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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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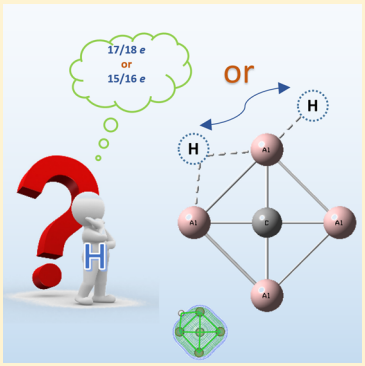
Supporting Information

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 the 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 Letter, we for the first time identified two hydrogenated ptC species, CAl_4H and CAl_4H^-, based on a photoelectron spectroscopic and quantum chemical study. The favorable site-selectivity of hydrogen was shown to be the bridge of the Al−Al bond rather than the terminus of Al, manifesting the thermodynamic preference of the 17e/18e counting rule over the 15e/16e rule.



Planar tetracoordinate carbon (ptC) has witnessed tremendous advancement in the past 50 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. On the basis of the above two strategies, Schleyer and co-workers theoretically designed the first group of ptC molecules (even though not global minima) in 1976.[5] Since then, ptC chemistry has been widely developed theoretically[1,2] and has been extended to planar high-coordinate carbon[6−8] or planar tetra-/high-coordinate X (X could be other main group elements)[9−11] as well as the nanosized 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 has been synthesized in the solid state,[16] but such compounds are usually structurally complicated and involve metals or transition metals as ligands to kinetically stabilize the ptC unit. By contrast, in 1999, a simple penta-atomic ptC cluster CAl_4^- was detected in the gas phase.[17] One year later, several new ptC species, that is, CAl_3Si^-, CAl_3Ge^-, CAl_4^{2-}, and $NaCAl_4^-$, 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 $Cr(C_6H_6)_2$ and $Fe(C_5H_5)_2$ 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 have the lowest energy (or be the global minimum) to allow its experimental observation under annealing conditions.[26] Moreover, the simplicity of these penta-atomic species has allowed them to act as building blocks for more complicated complexes.[27−29]

Clearly, in all of the known ptC compounds (except the simplest penta-atomic ptCs), the ptC cores are stabilized by metallic or organometallic ligands. No hydrogenated ptCs have been reported in experiments. By occupying the terminal, bridge or face sites to adjust the skeletal electrons, fascinating hydrogenated topologies can be achieved in compounds such as boranes, alanes, and carboranes.[30] A plausible explanation for the absence of hydrogenated ptCs could be the structural fragility of ptC, whose stability highly relies on the subtle balance between the electronic and steric factors. Presumably, being promiscuous in bonding possibilities, hydrogenation

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would cause undesired competition from other nonplanar structures. In this sense, identifying a global minimum hydrogenated ptC should represent a big challenge for both experiment and theory.

In this Letter, on the basis of anion photoelectron spectroscopy (PES), global structural search, and high-level ab initio calculations (see the SI for details), we successfully identified two hydrogenated species, $CAl_4H^{-/0}$, both featuring the global minimum ptC. Due to the hydrogen atom's site-selectivity, the observed isomer that fulfills the 17e/18e rule is energetically more favorable than the one with 15e/16e, this being the first time to experimentally prove the preference of 17e/18e ptC over 15e/16e ptC. The present work not only expands the diversity of ptC but more importantly opens a new avenue for hydrogenated ptC chemistry using the tested electronic counting rules.

Experimental details are presented in the SI. Figure 1 presents a typical mass spectrum containing hundreds of

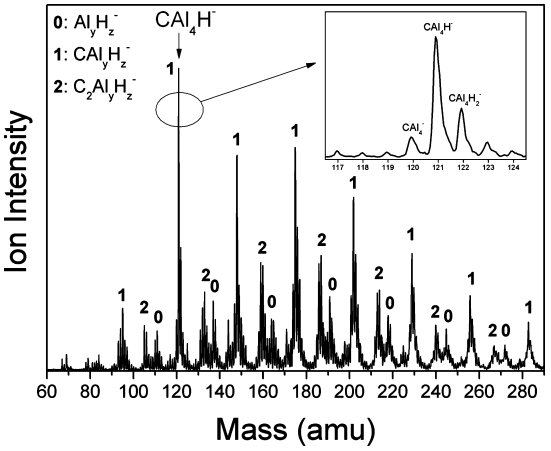

Figure 1. Mass spectrum of the $C_xAl_yH_z^-$ (x = 0−2, y = 1−9, z = 1−4) clusters.

