

Supporting Materials
for
Impact of the olefin structure on the catalytic cycle and
decomposition rates of Hoveyda-Grubbs metathesis
catalyst

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Table S1. Total energy values (E) and Gibbs free energy values (G; as defined in the manuscript) for catalyst **1** and its complexes with chloroethene (**2**) and dichloroethene (**3.4**).

structure	M06 Gas Phase. LACV3P**++ (Hartrees)	Solvation E in Toluene (Hartrees)	Zero-point E (kcal/mol)	Entropy E (cal/mol)	Thermal correction to enthalpy (Hartrees)	G (Hartrees)
monochloro						
pre	-2402.603	-0.002	386.2	226.3	0.038	-2402.058
2-ts1	-2940.728	0.000	412.7	251.4	0.043	-2940.147
2-ts1_geom2	-2940.726	-0.001	413.5	251.2	0.043	-2940.144
2-ts1_geom3	-2940.729	-0.001	413.5	246.2	0.042	-2940.146
2-ts1_geom4	-2940.727	0.000	412.8	252.5	0.043	-2940.147
2-int1	-2940.736	-0.001	414.0	251.6	0.043	-2940.154
2-int1-geom2	-2940.733	-0.001	413.6	248.3	0.043	-2940.150
2-int1-geom3	-2940.738	-0.001	413.9	241.1	0.042	-2940.152
2-int1-geom4	-2940.730	0.000	413.6	249.9	0.043	-2940.147
2-ts2	-2940.732	0.000	414.4	240.3	0.041	-2940.145
2-ts2-geom2	-2940.724	-0.001	414.3	240.9	0.041	-2940.138
2-ts2-geom3	-2940.733	-0.001	414.5	239.0	0.041	-2940.145
2-ts2-geom4	-2940.719	0.000	414.4	237.6	0.041	-2940.131
2-int2	-2940.747	-0.001	415.3	242.4	0.041	-2940.160
2-int2-geom2	-2940.736	-0.001	415.1	244.9	0.041	-2940.150
2-int2-geom3	-2940.749	-0.001	415.4	241.8	0.041	-2940.161
2-int2-geom4	-2940.726	-0.001	415.3	240.5	0.041	-2940.138
2-ts1_vr1	-2940.690	-0.001	414.3	238.8	0.041	-2940.103
2-ts1_vr1_geom2	-2940.703	-0.001	412.6	241.7	0.041	-2940.120
2-ts1_vr1_geom4	-2940.692	0.001	412.3	241.3	0.041	-2940.108
2-int1_vr1	-2940.722	0.000	414.0	248.8	0.043	-2940.139
2-int1_vr1_geom2	-2940.745	0.000	414.2	248.8	0.042	-2940.161
2-int1_vr1_geom4	-2940.739	0.000	413.9	246.4	0.042	-2940.154
2-int2_vr1	-2940.713	-0.001	413.1	242.7	0.041	-2940.130
2-int2_vr1_geom2	-2940.726	-0.001	414.2	245.9	0.042	-2940.142
2-int2_vr1_geom4	-2940.726	-0.001	413.7	245.0	0.042	-2940.143
2-ts3	-2940.741	0.000	414.6	241.8	0.041	-2940.154
2-ts3-geom2	-2940.727	-0.001	414.1	241.6	0.041	-2940.141
2-ts3-geom3	-2940.742	0.000	414.5	241.3	0.041	-2940.155
2-ts3-geom4	-2940.718	-0.001	413.5	230.6	0.040	-2940.130
2-int3	-2940.747	0.000	413.9	248.6	0.043	-2940.163
2-int3-geom2	-2940.732	-0.001	413.1	248.9	0.043	-2940.149
2-int3-geom3	-2940.747	0.000	414.0	249.0	0.043	-2940.163
2-int3-geom4	-2940.717	0.000	412.9	242.1	0.041	-2940.133
int4	-2438.156	-0.003	274.2	193.0	0.030	-2437.783
2-int5	-2976.315	-0.001	302.1	214.8	0.035	-2975.903
2-int5-geom1	-2976.315	-0.001	302.1	213.4	0.035	-2975.902
2-int5-geom3	-2976.318	-0.001	302.2	209.0	0.034	-2975.903
