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Computational Predictions of the Beryllium Analogue of Borole, Cp^+, and the Fluorenyl Cation: Highly Stabilized, non-Lewis Acidic Antiaromatic Ring Systems

Terri E. Field-Theodore, David J. D. Wilson,* and Jason L. Dutton*

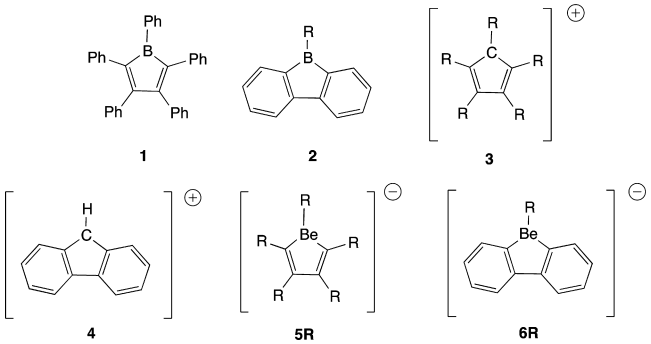
Department of Chemistry and Physics, La Trobe Institute for Molecular Science, La Trobe University, Melbourne, Victoria, Australia

Supporting Information

ABSTRACT: A computational study of a set of synthetically unknown beryllium-containing rings, anionic analogues of antiaromatic boroles, has been carried out to investigate their structure, stability, and potential reactivity. The results indicate that these compounds should be electronically viable (as assessed from HOMO−LUMO and singlet−triplet gaps) and therefore potential targets for synthesis. In strong contrast with boroles, these beryllium species are predicted to be not Lewis acidic but rather Lewis basic, with reactivity centered on the endocyclic Be−C bond.

INTRODUCTION

The chemistry of antiaromatic borole rings has seen a surge of interest in the past decade. While first reported in 1969,[1] the chemistry of this system has remained quite underdeveloped until the structural determination of 1,2,3,4,5-pentaphenylborole (**1**) by Braunschweig et al. in 2008.[2] Since that time, it has been shown that boroles possess a rich chemistry.[3] They are extremely Lewis acidic at the boron center yet have nucleophilic B−C bonds, which has been taken advantage of in the activation of a wide variety of small molecules and unusual bond transformations.[4−12] Two-electron reduction of the boroles to give 6π aromatic rings allows for the use of the dianionic derivatives as ligands for transition metals.[13] The related 9-borafluorene system **2**, stabilized by flanking fused phenyl rings, has also attracted attention.[14] The parent all-carbon systems, the cyclopentadienyl cation (Cp^+, e.g., **3**) and fluorenyl cation **4**, have also been of long-term interest because of them being considered the quintessential antiaromatic carbon compounds. No monocyclic derivative of Cp^+ has been isolated,[15−17] but the fluorenyl cation was recently isolated in a water−ice matrix at temperatures as high as 30 K.[18]



The increased stability of boroles over Cp^+ is due to the smaller electronegativity of boron (Pauling value of 2.04 compared to carbon at 2.55), which results in a lifting of the degeneracy of Hückel π orbitals. The bonding molecular orbital (MO) with a contribution from boron is raised in energy relative to the π MO without a contribution from boron, with the boron-containing π MO becoming the lowest unoccupied molecular orbital (LUMO; Figure 1). Destabilization of the

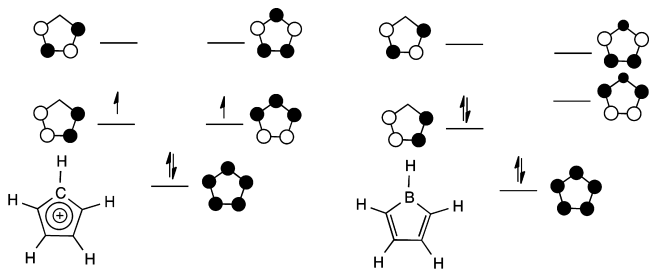


Figure 1. Qualitative diagram of the π MOs in $[Cp]^+$ and the parent borole.

boron-centered π MO of the borole is sufficient enough that the electronic ground state for boroles such as **1** is a singlet in contrast to the triplet ground state for Cp^+ (Figure 1). On the basis of this rationale, we hypothesized that the synthetically unknown beryllium analogues of this system (e.g., **5R**, **6R**) could display even greater electronic stability because of the smaller electronegativity of beryllium (1.57).

