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Aromaticity in Three Dimensions. 4.[1] Influence of Orbital Compatibility on the Geometry and Stability of Capped Annulene Rings with Six Interstitial Electrons

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Abstract: A $4n + 2$ interstitial electron rule extends the concept of aromaticity to three-dimensional, delocalized systems. Thus, pyramidal molecules are divided conceptually into caps and rings. The π electrons of the ring and the electrons available from the cap for ring–cap binding constitute the interstitial electrons; e.g., η^5-C_5H_5BeH (C_{5v}) has six interstitial electrons—five from the C_5H_5 ring and one from BeH. Since the interaction of the lowest a and e π orbitals of an annulene ring with the sp and p orbitals of a first-row cap, X or X–H, leads to three stabilized orbitals, pyramidal systems with $4n + 2$ interstitial electrons are generally expected to be stable. Ab initio SCF MO calculations were carried out to assess the strength of such cap–ring interactions and to find which ring–cap combinations should be optimum; STO-3G and 3-21G basis sets were used on a series of pyramidal systems with six-, five-, four-, and three-membered carbocyclic rings and caps selected from the set Li, LiH, Be, BeH, B, BH, C, CH, N, and NH. Appropriate charges were assigned to give six interstitial electrons. Geometry optimizations were carried out within C_{nv} (n = 3–6) symmetry (expected to give local minima). The C–H bonds of the ring bend out of the ring plane. This bending was away from the cap for small rings and for caps with highly diffuse orbitals. With large rings and with caps with less diffuse orbitals, the C–H bonds of the ring bend toward the cap. The out-of-plane ring C–H bending increases the ring–cap overlap by rehybridizing the π orbitals of the ring. Optimum ring–cap combinations have little C–H out-of-plane bending; isodesmic reactions evaluating energies provide support for this conclusion. Smaller rings prefer caps having less diffuse orbitals, and vice versa. The following ring–cap combinations are indicated to be best: six-membered rings with Li, five-membered rings with Be, and four-membered rings with B or C. These concepts can be extended to transition-metal complexes by using isolobal analogies.

Ever since Kekulé's intuitive suggestion for the structure of benzene,[3] the concept of aromaticity has played a central role in chemistry. Robinson's "aromatic sextet" theory[4a] and the $4n + 2$ rule of Hückel[4b] not only extended the concept of aromaticity beyond benzene but also led to the fundamental appreciation that the properties of seemingly similar systems (both ground and transition states) are strongly influenced by the number of electron with which they are associated. How much new and intriguing chemistry has been discovered as a consequence![5] But the terms "aromatic" and "antiaromatic" are now used in so many contexts and are so ill defined as to encourage criticisms of being "antipedagogical and outmoded" or worse, "dangerous and nonscientific".[5] If the term "aromaticity" is to retain its usefullness, we agree with Balaban[5e] that "narrower, more precisely defined areas" of application need to be specified and that other terms should be employed for other situations. We do not agree, however, that "aromticity" should be reserved only for "phenomena associated with the presence of odd number of electron pairs interacting in an approximately planar ring with contiguous conjugation".

"Aromaticity" must also be associated with three-dimensional systems, e.g., those symbolized by **1**.[1,6] Ferrocene exhibits the same classical substitution reactions as does benzene.[7a,b] Only a myopic chemist could look solely at the carbon rings in metallocenes, ignore the metal, and count to six! The cyclopentadienyl anion is surely aromatic. Should association with its counterion at a face (compare the C_{5v} structure (**2**) calculated for C_5H_5Li)[7c] require or even justify the introduction of a new term? The present paper will develop the thesis that a $4n + 2$ *interstitial* electron rule[1] easily extends the classical aromatic bonding concepts to half-sandwich molecules, **1**, comprised of $(CH)_n$ annulene rings interacting with "capping" atoms or groups, X. We will consider a large number of cap–ring combinations and will present criteria for determining which caps should provide the best match for any given ring.

We stress that the principle of what we term the "$4n + 2$ interstitial electron rule" has long been recognized.[6] The application to the boranes and carboranes was clearly explained both for singly and doubly capped ring systems by Lipscomb in 1963[6a] and was anticipated in earlier papers.[6m] An indefinitely large set of molecules, including many transition-metal systems, can be described similarly.

Computational Details

All ab initio calculations were performed with the GAUSSIAN 70 and 76 series of programs[8] with the STO-3G minimal and the 3-21G split-

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Table I. Optimized Geometries (Distances in Å, Angles in Deg) and Energies (in au) of C_{nv} Molecules **3–6** at STO-3G and 3-21G Levels[i]

molecule	energy	a[a]	b[a]	C–C	C–H	X–H	X–C	θ[b]
C_6H_6 (D_{6h})[c]	−227.89136	1.387		1.387	1.083			
$C_6H_6Li^+$, **3a**	−235.16237	1.409	1.712	1.409	1.086		2.217	2.5
C_6H_6LiH, **3b**	−235.82822	1.399	1.829	1.399	1.084	1.053	2.303	1.4
$C_6H_6BeH^+$, **3c**	−242.77393	1.412	1.490	1.412	1.080	1.284	2.053	−3.1
$C_5H_5^-$ (D_{5h})	−189.73142	1.185		1.393	1.080			
3-21G	−191.10947	1.196		1.406	1.075			
C_5H_5Li,[d] **4a**	−197.29375	1.206	1.644	1.417	1.079		2.039	6.4
3-21G	−198.59689	1.204	1.790	1.416	1.069		2.157	2.8
C_5H_5BeH,[e] **4b**	−204.97063	1.226	1.461	1.419	1.079	1.280	1.901	−0.9
3-21G	−206.30913	1.206	1.585	1.418	1.066	1.344	1.992	−0.5
$C_5H_5Be^+$, **4c**	−204.18005	1.222	1.367	1.436	1.081		1.834	−0.1
3-21G	−205.47194	1.217	1.420	1.430	1.067		1.870	0.5
$C_5H_5BH^+$, **4d**	−214.66612	1.220	1.256	1.434	1.087	1.148	1.751	−8.1
3-21G	−216.00853	1.214	1.332	1.427	1.066	1.157	1.802	−4.4
C_5H_5B, **4g** 3-21G	−215.58520	1.230	1.764	1.414	1.065		2.136	−2.6
$C_5H_5CH^{2+}$, **4e**	−227.14122	1.240	1.180	1.458	1.082	1.089	1.712	−11.7
3-21G	−228.53928	1.227	1.234	1.442	1.073		1.740	−8.2
$C_5H_5C^+$,[f] **4f**	−226.94806	1.216	1.357	1.427	1.088		1.819	−8.6
3-21G	−228.38835	1.212	1.507	1.424	1.060		1.934	−4.4
$C_4H_4Li^-$, **5a**	−159.03974	1.015	1.638	1.436	1.077		1.927	17.2
3-21G	−160.16036	1.037	1.786	1.467	1.070		2.065	12.1
C_4H_4Be, **5b**	−166.21782	1.035	1.370	1.463	1.077		1.717	7.1
3-21G	−167.31662	1.045	1.442	1.477	1.063		1.781	6.6
C_4H_4BH, **5c**	−176.77162	1.032	1.266	1.459	1.077	1.140	1.633	−1.2
3-21G	−177.92043	1.038	1.334	1.467	1.061	1.164	1.690	1.0
$C_4H_4CH^+$,[g] **5d**	−189.56069	1.044	1.195	1.477	1.078	1.100	1.589	−5.4
3-21G	−190.73641	1.041	1.232	1.472	1.062	1.053	1.613	−2.7
C_4H_4C, **5e**	−189.08757	1.025	1.311	1.449	1.078		1.672	−2.4
3-21G	−190.33287	1.029	1.435	1.455	1.060		1.766	−1.0
$C_3H_3Be^-$, **6a**	−128.00352	0.871	1.350	1.509	1.075		1.607	47.1
3-21G	−128.97214	0.915	1.403	1.585	1.073		1.675	49.6
$C_3H_3BH^-$, **6b**	−138.58660	0.868	1.270	1.503	1.070	1.147	1.538	31.8
3-21G	−139.61156	0.881	1.328	1.525	1.063	1.190	1.594	34.8
C_3H_3CH,[h] **6c**	−151.70782	0.850	1.203	1.473	1.069	1.069	1.473	19.5
3-21G	−152.70836	0.860	1.215	1.489	1.051	1.051	1.489	19.5
$C_3H_3NH^+$, **6d**	−167.86537	0.860	1.214	1.490	1.086	1.034	1.487	10.1
3-21G	−168.95102	0.846	1.239	1.466	1.056	1.000	1.501	10.6
C_3H_3N, **6e** 3-21G	−168.59895	0.838	1.292	1.452	1.051		1.540	12.6

