Supporting Information

Roles of the Lewis Acid and Base in the Chemical Reduction of CO_2 Catalyzed by Frustrated Lewis Pairs

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Contents

1. Computational Details

All ab initio calculations were conducted using GAMESS[1] and GAUSSIAN 09[2] computational chemistry software. All geometries and the relevant transition state (TS) structures, unless otherwise noted, were obtained using the B97-D density functional.[3] The B97-D functional was developed to correctly describe dispersion effects. Grimme *et al.* previously used the B97-D functional to describe the heterolytic cleavage of dihydrogen by a bulky Frustrated Lewis Pair (FLP) catalyst and demonstrated the erroneous results of the B3LYP functional in describing this system due to the incorrect description of dispersion effects.[4] The bulky ligands in the trichloroaluminum ($AlCl_3$) and trimesitylenephosphine ($PMes_3$, Mes = 2,4,6-$C_6H_2Me_3$) FLP system[5] of the present study also suggest significant dispersion effects and the B97-D functional was thus selected for describing this system. For accurate energies, we performed single point MP2[6] energy calculations at the optimized geometries of B97-D. A benchmarking study (Section 2) validated the MP2//B97-D method for describing the FLP system. The energy difference between MP2//B97-D and the high level CCSD(T)//MP2 was within 1 kcal mol^{-1} for both hydride transfer (HT) and complexation energy calculations. A moderate size 6-311G (d,p) Pople basis set was used for geometry optimizations with B97-D while the more extensive 6-311++G(d,p) Pople basis set was used for single point energy calculations with MP2, denoted as MP2/6-311++G(d,p)// B97-D/6-311G(d,p).

Solvation effects were described using the Polarizable Continuum Model (PCM).[7,8] Also, the use of C_6H_5Cl as the solvent instead of the experimentally used C_6H_5Br solvent[5] should give quantitatively similar TS structures and reaction energies because the main parameters in the PCM model of cavity size and dielectric constant are similar between C_6H_5Cl and C_6H_5Br. Hessian calculations on all TS structures verified that only one imaginary frequency was obtained and corresponded to the normal mode of the reaction pathway. The TS structures were further verified by Intrinsic Reaction Coordinate (IRC) calculations to confirm the correct corresponding reactants and products were connected by the TS identified. The reaction activation barrier was referenced to reactants determined from converged IRC calculations. Hessian calculations were also performed on the reactants to verify that those reactants correspond to stationary points along the reaction pathway.

Thermochemistry properties for a number of LA or/and LB catalyzed complexes were computed referencing to dimeric LA $(AlCl_3)_2$, free CO_2 and free LB ($PMes_3$) at T=298K and P= 1atm. $AlCl_3$ has been known to form dimers[9] at moderate temperatures in both non-coordinating solvent[10,11] and in gas phase.[12] The $AlCl_3$ dimer was thus chosen as the thermodynamic reference. The reported enthalpies, H, are zero point energy (ZPE) and thermally corrected (T=298.15K) at each stationary point. Solvation energy is implicitly included in the energy of converged geometries. The reported entropies, S, are determined using the ideal gas approximation (P = 1 atm, T=298.15K) for the associated partition functions. The calculated gas phase values for S provide an upper estimate due to the reduction in translational degrees of freedom from the gas phase system as compared to the experimental condensed phase system. The approximations imposed on entropy calculations do not affect the conclusions drawn on the role of LB, which is justified by the dominating enthalpic driving force leading to the formation of a high concentration of the activated FLP•CO_2 complex.

2. Benchmarking Studies

A HT benchmarking study was performed using a model system of $2AlCl_3•PH_3•CO_2$ + AB, where the TS structure is shown in Figure S1a. In this structure, we replace the bulky trimesitylenephosphine base ($PMes_3$), with a phosphine base (PH_3). The HT barrier at MP2/6-311++G(d,p)//B97-D/6-311G(d,p) was compared to CCSD(T)/6-311++G(d,p)// MP2/6-311G(d,p). Both calculations were done in gas phase at T=0K and not ZPE corrected. Table S1 (system **a**) shows that MP2//B97-D differs by -0.1 kcal mol^{-1} as compared to the high level CCSD(T)//MP2 calculation. Thus, the chosen MP2//B97-D method should describe HT reactions correctly. The $AlCl_3•PH_3$ model system was chosen to benchmark the complexation energy (Figure S1b). The complexation energy was calculated based on the difference in energy of the $AlCl_3•PH_3$ complex and the infinitely separated reactants of $AlCl_3$ and PH_3. Results from Table S1 (system **b**) shows that MP2//B97-D differs by -0.8 kcal mol^{-1} as compared to the CCSD(T)//MP2 calculation. Table S1 (system **c**) shows strong evidence that B3LYP functional significantly underestimates the complexation energy due to an insufficient description of the dispersion interaction in the bulky $AlCl_3•PMes_3$ complex. B3LYP predicts a complexation energy of -15.8 kcal mol^{-1} while MP2//B97-D yields -40.0 kcal mol^{-1}. Not shown in Table S1, B97-D results in a complexation energy of -32.5 kcal mol^{-1} and is in agreement with the MP2//B97-D results. Based on the results of this benchmarking study, the MP2//B97-D level of theory was selected to describe the FLP systems of this investigation.

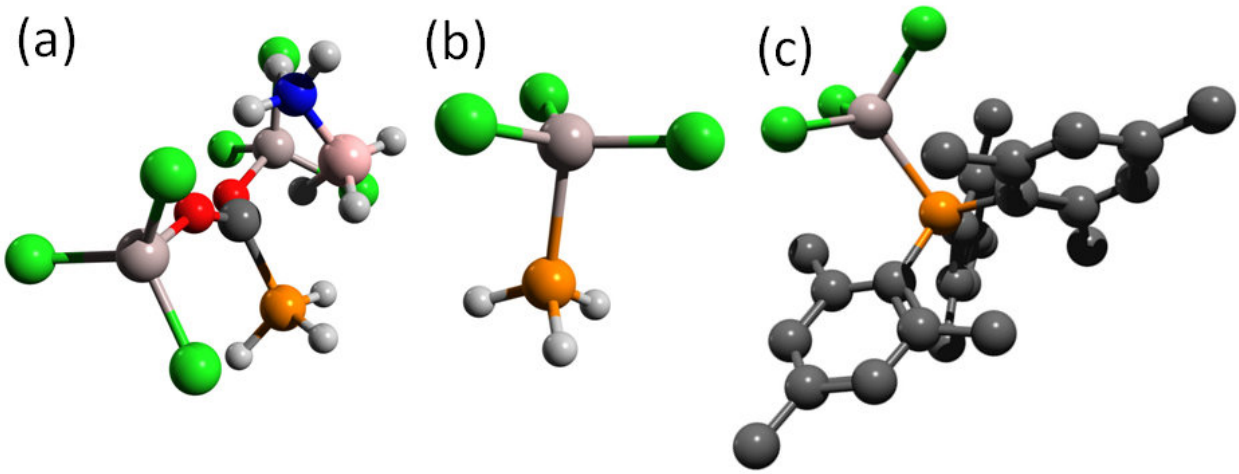


Figure S1. a) TS structure for hydride transfer for $2AlCl_3•PH_3•CO_2$ + AB b) $AlCl_3•PH_3$ complex c) $AlCl_3•PMes_3$ complex. H atoms in (c) omitted for clarity. Al, light gray; B, pink; C, gray; Cl, green; H, white; N, blue; O, red; P, orange.

Table S1. Benchmarking studies comparing different quantum chemical methods

System[a]	CCSD(T)//MP2[b]	MP2//B97-D[b]	B3LYP [c]
a) $2AlCl_3•PH_3•CO_2$ + AB, $\Delta E_{hydride}$	9.0	8.9	8.9
b) $AlCl_3•PH_3$, $\Delta E_{complex}$	-21.2	-22.0	-16.5
c) $AlCl_3•PMes_3$, $\Delta E_{complex}$	N/A	-40.0	-15.8

[a] Calculations performed in gas phase at T=0K, not ZPE and thermally corrected. [b] Basis sets: Single point energy at 6-311++G(d,p) and geometry optimizations at 6-311G(d,p), unit in kcal mol^{-1}. [c] Energy and geometry optimizations 6-311G(d,p), unit in kcal mol^{-1}.

3. Results

a. Hydride transfer reactants and TS energies

Table S2 below supplements the information reported in Table 1 of the paper with additional structural information of the C-H bond distance and imaginary frequency corresponding to the TS structures. In Table S3, we report energies of TS structures and reactants determined from IRC calculations, which were used to calculate the HT activation barriers.

Table S2. Hydride transfer TS properties and activation barriers at T=298K, P=1atm.

System[a]	$\Delta H_{hydride}$ [b]	C-H bond [c]	Freq. [d]
a) CO_2 + AB	25.3	1.21	947.4*i*
b) FLP•CO_2 + AB	7.9	1.48	227.6*i*
c) LA-O=C=O-LA + AB	–0.2	1.89	182.3*i*
d) CO_2•$(LA)_2$ + AB	4.1	1.83	210.2*i*
e) CO_2•(LA) + AB	3.8	1.84	314.5*i*

[a] All but case **c** were calculated at MP2/6-311++G(d,p)//B97-D/6-311G(d,p). Case **c** was calculated using CCSD(T)/6-311++G(d,p)// MP2/6-311G(d,p) because B97-D does not identify a HT TS. Solvation in C_6H_5Cl was treated with the CPCM model. LA=$AlCl_3$, AB=NH_3BH_3. [b] HT activation barriers referenced to reactants from IRC calculations, unit in kcal mol^{-1}. All calculations were zero-point energy (ZPE) and thermally corrected (298K). [c] Carbon-hydride bond distance at TS in Å. [d] Imaginary frequency at TS in cm^{-1}.

