

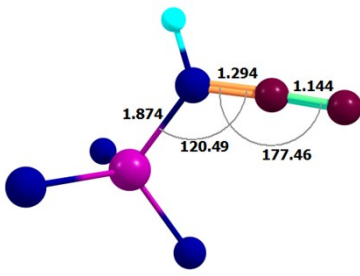
Supporting Information for

A Thorium Metallacyclopentadiene Complex: A Combined Experimental and Computational Study

Bo Fang, Guohua Hou, Guofu Zi,* De-Cai Fang,* and Marc D. Walter*

Table S1. The optimized Cartesian Coordinates (in Å) and structures (the hydrogen atoms omitted for clarity) of stationary points for **2**+Me₃SiCHN₂, obtained with B3PW91-PCM+D3 method.

Species	Cartesian coordinates				
2	C	-1.33992	2.49129	0.92437	
	C	0.00000	2.85439	1.24166	
	C	0.24755	2.47784	2.59294	
	C	-0.93988	1.87975	3.10299	
	C	-1.92356	1.89793	2.07449	
	C	-2.01418	2.85918	-0.36085	
	H	-2.14023	3.94881	-0.43271	
	H	-3.00160	2.40144	-0.44240	
	H	-1.42715	2.53477	-1.22734	
	C	0.85509	3.68492	0.32778	
	H	0.33377	4.61672	0.07063	
	H	1.07741	3.16153	-0.60883	
	H	1.80934	3.96052	0.78478	
	C	1.50949	2.69343	3.38259	
	H	2.17422	3.40649	2.88556	
	H	2.09390	1.77205	3.53740	
	H	1.28594	3.09245	4.37862	
	C	-1.15944	1.39445	4.50716	
	H	-0.21374	1.23467	5.03377	
	H	-1.71682	0.44873	4.53983	
	H	-1.74338	2.11957	5.09062	
	C	-3.35039	1.46741	2.24758	
	H	-3.91367	2.22064	2.81582	
	H	-3.43425	0.52347	2.79993	
	H	-3.85374	1.31711	1.28970	
	C	3.32889	1.38969	0.49156	
	H	2.61275	1.92533	1.10622	
	C	4.68737	1.52261	0.76493	
	H	5.01176	2.15679	1.58716	
	C	5.62233	0.82933	-0.00123	
	H	6.68480	0.91495	0.21236	
	C	5.17319	0.01746	-1.04698	
	H	5.89055	-0.53358	-1.65151	
	C	3.81608	-0.09502	-1.33012	
	H	3.49343	-0.72997	-2.14791	
	C	2.84596	0.58755	-0.56189	
	C	1.39483	0.39539	-0.69488	
	C	0.72419	0.18438	-1.87283	
	C	1.41311	0.28812	-3.19334	
	C	1.46788	-0.80207	-4.07327	
	H	0.95695	-1.72402	-3.80819	
	C	2.16431	-0.71216	-5.27574	
H	2.20080	-1.57006	-5.94324		
C	2.80801	0.47549	-5.62674		
H	3.34730	0.54757	-6.56820		
C	2.75173	1.57034	-4.76393		
H	3.24842	2.50069	-5.02981		
C	2.06295	1.47414	-3.55736		
H	2.03100	2.31963	-2.87455		
Th	0.00000	0.00000	1.30686		
C	-3.32889	-1.38969	0.49156		
H	-2.61275	-1.92533	1.10622		

	C -4.68737 -1.52261 0.76493 H -5.01176 -2.15679 1.58716 C -5.62233 -0.82933 -0.00123 H -6.68480 -0.91495 0.21236 C -5.17319 -0.01746 -1.04698 H -5.89055 0.53358 -1.65151 C -3.81608 0.09502 -1.33012 H -3.49343 0.72997 -2.14791 C -2.84596 -0.58755 -0.56189 C -1.39483 -0.39539 -0.69488 C -0.72419 -0.18438 -1.87283 C -1.41311 -0.28812 -3.19334 C -1.46788 0.80207 -4.07327 H -0.95695 1.72402 -3.80819 C -2.16431 0.71216 -5.27574 H -2.20080 1.57006 -5.94324 C -2.80801 -0.47549 -5.62674 H -3.34730 -0.54757 -6.56820 C -2.75173 -1.57034 -4.76393 H -3.24842 -2.50069 -5.02981 C -2.06295 -1.47414 -3.55736 H -2.03100 -2.31963 -2.87455 C 1.33992 -2.49129 0.92437 C 0.00000 -2.85439 1.24166 C -0.24755 -2.47784 2.59294 C 0.93988 -1.87975 3.10299 C 1.92356 -1.89793 2.07449 C 2.01418 -2.85918 -0.36085 H 2.14023 -3.94881 -0.43271 H 3.00160 -2.40144 -0.44240 H 1.42715 -2.53477 -1.22734 C -0.85509 -3.68492 0.32778 H -0.33377 -4.61672 0.07063 H -1.07741 -3.16153 -0.60883 H -1.80934 -3.96052 0.78478 C -1.50949 -2.69343 3.38259 H -2.17422 -3.40649 2.88556 H -2.09390 -1.77205 3.53740 H -1.28594 -3.09245 4.37862 C 1.15944 -1.39445 4.50716 H 0.21374 -1.23467 5.03377 H 1.71682 -0.44873 4.53983 H 1.74338 -2.11957 5.09062 C 3.35039 -1.46741 2.24758 H 3.91367 -2.22064 2.81582 H 3.43425 -0.52347 2.79993 H 3.85374 -1.31711 1.28970	
Me ₃ SiCHN ₂	C 4.44157 1.47888 -0.26779 H 4.12656 2.43605 -0.67754 C 6.15206 -0.87627 0.53259 H 5.47436 -1.57112 0.02294 H 5.82492 -0.78938 1.57529 H 7.15239 -1.32502 0.53263 C 7.34776 1.98881 0.57603 H 8.38347 1.62982 0.52811 H 7.07019 2.08869 1.63141 H 7.32024 2.98773 0.12451 C 6.74064 0.63191 -2.11638	

