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# Globally stabilized bent carbon–carbon triple bond by hydrogen-free inorganic–metallic scaffolding $\text{Al}_4\text{F}_6^\dagger$

Ying-ying Xue,<sup>a</sup> Ying Zhang,<sup>a</sup> Zhong-hua Cui<sup>✉</sup> and Yi-hong Ding<sup>✉</sup>

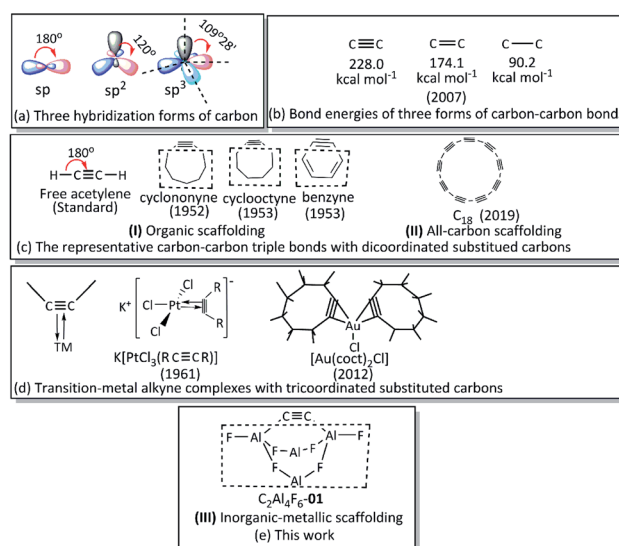
For over 100 years, known bent  $\text{C}\equiv\text{C}$  compounds have been limited to those with organic (I) and all-carbon (II) scaffoldings. Here, we computationally report a novel type (III) of bent  $\text{C}\equiv\text{C}$  compound, *i.e.*,  $\text{C}_2\text{Al}_4\text{F}_6$ -01, which is the energetically global minimum isomer and bears an inorganic–metallic scaffolding and unexpected click reactivity.

## 1. Introduction

Carbon, the element with  $2s^22p^2$  electron configuration, has three different hybridization forms of the valence atomic orbitals, *i.e.*,  $\text{sp}$ ,  $\text{sp}^2$  and  $\text{sp}^3$  hybrid orbitals, with significantly more acute bond angles and decreased homo-atomic bond strength (see Schemes 1a and b).<sup>1</sup> Understandably, bending a  $\text{C}\equiv\text{C}$  bond is in most cases geometrically and electronically unfavourable. In fact, in acyclic or less strained cyclic compounds, the  $\angle\text{CCR}$  angle of  $\text{C}\equiv\text{C}$  is strictly  $180^\circ$  (*e.g.*, acetylene in Scheme 1c) or very close to  $180^\circ$  (*e.g.*, acyclic alkynes<sup>1b,2</sup> and other substituted compounds<sup>3</sup>). A significantly bent  $\text{C}\equiv\text{C}$  without additional coordination is only possible when it is embedded in highly strained or cyclic scaffoldings. As for most exotic species,<sup>4</sup> the conceptual and synthetic challenges of developing compounds with a significantly bent  $\text{C}\equiv\text{C}$  bond have been long attempted.<sup>5</sup> The first postulation of a bent  $\text{C}\equiv\text{C}$  constrained in an aromatic framework as an reactive intermediate was published more than one century ago (in 1902).<sup>6</sup> Since then, related species with bent  $\text{C}\equiv\text{C}$  bonds in organic scaffolding (see type I in Scheme 1c) have witnessed fruitful achievements, including applications in the pharmaceutical chemistry, materials chemistry, natural products synthesis, and organometallic chemistry.<sup>5c,7</sup> Cycloalkynes or angle-strained alkynes have received great attention due to their closeness to alkenes (obtained by simply losing two ligands).<sup>5b–5h,7</sup> Besides, mono-cyclic all-carbon molecules, *i.e.*, cyclocarbon[ $n$ ], present

the second class (see type II in Scheme 1c), each of which possess alternating  $\text{C}\equiv\text{C}$  and  $\text{C}-\text{C}$  bonds.<sup>5a,8</sup> After lengthy pursuit, the first ring-shaped molecule of pure carbon, *i.e.*, cyclocarbon ( $\text{C}_{18}$ ), was recently synthesized, representing a breakthrough and possibly advancing potential molecular-scale electronic applications (*e.g.*, semiconductors).<sup>5a,9</sup>

