2012

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Recommended Citation

Crigger, Chad, Bernard K. Wittmaack, Marina Tawfik, Gabriel Merino, and Kelling J. Donald. "Plane and Simple: Planar Tetracoordinate Carbon Centers in Small Molecules." *Physical Chemistry, Chemical Physics* 14 (2012): 14775-14783. doi:10.1039/c2cp41986f.

PAPER

Plane and simple: planar tetracoordinate carbon centers in small molecules†

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A class of neutral 18-electron molecules with planar tetracoordinate carbon (ptC) centers is introduced. We show computationally that when $n = 3$ the neutral singlet molecule $C(BeH)_n(BH_2)_{4-n}$ and other isoelectronic (18-valence electron) molecules of main group elements collapse from locally tetrahedral arrangements at the C-center to (near) planar tetracoordinate structures. For $C(BeH)_3BH_2$ and $C(CH_3)(BH_2)Li_2$, for example, the tetrahedral type conformation is not even a minimum on the potential energy surface at the B3PW91, MP2(full), or CCSD levels of theory. The Mg analogue $C(MgH)_3BH_2$ of the Be system also features a completely flat global minimum (with even higher energy planar minima in both cases as well). Other neutral compounds that may prefer planar geometries are apparent, and new openings for experimental investigations and theoretical analyses of planar tetracoordinate main group systems are identified. The planar conformation persists at one center in the $C(BeH)_3BH_2$ dimer, and may be identifiable in higher order clusters of ptC molecules as well.

1. Introduction

Nearly a century after van't Hoff and Le Bel's seminal papers that convinced us, eventually, of the tetrahedral arrangement around carbon in many of its compounds,[1–3] Hoffmann *et al.*[4] published a letter to "open the problem of stabilizing tetra-coordinate planar carbon". In that work, they posited several organic and organometallic molecular motifs in which planar tetracoordinate carbon (ptC) centers could be stabilized. The quest to prepare such compounds and to augment the list of candidate structures has been ongoing since then,[5–13] - with some experimental successes,[12,14,15] and a small stream of theoretical proposals in the past few years.[16–19]

The challenge in stabilizing ptC centers is that going from the tetrahedral CH_4, for example, to the planar form involves a significant re-hybridization from sp^3 to sp^2 at the central carbon. This change results in the potentially destabilizing outcome of a doubly occupied p orbital – a lone pair – perpendicular to the plane of the molecule.[4,18,20] The latter situation is particularly unfavorable when the substituents are poor π-acceptors, and when other opportunities for the delocalization of these lone pair electrons are unavailable within the hypothetical planar structure.[4,5,11] For this reason, the stabilization of ptCs often involves a substantial degree of coercion either by strain,[8,17] entrapment in elaborate cage-like structures,[6,8,10a] or electronic effects (such as a π-system) that favor planar C centers.[13,11a,14,16]

Boldyrev and Simons showed over a decade ago that 18-electron (18e) pentatomic ($CR'_2R''_2$) clusters such as CSi_2Ga_2, and CGe_2Al_2, tend to favor a planar tetracoordinate arrangement at the central carbon.[16] That category of 18e clusters generalizes, too, to include CAl_4^{2-}, for example, (where R', R'' = Al) and other such species that are planar as well.[21] Several classical CR_4 type neutral compounds, such as CLi_4 and $C(BH_2)_4$ with good σ-donor and π acceptor substituents have been studied, too, but with little success to date. CLi_4 and $C(BH_2)_4$ are tetrahedral (T_d)[3] in geometry, even though the barriers to the planar transition structures are quite low.[5,11] Indeed, no neutral molecule with four independent R substituents around a C center is known for which the planar structure is preferred. The neutral CAl_4 molecule, for example, is tetrahedral (the planar form is a saddle point) even though the dianion CAl_4^{2-} is a computationally well established planar species.[21]

Informed by the earlier observations of Boldyrev and Simons on pentatomic 18e cluster,[14,16] we wanted to examine more broadly the preference for a planar geometry in small molecules. In particular, we wanted to identify compounds that satisfy the following conditions: (i) neutral 18e main group molecules,

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† Electronic supplementary information (ESI) available: The complete *Gaussian 03* citation, Geometrical data and coordinates for system considered in this work. See DOI: 10.1039/c2cp41986f

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with (ii) planar singlet minimum energy structures, even though they have (iii) acceptable Lewis structures in the T_d type geometry[3] and (unlike fenestranes) (iv) no structural constraint mandating the planar geometry.

To consider only neutral species, we allow in this work for polyatomic substituents in which the atom bonded to the central C is saturated by H atoms. Moreover, we include the electrons from those H atoms in the total valence electron count. So, the substituents -BeH and -BH$_2$ contribute three and five, respectively, to the total electron count. By considering such polyatomic substituents, we make the tacit assumption that in the theoretical C(AlH)$_4^{2+}$ system, for instance, the Al—H bonds would play a similar role in the bonding preference to that of the Al lone pairs in the planar and isoelectronic CAl$_4^{2-}$ anion.

We have been gratified to find that the 18e C(BeH)$_3$BH$_2$ molecule and its isovalent C(MgH)$_3$BH$_2$ analogue are both completely flat with planar tetracoordinate C atoms at their centers. More broadly, the 18e systems that we identify in this work show a substantial preference for non-tetrahedral type geometries. Even so, a question we considered is the importance of this particular electron count. We find for the C(BeH)$_n$(BH$_2$)$_{4-n}$ series of molecules that it is only when $n = 3$ (for $n = 0 - 4$) that the planar tetracoordinate structure is stable relative to the tetrahedral alternative. *The tetrahedral type isomer is not even a local minimum on the potential energy surface.* The preferred structure is an unstrained, electronically stabilized, planar tetracoordinate compound. The molecule represents an intriguing lead compound; a novel reference point *en route* to the possible synthesis of molecular objects with planar tetracoordinate carbon centers.

