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Planar Pentacoordinate Carbons in CBe_5^{4-} Derivatives

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Abstract

The potential energy surfaces of a series of clusters with formula $CBe_5Li_n^{n-4}$ (n=1-5) are systematically explored. Our computations show that the lithium cations preserve the CBe_5^{4-} pentagon, such that the global minimum structure for these series of clusters has a planar pentacoordinate carbon (ppC). The systems are primarily connected by a network of multicenter σ-bonds, in which C atom acts as σ-acceptor and this acceptance of charge is balanced by the donation of the $2p_z$ electrons to the π-cloud. The induced magnetic field analysis suggests that the clusters with formula $CBe_5Li_n^{n-4}$ (n=1-5) are fully delocalized. The fact that these ppC-containing clusters are the lowest-energy forms on the corresponding potential energy surfaces raises expectations that these species can be prepared experimentally in the gas phase.

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Molecules containing a planar tetracoordinate carbon (ptC) atom have been pursued for the last 40 years.[1] The smallest viable ptC species were predicted computationally by Schleyer and Boldyrev in 1991.[2] Notable predictions show also the viability of systems having planar pentacoordinate[3] and hexacoordinate carbon atoms.[4] So, planar hypercoordinate carbon (phC) chemistry has now been extended much further to planar bonding patterns involving main group, as well as transition metal elements.[5] Such species are attractive not only because of their unusual geometries and bonding patterns, but also because of their potential applications in custom materials design.

The first global minimum containing a planar pentacoordinate carbon (ppC) with the highest possible D_{5h} symmetry, CAl_5^+, was reported by Pei et al. in 2008.[3c] More recently, our group showed that substitution of one or two aluminum atoms by Be in CAl_5^+, preserving the 18 valence-electrons, results also in global minima with a ppC.[3e] So, beryllium seems to be a choice to figure planar hypercoordinate carbon atoms. In 2008, Luo suggested that CBe_5^{4-} tetraanion could adopt a ppC structure either.[6] This tetraanion is isoelectronic to CAl_5^+ but it is strongly destabilized by Coulomb repulsion. Inclusion of counterions could stabilize the CBe_5^{4-} skeleton, but the possible rupture of the ppC framework is latent.

In this manuscript, we propose *in silico* new ppC clusters based on the hypothetical CBe_5^{4-} moiety. Our computations show that lithium cations preserve the CBe_5^{4-} pentagon yielding a novel family of ppC clusters with formula $CBe_5Li_n^{n-4}$ (n=1-5). Bonding and electron delocalization are analyzed using the natural population analysis (NPA)[7] and the induced magnetic field ($\mathbf{B}^{ind}$), respectively. Our results reveal that sequential inclusion of lithium cation on the CBe_5^{4-} skeleton enhances C-Be attraction.

Our computational procedure employs a modified kick algorithm called Bilatu.[8] The initial search was done using the PBE0[9] functional in conjunction with a D95V basis set

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on both the singlet and the triplet state potential energy surfaces.[10] The located structures were reoptimized at the PBE0/def2-TZVP[11] level to establish an order of the isomers based on the computed energies. Highly correlated CCSD(T)/def2-TZVP[12]//PBE0/def2-TZVP relative energies were used to unequivocally identify the lowest energy structure. Zero point energy corrections were computed at the PBE0/def2-TZVP level. All these computations were done using the Gaussian 09 suite of programs.

To assess the existence of a multireference character of the title systems, a series of CASPT2[13]/ANO-L-TZVP//PBE0/def2-TZVP computations was performed using the MOLCAS 6.8 package.[14] Born-Oppenheimer molecular dynamics (BOMD) simulations at the PBE/def2-SVP level, using the resolution of identity, were done for each cluster at 1000 K for 20 ps using Turbomole.[15] The temperature was kept constant with a Nosé-Hoover thermostat with a relaxation time of 720.0 a.u and a time step of 80 a.u. (1.935 fs).

