Pentaatomic planar tetracoordinate carbon molecules $[XCAl_3]^q$ [(X,q)=(B,-2), (C,-1), (N,0)] with C–X multiple bonding

Supporting Information.

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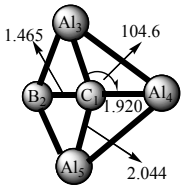
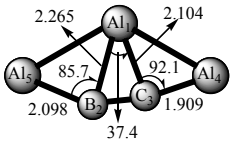
SI1-Figure 1~3. Calculated structures and relative energies for the isomer of the $[BCAl_3]^{2-}$, $[C_2Al_3]^-$ and $[NCAl_3]$, respectively. The parentheses and square bracket values obtained at the CCSD(T)/6-311+G(2df)//B3LYP/6-311+G(d) and B3LYP/6-311+G(d) levels, respectively. The energy values are in kcal/mol, bond lengths are in angstroms, bond angles in degrees.

SI1-Figure 4~6. Optimized geometries of interconversion transition states of $[BCAl_3]^{2-}$, $[C_2Al_3]^-$ and $[NCAl_3]$ at the B3LYP/6-311+G(d) level, respectively. The parentheses and square bracket values obtained at the CCSD(T)/6-311+G(2df)//B3LYP/6-311+G(d) and B3LYP/6-311+G(d) levels, respectively. The energy values are in kcal/mol, bond lengths are in angstroms, bond angles in degrees.

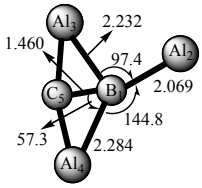
SI1-Figure 1



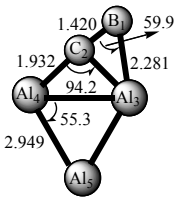
(0.0)
[0.0]
B-01 C_{2V}



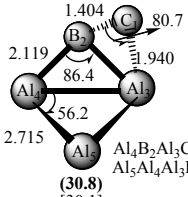
(0.8)
[-1.6]
B-02 Cs



(5.1)
[2.7]
B-03 Cs

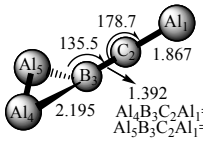


(26.4)
[24.3]
B-04 Cs



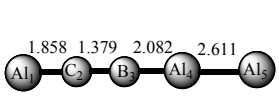
$Al_4B_2Al_3C_1$=152.8
$Al_5Al_4Al_3B_2$=-131.9

(30.8)
[30.1]
B-05 C_1

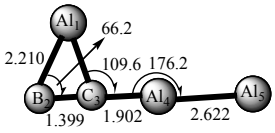


$Al_4B_3C_2Al_1$=120.9
$Al_5B_3C_2Al_1$=-120.9

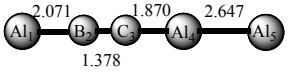
(31.4)
[23.5]
B-06 Cs



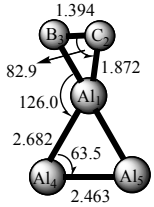
(35.7)
[24.4]
B-07 C∞



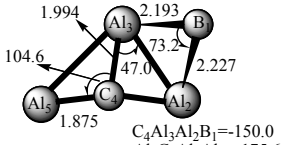
(39.3)
[33.0]
B-08 Cs



(46.1)
[33.3]
B-09 C∞

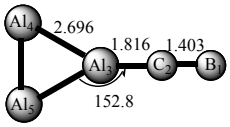


(51.3)
[53.5]
B-10 Cs

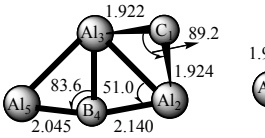


$C_4Al_3Al_2B_1$=-150.0
$Al_5C_4Al_3Al_2$=-175.6

(56.1)
[58.2]
B-11 C_1

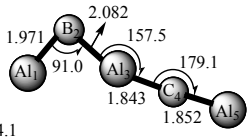


(60.2)
[56.2]
B-12 C_{2V}

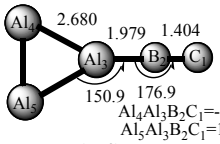


$Al_5B_4Al_3Al_2$=-164.1
$B_4Al_2Al_3C_1$=146.1

(65.6)
[73.1]
B-13 C_1

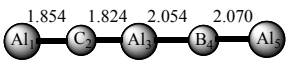


(77.0)
[75.7]
B-14 Cs

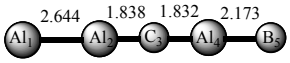


$Al_4Al_3B_2C_1$=-106.9
$Al_5Al_3B_2C_1$=106.9

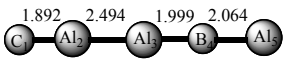
(77.9)
[74.9]
B-15 Cs



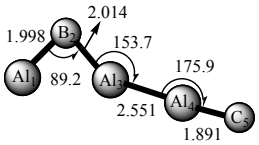
(79.6)
[70.3]
B-16 C∞



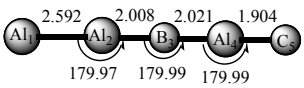
[115.6]
B-17 C∞



[131.4]
B-18 C∞

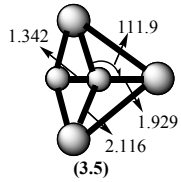


[131.7]
B-19 Cs

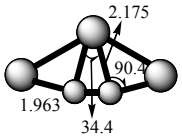


[135.0]
B-20 Cs

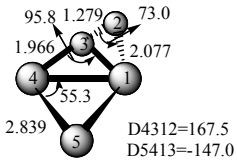
SI1-Figure 2



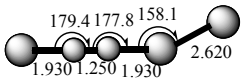
(3.5)
[4.0]
C-01 C_{2v}



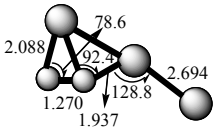
(0.0)
[0.0]
C-02 C_{2v}



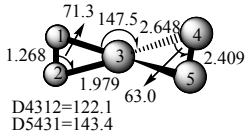
(26.0)
[26.3]
C-03 C_1



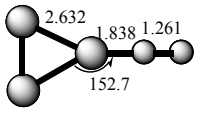
(42.7)
[34.3]
C-04 C_s



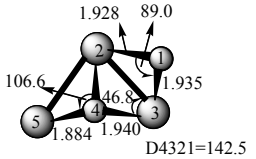
(40.7)
[37.6]
C-05 C_s



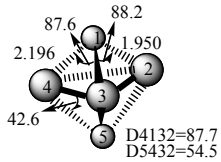
(38.7)
[43.0]
C-06 C_{2v}



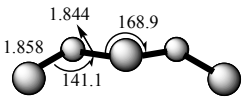
(44.2)
[44.7]
C-07 C_{2v}



[83.0]
C-08 C_1



[89.2]
C-09 C_{2v}



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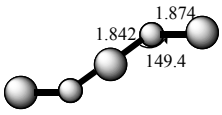
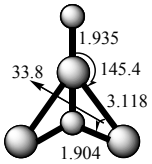
C-10 C_{2v}



[100.0]
C-11 C_{2h}



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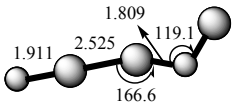
C-12 C_{2v}



