Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Plane and Simple: Planar Tetracoordinate Carbon Centers in Small Molecules

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Supporting Information

Complete Citation for the Gaussian 03 Suite of Programs

Gaussian 03, Revision E.01,
M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

Additional Figures

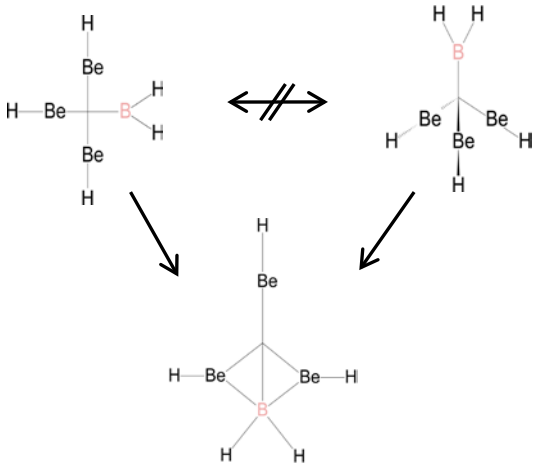


***Figure S.1a**: Representation of the computed (B3PW91, MP2(full), and CCSD) minimum energy structure of $C(BeH)_3BH_2$. The structure was obtained from the two starting structures shown in the upper half of the figure.*

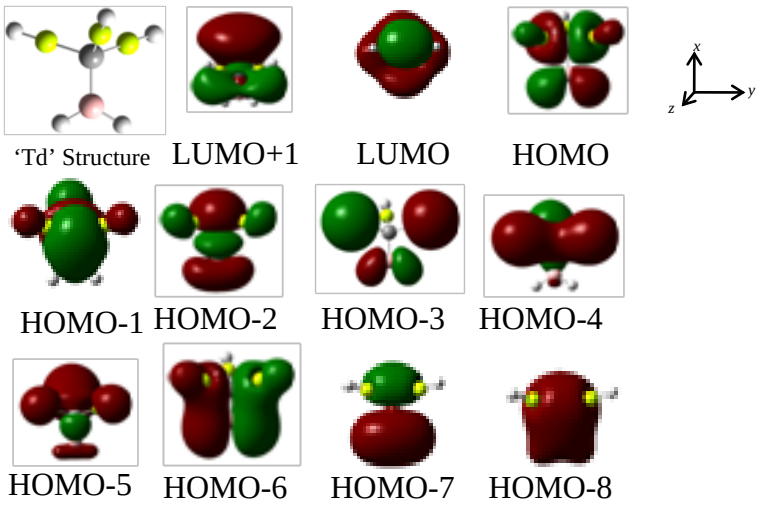


***Figure S.1b**: Larger views of the MO pictures for the tetrahedral type $C(BeH)_3BH_2$ structure studied for comparison with the stable planar structure. Miniature versions of these pictures are included in the main article.*

Notes on Molecular Orbital (MO) Composition.

Orbital	**Primary Atomic Orbital Compositions of MOs in Figure S.1b.**
LUMO+1:	p_x orbitals of Be and C.
LUMO:	p_z orbitals of B and Be
HOMO	p_y orbitals of B, Be, and C, and the *s* orbitals of H atoms bonded to Be and B centers.
HOMO-1	p_z on C and the s orbitals on H atoms on Be centers
HOMO-2	p_x orbitals of B and C, p_y orbital on Be centers and *s* orbitals of H atoms bonded to Be and B centers.
HOMO-3	p_y orbitals of B and *s* orbitals of H atoms bonded to Be and B centers.
HOMO-4	p_x orbitals of B and C, and *s* orbitals of H atoms bonded to Be centers.
HOMO-5	p_z orbitals of B and C, and *s* orbitals of H atoms bonded to Be centers.
HOMO-6	p_y orbitals of B and C, and *s* orbitals of H atoms bonded to Be centers.
HOMO-7	*s* orbital of B, p_x on C, and *s* orbitals of H atoms bonded to B.
HOMO-8	*s* orbital of B and C, and *s* orbitals of H atoms bonded to B.

