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 D_{3h} $CN_3Be_3^+$ and $CO_3Li_3^+$: viable planar hexacoordinate carbon prototypes†Yan-Bo Wu,^{*a} Yan Duan,^a Gang Lu,^b Hai-Gang Lu,^a Pin Yang,^a Paul von Ragué Schleyer,^c Gabriel Merino,^d Rafael Islas^{ef} and Zhi-Xiang Wang^{*b}

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Searches for planar hexacoordinate carbon (phC) species comprised of only seven atoms uncovered good CX_3M_3 prototypes, D_{3h} $CN_3Be_3^+$ and $CO_3Li_3^+$. The latter is the global minimum. It might also be possible to detect the deep-lying kinetically-viable D_{3h} $CN_3Be_3^+$ local minimum, based on its robustness toward molecular dynamic simulations and its very high isomerization barrier.

Violations of the strong preference of tetra-coordinate carbon for tetrahedral geometries have intrigued chemists, especially since Hoffmann *et al.* proposed strategies to reduce stereomutation barriers via planar tetra-coordinate carbon (ptC) arrangements in 1970¹ and the Schleyer–Pople computations predicted the first molecule with a ptC (1,1-dilithiocyclopane) in 1976.² Since then numerous compounds with ptC's have been characterized experimentally and explored computationally.³ Such “planar hypercoordinate” chemistry has broadened significantly more recently to include planar species where the central atom is not limited to carbon and the coordination number is more than four. Species with planar pentacoordinate and hexacoordinate carbons (ppC's or phC's) have been designed *in silico*.⁴

Planar tetra-coordinate or hyper-coordinate arrangements with other main group atoms (*e.g.* N, O, and Si) or transition metals (*e.g.* Ag, Au, Co, Ru, Cd, and Hg) have also been reported.⁵ Moreover, the appreciation of “planar chemistry” prospects has led to proposed applications of planar hyper-coordinate carbon structural units to design solid or nano-materials with novel properties.⁶

Unlike ptCs where carbon planarity is forced by a rigid molecular framework,⁷ ptCs in simple unconstrained pentaatomic systems were predicted by Schleyer and Boldyrev in 1991.^{5a} The Wang–Boldyrev group detected isoelectronic species (*e.g.*, CA_4^- , $NaCA_4^-$, CA_3Si^- , and CA_3Ge^-) experimentally in 1999–2000.⁸ Recent experimental evidence for D_{8h} CoB_8^- and D_{9h} RuB_9^- reported by the Wang–Boldyrev group⁵ⁱ also verified the theoretically predicted planar bonding.^{5f} D_{10h} NbB_{10}^- and TaB_{10}^- further extended the predicted coordination number in planar clusters.^{5j,k} However, experimental realization is often limited since most theoretically predicted species with planar hypercoordinate bonding are not both thermodynamically and kinetically viable. Under the Wang–Boldyrev gas phase experimental conditions, the isomer abundance is governed by thermodynamic stability and global minima are generated preferentially. Nevertheless, kinetic persistence is equally important for viability. A vast number of common but higher energy “metastable” molecules owe their existence to the large barriers precluding their isomerization to more stable forms or their further reaction.

However, the thermodynamic stability criterion encourages searches for lower-lying minima with planar hypercoordinate bonding, since they might be observable in the gas phase. Thus, CCu_4^{2+} , CCu_3Ni^+ , CCu_2Ni_2 , CE_4^{2-} ($E = Ga, In, Tl$), CA_3Sn^- , CA_3Pb^- , CB_4^+ , CBA_3^{2-} , and CNA_3 *etc.* possess ptC global minima.⁹ More elaborate examples include the D_{2h} C_2Al_4 global minimum with two ptCs,¹⁰ the star-like D_{5h} $C_5Al_5^-$ with five ptCs (nearly a global minimum),¹¹ and the planar pentacoordinate carbon (ppC) global minima CA_5^+ , CA_4Be , $CA_3Be_2^-$, CA_2Be^{2-} , $LiCA_2Be_3^-$ and $CEBe_5^-$ ($E = Al, Ga, In, Tl$).^{4e–h} Due to crowding around the small carbon, a 7-atom phC species is less likely to be a global minima. But how near can one approach this goal? The searches employed here can help guide future design strategies. Both D_{3h} $CO_3Li_3^+$, the global minimum, and D_{3h} $CN_3Be_3^+$, a kinetically viable local minimum, illustrate such species. Although the

