.575782 -4.739498 -3.400850 H 4.979132 4.569925 -0.983488 O -6.694027 -3.600429 -1.175766 O -2.780922 5.946711 1.684524 O -0.243378 0.828164 -3.334279 O -4.943031 0.987047 -1.194220 H -2.832637 -3.023772 -4.404478 H 5.866336 3.923162 -3.188535 O 1.511779 4.433343 -1.004299 H 4.219073 -1.536194 -4.679853 H -7.383566 -4.949485 0.853053 H -5.071550 6.090112 2.817397 O -2.878137 0.957347 -2.945690 H -7.135499 1.842025 -0.178498

	O -4.869208 -2.630435 -2.935018 O 3.356417 3.957428 -2.886475 O -0.688149 5.543914 0.016763 O 1.991268 -0.396377 -4.268726 H -7.269236 -3.232846 -3.608447 H -3.100816 5.101682 -0.721543 H -0.281773 -0.712222 -5.378819 H -4.469481 2.959467 -2.758866 H 1.660548 5.853799 -3.129746 H -6.870857 -1.250174 -2.207162 H -5.279541 0.851970 -3.731664 H -2.350616 7.412496 -0.349130 H 0.835606 1.475480 -5.534630 H 0.883399 3.533760 -3.336709 H -4.191616 0.485523 3.363087 H -1.305514 -2.748863 0.749181 H -4.211131 -1.600950 2.959101 H -7.534494 -1.397718 2.632426 Zr 0.017929 -1.115143 2.139087 C 0.009019 -4.490969 2.890548 H -0.058097 -4.745937 1.821627 H -1.010124 -4.380731 3.285272 C 0.865798 -5.489693 3.675000 H 1.467440 -6.102200 2.986941 H 0.252981 -6.174283 4.277906 C 1.965160 -3.411126 3.603848 H 2.693480 -3.618402 2.801241 H 2.248817 -2.478774 4.110882 C 1.773611 -4.599738 4.520257 H 2.723471 -5.083496 4.788021

	H 1.274906 -4.283880 5.450244 O 0.660888 -3.211614 3.034968 Zr 6.874115 -1.222476 0.712369 C 5.680493 0.327780 3.606769 H 6.546201 0.879856 4.018115 H 5.767688 -0.729007 3.892092 C 5.245327 1.720415 1.858185 H 6.081234 2.432438 1.986817 H 4.945488 1.721257 0.803736 C 4.357852 0.981518 3.989222 H 3.561425 0.223548 4.004809 H 4.399283 1.441726 4.986177 C 4.116129 2.000263 2.855350 H 4.152529 3.040484 3.208388 H 3.130807 1.849952 2.391009 O 5.710056 0.409423 2.187536 H 1.223150 -3.741903 -0.266357 C 1.985897 -1.266348 1.069557 H 2.706914 -0.752817 1.739668 H 2.423620 -2.247721 0.827496 H 1.983478 -0.678171 0.133933 C -2.127605 -2.069111 2.314567 H -2.625909 -1.093488 2.163205 H -2.740990 -2.839519 1.812281 H -2.139492 -2.283593 3.401449 C 0.416251 -0.238181 4.163445 H 0.687427 -0.942851 4.968964 H 1.175626 0.563781 4.136628 H -0.532120 0.249623 4.465376 C 5.725884 -2.742185 1.923737

	H 4.713802 -2.392785 2.194665 H 5.609573 -3.666372 1.328572 H 6.258868 -3.022952 2.853478 C 7.970742 -2.732762 -0.536842 H 7.280254 -3.326853 -1.164830 H 8.695014 -2.247846 -1.218734 H 8.540580 -3.448600 0.085236 C 8.688925 -0.358428 1.717610 H 9.620945 -0.716389 1.245250 H 8.713875 0.746806 1.712657 H 8.718154 -0.682901 2.777266

Model2-$Zr_2(Me)_4(THF)_2$	
	154 a2-ZrCH34THF2 SCF Done: -8954.51355720 A.U. Si -4.688336 2.298755 2.523137 Si -1.710303 -2.669873 -2.159200 Si 4.643715 1.283613 -2.736455 Si -5.666968 -2.821070 2.105961 Si -1.921399 1.843562 0.936637 Si 1.035110 -3.040346 -3.487037 Si -6.436611 -4.860166 -0.177828 Si -5.612091 5.294359 1.923782 Si -2.366706 0.364272 -1.899054 Si -6.332946 0.124624 0.871909 Si -4.052183 -3.580613 -4.082737 Si 3.946535 4.353536 -2.429541 Si -0.644621 4.670661 0.182201 Si 2.340856 -0.210906 -4.271392 Si -6.959426 -3.240282 -2.988391