One should be aware that when an alkyne perpendicularly interacts with a transition metal (TM) complex, so-called “transition-metal alkyne complexes” form (see Scheme 1d).<sup>10</sup> However, rather than the strain in type I and II, the synergistic bonding interactions between  $\text{C}\equiv\text{C}$  and TM in these complexes bend the  $\text{C}\equiv\text{C}$ , and the coordination number of the carbon atoms is increased to three rather than two in I and II. Thus,



**Scheme 1** Hybridization forms and homo-nuclear bond energies of carbon, and representative compounds with carbon–carbon triple bonds.

<sup>a</sup>Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130023, P. R. China. E-mail: yhdd@jlu.edu.cn

<sup>b</sup>Institute of Atomic and Molecular Physics, Jilin University, Changchun 130023, P. R. China. E-mail: zcui@jlu.edu.cn

<sup>c</sup>Key Laboratory of Carbon Materials of Zhejiang Province, College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, P. R. China

<sup>†</sup> Electronic supplementary information (ESI) available: Method details, Cartesian coordinates and total energies computed of key structures of  $\text{C}_2\text{Al}_4\text{F}_6$  at the CBS-QB3 level, and some important information of the reactivity. See DOI: 10.1039/d0ra02280b



such compounds are not the topic of the present work. Moreover, one should note that in numerous cases, the TM-C $\equiv$ C interactions may be so strong that the hybridization state of the ethynyl carbon atoms can change from sp to sp<sup>2</sup> upon coordination, greatly reducing or even diminishing the C $\equiv$ C feature.<sup>10a,10d,10g</sup>

Can a significantly bent C $\equiv$ C bond be stabilized by a non-carbon-based scaffolding while maintaining the dicoordinate carbons? We speculated that fluorinated metal dicarbides might possess the desired bent C $\equiv$ C bond if metal fluorides can form stable and closed structures. During our study on F-persubstituted dicarbides (C<sub>2</sub>Al<sub>4</sub>F<sub>6</sub>), by means of an extensive structural search and high-level energy calculations, we fortunately found a novel type (**III**) in which a bent C $\equiv$ C bond can be globally stabilized by the novel scaffolding Al<sub>4</sub>F<sub>6</sub> that is hydrogen-free and non-carbon-based. The global structure of C<sub>2</sub>Al<sub>4</sub>F<sub>6</sub>-**01** has an interesting “flower-basket” shape (with an Al-F alternative 8-member ring tray and a C-C handle). The nature and reactivity of C $\equiv$ C within the global C<sub>2</sub>Al<sub>4</sub>F<sub>6</sub>-**01** was further studied *via* numerous analytic methods.

## 2. Theoretical methods

Due to the good balance between reliability and computational cost, the density function theory (DFT) method is now indispensable for studying molecules and materials, though debates still exist.<sup>11</sup> First, to obtain the global structure, we reasonably assumed that the fluorine atoms act as ligands around the C<sub>2</sub>Al<sub>4</sub>-core. We then applied our locally developed “skeleton-ligand cluster-growth” method<sup>12</sup> at the level of B3LYP<sup>13</sup>/6-311G(d), which has been shown to be quite cost-effective for initial large-scale isomeric searches. Further, those with energies lower than 20 kcal mol<sup>-1</sup> were refined at the composite CBS-QB3 (ref. 14) level, which reliably gives accurate thermochemical properties in numerous fields. Second, similar to most DFT methods, the presently applied B3LYP is of single-reference nature and is constructed empirically *via* parameterization. The geometries, energetics and T1 diagnostics<sup>15</sup> of the former two lowest-energy isomers were computed using wave function-based methods, *i.e.*, CCSD(T)/aug-cc-pVTZ//CCSD/cc-pVTZ. The single-point CBS-QB3 energies were recomputed at CCSD/cc-pVTZ and CCSD/6-311G(2d,d,p) geometries. Their geometries were also optimized at the M062X/6-311G(2d,d,p) level.