Table S3. Hydride transfer reactants and TS energies

System[a]	E(0K) [b]	H(298K) [c]
a) CO_2 + AB (TS)	-271.15296	-271.06874
CO_2 + AB (reactants)	-271.19964	-271.10910
b) FLP•CO_2 + AB (TS)	-4900.32847	-4899.67039
FLP•CO_2 + AB (reactants)	-4900.34234	-4899.68293
c) LA-O=C=O-LA + AB (TS)	-3513.65340	-3513.53432
LA-O=C=O-LA + AB (reactants)	-3513.65502	-3513.53400
d) CO_2•$(LA)_2$ + AB (TS)	-3513.53745	-3513.42267
CO_2•$(LA)_2$ + AB (reactants)	-3513.54550	-3513.42923
e) CO_2•(LA) + AB (TS)	-1892.36069	-1892.25694
CO_2•(LA) + AB (reactants)	-1892.36727	-1892.26298

[a] All but case **c** were calculated at MP2/6-311++G(d,p)//B97-D/6-311G(d,p). Case **c** was calculated using CCSD(T)/6-311++G(d,p)//MP2/6-311G(d,p) because B97-D does not identify a HT TS. Solvation in C_6H_5Cl was treated with the CPCM model. LA=$AlCl_3$, LB=$PMes_3$, AB=NH_3BH_3. [b] Energy at T=0K, in Hartrees. [c] ZPE and thermally (T=298K) corrected energy, in Hartrees.

b. Formation of CO_2•$(LA)_2$ from free CO_2 and LA dimer

CO_2•$(LA)_2$ is an active complex for catalyzing HT to CO_2 (Table S2, case **d**). The activation barrier for the formation of CO_2•$(LA)_2$ from free CO_2 and LA dimer is 10.6 kcal mol^{-1}. The change of enthalpy for the formation of CO_2•$(LA)_2$ is +0.7 kcal mol^{-1}. Figure S2 shows the reactants, TS and product for the formation of CO_2•$(LA)_2$ complex. Table S4 below reports the energies used in determination of the activation barrier and complex formation energy.

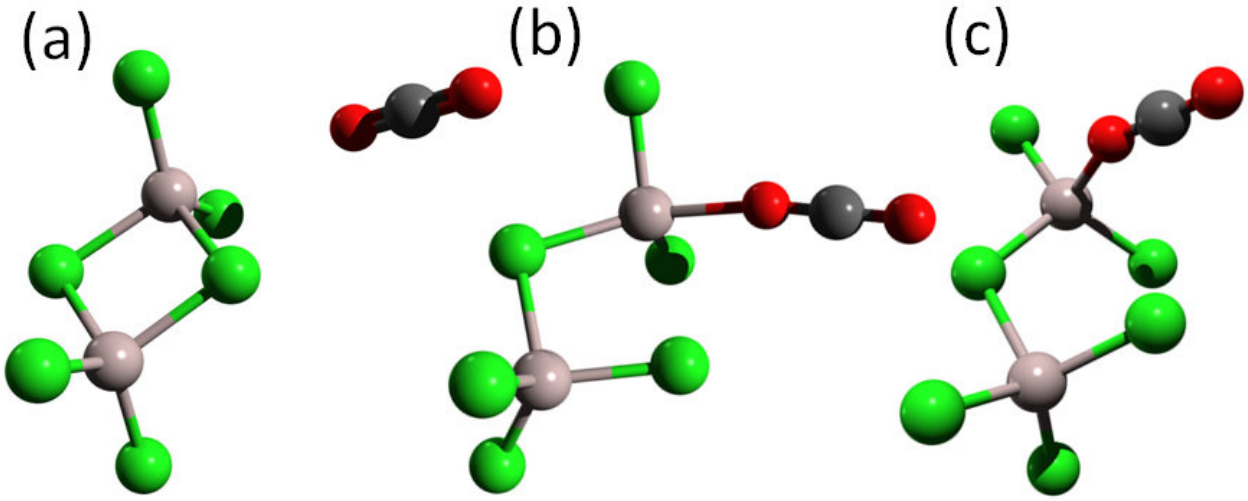


Figure S2. a) CO_2•$(LA)_2$ reactants b) CO_2•$(LA)_2$ TS structure c) CO_2•$(LA)_2$ product. Al, light gray; C, gray; Cl, green; and O, red.

Table S4. Energies for the formation of CO_2•$(LA)_2$ from free CO_2 and LA dimer

System[a]	E(0K) [b]	H(298K) [c]
CO_2 + $(LA)_2$ (TS)	-3430.54107	-3430.50192
CO_2 + $(LA)_2$ (reactants)	-3430.55871	-3430.51878
CO_2 + $(LA)_2$ (product)	-3430.55404	-3430.51765

[a] Calculations performed at MP2/6-311++G(d,p)//B97-D/6-311G(d,p). Solvation in C_6H_5Cl was treated with the CPCM model. LA=$AlCl_3$ [b] Energy at T=0K, in Hartrees. [c] ZPE and thermally (T=298K) corrected energy, in Hartrees.

c. Thermochemistry energies

Table S5 reports the energies used to calculate the thermochemical properties of LA or/and LB catalyzed complexes.

Table S5. Energies used to calculate thermochemical properties of LA or/and LB catalyzed complexes

Species[a]	E(0K) [b]	H(298K) [c]	G(298K) [d]
$(LA)_2$ dimer	-3,242.33636	-3,242.31275	-3,242.36891
CO_2	-188.21739	-188.20248	-188.22745
LB	-1,386.70731	-1,386.16815	-1,386.26220
LA	-1,621.14507	-1,621.13418	-1,621.17185
LA-O=C=O-LA	-3,430.53481	-3,430.49471	-3,430.56779
CO_2•(LA)	-1,809.38226	-1,809.35494	-1,809.40355
CO_2•$(LA)_2$	-3,430.55404	-3,430.51394	-3,430.58056
FLP•CO_2	-4,817.34610	-4,816.76139	-4,816.89432
$AlCl_3H^-$	-1621.88331	-1621.86553	-1621.90398
$NH_3BH_2^+$•CO_2	-270.42207	-270.34031	-270.37956
LA•AB	-1704.16852	-1704.08114	-1704.12923
AB	-82.97829	-82.90524	-82.93357
LA•LB	-3007.91636	-3007.36170	-3007.46822

[a] Calculations performed at MP2/6-311++G(d,p)//B97-D/6-311G(d,p). Solvation in C_6H_5Cl was treated with the CPCM model. LA=$AlCl_3$, LB=$PMes_3$. [b] Enthalpic energy at T=0K, in hartrees. [c] ZPE and thermally (T=298K) corrected energy, in hartrees. [d] Gibbs free energy, ZPE and thermally (298K) corrected, in hartrees.

4. FLP•CO_2 + AB Hydride Transfer (B3LYP)

Employing the B3LYP functional with a 6-311G(d,p) basis set, we located a TS corresponding to HT for the FLP•CO_2 + AB system at a C-H distance of 1.50 Å and with an imaginary frequency of 371*i* cm^{-1} (Figure S3a), consistent with our MP2//B97-D TS structure of 1.48 Å and 228*i* cm^{-1}. Also using the B3LYP functional, but with a 6-31+G(d,p) basis set (as used by Roy *et al.*[13]), we located a similar HT TS with a 1.50 Å C-H bond distance and a 428*i* cm^{-1} imaginary frequency, showing minimal difference between the 6-311G(d,p) and 6-31+G(d,p) basis sets in describing this reaction. A second TS (TS-B2) was identified, occurring after the initial HT along the reaction path, and corresponds to the dissociation of oxidized $NH_3BH_2^+$ from the reduced FLP•HCO_2^- complex with a 1.12 Å C-H distance and a 39*i* cm^{-1} imaginary frequency(Figure S3b), consistent with Roy *et al.*'s reported result of 1.12 Å and 41*i* cm^{-1}.[13] We believe the TS reported by Roy *et al.* was actually TS-B2, instead of the HT TS.

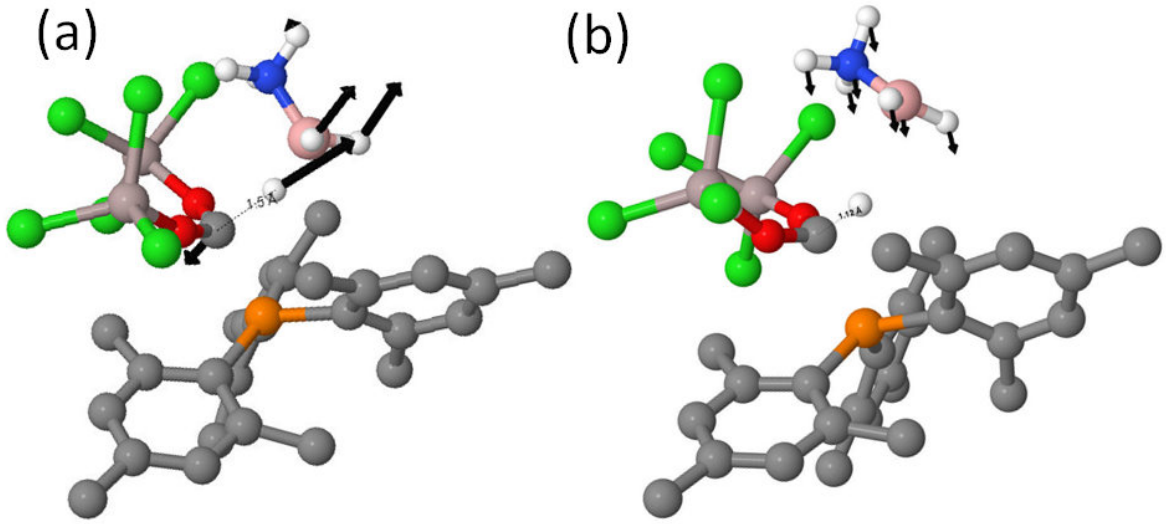


Figure S3. a) Hydride transfer TS structure for FLP•CO_2 + AB system with 1.50 Å C-H distance and 371*i* cm^{-1} imaginary frequency. Arrows indicate normal mode for HT reaction. b) TS-B2 structure with 1.12 Å C-H distance and 39*i* cm^{-1} imaginary frequency. Arrows indicate normal mode for dissociation of oxidized $NH_3BH_2^+$ from the reduced FLP•HCO_2^- complex after the initial HT. Calculations were performed using B3LYP/6-311G(d,p)/CPCM-C_6H_5Cl. Al, gray; B, pink; C, gray; Cl, green; H, white; O, red; N, blue; P, orange.

