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Influence of stepwise oxidation on the structure, stability, and properties of planar pentacoordinate carbon species  $CAI_5^+$ 

The milestone planar pentacoordinate carbon (ppC) species CAl<sub>5</sub><sup>+</sup> would be as vulnerable in the air as a naked hermit crab in the sea because the exposed AI atoms lead to high oxygen affinity (OA). Nevertheless, if the oxidation can be delicately controlled to give the new ppC species  $CAI_5O_5^+$ , the exposed Al atoms would be protected by O atoms. Being a kinetically stable global energy minimum with significantly lowered OA,  $CAI_5O_5^+$  might be resistant to further oxidation, like a hermit crab protected by the sturdy seashell.



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## Introduction

It is always exciting to predict the new molecules, especially those with non-classical exotic structures. The novel planar hyper-coordinate carbon  $(phC)^1$  has been the most-studied exotic structure since 1970, when Hoffmann *et al.* sponsored a project to obtain the planar tetracoordinate carbon in equilibrium structures.<sup>2</sup> Herein, the prefix "hyper-" denotes "tetra-", "penta-", "hexa-", or "hepta-", which correspond to ptC, ppC, p6C, or p7C, respectively. The majority of the numerous phC species reported to date were previously computationally predicted to exist, but with often limited or unknown stability levels. Originally, to be called "stable", it is only necessary for a phC species to be an energy minimum. Subsequently, "stable" was defined as "thermodynamically favorable"<sup>3</sup> by the positive<sup>4</sup>

# Influence of stepwise oxidation on the structure, stability, and properties of planar pentacoordinate carbon species $CAl_5^+$ ;

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Computational design has played an important role in planar hyper-coordinate carbon (phC) chemistry. However, none of numerous computationally predicted phC species were subsequently successfully synthesized in the condensed phase, perhaps due to the frustrating issue of oxidation. In the present work, we studied the influence of stepwise oxidation on the structure, stability, and properties of phC species using the milestone planar pentacoordinate carbon (ppC) species  $CAl_5^+$  as an example. Our results indicated that the ppC structure of  $CAl_5^+$  would be directly destroyed with one, two, or six O atom(s) per molecule present and indirectly with three or four O atoms, but maintained with five O atoms due to the ppC isomer of  $CAl_5O_5^+$  being a kinetically stable global energy minimum displaying  $\sigma$  and  $\pi$  double aromaticity. Moreover, the magnitudes of the first to fifth vertical oxygen affinities (VOAs) for  $CAl_5^+$  were determined to be very high (-85.5 to -116.3 kcal mol<sup>-1</sup>), probably due to the existence of peripheral diffuse Al–Al bond(s). However, the sixth VOA was reduced significantly to -50.2 kcal mol<sup>-1</sup>, consistent with the absence of any diffuse Al–Al bond in the corresponding  $CAl_5O_5^+$  species. So  $CAl_5O_5^+$  may be insensitive to oxidation. Therefore, the ppC species  $D_{5h}$   $CAl_5O_5^+$  might be resistant to being degraded under a delicate control of oxidation level (producing five O atoms per CAl\_5^+ molecule).

and negative<sup>5</sup> results from gas-phase spectroscopic studies. Under such a criterion, the species with ppC played the crucial role in phC chemistry because carbon could fit five-membered rings nicely, due to geometric and electronic considerations. In particular, the discovery of  $D_{5h} \text{ CAl}_5^+$  was a milestone because it was the first ppC global energy minimum known to chemists<sup>6</sup> and also a good template for designing dozens of global energy minima species with ppC.<sup>7</sup>

Nevertheless, none of the predicted phC species, including those global minima, had been subsequently synthesized in the condensed phase, which suggested that these species were not "chemically stable". The inability to carry out these syntheses may have been due to the overly simplified model employed for the prediction, which did not consider or at least not effectively study some crucial influential factors, including but not limited to intermolecular interactions, the solvation effect, and oxidation. Each of them may significantly change the desired phC structures. Although it would be very difficult to comprehensively consider all of these factors using current computational resources, effectively studying the influence of one factor may be feasible.

