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### Introduction

The investigation of non-classical molecules with exotic electronic structures has enriched the chemical bonding theory and provided support for the development and application of new materials due to their unusual properties.<sup>1</sup> A seminal example of non-classical molecules is planar hypercoordinate carbon (phC). In 1970, Hoffmann *et al.* first presented planar tetracoodinated carbon (ptC),<sup>2</sup> which violates the classical tetrahedral tetracoordinate carbon (ttC) independently deduced by van't Hoff and Le Bel.<sup>3,4</sup> However, the ptC arrangement is electronically unstable, for which the out-of-plane  $p_z$ atomic orbital of the central carbon has very high energy.<sup>2,5</sup> Besides, the implementation is pretty hard from the ttC to the ptC arrangement because the energy difference is extremely high. In the case of CH<sub>4</sub>, the energy difference is 130 kcal mol<sup>-1</sup>



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The exploration of planar hypercoordinate carbon (phC) is challenging and significant. It is often puzzling to chemists whether the designed phC species should satisfy the 18-valence-electron rule, an authoritative rule in the phC field. In this study, we introduced a zinc atom into the extremely unstable 16-valence-electron planar tetracoordinate carbon (ptC) species CAl<sub>4</sub> and its isoelectronic structure  $NAl_4^+$  with a planar tetracoordinate nitrogen (ptN), and designed the 18-valence-electron  $CAl_4Zn$  and NAl₄Zn<sup>+</sup> possessing a ptC and ptN, respectively. The thermodynamic results indicate that the ptC/N species CAl<sub>4</sub>Zn and NAl<sub>4</sub>Zn<sup>+</sup> are the global energy minima, and also showed that the 18-valenceelectron rule is more appropriate in designing ptC/N species having the CAl<sub>4</sub> and NAl<sub>4</sub><sup>+</sup> skeletons, compared with the 16-valence-electron rule. Simultaneously, the BOMD simulations found that CAl₄Zn is dynamically stable. Although NAl<sub>4</sub>Zn<sup>+</sup> was isomerized at 298 and 500 K, it is dynamically viable. The excellent stability may be explained by the perfect electronic structure. First, the HOMO-LUMO gaps became much wider after the introduction of the Zn atom. Second, AdNDP analysis indicated that the introduction of the Zn atom promoted the formation of peripheral Al-Al and Al-Zn covalent bonds, providing a stable and comfortable bonding environment for ptC/N. In addition, the  $\sigma$  and  $\pi$  double aromaticity further stabilized the ptC/N species. Hence, as dynamic global energy minima display  $\sigma$  and  $\pi$ double aromaticity, the ptC/N species CAl<sub>4</sub>Zn and NAl<sub>4</sub>Zn<sup>+</sup> are promising in gas phase generation.

> from methane to planar methane, even 27 kcal mol<sup>-1</sup> higher than the dissociation energy (103 kcal mol<sup>-1</sup>) of the C–H bond.<sup>6</sup> Nevertheless, studies<sup>7</sup> have confirmed that the planar hypercoordinate carbon can be designed by creating a comfortable bonding environment for central carbon using the electronic effect. To our knowledge, the 18-valence-electron rule has been a widely accepted principle for the design of phC, although some planar tetracoodinated structures having fewer than 18ve were explored. For example, the 12ve CLi<sub>3</sub>E (E = As, Sb, and Bi) and CLi<sub>3</sub>E<sup>+</sup> (E = O, S, Se, Te, Po),<sup>8a</sup> the 14ve CSi<sub>2</sub>H<sub>2</sub> and CGe<sub>2</sub>H<sub>2</sub>,<sup>8b</sup> and 16ve CAl<sub>3</sub>Tl<sup>8c</sup> and CLiAl<sub>2</sub>E (E = P, As, Sb, Bi),<sup>8d</sup> *etc.* In addition to the electronic factor, the selection of ligand atoms is also key to the phC.

