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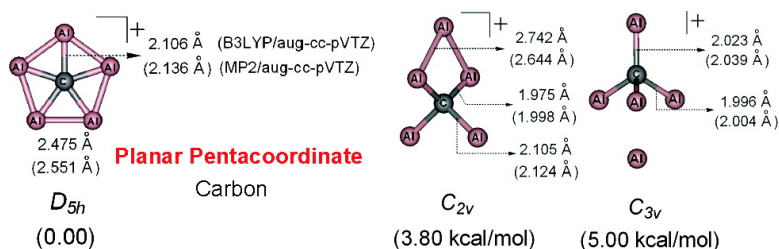# Planar Pentacoordinate Carbon in CAl: A Global Minimum

Yong Pei, Wei An, Keigo Ito, Paul von Rague# Schleyer, and Xiao Cheng Zeng

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Planar Pentacoordinate Carbon in CAl_5^+: A Global Minimum

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Abstract: We report evidence for the first global-minimum structure having a *planar* pentacoordinate carbon. High-level *ab initio* computations and quantum molecular dynamics simulations at 300 and 400 K reveal that the most stable CAl_5^+ isomer has D_{5h} symmetry and is ~3.80 kcal/mol lower in energy than the second most stable alternative. The latter has a nonplanar structure based on a tetrahedral CAl_4 moiety. The unexpectedly high proclivity for two-dimensional chemical bonding of the carbon in D_{5h} CAl_5^+, the robust thermal stability indicated computationally, and its mass spectrometric detection suggest that experimental characterization of this planar pentacoordinate carbon cation at room temperature is a likely prospect.

1. Introduction

The main-group elements in the periodic table generally obey well-precedented rules of chemical bonding.[1] In particular, the saturated carbons in the vast majority of organic compounds are *tetracoordinate* (Kekulé, 1857)[2] and favor (near) *tetrahedral geometries* (van't Hoff and Le Bel, 1874).[3] Consequently, carbon compounds that violate *both* of these conventional bonding constraints *simultaneously* are of fundamental importance. CH_5^+, the simplest pentacoordinate carbon species, was discovered in 1952,[4] but it has a highly fluxional three-dimensional (3D) structure. A large number of hypercoordinate carbon species have been described, but those also are 3D.[5] Following Hoffmann, Alder, and Wilcox's intriguing planar tetracoordinate carbon (ptC) concepts (1970),[6] a systematic computational investigation by Schleyer, Pople, et al. (1976) led to 1,1-dilithiocyclopropane, the first molecule found to favor a ptC geometry.[7] Although unrecognized at the time, the first experimental realization and X-ray structure of a ptC compound was published only a year later.[8] Since then, considerable effort has been devoted to exploration of compounds with novel electronic structures and unusual geometries, both experimen-

tally and theoretically.[9] Realization of "anti-van't Hoff/LeBel" geometries in the laboratory is still nontrivial.[10] This is especially true of unconstrained species where the atoms are free to assume lowest-energy conformations. According to valence-shell electron-pair repulsion (VSEPR) theory,[11] spatial orientations of chemical bonds tend to reduce repulsions among pairs of valence-shell electrons to the maximum degree. Consequently, planar coordination higher than three ("planar hypercoordination"), as in ptC molecules, is generally unfavorable.

Strategies to help stabilize planar hypercoordinate species are both steric and electronic and utilize small ring strain and other geometric constraints as well as σ-donating/π-accepting substituents. The latter delocalize the p_z lone pair on the central atom into the peripheral π-electron system.[6,7] Numerous ptC

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species were theoretically predicted on the basis of these considerations.[7,9,10] While ptC units may be incorporated into rigid steric systems,[12–20] this may result in considerable strain, complicating implementation in the laboratory. Like the first ptC-containing molecule (with the ptC coordinated by two vanadium atoms[8]), most of the experimentally known ptC compounds are transition-metal derivatives. Group IVB transition-metal-based bent metallocenes, i.e., titanocene, zirconocene, and hafnocene, have been found especially useful for making carbon compounds with unusual planar tetracoordinate structures.[21]

