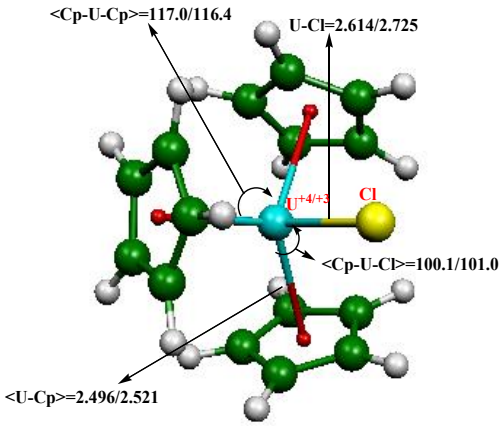
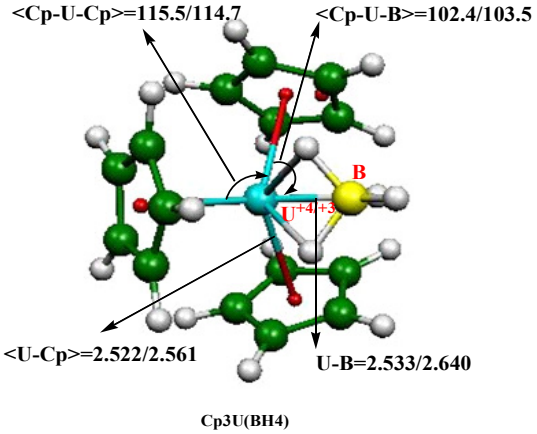
SUPPLEMENTARY MATERIAL

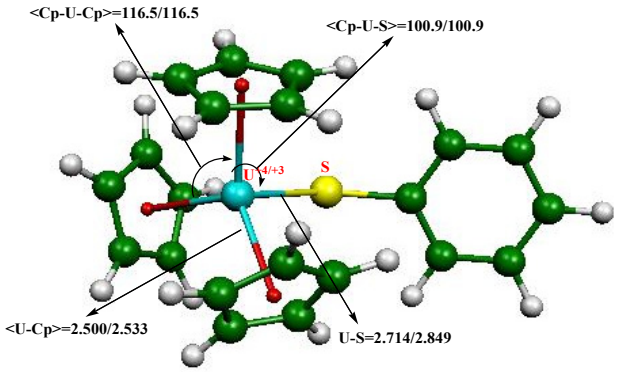
Suppl. S1: optimized geometries of Cp_3UX complexes at the ZORA/BP86/TZP level (in gas phase)



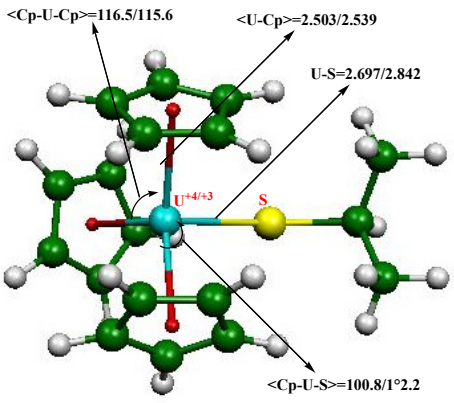
Cp3UCl



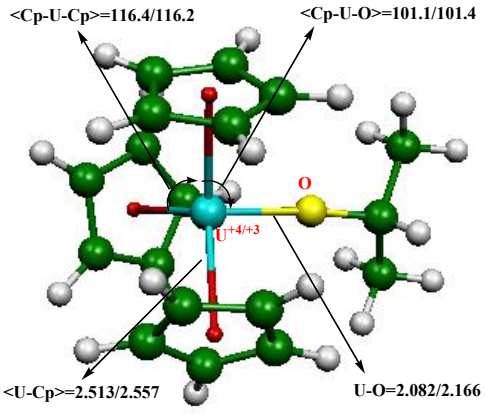
Cp3U(BH4)



$Cp_3U(SPh)$



$Cp_3U(S\,^{i}Pr)$



$Cp_3U(O^{i}Pr)$

Suppl. S2: optimized coordinates (ZORA/BP86/TZP)

Optimized coordinates of Cp_3UCl_U(IV)

