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Formation and hydrogen release of hydrazine bisborane: Transfer vs. attachment of a borane

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Supporting Information Available. Optimized geometries (Cartesian coordinates and figures with selected parameters). Table S-1 lists the reaction Enthalpies and Free Energies. Table S-2 lists the coordinates of all MP2/aVTZ optimized geometries. Figures S-1 shows the geometrical parameters of all 9 conformers optimized at the MP2/aVTZ. Figure S-2 illustrates the **c**ombination of IRC plots along with the total energy and B2─N4 and B4─H7 bond lengths. Figure S-3 displays geometrical parameters of all TSs for 1,2-H_2, 1,3-H_2 eliminations and BH_3-catalyzed H_2-loss.

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Table S-1: Reaction Enthalpies at 0 K and 298 K and Gibbs Free Energies at 298 K of the reactants, adducts, transition states, and products in kcal mol^{-1} [a] and imaginary frequencies[b]

Structures	ΔH (0 K)	ΔH (298 K)	ΔG (298 K)	Transition frequency (cm^{-1})
$B_2H_6 + N_2H_4$ (**db + hyz**)	0.0	0.0	0.0	
$2BH_3 + N_2H_4$ (**2b + hyz**)	36.4	38.3	28.8	
$BH_3 + BH_3N_2H_4$ (**b + bhyz**)	5.7	6.2	7.1	
dbhyz-com	−2.6	−2.2	4.7	
dbhyz-C	−8.1	−8.7	2.1	
dbhyz-T	−10.8	−11.3	−0.3	
bhyzb	−23.8	−24.7	−13.1	
$BH_3 + BH_2N_2H_3 + H_2$	0.9	3.3	−4.8	
Prod-dbhyz-TS2 + H_2	−17.1	−16.1	−13.0	
Prod-dbhyz-TS3 + H_2	2.9	3.8	6.9	
Prod-bhyzb-TS1 + H_2	−28.3	−27.3	−25.1	
Prod-bhyzb-TS2 + H_2	−17.4	−16.9	−12.8	
dbhyz-com-ts	2.7	2.0	12.9	315*i*
TS-dbhyz-T-C	1.6	1.3	11.1	389*i*
TS-dbhyz-bhyzb	3.6	3.5	13.1	163*i*
dbhyz-C-TS1	15.9	15.1	26.5	713*i*
dbhyz-C-TS2	36.6	36.0	46.8	1363*i*
dbhyz-C-TS3	50.4	49.2	61.6	1038*i*
dbhyz-T-TS1	13.6	12.9	24.2	813*i*
dbhyz-T-TS2	35.8	35.1	46.4	1384*i*
dbhyz-T-TS3	49.5	48.4	60.4	765*i*
bhyzb-TS1	17.8	16.7	28.6	1483*i*
bhyzb-TS2	18.6	17.4	29.8	239*i*

[a] Relative values obtained from CCSD(T)/aVTZ total energies
[b] Vibrational frequency modes were obtained from MP2/aVDZ calculations.

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Table S-2: Geometries of the Structures Considered Optimized at the MP2/aug-cc-pVTZ Level of Theory, Given in Cartesian Coordinates (Å)

1. bhyz

N	0.042692	0.548716	0.002598
H	0.074294	1.098623	0.856840
N	1.191725	-0.308406	-0.125800
H	1.939858	0.046268	0.458858
H	0.054408	1.189569	-0.784396
H	0.893111	-1.202276	0.251724
H	-2.216569	0.547128	0.099930
B	-1.353843	-0.292497	0.005938
H	-1.254562	-1.000060	0.984365
H	-1.362250	-0.898934	-1.034599

2. dbhyz-com

N	-1.346757	0.758156	0.066974
N	-2.044050	-0.456222	-0.246228
B	1.310994	-0.740879	0.208880
B	2.580186	0.396781	-0.159348
H	2.957337	0.499368	-1.278856
H	-1.425540	0.991266	1.051185
H	1.277545	0.518585	-0.141739
H	3.040632	1.044683	0.721191
H	2.622297	-0.864891	0.181742
H	-1.790314	1.499105	-0.459204
H	0.946220	-0.850970	1.332820
H	0.857302	-1.401852	-0.666029
H	-2.818592	-0.612778	0.388658
H	-1.387141	-1.215561	-0.122647

