DFT computations support the σ-complex assisted metathesis (σ-CAM) mechanism for the 1,4-Rh shift of Cp*Rh(III)-(η^1-β-styryl) complexes

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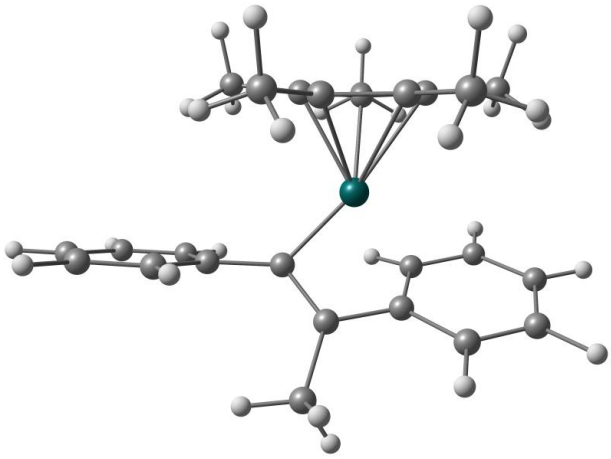
Computational methods

All computations were executed on Gaussian 09 (AM64L-G09RevA.02).[1] Optimizations were performed with the default IEFPCM/PBE0/DGDZVP and SMD/ωB97xD/DGDZVP methods in implicit solvent (1,2-dichloroethane) by using cut-off values for maximum force of 0.0001500, root-mean-square (RMS) force of 0.0001000, maximum displacement of 0.001800, and RMS displacement of 0.001200. In all cases, the predicted change in energy was confirmed to be less than 1×10^{-6}. All stationary points were confirmed to reside in their respective PEHS minima by having only positive vibrational frequencies for intermediates or one negative frequency for transition states, within the computational error (25 cm^{-1}). The frequency calculations were corrected for the reaction temperature (333.15 K) in order to obtain the vibrational partition function hence ΔS and ΔG. The pathways incorporating the transition states were found by IRC calculations taking 40 points in each direction with force constants check-pointed from the previous TS frequency calculations using the local quadratic approximation (LQA) algorhytm. AIM analyses were performed by the AIMall[2] software suite with the default parameters.

Computational results

Structure plots, Cartesian coordinates, energies asn first 3 frequences (IEFPCM/PBE0/DGDZVP level of theory)

1a



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	-0.433810	-0.160820	-0.007096
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3	6	0	0.422421	2.131966	0.296417
4	6	0	0.992457	3.246108	1.126608
5	6	0	-1.019150	2.140015	-0.044448
6	6	0	-2.000467	2.678945	0.826272
7	6	0	-3.335117	2.645369	0.479430
8	6	0	-3.749691	2.082114	-0.744729
9	6	0	-2.811356	1.576421	-1.621099

10	6	0	-1.439062	1.606868	-1.292515
11	6	0	-2.006821	-1.825068	-0.090844
12	6	0	-0.886169	-2.013830	-1.002903
13	6	0	0.316759	-2.187514	-0.221655
14	6	0	-0.043876	-1.965950	1.142893
15	6	0	-1.491339	-1.767319	1.212701
16	6	0	-3.443009	-1.725632	-0.483216
17	6	0	-0.991077	-2.202423	-2.477162
18	6	0	1.656874	-2.589135	-0.736832
19	6	0	0.854184	-2.075070	2.326271
20	6	0	-2.259877	-1.580779	2.476237
21	1	0	2.083372	3.232108	1.092951
22	1	0	0.690684	3.150762	2.174962
23	1	0	0.634127	4.215946	0.768155
24	1	0	-1.698015	3.105962	1.777804
25	1	0	-4.076476	3.054185	1.160369
26	1	0	-4.803701	2.074657	-1.006588
27	1	0	-3.115022	1.189002	-2.589598
28	1	0	-3.559994	-1.410825	-1.521085
29	1	0	-3.987483	-1.018265	0.146325
30	1	0	-3.922738	-2.705632	-0.378458
31	1	0	-1.194882	-3.258764	-2.691093
32	1	0	-0.063159	-1.932246	-2.983926
33	1	0	-1.803286	-1.614412	-2.907877
34	1	0	1.817761	-2.239323	-1.758053
35	1	0	1.735688	-3.682473	-0.739117
36	1	0	2.462616	-2.193938	-0.115184
37	1	0	0.767442	-3.081304	2.754043
38	1	0	0.580474	-1.361308	3.106258
39	1	0	1.899309	-1.913218	2.057829
40	1	0	-2.405066	-2.550254	2.967008
41	1	0	-3.244708	-1.149515	2.289876
42	1	0	-1.729383	-0.936107	3.180910
43	1	0	-0.706762	1.417551	-2.072121
44	6	0	2.554024	0.798972	-0.196790
45	6	0	3.220816	0.732339	-1.430162
46	6	0	3.289523	0.591556	0.981504
47	6	0	4.589186	0.480934	-1.482194
48	1	0	2.659775	0.881861	-2.349146
49	6	0	4.657699	0.334178	0.923804
50	1	0	2.786772	0.636069	1.944393
51	6	0	5.312957	0.278530	-0.306288
52	1	0	5.091556	0.438986	-2.444936
53	1	0	5.213492	0.178182	1.844677
54	1	0	6.379761	0.077226	-0.348591

SCF Done: E(RPBE1PBE) = -5655.53762057 A.U. after 1 cycles
Convg = 0.2657D-08 -V/T = 2.0041

Zero-point correction= 0.458574 (Hartree/Particle)
Thermal correction to Energy= 0.485681
Thermal correction to Enthalpy= 0.486625
Thermal correction to Gibbs Free Energy= 0.401865
Sum of electronic and zero-point Energies= -5655.079047
Sum of electronic and thermal Energies= -5655.051939
Sum of electronic and thermal Enthalpies= -5655.050995
Sum of electronic and thermal Free Energies= -5655.135755

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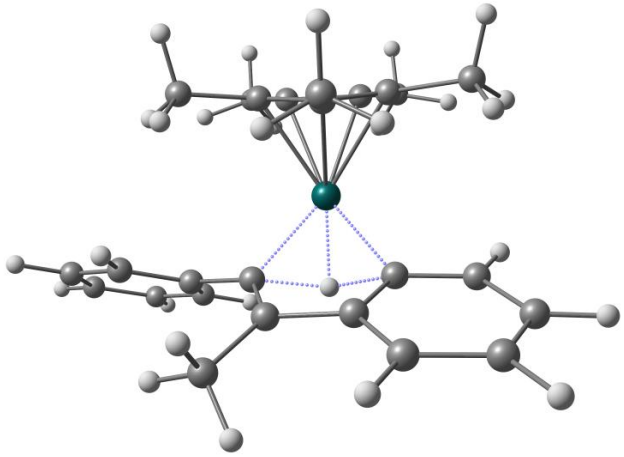
Frequencies --	29.8943	33.8170	42.5392

1b



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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3	6	0	0.209466	2.301572	0.258188
4	6	0	0.799631	3.514861	0.899264
5	6	0	-1.243129	2.254402	-0.042831
6	6	0	-2.199596	3.206282	0.295947
7	6	0	-3.494322	3.091818	-0.226835
8	6	0	-3.826001	2.047450	-1.085388
9	6	0	-2.876288	1.064583	-1.403401
10	6	0	-1.603604	1.159323	-0.863102
11	6	0	-1.869079	-1.851035	0.517751
12	6	0	-0.997126	-2.675294	-0.209909
13	6	0	0.362428	-2.529698	0.342410
14	6	0	0.311285	-1.613868	1.403840
15	6	0	-1.051418	-1.089380	1.455782
16	6	0	-3.353634	-1.777543	0.402120
17	6	0	-1.343543	-3.599727	-1.324103
18	6	0	1.546035	-3.306109	-0.123184
19	6	0	1.411481	-1.256453	2.340557
20	6	0	-1.574662	-0.153386	2.486995
21	1	0	-0.205839	1.019412	-1.200071
22	1	0	1.884815	3.545271	0.796211
23	1	0	0.558479	3.538084	1.968836
24	1	0	0.381621	4.424817	0.456908
25	1	0	-1.952318	4.038553	0.949775
26	1	0	-4.241819	3.838549	0.026708
27	1	0	-4.824478	1.989180	-1.510214
28	1	0	-3.148539	0.240217	-2.057020
29	1	0	-3.697525	-2.052298	-0.596648
30	1	0	-3.730589	-0.779021	0.628390
31	1	0	-3.806637	-2.475096	1.116041
32	1	0	-1.321845	-4.635028	-0.963615
33	1	0	-0.620317	-3.528263	-2.140551
34	1	0	-2.338210	-3.400575	-1.724724
35	1	0	1.548805	-3.424039	-1.209372
36	1	0	1.522384	-4.312141	0.312707
37	1	0	2.482710	-2.831841	0.174145
38	1	0	1.389719	-1.940145	3.197321
39	1	0	1.301967	-0.241463	2.726224
40	1	0	2.391768	-1.340479	1.868657
41	1	0	-1.868759	-0.729495	3.373096

42	1	0	-2.452361	0.388249	2.130485
43	1	0	-0.819045	0.572139	2.792450
44	6	0	2.338863	1.017959	-0.330783
45	6	0	3.207900	1.236383	0.752070
46	6	0	2.891306	0.577218	-1.547153
47	6	0	4.579583	1.034040	0.616324
48	1	0	2.806907	1.554543	1.709909
49	6	0	4.261262	0.379464	-1.681778
50	1	0	2.234777	0.408013	-2.397876
51	6	0	5.113072	0.607362	-0.599121
52	1	0	5.233386	1.207567	1.467019
53	1	0	4.666859	0.049486	-2.634460
54	1	0	6.183314	0.451339	-0.702379

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SCF Done:  E(RPBE1PBE) =  -5655.46789019     A.U. after    1 cycles
             Convg  =    0.2731D-08             -V/T =  2.0041
Zero-point correction=                           0.453751 (Hartree/Particle)
 Thermal correction to Energy=                    0.480462
 Thermal correction to Enthalpy=                  0.481406
 Thermal correction to Gibbs Free Energy=         0.398102
 Sum of electronic and zero-point Energies=          -5655.014139
 Sum of electronic and thermal Energies=             -5654.987428
 Sum of electronic and thermal Enthalpies=           -5654.986484
 Sum of electronic and thermal Free Energies=        -5655.069788
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                     A                      A                      A
 Frequencies -- -1574.7999               20.8701                41.4294
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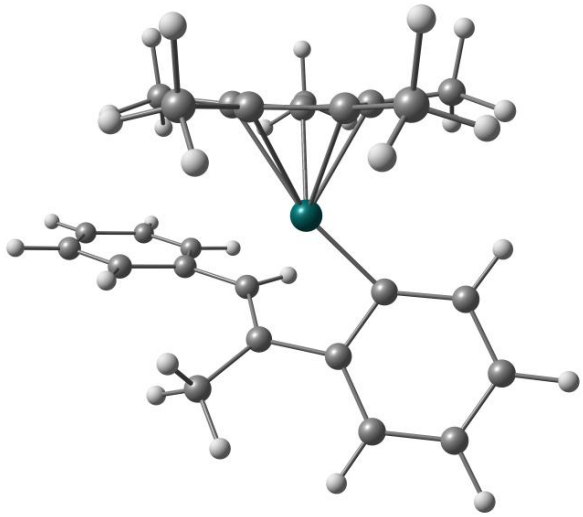
1c