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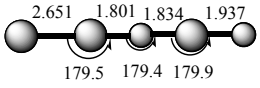
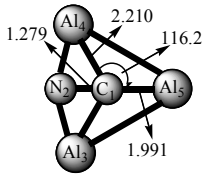
C-13 C_s

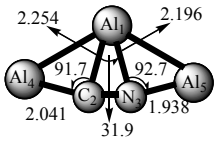


[161.1]
C-14 C_s

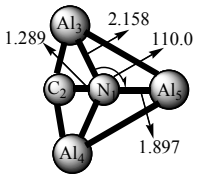
SI1-Figure 3



(0.0)
[0.0]
N-01 C_{2V}



(0.4)
[0.5]
N-02 Cs



(4.0)
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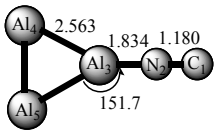
N-03 C_{2V}



(6.8)
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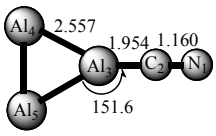

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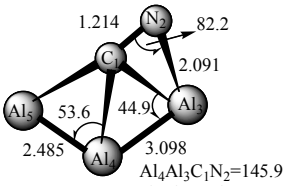
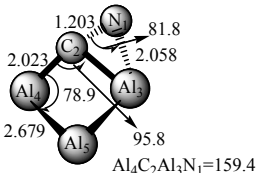
N-05 C_{2V}



(12.4)
[15.1]
N- 06 C_1



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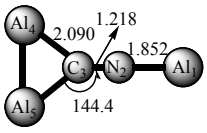
N-07 C_1



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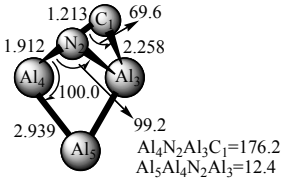
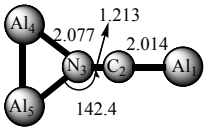
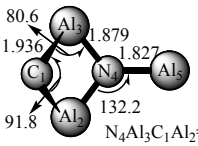
[13.1]
N-08 C_{2V}