3. dbhyz-C

N	0.718160	0.277099	0.503882
B	-0.461642	0.939662	-0.350483
N	1.519640	-0.632254	-0.267148
B	-2.043907	-0.584586	0.047882
H	-0.999418	1.757673	0.326269
H	1.268457	1.023514	0.924970
H	-1.135595	-0.028548	-0.796609
H	0.036202	1.341907	-1.371136
H	-1.614067	-0.633032	1.174555
H	0.265472	-0.261199	1.242687
H	-3.038954	0.061204	-0.090838
H	-1.988578	-1.625462	-0.549004
H	2.429200	-0.730389	0.169454
H	1.640434	-0.194964	-1.174483

4. dbhyz-T

N	0.678167	0.322231	0.495546
B	-0.418008	1.076359	-0.368546
N	1.485861	-0.679014	-0.179353
B	-1.838397	-0.634515	0.059993
H	-0.885734	1.968957	0.269125
H	-1.854995	-0.217693	1.185534
H	0.100099	1.376532	-1.412025
H	-1.289042	0.250837	-0.791917
H	0.221740	-0.151555	1.276270
H	1.330512	0.989967	0.899960
H	-1.132461	-1.598276	-0.120870
H	-2.899024	-0.675237	-0.490189
H	1.726745	-0.246772	-1.068510
H	0.815990	-1.408499	-0.417959

5. bhyzb

N	0.517885	-0.503602	0.000000
B	2.004934	0.143694	0.000000
N	-0.517889	0.503614	0.000000
B	-2.004933	-0.143705	0.000000
H	2.028453	0.805951	-1.012538
H	0.321362	-1.087562	-0.813558
H	2.761831	-0.791343	0.000000
H	2.028454	0.805951	1.012537
H	-2.028439	-0.805961	-1.012537
H	0.321362	-1.087562	0.813558
H	-2.028439	-0.805961	1.012538
H	-2.761846	0.791319	0.000000
H	-0.321359	1.087570	0.813559
H	-0.321359	1.087570	-0.813559

6. $BH_2N_2H_3$

N	0.120974	-0.438349	-0.000004
N	-1.206605	0.080892	-0.000057
B	1.306936	0.288030	0.000028
H	2.328224	-0.323245	-0.000013
H	0.104708	-1.445011	-0.000121
H	1.247127	1.478488	0.000083
H	-1.307489	0.676247	-0.813325
H	-1.307834	0.675571	0.813664

7. Prod-dbhyz-TS2

N	0.791075	0.613598	-0.000118
B	-0.612696	0.789983	-0.000055
B	-1.759474	-0.581066	0.000173
N	1.478245	-0.625078	-0.000018
H	-1.053207	1.891249	-0.000157
H	-1.248801	0.045091	0.981148
H	-1.248917	0.044862	-0.981010
H	1.422775	1.393627	-0.000259
H	-1.350598	-1.696674	0.000278
H	-2.917949	-0.327163	0.000211
H	1.186081	-1.157717	-0.812741
H	1.186231	-1.157503	0.812899

8. Prod-dbhyz-TS3

N	0.743656	0.751044	0.161185
N	1.178398	-0.521731	-0.471307
B	0.113849	-0.590056	0.596184
B	-1.905587	0.097291	-0.159818
H	-2.805373	-0.681935	-0.275846
H	0.179872	1.364859	-0.415391
H	-1.992776	0.887301	0.735270
H	-1.436937	0.503911	-1.197267
H	-1.044845	-0.884172	0.207675
H	1.502366	1.190821	0.661050
H	0.325844	-1.019631	1.679303
H	0.776159	-0.502523	-1.405777

9. Prod-bhyzb-TS1

N	0.456028	0.529917	-0.001549
N	-0.650443	-0.368202	-0.001638
B	-1.988026	0.019249	0.001626
B	1.885230	-0.257950	0.001959
H	1.856903	-0.914548	1.015023
H	0.391328	1.126632	0.818699
H	2.716722	0.615182	0.000424
H	1.858705	-0.919544	-1.007988
H	0.394038	1.123847	-0.824044
H	-2.232742	1.184605	0.004416
H	-2.806698	-0.838238	0.001472
H	-0.303379	-1.316432	-0.003614

10. Prod-bhyzb-TS2

N	-0.158548	-0.198562	-0.468145
B	-1.636047	-0.091226	0.161215
N	0.744307	0.790983	0.142443
B	1.117426	-0.761596	0.192825
H	-1.429279	-0.031217	1.356717
H	-2.219520	-1.087340	-0.181410
H	-2.100438	0.936137	-0.287723
H	2.006948	-1.032439	-0.548283
H	-0.122489	-0.084255	-1.475484
H	0.968314	-1.253250	1.258472
H	0.230959	1.230566	0.901330
H	1.158299	1.438959	-0.513898