Since  $O_2$  is ubiquitous, and since phC species may exhibit high affinity for oxygen because the atoms that exhibit high oxygen affinity, such as B, Al, and Be, are often exposed, most

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**Fig. 1** Optimized structures of  $CAl_5O_n^+$  (n = 0-6). The point groups are shown in parentheses and the necessary interatomic distances with regard to the point groups are given in Å.

phC species would be expected to be highly sensitive to oxidation. Currently, little is known about how oxidation changes a phC species, which is an important issue. Therefore, we set out to investigate such an oxidation effect using the milestone ppC species  $CAl_5^+$  (see **0** in Fig. 1) as an example.

## Computational methods

The structures of  $CAl_5O_n^+$  (n = 0-6), shown in Fig. 1, were optimized and vibrational frequencies were analyzed at the B3LYP/aug-cc-pVTZ, TPSS/aug-cc-pVTZ and MP2/aug-cc-pVTZ levels, which gave almost the same structures and frequencies. Here, the B3LYP/aug-cc-pVTZ results are discussed in the text, while the Cartesian coordinates optimized at the TPSS/aug-ccpVTZ and MP2/aug-cc-pVTZ levels are given in ESI.<sup>†</sup> Adaptive natural density partitioning (AdNDP)<sup>8</sup> analyses were performed at the B3LYP/6-31G(d) level to better understand the electronic structures of selected species. The potential energy surfaces (PESs) were analyzed using a stochastic search algorithm.<sup>9</sup> The generated random structures were initially optimized at the B3LYP/6-31G(d) level. Then, the six lowest-energy isomers for each component were re-optimized and the vibrational frequencies were analyzed at the B3LYP/aug-cc-pVTZ level. Finally, their energies were further improved at the CCSD(T)/ aug-cc-pVTZ level based on the B3LYP/aug-cc-pVTZ-optimized PCCP

structures. Their relative energies were compared at the CCSD(T)/aug-cc-pVTZ level considering the B3LYP/aug-cc-pVTZ zero-point energy corrections (CCSD(T) +  $ZPE_{B3LYP}$ ). The binding energies were also calculated at the CCSD(T) +  $ZPE_{B3LYP}$  level. The Born–Oppenheimer molecular dynamic (BOMD)<sup>10</sup> simulations were carried out at the B3LYP/6-31G(d) level. The nucleus-independent chemical shifts (NICSs)<sup>11</sup> were calculated at the B3LYP/aug-cc-pVTZ level. The stochastic search algorithm was realized using the GXYZ 2.0 program,<sup>12</sup> the AdNDP analyses were run using the AdNDP program,<sup>13</sup> the CCSD(T) calculations were carried out using the MolPro 2012.1 package,<sup>14</sup> the dissected NICS contributions were analyzed using the NBO 6.0 package,<sup>15</sup> and all other calculations were performed using the Gaussian 09 package.<sup>16</sup>

## Results and discussion

#### Structures designed and properties analyzed

First, we analyzed the electronic structures of  $\text{CAl}_5^+$  (**0**) using the AdNDP procedure. As shown in Fig. 2, of the nine pairs of valence electrons in **0**, four pairs were partitioned by this procedure to form six-center two-electron (6c-2e) bonds (three  $\sigma$  and one  $\pi$ ), with occupation numbers (ONs) of 2.00 |e| (orbitals labeled **A–D**). The corresponding eight electrons would support a stable octet shell structure around the central ppC. However, the remaining five pairs were partitioned to form 2c-2e Al–Al  $\sigma$ -bonds with ONs of 1.95 |e| (orbital labeled **E**), which may cause the high reactivity of **0** due to the diffuse nature of their orbitals with electron clouds distributed far away from the Al nuclei.

Consequently, we selected the Al–Al edges of **0** as the main binding sites of oxygen and constructed the species having one to six oxygen atom(s) as the demonstration. As shown in Fig. 1, introducing an oxygen atom significantly elongated, from 2.105 Å in **0** to 2.453 Å in **1a**, the C–Al bond on the side of the molecule opposite the introduced oxygen, resulting in CAl<sub>5</sub>O<sup>+</sup> (**1a**), a ptC rather than ppC species. Introducing a second O atom would yield two possible structures for CAl<sub>5</sub>O<sub>2</sub><sup>+</sup>: one with the two



Fig. 2 AdNDP view of chemical bonding in  $D_{5h}$  CAl<sub>5</sub><sup>+</sup>.