2. Computational methods

The computational results presented in this work, including the geometrical and harmonic vibrational frequency data have been obtained at the B3PW91,[22] Møller–Plesset (MP2(full)),[23] and the CCSD[24] levels of theory. The relevant method is indicated at each stage as necessary in the results section. In each case, we employed the correlation consistent triple-zeta cc-pVTZ all electron basis sets[25] and in several cases the 6-311+G*[26] basis sets were used as well for comparison and to estimate basis set effects. All of our computational studies have been performed using the Gaussian 03 suite of programs.[27] The Gaussview program has been used to generate representations of molecular geometries and molecular orbitals (MOs).

We used the Gradient Embedded Genetic Algorithm (GEGA) proposed by Alexandrova *et al.*[28] to explore in detail the potential energy surfaces of a few of the molecules that converged to planar tetracoordinate minima. This approach enabled us to identify the most competitive (the lowest energy) isomers from a scan of the potential energy surfaces (PES) of the molecules. The algorithm starts out with an initial guess structure from which it derives generations of increasingly viable (more and more stable) minimum energy geometries. The ten most stable minimum energy structures obtained in this way (confirmed by frequency analyses to be minima at the B3LYP/LANL2DZ level of theory) were then selected for re-optimization and frequency analyses at the more demanding levels of theory mentioned above. The GEGA has been quite

successful in finding global and low-energy local minima on the PES of atomic clusters.[29] For the details of the algorithm, the reader is referred to ref. 28.

3. Results and discussion

3.1. All fall down: neutral singlet molecules that prefer to be planar

3.1.1 Ten non-classical 18e species. Classical tetrahedral CR$_4$ type molecules such as CH$_4$ or CF$_4$ usually have substantial barriers to the square planar distortion ($\sim 5.0 \pm 1.0$ eV).[4,11,20] Yet, Schleyer *et al.* have shown that the barriers to planarity ($\Delta E_{Td \to Pl}$) in simple CR$_4$ type molecules are far lower in cases where the substituents are good σ-donors and π-acceptors. Take the isovalent CH$_4$ and CLi$_4$ molecules, for instance;[11a] the $\Delta E_{Td \to Pl}$ values reported in ref. 5 are 5.7 eV for CH$_4$ and 0.54 eV (a full order lower) for CLi$_4$.[30] The latter molecule has a relatively small barrier to planarity because of the delocalization of electron density from the p_Z lone pair at C into the energetically accessible and empty p orbitals of terminal Li atoms. Nevertheless, CLi$_4$ and several other molecules with various (σ-donor/ π-acceptor) substituents (like CH$_n$Li$_{4-n}$, CH$_n$(BeH)$_{4-n}$, and CH$_n$(BH$_2$)$_{4-n}$) have been found computationally to persist in the tetrahedral arrangement (and the planar conformers are not minimum energy structures) even though the $\Delta E_{Td \to Pl}$ values are low.[11]

Large rigid frameworks such as the fenestranes or aromatic ring systems in which planar tetracoordinate group 14 atoms may be stabilized, or charged species such as the C$_5^{2-}$ D_{2h} cluster,[17c] or CAl$_4^{2-}$ are interesting instances of the ptC phenomenon. Our objective in this project has been to locate simple neutral molecules that prefer the planar conformation without structural constraints, in accordance with the criteria mentioned in the introduction.

To identify candidate structures that satisfy those criteria, we started out at the 8e CLi$_4$ extreme and modified the structure by replacing the Li atoms with *monovalent* period 2 main group substituents (R) to obtain neutral 18e molecules. To be clear, an 'x electron compound' in this work is one in which the valence electrons of all the atoms in the structure sums to x. These x electrons are not necessarily involved in bonding to the central C atom. No link to the classical monocentric 18e rule is implied. Not all 18 electrons in CAl$_4^{2-}$, for example, are involved in C–Al bonding; there are four Al lone pairs pointing away from the C–Al bonding region.

The set of (R) substituents that we considered were: –F, –OH, –NH$_2$, and –CH$_3$ (all 7 electron substituents), –BH$_2$ (5 electrons), –BeH (3 electrons), and –Li (1 electron).[31] The previously identified 18e systems with stable ptCs have been pentatomic structures (such as CGe$_2$Al$_2$, and CAl$_4^{2-}$)[16,21] with only four atoms around the planar C center. We allowed in this work, however, for simple $-$AH$_x$ polyatomic substituents, as well, and we included the H electrons in the total electron count. The slate of substituents that we considered afforded us ten 18e candidate molecules,[31] and we optimized all ten – without constraints, starting in each case with a locally tetrahedral type coordination at the central carbon, with all the R–C–R' bond angles at 109.5° (see Fig. S.1).
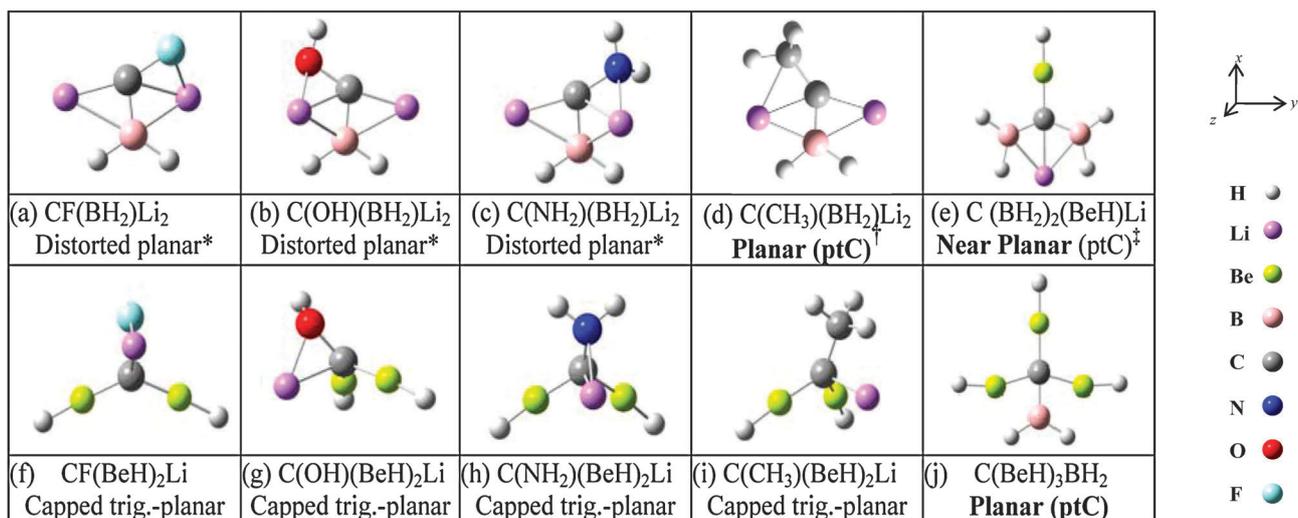
Fig. 1 Minimum energy 18*e* structures obtained at the B3PW91/cc-pVTZ level of theory. In each case, the optimization began with a tetrahedral type arrangement at the C center. The optimized coordinates are given in the supporting information.† *'Distorted planar': in (a), (b), and (c) the atoms bonded to C are all coplanar, except for the Li atom that is bonded to the C center and to the F, OH, and NH₂, respectively. The H–B–C–Li dihedral angle in these structures is between 33°–42°. †The central C is coplanar with the four atoms bonded to it. ‡The system is not quite planar: The Be–C–Li bond angle is 170°. The B–C–Li–B dihedral angle is 166°.

