Supporting Information

Facile Cyclization of Sodium Aminodiboranate to Construct Boron–nitrogen–hydrogen Ring

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This Electronic Supplementary Information replaces the version originally published on 31st October 2020, which contained errors in the ^{11}B NMR data in Section 1.

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1. General Experimental Details

General Procedures: All manipulations were carried out by using Schlenk-line techniques or in a glovebox filled with high-purity nitrogen. ^{11}B NMR spectra were obtained at 192 MHz and externally referenced to $BF_3{\cdot}OEt_2$ in C_6D_6 (δ = 0.00 ppm). ^{11}H NMR spectra were obtained at 600 MHz and externally referenced to TMS in d_6-Beneze (δ = 0.00 ppm). X-ray diffraction data was collected on a Rigaku D/max 2500 diffractometer by using Cu-*K* a radiation (λ = 0.1542 nm, 40 kV, 100 mA). Na[NR1R2(BH_3)$_2$] (R1, R2 = H, Me) were purchased from United Boron (Zhengzhou) Energy Materials S&T LLC. The HCl·Et_2O solution was prepared by passing dried HCl gas into Et_2O and titrated by 0.1 M standard KOH solution. The solvents (THF, DME, Et_2O) were dried over sodium/benzophenone and freshly distilled prior to use.

Reactions of Na[$NH_2(BH_3)_2$] with HCl·Et_2O:

A very rapid reaction was initiated when HCl·Et_2O solution (1.785 mL, 2 mmol) was injected into the flask filled with Na[$NH_2(BH_3)_2$] (0.134 g, 2 mmol) at 0 ℃. A white precipitate and a large amount of H_2 (23.16 mL, 1.035 mmol, Figure S1b) formed immediately and the reaction was followed by the ^{11}B NMR. ADB was purified by fractionally condensation with high yield (75%, Table 1, entry 7, Figure S1a).[1-2] The white solid was dried under a dynamic vacuum and further confirmed to be NaCl (0.116g, 1.992 mmol, Figure S1c). ^{11}B NMR (192 MHz, δ) -26.8 (br). ^{1}H NMR (d_6-Beneze, 600 MHz, δ) 4.2 (s, H_2). XRD(2θ): 27.1, 31.4, 45.0, 53.4, 56.0, 65.8, 74.7. The reaction also can occur at room temperature/-20 ^{o}C in THF or DME/Et_2O with similar results (Figures S2, 3).

Reactions of Na[$MeNH(BH_3)_2$] (2) with HCl·Et_2O

A very rapid reaction was initiated when HCl·Et_2O solution (0.4463 mL, 0.5 mmol) was injected into the flask filled with Na[$MeNH(BH_3)_2$](0.0405 g, 0.5 mmol) at 0 ℃. A white precipitate and a large amount of H_2 formed immediately and the reaction was followed by the ^{11}B NMR. $NMeB_2H_6$ was purified by fractionally condensation (yield, 38%, Table 1, entry 6, Figure S4).[1-2] The white solid was dried under a dynamic vacuum and further confirmed to be NaCl. ^{11}B NMR (192 MHz, δ) -22.15 (br, sextet). ^{1}H NMR (d_6-Beneze, 600 MHz): δ 4.2 (s, H_2). XRD (2θ, NaCl): 27.4, 31.7, 45.2, 53.5, 56.1, 65.6, 74.5.

Reactions of Na[$Me_2N(BH_3)_2$] (3) with HCl·Et_2O

A very rapid reaction was initiated when HCl·Et_2O solution (0.4463 mL, 0.5 mmol) was injected into the flask filled with Na[$Me_2N(BH_3)_2$] (0.0475 g, 0.5 mmol) at 0 ℃. A white precipitate and a large amount of H_2 formed immediately and the reaction was followed by the ^{11}B NMR. $NMe_2B_2H_5$ was purified by fractionally condensation (yield, 49%, Table 1, entry 7, Figure S5).[1-2] The white solid was dried under a dynamic vacuum and further confirmed to be NaCl. ^{11}B NMR (192 MHz, δ) -17.48 (br, sextet). ^{1}H NMR (d_6-Beneze, 600 MHz): δ 4.2 (s, H_2). XRD (2θ, NaCl): 26.9, 31.5, 45.6, 53.1, 56.2, 65.4, 74.2.

