Supporting information

Mechanism of Cp_2ZrCl_2-Catalyzed Olefin Cycloalumination with $AlEt_3$: Quantum Chemical Approach

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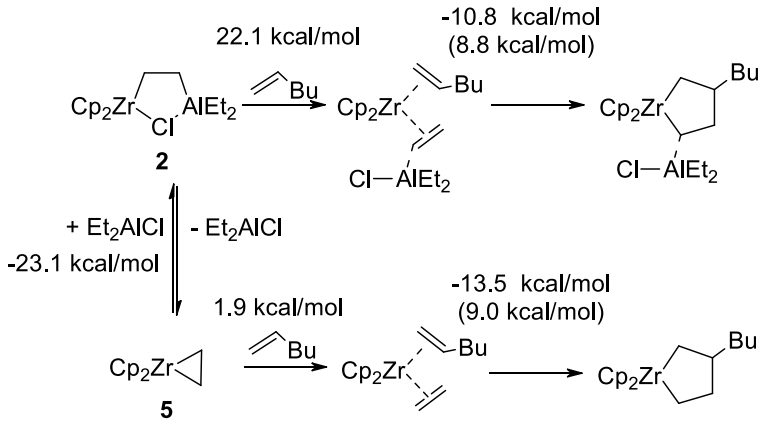
Contents:

The supplemental file FILENAME contains the computed Cartesian coordinates of all of the molecules reported in this study. The file may be opened as a text file to read the coordinates, or opened directly by a molecular modeling program such as Mercury (version 3.3 or later, http://www.ccdc.cam.ac.uk/pages/Home.aspx) for visualization and analysis.

Scheme S1.

Bimetallic complex **2** and zirconacyclopropane **5** as active sites in the alkene cyclometalation. There are ΔG values (298.15 K, 1 atm) above the arrows ($\Delta G^{\#}$ in parentheses).



Scheme S2.

Mechanism of intermediates **2** and 3 formation upon the reaction of $AlEt_3$ with $Cp_2ZrEtCl$ and Cp_2ZrEtH.

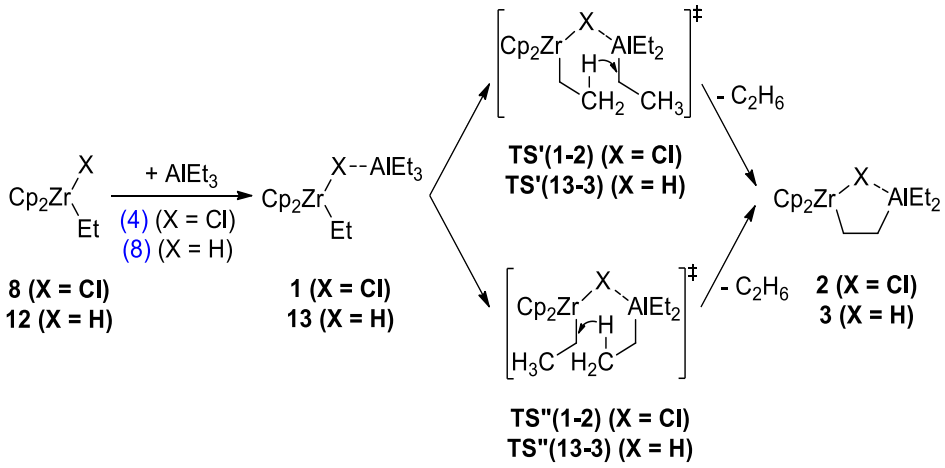


Figure S1.

Energy profile of the intermediates **2** and **3** formation by the reaction of $AlEt_3$ with $Cp_2ZrEtCl$ (reaction 4) (a) and $AlEt_3$ with Cp_2ZrEtH (reaction 8) (b).