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† Electronic supplementary information (ESI) available: The structures of higher-lying isomers of $CN_3Be_3^+$ and $CO_3Li_3^+$, the scheme describing the designing ideal of this work, the figure of occupied π MOs, the energies and Cartesian coordinates of mentioned species in the text and the full form of ref. 17 and 18. See DOI: 10.1039/c2cp41822c

latter is the lowest local minimum (6.1 kcal mol⁻¹ higher in energy than the global minimum), its good kinetic stability, suggested by our *ab initio* Born–Oppenheimer molecular dynamic (BOMD) simulations, and the high barriers toward isomerization hold promise for experimental realization.

All key species in this study were optimized and then characterized to be energy minima or saddle points at both B3LYP and MP2 levels, combined with aug-cc-pVTZ basis sets. The geometries were reoptimized at the CCSD(T)/aug-cc-pVTZ level. The latter refined geometric and energetic results are discussed here. The stochastic search method used previously¹² was applied again to explore potential energy surfaces (PESs).^{4e,10,11} To guarantee the convergence of PES exploration, we ran four sets of searches for singlet surfaces and two sets for triplet surfaces. Each set generated random structures for optimization and vibrational frequency analysis at B3LYP/6-31G(d). The minima at this level were then subjected to above B3LYP/, MP2/ and CCSD(T)/aug-cc-pVTZ computations. The four lowest energy isomers of CN₃Be₃⁺ and CLi₃O₃⁺ are shown in Fig. 1; other minima are given in the ESI.† The kinetic stability of *D*_{3h} CN₃Be₃⁺ (**2a**) was examined by the BOMD¹³ simulations (Fig. 2) and by the following ring-opening reaction to the global minimum (at B3LYP/6-31G(d) and B3LYP/aug-cc-pVTZ levels, respectively). The natural bond orbital (NBO)¹⁴ and the nucleus-independent chemical shift (NICS)¹⁵ analyses were performed at the B3LYP/aug-cc-pVTZ level. The electron affinities (EAs) of these cationic species were computed at OGVF/aug-cc-pVTZ. For a deeper analysis of the aromatic behavior, the induced magnetic field was computed perpendicular to the molecular plane for **2a** and **3a**.¹⁶ For both systems, a profile of the z-component of the **B**^{ind} (or NICS_{zz}) was computed at the middle of the C–Be or C–Li contact. For **3a**, the ring selected was one of the four-membered rings formed by the phC, one lithium and two oxygen atoms. The shielding tensors were computed at the PW91/DZVP level in the deMon-NMR package, the CCSD(T) computations were performed with MOLPRO 2008.1,¹⁷ while other calculations used the GAUSSIAN 03 program.¹⁸

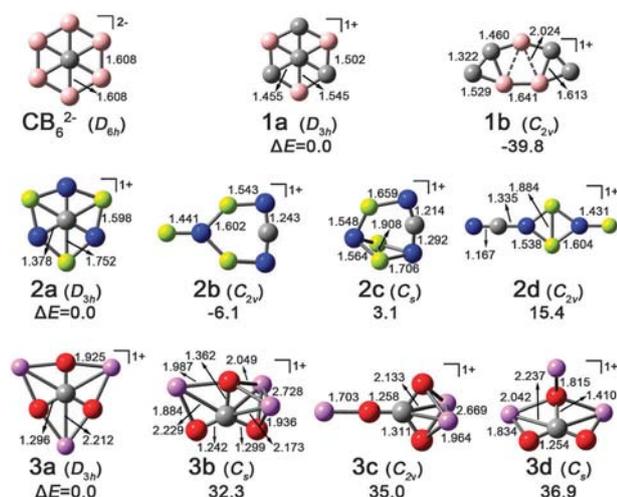


Fig. 1 CCSD(T)/aug-cc-pVTZ optimized structures and relative energies (ΔE, in kcal mol⁻¹) of *D*_{6h} CB₆²⁻, **1a**, **1b**, and four lowest energy isomers of CN₃Be₃⁺, and Li₃CO₃⁺. Bond lengths are in Å. Color codes: C: grey, N: blue, O: red, B: pink, Be: yellow, and Li: purple.

