Electronic Supplementary Material (ESI) for Chemical Communications

Splitting of Dihydrogen by Five-membered Zirconacycloallenoids: A Novel Pathway to Conjugated Diene Zirconocene Complexes

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‡ X-ray crystal structure analyses.

§ Computational chemistry

SUPPORTING INFORMATION

General Procedures. All syntheses involving air- and moisture-sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of argon. Solvents were dried with the procedure according to Grubbs (A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics*, 1996, **15**, 1518) or were distilled from appropriate drying agents and stored under an argon atmosphere. Dichlorobis(*η*^{5}-cyclopentadienyl)zirconium (J. J. Eisch, F. A. Owuor, P. O. Otieno, *Organometallics*, 2001, **20**, 4132) and 2-methyl-4-trimethylsilylbutenyne (**1b**) (J. Waser, J. C. Gonzalez-Gomez, H. Nambu, P. Huber, E. M. Carreira, *Org. Lett.*, 2005, **7**, 4249) were prepared according to published procedures and fully characterized by NMR spectroscopy. Purchased starting materials and other chemicals or reagents (Aldrich, Fluka, ABCR and Acros) were used without further purification. The following instruments were used for physical characterization of the compounds: NMR spectra: *Bruke*r AV 300 spectrometer (^{1}H: 300 MHz, ^{13}C: 75 MHz), *Varian* Inova 500 (^{1}H: 500 MHz, ^{13}C: 126 MHz), *Varian* UnityPlus 600 (^{1}H: 600 MHz, ^{13}C: 151 MHz). ^{1}H NMR and ^{13}C NMR: chemical shift δ, reported in ppm, is given relative to TMS and referenced to the solvent signal {$CDCl_3$ (δ_H = 7.26, δ_C = 77.0), [d_6]-benzene (δ_H = 7.15, δ_C = 128.0), [d_8]-toluene (δ_H = 2.03, δ_C = 20.4)}. NMR assignments are supported by additional 2D NMR experiments. Elemental analyses were performed on a *Elementar Vario El III*. IR spectra were recorded on a *Varian* 3100 FT-IR (Excalibur Series). Melting points were obtained with a DSC Q20 (*TA Instruments*). Mass spectra were recorded on a Orbitrap LTQ XL (*Thermo Scientific*).

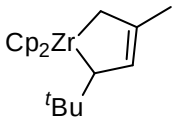
X-Ray diffraction: Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (Nonius B.V., 1998); data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr*. **2003**, *A59*, 228-234); structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr*. **1990**, *A46*, 467-473); structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr*. **2008**, *A64*, 112-122) and graphics, XP (BrukerAXS, 2000). Thermals ellipsoids are shown with 30% probability, *R*-values are given for observed reflections, and *w*R^2 values are given for all reflections.

1,1-Bis(η^5-cyclopentadienyl)-4-methyl-2-*tert*-butyl-1-zirconacyclopenta-3-ene (3a)

At –78 °C *n*-butylmagnesium chloride solution (0.34 ml, 2 M diethyl ether solution, 0.68 mmol, 2 eq) was added to a solution of dichlorobis(η^5-cyclopentadienyl)zirconium (100 mg, 0.34 mmol, 1 eq) and 2,5,5-trimethyl-1-hexen-3-yne (42 mg, 0.34 mmol, 1 eq) in THF (5 ml). After removal of the dry ice bath, the mixture was allowed to warm up to room temperature and stirred for 1 h. Then the yellow solution was heated to 60 °C for additional 1 h. The volatiles were removed *in vacuo* and the residue was extracted with *n*-pentane (3×5 ml) and filtered. After removing the solvent, toluene (5 ml) was added to the residue and the Schlenk flask was filled with 2 bar dihydrogen and stirred for 10 min at room temperature. The volatiles were concentrated *in vacuo* and the residue was extracted with *n*-pentane (3×5 ml) and filtered. The filtrate was cooled to –30 °C. Complex **3a** was obtained as orange crystals (50 mg, 42 %), which were suitable for X-ray crystal structure analysis.

Method B (NMR-experiment)

A solution of diphenylzirconocene (50 mg, 0.13 mmol, 1 eq) and 2,5,5-trimethyl-1-hexen-3-yne (17 mg, 0.14 mmol, 1 eq) in d_8-toluene (3 ml) was irradiated (Philips HPK 125, pyrex filter) for 4 h, then the NMR tube was filled with 1.5 bar dihydrogen. The product **3a** was detected by NMR.



^{1}H NMR (500 MHz, 299 K, [d_8]-toluene): δ = 5.42 (s, 5H, Cp^A), 4.92 (s, 5H, Cp^B), 4.56 (dm, $^3J_{HH}$ = 12.1 Hz, 1H, $CH^=$), 3.16 (ddd, $^2J_{HH}$ = 9.1, J_{HH} = 1.8, 0.5 Hz, 1H, $ZrCH_2$), 1.76 (m, 3H, Me), 1.14 (s, 9H, ^{t}Bu), -0.68 (dm, $^3J_{HH}$ = 12.1 Hz, 1H, ZrCH), -1.00 (dd, $^2J_{HH}$ = 9.1, J_{HH} = 1.4 Hz, 1H, $ZrCH_2$).

^{13}C{^{1}H} NMR (126 MHz, 299 K, [d_8]-toluene): δ = 119.0 ($C^=$), 110.8 ($CH^=$), 103.5 ($^1J_{CH}$ ~ 170 Hz, Cp^A)[1], 100.1 ($^1J_{CH}$ ~ 170 Hz, Cp^B)[1], 85.9 (ZrCH), 53.1 ($ZrCH_2$), 35.8 (^{t}Bu), 33.8 ($^1J_{CH}$ ~ 125 Hz, ^{t}Bu)[1], 29.2 (Me), [[1] from the ghmbc NMR experiment].

^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, 299 K, [d_8]-toluene): δ ^{1}H / ^{1}H = 4.56 / 3.16, 1.76, -0.68, -1.00 ($CH^=$ / $ZrCH_2$, Me, ZrCH, $ZrCH_2$), 3.16 / 4.56, -1.00 ($ZrCH_2$ / $CH^=$, $ZrCH_2$), 1.76 / 4.56, -0.68 (Me / $CH^=$, ZrCH), -0.68 / 4.56, 1.76 (ZrCH / $CH^=$, Me), -1.00 / 4.56, 3.16 ($ZrCH_2$ / $CH^=$, $ZrCH_2$).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 299 K, [d_8]-toluene): δ ^{1}H / δ ^{13}C = 5.42 / 103.5 (Cp^A), 4.92 / 100.1 (Cp^B), 4.56 / 110.8 ($CH^=$), 3.16 / 53.1 ($ZrCH_2$), 1.76 / 29.2 (Me), 1.14 / 33.8 (^{t}Bu), -0.68 / 85.9 (ZrCH), -1.00 / 53.1 ($ZrCH_2$).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 299 K, [d_8]-toluene): δ ^{1}H / δ ^{13}C = 4.56 / 53.1, 35.8, 29.2 ($CH^=$ / $ZrCH_2$, ^{t}Bu, Me), 3.16 / 119.0, 110.8, 29.2 ($ZrCH_2$ / $C^=$, $CH^=$, Me), 1.76 / 119.0,

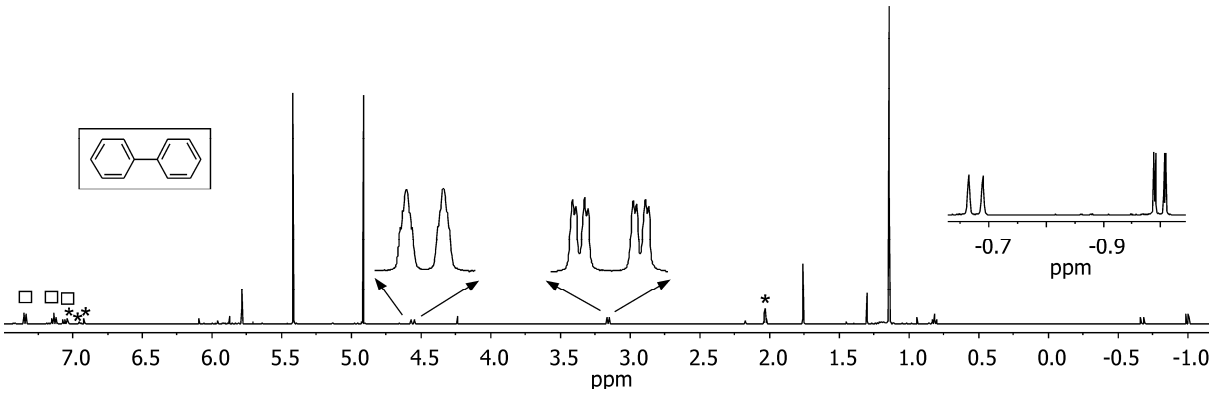
110.8 (Me / $C^{=}$, $CH^{=}$), 1.14 / 85.9, 35.8, 33.8 (^{t}Bu / ZrCH, ^{t}Bu, ^{t}Bu), -0.68 / 119.0, 33.8 (ZrCH / $C^{=}$, ^{t}Bu), -1.00 / 29.2 ($ZrCH_2$ / Me).