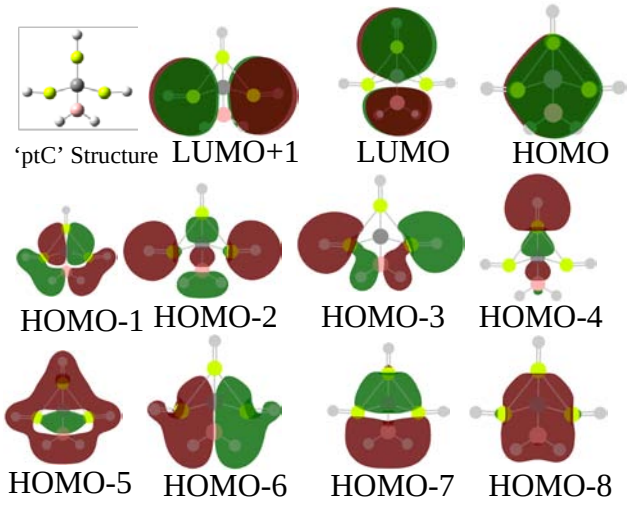


***Figure S.1c**: Larger views of the MO pictures for the minimum energy $C(BeH)_3BH_2$ structure. Miniature versions of these pictures are included in the main article.*

Notes on Molecular Orbital (MO) Composition.

Orbital	**Primary Atomic Orbital Compositions of MOs in Figure S.1c.**
LUMO+1:	p_z orbitals of $Be_{(2)}$ centers.
LUMO:	p_z orbitals of B and $Be_{(1)}$ with a small contribution from the C p_z as well.
HOMO	Contributions from p_z orbitals of B, $Be_{(1)}$, $Be_{(2)}$, and C.
HOMO-1	p_y orbitals of B, $Be_{(1)}$, $Be_{(2)}$, and C, and *s* orbitals of H atoms bonded to B and $Be_{(2)}$ centers.
HOMO-2	p_x orbitals of B and C, p_y orbital on $Be_{(2)}$ centers and *s* orbitals of H atoms bonded to B and $Be_{(2)}$ centers.
HOMO-3	p_y orbitals of B, and $Be_{(2)}$, and *s* orbitals of H atoms bonded to $Be_{(2)}$ and B centers.
HOMO-4	p_x orbitals of B, $Be_{(1)}$, and C, and *s* orbitals of H atoms on $Be_{(1)}$.
HOMO-5	p_x orbitals of B and C, p_y orbital on $Be_{(2)}$ centers and *s* orbitals of H atoms bonded to B and all Be centers.
HOMO-6	p_y orbitals of B, and C, and *s* orbitals of H atoms bonded to B with very small contributions from Hs on the $Be_{(2)}$ centers.
HOMO-7	p_x orbital on $Be_{(2)}$, and *s* orbitals of H atoms bonded to B.
HOMO-8	*s* orbital of B and C, and *s* orbitals of H atoms bonded to B.