Remarkably, none of the ten structures that we optimized persisted in a tetrahedral type geometry (Fig. 1). Six of the molecules (a–e, and j in Fig. 1) collapsed to planar or nearly planar arrangements.

For the other four structures (f–i), the pernicious insistence of the Li atom on occupying bridging positions made it difficult to achieve co-planar arrangements of the atoms. Instead, the optimized structures in those four cases have roughly trigonal planar C(BeH)₂X bases (where X = F, OH, NH₂, or CH₃), with the Li atom capping the C–X bond.

In the C(CH₃)(BH₂)Li₂ and C(BeH)₃BH₂ molecules ((d) and (j) in Fig. 1) *the four bonds to the central C atom are completely coplanar*. Our data for structure (d) are somewhat ambiguous, since the planar structure is a minimum at the B3PW91 and MP2(full) levels and a first order saddle point at the CCSD level (with $\nu_{min} = i30.7$; see Table S.1 in the supporting information†). A re-optimization of (d) at the CCSD level, following the trajectory of that imaginary frequency, led us to a very similar structure with one of the Li atoms in that case out of the plane by 21.5°.

For C(BeH)₃BH₂ ((j) in Fig. 1), our analyses at the B3PW91, MP2(full), and the CCSD levels of theory are unequivocal. Using both the 6-311+G* and the cc-pVTZ basis sets for all elements, we found that the tetrahedral type starting structure collapses spontaneously to the flat C_{2v} structure (Fig. 2j) with $\nu_{min} \geq 129$ cm⁻¹ in each case (Table 1).

3.1.2 C(BeH)₃BH₂ – planar preferred. We have been surprised by the remarkable stability of the planar C_{2v} structure of C(BeH)₃BH₂ relative to the starting tetrahedral-type geometry. The latter conformation, which the valence shell electron pair repulsion model and simple qualitative descriptors predict to be the global minimum energy structure for this molecule, is not even a local minimum. Indeed, it has been impossible to optimize a tetrahedral type structure for this compound. Tetrahedral input structures collapse readily for all five of the model chemistries we

considered (Table 1), eventually optimizing to the planar conformation (Fig. 1(j)).

In the absence of any optimized tetrahedral geometry with which to compare the planar structure, we computed instead the orbital energies of a model tetrahedral structure using reasonable values for the C–Be, C–B, Be–H, and B–H bond distances (1.660 Å, 1.550 Å, 1.320 Å, and 1.180 Å, respectively), and compared the nature and energies of its molecular orbitals with those of the planar structure (See Fig. 2). Fig. 2a compares the MO energy levels of the tetrahedral type and the planar (C_{2v}) structures. Fig. 2b provides a detailed look at the latter; the MO energy levels in 2b are precisely the same as they are for the planar isomer in 2a, but 2b includes the associated molecular orbital pictures, as well. Larger pictures of the orbitals in Fig. 2a and a summary of the atomic orbital parentage of the MOs are provided in the supporting information.†

The energy level diagrams in Fig. 2 help a lot with deepening our understanding of the bonding in the molecule. The results show, for example, that several of the MOs that include antibonding interactions between the substituents in the T_d structure (in Fig. 2a, and S.1b) become stabilized as the molecule becomes planar. That is, several of the atomic orbitals involved in the MOs of the T_d structure are reoriented in the planar conformations in ways that minimize antibonding interactions among the substituents. The HOMO−1, −5, −6, −7 and −8 in Fig. 2b (*cf.* Fig. 2a) are instances of this relaxation.

