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A Theoretical Study of the Mechanism for the Homogeneous Catalytic Reversible Dehydrogenation – Hydrogenation of Nitrogen Heterocycles

Xiang-BiaoZhang[a] and ZhaoXi[b]

[a]Room 302, 5 Building, Beiyuan District, Suzhou, Anhui 234000, People's Republic of China

[b]State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130023, People's Republic of China

xbzhtc@gmail.com

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Details on calculations

In the calculations, two kinds of model were adopted for geometry optimization and calculation of electronic energies, respectively. In the first model, the Iridium and

chlorine were described using the LANL2DZ basis set including a double – ζ valence basis set with the Hay and Wadt effective core potential (ECP),[1] additional f and d polarization shells were added for iridium and chlorine, with exponents of 0.938 and 0.640,[2] respectively; the 6-31G basis set was used for other elements, and polarization functions were added for carbon and nitrogen directly connected to iridium as well as those elements in substrate except for that in benzene and substituent on substrate. In the second model, description of iridium is the same with that in the first model, except for without polarization function; the 6-311+G(d) was used for nitrogen, chlorine and oxygen as well as 6-311G(d,p) for carbon and hydrogen. Based on the first model, the geometric structures and frequencies of complexes were calculated at the level of DFT/B3LYP.[3] Intrinsic reaction coordinate (IRC) analysis was carried out to confirm that all stationary points are smoothly connected to each other. To obtain accurate energy, based on the optimized geometries, the second model was used to calculate electronic energy of complexes at the same theoretical level. The free energies are obtained by adding free energy corrections at 298.15K to electronic energies. All the calculations were performed with the Gaussian03 package[4].

Cartesian coordinates

For the catalyst **1-H**

Atomic number		X	Y	Z
77	0	0.185971	-0.141929	-0.113448
17	0	-0.312970	-2.508176	-0.213395
8	0	-1.256232	0.103872	-1.749226
7	0	-1.844689	0.085307	0.364579
6	0	1.357857	1.681033	-0.222986
6	0	1.218003	1.280296	1.154177
6	0	1.795598	-0.043169	1.310256
6	0	2.369968	-0.421105	0.025054
6	0	2.076865	0.613829	-0.916148
6	0	0.951102	2.991251	-0.832717
6	0	0.583830	2.093199	2.245033
6	0	1.939524	-0.822014	2.585430
6	0	3.104479	-1.703245	-0.233789
6	0	2.439680	0.637654	-2.372411

6	0	-2.273094	0.128487	-0.933697
6	0	-3.654157	0.182858	-1.230223
6	0	-4.546523	0.187772	-0.166996
6	0	-4.083220	0.122327	1.165591
6	0	-2.714340	0.057289	1.393400
1	0	0.555602	2.848342	-1.842616
1	0	1.807073	3.677060	-0.897053
1	0	0.172778	3.482061	-0.241679
1	0	-0.207114	2.739462	1.854996
1	0	1.334589	2.732279	2.728793
1	0	0.145469	1.455409	3.017902
1	0	1.150220	-0.569957	3.299702
1	0	2.906231	-0.617893	3.066572
1	0	1.873992	-1.895825	2.390819
1	0	2.505944	-2.562662	0.083515
1	0	4.054561	-1.713143	0.315987
1	0	3.327126	-1.833384	-1.295275
1	0	2.635839	-0.367119	-2.753937
1	0	3.339019	1.246800	-2.535592
1	0	1.629875	1.064513	-2.971520
1	0	-3.977948	0.208316	-2.262569
1	0	-5.613630	0.230804	-0.361506
1	0	-2.294555	-0.017347	2.390050
1	0	-4.775076	0.112917	1.998505

For the catalyst **1-CF_3**

Atomic number		X	Y	Z
77	0	1.011142	-0.140230	-0.093635
17	0	0.549760	-2.515588	-0.088129
8	0	-0.525769	0.026478	-1.653311
7	0	-1.001947	0.072333	0.489567
6	0	2.110644	1.739963	-0.122109
6	0	2.176434	1.154965	1.199624
6	0	2.805108	-0.143419	1.099390
6	0	3.179730	-0.344638	-0.297059
6	0	2.741081	0.800504	-1.038511

