Anal. Calcd for $C_{10}H_{23}BO_2$: C, 64.54; H, 12.46; B, 5.80. Found: C, 64.55; H, 12.58; B, 5.88.

Preparation of Diisopropoxy-*tert*-butylborane. The reaction was conducted as described in the general procedure, except that 50 mmol (38.5 mL) of *tert*-butyllithium was added to triisopropoxyborane at –98 °C in a methanol/liquid nitrogen cold bath. Distillation yielded 6.33 g (68%), bp 136–138 °C (754 mmHg), of the *tert*-butylboronic ester: n^{20}_D 1.3898; proton NMR (neat) δ 4.50 (septet, 2 H), 1.15 (d, 12 H), 0.98 (s, 9 H); boron NMR (neat) +29.5 ppm (s). Anal. Calcd for $C_{10}H_{23}BO_2$: C, 64.54; H, 12.46; B, 5.80. Found: C, 64.63; H, 12.74; B, 5.94.

Preparation of Diisopropoxyphenylborane. The reaction was carried out as described in the general procedure by using 50 mmol (22.8 mL) of phenyllithium. Distillation of the residue, bp 98–101 °C (9 mmHg), gave an 8.85-g (84% overall) yield of the phenylboronic ester: n^{20}_D 1.4630; proton NMR (neat) δ 7.4 (m, 5 H), 4.6 (septet, 2 H), 1.10 (d, 12 H); boron NMR (neat) +27.7 ppm (s). Anal. Calcd for $C_{12}H_{19}BO_2$: C, 69.94; H, 9.29; B, 5.24. Found: C, 69.91; H, 9.31; B, 5.32.

Preparation of Diisopropoxy(dichloromethyl)borane. The procedure according to Rathke[22] was used in the preparation of dichloromethyllithium and was reacted with 50 mmol of triisopropoxyborane at –98 °C. Distillation of the residue, bp 66–68 °C (10 mmHg), gave an 8.91 g (84%) overall yield of the dichloromethylboronic ester: n^{20}_D 1.4180; proton NMR (neat) δ 5.25

(s, 1 H); 4.7 (septet, 2 H), 1.15 (d, 12 H); boron NMR (neat) +23.5 ppm (s). Anal. Calcd for $C_7H_{15}BCl_2O_2$: C, 39.49; H, 7.10; Cl, 33.30; B, 5.08. Found: C, 39.67; H, 7.26; Cl, 33.10; B, 4.90.

Molecular Orbital Study of Bonding, Structure, and Substitution Reactions of Bis(borabenzene)iron

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We carried out nonparametrized molecular orbital calculations on borabenzene anion ($C_5H_6B^-$, designated BBz⁻) and on its "sandwich" complexes (BBz)₂Fe and (BBz)₂Co. The π electrons in BBz⁻ are delocalized. The main bonding interactions between the transition-metal atom and the BBz⁻ ring are similar to those in metallocenes and bis(arene) complexes, namely, π donation from the ring to the metal atom and δ back-donation from the metal atom to the ring. Transition-metal 4p orbitals seem to contribute significantly to the metal–ring bonding. The sequence of the predominantly 3d molecular orbitals in both complexes is the following: $d_\delta(x^2 - y^2, xy) < d_\sigma(z^2) \ll d_{\pi^*}(xz,yz)$. Crystallographic studies have shown that transition-metal atom in borabenzene complexes is closer to the *p*-C atom than to the B atom in the ring. This slippage seems to maximize the important π and δ overlaps between metal and ring orbitals and also to minimize summed energy of those occupied molecular orbitals that are significantly delocalized over the metal atom and the rings. The predicted degree of slippage in (BBz)₂Fe agrees well with the observed slippage in two (BBz)₂Co complexes. Although borabenzene orbitals are polarized, the important Fe–BBz overlaps are practically insensitive to rotation of the rings because iron d_π and d_δ orbitals are not tilted. We cannot predict the optimal conformation of (BBz)₂Fe on the basis of overlaps. But comparison of orbital energies in three conformations points at a small preference for the conformation in which the B atoms are trans to each other. This apparent discrepancy between the criteria of maximum overlap and minimum orbital energy indicates that noncovalent intramolecular interactions can affect conformations. Electrophilic substitution at the α-C atoms of the BBz⁻ ligands appears to be charge controlled. Nucleophilic substitution at the B atoms appears to be frontier controlled and assisted by slippage of the BBz⁻ rings.

