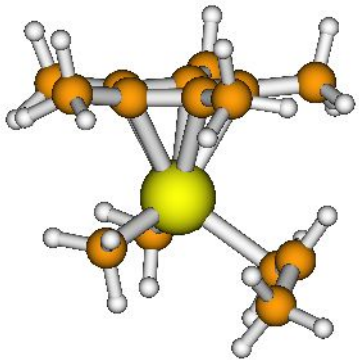
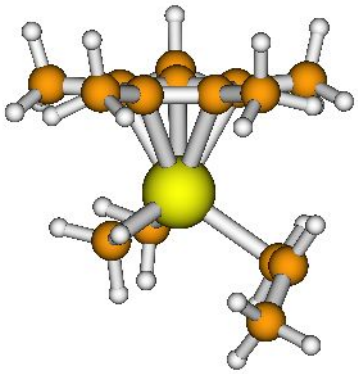
Supplementary Information
Cartesian Coordinates for **1**



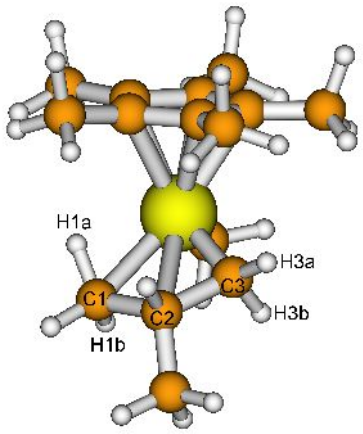
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.405316	-1.235460	-0.644911
2	6	0	-1.289859	-1.190166	0.775832
3	6	0	0.104173	-1.232050	1.101169
4	6	0	0.843250	-1.323657	-0.120391
5	6	0	-0.085042	-1.317120	-1.202683
6	22	0	-0.285021	0.776759	-0.115345
7	6	0	2.222865	1.829850	1.076104
8	6	0	3.141713	2.506866	0.116271
9	6	0	-2.419799	-1.220634	1.766095
10	6	0	0.659513	-1.315889	2.498909
11	6	0	2.330358	-1.499719	-0.267889
12	6	0	0.242387	-1.577728	-2.644938
13	6	0	-2.678943	-1.294988	-1.439167
14	6	0	0.194222	1.521774	-1.979007
15	6	0	-2.082093	1.708301	0.286573
16	6	0	0.963684	2.228972	1.380457
17	1	0	1.151110	1.189261	-2.396557
18	1	0	-0.592668	1.333001	-2.719850
19	1	0	0.238108	2.611946	-1.809180
20	1	0	-2.934042	1.380102	-0.317846
21	1	0	-2.362235	1.644949	1.346339
22	1	0	-1.876942	2.763686	0.037706
23	1	0	0.424854	1.775338	2.215526
24	1	0	0.559874	3.160053	0.981541
25	1	0	2.626367	0.960571	1.594443
26	1	0	4.004416	2.897079	0.674464
27	1	0	3.548816	1.795745	-0.612720
28	1	0	2.665052	3.337123	-0.410912
29	1	0	0.096429	-0.702095	3.209905
30	1	0	0.603329	-2.349998	2.862974
31	1	0	1.711038	-1.019950	2.552661
32	1	0	-2.876325	-2.329938	-1.748144
33	1	0	-3.541408	-0.957256	-0.860339
34	1	0	-2.625148	-0.693613	-2.352382
35	1	0	-2.643497	-2.257985	2.047172
36	1	0	-2.178439	-0.683178	2.688548
37	1	0	-3.336512	-0.788466	1.357992
38	1	0	2.868736	-1.294282	0.660984
39	1	0	2.558748	-2.537153	-0.544055
40	1	0	2.750203	-0.865215	-1.056709
41	1	0	1.244030	-1.228941	-2.910743
42	1	0	0.210298	-2.657114	-2.843623
43	1	0	-0.470424	-1.102480	-3.324142

Cartesian Coordinates for **TS-1,2**



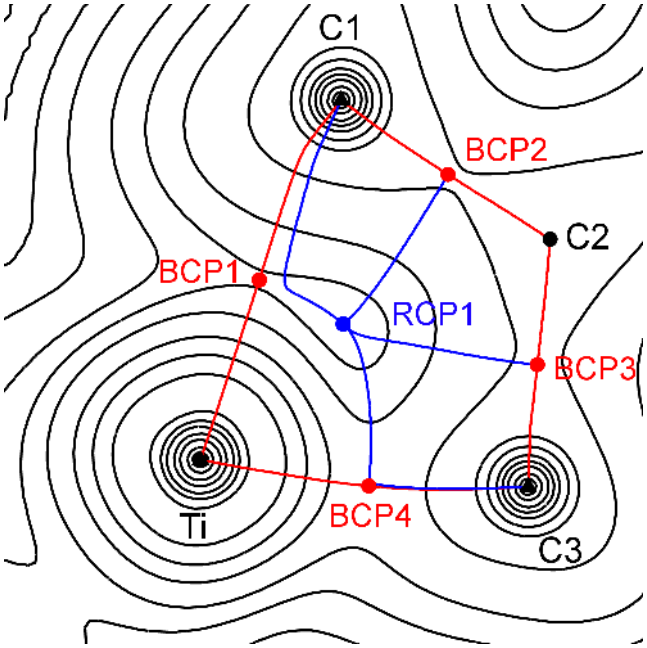
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	0.737680	-0.259804	0.112140
2	6	0	1.006533	-0.815076	3.950979
3	6	0	2.505531	-0.038717	-0.928996
4	6	0	-0.770201	1.454724	-0.536309
5	6	0	-1.539401	0.427787	0.096970
6	6	0	-1.441818	-0.755082	-0.697293
7	6	0	-0.608688	-0.454846	-1.821888
8	6	0	-0.201475	0.912640	-1.730758
9	6	0	1.571714	0.842465	2.121582
10	6	0	0.721832	0.337387	3.049269
11	6	0	0.541310	1.687972	-2.780988
12	1	0	2.590614	0.464057	2.033975
13	1	0	1.968728	-1.288350	3.739489
14	1	0	-1.084789	-1.324776	-3.718144
15	1	0	1.106380	2.523075	-2.357029
16	1	0	-2.400994	-0.297319	1.957744
17	1	0	-0.052005	-2.594053	1.273295
18	1	0	0.788406	-2.918060	-0.260777
19	1	0	1.720001	-2.372355	1.150740
20	1	0	2.543995	-0.516641	-1.913395
21	1	0	2.800566	1.013171	-1.042115
22	1	0	3.239112	-0.544943	-0.278138
23	1	0	1.352525	1.792762	1.629754
24	6	0	-0.662102	2.893016	-0.102439
25	1	0	-0.245841	0.821252	3.181740
26	1	0	1.015336	-0.453474	4.988831
27	1	0	0.209926	-1.567036	3.897799
28	6	0	-2.420830	0.583961	1.307669
29	1	0	0.325304	3.317759	-0.313114
30	1	0	-1.390912	3.506208	-0.648220
31	1	0	-0.870835	3.026723	0.963191
32	6	0	-2.223300	-2.020935	-0.491305
33	1	0	0.648144	-1.149897	-3.443633
34	1	0	-0.256392	-2.434899	-2.627392
35	1	0	-0.169424	2.110985	-3.502901
36	6	0	-0.298828	-1.391927	-2.953961
37	1	0	1.239255	1.061435	-3.341963
38	1	0	-2.156408	1.461013	1.905223
39	1	0	-3.463955	0.719348	0.993441
40	6	0	0.760125	-2.260763	0.617059
41	1	0	-2.449307	-2.198583	0.564005
42	1	0	-3.181932	-1.958203	-1.022705
43	1	0	-1.696866	-2.899155	-0.874322

Cartesian Coordinates for **2**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	0.664930	-0.105699	0.249001
2	6	0	0.679559	-0.207724	2.619628
3	6	0	2.496726	-0.801039	-0.416550
4	6	0	-0.106431	-0.927380	-1.814747
5	6	0	-0.433006	0.470901	-1.743795
6	6	0	-1.384746	0.657182	-0.697203
7	6	0	-1.616959	-0.614800	-0.087247
8	6	0	-0.831207	-1.592243	-0.781425
9	6	0	0.948976	1.784825	0.910797
10	6	0	0.590319	1.343603	2.358941
11	6	0	1.493731	2.041915	3.394758
12	1	0	-0.077649	-0.846646	2.100007
13	1	0	1.691108	-0.618263	2.463611
14	1	0	0.436420	-0.406435	3.667681
15	1	0	2.541252	-1.872063	-0.644704
16	1	0	2.856420	-0.246689	-1.293183
17	1	0	3.192391	-0.589604	0.414402
18	1	0	0.432158	2.693610	0.608307
19	1	0	2.037819	1.921319	0.799574
20	1	0	-0.452175	1.622640	2.548798
21	1	0	1.427337	3.127007	3.277526
22	1	0	1.192523	1.786171	4.417154
23	1	0	2.542465	1.751457	3.261853
24	6	0	0.074174	1.528297	-2.683608
25	1	0	-0.545378	1.554279	-3.589901
26	1	0	0.041805	2.525657	-2.237732
27	1	0	1.102365	1.334250	-3.003346
28	6	0	0.697854	-1.586655	-2.898332
29	1	0	1.150476	-2.524738	-2.566283
30	1	0	0.046002	-1.822651	-3.749490
31	1	0	1.497677	-0.941778	-3.272264
32	6	0	-2.110997	1.929620	-0.367541
33	1	0	-1.580423	2.811387	-0.734391
34	1	0	-3.100647	1.927205	-0.842833
35	1	0	-2.275438	2.054625	0.707905
36	6	0	-2.625372	-0.889900	0.998675
37	1	0	-3.621035	-1.027981	0.557835
38	1	0	-2.398025	-1.801882	1.559124
39	1	0	-2.706715	-0.062891	1.711628
40	6	0	-0.808928	-3.072118	-0.508664
41	1	0	-1.539127	-3.585410	-1.147996
42	1	0	0.169179	-3.514874	-0.720392
43	1	0	-1.071398	-3.309212	0.526959

Bader analysis:



	$\rho(\boldsymbol{r})$	$\nabla\rho(\boldsymbol{r})$
BCP1	0.0387	-0.04150
BCP2	0.2214	0.11264
BCP3	0.2285	0.11569
BCP4	0.1187	-0.03113
RCP1	0.0294	-0.04030

*Figure S1: Electron density map of **2**: Ti, C(1) and C(3) in plane, C(2) out of plane, view from the bottom*

NBO analysis:

Figure S2: C(1)-C(2) bond, 47.79% C(2)($sp^{3.42}$) and 52.21% C(1)($sp^{2.56}$)

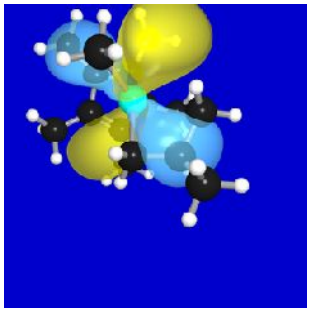


Figure S3: empty Ti($sd^{10.95}$) orbital

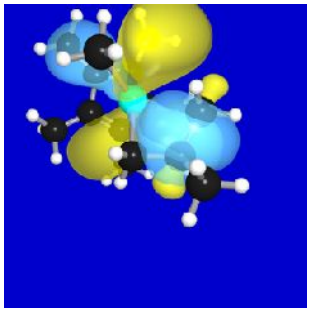


Figure S4: C(1)-C(2) -> Ti($sd^{10.95}$); 34.50 kJ/mol

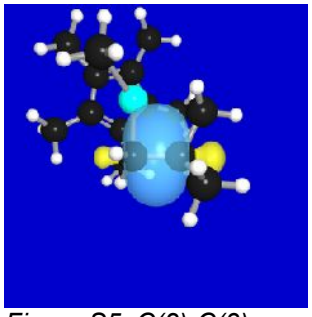


Figure S5: C(2)-C(3) bond, 52.03% C(2)($sp^{2.88}$) and 47.97% C(3)($sp^{2.51}$)

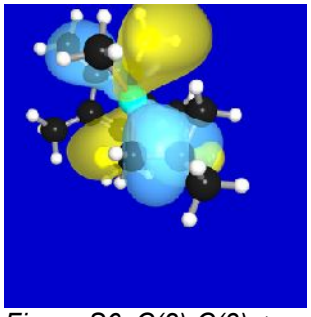


Figure S6: C(2)-C(3) -> Ti($sd^{10.95}$); 39.23 kJ/mol

Figure S7: C(1)-H(1b) bond, 63.04% C(1)($sp^{3.13}$) and 36.96% H(1b)(s)

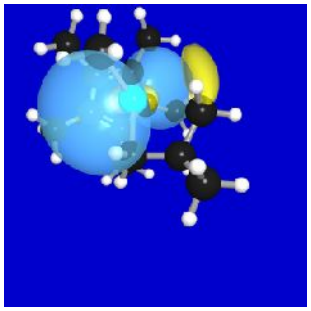


Figure S8: empty Ti($sd^{10.95}$) orbital

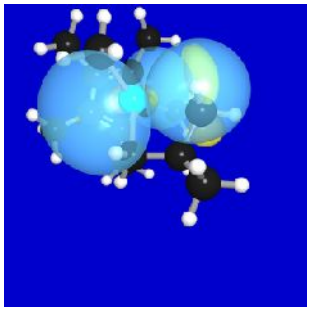


Figure S9: C(1)H(1b) -> Ti($sp^{0.32}d^{99.99}$); 22.52 kJ/mol

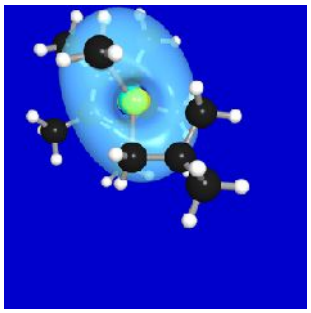


Figure S10: empty Ti($sd^{0.99}$) orbital

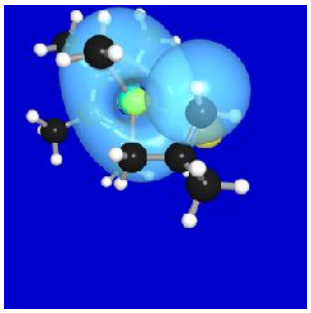


Figure S11: C(1)-H(1b) -> Ti($sd^{0.99}$); 24.41 kJ/mol

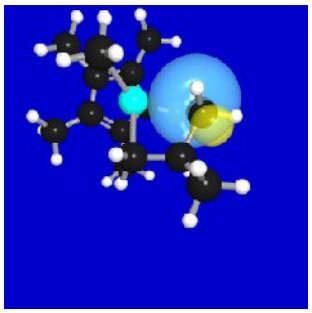


Figure S12: C(1)-H(1a) bond, 60.57% C(1)($sp^{3.31}$) and 39.43% H(1a)(s)

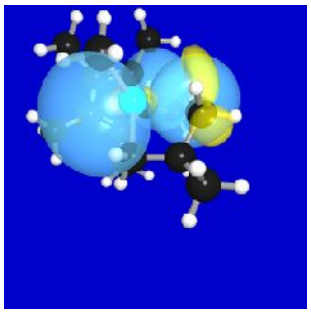


Figure S13: C(1)-H(1b) -> Ti($sd^{10.95}$); 25.62 kJ/mol

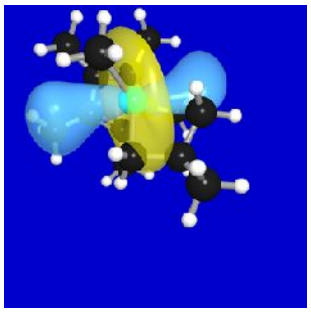


Figure 14: empty Ti($sd^{11.69}$) orbital

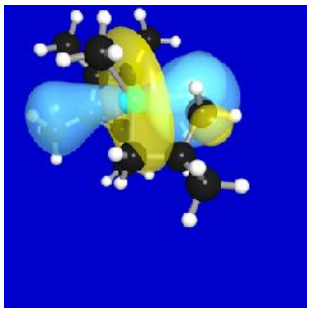


Figure 15: C(1)-H(1a) -> Ti($sd^{11.69}$); 71.59 kJ/mol

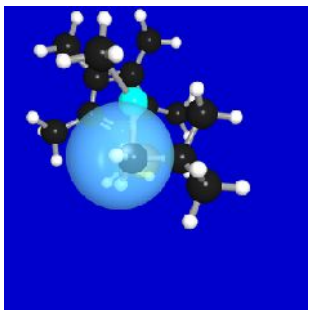


Figure S16: C(3)-H(3b) bond, 61.93% C(3)($sp^{2.92}$) and 38.07% H(3b)(s)

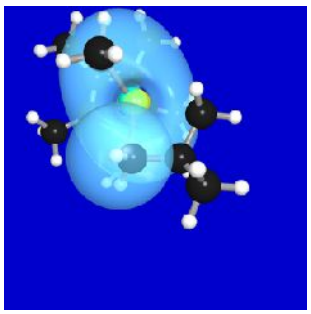


Figure S17: C(3)-H(3b) -> Ti($sd^{0.99}$); 23.78 kJ/mol

Figure S18: empty Ti($sp^{1.16}d^{99.99}$) orbital

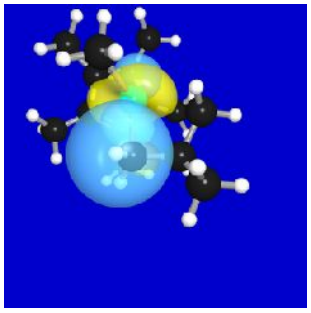
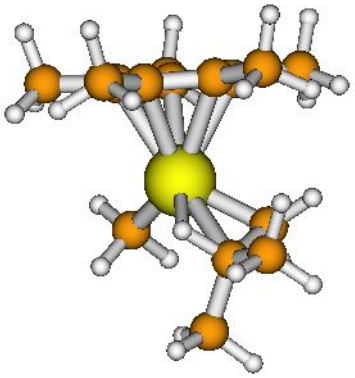


Figure S19: C(3)-H(3b) -> Ti($sp^{1.16}d^{99.99}$); 22.15 kJ/mol

Cartesian Coordinates for **TS-2,3**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	0.547391	-0.119839	0.438360
2	6	0	0.550762	0.315394	3.742286
3	6	0	2.485451	-0.773246	0.669056
4	6	0	0.826249	-0.142081	-1.874795
5	6	0	-0.097476	0.921825	-1.556864
6	6	0	-1.281651	0.333546	-1.029169
7	6	0	-1.074674	-1.080606	-0.950202
8	6	0	0.213748	-1.375648	-1.513685
9	6	0	0.222315	1.584510	1.528666
10	6	0	-0.396289	0.657305	2.578142
11	6	0	-1.778014	1.114233	3.074441
12	1	0	1.535317	-0.024728	3.401756
13	1	0	0.708096	1.215643	4.346060
14	1	0	0.124766	-0.458865	4.388265
15	1	0	3.026886	-1.299281	-0.118923
16	1	0	3.090603	0.087127	0.997673
17	1	0	2.393584	-1.459265	1.535518
18	1	0	-0.443313	2.371250	1.175867
19	1	0	1.191447	1.999191	1.832782
20	1	0	-0.635610	-0.363284	2.075824
21	1	0	-2.458251	1.322848	2.244593
22	1	0	-2.235637	0.358595	3.721180
23	1	0	-1.658997	2.034653	3.655298
24	6	0	0.110811	2.373991	-1.886534
25	1	0	-0.131337	2.557372	-2.941659
26	1	0	-0.528611	3.027067	-1.287270
27	1	0	1.148527	2.686941	-1.736188
28	6	0	2.136645	0.044220	-2.587052
29	1	0	2.790150	-0.824799	-2.483361
30	1	0	1.958048	0.194393	-3.659819
31	1	0	2.682198	0.921475	-2.225644
32	6	0	-2.550820	1.059565	-0.686505
33	1	0	-2.365931	2.076507	-0.329210
34	1	0	-3.179190	1.144755	-1.582940
35	1	0	-3.142472	0.532082	0.066967
36	6	0	-2.082333	-2.104903	-0.492963
37	1	0	-2.669975	-2.463764	-1.348003
38	1	0	-1.607673	-2.983846	-0.044724
39	1	0	-2.789734	-1.695555	0.234090
40	6	0	0.780142	-2.753396	-1.716607
41	1	0	0.385419	-3.186325	-2.645061
42	1	0	1.869395	-2.742405	-1.799286
43	1	0	0.510499	-3.439589	-0.906983

Bader analysis:

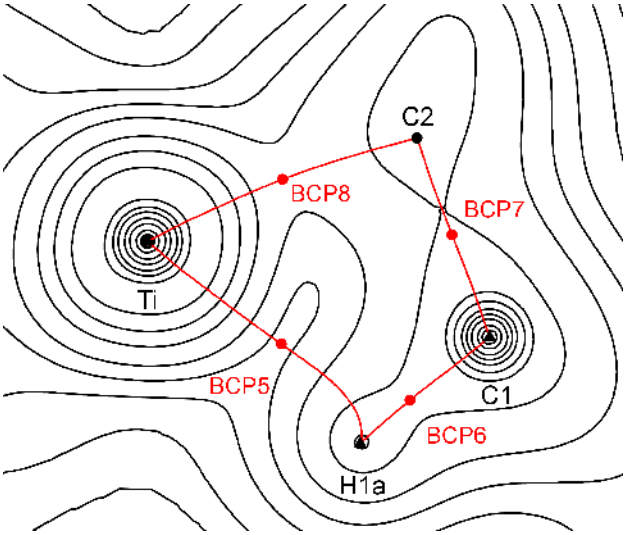


*Figure S20: Electron density map of **TS-2,3**, plane through Ti-H(1a)-C(1), C(2) out of plane.*

	$\rho(\boldsymbol{r})$	$\nabla\rho(\boldsymbol{r})$
BCP5	0.0371	-0.03894
BCP6	0.2230	0.13405
BCP7	0.2409	0.12746
BCP8	0.1125	-0.0306

NBO analysis

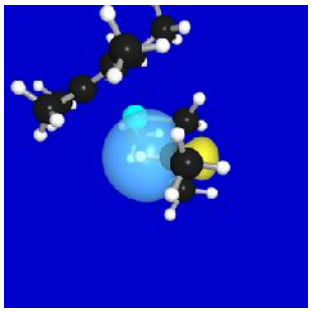


Figure S21: C(1)-H(1a) bond, 57.00% C(1)($sp^{4.89}$) and 43.00% H(1a)(s)

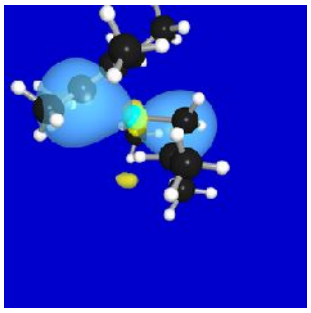


Figure S22: empty Ti($sd^{12.38}$) orbital

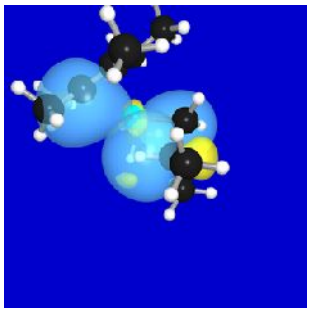


Figure S23: C(1)-H(1a) -> Ti($sd^{12.38}$) (33.62 kJ/mol); 33.62 kJ/mol

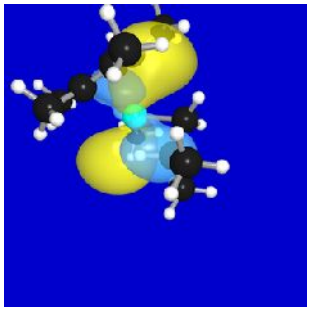


Figure S24: empty Ti($sd^{25.18}$)

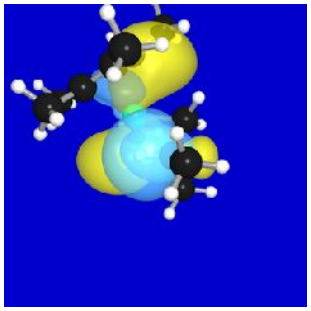


Figure S25: C(1)-H(1a) -> Ti($sd^{25.18}$); 59.83 kJ/mol

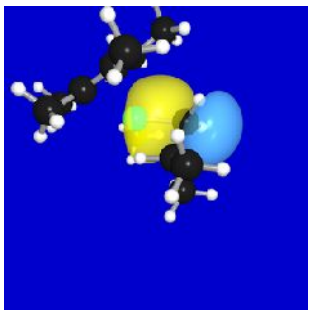


Figure S26: Ti-C(2) bond, 25.10% Ti($sd^{15.89}$) and 74.90% C(2)($sp^{5.42}$)

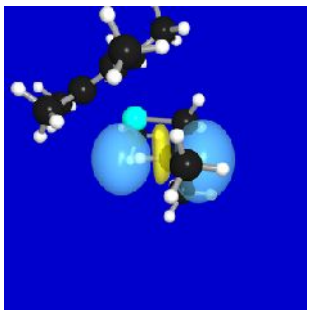


Figure S27: C(1)-H(1a) antibond, 43.00% C(1) ($sp^{4.89}$) and 57.00% H(1a)(s)

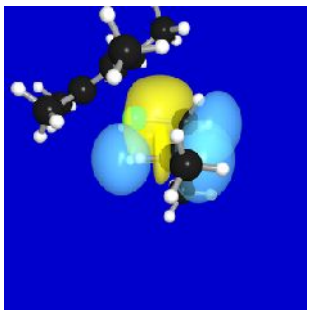


Figure S28: Ti-C(2) -> C(1)-H(1a) antibond; 24.53 kJ/mol

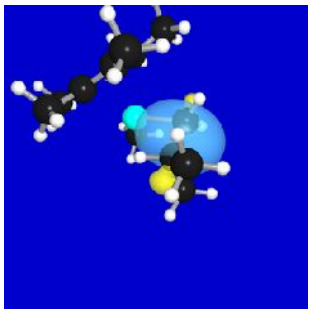


Figure S29: C(1)-C(2) bond, 47.10% C(2)($sp^{2.47}$) 52.90% C(1)($sp^{2.69}$)

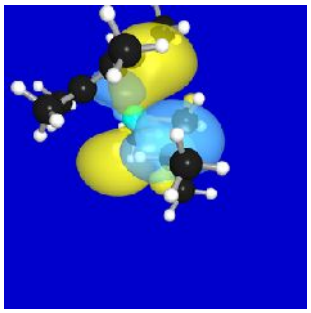
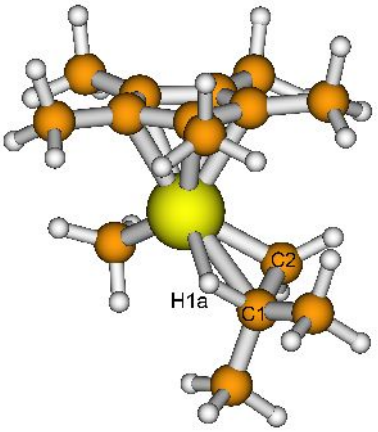


Figure S30: C(1)-C(2) -> Ti($sd^{25.18}$); 37.64 kJ/mol

Cartesian Coordinates for **3**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	0.639052	-0.052995	0.350166
2	6	0	0.904748	-0.302324	3.727469
3	6	0	2.687960	-0.153684	0.174611
4	6	0	0.644519	-0.093869	-1.996104
5	6	0	-0.062587	1.079988	-1.558270
6	6	0	-1.253610	0.667387	-0.884752
7	6	0	-1.254913	-0.762816	-0.842835
8	6	0	-0.088877	-1.228853	-1.538964
9	6	0	0.117465	1.258270	1.831798
10	6	0	-0.177057	0.020022	2.681488
11	6	0	-1.586582	0.011874	3.294867
12	1	0	1.912752	-0.324967	3.299258
13	1	0	0.893907	0.474178	4.499782
14	1	0	0.716462	-1.266595	4.210306
15	1	0	3.097225	-0.974985	-0.423486
16	1	0	3.124576	0.787481	-0.187756
17	1	0	3.016888	-0.287196	1.222316
18	1	0	-0.714791	1.954714	1.744394
19	1	0	1.037604	1.780085	2.128537
20	1	0	-0.199172	-0.911318	1.984908
21	1	0	-2.359031	0.205459	2.545395
22	1	0	-1.803045	-0.946291	3.778011
23	1	0	-1.647585	0.798762	4.053717
24	6	0	0.342284	2.498813	-1.848374
25	1	0	-0.054913	2.810766	-2.823505
26	1	0	-0.043727	3.197871	-1.101283
27	1	0	1.429139	2.615442	-1.892911
28	6	0	1.838774	-0.111394	-2.906612
29	1	0	2.419687	-1.032034	-2.807943
30	1	0	1.507799	-0.045410	-3.951196
31	1	0	2.511564	0.731414	-2.725666
32	6	0	-2.366952	1.567259	-0.430749
33	1	0	-2.012465	2.574042	-0.194373
34	1	0	-3.112212	1.666755	-1.230773
35	1	0	-2.889944	1.176678	0.446777
36	6	0	-2.362071	-1.628982	-0.299228
37	1	0	-3.103893	-1.823681	-1.084577
38	1	0	-2.000365	-2.602404	0.045726
39	1	0	-2.891384	-1.152404	0.530459
40	6	0	0.281717	-2.668640	-1.773736
41	1	0	-0.135940	-3.014080	-2.728651
42	1	0	1.365109	-2.812296	-1.826935
43	1	0	-0.112311	-3.332402	-0.997832

