Supporting Information

Probing β-alkyl Elimination and Selectivity in Polyolefin Hydrogenolysis through DFT

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Structure	E(TPSSh/cc-pVDZ)	E(M06-2X(PCM)/cc-pVTZ)	ZPE-C	ε_0	D_0	$H_{correction}$	$S_{correction}$	$G_{298.15}$	$G_{423.15}$
H_2	-1.179034485	-1.16880845	0.010144	-1.168890485	0	0.013449	0.014791	-1.16526942	-1.17022623
Methane	-40.5294983	-40.5014633	0.044873	-40.4846253	-0.00000015	0.048684	0.021133	-40.46693856	-40.47728575
Ethane	-79.85073321	-79.80542576	0.074559	-79.77617421	-0.00000892	0.078991	0.025863	-79.74377189	-79.75844981
Butane	-158.4968041	-158.4194341	0.131559	-158.3652451	-0.00016281	0.138317	0.034812	-158.304604	-158.3275992
2M_Butane	-197.8194729	-197.7278481	0.159437	-197.6600359	-0.00030243	0.167523	0.038162	-197.586196	-197.6129596
R_3M_Hexane	-276.463766	-276.3406321	0.21613	-276.247636	-0.00065737	0.226972	0.045601	-276.1448701	-276.1795373
2M_Heptane	-315.7881537	-315.6486953	0.244385	-315.5437687	-0.00078746	0.256584	0.049291	-315.4259237	-315.4645232
2M_Nonane	-394.4328075	-394.2617229	0.301175	-394.1316325	-0.00113568	0.316018	0.056486	-393.9846862	-394.0311215
2M_Decane	-433.7545357	-433.5679321	0.329599	-433.4249367	-0.00133644	0.345786	0.060248	-433.2638487	-433.3142533
S_3M_Decane	-433.7554759	-433.5685344	0.32926	-433.4262159	-0.00127397	0.345662	0.06052	-433.2646948	-433.3151586
S_28M_Decane	**-473.0778327**	**-472.8765247**	**0.357159**	**-472.7206737**	**-0.00152408**	**0.374881**	**0.063896**	**-472.5459781**	**-472.6002213**
1E_4M_Hexene	-275.2248132	-275.1120828	0.192768	-275.0320452	-0.00058776	0.203024	0.04451	-274.9394683	-274.971379
1E_6M_Heptene	-314.5492449	-314.4201198	0.220949	-314.3282959	-0.00072296	0.232569	0.048097	-314.2204987	-314.2563055
C2E_8M_Nonene	-393.1981228	-393.0362847	0.277461	-392.9206618	-0.00105797	0.291941	0.055829	-392.7828071	-392.8265868
T2E_8M_Nonene	-393.2002078	-393.0380766	0.277421	-392.9227868	-0.00101303	0.291871	0.055068	-392.7841142	-392.8276725
T3E_9M_Decene	-432.5230915	-432.3445705	0.305838	-432.2172535	-0.00117261	0.32165	0.059099	-432.0636894	-432.1112935
C3E_9M_Decene	-432.5208861	-432.3426106	0.306154	-432.2147321	-0.00122038	0.321875	0.059238	-432.0616454	-432.1093169
T2E_8M_Decene	-432.521639	-432.3439772	0.305495	-432.216144	-0.00120595	0.321461	0.059328	-432.0634719	-432.1111158
C3E_39M_Decene	-471.8472896	-471.6538739	0.333807	-471.5134826	-0.00146447	0.351083	0.062722	-471.3462791	-471.3977562
T4E_39M_Decene	-471.8456426	-471.6524138	0.333548	-471.5120946	-0.00139469	0.350846	0.062487	-471.3448288	-471.3962084
C4E_39M_Decene	-471.8433483	-471.6505014	0.333977	-471.5093713	-0.00152612	0.351132	0.062621	-471.3428515	-471.3943038
LsZrH	**-1667.686076**	**-1667.710973**	**0.045522**	-1667.640554	**-0.00027667**	**0.059419**	**0.0528**	**-1667.687207**	**-1667.705545**
LsZr_S_28M_Decane_SBM_TSC1	-2140.729994	-2140.550233	0.399429	**-2140.330565**	-0.00333743	0.431357	0.097805	-2140.187743	-2140.255016
LsZr_S_28M_Decane_SBM_TSC2	-2140.726547	-2140.545651	0.399281	-2140.327266	-0.00351662	0.431339	0.096108	-2140.182221	-2140.248997

