Supporting Information available for

Globally stabilize a bent carbon-carbon triple bond by a hydrogen-free inorganic-metallic scaffolding Al_4F_6

Ying-ying Xue[a], Ying Zhang[a], Zhong-hua Cui*[b] and Yi-hong Ding*[ac]

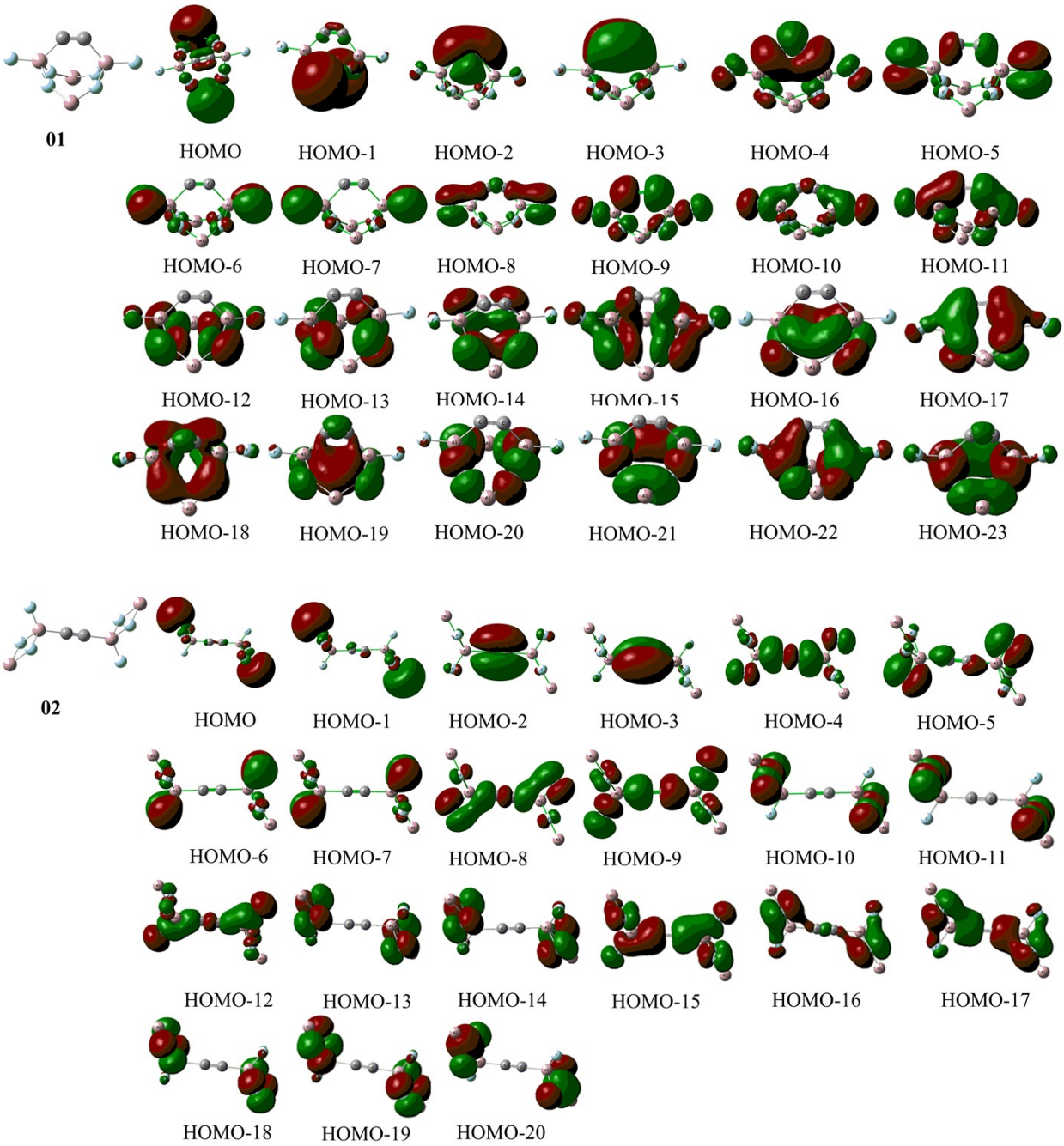
[a] Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130023, P. R. China. Email: yhdd@jlu.edu.cn

[b] Institute of Atomic and Molecular Physics, Jilin University, Changchun 130023, P. R. China. Email: zcui@jlu.edu.cn

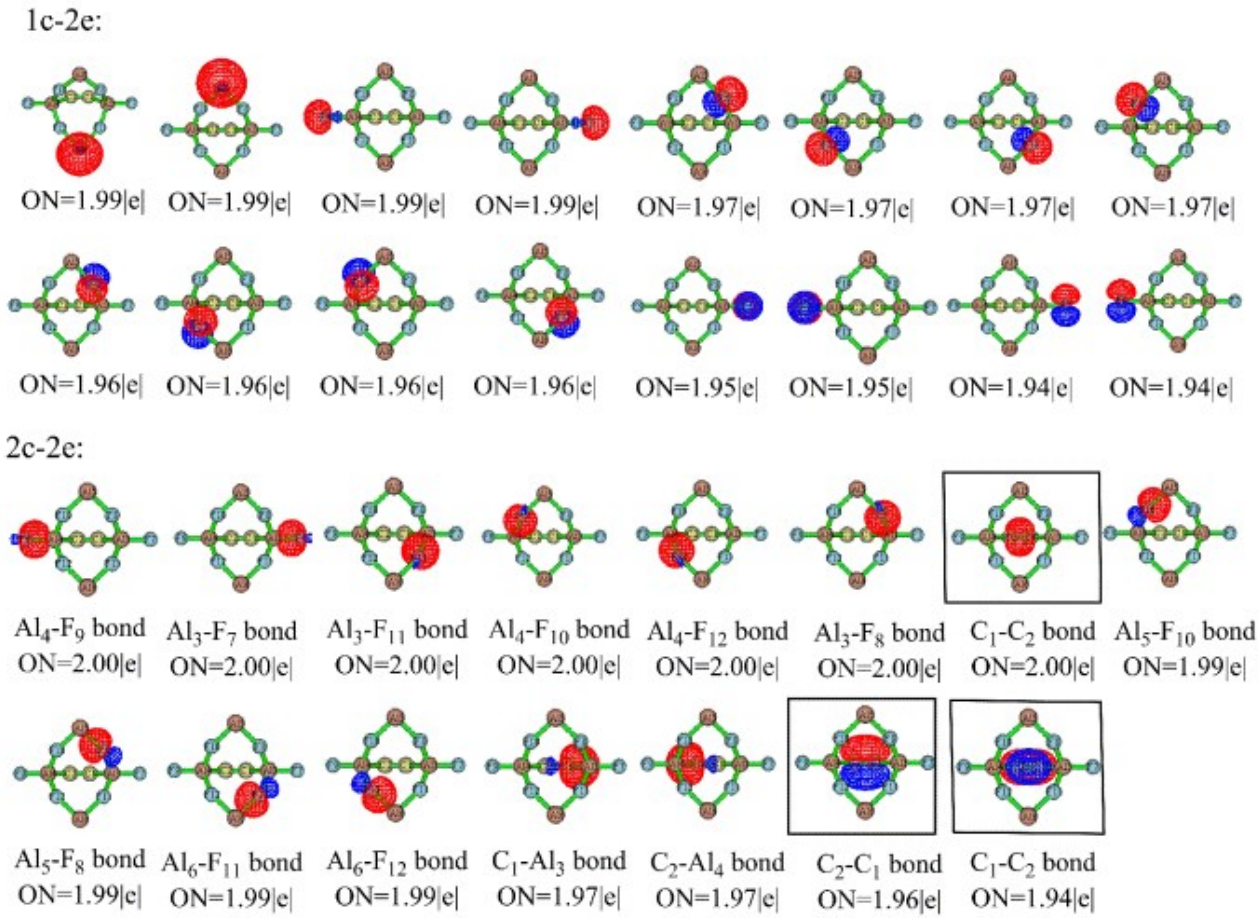
[c] Key Laboratory of Carbon Materials of Zhejiang Province, College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, P. R. China.