Tetraanions are completely unrealistic species having very much instability towards the spontaneous loss of electrons. One first approach to stabilize a ppC atom is to remove the extra-negative charge to form the neutral CBe_5 cluster. This species was considered by Pei et al.[3c] and later on analyzed by Luo.[6] However, the ppC structure is not the lowest-energy isomer. The experimentally characterized phC molecules are predominantly organometallic compounds or small clusters created in the gas-phase. Particularly, gas phase experimental detection of phC molecules predicted *in silico* is not easy and it could be effective only if the suggested arrangement is thermodynamically favored.[16] This is the reason why a systematic search of the global minimum is required. Actually, the D_{5h} symmetry of CBe_5^{4-} is not a global minimum. This perfect pentagon structure is less stable by 9.7 kcal·mol^{-1} than a classical tetracoordinate carbon form with C_{3v} symmetry (Figure 1). Of course, the HOMO energies of both structures are positive (7.5 and 8.4 eV, respectively), precluding the existence of this tetraanion in the gas phase.

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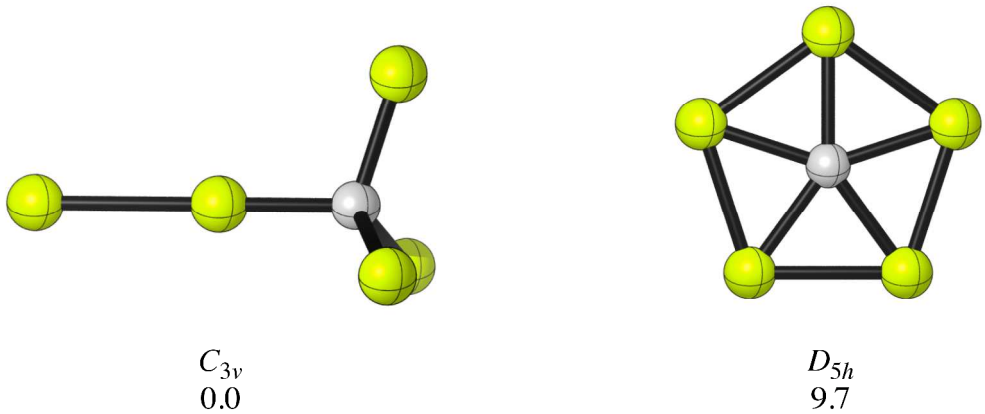

Figure 1. The lowest lying structure of the CBe_5^{4-} tetraanion (**1**) and its perfect pentagon isomer. Relative energies are in kcal·mol^{-1}.

To explore whether counterions might preserve the pentagon CBe_5^{4-} moiety, we survey the possibility to use lithium cations, maintaining 18 valence electrons around the carbon atom. Considering the electronegativity difference between lithium and beryllium and the propensity of lithium to be in a bridging position, one expects the most stable structure to contain a CBe_5 pentagon, where each lithium atom interacts with a Be-Be side. The lowest-lying energy structures of the resultant clusters are shown in Figure 2. Gratifyingly, all the global minima of the proposed clusters have a ppC atom. The lowest vibrational frequencies computed at the PBE0/def2-TZVP level range from 63 to 139 cm^{-1}. Local minima found within 15 kcal·mol^{-1} above their corresponding global minimum are shown in Figures 1-SI to 6-SI. For CBe_5Li^{3-} (**2**), the nearest energy isomer is 5.5 kcal·mol^{-1} higher in energy than the ppC structure. This energy difference between the global minimum and the nearest energy isomer increases proportionally to the number of lithium atoms. In the extreme case, $CBe_5Li_5^{+}$ (**6**), the second form is destabilized by 11.4 kcal·mol^{-1} over the perfectly planar star arrangement. Interestingly, when more than two lithium atoms are

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incorporated, the closer isomers to the global minimum preserve the CBe_5 pentagon skeleton.