Figure S4 demonstrates the effect of dispersion on HT barriers for the FLP•CO_2 + AB system. Our B3LYP results show that the HT TS enthalpy is 14.9 kcal mol^{-1} higher than the separated reactants **R**; Meanwhile MP2//B97-D predicts the HT TS enthalpy to be -2.3 kcal mol^{-1}. This demonstrates that B3LYP, which neglects the effect of dispersion, produces qualitatively different results than the more accurate MP2//B97-D method.

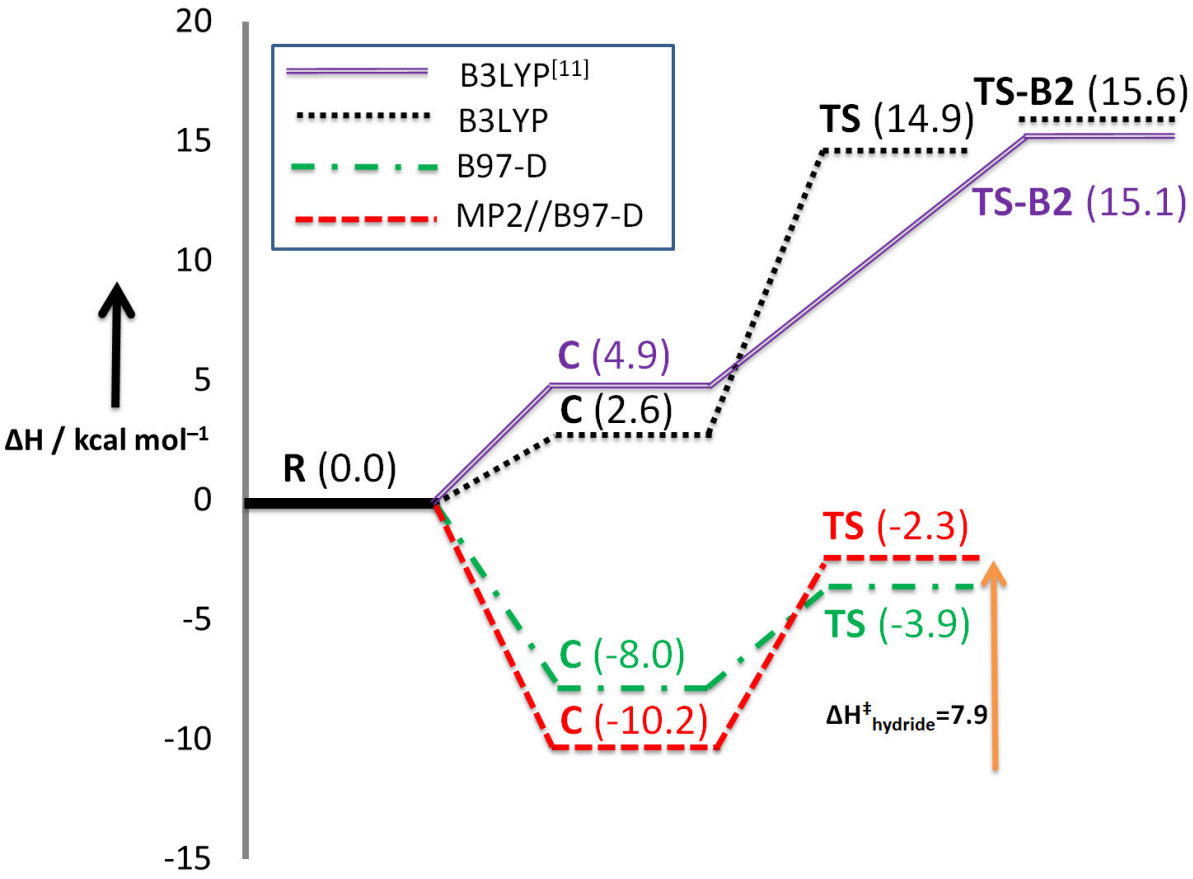


Figure S4. Comparison of various methods in determining hydride transfer barriers for FLP•CO_2 + AB system . **R** is infinitely separated reactants (FLP•CO_2 + AB); **C** is the reactant complex; **TS** is hydride transfer TS. **TS-B2** is the transition state corresponding to the dissociation of oxidized $NH_3BH_2^+$ from the reduced FLP•HCO_2^- complex after the initial HT.

5. Thermodynamics of Complex Formation Reported in Table 2

Table 2 of the manuscript reports the changes in enthalpy and entropy for reactions that form several complexes. The reference energy is that of the starting reactants, which are shown as case 1 and consist of two free CO_2 molecules, a free LA dimer (LA_2), two free Lewis bases and two free ammonia borane molecules. Equation 1 of the manuscript describes these reactions as $2CO_2 + (LA)_2 + 2LB + 2AB \xleftrightarrow{\Delta H;\, T\Delta S;\, Keq}$ Complexes 1 to 11 and conserves the number of molecular species, namely, we have two CO_2, two LA, two LB and two AB on both sides of the equation. The following examples explain how the thermodynamics of complexes 4 and 11 are determined:

Example 1

In complex 4 of Table 2, we have $2CO_2 + (LA)_2 + 2LB + 2AB =$ **CO_2•$(LA)_2$** $+ CO_2 + 2LB + 2AB$. This equation is equivalent to $CO_2 + (LA)_2 =$ **CO_2•$(LA)_2$** when the spectator species are omitted. Thus, for complex 4 as written in Table 2, we are evaluating the thermodynamics (ΔH, $T\Delta S$ and K_{eq}) of forming CO_2•$(LA)_2$ from $CO_2 + (LA)_2$.

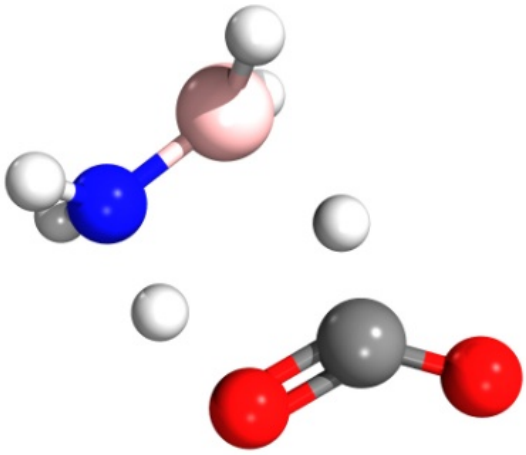
Example 2

In complex 11 of Table 2, we have $2CO_2 + (LA)_2 + 2LB + 2AB = 2CO_2 +$ **LA•LB** + **LA•AB** + LB + AB. This equation is equivalent to $(LA)_2 + LB + AB =$ **LA•LB** + **LA•AB** when the spectator species are omitted. Thus, for complex 11 as written in Table 2, we are evaluating the thermodynamics (ΔH, $T\Delta S$ and K_{eq}) of forming **LA•LB** + **LA•AB** from $(LA)_2 + LB + AB$.

6. Coordinates

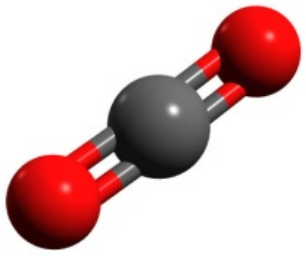
All coordinates are reported in XYZ format. Al, gray; B, pink; C, gray; Cl, green; H, white; O, red; N, blue; P, orange. LA=$AlCl_3$, LB=$PMes_3$, AB=NH_3BH_3. . 0 K energies (not ZPE corrected) reported are calculated using MP2/6-311++G(d,p)//B97-D/6-311G(d,p). Except in the case of LA-O=C=O-LA + AB, energies were calculated at CCSD(T)/6-311++G(d,p)//MP2/6-311G(d,p). Solvation in C_6H_5Cl is modeled using CPCM. Reported energies in hartrees.