2. Computational method

All density functional theory (DFT) calculations were performed using the Gaussian 09W program.[3] The geometries, natural population analysis (NPA) of all the species are calculated at M06-2X/6-311++G(d,p) level of theory. As well as the corresponding frequencies of the optimized geometries are computed at the same level to prove the characteristics of the transition states with one imaginary frequency (Figures S6-8), and the stationary points without imaginary frequency. To get more accurate energies, the single point energy of all the species are calculated at CCSD(T)/aug-cc-pVDZ level of theory with SMD solvent model in THF. The intrinsic reaction coordinate (IRC)[4-6] theory are used to confirm that the transition states really connect to minima along the reaction path. The rate constants are calculated by the conventional transition state theory (TST)[7-9] with Winger tunneling correction and performed using the VKLab[10] program coupled with the steady state approximation. The calculated structure of ADB is consistent with the microwave structure.[11] As presented in Figures S6-8, the geometries are in good accordance with the experiment. Otherwise, the N-H bond distance is shorter and the B-μH bond distance is longer by 0.008 and 0.014 Å, respectively. Furthermore, the dipole moment (2.67 D) is calculated at the M06-2X/dft2-T2VPD level of theory, which is same with the measured value of 2.67 D.[11]

References

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3. Supporting Results

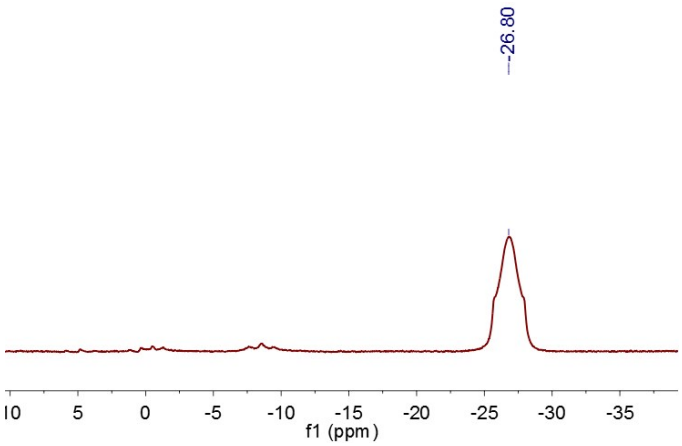

Figure S1a. ^{11}B NMR spectrum of ADB in the solution mixture of **1** + HCl (adding 1 equiv. HCl solution to **1** solution) in THF at room temperature.

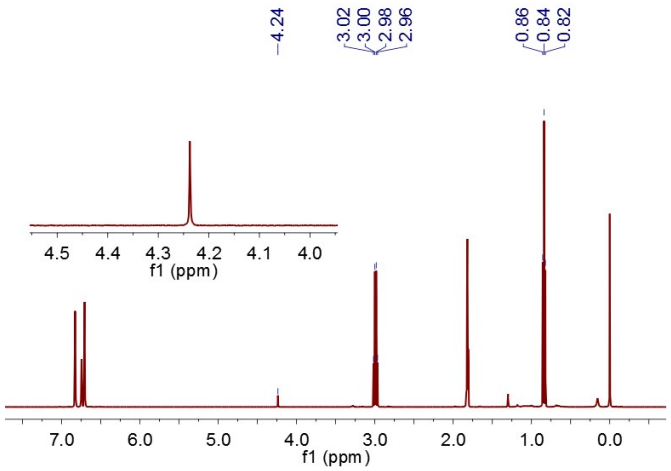

Figure S1b. ^{1}H NMR spectrum of the product H_2 in d_8-Toluene.