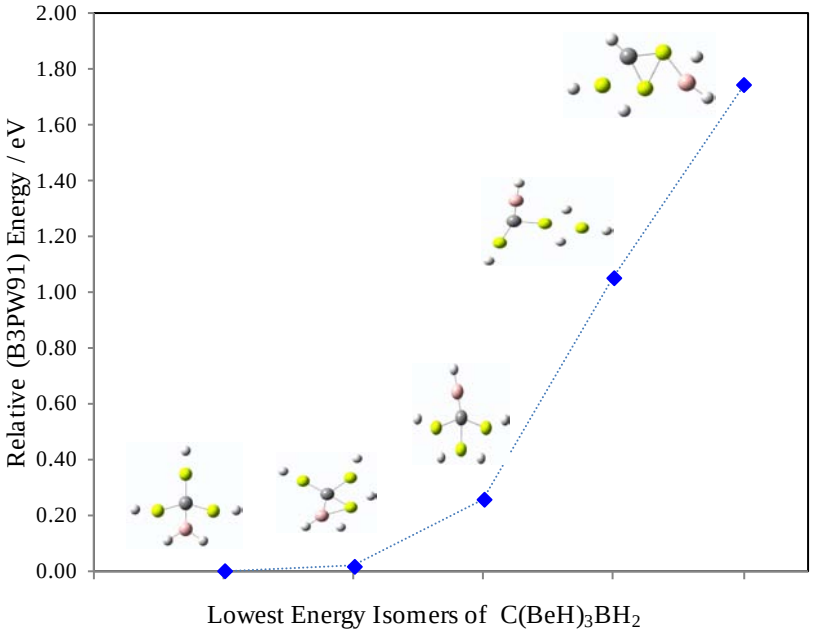


Figure S.2*: B3PW91 energies (relative to the global minimum) and geometries obtained using the cc-pVTZ basis sets for the lowest energy isomers of the $C(BeH)_3BH_2$ molecule obtained from a general search of the potential energy surface using the GEGA computational program, and reoptimized at the B3PW91 level of theory.*

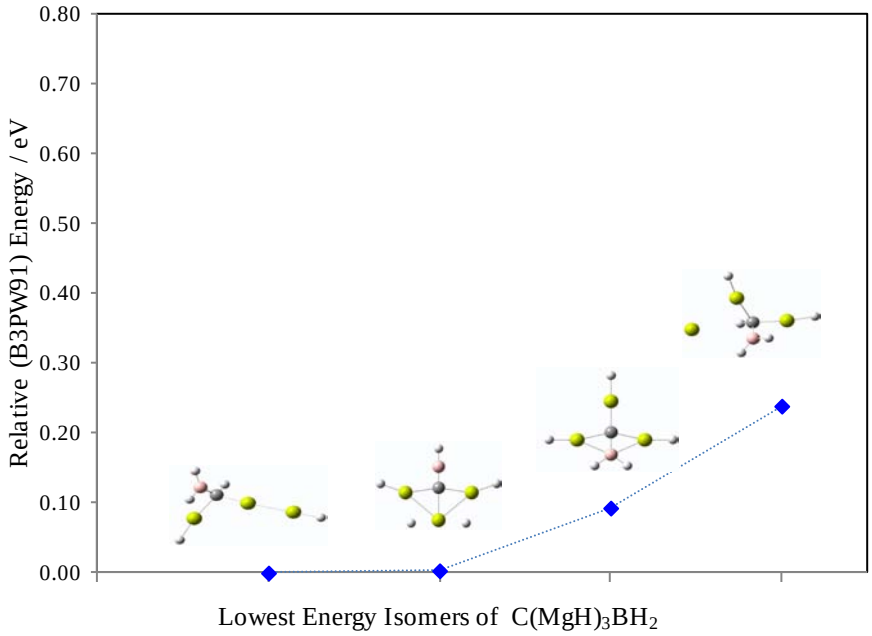


Figure S.3*: B3PW91 energies (relative to the global minimum) and geometries obtained using the cc-pVTZ basis sets for the lowest energy isomers of the $C(MgH)_3BH_2$ molecule obtained from a general search of the potential energy surface using the GEGA computational program, and reoptimized at the B3PW91 level of theory.*

