Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Platinum-catalyzed reduction of amides with hydrosilanes bearing dual Si-H group: a theoretical study of the reaction mechanism

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The DFT-optimized geometries (in XYZ file format) which discussed in the main text, using the B3LYP functional.

Complex **1**.

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Complex 1

Pt	-0.452500	-0.000071	-0.069893
S	-2.209073	1.859531	-0.092873
S	-2.208855	-1.859928	-0.091573
Si	1.302678	1.572988	-0.096000
Si	1.302830	-1.572941	-0.096499
C	2.991674	0.704940	0.027860
C	4.215327	1.389582	0.101771
H	4.233280	2.476493	0.101354
C	5.420919	0.697878	0.176602
H	6.358761	1.241088	0.235195
C	5.420993	-0.697506	0.176272
H	6.358893	-1.240644	0.234603
C	4.215475	-1.389305	0.101124
H	4.233545	-2.476213	0.100210
C	2.991746	-0.704760	0.027539
C	1.190980	2.825306	1.342862
H	1.157718	2.320687	2.312228
H	2.064698	3.486665	1.343013
H	0.305284	3.463389	1.254736
C	1.298285	2.616424	-1.691809
H	0.366211	3.179963	-1.797584
H	2.124938	3.336183	-1.685957
H	1.412404	1.984244	-2.576252
C	1.191463	-2.825635	1.342054
H	0.305312	-3.463155	1.254476
H	2.064785	-3.487519	1.341309
H	1.159300	-2.321265	2.311588
C	1.298335	-2.615950	-1.692584
H	1.411962	-1.983507	-2.576901
H	2.125221	-3.335442	-1.687173
H	0.366413	-3.179774	-1.798210
C	-3.781822	1.305346	-0.868117
H	-4.487184	2.130495	-0.740279
H	-3.544851	1.247547	-1.933342
C	-4.422052	-0.000395	-0.383991
H	-4.523363	0.000306	0.705084
H	-5.450545	-0.000513	-0.766663
C	-3.782233	-1.306950	-0.866434
H	-3.546169	-1.250927	-1.931958
H	-4.487520	-2.131862	-0.736646
C	-2.750429	2.152006	1.627653
H	-1.879952	2.536544	2.156852
H	-3.546100	2.898847	1.643474
H	-3.078445	1.233328	2.111711
C	-2.748826	-2.149828	1.629843
H	-3.075674	-1.230254	2.112975
H	-3.545032	-2.896068	1.647374
H	-1.878143	-2.534328	2.158728

Complex **2**

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Complex 2

Pt	-0.023255	0.677103	-0.146824
S	0.463357	3.223596	0.367981
Si	-2.451631	0.748981	0.461939
Si	-0.796219	-1.219531	-1.355546
Si	2.382895	0.528930	-0.906506
Si	0.880419	-0.689939	1.559792
C	-3.501702	1.981620	-0.567023
H	-3.429846	1.765068	-1.636670
H	-4.558551	1.899432	-0.289100
H	-3.208459	3.025967	-0.421507
C	-2.839487	1.169649	2.287487
H	-2.531813	2.185070	2.549705
H	-3.917368	1.101182	2.471581
H	-2.344309	0.484750	2.980514
C	0.358441	-2.702158	-1.590046
H	0.518097	-3.260511	-0.665625
H	-0.089424	-3.386414	-2.319706
H	1.339599	-2.410088	-1.967144
C	-1.121593	-0.471911	-3.079237
H	-0.214443	-0.091709	-3.552253
H	-1.531287	-1.261254	-3.720313
H	-1.858149	0.333717	-3.042547
C	-3.213552	-0.966245	0.113556
C	-2.452291	-1.853039	-0.676727
C	-2.962246	-3.126422	-0.972494
H	-2.385333	-3.821126	-1.575924
C	-4.207481	-3.526582	-0.492915
H	-4.585919	-4.517532	-0.721309
C	-4.963435	-2.651282	0.284895
H	-5.932705	-2.959670	0.663217
C	-4.469403	-1.382253	0.579735
H	-5.073268	-0.715725	1.189672
C	3.530347	2.002682	-0.487015
H	3.549727	2.221240	0.583388
H	4.553467	1.755535	-0.792025
H	3.252275	2.924666	-1.007469
C	2.588816	0.346547	-2.799484
H	2.164400	1.203421	-3.332806
H	3.654661	0.307332	-3.051703
H	2.121426	-0.555537	-3.198479
C	1.215862	0.557088	2.952264
H	0.297108	1.036141	3.298888
H	1.652616	0.015030	3.799387
H	1.925195	1.330063	2.650608
C	-0.302863	-1.992471	2.246713
H	-0.500459	-2.803592	1.544516
H	0.148993	-2.427726	3.145946
H	-1.263454	-1.561803	2.533198
C	3.189663	-0.976053	-0.058329
C	4.415132	-1.541030	-0.439434
H	4.961379	-1.135161	-1.286453
C	4.947740	-2.630701	0.245791
H	5.892341	-3.062661	-0.068361
C	4.262872	-3.170127	1.333884
H	4.672832	-4.021296	1.867277
C	3.047665	-2.617077	1.730844
H	2.525492	-3.052735	2.577841
C	2.500631	-1.522215	1.043412

C	0.253113	3.995729	-1.276746
H	-0.753698	3.829290	-1.659192
H	0.457696	5.064265	-1.200153
H	0.979327	3.537192	-1.945880
C	-0.806371	4.154229	1.294950
H	-0.774380	3.796259	2.322829
H	-0.547905	5.214283	1.277321
H	-1.801300	3.997006	0.883261

Complex **3**.

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Complex 3

Pt	-0.027717	0.418098	0.026707
S	-0.937398	2.323149	1.703420
S	0.257514	2.334130	-1.836651
Si	-2.372992	0.106523	-0.891982
Si	-0.726966	-1.378353	1.475172
Si	0.889782	-1.238497	-1.470361
Si	2.308454	0.373870	0.982254
C	-3.015866	-1.568084	-0.248080
C	-4.191451	-2.166905	-0.727085
H	-4.754021	-1.694766	-1.528079
C	-4.656188	-3.368531	-0.199589
H	-5.562770	-3.821105	-0.588236
C	-3.951276	-3.989226	0.830754
H	-4.307342	-4.925427	1.248219
C	-2.785324	-3.405930	1.319071
H	-2.248291	-3.907020	2.119249
C	-2.300697	-2.199054	0.787417
C	-2.578240	0.126248	-2.794670
H	-1.995458	-0.648995	-3.295831
H	-3.630578	-0.029145	-3.057996
H	-2.274865	1.088118	-3.219608
C	-3.743633	1.334637	-0.334075
H	-3.674670	2.307997	-0.830351
H	-4.716878	0.910620	-0.604428
H	-3.753618	1.495141	0.747489
C	0.513057	-2.772563	1.827371
H	1.435470	-2.416290	2.285832
H	0.041908	-3.465818	2.533457
H	0.788874	-3.341179	0.939354
C	-1.206334	-0.691193	3.184678
H	-2.031185	0.020091	3.125867
H	-1.541249	-1.538740	3.793408
H	-0.374800	-0.217100	3.711089
C	2.585451	-1.821871	-0.832579
C	3.246433	-2.910065	-1.427126
H	2.766743	-3.474741	-2.221486
C	4.519844	-3.290801	-1.014239
H	5.013012	-4.137505	-1.480498
C	5.157461	-2.580318	0.001854
H	6.150855	-2.870502	0.328561
C	4.512565	-1.500188	0.597579
H	5.026010	-0.960010	1.388528
C	3.224735	-1.106742	0.198609
C	1.246211	-0.483949	-3.182955
H	2.018109	0.288039	-3.153611
H	1.633314	-1.296835	-3.808221
H	0.362849	-0.072299	-3.672496
C	-0.155976	-2.774845	-1.856148
H	-1.094515	-2.517942	-2.349716
H	0.416933	-3.404641	-2.545971
H	-0.403856	-3.376096	-0.981966
C	3.463646	1.875290	0.656614
H	3.001346	2.832938	0.915034
H	4.363676	1.773246	1.273460
H	3.790834	1.926296	-0.383150
C	2.521564	0.174108	2.880790
H	1.818110	-0.517380	3.344097
H	3.529778	-0.203952	3.082256
H	2.440599	1.134893	3.396252
C	-1.568583	3.856344	0.905377
H	-2.559979	3.593930	0.538751
H	-1.705212	4.561552	1.728529
C	-0.740944	4.501578	-0.206128
H	0.298070	4.640086	0.106583
H	-1.144038	5.512564	-0.347951
C	-0.816961	3.796349	-1.562948
H	-0.560042	4.492660	-2.364813
H	-1.831758	3.445199	-1.757364
C	0.317078	3.081527	2.793743
H	1.156801	3.492532	2.234692
H	-0.160855	3.861467	3.389234
H	0.675670	2.298833	3.457075
C	1.857369	3.198821	-2.022776
H	2.599687	2.442642	-2.267796
H	1.777060	3.904157	-2.851896
H	2.160834	3.708932	-1.110910

TS from Pt(0) to **A1**.

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TS to A1

Pt	1.452368	0.143351	-0.027758
H	-1.516016	1.383014	1.793342
H	-0.278895	-0.080063	0.139605
Si	-2.569905	0.344627	1.957441
Si	-0.864758	-1.005882	-1.009918
C	-3.382092	-0.015659	0.269887
C	-2.714230	-0.502511	-0.890309
C	-4.761768	0.244771	0.184240
H	-5.292606	0.616946	1.053177
C	-3.470754	-0.687936	-2.060920
H	-2.986034	-1.051029	-2.961187
C	-5.488225	0.045912	-0.987254
H	-6.551555	0.259640	-1.010374
C	-4.836831	-0.422933	-2.119888
H	-5.382199	-0.581859	-3.044293
C	-3.853771	1.050732	3.155272
H	-4.658518	0.341939	3.371477
H	-3.361035	1.285566	4.103880
H	-4.305197	1.974809	2.784409
C	-1.806048	-1.185928	2.758638
H	-0.919958	-1.528285	2.221970
H	-1.499992	-0.950944	3.782939
H	-2.526028	-2.008509	2.802412
C	-0.780636	-2.861435	-0.645049
H	0.219590	-3.255286	-0.837705
H	-1.044709	-3.088118	0.390179
H	-1.488014	-3.393636	-1.290049
C	-0.303277	-0.713590	-2.795185
H	-0.485441	0.314375	-3.117282
H	0.766977	-0.907822	-2.888220
H	-0.829175	-1.383351	-3.484401
S	1.576493	2.378338	-0.880280

C	0.017301	3.299062	-0.588352
H	0.133247	4.335621	-0.911601
H	-0.753770	2.814839	-1.185854
H	-0.263629	3.251725	0.463436
C	2.670631	3.382893	0.193190
H	2.663804	4.422223	-0.142603
H	2.353043	3.314715	1.233258
H	3.673468	2.971151	0.093433
S	3.061186	-1.229994	0.912931
C	2.758289	-3.040596	0.794757
H	2.645748	-3.350118	-0.244481
H	3.586514	-3.577877	1.261905
H	1.837324	-3.244315	1.337974
C	4.627802	-1.200360	-0.045862
H	4.452487	-1.497192	-1.079751
H	4.992998	-0.175263	-0.020681
H	5.356968	-1.864756	0.423464

Intermediate **A1**.

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Intermediate A1

Pt	0.962036	-0.381273	-0.220107
H	-0.522347	1.879588	-0.274719
H	0.308799	-0.819182	-1.586578
Si	-1.894507	2.019674	0.294036
Si	-0.934970	-1.560998	0.483008
C	-2.983709	0.542153	-0.194154
C	-2.611743	-0.832514	-0.142167
C	-4.275644	0.875936	-0.640158
H	-4.574063	1.917613	-0.691667
C	-3.567517	-1.779631	-0.551754
H	-3.315196	-2.833639	-0.533690
C	-5.202070	-0.086374	-1.033043
H	-6.188312	0.212301	-1.372575
C	-4.842065	-1.425843	-0.989566
H	-5.543336	-2.195544	-1.295670
C	-2.621786	3.628902	-0.396033
H	-3.578681	3.890519	0.064985
H	-1.929389	4.452847	-0.195714
H	-2.771248	3.577547	-1.477992
C	-1.747418	2.227015	2.171054
H	-1.208583	1.401617	2.640047
H	-1.219965	3.156184	2.412129
H	-2.737970	2.279844	2.632577
C	-1.126817	-1.739865	2.376172
H	-0.264040	-2.256304	2.809214
H	-1.232151	-0.783796	2.892806
H	-2.019249	-2.335410	2.598294
C	-0.832732	-3.358318	-0.145575
H	-0.915792	-3.410598	-1.234326
H	0.143238	-3.771430	0.125877
H	-1.598089	-4.007022	0.293768
S	2.940558	0.673771	-1.514516
C	3.496136	-0.670375	-2.617713
H	4.212998	-0.283032	-3.343377
H	3.979166	-1.419107	-1.991198
H	2.638306	-1.121250	-3.115200
C	2.138885	1.769475	-2.735135
H	2.875376	2.124458	-3.457560
H	1.326674	1.239245	-3.230608
H	1.728855	2.614062	-2.183362
S	1.883591	0.166680	2.007486
C	3.498028	-0.682145	2.134224
H	4.143219	-0.409547	1.298817
H	3.972029	-0.424387	3.082525
H	3.295606	-1.751687	2.105238
C	2.463006	1.901035	2.000654
H	3.149064	2.076998	1.172022
H	1.578665	2.525853	1.885170
H	2.946598	2.127194	2.952131

TS from **A1** to **A2**.

