

## Supplementary Information for:

### **DFT investigation of methane metathesis with $L_2AnCH_3$ actinide complexes catalysts (L = Cl, Cp, Cp\*; An = Ac, Th, Pa, U, Np, Pu).**

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## SI.1.

### a) Optimized coordinates of $L_2AnCH_3 + CH_4$ systems

#### Highest spin state

##### 1. $Cl_2AnCH_3 + CH_4$

###### • $Cl_2AcCH_3 + CH_4$

#### Reactant: $Cl_2AcCH_3$

1.Ac	1.578951	0.317881	0.000000
2.Cl	2.675417	1.273551	2.256613
3.Cl	2.675417	1.273551	-2.256613
4.C	-0.792829	1.220633	0.000000
5.H	-1.018403	1.837073	0.887678
6.H	-1.018403	1.837073	-0.887678
7.H	-1.527941	0.390590	0.000000

#### Transition state: $Cl_2AcCH_3 + CH_4$

1.Ac	-0.385194	-0.027233	0.042464
2.Cl	0.765163	-0.004114	-2.418876
3.Cl	0.960034	-0.188143	2.397615
4.C	-2.599329	-1.513963	0.073368
5.H	-3.692034	-1.620475	0.116894
6.H	-2.207189	-2.101574	0.928914
7.H	-2.285871	-2.029501	-0.857765
8.C	-2.632673	1.415134	0.184136
9.H	-3.727637	1.490863	0.237272
10.H	-2.649597	-0.052814	0.131271
11.H	-2.336962	2.006816	-0.706746
12.H	-2.253934	1.948617	1.080367

###### • $Cl_2ThCH_3 + CH_4$

#### Reactant: $Cl_2ThCH_3$

1.Th	1.597469	0.521244	0.000000
2.Cl	2.617549	0.795693	2.364385
3.Cl	2.617549	0.795693	-2.364385
4.C	-0.804851	0.424836	0.000000
5.H	-1.287965	0.860044	0.892340
6.H	-1.287965	0.860044	-0.892340
7.H	-1.046310	-0.661380	0.000000

#### Transition state: $Cl_2ThCH_3 + CH_4$

1.Th	-0.326409	-0.100002	0.136419
2.Cl	0.906163	0.154431	-2.127505
3.Cl	0.829888	-0.225705	2.450801
4.C	-2.438146	-1.647550	-0.061921
5.H	-3.539046	-1.664775	-0.106278
6.H	-2.133917	-2.294989	0.779665
7.H	-2.067287	-2.117464	-0.990880
8.C	-2.600712	1.208561	0.240958
9.H	-3.697702	1.108498	0.211892
10.H	-2.507562	-0.218495	0.089358
11.H	-2.313446	1.896894	-0.573907
12.H	-2.343046	1.701301	1.195813

###### • $Cl_2PaCH_3 + CH_4$

**Reactant: Cl<sub>2</sub>PaCH<sub>3</sub>**

1.Pa	1.599481	0.404411	0.000000
2.Cl	2.587775	1.076611	2.246276
3.Cl	2.587775	1.076611	-2.246276
4.C	-0.697295	0.896410	0.000000
5.H	-1.079011	1.416089	0.894651
6.H	-1.079011	1.416089	-0.894651
7.H	-1.130583	-0.131871	0.000000

**Transition state: Cl<sub>2</sub>PaCH<sub>3</sub> + CH<sub>4</sub>**

1.Pa	-0.415279	-0.072375	0.051608
2.Cl	0.760493	0.172767	-2.217467
3.Cl	0.969055	-0.157530	2.212424
4.C	-2.355824	-1.658102	0.024039
5.H	-3.427898	-1.891470	0.052362
6.H	-1.877468	-2.212884	0.861011
7.H	-1.953402	-2.082468	-0.922223
8.C	-2.551100	1.224604	0.246775
9.H	-3.644360	1.305287	0.299823
10.H	-2.554982	-0.225596	0.139481
11.H	-2.218948	1.838479	-0.619541
12.H	-2.141956	1.704206	1.163282

**• Cl<sub>2</sub>UcH<sub>3</sub> + CH<sub>4</sub>****Reactant: Cl<sub>2</sub>UcH<sub>3</sub>**

1.U	1.597868	0.305190	0.000000
2.Cl	2.562723	1.345507	2.093274
3.Cl	2.562723	1.345507	-2.093274
4.C	-0.564053	1.261634	0.000000
5.H	-0.772395	1.874300	0.892524
6.H	-0.772395	1.874300	-0.892524
7.H	-1.288297	0.418929	0.000000

**Transition state: Cl<sub>2</sub>UcH<sub>3</sub> + CH<sub>4</sub>**

1.U	-0.404353	-0.030445	0.042645
2.Cl	0.726630	-0.004142	-2.264052
3.Cl	0.905964	-0.176236	2.246906
4.C	-2.363283	-1.496820	0.067054
5.H	-3.433535	-1.729467	0.113982
6.H	-1.879590	-2.021550	0.922428
7.H	-1.972832	-1.944932	-0.874598
8.C	-2.396945	1.421502	0.179532
9.H	-3.475975	1.607297	0.251271
10.H	-2.510914	-0.036452	0.131146
11.H	-2.039635	1.958840	-0.727463
12.H	-1.932498	1.904825	1.069107

**• Cl<sub>2</sub>NpCH<sub>3</sub> + CH<sub>4</sub>****Reactant: Cl<sub>2</sub>NpCH<sub>3</sub>**

1.Np	1.610495	0.304649	0.000000
2.Cl	2.515157	1.339643	2.124588
3.Cl	2.515157	1.339643	-2.124588
4.C	-0.542227	1.279280	0.000000
5.H	-0.737817	1.893377	0.893437
6.H	-0.737817	1.893377	-0.893437
7.H	-1.275688	0.446124	0.000000

**Transition state: Cl<sub>2</sub>NpCH<sub>3</sub> + CH<sub>4</sub>**

1.Np	-0.395763	-0.036573	0.042030
2.Cl	0.696584	0.014558	-2.284067
3.Cl	0.878980	-0.158455	2.270671
4.C	-2.383320	-1.487162	0.067936
5.H	-3.465165	-1.668164	0.104225
6.H	-1.936413	-2.023064	0.933170
7.H	-2.008468	-1.955434	-0.867966
8.C	-2.376286	1.423561	0.179382
9.H	-3.458782	1.598098	0.228262
10.H	-2.489941	-0.036269	0.127512
11.H	-2.002375	1.963233	-0.717074
12.H	-1.931665	1.893192	1.083109

**• Cl<sub>2</sub>PuCH<sub>3</sub> + CH<sub>4</sub>****Reactant: Cl<sub>2</sub>PuCH<sub>3</sub>**

1.Pu	1.634394	0.318021	0.000000
2.Cl	2.433528	1.340377	2.177145
3.Cl	2.433528	1.340377	-2.177145
4.C	-0.562060	1.179081	0.000000
5.H	-0.773155	1.781280	0.897010
6.H	-0.773155	1.781280	-0.897010
7.H	-1.244033	0.304889	0.000000

**Transition state: Cl<sub>2</sub>PuCH<sub>3</sub> + CH<sub>4</sub>**

1.Pu	-0.371018	-0.043914	0.041042
2.Cl	0.603569	0.037610	-2.337333
3.Cl	0.791805	-0.140455	2.332575
4.C	-2.390096	-1.469247	0.067999
5.H	-3.476331	-1.616753	0.107242
6.H	-1.956917	-2.008181	0.935155
7.H	-2.032261	-1.934473	-0.873065
8.C	-2.352347	1.426923	0.175668
9.H	-3.434515	1.598140	0.228729
10.H	-2.465605	-0.020646	0.128657
11.H	-1.983700	1.950880	-0.729630
12.H	-1.905024	1.889743	1.078887

**2. Cp<sub>2</sub>AnCH<sub>3</sub> + CH<sub>4</sub>****• Cp<sub>2</sub>AcCH<sub>3</sub> + CH<sub>4</sub>****Reactant : Cp<sub>2</sub>AcCH<sub>3</sub>**

1.Ac	-0.473898	-0.416968	0.005504
2.H	-2.105381	-0.330341	-3.130970
3.H	-1.945482	-0.355968	3.218929
4.C	-2.857016	-1.504147	0.057845
5.C	0.092376	-0.679674	-2.881426
6.H	-2.999475	-2.162603	0.936627
7.H	-3.050005	-2.132441	-0.833496
8.H	-1.570653	2.139227	-2.182568
9.H	2.191219	-0.068949	-2.376033
10.H	-3.690495	-0.776893	0.093389
11.H	1.083368	2.296067	-1.704825
12.H	0.220794	-1.690049	-3.267063
13.C	1.285448	-0.084030	2.368712
14.C	0.796790	1.221158	2.105372

15.C	-0.591584	1.239393	2.415056
16.C	-0.957527	-0.052643	2.881731
17.C	0.200341	-0.871584	2.845249
18.H	1.386945	2.067775	1.760974
19.H	2.318875	-0.411511	2.266858
20.H	0.258783	-1.908054	3.174365
21.H	-1.245505	2.108049	2.362358
22.C	1.130692	0.174142	-2.415605
23.C	0.548970	1.418949	-2.063614
24.C	-0.849761	1.333697	-2.310172
25.C	-1.130115	0.039066	-2.824286

**Transition state: Cp<sub>2</sub>AcCH<sub>3</sub> + CH<sub>4</sub>**

1.Ac	-0.626533	-0.572320	-1.575287
2.H	-3.260310	-0.363001	-3.976778
3.H	-0.022146	0.771158	1.680912
4.C	-3.057867	-0.098018	-0.378170
5.C	-1.488902	-1.718013	-4.158051
6.H	-2.709202	0.435067	0.525172
7.H	-4.070933	-0.464270	-0.153783
8.H	-1.457165	1.629737	-4.248164
9.H	0.685477	-2.167495	-4.472164
10.H	-3.195691	0.660418	-1.178083
11.H	0.981592	0.512756	-4.546627
12.H	-1.938770	-2.707662	-4.119226
13.C	2.123709	-0.601394	-0.494595
14.C	1.975911	0.714129	-1.008696
15.C	1.060212	1.409542	-0.174740
16.C	0.648034	0.525925	0.859707
17.C	1.304681	-0.716508	0.661973
18.H	2.498269	1.126752	-1.869100
19.H	2.787554	-1.369191	-0.887806
20.H	1.227983	-1.589353	1.306921
21.H	0.767084	2.452720	-0.279182
22.C	-0.107168	-1.433756	-4.337541
23.C	0.049096	-0.022480	-4.381900
24.C	-1.234582	0.564476	-4.220001
25.C	-2.184809	-0.484295	-4.085464
26.C	-1.876309	-2.769130	-0.481320
27.H	-1.403999	-3.329843	-1.316169
28.H	-2.827486	-3.288838	-0.291209
29.H	-1.247941	-2.924059	0.414386
30.H	-2.475631	-1.434271	-0.494779

• **Cp<sub>2</sub>ThCH<sub>3</sub> + CH<sub>4</sub>**

**Reactant: Cp<sub>2</sub>ThCH<sub>3</sub>**

1.Th	-0.458488	-0.395701	0.020743
2.H	-2.228269	-0.238554	-2.939863
3.H	-1.908046	-0.268844	3.150230
4.C	-1.812588	-2.495017	0.111147
5.C	-0.064342	-0.770608	-2.759833
6.H	-1.579916	-3.150363	0.970407
7.H	-1.748121	-3.124867	-0.794679
8.H	-1.462126	2.186975	-2.041777
9.H	2.090088	-0.353579	-2.300492
10.H	-2.881973	-2.215690	0.217500
11.H	1.209940	2.115905	-1.633426
12.H	-0.042131	-1.804286	-3.097993
13.C	1.286775	0.044634	2.186947

14.C	0.751358	1.329904	1.889211
15.C	-0.626989	1.330021	2.242271
16.C	-0.935578	0.048967	2.780173
17.C	0.239564	-0.739934	2.747248
18.H	1.303591	2.170419	1.474026
19.H	2.320113	-0.266856	2.060260
20.H	0.327767	-1.769305	3.087679
21.H	-1.311501	2.170199	2.162043
22.C	1.058203	-0.013471	-2.319352
23.C	0.593539	1.289124	-1.980123
24.C	-0.813232	1.327358	-2.187524
25.C	-1.213428	0.052603	-2.677125

**Transition state: Cp<sub>2</sub>ThCH<sub>3</sub> + CH<sub>4</sub>**

1.Th	-0.627457	-0.563034	-1.601708
2.H	-3.137328	-0.192217	-3.996216
3.H	-0.232280	0.817149	1.577430
4.C	-3.026029	-0.167839	-0.442703
5.C	-1.417074	-1.613251	-4.131210
6.H	-2.622018	0.562987	0.279522
7.H	-3.905907	-0.631041	0.031143
8.H	-1.247223	1.734060	-4.064737
9.H	0.748124	-2.160542	-4.306752
10.H	-3.392947	0.393544	-1.319722
11.H	1.166687	0.515204	-4.246453
12.H	-1.911280	-2.581963	-4.148667
13.C	1.926622	-0.722643	-0.473807
14.C	1.825921	0.576942	-1.057100
15.C	0.914332	1.348282	-0.272688
16.C	0.462086	0.521813	0.793741
17.C	1.083088	-0.746579	0.670254
18.H	2.387724	0.934616	-1.916250
19.H	2.569525	-1.531431	-0.810426
20.H	0.945176	-1.591383	1.341451
21.H	0.656457	2.392727	-0.426012
22.C	-0.013990	-1.393958	-4.195946
23.C	0.204427	0.017207	-4.159487
24.C	-1.067220	0.662468	-4.064892
25.C	-2.062878	-0.354097	-4.049950
26.C	-1.802864	-2.784686	-0.634214
27.H	-1.636833	-3.314162	-1.588560
28.H	-2.706246	-3.222279	-0.180674
29.H	-0.959713	-3.025817	0.035993
30.H	-2.404466	-1.470006	-0.563913

• **Cp<sub>2</sub>PaCH<sub>3</sub> + CH<sub>4</sub>**

**Reactant: Cp<sub>2</sub>PaCH<sub>3</sub>**

1.Pa	-0.551671	-0.409692	-0.040641
2.H	-1.368393	-1.010433	-3.174506
3.H	-0.965763	-1.294663	3.200751
4.C	-1.897352	-2.419768	0.366241
5.C	0.686186	-0.479438	-2.435761
6.H	-1.381837	-3.244992	0.890089
7.H	-2.213694	-2.819399	-0.620057
8.H	-2.034215	1.497902	-2.400355
9.H	2.215881	0.912976	-1.569122
10.H	-2.825196	-2.206206	0.930654
11.H	0.180788	2.674716	-1.406110
12.H	1.272931	-1.361931	-2.676057

13.C	1.196738	0.770239	1.673042
14.C	0.009115	1.557661	1.718278
15.C	-1.008740	0.780345	2.351107
16.C	-0.445595	-0.477303	2.707753
17.C	0.908672	-0.488362	2.275160
18.H	-0.095711	2.581795	1.370968
19.H	2.159821	1.082817	1.279099
20.H	1.611788	-1.309756	2.394668
21.H	-2.024154	1.109265	2.558152
22.C	1.186342	0.729788	-1.866015
23.C	0.116472	1.658538	-1.786712
24.C	-1.057549	1.033171	-2.294494
25.C	-0.700934	-0.285561	-2.712166

**Transition state: Cp<sub>2</sub>PaCH<sub>3</sub> + CH<sub>4</sub>**

1.Pa	-0.623238	-0.543532	-1.539658
2.H	-3.210590	-0.279342	-3.832744
3.H	-0.095946	0.799468	1.433346
4.C	-3.048669	-0.164853	-0.625060
5.C	-1.471639	-1.677536	-3.949147
6.H	-2.832484	0.176673	0.402761
7.H	-4.094352	-0.501880	-0.651652
8.H	-1.347555	1.672087	-3.979702
9.H	0.703060	-2.196211	-4.149704
10.H	-2.989904	0.721009	-1.295024
11.H	1.079336	0.487547	-4.172199
12.H	-1.953239	-2.652355	-3.931143
13.C	1.987957	-0.687837	-0.751770
14.C	1.873853	0.626407	-1.279425
15.C	0.983217	1.370247	-0.457118
16.C	0.535204	0.508493	0.596375
17.C	1.159872	-0.770094	0.412401
18.H	2.397216	1.007130	-2.152394
19.H	2.619021	-1.480937	-1.145783
20.H	1.083699	-1.623962	1.081725
21.H	0.723337	2.418831	-0.582318
22.C	-0.069161	-1.440507	-4.031120
23.C	0.131333	-0.022070	-4.035351
24.C	-1.153200	0.602636	-3.949253
25.C	-2.134902	-0.426673	-3.898728
26.C	-1.818444	-2.773012	-0.796049
27.H	-1.003338	-3.184581	-1.432859
28.H	-2.714656	-3.367658	-1.023906
29.H	-1.541081	-2.964874	0.253798
30.H	-2.473347	-1.487577	-0.797874