Atom	X	Y	Z (Angstrom)
1.U	.000000	.000000	.560166
2.C	2.268820	.708582	-.845657
3.C	2.268820	-.708582	-.845657
4.C	2.524593	-1.145529	.487745
5.C	2.696955	.000000	1.301014
6.C	2.524593	1.145529	.487745
7.H	2.149703	1.346840	-1.715848
8.H	2.149703	-1.346840	-1.715848
9.H	2.611429	-2.175332	.819988
10.H	2.892161	.000000	2.368804
11.H	2.611429	2.175332	.819988
12.C	-.520760	-2.319147	-.845657
13.C	-1.748060	-1.610565	-.845657
14.C	-2.254354	-1.613597	.487745
15.C	-1.348477	-2.335632	1.301014
16.C	-.270239	-2.759126	.487745
17.H	.091546	-2.535118	-1.715848
18.H	-2.241250	-1.188277	-1.715848
19.H	-3.189607	-1.173898	.819988
20.H	-1.446080	-2.504685	2.368804
21.H	.578178	-3.349230	.819988
22.C	-1.748060	1.610565	-.845657
23.C	-.520760	2.319147	-.845657
24.C	-.270239	2.759126	.487745
25.C	-1.348477	2.335632	1.301014
26.C	-2.254354	1.613597	.487745
27.H	-2.241250	1.188277	-1.715848
28.H	.091546	2.535118	-1.715848
29.H	.578178	3.349230	.819988
30.H	-1.446080	2.504685	2.368804
31.H	-3.189607	1.173898	.819988
32.Cl	.000000	.000000	3.175060

Optimized coordinates of Cp_3UCl_U(III)

Atom	X	Y	Z (Angstrom)
1.U	.000000	.000000	.572264
2.C	2.302849	.709870	-.883850
3.C	2.302849	-.709870	-.883850
4.C	2.554469	-1.150301	.447905
5.C	2.711962	.000000	1.266414
6.C	2.554469	1.150301	.447905
7.H	2.158803	1.346532	-1.752967
8.H	2.158803	-1.346532	-1.752967
9.H	2.626724	-2.182476	.778352
10.H	2.881418	.000000	2.339126
11.H	2.626724	2.182476	.778352
12.C	-.536660	-2.349261	-.883850
13.C	-1.766190	-1.639391	-.883850
14.C	-2.273425	-1.637084	.447905

15.C	-1.355981	-2.348628	1.266414
16.C	-.281044	-2.787385	.447905
17.H	.086729	-2.542844	-1.752967
18.H	-2.245532	-1.196312	-1.752967
19.H	-3.203442	-1.183571	.778352
20.H	-1.440709	-2.495381	2.339126
21.H	.576718	-3.366048	.778352
22.C	-1.766190	1.639391	-.883850
23.C	-.536660	2.349261	-.883850
24.C	-.281044	2.787385	.447905
25.C	-1.355981	2.348628	1.266414
26.C	-2.273425	1.637084	.447905
27.H	-2.245532	1.196312	-1.752967
28.H	.086729	2.542844	-1.752967
29.H	.576718	3.366048	.778352
30.H	-1.440709	2.495381	2.339126
31.H	-3.203442	1.183571	.778352
32.Cl	.000000	.000000	3.305177

