Supplementary Information (SI)

Cartesian coordinates (xyz) and total energies (in a.u.) for all optimized geometries of the studied complexes in this paper.

1 – Ti-Alpha-Baird (Tables 4 and 5): we optimized this structure following the Ref. 63.

Complex

43
B3LYP/6-311++G(2d,2p) Charge = 1 Multiplicity = 1 E(RB3LYP) = -1512.33058978

C	0.657430	2.068169	0.860778
C	0.457399	2.218499	-0.528488
C	1.714316	2.095384	-1.173271
C	2.693729	1.885431	-0.180947
C	2.041456	1.844334	1.078617
Ti	1.245128	-0.002321	-0.127494
C	1.590265	-2.257465	-0.769156
C	2.750779	-1.540572	-1.159904
C	3.385885	-1.070382	0.007758
C	2.605996	-1.466339	1.122699
C	1.506422	-2.222870	0.641930
C	-0.784827	-0.500077	0.006265
C	-2.037106	0.184372	0.532017
C	-2.161888	-0.174784	2.025612
C	-3.340644	-0.130592	-0.303949
C	-4.515552	0.676202	0.281620
H	3.751101	1.785494	-0.351380
H	2.521051	1.718485	2.035272
H	1.891066	2.167091	-2.235090
H	-0.102910	2.121119	1.620178
H	-0.485538	2.392773	-1.017942
H	4.302275	-0.508617	0.047730
H	2.834246	-1.268908	2.157420
H	0.753790	-2.696807	1.246779
H	0.899220	-2.749311	-1.433883
H	3.094293	-1.393803	-2.171783
H	-0.555790	-0.228999	-1.077218
H	-0.926380	-1.575328	0.030883
H	-1.919199	1.267451	0.463616
H	-3.013498	0.320001	2.485620
H	-2.278210	-1.248383	2.172721
H	-1.270107	0.131912	2.573655
C	-3.137791	0.326068	-1.760732
C	-3.705617	-1.624671	-0.294278
H	-5.391205	0.577316	-0.360128
H	-4.803142	0.329856	1.272739
H	-4.276935	1.739494	0.349518
H	-4.619572	-1.784695	-0.866599
H	-2.932078	-2.243099	-0.751690
H	-3.888941	-1.996921	0.713206

H	-4.061872	0.205310	-2.325564
H	-2.862493	1.381976	-1.815002
H	-2.373497	-0.256590	-2.277609

2 – Ti-Beta-Baird (Tables 4 and 5): we optimized this structure following the Ref. 63.

Complex

43
B3LYP/6-311++G(2d,2p) Charge = 1 Multiplicity = 1 E(RB3LYP) = -1512. 32705997

C	-1.460088	1.981474	1.261676
C	-0.193027	2.172004	0.654572
C	-0.376579	2.227235	-0.745627
C	-1.759189	2.060267	-1.003705
C	-2.427083	1.945145	0.238936
Ti	-0.974319	0.032955	-0.051126
C	-2.746066	-1.068782	1.051871
C	-1.657836	-1.972513	1.015943
C	-1.427903	-2.322387	-0.336317
C	-2.358318	-1.627652	-1.135081
C	-3.182526	-0.862958	-0.280396
C	0.735914	-0.519656	-1.259262
C	1.557733	-0.678565	0.007370
C	1.760959	-2.151344	0.425809
C	2.956712	0.100935	0.055483
C	4.018978	-0.753620	-0.671465
H	-2.226390	2.060603	-1.975486
H	-3.488084	1.840454	0.380152
H	0.383628	2.403946	-1.482535
H	0.960689	-0.206199	0.870920
H	0.608838	-1.434983	-1.823302
H	1.070696	0.269654	-1.916557
H	-1.650941	1.911175	2.320276
H	0.735420	2.288102	1.184220
H	-0.687488	-3.009401	-0.700315
H	-2.428788	-1.676140	-2.209749
H	-4.012085	-0.253290	-0.592179
H	-3.183498	-0.637990	1.936715
H	-1.121904	-2.348250	1.872613
H	2.184403	-2.718817	-0.399819
H	2.439147	-2.234685	1.270588
H	0.839701	-2.637339	0.719367
C	2.954807	1.474946	-0.636037
C	3.379363	0.311205	1.521173
H	3.955431	1.899632	-0.561505
H	2.724679	1.409739	-1.698392
H	2.282381	2.190843	-0.173122
H	4.951476	-0.192601	-0.725231
H	4.235018	-1.687504	-0.158747
H	3.715347	-0.984020	-1.693487
H	4.354634	0.795383	1.562457
H	2.675915	0.954904	2.053902
H	3.461669	-0.622631	2.074334

Free ligand

23
B3LYP/6-311++G(2d,2p) Charge = 0 Multiplicity = 1 E(RB3LYP) = - 276.4851295
C 1.638500 -1.250867 -0.016359
C 0.856540 -0.000005 -0.447121
C 1.638485 1.250856 -0.016309
C -0.645785 -0.000040 0.000562
C -1.357807 -1.241340 -0.571676
C -0.796020 -0.003872 1.532301
C -1.356051 1.245212 -0.565218
H 0.831229 0.000099 -1.542623
H 1.180690 2.173493 -0.368892
H 1.729488 1.313421 1.069440
H 2.650720 1.214837 -0.421772
H -2.426827 1.197271 -0.360292
H -0.982135 2.168357 -0.124182
H -1.229084 1.313709 -1.647843
H -1.852407 -0.002838 1.807468
H -0.344032 -0.887967 1.982493
H -0.341118 0.876329 1.987191
H -2.428312 -1.193666 -0.365275
H -1.232106 -1.303520 -1.654822
H -0.984287 -2.167446 -0.136571
H 1.179053 -2.173742 -0.366178
H 2.649720 -1.216360 -0.424471
H 1.732238 -1.311645 1.069248

3 – Ti-Beta-Si-Baird (Table 6):
For this compound, the optimized geometry suggested in the supporting information of Ref. 64 has been used.

4 – Ti-Gamma-Si-Baird (Table 6):
For this compound, the optimized geometry suggested in the supporting information of Ref. 64 has been used.

5 – Ti-Popelier (Table 7): we optimized this structure following the Ref. 18.

Complex

10
B3LYP/6-311++G(2d,2p) Charge = 1 Multiplicity = 1 E(RB3LYP) = - 1849. 0196674
Ti 0.196616 -0.046068 0.000000
C -1.248979 -1.439750 0.000000
Cl 0.196616 1.031981 1.858516
Cl 0.196616 1.031981 -1.858516
C -0.105969 -2.431760 0.000000
H -1.847134 -1.407826 -0.906987
H -1.847134 -1.407826 0.906987
H -0.058533 -3.043135 -0.898012
H -0.058533 -3.043135 0.898012
H 0.930540 -1.942875 0.000000

Free ligand

8

B3LYP/6-311++G(2d,2p) Charge = 0 Multiplicity = 1 E(RB3LYP) = - 79.860981

C	0.764167	0.000043	0.000000
H	1.161807	1.015719	0.000044
H	1.161767	-0.508023	0.879548
H	1.161767	-0.507947	-0.879592
C	-0.764166	-0.000021	0.000000
H	-1.161843	-1.015711	-0.000044
H	-1.161750	0.507877	0.879636
H	-1.161750	0.507954	-0.879592