	Si -5.370558 0.983361 -2.112811 Si -3.587351 5.864258 -0.480010 Si -0.653163 0.950724 -4.502620 Si 0.855021 5.098448 -2.578192 O -4.305263 1.805765 4.049460 O -1.068083 -3.606374 -0.954994 O 5.490812 0.441729 -1.634550 O -4.315564 -2.906936 3.033189 O -1.142896 0.748787 1.839159 O 1.499727 -3.788930 -2.095146 O -3.333975 2.316714 1.628342 O -0.543549 -2.527299 -3.300945 H 5.427533 1.475487 -3.983885 H -5.640523 -6.081738 -0.459180 O -5.315847 3.807507 2.568538 O -2.145295 -1.222677 -1.532810 O 4.275661 2.773736 -2.109614 O -5.829054 1.286622 1.920215 O -3.031013 -3.387607 -2.798098 O -5.849051 -1.326825 1.446053 H -4.217306 -5.042168 -4.310331 H 0.005226 5.446898 1.255732 O 3.227803 0.521541 -3.107442 O -5.584994 -3.922093 0.880077 O -0.988647 3.173751 0.741046 O 1.979888 -1.746666 -3.820465 H -5.758676 6.254260 3.045620 O -2.308960 1.248819 -0.541302 H 1.111945 -3.962331 -4.639470 H 4.201796 5.121410 -1.178402

	O -6.697947 -4.050374 -1.582675 O -4.357797 5.797283 0.978969 O -1.230856 0.861687 -2.953669 O -5.687660 0.384566 -0.607728 H -3.504499 -2.884409 -5.274771 H 4.807482 4.831281 -3.545577 O 0.363640 4.533851 -1.105061 H 3.100599 -0.252460 -5.539373 H -7.759054 -5.193626 0.425220 H -6.851029 5.218674 1.098779 O -3.853283 0.526387 -2.582507 H -7.807584 0.173783 0.800555 O -5.524057 -2.907678 -3.739082 O 2.376149 4.555271 -2.895403 O -2.007068 5.445648 -0.314926 O 0.958934 0.640620 -4.522102 H -7.787721 -4.096766 -3.881151 H -4.249019 4.928422 -1.431666 H -1.369528 -0.040598 -5.351412 H -5.451266 2.469033 -2.057986 H 0.861012 6.589565 -2.548652 H -7.631131 -1.948453 -2.696601 H -6.334257 0.421702 -3.090735 H -3.635730 7.265139 -0.972935 H -0.856390 2.335214 -4.998202 H -0.044447 4.585602 -3.641761 H -5.030133 1.402599 4.535785 H -1.360977 -3.418707 -0.050666 H -3.451186 -2.819847 2.600770 H -6.811695 -3.111785 2.995566

	Zr 0.137324 -0.733764 2.176085 C 2.023412 -3.528176 1.583893 H 2.882679 -3.159949 0.999651 H 1.168473 -3.641709 0.909816 C 2.371243 -4.782660 2.382230 H 3.185385 -5.340275 1.898298 H 1.505545 -5.457172 2.449808 C 2.635662 -2.726540 3.624385 H 3.591898 -2.265839 3.321474 H 2.260298 -2.210725 4.515729 C 2.758834 -4.241323 3.772592 H 3.775650 -4.528664 4.076305 H 2.068418 -4.612619 4.544269 O 1.688819 -2.544163 2.570193 Zr 6.799189 -0.514325 -0.487311 C 7.058832 2.398581 1.763773 H 7.235982 3.186846 1.007349 H 8.026430 1.952931 2.028863 C 4.896592 1.888741 1.258472 H 4.706985 2.477015 0.345186 H 4.217134 1.027711 1.252906 C 6.273147 2.934453 2.955155 H 6.496608 2.339589 3.853642 H 6.529899 3.979895 3.178841 C 4.806516 2.746004 2.527751 H 4.308356 3.702653 2.313991 H 4.221087 2.242935 3.310450 O 6.232628 1.384262 1.220040 H 0.758476 -3.871108 -1.468321 C 1.115348 -0.640150 0.154677

	H 2.124318 -0.199819 0.286042 H 1.273644 -1.603823 -0.358418 H 0.588371 0.019995 -0.555720 C -1.268627 -2.582104 2.040224 H -2.065762 -2.264161 1.337554 H -0.812667 -3.521719 1.682105 H -1.734360 -2.836175 3.005027 C 1.645196 0.280502 3.560661 H 2.635891 0.227215 3.069379 H 1.372629 1.351765 3.607387 H 1.768398 -0.069489 4.599230 C 5.480091 -1.506703 1.096007 H 4.432031 -1.172776 0.993721 H 5.476211 -2.592782 0.870832 H 5.788167 -1.376284 2.149698 C 7.274448 -2.133460 -1.986097 H 6.525248 -2.948869 -1.975567 H 7.248588 -1.700541 -3.003179 H 8.272360 -2.589149 -1.851637 C 8.648253 0.814257 -0.706283 H 8.376925 1.387724 -1.620294 H 8.975095 1.561854 0.037856 H 9.534713 0.205925 -0.977652 C 9.415453 -1.039638 1.723189 O 8.396040 -1.672219 0.932476 C 8.340214 -3.073753 1.216952 C 9.695265 -3.394271 1.815674 C 9.969240 -2.132621 2.626944 H 10.175983 -0.633484 1.039286 H 8.968053 -0.200526 2.277193