	H 6.10253 -0.07404 -2.65981	
	H 7.77472 0.26930 -2.17155	
	H 6.69726 1.59549 -2.63799	
	N 2.68385 0.16133 0.78908	
	N 3.49062 0.79879 0.28754	
	Si 6.18811 0.80255 -0.32120	
COM3	C 1.77062 -2.41787 -1.81407	
	C 1.08315 -1.41845 -2.56106	
	C -0.29194 -1.77537 -2.61395	
	C -0.45217 -3.01416 -1.93019	
	C 0.81792 -3.39560 -1.41619	
	C 3.25738 -2.53845 -1.64318	
	H 3.53800 -2.82369 -0.62236	
	H 3.76542 -1.59828 -1.87833	
	H 3.66755 -3.30695 -2.31268	
	C 1.71347 -0.29891 -3.33342	
	H 2.15291 -0.67554 -4.26800	
	H 2.50846 0.20624 -2.77689	
	H 0.96944 0.45527 -3.60601	
	C -1.35552 -1.00855 -3.34518	
	H -2.35077 -1.38670 -3.10142	
	H -1.22123 -1.07803 -4.43351	
	H -1.34205 0.05429 -3.07403	
	C -1.65446 -3.91071 -1.97934	
	H -2.58094 -3.36061 -2.15401	
	H -1.78955 -4.47714 -1.05362	
	H -1.53377 -4.63918 -2.79397	
	C 1.12995 -4.69746 -0.73984	
	H 1.33732 -5.48531 -1.47813	
	H 0.29710 -5.04758 -0.12179	
	H 2.01329 -4.62148 -0.09710	
	C 1.52757 -1.88410 2.41776	
	C 1.33998 -0.48515 2.61701	
	C -0.04267 -0.25937 2.83123	
	C -0.70653 -1.51548 2.81901	
	C 0.26015 -2.52536 2.56053	
	C 2.85376 -2.56496 2.23922	
	H 3.34217 -2.75871 3.20447	
	H 3.54481 -1.95599 1.64732	
	H 2.75418 -3.52985 1.73146	
	C 2.42010 0.54354 2.77500	
	H 2.22107 1.45755 2.20672	
	H 3.39455 0.16343 2.45453	
	H 2.51746 0.83159 3.83066	
	C -0.71564 1.02524 3.20075	
	H -1.60714 1.19124 2.58663	
	H -0.05390 1.88327 3.06743	
	H -1.03682 1.00923 4.25239	
	C -2.11197 -1.69124 3.31385	
	H -2.18199 -1.34736 4.35556	
	H -2.43112 -2.73697 3.29639	
	H -2.83243 -1.10983 2.72875	
	C 0.02218 -4.00815 2.65775	
	H 0.84941 -4.58118 2.22993	
	H -0.89295 -4.31991 2.13904	
	H -0.08072 -4.31621 3.70693	
	C -2.26465 -0.50143 -0.09588	
	C -2.51596 0.84506 -0.10322	