The overall charge of the ring in this case would be 1−, with the formal charge located on the beryllium atom. Beryllium chemistry is highly underdeveloped because of the high toxicity

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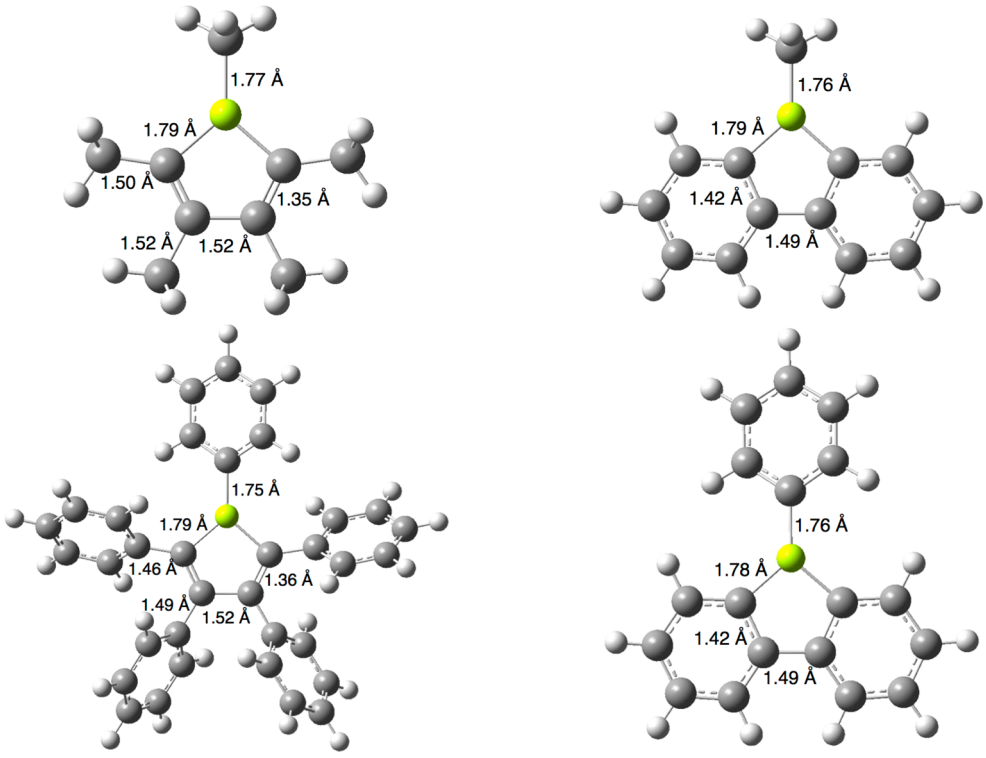

Figure 2. B3LYP/def2-TZVP-optimized gas-phase geometries and selected calculated bond distances (Å) for **5R** and **6R**.