11. dbhyz-com-ts

N	0.909384	-0.619531	-0.012216
N	2.002836	0.296934	-0.100369
B	-0.788659	0.560418	-0.030221
B	-2.477413	-0.154054	0.026140
H	-2.995336	-0.497408	-0.990110
H	-2.913581	-0.491255	1.082515
H	-0.447831	1.040322	1.007570
H	-1.302693	-0.664471	-0.026913
H	-2.237549	1.058319	0.009605
H	-0.489365	1.033470	-1.078331
H	0.919121	-1.157932	0.849099
H	0.971185	-1.257482	-0.797415
H	1.665430	1.177009	0.276268
H	2.775435	-0.014214	0.476210

12. TS-dbhyz-T-C

N	0.723797	-0.144691	0.500407
N	1.799500	-0.380854	-0.425286
B	-0.311722	0.972008	-0.041480
B	-2.529704	-0.447690	-0.139547
H	-1.146376	1.071676	0.825878
H	1.064082	0.147682	1.413109
H	-1.817305	-1.344414	0.207996
H	0.337075	1.981896	-0.171587
H	-0.723639	0.547013	-1.091321
H	0.218788	-1.020157	0.613826
H	-2.797038	-0.341790	-1.290526
H	-3.178175	0.117192	0.678748
H	2.641878	-0.607278	0.091222
H	1.944754	0.505398	-0.898063

13. TS-dbhyz-bhyzb

N	0.855216	-0.132592	0.521364
N	0.338707	-1.173643	-0.320894
B	0.970268	1.262765	-0.304871
B	-2.436310	0.214758	0.061948
H	1.362923	2.075660	0.495024
H	1.768048	-0.361744	0.907231

14. dbhyz-C-TS1

N	0.623731	0.223085	0.470692
N	1.467460	-0.624506	-0.313978
B	-0.220816	1.209884	-0.251669
B	-1.930440	-0.572352	-0.130713
H	-0.550319	2.146619	0.411351
H	1.066202	0.574491	1.312410

H	-0.146522	1.470613	-0.714040
H	1.765824	1.011474	-1.183291
H	-1.926591	0.167491	1.139558
H	0.199283	-0.014753	1.288890
H	-2.702875	1.269056	-0.408824
H	-2.750504	-0.792494	-0.479742
H	0.668563	-2.075481	0.005028
H	0.734599	-0.993788	-1.238510

15. dbhyz-C-TS2

N	0.568607	-0.284074	0.293735
N	1.909079	-0.300938	-0.181041
B	-0.382239	0.851931	-0.131116
B	-2.200147	-0.425529	-0.102914
H	-0.597136	1.464057	1.045978
H	-0.006722	0.705278	1.159891
H	-1.537928	0.687035	-0.575281
H	0.113763	1.694149	-0.811253
H	-1.897296	-0.652094	1.033742
H	0.170606	-1.210612	0.310415
H	-3.256416	0.115016	-0.256034
H	-1.862771	-1.234602	-0.919359
H	2.491900	0.214672	0.466674
H	1.950123	0.180176	-1.073482

16. dbhyz-C-TS3

N	-0.768118	0.472785	-0.418948
N	-1.356017	-0.756368	0.108767
B	0.638858	0.685699	0.222796
B	1.868244	-0.541505	-0.130582
H	0.977999	1.776153	0.529699
H	-1.326248	1.298257	-0.188522
H	1.117769	-0.321007	0.910764
H	-0.431688	0.423802	1.818625
H	1.479134	0.403696	-0.877805
H	-0.699592	0.409636	-1.432718
H	2.979264	-0.283764	0.194621
H	1.532023	-1.591720	-0.560113
H	-2.357558	-0.656774	-0.066844
H	-0.937671	-0.194172	1.382489

17. dbhyz-T-TS1

N	-0.598155	0.151485	0.490059
N	-1.665848	-0.573685	-0.131629
B	0.144936	1.196489	-0.238873
B	2.058166	-0.463536	-0.069108
H	-0.166457	1.380238	-1.375683
H	0.600358	-0.786445	0.370099
H	1.134714	-1.422882	0.050267
H	0.677854	2.032264	0.413459
H	1.491176	0.376428	-0.782227
H	-0.825703	0.322850	1.458716
H	2.348898	-0.067228	1.016493
H	2.859886	-1.113786	-0.670907
H	-1.275011	-1.416249	-0.545927
H	-2.013200	-0.014553	-0.903400