6	0	1.616350	3.112965	-0.475891
6	0	1.690629	1.801525	2.463953
6	0	3.138239	-1.082677	2.221245
6	0	3.899470	-1.551869	-0.821735
6	0	2.870479	1.009725	-2.518473
6	0	-1.493218	0.055891	-0.786990
6	0	-2.888148	0.063709	-1.020426
6	0	-3.723310	0.096769	0.086442
6	0	-3.200123	0.096711	1.398698
6	0	-1.821997	0.071016	1.557257
1	0	1.163593	3.127272	-1.471507
1	0	2.440961	3.839114	-0.471855
1	0	0.861871	3.463069	0.234327
1	0	0.827574	2.447571	2.280088
1	0	2.485232	2.421569	2.900260
1	0	1.403753	1.057869	3.212557
1	0	2.524058	-0.888903	3.104972
1	0	4.192015	-0.980563	2.514136
1	0	2.962674	-2.119114	1.920342
1	0	3.403431	-2.469841	-0.492349
1	0	4.936539	-1.565354	-0.461611
1	0	3.921988	-1.563937	-1.914064
1	0	3.029925	0.065611	-3.044150
1	0	3.719314	1.670810	-2.738445
1	0	1.967434	1.468283	-2.931686
1	0	-3.267008	0.043705	-2.032429
1	0	-1.358837	0.053139	2.536480
1	0	-3.854702	0.121612	2.259155
6	0	-5.206441	0.056624	-0.094311
9	0	-5.602351	0.454685	-1.365418
9	0	-5.863557	0.882679	0.817778
9	0	-5.724477	-1.223354	0.102832

For the catalyst **2**

Atomic number		X	Y	Z
77	0	-0.244019	-0.287105	-0.048547

17	0	-0.232416	-2.576389	-0.672029
8	0	1.896946	1.941017	-0.788020
7	0	1.807265	-0.261961	-0.047711
6	0	-1.296722	1.522608	-0.689950
6	0	-2.199315	0.367017	-0.769032
6	0	-2.358578	-0.164957	0.542936
6	0	-1.509536	0.614694	1.432740
6	0	-0.908341	1.699201	0.680669
6	0	-0.929301	2.418316	-1.830322
6	0	-2.866041	-0.130042	-2.016567
6	0	-3.209196	-1.338593	0.932027
6	0	-1.377428	0.401334	2.910385
6	0	-0.130073	2.847015	1.250036
6	0	2.510000	0.927234	-0.383251
6	0	3.951160	0.902696	-0.245523
6	0	4.619985	-0.218242	0.170322
6	0	3.887942	-1.395585	0.476594
6	0	2.519838	-1.373063	0.348791
1	0	0.147959	2.601570	-1.820100
1	0	-1.455976	3.378417	-1.738342
1	0	-1.201925	1.976633	-2.792097
1	0	-2.215505	-0.016076	-2.887883
1	0	-3.788564	0.434806	-2.208268
1	0	-3.123915	-1.188000	-1.933545
1	0	-3.193670	-2.111759	0.160038
1	0	-4.249650	-1.023173	1.086563
1	0	-2.857203	-1.798692	1.858841
1	0	-1.443010	-0.658392	3.171016
1	0	-2.182400	0.928767	3.441142
1	0	-0.423857	0.782091	3.284574
1	0	-0.797719	3.702635	1.423923
1	0	0.669069	3.142231	0.568667
1	0	0.327997	2.584656	2.208157
1	0	4.463213	1.823448	-0.496853
1	0	5.702425	-0.210566	0.262323
1	0	1.929039	-2.253695	0.555818
1	0	4.383910	-2.301891	0.800952

For the **TS-34**

Atomic number		X	Y	Z
77	0	0.987621	-0.384452	-0.186239
17	0	1.402571	-0.320011	-2.613062
8	0	-0.716980	2.068936	1.219091
7	0	1.111718	1.752250	-0.198140
6	0	0.733283	-1.196987	1.812729
6	0	0.717857	-2.296506	0.854613
6	0	1.992313	-2.323031	0.196496
6	0	2.840659	-1.291529	0.775061
6	0	2.053943	-0.601984	1.756313
6	0	-0.340163	-0.846790	2.804697
6	0	-0.406519	-3.275400	0.662728
6	0	2.437283	-3.295528	-0.857145
6	0	4.284047	-1.058756	0.433233
6	0	2.514072	0.538131	2.618465
6	0	0.306809	2.557397	0.603607
6	0	0.645888	3.944075	0.724998
6	0	1.728491	4.482303	0.058813
6	0	2.510884	3.648951	-0.764234
6	0	2.165250	2.311493	-0.859894
1	0	-0.481034	0.236952	2.847795
1	0	-0.090620	-1.217245	3.808974
1	0	-1.299917	-1.286354	2.516888
1	0	-1.377731	-2.805590	0.842445
1	0	-0.309836	-4.119093	1.360355
1	0	-0.416066	-3.681131	-0.352698
1	0	1.593026	-3.850421	-1.273315
1	0	3.144846	-4.021676	-0.434118
1	0	2.926861	-2.777023	-1.686417
1	0	4.461325	-1.180229	-0.640047
1	0	4.937741	-1.769226	0.960259
1	0	4.604995	-0.050270	0.710724
1	0	1.679538	1.192010	2.883912
1	0	3.269599	1.146939	2.114017