	H 7.523656 -3.265593 1.934409 H 8.117793 -3.608992 0.282477 H 9.683383 -4.312839 2.419458 H 10.447626 -3.517709 1.020037 H 9.417930 -2.166202 3.580218 H 11.032571 -1.978783 2.859217 C -1.366896 -1.821418 5.315819 O -1.039421 -0.742202 4.441209 C -1.351090 0.518929 5.062152 C -2.064747 0.166928 6.357549 C -1.472147 -1.196171 6.695108 H -2.330420 -2.267145 5.008970 H -0.586569 -2.594228 5.234478 H -0.405155 1.053842 5.244849 H -1.973215 1.105822 4.374924 H -1.909279 0.923384 7.139824 H -3.148646 0.081681 6.181870 H -0.471669 -1.082682 7.144054 H -2.089179 -1.792869 7.382252

Model3-Zr$(Me)_2$	
	85 a3-ZrCH34 SCF Done: -7820.09208042 A.U. Si 1.329116 -2.781910 1.141102 Si 0.904696 2.309107 0.521929 Si -4.713569 1.692871 1.613762 Si 5.075130 -0.039704 1.271954 Si -1.317118 -1.356614 0.221814 Si -1.138850 4.251149 1.927578 Si 7.386217 1.148929 -0.420222

	Si 0.699641 -5.874224 1.117812 Si -0.621845 0.831306 -1.845537 Si 3.680501 -1.991287 -0.828971 Si 2.925023 3.411879 -1.538866 Si -5.859978 0.463430 -1.023311 Si -3.355134 -3.457562 -0.775341 Si -3.622702 4.075980 -0.063417 Si 5.377288 1.826960 -2.813177 Si 1.752304 -0.833118 -3.133558 Si -0.996722 -5.506505 -1.587223 Si -2.736639 2.875748 -2.912874 Si -4.321961 -1.392190 -2.999850 O 1.443060 -1.805162 2.452246 O 1.234760 1.006685 1.512244 O -3.260644 1.284287 2.292057 O 3.854197 1.059310 1.570985 O -1.336152 -0.400707 1.562477 O -1.783043 3.383456 3.151828 O 0.085200 -2.229312 0.196160 O 0.250268 3.533992 1.352020 H -5.748726 1.755148 2.660205 H 8.426442 2.101571 0.031733 O 1.028073 -4.321750 1.586171 O -0.105733 1.856917 -0.670535 O -5.107686 0.599229 0.447646 O 2.702378 -2.751916 0.246513 O 2.374414 2.762252 -0.096790 O 4.699335 -0.973732 -0.029940 H 3.722641 4.619702 -1.204361 H -4.304232 -4.236540 0.037354

	O -4.581119 3.199617 0.948481 O 6.446344 0.782482 0.897279 O -2.597518 -2.370561 0.214391 O -2.172518 4.382063 0.643710 H 0.140605 -6.588575 2.289654 O -1.370812 -0.450235 -1.149310 H -0.757523 5.586250 2.414993 H -6.936412 -0.555031 -0.890926 O 6.465724 1.893661 -1.573880 O -0.427559 -5.888960 -0.086634 O -1.659207 1.620677 -2.814176 O 2.793376 -1.097167 -1.878339 H 1.762721 3.715389 -2.409092 H -6.397623 1.786389 -1.432889 O -4.171532 -2.666340 -1.956261 H -4.298696 5.346589 -0.383110 H 7.968310 -0.100405 -0.981870 H 1.954419 -6.504444 0.623428 O 0.667978 0.340050 -2.716974 H 4.485426 -2.998794 -1.542749 O 3.884056 2.286791 -2.264724 O -4.776854 -0.031139 -2.170665 O -2.233882 -4.425024 -1.479888 O -3.393992 3.189481 -1.432109 H 5.821909 2.779200 -3.863319 H 0.092168 -4.894639 -2.397399 H -2.005218 4.081199 -3.391091 H 1.028732 -2.094424 -3.447427 H -5.390987 -1.754690 -3.967528 H 5.260202 0.439354 -3.328405

	H 2.524080 -0.327958 -4.295091 H -1.513530 -6.748763 -2.216104 H -3.811708 2.477204 -3.850605 H -3.037644 -1.105858 -3.683413 H 2.214128 0.894503 1.660885 H -2.676382 0.576943 1.922503 H 3.765746 1.814490 0.962773 H -2.330437 2.596767 2.931490 H 5.237495 -0.836116 2.497430 Zr 0.055195 -0.521810 3.064263 C 0.616314 1.059667 4.528285 H 1.691591 1.314794 4.489323 H 0.045480 1.989457 4.346848 H 0.387381 0.722446 5.556059 C -1.155918 -1.775483 4.453151 H -0.547408 -2.132048 5.305155 H -1.999829 -1.196420 4.873821 H -1.586190 -2.666400 3.960297

