Theoretical Study of the Regioselectivity of the Interaction of 3-Methyl-4-Pyrimidone and 1-Methyl-2-Pyrimidone with Lewis Acids

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SUPPORTING INFORMATION

Manuscript submitted to the Journal of Physical Chemistry A

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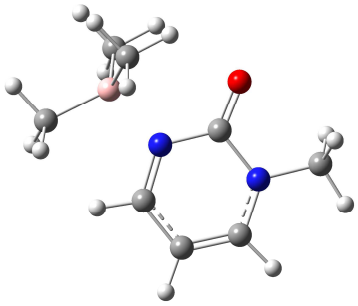
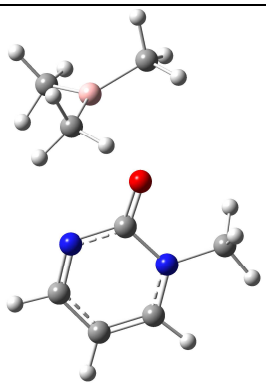
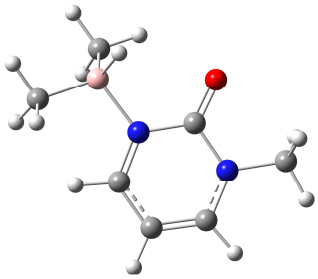
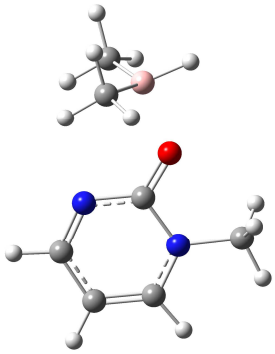
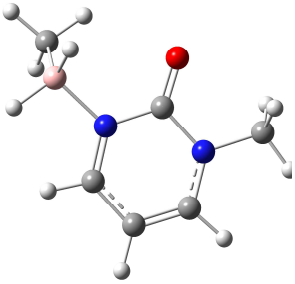
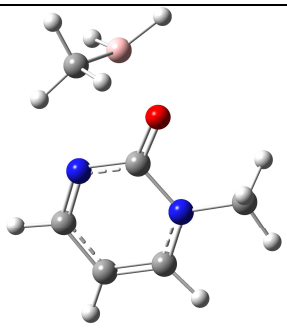
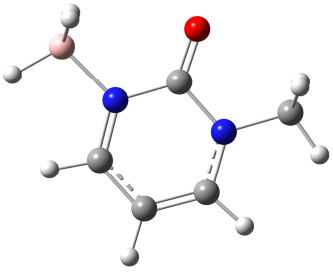
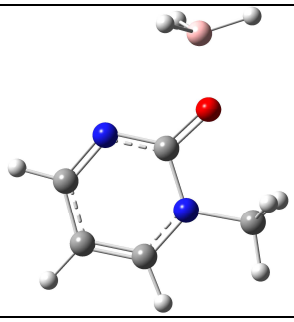
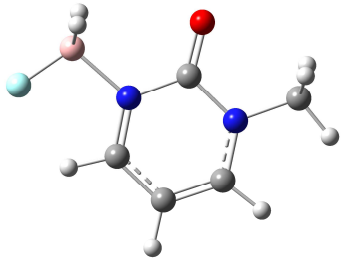
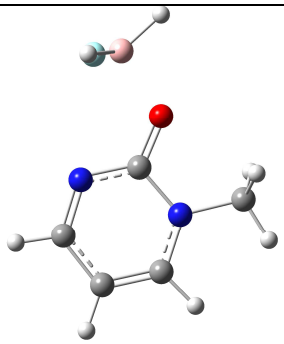
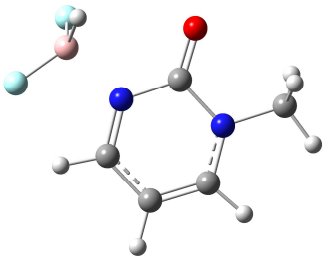
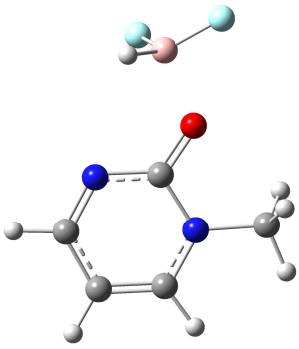
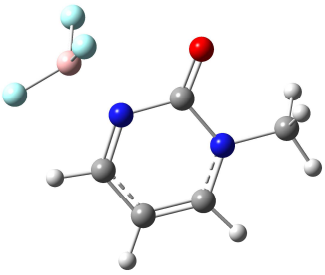
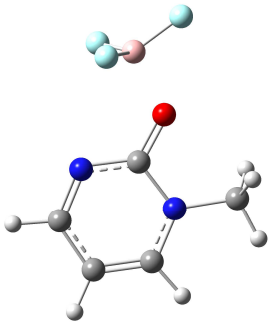
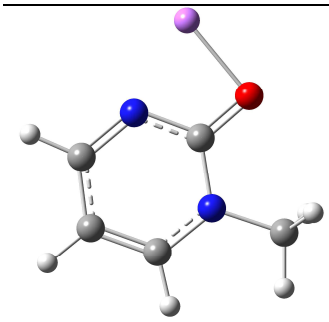
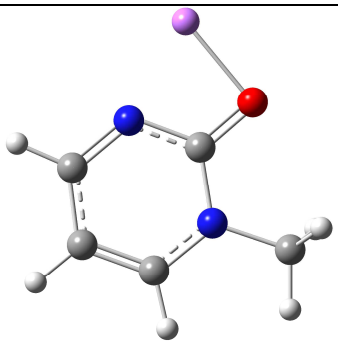
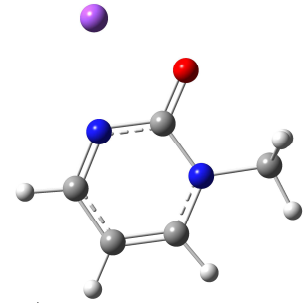
Version: April, 20, 2012

1. Structures of the pyrimidone complexes

The DFT geometry optimizations were performed using the B3LYP functional with a Pople type basis set 6-311++G(d,p).