Bader analysis

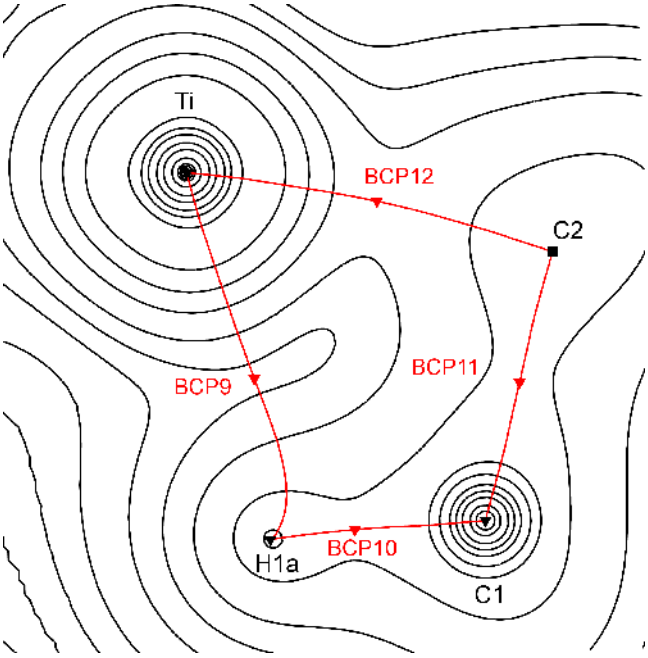


*Figure S31: Electron density map of **3**, plane through Ti-H(1a)-C1 with C(2) out of plane*

	$\rho(\boldsymbol{r})$	$\nabla\rho(\boldsymbol{r})$
BCP9	0.0372	-0.03874
BCP10	0.2226	0.13333
BCP11	0.2410	0.12758
BCP12	0.1129	-0.03138

NBO analysis

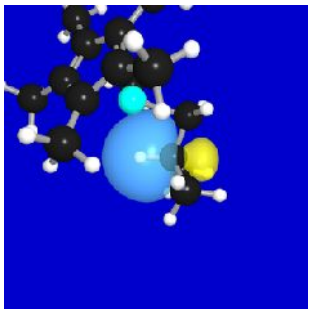


Figure S32: C(1)-H(1a) bond, 56.88% C(1)($sp^{4.91}$) and 43.12% H(1a)(s)

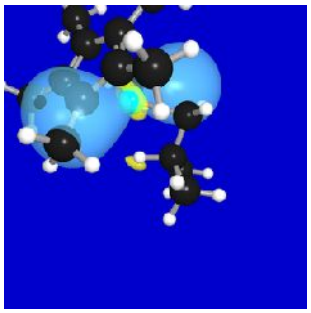


Figure S33: empty Ti($sd^{10.35}$) orbital

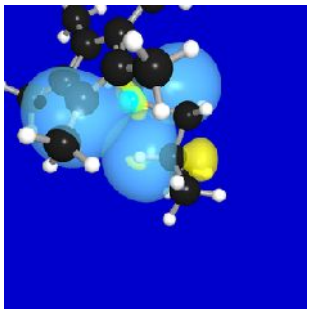


Figure S34: C(1)-H(1a) -> Ti($sd^{10.35}$); 39.48 kJ

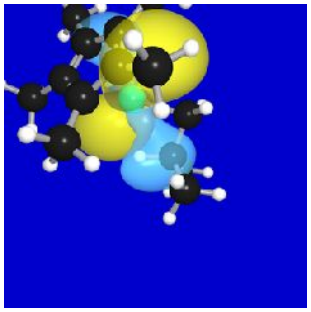


Figure S35: empty Ti($sd^{26.88}$) orbital

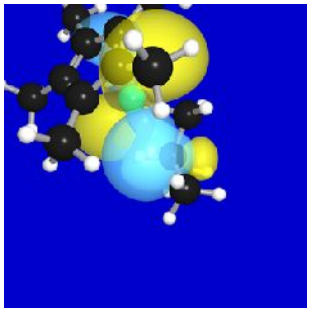


Figure S36: C(1)-H(1a) -> Ti($sd^{26.88}$); 54.34 kJ/mol

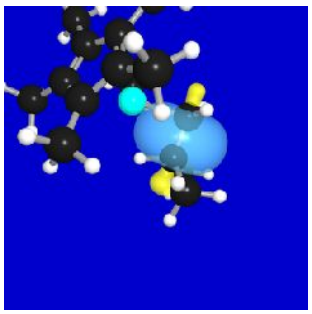


Figure S37: C(2)-C(1) bond, 47.20% C(2)($sp^{2.47}$) and 52.80% C(1)($sp^{2.68}$)

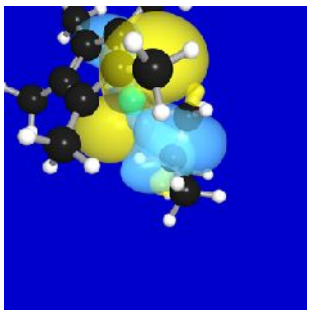
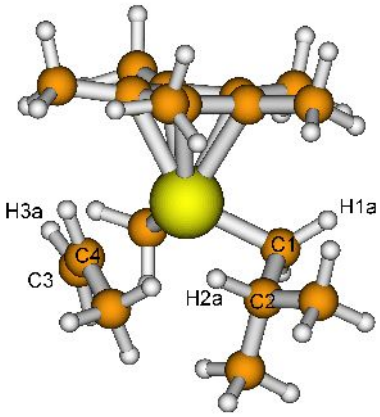


Figure S38: C(2)-C(1) -> Ti($sd^{26.88}$); 31.40 kJ/mol

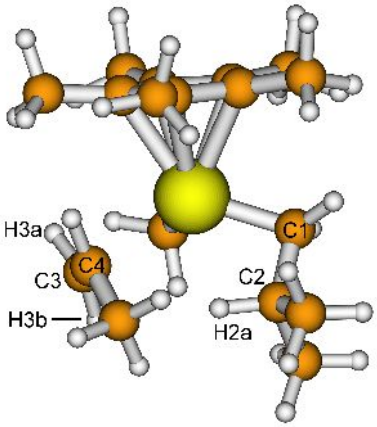
Cartesian Coordinates for **4**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.030997	-0.070481	-0.585593
2	6	0	-3.255418	-1.191088	-1.418940
3	6	0	0.454108	-0.002522	-2.606938
4	6	0	2.312239	0.116416	-0.369567
5	6	0	1.920720	-1.120051	0.243496
6	6	0	1.133547	-0.813780	1.393063
7	6	0	1.003597	0.603404	1.476545
8	6	0	1.736089	1.180117	0.389611
9	6	0	-0.943726	-1.930429	-0.595214
10	6	0	-2.283938	-1.289660	-0.229242
11	6	0	-2.953574	-1.945269	0.992054
12	1	0	-2.802431	-0.703710	-2.290216
13	1	0	-3.551855	-2.199142	-1.729028
14	1	0	-4.164690	-0.640940	-1.152732
15	1	0	0.973401	0.894879	-2.958943
16	1	0	1.026730	-0.882040	-2.922661
17	1	0	-0.532397	-0.052935	-3.099948
18	1	0	-0.630558	-2.717628	0.088217
19	1	0	-0.905058	-2.298985	-1.626419
20	1	0	-2.099460	-0.217648	0.101234
21	1	0	-2.278772	-1.984216	1.852162
22	1	0	-3.858244	-1.402764	1.287341
23	1	0	-3.240263	-2.972678	0.743600
24	6	0	2.389436	-2.482713	-0.180268
25	1	0	3.391440	-2.678697	0.223982
26	1	0	1.731942	-3.276394	0.183157
27	1	0	2.456681	-2.572764	-1.268608
28	6	0	3.335067	0.264905	-1.459341
29	1	0	3.206445	1.190006	-2.027454
30	1	0	4.340798	0.290151	-1.019478
31	1	0	3.311510	-0.568488	-2.166269
32	6	0	0.652460	-1.789259	2.429098
33	1	0	0.459503	-2.781630	2.013720
34	1	0	1.419819	-1.911628	3.205329
35	1	0	-0.256878	-1.446733	2.931979
36	6	0	0.366387	1.337657	2.628420
37	1	0	0.990906	1.234404	3.525065
38	1	0	0.269119	2.408514	2.434087
39	1	0	-0.623751	0.946511	2.888435
40	6	0	1.999404	2.644193	0.158915
41	1	0	2.944401	2.935298	0.635925
42	1	0	2.095623	2.884074	-0.904676
43	1	0	1.221422	3.286081	0.582206
44	1	0	-0.339042	2.491441	-1.507945
45	6	0	-1.308596	2.140926	-1.163234
46	6	0	-1.770030	2.481991	0.060812

47	1	0	-1.096265	3.006378	0.736317
48	1	0	-1.972970	1.712771	-1.912208
49	6	0	-3.160103	2.270643	0.567114
50	1	0	-3.784377	1.717839	-0.139830
51	1	0	-3.624315	3.250978	0.741600
52	1	0	-3.162506	1.757402	1.536817

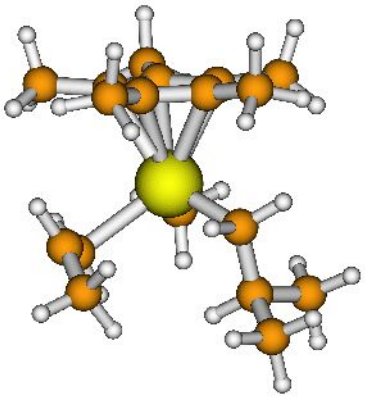
Cartesian Coordinates for **TS-4,5**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.091305	-0.144849	-0.434172
2	6	0	-3.296887	-2.062174	-1.131047
3	6	0	0.134312	-0.715844	-2.417575
4	6	0	2.283754	-0.117157	-0.550598
5	6	0	1.900611	-1.167234	0.348217
6	6	0	1.280661	-0.574092	1.488172
7	6	0	1.238420	0.835658	1.279659
8	6	0	1.870576	1.120392	0.026319
9	6	0	-1.140441	-1.792462	0.233731
10	6	0	-2.516936	-1.211840	-0.111278
11	6	0	-3.349630	-0.933270	1.152516
12	1	0	-2.719505	-2.229569	-2.046650
13	1	0	-3.525282	-3.041417	-0.696206
14	1	0	-4.243411	-1.583728	-1.406621
15	1	0	0.642683	0.014994	-3.055526
16	1	0	0.614890	-1.690459	-2.553610
17	1	0	-0.914648	-0.807061	-2.749067
18	1	0	-1.060654	-2.134388	1.265456
19	1	0	-0.836259	-2.603755	-0.440369
20	1	0	-2.382776	-0.211483	-0.612508
21	1	0	-2.805918	-0.312516	1.875431
22	1	0	-4.291497	-0.429755	0.910696
23	1	0	-3.592002	-1.879173	1.649336
24	6	0	2.214728	-2.625441	0.169862
25	1	0	3.215651	-2.846946	0.563339
26	1	0	1.506749	-3.267149	0.701188
27	1	0	2.210924	-2.919220	-0.883754
28	6	0	3.155549	-0.275723	-1.763078
29	1	0	2.992697	0.516597	-2.499183
30	1	0	4.212075	-0.232395	-1.467718
31	1	0	2.998574	-1.234262	-2.264393
32	6	0	0.887614	-1.267060	2.761466
33	1	0	0.763438	-2.343897	2.625209
34	1	0	1.673554	-1.126258	3.515408
35	1	0	-0.039335	-0.868752	3.187631
36	6	0	0.760579	1.832048	2.304558
37	1	0	1.431668	1.826112	3.172984
38	1	0	0.754337	2.853880	1.917119
39	1	0	-0.242778	1.604185	2.684553
40	6	0	2.206945	2.482912	-0.518658
41	1	0	3.206728	2.784278	-0.179610
42	1	0	2.228204	2.498714	-1.612865
43	1	0	1.513175	3.258372	-0.181076
44	1	0	-0.155482	2.213758	-1.822878
45	6	0	-1.157259	2.033582	-1.440704
46	6	0	-1.569641	2.599267	-0.283969

47	1	0	-0.838627	3.137521	0.317986
48	6	0	-2.973749	2.621405	0.227818
49	1	0	-1.868478	1.576686	-2.126250
50	1	0	-3.658271	2.042313	-0.397712
51	1	0	-3.323936	3.662573	0.247313
52	1	0	-3.033020	2.261074	1.261667

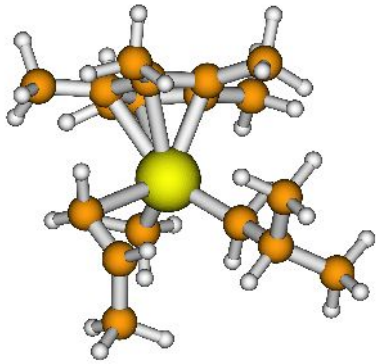
Cartesian Coordinates for **5**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.048996	-0.025398	-0.463224
2	6	0	-3.104734	-2.312177	-0.644336
3	6	0	-0.095042	-1.058500	-2.256934
4	6	0	2.228734	-0.708699	-0.466701
5	6	0	1.542416	-1.459544	0.540438
6	6	0	1.111307	-0.556022	1.560193
7	6	0	1.507227	0.759096	1.172226
8	6	0	2.195220	0.666621	-0.079343
9	6	0	-1.696617	-0.621804	0.630490
10	6	0	-2.971436	-0.842090	-0.219231
11	6	0	-4.224277	-0.390469	0.559114
12	1	0	-2.234001	-2.660544	-1.209468
13	1	0	-3.210974	-2.954931	0.238430
14	1	0	-3.991486	-2.459308	-1.269946
15	1	0	0.611362	-0.679757	-3.005808
16	1	0	0.063081	-2.137830	-2.153879
17	1	0	-1.120987	-0.900907	-2.627606
18	1	0	-1.755642	0.347153	1.178386
19	1	0	-1.611985	-1.396050	1.397630
20	1	0	-2.930501	-0.228817	-1.137069
21	1	0	-4.173792	0.670205	0.832090
22	1	0	-5.129706	-0.541576	-0.039996
23	1	0	-4.331529	-0.968708	1.484296
24	6	0	1.380636	-2.952864	0.570257
25	1	0	2.192360	-3.407839	1.153494
26	1	0	0.438267	-3.255544	1.036710
27	1	0	1.417459	-3.389838	-0.430985
28	6	0	3.003407	-1.278266	-1.620697
29	1	0	3.071577	-0.580389	-2.460273
30	1	0	4.029704	-1.504416	-1.303099
31	1	0	2.566994	-2.207914	-1.994164
32	6	0	0.527288	-0.927150	2.892718
33	1	0	0.082616	-1.925301	2.883007
34	1	0	1.317805	-0.933714	3.654676
35	1	0	-0.238286	-0.219801	3.227414
36	6	0	1.364265	1.983098	2.038127
37	1	0	2.080696	1.934627	2.868469
38	1	0	1.576550	2.906789	1.493361
39	1	0	0.368746	2.068624	2.488013
40	6	0	2.883039	1.790630	-0.808263
41	1	0	3.934630	1.852966	-0.499231
42	1	0	2.881522	1.642431	-1.892933
43	1	0	2.433795	2.766233	-0.598294
44	1	0	0.233992	1.973905	-2.149886
45	6	0	-0.719845	2.046952	-1.625125
46	6	0	-0.861849	2.882564	-0.568841

47	1	0	0.028288	3.371173	-0.174186
48	6	0	-2.152050	3.249730	0.084642
49	1	0	-2.099463	3.125661	1.172995
50	1	0	-2.999374	2.682291	-0.308308
51	1	0	-2.338947	4.318700	-0.090052
52	1	0	-1.590991	1.624544	-2.125269

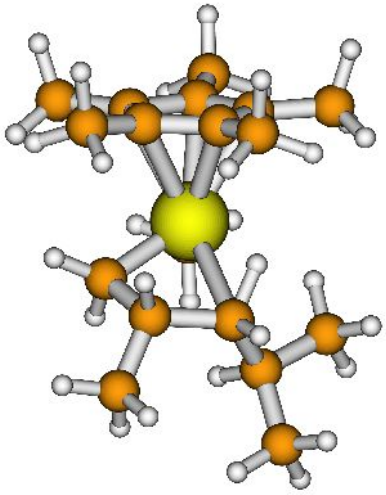
Cartesian Coordinates for **TS-5,6**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	0.065831	0.372775	-0.401242
2	6	0	-4.123168	-1.310635	-1.088563
3	6	0	0.520564	1.361183	-2.180535
4	6	0	1.544531	-1.423129	-0.645787
5	6	0	0.900842	-1.593209	0.627429
6	6	0	1.309925	-0.518792	1.464068
7	6	0	2.221619	0.306127	0.722826
8	6	0	2.387594	-0.270319	-0.572452
9	6	0	-1.829711	-0.303905	-0.665123
10	6	0	-3.231107	-0.543875	-0.092572
11	6	0	-3.211689	-1.247137	1.272001
12	1	0	-4.185502	-0.795179	-2.053510
13	1	0	-3.729924	-2.318740	-1.269322
14	1	0	-5.141048	-1.414936	-0.696432
15	1	0	1.388381	2.025611	-2.099262
16	1	0	0.702857	0.666445	-3.010804
17	1	0	-0.361388	1.965515	-2.438905
18	1	0	-1.355591	-1.272754	-0.966333
19	1	0	-1.900945	0.281942	-1.607521
20	1	0	-3.686537	0.447446	0.049924
21	1	0	-2.594850	-0.708381	2.001992
22	1	0	-4.225859	-1.318051	1.679532
23	1	0	-2.822576	-2.267683	1.186149
24	6	0	0.104471	-2.794118	1.057348
25	1	0	0.785273	-3.589002	1.389674
26	1	0	-0.564499	-2.566438	1.890010
27	1	0	-0.498574	-3.210808	0.244908
28	6	0	1.467669	-2.377303	-1.807206
29	1	0	1.562871	-1.865701	-2.769609
30	1	0	2.286001	-3.107152	-1.747722
31	1	0	0.532501	-2.944594	-1.816446
32	6	0	0.941281	-0.366924	2.915325
33	1	0	-0.115697	-0.584942	3.102472
34	1	0	1.524048	-1.069923	3.524567
35	1	0	1.157563	0.633918	3.299369
36	6	0	3.004630	1.475245	1.255314
37	1	0	3.987762	1.138268	1.608886
38	1	0	3.186199	2.236171	0.489469
39	1	0	2.513178	1.960165	2.103438
40	6	0	3.389826	0.153594	-1.606433
41	1	0	4.334291	-0.383791	-1.449162
42	1	0	3.056562	-0.068981	-2.623641
43	1	0	3.614165	1.222546	-1.552685
44	1	0	0.081386	1.990400	1.896348
45	6	0	-0.255017	2.403204	0.950542
46	6	0	-1.581405	2.425288	0.653152

47	1	0	-2.262623	1.891916	1.314560
48	6	0	-2.218124	3.211132	-0.445844
49	1	0	-2.905860	2.599242	-1.040500
50	1	0	-1.487178	3.689093	-1.102770
51	1	0	-2.831632	3.998803	0.014361
52	1	0	0.452595	3.019955	0.395366

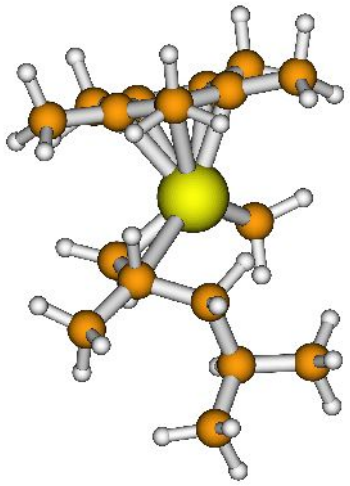
Cartesian Coordinates for **6**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	0.076703	-0.162839	-0.457255
2	6	0	-2.317370	-2.349614	0.126258
3	6	0	0.210979	-1.336560	-2.161745
4	6	0	2.358364	-0.739332	-0.264040
5	6	0	1.732273	-0.995060	0.992824
6	6	0	1.293691	0.255734	1.536269
7	6	0	1.640258	1.287905	0.611222
8	6	0	2.273606	0.671649	-0.511042
9	6	0	-2.209232	0.135491	0.661980
10	6	0	-2.887431	-0.960503	-0.213131
11	6	0	-4.416806	-0.968794	-0.033295
12	1	0	-1.228252	-2.422294	-0.041221
13	1	0	-2.499617	-2.601457	1.177966
14	1	0	-2.773292	-3.128408	-0.492989
15	1	0	0.805850	-0.828245	-2.931984
16	1	0	0.603869	-2.350274	-2.033748
17	1	0	-0.825154	-1.405204	-2.532276
18	1	0	-2.809921	0.292776	1.566855
19	1	0	-1.282383	-0.283508	1.148478
20	1	0	-2.684106	-0.752424	-1.274482
21	1	0	-4.869089	-0.006085	-0.282417
22	1	0	-4.870556	-1.728231	-0.678208
23	1	0	-4.678772	-1.209124	1.004195
24	6	0	1.630062	-2.339186	1.663320
25	1	0	2.538977	-2.541594	2.245038
26	1	0	0.787236	-2.394085	2.358825
27	1	0	1.525771	-3.154003	0.940156
28	6	0	3.131949	-1.732040	-1.082816
29	1	0	3.110924	-1.498059	-2.150248
30	1	0	4.183716	-1.727695	-0.768242
31	1	0	2.760135	-2.752328	-0.955259
32	6	0	0.706638	0.473053	2.906480
33	1	0	0.188692	-0.413334	3.284560
34	1	0	1.506085	0.704889	3.622116
35	1	0	0.005572	1.313296	2.929984
36	6	0	1.512593	2.764353	0.852211
37	1	0	2.374567	3.121124	1.431279
38	1	0	1.495210	3.333419	-0.080726
39	1	0	0.616009	3.020461	1.424827
40	6	0	2.846961	1.390224	-1.699467
41	1	0	3.870883	1.721632	-1.480714
42	1	0	2.897430	0.747648	-2.582514
43	1	0	2.266817	2.279843	-1.961409
44	1	0	-0.389369	2.525750	-1.208870
45	6	0	-0.838875	1.542752	-1.073677
46	6	0	-1.927000	1.546401	0.037259

47	1	0	-1.540963	2.154900	0.864374
48	6	0	-3.221666	2.215417	-0.461244
49	1	0	-1.256774	1.209571	-2.040213
50	1	0	-3.647302	1.685299	-1.319357
51	1	0	-3.005742	3.239670	-0.779743
52	1	0	-3.977885	2.257217	0.331387

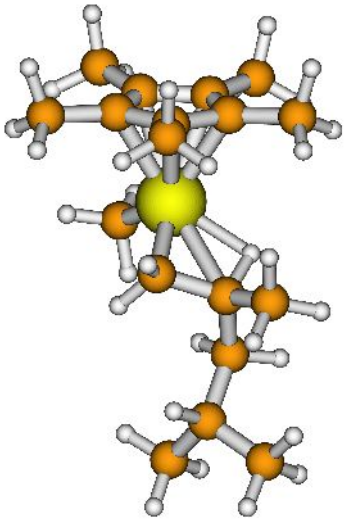
Cartesian Coordinates for **TS-6,7**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	0.169892	-0.289635	-0.264707
2	6	0	-3.542298	-2.239296	0.298477
3	6	0	-0.004384	-2.037793	-1.348723
4	6	0	2.453499	-0.854937	-0.245667
5	6	0	2.009249	-0.769552	1.108775
6	6	0	1.623291	0.583863	1.368998
7	6	0	1.844384	1.344410	0.176165
8	6	0	2.329871	0.452966	-0.826024
9	6	0	-2.359416	-0.026957	0.584652
10	6	0	-3.438513	-0.793343	-0.221621
11	6	0	-4.823417	-0.124396	-0.141075
12	1	0	-2.594082	-2.782983	0.207723
13	1	0	-3.840315	-2.254348	1.354382
14	1	0	-4.296967	-2.797099	-0.264329
15	1	0	0.502694	-1.942536	-2.318595
16	1	0	0.344431	-2.957167	-0.865540
17	1	0	-1.085120	-2.129477	-1.546341
18	1	0	-2.755289	0.221718	1.578158
19	1	0	-1.577492	-0.797014	0.861831
20	1	0	-3.134034	-0.829607	-1.277058
21	1	0	-4.849148	0.869007	-0.592321
22	1	0	-5.560125	-0.741456	-0.665593
23	1	0	-5.152518	-0.033983	0.901541
24	6	0	1.989696	-1.902508	2.098834
25	1	0	2.972810	-2.002600	2.577611
26	1	0	1.261114	-1.742274	2.899500
27	1	0	1.766710	-2.862389	1.622693
28	6	0	3.116920	-2.040851	-0.884955
29	1	0	2.954424	-2.075181	-1.965568
30	1	0	4.201155	-1.990100	-0.720830
31	1	0	2.768816	-2.987331	-0.463173
32	6	0	1.189388	1.134464	2.703634
33	1	0	0.595004	0.418634	3.280821
34	1	0	2.070017	1.378032	3.312080
35	1	0	0.607517	2.055373	2.603210
36	6	0	1.698827	2.833333	0.042054
37	1	0	2.598161	3.332057	0.426247
38	1	0	1.581020	3.141456	-0.999830
39	1	0	0.849988	3.226728	0.610722
40	6	0	2.733257	0.824686	-2.225213
41	1	0	3.797548	1.093796	-2.251829
42	1	0	2.593880	-0.004642	-2.924683
43	1	0	2.169399	1.681958	-2.602498
44	1	0	-0.475615	2.071384	-1.635892
45	6	0	-0.866024	1.115683	-1.288128
46	6	0	-1.704705	1.278685	0.017679

47	1	0	-1.013908	1.614969	0.816823
48	6	0	-2.708697	2.445351	-0.136449
49	1	0	-1.435041	0.628114	-2.090857
50	1	0	-3.353988	2.296957	-1.004730
51	1	0	-2.160742	3.380217	-0.285664
52	1	0	-3.333497	2.548918	0.757067

Cartesian Coordinates for **7**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.408795	-0.499995	-0.102847
2	6	0	4.715908	-1.855253	0.216994
3	6	0	-0.377250	-2.551059	-0.321875
4	6	0	-2.744651	-0.753564	-0.091825
5	6	0	-2.404892	0.135005	-1.155145
6	6	0	-1.825755	1.319255	-0.587834
7	6	0	-1.807936	1.166002	0.834317
8	6	0	-2.340516	-0.126712	1.136574
9	6	0	2.892465	-0.328575	-0.674279
10	6	0	4.183179	-0.412880	0.190528
11	6	0	5.278619	0.545463	-0.307985
12	1	0	3.985139	-2.549679	0.649580
13	1	0	4.954468	-2.204655	-0.795416
14	1	0	5.631863	-1.921302	0.813500
15	1	0	-0.715760	-3.073325	0.583746
16	1	0	-0.929133	-2.958754	-1.176812
17	1	0	0.694377	-2.783271	-0.456704
18	1	0	3.152417	-0.013631	-1.693462
19	1	0	2.466662	-1.337229	-0.770241
20	1	0	3.924031	-0.134814	1.222508
21	1	0	4.947142	1.587997	-0.341488
22	1	0	6.155942	0.498498	0.345853
23	1	0	5.603717	0.266571	-1.318032
24	6	0	-2.654540	-0.108203	-2.619662
25	1	0	-3.649641	0.262695	-2.898695
26	1	0	-1.932917	0.411806	-3.257665
27	1	0	-2.626925	-1.172415	-2.871971
28	6	0	-3.525571	-2.030175	-0.213942
29	1	0	-3.266161	-2.751510	0.565519
30	1	0	-4.598204	-1.817731	-0.117007
31	1	0	-3.377341	-2.515016	-1.182536
32	6	0	-1.457639	2.566128	-1.349341
33	1	0	-1.111256	2.348561	-2.364132
34	1	0	-2.337198	3.216144	-1.444071
35	1	0	-0.682022	3.147905	-0.844734
36	6	0	-1.447853	2.224996	1.836726
37	1	0	-2.327454	2.845487	2.052808
38	1	0	-1.114833	1.797002	2.785973
39	1	0	-0.664153	2.896078	1.474238
40	6	0	-2.535277	-0.702176	2.512447
41	1	0	-3.533202	-0.441982	2.889891
42	1	0	-2.465864	-1.793899	2.514499
43	1	0	-1.806385	-0.314002	3.229243
44	1	0	0.968479	0.862101	1.919965
45	6	0	1.097452	0.111313	1.142118
46	6	0	1.789551	0.612972	-0.125355

