Ab Initio SCF–MO Study of Cyclopentadienylberyllium Hydride and of Beryllocene[1]

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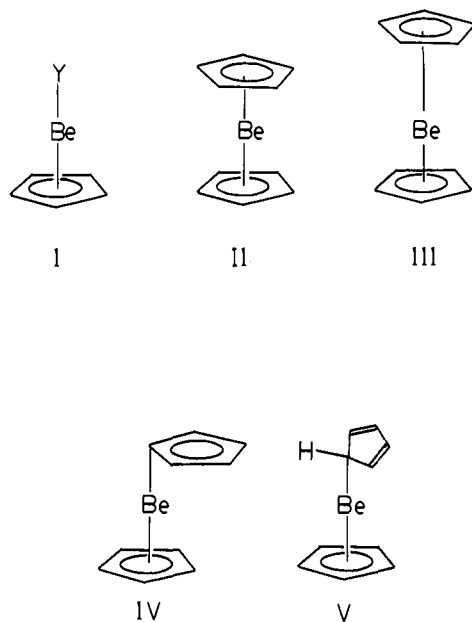
Abstract: Ab initio molecular orbital calculations show that cyclopentadienylberyllium hydride (I, Y = H) strongly prefers C_{5v} symmetry and pentahapto bonding with a high degree of covalent character. The direction of the dipole moment, revealed by the calculations to have the negative end toward the BeH group, argues against ionic bonding, $Cp^- BeH^+$, and implies considerable electron donation from the ring into the Be p orbitals. The fully optimized (RHF/STO-3G) and partially optimized (RHF/4-31G) structures agree closely with the experimental geometry and indicate additionally that the C–H hydrogens are bent out of the ring plane toward beryllium. This is opposite the direction of bending calculated for cyclopentadienyllithium. CpLi also prefers a pentahapto structure but the direction of the dipole moment, Cp^-Li^+, indicates greater ionic character in the bonding. Various structures for beryllocene (Cp$_2$Be) were probed by fixed geometry calculations at the minimal STO-3G basis level. The lowest energy form was found to have one pentahapto and one monohapto ring. Neither the "slipped sandwich" nor the C_{5v} off-center double well potential structures suggested experimentally were indicated to be favorable; even the symmetrical D_{5d} sandwich was found to be more stable than the C_{5v} form. In η^5,η^5-Cp$_2$Be (D_{5d}, II) the average binding energy of the two pentahapto rings is much less than the binding of a single pentahapto ring in CpBeH (I, Y = H). This relative destabilization in II, estimated to be nearly 60 kcal/mol, is due to the necessity of occupying doubly degenerate orbitals (e_{1g}) with nonbonding or even antibonding character between the cyclopentadienyl rings. Isostructural species with four fewer electrons seem better suited as candidates for symmetrical sandwiches involving first short period elements.

Our individual interests in organometallic bonding[3,4] have led to the common study of cyclopentadienylberyllium compounds. Experimental structures of a number of mono-Cp compounds of the type CpBeY (Y = H,[5a] Cl,[6] Br,[7] C≡CH,[7] and BH$_4$[8]), summarized in Table I, allow the generalization that Be is above the midpoint of a planar Cp ring in pentahapto π bonding (I). The di-Cp compound, beryllocene (Cp$_2$Be), was

first prepared in 1959,[9] but a number of recent spectroscopic and diffraction studies[10] have led to conflicting conclusions concerning structure.[11a] While it is always assumed that one of the rings is pentahapto, the arrangement of the second cyclopentadienyl unit has been variously described. Since beryllocene has a dipole moment,[9] metallocene D_{5d} (II) or D_{5h} structures are not possible; both C_{5v} (III) and less symmetrical structures, e.g., IV and V, have been proposed.[11a] On the NMR time scale, both rings are equivalent, so that rapidly fluctuating structures are involved.[10h] Previous MO calculations of these

systems have employed various semiempirical SCF methods[12] culminating in the PRDDO[13] investigation of Marynick[11] and the MNDO calculations of Dewar and Rzepa.[14] Our ab initio SCF–MO study of these compounds, the subject of the present paper, was in progress when PRDDO, MNDO and other ab initio[15] results came to our attention.

Quantum Mechanical Methods

Single-determinant self-consistent field molecular orbital (SCF–MO) theory[16] within the restricted Hartree–Fock (RHF) formalism[17] was used throughout. The minimal STO-3G basis set with the suggested standard exponents was employed for most of the calculations.[18] The pentahapto structure of CpBeH (I, Y = H) was partially optimized using the split valence 4-31G (5-21G for beryllium) basis set.[19] All calculations were carried out using the Gaussian 70 series of programs[20] adapted to the CDC 6400 and 7600 computers at Berkeley[21] and to the Telefunken TR 440 computer at Erlangen.[22] Details of the geometric models employed for CpBeH and for beryllocene are discussed in the text. Since it is not practical to optimize all geometrical parameters of beryllocene the following values were employed. The pentahapto Cp ring was assumed to have D_{5h} symmetry with the optimum r(C–C) and r(C–H) parameters obtained from the structure of optimized cyclopentadienyllithium (1.417 and 1.079 Å, respectively).[3b] For the monohapto Cp group the geometry was taken from the microwave structure of cyclopentadiene;[23] the Be–C and Be–H distances employed were those of the STO-3G optimized structure of CH$_3$BeH.[24]