2-int5-geom4	-2976.317	-0.001	302.2	210.9	0.034	-2975.904
2-ts6	-2976.309	-0.002	302.9	200.5	0.032	-2975.891
2-ts6-geom1	-2976.310	-0.002	302.9	201.2	0.032	-2975.893
2-int6	-2976.318	-0.002	303.7	202.3	0.032	-2975.900
2-int6-geom1	-2976.320	-0.002	303.7	201.1	0.032	-2975.902
2-ts1_vr2	-2976.277	0.000	300.0	198.0	0.032	-2975.861
2-ts1_vr2_geom1	-2976.277	-0.001	301.5	199.6	0.032	-2975.860
2-int1_vr2	-2976.316	-0.001	301.9	200.0	0.032	-2975.899
2-int1_vr2_geom1	-2976.300	-0.002	302.4	209.6	0.034	-2975.886
2-int2_vr2	-2976.304	-0.001	302.1	206.2	0.033	-2975.889
2-int2_vr2_geom1	-2976.288	-0.002	303.1	214.5	0.034	-2975.875
2-ts7 E	-2976.303	-0.001	302.8	200.6	0.032	-2975.885
2-ts7 Z	-2976.302	-0.002	302.8	199.8	0.032	-2975.883
2-int7 E	-2976.309	-0.002	303.7	202.0	0.032	-2975.890
2-int7 Z	-2976.307	-0.002	303.7	202.0	0.032	-2975.889
2-ts1_vr3_geom2 (E)	-2976.270	0.000	301.1	199.5	0.032	-2975.852
2-ts1_vr3_geom3 (Z)	-2976.264	0.000	301.2	197.6	0.032	-2975.846
2-int1_vr2_geom2 (E)	-2976.313	-0.001	302.0	200.8	0.033	-2975.895
2-int1_vr2_geom3 (Z)	-2976.304	-0.001	301.9	211.1	0.034	-2975.890

2-int2_vr2_geom2 (E)	-2976.298	-0.001	301.0	200.0	0.032	-2975.882
2-int2_vr2_geom3 (Z)	-2976.297	-0.001	302.4	198.6	0.032	-2975.878
2-ts8 E	-2976.293	-0.002	302.6	200.6	0.032	-2975.876
2-ts8 Z	-2976.293	-0.002	302.6	199.4	0.032	-2975.875
1-int4 = int8	-1978.544	-0.003	279.2	198.3	0.031	-1978.165
2	-538.134	0.002	26.5	63.1	0.005	-538.115
ethylene	-78.539	0.003	31.8	52.4	0.004	-78.506
benzylidene	-502.556	0.003	138.6	106.9	0.013	-502.371
dichloro E (trans)						
3-ts1	-3400.317	-0.001	407.6	256.9	0.043	-3399.746
3-ts1_geom2	-3400.317	-0.001	407.7	254.2	0.044	-3399.747
3-int1	-3400.328	-0.001	408.2	255.9	0.044	-3399.755
3-int1_geom2	-3400.326	0.000	408.2	249.4	0.043	-3399.751
3-ts2	-3400.321	0.000	408.6	246.9	0.042	-3399.745
3-ts2_geom2	-3400.310	0.000	408.5	245.2	0.042	-3399.733
3-int2	-3400.331	0.000	409.4	250.5	0.043	-3399.756
3-int2_geom2	-3400.323	-0.001	409.5	247.5	0.043	-3399.746
3-ts1_vr1_geom2	-3400.293	0.000	406.5	247.1	0.042	-3399.720
3-int1_vr1_geom2	-3400.337	0.000	407.9	250.2	0.043	-3399.764
3-int2_vr1_geom2	-3400.318	-0.001	407.2	247.7	0.042	-3399.746
3-ts3	-3400.323	0.000	408.4	249.4	0.043	-3399.748
3-ts3_geom2	-3400.314	0.001	408.6	248.1	0.042	-3399.738
3-int3	-3400.340	0.000	408.0	254.4	0.044	-3399.767
3-int3_geom2	-3400.332	-0.002	408.0	256.4	0.044	-3399.761
3-int5	-3435.905	-0.001	296.3	217.4	0.035	-3435.502
3-int5_geom2	-3435.906	-0.001	296.4	214.9	0.035	-3435.501
3-ts6	-3435.890	-0.001	297.0	205.8	0.033	-3435.481
3-ts6_geom2	-3435.890	-0.001	296.8	207.9	0.034	-3435.483
3-int6	-3435.901	-0.001	298.0	208.2	0.034	-3435.492
3-int6_geom2	-3435.901	-0.002	297.8	207.3	0.034	-3435.493