Optimized coordinates of $Cp_3U(SPh)\_U(IV)$

Atom	X	Y	Z (Angstrom)
1.U	-.085036	6.443641	11.800857
2.S	-.891633	3.897270	11.322508
3.C	-1.875062	6.900422	9.716864
4.C	-1.267678	8.156872	9.981750
5.H	-1.758817	9.037170	10.385435
6.C	.093107	8.076760	9.589648
7.H	.812944	8.889052	9.627265
8.C	.319138	6.772049	9.061232
9.H	1.249972	6.404563	8.641533
10.C	-.896237	6.053616	9.136205
11.H	-1.055214	5.029683	8.813542
12.C	-1.151971	8.292750	13.597680
13.C	-2.270074	7.723364	12.925604
14.H	-2.945127	8.243860	12.254843
15.C	-2.379502	6.368793	13.328795
16.H	-3.131756	5.660734	12.995656
17.C	-1.339848	6.102318	14.263286
18.H	-1.159168	5.149549	14.756068
19.C	-.601431	7.296592	14.442758
20.H	.239440	7.432789	15.114864
21.C	2.273565	5.174472	12.461646
22.C	2.120108	6.182101	13.444478
23.H	1.946895	6.012023	14.502419
24.C	2.284879	7.447640	12.809073
25.H	2.250111	8.419595	13.295276
26.C	2.553776	7.212732	11.438229
27.H	2.763506	7.969874	10.689656
28.C	2.530358	5.808579	11.216873
29.H	2.710963	5.301181	10.273950
30.H	2.211432	4.104084	12.632130
31.H	-.811486	9.323292	13.519934
32.H	-2.907609	6.628957	9.918143
33.C	-1.057751	2.761578	12.699457
34.C	-2.327041	2.533852	13.262074
35.C	-2.508318	1.553101	14.239680
36.C	-1.427926	.778562	14.675139
37.C	-.161770	1.000241	14.123666
38.C	.024087	1.980983	13.145071

39.H	-3.177706	3.115307	12.906664
40.H	-3.504517	1.383882	14.652080
41.H	-1.574128	.001430	15.426501
42.H	.687423	.394902	14.445469
43.H	1.007868	2.123988	12.697182

Optimized coordinates of $Cp_3U(SPh)\_U(III)$

Atom	X	Y	Z (Angstrom)
1.U	-.088782	6.460246	11.798956
2.S	-.838290	3.756502	11.301628
3.C	-1.915919	6.932930	9.749975
4.C	-1.261061	8.182529	9.936042
5.H	-1.709102	9.092957	10.323805
6.C	.084017	8.045207	9.499312
7.H	.833755	8.832456	9.499587
8.C	.259803	6.711970	9.030576
9.H	1.173380	6.294697	8.616347
10.C	-.974647	6.027537	9.184861
11.H	-1.170891	4.993969	8.913859
12.C	-.936202	8.172377	13.867528
13.C	-2.074305	8.057610	13.022637
14.H	-2.508773	8.855194	12.427056
15.C	-2.556977	6.725491	13.106449
16.H	-3.408482	6.315297	12.568870
17.C	-1.726530	6.015282	14.018621
18.H	-1.833812	4.970618	14.301021
19.C	-.733191	6.909321	14.495417
20.H	.027426	6.679517	15.234831
21.C	2.343493	5.247119	12.461385
22.C	2.196848	6.265487	13.439606
23.H	2.037238	6.108601	14.501689
24.C	2.339389	7.525147	12.789557
25.H	2.290351	8.501773	13.266883
26.C	2.589380	7.279149	11.413329
27.H	2.762498	8.034063	10.651223
28.C	2.583263	5.873030	11.206128
29.H	2.742754	5.360848	10.261033
30.H	2.277265	4.176898	12.637003
31.H	-.352965	9.075385	14.037048
32.H	-2.951718	6.707053	9.989373
33.C	-1.022280	2.662502	12.692732
34.C	-2.288345	2.483639	13.293881
35.C	-2.487196	1.543772	14.306941
36.C	-1.425064	.750809	14.761609
37.C	-.158670	.927735	14.188903
38.C	.041132	1.867632	13.174085
39.H	-3.120458	3.090936	12.934573
40.H	-3.484140	1.424587	14.740562
41.H	-1.582738	.007045	15.545520
42.H	.682954	.317790	14.530257
43.H	1.027529	1.985824	12.722437

Optimized coordinates of $Cp_3U(BH_4)\_U(IV)$

Atom	x	y	z (Angstrom)
1.U	0.01435661	-1.16308973	0.01336609
2.C	2.76170113	-0.68350659	0.01128448
3.C	2.53360788	-1.48444982	1.15819840
4.C	2.19186782	-2.79368657	0.71651684