6 – EtTiCl$_3$(dmpe) -McGrady (Table 7): we optimized this structure following the Ref. 67

Complex

35

B3LYP/6-311++G(2d,2p) Charge = 0 Multiplicity = 1 E(RB3LYP) = - 3230.7758828

Cl	-0.266018	-0.762396	-2.317758
Ti	-0.273089	-0.928984	0.009260
H	0.414833	2.845101	-1.358445
H	1.901848	-2.358383	-0.980815
H	1.905398	-2.427581	0.808275
H	-0.825414	-3.039825	-0.064531
C	1.293051	-2.383360	-0.084116
C	0.209973	-3.448890	-0.120248
Cl	-2.613095	-1.304682	0.192059
Cl	0.011615	-0.723961	2.325001
P	1.909982	0.546046	-0.021786
P	-1.134157	1.564707	-0.019455
C	0.246345	2.781498	-0.282350
H	0.260289	-4.124177	0.732100
H	0.210311	-4.013890	-1.050017
C	2.791256	0.709822	-1.627703
C	3.269568	0.131292	1.140775
C	1.514587	2.304898	0.434383
C	-1.937672	2.118331	1.534499
C	-2.358273	1.986195	-1.314984
H	-0.051925	3.775014	0.055921
H	3.649555	1.374822	-1.532181
H	2.111451	1.084888	-2.388197
H	3.131140	-0.273117	-1.948345
H	4.032781	0.909255	1.132233
H	3.723575	-0.812512	0.846010
H	2.862601	0.023211	2.143176
H	1.369742	2.315652	1.515769
H	2.366336	2.950305	0.212587
H	-2.304363	3.140295	1.439321
H	-1.232473	2.049921	2.359153
H	-2.766635	1.446090	1.745957
H	-2.635855	3.038881	-1.263649
H	-3.238323	1.364205	-1.166990
H	-1.939845	1.757155	-2.292082

7 – CpTiN*i*Pr$_2$Cl$_2$-McGrady (Table 7): we optimized this structure following the Ref. 67

Complex

34
B3LYP/6-311++G(2d,2p) Charge = 0 Multiplicity = 1 E(RB3LYP) = - 2255.6314855
Ti -0.690203 -0.255408 0.008993
Cl -0.943036 -1.576055 1.871873
Cl -1.010319 -1.697312 -1.754077
C -2.890491 0.587962 0.491736
C -1.194044 2.093835 0.235803
C -1.972765 1.408759 1.189414
C -1.613603 1.686066 -1.053066
C -2.675116 0.767209 -0.889678
N 1.147531 0.190645 -0.038076
C 1.808084 -1.152965 -0.033185
H 1.007532 -1.898377 0.008544
H -3.591258 -0.094673 0.940841
H -0.426739 2.810732 0.452425
H -1.867645 1.468349 2.258943
H -1.197961 2.009403 -1.991999
H -3.189589 0.252161 -1.680753
C 2.109059 1.313552 -0.066327
C 2.572421 -1.433705 -1.333173
C 2.661706 -1.390773 1.217883
C 2.182958 2.072313 1.266566
C 1.905748 2.247364 -1.265040
H 3.094834 0.869012 -0.207291
H 1.924131 -1.304061 -2.197354
H 2.932590 -2.462905 -1.331045
H 3.441120 -0.783599 -1.442711
H 3.533595 -0.736247 1.245370
H 2.074511 -1.235473 2.120945
H 3.024086 -2.419205 1.222023
H 1.261282 2.602178 1.496296
H 2.988574 2.807659 1.227440
H 2.385559 1.390581 2.090089
H 2.738772 2.949313 -1.327539
H 0.991333 2.830987 -1.190834
H 1.870306 1.678161 -2.192844

34
wB97XD/6-311++G(2d,2p) Charge = 0 Multiplicity = 1 E(RwB97XD) = - 2255.4338709
Ti -0.693847 -0.233972 0.017376
Cl -0.941079 -1.484981 1.920994
Cl -1.090160 -1.710760 -1.693020
C -2.853869 0.637092 0.407054
C -1.096743 2.080207 0.294376
C -1.950937 1.400583 1.177872
C -1.458477 1.729992 -1.026015
C -2.559000 0.853489 -0.950900
N 1.125163 0.172971 -0.069354
C 1.734665 -1.180988 -0.063040
H 0.915672 -1.906076 0.007728
H -3.595158 -0.041588 0.794158
H -0.311614 2.754007 0.577978
H -1.895254 1.417185 2.252702
H -0.974035 2.059140 -1.929227

H	-3.045575	0.381736	-1.785607
C	2.114715	1.256333	-0.105322
C	2.450115	-1.494313	-1.376252
C	2.610576	-1.433438	1.162003
C	2.274247	1.944373	1.250984
C	1.882394	2.245832	-1.244371
H	3.077813	0.789669	-0.318557
H	1.781366	-1.337134	-2.220642
H	2.768576	-2.536856	-1.382074
H	3.340185	-0.877745	-1.508366
H	3.512002	-0.818662	1.145768
H	2.057793	-1.230032	2.077801
H	2.923947	-2.477309	1.177448
H	1.359376	2.438374	1.570990
H	3.062837	2.696526	1.196470
H	2.542260	1.222244	2.019483
H	2.762117	2.880421	-1.358721
H	1.032086	2.900597	-1.066460
H	1.719058	1.714728	-2.181561

34

B2PLYPD3/6-311++G(2d,2p) Charge = 0 Multiplicity = 1 E(RB2PLYPD3) = - 2253.77799474

Ti	-0.696542	-0.260058	0.013275
Cl	-0.936157	-1.531106	1.913319
Cl	-1.036649	-1.690463	-1.756707
C	-2.869631	0.625482	0.464425
C	-1.128062	2.090451	0.265264
C	-1.946981	1.415047	1.193134
C	-1.532363	1.712953	-1.040007
C	-2.621495	0.820253	-0.911797
N	1.139108	0.190687	-0.051990
C	1.751018	-1.170807	-0.042793
H	0.929787	-1.892175	0.015839
H	-3.588415	-0.052665	0.888847
H	-0.343279	2.777005	0.509263
H	-1.855296	1.448242	2.263739
H	-1.082884	2.029920	-1.963848
H	-3.125882	0.323696	-1.719413
C	2.125745	1.281172	-0.090613
C	2.485460	-1.469183	-1.349550
C	2.610302	-1.409854	1.197400
C	2.237971	2.003296	1.254328
C	1.891437	2.236912	-1.259611
H	3.095168	0.817422	-0.270722
H	1.824893	-1.322426	-2.199430
H	2.820929	-2.504853	-1.352010
H	3.363957	-0.836933	-1.467173
H	3.494277	-0.774092	1.198087
H	2.035710	-1.224695	2.100943
H	2.946782	-2.445070	1.212098
H	1.315772	2.509177	1.522723
H	3.031868	2.748383	1.207970
H	2.472479	1.301289	2.049373
H	2.739077	2.914918	-1.351644
H	0.999410	2.840794	-1.127231