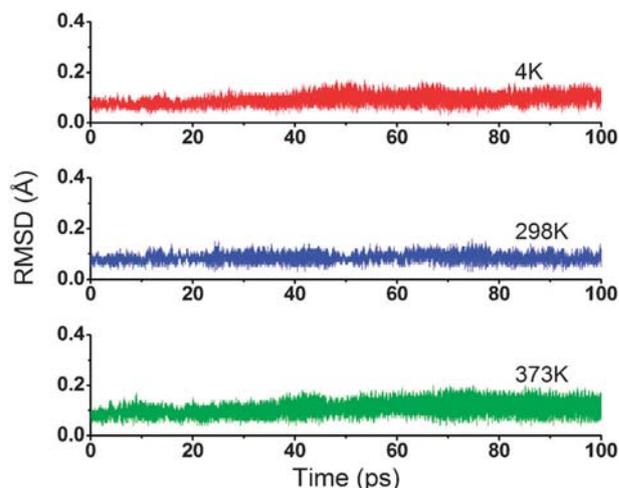


Fig. 2 RMSD vs. time in the BOMD simulations of **2a** at 4, 298, and 373 K, respectively.

The present study was inspired by *D*_{6h} CB₆²⁻,^{4a} a phC local minimum that is 34.4 kcal mol⁻¹ higher in energy than its most stable form.¹⁹ As is well known, the “rigidity” of tetrahedral carbon can be “softened” by electropositive substituents.^{6i,10,11,20} Indeed, most of the identified ptC and ppC global minima have metal ligands (*e.g.* Li, Be, B, Al, Cu, Ni, *etc.*).^{9–11} Since sigma donating electronic effects also should favor phC’s, we replaced the boron perimeter of CB₆²⁻ isoelectronically with CBe or NLi units in alternation. However, the resulting *D*_{3h} C₄Be₃²⁻ and *D*_{3h} CN₃Li₃²⁻ structures (Scheme S1, ESI†) proved to be second-order saddle points. The double negative charge evidently is not accommodated well. Hence, we explored the isoelectronic 24 valence electron species with +1 charge: *D*_{3h} C₄B₃⁺ (**1a**), CN₃Be₃⁺ (**2a**), and CLi₃O₃⁺ (**3a**). B3LYP/ and MP2/aug-cc-pVTZ computations levels revealed true minima. The lowest energy isomers, shown in Fig. 1, were located by extensive PES searches. As expected, changing the key ligand atom from B to Be and then to Li improves the relative thermodynamic stability of the isoelectronic *D*_{3h} species **1a**, **2a**, and **3a**. While **1a** is a local minimum, 39.8 kcal mol⁻¹ less stable than the C₄B₃⁺ global minimum (**1b**), this difference diminishes in CN₃Be₃⁺: *D*_{3h} **2a** is the second lowest minimum but its energy is only 6.1 kcal mol⁻¹ higher than its global minimum (**2b**). The extreme case, CO₃Li₃⁺, has a *D*_{3h} **3a** global minimum, which is 32.3 kcal mol⁻¹ more stable than the second lowest isomer (**3b**). We note that a study in 2005 analysing CO₃M₃⁺ had included CO₃Li₃⁺,²¹ and a recent study of superalkali cations also explored the PES of CO₃Li₃⁺. The later work only located **3a** and **3b**, but reported much higher third and fourth lowest isomers, rather than **3c** and **3d**.²² The triplet state PES’s of CN₃Be₃⁺ and CLi₃O₃⁺ were also explored, but these are unfavorable; the best triplet isomers are 30.2 and 110.7 kcal mol⁻¹ higher in energy than singlet **2a** and **3a**, respectively, at the B3LYP/aug-cc-pVTZ level. The global minimum character of **3a** should guarantee its experimental realization. Indeed, an ion with the corresponding mass (*m/z* = 81) has been detected recently by laser vaporization mass spectrometry of lithium carbonate.²³