^{1}H{^{1}H} NOE-DIFF (500 MHz, 298 K, [d_8]-toluene) [selective experiment]: δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 4.56 / 4.92, 1.76, 1.14 ($CH^{=}$ / Cp^{B}, Me, ^{t}Bu), 3.16 / -1.00 ($ZrCH_2$ / $ZrCH_2$), 1.76 / 4.92, 4.56, 3.16, 1.14 (Me / Cp^{B}, $CH^{=}$, $ZrCH_2$, ^{t}Bu), 1.14 / 5.42, 4.92, 4.56, -0.68 (^{t}Bu / Cp^{A}; Cp^{B}, $CH^{=}$, ZrCH), -0.68 / 5.42, 1.14, -1.00 (ZrCH / Cp^{A}, ^{t}Bu, $ZrCH_2$), -1.00 / 5.42, 3.16, -0.68 ($ZrCH_2$ / Cp^{A}, $ZrCH_2$, ZrCH).

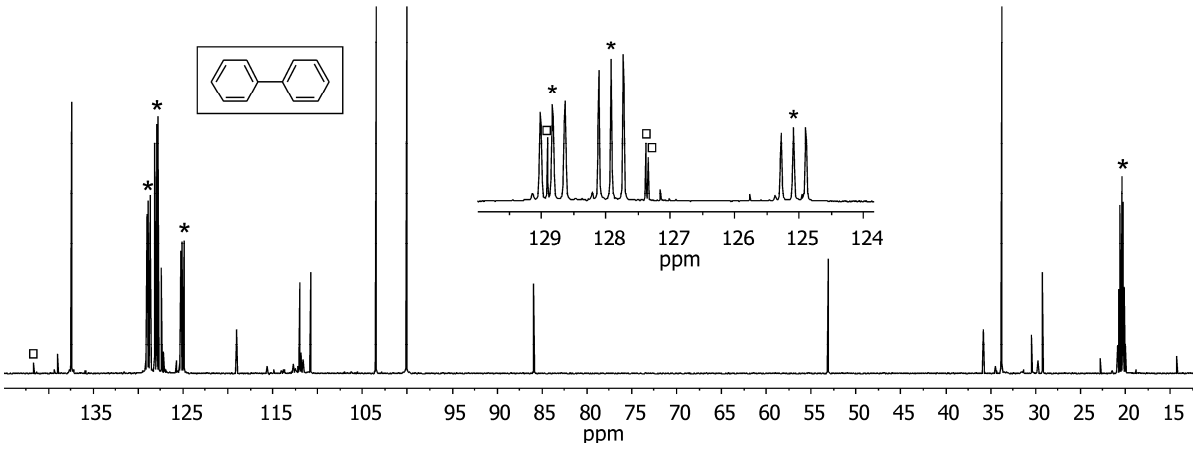
IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3079 (s), 2957 (br), 2858 (m), 1685 (s), 1515 (m), 1470 (m), 1439 (m), 1355 (m), 1228 (m), 1014 (w), 969 (m), 908 (m), 848 (w), 825 (w), 803 (br), 568 (m), 449 (m).

m. p. (DSC): 132 °C

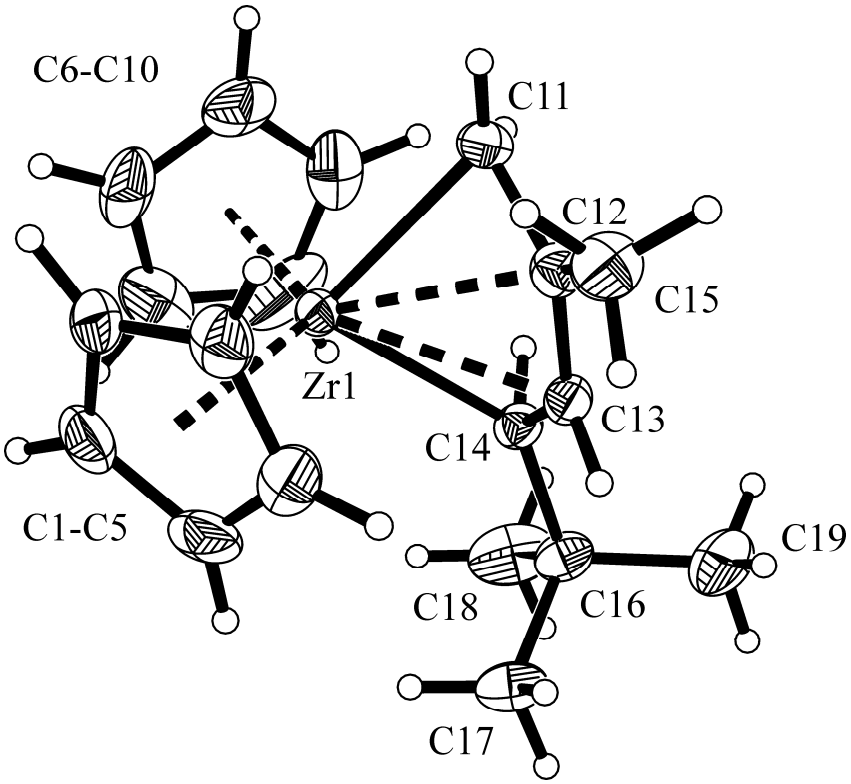
Elemental Analysis: $C_{19}H_{26}Zr$ (345.63 g/mol) requires C 66.02, H 7.58, found: C 65.82, H 7.31.



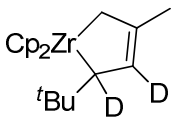
^{1}H NMR (500 MHz, 299 K, [d_8]-toluene (*), squares: the signals of biphenyl)



^{13}C{^{1}H} NMR (126 MHz, 299 K, [d_8]-toluene (*), squares: the signals of biphenyl)



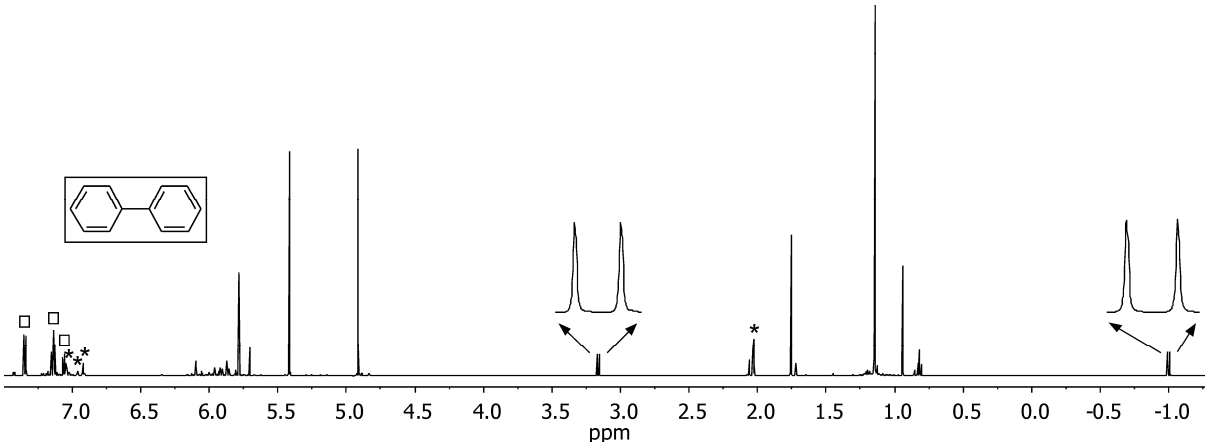
X-ray crystal structure analysis of 3a: formula $C_{19}H_{26}Zr$, M = 345.62, orange crystal, 0.12 x 0.07 x 0.05 mm, a = 16.5305(5), b = 8.3871(3), c = 25.2496(8) Å, β = 105.052(1) º, V = 3380.57(19) Å^3, ρ_{calc} = 1.358 gcm^{-3}, μ = 0.640 mm^{-1}, empirical absorption correction (0.927 ≤ T ≤ 0.968), Z = 8, monoclinic, space group $C2/c$ (No. 15), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 16247 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 4085 independent (R_{int} = 0.042) and 3355 observed reflections [I>2σ(I)], 201 refined parameters, R = 0.036, wR^2 = 0.096, max. (min.) residual electron density 0.33 (-0.64) e.Å^{-3}, hydrogen atoms at C11, C13 and C14 were refined freely, others were refined as riding atoms.



