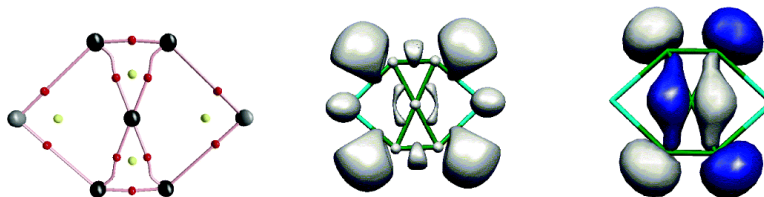Communication

(CM) (M = Li, Na, K, and *n* = 0, 1, 2). A New Family of Molecules Containing Planar Tetracoordinate Carbons

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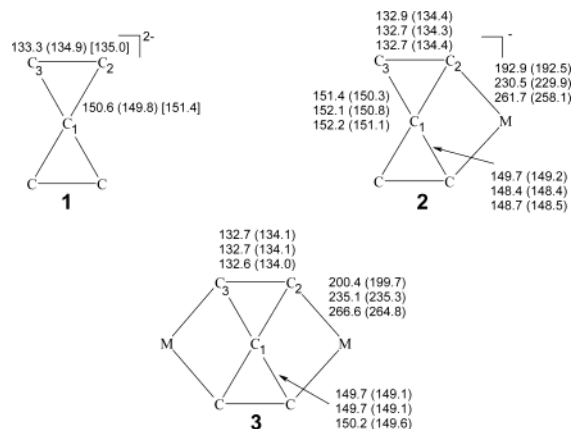# (C₅M₂−ₙ)ⁿ⁻ (M = Li, Na, K, and n = 0, 1, 2). A New Family of Molecules Containing Planar Tetracoordinate Carbons

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Américas-Puebla.Ex-Hda. de Sta. Catarina Mártir, A. P. 100, Cholula 72820, Puebla, Mexico*
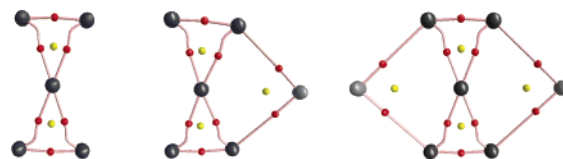
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One of the better known and well-established paradigms in chemistry is the tetrahedral symmetry adopted by tetracoordinate carbon atoms.[1] Almost a century after this bonding model was proposed, the quest to find compounds containing planar tetracoordinate carbon (ptC) atoms continues.[2] The accumulated evidence suggests that molecules containing ptC atoms can be stabilized by two general mechanisms: electronic and mechanic.[3] In the first approach, the stabilization arises from the redistribution of the lone pair of electrons located on one of the p-orbitals of the central carbon, enhancing the delocalization in the aromatic system, or by using the σ-donor/π-acceptor capabilities of substituents.[2a] A four-center peripheral bond could also be used to stabilize a ptC.[4a] These ideas were extended to stabilize penta- and hexacoordinate carbon atoms.[4b] In the second mechanism, the bonds are constrained by rings and cages. This mechanical approach has been used in the design of neutral planar tetracoordinate carbon molecules with a C(C)₄ skeleton.[2f] A combined approach, mechanical and electronic, has been recently proposed.[4c]

The aim of the present work is to show that ab initio calculations predict the possible existence of a family of compounds containing ptC atoms, which are stabilized only by electronic effects.[5] The lead molecular fragment with a ptC atom is the "naked" ionic cluster C₅²⁻, **1**. The optimized geometries of C₅²⁻ with B3LYP, MP2, and CCSD(T), are shown in Figure 1. As it can be seen, the three theoretical methodologies yield very similar values for the geometrical parameters of **1**. The planar structure is a minimum in the potential energy surface (PES). The harmonic analysis (Table 1S) shows that the smallest frequency corresponds to a soft mode with 172 and 182 cm⁻¹, for B3LYP and MP2, respectively. An extensive search on the PES of C₅²⁻, with B3LYP and MP2, was done. This search produces four additional local minima where three of them have a lower energy than the planar structure (as can be seen in Figure 1S, one is very close to the linear structure reported by Watts and Bartlett[7]). The HOMO of C₅²⁻ has a positive eigenvalue (Table 2S), similar to CAl₄²⁻,[2h,k] precluding the existence of this anion. Thus, considering this fact, one can think of adding alkaline metals to lower the HOMO eigenvalue and, consequently, enhance the stability of the molecule. The proposed compounds with one and two alkaline metals are C₅M⁻, **2**, and C₅M₂, **3** (M = Li, Na, and K), whose optimized geometries with C₂ᵥ and D₂ₕ symmetry, respectively, are presented in Figure 1. The harmonic analysis of these species is presented in Tables 3S and 4S. In all cases, the incorporation of the counterions in the long side of the rectangle does not modify the planar structure of the C₅²⁻ (see Figure 1). Similar to the naked dianion, the scan of the PES of these structures, preserving planarity, finds one additional local minimum for C₅M⁻,

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Figure 1. B3LYP, MP2, and CCSD(T) optimized geometries. Bond lengths are in picometers.


Figure 2. Molecular graphs of the C₅²⁻, C₅Li⁻, and C₅Li₂. Red and yellow spheres are the bond and ring critical points, respectively.

and two more isomers for C₅M₂ (see Figure 2S). The additional isomers correspond to placing alkali ions on the short side(s) or a mixed arrangement, one on a short side and one on a long side. In contrast to **1**, all of these minima have higher energy than the planar structures **2** and **3**.

