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Sandwich-Type Molecules of First-Row Atoms. Instability of Bis-(η^3-cyclopropenyl)beryllium

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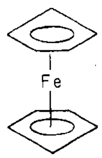
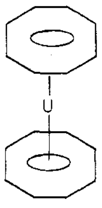
No symmetrical "sandwich" molecules involving only first short period elements and hydrogens are known. Beryllocene (IV) comes closest but possesses a fluctuating structure with nonequivalent cyclopentadienyl rings. Analysis of the more symmetrical (D_{5h} or D_{5d}) alternatives reveals that the HOMO's, degenerate pairs, possess two nodal planes passing through the central atom. Consequently, occupation of these orbitals does not contribute to binding between the rings and the central atom and less symmetrical structures are more stable. Only the lowest four valence molecular orbitals provide this bonding; therefore the optimum number of *interstitial* electrons is 8, provided that the ligand rings are large enough to accommodate six of these electrons in π orbitals which are bonding with respect to the rings themselves. Three- and four-membered ring sandwich complexes in the first short period should be possible only with *four* interstitial electrons. STO-3G ab initio calculations on partially optimized bis(η^3-cyclopropenyl)beryllium (IIIc) bears this out. The η^1,η^1 alternative is more stable. A first short period sandwhich complex was achieved computationally (if only marginally) with the four interstitial electron system VIIb. Other possible first-row sandwich complexes are suggested.

Introduction

Since E. O. Fischer and Wilkinson postulated the bonding scheme in ferrocene (I) (bis-(η^5-cyclopentadienyl)iron) nearly 25 years ago,[2] interest in such π-bonded sandwhich complexes has grown steadily.[3] It was proposed that metal orbitals of d symmetry were ideally disposed for interacting with π molecular orbitals of the two cyclopentadienyl rings, attaching the rings to the central metal in a highly symmetrical fashion.[2] R. D. Fischer[4a] and Streitwieser[4b] extended this idea to predict the stability of uranocene (II) (bis-(η^8-cyclooctatetraene)-uranium) in which orbitals of f symmetry are thought to help bind the ligands to the central atom.



I



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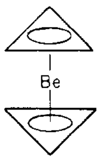
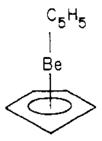


III



IV

We have investigated, by ab initio LCAO-MO-SCF calculations, the possibility of an extension of this idea in the opposite sense, namely, to symmetrical π complexes, such as III, comprised only of elements of the first short period in which the central atom is restricted to s and p orbitals.

Several half-sandwhich complexes of Be are known experimentally[5] as is "beryllocene" (bis(cyclopentadienyl)-beryllium) (IV).[6] However, IV has a dipole moment and the gas-phase structure confirms that the rings are not equivalent.[5b,7] In the gas the molecule possesses C_{5v} symmetry in which the Be atom oscillates in a double-well potential. In the solid a further distortion occurs to a structure described as having one π-bonded (η^5) and one σ-bonded (η^1) ligand.[8] A steric argument is generally offered[8] to account for this distortion. In the D_{5h} structures the rings are thought to approach too closely, thereby introducing strain which is relieved in the lower symmetry orientation.

Alternatively, it can be argued (vide infra), on the basis of orbital interaction diagrams (Figures 1 and 2), that D_{5h} or D_{5d} beryllocene has four too many electrons for the number of available ligand-metal bonding orbitals and relieves this surplus by a structural distortion.

Our search for symmetrical sandwich molecules utilized ligands designed to provide fewer electrons than cyclopentadienyl. The simpliest choice, and one that is both experimentally and computationally accessible, is cyclopropenyl (e.g., III). Several substituted cyclopropenyl complexes of transition metals have been reported and have been shown to possess local threefold axes.[9] In addition to cyclopropenyl we have studied the hypothetical ligands boracyclobutenyl, which has the same number of π electrons as cyclopropenyl, and diboracyclopropyl, which has two fewer π electrons.

Computational Method

All calculations were performed with the Gaussian 70[10] series of programs using the STO-3G basis set of Hehre et al.[11] in the restricted Hartree-Fock approximation (RHF/STO-3G).[12] Two levels of sophistication were employed in selecting the geometrical parameters of the molecules (Figure 3). In the first level a geometrical model was constructed from standard metal-carbon bond lengths[13] combined with calculated structures for the free ligands, where these are available, or standard geometries,[14] where they are not. For η^3-cyclopropenyl, the structure of $C_3H_3^+$ was employed;[15] for η^1-cyclopropenyl, the structure of cyclopropene itself[16] was used. In the second level the Be-ring distance was optimized since this parameter is subject to the greatest uncertainty, especially in the π complexes. In addition, some ligand parameters were optimized in the smaller complexes.[17] Total energies and optimized metal-ligand distances are given in Table I. Ligand geometries are found in Figure 3.