Natural bond orbital (NBO)<sup>16</sup> analysis and adaptive natural density partitioning (AdNDP) analysis<sup>17</sup> were conducted to understand their electronic structures at the B3LYP/6-311G(2d,d,p) level. The AdNDP analysis was analyzed by the Multiwfn program.<sup>17b</sup> All these calculations were performed using the commercial Gaussian 16 (ref. 18) and Gaussian 09 (ref. 19) packages.

## 3. Results and discussion

An amazingly large number, *i.e.*, 28600, of C<sub>2</sub>Al<sub>4</sub>F<sub>6</sub> isomers were obtained as local energy minima at the B3LYP/6-311G(d) level. For brevity and easy discussion, we only show the first two low-energy isomers with the respective bent and linear forms of

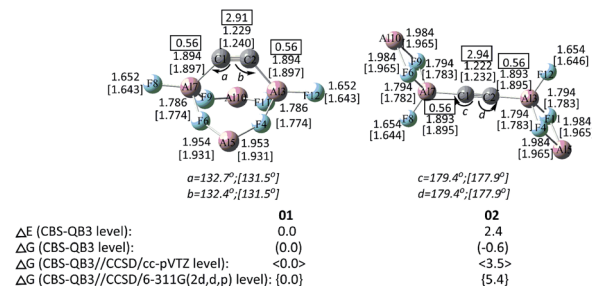


Fig. 1 The key geometrical parameters (distances in Å and angles in °) at the CBS-QB3 and CCSD(T)/aug-cc-pVTZ//CCSD/cc-pVTZ (in []) levels. The Wiberg bond indexes are shown in rectangular boxes. The relative CBS-QB3 energies (in kcal mol<sup>-1</sup>) with zero-point correction (ΔE) and the relative Gibbs free energies (ΔG) of the former two isomers of C<sub>2</sub>Al<sub>4</sub>F<sub>6</sub> at different levels are shown.

C $\equiv$ C, *i.e.*, **01** and **02**, at the CBS-QB3 level (see Fig. 1). Notably, the zero-point energy (ZPE)-corrected CBS-QB3 energy of **01** is lower than that of **02** by 2.4 kcal mol<sup>-1</sup>. However, the relative Gibbs free energy between **01** and **02** is very close, with the latter lower by 0.6 kcal mol<sup>-1</sup>. This suggests the profound influence of the Gibbs free energies on the stability of **01** and **02**. Thus, we performed additional calculations at the CBS-QB3 level using the costly CCSD/cc-pVTZ and CCSD/6-311G(2d,d,p)-optimized geometries. At the two CBS-QB3//CCSD levels, the Gibbs free energy of **01** is slightly more stable than **02** by 3.5 and 5.4 kcal mol<sup>-1</sup>, respectively. Thus, **01** can be viewed as the global minimum.

Besides, since the T1 values of **01** and **02**, *i.e.*, 0.0137 and 0.0136, respectively, are considerably smaller than the recommended threshold value 0.02,<sup>15</sup> there should be negligible multi-reference characters for both structures. Note that the main bond distances and angles of C<sub>2</sub>Al<sub>4</sub>F<sub>6</sub>-**01** and **02** are consistent among the CBS-QB3, CCSD and M062X levels (see Table S1†). Thus, for consistency, the following discussions are based on the CBS-QB3 values unless otherwise specified.

### Bonding features of C $\equiv$ C bond and C-Al bonds in C<sub>2</sub>Al<sub>4</sub>F<sub>6</sub>-**01** and **02**

By comparing the corresponding typical triple and double carbon-carbon bond distances, *i.e.*, 1.198 Å in HC $\equiv$ CH and 1.327 Å in H<sub>2</sub>C=CH<sub>2</sub> at the B3LYP/6-311G(2d,d,p) level (see Fig. S7†), both **01** and **02** with very short CC distances (1.229 and 1.222 Å, respectively) can be viewed as containing a C $\equiv$ C moiety, which is further supported by their large WBI values of 2.91 and 2.94, respectively. The C $\equiv$ C bond of **01** is heavily bent, with two acute ∠CCAl angles of 132.7° and 132.4°. By contrast, **02** has an almost linear C $\equiv$ C bond with a ∠CCAl angle of 179.4°.