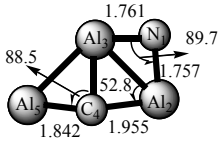
(20.2)
[20.3]
N-09 C_1



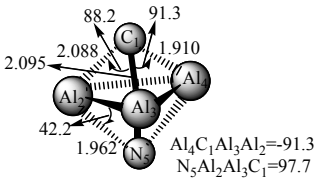
(38.1)
[31.9]
N-10 C_{2V}



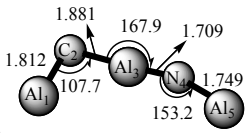
[59.0]
N-11 Cs



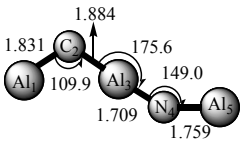
[63.6]
N-12 Cs



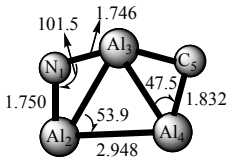
[68.3]
N-13 C_1



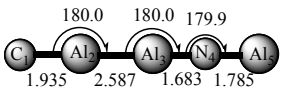
[68.0]
N-14 Cs



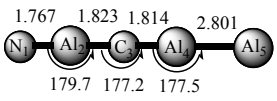
[69.4]
N-15 Cs



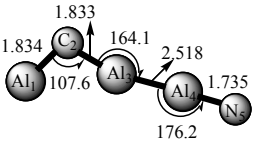
[78.0]
N-16 Cs



[123.4]
N-17 Cs

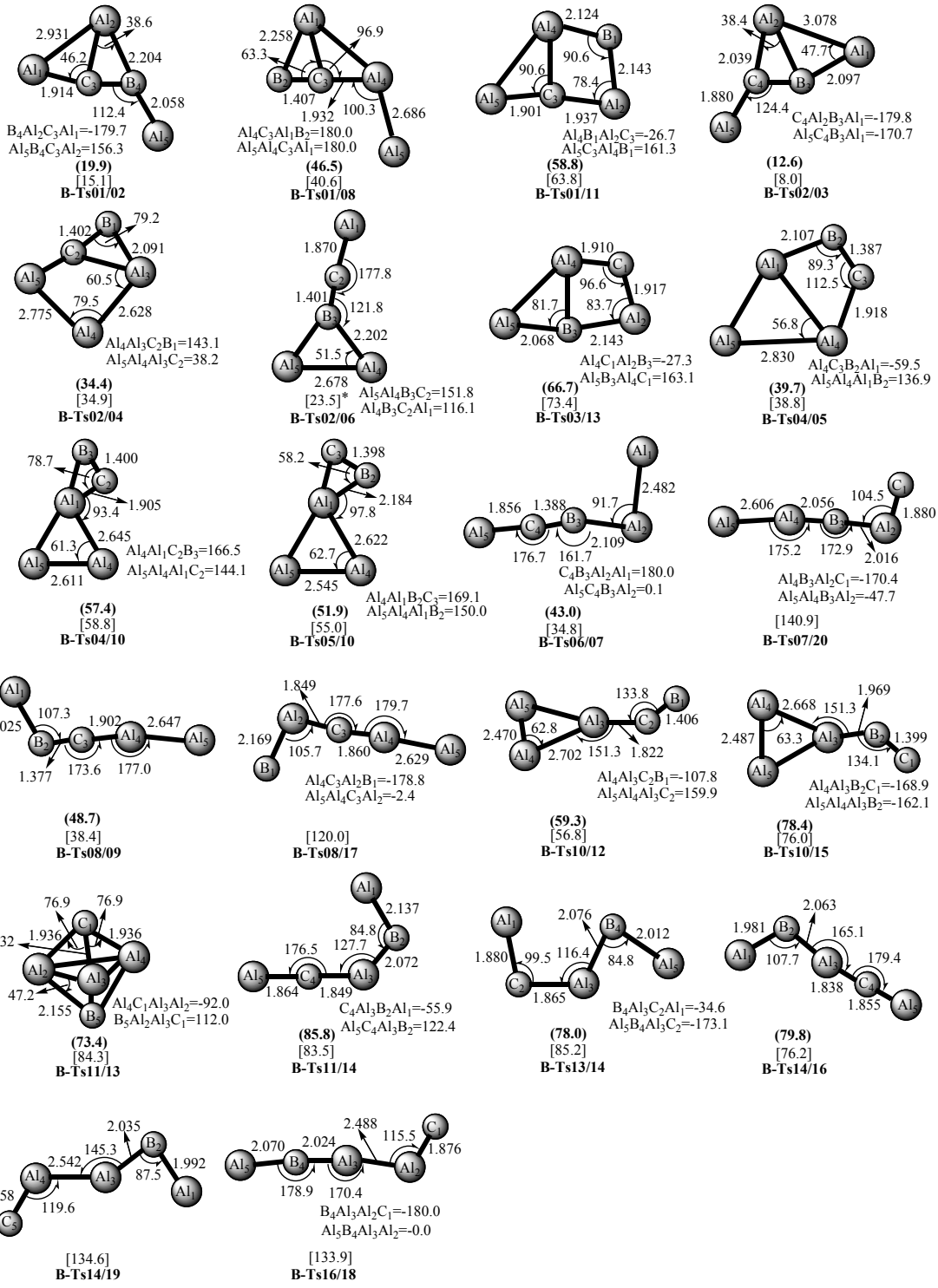


[153.4]
N-18 C_1

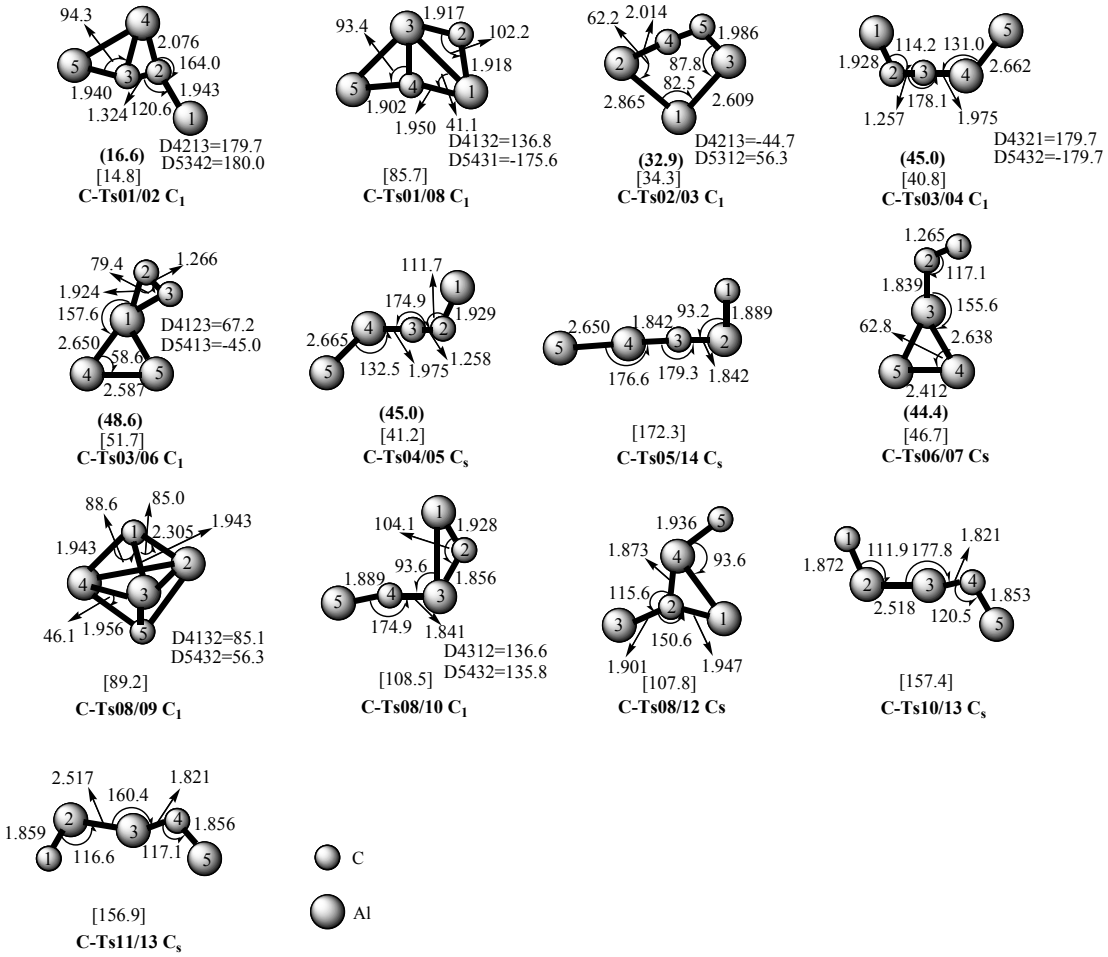


[154.8]
N-19 Cs

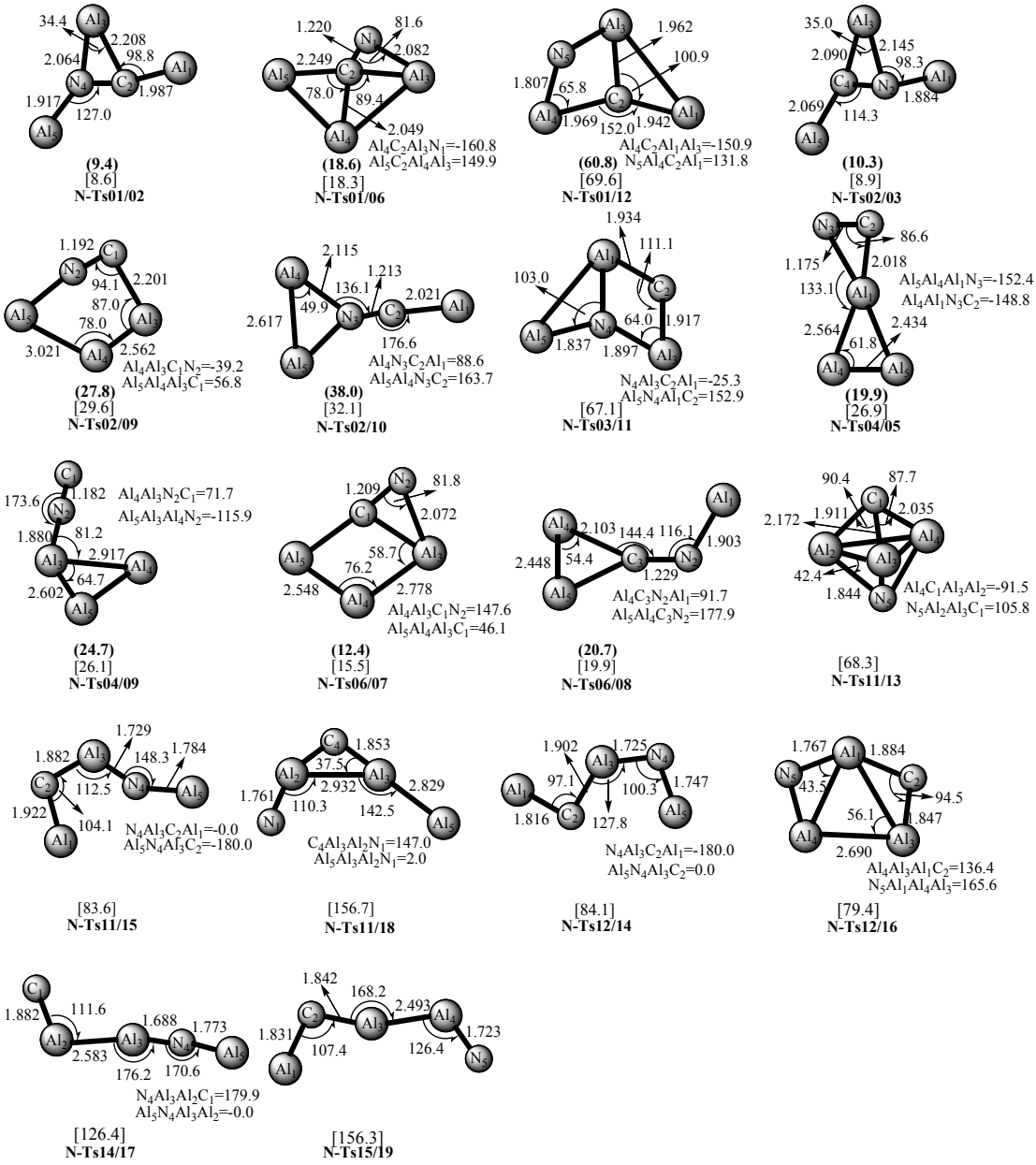
SI1-Figure 4


B4Al2C3Al1=-179.7
Al5B4C3Al2=156.3
(19.9)
[15.1]
B-Ts01/02
Al4Al3C2B1=143.1
Al5Al4Al3C2=38.2
(34.4)
[34.9]
B-Ts02/04
Al4C3Al1B2=180.0
Al5Al4C3Al1=180.0
(46.5)
[40.6]
B-Ts01/08
Al5Al4B3C2=151.8
Al4B3C2Al1=116.1
[23.5]*
B-Ts02/06
Al4B1Al2C3=-26.7
Al5C3Al4B1=161.3
(58.8)
[63.8]
B-Ts01/11
Al4C1Al2B3=-27.3
Al5B3Al4C1=163.1
(66.7)
[73.4]
B-Ts03/13
C4Al2B3Al1=-179.8
Al5C4B3Al1=-170.7
(12.6)
[8.0]
B-Ts02/03
Al4C3B2Al1=-59.5
Al5Al4Al1B2=136.9
(39.7)
[38.8]
B-Ts04/05
Al4Al1C2B3=166.5
Al5Al4Al1C2=144.1
(57.4)
[58.8]
B-Ts04/10
Al4Al1B3C3=169.1
Al5Al4Al1B2=150.0
(51.9)
[55.0]
B-Ts05/10
C4B3Al2Al1=180.0
Al5C4B3Al2=0.1
(43.0)
[34.8]
B-Ts06/07
Al4B3Al2C1=-170.4
Al5Al4B3Al2=-47.7
[140.9]
B-Ts07/20
Al4C1Al3Al2=-92.0
B5Al2Al3C1=112.0
(73.4)
[84.3]
B-Ts11/13
C4Al3B2Al1=-55.9
Al5C4Al3B2=122.4
(85.8)
[83.5]
B-Ts11/14
B4Al3C2Al1=-34.6
Al5B4Al3C2=-173.1
(78.0)
[85.2]
B-Ts13/14
(78.4)
[76.0]
B-Ts10/15
Al4Al3C2B1=-107.8
Al5Al4Al3C2=159.9
(59.3)
[56.8]
B-Ts10/12
Al4C3Al2B1=-178.8
Al5Al4C3Al2=-2.4
[120.0]
B-Ts08/17
Al4Al3B2C1=-168.9
Al5Al4Al3B2=-162.1
(48.7)
[38.4]
B-Ts08/09
B4Al2C3Al1=-170.4
Al5B4C3Al2=-0.0
[133.9]
B-Ts16/18
[134.6]
B-Ts14/19

SI1-Figure 5


94.3
2.076
164.0
1.940
1.943
1.324
120.6
D4213=179.7
(16.6) D5342=180.0
[14.8]
C-Ts01/02 C1
93.4
1.917
102.2
1.918
1.902
1.950
41.1
D4132=136.8
D5431=-175.6
[85.7]
C-Ts01/08 C1
62.2
2.014
1.986
87.8
82.5
2.865
2.609
D4213=-44.7
(32.9) D5312=56.3
[34.3]
C-Ts02/03 C1
1.928
114.2
131.0
2.662
178.1
1.257
1.975
D4321=179.7
(45.0) D5432=-179.7
[40.8]
C-Ts03/04 C1
79.4
1.266
1.924
157.6
D4123=67.2
2.650
D5413=-45.0
58.6
2.587