C	-1.40679	1.84675	-0.15786
C	-0.08362	1.50120	-0.27465
C	-3.33251	-1.50122	-0.27753
C	-3.32713	-2.70878	0.44642
H	-2.53433	-2.87725	1.16748
C	-4.28498	-3.69847	0.24575
H	-4.24663	-4.61095	0.83732
C	-5.26717	-3.53608	-0.72979
H	-6.00910	-4.31178	-0.90254
C	-5.27187	-2.36681	-1.49445
H	-6.02049	-2.22871	-2.27192
C	-4.33137	-1.36724	-1.26755
H	-4.35911	-0.46312	-1.86696
C	-3.91281	1.38243	-0.08155
C	-4.77192	1.05061	0.97324
H	-4.39783	0.41492	1.77165
C	-6.08520	1.51408	1.00320
H	-6.73401	1.24530	1.83387
C	-6.56683	2.31768	-0.02985
H	-7.59174	2.68067	-0.00981
C	-5.72241	2.65461	-1.08900
H	-6.08805	3.28076	-1.89980
C	-4.40862	2.19534	-1.11097
H	-3.75285	2.46843	-1.93320
C	-1.80139	3.29094	-0.06214
C	-2.40820	3.79215	1.09664
H	-2.62995	3.11424	1.91586
C	-2.74655	5.13872	1.20254
H	-3.21588	5.50632	2.11242
C	-2.49167	6.01158	0.14458
H	-2.75927	7.06260	0.22451
C	-1.89527	5.52391	-1.01811
H	-1.69471	6.19400	-1.85116
C	-1.55259	4.17770	-1.11724
H	-1.08115	3.80086	-2.02054
C	0.91611	2.58617	-0.34027
C	1.24291	3.37888	0.77503
H	0.69954	3.22356	1.70143
C	2.20139	4.38724	0.69814
H	2.42158	4.98461	1.58039
C	2.85852	4.64949	-0.50568
H	3.59724	5.44459	-0.57046
C	2.54254	3.87943	-1.62792
H	3.03723	4.07197	-2.57767
C	1.59887	2.85922	-1.53994
H	1.35854	2.26959	-2.41807
C	4.48558	1.49044	-0.07543
H	4.26694	2.55681	-0.01058
C	6.16768	-0.93413	0.66864
H	5.47465	-1.61014	0.15527
H	5.85289	-0.85229	1.71504
H	7.15883	-1.40278	0.64859
C	7.33950	1.95858	0.73553
H	8.38152	1.61959	0.69711
H	7.05127	2.05418	1.78833
H	7.29463	2.95457	0.27956
C	6.72376	0.56486	-1.97074
H	6.04159	-0.11025	-2.50111

	H 7.73663 0.15088 -2.05090	
	H 6.71023 1.53087 -2.48808	
	N 2.52339 0.07293 -0.20285	
	N 3.44393 0.75668 -0.14589	
	Si 6.21579 0.75139 -0.16640	
	Th 0.19273 -1.04265 0.08439	
TS3	C 1.81302 -2.72533 -1.57121	
	C 1.13591 -1.81027 -2.41920	
	C -0.23608 -2.17862 -2.46498	
	C -0.40700 -3.34335 -1.66933	
	C 0.85656 -3.67374 -1.09908	
	C 3.29068 -2.72515 -1.30954	
	H 3.57313 -3.48403 -0.57478	
	H 3.63906 -1.75213 -0.93939	
	H 3.85424 -2.93286 -2.22896	
	C 1.75847 -0.75213 -3.27912	
	H 1.87018 -1.11724 -4.31035	
	H 2.74740 -0.46284 -2.91659	
	H 1.14581 0.15526 -3.31250	
	C -1.25026 -1.51703 -3.35032	
	H -2.22929 -1.99050 -3.25916	
	H -0.94105 -1.57591 -4.40278	
	H -1.37873 -0.45505 -3.10541	
	C -1.62412 -4.21973 -1.61794	
	H -2.53073 -3.68281 -1.90402	
	H -1.80173 -4.62645 -0.61704	
	H -1.50234 -5.07307 -2.30006	
	C 1.15255 -4.95377 -0.37426	
	H 1.38478 -5.75770 -1.08784	
	H 0.29735 -5.29154 0.21991	
	H 2.01160 -4.86513 0.29746	
	C 1.64572 -2.06014 2.48028	
	C 1.60285 -0.64227 2.59120	
	C 0.27017 -0.26978 2.90602	
	C -0.51480 -1.44903 2.98760	
	C 0.33238 -2.56364 2.72503	
	C 2.90549 -2.85982 2.32041	
	H 3.46038 -2.90380 3.26769	
	H 3.58214 -2.42137 1.57846	
	H 2.70405 -3.89044 2.01717	
	C 2.78347 0.27910 2.53530	
	H 2.51623 1.26291 2.13906	
	H 3.57800 -0.11360 1.89488	
	H 3.21529 0.42574 3.53558	
	C -0.21044 1.09603 3.29566	
	H -0.72686 1.61289 2.48310	
	H 0.62693 1.72614 3.61115	
	H -0.90745 1.03176 4.13996	
	C -1.91752 -1.47444 3.52311	
	H -1.92676 -1.14563 4.57223	
	H -2.34947 -2.47919 3.50270	
	H -2.58595 -0.80797 2.96643	
	C -0.04241 -4.00501 2.92989	
	H 0.63243 -4.68171 2.40106	
	H -1.05999 -4.22140 2.58289	
	H 0.00014 -4.26912 3.99520	
	C -2.08579 -0.42647 -0.13834	
	C -2.28840 0.92057 -0.23508	