The simplest molecules having a planar tetracoordinate carbon are comprised of only five atoms. The first examples, e.g., CAl_2Si_2, were predicted theoretically in 1991 by Schleyer and Boldyrev,[22] who also codified design rules for achieving planar hypercoordinate structures. There should be a good "fit", both geometric (the ring size and the covalent radius of the central atom should match) and electronic (degenerate molecular orbitals should be equally occupied and a Hückel π-electron count is helpful, but not always mandatory). It also was recognized that the σ as well as the π system contributed to the planar stabilization. In 1998, high-level *ab initio* calculations suggested that the CAl_2Ge_2 and CGa_2Si_2 *global-minimum* structures both have ptC's.[23] Stimulated by these theoretical findings, a series of *planar tetracoordinate carbon* molecules, such as CAl_4^-,[24a] CAl_3Si^-,[24b] CAl_3Ge^-,[24b] CAl_4^{2-},[24c] and their relatives, were identified in gas-phase photoelectron spectroscopy (PES) experiments. The penta-atomic pure carbon ptC D_{5h} dianion C_5^{2-} also is a local minimum,[25,26] but it is not a viable species in isolation, and no derivatives have been observed experimentally.

The next breakthrough also was dramatic. The Schleyer–Boldyrev design principles were employed to predict numerous hexa- (in 2000) and then (in 2001) pentacoordinate carbon[27–29] minima theoretically. "Planar hypercoordinate element chemistry" has since become a source of fascination for chemists interested in new manifestations of chemical bonding.[9o] Very many examples of 3D penta- and hexacoordinated carbon are well known experimentally, e.g., in carborane cages, carbido-metal carbonyl clusters, and nonclassical carbocations,[5,30] but as yet the *planar* penta-, hexa-, and higher-coordinate carbon molecules predicted by theoretical computations, for example, mixed carbon–boron clusters,[27a] hyparene molecules,[27b,29] and hydrocopper complex,[31] have not been confirmed experimentally. There is a further impediment, as the predicted penta- or hexacoordinate carbon (ppC or phC)-containing minima are generally only metastable. There are lower-energy isomers, often having hypercoordinate elements other than carbon, that are lower in energy than the ppC or phC local minima. Although organic chemistry teaches us that chemists are as interested in isolable high-energy ("strained") molecules as they are in their global-minima isomers, the preparation, isolation, or even the detection of metastable molecules in the gas phase or in matrix isolation can be very challenging. Gas-phase methods under "annealing" conditions tend to generate low-energy isomers. As demonstrated in a recent PES experiment,[32] the 3D (global-minimum) structures for ppC- or phC-containing species overwhelm their 2D ppC or phC isomers in the cluster beam. On the other hand, pentagonal-planar coordinate indium,[34] sulfur,[35] rhodium,[36] iron,[37] and zinc[38] derivatives have been prepared. Small clusters of silver and gold have planar penta-coordinate and hexacoordinate Au[39a] and Ag[39b] atoms. The stabilization of hypercoordinate group 14 elements Si, Ge, and Sn in the center of boron rings also has been predicted theoretically.[40,41]

The search for the lowest-energy ppC or phC structures thus becomes highly relevant to address this important concept in chemistry as well as to guide future experimental confirmation.

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Scheme 1. Summary of Simple Species That Have (a) ptC, (b) ppC, and (c) phC Minima (Red Denotes Global Minima)
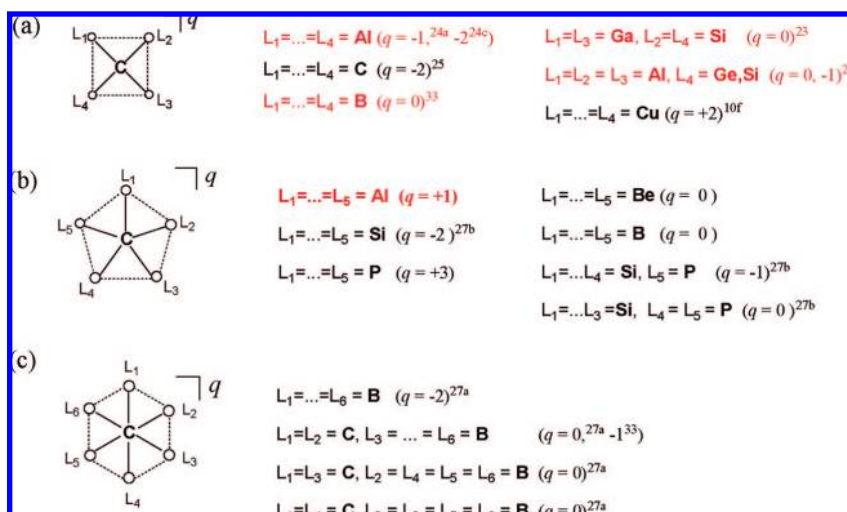
The requirements for stable ppC or phC units are very strict: the constituent atoms not only should satisfy both geometrical and electronic requirements impeccably, but they also should adopt the most energetically favored configuration and resist spatial isomerization or atomic exchange between the central carbon and a peripheral non-carbon atom. Highly stable ppC or phC structures might be achieved by anchoring the carbon atom into a rigid molecular framework such as a *fenestrane*,[15] *hyperene*,[27b] or some organometallic derivative.[21h] However, compounds constructed in this way are generally quite complicated, which renders not only their preparation but also the computational search for their global-minimum structures difficult.

