Computational Study of the Stereochemistry of Intramolecular Carbolithiation of an Unsaturated Secondary Alkyllithium to Produce 2-Methylcyclopentylmethyllithium: Stereochemistry Change Caused by a Single THF Molecule of Solvation

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SUPPORTING INFORMATION:

Full authorship of reference 20. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, Revision C.01. In Gaussian, Inc., Wallingford CT, 2004.

Table S1 Calculated B3LYP/6-31+G(d) energies and activation barriers for the gas phase cyclization of **1**. The units of energy are Hartree unless specified otherwise.

	***Cis*-complex**	***Trans*-complex**	***Cis*-TS(chair)**	***Trans*-TS(twist)**	***Trans*-TS(chair)**	***Cis*-product**	***Trans*-product**
Energy	-282.0613	-282.0608	-282.0496	-282.0484	-282.0486	-282.7259	-282.0755
Zero-point correction	0.1821	0.1823	0.1831	0.18228	0.18281	0.18478	0.18418
Thermal correction to free energies	0.1625	0.1628	0.1638	0.1632	0.1638	0.1656	0.1644
Sum of electronic and thermal free Energies (T = -78˚C)	-281.8989	-281.8981	-281.8854	-281.8852	-281.8847	-281.9070	-281.9111
$\Delta G^{\#}$(kcal/mol)[a]	8.46	8.88 (twisted) 8.61(chair)					

[a] $\Delta G^{\#}$ gives the free energies of activation

Table S2 Calculated B3LYP/6-31+G(d) energies and activation barriers for the cyclization of **1** with explicit inclusion of one THF molecule. The units of energy are Hartree unless specified otherwise.

	Cis-complex-THF	*Trans*-complex-THF	*Cis*-TS(chair)-THF	*Trans*-TS(twist)	*Trans*-TS(chair)-THF	*Cis*-product-THF	*Trans*-product-THF
Energy	-514.5471	-514.5469	-514.5313	-514.5342	-514.5351	-514.5644	-514.5682
Zero-point correction	0.3010	0.3009	0.3013	0.3010	0.3013	0.3036	0.3032
Thermal correction to free energies	0.2753	0.2752	0.2756	0.2755	0.2754	0.2773	0.2763
Sum of electronic and thermal free Energies (T = -78˚C)	-514.2719	-514.2716	-514.2557	-514.2587	-514.2597	-514.2872	-514.2919
$\Delta G^{\#}$(kcal/mol)[a]	10.14	7.63 (chair) 8.17 (twisted)					

[a]$\Delta G^{\#}$ gives the free energies of activation

Table S3 Calculated B3LYP/6-31+G(d) energies and activation barriers for the cyclization of **1** with explicit inclusion of two THF molecules. (Structures are depicted in Figure S1.) The units of energy are Hartree unless specified otherwise.

	Cis-complex-2THF	*Trans*-complex-2THF	*Cis*-TS(chair)-2THF	*Trans*-TS(twist)	*Trans*-TS(chair)-2THF	*Cis*-product-2THF	*Trans*-product-2THF
HF energy	-747.0190	-747.0177	-746.9993	-747.0021	-747.0070	-747.0421	-747.0460
Zero-point correction	0.4188	0.4190	0.4197	0.4191	0.4196	0.4217	0.4214
Sum of electronic and thermal free Energies(T = -78˚C)	-746.6325	-746.6298	-746.6107	-746.6141	-746.6191	-746.6534	-746.6582
$\Delta G^{\#}$(kcal/mol)[a]	13.67	8.37 (chair) 11.55 (twisted)					

[a]$\Delta G^{\#}$ gives the free energies of activation

Table S4 Calculated MP2/6-31+G(d) energies and activation barriers for the gas phase cyclization of **1.** The units of energy are Hartree unless specified otherwise.

	Cis-complex	*Trans*-complex	*Cis*-TS(chair)	*Trans*-TS(twist)	*Trans*-TS(chair)	*Cis*-product	*Trans*-product
Energy	-280.971	-280.971	-280.960	-280.957	-280.959	-280.995	-280.997
Thermal correction to free energies	0.1625	0.1628	0.1638	0.1632	0.1638	0.1656	0.1644
Sum of electronic and thermal free Energies (T = -78˚C)[a]	-280.808	-280.808	-280.796	-280.794	-280.795	-280.830	-280.833
$\Delta G^{\#}$(kcal/mol)[a]	7.65	8.94 (twisted) 8.21 (chair)					

[a]Zero-point energies and thermal corrections to the free energies use B3LYP/6-31+G(d) frequencies
[b]$\Delta G^{\#}$ gives the free energies of activation

Table S5 Calculated MP2/6-31+G(d) energies and activation barriers for the cyclization of **1** with explicit inclusion of one THF molecule. The units of energy are Hartree unless specified otherwise.

	***Cis*-complex-THF**	***Trans*-complex-THF**	***Cis*-TS(chair)-THF**	***Trans*-TS(twist)**	***Trans*-TS(chair)-THF**	***Cis*-product-THF**	***Trans*-product-THF**
Energy	-512.6893	-512.6889	-512.6770	-512.6778	-512.6787	-512.7173	-512.7197
Thermal correction to free energies	0.2753	0.2752	0.2756	0.2755	0.2754	0.2773	0.2763
Sum of electronic and thermal free Energies (T = -78°C)[b]	-512.4140	-512.4137	-512.4013	-512.4022	-512.4033	-512.4400	-512.4434
$\Delta G^{\#}$(kcal/mol)[a]	7.98	6.74 (chair) 7.40 (twisted)					

[a]Zero-point energies and thermal corrections to the free energies use B3LYP/6-31+G(d) frequencies
[b]$\Delta G^{\#}$ gives the free energies of activation

Table S6 Geometries of the optimized structures of **1**, **1(THF)**, and **1(THF)$_2$**. The geometries of **1** and **1(THF)** were optimized at the MP2/6-31+G(d) level of theory and the geometry of **1(THF)$_2$** was optimized at the B3LYP/6-31+G(d) level of theory. Coordinates are in units of Angstroms.