[a] Ring center–ring carbon distance = a; ring center–cap distance = b (see **1**). [b] Positive value indicates that ring hydrogens are bent away from the cap. [c] Radom, L.; Schafer, H. F., III, *J. Am. Chem. Soc.* 1977, *99*, 7522. [d] Reference 7a. [e] Reference 1b. [f] Reference 1c. [g] Reference 40b. [h] Reference 45a. [i] The 3-21G energies are indicated, the remainder are at STO-3G, as given.

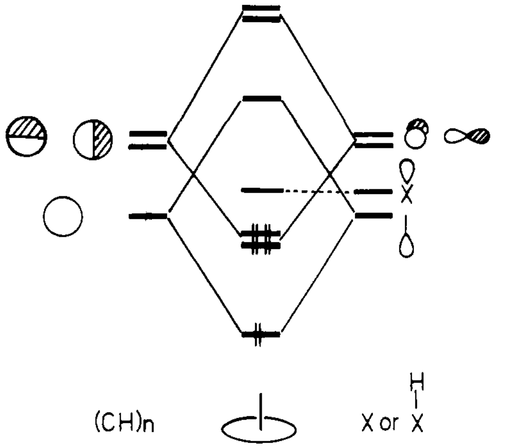

Figure 1. Diagram showing the interaction of the lowest a and e π orbitals (shown schematically) of a $(CH)_n$ annulene ring and the sp and p orbitals of a capping atom, X, or group, XH. The six interstitial electrons in the resulting stabilized orbitals (center) convey aromatic character to the pyramidal structure.

valence basis sets.[9] A single precision Telefunken TR 440 version with a modified Fletcher–Powell routine for optimization was used for the earlier calculations;[10] later, analytic gradient optimization was employed.[10b]

The molecules studied, **3–6**, have three- to six-membered carbocyclic rings and caps selected from the set Li, LiH, Be, BeH, B, BH, C, CH, N, and NH and were charged or neutral, in order to satisfy the six interstitial electron rule. Geometries were completely optimized within C_{nv} symmetry unless otherwise specified; the ring hydrogens were allowed to move out of the plane of the ring. Since isomers of lower symmetry were calculated in some cases but were found to be less stable, they were not considered in each instance.[1c,7c,11] Table I summarizes the geometries and energies of the systems investigated.

Discussion and Results

The $4n + 2$ Interstitial Electron Rule. The pyramidal molecules **3–6**, represented by **1**, can be conceptually divided into a carbocyclic ring and a capping group, X.[6a] The electrons involved in skeletal C–C and C–H bonding of the $(CH)_n$ ring are assigned in the conventional manner, i.e., two electrons to each single bond.[6a] Delocalization of the π electrons of the ring to the cap will bind these two units together. The cap also may contribute such binding electrons. Since "π" is a symmetry designation, which is inap-

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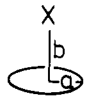
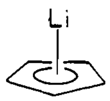
(11) Standard geometry STO-3G calculations indicate that **8**, X = Li, is less stable than **3a** by 61 kcal/mol and **8**, X = BeH$^+$, is less stable than **3c** by 39 kcal/mol. η^2-**9**, as well as η^3, η^4, and η^5 alternatives, are also unfavorable (Chandrasekhar, J., unpublished calculation).



1



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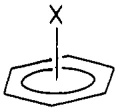
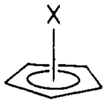


C_{6v}

3

X
(a) Li^+
(b) LiH
(c) BeH^+



C_{5v}

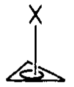
4

X
(a) Li
(b) BeH
(c) Be^+
(d) BH^+
(e) CH^{+2}
(f) C^+
(g) B

C_{4v}

5

X
(a) Li^-
(b) Be
(c) BH
(d) CH^+
(e) C



C_{3v}

6

X
(a) Be^-
(b) BH^-
(c) CH (Td)
(d) NH^+
(e) N

propriate in molecules like **1**, the descriptive term "interstitial" is used to designate the electrons that bind caps and rings together.[1a] How do six interstitial electrons lead to aromatic pyramidal systems? Consider cyclopentadienyllithium (**2**), assumed to be ionic. The parent cyclopentadienyl anion is aromatic, with six π electrons delocalized over the ring. In cyclopentadienyllithium, the lithium cation prefers to be located above a ring face, on the C_5 axis.[7c] The total number of valence electrons in cyclopentadienyllithium is the same as in the cyclopentadienyl anion. However, the six π electrons of the latter are further delocalized to the cap, Li^+, in **2**. This is shown by the familiar interaction diagram, Figure 1.[6a,f] The a and e π orbitals of cyclopentadienyl interact with the lithium s and p orbitals of the same symmetry, giving three stabilized MO's. In general, a favorable system is expected to have six interstitial electrons (in addition to the electrons involved in localized σ bonding in the ring and in the cap). The "one below two" Hückel pattern of the three lowest energy π orbitals is found in all $(CH)_n$ annulenes. Similarly, the orbitals of the appropriate a and e symmetry are available when the cap is a single atom like Li, Be, B, C, and N or a group like LiH, BeH, BH, CH, NH, etc. The six-electron rule can thus be applied to any pyramidal system. Cyclopentadienylberyllium hydride, for example, has six interstitial electrons, five from C_5H_5 and one from Be–H. Here we count only the one electron donated to ring–cap bonding from Be–H and not the electron pair involved in Be–H σ bonding.

