CO_2 activation through silylimido and silylamido zirconium hydrides supported on N-donor chelating SBA15 surface ligand

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Supporting Information

Computational Details: All the calculations have been performed using a cluster silica (2T) model. Plausible elementary steps for CO2 insertion process for these different hydrides were designed. The study performed using M06/TZVP density functional theory (DFT) [1] method over Gaussian 09 package.[2] Zirconium [Zr] described by effective core pseudo-potentials (SDD) and the associated basis sets with a polarization function.[3-5] The calculation were performed assuming the singlet state of [Zr] because of the stability. The transition states were located using the synchronous transit-guided quasi-newton (QST2) approach and the character of the stationary points has been checked by analytical frequency calculations. The Gibbs Free energies were computed assuming an ideal gas, unscaled harmonic vibrational frequencies and the rigid rotor approximation at 298.15 K and 1 atm. Since we discussed several reaction steps, heavily interconnected, we decided to assume the initial Zr hydride as reference states at 0 kcal mol^{-1}. All other species are thus referred to this reference state, by adding/subtracting the energy of the CO_2.

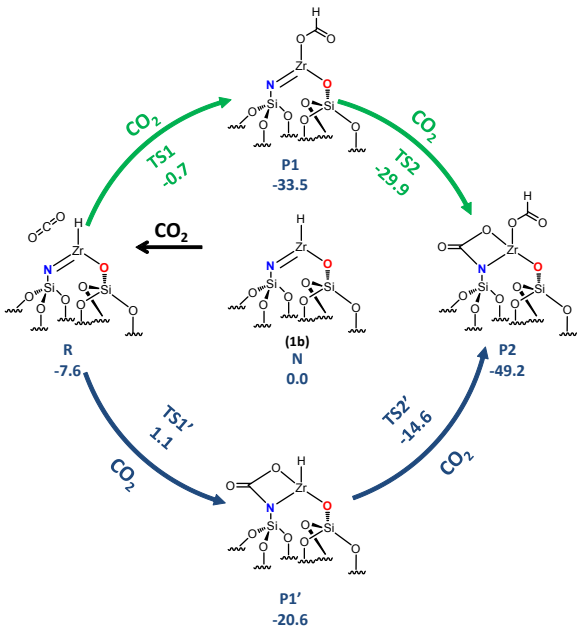


Fig. S1: CO_2 insertion into [(≡Si-O-)(Si-N=)[Zr]H], **1b.**

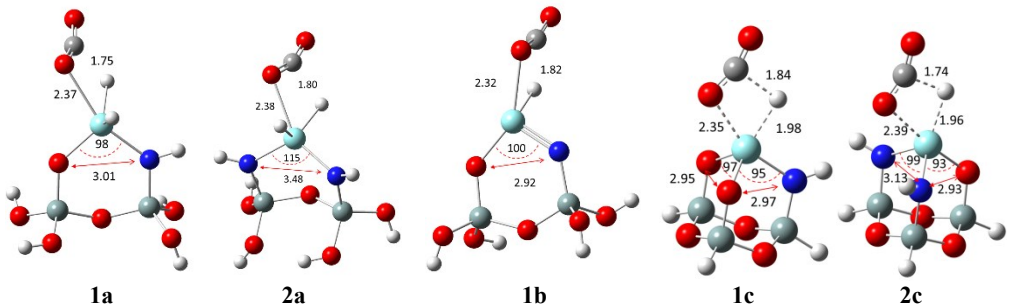


Fig. S2. The first transition state for complexes **1a**, **2a**, **1b, 1c** and **2c**. oxygen (red), nitrogen (blue), carbon (black), zirconium (cyan)

silica (grey) and hydrogen (white).

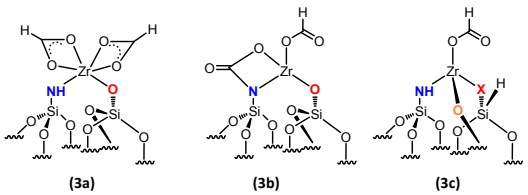
Table S1: The natural population analysis (NPA) charges on Zr atom in different supported complexes.