1M2P-complexes	
 $B(CH_3)_3$	
 $BH(CH_3)_2$	
 $BH_2(CH_3)$	
 BH_3	

 BH_2F	
 BHF_2	
 BF_3	
 Li^+	



Na^+

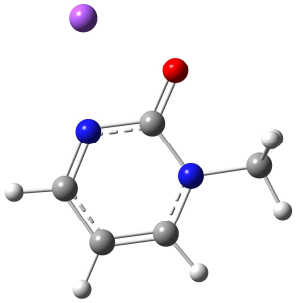
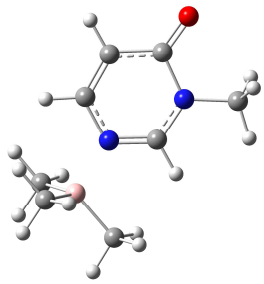
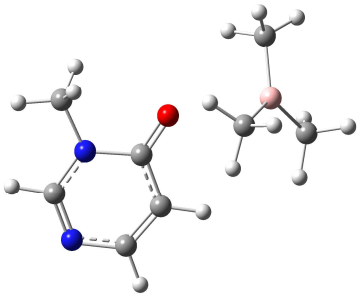
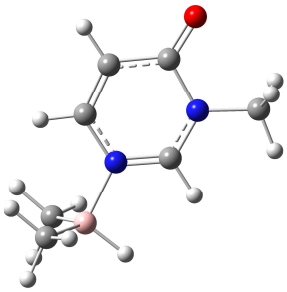
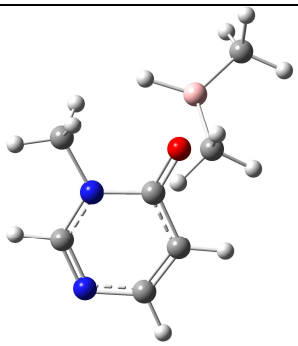
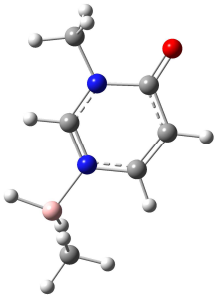
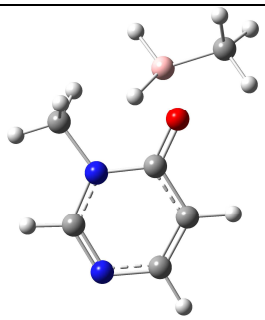
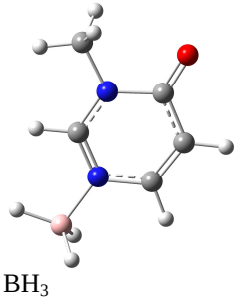
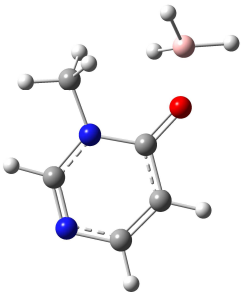
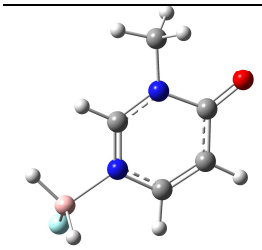
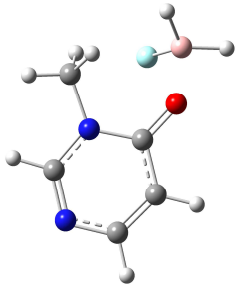
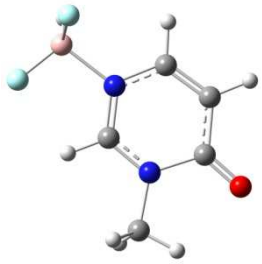
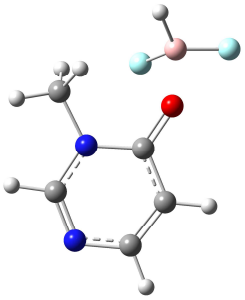
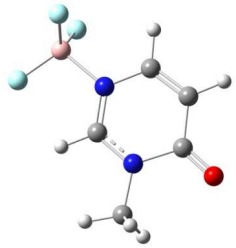
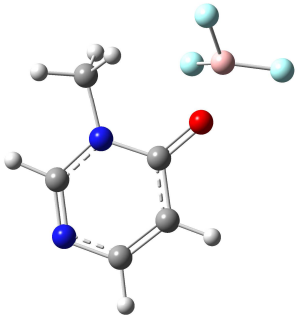
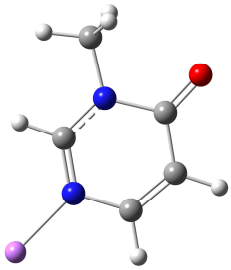
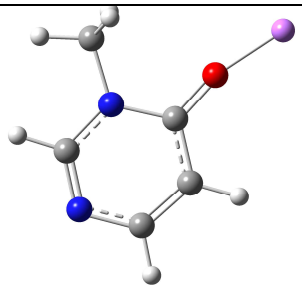
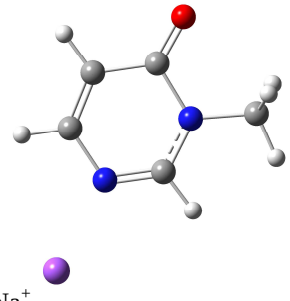
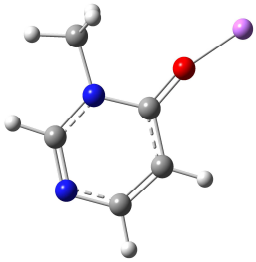
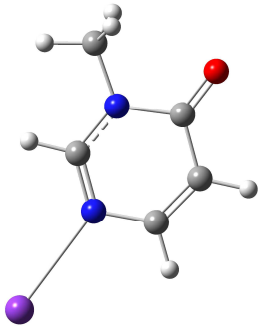


Figure.S1 Optimized geometries of 1 M2P-complexes

3M4P-complexes	
 $B(CH_3)_3$	
 $BH(CH_3)_2$	
 $BH_2(CH_3)$	
 BH_3	

 BH_2F	
 BHF_2	
 BF_3	
 Li^+	
 Na^+	



K^+

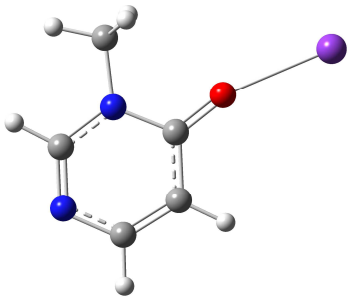


Figure S2. Optimized geometries of 3M4P complexes

2. Geometries of the 1M2P complexes

The upper Cartesian coordinates and that bellow separated by a horizontal line are related to complexes formed by the attack of Lewis acids on the N and O sites respectively. The total electronic energies (E) and the zero-point corrections in parenthesis are given in a.u.