Supporting Information Available.

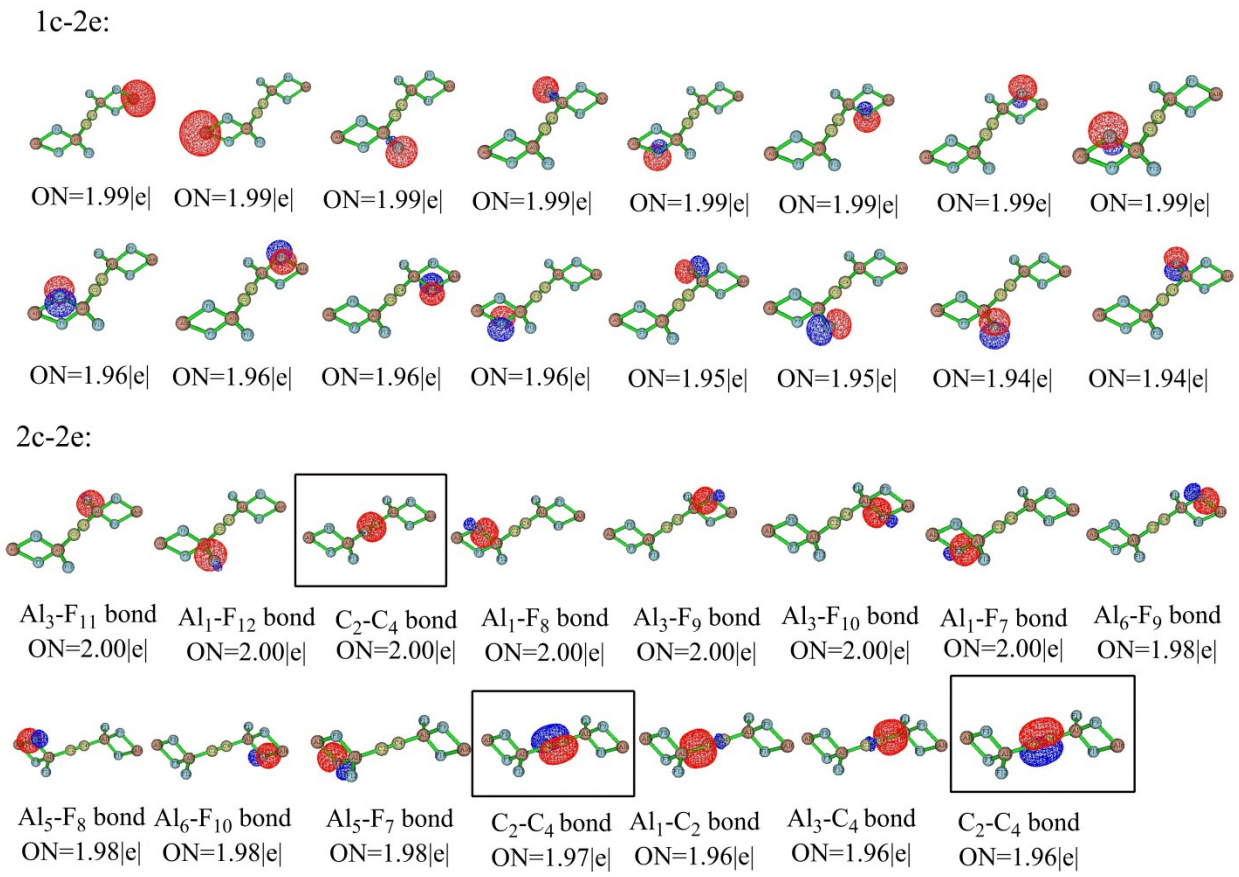
1. Fig. S1 Selected Molecular orbitals of the isomers $C_2Al_4F_6$-01 and $C_2Al_4F_6$-02 at the level of B3LYP/6-311G(2d,d,p).



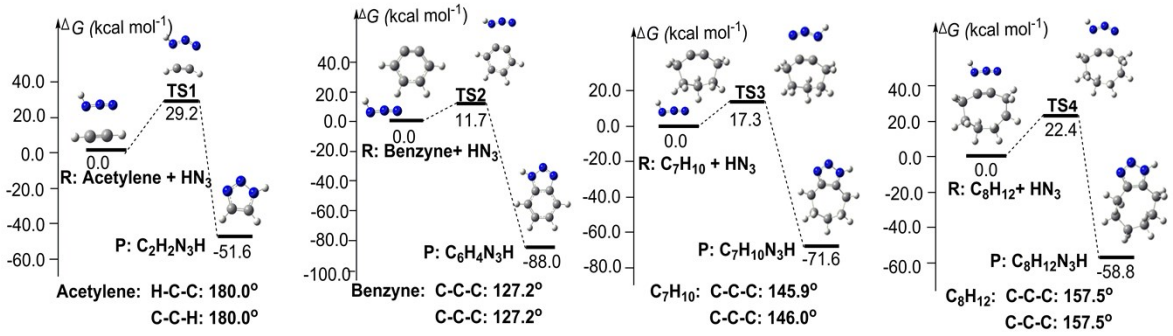
2. Fig. S2 Localized molecular orbitals of $C_2Al_4F_6$-01 obtained by AdNDP analysis at the B3LYP/6-311G(2d,d,p) level. "ON" denotes the occupation number on the localized orbital.