Results and Discussion

A. Cyclopentadienylberyllium Hydride. The structures of CpBeH, completely optimized at the STO-3G and partially optimized at the 4-31G/5-21G levels, are summarized in Table II. In agreement with the experimental results and with other theoretical calculations,[5b,11b,14,15] the C_{5v} (pentahapto) geometry (I, Y = H) was found to have the lowest energy. The STO-3G and the experimental structures are in remarkably close agreement (compare Tables I and II), but the skeletal distances given by PRDDO[11b] are somewhat short and by

Table I. Experimental Structural Parameters for η^5-CpBeY (I)

distance, Å	Y					
	H[a]	CH₃[b]	BH₄[c]	C≡CH[d]	Cl[e]	Br[d]
C–C	1.423	1.420	1.422	1.428	1.424	1.424
C–H	1.09[f]	1.084	1.116	1.127	1.097	1.087
Be-φ[g]	1.49[f]	1.497	1.484	1.487	1.487	1.528
Be-Y	1.32	1.706	1.88	1.634	1.837	1.943

[a] Reference 5a. [b] Reference 5b. [c] Reference 8. [d] Reference 7. [e] Reference 6. [f] Assumed values. [g] φ is the center of the Cp ring.

Table II. Structural Parameters for CpBeH (C_{5v})

| parameter[a]	exptl[b]	STO-3G	4-31G	PRDDO[c]	MNDO[d]
C–C	1.423	1.419	1.421[h]	1.40	1.458
C–H	1.09[e]	1.079	1.079	1.06	1.084
Be–C	1.920	1.901	1.976[h]	1.83	1.991
Be-φ[f]	1.49[e]	1.461	1.563[h]	1.39	1.557
Be–H	1.32	1.280	1.280	1.26	1.285
φ-CH[f,g]	180.[e]	179.1[g]	179.2[g,h]	−177.6[g]	−172.0[g]
dipole moment	2.08 D	2.80 D	1.792 D		

[a] Bond lengths in Ångströms and bond angles in degrees. [b] Reference 5a. [c] Reference 11b. [d] Reference 14. [e] Assumed values. [f] φ is the center of the Cp ring. [g] Positive values indicate CH bending toward Be, negative values away from Be. [h] Only these parameters are optimized at 4-31G.

Table III. Total and Relative Energies of Various CpBeH Structures at the STO-3G Level

structure	total energy, au	rel energy, kcal/mol	Be–ring distance, Å
I (Y = H)[a]	−204.970 63	0.00	1.461
VI[b,c]	−204.970 53	0.06	1.466
VII[b,d]	−204.901 34	43.48	1.659
VIII[b,e]	−204.877 33	58.55	1.700
IX[f]	−204.889 18	51.11	

[a] Fully optimized structure. [b] Cp ring structures (D_{5h}) taken from CpLi optimized values (ref 3b): r(C–C) = 1.417 Å, r(C–H) = 1.079 Å. r(BeH) was fixed at 1.283 Å perpendicular to the ring and the ring–Be distances optimized. [c] C_{5v} symmetry, η^5. [d] C_s symmetry, η^2, BeH above a C–C bond center. [e] C_s symmetry, η^1, BeH above a carbon atom. [f] C_s symmetry, η^1, optimized cyclopentadiene structure (Table IV) with a methylene hydrogen replaced by a BeH group; r(Be–C) = 1.69 Å and (BeH) = 1.29 Å, ∠CBeH = 180°.

MNDO[14] are too long. The 4-31G structure, also in reasonable agreement with experiment, was determined in order to check the basis set dependence and a point which interested us in particular—the direction and degree of bending of the ring hydrogens. None of the experimental results (Table I) gave any information in this respect, and STO-3G on the one hand and PRDDO and MNDO on the other gave opposite results. An analysis is presented separately below. The interaction surface above the cyclopentadienyl ligand was probed in one set of calculations by keeping the ring geometry fixed at the value calculated for η^5-CpLi (C_{5v}, r(C–C) = 1.417 Å, r(C–H) = 1.079 Å).[3b] The BeH group (r(Be–H) fixed at 1.283 Å) was positioned perpendicular to the ring first above the center (pentahapto, VI), then above the midpoint of the C–C bonds (dihapto, VII), and finally above one of the C atoms (mono-

VI   VII   VIII
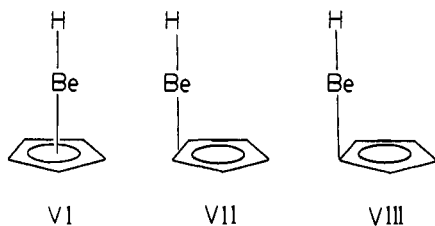
hapto, VIII). This procedure amounts to what has been termed a "haptotropic" search,[25a] and has been employed for a parallel study of cyclopentadienyllithium[3b] as well as for other systems.[25b] VI was extremely close in geometry and energy to fully optimized CpBeH (I, Y = H) (Table III).