Let us illustrate the $4n + 2$ interstitial electron rule further, starting with benzene, the aromatic prototype (Figure 2). The 18 valence electrons involved in C–C bonding will concern us: there are six two-electron C–C single bonds and six π electrons. With two fewer electrons, the planar dication, $C_6H_6^{2+}$, is not aromatic. $C_6H_6^{2+}$ can regain stabilized six-electron multicenter bonding in the pyramidal geometry (**4e**). The C_5H_5 ring in **4e** has only five C–C bonds, assigned two electrons each. Hence, there are six interstitial electrons to bind all six carbons together. There is an easier way to count electrons in **4e**. Its $C_5H_5^+$ ring (charge assigned arbitrarily) has four π electrons; the CH^+ cap donates two more to complete the set of six for interstitial bonding. The generalized interaction diagram (Figure 1) shows how stable closed-shell species result from combination of annulene fragments.

In principle, two additional electrons can be removed from **4e**; $C_6H_6^{4+}$ would result. This species could achieve six interstitial electron character by yet another structural change to give **7**, which can be considered to be made up of one $C_4H_4^{2+}$ ring (arbitrarily chosen; **7** has octahedral symmetry) and two CH^+ caps. Each of these three components contributes 2 electrons to the six interstitial electron bonding (dashed lines in **7**). Similar structural relationships, e.g., between arachno (like benzene), nido (like **1**),

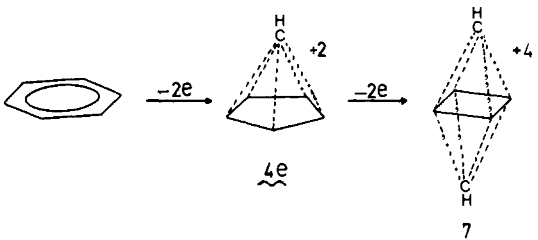


Figure 2. Favored aromatic structures corresponding to six π (C_6H_6) or six interstitial electrons ($C_6H_6^{2+}$ and $C_6H_6^{4+}$).

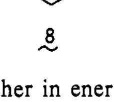
and closo (like **7**) carboranes, involving differences of two valence electrons, are familiar.[6b] In a subsequent paper, we will show how the $4n + 2$ interstitial electron rule can be applied to doubly capped (closo) ring systems.

An alternative eight-electron rule, including all electrons of the cap, has been suggested for such pyramidal structures.[12] However, the six interstitial electron rule is more general. The electronic structures of cyclopentadienyllithium and cyclopentadienylberyllium hydride are similar. Both have the expected C_{5v} symmetry. The interaction diagram, Figure 1, accounts for the ring–cap bonding. Yet according to the eight-electron rule, only cyclopentadienylberyllium hydride should be stable. $C_5H_5Be^+$ (**4c**) and C_4H_4Be (**5b**) are similar examples. We prefer to emphasize the Hückel $4n + 2$ analogy between aromatic annulenes and their pyramidal counterparts, **1**.

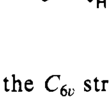
Optimum Ring–Cap Combinations. The symmetry properties and the "one below two" pattern of the three lowest energy annulene π orbitals do not change, but a regular decrease in the energy of these orbitals accompanies an increase in the size of the ring. Similarly, the energies and the overlap propensities, but not the symmetries of the orbitals, will vary with the nature of the cap, X. A large number of cap–ring combinations with six interstitial electrons are possible. But our chemical intuition tells us that all possibilities will not be equally favorable. For example, **7** is unrealistic electrostatically, although many isoelectronic analogues (e.g., $C_2B_4H_6$ and $B_6H_6^{2-}$) are well-known.[6b] We have studied the interaction between annulene rings and first-row caps in half-sandwich systems with six interstitial electrons, **3**–**6**. Which cap interacts best with each ring? Which ring is needed for optimal interaction with a given cap? The concepts resulting from our analysis can be extended to similar transition-metal organometallic complexes.

The pyramidal structures we considered are based on six-, five-, four-, and three-membered rings. The caps are selected from first-row elements, and hydrogen and the charges are chosen so that six interstitial electrons result. The discussion is arranged according to the size of the ring. A general comparison follows.

Interaction of C_6H_6 with Caps. As benzene already has six electrons, an appropriate cap should not add any more electrons. Having three vacant orbitals of the right symmetry, Li^+, LiH, BeH^+, and perhaps Be, are suitable. Structures **3a–c** have six interstitial electrons. Optimized geometries and corresponding energies are given in Table I. (The ring midpoint–C distance is "*a*"; "*b*" is the ring midpoint–X distance.) Alternatives to **3**, e.g., ortho protonated and bridged benzenes, **8** and **9** (X = Li, BeH),



8



are much higher in energy.[11] Only the C_{6v} structure, **3b**, was considered for C_6H_6LiH. If the beryllium atom in C_6H_6Be (C_{6v}) could accommodate a lone pair effectively, a six interstitial electron system similar to C_5H_5In[13] and C_5H_5Tl[14] would result. However

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Table II. Supplementary Energies (au)

species	point group	energy[a] STO-3G	3-21G
Li		−7.31553	−7.38151
Li^+		−7.13545	−7.18709
LiH	$C_{\infty v}$	−7.86338	−7.92984
Be		−14.35188	−14.48682
BeH	$C_{\infty v}$	−14.93532	−15.05931
BeH^+	$C_{\infty v}$	−14.66477	−14.76035
B		−24.14899	−24.38976
B^+		−24.76273	−24.09638
BH	$C_{\infty v}$	−24.75299	−24.97680
CH^+	$C_{\infty v}$	−37.45638	−37.67919
NH_4^+	T_d	−55.86885	−56.23386
NH_3	C_{3v}	−55.45542	−55.87220
CH_4	T_d	−39.72686	−39.97688
C_4H_4	D_{2h} (singlet)	−151.74812	−152.77152[b]
C_4H_4Be	C_{2v}	−166.27432[b]	
C_4H_4BH	C_{2v}	−176.82013[b]	
$C_5H_5^+$	D_{5h} (triplet)	−189.63325[b]	

[a] Unless otherwise specified energies taken from ref 57. Species are singlets, unless otherwise indicated. [b] This study; see eq 10, 11, and 12.

we could not find a C_{6v} bound structure for C_6H_6Be at the minimal basis STO-3G level; the Be–ring distance increases to infinity on optimization. Similar cases of the failure of Be to bind to π systems have been described.[15] The 2 s electrons of Be are low in energy; the gain in bonding energy in C_6H_6Be (C_{6v}) is insufficient to overcome the energy required for sp hybridization. In short, Be behaves somewhat like He in such contexts. However, as will be discussed below, Be does bond to cyclobutadiene.

The interactions of the electrophiles, Li^+, BeH^+, and LiH, with benzene (STO-3G) are quite exothermic (eq 1–3; see Table II).