Triplet states were also considered, however, the closest triplet forms are higher in energy than the singlet structures by 37.6 (**2**), 11.3 (**3**), 14.3 (**4**), 20.1 (**5**), and 31.9 (**6**) kcal/mol. In order to judge the reliability of our DFT and CCSD(T) computations, we employed the T1 diagnostic. Empirically, if T1 is less than 0.02 then a CCSD result is reliable. The T1 values computed for the global minima are lower than 0.03, except for **2** (0.06). So, in principle perhaps higher order excitation levels can correct for some amount of multireference character. In order to avoid any doubt about our results, we performed a series of CASPT2/ANO-L-TZVP computations. In all cases, the total wavefunction is dominated by a single-reference determinant with contributions varying from 83% for **2** up to 92% for **4**, **5**, and **6**. This indicates unambiguously that accurate mono-determinantal methodologies like DFT and/or CCSD(T) can be safely employed.

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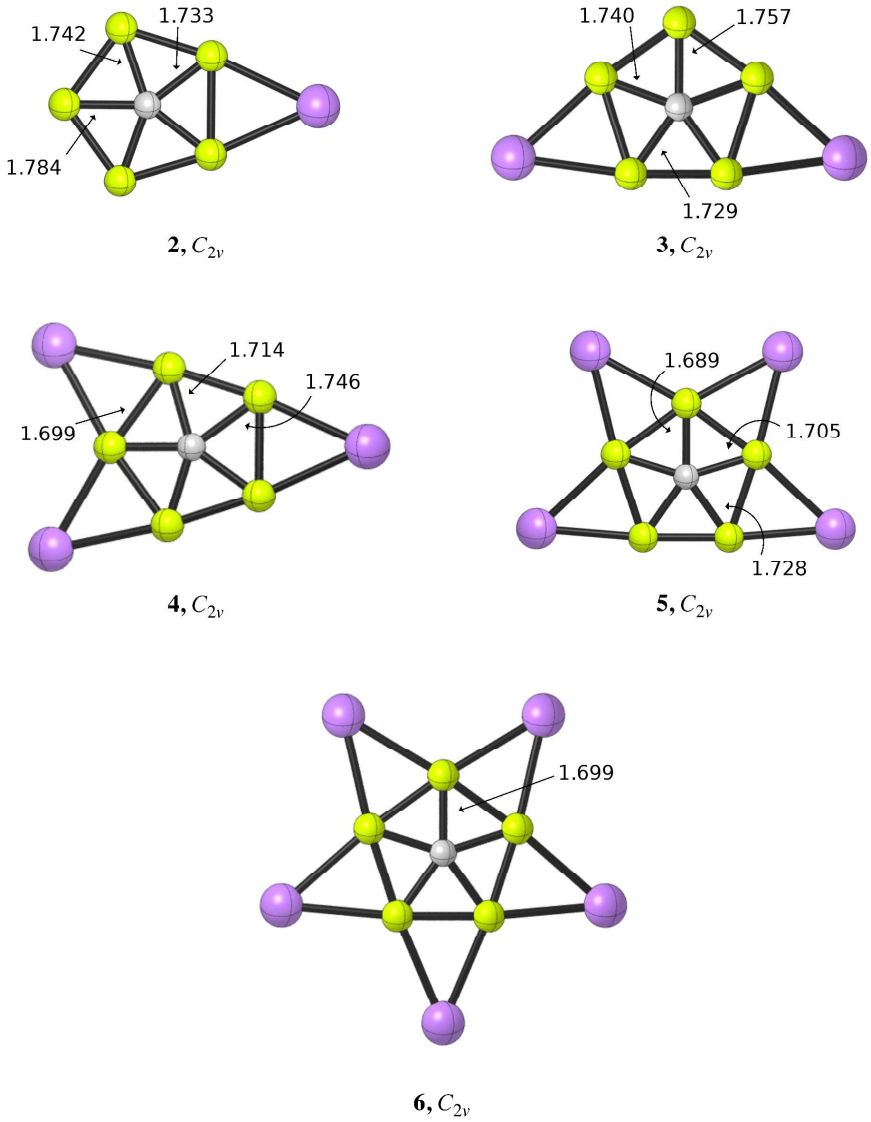

Figure 2. Global minimum structures of CBe_5Li^{3-} (**2**), $CBe_5Li_2^{2-}$ (**3**), $CBe_5Li_3^{-}$(**4**), CBe_5Li_4 (**5**), and $CBe_5Li_5^{+}$ (**6**). Bond lengths are in Å.