47	1	0	0.999136	0.625186	-0.985020
48	6	0	2.197038	2.092833	-0.048873
49	1	0	1.539177	-0.806747	1.552476
50	1	0	2.987741	2.214756	0.696303
51	1	0	1.356420	2.722661	0.254895
52	1	0	2.571244	2.454179	-1.011895

Bader Analysis

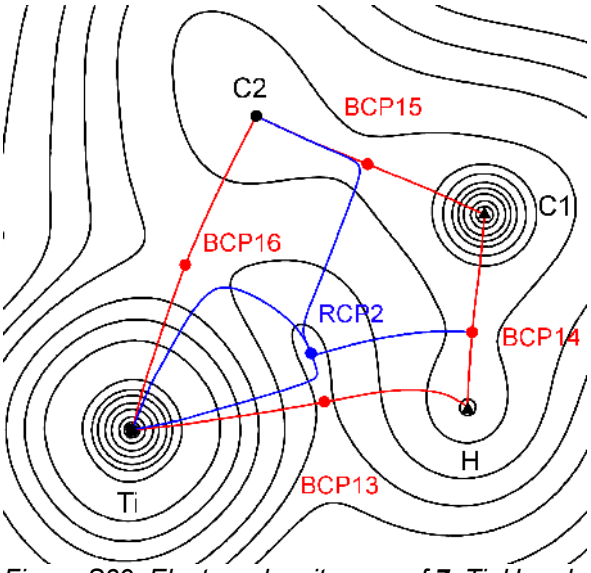


*Figure S39: Electron density map of **7**: Ti, H and C(1) in plane, C(2) out of plane, view from the bottom*

	$\rho(\boldsymbol{r})$	$\nabla\rho(\boldsymbol{r})$
BCP13	0.0389	-0.03964
BCP14	0.2197	0.12862
BCP15	0.2417	0.12807
BCP16	0.1123	-0.03140
RCP2	0.0371	-0.05103

NBO Analysis

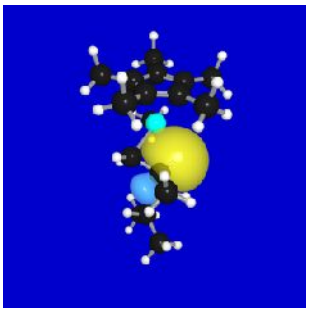


Figure S40: C(1)-H bond, 56.75% C(1)($sp^{5.05}$) and 43.25% H(s)

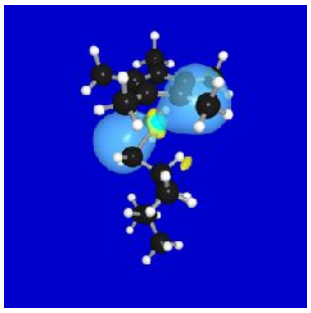


Figure S41: empty Ti($sd^{11.14}$) orbital

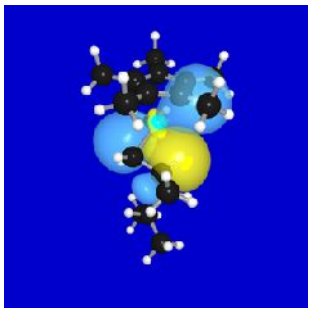


Figure S42: C(1)-H -> Ti($sd^{11.14}$); 37.85 kJ/mol

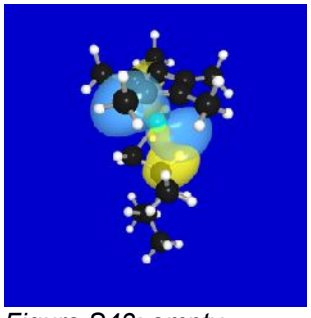


Figure S43: empty Ti($sd^{26.64}$) orbital

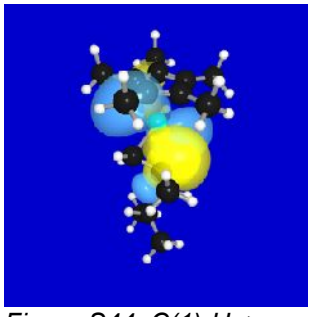


Figure S44: C(1)-H -> Ti($sd^{26.64}$); 59.70 kJ/mol

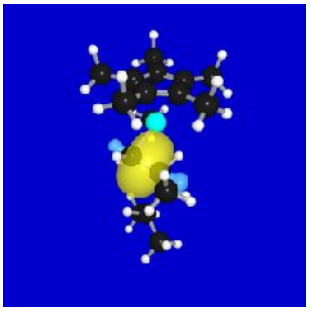


Figure S45: C(1)-C(2) bond, 52.73%)C(1) ($sp^{2.71}$) and 47.27% C(2) ($sp^{2.46}$)

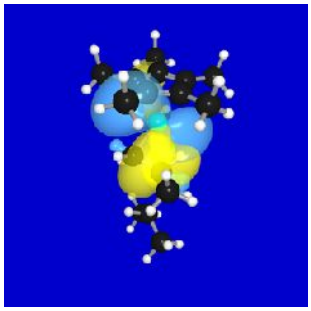


Figure S46: C(1)-C(2) -> Ti($sd^{26.64}$); 31.40 kJ/mol

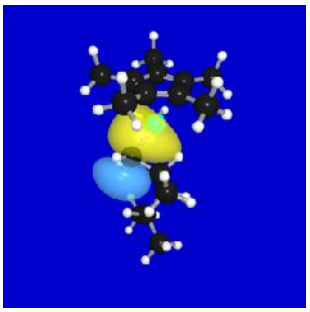


Figure S47: Ti-C(2) bond, 25.46% Ti($sd^{16.76}$) and 74.54% C(2)($sp^{5.47}$)

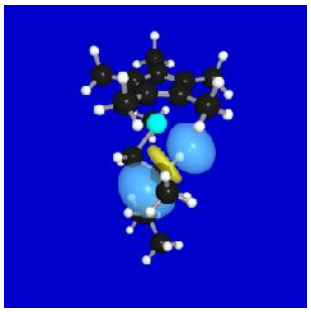


Figure S48: C(1)-H antibond, 43.25% C(1) ($sp^{5.05}$) and 56.75% H(s)

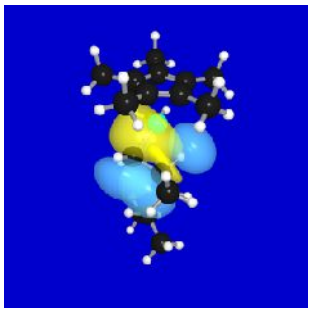
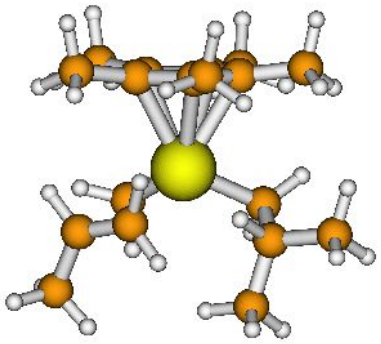


Figure S49: Ti-C(2) -> C(1)-H; 25.25 kJ/mol

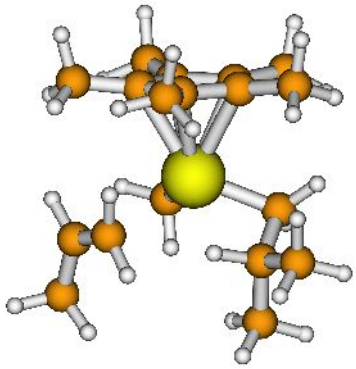
Cartesian Coordinates for **8**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.243254	0.081678	-0.316926
2	6	0	-3.399559	-1.250745	-0.612336
3	6	0	-0.471913	1.289617	-1.994419
4	6	0	2.007833	0.773800	-0.543357
5	6	0	1.977736	-0.647287	-0.731025
6	6	0	1.599626	-1.250320	0.505528
7	6	0	1.350423	-0.208740	1.447728
8	6	0	1.615575	1.041867	0.804150
9	6	0	-0.937321	-1.675199	-1.172898
10	6	0	-2.035434	-1.757023	-0.112511
11	6	0	-2.155371	-3.146727	0.539145
12	1	0	-3.336130	-0.254433	-1.066411
13	1	0	-3.779634	-1.932330	-1.381234
14	1	0	-4.136276	-1.212234	0.197835
15	1	0	-0.167604	2.337509	-1.914073
16	1	0	0.051606	0.840944	-2.847434
17	1	0	-1.553377	1.245343	-2.205386
18	1	0	-0.314887	-2.565711	-1.237273
19	1	0	-1.313081	-1.412653	-2.168316
20	1	0	-1.752318	-1.076128	0.754635
21	1	0	-1.194794	-3.496519	0.926669
22	1	0	-2.877425	-3.135929	1.362799
23	1	0	-2.500969	-3.869269	-0.207904
24	6	0	2.412316	-1.371349	-1.973276
25	1	0	3.504103	-1.489495	-1.978840
26	1	0	1.977642	-2.371981	-2.038654
27	1	0	2.142374	-0.827174	-2.883195
28	6	0	2.574730	1.768606	-1.515518
29	1	0	2.162931	2.771678	-1.374249
30	1	0	3.661760	1.840900	-1.379383
31	1	0	2.396833	1.478038	-2.554245
32	6	0	1.624932	-2.718767	0.818577
33	1	0	1.358091	-3.339139	-0.041122
34	1	0	2.640191	-3.010985	1.118646
35	1	0	0.960865	-2.978031	1.647914
36	6	0	1.032590	-0.412591	2.906835
37	1	0	1.945346	-0.675992	3.456975
38	1	0	0.633269	0.491025	3.376772
39	1	0	0.316438	-1.224439	3.072541
40	6	0	1.655423	2.389420	1.473895
41	1	0	2.636232	2.542321	1.943119
42	1	0	1.515442	3.208379	0.762279
43	1	0	0.909427	2.493809	2.268146
44	1	0	-0.881404	3.119277	0.623491
45	6	0	-1.792056	2.523801	0.573029
46	6	0	-1.869678	1.393138	1.311373

47	1	0	-1.106653	1.149910	2.049354
48	1	0	-2.799485	0.832637	1.364451
49	6	0	-2.893193	3.084107	-0.266612
50	1	0	-2.545717	3.325425	-1.277229
51	1	0	-3.754750	2.413488	-0.327936
52	1	0	-3.226405	4.031200	0.179785

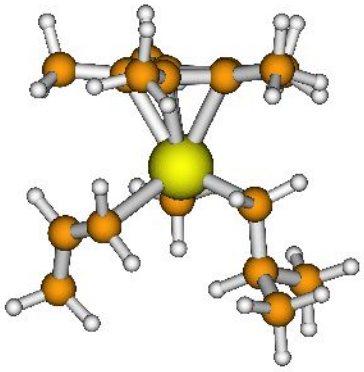
Cartesian Coordinates for **TS-8,9**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.233035	0.043205	-0.275534
2	6	0	-3.518487	-1.305049	-0.910714
3	6	0	-0.506523	1.133766	-2.018636
4	6	0	2.030002	0.613032	-0.691551
5	6	0	1.928361	-0.816938	-0.732428
6	6	0	1.596027	-1.275073	0.578342
7	6	0	1.445057	-0.134986	1.419255
8	6	0	1.722324	1.032819	0.637879
9	6	0	-0.992717	-1.762648	-0.963048
10	6	0	-2.235695	-1.573950	-0.102932
11	6	0	-2.433850	-2.693856	0.933190
12	1	0	-3.392090	-0.480310	-1.620701
13	1	0	-3.779771	-2.199725	-1.486376
14	1	0	-4.362402	-1.067276	-0.253653
15	1	0	-0.187314	2.180396	-2.008151
16	1	0	-0.055311	0.640545	-2.886972
17	1	0	-1.603478	1.094478	-2.140099
18	1	0	-0.470464	-2.701934	-0.792521
19	1	0	-1.173992	-1.624654	-2.035184
20	1	0	-2.100648	-0.635059	0.526985
21	1	0	-1.532167	-2.858445	1.531809
22	1	0	-3.260400	-2.463308	1.613792
23	1	0	-2.669948	-3.631725	0.418944
24	6	0	2.260315	-1.679903	-1.916522
25	1	0	3.336111	-1.899183	-1.935436
26	1	0	1.733960	-2.637755	-1.889676
27	1	0	2.014707	-1.188283	-2.862403
28	6	0	2.584384	1.481988	-1.784052
29	1	0	2.213859	2.509306	-1.728444
30	1	0	3.678273	1.526170	-1.701760
31	1	0	2.350325	1.096119	-2.779513
32	6	0	1.559051	-2.702830	1.042582
33	1	0	1.356536	-3.401960	0.227680
34	1	0	2.535136	-2.977020	1.464784
35	1	0	0.815660	-2.868732	1.828450
36	6	0	1.200123	-0.185763	2.905844
37	1	0	2.111867	-0.508701	3.424948
38	1	0	0.934114	0.791838	3.317820
39	1	0	0.412438	-0.896021	3.181984
40	6	0	1.854862	2.438645	1.159542
41	1	0	2.878801	2.608495	1.517655
42	1	0	1.664401	3.186343	0.383771
43	1	0	1.189341	2.643895	2.003712
44	1	0	-0.710117	3.152161	0.450928
45	6	0	-1.648230	2.609622	0.557663
46	6	0	-1.704643	1.578053	1.429092

47	1	0	-0.878982	1.359619	2.103019
48	1	0	-2.649910	1.085084	1.642423
49	6	0	-2.803219	3.132023	-0.234975
50	1	0	-2.547220	3.242005	-1.294611
51	1	0	-3.692001	2.501539	-0.140458
52	1	0	-3.055403	4.137860	0.127816

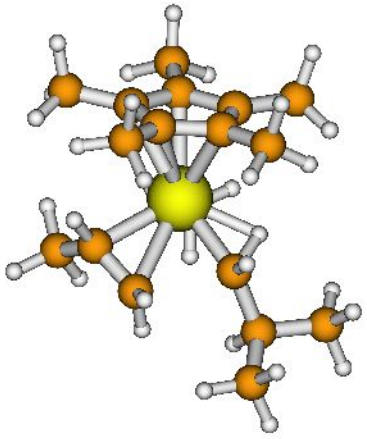
Cartesian Coordinates for **9**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.141201	0.170248	-0.094258
2	6	0	-3.412067	-1.389151	-1.302824
3	6	0	-0.544610	0.743329	-2.047003
4	6	0	2.046928	-0.174385	-0.968943
5	6	0	1.475013	-1.458529	-0.701563
6	6	0	1.279113	-1.579518	0.708230
7	6	0	1.698764	-0.355280	1.312055
8	6	0	2.175573	0.511181	0.278015
9	6	0	-1.614326	-1.151137	0.478052
10	6	0	-3.001339	-0.669400	-0.009887
11	6	0	-4.062464	-0.866252	1.092176
12	1	0	-2.674230	-1.253721	-2.100799
13	1	0	-3.516198	-2.465901	-1.121452
14	1	0	-4.375391	-1.018901	-1.669433
15	1	0	0.105246	1.530081	-2.446841
16	1	0	-0.509958	-0.107967	-2.738242
17	1	0	-1.581606	1.114080	-2.022808
18	1	0	-1.483753	-0.941548	1.563379
19	1	0	-1.510731	-2.232647	0.361728
20	1	0	-2.976547	0.414645	-0.228882
21	1	0	-3.809937	-0.310839	2.003906
22	1	0	-5.046469	-0.524472	0.751004
23	1	0	-4.146377	-1.925911	1.359659
24	6	0	1.210240	-2.533550	-1.717134
25	1	0	2.077329	-3.203103	-1.792681
26	1	0	0.347331	-3.150079	-1.447705
27	1	0	1.032716	-2.121195	-2.714026
28	6	0	2.587447	0.291598	-2.290471
29	1	0	2.592477	1.382222	-2.375239
30	1	0	3.625113	-0.047261	-2.407509
31	1	0	2.019266	-0.106853	-3.134898
32	6	0	0.890322	-2.825452	1.449937
33	1	0	0.344487	-3.529178	0.816611
34	1	0	1.792988	-3.341638	1.802281
35	1	0	0.274860	-2.615445	2.330355
36	6	0	1.743603	-0.099145	2.795785
37	1	0	2.594794	-0.629363	3.242332
38	1	0	1.873421	0.960875	3.033105
39	1	0	0.845049	-0.457268	3.310931
40	6	0	2.831899	1.852714	0.472700
41	1	0	3.917442	1.728840	0.580068
42	1	0	2.673897	2.519821	-0.380846
43	1	0	2.483419	2.362833	1.376224
44	1	0	0.427540	3.410428	0.309350
45	6	0	-0.604632	3.068242	0.388936
46	6	0	-0.890007	2.092928	1.285509

47	1	0	-0.141666	1.773917	2.012542
48	1	0	-1.919877	1.789768	1.470499
49	6	0	-1.594794	3.764233	-0.482421
50	1	0	-1.276588	3.756415	-1.531243
51	1	0	-2.598758	3.338732	-0.401922
52	1	0	-1.640842	4.820619	-0.182675

Cartesian Coordinates for **TS-9,10**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	0.003443	0.226068	-0.348484
2	6	0	-3.879201	-1.534000	-0.767962
3	6	0	-0.158979	0.124507	-2.410596
4	6	0	2.158964	-0.733814	-0.670445
5	6	0	1.305445	-1.722436	-0.099371
6	6	0	0.935358	-1.285732	1.217377
7	6	0	1.570632	-0.034531	1.460771
8	6	0	2.308619	0.323650	0.289767
9	6	0	-1.998002	-0.204027	0.252685
10	6	0	-3.415582	-0.126087	-0.337303
11	6	0	-4.423066	0.478462	0.655347
12	1	0	-3.216931	-1.965137	-1.527877
13	1	0	-3.915478	-2.218943	0.087758
14	1	0	-4.886108	-1.482286	-1.195553
15	1	0	0.607355	0.721902	-2.920580
16	1	0	-0.157721	-0.880518	-2.846591
17	1	0	-1.141947	0.586740	-2.611225
18	1	0	-2.021381	-0.532597	1.297579
19	1	0	-1.453518	-1.034107	-0.316584
20	1	0	-3.386793	0.499343	-1.241402
21	1	0	-4.169598	1.498875	0.958037
22	1	0	-5.419092	0.511262	0.202703
23	1	0	-4.490337	-0.136493	1.561323
24	6	0	0.949726	-3.045481	-0.720752
25	1	0	1.711143	-3.795269	-0.468316
26	1	0	-0.008757	-3.430688	-0.359390
27	1	0	0.901863	-2.989371	-1.811793
28	6	0	2.903668	-0.851659	-1.970286
29	1	0	3.111981	0.124381	-2.418297
30	1	0	3.870575	-1.344327	-1.804305
31	1	0	2.357206	-1.447293	-2.705977
32	6	0	0.148717	-2.084242	2.222092
33	1	0	-0.603738	-2.723470	1.749559
34	1	0	0.818903	-2.744641	2.787434
35	1	0	-0.359523	-1.446233	2.952186
36	6	0	1.537251	0.715807	2.764156
37	1	0	2.212440	0.240097	3.487111
38	1	0	1.868746	1.752074	2.656719
39	1	0	0.540781	0.722756	3.219718
40	6	0	3.228598	1.504552	0.142734
41	1	0	4.242691	1.234630	0.465263
42	1	0	3.304583	1.841592	-0.895649
43	1	0	2.915986	2.357387	0.751974
44	1	0	0.478084	2.532725	1.054460
45	6	0	-0.186595	2.370397	0.210097
46	6	0	-1.495238	1.966548	0.513776

47	1	0	-1.801304	1.853017	1.548515
48	1	0	-2.294865	2.199110	-0.183012
49	6	0	0.125342	3.183648	-1.041579
50	1	0	1.125740	2.985143	-1.439917
51	1	0	-0.602433	3.011752	-1.840566
52	1	0	0.091749	4.251709	-0.789698

Bader Analysis:

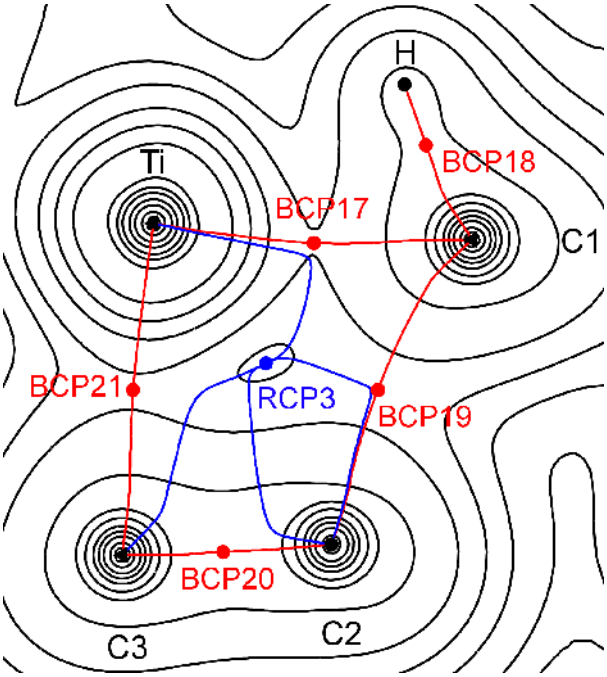


*Figure S50: Electron density map of **TS-9,10**: Ti, C(1), C(2) and C(3) in plane, H out of plane, view from the top*

	$\rho(\boldsymbol{r})$	$\nabla\rho(\boldsymbol{r})$
BCP17	0.0811	-0.05049
BCP18	0.2348	0.15098
BCP19	0.0588	-0.01152
BCP20	0.3058	0.20190
BCP21	0.0715	-0.03351
RCP3	0.0375	-0.03566

NBO Analysis:

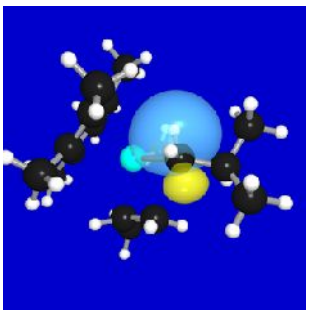


Figure S51: C(1)-H bond, 58.35% C($sp^{4.06}$) and 41.65% H(s)

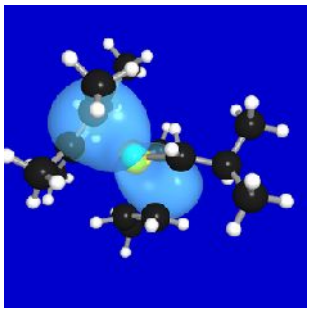


Figure S52: empty Ti($sd^{22.04}$) orbital

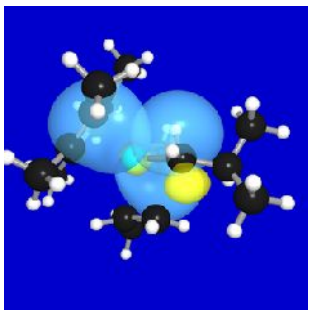


Figure S53: C(1)-H -> Ti($sd^{22.04}$), 47.06 kJ/mol

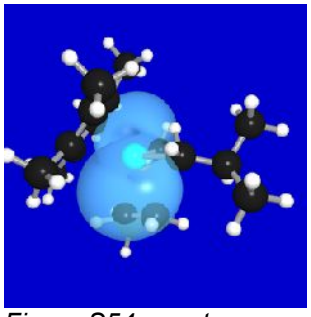


Figure S54: empty Ti($sd^{0.99}$) orbital

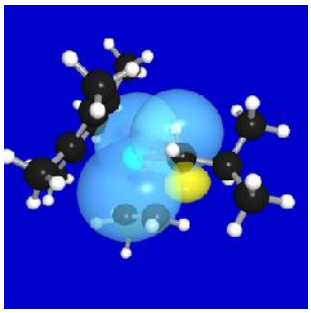


Figure S55: C(1)H -> Ti($sd^{0.99}$); 57.48 kJ/mol

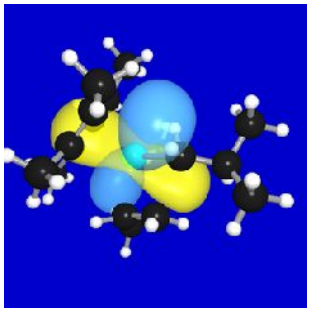


Figure S56: empty Ti($sp^{2.21}d^{99.99}$) orbital

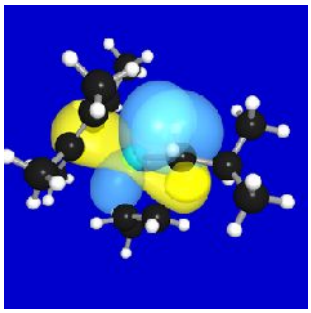
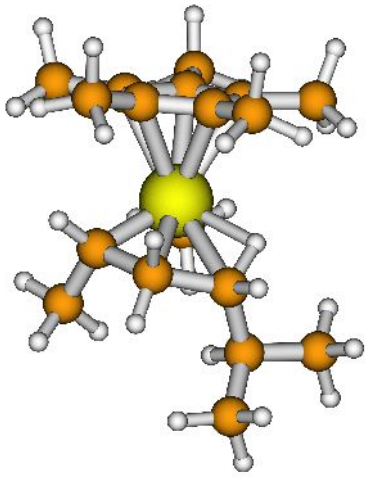


Figure 57: C(1)H -> Ti($sp^{2.21}d^{99.99}$); 32.15 kJ/mol

Cartesian Coordinates for **10**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.030679	-0.079390	-0.396234
2	6	0	3.492146	1.979501	-0.383402
3	6	0	0.149301	0.497808	-2.376935
4	6	0	-2.216502	0.767765	-0.651289
5	6	0	-1.585033	1.494797	0.400699
6	6	0	-1.323105	0.585445	1.477193
7	6	0	-1.803543	-0.704445	1.094442
8	6	0	-2.322359	-0.601583	-0.230089
9	6	0	2.124902	0.196901	0.771680
10	6	0	3.264457	0.465658	-0.245212
11	6	0	4.561321	-0.243808	0.178598
12	1	0	2.597863	2.496247	-0.754504
13	1	0	3.767324	2.426447	0.580026
14	1	0	4.305025	2.183683	-1.086788
15	1	0	-0.389578	-0.210953	-3.022527
16	1	0	-0.161779	1.511304	-2.646764
17	1	0	1.224396	0.393431	-2.601386
18	1	0	2.473334	0.493255	1.768716
19	1	0	1.330425	0.994347	0.632918
20	1	0	2.975989	0.075220	-1.229864
21	1	0	4.458433	-1.333390	0.213764
22	1	0	5.358684	-0.018496	-0.536345
23	1	0	4.892862	0.099917	1.166087
24	6	0	-1.300952	2.972684	0.394068
25	1	0	-2.198137	3.533552	0.686973
26	1	0	-0.509943	3.246099	1.098742
27	1	0	-1.008703	3.331294	-0.598126
28	6	0	-2.836948	1.354833	-1.886945
29	1	0	-2.788301	0.674176	-2.741336
30	1	0	-3.897372	1.569238	-1.700787
31	1	0	-2.362394	2.295112	-2.179280
32	6	0	-0.780852	0.947915	2.834711
33	1	0	-0.143991	1.836953	2.806233
34	1	0	-1.607538	1.169415	3.522035
35	1	0	-0.205764	0.132484	3.285372
36	6	0	-1.875877	-1.911342	1.984999
37	1	0	-2.735638	-1.821890	2.661707
38	1	0	-2.011347	-2.834833	1.416614
39	1	0	-0.988438	-2.026894	2.616188
40	6	0	-2.966404	-1.706179	-1.020464
41	1	0	-4.048025	-1.726627	-0.831671
42	1	0	-2.831463	-1.570102	-2.097636
43	1	0	-2.570127	-2.689491	-0.752116
44	1	0	0.075430	-2.728637	0.380890
45	6	0	0.665767	-1.966563	-0.125725
46	6	0	1.609362	-1.288352	0.934677

47	1	0	1.147713	-1.369349	1.922075
48	1	0	2.529459	-1.882062	0.965669
49	6	0	1.368677	-2.559087	-1.353178
50	1	0	0.639045	-3.038529	-2.013636
51	1	0	1.919652	-1.826512	-1.952713
52	1	0	2.091692	-3.329513	-1.048369