The pentahapto structure (VI) was much lower in energy than either of the alternatives (VII or VIII, Table III). Quantitatively similar results were obtained at the PRDDO level; Marynick's study also included a larger number of geometries.[11b] The similarity of the results to those found for CpLi[3b] should also be noted. The ring–Be distances (Table III) were shorter by 0.2 Å than the comparable ring–Li values, but the energies relative to the respective pentahapto values are almost identical.[3b]

Another model for the hypothetical monohaptocyclopentadienylberyllium hydride (IX) was examined. Cyclopenta-

IX   X
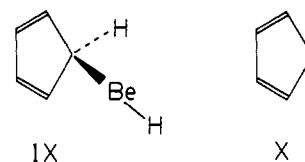
diene (X) was first optimized at the STO-3G level (Table IV). The resulting energy was 6.24 kcal/mol lower than that obtained by carrying out a single point calculation on the experimental geometry.[23] A methylene hydrogen on the optimized structure was replaced by a Be–H group, keeping all angles the same and using standard geometries (∠CBeH = 180°, r(C–Be) = 1.69 Å, r(Be–H) = 1.29 Å). The resulting structure (IX) was 51 kcal/mol less stable than the pentahapto form (I, Y = H) at the STO-3G level (Table III). Although we did not specifically examine the possibility, it seems unlikely in view of the large energy differences and the parallel CpBeH PRDDO[11b] and CpLi STO-3G[3b] results that any form besides I will be an energy minimum. This contrasts with Dewar's MNDO study,[14] in which a monohapto form was indicated to be a local minimum, only 9 kcal/mol higher in energy than the pentahapto form.

Ring C–H Out of Plane Bending. The C–H bonds in CpBeH (I, Y = H) are bent toward beryllium by 0.9° at the STO-3G and by 0.8° at the 4-31G/5-21G levels (Table II). This contrasts with η^5-CpLi where the C–H's are bent away from Li, by 3.6° with a double ζ basis[3b] and by 6.8° with the STO-3G

Table IV. Experimental[a] and STO-3G Geometries of Cyclopentadiene

parameter[b]	exptl	STO-3G optimized X
C_1-C_2	1.342	1.320
C_2-C_3	1.469	1.495
C_1-C_5	1.509	1.518
C_1-H	1.08[c]	1.080
C_2-H	1.08[c]	1.082
C_5-H	1.09[c]	1.092
HC_5 plane	126.5	126.7
$C_5C_1C_2$	109.3	109.3
$C_1C_5C_4$	102.6	102.6
$C_1C_2C_3$	109.4	112.7
calcd energies, au	−190.446 93	−190.456 87[d]

[a] Reference 23. [b] Bond lengths in ångströms and bond angles in degrees. [c] Assumed values. [d] A recently published energy, −190.45711 av, is slightly lower (J. Kad and L. Radon, *J. Am. Chem. Soc.*, **100**, 760 (1978)).

Table V. STO-3G Energies Used in Isodesmic Reactions

| species	energy, au	species	energy, au
Li^a	−7.315 52	$CH_4{}^c$	−39.726 86
Li^{+b}	−7.135 45	CH_3Li^a	−46.421 59
BeH^a	−14.935 33	CH_3BeH^d	−54.153 22
BeH^{+b}	−14.664 77	$CpLi^e$	−197.293 75
$BeH_2{}^b$	−15.561 35	C_5H_6	−190.456 90

[a] J. D. Dill and J. A. Pople, *J. Chem. Phys.*, **62**, 2921 (1975). [b] Reference 32. [c] W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 6377 (1971). [d] J. B. Collins, J. D. Dill, E. D. Jemmis, Y. Apeloig, P. v. R. Schleyer, R. Seeger, and J. A. Pople, *ibid.*, **19**, 5419 (1976). [e] Fully optimized value, ref 26. Partially optimized values are given in ref 3b and in footnote *d*.

basis.[26] Assuming that the bonding in η^5-CpLi is largely ionic, it was suggested that the C–H bonds bend away from Li in order to increase the sp hybrid character of the π orbitals and consequently to enhance the negative charge between the ring and Li+. However, an alternative to this ionic character explanation is based on significant covalent interaction involving diffuse p orbitals on Li. This alternative explanation is supported by calculations on a series of sandwich molecules involving first-row elements[26] and is similar to effects suggested by Kettle[27] and by Hoffmann and co-workers[28] for transition metal π complexes. The π orbitals of a given ring require a specific "size" for the p_x and p_y orbitals on Li or BeH for maximum overlap. Depending on the diffuse nature of these orbitals, the π orbitals of the ring can rehybridize (see Figure 1 for a schematic representation) by bending the C–H bonds out of the plane of the ring. The direction of bending obviously depends on the diameter of the ring as well. The compatibility of orbital size will be discussed in detail elsewhere, where results on a large set of electronically similar sandwich molecules will be presented.[26]
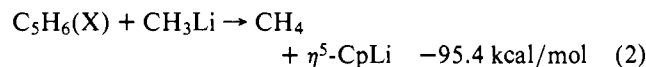
Energy and Bonding. The multicenter bonding in cyclopentadienylberyllium compounds[10] can readily be understood by considering the interaction of Cp and BeH fragments. The degenerate Cp π orbitals (e_1) interact with the p_x and p_y BeH orbitals while the lowest Cp π orbital (a_1) interacts with the BeH sp orbital. The three stabilized orbitals resulting are occupied by six electrons; hence, the pentahapto arrangement is favored. The bonding pattern is the same in the many known isoelectronic and isoconjugate systems.[29,30] Figure 2B, discussed in more detail below, presents an equivalent interpretation.
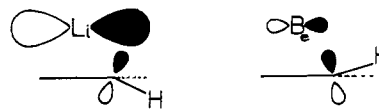
Figure 1. Schematic presentation of the dependance of out of plane bending on the diffuse nature of Li and Be p orbitals.
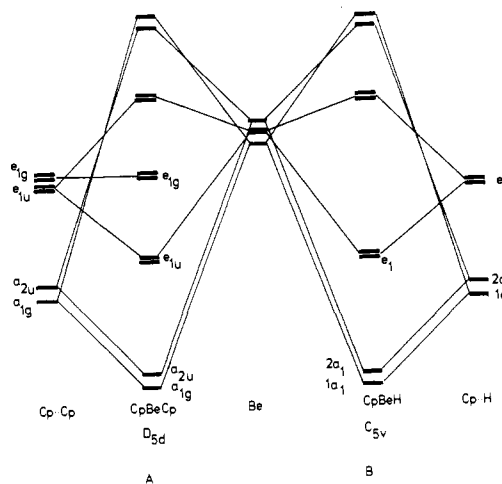
Figure 2. Schematic interaction diagram using an approximate energy scale to emphasize the difference in bonding in D_{5d} Cp$_2$Be (A) and in C_{5v} CpBeH (B). In B, the $1a_1$ and $2a_1$ designations are used for convenience.