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TS from A1 to A2

Pt	0.690186	-0.062573	-0.181001
H	0.441973	1.758991	0.158786
H	0.229598	-0.037678	-1.685938
Si	-1.167765	1.860536	0.199932
Si	-0.990715	-1.690076	-0.351738
C	-2.665673	0.685472	-0.046895
C	-2.631397	-0.711075	-0.256636
C	-3.917010	1.327890	0.018559
H	-3.970945	2.401106	0.179632
C	-3.849522	-1.399632	-0.392729
H	-3.840843	-2.473898	-0.556756
C	-5.110839	0.626965	-0.119183
H	-6.059012	1.151898	-0.065821
C	-5.077390	-0.749451	-0.327044
H	-6.000224	-1.309614	-0.437661
C	-1.359654	3.245585	-1.085231
H	-2.364793	3.676591	-1.077907
H	-0.643412	4.051531	-0.898319
H	-1.175353	2.858626	-2.091607
C	-1.364815	2.590611	1.944501
H	-1.203963	1.824048	2.708715
H	-0.648973	3.400517	2.117369
H	-2.371177	2.991621	2.097186
C	-1.031902	-2.963866	1.071661
H	-0.175478	-3.644185	1.015500
H	-1.027304	-2.486543	2.055130
H	-1.938168	-3.576440	1.006473
C	-1.055255	-2.738814	-1.940324
H	-1.147208	-2.106424	-2.827316
H	-0.140303	-3.330189	-2.046696
H	-1.901371	-3.435093	-1.932988
S	3.209957	0.393126	-0.963675
C	3.418270	-0.711184	-2.401581
H	4.382974	-0.529549	-2.878852
H	3.379969	-1.731610	-2.023857
H	2.600910	-0.564088	-3.106752
C	3.257382	2.008440	-1.814713
H	4.218659	2.145676	-2.312867
H	2.440078	2.078586	-2.532474
H	3.129213	2.775040	-1.051496
S	1.330025	-0.503952	2.181657
C	2.564335	-1.851072	2.193678
H	3.403790	-1.606819	1.543134
H	2.907445	-2.016968	3.216174
H	2.060052	-2.742428	1.826428
C	2.391448	0.862416	2.771369
H	3.239068	1.006484	2.100957
H	1.774277	1.759538	2.781665
H	2.737149	0.645032	3.783191

Complex **A2**.

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Complex A2

Pt	-0.708059	-0.288263	-0.373497
H	-1.426789	-1.648074	-1.022123
H	-0.443607	0.206340	-1.824625
Si	1.332452	-1.431309	-0.777286
Si	0.716364	1.636625	0.251155
C	2.772210	-0.325091	-0.209540
C	2.517586	0.992482	0.228789
C	4.095609	-0.797937	-0.232584
H	4.307987	-1.809999	-0.567639
C	3.602268	1.790886	0.628859
H	3.429341	2.808615	0.969046
C	5.156343	0.007150	0.171117
H	6.171222	-0.376562	0.149871
C	4.907750	1.309066	0.604118
H	5.729508	1.943310	0.921040
C	1.569766	-1.844745	-2.611049
H	2.518851	-2.369873	-2.764924
H	0.761778	-2.485788	-2.973297
H	1.585669	-0.939721	-3.223387
C	1.427526	-3.073668	0.171995
H	1.318183	-2.932989	1.250034
H	0.656447	-3.769142	-0.171225
H	2.401458	-3.544977	-0.000067
C	0.472280	2.444050	1.973113
H	-0.532948	2.864453	2.090229
H	0.639468	1.727732	2.783153
H	1.182032	3.266040	2.119042
C	0.676969	3.114524	-0.962259
H	0.834189	2.784623	-1.992975
H	-0.275472	3.652167	-0.923951
H	1.466888	3.834210	-0.720314
S	-3.109038	0.755850	-0.399621
C	-3.104251	2.570134	-0.601649
H	-4.124913	2.929708	-0.741605
H	-2.691933	2.994218	0.312793
H	-2.477896	2.857146	-1.445491
C	-3.772362	0.274893	-2.029174
H	-4.774495	0.687103	-2.156995
H	-3.108314	0.618757	-2.821765
H	-3.807080	-0.812608	-2.041966
S	-1.004034	-1.190511	1.955141
C	-2.070333	-0.089684	2.948960
H	-3.012039	0.101841	2.434971
H	-2.252929	-0.557621	3.917222
H	-1.527817	0.842162	3.091321
C	-2.121374	-2.631385	1.841294
H	-3.056309	-2.347031	1.359559
H	-1.612717	-3.374443	1.231078
H	-2.303367	-3.028966	2.841327

Complex **A3a**.

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Complex A4a

Pt	-0.939107	-0.317031	0.027849
H	-0.404497	1.037156	-0.868141
H	-1.473325	-1.684707	0.661716
Si	0.687722	1.691459	0.192646
Si	0.996493	-1.648215	0.018996
C	2.383579	0.901707	-0.052055
C	2.525026	-0.502165	-0.109853
C	0.621369	3.352720	-0.723210
H	-0.379192	3.790807	-0.655687
H	1.320473	4.071192	-0.283787
H	0.872980	3.243135	-1.781310
C	0.283757	2.064712	2.001442
H	0.362263	1.178103	2.631281
H	0.991124	2.816298	2.371493
H	-0.725324	2.472074	2.104997
C	1.254205	-2.728530	1.559668
H	0.463775	-3.480102	1.640086
H	2.216448	-3.250366	1.518145
H	1.238145	-2.128659	2.473438
C	1.008239	-2.805991	-1.488448
H	0.921451	-2.245318	-2.422559
H	1.934475	-3.389852	-1.530600
H	0.171494	-3.508610	-1.439059
C	3.525413	1.715843	-0.145135
H	3.430496	2.797186	-0.109209
C	4.794127	1.162269	-0.289572
H	5.664224	1.806126	-0.361630
C	3.814126	-1.038831	-0.255734
H	3.948304	-2.115901	-0.304479
C	4.938172	-0.222275	-0.345929
H	5.922882	-0.662878	-0.463042
S	-3.291857	0.716383	0.024681
C	-3.828341	0.687550	-1.722213
H	-4.876812	0.980830	-1.789805
H	-3.214012	1.411027	-2.256771
H	-3.677196	-0.302132	-2.152232
C	-4.407003	-0.551810	0.717259
H	-5.442427	-0.217498	0.637150
H	-4.262940	-1.503068	0.206345
H	-4.137760	-0.665140	1.766214

Complex **A3b**.

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Complex A3b

Pt	-0.891827	-0.463418	-0.013331
H	-1.852497	-2.116814	-0.394811
H	-1.864830	-2.103368	0.394429
Si	0.431548	1.490329	-0.031302
Si	1.191246	-1.579401	0.012399
C	2.278117	1.045117	-0.002954
C	2.618578	-0.323118	0.013540
C	0.085788	2.536993	-1.582381
H	-0.956144	2.868933	-1.618927
H	0.718965	3.431431	-1.586986
H	0.297150	1.974347	-2.495151
C	0.049726	2.587247	1.477016
H	0.238544	2.055074	2.412736
H	0.683096	3.481452	1.467669
H	-0.992150	2.921968	1.477299
C	1.363883	-2.687925	1.552055
H	0.597486	-3.469255	1.571740
H	2.341039	-3.183856	1.562154
H	1.275370	-2.105855	2.472841
C	1.391307	-2.718763	-1.501137
H	1.319234	-2.155958	-2.435219
H	2.368482	-3.214448	-1.483527

H	0.625397	-3.500624	-1.518434
C	3.301321	2.006802	-0.001822
H	3.056113	3.065688	-0.014658
C	4.640453	1.628263	0.015001
H	5.420415	2.382767	0.015568
C	3.973944	-0.689525	0.030145
H	4.255783	-1.739116	0.042845
C	4.977898	0.274523	0.030827
H	6.020880	-0.025027	0.043701
S	-3.113268	0.844403	-0.023475
C	-4.180580	0.109804	-1.311306
H	-3.700148	0.306344	-2.268996
H	-4.277501	-0.967200	-1.168739
H	-5.162611	0.584397	-1.293556
C	-4.028366	0.337936	1.474662
H	-3.448414	0.683381	2.329435
H	-5.010914	0.811679	1.485785
H	-4.129437	-0.746911	1.520946

Complex **A3c**.

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Complex A3c

Pt	-1.114972	-0.000313	-0.714901
H	-0.693608	-0.001021	-2.215165
H	-2.639699	-0.001543	-1.386131
Si	0.752838	-1.480982	-0.268390
Si	0.752691	1.480953	-0.268867
C	2.380576	-0.703571	0.312966
C	2.380389	0.703973	0.313141
C	0.153533	-2.715919	1.047020
H	-0.742784	-3.251200	0.721696
H	0.936274	-3.464754	1.213991
H	-0.048750	-2.233055	2.006225
C	1.055918	-2.460986	-1.860954
H	1.469640	-1.821865	-2.644388
H	1.768298	-3.272702	-1.674053
H	0.130125	-2.902181	-2.239524
C	1.056391	2.459688	-1.862123
H	0.131179	2.902292	-2.240460
H	1.770251	3.270271	-1.675914
H	1.468703	1.819539	-2.645457
C	0.152908	2.717020	1.045267
H	-0.049426	2.235019	2.004898
H	0.935258	3.466384	1.211670
H	-0.743571	3.251597	0.719212
C	3.535607	-1.394594	0.709783
H	3.553477	-2.480970	0.713471
C	4.673185	-0.697835	1.107025
H	5.561485	-1.238235	1.417179
C	3.535206	1.395199	0.710215
H	3.552756	2.481580	0.714224
C	4.672971	0.698648	1.107278
H	5.561101	1.239206	1.417642
S	-2.204008	0.000665	1.574329
C	-3.391281	-1.385990	1.498400
H	-4.043953	-1.345734	2.371656
H	-3.964255	-1.330884	0.573663
H	-2.814209	-2.308376	1.519619
C	-3.391910	1.386704	1.497050
H	-4.044642	1.346913	2.370283
H	-2.815278	2.309383	1.517513
H	-3.964823	1.330509	0.572337

TS from **A3a** to **A3b**.

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TS from A3a to A3b

Pt	-0.883984	-0.447805	-0.272224
H	0.099694	-0.192233	-1.450973
H	-1.444315	-2.023681	-0.113986
Si	0.386310	1.638668	-0.128473
Si	1.101656	-1.693283	0.019419
C	2.186787	1.015699	0.040681
C	2.476570	-0.369272	0.098402
C	0.308782	2.906316	-1.544671
H	-0.708820	3.287655	-1.677687
H	0.958257	3.766715	-1.350508
H	0.619686	2.460181	-2.493111
C	-0.014011	2.590600	1.476656
H	-0.005075	1.928247	2.345982
H	0.737637	3.369783	1.646284
H	-0.990969	3.082644	1.439690
C	1.032451	-2.582367	1.689235
H	0.330161	-3.418532	1.656237
H	2.024914	-2.970473	1.945044
H	0.722687	-1.907106	2.490254
C	1.510334	-2.952471	-1.328240
H	1.573938	-2.480804	-2.311789
H	2.470520	-3.439331	-1.126874
H	0.740240	-3.726653	-1.373499
C	3.248991	1.930428	0.131774
H	3.047955	2.997779	0.090514
C	4.567710	1.507272	0.270053
H	5.370233	2.234948	0.332079
C	3.812832	-0.778327	0.246484
H	4.054811	-1.836968	0.295583
C	4.851543	0.144479	0.328011
H	5.876010	-0.196362	0.435330
S	-3.029088	0.328938	0.776272
C	-3.638418	1.832371	-0.070927
H	-4.612424	2.106297	0.336882
H	-2.921848	2.625859	0.130816
H	-3.706971	1.665722	-1.145274
C	-4.331765	-0.850211	0.274784
H	-5.291804	-0.520646	0.674496
H	-4.373462	-0.936965	-0.810338
H	-4.057259	-1.812804	0.701260

TS from **A3c** to **A3b**.

40
TS from A3c to A3b

Pt	-0.997153	-0.588823	-0.275278
H	-0.678558	-2.002908	-0.887029
H	-2.129330	-1.754018	-0.526737
Si	0.408072	1.465081	-0.158681
Si	1.197328	-1.551022	0.160120
C	2.259512	1.072549	-0.012205
C	2.607573	-0.285464	0.101829
C	0.129043	2.436258	-1.773995
H	-0.914258	2.748668	-1.879821
H	0.748645	3.339937	-1.793045
H	0.390256	1.833004	-2.647161
C	-0.009206	2.669366	1.265901
H	0.124893	2.197314	2.243612

H	0.658170	3.537326	1.229235
H	-1.033485	3.049432	1.203105
C	1.046755	-2.248038	1.919309
H	0.250556	-2.993953	1.989189
H	1.988563	-2.729615	2.206039
H	0.839710	-1.458066	2.644761
C	1.689095	-2.993208	-0.975630
H	1.751345	-2.675312	-2.019841
H	2.670728	-3.386339	-0.690373
H	0.972815	-3.818271	-0.915735
C	3.275771	2.041130	-0.019508
H	3.025778	3.095022	-0.107321
C	4.614488	1.673175	0.075857
H	5.390417	2.431674	0.062812
C	3.961895	-0.645740	0.196807
H	4.247991	-1.690315	0.281741
C	4.958820	0.325088	0.184070
H	6.001893	0.035056	0.256569
S	-2.895324	0.965180	0.155864
C	-4.385011	0.216019	-0.593139
H	-4.231568	0.221427	-1.671102
H	-4.503837	-0.810054	-0.248943
H	-5.256374	0.823187	-0.342465
C	-3.266576	0.694354	1.925051
H	-2.426633	1.093939	2.490171
H	-4.176148	1.237884	2.183551
H	-3.376955	-0.369450	2.130392

TS from [Pt(II)(BDSB)(SMe_2)] to **A4a**.