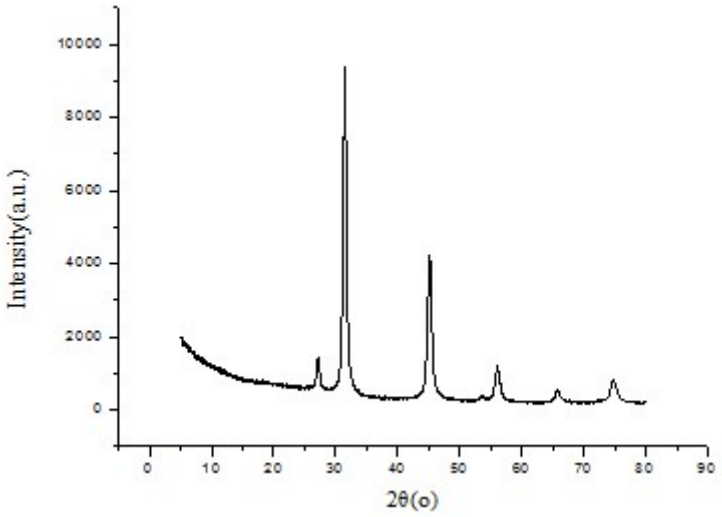

Figure S1c. XRD spectrum of the product NaCl.

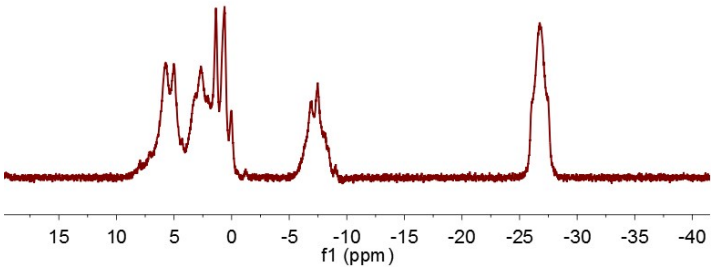

Figure S1d. ^{11}B NMR spectrum of the solution mixture of **1** + HCl (adding 1.5 equiv. HCl solution to **1** solution) in THF at room temperature.

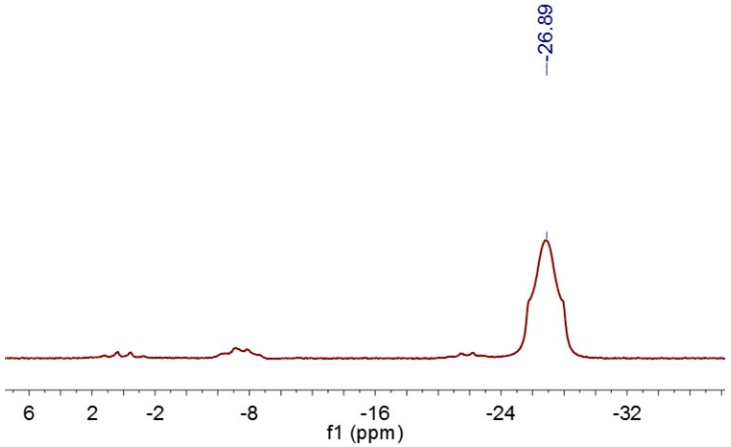

Figure S1e. ^{11}B NMR spectrum of the solution mixture of **1** + HCl (adding **1** solution to 1 equiv. HCl solution) in THF at room temperature.

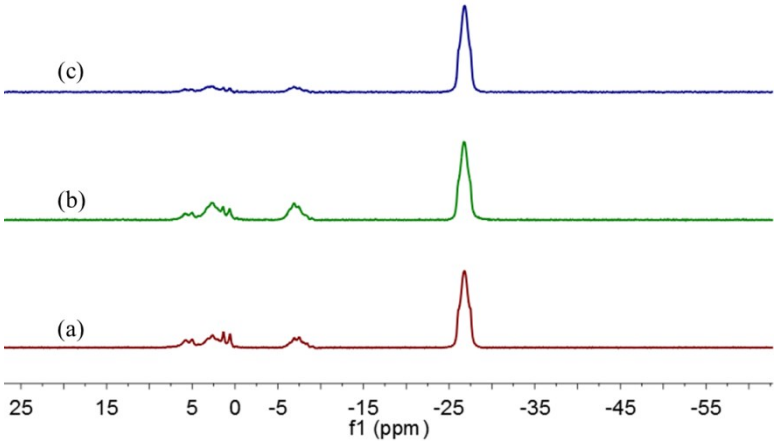

Figure S2. ^{11}BNMR spectrum of the solution mixture of **1** + HCl in THF at different temperature. a) RT, b) 0 ^{o}C, c) -20 ^{o}C