The isodesmic reaction[31] (eq 1) indicates the large stabilization of η^5-CpBeH relative to CH_3BeH (Table V).

$$C_5H_6(X) + CH_3BeH \rightarrow CH_4$$
$$+ \eta^5\text{-CpBeH (I, Y = H)} \quad -54.8 \text{ kcal/mol} \quad (1)$$
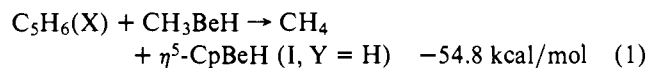
The corresponding reaction (eq 2) for η^5-CpLi is even more exothermic:

$$C_5H_6(X) + CH_3Li \rightarrow CH_4$$
$$+ \eta^5\text{-CpLi} \quad -95.4 \text{ kcal/mol} \quad (2)$$

This comparison gives the impression that the interaction between Li and Cp is more exothermic than that between BeH and Cp, but the lower C–M bond energy in CH_3Li relative to CH_3BeH is also responsible. The equation

$$\eta^5\text{-CpLi} + BeH^+ \rightarrow \eta^5\text{-CpBeH (I, Y = H)}$$
$$+ Li^+ \quad -92.6 \text{ kcal/mol} \quad (3)$$
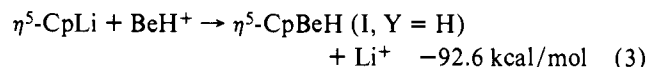
also compares the relative stabilities of CpLi and CpBeH. While the products are more stable than the reactants by −92.6 kcal/mol, this is also misleading owing to the difference in electron affinities of Li and BeH (relative STO-3G values are given by eq 4).

$$Li + BeH^+ \rightarrow BeH + Li^+ \quad -56.8 \text{ kcal/mol} \quad (4)$$
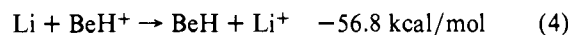
Thus, the most reasonable way to estimate the difference between Li and BeH bonding to Cp probably is eq 5, but the value obtained with the STO-3G minimal basis set, −38.5 kcal/mol, should only be considered to be illustrative, even though reaction energies at higher levels (−68.6 kcal/mol at UHF/6-31G* and −69.8 kcal/mol at UMP2/6-31G*) are not far from the STO-3G value for eq 4.[32]

$$\eta^5\text{-CpLi} + BeH \rightarrow \eta^5\text{-CpBeH (I, Y = H)}$$
$$+ Li \quad -35.8 \text{ kcal/mol} \quad (5)$$
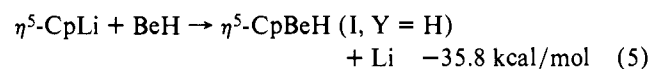
There is very little energetic difference between the Be–C

Table VI. Total and Relative Energies (STO-3G) of Various Structures of Beryllocene[a]

structure	point group	inter-ring distance, b, Å[b]	ring–Be distance, a, Å[b]	E, au	E rel, kcal/mol
V[c]	C_s			−394.290 56	0.0
II(a)	D_{5d}	3.247	1.6235	−394.278 76	7.4
(b)		3.375	1.6875	−394.274 35	10.2
(c)		3.700	1.850	−394.232 01	35.2
III(a)	C_{5v}	3.375	1.6182	−394.274 34	10.2
(b)		3.375	1.5375	−394.265 86	15.5
(c)		3.375	1.3875	−394.238 84	32.5
(d)		3.700	1.700	−394.232 01	37.6
IV(a)	C_s	3.247	1.6235	−394.239 97	31.7
(b)		3.375	1.6875	−394.239 46	32.1

[a] See text and Figures 3 and 4 for designation of the structural assumptions employed. [b] See Figures 3. [c] See Figure 4.
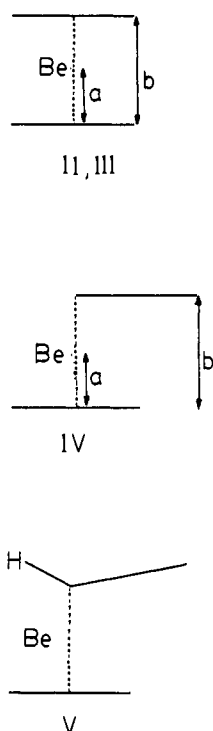

Figure 3. Side view of the three beryllocene structures considered; b is the inter-ring distance, a is the ring–Be distance. II is the symmetrical D_{5d} form, IV is the "slipped sandwich" form where both rings are parallel and maintain identical C–C and C–H bond lengths, and V is the η^5,η^1 form (for the geometry used, see Figure 4).

bonds in CH_3BeH and in η^1-CpBeH (IX):

$$\eta^1\text{-CpBeH (IX)} + CH_4 \rightarrow CH_3BeH$$
$$+ C_5H_6 \text{ (X)} \quad +3.7 \text{ kcal/mol} \quad (6)$$
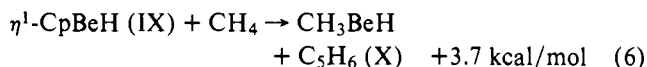
Evidently, there is no appreciable π bonding involving beryllium in this geometry (IX). A large increase in such bonding occurs when the BeH group is moved to a central position above the ring, and η^1-CpBeH (IX) is 51.1 kcal/mol less stable than η^5-CpBeH (I, Y = H).