Why are these species minima? A first clue is provided by the behavior of the HOMO, the hardness (HOMO−LUMO gap), and the electrophilicity[8] of **1**, **2**, and **3** (Table 2S). The first feature to be noted is that, indeed, the addition of the alkaline metals lowers the energy of the HOMO, making it negative. Second, the compounds become harder with the addition of the alkali ions, and the hardest species is that with the hardest ion, lithium. Finally, it is very interesting to note that the largest electrophilicity corresponds to the C₅²⁻ dianion, which, after considering that the chemical potential is positive, indicates the large tendency of this species to give away electrons. To gain further insight about the nature of the chemical bonding in these species, the following molecular scalar fields are considered: the electronic density, ρ(**r**), the electron localization function, ELF(**r**), and the molecular orbitals (MOs), {φᵢ(**r**)}. Below, these fields are analyzed and compared with planar CH₄ and CAl₄²⁻, which are molecules containing a ptC. The analysis of ρ(**r**)[9] for C₅²⁻ is depicted in Figure 2 and shows critical points (CPs) along the C₁−C₂ and C₂−C₃ directions. The values of the descriptors at these CPs (Table 5S) allow one to classify
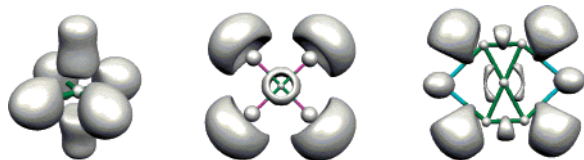
Figure 3. ELF isosurfaces ($\eta = 0.80$) for the planar CH_4, CAl_4^{2-}, and C_5Li_2.

Figure 4. HOMO isosurfaces ($|\varphi| = 0.05$) for the C_5^{2-}, C_5Li^-, and C_5Li_2.

these interactions as covalent bonds. The value of ρ at $CP(C_1-C_2)$ is smaller than that at $CP(C_2-C_3)$, in agreement with the bond lengths. As it can be seen in Figure 2, the gradient paths connecting the ptC with the outer carbon atoms have a noticeable curvature, and the CPs associated to these paths have a large ellipticity. These facts point toward the existence of multicenter bonds. On the other hand, the values of ρ at $CP(C-M)$ are small, and $-\nabla^2\rho$ is negative. Moreover, the interaction of C_5^{2-} with the cation does not alter the distribution of the electron density in the carbon fragment (see Figure 1 and Table 5S). The Bader charges of the metallic cations in C_5M^- (C_5M_2) are 0.86 (0.90), 0.76 (0.87), and 0.75 (0.86) e$^-$ for Li, Na, and K, respectively. Thus, the bonding of the alkaline metals to C_5^{2-} is basically ionic.

A key question is the distribution of the lone pairs, because the delocalization of the ptC lone pair stabilizes the central carbon arrangement. The results of the analysis of the ELF[10] for the planar structures of CH_4, CAl_4^{2-}, and C_5Li_2 are presented in Figure 3 and in Table 6S.

Around the carbon atom in planar CH_4, there are six basins, four corresponding to C—H bonds, V(C—H), and two monosynaptic basins corresponding to the carbon lone pair, V(C). The population of the V(C—H) and V(C) basins is 1.40 and 1.05 e$^-$, respectively, and they support the multicenter bonding scheme. In CAl_4^{2-}, there are four basins around the carbon atom, V(C—Al), integrating to 1.75 e$^-$. In this system, the ELF does not have a maximum related to a lone pair. In C_5^{2-}, C_5M^-, and C_5M_2, there are only four basins around the carbon atom, V(C—C), whose populations are approximately 1.5 e$^-$. Similar to CAl_4^{2-}, the planar carbon atom does not have a lone pair perpendicular to the molecular plane. The external carbons have a V(C) with 2.6 e$^-$ attributed to a lone pair. The interaction between the metal cation and C_5^{2-} is purely ionic because the metal basin is detached from the remaining part of the molecular system, which is in agreement with the results discussed above.

The analysis of the MOs of structures **1**−**3** reveals that the C_4 fragment has an orbital, with the proper symmetry, that interacts with the p-orbital of the ptC perpendicular to the molecular plane (see the $1b_{3u}$ MO in Figure 3S). This MO is a highly delocalized π-orbital. On the other hand, the transfer of electrons to the C_5 fragment is of paramount importance to enhance the stability of the molecule. These electrons occupy the bonding MOs (the HOMOs) depicted in Figure 4, which hold together the C_5 fragment.

In conclusion, the theoretical study presented in this Communication shows that alkaline metals stabilize ptC-containing molecules with the $C(C_4)$ skeleton, making them candidates for experimental detection. The structures reported here are the first with a ptC, surrounded only by other carbon atoms which are stabilized, only, by electronic factors.
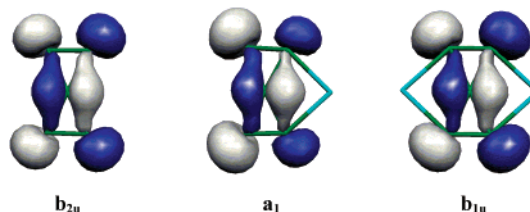
Supporting Information Available: Frequencies, IR intensities, frontier orbital eigenvalues, chemical potentials, hardness, electrophilicities, the geometries of other stationary points, and the molecular orbitals of C_5Li_2 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) B3LYP, MP2 (full), and CCSD(T) (frozen core) calculations were carried out with the Gaussian 98 program using 6-311++G(2df) basis sets.[6a] The harmonic frequencies were calculated to characterize the nature of the stationary points and to determine the zero point energy correction (ZPE). The topological analysis of $\rho(\mathbf{r})$ and ELF($\mathbf{r}$) was done with the AIM2000[6b] and TopMod[6c] programs, respectively. The lead dianion C_5^{2-} was calculated with B3LYP in a singlet and triplet state, and it was found that the latter was 47.1 kcal/mol higher in energy than the former.

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