Scheme 1 summarizes a number of simple systems with ptC, ppC, and phC minima. More details are provided in the Supporting Information. Except for CAl_5^+, the planar penta- and hexa-hypercoordinate carbon minima are local rather than global. The high stability of CAl_4^-,[24a] CAl_3Si^-,[24b] CAl_3Ge^-,[24b] and CAl_4^{2-} [24c] species is attributed to the formation of peripheral four-center bonds.[22] In stark contrast to the global-minimum ptC structures (CAl_4^-,[24a] CAl_3Si^-,[24b] etc.), the reported 2D ppC and phC structures[27] generally are significantly higher in energy than the global-minimum (2D or 3D) isomers (see the Supporting Information and refs 27b, 33). For the ppC- and phC-containing mixed boron−carbon clusters, exchanging a peripheral boron atom with the central carbon atom generally leads to significant reduction in total energy (>1.0 eV).[27b,33] Thus far, the demonstration of global minima with hypercoordinate carbons has been elusive.

We now report the first compelling evidence that the CAl_5^+ cation favors a D_{5h} global-minimum ppC structure. Various levels of theory agree on the lowest-energy characteristics of this ppC-containing species. The thermal stability of the CAl_5^+ cation is also confirmed by performing *ab initio* molecular dynamics (MD) simulations at 300 and 400 K. The electronic structure, thermal stability, aromaticity, and effect of a counterion are discussed. The predicted infrared spectrum and

ionization potential of ppC D_{5h} CAl_5^+ should aid its eventual experimental identification.

2. Computational Methods

Both the basin-hopping (BH) global-search algorithm[42] and stochastic search ("kick") methods[43] combined with the density functional theory (DFT)[44] optimization were used to sample the potential energy surface of CAl_5^+ and other clusters. Both search methods, employed independently by the authors in Nebraska and in Georgia, located the same isomers and led to the same conclusions. The Perdew−Burke−Ernzerhof (PBE) exchange-correlation functional,[45] implemented in the DMol3 program (see ref 46), and an all-electron d-polarization function including double-numerical (DND) basis set[46] were employed in Nebraska. Both the singlet and triplet spin states of the clusters were examined in the BH search. The structures of isomers obtained from the DMol3 search were reoptimized (guided by the vibrational frequency compuations) using the Becke and Lee−Yang−Parr exchange-correlation functional (B3LYP) correlation functional[47] and the aug-cc-pVTZ basis set, as implemented in the Gaussian03 package.[48] The structures of the most stable isomers, with energy differences less than 5 kcal/mol, were reoptimized (and their frequencies computed) at the Møller−Plesset second-order perturbation (MP2)/aug-cc-pVTZ level of theory.[49] Using these geometries, single-point energies were evaluated at the CCSD(T)/aug-cc-pVTZ level using coupled-cluster theory with inclusion of triple excitation.[50]

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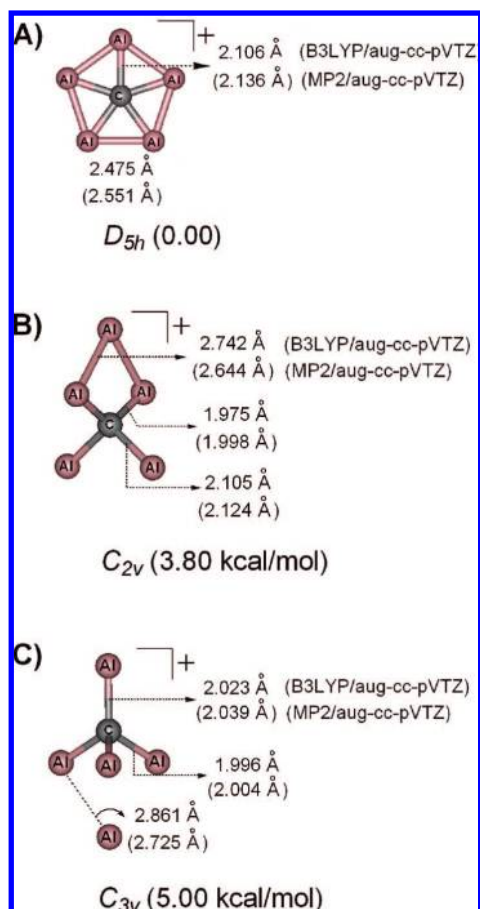
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Figure 1. Geometric structures and relative energy of the three lowest-lying isomers of CAl$_5^+$. **A** is the planar pentacoordinate carbon structure. **B** and **C** are two tetracoordinate carbon-containing structures. The relative energies are computed at the CCSD(T)/aug-cc-pVTZ level theory using the coordinates optimized from the MP2/aug-cc-pVTZ level theory.