• **Cp<sub>2</sub>UcH<sub>3</sub> + CH<sub>4</sub>**

**Reactant: Cp<sub>2</sub>UcH<sub>3</sub>**

1.U	-0.571780	-0.249336	0.028966
2.H	-1.702349	-1.078794	-3.096054
3.H	-1.520549	-1.094025	3.131938
4.C	-2.617423	-1.645432	0.094270
5.C	0.435212	-0.921453	-2.453026
6.H	-2.400143	-2.655829	0.495220
7.H	-3.122526	-1.795895	-0.876230
8.H	-1.810768	1.559548	-2.571070
9.H	2.260659	0.177398	-1.745934
10.H	-3.372635	-1.213539	0.780835
11.H	0.638971	2.349236	-1.725942

12.H	0.802949	-1.934851	-2.605228
13.C	1.368059	0.093513	1.897049
14.C	0.564175	1.269513	1.974307
15.C	-0.712233	0.895249	2.488428
16.C	-0.697121	-0.505852	2.734526
17.C	0.583979	-1.002831	2.363791
18.H	0.882367	2.278577	1.722463
19.H	2.407226	0.049211	1.579804
20.H	0.918718	-2.034265	2.461821
21.H	-1.540895	1.569516	2.698396
22.C	1.201163	0.188460	-1.990016
23.C	0.345650	1.332457	-1.976915
24.C	-0.941954	0.918156	-2.432828
25.C	-0.879956	-0.467381	-2.733607

**Transition state: Cp<sub>2</sub>UCh<sub>3</sub> + CH<sub>4</sub>**

1.U	-0.665350	-0.486620	-1.594412
2.H	-3.100242	-0.996899	-3.858899
3.H	0.028117	0.132093	1.636189
4.C	-2.898864	-0.083800	-0.439998
5.C	-1.016518	-1.826845	-3.935145
6.H	-2.391523	0.652661	0.217530
7.H	-3.825602	-0.381787	0.067786
8.H	-1.884778	1.408941	-4.102383
9.H	1.211604	-1.675164	-4.161680
10.H	-3.201331	0.435753	-1.374515
11.H	0.774552	0.985775	-4.284641
12.H	-1.184260	-2.900566	-3.887040
13.C	2.005465	-0.571289	-0.986220
14.C	1.715657	0.807044	-1.187078
15.C	0.856992	1.235507	-0.135908
16.C	0.614012	0.121078	0.719832
17.C	1.323818	-0.995260	0.190567
18.H	2.110697	1.433053	-1.982705
19.H	2.665737	-1.179974	-1.598966
20.H	1.367617	-1.989236	0.630663
21.H	0.485413	2.248106	0.011919
22.C	0.246329	-1.182592	-4.075436
23.C	0.016153	0.220342	-4.143363
24.C	-1.386524	0.442523	-4.046117
25.C	-2.028079	-0.824109	-3.918339
26.C	-1.665010	-2.718198	-0.601090
27.H	-0.732081	-3.091644	-1.076970
28.H	-2.487128	-3.303316	-1.039318
29.H	-1.590975	-2.971762	0.467259
30.H	-2.294938	-1.438163	-0.521778

• **Cp<sub>2</sub>NpCH<sub>3</sub> + CH<sub>4</sub>**

**Reactant: Cp<sub>2</sub>NpCH<sub>3</sub>**

1.Np	-0.580778	-0.319619	0.020552
2.H	-1.749109	-0.812831	-3.093729
3.H	-1.539342	-0.840536	3.201473
4.C	-2.670494	-1.621312	0.131430
5.C	0.409949	-0.790806	-2.497613
6.H	-2.677736	-2.356745	0.957756
7.H	-2.879137	-2.182790	-0.798510
8.H	-1.730011	1.781315	-2.360511
9.H	2.291072	0.178366	-1.751692
10.H	-3.544943	-0.961122	0.298638



11.H	0.768810	2.396500	-1.523229
12.H	0.733536	-1.802247	-2.737837
13.C	1.385014	0.142045	1.883899
14.C	0.621243	1.340555	1.849258
15.C	-0.666831	1.053569	2.385494
16.C	-0.695424	-0.316564	2.759202
17.C	0.568547	-0.883167	2.442716
18.H	0.972595	2.312608	1.512838
19.H	2.423155	0.036557	1.577346
20.H	0.873410	-1.911008	2.634259
21.H	-1.476198	1.768148	2.526004
22.C	1.229806	0.251735	-1.977918
23.C	0.428226	1.419226	-1.855799
24.C	-0.886614	1.095703	-2.299883
25.C	-0.893764	-0.266068	-2.703825

**Transition state : Cp<sub>2</sub>NpCH<sub>3</sub> + CH<sub>4</sub>**

1.Np	-0.678681	-0.555441	-1.440498
2.H	-3.048385	-0.865153	-3.828262
3.H	0.239294	-0.310001	1.795334
4.C	-2.842032	0.454482	-0.504882
5.C	-1.073999	-1.924058	-3.785395
6.H	-2.329299	1.053919	0.270042
7.H	-3.893642	0.355297	-0.202947
8.H	-1.556879	1.376213	-4.085458
9.H	1.161932	-2.036170	-3.892224
10.H	-2.841261	1.036157	-1.451504
11.H	1.038919	0.652115	-4.118106
12.H	-1.364347	-2.970104	-3.711872
13.C	2.049490	-0.347627	-1.027513
14.C	1.569826	0.991329	-0.994992
15.C	0.767974	1.138886	0.168066
16.C	0.745824	-0.105552	0.854566
17.C	1.540997	-1.024052	0.111702
18.H	1.810066	1.775238	-1.708620
19.H	2.712396	-0.770202	-1.777819
20.H	1.749682	-2.056071	0.387854
21.H	0.276109	2.054134	0.491656
22.C	0.257452	-1.433073	-3.872829
23.C	0.191696	-0.017673	-3.999965
24.C	-1.175201	0.362130	-3.982326
25.C	-1.961875	-0.817169	-3.849711
26.C	-2.104485	-2.354726	-0.310686
27.H	-2.064654	-2.989469	-1.215838
28.H	-2.976598	-2.677471	0.274320
29.H	-1.208730	-2.574595	0.307873
30.H	-2.535927	-0.962719	-0.428953

• **Cp<sub>2</sub>PuCH<sub>3</sub> + CH<sub>4</sub>**

**Reactant: Cp<sub>2</sub>PuCH<sub>3</sub>**

1.Pu	-0.575418	-0.391416	0.017478
2.H	-1.711922	-0.677321	-3.121243
3.H	-1.504673	-0.727675	3.217252
4.C	-2.825798	-1.369693	0.184551
5.C	0.445024	-0.663426	-2.510239
6.H	-2.914439	-2.103902	1.007329
7.H	-3.079497	-1.903531	-0.752228
8.H	-1.733940	1.865988	-2.224584
9.H	2.303064	0.287947	-1.689204

10.H	-3.616919	-0.613502	0.345276
11.H	0.744574	2.460674	-1.338997
12.H	0.787060	-1.652368	-2.810836
13.C	1.386231	0.251762	1.830050
14.C	0.590652	1.426556	1.737524
15.C	-0.682157	1.140155	2.294142
16.C	-0.677068	-0.209780	2.738855
17.C	0.601949	-0.759867	2.451254
18.H	0.912561	2.384166	1.337843
19.H	2.424532	0.158879	1.519739
20.H	0.934755	-1.765946	2.701244
21.H	-1.512547	1.837579	2.386854
22.C	1.242835	0.356592	-1.921619
23.C	0.422210	1.503359	-1.739135
24.C	-0.879683	1.191958	-2.208855
25.C	-0.867173	-0.146090	-2.688478

**Transition state: Cp<sub>2</sub>PuCH<sub>3</sub> + CH<sub>4</sub>**

1.Pu	-0.648270	-0.580795	-1.564795
2.H	-3.009849	0.150769	-3.846673
3.H	-0.049583	0.342468	1.615735
4.C	-2.958900	-0.010850	-0.488924
5.C	-1.568475	-1.560639	-3.943361
6.H	-3.064365	0.149882	0.594602
7.H	-3.955393	-0.222312	-0.904168
8.H	-0.805393	1.700648	-4.072744
9.H	0.467211	-2.475662	-4.160648
10.H	-2.635971	0.960508	-0.927036
11.H	1.337644	0.071148	-4.257423
12.H	-2.222710	-2.428555	-3.897893
13.C	2.020179	-0.407414	-0.911986
14.C	1.644746	0.931786	-1.212712
15.C	0.749772	1.374683	-0.205761
16.C	0.567017	0.312358	0.720162
17.C	1.356314	-0.787760	0.285163
18.H	2.001657	1.522217	-2.052674
19.H	2.724438	-1.014906	-1.475616
20.H	1.455692	-1.743182	0.796195
21.H	0.297686	2.362493	-0.141385
22.C	-0.153228	-1.585037	-4.079520
23.C	0.305082	-0.244141	-4.133809
24.C	-0.823759	0.613517	-4.029018
25.C	-1.983058	-0.201180	-3.914624
26.C	-1.768643	-2.649386	-0.487687
27.H	-1.212952	-3.166069	-1.299724
28.H	-2.714008	-3.198462	-0.372587
29.H	-1.197637	-2.758383	0.448947
30.H	-2.379126	-1.322790	-0.532180

**3. Cp\*<sub>2</sub>AnCH<sub>3</sub> + CH<sub>4</sub>**

• **Cp\*<sub>2</sub>AcCH<sub>3</sub> + CH<sub>4</sub>**

**Reactant: Cp\*<sub>2</sub>AcCH<sub>3</sub>**

1.Ac	-0.577440	-0.523341	-1.647819
2.C	-3.664380	-0.019516	-3.899775
3.C	-0.427263	-0.090852	2.193160
4.H	-2.814671	-3.386155	-4.960134
5.C	-1.711425	-1.750129	-4.071287

6.H	1.654496	-2.619797	-4.301021
7.H	-3.454504	-2.855663	-3.397034
8.C	-1.243509	1.967569	-4.523396
9.C	0.605804	-2.862255	-4.528102
10.H	0.584212	-3.217040	-5.572734
11.C	1.389820	0.207515	-4.953374
12.C	-2.525562	-3.011858	-3.962893
13.C	2.123526	-0.121689	-0.583925
14.C	1.605282	1.203726	-0.709565
15.C	0.576584	1.366164	0.265046
16.C	0.470450	0.148589	1.006880
17.C	1.426072	-0.770628	0.484657
18.C	2.129897	2.284512	-1.618516
19.C	3.309530	-0.681350	-1.328016
20.C	1.733345	-2.135802	1.042095
21.C	-0.197110	2.634418	0.522622
22.C	-0.309061	-1.680668	-4.330084
23.C	0.044828	-0.306433	-4.509423
24.C	-1.136826	0.474670	-4.344826
25.C	-2.219168	-0.416450	-4.068265
26.C	-1.549230	-2.725185	-0.574093
27.H	-1.976411	-3.818210	-3.457731
28.H	-4.199257	-0.012646	-4.864776
29.H	-4.213255	-0.711801	-3.243631
30.H	0.318579	-3.716924	-3.898370
31.H	4.253007	-0.476797	-0.793766
32.H	3.413882	-0.244213	-2.331665
33.H	3.249003	-1.773145	-1.448612
34.H	2.868559	2.920805	-1.101345
35.H	1.334659	2.957832	-1.975338
36.H	2.632944	1.871821	-2.504276
37.H	2.443814	-2.073910	1.884210
38.H	2.190376	-2.794792	0.290033
39.H	0.831758	-2.643261	1.412030
40.H	0.074940	0.176779	3.138677
41.H	-0.727363	-1.145105	2.275171
42.H	-1.348382	0.510619	2.149556
43.H	0.342908	3.310033	1.207856
44.H	-1.174783	2.438929	0.988625
45.H	-0.378095	3.209693	-0.399241
46.H	2.217654	-0.416263	-4.585015
47.H	1.575521	1.236581	-4.612961
48.H	1.470295	0.218882	-6.053996
49.H	-0.307262	2.485254	-4.265744
50.H	-2.043373	2.407932	-3.907508
51.H	-1.474786	2.236755	-5.568387
52.H	-3.774045	0.992764	-3.480331
53.H	-0.999846	-3.635707	-0.882901
54.H	-2.602852	-2.903014	-0.865462
55.H	-1.530765	-2.722203	0.532237

**Transition state: Cp\*<sub>2</sub>AcCH<sub>3</sub> + CH<sub>4</sub>**

1.Ac	-0.593941	-0.446426	-1.654155
2.C	-3.714617	-0.983296	-3.919878
3.C	-0.160359	-0.368514	2.212566
4.C	-2.928408	0.629873	-0.613986
5.C	-1.294351	-1.957638	-4.073922
6.H	-2.646092	1.149620	0.317242
7.H	-4.013248	0.445878	-0.561649
8.C	-2.082837	1.700057	-4.522617

9.C	1.246609	-2.251905	-4.593279
10.H	-2.799481	1.358153	-1.442984
11.C	0.969221	0.919063	-4.974446
12.C	-1.638966	-3.419480	-3.950914
13.C	2.191399	-0.268079	-0.735472
14.C	1.733294	1.083531	-0.708747
15.C	0.782736	1.206385	0.351327
16.C	0.652521	-0.068617	0.980021
17.C	1.518369	-0.980762	0.304091
18.C	2.270332	2.222230	-1.537420
19.C	3.302809	-0.812937	-1.594986
20.C	1.775331	-2.414399	0.692765
21.C	0.146379	2.492772	0.810688
22.C	0.004134	-1.432362	-4.355590
23.C	-0.118729	-0.020322	-4.522204
24.C	-1.491791	0.325922	-4.336559
25.C	-2.219384	-0.871963	-4.065987
26.C	-2.278263	-2.188976	-0.313013
27.H	-1.329568	-2.724013	-0.094317
28.H	-2.797034	-2.761985	-1.100457
29.H	-2.880070	-2.289218	0.604098
30.H	-2.557555	-0.771274	-0.491403
31.H	4.276284	-0.745859	-1.079272
32.H	3.407508	-0.257700	-2.538427
33.H	3.157509	-1.873050	-1.851689
34.H	3.118511	2.718153	-1.034760
35.H	1.514625	3.002665	-1.714195
36.H	2.634400	1.889839	-2.519926
37.H	2.631326	-2.497944	1.383903
38.H	2.014868	-3.048160	-0.175294
39.H	0.912851	-2.866141	1.203089
40.H	0.422131	-0.181531	3.130709
41.H	-0.487533	-1.417131	2.248482
42.H	-1.063825	0.254545	2.274781
43.H	0.806049	3.040356	1.504910
44.H	-0.800165	2.320253	1.341018
45.H	-0.067150	3.177952	-0.023676
46.H	1.969999	0.562236	-4.690789
47.H	0.851506	1.931655	-4.560428
48.H	0.972090	1.027580	-6.072746
49.H	-1.394230	2.499417	-4.207517
50.H	-3.017487	1.828326	-3.958531
51.H	-2.322608	1.895827	-5.581707
52.H	-4.155531	-0.084292	-3.466522
53.H	-4.006465	-1.838126	-3.293617
54.H	-4.202462	-1.122201	-4.899680
55.H	-0.828746	-4.004126	-3.489526
56.H	-1.827719	-3.871566	-4.939334
57.H	-2.543335	-3.583692	-3.348801
58.H	2.166235	-1.690296	-4.375757
59.H	1.315214	-2.580011	-5.644784
60.H	1.267823	-3.166171	-3.980750

• **Cp\*<sub>2</sub>ThCH<sub>3</sub> + CH<sub>4</sub>**

**Reactant: Cp\*<sub>2</sub>ThCH<sub>3</sub>**

1.Th	-0.520764	-0.485128	-1.698034
2.C	-3.629835	-0.233606	-3.849060
3.C	-0.328233	-0.590192	2.124716
4.H	-2.578122	-3.676958	-4.603268