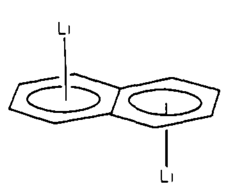
$$C_6H_6 + Li^+ \rightarrow \underset{\mathbf{3a}}{C_6H_6Li^+} \quad -84.3\ \text{kcal/mol} \qquad (1)$$

$$C_6H_6 + LiH \rightarrow \underset{\mathbf{3b}}{C_6H_6LiH} \quad -46.1\ \text{kcal/mol} \qquad (2)$$

$$C_6H_6 + BeH^+ \rightarrow \underset{\mathbf{3c}}{C_6H_6BeH^+} \quad -136.7\ \text{kcal/mol} \qquad (3)$$

However, these equations are not isodesmic; errors inherent in the method and in the neglect of electron correlation may not cancel.[16] As the minimal STO-3G basis tends to overestimate binding energies, the exothermicity of these reactions probably is exaggerated.[17] An energy of −37.9 kcal/mol has been reported experimentally for the binding of Li^+ to benzene (corresponding to eq 1), but the STO-3G value is twice as large.[18] A recent semiempirical calculation using the CNDO/2-FK method also overestimates the energy of eq 1, but the lowest energy structure of $C_6H_6Li^+$ is found to have C_{6v} symmetry.[19] Single-point 4-31G/5-21G//STO-3G calculations indicate a value of −40 kcal/mol for eq 1, in good agreement with experiment.

X-ray studies of Li complexes of condensed aromatic compounds provide evidence for symmetrical (local C_{6v}) bridging. Lithium is located approximately at the center of the six-membered rings in **10** and **11**.[20,21] The involvement of the p orbitals of Li has been invoked to explain these structures.[21] The average distance of lithium to the carbons of the nearest six-membered ring in these complexes is 2.44 Å, in reasonable agreement with the calculated distance in C_{6v} $C_6H_6Li^+$ (**3c**) of 2.2 Å; the STO-3G basis is known to underestimate C–Li bond lengths.[22,23]



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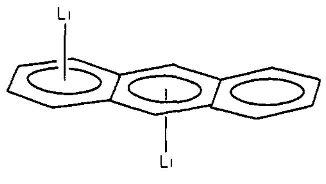

11

The higher exothermicity of eq 3 compared to eq 1 may be due either to the greater stability of $C_6H_6BeH^+$ than $C_6H_6Li^+$ or to a higher energy of BeH^+ relative to Li^+. A better way of comparing the relative interactions of Li^+ and BeH^+ with benzene may be eq 4 (although this is also not free of objections). The

$$\underset{\mathbf{3a}}{C_6H_6Li^+} + BeH \rightarrow \underset{\mathbf{3c}}{C_6H_6BeH^+} + Li \quad +5.2\ \text{kcal/mol} \qquad (4)$$

near thermoneutrality of eq 4 (Table II) indicates that there may be only a relatively small difference in the bonding energy of Li^+ and BeH^+ with benzene, at least at the STO-3G level.

In contrast to the number of X-ray structures of lithium derivatives,[20,21] there is surprisingly little experimental data available on open (half) sandwiches involving aromatic ring systems and beryllium (besides C_5H_5BeX derivatives and beryllocene discussed below). Since both Li and BeH are found to have approximately the same complexation energy with benzene (eq 4), many beryllium-capped systems appear to be possible. Dewar and McKee's MNDO study of indenyl-BeH indicates the BeH to prefer η^5 bonding over the five ring rather than the six ring.[24] The notoriety of beryllium compounds as poisons deters the experimentalist but not the computer chemist! However, preliminary results indicate the existence of a η^1–η^6 structure for $C_6H_5BeC_6H_6^+$, prepared by protonating diphenylberyllium.[25]

The C–C bond lengths in these compounds do not vary significantly with changes in the cap, but the C–X distances do. The C–Li distance in $C_6H_6Li^+$ (**3a**), 0.1 Å less than that in C_6H_6LiH (**3b**) (2.217 vs. 2.303 Å, STO-3G), indicates a stronger interaction of benzene to a positively charged lithium than to a neutral LiH acceptor (cf. eq 1 and 2). The Be–C distance in $C_6H_6BeH^+$ (**3c**) (2.053 Å) is shorter than the C–Li distance in $C_6H_6Li^+$ (**3a**) (2.217 Å), but the difference is less than in conventional σ-bonded compounds, e.g., 1.691 Å in CH_3–BeH vs. 2.009 Å in CH_3–Li, STO-3G.[26] A point of special interest: the ring hydrogens bend toward the cap X in $C_6H_6BeH^+$ (**3c**) but away from X in C_6H_6LiH (**3b**).

Interaction of C_5H_5 with Caps. Since the cyclopentadienyl radical has five π electrons, a cap should contribute only one more to give a total of six interstitial electrons. Structures **4a–g** all have six interstitial electrons. Detailed MO studies of cyclopentadienyllithium **4a**[7c,27] and of the pyramidal phenyl cation isomer **4f**[1c,28] have appeared.[7c,27,28a] The results on cyclopentadienylberyllium hydride[1b] are also included here for completeness (Table I). The C_{5v} structures **4a–c** are found to be the most stable; deformations to lower symmetries result in increases

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in energy. Even though we have not examined other alternatives, **4f** and **4g** also should be minima on their potential energy surfaces.

The interaction of C_5H_5 with BeH is stronger than with Li at the STO-3G (3-21G) level (eq 5). The C–X distances in **4a–e**

$$\underset{\mathbf{4a}}{C_5H_5Li} + BeH \rightarrow \underset{\mathbf{4b}}{C_5H_5BeH} + Li \quad -35.8\ (-21.6)\ \text{kcal/mol} \qquad (5)$$

decrease from 2.157 Å (X = Li) to 1.740 Å (X = CH^2) (3-21G) as expected (Table I). The C–C bond lengths in the C_5H_5 ring do not vary greatly. The longest C–C bond, 1.442 Å, is found in $C_5H_5CH^{2+}$ (**4e**), which also has the largest out-of-plane bending of the ring hydrogens toward the cap. C_5H_5B (**4g**) has the shortest ring C–C bond length.