Introduction

Various carbocycles form a myriad of π complexes with transition metals, but few heterocycles form such compounds.[1] Several cyclic molecules or ions containing heteroatoms are isoelectronic with cyclopentadiene anion and benzene, and they also form "half-sandwich" and "sandwich" complexes with metals. One such ligand is the borabenzene (or borine) anion $C_5R_5Br'^-$, drawn schemat-

ically in 1. Regardless of the nature of groups R and R', which in our study are H atoms ($C_5H_6B^-$), we will designate this ligand BBz⁻. Borabenzene complexes with transition metals have been known for 12 years, and this knowledge has recently been reviewed.[2–4] Among the most studied such complexes are the (BBz)₂M "sandwiches" (shown in

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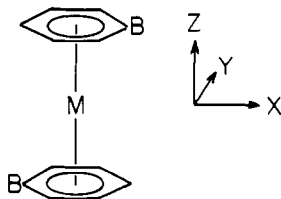(3) Grimes, R. N. *Coord. Chem. Rev.* **1979**, *28*, 47–96.
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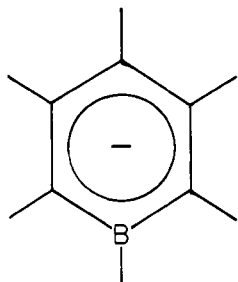
2), particularly bis(borabenzene)iron, $(BBz)_2Fe$.[5-9] Bor-

2

abenzene ligands in it undergo electrophilic substitution at α-C atoms (those adjacent to the B atoms) and nucleophilic substitution at the B atom. The presence of heteroatoms in the ligands permits conformational isomerism, the conformers being converted into one another by rotation of the rings about the axis that connects them to the Fe atom. No experimentally established properties of $(BBz)_2F$ permit conclusions about its actual conformation, so we sought the answer in theory. All crystallographic studies of borabenzene complexes have shown that transition-metal atoms are nearer to the p-C atom than to the B atom in the BBz^- ring; we wanted to learn about the causes of this slippage. Since both reactivity and structure of complexes depend on the nature of metal–ligand bonding in them, we decided to examine properties of $(BBz)_2Fe$ by molecular orbital calculations. We also examined the electronic structure of the paramagnetic compound $(BBz)_2Co$ because its ESR spectrum has been interpreted by invoking two different electron configurations of the Co(II) atom.[10-12] Two recent molecular orbital studies of borabenzene complexes were focused on the nature of the ground states and the electron configurations of the metal atoms in these complexes.[11-13]

This work is a part of our wider study of the nature of bonding in transition-metal π complexes,[14-16] of the conformations of transition-metal compounds,[16-18] and of the

regioselectivity of nucleophilic and electrophilic attacks at organic ligands.[16,19-21]

Details of the Calculations

An approximation of the Hartree–Fock–Roothaan technique, the Fenske–Hall method, has been described elsewhere.[22] The method is devoid of adjustable or empirical parameters, so that results of a calculation (eigenvalues and eigenvectors) are determined completely by molecular geometry and basis functions.

We divided each "sandwich" molecule into two closed-shell fragments, "cleaving" it in a manner that best shows the orbital interactions important for the property under study. To examine slippage of the rings with respect to the Fe atom, we divided a molecule of $(BBz)_2Fe$ into $(BBz^-)_2$ and Fe^{2+} fragments; $(BBz)_2Co$ was partitioned in the same way. To examine rotation of the rings with respect to each other, we divided the molecule into $(BBz)Fe^+$ and BBz^- fragments. We first carried out calculations on the separate fragments and then on the "sandwich" molecule composed of these fragments. After the iterative calculation on the complete "sandwich" molecule would converge with the atomic basis set, the molecular orbitals would be transformed into the basis set of the fragment orbitals. The large fragments themselves were built from "subfragments": $(BBz^-)_2$ from two BBz^- rings and $(BBz)_2Fe^+$ from a BBz^- ring and an Fe^{2+} ion. The redistribution of electrons between the fragments to make them closed shells and the transformation of basis set do not affect numerical results of the calculations but render them easier to interpret.

In the computation of diagonal and off-diagonal elements in the Fock matrices, the small but discernible effects of the intramolecular electrostatic interactions are taken into account.[22] This means that energies of the fragment orbitals reflect influences of the molecular environment upon the fragments "ready for bonding" and that energies of the molecular orbitals depend somewhat upon the overall distribution of charges in the molecule. These features of the method add to its usefulness for conformational studies of large molecules with low symmetry. We estimated relative stabilities of different structures by comparing summed eigenvalues (energies) of those occupied molecular orbitals in them that are affected by the motion of fragments with respect to each other.