C	-1.21264	1.94726	-0.09959
C	0.14336	1.79764	-0.11189
C	-3.18272	-1.39221	-0.35174
C	-3.35681	-2.46279	0.54248
H	-2.68789	-2.54668	1.39316
C	-4.35757	-3.41636	0.36747
H	-4.46471	-4.22236	1.09026
C	-5.20148	-3.34915	-0.73882
H	-5.97669	-4.09639	-0.88886
C	-5.03080	-2.31112	-1.65914
H	-5.67686	-2.24693	-2.53210
C	-4.04804	-1.34650	-1.46522
H	-3.94331	-0.53729	-2.18004
C	-3.65815	1.47501	-0.48947
C	-4.70750	1.21549	0.39946
H	-4.50675	0.62448	1.28951
C	-5.99139	1.69143	0.14710
H	-6.79315	1.48112	0.85131
C	-6.24962	2.43190	-1.00653
H	-7.25207	2.80297	-1.20610
C	-5.21213	2.69555	-1.90178
H	-5.40337	3.27279	-2.80358
C	-3.92764	2.22515	-1.64111
H	-3.11821	2.43810	-2.33533
C	-1.73308	3.33366	0.19643
C	-2.40373	3.56560	1.40423
H	-2.56988	2.73665	2.08715
C	-2.88401	4.83236	1.72634
H	-3.40155	4.98847	2.67014
C	-2.70889	5.89341	0.83835
H	-3.08355	6.88357	1.08645
C	-2.05776	5.67112	-0.37488
H	-1.92484	6.48809	-1.08037
C	-1.57741	4.40293	-0.69230
H	-1.07520	4.23649	-1.63987
C	1.01677	2.97830	-0.06695
C	1.41207	3.59183	1.12971
H	1.01274	3.22621	2.06849
C	2.29459	4.66918	1.11908
H	2.59426	5.12799	2.05856
C	2.79053	5.16317	-0.08906
H	3.48414	6.00022	-0.09452
C	2.37532	4.58459	-1.29089
H	2.74570	4.96950	-2.23810
C	1.50520	3.50002	-1.27773
H	1.20471	3.02492	-2.20842
C	3.78860	1.56516	-0.45468
H	3.60208	2.58469	-0.11077
C	6.13013	-0.25932	0.46176
H	5.49833	-1.15522	0.43927
H	6.09799	0.14905	1.47839
H	7.16068	-0.57452	0.25538
C	6.59491	2.58174	-0.68214
H	7.65392	2.37385	-0.87422
H	6.51459	3.02723	0.31671
H	6.25932	3.33128	-1.40865
C	5.67620	0.27010	-2.53577
H	5.09910	-0.65811	-2.61108

	H 6.71879 0.03496 -2.78397 H 5.29469 0.96516 -3.29265 N 1.61823 0.43573 -0.57641 N 2.80222 0.75438 -0.60851 Si 5.55106 1.01656 -0.80686 Th 0.24666 -1.22948 0.19484	
3	C 3.24001 -1.25255 -1.89393 C 2.34543 -0.29843 -2.45920 C 1.12147 -0.96354 -2.75537 C 1.26926 -2.33078 -2.40495 C 2.55648 -2.49794 -1.82392 C 4.70673 -1.07584 -1.60933 H 4.96728 -1.24459 -0.55612 H 5.04983 -0.07320 -1.87300 H 5.29500 -1.79155 -2.19786 C 2.65889 1.11008 -2.86636 H 2.82533 1.17263 -3.95079 H 3.55775 1.48528 -2.37309 H 1.84458 1.79845 -2.61942 C -0.07911 -0.33581 -3.40094 H -0.99299 -0.88363 -3.15124 H 0.01398 -0.30566 -4.49594 H -0.22331 0.69211 -3.05090 C 0.38058 -3.45453 -2.83507 H -0.62520 -3.11081 -3.07799 H 0.28185 -4.23502 -2.07708 H 0.80006 -3.92207 -3.73765 C 3.13991 -3.80263 -1.36433 H 3.56369 -4.37542 -2.20187 H 2.38023 -4.44073 -0.89594 H 3.94607 -3.65231 -0.63731 C 2.75615 -1.45789 2.38138 C 2.31357 -0.12159 2.57914 C 0.90788 -0.14933 2.78224 C 0.48629 -1.50598 2.77916 C 1.63100 -2.31740 2.52034 C 4.17764 -1.92361 2.24877 H 4.59312 -2.22086 3.22221 H 4.82877 -1.14033 1.84589 H 4.26181 -2.79442 1.58771 C 3.18501 1.07008 2.81783 H 2.75054 1.98035 2.39752 H 4.18440 0.94504 2.39547 H 3.30684 1.23607 3.89739 C 0.03120 1.03303 3.07326 H -0.96853 0.90403 2.64474 H 0.44657 1.95223 2.64663 H -0.08532 1.19262 4.15477 C -0.88603 -1.94181 3.20068 H -1.01035 -1.81243 4.28474 H -1.09167 -2.98944 2.96657 H -1.65336 -1.34118 2.70329 C 1.73179 -3.81780 2.56715 H 2.09179 -4.25258 1.62425 H 0.76882 -4.28381 2.79640 H 2.43744 -4.13069 3.34779 C -1.34323 -1.24494 -0.11177 C -2.39873 -0.36470 -0.00673	