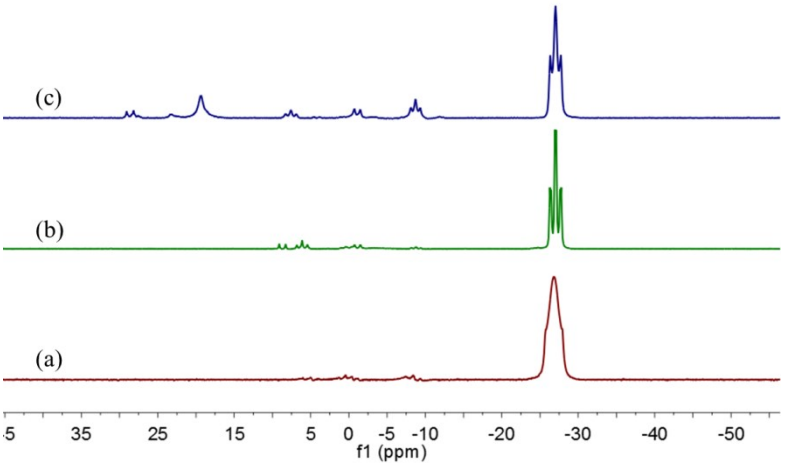

Figure S3. ^{11}BNMR spectrum of the solution mixture of **1** + HCl in different solvent at room temperature. a) THF, b) Et_2O, c) DME.

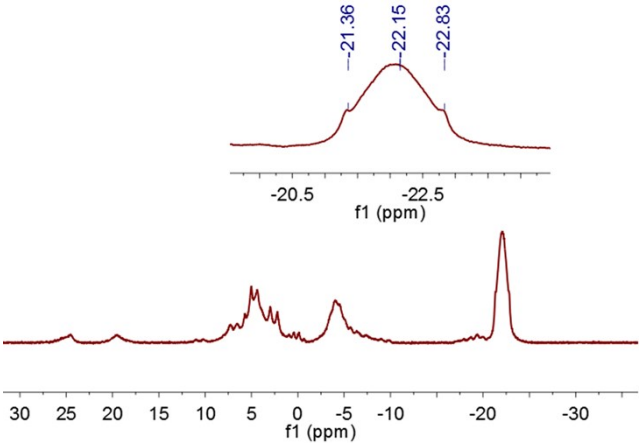

Figure S4. ^{11}B NMR spectrum of MeADB in the solution mixture of **2** + HCl (adding 1 equiv. HCl solution to **2** solution) in THF at 0 ℃.

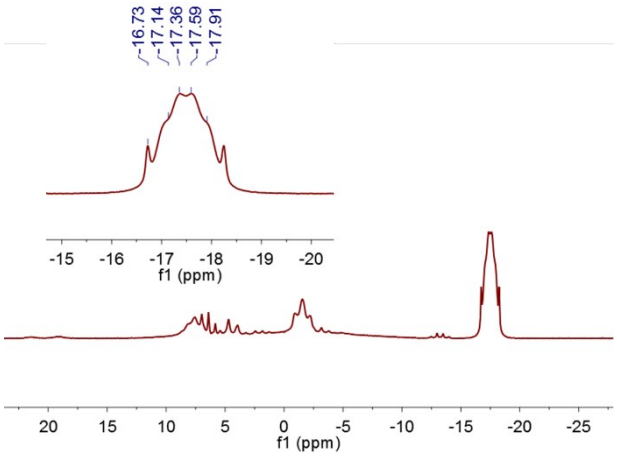

Figure S5. ^{11}B NMR spectrum of Me_2ADB in the solution mixture of **3** + HCl (adding 1 equiv. HCl solution to **3** solution) in THF at 0 ℃.