5.C	2.19039241	-2.79235060	-0.69647751
6.C	2.53180061	-1.48245483	-1.13669238
7.H	2.64777270	-1.16292006	-2.16764231
8.H	3.05334126	0.36213149	0.01187350
9.H	2.65056282	-1.16638789	2.18947610
10.H	2.00938875	-3.65573257	1.35013116
11.H	2.00747911	-3.65370087	-1.33103681
12.C	-1.33060387	-0.51882193	2.37594540
13.C	-2.24789470	-1.30308570	1.63336967
13.C	-1.76067975	-2.64059297	1.60840751
14.C	-0.53912880	-2.67405462	2.31846655
15.C	-0.26342026	-1.35767065	2.78397216
16.H	0.58523344	-1.05628777	3.39008580
17.H	-1.42381792	0.54188780	2.58733853
18.H	-3.18243141	-0.95325089	1.20610362
19.H	-2.26134806	-3.49552629	1.16502207
20.H	0.05722461	-3.55937012	2.51469267
21.C	-1.35647886	-0.52096718	-2.33607571
22.C	-0.27911802	-1.34246940	-2.75359617
23.C	-0.53730467	-2.66622535	-2.29907688
24.C	-1.75706184	-2.65442461	-1.58543905
25.C	-2.26164945	-1.32322545	-1.59824693
26.H	-3.20047386	-0.98978648	-1.16717216
27.H	-1.46434887	0.54003334	-2.53884298
28.H	0.56432432	-1.02485047	-3.35878144
29.H	0.06940992	-3.54229104	-2.50450204
30.H	-2.24524821	-3.51942596	-1.14737002
31.H	0.67305007	0.84271187	0.99648549
32.B	0.10655703	1.36151951	0.01313719
33.H	-1.05557422	0.90692245	0.02351543
34.H	0.65200311	0.85538389	-0.98789762
35.H	0.14305760	2.56303008	0.02270639

Optimized coordinates of $Cp_3U(BH_4)$_U(III)

Atom	x	y	z (Angstrom)
1.U	0.00394889	0.13352495	-0.00177890
2.C	2.79851559	0.60801432	-0.00459915
3.C	2.57640472	-0.19410096	1.14587640
4.C	2.22826103	-1.50271043	0.70607031
5.C	2.22620720	-1.50302000	-0.71257497
6.C	2.57332544	-0.19462996	-1.15409276
7.H	2.66594027	0.13031864	-2.18680024
8.H	3.05716950	1.66281357	-0.00519161
9.H	2.67370026	0.13100705	2.17809542
10.H	2.02500657	-2.35969918	1.34211322
11.H	2.02134441	-2.36053589	-1.34741213
12.C	-1.36089764	0.77237834	2.39828128
13.C	-2.28633839	-0.01255511	1.66094257
14.C	-1.79915711	-1.35019830	1.63038312
15.C	-0.57157220	-1.38609640	2.34106538
16.C	-0.29606930	-0.07110008	2.81193030
17.H	0.56626286	0.23304978	3.39892756
18.H	-1.43687897	1.83982363	2.58390582
19.H	-3.21098584	0.34391594	1.21548538
20.H	-2.29259438	-2.20130548	1.16945742
21.H	0.03542617	-2.26964396	2.51763376
22.C	-1.38645990	0.77051715	-2.38508299
23.C	-0.31143511	-0.05442411	-2.81063292
24.C	-0.56666438	-1.37713295	-2.35001111

25.C	-1.79083034	-1.36436088	-1.63303329
26.C	-2.29702977	-0.03351457	-1.65010389
27.H	-3.22501639	0.30532189	-1.19785545
28.H	-1.47858071	1.83821790	-2.56172944
29.H	0.54450763	0.26690137	-3.39779680
30.H	0.05202151	-2.25044514	-2.53601058
31.H	-2.27000495	-2.22646575	-1.17700344
32.H	0.67311741	2.28072626	0.99405170
33.B	0.10898674	2.77079284	0.00181888
34.H	-1.06184002	2.35235066	0.01229355
35.H	0.65756403	2.28850842	-1.00330871
36.4)H	0.15464517	3.98375644	0.00668630