Table S1 Cont. Final Energies, Enthalpy and Entropy Corrections, Gibbs Free Energies from TPSSh functional with Zero Damping Dispersion Correction-D0. In Hartree. See Computational Details for Methods.

Structure	E(TPSSh/cc-pVDZ)	E(M06-2X(PCM)/cc-pVTZ)	ZPE-C	ε_0	D_0	$H_{correction}$	$S_{correction}$	$G_{298.15}$	$G_{423.15}$
LsZr_S_28M_Decane_SBM_TSC3	-2140.727601	-2140.547836	0.399701	-2140.3279	-0.00351834	0.431672	0.096335	-2140.184227	-2140.251111
LsZr_S_28M_Decane_SBM_TSC4	-2140.728495	-2140.549097	0.399574	-2140.328921	-0.00372516	0.431587	0.096802	-2140.186092	-2140.253101
LsZr_S_28M_Decane_SBM_TSC5	-2140.728057	-2140.549294	0.399802	-2140.328255	-0.00386626	0.431588	0.095266	-2140.1854	-2140.251982
LsZr_S_28M_Decane_SBM_TSC6	-2140.728781	-2140.549006	0.3994	-2140.329381	-0.00368435	0.431341	0.096578	-2140.186056	-2140.252977
LsZr_S_28M_Decane_SBM_TSC7	-2140.727989	-2140.548654	0.400268	-2140.327721	-0.00392507	0.431883	0.094512	-2140.184019	-2140.250429
LsZr_S_28M_Decane_SBM_TSC8	-2140.726767	-2140.546601	0.399434	-2140.327333	-0.00363491	0.431407	0.095746	-2140.182979	-2140.249662
LsZr_S_28M_Decane_SBM_TSC8M	-2140.729809	-2140.550529	0.399796	-2140.330013	-0.00327676	0.431538	0.095891	-2140.186515	-2140.253276
LsZr_S_28M_Decane_SBM_TSC9	-2140.727156	-2140.546025	0.399436	-2140.32772	-0.00350384	0.431366	0.095752	-2140.182317	-2140.249007
LsZr_S_28M_Decane_SBM_TSC10	-2140.72917	-2140.549484	0.399692	-2140.329478	-0.00309707	0.431391	0.096055	-2140.185547	-2140.252334
LsZr_S_28M_Decane_C3	-2139.57229	-2139.402574	0.384507	-2139.187783	-0.00330823	0.416352	0.097649	-2139.054955	-2139.120695
LsZr_S_28M_Decane_C6	-2139.575839	-2139.408355	0.384511	-2139.191328	-0.00374297	0.415928	0.094404	-2139.05942	-2139.124208
LsZr_S_28M_Decane_C7	**-2139.574071**	**-2139.404469**	**0.384329**	**-2139.189742**	**-0.00340748**	**0.415981**	**0.095939**	**-2139.056175**	**-2139.121393**
LsZr_S_28M_Decane_C6_TSH7_E	-2139.537598	-2139.367615	0.379958	-2139.15764	-0.00376716	0.411095	0.09352	-2139.022946	-2139.086977
LsZr_S_28M_Decane_C7_TSH6_E	-2139.535402	-2139.365469	0.379794	-2139.155608	-0.00341548	0.41109	0.0951	-2139.021511	-2139.085986
LsZr_S_28M_Decane_C7_TSH6_Z	-2139.531565	-2139.361812	0.379765	-2139.1518	-0.003317	0.411216	0.096137	-2139.018324	-2139.083097
LsZr_S_28M_Decane_C7_TSH8_Z	-2139.538792	-2139.369154	0.379968	-2139.158824	-0.00351166	0.411125	0.093505	-2139.024189	-2139.08822
LsZr_S_28M_Decane_C8_TSH7_Z	-2139.533515	-2139.363219	0.37986	-2139.153655	-0.00330805	0.411169	0.09369	-2139.018131	-2139.082222
LsZr_S_28M_Decane_C3_TSC1	-2139.527084	-2139.357131	0.381527	-2139.145557	-0.00336816	0.413051	0.094613	-2139.010839	-2139.07536
LsZr_S_28M_Decane_C3_TSC2M	-2139.530145	-2139.359465	0.381289	-2139.148856	-0.00335402	0.412847	0.094699	-2139.01342	-2139.077943
LsZr_S_28M_Decane_C6_TSC4	-2139.528303	-2139.35749	0.38209	-2139.146213	-0.00346968	0.413546	0.094598	-2139.010795	-2139.075376
LsZr_S_28M_Decane_C6_TSC8	-2139.526495	-2139.354394	0.382267	-2139.144228	-0.00384052	0.41363	0.094202	-2139.00772	-2139.072213
LsZr_S_28M_Decane_C7_TSC8M	-2139.529459	-2139.358484	0.381485	-2139.147974	-0.00344945	0.41288	0.09439	-2139.012295	-2139.076738
LsZr_S_28M_Decane_C7_TSC9	-2139.524006	-2139.352788	0.381776	-2139.14223	-0.00345596	0.413331	0.096277	-2139.007419	-2139.072454