Dipole Moment. The calculated dipole moments for CpBeH (2.80 D at STO-3G; 1.79 D at 4-31G) are in agreement with the gas-phase experiment value of 2.08 D.[5a] However, the direction of the dipole moment is not known experimentally. Although the relative electronegativities of C and Be and the usual assumption that the cyclopentadienyl anion should be stabilized suggest that the negative end of the dipole should be directed toward Cp, the calculation shows the opposite: BeH is the negative end. This result indicates the high degree of covalency present in CpBeH; ionic bonding, Cp^-BeH^+, would

have given a dipole moment oriented in the opposite direction as is found for Cp^-Li^+ (−0.79 D at STO-3G, lithium positive). The observed dipole moment, 4.26 D for CpBeCl (I, Y = Cl),[33] is consistent with this conclusion. A decrease in the dipole moment is expected by substitution of the chlorine (I, Y = Cl) by hydrogen (I, Y = H). In addition, the dipole moments of CH_3BeH[34a] and CH_3BeF[34b] have been calculated to be in the same direction (methyl positive), 0.45 vs. 1.75 D, respectively; the change in magnitude parallels the behavior in going from CpBeH to CpBeCl.[35] Monohapto CpBeH (IX) is calculated (STO-3G) to have a dipole moment of 0.53 D, similar to that of CH_3BeH (BeH in both cases negative), with the component perpendicular to the ring being 0.47 D. The large increase in dipole moment in going to η^5-CpBeH (I, Y = H) (2.80 D) also indicates that π Cp electrons are donated into the beryllium p orbitals in pentahapto bonding. The Mulliken populations show parallel behavior. At STO-3G the charges on Be are +0.222 in IX, but only −0.016 in I (Y = H). (The charges on the BeH hydrogen remain essentially unchanged, −0.045 and −0.053, in IX and I, respectively.)
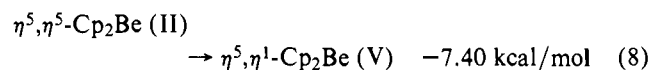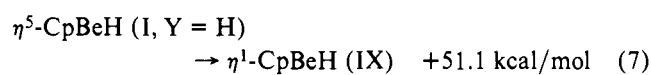
B. Beryllocene. The relative energies obtained for various Cp_2Be structures are given in Table VI. The more symmetrical structures, C_{5v} (III) and D_{5d} (II), were considered in order to probe the double well potential indicated by electron diffraction studies and supported by the two earlier semiempirical calculations.[12] The Cp rings, each with local D_{5d} symmetry, r(C–C) = 1.417 Å, and r(C–H) = 1.079 Å, were held at the experimental (gas phase) inter-ring distance (3.375 Å)[10b] and the position of the Be atom was varied. As the data in Table VI show, Cp_2Be prefers D_{5d} symmetry; no evidence for preferred off-center (C_{5v}) arrangements was found. The inter-ring distance was then expanded to 3.70 Å so that any tendency to distort toward C_{5v} symmetry would be increased, but distortion again was found to be unfavorable (Table VI). In contrast to the two previous semiempirical[12] and gas-phase[10b] results, D_{5d} structures are preferred over C_{5v} at the STO-3G level. The PRDDO and MNDO studies came to the same conclusion. The optimum D_{5d} inter-ring distance, determined to be 3.247 Å (STO-3G), is comparable to 3.220 (PRDDO)[11a] and 3.330 Å (MNDO),[14] but is shorter than the experimental distance of 3.375 Å found for a structure assigned C_{5v} symmetry.[10b]

The "slipped-ring" x-ray structures of beryllocene were proved by moving one of the rings of the D_{5d} structure in a parallel plane by 1.2053 Å sideways so that the Be is directly above one of the carbon atoms, IV. This η^1,η^5-Cp_2Be (IVa) with inter-ring distance b = 3.247 Å and Be–ring distance a = 1.6235 Å gave a total energy of −394.239 97 au; with b = 3.375 Å (Figure 3) the energy is −394.239 46 au. These structures are thus 24.3 and 24.7 kcal/mol, respectively, *less stable* than the D_{5d} form. The x-ray structure is also found by PRDDO to be unfavorable relative to the D_{5d} alternative.
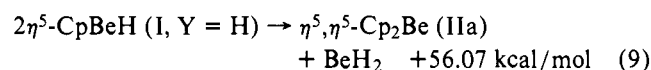
In contrast to the situation in CpBeH, monohapto Be–C