Bader Analysis:

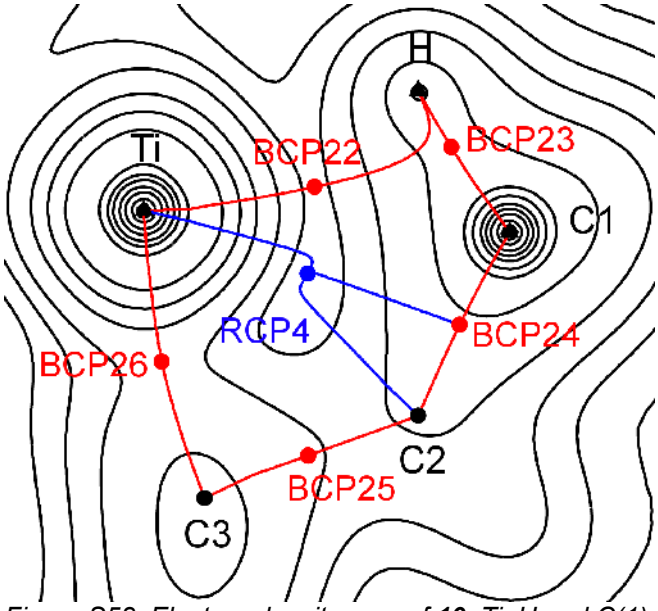


*Figure S58: Electron density map of **10**: Ti, H and C(1) in plane, C(2) and C(3) out of plane, view from the top*

	$\rho(\boldsymbol{r})$	$\nabla\rho(\boldsymbol{r})$
BCP22	0.0368	-0.04175
BCP23	0.2403	0.16065
BCP24	0.2184	0.10794
BCP25	0.2189	0.10402
BCP26	0.1171	-0.03133
RCP4	0.0311	-0.04020

NBO Analysis:

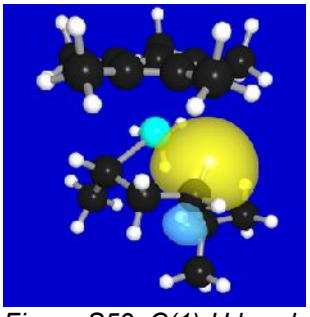


Figure S59: C(1)-H bond, 58.41% C(1)($sp^{3.78}$) and 41.59% H(s)

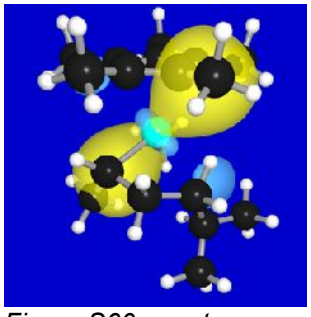


Figure S60: empty Ti($sd^{9.48}$) orbital

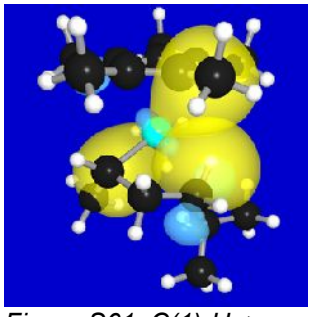


Figure S61: C(1)-H -> Ti($sd^{9.48}$), 39.31 kJ/mol

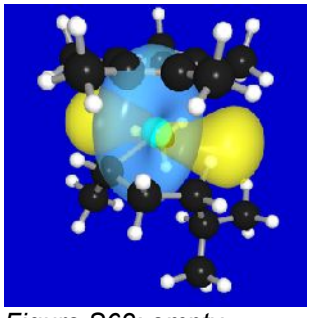


Figure S62: empty Ti($sd^{13.96}$) orbital

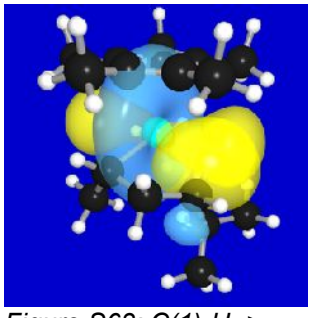
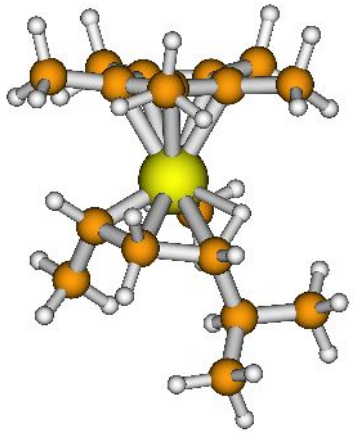


Figure S63: C(1)-H -> Ti($sd^{13.96}$); 79.42 kJ/mol

Cartesian Coordinates for **TS-10,11**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.015681	-0.118347	-0.384644
2	6	0	3.400898	1.974722	-0.483864
3	6	0	0.178143	0.363983	-2.390471
4	6	0	-1.995925	1.209378	-0.437138
5	6	0	-1.388749	1.369546	0.846557
6	6	0	-1.431922	0.107717	1.522728
7	6	0	-2.027190	-0.845031	0.645395
8	6	0	-2.361481	-0.163062	-0.574685
9	6	0	2.127692	0.191172	0.783839
10	6	0	3.251796	0.462995	-0.250805
11	6	0	4.583217	-0.148886	0.216992
12	1	0	2.484812	2.418426	-0.894549
13	1	0	3.641405	2.496216	0.450963
14	1	0	4.209849	2.177176	-1.192312
15	1	0	-0.330597	-0.408117	-2.986636
16	1	0	-0.166726	1.344247	-2.729616
17	1	0	1.257031	0.283682	-2.603882
18	1	0	2.485236	0.505151	1.772236
19	1	0	1.317511	0.972832	0.650905
20	1	0	2.987168	-0.005266	-1.207847
21	1	0	4.529682	-1.234745	0.348639
22	1	0	5.364640	0.048855	-0.523283
23	1	0	4.904304	0.294214	1.167540
24	6	0	-0.918242	2.676356	1.429895
25	1	0	-1.769149	3.235295	1.841023
26	1	0	-0.206075	2.532626	2.247920
27	1	0	-0.448839	3.320635	0.679040
28	6	0	-2.301413	2.321217	-1.400085
29	1	0	-2.439838	1.957012	-2.420743
30	1	0	-3.232341	2.821952	-1.103311
31	1	0	-1.517069	3.084555	-1.416337
32	6	0	-1.033457	-0.130963	2.954201
33	1	0	-0.144130	0.437678	3.246452
34	1	0	-1.843690	0.184640	3.624255
35	1	0	-0.844484	-1.188122	3.160450
36	6	0	-2.438304	-2.247835	0.993270
37	1	0	-3.468555	-2.252862	1.372535
38	1	0	-2.409926	-2.912826	0.125201
39	1	0	-1.808303	-2.684963	1.773267
40	6	0	-3.087888	-0.780807	-1.736726
41	1	0	-4.165217	-0.817642	-1.527574
42	1	0	-2.952810	-0.208016	-2.657130
43	1	0	-2.764499	-1.809253	-1.926765
44	1	0	0.079197	-2.739230	0.487658
45	6	0	0.666920	-2.000166	-0.053486
46	6	0	1.644135	-1.303175	0.966266

47	1	0	1.225394	-1.392184	1.970540
48	1	0	2.575065	-1.880535	0.952893
49	6	0	1.340477	-2.640767	-1.273843
50	1	0	0.593522	-3.123376	-1.912366
51	1	0	1.898679	-1.935845	-1.899323
52	1	0	2.051487	-3.416939	-0.955927

Bader Analysis:

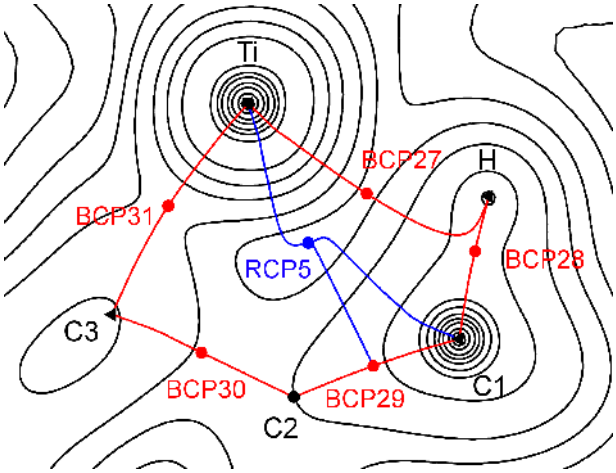


*Figure S64: Electron density map of **TS-10,11**: Ti, H and C(1) in plane, C(2) and C(3) out of plane, view from the top*

	$\rho(\boldsymbol{r})$	$\nabla\rho(\boldsymbol{r})$
BCP27	0.0373	-0.04241
BCP28	0.2409	0.16135
BCP29	0.2182	0.10763
BCP30	0.2180	0.10313
BCP31	0.1172	-0.03146
RCP5	0.0310	-0.04015

NBO Analysis:

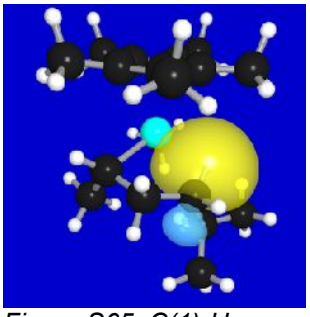


Figure S65: C(1)-H bond,58.47% C($sp^{3.75}$) and 41.53% H(s)

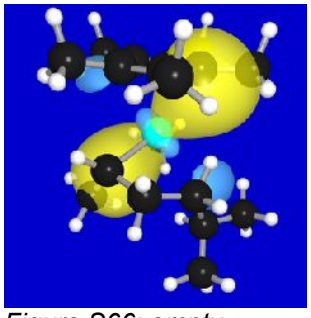


Figure S66: empty Ti($sd^{8.98}$) orbital

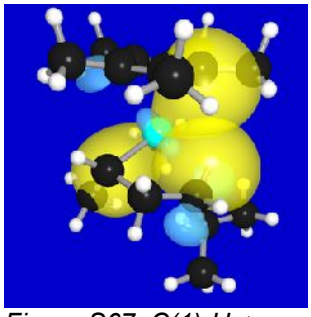


Figure S67: C(1)-H -> Ti(sd8.98);37.85 KJ/mol

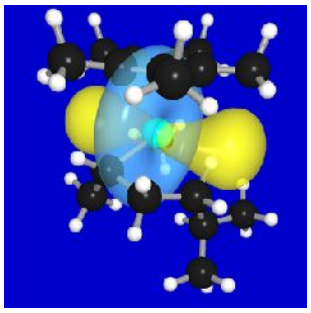


Figure S68: empty Ti($sd^{13.96}$) orbital

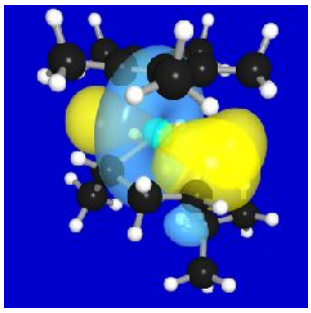
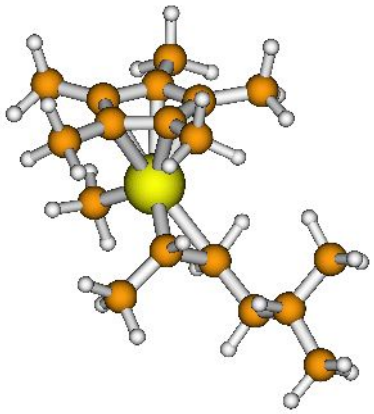


Figure S69: C(1)-H -> Ti($sd^{13.96}$); 79.47 kJ/mol

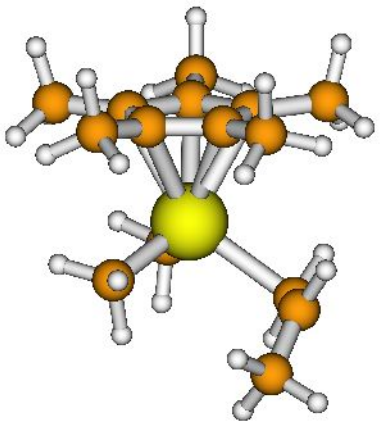
Cartesian Coordinates for **11**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.596297	-0.471932	-0.586971
2	6	0	5.524708	-0.101516	-0.037419
3	6	0	-1.486395	-1.978093	-1.702935
4	6	0	-2.792889	-0.052164	0.152160
5	6	0	-2.353930	1.069169	-0.607818
6	6	0	-1.247223	1.671363	0.081171
7	6	0	-1.022165	0.936951	1.287895
8	6	0	-1.942836	-0.152071	1.311148
9	6	0	3.252952	-0.593474	-0.980676
10	6	0	4.020665	0.185968	0.103670
11	6	0	3.751187	1.696742	0.042957
12	1	0	5.738492	-1.173012	0.046179
13	1	0	5.903713	0.242877	-1.007616
14	1	0	6.092759	0.414850	0.743329
15	1	0	-1.859749	-2.780439	-1.051083
16	1	0	-2.301878	-1.676079	-2.368850
17	1	0	-0.677325	-2.406824	-2.319692
18	1	0	3.539935	-0.215424	-1.970841
19	1	0	3.546741	-1.649310	-0.951979
20	1	0	3.702035	-0.184294	1.088620
21	1	0	2.694222	1.944049	0.208467
22	1	0	4.326714	2.223757	0.811000
23	1	0	4.044011	2.109875	-0.930783
24	6	0	-2.967163	1.566688	-1.889023
25	1	0	-3.745861	2.309419	-1.670921
26	1	0	-2.235776	2.058900	-2.538565
27	1	0	-3.438992	0.761609	-2.459353
28	6	0	-4.020440	-0.877975	-0.104983
29	1	0	-3.915054	-1.902393	0.262776
30	1	0	-4.879937	-0.433463	0.413489
31	1	0	-4.272073	-0.927288	-1.167422
32	6	0	-0.548473	2.943797	-0.327034
33	1	0	-0.479265	3.053936	-1.414320
34	1	0	-1.106069	3.813773	0.043773
35	1	0	0.462480	3.012353	0.084694
36	6	0	-0.059238	1.310763	2.377871
37	1	0	-0.511752	2.070874	3.028074
38	1	0	0.196759	0.457237	3.010837
39	1	0	0.871203	1.736371	1.988845
40	6	0	-2.087738	-1.170046	2.408125
41	1	0	-2.837569	-0.835932	3.137393
42	1	0	-2.422250	-2.139838	2.027118
43	1	0	-1.151353	-1.324347	2.950736
44	1	0	1.397300	-0.644054	1.277113
45	6	0	1.060864	-1.168010	0.381922
46	6	0	1.701261	-0.558103	-0.887545

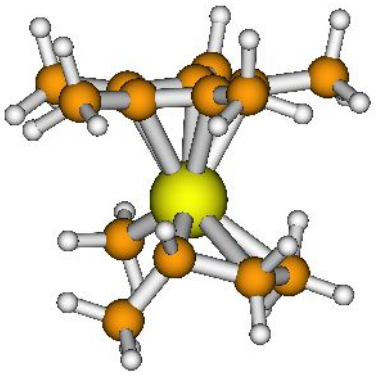
47	1	0	1.340287	-1.087896	-1.794741
48	1	0	1.401083	0.516063	-0.996805
49	6	0	1.206905	-2.682888	0.515790
50	1	0	0.644845	-3.051094	1.380273
51	1	0	0.853527	-3.226473	-0.368608
52	1	0	2.257017	-2.967899	0.670583

Cartesian Coordinates for **TS-1,12**



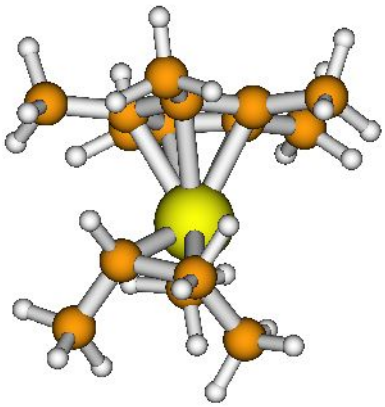
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.429743
3	6	0	1.357917	0.000000	1.882515
4	6	0	2.198886	-0.012138	0.728313
5	6	0	1.362525	-0.018130	-0.432626
6	22	0	0.963710	-2.044953	0.736434
7	6	0	-0.815682	-2.864004	0.087531
8	6	0	-1.213959	0.085543	2.309917
9	6	0	3.699634	0.107265	0.752818
10	6	0	1.815705	0.062949	-1.866734
11	6	0	1.814309	0.174013	3.302710
12	6	0	-1.201445	0.164548	-0.886175
13	6	0	1.184889	-2.877792	2.611733
14	6	0	2.346140	-3.466917	-0.683173
15	6	0	3.525424	-3.406378	-0.017116
16	6	0	4.031051	-4.424996	0.946764
17	1	0	1.129407	-3.961896	2.411055
18	1	0	3.306213	-5.220109	1.138966
19	1	0	2.130866	-2.658605	3.120037
20	1	0	-1.718496	-2.510959	0.596674
21	1	0	4.943483	-4.876318	0.532340
22	1	0	-0.692655	-3.935629	0.320998
23	1	0	0.360288	-2.621375	3.288278
24	1	0	1.706444	-4.346589	-0.605777
25	1	0	1.166201	-0.505846	-2.540806
26	1	0	-0.962053	-2.753059	-0.995320
27	1	0	2.842164	-0.290327	-2.003095
28	1	0	2.134955	-2.771384	-1.498428
29	1	0	4.187005	-2.562539	-0.212843
30	1	0	4.155896	-0.177840	-0.199417
31	1	0	4.325365	-3.961525	1.896200
32	1	0	-1.449027	1.137977	2.518119
33	1	0	1.790137	1.105060	-2.210824
34	1	0	-1.052654	-0.283375	-1.872920
35	1	0	-1.404752	1.232047	-1.042239
36	1	0	-1.060543	-0.406398	3.274642
37	1	0	-2.101145	-0.276625	-0.449970
38	1	0	-2.097262	-0.354976	1.839986
39	1	0	4.155354	-0.491500	1.548710
40	1	0	3.986839	1.150109	0.940358
41	1	0	2.810541	-0.245443	3.469732
42	1	0	1.866170	1.242483	3.549651
43	1	0	1.130076	-0.291275	4.017158

Cartesian Coordinates for **12**



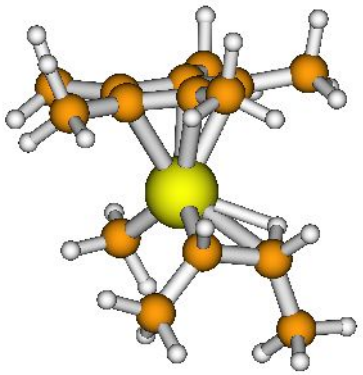
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.872178	0.176825	-0.485357
2	6	0	-1.244779	1.327084	0.095138
3	6	0	-0.573179	0.913006	1.287097
4	6	0	-0.740143	-0.495303	1.419868
5	6	0	-1.562353	-0.951514	0.326884
6	22	0	0.461326	-0.182968	-0.580461
7	6	0	2.208015	-0.296432	0.468031
8	6	0	3.075284	-1.491676	0.051102
9	6	0	-1.414717	2.747235	-0.381369
10	6	0	0.108494	1.818729	2.273581
11	6	0	-0.299347	-1.337003	2.584785
12	6	0	-2.129478	-2.336267	0.189207
13	6	0	-2.754028	0.187397	-1.703191
14	6	0	0.293239	-1.809054	-1.852342
15	6	0	1.898667	1.369391	-1.622891
16	6	0	2.592258	1.038089	-0.247009
17	1	0	0.410546	-2.739870	-1.279987
18	1	0	-0.617261	-1.885517	-2.454240
19	1	0	1.156316	-1.734879	-2.536478
20	1	0	0.814335	1.644775	-1.584706
21	1	0	2.334114	2.288450	-2.024633
22	1	0	2.053902	0.593870	-2.387476
23	1	0	2.438707	1.890369	0.419255
24	1	0	3.660002	0.992511	-0.491852
25	1	0	2.222774	-0.158904	1.548289
26	1	0	4.118926	-1.329453	0.356061
27	1	0	2.732883	-2.413946	0.531400
28	1	0	3.084982	-1.668506	-1.031367
29	1	0	0.492739	2.731418	1.807604
30	1	0	-0.606523	2.133577	3.044952
31	1	0	0.935926	1.325197	2.791735
32	1	0	-3.762413	0.528407	-1.434361
33	1	0	-2.386978	0.866092	-2.480943
34	1	0	-2.854225	-0.806709	-2.145011
35	1	0	-2.312651	3.188086	0.070681
36	1	0	-0.572182	3.387399	-0.101860
37	1	0	-1.544918	2.809494	-1.466598
38	1	0	0.575842	-0.918015	3.088180
39	1	0	-1.104210	-1.396564	3.329364
40	1	0	-0.060340	-2.362973	2.289127
41	1	0	-1.440818	-3.102551	0.556411
42	1	0	-3.050664	-2.418528	0.780606
43	1	0	-2.382512	-2.580973	-0.845210

Cartesian Coordinates for **TS-12,13**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	0.457894	-0.173039	-0.492185
2	6	0	0.460124	-1.883978	-1.668050
3	6	0	2.792190	0.829026	-1.679871
4	6	0	-1.321226	1.325212	-0.131624
5	6	0	-0.780504	1.037672	1.161495
6	6	0	-0.927064	-0.359434	1.398290
7	6	0	-1.622752	-0.931291	0.271117
8	6	0	-1.872781	0.114155	-0.663970
9	6	0	2.439300	1.063528	-0.194787
10	6	0	2.116562	-0.183318	0.693070
11	6	0	3.082149	-1.361468	0.577432
12	1	0	0.454730	-2.752354	-0.992424
13	1	0	-0.361486	-2.004219	-2.381924
14	1	0	1.410099	-1.910369	-2.224424
15	1	0	1.983241	0.375894	-2.287975
16	1	0	3.021593	1.782328	-2.163941
17	1	0	3.651597	0.162399	-1.785993
18	1	0	1.601596	1.797670	-0.130971
19	1	0	3.259264	1.614245	0.281106
20	1	0	2.021186	0.142263	1.729844
21	1	0	4.102559	-1.065747	0.861864
22	1	0	2.776493	-2.162532	1.258075
23	1	0	3.135507	-1.790775	-0.428444
24	6	0	-0.220498	2.040921	2.130305
25	1	0	0.160637	2.937309	1.632041
26	1	0	-1.009522	2.371135	2.818360
27	1	0	0.582418	1.624094	2.745274
28	6	0	-2.622461	-0.005385	-1.961953
29	1	0	-3.650013	0.359969	-1.835839
30	1	0	-2.172191	0.589204	-2.764581
31	1	0	-2.683855	-1.040792	-2.304521
32	6	0	-1.413771	2.683227	-0.780209
33	1	0	-2.366619	3.162120	-0.519167
34	1	0	-0.617952	3.359125	-0.452334
35	1	0	-1.380540	2.625260	-1.873297
36	6	0	-0.576349	-1.091904	2.663134
37	1	0	0.213928	-0.586882	3.224666
38	1	0	-1.454298	-1.153814	3.319463
39	1	0	-0.248248	-2.117064	2.466606
40	6	0	-2.139330	-2.340293	0.197641
41	1	0	-1.479305	-3.047781	0.707695
42	1	0	-3.119240	-2.400703	0.688743
43	1	0	-2.266783	-2.683138	-0.831958

Cartesian Coordinates for **13**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	0.353621	-0.356527	-0.437748
2	6	0	0.214627	-2.037019	-1.629536
3	6	0	3.752763	0.542173	-1.184064
4	6	0	-1.013677	1.509651	-0.046981
5	6	0	-0.712499	0.953636	1.237524
6	6	0	-1.231452	-0.374010	1.266696
7	6	0	-1.923002	-0.621440	0.025449
8	6	0	-1.781815	0.543714	-0.782291
9	6	0	2.511142	0.800412	-0.318730
10	6	0	2.079329	-0.271540	0.684759
11	6	0	2.793776	-1.628506	0.658486
12	1	0	0.190723	-2.966204	-1.041935
13	1	0	-0.596060	-2.074974	-2.364341
14	1	0	1.176693	-2.025404	-2.179303
15	1	0	3.669724	-0.377304	-1.770911
16	1	0	3.921650	1.373269	-1.875271
17	1	0	4.633897	0.451959	-0.541563
18	1	0	1.666112	1.023829	-1.076571
19	1	0	2.578902	1.773135	0.177986
20	1	0	2.024239	0.129238	1.696021
21	1	0	3.856178	-1.515761	0.914989
22	1	0	2.354123	-2.301397	1.402305
23	1	0	2.758958	-2.138531	-0.310717
24	6	0	-0.723404	2.923100	-0.482593
25	1	0	-1.537396	3.587306	-0.164266
26	1	0	0.198290	3.312882	-0.039985
27	1	0	-0.643045	3.016712	-1.569841
28	6	0	-0.058972	1.685369	2.374632
29	1	0	0.755240	2.337639	2.041804
30	1	0	-0.795076	2.326719	2.876406
31	1	0	0.339413	1.002884	3.129779
32	6	0	-1.158367	-1.333421	2.423393
33	1	0	-0.295163	-1.138181	3.065267
34	1	0	-2.057440	-1.241870	3.047018
35	1	0	-1.106416	-2.375457	2.092096
36	6	0	-2.763699	-1.828023	-0.282967
37	1	0	-3.778483	-1.683647	0.110189
38	1	0	-2.852784	-2.006001	-1.357567
39	1	0	-2.365300	-2.737565	0.175182
40	6	0	-2.364289	0.746675	-2.154498
41	1	0	-3.349632	1.224955	-2.076812
42	1	0	-1.745332	1.399152	-2.779047
43	1	0	-2.504431	-0.198405	-2.686135

Bader Analysis:

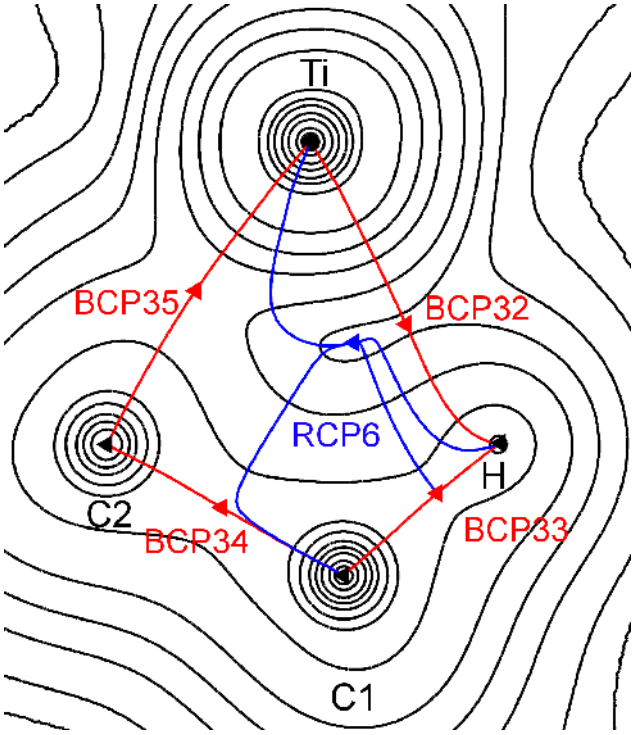


*Figure S70: Electron density map of **13**: Ti, H and C(1) in plane, C(2) out of plane, view from the top*

	$\rho(\boldsymbol{r})$	$\nabla\rho(\boldsymbol{r})$
BCP32	0.0386	-0.03954
BCP33	0.2244	0.13495
BCP34	0.2405	0.12675
BCP35	0.1116	-0.02865
RCP6	0.0367	-0.05163

NBO Analysis:

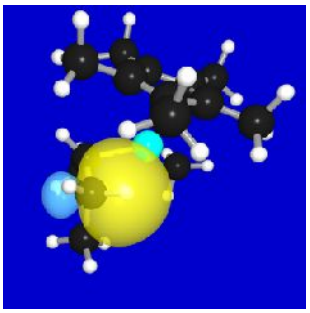


Figure S71: C(1)-H bond,56.77% C($sp^{4.57}$) and 43.23% H(s)