***Cis*_complex**

C	1.464455	0.978821	-0.28493
H	1.414157	0.817689	-1.37118
H	2.280735	1.698295	-0.11593
C	0.154774	1.611346	0.216224
H	0.156691	2.658315	-0.11692
H	0.166458	1.639058	1.316142
C	1.880019	-0.28905	0.399795
H	1.828722	-0.27872	1.491216
C	2.377435	-1.38934	-0.20935
H	2.753495	-2.23462	0.363587
H	2.492669	-1.43412	-1.29178
C	-1.13779	0.93773	-0.25842
H	-1.10124	0.867681	-1.36032
C	-1.43567	-0.43683	0.34917
H	-1.50297	-0.28192	1.443977
C	-2.82621	-0.88721	-0.12276
H	-3.15292	-1.80982	0.375265
H	-3.61067	-0.12639	0.06161
H	-2.84242	-1.08579	-1.20456
Li	0.072925	-1.74432	-0.02692
H	-1.9636	1.650505	-0.04873

***Trans*_complex**

C	1.216269	1.144075	-0.094258
H	1.827338	1.840758	-0.689201
H	1.485154	1.318259	0.957521
C	-0.263482	1.48707	-0.329052
H	-0.535976	1.206161	-1.355784
H	-0.35348	2.581277	-0.282338
C	1.637028	-0.235419	-0.506601
H	1.264911	-0.576882	-1.47566
C	2.492675	-1.035328	0.170593
H	2.834601	-1.981445	-0.244183
H	2.932705	-0.721695	1.116809
C	-1.255541	0.86667	0.664794
H	-2.228496	1.370607	0.479077
C	-1.408394	-0.656693	0.598374
H	-2.079674	-0.930254	1.432223
C	-2.130613	-1.056229	-0.697067
H	-2.448953	-2.107121	-0.671216
H	-3.039593	-0.449351	-0.885135
H	-1.501597	-0.945569	-1.592518
H	-0.951186	1.177374	1.678232
Li	0.355532	-1.622333	0.897161

***Cis*_TS**

C	1.427174	0.853456	-0.220592
H	1.503989	0.718612	-1.31015
H	2.408961	1.215211	0.117049
C	0.334543	1.869587	0.091019
H	0.493516	2.805201	-0.460321
H	0.35299	2.119128	1.161606
C	1.172834	-0.49032	0.424375
H	1.137934	-0.460055	1.516014
C	1.724406	-1.659816	-0.148407
H	2.03149	-2.48747	0.488456
H	2.182603	-1.609409	-1.135425
C	-1.000654	1.219563	-0.257063
H	-1.05235	1.0796	-1.350566
C	-1.069999	-0.121462	0.430687
H	-1.151843	-0.01845	1.519519
C	-2.198121	-1.00707	-0.094167
H	-2.288511	-1.962048	0.454856
H	-3.194049	-0.540961	-0.038782
H	-2.077578	-1.252456	-1.171537
Li	-0.280928	-1.823652	-0.38372
H	-1.845466	1.880431	0.005328

***Trans*_TS(chair like)**

C	0.829119	1.33319	-0.213221
H	1.369713	1.899558	-0.985251
H	1.225706	1.669914	0.756434
C	-0.666879	1.610219	-0.287197
H	-1.028717	1.419014	-1.306471
H	-0.889234	2.662042	-0.066174
C	1.148767	-0.132201	-0.397593
H	0.792877	-0.548794	-1.344452
C	2.362308	-0.666275	0.089852
H	2.858784	-1.470534	-0.45039
H	2.987623	-0.068088	0.751956
C	-1.355483	0.672837	0.706382
H	-2.453372	0.744892	0.612878
C	-0.849701	-0.738139	0.486608
H	-1.018822	-1.328205	1.424307
C	-1.518121	-1.472718	-0.663917
H	-1.101847	-2.480059	-0.81
H	-2.60442	-1.587604	-0.520644
H	-1.377576	-0.934486	-1.609062
H	-1.108485	1.00734	1.725364
Li	0.882568	-1.542153	1.165342

***Trans*_TS(twist)**

C	1.454203	0.916619	-0.16106
H	1.895152	1.300586	-1.09313
H	2.259164	0.935986	0.585286
C	0.284828	1.822987	0.264706
H	0.4314	2.8456	-0.10885
H	0.254128	1.890248	1.361448
C	1.058418	-0.52088	-0.4221
H	0.466106	-0.68403	-1.32459
C	1.824068	-1.59327	0.022449
H	1.777392	-2.56096	-0.47415
H	2.637487	-1.44297	0.730972
C	-1.03456	1.215156	-0.20743
H	-1.01743	1.105668	-1.30426
C	-1.17172	-0.14229	0.437802
H	-1.46746	-0.00503	1.502271
C	-2.12945	-1.1035	-0.25105
H	-2.12563	-2.11723	0.195709
H	-3.18518	-0.78333	-0.2363
H	-1.85102	-1.22939	-1.30706
H	-1.87283	1.89899	0.010434
Li	0.027989	-1.57437	1.120753