3. Results and Discussion

Structures and Relative Stabilities. The global-minimum singlet ppC structure of CAl$_5^+$ (**A** in Figure 1) is appreciably lower in energy than the second and third lowest-energy isomers containing a spatially tetracoordinated C atom (isomers **B** and **C** in Figure 1), in which the fifth Al is bound to a tetrahedral CAl$_4$ "core". The relative energies of isomers **B** and **C** with respect to **A** at various levels are: B3LYP/aug-cc-pVTZ, 1.00 and 8.40 kcal/mol; MP2/aug-cc-pVTZ, 15.49 and 16.02 kcal/mol; MP3/aug-cc-pVTZ//MP2/aug-cc-pVTZ, 3.63 and 4.95 kcal/mol; MP4(SDQ)/aug-cc-pVTZ//MP2/aug-cc-pVTZ, −0.79 and 1.51 kcal/mol; CCSD/aug-cc-pVTZ//MP2/aug-cc-pVTZ, −1.50 and 1.57 kcal/mol; and CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ, 3.80 and 5.00 kcal/mol.[51,52]

The binding energy of the ppC D_{5h} CAl$_5^+$ cation (**A**) at the B3LYP/aug-cc-pVTZ level (−10.09 eV) was evaluated from the computed binding energy of neutral D_{5h} CAl$_5$ (−15.71 eV) and its vertical ionization potential (5.62 eV). The computed dissociation energy of the ppC CAl$_5^+$ cation (**A**) is ~2.5 eV into an Al$^+$ cation and tetrahedral CAl$_4$ and is ~2.6 eV into the CAl$_4^+$ cation and an Al atom.
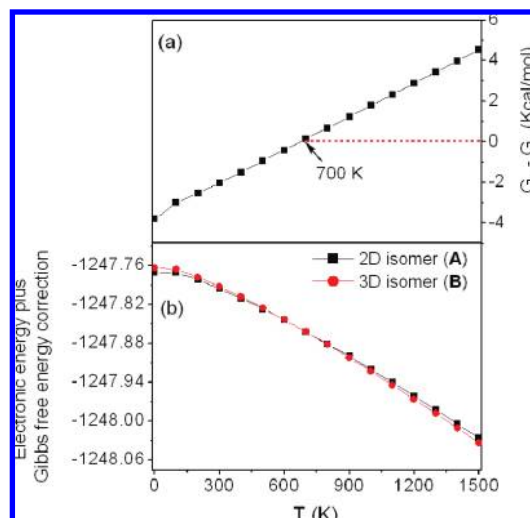

Figure 2. (a) Gibbs free energy difference between 2D isomer (**A**) and 3D isomer (**B**) at different temperatures. (b) Absolute electronic energies (from CCSD(T)/aug-cc-pVTZ single-point energy computations) of 2D and 3D isomers of CAl$_5^+$, including the Gibbs energy corrections (from MP2/aug-cc-pVTZ computations) at various temperatures.

The lowest vibrational frequency of ppC CAl$_5^+$ (**A**) in D_{5h} symmetry is 69.4 cm^{-1} at MP2/aug-cc-pVTZ. The simulated IR spectrum (see the Supporting Information) shows only an intense e$_1'$ mode at 627.7 cm^{-1}, but this feature, along with the computed ionization potential (IP; adiabatic, 6.00 eV from the C_{2v} CAl$_5$ neutral global minimum[61] to **A**), may aid the spectroscopic identification of **A** in the gas phase. The vertical IP of C_{2v} CAl$_5$ to C_{2v} CAl$_5^+$ is 6.72 eV. The CAl$_5^+$ ion has been detected mass spectrometrically in Leuven, Belgium, along with many other C−Al stoichiometries,[53] but no IP or IR measurements have been made as yet. The optimized structures (**A**−**C**) using both B3LYP and MP2 methods (both with the aug-cc-pVTZ basis set) are shown in Figure 1. Both B3LYP and MP2 levels yield very similar bond lengths and angles. In the ppC CAl$_5^+$ (**A**), the Al−C bond length is 2.11 Å (B3LYP) and 2.14 Å (MP2), slightly longer than the experimental value of the Al−C bond length (~2.00 Å)[54] and that in **B** (2.00−2.12 Å). The other low-energy isomers for the CAl$_5^+$ are listed in the Supporting Information.

