Letter

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Identifying the Hydrogenated Planar Tetracoordinate Carbon: a Combined Experimental and Theoretical Study of CAl_4H and CAl_4H^-

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ABSTRACT The chemical curiosity “planar tetracoordinate carbon” (ptC) has greatly broadened one’s knowledge of molecular bonding motifs apart from the traditional, tetrahedral, van’t Hoff and LeBel’s concept. Synthesized ptC examples have been reported either in solid state or in the gas phase, where the ptC core is usually metalized or organometallized. Surprisingly, there has been no experimental report on hydrogenated ptC to date. A possible answer to this situation could be the “promiscuity” of hydrogen when binding to other elements, which frustrates the formation of stable ptC that is in competition with other structures. In this paper, we for the first time identified two hydrogenated ptC species, CAI_4H and CAI_4H^- , based on a photoelectron spectroscopic and quantum chemical study. The favorable site-selectivity of hydrogen was shown to be the bridge of Al-Al bond rather than the terminus of Al, manifesting the thermodynamic preference of 17e/18e counting rule over the 15e/16e rule.

TOC GRAPHICS

Planar tetracoordinate carbon (ptC) has witnessed tremendous advancement in the past fifty years.^{1,2} First proposed by H. J. Monkhorst in 1968,³ the designed planar methane was nevertheless an unstable transition state. Subsequently, Hoffmann *et al.* proposed two strategies to stabilize ptC,⁴ which have been a general guide to design ptC species. One is the mechanical strategy, which often makes use of transition metals, conjugative rings or cages to forcibly form ptC. The other is the electronic strategy, which introduces strong σ -donor and π -acceptor ligands or aromatic delocalization to stabilize the *p*-type lone pair on the ptC center. Based on the above two strategies, Schleyer and coworkers theoretically designed the first group of ptC molecules (even though not global minimum) in 1976.⁵ Since then, the ptC chemistry has been widely developed theoretically,^{1,2} and has been extended to planar high-coordinate carbon⁶⁻⁸ or planar tetra-/high-coordinate X (X could be other main group elements)⁹⁻¹¹ as well as the nano-sized systems for potential applications in materials science.¹²⁻¹⁴

In parallel, there have been some experimental investigations on ptC.¹⁵ A class of organometallic ptC have been synthesized in solid state,¹⁶ but such compounds are usually structurally complicated and involve metals or transitional metals as ligands to kinetically stabilize the ptC unit. By contrast, in 1999, a simple penta-atomic ptC cluster CAI_4^- was detected in the gas phase.¹⁷ One year later, several new ptC species, i.e., CAI_3Si^- , CAI_3Ge^- , CAI_4^{2-} and NaCAI_4^- , were characterized.¹⁸⁻²⁰ To understand the bonding and stability of these species, an effective valence electron-counting rule, namely the “18ve-rule”,²¹ has been devised and found applicable in many systems.²² Note that this rule differs sharply from the one mainly associated with compounds composed of transition metal atoms such as $\text{Cr}(\text{C}_6\text{H}_6)_2$ and $\text{Fe}(\text{C}_5\text{H}_5)_2$ where 18 valence electrons are needed to close the s, p, and d shells.²³⁻²⁵ Besides, there is an increasing consensus that a ptC structure should better have the lowest energy (or be the global minimum)