The Al-F bonds in both **01/02** can be categorized into three classes, *i.e.*, 1.652/1.654, 1.786/1.794, and 1.954/1.984 Å, respectively, with increasing bond distances. The first two are comparable to the corresponding terminal (1.638 Å) and bridge (1.821 Å) Al-F bonds of the model Al<sub>2</sub>F<sub>6</sub> (see Fig. S7†). The third type with the longer Al-F distance can be viewed as the dative



bonding, indicating the presence of two  $\text{Al}^+$ -ions in **01/02**. The low-valent  $\text{Al}^+$ -subunits<sup>20</sup> are effectively stabilized by the neighbouring  $\text{F} \rightarrow \text{Al}$  donor-acceptor interactions rather than the electron-sharing one. The situation is quite similar to the reference molecule  $\text{Al}_2\text{F}_4$ ,<sup>21</sup> which has a ground ionic structure  $\text{Al}^+[\text{AlF}_4]^-$  with the two types of  $\text{Al}-\text{F}$  bonds, *i.e.*, 1.993 Å between  $\text{Al}^+$  and  $\text{F}$  and 1.648/1.783 Å between  $\text{Al}^{3+}$  and  $\text{F}$  (see Fig. S7†). Compared to the typical  $\text{C}-\text{Al}$  single bond of the model molecule  $\text{Al}(\text{CH}_3)_3$  (1.967 Å), the  $\text{C}-\text{Al}$  bonds of **01** and **02**, *i.e.*, 1.894, 1.894, 1.893 and 1.893 Å, can be viewed as covalent single bonding. The somewhat shortened (smaller by 3.7%) bond of  $\text{C}-\text{Al}$  could result from the additional interaction between the  $\text{Al}$ -center and the similar  $\text{C}\equiv\text{C}$   $\pi$  bond in **01** and **02**.

Note that the isomer **02** has a rather small low frequency ( $2.2\text{ cm}^{-1}$ ). Its local minimum was confirmed at the MP2/6-311G(2d,d,p) level ( $5.4\text{ cm}^{-1}$ ) (see Fig. S10†). The small low frequency indicates that **02** is a very floppy structure due to the two  $\text{Al}^+$ -ions stabilized by dative bonding. In fact, in bonds associated with easy rotation or wagging, very small low frequencies are evident. For example, in a small H-terminated cluster of graphene with 6 benzene units and 6 CC units, the first two imaginary frequencies are as small as  $7.1\text{ cm}^{-1}$  and  $7.2\text{ cm}^{-1}$  at the B3LYP/6-311G(2d,d,p) level, which correspond to the up-and-down wagging of the benzene unit.

The main molecular orbitals of isomers **01** and **02** are shown in Fig. 2. Both possess one  $\sigma$  bond, HOMO-4 (**01**) and HOMO-4 (**02**), and two  $\pi$  bonds (HOMO-2 and HOMO-3 for **01** and HOMO-2 and HOMO-3 for **02**). Each has two  $\sigma$   $\text{C}-\text{Al}$  bonds (HOMO-10 and HOMO-11 in **01** and HOMO-12 and HOMO-15 in **02**). The widely used and efficient method, namely adaptive natural density partitioning (AdNDP) analysis,<sup>17</sup> was adopted at the B3LYP/6-311G(2d,d,p) level. The one  $2\text{c}-2\text{e}$   $\sigma$  (two centers and two electrons) bond and two  $2\text{c}-2\text{e}$   $\pi$  bonds with high occupation numbers (close to 2.0) support the presence of a triple  $\text{C}\equiv\text{C}$  bond and the high occupation numbers (close to 2.0) of two  $2\text{c}-2\text{e}$   $\text{C}-\text{Al}$  bonds well support the presence of the two  $\text{C}-\text{Al}$  the single bonds in both **01** and **02**. The detailed orbital and AdNDP analysis can be found in Fig. S2 and S3.†