H 1.793109 1.680859 -2.189026

Free ligand

22
B3LYP/6-311++G(2d,2p) Charge = 0 Multiplicity = 1 E(RB3LYP) = - 292.5224781
C -2.081515 -1.178022 -0.090719
C -1.063917 -0.037807 -0.211895
C -1.766228 1.325630 -0.171481
N -0.029128 -0.173031 0.830136
C 1.386573 -0.053570 0.445512
C 1.829771 -1.268282 -0.374964
C 1.773425 1.262190 -0.253971
H -0.227207 0.456049 1.596560
H 1.932695 -0.090131 1.391678
H -0.573419 -0.134854 -1.182381
H 1.594299 -2.190725 0.153977
H 2.904602 -1.235893 -0.557727
H 1.335736 -1.299239 -1.347652
H 1.280149 1.363684 -1.222368
H 1.502353 2.125101 0.356051
H 2.850102 1.302026 -0.429712
H -2.255687 1.470881 0.795323
H -2.536843 1.397117 -0.940790
H -1.061868 2.143532 -0.319814
H -2.836342 -1.122228 -0.877994
H -2.591511 -1.131417 0.873482
H -1.581819 -2.143520 -0.154476

8 – Rh-butene-Milstein (Table 7): we optimized this structure following the Ref. 66

Complex

46
PBE1PBE/Def2TZVP Charge = 1 Multiplicity = 1 E(RPBE1PBE) = - 2175.8359543
C 0.946911 -1.858174 0.322336
C 0.832179 -2.716118 1.411682
C -0.405645 -3.097517 1.894337
C -1.538564 -2.513942 1.357483
C -1.456383 -1.652766 0.268666
C -0.207138 -1.375566 -0.349798
H 1.721509 -3.089692 1.902624
H -0.483887 -3.792435 2.720716
H -2.499151 -2.729257 1.807504
P -2.925164 -0.684575 -0.158882
P 2.577323 -1.161329 -0.045169
S 2.357906 0.818373 -0.194841
S -2.360920 1.230700 -0.252282
C -3.729157 -1.279236 -1.663173
H -3.984969 -2.336060 -1.561435
H -4.643208 -0.697552 -1.803255
H -3.097411 -1.132960 -2.537049
C 3.335303 -1.924982 -1.495971
H 4.336469 -1.502970 -1.610120
H 3.412146 -3.005516 -1.357517

H	2.770338	-1.706623	-2.400049
C	3.686894	-1.602986	1.305067
H	3.880795	-2.676384	1.348018
H	4.627926	-1.081715	1.116525
H	3.281106	-1.246054	2.251398
C	-4.165248	-0.945081	1.122362
H	-4.990487	-0.265919	0.897237
H	-4.543333	-1.969169	1.128039
H	-3.757759	-0.678109	2.096984
Rh	-0.017154	0.982047	0.028860
C	-0.126540	-0.767250	-1.725672
H	0.733085	-1.153046	-2.268750
H	-1.022229	-0.993155	-2.299065
H	-0.021782	0.356220	-1.806724
C	0.060078	3.106862	0.187180
H	-0.876977	3.445893	-0.250857
C	-0.024938	2.511671	1.466912
H	-1.024109	2.459197	1.896069
C	1.248794	3.841225	-0.343744
H	2.193519	3.506115	0.084414
H	1.314244	3.762040	-1.430480
H	1.144193	4.906324	-0.104823
C	1.063049	2.533504	2.496204
H	0.943797	3.421209	3.128520
H	1.000541	1.663306	3.153390
H	2.062677	2.561344	2.065874

Free ligand

39

B3LYP/ Def2TZVP Charge = 0 Multiplicity = 1 E(RB3LYP) = - 586.2601147

C	-1.193598	1.799559	-0.014914
C	-1.234851	0.403091	-0.006261
C	0.000005	-0.305849	0.012878
C	1.234874	0.403051	-0.006274
C	1.193715	1.799510	-0.014965
C	0.000076	2.492992	-0.013546
C	0.000040	-1.821694	0.030623
H	-2.106750	2.371285	-0.025702
H	2.106913	2.371172	-0.025819
H	0.000104	3.576213	-0.018507
H	-0.867653	-2.225290	0.535941
H	0.000485	-2.229905	-0.982412
H	0.867358	-2.225214	0.536660
C	2.641899	-0.269144	-0.001022
C	-2.641915	-0.269095	-0.001027
C	-3.771602	0.759783	-0.230624
C	-2.807606	-1.300853	-1.141686
C	-2.939583	-0.906606	1.376359
C	3.771471	0.759798	-0.230945
C	2.939603	-0.906322	1.376514
C	2.807519	-1.301207	-1.141441
H	3.851062	-1.619664	-1.195286
H	2.206377	-2.195782	-1.018768
H	2.548737	-0.852006	-2.102793

H	4.726039	0.231789	-0.254675
H	3.660718	1.285260	-1.181031
H	3.833934	1.498548	0.568483
H	3.934152	-1.359860	1.371361
H	2.925115	-0.141045	2.155007
H	2.229653	-1.677479	1.666742
H	-3.851107	-1.619509	-1.195374
H	-2.549137	-0.851286	-2.102960
H	-2.206229	-2.195332	-1.019423
H	-3.934172	-1.360054	1.371143
H	-2.229700	-1.677894	1.666379
H	-2.924996	-0.141519	2.155034
H	-4.726124	0.231683	-0.254324
H	-3.834028	1.498376	0.568951
H	-3.661034	1.285416	-1.180632

9 – Rh-H_2CO-Milstein (Table 7): we optimized this structure following the Ref. 66

Complex

38
PBE1PBE/Def2TZVP Charge = 1 Multiplicity = 1 E(RPBE1PBE) = - 2133.1531595

C	0.126199	3.127194	1.478545
C	1.298124	2.521471	1.055055
C	1.287806	1.491357	0.124981
C	0.064237	1.034761	-0.449951
C	-1.131151	1.583568	0.103600
C	-1.080346	2.613035	1.033960
Rh	-0.027556	-1.257832	-0.210110
H	2.237643	2.854044	1.480474
H	-1.999313	3.016312	1.442847
H	0.150961	3.940136	2.191843
C	0.050201	0.286093	-1.747433
H	-0.819693	0.533317	-2.352500
H	0.952983	0.458168	-2.329104
H	-0.006279	-0.931192	-1.842422
C	3.710601	1.166984	-1.585458
H	3.968842	2.217518	-1.436305
H	4.623740	0.578323	-1.695878
H	3.121429	1.062227	-2.495468
C	3.899189	0.822929	1.238725
H	4.754968	0.157585	1.106478
H	4.255802	1.853751	1.279387
H	3.391226	0.558086	2.165793
C	-3.547450	1.434895	-1.645689
H	-4.503147	0.920016	-1.763890
H	-3.722585	2.503924	-1.507279
H	-2.956497	1.276295	-2.546777
C	-3.802982	1.113449	1.177787
H	-4.083694	2.167676	1.212290
H	-4.703293	0.512561	1.033662
H	-3.328280	0.816559	2.112748
P	-2.700487	0.756193	-0.201997
P	2.795036	0.544628	-0.157680
S	-2.389870	-1.225005	-0.372310

S	2.341739	-1.404883	-0.324227
O	-0.049954	-2.447426	1.468925
C	-0.633211	-3.494462	1.659969
H	-0.515937	-4.001759	2.625756
H	-1.274654	-3.953461	0.897088