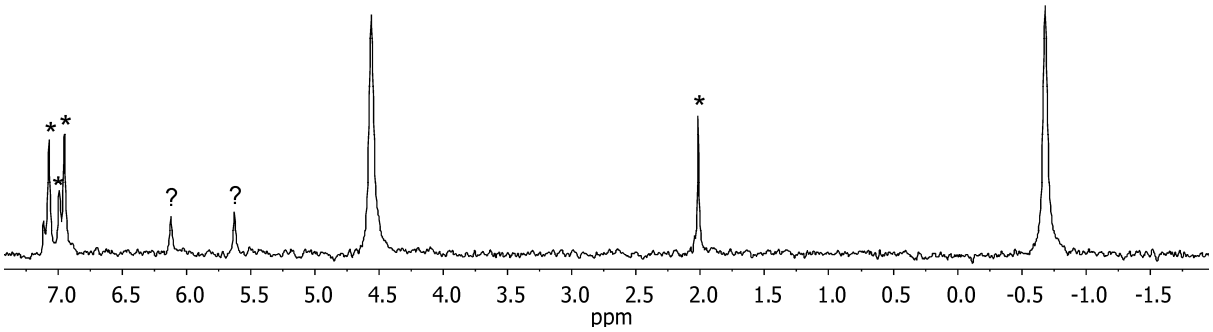
^{1}H NMR (500 MHz, 299 K, [d_8]-toluene): δ = 5.42 (s, 5H, Cp^A), 4.91 (s, 5H, Cp^B), 3.16 (d, $^2J_{HH}$ = 9.1 Hz, 1H, ZrCH$_2$), 1.75 (s, 3H, Me), 1.14 (s, 9H, ^{t}Bu), -1.00 (d, $^2J_{HH}$ = 9.1 Hz, 1H, ZrCH$_2$).

^{2}H NMR (92 MHz, 299 K, [h_8]-toluene): δ = 4.57 (s, 1D, CD$^=$), -0.67 (s, 1D, ZrCD).

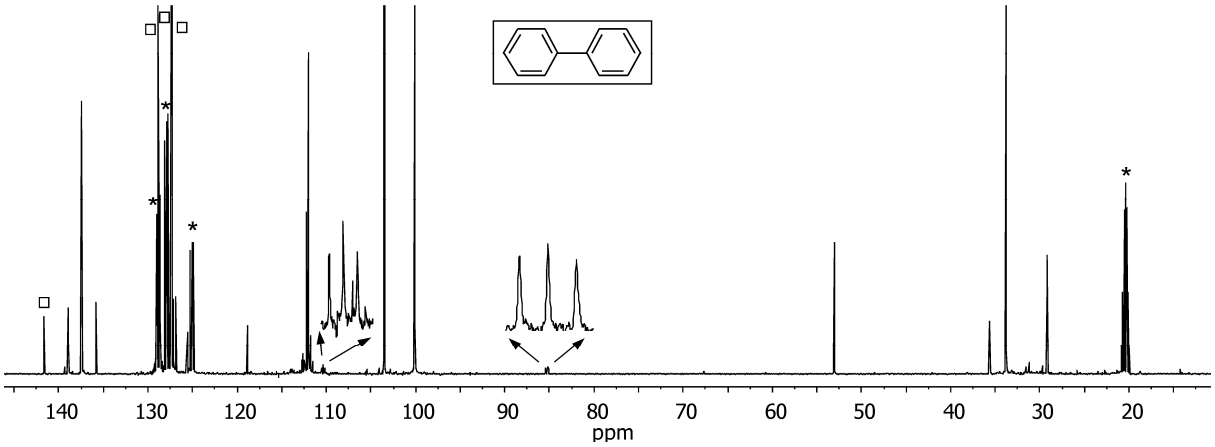
^{13}C{^{1}H} NMR (126 MHz, 299 K, [d_8]-toluene): δ = 118.9 (C$^=$), 110.4 (t, $^1J_{CD}$ = 22.8 Hz, CD$^=$), 103.5 (Cp^A), 100.1 (Cp^B), 85.2 (t,$^1J_{CD}$ = 19.0 Hz, ZrCD), 53.1 (ZrCH$_2$), 35.7 (^{t}Bu) 33.8 (^{t}Bu), 29.2 (Me).



^{1}H NMR (500 MHz, 299 K, [d_8]-toluene (*), squares: the signals of biphenyl)



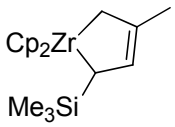
^{2}H NMR (92 MHz, 299 K, [h_8]-toluene, (*) trace of [d_8]-toluene)



^{13}C{^{1}H} NMR (126 MHz, 299 K, [d_8]-toluene (*), squares: the signals of biphenyl)

1,1-Bis(η^5-cyclopentadienyl)-4-methyl-2-trimethylsilyl-1-zirconacyclopenta-3-ene (3b)

At –78 °C *n*-butylmagnesium chloride solution (0.34 ml, 2 M diethyl ether solution, 0.68 mmol, 2 eq) was added to a solution of dichlorobis(η^5-cyclopentadienyl)zirconium (100 mg, 0.34 mmol, 1 eq) and 2-methyl-4-trimethylsilylbutenyne (38 mg, 0.27 mmol, 0.8 eq) in THF (5 ml). After removal of the dry ice bath, the mixture was allowed to warm up to room temperature and stirred for 1 h, then the yellow solution was heated to 60 °C for additional 1 h. The volatiles were removed *in vacuo* and the residue was extracted with *n*-pentane (3×5 ml) and filtered. After removing the solvent, toluene (5 ml) was added to the residue and the Schlenk flask was filled with 2 bar dihydrogen and stirred for 10 min. The volatiles were removed *in vacuo* and the residue was extracted with *n*-pentane (3×5 ml) and filtered. The red coloured filtrate was concentrated *in vacuo* to give the five-membered compound **3b** as red oil (73 mg, 75%).



^{1}H NMR (500 MHz, 299 K, [d_6]-benzene): δ = 5.48 (s, 5H, Cp^A), 5.04 (s, 5H, Cp^B), 4.70 (dm, $^3J_{HH}$ = 13.1 Hz, 1H, $CH^=$), 3.16 (dd, $^3J_{HH}$ = 9.3 Hz, J_{HH} = 1.8 Hz, 1H, $ZrCH_2$), 1.81 (s, 3H, Me), 0.25 (s, $^2J_{SiH}$ = 6.3 Hz, 9H, $SiMe_3$), -0.64 (dd, $^3J_{HH}$ = 9.3 Hz, J_{HH} = 1.6 Hz, 1H, $ZrCH_2$), -1.26 (d, $^3J_{HH}$ = 13.1 Hz, 1H, ZrCH).

^{13}C{^{1}H} NMR (126 MHz, 299 K, [d_6]-benzene): δ = 123.9 ($C^=$), 113.3 ($CH^=$), 104.4 (Cp^A), 100.9 (Cp^B), 58.7 ($^1J_{SiC}$ = 67.4 Hz, ZrCH), 52.6 ($ZrCH_2$), 28.8 (Me), 1.7 ($^1J_{SiC}$ = 51.1 Hz, $SiMe_3$).