***Cis*_product**

C	-1.50884	0.673743	0.603906
H	-1.99094	1.632532	0.383023
H	-1.84913	0.353389	1.601014
C	-1.8419	-0.4171	-0.43899
H	-2.1053	0.032623	-1.40195
H	-2.70011	-1.02411	-0.12894
C	0.030022	0.786873	0.577685
H	0.386952	1.195067	1.538314
C	0.599733	1.648481	-0.56168
H	0.319393	2.695351	-0.3686
H	0.103189	1.381286	-1.51142
C	-0.55292	-1.2672	-0.57103
H	-0.10639	-1.13847	-1.56583
C	0.406331	-0.71119	0.494495
H	0.146008	-1.16842	1.462931
C	1.873113	-1.03494	0.22402
H	2.539956	-0.48249	0.906896
H	2.092431	-2.09935	0.368648
H	2.133331	-0.81868	-0.82382
Li	2.578076	1.236812	-0.66303
H	-0.73683	-2.34124	-0.44166

***Trans*_product**

C	1.008646	-1.34596	0.050125
H	1.210518	-2.20799	-0.59693
H	0.939014	-1.72749	1.078299
C	2.083455	-0.24002	-0.05551
H	2.663328	-0.33222	-0.98097
H	2.801987	-0.29512	0.770347
C	-0.33038	-0.66581	-0.29456
H	-0.33263	-0.49034	-1.38908
C	-1.61044	-1.40794	0.094769
H	-1.6455	-2.36896	-0.44296
H	-1.54592	-1.66641	1.1676
C	1.296597	1.09562	-0.03114
H	1.280194	1.550663	-1.03204
C	-0.1364	0.713033	0.359617
H	-0.18352	0.564584	1.451976
C	-1.1586	1.775214	-0.02823
H	-2.13615	1.597674	0.447229
H	-0.85142	2.775545	0.299993
H	-1.28623	1.809904	-1.11977
H	1.735417	1.83796	0.647491
Li	-3.18878	-0.19755	-0.29054

***Cis*_complex with 1THF**

C	-0.955454	2.75177	-0.244483
H	-0.185666	2.99586	-0.990856
H	-1.688751	3.584928	-0.260444
H	-0.472229	2.800703	0.744844
C	-1.592677	1.377449	-0.495597
H	-2.031768	1.413429	-1.512924
C	-2.764852	1.211306	0.472181
H	-3.443246	2.093017	0.445795
H	-2.397842	1.171635	1.514349
C	-3.637362	-0.02301	0.231231
H	-4.530697	0.031251	0.86959
H	-3.999891	-0.009783	-0.807896
C	-2.960845	-1.373306	0.503631
H	-2.510826	-1.374091	1.507013
H	-3.73825	-2.153574	0.512692
C	-1.938914	-1.79617	-0.510369
H	-2.205636	-1.626929	-1.5556
C	-0.785685	-2.44418	-0.235402
H	-0.135597	-2.805151	-1.029027
H	-0.48992	-2.668858	0.788406
Li	-0.210695	-0.145239	-0.374407
O	1.691398	-0.199324	-0.185354
C	2.37835	1.089868	-0.169645
C	3.702099	0.812626	0.522723
C	4.012888	-0.605585	0.040761
C	2.640691	-1.264017	0.095714
H	1.726737	1.799052	0.342603
H	2.519407	1.413856	-1.207321
H	3.576298	0.829859	1.611182
H	4.472499	1.540889	0.252588
H	4.746302	-1.128206	0.661958
H	4.387002	-0.583879	-0.988881
H	2.419425	-1.663449	1.09235
H	2.494118	-2.050764	-0.64884

***Trans*_complex with 1THF**

C	3.040841	1.33779	-0.31085
H	3.849233	2.031062	-0.0293
H	2.747256	1.604068	-1.33644
C	3.600472	-0.0906	-0.27465
H	3.804266	-0.36597	0.769887
H	4.577449	-0.0759	-0.77894
C	1.901035	1.605155	0.627562
H	1.996035	1.173183	1.6268
C	0.843964	2.409075	0.373802
H	0.105903	2.633982	1.14036
H	0.72008	2.896828	-0.59226
C	2.712361	-1.15456	-0.93174
H	3.325393	-2.08251	-0.97989
C	1.370086	-1.40018	-0.24377
H	0.811021	-2.08903	-0.90915
C	1.584839	-2.14846	1.079594
H	0.636956	-2.52754	1.489946
H	2.262738	-3.02308	0.983597
H	2.023828	-1.5118	1.862371
H	2.55087	-0.85101	-1.97984
Li	0.115584	0.211322	-0.05768
H	-1.71348	-1.80686	-0.32569
C	-2.38026	-1.11042	0.186376
O	-1.78729	0.219205	0.06819
C	-3.76478	-0.96793	-0.42281
H	-2.42784	-1.36937	1.250656
C	-2.82705	1.199158	-0.19821
C	-4.14174	0.454497	-0.00324
H	-3.71219	-1.04614	-1.51455
H	-4.46149	-1.72692	-0.05479
H	-2.68259	2.037385	0.488758
H	-2.70742	1.551531	-1.22938
H	-4.95233	0.886156	-0.59782
H	-4.44071	0.473233	1.050742

