Proton-Transfer and H_2-Elimination Reactions of Trimethylamine Alane: Role of Dihydrogen Bonding and Lewis Acid-base Interactions.

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Supporting Information

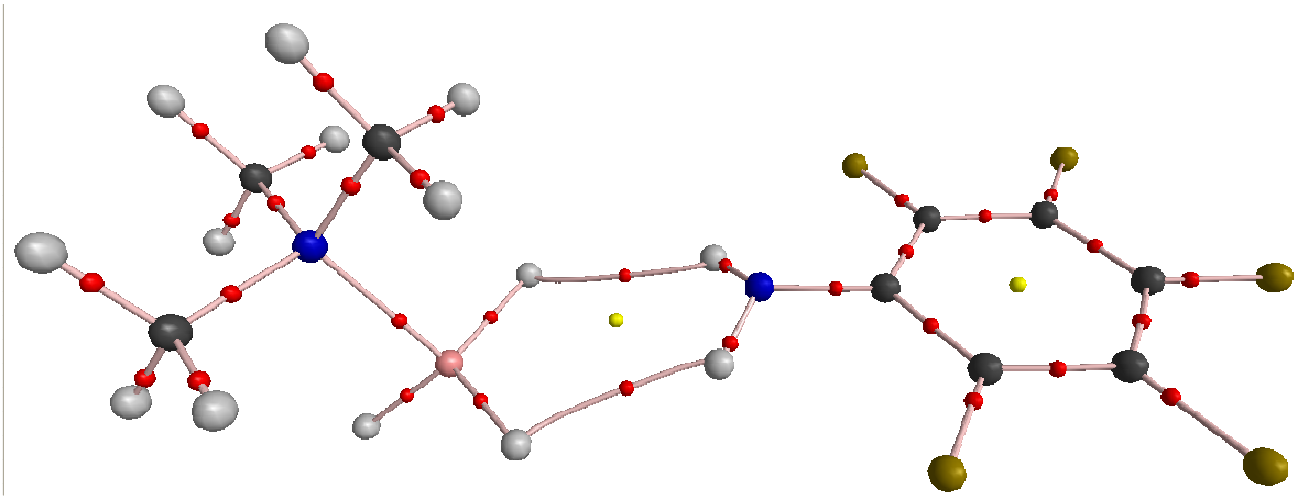


Figure S1. Molecular graph of TMAA/PFA bidentate cycle complex, color codes: ● - bond critical points, ● - ring points, ● - fluorine atoms, ● - carbon atoms, ● - nitrogen atoms, ● - hydrogen atoms, ● - aluminum atom.

B3LYP optimized structures of reactants (Cartesian coordinates)

Table S1. $(NMe_3)AlH_3$

13	0.000000000	0.000000000	1.690869000
1	-1.367198000	0.789352000	1.967838000
1	1.367198000	0.789352000	1.967838000
1	0.000000000	-1.578705000	1.967838000
7	0.000000000	0.000000000	-0.406505000
6	1.215362000	-0.701690000	-0.889642000
6	-1.215362000	-0.701690000	-0.889642000
6	0.000000000	1.403380000	-0.889642000
1	0.000000000	1.435016000	-1.985894000
1	-0.886598000	1.913370000	-0.511339000
1	0.886598000	1.913370000	-0.511339000
1	-1.242760000	-0.717508000	-1.985894000
1	-1.213728000	-1.724502000	-0.511339000
1	-2.100326000	-0.188868000	-0.511339000
1	1.242760000	-0.717508000	-1.985894000
1	2.100326000	-0.188868000	-0.511339000
1	1.213728000	-1.724502000	-0.511339000

Table S2. CH_3OH

8	-0.749439000	0.122069000	-0.000076000
1	-1.149610000	-0.752034000	0.000650000

6	0.667155000	-0.020471000	-0.000075000
1	1.083807000	0.987216000	0.000236000
1	1.029277000	-0.544218000	0.893179000
1	1.029106000	-0.544686000	-0.893002000

Table S3. CF_3CH_2OH

8	2.012519000	-0.081547000	0.112739000
1	2.056079000	-0.721691000	-0.606260000
6	0.904910000	0.763675000	-0.085476000
1	0.922559000	1.516525000	0.703077000
1	0.923475000	1.269606000	-1.057757000
6	-0.418552000	0.015894000	0.007179000
9	-0.624429000	-0.538821000	1.213012000
9	-0.470499000	-0.986193000	-0.908436000
9	-1.451785000	0.848405000	-0.245819000

Table S4. CF_3OH

8	-1.285390000	0.448626000	0.005641000
1	-1.877422000	-0.314840000	0.006359000
6	-0.008670000	0.024862000	-0.000061000
9	0.792601000	1.086064000	-0.006415000
9	0.288014000	-0.730688000	1.083595000
9	0.276337000	-0.735747000	-1.082860000

Table S5. Pyrrole

6	0.000000000	1.124762000	0.331131000
6	0.000000000	0.712306000	-0.982494000
6	0.000000000	-0.712306000	-0.982494000
6	0.000000000	-1.124762000	0.331131000
1	0.000000000	2.111941000	0.763695000
1	0.000000000	1.360480000	-1.844896000
1	0.000000000	-1.360480000	-1.844896000
1	0.000000000	-2.111941000	0.763695000
7	0.000000000	0.000000000	1.121601000
1	0.000000000	0.000000000	2.127542000