O atoms on adjacent Al-Al edges (2a) and the other with the two O atoms on separated Al-Al edges (2a'). We evaluated their relative energies at the  $CCSD(T) + ZPE_{B3LYP}$  level; 2a was determined to be 15.1 kcal mol<sup>-1</sup> lower in energy than 2a', so only 2a is discussed in the following. Note the presence of a quite long C-Al distance (2.494 Å) in 2a, so 2a was considered to be a ptC species as well. When three O atoms are anchored on Al-Al edges, two isomers would result: one with all three O atoms on three adjacent Al-Al edges (3a), and the other with one O atom separated from the other two (3a'). Likewise, 3a was computed to be 8.3 kcal mol<sup>-1</sup> lower in energy than 3a' at the CCSD(T) + ZPE<sub>B3LYP</sub> level. The introduction of the third O atom significantly shortened the long C-Al distance (from 2.494 Å in 2a to 2.221 Å in 3a), so 3a was considered to be a ppC species. The introduction of a fourth O atom led to a further shortening of the C-Al distance (from 2.221 Å in 3a to 2.063 Å in 4a). For 4a, a non-planar  $C_2$  symmetry was indicated, but with just a slight deviation from planarity (see the bottom view in Fig. 1), and the carbon atom in 4a can be regarded as a quasi-ppC. With all five Al–Al edges anchored by O atoms, 5a had a planar  $D_{5h}$  structure with five equivalent C-Al distances of 2.068 Å, making 5a a ppC species. With no empty Al-Al edge in 5a, an added sixth O atom would have to be located above a C-Al-Al triangle (see 6a), leading to the destruction of the ppC arrangement—with carbon forming an out-of-plane C–O contact ( $r_{C-O}$  =1.561 Å) and simultaneously losing two in-plane C–Al contacts ( $r_{C-Al} = 2.354$  Å). The above results indicated that introducing one, two, and six O atom(s) would disrupt the ppC arrangement of their CAl<sub>5</sub> cores.

As shown in Fig. 3A, compared to **0** with its HOMO–LUMO gap (Gap) of 2.82 eV, introducing one O atom was determined



Fig. 3 HOMO-LUMO gaps (A) and vertical oxygen-affinities (B) with the stepwise introduction of O atoms.

to result in an obviously narrowed gap of 1.86 eV in **1a**. Nevertheless, introducing the second to fifth O atoms gradually increased the gaps (2.63, 2.71, 3.58, and 3.83 eV for **2a–5a**, respectively). With a large gap of 3.83 eV, it would be difficult for the electrons in **5a** to be excited. Note that a further introduction of an O atom was determined to lead to a decrease in the gap to 3.51 eV in **6a**.

The vertical oxygen-affinities (VOAs) with stepwise introduction of O atoms were calculated by using eqn (1).

$$\operatorname{CAl}_{5}\operatorname{O}_{n-1}^{+} + 0.5\operatorname{O}_{2} \to \operatorname{CAl}_{5}\operatorname{O}_{n}^{+} + \operatorname{VOA}$$
(1)

In eqn (1), n = 1-6 and  $O_2$  was computed in the triplet state. As shown in Fig. 3B, the VOA with one O atom introduced (the "first" VOA) was calculated to be -85.5 kcal mol<sup>-1</sup>, at the  $CCSD(T) + ZPE_{B3LYP}$  level, obviously lower in magnitude than those of the second to fifth VOAs (being -111.7, -103.6,-113.2, -116.3 kcal mol<sup>-1</sup>, respectively). This result may have been caused by a breaking of the integrity of peripheral Al-Al bonding in 0 upon the introduction of first O atom. Correspondingly, upon the formation of integrate peripheral O-Al bonding framework, a peak VOA value of -116.3 kcal mol<sup>-1</sup> was observed. Without any empty Al-Al edge in 5a, further introduction of an O atom would break its integrate O-Al bonding framework, and the sixth VOA was calculated to be only -50.2 kcal mol<sup>-1</sup>, much lower than those of the first to fifth VOAs, *i.e.* the oxidation of 5a was not as easy as those of 0 and 1a-4a.