C	-2.29783	1.10596	0.01065
C	-1.13009	1.82540	-0.11954
C	-1.59447	-2.68116	-0.34542
C	-0.80143	-3.63903	0.31676
H	-0.08485	-3.30039	1.05660
C	-0.94637	-5.01106	0.11209
H	-0.31932	-5.70542	0.66730
C	-1.89115	-5.48022	-0.79686
H	-2.01835	-6.54681	-0.96334
C	-2.66466	-4.55298	-1.50344
H	-3.39370	-4.90117	-2.23209
C	-2.51544	-3.18841	-1.29159
H	-3.12192	-2.49357	-1.86192
C	-3.80980	-0.88648	0.03820
C	-4.22579	-1.71556	1.08555
H	-3.51718	-1.97098	1.86768
C	-5.51997	-2.23095	1.12511
H	-5.81985	-2.87158	1.95151
C	-6.42503	-1.93086	0.10827
H	-7.43527	-2.33233	0.13616
C	-6.02201	-1.11175	-0.94776
H	-6.71702	-0.87395	-1.74996
C	-4.73078	-0.59370	-0.97802
H	-4.42407	0.04552	-1.80133
C	-3.56031	1.89181	0.15771
C	-4.26379	1.84709	1.36863
H	-3.88898	1.21724	2.17170
C	-5.43245	2.58314	1.54403
H	-5.96367	2.53483	2.49183
C	-5.92116	3.37898	0.50709
H	-6.83443	3.95361	0.64204
C	-5.23170	3.42999	-0.70413
H	-5.60480	4.04582	-1.51926
C	-4.06299	2.69201	-0.87540
H	-3.52375	2.73583	-1.81789
C	-1.13780	3.29532	-0.35793
C	-1.55851	4.20841	0.61586
H	-1.94378	3.83403	1.55967
C	-1.47878	5.57807	0.37692
H	-1.80312	6.27815	1.14300
C	-0.98285	6.05273	-0.83895
H	-0.91675	7.12246	-1.02127
C	-0.57939	5.14803	-1.82213
H	-0.19938	5.50935	-2.77468
C	-0.65883	3.77847	-1.58314
H	-0.32844	3.06943	-2.33825
C	1.71504	2.84691	0.21210
H	0.95842	3.61093	0.38855
C	3.76781	4.64576	1.55343
H	3.82347	4.09065	2.49626
H	2.96372	5.38612	1.64380
H	4.71063	5.19240	1.42818
C	3.48018	4.56942	-1.48689
H	4.42327	5.12202	-1.58135
H	2.65952	5.29617	-1.45862
H	3.35050	3.95659	-2.38540
C	4.75820	2.13510	-0.00942
H	5.44487	2.18373	0.84234

H	5.35591	2.20496	-0.92491
H	4.27299	1.15392	0.00304
N	0.06720	1.14769	-0.14310
N	1.32138	1.63306	-0.03913
Si	3.46483	3.50750	0.07731
Th	1.16514	-0.87283	0.05751

Table S2. Frequencies of the stationary points optimized for **2**+Me₃SiCHN₂, obtained with B3PW91-PCM+D3 method.