The basis functions were the same as in our previous studies.[19-21] The interatomic distances and angles in the fragments and complete molecules were taken from the crystallographic data for $(C_5H_5BCH_3)_2Co$.[23] The metal atom occupied the origin of the right-hand coordinate system, and the BBz^- rings lay in the positive and negative z directions, as drawing 2 shows.

Borabenzene Ligand. We will discuss electronic structure of $C_5H_6B^-$ anion by comparing it with the isoelectronic molecule of benzene, whose orbitals are well-known. It is the π orbitals in the unsaturated ligands that are chiefly responsible for bonding with metal atoms. We will emphasize the effect of replacement of a carbon atom by a boron atom upon these π orbitals.[24,25]

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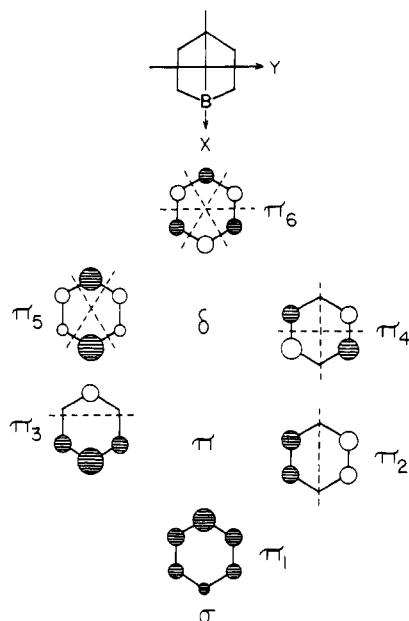(21) Kostić, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974–982.

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Table I. Energies and Percent Compositions of the Important MO's in $(C_5H_6B)Fe^+$

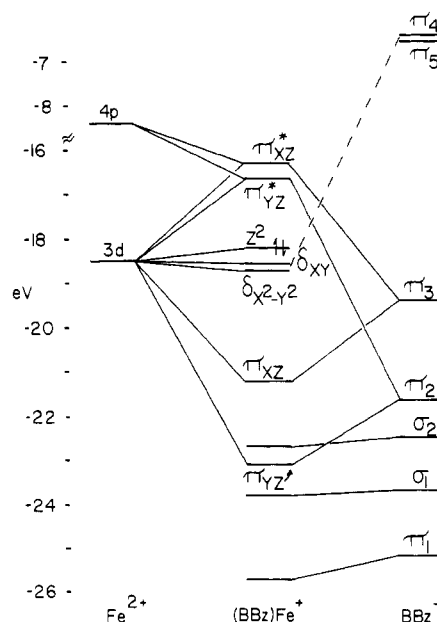| ε, eV	Fe							BBz					
	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	d_{xz}	d_{yz}	4s	4p	π_1	σ_1,σ_2	π_2	π_3	π_4	π_5
−16.31				63			14				19		
−16.65 (LUMO)					75		10			13			
−18.19 (HOMO)	96												
−18.55			88							6			5
−18.70		88								2		5	
−21.22				22			3				65		
−22.67			6							91			
−23.09					17		4				73		
−23.78		2								92			
−25.76						5	3	86					

Figure 1. The most important π orbitals of borabenzene anion, $C_5H_6B^-$, designated according to their bonding abilities (σ, π, or δ) toward d orbitals of transition metals.

The most important molecular oribtals of BBz⁻ are depicted schematically in Figure 1 and designated π_1 through π_6. Clearly, the following resemblances exist between the borabenzene and benzene orbitals: π_1 corresponds to a_{2u}, π_2 and π_3 to e_{1g}, π_4 and π_5 to e_{2u}, and π_6 to b_{2g}. Substitution of a B atom for a C atom perturbs benzene orbitals in two ways: lifts degeneracies and causes polarizations. Since C_{2v} symmetry of BBz⁻ does not permit degeneracy, the "e levels" become split in this molecule. Boron is less electronegative than carbon, so that orbital π_3, which is partly localized on the B atom, lies about 2 eV above orbital π_2, which has a node at the B atom. Polarization, caused by the difference in electronegativities, is evident in orbitals π_1 and π_3. The completely bonding orbital π_1 is polarized toward the C_3 side of the ring, whereas the partly antibonding orbital π_3 is polarized toward the BC_2 side. Our calculations agree with the conclusions from the ion cyclotron resonance[26] and NMR[27] spectra, namely, that π electrons in the BBz⁻ anion are delocalized over the whole ring.