68
TS to A4a

Pt	-0.055680	0.250082	-0.330233
Si	-2.164065	-0.263215	-1.330486
Si	-1.451745	0.162003	1.706255
C	-3.338580	-1.029036	-0.048580
C	-3.049967	-0.796507	1.312779
C	-4.495610	-1.744788	-0.394258
H	-4.730985	-1.936336	-1.437321
C	-3.934758	-1.279763	2.288098
H	-3.729076	-1.110745	3.341739
C	-5.358164	-2.227000	0.587363
H	-6.244500	-2.786216	0.305975
C	-5.077800	-1.991977	1.932723
H	-5.746200	-2.367916	2.700599
C	-2.918241	1.375652	-1.933414
H	-3.907046	1.165549	-2.357330
H	-3.043980	2.106417	-1.133384
H	-2.309507	1.831122	-2.719798
C	-2.144707	-1.362652	-2.879590
H	-3.167280	-1.435575	-3.266352
H	-1.532530	-0.917041	-3.667875
H	-1.788975	-2.378248	-2.698996
C	-0.558737	-0.749958	3.124315
H	0.338139	-0.208391	3.440133
H	-1.214826	-0.835198	3.997859
H	-0.256415	-1.759842	2.837194
C	-1.950653	1.851874	2.439810
H	-1.071937	2.405500	2.786791
H	-2.475904	2.472541	1.709281
H	-2.614794	1.715740	3.300542
Si	1.075615	-1.728184	-1.038217
Si	2.784887	0.964386	0.764205
C	2.806800	-1.792924	-0.209090
C	3.470431	-0.767793	0.502958
C	3.465668	-3.027881	-0.352879
H	2.982536	-3.837422	-0.890828
C	4.749819	-1.018145	1.032971
H	5.268187	-0.241701	1.587908
C	4.731999	-3.259051	0.175160
H	5.206044	-4.225784	0.043372
C	5.381578	-2.246494	0.873230
H	6.367674	-2.411995	1.293129
C	0.088763	-3.175814	-0.306436
H	0.597101	-4.120593	-0.529307
H	0.004619	-3.084035	0.777849
H	-0.922079	-3.236365	-0.713541
C	1.388495	-2.120759	-2.867062
H	1.774221	-3.139568	-2.976874
H	0.479196	-2.045190	-3.464582
H	2.127072	-1.433687	-3.287836
C	3.366642	2.165099	-0.562044
H	4.455798	2.265994	-0.515503
H	3.098692	1.812879	-1.559356
H	2.930000	3.156151	-0.417906
C	3.236609	1.631208	2.471446
H	4.314736	1.793479	2.563866
H	2.744496	2.591412	2.650071
H	2.930350	0.941920	3.261817
H	0.924572	0.229114	-1.680634
H	1.245898	0.903849	0.841549
S	-0.448917	3.617090	-0.562274
C	0.256843	4.231307	-2.128529
H	-0.054064	5.261240	-2.313161
H	1.345776	4.163426	-2.126144
H	-0.134094	3.593884	-2.921309
C	0.310398	4.794651	0.607062
H	-0.003098	5.815260	0.379807
H	-0.049045	4.528565	1.601056
H	1.400274	4.732655	0.591239

Complex **A4a**.

68
Complex A4a

Pt	-0.077000	0.692157	-0.342358
Si	-2.268999	0.269554	-1.199038
Si	-1.000130	-0.336089	1.730204
C	-3.159507	-0.955817	-0.049717
C	-2.623937	-1.213652	1.230747
C	-4.362170	-1.572272	-0.431995
H	-4.785801	-1.384649	-1.414977
C	-3.316111	-2.084060	2.087004
H	-2.921783	-2.298175	3.076740
C	-5.030564	-2.438270	0.429614
H	-5.954585	-2.913049	0.116260
C	-4.504427	-2.695224	1.694457
H	-5.018369	-3.371461	2.370036
C	-3.289334	1.874943	-1.202654
H	-4.298421	1.620548	-1.546647
H	-3.380599	2.324705	-0.213330
H	-2.888884	2.623061	-1.892755
C	-2.367327	-0.328411	-2.997001
H	-3.419948	-0.359799	-3.299808
H	-1.854770	0.375092	-3.658408
H	-1.947350	-1.320472	-3.163263

C	0.112176	-1.595118	2.635078
H	0.979285	-1.090483	3.073556
H	-0.430927	-2.079040	3.454454
H	0.492079	-2.376311	1.974040
C	-1.491042	0.892498	3.117667
H	-0.608603	1.348839	3.579258
H	-2.140836	1.694772	2.756052
H	-2.032659	0.366944	3.911904
Si	0.729238	-1.367429	-1.258337
Si	3.055135	0.857904	0.366233
C	2.394153	-1.865678	-0.414919
C	3.337269	-0.986244	0.167007
C	2.733803	-3.228514	-0.487212
H	2.035025	-3.936135	-0.918242
C	4.561335	-1.493692	0.637481
H	5.286949	-0.826279	1.092996
C	3.950101	-3.717547	-0.016860
H	4.169598	-4.777628	-0.087961
C	4.874378	-2.845916	0.547180
H	5.824195	-3.213284	0.920008
C	-0.399563	-2.885654	-1.087363
H	-0.017385	-3.704508	-1.705543
H	-0.459005	-3.235924	-0.054924
H	-1.420139	-2.685223	-1.412495
C	1.194786	-1.222250	-3.094851
H	1.576921	-2.181381	-3.461825
H	0.344048	-0.931798	-3.713370
H	1.977122	-0.472349	-3.234304
C	3.692989	1.887650	-1.073831
H	4.776427	1.763098	-1.170449
H	3.227514	1.585192	-2.013028
H	3.492824	2.952632	-0.922740
C	3.804356	1.486949	1.981895
H	4.893482	1.380186	1.973708
H	3.585252	2.547056	2.135240
H	3.420133	0.931369	2.840600
H	0.417857	1.295603	-1.805110
H	1.546081	1.072492	0.557035
S	-0.659288	3.157791	0.370811
C	-0.137516	4.230393	-1.011385
H	-0.295382	5.276656	-0.743673
H	0.905678	4.044497	-1.263992
H	-0.760078	3.970910	-1.865101
C	0.503298	3.748395	1.645589
H	0.281017	4.790668	1.878766
H	0.347948	3.137896	2.532520
H	1.534382	3.652612	1.307305

TS from **A4a** to **A4b**.

68
TS from A4a to A4b

Pt	0.017954	0.688503	-0.440216
Si	-2.374839	0.139655	-1.120007
Si	-0.725339	-0.484039	1.620531
C	-3.053173	-1.167564	0.077687
C	-2.347718	-1.428456	1.267198
C	-4.261015	-1.840149	-0.168216
H	-4.816060	-1.650398	-1.082879
C	-2.876533	-2.355865	2.180065
H	-2.349595	-2.572762	3.104693
C	-4.767740	-2.763093	0.742340
H	-5.697918	-3.281146	0.533185
C	-4.072362	-3.020760	1.922692
H	-4.459725	-3.739907	2.637027
C	-3.562499	1.627718	-1.016852
H	-4.577698	1.269468	-1.220670
H	-3.571155	2.098627	-0.032217
H	-3.335084	2.395216	-1.763302
C	-2.605560	-0.481090	-2.905593
H	-3.656649	-0.736172	-3.078732
H	-2.337476	0.301087	-3.622759
H	-2.011118	-1.365042	-3.140623
C	0.449390	-1.746204	2.425864
H	1.397892	-1.305948	2.735113
H	-0.029124	-2.155693	3.322120
H	0.684223	-2.582478	1.765314
C	-1.151555	0.767625	2.997259
H	-0.273036	1.307614	3.359832
H	-1.896730	1.496671	2.668397
H	-1.579446	0.227843	3.849096
Si	0.893714	-1.375631	-1.342334
Si	2.337771	0.917350	0.517796
C	2.582172	-1.729168	-0.548272
C	3.217278	-0.743340	0.231030
C	3.237008	-2.951026	-0.776285
H	2.761808	-3.723608	-1.373802
C	4.491907	-1.008793	0.756548
H	4.999635	-0.260532	1.358723
C	4.497829	-3.201138	-0.242353
H	4.985991	-4.153100	-0.422799
C	5.128779	-2.224875	0.526731
H	6.111310	-2.413384	0.946725
C	-0.177496	-2.927311	-1.179583
H	0.369897	-3.763392	-1.629632
H	-0.401997	-3.192681	-0.146745
H	-1.126987	-2.836252	-1.708027
C	1.195346	-1.114118	-3.198294
H	1.633395	-2.024608	-3.622266
H	0.273548	-0.899365	-3.743709
H	1.896981	-0.295362	-3.374771
C	3.381437	2.237187	-0.387953
H	4.394002	2.280820	0.028632
H	3.469496	2.005108	-1.452730
H	2.950700	3.240273	-0.302359
C	2.566789	1.371029	2.356759
H	3.631427	1.284231	2.600657
H	2.280925	2.403980	2.564448
H	2.021210	0.724012	3.043233
H	-0.340476	1.210743	-1.959864
H	0.901854	1.476856	-1.591346
S	-0.846874	3.117248	0.380567
C	-0.698036	4.163819	-1.107440
H	-1.035892	5.174349	-0.873563
H	0.330843	4.178737	-1.467472
H	-1.343652	3.735007	-1.871043
C	0.266196	4.052297	1.482217
H	-0.139574	5.056161	1.617100
H	0.277076	3.538286	2.440561
H	1.275768	4.104529	1.077176

Complex **A4b**.

68
Complex A4b

Pt	-0.010899	0.672848	-0.356081

Si	-2.382540	0.182956	-1.104109
Si	-0.719399	-0.522843	1.595868
C	-3.053616	-1.173377	0.052435
C	-2.322905	-1.477922	1.218316
C	-4.254573	-1.856210	-0.195170
H	-4.831116	-1.636155	-1.089623
C	-2.814727	-2.453920	2.100564
H	-2.264299	-2.703496	3.003139
C	-4.727812	-2.827022	0.683684
H	-5.654071	-3.350571	0.470459
C	-4.005045	-3.126579	1.837299
H	-4.365880	-3.883711	2.525694
C	-3.632995	1.626917	-0.975815
H	-4.641557	1.238186	-1.155558
H	-3.635192	2.102590	0.007515
H	-3.451173	2.400866	-1.728814
C	-2.600769	-0.393199	-2.912361
H	-3.653678	-0.621966	-3.111385
H	-2.306077	0.398486	-3.609409
H	-2.018634	-1.283121	-3.157318
C	0.507692	-1.738355	2.377474
H	1.446952	-1.257955	2.654284
H	0.060424	-2.139919	3.293613
H	0.751498	-2.581113	1.729762
C	-1.130468	0.737769	2.960853
H	-0.247029	1.279245	3.308921
H	-1.886172	1.460675	2.646548
H	-1.538842	0.189179	3.817068
Si	0.877404	-1.360871	-1.293393
Si	2.369709	0.939981	0.432898
C	2.581437	-1.738614	-0.542896
C	3.256374	-0.726603	0.168475
C	3.214477	-2.975688	-0.746945
H	2.706992	-3.768298	-1.289039
C	4.550864	-0.982386	0.646871
H	5.089617	-0.215183	1.196162
C	4.496028	-3.215043	-0.258234
H	4.968421	-4.178558	-0.418632
C	5.168265	-2.212935	0.439288
H	6.167401	-2.392953	0.822503
C	-0.178838	-2.929381	-1.212614
H	0.346629	-3.725049	-1.752670
H	-0.357865	-3.278092	-0.195075
H	-1.151463	-2.796377	-1.687402
C	1.172467	-0.996512	-3.138311
H	1.579172	-1.897326	-3.611024
H	0.256265	-0.723998	-3.666318
H	1.904164	-0.196653	-3.275972
C	3.362531	2.231491	-0.577918
H	4.403920	2.269372	-0.238734
H	3.375861	1.982309	-1.643123
H	2.952035	3.242165	-0.477795
C	2.702782	1.446124	2.246882
H	3.769564	1.320394	2.461964
H	2.465872	2.496258	2.430799
H	2.152764	0.844786	2.972714
H	-0.010788	1.502032	-2.098774
H	0.734591	1.665159	-1.844659
S	-0.859810	3.110288	0.447322
C	-0.859121	4.163105	-1.044376
H	-1.204503	5.162588	-0.777369
H	0.137382	4.214514	-1.484387
H	-1.553931	3.723289	-1.756590
C	0.313947	4.077689	1.456141
H	-0.108340	5.067554	1.636371
H	0.426776	3.556469	2.403982
H	1.282970	4.162407	0.965759

Precursory complex **4a**.