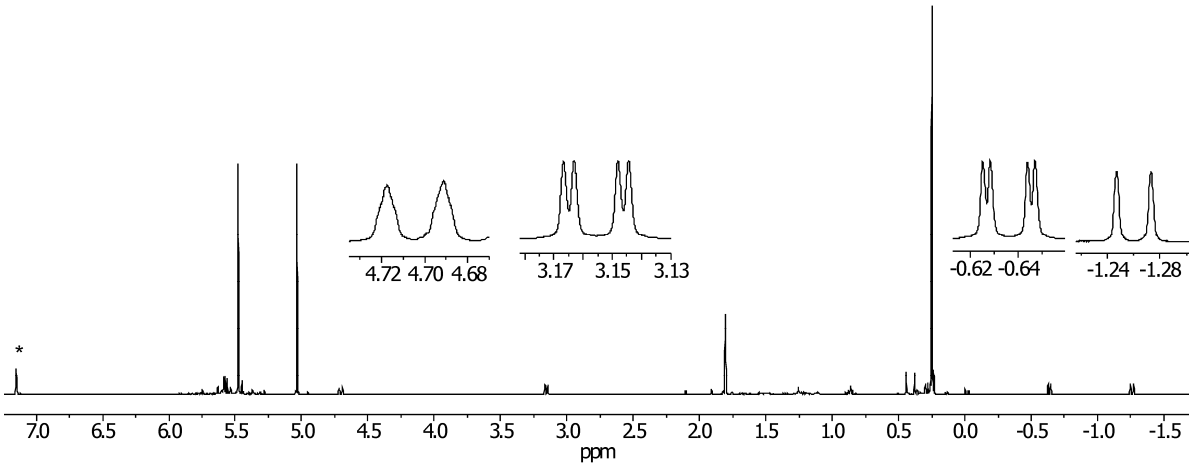
^{29}Si{^{1}H} DEPT NMR (99 MHz, 299 K, [d_6]-benzene): δ = -1.7 ($SiMe_3$).

^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, 299 K, [d_6]-benzene): δ ^{1}H / ^{1}H = 4.70 / 3.16, 1.81, -0.64, -1.26 ($CH^=$ / $ZrCH_2$, Me, $ZrCH_2$, ZrCH), 3.16 / 4.70, -0.64 ($ZrCH_2$ / $CH^=$, $ZrCH_2$), -0.64 / 4.70, 3.16 ($ZrCH_2$ / $CH^=$, $ZrCH_2$), -1.26 / 4.70, 1.81 (ZrCH / $CH^=$, Me).

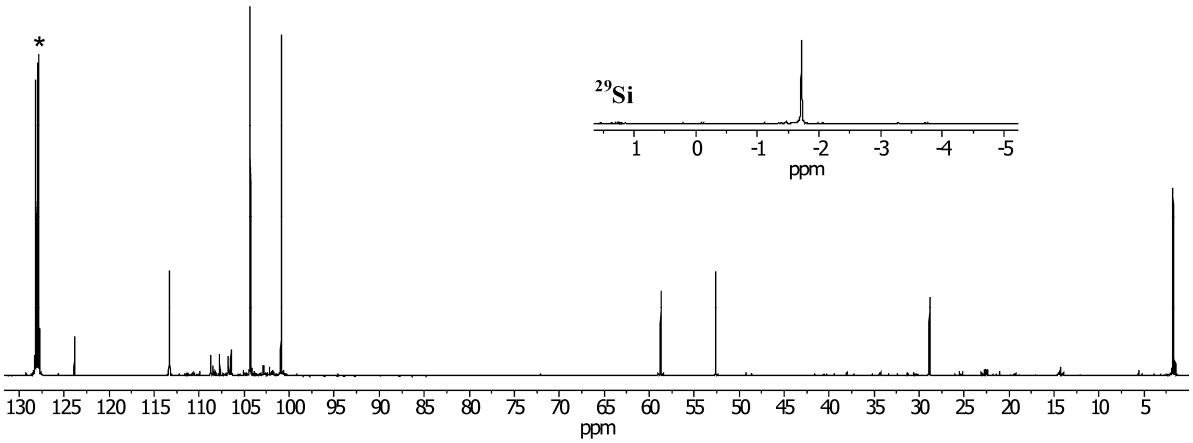
^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 299 K, [d_6]-benzene): δ ^{1}H / δ ^{13}C = 5.48 / 104.4 (Cp^A), 5.04 / 100.9 (Cp^B), 4.70 / 113.3 ($CH^=$), 3.16 / 52.6 ($ZrCH_2$), 1.81 / 28.8 (Me), 0.25 / 1.7 ($^1J_{SiC}$ = 51.2 Hz, $SiMe_3$), -0.64 / 52.6 ($ZrCH_2$), -1.26 / 58.7 (ZrCH).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 299 K, [d_6]-benzene): δ ^{1}H / δ ^{13}C = 4.70 / 58.7, 52.6, 28.8 ($CH^=$ / ZrCH, $ZrCH_2$, Me), 3.16 / 123.8, 113.3, 28.8 ($ZrCH_2$ / $C^=$, $CH^=$, Me), 1.81 / 123.9, 113.3, 52.6 (Me / $C^=$, $CH^=$, $ZrCH_2$), -0.64 / 113.3, 28.8 ($ZrCH_2$ / $CH^=$, Me), -1.26 / 123.9, 113.3 (ZrCH / $C^=$, $CH^=$).

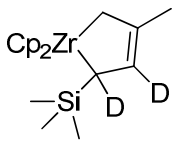
EI-MS: *m/z* 360.1 (M^+, 12%), 254.9 (20), 219.9 (100), 193.9 (14), 125.0 (24).



^{1}H NMR (500 MHz, 299 K, [d_6]-benzene (*))

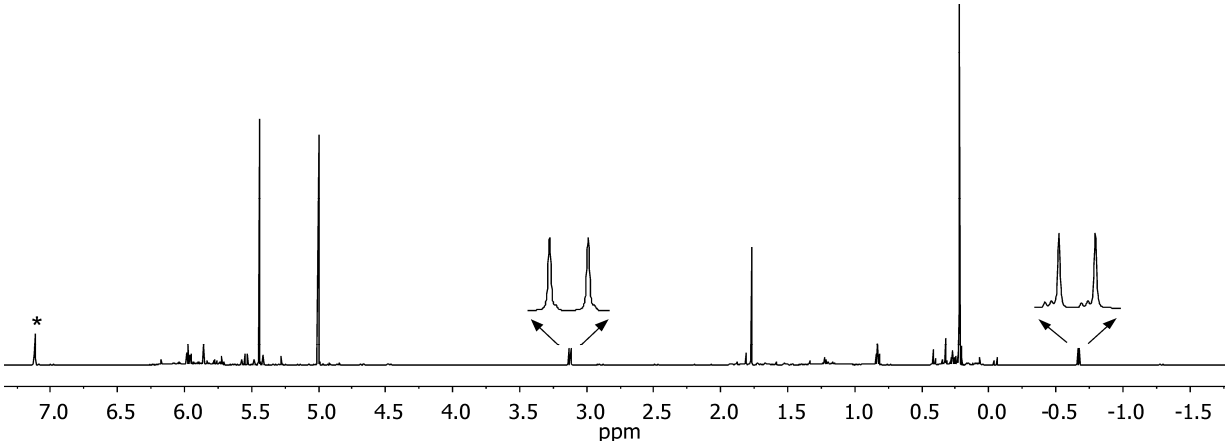


^{13}C{^{1}H} NMR (126 MHz, 299 K, [d_6]-benzene (*)) and ^{29}Si{^{1}H, DEPT} NMR (99 MHz, 299 K, [d_6]-benzene)

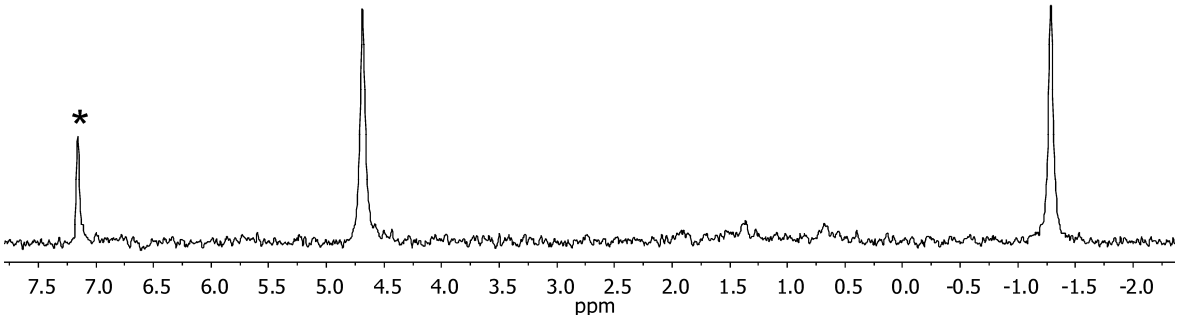


^{1}H NMR (600 MHz, 299 K, [d_6]-benzene): δ = 5.48 (s, 5H, Cp^{A}), 5.03 (s, 5H, Cp^{B}), 3.16 (d, $^{2}J_{HH}$ = 9.3 Hz, 1H, $ZrCH_2$), 1.80 (s, $^{2}J_{SiH}$ = 6.4 Hz, 3H, Me), 0.25 (s, 9H, $SiMe_3$), -0.64 (d, $^{2}J_{HH}$ = 9.3 Hz, 1H, $ZrCH_2$).