We studied the kinetic viability of **2a** as a potential phC species, albeit it is the second lowest energy isomer on the CN₃Be₃⁺ PES. Fig. 2 shows the *ab initio* BOMD simulation

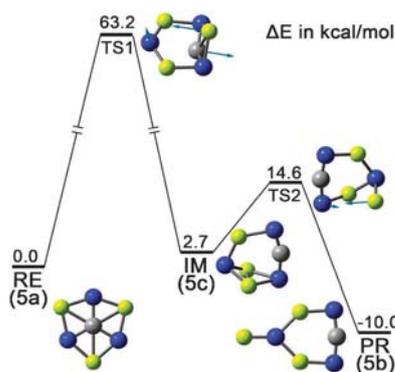


Fig. 3 Energy profile for the isomerization of **2a** to **2b** at B3LYP/aug-cc-pVTZ. The arrows shown in TS1 and TS2 depict the vibrational modes of the imaginary frequencies.

runs at 4, 298, and 373 K for 100 ps. The structural undulations are depicted by the curve of root-mean-square deviations (RMSD, in Å) vs. simulation time. As Fig. 2 also shows, all three RMSD curves have no sharp increase. This implies that the basic structure of **2a** is maintained well during the simulation. The fluctuations of the curves are small. The RMSD values of simulations at 4, 298, and 373 K, range from 0.03, 0.03, and 0.04 to 0.16, 0.17, and 0.20 Å, respectively. The average RMSD values for these three sets of simulations are only 0.08, 0.09, and 0.11 Å, respectively. The dynamic simulations suggest that the structure of **2a** is rather rigid at all three temperatures. Likewise, the computed barrier for isomerization of **2a** to the global minimum **2b** (Fig. 3) is prohibitively high, 63.2 kcal mol⁻¹ at B3LYP/aug-cc-pVTZ. The third lowest energy isomer, **2c**, is an intermediate on the PES but is not as viable kinetically.

The interatomic distances, $r_{C-C} = 1.455$ and $r_{C-B} = 1.545$ Å in **1a**, and $r_{C-N} = 1.378$ and $r_{C-Be} = 1.752$ Å in **2a**, are all well within the normal bond lengths, so that **1a** and **2a** can be regarded unambiguously as phC species. However, the longer C–Li distance (2.212 Å) in **3a** raises the issue of the degree of coordination. This key point is discussed below.

The Wiberg bond indices (WBI's) to the central carbon in CB_6^{2-} (C–B = 0.65), **1a** (C–C = 0.94, C–B = 0.44), **2a** (C–N = 1.28, C–Be = 0.07) and **3a** (C–O = 1.28, C–Li = 0.01) reveal the expected electronegativity influence. However, the total WBI's of the central carbon atoms in these species (3.92, 4.14, 4.05, and 3.86, respectively) are all close to 4. Although the central carbons in CB_6^{2-} and **1a** are more evenly bound covalently to the perimeter, the partial ionic character of the bonding interactions in **2a** and **3a** increases their thermodynamic stability relative to their isomers.

Besides the direct central atom–ligand bonding, ligand–ligand interactions also stabilize planar hypercoordinate species importantly. These interactions differ somewhat in **2a** and in **3a**. In addition to the obvious ionic interactions between the Be's ($q_{Be} = 0.92 |e|$) and the CN_3 moiety ($q_{total} = -1.76 |e|$) in **2a**, the significant $WBI_{Be-N} = 0.44$ values suggest that the Be–N covalent interactions also are efficient, and help decrease the Be–N distance. As the C–Be distance in **2a** (1.752 Å) is well within typical (*ca.* 1.93 Å) C–Be bond lengths C–Be atoms are close enough to C to qualify as ligands in **2a**, the $WBI_{Be-C} = 0.07$ values are small, so that the C–Be bonding is largely ionic.