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3	6	0	0.166570	2.001190	0.590504
4	6	0	0.645343	2.478972	1.930182
5	6	0	-1.241397	2.222003	0.211675
6	6	0	-2.011530	3.352121	0.549338
7	6	0	-3.285633	3.467088	0.018087
8	6	0	-3.820289	2.459177	-0.806113
9	6	0	-3.094025	1.307701	-1.082110
10	6	0	-1.804544	1.178079	-0.552744

11	6	0	-1.442177	-2.075735	-0.802964
12	6	0	-0.020852	-1.983373	-1.057908
13	6	0	0.689504	-2.178620	0.204530
14	6	0	-0.267326	-2.242890	1.221678
15	6	0	-1.598416	-2.153331	0.609384
16	6	0	-2.509839	-2.161689	-1.840364
17	6	0	0.619331	-1.951888	-2.401012
18	6	0	2.165592	-2.337929	0.327267
19	6	0	-0.034305	-2.415985	2.683414
20	6	0	-2.877742	-2.276803	1.362618
21	1	0	0.598470	1.452113	-1.393844
22	1	0	1.659781	2.880147	1.877640
23	1	0	0.639880	1.669927	2.666845
24	1	0	-0.018585	3.253479	2.317282
25	1	0	-1.605640	4.151892	1.163132
26	1	0	-3.877401	4.353596	0.228519
27	1	0	-4.822574	2.577344	-1.210230
28	1	0	-3.538998	0.518944	-1.683325
29	1	0	-2.291557	-1.524056	-2.699250
30	1	0	-3.486480	-1.882724	-1.441680
31	1	0	-2.581594	-3.193975	-2.201646
32	1	0	0.809871	-2.981764	-2.728359
33	1	0	1.578271	-1.430146	-2.380848
34	1	0	-0.023123	-1.477314	-3.144601
35	1	0	2.706868	-1.685627	-0.360823
36	1	0	2.436775	-3.371957	0.083192
37	1	0	2.517766	-2.129382	1.338490
38	1	0	-0.275115	-3.444053	2.977779
39	1	0	-0.673009	-1.753356	3.273140
40	1	0	1.004495	-2.223558	2.955283
41	1	0	-3.061765	-3.332999	1.593970
42	1	0	-3.726488	-1.903668	0.787959
43	1	0	-2.839038	-1.736741	2.311238
44	6	0	2.423357	1.146643	-0.294809
45	6	0	3.150101	1.173920	-1.498144
46	6	0	3.121498	0.865100	0.892120
47	6	0	4.524020	0.956080	-1.515856
48	1	0	2.628052	1.378295	-2.430230
49	6	0	4.496208	0.649124	0.874146
50	1	0	2.593397	0.781182	1.835556
51	6	0	5.205161	0.698077	-0.326173
52	1	0	5.063223	0.988630	-2.458544
53	1	0	5.015224	0.429906	1.803298
54	1	0	6.278113	0.527749	-0.335151

SCF Done: E(RPBE1PBE) = -5655.53570438 A.U. after 1 cycles
Convg = 0.4562D-08 -V/T = 2.0041
Zero-point correction= 0.459255 (Hartree/Particle)
Thermal correction to Energy= 0.486031
Thermal correction to Enthalpy= 0.486976
Thermal correction to Gibbs Free Energy= 0.403134
Sum of electronic and zero-point Energies= -5655.076449
Sum of electronic and thermal Energies= -5655.049673
Sum of electronic and thermal Enthalpies= -5655.048729
Sum of electronic and thermal Free Energies= -5655.132570

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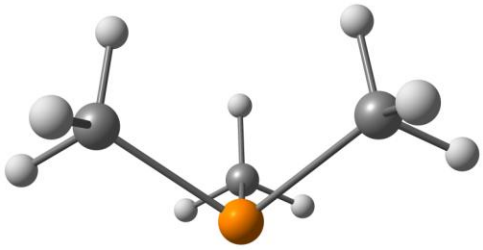
Frequencies --	20.0678	36.1929	45.0802

PMe_3



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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4	6	0	-1.581376	-0.401911	0.274633
5	1	0	0.906932	-2.196374	-0.020017
6	1	0	1.063259	-1.089722	1.364942
7	1	0	2.172281	-0.963277	-0.021057
8	1	0	0.413415	1.464940	1.365018
9	1	0	-0.252092	2.362525	-0.020267
10	1	0	1.448600	1.883630	-0.020763
11	1	0	-1.475999	-0.372717	1.365193
12	1	0	-1.918970	-1.400506	-0.018671
13	1	0	-2.356100	0.311360	-0.022262

SCF Done: E(RPBE1PBE) = -460.775009236 A.U. after 1 cycles
Convg = 0.2706D-08 -V/T = 2.0079
Zero-point correction= 0.113592 (Hartree/Particle)
Thermal correction to Energy= 0.120267
Thermal correction to Enthalpy= 0.121212
Thermal correction to Gibbs Free Energy= 0.084297
Sum of electronic and zero-point Energies= -460.661417
Sum of electronic and thermal Energies= -460.654742
Sum of electronic and thermal Enthalpies= -460.653798
Sum of electronic and thermal Free Energies= -460.690712

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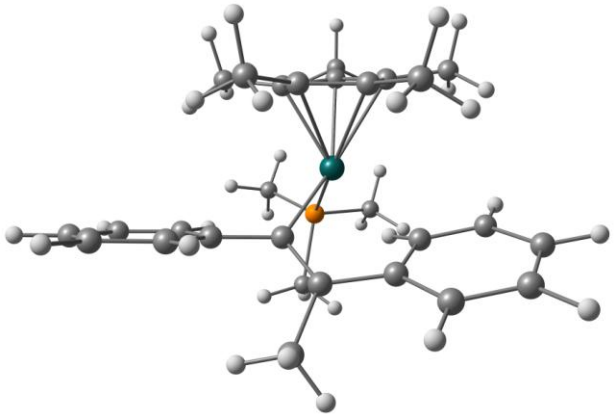
Frequencies --	175.4716	203.3824	210.7505

2a



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

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3	6	0	-0.885030	1.143271	0.368486
4	6	0	-0.261458	2.307537	0.696590
5	6	0	-0.962233	3.599188	1.049934
6	6	0	1.208951	2.335969	0.717569
7	6	0	1.948165	3.492890	0.421455
8	6	0	3.338614	3.453905	0.362466
9	6	0	4.038157	2.269316	0.614313
10	6	0	3.327462	1.118034	0.938215
11	6	0	1.932954	1.161174	0.988483
12	6	0	1.873009	-1.453281	-1.495510
13	6	0	0.821690	-2.352815	-1.266594
14	6	0	-0.424797	-1.683956	-1.637548
15	6	0	-0.077503	-0.417733	-2.245237
16	6	0	1.314623	-0.231976	-2.078709
17	6	0	3.328535	-1.731735	-1.318656
18	6	0	0.963720	-3.785808	-0.873753
19	6	0	-1.768571	-2.324971	-1.718044
20	6	0	-1.007461	0.464380	-3.003525
21	6	0	2.116405	0.918330	-2.588103
22	6	0	-1.345555	-2.955614	2.033444
23	6	0	1.325810	-2.290485	2.726622
24	6	0	-0.755289	-0.458555	3.357752
25	1	0	1.420747	0.323313	1.499978
26	1	0	-2.014150	3.435271	1.287518
27	1	0	-0.920370	4.332810	0.236311
28	1	0	-0.483990	4.061154	1.920814
29	1	0	1.433885	4.426086	0.211088
30	1	0	3.887074	4.359753	0.117492
31	1	0	5.123601	2.254434	0.579922
32	1	0	3.850888	0.198441	1.185747
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34	1	0	3.901468	-0.814644	-1.173323
35	1	0	3.718685	-2.224540	-2.217418
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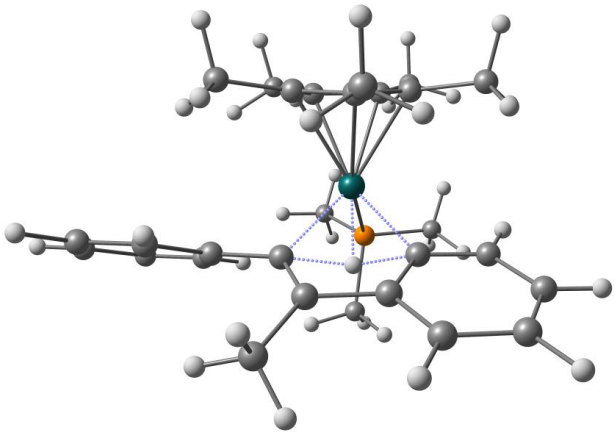
37	1	0	0.060533	-4.183699	-0.409753
38	1	0	1.805216	-3.949380	-0.197407
39	1	0	-1.878935	-3.135859	-0.996009
40	1	0	-1.912390	-2.750575	-2.718877
41	1	0	-2.567335	-1.601004	-1.542694
42	1	0	-1.000732	0.158880	-4.056929
43	1	0	-0.706847	1.512774	-2.959097
44	1	0	-2.033480	0.385366	-2.642464
45	1	0	2.521691	0.673998	-3.577473
46	1	0	2.958453	1.150429	-1.932708
47	1	0	1.506846	1.817933	-2.688675
48	1	0	-2.292062	-2.723975	1.544030
49	1	0	-1.543062	-3.231926	3.073639
50	1	0	-0.894262	-3.813899	1.532420
51	1	0	1.079992	-2.821879	3.651325
52	1	0	2.060891	-1.514227	2.953176
53	1	0	1.771939	-2.991989	2.019193
54	1	0	-0.809186	-1.028276	4.290437
55	1	0	-1.736567	-0.036504	3.135558
56	1	0	-0.052911	0.368719	3.487537
57	6	0	-2.336771	1.086386	0.108527
58	6	0	-3.171786	0.082949	0.624619
59	6	0	-2.939628	2.050458	-0.724292
60	6	0	-4.539018	0.059880	0.363484
61	1	0	-2.750013	-0.695272	1.248525
62	6	0	-4.303574	2.024697	-1.001364
63	1	0	-2.322429	2.822520	-1.174350

64	6	0	-5.115762	1.032372	-0.453224
65	1	0	-5.153937	-0.726428	0.793810
66	1	0	-4.731783	2.782163	-1.653033
67	1	0	-6.180856	1.010794	-0.667058

SCF Done: E(RPBE1PBE) = -6116.34817123 A.U. after 1 cycles
Convg = 0.2243D-08 -V/T = 2.0044
Zero-point correction= 0.575382 (Hartree/Particle)
Thermal correction to Energy= 0.609785
Thermal correction to Enthalpy= 0.610729
Thermal correction to Gibbs Free Energy= 0.511996
Sum of electronic and zero-point Energies= -6115.772789
Sum of electronic and thermal Energies= -6115.738386
Sum of electronic and thermal Enthalpies= -6115.737442
Sum of electronic and thermal Free Energies= -6115.836175

	1	2	3
	A	A	A
Frequencies --	19.5830	36.1532	49.0819

2b



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	0.388385	-0.401286	-0.095171
2	15	0	0.435413	-1.549659	1.979662
3	6	0	-1.014960	1.242804	0.364059
4	6	0	-0.466029	2.491897	0.353171
5	6	0	-1.214476	3.790794	0.405762
6	6	0	1.006887	2.518266	0.433702
7	6	0	1.811477	3.659894	0.441469
8	6	0	3.186285	3.534365	0.646305
9	6	0	3.757863	2.280779	0.859832
10	6	0	2.961070	1.130235	0.841263
11	6	0	1.597681	1.248138	0.604119
12	6	0	1.768948	-0.908243	-1.848404
13	6	0	1.151134	-2.098541	-1.381172
14	6	0	-0.288171	-1.970035	-1.575613
15	6	0	-0.525396	-0.712030	-2.186306
16	6	0	0.727396	-0.009734	-2.281336
17	6	0	3.235693	-0.662676	-1.964272
18	6	0	1.854762	-3.361476	-1.006997
19	6	0	-1.302935	-3.055764	-1.414072
20	6	0	-1.829465	-0.257464	-2.740404
21	6	0	0.932464	1.322347	-2.924116
22	6	0	-0.629885	-3.021666	2.174821
23	6	0	2.090081	-2.181317	2.430797