10 – Ni-Jones (Table 7): we optimized this structure following the Ref. 65

Complex

31
B3LYP/6-311++G(2d,2p) SCRF=(PCM,solvent=THF) Charge = 0 Multiplicity = 1
E(RB3LYP) = - 2562.2742036

H	0.120487	1.927553	-1.685892
C	0.180404	2.910122	-1.139298
H	1.113239	3.387048	-1.432629
H	-0.664569	3.510881	-1.469778
C	0.140382	2.746993	0.332669
N	0.121354	3.016281	1.474328
Ni	0.028902	0.848353	-0.234815
P	-1.655278	-0.543134	-0.025496
C	-0.795408	-2.204234	-0.163492
C	0.580824	-2.185754	0.517505
P	1.586601	-0.687740	0.008382
C	2.939371	-0.720923	1.269270
H	3.403566	-1.706027	1.336021
H	2.534194	-0.447522	2.242112
H	3.698143	0.011960	0.997982
C	2.488732	-1.326173	-1.478855
H	1.781771	-1.505613	-2.287304
H	3.021667	-2.251592	-1.255717
H	3.202547	-0.574939	-1.814448
H	0.461192	-2.116494	1.600527
H	1.132120	-3.106414	0.314274
H	-0.685881	-2.404149	-1.231363
H	-1.427229	-2.994862	0.247406
C	-3.117116	-0.815119	-1.128365
H	-3.651130	-1.731349	-0.871515
H	-3.796767	0.030865	-1.034283
H	-2.784800	-0.872495	-2.163834
C	-2.457179	-0.662175	1.638575
H	-1.693666	-0.667951	2.414156
H	-3.066574	-1.562897	1.723975
H	-3.086960	0.212841	1.793512

Free ligand

6
B3LYP/6-311++G(2d,2p) SCRF=(PCM,solvent=THF) Charge = 0 Multiplicity = 1
E(RB3LYP) = - 132.8004878

c	-0.279760	-0.000002	0.000506
c	1.175175	0.000001	-0.000113
n	-1.430568	0.000001	-0.000231
h	1.547002	-0.883280	-0.516432
h	1.547003	0.888676	-0.507089

h 1.547482 -0.005393 1.022776

11 – Zr-NH_2BH_3-a-Forster (Table 9): we optimized this structure following the Ref. 68.

Complex

29
B3LYP/Def2-TZVPD Charge = 0 Multiplicity = 1 E(RB3LYP) = - 977.3570775

H	1.516495	-0.992397	-2.484241
C	1.758795	-0.926150	-1.435620
C	1.520387	-1.919278	-0.451347
C	2.412972	0.157692	-0.805075
Zr	-0.000262	0.051268	0.109275
C	1.983593	-1.430761	0.784598
H	1.066802	-2.882462	-0.619552
C	2.531804	-0.137854	0.564424
H	2.708662	1.074401	-1.285399
C	-1.629683	-1.513803	-1.090414
C	-1.675367	-1.854332	0.288015
C	-2.282941	-0.781383	0.977804
C	-2.567714	0.235194	0.042901
C	-2.177187	-0.227319	-1.239109
B	0.087417	0.728461	2.735445
N	0.060155	1.778542	1.616059
Cl	-0.020767	2.053059	-1.452925
H	0.033248	-0.399977	2.088518
H	0.873598	2.367693	1.501123
H	-0.754154	2.374447	1.552210
H	1.941630	-1.943543	1.731184
H	2.970912	0.492691	1.320678
H	-1.250022	-2.134038	-1.886627
H	-1.347749	-2.782233	0.728845
H	-2.459656	-0.733619	2.039144
H	-3.019779	1.190733	0.255798
H	-2.254611	0.327469	-2.157986
H	-0.903937	0.714188	3.416469
H	1.135979	0.669775	3.321862

Free ligand
B3LYP/Def2-TZVPD Charge = 0 Multiplicity = 1 E(RB3LYP) = - 83.2570969
8

B	0.000052	0.930564	0.000000
N	0.000052	-0.729020	0.000000
H	-1.167229	1.242263	0.000000
H	0.583462	1.242462	1.011022
H	0.583462	1.242462	-1.011022
H	0.948679	-1.092687	0.000000
H	-0.474501	-1.092091	0.821678
H	-0.474501	-1.092091	-0.821678

12 – Zr-NH_2BH_3-b-Forster (Table 9): we optimized this structure following the Ref. 68.

Complex

29
B3LYP/Def2-TZVPD Charge = 0 Multiplicity = 1 E(RB3LYP) = - 977.3476798

H	1.812662	-2.305297	-1.291880
C	1.928737	-1.259802	-1.053860
C	1.576008	-0.179796	-1.889583
C	2.495719	-0.723022	0.131669
Zr	0.000917	-0.040768	0.137090
C	1.892669	1.020930	-1.213406
H	1.158966	-0.258568	-2.879445
C	2.479903	0.678321	0.027178
H	2.863987	-1.283064	0.976831
C	-2.476391	-0.783911	0.111475
C	-1.898060	-1.260953	-1.093657
C	-1.580589	-0.139865	-1.890616
C	-1.926360	1.024356	-1.169329
C	-2.496134	0.620003	0.061443
B	0.012256	-1.344579	2.504356
N	0.010876	-2.119892	1.151388
H	0.034857	-0.112297	2.174123
H	-0.800962	-2.702912	1.009112
H	0.827305	-2.695581	1.005384
Cl	-0.012576	2.275963	1.136261
H	1.724901	2.022072	-1.574875
H	2.803005	1.373907	0.782705
H	-2.827954	-1.384373	0.935740
H	-1.755052	-2.293536	-1.370604
H	-1.165702	-0.168440	-2.884153
H	-1.785500	2.042348	-1.492669
H	-2.834297	1.278134	0.843659
H	1.022604	-1.507193	3.136704
H	-1.012145	-1.481250	3.119952

13 – Ti- NH_2BH_3-a-McGrady (Table 9): we optimized this structure following the Ref. 67.

Complex

29
B3LYP/TZVP/SDD Charge = 0 Multiplicity = 1 E(RB3LYP) = - 528.8512043

H	1.209237	-2.634585	-0.737926
C	1.536423	-1.681353	-0.357626
C	1.566886	-1.290108	1.006306
C	2.048065	-0.616622	-1.133436
Ti	0.000024	0.131048	-0.142704
C	2.094759	0.012075	1.072731
H	1.259250	-1.889473	1.847291
C	2.376409	0.437775	-0.247231
H	2.191941	-0.620240	-2.200231
C	-1.536816	-1.681126	-0.357554
C	-1.567197	-1.289843	1.006361
C	-2.094775	0.012464	1.072755
C	-2.376348	0.438179	-0.247216
C	-2.048217	-0.616305	-1.133396
B	0.000508	2.528451	0.789003
N	0.000130	2.253613	-0.716314
H	-0.000054	0.206357	-1.803310

H	0.000228	1.339312	1.312787
H	0.816930	2.528549	-1.241018
H	-0.816958	2.528551	-1.240566
H	2.232785	0.599717	1.964738
H	2.790135	1.394888	-0.521018
H	-1.209819	-2.634435	-0.737832
H	-1.259692	-1.889256	1.847361
H	-2.232662	0.600165	1.964744
H	-2.789885	1.395364	-0.521036
H	-2.192058	-0.619909	-2.200196
H	-1.022040	3.022093	1.192595
H	1.023546	3.021473	1.192124

14 – Ti- NH_2BH_3-b-McGrady (Table 9): we optimized this structure following the Ref. 67.