The effect of temperature on the relative stability of **A** and **B** (as depicted in Figure 2) was based on the Gibbs free-energy correction at finite temperature computed at the MP2/aug-cc-pVTZ level, which was added to the single-point CCSD(T)/aug-cc-pVTZ energies. **A** is more stable than **B** in the 0−700 K temperature range, but isomer **B** is more stable above 700 K.

Thermal Stability and Quantum Molecular Dynamics. To further confirm the thermal stability of the predicted ppC structure (**A**) at room temperature, we carried out two independent Born−Oppenheimer quantum molecular dynamics simulations at 300 and 400 K, each for 10 ps (MD time step is 0.7 fs), using the Dmol3 program.[46] We recorded a movie of the MD simulation at 300 K. Both simulations show that the structure of ppC CAl$_5^+$ remains intact during the 10 ps run. Analysis of both MD trajectories in the equilibrium stage reveals that the ppC CAl$_5^+$ is slightly distorted at 300 and 400 K due to the

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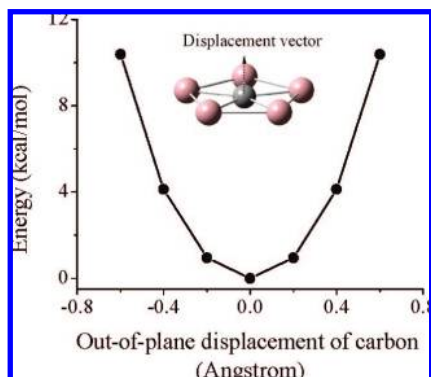
Figure 3. Computed potential energy curve describing the out-of-plane displacement of the central C atom. Its equilibrium position is at the center of the five-membered ring.

thermal effect. The three torsion angles, $\delta(Al_1-Al_2-C-Al_3)$, $\delta(Al_1-Al_2-C-Al_4)$, and $\delta(Al_1-Al_2-C-Al_5)$ (see Scheme 1), can be used to describe the out-of-plane distortion of the ppC CAl_5^+ (**A**), which exhibits average values of 16.90, 14.13, and 18.29°, respectively, at 300 K and 22.83, 11.20, and 19.75° at 400 K. The average Al–C bond length ranges from 2.14 to 2.18 Å (300 K) and from 2.17 to 2.21 Å (400 K), slightly longer than the Al–C bond length at 0 K (2.11 Å).

The bond stretching shown in the MD movies correlates with the two lowest vibrational modes (out-of-plane vibration and in-plane stretching vibration) of the ppC CAl_5^+(**A**). The calculated potential energy curve [at the CCSD(T)/aug-cc-pVTZ level] for the out-of-plane displacement of the central C atom also indicates the preference of the CAl_5^+ for the planar geometry over 3D structure (see Figure 3).

MD simulations of the 3D isomer (**B** and **C** in Figure 1) at 300 and 400 K also were performed. Interestingly, a 3D-to-2D structure transition (**B** → **A**) is clearly seen during the 300 K MD run starting from the secondary lowest-energy structure **B**. A low transition barrier (5.98 kcal/mol) between the 2D isomer **A** and 3D structure **B** (computed at the B3LYP/aug-cc-pVTZ level theory) is found, consistent with the MD simulation. The 3D structure of isomer **C** always remains intact and resists isomerization, even at 400 K. Moreover, the average Al–C bond length in the 3D isomer **C** at 300 and 400 K only fluctuates in the 2.11–2.18 Å range, indicating much stronger bonding between the tetrahedrally coordinated C atom and the Al ligand. Although the free energy analysis (based on harmonic approximation) shown in Figure 2 suggests that the 2D-to-3D transition between the isomers **A** and **B** would occur beyond 700 K, the realistic dynamics trajectory of 2D ppC CAl_5^+ at 400 K already indicates much enhanced out-of-plane vibration and in-plane stretching vibration due to the thermal effect. Accordingly, we conclude that the integrity of the ppC CAl_5^+ (**A**) may not be capable of withstanding much higher temperatures than 400 K, since our MD simulations show that very large thermal fluctuations destabilize the planar structure at, e.g., 600–800 K.