> Aluminum is one of the most popular ligand atoms in the planar hypercoordinate field, and abundant planar hypercoordinate structures have been reported. Among them, the great breakthrough has included ptC species  $CAl_4^{2-}$  and  $CAl_4^{-}$ , which were experimentally and theoretically proven to be the global energy minimum structures by Wang and Boldyrev *et al.*<sup>9,10</sup> However, for the neutral 16-valence-electron  $CAl_4$ , the  $D_{4h}$  ptC structure is extremely unstable electronically and thermodynamically. The isoelectronic species of  $CAl_4$ ,  $NAl_4^+$  also have the same phenomenon, as shown in Fig. S1 in the ESI.†

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Paper



Fig. 1 Optimized structures of  $CAl_4Zn$  and  $NAl_4Zn^+$  (**1a** and **2a**) regarding symmetry. The bond lengths (in Å) and the Wiberg bond orders calculated at the B2PLYP-D3(BJ)/aug-cc-pVTZ level are given in red and italic blue font, respectively.

According to the view proposed by Wang, in the  $CAl_3Si^{0/-}$  and  $CAl_3Ge^{0/-}$  with a tetracoordinate carbon, 16 valence electrons prefer to form a classical ttC arrangement and the 18-valence-electron rule may be more suitable for the design of ptC.<sup>11</sup> Therefore, it is natural to ask whether it is possible to achieve structural stability by introducing other elements to cause the ptC/N species  $CAl_4$  and  $NAl_4^+$  to meet the 18-valence-electron rule.

To answer this question, we introduced a zinc atom into the  $CAl_4$  and  $NAl_4^+$  skeletons and designed the 18-valence-electron ptC/N species  $CAl_4Zn$  (1a) and  $NAl_4Zn^+$  (2a), as shown in Fig. 1. Here, the zinc atom was selected due to its particular properties, which are the active  $4s^2$  valence electron and ten inert 3d electrons. Surprisingly, the ptC/N species are the global energy minima displaying  $\sigma$  and  $\pi$  double aromaticity.

### Computational method

For ptC/N species 1a and 2a, the geometry optimizations and harmonic vibrational frequency analyses were performed at both the B3LYP/aug-cc-pVTZ and B2PLYP-D3(BJ)/aug-cc-pVTZ levels, which gave almost the same structures and frequencies. In the text, we reported the structural parameters at the B2PLYP-D3(BJ)/aug-cc-pVTZ level. The potential energy surfaces (PESs) of CAl<sub>4</sub>Zn and NAl<sub>4</sub>Zn<sup>+</sup> were explored to evaluate thermodynamic stabilities of 1a and 2a using the stochastic search algorithm,<sup>12</sup> and the randomly generated singlet and triplet structures were initially optimized at the B3LYP/6-31G(d) level. The fifteen lowest isomers were then re-optimized and the vibrational frequencies were re-analyzed at both the B3LYP/ aug-cc-pVTZ and B2PLYP-D3(BJ)/aug-cc-pVTZ levels. Finally, the energies of the five lowest isomers were refined at the CCSD(T)/ aug-cc-pVTZ level based on the optimized geometries at the B2PLYP-D3(BJ)/aug-cc-pVTZ level. The relative energies of isomers were compared via the CCSD(T)/aug-cc-pVTZ single-point energies with the B2PLYP-D3(BJ)/aug-cc-pVTZ zero-point energy (ZPE) corrections. The dynamic stabilities of 1a and 2a were evaluated by Born-Oppenheimer molecular dynamic (BOMD)<sup>13</sup> simulations at the PBE/DZVP level for 100 ps. To get more accurate electronic structures of 1a and 2a, the adaptive natural density partitioning (AdNDP)<sup>14</sup> analyses were performed at the B3LYP/6-31G(d) level and the natural bond orbital (NBO)<sup>15</sup> was analyzed at the B2PLYP-D3(BJ)/aug-cc-pVTZ level. The nucleusindependent chemical shifts (NICS)<sup>16</sup> were analyzed at the B3LYP/aug-cc-pVTZ level. The stochastic search algorithm was performed using the GXYZ 2.0 program,<sup>17</sup> the BOMD was analyzed using the CP2K package,<sup>18</sup> the AdNDP was carried out using the AdNDP program,<sup>19</sup> the cross sections of NICS (CS-NICS) were generated with the Multiwfn 3.8 code,<sup>20</sup> the CCSD(T) calculations were carried out using MolPro 2012.1 package,<sup>21</sup> and all other calculations were performed using the Gaussian 16 package.<sup>22</sup>