There are a few interactions that are evidently more destabilizing in the planar geometry, such as the HOMO and HOMO−4 in Fig. 2b. But such interactions are more than compensated for by the several other bonding interactions that are facilitated by the planar conformation (Fig. 2).[32] This substantial stabilization occurs in the planar C(BeH)₃BH₂, and not in planar forms of CH₄ or CF₄, for example, partly because of the unavailability of any empty valence p orbital on the substituents for electron delocalization in the latter systems. Moreover, the abundance of lone pairs on
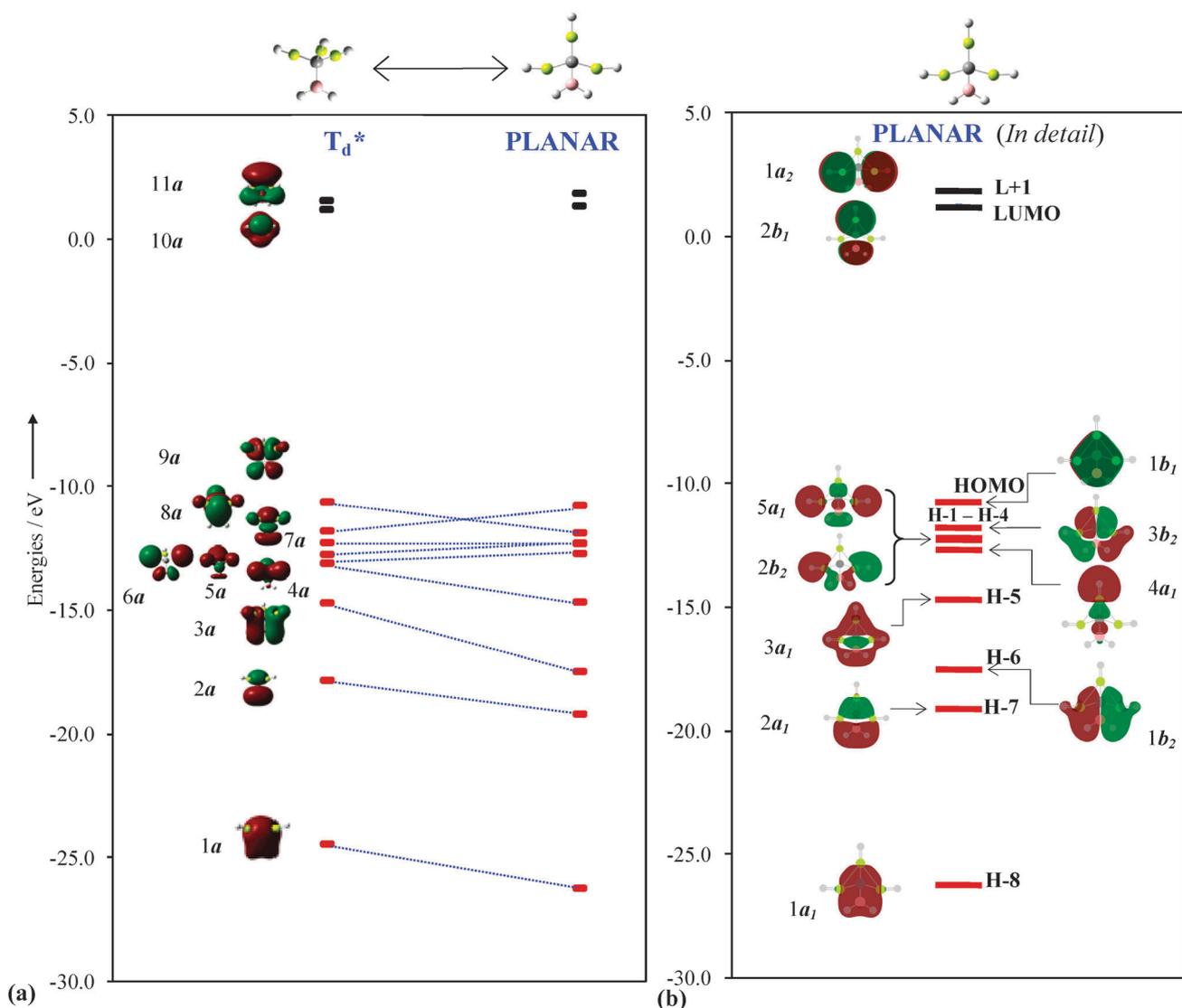
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Fig. 2 (a) Simple Walsh diagram for the collapse from the local T_d geometry to a planar conformation for $C(BeH)_3BH_2$ at the MP2 (full) level of theory. We used the label T_d* to remind ourselves that the molecule does not formally have tetrahedral symmetry. The T_d* energies and orbitals were obtained from a single point calculation. (b) The MO energy level diagram for $C(BeH)_3BH_2$ and the corresponding orbital pictures. The occupied MOs are in red, and the unoccupied MOs are in black. The highest occupied and lowest unoccupied MOs (the HOMO and the LUMO) are abbreviated 'H' and 'L', respectively. H-1 is the MO that is just below the HOMO in energy. L + 1 is just above the LUMO.

halides in their compounds means a great deal of repulsion between terminal sites in planar conformers of halomethanes.

The HOMO–LUMO gap in the planar structure in Fig. 2 is substantial, and that characteristic is consistent with the observed stability. But that gap is about the same for both the planar and the tetrahedral structures in Fig. 2. So, the strong preference for the planar conformer is to be understood primarily in terms of a redistribution of the electron density (to better engage the valence p orbitals of the hypovalent centers) plus associated changes in orbital interactions as the molecule relaxes to two-dimensions, with no big change in the HOMO–LUMO gap.

3.2. The planar molecule is the global minimum

We wanted to find out conclusively whether this non-classical $C(BeH)_3BH_2$ planar structure is the global minimum on its potential energy surface or not. To answer that question, we employed the GEGA program described in the methods section to obtain the ten lowest energy isomers for this group of atoms, and re-optimized the resulting structures at the B3PW91 and the MP2(full) levels of theory. And the outcomes were fascinating.

As shown in Fig. 3, the planar structure identified initially in Fig. 1(j) is in fact the global minimum energy isomer for $C(BeH)_3BH_2$. Although we considered the ten lowest energy structures derived from the GEGA search, a number of those structures looked very similar and gave identical geometries and energies to one of the five points shown in Fig. 3 after re-optimizations at the B3PW91 and MP2(full) levels.[33] Remarkably, all five of the low energy structures in Fig. 3, spanning some 2.0 eV relative to the global minimum, are completely planar. Moreover, the central C is tetracoordinate

Table 1 Computed distances in angstrom (Å) and angles in degree (°) units, Wiberg bond indices (WBIs), point charges (q/e), vibrational frequencies (ν/cm^{-1}), and energy differences between the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbitals ($\Delta E_{\mathrm{H-L}}/\mathrm{eV}$) for planar $C(BeH)_3(BH_2)$ at three different levels of theory