3-ts1_vr2	-3435.863	0.001	295.0	207.7	0.033	-3435.458
3-int1_vr2	-3435.903	0.000	296.4	214.7	0.035	-3435.498
3-int2_vr2	-3435.903	0.000	296.4	214.0	0.035	-3435.498
3	-997.725	0.003	21.1	70.8	0.005	-997.716
dichloro Z (cis)						
4-ts6	-3435.894	-0.001	297.0	207.1	0.033	-3435.487
4-ts6_geom2	-3435.893	-0.002	297.2	205.9	0.033	-3435.486
4-int6	-3435.901	-0.002	297.8	207.5	0.034	-3435.493
4-int6_geom2	-3435.899	-0.002	297.8	207.5	0.034	-3435.491
4-ts1_vr2_geom1	-3435.851	0.001	295.1	207.4	0.033	-3435.445
4-ts1_vr2_geom2	-3435.864	0.001	295.4	205.6	0.034	-3435.456
4-int1_vr2_geom1	-3435.891	0.000	295.9	210.7	0.033	-3435.485
4-int1_vr2_geom2	-3435.891	0.000	295.9	210.7	0.035	-3435.485
4-int2_vr2_geom1	-3435.911	-0.001	297.8	213.4	0.035	-3435.504
4-int2_vr2_geom2	-3435.911	-0.001	297.8	213.4	0.036	-3435.504
4	-997.726	0.003	21.3	70.6	0.005	-997.718

Table S2. Total energy values (E) and Gibbs free energy values (G; as defined in the manuscript) for catalyst **1** and its complexes with methoxyethene (**5**) and 1,2-dimethoxyethene (**6,7**).

structure	M06 Gas Phase. LACV3P*** (Hartrees)	Solvation E in Toluene (Hartrees)	Zero-point E (kcal/mol)	Entropy E (cal/mol)	Thermal correction to enthalpy (Hartrees)	G (Hartrees)
monomethoxy						
5-ts1	-2595.628	-0.001	439.7	256.2	0.044	-2595.005
5-ts1_geom2	-2595.631	-0.001	439.8	255.7	0.044	-2595.008
5-ts1_geom3	-2595.630	-0.001	439.4	245.8	0.042	-2595.005
5-ts1_geom4	-2595.624	-0.002	439.6	252.1	0.044	-2595.001
5-int1	-2595.637	-0.001	440.3	259.9	0.045	-2595.014
5-int1_geom2	-2595.641	-0.001	440.5	256.4	0.045	-2595.017
5-int1_geom3	-2595.637	-0.001	439.8	256.0	0.044	-2595.014

5-int1_geom4	-2595.639	0.000	440.3	253.4	0.044	-2595.014
5-ts2	-2595.640	0.000	440.5	241.8	0.042	-2595.012
5-ts2_geom2	-2595.626	-0.001	440.3	248.3	0.043	-2595.000
5-ts2_geom3	-2595.618	0.000	440.4	250.1	0.043	-2594.992
5-ts2_geom4	-2595.638	-0.002	440.6	245.3	0.043	-2595.012
5-int2	-2595.649	-0.001	441.5	246.5	0.043	-2595.021
5-int2_geom2	-2595.630	-0.002	440.8	249.6	0.043	-2595.005
5-int2_geom3	-2595.619	-0.001	440.9	249.6	0.043	-2594.992
5-int2_geom4	-2595.647	-0.002	441.3	237.8	0.041	-2595.017
5-ts1_vr1	-2595.617	-0.001	438.8	237.7	0.041	-2594.990
5-ts1_vr1_geom2	-2595.593	0.000	439.3	246.6	0.042	-2594.968
5-ts1_vr1_geom3	-2595.577	-0.001	438.9	240.7	0.042	-2594.951
5-ts1_vr1_geom4	-2595.618	-0.001	439.1	242.7	0.042	-2594.992
5-int1_vr1	-2595.659	0.000	440.1	245.5	0.042	-2595.032
5-int1_vr1_geom2	-2595.643	0.000	440.1	249.0	0.043	-2595.017
5-int1_vr1_geom3	-2595.642	-0.001	440.3	244.5	0.043	-2595.014
5-int1_vr1_geom4	-2595.658	-0.001	439.9	235.7	0.041	-2595.029
5-int2_vr1	-2595.636	-0.001	439.3	243.8	0.042	-2595.011