Important geometric parameters of the title clusters are also mentioned in Figure 2. It is apparent that the counterion insertion has an impact on the C-Be bond lengths. The most prominent structural changes are perceived in **6**, where the C-Be distances are 0.065 Å shorter than those computed for the D_{5h} form of **1**. So, the lithium cations strengthen the C-Be interactions, stabilizing the CBe_5^{4-} fragment.

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Natural population analysis (NPA) charges provided us important insights about bonding. From Table 1, it is apparent a substantial electron transfer from the peripheral atoms to carbon. The charge on carbon is -2.39 |e| for **1**. The electron transfer is gradually reduced when the number of counterions increases. For **6**, the charge on C is -2.07 |e|; supporting the stabilization of the CBe_5 core as a consequence of the Li cation interactions. The carbon atom acts as a σ-acceptor; this charge acceptance is balanced by the incorporation of the $2p_z$ electrons as part of the π-cloud (see Table 1). Note that the occupancies of $2p_z$ orbitals are lower than those of the $2p_x$ and $2p_y$ orbitals, indicating a back-donation.

The total Wiberg bond indices (WBIs)[17] of the ppC ranges from 2.48 to 2.84, i.e., the average of C-Be WBIs is 0.5, which denotes that each C-Be bond is weak, but the number of C-Be bonds compensates it. Notice that hypercoordination does not lead to violations of the octet rule.

Table 1. Smallest frequencies (ν□□□, cm^{-1}); NPA charge on ppC (q(C), |e|); total Wiberg bond indices on ppC (WBI_C), carbon valence populations (Pop), HOMO energy (E_{HOMO}, eV), HOMO-LUMO gap (gap, eV).

	ν□□□	q(C)	WBI_C	Pop	E_{HOMO}	gap
1	241	-2.39	2.48	$2s^{1.44}2p_x^{1.77}2p_y^{1.77}2p_z^{1.39}$	8.40	5.04
2	139	-2.29	2.65	$2s^{1.43}2p_x^{1.74}2p_y^{1.69}2p_z^{1.40}$	4.95	3.48
3	103	-2.24	2.69	$2s^{1.41}2p_x^{1.71}2p_y^{1.70}2p_z^{1.36}$	1.77	3.92
4	70	-2.17	2.74	$2s^{1.39}2p_x^{1.70}2p_y^{1.70}2p_z^{1.36}$	-1.33	4.41
5	63	-2.13	2.79	$2s^{1.36}2p_x^{1.70}2p_y^{1.69}2p_z^{1.35}$	-4.44	4.91
6	75	-2.07	2.84	$2s^{1.33}2p_x^{1.68}2p_y^{1.68}2p_z^{1.34}$	-9.07	7.11

The valence molecular orbitals of **6** are depicted in Figure 3. Like other phC systems,

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there is a substantial contribution of the $2p_z$ orbital of C atom to the π-orbital, in line with the mechanism proposed by Hoffmann et al.[1a] Clearly, the multicenter bonds maintain the planar pentacoordinate carbon skeleton. The HOMO-LUMO gap increases gradually with the number of counterions from **2** (3.47 eV) to **6** (7.11 eV), implying enhanced stability according to the principle of maximum hardness.[18]