	B3PW91		MP2(full)		CCSD
	6-311+G*	cc-pVTZ	6-311+G*	cc-pVTZ	cc-pVTZ
C–Be(a)	1.618	1.617	1.625	1.615	1.626
C–Be(b)	1.667	1.668	1.677	1.666	1.677
C–B	1.457	1.454	1.469	1.457	1.463
Be(b)–B	1.906	1.896	1.909	1.893	1.914
Be(a)–H	1.330	1.329	1.330	1.320	1.329
Be(b)–H	1.335	1.334	1.333	1.324	1.333
B–H	1.229	1.226	1.227	1.215	1.223
H–B–H	114.5	114.7	114.7	115.0	115.0
Be–C–Be	105.2	105.5	105.6	105.7	105.2
WBIs					
C–Be(a)	0.51	0.51	0.48	0.48	0.48
C–Be(b)	0.51	0.51	0.47	0.47	0.49
C–B	1.55	1.57	1.43	1.44	1.52
Be(b)–B	0.21	0.22	0.20	0.20	0.19
Be(a)–H	0.84	0.84	0.81	0.79	0.81
Be(b)–H	0.88	0.88	0.85	0.84	0.86
B–H	0.82	0.81	0.79	0.79	0.84
C center	3.13	3.16	2.90	2.91	3.04
Charges/e					
q_C	−1.66	−1.62	−1.61	−1.59	−1.63
$q_{Be(a)}$	1.03	1.04	1.03	1.05	1.05
$q_{Be(b)}$	0.82	0.81	0.82	0.83	0.84
q_B	−0.09	−0.13	−0.09	−0.10	−0.08
$q_{H(a)}$	−0.39	−0.39	−0.39	−0.41	−0.40
$q_{H(b)}$	−0.32	−0.32	−0.32	−0.34	−0.34
q_H	0.05	0.06	0.04	0.04	0.03
Lowest ν/cm^{-1}	129.0	128.9	149.5	146.1	135.7
$\Delta E_{\mathrm{H-L}}/\mathrm{eV}$	[a]	[b]	11.5	12.0	12.0

The HOMO–LUMO gaps obtained from the B3PW91 density functional theory (DFT) method were[a] 6.70 eV and [b] 6.61 eV. However, we exclude these values from the table since it is well known that gaps obtained from several DFT methods are generally unreliable.
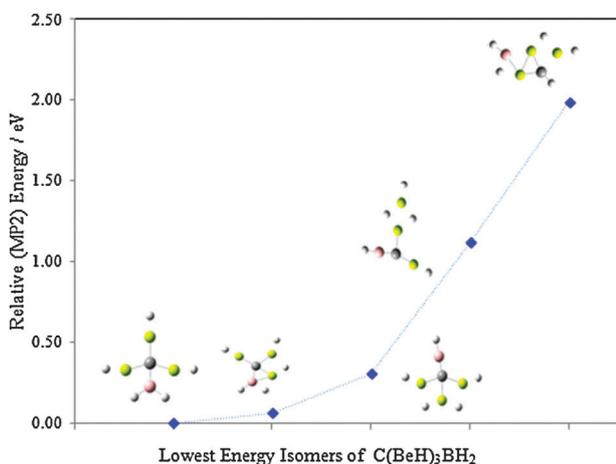

Fig. 3 MP2(full) energies (relative to the global minimum) and geometries obtained using the cc-pVTZ basis sets for the lowest energy isomers of the $C(BeH)_3BH_2$ molecule obtained from a general search of the potential energy surface using the GEGA computational program, and reoptimized at the MP2(full) level of theory. The corresponding B3PW91 values are included in the supporting information (Fig. S.2).†

in all but one case (the fourth highest energy structure in Fig. 3) in which the C atom forms essentially a double bond to the boron atom (with a C=B bond distance of 1.358 Å) and σ-bonds to the two Be centers with far weaker π contributions.

3.3. Structure and bonding in $C(BeH)_3BH_2$

The computed geometrical and bonding information obtained for the optimized $C(BeH)_3BH_2$ structure are summarized in Fig. 4 and Table 1. A simple view of the bonding in the $C(BeH)_3BH_2$ molecule assigns four electrons to the two B–H bonds and six electrons to the three Be–H bonds (a total of ten electrons), leaving eight electrons for three C–Be and one C–B single bonds. That would be a straightforward Lewis description of the tetrahedral conformation, but it is quite inadequate for the planar structure. There are, for example, a substantial π contribution to the bonding and clear evidence of multicenter bonding involving ligand-ligand (*i.e.* Be–B) interactions, as well.

The small Be(b)–B Wiberg bond indices (WBI) ∼0.20(2) in Table 1, the short Be(b)–B bond distances, and the large Be(a)–C–Be(b) bond angles (Table 1, and Fig. 4) are consistent with a significant degree of bonding between the Be(b) atoms and the B center. The non-linearity of the C–Be(b)–H fragment is evidence of a substantial rehybridization at the Be(b) center (from *sp* toward sp²) in order to facilitate the Be(b)–B interaction. The bending also signals the possible influence of repulsive H···H interactions between the H atoms on the Be(b) and the B centers. However, the stabilization won by forming the Be(b)–B bonds more than compensate for the costs in energy of such H···H interactions.

To be sure, the Be(b)–B bonds that are formed during the optimization are not simple 2-center–2-electron bonds. There are not enough electrons to go around. The ptC center in Fig. 4 is supported by a nuanced bonding pattern that includes two 3-center (B–Be(b)–C) 2-electron bonds. The large negative charge on the C center (∼−1.60e), the positive charge at Be(b) (∼+0.82e), and the low C–Be(b) bond order (Table 1) suggest that the electron density is polarized, however, towards the C–B region.