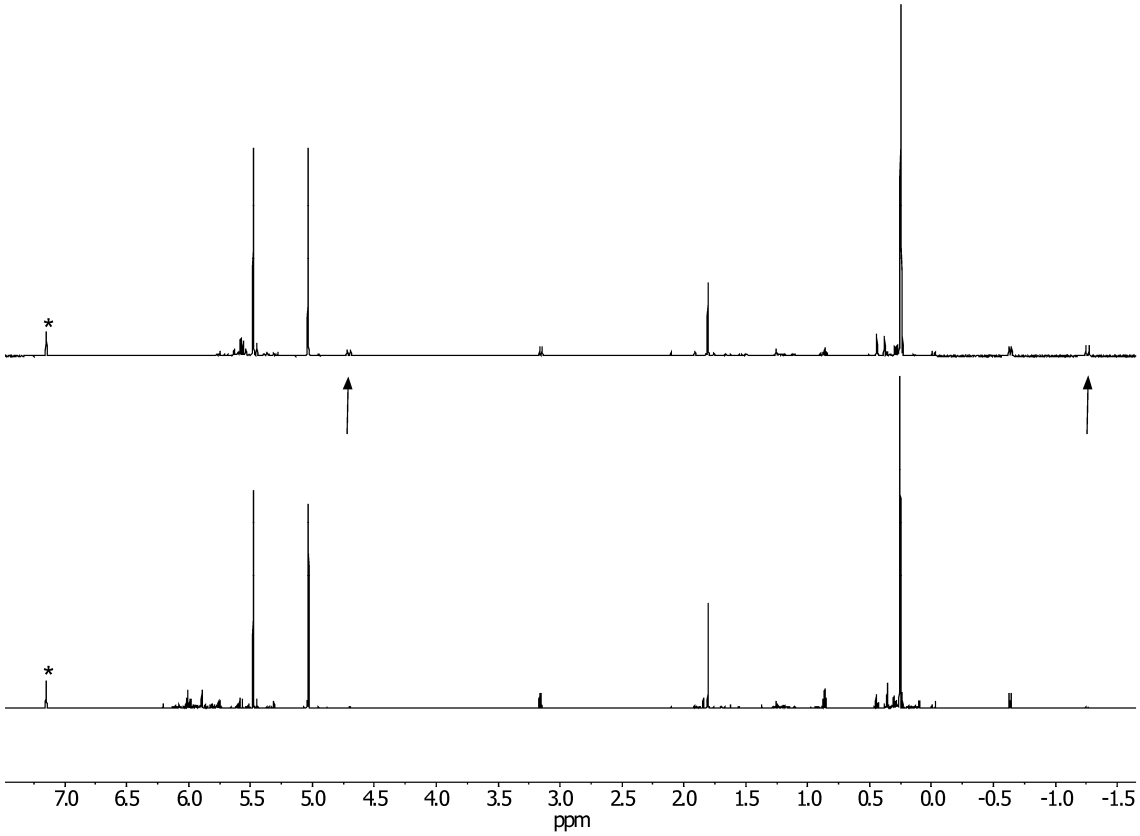
^{2}H NMR (92 MHz, 299 K, [h_6]-benzene): δ = 4.68 (s, 1D, $CD^{=}$), -1.29 (s, 1D, ZrCD).



^{1}H NMR (600 MHz, 299 K, [d_6]-benzene (*))



^{2}H NMR (92 MHz, 299 K, [h_6]-benzene, (*) trace of [d_1]-benzene)



a.) top: ^{1}H NMR (500 MHz, 299 K, [d_6]-benzene (*) Addition of H_2 to complex **2b**); b.) bottom: ^{1}H NMR (600 MHz, 299 K, [d_6]-benzene (*) Addition of D_2 to complex **2b**)

Theoretical Details: All minimum and transition state structures were optimized on the TPSS/def2-TZVP[1,2] level of theory, with an m4 numerical integration grid and a convergence criterion of 10^{-7} E_h in the SCF iterations. Transition states were verified to have exactly one imaginary frequency at the same level of theory. Single point energies were calculated with the PW6B95[3] functional and the very large def2-QZVP[2] AO basis in order to avoid basis set truncation errors. A finer m5 grid was used for these calculations. Where applicable, the resolution of the identity (RI) approximation for two electron integrals was applied[4]. The DFT calculations were corrected for missing dispersion interactions with DFT-D3[5], employing the Becke-Johnson damping function[6]. All calculations were carried out using the TURBOMOLE program package, version 6.4[7].

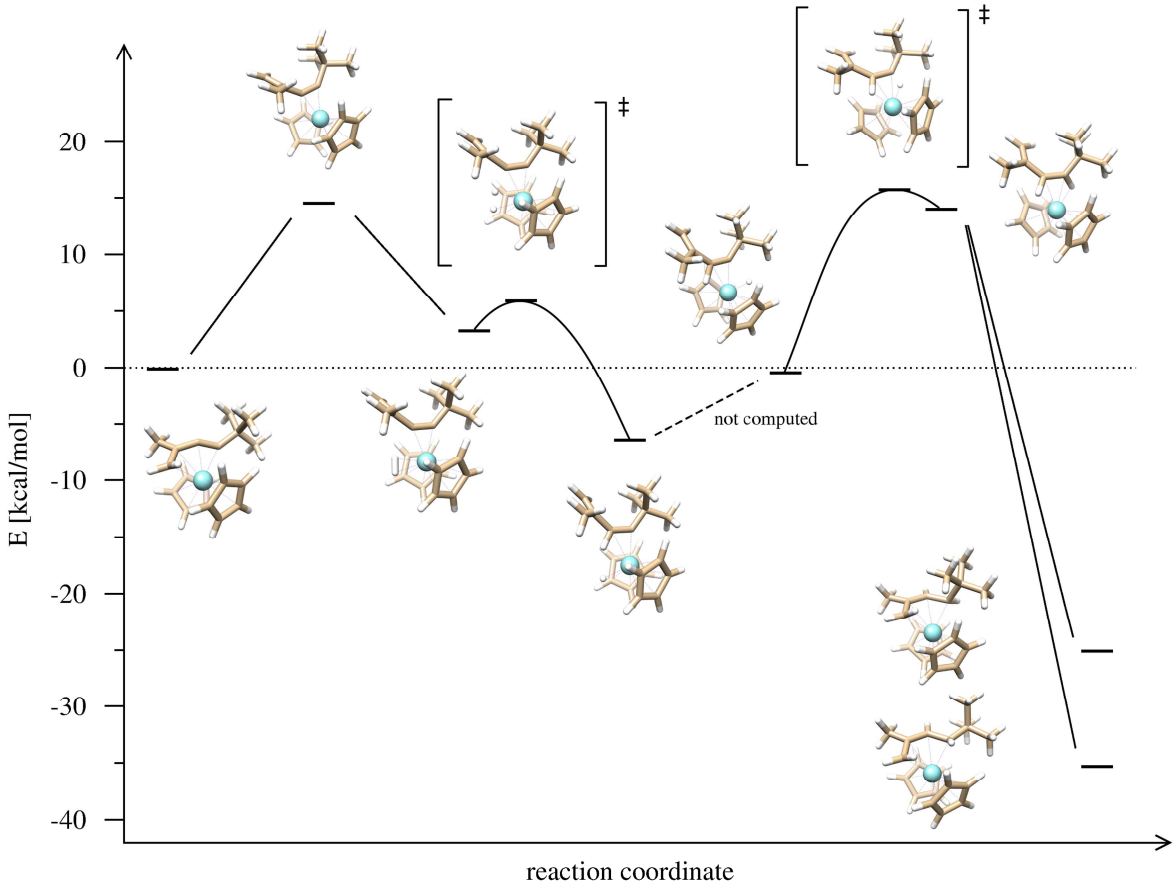


Figure: Full DFT calculated pathway of the reaction of the zirconacycloallenoid … with dihydrogen to give … . The pathway from X to Y (dashed line) was not investigated.