a. 1M2P-B(CH_3)$_3$

E = -523.64018 (0.22607)

N	-1.673397	0.667556	-0.000016
C	-2.275579	-0.631700	-0.000002
C	-1.298008	-1.696255	-0.000013
C	0.027795	-1.425306	-0.000011
N	0.528051	-0.140146	-0.000008
C	-0.339149	0.839963	-0.000010
O	-3.486847	-0.736677	0.000020
B	2.217134	0.114052	0.000005
C	2.749082	-0.595187	-1.363777
C	-2.583153	1.819706	0.000000
H	0.775906	-2.205126	-0.000012
H	-1.668332	-2.711937	-0.000014
H	-1.995522	2.735887	-0.000272
H	-3.220233	1.780823	-0.883337
H	-3.219865	1.781121	0.883621
H	0.035074	1.854187	-0.000011
C	2.749058	-0.595195	1.363792
C	2.462818	1.719458	0.000008
H	3.834967	-0.460825	-1.438500
H	2.578170	-1.679111	-1.412564
H	2.317523	-0.158374	-2.274179
H	3.543990	1.897883	0.000014
H	2.078560	2.241099	-0.888932
H	2.078550	2.241099	0.888943
H	3.834941	-0.460839	1.438536
H	2.317485	-0.158384	2.274188
H	2.578138	-1.679118	1.412571

E = -523.63449 (0.22273)

C	0.696584	0.061405	-0.029856
N	0.862807	-1.304441	-0.037670
C	2.066253	-1.813615	-0.009427
C	3.259379	-1.053505	0.025464
C	3.109565	0.304342	0.022808
N	1.876705	0.861087	-0.007121
C	1.685235	2.313481	-0.010946
O	-0.367985	0.627638	-0.041690
B	-2.907459	-0.141274	0.014697
H	2.125850	-2.900861	-0.016089
H	4.235954	-1.514070	0.049663
H	3.947220	0.991443	0.043406
H	1.133731	2.609622	-0.903553
H	1.100659	2.610686	0.859972

H	2.660164	2.799369	0.006726
C	-2.824385	-0.724483	1.481686
C	-3.383857	1.349317	-0.207510
C	-2.818545	-1.127263	-1.216796
H	-3.843885	-1.006697	1.789200
H	-2.210635	-1.624978	1.564403
H	-2.475981	0.007736	2.216786
H	-3.765169	-1.687624	-1.272098
H	-2.689410	-0.628781	-2.182401
H	-2.027663	-1.871901	-1.096749
H	-4.479956	1.338210	-0.316850
H	-3.157741	2.019009	0.627211
H	-2.989920	1.789498	-1.128599

b. 1M2P-HB(CH_3)$_2$

E = -484.30771 (0.19824)

C	2.014925	1.236792	0.216725
N	1.848476	-0.081651	-0.015281
C	0.566865	-0.680530	-0.188822
N	-0.527074	0.202807	-0.125617
C	-0.332117	1.489338	0.101002
C	0.932989	2.069077	0.285233
C	2.990337	-1.000156	-0.095662
O	0.486378	-1.867683	-0.378107
B	-2.060014	-0.426228	-0.335386
C	-2.389447	-1.315166	0.985050
C	-3.097611	0.796600	-0.568525
H	-1.228535	2.094871	0.135669
H	1.044167	3.126685	0.469155
H	3.034332	1.580985	0.340616
H	2.904793	-1.762750	0.678385
H	2.991969	-1.498214	-1.065033
H	3.908250	-0.429987	0.036739
H	-1.928816	-1.103405	-1.333121
H	-3.384877	-1.761555	0.874495
H	-1.690123	-2.140544	1.148642
H	-2.418944	-0.708180	1.902108
H	-4.072580	0.361819	-0.816192
H	-3.273259	1.430137	0.314936
H	-2.842782	1.458926	-1.408339

E = -484.29455 (0.19658)

C	-0.209915	0.131199	-0.000040
N	-0.187683	-1.230680	-0.000073
C	-1.320555	-1.890363	-0.000047
C	-2.596116	-1.283189	0.000022
C	-2.615915	0.083047	0.000023
N	-1.460675	0.787347	-0.000011
C	-1.452049	2.256187	0.000002
O	0.789335	0.861164	-0.000076
B	2.578986	0.454482	0.000044
H	-1.240236	-2.975483	-0.000045
H	-3.509425	-1.859637	0.000064
H	-3.530231	0.663387	0.000059
H	-0.925365	2.618762	0.882402
H	-0.925327	2.618775	-0.882369
H	-2.481184	2.611883	-0.000018

C	2.811421	-0.330564	-1.374763
H	2.951736	1.602890	0.000096
C	2.811222	-0.330592	1.374871
H	3.892392	-0.472870	-1.511917
H	2.355157	-1.326872	-1.393439
H	2.463011	0.223127	-2.255149
H	3.892175	-0.472845	1.512215
H	2.462632	0.223068	2.255206
H	2.355005	-1.326923	1.393455

c. 1M2P-$H_2B(CH_3)$

E = -444.97438 (0.17004)

N	1.474803	-0.303067	0.049754
C	0.110419	-0.636640	-0.192401
N	-0.771660	0.455195	-0.271380
C	-0.326931	1.689397	-0.117139
C	1.017338	2.009237	0.126387
C	1.900267	0.967656	0.203478
O	-0.210418	-1.791350	-0.317105
B	-2.367981	0.178125	-0.561389
H	-2.793135	1.298993	-0.764000
C	2.398873	-1.440876	0.125191
C	-3.035528	-0.539062	0.727539
H	-1.087357	2.456931	-0.197970
H	1.338771	3.032449	0.245795
H	2.958955	1.103887	0.386914
H	2.096306	-2.106894	0.933169
H	2.366005	-2.001842	-0.808671
H	3.404614	-1.064441	0.303585
H	-2.384304	-0.500561	-1.563717
H	-4.109534	-0.662008	0.543949
H	-2.632457	-1.536343	0.931253
H	-2.943246	0.056832	1.646525