carbon aluminum hydride cluster anions, $C_xAl_yH_z^-$ (x = 0−2, y = 1−9, z = 1−4), 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; it is the $CAl_4H_n^-$ (n = 0−3) clusters. Those small peaks to the left of CAl_4^- correspond to the $C_3Al_3H_n^-$ series. By minimizing the carbon powder ratio in the carbon aluminum mixture, we managed to lower the $C_3Al_3H_n^-$ signal as much as possible in order to make sure that $C_3Al_3H_n^-$ did not contaminate the photoelectron spectra of $CAl_4H_n^-$. In the $CAl_4H_n^-$ (n = 0−3) series, CAl_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 $CAl_4H_1^-$ cluster. This observation is reasonable in the sense that CAl_4H^- is closed-shell and $CAl_4H_{0,2}^-$ are open-shell. However, this conventional wisdom does not apply to $CAl_4H_3^-$, which is also closed-shell, suggesting that there must be more stabilizing effect contributing to the high intensity of CAl_4H^- (vide infra).

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

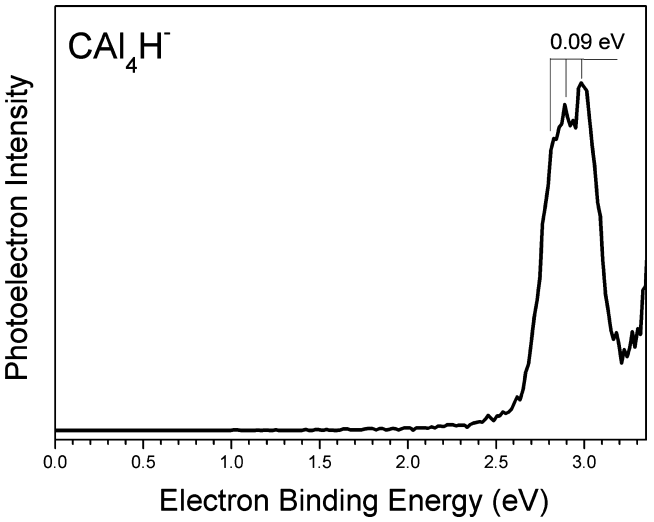

Figure 2. Photoelectron spectrum of the CAl_4H^- cluster.

The experimental electron affinity (EA) of neutral CAl_4H can be determined to be ∼2.6 eV from the threshold of the spectrum when there is enough Franck−Condon overlap between the anion and the neutral counterpart and when there is not too much hot band present. The experimental vertical detachment energy (VDE) of CAl_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 CAl_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 CAl_4H cluster (**CAl_4H-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 (MO) that is delocalized within the whole cluster, which causes the bond displacement of the entire skeleton.

The global, unbiased, isomeric search utilizing the "grid" program (see the SI for detail) obtained 32 local minima for CAl_4H^- and 41 local minima for CAl_4H at the level of CBS-QB3. 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 were performed for all of the low-lying isomers (ΔE < 10 kcal/mol at the CBS-QB3 level). Most of the isomers of $CAl_4H^{-/0}$ 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, **CAl_4H-01** and **CAl_4H^--01** featuring a ptC core are the ground-state structures in each system. Unlike CAl_4 and CAl_4^- that have tetrahedral and planar skeletons, respectively, **CAl_4H-01** and **CAl_4H^--01** possess very similar skeletons 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 CAl_4^-, forming a H-bridged ptC. Similar H-bridged structures have been found in many boranes and alanes.[30] All of the remaining isomers with higher energy in each system have terminal H, among which **CAl_4H-03**, **CAl_4H-04**, and **CAl_4H^--02** also possess ptC structures.