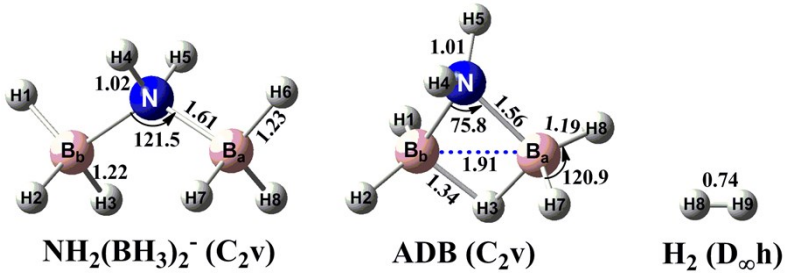

Figure S6 The optimized geometries for $[NH_2(BH_3)_2]^-$, ADB and H_2. Colors: N, blue; B, pink; H, white (bond length is shown in Å, bond angle shown in °)

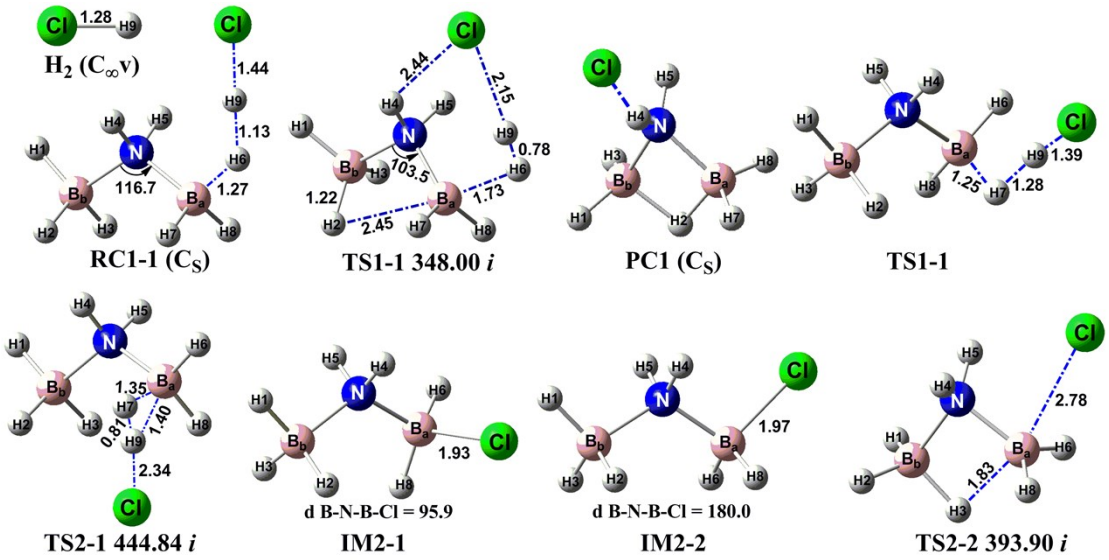

Figure S7 The optimized geometries for all the species of the $[NH_2(BH_3)_2]^-$ + HCl reactions. Colors: N, blue; B, pink; Cl, green; H, white (bond length is shown in Å, bond angle shown in °).