18. dbhyz-T-TS2

N	0.583047	-0.211412	-0.414620
N	1.843845	-0.119601	0.234925
B	-0.441948	0.809144	0.149000
B	-2.146643	-0.465980	0.111787
H	-0.296231	1.304009	1.214823
H	0.204613	-1.142542	-0.543606
H	-1.567615	-0.849133	1.090240
H	-0.176851	1.823589	-0.728187
H	-1.605089	0.712452	-0.315205
H	0.293822	1.026383	-1.003667
H	-2.004526	-1.122197	-0.882704
H	-3.222667	0.018020	0.301847
H	2.533478	-0.603354	-0.325861
H	1.795773	-0.565955	1.146252

19. dbhyz-T-TS3

N	-0.610590	-0.527325	0.093814
N	-1.884103	0.167700	-0.019325
B	0.578173	0.439740	0.361779
B	2.151529	-0.157145	-0.206194
H	3.157648	0.366852	0.134456
H	-0.384972	-1.110312	-0.716814
H	1.534840	-0.487574	0.844409
H	2.116446	-1.029597	-1.014324
H	1.384811	0.788671	-0.632492

20. bhyzb-TS1

N	-0.676149	-0.610321	0.256645
B	-1.609453	0.684871	-0.122599
N	0.626941	-0.586534	-0.320977
B	1.634358	0.535317	0.240042
H	-1.083582	1.642200	0.378365
H	-0.600730	-0.698775	1.271162
H	-2.676417	0.401903	0.368223
H	-1.608764	0.692151	-1.330906
H	1.394213	1.423277	-0.691053

H	-0.642676	-1.157983	0.897887	H	-1.170602	-1.423047	-0.100627
H	-0.314439	1.694020	-0.827845	H	1.297229	1.023977	1.272333
H	0.486100	1.216423	1.242936	H	2.750315	0.161222	0.058281
H	-2.476840	-0.479665	-0.539982	H	1.028703	-1.505323	-0.429360
H	-1.046575	1.303566	-0.687586	H	0.889561	0.559469	-0.933312

21. bhyzb-TS2

N	-0.511106	0.546118	-0.176052
B	-1.969963	-0.057590	0.063023
N	0.426831	-0.564059	-0.081888
B	1.842048	-0.001852	0.187201
H	-2.218714	-0.771698	-0.892121
H	1.255603	1.277100	-0.465476
H	-2.732574	0.867728	0.191246
H	-1.872159	-0.735992	1.092803
H	1.961398	0.426984	1.286898
H	-0.333119	1.058982	0.691271
H	2.761960	-0.540256	-0.341694
H	1.998801	1.112637	-0.710831
H	0.317744	-1.074751	-0.956748
H	0.090560	-1.197935	0.659114

Fig. S-1. The LUMOs and HOMOs of BH_3, $BH_3N_2H_4$ and **TS-dbhyz-bhyzb**.