5-int2_vr1_geom2	-2595.630	-0.002	439.7	250.2	0.043	-2595.007
5-int2_vr1_geom3	-2595.629	-0.002	439.1	244.3	0.043	-2595.005
5-int2_vr1_geom4	-2595.627	-0.002	439.3	247.8	0.043	-2595.004
5-ts3	-2595.645	-0.001	440.4	246.0	0.042	-2595.019
5-ts3_geom2	-2595.621	-0.001	440.5	246.5	0.042	-2594.995
5-ts3_geom3	-2595.614	0.000	440.3	242.6	0.042	-2594.986
5-ts3_geom4	-2595.646	-0.002	440.5	245.0	0.042	-2595.020
5-int3	-2595.655	-0.002	439.9	253.4	0.043	-2595.033
5-int3_geom2	-2595.639	-0.001	439.9	250.9	0.044	-2595.014
5-int3_geom3	-2595.625	-0.001	439.3	258.5	0.044	-2595.005
5-int3_geom4	-2595.656	-0.002	440.2	256.3	0.044	-2595.034
5-int4	-2093.056	-0.006	300.2	192.7	0.030	-2092.645
5-int5_geom1	-2286.128	-0.004	354.5	217.3	0.036	-2285.635
5-int5_geom2	-2286.127	-0.004	354.4	218.3	0.036	-2285.633
5-int5_geom3	-2286.124	-0.005	354.4	221.8	0.037	-2285.633
5-int5_geom4	-2286.126	-0.004	354.4	213.7	0.035	-2285.632
5-ts6	-2286.119	-0.005	354.7	206.6	0.034	-2285.623
5-ts6_geom4	-2286.117	-0.005	354.7	205.8	0.034	-2285.621
5-int6	-2286.123	-0.005	355.6	207.1	0.034	-2285.626
5-int6_geom4	-2286.122	-0.005	356.0	212.5	0.035	-2285.625
5-ts7 E	-2286.102	-0.005	354.9	209.9	0.035	-2285.607
5-ts7 Z	-2286.101	-0.005	354.9	209.3	0.034	-2285.606
5-int7 E	-2286.104	-0.005	355.5	210.3	0.035	-2285.608
5-int7 Z	-2286.103	-0.005	355.4	209.7	0.035	-2285.606
5-ts8 E	-2286.087	-0.005	353.9	205.7	0.034	-2285.592
5-ts8 Z	-2286.092	-0.005	354.4	210.3	0.035	-2285.597
5-ts1_vr2	-2286.085	-0.002	353.6	205.9	0.034	-2285.588
5-ts1_vr2_geom4	-2286.064	-0.003	353.7	209.8	0.034	-2285.568
5-ts1_vr3 E	-2286.064	-0.002	353.5	213.6	0.035	-2285.569
5-ts1_vr3 Z	-2286.056	-0.002	353.7	208.7	0.034	-2285.560
5-int1_vr2	-2286.118	-0.003	353.8	212.8	0.035	-2285.623
5-int1_vr2_geom4	-2286.111	-0.004	354.4	213.1	0.035	-2285.616
5-int1_vr3 E	-2286.116	-0.002	353.8	213.1	0.035	-2285.620
5-int1_vr3 Z	-2286.110	-0.002	354.1	212.1	0.035	-2285.613
5-int2_vr2	-2286.096	-0.003	354.4	213.6	0.035	-2285.600
5-int2_vr2_geom4	-2286.092	-0.004	353.9	222.4	0.037	-2285.601
5-int2_vr3 E	-2286.107	-0.002	354.1	216.1	0.036	-2285.612
5-int2_vr3 Z	-2286.089	-0.003	354.0	212.4	0.035	-2285.594
5	-193.037	0.002	53.1	68.5	0.006	-192.977
dimethoxy E (trans)						
6-ts1	-2710.115	-0.001	460.0	269.2	0.047	-2709.464
6-ts1_geom2	-2710.108	-0.002	459.4	264.9	0.046	-2709.457
6-int1	-2710.127	-0.001	460.3	259.8	0.046	-2709.472
6-int1_geom2	-2710.123	-0.002	460.0	275.4	0.048	-2709.475
6-ts2	-2710.104	-0.002	460.3	250.2	0.044	-2709.448
6-ts2_geom2	-2710.116	-0.002	460.3	257.8	0.045	-2709.462
6-int2	-2710.117	-0.001	461.2	258.1	0.045	-2709.461
6-int2_geom2	-2710.127	-0.002	461.3	261.0	0.046	-2709.472

6-ts1_vr1	-2710.082	-0.002	459.0	258.1	0.045	-2709.430