Electronic Structure. CAl_5^+ has 18 valence electrons with the electronic configuration $1a_1'^{(2)} 1e_1'^{(2)} 1e_1'^{(2)} 2a_1'^{(2)} 1a_2''^{(2)} 1e_2'^{(2)} 1e_2'^{(2)} 2e_1'^{(2)} 2e_1'^{(2)}$. The canonical molecular orbitals of the ppC CAl_5^+ (**A**), shown in Figure 4, include two degenerate highest occupied molecular orbitals [HOMO, e_1'(radial)], an occupied π-orbital [HOMO−2, $a_2''(\pi)$], a peripheral five-center molecular orbital [HOMO−3, a_1'-(radial)], and other σ-orbitals. A significant contribution of
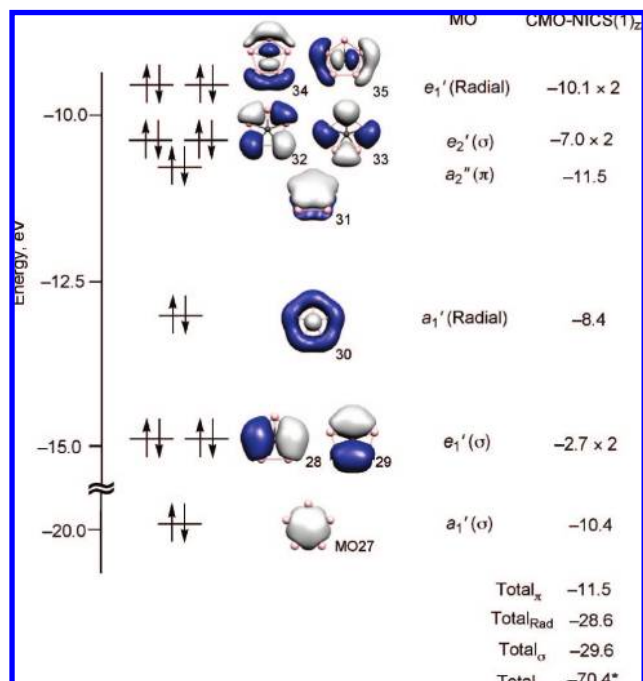

Figure 4. Canonical molecular orbitals of D_{5h} CAl_5^+ and their CMO-NICS(1)$_{zz}$ contributions (in ppm) at PW91/IGLO-III. [Perdew, J. P.; Burke, K.; Wang, Y. *Phys. Rev. B* **1996**, *54*, 16533. Kutzelnigg, W., et al. *The IGLO-Method: Ab Initio Calculation and Interpretation of NMR Chemical Shifts and Magnetic Susceptibilities*; Springer-Verlag: Heidelberg, 1990.] *The −70.4 total value includes −0.7 contribution from core MOs (not shown).

the perpendicular $2p_z$ orbital of the central C atom to the π-orbital [HOMO−2, $a_2''(\pi)$] is found, consistent with the electronic stabilization mechanism proposed by Hoffmann et al.[6a] In addition, the highly delocalized radical bonding [HOMO−3, a_1'(radial)] also favors the planar structure. Furthermore, the large HOMO−LUMO gap (1.65 eV at the PBEPBE/aug-cc-pVTZ level or 2.82 eV at the B3LYP/aug-cc-pVTZ level) also suggests high stability of the ppC CAl_5^+ (**A**).

Natural bonding orbital (NBO) analysis[55] indicates considerable charge transfer from the peripheral Al ligands to the central electronegative C atom. The natural population analysis (NPA) charges on the peripheral Al and central C atoms are +0.78 and −2.91, respectively. Note that the carbon acts as a σ acceptor, and this compensates for the donation of the carbon $2p_z$ electrons to the π bonding; the $2s^{1.65} 2p_x^{1.79} 2p_y^{1.79} 2p_z^{1.53}$ valence population of the ppC results. The relatively high $2p_x$ and $2p_y$ occupancies and lower occupancies in $2p_z$ orbitals are manifestations of the back-donation. The 1.53 electron occupancy of the $2p_z$ orbital of ppC is close to that of the central carbon in the D_{5h} CAl_4^{2-} ptC cluster[24c] (also at the MP2/aug-cc-pVTZ level), where the ptC population is $2s^{1.62} 2p_x^{1.77} 2p_y^{1.77} 2p_z^{1.61}$.