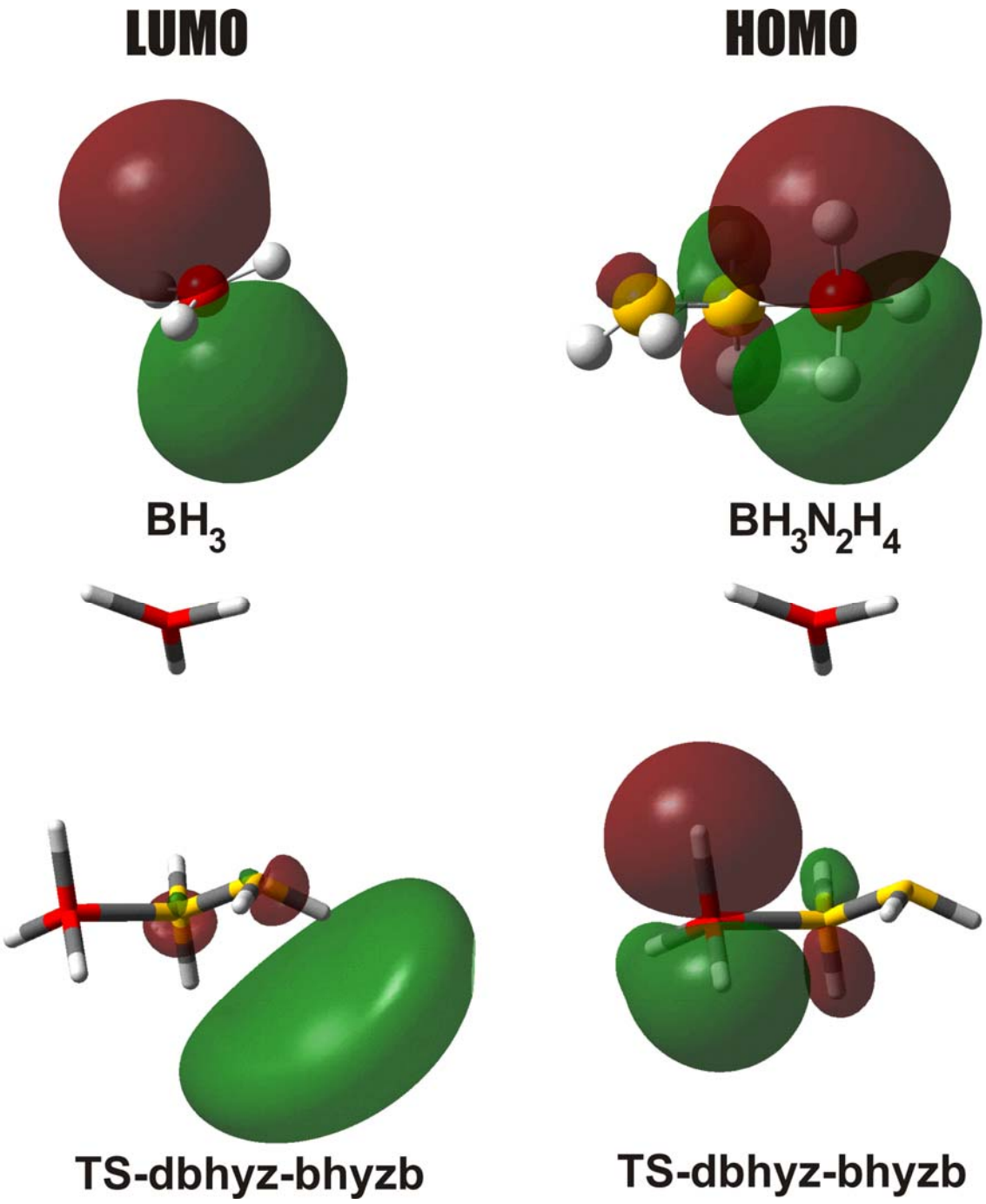
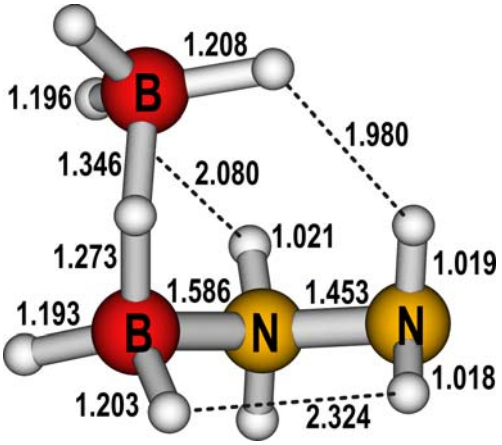
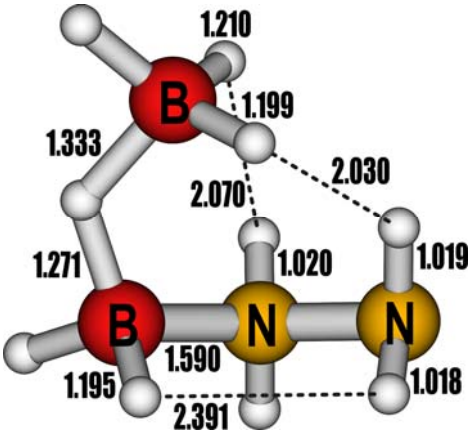


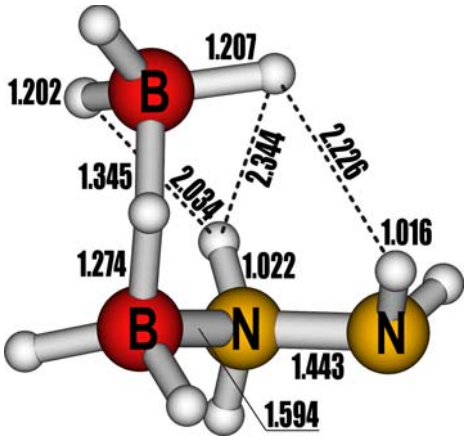
Figure S-2. Selected MP2/aVTZ geometry parameters of 9 conformers. Bond distances in angstroms and bond angles in degrees.