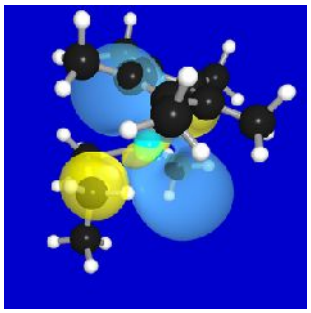


Figure S72: empty Ti($sd^{5.73}$) orbital

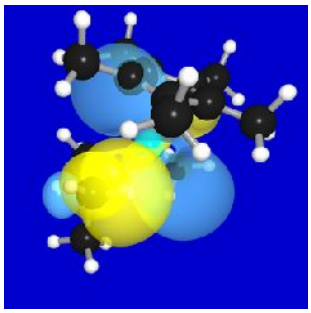


Figure S73: C(1)-H -> Ti($sd^{5.73}$); 75.70 kJ/mol

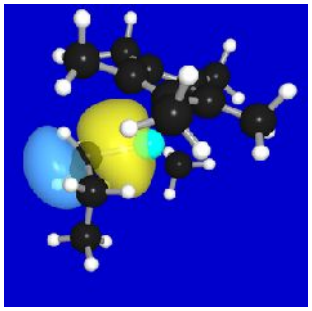


Figure S74: Ti-C(2) bond, 26.38% Ti($sd^{30.81}$) and C($sp^{6.52}$)

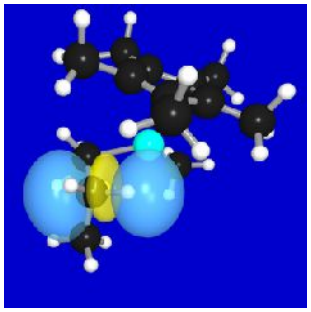


Figure S75: C(1)-H antibond, 43.23% C(1) ($sp^{4.57}$) and 56.77% H(s)

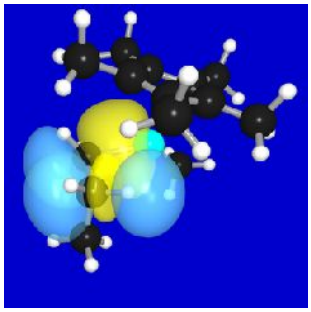
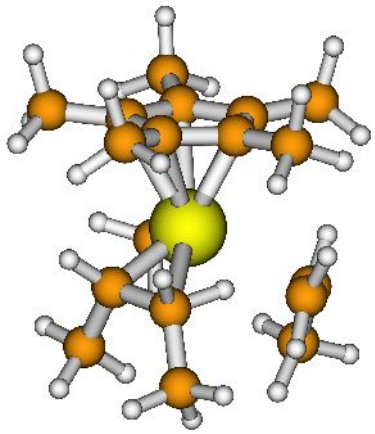


Figure S76: Ti-C(2) -> C(1)-H; 30.31 kJ/mol

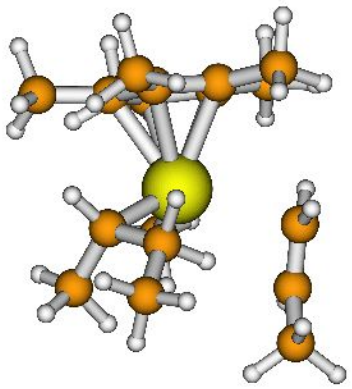
Cartesian Coordinates for **14**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	0.298376	0.028254	-0.241167
2	6	0	0.720991	1.138996	-1.956784
3	6	0	2.756265	-2.690668	0.852752
4	6	0	-1.414047	-0.076825	1.432919
5	6	0	-1.757519	-1.060806	0.454823
6	6	0	-1.987705	-0.390043	-0.781282
7	6	0	-1.834577	1.017287	-0.564714
8	6	0	-1.472082	1.206938	0.805269
9	6	0	1.334913	-2.152688	0.619669
10	6	0	0.889882	-1.886099	-0.823652
11	6	0	2.007418	-1.789881	-1.870127
12	1	0	0.191475	0.668736	-2.797291
13	1	0	0.470596	2.204124	-1.952876
14	1	0	1.798957	1.026568	-2.140396
15	1	0	3.527702	-2.029192	0.446601
16	1	0	2.947209	-2.816607	1.923441
17	1	0	2.872290	-3.668398	0.374593
18	1	0	1.269432	-1.208088	1.237458
19	1	0	0.608388	-2.804757	1.110500
20	1	0	0.124491	-2.589980	-1.149725
21	1	0	2.554073	-2.740570	-1.937760
22	1	0	1.596852	-1.574565	-2.860514
23	1	0	2.758600	-1.020200	-1.649664
24	6	0	-1.198995	-0.334048	2.902229
25	1	0	-2.164591	-0.387073	3.421872
26	1	0	-0.681505	-1.279568	3.091501
27	1	0	-0.627009	0.464378	3.385182
28	6	0	-2.028316	-2.515080	0.717630
29	1	0	-1.634060	-2.840841	1.683394
30	1	0	-3.112215	-2.687422	0.740054
31	1	0	-1.622369	-3.171837	-0.058768
32	6	0	-2.443779	-1.039168	-2.057165
33	1	0	-2.072758	-2.063838	-2.151865
34	1	0	-3.540761	-1.087541	-2.085287
35	1	0	-2.123844	-0.480515	-2.941487
36	6	0	-2.219158	2.097605	-1.534192
37	1	0	-3.293554	2.306158	-1.446716
38	1	0	-1.691251	3.036261	-1.343750
39	1	0	-2.028060	1.810619	-2.571336
40	6	0	-1.340972	2.536503	1.499589
41	1	0	-2.311118	2.840306	1.914310
42	1	0	-0.636934	2.508974	2.337556
43	1	0	-1.028277	3.330910	0.815382
44	1	0	1.336034	3.001742	0.652616
45	6	0	2.140312	2.272203	0.563334
46	6	0	2.065955	1.139291	1.300431

47	1	0	1.308513	1.031598	2.076493
48	1	0	2.898321	0.438105	1.323729
49	6	0	3.281668	2.659412	-0.317144
50	1	0	4.015268	1.856109	-0.430059
51	1	0	3.787198	3.525498	0.132496
52	1	0	2.937106	2.981748	-1.305514

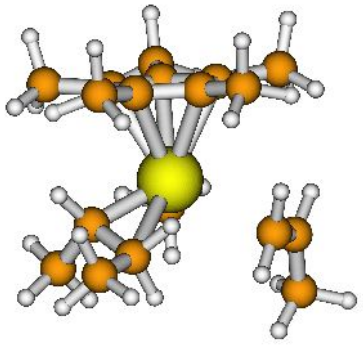
Cartesian Coordinates for **TS-14,15**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.177306	0.110915	-0.701794
2	6	0	-1.924451	1.107495	0.287458
3	6	0	-1.410086	0.457259	1.452552
4	6	0	-1.374753	-0.947412	1.192359
5	6	0	-1.829782	-1.162617	-0.141083
6	22	0	0.159643	0.126052	-0.331589
7	6	0	2.074605	-1.242613	0.714298
8	6	0	3.419158	-1.991279	0.849783
9	6	0	-2.275428	2.563832	0.144136
10	6	0	-1.109841	1.105684	2.779159
11	6	0	-1.048494	-2.018000	2.195836
12	6	0	-2.083295	-2.490219	-0.797374
13	6	0	-2.911831	0.323343	-1.994336
14	6	0	1.160480	-1.703747	-0.434778
15	6	0	1.870852	-1.922645	-1.775610
16	6	0	0.151169	0.779741	-2.301632
17	6	0	2.288330	2.452199	-0.347834
18	6	0	1.279892	2.336918	0.546548
19	1	0	-0.284884	0.043766	-2.986239
20	1	0	-0.340000	1.745177	-2.467883
21	1	0	1.219718	0.878670	-2.554212
22	1	0	4.041107	-1.866316	-0.040496
23	1	0	3.979526	-1.619761	1.713764
24	1	0	3.240212	-3.061586	0.993756
25	1	0	2.342063	-0.168627	0.596685
26	1	0	1.542266	-1.318880	1.671151
27	1	0	0.615282	-2.603747	-0.149723
28	1	0	2.560826	-2.775095	-1.715369
29	1	0	1.153737	-2.144241	-2.572203
30	1	0	2.464665	-1.057685	-2.097916
31	1	0	-1.977916	1.019055	3.445301
32	1	0	-0.266881	0.634354	3.295642
33	1	0	-0.889167	2.172144	2.681345
34	1	0	-0.435073	-1.640993	3.019208
35	1	0	-1.975002	-2.404867	2.640025
36	1	0	-0.530728	-2.871704	1.748310
37	1	0	-1.541096	-3.302767	-0.307846
38	1	0	-3.152195	-2.735622	-0.743905
39	1	0	-1.807030	-2.489163	-1.856716
40	1	0	-3.992509	0.227850	-1.824278
41	1	0	-2.735780	1.317198	-2.413953
42	1	0	-2.637952	-0.415492	-2.752603
43	1	0	-3.363824	2.692840	0.203368
44	1	0	-1.842449	3.178136	0.938387
45	1	0	-1.961009	2.977804	-0.820582
46	1	0	2.060151	2.883322	-1.322803

47	1	0	0.318876	2.800473	0.342920
48	6	0	3.718069	2.087206	-0.118774
49	1	0	3.893381	1.658761	0.871947
50	1	0	4.082055	1.393475	-0.887575
51	1	0	4.333011	2.992448	-0.215067
52	1	0	1.470749	2.011586	1.569038

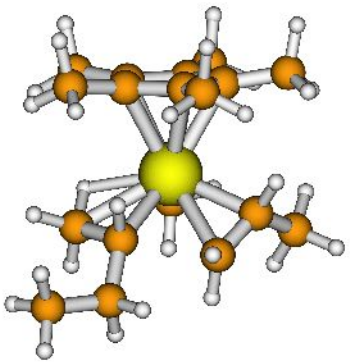
Cartesian Coordinates for **15**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.138495	0.318447	-0.219903
2	6	0	-1.178884	0.555085	-2.000282
3	6	0	2.632496	2.807427	1.169949
4	6	0	0.060267	-1.416467	1.437623
5	6	0	1.307367	-1.365601	0.744556
6	6	0	1.068019	-1.686922	-0.623266
7	6	0	-0.332727	-1.964143	-0.775456
8	6	0	-0.950220	-1.797726	0.502310
9	6	0	1.357851	2.224338	0.527742
10	6	0	1.611907	1.350675	-0.708927
11	6	0	1.678785	2.122041	-2.027673
12	1	0	-0.543946	0.231802	-2.834472
13	1	0	-2.154346	0.068412	-2.101371
14	1	0	-1.313204	1.645626	-2.088630
15	1	0	3.154382	3.441139	0.446626
16	1	0	2.391841	3.416036	2.047599
17	1	0	3.315394	2.009794	1.477722
18	1	0	0.668911	3.045474	0.284420
19	1	0	0.855048	1.638703	1.341876
20	1	0	2.528590	0.775513	-0.570665
21	1	0	2.529515	2.818891	-2.024630
22	1	0	1.820294	1.445429	-2.876662
23	1	0	0.778039	2.715895	-2.220635
24	6	0	-0.109122	-1.258059	2.926750
25	1	0	0.215716	-2.172500	3.439936
26	1	0	0.489908	-0.437215	3.336133
27	1	0	-1.151941	-1.091666	3.212329
28	6	0	2.645056	-1.146036	1.392615
29	1	0	2.599974	-0.418911	2.209794
30	1	0	3.006140	-2.088850	1.824429
31	1	0	3.403883	-0.811971	0.680758
32	6	0	2.105505	-1.866675	-1.694999
33	1	0	3.009610	-1.284348	-1.499197
34	1	0	2.405314	-2.921309	-1.755122
35	1	0	1.729616	-1.582409	-2.682348
36	6	0	-0.974146	-2.568063	-1.992111
37	1	0	-0.862371	-3.660025	-1.965557
38	1	0	-2.044508	-2.352782	-2.047869
39	1	0	-0.514167	-2.218274	-2.920091
40	6	0	-2.385172	-2.115922	0.824029
41	1	0	-2.487079	-3.182466	1.064522
42	1	0	-2.755650	-1.561784	1.692129
43	1	0	-3.051808	-1.918370	-0.020989
44	1	0	-3.358169	0.494888	0.435764
45	6	0	-2.867711	1.466283	0.488875
46	6	0	-1.815299	1.615009	1.325446

47	1	0	-1.557826	0.837163	2.043117
48	1	0	-1.367682	2.593849	1.479580
49	6	0	-3.473639	2.551313	-0.338806
50	1	0	-2.892377	3.477272	-0.305700
51	1	0	-4.480837	2.764121	0.045582
52	1	0	-3.601371	2.237694	-1.380750

Cartesian Coordinates for **TS-15,16**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.990673	0.221371	0.849462
2	6	0	-1.014825	-0.527317	1.586181
3	6	0	-0.654359	-1.664604	0.810704
4	6	0	-1.404681	-1.624767	-0.411740
5	6	0	-2.236554	-0.467946	-0.382019
6	22	0	0.055537	0.278001	-0.379119
7	6	0	1.544236	2.066772	0.387115
8	6	0	0.167853	2.358123	0.404017
9	6	0	-0.436531	3.368066	-0.565784
10	6	0	-0.534161	-0.218769	2.978762
11	6	0	0.243201	-2.789967	1.253118
12	6	0	-1.428901	-2.695108	-1.468766
13	6	0	-3.303953	-0.122910	-1.380846
14	6	0	-2.811655	1.364615	1.377919
15	6	0	-0.345237	0.703401	-2.378682
16	6	0	2.263941	-0.007340	-0.038202
17	6	0	2.009196	-0.958272	-1.214428
18	6	0	3.725889	0.455705	-0.031286
19	6	0	4.736971	-0.693639	0.121913
20	1	0	-0.540147	-0.147311	-3.039675
21	1	0	-1.176265	1.410552	-2.471250
22	1	0	0.576707	1.204758	-2.721135
23	1	0	4.718386	-1.381182	-0.729687
24	1	0	5.750510	-0.286495	0.191699
25	1	0	4.548275	-1.272040	1.034090
26	1	0	3.930987	0.998537	-0.964204
27	1	0	3.892018	1.163083	0.787402
28	1	0	2.031627	-0.501419	0.918250
29	1	0	2.413027	-1.949996	-0.983765
30	1	0	0.955178	-1.202709	-1.479637
31	1	0	2.464706	-0.574870	-2.131029
32	1	0	-1.203418	-0.674080	3.720535
33	1	0	0.468058	-0.615063	3.170138
34	1	0	-0.516425	0.855673	3.185914
35	1	0	1.026283	-2.457379	1.941293
36	1	0	-0.345554	-3.548141	1.785636
37	1	0	0.723615	-3.297830	0.411719
38	1	0	-0.481897	-3.239579	-1.536732
39	1	0	-2.204399	-3.436214	-1.234726
40	1	0	-1.658392	-2.291584	-2.458953
41	1	0	-4.249776	-0.603597	-1.098129
42	1	0	-3.491743	0.953696	-1.429853
43	1	0	-3.053745	-0.465873	-2.388160
44	1	0	-3.737666	0.978848	1.824011
45	1	0	-2.294459	1.926335	2.160592
46	1	0	-3.103609	2.067875	0.592639

47	1	0	-0.297049	2.342097	1.386871
48	1	0	2.053762	1.905826	1.330253
49	1	0	2.166681	2.471943	-0.406820
50	1	0	0.101732	3.400783	-1.517506
51	1	0	-0.374616	4.368301	-0.117514
52	1	0	-1.492762	3.176555	-0.776273

Bader Analysis:

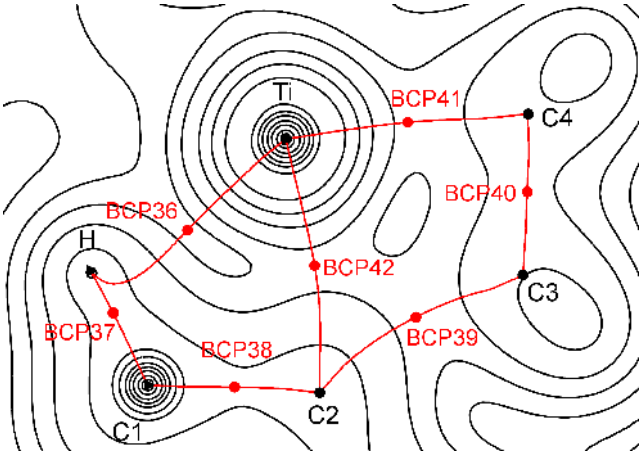


*Figure S77: Electron density map of **TS-15,16**: Ti, H and C(1) in plane, C(2), C(3) and C(4) out of plane, view from the top*

	$\rho(\boldsymbol{r})$	$\nabla\rho(\boldsymbol{r})$
BCP36	0.0351	-0.04169
BCP37	0.2534	0.18634
BCP38	0.2377	0.12586
BCP39	0.0601	-0.01046
BCP40	0.3046	0.20107
BCP41	0.0730	-0.03183
BCP42	0.06185	-0.03597

NBO Analysis:

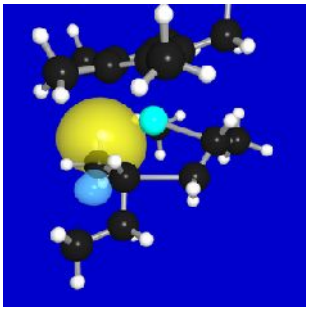


Figure S78: C(1)-H bond, 60.58% C(1)($sp^{3.35}$) and H(s)

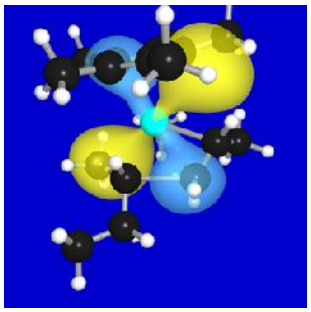


Figure S79: empty Ti($sp^{0.54}d^{99.99}$) orbital

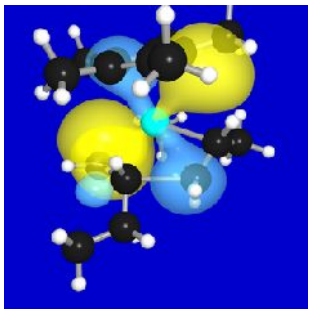


Figure S80: C(1)-H -> Ti($sp^{0.54}d^{99.99}$); 26.38 kJ/mol

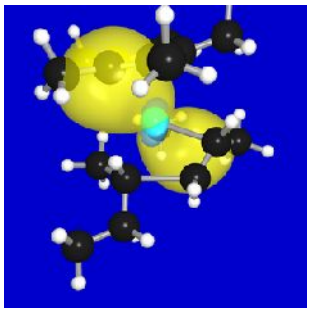


Figure S81: empty Ti($sd^{3.49}$) orbital

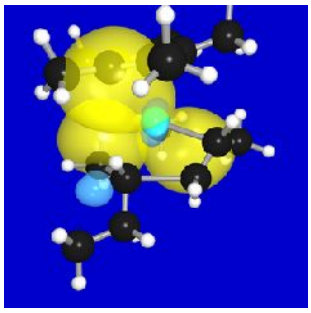


Figure S82: C(1)-H -> Ti($sd^{3.49}$); 22.40 kJ/mol

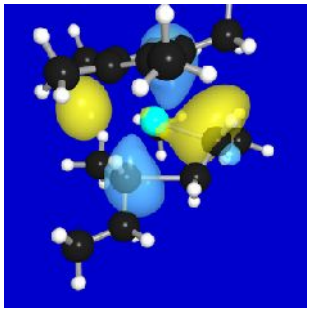


Figure S84: antibonding Ti-C(4) orbital, 76.13% Ti($sd^{8.41}$) and 23.87% C(4)($sp^{10.93}$)

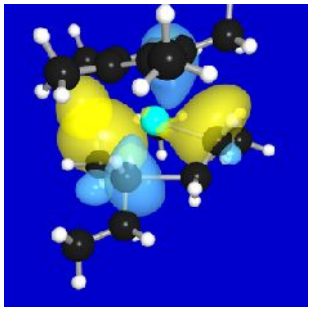
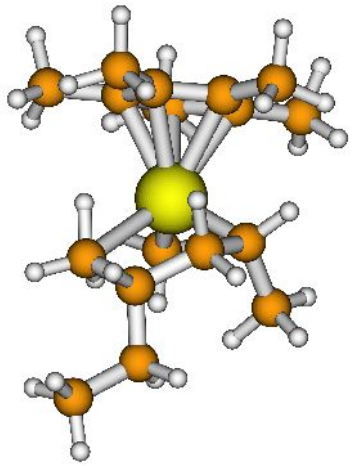


Figure S83: C(1)-H -> Ti-C(4); 26.63 kJ/mol

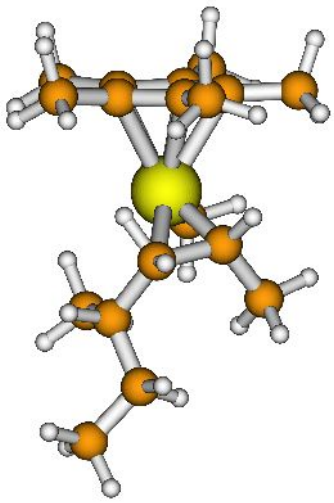
Cartesian Coordinates for **16**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	0.084502	-0.057950	-0.430043
2	6	0	0.162646	-0.322703	-2.492653
3	6	0	-5.047094	0.978795	-0.562142
4	6	0	1.663579	-0.440923	1.325510
5	6	0	1.408719	0.964076	1.248903
6	6	0	1.868625	1.430857	-0.024406
7	6	0	2.406040	0.317990	-0.738299
8	6	0	2.251492	-0.843692	0.088795
9	6	0	-4.032550	-0.120225	-0.221938
10	6	0	-2.806863	0.377655	0.573562
11	6	0	-1.963377	1.368831	-0.258318
12	1	0	0.567718	0.522736	-3.059879
13	1	0	0.746591	-1.216796	-2.746603
14	1	0	-0.872386	-0.503623	-2.823274
15	1	0	-4.639107	1.728115	-1.250636
16	1	0	-5.928788	0.547130	-1.045621
17	1	0	-5.386971	1.499308	0.341167
18	1	0	-3.709354	-0.618112	-1.144830
19	1	0	-4.530286	-0.890559	0.380390
20	1	0	-3.196933	0.956773	1.421613
21	1	0	-2.494417	2.304013	-0.459356
22	1	0	-1.051042	1.714882	0.278158
23	1	0	-1.724903	0.991842	-1.272220
24	6	0	1.504417	-1.292840	2.551879
25	1	0	2.343719	-1.113711	3.236571
26	1	0	0.587389	-1.071535	3.107518
27	1	0	1.507435	-2.359524	2.314497
28	6	0	0.890320	1.817802	2.377163
29	1	0	0.167085	1.286778	3.004074
30	1	0	1.720408	2.115120	3.031316
31	1	0	0.420600	2.740980	2.023862
32	6	0	1.858010	2.857106	-0.506486
33	1	0	1.081128	3.455603	-0.020924
34	1	0	2.818108	3.339567	-0.280924
35	1	0	1.712646	2.927573	-1.589249
36	6	0	3.170508	0.383378	-2.029034
37	1	0	4.239261	0.516992	-1.816933
38	1	0	3.069248	-0.530538	-2.620021
39	1	0	2.856930	1.223795	-2.654127
40	6	0	2.718338	-2.229529	-0.257864
41	1	0	3.758149	-2.370586	0.065769
42	1	0	2.118345	-3.001079	0.232841
43	1	0	2.689347	-2.413497	-1.335642
44	1	0	-0.437539	-2.267114	1.104821
45	6	0	-0.970363	-1.634928	0.392790
46	6	0	-1.959523	-0.759199	1.228699

47	1	0	-1.394140	-0.307897	2.057331
48	1	0	-2.667919	-1.447707	1.713345
49	6	0	-1.606724	-2.537674	-0.677882
50	1	0	-2.059798	-1.998696	-1.515640
51	1	0	-2.403029	-3.149492	-0.229283
52	1	0	-0.863738	-3.224510	-1.096846

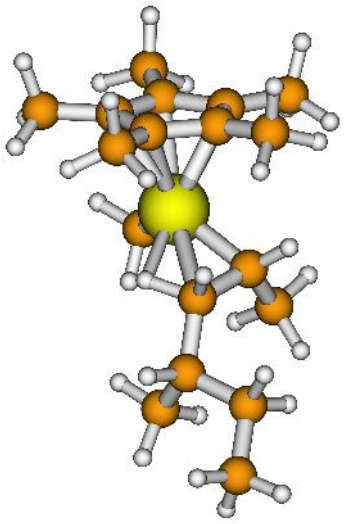
Cartesian Coordinates for **TS-16,17**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	0.186531	-0.063547	-0.434814
2	6	0	0.285547	-0.568707	-2.452625
3	6	0	-5.428713	0.642134	-0.255348
4	6	0	1.629907	-0.144755	1.485319
5	6	0	1.561112	1.208815	1.022324
6	6	0	2.124621	1.256778	-0.292509
7	6	0	2.527653	-0.064662	-0.652331
8	6	0	2.194039	-0.935175	0.443573
9	6	0	-4.219195	-0.213122	0.144233
10	6	0	-2.909751	0.593897	0.267457
11	6	0	-2.416276	1.145423	-1.080820
12	1	0	0.765041	0.176813	-3.098424
13	1	0	0.821013	-1.518940	-2.582038
14	1	0	-0.742859	-0.722133	-2.810247
15	1	0	-5.318433	1.072116	-1.257176
16	1	0	-6.339141	0.034935	-0.262778
17	1	0	-5.585163	1.466059	0.450949
18	1	0	-4.096514	-1.028286	-0.577182
19	1	0	-4.421507	-0.686479	1.114194
20	1	0	-3.140173	1.465770	0.897360
21	1	0	-3.100494	1.890594	-1.497395
22	1	0	-1.454247	1.699429	-0.980916
23	1	0	-2.301664	0.366468	-1.840632
24	6	0	1.269893	-0.614367	2.865798
25	1	0	2.096693	-0.404577	3.556789
26	1	0	0.385619	-0.108069	3.266226
27	1	0	1.089906	-1.691791	2.901921
28	6	0	1.120687	2.401091	1.832977
29	1	0	0.411128	2.128937	2.619780
30	1	0	1.987737	2.858352	2.327187
31	1	0	0.660670	3.180517	1.216744
32	6	0	2.320852	2.495234	-1.124769
33	1	0	1.577932	3.268092	-0.903442
34	1	0	3.306449	2.934089	-0.920429
35	1	0	2.280173	2.281967	-2.196850
36	6	0	3.351911	-0.442269	-1.849029
37	1	0	4.417750	-0.342771	-1.604990
38	1	0	3.186028	-1.478110	-2.156733
39	1	0	3.154263	0.200387	-2.710694
40	6	0	2.497898	-2.406271	0.500642
41	1	0	3.542767	-2.564682	0.798625
42	1	0	1.869523	-2.929266	1.226195
43	1	0	2.365298	-2.891071	-0.471732
44	1	0	-0.622141	-1.925982	1.388377
45	6	0	-1.038286	-1.407972	0.523893
46	6	0	-1.774552	-0.132971	1.033789

47	1	0	-1.001189	0.666935	1.222030
48	1	0	-2.103134	-0.328777	2.062009
49	6	0	-1.758573	-2.412246	-0.378806
50	1	0	-2.128533	-1.989889	-1.317738
51	1	0	-2.619924	-2.855429	0.138841
52	1	0	-1.079214	-3.232296	-0.634537

Cartesian Coordinates for **17**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	0.461993	-0.537585	-0.207300
2	6	0	0.796722	-2.498806	-0.781803
3	6	0	-5.719351	0.541587	-0.088095
4	6	0	1.460730	1.346282	0.846023
5	6	0	1.538541	1.512804	-0.573045
6	6	0	2.374297	0.470387	-1.100231
7	6	0	2.791209	-0.356995	-0.017611
8	6	0	2.193544	0.168539	1.182843
9	6	0	-4.269368	0.526578	0.411270
10	6	0	-3.243786	0.123353	-0.671167
11	6	0	-3.448364	-1.297808	-1.216975
12	1	0	1.566319	-2.675241	-1.539962
13	1	0	0.991765	-3.167227	0.069127
14	1	0	-0.181086	-2.796683	-1.208560
15	1	0	-6.067130	-0.457332	-0.370272
16	1	0	-6.387664	0.911415	0.695979
17	1	0	-5.833718	1.198254	-0.958838
18	1	0	-4.185952	-0.150260	1.271057
19	1	0	-4.011239	1.528087	0.781838
20	1	0	-3.385854	0.812539	-1.516892
21	1	0	-4.391212	-1.358658	-1.767551
22	1	0	-2.654014	-1.577480	-1.922317
23	1	0	-3.485052	-2.052295	-0.426015
24	6	0	0.826007	2.308971	1.808141
25	1	0	1.511760	3.142758	2.007008
26	1	0	-0.098798	2.745474	1.416945
27	1	0	0.600554	1.842172	2.770552
28	6	0	0.977344	2.671658	-1.355531
29	1	0	0.056367	3.063591	-0.913732
30	1	0	1.700611	3.497286	-1.372496
31	1	0	0.768283	2.409867	-2.397249
32	6	0	2.767762	0.307721	-2.543558
33	1	0	1.986293	0.650081	-3.229904
34	1	0	3.662873	0.905698	-2.759717
35	1	0	3.004237	-0.730644	-2.791216
36	6	0	3.793913	-1.473737	-0.076823
37	1	0	4.796146	-1.083437	0.143272
38	1	0	3.583480	-2.258795	0.654875
39	1	0	3.836376	-1.939203	-1.064537
40	6	0	2.396063	-0.390173	2.564743
41	1	0	3.332425	-0.008484	2.992890
42	1	0	1.588664	-0.108234	3.246024
43	1	0	2.470858	-1.482223	2.559337
44	1	0	-1.079767	0.433431	1.879422
45	6	0	-1.155497	-0.255229	1.039637
46	6	0	-1.797154	0.420182	-0.170652