5.C	-1.592530	-1.880047	-3.911412
6.H	1.806384	-2.611467	-4.131466
7.H	-3.254300	-3.017956	-3.102598
8.C	-1.336223	1.807028	-4.643637
9.C	0.769891	-2.909181	-4.344671
10.H	0.756272	-3.306960	-5.374891
11.C	1.400578	0.180938	-4.922767
12.C	-2.319074	-3.173652	-3.656307
13.C	2.104669	-0.082949	-0.708131
14.C	1.496901	1.205819	-0.642655
15.C	0.481836	1.165290	0.363221
16.C	0.469937	-0.148056	0.926914
17.C	1.462393	-0.927756	0.250397
18.C	1.906160	2.428885	-1.420279
19.C	3.276490	-0.478390	-1.568232
20.C	1.888646	-2.325318	0.615527
21.C	-0.327563	2.341665	0.841091
22.C	-0.193405	-1.761542	-4.192562
23.C	0.082615	-0.385594	-4.462141
24.C	-1.134418	0.350482	-4.318321
25.C	-2.171989	-0.581157	-3.992381
26.C	-2.573060	-1.161492	-0.419068
27.H	-1.707576	-3.878641	-3.073323
28.H	-4.098552	-0.082872	-4.836161
29.H	-4.191455	-1.026433	-3.338590
30.H	0.522634	-3.741499	-3.671351
31.H	4.219153	-0.443098	-0.996485
32.H	3.401360	0.191503	-2.429936
33.H	3.180218	-1.505096	-1.955425
34.H	2.614744	3.048500	-0.844382
35.H	1.044225	3.068067	-1.664090
36.H	2.405171	2.171518	-2.365370
37.H	2.651771	-2.312085	1.414069
38.H	2.324218	-2.857116	-0.241260
39.H	1.048291	-2.929760	0.983102
40.H	0.219881	-0.383222	3.059837
41.H	-0.537985	-1.668813	2.104974
42.H	-1.295448	-0.073660	2.192301
43.H	0.191866	2.876224	1.655711
44.H	-1.307822	2.035910	1.231780
45.H	-0.505957	3.068682	0.036763
46.H	2.254271	-0.416165	-4.572254
47.H	1.552395	1.214912	-4.578250
48.H	1.459035	0.203787	-6.024140
49.H	-0.437801	2.405838	-4.438387
50.H	-2.160494	2.243812	-4.063571
51.H	-1.579054	1.945955	-5.712483
52.H	-3.780173	0.694909	-3.276670
53.H	-2.359651	-2.002482	0.268520
54.H	-3.430386	-1.470999	-1.042262
55.H	-2.929719	-0.324636	0.213118

**Transition state: Cp\*<sub>2</sub>ThCH<sub>3</sub> + CH<sub>4</sub>**

1.Th	-0.567754	-0.433379	-1.672003
2.C	-3.682698	-1.037388	-3.802305
3.C	-0.264109	-0.298879	2.132276
4.C	-2.865833	0.611720	-0.679428
5.C	-1.227185	-1.916146	-3.987431
6.H	-2.450265	1.272228	0.098429
7.H	-3.888588	0.341313	-0.365842

8.C	-2.168819	1.711612	-4.427573
9.C	1.301248	-2.115368	-4.567045
10.H	-2.960154	1.205163	-1.604600
11.C	0.904044	1.067828	-4.876754
12.C	-1.520794	-3.391412	-3.931501
13.C	2.125471	-0.373442	-0.783320
14.C	1.725944	0.997163	-0.794454
15.C	0.753912	1.185029	0.235444
16.C	0.558072	-0.072674	0.888887
17.C	1.399771	-1.041933	0.252556
18.C	2.319691	2.100009	-1.629715
19.C	3.222031	-0.993559	-1.608564
20.C	1.646528	-2.448638	0.729101
21.C	0.193723	2.511129	0.675036
22.C	0.042438	-1.336358	-4.292532
23.C	-0.134503	0.073833	-4.428243
24.C	-1.514878	0.374306	-4.203338
25.C	-2.191922	-0.860577	-3.940275
26.C	-2.184320	-2.169316	-0.355639
27.H	-1.300296	-2.588424	0.154155
28.H	-2.428898	-2.834566	-1.199170
29.H	-3.023525	-2.225802	0.358649
30.H	-2.473373	-0.768470	-0.555599
31.H	4.164115	-1.044396	-1.036953
32.H	3.432456	-0.415522	-2.518932
33.H	2.979714	-2.021524	-1.917001
34.H	3.098284	2.643123	-1.067549
35.H	1.563547	2.841464	-1.929078
36.H	2.790995	1.721498	-2.546283
37.H	2.440633	-2.474378	1.496996
38.H	1.962847	-3.109581	-0.089689
39.H	0.751650	-2.896354	1.183286
40.H	0.327493	-0.085491	3.039096
41.H	-0.615115	-1.336875	2.213929
42.H	-1.151151	0.349737	2.168526
43.H	0.871566	3.009534	1.390313
44.H	-0.776369	2.403839	1.178951
45.H	0.049048	3.197522	-0.171022
46.H	1.926655	0.704957	-4.704457
47.H	0.804024	2.034765	-4.361651
48.H	0.814061	1.269725	-5.957459
49.H	-1.491279	2.544285	-4.193439
50.H	-3.070641	1.840895	-3.813308
51.H	-2.481222	1.829138	-5.480795
52.H	-4.167346	-0.148722	-3.375087
53.H	-3.942436	-1.891502	-3.160597
54.H	-4.149780	-1.219543	-4.785373
55.H	-0.683498	-3.961786	-3.505344
56.H	-1.712951	-3.794868	-4.941405
57.H	-2.410298	-3.613968	-3.326656
58.H	2.202927	-1.495336	-4.476871
59.H	1.293917	-2.526804	-5.590756
60.H	1.415980	-2.967115	-3.879402

• **Cp\*<sub>2</sub>PaCH<sub>3</sub> + CH<sub>4</sub>**

**Reactant: Cp\*<sub>2</sub>PaCH<sub>3</sub>**

1.Pa	-0.463498	-0.524250	-1.729473
2.C	-3.741111	-0.327673	-3.554317
3.C	-0.304134	-0.651903	2.099871

4.H	-2.442529	-3.744676	-4.561155
5.C	-1.644790	-1.868092	-3.846903
6.H	1.767538	-2.439002	-4.205433
7.H	-3.259847	-3.117326	-3.117463
8.C	-1.593044	1.865966	-4.341780
9.C	0.740927	-2.755567	-4.439698
10.H	0.732455	-3.052756	-5.504163
11.C	1.194487	0.385734	-4.895906
12.C	-2.283851	-3.209247	-3.610200
13.C	2.084892	0.013840	-0.731934
14.C	1.397221	1.259752	-0.662752
15.C	0.375995	1.149284	0.331649
16.C	0.450272	-0.163966	0.892604
17.C	1.490444	-0.876962	0.215362
18.C	1.722401	2.508414	-1.437967
19.C	3.276090	-0.308218	-1.594037
20.C	2.005108	-2.244806	0.576061
21.C	-0.494136	2.274900	0.822948
22.C	-0.263597	-1.668036	-4.167518
23.C	-0.058493	-0.259205	-4.362234
24.C	-1.310896	0.403422	-4.125150
25.C	-2.285970	-0.599535	-3.821707
26.C	-2.315843	-1.489323	-0.425670
27.H	-1.657047	-3.856693	-2.977236
28.H	-4.281752	-0.114909	-4.491653
29.H	-4.236633	-1.181484	-3.075520
30.H	0.534049	-3.657568	-3.847841
31.H	4.213216	-0.244916	-1.015089
32.H	3.374294	0.386011	-2.439538
33.H	3.225001	-1.329229	-2.004598
34.H	2.337741	3.199965	-0.837305
35.H	0.814804	3.059429	-1.729700
36.H	2.288335	2.290895	-2.354282
37.H	2.765905	-2.184911	1.375055
38.H	2.473427	-2.744297	-0.282817
39.H	1.204953	-2.902013	0.942154
40.H	0.257253	-0.432743	3.024432
41.H	-0.473943	-1.737340	2.073275
42.H	-1.287798	-0.172228	2.195857
43.H	-0.005146	2.823792	1.647461
44.H	-1.458557	1.913417	1.204338
45.H	-0.706864	3.002680	0.028058
46.H	2.102336	-0.155614	-4.592326
47.H	1.301206	1.427380	-4.559201
48.H	1.192169	0.407949	-6.000173
49.H	-0.727779	2.496233	-4.090735
50.H	-2.437849	2.211799	-3.730742
51.H	-1.845249	2.073764	-5.397514
52.H	-3.881708	0.543833	-2.896190
53.H	-1.920667	-2.334215	0.173470
54.H	-3.185156	-1.870582	-0.985655
55.H	-2.697216	-0.742494	0.297638

**Transition state: Cp\*<sub>2</sub>PaCH<sub>3</sub> + CH<sub>4</sub>**

1.Pa	-0.464834	-0.425100	-1.730732
2.C	-3.768065	-0.546123	-3.784291
3.C	-0.234679	-0.750321	2.130434
4.C	-2.701919	0.576503	-0.730412
5.C	-1.590989	-1.980956	-3.836365
6.H	-2.793257	0.865375	0.326429

7.H	-3.712648	0.435469	-1.139850
8.C	-1.652545	1.721572	-4.539070
9.C	0.830535	-2.817457	-4.320747
10.H	-2.262929	1.448805	-1.267517
11.C	1.201464	0.342668	-4.855826
12.C	-2.222788	-3.335147	-3.663712
13.C	1.999815	0.012195	-0.815164
14.C	1.378186	1.285730	-0.598447
15.C	0.443544	1.140001	0.468186
16.C	0.474453	-0.213140	0.915560
17.C	1.428050	-0.929299	0.115773
18.C	1.745786	2.581797	-1.270333
19.C	3.154443	-0.284764	-1.735708
20.C	1.946102	-2.316704	0.393318
21.C	-0.335107	2.262129	1.098544
22.C	-0.212787	-1.750064	-4.123170
23.C	-0.041633	-0.342799	-4.351402
24.C	-1.323960	0.295600	-4.180000
25.C	-2.276841	-0.732895	-3.874971
26.C	-1.967029	-2.194743	-0.463956
27.H	-1.065218	-2.791107	-0.734585
28.H	-2.828320	-2.683840	-0.940606
29.H	-2.079887	-2.278591	0.626707
30.H	-2.306637	-0.800432	-0.616465
31.H	4.104113	-0.349242	-1.176682
32.H	3.283226	0.493900	-2.499884
33.H	3.039856	-1.248774	-2.259713
34.H	2.583900	3.077405	-0.749056
35.H	0.904978	3.289456	-1.278601
36.H	2.065081	2.438247	-2.312917
37.H	2.761158	-2.301430	1.140796
38.H	2.348738	-2.795204	-0.510591
39.H	1.161889	-2.977160	0.788597
40.H	0.328266	-0.516899	3.050337
41.H	-0.344560	-1.842494	2.091662
42.H	-1.241014	-0.323632	2.251668
43.H	0.293071	2.822241	1.811251
44.H	-1.205328	1.894637	1.657229
45.H	-0.703412	2.983862	0.355049
46.H	2.105067	-0.255891	-4.675459
47.H	1.358528	1.329176	-4.389044
48.H	1.145455	0.521271	-5.944011
49.H	-0.810007	2.401015	-4.347791
50.H	-2.511903	2.100904	-3.968861
51.H	-1.908420	1.819519	-5.610630
52.H	-4.036581	0.464852	-3.448649
53.H	-4.236898	-1.257566	-3.089501
54.H	-4.243378	-0.694304	-4.768974
55.H	-1.597906	-4.015387	-3.066889
56.H	-2.384907	-3.817934	-4.641838
57.H	-3.201254	-3.271643	-3.170543
58.H	1.841825	-2.467649	-4.067190
59.H	0.866468	-3.150556	-5.373489
60.H	0.626889	-3.705830	-3.706597

•  $\text{Cp}^*_2\text{UCH}_3 + \text{CH}_4$

**Reactant:  $\text{Cp}^*_2\text{UCH}_3$**

1.U	-0.499082	-0.428818	-1.716778
2.C	-3.741394	-0.954939	-3.630633



3.C	-0.381317	-0.568756	2.099472
4.H	-1.968109	-3.933678	-4.483567
5.C	-1.336573	-1.975385	-3.796208
6.H	2.110016	-1.804849	-4.300736
7.H	-2.545568	-3.517398	-2.861316
8.C	-2.096821	1.677020	-4.333289
9.C	1.165262	-2.337801	-4.479779
10.H	1.170713	-2.654541	-5.538290
11.C	0.928871	0.822102	-4.928334
12.C	-1.693134	-3.417912	-3.547568
13.C	2.061081	-0.338380	-0.765386
14.C	1.564377	1.006139	-0.723895
15.C	0.552596	1.069656	0.292105
16.C	0.439094	-0.224477	0.887042
17.C	1.353629	-1.096134	0.219917
18.C	2.123001	2.184671	-1.478896
19.C	3.236589	-0.815802	-1.576133
20.C	1.614844	-2.536271	0.576716
21.C	-0.153149	2.317999	0.755548
22.C	-0.039251	-1.487373	-4.169947
23.C	-0.156175	-0.075679	-4.394395
24.C	-1.514563	0.299388	-4.152351
25.C	-2.248647	-0.876146	-3.800953
26.C	-2.527081	-0.972361	-0.389417
27.H	-0.854493	-3.984655	-3.115051
28.H	-4.245273	-1.016416	-4.610781
29.H	-4.042195	-1.839832	-3.054987
30.H	1.189467	-3.257292	-3.876894
31.H	4.188648	-0.620913	-1.051009
32.H	3.305224	-0.307808	-2.549694
33.H	3.194843	-1.896623	-1.772420
34.H	2.948809	2.663023	-0.922829
35.H	1.367563	2.967391	-1.647545
36.H	2.525237	1.899901	-2.461911
37.H	2.385023	-2.622464	1.362093
38.H	1.976722	-3.116811	-0.284670
39.H	0.714470	-3.037406	0.960182
40.H	0.166735	-0.325174	3.025918
41.H	-0.626352	-1.638901	2.140676
42.H	-1.333660	-0.021748	2.128699
43.H	0.434656	2.852317	1.522420
44.H	-1.132013	2.094233	1.202205
45.H	-0.319023	3.034584	-0.063335
46.H	1.928561	0.518156	-4.582748
47.H	0.784618	1.872382	-4.635288
48.H	0.957131	0.801392	-6.031989
49.H	-1.361132	2.470314	-4.132200
50.H	-2.960657	1.850099	-3.674517
51.H	-2.451239	1.834399	-5.366268
52.H	-4.151753	-0.077415	-3.110408
53.H	-2.363927	-1.772743	0.356844
54.H	-3.438950	-1.236016	-0.949275
55.H	-2.773923	-0.066505	0.203102

**Transition state: Cp\*<sub>2</sub>UCH<sub>3</sub> + CH<sub>4</sub>**

1.U	-0.518706	-0.445769	-1.702554
2.C	-3.642190	-0.316415	-3.895539
3.C	-0.067342	-0.872792	2.067045
4.C	-2.749907	0.530975	-0.746153
5.C	-1.570472	-1.902786	-3.823554

6.H	-2.821331	0.881259	0.293915
7.H	-3.770449	0.359080	-1.120530
8.C	-1.331365	1.791016	-4.547128
9.C	0.817590	-2.898845	-4.165710
10.H	-2.348636	1.385986	-1.339317
11.C	1.389890	0.174019	-4.898394
12.C	-2.305478	-3.207939	-3.678670
13.C	2.023713	0.111374	-0.921313
14.C	1.305085	1.323454	-0.668347
15.C	0.412255	1.097497	0.424591
16.C	0.559294	-0.259524	0.843192
17.C	1.545230	-0.873941	0.006211
18.C	1.542709	2.648799	-1.343857
19.C	3.230263	-0.046416	-1.808375
20.C	2.109353	-2.260880	0.176172
21.C	-0.393869	2.157391	1.125369
22.C	-0.170088	-1.764850	-4.075616
23.C	0.106418	-0.386938	-4.346260
24.C	-1.129889	0.332281	-4.226248
25.C	-2.165543	-0.607796	-3.916090
26.C	-1.945528	-2.233147	-0.430113
27.H	-1.003404	-2.791120	-0.644837
28.H	-2.752498	-2.780753	-0.938480
29.H	-2.102471	-2.322084	0.655746
30.H	-2.330298	-0.845216	-0.597647
31.H	4.162992	0.105085	-1.235589
32.H	3.237737	0.679756	-2.632151
33.H	3.296621	-1.050596	-2.254345
34.H	2.333427	3.224442	-0.832289
35.H	0.642304	3.281046	-1.343396
36.H	1.864938	2.531408	-2.389412
37.H	3.022965	-2.251974	0.796176
38.H	2.389105	-2.721110	-0.784034
39.H	1.396862	-2.936645	0.669601
40.H	0.526367	-0.647326	2.969752
41.H	-0.134870	-1.966769	1.993492
42.H	-1.084170	-0.495983	2.247241
43.H	0.230809	2.716054	1.842984
44.H	-1.229937	1.729671	1.694263
45.H	-0.817919	2.894912	0.428551
46.H	2.264094	-0.423686	-4.607018
47.H	1.573149	1.207879	-4.568333
48.H	1.367231	0.195660	-6.002922
49.H	-0.471216	2.409909	-4.248633
50.H	-2.221004	2.202330	-4.049084
51.H	-1.471708	1.950188	-5.630800
52.H	-3.859500	0.708308	-3.564129
53.H	-4.189893	-0.996121	-3.227795
54.H	-4.080483	-0.429132	-4.902100
55.H	-1.734139	-3.951799	-3.104778
56.H	-2.513691	-3.654393	-4.665943
57.H	-3.272577	-3.081337	-3.174012
58.H	1.838089	-2.584713	-3.899475
59.H	0.870173	-3.307012	-5.189823
60.H	0.545938	-3.737133	-3.506863