Optimized Coordinates of $Cp_3U(S^iPr)\_U(IV)$

Atom	X	Y	Z (Angstrom)
1.U	-.014109	-.016487	.587313
2.C	2.324772	.691568	-.711077
3.C	2.303039	-.725324	-.742588
4.C	2.498073	-1.196306	.589318
5.C	2.650869	-.069848	1.433583
6.C	2.527472	1.095520	.638773
7.H	2.245570	1.350699	-1.570289
8.H	2.211414	-1.341026	-1.632234
9.H	2.559908	-2.236750	.895745
10.H	2.822703	-.086743	2.503166
11.H	2.610108	2.115613	1.000800
12.C	-.446632	-2.333727	-.852401
13.C	-1.650997	-1.600648	-.994820
14.C	-2.301474	-1.576869	.271290
15.C	-1.508156	-2.306340	1.188182
16.C	-.352688	-2.761913	.505018
17.H	.249899	-2.573730	-1.649614
18.H	-2.032440	-1.174865	-1.918401
19.H	-3.252097	-1.102687	.496071
20.H	-1.743496	-2.472932	2.232823
21.H	.440834	-3.370913	.929249
22.C	-1.744314	1.589733	-.840534
23.C	-.497152	2.262491	-.905193
24.C	-.206480	2.768127	.394932
25.C	-1.270961	2.411514	1.254310
26.C	-2.215357	1.670662	.501753
27.H	-2.268035	1.137507	-1.676629
28.H	.102133	2.410544	-1.798797
29.H	.664754	3.351678	.676201
30.H	-1.340339	2.637431	2.313388
31.H	-3.148332	1.267076	.884261
32.S	-.327767	.226589	3.255274
33.C	.190591	-.902776	4.658793
34.H	-.104791	-.312415	5.538640
35.C	-.590163	-2.216068	4.680645
36.H	-1.671733	-2.040129	4.613117
37.H	-.389543	-2.757135	5.620602
38.H	-.289373	-2.867110	3.848063
39.C	1.697426	-1.139297	4.723732
40.H	2.252528	-.192125	4.732392
41.H	1.951572	-1.691575	5.643772
42.H	2.039210	-1.736869	3.867347

Optimized coordinates of $Cp_3U(S^iPr)\_U(III)$

Atom	X	Y	Z (Angstrom)
1.U	-.015715	-.018929	.607101
2.C	2.357186	.657777	-.783890
3.C	2.336646	-.761426	-.783362
4.C	2.532457	-1.206046	.555478
5.C	2.678970	-.054902	1.378415
6.C	2.565038	1.095910	.553349
7.H	2.252188	1.295841	-1.658323
8.H	2.215500	-1.394793	-1.658516
9.H	2.587962	-2.241139	.882970
10.H	2.842626	-.045732	2.450517
11.H	2.644055	2.125837	.888831
12.C	-.467838	-2.362304	-.921165
13.C	-1.667138	-1.613904	-1.051141
14.C	-2.312188	-1.589934	.217326
15.C	-1.511938	-2.329827	1.128787
16.C	-.365781	-2.802924	.429084
17.H	.235925	-2.576522	-1.721358
18.H	-2.036486	-1.160231	-1.968311
19.H	-3.257870	-1.108923	.449152
20.H	-1.740600	-2.492621	2.176779
21.H	.431464	-3.415705	.842572
22.C	-1.731585	1.621057	-.887102
23.C	-.479264	2.292664	-.912992
24.C	-.208883	2.768223	.401676
25.C	-1.292442	2.386625	1.237688
26.C	-2.232884	1.675198	.443822
27.H	-2.225832	1.164783	-1.740246
28.H	.145714	2.438142	-1.790376
29.H	.662386	3.338020	.712531
30.H	-1.380406	2.588452	2.302078
31.H	-3.172725	1.259363	.796663
32.S	-.372835	.313673	3.406429
33.C	.196728	-.903740	4.706659
34.H	-.060990	-.396799	5.650719
35.C	-.564906	-2.230644	4.663244
36.H	-1.650045	-2.059907	4.641850
37.H	-.325114	-2.851640	5.546945
38.H	-.293618	-2.802337	3.764486
39.C	1.707306	-1.142363	4.698007
40.H	2.255614	-.191718	4.743847
41.H	2.012694	-1.763989	5.560457
42.H	2.009867	-1.663136	3.778279