bonding in Cp_2Be is enhanced by using a localized cyclopentadienyl group with a tetrahedral arrangement around the carbon atom bonded by beryllium. As detailed above, the geometry (Figure 4) used for calculation employed the microwave structure of cyclopentadiene,[23] a Be–C distance identical with the optimized (STO-3G) CH_3–BeH value,[24] and η^5-ring–Be distance taken from the optimized CpBeH structure (I, Y = H). This σ,π (monohapto-pentahapto) structure, V, is found to be 7.4 kcal/mol more stable than the best D_{5d} structure even without any geometry optimization. Tables III and IV indicate that use of the STO-3G optimized instead of the experimental cyclopentadiene structure might lead to a further stabilization. Since the size and the low symmetry of some of the competitive Cp_2Be structures preclude complete STO-3G optimizations, we were contented with the qualitative conclusion that the η^1,η^5-Cp_2Be (V) should be the most stable form. The PRDDO and MNDO results agree: PRDDO indicates the η^1,η^5 structure to be more stable than the D_{5d} structure by 6.4 kcal/mol while the MNDO value is 15.6 kcal/mol. It should be recalled that only one sharp proton singlet is found in the NMR spectrum of Cp_2Be down to $-135\ °C$.[10h] However, since the chemical shift differences in known fluctuating η^1-cyclopentadienyl derivatives do not differ much from η^5 analogues,[10i] the height of the barrier cannot be estimated very well.

Energy and Bonding. There is a dramatic change in the energy difference between monohapto and pentahapto bonding in CpBeH and Cp_2Be (compare eq 7 and 8).

$$\eta^5\text{-CpBeH (I, Y = H)}$$
$$\rightarrow \eta^1\text{-CpBeH (IX)} \quad +51.1\ \text{kcal/mol} \quad (7)$$

$$\eta^5,\eta^5\text{-Cp}_2\text{Be (II)}$$
$$\rightarrow \eta^5,\eta^1\text{-Cp}_2\text{Be (V)} \quad -7.40\ \text{kcal/mol} \quad (8)$$

Since C–Be bonding in η^1-CpBeH (IX) and in CH_3BeH is similar (eq 6), the difference in energy between eq 7 and 8 (58.5 kcal/mol) must arise from the destabilizing interaction between the two rings in η^5,η^5-Cp_2Be (II). This is shown in another way by isodesmic reactions (eq 9);[10j] two pentahapto rings in the same molecule (IIa) are bound less effectively than in separate molecules (I, Y = H).

$$2\eta^5\text{-CpBeH (I, Y = H)} \rightarrow \eta^5,\eta^5\text{-Cp}_2\text{Be (IIa)}$$
$$+ \text{BeH}_2 \quad +56.07\ \text{kcal/mol} \quad (9)$$

A comparison of orbital interaction diagrams (Figure 2) for η^5-CpBeH (I, Y = H) and for η^5,η^5-Cp_2Be (D_{5d}, II) indicates why a single pentahapto ring is bound strongly, but simultaneous pentahapto bonding of two rings is unfavorable. The interaction of the π MOs of a η^5-Cp ligand with the a_1 (s or sp) orbital of a η^1-X ligand (e.g., H, CH_3, η^1-Cp) results in the pattern shown on the right side of Figure 2B. The four lowest energy orbitals have the proper symmetry to interact with the valence atomic orbitals of beryllium, and the four stabilized orbitals (shown in the center of Figure 2B) result. Eight electrons, which have been termed "interstitial" electrons,[4a] fill these four orbitals giving rise to highly stable C_{5v} structures (I). This type of bonding has already been recognized many times in the literature.[3b,4a,29,30]

Following Collins and Schleyer,[4a] the bonding in η^5,η^5-Cp_2Be (D_{5d}, II) can be developed similarly (Figure 2A). The interaction of the π orbitals of two cyclopentadienyl rings lying face to face produces the orbital pattern shown at the left side of Figure 2A. In contrast to the situation in Figure 2B, only four of the six lowest orbitals have the proper symmetry to interact with the s and p orbitals of Be in II; the two e_{1g} orbitals remaining (center of Figure 2A) have antibonding character with regard to interactions between the two Cp rings. As there are now 12 interstitial electrons, these two unfavorable orbitals
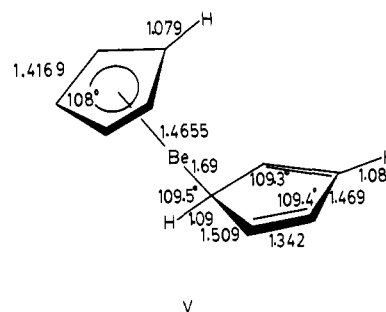

Figure 4. Structural details of η^5,η^1-Cp_2Be (V).

(e_{1g}) as well as the four favorable ones (a_{1g}, a_{2u}, and e_{1u}) must be occupied. Comparison of Figures 2A and 2B shows that the extra four interstitial electrons in η^5,η^5-Cp_2Be (II) are certainly no advantage and actually seem to be detrimental as less symmetrical structural alternatives (e.g., η^1,η^5-Cp_2Be (V)) are known to be more stable. This explanation may be looked at as a molecular orbital equivalent of the ring–ring repulsion rationalization offered earlier,[10] but the repulsion is better regarded as an electronic rather than as a steric effect. Note that two e_{1g} orbitals are those involved in overlap with d_{xz} and d_{yz} orbitals of transition metals to provide the substantial ring–metal bonding in transition metal metallocenes.[36] The absence of available d orbitals on Be renders the metallocene structure less favorable.

Conclusions

Ab initio molecular orbital calculations at the levels of approximation employed in this work cannot be considered to be definitive. Still, the general ability of the minimal STO-3G and the split valence 4-31G/5-21G basis sets to give optimized geometries in close agreement with experiment[37] is confirmed by the results with CpBeH (I, Y = H) (Tables I and II). The experimental dipole moment is also well reproduced in magnitude; the dipole is found to be directed toward BeH, a surprising result indicating the high degree of back-bonding into the beryllium p orbitals. No experimental energy data are available with which comparisons can be made.