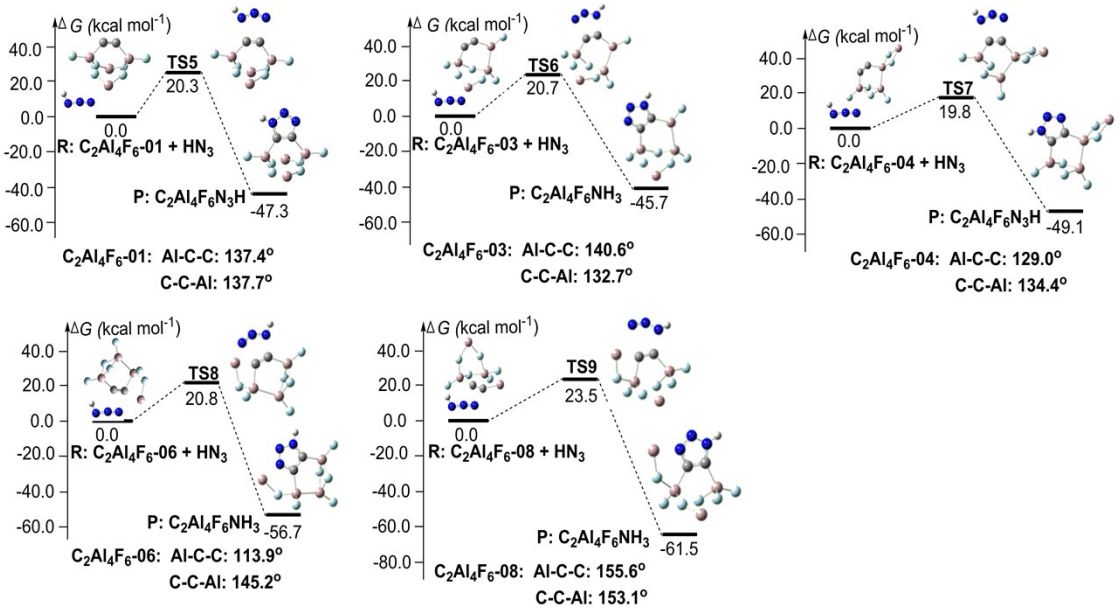
3. Fig. S3 Localized molecular orbitals of $C_2Al_4F_6$-02 obtained by AdNDP analysis at the B3LYP/6-311G(2d,d,p) level. "ON" denotes the occupation number on the localized orbital.



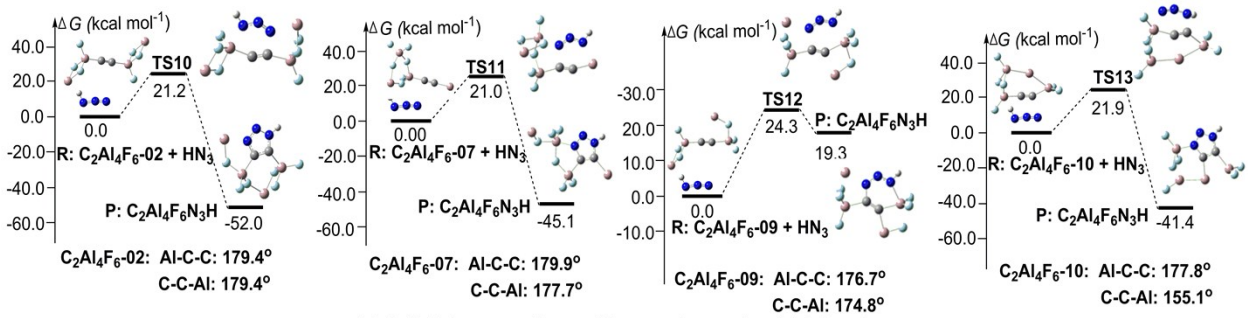
4. Fig. S4 The HN_3-click reaction process and the Gibbs free energy barrier (in kcal mol^{-1}) of the main isomers at the CBS-QB3 level.



(a) Standard acetylene, Aromatic benzyne and Clycloalkynes

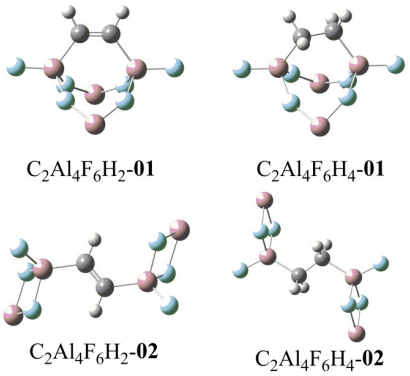


(b) $C_2Al_4F_6$ isomers with signifcant bent carbon-carbon triple bond

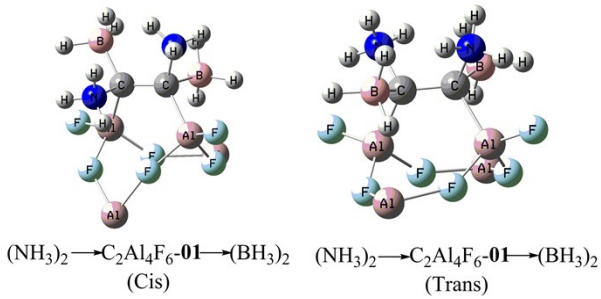


(c) $C_2Al_4F_6$ isomers with quast linear carbon-carbon triple bond

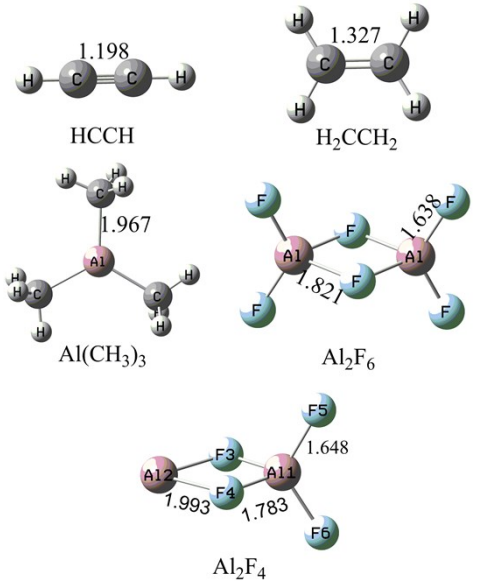
5. Fig. S5 The products of adding one and two H_2 molecules to $C_2Al_4F_6$-01 and 02.