Complex

29
B3LYP/TZVP/SDD Charge = 0 Multiplicity = 1 E(RB3LYP) = - 528.8489583

H	2.313392	0.798315	1.809174
C	2.128753	0.130357	0.983393
C	1.596555	-1.165669	1.088101
C	2.369537	0.404588	-0.384961
Ti	-0.000020	0.128307	-0.200144
C	1.529407	-1.713171	-0.219597
H	1.309006	-1.660540	2.001595
C	2.018343	-0.748962	-1.128678
H	2.754903	1.324384	-0.792389
C	-2.130632	0.132063	0.980803
C	-1.596699	-1.162891	1.090198
C	-1.527418	-1.714383	-0.215760
C	-2.016313	-0.753542	-1.128400
C	-2.369934	0.401867	-0.388577
B	-0.000915	2.628308	-0.663894
N	-0.000310	2.118522	0.786563
H	-0.000682	1.543719	-1.399667
H	-0.815408	2.360955	1.329003
H	0.815177	2.361152	1.328349
H	-0.000005	-0.053192	-1.840779
H	1.191025	-2.703147	-0.475686
H	2.135742	-0.878340	-2.190788
H	-2.317244	0.802303	1.804283
H	-1.309826	-1.654597	2.005611
H	-1.187726	-2.704823	-0.468289
H	-2.132431	-0.886344	-2.190226
H	-2.755893	1.319979	-0.799215
H	1.017102	3.187721	-0.982011
H	-1.019535	3.186970	-0.981383

15 – $TiCp_2NH_2BH_3$-McGrady (Table 9): we optimized this structure following the Ref. 67.

Complex

28
B3LYP/Def2-TZVPD Charge = 0 Multiplicity = 2 E(UB3LYP) = - 1319.4466408

H	1.769656	-0.890251	2.278237
C	1.834357	-0.778233	1.207506
C	1.441986	-1.734275	0.240983
C	2.361314	0.334436	0.511590
Ti	0.000773	0.143317	-0.034531
C	1.709607	-1.204183	-1.044537
H	1.017351	-2.702651	0.448205
C	2.285199	0.072771	-0.872029
H	2.754270	1.234278	0.956738
C	-2.129136	-0.109911	1.081097
C	-1.649309	-1.408286	0.820378
C	-1.597547	-1.583308	-0.585831
C	-2.036072	-0.391330	-1.193091
C	-2.358627	0.524880	-0.162611
B	0.093227	2.584149	-0.730553
N	0.017947	2.172114	0.765459
H	0.057094	1.464689	-1.388115
H	-0.820669	2.465902	1.245335
H	0.808849	2.453236	1.325766
H	1.518384	-1.691284	-1.987441
H	2.581731	0.747918	-1.657243
H	-2.282649	0.322057	2.057480
H	-1.374149	-2.141027	1.561996
H	-1.268839	-2.471717	-1.100791
H	-2.104012	-0.200777	-2.251983
H	-2.706241	1.533895	-0.311923
H	1.149395	3.079616	-1.029248
H	-0.879571	3.182238	-1.113503

16 – R1-R2-Ti Beta and Gamma (Table 12):

- **β-agostic structure:** R^1 = Cp and R^2 = OCH_2

37

B3LYP/TZVP Charge = 0 Multiplicity = 1 E(RB3LYP) = -1684.94435211

C	-3.182017	-0.733191	-1.191523
C	-3.594070	0.405958	-0.462330
C	-3.430037	0.108395	0.917279
C	-2.927438	-1.218953	1.032349
C	-2.781069	-1.734055	-0.273389
Ti	-1.278361	0.183886	-0.000302
O	-0.848029	1.977748	0.057431
C	0.243353	-0.763485	-1.114828
C	1.063408	-0.769317	0.180190
C	1.113702	-2.157572	0.842996
Si	2.825720	-0.002894	-0.028485
C	3.841465	-1.116790	-1.178930
C	2.697962	1.736840	-0.763819
C	3.679535	0.108129	1.665144
H	-3.663901	0.771653	1.737160
H	-3.973643	1.327975	-0.873928
H	-2.732386	-1.750136	1.951862
H	-2.409844	-2.713398	-0.531505
H	-3.164126	-0.823753	-2.267096
H	0.113179	-1.759405	-1.532276
H	0.616794	-0.085458	-1.886638

H	1.536542	-2.116645	1.849213
H	1.725943	-2.841313	0.250370
H	0.117025	-2.598655	0.919488
H	0.605157	-0.062253	0.939170
H	3.099782	0.716812	2.363967
H	4.664524	0.571910	1.566449
H	3.823246	-0.876225	2.116478
H	3.990586	-2.112495	-0.755426
H	4.829129	-0.681387	-1.351826
H	3.353947	-1.233736	-2.149198
H	2.130048	2.401822	-0.109859
H	2.210114	1.733990	-1.740483
H	3.696340	2.163361	-0.893137
C	-0.703447	3.236135	0.287199
H	-1.328103	3.719337	1.031682
H	-0.020338	3.808474	-0.330492

- **β-agostic structure:** R^1 = Cp and R^2 = Cl

37
B3LYP/TZVP Charge = 1 Multiplicity = 1 E(RB3LYP) = -2030.4608958

C	-3.583345	0.204549	-0.080678
C	-3.136153	-0.275466	1.169964
C	-2.406467	-1.476049	0.944710
C	-2.424645	-1.744454	-0.447228
C	-3.131235	-0.699041	-1.080883
Ti	-1.238390	0.289126	-0.055646
C	0.237463	-0.469551	-1.273006
C	0.976247	-0.748306	0.010884
Si	2.800961	0.063518	0.048032
C	2.666191	1.903477	-0.331644
C	1.038904	-2.232718	0.406893
C	3.485492	-0.222882	1.781015
C	3.800973	-0.836175	-1.271734
H	-3.303913	0.198937	2.125785
H	-4.145771	1.109824	-0.249440
H	-1.954148	-2.092619	1.707019
H	-1.983504	-2.594312	-0.941168
H	-3.299370	-0.601862	-2.143624
H	0.106035	-1.327289	-1.922557
H	0.560223	0.414937	-1.830695
H	1.385310	-2.357538	1.432744
H	1.742974	-2.751963	-0.244639
H	0.082633	-2.746237	0.312551
H	0.534372	-0.161015	0.886840
H	2.845377	0.209802	2.553734
H	4.463368	0.257687	1.867185
H	3.624813	-1.281820	2.004599
H	3.910182	-1.901664	-1.063504
H	4.806562	-0.408911	-1.307094
H	3.363168	-0.722564	-2.265439
H	2.085546	2.447049	0.415284
H	2.237026	2.108602	-1.314248
H	3.673400	2.328899	-0.329349
Cl	-1.049630	2.482454	0.111060