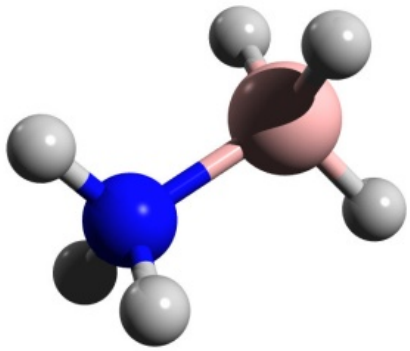
CO_2 + AB (TS) (-271.15296)



C	0.95836	-0.03588	-0.00590
O	2.09690	-0.45502	-0.00457
O	0.44519	1.12648	-0.01594
N	-1.91750	0.31998	0.00657
H	-2.42817	0.61533	-0.82506
H	-0.82811	0.88606	-0.00836
H	-2.41214	0.64229	0.83896
H	-1.53213	-1.72115	-1.02585
H	0.10804	-0.89932	0.00510
H	-1.51507	-1.70263	1.07755
B	-1.51341	-1.14179	0.02104

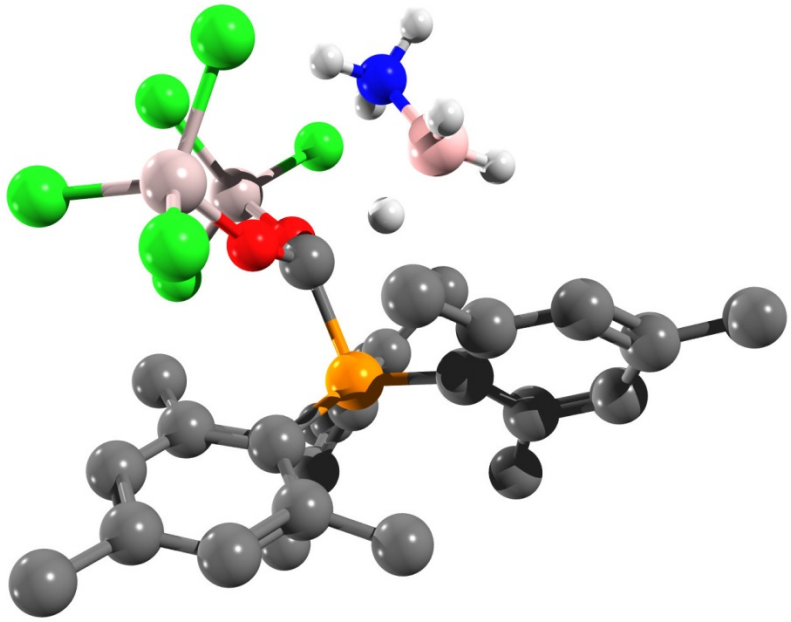
CO_2 + AB (reactants) (-271.19964)





C	1.37846	0.28556	0.01737
O	2.07501	-0.64991	-0.00376
O	0.71234	1.24778	0.04092
N	-2.34404	0.22501	-0.03844
H	-2.78584	0.39856	-0.94281
H	-1.70776	1.00419	0.14052
H	-3.07874	0.26830	0.66947
H	-2.38294	-2.09616	-0.16314
H	-0.72128	-1.19184	-0.89876
H	-1.01471	-1.28398	1.10644
B	-1.54027	-1.22798	0.00392

FLP•CO_2 + AB (TS) (-4900.32847)

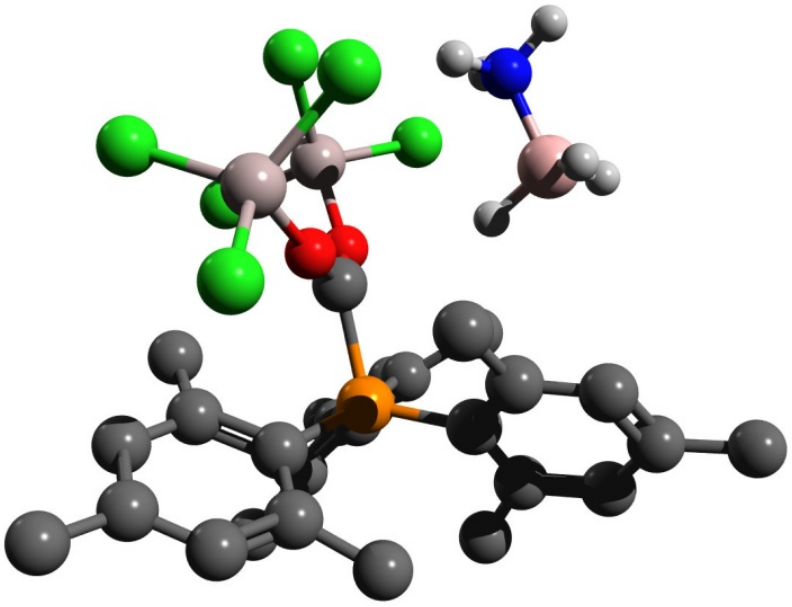


P	-0.00697	0.00478	0.00129
C	-0.01574	0.00735	2.02978
O	1.17254	0.00409	2.52390
Al	2.55353	0.11531	3.68747
Cl	1.86058	1.38058	5.30819
O	-0.96385	-0.72920	2.51486
Al	-1.62894	-1.92000	3.70737
Cl	-3.63994	-1.18412	4.08865
Cl	4.22418	1.02110	2.66395
Cl	3.11746	-1.85614	4.34217
Cl	-1.66898	-3.87987	2.83863
Cl	-0.46713	-1.76489	5.51004
H	-0.49915	1.39154	2.21320
B	-1.03677	2.38935	2.93642
N	-1.50400	1.68666	4.29634
H	-0.12622	3.13997	3.15231
H	-1.98055	2.76269	2.29395
H	-1.95266	2.38193	4.89959
H	-2.19414	0.93920	4.16120
H	-0.71720	1.30511	4.83472
C	-1.36160	-1.13059	-0.45746
C	-2.64720	-0.90820	0.11342
C	-1.14188	-2.26187	-1.29886
C	-3.62723	-1.89727	-0.02890
C	-2.16962	-3.20799	-1.40954
C	-3.39823	-3.07434	-0.74955

H	-4.60196	-1.72912	0.42816
H	-2.00413	-4.07510	-2.04841
C	-0.29318	1.71912	-0.54610
C	-1.27644	2.02175	-1.53424
C	0.44625	2.76873	0.06976
C	-1.61290	3.36642	-1.73535
C	0.06237	4.09233	-0.17998
C	-0.99444	4.41416	-1.03841
H	-2.36234	3.60279	-2.49035
H	0.62982	4.89225	0.29493
C	1.65370	-0.64365	-0.38789
C	2.50732	0.00227	-1.33012
C	2.11190	-1.79005	0.32323
C	3.83460	-0.43581	-1.42435
C	3.45066	-2.17426	0.18323
C	4.34064	-1.48940	-0.65111
H	4.48949	0.05528	-2.14365
H	3.79722	-3.04820	0.73415
C	1.69072	2.55986	0.90443
H	1.47071	2.59425	1.97538
H	2.19447	1.61428	0.70061
H	2.40205	3.36768	0.69332
C	-1.91346	1.01041	-2.47019
H	-1.21804	0.21048	-2.74595
H	-2.80166	0.53412	-2.03883
H	-2.22160	1.52433	-3.38869
C	0.08960	-2.49846	-2.15254
H	0.50754	-1.56815	-2.55028
H	0.88963	-3.00395	-1.59811
H	-0.18506	-3.13852	-2.99957
C	-3.09061	0.38736	0.75453
H	-3.68386	0.95778	0.02404
H	-3.73052	0.18492	1.61956
H	-2.27994	1.03891	1.07448
C	1.23719	-2.68860	1.17292
H	1.45153	-2.55496	2.23897
H	0.16749	-2.54338	1.01670
H	1.45863	-3.73535	0.92927
C	2.07644	1.09052	-2.29488
H	1.06921	0.92074	-2.69108
H	2.07878	2.08321	-1.82818
H	2.77447	1.11601	-3.14008
C	5.79513	-1.88293	-0.72765
H	6.36541	-1.35752	0.05412

H	5.92418	-2.96034	-0.56244
H	6.23061	-1.61214	-1.69793
C	-1.42858	5.84569	-1.23926
H	-1.83989	5.99928	-2.24518
H	-2.21608	6.10589	-0.51483
H	-0.59266	6.53946	-1.08279
C	-4.44513	-4.15789	-0.82508
H	-4.34839	-4.74134	-1.74952
H	-4.32628	-4.85102	0.02226
H	-5.45738	-3.73722	-0.76884

FLP•CO_2 + AB (reactants) (-4900.34234)

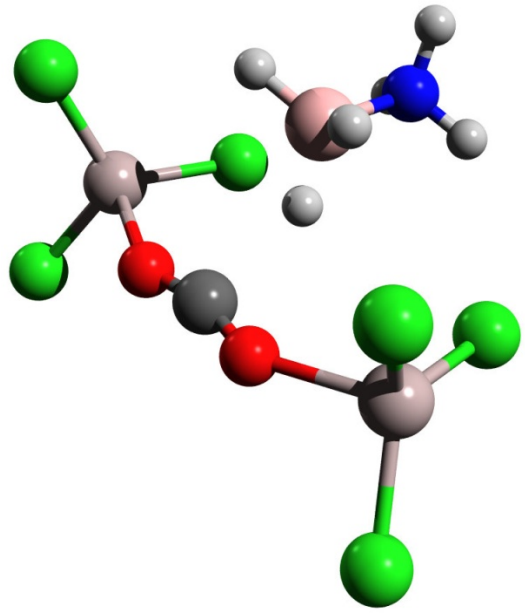


P	-0.05518	0.07217	-0.01144
C	-0.16923	0.08188	1.95094
O	0.90763	0.06039	2.58450
Al	2.31696	-0.10162	3.78125
Cl	2.20248	1.64452	5.03028
O	-1.32043	-0.03254	2.43460
Al	-2.34059	-0.43424	3.94621
Cl	-3.96042	0.97970	3.88791
Cl	4.11522	-0.12576	2.60537
Cl	2.03705	-1.97556	4.78580
Cl	-2.92480	-2.46715	3.61004
Cl	-1.13810	-0.12176	5.69257
H	-0.66018	2.62554	2.42375
B	-0.75799	3.68426	3.01751
N	-1.06392	3.29573	4.59323
H	0.29327	4.30455	3.01059
H	-1.70880	4.34445	2.62590
H	-1.10038	4.12333	5.19022
H	-1.95816	2.81166	4.70294
H	-0.34159	2.68030	4.97690
C	-1.67038	-0.62374	-0.48822
C	-2.83854	0.08502	-0.07321
C	-1.78617	-1.84368	-1.21504
C	-4.08236	-0.53302	-0.25256
C	-3.06496	-2.39520	-1.37261
C	-4.21846	-1.78516	-0.86419