Table S6. C_6H_5CCH

6	0.000000000	0.000000000	0.593767000
6	0.000000000	1.210911000	-0.119257000
6	0.000000000	-1.210911000	-0.119257000
1	0.000000000	2.146458000	0.426866000
1	0.000000000	-2.146458000	0.426866000
6	0.000000000	1.206570000	-1.509967000

6	0.000000000	-1.206570000	-1.509967000
1	0.000000000	2.147174000	-2.049046000
1	0.000000000	-2.147174000	-2.049046000
6	0.000000000	0.000000000	-2.209578000
1	0.000000000	0.000000000	-3.293640000
6	0.000000000	0.000000000	2.021950000
6	0.000000000	0.000000000	3.227054000
1	0.000000000	0.000000000	4.289532000

Table S7. $C_6F_5NH_2$

7	0.078804000	2.787719000	0.000000000
1	-0.213775000	3.247975000	0.848552000
1	-0.213775000	3.247975000	-0.848552000
9	-0.006176000	1.344244000	-2.357580000
6	0.003306000	0.670941000	-1.188189000
6	-0.000387000	-0.715889000	-1.198892000
9	-0.006176000	-1.375613000	-2.361574000
9	0.000161000	-2.758861000	0.000000000
6	0.000981000	-1.420252000	0.000000000
6	-0.000387000	-0.715889000	1.198892000
9	-0.006176000	-1.375613000	2.361574000
9	-0.006176000	1.344244000	2.357580000
6	0.003306000	0.670941000	1.188189000
6	0.009313000	1.407552000	0.000000000

Table S8. $(NMe_3)AlH_4^+$

13	-1.561660000	0.288185000	-0.000213000
1	-2.063714000	0.556431000	1.452220000
1	-2.120705000	-1.779958000	0.380738000
1	-2.064577000	0.550082000	-1.453505000
7	0.409902000	-0.017471000	0.000014000
6	0.872391000	-0.747519000	-1.226476000
1	1.963644000	-0.795192000	-1.235651000
1	0.475191000	-1.763028000	-1.222300000
1	0.525787000	-0.225547000	-2.117996000
6	0.872641000	-0.744455000	1.228223000
1	0.525958000	-0.220404000	2.118496000
1	0.475758000	-1.760097000	1.226564000
1	1.963911000	-0.791851000	1.237506000
6	0.994953000	1.369339000	-0.001787000
1	0.673926000	1.907777000	0.892039000
1	2.085549000	1.307840000	-0.002355000
1	0.672955000	1.905890000	-0.896416000
1	-2.121324000	-1.780239000	-0.376428000

B3LYP optimized structures of dihydrogen bonded complexes of $(NMe_3)AlH_3$ (Cartesian coordinates)

Table S9. CH_3OH

13	-0.844614000	1.687709000	-0.000055000
1	0.766388000	1.749811000	0.000042000
1	-1.540646000	2.119951000	1.372734000
1	-1.540779000	2.119699000	-1.372843000
7	-1.224653000	-0.361100000	0.000155000
6	-2.699860000	-0.535119000	0.000948000
1	-2.958976000	-1.600016000	0.000930000
1	-3.119596000	-0.060610000	0.888277000
1	-3.120593000	-0.060377000	-0.885793000
6	-0.645673000	-0.993710000	1.216482000
1	0.440041000	-0.901956000	1.190725000
1	-1.035561000	-0.490077000	2.101620000
1	-0.915876000	-2.055380000	1.254849000
6	-0.647001000	-0.993769000	-1.216759000
1	0.438734000	-0.901910000	-1.192392000
1	-0.917064000	-2.055493000	-1.254663000
1	-1.038020000	-0.490329000	-2.101507000
1	2.024759000	0.604066000	-0.002920000
8	2.484219000	-0.252880000	-0.002517000
6	3.890364000	-0.038052000	0.001481000
1	4.367430000	-1.019201000	0.004280000
1	4.223496000	0.506938000	-0.890044000
1	4.218077000	0.509311000	0.893564000

Table S10. CF_3CH_2OH

13	2.329706000	1.495394000	-0.680340000
1	3.200162000	2.319480000	0.373542000
1	0.736415000	1.758616000	-0.610844000
1	2.898814000	1.277511000	-2.155831000
7	2.467376000	-0.429315000	0.093575000
6	1.677484000	-1.367886000	-0.747334000
1	1.773669000	-2.391495000	-0.368313000
1	0.627866000	-1.077505000	-0.732980000
1	2.043496000	-1.325718000	-1.773396000
6	1.964882000	-0.462052000	1.494240000
1	2.529214000	0.252431000	2.093932000
1	0.909722000	-0.190108000	1.515446000
1	2.086534000	-1.466195000	1.915908000
6	3.899798000	-0.824982000	0.070285000
1	4.476832000	-0.128681000	0.679240000
1	4.021825000	-1.839921000	0.464798000
1	4.268773000	-0.788207000	-0.954962000
9	-3.954770000	-0.198247000	-0.684156000

6	-2.720938000	-0.193846000	-0.129948000
9	-1.840344000	-0.526635000	-1.106529000
6	-2.411125000	1.169789000	0.475809000
1	-3.160337000	1.353293000	1.249547000
1	-2.540175000	1.913678000	-0.317714000
8	-1.138332000	1.210944000	1.062775000
1	-0.472642000	1.473575000	0.395940000
9	-2.683988000	-1.185048000	0.783414000