- **γ-agostic structure:** R^1 = Cp and R^2 = OCH_2

37
B3LYP/TZVP Charge = 0 Multiplicity = 1 E(RB3LYP) = -1684.94265911

C	3.526154	-0.395477	0.894610
C	3.731230	-0.215572	-0.494295
C	2.995879	-1.203416	-1.183915
C	2.337316	-2.019475	-0.231197
C	2.659594	-1.517169	1.056089
Ti	1.394951	0.174394	0.063029
O	1.477259	2.026429	0.047447
C	-0.392147	-0.319957	1.061062
C	-1.220318	0.311560	-0.095660
Si	-3.087607	-0.141530	0.047820
C	-3.335901	-2.012276	-0.153666
C	-0.681258	-0.022124	-1.510957
C	-4.085019	0.759868	-1.297771
C	-3.717201	0.411430	1.746885
H	4.314549	0.570666	-0.948878
H	3.973594	0.190079	1.682574
H	2.940004	-1.312778	-2.257264
H	1.716443	-2.875079	-0.446168
H	2.323686	-1.927255	1.995484
H	-0.588177	-1.387662	1.182755
H	-0.589790	0.186167	2.008427
H	-1.269769	0.488591	-2.276722
H	-0.698544	-1.091013	-1.724131
H	0.343875	0.357210	-1.748277
H	-1.194379	1.401830	0.010720
H	-3.810098	0.433446	-2.303456
H	-3.937447	1.841598	-1.245089
H	-5.154154	0.567173	-1.174144
H	-4.789867	0.222127	1.838119
H	-3.555064	1.481344	1.900250
H	-3.213080	-0.122583	2.554272
H	-2.994807	-2.365505	-1.129918
H	-4.396373	-2.262935	-0.067465
H	-2.799948	-2.574602	0.613616
C	1.629291	3.298925	0.039829
H	2.449212	3.737583	-0.520980
H	0.963925	3.917022	0.634492

- **γ-agostic structure:** R^1 = OCH_2 and R^2 = OCH_2

37
B3LYP/TZVP Charge = 1 Multiplicity = 1 E(RB3LYP) = - 1605.6941833

Ti	1.706335	-0.036716	-0.111496
C	0.017530	0.078668	-1.227789
C	-0.649788	-0.317345	0.111770
Si	-2.594600	0.009213	-0.025553
C	-2.893556	1.859943	-0.235953
C	-0.122529	0.351985	1.415262
C	-3.381456	-0.633411	1.567499
C	-3.201510	-0.974580	-1.513198
H	-0.194294	1.098722	-1.551688
H	-0.179674	-0.638320	-2.020466
H	-0.657700	-0.068553	2.265870

H	-0.243610	1.434823	1.429225
H	0.943021	0.134202	1.734189
H	-0.591408	-1.403551	0.241139
H	-3.110977	-0.040916	2.443945
H	-3.115520	-1.675117	1.762487
H	-4.469838	-0.590132	1.476020
H	-4.290549	-0.907251	-1.575388
H	-2.946475	-2.033738	-1.431502
H	-2.796187	-0.596404	-2.453074
H	-2.530580	2.442542	0.613415
H	-3.968982	2.040757	-0.310896
H	-2.437392	2.255964	-1.145022
O	2.364905	-1.800332	0.081827
O	2.554059	1.654096	-0.045760
C	3.289374	2.677510	-0.025819
H	2.902960	3.617522	-0.412656
H	4.299523	2.614906	0.373232
C	2.992872	-2.894580	0.067682
H	2.468204	-3.806267	-0.207500
H	4.047177	-2.919680	0.334060

- **γ-agostic structure:** R^1 = Cp and R^2 = Cl

34
B3LYP/TZVP Charge = 1 Multiplicity = 1 E(RB3LYP) = -2030.4671222

C	-2.406427	1.357949	1.214068
C	-3.303244	0.298658	0.916400
C	-3.541634	0.298247	-0.480557
C	-2.786013	1.348659	-1.047301
C	-2.086967	2.003074	-0.002279
Ti	-1.264521	-0.229686	-0.104743
C	0.328170	0.197622	1.092623
C	1.055805	-0.247717	-0.183395
C	0.607712	0.360273	-1.534693
Cl	-1.639930	-2.416838	-0.019966
Si	3.010953	0.098877	0.075869
C	3.506751	-0.849246	1.621989
C	3.268418	1.956230	0.254123
C	3.869705	-0.585906	-1.456478
H	-4.169366	-0.397291	-1.015248
H	-3.727697	-0.393018	1.627774
H	-2.757597	1.612050	-2.094321
H	-1.428061	2.850890	-0.115146
H	-2.057396	1.634976	2.195223
H	0.485876	1.230869	1.387396
H	0.484753	-0.486816	1.922758
H	1.180717	-0.082645	-2.347520
H	0.702703	1.444800	-1.578430
H	-0.449006	0.147082	-1.905813
H	1.050948	-1.339080	-0.269117
H	3.666220	-0.003428	-2.356891
H	3.600676	-1.627072	-1.648290
H	4.950862	-0.557258	-1.296056
H	4.592926	-0.804202	1.736146
H	3.230921	-1.904340	1.560728
H	3.066852	-0.430283	2.528157

H	2.939144	2.516628	-0.623263
H	4.337871	2.150777	0.371993
H	2.769927	2.365384	1.134510

- **γ-agostic structure:** R^1 = Cl and R^2 = Cl

25
B3LYP/TZVP Charge = 1 Multiplicity = 1 E(RB3LYP) = -2297.1156531

Ti	1.623314	-0.027165	0.104512
Cl	2.574462	-1.977639	0.046376
C	0.054835	0.060404	-1.138219
C	-0.610611	-0.221658	0.207983
Si	-2.619297	-0.018008	-0.075759
C	-3.386380	-0.590254	1.544791
C	-0.207855	0.637005	1.430094
C	-3.044877	-1.161607	-1.500662
C	-2.954185	1.793712	-0.441675
H	-0.083556	1.060261	-1.546339
H	-0.075219	-0.725277	-1.875290
H	-0.779567	0.339478	2.307147
H	-0.321441	1.708636	1.265245
H	0.852841	0.518114	1.851463
H	-0.554747	-1.287327	0.463055
H	-3.204654	0.096179	2.373619
H	-3.047732	-1.587182	1.834729
H	-4.470429	-0.646488	1.410893
H	-4.133062	-1.209264	-1.596654
H	-2.692262	-2.181666	-1.333949
H	-2.650438	-0.808178	-2.454266
H	-2.671315	2.454391	0.379916
H	-4.030739	1.917321	-0.590761
H	-2.464394	2.140297	-1.353092
Cl	2.847797	1.739687	-0.222154

17 – β model compound (Table 13):

- **β-agostic structure: M = Ti**

10
TPSSh/Def2-TZVPD Charge = 1 Multiplicity = 1 E(RTPSSh) = -1849.05747202

Ti	-0.205274	0.055567	0.000000
C	1.271302	1.418788	0.000000
Cl	-0.205274	-1.030732	1.844498
Cl	-0.205274	-1.030732	-1.844498
C	0.140690	2.423256	0.000000
H	1.868374	1.381672	-0.910568
H	1.868374	1.381672	0.910568
H	0.095266	3.033686	-0.901438
H	0.095266	3.033686	0.901438
H	-0.903866	1.939434	0.000000

- **β-agostic structure: M = Zr**

10
TPSSh/Def2-TZVPD Charge = 1 Multiplicity = 1 E(RTPSSh) = -1046.64752726

Zr	0.315171	0.023104	0.000000
C	-1.263844	-1.433627	0.000000
Cl	0.202403	1.211024	1.952685
Cl	0.202403	1.211024	-1.952685

C	-0.162482	-2.484465	0.000000
H	-1.877299	-1.437520	-0.901550
H	-1.877299	-1.437520	0.901550
H	-0.137333	-3.102240	-0.897110
H	-0.137333	-3.102240	0.897110
H	0.906363	-2.043042	0.000000

- **β-agostic structure: M = Hf**

10
TPSSh/Def2-TZVPD Charge = 1 Multiplicity = 1 E(RTPSSh) = -1047.61169723

Hf	-0.181884	0.034619	0.000000
C	1.269308	1.607842	0.000000
Cl	0.067356	-1.157414	1.935383
Cl	0.067356	-1.157414	-1.935383
C	0.067356	2.567122	0.000000
H	1.882390	1.700296	-0.896793
H	1.882390	1.700296	0.896793
H	-0.007733	3.182989	-0.895722
H	-0.007733	3.182989	0.895722
H	-0.963744	2.043151	0.000000

18 – Os,H-MeB-Alcaraz, Os,Cl-MeB-Alcaraz (Tables 14 and 15):
For these compounds, the optimized geometries suggested in the supporting information of Ref. 69 have been used.

