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Planar Tetracoordinate Carbon Species Involving Beryllium Substituents

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Planar tetracoordinate carbon (ptC) arrangements can be achieved by employing multiple substituents based on beryllium, despite its rather weak π-acceptor ability. A variety of ptC-containing examples, some with more than one ptC, have been designed computationally by elaborating the planar $C(BeH)_4^{2-}$ prototype at B3LYP/6-311++G(3df,2p) and MP2/6-311++G(3df,2p) levels of theory for some small ptC representatives. The prototype prefers a D_{2h} paramagnetic triplet ground state due to Hund's rule, rather than a singlet. The highly polarized C−Be bonding weakens the rigidity of the tetrahedral carbon in T_d $C(BeH)_4$ enormously, and the enhancement of both C−Be and Be_4 peripheral covalent bonding exerted by the extra electrons stabilizes the ptC eventually. The delocalization of the two p_π electrons is only modest, but their density on the most electronegative carbon atom helps stabilize the ptC arrangement. This is in contrast to the conventional strategy to delocalize p_π lone pairs for stabilizing the ptC arrangement. Various strategies to achieve neutral derivatives with ptCs are demonstrated.

Introduction

A curious exception to the usual bonding patterns of organic compounds, planar tetracoordinate carbon (ptC), has fascinated chemists[1] since the 1970s, when Hoffmann et al.[2] suggested ways to reduce the unfavorable energies of ptC dispositions and the systematic Schleyer−Pople computational investigations predicted the first ptC minimum, 1,1-dilithiocyclopropane.[3] PtC species comprised of only five atoms, the smallest possible number (e.g., *cis*- and *trans*-CAl_2Si_2), were first designed computationally by Schleyer and Boldyrev in 1991.[4] Their predictions stimulated a continuing number of theoretical studies[5–8] and culminated in the remarkable experimental realization of the close isoelectronic analogs, CAl_3Si^- and CAl_3Ge^-, by Wang et al. in 2000.[6] CAl_4^- and $NaCAl_4^-$ also have been detected experimentally.[7,8] The smallest all-carbon ptC species, C_5^{2-}, has been predicted.[9,10] The potential of using small ptC building blocks, such as C_5^{2-},[11] CAl_3Si,[12] and CAl_4^{2-},[13] to construct novel materials has been explored theoretically.

The electronic structure of planar D_{4h} methane is unfavorable:[2] only six electrons are available for the four CH bonds, and a nonbonding p_π lone pair resides on the central ptC. The "electronic" strategy of Hoffmann et al.[2] uses σ donors and π acceptors to stabilize the ptC arrangement. To

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overcome bond angle strain, the "mechanical" strategy incorporates ptC's into three- or four-membered rings. The two approaches can be combined successfully to achieve ptC's, as exemplified by 1,1-dilithiocyclopropane ($C_2H_4C_{ptc}Li_2$)[3] and $C_2H_2C_{ptc}B_2H_2$.[14] Nevertheless, Rasmussen and Radom[15] succeeded in designing alkaplanes with ptC's computationally using purely "mechanical" strategies. By combining electronic with such "brute-force" cage effects, Wang and Schleyer[16] conceived a family of boraplane molecules with ptC's. The boraplanes accommodate the two electrons corresponding to the p_π lone pair in D_{4h} methane in a low-energy tangential molecular orbital (MO) involving B_4 perimeters around the periphery of the central ptC. Isoelectronic substitution can mutate boraplanes further to achieve CC_4-type ptC's.[17] The electron deficiency of boron atoms also has been used to realize molecules with planar penta- and hexacoordinated carbons.[18–21]

Are electron-deficient group 2 atoms, beryllium in particular, capable of stabilizing ptC's? The favorable effect of substituting BeH groups was pointed out by the Schleyer group[3] in 1976, and later the effect was also revealed by Dewar and Rzepa's[22] modified neglect of diatomic overlap calculations, which predicted that D_{4h} $C(BeH)_4$ was 25.5 kcal/mol less favorable than T_d $C(BeH)_4$. However, no experimental or computed ptC molecules using group 2 atoms have been achieved. We now show how beryllium can be employed to stabilize ptC arrangements by means of theoretical computations.