Model3-$Zr(Me)_2(THF)_1$	
Zero-point correction= 0.603322 (Hartree/Particle)	98
Thermal correction to Energy= 0.677436	a3-ZrCH34THF SCF Done: -8052.32047443 A.U.
Thermal correction to Enthalpy= 0.678380	Si -0.335067 2.852099 1.123170
Thermal correction to Gibbs Free Energy= 0.485466	Si -2.315387 -2.321869 0.454305
Sum of electronic and zero-point Energies= -8051.717152	Si 4.960493 -1.452827 -0.710283
Sum of electronic and thermal Energies= -8051.643038	Si -4.357101 1.379543 1.804319
Sum of electronic and thermal Enthalpies= -8051.642094	Si 1.273998 0.724743 -0.227033
Sum of electronic and thermal Free Energies= -8051.835008	Si 0.138714 -3.259353 1.814399
	Si -6.189726 -0.882495 0.772619
	Si 1.366221 5.487755 1.251541

	Si -0.893296 -0.793888 -1.731313 Si -3.019205 3.225742 -0.344760 Si -4.153072 -3.315321 -1.870387 Si 4.186973 -1.773136 -3.678724 Si 3.140774 2.164010 -2.146489 Si 2.467449 -3.499364 -0.257835 Si -5.341934 -0.502519 -2.299647 Si -1.808900 1.897917 -3.049304 Si 1.626725 4.973541 -1.877690 Si 0.297225 -3.490541 -2.703791 Si 1.981178 0.321235 -4.445425 O -0.564043 1.776843 2.335701 O -2.762727 -1.886956 1.977726 O 4.948771 -0.074975 0.167953 O -3.154108 1.298776 2.889614 O 1.446697 0.071534 1.228622 O -0.150349 -1.847082 2.675876 O 0.286305 2.055969 -0.188988 O -1.050760 -3.362182 0.673164 H 6.176358 -2.208448 -0.351385 H -6.157343 -2.323519 1.119490 O 0.711391 4.009969 1.604012 O -1.797861 -0.993914 -0.367165 O 4.930239 -1.150477 -2.337727 O -1.738084 3.552481 0.641800 O -3.515232 -3.068274 -0.353703 O -3.917288 2.036744 0.357347 H -5.433776 -4.039479 -1.664533 H 4.601753 2.084691 -2.304039 O 3.619209 -2.358904 -0.383517

	O -4.842551 -0.194563 1.485394 O 2.741173 1.214660 -0.835797 O 1.612868 -3.192652 1.124526 H 2.685229 5.557309 1.927672 O 0.619564 -0.299250 -1.339812 H 0.074808 -4.418629 2.726365 H 5.060236 -1.482692 -4.845889 O -6.138674 -0.692449 -0.860391 O 1.568990 5.651203 -0.377954 O -0.767414 -2.236653 -2.487596 O -2.522443 2.724512 -1.816637 H -3.203714 -4.082191 -2.709914 H 3.949978 -3.230211 -3.506109 O 2.344350 1.606772 -3.470989 H 3.089702 -4.833694 -0.133540 H -7.407173 -0.198067 1.279290 H 0.447818 6.561409 1.709590 O -1.641277 0.294442 -2.677614 H -3.813408 4.457269 -0.494656 O -4.422236 -1.852713 -2.589010 O 2.714178 -1.056911 -3.900967 O 2.696237 3.711403 -1.879909 O 1.476236 -3.483385 -1.552547 H -6.367367 -0.389033 -3.367104 H 0.272803 4.493899 -2.256223 H -0.484371 -4.746571 -2.579241 H -0.472535 2.480799 -3.319159 H 2.483684 0.638576 -5.809953 H -4.466945 0.688058 -2.237760 H -2.704598 1.973748 -4.229510

	H 2.130813 6.006650 -2.816301 H 0.934245 -3.362088 -4.035644 H 0.519087 0.089566 -4.442293 H -3.510441 -1.254049 2.025334 H 4.184937 0.504154 -0.020696 H -2.209686 1.504579 2.697017 H -1.118599 -1.745824 2.829277 H -5.527263 2.099123 2.350189 Zr 0.720032 0.402974 3.142110 O 2.366308 -1.080226 3.760841 C 2.339120 -1.972696 4.886357 C 3.611368 -1.193785 3.036683 H 1.536706 -2.708332 4.716354 H 3.380428 -1.099594 1.971439 C 3.719981 -2.609911 4.920967 H 3.692367 -3.631584 5.324708 C 4.155399 -2.539249 3.460595 H 4.268860 -0.362359 3.339187 H 2.095533 -1.395695 5.790375 H 4.400092 -2.015742 5.551148 H 5.243245 -2.610223 3.324095 H 3.677993 -3.337648 2.871984 C -0.687164 -0.104630 4.845076 H -1.748031 -0.205197 4.554081 H -0.420447 -0.996183 5.440148 H -0.638431 0.771894 5.523028 C 2.138394 1.854764 4.073799 H 1.700149 2.867875 4.088793 H 2.376968 1.569758 5.115029 H 3.091878 1.918023 3.518678