H	-4.97319	-0.00257	0.08220
H	-3.15898	-3.32859	-1.92673
C	0.11648	1.77004	-0.65794
C	-0.61826	2.15128	-1.82256
C	0.94415	2.71667	0.00652
C	-0.63063	3.50710	-2.17138
C	0.88114	4.05692	-0.39363
C	0.06628	4.48431	-1.44672
H	-1.18358	3.80343	-3.06241
H	1.51129	4.77802	0.12511
C	1.38860	-1.01538	-0.23560
C	2.46205	-0.66425	-1.10540
C	1.44950	-2.21164	0.54070
C	3.60345	-1.47746	-1.09831
C	2.61891	-2.97685	0.49545
C	3.71890	-2.61517	-0.29062
H	4.42642	-1.21359	-1.76158
H	2.66256	-3.88962	1.08891
C	1.95414	2.35827	1.06698
H	1.52058	2.47924	2.06684
H	2.32904	1.33735	0.95303
H	2.81113	3.03846	0.99452
C	-1.31177	1.20142	-2.78355
H	-0.79002	0.24250	-2.87685
H	-2.34491	0.98336	-2.48576
H	-1.33879	1.66497	-3.77698
C	-0.64533	-2.56614	-1.90632
H	0.08593	-1.87748	-2.34264
H	-0.09855	-3.23086	-1.22668
H	-1.05534	-3.18286	-2.71471
C	-2.86777	1.51625	0.42576
H	-2.98199	2.18818	-0.43783
H	-3.73086	1.65894	1.08376
H	-1.98133	1.84732	0.96919
C	0.32080	-2.76001	1.39627
H	0.49829	-2.55479	2.45956
H	-0.67175	-2.38418	1.13020
H	0.28754	-3.85074	1.28781
C	2.45694	0.49823	-2.07946
H	1.50613	0.59086	-2.61457
H	2.64210	1.45559	-1.57717
H	3.25045	0.34933	-2.82073
C	4.98976	-3.42710	-0.26760
H	5.64910	-3.06296	0.53557

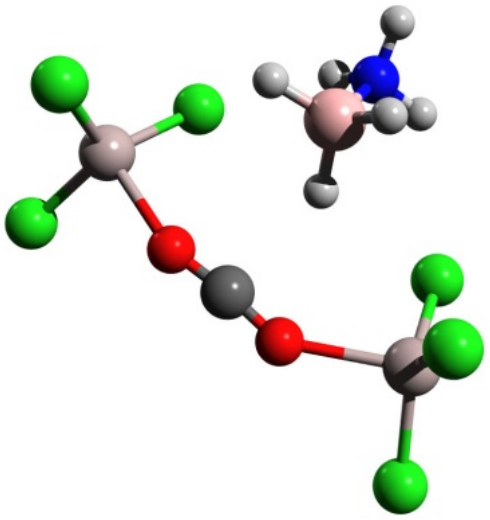
H	4.78065	-4.48617	-0.06976
H	5.53662	-3.33780	-1.21475
C	-0.03145	5.94413	-1.81450
H	-0.26224	6.07198	-2.87981
H	-0.83847	6.42226	-1.23776
H	0.90031	6.47519	-1.58151
C	-5.56943	-2.44602	-0.98701
H	-5.58630	-3.16655	-1.81431
H	-5.80507	-2.99201	-0.06033
H	-6.36201	-1.70226	-1.14112

LA-O=C=O-LA + AB (TS) (-3513.65340)



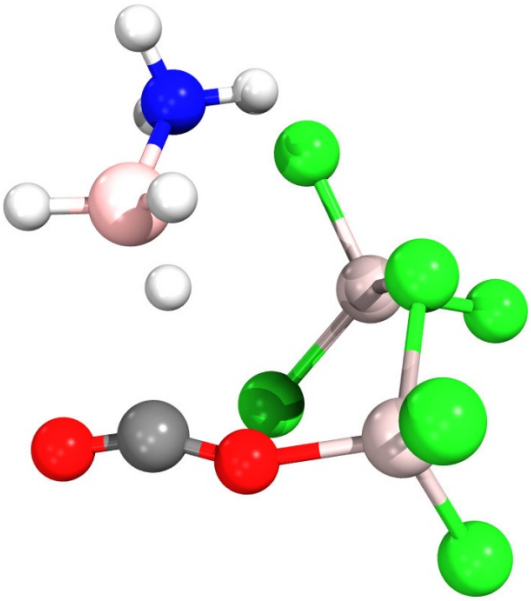
Al	3.09732	-0.17899	0.05690
Cl	2.68262	1.13950	-1.52129
Cl	3.63807	0.61511	1.91076
Cl	3.94861	-2.01579	-0.47308
Al	-3.10611	-0.21610	0.09243
Cl	-2.72058	1.10458	-1.49068
Cl	-3.88003	-2.08710	-0.43853
Cl	-3.70421	0.56793	1.93253
C	0.00296	-0.70038	0.48999
O	1.16231	-0.87474	0.50577
O	-1.15549	-0.86740	0.55643
N	0.00487	3.28891	-0.55018
H	-0.78464	3.19731	-1.18908
H	0.85854	3.21329	-1.10287
H	-0.03023	4.22967	-0.16020
H	-1.07891	2.26675	1.19003
H	0.00208	1.11914	-0.03224
H	0.94255	2.29163	1.28466
B	-0.03666	2.16914	0.59664

LA-O=C=O-LA + AB (reactants) (-3513.65502)



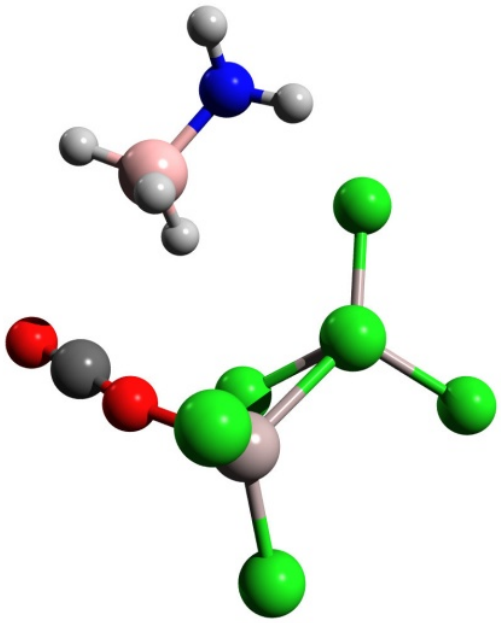
Al	3.11583	-0.21149	-0.02715
Cl	2.54272	1.00055	-1.63561
Cl	3.59433	0.66770	1.79816
Cl	4.01052	-2.03633	-0.50877
Al	-3.14497	-0.19679	0.05449
Cl	-2.63595	1.12947	-1.48636
Cl	-3.80955	-2.08958	-0.52791
Cl	-3.83108	0.56650	1.86549
C	0.00753	-0.85484	0.55593
O	1.15917	-1.03080	0.50344
O	-1.15333	-0.80246	0.63073
N	-0.06967	3.30975	-0.51362
H	-0.81228	2.95947	-1.11705
H	0.80100	3.23095	-1.03699
H	-0.25027	4.29990	-0.35988
H	-1.10768	2.44848	1.33672
H	0.38530	1.37125	0.54052
H	0.81777	3.02300	1.57321
B	0.00507	2.47284	0.86867

CO_2•$(LA)_2$ + AB (TS) (-3513.53745)



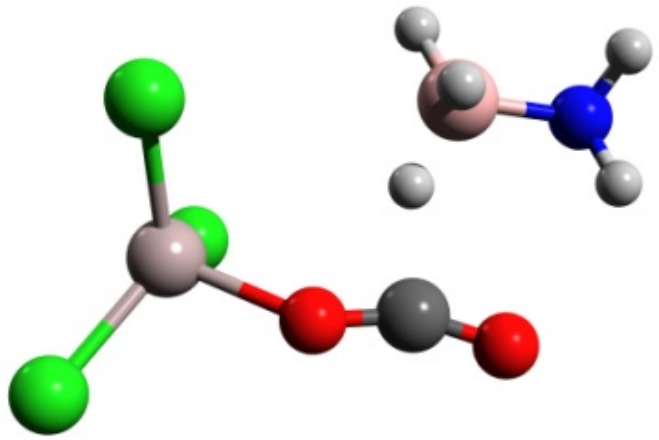
Al	-1.73413	0.97877	-0.26580
Cl	-1.36074	2.74242	0.82333
Cl	0.12258	0.29016	-1.34683
Cl	-3.35783	0.86212	-1.60414
Al	2.02551	0.12773	0.09931
Cl	2.95273	-1.63310	-0.70181
Cl	1.17630	-0.14453	2.04170
Cl	3.09048	1.94158	-0.20436
C	-1.87309	-1.47593	1.52500
O	-1.98195	-0.37831	1.03524
O	-1.98619	-2.30494	2.32543
N	0.12036	-3.49587	-1.46723
H	0.04877	-4.32591	-2.06200
H	0.91448	-3.64526	-0.83963
H	0.37848	-2.72090	-2.08234
H	-2.11327	-2.85163	-1.46105
H	-1.55554	-4.23088	-0.04171
H	-1.01073	-2.30873	0.14850
B	-1.27886	-3.23346	-0.66985