#### Stability consideration

The thermodynamic stability of 1a-6a was investigated by extensively exploring their PESs using the stochastic search algorithm. As shown in Fig. 4, the carbon atoms in the lowenergy isomers were generally in the classical sp,  $sp^2$ , or  $sp^3$ hybridization. According to the comparison of their relative energies at the final  $CCSD(T) + ZPE_{B3LYP}$  level, 1a-4a are all high-energy local minima, which are 31.1, 30.2, 17.9, and 13.1 kcal mol<sup>-1</sup>, respectively, higher in energy than corresponding located lowest-energy isomers (1b-4b). As expected, 5a, a species with the integrate peripheral O-Al bonding framework, was calculated to be a global energy minimum. Though the energy of 5a was calculated to be only 0.5 kcal  $mol^{-1}$  lower than that of the next-lowest-energy isomer (5b), such a result was deemed to be significant because the ppC structure was energetically competitive again, *i.e.*, even after the introduction of O atoms. In contrast, 6a, with an obviously out-of-plane O atom, was found to be a local minimum, and 45.2 kcal  $mol^{-1}$ higher in energy than the lowest-energy isomer (6b). The PES investigations indicated that the ppC arrangement of the CAl<sub>5</sub> core moiety would be disrupted indirectly in the presence of three or four O atoms due to the strong thermodynamic driving force. Nonetheless, the ppC arrangement of **0** survived in the presence of five O atoms in that the ppC isomer 5a was the global energy minimum. The above results suggested that the ppC structure may be achievable for the CAl<sub>5</sub><sup>+</sup> system under a delicately controlled oxidation level (five O atoms per CAl<sub>5</sub><sup>+</sup> molecule).



Fig. 4 Structures and relative energies ( $\Delta E$ , in kcal mol<sup>-1</sup> at the CCSD(T) + ZPE<sub>B3LYP</sub> level) of **1a–6a** and their low-energy isomers.

Since it is possible for a global energy minimum to be kinetically unstable,<sup>17</sup> the kinetic stability of the global minimum **5a** was explored by carrying out 100-picosecond Born-Oppenheimer molecular dynamics (BOMD)<sup>12</sup> simulations at 4, 298, 500, and 1000 K, respectively. The structural evolution was described by the root-mean-square deviation (RMSD, in Å) relative to the B3LYP/6-31G(d)-optimized structure. As shown in Fig. 5, these simulations showed no irreversible upward jump in the RMSD values at the four selected temperatures and showed very small fluctuations of RMSD values, specifically 0.05–0.31 Å for 4 K, 0.06–0.38 Å for 298 K, 0.06–0.37 Å for 500 K, and 0.08–0.39 Å for 1000 K, and with average RMSD values of 0.17, 0.19, 0.23, and 0.22 Å, respectively. The BOMD results

revealed the good kinetic stability and structural rigidity of **5a** against isomerization and dissociation.

#### Electronic structure analysis

The excellent stability of 5a can be explained with the aid of an AdNDP analysis. As shown in Fig. 6, the analysis showed 5a possessing four delocalized 6c-2e bonds (orbitals labeled F-I), including three  $\sigma$  bonds (ON = 1.98–1.99 |e|) and a  $\pi$  bond (ON = 1.94 |e|), similar to 0 in that these four orbitals also supported a stable octet electronic structure around the ppC. However, 5a was significantly different from 0 with regards to their peripheral bonding environments, with the diffuse Al-Al 2c-2e  $\sigma$  bonds in **0** replaced by considerably less-diffuse orbitals in 5a (pictures J-L), including a 1c-2e O lone pair (ON = 1.95 |e|), two O–Al 2c-2e  $\sigma$  bonds (ON = 1.96 |e|), and a 3c-2e Al–O–Al  $\pi$ bond (ON = 2.00 |e|). Surrounded geometrically by the saturated O atoms and electronically by the less-diffuse orbitals, 5a would be expected to be chemically more stable than its parent species **0**. Nevertheless, the 3c-2e Al–O–Al  $\pi$  bonds represent indirect Al-Al interactions, and if five such bonds are counted, the CAl<sub>5</sub> moiety in 5a would still meet the 18 valence electron rule, similar to 0. Note, interestingly, that the obvious Al  $\rightarrow$  O  $\sigma$ -donation and  $O \rightarrow Al \pi$ -backdonation features of the 2c-2e O–Al  $\sigma$  bonds and 3c-2e Al–O–Al  $\pi$  bonds, respectively, features were somewhat similar to the C  $\,\rightarrow\,$  O  $\,\sigma\text{-donation}\,$  and O  $\,\rightarrow\,$  C  $\pi\text{-backdonation}\,$ found in carbon-monoxide (CO) and were expected to contribute to the stabilization of 5a.