Model3-Zr(Me)$_2$(THF)$_2$	
	111 a3-ZrCH34THF2 SCF Done: -8284.15638103 A.U. Si 1.927147 -2.608283 -0.605092 Si -0.299164 3.756564 -0.170885 Si -4.860085 -0.942388 2.106904 Si 5.219400 0.289422 -0.874520 Si -0.843062 -1.555689 -0.052591 Si -2.411171 4.362820 1.909313 Si 4.628123 3.385260 -0.790432 Si 2.010402 -5.727455 -0.992662 Si -1.257508 1.182459 -1.570346 Si 3.297852 -1.047742 -2.973383 Si 0.545024 4.662012 -3.096948 Si -6.351580 -1.076997 -0.711251 Si -2.869585 -3.769755 -0.789642 Si -4.692919 2.166865 1.451137 Si 3.472120 3.627412 -3.771531 Si 0.576655 0.282285 -4.022973 Si -0.826580 -5.476493 -2.492657 Si -4.179868 2.542581 -1.705508 Si -4.252998 -1.814903 -2.931384 O 2.414134 -1.767517 0.713619 O 0.785178 3.936825 1.065453 O -3.582940 -1.908734 2.442496 O 4.949900 -0.799070 0.318818 O -0.250705 -1.133161 1.390247 O -1.222820 4.120886 3.025430 O 0.344192 -2.263568 -0.957729

	O -1.722157 4.354345 0.393503 H -5.793526 -1.020415 3.247762 H 3.524402 4.007705 -0.014506 O 2.077484 -4.214666 -0.324622 O -0.442939 2.153948 -0.516022 O -5.615796 -1.434023 0.721937 O 2.825707 -2.226371 -1.924363 O 0.143660 4.596368 -1.493663 O 4.482343 -0.142145 -2.288304 H 0.871389 6.078601 -3.409756 H -3.910425 -4.375614 0.056599 O -4.367569 0.626419 1.911124 O 4.629582 1.771922 -0.426604 O -2.093322 -2.629033 0.141995 O -3.497569 3.133126 2.027961 H 2.026384 -6.701652 0.126960 O -1.464276 -0.286728 -0.888900 H -3.118659 5.644003 2.101315 H -7.277401 -2.197246 -1.029355 O 4.391859 3.633773 -2.403273 O 0.625917 -5.925420 -1.864520 O -2.703509 1.835783 -1.922803 O 2.030153 -0.061251 -3.319192 H -0.591468 4.157257 -3.907328 H -7.066879 0.221331 -0.618951 O -3.513304 -3.049772 -2.117361 H -5.993346 2.604263 1.998735 H 5.948880 3.972660 -0.441957 H 3.166684 -5.919178 -1.907780 O -0.395478 1.071957 -2.949779

	H 3.812231 -1.686435 -4.198999 O 1.862560 3.710504 -3.393197 O -5.218799 -0.941718 -1.911129 O -1.813242 -4.918262 -1.283732 O -4.758843 2.247996 -0.187780 H 3.847795 4.825720 -4.570678 H -0.629042 -4.407275 -3.508786 H -4.024697 4.008948 -1.891523 H -0.081971 -0.986203 -4.439588 H -5.087235 -2.432236 -3.996790 H 3.701026 2.369302 -4.521860 H 0.798249 1.190908 -5.174158 H -1.449931 -6.687469 -3.083928 H -5.129144 1.962836 -2.684275 H -3.233373 -0.898143 -3.496126 H 1.396654 3.200019 1.236711 H -3.003824 -2.189315 1.710764 H 4.036862 -1.131978 0.477903 H -0.336940 4.143397 2.618831 H 6.676703 0.377607 -1.097165 Zr 1.494706 -0.979940 2.387397 O 0.023672 -0.015861 3.950454 C 0.428734 0.384227 5.264654 C -1.287322 0.514489 3.635323 H 1.483249 0.700382 5.228047 H -1.165808 1.318881 2.894443 C -0.529773 1.497101 5.649293 H -0.194210 2.460938 5.235108 C -1.810899 1.057912 4.949577 H -1.889078 -0.291766 3.202239