At energies between π_1 and π_2 lie two σ-type orbitals of the ring, designated σ_1 and σ_2, both of them with sizeable contributions from the boron p orbitals. Since B is less electronegative than C, these σ orbitals have higher en-

Table II. Iron–Borabenzene Overlaps in $(C_5H_6B)Fe^+$

BBz	Fe				
	$d_{x^2-y^2}$	d_{xy}	d_{xz}	d_{yz}	4s
π_1					0.388
π_2				0.122	
π_3			0.110		
π_4	0.110				
π_5		0.103			

Figure 2. The most important interactions between the iron and borabenzene orbitals in $(C_5H_6B)Fe^+$. Orbital designated z^2 is the HOMO. The dashed line represents minor contribution.

ergies than do corresponding σ orbitals of benzene.[11,12]

The orbitals in the $(BBz^-)_2$ fragment are simply sums and differences of the corresponding orbitals in the BBz⁻ rings. We combined the two ligands into a single fragment because this enables us to examine a molecule of $(BBz)_2M$ in terms of just two fragments, which simplifies the analysis of orbital interactions.

Iron–Borabenzene Bonding in (BBz)Fe⁺. From the preceding discussion of orbitals in BBz⁻ ring and from Figure 1, it is clear how this ligand can bind to a transition-metal atom. One can expect three main kinds of interactions. With the coordinate system shown in **2** as a reference, they can be identified as follows: σ donation from the ligand π_1 orbital into the vacant $4s-4p_z$ hybrid of the metal; π donation from the π_2 and π_3 orbitals into the formally vacant $3d_{xz}$ and $3d_{yz}$ orbitals of the Fe^{2+} ion; and δ back-donation from the filled $3d_{x^2-y^2}$ and $3d_{xy}$ orbitals of the metal into the vacant π_4 and π_5 orbitals of the BBz⁻ ligand. Orbital π_6 does not have a counterpart of appropriate symmetry in an atom of a 3d transition metal; even

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Table III. Populations (in Electrons) of the Important
Orbitals of Iron and Borabenzene in $(C_5H_6B)Fe^+$

Fe		BBz	
orbital	pop.	orbital	pop.
$3d\, z^2$	1.97	π_1	1.81
$x^2 - y^2$	1.87	π_2	1.52
xy	1.88	π_3	1.35
xz	0.66	π_4	0.12
yz	0.43	π_5	0.12
4s	0.13		
4p x	0.09		
y	0.11		
z 0.06	0.11		

if a metal atom had the needed orbital (e.g., an f orbital), the resulting interaction would be weak because π_6 has very high energy.

The expected σ, π, and δ interactions are evident in Figure 2 and in the accompanying Tables I and II. The transfers of electrons resulting from these interactions can be estimated from the data in Table III. The qualitative features of metal–ring bonding are very similar to those found in metallocenes and bis(arene) complexes of transition metals[11] and in phosphaferrocenes.[16] The extent of these interactions deserve some comment.

Despite the sizeable overlaps of π_1 with the 4s and $4p_z$ orbitals of iron, the corresponding σ interaction is weak because the energy gap between the iron and borabenzene orbitals is wide. Figure 2 shows that stabilization of π_1 is small; Table III shows that donation from π_1 to 4s and $4p_z$ orbitals is also small. The overlap between π_1 and d_{z^2} is negligible because lobes of π_1 largely coincide with the conical nodal surface of d_{z^2}; this has been found in other π complexes as well.[11] The polarization of π_1 gives this orbital some π character, but its interaction with d_{xz} is negligible. Orbitals σ_1 and σ_2 of the BBz$^-$ ring interact very weakly with the iron orbitals and remain practically filled and nonbonding with respect to the metal atom.

The prinicipal covalent bonding between Fe^{2+} and BBz$^-$ occurs through π interactions between π_2 and d_{yz} and between π_3 and d_{xz}. The corresponding pairs of filled and empty molecular orbitals are evident in Figure 2. Although π_2 overlaps with d_{yz} better than π_3 does with d_{xz} (see Table II), the former two oribtals mix with each other somewhat less than the latter two orbitals do (see Table I) because the energy gap between π_2 and d set is wider then the gap between π_3 and d set (see Figure 2). The difference between these two π interactions is evident in Table III; electron donation from π_2 to d_{yz} is smaller than from π_3 to d_{xz}.