Results and Discussion

An analysis of the orbital interaction diagram in Figure 1 shows that first-row π complexes can accommodate no more than eight electrons in orbitals which bind ligands to a central

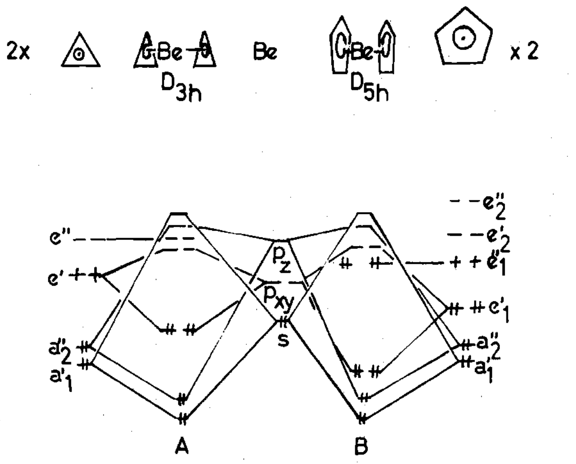


Figure 1. Schematic molecular orbital interaction diagram showing the interaction of Be with (A) three- and (B) five-electron ligands. The degenerate p_x, p_y, and p_z Be orbitals are separated for clarity.

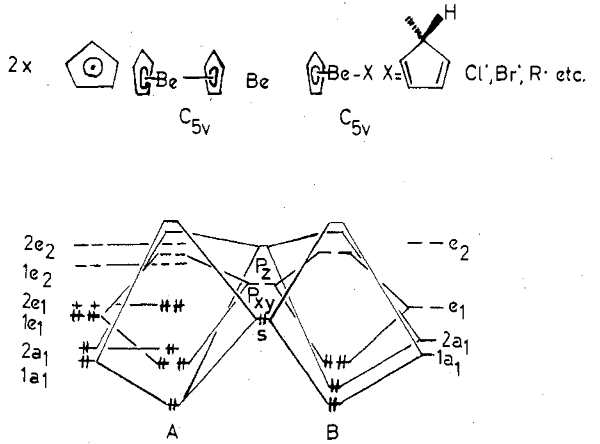


Figure 2. Schematic molecular orbital interaction diagram showing the interaction of Be with (A) nonequivalent cyclopentadienyl ligands and (B) a combination of a five- and a one-electron ligand. The degenerate p_x, p_y, and p_z orbitals of Be are separated for clarity.

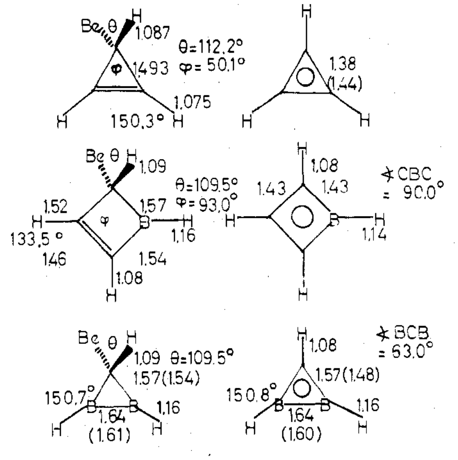
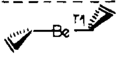
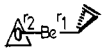
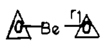
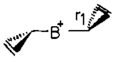
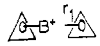
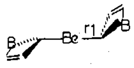
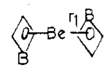
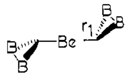
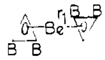


Figure 3. Standard and partially optimized ligand geometries (distances in angstroms, angles in degrees, and optimized values in parentheses). In the sandwich complexes, the Be atom lies on the normal passing through the point of intersection of the bisectors of the ring angles.

atom. We call these *interstitial* electrons. Each cyclopentadienyl ring possesses a doubly degenerate e_1'' pair of orbitals. The face-to-face approach of two such rings leads to an interaction of these orbitals, and to the formation of two new pairs of e_1' and e_2'' symmetry. The lower lying orbital (e_1') is further stabilized by interaction with the $2p_x$ and $2p_y$ orbitals on Be. The higher lying orbital (e_2'') can interact only with a metal orbital of d symmetry and is destabilized with respect to the situation which would pertain if the two rings were at infinite separation.