The four C−Al bond lengths and the corresponding Wiberg bond indices (WBIs)[31] of two ground-state structures are

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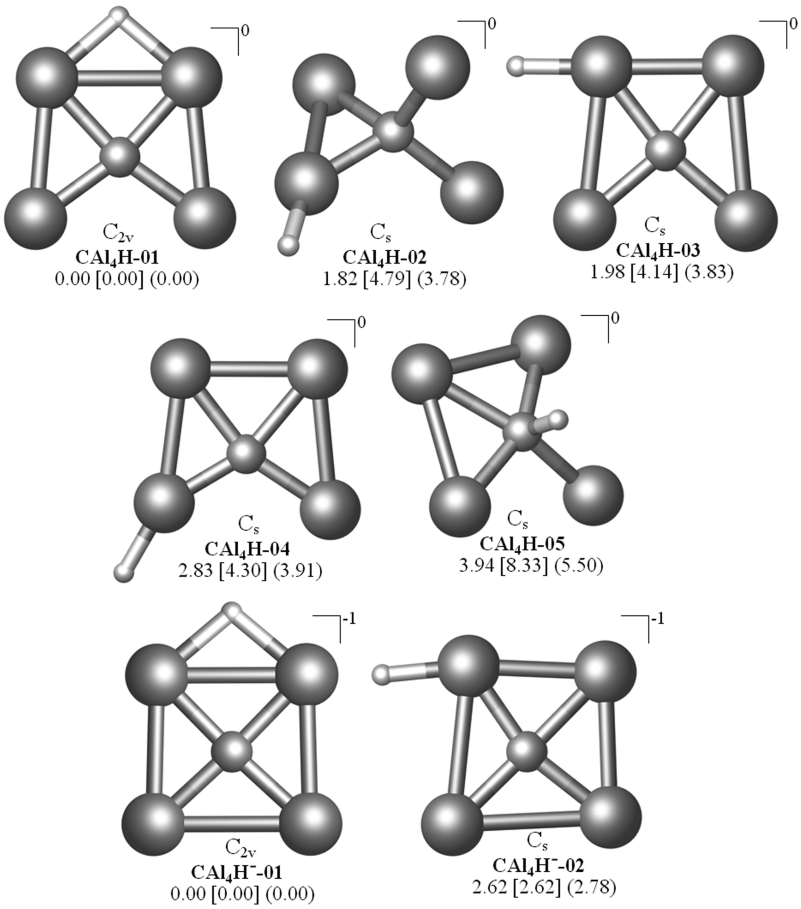

Figure 3. Structures and relative energies (in kcal/mol) of the ground-state and low-lying ptC structures at the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ levels of theory. The values in square brackets are at the level of CBS-QB3, and the values in parentheses are at the B3LYP/aug-cc-pVTZ level. All of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

shown in Figure 4. The C−Al bond lengths range from 1.966 to 2.017 Å, and each WBI_{C-Al} is around 0.5. These values indicate

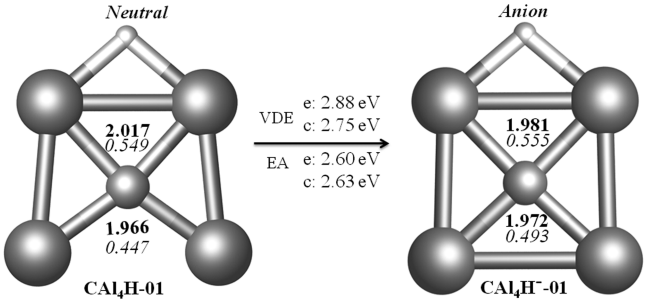

Figure 4. Key structural parameters, WBIs of C−Al bonds, experimental and calculated VDEs, and adiabatic EA of neutral CAl_4H and anion CAl_4H^- ground-state structures. e is short for experiment, and c is short for calculation.