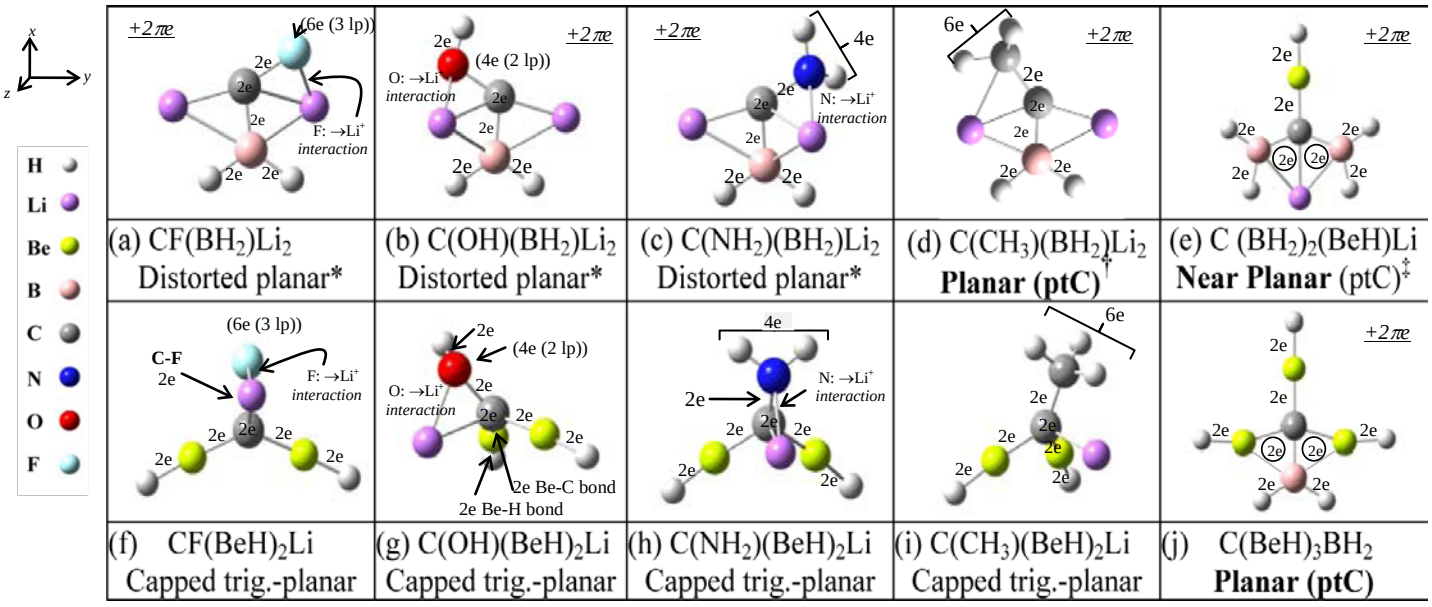


Figure S.4: Lewis type localized interpretations of the bonding in the ten molecules shown in Figure 1 in the main text.

Summary of simple localized bonding pictures shown in Figure S.4 based on a natural bond orbital NBO analysis of the structures, and test of alternative Lewis structures.

System	Proposed Lewis Type Description*
System (a)	The molecule may be viewed as having two 3c-2*e* (C-Li-B) bonds. However, the large charge on Li (+0.91*e* obtained from a natural population analysis (NPA)) and the substantial Wiberg bond index (WBI) of 1.953 for the C-B contact suggest that, for the valence electrons, the electron density is primarily in the C-B and C-F bonding regions. The following alternative seems to be a better description of the bonding in this compound and structures (b) (c) and (d) that follow the same basic structural motif. - Two polar covalent B-H bonds - A C-F single bond - Three lone pairs are on the F center. The F is negatively charged, and has a strong primarily electrostatic interaction (what may be viewed as a highly polar dative bond) with Li. - The Li atoms donate their valence electrons into the C-B fragment, primarily into a p_y orbital on the C center. - A strong C-B σ bond, supported by a π bond.
System (b)	A similar arrangement to (a), except that now the 3 lone pairs are replaced by two lone pairs and one O-H bond.
System (c)	A similar arrangement to (a), except that now the 3 lone pairs are replaced by one lone pairs and two N-H bond.
System (d)	A similar arrangement to (a), except that now the 3 lone pairs are replaced by three C-H bonds.
System (e)	The C-B Wiberg Bond indices are 1.38, indicative of a significant π contribution reinforcing the σ bond. Electrons contributing to this high bond order are from the Li centers, which have a correspondingly high charge of 0.91*e*. So although the structure may be seen as having two 3c-2*e* (C-Li-B) bonds (see the accounting