	1a	2a	1b	1c	2c
R	1.86	1.73	1.89	1.8	1.7
TS1	1.87	1.72	1.9	1.81	1.72
TS2	2.05	1.88	2.17	-	-
P2	2.26	2.17	2.26	2.06	1.697

Solid-State Nuclear Magnetic Resonance Spectroscopy

One-dimensional ^{1}H MAS and ^{13}C CP/MAS solid state NMR spectra were recorded on Bruker AVANCE III spectrometers operating at 400 MHz resonance frequencies for ^{1}H. Experiments at 400 MHz employed a conventional double-resonance 3.2 mm CP/MAS probe. In all cases the samples were packed into rotors under an inert atmosphere inside gloveboxes. Dry nitrogen gas was utilized for sample spinning to prevent degradation of the samples. NMR chemical shifts are reported with respect to the external references TMS and adamantane. For ^{13}C CP/MAS NMR experiments, the following sequence was used: 90° pulse on the proton (pulse length 2.4 s), then a cross-polarization step with a contact time of typically 2 ms, and finally acquisition of the ^{13}C NMR signal under high-power proton decoupling. The delay between the scans was set to 5 s to allow the complete relaxation of the ^{1}H nuclei, and the number of scans ranged between 3000 and 5000 for ^{13}C and was 32 for ^{1}H. An exponential apodization function 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: 90° proton pulse, t_1 evolution period, CP to ^{13}C, and detection of the ^{13}C magnetization under TPPM decoupling. For the cross-polarization step, a ramped radio frequency (RF) field centered at 75 kHz was applied to the protons, while the 13C channel RF field was matched to obtain an optimal signal. A total of 32 t1 increments with 2000 scans each were collected. The sample spinning frequency was 8.5 kHz. Using a short contact time (0.5 ms) for the CP step, the polarization transfer in the dipolar correlation experiment was verified to be selective for the first coordination, to lead to correlations only between pairs of attached $^{1}H-^{13}C$ spins (C−H directly bonded).



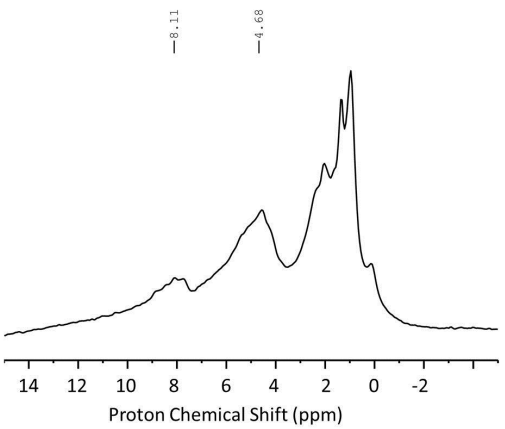


Fig. S3: ^{1}H Solid State NMR spectrum of **1a**, **1b** and **1c** after CO_2 insertion to yield **3a**, **3b** and **3c**

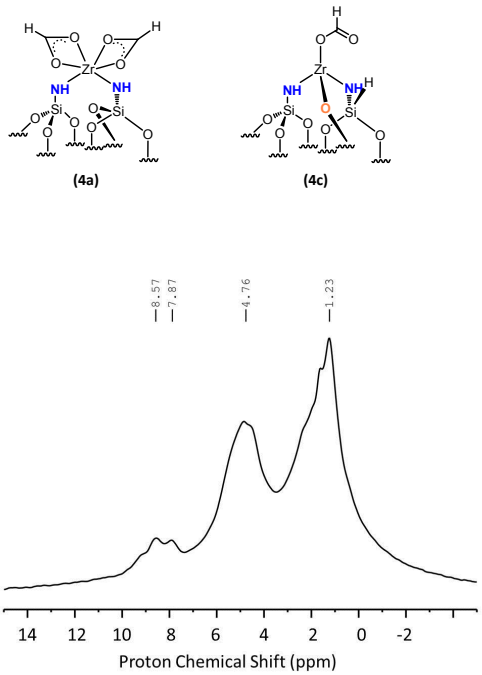


Fig. S4: ^{1}H Solid State NMR spectrum of **2a** and **2c** after CO_2 insertion to yield **4a** and **4c**

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(2) M. J. Frisch, G. W. T., H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, ; 09 ed.; Gaussian, Inc.: Wallingford CT, 2009, 2009.