Our results indicate CpBeH to be a stable species with a strong preference for a C_{5v} structure with pentahapto bonding. The covalent character is considerably greater in CpBeH than in CpLi, and the calculated dipole moments are in opposite directions.

All theoretical and experimental methods find D_{5d} or D_{5h} sandwich structures for Cp_2Be to be less stable than alternatives with lower symmetry, but there is considerable disagreement concerning the most stable structure. The rather flat energy surface indicated both experimentally and by various calculations undoubtedly contributes to this uncertainty. No support for the off-center C_{5v} electron diffraction structure was found in our ab initio or in any of the other recent theoretical results.[11a,14,15] D_{5d} or D_{5h} and monohapto-pentahapto forms are indicated to be lower in energy. However, a reinvestigation by electron diffraction of the structure of beryllocene confirms the earlier conclusion that a C_{5v} geometry best fits the data.[39] This structure may have one cyclopentadienyl ring covalently bound to Be and the other ionically bound, in agreement with the largely ionic bonding deduced from infrared spectra.[10e] The discrepancy with the theoretical results remains. However, none of the calculations were carried out with a full geometry optimization, with a truly large basis set, or with the inclusion of electron correlations which might alter the relative energies of different structures significantly.

The "slipped sandwich" form proposed on the basis of x-ray studies was also found to be less favorable than the D_{5d} form.

Of course, the calculations refer to the gas phase, rather than to the solid state. The pentahapto-monohapto structure favored theoretically would seem to be a reasonable alternative, especially when the fluctional nature of the system is taken into account.

Why is not the symmetrical sandwich (D_{5d} or D_{5h}) structure favored for beryllocene? Cotton and Wilkinson suggest that "the Be radius is so small that even at the closest distance of approach of the two C_5H_5 rings the Be atom cannot make good bonds to both simultaneously".[38] While we agree that two Cp rings cannot both be bound effectively, it is the unavailability of orbitals of the proper symmetry on beryllium rather than the small size of the Be atom which is responsible.[4a] Beryllocene possesses 12 interstitial electrons, but only four stabilized molecular orbitals are available (Figure 2A). The extra four electrons occupy orbitals (e_{1g}) which are probably antibonding with regard to the two Cp rings, and distortion to the η^1,η^5 form, with eight interstitial electrons, occurs. Symmetrical sandwiches involving beryllium (or other first-row elements as the central atom) may be possible in systems possessing four fewer electrons.[4a]

References and Notes

(1) This work was supported in part by NSF Grant 29383 at Berkeley and by the Fonds der Chemischen Industrie at Erlangen. Taken, in part, from the Ph.D. theses of E.D.J. (Princeton University, 1978) and S.A. (University of California, 1972).

(2) (a) Universität Erlangen-Nürnberg; (b) University of California, Berkeley.

(3) (a) A. Streitwieser, Jr., J. E. Williams, J. M. McKelvey, and S. Alexandratos, *J. Am. Chem. Soc.*, **98**, 244 (1976); (b) S. Alexandratos, A. Streitwieser, Jr., and H. F. Schaefer, III, *ibid.*, **98**, 7959 (1976).

(4) (a) J. B. Collins and P. v. R. Schleyer, *Inorg. Chem.*, **16**, 152 (1977); (b) E. D. Jemmis, D. Poppinger, P. v. R. Schleyer, and J. A. Pople, *J. Am. Chem. Soc.*, **99**, 5796 (1977); (c) J. D. Dill, P. v. R. Schleyer, J. S. Binkley, and J. A. Pople, *ibid.*, **99**, 6159 (1977); and references cited in these papers.

(5) (a) T. C. Bartke, A. Bjorseth, A. Haaland, K.-M. Marstokk, and H. Møllendal, *J. Organomet. Chem.*, **85**, 271 (1975); (b) D. A. Drew and A. Haaland, *Acta Chem. Scand.*, **26**, 3079 (1972).

(6) D. A. Drew and A. Haaland, *Acta Chem. Scand.*, **26**, 3351 (1972).

(7) A. Haaland and D. P. Novak, *Acta Chem. Scand., Ser. A*, **28**, 153 (1974).

(8) D. A. Drew, G. Gundersen, and A. Haaland, *Acta Chem. Scand.*, **26**, 2147 (1972).

(9) E. O. Fischer and H. P. Hofmann, *Chem. Ber.*, **92**, 482 (1959).

(10) (a) A. Almenningen, O. Bastiansen, and A. Haaland, *J. Chem. Phys.*, **40**, 3434 (1964); (b) A. Haaland, *Acta Chem. Scand.*, **22**, 3030 (1968); (c) C. Wong, T. Y. Lee, K. J. Chao, and S. Lee, *Acta Crystallogr., Sect. B*, **28**, 1662 (1972); (d) C. Wong, T. Y. Lee, T. W. Chang, and C. S. Liu, *Inorg. Nucl. Chem. Lett.*, **9**, 667 (1973); (e) G. B. McVicker and G. L. Morgan, *Spectrochim. Acta, Part A*, **26**, 23 (1970); (f) D. A. Drew and A. Haaland, *Acta Crystallogr., Sect. B*, **28**, 3671 (1972); (g) E. O. Fischer and S. Schreiner, *Chem. Ber.*, **92**, 938 (1959); (h) C. Wong and S. Wang, *Inorg. Nucl. Chem.*

Lett., **11**, 677 (1975); (i) P. Fischer, J. Stadelhofer, and J. Weidlein, *J. Organomet. Chem.*, **116**, 65 (1976); (j) D. A. Drew and G. L. Morgan, *Inorg. Chem.*, **16**, 1704 (1977).