	H 0.346908 -0.485396 5.938914 H -0.630124 1.603654 6.738805 H -2.320041 0.266820 5.523674 H -2.518683 1.881455 4.786147 C 1.978167 1.239430 2.245861 H 2.765298 1.424365 1.493058 H 1.002836 1.552884 1.830730 H 2.181434 1.839844 3.147055 C 1.395035 -2.601822 3.964852 H 1.885019 -3.526059 3.605251 H 1.825502 -2.362183 4.953449 H 0.327129 -2.845022 4.116419 C 4.612105 0.104491 3.451224 O 3.739930 -1.009268 3.172873 C 4.476355 -2.249613 3.246313 C 5.936788 -1.843988 3.289205 C 5.869753 -0.514684 4.031570 H 4.813935 0.628655 2.505934 H 4.095206 0.786647 4.139466 H 4.163819 -2.780995 4.159156 H 4.209334 -2.857614 2.370804 H 6.561193 -2.597411 3.789906 H 6.309586 -1.691113 2.266149 H 5.759510 -0.677820 5.116241 H 6.751796 0.121852 3.872647

Model3-Zr$(Me)_2(THF)_2$ methylated	
	116 a3-ZrCH34THF2+CH3Hf SCF Done: -8324.55270574 A.U. Si 1.458053 -3.080481 0.317792

	Si 0.367629 3.602688 -1.135957 Si -4.723067 0.754747 2.355929 Si 5.178827 -1.054797 -0.877154 Si -1.019208 -1.307128 0.539165 Si -1.523030 5.243195 0.582701 Si 5.364609 2.063788 -1.437667 Si -0.992838 -5.207951 -2.585654 Si -1.097020 0.928020 -1.741441 Si 2.805000 -2.391895 -2.458293 Si 1.455016 3.519380 -4.123124 Si -6.388430 -0.088939 -0.231077 Si -3.535825 -3.156481 0.689631 Si -4.169295 3.464428 0.793719 Si 4.143799 1.830488 -4.377878 Si 0.484826 -0.716994 -3.994480 Si -2.549699 -6.081920 0.010611 Si -3.750751 2.710069 -2.291983 Si -4.544315 -1.877988 -2.047845 O 2.172972 -1.980322 1.321555 O 1.473071 3.913883 0.055623 O -3.583796 -0.223272 3.009864 O 4.811649 -1.757159 0.557767 O -0.247436 -0.609956 1.773690 O -0.361353 5.166512 1.749120 O -0.076739 -2.519607 -0.092219 O -0.908797 4.584652 -0.818058 H -5.596120 1.223927 3.450528 H 4.391890 3.015923 -0.838671 O -1.124771 -3.569545 -2.440901 O -0.072042 2.021032 -1.050598

	O -5.612490 -0.060894 1.227708 O 2.277250 -3.179463 -1.112316 O 0.953006 3.960061 -2.612969 O 4.118421 -1.479656 -2.068826 H 2.023536 4.728376 -4.775644 H -4.601761 -3.093629 1.703861 O -4.011101 2.055748 1.621905 O 5.123642 0.593274 -0.722817 O -2.444903 -1.959450 1.073072 O -2.827337 4.368274 1.070898 H 0.399031 -5.643046 -2.888597 O -1.391284 -0.264064 -0.664830 H -1.955166 6.627785 0.310341 H -7.507264 -1.062959 -0.119691 O 5.136276 1.979619 -3.068973 O -1.391192 -5.968764 -1.158388 O -2.494799 1.653378 -2.135871 O 1.634905 -1.395348 -3.023257 H 0.302824 2.968542 -4.880712 H -6.872619 1.271440 -0.581281 O -4.130538 -2.912652 -0.818192 H -5.364579 4.203201 1.247853 H 6.768260 2.494025 -1.206610 H -1.935571 -5.612789 -3.662139 O -0.413529 0.340005 -3.097034 H 3.174278 -3.393009 -3.476978 O 2.619215 2.353172 -4.004110 O -5.346478 -0.569071 -1.421423 O -2.790076 -4.615496 0.747050 O -4.332957 3.144729 -0.808750

	H 4.701539 2.679835 -5.465385 H -3.832151 -6.543972 -0.590886 H -3.266890 3.926388 -2.996364 H -0.398438 -1.768038 -4.551992 H -5.454796 -2.631573 -2.949374 H 4.062335 0.404423 -4.778005 H 1.148834 0.062666 -5.069240 H -2.054258 -7.019531 1.047686 H -4.842527 2.040311 -3.037373 H -3.341705 -1.384286 -2.753484 H 1.991863 3.164472 0.397661 H -3.116177 -0.840441 2.419433 H 3.872437 -1.799423 0.847661 H 0.484648 4.837665 1.391698 H 6.546599 -1.468319 -1.251441 Zr 1.574354 -0.505944 2.625840 O 0.438773 1.198043 3.790474 C 1.001532 1.876185 4.920482 C -0.733627 1.898725 3.306239 H 2.094397 1.932832 4.791466 H -0.469047 2.405414 2.365295 C 0.319762 3.233037 4.948537 H 0.830506 3.941325 4.277053 C -1.060422 2.902734 4.392318 H -1.520249 1.160467 3.115872 H 0.786959 1.285386 5.826924 H 0.301689 3.669551 5.957236 H -1.696700 2.444459 5.166562 H -1.579645 3.778328 3.980780 C 2.424554 1.389476 1.696508