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46
Precursory complex 4a
```

Pt	-0.414185	-0.513063	0.032479
Si	1.632325	-1.589349	0.126516
Si	0.897444	1.710613	-0.032261
C	3.003020	-0.261393	-0.054407
C	2.687297	1.114320	-0.126280
C	4.354493	-0.639150	-0.105423
H	4.623168	-1.690737	-0.054864
C	3.724553	2.054976	-0.246339
H	3.495349	3.114961	-0.308955
C	5.373099	0.302735	-0.222943
H	6.408995	-0.018182	-0.262773
C	5.057545	1.657784	-0.292258
H	5.844296	2.398970	-0.385333
C	1.987321	-2.514186	1.746739
H	1.292390	-3.348807	1.875309
H	3.006694	-2.915234	1.757255
H	1.877915	-1.853803	2.610912
C	1.843661	-2.837717	-1.290711
H	1.705811	-2.361564	-2.264637
H	2.843239	-3.286245	-1.272041
H	1.112040	-3.646336	-1.204597
C	0.671296	3.224980	-1.153459
H	-0.380050	3.527175	-1.179567
H	1.249158	4.079394	-0.787196
H	0.988505	3.018183	-2.178848
C	0.367708	2.241192	1.703201
H	0.567060	1.465425	2.443203
H	0.919196	3.145022	1.987627
H	-0.700592	2.470876	1.729052
O	-2.614546	0.414911	0.002299
N	-4.865982	0.538273	0.008954
C	-3.704677	-0.131322	-0.220670
H	-0.029969	0.781706	-1.020935
H	-0.837824	-1.845583	0.808439
C	-3.774656	-1.546599	-0.754200
H	-4.343528	-2.199724	-0.088229
H	-4.240868	-1.574610	-1.742498
H	-2.756983	-1.923830	-0.829304
C	-6.197055	0.013592	-0.263999
H	-6.153714	-1.006041	-0.633617
H	-6.799872	0.024102	0.649891
H	-6.702453	0.632406	-1.013449
C	-4.833177	1.904002	0.524764
H	-3.806464	2.174183	0.752019
H	-5.236223	2.600987	-0.217499
H	-5.439988	1.972007	1.432587

Precursory complex **4b**.

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46
Precursory complex 4b
```

Pt	0.334219	-0.786796	-0.196050
Si	-1.887403	-1.428932	0.062523
Si	-0.528462	1.394431	-0.258519

C	-3.013244	0.101505	0.176636
C	-2.405155	1.367089	0.037855
C	-4.399790	0.028652	0.384892
H	-4.885057	-0.937870	0.493845
C	-3.200918	2.521335	0.112967
H	-2.748903	3.504411	0.008419
C	-5.176156	1.181825	0.457696
H	-6.246684	1.108811	0.620450
C	-4.574422	2.433162	0.321588
H	-5.176233	3.334534	0.378205
C	-2.488735	-2.507789	-1.386238
H	-1.901660	-3.427569	-1.471827
H	-3.536780	-2.794925	-1.243717
H	-2.414284	-1.972094	-2.335818
C	-2.119563	-2.465456	1.644275
H	-1.822138	-1.904192	2.533637
H	-3.169670	-2.754800	1.765775
H	-1.526366	-3.384711	1.610560
C	0.275042	2.526038	1.049077
H	1.353564	2.613670	0.885032
H	-0.148340	3.535171	0.993735
H	0.110907	2.151455	2.062712
C	-0.175050	2.196952	-1.947265
H	-0.658187	1.645016	-2.757161
H	-0.545883	3.227940	-1.973056
H	0.899729	2.219096	-2.150257
O	2.627020	-0.159661	-0.439807
N	4.724148	0.501144	0.059472
C	3.471536	0.122502	0.423829
H	1.058317	-2.581937	0.166574
H	1.008334	-2.576585	-0.617641
C	3.128742	0.047541	1.897563
H	3.729470	-0.710807	2.406796
H	3.288069	1.004013	2.400114
H	2.075503	-0.219948	1.975164
C	5.794560	0.836720	0.989058
H	5.479558	0.708259	2.019913
H	6.661053	0.191681	0.810518
H	6.107821	1.876599	0.848331
C	5.077703	0.594702	-1.355055
H	4.204359	0.361704	-1.956794
H	5.422606	1.607000	-1.586640
H	5.881431	-0.110247	-1.590133

Precursory complex **A5c**.

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46
Precursory complex 4c
```

Pt	0.461546	-1.164797	-0.444313
Si	-0.961975	-0.527819	1.391524
Si	-1.206813	0.270810	-1.447023
C	-2.526307	0.470451	0.998753
C	-2.643212	0.851202	-0.351958
C	-3.528140	0.838952	1.909755
H	-3.455358	0.548779	2.954504
C	-3.759798	1.594139	-0.765231
H	-3.867496	1.892805	-1.804451
C	-4.630703	1.576154	1.487429
H	-5.402870	1.855453	2.196865
C	-4.746558	1.954284	0.148050
H	-5.608387	2.526598	-0.179511
C	-1.452356	-2.152509	2.236368
H	-0.575782	-2.765785	2.461293
H	-1.972486	-1.945639	3.178890
H	-2.120895	-2.740053	1.602854
C	0.112081	0.458512	2.611284
H	0.445673	1.399775	2.169586
H	-0.469553	0.690722	3.510508
H	0.993201	-0.109565	2.923061
C	-0.301169	1.785733	-2.148961
H	0.563772	1.490172	-2.748695
H	-0.979754	2.357436	-2.792111
H	0.043348	2.442660	-1.347602
C	-1.894391	-0.720012	-2.909835
H	-2.472082	-1.581592	-2.567192
H	-2.554467	-0.087357	-3.514649
H	-1.092771	-1.086363	-3.556631
O	2.002837	0.503034	-0.170804
N	3.886812	1.651492	0.250732
C	3.159602	0.507812	0.289453
H	1.643041	-2.279316	-0.822862
H	-0.452232	-2.374511	-0.701096
C	3.775229	-0.733258	0.891389
H	4.792714	-0.902432	0.535444
H	3.799583	-0.659028	1.982593
H	3.152445	-1.580752	0.608844
C	5.194051	1.823704	0.872433
H	5.490178	0.937163	1.424095
H	5.954596	2.037703	0.114384
H	5.160477	2.665185	1.571661
C	3.330559	2.854166	-0.366588
H	2.469781	2.585807	-0.971045
H	3.021425	3.574005	0.398746
H	4.092655	3.319699	-0.996852

TS from **A5a** to **A5b**.

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46
TS from 4a to 4b
```

Pt	-0.376958	-0.558737	-0.445122
Si	1.562270	-1.607935	0.319017
Si	0.777737	1.589007	-0.478274
C	2.875802	-0.221955	0.371436
C	2.556046	1.119420	0.048159
C	4.188450	-0.533297	0.764862
H	4.452380	-1.557415	1.016332
C	3.567417	2.090703	0.132108
H	3.343272	3.125590	-0.113441
C	5.176578	0.444260	0.838178
H	6.184532	0.178709	1.139827
C	4.863867	1.764260	0.519894
H	5.627507	2.533528	0.572756
C	1.280293	-2.239552	2.081880
H	0.600206	-3.094388	2.083685
H	2.233765	-2.551149	2.523617
H	0.855386	-1.462863	2.722234
C	2.193504	-3.034751	-0.747073
H	2.378354	-2.714016	-1.775191
H	3.131877	-3.432920	-0.346224
H	1.461538	-3.845812	-0.771754
C	0.874286	2.608223	-2.082668
H	-0.127157	2.892545	-2.421335
H	1.447884	3.530609	-1.938821
H	1.349226	2.041654	-2.888194
C	0.053202	2.749401	0.848971
H	0.009335	2.263251	1.827012

H	0.666798	3.651767	0.950247
H	-0.961058	3.056873	0.578477
O	-2.403206	0.347700	0.211829
N	-4.581122	0.583847	0.719593
C	-3.578856	-0.030582	0.047069
H	0.656959	-0.471181	-1.583733
H	-0.974356	-2.112716	-0.147125
C	-3.902444	-1.159263	-0.902196
H	-4.682286	-1.821795	-0.526167
H	-4.222505	-0.758241	-1.868844
H	-2.985440	-1.730915	-1.048576
C	-5.999120	0.295505	0.536680
H	-6.171171	-0.292307	-0.360106
H	-6.404672	-0.244085	1.399470
H	-6.545922	1.236756	0.433441
C	-4.277892	1.628159	1.697160
H	-3.203210	1.684979	1.840276
H	-4.646773	2.596783	1.345395
H	-4.765175	1.391556	2.647332

TS from **A5c** to **A5b**.

46
TS from 4c to 4b

Pt	0.382530	-0.808396	-0.582405
Si	-1.757366	-1.404362	0.235213
Si	-0.568699	1.443268	-0.206998
C	-2.965498	0.057622	0.336931
C	-2.430928	1.350474	0.165567
C	-4.335573	-0.091701	0.606194
H	-4.765050	-1.081355	0.735975
C	-3.281623	2.461028	0.276484
H	-2.885981	3.464921	0.146703
C	-5.167421	1.019975	0.707828
H	-6.225388	0.891220	0.912225
C	-4.638522	2.300604	0.543473
H	-5.285645	3.168499	0.619919
C	-2.585066	-2.796235	-0.754853
H	-1.946295	-3.683255	-0.799514
H	-3.530679	-3.091621	-0.287374
H	-2.804358	-2.483454	-1.779174
C	-1.449615	-2.078141	1.986867
H	-1.021769	-1.314997	2.641228
H	-2.398222	-2.404820	2.428351
H	-0.772768	-2.936907	1.970092
C	0.256064	2.422349	1.208874
H	1.328085	2.544267	1.029393
H	-0.184372	3.421774	1.298554
H	0.126704	1.916939	2.170078
C	-0.308942	2.468818	-1.791538
H	-0.808440	2.007224	-2.647003
H	-0.709389	3.482340	-1.673444
H	0.755108	2.555769	-2.030961
O	2.423259	0.268332	-0.302811
N	4.521929	0.698073	0.382334
C	3.365848	-0.003686	0.462040
H	1.173207	-2.208503	-1.000137
H	-0.122552	-1.932581	-1.534045
C	3.242361	-1.108385	1.487047
H	4.091234	-1.793959	1.458346
H	3.168055	-0.693023	2.496020
H	2.330028	-1.661855	1.269085
C	5.652485	0.539483	1.288920
H	5.435761	-0.181317	2.071140
H	6.538852	0.205582	0.739752
H	5.883531	1.498881	1.762363
C	4.674496	1.748894	-0.622661
H	3.848270	1.697179	-1.325096
H	4.681939	2.734756	-0.146779
H	5.619737	1.608752	-1.154002

TS from **A5c** to **C1**.

46
TS from 4c to 5a

Pt	0.644179	0.027408	-0.278864
Si	-1.048793	-1.598062	-0.079107
Si	-1.105896	1.603674	0.168925
C	-2.728818	-0.727806	-0.055204
C	-2.764475	0.677692	0.071987
C	-3.932903	-1.446415	-0.125345
H	-3.920848	-2.528035	-0.228379
C	-4.010512	1.320535	0.127905
H	-4.061030	2.401647	0.223818
C	-5.159807	-0.790962	-0.070361
H	-6.082770	-1.357969	-0.129536
C	-5.198044	0.596865	0.057250
H	-6.152089	1.111921	0.098482
C	-1.001411	-2.926928	-1.419934
H	-0.011529	-3.387695	-1.475860
H	-1.726068	-3.717646	-1.196821
H	-1.241299	-2.516998	-2.403722
C	-0.708583	-2.432750	1.586544
H	-0.689370	-1.714646	2.408521
H	-1.506757	-3.156746	1.788697
H	0.240423	-2.974435	1.574549
C	-0.917890	2.394560	1.880467
H	0.061531	2.870112	1.980933
H	-1.687431	3.157203	2.044120
H	-1.006408	1.650045	2.675322
C	-1.079260	2.993775	-1.124503
H	-1.213522	2.605107	-2.136799
H	-1.882166	3.713652	-0.930083
H	-0.132045	3.540144	-1.093306
O	2.124953	0.634651	1.153155
N	4.107444	0.329202	0.004087
C	3.011599	-0.215953	0.673921
H	2.201378	-0.899827	-0.487805
H	-0.041072	-0.250719	-1.642439
C	3.284238	-1.449757	1.524695
H	3.671751	-2.292704	0.954099
H	4.005388	-1.180853	2.303327
H	2.351820	-1.744584	2.001111
C	4.996246	-0.588618	-0.698680
H	5.391782	-1.346192	-0.024065
H	4.482319	-1.089839	-1.534793
H	5.840257	-0.025602	-1.097842
C	3.856887	1.572702	-0.716013
H	3.355863	2.281898	-0.062516
H	4.810361	1.991222	-1.040467
H	3.225872	1.401866	-1.604848

Intermediate **C1**.