### Results and discussion

#### Structures designed

To stabilize the planar tetracoordinate carbon and nitrogen in CAl<sub>4</sub> and NAl<sub>4</sub><sup>+</sup> skeletons, two main tasks need to be completed. First, making the ptC/N structures meet the 18-electron rule; second, eliminating mutual repulsions of the  $3s^2$  lone electron pairs on the four Al atoms that may hinder the bonding of Al–Al, as shown in Fig. S2 (ESI<sup>†</sup>). Hence, we introduced the Zn atom and designed ptC/N species CAl<sub>4</sub>Zn and NAl<sub>4</sub>Zn<sup>+</sup>, which meet the 18-electron-rule and all the  $3s^2$  electrons of Al atoms are used for the formation of peripheral Al–Al and Al–Zn covalent bonds. Satisfactorily, the ptC/N species have no imaginary frequencies. In addition, the binding energy for CAl<sub>4</sub> + Zn to generate CAl<sub>4</sub>Zn is -30.1 kcal mol<sup>-1</sup> at the B2PLYP-D3(BJ)/aug-cc-pVTZ level, showing that the formation of CAl<sub>4</sub>Zn (from CAl<sub>4</sub> + Zn) is energetically favorable.

As shown in Fig. 1, 1a and 2a adopt the perfect planar arrangement with a central carbon/nitrogen atom. According to the criterion of Pyykkö,<sup>23</sup> the covalent radii of C, N, Al and Zn are about 0.75, 0.71, 1.26 and 1.18 Å, respectively, so the standard covalent bond lengths of C–Al, N–Al, C–Zn and N–Zn are 2.01, 1.97, 1.93 and 1.89 Å, respectively. In this text, the distances of C–Al and N–Al are 2.000  $\pm$  0.069 and 1.975  $\pm$  0.092 Å, respectively, which are in reasonable agreement with the bond lengths of the standard covalent C/N–Al single bonds. However, the distances of C–Zn (3.119 Å) and N–Zn (3.151 Å) are far beyond the standard C/N–Zn single bonds, and their Wiberg bond orders are very small, showing that there is no direct covalent interaction between C/N and Zn atoms. Therefore, **1a** and **2a** are eligible ptC/N species.

#### Stability consideration

**Thermodynamic stability.** The stability of the designed ptC/N species **1a** and **2a** may be seen as a crucial indicator in the assessment of experimental feasibility. First, their thermodynamic stabilities were investigated by extensively exploring both singlet and triple potential energy surfaces (PESs) using the stochastic search algorithm. Fig. 2 shows the five lowest energy isomers on the PESs of CAl<sub>4</sub>Zn and NAl<sub>4</sub>Zn<sup>+</sup>. According to the relative energies, **1a** and **2a** are the global energy minimum structures and their energies are 18.3 and 27.1 kcal mol<sup>-1</sup> lower than their homologous isomers with triplet spin (**1e** and **2e**), respectively, at the CCSD(T)/ aug-cc-pVTZ level considering the zero-point energy (ZPE)

Paper



Fig. 2 Structures and relative energies ( $\Delta E$ , in kcal mol<sup>-1</sup> at the CCSD(T) + ZPE<sub>B2PLYP-D3(BJ)</sub> level) of CAl<sub>4</sub>Zn (**1a**), and NAl<sub>4</sub>Zn<sup>+</sup> (**2a**) and their low-energy isomers.

corrections at the B2PLYP-D3(BJ)/aug-cc-pVTZ level (abbreviated as CCSD(T) + ZPE<sub>B2PLYP-D3(BJ)</sub>). Interestingly, the isomers (**1b** and **2d**) possessing ttC/N are located at 0.8 and 2.6 kcal mol<sup>-1</sup> on their PESs, respectively. The thermodynamic stabilities of CAl<sub>4</sub>Zn and NAl<sub>4</sub>Zn<sup>+</sup> show that the ptC/N species is significantly more stable than the ttC/N species. This proves that the introduction of the Zn atom improved the stability of the planar tetracoordinate carbon and nitrogen. In other words, the 18-valence-electron rule favours the planar tetracoordinate carbon and nitrogen in this case.