The C–B interaction is particularly interesting, since the C–B σ component is reinforced by a substantial π-type interaction in which the C p$_z$ electrons are delocalized into the empty B p$_z$ orbital on boron. The structural evidence of this π-contribution to the bonding includes a relatively short
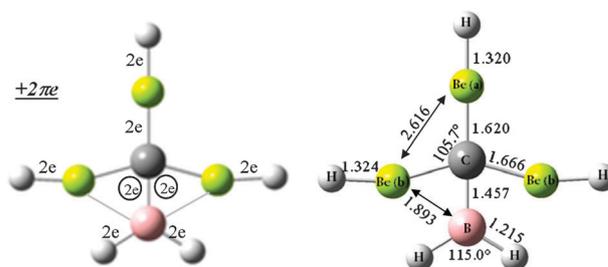

Fig. 4 A simple Lewis structure and computed geometrical data for the planar tetracoordinate $C(BeH)_3BH_2$ molecule optimized at the MP2(full)/cc-pVTZ level of theory. All the bond lengths are in angstrom (Å) units. Additional bonding and frequency data are in Table S.2 in the supporting information.†

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C–B bond distance ($\sim$1.454 Å–1.469 Å in Table 1) compared to a typical C–B single bond length of 1.58 Å or the sum of the covalent radii[34] for C (0.85 Å) and B (0.75 Å) (= 1.60 Å). Moreover, the WBI for the C–B bond is well in excess of 1.0 Å for all five of the model chemistries in Table 1, and natural bond orbital analyses confirm, as well, the presence of this π component in the C–B bond. The elongation of the B–H bond (1.22 Å; cf. 1.17 Å for the sum of the B and H radii)[34] is consistent, too, with a π type interaction at B in addition to the σ bonding.

The relatively short C–Be bonds (at 1.62 Å and 1.67 Å in Table 1, cf. 1.77 Å for the sum of radii in ref. 34) suggest that π delocalization from the central C atom is not isolated to B. The Be p_z orbitals are involved to a lesser extent, as well, as is also apparent in the HOMO shown in Fig. 2b.

Consistent with the criteria that we outlined in the introduction, therefore, and in line with the observations of Boldyrev et al. for pentatomic main group clusters,[14,16] the C(BeH)$_3$BH$_2$ molecule and other 18e systems in Fig. 1 combine a range of σ and π covalent interactions to stabilize planar (and near planar) conformations over the classically expected tetrahedral type geometry. In the systems considered herein, this is achieved with simple substituents, and without engineering the chemical environment using strain, aromaticity, or externally imposed constraints to clamp them in place.

The planar tetracoordinate conformation of the C(BeH)$_3$BH$_2$ molecule optimizes the bonding between the C center and the electropositive terminal groups, which are substantial σ donors (notice the large negative charge at C in Table 1) and π-acceptors. In particular, the molecule utilizes, quite creatively, multicenter interactions to stabilize the planar geometry. We comment briefly on the structure and bonding in the other molecules shown in Fig. 1 (a–i) in the supporting information.†

3.4. A preliminary assessment of transferability

3.4.1 The case of C(MgH)$_3$BH$_2$. To test the transferability of our observations for the bonding and geometrical preferences in C(BeH)$_3$BH$_2$ we carried out a search for the global minimum of the isoelectronic C(MgH)$_3$BH$_2$ system, and re-optimized the most stable isomers at the MP2(full) and B3PW91 levels that we employed for the lighter Be analogue.

Indeed, the Mg systems converged readily, as well, to planar tetracoordinate C-centered structures (see the MP2 results in Fig. 5 and 6). The DFT (B3PW91) calculations (see Fig. S.3) give roughly the same energies for isomer (b) in Fig. 6 and the third lowest energy structure in Fig. 5, which is non-planar. However, the preference for the planar tetracoordinate geometry in the global minimum energy structure appears to be well established at the MP2(full) level (Fig. 5).

3.4.2 The C(BeH)$_n$(BH$_2$)$_{4-n}$ is planar only when n = 3. We wanted to understand better the possible influences of substitutions on the stability of the ptCs, and C(BeH)$_3$BH$_2$ in particular. So, we carried out a series of geometrical optimizations on the five C(BeH)$_n$(BH$_2$)$_{4-n}$ molecules for n = 0 to 4, where the 18e structure (3j) is attained only when n = 3. Our results are illustrated in Fig. 7. Again, all five of the
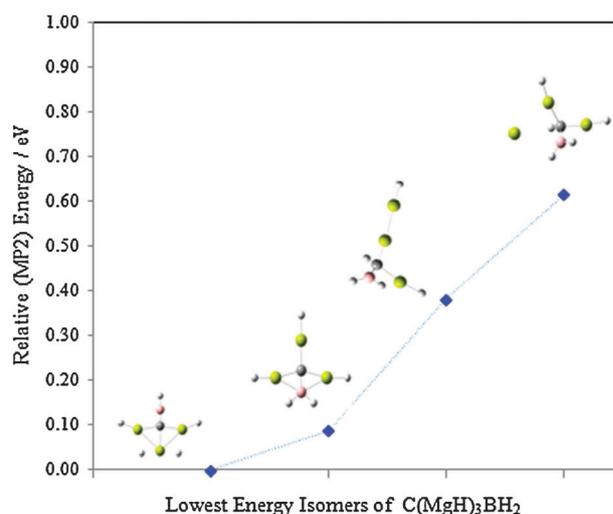

Fig. 5 MP2(full) energies (relative to the global minimum) and geometries obtained using the cc-pVTZ basis sets for the lowest energy isomers of the C(MgH)$_3$BH$_2$ molecule. The structures were identified in a general search of the potential energy surface using the GEGA computational program, and reoptimization at the MP2(full) level of theory. The corresponding B3PW91 values are included in Fig. S.3.
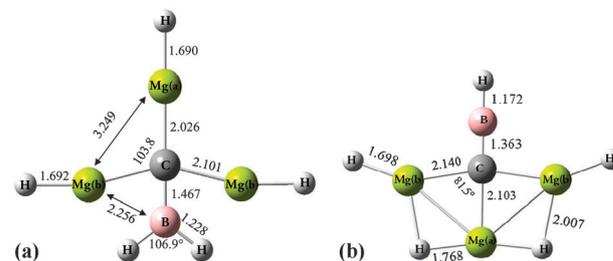

Fig. 6 Geometrical data for the planar tetracoordinate C(MgH)$_3$BH$_2$ molecules optimized at the MP2(full)/cc-pVTZ level of theory. All the bond lengths are in angstrom (Å) units. Additional data are provided in Table 1 and S.2 in the supporting information.†

structures were optimized starting from the tetrahedral-type conformation at the C center.