24	6	0	0.035609	-0.512713	3.433776
25	1	0	0.290218	0.772428	1.074391
26	1	0	-2.264949	3.652024	0.662022
27	1	0	-1.165993	4.312944	-0.557083
28	1	0	-0.765867	4.453612	1.152686
29	1	0	1.375979	4.644144	0.291336
30	1	0	3.812744	4.422212	0.652656
31	1	0	4.826000	2.192034	1.039614
32	1	0	3.423822	0.158795	0.988356
33	1	0	3.803333	-1.204047	-1.204510
34	1	0	3.479603	0.397609	-1.877162
35	1	0	3.585554	-1.005708	-2.945352
36	1	0	1.930347	-4.002708	-1.893353
37	1	0	1.317969	-3.932544	-0.246611
38	1	0	2.869610	-3.176811	-0.650433
39	1	0	-0.967190	-3.831806	-0.724778
40	1	0	-1.488836	-3.537278	-2.381647
41	1	0	-2.256509	-2.666601	-1.048856
42	1	0	-1.951533	-0.687615	-3.742340
43	1	0	-1.878964	0.827520	-2.839046
44	1	0	-2.673311	-0.588964	-2.132601
45	1	0	1.018534	1.209019	-4.011217
46	1	0	1.843545	1.803874	-2.563872
47	1	0	0.095755	1.995095	-2.722950
48	1	0	-1.667435	-2.796294	1.922534
49	1	0	-0.580751	-3.376426	3.208990
50	1	0	-0.281330	-3.821752	1.518813
51	1	0	2.022675	-2.774919	3.347964
52	1	0	2.767096	-1.342766	2.606551
53	1	0	2.501024	-2.803660	1.635083
54	1	0	0.162241	-1.093554	4.352050
55	1	0	-0.988870	-0.139519	3.388015
56	1	0	0.713857	0.344239	3.461654
57	6	0	-2.448771	0.933223	0.344101
58	6	0	-3.322736	1.645299	-0.499436
59	6	0	-3.004394	-0.080402	1.141660
60	6	0	-4.688185	1.373449	-0.519595
61	1	0	-2.923857	2.402986	-1.166755
62	6	0	-4.368393	-0.350963	1.127627
63	1	0	-2.358869	-0.661874	1.789226
64	6	0	-5.221156	0.377297	0.296887
65	1	0	-5.335588	1.937164	-1.186249
66	1	0	-4.766807	-1.135573	1.765480
67	1	0	-6.286126	0.162887	0.279371

SCF Done: E(RPBE1PBE) = -6116.29975088 A.U. after 1 cycles
Convg = 0.4853D-08 -V/T = 2.0044

Zero-point correction= 0.571932 (Hartree/Particle)
Thermal correction to Energy= 0.605599
Thermal correction to Enthalpy= 0.606543
Thermal correction to Gibbs Free Energy= 0.510285
Sum of electronic and zero-point Energies= -6115.727819
Sum of electronic and thermal Energies= -6115.694152
Sum of electronic and thermal Enthalpies= -6115.693208
Sum of electronic and thermal Free Energies= -6115.789466

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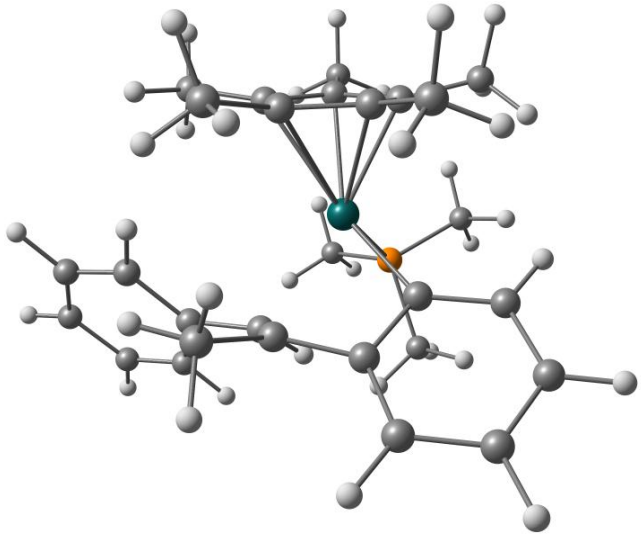
	A	A	A
Frequencies --	-1479.0602	21.4012	36.4038

2c



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	0.460381	-0.332725	-0.022939
2	15	0	0.417479	-0.189188	2.317115
3	6	0	-1.283767	1.377363	0.090148
4	6	0	-0.488988	1.842477	-0.946562
5	6	0	-0.960577	2.105731	-2.341275
6	6	0	0.877310	2.325055	-0.601640
7	6	0	1.419860	3.575524	-0.905810
8	6	0	2.732431	3.845871	-0.517271
9	6	0	3.488522	2.866683	0.131855
10	6	0	2.949150	1.602555	0.396672
11	6	0	1.631974	1.335922	0.029764
12	6	0	1.715191	-1.308770	-1.628528
13	6	0	1.801440	-2.018426	-0.377803
14	6	0	0.502383	-2.641514	-0.135817
15	6	0	-0.374084	-2.232607	-1.151186
16	6	0	0.374453	-1.397642	-2.081325
17	6	0	2.860986	-0.685465	-2.355687
18	6	0	3.085516	-2.387669	0.292242
19	6	0	0.193203	-3.689444	0.881391
20	6	0	-1.758022	-2.765115	-1.352385
21	6	0	-0.120863	-0.974247	-3.422763
22	6	0	-1.116595	-0.873395	3.035353
23	6	0	1.738037	-1.083678	3.208996
24	6	0	0.566180	1.455975	3.108976
25	1	0	-0.961682	1.705987	1.071215
26	1	0	-1.955724	1.720509	-2.554153
27	1	0	-0.253482	1.745202	-3.089942
28	1	0	-0.998890	3.196657	-2.457945
29	1	0	0.837496	4.332644	-1.426154
30	1	0	3.169571	4.818643	-0.725238
31	1	0	4.511682	3.085625	0.428440
32	1	0	3.569897	0.852773	0.882814
33	1	0	3.649253	-0.373906	-1.668512
34	1	0	2.552008	0.192171	-2.926899
35	1	0	3.293785	-1.409376	-3.056268
36	1	0	3.594722	-3.152097	-0.307093
37	1	0	2.930996	-2.805829	1.287015
38	1	0	3.765351	-1.537236	0.379583

39	1	0	0.780696	-3.589521	1.794770
40	1	0	0.430140	-4.673930	0.459039
41	1	0	-0.865983	-3.695889	1.147539
42	1	0	-1.722649	-3.855197	-1.459116
43	1	0	-2.218831	-2.367754	-2.258067
44	1	0	-2.417650	-2.538016	-0.510805
45	1	0	-0.131660	-1.848993	-4.084721
46	1	0	0.527580	-0.227293	-3.883006
47	1	0	-1.139314	-0.581285	-3.397524
48	1	0	-1.980750	-0.320508	2.660255
49	1	0	-1.091961	-0.807662	4.127488
50	1	0	-1.225447	-1.919228	2.741929
51	1	0	1.642310	-0.892466	4.282154
52	1	0	2.720105	-0.741101	2.877094
53	1	0	1.663524	-2.158599	3.046469
54	1	0	0.490755	1.328279	4.192938
55	1	0	-0.212401	2.151218	2.793549
56	1	0	1.536532	1.892151	2.865601
57	6	0	-2.712298	1.005490	0.045360
58	6	0	-3.534497	1.463899	1.088716
59	6	0	-3.304368	0.236644	-0.966119
60	6	0	-4.897993	1.183829	1.108533
61	1	0	-3.103259	2.062401	1.888258
62	6	0	-4.666734	-0.046554	-0.948073
63	1	0	-2.693738	-0.165379	-1.766613
64	6	0	-5.472204	0.427510	0.087334
65	1	0	-5.511842	1.557003	1.923766
66	1	0	-5.099218	-0.648831	-1.742578
67	1	0	-6.535121	0.203249	0.101658

SCF Done: E(RPBE1PBE) = -6116.35391134 A.U. after 1 cycles
Convg = 0.7323D-08 -V/T = 2.0044
Zero-point correction= 0.576045 (Hartree/Particle)
Thermal correction to Energy= 0.610434
Thermal correction to Enthalpy= 0.611378
Thermal correction to Gibbs Free Energy= 0.513170
Sum of electronic and zero-point Energies= -6115.777866
Sum of electronic and thermal Energies= -6115.743478
Sum of electronic and thermal Enthalpies= -6115.742533
Sum of electronic and thermal Free Energies= -6115.840742

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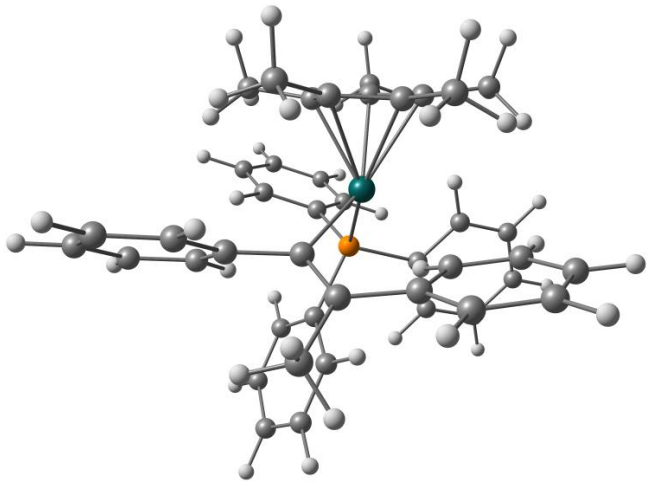
	A	A	A
Frequencies --	29.3754	43.6552	53.1456