Table S11. CF_3OH

13	-2.133540000	-1.193417000	0.000000000
1	-1.476142000	0.286330000	0.000000000
1	-2.813942000	-1.604447000	1.380806000
1	-2.813942000	-1.604447000	-1.380806000
7	-0.444181000	-2.404036000	0.000000000
6	-0.915213000	-3.814738000	0.000000000
1	-0.061962000	-4.501773000	0.000000000
1	-1.522936000	-3.992903000	0.887425000
1	-1.522936000	-3.992903000	-0.887425000
6	0.373645000	-2.153286000	1.217608000
1	0.743419000	-1.128382000	1.206059000
1	-0.244700000	-2.301687000	2.103084000
1	1.226527000	-2.840315000	1.250937000
6	0.373645000	-2.153286000	-1.217608000
1	0.743419000	-1.128382000	-1.206059000
1	1.226527000	-2.840315000	-1.250937000
1	-0.244700000	-2.301687000	-2.103084000
1	-0.172365000	0.981810000	0.000000000
8	0.787222000	1.243227000	0.000000000
6	0.933797000	2.568394000	0.000000000
9	0.373645000	3.159822000	-1.084363000
9	0.373645000	3.159822000	1.084363000
9	2.240043000	2.867407000	0.000000000

Table S12. Pyrrole

13	-2.094222000	1.612070000	-0.153291000
1	-3.048679000	1.776351000	-1.424956000
1	-0.534075000	1.909518000	-0.414348000
1	-2.651262000	2.050994000	1.279263000
7	-2.094614000	-0.465321000	0.054551000
6	-1.239969000	-0.865533000	1.203315000
6	-3.494837000	-0.897462000	0.299727000
6	-1.587782000	-1.096571000	-1.191252000
1	-1.624267000	-2.188832000	-1.109866000
1	-2.200634000	-0.774564000	-2.033404000
1	-0.556588000	-0.786907000	-1.360045000
1	-3.545537000	-1.986331000	0.412941000

1	-3.865186000	-0.420974000	1.207573000
1	-4.119359000	-0.590506000	-0.539481000
1	-1.279859000	-1.950925000	1.348869000
1	-0.208344000	-0.570744000	1.011979000
1	-1.594340000	-0.366279000	2.105391000
1	4.298393000	-1.360750000	-1.135738000
6	3.650525000	-0.682883000	-0.601862000
6	3.677119000	-0.395314000	0.792718000
1	4.349067000	-0.811927000	1.527005000
6	2.687691000	0.532941000	1.039374000
1	2.384851000	1.017682000	1.953532000
1	1.265994000	1.425569000	-0.265659000
7	2.068651000	0.816217000	-0.153361000
6	2.645326000	0.079360000	-1.158649000
1	2.308020000	0.168208000	-2.178838000

Table S13. C_6H_5CCH

13	4.116858000	1.336449000	-0.099672000
1	2.730562000	2.142662000	-0.153552000
1	4.940873000	1.242512000	-1.469035000
1	4.952691000	1.446660000	1.261162000
7	3.422841000	-0.631452000	0.050515000
6	4.595410000	-1.538717000	0.123729000
1	4.269638000	-2.582383000	0.203387000
1	5.202389000	-1.415365000	-0.773434000
1	5.197557000	-1.279025000	0.994471000
6	2.605454000	-0.962345000	-1.144735000
1	1.742919000	-0.297567000	-1.189533000
1	3.208997000	-0.823825000	-2.042007000
1	2.257243000	-2.000730000	-1.095845000
6	2.599428000	-0.774842000	1.278282000
1	1.737106000	-0.111325000	1.215659000
1	2.250892000	-1.808419000	1.388084000
1	3.198470000	-0.499754000	2.146647000
6	-2.766136000	0.503455000	-0.039391000
6	-3.426853000	0.315690000	1.186799000
6	-3.376971000	0.043812000	-1.218888000
1	-2.961824000	0.672231000	2.098026000
1	-2.873495000	0.190472000	-2.166911000
6	-4.665083000	-0.316388000	1.228268000
6	-4.615328000	-0.587439000	-1.169058000
1	-5.165395000	-0.453608000	2.180297000
1	-5.076830000	-0.935973000	-2.086113000
6	-5.263156000	-0.769922000	0.052632000
1	-6.228910000	-1.261050000	0.088127000
6	-1.495344000	1.154129000	-0.086655000
6	-0.423515000	1.705703000	-0.126823000
1	0.530641000	2.181998000	-0.162259000

Table S14. $C_6F_5NH_2$ monodentate

13	3.906663000	1.624949000	-0.463067000
1	4.831699000	2.351294000	0.618978000
1	4.341138000	1.684293000	-2.000030000
1	2.323139000	1.700877000	-0.185875000
7	4.285235000	-0.375563000	-0.023152000
6	3.509526000	-1.246907000	-0.944410000
6	3.897119000	-0.658838000	1.383014000
6	5.738741000	-0.624896000	-0.202650000
1	5.978551000	-1.671455000	0.016625000
1	6.301972000	0.024477000	0.467789000
1	6.018577000	-0.397710000	-1.231576000
1	4.118535000	-1.701195000	1.638970000
1	2.829694000	-0.478152000	1.506549000
1	4.450346000	0.003445000	2.049263000
1	3.721550000	-2.302651000	-0.740779000
1	3.782422000	-1.014219000	-1.973815000
1	2.444851000	-1.061998000	-0.806183000
7	-0.428919000	1.985167000	0.462954000
1	0.544889000	1.774444000	0.261861000
1	-0.707546000	2.924627000	0.224248000
9	-3.085805000	2.603791000	0.029385000
6	-2.719494000	1.304709000	0.048836000
6	-3.685254000	0.324914000	-0.120132000
9	-4.965613000	0.669583000	-0.296630000
9	-4.249467000	-1.973462000	-0.274985000
6	-3.324070000	-1.017987000	-0.111608000
6	-1.987347000	-1.352650000	0.066913000
9	-1.615357000	-2.639422000	0.076429000
9	0.257047000	-0.712939000	0.414784000
6	-1.036814000	-0.357531000	0.237118000
6	-1.363720000	1.003252000	0.235319000