Table S1 Cont. Final Energies, Enthalpy and Entropy Corrections, Gibbs Free Energies from TPSSh functional with Zero Damping Dispersion Correction-D0. In Hartree. See Computational Details for Methods.

Structure	E(TPSSh/cc-pVDZ)	E(M06-2X(PCM)/cc-pVTZ)	ZPE-C	ε_0	D_0	$H_{correction}$	$S_{correction}$	$G_{298.15}$	$G_{423.15}$
LsZr_R_28M_Decane_C7_TSC8M	-2139.528081	-2139.358932	0.382068	-2139.146013	-0.00358667	0.413349	0.093294	-2139.011676	-2139.075865
LsZr_R_28M_Decane_C7_TSC9	-2139.529117	-2139.357776	0.381794	-2139.147323	-0.00349929	0.413285	0.094564	-2139.011348	-2139.075898
LsZr_Methane	-1707.027174	-1707.032282	0.073224	-1706.95395	-0.00051255	0.088872	0.056778	-1706.981964	-1707.004306
LsZr_Ethane	-1746.345319	-1746.331844	0.1023	-1746.243019	-0.00069	0.120197	0.062947	-1746.254511	-1746.281602
LsZr_Butane_C2	-1824.989548	-1824.94349	0.158619	-1824.830929	-0.00110657	0.178645	0.068348	-1824.811744	-1824.846131
LsZr_2M_Butane_C4	-1864.315371	-1864.255493	0.186832	-1864.128539	-0.00119739	0.208752	0.073713	-1864.097326	-1864.136073
LsZr_S_3M_Decane_C8	-2100.249911	-2100.093997	0.356531	-2099.89338	-0.00294462	0.386992	0.094317	-2099.773142	-2099.835102
LsZr_Methane_SBM_TSC1	-1708.178345	-1708.171235	0.088095	-1708.09025	-0.00062702	0.105043	0.059753	-1708.106853	-1708.131554
LsZr_S_3M_Decane_SBM_TSC8	-2101.404546	-2101.240513	0.371699	-2101.032847	-0.00346111	0.402144	0.092693	-2100.903935	-2100.966934
LsZr_S_3M_Decane_C8_TSH9_E	-2100.212438	-2100.056178	0.352108	-2099.86033	-0.00269194	0.382065	0.092324	-2099.738662	-2099.799546
LsZr_S_28M_Decane_C1	-2139.573584	-2139.405527	0.384791	-2139.188793	-0.00288378	0.416277	0.097384	-2139.057381	-2139.123052
LsZr_S_28M_Decane_C2	-2139.573259	-2139.403116	0.384072	-2139.189187	-0.00305887	0.415852	0.095901	-2139.054577	-2139.119768
LsZr_S_28M_Decane_C4	-2139.574281	-2139.405613	0.384731	-2139.18955	-0.00336707	0.416137	0.094698	-2139.056291	-2139.121182
LsZr_S_28M_Decane_C5	-2139.573401	-2139.40381	0.384628	-2139.188773	-0.00346729	0.416167	0.095309	-2139.054967	-2139.120031
LsZr_S_28M_Decane_C8M	-2139.57119	-2139.404571	0.384979	-2139.186211	-0.00305136	0.416231	0.095689	-2139.055503	-2139.120693
LsZr_S_28M_Decane_C9	-2139.573624	-2139.40414	0.384483	-2139.189141	-0.00307268	0.416034	0.095508	-2139.055169	-2139.120275
LsZr_S_28M_Decane_C10	-2139.574793	-2139.40606	0.384729	-2139.190064	-0.00269502	0.416088	0.096146	-2139.057084	-2139.122383