• **Cp\*<sub>2</sub>NpCH<sub>3</sub> + CH<sub>4</sub>**

**Reactant: Cp\*<sub>2</sub>NpCH<sub>3</sub>**

1.Np	-0.509559	-0.532464	-1.543670
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2.C	-3.636446	-0.946597	-3.565339
3.C	-0.173071	-0.686969	2.194456
4.C	-2.479428	-1.227505	-0.213256
5.C	-1.250010	-2.010210	-3.715307
6.H	1.298684	-3.275293	-3.633568
7.H	2.072905	0.402075	-4.500428
8.C	-1.930816	1.661540	-4.209734
9.C	1.262137	-2.405407	-4.307019
10.H	1.252932	-2.807476	-5.335114
11.C	1.074448	0.760599	-4.788401
12.C	-1.639112	-3.451959	-3.510633
13.C	2.136293	-0.253136	-0.758382
14.C	1.568453	1.052935	-0.665225
15.C	0.600606	1.040778	0.391806
16.C	0.582660	-0.267317	0.962927
17.C	1.512022	-1.072579	0.236390
18.C	2.016205	2.276643	-1.419939
19.C	3.312486	-0.650874	-1.609583
20.C	1.868763	-2.502922	0.548986
21.C	-0.172798	2.233824	0.892455
22.C	0.060460	-1.534302	-4.051641
23.C	-0.020570	-0.124546	-4.256711
24.C	-1.376380	0.271828	-4.032146
25.C	-2.139954	-0.894699	-3.722479
26.H	0.981314	1.797252	-4.433905
27.H	1.054659	0.798491	-5.891678
28.H	-2.818867	1.835329	-3.584024
29.H	-1.192052	2.438921	-3.963248
30.H	-2.241700	1.843241	-5.252849
31.H	0.393990	2.791729	1.657682
32.H	-1.126952	1.941806	1.354000
33.H	-0.399222	2.951447	0.089138
34.H	2.783324	2.834786	-0.855150
35.H	1.190239	2.981116	-1.602371
36.H	2.454575	2.024063	-2.394883
37.H	4.264695	-0.483064	-1.076143
38.H	3.363455	-0.070321	-2.541583
39.H	3.287015	-1.714986	-1.884841
40.H	0.427693	-0.508057	3.102962
41.H	-0.429269	-1.755331	2.180990
42.H	-1.114773	-0.134126	2.312106
43.H	2.693957	-2.563030	1.279159
44.H	2.200546	-3.053096	-0.344295
45.H	1.022415	-3.054271	0.983903
46.H	-1.938271	-3.928474	-4.460119
47.H	-2.485853	-3.556313	-2.817579
48.H	-0.809220	-4.052265	-3.108576
49.H	-4.034569	-0.075958	-3.023874
50.H	-3.959824	-1.841782	-3.018480
51.H	-4.134149	-0.968174	-4.550251
52.H	2.204742	-1.855097	-4.184717
53.H	-2.250775	-2.144530	0.366166
54.H	-3.385642	-1.446435	-0.804232
55.H	-2.768037	-0.465497	0.536509

**Transition state: Cp\*<sub>2</sub>NpCH<sub>3</sub> + CH<sub>4</sub>**

1.Np	-0.530336	-0.475654	-1.544047
2.C	-3.579236	-1.189403	-3.633632
3.C	-0.037869	-0.882914	2.180994
4.C	-2.396336	1.230975	-0.912057

5.C	-1.115901	-2.071348	-3.674184
6.H	-2.565659	1.692135	0.072610
7.H	-3.335364	1.297078	-1.483208
8.C	-2.064294	1.491913	-4.431210
9.C	1.409496	-2.322702	-4.250281
10.H	-1.661385	1.882558	-1.435427
11.C	1.015710	0.822812	-4.815176
12.C	-1.387873	-3.532186	-3.423685
13.C	2.126913	-0.274097	-0.849561
14.C	1.589133	1.031972	-0.627800
15.C	0.695239	0.963281	0.485988
16.C	0.662576	-0.388607	0.942793
17.C	1.537756	-1.154245	0.113114
18.C	2.029680	2.298185	-1.314047
19.C	3.294776	-0.603885	-1.739924
20.C	1.881401	-2.609567	0.298188
21.C	0.072700	2.142900	1.182533
22.C	0.161807	-1.515143	-4.009792
23.C	-0.021163	-0.125363	-4.274663
24.C	-1.408447	0.176227	-4.108157
25.C	-2.086541	-1.028216	-3.752097
26.C	-2.441316	-1.574333	-0.181566
27.H	-3.183080	-2.025852	-0.858020
28.H	-2.911506	-1.461051	0.806857
29.H	-1.622346	-2.316132	-0.034812
30.H	-2.388191	-0.167343	-0.524822
31.H	0.780680	2.593530	1.899012
32.H	-0.823162	1.860128	1.751528
33.H	-0.222985	2.936521	0.482080
34.H	2.875434	2.768220	-0.781957
35.H	1.226252	3.048604	-1.352653
36.H	2.361407	2.115924	-2.345618
37.H	4.249546	-0.419130	-1.215958
38.H	3.310000	0.009363	-2.652156
39.H	3.300129	-1.657974	-2.049340
40.H	0.592907	-0.738953	3.074937
41.H	-0.273013	-1.955072	2.126006
42.H	-0.982592	-0.352386	2.364085
43.H	2.765538	-2.736129	0.946569
44.H	2.118365	-3.106710	-0.654767
45.H	1.062404	-3.171735	0.770202
46.H	-1.500379	-4.089915	-4.369373
47.H	-2.310593	-3.688822	-2.848317
48.H	-0.570383	-4.020447	-2.870473
49.H	-4.055320	-0.340686	-3.122119
50.H	-3.853316	-2.099685	-3.083039
51.H	-4.045344	-1.267690	-4.630641
52.H	2.310754	-1.696986	-4.262461
53.H	1.360066	-2.840025	-5.224397
54.H	1.561521	-3.105107	-3.490270
55.H	2.033590	0.535312	-4.517464
56.H	0.851911	1.855602	-4.475223
57.H	0.998675	0.844640	-5.918790
58.H	-1.407519	2.347633	-4.216776
59.H	-2.992131	1.641183	-3.863138
60.H	-2.326956	1.552564	-5.501301

•  $\text{Cp}^*_2\text{PuCH}_3 + \text{CH}_4$

Reactant:  $\text{Cp}^*_2\text{PuCH}_3$

1.Pu	-0.577241	-0.493767	-1.512481
2.C	-3.590816	-0.753656	-3.597479
3.C	0.018075	-0.892818	2.147467
4.C	-2.308633	-1.675458	-0.185395
5.C	-1.294658	-2.008949	-3.667642
6.H	1.155790	-3.448224	-3.427580
7.H	2.216166	0.059878	-4.552211
8.C	-1.667214	1.681423	-4.341608
9.C	1.195776	-2.618488	-4.149172
10.H	1.181136	-3.074797	-5.154092
11.C	1.253425	0.529202	-4.792719
12.C	-1.801255	-3.407055	-3.430632
13.C	2.135418	-0.105704	-0.867269
14.C	1.480488	1.147889	-0.668152
15.C	0.573042	1.002568	0.429806
16.C	0.670713	-0.339255	0.910604
17.C	1.619853	-1.026723	0.091912
18.C	1.798096	2.442161	-1.369217
19.C	3.306977	-0.357592	-1.776801
20.C	2.083351	-2.445260	0.296355
21.C	-0.254245	2.105965	1.038220
22.C	0.056350	-1.649685	-3.970375
23.C	0.091009	-0.246820	-4.236346
24.C	-1.235048	0.261672	-4.084018
25.C	-2.094166	-0.826524	-3.746376
26.H	1.284751	1.563527	-4.419426
27.H	1.193461	0.591212	-5.893458
28.H	-2.576686	1.946527	-3.781987
29.H	-0.886168	2.408899	-4.073366
30.H	-1.898063	1.846473	-5.408197
31.H	0.311877	2.661267	1.805895
32.H	-1.159601	1.721500	1.530123
33.H	-0.572800	2.849335	0.291061
34.H	2.529350	3.039439	-0.796938
35.H	0.909572	3.079845	-1.497892
36.H	2.230223	2.275279	-2.365261
37.H	4.259581	-0.186379	-1.245753
38.H	3.304249	0.308613	-2.649656
39.H	3.332989	-1.392092	-2.147809
40.H	0.679992	-0.778049	3.023498
41.H	-0.213235	-1.962134	2.051128
42.H	-0.924226	-0.380647	2.384057
43.H	2.883847	-2.503171	1.053837
44.H	2.488127	-2.883090	-0.627308
45.H	1.270710	-3.099026	0.646534
46.H	-2.102542	-3.888627	-4.376847
47.H	-2.673660	-3.423008	-2.763615
48.H	-1.033726	-4.052098	-2.978831
49.H	-3.924496	0.190903	-3.140886
50.H	-3.981061	-1.571047	-2.977159
51.H	-4.090471	-0.821886	-4.579244
52.H	2.172211	-2.128925	-4.033725
53.H	-1.995170	-2.660200	0.208936
54.H	-3.225075	-1.851919	-0.779427
55.H	-2.619061	-1.076514	0.692852

**Transition state: Cp\*<sub>2</sub>PuCH<sub>3</sub> + CH<sub>4</sub>**

1.Pu	-0.644953	-0.149818	-1.591928
2.C	-3.609568	-0.981957	-3.669260
3.C	0.068390	-1.375940	1.871941

4.C	-2.805856	-0.749848	-0.217652
5.C	-1.261150	-2.110002	-3.435505
6.H	1.186528	-3.476382	-3.035672
7.H	2.189613	-0.077429	-4.590268
8.C	-1.761769	1.351038	-4.838003
9.C	1.237774	-2.714756	-3.826223
10.H	1.252543	-3.254807	-4.789298
11.C	1.217525	0.300878	-4.930630
12.C	-1.715363	-3.467111	-2.965393
13.C	2.083276	0.085512	-0.953068
14.C	1.443094	1.256249	-0.447389
15.C	0.583415	0.867043	0.624536
16.C	0.680938	-0.551341	0.770826
17.C	1.604270	-1.035660	-0.205948
18.C	1.725954	2.669525	-0.885315
19.C	3.240595	0.080005	-1.914385
20.C	2.140814	-2.441563	-0.264742
21.C	-0.176222	1.796989	1.533000
22.C	0.079993	-1.755158	-3.770052
23.C	0.068884	-0.415281	-4.270571
24.C	-1.281952	0.049148	-4.252678
25.C	-2.105966	-0.999586	-3.740988
26.H	1.200932	1.385078	-4.742196
27.H	1.186133	0.171861	-6.026824
28.H	-2.721446	1.669687	-4.409881
29.H	-1.044378	2.170085	-4.680365
30.H	-1.907927	1.265146	-5.928534
31.H	0.419873	2.049202	2.426937
32.H	-1.118028	1.356108	1.889920
33.H	-0.427037	2.744433	1.036883
34.H	2.592627	3.091097	-0.347696
35.H	0.876891	3.340110	-0.692035
36.H	1.959627	2.732895	-1.958499
37.H	4.194641	0.224637	-1.377463
38.H	3.168931	0.885908	-2.657651
39.H	3.325241	-0.869367	-2.460456
40.H	0.780932	-1.517536	2.702680
41.H	-0.223720	-2.380906	1.532557
42.H	-0.826410	-0.900996	2.295444
43.H	2.933167	-2.595824	0.488754
44.H	2.578348	-2.675490	-1.243722
45.H	1.364769	-3.194955	-0.061573
46.H	-1.868699	-4.155151	-3.814425
47.H	-2.668103	-3.417769	-2.420443
48.H	-0.979629	-3.946018	-2.301727
49.H	-4.002990	0.015478	-3.426731
50.H	-3.995396	-1.678090	-2.912166
51.H	-4.053917	-1.276731	-4.635448
52.H	2.206413	-2.205203	-3.733322
53.H	-2.411105	-1.764074	-0.445925
54.H	-3.876974	-0.778594	-0.469155
55.H	-2.717795	-0.603694	0.869657
56.C	-2.297923	1.880840	-1.305640
57.H	-2.557754	2.450703	-0.400507
58.H	-3.117535	2.003885	-2.029798
59.H	-1.404633	2.381319	-1.740601
60.H	-2.516085	0.548300	-0.786663

**Low spin state**

- **Cl<sub>2</sub>PaCH<sub>3</sub> [1] + CH<sub>4</sub>**

**Reactant: Cl<sub>2</sub>PaCH<sub>3</sub>**

1.Pa	1.593589	0.359491	0.000000
2.Cl	2.588834	1.221542	2.124919
3.Cl	2.588834	1.221542	-2.124919
4.C	-0.615376	1.022612	0.000000
5.H	-1.000071	1.525430	0.900512
6.H	-1.000071	1.525430	-0.900512
7.H	-1.014536	-0.028908	0.000000

**Transition state: Cl<sub>2</sub>PaCH<sub>3</sub> + CH<sub>4</sub>**

1.Pa	-0.460763	-0.041920	0.042898
2.Cl	0.937007	0.018654	-2.075255
3.Cl	1.092890	-0.142883	2.046107
4.C	-2.436049	-1.468748	0.088301
5.H	-3.498227	-1.732433	0.144143
6.H	-1.924432	-1.992632	0.935915
7.H	-2.043215	-1.892249	-0.871421
8.C	-2.387179	1.437353	0.183366
9.H	-3.439104	1.734216	0.261536
10.H	-2.608075	-0.014530	0.157781
11.H	-1.979902	1.912424	-0.745838
12.H	-1.855696	1.883138	1.063505

**b) Optimized coordinates of Cp<sub>2</sub>An(Me)<sub>2</sub> + CH<sub>4</sub> systems (An=U, Np)**

**Reactant: Cp<sub>2</sub>U(Me)<sub>2</sub>**

1.U	-0.400022	0.028695	-0.145949
2.C	0.572246	-0.041399	-2.687885
3.C	1.274989	1.033129	-2.073661
4.C	1.040674	-1.256755	-2.116749
5.C	2.169483	0.480698	-1.118893
6.C	2.022558	-0.930404	-1.144883
7.C	-1.318726	0.105376	2.418173
8.C	-0.399361	-0.980678	2.411907
9.C	-0.576548	1.311191	2.288275
10.C	0.797439	0.967908	2.190365
11.C	0.907915	-0.444983	2.268582
12.H	-0.654427	-2.033508	2.506853
13.H	1.833891	-1.014648	2.239708
14.H	1.624625	1.667069	2.087740
15.H	-0.988836	2.316712	2.270322
16.H	-2.398246	0.027488	2.524922
17.H	2.858274	1.038437	-0.488667
18.H	2.576057	-1.639832	-0.533299
19.H	0.707201	-2.257199	-2.380064
20.H	-0.176949	0.050029	-3.470977
21.H	1.151547	2.089427	-2.301267
22.C	-1.930589	-1.759023	-0.605114
23.C	-1.893089	1.798754	-0.769413
24.H	-2.235382	-1.694741	-1.667088
25.H	-1.607093	-2.795935	-0.414704
26.H	-2.837452	-1.577101	0.003756
27.H	-2.805288	1.722443	-0.147616
28.H	-1.533451	2.839339	-0.703529

29.H -2.199974 1.618217 -1.817975

**Transition state: Cp<sub>2</sub>U(Me)<sub>2</sub> + CH<sub>4</sub>**

1.C -0.995768 0.253045 3.334729  
2.C 0.069473 1.191468 3.233045  
3.C 1.278500 0.469507 3.071788  
4.C 0.965505 -0.917824 3.090907  
5.C -0.434677 -1.052328 3.261120  
6.U -0.163907 0.041339 0.739730  
7.C -0.204092 2.712134 0.447678  
8.C 2.149071 -1.190987 -0.039730  
9.C 1.205526 -1.637461 -0.998836  
10.C 0.826522 -0.522784 -1.790226  
11.C 1.539815 0.614078 -1.328420  
12.C 2.356870 0.203674 -0.239767  
13.C -2.165520 0.957197 -0.638405  
14.C -1.469145 -2.025796 0.617781  
15.H 1.678645 -1.734421 3.017407  
16.H 2.272816 0.899205 2.979488  
17.H -0.024786 2.272457 3.280279  
18.H -2.046190 0.490054 3.491784  
19.H -0.981277 -1.986708 3.334035  
20.H 3.053451 0.831274 0.310571  
21.H 2.653231 -1.813193 0.694427  
22.H 0.837051 -2.653258 -1.107097  
23.H 0.119678 -0.539590 -2.616571  
24.H 1.483572 1.616278 -1.743980  
25.H -1.748883 -2.173588 -0.441913  
26.H -0.992304 -2.955841 0.964571  
27.H -2.406705 -1.902442 1.191501  
28.H -1.144399 1.781787 -0.132252  
29.H -2.012055 0.155859 -1.379754  
30.H -2.868974 0.589708 0.131971  
31.H -0.787012 3.264552 1.198281  
32.H 0.828802 2.608404 0.826222  
33.H -2.652248 1.794754 -1.155268  
34.H -0.150827 3.326751 -0.463296