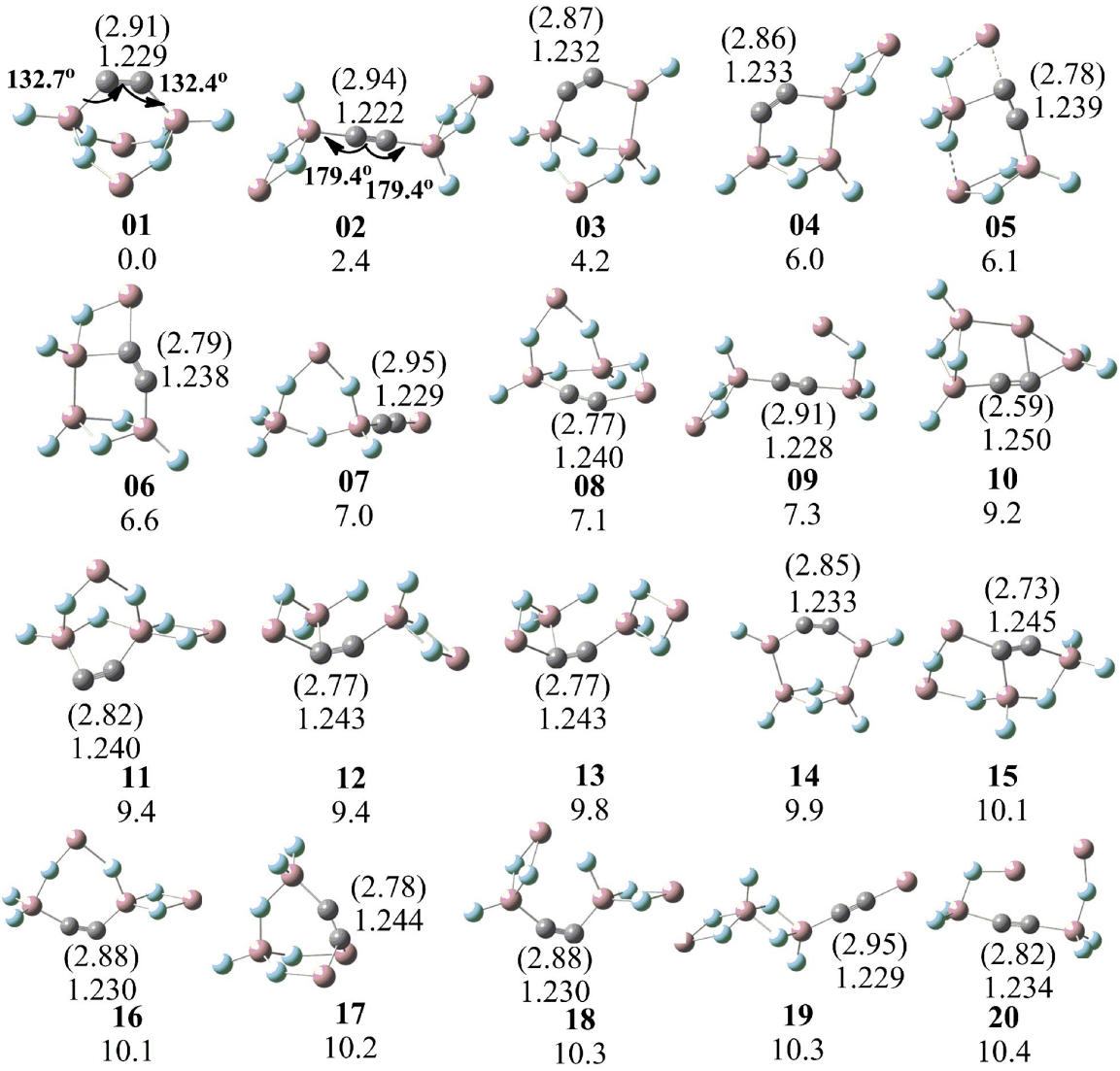
6. Fig. S6 The products of adding two BH_3NH_3 to $C_2Al_4F_6$-01.



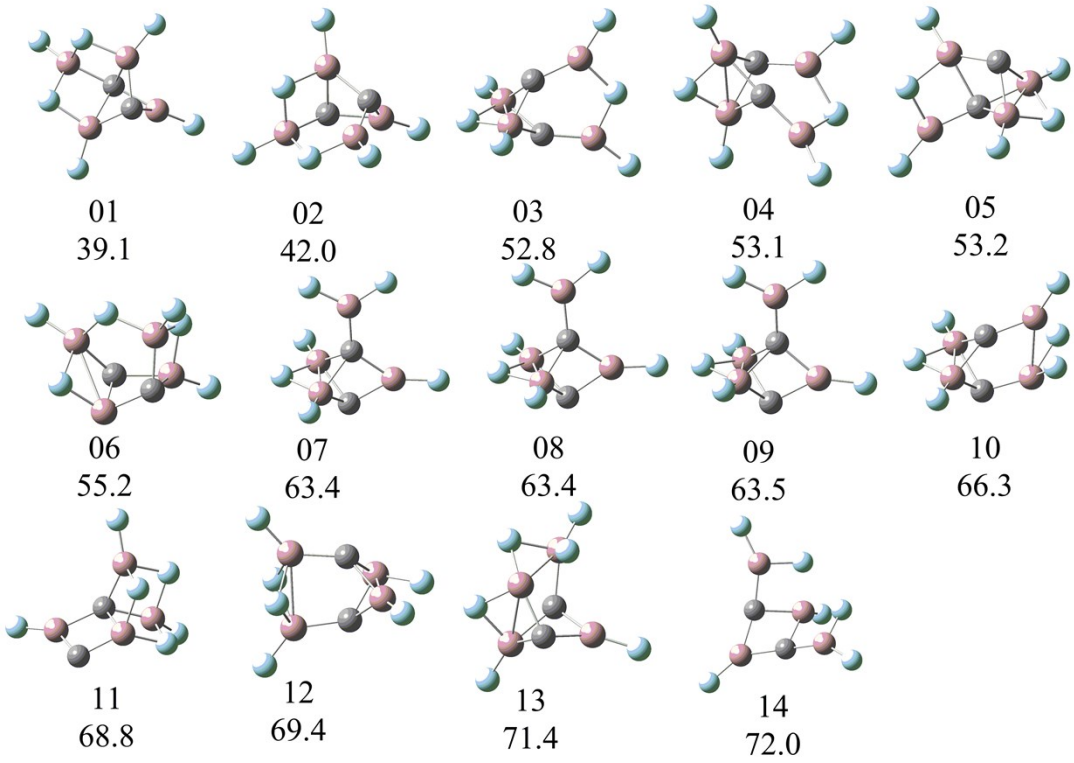
7. Fig. S7 The key geometrical parameters of models HCCH, H_2CCH_2, $Al(CH_3)_3$, Al_2F_6 and Al_2F_4 at the B3LYP/6-311G(2d,d,p) level.