Relative Enthalpies and Gibbs Free Energies for Probing β-alkyl elimination

Table S2. Relative Energies (zero damping corrections, M06-2X/PCM(PhMe) corrected SPE) --Table sorted by figure. All values are in kcal/mol at 423.15 K and 1 atm.

Figure	Structure	Δ*H*	Δ*G*	Figure	Structure	Δ*H*	Δ*G*
Figure 3	**LsZrH + S_28M_Decane + H_2**	**0**	**0**	**Figure 6**	**(2 * LsZrH) + H_2 + S_28M_Decane**	**0**	**0**
	LsZr_S_28M_Decane_SBM_TSC1 + H_2	21.1	31.8		LsZrH + H_2 + LsZr_S_28M_Decane_SBM_TSC3	22.7	34.3
	LsZr_S_28M_Decane_SBM_TSC2 + H_2	24.0	35.6		LsZrH + (2 * H_2) + LsZr_S_28M_Decane_C3	7.7	9.3
	LsZr_S_28M_Decane_SBM_TSC3 + H_2	22.7	34.3		LsZrH + (2 * H_2) + LsZr_S_28M_Decane_C3_TSC2M	32.8	36.1
	LsZr_S_28M_Decane_SBM_TSC4 + H_2	21.7	33.0		LsZr_Methane + LsZrH + (2 * H_2) + T2E_8M_Decene	21.4	12.6
	LsZr_S_28M_Decane_SBM_TSC5 + H_2	21.5	33.8		LsZr_Methane + (2 * H_2) + LsZr_S_3M_Decane_C8_TSH2_E	20.8	23.4
	LsZr_S_28M_Decane_SBM_TSC6 + H_2	21.7	33.1		LsZr_Methane + (2 * H_2) + LsZr_S_3M_Decane_C8	-0.3	1.1
	LsZr_S_28M_Decane_SBM_TSC7 + H_2	22.0	34.7		LsZr_Methane + H_2 + LsZr_S_3M_Decane_SBM_TSC8	13.7	25.1
	LsZr_S_28M_Decane_SBM_TSC8 + H_2	23.3	35.2		LsZrMe + LsZrH + H_2 + S_3M_Decane	-8.3	-8.6
	LsZr_S_28M_Decane_SBM_TSC8M + H_2	21.0	32.9		LsZrH + S_3M_Decane + LsZr_Methane_SBM_TSC1	11.6	18.4
	LsZr_S_28M_Decane_SBM_TSC9 + H_2	23.7	35.6		(2 * LsZrH) + Methane + S_3M_Decane	-12.6	-13.8
	LsZr_S_28M_Decane_SBM_TSC10 + H_2	21.7	33.5	**Table 1**	**LsZr_S_28M_Decane_C3 + 2H_2**	**0**	**0**
Figure 5	**LsZrH + S_28M_Decane + H_2**	**0**	**0**		LsZr_S_28M_Decane_C3_TSC1 + 2H_2	26.7	28.5
	LsZr_S_28M_Decane_C7_TSC8M + 2H_2	33.4	36.9		LsZr_S_28M_Decane_C3_TSC2M + 2H_2	25.1	26.8
	LsZr_S_28M_Decane_C7_TSC9 + 2H_2	37.1	39.6		**LsZr_S_28M_Decane_C6 + 2H_2**	**0**	**0**
	LsZr_R_28M_Decane_C7_TSC8M + 2H_2	33.3	37.4		LsZr_S_28M_Decane_C6_TSC4 + 2H_2	30.8	30.7
	LsZr_R_28M_Decane_C7_TSC9 + 2H_2	34.0	37.4		LsZr_S_28M_Decane_C6_TSC8 + 2H_2	32.5	32.6
	LsZr_Methane + T3E_9M_Decene + 2H_2	21.2	12.5		**LsZr_S_28M_Decane_C7 + 2H_2**	**0**	**0**
	LsZr_Methane + C3E_9M_Decene + 2H_2	22.5	13.8		LsZr_S_28M_Decane_C7_TSC8M + 2H_2	27.2	28.0
	LsZr_Ethane + T2E_8M_Nonene + 2H_2	26.6	16.5		LsZr_S_28M_Decane_C7_TSC9 + 2H_2	30.9	30.7
	LsZr_Ethane + C2E_8M_Nonene + 2H_2	27.7	17.2				