that the bonds between the central C atom and the ligand Al atoms are single bonds. The ptC feature also can be demonstrated from the MOs. In Figure 5, the MOs HOMO−3 (for CAl_4H) and HOMO−4 (for CAl_4H^-) are delocalized π orbitals, which are crucial for achieving the planar geometry and are aromatic. Meanwhile, HOMO−4 (for CAl_4H) and HOMO−3 (for CAl_4H^-) are delocalized ligand−ligand σ-bonding. Addition of one electron reverses

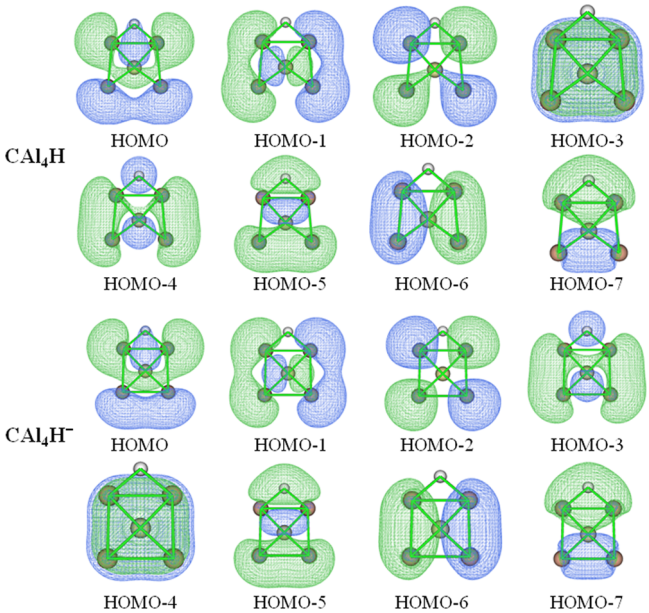

Figure 5. MOs of neutral CAl_4H and anion CAl_4H^- ground-state structures at the level of B3LYP/aug-cc-pVTZ.

the order of delocalized π and σ orbitals. One can observe that the hydrogen is actively hybridized in several MOs (ligand−

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ligand and center−ligand), making the electron of hydrogen part of the skeleton. Interestingly, with reference to the 18e-CAl_4^{2-}, the hydrogen in CAl_4H^- strengthens the neighboring Al−Al bonds, whereas Na weakens them in $NaCAl_4^-$ (Figure S1).

To compare with the experiment, the VDE and the adiabatic 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 CAl_4H^- in its ground state and neutral CAl_4H having the anion geometry. The 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 CAl_4H^-, the calculated VDE is 2.75 eV for **CAl_4H^--01** and 2.78 eV for **CAl_4H^--02**; both agree well with the experimental 2.88 eV. The calculated EA and ADE are 2.63 eV for **CAl_4H^--01** and 2.60 eV for **CAl_4H^--02**, which are also very close to the experimental value of 2.60 eV. However, **CAl_4H^--02**, a terminal-H ptC, has a slightly higher energy (around 2 kcal/mol at three different levels) than **CAl_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 at 0.01 kcal/mol for the neutral system and 0.03 kcal/mol for the 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 and 450 K (experimental temperature), respectively. Therefore, the terminal-H structure is very easy to transfer to the H-bridged structure, and coexistence of **CAl_4H^--02** is unlikely in the experiment. The good agreement between theory and experiment indicates that the ground ptC H-bridged ptC states of $CAl_4H^{-/0}$ were detected.

On the basis of the above discussion, the most stable **CAl_4H-01** and **CAl_4H^--01** are demonstrated as ptC with a bridging H. The hydrogen atom effectively donates its electron to the skeleton by hybridization in several MOs, which is supported by the MOs in Figure 5. Thus, for anionic **CAl_4H^--01** with a bridging-H motif, the skeleton has 4 + 3 × 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 **CAl_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 MOs are shown in Figure S3. This directly demonstrates that the bridging-H isomers with 17e/18e are more stable than the terminal-H isomers with 15e/16e. While previously studied 17e/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 ptC species CAl_4H and CAl_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 binds 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 CAl_4H^-, which can be understood by its electronic structures and MOs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.7b00732.

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

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Notes

The authors declare no competing financial interest.

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