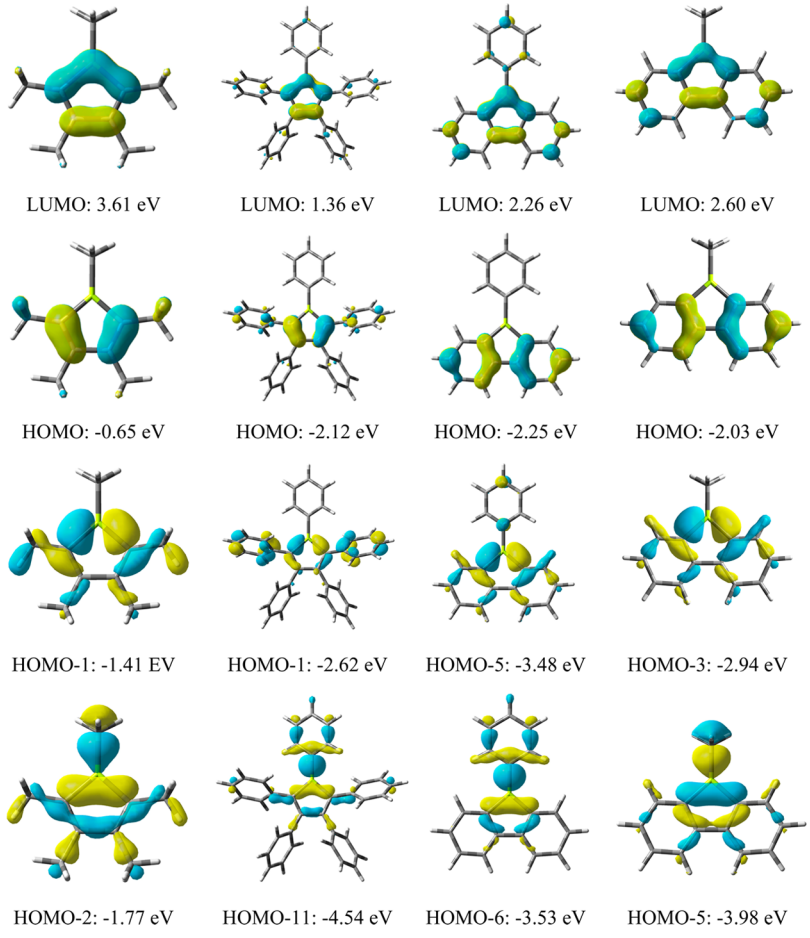

Figure 3. Important MOs of **5R** and **6R** (R = Me, Ph). B3LYP/def2-TZVP.

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of elemental beryllium, beryllium salts, and beryllium-containing compounds.[19] Nonetheless, the past few years have seen increasing interest in the organochemistry and coordination chemistry of beryllium.[20−31] Employing a computational approach is particularly attractive for exploring new beryllium-based systems[32−36] because beryllium is a light atom with typically well-defined electronic properties, while also avoiding toxicity issues. The parent beryllium analogue of borole, the $[C_4H_4BeH]^-$ ring, has previously been considered but only peripherally as one member of a large set of ring systems investigated for aromaticity using nucleus independent chemical shift (NICS)[37] and aromatic stabilization energy,[37−39] with no investigation of the stability and structure of the molecules themselves. The purpose of the current study was to evaluate the stability and likely reactivity of the **5R** and **6R** (R = Me, Ph) family of beryllium ring compounds using theoretical methods, from the perspective of predicting the chemistry of a new class of beryllium compounds and also from the perspective of a potential new addition to the "ole" rings, in this case having unusual properties. **5R** and **6R** were chosen as model systems because these more highly substituted analogues have a much greater likelihood of a synthesis being realized than the parent $[C_4H_4BeH]^-$ ring.

RESULTS AND DISCUSSION

Geometrical Properties. The properties of compounds **5R** and **6R** were considered with R = Me, Ph, with B3LYP/def2-TZVP-optimized gas-phase geometries presented in Figure 2. Geometry optimizations inclusive of the solvent (self-consistent reaction field with CH_2Cl_2) produced Be−C and C−C distances within 0.004 Å of the gas-phase results and are not discussed further. For **5R**, the optimized gas-phase geometries gave similar structures within the five-membered rings, with localized bonding in a planar ring that is consistent with antiaromatic character. The C_2-C_3 bond distances were calculated to be 1.350 Å (**5Me**) and 1.356 Å (**5Ph**), with the C_3-C_4 bond distance being in the range of 1.521−1.513 Å in both rings. The endocyclic Be−C bonds (Be_1-C_2) were consistent at 1.791−1.792 Å, with the exocyclic Be_1-C_1 bond distances calculated to be 1.772 and 1.750 Å for **5Me** and **5Ph**, respectively. The Be−C bonds are similar to those of other trigonal-planar triorganoberyllium species. For example, the N-heterocyclic carbene (NHC) adduct of Ph_2Be has Be−C bond distances of 1.75 Å (Be−Ph) and 1.81 Å (Be−NHC).[40]