46

Intermediate 5a

Pt	0.488289	-0.163700	-0.488549
Si	-1.333455	-1.628633	-0.130180
Si	-0.938266	1.607748	0.108397
C	-2.852883	-0.527444	0.127957
C	-2.677488	0.870644	0.223889
C	-4.145172	-1.061592	0.243594
H	-4.300966	-2.134149	0.169216
C	-3.798130	1.689360	0.433035
H	-3.683385	2.767219	0.508435
C	-5.247965	-0.236585	0.448575
H	-6.240340	-0.666406	0.531720
C	-5.073941	1.142694	0.543556
H	-5.930072	1.789803	0.700689
C	-1.630164	-2.893602	-1.502588
H	-0.716027	-3.452717	-1.723151
H	-2.390948	-3.619827	-1.197165
H	-1.966120	-2.417273	-2.426391
C	-0.919501	-2.576355	1.455793
H	-0.735387	-1.901752	2.294197
H	-1.758085	-3.230156	1.722539
H	-0.034891	-3.205515	1.323280
C	-0.335190	2.267515	1.760768
H	0.745949	2.418291	1.728661
H	-0.826950	3.220654	1.986428
H	-0.554295	1.568982	2.570754
C	-0.827602	2.932826	-1.226439
H	-1.129271	2.549265	-2.202878
H	-1.488766	3.768611	-0.969830
H	0.189415	3.324516	-1.305545
O	2.081388	0.461043	0.604466
N	4.401332	0.483556	0.267153
C	3.232508	-0.339663	0.614153
H	3.144034	-1.159083	-0.147621
H	-0.472202	-0.329381	-1.718286
C	3.384839	-0.985473	1.994646
H	4.187468	-1.725365	2.032991
H	3.575233	-0.207022	2.736955
H	2.449736	-1.488084	2.248168
C	5.641947	-0.281743	0.219280
H	5.885042	-0.697387	1.196798
H	5.608402	-1.111365	-0.513953
H	6.459554	0.382747	-0.068385
C	4.207260	1.216174	-0.978930
H	3.319920	1.839744	-0.904263
H	5.074101	1.857168	-1.156304
H	4.094873	0.545705	-1.854781

TS from **C1** to **C2**.

46
TS from 5a to 5b

Pt	-0.561898	0.059317	-0.370005
Si	1.070312	-1.620260	-0.156696
Si	1.121504	1.617003	0.182725
C	2.734708	-0.736293	0.028600
C	2.760131	0.666968	0.183089
C	3.943038	-1.449797	0.046457
H	3.943041	-2.530029	-0.070651
C	3.994746	1.312633	0.348886
H	4.034945	2.392001	0.465740
C	5.160113	-0.793319	0.209040
H	6.085748	-1.358738	0.215565
C	5.186006	0.591839	0.360606
H	6.132085	1.107559	0.485372
C	0.649829	-2.622344	1.378439
H	-0.381476	-2.975939	1.326186
H	1.322853	-3.483814	1.457780
H	0.753083	-2.021918	2.284257
C	1.030627	-2.716760	-1.690013
H	1.264767	-2.152776	-2.594913
H	1.767344	-3.522105	-1.589909
H	0.047620	-3.177806	-1.815089
C	1.209124	3.111342	-0.972077
H	0.242735	3.620035	-1.033789
H	1.938003	3.838130	-0.597310
H	1.505723	2.823788	-1.983164
C	0.722265	2.241620	1.924952
H	0.634249	1.418309	2.636620
H	1.522381	2.906772	2.270224
H	-0.213644	2.806903	1.942872
O	-2.005557	-0.800718	0.762494
C	-3.350187	-0.446928	0.892018
N	-3.843526	0.368001	-0.246158
H	0.327749	0.429046	-1.604889
H	-3.465023	0.156476	1.819544
C	-4.146449	-1.743253	1.061889
H	-5.173761	-1.572785	1.392223
H	-4.153647	-2.306928	0.125150
H	-3.639615	-2.341024	1.820040
C	-5.300115	0.463944	-0.333951
H	-5.741777	-0.515881	-0.506764
H	-5.765160	0.903554	0.567834
H	-5.562258	1.097050	-1.184821
C	-3.267640	1.702793	-0.254210
H	-2.170898	1.671141	-0.366796
H	-3.644674	2.264270	-1.111222
H	-3.475829	2.278632	0.666699

Intermediate **C2**.

46
Intermediate 5b

Pt	-0.687131	-0.140909	-0.279191
Si	1.135890	-1.616132	-0.030533
Si	0.873500	1.558984	0.179386
C	2.731816	-0.587531	0.007355
C	2.611539	0.816432	0.091303
C	4.012405	-1.159815	-0.024500
H	4.126547	-2.238328	-0.089935
C	3.771161	1.605243	0.139761
H	3.695827	2.687467	0.201177
C	5.155137	-0.365224	0.021366
H	6.137852	-0.823877	-0.009058
C	5.034627	1.021161	0.103636
H	5.922637	1.643436	0.136887
C	0.928922	-2.581513	1.578662
H	-0.059320	-3.046483	1.614405
H	1.691108	-3.363981	1.663923
H	1.016588	-1.923941	2.446682
C	1.168196	-2.827170	-1.485590
H	1.283088	-2.306664	-2.439018
H	2.004351	-3.527343	-1.378618
H	0.246923	-3.414937	-1.524612
C	0.731580	3.073593	-0.944791
H	-0.289628	3.465249	-0.956551

H	1.385596	3.875915	-0.586277
H	1.016322	2.838765	-1.972945
C	0.494287	2.114710	1.951993
H	0.542922	1.279218	2.653159
H	1.232846	2.862714	2.263455
H	-0.496285	2.571058	2.033135
O	-2.042854	-1.111923	0.965634
N	-2.984629	0.611401	-0.290754
C	-3.114722	-0.239402	0.971787
H	0.054830	0.367204	-1.563974
H	-3.025410	0.493372	1.790778
C	-4.445099	-0.969954	1.130942
H	-5.296965	-0.283315	1.082922
H	-4.563965	-1.746521	0.373198
H	-4.454112	-1.454359	2.109320
C	-3.631944	0.034901	-1.480668
H	-3.354098	-1.014440	-1.580643
H	-4.726898	0.109315	-1.430081
H	-3.289694	0.566849	-2.370467
C	-3.387972	2.008287	-0.106954
H	-2.864273	2.435537	0.749253
H	-3.125280	2.583705	-0.997450
H	-4.471093	2.108631	0.058723

TS from **C2** to **D1**.

46
TS from 5b to 6

Pt	-0.719569	-0.803225	0.178582
Si	1.462254	-1.610771	-0.045232
Si	0.311867	1.314602	0.854240
C	2.541016	-0.063028	-0.298817
C	2.006178	1.203293	0.029869
C	3.835647	-0.132476	-0.832256
H	4.263369	-1.095660	-1.096472
C	2.776295	2.354437	-0.194583
H	2.375407	3.335030	0.041194
C	4.593339	1.017608	-1.042993
H	5.592704	0.942049	-1.458764
C	4.061184	2.264740	-0.725414
H	4.642805	3.164735	-0.894636
C	2.179214	-2.641350	1.373630
H	3.217379	-2.918916	1.161423
H	2.168319	-2.092455	2.318413
H	1.605035	-3.561859	1.513989
C	1.520554	-2.680196	-1.612851
H	2.544577	-3.017562	-1.808944
H	0.895132	-3.570905	-1.503710
H	1.175105	-2.124669	-2.487751
C	-0.326825	3.094539	0.827793
H	-1.329991	3.182341	1.253278
H	0.330542	3.706709	1.456165
H	-0.340418	3.507888	-0.180109
C	0.435708	0.947416	2.723055
H	-0.556354	0.919943	3.183263
H	0.929143	-0.000863	2.935448
H	1.005185	1.753845	3.201303
O	-0.897681	0.975165	-1.046419
N	-2.938291	0.058584	-0.306632
C	-2.260495	0.907453	-1.362929
H	-0.702274	-1.946929	1.249331
H	-2.367894	0.324492	-2.287928
C	-2.879901	2.280607	-1.602744
H	-2.799635	2.928963	-0.730278
H	-3.934214	2.192789	-1.884720
H	-2.348344	2.758356	-2.428018
C	-3.540148	0.794636	0.814872
H	-3.797246	0.086437	1.604582
H	-2.829353	1.510519	1.223145
H	-4.451756	1.331751	0.517952
C	-3.906098	-0.894429	-0.866514
H	-4.237345	-1.574939	-0.079662
H	-4.791636	-0.390979	-1.282611
H	-3.434051	-1.483068	-1.654364

Intermediate **D1**.

46
Intermediate 6

Pt	-0.860114	-1.107624	0.025920
Si	0.493931	1.907207	0.817880
Si	1.340513	-1.663784	0.331157
C	1.993546	1.248435	-0.127219
C	2.357232	-0.123580	-0.275347
C	2.841784	2.237276	-0.660676
H	2.581991	3.285241	-0.561297
C	3.554112	-0.404204	-0.955915
H	3.856020	-1.435825	-1.094742
C	4.023963	1.923733	-1.326473
H	4.650214	2.713867	-1.726505
C	4.382010	0.591147	-1.472015
H	5.297974	0.320895	-1.987369
C	0.376803	3.781998	0.647492
H	-0.522410	4.146637	1.151252
H	1.232376	4.257507	1.136267
H	0.353248	4.131373	-0.387820
C	0.489139	1.473356	2.640496
H	0.258401	0.418107	2.793418
H	1.462033	1.681495	3.094749
H	-0.267029	2.064320	3.166170
C	1.898173	-2.059326	2.109715
H	1.374271	-2.947291	2.476226
H	2.973476	-2.270027	2.128602
H	1.707096	-1.246804	2.812989
C	1.924565	-3.152068	-0.700750
H	1.760310	-2.994500	-1.769887
H	2.981372	-3.392384	-0.544088
H	1.343067	-4.030606	-0.406535
O	-0.970285	1.205492	0.266151
N	-2.822178	0.226210	-0.652696
C	-1.958157	1.423362	-0.747563
H	-0.938222	-2.636576	-0.152467
H	-1.475091	1.366862	-1.727414
C	-2.665948	2.763682	-0.591529
H	-3.507397	2.822249	-1.287916
H	-3.041529	2.901575	0.423393
H	-1.986575	3.583714	-0.823925
C	-3.813169	0.269251	0.433851
H	-3.325392	0.564829	1.361996
H	-4.643905	0.957764	0.221468
H	-4.220601	-0.733136	0.570173
C	-3.437066	-0.141626	-1.932617
H	-2.664383	-0.244369	-2.695333
H	-3.931723	-1.107047	-1.819862
H	-4.185307	0.592883	-2.268822

TS from **D1** to **D2**.

```
46
TS from 6 to 7
Pt   -0.885028   -1.213174    0.401678
Si    1.223874   -1.663731   -0.309147
Si    0.373763    1.530272    1.328463
C     2.187220    0.000499   -0.476554
C     1.884430    1.229595    0.176950
C     3.333138   -0.056577   -1.291685
H     3.583970   -0.981597   -1.801879
C     2.755431    2.316715   -0.023417
H     2.547203    3.264165    0.463058
C     4.178270    1.035951   -1.472517
H     5.053456    0.948031   -2.108221
C     3.887886    2.233168   -0.830638
H     4.532945    3.096821   -0.956436
C     2.189067   -2.746803    0.913055
H     3.224297   -2.873411    0.576564
H     2.212616   -2.300227    1.909811
H     1.729365   -3.735141    0.997326
C     1.278066   -2.538680   -1.997643
H     2.297950   -2.808089   -2.291417
H     0.692529   -3.459920   -1.942533
H     0.852794   -1.919848   -2.792973
C     0.125122    3.406295    1.511253
H    -0.789486    3.581843    2.088012
H     0.941396    3.897422    2.049550
H     0.012890    3.912420    0.546875
C     0.769693    0.860356    3.051819
H    -0.052375    1.073707    3.743206
H     0.911389   -0.223114    3.031519
H     1.679823    1.315023    3.457126
O    -0.998212    0.899689    0.682833
N    -3.069109    1.186451   -1.257949
C    -1.908881    0.872415   -1.740692
H    -0.981816   -2.773297    0.230631
H    -1.719065   -0.190644   -1.867724
C    -0.885742    1.820615   -2.234663
H     0.102242    1.416281   -2.013778
H    -0.960377    2.816061   -1.805375
H    -0.978236    1.888649   -3.327323
C    -3.416255    2.552430   -0.843992
H    -4.499571    2.627609   -0.765039
H    -2.951583    2.736289    0.127513
H    -3.064849    3.278668   -1.572782
C    -3.982566    0.139084   -0.784021
H    -4.097943    0.241683    0.296700
H    -4.952811    0.254036   -1.271356
H    -3.561288   -0.840472   -1.002889
```

Intermediate **D2**.

```
46
Intermediate 7
Pt   -0.975957   -0.324343   -0.478664
Si    0.703753   -1.614340    0.507944
Si    1.386049    1.952211    0.378339
C     2.354706   -0.839627   -0.043130
C     2.634192    0.554249   -0.037649
C     3.373395   -1.734555   -0.420683
H     3.174597   -2.800617   -0.447591
C     3.933698    0.965524   -0.379234
H     4.175214    2.024418   -0.380856
C     4.650345   -1.296177   -0.760765
H     5.413576   -2.013017   -1.044746
C     4.934429    0.064112   -0.733058
H     5.924250    0.423768   -0.994270
C     0.519212   -1.485640    2.388473
H     1.354505   -1.999927    2.876313
H     0.519901   -0.444946    2.717073
H    -0.407945   -1.953582    2.732281
C     0.644580   -3.444342    0.037838
H     1.407001   -4.021852    0.571234
H    -0.331485   -3.858261    0.304516
H     0.784812   -3.593506   -1.035230
C     1.625248    3.333011   -0.895967
H     0.903398    4.133598   -0.703559
H     2.623886    3.779380   -0.869513
H     1.449069    2.964380   -1.910867
C     1.824562    2.650083    2.081661
H     1.157415    3.479970    2.336770
H     1.724624    1.889633    2.861392
H     2.852351    3.025671    2.114527
O    -0.159122    1.422146    0.359153
N    -3.342911    0.820613   -0.117463
C    -2.698726   -0.083634    0.716185
H    -1.563887   -1.621460   -1.147809
H    -2.245700    0.425661    1.564817
C    -3.400204   -1.366610    1.100654
H    -3.729199   -1.946686    0.240299
H    -4.275378   -1.130297    1.720703
H    -2.727089   -1.989478    1.688949
C    -4.402821    0.410917   -1.029316
H    -4.435792    1.103071   -1.872449
H    -4.205199   -0.586499   -1.419165
H    -5.386715    0.416109   -0.541242
C    -3.189332    2.254145    0.134102
H    -3.307596    2.801719   -0.802971
H    -3.943827    2.613132    0.846312
H    -2.183701    2.438032    0.517279
```