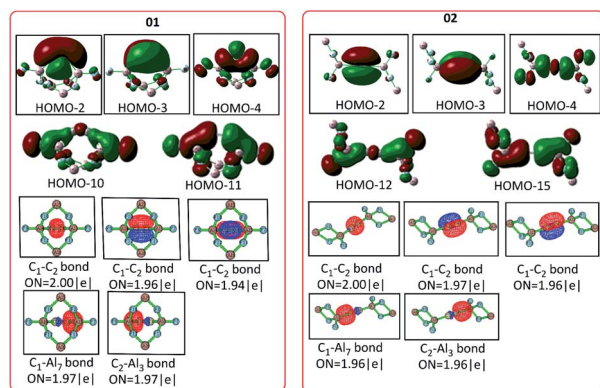
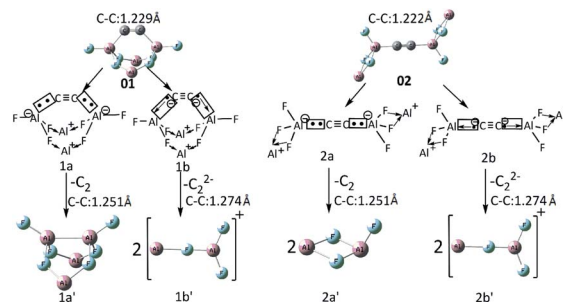


Fig. 2 The selected molecular orbitals of  $\text{C}_2\text{Al}_4\text{F}_6$ -**01** and **02** at the level of B3LYP/6-311G(2d,d,p). "ON" denotes the occupation number on the localized orbital.



Scheme 2 The path of eliminating  $\text{C}_2$  and  $\text{C}_2^{2-}$  in  $\text{C}_2\text{Al}_4\text{F}_6$ -**01** and **02** at the level of B3LYP/6-311G(2d,d,p).

Based on the above structural and electronic analysis, we can deduce that the connection between  $\text{C}$  and  $\text{Al}$  should be of the "electron-sharing" type for both **01** and **02** (see **1a** and **2a** in Scheme 2) rather than the "electron dative" type (see **1b'** and **2b'** in Scheme 2). According to the "electron-sharing" mode, if  $\text{C}_2$  is removed, the radical centers should be positioned at the neighbouring  $\text{Al}$  centers. This is well supported by the optimized  $\text{Al}_2\text{F}_3^+$  and an  $\text{Al}-\text{Al}$  connected  $\text{Al}_4\text{F}_6$  structure (see **1a'** and **2a'** in Scheme 2). However, the optimized fragments based on the "electron dative" mode, *i.e.*,  $\text{Al}_2\text{F}_3^+$  and  $\text{Al}_4\text{F}_6^{2+}$ , differ rather dramatically from the structures of **01** and **02**.