1	0	2.955190	0.157537	3.549860
1	0	0.006338	4.542776	1.362120
1	0	1.968146	5.536697	0.162425
1	0	2.715198	1.633673	-1.499559
1	0	3.359865	4.029147	-1.319096
7	0	-2.482643	1.134066	-0.403324
6	0	-1.833241	0.682258	-1.459230
1	0	-0.981341	1.256013	-1.800550
1	0	-0.557902	-0.268052	-0.679980
6	0	-2.476481	-0.336526	-2.366834
1	0	-2.105886	-0.195140	-3.384569
1	0	-2.134771	-1.328489	-2.050064
6	0	-4.010807	-0.253576	-2.294219
1	0	-4.456656	-1.113794	-2.802537
1	0	-4.352965	0.641490	-2.834606
6	0	-3.685591	0.548491	0.053002
6	0	-4.080515	0.721178	1.386592
6	0	-4.482803	-0.175151	-0.858873
6	0	-5.282110	0.156650	1.822985
1	0	-3.446204	1.286037	2.061534
6	0	-5.678897	-0.734064	-0.399718
6	0	-6.080463	-0.573341	0.933396
1	0	-5.592504	0.285004	2.854493
1	0	-6.301823	-1.295419	-1.090111
1	0	-7.011853	-1.013664	1.273620
1	0	-1.854273	1.662044	0.302218

For the **TS-52**

Atomic number		X	Y	Z
77	0	-0.058036	0.003163	0.079514
17	0	-0.093157	-0.295285	2.454763
8	0	2.548941	0.097092	-1.540533
7	0	1.642174	1.184081	0.286996
6	0	-0.685201	-0.672319	-1.920273
6	0	-1.600741	-1.238689	-0.920408
6	0	-2.224946	-0.162490	-0.233936

6	0	-1.656379	1.089163	-0.745967
6	0	-0.759339	0.752602	-1.849931
6	0	0.140064	-1.447793	-2.902533
6	0	-1.862070	-2.702437	-0.713722
6	0	-3.255006	-0.257269	0.851039
6	0	-2.097584	2.469001	-0.358280
6	0	-0.052455	1.715563	-2.756486
6	0	2.658145	1.006941	-0.669357
6	0	3.794026	1.890184	-0.580576
6	0	3.887867	2.843387	0.406587
6	0	2.854219	2.967900	1.366114
6	0	1.768459	2.121763	1.270884
1	0	1.155416	-1.045026	-2.934552
1	0	-0.304389	-1.382261	-3.904805
1	0	0.200272	-2.505106	-2.632766
1	0	-0.965983	-3.299631	-0.901737
1	0	-2.645889	-3.053705	-1.398600
1	0	-2.188491	-2.909281	0.308282
1	0	-3.252233	-1.241519	1.323799
1	0	-4.256109	-0.078555	0.435951
1	0	-3.072329	0.479331	1.637500
1	0	-2.399685	2.508476	0.691410
1	0	-2.955095	2.781671	-0.970373
1	0	-1.296335	3.197986	-0.504940
1	0	-0.623931	1.851686	-3.684731
1	0	0.943335	1.343337	-3.008333
1	0	0.063765	2.697036	-2.289059
1	0	4.567655	1.753364	-1.326323
1	0	4.756068	3.494598	0.456000
1	0	0.963665	2.150311	1.994044
1	0	2.905688	3.696886	2.165170
1	0	1.456941	-1.746113	0.362778
1	0	1.814809	-1.396269	-0.213597