TS from **D2** to **D3**.

```
46
TS from 7 to 8
Pt   -1.056931   -0.165507    0.276538
Si    0.802071   -1.539566    0.685703
Si    1.490344    1.901270    0.321170
C     2.335352   -0.856833   -0.223294
C     2.628973    0.525847   -0.340579
C     3.240848   -1.782998   -0.771669
H     3.035949   -2.846404   -0.702930
C     3.816321    0.908819   -0.985583
H     4.058283    1.964177   -1.083794
C     4.411945   -1.379646   -1.408790
H     5.089676   -2.120946   -1.819508
C     4.704030   -0.023984   -1.515098
H     5.612356    0.305086   -2.009160
C     1.138480   -1.595729    2.547579
H     2.047165   -2.171172    2.755826
H     1.266373   -0.586075    2.941626
H     0.307197   -2.064418    3.082653
C     0.502783   -3.327245    0.109251
H     1.338709   -3.981941    0.377189
```

H	-0.389853	-3.730915	0.596845
H	0.357720	-3.391692	-0.972647
C	1.065693	3.053939	-1.119891
H	0.406701	3.860161	-0.781426
H	1.956720	3.515350	-1.557428
H	0.551600	2.507184	-1.916053
C	2.406083	2.892789	1.639016
H	1.769607	3.694047	2.026779
H	2.688110	2.252543	2.479039
H	3.318651	3.349390	1.243103
O	0.145080	1.263228	1.016796
N	-3.240396	0.597461	-0.441374
C	-2.996669	-0.815436	-0.641072
H	-1.909687	-1.494027	-0.141318
H	-3.683152	-1.379298	-0.007036
C	-3.039655	-1.355361	-2.064832
H	-2.285115	-0.898715	-2.703251
H	-4.027938	-1.186309	-2.503321
H	-2.853790	-2.431151	-2.049154
C	-3.236262	1.497890	-1.595699
H	-3.130019	2.520626	-1.231797
H	-2.385807	1.285927	-2.240105
H	-4.163396	1.428957	-2.182627
C	-4.246522	0.935669	0.567651
H	-4.119857	1.977637	0.864808
H	-5.270336	0.798743	0.188560
H	-4.105329	0.314556	1.452244

Intermediate **D3**.

48
Intermediate 8

Pt	-0.885266	-0.165092	0.089923
Si	0.905739	-1.527759	0.769322
Si	1.848974	1.824036	0.259826
C	2.514340	-1.011822	-0.120198
C	2.907594	0.340414	-0.288975
C	3.372608	-2.022239	-0.589187
H	3.091262	-3.064205	-0.481671
C	4.145203	0.610193	-0.895548
H	4.464700	1.639928	-1.030232
C	4.593157	-1.730563	-1.194300
H	5.231284	-2.535256	-1.544903
C	4.985851	-0.405279	-1.344279
H	5.934491	-0.162534	-1.811851
C	1.138249	-1.292945	2.639789
H	2.021455	-1.841257	2.986059
H	1.264640	-0.238800	2.891963
H	0.269266	-1.665349	3.190985
C	0.657830	-3.393981	0.502854
H	1.498710	-3.951119	0.929107
H	-0.246687	-3.738914	1.011291
H	0.568620	-3.667975	-0.551531
C	1.883840	3.109492	-1.133739
H	1.290830	3.987967	-0.858102
H	2.897966	3.460294	-1.348246
H	1.474029	2.698625	-2.061321
C	2.632774	2.612429	1.788385
H	2.056110	3.483771	2.115136
H	2.669320	1.904270	2.620583
H	3.656716	2.944127	1.588125
O	0.306921	1.392279	0.615709
S	-2.246998	-1.928479	-0.501312
C	-3.759604	-1.860096	0.532135
H	-4.448168	-2.638761	0.200281
H	-3.450598	-2.054319	1.557957
H	-4.225515	-0.877813	0.464182
C	-3.000339	-1.530741	-2.122707
H	-3.691271	-2.330458	-2.393924
H	-3.518297	-0.573121	-2.081093
H	-2.187070	-1.484913	-2.844998
S	-2.808160	1.733999	-0.306736
C	-2.021126	2.838565	-1.526316
H	-2.559191	3.786416	-1.573114
H	-0.979549	2.992943	-1.251673
H	-2.074315	2.343368	-2.495614
C	-2.505591	2.690028	1.219195
H	-2.957750	3.678800	1.130865
H	-2.978929	2.145398	2.035899
H	-1.428809	2.740882	1.384207

TS from **D3** to product + Pt(0).

48
TS from 8 to product

Pt	-0.656987	-0.429538	-0.131632
Si	1.365870	-0.931080	1.088547
Si	1.721863	1.962237	-0.216267
C	3.010729	-0.476838	0.226939
C	3.201182	0.803721	-0.345337
C	4.066530	-1.400601	0.162170
H	3.947980	-2.394390	0.580346
C	4.424443	1.118205	-0.950702
H	4.575801	2.098092	-1.396189
C	5.281335	-1.071370	-0.435872
H	6.083462	-1.801275	-0.468932
C	5.462750	0.191049	-0.995610
H	6.405693	0.448899	-1.466211
C	1.323751	-0.512167	2.929869
H	2.047386	-1.134023	3.467714
H	1.551124	0.537496	3.117270
H	0.334065	-0.722548	3.346276
C	1.280648	-2.846119	1.049889
H	2.109581	-3.269934	1.630165
H	0.352086	-3.196825	1.507580
H	1.331204	-3.246663	0.035175
C	1.104855	2.532810	-1.900310
H	0.203994	3.146373	-1.801941
H	1.861534	3.137036	-2.411772
H	0.868581	1.677508	-2.538363
C	2.085157	3.454509	0.869775
H	1.193469	4.075904	0.995525
H	2.421148	3.140707	1.861242
H	2.870246	4.079734	0.432284
O	0.638177	0.979990	0.589489
S	-1.903671	-2.210172	-0.795640
C	-3.448922	-2.275122	0.195544
H	-4.072616	-3.083692	-0.189274
H	-3.154469	-2.494313	1.220546
H	-3.971859	-1.320089	0.152413
C	-2.641258	-1.798691	-2.425724
H	-3.275114	-2.629203	-2.739549
H	-3.220577	-0.878304	-2.364855
H	-1.817330	-1.677040	-3.126663
S	-4.585097	1.640671	0.336055
C	-3.522032	2.682756	-0.721479

H	-3.426252	3.686271	-0.302740
H	-2.534262	2.233947	-0.840609
H	-4.007323	2.752310	-1.695677
C	-3.585778	1.643315	1.865812
H	-3.482069	2.657337	2.256156
H	-4.122658	1.037880	2.597051
H	-2.601582	1.205891	1.686074

Intermediate **D3'**.

69
Intermediate 8'

Pt	-0.256252	-0.983287	-0.537103
Si	2.081261	-1.279940	-0.790692
Si	1.270532	0.543395	2.172641
C	3.035151	0.250222	-0.190719
C	2.724107	0.962742	0.996827
C	4.154237	0.642417	-0.946748
H	4.401638	0.114194	-1.861805
C	3.558689	2.032730	1.361535
H	3.340982	2.597582	2.263236
C	4.966477	1.705253	-0.559713
H	5.823222	1.983553	-1.164415
C	4.665412	2.406270	0.602887
H	5.285179	3.239770	0.916922
C	2.584815	-2.740089	0.306339
H	3.678638	-2.807364	0.300745
H	2.261901	-2.598007	1.338637
H	2.181457	-3.687777	-0.056378
C	2.584157	-1.753580	-2.553586
H	3.640205	-2.041977	-2.584847
H	1.998627	-2.621381	-2.869074
H	2.427121	-0.960921	-3.286551
C	0.487733	2.161122	2.761751
H	-0.335467	1.939202	3.448781
H	1.197502	2.795159	3.302215
H	0.079138	2.741576	1.931374
C	2.007292	-0.305790	3.699276
H	1.220077	-0.555092	4.418774
H	2.527809	-1.230966	3.435684
H	2.727306	0.342693	4.208912
O	0.175518	-0.446390	1.470997
Si	-0.468667	0.986230	-1.857145
Si	-3.177763	0.377737	0.376216
C	-1.301088	2.323703	-0.768928
C	-2.425653	2.077349	0.057964
C	-0.822429	3.641736	-0.858650
H	0.047709	3.858286	-1.467471
C	-3.030463	3.153380	0.727826
H	-3.893052	2.980297	1.366273
C	-1.431891	4.696073	-0.181750
H	-1.032935	5.700667	-0.273423
C	-2.547482	4.453803	0.611340
H	-3.032014	5.265383	1.143129
C	1.066975	1.744449	-2.654553
H	0.764150	2.593838	-3.276075
H	1.806902	2.087335	-1.931015
H	1.552880	1.023418	-3.314815
C	-1.668459	0.640197	-3.291109
H	-1.922012	1.577428	-3.798065
H	-1.210428	-0.031160	-4.023331
H	-2.599104	0.176958	-2.955607
C	-4.876431	0.208722	-0.432105
H	-5.569557	0.950099	-0.022089
H	-4.824685	0.367142	-1.512084
H	-5.305401	-0.781556	-0.252046
C	-3.263171	-0.002101	2.214233
H	-3.764012	0.801968	2.760975
H	-3.815913	-0.926557	2.405916
H	-2.248213	-0.107434	2.603600
H	-0.514881	-1.563419	-1.968571
H	-2.291575	-0.677668	-0.276885
S	-0.755520	-3.483681	0.480061
C	-2.384693	-4.007438	-0.151081
H	-2.676529	-4.954682	0.303946
H	-3.140368	-3.245912	0.042869
H	-2.278552	-4.141876	-1.227357
C	-1.113602	-3.216389	2.249886
H	-0.968910	-4.140559	2.809000
H	-0.426600	-2.434764	2.574727
H	-2.133595	-2.853673	2.371494

TS from **D3'** to product + **A5a**.

69
TS from 8' to product

Pt	-0.301559	-1.063618	-0.579398
Si	2.139120	-1.195666	-0.588435
Si	1.594286	0.481091	2.103238
C	3.132368	0.394535	-0.239363
C	2.926567	1.145072	0.942693
C	4.126317	0.815819	-1.138416
H	4.300623	0.263441	-2.055231
C	3.708615	2.282368	1.181410
H	3.551911	2.868299	2.083179
C	4.900691	1.945797	-0.883106
H	5.662614	2.251417	-1.592520
C	4.690025	2.684931	0.278629
H	5.286259	3.569349	0.477727
C	2.843249	-2.697107	0.326556
H	3.879238	-2.841532	0.000097
H	2.833213	-2.577440	1.409256
H	2.294168	-3.607959	0.073483
C	2.465516	-1.666500	-2.415956
H	3.528137	-1.903456	-2.550768
H	1.895326	-2.563553	-2.670247
H	2.197019	-0.886151	-3.128460
C	0.415511	1.819686	2.700333
H	-0.342286	1.398157	3.368485
H	0.963747	2.577252	3.271192
H	-0.096247	2.322226	1.878821
C	2.387888	-0.300008	3.630467
H	1.631724	-0.758771	4.276004
H	3.114436	-1.070153	3.358967
H	2.912726	0.454637	4.225629
O	0.908959	-0.709342	1.182058
Si	-0.662480	0.939621	-1.807105
Si	-3.434877	0.442086	0.448744
C	-1.400424	2.276120	-0.636257
C	-2.535615	2.085157	0.196641
C	-0.820551	3.556466	-0.672015
H	0.057514	3.730874	-1.282452
C	-3.042132	3.178123	0.919929
H	-3.910261	3.047832	1.560632
C	-1.335147	4.626274	0.057529
H	-0.857076	5.598567	0.001900

C	-2.458334	4.440223	0.854201
H	-2.872320	5.263777	1.425837
C	0.801335	1.713328	-2.723291
H	0.464068	2.595954	-3.277044
H	1.624777	2.005239	-2.070306
H	1.192586	1.004073	-3.456357
C	-1.976214	0.656822	-3.156904
H	-2.277948	1.614499	-3.594280
H	-1.568286	0.030864	-3.956451
H	-2.872950	0.160908	-2.779120
C	-5.077425	0.387695	-0.481652
H	-5.748997	1.171160	-0.116811
H	-4.937134	0.546588	-1.553300
H	-5.580677	-0.574056	-0.342921
C	-3.739373	0.120168	2.285120
H	-4.382698	0.886627	2.726717
H	-4.234729	-0.844557	2.432614
H	-2.800634	0.111946	2.844571
H	-0.875363	-1.556570	-1.941677
H	-2.550806	-0.664973	-0.062864
S	-0.647438	-3.499642	0.469656
C	-2.331663	-4.008092	-0.012794
H	-2.594266	-4.943941	0.482150
H	-3.055133	-3.230504	0.232412
H	-2.319229	-4.160354	-1.091564
C	-0.868558	-3.216395	2.257048
H	-0.961904	-4.168131	2.780969
H	0.021193	-2.681307	2.583521
H	-1.743992	-2.591819	2.435252

TS from **A5a** to **M1a**.