Table S2 Cont. Relative Energies (zero damping corrections, M06-2X/PCM(PhMe) corrected SPE) --Table sorted by figure. All values are in kcal/mol at 298 K and 1 atm.

Figure	Structure	Δ*H*	Δ*G*	Figure	Structure	Δ*H*	Δ*G*
Scheme 1	**LsZrH + S_28M_Decane + H_2**	**0**	**0**		LsZrH + (2 * H_2) + T4E_39M_Decene	29.6	21.2
	LsZr_S_28M_Decane_C6 + (2 * H_2)	3.5	7.1		LsZrH + (2 * H_2) + C4E_39M_Decene	30.8	22.4
	LsZr_S_28M_Decane_C8 + (2 * H_2)	7.3	9.9		LsZrH + (2 * H_2) + C3E_39M_Decene	28.7	20.2
	LsZr_S_28M_Decane_C6_TSH7_E + (2 * H_2)	26.3	30.5		LsZr_2M_Butane_C4 + (2 * H_2) + 1E_4M_Hexene	27.9	17.6
	LsZr_S_28M_Decane_C7_TSH6_E + (2 * H_2)	27.9	31.1		LsZr_Butane_C2 + (2 * H_2) + 1E_6M_Heptene	29.7	20.8
	LsZr_S_28M_Decane_C7_TSH6_Z + (2 * H_2)	30.4	32.9		LsZr_Methane + (2 * H_2) + T3E_9M_Decene	21.2	12.5
	LsZr_S_28M_Decane_C7_TSH8_Z + (2 * H_2)	25.5	29.7		LsZr_Ethane + (2 * H_2) + C2E_8M_Nonene	27.7	17.2
	LsZr_S_28M_Decane_C8_TSH7_Z + (2 * H_2)	29.4	33.5		LsZrH + 3M_Hexane + 2M_Butane	-11.5	-13.8
	LsZr_S_28M_Decane_C6_TSC4 + (2 * H_2)	34.3	37.8		LsZrH + Butane + 2M_Heptane	-11.1	-13.6
	LsZr_S_28M_Decane_C6_TSC8 + (2 * H_2)	36.0	39.7		LsZrH + Methane + 2M_Decane	-12.3	-13.2
	LsZr_S_28M_Decane_C7_TSC8M + (2 * H_2)	33.4	36.9		LsZrH + Ethane + 2M_Nonane	-10.6	-12.0
	LsZr_S_28M_Decane_C7_TSC9 + (2 * H_2)	37.1	39.6				