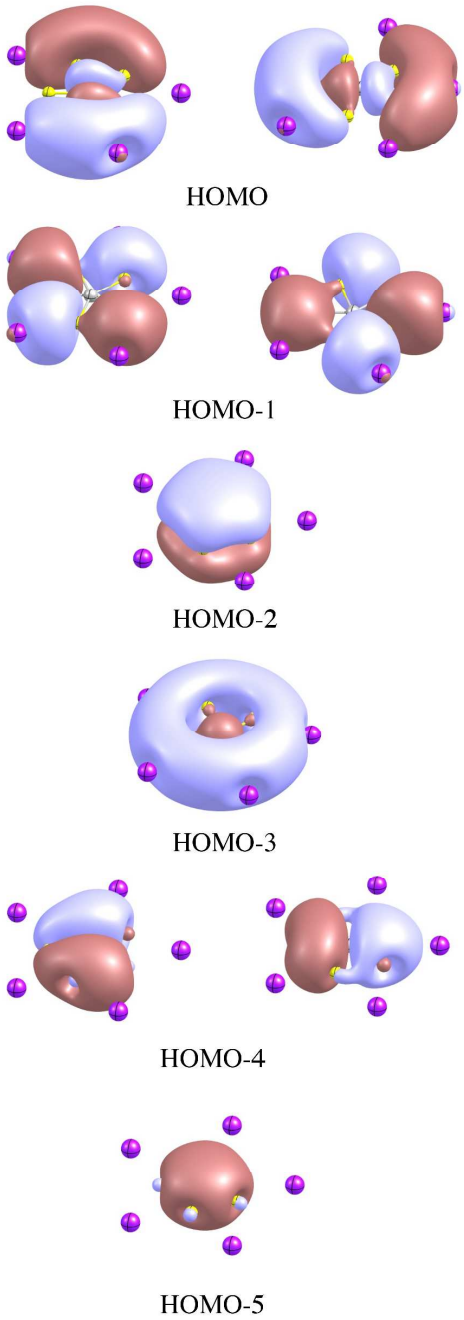

Figure 3. Valence Molecular Orbitals of **6**.

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In order to understand electron delocalization, we carried out the induced magnetic field analysis.[19] Figure 4a shows the profiles for the σ-, π-, and core contributions of the z-component of the induced magnetic field (B^{ind}_z) for the most stable form of the $CBe_5Li_5^+$ cluster. We selected the Be-C-Be triangles to compute B^{ind}_z. The external magnetic field was applied perpendicular to the molecular plane along the z-axis. The $B^{ind}_z(0)$ is lower than -50 ppm. The σ-skeleton is diatropic and similar in shape to that described for other pptC clusters. The π-system contribution is also diatropic, but its contribution is too small compared to the σ one (only 10%).

B^{ind}_z, as NICS, can be computed at any point of the space. Information provides by a grid is richer than a simple point calculation. Figure 4b depicts the B^{ind}_z contour lines of **6**, showing in which areas the magnetic response is the shielding (diatropic) or enforcing (paratropic) the external field. Clearly, these plots show that fields induced by the σ- and π-electrons have the same sign, but the intensity of σ-skeleton is stronger. Similar responses are computed for the rest of the title clusters (see Figures 7-SI to 9-SI). So, CBe_5^{4-} and its derivatives are doubly delocalized systems (σ– and π–delocalization).[20]

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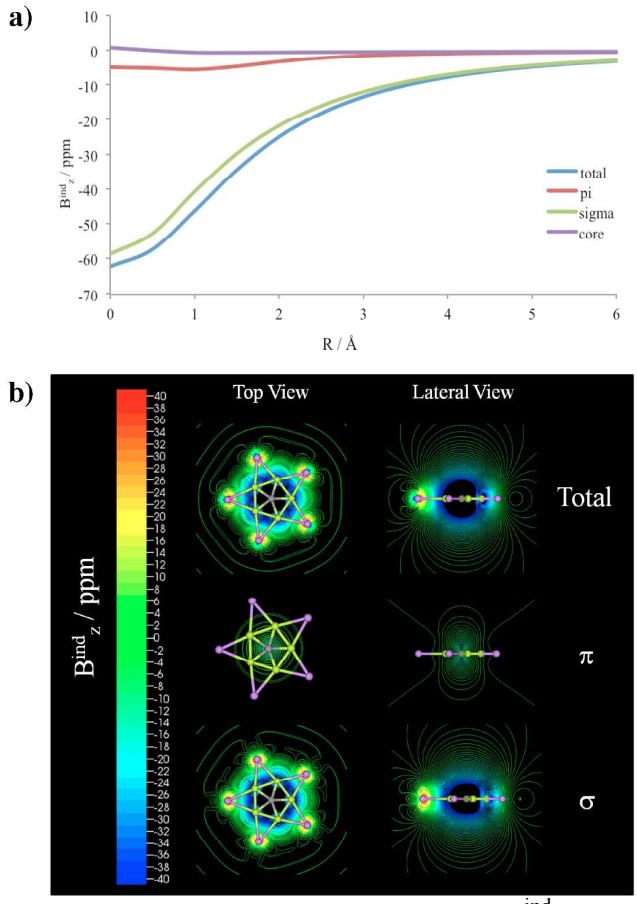