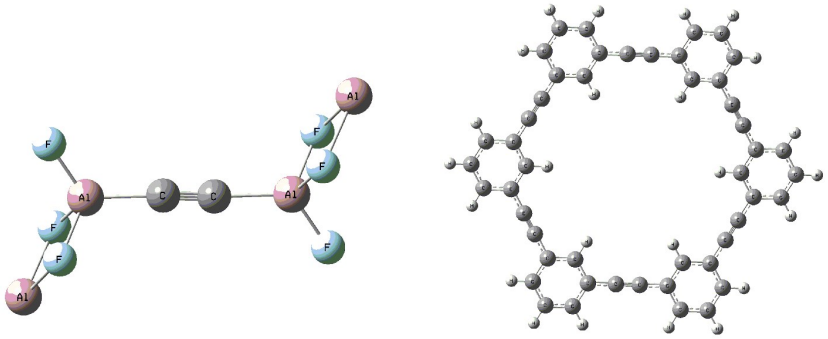
8. Fig. S8 The key geometrical parameters of the former twenty isomers of $C_2Al_4F_6$ at CBS-QB3 level. Note that the values beside the carbon-carbon bond represent the bond distances (in Å) at CBS-QB3 level and Wiberg bond indexes in the parentheses. The selected angles are shown.



9. **Fig. S9 The structures and relative energies (in kcal mol^{-1})(relative to the $C_2Al_4F_6$-01) of the $C_2Al_4F_6$ isomers with separated carbon atoms at the B3LYP/6-31G(d) level.**

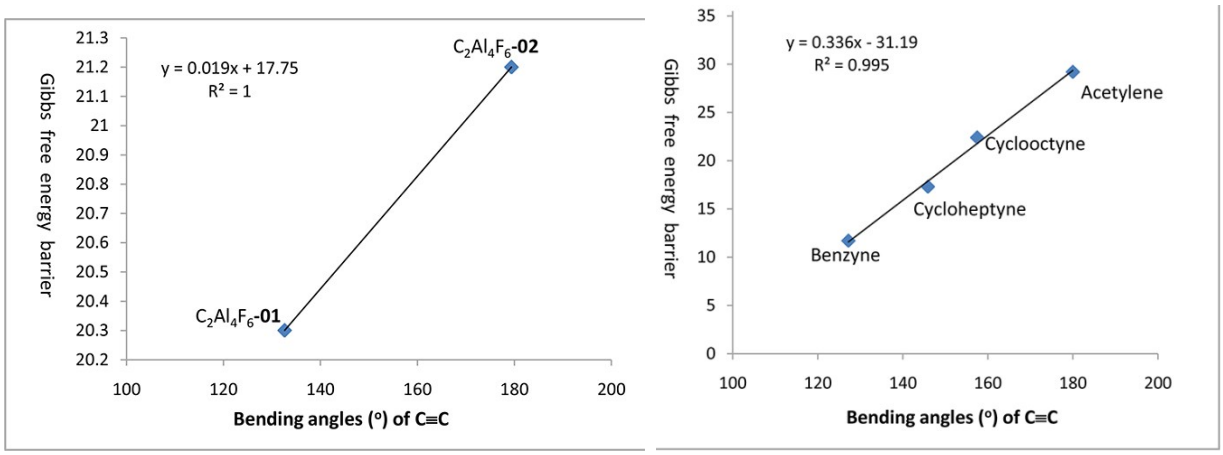


10. Fig. S10 The structures of representative local minima with small low frequencies, $C_2Al_4F_6$-02 (at the MP2/6-311G(2d,d,p) level) and $C_{48}H_{24}$ (at the B3LYP/6-311G(2d,d,p) level).

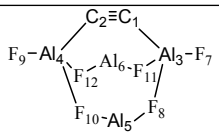


$C_2Al_4F_6$-**02** $C_{48}H_{24}$

11. Fig. S11 The correction of Gibbs free energy barriers (in kcal mol^{-1}) and the bending angles (°) of C≡C in the representative molecules at the CBS-QB3 level.



12.Table S1 Wiberg bond indexes (WBI) at the B3LYP/6-311G(2d,d,p) level, bond distances (Å), and selected angles (°) for $C_2Al_4F_6$-01 at the CBS-QB3 level, M062X/6-311G(2d,d,p) , CCSD/cc-pVTZ and CCSD/6-311G(2d,d,p) levels, respectively.