Coordinates of all structures in Xmol format:

1:

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44
Energy =
Zr    -0.3851239   -0.6268902    0.8267755
C     -1.3577051    0.3865018    2.9525256
C     -0.9006855    0.3903734   -1.1936535
C     -2.0078222   -0.4083273   -1.0198331
C     -2.7132573   -0.4372007    0.2379397
C     -0.9280926    1.4871169    2.1598797
C      0.4829936    1.4422874    2.0759666
C     -2.3747972   -1.4033535   -2.1056110
C      0.9337545    0.3124994    2.8018120
C     -0.2063950   -0.3309075    3.3559954
C      1.3384386   -2.2872881    0.0593261
C      0.3247726    0.7169237   -0.9009210
C      1.2554484    1.7644533   -1.4662277
C      2.6682467    1.6136287   -0.8769307
C      0.1436950   -2.6496541   -0.6139101
C     -0.7899500   -3.1063358    0.3532377
C     -0.1705390   -3.0383959    1.6248395
C      1.3293206    1.5557058   -2.9950448
C      1.1437303   -2.5357377    1.4455142
C      0.7027547    3.1770391   -1.1844359
H     -2.3793606    0.1430539    3.2091548
H      1.6921466    0.5494774   -3.2297710
H      0.6289618    3.3721153   -0.1105736
H     -0.2960844    3.2853558   -1.6186187
H      1.3611111    3.9359151   -1.6243052
H      0.3380763    1.6756578   -3.4427691
H      1.8734327   -2.3744162    2.2268246
H      2.0134421    2.2847115   -3.4461269
H     -0.6283387   -3.3108007    2.5663199
H      2.6637392    1.7341267    0.2100244
H     -1.7969719   -3.4486181    0.1619715
H      3.0698092    0.6195070   -1.0998113
H     -0.0234499   -2.5743384   -1.6774491
H      3.3445557    2.3627833   -1.3046651
H      2.2387083   -1.9067303   -0.4016084
H     -3.2503245   -1.0227814   -2.6460627
H     -0.1967272   -1.2198198    3.9719880
H     -1.5658524   -1.5339121   -2.8285020
H      1.9651313    0.0137467    2.9315902
H     -2.6461443   -2.3756839   -1.6832686
H      1.1116937    2.1509697    1.5599718
H     -3.5581534   -1.1184843    0.3079501
H     -1.5647415    2.2239190    1.6883132
H     -2.8834464    0.5118074    0.7421789
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2:

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44
Energy =
Zr     0.1903659   -0.7519199    1.1506670
C     -1.2802093    0.4749468    2.8395975
C     -0.9008576    0.0871953   -0.5533416
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C	-2.1546292	0.2144132	-1.2721858
C	-2.3881793	-0.4103033	-2.4430817
C	-0.4224002	1.4748284	2.3214040
C	0.9040851	1.1548226	2.6882794
C	-3.2309020	1.0277900	-0.5899232
C	0.8716907	-0.0449117	3.4626185
C	-0.4813407	-0.4609769	3.5600992
C	1.7405145	-2.7570986	0.8826761
C	0.3719847	0.4570077	-0.6556740
C	1.1453281	1.3083629	-1.6372260
C	2.2600239	2.0653172	-0.8901244
C	0.9881808	-2.6508164	-0.3187426
C	-0.3726858	-2.9079158	-0.0074094
C	-0.4537141	-3.1795201	1.3889080
C	1.7902283	0.3713632	-2.6801542
C	0.8538977	-3.1010475	1.9347341
C	0.2285848	2.3203775	-2.3493042
H	-2.3555185	0.4394177	2.7236221
H	2.4473801	-0.3564455	-2.1911710
H	-0.2379863	2.9918073	-1.6196085
H	-0.5679700	1.8074934	-2.8950208
H	0.8031469	2.9310152	-3.0570767
H	1.0216077	-0.1747952	-3.2361833
H	1.1224465	-3.2472601	2.9724604
H	2.3905002	0.9499950	-3.3932816
H	-1.3565463	-3.4190846	1.9374817
H	1.8328520	2.7325302	-0.1331920
H	-1.1991776	-2.8919400	-0.7047209
H	2.9290782	1.3598049	-0.3837792
H	1.3778285	-2.3977209	-1.2938060
H	2.8546697	2.6714720	-1.5846411
H	2.8100921	-2.6099150	0.9774660
H	-3.4589004	0.6119174	0.3989083
H	-0.8432817	-1.3311723	4.0915922
H	-2.8909837	2.0589293	-0.4326199
H	1.7239948	-0.5344668	3.9161960
H	-4.1489690	1.0491409	-1.1841509
H	1.7880288	1.7228238	2.4279489
H	-1.6200521	-1.0019934	-2.9327472
H	-0.7225246	2.2999404	1.6917791
H	-3.3596814	-0.3534088	-2.9272721

3:

46

Energy =

Zr	-0.2405806	-0.8072745	1.1192597
C	-1.2037651	-0.0142232	3.3116606
C	-0.9386321	0.1539316	-0.8235886
C	-2.0316830	0.4133628	-1.7438531
C	-2.1467753	-0.1909556	-2.9414177
C	-1.2495168	1.1079036	2.4249706
C	0.0805380	1.5045371	2.1568112
C	-3.0848446	1.3777386	-1.2452343
C	0.9524167	0.6223344	2.8440918
C	0.1557964	-0.3004487	3.5778977
C	1.4440076	-2.3381017	0.0356562
C	0.3294233	0.4161429	-0.6408155

C	1.3814797	1.2013320	-1.3889492
C	2.6630080	1.3488671	-0.5514333
C	0.1690689	-2.8637842	-0.3034974
C	-0.4376679	-3.3415578	0.8883219
C	0.4532793	-3.1075149	1.9659491
C	1.7113597	0.4573051	-2.7015769
C	1.6150310	-2.4812766	1.4400058
C	0.8213400	2.5970545	-1.7335372
H	-2.0574027	-0.5278186	3.7344672
H	2.0781069	-0.5541667	-2.4980299
H	0.5595159	3.1465108	-0.8224963
H	-0.0782509	2.5046906	-2.3495825
H	1.5645112	3.1855972	-2.2860034
H	0.8193969	0.3786412	-3.3289142
H	2.4859251	-2.1794707	2.0078310
H	2.4881052	0.9963959	-3.2585114
H	0.2746059	-3.3582976	3.0026875
H	2.4654559	1.9047682	0.3709025
H	-1.4102052	-3.8109243	0.9619473
H	3.0565562	0.3654904	-0.2718046
H	-0.2699368	-2.8801263	-1.2911436
H	3.4373285	1.8843895	-1.1139099
H	2.1630247	-1.9191449	-0.6521135
H	-3.5245706	1.0193684	-0.3054017
H	0.5268866	-1.0945741	4.2110937
H	-2.6376004	2.3564553	-1.0326523
H	2.0340131	0.6595755	2.8292022
H	-3.8856723	1.5067128	-1.9789711
H	0.3806790	2.3146624	1.5092130
H	-1.4003031	-0.8954598	-3.2961746
H	-2.1431717	1.5773831	2.0367589
H	-3.0014762	-0.0026840	-3.5858373
H	-2.2091930	-1.3854850	1.2008861
H	-2.1596117	-0.9478616	0.5158353

TS34:

46
Energy =

Zr	-0.2159907	-0.8315008	1.1642554
C	-1.2176655	0.0034792	3.3286521
C	-0.9813528	0.1355471	-0.8156347
C	-2.0447786	0.4526430	-1.7683470
C	-2.0935336	-0.0699150	-3.0051140
C	-1.2104118	1.1193934	2.4394642
C	0.1349786	1.4770244	2.1943242
C	-3.1276518	1.3680234	-1.2462647
C	0.9674679	0.5720807	2.9011732
C	0.1270146	-0.3246208	3.6213254
C	1.4827632	-2.3650832	0.0929507
C	0.2959150	0.3810711	-0.6242297
C	1.3251215	1.1744950	-1.3959028
C	2.6134695	1.3403526	-0.5709642
C	0.2103241	-2.8836848	-0.2609104
C	-0.4197114	-3.3536477	0.9213728
C	0.4593427	-3.1213338	2.0096922
C	1.6587621	0.4217941	-2.7029283
C	1.6347944	-2.5063224	1.4985875