CO_2•$(LA)_2$ + AB (reactants) (-3513.54550)



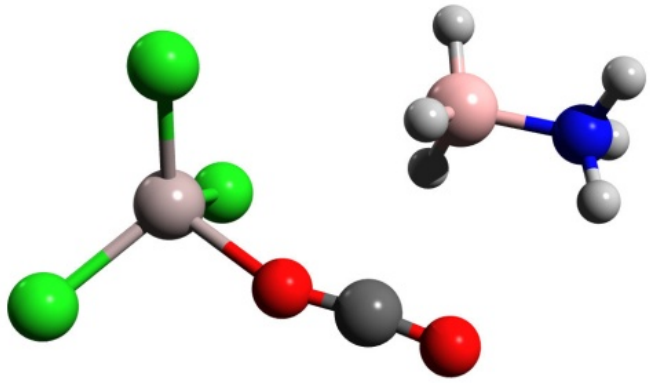
Al	-1.75134	1.00035	-0.31622
Cl	-1.47345	2.73134	0.84749
Cl	0.12842	0.38833	-1.35895
Cl	-3.37328	0.83127	-1.64451
Al	1.99840	0.07579	0.10708
Cl	2.87984	-1.70147	-0.69720
Cl	1.13701	-0.11802	2.05717
Cl	3.14842	1.84759	-0.17283
C	-1.88749	-1.33615	1.72385
O	-2.01492	-0.41190	0.99436
O	-1.84182	-2.19544	2.48418
N	0.18452	-3.64843	-1.70033
H	-0.20410	-4.37504	-2.30554
H	0.98587	-4.05905	-1.21717
H	0.55861	-2.91880	-2.31000
H	-1.78949	-2.50129	-1.28197
H	-1.36086	-4.04876	-0.03084
H	-0.31700	-2.32397	0.10667
B	-0.93184	-3.08041	-0.63382

CO_2•(LA) + AB (TS) (-1892.36069)



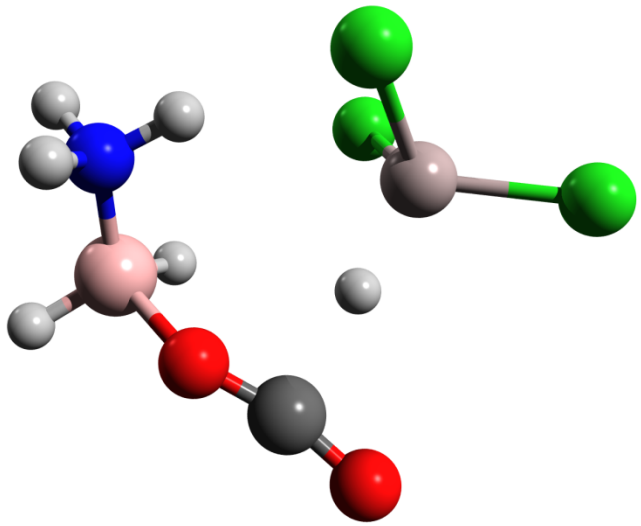
C	1.56482	1.35372	0.23468
O	0.44716	1.18255	-0.17686
O	2.51898	1.95621	0.52323
Al	-1.08258	-0.07014	-0.18758
Cl	-2.67647	1.27613	-0.64968
Cl	-0.59607	-1.45128	-1.73545
Cl	-1.10638	-0.84585	1.80131
N	4.18977	-0.65676	0.92191
H	4.17951	-0.86475	1.92313
H	4.39035	0.34048	0.81815
H	4.97841	-1.16319	0.51484
H	2.54013	-2.22929	0.42730
H	1.92377	-0.37179	0.76990
H	2.88746	-0.78829	-0.98695
B	2.78957	-1.06944	0.18743

CO_2•(LA) + AB (reactants) (-1892.36727)



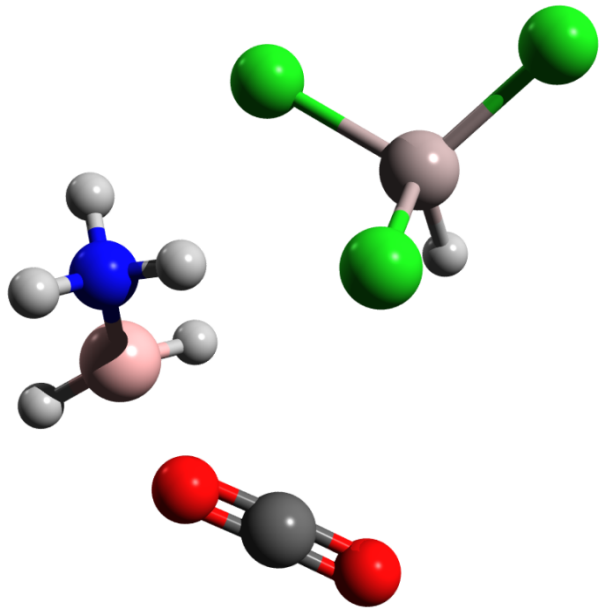
C	1.51086	1.55184	0.22557
O	0.43201	1.18549	-0.08299
O	2.52058	2.03446	0.50823
Al	-1.13520	-0.11220	-0.25631
Cl	-2.66226	1.28097	-0.77862
Cl	-0.49690	-1.40046	-1.81895
Cl	-1.25697	-0.92143	1.70509
N	4.35384	-0.75549	0.84276
H	4.54420	-1.00102	1.81592
H	4.53429	0.24520	0.74103
H	5.05200	-1.24019	0.27686
H	2.76711	-2.37482	0.32556
H	2.07342	-0.71418	1.24756
H	2.64720	-0.63263	-0.70674
B	2.81313	-1.15859	0.38148

$NH_3BH_2^+ \bullet CO_2 + AlCl_3H^-$ (TS) (-1892.33428)



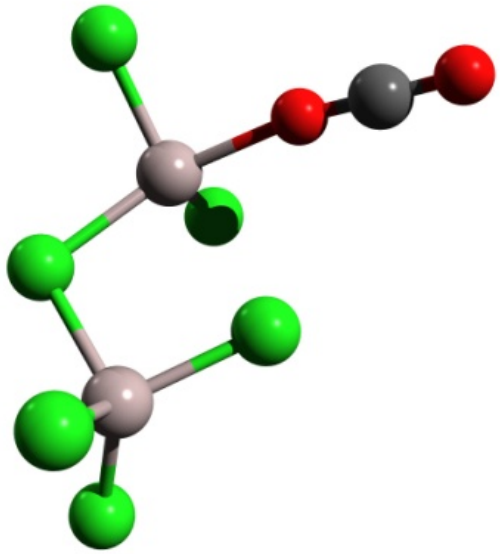
Al	3.72681	-0.59973	-0.17319
Cl	3.16352	-0.66469	-2.27366
Cl	2.04175	-1.04875	1.12012
Cl	5.32888	-2.09211	0.17302
N	7.67900	-0.03723	-0.92580
H	8.52449	-0.07026	-0.34999
H	7.95405	-0.32971	-1.86895
H	7.02189	-0.75736	-0.57451
H	4.36099	0.82898	0.18149
H	7.82624	2.25747	-1.23710
H	5.96440	1.38394	-1.55532
B	7.02403	1.40153	-1.01065
C	5.68013	1.94898	1.29066
O	6.66383	1.67926	0.66407
O	4.93942	2.35791	2.07923

$NH_3BH_2^+ \bullet CO_2 + AlCl_3H^-$ (reactant) (-1892.33969)



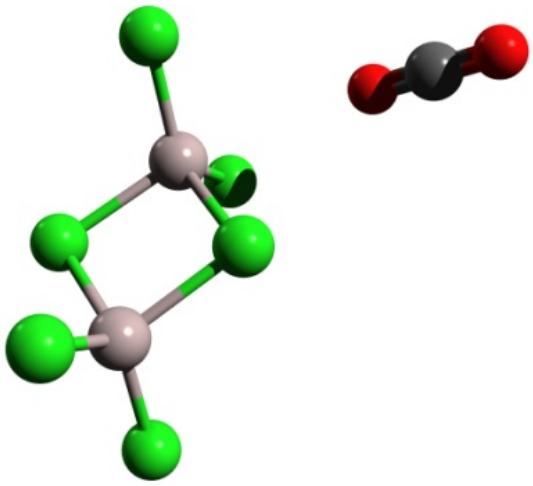
Al	-1.16271	-0.37288	-0.26992
Cl	-0.26704	-0.69965	-2.26681
Cl	-2.66532	-1.91033	0.09000
Cl	0.51788	-0.72953	1.17206
N	2.75007	0.15569	-1.03524
H	3.72281	-0.13397	-0.90759
H	2.42291	-0.21922	-1.93595
H	2.16101	-0.31549	-0.32074
H	-1.69211	1.11002	-0.10621
H	3.44623	2.35766	-1.38942
H	1.38847	2.02821	-1.10236
B	2.52774	1.70069	-1.02041
C	2.00267	2.29962	1.75077
O	2.77316	1.96811	0.91758
O	1.28432	2.63957	2.58826