E = -444.95807 (0.16905)

C	-0.084830	0.063146	-0.171636
N	0.010366	-1.288331	-0.243713
C	1.186357	-1.852647	-0.104749
C	2.386273	-1.143100	0.120389
C	2.281440	0.217721	0.190895
N	1.079372	0.822476	0.047871
C	0.936261	2.283734	0.115671
O	-1.138802	0.713221	-0.286321
B	-2.700965	0.110308	-0.633098
H	1.204372	-2.938431	-0.169830
H	3.338411	-1.640311	0.233178
H	3.128313	0.870845	0.359545
H	0.499027	2.650110	-0.812599
H	0.267978	2.548304	0.934726
H	1.919864	2.723737	0.271757
C	-3.262749	-0.511204	0.735341
H	-3.228334	1.136300	-0.988858
H	-2.503746	-0.674879	-1.528090
H	-4.296948	-0.842754	0.573753
H	-2.702830	-1.389457	1.079290
H	-3.295539	0.214303	1.558616

d. 1M2P-H_2BF

E = -504.97848 (0.13260)

C	0.393788	-0.774208	0.000028
N	-0.818385	-0.072133	-0.000044
C	-0.851767	1.248525	-0.000091
C	0.306083	2.040214	-0.000049
C	1.508419	1.387634	0.000057
N	1.560389	0.038209	0.000109
B	-2.214719	-0.936654	-0.000086
C	2.836729	-0.687110	0.000214
O	0.486224	-1.976266	0.000088
H	-1.848854	1.673557	-0.000157
H	0.249961	3.117930	-0.000086
H	2.459510	1.905572	0.000107
H	2.896987	-1.323077	0.883271
H	2.897234	-1.322920	-0.882942
H	3.650343	0.035920	0.000391
H	-2.191594	-1.589354	-1.016206
H	-2.191753	-1.589203	1.016133
F	-3.232396	0.059122	-0.000244

E = -504.96103 (0.13528)

C	0.132149	0.071711	-0.198165
N	0.037898	-1.276294	-0.269906
C	-1.136048	-1.842127	-0.116558
C	-2.332353	-1.131651	0.120674
C	-2.227266	0.229421	0.182108
N	-1.025162	0.832670	0.025388
C	-0.879963	2.294477	0.095321
O	1.190552	0.722655	-0.322025
B	2.748400	0.042978	-0.440014
H	-1.154286	-2.927540	-0.184398
H	-3.283342	-1.628177	0.246039
H	-3.071940	0.884217	0.354414
H	-0.192341	2.553198	0.899873
H	-0.465504	2.665497	-0.841483
H	-1.859584	2.733481	0.276416
H	2.672082	-0.710535	-1.375200
H	3.402163	1.043674	-0.580298
F	2.917563	-0.581728	0.799139

e. 1M2P-HBF_2

E = -604.32198 (0.13005)

C	0.528888	-0.703283	-0.157562
N	-0.556419	0.176703	-0.143873
C	-0.393100	1.477833	0.003778
C	0.863340	2.077657	0.160773
C	1.951753	1.245201	0.158486
N	1.806484	-0.084178	0.004803
B	-2.127776	-0.464810	-0.291819
C	2.957041	-0.996208	-0.001582
O	0.449951	-1.896628	-0.297160
H	-1.311826	2.053776	-0.005997

H	0.969379	3.144698	0.281294
H	2.965903	1.607725	0.276583
H	2.852640	-1.721640	0.805035
H	2.987910	-1.538612	-0.946368
H	3.867232	-0.413806	0.129553
H	-2.119747	-1.160150	-1.267774
F	-2.346566	-1.104684	0.919256
F	-2.916790	0.690263	-0.413238

E = -604.31198 (0.12932)

C	-0.219036	-0.024852	-0.133920
N	-0.509465	-1.341793	-0.251457
C	-1.763076	-1.725744	-0.181398
C	-2.849859	-0.846756	0.009916
C	-2.544902	0.481117	0.121007
N	-1.259054	0.897967	0.050184
C	-0.897353	2.318770	0.173891
O	0.930036	0.458712	-0.180467
B	2.404165	-0.420718	-0.280518
H	-1.940346	-2.793984	-0.282478
H	-3.870596	-1.195395	0.065654
H	-3.290196	1.252415	0.267668
H	-0.229815	2.450850	1.024759
H	-0.372376	2.640645	-0.724790
H	-1.808069	2.899263	0.310643
H	2.278036	-1.128497	-1.237525
F	3.291401	0.621804	-0.403715
F	2.463847	-1.044008	0.947529

f. 1M2P-BF_3

E = -703.66865 (0.12365)

C	-0.650707	-0.666155	-0.000071
N	0.338367	0.326259	-0.000037
C	0.030149	1.611396	0.000013
C	-1.287565	2.082398	0.000048
C	-2.283462	1.139886	0.000017
N	-1.993404	-0.172624	-0.000062
B	1.968490	-0.145826	-0.000012
C	-3.041815	-1.201134	-0.000049
O	-0.444669	-1.850004	0.000154
H	0.879737	2.283840	0.000030
H	-1.509065	3.138298	0.000109
H	-3.335104	1.400917	0.000040
H	-2.934859	-1.830829	-0.883042
H	-2.935136	-1.830567	0.883170
H	-4.013643	-0.710981	-0.000270
F	2.149461	-0.855622	1.159773
F	2.149413	-0.855900	-1.159632
F	2.650974	1.067599	-0.000172

E = -703.66041 (0.12317)

N	-1.529089	0.888912	0.000085
C	-0.419647	0.039393	0.000056
N	-0.595468	-1.297175	-0.000063
C	-1.818468	-1.777311	-0.000133

C	-2.978616	-0.975876	-0.000086
C	-2.783022	0.377110	0.000026
O	0.694279	0.615780	0.000169
B	2.188477	-0.112313	-0.000130
F	2.227496	-0.848506	1.156041
C	-1.285599	2.341056	0.000195
F	2.227012	-0.847770	-1.156030
F	3.014327	0.979841	-0.000183
H	-1.904629	-2.861180	-0.000233
H	-3.972370	-1.399095	-0.000140
H	-3.592176	1.096001	0.000064
H	-0.708786	2.612546	0.883523
H	-0.708545	2.612628	-0.882949
H	-2.245620	2.853951	0.000090

g. 1M2P-Li^+

E = -386.36900 (0.11217)