For the beryllium fluorenyl derivative **6R**, the Be−C bonds have similar distances of 1.760 Å (exocyclic) and 1.776−1.789 Å (endocyclic) for both rings. In this case, the C_2-C_3 bonds were calculated to be 1.420 Å, and the C_3-C_4 bond was calculated to be 1.493 Å for both rings, indicating the possibility of greater delocalization in **6R** than is present in **5R**, induced by the fused phenyl rings.

Electronic Properties. The framework of the calculated MOs of **5R** and **6R** are typical of an antiaromatic five-membered ring (Figure 3). The highest occupied molecular orbital (HOMO) is composed of endocyclic π interactions between the C_2-C_3 and C_4-C_5 carbons, while the LUMO contains π interactions between $C_2-Be_1-C_5$ and C_3-C_4 (Figure 3). In **5Ph**, there is very little delocalization of these orbitals into the π systems of the various flanking phenyl groups. The endocyclic Be−C σ bond is found to be relatively high in energy, being the HOMO−1 for both **5Me** and **5Ph**, indicating that these bonds would be potentially reactive. In **6R**, the corresponding Be−C σ binds are stabilized somewhat, being found in the HOMO−5 for **6Ph** and the HOMO−3 for **6Me**. The exocyclic Be−C σ bonds are stabilized compared to the endocyclic bonds, being found in the HOMO−2 for **5Me**. For the other derivatives, the corresponding orbital is further stabilized, being found in the HOMO−11 for **5Ph** and the HOMO−6 and HOMO−5 for **6Ph** and **6Me**, respectively.

A key consideration for the potential electronic stability of antiaromatic systems and hence the synthetic viability of a proposed species is the magnitude of the HOMO−LUMO gap.[41] Borole **1** and the derivative containing C_6F_5 rings rather than Ph have B3LYP/def2-TZVP-calculated HOMO−LUMO gaps of 2.62 and 2.69 eV, respectively.[42] This allows for these boroles to exist as ground-state singlets and subsequently be isolated in the solid state at room temperature and handled in compatible solvents. In contrast, a homoleptic Cp^+ system such as Me_5Cp^+ would have (nearly) degenerate frontier orbitals, giving a ground-state triplet, and these are not isolatable. For compounds **5Me** and **5Ph**, the HOMO−LUMO gap widens appreciably from the borole rings, with calculated values of 3.47 and 4.25 eV, respectively. The singlet−triplet gaps were calculated to be 127.4 kJ/mol (**5Me**) and 295.0 kJ/mol (**5Ph**), respectively. For comparison, the corresponding value for borole **1** is 128 kJ/mol.[42] The anionic beryllium derivatives of fluorenyl are more electronically stable, with calculated HOMO−LUMO gaps of 4.63 and 4.51 eV for **6Me** and **6Ph**, respectively, with substantial delocalization of the HOMO into the fused phenyl groups.

NICS calculations can be used to quantify the aromaticity of a ring system.[43] Broadly, large negative NICS values (ppm) denote aromaticity, while large positive NICS values represent antiaromaticity. The NICS values considered here are NICS(0) and $NICS(1)_{zz}$, where the z axis is perpendicular to the plane of the five-membered ring (the origin is the centroid of the ring plane). The $NICS(1)_{zz}$ metric is considered to provide a more reliable measure of the aromaticity for planar rings than the first generation of NICS(0), where shielding is calculated at the centroid of the molecular ring plane.[37] For reference, borole **1** has a B3LYP/def2-TZVP-calculated $NICS(1)_{zz}$ value of 24.2 ppm, while aromatic $[C_5H_5]^-$ has a $NICS(1)_{zz}$ value of −34.4 ppm. The parent $[C_4H_4BeH]^-$ ring has a calculated $NICS(1)_{zz}$ of 9.7 ppm. The $NICS(1)_{zz}$ values for **5Me** and **5Ph** are calculated to be 12.7 and 13.4 ppm, respectively. The fluorenyl derivatives give similar values of 12.6 ppm (**6Me**) and 13.7 ppm (**6Ph**). From these results, all **5R** and **6R** are concluded to be antiaromatic, as may be expected.