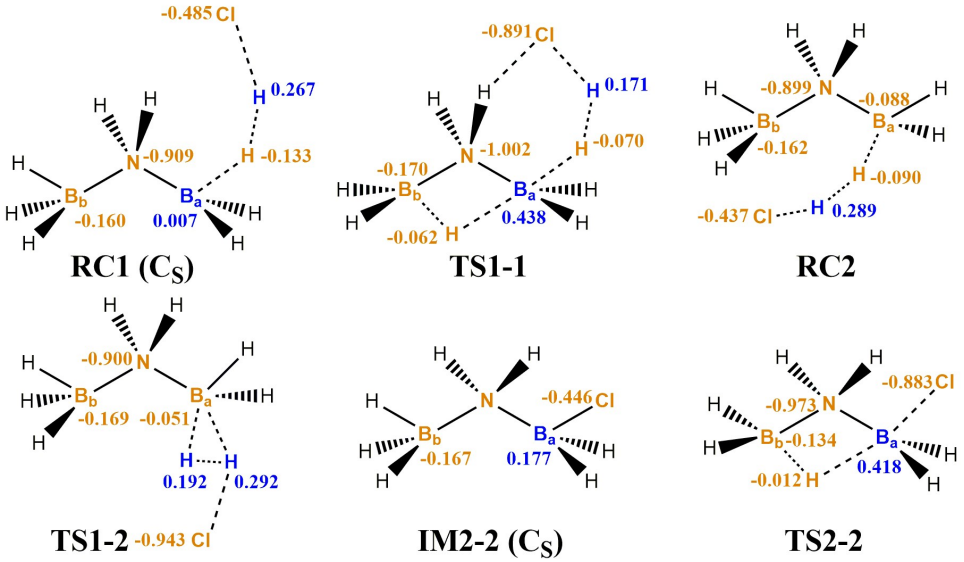

Figure S8 The nature population analysis of reactant complexes and transition states of the $[NH_2(BH_3)_2]^-$ + HCl reactions.

Table S1 Calculated zero point energies (ZPE), relative energies (△(E + ZPE) kcal·mol^{-1}), enthalpies (△H kcal·mol^{-1}), gibbs free energies (△G kcal·mol^{-1}) and entropy (S cal·mol^{-1}) of the reaction $[NH_2(BH_3)_2]^-$ + HCl → ADB + H_2 + Cl^-

Species	ZPE	△E	△(E+ZPE)	△H	△G	S
$[NH_2(BH_3)_2]^-$ + HCl	60.20	0.00	0.00	0.00	0.00	112.78
RC1	61.64	-3.21	-1.77	-2.52	5.84	84.75
TS1-1	61.53	1.31	2.64	2.00	10.46	84.41
PC1 + H_2	59.31	-15.29	-16.18	-15.66	-14.54	77.90
RC2	61.55	-4.80	-3.45	-4.28	4.51	83.29
TS1-2	63.11	5.13	8.04	7.19	15.88	83.63
IM1-2 + H_2	58.71	-16.68	-18.17	-17.64	-16.38	77.43
IM2-2 + H_2	58.78	-19.04	-20.46	-19.91	-18.35	76.42
TS2-2 + H_2	58.35	-3.66	-5.51	-5.00	-3.57	76.87
ADB + H_2 + Cl^-	59.47	-9.09	-9.81	-9.06	-13.92	129.06

4. Cartesian coordinates and vibrational frequencies on the studied models

$[NH_2(BH_3)_2]^-$

Cartesian coordinates

B	1.40427600	-0.29218800	-0.00001800
H	1.45259200	-0.97257100	-1.01179500
H	2.29650300	0.55850800	0.00011600
B	-1.40432900	-0.29225100	-0.00004000
H	-1.45260700	-0.97241700	1.01183600
H	-1.45258700	-0.97274600	-1.01172000
H	1.45234400	-0.97300400	1.01147300
N	0.00002600	0.49449700	-0.00004200
H	0.00021900	1.11653000	0.80735700
H	-0.00004800	1.11767000	-0.80656200
H	-2.29632900	0.55874800	-0.00011900

Vibrational frequencies

155.4854	236.9410	280.7759
576.7250	695.5078	799.2926
818.0507	885.5216	1026.9020
1070.6064	1184.8017	1196.6696
1208.7228	1211.5935	1226.1517
1226.1901	1227.5819	1228.6904
1657.7065	2379.4123	2393.3151
2455.8671	2473.0802	2483.2709
2497.9449	3486.9113	3558.2377

The reaction of $[NH_2(BH_3)_2]^-$ + HCl

Complex (RC1)

Cartesian coordination

B	0.80856100	1.36946300	0.22184400
H	1.69657800	1.93782400	0.81641100
H	0.21464800	2.08855800	-0.56399500
B	2.23080400	-0.99357400	0.31174500
H	1.50837700	-1.40565600	1.20203100
H	3.21794200	-0.42406800	0.74516200
H	0.01274500	0.95426800	1.09456500
N	1.38027500	0.09630300	-0.52713100
H	0.60849300	-0.39133700	-0.98592000
H	1.96920700	0.42780800	-1.28997400
H	2.53684600	-1.88806400	-0.47085400
Cl	-2.09607000	-0.25120000	-0.00184300
H	-0.99039400	0.41749700	0.50586800