***Cis*_TS with 1THF**

C	0.868246	-0.75834	1.713034
H	-0.08889	-1.25335	1.927693
H	1.58397	-1.0932	2.472207
H	0.725755	0.338266	1.961944
C	1.381338	-0.97182	0.306944
H	0.674246	-1.52916	-0.32556
C	2.793957	-1.50418	0.172416
H	2.809538	-2.56314	-0.12989
H	3.295998	-1.45977	1.151042
C	3.607948	-0.65728	-0.80626
H	4.676147	-0.91283	-0.77212
H	3.266283	-0.83441	-1.83667
C	3.361338	0.796285	-0.43801
H	3.71817	0.993124	0.584201
H	3.92012	1.471038	-1.10339
C	1.897405	1.144355	-0.5303
H	1.494657	0.988502	-1.54051
C	1.326211	2.204951	0.191233
H	0.537691	2.817126	-0.24911
H	1.817996	2.610055	1.072403
Li	0.038353	0.571686	0.248936
O	-1.78786	0.234754	-0.12698
C	-2.88953	1.088526	0.29456
C	-4.10017	0.169342	0.343018
C	-3.80359	-0.79494	-0.80714
C	-2.30744	-1.02209	-0.6474
H	-3.00947	1.884356	-0.44964
H	-2.61506	1.529961	1.255734
H	-5.04065	0.714856	0.221675
H	-4.13353	-0.37015	1.296181
H	-4.01861	-0.31791	-1.76986
H	-4.37155	-1.72816	-0.75049
H	-1.78169	-1.2364	-1.58098
H	-2.0875	-1.81074	0.081523

***Trans*_TS(chair) with 1THF**

C	3.292622	0.987067	-0.300042
H	4.041025	1.666244	0.133992
H	3.155304	1.298092	-1.346726
C	3.771619	-0.456712	-0.241656
H	4.026486	-0.716857	0.795487
H	4.682741	-0.603028	-0.836765
C	1.993927	1.178622	0.448691
H	2.043222	0.857986	1.495004
C	1.175315	2.297513	0.200484
H	0.601235	2.748975	1.008434
H	1.330063	2.905432	-0.690276
C	2.624812	-1.333991	-0.745739
H	2.86512	-2.404542	-0.608378
C	1.337675	-0.937004	-0.052427
H	0.485631	-1.219527	-0.707987
C	1.143043	-1.57219	1.314936
H	0.231485	-1.209366	1.814974
H	1.079119	-2.673521	1.277952
H	1.979195	-1.328798	1.983377
H	2.524826	-1.175916	-1.830333
Li	0.035804	0.650755	-0.267377
H	-2.027388	-1.645178	-1.197299
C	-2.403551	-1.109263	-0.322466
O	-1.819409	0.227518	-0.33198
C	-3.910382	-0.887597	-0.328032
H	-2.063705	-1.61838	0.585634
C	-2.864958	1.221458	-0.131592
C	-4.04238	0.437773	0.4243
H	-4.280118	-0.780354	-1.353919
H	-4.448655	-1.713611	0.145908
H	-2.464401	1.985417	0.538348
H	-3.099481	1.676066	-1.101436
H	-4.99743	0.94256	0.250963
H	-3.922874	0.281837	1.502283

***Trans*_TS(twist) with 1THF**

C	3.135716	1.009673	-0.6865
H	4.117438	1.360922	-0.33443
H	2.840154	1.694804	-1.49228
C	3.256951	-0.43451	-1.20288
H	4.278573	-0.64427	-1.54892
H	2.595179	-0.57363	-2.06996
C	2.164017	1.163044	0.46842
H	2.50696	0.746379	1.418542
C	1.314084	2.265206	0.550006
H	0.917746	2.60267	1.506189
H	1.165628	2.922914	-0.30572
C	2.803264	-1.39119	-0.10304
H	3.445125	-1.25903	0.784007
C	1.375491	-1.039	0.241052
H	0.715004	-1.42234	-0.56518
C	0.906721	-1.5399	1.598094
H	-0.13331	-1.25185	1.826493
H	0.956665	-2.63754	1.71479
H	1.53246	-1.11393	2.397032
H	2.940002	-2.4411	-0.41651
Li	0.1275	0.572496	0.13114
H	-1.77004	-1.41363	-1.38269
C	-2.30299	-1.04286	-0.50408
O	-1.72418	0.246755	-0.14532
C	-3.78077	-0.76301	-0.7384
H	-2.14058	-1.7307	0.332704
C	-2.78606	1.21407	0.091714
C	-4.04756	0.379191	0.243589
H	-3.95061	-0.42757	-1.76763
H	-4.40062	-1.64611	-0.55787
H	-2.51265	1.791509	0.977949
H	-2.84158	1.883741	-0.77453
H	-4.95289	0.948577	0.013201
H	-4.13097	-0.00565	1.266117

***Cis*_product with 1THF**

C	-0.895	1.504877	-0.281179
H	-0.306013	1.303082	-1.188792
H	-0.925648	2.594329	-0.149759
H	-0.370684	1.097264	0.593776
C	-2.294956	0.911785	-0.389383
H	-2.837094	1.48294	-1.161565
C	-3.102313	0.993184	0.917261
H	-3.518396	1.995256	1.084137
H	-2.440695	0.777154	1.766456
C	-4.197452	-0.095883	0.787332
H	-4.153704	-0.787737	1.635066
H	-5.204905	0.336629	0.784009
C	-3.88625	-0.831332	-0.535718
H	-4.119816	-1.901191	-0.490944
H	-4.481837	-0.395065	-1.353677
C	-2.38144	-0.582414	-0.777673
H	-2.160172	-0.687919	-1.853662
C	-1.430647	-1.498973	0.009556
H	-1.576815	-2.526467	-0.36457
H	-1.748468	-1.531708	1.068447
Li	0.482884	-0.788468	-0.140947
O	2.327094	-0.323357	-0.116813
C	3.382073	-1.290385	0.166216
C	4.568187	-0.451917	0.613512
C	4.405685	0.800296	-0.250016
C	2.899718	1.01495	-0.214581
H	3.596408	-1.842562	-0.755731
H	3.00165	-1.979837	0.923482
H	5.520877	-0.966197	0.45729
H	4.480621	-0.199974	1.67612
H	4.742277	0.604194	-1.274012
H	4.95355	1.666298	0.132446
H	2.491939	1.486577	-1.111712
H	2.585885	1.582079	0.668578