Predicted Lewis Acidic/Basic Behavior. Antiaromatic borole rings are very strong boron-based Lewis acids. Typically, coordination of a substrate to the boron center is the starting point for reactions of the boroles, which can even coordinate (at least transiently) very weak Lewis bases such as H_2 and make adducts with CO, which is very rare for a main-group Lewis acid.[7−9] Because of the LUMO having an appreciable coefficient at beryllium and the beryllium being coordinately unsaturated and having only three bonds, we hypothesized that the beryllium ring would be a strong Lewis acidic anion. Despite the negative charge on the rings, formally located at beryllium, the calculated natural population analysis (NPA) charges at beryllium in **5Me** and **5Ph** are 0.98+ (0.94+ in the CH_2Cl_2 solvent field) and 1.02+ (1.01+ in the CH_2Cl_2 solvent field), respectively. The NPA charge on beryllium is greater than that on boron in the analogous borole **1** (0.85+), owing to the smaller electronegativity of beryllium compared to that of boron, which lends support to our hypothesis. The NPA charge

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on beryllium in **6Me** was calculated to be 0.96+ (0.94+ in the CH_2Cl_2 solvent field), and for **6Ph**, the charge was calculated to be 0.94+ (0.93+ in the CH_2Cl_2 solvent field).

The Lewis acidity of the beryllium analogues was evaluated from fluoride-ion affinities and binding energies of pyridine of **5R** and **6R** (calculated as $\Delta G_{298\ K}$). The fluoride affinity was considered because it is a standard measure of Lewis acidity. Pyridine binding was additionally included because it is neutral (anion−anion repulsion could be a factor for $[F]^-$) in addition to the known ability of analogous boroles to easily coordinate pyridine ligands.[4,8] Fluoride affinities were calculated in both the gas and solvent phases (CH_2Cl_2 solvent). Additionally, $[OCF_3]^-$ was used as a "softer" fluoride source, which has been considered to give more reliable fluoride affinities than those using $[F]^-$.[44,45] The fluoride affinity of borole **1** is calculated to be −68 kJ/mol at the B3LYP/def2-TZVP level of theory, using $[OCF_3]^-$, corrected for the CH_2Cl_2 field (Table 1).

Table 1. B3LYP/def2-TZVP-Calculated ΔG Values (kJ/mol) for the Addition of $[F]^-$ (Using Both $[F]^-$ and $[OCF_3]^-$ as Fluoride Sources) and Pyridine to 5R and 6R[a]

	$[F]^-$	$[OCF_3]^-$	pyridine
1	−357 (−149)	−146 (−68)	N/A
5Me	177 (−2)	388 (79)	53 (54)
5Ph	3 (−52)	214 (29)	34 (34)
6Me	134 (−17)	345 (64)	53 (45)
6Ph	83 (−29)	294 (52)	48 (45)

[a]Solvent (CH_2Cl_2)-corrected values are given in parentheses.

In all cases, the addition of the Lewis base resulted in the geometry optimizing to the expected tetrahedral geometry about the newly four-coordinate beryllium atom. To our surprise, the calculated ΔG for the reaction of the Lewis base to the beryllium center was unfavorable in all cases. For the addition of $[F]^-$ using $[OCF_3]^-$ as the fluoride source, solvent-corrected values ranged from +29 to +79 kJ/mol (which gives a negative fluoride affinity), indicating a lack of Lewis acidity toward fluoride. Using $[F]^-$ as the fluoride source only gave negative ΔG values in solvent-corrected cases, up to a maximum of −52 kJ/mol for **5Ph**. The addition of a neutral pyridine also resulted in a positive ΔG value, ranging from +34 to +53 kJ/mol. The data indicates that this class of five-membered antiaromatic rings would not be expected to display Lewis acidic behavior, in strong contrast with the boron analogues.