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3 to allow its experimental observation under annealing conditions.²⁶ Moreover, the simplicity of
4 these penta-atomic species has allowed them to act as building blocks for more complicated
5 complexes.^{27–29}
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10 Clearly, in all the known ptC compounds (except the simplest penta-atomic ptCs), the ptC
11 cores are stabilized by metallic or organometallic ligands. No hydrogenated ptCs have been
12 reported in experiments. By occupying the terminal, bridge or face-sites to adjust the skeletal
13 electrons, fascinating hydrogenated topologies can be achieved in compounds such as boranes,
14 alanes and carboranes.³⁰ A plausible explanation for the absence of hydrogenated ptCs could be
15 the structural fragility of ptC, whose stability highly relies on the subtle balance between the
16 electronic and steric factors. Presumably, being promiscuous in bonding possibilities,
17 hydrogenation would cause undesired competition from other nonplanar structures. In this sense,
18 identifying a global minimal hydrogenated ptC should represent a big challenge for both
19 experiment and theory.
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34 In this paper, based on the anion photoelectron spectroscopy (PES), global structural search
35 and high-level *ab initio* calculations (see SI for details), we successfully identified two
36 hydrogenated species, $\text{CAI}_4\text{H}^{-/0}$, both featuring the global minimal ptC. Due to the hydrogen
37 atom's site-selectivity, the observed isomer that fulfills the 17e/18e rule is energetically more
38 favorable than the one with 15e/16e, this being the first time to experimentally prove the
39 preference of 17e/18e ptC over 15e/16e ptC. The present work not only expands the diversity of
40 ptC, but more importantly, opens a new avenue for the hydrogenated ptC chemistry using the
41 tested electronic counting rules.
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53 Experimental details are presented in the SI. Figure 1 presents a typical mass spectrum
54 containing hundreds of carbon aluminum hydride cluster anions, $\text{C}_x\text{Al}_y\text{H}_z^-$ ($x=0-2$, $y=1-9$, $z=1-4$),
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and different ion groups are marked by the number of carbon atoms as **0**, **1**, or **2**. Here we highlight only the group with the highest intensity, circled and expanded in Figure 1; they are the CAI_4H_n^- ($n = 0-3$) clusters. Those small peaks to the left of CAI_4^- are corresponding to the $\text{C}_3\text{Al}_3\text{H}_n^-$ series. By minimizing the carbon powder ratio in the carbon aluminum mixture, we managed to lower the $\text{C}_3\text{Al}_3\text{H}_n^-$ signal as much as possible in order to make sure $\text{C}_3\text{Al}_3\text{H}_n^-$ did not contaminate the photoelectron spectra of CAI_4H_n^- . In the CAI_4H_n^- ($n = 0-3$) series, CAI_4H^- possesses overwhelmingly higher intensity. It is not only the strongest peak in the neighborhood, but also the strongest peak in the entire mass spectrum that contains hundreds of clusters, indicating highly unusual stability of the CAI_4H_1^- cluster. This observation is reasonable in the sense that CAI_4H^- is closed shell and $\text{CAI}_4\text{H}_{0,2}^-$ are open shell. However, this conventional wisdom does not apply to CAI_4H_3^- , which is also closed shell, suggesting that there must be more stabilizing effect contributing to the high intensity of CAI_4H^- (*vide infra*).

Figure 1. Mass spectrum of the $\text{C}_x\text{Al}_y\text{H}_z^-$ ($x=0-2$, $y=1-9$, $z=1-4$) clusters.

When a cluster has reproducible intense mass spectral peak relative to its neighbors, it is a magic number species. To further investigate this magic cluster CAI_4H^- , we present its

photoelectron spectrum in Figure 2, where an electron binding energy (EBE) band starts from 2.6 eV and peaks at 2.88 eV. The experimental electron affinity of neutral CAI_4H can be determined to be ~ 2.6 eV from the threshold of the spectrum when there is enough Frank-Condon overlap between the anion and the neutral counterpart and when there is not too much hot band present. The experimental vertical detachment energies (VDE) of CAI_4H^- is determined to be the peak position, 2.88 eV, which is the middle one of the three vibrational progressions. This high detachment energy needed for CAI_4H^- again confirms its high stability, consistent with its high mass spectral intensity. The splitting of this EBE band, 0.09 eV, is close to the calculated 725.6 cm^{-1} vibrational mode of the neutral CAI_4H cluster (**CAI₄H-01** at B3LYP/aug-cc-pVTZ level), which is associated with the in-plane swing of the central carbon and ligand hydrogen perpendicular to the Al-Al bond. This is reasonable because the photoelectron is detached from a molecular orbital that is delocalized within the whole cluster, which causes the bond displacement of the entire skeleton.