Structure **01**

Bond	WBI	Bond distances (Å)/ selected angles (°)			
		CBS-QB3	M062X/6-311G(2d,d,p)	CCSD/cc-pVTZ	CCSD/6-311G(2d,d,p)
C1-C2	2.905	1.229	1.226	1.233	1.240
C2-Al4	0.561	1.894	1.894	1.902	1.897
Al4-F9	0.523	1.652	1.641	1.648	1.643
Al4-F10	0.289	1.786	1.759	1.781	1.774
Al4-F12	0.289	1.786	1.759	1.781	1.774
F10-Al5	0.148	1.954	1.933	1.931	1.931
Al5-F8	0.148	1.954	1.926	1.931	1.931
F8-Al3	0.289	1.786	1.762	1.781	1.774
F11-Al3	0.289	1.786	1.762	1.781	1.774
Al6-F11	0.148	1.954	1.926	1.931	1.931
Al6-F12	0.148	1.954	1.933	1.931	1.931
Al3-F7	0.523	1.652	1.641	1.648	1.643
C1-Al3	0.561	1.894	1.891	1.902	1.897
		C1-C2-Al4 132.7° C2-C1-Al3 132.4°	C1-C2-Al4 134.7° C2-C1-Al3 128.2°	C1-C2-Al4 132.7° C2-C1-Al3 132.7°	C1-C2-Al4 131.5° C2-C1-Al3 131.5°

13. Table S2 The Cartesian coordinates and total energies of the former twenty low-lying $C_2Al_4F_6$ at the level of CBS-QB3.

"level"----"CBS-QB3"
"mol"----"Stoichiometry"
"lf"----"lowest frequency(cm-1)"
"te_zpe"----"total energy with zero-point energy (a.u.) at RB3LYP/6-311G(2d,d,p)"
"te_gfe"----"total energy with Gibbs free energy (a.u.) at RB3LYP/6-311G(2d,d,p)"
"te_ms_zpe"----"total energy with zero-point energy (a.u.) at CBS-QB3"
"te_ms_gfe"----"total energy with Gibbs free energy (a.u.) at CBS-QB3"

##

$C_2Al_4F_6$-01

lf=44.1 te_zpe=-1645.788576 te_gfe=-1645.833080 te_ms_zpe=-1643.229442 te_ms_gfe=-1643.274078

6	0.615500	-0.001353	1.930447
6	-0.613015	-0.001899	1.928257
13	1.895044	-0.000029	0.533600
13	-1.894946	-0.000487	0.533542
13	0.000181	-2.598060	-1.143927
13	-0.000432	2.598352	-1.143652
9	3.544029	-0.000568	0.626939
9	1.355928	-1.338978	-0.517761
9	-3.543751	-0.000386	0.629606
9	-1.356919	-1.339454	-0.518016
9	1.356284	1.341110	-0.514994
9	-1.357005	1.340768	-0.515391

$C_2Al_4F_6$-02

lf=2.2 te_zpe=-1645.783953 te_gfe=-1645.833134 te_ms_zpe=-1643.225657 te_ms_gfe=-1643.274970

13	2.396159	-0.728353	0.012453
6	0.583216	-0.182571	0.012360
13	-2.396167	0.728367	0.012458
6	-0.583210	0.182633	0.012395
13	4.621395	1.202469	-0.032706
13	-4.621372	-1.202497	-0.032720
9	3.418072	0.183936	1.171055
9	3.405384	0.143258	-1.187871
9	-3.405365	-0.143273	-1.187855
9	-3.418063	-0.183945	1.171068
9	-2.812941	2.329127	0.037802
9	2.812887	-2.329124	0.037819

$C_2Al_4F_6$-03

lf=42.2 te_zpe=-1645.776776 te_gfe=-1645.820510 te_ms_zpe=-1643.222781 te_ms_gfe=-1643.266644

 6 -0.016154 -2.132693 -0.570349
 6 1.185292 -1.979303 -0.797773
13 -1.470224 -1.262455 0.283689
13 2.422582 -0.600437 -0.342268
13 0.822837 1.083714 0.706250
13 -1.912155 1.743114 -1.590342
 9 -2.659604 -1.936046 1.204849
 9 -2.154383 -0.052510 -0.817315
 9 -0.232427 1.755294 -0.599054
 9 4.050874 -0.631479 -0.649554
 9 0.968177 2.245310 1.882220
 9 -0.554232 -0.031591 1.252572

$C_2Al_4F_6$-04

lf=38.4 te_zpe=-1645.768046 te_gfe=-1645.811316 te_ms_zpe=-1643.219847 te_ms_gfe=-1643.263243

 6 0.935518 -2.066508 -0.000274
13 2.382654 -0.852108 0.000025
 6 -0.274863 -1.831274 -0.000502
13 -1.332006 -0.230503 -0.000308
13 0.660082 1.357418 -0.000103
13 -4.302516 -0.144981 0.000503
 9 1.826223 0.437550 1.169025
 9 1.051486 2.968027 -0.000018
 9 1.826556 0.437700 -1.168978
 9 4.009647 -1.094125 0.000257
 9 -2.705099 -0.169266 1.175849
 9 -2.705560 -0.168890 -1.175787

$C_2Al_4F_6$-05

lf=33.5 te_zpe=-1645.772324 te_gfe=-1645.817249 te_ms_zpe=-1643.219762 te_ms_gfe=-1643.264819

 6 -0.087559 1.341357 0.400089
 6 -1.326712 1.361545 0.412736
13 -1.398765 -0.657783 0.396019
13 -3.217614 1.497088 -0.727772
13 1.912864 -1.898988 -0.793633

13 1.821346 0.965686 0.190700
 9 -1.741430 -1.415386 1.821672
 9 -0.149730 -1.480876 -0.470634
 9 -2.799369 -0.531449 -0.651508
 9 1.955638 0.160629 -1.355472
 9 2.051558 -0.572725 0.966713
 9 2.900423 2.173646 0.497447

$C_2Al_4F_6$-06

lf=46.5 te_zpe=-1645.764265 te_gfe=-1645.807629 te_ms_zpe=-1643.219001 te_ms_gfe=-1643.262492

 6 1.214685 -1.303007 0.523265
13 -1.780430 -1.176900 0.198765
13 -0.910601 1.440569 -0.309368
 6 0.033735 -1.673159 0.557100
13 3.058676 -1.554910 -0.726919
13 1.448530 0.756031 0.357288
 9 -1.532934 -0.112412 -1.241199
 9 2.695908 0.398675 -0.880025
 9 -1.858606 2.711383 -0.783541
 9 -1.868096 0.422890 1.016820
 9 2.241552 1.442321 1.651638
 9 -3.133469 -2.105663 0.209735

$C_2Al_4F_6$-07

lf=17.0 te_zpe=-1645.774657 te_gfe=-1645.822899 te_ms_zpe=-1643.218241 te_ms_gfe=-1643.266620