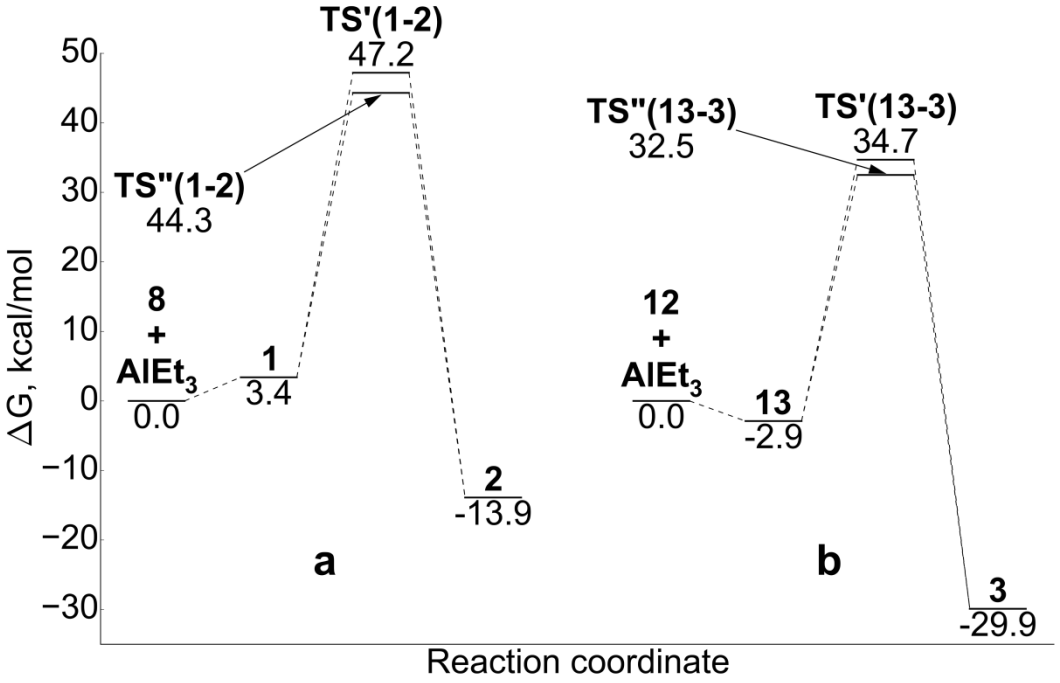
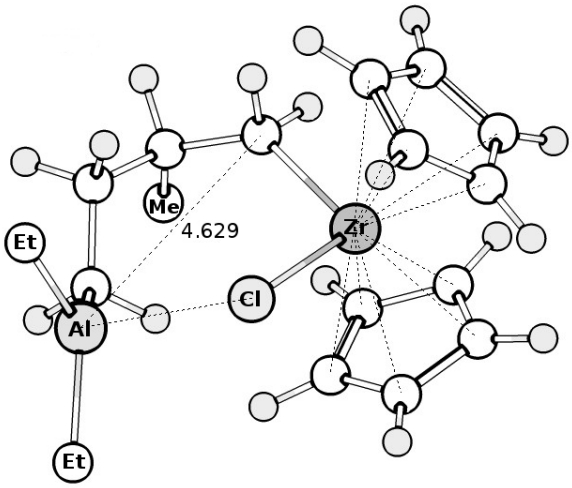
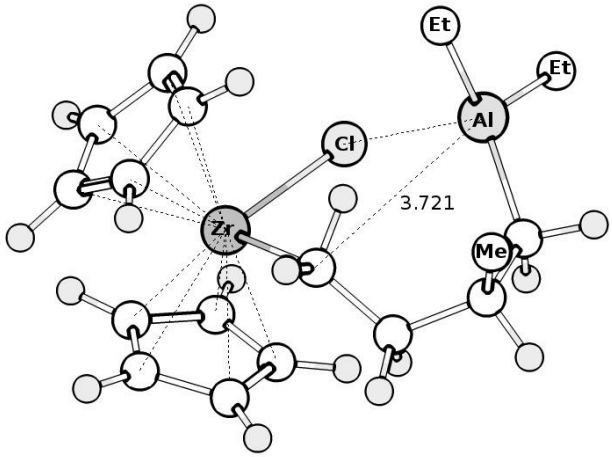


Figure S2.

Optimized (PBE/3ζ) structures of intermediates **18a** and **18b**.



18a



18b

Table S1.

Thermodynamic parameters of the catalytic alkene cycloalumination by $AlEt_3$ in the presence of Cp_2ZrCl_2 calculated by M06-2X/cc-pVDZ(for H, C, Al, and Cl)//cc-pVDZ-PP(for Zr) method at T = 298 K (ΔS [cal/(mol K]); ΔH, ΔG [kcal/mol]).