For the **TS-67**

Atomic number	X	Y	Z

77	0	1.103649	-0.088831	-0.220484
17	0	1.168198	0.405887	-2.605234
8	0	-1.431411	0.407546	1.293255
7	0	-0.030363	1.667404	-0.008465
6	0	1.661153	-1.244365	1.569250
6	0	2.296109	-1.854969	0.399669
6	0	3.166455	-0.880739	-0.183081
6	0	3.057990	0.354715	0.577012
6	0	2.148169	0.099799	1.686408
6	0	0.750624	-1.923454	2.550828
6	0	2.166074	-3.287683	-0.033805
6	0	4.052734	-1.081377	-1.375734
6	0	3.884992	1.590089	0.368209
6	0	1.812118	1.061869	2.788026
6	0	-1.106704	1.584805	0.850222
6	0	-1.815638	2.767678	1.194171
6	0	-1.433432	3.981682	0.653292
6	0	-0.353648	4.036425	-0.252356
6	0	0.311856	2.861470	-0.560369
1	0	-0.053574	-1.254716	2.868122
1	0	1.314725	-2.236773	3.439810
1	0	0.282773	-2.812585	2.123108
1	0	1.214224	-3.720605	0.282609
1	0	2.967529	-3.897888	0.404845
1	0	2.228894	-3.384979	-1.121062
1	0	3.741487	-1.944981	-1.967232
1	0	5.087921	-1.246777	-1.047519
1	0	4.032638	-0.212064	-2.037236
1	0	4.122248	1.732641	-0.689505
1	0	4.833324	1.522001	0.919406
1	0	3.362398	2.485557	0.716814
1	0	1.859029	2.099204	2.445282
1	0	2.524449	0.950755	3.616681
1	0	0.807410	0.882575	3.178627
1	0	-2.655252	2.670511	1.869816
1	0	-1.973391	4.886613	0.913583

1	0	1.128810	2.829129	-1.269332
1	0	-0.046190	4.968401	-0.709917
7	0	-2.871084	-2.562645	0.307844
6	0	-1.657791	-2.387271	-0.077444
1	0	-0.957806	-3.192621	0.160611
6	0	-1.112715	-1.197214	-0.792258
1	0	-1.012640	-0.392103	0.350673
1	0	-0.346347	-1.542841	-1.486993
6	0	-2.208886	-0.452789	-1.579341
1	0	-2.342037	-0.951144	-2.551862
1	0	-1.897416	0.569049	-1.812488
6	0	-3.808436	-1.531012	0.040416
6	0	-5.050404	-1.600365	0.688884
6	0	-3.532953	-0.462534	-0.844466
6	0	-6.018259	-0.614816	0.475805
1	0	-5.230764	-2.434291	1.358789
6	0	-4.510642	0.515740	-1.050342
6	0	-5.748348	0.446730	-0.395866
1	0	-6.975892	-0.674935	0.983715
1	0	-4.302365	1.339336	-1.728655
1	0	-6.495652	1.215297	-0.568896

For the **TS-89**

Atomic number		X	Y	Z
77	0	-1.540474	-0.126877	0.004624
17	0	-0.283634	0.537729	1.974671
8	0	4.711055	0.674875	0.554013
7	0	4.420478	-1.407918	-0.425107
6	0	-3.760194	-0.524444	-0.044759
6	0	-3.097180	-1.169033	-1.168490
6	0	-2.196134	-2.172204	-0.633388
6	0	-2.215263	-2.068295	0.793921
6	0	-3.210791	-1.052189	1.160616
6	0	-4.853116	0.501622	-0.153244
6	0	-3.466300	-1.006483	-2.617091
6	0	-1.401985	-3.154039	-1.446302