	for the electrons in the figure above)., these bonds are strongly polarized towards the C-B bonding regions.
System (f)	The bonding in this structure and in (g), (h), and (i) is probably best understood in a Lewis picture as a sp^2 C center interacting with a Li^+ site above the C-M bonds where M = F, O, N, and C in (g), (h), and (i) respectively. 2 × C-Be-H C-M (with lone pair and any M-H bonds) A filled $2p_z$ (hence the relatively flat geometry of the fragment without the bridging Li)
System (g)	See comments on system (f)
System (h)	See comments on system (f)
System (i)	See comments on system (f)
System (j)	The C-B Wiberg Bond index is 1.76. This is indicative of a significant π contribution reinforcing the σ bond. Electrons contributing to this high bond order are from the Be centers, which have a relatively high charge of 1.39*e* for the bridging Be atoms and 1.38*e* for isolated Be center. The structure may be seen as having two 3c-2*e* (C-Be-B) bonds (see the accounting for the electrons in the figure above). However, these 3c-2*e* bonds are strongly polarized towards the C-B bonding regions. The C-Be bond orders are quite low (~ 0.16 to 0.25) for the three Be centers in the molecule. So, the two 3c-2*e* (C-Be-B) bonds may be viewed instead as a C-B bond and a filled p_y orbital on the C center.

* The NPA analyses on which these deductions are based were carried out on the charged densities obtained at the B3PW91 level using the cc-pVTZ basis sets for all atoms.

Unconstrained Minimum Energy Structures of the 18-electron molecules considered in this work. The structures included here have no imaginary frequency at the levels of theory we considered.

$CF(BH_2)Li_2$

RB3PW91/CC-pVTZ E=-179.0139064 au

```
C  -0.2544589776   0.0316317361    0.2127220788
F  -1.0297031804   0.8044806511    1.2145620729
B  -0.1104146708   0.6598382857   -1.0975880822
H   0.5007313131   0.0153115181   -1.9418863354
H  -0.5488007185   1.736423657    -1.4943685457
Li -1.9514344534   1.1263952294   -0.2462891344
Li  0.8473801777  -1.2366642975   -0.550006444
```

$C(OH)(BH_2)Li_2$

RB3PW91/CC-pVTZ E=-155.0038955 au

```
C  -0.1025651925   0.1046359104    0.240762173
B  -0.107849149    0.6355529575   -1.1259050469
H   0.4254693527  -0.0212957196   -2.0146067522
H  -0.6073085657   1.6894604684   -1.5236310837
Li -1.856288883    1.1235097398   -0.1363392501
Li  0.8702796038  -1.189062277    -0.6611455774
O  -0.760423842    0.895872869     1.2676543841
H  -0.7554021144   0.3731894516    2.06738074
```

$C(NH_2)(BeH)_2Li$

RB3PW91/CC-pVTZ E=-132.2437373 au

```
C  -0.2320149963   0.2746320958    0.1052851968
Li -2.1744201063   0.3721441127    0.2741391611
Be  0.0970644472  -1.2904513282   -0.1062374144
H   0.3672954028  -2.5701599571   -0.4167594719
Be  0.0970913218   0.8739834198   -1.3558746907
H   0.3673427891   1.244912298    -2.6193931133
N  -0.7007383176   0.9751452419    1.3185992671
H  -0.3886907116   1.9366033028    1.3620909662
H  -0.3887081591   0.5320754415    2.1729956455
```

$C(CH_3)(BH_2)Li_2$

RB3PW91/CC-pVTZ E=-119.0839375 au

```
C   0.1174216585    0.3241443037   0.0919720549
B  -0.3017724558    0.4503894617  -1.2844801591
H   0.2008665651   -0.2362253714  -2.1871696426
H  -1.1659008931    1.1951976155  -1.8058374725
Li -1.3148544364    1.6858020348  -0.1284800134
Li  1.1848885723   -0.932893288   -0.8575776216
C  -0.1624176563    0.886034417    1.4414753788
H  -0.961804784     1.7056947354   1.5890568866
H  -0.4928208538    0.1204936628   2.1504812672
H   0.7211335253    1.3521594782   1.8887053517
```