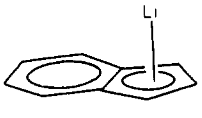
$C_5H_5C^+$ (**4f**) has a lone pair on the bare carbon directed away from the ring. Despite the presence of the positive charge in **4f** (Coulombic repulsion), the calculated proton affinity (to give dication **4e** (eq 6)) is rather large; this indicates the relative

$$\underset{\mathbf{4f}}{C_5H_5C^+} + H^+ \rightarrow \underset{\mathbf{4e}}{C_5H_5CH^{2+}} \ -121.2\ \text{kcal/mol (STO-3G)}; \quad -94.7\ \text{kcal/mol (3-21G)} \qquad (6)$$

instability of the carbene-like structure. As has been discussed separately, **4f** is appreciably less stable than its $C_6H_5^+$ isomer, the phenyl cation.[1c] Similarly, **4e** is not the lowest energy $C_6H_6^{2+}$ isomer.[28a]

Some geometrical contrasts due to the removal of a proton from a cap (BeH and Be$^+$ vs. CH^{2+} and C$^+$) are striking. The Be–center distances *decrease* in going from C_5H_5BeH (**4b**) to $C_5H_5Be^+$ (**4c**) (1.461 vs. 1.367 Å), but the C–C bonds *elongate* (1.419 vs. 1.436 Å). A similar change from $C_5H_5CH^{2+}$ (**4e**) to $C_5H_5C^+$ (**4f**) *increases* the C(cap)–ring distance (1.180 vs. 1.57 Å) but *decreases* the ring C–C bond length (1.458 vs. 1.427 Å (Table I)). The lone pair on **4f** decreases the delocalization of the π electrons of the ring to the carbon caps. However, the Be in $C_5H_5Be^+$ (**4c**) has an empty sp orbital; hence, donation of π electrons from the ring to Be in **4c** will be greater than in **4b**. The more the electrons are shifted away from the C–C bonding π orbitals and are donated to the cap, the longer the ring C–C bond will be. 3-21G X–center distances show similar trends; STO-3G data are given in Table I.

Direct or indirect experimental evidence exists for all these pyramidal structures involving five-membered rings (except **4f**). X-ray studies show Li to be above the five-membered ring in indenyllithium **12**.[29] Li NMR spectroscopic studies support such a structure in solution. Cyclopentadienyllithium is also found to have η^5 structures by ^{7}Li NMR.[30–32] η^5 bonding has been demonstrated in large numbers of cyclopentadienylberyllium compounds **4** (X = BeH, BeCH$_3$, BeCCH, BeBr, BeCl, BeBH$_4$, BeCp) by electron diffraction and X-ray structural studies.[33] The large η^5 bonding energy in cyclopentadienylberyllium compounds is also indicated by the appearance of the $C_5H_5Be^+$ ion as the base peak in the mass spectra of these compounds.[34] Spectroscopic studies support a η^5 structure **13** for $(CCH_3)_5BI^+$, a derivative of **4d**.[35] Several derivatives of the dication **4e** are known in solution.[36] While there is no direct experimental evidence available on the pyramidal bare carbon molecule **4f**, the relative instability of **14a** relative to **14b** may be due to the decomposition of the former to a derivative of the bare carbon cation **4f** and the isopropyl cation. The corresponding decomposition of **14b** may be slower because Et$^+$ is less stable than the isopropyl cation. Similar structures have been suggested for isoelectronic species **15**.[37] Even though the neutral boron analogue is not known, C_5H_5In[13] and C_5H_5Tl[14] are found to have C_{5v} structures (**15**).



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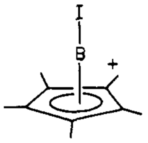

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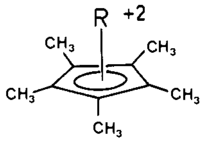
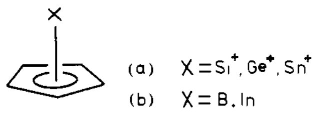


14 a, R = Me$_2$CHC
b, R = MeCH$_2$C



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The ionic vs. covalent nature of the cyclopentadienyl derivatives has been debated[1b,7c] with the assumption that cyclopentadienylsodium is completely ionic, 20% covalent character has been assigned to CpLi on the basis of correlations for ^{19}F NMR chemical shifts of *p*-fluorophenyl-substituted cyclopentadienyl rings.[38] That the π electrons of the Cp ring in CpBeH are donated to the vacant p orbitals of the BeH cap is shown by the direction of its dipole moment; BeH is the negative end.[1b] MO calculations also indicated partial *negative* charge on the Fe relative to the Cp rings in covalent ferrocene, even though conventional assumption is that the rings are negatively charged.[39] (See Note Added in Proof.)

Interaction of C_4H_4 with Caps. The antiaromatic cyclobutadiene can be stabilized by caps that donate two electrons. The isolobal Fe(CO)$_3$ complex, discussed below, is the best known example. The resulting six interstitial electrons occupy the three stabilized MO's. The following caps were considered in this study: Li$^-$, Be, BH, CH$^+$, and C (**5a–e**). Detailed discussions of the potential energy surface[6f] and structure[40] of $C_5H_5^+$ have been published. The pyramidal carbene C_4H_4C (**5e**) has been suggested to be a local minimum on the potential energy surface of C_5H_4 by ab initio calculations.[41,12]

The STO-3G (3-21G) interaction energies of C_4H_4 with caps increase in the order Be < BH < CH$^+$ (eq 7–9, using the energy

$$C_4H_4 + Be \rightarrow \underset{\mathbf{5b}}{C_4H_4Be} \quad -73.8\ (-36.6)\ \text{kcal/mol} \qquad (7)$$

$$C_4H_4 + BH \rightarrow \underset{\mathbf{5c}}{C_4H_4BH} \quad -169.7\ (-108.0)\ \text{kcal/mol} \qquad (8)$$

$$C_4H_4 + CH^+ \rightarrow \underset{\mathbf{5d}}{C_5H_5^+} \quad -223.5\ (-179.3)\ \text{kcal/mol} \qquad (9)$$

of singlet cyclobutadiene). However, these comparisons are complicated by the energies of the capping fragments. Thus, the instability and charge of the fragment ion, CH$^+$, contributes to the large exothermicity of eq 9 relative to eq 8. Alternative five-membered planar structures are less strained and are calculated to be more stable (STO-3G) despite the four π electron arrangements, eq 10–12 (Table II). The energy differences among **5b–d** are much smaller on this basis.

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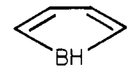
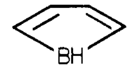
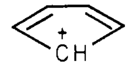
C_4H_4BH (5a) →

−30.4 kcal/mol (10)

C_4H_4Be (5b) →

−35.5 kcal/mol (11)

$C_5H_5^+$ (5d) →

−45.3 kcal/mol (12)

In the C_{4v} C_4H_4X series, the ring center–cap distance decreases from Li to C as expected (Table I). As in the case of **4e** and **4f**, the distance of the cap to the center of the ring increases considerably in going from **5d** to **5e** (3-21G, 1.232 vs. 1.435 Å). The high energy of the lone pair on the bare carbon cap in C_5H_4, **5e**, is indicated by the large calculated proton affinity of 253.2 kcal/mol (eq 13, 3-21G). The ring CH's bend away from the

$$\underset{\mathbf{5e}}{C_4H_4C} + H^+ \rightarrow \underset{\mathbf{5d}}{C_5H_5^+} \quad -296.9\ \text{kcal/mol (STO-3G)}, \quad -253.2\ \text{kcal/mol (3-21G)} \quad (13)$$

cap in **5a** and **5b**. In contrast, the ring hydrogens bend toward boron and carbon caps.