3a



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	0.751364	-0.329049	-0.626331
2	15	0	-1.493645	-0.131563	0.299058
3	6	0	1.632166	1.081718	0.645950
4	6	0	2.492670	0.572050	1.567349
5	6	0	3.266543	1.397561	2.569503
6	6	0	2.673823	-0.885544	1.640963
7	6	0	3.867607	-1.477352	2.085400
8	6	0	4.022401	-2.860460	2.081304
9	6	0	2.988004	-3.699174	1.653082
10	6	0	1.787566	-3.136043	1.233482
11	6	0	1.639241	-1.747506	1.231992
12	6	0	1.510723	2.535857	0.414473
13	6	0	0.276267	3.203031	0.387632
14	6	0	0.191755	4.574491	0.165460
15	6	0	1.346246	5.325822	-0.055753
16	6	0	2.584734	4.685951	-0.033751
17	6	0	2.664460	3.315715	0.202276
18	6	0	2.337290	-1.132989	-2.012131
19	6	0	1.102461	-1.814651	-2.396047
20	6	0	0.179627	-0.843999	-2.808908
21	6	0	0.808676	0.469673	-2.645037
22	6	0	2.181631	0.250961	-2.263888
23	6	0	3.612706	-1.821257	-1.666477
24	6	0	0.967459	-3.298396	-2.487004
25	6	0	-1.141480	-1.079019	-3.460422
26	6	0	0.277928	1.759697	-3.171675
27	6	0	3.271669	1.263605	-2.294876
28	6	0	-2.812081	0.432000	-0.837905
29	6	0	-2.720376	1.708562	-1.410115
30	6	0	-3.718432	2.174301	-2.261079
31	6	0	-4.815202	1.365883	-2.562044
32	6	0	-4.911040	0.094786	-2.000016
33	6	0	-3.917864	-0.371138	-1.138712
34	6	0	-2.055954	-1.804793	0.816504
35	6	0	-1.727855	-2.911354	0.023935
36	6	0	-2.172963	-4.186576	0.362082
37	6	0	-2.943927	-4.373312	1.508832
38	6	0	-3.270427	-3.278766	2.307822
39	6	0	-2.832647	-2.000465	1.965256
40	6	0	-1.785355	0.850906	1.818747
41	6	0	-0.866599	0.750884	2.872514
42	6	0	-1.077175	1.448398	4.057929
43	6	0	-2.203836	2.258279	4.204184
44	6	0	-3.124568	2.357323	3.163304
45	6	0	-2.921221	1.653989	1.976500
46	1	0	2.859427	2.405484	2.659606
47	1	0	4.324491	1.493570	2.297317
48	1	0	3.231420	0.925699	3.557731
49	1	0	4.691296	-0.851352	2.415797
50	1	0	4.961150	-3.293096	2.417404
51	1	0	3.113091	-4.777971	1.670348
52	1	0	0.951221	-3.767885	0.946901
53	1	0	-0.631422	2.646994	0.586239
54	1	0	-0.781830	5.058396	0.167338
55	1	0	1.281339	6.395006	-0.238681
56	1	0	3.496353	5.254340	-0.200446
57	1	0	3.638993	2.837231	0.219006
58	1	0	4.289688	-1.166503	-1.115913
59	1	0	4.117032	-2.122844	-2.593140
60	1	0	3.444950	-2.721487	-1.072359

61	1	0	-0.059294	-3.608346	-2.688853
62	1	0	1.309989	-3.799048	-1.578631
63	1	0	1.587892	-3.666602	-3.312629
64	1	0	-1.859447	-0.289424	-3.235243
65	1	0	-1.584622	-2.034189	-3.173064
66	1	0	-0.998979	-1.092328	-4.547840
67	1	0	-0.807297	1.742735	-3.275244
68	1	0	0.703737	1.942544	-4.166229
69	1	0	0.553436	2.602255	-2.532200
70	1	0	2.891744	2.278316	-2.177976
71	1	0	3.771183	1.203998	-3.269729
72	1	0	4.023951	1.082179	-1.524976
73	1	0	-1.871003	2.349182	-1.192550
74	1	0	-3.635227	3.167962	-2.692632
75	1	0	-5.591365	1.726752	-3.231115
76	1	0	-5.762636	-0.540496	-2.227330
77	1	0	-4.011573	-1.361979	-0.705029
78	1	0	-1.120484	-2.776045	-0.865220
79	1	0	-1.911143	-5.033164	-0.266921
80	1	0	-3.286576	-5.367998	1.780112
81	1	0	-3.869868	-3.416425	3.203475
82	1	0	-3.101587	-1.159394	2.597056
83	1	0	0.020479	0.133468	2.772876
84	1	0	-0.356302	1.362951	4.866279
85	1	0	-2.363159	2.808888	5.127223
86	1	0	-4.008066	2.980362	3.271869
87	1	0	-3.653428	1.734265	1.178746
88	1	0	0.607837	-1.357226	1.143788

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SCF Done:  E(RPBE1PBE) =  -6690.88857645     A.U. after    1 cycles
             Convg  =    0.1782D-08             -V/T =  2.0053
Zero-point correction=                           0.736754 (Hartree/Particle)
 Thermal correction to Energy=                    0.780581
 Thermal correction to Enthalpy=                  0.781525
 Thermal correction to Gibbs Free Energy=         0.660984
 Sum of electronic and zero-point Energies=          -6690.151823
 Sum of electronic and thermal Energies=             -6690.107995
 Sum of electronic and thermal Enthalpies=           -6690.107051
 Sum of electronic and thermal Free Energies=        -6690.227593
                     1                      2                      3
                     A                      A                      A
 Frequencies --    24.5958                25.5011                29.9332
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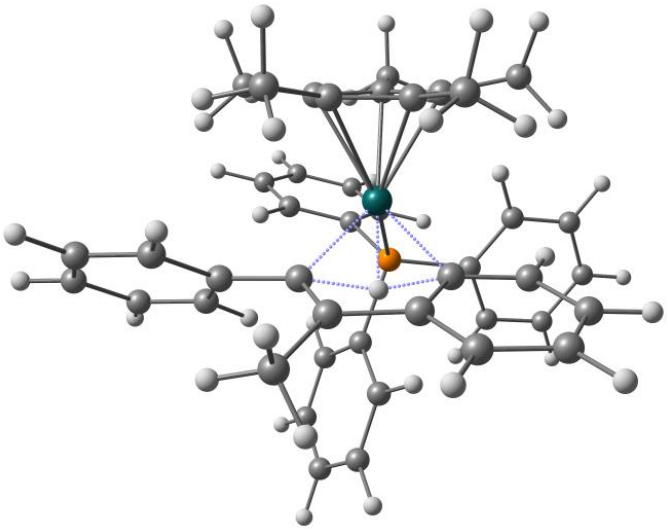
3b



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	0.612686	-0.532810	-0.627170
2	15	0	-1.476894	0.272721	0.249251
3	6	0	2.069772	0.375062	0.786484
4	6	0	2.797381	-0.540371	1.485387
5	6	0	4.033007	-0.254180	2.283951
6	6	0	2.205460	-1.890987	1.544492
7	6	0	2.734879	-2.997852	2.210872
8	6	0	1.989891	-4.176139	2.289135
9	6	0	0.714738	-4.248390	1.729202
10	6	0	0.178543	-3.147397	1.050998
11	6	0	0.935076	-1.989279	0.939343
12	6	0	0.394754	-1.887176	-2.470462
13	6	0	0.047827	-0.542750	-2.837490
14	6	0	1.202745	0.296987	-2.657120
15	6	0	2.270203	-0.546850	-2.206718
16	6	0	1.766627	-1.878411	-2.062699
17	6	0	-0.392286	-3.134191	-2.718230
18	6	0	-1.210369	-0.127591	-3.523462
19	6	0	1.352084	1.721085	-3.085293
20	6	0	3.707944	-0.168680	-2.121095
21	6	0	2.575179	-3.087494	-1.735048
22	1	0	0.826609	-0.533257	1.030571
23	1	0	4.227199	0.814789	2.372957
24	1	0	4.910457	-0.721625	1.821532
25	1	0	3.939911	-0.672167	3.291763
26	1	0	3.717783	-2.948727	2.672071
27	1	0	2.401038	-5.038272	2.807314
28	1	0	0.130678	-5.160358	1.820811
29	1	0	-0.815809	-3.207007	0.618946
30	1	0	-1.393650	-2.923531	-3.097655
31	1	0	-0.481515	-3.756393	-1.823345
32	1	0	0.117403	-3.736609	-3.479109
33	1	0	-1.065875	-0.250292	-4.603948
34	1	0	-1.456894	0.918717	-3.340188
35	1	0	-2.070058	-0.735582	-3.237446
36	1	0	0.383362	2.202107	-3.227389
37	1	0	1.889525	1.771897	-4.039793
38	1	0	1.917475	2.306069	-2.354251

39	1	0	4.218919	-0.541142	-3.017449
40	1	0	4.202837	-0.611899	-1.254026
41	1	0	3.840838	0.912390	-2.090784
42	1	0	2.915126	-3.558253	-2.665844
43	1	0	1.992469	-3.826422	-1.180981
44	1	0	3.460180	-2.837710	-1.147593
45	6	0	-2.294211	1.530781	-0.792934
46	6	0	-3.634070	1.420029	-1.178707
47	6	0	-1.549063	2.644165	-1.204481
48	6	0	-4.217995	2.410143	-1.969051
49	1	0	-4.226990	0.564827	-0.868239
50	6	0	-2.139307	3.636183	-1.981630
51	1	0	-0.505056	2.738601	-0.917941
52	6	0	-3.474865	3.518302	-2.370037
53	1	0	-5.257820	2.312580	-2.268459
54	1	0	-1.553118	4.497351	-2.290625
55	1	0	-3.933191	4.288340	-2.984336
56	6	0	-1.420224	1.048422	1.911292
57	6	0	-0.764814	0.383748	2.957492
58	6	0	-2.051222	2.270886	2.170215
59	6	0	-0.728562	0.940832	4.232180
60	1	0	-0.295320	-0.583451	2.794277
61	6	0	-2.008298	2.828010	3.447938
62	1	0	-2.577456	2.795468	1.378531
63	6	0	-1.344360	2.168193	4.479396
64	1	0	-0.216912	0.414313	5.032935
65	1	0	-2.498660	3.779694	3.633107
66	1	0	-1.309576	2.605032	5.473501
67	6	0	-2.753728	-1.022091	0.483154
68	6	0	-3.614831	-1.009278	1.587271
69	6	0	-2.905664	-2.022329	-0.482257
70	6	0	-4.606377	-1.980498	1.715806
71	1	0	-3.520607	-0.243036	2.350409
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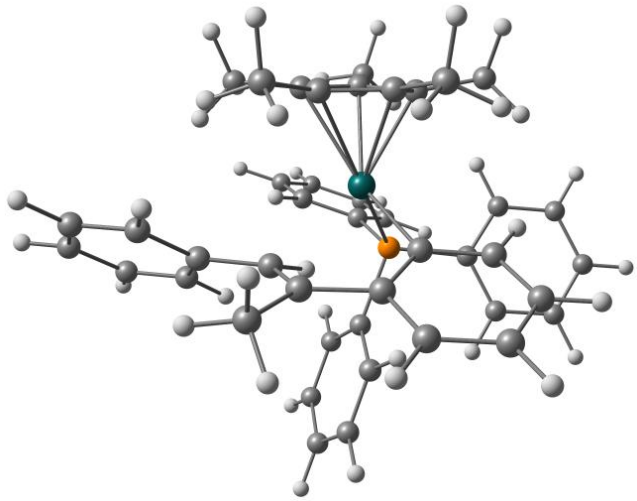
73	1	0	-2.238092	-2.049745	-1.335628
74	6	0	-4.753088	-2.970190	0.745671
75	1	0	-5.265843	-1.960077	2.579019
76	1	0	-4.002962	-3.757610	-1.118050
77	1	0	-5.526090	-3.726402	0.850339
78	6	0	2.393359	1.802458	0.656137
79	6	0	3.681412	2.215278	0.266396
80	6	0	1.452352	2.803519	0.945986
81	6	0	4.005195	3.565776	0.157920
82	1	0	4.441622	1.472019	0.050407
83	6	0	1.776981	4.152790	0.845650
84	1	0	0.462308	2.521110	1.285175
85	6	0	3.054398	4.544087	0.443031
86	1	0	5.008010	3.851333	-0.149255
87	1	0	1.027710	4.902074	1.088283
88	1	0	3.306530	5.597627	0.359054

SCF Done: E(RPBE1PBE) = -6690.84124970 A.U. after 1 cycles
Convg = 0.4731D-08 -V/T = 2.0053

Zero-point correction= 0.732994 (Hartree/Particle)
Thermal correction to Energy= 0.776316
Thermal correction to Enthalpy= 0.777260
Thermal correction to Gibbs Free Energy= 0.658387
Sum of electronic and zero-point Energies= -6690.108256
Sum of electronic and thermal Energies= -6690.064934
Sum of electronic and thermal Enthalpies= -6690.063990
Sum of electronic and thermal Free Energies= -6690.182863