CO_2 + $(LA)_2$ (TS) (-3430.54107)



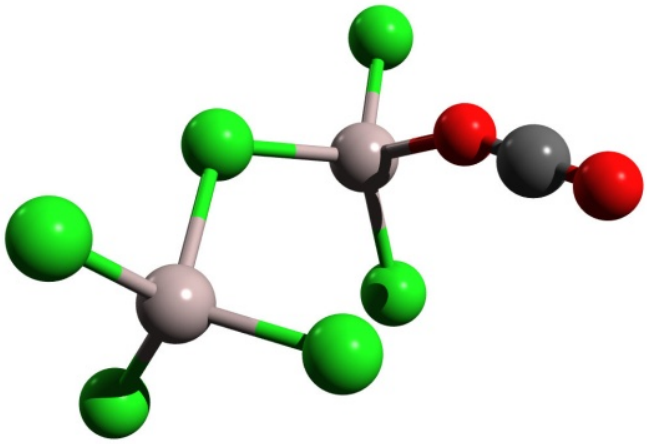
Al	-1.37226	-0.51542	0.20597
Cl	-1.79353	-1.39419	-1.66360
Cl	0.58137	-1.43637	1.04722
Cl	-2.63401	-0.86639	1.88256
Al	2.15175	-0.02886	0.09367
Cl	3.19405	0.92906	1.67657
Cl	0.64356	1.25151	-0.86070
Cl	3.30486	-1.14722	-1.29219
C	-2.61716	2.46008	-0.36802
O	-2.27540	1.36653	-0.09592
O	-2.96696	3.52795	-0.62669

CO_2 + $(LA)_2$ (reactants) (-3430.55871)



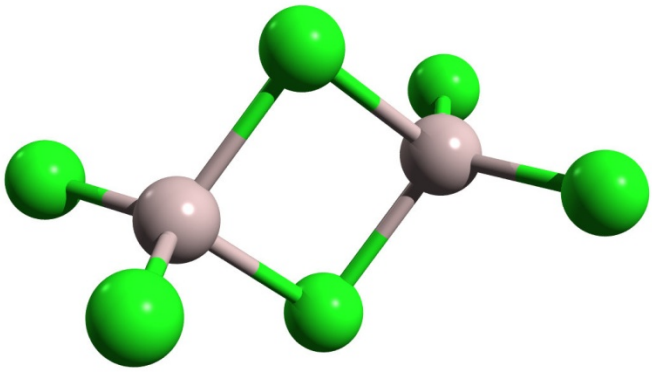
Al	-1.02849	-0.76847	0.22995
Cl	-1.80944	-1.65495	-1.51034
Cl	0.86900	-1.94825	0.88006
Cl	-2.19829	-0.39283	1.93741
Al	2.18870	-0.18601	0.22748
Cl	3.19625	0.64310	1.88050
Cl	0.30442	1.03761	-0.29685
Cl	3.23402	-0.69212	-1.53006
C	-3.04747	2.92852	-0.86770
O	-2.87406	1.77138	-0.86171
O	-3.22143	4.08180	-0.87506

CO_2 + $(LA)_2$ (product) (-3430.55404)



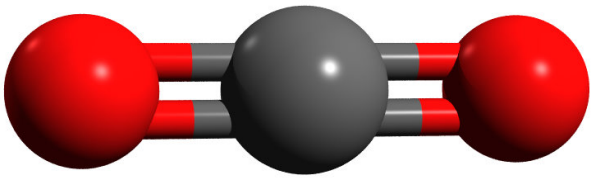
Al	-1.62802	-0.80121	0.36278
Cl	-1.54070	-1.33688	-1.66373
Cl	0.35128	-0.70799	1.37586
Cl	-3.05934	-1.58813	1.68411
Al	2.07011	0.22569	-0.04265
Cl	3.39785	1.04812	1.40463
Cl	0.97167	1.67292	-1.18730
Cl	2.78465	-1.44124	-1.15279
C	-2.08375	2.23429	-0.11903
O	-2.01614	1.15129	0.35560
O	-2.17421	3.29686	-0.54476

$(LA)_2$ dimer (-3,242.33636)



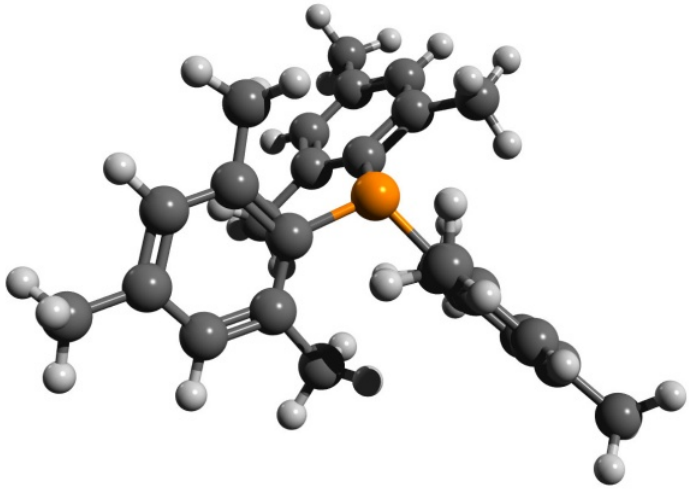
Al	0.09687	0.45942	0.24789
Cl	-0.10913	1.88272	1.78332
Cl	2.32144	-0.11537	0.02153
Cl	-0.78036	0.74273	-1.64347
Al	1.84678	-2.23623	0.80304
Cl	-0.37782	-1.66147	1.02932
Cl	2.72380	-2.51956	2.69450
Cl	2.05259	-3.65972	-0.73222

CO_2 (-188.21739)



C	-0.78763	0.11991	-1.91756
O	-1.90224	0.13162	-2.26827
O	0.32696	0.10820	-1.56681

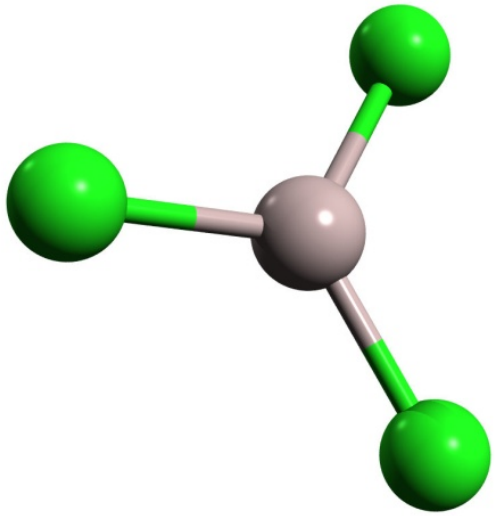
LB (-1,386.70731)



P	0.01596	0.00442	0.86400
C	1.58823	-0.74875	0.24239
C	1.99254	-1.92505	0.94329
C	3.21971	-2.52900	0.64140
C	4.08346	-2.00653	-0.33187
C	3.67167	-0.85857	-1.01678
C	2.44064	-0.22379	-0.76569
C	1.11069	-2.58758	1.98430
H	3.50268	-3.43392	1.18138
C	5.40901	-2.67209	-0.63304
H	4.31669	-0.45107	-1.79684
C	2.08245	0.95668	-1.64541
H	1.60748	-3.47576	2.39469
H	0.14902	-2.89906	1.55087
H	0.87454	-1.89896	2.80919
H	5.93942	-2.14997	-1.43964
H	5.26434	-3.71967	-0.93652
H	6.05625	-2.67840	0.25664
H	1.05664	0.87545	-2.02378
H	2.76823	1.00418	-2.50077
H	2.13926	1.91062	-1.10465
C	-0.12618	1.74417	0.24837
C	0.64705	2.69610	0.97496
C	0.51075	4.06285	0.69319
C	-0.37666	4.53365	-0.28354
C	-1.10702	3.58605	-1.01117
C	-0.99572	2.20495	-0.77905
C	1.66577	2.27737	2.01758
H	1.11808	4.77692	1.25115

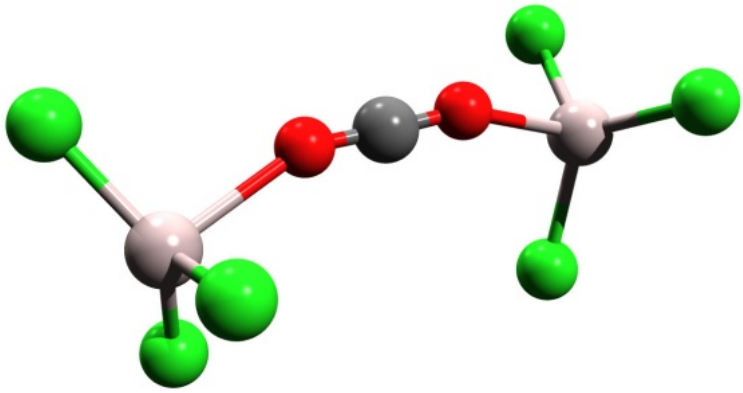
C	-0.54567	6.01537	-0.53729
H	-1.77271	3.92808	-1.80532
C	-1.77020	1.28321	-1.69782
H	2.45467	1.65534	1.56922
H	1.20114	1.67274	2.81044
H	2.13717	3.15755	2.47229
H	-0.72147	6.21945	-1.60253
H	0.34141	6.57645	-0.21417
H	-1.41021	6.41034	0.01947
H	-2.09157	1.83188	-2.59264
H	-2.66189	0.86391	-1.21223
H	-1.15797	0.43032	-2.01106
C	-1.42418	-0.97725	0.24329
C	-2.64979	-0.72937	0.93227
C	-3.77967	-1.50486	0.64090
C	-3.74726	-2.53841	-0.30578
C	-2.54760	-2.75179	-0.99252
C	-1.39013	-1.98882	-0.75392
C	-2.79457	0.39100	1.94384
H	-4.71002	-1.29144	1.16968
C	-4.97009	-3.38940	-0.56978
H	-2.51050	-3.52247	-1.76432
C	-0.19267	-2.26330	-1.64022
H	-2.59411	1.36995	1.48469
H	-2.07850	0.28174	2.77187
H	-3.81093	0.40424	2.35718
H	-5.87033	-2.76750	-0.67644
H	-5.15103	-4.08192	0.26698
H	-4.84785	-3.98804	-1.48180
H	-0.50249	-2.86185	-2.50661
H	0.60056	-2.80953	-1.11287
H	0.25965	-1.33263	-2.00280