6	0	-1.460092	-2.909445	1.781692
6	0	-3.591613	-0.707727	2.570450
6	0	5.208136	-0.527749	0.220664
6	0	6.548464	-0.811698	0.569624
6	0	7.075088	-2.050355	0.231113
6	0	6.265227	-2.979343	-0.444156
6	0	4.957597	-2.603638	-0.742042
1	0	-4.879620	1.152203	0.724480
1	0	-5.832766	0.011965	-0.239247
1	0	-4.724338	1.136888	-1.034526
1	0	-3.823706	0.005399	-2.831153
1	0	-4.267726	-1.703816	-2.898537
1	0	-2.614753	-1.204836	-3.275553
1	0	-1.082176	-2.728146	-2.402371
1	0	-2.009168	-4.041918	-1.670727
1	0	-0.507913	-3.487805	-0.913629
1	0	-0.645122	-3.458176	1.302161
1	0	-2.125950	-3.641719	2.258435
1	0	-1.019403	-2.283013	2.562700
1	0	-2.700582	-0.489192	3.167166
1	0	-4.129526	-1.541120	3.042170
1	0	-4.238158	0.173140	2.608043
1	0	7.126474	-0.058416	1.090276
1	0	8.101267	-2.295800	0.486847
1	0	4.295088	-3.291298	-1.263196
1	0	6.638267	-3.957079	-0.726169
7	0	2.159970	1.131788	-0.291129
6	0	1.482170	0.158042	-0.808671
1	0	2.003769	-0.797385	-0.865092
6	0	0.129861	0.260159	-1.335831
6	0	-0.530335	1.568529	-1.268824
1	0	-1.568183	1.521134	-0.284666
1	0	-1.178927	1.837071	-2.101993
6	0	1.586210	2.413832	-0.245013
6	0	2.373772	3.469382	0.251036
6	0	0.280271	2.685250	-0.721022
6	0	1.877090	4.770046	0.273954

1	0	3.370204	3.240784	0.612538
6	0	-0.201348	4.003429	-0.703065
6	0	0.586371	5.042653	-0.208776
1	0	2.491114	5.575471	0.663531
1	0	-1.203718	4.208749	-1.070979
1	0	0.201253	6.056931	-0.193882
1	0	3.758767	0.769281	0.240505
1	0	-0.063231	-0.365105	-2.205419

For the intermediate **5**

Atomic number		X	Y	Z
77	0	-0.335829	0.305445	0.370629
17	0	-0.664328	0.340344	2.790596
8	0	2.587502	0.173471	-0.797027
7	0	1.417556	1.480866	0.723358
6	0	-0.889616	0.683835	-1.717053
6	0	-1.412726	-0.593721	-1.283859
6	0	-2.326047	-0.340775	-0.196978
6	0	-2.494836	1.117339	-0.086545
6	0	-1.629194	1.734606	-1.004929
6	0	-0.005955	0.928933	-2.910460
6	0	-1.115546	-1.932183	-1.900333
6	0	-3.171503	-1.348164	0.530923
6	0	-3.402547	1.769829	0.913239
6	0	-1.431978	3.206219	-1.235178
6	0	2.561334	1.225537	0.039269
6	0	3.710515	2.022650	0.173846
6	0	3.677744	3.103135	1.044922
6	0	2.504921	3.360194	1.772283
6	0	1.408127	2.528544	1.590821
1	0	0.620050	1.815379	-2.768875
1	0	-0.609104	1.090150	-3.815375
1	0	0.662026	0.084813	-3.101733
1	0	-0.118073	-1.959588	-2.348450
1	0	-1.843981	-2.155110	-2.692163
1	0	-1.169073	-2.733559	-1.159036

1	0	-2.741108	-2.350991	0.462261
1	0	-4.187707	-1.387143	0.113429
1	0	-3.245209	-1.096643	1.592750
1	0	-3.116215	1.478581	1.931292
1	0	-4.443140	1.460105	0.752466
1	0	-3.363951	2.860823	0.849760
1	0	-1.902387	3.805265	-0.450940
1	0	-1.866536	3.513881	-2.196215
1	0	-0.368605	3.468830	-1.261446
1	0	4.590202	1.763883	-0.400462
1	0	4.552944	3.732071	1.166532
1	0	0.493451	2.648602	2.154894
1	0	2.444647	4.182473	2.474116
1	0	0.575537	-0.958923	0.669019
1	0	1.718221	-0.286022	-0.665950

Fo complex of 1-H and substrate

Atomic number		X	Y	Z
77	0	-1.450714	-0.154687	-0.180926
17	0	-1.912087	0.716154	-2.394110
8	0	0.354145	1.125447	-0.206965
7	0	-1.611993	1.848311	0.445200
6	0	-1.093781	-1.591323	1.416007
6	0	-2.505993	-1.314595	1.313063
6	0	-2.952191	-1.678109	-0.018318
6	0	-1.810089	-2.255755	-0.719128
6	0	-0.674662	-2.177972	0.146822
6	0	-0.233009	-1.442259	2.636477
6	0	-3.367895	-0.757910	2.408238
6	0	-4.354312	-1.629156	-0.551417
6	0	-1.858140	-2.809783	-2.112531
6	0	0.726531	-2.613032	-0.167969
6	0	-0.316214	2.182899	0.178652
6	0	0.131624	3.512802	0.326173
6	0	-0.789689	4.462754	0.747534
6	0	-2.130183	4.102293	1.002447