Optimized coordinates of $Cp_3U(O^iPr)\_U(IV)$

Atom	X	Y	Z (Angstrom)
1.U	.012669	.018403	.646978
2.C	2.260662	.310108	-1.043563
3.C	2.312658	-1.009562	-.528162
4.C	2.555883	-.925403	.873677
5.C	2.692371	.451820	1.208438
6.C	2.535419	1.206338	.024394
7.H	2.093294	.582564	-2.083427
8.H	2.200799	-1.924504	-1.101487
9.H	2.656617	-1.757565	1.565319
10.H	2.902183	.853228	2.195503
11.H	2.668425	2.281284	-.078201

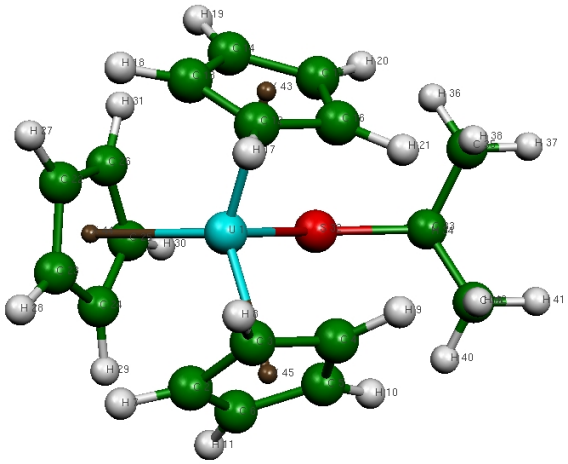
12.C	-.653810	-2.252989	-.826535
13.C	-1.867726	-1.543576	-.655362
14.C	-2.221714	-1.607512	.725628
15.C	-1.238322	-2.382588	1.391269
16.C	-.262291	-2.766124	.444716
17.H	-.134171	-2.408850	-1.768195
18.H	-2.450166	-1.076295	-1.443528
19.H	-3.113004	-1.186645	1.180956
20.H	-1.218430	-2.609612	2.453437
21.H	.626363	-3.355509	.652059
22.C	-1.602439	1.708570	-.860835
23.C	-.369897	2.391268	-.711710
24.C	-.241494	2.770361	.658520
25.C	-1.410034	2.346823	1.339027
26.C	-2.242335	1.676874	.414326
27.H	-2.014063	1.328202	-1.791599
28.H	.333422	2.620640	-1.506507
29.H	.586649	3.317875	1.100028
30.H	-1.613037	2.486733	2.396661
31.H	-3.211902	1.237759	.630776
32.O	.024952	.078950	2.727580
33.C	-.032529	.272443	4.135385
34.H	.278109	1.315514	4.338785
35.C	-1.468605	.085488	4.631086
36.H	-2.151295	.760809	4.099522
37.H	-1.540512	.294925	5.708545
38.H	-1.801452	-.947372	4.454787
39.C	.949124	-.675166	4.828514
40.H	1.967572	-.525307	4.447354
41.H	.955392	-.504923	5.915493
42.H	.661770	-1.720629	4.642177

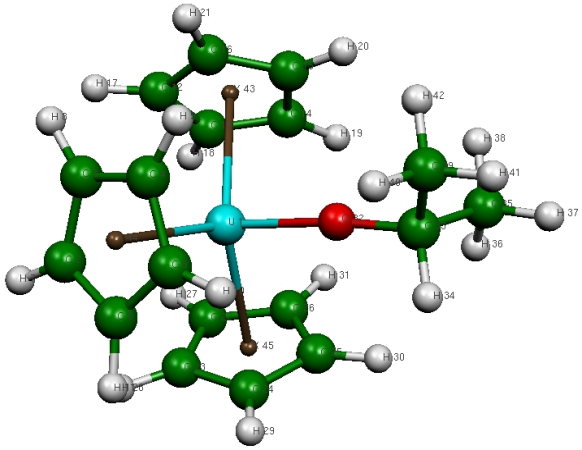
Optimized coordinates of $Cp_3U(O^iPr)$_U(III)