Figure 4. a) z-component of the induced magnetic field (B^{ind}_z) profiles computed at the midpoints of Be-C-Be triangles of **6**. The molecular plane lies in the *xy* plane and the B^{ind}_z profile was computed perpendicular to it at the PW91/DZVP//PBE0/def2-TZVP level. b) Contour lines of B^{ind}_z in the molecular plane and perpendicular to the molecular plane through the origin. The scale is given in ppm (or μT for an external field of 1 T).

Finally, to corroborate the kinetic stability of the title ppC clusters, BO-MD simulations were done for each cluster at 1000 K for 20 ps. The corresponding movies are included in the supplementary material. Given the strong Coulomb repulsion, structure **2** is broken after 5 ps. From **3** to **5**, the lithium atoms interchange bridged positions and even interact with the π-cloud. Note that the energy differences between the lowest-energy isomers containing a ppC are less than 10 kcal/mol. In the case of **6**, floppy behavior at this temperature is not perceived because the second most stable isomer is 11.4 kcal/mol higher

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in energy. Interestingly, in all cases the CBe_5 pentagon remains intact.

In summary, our computations show that the global minimum structures for CBe_5Li^{3-}, $CBe_5Li_2^{2-}$, $CBe_5Li_3^{-}$, CBe_5Li_4, and $CBe_5Li_5^{+}$ contain a ppC atom. Thus, the 18 valence electron preference rule suggested by Schleyer and Boldyrev[2] for planar tetracoordinate carbon systems can be extended to ppCs. The systems are primarily connected by a network of multicenter σ-bonds, in which C atom acts as σ-acceptor and this acceptance of charge is balanced by the donation of the $2p_z$ electrons to the π-cloud. The induced magnetic field analysis suggests that the clusters with formula $CBe_5Li_n^{n-4}$ (n=1-5) are doubly (σ– and π-) delocalized. The fact that these ppC-containing clusters are the lowest-lying energy forms on the corresponding potential energy surfaces raises expectations that these species can be prepared experimentally in the gas phase. The limitations of working experimentally with Be and possible dimerization of the title clusters do not escape to us, but clearly mixing Be and C leads to exotic clusters and perhaps some of them would contain planar hypercoordinate carbon centers.

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Supporting Information Available

Isomers and relative energies of CBe_5^{4-} (**1**), CBe_5Li^{3-} (**2**), $CBe_5Li_2^{2-}$ (**3**), $CBe_5Li_3^{-}$(**4**), CBe_5Li_4 (**5**), and $CBe_5Li_5^{+}$ (**6**), the Cartesian coordinates for all the reported local minima, and the z-component of the induced magnetic field (B^{ind}_z) counter lines for all the global minima.

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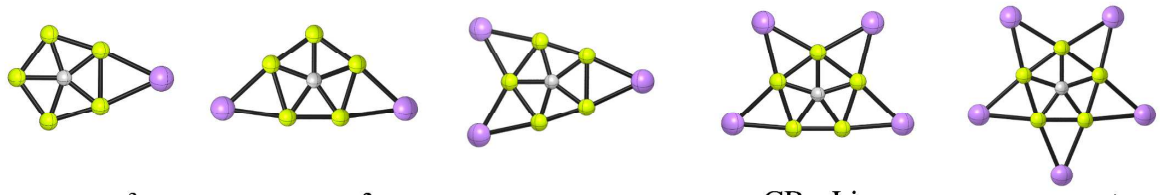
TOC



CBe_5Li^{3-} $CBe_5Li_2^{2-}$ $CBe_5Li_3^{-}$ CBe_5Li_4 $CBe_5Li_5^{+}$

Ab initio computations show that the global minimum structure of the $CBe_5Li_n^{n-4}$ clusters (n=1-5) contains a planar pentacoordinate carbon atom.

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