Reaction	ΔH	ΔG	ΔS	$\Delta H^{\neq}$	$\Delta G^{\neq}$	$\Delta S^{\neq}$
Cp_2ZrCl_2 + 2$AlEt_3$ → **6**	-25,1	4,3	-98,4			
6 → TS''(6-7) → 7	4,6	4,4	0,4	6,9	9,1	-7,3
7 → 1 + $ClAlEt_2$	9,9	-2,7	42,1			
1 → TS(1-9') → 9'	17,0	19,7	-9,0	17.1	21.0	-12.9
8' → TS(9'-10) → 10	-7,1	-10,1	10,1	0,1	0,7	-1,8
10 → 11 + $ClAlEt_2$	14,3	1,1	44,2			
11 → TS"(11-12) → 12	28.0	15.8	41.2	31.4	32.0	-1.8
12 + $AlEt_3$ → **13**	-21.0	-8.8	-40.7			
13 → TS'(13-11) → 11+ $HAlEt_2$	24.3	12.2	40.6	-	-	-
11 → TS(11-5) → 5 + C_2H_6	12,0	0,9	37,0	24,6	27,0	-8,2
5 + $ClAlEt_2$ → **2**	-41,2	-24,9	-54,5			
5 + $HAlEt_2$ → **3**	-49,4	-34,7	-49,5			
5 + propene → **16**	-13,1	1,6	-49,2			
16 → TS(16-17) → 17	-14,5	-14,1	-1,4	4.1	5.1	-3,4
17 + $ClAlEt_2$ → **22a**	-14,6	-1,4	81,6			
22a → TS(22a-23a) → 23a	-6,5	-4,4	-7,2	1,2	2,8	-5,1
23a → TS(23a-18a) → 18a	1,3	-0,6	6,6	11,3	8,4	9,6
18a + $ClAlEt_2$ → **24**	-13,0	2,0	-50,4			
24 → TS(24-25) → 25	-9,1	-11,0	6,2	3,3	5,7	-8,0
25 → 20 + Cp_2ZrCl_2	18,1	-0,8	63,3			
20 → TS(20-29) → 29	-16,9	-7,9	-30,4	-2,6	4,8	-24,7
29 → 21 + $AlEt_3$	24,2	6,0	61,2			

Table S2.
Calculated at different DFT levels thermodynamic parameters (298.15 K, 1 atm, [S] = cal/(mol*K); [H] = [G] = kcal/mol) for all the reactants, intermediates, transition states, and product considered in the text of the article.

Stationary point	PBE/3ζ			M06-2X/cc-pVDZ(for H, C, Al, and Cl)//cc-pVDZ-PP(for Zr)		
	H^0	G^0	S^0	H^0	G^0	S^0
1	-3103641.3	-3103701.9	203.1	-911659.2	-911714.7	186.1
2	-3053666.9	-3053716.5	166.4	-861655.5	-861703.0	159.5
3	-2765318.4	-2765366.4	160.9	-573206.5	-573253.2	156.5
5	-2513630.7	-2513664.8	114.3	-321394.7	-321428.4	113.2
6	-3643656.9	-3643736.3	266.2	-1451893.3	-1451966.1	244.3
7	-3643652.6	-3643730.8	262.2	-1451888.7	-1451961.7	244.7
8	-2802732.9	-2802770.6	126.2	-610598.9	-610635.6	123.1
10	-3103632.6	-3103692.5	200.9	-911649.3	-911705.1	187.1
11	-2563617.9	-2563658.1	134.9	-371415.4	-371454.3	130.6
12	-2514369.4	-2514404.4	117.5	-322135.0	-322169.8	116.7
13	-2815284.7	-2815342.1	192.6	-623202.2	-623256.6	182.7
14	-5555478.8	-5555536.4	192.9	-	-	-
15	-5555482.9	-5555540.7	193.8	-	-	-
16	-2587496.6	-2587535.9	131.9	-395302.5	-395340.4	127.2
17	-2587500.7	-2587539.6	130.7	-395316.9	-395354.4	125.9
20	-625692.8	-625748.6	187.2	-626003.0	-626058.1	184.8
21	-324788.2	-324819.2	103.9	-324950.1	-324980.8	102.8
24	-3667530.6	-3667605.0	249.7	-1475789.1	-1475858.3	232.1
25	-3667542.6	-3667617.8	252.0	-1475798.2	-1475869.2	238.4
26	-3667532.6	-3667607.2	250.2	-1475790.9	-1475859.4	229.6
27	-3667532.3	-3667605.4	245.2	-1475792.5	-1475860.5	228.1
28	-3667545.3	-3667622.7	259.7	-1475800.5	-1475871.1	236.7
29	-625704.0	-625752.6	162.8	-626019.9	-626066.0	154.4
18a	-3127519.6	-3127576.1	189.5	-935556.4	-935610.6	181.8
18b	-3127525.5	-3127581.6	188.0	-935563.0	-935616.2	178.2
19a	-3127507.2	-3127562.5	185.2	-935564.0	-935616.5	176.2
19b	-3127526.8	-3127583.9	191.5	-935562.8	-935616.8	181.0
22a	-3127515.6	-3127573.3	193.8	-935551.2	-935605.6	182.4
22b	-3127516.1	-3127574.4	195.8	-935551.4	-935607.0	186.4
23a	-3127521.1	-3127576.1	184.3	-935557.8	-935610.0	175.2
23b	-3127523.9	-3127579.5	186.7	-935559.5	-935613.4	180.8