(3) Andrae, D.; Haussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor Chim Acta* **1990**, *77*, 123.

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(5) Hollwarth, A.; Bohme, M.; Dapprich, S.; Ehlers, A. W.; Gobbi, A.; Jonas, V.; Kohler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem Phys Lett* **1993**, *208*, 237.

COORDINATES

3
CO2 Energy E= -188.572478404 A.U.
C 0.000000 0.000000 0.000000
O 0.000000 0.000000 1.154703
O 0.000000 0.000000 -1.154703

17
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O 1.540317 0.379455 -0.387372
Si 0.589032 1.678812 -0.053267
O 2.229273 -1.522690 1.295430
O 0.816207 1.931259 1.562103
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H 0.126006 2.425970 2.005596
H 2.131159 -2.392560 1.683041
H 2.691313 -2.056943 -1.630368
H 1.892385 3.319086 -0.870340
H -2.710061 -0.330368 1.696536
H -3.043965 -1.072264 -1.328229

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N 0.896379 -1.685910 -0.086707
Si 0.768326 1.791049 -0.060230
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N 0.308934 -1.643578 -0.297157
Si 1.308166 1.678100 0.143992
O 1.993482 0.279137 0.645111
Si 1.932059 -1.312134 0.215930
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O 2.448765 -2.181283 1.517331
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H 2.022096 3.107949 -1.419089
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H -1.635105 -0.593358 -2.324072

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23
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18
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Zr -0.002291 1.871029 -0.011573
N 1.676773 0.770051 -0.389196
N -1.678802 0.766070 -0.388727
Si 1.571563 -0.898300 0.017779
O 0.001245 -1.022798 0.524167
Si -1.569395 -0.902103 0.017787
O 1.937614 -1.856196 -1.260577
O -1.932957 -1.860594 -1.260849
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21
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21

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24

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O 1.767287 3.033194 0.178270
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H 0.086900 -2.858186 0.173390
C -2.742261 1.269701 1.353723
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O -3.042949 1.699642 2.387396
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H 2.671917 3.343398 0.244022
H 1.954772 -1.819692 2.822928
O -2.036602 -0.688781 -2.004618
C -2.758135 -1.532335 -1.409920
O -2.582174 -1.775527 -0.193068
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24

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H -1.399078 2.966066 0.400811
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C 3.530655 -0.732791 -0.928146
O 2.840076 0.149274 -1.504455
H 4.560250 -0.925425 -1.263641
H 0.500938 -2.914504 0.216071

15

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18

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C -2.756164 0.237197 1.381111
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O -3.187238 1.061582 2.041294
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18

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N 0.391451 1.285398 -0.278477
Si -1.938215 -1.285059 0.143819
O -2.188921 0.336359 0.178738
Si -1.246736 1.691175 0.017055
O -2.669948 -2.021221 -1.125485
O -1.803296 2.582273 -1.255012
O -2.560457 -1.936672 1.518740
O -1.475997 2.475164 1.455356
H 2.344609 -0.323429 1.222033
C 3.916774 -0.098788 0.315657
O 3.483583 -0.156507 -0.803278
O 4.708128 -0.000802 1.148817
H -2.737129 2.795002 -1.231713
H -3.581165 -2.277739 -0.982608
H -2.603420 -1.342869 2.269187
H -0.893224 3.220246 1.605427

18

1B_P1 Energy E= -1324.09658474 A.U.

Zr -1.322955 -0.240012 0.029106
O 0.077263 -1.590703 -0.296452
N -0.326262 1.298943 0.097499
Si 1.699364 -1.370671 -0.088725
O 2.098648 0.167141 -0.520359
Si 1.366886 1.576777 -0.034391
O 1.916011 -1.619199 1.522636
O 2.119422 1.935220 1.388678
O 2.608676 -2.399078 -0.979544
O 1.693138 2.785520 -1.106921
H -4.952087 0.314614 -0.064287
C -3.873416 0.108273 -0.024508
O -3.214805 0.080402 -1.102599
O -3.320931 -0.090816 1.088180
H 1.986336 2.823700 1.719453
H 2.734838 -1.285407 1.892655
H 2.965573 -2.033114 -1.789077
H 0.960985 3.005083 -1.683766

21

1B_TS2 Energy E= -1512.68166095 A.U.