Various derivatives of **5d** are known in solution.[42] The pentaphenyl derivative of C_4H_4BH known experimentally does *not* have a C_{4v} structure.[43] Isoelectronic boranes are known to have tetragonal-pyramidal structures.[6d,44] In fact, the possible existence of **5d** was first predicted by Williams by analogy with known boranes, e.g., B_5H_9.[44]

Interaction of C_3H_3 with Caps. The cyclopropenyl radical and caps that donate three bonding electrons, e.g., Be^-, BH^-, CH, N, and NH^+, should give pyramidal structures (**6a–e**). Tetrahedrane (**6c**) has been calculated to be a local minimum on the potential energy surface of C_4H_4;[45] tetra-*tert*-butyltetrahedrane has been prepared.[46] Experiments following a suggestion by Dill indicate that tetralithiotetrahedrane might have been prepared.[47] $C_3H_3Be^-$, $C_3H_3BH^-$, C_3H_3N, and $C_3H_3NH^+$ are not known experimentally. The calculated C–C distances in **6a–e** (Table I) are all close to that in cyclopropane (1.513 Å, 3-21G). The ring hydrogens in **6a** are bent out of plane away from Be by 49.6°; the corresponding angle in **6b** is 34.8°. By T_d symmetry, the hydrogens in tetrahedrane **6c** are bent by 19.5°. In the NH^+ analogue, **6d**, the bending is less (10.6°). The C–X distances in **6** are shorter than the 3-21G single-bond lengths calculated for CH_3BeH (1.71 Å),[23] CH_3BH_2 (1.58 Å),[48] and CH_3CH_3 (1.54 Å).[49] As is well-known, C_4H_4 (T_d) is not a very stable arrangement. Although alternative structures for **6a,b,d,e** were not calculated, geometries with lower symmetries are also expected to be more stable.

An alternative description of bonding is possible for pyramidal systems, **6**. With six interstitial electrons, a localized 2c–2e bond is possible between the cap and any carbon atom in the C_3H_3 ring. However, these two descriptions are equivalent; linear combinations of the three σ bonds yield the stabilized a and e type orbitals indicated in the general interaction diagram, Figure 1. Due to the high symmetry in tetrahedrane, **6c**, each CH group can be considered as a cap; with $4n + 2$ electrons ($n = 1$) a 2c–2e bond can be assigned between any two carbon atoms. As discussed below there are several transition-metal analogues of tetrahedrane where one or more CH groups are replaced by isolobal[50] transition-metal groups, e.g., $(Co(CO)_3)_n(CH)_m$, $m + n = 4$.[51e]

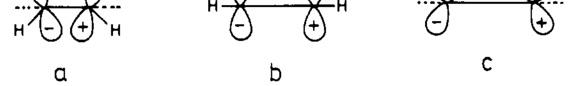
According to the $4n + 2$ Hückel rule for planar aromatic systems, $n = 0$ gives the optimum number of π electrons for three-membered rings, e.g., cyclopropenium cation. In three-dimensional systems also we expect delocalized, stable systems with two interstitial electrons bridging a three-membered ring and cap. These are difficult to realize with the carbocyclic ring systems that are used in this study. Systems with two interstitial electrons are known in boron chemistry. B_4Cl_4 and $B_4(t\text{-}Bu)_4$ are stable molecules having tetrahedral skeletons of boron atoms.[52] However, unlike tetrahedrane, an alternative localized 2c–2e bonding for B_4R_4 is not possible.

Table III. Out-of-Plane Bending (in Deg) of the Ring Hydrogens in Open Sandwiches Comprised of Carbocyclic Rings and Various Caps (1), at STO-3G (3-21G) Levels[a]

	ring			
cap	C_3H_3	C_4H_4	C_5H_5	C_6H_6
Li		17.2 (12.1) (**5a**)	6.4 (2.8) (**4a**)	2.5 (**3a**)
Be	47.1 (49.6) (**6a**)	7.1 (6.6) (**5b**)	−0.9 (−0.5) (**4b**)	−3.1 (**3c**)
B	31.8 (34.8) (**6b**)	−1.2 (1.0) (**5c**)	−8.1 (−4.4) (**4d**)	
C	19.5 (19.5) (**6c**)	−5.4 (−2.7) (**5d**)	−11.7 (−8.2) (**4e**)	
N	10.1 (10.6) (**6d**)			

[a] Positive values indicate that the hydrogens are bent away from the cap.

Effective Size of Orbitals and Out-of-Plane Bending of Ring CH Bonds. Even though these pyramidal molecules have six interstitial electrons, the magnitude of the stabilizing interaction between rings and caps varies widely. The six interstitial electron rule is only qualitative: the symmetry properties of the orbitals of the caps and the rings lead to three relatively stable MO's. The extent of this stabilization is determined by the energy difference between the interacting fragment orbitals and their degree of overlap. The overlap of the p orbitals of the cap with the orbitals of the ring depends on the number of carbons in the ring, the effective size of the orbitals of the cap, and the ring–cap distance. In the same period the effective size or the diffuse nature of the orbitals decreases with increasing atomic number. This is indicated by the magnitude of the STO-3G valence orbital exponents used in the calculations: Li = 0.8, Be = 1.15, B = 1.5, C = 1.72, and N = 1.95.[9] CH has "smaller" p orbitals than BH, which in turn has "smaller" orbitals than BeH. Lithium has the "largest" orbitals (smallest exponents) among the first-row elements. The overlap between the p orbitals of the cap and the π orbitals of the ring can be increased by changing the ring–cap distance or by reorienting the π orbitals of the ring (**16**). When the p orbitals



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of the caps are larger in size than optimum, the C–H hydrogens of the ring bend away from the cap (**16a**). When the ring is larger or the effective size of the orbitals of the cap is small, the ring hydrogens can bend toward the cap to increase overlap (**16c**). An ideal match is shown in **16b**; the hydrogens are nearly in the ring plane. The calculated out-of-plane bending thus indicates the match of the cap orbitals with those of a ring of given size (Table III, positive angle indicates bending away from the cap). The ring center–cap distance *b* (**1**) also increases as the effective size of the orbitals of the cap increases. Therefore the out-of-plane bending is also related to the ring center–cap distance, *b*. However, for a given cap, *b* does not vary significantly with ring size. For example, with BH (charged or neutral) as cap, the ring center–cap distances, *b* (in Å), are, at STO-3G: 1.256 (**4d**), 1.266 (**5c**), and 1.270 (**6b**); and at 3-21G: 1.332 (**4d**), 1.334 (**5c**), and 1.328 (**6b**). The corresponding CH out-of-plane bendings are, at STO-3G (3-21G): -8.1° (-4.4), -1.2° (1.0), and 31.8° (34.8), respectively. Therefore, for a given cap, the increase in ring size and consequent rehybridization to give better overlap is the main reason for the varying CH out-of-plane bending.