Table S15. $C_6F_5NH_2$ bidentate

13	-3.707198000	-0.012482000	1.405964000
1	-4.866310000	0.083843000	2.499063000
1	-2.927248000	-1.408509000	1.257617000
1	-2.780013000	1.281800000	1.186520000
7	-4.821186000	0.003863000	-0.354517000
6	-3.910809000	-0.096371000	-1.524562000
6	-5.592918000	1.271428000	-0.425030000
6	-5.754474000	-1.152168000	-0.343432000
1	-6.359461000	-1.166163000	-1.257100000
1	-6.410017000	-1.077990000	0.524345000
1	-5.181816000	-2.077290000	-0.274639000
1	-6.200001000	1.301028000	-1.336867000
1	-4.902032000	2.114595000	-0.422661000
1	-6.243755000	1.346251000	0.446321000

1	-4.484098000	-0.083165000	-2.458449000
1	-3.342207000	-1.023866000	-1.461645000
1	-3.215168000	0.742465000	-1.514964000
7	-0.220550000	-0.104438000	0.202162000
1	-0.696950000	0.718552000	0.546632000
1	-0.628183000	-0.964895000	0.540497000
9	1.312712000	-2.407861000	0.128406000
6	1.935340000	-1.212146000	0.064899000
6	3.315367000	-1.171300000	-0.065063000
9	4.015778000	-2.309752000	-0.130100000
9	5.305891000	0.102403000	-0.255085000
6	3.972713000	0.052150000	-0.127279000
6	3.227034000	1.223160000	-0.053607000
9	3.842440000	2.410316000	-0.106761000
9	1.140035000	2.308554000	0.150052000
6	1.847647000	1.162183000	0.075938000
6	1.155311000	-0.052485000	0.137414000

B3LYP optimized structures of Lewis complexes of $(NMe_3)AlH_3$ (Cartesian coordinates)

Table S16. CH_3OH

13	0.580042000	-0.185760000	-0.043570000
1	0.687325000	0.512942000	-1.487282000
1	0.468785000	-1.785397000	0.141613000
1	0.775191000	0.731717000	1.272272000
7	-1.609891000	0.046759000	0.006996000
6	-2.117350000	-0.480696000	1.289419000
1	-3.209914000	-0.385613000	1.351547000
1	-1.840824000	-1.531596000	1.379895000
1	-1.659701000	0.071562000	2.110788000
6	-2.192215000	-0.709934000	-1.119739000
1	-1.790084000	-0.324796000	-2.057354000
1	-1.915368000	-1.760735000	-1.028259000
1	-3.287120000	-0.622042000	-1.130827000
6	-1.939980000	1.480409000	-0.119195000
1	-1.535204000	1.860561000	-1.057561000
1	-3.026793000	1.638625000	-0.101278000
1	-1.481654000	2.027985000	0.704939000
1	2.968428000	-1.262830000	0.515780000
8	2.761416000	-0.550770000	-0.099380000
6	3.700641000	0.527346000	0.038630000
1	3.626586000	0.987797000	1.027278000
1	4.717733000	0.171905000	-0.143544000
1	3.433403000	1.260897000	-0.720215000

Table S17. CF_3CH_2OH

13	1.259328000	-0.242970000	0.009523000

1	0.967570000	0.808292000	1.187682000
1	1.370725000	-1.822297000	0.276901000
1	1.037778000	0.262196000	-1.506490000
7	3.394287000	0.082362000	0.004964000
6	4.009060000	-0.754064000	-1.049180000
1	5.098390000	-0.621342000	-1.068893000
1	3.775798000	-1.801824000	-0.857965000
1	3.593748000	-0.474424000	-2.017736000
6	3.932964000	-0.297269000	1.330013000
1	3.455852000	0.310256000	2.099507000
1	3.706954000	-1.346325000	1.522881000
1	5.019356000	-0.146512000	1.369399000
6	3.665058000	1.512206000	-0.260701000
1	3.186528000	2.117289000	0.509704000
1	4.744092000	1.713001000	-0.263135000
1	3.244592000	1.783334000	-1.229445000
9	-4.164310000	1.135935000	-0.388882000
6	-3.374676000	0.117006000	0.012960000
9	-3.783425000	-0.998984000	-0.643452000
6	-1.919811000	0.426732000	-0.298601000
1	-1.606240000	1.279326000	0.303445000
1	-1.842831000	0.686624000	-1.358560000
8	-1.071864000	-0.653351000	0.047721000
1	-1.258996000	-1.418912000	-0.510295000
9	-3.599514000	-0.086669000	1.320749000