Figure 2. Photoelectron spectrum of the CAI_4H^- cluster.

The global, unbiased, isomeric search utilizing the “grid” program (see SI for detail) obtained 32 local minima for CAI_4H^- and 41 local minima for CAI_4H at the level of CBS-QB3. In order to improve the accuracy, high level B3LYP/aug-cc-pVTZ (for geometry and vibrational frequencies) and CCSD(T)/aug-cc-pVTZ (for single-point energy) calculations are performed for all the low-lying isomers ($\Delta E < 10$ kcal/mol at CBS-QB3 level). Most of isomers of $\text{CAI}_4\text{H}^{-/0}$ have very high energies, for simplicity, we only show several low-lying isomers in Figure 3. Structures, Cartesian coordinates and total energies of high energy isomers can be found in the SI. As seen in Figure 3, **CAI₄H-01** and **CAI₄H⁻-01** featuring a ptC core are the ground state structures in each system. Unlike CAI_4 and CAI_4^- that have the tetrahedral and planar skeletons, respectively, **CAI₄H-01** and **CAI₄H⁻-01** possess very similar skeleton with C_{2v} symmetry, the major difference is that one ligand-ligand bond (Al-Al bond) is broken in the neutral system by removing one electron. The two structures can be viewed as one H-bridge is added to the skeleton of CAI_4^- , forming an H-bridged ptC. Similar H-bridged structures have been found in many boranes and alanes.³⁰ All the remaining isomers with higher energy in each system have terminal-H, among which **CAI₄H-03**, **CAI₄H-04** and **CAI₄H⁻-02** also possess ptC structures.

Figure 3. Structures and the relative energies (in kcal/mol) of the ground state and low-lying ptC structures at the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ levels of theory. The values in square brackets are at the level of CBS-QB3, and the values in parenthesis are at B3LYP/aug-cc-pVTZ level. All the energies are corrected by zero-point energy. The energies at CCSD(T)/aug-cc-pVTZ level were corrected using the zero-point energies obtained at B3LYP/aug-cc-pVTZ.

Figure 4. The key structural parameters, Wiberg Bond Indices (WBI) of C-Al bonds, experimental and calculated vertical detachment energies, adiabatic electron affinity of neutral CAI_4H and anion CAI_4H^- ground state structures. e is short for experiment and c is short for calculation.

The four C-Al bond lengths and the corresponding Wiberg Bond Indices (WBI)³¹ of two ground state structures are shown in Figure 4. The C-Al bond lengths range from 1.966 Å to 2.017 Å, and each $\text{WBI}_{\text{C-Al}}$ is around 0.5. These values indicate the bonds between the central C-atom and the ligand Al-atoms are single bonds. The ptC feature also can be demonstrated from the molecular orbitals. In Figure 5, the molecular orbitals (MO) HOMO-3 (for CAI_4H) and HOMO-4 (for CAI_4H^-) are delocalized π -orbitals, which are crucial to achieving the planar geometry and are aromatic. Meanwhile, HOMO-4 (for CAI_4H) and HOMO-3 (for CAI_4H^-) are

delocalized ligand-ligand σ bonding. Addition of one electron reverses the order of delocalized π and σ orbitals. One can observe that the hydrogen is actively hybridized in several MOs (ligand-ligand and center-ligand), making the electron of hydrogen part of the skeleton. Interestingly, with reference to the $18e\text{-CAI}_4^{2-}$, the hydrogen in CAI_4H^- strengthens the neighboring Al-Al bonds, whereas Na weakens them in NaCAI_4^- (Figure S1).

Figure 5. Molecular orbitals of neutral CAI_4H and anion CAI_4H^- ground state structures at the level of B3LYP/aug-cc-pVTZ.