46
TS from 4a to 9a

Pt	-0.905728	-0.792173	-0.343938
Si	1.139177	-1.748097	0.214912
Si	0.517927	1.893124	0.095020
C	2.476813	-0.406403	-0.007325
C	2.229761	0.984069	-0.045479
C	3.804396	-0.864323	-0.102406
H	4.011010	-1.930113	-0.065312
C	3.332103	1.848978	-0.179957
H	3.177698	2.923609	-0.204145
C	4.876538	0.008380	-0.254979
H	5.887191	-0.376857	-0.339528
C	4.635880	1.377677	-0.299826
H	5.456711	2.076332	-0.424431
C	1.198271	-2.373446	2.003630
H	0.467088	-3.170274	2.162813
H	2.193743	-2.770264	2.231776
H	0.991139	-1.572732	2.718088
C	1.518737	-3.209020	-0.934011
H	1.548344	-2.897289	-1.980743
H	2.485398	-3.662121	-0.689515
H	0.752719	-3.981960	-0.831101
C	0.363894	3.153273	-1.310896
H	-0.512386	3.789875	-1.159706
H	1.240525	3.807512	-1.315222
H	0.293795	2.683835	-2.294370
C	0.855124	2.879444	1.697098
H	0.857978	2.212763	2.565338
H	1.833938	3.365114	1.663783
H	0.085901	3.637143	1.865639
O	-1.313270	1.785028	0.739890
N	-3.011438	0.578056	-0.261607
C	-2.088526	0.737001	0.777833
H	-0.087523	0.601679	-0.954133
H	-1.608932	-2.143888	0.167319
C	-2.430123	0.224031	2.162934
H	-3.099162	0.955450	2.633484
H	-2.900147	-0.754419	2.175203
H	-1.511264	0.183641	2.744133
C	-4.206241	-0.258939	-0.103449
H	-4.999324	0.283574	0.425137
H	-4.569224	-0.529978	-1.095132
H	-3.967099	-1.175826	0.427098
C	-3.141632	1.611411	-1.296091
H	-2.229051	2.189969	-1.361691
H	-3.340871	1.133568	-2.256408
H	-3.974585	2.281373	-1.050536

Intermediate **M1a**.

46
Intermediate 9a

Pt	1.252406	-0.906122	0.086722
Si	-0.872681	-1.789476	0.445767
Si	-0.915067	1.974117	0.806195
C	-2.186535	-0.543550	-0.213681
C	-2.192792	0.876502	-0.075328
C	-3.265343	-1.140466	-0.888415
H	-3.281166	-2.216077	-1.019704
C	-3.279487	1.594477	-0.611142
H	-3.307898	2.674037	-0.523137
C	-4.331262	-0.406939	-1.405824
H	-5.142461	-0.915594	-1.916000
C	-4.340119	0.972485	-1.265414
H	-5.156863	1.565714	-1.662095
C	-1.078522	-3.435125	-0.478997
H	-0.259019	-4.102137	-0.195326
H	-2.015135	-3.942158	-0.223375
H	-1.028322	-3.301684	-1.561630
C	-1.285523	-2.180137	2.256753
H	-1.267985	-1.295456	2.894133
H	-2.282836	-2.629362	2.324591
H	-0.564124	-2.896319	2.661276
C	-0.740166	1.644948	2.641991
H	-0.123701	2.425702	3.098575
H	-1.722716	1.668026	3.123932
H	-0.268860	0.684285	2.842432
C	-1.334176	3.795459	0.588607
H	-1.437849	4.086683	-0.459472
H	-2.251761	4.071899	1.115773
H	-0.520150	4.387964	1.016781
O	0.641703	1.909310	0.089267
N	2.665580	1.023490	-0.578444
C	1.256511	1.028294	-0.743394
H	1.302768	-0.442264	1.682170
H	1.203876	-1.520958	-1.448268
C	0.704243	1.105920	-2.161003
H	0.853517	2.128857	-2.528536
H	1.166132	0.396268	-2.837977
H	-0.364159	0.899852	-2.134076
C	3.542932	0.822533	-1.734302
H	3.637079	1.735685	-2.336954
H	4.532321	0.545839	-1.368626

H	3.176639	0.009438	-2.355806
C	3.263839	1.806251	0.508332
H	2.628340	1.768822	1.385558
H	4.233598	1.370868	0.753643
H	3.407241	2.851820	0.206208

TS from **M1a** to **D1'**.

46
TS from 9a to 10a

Pt	1.082392	-0.920727	0.052611
Si	-1.060939	-1.785394	0.333025
Si	-0.655457	1.926957	0.771563
C	-2.306574	-0.395411	-0.169160
C	-2.101437	1.013758	-0.067826
C	-3.515341	-0.842048	-0.728533
H	-3.697902	-1.907696	-0.817314
C	-3.109201	1.871811	-0.550141
H	-2.978960	2.945625	-0.486875
C	-4.499241	0.027646	-1.194532
H	-5.414650	-0.366875	-1.623229
C	-4.291918	1.396765	-1.111707
H	-5.039091	2.093904	-1.475376
C	-1.376232	-3.284245	-0.790289
H	-0.617491	-4.044697	-0.585154
H	-2.355701	-3.741097	-0.614938
H	-1.303454	-3.021668	-1.848692
C	-1.499600	-2.333848	2.095958
H	-1.341147	-1.542399	2.831452
H	-2.551579	-2.635145	2.149976
H	-0.882784	-3.188770	2.387177
C	-0.301638	1.340040	2.522402
H	0.422142	2.008812	2.999431
H	-1.224845	1.382264	3.110028
H	0.088026	0.323486	2.571458
C	-1.011323	3.772067	0.877161
H	-1.137276	4.233131	-0.105296
H	-1.901379	3.985813	1.475340
H	-0.161639	4.263205	1.360534
O	0.793091	1.984434	-0.153232
N	2.752147	0.677415	-0.349591
C	1.438864	1.028820	-0.897214
H	1.438440	-2.052988	1.153948
H	0.384190	-0.252311	-1.249139
C	1.418802	1.419863	-2.370569
H	1.984322	2.348333	-2.506485
H	1.828331	0.649024	-3.021207
H	0.384617	1.602383	-2.662055
C	3.803643	0.268415	-1.290768
H	4.218367	1.122889	-1.841853
H	4.604501	-0.202373	-0.719989
H	3.420849	-0.467278	-1.995225
C	3.279103	1.487783	0.758024
H	2.501287	1.686924	1.486104
H	4.077712	0.923239	1.240469
H	3.680898	2.443192	0.395126

Intermediate **D1'**.

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Intermediate 10a

Pt	1.615431	-0.521532	0.244548
Si	-0.142168	-1.986050	0.158237
Si	-1.435472	1.371409	1.242006
C	-1.756076	-1.094213	-0.419833
C	-2.286686	0.135815	0.070539
C	-2.515567	-1.805488	-1.366157
H	-2.133277	-2.737730	-1.764863
C	-3.548680	0.551094	-0.395820
H	-3.978029	1.476659	-0.030603
C	-3.760119	-1.368549	-1.815627
H	-4.310370	-1.955458	-2.543702
C	-4.285745	-0.183869	-1.321270
H	-5.255974	0.172363	-1.650430
C	0.254518	-3.365548	-1.088510
H	1.195359	-3.837400	-0.794333
H	-0.516449	-4.143528	-1.099790
H	0.380516	-2.989217	-2.106737
C	-0.594679	-2.868291	1.776434
H	-0.812045	-2.174850	2.590109
H	-1.482400	-3.490905	1.619654
H	0.225430	-3.516517	2.097986
C	-0.703785	0.701136	2.831258
H	-0.330835	1.541120	3.426432
H	-1.464700	0.184998	3.424864
H	0.129083	0.021319	2.647343
C	-2.640538	2.735887	1.735045
H	-3.028379	3.296724	0.880994
H	-3.490968	2.349827	2.305350
H	-2.110944	3.446824	2.376628
O	-0.205534	2.177131	0.391811
N	1.539385	1.398716	-0.988506
C	0.179302	2.045204	-0.942926
H	1.974536	-1.751405	1.133147
H	-0.470974	1.342637	-1.473586
C	0.102263	3.419045	-1.611784
H	0.673549	4.161062	-1.051892
H	0.452385	3.398722	-2.646129
H	-0.941339	3.738528	-1.618472
C	1.916682	1.056834	-2.378490
H	2.077556	1.952219	-2.992095
H	2.836985	0.473351	-2.364046
H	1.133380	0.446127	-2.827891
C	2.581360	2.255278	-0.371581
H	2.237020	2.581196	0.608030
H	3.498999	1.673767	-0.254735
H	2.810338	3.129960	-0.991974

Assessments for DFT functionals

To check whether our computational results were reliable or not, here we performed a simple assessment using the five commonly used functionals; B3LYP, B3PW91, B97D, M06, and PBE0.

Table S1. The DFT-optimized geometry of the isolated complex **1**, using various functionals. Important bond lengths and bond angles are shown.

	B3LYP	B3PW91	B97D	M06	PBE0	exptl.
			bond lenghts [Å]			
Pt-Si1	2.356	2.350	2.343	2.352	2.346	2.323
Pt-Si2	2.356	2.350	2.343	2.352	2.346	2.320
Pt-S1	2.554	2.491	2.525	2.554	2.468	2.409
Pt-S2	2.553	2.491	2.525	2.554	2.468	2.403
			bond angles [degree]			
Si1-Pt-Si2	83.6	83.3	84.2	82.2	83.1	82.8
S1-Pt-S2	93.2	94.9	94.7	95.1	95.8	97.9

The DFT-optimized bond lengths overestimated those of the experimental values for all functionals, although the DFT-optimized bond angles agreed well with the experimental values. These results clearly indicate that a crystal packing effect must be taken into account for the experimental bond lengths. Moreover, because amounts of the functional dependency and crystal packing effect are likely in same order, it is difficult to conclude which functional is the most reliable only from the optimized geometry.

Thus, we also checked the functional dependency in energy calculations. Figure S1 showed the potential energy changes toward the reduction of amide as discussed in the manuscript. Note that the geometries were taken from the B3LYP calculations. It should be noted that all the functionals gave qualitatively the same results. Consequently, functional dependency was reasonably small in our system. Again, it is however, very difficult to conclude which functional is better to use. To keep robustness and generality in our computational results and discussions, we simply employed the B3LYP functional which have been well demonstrated for ground state reactions of 4d and 5d transition metal complexes.

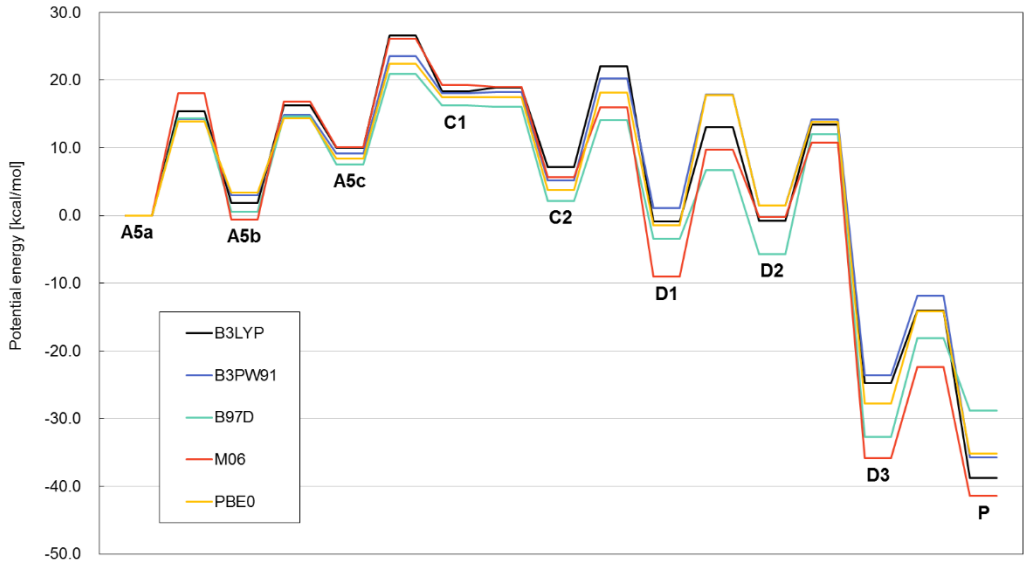


Figure S1. Potential energy changes (vacuum) for the platinum-catalyzed reduction of amide computed by several functionals. Geometries were optimized by the B3LYP functional and the energies were evaluated by the B3LYP, B3PW91, B97D, M06, and PBE0 functionals.

Chalk-Harrod mechanism from A5a

Figure S2 shows the potential energy curve toward the C=O bond insertion into the Pt-H bond of **A5a**. Around the C-H bonding region, there is a shelf structure but no energy minima. Moreover, because the energy barrier must be larger than 25-30 kcal/mol, the direct C=O bond insertion from **A5a** is unfavorable.