**Dynamic stability.** The dynamic stabilities of **1a** and **2a** were evaluated by performing the 100 picosecond (ps) BOMD simulations at three temperatures (4, 298 and 500 K). Fig. 3 shows the root-mean-square deviation (RMSD, in Å) plots of **1a** and **2a**, exhibiting the structural evolutions relative to the optimized structure. As shown in Fig. 3(A), **1a** has no meaningful upward jumps in the RMSD values at the three considered temperatures and has small fluctuations in the RMSD values, specifically 0.01–0.07 Å for 4 K, 0.03–0.47 Å for 298 K, and 0.02–0.77 Å for 500 K, and with the average RMSD values of 0.04, 0.15, and 0.22 Å, respectively. This illustrates that **1a** is dynamically stable at all three temperatures.

The dynamic results of the ptN species **2a** are shown in Fig. 3(B), at 4 K and 298 K. The RMSD plots for simulations have no meaningful upward jumps but two reversible upward jumps at 298 K appeared at about 32 and 39 ps, respectively. The structural samplings indicated that these two jumps correspond to a pseudo-isomerization of **2c**, which is 2.4 kcal mol<sup>-1</sup> higher in energy than **2a** (see Fig. 2). The isomerization of **2c** is not finished because the structure changed back to **2a** during the simulation at 298 K. According to the variation in the RMSD values at 500 K, **2a** and **2c** are always alternating in the simulation. Therefore, **2a** is dynamically viable.

#### Electronic structure analyses

The electronic structure analysis may provide some convincing clues about why **1a** and **2a** possess excellent stability. Fig. 4



Fig. 3 RMSD plots for the BOMD simulations (at the PBE/DVZP level) of **1a** (A) and **2a** (B) at 4, 298 and 500 K.

shows the changes in HOMO–LUMO gap values before and after introducing a Zn atom into the  $CAl_4$  and  $NAl_4^+$  skeleton at the B2PLYP-D3(BJ)/aug-cc-pVTZ level. The results indicate that the HOMO–LUMO gaps of the ptC/N arrangement increased after introducing a Zn atom, specifically  $CAl_4$  (**1** $\epsilon$ ' in Fig. S1,

Paper



Fig. 4 HOMO-LUMO gap values of the ttC/N and ptC/N species CAl<sub>4</sub>, CAl<sub>4</sub>Zn, NAl<sub>4</sub><sup>+</sup> and NAl<sub>4</sub>Zn<sup>+</sup> at the B2PLYP-D3(BJ)/aug-cc-pVTZ level.

ESI<sup>†</sup> 3.28 eV) *versus* CAl<sub>4</sub>Zn (**1a**, 4.08 eV) and NAl<sub>4</sub><sup>+</sup> (**2d**' in Fig. S1, ESI<sup>†</sup> 3.99 eV) *versus* NAl<sub>4</sub>Zn<sup>+</sup> (**2a**, 4.64 eV). In contrast, the values for the ttC/N arrangement decreased after introducing a Zn atom. It was indicated that the introduction of the Zn atom can enhance the stability of the ptC/N arrangement and weaken the stability of the ttC/N arrangement. In other words, the 18-valence-electron rule, commonly in combination with the delocalization of  $\sigma$  and  $\pi$  bonding, is more suitable for rationalizing the high stability of the ptC/N arrangement. It also explains the energetic priority of the ptC/N species as the global energy minima.

To further understand the electronic structures, the AdNDP of **1a** was analyzed and the bonding patterns are shown in Fig. 5. Here, **1a** has three five-centre two-electron (5c-2e)  $\sigma$  bonds (pictures **I-III**) with an occupation number (ON) of 1.99 |e| and one 5c-2e  $\pi$  bond (picture **IV**, ON = 1.99 |e|). The four delocalized bonds are critical to stabilizing the planar structure of **1a** because they support a stable octet electronic structure of the central carbon atom. Besides, the six  $\sigma$  and two

π delocalized electrons meet the Hückel 4*n* + 2 rule for *n* = 1 and 0, respectively, implying the double 6σ/2π aromaticity in the CAl<sub>4</sub> fragment of **1a**. The peripheral bonding environment consists of three diffuse Al–Al 2c–2e σ bonds (picture **V**, ON = 1.93 |*e*|) and two less-diffuse Al–Zn 2c–2e σ bonds (picture **VI**, ON = 1.93 |*e*|). Hence, the introduction of the Zn atom can promote the formation of peripheral Al–Al and Al–Zn covalent bonds, which are consistent with the calculated Wiberg bond orders for Al–Al and Al–Zn (see Fig. 1). This suggests that **1a** has a stable and comfortable bonding environment. The bonding in **2a** is similar to that in **1a**, so it is given in Fig. S3 (ESI<sup>†</sup>).