6	0	-2.510742	2.777674	0.826916
1	0	0.812557	-1.273527	2.365359
1	0	-0.276125	-2.348829	3.255996
1	0	-0.556226	-0.599889	3.255120
1	0	-2.799344	-0.100671	3.071789
1	0	-3.778613	-1.574965	3.016544
1	0	-4.211273	-0.187907	2.008310
1	0	-4.965094	-0.901225	-0.009921
1	0	-4.841608	-2.609827	-0.461635
1	0	-4.354994	-1.340046	-1.605817
1	0	-2.268251	-2.071979	-2.809108
1	0	-2.488885	-3.707827	-2.142497
1	0	-0.863483	-3.085437	-2.470789
1	0	0.890603	-2.690151	-1.245319
1	0	0.929304	-3.596085	0.277884
1	0	1.462798	-1.908761	0.230357
1	0	1.161921	3.757542	0.102270
1	0	-0.477938	5.494708	0.872803
1	0	-3.528359	2.439903	0.985726
1	0	-2.856541	4.839457	1.320775
1	0	3.540522	-0.485759	3.513916
6	0	4.003276	-0.470769	2.530692
6	0	5.260398	-1.058727	2.336826
6	0	3.341683	0.149651	1.470383
6	0	5.839950	-1.009252	1.064321
1	0	5.781556	-1.536100	3.160222
6	0	3.922636	0.195399	0.180958
1	0	2.376429	0.623868	1.620054
6	0	5.197040	-0.400199	-0.020657
1	0	6.819570	-1.453894	0.902800
7	0	3.266286	0.860986	-0.850579
6	0	5.838239	-0.369712	-1.396871
6	0	3.707064	0.666805	-2.222511
1	0	2.263185	0.975914	-0.719551
6	0	5.234871	0.728084	-2.284312
1	0	5.702368	-1.343340	-1.891482
1	0	6.921904	-0.229568	-1.300563

1	0	3.260018	1.452296	-2.840733
1	0	3.367150	-0.300303	-2.636256
1	0	5.560794	1.714155	-1.932731
1	0	5.574823	0.617075	-3.319710

For complex of 1-H and 3,4-dihydroquinoline

Atomic number		X	Y	Z
77	0	-1.645193	-0.220065	-0.186357
17	0	-2.769273	0.544683	-2.192955
8	0	-0.207840	1.431464	-0.529732
7	0	-2.090821	1.690597	0.569391
6	0	-0.594562	-1.568755	1.165908
6	0	-2.000144	-1.548793	1.482608
6	0	-2.744124	-1.988504	0.314013
6	0	-1.770346	-2.357527	-0.705031
6	0	-0.464147	-2.077359	-0.198325
6	0	0.543257	-1.247833	2.091664
6	0	-2.599856	-1.144789	2.797352
6	0	-4.226325	-2.205199	0.213607
6	0	-2.115699	-2.913322	-2.054938
6	0	0.835937	-2.299364	-0.913521
6	0	-0.983624	2.303380	0.053366
6	0	-0.813464	3.700577	0.183296
6	0	-1.799428	4.417442	0.847443
6	0	-2.942798	3.766663	1.359195
6	0	-3.060554	2.392998	1.186839
1	0	1.396015	-0.824908	1.551340
1	0	0.888764	-2.156705	2.604798
1	0	0.241317	-0.528445	2.858792
1	0	-1.980469	-0.404128	3.309969
1	0	-2.695831	-2.018355	3.456127
1	0	-3.598130	-0.717258	2.666570
1	0	-4.773449	-1.576282	0.922182
1	0	-4.484403	-3.252052	0.426140
1	0	-4.586487	-1.961107	-0.789432
1	0	-2.858236	-2.285011	-2.555936