Zr 1.273236 -0.342307 -0.130926
O -0.088615 -1.711083 -0.451737
N 0.187548 1.087550 0.460899
Si -1.727342 -1.501753 -0.401024
O -2.081180 -0.448765 0.817128
Si -1.443704 1.074222 1.013721
O -2.087250 -0.869390 -1.874297
O -2.431182 2.040109 0.108549
O -2.551554 -2.890039 -0.148744
O -1.470536 1.461799 2.607933
H 4.568195 -0.748077 1.484923
C 3.610454 -0.622649 0.960631
O 2.551106 -1.053897 1.507580
O 3.569341 -0.063477 -0.158031
H -2.035353 2.852313 -0.216042
H -2.960412 -0.485775 -1.970569
H -2.711760 -3.127339 0.764839
H -2.335400 1.542220 3.011326
C 0.520616 1.939775 -1.384389
O -0.057851 2.943211 -1.424622
O 1.252803 1.107629 -1.871129

21

1B_P2_new Energy E= -1512.71375789 A.U.

Zr -1.419386 0.107156 -0.343170
O -0.274130 1.659114 -0.308584
N 0.143461 -1.224389 0.030895
Si 1.382121 1.758750 -0.159793
O 1.911344 0.614164 0.874328
Si 1.643369 -1.018029 0.909338
O 2.053957 1.394266 -1.612712
O 2.794229 -1.925225 0.194414