Table I. Total Energies,[a] Relative Energies,[b] and Ring–Metal Distances[c] at Standard and Partially Optimized Geometries

Molecule		Standard Geometry	Partially Optimized Geometry
IIIa 	E	-242.07814	-242.07827
	r_1	1.69	1.70
	E(rel)	0	0
IIIb 	E	-241.89181	
	r_1	1.47	
	r_2	1.69	
	E(rel)	117	
IIIc 	E	-241.85645	-241.87821
	r_1	1.47	1.52
	E(rel)	139	126
Va 	E	-251.82274	
	r_1	1.57	
	E(rel)	0	
Vb 	E	-251.65459	
	r_1	1.35	
	E(rel)	106	
VIa 	E	-292.08057	-292.08084
	r_1	1.69	1.71
	E(rel)	0	0
VIb 	E	-291.98827	-291.99023
	r_1	1.69	1.65
	E(rel)	58	57
VIIa 	E	-190.04356	-190.04469
	r_1	1.69	1.65
	E(rel)	0	0
VIIb 	E	-189.99997	-190.05380
	r_1	1.55	1.71
	E(rel)	27	-6

[a] Total energies in au. [b] Relative energies in kcal/mol. [c] Bond lengths in Å.

Molecules such as D_{5h} and D_{5d} beryllocene have 12 such interstitial electrons and distort[5d] so as to avoid populating the destabilized e_2'' orbitals (Figures 1B, 2A).[18] Symmetrical lengthening of the Be–ring distances would reduce this destabilization but would also weaken the favorable interactions of Be with the a_1' and a_2'' orbitals. Asymmetrical distortion reduces the destabilization of the $2e_1$ orbitals and the stabilization of the lower lying ($1a_1$, $2a_1$, $1e_1$) orbitals; presumably the former predominates.[7d]

Ferrocene and other metallocenes can stabilize the higher lying e_2'' orbitals with iron d_{xz} and d_{yz} orbitals (perpendicular to the two rings).[2] For first-row atoms stable π complexes have been achieved experimentally only with a combination of a five-electron ligand (η^5-cyclopentadienyl) and a one-electron ligand (bromine, chlorine, ethynyl, CH_3, and BH_4).[5] η^1-Cyclopentadienyl falls into the same category. The stability of these half-sandwich complexes is indicated by the molecular orbital diagram in Figure 2.

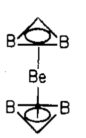
There is another factor to consider. In order for an axially symmetric π complex to be stable relative to other geometries, the π molecular orbitals must be bonding not only between each ligand and the metal but also with regard to the ligands themselves. Although the molecular orbitals in IIIc are well suited for binding the rings to beryllium,[19] the degenerate (e') highest occupied molecular orbitals in bis(η^3-cyclopropenyl)beryllium are antibonding with respect to the cyclopropenyl rings.[20] This unfavorable interaction overwhelms the metal–ligand stabilization[21] afforded by the D_{3h} structure. The unfavorable antibonding interactions in the ligands can be reduced somewhat by reducing the orbital coefficients of the ligand atoms. However, this results in transfer of electrons to Be. Since beryllium is electropositive with respect to carbon[22] such a charge transfer is unfavorable.[23]

This electronegativity problem can be reduced by substituting an isoelectronic, but positively charged, central atom. Replacement of Be by B^+ (Va, b) indeed results in a relative stabilization of the π complex by some 33 kcal/mol (standard model, Table I). However, this still falls short of the stabilization achieved by becoming σ bonded and Va is 106 kcal/mol more stable than Vb. Evidently, the principal source of the high relative energies of the symmetrical sandwhich structures, IIIc or Vb, is the unfavorable nodal properties of the HOMO; the transfer of charge to the metal is involved to a lesser extent. η^3-Cyclopropenyl complexes of transition metals[9] generally have a complementary anionic ligand so that the cyclopropenyl fragment bears a formal positive charge and is considered to be a two-π-electron donor.[3a] Thus the contribution of the ligand antibonding orbitals to the molecular orbitals is small.

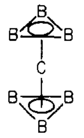
In order to prepare a symmetrical eight-interstitial-electron sandwhich (D_{nd} or D_{nh}) complex of a first row atom it will be necessary to incorporate the ligand π electrons into larger rings so that the resulting molecular orbitals are bonding between the ligand atoms themselves.