1	0	-2.524152	-3.927669	-1.954878
1	0	-1.237727	-2.965508	-2.703025
1	0	0.719402	-2.199953	-1.996048
1	0	1.208486	-3.312614	-0.706749
1	0	1.603829	-1.591586	-0.588542
1	0	0.061736	4.174458	-0.242032
1	0	-1.696332	5.491666	0.964774
1	0	-3.923299	1.837130	1.536036
1	0	-3.721373	4.320902	1.868192
1	0	8.604848	-1.042583	0.743935
6	0	7.551502	-0.817109	0.610522
6	0	6.587107	-1.473312	1.384841
6	0	7.155381	0.132750	-0.340134
6	0	5.232682	-1.179825	1.204299
1	0	6.888952	-2.210855	2.121674
6	0	5.803997	0.442766	-0.523604
1	0	7.903906	0.641446	-0.942031
6	0	4.832767	-0.223337	0.259939
1	0	4.466369	-1.678780	1.787903
6	0	5.316840	1.433596	-1.557158
7	0	3.438237	0.026846	0.115667
6	0	4.030433	2.114685	-1.072470
1	0	5.108391	0.901903	-2.498043
1	0	6.091525	2.173676	-1.782647
6	0	3.072098	1.095323	-0.496959
1	0	3.542321	2.671914	-1.877908
1	0	4.262046	2.845513	-0.281404
1	0	1.998699	1.275834	-0.584095

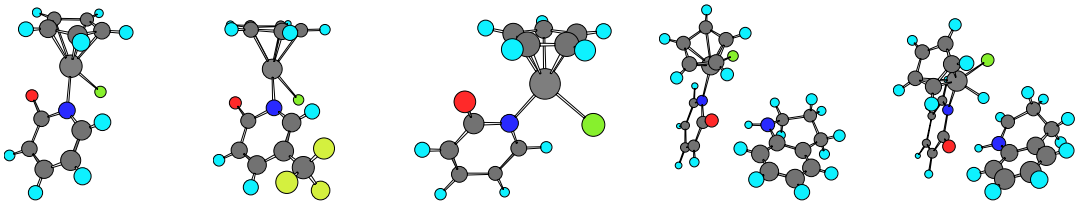
For **oxid-1**

Atomic number		X	Y	Z
77	0	0.773912	-0.161349	-0.269765
17	0	1.698854	-0.060502	-2.526396
8	0	0.592621	1.927758	-0.495498
7	0	-1.062225	2.743031	0.914971
6	0	1.094182	-0.053864	2.030911

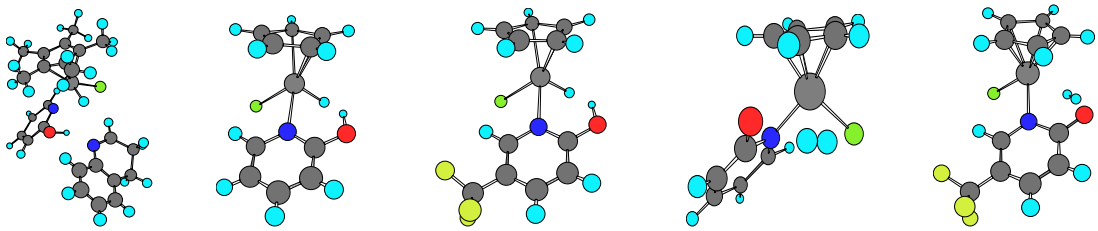
6	0	1.206907	-1.389080	1.518584
6	0	2.353869	-1.402353	0.607443
6	0	2.988832	-0.101638	0.665757
6	0	2.235567	0.712541	1.539408
6	0	-0.537110	2.618889	-0.328223
6	0	-1.110731	3.269004	-1.448433
6	0	-2.230578	4.072571	-1.271089
6	0	-2.768930	4.212376	0.016666
6	0	-2.148009	3.525212	1.060712
1	0	-0.650394	3.124065	-2.417819
1	0	-2.681698	4.581260	-2.117696
1	0	-2.540191	3.604607	2.072705
1	0	-3.640942	4.828670	0.203761
7	0	-1.223965	-0.204126	-0.809936
6	0	-1.501463	-0.442335	-2.237165
1	0	-2.509108	-0.039634	-2.422881
1	0	-0.799789	0.135845	-2.834280
6	0	-1.470773	-1.923618	-2.624436
1	0	-1.645980	-2.038642	-3.700204
1	0	-0.466003	-2.316078	-2.431512
6	0	-2.527841	-2.695243	-1.822878
1	0	-2.276810	-3.762725	-1.771384
1	0	-3.491588	-2.643717	-2.349827
6	0	-2.108292	-0.947932	0.015211
6	0	-2.441691	-0.430106	1.286482
6	0	-2.737749	-2.145001	-0.422758
6	0	-3.325382	-1.097745	2.132204
1	0	-2.017137	0.527213	1.559746
6	0	-3.625836	-2.800907	0.446984
6	0	-3.915733	-2.302007	1.718046
1	0	-3.577123	-0.670445	3.098729
1	0	-4.101756	-3.718574	0.108591
1	0	-4.608494	-2.828237	2.367321
1	0	0.543039	-1.622958	-0.760671
6	0	0.419915	-2.583983	1.968781
1	0	0.420980	-3.373921	1.213391
1	0	0.857818	-2.995342	2.888532