The first structure in the series, C(BH$_2$)$_4$, is non-planar, which is consistent qualitatively with the much earlier observations in ref. 20 that the planar structure is not preferred for that molecule. Notice, however, that the lowest energy geometry that we obtained for C(BH$_2$)$_4$, with no imaginary frequency, has three H bridges linking three of the boron atoms in the molecule, reminiscent of the H bridges in B$_2$H$_6$. Moreover, the isolated BH$_2$ group in the compound is coplanar with one face of the tetrahedron formed by the central C atom and the bridged B atoms. Curiously, we have been unable to find this stable C(BH$_2$)$_4$ isomer identified anywhere else in the literature.

The second structure (where n = 1) is a distorted pyramidal structure in which the BeH group is tilted somewhat towards one of the BH$_2$ centers (as indicated by the dashed line). The n = 2 case is an interesting C$_2$ structure in which we have identified in the assignment of the bonds two bridging hydrogens between the Be and B atoms.

The planar tetracoordinate C center is achieved only when n = 3. In that case, the entire structure is flat (Fig. 3, 4 and 7)
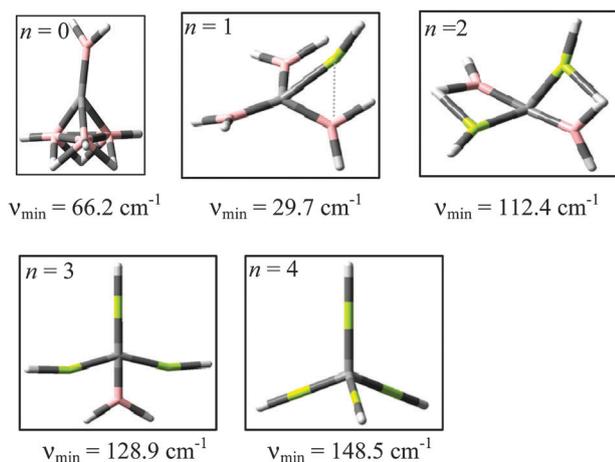
Fig. 7 Minimum energy geometries and the lowest vibrational frequencies obtained at the B3PW91/cc-pVTZ level of theory for the $C((BeH)_3)_n(BH_2)_{4-n}$ molecules for $n = 0$ to 4. All five structures were obtained by starting with a locally tetrahedral arrangement of the bonds to the C center.

Fig. 8 Structures and the numbers of imaginary frequencies obtained at the B3PW91/cc-pVTZ for the several test C_5 and small isoelectronic ions: $C(BH)_4^{2-}$, $CB_4H_5^{-}$, $CB_4H_5^{3+}$.

and the tetrahedral conformation is, as we mentioned above, not even a local minimum on the potential energy surface of the molecule. Replacing the remaining BH_2 group by a fourth BeH unit to form $C(BeH)_4$ gives the classical tetrahedral geometry.

3.4.3 Electron count alone is not enough. The 18-electron count is not unique for planar molecules. Several arbitrary assemblies of periods one and two atoms are possible that would achieve this electron count. Moreover, as we have already shown in Fig. 1(f–i), the number of electrons alone is no guarantee that a planar tetracoordinate minimum is achievable. The size of the atoms and the number of valence orbitals in the system are decisive as well. The planar tetra-coordinate C_5^{2-} bow-tie global minimum that Merino et al.[17c] identified computationally in 2004 is a 22e species (with its lowest vibrational frequency = 178.4 cm^{-1} at the B3PW91 level; Fig. 8). The neutral 20e C_5 bow-tie species is a third order saddle point, and the 18e C_5^{2+} species examined at the same level of theory reveals a very large imaginary frequency ($\nu_{min} = 620.5i$ cm^{-1}). Incidentally, we should mention that the vibrational motion associated with the imaginary frequency obtained for that bow-tie C_5^{2+} transition state geometry moves the central atom of the bow-tie out of the middle to form a V-shaped chain that optimizes ultimately to give the simple 5-carbon chain, which is, indeed, a minimum on the C_5^{2+} potential energy surface (Fig. 8). This one-dimensional structure is interesting but not surprising since 5-carbon and even longer carbon chains have been observed experimentally.[35]

Building from the C_5^{2-} bow-tie bonding motif, we found that, in fact, the corresponding $C(BH)_4^{2-}$ 22e species in which the four outer C atoms of C_5^{2-} are each replaced by a B–H fragment is stable, too, in the planar tetracoordinate arrangement (Fig. 8).

Interestingly, if we maintained the 22e count in $C(BH)_4^{2-}$, and add a proton (to obtain $C(BH)_3BH_2^{-}$, which is isovalent with $C(BeH)_3BH_2$), the bow-tie unravels to give a new minimum energy structure that preserves the ptC center with a very different geometry (see Fig. 8). Finally, if we remove four electrons to
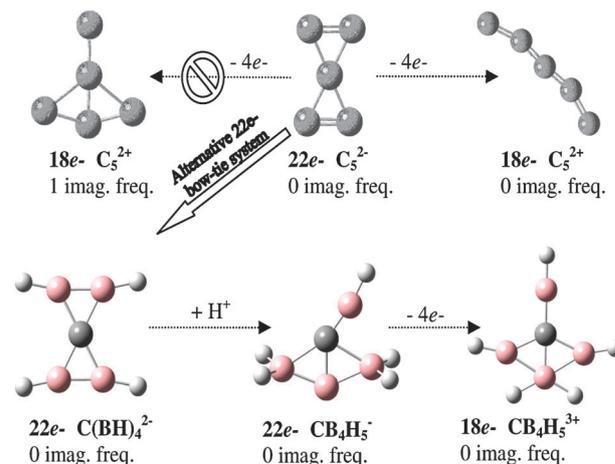
reduce the electron count to 18, the stable outcome is a $C(BH)_3BH_2^{3+}$ system that is isoelectronic with and isostructural to the planar $C(BeH)_3BH_2$ structure in Fig. 4

These observations evince the versatility and abundance of planar tetracoordinate carbon compounds in pentatomic frameworks (and some augmented by hydrogens). They support the claim, too, that there is no unique electron count that must be achieved to obtain ptC centers. The geometry evolves with the electron count, and the number of valence orbitals in the molecule. Put another way, different electron counts privilege different planar conformations. So, various electron counts may be considered as we probe computationally and experimentally - by photoelectron spectroscopy and other methods - for simple neutral molecules and ions with ptC centers. These ptC systems bring to mind, in fact, the non-classical carborane structures pioneered by Berndt et al.[36] Those somewhat more complicated molecules and the lead compounds identified herein may be instructive for the possible synthesis of simple main group compounds with stable ptC.