6-ts1_vr1_geom2	-2710.095	-0.001	458.9	250.2	0.044	-2709.440
6-int1_vr1	-2710.129	-0.002	459.8	259.0	0.045	-2709.476
6-int1_vr1_geom2	-2710.138	-0.001	459.9	254.9	0.045	-2709.482
6-int2_vr1	-2710.111	-0.001	459.5	257.8	0.045	-2709.458
6-int2_vr1_geom2	-2710.116	-0.002	459.4	265.9	0.046	-2709.466
6-ts3	-2710.115	-0.001	460.6	249.7	0.044	-2709.457
6-ts3_geom2	-2710.125	-0.003	460.5	256.7	0.045	-2709.471
6-int3	-2710.141	-0.002	460.1	267.4	0.046	-2709.491
6-int3_geom2	-2710.155	-0.002	460.4	270.7	0.047	-2709.505
6-int5	-2400.618	-0.005	374.8	228.1	0.039	-2400.095
6-int5_geom2	-2400.616	-0.004	374.9	229.9	0.039	-2400.093
6-ts6	-2400.594	-0.006	375.1	217.4	0.036	-2400.070
6-ts6_geom2	-2400.595	-0.006	374.8	217.3	0.037	-2400.070
6-int6	-2400.596	-0.006	375.8	218.5	0.037	-2400.070
6-ts1_vr2	-2400.560	-0.004	373.5	219.0	0.037	-2400.036
6-int1_vr2	-2400.611	-0.004	374.0	225.4	0.038	-2400.088
6-int2_vr2	-2400.594	-0.002	374.0	230.6	0.038	-2400.071
6	-307.521	0.001	74.1	81.1	0.008	-307.432
dimethoxy Z (cis)						
7-ts1	-2710.126	-0.002	460.4	256.4	0.046	-2709.469
7-ts1_geom2	-2710.121	-0.003	460.5	261.7	0.045	-2709.470
7-int1	-2710.132	-0.003	460.2	263.3	0.046	-2709.481
7-int1_geom2	-2710.126	-0.002	460.3	270.9	0.047	-2709.476
7-ts2	-2710.114	-0.001	460.2	252.4	0.044	-2709.458
7-ts2_geom2	-2710.114	-0.003	460.5	261.6	0.046	-2709.463
7-int2	-2710.119	-0.001	461.2	257.4	0.045	-2709.462
7-int2_geom2	-2710.123	-0.003	461.1	258.3	0.045	-2709.469
7-ts1_vr1	-2710.069	-0.001	459.6	259.2	0.045	-2709.415
7-ts1_vr1_geom2	-2710.095	-0.001	458.7	252.2	0.044	-2709.440
7-int1_vr1	-2710.119	-0.001	459.3	259.4	0.045	-2709.466
7-int1_vr1_geom2	-2710.132	-0.001	460.1	265.0	0.046	-2709.480
7-int2_vr1	-2710.099	-0.001	458.9	260.2	0.045	-2709.447
7-int2_vr1_geom2	-2710.106	-0.003	459.8	262.3	0.046	-2709.454
7-ts3	-2710.114	-0.001	460.7	256.7	0.045	-2709.458
7-ts3_geom2	-2710.125	-0.004	460.5	251.3	0.044	-2709.471
7-int3	-2710.145	-0.002	460.2	266.0	0.046	-2709.493
7-int3_geom2	-2710.157	-0.002	460.9	260.1	0.046	-2709.502
7-int5	-2400.619	-0.006	374.8	228.6	0.039	-2400.097
7-int5_geom2	-2400.615	-0.006	374.4	226.8	0.038	-2400.094
7-ts6	-2400.597	-0.006	375.4	219.6	0.037	-2400.072
7-ts6_geom2	-2400.600	-0.007	374.8	218.7	0.037	-2400.076
7-int6	-2400.597	-0.006	375.7	219.7	0.037	-2400.072
7-int6_geom2	-2400.595	-0.006	375.9	221.1	0.037	-2400.070
7-ts1_vr2	-2400.554	-0.003	373.8	225.5	0.037	-2400.031
7-ts1_vr2_geom2	-2400.542	-0.003	373.7	221.3	0.037	-2400.017
7-int1_vr2	-2400.600	-0.004	374.0	223.3	0.037	-2400.077
7-vr1_vr2_geom2	-2400.583	-0.004	373.9	226.0	0.037	-2400.060
7-int2_vr2	-2400.605	-0.004	376.9	226.2	0.037	-2400.076
7-int2_vr2_geom2	-2400.572	-0.003	374.9	224.7	0.037	-2400.046
7	-307.518	0.001	73.6	85.0	0.008	-307.432