dbhyz-C-0a



dbhyz-C-0b



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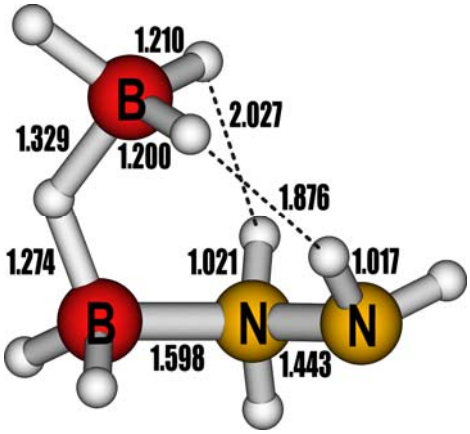

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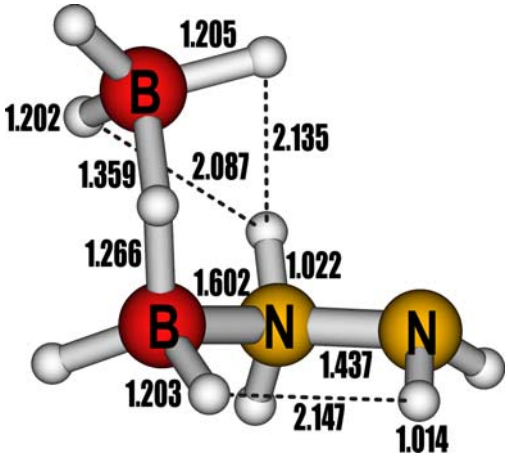

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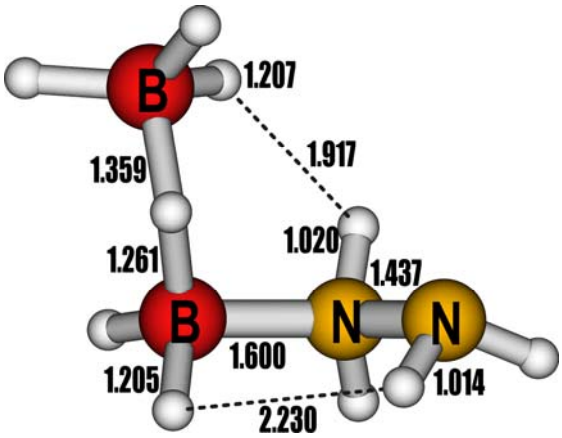

dbhyz-C-120b

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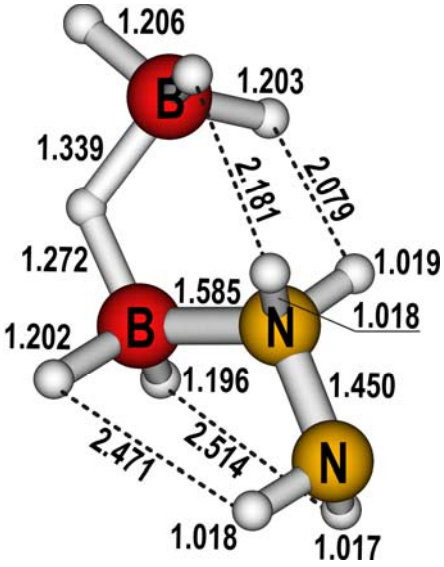

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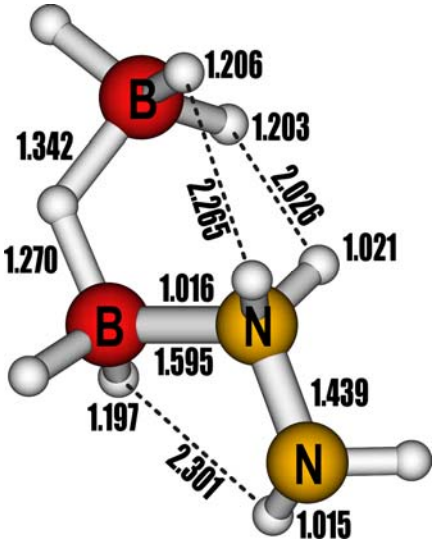

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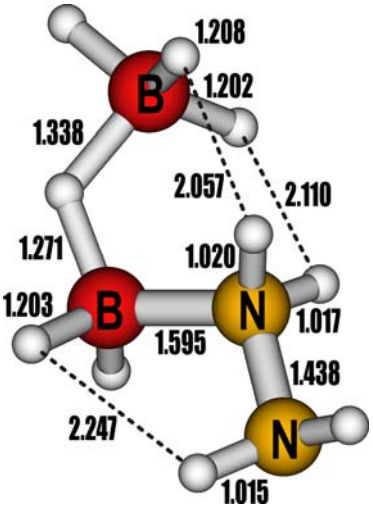


dbhyz-T-120

Figure S-3. Combination of IRC plots along with the total energy and B2─N4 and B4─H7 bond lengths