B3LYP optimized structures of transition states of proton transfer from dihydrogen bonded complexes of $(NMe_3)AlH_3$ (Cartesian coordinates)

Table S18. CH_3OH

13	-0.491433000	1.335277000	-0.193712000
1	0.343388000	2.238183000	0.822567000
1	-2.093915000	2.102349000	0.109834000
1	-0.390797000	1.319285000	-1.785632000
7	1.128091000	-0.188891000	0.003348000
6	0.910932000	-1.389257000	-0.828782000
1	1.796471000	-2.038621000	-0.822795000
1	0.066070000	-1.955700000	-0.439979000
1	0.696748000	-1.085752000	-1.854373000
6	1.279123000	-0.574052000	1.423716000
1	1.436269000	0.324054000	2.021369000
1	0.366361000	-1.063290000	1.763578000
1	2.131419000	-1.252808000	1.559403000
6	2.350483000	0.505763000	-0.457755000
1	2.501419000	1.404726000	0.139597000
1	3.227511000	-0.147341000	-0.363931000
1	2.229085000	0.795750000	-1.502406000
1	-2.246083000	1.018271000	0.473866000

8	-1.805764000	-0.015035000	0.526477000
6	-2.635383000	-0.902895000	-0.230429000
1	-3.412967000	-1.312659000	0.418502000
1	-3.106015000	-0.375984000	-1.068423000
1	-2.037801000	-1.723903000	-0.628673000

Table S19. CF_3CH_2OH

13	-1.555803000	1.607211000	-0.113093000
1	-1.613418000	1.733671000	-1.699401000
1	-0.370523000	2.820631000	0.431832000
1	-2.710447000	2.030245000	0.903371000
7	-2.283843000	-0.446700000	-0.000810000
6	-2.208032000	-0.919234000	1.403242000
1	-2.654453000	-1.916218000	1.502277000
1	-1.163616000	-0.959238000	1.712320000
1	-2.744126000	-0.219911000	2.045155000
6	-1.562729000	-1.390705000	-0.884006000
1	-1.538610000	-0.991199000	-1.898869000
1	-0.546538000	-1.524291000	-0.518913000
1	-2.061698000	-2.367498000	-0.896990000
6	-3.703014000	-0.374289000	-0.424437000
1	-3.755578000	-0.029192000	-1.458086000
1	-4.177726000	-1.359899000	-0.349535000
1	-4.233608000	0.334741000	0.210250000
1	0.261390000	1.884101000	0.496458000
8	0.359959000	0.780262000	0.298694000
1	1.744044000	1.491054000	-1.081072000
6	1.370333000	0.551439000	-0.657831000
1	1.009494000	-0.072879000	-1.479298000
6	2.547675000	-0.169207000	-0.019978000
9	3.096348000	0.532112000	0.988114000
9	2.192158000	-1.376634000	0.474555000
9	3.514015000	-0.383376000	-0.944348000

Table S20. CF_3OH

13	1.163930000	1.568443000	-0.136248000
1	2.301328000	2.412309000	0.578725000
1	-0.065047000	2.107589000	1.044296000
1	0.674089000	1.782289000	-1.612853000
7	1.972822000	-0.307417000	0.010897000
6	1.354478000	-1.274279000	-0.947775000
1	1.874743000	-2.234948000	-0.881321000
1	0.303236000	-1.397251000	-0.705471000
1	1.446118000	-0.882226000	-1.960654000
6	1.855208000	-0.837395000	1.402427000
1	2.293343000	-0.120618000	2.099288000
1	0.802326000	-0.984529000	1.634431000

1	2.393090000	-1.787322000	1.483068000
6	3.416987000	-0.150649000	-0.332530000
1	3.893230000	0.526583000	0.374676000
1	3.911904000	-1.125861000	-0.300312000
1	3.512780000	0.261237000	-1.338985000
1	-0.529665000	1.385098000	0.890569000
8	-0.969301000	0.093092000	0.556815000
6	-2.132471000	-0.092317000	0.042092000
9	-3.089955000	-0.474757000	0.946296000
9	-2.653918000	1.021928000	-0.582251000
9	-2.140919000	-1.080182000	-0.925190000

Table S21. Pyrrole

13	-0.759539000	1.628418000	0.000071000
1	-1.352544000	1.845376000	-1.460755000
1	0.433195000	2.923891000	0.000412000
1	-1.353018000	1.845294000	1.460728000
7	-1.664938000	-0.432273000	-0.000037000
6	-1.317325000	-1.204051000	1.212549000
6	-3.117679000	-0.149545000	-0.000337000
6	-1.316850000	-1.204184000	-1.212402000
1	-1.892232000	-2.138023000	-1.259098000
1	-1.538468000	-0.603534000	-2.095429000
1	-0.253157000	-1.439980000	-1.203754000
1	-3.694179000	-1.083142000	-0.000422000
1	-3.375237000	0.430597000	0.886721000
1	-3.374883000	0.430539000	-0.887535000
1	-1.892612000	-2.137958000	1.259055000
1	-0.253600000	-1.439707000	1.204397000
1	-1.539421000	-0.603354000	2.095422000
1	3.381315000	-1.374898000	-1.362276000
6	2.779120000	-0.751885000	-0.717847000
6	2.779064000	-0.752117000	0.717708000
1	3.381215000	-1.375331000	1.361984000
6	1.885817000	0.200144000	1.122958000
1	1.616104000	0.529439000	2.114602000
1	1.100614000	1.975317000	0.000290000
7	1.292988000	0.786948000	0.000118000
6	1.885904000	0.200506000	-1.122864000
1	1.616252000	0.530102000	-2.114425000