As Table I shows, the LUMO (π^*_{yz}) and the next vacant molecular orbital (π^*_{xz}) have contributions from the iron $4p_y$ and $4p_x$ orbitals, respectively. This partial p character in the predominantly d orbitals can be viewed as "3d–4p hybridization" of the iron orbitals that interact with the borabenzene orbitals π_2 and π_3. Orbitals π^*_{yz} and π^*_{xz} of $(BBz)Fe^+$ are depicted schematically in **3** and **4**, respectively. They are essential for bonding of this fragment to another BBz$^-$ ring in the complete "sandwich" molecule.
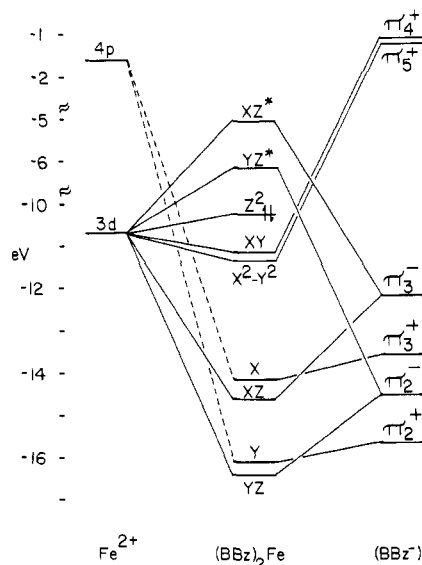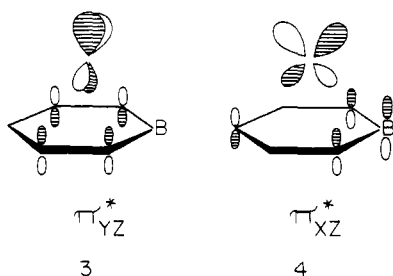
Figure 3. The most important π and δ interactions between the iron and bis(borabenzene) orbitals in *trans*-$(C_5H_6B)_2Fe$. Orbital designated z^2 is the HOMO. Dashed lines represent minor contributions.

The three highest occupied molecular orbitals are almost nonbonding between the metal and the ring. Orbitals d_{xy} and $d_{x^2-y^2}$ overlap appreciably with the high-lying orbitals π_4 and π_5, respectively (see Table II), but the resulting attractive δ interactions in the molecular orbitals $\delta_{x^2-y^2}$ and δ_{xy} are weak (see Tables I and III) and the stabilization of the d_δ orbitals is small (see Figure 2) because the energy gap is wide. Orbital d_{z^2} is destablized slightly by weak, repulsive σ interactions with low-lying, filled orbitals of the ring.

The iron d orbitals of π type (d_{xz} and d_{yz}) do not mix with the d orbitals of δ type ($d_{x^2-y^2}$ and d_{xy}). In this respect, $(BBz)Fe^+$ is similar to $(C_6H_6)M$ fragments and different from $M(CO)_3$ fragments.[28-30] The π–δ mixing in $M(CO)_3$ causes asymmetry or tilting of its uppermost filled molecular orbitals, a feature that profoundly affects conformations of complexes containing $M(CO)_3$ fragments.[29-33] In the absence of π–δ mixing, the frontier orbitals ($\delta_{x^2-y^2}$, δ_{xy}, π^*_{yz}, and π^*_{xz}) of $(BBz)Fe^+$ are not tilted. In particular, its LUMO (π^*_{yz}) lies in the yz plane and the next vacant molecular orbital (π^*_{xz}) lies in the xz plane. This is important for conformations of $(BBz)_2Fe$, which are discussed in a later section.

Structure of $(BBz)_2Fe$. Bonding of iron with two borabenzene rings in $(BBz)_2Fe$ is quite similar to its bonding with one ring in $(BBz)Fe^+$. This similarity is obvious upon comparison of Figures 2 and 3. The sequence of predominantly 3d molecular orbitals in both species is the following: $x^2 - y^2 \lesssim xy < z^2 \ll yz \lesssim xz$. It agrees with the ordering of one-electron orbitals calculated by an INDO method.[12]

The "sandwich" molecule can be viewed as consisting from an Fe^{2+} ion and a $(BBz^-)_2$ fragment. The corresponding orbitals of the two rings can be combined in phase (superscript "+") or out of phase (superscript "–").