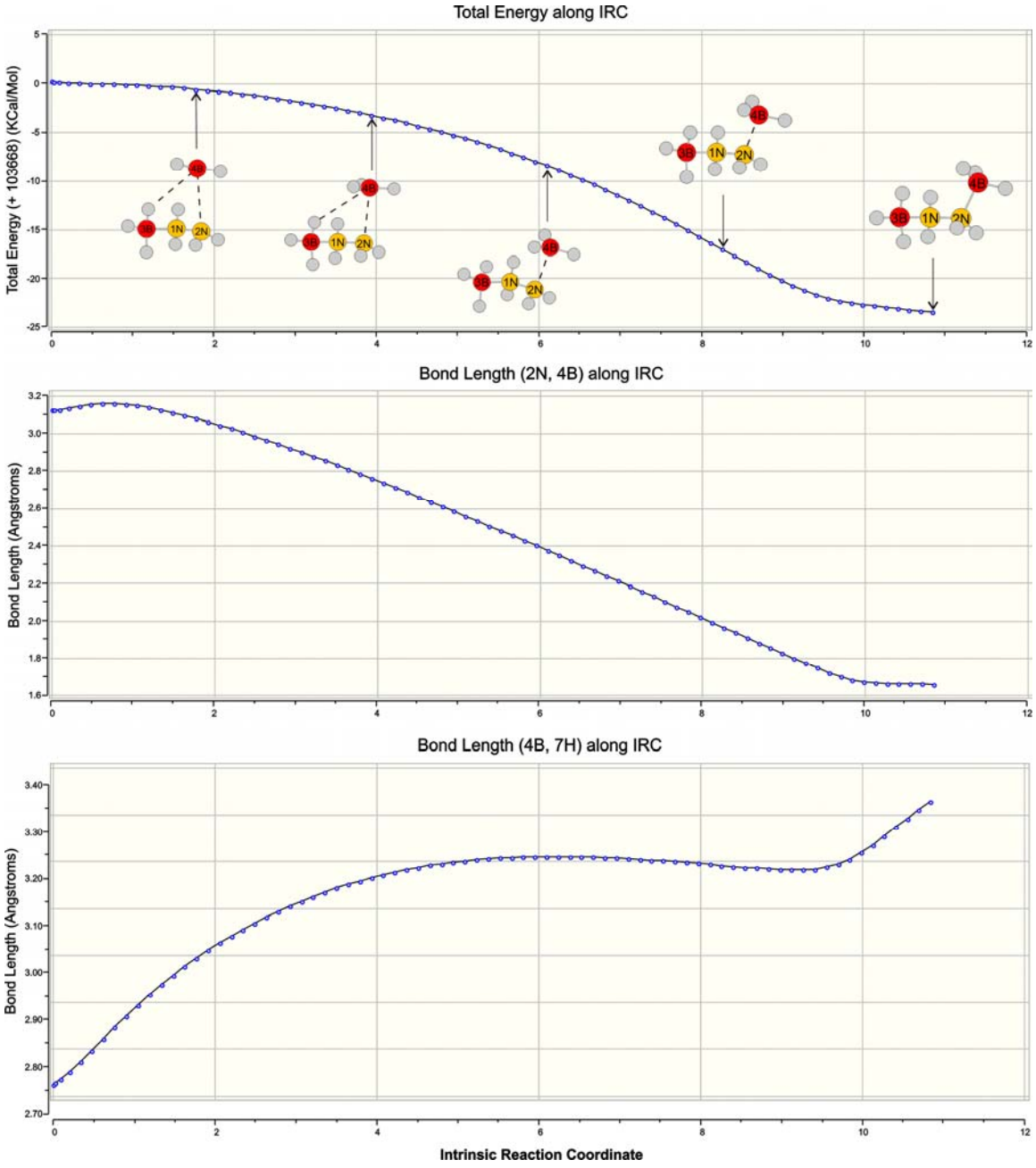
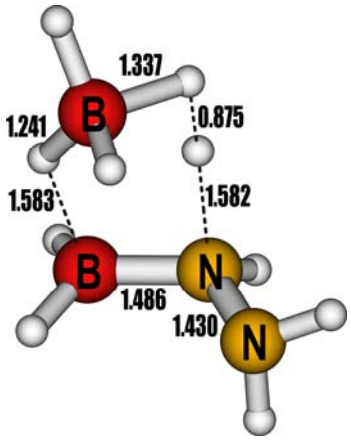


Figure S-4. Selected MP2/aVTZ geometrical parameters of all TSs for 1,2-H_2, 1,3-H_2 eliminations and BH_3-catalyzed H_2-loss. Bond distances in angstroms and bond angles in degrees.