Computational Methods

All reported structures were optimized with the Gaussian 03 program[23] at the B3LYP/6-311++G(3df,2p) level of theory, and the natures of the stationary points were ascertained by vibrational frequency analyses. The natural bond orbital (NBO) analyses,[24] performed at the same level, were used to characterize the electronic structures of molecules. Caveats about density functional theory reliability, recently raised by several authors,[25] were addressed by reoptimizing small ptC representatives [**4**$^{2-}$**-T**(D_{2h}), **5-D**(D_{4h}), **6**$^{2-}$**-S**(C_{2v}), **7-S**(D_{2h}), **8-S**(C_{2v}), **9-D**(C_{2v}), **11-S**(C_{2v}), **12-S**(C_{2v}), **13-S**(C_{2v}), and **14-S**(C_{2v})] at the MP2(fc)/6-311++G(3df,2p) level. The differences in geometries (see Figures 1 and 4) between the two levels are small. The planar structures are still minima, and the variations of the smallest vibrational frequencies are less than 28 cm^{-1}. Hence, the following discussion is based on the B3LYP/6-311++G(3df, 2p) results.

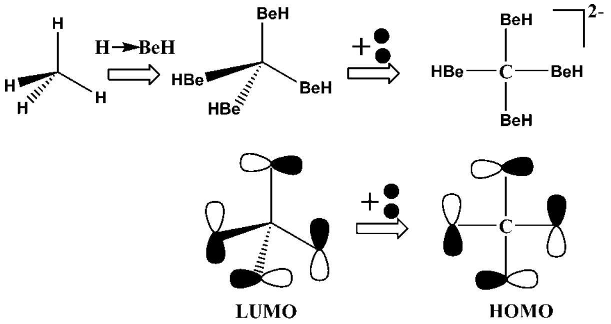

Figure 1. Basic idea to planarize T_d $C(BeH)_4$.

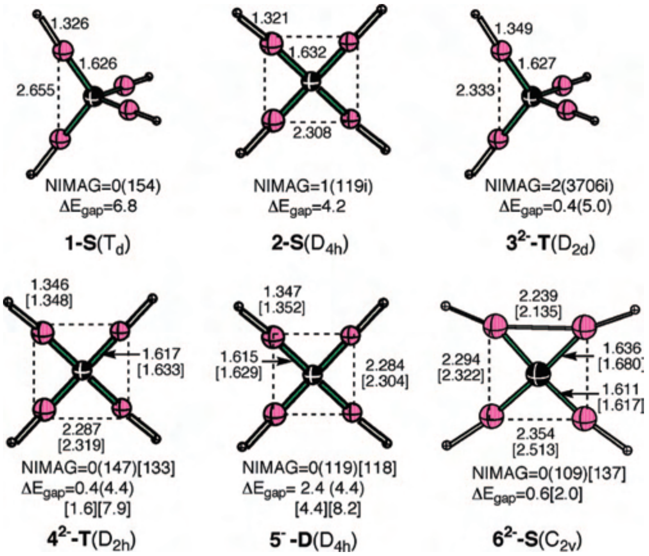

Figure 2. B3LYP/6-311++G(3df,2p) geometries of **1-S**(T_d)-**6**$^{2-}$−S(C_{2v}), including the important bond lengths in angstroms, the NIMAGs, and the smallest vibrational frequencies in centimeters^{-1}, and the HOMO–LUMO gaps (ΔE_{gap}) in electrovolts. In **3**$^{2-}$**-T**(D_{2d}), **4**$^{2-}$**-T**(D_{2h}), and **5**$^{-}$**-D**(D_{4h}), the HOMO–LUMO gaps in the parentheses are for β electrons. The values in the square brackets were calculated at the MP2(fc)/6–311++G(3df,2p) level. The black, red, and white balls represent carbon, beryllium, and hydrogen atoms, respectively.