LA (-1,621.14507)



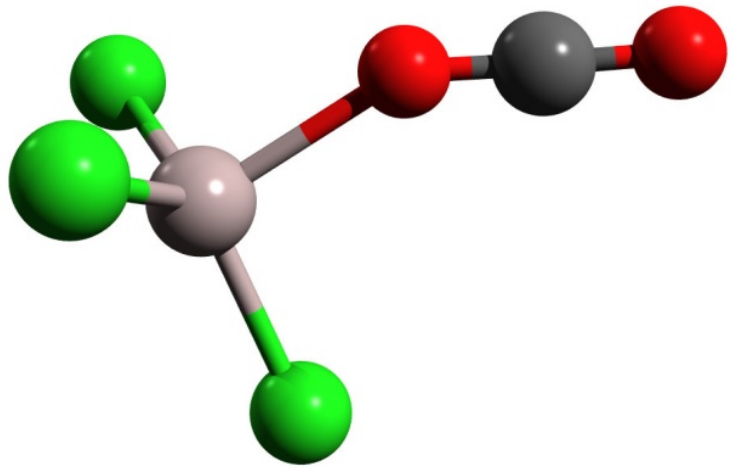
Al	0.43945	0.70786	0.01032
Cl	-0.57872	1.12612	1.79840
Cl	2.37702	-0.09896	0.06637
Cl	-0.45416	1.15186	-1.83687

LA-O=C=O-LA (-1,621.14507)



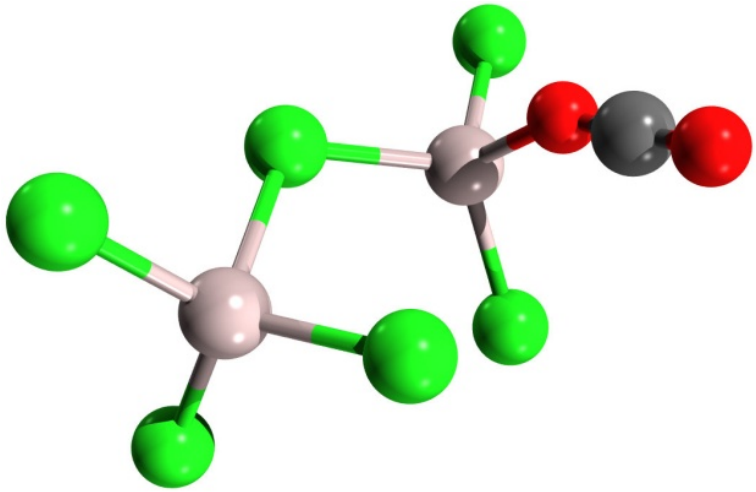
Al	3.27110	-0.46334	-0.04245
Cl	2.74885	0.56620	-1.81373
Cl	3.90493	0.66973	1.62479
Cl	3.87147	-2.48367	-0.17148
Al	-3.30171	-0.28698	-0.00091
Cl	-2.92888	1.33150	-1.30274
Cl	-3.42893	-2.23231	-0.81183
Cl	-4.17860	0.09435	1.87912
C	0.02003	-0.66243	0.70095
O	1.17059	-0.84081	0.66798
O	-1.12906	-0.49734	0.76285

CO_2•(LA) (-1,809.38226)



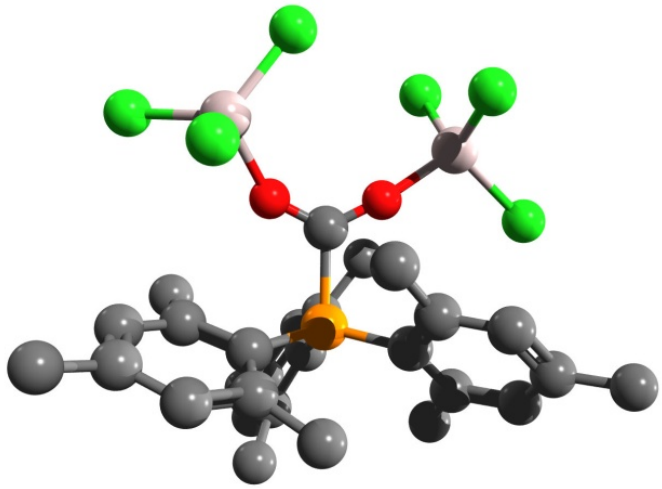
C	-0.56765	-2.61180	-0.13716
O	-0.63917	-1.43333	-0.10964
O	-0.52626	-3.76262	-0.16630
Al	0.28444	0.42269	-0.03144
Cl	-0.51849	1.16343	1.78777
Cl	2.31597	-0.20533	-0.01109
Cl	-0.43934	1.27491	-1.83488

CO_2•$(LA)_2$ (-3,430.55404)



Al	-1.62802	-0.80121	0.36278
Cl	-1.54070	-1.33688	-1.66373
Cl	0.35128	-0.70799	1.37586
Cl	-3.05934	-1.58813	1.68411
Al	2.07011	0.22569	-0.04265
Cl	3.39785	1.04812	1.40463
Cl	0.97167	1.67292	-1.18730
Cl	2.78465	-1.44124	-1.15279
C	-2.08375	2.23429	-0.11903
O	-2.01614	1.15129	0.35560
O	-2.17421	3.29686	-0.54476

FLP•CO_2 (-4,817.34610)



P	-0.00499	0.18287	-1.37669
C	-0.09451	0.21102	0.57242
O	0.97123	0.03291	1.19918
Al	2.45960	0.00951	2.31201
Cl	2.29388	1.76253	3.53675
O	-1.24283	0.28918	1.06898
Al	-2.30959	-0.22705	2.53218
Cl	-3.91625	1.19909	2.52715
Cl	4.15305	0.10428	0.98141
Cl	2.35693	-1.87618	3.33186
Cl	-2.90820	-2.21374	1.96732
Cl	-1.09968	-0.15116	4.29594
C	-1.64608	-0.48527	-1.81374
C	-2.78752	0.27136	-1.40073
C	-1.81445	-1.74367	-2.46037
C	-4.04353	-0.34156	-1.47529
C	-3.10510	-2.28675	-2.51718
C	-4.22234	-1.63422	-1.98236
H	-4.91094	0.22054	-1.13143
H	-3.23571	-3.25170	-3.00652
C	0.12730	1.87630	-2.05108
C	-0.48719	2.13908	-3.31067
C	0.74030	2.92844	-1.31839
C	-0.56264	3.46939	-3.74227
C	0.62216	4.23652	-1.80272
C	-0.05397	4.53699	-2.99190
H	-1.02716	3.67201	-4.70670
H	1.09140	5.04033	-1.23661
C	1.42455	-0.91152	-1.63733

C	2.50472	-0.55750	-2.50212
C	1.45549	-2.13684	-0.90627
C	3.58787	-1.44127	-2.58930
C	2.57779	-2.96175	-1.03339
C	3.65631	-2.63508	-1.86098
H	4.41116	-1.18029	-3.25302
H	2.59704	-3.89627	-0.47344
C	1.55940	2.71755	-0.06693
H	0.93161	2.61324	0.82771
H	2.20533	1.83636	-0.14720
H	2.20466	3.58618	0.10286
C	-1.02307	1.08444	-4.26074
H	-0.44674	0.15254	-4.23088
H	-2.06685	0.82905	-4.03803
H	-0.97728	1.46943	-5.28628
C	-0.72516	-2.52061	-3.17634
H	0.05425	-1.87803	-3.59536
H	-0.23015	-3.24645	-2.52019
H	-1.18245	-3.08247	-3.99968
C	-2.78788	1.73875	-1.00538
H	-2.86118	2.34953	-1.91723
H	-3.65970	1.95145	-0.37787
H	-1.90124	2.08100	-0.47062
C	0.35823	-2.66367	0.00338
H	0.66838	-2.59026	1.05380
H	-0.61561	-2.17674	-0.10353
H	0.19690	-3.72780	-0.20898
C	2.58574	0.70013	-3.34587
H	1.70867	0.83307	-3.98767
H	2.67622	1.60112	-2.72703
H	3.46899	0.64535	-3.99186
C	4.86602	-3.53114	-1.95442
H	5.62317	-3.21755	-1.21936
H	4.60442	-4.57476	-1.73920
H	5.32565	-3.47471	-2.94967
C	-0.21696	5.96418	-3.45369
H	-0.35278	6.01678	-4.54088
H	-1.10572	6.41092	-2.98173
H	0.64976	6.57368	-3.16764
C	-5.57819	-2.29459	-1.96500
H	-5.70781	-2.96372	-2.82532
H	-5.68418	-2.90141	-1.05238
H	-6.38303	-1.54874	-1.96394

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