O 1.705029 3.262755 0.385528
O 1.529291 -1.355255 2.504453
H -4.299885 0.142319 1.952565
C -3.444423 0.114222 1.264960
O -2.326500 -0.295050 1.665288
O -3.586939 0.493653 0.067225
H 2.507181 -2.268194 -0.667488
H 1.936435 2.001266 -2.343250
H 2.522994 3.379433 0.869793
H 1.680993 -2.269454 2.746027
C 0.087193 -1.687758 -1.274165
O 0.869859 -2.397494 -1.846512
O -1.024890 -1.154647 -1.859120
18
1B_TS1A_ Energy E= -1324.03660521 A.U.
Zr -0.890653 -1.446288 -0.417086
O 1.013049 -1.632016 0.054122
N -1.013631 0.420216 -0.541653
Si 2.100464 -0.413085 0.253748
O 1.643067 0.919566 -0.575711
Si 0.158132 1.673755 -0.422352
O 2.058106 0.090509 1.837568
O 0.159754 2.435135 1.044768
O 3.574840 -0.948616 -0.204427
O -0.047618 2.804567 -1.583957
H -1.172754 -2.055573 -2.149052
H 0.733109 2.014175 1.694279
H 2.421833 -0.493886 2.502850
H 4.181762 -0.289216 -0.541249
H 0.263998 3.681129 -1.355742
C -2.689880 0.280939 0.704553
O -3.094096 1.345454 0.878799
O -2.705538 -0.924802 0.855971
18
1B_P1A_ Energy E= -1324.07492188 A.U.
Zr -1.014018 -1.467561 -0.507696
O 0.927414 -1.573434 -0.394893
N -1.036079 0.557232 -0.294414
Si 1.969164 -0.522215 0.345626
O 1.633425 0.989766 -0.200698
Si 0.211716 1.791168 -0.419824
O 1.599637 -0.715108 1.933774
O -0.098219 2.933860 0.700917
O 3.545518 -0.839913 0.074797
O 0.338551 2.426043 -1.921824
H -1.671435 -1.915110 -2.180289
C -1.978086 0.488346 0.750327
O -2.377410 -0.785302 0.866817
O -2.334455 1.401813 1.447315
H -0.900643 2.735575 1.212910
H 2.107152 -0.227873 2.583447
H 3.952884 -0.374829 -0.656900
H -0.214182 3.186850 -2.103227
21
1B_TS2A Energy E= -1512.65375812 A.U.
Zr -1.292536 0.070641 -0.215364
O -0.108275 1.592589 -0.377721
N 0.229886 -1.231504 0.321558
Si 1.531943 1.793413 -0.200352
O 1.988953 0.723863 0.973831
Si 1.855311 -0.914651 0.841790
O 2.337437 1.420284 -1.578427
O 2.885477 -1.327669 -0.385061
O 1.765261 3.345612 0.226084
O 2.149068 -1.637852 2.271408
H -2.392938 0.085712 1.381217
C -3.903109 0.382096 0.615710
O -3.530170 0.464300 -0.531503
O -4.681371 0.393728 1.468646
H 2.625949 -2.152085 -0.821024
H 2.767397 0.554583 -1.560775
H 2.627587 3.717499 0.039784
H 3.010522 -1.515123 2.670927
C -0.056322 -2.069814 -0.762330
O -1.206308 -1.639613 -1.323024
O 0.623523 -2.969252 -1.175093
15
1C_N Energy E= -1349.82565546 A.U.
Zr -1.634483 -0.047360 -0.000009
O -0.603759 -0.872597 -1.460649
O -0.603778 -0.872499 1.460720
N -0.722892 1.790850 -0.000071
Si 1.055614 -0.825245 -1.434957
O 1.476242 0.775293 -1.316245
Si 1.022455 1.691657 -0.000047
Si 1.055572 -0.825157 1.435021
O 1.523677 -1.521867 0.000051
O 1.476260 0.775368 1.316185
H 1.677603 -1.472705 -2.584653
H 1.696695 2.992322 -0.000065
H 1.677608 -1.472537 2.584736
H -1.130865 2.717206 0.000145
H -3.501582 -0.252994 -0.000044
18
1C_R Energy E= -1538.40619501 A.U.
Zr 0.793327 -0.831062 0.000086
O 0.276707 0.365555 -1.488305
O 0.276028 0.364874 1.488877
N -0.924629 -1.950884 -0.000563
Si -1.179233 1.157280 -1.438936
O -2.355437 -0.007455 -1.316799
Si -2.404770 -1.028094 -0.000629
Si -1.179913 1.156548 1.439285
O -1.222018 1.990620 0.000361
O -2.356187 -0.008004 1.316033
H -1.401477 2.039981 -2.579891
H -3.627669 -1.835464 -0.001033
H -1.402710 2.038695 2.580563
H 2.360410 -1.907680 0.000034
H -1.001262 -2.960047 0.000873
C 4.073802 0.440106 0.000119
O 2.945030 0.714347 0.000870
O 5.193882 0.190350 -0.00063818
1C_TS Energy E= -1538.39695532 A.U.
Zr 1.005370 0.237375 0.000003
O 0.082258 -0.683578 1.476436
O 0.082204 -0.683306 -1.476574