C	0.509133	-1.524092	-0.000014
N	-0.576571	-0.712334	0.000008
C	-0.412122	0.665479	0.000012
N	0.851916	1.195159	0.000036
C	1.901821	0.391354	0.000010
C	1.779618	-1.006642	-0.000020
C	-1.956231	-1.240225	0.000006
O	-1.386979	1.439574	-0.000008
Li	-0.242169	2.953754	-0.000064
H	2.879432	0.863379	0.000027
H	2.643942	-1.654040	-0.000040
H	0.308831	-2.588081	-0.000024
H	-2.479247	-0.883653	0.886504
H	-2.479251	-0.883641	-0.886484
H	-1.912097	-2.326832	-0.000001

E = -386.36900 (0.11217)

C	0.509858	-1.523819	-0.000094
N	-0.576141	-0.712665	-0.000060
C	-0.412402	0.665244	-0.000012
N	0.851252	1.195495	0.000012
C	1.901651	0.392239	0.000067
C	1.780167	-1.005778	0.000027
C	-1.955579	-1.241032	0.000081
O	-1.387733	1.438916	0.000034
Li	-0.243743	2.953570	-0.000195
H	2.878894	0.864978	0.000248
H	2.644604	-1.653021	0.000016
H	0.310193	-2.587936	-0.000334
H	-2.478494	-0.885100	0.886877
H	-2.478980	-0.884292	-0.886114
H	-1.911066	-2.327608	-0.000466

h. 1M2P-Na^+

E = -541.14541 (0.11112)

C	-0.306053	-0.357108	-0.000479
N	-0.709240	0.956730	0.000033
C	0.196955	1.918778	0.000217
C	1.579013	1.672801	0.000100
C	1.974066	0.360207	-0.000053
O	-1.135359	-1.276625	0.000977
C	1.463198	-2.059940	0.000061
H	-0.177895	2.938176	0.000332
H	2.302360	2.474516	0.000208
H	3.014300	0.059663	0.000032
H	1.060987	-2.550265	0.885753
H	1.060904	-2.550575	-0.885415
H	2.549571	-2.115132	0.000026
Na	-2.967644	0.048557	-0.000600
N	1.062620	-0.640436	-0.000208

E = -541.14541 (0.11112)

N	-1.062738	-0.640257	0.000004
C	0.306078	-0.357309	0.000009
N	0.709359	0.956503	-0.000001
C	-0.196522	1.918647	-0.000003
C	-1.578673	1.672981	-0.000001
C	-1.973963	0.360534	0.000001
O	1.135098	-1.276872	-0.000012
C	-1.463477	-2.059691	0.000001
H	0.178555	2.937954	-0.000006
H	-2.301849	2.474818	-0.000004
H	-3.014253	0.060234	0.000000
H	-1.061194	-2.550223	-0.885530
H	-1.061206	-2.550223	0.885538
H	-2.549834	-2.114831	-0.000006
Na	2.967454	0.048415	0.000004

i. 1M2P-K^+

E = -978.79949 (0.11062)

N	1.465590	-0.648617	0.000093
C	0.095419	-0.343199	0.000256
N	-0.281139	0.978240	-0.000021
C	0.645131	1.918519	-0.000077
C	2.024787	1.651820	-0.000017
C	2.396260	0.333374	0.000026
O	-0.735984	-1.257040	-0.000289
C	1.840976	-2.073154	0.000014
H	0.291035	2.945908	-0.000152
H	2.761243	2.441455	-0.000068
H	3.430748	0.013380	-0.000017
H	1.430381	-2.557970	0.884984
H	1.430173	-2.557937	-0.884879
H	2.926265	-2.148299	-0.000117
K	-2.983609	0.036224	0.000045

E = -978.79949 (0.11062)

N	1.465477	-0.648729	0.000019
C	0.095318	-0.343098	0.001013
N	-0.280983	0.978442	0.001716
C	0.645435	1.918521	0.000680
C	2.025070	1.651604	-0.000843
C	2.396307	0.333106	-0.001002
O	-0.736177	-1.256786	0.001078
C	1.840588	-2.073319	-0.000231
H	0.291558	2.945990	0.001309
H	2.761632	2.441136	-0.001691
H	3.430737	0.012923	-0.001890
H	1.430312	-2.558065	0.884932
H	1.429266	-2.558049	-0.884915
H	2.925859	-2.148687	-0.000851
K	-2.983564	0.036325	-0.000809

Geometries of the 3M4P complexes

j. 3M4P-B(CH_3)$_3$

E = -532.65223 (0.22609)

N	-1.673397	0.667556	-0.000016
C	-2.275579	-0.631700	-0.000002
C	-1.298008	-1.696255	-0.000013
C	0.027795	-1.425306	-0.000011
N	0.528051	-0.140146	-0.000008
C	-0.339149	0.839963	-0.000010
O	-3.486847	-0.736677	0.000020
B	2.217134	0.114052	0.000005
C	2.749082	-0.595187	-1.363777
C	-2.583153	1.819706	0.000000
H	0.775906	-2.205126	-0.000012
H	-1.668332	-2.711937	-0.000014
H	-1.995522	2.735887	-0.000272
H	-3.220233	1.780823	-0.883337
H	-3.219865	1.781121	0.883621
H	0.035074	1.854187	-0.000011
C	2.749058	-0.595195	1.363792
C	2.462818	1.719458	0.000008
H	3.834967	-0.460825	-1.438500
H	2.578170	-1.679111	-1.412564
H	2.317523	-0.158374	-2.274179
H	3.543990	1.897883	0.000014
H	2.078560	2.241099	-0.888932
H	2.078550	2.241099	0.888943
H	3.834941	-0.460839	1.438536
H	2.317485	-0.158384	2.274188
H	2.578138	-1.679118	1.412571

E = -523.64126 (0.22237)