Species	Frequencies (cm ⁻¹)
2	22 24 36 40 46 48 50 56 57 65 67 73 81 82 90 94 97 107 112 114 120 121 133 138 148 148 160 163 171 172 173 180 185 186 190 195 199 203 207 211 215 217 228 236 252 271 279 282 283 292 298 300 300 305 307 314 318 357 378 386 400 402 412 412 414 429 429 459 500 501 534 540 552 553 554 555 556 567 568 604 604 607 624 627 627 629 632 634 634 639 639 644 701 710 716 716 720 720 747 771 782 790 802 817 822 823 833 833 856 856 862 862 873 924 924 926 927 966 967 969 975 976 978 979 986 986 992 992 995 996 1014 1014 1016 1017 1048 1049 1054 1058 1058 1060 1060 1063 1065 1066 1068 1068 1073 1073 1089 1092 1093 1096 1097 1116 1116 1119 1124 1127 1128 1193 1193 1194 1194 1196 1196 1197 1198 1200 1217 1217 1223 1224 1239 1286 1292 1337 1338 1340 1345 1372 1373 1375 1376 1424 1424 1425 1425 1434 1437 1439 1441 1442 1446 1451 1453 1460 1462 1475 1475 1482 1483 1487 1488 1488 1490 1492 1492 1494 1501 1504 1504 1506 1508 1509 1511 1511 1517 1518 1519 1526 1529 1529 1532 1534 1534 1537 1539 1543 1544 1546 1561 1562 1586 1628 1628 1643 1643 1660 1660 1668 1669 3008 3008 3033 3033 3037 3037 3038 3038 3044 3044 3084 3084 3091 3091 3094 3094 3106 3106 3109 3109 3135 3138 3140 3141 3147 3147 3161 3161 3170 3170 3182 3182 3183 3183 3190 3190 3190 3191 3201 3201 3208 3208 3210 3210 3215 3215 3231 3231 3236 3236
Me ₃ SiCHN ₂	29 109 140 153 164 165 187 215 224 274 440 497 578 613 693 695 700 714 779 797 877 883 892 1201 1311 1314 1323 1339 1475 1478 1479 1487 1489 1496 2227 3047 3048 3052 3129 3131 3138 3139 3140 3140 3194
COM3	11 25 28 30 33 37 43 43 52 57 58 63 64 72 74 76 83 86 89 99 101 105 111 114 114 122 127 128 138 141 144 147 152 158 161 163 166 168 170 171 179 179 180 186 193 198 200 204 214 219 225 228 228 235 240 245 249 254 258 264 275 280 285 288 292 294 299 304 306 309 316 322 325 365 379 384 392 397 412 415 417 423 435 465 484 488 498 515 534 542 552 552 555 557 559 562 564 566 606 612 612 614 620 627 630 631 631 633 635 637 640 643 684 697 701 703 711 712 713 715 718 719 738 770 777 782 787 798 800 813 825 827 831 834 852 854 855 859 864 881 883 888 912 920 921 923 962 963 964 968 972 974 978 982 986 987 988 988 989 1015 1017 1017 1018 1047 1048 1054 1054 1054 1057 1058 1061 1064 1064 1065 1067 1067 1071 1089 1094 1097 1099 1100 1108 1116 1117 1122 1129 1132 1191 1193 1195 1195 1196 1197 1198 1199 1201 1210 1213 1217 1219 1223 1236 1274 1289 1313 1314 1323 1326 1336 1340 1344 1369 1370 1373 1375 1376 1420 1422 1423 1424 1429 1431 1433 1434 1438 1442 1453 1454 1460 1461 1474 1476 1476 1477 1479 1483 1485 1486 1487 1487 1487 1491 1491 1492 1496 1497 1499 1502 1504 1506 1510 1512 1513 1514 1515 1516 1521 1525 1527 1528 1530 1532 1534 1536 1537 1539 1546 1550 1553 1554 1559 1578 1627 1629 1643 1645 1658 1664 1669 1670 2234 3034 3035 3036 3037 3037 3037 3038 3039 3040 3043 3048 3053 3055 3096 3096 3097 3102 3107 3107 3111 3112 3112 3121 3132 3137 3137 3139 3139 3140 3141 3144 3145 3146 3148 3149 3150 3160 3161 3168 3175 3179 3181 3181 3181 3187 3189 3190 3190 3202 3204 3208 3208 3209 3213 3215 3217 3226 3226 3230 3234
TS3	-242 13 21 30 38 43 47 48 49 54 58 61 66 68 74 77 82 86 94 96 99 104 104 112 114 117 126 130