47	1	0	-1.168979	0.234917	-1.121716
48	1	0	-1.696683	1.503172	-0.044002
49	6	0	-1.592446	-1.651698	1.501320
50	1	0	-1.535270	-2.423692	0.726700
51	1	0	-2.630123	-1.645538	1.857950
52	1	0	-0.969320	-1.978146	2.341688

Bader Analysis:

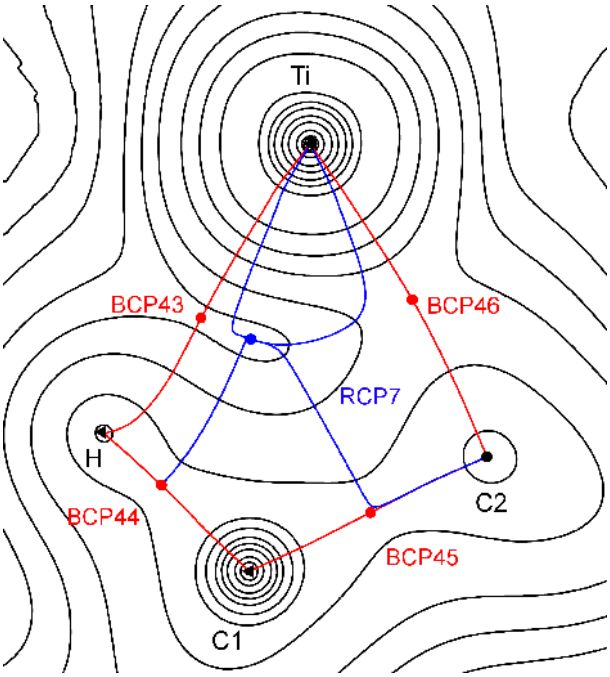


*Figure S85: Electron density map of **17**: Ti, H and C(1) in plane, C(2) out of plane, view from the top*

	$\rho(\boldsymbol{r})$	$\nabla\rho(\boldsymbol{r})$
BCP43	0.0379	-0.03793
BCP44	0.2255	0.13672
BCP45	0.2412	0.12745
BCP46	0.1114	-0.02809
RCP7	0.0362	-0.05053

NBO Analysis:

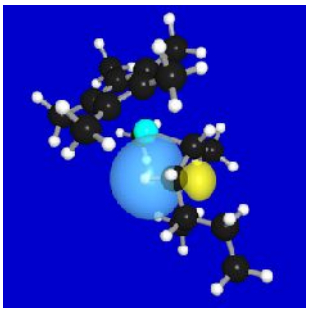


Figure S86: C(1)-H bond,56.85% C(1)($sp^{4.67}$) and 43.15% H(s)

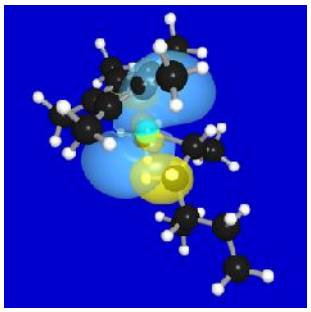


Figure S87: empty Ti($sd^{5.77}$) orbital

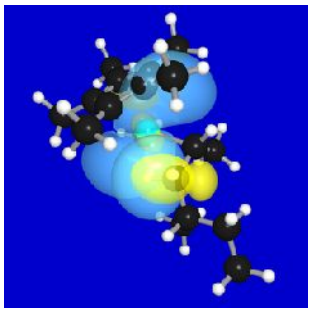
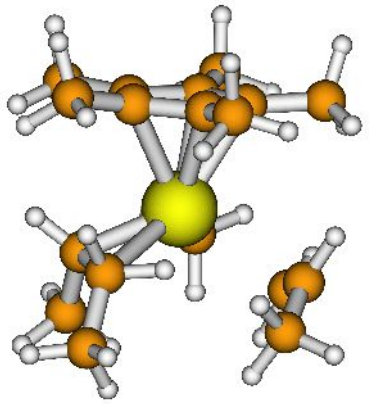


Figure S88: C(1)-H -> Ti($sd^{5.77}$); 69.50 kJ/mol

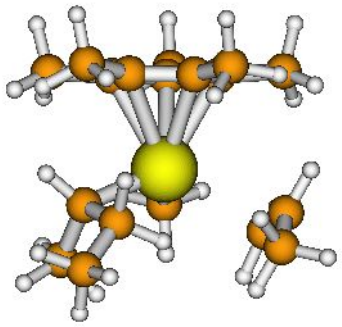
Cartesian Coordinates for **18**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.541180	1.391329	0.285815
2	6	0	-0.844255	0.878099	1.425959
3	6	0	-1.130155	-0.517758	1.524044
4	6	0	-1.969716	-0.874381	0.429379
5	6	0	-2.245695	0.310160	-0.327669
6	22	0	0.067817	-0.131317	-0.552579
7	6	0	0.955938	-1.982350	-0.183084
8	6	0	1.482769	-2.596237	-1.486927
9	6	0	-0.094052	1.683047	2.455947
10	6	0	-0.769522	-1.412101	2.676081
11	6	0	-2.582306	-2.224332	0.190286
12	6	0	-3.280722	0.434899	-1.408632
13	6	0	-1.658991	2.835022	-0.123838
14	6	0	-0.504183	-0.331669	-2.549031
15	6	0	1.997058	-1.269494	0.690673
16	6	0	3.471198	-1.676231	0.515460
17	6	0	1.557367	1.763365	-1.540785
18	6	0	2.063254	2.345719	-0.430188
19	1	0	-1.102506	-1.244179	-2.670808
20	1	0	-1.057703	0.501184	-2.993536
21	1	0	0.430517	-0.471151	-3.113674
22	1	0	3.828627	-1.517965	-0.506207
23	1	0	4.111943	-1.103842	1.193750
24	1	0	3.595934	-2.737509	0.752523
25	1	0	1.971992	-0.154203	0.510920
26	1	0	1.714901	-1.361586	1.742157
27	1	0	0.398463	-2.726629	0.385491
28	1	0	2.203204	-3.396967	-1.271498
29	1	0	0.667722	-3.034980	-2.069597
30	1	0	2.002588	-1.879802	-2.136142
31	1	0	-0.727688	1.849061	3.336651
32	1	0	0.812865	1.179782	2.807704
33	1	0	0.191311	2.669303	2.081640
34	1	0	0.037578	-0.996633	3.285055
35	1	0	-1.639211	-1.529385	3.335787
36	1	0	-0.477815	-2.418517	2.358706
37	1	0	-1.970887	-3.031913	0.601584
38	1	0	-3.566089	-2.282334	0.675390
39	1	0	-2.736681	-2.423282	-0.874346
40	1	0	-4.269116	0.585192	-0.954542
41	1	0	-3.093226	1.288195	-2.065849
42	1	0	-3.342194	-0.461290	-2.031578
43	1	0	-2.583425	3.265382	0.283069
44	1	0	-0.835015	3.447682	0.251514
45	1	0	-1.706646	2.956948	-1.210669
46	1	0	0.629706	2.120798	-1.980894

47	1	0	1.452396	3.086200	0.084753
48	1	0	2.170307	1.102296	-2.153459
49	6	0	3.430208	2.127446	0.131688
50	1	0	3.394921	1.899973	1.204143
51	1	0	3.999753	3.062507	0.038416
52	1	0	3.979414	1.339453	-0.390777

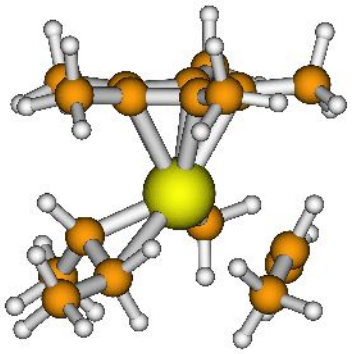
Cartesian Coordinates for **TS-18,19**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.276287	0.035040	-0.247232
2	6	0	-1.709359	1.226107	0.299747
3	6	0	-0.893885	0.857182	1.416768
4	6	0	-0.967639	-0.560265	1.567479
5	6	0	-1.799531	-1.071781	0.529572
6	22	0	0.066869	-0.087430	-0.574856
7	6	0	2.287907	-1.014765	0.443174
8	6	0	3.649490	-1.734386	0.567943
9	6	0	-2.043398	2.622779	-0.151753
10	6	0	-0.222528	1.789184	2.392403
11	6	0	-0.411211	-1.345124	2.720911
12	6	0	-2.226185	-2.501478	0.359042
13	6	0	-3.367482	-0.027921	-1.277122
14	6	0	1.162857	-1.828178	-0.223115
15	6	0	1.578073	-2.523320	-1.527025
16	6	0	-0.564722	-0.366045	-2.535031
17	6	0	1.278573	1.974759	-1.575191
18	6	0	1.726234	2.602089	-0.464231
19	6	0	3.122418	2.566111	0.065011
20	1	0	-1.066050	-1.334468	-2.650399
21	1	0	-1.205489	0.409404	-2.966151
22	1	0	0.375229	-0.406029	-3.109717
23	1	0	4.067835	-1.979523	-0.411767
24	1	0	4.369892	-1.101543	1.096325
25	1	0	3.533668	-2.664728	1.133265
26	1	0	2.488011	-0.084244	-0.130180
27	1	0	1.978086	-0.694283	1.446098
28	1	0	0.753606	-2.559086	0.474967
29	1	0	2.311180	-3.315748	-1.325849
30	1	0	0.722056	-2.993124	-2.020922
31	1	0	2.044451	-1.841272	-2.250578
32	1	0	-0.799370	1.831351	3.325221
33	1	0	0.788952	1.465617	2.662658
34	1	0	-0.161182	2.811918	2.012746
35	1	0	0.448024	-0.852450	3.185206
36	1	0	-1.178198	-1.447879	3.500067
37	1	0	-0.111539	-2.358034	2.437558
38	1	0	-1.489923	-3.202711	0.760777
39	1	0	-3.169309	-2.679250	0.893096
40	1	0	-2.398820	-2.756795	-0.690716
41	1	0	-4.345222	-0.000192	-0.778261
42	1	0	-3.334388	0.816568	-1.970674
43	1	0	-3.330653	-0.947486	-1.867167
44	1	0	-3.003934	2.936964	0.277043
45	1	0	-1.299533	3.357602	0.168538
46	1	0	-2.144704	2.694806	-1.239702

47	1	0	0.296350	2.204300	-1.982785
48	1	0	1.029934	3.235553	0.083098
49	1	0	1.961330	1.422608	-2.220832
50	1	0	3.144501	2.251714	1.116046
51	1	0	3.533750	3.584514	0.043647
52	1	0	3.780387	1.919453	-0.521918

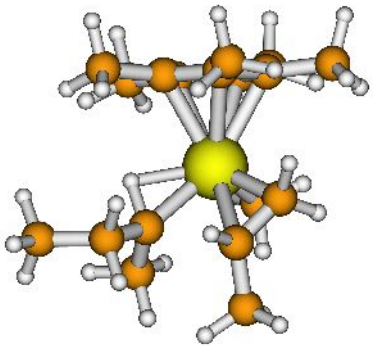
Cartesian Coordinates for **19**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.602180	1.365121	0.280391
2	6	0	-0.770599	1.023201	1.392748
3	6	0	-0.898482	-0.378891	1.625614
4	6	0	-1.791752	-0.911334	0.651315
5	6	0	-2.240170	0.172235	-0.178150
6	22	0	0.063733	-0.097381	-0.572563
7	6	0	0.965396	-1.956875	-0.281139
8	6	0	1.002821	-2.967062	-1.427577
9	6	0	-0.037059	1.972246	2.304969
10	6	0	-0.288285	-1.113324	2.786245
11	6	0	-2.304231	-2.321455	0.579078
12	6	0	-3.361503	0.102287	-1.175171
13	6	0	-1.871457	2.746704	-0.252978
14	6	0	-0.595090	-0.345174	-2.527305
15	6	0	2.270023	-1.181238	-0.058409
16	6	0	3.281930	-1.881682	0.869192
17	6	0	1.425769	1.860817	-1.664822
18	6	0	1.941030	2.434053	-0.554847
19	1	0	-1.183823	-1.265008	-2.624036
20	1	0	-1.162932	0.480204	-2.969116
21	1	0	0.333240	-0.481398	-3.107571
22	1	0	3.567545	-2.847871	0.442817
23	1	0	4.189355	-1.282373	0.995634
24	1	0	2.845085	-2.063092	1.856311
25	1	0	2.753292	-0.952040	-1.019523
26	1	0	2.069370	-0.183900	0.417386
27	1	0	0.672070	-2.453023	0.645965
28	1	0	1.714824	-3.776570	-1.210726
29	1	0	0.023070	-3.432733	-1.576373
30	1	0	1.305083	-2.516664	-2.379584
31	1	0	-0.583949	2.071096	3.251639
32	1	0	0.970641	1.625416	2.560169
33	1	0	0.044688	2.976619	1.882533
34	1	0	0.747310	-0.811164	2.977238
35	1	0	-0.855921	-0.898792	3.701344
36	1	0	-0.305658	-2.196910	2.647719
37	1	0	-1.608291	-3.039414	1.020408
38	1	0	-3.251226	-2.405922	1.128482
39	1	0	-2.500959	-2.633398	-0.450942
40	1	0	-4.322708	0.220118	-0.657673
41	1	0	-3.298636	0.893796	-1.926560
42	1	0	-3.391526	-0.856049	-1.700313
43	1	0	-2.797736	3.145495	0.180802
44	1	0	-1.075109	3.454659	-0.005595
45	1	0	-2.003617	2.751267	-1.339925
46	1	0	0.464713	2.180282	-2.060375

47	1	0	1.314111	3.129580	0.000509
48	1	0	2.043109	1.243031	-2.315803
49	6	0	3.335809	2.265704	-0.044553
50	1	0	3.348901	2.005902	1.021150
51	1	0	3.858537	3.228466	-0.128221
52	1	0	3.903196	1.520788	-0.608998

Cartesian Coordinates for **TS-19,20**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.211215	-0.383638	0.680199
2	6	0	1.359836	0.442452	1.479999
3	6	0	0.925693	1.536163	0.681055
4	6	0	1.510225	1.392319	-0.621812
5	6	0	2.330326	0.225036	-0.612407
6	22	0	0.036298	-0.428699	-0.335706
7	6	0	-1.744270	-1.800529	0.780325
8	6	0	-0.373261	-2.130773	0.932375
9	6	0	1.062325	0.272723	2.944839
10	6	0	0.133510	2.718106	1.175557
11	6	0	1.383346	2.365075	-1.763669
12	6	0	3.295204	-0.178138	-1.689760
13	6	0	2.984811	-1.584865	1.146853
14	6	0	0.501918	-1.508775	-2.062030
15	6	0	-2.041718	0.184658	-0.340979
16	6	0	-2.510714	-0.043336	-1.782172
17	6	0	-3.126612	0.726535	0.593229
18	6	0	-3.763413	2.055544	0.148807
19	1	0	0.661928	-0.874632	-2.943796
20	1	0	1.376268	-2.157284	-1.946438
21	1	0	-0.373973	-2.149267	-2.250379
22	1	0	-4.315541	1.954814	-0.790098
23	1	0	-4.471381	2.396994	0.910422
24	1	0	-3.010637	2.842251	0.020453
25	1	0	-3.917313	-0.029275	0.683845
26	1	0	-2.703827	0.858443	1.597174
27	1	0	-1.253880	1.007909	-0.362223
28	1	0	-2.895335	0.895309	-2.198875
29	1	0	-1.725298	-0.383508	-2.463838
30	1	0	-3.320864	-0.775850	-1.818450
31	1	0	1.683883	0.959504	3.534004
32	1	0	0.019117	0.499892	3.191985
33	1	0	1.283240	-0.736977	3.300541
34	1	0	-0.606939	2.437702	1.931393
35	1	0	0.806209	3.448546	1.643735
36	1	0	-0.387274	3.239581	0.366854
37	1	0	0.440423	2.919943	-1.734905
38	1	0	2.192163	3.106648	-1.724224
39	1	0	1.452192	1.867876	-2.736108
40	1	0	4.245707	0.353245	-1.550024
41	1	0	3.517980	-1.248213	-1.669137
42	1	0	2.929682	0.069322	-2.690133
43	1	0	3.979972	-1.282739	1.498673
44	1	0	2.493955	-2.098757	1.978140
45	1	0	3.134594	-2.313424	0.344195
46	1	0	0.073581	-1.990549	1.910945

47	1	0	-2.206872	-1.301491	1.626405
48	6	0	-2.670468	-2.674820	-0.026355
49	1	0	0.017017	-2.976925	0.363887
50	1	0	-3.639314	-2.212078	-0.225170
51	1	0	-2.225116	-3.002385	-0.970291
52	1	0	-2.860632	-3.575655	0.572652

Bader Analysis:

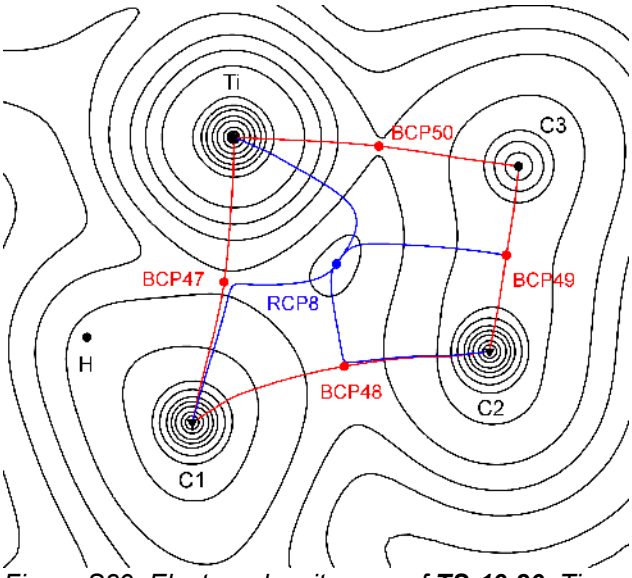


*Figure S89: Electron density map of **TS-19,20**: Ti, C(1) and C(2) in plane, C(3) and H out of plane, view from the top*

	$\rho(\boldsymbol{r})$	$\nabla\rho(\boldsymbol{r})$
BCP47	0.0743	-0.05027
BCP48	0.0550	-0.01026
BCP49	0.2977	0.19296
BCP50	0.0825	-0.03398
RCP8	0.03524	-0.03090

NBO Analysis:

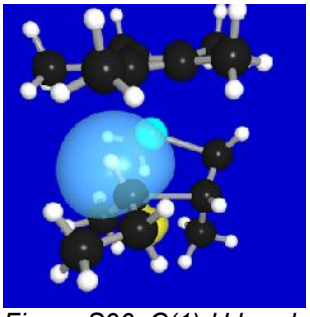


Figure S90: C(1)-H bond, 59.19% C(1)($sp^{3.33}$) and 40.81% H(s)

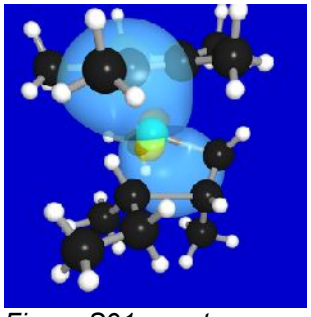


Figure S91: empty Ti($s^{3.55}$) orbital

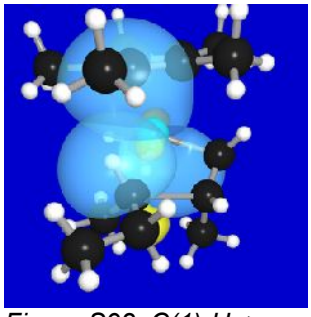


Figure S92: C(1)-H -> Ti($s^{3.55}$); 72.72 kJ/mol

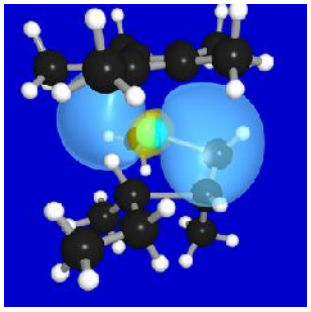


Figure S93: empty Ti($sd^{4.22}$) orbital

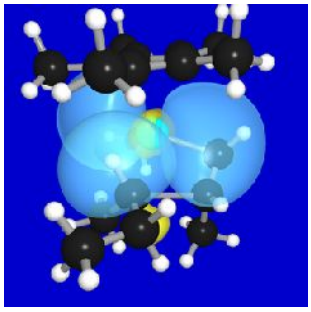
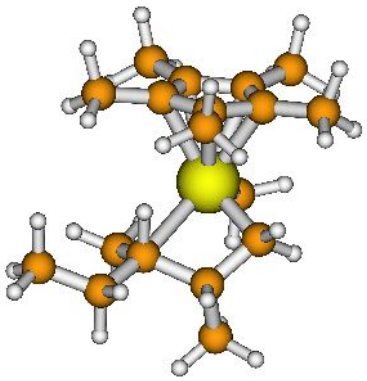


Figure 94: C(1)-H -> Ti($sd^{4.22}$); 85.37 kJ/mol

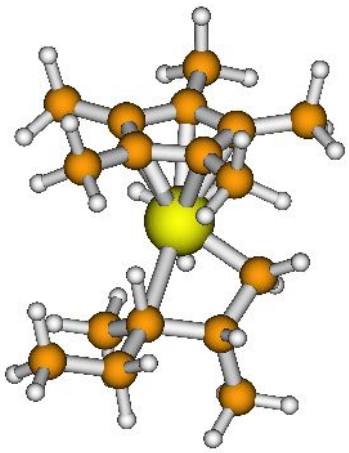
Cartesian Coordinates for **20**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.985474	-0.197012	1.144166
2	6	0	1.092468	0.890893	1.375156
3	6	0	1.018858	1.665715	0.174682
4	6	0	1.891402	1.073657	-0.790092
5	6	0	2.492949	-0.074547	-0.196194
6	22	0	0.169262	-0.496703	-0.321762
7	6	0	-2.046127	-1.492299	0.560592
8	6	0	-0.582068	-1.852224	0.982874
9	6	0	0.408179	1.203349	2.677257
10	6	0	0.265797	2.956700	-0.015636
11	6	0	2.173752	1.616854	-2.163598
12	6	0	3.607033	-0.894632	-0.780741
13	6	0	2.464813	-1.189453	2.166109
14	6	0	0.749187	-1.756510	-1.885733
15	6	0	-2.222048	-0.029114	-0.074125
16	6	0	-2.061856	0.095126	-1.609613
17	6	0	-3.601086	0.540943	0.366376
18	6	0	-3.904362	1.983366	-0.050240
19	1	0	1.144008	-1.259982	-2.779912
20	1	0	1.503040	-2.467351	-1.527132
21	1	0	-0.142408	-2.334595	-2.174483
22	1	0	-4.034425	2.094565	-1.131222
23	1	0	-4.837581	2.309953	0.418946
24	1	0	-3.116878	2.675230	0.273119
25	1	0	-4.378842	-0.128563	-0.021758
26	1	0	-3.648388	0.467682	1.459112
27	1	0	-1.499736	0.664922	0.425523
28	1	0	-2.238979	1.122471	-1.933183
29	1	0	-1.082707	-0.185612	-2.053854
30	1	0	-2.771785	-0.563226	-2.118036
31	1	0	1.072049	1.798435	3.317924
32	1	0	-0.506603	1.787822	2.538788
33	1	0	0.150851	0.298592	3.235623
34	1	0	-0.580318	3.051969	0.670912
35	1	0	0.929656	3.809920	0.175219
36	1	0	-0.111044	3.071926	-1.037282
37	1	0	1.283499	2.050129	-2.631842
38	1	0	2.924448	2.416057	-2.107176
39	1	0	2.567342	0.849212	-2.834377
40	1	0	4.572719	-0.445380	-0.514450
41	1	0	3.610856	-1.918375	-0.396035
42	1	0	3.560159	-0.944534	-1.871405
43	1	0	3.402233	-0.840430	2.618807
44	1	0	1.744926	-1.324854	2.977336
45	1	0	2.663625	-2.171272	1.726012
46	1	0	-0.430699	-1.780192	2.059267

47	1	0	-2.592207	-1.402605	1.505067
48	6	0	-2.720401	-2.588023	-0.277558
49	1	0	-0.271454	-2.844923	0.634757
50	1	0	-3.752404	-2.330405	-0.538925
51	1	0	-2.178705	-2.797618	-1.206437
52	1	0	-2.749809	-3.518242	0.297765

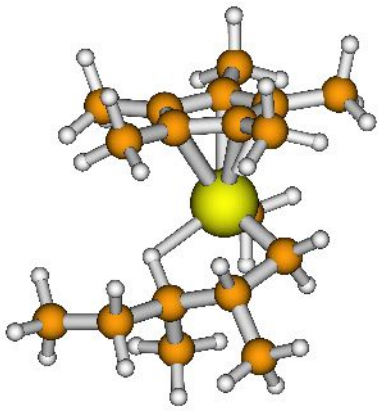
Cartesian Coordinates for **TS-20,21**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.042662	-0.481315	0.993279
2	6	0	1.108200	0.443172	1.546892
3	6	0	0.972964	1.534457	0.631944
4	6	0	1.835791	1.290800	-0.481023
5	6	0	2.510122	0.054115	-0.255649
6	22	0	0.207447	-0.427101	-0.481979
7	6	0	-2.063394	-1.430438	0.473106
8	6	0	-0.604294	-1.992641	0.511595
9	6	0	0.445216	0.333673	2.891110
10	6	0	0.186315	2.798824	0.862498
11	6	0	2.060912	2.217554	-1.644520
12	6	0	3.661537	-0.480094	-1.057237
13	6	0	2.580841	-1.716605	1.658348
14	6	0	0.897116	-1.362182	-2.229498
15	6	0	-2.233762	0.007639	-0.180984
16	6	0	-2.198479	0.055598	-1.724204
17	6	0	-3.525828	0.680092	0.363199
18	6	0	-3.751745	2.136002	-0.057181
19	1	0	1.245074	-0.659475	-2.997435
20	1	0	1.713782	-2.058300	-2.009308
21	1	0	0.068922	-1.952685	-2.649751
22	1	0	-3.941610	2.239733	-1.130123
23	1	0	-4.627723	2.536144	0.462666
24	1	0	-2.897790	2.773143	0.202557
25	1	0	-4.381164	0.072348	0.045712
26	1	0	-3.495166	0.621232	1.457774
27	1	0	-1.438232	0.689683	0.225894
28	1	0	-2.326679	1.077274	-2.088749
29	1	0	-1.281239	-0.332526	-2.205429
30	1	0	-2.999841	-0.562447	-2.139765
31	1	0	1.078859	0.791347	3.662131
32	1	0	-0.518504	0.851272	2.923460
33	1	0	0.280496	-0.706214	3.185987
34	1	0	-0.652241	2.650371	1.548757
35	1	0	0.834695	3.562528	1.311437
36	1	0	-0.206114	3.223206	-0.067211
37	1	0	1.173755	2.813560	-1.881381
38	1	0	2.867467	2.925886	-1.413214
39	1	0	2.356447	1.676897	-2.547964
40	1	0	4.595419	-0.024293	-0.702794
41	1	0	3.771005	-1.562859	-0.951645
42	1	0	3.571612	-0.251640	-2.122292
43	1	0	3.552611	-1.499819	2.121088
44	1	0	1.919405	-2.078925	2.448824
45	1	0	2.736979	-2.534520	0.948207
46	1	0	-0.323604	-2.350905	1.500330

47	1	0	-2.338871	-1.265246	1.520133
48	6	0	-3.029630	-2.462635	-0.133943
49	1	0	-0.457001	-2.805550	-0.216486
50	1	0	-4.067411	-2.113460	-0.137453
51	1	0	-2.751887	-2.721850	-1.161946
52	1	0	-2.992550	-3.383789	0.455135