In order to compare with the experiment, the vertical detachment energies (VDE) and the adiabatic electron affinity (EA) were calculated at the level of CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ (see Figure 4). The VDE represents the difference in energy between CAI_4H^- in its ground state and neutral CAI_4H having the anion geometry. EA is the energy difference between the ground states of the neutral and the anionic clusters. Due to the same structure between the neutral ground state and the neutral equilibrium structure with

anionic geometry, the EA and adiabatic detachment energy ADE have the same values. For the two low-lying isomers of CAI_4H^- , the calculated VDE is 2.75 eV for CAI_4H^- -01 and 2.78 eV for CAI_4H^- -02; both agree well with the experimental 2.88 eV. The calculated EA and ADE are 2.63 eV for CAI_4H^- -01 and 2.60 eV for CAI_4H^- -02, which are also very close to the experimental value 2.60 eV. However, **CAI_4H^- -02**, a terminal-H ptC, has a slightly higher energy (around 2 kcal/mol at three different levels) than **CAI_4H^- -01** with a H-bridged ptC. We further studied the interconversion between the terminal-H and H-bridged ptC structures. In Figure S2, at the B3LYP/6-311G(2d,d,p) level without zero-point energy correction, the barrier is negligibly small as 0.01 kcal/mol for neutral system and 0.03 kcal/mol for anion system. At the sophisticated CBS-QB3 level including zero-point energy correction, the barrier values become slightly negative, which is a reasonable result of computing the higher-level energy at a lower-level geometry. If the Gibbs free energy is concerned, the conversion barriers from the terminal-H ptC to H-bridged ptC structures are 0.67 and 1.33 kcal/mol at 298.15 K and 450 K (experimental temperature), respectively. Therefore, the terminal-H structure is very easy to transfer to the H-bridged structure, and coexistence of **CAI_4H^- -02** is unlikely in the experiment. The good agreement between theory and experiment indicates that the ground ptC H-bridged ptC states of $\text{CAI}_4\text{H}^{-/0}$ were detected.

Based on the above discussion, the most stable **CAI_4H -01** and **CAI_4H^- -01** are demonstrated as ptC with a bridging-H. The hydrogen atom effectively donates its electron to the skeleton by hybridization in several molecular orbitals, which is supported by the MOs in Figure 5. Thus, for anionic **CAI_4H^- -01** with a bridging-H motif, the skeleton has $4+3\times 4=16$ electrons available from the carbon and aluminum atoms, *plus* 1 electron from the bridged hydrogen atom *and* 1 electron from negative charge, summing to a total of 18 electrons. Similarly, the neutral **CAI_4H -01** has 17

electrons. In the terminal-H motif on the other hand, the Al-H bond consumes two electrons to form a localized σ bond (the occupation number is 1.96 according to NBO calculations), which cannot contribute to the delocalization of the skeleton. Thus, these higher energy anionic isomers with a terminal-H only have 16 electrons available. Accordingly, the higher energy neutral isomers with a terminal-H have 15 electrons, and the molecular orbitals are shown in Figure S3. This directly demonstrates that the bridging-H isomers with 17/18e are more stable than the terminal-H isomers with 15/16e. While previously studied 17/18e species mainly comprise the metalized or organometallized ptC cores, the presently identified hydrogenated ptCs have expanded our knowledge on ptC.

In summary, the hydrogenated planar tetracoordinate carbon species CAI_4H and CAI_4H^- have been identified theoretically and experimentally for the first time. They both contain the ptC core with a bridging-H as the global minima. The hydrogen atom, even though known to be able to bind to diverse sites, selectively bind to the bridging site in lieu of the terminal sites, demonstrating that the 17e/18e ptCs with bridging-H are more stable than 15e/16e ptCs with terminal-H, making it a good example of the success of the electron counting rules. Experiment and theory have demonstrated and interpreted the unusual stability of CAI_4H^- , which can be understood by its electronic structures and molecular orbitals.

ASSOCIATED CONTENT

Supporting Information. Detailed description of the experimental and theoretical methods; structures, total energies and the Cartesian coordinates of all the isomers; the barrier between the bridging-H ptC and the terminal-H ptC; molecular orbitals of the terminal-H ptC.

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Notes

The authors declare no competing financial interests.

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Figure 1

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Figure 2

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Figure 3

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Figure 4

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Figure 5
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