Three delocalized  $\sigma$  orbitals and a delocalized  $\pi$  orbital were noticed to correspond to six  $\sigma$  and two  $\pi$  delocalized electrons, meeting Hückel's 4n + 2 rule for n = 1 and 0, respectively, and hence suggesting the existence of  $\sigma$  and  $\pi$  double aromaticity. Note, in addition, a delocalized  $3c-2e \pi$  bond (two electrons) on each Al–O–Al triangle, meeting the 4n + 2 rule for n = 0. To verify the presence of aromaticity, the NICSs were calculated for the ghost atoms located at concerned points. As shown in Fig. 7A, obviously negative NICS values were calculated for the points within the molecular frame or near the molecule, suggesting an aromatic molecule, consistent with the deduction from the AdNDP analyses. The NICS values were calculated to gradually



Fig. 5 RMSD (in Å) *versus* simulation time (in ps) for the BOMD simulations of **5a** at the B3LYP/6-31G(d) level.



Fig. 6 AdNDP view of chemical bonding in CAl<sub>5</sub>O<sub>5</sub><sup>+</sup> (5a).



**Fig. 7** The NICS results for **5a**. The points with negative and positive NICS values (in ppm) are shown as red and green balls, respectively, without crossed solid lines (A) and the dissected contributions from individual canonical molecular orbitals for the point located 1 Å above the molecular center (B).

approach zero for points increasingly farther away from the molecule.

Here, we further focused on the aromaticity of the CAl<sub>5</sub> core moiety and chose the point located at 1 Å above the carbon atom as the representative. A total NICS value of -19.4 ppm was calculated at this point, which was significantly less negative than the value of -37.9 ppm for the similar point for the CAl<sub>5</sub><sup>+</sup> molecule. The dissected contributions from the individual orbitals to the NICS values were then studied. As shown in Fig. 7B, the contribution from the HOMO, mostly the delocalized 6c-2e  $\pi$  bond over the CAl<sub>5</sub> core moiety, was calculated to be -5.8 ppm, and those from HOMO-11 and degenerate HOMO-10 (three delocalized 6c-2e  $\sigma$  bonds) were -3.7 and -4.0 ppm, respectively. The sum of the contributions from these four orbital, i.e., -17.5 ppm, comprised 90.2% of total NICS value (-19.4 ppm) and verified the  $\sigma$  and  $\pi$  double aromaticity suggested by the AdNDP analysis. Note the obviously higher total contribution from the three delocalized  $\sigma$  orbitals (-11.7 ppm) than from one delocalized  $\pi$  orbital (-5.8 ppm), similar to the situation found in  $CAl_5^+$ . The aromaticity would be expected to contribute positively to the good thermodynamic and kinetic stability levels of 5a.

### Conclusions

In summary, we have shown that the presence of oxygen atoms can significantly influence the structure, properties, and stability of the milestone ppC species  $D_{5h} \text{ CAl}_5^+$  (**0**). In particular, the ppC structure was indicated to be stable under a properly controlled oxidation level. That is, our analyses indicated that the ppC arrangement of **0** would be directly destroyed with one, two, or six O atom(s) per molecule present and indirectly in the presence of three or four O atoms, but maintained with five O atoms due to  $D_{5h} \text{ CAl}_5O_5^+$  (**5a**) being a

kinetically stable global energy minimum with significantly reduced vertical oxygen-affinity. The good stability of **5a** can be rationalized as follows: the diffuse Al–Al 2c-2e bonds were replaced by the peripheral integrate less-diffuse O–Al bonding framework. Our study found it possible to effectively study the important factors that may influence the stability of phC species. Therefore, the systematic investigation of various influential factors may be a feasible way to computationally achieve the candidates of chemically stable phC species for future syntheses in the condensed phase.

## Conflicts of interest

There are no conflicts to declare.

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