	H 3.237728 1.182273 0.981171 H 1.511788 1.641905 1.125144 H 2.699038 2.242979 2.337561 C 1.325827 -1.464872 4.667841 H 1.612450 -2.533151 4.636199 H 1.873858 -1.005355 5.509460 H 0.248635 -1.431917 4.916170 C 4.907842 0.273746 3.185876 O 3.840822 -0.685856 3.333086 C 4.362739 -1.937492 3.828234 C 5.870067 -1.815108 3.715396 C 6.079808 -0.322719 3.941838 H 5.128176 0.385798 2.114404 H 4.564138 1.237313 3.585487 H 4.030403 -2.060173 4.871186 H 3.938106 -2.748893 3.220881 H 6.393138 -2.449806 4.444632 H 6.190063 -2.095956 2.701501 H 6.018722 -0.077402 5.014849 H 7.043427 0.047339 3.563815 C 1.336140 -4.763841 1.065540 H 2.339609 -5.176590 1.249059 H 0.794756 -4.725709 2.023122 H 0.796397 -5.446021 0.391615 H -0.682909 -3.159458 -1.672934

$Zr(Me)_4$	
Zero-point correction= 0.135424 (Hartree/Particle) Thermal correction to Energy= 0.147842 Thermal correction to Enthalpy= 0.148786	17 ZrCH34 SCF Done: -206.336105716 A.U. Zr -0.000095 -0.000005 0.000041

Thermal correction to Gibbs Free Energy= 0.097295	C -1.762463 1.333349 -0.243157
Sum of electronic and zero-point Energies= -206.200682	H -1.788331 1.791546 -1.249933
Sum of electronic and thermal Energies= -206.188264	H -2.711158 0.780424 -0.107321
Sum of electronic and thermal Enthalpies= -206.187320	H -1.751956 2.157659 0.494829
Sum of electronic and thermal Free Energies= -206.238811	C 1.267636 0.743864 1.668018
	H 0.844551 1.660026 2.121710
	H 1.362248 -0.009839 2.472492
	H 2.289889 0.988150 1.322262
	C 1.184553 -0.013344 -1.881255
	H 1.263368 -1.032837 -2.303893
	H 0.724403 0.630270 -2.654700
	H 2.214227 0.355581 -1.714248
	C -0.689385 -2.063900 0.456267
	H -0.305892 -2.413019 1.433628
	H -1.793586 -2.123145 0.494251
	H -0.345991 -2.784433 -0.309966

$Zr(Me)_4(THF)_1$	
Zero-point correction= 0.255142 (Hartree/Particle)	30
Thermal correction to Energy= 0.273450	ZrCH34THF SCF Done: -438.365712556 A.U.
Thermal correction to Enthalpy= 0.274394	Zr -1.169776 0.002268 0.001111
Thermal correction to Gibbs Free Energy= 0.208641	C -0.957912 2.112789 -0.744935
Sum of electronic and zero-point Energies= -438.110570	H -0.405083 2.189416 -1.700474
Sum of electronic and thermal Energies= -438.092263	H -1.975498 2.508306 -0.925498
Sum of electronic and thermal Enthalpies= -438.091319	H -0.475148 2.795186 -0.019799
Sum of electronic and thermal Free Energies= -438.157071	C -0.614232 -0.396441 2.142673
	H -0.018899 0.429453 2.578014
	H -1.527154 -0.499355 2.757660
	H -0.028932 -1.326996 2.272722
	C -0.938488 -1.686288 -1.464763

	H -1.945725 -1.967027 -1.826587 H -0.336324 -1.411550 -2.351389 H -0.491704 -2.599114 -1.027084 C -3.408182 -0.050140 0.225375 H -3.758253 -1.031213 0.599783 H -3.769532 0.714453 0.939395 H -3.928366 0.132910 -0.734135 C 2.128385 1.187572 0.035575 O 1.298957 0.044598 -0.215408 C 2.083729 -1.157374 -0.214552 C 3.443522 -0.751021 0.327676 C 3.552377 0.693314 -0.147364 H 1.838928 1.986724 -0.659855 H 1.948964 1.539327 1.066832 H 1.574445 -1.912961 0.400966 H 2.144999 -1.536441 -1.248266 H 3.446997 -0.794353 1.428629 H 4.251445 -1.399768 -0.039022 H 4.280071 1.290987 0.419570 H 3.838947 0.730024 -1.210773