**Reactant: Cp<sub>2</sub>Np(Me)<sub>2</sub>**

1.C 0.105730 0.028880 0.066616  
2.C 0.330038 0.044465 1.469034  
3.C 1.349398 -0.198043 -0.580694  
4.C 2.343372 -0.336484 0.424427  
5.C 1.713599 -0.186067 1.690351  
6.Np 0.748321 -2.541439 0.692518  
7.C 2.574359 -3.461301 2.508544  
8.C 1.492683 -4.378876 2.574377  
9.C 1.450472 -5.089637 1.345399  
10.C 2.512293 -4.623541 0.525005  
11.C 3.204499 -3.612634 1.242868  
12.C 0.282212 -3.216673 -1.553639  
13.C -1.358443 -2.827328 1.789271



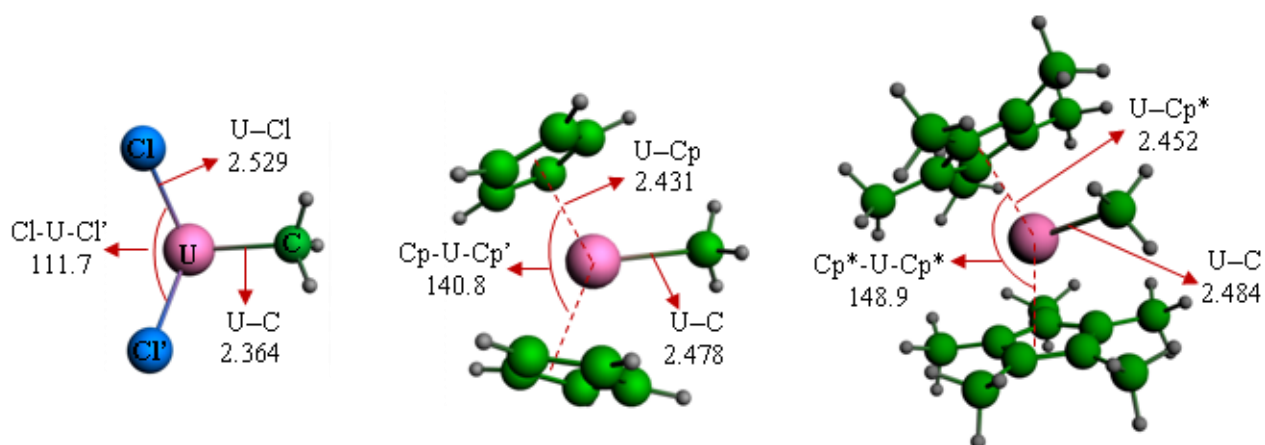
14.H	-0.561293	-2.579615	-1.887883
15.H	1.038854	-3.212722	-2.353302
16.H	-0.111537	-4.250005	-1.470613
17.H	-1.524201	-2.610701	2.855842
18.H	-2.075707	-2.212670	1.208250
19.H	-1.635420	-3.887206	1.616928
20.H	3.404561	-0.501000	0.255373
21.H	2.209324	-0.216733	2.657217
22.H	-0.425263	0.200931	2.234623
23.H	-0.853238	0.170515	-0.427202
24.H	1.508629	-0.258247	-1.654022
25.H	2.883283	-2.780819	3.297997
26.H	4.079117	-3.067875	0.896324
27.H	2.748390	-4.976465	-0.475374
28.H	0.731546	-5.861704	1.079839
29.H	0.813807	-4.511769	3.412544

**Transition state: Cp<sub>2</sub>Np(Me)<sub>2</sub> + CH<sub>4</sub>**

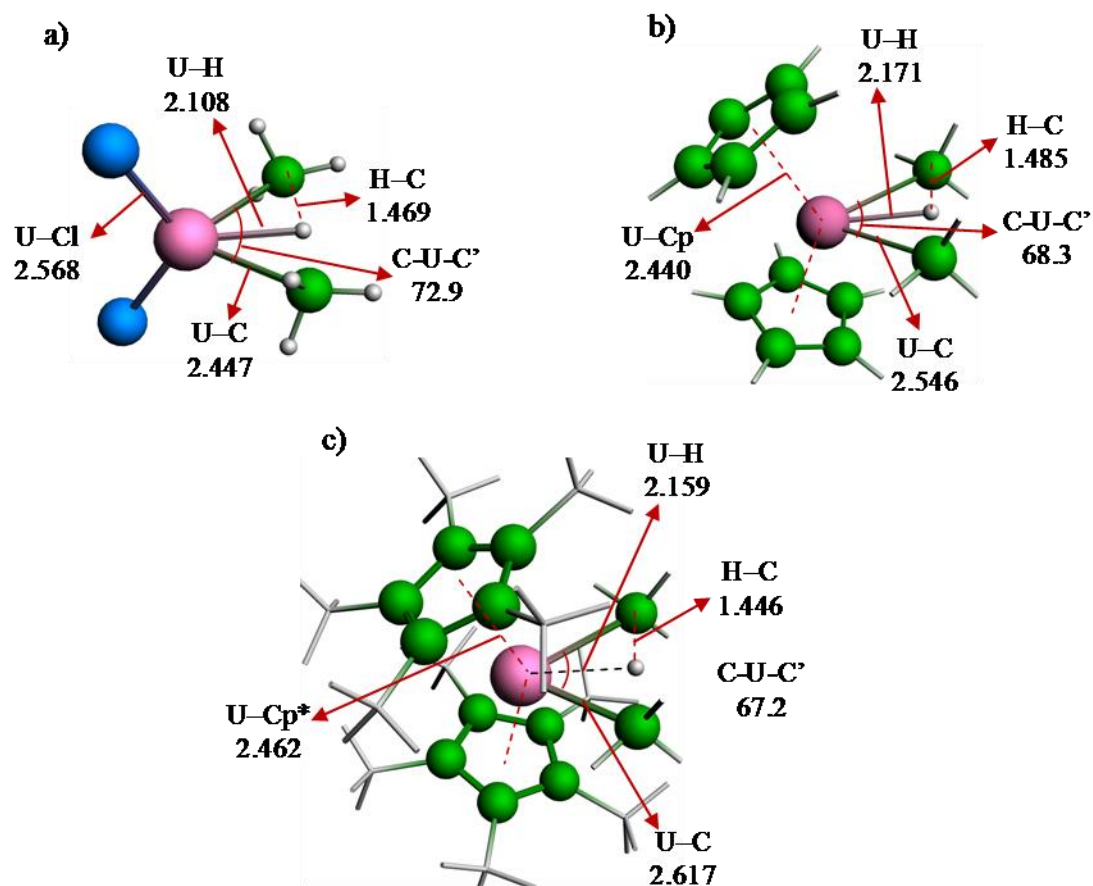
1.C	3.217423	-3.674930	1.006232
2.C	2.849279	-3.494791	2.368769
3.C	1.799326	-4.401382	2.660724
4.C	1.509050	-5.132676	1.477245
5.C	2.395748	-4.689689	0.458185
6.Np	0.695140	-2.586280	0.926698
7.C	0.608114	-3.147245	-1.450607
8.C	-0.755221	-2.453172	3.161547
9.C	2.006325	-0.262328	1.609961
10.C	0.627611	0.065004	1.635133
11.C	0.139285	0.010586	0.301293
12.C	1.225631	-0.329573	-0.550692
13.C	2.374623	-0.505756	0.257328
14.H	-0.171247	-2.523434	-1.925837
15.H	1.537506	-3.015336	-2.026313
16.H	0.295958	-4.202092	-1.554613
17.H	-1.206095	-2.943703	1.919324
18.H	3.370289	-0.754724	-0.098994
19.H	2.672076	-0.290635	2.468787
20.H	0.047596	0.320182	2.517911
21.H	-0.879748	0.224140	-0.015275
22.H	1.183806	-0.429450	-1.630420
23.H	3.313877	-2.807138	3.070802
24.H	4.011396	-3.148818	0.483813
25.H	2.441244	-5.067200	-0.558169
26.H	0.759177	-5.914573	1.377922
27.H	1.307707	-4.522239	3.622242
28.C	-1.777867	-3.430586	0.694944
29.H	-1.471258	-1.635024	3.323419
30.H	-1.051327	-3.306961	3.787230
31.H	0.234784	-2.109985	3.515732
32.H	-1.438956	-4.376826	0.244097
33.H	-2.725225	-3.629312	1.214471
34.H	-1.984214	-2.711039	-0.114645

## SI.2. Optimized geometries of $L_2AnCH_3 + CH_4$

- Reactants



- Transition states



### SI.3. Geometrical parameters

#### Complexes: $L_2AnCH_3$ ( $L = Cl, Cp$ )

$Cl_2AnCH_3$	Ac	Th	Pa	U	Np	Pu
An-Cl	2.685	2.590	2.544	2.529	2.531	2.535
An-C	2.538	2.404	2.349	2.364	2.363	2.359
Cl-An-Cl'	114.4	131.9	124.0	111.7	114.2	118.4
Cl-An-C	104.8	113.4	108.9	100.5	99.0	98.4
Sum of angles	324.0	358.7	341.8	312.7	312.2	315.2
$Cp_2AnCH_3$	Ac	Th	Pa	U	Np	Pu
An-Cp	2.688	2.554	2.447	2.431	2.465	2.471
An-Cp'	2.688	2.552	2.439	2.466	2.461	2.462
An-C	2.620	2.500	2.453	2.478	2.464	2.460
Cp-An-Cp'	138.6	137.6	126.7	140.8	134.1	127.7

#### Complexes: $Cp^*_2AnCH_3$ gaz and (solution) phase

$Cp^*_2AnCH_3$	Ac	Th	Pa	U	Np	Pu
An-Cp*	2.669 (2.662)	2.552 (2.548)	2.510 (2.504)	2.452 (2.445)	2.473 (2.466)	2.476 (2.470)
An-Cp*'	2.671 (2.663)	2.550 (2.544)	2.439 (2.434)	2.444 (2.439)	2.468 (2.458)	2.482 (2.471)
An-C	2.635 (2.629)	2.511 (2.523)	2.462 (2.476)	2.484 (2.504)	2.477 (2.487)	2.481 (2.499)
Cp*-An-Cp*'	142.2 (138.8)	146.0 (146.7)	150.596 (150.7)	148.963 (149.5)	141.72 (141.6)	136.684 (136.6)

#### Transition state: $L_2AnCH_3 + CH_4$ ( $L = Cl, Cp, Cp^*$ )

TS	An-Cl	An-C	An-C'	An-H	C-H	C'-H	C-H-C'	C-An-C'	Cl-An-Cl
Ac	2.717	2.667	2.674	2.266	1.463	1.469	177.4	66.6	125.2
Th	2.590	2.626	2.626	2.185	1.439	1.438	179.1	66.4	125.0
Pa	2.568	2.506	2.506	2.147	1.451	1.454	171.9	70.6	120.0
U	2.568	2.447	2.469	2.108	1.469	1.463	169.7	72.9	123.1
Np	2.570	2.461	2.464	2.100	1.456	1.465	171.3	72.5	125.1
Pu	2.572	2.472	2.471	2.100	1.452	1.453	172.5	71.8	130.8
TS	An-Cp An-Cp'	An-C	An-C'	An-H	C-H	C'-H	C-H-C'	C-An-C'	Cp-An- Cp'

Ac	2.687-2.699	2.751	2.754	2.309	1.462	1.463	174.9	64.1	132.5
Th	2.535-2.531	2.693	2.693	2.249	1.448	1.448	177.8	65.0	132.1
Pa	2.417-2.454	2.620	2.637	2.206	1.453	1.443	172.3	66.7	128.3
U	2.440-2.444	2.546	2.639	2.171	1.485	1.429	177.8	68.3	127.3
Np	2.468-2.474	2.564	2.559	2.154	1.452	1.462	174.7	69.3	123.8
Pu	2.463-2.472	2.612	2.587	2.148	1.435	1.461	176.4	67.7	126.0
TS	An-Cp* An-Cp*'	An-C	An-C'	An-H	C-H	C'-H	C-H-C'	C-An-C'	Cp*-An- Cp*'
Ac	2.675-2.674	2.770	2.773	2.305	1.456	1.455	175.7	63.3	140.217
Th	2.554-2.555	2.713	2.713	2.234	1.444	1.440	174.8	64.2	141.0
Pa	2.473-2.471	2.644	2.647	2.185	1.443	1.437	177.2	65.9	152.6
U	2.462-2.457	2.617	2.617	2.159	1.446	1.450	178.4	67.2	145.5
Np	2.473-2.486	2.607	2.591	2.141	1.451	1.449	177.0	67.8	139.4
Pu	2.486-2.484	2.634	2.630	2.153	1.447	1.447	176.3	66.6	134.2

#### SI.4. Vibration frequencies (cm<sup>-1</sup>) of the transition states

TS	Ac	Th	Pa	U	Np	Pu
Cl <sub>2</sub> AnCH <sub>3</sub> + CH <sub>4</sub>	-1160	-1083	-1097	-1090	-1095	-1114
Cp <sub>2</sub> AnCH <sub>3</sub> + CH <sub>4</sub>	-1162	-1146	-1120	-1097	-1106	-1113
Cp* <sub>2</sub> AnCH <sub>3</sub> + CH <sub>4</sub>	-1252	-1228	-1221	-1214	-1211	-1206

## SI. 5. Total bonding energy (eV)

**Complex: L<sub>2</sub>AnCH<sub>3</sub> (L = Cl, Cp, Cp\*)**

Complex	Ac	Th	Pa	U	Np	Pu
Cl <sub>2</sub> AnCH <sub>3</sub>	-31.521	-33.189	-33.455	-33.715	-34.640	-34.222
Cp <sub>2</sub> AnCH <sub>3</sub>	-148.597	-150.579	-150.994	-151.163	-152.310	-151.665
Cp* <sub>2</sub> AnCH <sub>3</sub>	-311.421	-313.575	-313.992	-314.055	-315.213	-314.514

As shown in this Table, the TBE increases in absolute value from the Cp\*<sub>2</sub>AcCH<sub>3</sub> complex (–311.421 eV), to the Cp\*<sub>2</sub>NpCH<sub>3</sub> complex (–315.213 eV), thus attributing to the latter, as its homolog Cl<sub>2</sub>NpCH<sub>3</sub>, the highest TBE. The solvation brings a slight decrease in TBE equal to an average of 0.3 eV (complete TBEs and their different compositions are available in SI. 5). Taking into account the spin–orbit coupling reduces the total bond energies with a significant degree. The calculated spin–orbit corrections are –2.770, –2.982, –3.730, –4.459, –4.966 and –5.505 eV for Ac, Th, Pa, U, Np and Pu complexes respectively. We note in addition, that this energy correction is almost the same in the gas phase or in THF solution since it is mainly of atomic nature, depending mainly on the oxidation state of the metal and not on the molecular environment.