3.5 Viability of the proposed structure and the persistence of the planarity

Hoffmann et al. have identified the propensity for dimerization as one of the definite tests for the viability of novel compounds.[37] An investigation that started off with three different relative orientations of two $C(BeH)_3BH_2$ monomers (see Fig. 9), turned up two energetically identical stereoisomeric dimers with no imaginary frequency. At the B3PW91/cc-pVTZ level, the dimerization energy ($E_{dimer} - 2E_{monomers}$) corrected for basis set super-position energy is −1.11 eV.

In both of these structures, the two $C(BeH)_3BH_2$ monomers are linked by a Be–H–Be and a Be–C–Be bridge. The C center invoved in the bridge is pentacoordinate, while, remarkably, the other C center remains planar tetracoordinate in the dimer (see Fig. 9).

So, although dimerization is likely for electron deficient compounds such as those considered in this work, our results suggest that the observed planarity in the monomer units can
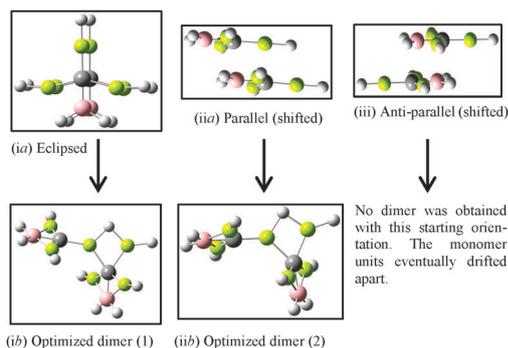
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Fig. 9 Starting $(C(BeH)_3BH_2)_2$ structures and the stereo–isomeric dimer units obtained from our geometry optimizations. The starting structures (ia) and (iia) converged to the energetically equivalent stereoisomers (ib) and (iib). Structure (iii) separated into two isolated $C(BeH)_3BH_2$ monomers.

persist in the dimers, and may be observable even in higher order oligomers, as well.

4. Summary and outlook

An unprecedented class of $18e$ compounds (Fig. 1) has been identified for which a (nearly) planar conformation is substantially more stable than the tetrahedral type conformation. Indeed, the latter alternative is not even a local minimum on the potential energy surfaces of the systems. The $C(BeH)_3BH_2$, and $C(MgH)_3BH_2$ molecules (Fig. 4 and 6), are particularly significant. The global minimum energy structures for both species (and even some of the higher energy isomers) are completely flat, each with a planar tetracoordinate carbon center.

These observations confirm that the $18e$ count in certain small main group compounds favors quite strongly the formation of ptCs. However, an $18e$ count is not a unique condition (neither necessary, nor sufficient) for stabilizing ptCs in simple compounds. Like the C_5^{2-} anion identified previously,[17c] we find, for instance, that the $22e$ $C(BH)_4^{2-}$, and $CB_4H_5^-$ anions, as well as the $18e$ $CB_4H_5^{3+}$ cations (Fig. 8), all prefer a planar tetracoordinate arrangement at the C center. The neutral systems identified in this paper are distinguished in part by their strong preference for the planar or near planar geometries even though simple bonding models predict classical T_d type geometries for them.

The investigations triggered by Hoffmann *et al.*[4] into unusual bonding patterns at C centers in molecules continue on both fronts. Synthetic chemistry has to be relied on to confirm or refute theoretical predictions of non-classical coordinations in compounds; the computational prediction of molecules is a job best held by the brave and the humble. Even so, other exotic and synthetically challenging systems with planar penta- and hexa- coordinate carbon centers have already been added to the discussion of bonding possibilities in carbon compounds.

In this work, we have identified a broad class of neutral $18e$ singlet molecules that are expected to be locally tetrahedral at the C center (like CLi_4, $C(BeH)_4$, and the $CH_n(BH_2)_{4-n}$ compounds),[11] but which strongly prefer the planar tetracoordinate geometry over the three-dimensional alternative. To the best of our knowledge, the minimum energy species in Fig. 1, 3, and 5, represent the first class of neutral compounds

(as distinguished from metal clusters[16] or ions)[17] to show this inversion (with the ptC more stable than the T_d conformation) on the potential energy surface.

Our observations on this class of simple compounds suggest new potential directions in the exploration of planar tetra-coordinate main group systems. They affirm the insights of others who have, over the past few decades, identified simple neutral species with low barriers to bending.[11] Despite the practical challenges in working with beryllium experimentally, the grand diversity in the stable planar structures identified in Fig. 1, 3, 5, and 8 present new challenges for experimental synthesis, and suggest the likelihood of detecting new ptC systems in gas phase or matrix isolation studies. And room for more theoretical investigation of non-canonical coordination at C centers is apparent as well.

The stability of the $C(BeH)_3BH_2$ and $C(MgH)_3BH_2$ molecules in particular, suggest that heavier 18-electron systems with the general formula ME_3E', where M is a group 14 atom, and E = $-MgH$, or E' = $-AlH_2$, for example, may be planar as well. To be sure, the stability of the period 2 compounds does not necessarily mean that the planar conformation will be preferred in heavier ME_3E' analogues, since shell structure and atomic sizes change dramatically in the main group beyond period 2. Yet, the stability of the class of systems with ptCs that we have identified (including the $C(BeH)_3BH_2$ dimer and $C(MgH)_3BH_2$) gives us reason to hope that intriguing ptC compounds will be identified and, in time, realized.

We find, admittedly, no obvious route to synthesizing the $C(BeH)_3BH_2$ monomer (or its analogues). However, as simple substituted methanes with uncomplicated ($-BeH$ and $-BH_2$) subsituents they stand as theoretical lead compounds that in the words of one reviewer "could act as a starting point" for the synthesis of molecules with planar tetracoordinate carbon centers.

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