$Zr(Me)_4(THF)_2$	
Zero-point correction= 0.375687 (Hartree/Particle)	43
Thermal correction to Energy= 0.399610	ZrCH34THF2 SCF Done: -670.387547782 A.U.
Thermal correction to Enthalpy= 0.400554	Zr 0.018758 0.881852 -0.060344
Thermal correction to Gibbs Free Energy= 0.321245	C 1.466991 2.632951 -0.047132
Sum of electronic and zero-point Energies= -670.011861	H 2.162194 2.591300 -0.908320
Sum of electronic and thermal Energies= -669.987938	H 0.955680 3.609257 -0.090134
Sum of electronic and thermal Enthalpies= -669.986993	H 2.088422 2.639246 0.869672
Sum of electronic and thermal Free Energies= -670.066302	C 0.249866 -0.131225 1.968389

	H 1.225251 0.176700 2.392038 H -0.517737 0.221844 2.682172 H 0.221970 -1.236678 1.979386 C -0.015316 0.055439 -2.175509 H -0.884371 0.469675 -2.721993 H 0.889305 0.463576 -2.667606 H -0.010946 -1.036779 -2.339580 C -1.637823 2.436956 0.089536 H -2.672163 2.045695 0.071006 H -1.528604 3.036914 1.013529 H -1.548600 3.155093 -0.747773 C 3.480690 0.111625 0.331730 O 2.234316 -0.295133 -0.241148 C 2.230279 -1.703434 -0.490984 C 3.432333 -2.249239 0.260642 C 4.407671 -1.081349 0.166299 H 3.824693 1.019003 -0.182904 H 3.320602 0.357975 1.395860 H 1.271903 -2.122405 -0.148432 H 2.313732 -1.872877 -1.578317 H 3.169125 -2.445796 1.312436 H 3.814086 -3.183197 -0.175778 H 5.200700 -1.105250 0.927214 H 4.889919 -1.062139 -0.824469 C -2.835003 -0.936464 -1.099090 O -2.029714 -0.604061 0.036620 C -2.813645 -0.682748 1.237223 C -4.241517 -0.952568 0.786124 C -4.028020 -1.683565 -0.533479 H -3.145960 -0.006902 -1.608535

	H -2.225436 -1.524436 -1.796997 H -2.412246 -1.499613 1.858809 H -2.708183 0.259248 1.794061 H -4.812409 -1.529725 1.527359 H -4.775202 -0.004336 0.613115 H -3.771887 -2.740918 -0.356009 H -4.900008 -1.653271 -1.202352

THF	
Zero-point correction= 0.117288 (Hartree/Particle) Thermal correction to Energy= 0.122137 Thermal correction to Enthalpy= 0.123081 Thermal correction to Gibbs Free Energy= 0.089248 Sum of electronic and zero-point Energies= -231.892327 Sum of electronic and thermal Energies= -231.887478 Sum of electronic and thermal Enthalpies= -231.886534 Sum of electronic and thermal Free Energies= -231.920366	13 THF SCF Done: -232.009614803 A.U. C 1.153335 -0.430411 0.133729 O -0.000082 -1.235150 -0.000162 C -1.153449 -0.430238 -0.133528 C -0.726560 0.987113 0.230891 C 0.726765 0.986941 -0.230985 H 1.526184 -0.474205 1.176318 H 1.950703 -0.823385 -0.518934 H -1.526780 -0.474116 -1.175932 H -1.950591 -0.823013 0.519544 H -1.345375 1.761037 -0.246157 H -0.780127 1.137018 1.321832 H 0.780388 1.136598 -1.321957 H 1.345709 1.760839 0.245936

TMS	
Zero-point correction= 0.147187 (Hartree/Particle) Thermal correction to Energy= 0.156522 Thermal correction to Enthalpy= 0.157466	17 TMS SCF Done: -448.656749682 A.U. Si -0.000009 -0.000004 -0.000005

Thermal correction to Gibbs Free Energy= 0.114764	C 0.745057 -0.989634 1.422670
Sum of electronic and zero-point Energies= -448.509563	H 0.135036 -0.895476 2.335402
Sum of electronic and thermal Energies= -448.500228	H 0.809686 -2.060548 1.171601
Sum of electronic and thermal Enthalpies= -448.499284	H 1.762057 -0.639286 1.661510
Sum of electronic and thermal Free Energies= -448.541986	C -1.736756 -0.637862 -0.367932
	H -2.392460 -0.536977 0.511810
	H -2.199127 -0.077970 -1.196667
	H -1.718010 -1.702360 -0.651795
	C -0.087927 1.822243 0.479839
	H 0.913752 2.224264 0.701394
	H -0.519810 2.427564 -0.333268
	H -0.713380 1.968330 1.375126
	C 1.079640 -0.194744 -1.534577
	H 1.150641 -1.251093 -1.839789
	H 0.668926 0.373049 -2.384868
	H 2.102735 0.170527 -1.350378

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