### Total bond energy decomposition

Cl <sub>2</sub> AnCH <sub>3</sub>	E <sub>Pauli</sub>	E <sub>ELEC</sub>	E <sub>STER</sub>	E <sub>ORR</sub>	TBE
Ac	72.970	-16.894	56.076	-87.597	-31.521
Th	79.046	-19.753	59.294	-92.482	-33.189
Pa	83.242	-20.049	63.194	-96.649	-33.455
U	81.485	-19.799	61.686	-95.401	-33.715
Np	80.230	-19.485	60.745	-95.385	-34.640
Pu	69.081	-18.100	50.981	-85.203	-34.222
Cp <sub>2</sub> AnCH <sub>3</sub>	E <sub>Pauli</sub>	E <sub>ELEC</sub>	E <sub>STER</sub>	E <sub>ORR</sub>	TBE
Ac	550.893	-115.189	435.704	-584.301	-148.597
Th	558.731	-119.123	439.608	-590.187	-150.579
Pa	565.518	-120.968	444.550	-595.543	-150.994
U	561.711	-119.849	441.861	-593.024	-151.163
Np	560.929	-119.313	441.616	-593.926	-152.310
Pu	550.781	-117.515	433.266	-584.931	-151.665
(Cp*) <sub>2</sub> AnC H <sub>3</sub>	E <sub>Pauli</sub>	E <sub>ELEC</sub>	E <sub>STER</sub>	E <sub>ORR</sub>	TBE
Ac	1105.038	-225.508	879.529	-1190.950	-311.421

Th	1112.319	-229.169	883.150	-1196.725	-313.575
Pa	1119.683	-230.731	888.951	-1202.942	-313.992
U	1116.423	-230.126	886.297	-1200.351	-314.055
Np	1114.919	-229.215	885.703	-1200.916	-315.213
Pu	1103.620	-227.223	876.396	-1190.910	-314.514

**Solvation energy E(solv) and spin-orbit E(SO)-gaz corrections of (Cp\*)<sub>2</sub>AnCH<sub>3</sub> complex**

Cp* <sub>2</sub> AnCH <sub>3</sub>	Ac	Th	Pa	U	Np	Pu
ESO-gaz	-2.770	-2.982	-3.730	-4.459	-4.966	-5.505
E(Solv)	-0.507	-0.275	-0.278	-0.337	-0.337	-0.341

**Transition state: L<sub>2</sub>AnCH<sub>3</sub> + CH<sub>4</sub> (L = Cl, Cp, Cp\*)**

TS	Ac	Th	Pa	U	Np	Pu
Cl <sub>2</sub> AnCH <sub>3</sub> +CH <sub>4</sub>	-54.603	-56.004	-56.620	-57.221	-58.288	-57.536
Cp <sub>2</sub> AnCH <sub>3</sub> +CH <sub>4</sub>	-171.665	-173.470	-174.088	-174.525	-175.686	-174.837
Cp* <sub>2</sub> AnCH <sub>3</sub> +CH <sub>4</sub>	-334.414	-336.254	-336.861	-337.236	-338.252	-337.555

## SI. 6. Mulliken Populations, Hirshfeld charges and Nalewajski-Mrozek Bond Orders

### Analyses

#### Complex: $L_2AnCH_3$ (L: Cl, Cp)

$Cl_2AnCH_3$	Net charge Mulliken-(Hirshfeld)					Bond orders		
		An	2Cl	$AnCl_2$	$CH_3$	An-C( $CH_3$ )	An-Cl	
Ac	0.00	1.286 (0.877)	-0.896 (-0.609)	0.390 (0.268)	-0.390 (-0.268)	0.870	1.023	
Th	1.04	0.996 (0.614)	-0.673 (-0.432)	0.323 (0.182)	-0.324 (-0.182)	0.919	1.082	
Pa	2.13	0.923 (0.636)	-0.643 (-0.446)	0.280 (0.190)	-0.280 (-0.190)	1.039	1.303	
U	3.17	1.047 (0.659)	-0.726 (-0.458)	0.322 (0.201)	-0.322 (-0.201)	1.011	1.274	
Np	4.20	1.053 (0.673)	-0.741 (-0.478)	0.313 (0.195)	-0.313 (-0.195)	0.999	1.234	
Pu	5.27	1.098 (0.783)	-0.789 (-0.572)	0.309 (0.211)	-0.309 (-0.211)	0.738	0.648	
$Cp_2AnCH_3$	Net charge Mulliken-(Hirshfeld)					Bond orders		
		An	2Cp	$AnCp_2$	$CH_3$	An- $CH_3$	An-(Cp)	An-(Cp)
Ac	0.00	1.083 (0.808)	-0.640 (-0.464)	0.443 (0.345)	-0.443 (-0.345)	0.763	0.415	0.414
Th	0.96	0.914 (0.570)	-0.468 (-0.296)	0.447 (0.274)	-0.447 (-0.274)	0.802	1.204	1.200
Pa	1.87	0.928 (0.658)	-0.464 (-0.387)	0.465 (0.271)	-0.465 (-0.271)	0.902	1.640	1.649
U	2.98	0.926 (0.717)	-0.518 (-0.417)	0.408 (0.300)	-0.408 (-0.300)	0.838	1.538	1.434
Np	4.17	0.893 (0.666)	-0.493 (-0.374)	0.400 (0.292)	-0.400 (-0.292)	0.845	1.350	1.343
Pu	5.28	0.946 (0.779)	-0.530 (-0.461)	0.416 (0.318)	-0.416 (-0.318)	0.580	/	/

#### Complex: $Cp^*_2AnCH_3$

$Cp^*_2AnCH_3$ (gas)	Net charge (Mulliken/Hirshfeld)					Bond orders		
		An	2Cp*	$AnCp^*_2$	$CH_3$	An-C( $CH_3$ )	An-Cp*	An-(Cp*)
Ac	0.00	0.923 (0.755)	-0.497 (-0.417)	0.426 (0.338)	-0.426 (-0.338)	0.763	0.210	0.203
Th	0.96	0.986 (0.570)	-0.636 (-0.303)	0.350 (0.267)	-0.350 (-0.267)	0.813	1.142	1.138
Pa	1.96	0.889 (0.627)	-0.405 (-0.357)	0.484 (0.270)	-0.484 (-0.270)	0.899	1.582	1.382
U	2.98	0.861 (0.674)	-0.484 (-0.381)	0.377 (0.293)	-0.377 (-0.293)	0.839	1.444	1.465
Np	4.19	0.830 (0.629)	-0.446 (-0.333)	0.384 (0.296)	-0.384 (-0.296)	0.826	1.291	1.307
Pu	5.30	0.915 (0.746)	-0.497 (-0.415)	0.418 (0.331)	-0.418 (-0.331)	0.539	/	/
$Cp^*_2AnCH_3$ (THF)	Net charge (Mulliken/Hirshfeld)					Bond orders		
		An	2Cp*	$AnCp^*_2$	$CH_3$	An- $CH_3$	An-(Cp)	An-(Cp*)

Ac	0.00	1.101 (0.785)	0.598 (0.430)	0.503 (0.355)	-0.503 (-0.355)	0.751	0.212	0.208
Th	0.98	1.003 (0.577)	0.439 (0.290)	0.564 (0.287)	-0.564 (-0.287)	0.797	1.143	1.140
Pa	1.97	0.911 (0.635)	0.406 (0.347)	0.505 (0.288)	-0.505 (-0.288)	0.880	1.391	1.584
U	2.98	0.918 (0.687)	0.485 (0.369)	0.433 (0.318)	-0.433 (-0.318)	0.813	1.453	1.465
Np	4.19	0.879 (0.640)	0.436 (0.321)	0.443 (0.319)	-0.443 (-0.319)	0.803	1.316	1.290
Pu	5.30	0.972 (0.761)	0.492 (0.404)	0.480 (0.357)	-0.480 (-0.357)	0.514	/	/

**Transition states :  $L_2AnCH_3 + CH_4$  (  $L = Cl, Cp$  )**

$Cl_2AnCH_3+CH_4$	Spin polarization	Mulliken - (Hirshfeld) net charges				
		An	AnCl <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub> '	H
Ac	0.00	1.241 (0.838)	0.311 (0.173)	-0.309 (-0.091)	-0.315 (-0.096)	0.313 (0.014)
Th	1.05	0.848 (0.567)	0.153 (0.119)	-0.240 (-0.069)	-0.239 (-0.069)	0.326 (0.019)
Pa	2.14	0.894 (0.616)	0.193 (0.104)	-0.210 (-0.059)	-0.212 (-0.061)	0.228 (0.016)
U	3.19	1.103 (0.606)	0.338 (0.067)	-0.259 (-0.042)	-0.264 (-0.046)	0.184 (0.021)
Np	4.22	1.066 (0.604)	0.271 (0.046)	-0.239 (-0.032)	-0.245 (-0.036)	0.213 (0.022)
Pu	5.31	1.131 (0.739)	0.277 (0.094)	-0.239 (-0.053)	-0.239 (-0.054)	0.201 (0.013)
$Cp_2AnCH_3+CH_4$	Spin polarization	Mulliken - (Hirshfeld) net charges				
		An	AnCp <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub> '	H
Ac	0.00	0.913 (0.740)	0.277 (0.283)	-0.313 (-0.145)	-0.318 (-0.147)	0.354 (0.010)
Th	0.91	0.717 (0.561)	0.208 (0.230)	-0.268 (-0.124)	-0.267 (-0.124)	0.327 (0.018)
Pa	1.79	0.785 (0.661)	0.205 (0.203)	-0.256 (-0.109)	-0.257 (-0.107)	0.309 (0.013)
U	2.96	0.768 (0.614)	0.232 (0.185)	-0.264 (-0.104)	-0.268 (-0.096)	0.301 (0.016)
Np	4.18	0.715 (0.568)	0.213 (0.190)	-0.240 (-0.100)	-0.244 (-0.105)	0.270 (0.015)
Pu	5.30	0.765 (0.706)	0.225 (0.240)	-0.267 (-0.118)	-0.276 (-0.127)	0.317 (0.006)



## SI. 7. Energies and composition of the frontier molecular orbitals

### Complexes : $L_2AnCH_3$ ( L : Cl, Cp, Cp\* )

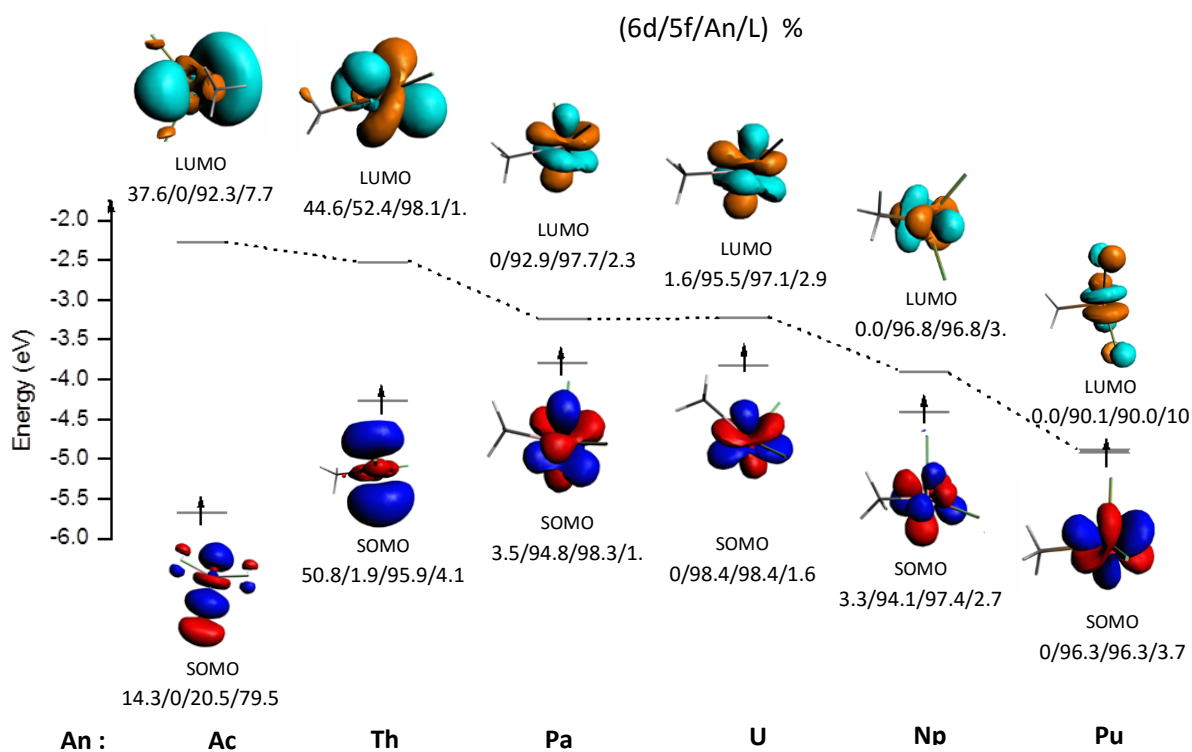
Orbital		SOMO		LUMO	
		Energy (eV)	Contribution % (6d/5f/An/L)	Energy (eV)	Contribution % (6d/5f/An/L)
Cl <sub>2</sub> AnCH <sub>3</sub>	Ac	-5.667	14.3/0/20.5/79.5	-2.266	37.6/0/92.3/7.7
	Th	-4.271	50.8/1.9/95.9/4.1	-2.524	44.6/52.4/98.1/1.9
	Pa	-3.787	3.5/94.8/98.3/1.7	-3.234	0/92.9/97.7/2.3
	U	-3.820	0/98.4/98.4/1.6	-3.229	1.6/95.5/97.1/2.9
	Np	-4.403	3.3/94.1/97.4/2.7	-3.900	0.0/96.8/96.8/3.2
	Pu	-4.922	0/96.3/96.3/3.7	-4.879	0.0/90.1/90.0/10.0
Complex/Parameters		Energy (eV)	Contribution % (6d/5f/An/L)	Energy (eV)	Contribution % (6d/5f/An/L)
Cp <sub>2</sub> AnCH <sub>3</sub>	Ac	-4.536	8.3/1.1/15.1/84.9	-1.520	52.0/0.0/84.9/15.1
	Th	-3.051	64.1/0.0/86.1/13.9	-1.691	50.8/22.4/73.2/26.8
	Pa	-2.936	9.4/73.2/82.6/17.4	-2.322	3.0/85.9/90.8/9.2
	U	-2.787	0.0/89.6/89.6/10.4	-2.184	4.1/86.5/94.0/6.0
	Np	-3.168	0.0/93.9/95.6/4.4	-2.526	3.9/86.5/91.5/8.5
	Pu	-3.614	1.7/88.0/89.7/10.3	-2.986	0.0/82.2/85.8/14.2
Complex/Parameters		Energy (eV)	Contribution % (6d/5f/An/L)	Energy (eV)	Contribution % (6d/5f/An/L)
Complexes Cp* <sub>2</sub> AnCH <sub>3</sub>	Ac	-4.127	1.54/0.0/24.72/75.28	-1.720	42.5/0.0/81.92/18.08
	Th	-2.668	60.3/0.0/85.1/14.9	-1.750	57.8/15.2/73.0/27
	Pa	-2.423	1.1/82.8/87.8/12.2	-2.233	2.0/87.9/89.9/10.1
	U	-2.275	10.2/74.2/85.9/14.1	-2.158	3.4/79.0/93.7/6.3
	Np	-2.602	1.2/86.6/93.6/6.4	-2.543	1.3/87.2/91.0/9.0
	Pu	-3.079	1.5/84.0/86.6/13.4	-2.971	0/79.7/82.9/17.1

### Transition states : $L_2AnCH_3 + CH_4$ ( L : Cl, Cp, Cp\* )

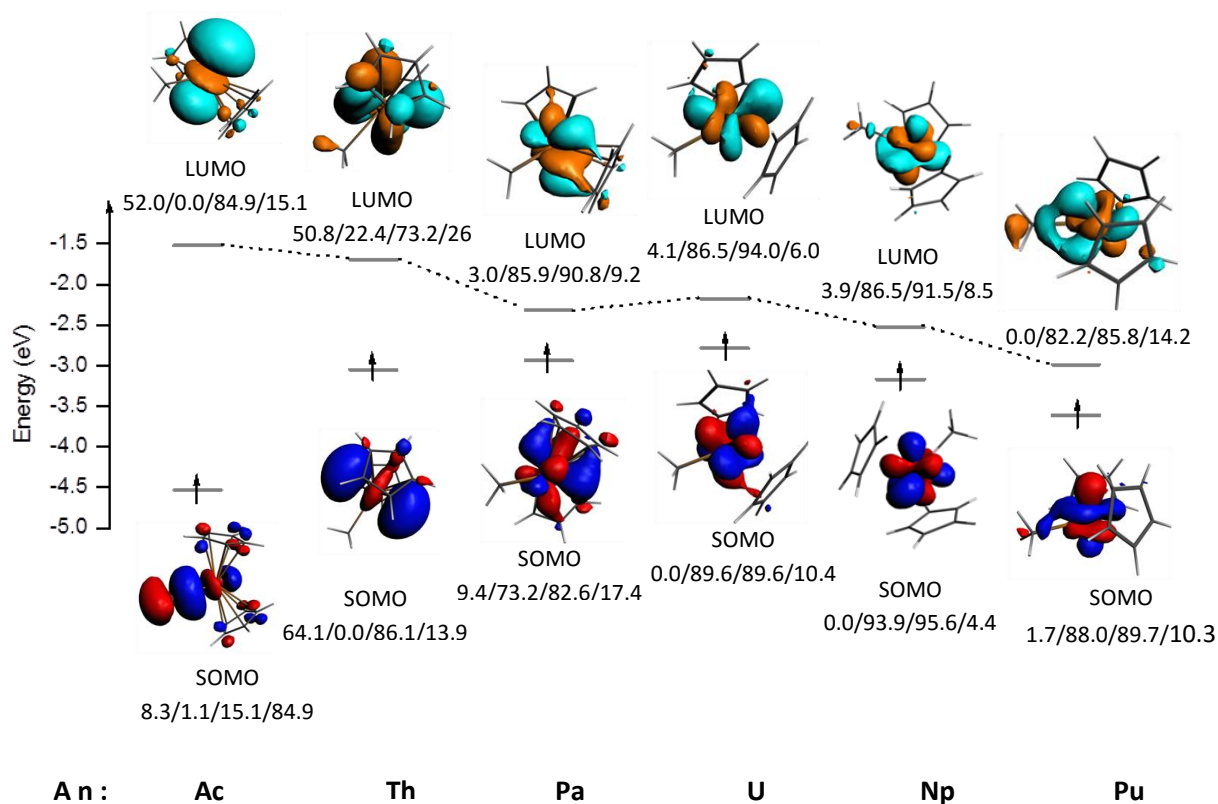
Orbitales		SOMO		LUMO	
		Energy (eV)	Contribution % (6d/5f/An/L)	Energy (eV)	Contribution % (6d/5f/An/L)
Cl <sub>2</sub> AnCH <sub>3</sub> + CH <sub>4</sub>	Ac	-5.929	8.2/3.15/11.3/88.7	-2.018	47.7/1.3/88.0/12
	Th	-3.586	47.0/5.3/91.0/9.0	-2.284	21.2/70.1/96.4/3.6
	Pa	-3.207	4.7/90.9/95.6/4.4	-2.598	18.1/78.4/96.5/3.5
	U	-3.541	2.3/93.0/95.3/4.7	-3.450	2.7/93.0/95.6/4.4
	Np	-4.139	1.2/93.9/95.1/4.9	-3.605	0.0/94.7/94.7/5.3