N -0.234885 1.875921 0.000146
Si -1.559738 -0.935261 1.437798
O -2.259901 0.561757 1.316325
Si -1.943876 1.536088 0.000144
Si -1.559788 -0.935008 -1.437931
O -1.883379 -1.705054 -0.000128
O -2.259981 0.561969 -1.316180
H -2.057163 -1.690556 2.582251
H -2.807120 2.719720 0.000245
H -2.057233 -1.690114 -2.582501
H 2.684172 1.295881 0.000079
H 0.051410 2.845909 -0.000039
C 3.851313 -0.130737 -0.000009
O 3.017432 -0.989512 -0.000071
O 4.895750 0.357185 0.000030
18
1C_P Energy E= -1538.46420535 A.U.
Zr -1.118084 -0.121230 0.000072
O -0.017159 -0.858108 -1.447982
O -0.017057 -0.857636 1.448379
N -0.184094 1.712679 -0.000263
Si 1.643554 -0.793311 -1.432100
O 2.049739 0.806983 -1.316776
Si 1.552285 1.706549 -0.000358
Si 1.643580 -0.792717 1.432371
O 2.118109 -1.491088 0.000241
O 2.049898 0.807489 1.316331
H 2.259085 -1.442616 -2.584534
H 2.183734 3.028829 -0.000631
H 2.259288 -1.441487 2.585009
H -4.844967 0.084903 -0.000296
H -0.677526 2.595558 -0.000276
C -3.745674 0.067862 -0.000103
O -3.146337 -1.047725 -0.000077
O -3.092872 1.132682 0.000074
16
2C_N Energy E= -1329.90763772 A.U.
Zr 1.645101 -0.000069 0.048776
N 0.697152 1.572655 -0.871785
O 0.565778 -0.000313 1.699297
N 0.696868 -1.572372 -0.872376
Si -1.043629 1.461098 -0.846740
O -1.451704 0.000356 -1.525861
Si -1.043851 -1.460709 -0.847293
Si -1.091884 -0.000263 1.639994
O -1.530720 1.326016 0.742091
O -1.530918 -1.326149 0.741617
H -1.727215 2.574698 -1.510943
H -1.727707 -2.573912 -1.511874
H -1.724398 -0.000496 2.955429
H 1.098457 -2.434299 -1.219656
H 1.098572 2.434336 -1.219862
H 3.511722 -0.000604 0.264386
19
2C_R Energy E= -1518.48828970 A.U.
Zr -0.807550 0.822282 -0.147133
N -0.230064 -0.509670 -1.618204
O -0.359375 -0.292004 1.423409
N 0.897325 1.962628 -0.101718
Si 1.316761 -1.256288 -1.332654
O 2.431086 -0.034146 -1.182054
Si 2.383293 1.066910 0.062699
Si 1.109382 -1.052592 1.540843
O 1.289247 -1.978708 0.175938
O 2.264474 0.135859 1.439078
H 1.718140 -2.233915 -2.349573
H 3.592496 1.895445 0.089813
H 1.252855 -1.847431 2.757608
H -2.407698 1.842925 -0.103238
H 0.964827 2.971466 -0.147049
C -4.045391 -0.440815 0.058998
O -2.978132 -0.746285 -0.286465
O -5.106261 -0.161907 0.395121
H -0.877527 -1.040496 -2.189392
19
2C_TS Energy E= -1518.48052226 A.U.
Zr 1.009223 -0.325549 0.002402
N 0.252619 1.423506 -0.815872
O -0.038667 -0.276126 1.650608
N -0.252636 -1.597307 -1.000621
Si -1.470789 1.618616 -0.718734
O -2.180028 0.314085 -1.469535
Si -1.957795 -1.233258 -0.900160
Si -1.677311 0.018294 1.673564
O -1.919589 1.452506 0.886202
O -2.345067 -1.158500 0.715726
H -1.978072 2.885259 -1.255446
H -2.819690 -2.176650 -1.617955
H -2.238600 0.022130 3.020365
H 2.736818 -1.272547 0.050797

H	0.020816	-2.123287	-1.823513
C	3.853143	0.151378	0.016216
O	3.009741	0.996695	-0.047256
O	4.907470	-0.316797	0.064055
H	0.802729	2.249352	-1.01596019

2C_P Energy E= -1518.54483798 A.U.

Zr	1.127267	-0.115712	0.028012
N	0.176526	1.616283	-0.571310
O	0.028998	-0.366578	1.627959
N	0.035907	-1.375961	-1.173221
Si	-1.557587	1.626703	-0.528095
O	-2.092989	0.359718	-1.466699
Si	-1.701760	-1.212783	-1.092953
Si	-1.631158	-0.277242	1.627847
O	-2.029813	1.209189	1.022315
O	-2.132941	-1.388802	0.504360
H	-2.186186	2.888713	-0.930802
H	-2.429765	-2.149626	-1.953827
H	-2.220140	-0.517300	2.941245
H	4.854690	0.132201	-0.003531
H	0.388941	-1.810622	-2.018188
C	3.755598	0.093285	0.004565
O	3.177883	-1.024781	0.129144
O	3.084159	1.141241	-0.110680
H	0.665850	2.489767	-0.717451