N	-1.949047	0.850214	-0.031600
C	-0.834122	0.010221	-0.304989
C	-1.170551	-1.392448	-0.273383
C	-2.442806	-1.790722	-0.000841
N	-3.476908	-0.928776	0.256539
C	-3.180607	0.334788	0.228166
O	0.260613	0.506322	-0.533227
B	3.210824	-0.132554	0.157939
C	3.187004	-1.555873	-0.522071
C	-1.713679	2.295988	-0.040137
H	-2.700704	-2.844527	0.024641
H	-0.376091	-2.098791	-0.473307
H	-2.650039	2.807509	0.177965
H	-0.964059	2.552893	0.708606
H	-1.338494	2.603007	-1.016588
H	-3.961091	1.064540	0.424710
C	2.910459	0.025382	1.697615
C	3.645904	1.122750	-0.686523
H	4.224502	-1.923425	-0.560195
H	2.603348	-2.310774	0.013245
H	2.849887	-1.515733	-1.563153
H	4.248667	0.891207	-1.570422
H	2.708038	1.566852	-1.052175

H	4.148726	1.900596	-0.102148
H	3.853472	-0.173666	2.232178
H	2.604033	1.035716	1.985405
H	2.182856	-0.693795	2.085767

k. 3M4P-HB(CH_3)$_2$

E = -484.31819 (0.19823)

C	-1.962937	-0.705338	-0.000026
C	-0.870705	-1.652729	0.000007
C	0.416231	-1.233537	0.000000
N	0.761759	0.100493	-0.000019
C	-0.208715	0.978271	-0.000034
N	-1.513534	0.655964	-0.000042
B	2.362511	0.589099	-0.000013
C	-2.548546	1.696993	-0.000019
O	-3.154131	-0.947318	0.000065
H	1.251556	-1.920469	0.000019
H	-1.124925	-2.703484	0.000045
H	-2.068472	2.673816	-0.000365
H	-3.176820	1.585792	-0.883457
H	-3.176401	1.586219	0.883776
H	0.064489	2.025796	-0.000044
C	3.030657	0.032165	1.366045
C	3.030703	0.032052	-1.365995
H	2.246733	1.802992	-0.000068
H	4.063594	0.393096	-1.436651
H	3.090880	-1.064916	-1.417249
H	2.518924	0.371578	-2.275619
H	4.063547	0.393210	1.436711
H	2.518846	0.371765	2.275622
H	3.090830	-1.064800	1.417390

E = -484.29905 (0.19471)

N	-1.221991	0.877218	0.009478
C	-0.478605	-0.236468	-0.461340
C	-1.252270	-1.451380	-0.504605
C	-2.557394	-1.451256	-0.117376
N	-3.221896	-0.340138	0.328921
C	-2.528098	0.756856	0.368796
O	0.696440	-0.098369	-0.782535
B	2.975371	0.231370	0.414415
C	3.818496	0.076853	-0.897810
C	-0.527011	2.166611	0.081860
H	-3.145167	-2.363012	-0.146630
H	-0.753988	-2.346148	-0.852660
H	-1.207571	2.910464	0.493472
H	0.356697	2.073534	0.712005
H	-0.203094	2.467490	-0.915020
H	-3.003879	1.670234	0.714211
C	2.771061	-0.933164	1.447623
H	2.662571	1.342956	0.750309
H	4.833475	0.449221	-0.685757
H	3.916922	-0.952440	-1.254575
H	3.436970	0.699114	-1.712450
H	3.635715	-0.898625	2.131261
H	1.887047	-0.818900	2.081749

H	2.766058	-1.931663	1.000600

l. 3M4P-$H_2B(CH_3)$

E = -444.98355 (0.17009)

C	1.609476	-0.732495	0.057772
C	0.498571	-1.638476	-0.138035
C	-0.755475	-1.172241	-0.334918
N	-1.048756	0.175753	-0.360782
C	-0.061514	1.017043	-0.186247
N	1.214795	0.643534	0.015689
B	-2.577335	0.678350	-0.601066
C	2.272366	1.644051	0.204178
O	2.775417	-1.021554	0.243302
H	-1.608915	-1.819905	-0.484624
H	0.712751	-2.697898	-0.120336
H	1.833305	2.638455	0.149680
H	2.746348	1.494462	1.173978
H	3.029502	1.523916	-0.570347
H	-0.291857	2.074034	-0.206623
H	-2.900315	0.234249	-1.678954
C	-3.585499	-0.063159	0.817090
H	-2.530350	1.886428	-0.575048
H	-4.627724	0.236243	0.716857
H	-3.515000	-1.149352	0.783405
H	-3.194236	0.296698	1.767530

E = -444.96051 (0.16909)

C	-0.031805	-0.345267	-0.266494
C	-0.830188	-1.529969	-0.227390
C	-2.158935	-1.448458	0.069593
N	-2.800026	-0.271164	0.322130
C	-2.072341	0.801162	0.248503
N	-0.738844	0.838458	-0.038978
C	-0.058935	2.138153	-0.198844
O	1.191476	-0.353595	-0.509883
H	-2.774351	-2.340031	0.124498
H	-0.331935	-2.470954	-0.415386
H	-0.804111	2.925795	-0.101692
H	0.720197	2.247638	0.550350
H	0.401291	2.179081	-1.185184
H	-2.534281	1.767596	0.421675
B	2.547482	0.414378	0.283888
H	2.064913	0.685314	1.362695
C	3.666586	-0.718643	0.282856
H	2.767997	1.379182	-0.406896
H	4.571051	-0.323990	0.765274
H	3.377690	-1.617345	0.840140
H	3.958118	-1.028330	-0.727260

m. 3M4P-H_2BF

E = -504.98345 (0.13617)

C	-0.770425	-1.233575	0.197618
N	-1.099788	0.104219	0.241684
C	-0.137564	0.983845	0.131836

N	1.156919	0.657476	0.005595
C	1.598179	-0.710198	-0.034389
C	0.507836	-1.655782	0.067638
C	2.192180	1.692207	-0.112704
O	2.781914	-0.954360	-0.147361
B	-2.674914	0.560502	0.430836
H	-1.612722	-1.908447	0.272012
H	0.758426	-2.706831	0.036187
H	2.906630	1.586416	0.703220
H	2.724960	1.566835	-1.054908
H	-0.409028	2.032001	0.147927
H	-3.016917	0.067292	1.481621
H	-2.639948	1.772079	0.421233
H	1.719730	2.671994	-0.074841
F	-3.339226	-0.004424	-0.682077