1	2	3
A	A	A
Frequencies -- -1490.7428	21.8464	29.4703

3c



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4	6	0	2.313615	-1.567536	1.434704
5	6	0	3.598384	-2.078022	2.015550
6	6	0	1.139360	-2.455032	1.417898
7	6	0	1.074740	-3.610148	2.218606
8	6	0	-0.066653	-4.404045	2.240921
9	6	0	-1.165077	-4.058336	1.454604
10	6	0	-1.106502	-2.930416	0.633456
11	6	0	0.034367	-2.129095	0.591820
12	6	0	3.170316	0.784250	0.860130
13	6	0	2.775555	2.099328	1.166506
14	6	0	3.669344	3.161138	1.076979
15	6	0	4.985796	2.937906	0.670947
16	6	0	5.394165	1.641753	0.360026
17	6	0	4.499288	0.578218	0.450570
18	6	0	0.801872	-2.171699	-2.329912
19	6	0	-0.356943	-1.391421	-2.678689
20	6	0	0.092964	-0.031797	-2.985787
21	6	0	1.461240	0.042891	-2.697156
22	6	0	1.903766	-1.288929	-2.275554
23	6	0	0.838491	-3.653983	-2.169756
24	6	0	-1.666391	-1.985586	-3.081584
25	6	0	-0.757906	1.005299	-3.637545
26	6	0	2.377814	1.205669	-2.887973
27	6	0	3.324965	-1.689323	-2.076226
28	6	0	-1.643147	2.255055	-0.546262
29	6	0	-0.512698	2.977314	-0.951383
30	6	0	-0.647330	4.245907	-1.507947
31	6	0	-1.915293	4.801245	-1.682505
32	6	0	-3.044238	4.087644	-1.284761
33	6	0	-2.911204	2.823683	-0.710579
34	6	0	-3.048384	-0.107993	0.374742
35	6	0	-3.743005	-0.364708	-0.814630
36	6	0	-5.000481	-0.959385	-0.788562
37	6	0	-5.579333	-1.316110	0.429569
38	6	0	-4.897232	-1.061858	1.617002
39	6	0	-3.640540	-0.457854	1.592902
40	6	0	-1.030630	1.150426	2.017627

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42	6	0	-0.375228	0.558435	4.278036
43	6	0	-0.505294	1.888945	4.673575
44	6	0	-0.902422	2.848307	3.744461
45	6	0	-1.166437	2.483998	2.425091
46	1	0	1.128940	0.094128	0.953973
47	1	0	4.333314	-1.286130	2.150456
48	1	0	4.036907	-2.858492	1.383084
49	1	0	3.420679	-2.527739	2.996047
50	1	0	1.919081	-3.898694	2.837114
51	1	0	-0.099278	-5.287931	2.872021
52	1	0	-2.065358	-4.668015	1.472556
53	1	0	-1.969596	-2.683330	0.019961
54	1	0	1.759063	2.286575	1.505482
55	1	0	3.338523	4.165176	1.328956
56	1	0	5.685293	3.765938	0.596709
57	1	0	6.414869	1.454957	0.036951
58	1	0	4.841347	-0.417488	0.188582
59	1	0	1.618019	-3.968285	-1.472994
60	1	0	1.048635	-4.116790	-3.141668
61	1	0	-0.115415	-4.044496	-1.811431
62	1	0	-2.388574	-1.225439	-3.380413
63	1	0	-2.110492	-2.595500	-2.291604
64	1	0	-1.507035	-2.640687	-3.946531
65	1	0	-0.288130	1.988868	-3.625486
66	1	0	-1.739266	1.102304	-3.168204
67	1	0	-0.922556	0.722692	-4.684383
68	1	0	1.827024	2.128910	-3.074978
69	1	0	3.033659	1.028217	-3.748379
70	1	0	3.019948	1.363312	-2.016222
71	1	0	3.948159	-0.840881	-1.794553
72	1	0	3.716505	-2.085132	-3.021623
73	1	0	3.431179	-2.472769	-1.323211
74	1	0	0.480435	2.551339	-0.829089
75	1	0	0.238445	4.797005	-1.811892
76	1	0	-2.022078	5.787756	-2.125034
77	1	0	-4.034482	4.516246	-1.412113
78	1	0	-3.799444	2.291072	-0.384156
79	1	0	-3.317091	-0.077601	-1.770576
80	1	0	-5.527740	-1.142101	-1.720814
81	1	0	-6.559650	-1.783919	0.451670
82	1	0	-5.343023	-1.328592	2.571225
83	1	0	-3.131360	-0.260707	2.530753
84	1	0	-0.529253	-0.850404	2.669790
85	1	0	-0.070206	-0.199198	4.994519
86	1	0	-0.298894	2.176220	5.700889
87	1	0	-1.010009	3.887370	4.043332
88	1	0	-1.478512	3.247835	1.720153

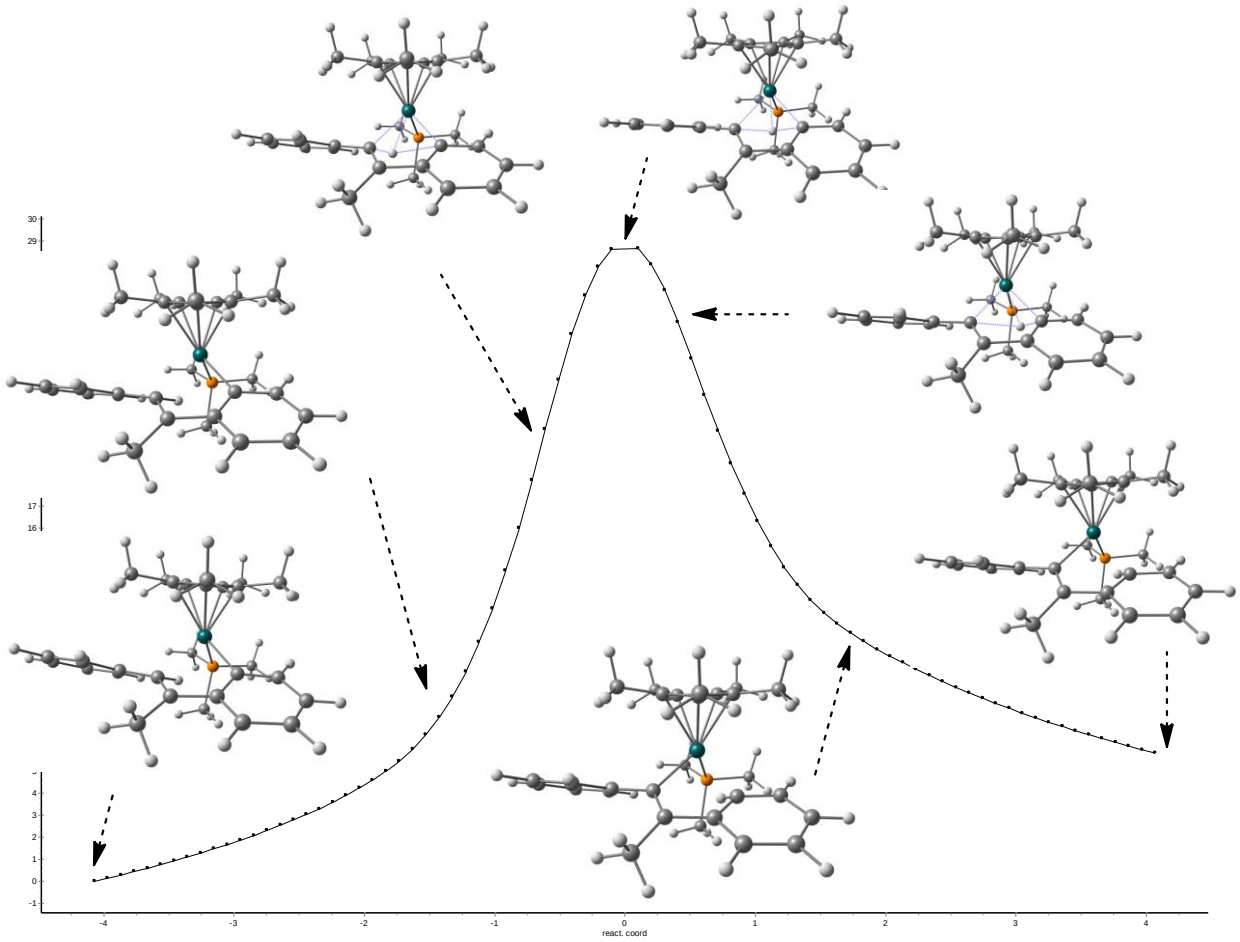
SCF Done: E(RPBE1PBE) = -6690.89665418 A.U. after 1 cycles
Convg = 0.1648D-08 -V/T = 2.0053

Zero-point correction= 0.736365 (Hartree/Particle)
Thermal correction to Energy= 0.780437
Thermal correction to Enthalpy= 0.781381
Thermal correction to Gibbs Free Energy= 0.658796
Sum of electronic and zero-point Energies= -6690.160290
Sum of electronic and thermal Energies= -6690.116217
Sum of electronic and thermal Enthalpies= -6690.115273
Sum of electronic and thermal Free Energies= -6690.237859