B3LYP optimized structures of transition states of proton transfer from Lewis complexes of $(NMe_3)AlH_3$ (Cartesian coordinates)

Table S22. CH_3OH

13	0.647190000	-0.447522000	-0.211554000

1	0.318186000	-1.993120000	-0.024049000
1	0.713392000	0.598558000	1.351047000
1	0.724423000	0.336470000	-1.603620000
7	-1.487690000	0.069469000	0.004654000
6	-1.687756000	1.532387000	-0.070085000
1	-2.754736000	1.785835000	-0.025374000
1	-1.171976000	2.011461000	0.762748000
1	-1.267250000	1.905139000	-1.004435000
6	-2.023160000	-0.453341000	1.280086000
1	-1.843436000	-1.527383000	1.331265000
1	-1.509309000	0.027425000	2.113048000
1	-3.100412000	-0.260346000	1.361426000
6	-2.172114000	-0.587346000	-1.131152000
1	-2.003825000	-1.663355000	-1.079474000
1	-3.250730000	-0.387628000	-1.105455000
1	-1.758239000	-0.211552000	-2.067364000
1	1.654720000	0.369630000	1.151583000
8	2.461409000	-0.284053000	0.438680000
6	3.551773000	0.351820000	-0.210811000
1	3.333258000	1.403460000	-0.439403000
1	4.436779000	0.307461000	0.430543000
1	3.775781000	-0.159250000	-1.152526000

Table S23. CF_3CH_2OH

13	-1.104972000	-0.617534000	0.039011000
1	-1.440373000	-1.654174000	1.192324000
1	-0.773673000	1.118341000	0.544248000
1	-1.079138000	-0.890420000	-1.534078000
7	-3.155167000	0.118239000	-0.022337000
6	-3.297917000	1.213573000	-1.007581000
1	-4.342934000	1.538778000	-1.080773000
1	-2.681800000	2.059549000	-0.701734000
1	-2.959041000	0.865929000	-1.983666000
6	-3.578209000	0.582898000	1.318366000
1	-3.443751000	-0.224883000	2.037867000
1	-2.960076000	1.428756000	1.620808000
1	-4.630717000	0.891735000	1.310123000
6	-3.986559000	-1.036142000	-0.436506000
1	-3.867588000	-1.844514000	0.285500000
1	-5.044653000	-0.752981000	-0.491727000
1	-3.656391000	-1.386269000	-1.415163000
1	0.138745000	0.714416000	0.501115000
8	0.840681000	-0.306148000	0.343849000
6	1.839968000	-0.312509000	-0.636033000
1	1.638944000	0.393596000	-1.452961000
1	1.952093000	-1.311011000	-1.071131000
9	4.134866000	0.091114000	-1.001054000
6	3.182020000	0.075002000	-0.034369000
9	3.593006000	-0.781081000	0.918764000

9	3.152116000	1.308374000	0.517223000

B3LYP optimized structures of H_2 elimination products (Cartesian coordinates)

Table S24. CH_3OH

13	-1.064623000	0.553821000	0.000000000
1	-1.397873000	1.307228000	1.371376000
1	-1.397873000	1.307228000	-1.371376000
7	1.006447000	0.566344000	0.000000000
6	1.488046000	-0.140158000	-1.215230000
1	2.583816000	-0.166225000	-1.233762000
1	1.088596000	-1.153452000	-1.211088000
1	1.121636000	0.379712000	-2.100828000
6	1.488046000	-0.140158000	1.215230000
1	1.121636000	0.379712000	2.100828000
1	1.088596000	-1.153452000	1.211088000
1	2.583816000	-0.166225000	1.233762000
6	1.488046000	1.968622000	0.000000000
1	1.112154000	2.479813000	0.887055000
1	2.583610000	2.000742000	0.000000000
1	1.112154000	2.479813000	-0.887055000
8	-1.226249000	-1.193313000	0.000000000
6	-2.318671000	-2.073805000	0.000000000
1	-1.959125000	-3.109953000	0.000000000
1	-2.954486000	-1.944761000	0.888351000
1	-2.954486000	-1.944761000	-0.888351000

Table S25. CF_3CH_2OH

13	1.265853000	1.474002000	-0.139564000
1	2.079513000	2.323427000	0.933233000
1	1.359096000	1.829885000	-1.693678000
7	2.242681000	-0.345682000	-0.006422000
6	1.671345000	-1.303774000	-0.989457000
1	2.188130000	-2.267926000	-0.924620000
1	0.611517000	-1.442707000	-0.782584000
1	1.785980000	-0.898408000	-1.995017000
6	2.067187000	-0.876901000	1.372082000
1	2.489570000	-0.169116000	2.085880000
1	1.003011000	-0.990056000	1.575395000
1	2.572353000	-1.843840000	1.474537000
6	3.684094000	-0.132358000	-0.288327000
1	4.090314000	0.584561000	0.425652000
1	4.234827000	-1.076206000	-0.209446000
1	3.800586000	0.267365000	-1.296691000
8	-0.339821000	0.965330000	0.388308000
6	-1.621821000	1.137073000	-0.096754000
1	-1.657240000	1.451061000	-1.150699000