The calculated Wiberg bond index (WBI)[56] is 0.40 for each Al−C bond in the ppC CAl_5^+ (**A**), and the WBI central C sum is 1.99. These data are similar to those of the ptC WBI in CAl_4^{2-} (WBI$_{Al-C}$ = 0.51 and WBI$_{C-Total}$ = 2.05). In both cases, the interaction between the central C and peripheral Al atoms is

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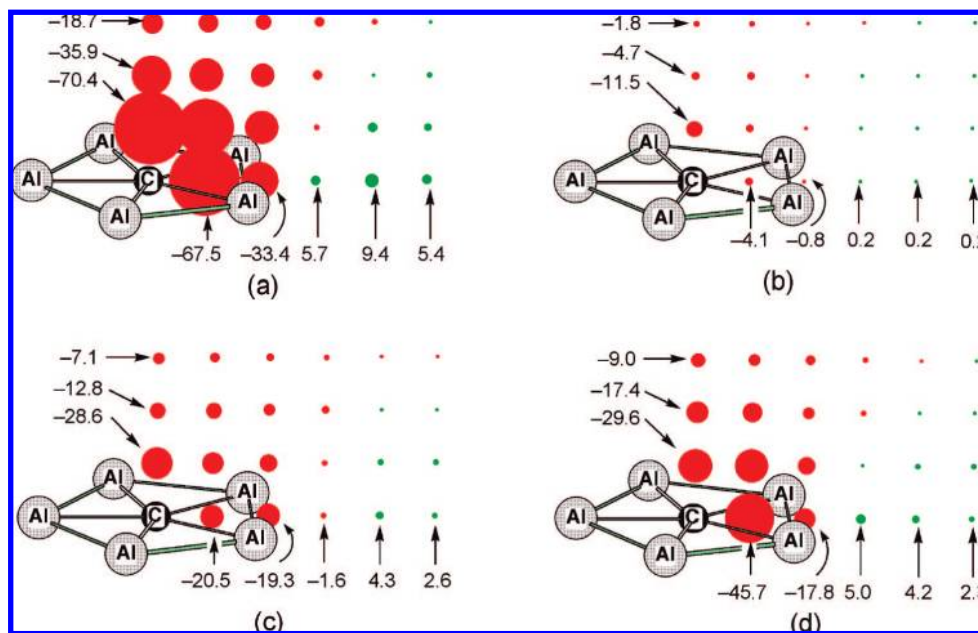(56) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083.

Figure 5. (a) NICS$_{zz}$, (b) NICS$_{\pi zz}$, (c) NICS$_{Rad.zz}$, and (d) NICS$_{\sigma zz}$ grids of the D_{5h} CAl$_5^+$ at the PW91/IGLO-III level. Diatropic tensors are shown in red and paratropic tensors in green. NICS values are in ppm.

much weaker than, e.g., the WBI$_{C-H}$ = 0.97 and WBI$_{C-Total}$ = 3.87 in T_d CH$_4$. The in-plane bonding between the peripheral Al ligand and the central C atom is electron-deficient. Eight valence electrons (four from the Al$_5^+$ perimeter and four from C) are responsible for the ppC bonding. Four valence electrons distribute among the multicenter in-plane Al$-$C σ-bonds, as depicted by two degenerate HOMO [e_1'(radial)] orbitals (Figure 4). In addition, two valence electrons delocalize in the multi-center ligand$-$ligand$-$ppC σ-orbital [HOMO-3, a_1'(radial)] orbitals (Figure 4), which sums up to six radial electrons. The remaining two π-electrons [distributed in HOMO-2, $a_2''(\pi)$], satisfy the Hückel ($4n$ + 2) π-electron aromatic rule (with n = 0). However, ppC CAl$_5^+$ (**A**) exhibits weak π-aromaticity, as is shown by the canonical molecular orbital (CMO) dissection of the out-of-plane tensor component of the nucleus-independent chemical shift,[57] probed 1.0 Å above the central carbon (CMO-NICS(1)$_{zz}$) (see Figure 4). Dissection of the total NICS(1)$_{zz}$ tensor (-70.4 ppm) suggests that the π MO (Figure 4, π MO) contributes only -11.5 ppm. The tensor contributions from the radial MOs (Figure 4, radial MOs; -28.6 ppm) are more diatropic (aromatic). This underscores the importance of the intrinsic delocalization of the σ radial framework in the D_{5h} CAl$_5^+$ (**A**) (like that reported in Al$_4^{2-}$).[58] In addition, the NICS$_{zz}$ grid and its dissection into π, radial, and σ contributions (NICS$_{\pi zz}$, NICS$_{Rad.zz}$, and NICS$_{\sigma zz}$, respectively), are shown in Figure 5. The large cone-shaped diatropic tensors (red NICS

probes) above the plane of the CAl$_5^+$ and the paratropic NICS tensors (green NICS) outside the ring are consistent with the ring current model[59] and document the magnetic aromaticity of CAl$_5^+$ (**A**). The dissected NICS grid analysis further supports the CMO-NICS(1)$_{zz}$ conclusions: the contribution to the diatropic NICS tensor from the π MO is rather small relative to that of the radial MOs. Hence, the radial MOs are more important than the π MO in favoring the planar geometry of D_{5h} CAl$_5^+$.