E = -504.96460 (0.13579)

C	1.586983	1.155885	0.172387
N	0.331361	0.775528	-0.204449
C	0.024453	-0.574538	-0.354824
C	1.121356	-1.463992	-0.156213
C	2.340140	-0.972215	0.211427
N	2.585794	0.355914	0.390746
C	-0.681912	1.807987	-0.500716
O	-1.120004	-0.976869	-0.673764
B	-2.657976	-0.575466	-0.076759
H	3.180368	-1.635158	0.387510
H	0.932554	-2.521139	-0.281391
H	-0.176899	2.770100	-0.563199
H	-1.154421	1.574192	-1.452661
H	-1.439612	1.815583	0.279529
H	1.730630	2.225368	0.283633
H	-3.116503	0.184252	-0.890362
H	-3.156895	-1.660486	0.017275
F	-2.368390	0.033412	1.161903

n. 3M4P-HBF$_2$

E = -604.33177 (0.13020)

C	0.528888	-0.703283	-0.157562
N	-0.556419	0.176703	-0.143873
C	-0.393100	1.477833	0.003778
C	0.863340	2.077657	0.160773
C	1.951753	1.245201	0.158486
N	1.806484	-0.084178	0.004803
B	-2.127776	-0.464810	-0.291819
C	2.957041	-0.996208	-0.001582
O	0.449951	-1.896628	-0.297160
H	-1.311826	2.053776	-0.005997
H	0.969379	3.144698	0.281294
H	2.965903	1.607725	0.276583
H	2.852640	-1.721640	0.805035
H	2.987910	-1.538612	-0.946368
H	3.867232	-0.413806	0.129553
H	-2.119747	-1.160150	-1.267774
F	-2.346566	-1.104684	0.919256
F	-2.916790	0.690263	-0.413238

E = -604.31399 (0.12950)

C	-0.219036	-0.024852	-0.133920
N	-0.509465	-1.341793	-0.251457
C	-1.763076	-1.725744	-0.181398
C	-2.849859	-0.846756	0.009916
C	-2.544902	0.481117	0.121007
N	-1.259054	0.897967	0.050184
C	-0.897353	2.318770	0.173891
O	0.930036	0.458712	-0.180467
B	2.404165	-0.420718	-0.280518
H	-1.940346	-2.793984	-0.282478
H	-3.870596	-1.195395	0.065654
H	-3.290196	1.252415	0.267668
H	-0.229815	2.450850	1.024759
H	-0.372376	2.640645	-0.724790
H	-1.808069	2.899263	0.310643
H	2.278036	-1.128497	-1.237525
F	3.291401	0.621804	-0.403715
F	2.463847	-1.044008	0.947529

o. 3M4P-BF_3

E = -703.67979 (0.12386)

C	-0.094103	-1.438465	-0.000237
N	-0.574915	-0.146732	-0.000281
C	0.281855	0.845402	-0.000338
N	1.607084	0.671321	-0.000260
C	2.207716	-0.638890	0.000128
C	1.230928	-1.706412	-0.000177
C	2.523018	1.820056	-0.000008
O	3.415745	-0.740698	0.000340
B	-2.212494	0.129071	0.000079
H	-0.853403	-2.208966	-0.000266
H	1.604322	-2.720687	-0.000141
H	3.158220	1.776149	0.884101
H	-0.117209	1.851734	-0.000428
F	-2.338082	1.510136	0.000499
F	-2.679752	-0.471179	-1.150808
F	-2.679360	-0.471768	1.150847
H	3.158465	1.776635	-0.883929
H	1.939206	2.738402	0.000279

E = -703.66320 (0.12364)

N	-1.529089	0.888912	0.000085
C	-0.419647	0.039393	0.000056
N	-0.595468	-1.297175	-0.000063
C	-1.818468	-1.777311	-0.000133
C	-2.978616	-0.975876	-0.000086
C	-2.783022	0.377110	0.000026
O	0.694279	0.615780	0.000169
B	2.188477	-0.112313	-0.000130
F	2.227496	-0.848506	1.156041
C	-1.285599	2.341056	0.000195
F	2.227012	-0.847770	-1.156030
F	3.014327	0.979841	-0.000183

H	-1.904629	-2.861180	-0.000233
H	-3.972370	-1.399095	-0.000140
H	-3.592176	1.096001	0.000064
H	-0.708786	2.612546	0.883523
H	-0.708545	2.612628	-0.882949
H	-2.245620	2.853951	0.000090

p. 3M4P-Li^+

E = -386.33420 (0.11148)

N	1.751857	-0.414686	-0.000528
C	0.642127	-1.132142	-0.000448
N	-0.593869	-0.631864	-0.000227
C	-0.844508	0.796723	0.000283
C	0.378851	1.574107	-0.000219
C	1.584445	0.965475	-0.000543
C	-1.782060	-1.502859	-0.000061
O	-1.979423	1.201447	0.000685
Li	3.528991	-1.119835	0.002581
H	2.495859	1.554434	-0.000947
H	0.283640	2.651403	-0.000234
H	-1.463724	-2.543663	-0.001898
H	-2.381020	-1.291685	0.885033
H	-2.382939	-1.289180	-0.883231
H	0.717544	-2.215359	-0.000733

E = -386.35551 (0.11192)

C	-1.787370	-1.067163	-0.000019
N	-2.146412	0.241132	-0.000014
C	-1.182504	1.109976	-0.000043
N	0.149224	0.798576	-0.000029
C	0.558778	-0.524975	0.000033
C	-0.481730	-1.486889	0.000020
C	1.164238	1.866288	0.000030
O	1.796119	-0.783486	0.000078
H	-2.602713	-1.782434	0.000055
H	-0.219610	-2.536179	0.000081
H	0.655482	2.827502	-0.000529
H	1.786667	1.783314	0.890293
H	1.787388	1.782674	-0.889658
H	-1.416444	2.169210	-0.000051
Li	3.330706	-1.545858	-0.000213

q. 3M4P-Na^+

E = -541.11449 (0.11057)