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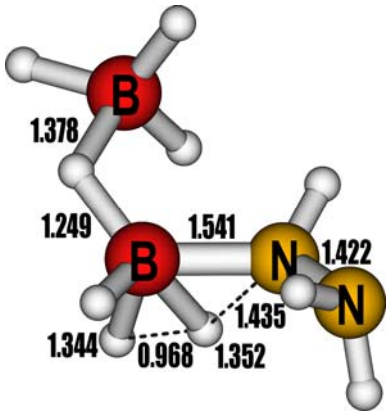

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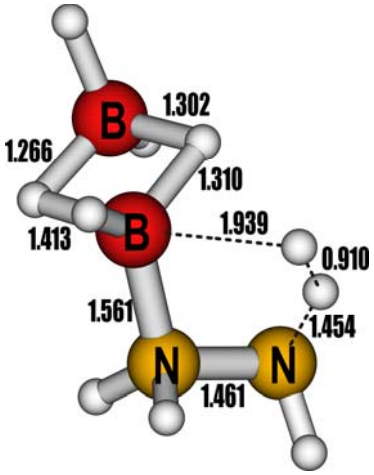

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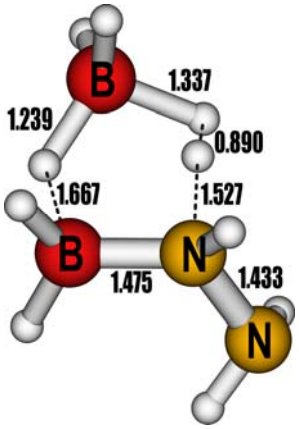

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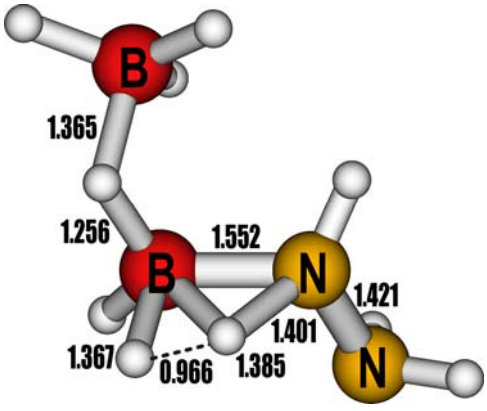

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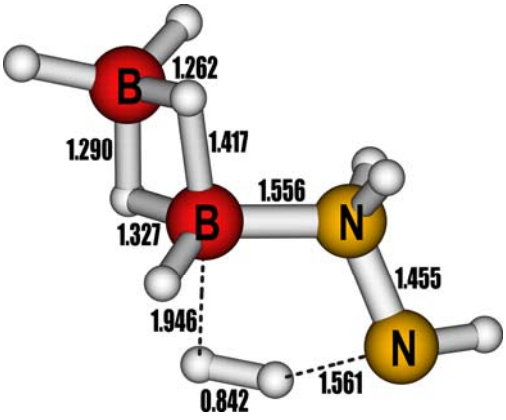

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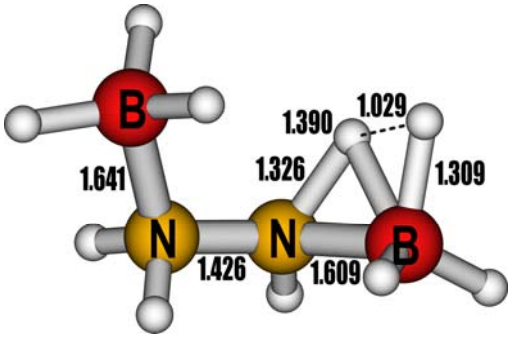
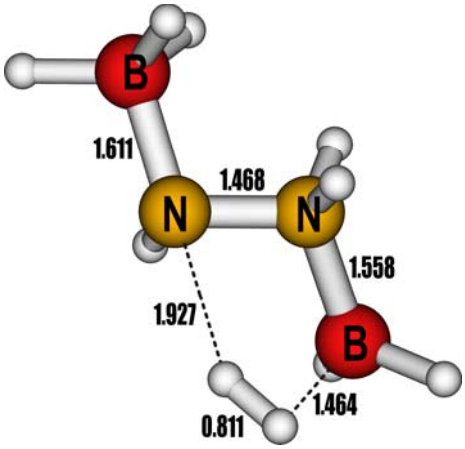


bhyzb-TS1



bhyzb-TS2