Chemical Reactivity and IR Spectrum. The peripheral Al atoms in D_{5h} CAl$_5^+$ have the same charge. However, planar Al$_5^q$ (q is in the -5 to $+5$ range) five-membered rings (without a central atom) are unstable. In contrast, the peripheral Al$_4^{2-}$, Al$_3$Si$^-$, Al$_3$Ge$^-$, and P$_5^-$ rings in the CAl$_4^{2-}$, CAl$_3$Si$^-$, CAl$_3$Ge$^-$, and CP$_5^{3+}$ ptC's all are stable and aromatic.[60]

The evenly distributed positive charges on the Al perimeter atoms suggest that the CAl$_5^+$ has no specific site for nucleophilic attack. A Cl$^-$ counteranion prefers attachment to one of the peripheral Al atoms in ppC CAl$_5^+$ (**A**). A deformed C_{2v} global-minimum structure with a ptC (Figure 6a) results. An alternative C_{2v} geometry, with the Cl$^-$ bridging two Al atoms (Figure 6b), as well as the 3D structures we have examined are substantially higher in energy.

Akin to CAl$_5$Cl (Figure 6a), neutral CAl$_5$ and monoanion CAl$_5^-$ clusters are most stable in planar C_{2v} geometries containing ptC subunits, as has been shown by previous PES anion experiments and high-level theoretical computations.[61] The CAl$_5^+$ cation has been detected mass spectroscopically, but its IP has not been measured yet.[53] The single intense peak at 627.7 cm^{-1} computed in the IR spectrum (see Figure S1,

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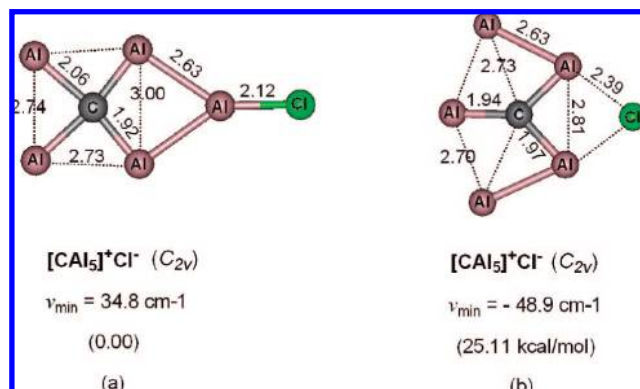(61) Boldyrev, A. I.; Simons, J.; Li, X.; Wang, L. S. *J. Chem. Phys.* **1999**, *111*, 4993.

Figure 6. Optimized structure of neutral $[CAl_5]^+Cl^-$ (B3LYP/aug-cc-pVTZ). (a) A Cl atom binds to a peripheral Al atom and (b) a Cl atom binds to the edge site. The lowest frequencies are given as ν_{min}. The bond lengths are in units of Å.

Supporting Information) also affords a means of identifying ppC CAl_5^+ in possible mass-selected photodissociation experiments.[62]

Conclusion

We have reported the first evidence of a hexatomic species having a global-minimum structure with a planar pentacoordinate carbon: CAl_5^+ prefers D_{5h} symmetry on the basis of extensive potential energy surface searches, high-level *ab initio* computations, and quantum molecular dynamics simulations at 300 and 400 K. Although both neutral and positively charged three-dimensional molecules with pentacoordinated carbons are well described,[5,30,63,64] experimental evidence of *planar* penta- or hexacoordinate carbon species is still lacking. We hope that the global-minimum character of D_{5h} CAl_5^+ (**A**), its predicted robust thermal stability at room temperature, and the mass spectrometric observation of CAl_5^+ will stimulate investigations to confirm the existence of the ppC CAl_5^+ species in the laboratory.

Supporting Information Available: Isomers and relative energies of CAl_5^+, CBe_5, CB_5, CP_5^{3+}, and CSi_5^{2-}; local minima ppC structures of CSi_4P^- and CSi_3P_2; and complete ref 48. This material is available free of charge via the Internet at http://pubs.acs.org.

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