1	-2.190299000	1.871442000	0.491000000
9	-3.670681000	0.010461000	-0.474609000
6	-2.407707000	-0.165227000	-0.017787000
9	-2.499086000	-0.646108000	1.239133000
9	-1.848259000	-1.148493000	-0.771044000

Table S26. CF_3OH

13	0.541387000	1.321231000	0.004313000
1	0.505764000	1.778042000	-1.512486000
1	1.053996000	2.252919000	1.177772000
7	1.956660000	-0.180963000	0.001024000
6	3.274132000	0.438294000	-0.298036000
1	4.061553000	-0.322814000	-0.304639000
1	3.233783000	0.921701000	-1.274967000
1	3.503291000	1.187349000	0.460635000
6	1.628346000	-1.192613000	-1.040679000
1	0.654139000	-1.630366000	-0.828245000
1	1.588757000	-0.705727000	-2.015094000
1	2.389832000	-1.979807000	-1.056331000
6	1.997022000	-0.830727000	1.339279000
1	1.020049000	-1.259339000	1.558640000
1	2.758529000	-1.617832000	1.355945000
1	2.231873000	-0.082069000	2.096262000
8	-0.870484000	0.336940000	0.534411000
6	-1.994806000	-0.081405000	0.045895000
9	-2.748070000	0.903486000	-0.523656000
9	-1.830746000	-1.032160000	-0.940093000
9	-2.776796000	-0.665562000	0.988774000

Table S27. Pyrrole

13	-0.507728000	-0.245108000	1.341979000
1	-0.891160000	1.007905000	2.244114000
1	-0.885037000	-1.737026000	1.744819000
7	-1.798078000	0.049563000	-0.275731000
6	-1.555802000	-0.988225000	-1.312295000
6	-3.189414000	-0.061300000	0.231096000
6	-1.580811000	1.398958000	-0.859430000
1	-2.271546000	1.569742000	-1.692883000
1	-1.747407000	2.153850000	-0.090631000
1	-0.553584000	1.476676000	-1.215226000
1	-3.907748000	0.084124000	-0.583431000
1	-3.336475000	-1.048645000	0.670014000
1	-3.355800000	0.695523000	0.998350000
1	-2.241543000	-0.851989000	-2.156248000
1	-0.525990000	-0.914098000	-1.661735000
1	-1.711565000	-1.976077000	-0.877689000
1	3.802303000	1.507363000	-0.667988000

6	3.049748000	0.792397000	-0.370295000
6	3.057694000	-0.611230000	-0.610809000
1	3.817720000	-1.177963000	-1.127827000
6	1.913289000	-1.120540000	-0.036155000
1	1.568991000	-2.142873000	0.019285000
7	1.186264000	-0.098465000	0.551304000
6	1.901161000	1.068592000	0.339525000
1	1.546818000	2.010298000	0.732519000

B3LYP optimized structures of complexes, transition states and H_2 elimination products of $(NMe_3)AlH_3$ with CH_3OH dimer (Cartesian coordinates)

Table S28. Cooperative dihydrogen bonded complex

13	-1.558248000	-1.730408000	-0.279911000
1	-2.319524000	-1.957515000	-1.666279000
1	-2.156517000	-2.406939000	1.039228000
1	0.049944000	-1.764590000	-0.378949000
7	-1.967701000	0.273303000	0.075017000
6	-1.343805000	0.718828000	1.351091000
6	-1.461698000	1.112472000	-1.045880000
6	-3.444707000	0.403289000	0.169420000
1	-3.723165000	1.447041000	0.353712000
1	-3.898583000	0.067049000	-0.763262000
1	-3.812035000	-0.218881000	0.986146000
1	-1.786390000	2.150922000	-0.913118000
1	-0.372365000	1.085814000	-1.053770000
1	-1.855381000	0.728641000	-1.987728000
1	-1.657717000	1.742568000	1.585245000
1	-1.657000000	0.052111000	2.155257000
1	-0.259221000	0.703589000	1.250246000
1	1.654978000	-1.490981000	-0.477983000
8	2.569864000	-1.157920000	-0.414677000
1	2.920556000	-2.120189000	1.414504000
6	3.332725000	-2.043776000	0.401963000
1	3.385332000	-3.044505000	-0.039619000
1	4.343081000	-1.637882000	0.463727000
1	2.199307000	0.584845000	-0.066620000
8	1.792103000	1.458912000	0.088966000
6	2.759684000	2.471635000	-0.140891000
1	3.605747000	2.397764000	0.554597000
1	2.273223000	3.436333000	0.016823000
1	3.147923000	2.444357000	-1.166972000

Table S29. Ring complex

1	-0.290141000	-0.798349000	0.785701000
1	0.116595000	0.687300000	-1.521758000

1	0.744585000	1.838776000	0.948970000
7	2.264508000	-0.238546000	-0.028775000
6	3.124071000	0.759385000	-0.694343000
1	4.159709000	0.401040000	-0.773263000
1	2.735167000	0.959581000	-1.693377000
1	3.106543000	1.687341000	-0.121905000
6	2.245911000	-1.490857000	-0.807145000
1	1.591581000	-2.211249000	-0.314804000
1	1.853804000	-1.287951000	-1.804344000
1	3.253573000	-1.920090000	-0.894685000
6	2.751277000	-0.495656000	1.340240000
1	2.092163000	-1.214911000	1.827982000
1	3.775463000	-0.893434000	1.329565000
1	2.731523000	0.434637000	1.908771000
1	-1.919640000	-1.310187000	0.733271000
8	-2.871048000	-1.170462000	0.556649000
6	-3.317085000	-2.106937000	-0.422807000
1	-2.746194000	-2.022907000	-1.354460000
1	-3.245783000	-3.133711000	-0.048941000
1	-4.364522000	-1.885054000	-0.629310000
1	-2.442073000	0.542490000	0.309012000
8	-1.793030000	1.279287000	0.323055000
6	-2.298720000	2.463779000	-0.299898000
1	-3.244820000	2.756513000	0.161611000
1	-2.433767000	2.316838000	-1.375556000
1	-1.562034000	3.249499000	-0.135245000
13	0.193586000	0.601906000	0.086944000