### Reactivity of $\text{C}\equiv\text{C}$ in $\text{C}_2\text{Al}_4\text{F}_6$ -**01** and **02**

Further, the presence of  $\text{C}\equiv\text{C}$  within the **01** and **02** isomers of  $\text{C}_2\text{Al}_4\text{F}_6$  is consistent with the computational observation that the  $\text{C}\equiv\text{C}$  bond can undergo the addition of two  $\text{H}_2$  molecules as well as  $[3+2]$  click reactions with  $\text{HN}_3$ . For known cycloalkynes, there is a clear linear correlation ( $R^2 = 0.995$ , see Fig. S11†) between the Gibbs free energy barriers and the bending angles of  $\text{C}\equiv\text{C}$ , *i.e.*, the higher bending degree of  $\text{C}\equiv\text{C}$ , the more reactive it becomes. The  $\text{HN}_3$  click reactivity of **01** and **02** was a great surprise. Both have comparable barrier heights ( $20.3$  and  $21.2\text{ kcal mol}^{-1}$ , respectively) despite the significantly different bending angles of  $\text{C}\equiv\text{C}$ . The unexpected click reactivity of  $\text{C}\equiv\text{C}$  can be ascribed to the involvement of the neighbouring acid  $\text{Al}$  centers of **02** (see Fig. S4†). One of the  $\text{Al}^+$  atoms of **02** could flip and attach to the nitrogen atom with the lone pair electrons of the  $\text{HN}_3$  unit. Such additional interaction lowers the barrier of **02** with linear  $\text{C}\equiv\text{C}$ , approaching that of **01** with the bent  $\text{C}\equiv\text{C}$  bond. Compared with known cycloalkynes (see Fig. 3), the  $\text{HN}_3$  click barrier ( $20.3\text{ kcal mol}^{-1}$ ) of **01** lies between cycloheptyne ( $\text{C}_7\text{H}_{10}$ ,  $17.3\text{ kcal mol}^{-1}$ ) and cyclooctyne ( $\text{C}_8\text{H}_{12}$ ,  $22.4\text{ kcal mol}^{-1}$ ), indicating the feasible existence of **01** at least *via* spectroscopic detection.

### Interconversion between $\text{C}_2\text{Al}_4\text{F}_6$ -**01** and **02**

For the intrinsic stability, we attempted to identify the isomerization of the global isomer of  $\text{C}_2\text{Al}_4\text{F}_6$ -**01**. The lowest barrier is associated with an indirect conversion to  $\text{C}_2\text{Al}_4\text{F}_6$ -**02** by sequentially breaking the  $\text{F} \rightarrow \text{Al}^+$  dative bond *via* an intermediate  $\text{C}_2\text{Al}_4\text{F}_6$ -**18** (see Fig. 4). The barrier is as high as  $14.8\text{ kcal mol}^{-1}$ . In addition, at the B3LYP/6-311G(2d,d,p) level,





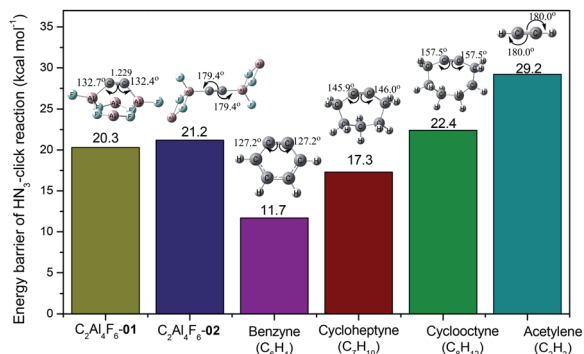


Fig. 3 Gibbs free energy barriers (in kcal mol<sup>-1</sup>) of the HN<sub>3</sub> click reaction with C<sub>2</sub>Al<sub>4</sub>F<sub>6</sub>-01, C<sub>2</sub>Al<sub>4</sub>F<sub>6</sub>-02, benzyne, cycloheptyne, cyclooctyne and acetylene at the CBS-QB3 level.

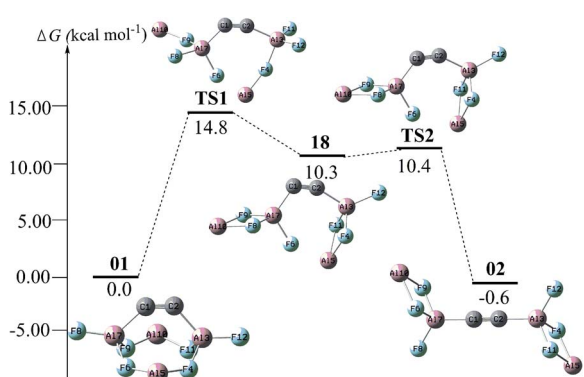


Fig. 4 The conversion pathways between C<sub>2</sub>Al<sub>4</sub>F<sub>6</sub>-01 and C<sub>2</sub>Al<sub>4</sub>F<sub>6</sub>-02 with the Gibbs free energy barriers at the CBS-QB3 level.