	1	2	3
	A	A	A
Frequencies --	17.9524	24.7906	28.2637

Intrinsic reaction coordinate (IRC) plot

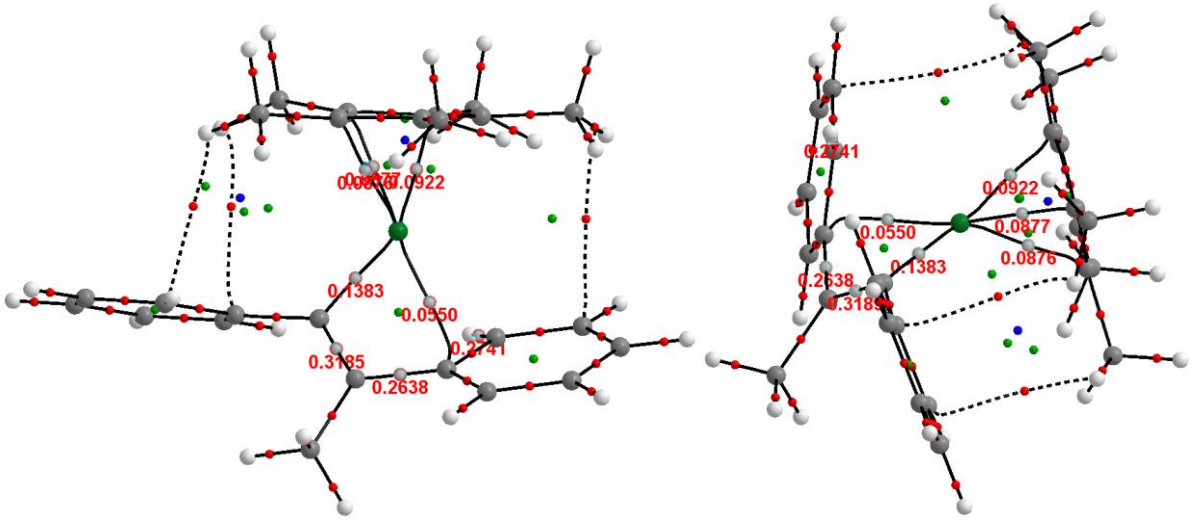
TS 2b



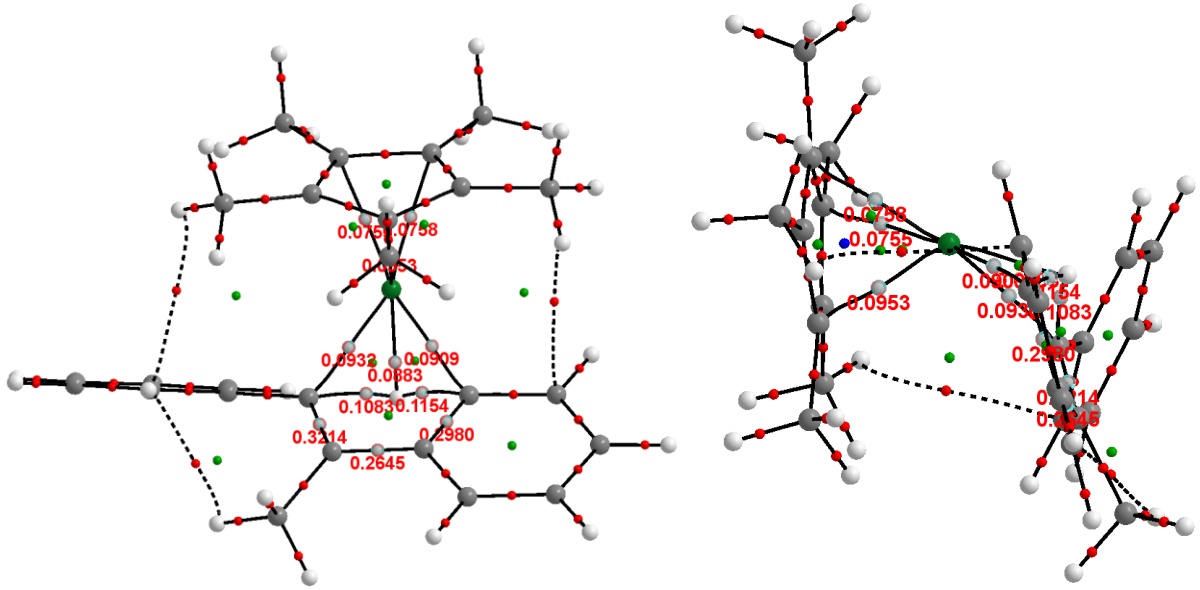
Atom-In-Molecules (AIM) plots

Selected BCP values are only are shown; 2 different orientations per structure.

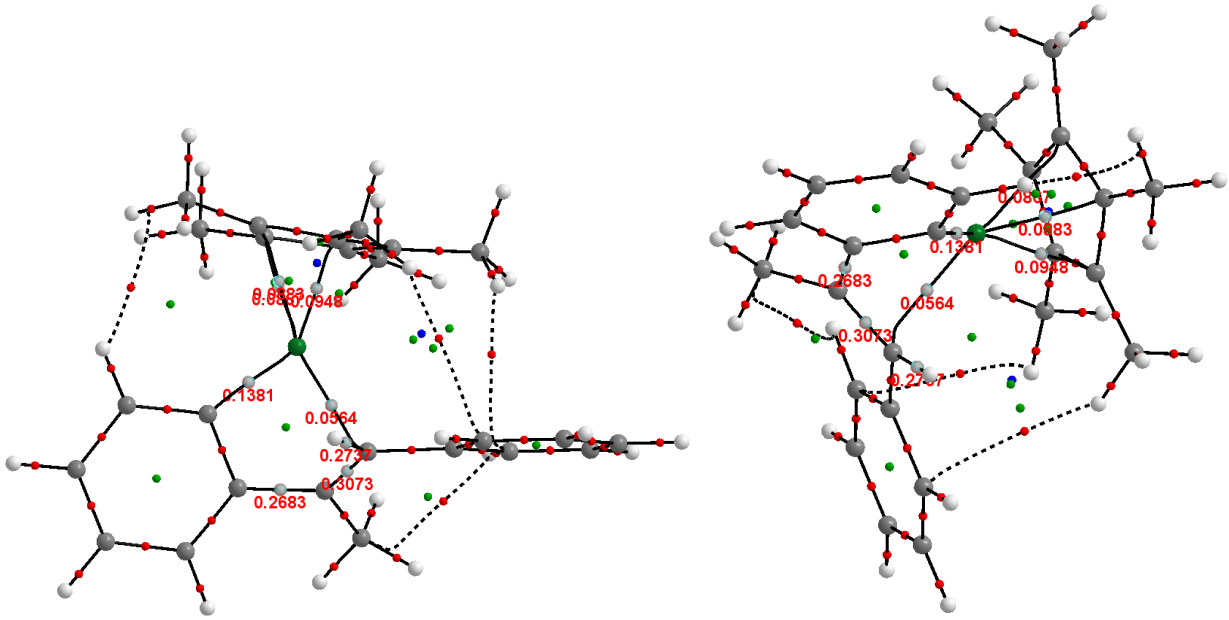
1a



1b



1c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0.3073
0.2683
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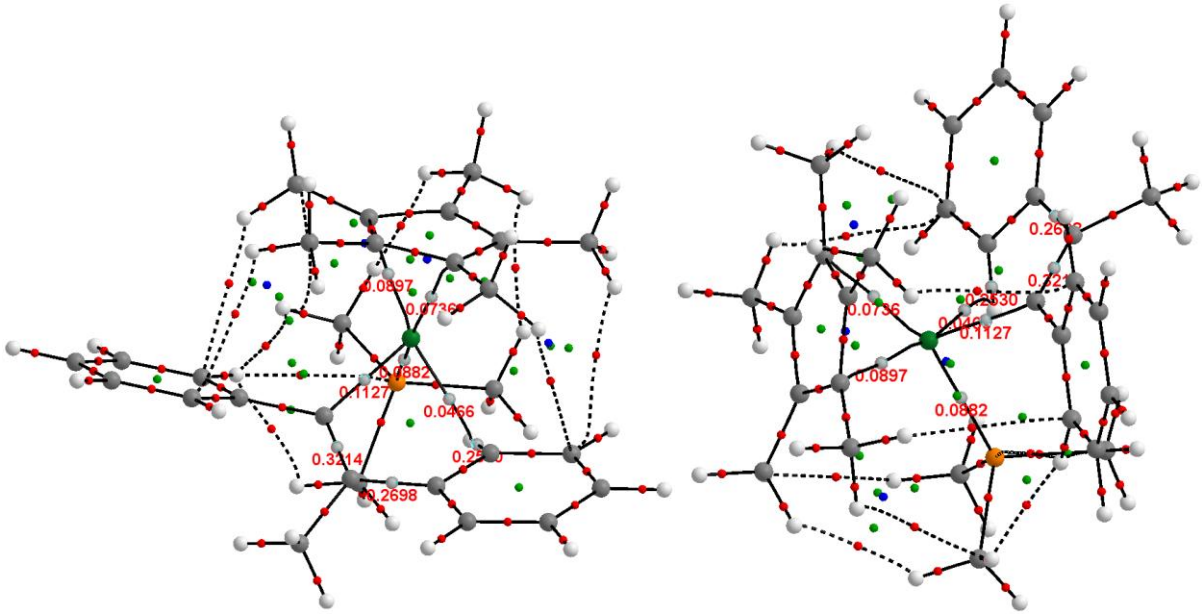
0.0883
0.1381
0.0948
0.2683
0.0564
0.3073

2a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0.0466
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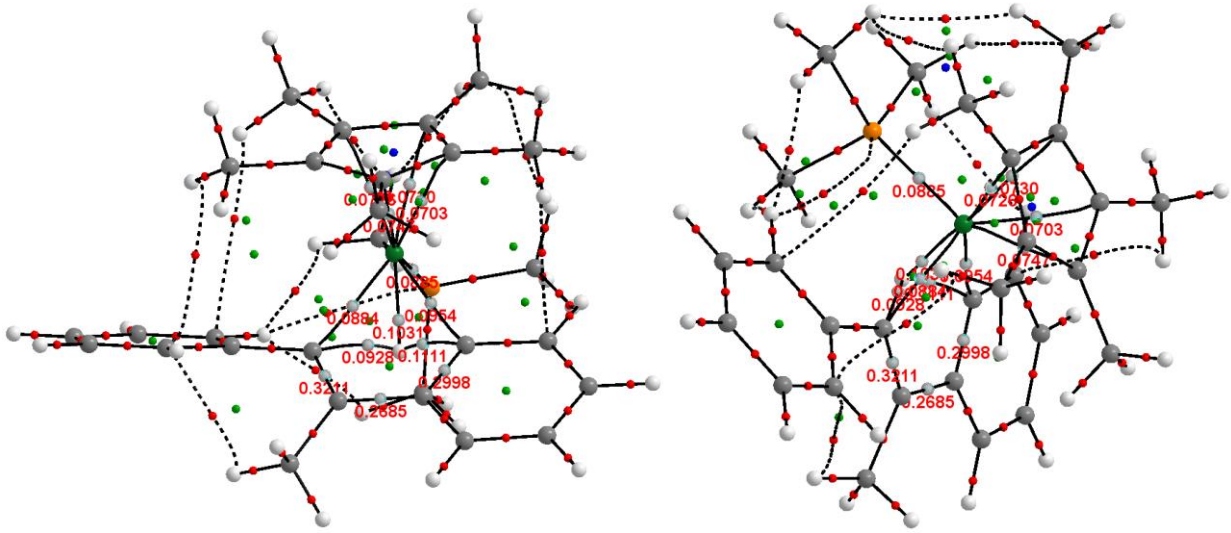
0.2698
0.0736
0.1127
0.0897
0.0882

2b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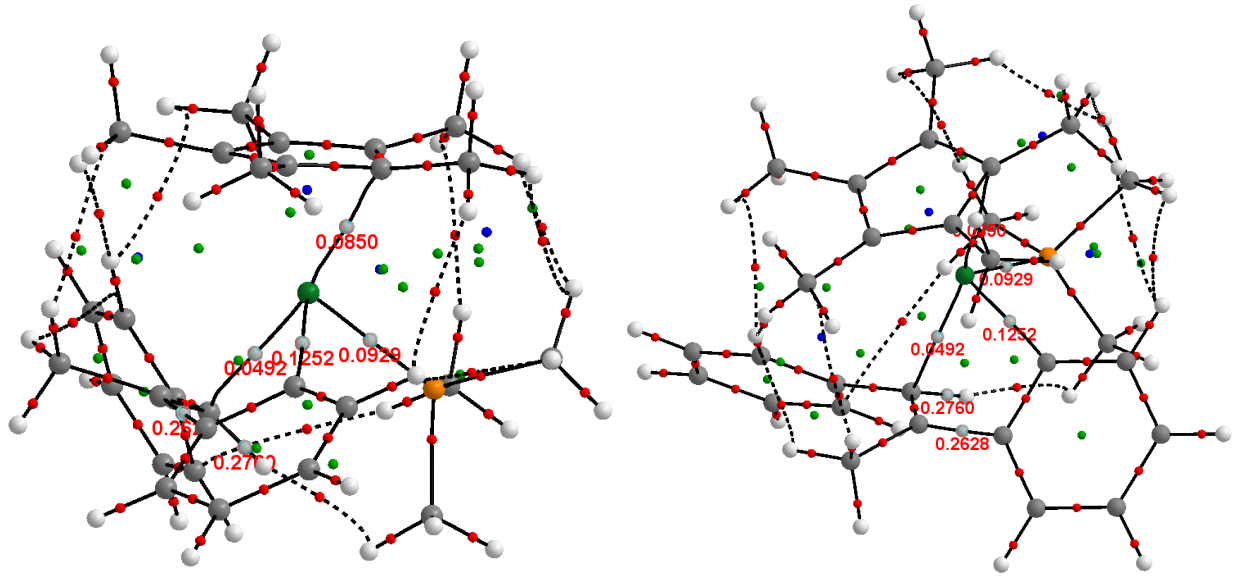
0.0928
0.2998
0.3211
0.2685