Table S30. Transition state of proton transfer from cooperative complex

13	-1.056258000	1.155554000	-1.039317000
1	-1.456273000	0.328772000	-2.344325000
1	0.083379000	2.260902000	-1.864887000
1	-2.007573000	2.124830000	-0.206874000
7	-1.514690000	-0.630351000	0.148985000
6	-1.194958000	-0.502095000	1.588181000
1	-1.584668000	-1.360541000	2.149514000
1	-0.114768000	-0.462860000	1.716663000
1	-1.645950000	0.410725000	1.980685000
6	-0.834836000	-1.828650000	-0.406860000
1	-1.050278000	-1.894190000	-1.473374000
1	0.242533000	-1.749865000	-0.258864000
1	-1.197141000	-2.736454000	0.091893000
6	-2.980351000	-0.784907000	-0.012843000
1	-3.220158000	-0.858577000	-1.073989000
1	-3.329173000	-1.689102000	0.500330000
1	-3.487550000	0.086166000	0.403210000
1	0.743853000	1.865821000	-1.024419000
6	1.048660000	2.158549000	1.017493000
1	2.121012000	2.300127000	1.169794000

1	0.580003000	3.126354000	0.813155000
1	0.610685000	1.738602000	1.923028000
1	2.015664000	-0.196182000	0.011720000
8	0.833388000	1.258294000	-0.084327000
8	2.444565000	-1.046577000	0.206060000
6	3.725347000	-1.085242000	-0.406808000
1	4.393918000	-0.307885000	-0.014703000
1	3.664657000	-0.977888000	-1.497257000
1	4.165216000	-2.058162000	-0.181920000

Table S31. Transition state of proton transfer from ring complex

1	-0.249367000	-0.952008000	0.349153000
1	0.323034000	0.812134000	-1.753604000
1	0.544966000	1.805014000	0.910573000
7	2.175169000	-0.180732000	0.010643000
6	3.088906000	0.895531000	-0.414679000
1	4.137293000	0.570169000	-0.363067000
1	2.853196000	1.183694000	-1.439964000
1	2.949455000	1.762698000	0.231616000
6	2.324496000	-1.347009000	-0.876172000
1	1.636950000	-2.134137000	-0.562795000
1	2.077854000	-1.055539000	-1.897715000
1	3.350131000	-1.741271000	-0.849532000
6	2.453241000	-0.556675000	1.407703000
1	1.762241000	-1.341868000	1.719000000
1	3.482834000	-0.922813000	1.526567000
1	2.305189000	0.311930000	2.050396000
1	-1.188124000	-1.170629000	0.496440000
8	-2.436626000	-1.205290000	0.618225000
6	-3.067470000	-2.028190000	-0.366835000
1	-2.649747000	-1.848791000	-1.363485000
1	-2.920550000	-3.074693000	-0.094191000
1	-4.138183000	-1.814125000	-0.385142000
1	-2.408549000	-0.145813000	0.326930000
8	-1.818134000	0.990599000	-0.045874000
6	-2.441581000	2.260727000	0.021963000
1	-3.453866000	2.159674000	0.427202000
1	-2.514148000	2.714662000	-0.973871000
1	-1.877226000	2.939068000	0.673147000
13	0.049459000	0.736845000	-0.177911000

Table S32. Product of H_2 elimination

1	0.911849000	0.858898000	-2.311863000
1	1.612023000	2.392839000	-0.110834000
7	1.581470000	-0.468578000	0.101385000
6	3.051250000	-0.365582000	-0.086270000
1	3.551141000	-1.247044000	0.330355000

1	3.276240000	-0.298566000	-1.152000000
1	3.421062000	0.531520000	0.410178000
6	1.084058000	-1.710683000	-0.555735000
1	0.007731000	-1.800033000	-0.402810000
1	1.297505000	-1.657665000	-1.623387000
1	1.587030000	-2.585263000	-0.126955000
6	1.260336000	-0.509138000	1.552652000
1	0.184075000	-0.617289000	1.678775000
1	1.769246000	-1.354448000	2.029813000
1	1.589714000	0.419387000	2.021084000
8	-2.089285000	-1.208060000	0.219469000
6	-3.405633000	-1.387106000	-0.275547000
1	-3.465002000	-1.227041000	-1.360162000
1	-3.703827000	-2.416215000	-0.064556000
1	-4.124612000	-0.716500000	0.213624000
1	-1.782365000	-0.296660000	0.019669000
8	-0.923868000	1.218857000	-0.166563000
6	-1.574401000	2.254854000	0.548660000
1	-2.080910000	1.843538000	1.430117000
1	-2.328898000	2.741560000	-0.080954000
1	-0.869484000	3.023518000	0.890129000
13	0.745289000	1.223466000	-0.771209000