Cartesian Coordinates for **21**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	0.274111	-0.185752	-0.654614
2	6	0	0.849176	-0.077736	-2.637993
3	6	0	-3.604989	2.281133	0.242073
4	6	0	1.372452	-0.577733	1.420730
5	6	0	0.927105	0.780929	1.399997
6	6	0	1.620295	1.460706	0.346344
7	6	0	2.491895	0.527002	-0.288139
8	6	0	2.313006	-0.742065	0.359298
9	6	0	-3.357307	0.807520	0.581556
10	6	0	-2.337827	0.090214	-0.337651
11	6	0	-2.792439	0.084593	-1.810086
12	1	0	1.234402	0.893471	-2.967659
13	1	0	1.587037	-0.847613	-2.899656
14	1	0	-0.073156	-0.297372	-3.201683
15	1	0	-4.057167	2.410156	-0.746050
16	1	0	-4.287278	2.725452	0.973111
17	1	0	-2.674307	2.863765	0.266924
18	1	0	-4.303311	0.256329	0.525466
19	1	0	-3.011576	0.725036	1.619154
20	1	0	-1.454964	0.807651	-0.248588
21	1	0	-2.800007	1.092641	-2.232779
22	1	0	-2.169491	-0.545254	-2.453244
23	1	0	-3.811827	-0.308537	-1.873525
24	6	0	1.022989	-1.602892	2.460517
25	1	0	1.667288	-1.474098	3.340088
26	1	0	-0.011224	-1.514584	2.807206
27	1	0	1.173078	-2.623193	2.098765
28	6	0	0.005572	1.416067	2.407861
29	1	0	-0.719857	0.703753	2.812179
30	1	0	0.587255	1.796021	3.257915
31	1	0	-0.546157	2.265607	1.994561
32	6	0	1.498020	2.919250	-0.004265
33	1	0	0.541258	3.344731	0.312813
34	1	0	2.285984	3.496914	0.496706
35	1	0	1.608191	3.095119	-1.079234
36	6	0	3.541190	0.850848	-1.311954
37	1	0	4.485113	1.093194	-0.806532
38	1	0	3.740160	0.012513	-1.984854
39	1	0	3.269918	1.715591	-1.923381
40	6	0	3.062834	-2.001095	0.026990
41	1	0	4.015060	-2.028281	0.573305
42	1	0	2.502106	-2.897925	0.302917
43	1	0	3.301199	-2.066782	-1.038602
44	1	0	-0.313218	-2.792115	0.254145
45	6	0	-0.657142	-1.960700	-0.360763
46	6	0	-1.969009	-1.338424	0.215843

47	1	0	-1.820386	-1.216547	1.296094
48	6	0	-3.135857	-2.332790	0.020668
49	1	0	-2.889806	-3.278303	0.512448
50	1	0	-3.309919	-2.545949	-1.038458
51	1	0	-4.067715	-1.960590	0.458699
52	1	0	-0.806920	-2.323229	-1.392898

Bader Analysis:

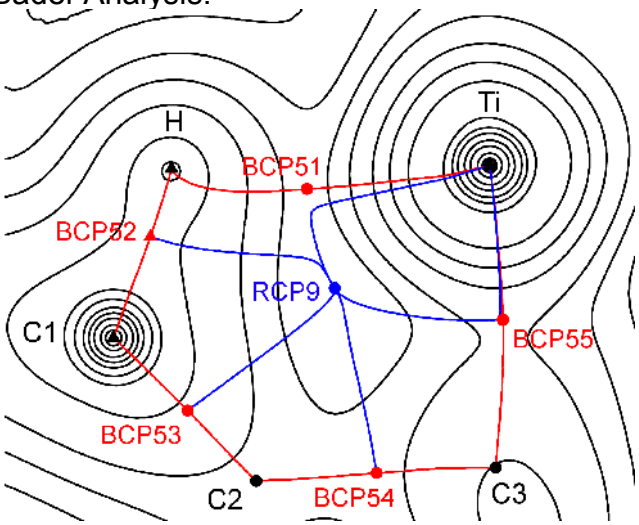


*Figure S95: Electron density map of **21**: Ti, H and C(2) in plane, C(2) and C(3) out of plane, view from the top*

	$\rho(\boldsymbol{r})$	$\nabla\rho(\boldsymbol{r})$
BCP51	0.0323	-0.03333
BCP52	0.2351	0.15300
BCP53	0.2282	0.12049
BCP54	0.2249	0.11254
BCP55	0.1195	-0.02999
RCP9	0.0216	-0.02650

NBO Analysis:

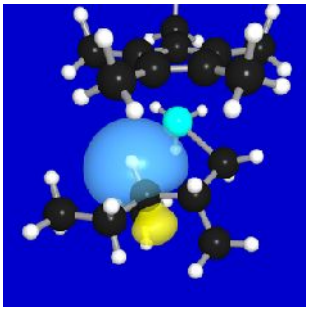


Figure S96: C(1)-H bond, 56.46% C(1)($sp^{4.36}$) 43.54% H(s)

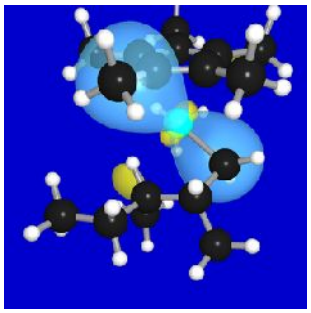


Figure S97: empty Ti($sd^{7.71}$) orbital

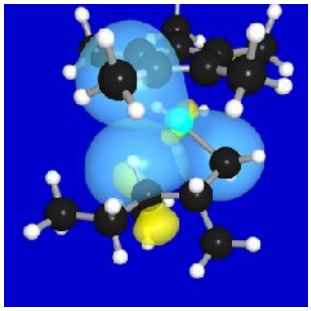


Figure S98: C(1)-H -> Ti($sd^{7.71}$);

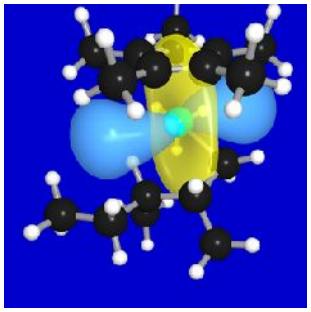


Figure S99: empty Ti($sd^{55.66}$) orbital

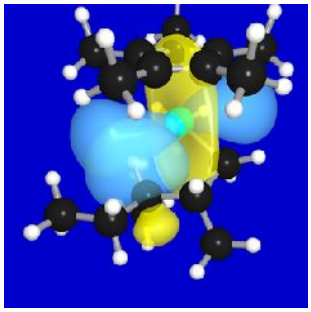
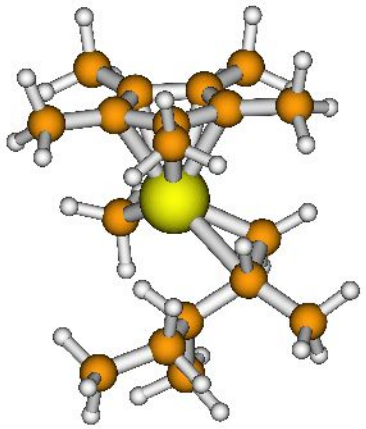


Figure S100: C(1)-H -> Ti($sd^{55.66}$); 45.80 kJ/mol

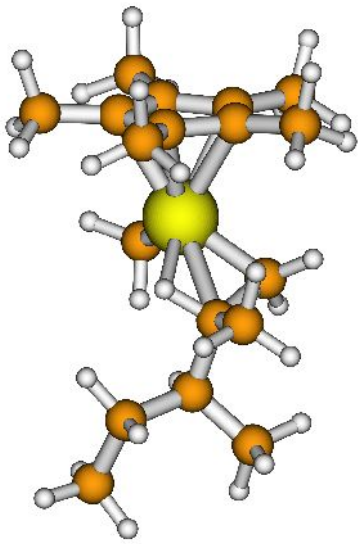
Cartesian Coordinates for **TS-21,22**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.201317	-0.061234	-0.555958
2	6	0	-0.406824	-0.990194	-2.391181
3	6	0	3.755094	-2.193136	0.572691
4	6	0	-1.603458	1.021804	1.033328
5	6	0	-1.183943	-0.234979	1.575206
6	6	0	-1.722328	-1.274416	0.751716
7	6	0	-2.462490	-0.666508	-0.307663
8	6	0	-2.368872	0.756620	-0.141116
9	6	0	3.348095	-0.727725	0.766347
10	6	0	2.495834	-0.140462	-0.384197
11	6	0	3.263668	-0.069697	-1.713106
12	1	0	-0.723696	-2.038941	-2.379946
13	1	0	-1.102169	-0.426422	-3.028433
14	1	0	0.592357	-0.929622	-2.853262
15	1	0	4.403681	-2.330344	-0.297727
16	1	0	4.304681	-2.551434	1.448456
17	1	0	2.878649	-2.842643	0.445638
18	1	0	4.248656	-0.112515	0.876566
19	1	0	2.790893	-0.629412	1.708289
20	1	0	1.708357	-0.942976	-0.540702
21	1	0	3.570606	-1.065824	-2.042026
22	1	0	2.673423	0.377951	-2.518140
23	1	0	4.169505	0.532100	-1.588778
24	6	0	-1.375432	2.367839	1.659396
25	1	0	-2.111782	2.537795	2.455652
26	1	0	-0.385109	2.457205	2.118118
27	1	0	-1.489363	3.180337	0.937523
28	6	0	-0.421301	-0.433304	2.860130
29	1	0	0.192323	0.435502	3.115726
30	1	0	-1.121349	-0.585892	3.691925
31	1	0	0.230764	-1.312552	2.831426
32	6	0	-1.573352	-2.754307	0.981360
33	1	0	-0.692371	-2.993350	1.584707
34	1	0	-2.446072	-3.142189	1.523158
35	1	0	-1.505845	-3.313711	0.042874
36	6	0	-3.338905	-1.382465	-1.294667
37	1	0	-4.352445	-1.481655	-0.884997
38	1	0	-3.423687	-0.843771	-2.242271
39	1	0	-2.976590	-2.390399	-1.513506
40	6	0	-3.038858	1.782494	-1.011518
41	1	0	-4.047562	1.997525	-0.634572
42	1	0	-2.488926	2.727368	-1.030968
43	1	0	-3.147864	1.435030	-2.042853
44	1	0	0.303116	2.694128	-0.580157
45	6	0	0.683827	1.725851	-0.902884
46	6	0	1.832029	1.224117	0.029624

47	1	0	1.399021	1.062237	1.037011
48	6	0	2.881068	2.347722	0.212187
49	1	0	2.396359	3.241529	0.614282
50	1	0	3.333106	2.615981	-0.746586
51	1	0	3.673068	2.050500	0.905925
52	1	0	0.992141	1.780083	-1.955189

Cartesian Coordinates for **22**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.420251	0.452528	-0.819531
2	6	0	-1.863485	1.353130	0.139383
3	6	0	-1.644109	0.619553	1.348286
4	6	0	-2.116234	-0.720821	1.145523
5	6	0	-2.609818	-0.826086	-0.188228
6	22	0	-0.308097	-0.384757	-0.302743
7	6	0	1.870193	0.761821	-0.065468
8	6	0	0.901291	0.982021	-1.227320
9	6	0	-1.682854	2.832657	-0.044255
10	6	0	-1.154697	1.190738	2.654376
11	6	0	-2.123193	-1.818981	2.174748
12	6	0	-3.344283	-1.996600	-0.776792
13	6	0	-2.834050	0.799078	-2.223214
14	6	0	-0.197963	-2.197083	-1.277572
15	6	0	3.099285	-0.135650	-0.413882
16	6	0	4.089411	0.617301	-1.320062
17	6	0	3.776967	-0.717324	0.844898
18	6	0	4.835863	-1.785953	0.546961
19	1	0	-0.608250	-3.063432	-0.746585
20	1	0	-0.636676	-2.171920	-2.284538
21	1	0	0.892007	-2.343153	-1.395065
22	1	0	5.686076	-1.374580	-0.005932
23	1	0	5.225326	-2.209045	1.478283
24	1	0	4.417055	-2.610296	-0.043498
25	1	0	4.235299	0.093632	1.425544
26	1	0	3.003970	-1.159692	1.494187
27	1	0	2.711750	-0.987421	-0.995093
28	1	0	4.829980	-0.073963	-1.731114
29	1	0	3.584409	1.096589	-2.165836
30	1	0	4.632888	1.390629	-0.766308
31	1	0	-2.598022	3.357127	0.260574
32	1	0	-0.867420	3.233379	0.564070
33	1	0	-1.491692	3.099431	-1.087062
34	1	0	-0.453703	2.017512	2.511054
35	1	0	-2.002267	1.584124	3.230658
36	1	0	-0.665967	0.438399	3.280641
37	1	0	-1.320389	-1.707307	2.910467
38	1	0	-3.068595	-1.805944	2.733077
39	1	0	-2.032806	-2.810035	1.720263
40	1	0	-4.419876	-1.894354	-0.582565
41	1	0	-3.215112	-2.063085	-1.860390
42	1	0	-3.024882	-2.947436	-0.342159
43	1	0	-3.884477	1.118996	-2.237166
44	1	0	-2.239062	1.617507	-2.637525
45	1	0	-2.750748	-0.057157	-2.899262
46	1	0	0.623495	2.020325	-1.400639

47	1	0	1.320100	0.141654	0.756131
48	6	0	2.213376	2.062937	0.679635
49	1	0	1.221728	0.500874	-2.162011
50	1	0	2.778762	1.871496	1.595646
51	1	0	2.814260	2.706957	0.031466
52	1	0	1.308286	2.615233	0.946110

Bader Analysis:

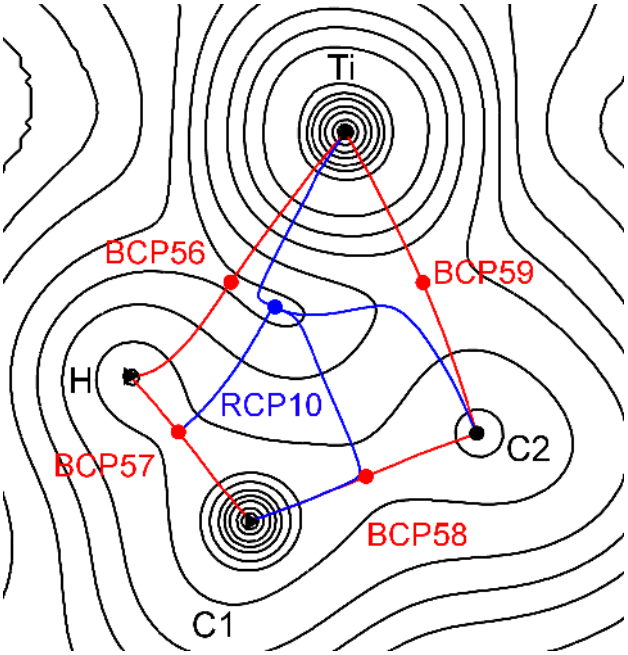


*Figure S101: Electron density map of **22**: Ti, H and C(1) in plane, C(2) out of plane, view from the top*

	$\rho(\boldsymbol{r})$	$\nabla\rho(\boldsymbol{r})$
BCP56	0.0388	-0.03818
BCP57	0.2199	0.12856
BCP58	0.2417	0.12796
BCP59	0.1129	-0.03130
RCP9	0.0368	-0.05012

NBO Analysis:

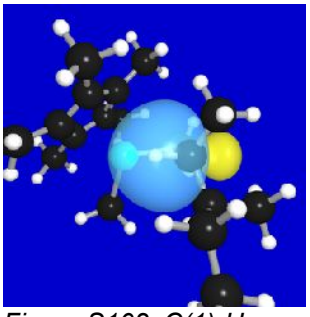


Figure S102: C(1)-H bond, 56.54% C($sp^{5.08}$) and 43.46% H(s)

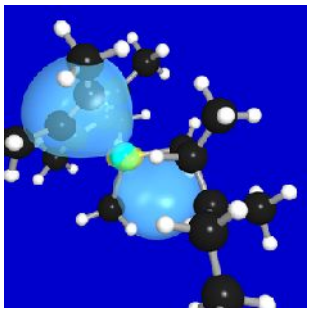


Figure S103: empty Ti($sd^{10.26}$) orbital

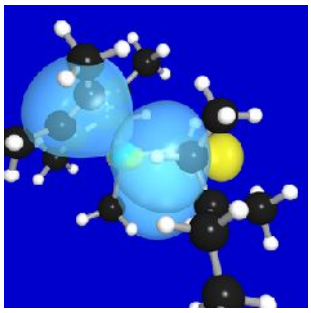


Figure S104: C(1)-H -> Ti(); 42.54 kJ/mol

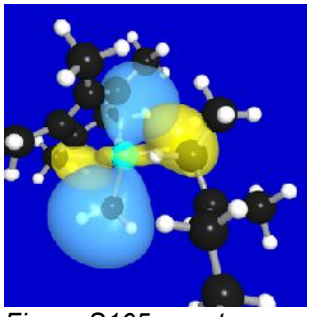


Figure S105: empty Ti($sd^{24.14}$) orbital

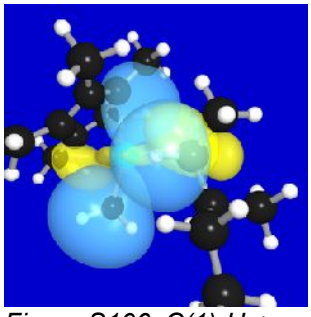
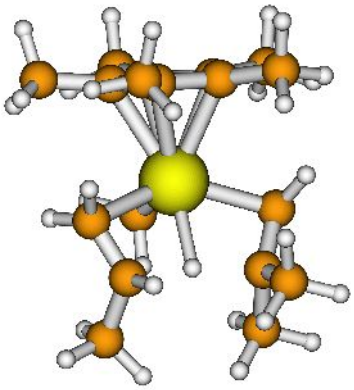


Figure S106: C(1)-H -> Ti(); 56.02 kJ/mol

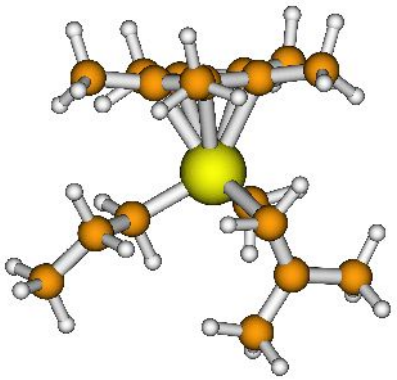
Cartesian Coordinates for **TS-4,23**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.016459	0.991846	0.162647
2	6	0	2.067054	0.095323	-0.949473
3	6	0	1.748256	-1.215377	-0.475113
4	6	0	1.517362	-1.127986	0.931978
5	6	0	1.679652	0.230076	1.324009
6	22	0	-0.204370	0.150397	-0.177002
7	6	0	-0.740324	2.158618	0.701436
8	6	0	-2.076010	1.716220	0.694087
9	6	0	-3.106478	2.349626	-0.220955
10	6	0	2.607641	0.421778	-2.311961
11	6	0	1.832645	-2.472288	-1.295128
12	6	0	1.290292	-2.268461	1.887738
13	6	0	1.643418	0.715810	2.748811
14	6	0	2.438978	2.434194	0.127538
15	6	0	-0.454011	0.742706	-2.159505
16	6	0	-1.228643	-1.821978	-0.411497
17	6	0	-2.446069	-1.194350	-0.042382
18	6	0	-2.978085	-1.450293	1.363778
19	6	0	-3.519587	-1.022448	-1.109449
20	1	0	-3.105420	-0.717027	-2.073260
21	1	0	-3.995369	-2.001560	-1.250139
22	1	0	-4.301474	-0.319318	-0.814829
23	1	0	0.054395	1.677355	-2.417193
24	1	0	-0.163909	-0.020166	-2.889321
25	1	0	-1.540034	0.904344	-2.239305
26	1	0	-0.767803	-2.496549	0.303484
27	1	0	-1.067178	-2.074520	-1.458002
28	1	0	-2.110469	0.265848	0.174404
29	1	0	-2.179708	-1.485639	2.112915
30	1	0	-3.719357	-0.706357	1.671428
31	1	0	-3.474700	-2.428504	1.369247
32	1	0	2.875065	-2.810101	-1.361563
33	1	0	1.257583	-3.294510	-0.860959
34	1	0	1.480266	-2.319346	-2.320223
35	1	0	2.424856	1.462269	-2.593764
36	1	0	3.694924	0.269045	-2.323977
37	1	0	2.183389	-0.215997	-3.092173
38	1	0	1.044177	-3.201078	1.373741
39	1	0	2.203305	-2.456883	2.467502
40	1	0	0.496088	-2.060409	2.614809
41	1	0	2.527223	0.353216	3.289661
42	1	0	1.656987	1.806563	2.817375
43	1	0	0.768628	0.351333	3.301259
44	1	0	3.532052	2.507739	0.196918
45	1	0	2.144120	2.926623	-0.804409
46	1	0	2.026720	3.012479	0.958856

47	1	0	-0.212845	2.195333	1.649011
48	1	0	-2.468608	1.371299	1.653592
49	1	0	-0.415787	2.875077	-0.050250
50	1	0	-2.699761	2.560469	-1.213486
51	1	0	-3.392189	3.308802	0.229188
52	1	0	-4.014336	1.753353	-0.325849

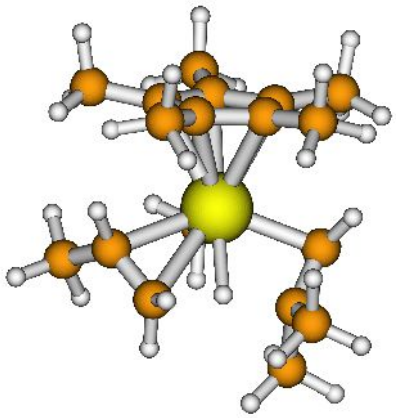
Cartesian Coordinates for **23**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.131018	-0.101728	-0.327919
2	6	0	-2.725063	-3.031519	-0.176031
3	6	0	-0.346721	-1.095594	-2.142146
4	6	0	2.097550	-0.959271	-0.437172
5	6	0	1.628954	-1.125957	0.901901
6	6	0	1.400968	0.171853	1.460303
7	6	0	1.730760	1.145321	0.468169
8	6	0	2.143728	0.442257	-0.707848
9	6	0	-1.795556	-1.098219	1.112449
10	6	0	-2.748066	-1.599486	0.271086
11	6	0	-3.895404	-0.764433	-0.216695
12	1	0	-1.839396	-3.568209	0.172541
13	1	0	-3.614631	-3.542431	0.216287
14	1	0	-2.784600	-3.103381	-1.268306
15	1	0	0.221544	-0.608198	-2.944948
16	1	0	-0.073054	-2.156636	-2.124745
17	1	0	-1.415205	-1.008893	-2.397318
18	1	0	-1.937076	-0.118213	1.575387
19	1	0	-1.096821	-1.775790	1.600535
20	1	0	-2.234722	2.122561	1.029034
21	1	0	-3.833150	0.275708	0.111082
22	1	0	-3.969923	-0.797789	-1.310586
23	1	0	-4.833096	-1.189924	0.165540
24	6	0	1.524629	-2.445802	1.619399
25	1	0	2.523810	-2.796641	1.907933
26	1	0	0.938244	-2.373934	2.539933
27	1	0	1.084895	-3.230672	0.993336
28	6	0	2.601460	-2.054946	-1.332201
29	1	0	2.476410	-1.816020	-2.391602
30	1	0	3.673600	-2.215505	-1.158620
31	1	0	2.097585	-3.007168	-1.141313
32	6	0	0.981089	0.477363	2.873759
33	1	0	0.448094	-0.356460	3.339833
34	1	0	1.862966	0.679277	3.495477
35	1	0	0.339414	1.362547	2.931761
36	6	0	1.858992	2.627366	0.678238
37	1	0	2.914039	2.886189	0.837847
38	1	0	1.512942	3.205241	-0.184165
39	1	0	1.308652	2.967634	1.558389
40	6	0	2.643461	1.085737	-1.970482
41	1	0	3.704920	1.346160	-1.862927
42	1	0	2.559494	0.420505	-2.833805
43	1	0	2.108960	2.012523	-2.201543
44	1	0	-0.378704	2.271415	-1.443332
45	6	0	-1.009174	1.723719	-0.726607
46	6	0	-1.620212	2.681387	0.307626

47	1	0	-0.823850	3.153930	0.892122
48	1	0	-1.822624	1.269242	-1.334464
49	6	0	-2.488950	3.778640	-0.329709
50	1	0	-3.325332	3.347974	-0.892914
51	1	0	-1.900857	4.390321	-1.023146
52	1	0	-2.904804	4.442148	0.436679

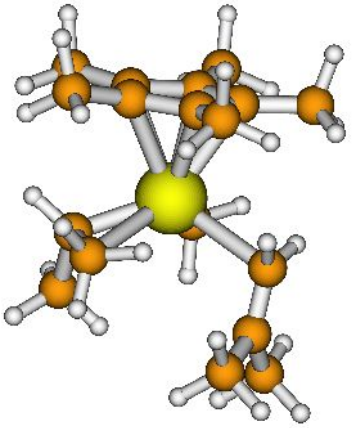
Cartesian Coordinates for **TS-8,24**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.274056	0.207787	-0.256360
2	6	0	-3.705053	0.139823	-1.143849
3	6	0	-0.209860	0.918124	-2.206932
4	6	0	1.968321	-0.414508	-0.825915
5	6	0	1.271952	-1.611350	-0.469009
6	6	0	0.933595	-1.526074	0.917851
7	6	0	1.400095	-0.277025	1.411349
8	6	0	2.045981	0.413166	0.336862
9	6	0	-1.743019	-1.420919	-0.753847
10	6	0	-2.744471	-0.579515	-0.204334
11	6	0	-3.348042	-0.965852	1.142309
12	1	0	-3.230131	0.431762	-2.083561
13	1	0	-4.518207	-0.555781	-1.386857
14	1	0	-4.160944	1.022327	-0.683249
15	1	0	0.554227	1.677667	-2.392794
16	1	0	-0.114845	0.133931	-2.965342
17	1	0	-1.201922	1.389956	-2.317529
18	1	0	-1.476395	-2.320338	-0.210773
19	1	0	-1.647712	-1.489081	-1.835942
20	1	0	-2.034833	0.630150	0.293247
21	1	0	-2.606376	-1.400850	1.819237
22	1	0	-3.829529	-0.118208	1.640672
23	1	0	-4.121852	-1.723585	0.968250
24	6	0	1.115584	-2.811336	-1.361007
25	1	0	2.047690	-3.391090	-1.377566
26	1	0	0.326696	-3.487441	-1.021154
27	1	0	0.894812	-2.530201	-2.395616
28	6	0	2.699510	-0.185790	-2.117805
29	1	0	2.808098	0.876492	-2.352994
30	1	0	3.710733	-0.608536	-2.052155
31	1	0	2.202383	-0.665871	-2.964906
32	6	0	0.334218	-2.613175	1.768555
33	1	0	-0.183065	-3.373601	1.177868
34	1	0	1.128535	-3.130744	2.322664
35	1	0	-0.367296	-2.227006	2.516689
36	6	0	1.347206	0.148220	2.855220
37	1	0	2.095685	-0.405195	3.437347
38	1	0	1.569068	1.210501	2.987864
39	1	0	0.375573	-0.056079	3.319985
40	6	0	2.878794	1.659536	0.449489
41	1	0	3.915484	1.390959	0.692132
42	1	0	2.907576	2.223168	-0.487523
43	1	0	2.534812	2.333533	1.238929
44	1	0	0.328583	2.258811	1.534195
45	6	0	-0.374264	2.370609	0.715988
46	6	0	-1.679727	1.914751	0.951236

47	1	0	-1.934312	1.538912	1.943274
48	1	0	-2.505534	2.403966	0.431702
49	6	0	-0.088429	3.499949	-0.249990
50	1	0	0.909571	3.439725	-0.690191
51	1	0	-0.821131	3.547239	-1.060856
52	1	0	-0.140561	4.451388	0.297859