$C(BH_2)_2(BeH)Li$

RB3PW91/CC-pVTZ E=-113.0704053 au

```
C  -0.6129234697    0.0197672602    -0.2532982696
Be -0.0292836425   -1.5224064924    -0.2747073763
H   0.4446123661   -2.7742145036    -0.2924321042
B   0.2435043918    0.9390192959    -1.0660843007
H   0.029183681     2.1636784187    -1.1901332988
H   1.2186579834    0.6202342629    -1.6857666147
B  -2.0133518839    0.0672769834     0.271762301
H  -2.6706304405    1.1208350492     0.4096957704
H  -2.6631532228   -0.8792462473     0.6158226289
Li -1.1586025128    1.9639960731     0.093020344
```

$CF(BeH)_2Li$

RB3PW91/CC-pVTZ E=-176.1086223 au

```
C  -0.3288930642   0.0849006214   -0.2233408434
Li -2.1683251759   0.4099679597    0.3396535368
Be  0.0743407632  -1.479421985     0.0231135548
H   0.3561357522  -2.7838309911    0.1595133466
Be  0.0743717902   1.0804901246   -1.4548527229
H   0.3561919084   1.8508149775   -2.5163013634
F  -0.6138938838   0.8443659482    1.0920854056
```

$C(NH_2)(BH_2)Li_2$

RB3PW91/CC-pVTZ E=-135.14304782 au

```
C   0.11564987   -0.47383281   -0.00137170
B   1.05814246    0.61419526   -0.28445170
H   2.27194537    0.42106089   -0.19845702
H   0.76335700    1.77596739   -0.58212001
Li -0.55486054    1.20831674    0.92476427
Li  1.76428069   -1.26670089    0.32385698
N  -1.31076431   -0.19900906   -0.09195841
H  -1.58945557    0.14662243   -1.00582599
H  -1.88336859   -1.00341426    0.11473684
```

$C(OH)(BeH)_2Li$

RB3PW91/CC-pVTZ E=-152.09456591 au

```
C  -0.23719803    0.01070923   -0.08689974
Li  0.92997675   -0.06125568    1.46974754
Be -1.15308349   -1.33450784   -0.08841006
H  -1.99469667   -2.37870760   -0.00274169
Be -1.09236600    1.38563033   -0.02089773
H  -1.80565887    2.52122861    0.07204823
O   1.23762749   -0.10731530   -0.33056391
H   1.51439144    0.63102309   -0.87540833
```

$C(CH_3)(BeH)_2Li$

RB3PW91/CC-pVTZ E=-116.1923234 au

```
C  -0.1420021544   0.2449903036   0.0375050097
Li -1.9947787725   0.1673395709   0.512876245
C  -0.0846631739   1.0143237806   1.3579827667
H   0.2568962295   2.0487929176   1.2579711757
H  -1.0704382135   1.1338551375   1.8902907647
H   0.5411568493   0.5442759203   2.1223091859
Be  0.2901456932  -1.2845250912  -0.2231071118
H   0.5853906924  -2.5574552445  -0.5443333834
Be -0.1178249887   0.854295007   -1.4531009223
H  -0.1425148713   1.2547756553  -2.7375227665
```

$C(BeH)_3BH_2$

RB3PW91/cc-pVTZ E=-110.1946125

```
6  0.000000    0.000000    0.229608
4  0.000000    1.606736   -0.217192
1  0.000000    2.939039   -0.153533
4  0.000000    0.000000    1.846795
1  0.000000    0.000000    3.175453
4  0.000000   -1.606736   -0.217192
1  0.000000   -2.939039   -0.153533
5  0.000000    0.000000   -1.224666
1  0.000000   -1.031954   -1.886173
1  0.000000    1.031954   -1.886173
```

Unconstrained Minimum Energy Structures of **$C(BeH)_3BH_2$** at different levels of theory.