C	0.7516655	2.5629567	-1.7473055
H	-2.0956157	-0.4929400	3.7188388
H	2.0151921	-0.5917744	-2.4917436
H	0.4906658	3.1159983	-0.8382136
H	-0.1495495	2.4612731	-2.3593545
H	1.4883063	3.1529530	-2.3064685
H	0.7734206	0.3493967	-3.3397524
H	2.5006839	-2.2107139	2.0770739
H	2.4450209	0.9528260	-3.2537318
H	0.2656573	-3.3690505	3.0444797
H	2.4209664	1.9002819	0.3496468
H	-1.3980783	-3.8097771	0.9831603
H	3.0187875	0.3627683	-0.2887425
H	-0.2168640	-2.8937072	-1.2542126
H	3.3760907	1.8795633	-1.1456419
H	2.2119461	-1.9474869	-0.5854643
H	-3.5958692	0.9383725	-0.3513107
H	0.4610593	-1.1253555	4.2667377
H	-2.7020485	2.3346728	-0.9501189
H	2.0496815	0.5806030	2.9125590
H	-3.9028501	1.5381463	-1.9986705
H	0.4701008	2.2789125	1.5534127
H	-1.3287074	-0.7508869	-3.3651011
H	-2.0832267	1.6029771	2.0217823
H	-2.9126356	0.1628511	-3.6806253
H	-2.0935645	-1.2685184	1.0355880
H	-1.8590928	-0.7041373	0.2116766

4:

46

Energy =

Zr	-0.2336611	-0.8958231	1.2315795
C	-1.1694375	-0.0292755	3.4273263
C	-1.1205026	0.1383724	-0.8727466
C	-2.0752784	0.6001722	-1.9108390
C	-2.0048714	0.2097415	-3.1896187
C	-1.2232326	1.0614786	2.5153939
C	0.1021095	1.4324278	2.1902791
C	-3.1722996	1.5019538	-1.4008910
C	0.9840616	0.5503669	2.8684507
C	0.1918707	-0.3382042	3.6523891
C	1.5122446	-2.3593165	0.1257837
C	0.1768637	0.3107463	-0.6141480
C	1.2201959	1.0930689	-1.3816149
C	2.4954482	1.2510350	-0.5299909
C	0.2606415	-2.9549284	-0.1749569
C	-0.3102941	-3.4261697	1.0342646
C	0.5827282	-3.1077113	2.0895696
C	1.5948826	0.3375597	-2.6768205
C	1.7104253	-2.4445744	1.5279960
C	0.6893465	2.4949628	-1.7494154
H	-2.0207017	-0.5360281	3.8581501
H	1.9046655	-0.6896581	-2.4587947
H	0.4173696	3.0534456	-0.8468224
H	-0.1936560	2.4219578	-2.3901916
H	1.4593981	3.0650591	-2.2832100
H	0.7474121	0.3029232	-3.3645000

H	2.5754668	-2.0873166	2.0708528
H	2.4281299	0.8463635	-3.1766782
H	0.4326069	-3.3373579	3.1355443
H	2.2936789	1.8240469	0.3798867
H	-1.2602819	-3.9291138	1.1357724
H	2.8858532	0.2729926	-0.2300959
H	-0.1939992	-3.0101574	-1.1551474
H	3.2734728	1.7757025	-1.0972436
H	2.1962780	-1.9223935	-0.5865931
H	-3.7226946	1.0117273	-0.5873937
H	0.5687735	-1.1177500	4.2998986
H	-2.7480949	2.4254877	-0.9876668
H	2.0647442	0.5762099	2.8288405
H	-3.8783604	1.7607981	-2.1948690
H	0.3903047	2.2312065	1.5230679
H	-1.2409142	-0.4785459	-3.5350589
H	-2.1251669	1.5155136	2.1270220
H	-2.7279921	0.5589488	-3.9224676
H	-1.9876995	-1.5078617	1.4062317
H	-1.7498337	-0.4520830	-0.1105247

5:

46

Energy =

Zr	0.1166775	-0.8016397	1.1981175
C	-1.0924946	-0.4470085	3.3869588
C	-0.9929173	0.3226190	-0.7947666
C	-2.0614953	0.6177621	-1.7750108
C	-1.9551133	0.2615629	-3.0621879
C	-1.3610275	0.6969721	2.5909760
C	-0.1396529	1.3985501	2.3995029
C	-3.2991771	1.2753083	-1.2174040
C	0.8837695	0.6915204	3.0838932
C	0.2948542	-0.4495222	3.6909137
C	0.5299758	-2.7277965	-0.3817592
C	0.3131019	0.5118365	-0.6412198
C	1.3445585	1.2617619	-1.4400620
C	2.1795557	2.1138808	-0.4586520
C	-0.8085838	-2.8692076	0.0692257
C	-0.7800137	-3.1485231	1.4594600
C	0.5828214	-3.1939848	1.8659270
C	2.2801501	0.2172584	-2.0868854
C	1.3912875	-2.9360620	0.7287681
C	0.7695453	2.1940875	-2.5227712
H	-1.8190207	-1.1787835	3.7140263
H	2.7048635	-0.4323890	-1.3153798
H	0.0458926	2.8925188	-2.0880252
H	0.2637838	1.6394395	-3.3159890
H	1.5783178	2.7796215	-2.9765942
H	1.7349772	-0.4016249	-2.8083723
H	2.4702320	-2.9094442	0.7086453
H	3.0977040	0.7218093	-2.6156371
H	0.9406602	-3.3959936	2.8665457
H	1.5630402	2.8995293	-0.0069871
H	-1.6415373	-3.3211335	2.0908807
H	2.5784740	1.4802302	0.3382373
H	-1.6971917	-2.7663242	-0.5406235

H	3.0076269	2.5964772	-0.9915412
H	0.8397521	-2.4907262	-1.3891900
H	-3.7114191	0.6810255	-0.3906703
H	0.8152813	-1.1911882	4.2816599
H	-3.0615952	2.2651647	-0.8089486
H	1.9239755	0.9746846	3.1394862
H	-4.0729326	1.3864620	-1.9817517
H	-0.0113173	2.3051542	1.8268029
H	-1.0760745	-0.2539916	-3.4354015
H	-2.3288315	0.9894040	2.2045841
H	-2.7485179	0.4759451	-3.7736606
H	1.9372733	-0.5024987	1.1110973
H	-1.5292382	-0.2327439	0.0637823

TS56:

46
Energy =

Zr	0.1947063	-0.7172211	1.2048331
C	-0.4835538	0.8927474	2.9990987
C	-1.0312162	0.1141891	-0.6227434
C	-2.1382030	-0.0547472	-1.5638001
C	-1.9694082	-0.2946087	-2.8788532
C	0.5694198	1.5104707	2.2775005
C	1.7614939	0.7512832	2.4906747
C	-3.5195159	0.0052523	-0.9564345
C	1.4378891	-0.3124130	3.3766431
C	0.0578552	-0.2371827	3.6789667
C	1.1936092	-3.0250598	1.4259169
C	0.2150735	0.6411134	-0.6087309
C	0.9449901	1.5891725	-1.5415379
C	2.0651609	2.3246885	-0.7787441
C	0.9187123	-2.8434105	0.0381926
C	-0.4821178	-2.7583676	-0.1220674
C	-1.0871112	-2.8716784	1.1703488
C	1.6179961	0.7966254	-2.6858157
C	-0.0440628	-3.0734165	2.1137940
C	-0.0427379	2.6192398	-2.1165426
H	-1.5092968	1.2328697	3.0495006
H	2.3017568	0.0455152	-2.2752634
H	-0.5202319	3.1830484	-1.3078852
H	-0.8266920	2.1341121	-2.7032623
H	0.4902553	3.3278085	-2.7610203
H	0.8811392	0.2847980	-3.3091508
H	-0.1702094	-3.2069543	3.1799155
H	2.1958058	1.4777033	-3.3219892
H	-2.1483724	-2.8861967	1.3797298
H	1.6552082	2.9993422	-0.0217485
H	-1.0069096	-2.6073133	-1.0553272
H	2.7245039	1.6044405	-0.2816408
H	1.6568362	-2.7853728	-0.7494832
H	2.6683784	2.9201567	-1.4732235
H	2.1748993	-3.1353272	1.8685031
H	-3.6012473	-0.7046813	-0.1222672
H	-0.4937005	-0.9144047	4.3174154
H	-3.7229848	1.0018429	-0.5451230
H	2.1234601	-1.0708088	3.7313887
H	-4.2891655	-0.2335649	-1.6942246