Having found a surprising lack of predicted Lewis acidic behavior for **5R** and **6R**, we turned to an evaluation of the potential Lewis basic activity. The endocyclic B−C bonds of boroles are nucleophilic, with a variety of ring insertion reactions based on this behavior after the initial coordination of a substrate to the boron center. Opening of the endocyclic B−C bond in boroles has now been observed with a variety of substrates (e.g., CO, azides, ketones, aldehydes).[5,6,8,10,11] To test the potential nature of **5Me** and **6Me** toward Lewis acids, we examined their interactions with model acids BH_3 and $[H]^+$. This portion of our study is quite speculative in nature, the resultant products may not be the final products of the proposed reactions but indicative of the kind of reactivity that may be expected. Placing BH_3 above the endocyclic Be−C bond with the boron atom most proximal to the bond in **5Me** and running a geometry optimization results in a structure where the Be−C interaction opens to 2.566 Å (Figure 4). The boron atom most closely associates with the carbon atom (C−B = 1.656 Å) with a Be−B distance of 2.100 Å. This compares to the distances of 1.870 and 1.954 Å in the only Be−B bonds reported to date, from bis-complexes of the anionic N-heterocyclic boryl base and Be^{2+} and $[BeNHC]^{2+}$, respectively.[46] There is a hydride bridging the beryllium and boron atoms with a Be−H distance of 1.566 Å. Be−H hydrides are rare, but this is likely due to the paucity of work in beryllium chemistry rather than an inherent instability of the bond. Hill and co-workers have shown that molecular complexes containing Be−H bridging interactions are stable entities.[47,48] The Be−H distance in the BH_3 addition product is very similar to that of 1.552 Å observed experimentally by Hill and co-workers, in that case bridging between two beryllium atoms. Significantly, the ΔG value for the addition of BH_3 to **5Me** is

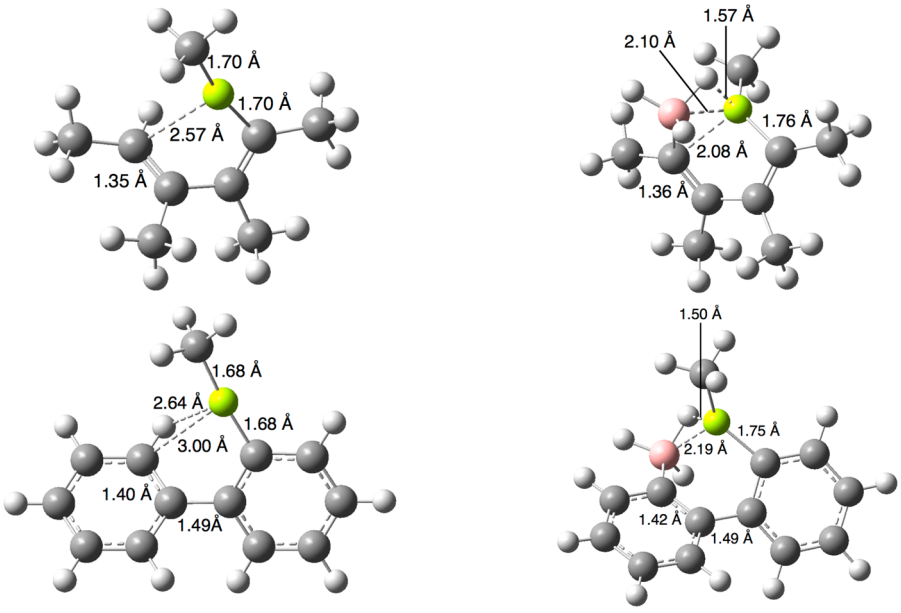

Figure 4. B3LYP/def2-TZVP-optimized geometries of the products of endocyclic attack of (a) $[H]^+$ and (b) BH_3 on **5Me** and **6Me**, respectively.