The same is true for **3a** ($WBI_{Li-C} = 0.01$), which has a much longer (2.212 Å) C–Li distance. Clearly, **3a** can be regarded simply as a planar CO_3^{2-} carbonate dianion stabilized electrostatically by the three bridging Li^+ counterions. But does it have a “planar hexacoordinate carbon”? The nature of the bonding (ionic or covalent) is *not* considered for this purpose. The “coordination” depends on “the number of nearest neighbors” or on “the number of atoms touching the given atom”.²⁴ As the 2.212 Å C–Li distances in **3a** are, in fact, shorter than the 2.31 Å C–Li distances in the methyl lithium tetramer and hexamer²⁵ (where each carbon is bonded to three H's and three Li's and is clearly hexacoordinate), we consider planar **3a** to be hexacoordinate as the carbon “touches” six atoms.

Like benzene and CB_6^{2-} , **1a–3a** possess six π electrons (the actual π occupancies are 5.98, 5.96, and 5.98, respectively.) The symmetries of the three occupied π orbitals of **1a–3a** (Fig. S3, ESI†) are like those of benzene. However, the π electron density resides to a greater extent on the more electronegative atoms (C, N, and O).

The B_z^{ind} studies were performed for **2a** and **3a**. In both cases, the B_z^{ind} values in the middle of any C–E bonds (E = Li, Be) are positive (Fig. 4). The minimum B_z^{ind} values (–8 and –5 ppm in **2a** and **3a**, respectively) are located at about 1.5 Å above the molecular plane. Clearly, the σ -contribution is the most important one. Note that the contribution of the π -system is almost negligible. Like in borazine or $Si_4C_4H_8$,²⁶ the inherent electronegativity difference between Be and N or Li and O polarizes the system, reducing electron delocalization. This magnetic index shows that **2a** and **3a** are less delocalized than other reported phC systems. So, electron delocalization is not the determining factor for the stability of **2a** and **3a**.

We computed the electron affinities (EA) of **2a–2c** and **3a** (4.04, 6.97, 5.14, and 2.81 eV, respectively) to facilitate experimental identification. The smaller EA of **2a** contributes to its stability vs. **2b** and **2c**. The EA of **3a** is even lower (2.81 eV).

In summary, we examined three phC candidates with D_{3h} symmetry, $C_4B_3^+$ (**1a**), $CN_3Be_3^+$ (**2a**), and $CLi_3O_3^+$ (**3a**), derived by isoelectronic substitution of the ligand atoms of the parent phC species, CB_6^{2-} . Both the lithium and the beryllium bonding are largely ionic. The C–Li distances in **3a**, the only global minimum in the Fig. 1 set, are not too long for the Li's to participate in the carbon hexacoordination. In contrast, all

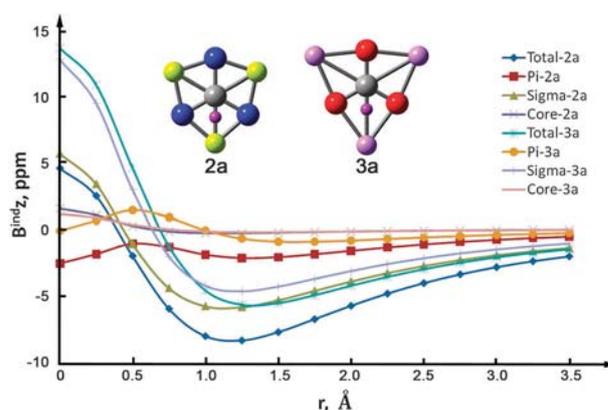


Fig. 4 Profile of the z-component of the induced magnetic field, B_z^{ind} . The external field is $|\mathbf{B}^{ext}| = 1.0$ T and the units of the B_z^{ind} are ppm.

the C–ligand distances in **1a** and **2a** are near normal bond lengths, so **1a** and **2a** are pH⁺C's as well. However, the energy of **1a** is 39.8 kcal mol⁻¹ higher than that of its global minimum, **1b**. Consequently, **2a**, the second lowest isomer on its PES, is our best kinetically viable pH⁺C prospect. Moreover, the *ab initio* BOMD simulations revealed that its structure is rather rigid and the isomerization pathway to the 6.1 kcal mol⁻¹ lower energy global minimum (**2b**) has a very high barrier. Hence, it might be possible to detect **2a** as a kinetically viable local minimum. Another promising approach would be to replace the Be atoms in **2a** by other metals.

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