In addition, the molecular orbital pictures of the valence electrons were drawn for **1a** and **2a** (Fig. S4, ESI<sup>†</sup>) similar to the WAu<sub>12</sub> system reported by Pyykkö,<sup>24</sup> in which the HOMO–13, HOMO–6, HOMO–7 and HOMO–4 correspond to the pictures **I–IV** in AdNDP bonding patterns, respectively. In contrast, though **1b** and **2d** have 18 valence electrons, they do not benefit from the aromatic stabilization effect (Fig. S5, ESI<sup>†</sup>), as mirrored by the absence of the delocalized  $\sigma$  and  $\pi$  bonding and thus they are less stable in energy than **1a** and **2a** possessing the  $6\sigma/2\pi$  double aromaticity.

To verify the existence of double  $6\sigma/2\pi$  aromaticity, the nucleus-independent chemical shift (NICS) calculations of **1a** and **2a** were performed, and the results are represented by color-filled cross sections of NICS (CS-NICS). As shown in Fig. 6, the CS-NICS (0) and CS-NICS (1) respectively represent the  $\sigma$  and  $\pi$  aromaticities, which correspond to the NICS distributions in the planes located 0 and 1 Å above the molecular plane, respectively. The ring-like cyan regions around the central carbon/nitrogen atom in Fig. 6(A) and (C) show the strong aromatic electron circulation and the C/NAl<sub>4</sub><sup>0/+</sup> fragment is almost filled with colors representing negative values of NICS. This verified the existence of  $\sigma$  aromaticity in the CAl<sub>4</sub> and NAl<sub>4</sub><sup>+</sup> fragments of **1a** and **2a**, consistent with the three delocalized



Fig. 5 AdNDP bonding patterns with occupation numbers (ONs) of CAl\_4Zn (1a).



Fig. 6 NICS results for CAl<sub>4</sub>Zn (**1a**) and NAl<sub>4</sub>Zn<sup>+</sup> (**2a**). Panels A and C correspond to the molecular planes, while panels B and D correspond to the planes parallel to and located 1 Å above the molecular planes.

#### PCCP

5c–2e σ bonds in AdNDP analysis. Fig. 6(B) and (D) show CS-NICS (1) plots of **1a** and **2a**, and the regions located 1 Å above the molecular plane are filled with green, red and yellow, indicating  $\pi$  aromaticity. Hence, this indicated the existence of double  $\sigma/\pi$  aromaticity in the CAl<sub>4</sub> and NAl<sub>4</sub><sup>+</sup> fragments of **1a** and **2a**. Simultaneously, the NICS calculations of **1b** and **2d** were conducted at the B3LYP/aug-cc-pVTZ level, and it was found that these ttC/N species have almost no aromaticity from the NICS values, as shown in Fig. S6. The  $\sigma$  and  $\pi$  double aromaticity further promoted the stabilization of the planar tetracoodinate carbon/nitrogen species CAl<sub>4</sub>Zn and NAl<sub>4</sub>Zn<sup>+</sup>.

# Conclusions

In summary, we have computationally demonstrated that the 18-valence-electron rule is more appropriate in achieving the stabilization of the ptC/N species CAl<sub>4</sub>Zn and NAl<sub>4</sub>Zn<sup>+</sup>. The introduction of the zinc atom greatly enhances the stability of the CAl<sub>4</sub> or NAl<sub>4</sub><sup>+</sup> skeleton, electronically and thermodynamically. In particular, the Zn atom promotes the formation of peripheral Al–Al and Al–Zn covalent bonds, providing a stable and comfortable bonding environment for ptC/N. Besides, the  $\sigma$  and  $\pi$  double aromaticity further stabilizes the ptC/N species. Consequently, as the dynamic global energy minima display double  $6\sigma/2\pi$  aromaticity, the ptC/N species CAl<sub>4</sub>Zn and NAl<sub>4</sub>Zn<sup>+</sup> are promising in gas phase generation.

### Conflicts of interest

There are no conflicts to declare.

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