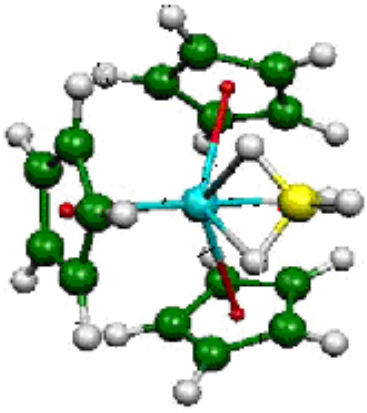
Atom	X	Y	Z (Angstrom)
1.U	.007731	.015310	.645106
2.C	2.296049	.231484	-1.050417
3.C	2.375121	-1.065929	-.476015
4.C	2.636318	-.922222	.914065
5.C	2.741101	.470503	1.194963
6.C	2.523305	1.181721	-.011268
7.H	2.136462	.454511	-2.103750
8.H	2.259979	-2.006001	-1.008291
9.H	2.743404	-1.728001	1.636818
10.H	2.915618	.914209	2.172790
11.H	2.522268	2.262711	-.120002
12.C	-.622386	-2.283174	-.886809
13.C	-1.850487	-1.578680	-.790707
14.C	-2.286963	-1.636147	.566064
15.C	-1.329794	-2.387642	1.299033
16.C	-.296607	-2.781423	.410273
17.H	-.040284	-2.426531	-1.794462
18.H	-2.374431	-1.094203	-1.610610
19.H	-3.199424	-1.201578	.966121
20.H	-1.360642	-2.590001	2.366638
21.H	.584501	-3.362794	.671309
22.C	-1.674574	1.752087	-.819494
23.C	-.432033	2.433046	-.728112
24.C	-.239443	2.816746	.632373
25.C	-1.368977	2.377867	1.372371

26.C	-2.253625	1.713106	.483557
27.H	-2.115143	1.348724	-1.727855
28.H	.250309	2.630180	-1.551420
29.H	.614284	3.356725	1.034890
30.H	-1.516031	2.507739	2.442074
31.H	-3.209961	1.268607	.745759
32.O	.017219	.014103	2.811076
33.C	-.012452	.301755	4.174516
34.H	.268719	1.367646	4.336564
35.C	-1.432096	.110408	4.734640
36.H	-2.140314	.732107	4.170153
37.H	-1.490169	.384530	5.801681
38.H	-1.740687	-.940398	4.620946
39.C	1.011254	-.566167	4.925957
40.H	2.012779	-.413744	4.501472
41.H	1.040674	-.324078	6.001794
42.H	.752558	-1.630181	4.809256

Suppl. S3: numbering of atoms of Suppl. S2

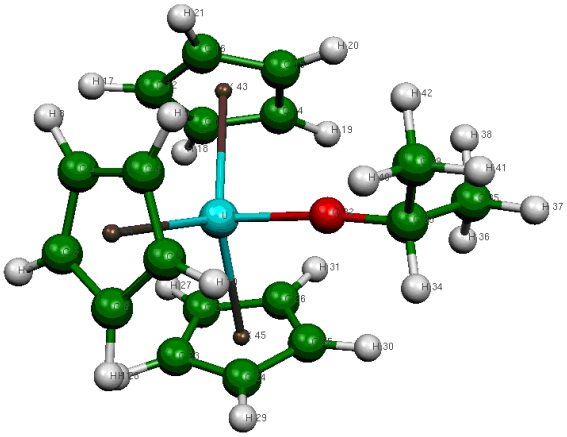




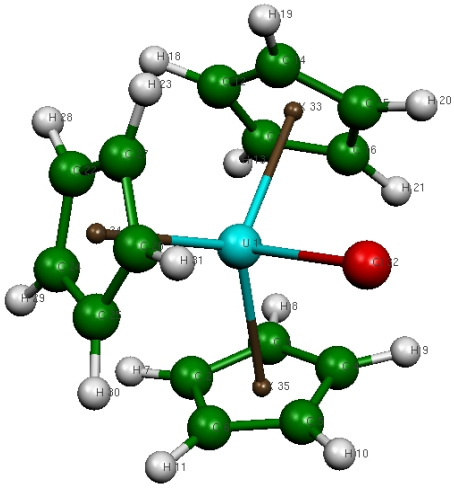


$Cp_3U(OiPr)$

Cp_3UBH_4



$Cp_3U(SPh)$



Cp_3UCl

Suppl. S4: Frontier MO diagrams of the U(IV) complexes (percentages 6d/5f/U/X between brackets)