The amount by which ring hydrogens can bend profitably is limited; the C–H bonds decrease in strength and angle strain increases. Bonding should be optimum when there is maximum overlap without bending. Thus, each ring will have an optimum cap and each cap an optimum ring. Columns and rows in Table III indicate the variations in angle bending. The ring hydrogens in $C_6H_6Li^+$ (**3a**) are bent away from lithium (**16a**) but in $C_6H_6BeH^+$ (**3c**) these hydrogens bend toward BeH$^+$ (**16c**). Since the bending in both cases are small, both BeH and Li seem to be suitable caps for a six-membered ring. In cyclopentadienyllithium, **4a**, the ring hydrogens bend away from lithium. This has been suggested to be an indication of the ionic character of CpLi.[7c] Bending toward the cap, on the other hand, has been suggested to indicate covalent bonding between a ring and a cap. We do not agree. On this basis, C_4H_4 (T_d) (tetrahedrane) should be ionic and η^4-$C_4H_4CH^+$ covalent. The magnitude and direction of the ring hydrogen bending generally is a function of the ring size, and cap X, and the ring center–cap distance. (See Note Added in Proof.) A π complex between Be and a four-membered ring may have ring hydrogens bent away from beryllium. Cyclopentadienylberyllium hydride **4b** has the ring hydrogens almost in the plane of the ring. Therefore, beryllium should prefer a five-membered ring to a four- or a six-membered ring (eq 14).

$$\underset{\mathbf{3c}}{C_6H_6BeH^+} + \underset{\mathbf{4a}}{C_5H_5Li} \rightarrow \underset{\mathbf{3a}}{C_6H_6Li^+} + \underset{\mathbf{4b}}{C_5H_5BeH} \quad -41.0\ \text{kcal/mol (STO-3G)} \quad (14)$$

The p orbitals on a BH cap are smaller. Therefore, the CH hydrogens bend toward BH in $C_5H_5BH^+$ (**4d**); the bonding is worse than in **4b**. This bending trend increases further in $C_5H_5CH^{2+}$ (**4e**). In the four-membered ring series, the extent of out-of-plane bending is largest in $C_4H_4Li^-$ (**5a**, Table III). C_4H_4Be (**5b**) also has the ring hydrogens bent away from the cap, Be. The ring hydrogens are nearly in the plane of the C_4H_4 ring in C_4H_4BH (**5c**). Caps with more diffuse orbitals interact better with larger rings. Energy evaluations (eq 15–17) support these

$$\underset{\mathbf{5b}}{C_4H_4Be} + \underset{\mathbf{4f}}{C_6H_5^+} \rightarrow \underset{\mathbf{5e}}{C_5H_4} + \underset{\mathbf{4e}}{C_5H_5Be^+} \quad -63.8\ (-62.6)\ \text{kcal/mol} \quad (15)$$

$$\underset{\mathbf{5b}}{C_4H_4Be} + \underset{\mathbf{4d}}{C_5H_5BH^+} \rightarrow \underset{\mathbf{5c}}{C_4H_4BH} + \underset{\mathbf{4c}}{C_5H_5Be^+} \quad -42.5\ (-42.2)\ \text{kcal/mol} \quad (16)$$

$$\underset{\mathbf{5c}}{C_4H_4BH} + \underset{\mathbf{4f}}{C_6H_5^+} \rightarrow \underset{\mathbf{5e}}{C_5H_4} + \underset{\mathbf{4a}}{C_5H_5BH^+} \quad -21.3\ (-20.5)\ \text{kcal/mol} \quad (17)$$

expectations. Beryllium prefers to cap a five- over a four-membered ring; carbon exhibits the opposite preference. Hence, eq 15 is strongly exothermic. The preference of boron for a four-membered ring over a five-membered ring is less than that for carbon. Hence, eq 16 is less exothermic. Equation 17 provides this comparison between boron and carbon directly. Values at STO-3G and at 3-21G (in parentheses) are comparable.

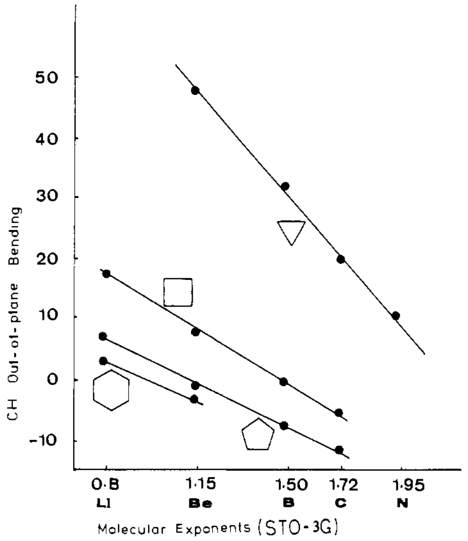

Figure 3. Relationship between CH out-of-plane bending angle and the STO-3G basis set exponents.

The variation in CH out-of-plane bending with XH or X caps (e.g., CH^{2+} and C$^+$, BeH and Be$^+$) is also reflected in the ring center–cap distance, *b* (**1**). This distance (STO-3G) in $C_5H_5CH^{2+}$ (**4e**) is 1.180 Å, but a larger value, 1.357 Å, is found in $C_5H_5C^+$ (**4f**). The ring hydrogens are bent toward the cap by 11.7° in **4e** and 8.6° in **4f**. In $C_4H_4CH^+$, **5d**, the ring center–cap distance is 1.195 Å. This increases to 1.311 Å in C_4H_4C (**5e**). The out-of-plane bending in the ring hydrogens in the former is 5.4° and in the latter 2.4°. The larger the ring–cap distance, *b*, the smaller the out-of-plane bending. Similar trends are seen in $C_6H_6Li^+$ (**3a**) and C_6H_6LiH (**3b**). $C_6H_6Li^+$ (**3a**) has smaller ring center–Li distance (1.712 vs. 1.829 Å) and larger out-of-plane CH bending (2.5 vs. 1.4°) compared to **3b**. The extent of out-of-plane bending of ring hydrogens increases considerably in pyramidal molecules with three-membered rings (**6**). In $C_3H_3Be^-$, **6a**, the ring hydrogens are bent away from Be by 47.1°. The preference of the caps with more diffuse orbitals for larger rings is again demonstrated by eq 18. Tetrahedrane has a CH angle

$$\underset{\mathbf{6a}}{C_3H_3Be^-} + \underset{\mathbf{5c}}{C_4H_4BH} \rightarrow \underset{\mathbf{6b}}{C_3H_3BH^-} + \underset{\mathbf{5b}}{C_4H_4Be} \quad -18.4\ \text{kcal/mol (STO-3G)},\ -22.3\ \text{(3-21G)} \quad (18)$$

bending of 19.5° (by symmetry). Each of the CH groups can be considered to be a cap in C_4H_4 (T_d) so that total overlap cannot be improved by reducing the symmetry; any deformation from T_d symmetry will favor one ring–cap interaction while disfavoring the other three.