 6 2.399550 0.120435 0.243184
 6 3.500379 -0.267551 -0.142733
13 -2.020363 -1.171210 0.017065
13 5.300714 -0.910329 -0.691269
13 -1.667702 2.066410 -1.536049
13 0.710511 0.714025 0.835979
 9 -0.488590 -0.640552 0.767036
 9 -2.278494 0.301021 -0.917640
 9 -3.165926 -1.297375 1.192741
 9 0.455813 1.465261 2.286628
 9 -0.133902 1.674329 -0.401987
 9 -1.677863 -2.414124 -1.008682

$C_2Al_4F_6$-08

lf=45.9 te_zpe=-1645.768348 te_gfe=-1645.811778 te_ms_zpe=-1643.218163 te_ms_gfe=-1643.261722

 6 -0.026233 -1.367348 -0.818318
13 1.745663 -0.967823 -0.152224
 6 -1.265381 -1.396224 -0.783582
13 -0.927050 0.110422 0.730975
13 1.485028 2.464384 -0.587702
13 -3.254958 -0.606997 -1.262771
 9 2.201197 0.606429 -0.803684
 9 -2.483379 0.686532 0.009580
 9 0.988517 -0.377349 1.310597
 9 3.024112 -1.999539 -0.069293
 9 -0.070733 1.586140 0.161601
 9 -1.424514 -0.104256 2.296068

$C_2Al_4F_6$-09

lf=8.3 te_zpe=-1645.773007 te_gfe=-1645.821808 te_ms_zpe=-1643.217826 te_ms_gfe=-1643.266763

13 2.836268 -0.842648 0.000088
 6 0.941546 -0.376156 0.000089
13 -2.046535 0.538833 0.000198
 6 -0.219184 0.023508 0.000112
13 2.020066 2.258548 -0.000381
13 -4.265153 -1.409271 -0.000443
 9 3.409984 -1.469142 1.423876
 9 3.410167 -1.468848 -1.423768
 9 -3.051381 -0.349253 -1.180653
 9 -3.051604 -0.349911 1.180455
 9 -2.419763 2.150885 0.000752
 9 3.323199 0.933478 -0.000018

$C_2Al_4F_6$-10

lf=44.9 te_zpe=-1645.753975 te_gfe=-1645.797356 te_ms_zpe=-1643.214847 te_ms_gfe=-1643.258352

13 -1.751742 -1.350492 0.000004
 6 0.203235 1.096716 -0.000017
 6 1.448312 0.984825 -0.000022
13 -1.690621 1.341282 -0.000007
13 3.150038 0.001262 -0.000001
13 0.845320 -1.216395 -0.000003

 9 -2.928315 -2.509167 0.000009
 9 -2.201135 0.060409 -1.178607
 9 3.994300 0.018300 1.427504
 9 -2.201117 0.060417 1.178612
 9 3.994348 0.018292 -1.427477
 9 -2.557883 2.732550 -0.000004

$C_2Al_4F_6$-11

lf=50.3 te_zpe=-1645.768142 te_gfe=-1645.811205 te_ms_zpe=-1643.214535 te_ms_gfe=-1643.257724

 6 -0.142067 -1.032076 1.486161
 6 -1.307561 -1.334496 1.784205
13 0.905493 -0.160658 0.134020
13 -2.003081 -0.852592 0.070277
13 3.865912 -0.296701 -0.265626
13 -1.330810 2.594876 -0.104020
 9 0.346883 1.516816 -0.075808
 9 -3.204670 -1.602426 -0.778899
 9 -2.285205 0.921708 0.054661
 9 2.500777 0.343369 0.918933
 9 -0.542452 -0.663975 -1.008329
 9 2.074677 -0.793780 -1.051966

$C_2Al_4F_6$-12

lf=34.0 te_zpe=-1645.763344 te_gfe=-1645.807533 te_ms_zpe=-1643.214385 te_ms_gfe=-1643.258703

 6 -0.300526 -0.722494 -0.834621
 6 -1.480793 -0.744263 -1.224240
13 -1.553209 0.869718 0.075510
13 -3.448165 -1.470373 -0.580608
13 3.801159 0.327994 -0.854696
13 1.209958 -0.416404 0.412870
 9 2.238103 1.027429 0.198731
 9 -0.191174 0.836193 1.164524
 9 -3.001342 0.172359 0.728102
 9 1.338141 -1.311328 1.802490
 9 2.588973 -1.127130 -0.604181
 9 -1.799229 2.375631 -0.549311

$C_2Al_4F_6$-13

lf=34.6 te_zpe=-1645.762488 te_gfe=-1645.806638 te_ms_zpe=-1643.213863 te_ms_gfe=-1643.258141

 6 -1.422257 -0.775035 -1.248082
 6 -0.271716 -0.319793 -1.128971
13 -2.811050 -2.168774 -0.286898
13 1.277411 0.539699 -0.240485
13 -1.752734 0.684573 0.190555
13 3.523021 -1.290147 0.451751
 9 1.974031 -0.255904 1.201280
 9 -2.650216 -0.521131 1.064590
 9 -2.679732 1.992953 -0.186740
 9 2.634156 -0.461302 -1.017786
 9 1.758025 2.083102 -0.600962
 9 -0.248774 1.119994 0.958320

$C_2Al_4F_6$-14

lf=42.2 te_zpe=-1645.760797 te_gfe=-1645.805003 te_ms_zpe=-1643.213659 te_ms_gfe=-1643.257993

13 -2.204321 -1.309695 -0.000002
 6 -0.616568 -2.365801 -0.000159
13 -1.439319 1.124276 0.000126
 6 0.616558 -2.365831 -0.000474
13 2.204305 -1.309724 -0.000144
13 1.439316 1.124248 -0.000072
 9 0.000070 1.226738 1.170194
 9 2.255522 2.563171 -0.000092
 9 3.733561 -1.944892 0.000286
 9 -0.000083 1.226869 -1.170122
 9 -2.255491 2.563218 0.000269
 9 -3.733544 -1.944946 0.000019

$C_2Al_4F_6$-15

lf=28.0 te_zpe=-1645.766162 te_gfe=-1645.811410 te_ms_zpe=-1643.213358 te_ms_gfe=-1643.258737

 6 -0.283902 1.291480 0.488147
13 -3.106759 -1.105611 -1.120333
 6 0.918490 1.254778 0.168923
13 2.562045 0.300336 -0.369561
13 -2.267230 2.242258 0.395200
13 -0.061431 -0.707142 0.668859
 9 -1.212586 -1.377789 -0.452540
 9 3.832664 0.356025 0.681194