H	2.7427231	0.9810334	2.1009016
H	-0.9855723	-0.3846358	-3.3242868
H	0.4822495	2.4005879	1.6747041
H	-2.8251390	-0.4228920	-3.5347319
H	-1.5260002	-0.1541421	0.4415140
H	1.3493265	-0.1436416	-0.1636441

6:

46

Energy =

Zr	0.1888499	-0.7634998	1.2076229
C	-0.4867727	0.8758817	2.9675309
C	-0.9291500	0.0112833	-0.6432911
C	-2.0272909	-0.1304625	-1.5871103
C	-1.8486672	-0.4311355	-2.8916579
C	0.5551247	1.4903481	2.2275136
C	1.7593567	0.7519634	2.4541181
C	-3.4162918	0.0072376	-1.0099096
C	1.4558984	-0.2924819	3.3655379
C	0.0738945	-0.2320849	3.6689806
C	1.1111693	-3.0882897	1.5363687
C	0.3269779	0.5583587	-0.6821073
C	0.9558940	1.6258198	-1.5704940
C	2.1185223	2.3069377	-0.8214971
C	0.8645101	-2.9437827	0.1385580
C	-0.5311950	-2.8145447	-0.0486769
C	-1.1598171	-2.8571865	1.2381603
C	1.5461390	0.9914887	-2.8517243
C	-0.1357925	-3.0641655	2.2049779
C	-0.1072230	2.6707233	-1.9439541
H	-1.5147852	1.2070237	3.0205132
H	2.2541324	0.1947787	-2.5965904
H	-0.5238818	3.1333272	-1.0426015
H	-0.9260427	2.2117392	-2.5042623
H	0.3406535	3.4583833	-2.5607124
H	0.7611745	0.5676744	-3.4812105
H	-0.2816189	-3.1574204	3.2725512
H	2.0825758	1.7506768	-3.4341965
H	-2.2238363	-2.8329719	1.4298524
H	1.7623401	2.8815790	0.0375750
H	-1.0356825	-2.6856230	-0.9960417
H	2.8362386	1.5597512	-0.4615773
H	1.6162955	-2.9400469	-0.6392090
H	2.6514706	2.9915301	-1.4908135
H	2.0809234	-3.2167068	1.9992901
H	-3.5320953	-0.6496289	-0.1373919
H	-0.4638404	-0.8986579	4.3293691
H	-3.5954071	1.0316071	-0.6599966
H	2.1537813	-1.0325701	3.7349904
H	-4.1807684	-0.2506490	-1.7468412
H	2.7356602	0.9839952	2.0517292
H	-0.8619753	-0.5887317	-3.3116906
H	0.4512907	2.3641277	1.6033623
H	-2.6987120	-0.5530004	-3.5558102
H	-1.4777438	-0.1329166	0.4531649
H	1.2757165	-0.0696781	-0.2723980

cis-product:

46
Energy =

Zr	-0.1119099	-0.9441104	0.5909275
C	-0.4662267	-1.3826109	3.0849033
C	-0.3684223	0.1983224	-1.6480886
C	-1.6746619	-0.0814747	-1.2693364
C	-2.1656370	0.0170282	0.0882327
C	-0.9707060	-0.0764961	2.8649076
C	0.1099577	0.7554592	2.5036765
C	-2.5880858	-0.7549200	-2.2673337
C	1.2985738	-0.0284166	2.5129541
C	0.9426127	-1.3398365	2.8980688
C	1.2037725	-2.5296555	-0.9521371
C	0.7406349	0.7131464	-0.8053558
C	0.9057032	2.2607306	-0.7008429
C	2.0682277	2.6111645	0.2388323
C	-0.1534704	-2.7208799	-1.3105892
C	-0.8369886	-3.2747137	-0.1997842
C	0.1214444	-3.4862120	0.8320282
C	1.2686168	2.7759996	-2.1145609
C	1.3723967	-3.0226142	0.3704319
C	-0.3757267	2.9910341	-0.2742718
H	-1.0467446	-2.2452025	3.3833697
H	2.1898932	2.3027090	-2.4741177
H	-0.6734024	2.7507710	0.7493908
H	-1.2053151	2.7290027	-0.9391137
H	-0.2250974	4.0759620	-0.3288298
H	0.4662567	2.5456710	-2.8241043
H	2.3018067	-3.0304205	0.9235912
H	1.4215977	3.8629996	-2.1082451
H	-0.0797602	-3.9115790	1.8048784
H	1.8461224	2.3523318	1.2761933
H	-1.8849545	-3.5398865	-0.1621143
H	2.9753965	2.0707819	-0.0574946
H	-0.5955706	-2.4729630	-2.2623472
H	2.2866030	3.6854195	0.1974834
H	1.9795623	-2.1188138	-1.5834938
H	-3.4246316	-0.0882581	-2.5092994
H	1.6210124	-2.1725577	3.0162821
H	-2.0683316	-1.0003374	-3.1987469
H	2.2967104	0.3235532	2.2928111
H	-3.0191271	-1.6719702	-1.8478876
H	0.0517699	1.8078564	2.2749586
H	-3.2014285	-0.2645231	0.2597073
H	-2.0072998	0.2200347	2.9430677
H	-1.8957055	0.9273231	0.6290222
H	-0.1068345	-0.1813664	-2.6383451
H	1.6773670	0.3625176	-1.2592786

trans-product:

46
Energy =

Zr	-0.3272202	-0.6510735	0.8829854
C	-1.1852908	-0.0699194	3.2171562
C	-0.8499391	0.3370942	-1.3731707
C	-2.0516076	-0.2442313	-0.9644896

C	-2.5580867	-0.1906680	0.3863624
C	-0.7605165	1.1685445	2.6587817
C	0.6433061	1.1234643	2.4954866
C	-2.7685084	-1.1511869	-1.9391133
C	1.0957363	-0.1398875	2.9453678
C	-0.0340822	-0.8682804	3.4104694
C	1.3122056	-2.2149523	-0.2365026
C	0.1035030	1.1052164	-0.6028027
C	1.2219789	1.8361668	-1.3565348
C	2.1653621	2.5209546	-0.3560376
C	0.0713925	-2.4690637	-0.8767696
C	-0.8183921	-3.0246029	0.0801189
C	-0.1137657	-3.1461467	1.3047957
C	2.0570839	0.8706491	-2.2138580
C	1.1977474	-2.6544682	1.1124842
C	0.6015697	2.9150086	-2.2722567
H	-2.2007109	-0.3413672	3.4707374
H	2.5580573	0.1339878	-1.5790532
H	0.0172361	3.6308124	-1.6828170
H	-0.0700250	2.4582778	-3.0073840
H	1.3796676	3.4686736	-2.8125680
H	1.4458076	0.3332455	-2.9463343
H	1.9768632	-2.6144380	1.8600347
H	2.8230294	1.4263400	-2.7672435
H	-0.5206962	-3.5395251	2.2262804
H	1.6192181	3.2332949	0.2741132
H	-1.8394353	-3.3308272	-0.0933393
H	2.6439415	1.7784284	0.2914244
H	-0.1554759	-2.2758710	-1.9137431
H	2.9500084	3.0755737	-0.8840260
H	2.1993648	-1.8139197	-0.7037874
H	-3.6894616	-0.6627456	-2.2822251
H	-0.0156826	-1.8619020	3.8354154
H	-2.1574359	-1.3746223	-2.8193271
H	2.1243612	-0.4732024	2.9630966
H	-3.0651409	-2.0955676	-1.4704536
H	1.2630700	1.9124139	2.0987824
H	-3.5001609	-0.6978352	0.5775030
H	-1.4007995	2.0030384	2.4040767
H	-2.5045592	0.7832572	0.8837155
H	-0.5094934	0.0179870	-2.3574117
H	-0.3740239	1.7738750	0.1320609

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