N	1.312011	0.001373	-0.004069
C	0.372659	0.923443	-0.003658
N	-0.944977	0.685343	-0.000518
C	-1.478662	-0.657060	0.000915
C	-0.438458	-1.665772	-0.000265
C	0.866505	-1.311719	-0.002590
C	-1.928519	1.780416	0.000657
O	-2.673978	-0.826537	0.003079
Na	3.585121	0.369739	0.003856

H	1.637672	-2.075407	-0.003774
H	-0.750296	-2.701374	0.000640
H	-1.403136	2.733741	-0.000856
H	-2.561881	1.697014	-0.881860
H	-2.558569	1.698013	0.885639
H	0.661327	1.970335	-0.005089

E = -541.13170 (0.11087)

C	-1.818744	-1.533579	-0.000074
N	-2.591942	-0.415428	-0.000137
C	-1.966019	0.720718	-0.000068
N	-0.607001	0.866118	0.000102
C	0.227588	-0.249430	0.000238
C	-0.450387	-1.501212	0.000073
C	-0.000555	2.206056	-0.000056
O	1.471871	-0.085477	0.000310
H	-2.353884	-2.477058	-0.000204
H	0.139883	-2.407659	0.000079
H	-0.795860	2.948228	-0.000489
H	0.616545	2.332468	0.889013
H	0.617136	2.332014	-0.888762
H	-2.535930	1.644029	-0.000188
Na	3.543495	-0.427124	-0.000216

r. 3M4P-K^+

E = -978.77245 (0.11011)

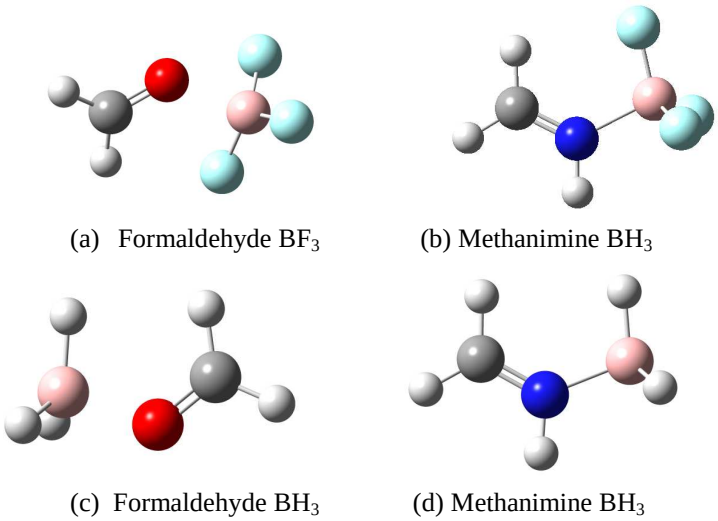
N	0.836013	-0.057025	-0.009269
C	-0.072817	0.890633	-0.006808
N	-1.401354	0.696211	-0.001365
C	-1.976468	-0.625084	0.002682
C	-0.969422	-1.666355	-0.000715
C	0.346874	-1.351257	-0.007057
C	-2.347419	1.822400	0.000772
O	-3.178179	-0.758234	0.008085
K	3.538251	0.199584	0.004771
H	1.092611	-2.140659	-0.010354
H	-1.314192	-2.691475	0.001318
H	-1.790346	2.757664	-0.001571
H	-2.985010	1.761222	-0.880656
H	-2.979591	1.762320	0.886152
H	0.248094	1.928380	-0.009020

E = -978.78928 (0.11046)

C	-2.206814	-1.590639	0.000000
N	-3.031186	-0.507787	-0.000014
C	-2.456217	0.654552	-0.000010
N	-1.105209	0.861556	0.000002
C	-0.215637	-0.215738	0.000006
C	-0.842631	-1.497433	0.000013
C	-0.560411	2.226309	0.000007
O	1.016701	0.000013	0.000008
H	-2.699337	-2.557077	0.000000
H	-0.212636	-2.376721	0.000022
H	-1.387845	2.932621	0.000000
H	0.051458	2.380458	0.888492
H	0.051479	2.380459	-0.888464

H	-3.067239	1.551361	-0.000015
K	3.461871	-0.223679	-0.000006

3. Geometries of formaldehyde and methanimine complexes with BH_3 and BF_3



(a) Formaldehyde BF_3 (b) Methanimine BH_3

(c) Formaldehyde BH_3 (d) Methanimine BH_3

Figure S3. Structures of formaldehyde and methanimine complexes with BF_3 and BH_3.

Coordinates of formaldehyde and methanimine complexes

Formaldehyde BH_3

E = -141.18457 (0.05948)

C	1.174718	0.202326	0.000005
H	1.114977	1.296841	-0.000042
H	2.146735	-0.299565	0.000069
O	0.160457	-0.474590	-0.000006
B	-1.355192	0.163864	0.000009
H	-1.169527	1.356923	-0.000139
H	-1.824054	-0.295501	-1.007481
H	-1.824134	-0.295251	1.007564

Formaldehyde BF_3

E = -439.21646 (0.04152)

C	2.066546	0.024515	0.000045
H	1.987345	1.119446	-0.000525
H	3.058997	-0.443771	0.000282
O	1.073882	-0.675171	0.000411
B	-0.646789	0.062168	-0.000048
F	-1.099473	-0.453352	1.153323
F	-0.334543	1.383127	-0.001304
F	-1.099621	-0.455579	-1.152360

Methanimine BH_3

E = -121.33520 (0.07325)

C	-1.227469	0.226742	-0.000008
H	-2.175690	-0.302845	0.000001
H	-1.210717	1.311289	-0.000015
B	1.348607	0.190132	-0.000004
N	-0.115913	-0.394662	0.000008
H	-0.183238	-1.411068	0.000036
H	1.255016	1.394142	-0.000155
H	1.873936	-0.270117	-0.993600
H	1.873864	-0.269882	0.993738

Methanimine BF_3

E = -419.35980 (0.05590)

C	-2.081992	0.043008	-0.000070
H	-3.048057	-0.455118	0.000038
H	-2.027438	1.127399	-0.000169
B	0.531361	0.043068	-0.000073
F	0.330536	1.410089	0.000036
F	1.108395	-0.441994	1.154219
F	1.108512	-0.442018	-1.154177
N	-0.994570	-0.607947	0.000007
H	-1.054358	-1.624730	0.000166