 9 1.544884 -1.215018 0.050693
 9 -2.949248 0.561475 -0.274171
 9 2.834178 0.264257 -1.998409
 9 -0.322517 -1.340669 2.170280

$C_2Al_4F_6$-16

lf=20.0 te_zpe=-1645.771649 te_gfe=-1645.818330 te_ms_zpe=-1643.213320 te_ms_gfe=-1643.260137

 6 0.196284 -1.717941 -0.002754
 6 -1.021312 -1.545519 -0.001628
13 1.473601 -0.387687 -0.000946
13 -2.730706 -0.621974 0.000157
13 -0.861894 2.526649 0.000179
13 4.430856 -0.211693 0.001140
 9 2.805098 -0.304031 -1.180494
 9 0.784487 1.208996 -0.000012
 9 -3.589616 -0.690109 -1.420190
 9 -2.005332 1.073117 0.000655
 9 2.803504 -0.305971 1.180475
 9 -3.587470 -0.691788 1.421722

$C_2Al_4F_6$-17

lf=29.2 te_zpe=-1645.763580 te_gfe=-1645.807936 te_ms_zpe=-1643.213254 te_ms_gfe=-1643.257741

13 -1.589015 -1.533075 1.901385
 6 -0.568948 -1.858527 -0.000113
13 -0.822479 1.409153 0.000020
13 -1.590193 -1.533196 -1.900831
 6 0.628214 -1.521070 -0.000131
13 2.103313 -0.251188 -0.000270
 9 2.913398 -0.109019 -1.436677
 9 -1.235488 2.998900 0.000062
 9 -1.403273 0.512411 1.354317
 9 -1.404274 0.512226 -1.353713
 9 2.913030 -0.108594 1.436312
 9 0.919191 1.203582 -0.000578

$C_2Al_4F_6$-18

lf=22.0 te_zpe=-1645.770839 te_gfe=-1645.816765 te_ms_zpe=-1643.213028 te_ms_gfe=-1643.259088

6 -0.875775 -1.745017 -0.000321
6 0.345652 -1.892802 0.000156
13 -2.459905 -0.663896 -0.000194
13 1.424965 -0.376844 0.000540
13 4.345319 0.078020 -0.000370
13 -1.506882 2.178198 0.000041
9 -3.997540 -1.266056 -0.000398
9 -2.151798 0.601211 -1.197424
9 0.553593 1.095833 0.000479
9 2.747821 -0.181047 -1.180214
9 2.748213 -0.181273 1.180303
9 -2.151924 0.600853 1.197341

$C_2Al_4F_6$-19

lf=19.5 te_zpe=-1645.764011 te_gfe=-1645.810953 te_ms_zpe=-1643.212983 te_ms_gfe=-1643.260058

6 2.732433 0.319974 -0.038193
6 3.870684 -0.140946 -0.087217
13 -1.354941 -0.614651 0.144460
13 5.712023 -0.893163 -0.157760
13 -4.205256 0.123547 -0.318165
13 0.990381 1.023556 0.037809
9 -2.651971 -0.678861 -1.141868
9 -2.688407 0.204814 0.998531
9 -1.054441 -2.199064 0.495722
9 -0.100908 0.258881 1.246603
9 0.654725 2.639514 -0.038262
9 -0.210929 0.176391 -1.052951

$C_2Al_4F_6$-20

lf=7.2 te_zpe=-1645.762257 te_gfe=-1645.810310 te_ms_zpe=-1643.212891 te_ms_gfe=-1643.261079

6 0.226888 -0.862690 -0.000427
6 -1.006972 -0.835728 -0.000492
13 -2.911220 -0.335392 -0.000562
13 2.182315 -1.106590 0.000177
13 -0.439730 1.458822 0.003140
13 2.557404 2.496407 -0.002042
9 2.701921 0.643360 -0.004987
9 -3.703511 -0.573440 1.429840
9 -3.702673 -0.569844 -1.432017
9 2.757408 -1.697412 1.436447
9 2.757884 -1.707260 -1.431733
9 -2.296971 1.406630 0.002031

14. Table S3 The Cartesian coordinates of the transition state structures(TS) between $C_2Al_4F_6$-01, $C_2Al_4F_6$-18 and $C_2Al_4F_6$-02 at the level of CBS-QB3.

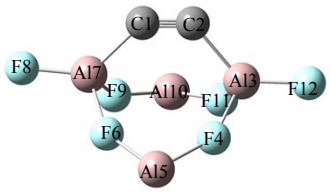
TS1: $C_2Al_4F_6$-01/$C_2Al_4F_6$-18

6	0	0.248779	-1.228544	1.179636
6	0	-0.932460	-1.305252	0.850772
13	0	-2.587511	-0.742243	0.017424
9	0	-1.971336	0.912580	-0.508393
13	0	-0.902074	2.394706	-0.820225
9	0	0.712235	1.422832	-0.036365
13	0	1.496408	0.099742	0.813299
9	0	2.700797	0.704153	1.789121
9	0	2.608767	-0.482778	-0.568640
9	0	-2.946872	-1.499474	-1.421093
9	0	-3.862985	-0.403339	1.028309
13	0	4.219073	-1.035513	-1.143491

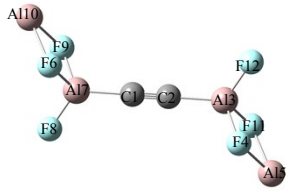
TS2: $C_2Al_4F_6$-02/ $C_2Al_4F_6$-18

6	0	-0.358139	-1.669488	-0.000140
13	0	-1.548794	-0.228529	0.000013
13	0	-4.497572	-0.046666	-0.000092
9	0	-2.889285	-0.159619	1.179367
6	0	0.868172	-1.709029	-0.000004
13	0	2.515025	-0.749431	-0.000100
9	0	2.314571	0.559301	-1.189591
13	0	1.823645	2.148969	0.000303
9	0	-0.745927	1.255137	0.000248
9	0	2.314910	0.559019	1.189743
9	0	4.021564	-1.426262	-0.000412
9	0	-2.889182	-0.159282	-1.179436

15. Table S4. The oxidation state of atoms of 01 and 02 compounds.



01



02

Atom (oxidation state)	Atom (oxidation state)
Al3 (+3)	Al3 (+3)
Al5 (+1)	Al5 (+1)
Al7 (+3)	Al7 (+3)
Al10 (+1)	Al10 (+1)