30	-3127521.9	-3127579.6	193.4	-935556.5	-935611.4	184.0
31a_R=Bu	-2913045.5	-2913106.3	203.7	-721024.7	-721083.1	195.8
31a_R=Ph	-2959344.4	-2959404.3	200.8	-767357.7	-767415.0	192.2
31b_R=Bu	-2913038.8	-2913098.8	201.1	-721020.4	-721077.4	191.0
31b_R=Ph	-2959342.7	-2959401.3	196.5	-767362.5	-767417.1	183.2
9'	-3103622.6	-3103678.4	187.0	-911642.2	-911695.0	177.0
9''	-3103624.7	-3103682.4	193.6	-911645.2	-911698.2	178.0
$AlEt_3$	-300901.4	-300934.8	112.0	-301046.2	-301078.0	106.7
C_2H_4	-49227.3	-49243.7	55.2	-	-	-
C_2H_6	-49985.3	-50002.6	58.1	-50008.8	-50025.0	54.4
C_3H_6	-73855.9	-73874.9	63.5	-73894.7	-73913.6	63.2
Cp_2ZrCl_2	-3041843.2	-3041878.6	118.7	-849777.1	-849811.9	116.9
Et_2AlCl	-540007.8	-540038.1	101.6	-540219.6	-540249.7	100.8
Et_2AlH	-251646.1	-251673.9	93.5	-251762.4	-251790.1	92.7
Hexene-1	-147730.0	-147755.8	86.7	-147812.0	-147837.6	85.9
Styrene	-194030.9	-194055.8	83.4	-194146.3	-194171.1	83.3
TS''(1-2)	-3103603.5	-3103658.1	183.1	-	-	-
TS''(11-12)	-2563590.9	-2563630.2	131.8	-371384.0	-371422.4	128.7
TS''(13-11)	-2815279.4	-2815332.8	178.9	-	-	-
TS''(13-3)	-2815252.7	-2815304.5	173.8	-	-	-
TS''(6-7)	-3643646.5	-3643721.2	250.5	-	-	-
TS'(1-2)	-3103605.9	-3103661.0	184.8	-	-	-
TS'(11-12)	-2563584.5	-2563624.0	132.4	-371380.0	-371417.0	124.2
TS'(13-11)	-2815281.0	-2815334.6	179.7	-	-	-
TS'(13-3)	-2815253.0	-2815306.7	180.2	-	-	-
TS'(6-7)	-3643649.9	-3643725.1	252.2	-1451886.4	-1451957.0	237.0
TS(1-9'')	-3103625.1	-3103679.3	182.0	-	-	-
TS(1-9')	-3103622.9	-3103677.0	181.5	-911642.1	-911693.7	173.2
TS(11-5)	-2563600.6	-2563639.1	128.9	-371390.8	-371427.3	122.4
TS(14-15)	-5555462.8	-5555518.1	185.4	-	-	-
TS(16-17)	-2587488.7	-2587526.7	127.2	-395298.4	-395335.3	123.8
TS(18a-19a)	-3127506.9	-3127560.8	180.8	-	-	-
TS(18b-19b)	-3127521.8	-3127578.4	189.9	-	-	-
TS(19a-30)	-3127503.5	-3127555.0	172.8	-935541.2	-935589.9	163.4
TS(19b-30)	-3127481.2	-3127534.1	177.4	-	-	-
TS(2-31a)_R=Bu	-2913013.9	-2913075.3	205.7	-	-	-
TS(2-31a)_R=Ph	-2959314.5	-2959374.0	199.4	-	-	-

TS(2-31b)_R=Bu	-2912998.3	-2913057.0	196.7	-	-	-
TS(2-31b)_R=Ph	-2959314.8	-2959374.5	200.0	-	-	-
TS(20-29)	-625690.8	-625744.0	178.5	-626005.6	-626053.4	160.0
TS(22a-23a)	-3127514.1	-3127569.6	186.1	-935550.0	-935602.8	177.3
TS(22b-23b)	-3127515.5	-3127571.9	189.3	-3127500.0	-3127554.9	184.4
TS(23a-18a)	-3127511.8	-3127568.4	189.8	-935546.5	-935601.6	184.8
TS(23b-18b)	-3127516.5	-3127573.2	190.3	-	-	-
TS(24-25)	-3667526.2	-3667598.2	241.5	-1475785.8	-1475852.6	224.1
TS(26-27)	-3667522.5	-3667595.4	244.4	-	-	-
TS(27-28)	-3667532.5	-3667604.3	240.8	-1475791.7	-1475859.7	228.0
TS(8-15)	-5605411.3	-5605475.9	216.8	-	-	-
TS(9'-10)	-3103621.7	-3103677.1	186.0	-911642.1	-911694.3	175.2
TS(9''-10)	-3103624.0	-3103680.6	189.9	-911643.2	-911696.8	179.8