	<p>132 135 139 145 145 156 159 164 165 167 174 176 177 182 188 192 193 199 202 206 208 212 215 222 227 234 235 245 255 263 268 277 282 284 289 293 295 298 305 306 312 315 318 327 331 371 379 382 386 403 410 414 418 423 431 458 483 485 507 538 541 549 549 555 558 562 563 564 581 595 600 610 612 615 625 627 630 631 632 635 636 642 647 680 690 694 701 706 709 713 714 717 718 740 755 771 779 786 789 796 802 811 825 825 831 836 853 856 858 859 866 876 877 891 921 922 925 925 960 965 968 972 972 974 978 986 987 989 989 991 991 1016 1017 1017 1018 1048 1049 1051 1053 1058 1059 1060 1061 1062 1064 1065 1067 1074 1074 1083 1095 1096 1097 1101 1114 1116 1117 1121 1128 1132 1164 1194 1195 1196 1196 1196 1197 1198 1199 1205 1214 1216 1220 1223 1242 1267 1281 1308 1311 1319 1333 1338 1342 1343 1369 1372 1372 1375 1379 1422 1423 1424 1426 1430 1433 1435 1436 1440 1444 1455 1455 1460 1461 1475 1476 1478 1479 1480 1485 1486 1488 1488 1489 1489 1490 1492 1493 1495 1496 1499 1503 1504 1505 1510 1513 1514 1517 1519 1520 1523 1524 1528 1529 1531 1533 1536 1537 1539 1540 1550 1552 1557 1559 1562 1589 1632 1634 1645 1646 1663 1666 1669 1670 1803 3034 3034 3035 3037 3038 3038 3039 3041 3043 3047 3050 3051 3058 3092 3093 3100 3100 3104 3105 3108 3111 3121 3126 3129 3132 3134 3137 3137 3138 3142 3143 3144 3147 3153 3154 3157 3158 3164 3168 3172 3181 3181 3183 3185 3188 3190 3192 3192 3198 3203 3204 3205 3209 3213 3214 3215 3224 3225 3230 3248</p>
3	<p>19 28 31 37 46 52 53 55 56 68 69 74 79 80 84 86 90 91 97 104 108 108 111 117 121 132 135 137 143 144 147 154 157 158 163 169 171 174 177 180 184 189 189 194 198 207 208 217 218 221 226 232 234 251 256 260 268 275 279 283 286 292 295 300 301 302 303 311 314 319 329 367 376 381 384 390 398 401 411 415 418 423 431 481 497 528 535 547 551 554 557 560 564 566 566 579 608 614 617 619 626 627 629 632 633 634 639 640 653 667 690 695 713 715 716 718 718 720 724 742 756 770 772 785 791 797 810 827 829 833 834 846 857 858 859 861 866 870 882 888 914 916 925 928 935 950 967 968 971 974 977 980 987 989 990 991 991 997 1015 1017 1019 1019 1048 1049 1049 1057 1059 1060 1061 1061 1063 1065 1066 1068 1069 1070 1075 1096 1097 1100 1101 1105 1114 1115 1116 1124 1131 1134 1193 1196 1196 1197 1198 1199 1199 1200 1201 1216 1217 1219 1224 1233 1285 1308 1309 1310 1318 1337 1337 1341 1344 1364 1371 1375 1379 1379 1382 1423 1425 1425 1427 1430 1432 1436 1438 1439 1443 1455 1456 1460 1460 1475 1478 1479 1479 1481 1484 1485 1487 1488 1489 1490 1492 1493 1494 1495 1497 1501 1501 1504 1505 1507 1509 1512 1514 1516 1517 1520 1522 1526 1529 1530 1531 1535 1537 1538 1543 1545 1547 1550 1558 1559 1574 1597 1628 1644 1646 1648 1659 1670 1671 1673 3027 3030 3031 3032 3033 3035 3040 3041 3042 3043 3047 3048 3059 3084 3087 3092 3093 3101 3106 3116 3116 3119 3121 3124 3127 3130 3133 3135 3137 3138 3139 3141 3143 3152 3155 3159 3162 3168 3169 3183 3183 3184 3184 3188 3190 3191 3191 3197 3199 3203 3205 3206 3209 3210 3213 3213 3220 3222 3227 3231</p>

Table S3. The energies, enthalpies and free energies (in au at 298 K) and corresponding relative values (in kcal/mol) for **2**+Me₃SiCHN₂, obtained with B3PW91-PCM+D3 method

species	E	H	G (gas)	G (sol)
2	-1894.67895	-1893.79112	-1893.92362	-1893.91355
Me ₃ SiCHN ₂	-557.28607	-557.13860	-557.18644	-557.17631
2 +Me ₃ SiCHN ₂	-2451.96502(0.0)	-2450.92972(0.0)	-2451.11006(0.0)	-2451.08986(0.0)
COM3	-2451.98585(-13.1)	-2450.94805(-11.5)	-2451.10651(2.2)	-2451.09662(-4.2)
TS3	-2451.95400(6.9)	-2450.91741(7.7)	-2451.07265(23.5)	-2451.06283(17.0)
3	-2452.04723(-51.6)	-2451.00721(-48.6)	-2451.15952(-31.0)	-2451.14954(-37.4)

Table S4. The optimized Cartesian Coordinates (in Å) and structures (the hydrogen atoms omitted for clarity) of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}(\eta^2\text{-C}_4\text{Ph}_4)$, obtained with B3PW91-PCM+D3 method.