2c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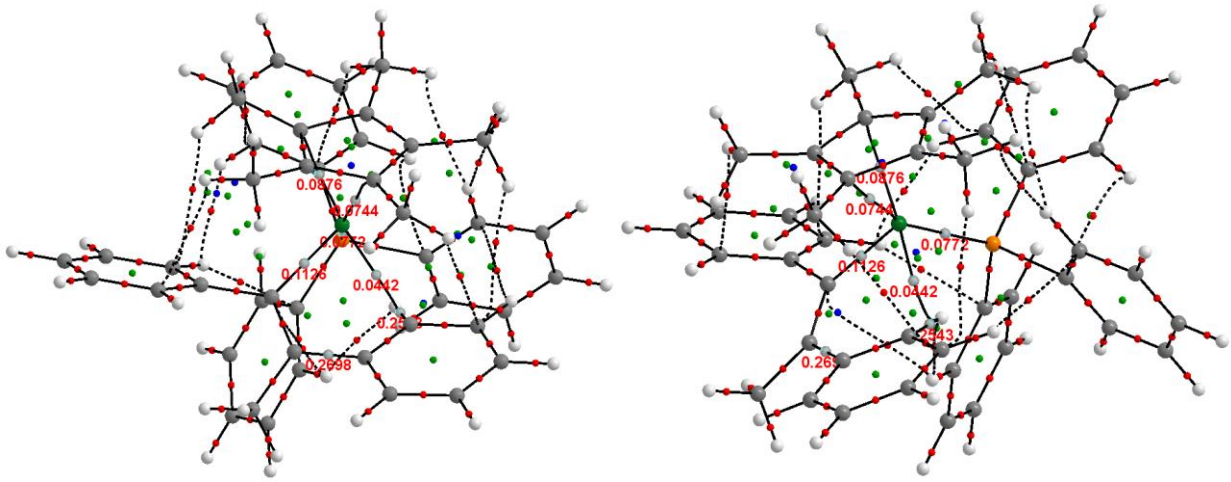
0.1252
0.0929
0.2760
0.2628

3a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0.0744
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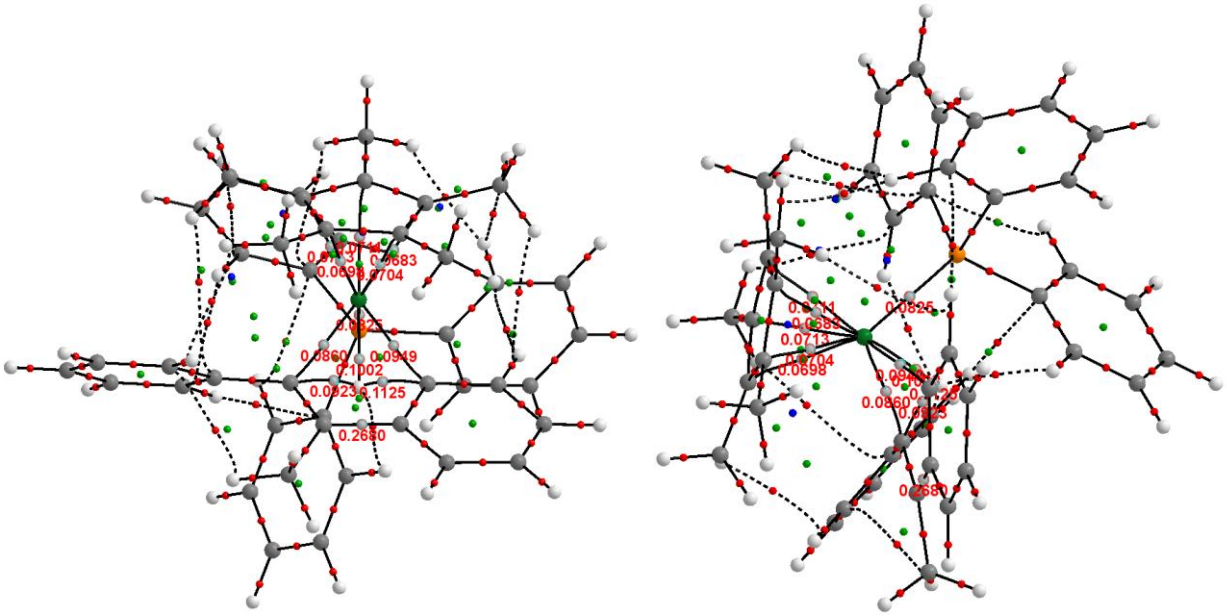
0.1126
0.0442

3b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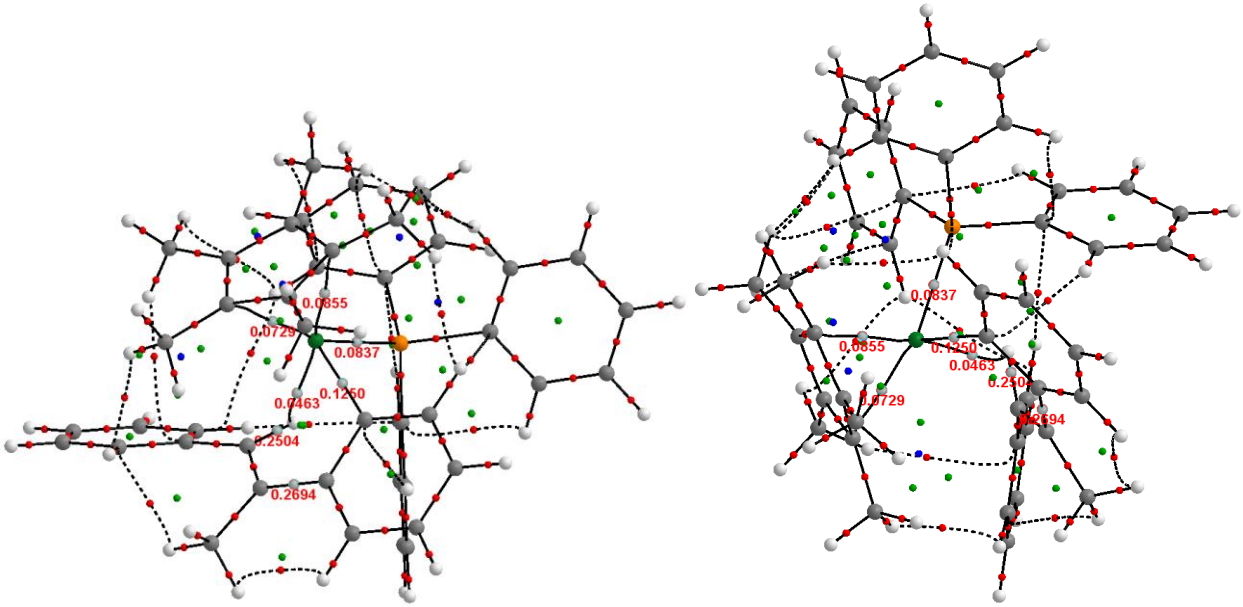
3c



Extended tables

Table S1. Reaction free energies ($\Delta G^{\ddagger}$, ΔG) (including breakdown to enthalpy (ΔH) and entropy ($-T\Delta S$)) terms) for the 1,4-Rh shift reaction in Cp*Rh(III)-(η^1-β-styryl) complexes **1a-c** in 1,2-dichloroethane at 25°C.

Structures	Phosphane	Reaction energies, kcal mol^{-1}											
		PCM/PBE0/DGDZVP						*SMD/ωB97xD/DGDZVP*					
		$\Delta G^{\ddagger a}$	$\Delta H^{\ddagger b}$	$-T\Delta S^{\ddagger c}$	ΔG^{d}	ΔH^{e}	$-T\Delta S^{f}$	$\Delta G^{\ddagger a}$	$\Delta H^{\ddagger b}$	$-T\Delta S^{\ddagger c}$	ΔG^{d}	ΔH^{e}	$-T\Delta S^{f}$
1a-3a	none	41.4	40.5	0.9	2.0	1.4	0.6	41.4	40.7	0.7	1.0	0.6	0.4
1b-3b	PMe_3	29.3	27.6	1.6	–2.9	–3.2	0.3	33.6	32.6	1.0	–2.8	–3.0	0.2
1c-3c	PPh_3	28.1	27.0	1.1	–6.4	–5.2	–1.2	33.4	31.2	1.8	–4.3	–3.9	–0.4
		PCM/ωB97xD/DGDZVP						*SMD/M06/DGDZVP*					
		$\Delta G^{\ddagger a}$	$\Delta H^{\ddagger b}$	$-T\Delta S^{\ddagger c}$	ΔG^{d}	ΔH^{e}	$-T\Delta S^{f}$	$\Delta G^{\ddagger a}$	$\Delta H^{\ddagger b}$	$-T\Delta S^{\ddagger c}$	ΔG^{d}	ΔH^{e}	$-T\Delta S^{f}$
1a-3a	none	44.8	42.3	2.5	2.8	1.8	1.0	40.0	39.0	1.0	1.5	0.8	0.7
1b-3b	PMe_3	32.9	31.9	1.0	–2.0	–2.4	0.4	31.0	30.6	0.4	–2.2	–2.7	0.5
1c-3c	PPh_3	32.5	30.9	1.6	–4.7	–3.8	–0.9	32.9	30.5	2.4	–1.6	–3.4	1.8
		PCM/M06/DGDZVP											
		$\Delta G^{\ddagger a}$	$\Delta H^{\ddagger b}$	$-T\Delta S^{\ddagger c}$	ΔG^{d}	ΔH^{e}	$-T\Delta S^{f}$						
1a-3a	none	41.1	41.3	–0.2	0.2	2.2	–2.2						
1b-3b	PMe_3	29.9	29.0	0.9	–1.6	–3.1	1.4						
1c-3c	PPh_3	32.2	30.1	2.1	–1.8	–3.2	1.4						

[a] $\Delta G^{\ddagger}$ = ΔG(**2**)–ΔG(**1**). [b]$\Delta H^{\ddagger}$ = ΔH(**2**)–ΔH(**1**). [c]$-T\Delta S^{\ddagger}$= $-T[\Delta S$(**2**)–ΔS(**1**)]. [d] ΔG = ΔG(**3**) –ΔG(**1**). [e] ΔH = ΔH(**3**) –ΔH(**1**). [e]$-T\Delta S^{\ddagger}$= $-T[\Delta S$(**2**)–ΔS(**1**)].

Table S2. Key structural parameters for **1-3** using various DFT methods.