Results and Discussion

Figure 1 describes the strategy to achieve a ptC arrangement. The replacement of the four H's in methane by four

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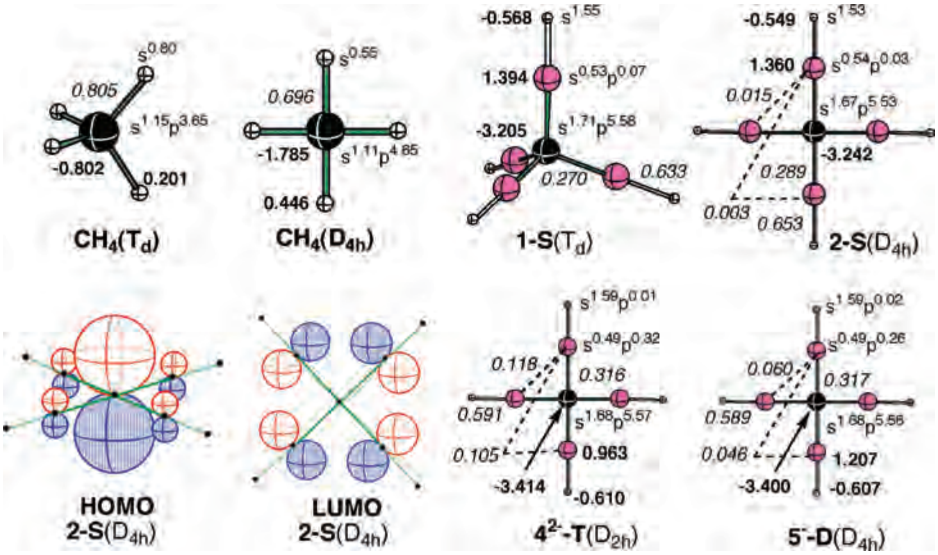

Figure 3. Comparison of methane and C(BeH)$_4$ NBO charges (bold), Wiberg bond indices (italic), and natural electron configurations in planar and T_d geometries. NBO results of **4**$^{2-}$**-T**(D_{2h}) and **5**$^{-}$-**D**(D_{4h}) are also given, as well as the HOMO and LUMO of **2-S**(D_{4h}). The red, black, and white balls represent beryllium, carbon, and hydrogen atoms, respectively.

BeH groups results in a "classical" T_d minimum, C(BeH)$_4$ [**1-S**(T_d), Figure 2]. While there are four formal C−Be and four formal Be−H single bonds, these are highly polarized and have only partial covalent character. Consequently, the BeH substituents weaken the rigidity of the tetrahedral carbon geometry enormously. While the $T_d - D_{4h}$ methane energy difference is ~130.0 kcal/mol,[26] T_d C(BeH)$_4$ is only 13.4 kcal/mol more stable than the planar singlet geometry [**2-S**(D_{4h})]. As **2-S**(D_{4h}) is a first-order saddle point with a smallest vibrational frequency (SVF) of 119i cm^{-1}, the D_{4h} CH$_4$ has *four* imaginary frequencies (SVF = 4189i cm^{-1}).

Figure 3 compares the electronic structures of methane and C(BeH)$_4$, given by NBO analyses, in planar and tetrahedral geometries. Unlike the large differences between T_d and D_{4h} methane, the **1-S**(T_d) and **2-S**(D_{4h}) structures of C(BeH)$_4$ have similar carbon natural electron configurations (2s$^{1.71}$2p$^{5.58}$ and 2s$^{1.67}$2p$^{5.53}$), NBO charges (−3.205 and −3.242e), and total Wiberg bond indices (WBI; 1.292 and 1.373, respectively). The total WBI, not shown in Figure 3, includes the four WBIs of the C−Be bonds and the four small contributions due to the 1–3 C and H interactions. The individual 1–3 contributions in **1-S**(T_d) and **2-S**(D_{4h}) are 0.053 and 0.055, respectively. As expected, the C−H bonds in D_{4h} methane (WBI = 0.696) are weaker than those in the T_d form (WBI = 0.805). In contrast, the C−Be WBI (0.289) in planar **2-S**(D_{4h}) is larger than that (0.270) in **1-S**(T_d). Reflecting their ionic character, both of these CBe WBIs are much smaller than the CH WBIs in CH$_4$. The σ-electron donation by beryllium, resulting in partial ionic bonding, also is found for lithium in CLi$_4$. D_{4h} CLi$_4$ [**SI1-S**(D_{4h})] is 12.4 kcal/mol less stable than the T_d form [**SI2-S**(D_{4h})]. The effects of substitution also are substantial in O(BeH)$_2$ [**SI3-S**($D_{\infty h}$)] and N(BeH)$_3$ [**SI4-S**(D_{3h})], which prefer linear and D_{3h} geometries, rather than the C_{2v} of H$_2$O and C_{3v} of NH$_3$, respectively. How can the ptC in **2-S**(D_{4h}) be stabilized?