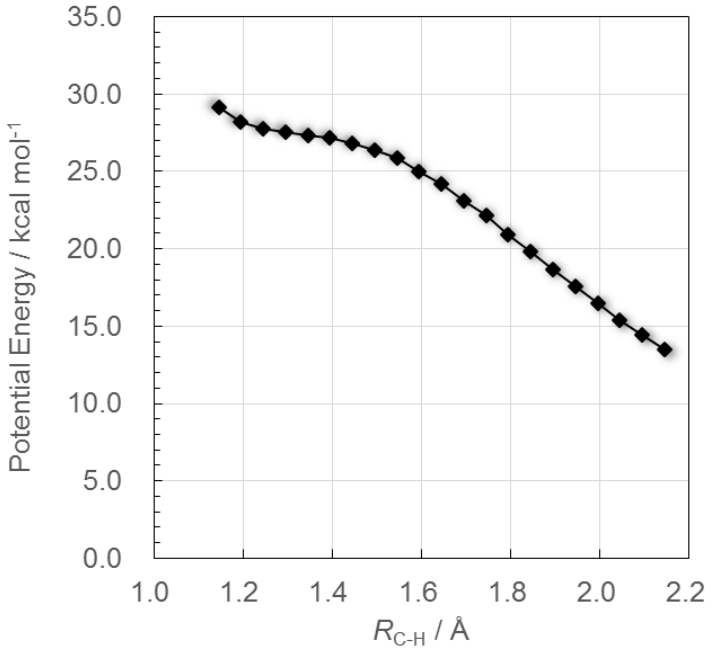


Figure S2. Potential energy curve toward the C=O insertion into the Pt-H bond of **A5a**.

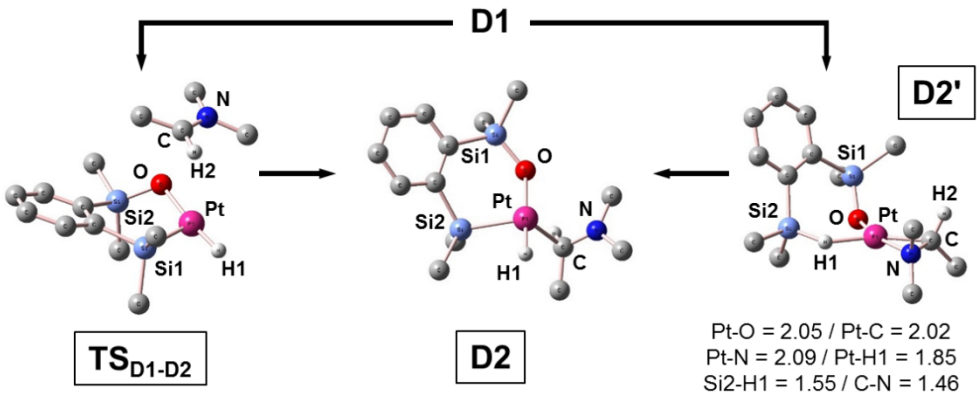


Figure S3. Optimized geometry of the iminium complex **D2'** involved in the formation of the intermediate **D2**. Important bond lengths of **D2'** are shown in Å.

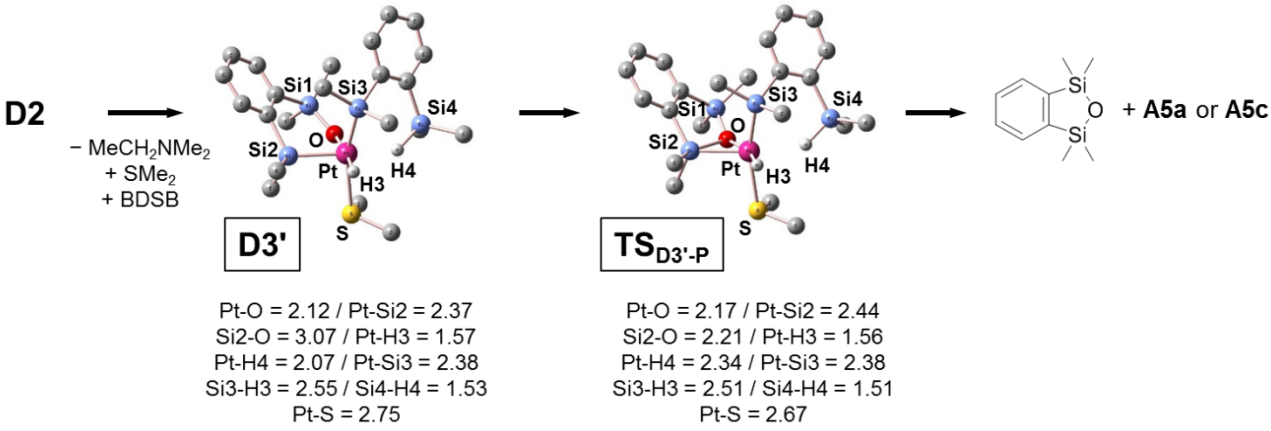


Figure S4. Optimized geometries obtained from the BDSB-supported siloxane formation. Important bond lengths are shown in Å.

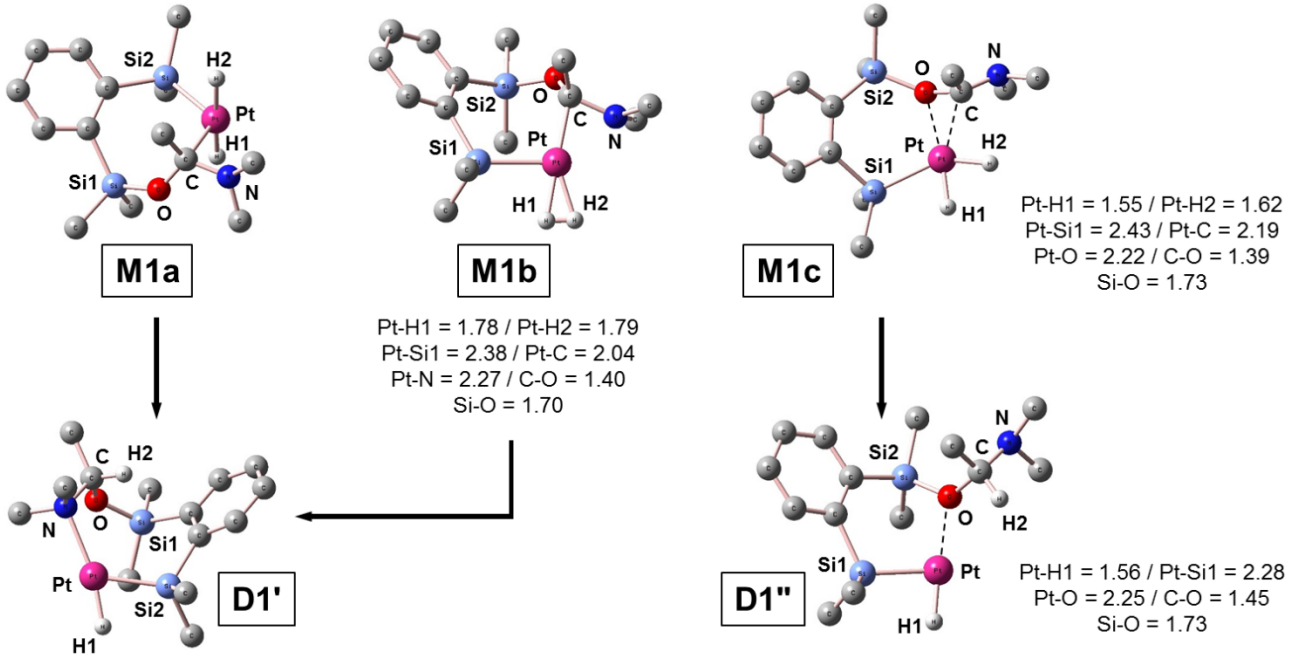
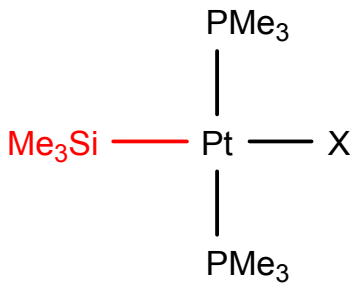


Figure S5. Optimized geometries obtained from the modified Chalk-Harrod cycles.

Order of Trans-Influence for Related Ligands

As summarized in Table S2, the binding energies were estimated in the order of $SiMe_3$ < SiH_2CH_3 < CH_2CH_3 < H < OCH_3 and the Pt-Si bond length that was in the trans position to the ligand X changed in the order of SiH_2CH_3 > $SiMe_3$ > CH_2CH_3 > H > OCH_3. From these results, trans influence of these ligands are estimated to be in the order of SiH_2CH_3 = $SiMe_3$ > CH_2CH_3 > H > OCH_3.

Table S2. Calculated binding energy (BE) of $SiMe_3$ group and the Pt-Si length (red colored) in square planer Pt(II) complex [$Pt(PMe_3)_2(X)(SiMe_3)$], where X = H, CH_2CH_3, OCH_3, SiH_2CH_3, and $SiMe_3$ at the position trans to the $SiMe_3$ group. The BE was estimated as a homolytic cleavage of the Pt-Si bond, where the geometry of the remaining fragment, [$Pt(PMe_3)_2(X)$] was fixed to that of the binding complex [$Pt(PMe_3)_2(X)(SiMe_3)$], to account for only electronic effects into account. Computational details were the same as mentioned in the main text.



X	BE / kcal mol^{-1}	Pt–Si / Å
H	63.0	2.489
CH_2CH_3	60.1	2.497
OCH_3	65.5	2.382
SiH_2CH_3	54.8	2.514
$SiMe_3$	51.6[a]	2.498[a]

[a] Values of two $SiMe_3$ groups were averaged.

Natural Bonding Orbitals (NBOs) of A3c

As discussed in the manuscript, we found the five-coordinate Pt(IV) complex **A3c** is an important intermediate to proceed the platinum-catalyzed hydrosilylation of carbonyl group. It is curious that **A3c** takes a trigonal bipyramidal structure which is not common in Pt(IV) species. We carried out the natural bonding orbitals (NBOs) analysis of **A3c** to investigate occupation numbers of d-orbital space. As shown in Figure S6, three d-orbitals (d_z2, d_{xy}, and d_{yz}) were found to be almost doubly-occupied (> 1.9e), d_{xz} orbital was found with occupation number of 1.776e, and the $d_x2_{-y}2$ orbital could not be found within the occupied orbital space, meaning that the $d_x2_{-y}2$ orbital was in the unoccupied space. These four occupied d-orbitals were therefore, occupied by 7.69e in total, which was close to 8e rather than 6e.

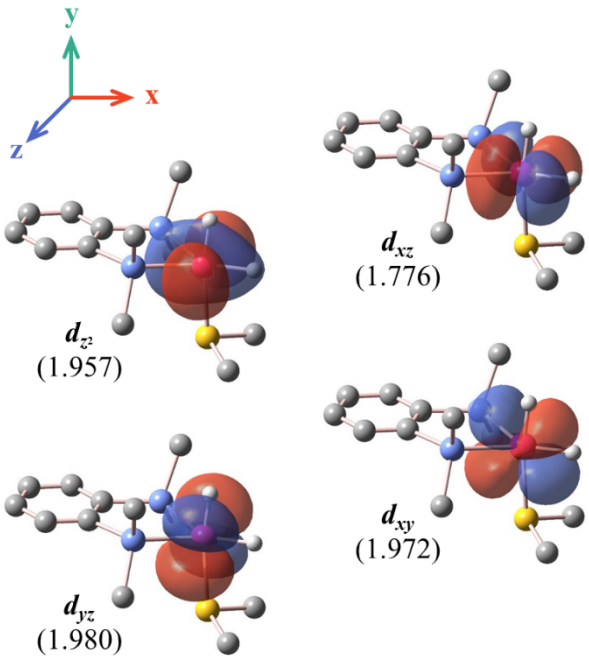
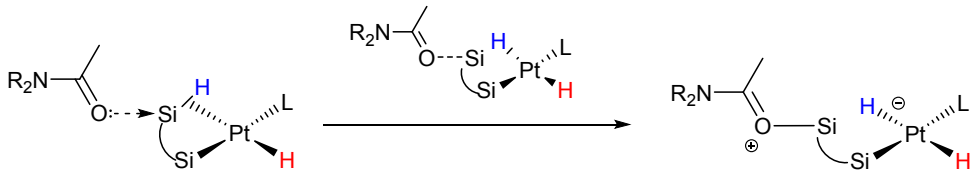
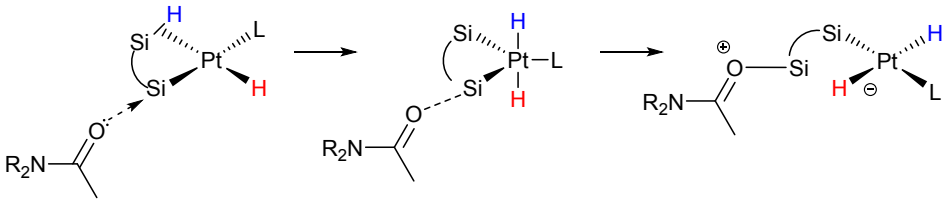


Figure S6. Natural atomic orbitals (NAOs) and their occupation numbers of the four 5d-orbitals of **A3c**.

(A) Ionic outer-sphere mechanism for the Pt-catalyzed amide reduction



(B) Chan's alternative "outer-sphere" modified Chalk-Harrod mechanism



Scheme S1. (A) Ionic outer sphere mechanism and (B) Chan's outer sphere mechanism.