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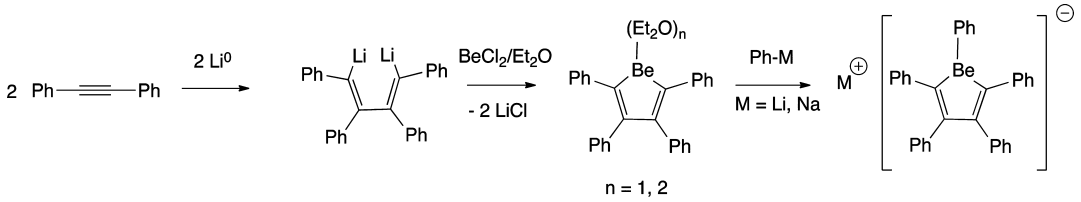
Table 2. B3LYP/def2-TZVP-Calculated $\Delta G_{298\ K}$ Values for the Addition of BH_3 and $[H]^+$ to 5R and 6R[a]

	BH_3		$[H]^+$	
	endocyclic	exocyclic	endocyclic	exocyclic
5Me	−138 (−135)	−112 (−103)	−1469 (−800)	N/A
5Ph	−107 (−110)	−96 (−96)	−1372 (−755)	N/A
6Me	−107 (−103)	−103 (−96)	−1401 (−755)	−1324 (−693)
6Ph	−103 (−102)	−99 (−97)	−1374 (−747)	−1315 (−687)

[a]Solvent (CH_2Cl_2)-corrected values are given in parentheses.

Scheme 1. Proposed Synthetic Route to 5Ph



−135 kJ/mol (CH_2Cl_2-corrected; gas phase −138 kJ/mol; Table 2), indicating that the ring is strongly Lewis basic. Compound **5Ph** optimizes to a similar geometry with BH_3, with a ΔG value of −107 kJ/mol. For comparison, the BH_3 binding energy with NH_3 is −124 kJ/mol.[49] For **6R**, attack from the exocyclic bond is predicted to be competitive with attack from the endocyclic Be−C bond on BH_3. Endocyclic attack gives products analogous to that calculated for **5Me** with ΔG values of −103 and −107 kJ/mol for **6Ph** and **6Me**, respectively. Exocyclic attack gives a product with an intact berylfluorenyl ring system, with a bridging Be−H−B interaction and the boron bound to the formally exocyclic methyl or phenyl fragment. The calculated ΔG value for these potential transformations are only slightly less than endocyclic attack at −99 and −103 kJ/mol for **6Ph** and **6Me**, respectively (CH_2Cl_2-corrected results are −96 and −97 kJ/mol).

The addition of a proton to the Be−C bond in **5Me** results in a complete ring opening, with the proton binding to the carbon atom and the formation of an essentially linear C−Be−C motif (C−Be−C 167°), as would be expected for a diorganoberyllium species, on the other side of the opened ring. The free energy for this transformation is −800 kJ/mol corrected for CH_2Cl_2 and −1469 kJ/mol in the gas phase. This is again consistent with the strongly basic behavior of the rings.

The ΔG values of protonation for **6Me** and **6Ph** were calculated to be −1401 and −1374 kJ/mol in the gas phase, respectively. The corresponding CH_2Cl_2-corrected ΔG values were calculated to be −867 and −855 kJ/mol. For **5Me** and **5Ph**, attempts to induce exocyclic attack resulted in the proton migrating to the endocyclic attack minima. For **6Me** and **6Ph**, a minimum could be located for the proton rupturing the exocyclic Be−C bond, essentially giving either a molecule or methane or benzene weakly interacting with an intact beryllium fluorenyl moiety. However, the gas-phase free-energy change associated with this transformation is not as favorable as the endocyclic attack by 60−75 kJ/mol.