The electronic configuration, $1a_1^2 2a_1^2 1t_2^6 3a_1^2 2t_2^6 4a_1^2 3t_2^6 e^0$, of T_d C(BeH)$_4$ [**1-S**(T_d)] differs from $1a_1^2 2a_1^2 1t_2^6 3a_1^0$ for T_d methane. As the LUMO of **1-S**(T_d) is a doubly degenerate pair of antibonding MOs, equal occupation of these MOs, as in the triplet state of the dianion, D_{2d} C(BeH)$_4^{2-}$ [**3**$^{2-}$**-T**(D_{2d})], is unfavorable; the D_{2d} structure has two imaginary frequencies (SVF = 3706i cm^{-1}) and is 28.0 kcal/mol less stable than the planar triplet minimum **4**$^{2-}$**-T**(D_{2h}) (see below). There are better possibilities. As emphasized in Figure 1, one LUMO component of **1-S**(T_d) correlates with a favorable tangential bonding orbital in planar **2-S**(D_{4h}). The possibility of stabilizing the ptC by occupying this tangential MO obviously is not shared by methane. The large negative orbital energy of the LUMO (−3.3 eV) of **2-S**(D_{4h}) facilitates its accommodation of extra electrons. Analogous tangential bonding orbitals are important in stabilizing other ptC molecules such as boraplanes[14] and pentatomic species (e.g., CAl$_2$Si$_2$[4] and their isoelectronic analogs such as CAl$_4^-$ and CAl$_4^{2-}$).[6–8] BeH and Al are isoelectronic, but the electrons used to form the BeH bond in C(BeH)$_4^{2-}$ occupy the nonbonding orbitals in (Al$_4^{2-}$).[7,8] The optimization of doublet [**5**$^-$**-D**(D_{4h})], singlet [**6**$^{2-}$**-S**(C_{2v})], and triplet [**4**$^{2-}$**-T**(D_{2h})] C(BeH)$_4^-$ led to true minima with ptC's. However, the HOMO–LUMO gap of singlet **6**$^{2-}$**-S**(C_{2v}) is small (0.6 eV), and it is 4.4 kcal/mol less stable than the triplet. Hence, C(BeH)$_4^{2-}$ has a D_{2h} paramagnetic triplet ground state [**4**$^{2-}$**-T**(D_{2h})]. Multireference methods are required to describe the excited singlet reliably. Hund's rule elucidates the triplet over singlet preference for C(BeH)$_4^{2-}$.

The D_{4h} methane HOMO is a p$_\pi$ lone pair on the central ptC.[2] The corresponding orbitals in **4**$^{2-}$**-T**(D_{2h}) and **5**$^-$**-D**(D_{4h}) are doubly occupied, similar to the LUMO of neutral D_{4h} C(BeH)$_4$ shown in Figure 3, and the lone pair is slightly delocalized to the Be p$_\pi$ atomic orbitals (AOs) of the CBe$_4$ moiety. This is different from Gribanova et al.'s[14] C$_2$H$_2$C$_{\text{ptc}}$B$_2$H$_2$ [**SI5-S**(C_{2v})] in which the p$_\pi$ electrons are effectively delocalized among the two three-membered rings