***Trans*_prodcut with 1THF**

C	3.764094	1.083886	0.241436
H	4.048247	1.78176	1.038677
H	3.934869	1.602466	-0.71264
C	4.545044	-0.248	0.291312
H	4.961842	-0.42868	1.289169
H	5.391723	-0.24945	-0.40533
C	2.271381	0.703406	0.309205
H	2.065856	0.384489	1.351456
C	1.25974	1.778037	-0.09563
H	1.395015	2.649639	0.568972
H	1.537447	2.136553	-1.10566
C	3.505888	-1.33906	-0.07496
H	3.243271	-1.93297	0.812705
C	2.258578	-0.57693	-0.54308
H	2.400389	-0.26555	-1.59255
C	0.988365	-1.41309	-0.4561
H	0.140379	-0.90894	-0.93745
H	1.108148	-2.38157	-0.95889
H	0.733038	-1.61071	0.594847
H	3.876354	-2.04541	-0.8292
Li	-0.6645	1.080909	-0.03035
H	-2.53532	-1.6003	-0.51734
C	-2.79764	-0.97604	0.343684
O	-2.44229	0.403843	0.026433
C	-4.29744	-0.94798	0.592475
H	-2.20218	-1.28137	1.207369
C	-3.65291	1.178758	-0.22323
C	-4.75625	0.143661	-0.37596
H	-4.76428	-1.91912	0.404531
H	-4.51049	-0.65648	1.626855
H	-3.82263	1.833071	0.639064
H	-3.47812	1.787115	-1.1138
H	-4.78316	-0.24044	-1.40162
H	-5.74163	0.552494	-0.13448

***Cis*_complex with 2THF**

C	-1.03632	0.508524	2.591064
H	-0.24434	-0.176587	2.935906
H	-1.39199	1.052838	3.495983
H	-1.88483	-0.128444	2.284167
C	-0.56656	1.425334	1.448152
H	0.297226	2.005603	1.838972
C	-1.66227	2.44954	1.143538
H	-2.01473	2.975614	2.061887
H	-2.56883	1.939997	0.76092
C	-1.27073	3.537351	0.131
H	-2.05374	4.309281	0.097554
H	-0.35884	4.044432	0.485031
C	-1.03589	3.052077	-1.31273
H	-1.92572	2.522267	-1.683769
H	-0.92476	3.942047	-1.954949
C	0.187463	2.201951	-1.527777
H	1.08496	2.534945	-1.004038
C	0.286305	1.169005	-2.386244
H	1.232998	0.665152	-2.567799
H	-0.57089	0.811774	-2.955053
Li	0.058508	0.141702	-0.092734
O	-1.10655	-1.417116	-0.601504
C	-0.98262	-2.673476	0.105924
C	-2.50364	-1.127611	-0.864078
C	-2.33957	-3.364572	-0.040833
C	-3.3043	-2.167621	-0.075552
H	-2.67102	-1.216553	-1.94571
H	-2.6996	-0.097934	-0.552936
H	-4.26386	-2.399366	-0.548825
H	-3.5017	-1.806163	0.940033
H	-2.38656	-3.925375	-0.982667
H	-2.54305	-4.059376	0.7803
H	-0.15306	-3.229664	-0.341439
H	-0.74595	-2.462805	1.1565
O	1.867663	-0.695229	0.166633
C	2.721984	-1.487822	-0.67209
C	2.667487	-0.285792	1.292163
C	4.134292	-0.868041	-0.550551
H	2.710749	-2.527838	-0.313264
H	2.305055	-1.461556	-1.681811
C	4.027656	0.073071	0.681472
H	2.142539	0.539666	1.774415
H	2.7504	-1.127634	1.996808
H	4.404377	-0.309683	-1.452062
H	4.890461	-1.646954	-0.408334
H	4.032808	1.121893	0.367713
H	4.847684	-0.067424	1.392881

***Trans*_complex with 2THF**

C	-1.766728	-2.475929	1.518324
H	-1.852183	-3.336329	2.203161
H	-2.437216	-1.702357	1.921791
C	-2.254285	-2.930125	0.129505
H	-1.582725	-3.719405	-0.239886
H	-3.235203	-3.410257	0.263968
C	-0.341936	-1.997055	1.592255
H	0.383119	-2.59686	1.039607
C	0.107762	-0.994689	2.373383
H	1.167907	-0.768993	2.460412
H	-0.570997	-0.390872	2.974302
C	-2.368384	-1.815869	-0.928505
H	-2.941708	-2.256304	-1.777971
C	-1.039955	-1.205018	-1.391973
H	-1.314238	-0.347033	-2.043544
C	-0.276638	-2.193618	-2.287346
H	0.534644	-1.696487	-2.841368
H	-0.914305	-2.692219	-3.053156
H	0.195574	-3.014209	-1.720491
H	-3.025888	-1.029298	-0.515117
Li	0.041257	-0.10108	0.031701
C	-1.931271	1.915664	1.075402
O	-0.678885	1.76836	0.35863
C	-2.694476	3.039802	0.368026
H	-1.698323	2.134786	2.12243
H	-2.470839	0.962832	1.020035
C	-0.707296	2.562465	-0.853655
C	-2.175255	2.925778	-1.074809
H	-2.430784	4.015362	0.795198
H	-3.779101	2.916253	0.447948
H	-0.278573	1.95956	-1.658663
H	-0.085518	3.455463	-0.698315
H	-2.295238	3.848566	-1.65172
H	-2.687218	2.115499	-1.606101
O	1.99584	0.291868	-0.186315
C	2.783414	1.300626	0.468471
C	2.882962	-0.416864	-1.068552
C	4.20072	0.700318	0.629674
H	2.284687	1.540197	1.410157
H	2.800082	2.203331	-0.159227
C	4.17713	-0.5713	-0.261874
H	3.041947	0.182356	-1.978498
H	2.393342	-1.352159	-1.342312
H	4.963941	1.413787	0.302268
H	4.414013	0.448663	1.673011
H	5.057941	-0.653031	-0.90665
H	4.128866	-1.474537	0.355155