we obtained an optimized complex by adding two BH<sub>3</sub>NH<sub>3</sub> to **01** (see Fig. S6†), which comprises four dative bonds, *i.e.*, two C → BH<sub>3</sub> and two NH<sub>3</sub> → C. This indicates that the bent C≡C bond in **01** does have the “hidden carbene” feature as was proposed very recently.<sup>3a</sup>

The unique stability of isomer **01** could be attributed to the balance of two opposite effects. On one hand, bending the C≡C bond leads to an energetic destabilization. On the other hand, the recombination of the two Al<sub>2</sub>F<sub>3</sub> units causes energetic stabilization. Fig. 4 vividly shows this energetic change during the interconversion between **01** and **02**.

## Implications

Two computational facts from the present work deserve the interest of the chemical community. First, our global isomeric search unexpectedly identified a bent C≡C bond (both C-atoms are in dicoordination) supported by a scaffolding that is neither of the two known carbon-based systems, *i.e.*, type-I and II. **01** presents the first example of a bent C≡C bond stabilized by an inorganic metal cluster composed of Al and F, despite the typical expectation that a polyatomic cluster such as C<sub>2</sub>Al<sub>4</sub>F<sub>6</sub> could sufficiently undergo complex structural rearrangement to avoid a global bent C≡C. Second, we observed an inverse click

reactivity for C≡C between the inorganic metal-supported structures **01** (bent C≡C) and **02** (linear C≡C) due to the active involvement of the attached Al-atoms. We postulated that this structure could be versatile in such metal-inorganic C≡C compounds.

A large number of organometallic fluorides have been synthesized,<sup>22</sup> among which various C, Al, and F-based species are known.<sup>23</sup> Numerous general synthetic methods for generating angle-strained cycloalkynes have been reported.<sup>5e</sup> In our study, the lowest-energy C<sub>2</sub>Al<sub>4</sub>F<sub>6</sub>-**01** with the bent C≡C bond has a high likelihood to be synthesized in future. Here, we tentatively supposed a possible synthetic method *via* the photochemical reactions of compounds C<sub>2</sub>Al<sub>4</sub>F<sub>6</sub>HCl or C<sub>2</sub>Al<sub>4</sub>F<sub>6</sub>CO. We calculated the adsorption energy for removing HCl from C<sub>2</sub>Al<sub>4</sub>F<sub>6</sub>HCl at 273.15 K, which is 20.0 kcal mol<sup>-1</sup> at the CBS-QB3 level. The process of removing CO from C<sub>2</sub>Al<sub>4</sub>F<sub>6</sub>CO was predicted to be exothermic by 9.3 kcal mol<sup>-1</sup> at the CBS-QB3 level.

## 4. Conclusion

The unexpected finding of a bent C≡C bond stabilized globally within the chemical formula C<sub>2</sub>Al<sub>4</sub>F<sub>6</sub> contrasts sharply with the current knowledge of 6-vertex dicarbalanes, *i.e.*, C<sub>2</sub>Al<sub>4</sub>R<sub>6</sub> with R = H and CH<sub>3</sub> shows a distorted octahedral structure as the lowest energy isomer with the two carbons being well separated.<sup>24</sup> Besides providing of the great possibility to regulate the ground shape of dicarbalanes by substituent engineering, the strong tendency to form the triply bonded CC moiety indicates that a variety of low-lying bent C≡C with inorganic-metallic scaffoldings could be found in similar dicarbon metal fluorides (*i.e.*, C<sub>2</sub>M<sub>x</sub>F<sub>y</sub>, M = heavier than group 13).

In summary, in this study, through our locally developed “skeleton-ligand cluster-growth” method, we report the first example of a main-group metal-inorganic compound isomer (C<sub>2</sub>Al<sub>4</sub>F<sub>6</sub>-**01**) with a globally stabilized bent carbon-carbon triple bond. *Via* bonding analysis, we determined that C<sub>2</sub>Al<sub>4</sub>F<sub>6</sub>-**01** exhibits a salt-like character with two [−AlF<sub>3</sub>]<sup>−</sup> and two Al<sup>+</sup> units.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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