(48.6)
[51.7]
C-Ts03/06 C1
111.7
174.9
1.929
2.665
132.5
1.975
1.258
(45.0)
[41.2]
C-Ts04/05 Cs
2.650
1.842
93.2
1.889
176.6
179.3
1.842
[172.3]
C-Ts05/14 Cs
1.265
117.1
1.839
155.6
62.8
2.638
2.412
(44.4)
[46.7]
C-Ts06/07 Cs
88.6
85.0
1.943
2.305
1.943
46.1
1.956
D4132=85.1
D5432=56.3
[89.2]
C-Ts08/09 C1
104.1
1.928
93.6
1.889
1.856
174.9
1.841
D4312=136.6
D5432=135.8
[108.5]
C-Ts08/10 C1
1.936
1.873
93.6
115.6
150.6
1.901
1.947
[107.8]
C-Ts08/12 Cs
1.872
111.9
177.8
1.821
2.518
120.5
1.853
[157.4]
C-Ts10/13 Cs
2.517
160.4
1.821
1.859
116.6
117.1
1.856
[156.9]
C-Ts11/13 Cs
C
Al

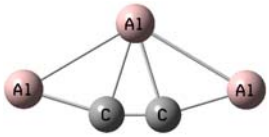
SI1-Figure 6


34.4
2.208
2.064
98.8
1.987
1.917
127.0
(9.4)
[8.6]
N-Ts01/02
1.220
81.6
2.082
2.249
78.0
89.4
2.049
Al4C2Al3N1=-160.8
Al5C2Al4Al3=149.9
(18.6)
[18.3]
N-Ts01/06
1.962
100.9
1.807
65.8
1.969
152.0
1.942
Al4C2Al1Al3=-150.9
(60.8)
N5Al4C2Al1=131.8
[69.6]
N-Ts01/12
35.0
2.145
2.090
98.3
1.884
2.069
114.3
(10.3)
[8.9]
N-Ts02/03
1.192
94.1
2.201
87.0
78.0
3.021
2.562
Al4Al3C1N2=-39.2
Al5Al4Al3C1=56.8
(27.8)
[29.6]
N-Ts02/09
2.115
1.213
136.1
49.9
2.021
2.617
176.6
Al4N3C2Al1=88.6
Al5Al4N3C2=163.7
(38.0)
[32.1]
N-Ts02/10
1.934
111.1
103.0
64.0
1.917
1.837
1.897
N4Al3C2Al1=-25.3
Al5N4Al1C2=152.9
[67.1]
N-Ts03/11
86.6
1.175
2.018
133.1
Al5Al4Al1N3=-152.4
Al4Al1N3C2=-148.8
2.564
2.434
61.8
(19.9)
[26.9]
N-Ts04/05
1.182
Al4Al3N2C1=71.7
173.6
Al5Al3Al4N2=-115.9
1.880
81.2
2.917
64.7
2.602
(24.7)
[26.1]
N-Ts04/09
1.209
81.8
2.072
58.7
76.2
2.548
2.778
Al4Al3C1N2=147.6
Al5Al4Al3C1=46.1
(12.4)
[15.5]
N-Ts06/07
2.103
144.4
116.1
1.903
2.448
54.4
1.229
Al4C3N2Al1=91.7
Al5Al4C3N2=177.9
(20.7)
[19.9]
N-Ts06/08
90.4
87.7
2.035
2.172
1.911
42.4
1.844
Al4C1Al3Al2=-91.5
N5Al2Al3C1=105.8
[68.3]
N-Ts11/13
1.729
1.882
148.3
1.784
112.5
1.922
104.1
N4Al3C2Al1=-0.0
Al5N4Al3C2=-180.0
[83.6]
N-Ts11/15
1.853
37.5
1.761
110.3
2.932
142.5
2.829
C4Al3Al2N1=147.0
Al5Al3Al2N1=2.0
[156.7]
N-Ts11/18
1.902
1.725
97.1
100.3
1.747
1.816
127.8
N4Al3C2Al1=-180.0
Al5N4Al3C2=0.0
[84.1]
N-Ts12/14
1.767
1.884
43.5
94.5
56.1
1.847
2.690
Al4Al3Al1C2=136.4
N5Al1Al4Al3=165.6
[79.4]
N-Ts12/16
1.882
111.6
1.688
1.773
2.583
176.2
170.6
N4Al3Al2C1=179.9
Al5N4Al3Al2=-0.0
[126.4]
N-Ts14/17
1.842
168.2
2.493
1.831
107.4
126.4
1.723
[156.3]
N-Ts15/19