Overall, these data should be used to indicate that **5R** and **6R** are likely to react as Lewis bases, given the clearly strongly favorable ΔG values from the addition of $[H]^+$ and BH_3. We would reiterate that the calculated minima may not represent the final products of these transformations in an actual reaction but do give an indication of how the processes might begin.

Finally, given that these compounds are anionic, they must therefore be paired with a cation. Realistic choices would be ions such as Li^+ or Na^+. These cations are Lewis acidic, and we have shown that ring-opening reactions are likely with Lewis acids. Therefore, as a final check on the viability of these compounds, a test pairing **5Me** with Li^+ and Na^+ was carried out. To complete a reasonable environment about the cations, two Me_2O solvates were explicitly incorporated bound to the metal cations. A geometry optimization analogous to that performed with BH_3 and $[H]^+$, with the metal cations initially placed above the beryllium, showed that these cations are not predicted to result in an opening of the ring because the Be−C bonds are essentially unperturbed. The exocyclic Be−C bond bends slightly out of the plane in the presence of the cation, but the antiaromatic π-MO framework remains intact.

CONCLUSIONS

In summary, our calculations indicate that anionic, five-membered "Beryloles" should be electronically viable species and hence potential targets for synthetic chemists with the appropriate skills to carefully handle beryllium-containing compounds. NICS calculations indicate that these are antiaromatic in character, albeit somewhat less than the most common borole rings. In strong contrast with boroles, the beryllium analogues are predicted to have no Lewis acidic tendencies but possess quite strong Lewis basic character, which may lead to a rich variety of reactivity if a synthesis can be achieved. This synthesis, using **5Ph** as an example, could potentially be as straightforward as reacting lithium-reduced coupled diphenylacetylene with commercially available $BeCl_2$, following the standard protocol for the formation of borole and other main-group "ole" rings (Scheme 1).[1,50] The redox-inert nature of beryllium(II) should aid in avoiding complications at this step. This could be followed by the addition of a strong nucleophile such as MeLi or PhLi (or PhNa) to complete the triorganoberyllium fragment. Any ethers present (e.g., Et_2O, tetrahydrofuran) in the reaction should not bind to the final product because of their predicted nonacidic nature, avoiding this potential complication.

COMPUTATIONAL DETAILS

All calculations were carried out using the *Gaussian 09* package.[51] All geometries were optimized with density functional theory using the

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B3LYP[52,53] functional. The def2-TZVP basis set was used for all calculations.[54] Stationary points were characterized as minima by calculating the Hessian matrix analytically at this level of theory. Thermodynamic corrections were taken from these calculations at the same level of theory (1 atm, 298.15 K). Solvent effects for geometry optimizations of **5R** and **6R** were considered using the integral equation formulation of the polarizable continuum model (IEFPCM)[55−57] with a CH_2Cl_2 solvent. All reported solvent-corrected energetics were calculated with the SMD solvation model[58] within IEFPCM as single-point energies at the optimized gas-phase geometries (thermodynamic corrections are the gas-phase-calculated values). MO analysis was carried out at the B3LYP/def2-TZVP level of theory at the optimized gas-phase geometries. NICS[43] shielding values were computed through the gauge, including the atomic orbital (GIAO) method at the B3LYP/def2-TZVP level of theory (gas phase). Both NICS(0) and NICS(1) were calculated. The in-plane NICS(0) component was calculated at the centroid of the five-membered ring plane. The out-of-plane $NICS(1)_{zz}$ component was also calculated, where the z axis is perpendicular to the plane of the five-membered ring and the origin is at the centroid of the ring plane, at a distance of 1.0 Å above and below the centroid of the ring.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01255.

Cartesian coordinates and energies for optimized geometries (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: david.wilson@latrobe.edu.au.

*E-mail: j.dutton@latrobe.edu.au; Twitter, @DuttonChemistry.

Notes

The authors declare no competing financial interest.

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