	Pu	-4.721	1.0/92.5/93.5/6.5	-4.058	0.0/87.7/87.7/12.3
Parameters		Energy (eV)	Contribution % (6d/5f/An/L)	Energy (eV)	Contribution % (6d/5f/An/L)
Cp <sub>2</sub> AnCH <sub>3</sub> + CH <sub>4</sub>	Ac	-4.833	2.8/2.0/4.7/95.3	-1.308	56.7/0.0/72.8/27.2
	Th	-2.632	61.7/2.8/76.1/23.9	-1.231	23.9/47.5/71.5/98.5
	Pa	-2.482	14.3/67.1/81.4/18.6	-1.793	1.8/89.3/91.1/8.9
	U	-2.597	5.3/83.6/89.0/11.0	-2.025	4.8/87.5/92.3/7.7
	Np	-3.070	0.0/93.5/93.5/6.5	-2.485	1.9/91.9/93.7/6.3
	Pu	-3.563	4.7/84.9/89.6/10.4	-2.860	1.8/80.4/82.3/17.7
Parameters		Energy (eV)	Contribution % (6d/5f/An/L)	Energy (eV)	Contribution % (6d/5f/An/L)
Cp* <sub>2</sub> AnCH <sub>3</sub> + CH <sub>4</sub>	Ac	-4.421	0.0/0.0/0.0/100	-1.506	46.7/0.0/73.3/26.7
	Th	-2.279	63.1/0.0/78.0/22.0	-1.491	31.3/42.6/73.9/26.1
	Pa	-2.092	1.2/82.1/83.3/16.7	-1.857	4.8/78.6/86.2/13.8
	U	-2.169	7.9/77.5/85.4/14.6	-1.995	11.0/75.2/89.9/10.1
	Np	-2.634	0.0/89.9/93.9/6.1	-2.526	8.0/81.9/89.9/10.1
	Pu	-3.075	6.0/78.2/84.2/15.8	-2.971	2.6/77.8/82.3/17.7

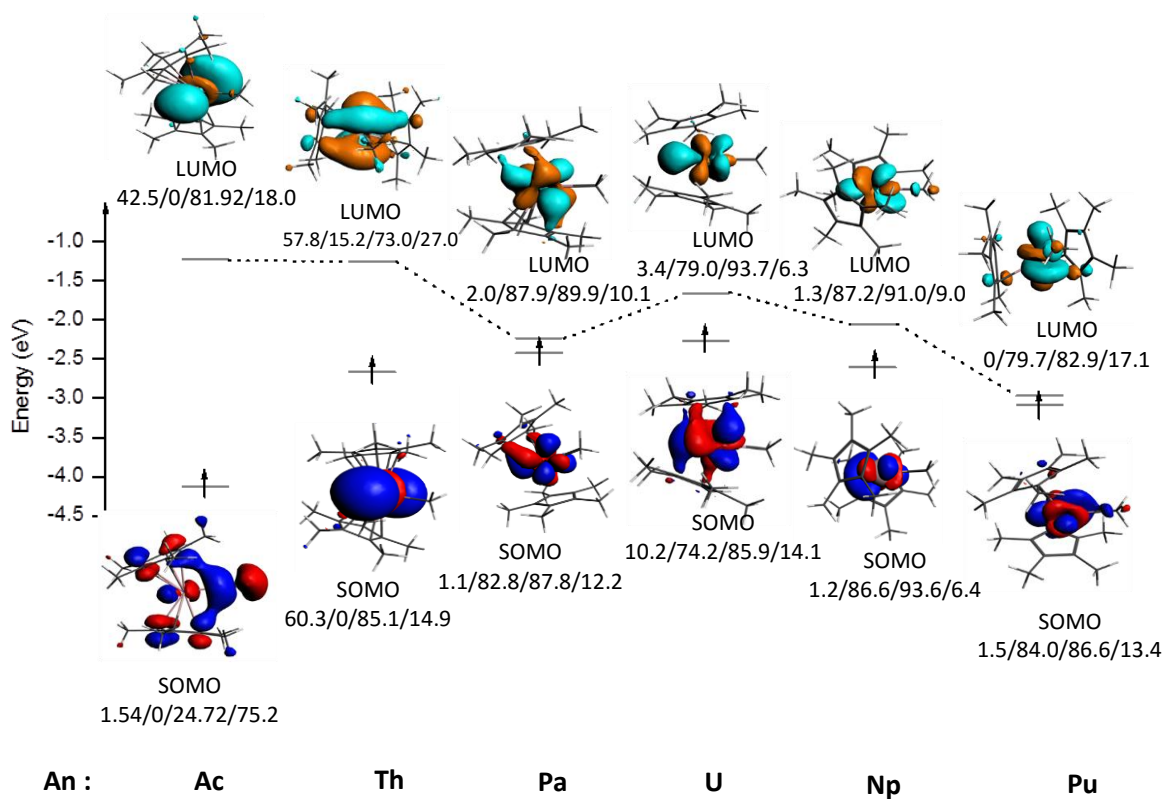
### Complex Cl<sub>2</sub>AnCH<sub>3</sub>



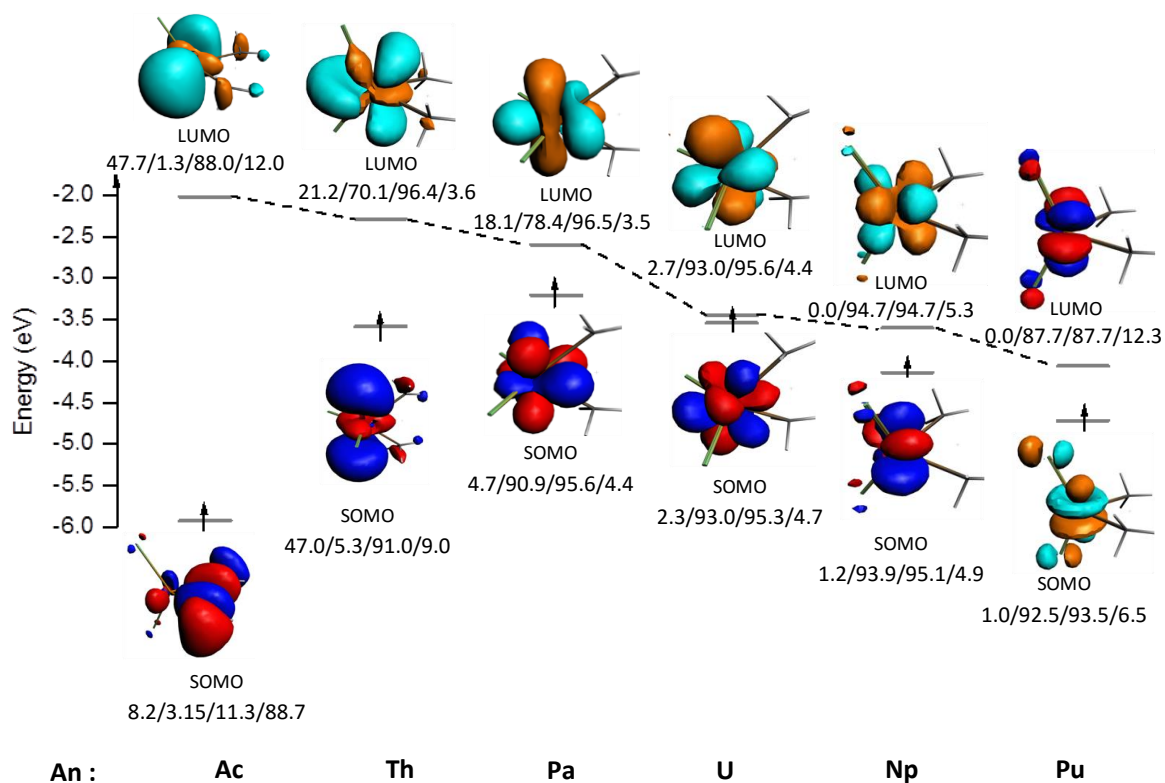
### Complex Cp<sub>2</sub>AnCH<sub>3</sub>



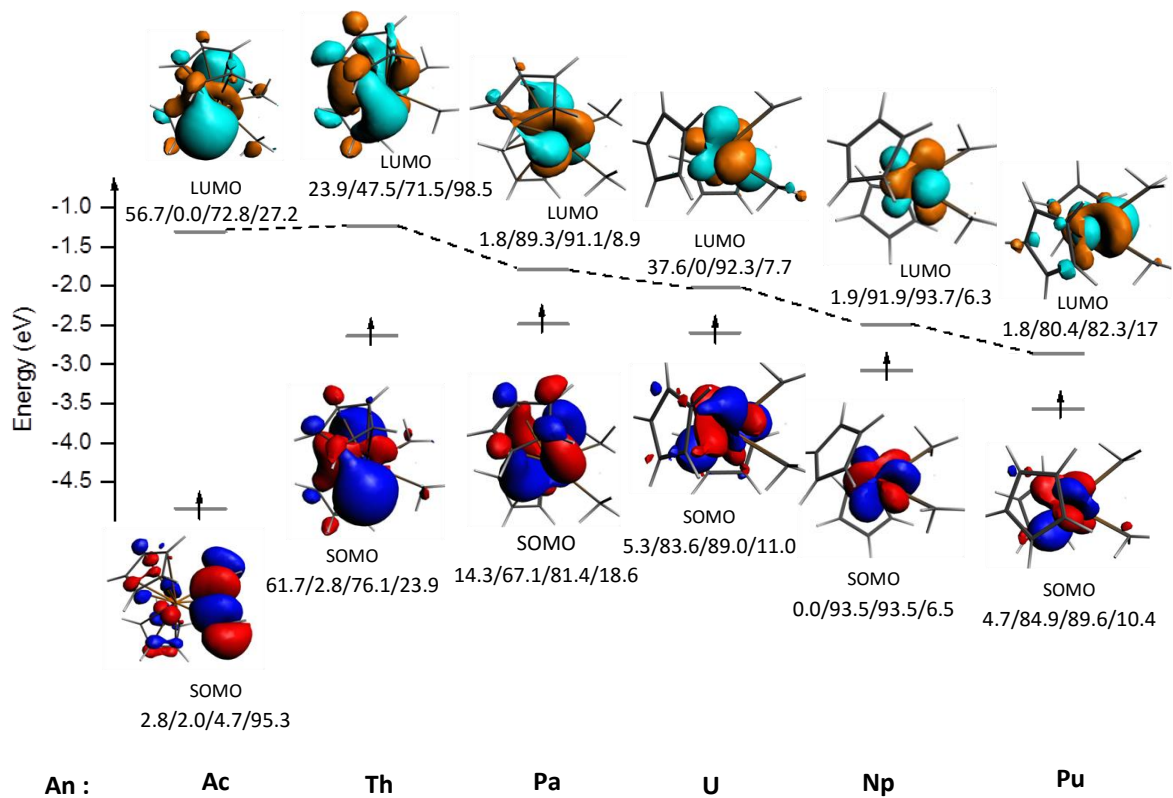
### Complex Cp\*<sub>2</sub>AnCH<sub>3</sub>



### Cl<sub>2</sub>AnCH<sub>3</sub>\_TS



### (Cp)<sub>2</sub>AnCH<sub>3</sub>\_TS



## SI. 8. Optimized coordinates of $L_2AnCH_3^+ + CH_4$ systems

### 1 - $Cl_2AnCH_3^+ + CH_4$

- $Cl_2ThCH_3^+ + CH_4$

#### Reactant: $Cl_2ThCH_4^+$

1.Th	1.574086	0.281801	0.000000
2.Cl	2.636140	1.393613	1.967857
3.Cl	2.636140	1.393613	-1.967857
4.C	-0.534222	1.296989	0.000000
5.H	-0.732870	1.916881	0.892010
6.H	-0.732870	1.916881	-0.892010
7.H	-1.285240	0.476375	0.000000

#### Transition state: $Cl_2ThCH_3^+ + CH_4$

1.Th	-0.363805	-0.097956	0.127963
2.Cl	0.784677	0.138066	-2.130506
3.Cl	0.746156	-0.233486	2.413681
4.C	-2.287289	-1.668047	-0.027528
5.H	-3.365420	-1.874684	-0.002552
6.H	-1.852202	-2.271329	0.801438
7.H	-1.922989	-2.082206	-0.993195
8.C	-2.465180	1.233690	0.217452
9.H	-3.560304	1.307269	0.248191
10.H	-2.513353	-0.223230	0.100522
11.H	-2.147027	1.850230	-0.651993
12.H	-2.108908	1.726975	1.149908

- $Cl_2PaCH_3^+ + CH_4$

#### Reactant: $Cl_2PaCH_4^+$

1.Pa	1.574833	0.275669	0.000000
2.Cl	2.616525	1.404812	1.904054
3.Cl	2.616525	1.404812	-1.904054
4.C	-0.456624	1.323969	0.000000
5.H	-0.659061	1.935788	0.895609
6.H	-0.659061	1.935788	-0.895609
7.H	-1.180988	0.475577	0.000000

#### Transition state: $Cl_2PaCH_3^+ + CH_4$

1.Pa	-0.357539	-0.091202	0.048413
2.Cl	0.487441	0.144393	-2.307205
3.Cl	0.703554	-0.204244	2.325093
4.C	-2.204655	-1.653212	0.017632
5.H	-3.270354	-1.914579	0.015537
6.H	-1.750404	-2.189778	0.882693
7.H	-1.780167	-2.073645	-0.924946
8.C	-2.372742	1.235843	0.242564
9.H	-3.461397	1.369460	0.274051
10.H	-2.454163	-0.216792	0.132998
11.H	-2.010512	1.841543	-0.621658
12.H	-1.973594	1.682052	1.182734

- $Cl_2UCh_3^+ + CH_4$

#### Reactant: $Cl_2UCh_4^+$

1.U	1.587524	0.263213	0.000000
2.Cl	2.557123	1.459044	1.893800

3.Cl	2.557123	1.459044	-1.893800
4.C	-0.380104	1.390190	0.000000
5.H	-0.502518	2.023488	0.895507
6.H	-0.502518	2.023488	-0.895507
7.H	-1.186385	0.626132	0.000000

**Transition state: Cl<sub>2</sub>UCh<sub>3</sub><sup>+</sup> + CH<sub>4</sub>**

1.U	-0.314143	-0.044888	0.038448
2.Cl	0.328660	0.051220	-2.366830
3.Cl	0.518303	-0.131899	2.385640
4.C	-2.193580	-1.485253	0.062393
5.H	-3.263600	-1.724244	0.088526
6.H	-1.729225	-1.980938	0.948681
7.H	-1.785112	-1.934847	-0.874827
8.C	-2.180596	1.406862	0.166851
9.H	-3.247674	1.652926	0.227133
10.H	-2.384891	-0.037547	0.111302
11.H	-1.780789	1.915343	-0.743088
12.H	-1.698883	1.836676	1.078462

• **Cl<sub>2</sub>NpCH<sub>3</sub><sup>+</sup> + CH<sub>4</sub>**

**Reactant: Cl<sub>2</sub>NpCH<sub>4</sub><sup>+</sup>**

1.Np	1.590900	0.251172	0.000000
2.Cl	2.542838	1.494854	1.858525
3.Cl	2.542838	1.494854	-1.858525
4.C	-0.371845	1.396752	0.000000
5.H	-0.476087	2.021063	0.902742
6.H	-0.476087	2.021063	-0.902742
7.H	-1.141000	0.596886	0.000000

**Transition state: Cl<sub>2</sub>NpCH<sub>3</sub><sup>+</sup> + CH<sub>4</sub>**

1.Np	-0.374646	0.074833	0.049516
2.Cl	0.572392	-0.282746	-2.206715
3.Cl	0.769600	-0.470606	2.173346
4.C	-2.047899	-1.606076	0.065219
5.H	-3.070583	-1.999965	0.053534
6.H	-1.534759	-2.003598	0.970046
7.H	-1.536257	-1.965999	-0.858387
8.C	-2.512271	1.219978	0.114632
9.H	-3.609174	1.240654	0.137148
10.H	-2.437053	-0.222784	0.101039
11.H	-2.189374	1.763098	-0.801723
12.H	-2.151915	1.748370	1.025459

• **Cl<sub>2</sub>PuCH<sub>3</sub><sup>+</sup> + CH<sub>4</sub>**

**Reactant: Cl<sub>2</sub>PuCH<sub>4</sub><sup>+</sup>**

1.Pu	1.658890	0.301707	0.000000
2.Cl	2.316223	1.355450	2.104464
3.Cl	2.316223	1.355450	-2.104464
4.C	-0.430276	1.378274	0.000000
5.H	-0.544752	1.966342	0.918909
6.H	-0.544752	1.966342	-0.918909
7.H	-1.060361	0.466700	0.000000