SI2-Table 1~4. The structures and relative energies for low-lying isomers of $Na^+[C_2Al_3]^-$, Na^+ $[BCAl_3]^{2-}$, $(Na^+)_2[BCAl_3]^{2-}$ and $Mg^{2+}[BCAl_3]^{2-}$ at the B3LYP/6-311+G(d). Single-point calculations for the low-lying isomers at the CCSD(T)/6-311+G(2df)//B3LYP/6-311+G(d) level. The relative energy values (ΔE) are in kcal/mol.

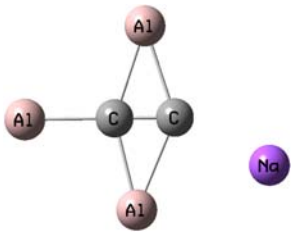
SI2-Table 1.

$Na^+[C_2Al_3]^-$	B3LYP/6-311+G(d)	ΔE	CCSD(T)/6-311+G(2df)//B3LYP/6-311+G(d)	**ΔE**
01	-965.832999	0.0	-963.8725942	**0.0**
02	-965.8316392	0.9	-963.8716098	**0.6**
03	-965.8320355	0.6	-963.8678769	**3.0**
04	-965.8281077	3.1	-963.8632199	**5.9**



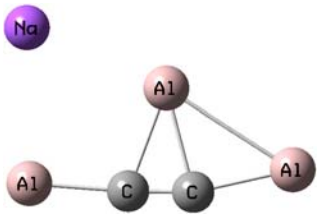
01

Al,0,0.,2.5609065278,0.3031394279
Al,0,0.,-2.5609065278,0.3031394279
C,0,0.,0.6515396918,-0.2657966055
Al,0,0.,0.,1.8090792025
C,0,0.,-0.6515396918,-0.2657966055
Na,0,0.,0.,-2.5678904773



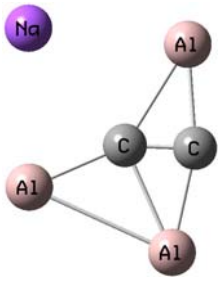
02

C,0,-0.44600442,0.65282595,0.
Al,0,-2.1061999,-0.64379837,0.
C,0,0.01885332,-0.59017769,0.
Al,0,0.71157564,-2.43816384,0.
Al,0,1.73723874,0.54650229,0.
Na,0,-0.17191651,2.96228086,0.



03

C,0,-1.13106686,-0.14298698,0.
Al,0,1.0399603,-0.2541049,0.
C,0,-0.76922327,-1.36921785,0.
Al,0,0.23416429,-3.103525,0.
Al,0,-1.56234394,1.75366069,0.
Na,0,1.37714476,2.72043898,0.



04

Al,0,1.19008209,-1.82253057,0.

Al,0,-0.38647229,1.90348458,0.

C,0,-0.72313675,-1.295904,0.

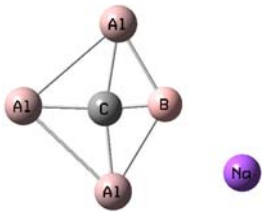
C,0,-0.23477685,-0.06433807,0.

Al,0,-2.45631638,-0.2267274,0.

Na,0,2.47771218,0.91271447,0.

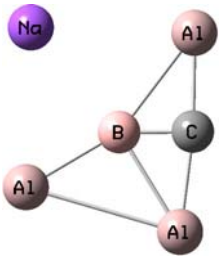
SI2-Table 2

$Na^+[CBAl_3]^{2-}$	B3LYP/6-311+G(d)	ΔE	CCSD(T)/6-311+G(2df)//B3LYP/6-311+G(d)	**ΔE**
01	-952.6285527	0.0	-950.6790271	**0.0**
02	-952.6252952	2.0	-950.671561	**4.7**
03	-952.6204914	5.1	-950.6699927	**5.7**
04	-952.6214533	4.5	-950.6697465	**5.8**
05	-952.6217607	4.3	-950.6669196	**7.6**
06	-952.6210016	4.7	-950.6659539	**8.2**
07	-952.621378	4.5	-950.6656635	**8.4**
08	-952.6153923	8.3	-950.664556	**9.1**



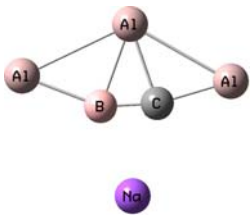
01

Al,0,2.144895832,-1.0137112145,0.
Al,0,-0.7626408381,-1.5767339899,0.
Al,0,1.2938314552,1.8730690985,0.
C,0,0.4717983674,-0.0091743653,0.
B,0,-0.6820775572,0.8519812417,0.
Na,0,-3.1173180394,0.4679775895,0.



02

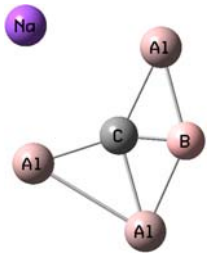
C,0,-0.4669386849,-1.3532036934,0.
Al,0,1.3940940679,-1.8473518338,0.
Al,0,-2.3071263242,-0.6398897305,0.
Al,0,-0.7346129134,2.0625603516,0.
B,0,-0.1313860274,0.04178998,0.
Na,0,2.266526162,1.2182448961,0.



03

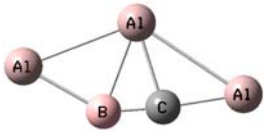
C,0,0.7200165362,0.2171932223,0.
Al,0,2.526024782,-0.447745479,0.
Al,0,-2.7052368827,-0.2655243312,0.

Al,0,-0.0814191397,-1.7406133899,0.
B,0,-0.6942593042,0.3802317225,0.
Na,0,0.2462593384,2.5950681653,0.



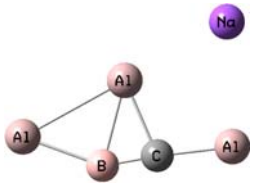
04

Al,0,0.3143568735,-1.7217214405,0.
Al,0,2.4858727209,0.0804125254,0.
Al,0,-1.169241658,1.6938259396,0.
C,0,0.3415279905,0.2149441028,0.
B,0,0.9207919833,1.5412900368,0.
Na,0,-2.5587330102,-0.9021575341,0.



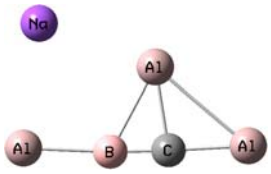
05 

Al,0,1.8926337782,1.2518177298,0.
C,0,-0.9589862682,-0.628295464,0.
Al,0,-0.9543805901,1.4662845098,0.
Al,0,-2.855266333,-0.8872428464,0.
B,0,0.4091941074,-0.3210383071,0.
Na,0,2.6008208858,-1.6863122021,0.