Species	Cartesian coordinates				
$\text{Cp}^*_2\text{U}(\text{C}_4\text{Ph}_4)$	C	0.00000	-2.79241	1.07504	
	C	-1.35878	-2.46531	1.36391	
	C	-1.40951	-1.93926	2.68729	
	C	-0.08428	-1.94811	3.21661	
	C	0.78350	-2.48113	2.22018	
	C	0.43745	-3.56704	-0.13176	
	H	0.13642	-4.62146	-0.03997	
	H	1.52221	-3.54537	-0.25827	
	H	-0.01081	-3.18088	-1.05347	
	C	-2.50795	-2.89035	0.49219	
	H	-2.48395	-3.97964	0.34838	
	H	-2.47949	-2.43153	-0.50239	
	H	-3.47796	-2.64944	0.93597	
	C	-2.64096	-1.56849	3.46704	
	H	-3.55343	-1.73193	2.88608	
	H	-2.64904	-0.51945	3.79144	
	H	-2.72558	-2.17822	4.37612	
	C	0.29106	-1.71079	4.65115	
	H	-0.45742	-1.11169	5.17633	
	H	1.25772	-1.20492	4.76079	
	H	0.37589	-2.66652	5.18899	
	C	2.23069	-2.82332	2.43024	
	H	2.32692	-3.79584	2.93495	
	H	2.74440	-2.08996	3.06279	
	H	2.78254	-2.88350	1.48877	
	C	-3.70124	0.34988	0.33156	
	H	-3.35522	-0.45645	0.97014	
	C	-5.00321	0.82368	0.47693	
	H	-5.65826	0.37742	1.22211	
	C	-5.46019	1.87197	-0.32008	
	H	-6.47241	2.25213	-0.20694	
	C	-4.59325	2.43167	-1.26078	
	H	-4.92890	3.25687	-1.88525	
C	-3.30004	1.94085	-1.41729		
H	-2.65198	2.39140	-2.16114		
C	-2.81316	0.87505	-0.62787		
C	-1.42488	0.37335	-0.68757		
C	-0.72307	0.19520	-1.85981		
C	-1.38230	0.38198	-3.19590		
C	-0.96887	1.38403	-4.08650		
H	-0.13067	2.02273	-3.82068		
C	-1.61912	1.57349	-5.30391		
H	-1.28506	2.36086	-5.97564		
C	-2.68976	0.75416	-5.66390		
H	-3.19345	0.89729	-6.61676		
C	-3.10681	-0.25083	-4.79171		
H	-3.93955	-0.89648	-5.06108		
C	-2.46197	-0.42970	-3.56909		
H	-2.79950	-1.20658	-2.88764		
U	0.00000	0.00000	1.22501		
C	3.70124	-0.34988	0.33156		
H	3.35522	0.45645	0.97014		

C	5.00321	-0.82368	0.47693
H	5.65826	-0.37742	1.22211
C	5.46019	-1.87197	-0.32008
H	6.47241	-2.25213	-0.20694
C	4.59325	-2.43167	-1.26078
H	4.92890	-3.25687	-1.88525
C	3.30004	-1.94085	-1.41729
H	2.65198	-2.39140	-2.16114
C	2.81316	-0.87505	-0.62787
C	1.42488	-0.37335	-0.68757
C	0.72307	-0.19520	-1.85981
C	1.38230	-0.38198	-3.19590
C	0.96887	-1.38403	-4.08650
H	0.13067	-2.02273	-3.82068
C	1.61912	-1.57349	-5.30391
H	1.28506	-2.36086	-5.97564
C	2.68976	-0.75416	-5.66390
H	3.19345	-0.89729	-6.61676
C	3.10681	0.25083	-4.79171
H	3.93955	0.89648	-5.06108
C	2.46197	0.42970	-3.56909
H	2.79950	1.20658	-2.88764
C	0.00000	2.79241	1.07504
C	1.35878	2.46531	1.36391
C	1.40951	1.93926	2.68729
C	0.08428	1.94811	3.21661
C	-0.78350	2.48113	2.22018
C	-0.43745	3.56704	-0.13176
H	-0.13642	4.62146	-0.03997
H	-1.52221	3.54537	-0.25827
H	0.01081	3.18088	-1.05347
C	2.50795	2.89035	0.49219
H	2.48395	3.97964	0.34838
H	2.47949	2.43153	-0.50239
H	3.47796	2.64944	0.93597
C	2.64096	1.56849	3.46704
H	3.55343	1.73193	2.88608
H	2.64904	0.51945	3.79144
H	2.72558	2.17822	4.37612
C	-0.29106	1.71079	4.65115
H	0.45742	1.11169	5.17633
H	-1.25772	1.20492	4.76079
H	-0.37589	2.66652	5.18899
C	-2.23069	2.82332	2.43024
H	-2.32692	3.79584	2.93495
H	-2.74440	2.08996	3.06279
H	-2.78254	2.88350	1.48877