1	0	-0.620759	-2.323403	2.174307
6	0	2.960655	-2.601717	-0.062704
1	0	3.826024	-2.958920	0.511852
1	0	2.246046	-3.424930	-0.142597
1	0	3.298247	-2.351212	-1.072073
6	0	4.223747	0.278157	-0.095111
1	0	5.062634	-0.375888	0.174429
1	0	4.050781	0.185026	-1.173628
1	0	4.516157	1.311017	0.106950
6	0	2.468272	2.155379	1.816706
1	0	3.531534	2.409926	1.790728
1	0	1.948354	2.729080	1.034120
1	0	2.053556	2.453940	2.782844
6	0	0.190850	0.429766	3.125707
1	0	0.773572	0.568518	4.047351
1	0	-0.259619	1.388639	2.850621
1	0	-0.606794	-0.283398	3.337103

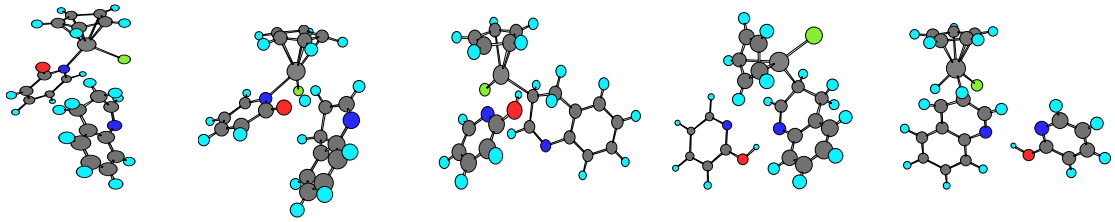
Geometric structures (for clarity, the Cp* substituted by Cp in all of complexes)



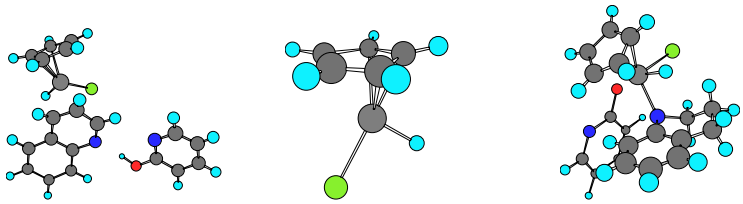
1-H **1-CF_3** **2** **3** **TS-34**



4 **5** **5-CF_3** **TS-52** **TS-52-CF_3**



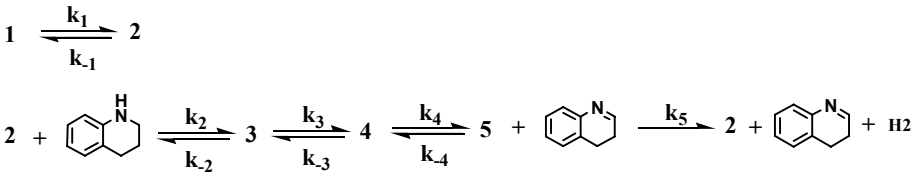
6 **TS-67** **7** **8** **TS-89**



9 **10** **oxid-1**

Deduction of rate constant for the first stage of reaction

Suppose:



S1 =  S2 =  c stands for concentration

$$\frac{dc_1}{dt} = k_{-1}c_2 - k_1c_1 = 0 \qquad (1)$$

$$\frac{dc_2}{dt} = k_1c_1 - k_{-1}c_2 - k_2c_2c_{s1} + k_{-2}c_3 = 0 \qquad (2)$$

$$\frac{dc_3}{dt} = k_2c_{s1} - k_{-2}c_3 - k_3c_3 + k_{-3}c_4 = 0 \qquad (3)$$

$$\frac{dc_4}{dt} = k_3 c_3 - k_{-3} c_4 - k_4 c_4 + k_{-4} c_5 c_{s2} = 0 \qquad (4)$$

therefore, $k_{\text{the first state}} = (k_1 k_2 k_3 k_4 k_5 / k_{-1} k_{-2} k_{-3} k_{-4}) c_1 c_{s1}$

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