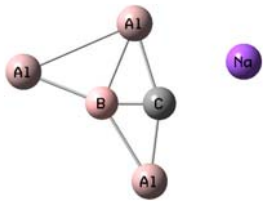
06

C,0,0.0762316218,1.1753906014,0.
Al,0,-1.7944548256,1.5392250283,0.
Al,0,3.1510407134,-0.3191440156,0.
Al,0,0.2693185183,-0.88323773,0.
B,0,1.4649365671,0.9898506809,0.
Na,0,-2.6322590351,-1.499319565,0.



07

C,0,1.2867301641,-0.7097612013,0.
Al,0,3.1174476883,-0.1357869549,0.
Al,0,-2.1049998135,-1.5177027751,0.
Al,0,0.4860380769,1.1685866939,0.
B,0,-0.0600052293,-1.0888599315,0.
Na,0,-2.4795180565,1.513102149,0.

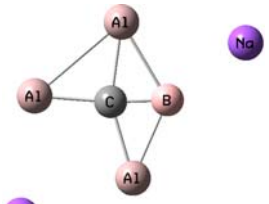


08

C,0,0.6777017979,0.3130773128,0.
Al,0,0.5960119421,2.2735304287,0.
Al,0,-0.1114688534,-1.6252728896,0.
Al,0,-2.776812814,-0.1766927293,0.
B,0,-0.7611635149,0.4300412828,0.
Na,0,2.6909687923,-0.9108006653,0.

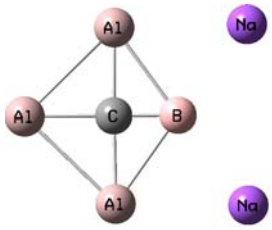
SI2-Table 3

$(Na^+)_2[CBAl_3]^{2-}$	B3LYP/6-311+G(d)	ΔE	CCSD(T)/6-311+G(2df)//B3LYP/6-311+G(d)	**ΔE**
01	-1114.9116513	0.0	-1112.5312561	**0.0**
02	-1114.9100098	1.0	-1112.5292324	**1.3**
03	-1114.9033718	5.2	-1112.5233931	**4.9**
04	-1114.902835	5.5	-1112.521527	**6.1**
05	-1114.9027882	5.6	-1112.521366	**6.2**
06	-1114.8970464	9.2	-1112.5137537	**11.0**
07	-1114.9002565	7.2	-1112.5125249	**11.8**
08	-1114.8982815	8.4	-1112.5124858	**11.8**
09	-1114.8941444	11.0	-1112.5102597	**13.2**



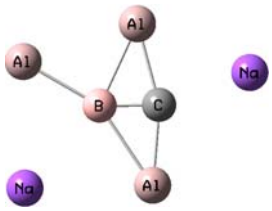
01

Al,0,-1.2874121561,1.5606318141,0.
Al,0,1.5980087366,1.5211731666,0.
Al,0,-0.8068713555,-1.6566956012,0.
C,0,0.0525267591,0.1785154474,0.
B,0,1.158428817,-0.7383792992,0.
Na,0,3.600673194,-0.9522261761,0.
Na,0,-3.5591543252,-0.4891350616,0.



02

Al,0,0.,0.,-2.6512163474
Al,0,0.,-1.9950113313,-0.6354626294
Al,0,0.,1.9950113313,-0.6354626294
C,0,0.,0.,-0.6618583669
B,0,0.,0.,0.7730321236
Na,0,0.,-2.0447339544,2.3264023947
Na,0,0.,2.0447339544,2.3264023947



03

C,0,-0.9193134434,0.3342084875,0.

Al,0,-0.1067429135,2.1175625686,0.
Al,0,-1.0960186779,-1.6946698322,0.
Al,0,1.8163598376,-1.7717197788,0.
B,0,0.4421108215,-0.1382330145,0.
Na,0,-3.2504064019,0.3433548046,0.
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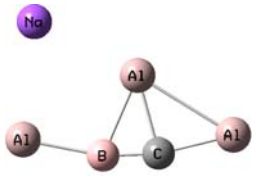
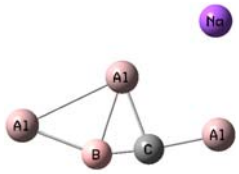


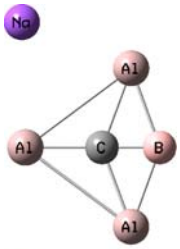
04

C,0,-1.1954310018,-0.1376073235,0.
Al,0,-2.3301381502,-1.7327641155,0.
Al,0,1.6476535831,1.8418815702,0.
Al,0,0.4999663809,-1.2999655508,0.
B,0,-0.1573401257,0.8207105245,0.
Na,0,3.3881891952,-0.635568401,0.
Na,0,-2.4093810017,1.9028242561,0.



05

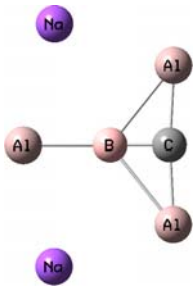
C,0,0.2048008777,0.713973951,0.
Al,0,-1.5319061867,1.5356956088,0.
Al,0,2.5568292516,-1.8427667157,0.
Al,0,-0.3820154835,-1.2743883531,0.
B,0,1.4144960085,-0.0191875337,0.
Na,0,-3.3189490727,-0.9764647133,0.
Na,0,1.793726725,2.467252286,0.



06

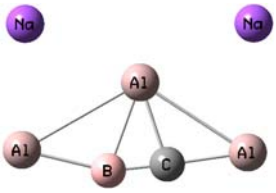
Al,0,0.,0.,-1.309986408
Al,0,0.,-1.9819195414,1.3149199402

Al,0,0.,1.9819195414,1.3149199402
C,0,0.,0.,0.5918942511
B,0,0.,0.,2.0236680844
Na,0,0.,-3.1372504036,-1.399090574
Na,0,0.,3.1372504036,-1.399090574



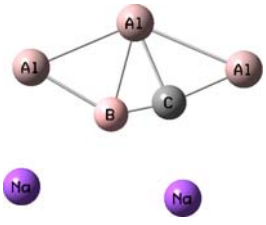
07

Al,0,0.,0.,-1.8814260198
Al,0,0.,-1.9189636801,1.7260853256
Al,0,0.,1.9189636801,1.7260853256
Na,0,0.,-2.9296315361,-1.1359176144
Na,0,0.,2.9296315361,-1.1359176144
B,0,0.,0.,0.2061196176
C,0,0.,0.,1.6322056397



08

C,0,0.6688491827,-1.4731392006,0.
Al,0,2.5631220345,-1.2153523665,0.
Al,0,-2.7402870619,-1.0994152035,0.
Al,0,0.0550236834,0.4671121536,0.
B,0,-0.7170288501,-1.6095764957,0.
Na,0,2.7349339381,1.836849794,0.
Na,0,-2.6333407266,1.8805362987,0.

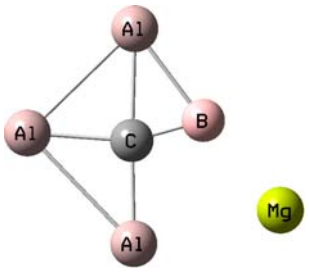


09

C,0,0.9910348972,0.1075948199,0.
Al,0,2.8759549535,-0.4249668327,0.
Al,0,-2.1682470689,-1.1888504528,0.
Al,0,0.4540672659,-1.8947093052,0.
B,0,-0.4282429082,0.1965624351,0.
Na,0,-2.7945548432,1.6099229378,0.
Na,0,0.9929167437,2.4260804579,0.