***Cis*_complex with 2THF**

C	-1.03632	0.508524	2.591064
H	-0.24434	-0.176587	2.935906
H	-1.39199	1.052838	3.495983
H	-1.88483	-0.128444	2.284167
C	-0.56656	1.425334	1.448152
H	0.297226	2.005603	1.838972
C	-1.66227	2.44954	1.143538
H	-2.01473	2.975614	2.061887
H	-2.56883	1.939997	0.76092
C	-1.27073	3.537351	0.131
H	-2.05374	4.309281	0.097554
H	-0.35884	4.044432	0.485031
C	-1.03589	3.052077	-1.31273
H	-1.92572	2.522267	-1.683769
H	-0.92476	3.942047	-1.954949
C	0.187463	2.201951	-1.527777
H	1.08496	2.534945	-1.004038
C	0.286305	1.169005	-2.386244
H	1.232998	0.665152	-2.567799
H	-0.57089	0.811774	-2.955053
Li	0.058508	0.141702	-0.092734
O	-1.10655	-1.417116	-0.601504
C	-0.98262	-2.673476	0.105924
C	-2.50364	-1.127611	-0.864078
C	-2.33957	-3.364572	-0.040833
C	-3.3043	-2.167621	-0.075552
H	-2.67102	-1.216553	-1.94571
H	-2.6996	-0.097934	-0.552936
H	-4.26386	-2.399366	-0.548825
H	-3.5017	-1.806163	0.940033
H	-2.38656	-3.925375	-0.982667
H	-2.54305	-4.059376	0.7803
H	-0.15306	-3.229664	-0.341439
H	-0.74595	-2.462805	1.1565
O	1.867663	-0.695229	0.166633
C	2.721984	-1.487822	-0.67209
C	2.667487	-0.285792	1.292163
C	4.134292	-0.868041	-0.550551
H	2.710749	-2.527838	-0.313264
H	2.305055	-1.461556	-1.681811
C	4.027656	0.073071	0.681472
H	2.142539	0.539666	1.774415
H	2.7504	-1.127634	1.996808
H	4.404377	-0.309683	-1.452062
H	4.890461	-1.646954	-0.408334
H	4.032808	1.121893	0.367713
H	4.847684	-0.067424	1.392881

***Trans*_complex with 2THF**

C	-1.766728	-2.475929	1.518324
H	-1.852183	-3.336329	2.203161
H	-2.437216	-1.702357	1.921791
C	-2.254285	-2.930125	0.129505
H	-1.582725	-3.719405	-0.239886
H	-3.235203	-3.410257	0.263968
C	-0.341936	-1.997055	1.592255
H	0.383119	-2.59686	1.039607
C	0.107762	-0.994689	2.373383
H	1.167907	-0.768993	2.460412
H	-0.570997	-0.390872	2.974302
C	-2.368384	-1.815869	-0.928505
H	-2.941708	-2.256304	-1.777971
C	-1.039955	-1.205018	-1.391973
H	-1.314238	-0.347033	-2.043544
C	-0.276638	-2.193618	-2.287346
H	0.534644	-1.696487	-2.841368
H	-0.914305	-2.692219	-3.053156
H	0.195574	-3.014209	-1.720491
H	-3.025888	-1.029298	-0.515117
Li	0.041257	-0.10108	0.031701
C	-1.931271	1.915664	1.075402
O	-0.678885	1.76836	0.35863
C	-2.694476	3.039802	0.368026
H	-1.698323	2.134786	2.12243
H	-2.470839	0.962832	1.020035
C	-0.707296	2.562465	-0.853655
C	-2.175255	2.925778	-1.074809
H	-2.430784	4.015362	0.795198
H	-3.779101	2.916253	0.447948
H	-0.278573	1.95956	-1.658663
H	-0.085518	3.455463	-0.698315
H	-2.295238	3.848566	-1.65172
H	-2.687218	2.115499	-1.606101
O	1.99584	0.291868	-0.186315
C	2.783414	1.300626	0.468471
C	2.882962	-0.416864	-1.068552
C	4.20072	0.700318	0.629674
H	2.284687	1.540197	1.410157
H	2.800082	2.203331	-0.159227
C	4.17713	-0.5713	-0.261874
H	3.041947	0.182356	-1.978498
H	2.393342	-1.352159	-1.342312
H	4.963941	1.413787	0.302268
H	4.414013	0.448663	1.673011
H	5.057941	-0.653031	-0.90665
H	4.128866	-1.474537	0.355155