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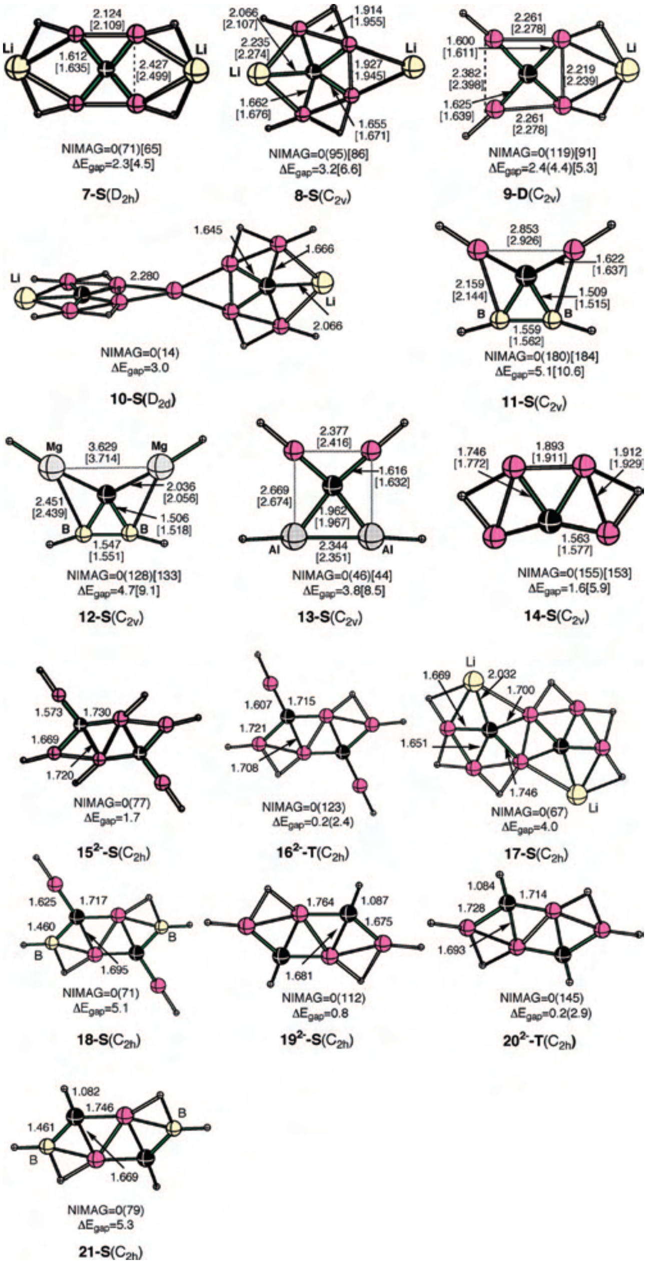

Figure 4. B3LYP/6-311++G(3df,2p) geometries of **7-S**(D_{2h})−**21-S**(C_{2h}), including the important bond lengths in angstroms, the number of imaginary frequencies (NIMAG), and the smallest vibrational frequencies in centimeters^{-1}, and the highest occupied MO−lowest unoccupied MO (HOMO–LUMO) gaps (ΔE_{gap}) in electrovolts. The values in the square brackets were calculated at the MP2(fc)/6-311++G(3df,2p) level. The unlabeled red, black, and white balls represent beryllium, carbon, and hydrogen atoms, respectively.