Vibrational frequencies

54.4933	102.2783	145.1856
208.7867	249.5628	403.9567
609.2092	719.2137	811.7023
818.2570	845.8907	915.1127
938.8328	1001.7038	1068.8752

1130.4702	1192.7879	1196.9898
1214.7630	1215.6399	1232.2974
1238.5800	1310.4885	1480.4633
1664.0368	2129.6320	2435.9723
2489.1732	2516.9202	2559.7038
2616.2136	3488.6287	3556.2643

TS1-1

Cartesian coordination

B	-1.15811700	-1.25788300	0.12147100
H	-1.72188100	-1.91677200	-0.69944100
H	0.31888200	-2.02725100	-0.37806200
B	-2.49968100	0.81274900	0.07683300
H	-3.03954600	0.10124100	0.90914100
H	-3.06546300	0.74357600	-0.99602500
H	-1.07063600	-1.60636200	1.25533800
N	-0.99021400	0.19578800	-0.16559700
H	-0.25305100	0.60700200	0.41684500
H	-0.68765200	0.38498600	-1.11863600
H	-2.36637500	1.94904400	0.47793800
Cl	2.13324800	0.23997900	0.03189200
H	0.84098800	-1.45995200	-0.24159600

Vibrational frequencies

-348.0000	61.4394	116.4299
149.4126	181.0077	277.0422
420.5498	498.8491	662.3227
675.6495	754.2144	788.3601
836.0691	864.4469	1029.0274
1051.3582	1069.1918	1105.1261
1189.6635	1205.6861	1215.3086
1218.8669	1232.6868	1270.3106
1672.6837	2474.6901	2522.4024
2557.8330	2685.3677	2784.7720
3437.0002	3567.7874	3642.0027

Complex (PC1)

Cartesian coordination

B	-1.91819100	0.95659800	-0.17765500
H	-2.60606700	1.52062100	0.62925300
B	-1.91727400	-0.95707900	-0.17739900
H	-2.74864300	-0.00065500	-0.65254600
H	-2.60466600	-1.52157500	0.62957900
H	-1.57711500	1.53124400	-1.16953600
N	-0.86689300	0.00033900	0.41816500
H	0.11092800	0.00059700	0.03615800
H	-0.80097400	0.00048800	1.42870500
H	-1.57560400	-1.53153700	1.16917800
Cl	2.17927700	0.00005000	-0.05201900

Vibrational frequencies

91.7835	98.6325	200.0351
349.6660	659.4351	727.8027
757.0251	794.0867	926.6960
941.1925	972.6072	1050.7916
1084.6406	1124.2028	1160.6586
1196.6034	1220.5099	1237.6412
1674.2465	1715.4779	1994.7341
2611.8688	2626.2559	2702.7629
2712.0955	3039.6733	3625.0033

Complex (RC2)

Cartesian coordination

B	0.74454800	1.02047800	0.28470400
H	0.67255100	0.95060400	1.47744800
H	0.42623300	2.08632200	-0.16881300
B	2.45506300	-1.10831600	0.11872500
H	1.54621600	-1.80329900	-0.28436200
H	2.56339300	-1.12648100	1.32796300
H	-0.12120579	0.48040559	-0.34679593
N	2.06582600	0.42967000	-0.27597800
H	2.09794200	0.52238600	-1.29067800
H	2.82119800	1.02150100	0.06847300
H	3.51032400	-1.34267600	-0.44787600
Cl	-2.44098209	-0.18500078	-0.01919546
H	-0.30527868	0.02051252	0.30551240

Vibrational frequencies

52.1755	107.6473	166.7768
253.7268	289.0881	406.7848
607.5985	699.2373	713.3319
770.1611	825.1427	843.9224
896.4329	1022.3009	1065.2322
1172.3049	1198.6419	1203.0738
1212.7605	1222.0020	1225.9752
1242.9989	1293.3079	1552.6771
1670.7268	2286.7338	2426.3517
2486.4986	2493.5456	2516.0718