$C(BeH)_3BH_2$

RB3PW91/cc-pVTZ E=-110.1946125

6	0.000000	0.000000	0.229608
4	0.000000	1.606736	-0.217192
1	0.000000	2.939039	-0.153533
4	0.000000	0.000000	1.846795
1	0.000000	0.000000	3.175453
4	0.000000	-1.606736	-0.217192
1	0.000000	-2.939039	-0.153533
5	0.000000	0.000000	-1.224666
1	0.000000	-1.031954	-1.886173
1	0.000000	1.031954	-1.886173

MP2(full)/cc-pVTZ E(MP2)=-109.9128958

6	0.000000	0.000000	0.231747
4	0.000000	1.603846	-0.219410
1	0.000000	2.926365	-0.152310
4	0.000000	0.000000	1.846776
1	0.000000	0.000000	3.166372
4	0.000000	-1.603846	-0.219410
1	0.000000	-2.926365	-0.152310
5	0.000000	0.000000	-1.225537
1	0.000000	-1.024950	-1.878187
1	0.000000	1.024950	-1.878187

CCSD/cc-pVTZ E (CCSD)=-109.8743393

6	0.000000	0.000000	0.227546
4	0.000000	1.617980	-0.213189
1	0.000000	2.949588	-0.144609
4	0.000000	0.000000	1.853058
1	0.000000	0.000000	3.181952
4	0.000000	-1.617980	-0.213189
1	0.000000	-2.949588	-0.144609
5	0.000000	0.000000	-1.235945
1	0.000000	-1.031318	-1.892504
1	0.000000	1.031318	-1.892504

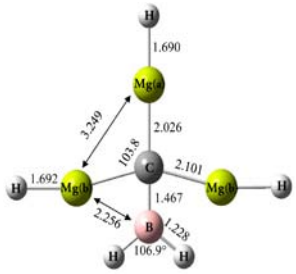
Additional Tables

Table S.1: Computed geometries (with distances in angstrom (Å) units), WBIs, point charges, *q*, and vibrational and electronic data for the planar $C(CH_3)(BH_2)Li_2$ molecule at three different levels of theory using the all electron cc-pVTZ basis sets for all the elements.

	B3PW91	MP2(full)	CCSD [a]
Bond Lengths			
C-Li(a)	1.903	1.908	1.917
C-Li(b)	1.988	1.990	2.019
C-B	1.444	1.448	1.456
C(b)-Li(b)	2.105	2.100	2.124
C-C(b)	1.488	1.492	1.508
*WBI*s			
C-B	1.864	1.704	1.695
C-Li(a)	0.204	0.207	0.190
C-Li(b)	0.188	0.171	0.144
C-C(b)	1.134	1.043	1.027
C(b)-Li(b)	0.053	0.047	0.044
Li(a)-B	0.075	0.067	0.063
Li(b)-B	0.106	0.100	0.096
Ccenter	3.524	3.240	3.162
Charges / e			
q_C	-0.883	-0.881	-0.899
$q_{Li(a)}$	0.807	0.778	0.793
$q_{Li(b)}$	0.744	0.737	0.759
q_B	-0.368	-0.318	-0.315
$q_{C(b)}$	-0.628	-0.603	-0.570
Lowest ν / cm^{-1}	51.1	32.4	*i*30.7 [a]
$\Delta E_{H\text{-}L}$ / eV	*3.75**	7.18	7.12

Note: C(b) is the methyl C in the structure; Li(a) is the Li atom not bonded directly to C(b). Li(b) is bonded to C(b). The CCSD optimized structure has one imaginary frequency. * The HOMO-LUMO gaps obtained from the B3PW91 density functional theory (DFT) method is included for completeness. However, it is well known that gaps obtained from DFT methods in general are unreliable as estimates of the excitation energies or relative stabilities of compounds.

Table S.2: Computed geometries (with distances in angstrom (Å) and angles in degree (^{o}) units), and vibrational and electronic data for the planar $C(MgH)_3(BH_2)$ molecule that is an isomer of the global minimum in the Be analogue at two different levels of theory using the all electron cc-pVTZ basis sets for all the elements.