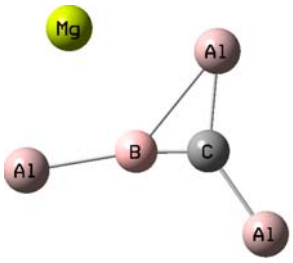
SI2-Table 4

$Mg^{2+}[CBAl_3]^{2-}$	B3LYP/6-311+G(d)	ΔE	CCSD(T)/6-311+G(2df)//B3LYP/6-311+G(d)	**ΔE**
01	-990.3551597	1.9	-988.3924972	**0.0**
02	-990.3581933	0.0	-988.3889679	**2.2**
03	-990.349854	5.2	-988.3881677	**2.7**
04	-990.3495738	5.4	-988.3816949	**6.8**
05	-990.3446231	8.5	-988.376762	**9.9**
06	-990.3396081	11.7	-988.3757267	**10.5**
07	-990.3359297	14.0	-988.3713082	**13.3**
08	-990.3306183	17.0	-988.3698041	**14.2**



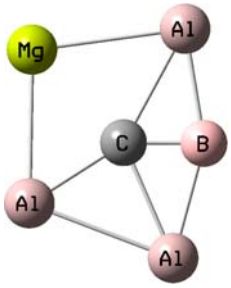
01

Al,0,2.0506138131,-0.9458660299,0.
Al,0,-0.8041791165,-1.6847443872,0.
Al,0,1.3605299246,1.8495486219,0.
C,0,0.2745825511,-0.0119414555,0.
B,0,-0.6838963911,1.0391811969,0.
Mg,0,-2.8491615612,0.3472304137,0.



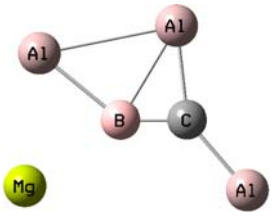
02

C,0,1.165654151,-0.0361909761,0.
Al,0,2.8549260523,-1.0258900068,0.
Al,0,-1.8807602312,-1.8656892943,0.
Al,0,0.5019762208,1.8014130793,0.
B,0,-0.1017539242,-0.6348967963,0.
Mg,0,-2.2943494387,0.9908319742,0.



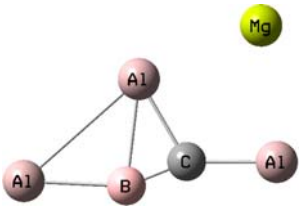
03

Al,0,0.4225678703,-1.8716006916,0.
Al,0,2.3743589103,0.0419397204,0.
Al,0,-1.2717947072,1.9376824226,0.
C,0,0.131037683,0.0972191094,0.
B,0,0.7353038574,1.3907073295,0.
Mg,0,-2.0568987138,-0.6893542603,0.



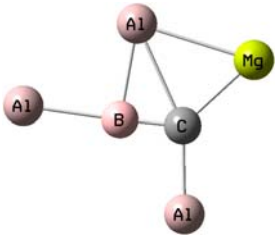
04

Al,0,2.0524782381,1.0729418515,0.
C,0,-1.1234694099,-0.1512110681,0.
Al,0,-0.7908924864,1.8225706244,0.
Al,0,-2.4720553462,-1.5670507098,0.
B,0,0.2727775147,-0.2358689118,0.
Mg,0,2.1951770697,-1.7461683661,0.



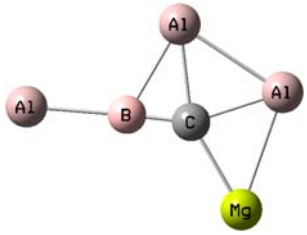
05

C,0,-0.0236664379,0.8837775881,0.
Al,0,-1.8041916366,1.6236815729,0.
Al,0,3.3546801894,-0.0515426806,0.
Al,0,0.2487145902,-1.1320382657,0.
B,0,1.3651614041,0.8764208264,0.
Mg,0,-2.6058845491,-1.1975340412,0.



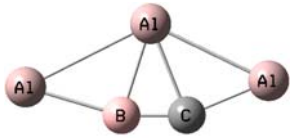
06

C,0,0.7510561599,0.4858521408,0.
Al,0,0.6636390563,2.4666204894,0.
Al,0,-0.1229051592,-1.8564289707,0.
Al,0,-2.7686424501,-0.1723356725,0.
B,0,-0.6371505872,0.2642019301,0.
Mg,0,2.4292403304,-0.8840271771,0.



07

C,0,0.3354489019,0.2361475116,0.
Al,0,2.1508210877,-0.7779171174,0.
Al,0,-3.2204068711,0.5896311828,0.
Al,0,-0.3159315422,-1.8068443134,0.
B,0,-1.0545786402,0.3460936847,0.
Mg,0,1.7726120439,1.8997283917,0.



08

C,0,0.8153614527,0.3042124559,0.
Al,0,2.5732002017,-0.5406763602,0.
Al,0,-2.7430635468,-0.1619470403,0.
Al,0,-0.0678298806,-1.6959458351,0.
B,0,-0.6141485071,0.3742623478,0.
Mg,0,0.0478656102,2.4587043419,0.

SI3-1 The details of MD simulations.

General parameters:

Max. points for each Traj. = 3500 and 4000
Total Number of Trajectories = 1
Random Number Generator Seed = 398465
Trajectory Step Size = 0.500 sqrt(amu)*bohr

Sampling parameters:

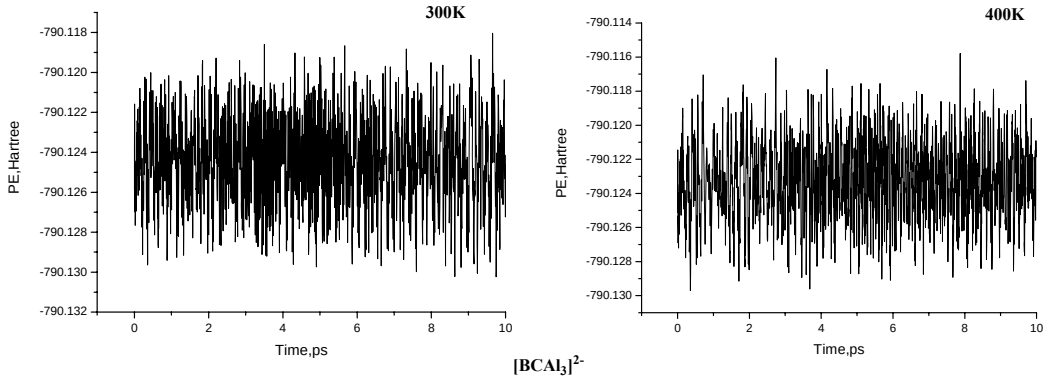
Vib Energy Sampling Option = Thermal sampling
TS Sampling direction = Forward
Vib Sampling Temperature = 300.0 K and 400.0 K
Rot Energy Sampling Option = Thermal distribution (symmetric top)
Rot Sampling Temperature = 300.0 K and 400.0 K
Start point scaling criteria = 1.000D-05 Hartree

Integration parameters:

Correction Scheme = Fifth order polynomial fit
Project trans/rot in grad. = True
Project in prediction step = True
Project in correction step = True
Integration Scheme = Bulirsch-Stoer method
Integration Step Size = 2.000D-01 femtosec
Truncation Error Criteria = 1.000D-08 bohr
Energy Error Criteria = 1.000D-04 Hartree
Hessian evaluation = Full Hessian always

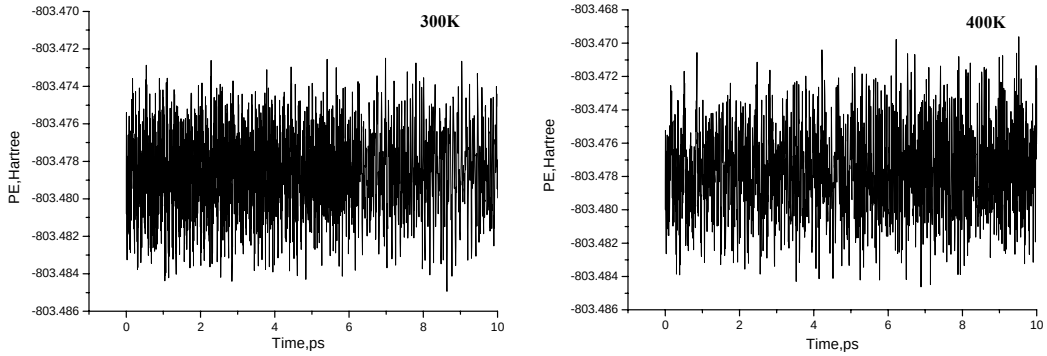
SI3-2 Potential energy of three designed systems $[XCAl_3]^q$ (X,q)=(B,-2), (C,-1) and (N,0). (a) $[BCAl_3]^{2-}$, (b) $[C_2Al_3]^-$, and (c) $[NCAl_3]$ along the MD trajectory at B3LYP/6-31G(d) level, respectively. Born-Oppenheimer molecular dynamics simulation is performed for 10ps at 300K and 400K. Potential energy (in au) versus time (in ps).

(a)



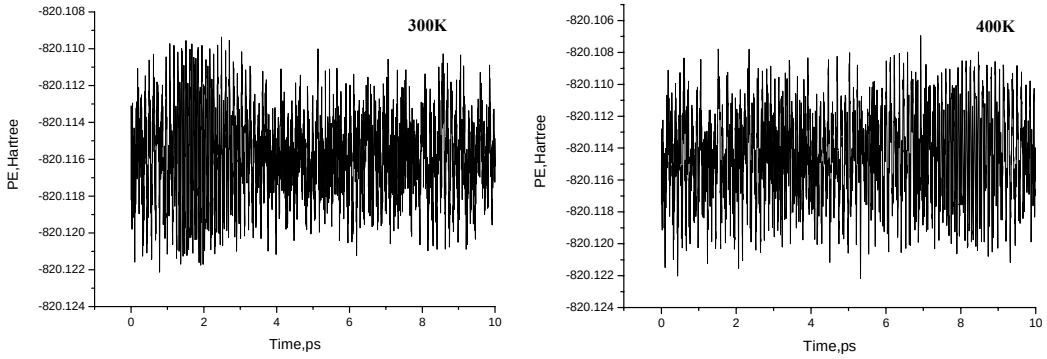
$[BCAl_3]^{2-}$

(b)



$[C_2Al_3]^-$

(c)



$[NCAl_3]$

SI4-Table 1 Calculated molecular properties of the $[BCAl_3]^{2-}$ (pptC) structures.

$BCAl_3^{2-}$, C_{2v}, $^1A_1$	B3LYP/aug-cc-pVTZ	MP2/ aug-cc-pVTZ	CCSD(T)/ aug-cc-pVTZ
$R(C_1\text{-}B_2)$, Å	1.461	1.485	1.486
$R(C_1\text{-}Al_{3,4})$, Å	2.044	2.030	2.035
$R(C_1\text{-}Al_5)$, Å	1.917	1.938	1.939
$<Al_5C_1Al_3$ °	105.0	103.3	103.3
-Etot, au	-790.2375416	-788.679885	-788.7317903
$\omega_1(a_1)$, cm^{-1}	1190	1209	1165
$\omega_2(a_1)$, cm^{-1}	544	535	539
$\omega_3(a_1)$, cm^{-1}	325	350	340
$\omega_4(a_1)$, cm^{-1}	158	177	162
$\omega_5(b_1)$, cm^{-1}	210	202	197
$\omega_6(b_1)$, cm^{-1}	122	111	112
$\omega_7(b_2)$, cm^{-1}	656	721	708
$\omega_8(b_2)$, cm^{-1}	528	510	514
$\omega_9(b_2)$, cm^{-1}	79	96	99

SI4-Table 2 Calculated molecular properties of the $[C_2Al_3]^-$ (pptC) structures.

$C_2Al_3^-$, C_{2v}, $^1A_1$	B3LYP/aug-cc-pVTZ	MP2/ aug-cc-pVTZ	CCSD(T)/aug-cc-pVTZ
R(C_1-C_2), Å	1.337	1.3527	1.359
R(C_1-$Al_{3,4}$), Å	2.107	2.0911	2.107
R(C_1-Al_5), Å	1.925	1.9394	1.935
$<Al_5C_1Al_3$ °	111.6	110.0	110.7
-Etot, au	-803.5806862	-802.0023153	-802.0580572
$\omega_1(a_1)$, cm^{-1}	1453	1454	1408
$\omega_2(a_1)$, cm^{-1}	555	547	560
$\omega_3(a_1)$, cm^{-1}	339	350	349
$\omega_4(a_1)$, cm^{-1}	168	170	174
$\omega_5(b_1)$, cm^{-1}	222	224	216
$\omega_6(b_1)$, cm^{-1}	121	101	105
$\omega_7(b_2)$, cm^{-1}	672	662	666
$\omega_8(b_2)$, cm^{-1}	609	643	649
$\omega_9(b_2)$, cm^{-1}	60	53	60

SI4-Table 3 Calculated molecular properties of the [$NCAl_3$] (pptC) structures.

$NCAl_3$, C_{2v}, $^1A_1$	B3LYP/aug-cc-pVTZ	MP2/ aug-cc-pVTZ	CCSD(T)/ aug-cc-pVTZ
$R(C_1\text{-}N_2)$, Å	1.275	1.293	1.298
$R(C_1\text{-}Al_{3,4})$, Å	2.197	2.171	2.192
$R(C_1\text{-}Al_5)$, Å	1.986	1.988	1.976
$<Al_5C_1Al_3$ °	116.1	114.0	116.3
-Etot, au	-820.2221039	-818.6223296	-818.678994
$\omega_1(a_1)$, cm^{-1}	1549	1490	1496
$\omega_2(a_1)$, cm^{-1}	483	493	496
$\omega_3(a_1)$, cm^{-1}	315	319	329
$\omega_4(a_1)$, cm^{-1}	157	163	162
$\omega_5(b_1)$, cm^{-1}	192	199	201
$\omega_6(b_1)$, cm^{-1}	114	107	112
$\omega_7(b_2)$, cm^{-1}	594	581	606
$\omega_8(b_2)$, cm^{-1}	486	563	525
$\omega_9(b_2)$, cm^{-1}	47	42	37