The dependence of the CH out-of-plane bending on the diffuse nature or the effective size of the orbitals of the cap is demonstrated in Figure 3, where the extent of CH bending is plotted against the molecular exponents of the valence shell orbitals employed in the STO-3G basis set. For a given ring the CH out-of-plane bending varies linearly with the exponents. The orbitals of a cap and a ring are ideally compatible when the optimum out-of-plane ring CH bending is near 0°. When the orbitals of the cap are small, the ring CH hydrogens bend toward the cap (**16c**). This is undesirable especially when the magnitude of bending is large; the hybrid ring orbitals point away from the cap and overlap decreases. When the ring is too small, as in tetrahedrane, the orbitals of the cap should also be as small as possible to have optimum overlap. On this basis protonated azatetrahedrane (**6d**) should be more favorable than tetrahedrane itself; the CH out-of-plane bending in **6d** at STO-3G (3-21G) is only 10.1°

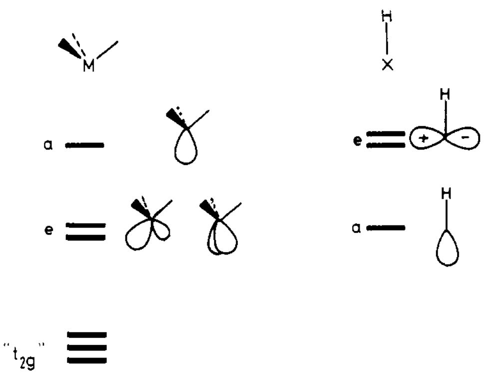

Figure 4. Isolobal orbitals of ML_3 and XH fragments.

(10.6) (Table III). The two basis sets employed give differing answers in this case (eq 19 and 20). The concept of compatibility

$$\underset{\mathbf{6c}}{C_4H_4} + NH_4^+ \rightarrow \underset{\mathbf{6d}}{C_3H_3NH^+} + CH_4$$
$$-9.8 \text{ kcal/mol (STO-3G)}, +9.0 \text{ kcal/mol (3-21G)} \quad (19)$$

$$\underset{\mathbf{6c}}{C_4H_4} + NH_3 \rightarrow \underset{\mathbf{6e}}{C_3H_3N} + CH_4 \quad 3.0 \text{ kcal/mol (3-21G)} \quad (20)$$

of orbitals should also apply to systems in which the ring hydrogens are replaced by different substituents.

Extension to Transition-Metal Complexes. The six-electron rule and the concept of orbital matching can be extended to transition-metal complexes by using the isolobal analogy.[50] Transition-metal fragments can be compared to first-row groups in the number, symmetry, and extension in space of the available orbitals. Here we specifically compare transition-metal fragments, ML_3, which are similar to X–H groups.[50]

Frontier orbitals of an ML_3 fragment are represented in Figure 4. Above the three low-lying metal-based "t_{2g}" orbitals, which do not contribute significantly to bonding between L_3M and the cyclopolyene ligand, there are three orbitals, one e pair and an a. The ordering of the e and a orbitals is reversed relative to that in X–H group, but this does not alter the symmetry-based arguments. The e orbitals of ML_3 are better oriented for interaction in comparison to the unhybridized e set (p_x and p_y) of an X–H group. Depending on the number of valence electrons in the X–H group, an isolobal ML_3 group can be found, **17**. A C–H group

H–C	H–B	H–Be	Li^+
d^9 ML_3	d^8 ML_3	d^7 ML_3	d^6 ML_3
CpNi	$Fe(CO)_3$	CpFe	$Cr(CO)_3$
$Co(CO)_3$		$Mn(CO)_3$	$Cr(C_6H_6)$

17

with three electrons in the three (a + e) orbitals can be replaced by a ML_3 fragment with a d^9 metal, i.e., six electrons in the t_{2g} set and three in the (e + a) orbitals. An example is CpNi. CpNi needs three more electrons in order to achieve a closed shell. Indeed $CpNiC_3R_3$ is a well-characterized complex with an η^3-bonded C_3R_3 group.[51b] Other known complexes of this type are $Py_2ClNiC_3R_2$ and $Br(CO)_2NiC_3R_3$.[51] With a d^8 metal, a four-membered ring is necessary to fulfill the six-electron rule, e.g., $(CO)_3FeC_4R_4$.[53] $Fe(CO)_3$ has two (= 8 − 6) electrons in the e + a orbitals, so that C_4R_4 completes the sextet. Fe is d^7 (1+ oxidation state) in CpFe; since there is only one electron in the a + e set, five more electrons are required to fill the sextet. Of course, the stability and aromatic character of CpFeCp, ferrocene, are well established.[54] Once the isolobal analogues are recognized, one can explain the bonding in many transition-metal complexes. Polynuclear complexes can be looked at similarly. It is not hard to recognize $(CpNi)_4$ and $(Co(CO)_3)_3CR$ as different types of tetrahedranes, despite their absence in organic textbooks.[55]

The variation of the C–H (CR) bonds out of the ring plane in $L_xM(CH)_m$ complexes has been discussed by Hoffmann and co-workers[50] and was anticipated by Kettle.[56] The variation in the diffuse nature of d orbital in a given transition-metal series is not as large as that in the p orbitals of the first short period elements. Therefore major changes in the out-of-plane C–H bending of $(CH)_n$ ligands are found as a function of n only. The published extended Hückel out-of-plane bending in $(CH)_nM$ fragment (M is a metal of the first transition series) ranges from +25° in C_3H_3M to −3° in C_6H_6M, with the change over from $+\theta$ to $-\theta$ taking place around C_5H_5M. The values are comparable to those calculated for Be and even better for Li as caps. Bond lengths, e.g., Li–C and M–C, are also comparable. Thus, orbitals of Li, and to a lesser extent of Be, are as diffuse as the d orbitals of the transition metals. Finally, C–H bendings also change in going down a group, e.g., from C to Si caps.[1c]

Conclusions

Favorable pyramidal structures of type **1** follow a Hückel-like $4n + 2$ interstitial electron rule. However, the detailed geometries and stabilities of pyramidal structures **3–6** depend on the particular ring–cap combinations. With larger rings or with caps with contracted orbitals, the ring C–H bonds bend toward the cap. With smaller rings or with caps with more diffuse orbitals, the ring C–H bonds bend away from the cap. Optimum combinations of caps and rings display little out-of-plane bending. By use of isolobal analogies these concepts can be extended to transition-metal organometallic systems with cyclic polyene ligands.

Note Added in Proof. Professor A. Streitwieser has kindly informed us that calculations on cyclopentadienyllithium (**4a**) using a basis set in which p orbitals on lithium have been omitted give nearly the identical degree of C–H out-of-plane bending as the 3-21G results in Tables I and III.[58] Likewise, our own examination of the related hydrogen bendings out of the carbon plane in allyllithium[59] reveals lithium p orbitals not to be involved.[60] While such ionic contributions probably influence systems with Be, B, C, and N caps to a lesser extent, the degree of involvement has not yet been established.

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Registry No. 4a, 16733-97-4; **4b**, 65887-14-1; **4c**, 54628-72-7; **4d**, 82168-23-8, 55574-89-5; **4g**, 82168-24-9; **5a**, 82168-25-0; **5b**, 82190-57-6; **5c**, 79010-89-2; **5d**, 58252-09-8; **5e**, 70388-04-4; **6a**, 82182-08-9; **6b**, 82182-09-0; **6c**, 82228-56-6; **6d**, 82228-55-5; **6e**, 82228-54-4; $C_5H_5^-$, 12127-83-2.

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