and the boron atoms function as π acceptors. As indicated by the WBI values, relative to neutral **2-S**(D_{4h}), the covalent bonding between ptC and Be in **4^{2-}-T**(D_{2h}) and **5^{-}-D**(D_{4h}) is enhanced, so is the peripheral covalent bonding involved in the Be_4 perimeter. Note the substantially larger peripheral Be−Be WBI values [0.118 and 0.060 in **4^{2-}-T**(D_{2h}) and **5^{-}-D**(D_{4h}), respectively] than that (0.015) in **2-S**(D_{4h}).The enhancement of covalent bonding stabilizes the ptC's in **4^{2-}-T**(D_{2h}) and **5^{-}-D**(D_{4h}). Recall that the neutral T_d **1-S**(T_d) is only 13.4 kcal/mol more favorable than the planar **2-S**(D_{4h}). Despite the small energy difference between D_{4h} and T_d CLi_4 (12.4 kcal/mol), the addition of extra electrons does not help stabilize the ptC in D_{4h} CLi_4. The planar singlet [**SI6-S**(D_{4h})] and triplet [**SI7-S**(D_{4h})] CLi_4^{2-} and doublet CLi_4^{-} [**SI8-S**(D_{4h})] are all not minima. This indicates that the enhancement of covalent bonding is important to stabilize the ptC's in **4^{2-}-T**(D_{2h}) and **5^{2-}-D**(D_{4h}); lithium is less powerful to bond covalently than beryllium.

The similar tangential MO in the B_4 perimeter of the boraplanes[16] accepts the electrons corresponding to the nonbonding p_π lone pair in D_{4h} methane. In contrast, the p_π orbital (A_{2u}) in neutral D_{4h} **2-S**(D_{4h}) is occupied in preference to the tangential (B_{2g}) MO. We suggest two reasons. Since the C versus Be electronegativity difference is greater than that for C versus B, the carbon electron density is greater in **2-S**(D_{4h}) than in the boraplanes. Due to the relatively smaller attraction of electrons to beryllium than to boron nuclei (i.e., the smaller π-acceptor ability of Be p AOs than that of B p AOs), occupation of the peripheral Be_4 tangential orbital is not as favorable energetically as that of the B_4 tangential orbital in boraplanes.[16] This also explains why $C(BeH)_4^{2-}$ follows Hund's rule and prefers a triplet, rather than a singlet, ground state, by doubly occupying the tangential orbital. The occupation of the p_π lone pair MO in **4^{2-}-T**(D_{2h}) and **5^{-}-D**(D_{4h}) also implies that such lone pairs do not necessarily preclude ptC arrangements. The geometrical preference also depends on the surrounding chemical environment. The anionic electrons in **4^{2-}-T**(D_{2h}) and **5^{-}-D**(D_{4h}) are stabilized by occupying the p_π MO largely involving the electronegative carbon. In contrast, because the π lone pair in the D_{4h} methane is unfavorable, how to delocalize the lone pair is the basis for stabilizing ptC in the conventional strategies.[1,2]

The paramagnetic polyanionic triplet [**4^{2-}-T**(D_{2h})] discussed here illustrates how the ptC's can be stabilized, but they are not good candidates for experimental realization. Neutral species avoid Coulomb repulsion and are more promising. Several basic strategies, including counterion stabilization and isoelectronic replacement, can be used to achieve neutral species with ptC's. When added to **4^{2-}-T**(D_{2h}), lithium cations result in planar minima, **7-S**(D_{2h}) and **8-S**(C_{2v}) (Figure 4). Relatively large HOMO–LUMO gaps for **7-S**(D_{2h}) and **8-S**(C_{2v}), 2.3 and 3.2 eV, respectively, characterize their singlet ground states. Structure **SI9-S**(D_{2d}), with an imposed T_d-like carbon, has six imaginary frequencies and is 38.2 and 52.7 kcal/mol higher in energy than **7-S**(D_{2h}) and **8-S**(C_{2v}), respectively. The doublet **9-D**(C_{2v}), isoelectronic with **5^{-}-D**(D_{4h}), is also a minimum. Two $C(BeH)_4^{2-}$ units can be neutralized in a joined Li−C(BeH)$_4$−Be−C(BeH)$_4$−Li arrangement; the perpendicular [**10-S**(D_{2d})] is a minimum, but the slightly less stable (0.3 kcal/mol) coplanar D_{2h} **SI10-S**(D_{2h}) is a first-order saddle point. Replacing two BeH^{-} units in **4^{2-}-T**(D_{2h}) by isoelectronic BHs resulted in C_{2v} cis [**11-S**(C_{2v})] and 24.0 kcal/mol less stable C_s trans minima [**SI11-S**(C_s)]. Tetrahedral-like structure **SI12-S**(C_{2v}) is a first-order saddle point and 22.0 kcal/mol less stable than **11-S**(C_{2v}). The boron atoms in **11-S**(C_{2v}) also serve as the p_π lone-pair acceptors. This is indicated by the small p_π occupancy of the ptC (1.20e) and the large HOMO–LUMO gap (5.1 eV) of **11-S**(C_{2v}). Because of the strong attraction of electrons to boron, the Mg analog of **11-S**(C_{2v}), $C(MgB)_2H_4$, **12-S**(C_{2v}), also has a planar minimum (HOMO–LUMO gap = 4.7 eV), 16.6 kcal/mol more stable than its T_d-like isomer [**SI13-S**(C_{2v})]. The isoelectronic replacement of $(BeH)_2^{2-}$ by $(AlH)_2$ also resulted in a C_{2v} planar minimum [**13-S**(C_{2v})], 2.7 kcal/mol more stable than its tetrahedral-like isomer [**SI14-S**(C_{2v})]. Finally, when two H atoms are removed, the two electrons remaining participate in peripheral bonding. Indeed, CBe_4H_2 has a planar C_{2v} minimum [**14-S**(C_{2v})] with a 155 cm^{-1} lowest frequency. However, its HOMO–LUMO gap is small, 1.6 eV.