Parameter[a]	No phosphane			PMe_3				PPh_3	
	1a	**2a**	**3a**	**1b**	**2b**	**3b**	**1c**	**2c**	**3c**
				PCM/PBE0/DGDZVP					
Rh-C_b (Å)	1.971	2.169	(2.374)	2.094	2.210	(2.445)	2.094	2.224	(2.532)
Rh-C_2 (Å)	(2.406)	2.173	1.983	(2.479)	2.161	2.040	(2.501)	2.163	2.043
Rh-H_m (Å)	(2.613)	1.736	(2.578)	(2.022)	1.660	(2.716)	(2.052)	1.671	(2.015)
C_b-H_m (Å)	(2.661)	1.479	1.088	(2.696)	1.559	1.084	(2.691)	1.559	1.112
C_2-H_m (Å)	1.086	1.445	(2.561)	1.107	1.469	(2.819)	1.106	1.463	(2.504)
Rh-P (Å)	-	-	-	2.370	2.372	2.312	2.436	2.405	2.393
Rh-Cp* (1) (Å)	2.152	2.244	2.137	2.287	2.262	2.183	2.314	2.281	2.321
Rh-Cp* (2) (Å)	2.292	2.249	2.168	2.304	2.288	2.154	2.337	2.298	2.184
Rh-Cp* (3) (Å)	2.278	2.128	2.182	2.257	2.247	2.259	2.254	2.281	2.246
Rh-Cp* (4) (Å)	2.176	2.246	2.299	2.254	2.303	2.319	2.250	2.290	2.267
Rh-Cp* (5) (Å)	2.172	2.246	2.311	2.160	2.261	2.362	2.172	2.271	2.332
C_b-Rh-C_2 (°)	(80.5)	72.8	(79.5)	(77.1)	73.8	(80.5)	(77.3)	73.6	(76.1)
C_b-H_m-C_2 (°)	(88.4)	123.6	(91.1)	(88.5)	120.1	(84.1)	(88.8)	120.7	(96.1)
H_m-Rh-C_b (°)	(69.3)	42.8	(25.0)	(81.5)	44.8	(23.5)	(81.0)	44.4	(25.1)
H_m-Rh-C_2 (°)	(24.6)	41.5	(66.8)	(24.8)	42.7	(71.1)	(25.8)	42.5	(76.2)
C_b-Rh-P (°)	-	-	-	92.0	101.0	85.9	95.9	101.6	98.7
H_m-C_b-C_a-C_1 (°)	(33)	22	18	(30)	24	19	(28)	22	20.1
H_m-C_2-C_1-C_a (°)	−14	−16	(−39)	−15	−19	(−48)	−18	−18	(−24)
C_2-C_1-C_a-C_b (°)	−35	−5	39	−32	−4	58	−27	−4	18
				SMD/ωB97xD/DGDZVP					
Rh-C_b (Å)	2.004	2.171	(2.438)	2.094	2.212	(2.578)	2.092	2.225	(2.625)
Rh-C_2 (Å)	(2.550)	2.190	2.023	(2.566)	2.167	2.037	(2.628)	2.168	2.049
Rh-H_m (Å)	(2.669)	1.730	(2.578)	(2.107)	1.658	(2.727)	(2.290)	1.672	(2.208)
C_b-H_m (Å)	(2.776)	1.468	1.089	(2.745)	1.547	1.083	(2.793)	1.538	1.095
C_2-H_m (Å)	1.086	1.452	(2.665)	1.099	1.456	(2.864)	1.091	1.451	(2.573)
Rh-P (Å)	-	-	-	2.374	2.379	2.355	2.437	2.404	2.394
Rh-Cp* (1) (Å)	2.128	2.250	2.165	2.283	2.251	2.301	2.305	2.268	2.312
Rh-Cp* (2) (Å)	2.291	2.257	2.157	2.298	2.279	2.154	2.321	2.285	2.163
Rh-Cp* (3) (Å)	2.277	2.127	2.292	2.251	2.234	2.258	2.235	2.270	2.241
Rh-Cp* (4) (Å)	2.155	2.248	2.316	2.248	2.294	2.310	2.234	2.285	2.263
Rh-Cp* (5) (Å)	2.165	2.249	2.131	2.138	2.249	2.347	2.147	2.268	2.323
C_b-Rh-C_2 (°)	(79.1)	72.2	(79.1)	(77.1)	73.2	(79.1)	(75.8)	73.0	(75.1)
C_b-H_m-C_2 (°)	(86.1)	123.4	(88.8)	(88.5)	120.9	(84.8)	(88.4)	120.0	(95.2)
H_m-Rh-C_b (°)	(71.3)	42.3	(24.9)	(81.5)	44.3	(23.3)	(79.0)	43.7	(24.3)
H_m-Rh-C_2 (°)	(23.9)	41.4	(69.6)	(24.8)	42.2	(72.3)	(23.7)	42.0	(74.2)
C_b-Rh-P (°)	-	-	-	92.0	101.3	85.9	95.2	101.1	97.4
H_m-C_b-C_a-C_1 (°)	(39)	22	16	(30)	23	16	(32)	22	15.2
H_m-C_2-C_1-C_a (°)	−12	−16	(−42)	−15	−12	(−47)	−11	−17	(−32)
C_2-C_1-C_a-C_b (°)	−46	−5	46	−32	−5	58	−37	−4	32
				PCM/wB97xD/DGDZVP					
Rh-C_b (Å)	1.972	2.162	(2.406)	2.091	2.206	(2.482)	2.090	2.220	(2.556)
Rh-C_2 (Å)	(2.435)	2.179	2.003	(2.532)	2.165	2.041	(2.572)	2.167	2.045
Rh-H_m (Å)	(2.677)	1.738	(2.586)	(2.168)	1.659	(2.733)	(2.178)	1.671	(2.153)
C_b-H_m (Å)	(2.706)	1.466	1.088	(2.765)	1.542	1.081	(2.745)	1.533	1.097
C_2-H_m (Å)	1.084	1.449	(2.674)	1.095	1.457	(2.864)	1.095	1.447	(2.543)
Rh-P (Å)	-	-	-	2.378	2.378	2.357	2.424	2.397	2.390
Rh-Cp* (1) (Å)[c]	2.134	2.243	2.126	2.278	2.248	2.298	2.298	2.264	2.312
Rh-Cp* (2) (Å)[c]	2.170	2.243	2.316	2.142	2.290	2.345	2.151	2.258	2.312
Rh-Cp* (3) (Å)[c]	2.167	2.245	2.294	2.239	2.225	2.298	2.238	2.280	2.243
Rh-Cp* (4) (Å)[c]	2.270	2.126	2.166	2.239	2.277	2.249	2.237	2.271	2.231
Rh-Cp* (5) (Å)[c]	2.286	2.253	2.165	2.291	2.248	2.164	2.315	2.283	2.163
C_b-Rh-C_2 (°)	(80.2)	72.6	(79.9)	(77.9)	73.4	(80.6)	(77.1)	73.6	(76.0)
C_b-H_m-C_2 (°)	(86.9)	123.8	(87.8)	(87.3)	121.1	(83.5)	(88.5)	120.7	(95.3)
H_m-Rh-C_b (°)	(69.2)	42.4	(24.8)	(80.9)	44.2	(23.3)	(80.0)	44.4	(25.1)
H_m-Rh-C_2 (°)	(23.9)	41.6	(70.0)	(25.4)	42.2	(72.1)	(24.9)	42.5	(74.5)
C_b-Rh-P (°)	-	-	-	92.2	100.8	84.5	95.1	101.6	96.7
H_m-C_b-C_a-C_1 (°)	(37)	22	18	(33)	24	18	(31)	22	17
H_m-C_2-C_1-C_a (°)	−14	−15	(−42)	−17	−18	(−49)	−14	−18	(−31)
C_2-C_1-C_a-C_b (°)	−41	−5	45	−36	−5	60	−33	−4	29
				SMD/M06/DGDZVP					

Rh-C_b (Å)	1.992	2.198	(2.415)	2.117	2.246	(2.483)	2.115	2.246	(2.585)
Rh-C_2 (Å)	(2.464)	2.208	2.029	(2.537)	2.192	2.059	(2.627)	2.205	2.058
Rh-H_m (Å)	(2.692)	1.756	(2.596)	(2.084)	1.722	(2.756)	(2.130)	1.708	(2.175)
C_b-H_m (Å)	(2.708)	1.484	1.093	(2.718)	1.547	1.087	(2.742)	1.545	1.101
C_2-H_m (Å)	1.087	1.437	(2.674)	1.104	1.421	(2.800)	1.101	1.434	(2.560)
Rh-P (Å)	-	-	-	2.397	2.388	2.366	2.488	2.443	2.435
Rh-Cp* (1) (Å)[c]	2.167	2.245	2.151	2.301	2.247	2.329	2.332	2.294	2.339
Rh-Cp* (2) (Å)[c]	2.192	2.273	2.338	2.165	2.282	2.381	2.181	2.283	2.341
Rh-Cp* (3) (Å)[c]	2.185	2.156	2.312	2.273	2.286	2.344	2.259	2.302	2.267
Rh-Cp* (4) (Å)[c]	2.278	2.271	2.159	2.274	2.319	2.283	2.259	2.287	2.258
Rh-Cp* (5) (Å)[c]	2.298	2.265	2.182	2.319	2.266	2.193	2.346	2.304	2.193
C_b-Rh-C_2 (°)	(79.8)	71.5	(79.5)	(76.8)	71.7	(78.9)	(75.8)	72.0	(75.5)
C_b-H_m-C_2 (°)	(87.9)	123.5	(88.3)	(88.6)	122.2	(84.5)	(89.2)	122.6	(95.0)
H_m-Rh-C_b (°)	(68.7)	42.2	(24.8)	(80.6)	43.4	(23.2)	(80.5)	43.4	(24.9)
H_m-Rh-C_2 (°)	(23.8)	40.5	(69.4)	(25.3)	40.3	(69.4)	(24.0)	40.6	(74.4)
C_b-Rh-P (°)	-	-	-	92.7	101.6	84.0	94.5	101.1	96.9
H_m-C_b-C_a-C_1 (°)	(34)	22	18	(29)	20	19	(29)	20	17
H_m-C_2-C_1-C_a (°)	−13	−16	(−41)	−17	−17	(−48)	−14	−17	(−31)
C_2-C_1-C_a-C_b (°)	−37	−5	44	−29	−4	56	−30	−4	29
				PCM/M06/DGDZVP					
Rh-C_b (Å)	1.984	2.194	(2.375)	2.111	2.236	(2.448)	2.109	2.237	(2.551)
Rh-C_2 (Å)	(2.427)	2.188	2.006	(2.496)	2.186	2.060	(2.541)	2.197	2.057
Rh-H_m (Å)	(2.668)	1.736	(2.588)	(2.142)	1.713	(2.731)	(2.165)	1.709	(2.103)
C_b-H_m (Å)	(2.699)	1.496	1.092	(2.738)	1.550	1.087	(2.736)	1.545	1.105
C_2-H_m (Å)	1.087	1.432	(2.647)	1.101	1.420	(2.813)	1.100	1.432	(2.523)
Rh-P (Å)	-	-	-	2.398	2.391	2.367	2.457	2.434	2.422
Rh-Cp* (1) (Å)[c]	2.161	2.231	2.148	2.300	2.249	2.319	2.325	2.288	2.345
Rh-Cp* (2) (Å)[c]	2.191	2.261	2.331	2.173	2.284	2.366	2.179	2.270	2.342
Rh-Cp* (3) (Å)[c]	2.188	2.154	2.310	2.263	2.266	2.331	2.263	2.297	2.265
Rh-Cp* (4) (Å)[c]	2.278	2.260	2.194	2.260	2.309	2.272	2.269	2.291	2.255
Rh-Cp* (5) (Å)[c]	2.299	2.263	2.182	2.316	2.264	2.191	2.345	2.300	2.197
C_b-Rh-C_2 (°)	(80.3)	72.1	(80.2)	(77.6)	72.0	(79.9)	(77.0)	72.3	(75.7)
C_b-H_m-C_2 (°)	(87.6)	123.4	(88.4)	(87.3)	122.2	(84.1)	(88.1)	122.8	(95.6)
H_m-Rh-C_b (°)	(69.1)	42.7	(25.0)	(80.1)	43.8	(23.4)	(79.6)	43.6	(25.2)
H_m-Rh-C_2 (°)	(24.1)	40.7	(69.0)	(26.0)	40.5	(70.3)	(25.5)	40.7	(74.7)
C_b-Rh-P (°)	-	-	-	92.8	100.9	84.5	94.6	101.0	97.7
H_m-C_b-C_a-C_1 (°)	(34)	22	19	(33)	20	20	(31)	20	19
H_m-C_2-C_1-C_a (°)	−15	−16	(−40)	−19	−18	(−48)	−16	−17	(−27)
C_2-C_1-C_a-C_b (°)	−37	−5	42	−33	−3	57	−32	−4	24

[a] Parameters connecting non-bonded atoms are shown in brackets.

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