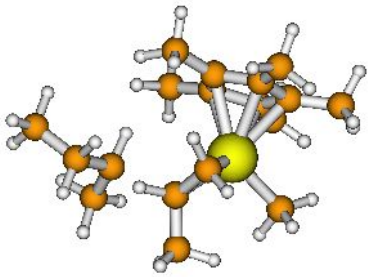
Cartesian Coordinates for **24**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.131121	0.155278	-0.281574
2	6	0	-3.929031	-0.845154	-1.153415
3	6	0	-0.478316	-0.205530	-2.303132
4	6	0	1.914000	-0.907336	-0.813644
5	6	0	1.334375	-1.617991	0.283364
6	6	0	1.305178	-0.743125	1.413363
7	6	0	1.889056	0.502010	1.021232
8	6	0	2.244158	0.408736	-0.354785
9	6	0	-2.012980	-1.373384	0.371545
10	6	0	-3.213136	-0.761689	0.163923
11	6	0	-3.928243	-0.023519	1.259402
12	1	0	-3.358003	-1.384998	-1.911393
13	1	0	-4.887291	-1.361699	-1.009301
14	1	0	-4.176886	0.154594	-1.532461
15	1	0	0.184109	0.409353	-2.925263
16	1	0	-0.387571	-1.246398	-2.631688
17	1	0	-1.510793	0.131571	-2.480756
18	1	0	-1.616483	-1.459570	1.383479
19	1	0	-1.618332	-2.060957	-0.374314
20	1	0	-1.215557	1.016525	1.460042
21	1	0	-3.359476	0.009847	2.191997
22	1	0	-4.177377	0.999479	0.950927
23	1	0	-4.885295	-0.522053	1.461860
24	6	0	0.959250	-3.075589	0.269478
25	1	0	1.849680	-3.692881	0.446540
26	1	0	0.235747	-3.329821	1.049240
27	1	0	0.544276	-3.387730	-0.694334
28	6	0	2.338122	-1.504725	-2.124439
29	1	0	2.318820	-0.775447	-2.938577
30	1	0	3.368422	-1.875728	-2.043800
31	1	0	1.711603	-2.351316	-2.417767
32	6	0	0.887668	-1.108271	2.814691
33	1	0	0.204361	-1.962413	2.835499
34	1	0	1.766126	-1.392726	3.408276
35	1	0	0.405714	-0.276652	3.339399
36	6	0	2.227954	1.643454	1.937743
37	1	0	3.290102	1.593684	2.211048
38	1	0	2.068036	2.621659	1.473023
39	1	0	1.657611	1.609154	2.869786
40	6	0	2.968472	1.452517	-1.156377
41	1	0	4.048784	1.255233	-1.143195
42	1	0	2.656166	1.457618	-2.205200
43	1	0	2.818829	2.457920	-0.754180
44	1	0	0.566351	2.835937	-0.147917
45	6	0	-0.333681	2.224587	-0.201409
46	6	0	-1.004473	2.079430	1.169583

47	1	0	-0.390109	2.467570	1.983762
48	1	0	-1.990667	2.555848	1.204418
49	6	0	-1.277044	2.752188	-1.289910
50	1	0	-0.783579	2.801950	-2.264892
51	1	0	-2.182050	2.140660	-1.408162
52	1	0	-1.618587	3.766019	-1.034740

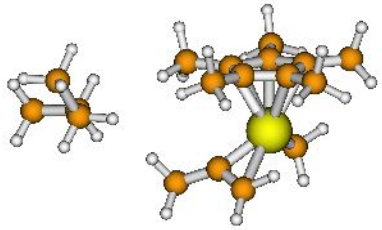
Cartesian Coordinates for **TS-18,25**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.130216	-0.447829	1.173281
2	6	0	2.674254	-0.368279	-0.140050
3	6	0	1.785053	-1.058081	-1.032242
4	6	0	0.723852	-1.611150	-0.253804
5	6	0	0.910279	-1.204910	1.100850
6	22	0	0.605688	0.801761	-0.132104
7	6	0	-1.433625	1.382370	-0.584179
8	6	0	-1.780396	2.862152	-0.399896
9	6	0	3.995560	0.232448	-0.532953
10	6	0	2.037446	-1.313147	-2.493496
11	6	0	-0.321353	-2.558861	-0.775324
12	6	0	0.086497	-1.620626	2.293622
13	6	0	2.758465	0.072195	2.438012
14	6	0	-2.797071	0.098578	0.256212
15	6	0	-3.958156	-0.379216	-0.637989
16	6	0	-4.695500	-1.569870	0.002880
17	6	0	1.638277	2.577130	0.172634
18	6	0	-0.636621	0.929309	-1.779067
19	6	0	-3.186856	0.808778	1.526710
20	1	0	1.052202	3.111942	0.942791
21	1	0	2.683354	2.571483	0.489134
22	1	0	1.566003	3.162807	-0.759273
23	1	0	-5.185481	-1.293815	0.940783
24	1	0	-5.469434	-1.924841	-0.684047
25	1	0	-4.014791	-2.405709	0.199043
26	1	0	-4.657345	0.447193	-0.812952
27	1	0	-3.567774	-0.690949	-1.614686
28	1	0	-2.063823	-0.688821	0.392706
29	1	0	-3.819427	1.679989	1.333211
30	1	0	-3.774355	0.109570	2.134282
31	1	0	-2.319612	1.117131	2.114312
32	1	0	2.657768	-2.209893	-2.624895
33	1	0	1.109345	-1.477358	-3.048608
34	1	0	2.568275	-0.482807	-2.969015
35	1	0	-0.718834	-2.256225	-1.750175
36	1	0	0.116089	-3.556385	-0.912597
37	1	0	-1.160883	-2.681091	-0.084256
38	1	0	-0.927426	-1.926583	2.018075
39	1	0	0.549423	-2.479656	2.796764
40	1	0	0.005721	-0.824761	3.042282
41	1	0	3.361177	-0.712217	2.914449
42	1	0	3.420007	0.921370	2.248608
43	1	0	2.011762	0.389828	3.173472
44	1	0	4.745634	-0.559665	-0.656250
45	1	0	3.940456	0.773796	-1.483055
46	1	0	4.374044	0.922955	0.224285

47	1	0	-0.919167	-0.022140	-2.229633
48	1	0	-2.457509	0.893148	-0.818133
49	1	0	-0.474678	1.696848	-2.542746
50	1	0	-2.070073	3.107896	0.625668
51	1	0	-2.574531	3.200374	-1.077654
52	1	0	-0.893178	3.461881	-0.626821

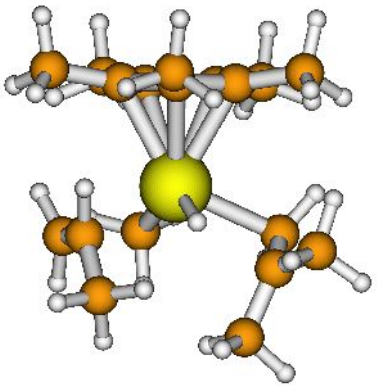
Cartesian Coordinates for **25**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.177983	-0.264441	1.432360
2	6	0	2.823248	-1.077689	0.466132
3	6	0	1.813030	-1.627415	-0.400476
4	6	0	0.533999	-1.209664	0.083767
5	6	0	0.752438	-0.325155	1.180747
6	22	0	1.729953	0.688199	-0.664045
7	6	0	0.094643	1.697657	-1.232869
8	6	0	-0.961442	2.685681	-0.858286
9	6	0	4.298204	-1.342005	0.353148
10	6	0	2.066863	-2.592408	-1.531431
11	6	0	-0.796755	-1.645821	-0.459665
12	6	0	-0.299155	0.298960	2.056267
13	6	0	2.816584	0.425818	2.603581
14	6	0	-4.595394	0.310732	0.405264
15	6	0	-5.174265	-0.652061	-0.646883
16	6	0	-6.038160	-1.777528	-0.066069
17	6	0	3.168186	2.094537	-0.220616
18	6	0	0.409146	1.290491	-2.473922
19	6	0	-5.648651	1.114916	1.177374
20	1	0	2.745248	2.795164	0.517054
21	1	0	4.142167	1.757154	0.145997
22	1	0	3.311298	2.658691	-1.158284
23	1	0	-6.929764	-1.387657	0.435958
24	1	0	-6.378018	-2.457300	-0.854944
25	1	0	-5.477221	-2.371458	0.667005
26	1	0	-5.764615	-0.074415	-1.371812
27	1	0	-4.344825	-1.095648	-1.217205
28	1	0	-3.981901	-0.262450	1.118439
29	1	0	-6.279827	1.693366	0.492014
30	1	0	-6.304999	0.462994	1.762869
31	1	0	-5.179715	1.819366	1.873783
32	1	0	2.166779	-3.613255	-1.140079
33	1	0	1.247266	-2.605281	-2.255488
34	1	0	2.994505	-2.370732	-2.070216
35	1	0	-0.771096	-1.809204	-1.541224
36	1	0	-1.090117	-2.597438	0.002822
37	1	0	-1.588008	-0.922805	-0.247724
38	1	0	-1.277074	0.321110	1.570050
39	1	0	-0.406063	-0.281856	2.981786
40	1	0	-0.041710	1.321850	2.349335
41	1	0	2.797655	-0.235475	3.479643
42	1	0	3.860400	0.685942	2.412282
43	1	0	2.286331	1.341815	2.879569
44	1	0	4.536381	-2.324862	0.780491
45	1	0	4.642570	-1.359394	-0.686987
46	1	0	4.889978	-0.598642	0.892187

47	1	0	1.166186	0.495837	-2.680108
48	1	0	-3.914139	1.012953	-0.100447
49	1	0	-0.042186	1.615467	-3.412230
50	1	0	-1.713528	2.203383	-0.222188
51	1	0	-1.470496	3.108281	-1.732425
52	1	0	-0.533440	3.506469	-0.271468

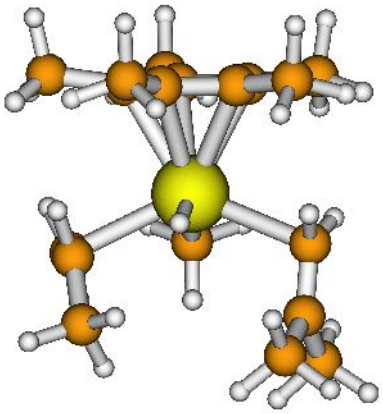
Cartesian Coordinates for **TS-4-26**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.146427	0.071505	-0.509932
2	6	0	-3.431884	-0.778868	-1.064733
3	6	0	0.027381	0.388850	-2.584280
4	6	0	2.215096	0.222191	-0.464804
5	6	0	1.874550	-1.134838	-0.175386
6	6	0	1.205879	-1.166852	1.089984
7	6	0	1.096389	0.168362	1.570135
8	6	0	1.730569	1.028180	0.614381
9	6	0	-1.219207	-1.958196	-0.954024
10	6	0	-2.347823	-1.492261	-0.292417
11	6	0	-2.763053	-2.043532	1.048744
12	1	0	-3.051961	-0.256035	-1.946747
13	1	0	-4.137812	-1.542989	-1.419776
14	1	0	-3.995031	-0.082928	-0.440102
15	1	0	0.586420	1.282794	-2.880505
16	1	0	0.538310	-0.481068	-3.022068
17	1	0	-0.974603	0.450838	-3.035897
18	1	0	-0.624394	-2.744166	-0.501277
19	1	0	-1.172066	-1.885488	-2.038221
20	1	0	-1.553893	0.100551	0.509403
21	1	0	-1.925288	-2.463617	1.606251
22	1	0	-3.269983	-1.295141	1.663424
23	1	0	-3.480735	-2.855170	0.862622
24	6	0	2.290544	-2.329107	-0.989581
25	1	0	3.317661	-2.619387	-0.731726
26	1	0	1.656795	-3.200771	-0.804077
27	1	0	2.274972	-2.122726	-2.063767
28	6	0	3.093719	0.684748	-1.593168
29	1	0	2.893960	1.721436	-1.878417
30	1	0	4.148388	0.627869	-1.293208
31	1	0	2.975435	0.066440	-2.486749
32	6	0	0.863051	-2.400294	1.876660
33	1	0	0.569263	-3.244866	1.246523
34	1	0	1.745061	-2.726785	2.444038
35	1	0	0.067418	-2.217975	2.603714
36	6	0	0.598430	0.572027	2.932172
37	1	0	1.385009	0.418885	3.682815
38	1	0	0.323976	1.629788	2.974681
39	1	0	-0.271367	-0.012071	3.245961
40	6	0	2.062455	2.480653	0.833199
41	1	0	2.962377	2.558576	1.457290
42	1	0	2.282272	3.003047	-0.102204
43	1	0	1.271585	3.030006	1.352690
44	1	0	0.180375	2.778489	-0.837810
45	6	0	-0.873617	2.528324	-0.802422
46	6	0	-1.539331	2.426632	0.375770

47	1	0	-0.969046	2.470770	1.301935
48	1	0	-1.414510	2.577034	-1.743602
49	6	0	-3.029323	2.463179	0.533990
50	1	0	-3.551300	2.311840	-0.414522
51	1	0	-3.304378	3.457827	0.911816
52	1	0	-3.384460	1.736695	1.270713

Cartesian Coordinates for **26**



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-0.140456	0.077296	-0.273781
2	6	0	-3.811204	-1.468750	-0.979785
3	6	0	-0.729523	-0.397931	-2.244266
4	6	0	2.000225	-0.711076	-0.816354
5	6	0	1.460284	-1.610307	0.155634
6	6	0	1.315409	-0.901253	1.391259
7	6	0	1.756756	0.437953	1.187929
8	6	0	2.182907	0.557380	-0.174153
9	6	0	-1.856342	-1.486829	0.586999
10	6	0	-3.081676	-0.994320	0.242616
11	6	0	-3.808378	-0.006097	1.108175
12	1	0	-3.206413	-2.129678	-1.603778
13	1	0	-4.710324	-2.016649	-0.666227
14	1	0	-4.163389	-0.624533	-1.585047
15	1	0	-0.072597	-0.007602	-3.029906
16	1	0	-0.696858	-1.497647	-2.309366
17	1	0	-1.755154	-0.077908	-2.470029
18	1	0	-1.463861	-1.284167	1.581549
19	1	0	-1.443804	-2.334799	0.043663
20	1	0	-0.791304	0.992253	1.003422
21	1	0	-3.213757	0.317224	1.965127
22	1	0	-4.112416	0.874104	0.529177
23	1	0	-4.736329	-0.464370	1.475842
24	6	0	1.228412	-3.081156	-0.064818
25	1	0	2.182670	-3.620505	-0.003705
26	1	0	0.567314	-3.516252	0.689383
27	1	0	0.807595	-3.292819	-1.053211
28	6	0	2.474673	-1.088065	-2.191861
29	1	0	2.465076	-0.238030	-2.879658
30	1	0	3.507616	-1.457401	-2.145019
31	1	0	1.864690	-1.879690	-2.634946
32	6	0	0.898419	-1.472376	2.718300
33	1	0	0.361264	-2.419080	2.616079
34	1	0	1.785661	-1.673272	3.332821
35	1	0	0.267901	-0.778409	3.284255
36	6	0	1.924528	1.471913	2.266525
37	1	0	2.876171	1.314848	2.791698
38	1	0	1.950175	2.489114	1.865542
39	1	0	1.125606	1.421780	3.011191
40	6	0	2.914530	1.735929	-0.759222
41	1	0	3.978540	1.674959	-0.495648
42	1	0	2.860367	1.758472	-1.851528
43	1	0	2.549210	2.695003	-0.379024
44	1	0	0.652918	2.254517	-1.779157
45	6	0	-0.359619	2.307750	-1.395782
46	6	0	-0.624061	2.793359	-0.150280

47	1	0	0.211292	3.018861	0.509293
48	1	0	-1.156620	2.202967	-2.125305
49	6	0	-1.966595	3.290237	0.301734
50	1	0	-2.775630	2.925264	-0.338166
51	1	0	-1.961228	4.387145	0.236480
52	1	0	-2.176822	3.027620	1.341462

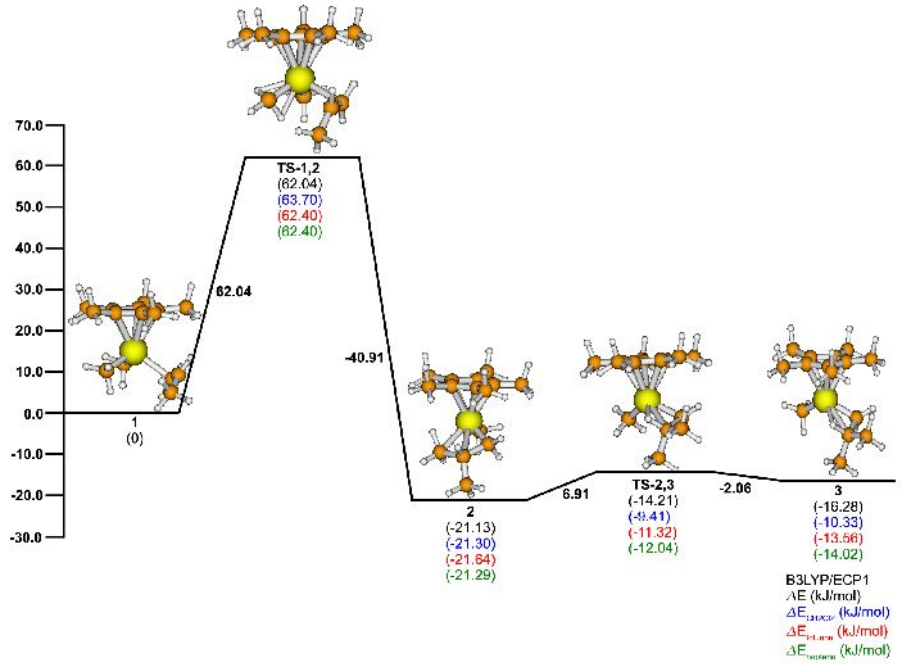


Figure S107: Reaction Pathway for the initial 1,2 insertion, energies for the PCM calculations are in colour.

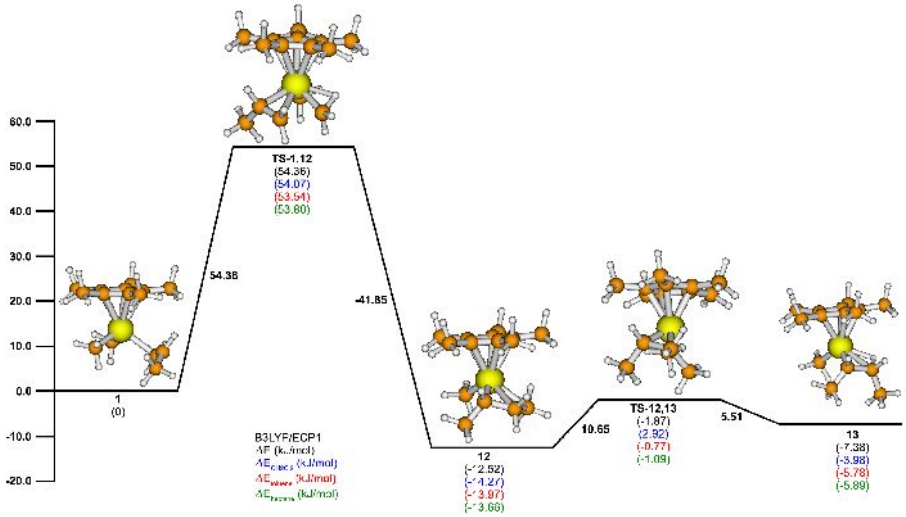


Figure S108: Reaction Pathway for the initial 2,1 insertion, energies for the PCM calculations are in colour.

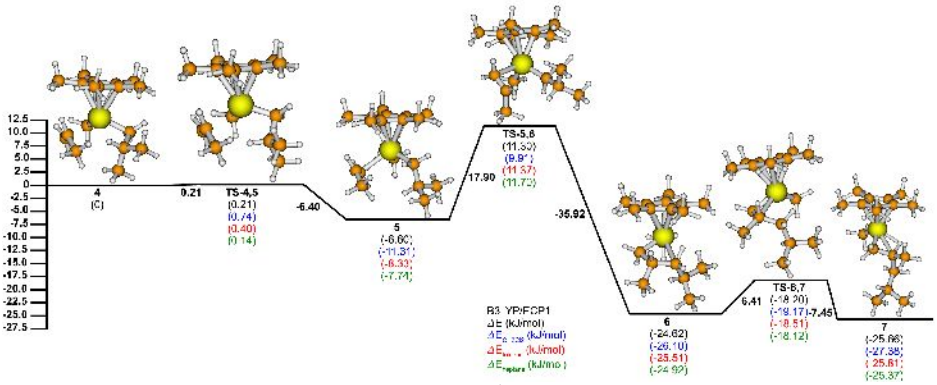


Figure S109: Reaction Pathway for the 2nd 1,2 insertion, energies for the PCM calculations are in colour.

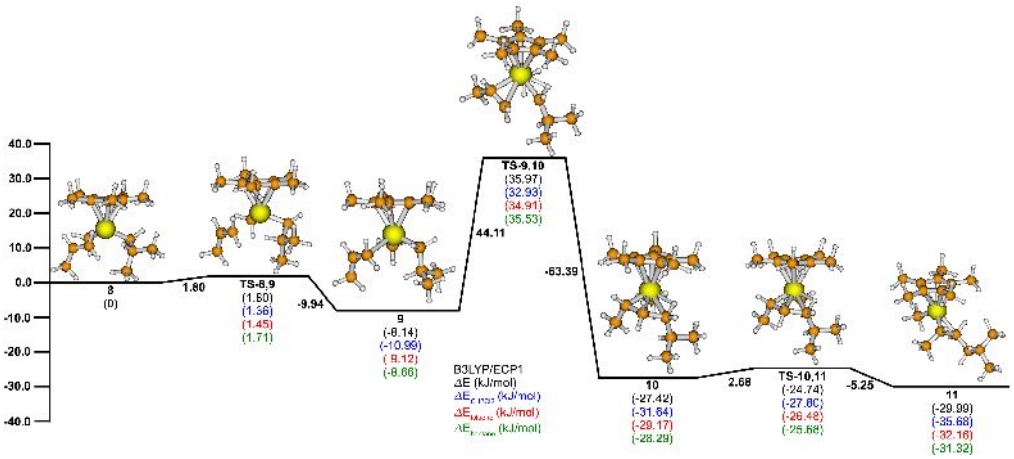


Figure S110: Reaction Pathway for the 2,1 insertion following an initial 1,2 insertion, energies for the PCM calculations are in colour.

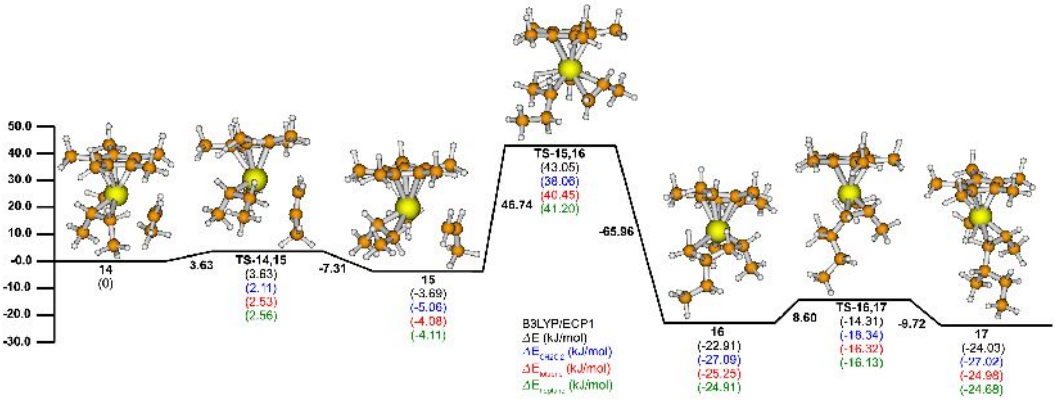


Figure S111: Reaction Pathway for the 2nd 2,1 insertion, energies for the PCM calculations are in colour.

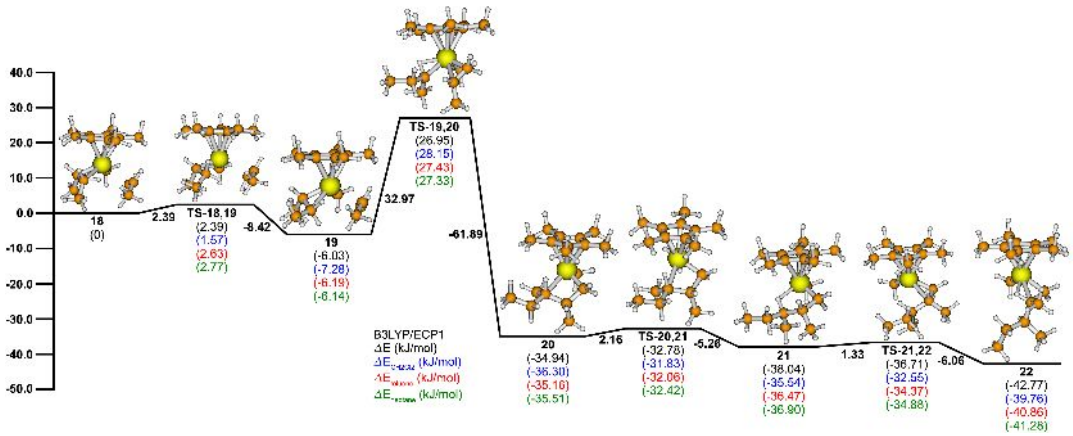


Figure S112: Reaction Pathway for the 1,2 insertion following an initial 2,1 insertion, energies for the PCM calculations are in colour.

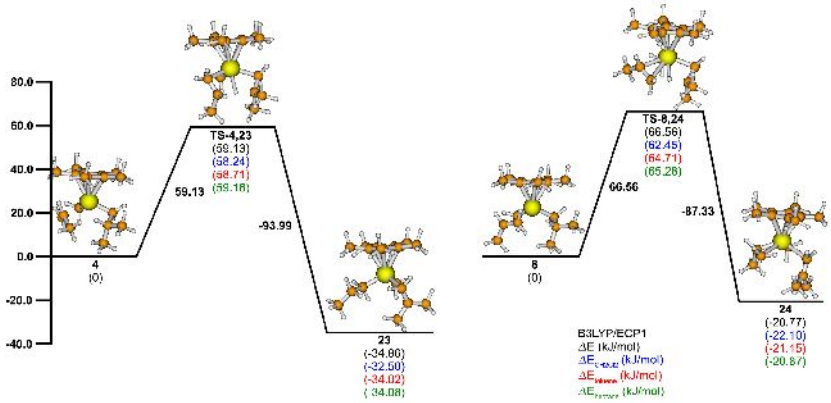


Figure S113: β-H Elimination, energies for the PCM calculations are in colour.

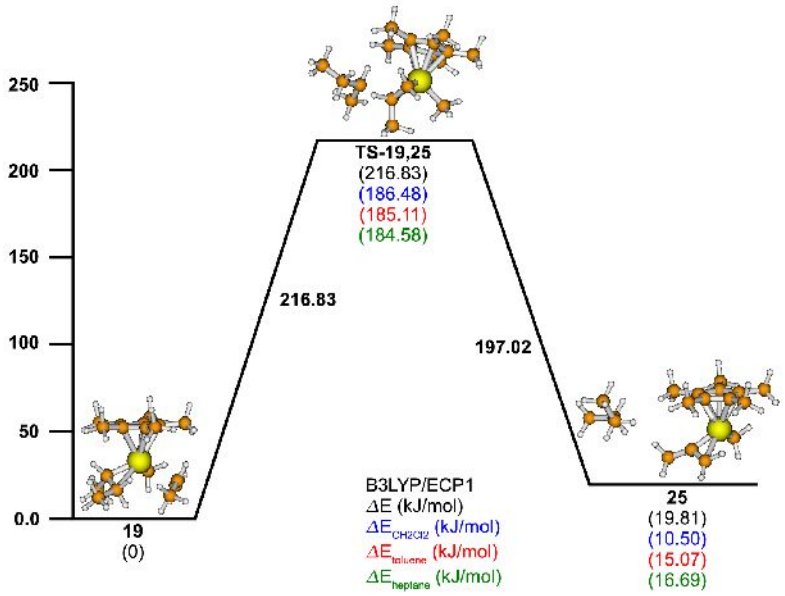


Figure S114: β-H Elimination,energies for the PCM calculations are in colour.

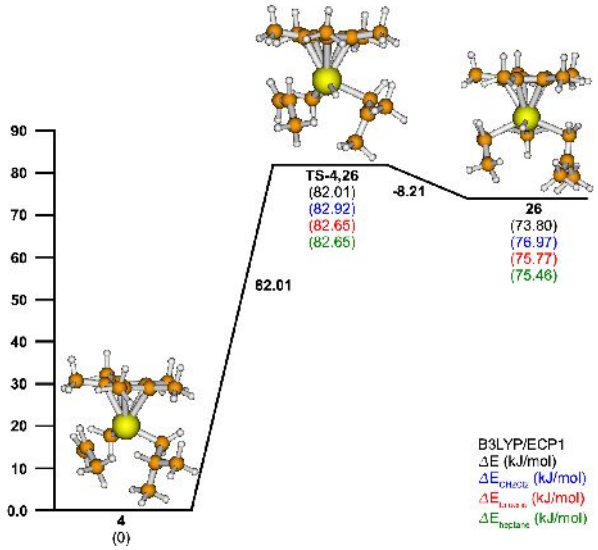


Figure S115: β-H Elimination with Ti-H formation, energies for the PCM calculations are in colour.