Such ligands, large enough to possess several π-bonding levels, present a ponderous computational burden at the ab initio level. However, we examined the effect of such a larger ring by constraining a pair of 1-boracyclobutenyl ligands to be symmetrically arranged around Be. In the resulting system (VIa, b), the HOMO is no longer antibonding since the ring has been enlarged without increasing the number of electrons. The resulting σ-bonded structure is still calculated to be favored, but by only 57 kcal/mol.

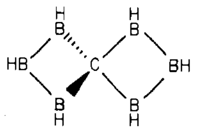
Further analysis of Figure 1A shows that a π complex with only four interstitial electrons should also be favorable. The σ-bonded complexes, IIIa, Va, and VIa, are trivial examples of this type. In order to investigate π-bonded complexes we have replaced four carbon atoms in bis(η^3-cyclopropenyl)-beryllium with boron atoms. This achieves our objectives. A complex (VIIb) in which the planes of the ligands are parallel is 6 kcal/mol more stable than the σ-bonded structure. The isoelectronic species $C(B_3H_3)_2$ (VIII) is also expected to demonstrate this behavior, especially since no corresponding σ-bonded Lewis structure is especially attractive (although IX should be the best alternative).[24] However, four-interstitial-electron sandwich systems, like BeH_2, $Be(CH_3)_2$, etc., are still highly electron deficient and may associate or otherwise react to form more stable molecular arrangements.[25]



VII



VIII

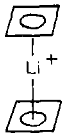


IX

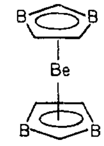
Speculations on Stabilized π Complexes

Symmetrical sandwich complexes of first-row atoms and ions will be preferred over corresponding σ-bonded isomers if the number of interstitial electrons involved in ligand–metal bonding does not exceed 8 for larger ring ligands or 4 for three-membered-ring ligands.

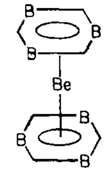
A variety of structures that meet these criteria come to mind. Bis(cyclobutadiene)lithium(1+) (X), bis(1,3-dibora-cyclopent-4-ene-2-yl)beryllium (XI), and bis(1,3,5-triborabenzene)beryllium (XII) are illustrative. X is just centrally lithiated cubane (although an antiprismatic structure may be preferred). XI not only should be more favorable but also should allow differentiation between the steric and the electronic explanations for the distorted structure of beryllocene. The five-membered rings in XI, although similar sterically to those in IV, provide a total of four fewer interstitial electrons. XII is a further extension of the same principle. A particularly attractive example employs the known ligand $CB_{10}H_{11}$.[26] The neutral ligand is a three-electron donor in transition metal complexes but also exists as the triply negative salt of alkali metals.[26] A sandwich compound such as $Be(CB_{10}H_{11})_2$ (XIII) meets all the requirements of an eight-interstitial-electron complex and could be expected to exist in D_{5d} or D_{5h} symmetry.



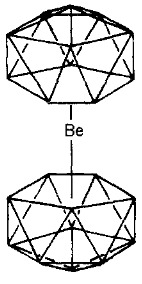
X



XI



XII



XIII, $Be(CB_{10}H_{11})_2$
(each vertex represents a BH or CH group)

We wish to emphasize that these predictions apply only to monohapto vs. polyhapto alternatives in the gas phase. We have not considered other structural arrangements or the effects of self-association, solvation, etc., which may influence the absolute rather than the relative stability of such species.

Acknowledgment. This work was carried out in part at Princeton University and at the University of Munich, the latter during the tenure of an award of the Alexander von Humboldt Foundation (to P. v. R. Schleyer). Computer time was donated by Princeton University and by the University of Munich, and the project was supported at Princeton by NSF Grant GP-29078X. We thank Dr. H.-U. Wagner for assistance with the calculations and J. A. Pople, W. E. Watts, R. Hoffmann, P. Hofmann, J. Schwartz, J. Norton, T. G. Spiro, and M. Chisolm for helpful discussions.

Registry No. IIIa, 60489-99-8; IIIb, 60525-59-9; IIIc, 60553-49-3; Va, 60490-00-8; Vb, 60553-50-6; VIa, 60490-01-9; VIb, 60525-57-7; VIIa, 60490-02-0; VIIb, 60525-58-8.