2561.5643	3480.2855	3551.4375	

TS1-2

Cartesian coordination

B	0.74454800	1.02047800	0.28470400
H	0.67255100	0.95060400	1.47744800
H	0.42623300	2.08632200	-0.16881300
B	2.45506300	-1.10831600	0.11872500
H	1.54621600	-1.80329900	-0.28436200
H	2.56339300	-1.12648100	1.32796300
H	-0.22970000	0.41272500	-0.42593400
N	2.06582600	0.42967000	-0.27597800
H	2.09794200	0.52238600	-1.29067800
H	2.82119800	1.02150100	0.06847300
H	3.51032400	-1.34267600	-0.44787600
Cl	-2.56476400	-0.19691200	-0.03801500
H	-0.26600700	0.05791900	0.30473400

Vibrational frequencies

-444.8370	75.2835	97.0214
175.8728	222.8265	286.0882
384.8228	604.0508	691.1112
733.7156	781.4365	918.8783
952.2767	983.4064	1089.0041
1145.9921	1184.9491	1205.0736
1211.4355	1217.7351	1224.9684
1239.9438	1405.7020	1634.8332
1669.2140	2472.9946	2529.8435
2563.8608	2629.2800	2702.6951
3492.0883	3518.8287	3560.7857

Intermediate (IM1-2)

Cartesian coordination

B	-0.15077700	0.88554300	0.37932000
H	0.06780000	0.84324800	1.56179600
H	-0.47650700	1.98194900	-0.02957200
B	2.20175100	-0.60494200	0.24095600
H	1.61921000	-1.58398800	0.66429200
H	2.73374700	0.03839900	1.13026500
N	1.10248600	0.36629200	-0.44730900
H	0.74319300	-0.09609400	-1.28245100
H	1.60132400	1.18610400	-0.79055700
H	3.00744100	-0.89875700	-0.63848100
Cl	-1.60402800	-0.31987700	-0.03444200

Vibrational frequencies

44.6975	189.6029	267.3608
315.2891	524.0451	644.5263
707.6032	813.9901	871.2733
926.5500	962.8205	1035.8088
1133.9935	1197.4782	1211.7622
1213.7695	1226.6814	1233.2508
1245.1981	1653.0055	2418.6568
2483.3307	2510.1710	2539.7445
2619.3951	3478.2958	3552.9246

Intermediate (IM2-2)

Cartesian coordination

B	0.03125600	0.61620000	-0.01671800
H	-0.00456500	1.23289700	1.01003600
H	-0.04238000	1.16952000	-1.09041300
B	2.77151700	0.05958400	0.02623700
H	2.86225700	1.10853900	-0.59009000
H	3.36244900	-0.83861500	-0.52886500
N	1.18610100	-0.37113900	-0.02201900
H	0.99873700	-0.99595200	0.77795500
H	1.02050600	-0.94206100	-0.87324500
H	3.07643700	0.16301800	1.21334500
Cl	-1.97588300	-0.09872300	0.01104800

Vibrational frequencies

94.1755	181.7379	200.0353
292.7802	525.0738	619.9082
756.2472	777.6440	865.0690
903.4346	971.0274	1084.2071
1108.6898	1197.0194	1208.8515
1214.5139	1224.9714	1226.6744
1237.5005	1666.2438	2425.6949
2495.1388	2520.3036	2581.3466
2637.2102	3486.1733	3557.0086

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Cartesian frequencies

B	0.62895700	0.93723400	-0.00006300
H	0.51490900	1.47872300	1.05096300
H	0.51504500	1.47882000	-1.05105800
B	2.52290500	-0.14615300	0.00011800
H	2.45616200	1.10236000	0.00009800
H	3.04889100	-0.51114300	-1.02507800
N	0.97169300	-0.53074400	-0.00011300
H	0.57982600	-0.99042900	0.81554300
H	0.58009100	-0.99034400	-0.81594300
H	3.04857300	-0.51113000	1.02547900
Cl	-1.95909800	-0.07629700	0.00003000

Vibrational frequencies

-393.8976	91.8889	152.2346
193.0446	281.5897	699.9794
738.1183	781.2947	787.3471
838.5651	969.9181	1042.1569
1073.5648	1101.3443	1139.2316
1195.8370	1203.7985	1240.2731
1275.4583	1669.1861	2285.3530
2550.6233	2607.6024	2706.7100
2814.1057	3559.0052	3627.3796