Two ptC's can be joined by utilizing the same strategy of adding electrons to enhance the covalent bonding. Unlike $C(BeH)_4^{2-}$, the relatively large $C_2(BeH)_6^{2-}$ favors a singlet ground state [**15^{2-}-S**(C_{2h})]; the triplet [**16^{2-}-T**(C_{2h})] is 26.5 kcal/mol higher in energy than the singlet. Both (**15^{2-}-S**(C_{2h}) and **16^{2-}-T**(C_{2h}) have small HOMO–LUMO gaps, but the gaps of the neutral minima, with Li^+ counterions [**17-S**(C_{2h})] or with isoelectronic replacement of BeH^- by BH [**18-S**(C_{2h})], are large (4.0 and 5.1 eV, respectively). The protruding BeH groups in **15^{2-}-S**(C_{2h}) and **16^{2-}-T**($C_{2\,h}$) only bond to carbon and can even be replaced by H's; **19^{2-}**-**S**(C_{2h}) and **20^{2-}**-**T**(C_{2h}) result. Like $C_2(BeH)_6^{2-}$, singlet **19^{2-}**-**S**(C_{2h}) is favored by 8.6 kcal/mol over singlet **20^{2-}**-**T**(C_{2h}). Isoelectronic replacement of BeH by BH leads to minima **21-S**(C_{2h}) with a large HOMO–LUMO gap (5.3 eV).

Summary

Beryllium substituents can be employed successfully to stabilize molecules with ptC, although they are not good π acceptors. Due to the highly polarized C−Be bond, the rigidity of tetrahedral carbon in T_d $C(BeH)_4$ is weakened enormously. Adding extra electrons to D_{4h} $C(BeH)_4$ enhances both C−Be and peripheral Be_4 covalent bonding and therefore stabilizes ptC. Due to Hund's rule, the $C(BeH)_4$ dianion prefers a planar D_{2h} triplet ground state, rather than a singlet. The delocalization of the two p_π electrons is only modest, but their density on the most electronegative carbon atom helps stabilize the ptC arrangement. This is in contrast to the conventional strategy for stabilizing ptC by delocalizing the p_π lone pair. A number of ptC derivatives involving beryllium, including some neutral examples with multiple ptC's, have been predicted on the basis of elaborations of the parent $C(BeH)_4^{2-}$ dianion.

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Supporting Information Available: The structures **SI1-S**(D_{4h})−**SI14-S**(C_{2v}) and B3LYP/6-311++G (3df,2p) geometries of **SI1-S**(D_{4h})−**SI14-S**(C_{2v}), including the important bond lengths in angstroms, the number of imaginary frequencies, and the smallest vibrational frequencies in centimeters^{-1}. This material is available free of charge via the Internet at http://pubs.acs.org.

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