19 – Fe-X-BH_2 (Table 15):

- **Fe-H-MeB**

41
B3LYP/Def2-TZVP Charge = 0 Multiplicity = 1 E(RB3LYP) = -2348.05892754

Fe	-0.004210	-0.331095	-0.000288
B	0.013918	1.538009	-0.000012
H	0.006769	0.929764	1.120243
H	-0.012465	-1.390880	1.099966
H	-0.014022	-1.390414	-1.100942
H	0.006135	0.930080	-1.120441
N	0.030666	2.937385	0.000220
C	0.040767	3.727908	1.218319
C	0.040469	3.728337	-1.217598
H	-0.835672	4.384369	1.269594
H	-0.835970	4.384831	-1.268429
H	0.032733	3.074865	2.088894
H	0.032232	3.075597	-2.088398
H	0.933463	4.362162	1.269306
H	0.933166	4.362589	-1.268574
P	-2.115146	-0.858896	-0.000169
P	2.096619	-0.895111	0.000032
C	-3.152327	-0.297631	1.419762
C	3.139139	-0.358131	1.425290
C	-3.150237	-0.302692	-1.423548
C	3.143675	-0.348663	-1.418377
C	-2.481801	-2.660056	0.002999
C	2.432467	-2.702219	-0.005871
H	-4.176842	-0.671766	1.356610
H	2.680063	-0.706367	2.350965

H	-2.700625	-0.647433	2.348492
H	4.157985	-0.747054	1.362263
H	-3.173343	0.792683	1.444891
H	3.176244	0.731479	1.456752
H	-4.175032	-0.676037	-1.360230
H	2.686959	-0.689871	-2.347833
H	-2.697485	-0.656276	-2.350333
H	4.161979	-0.738985	-1.355337
H	-3.170677	0.787531	-1.452906
H	3.181803	0.741104	-1.441925
H	-3.556795	-2.853616	0.002154
H	1.971811	-3.152545	0.872733
H	-2.032149	-3.113154	0.885888
H	1.976120	-3.145869	-0.890104
H	-2.030090	-3.116725	-0.876993
H	3.503893	-2.914353	-0.004084

- **Fe-Cl-MeB**

41

B3LYP/Def2-TZVP Charge = 0 Multiplicity = 1 E(RB3LYP) = -2807.74959580

Fe	0.000539	-0.237953	-0.074514
B	-0.002581	1.626871	0.218174
H	-0.001285	1.115997	-0.967660
H	0.001541	-1.022154	-1.362886
Cl	0.003115	-2.069053	1.405040
H	-0.001252	0.945257	1.259561
N	-0.005110	3.018924	0.275698
C	-0.006254	3.870697	-0.902745
C	-0.007265	3.750359	1.533474
H	0.876901	4.518559	-0.918181
H	0.876271	4.392899	1.613199
H	-0.004391	3.263461	-1.805824
H	-0.006362	3.055319	2.370600
H	-0.892150	4.514763	-0.919249
H	-0.893482	4.389306	1.612196
P	2.200428	-0.592086	-0.290653
P	-2.198172	-0.598275	-0.290871
C	3.103916	0.458470	-1.502999
C	-3.103969	0.449189	-1.504093
C	3.234794	-0.416270	1.217721
C	-3.233333	-0.424294	1.217147
C	2.641308	-2.276907	-0.858513
C	-2.634660	-2.284514	-0.857832
H	4.150942	0.161821	-1.592511
H	-2.626732	0.362841	-2.480811
H	2.626849	0.372063	-2.479810
H	-4.150360	0.150230	-1.593280
H	3.059357	1.503227	-1.192759
H	-3.061596	1.494336	-1.194889
H	4.272407	-0.703037	1.034180
H	-2.807879	-1.059374	1.993818
H	2.810924	-1.053055	1.993860
H	-4.270121	-0.714063	1.033626
H	3.206288	0.617114	1.566059
H	-3.207748	0.609391	1.564794

H	3.723944	-2.418426	-0.874679
H	-2.230850	-2.442372	-1.857609
H	2.238470	-2.434988	-1.858611
H	-2.173394	-3.003904	-0.183139
H	2.181296	-2.997807	-0.184612
H	-3.716969	-2.428509	-0.874532

20 – Ru,dimethylaminoborane-Alcaraz (Table 15): we optimized this structure following the Ref. 70.

130
B3LYP/Lanl2DZ Charge = 0 Multiplicity = 1 E(RB3LYP) = -1895.0938011

C	-0.819650	3.263304	-0.201051
C	-0.783237	4.119410	0.952159
C	-1.205669	5.460677	0.859054
H	-1.164234	6.091280	1.746180
C	-1.677812	6.009842	-0.348991
C	-1.704006	5.178156	-1.485928
H	-2.054819	5.587060	-2.432681
C	-1.285793	3.834116	-1.434276
C	-0.278521	3.633440	2.303918
H	-0.869151	2.788873	2.680450
H	-0.327846	4.437300	3.047504
H	0.761273	3.287526	2.248148
C	-1.345271	3.026496	-2.722963
H	-1.754592	3.630411	-3.541133
H	-1.971207	2.133344	-2.615021
H	-0.350012	2.676540	-3.027602
C	-2.161153	7.446994	-0.420277
H	-1.960516	7.888827	-1.404040
H	-1.677214	8.071786	0.340160
H	-3.246698	7.506087	-0.250953
C	3.458500	-0.330382	1.585329
H	3.380146	-1.381075	1.905994
C	2.698133	0.518392	2.636602
H	1.641174	0.229559	2.645540
H	2.735355	1.581899	2.352268
C	3.317165	0.347954	4.044272
H	2.779420	0.980773	4.765709
H	3.181365	-0.695113	4.373146
C	4.824158	0.692342	4.051413
H	4.950760	1.767096	3.842744
H	5.253382	0.508080	5.046822
C	5.585338	-0.124745	2.982517
H	5.560794	-1.191717	3.256285
H	6.643875	0.173744	2.958651
C	4.961269	0.055048	1.575232
H	5.521611	-0.544161	0.848107
H	5.074126	1.106830	1.275240
C	3.120715	-2.013506	-0.943227
H	2.540690	-2.017285	-1.878001
C	2.661248	-3.239337	-0.115313
H	3.219490	-3.277568	0.834067
H	1.599914	-3.136520	0.134786
C	2.909759	-4.556959	-0.889133