(11) (a) A thorough historical introduction to the problem is given by D. S. Marynick, *J. Am. Chem. Soc.*, **99**, 1436 (1977); (b) D. S. Marynick, private communication.

(12) (a) M. Sundbom, *Acta Chem. Scand.*, **20**, 1608 (1966); (b) O. Y. Lopatko. N. M. Klimenko, and M. E. Dyatkina, *Zh. Strukt. Khim.*, **13**, 1128 (1972).

(13) T. A. Halgren and W. N. Lipscomb, *J. Chem. Phys.*, **58**, 1596 (1973).

(14) M. J. S. Dewar and H. S. Rzepa, *J. Am. Chem. Soc.*, **100**, 777 (1978). We are indebted to Professor Dewar for a preprint of this manuscript.

(15) Ab initio calculations have also been performed on (a) CpBeH and Cp2Be by E. Wisløff Nilssen and A. Haaland (private communication, see ref 5a), and on (b) Cp2Be by J. Demuynck and M. M. Rohmer, *Chem. Phys. Lett,* **54**, 567 (1978), and N.-S. Chiu and L, Schäfer, *J. Am. Chem. Soc.*, **100**, 2604 (1978). We thank Professors A. Veillard and L. Schäfer for preprints of these papers.

(16) H. F. Schaefer, III, "The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results", Addison-Wesley, Reading, Mass., 1972.

(17) C. C. J. Roothan, *Rev. Mod. Phys.*, **23**, 69 (1951).

(18) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

(19) (a) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971); (b) W. J. Hehre and J. A. Pople, *ibid.*, **56**, 4233 (1972); (c) J. D. Dill and J. A. Pople, *ibid.*, **62**, 2921 (1975); (d) J. S. Binkley and J. A. Pople, *Ibid.*, **66**, 879 (1977).

(20) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.

(21) The QCPE version was adapted to the CDC computer by Dr. J. M. McKelvey at Berkeley.

(22) Many calculations were carried out using a single precision version of the program. We thank Dr. Hans-Ulrich Wagner for making this program available to us.

(23) L. H. Scharpen and V. W. Laurie, *J. Chem Phys.*, **43**, 2765 (1965).

(24) J. D. Dill, P. v. R. Schleyer, and J. A. Pople, *J. Am. Chem. Soc.*, **98**, 1663 (1976).

(25) (a) The term "haptotropic" search was first suggested by Dr. P. Hofmann, Erlangen; see (b) N. T. Anh, M. Elian, and R. Hoffmann, *J. Am. Chem. Soc.*, **100**, 110 (1978).

(26) E. D. Jemmis, P. v. R. Schleyer, and J. A. Pople, manuscript in preparation; E. D. Jemmis, Ph.D. Thesis, Princeton University, 1978.

(27) S. F. A. Kettle, *Inorg. Chim. Acta*, **1**, 303 (1967).

(28) M. Elian, M. M. L. Chen, D. M. P. Mingos, and R. Hoffmann, *Inorg. Chem.*, **15**, 1148 (1976).

(29) (a) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179 (1962); (b) W. D. Stohrer and R. Hoffmann, *J. Am. Chem. Soc.*, **94**, 1661 (1972).

(30) (a) H. Hogeveen and P. W. Kwant, *Acc. Chem. Res.*, **8**, 413 (1975); (b) H. C. Brown, "The Nonclassical Ion Problem", with comments from P. v. R. Schleyer, Plenum Press, New York, N.Y., 1977, p 15 ff; (c) E. L. Muetterties, Ed., "Boron Hydride Chemistry", Academic Press, New York, N.Y., 1975.

(31) W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 4796 (1970).

(32) J. B. Collins, P. v. R. Schleyer, J. S. Binkley, J. A. Pople, and L. Radom, *J. Am. Chem. Soc.*, **98**, 3436 (1976).

(33) A. Bjorseth, D. A. Drew, K.-M. Marstokk, and H. Mollendal, *J. Mol. Struct.*, **13**, 233 (1972).

(34) (a) J. D. Dill, unpublished; see ref 24. (b) C. P. Baskin, C. F. Bender, R. R. Lucchese, C. W. Bauschlicher, Jr., and H. F. Schaefer III, *J. Mol. Struct.*, **32**, 125 (1976).

(35) Unlike charge distributions obtained from population analyses, dipole moments do not depend as markedly on the basis set used. Population analysis indicates the BeH group in I (Y = H) to be negatively charged at STO-3G and positively charged at 4-31G levels. However, the direction of the dipole moment remains unchanged.

(36) M. Tsutsui, M. Levy, A. Nakamura, M. Ichikawa, and K. Mori, "Introduction to Metal Pi-Complex Chemistry", Plenum Press, New York, N.Y., 1970, Chapters 5 and 6.

(37) J. A. Pople in "Modern Theoretical Chemistry", Vol. 4, H. F. Schaefer, Ed., Plenum Press, New York, N.Y., 1977, Chapter 1.

(38) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed, Interscience, New York, N.Y., 1972, p 743.

(39) A. Haaland, private communication.

(40) D. Poppinger, *Chem. Phys. Lett.*, **34**, 332 (1975).