**Transition state: Cl<sub>2</sub>PuCH<sub>3</sub><sup>+</sup> + CH<sub>4</sub>**

1.Pu	-0.246501	-0.059289	0.035574
2.Cl	0.093217	0.088029	-2.416665

3.Cl	0.290214	-0.093237	2.457287
4.C	-2.261187	-1.435540	0.062167
5.H	-3.349795	-1.558548	0.096045
6.H	-1.831489	-1.927645	0.958420
7.H	-1.893965	-1.879779	-0.885301
8.C	-2.162224	1.413944	0.164609
9.H	-3.235206	1.632669	0.202042
10.H	-2.335167	-0.002660	0.103802
11.H	-1.743894	1.889108	-0.747055
12.H	-1.697898	1.793501	1.098273

## 2 - Cp<sub>2</sub>AnCH<sub>3</sub><sup>+</sup> + CH<sub>4</sub>

### • Cp<sub>2</sub>ThCH<sub>3</sub><sup>+</sup> + CH<sub>4</sub>

#### Reactant: Cp<sub>2</sub>ThCH<sub>3</sub><sup>+</sup>

1.Th	-0.282413	-0.534362	0.015861
2.H	-2.514436	-0.064292	-2.528956
3.H	-2.158995	-0.282644	2.872507
4.C	-2.427598	-1.631869	0.123261
5.C	-0.347503	-0.573663	-2.780117
6.H	-2.347486	-2.305723	1.002528
7.H	-2.465038	-2.280713	-0.776339
8.H	-1.594631	2.223281	-1.425939
9.H	1.853123	-0.154449	-2.663919
10.H	-3.405391	-1.134885	0.196403
11.H	1.105879	2.169426	-1.518263
12.H	-0.381673	-1.538497	-3.284175
13.C	1.081300	0.348312	2.282959
14.C	0.450482	1.495170	1.737397
15.C	-0.957704	1.340318	1.903871
16.C	-1.191053	0.106158	2.569830
17.C	0.067877	-0.515266	2.787381
18.H	0.952096	2.359670	1.309737
19.H	2.154867	0.172225	2.332225
20.H	0.234227	-1.463454	3.296938
21.H	-1.716247	2.070436	1.630111
22.C	0.830313	0.155879	-2.455120
23.C	0.439266	1.375062	-1.845290
24.C	-0.985634	1.399854	-1.792081
25.C	-1.470985	0.200994	-2.385363

#### Transition state: Cp<sub>2</sub>ThCH<sub>3</sub><sup>+</sup> + CH<sub>4</sub>

1.Th	-0.633290	-0.587592	-1.581306
2.H	-3.139055	-0.164107	-3.933827
3.H	-0.230590	0.756107	1.570217
4.C	-2.976414	-0.063349	-0.618305
5.C	-1.430204	-1.602018	-4.079460
6.H	-2.753499	0.281438	0.406106
7.H	-4.032746	-0.364325	-0.634340
8.H	-1.226970	1.742209	-4.032017
9.H	0.733120	-2.149570	-4.313029
10.H	-2.921425	0.820672	-1.293541
11.H	1.162553	0.514035	-4.286740
12.H	-1.929115	-2.567718	-4.110637
13.C	1.973838	-0.640868	-0.532507
14.C	1.839448	0.669020	-1.065040
15.C	0.896053	1.371045	-0.267575
16.C	0.455106	0.498344	0.765963
17.C	1.121075	-0.745935	0.601998

18.H	2.394132	1.077281	-1.906259
19.H	2.649091	-1.412533	-0.897872
20.H	1.037067	-1.608153	1.260002
21.H	0.600824	2.411148	-0.394348
22.C	-0.027754	-1.381662	-4.184504
23.C	0.200462	0.021485	-4.169953
24.C	-1.059379	0.666544	-4.037416
25.C	-2.066962	-0.337522	-3.987935
26.C	-1.810166	-2.713547	-0.742566
27.H	-1.250204	-3.235112	-1.550776
28.H	-2.747085	-3.275992	-0.634228
29.H	-1.249223	-2.848584	0.200946
30.H	-2.486250	-1.416685	-0.757570

• **Cp<sub>2</sub>PaCH<sub>3</sub><sup>+</sup> + CH<sub>4</sub>**

**Reactant: Cl<sub>2</sub>PaCH<sub>4</sub><sup>+</sup>**

1.Pa	-0.289012	-0.526057	-0.009779
2.H	-2.700870	0.093662	-2.269625
3.H	-2.450606	0.127419	2.486516
4.C	-2.321449	-1.686841	0.103145
5.C	-0.580870	-0.458330	-2.730112
6.H	-2.128385	-2.343196	0.981231
7.H	-2.263577	-2.324022	-0.806266
8.H	-1.627831	2.301150	-1.148898
9.H	1.635257	-0.124763	-2.754204
10.H	-3.356078	-1.330887	0.187354
11.H	1.063509	2.159723	-1.438121
12.H	-0.688561	-1.398597	-3.268659
13.C	0.895653	0.149843	2.338130
14.C	0.563003	1.360423	1.670360
15.C	-0.861939	1.470095	1.649619
16.C	-1.397885	0.326501	2.308435
17.C	-0.311804	-0.486846	2.727345
18.H	1.268242	2.100228	1.300109
19.H	1.903189	-0.216391	2.531728
20.H	-0.392463	-1.430286	3.265144
21.H	-1.432504	2.319825	1.287453
22.C	0.641990	0.210805	-2.457940
23.C	0.345165	1.404037	-1.745566
24.C	-1.073413	1.472586	-1.579106
25.C	-1.641361	0.320507	-2.194873

**Transition state: Cp<sub>2</sub>PaCH<sub>3</sub><sup>+</sup> + CH<sub>4</sub>**

1.Pa	-0.687420	-0.440944	-1.584674
2.H	-3.093304	-1.030522	-3.920272
3.H	0.122663	0.096730	1.661934
4.C	-2.917014	-0.227939	-0.506412
5.C	-1.023151	-1.881994	-3.879835
6.H	-2.473625	0.454458	0.251280
7.H	-3.854282	-0.605662	-0.080927
8.H	-1.846393	1.349515	-4.181107
9.H	1.211876	-1.771286	-4.018576
10.H	-3.197615	0.374832	-1.399761
11.H	0.815041	0.896989	-4.262849
12.H	-1.206625	-2.950973	-3.804780
13.C	1.967926	-0.658320	-1.037352
14.C	1.732281	0.736294	-1.213889
15.C	0.933238	1.183765	-0.124296
16.C	0.683010	0.074531	0.729056



17.C	1.319771	-1.061992	0.164644
18.H	2.142348	1.360402	-2.003257
19.H	2.591015	-1.287603	-1.667516
20.H	1.339875	-2.060010	0.596207
21.H	0.599171	2.206775	0.045241
22.C	0.254614	-1.258967	-3.973176
23.C	0.045509	0.146585	-4.103268
24.C	-1.359410	0.380394	-4.079636
25.C	-2.017349	-0.871982	-3.947773
26.C	-1.472026	-2.721078	-0.727517
27.H	-0.499236	-2.996546	-1.197774
28.H	-2.226139	-3.370765	-1.190663
29.H	-1.387956	-2.988549	0.335038
30.H	-2.261648	-1.535781	-0.617617

•  $\text{Cp}_2\text{UCH}_3^+ + \text{CH}_4$

**Reactant:  $\text{Cp}_2\text{UCH}_4^+$**

1.U	-0.706897	-0.219268	0.006885
2.H	-1.538901	-0.819018	-3.132882
3.H	-1.245713	-1.123638	3.233081
4.C	-2.050645	-2.046295	0.473891
5.C	0.513538	-0.968424	-2.232025
6.H	-1.281916	-2.832816	0.286118
7.H	-2.654848	-1.967835	-0.463894
8.H	-1.302859	1.827137	-2.627286
9.H	2.398106	-0.122478	-1.365574
10.H	-2.705995	-2.399262	1.278191
11.H	1.120081	2.248762	-1.519269
12.H	0.748343	-2.026293	-2.339980
13.C	1.414130	0.083936	1.584292
14.C	0.625408	1.251994	1.784234
15.C	-0.560191	0.869163	2.472330
16.C	-0.504774	-0.530884	2.705148
17.C	0.705072	-1.018373	2.143179
18.H	0.901284	2.266435	1.502784
19.H	2.407212	0.048627	1.146224
20.H	1.051466	-2.049859	2.177029
21.H	-1.353894	1.540535	2.797413
22.C	1.383020	0.033929	-1.719193
23.C	0.713993	1.284181	-1.816243
24.C	-0.564001	1.061678	-2.394561
25.C	-0.690064	-0.329776	-2.657676

**Transition state:  $\text{Cp}_2\text{UCH}_3^+ + \text{CH}_4$**

1.U	-0.679522	-0.471897	-1.587657
2.H	-3.067781	-1.088429	-3.843306
3.H	0.056332	-0.006052	1.630994
4.C	-2.832506	-0.051730	-0.495075
5.C	-0.970684	-1.870268	-3.918078
6.H	-2.292505	0.664040	0.162347
7.H	-3.768102	-0.317090	0.009700
8.H	-1.903288	1.345126	-4.081368
9.H	1.249850	-1.672622	-4.121952
10.H	-3.108626	0.468451	-1.439252
11.H	0.764919	0.974859	-4.272264
12.H	-1.113167	-2.947577	-3.873608
13.C	2.005911	-0.567219	-1.035051
14.C	1.691186	0.807821	-1.186100
15.C	0.831919	1.177585	-0.115741

16.C	0.627619	0.028762	0.705741
17.C	1.355515	-1.048148	0.133380
18.H	2.071220	1.469252	-1.960342
19.H	2.661243	-1.145790	-1.682708
20.H	1.429432	-2.055667	0.536654
21.H	0.442250	2.176881	0.073697
22.C	0.273831	-1.197593	-4.050189
23.C	0.020765	0.197060	-4.122206
24.C	-1.384251	0.389600	-4.019951
25.C	-1.999237	-0.891607	-3.897608
26.C	-1.606305	-2.640804	-0.657325
27.H	-0.671768	-2.966736	-1.174008
28.H	-2.416729	-3.251765	-1.075661
29.H	-1.487597	-2.893958	0.404958
30.H	-2.290023	-1.398426	-0.557379

•  $\text{Cp}_2\text{NpCH}_3^+ + \text{CH}_4$

**Reactant:  $\text{Cp}_2\text{NpCH}_3^+$**

1.Np	-0.663757	-0.331618	0.015643
2.H	-1.455089	-0.804040	-3.159092
3.H	-1.282768	-0.870817	3.223076
4.C	-2.579718	-1.649136	0.290011
5.C	0.619527	-0.754257	-2.307070
6.H	-2.381621	-2.602869	0.808355
7.H	-2.922357	-1.870233	-0.740612
8.H	-1.566304	1.785905	-2.395762
9.H	2.394595	0.248584	-1.381960
10.H	-3.383276	-1.110356	0.821716
11.H	0.817246	2.437693	-1.310360
12.H	0.987167	-1.759207	-2.510650
13.C	1.457393	0.196995	1.607611
14.C	0.658177	1.370166	1.651479
15.C	-0.562665	1.044441	2.305793
16.C	-0.510841	-0.325008	2.685363
17.C	0.730308	-0.852923	2.235289
18.H	0.946062	2.354359	1.292279
19.H	2.465639	0.123427	1.209303
20.H	1.082888	-1.872276	2.388062
21.H	-1.376417	1.735862	2.520879
22.C	1.359866	0.301603	-1.708859
23.C	0.529353	1.453916	-1.671025
24.C	-0.724400	1.110936	-2.246777
25.C	-0.664697	-0.250778	-2.654975

**Transition state:  $\text{Cp}_2\text{NpCH}_3^+ + \text{CH}_4$**

1.Np	-0.661353	-0.634666	-1.426660
2.H	-2.884377	-1.600727	-3.718523
3.H	0.255599	-0.388902	1.759948
4.C	-2.526790	0.939630	-0.778457
5.C	-0.659662	-1.890494	-3.790490
6.H	-2.554877	1.300312	0.259385
7.H	-3.520463	1.071862	-1.224549
8.H	-2.300787	1.027257	-3.860323
9.H	1.456476	-1.190113	-3.992951
10.H	-1.833192	1.603682	-1.344201
11.H	0.378793	1.283865	-4.022131
12.H	-0.554691	-2.974573	-3.780932
13.C	2.022212	-0.329533	-1.090193
14.C	1.497221	0.988613	-1.032234

15.C	0.705554	1.095694	0.142246
16.C	0.736226	-0.158095	0.811048
17.C	1.546804	-1.041138	0.043576
18.H	1.704369	1.791366	-1.735065
19.H	2.704285	-0.712944	-1.843766
20.H	1.793168	-2.070123	0.302162
21.H	0.196751	1.992128	0.488833
22.C	0.401261	-0.951345	-3.894965
23.C	-0.166683	0.350406	-3.910971
24.C	-1.578999	0.214843	-3.830631
25.C	-1.886510	-1.169413	-3.758469
26.C	-2.436588	-1.880939	-0.301299
27.H	-2.344730	-2.591595	-1.151497
28.H	-3.428296	-2.030249	0.140689
29.H	-1.683408	-2.138210	0.475394
30.H	-2.580419	-0.479545	-0.556912

•  $\text{Cp}_2\text{PuCH}_3^+ + \text{CH}_4$

**Reactant:  $\text{Cp}_2\text{PuCH}_4^+$**

1.Pu	-0.616967	-0.342875	0.018989
2.H	-1.660496	-0.688431	-3.123394
3.H	-1.429836	-0.772616	3.220073
4.C	-2.576818	-1.649636	0.175323
5.C	0.462293	-0.749263	-2.404628
6.H	-2.462659	-2.405483	0.968494
7.H	-2.650160	-2.139948	-0.812086
8.H	-1.628079	1.869002	-2.272637
9.H	2.326552	0.154744	-1.546913
10.H	-3.459345	-1.016433	0.358730
11.H	0.844477	2.396391	-1.312408
12.H	0.777835	-1.756810	-2.670560
13.C	1.411464	0.191537	1.723630
14.C	0.633101	1.378981	1.686260
15.C	-0.628045	1.096709	2.285668
16.C	-0.618198	-0.257630	2.710527
17.C	0.632010	-0.826800	2.339758
18.H	0.958643	2.344762	1.308850
19.H	2.433995	0.086859	1.368258
20.H	0.957093	-1.844450	2.550018
21.H	-1.438454	1.807809	2.438328
22.C	1.278780	0.258786	-1.819161
23.C	0.497409	1.438257	-1.690163
24.C	-0.803369	1.161581	-2.199647
25.C	-0.815863	-0.180714	-2.661533

**Transition state:  $\text{Cp}_2\text{PuCH}_3^+ + \text{CH}_4$**

1.Pu	-0.605013	-0.665543	-1.568337
2.H	-2.531614	0.903832	-3.866462
3.H	0.318557	-0.561294	1.650896
4.C	-2.791325	0.362136	-0.763484
5.C	-1.862922	-1.229662	-3.886784
6.H	-3.014465	0.667538	0.265931
7.H	-3.727668	0.205077	-1.312626
8.H	0.096836	1.476432	-4.108182
9.H	-0.337268	-2.868327	-4.047217
10.H	-2.243278	1.199626	-1.251596
11.H	1.450665	-0.851128	-4.221913
12.H	-2.801799	-1.776440	-3.826803
13.C	1.865537	0.363228	-1.175960

14.C	0.977712	1.446661	-0.948146
15.C	0.237404	1.170323	0.236490
16.C	0.671497	-0.082592	0.739717
17.C	1.665821	-0.592027	-0.141739
18.H	0.908314	2.351491	-1.547320
19.H	2.592076	0.292437	-1.981536
20.H	2.216167	-1.522969	-0.014188
21.H	-0.491047	1.828027	0.703359
22.C	-0.563228	-1.804794	-3.989827
23.C	0.376357	-0.742848	-4.091091
24.C	-0.335280	0.482524	-4.024962
25.C	-1.720939	0.180190	-3.901071
26.C	-1.950943	-2.324220	-0.350915
27.H	-1.910377	-2.919803	-1.286339
28.H	-2.798057	-2.680853	0.244687
29.H	-1.024873	-2.482535	0.240318
30.H	-2.405476	-0.994666	-0.510483

### SI. 9. Total bonding energy (eV) of $L_2AnCH_3^+ + CH_4$ systems

**Complex :  $L_2AnCH_3^+$  ( L : Cl, Cp )**

Complexe	Th	Pa	U	Np	Pu
$Cl_2AnCH_3$	-26.9217	-27.0744	-26.8095	-27.1810	-25.8492
$Cp_2AnCH_3$	-145.4949	-145.7724	-145.6526	-146.1996	-145.1075

**Transition state :  $L_2AnCH_3^+ + CH_4$  ( L : Cl, Cp)**

Complexe	Th	Pa	U	Np	Pu
$Cl_2AnCH_3^+ + CH_4$	-50.2540	-50.5483	-50.6026	-50.8063	-49.5118
$Cp_2AnCH_3^+ + CH_4$	-168.6201	-168.9871	-168.9677	-169.5321	-168.4163