***Cis*_TS with 2THF**

C	0.601147	-1.018372	-1.964581
H	0.075568	-0.063708	-2.115077
H	0.885111	-1.368439	-2.975484
H	-0.13051	-1.754035	-1.593757
C	1.82221	-0.911933	-1.037402
H	2.455377	-0.07985	-1.380326
C	2.613673	-2.212486	-1.082177
H	3.105625	-2.372195	-2.059225
H	1.918888	-3.060224	-0.953614
C	3.621646	-2.235917	0.067336
H	4.09952	-3.218171	0.183224
H	4.425385	-1.507451	-0.121706
C	2.836238	-1.830223	1.313075
H	2.151898	-2.642762	1.601064
H	3.499102	-1.662616	2.174618
C	2.026447	-0.562405	1.084182
H	2.670841	0.293356	0.862087
C	0.926932	-0.2795	1.952439
H	0.83644	0.727194	2.365517
H	0.587315	-1.077428	2.61557
Li	0.039495	-0.038049	0.111385
O	-1.97496	-0.520083	0.074491
C	-2.92397	-0.702505	-0.988363
C	-2.60157	-1.046275	1.258687
C	-3.61867	-2.053104	-0.704525
C	-3.29565	-2.333224	0.790438
H	-3.33011	-0.310091	1.633514
H	-1.81297	-1.18333	1.999613
H	-4.19003	-2.552956	1.382344
H	-2.61467	-3.185077	0.884956
H	-4.69554	-1.988158	-0.891751
H	-3.21991	-2.844224	-1.346895
H	-3.64485	0.128969	-0.968525
H	-2.37389	-0.669271	-1.930789
O	-0.08254	1.934967	-0.402802
C	-1.0271	2.733755	0.351465
C	1.054613	2.742711	-0.791156
C	-0.55514	4.18421	0.212961
H	-2.02533	2.554394	-0.058994
H	-1.00617	2.392261	1.393745
C	0.964607	4.016068	0.051492
H	1.960262	2.157094	-0.615436
H	0.975545	2.960186	-1.865212
H	-0.83352	4.795001	1.077762
H	-0.98623	4.647619	-0.683215
H	1.439695	3.862325	1.027638
H	1.446157	4.871873	-0.432535

***Trans*_TS(chair) with 2THF**

C	-2.536491	-1.921332	1.097504
H	-2.894186	-2.514828	1.951778
H	-3.057846	-0.953115	1.155161
C	-2.86694	-2.609213	-0.228096
H	-2.520923	-3.652744	-0.201531
H	-3.949613	-2.641611	-0.411763
C	-1.042633	-1.685058	1.271075
H	-0.466279	-2.613194	1.290907
C	-0.596962	-0.675815	2.167889
H	0.273821	-0.866443	2.795446
H	-1.331654	0.015283	2.585173
C	-2.121085	-1.834838	-1.326026
H	-2.196616	-2.362617	-2.295284
C	-0.681183	-1.606457	-0.884003
H	-0.273572	-0.730286	-1.425205
C	0.240091	-2.791195	-1.148242
H	1.270958	-2.581096	-0.828149
H	0.282326	-3.076866	-2.215401
H	-0.082336	-3.689257	-0.601324
H	-2.62758	-0.865969	-1.465077
Li	0.120438	-0.002847	0.353893
C	-0.62632	2.841661	0.711271
O	-0.464067	1.832053	-0.302279
C	-2.137828	3.129004	0.760422
H	-0.05383	3.734399	0.416188
H	-0.216887	2.434542	1.638059
C	-1.384772	2.173424	-1.352185
C	-2.651202	2.681604	-0.638095
H	-2.337722	4.186279	0.962503
H	-2.611702	2.541295	1.551929
H	-1.53709	1.27893	-1.959758
H	-0.93383	2.958652	-1.977956
H	-3.121516	3.498812	-1.194538
H	-3.387562	1.878311	-0.541184
O	2.096047	0.058452	0.120913
C	3.037338	-0.457957	1.09353
C	2.792921	0.551761	-1.043814
C	4.402181	-0.452226	0.396547
H	2.703216	-1.453575	1.398563
H	3.016878	0.202463	1.9692
C	4.252938	0.699337	-0.612097
H	2.316932	1.49001	-1.34285
H	2.683696	-0.178339	-1.857625
H	5.226957	-0.306112	1.101266
H	4.569689	-1.399766	-0.129627
H	4.411101	1.666212	-0.118534
H	4.947701	0.628934	-1.455196

***Trans*_TS(twist) with 2THF**

C	-2.61354	-1.65239	1.435978
H	-2.96877	-2.507298	2.030735
H	-2.66329	-0.784624	2.107611
C	-3.51786	-1.450155	0.199788
H	-4.50622	-1.908985	0.337716
H	-3.69317	-0.375769	0.035147
C	-1.14941	-1.918671	1.077921
H	-0.96985	-2.928283	0.698461
C	-0.14195	-1.39201	1.918201
H	0.791349	-1.935789	2.062322
H	-0.40648	-0.682129	2.702272
C	-2.77715	-2.015742	-1.014408
H	-2.69679	-3.111207	-0.90973
C	-1.38485	-1.410781	-1.039829
H	-1.47263	-0.351385	-1.348016
C	-0.42722	-2.160042	-1.959154
H	0.503567	-1.608722	-2.14993
H	-0.86293	-2.382874	-2.951493
H	-0.14378	-3.133521	-1.524268
H	-3.34469	-1.845895	-1.946461
Li	0.088862	-0.32638	0.132671
C	-1.27837	2.279039	0.967606
O	-0.33811	1.652399	0.059151
C	-1.85945	3.480158	0.211875
H	-0.72559	2.583308	1.865175
H	-2.02914	1.536873	1.252806
C	-0.19635	2.446063	-1.139955
C	-0.73208	3.830295	-0.774092
H	-2.11962	4.305206	0.882518
H	-2.76491	3.189171	-0.333833
H	-0.78561	1.985528	-1.945174
H	0.859666	2.431227	-1.424048
H	0.045378	4.423638	-0.276999
H	-1.08084	4.38865	-1.648749
O	2.084518	-0.120081	-0.359439
C	2.767608	0.655285	0.659097
C	2.94307	-1.191949	-0.82265
C	4.005173	-0.156941	1.043922
H	2.068874	0.80931	1.485526
H	3.037494	1.628616	0.226562
C	4.336241	-0.882363	-0.269961
H	2.898574	-1.212961	-1.915473
H	2.55358	-2.141309	-0.434356
H	4.821816	0.475164	1.407751
H	3.75514	-0.880181	1.828923
H	4.882281	-0.216648	-0.949955
H	4.935491	-1.787295	-0.126779