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(17) Calculations were performed on the D_{3h} structures of $(\eta^3\text{-}C_3H_3)_2Be$ (III). Corresponding geometries for other complexes are found in Figure 3. We assume that the energy difference arising from rotation to the D_{3d} geometry will be small. This is found to be the case from MINDO/3 calculations on the D_{3h} and D_{3d} geometries of VIII (E. D. Jemmis, unpublished work). See also ref 5f.
(18) That significant metal–ligand stabilization is occurring is evident in the relative energies of the π-bonded (η^3,η^3), half-sandwich (η^1,η^3), and σ-bonded (η^1,η^1) structures (Table I). Bridging of one ligand (IIIa → IIIb) costs 117 kcal/mol while bridging the second ring (IIIb → IIIc) costs only an additional 22 kcal/mol.
(19) This is shown by the short Be···ring distance in IIIc (1.52 Å), comparable to those in η^5-cyclopentadienylberyllium derivatives (1.48–1.53 Å).[5] VIIIb, with four fewer valence electrons than IIIc has a longer Be···ring distance (1.71 Å).
(20) Bis(η^3-allyl)beryllium (v. G. Wiegand and K.-H. Thiele, *Z. Anorg. Allg. Chem.*, **405**, 101 (1974)) is an interesting possibility which may overcome this problem (J. Schwartz, private communication).
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(23) A referee has kindly pointed out that the "slipping" motion of the cyclopropenyl rings leading to IIIa is symmetry forbidden. Thus, structures such as IIIa might be attainable in spite of the unfavorable enthalpy.
(24) MINDO/3 finds IX to be 100 kcal/mol more stable than VIII. However, the lower symmetry of IX allows four hydrogen atoms to bridge boron–boron bonds. This tendency toward bridging of boron bonds has been found to be excessive in MINDO/3 and often leads to unrealistic structures (K. Krogh-Jespersen, private communication).
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Investigation of Isomerization and Oxidation–Reduction Reactions of Halotricarbonylbis(diphenylphosphino)methanemanganese(I) Complexes Using Chemical and Electrochemical Techniques

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Electrochemical and chemical investigations of $Mn(CO)_3dpmX$ [dpm = $Ph_2PCH_2PPh_2$, X = Cl, Br] have allowed the elucidation of the structural, kinetic, and thermodynamic properties of the $[Mn(CO)_3dpmX]^{0,+}$ system. The equilibrium *fac*-Mn(I) + *mer*-Mn(II) ⇌ *mer*-Mn(I) + *fac*-Mn(II) is shown to lie substantially to the left. The various isomers for this system have all been individually identified and characterized by a variety of physical measurements. Electrochemistry is demonstrated to be particularly valuable in distinguishing the different species as well as providing information about redox properties. The reactions occurring in solution are summarized by the equations

$$\textit{fac}\text{-Mn(I)} \underset{e^-}{\overset{-e^-/\mathrm{NOPF_6}}{\rightleftharpoons}} \textit{fac}\text{-Mn(II)} \rightarrow \textit{mer}\text{-Mn(II)}$$

$$\textit{mer}\text{-Mn(II)} \underset{-e^-/\mathrm{NOPF_6}}{\overset{e^-/\text{solvent}}{\rightleftharpoons}} \textit{mer}\text{-Mn(I)} \rightarrow \text{decompose}$$

The most interesting feature of this system is that both *mer*- and *fac*-$[Mn(CO)_3dpmX]^+$ are low spin, as shown by ESR and direct magnetic susceptibility measurements (*mer* only). Reduction of Mn(I) (2e) and oxidation of Mn(II) were also observed.

Introduction

A study[1] of a series of complexes of the type $Mn(CO)_3(PR_3)_2X$ has shown that they can exist in two distinct isomeric forms and that the rate of isomerism from cis to trans (referring to the phosphine groups) increases with increasing size of R. The complexes $Mn(CO)_3dpmX$ cannot of course isomerize in this manner because of the bidentate nature of dpm, but isomerism from facial to meridional (referring to carbonyls), which always accompanies the cis–trans type noted above, is still possible. However, only facial isomers of $Mn(CO)_3dpmX$ have been previously reported.[2]

In two separate publications Reimann and Singleton have reported two compounds to result from the oxidation of $Mn(CO)_3dpmBr$ with $NOPF_6$: one green[3] and one violet.[4] Both were described as *fac*-$[Mn(CO)_3dpmBr]^+$, but there is only one possible isomer with this formula. Violet *fac*-