H	2.607123	-5.413535	-0.269101
H	2.271108	-4.572226	-1.786384
C	4.389756	-4.702445	-1.311812
H	5.013561	-4.822758	-0.411383
H	4.525719	-5.610809	-1.916693
C	4.870666	-3.461455	-2.098207
H	4.333601	-3.408855	-3.058612
H	5.940766	-3.553623	-2.336046
C	4.621443	-2.153835	-1.304126
H	5.224487	-2.183501	-0.385588
H	4.972438	-1.298152	-1.894836
C	3.472602	0.974886	-1.196005
H	4.545898	0.741791	-1.127933
C	3.041471	0.888066	-2.682411
H	3.237699	-0.114499	-3.086073
H	1.955170	1.046554	-2.746519
C	3.772160	1.941213	-3.551160
H	4.848982	1.707955	-3.576687
H	3.409198	1.878828	-4.587574
C	3.576245	3.372207	-3.001436
H	2.514775	3.653860	-3.088416
H	4.147939	4.092355	-3.604578
C	4.001600	3.457854	-1.519003
H	3.805234	4.465443	-1.125544
H	5.088191	3.289891	-1.442241
C	3.255576	2.410696	-0.657046
H	3.591925	2.488558	0.385285
H	2.181532	2.643694	-0.661177
C	-2.086425	-3.033229	0.409991
H	-1.217686	-3.144593	1.075358
C	-3.301572	-3.707655	1.099309
H	-3.535709	-3.221702	2.053993
H	-4.196122	-3.620830	0.467096
C	-3.013539	-5.208522	1.364197
H	-2.188370	-5.291635	2.089450
H	-3.893953	-5.676801	1.829056
C	-2.628606	-5.961378	0.070921
H	-3.497440	-5.986348	-0.606701
H	-2.375477	-7.006247	0.301977
C	-1.447780	-5.267216	-0.644523
H	-0.542729	-5.349440	-0.022047
H	-1.227902	-5.775408	-1.594850
C	-1.748789	-3.772779	-0.908684
H	-2.602481	-3.706204	-1.599982
H	-0.891484	-3.293839	-1.396474
C	-3.108739	-0.539679	1.761553
H	-4.019502	-1.156267	1.796770
C	-2.280828	-0.811817	3.043639
H	-1.994583	-1.870843	3.102682
H	-1.343323	-0.241586	2.987990
C	-3.060683	-0.411594	4.318661
H	-2.433822	-0.586887	5.205350
H	-3.948722	-1.056032	4.423321
C	-3.508468	1.066467	4.264133
H	-4.102897	1.318636	5.154268

H	-2.617800	1.714970	4.281843
C	-4.322080	1.351821	2.981815
H	-4.584434	2.418385	2.926477
H	-5.270348	0.791665	3.024912
C	-3.547915	0.943462	1.703463
H	-4.186964	1.126065	0.828905
H	-2.663538	1.584521	1.589501
C	-3.355165	-0.663648	-1.232624
H	-3.483223	0.421446	-1.090056
C	-4.757980	-1.316750	-1.154433
H	-4.668069	-2.401746	-1.308013
H	-5.207346	-1.167968	-0.163093
C	-5.697020	-0.737647	-2.242057
H	-5.866498	0.332385	-2.041852
H	-6.678488	-1.231419	-2.188549
C	-5.093343	-0.901366	-3.655687
H	-5.031471	-1.973935	-3.900553
H	-5.753213	-0.441058	-4.405123
C	-3.679142	-0.280312	-3.733410
H	-3.757948	0.811625	-3.608772
H	-3.242335	-0.455224	-4.727508
C	-2.742230	-0.856059	-2.643451
H	-1.756574	-0.377629	-2.688301
H	-2.582402	-1.923930	-2.843442
P	2.551130	-0.347049	-0.131273
P	-2.124250	-1.099627	0.195164
Ru	0.118141	-0.213747	-0.023578
B	-0.350164	1.784734	-0.123734
H	0.368098	-1.338019	1.114102
H	0.215670	-1.452162	-1.050364
H	-0.143005	1.183507	-1.237096
H	0.010746	1.348160	1.019514

21 – Model systems (Table 16):

- **Model system-1 : bi-agostic BH_2**

19

wB97XD/Def2-TZVP Charge = 1 Multiplicity = 1 E(RwB97XD) = -1117.77965030

P	0.691236	1.997824	-0.000543
Ru	-0.203370	-0.134163	-0.000119
B	1.656626	-0.641227	0.002582
H	-0.273552	3.012052	-0.078923
H	1.558710	2.394313	-1.028712
H	1.422190	2.431416	1.115203
C	-1.867170	-1.592485	0.052359
C	-1.977959	-0.811287	-1.130973
C	-1.993733	-0.710244	1.163667
C	-2.154043	0.543181	-0.761890
C	-2.168439	0.603882	0.674802
H	-1.732053	-2.660643	0.100602
H	-1.940739	-0.990908	2.203765
H	-1.908341	-1.182929	-2.141244
H	-2.303538	1.367354	-1.440309
H	-2.325837	1.484707	1.276114
H	0.944168	-0.758284	1.134956

H	0.942653	-0.760974	-1.130524
Cl	3.345943	-0.787790	0.000101

- **Model system-2 : mono-agostic BH_2**

19
wB97XD/Def2-TZVP Charge = 1 Multiplicity = 1 E(RwB97XD) = -1117. 7637616

Ru	0.015224	0.009262	-0.148307
P	-1.012188	2.122851	-0.020495
H	-0.287191	3.129041	0.633645
H	-2.241125	2.216655	0.651056
H	-1.326165	2.783421	-1.217124
C	1.644120	-1.469169	-0.048534
C	1.964571	-0.439286	-0.977485
C	1.508711	-0.863519	1.233665
C	2.014439	0.795113	-0.274233
C	1.740113	0.523180	1.110243
H	2.276413	1.749547	-0.701954
H	1.737152	1.238084	1.916865
H	1.235905	-1.375305	2.144040
H	2.134687	-0.568498	-2.034673
H	1.565671	-2.522531	-0.263967
B	-1.174874	-1.387022	-1.050484
H	-0.843194	-0.212234	-1.635374
Cl	-2.107046	-1.218192	0.476138
H	-1.276761	-2.322031	-1.763470

- **Model system-3 : bi-agostic CH_2**

20
wB97XD/Def2-TZVP Charge = 1 Multiplicity = 1 E(RwB97XD) = -1591.16166163

Cl	2.544958	-1.821827	0.000175
C	1.773255	-0.246613	-0.000561
Ru	-0.593644	0.065506	-0.000778
P	-0.508852	2.433642	0.000192
C	-1.333932	-1.989041	0.002040
C	-1.795700	-1.285415	1.144955
C	-2.582284	-0.172946	0.712338
C	-2.582539	-0.174916	-0.712735
C	-1.796390	-1.288883	-1.142481
H	-1.747346	3.091750	0.003890
H	-1.583123	-1.536266	2.172997
H	-3.096539	0.524024	1.354336
H	-3.097109	0.520150	-1.356534
H	-1.584014	-1.542534	-2.169890
H	-0.713560	-2.871064	0.003163
H	0.119775	3.087537	-1.072442
H	0.126013	3.087434	1.069174
H	1.183438	-0.177814	0.950795
H	1.184785	-0.177915	-0.952614
Cl	2.917769	1.089749	0.000245