Structure (with parameters)		B3PW91	MP2(full)
	C-Be(a)	2.024	2.026
	C-Be(b)	2.106	2.101
	C-B	1.465	1.467
	Be(a)-H	1.700	1.690
	Be(b)-H	1.703	1.692
	B-H	1.241	1.228
	H-B-H	106.3	106.9
	Be-C-Be	103.0	103.8
	Lowest ν / cm^{-1}	22.9	45.9
	$\Delta E_{H\text{-}L}$ / eV	*5.20**	10.1

* The HOMO-LUMO gaps obtained from the B3PW91 density functional theory (DFT) method is included for completeness. However, it is well known that gaps obtained from DFT methods in general are unreliable as estimates of the excitation energies or relative stabilities of compounds.

Table S.3: Optimized $C(BeH)_n(BH_2)_{4-n}$ Structures for $n = 0 – 4$ obtained at the B3PW91 level of theory using the cc-pVTZ basis sets for all the elements.

***n* = 0**			***n* = 1**		
B	-1.93866900	0.00093900	-0.05665700	C	-0.31042850	-0.03411573	0.01510241
H	-2.55165400	1.02840100	-0.01792100	Be	1.41149739	0.00629068	0.70235879
H	-2.54765400	-1.02882900	-0.01672000	H	2.24940952	-0.01141347	1.74800648
B	0.76267100	0.92140600	-0.46056400	B	0.51109212	-1.15840094	-0.51902896
H	0.91022900	1.95356800	-1.01762400	H	0.18022249	-2.17473615	-1.03220270
H	1.62270400	0.01250800	-1.02110100	H	1.75287830	-1.02986081	-0.44886860
C	-0.42980700	0.00360500	-0.12432000	B	0.37305548	1.23866840	-0.38550504
B	0.58784600	-0.01544800	1.05434200	H	1.60320107	1.30994488	-0.20153415
H	1.44717500	0.99130600	0.71549600	H	-0.09326866	2.23917692	-0.81809034
H	0.48018400	-0.03274000	2.23049100	B	-1.81513670	-0.07690800	0.30462684
B	0.76189700	-0.90834700	-0.48529200	H	-2.56365036	0.65368943	-0.27412329
H	0.90273000	-1.92494800	-1.07186900	H	-2.25726541	-0.82406644	1.12629882
H	1.44640400	-1.01364900	0.68602200				

***n* = 2**			***n* = 3**		
C	0.00050232	-0.00144135	-0.45369032	C	0.000000	0.000000	0.229608
Be	-0.90562776	-1.10980893	0.48456997	Be	0.000000	1.606736	-0.217192
H	-1.14308628	-2.22875766	1.16909405	H	0.000000	2.939039	-0.153533
Be	0.90199766	1.10936577	0.48595530	Be	0.000000	0.000000	1.846795
H	1.13713781	2.23007994	1.16812659	H	0.000000	0.000000	3.175453
B	-1.31268978	0.58623868	-0.29056636	Be	0.000000	-1.606736	-0.217192
H	-1.84493629	1.51727177	-0.79574540	H	0.000000	-2.939039	-0.153533
H	-2.07221632	-0.04541039	0.49383077	B	0.000000	0.000000	-1.224666
B	1.31545924	-0.58518117	-0.28904583	H	0.000000	-1.031954	-1.886173
H	1.84942541	-1.51507077	-0.79454181	H	0.000000	1.031954	-1.886173
H	2.07133485	0.04702038	0.49733761				

***n* = 4**			
C	-0.00002727	-0.00001054	-0.00003842
Be	-0.63307731	1.49932947	0.06337048
H	-1.15087622	2.72557152	0.11523077
Be	-1.16712409	-1.06587151	-0.39324073
H	-2.12157059	-1.93769792	-0.71480807
Be	0.62247929	-0.38840269	1.45407810
H	1.13166158	-0.70607961	2.64330870
Be	1.17772056	-0.04504144	-1.12418732
H	2.14095508	-0.08178607	-2.04358306