***Cis*_product with 2THF**

C	1.7418	0.167293	1.896563
H	0.904446	-0.435171	2.277063
H	2.228977	0.639066	2.762045
H	1.326731	0.964837	1.26775
C	2.72906	-0.689495	1.103187
H	3.144081	-1.439238	1.798159
C	3.924067	0.106706	0.521806
H	4.694852	0.294549	1.281146
H	3.581406	1.089979	0.171759
C	4.453943	-0.742565	-0.670596
H	4.428139	-0.158164	-1.597442
H	5.495131	-1.056004	-0.524169
C	3.493897	-1.957039	-0.765041
H	3.350015	-2.302625	-1.795598
H	3.911272	-2.801111	-0.190212
C	2.163678	-1.472159	-0.120811
H	1.610695	-2.353498	0.251587
C	1.233198	-0.655518	-1.044915
H	1.030032	-1.292858	-1.931571
H	1.816028	0.19116	-1.466055
Li	-0.57907	0.00892	-0.313407
O	-1.23808	1.862386	-0.384606
C	-1.70023	2.654955	0.737672
C	-0.53776	2.706318	-1.338238
C	-1.36015	4.112266	0.398816
C	-0.16306	3.962752	-0.555785
H	-1.22096	2.933435	-2.168221
H	0.312195	2.13083	-1.712161
H	-0.02037	4.83257	-1.204901
H	0.763482	3.798171	0.006616
H	-2.20034	4.593996	-0.115968
H	-1.13014	4.70029	1.29289
H	-2.77358	2.47891	0.866485
H	-1.17469	2.310372	1.636759
O	-2.03417	-1.160964	0.26088
C	-3.46399	-0.969591	0.131503
C	-1.71787	-2.577594	0.252309
C	-4.08095	-2.37528	0.062933
H	-3.81767	-0.387392	0.989711
H	-3.6437	-0.392567	-0.783322
C	-2.90862	-3.237218	-0.43769
H	-0.76316	-2.687908	-0.265675
H	-1.60978	-2.920635	1.290623
H	-4.95554	-2.410185	-0.594413
H	-4.39603	-2.705919	1.059921
H	-2.80629	-3.160879	-1.52688
H	-3.01211	-4.295126	-0.176168

***Trans*_product with 2THF**

C	3.768324	0.501303	-1.271363
H	3.828337	1.426863	-1.858391
H	3.824904	-0.331118	-1.988114
C	4.892094	0.381066	-0.211444
H	5.28783	1.367631	0.062162
H	5.744552	-0.201366	-0.58333
C	2.424785	0.383065	-0.502258
H	2.284064	1.342357	0.037892
C	1.164475	0.084663	-1.331029
H	1.090861	0.872338	-2.112171
H	1.374457	-0.838451	-1.915224
C	4.220763	-0.297243	1.020401
H	4.167457	0.409364	1.86179
C	2.786994	-0.670852	0.576583
H	2.822463	-1.648221	0.064674
C	1.80946	-0.784417	1.74687
H	0.811739	-1.082435	1.39971
H	2.142821	-1.527423	2.485117
H	1.710735	0.178812	2.26868
H	4.783474	-1.167936	1.38235
Li	-0.691363	0.045761	-0.436221
C	-1.580828	-2.55837	-1.28239
O	-1.93327	-1.47784	-0.376189
C	-1.56532	-3.813148	-0.41318
H	-2.347026	-2.617646	-2.06778
H	-0.618034	-2.299053	-1.728571
C	-2.569276	-2.012098	0.812341
C	-2.701326	-3.523915	0.583146
H	-1.726504	-4.72682	-0.994162
H	-0.604738	-3.901785	0.107754
H	-1.928617	-1.782152	1.672467
H	-3.532612	-1.508395	0.946197
H	-3.672662	-3.761519	0.132607
H	-2.614415	-4.090836	1.515415
O	-1.605599	1.616859	0.278774
C	-2.992886	1.97974	0.121922
C	-0.784404	2.81703	0.383673
C	-2.971163	3.404125	-0.429908
H	-3.455015	1.244862	-0.543499
H	-3.490491	1.935714	1.101893
C	-1.75633	4.003137	0.300456
H	-0.235279	2.773012	1.329077
H	-0.067126	2.790351	-0.441738
H	-3.902268	3.945767	-0.233974
H	-2.803027	3.388293	-1.513336
H	-2.045241	4.339465	1.303565
H	-1.317771	4.856386	-0.225994

Figure **S1**. Calculated stationary points for **1** complexed with two THF molecules. The numbers within parentheses denote the relative energies in kcal/mol, obtained from B3LYP/6-31+G(d) level of theory.