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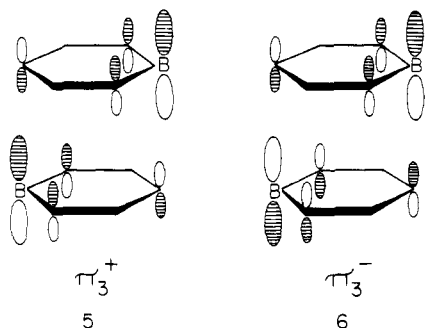
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For example, these two combinations of the π_3 orbitals are shown schematically in **5** and **6**. The symmetries of these
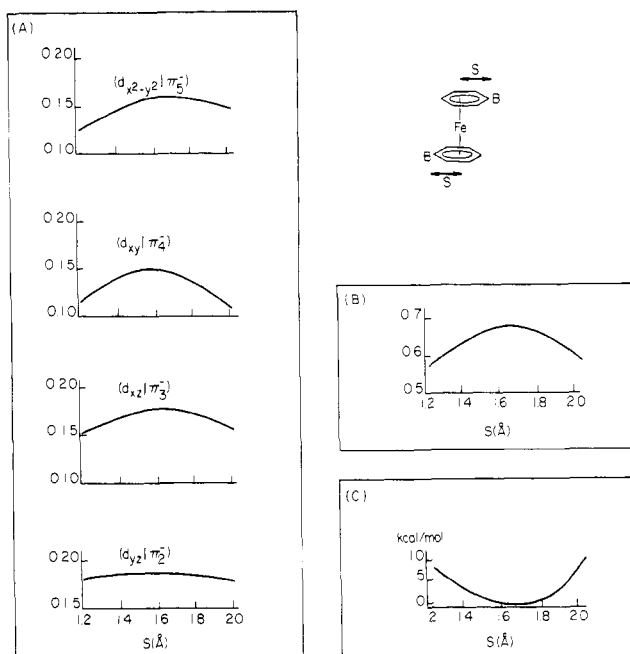

fragment orbitals are such that π_3^+ (and π_2^+) can interact with the iron 4p orbitals, whereas π_3^- (and π_2^-) can interact with its 3d orbitals; both these Fe–(BBz)₂ interactions are of π type. Fragment orbitals π_4^+ and π_5^+ have proper symmetry for δ interactions with orbitals d_{xy} and $d_{x^2-y^2}$, respectively. Only the π and δ interactions are shown in Figure 3. The (BBz⁻)₂ orbitals arising from the ring orbitals π_1, σ_1, and σ_2 and the corresponding molecular orbitals of the "sandwich" complex are omitted from the diagram because they contribute little to the metal–ligand bonding.

All crystallographic studies of borabenzene complexes have shown that the metal atom is nearer to the p-C atom than to the B atom of the ring.[3,23] Such slippage is found in several other kinds of π complexes as well.[15,34-37] We examined both slippage and rotation of the rings in (BBz)₂Fe. The three kinds of conformational isomers are shown in **7**, **8**, and **9**; structures are designated according
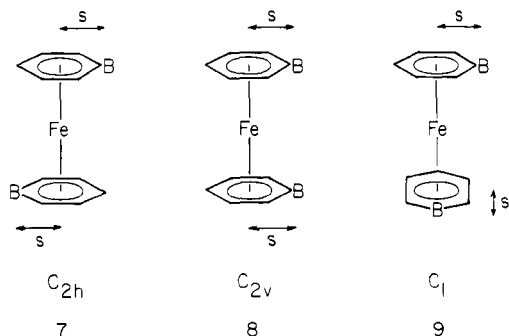
to their idealized symmetry. The degree of slippage is measured by distance S between the B atom and the projection of the Fe atom on the ligand plane; when $S = 1.45$ Å, the Fe atom is equidistant from the B and p-C atoms. We examined all three rotamers with various degrees of slippage, keeping S the same for both rings.

Slippage of the Borabenzene Rings. From the preceding discussions it is clear that four covalent interactions are chiefly responsible for iron–borabenzene bonding. These are π donation from π_2 and π_3 into d_π orbitals and δ back-donation from $d\delta$ into δ_4 and π_5 orbitals. In Figure 4a we present calculated overlaps for all these interactions in the C_{2h} rotamer (structure **7**) for various degrees of slippage, S. The shapes of these four curves can be understood by referring to the shapes of the BBz⁻ orbitals, shown in Figure 1. As the Fe atom approaches either the

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Figure 4. Slippage of the borabenzene rings in *trans*-(C₅H₆B)₂Fe. One scale of values S belongs to part a and the other such scale to parts b and c: (a) the four most important π and δ overlaps between the iron and bis(borabenzene) orbitals; (b) sum of the most important π and δ overlaps; (c) summed energy of the nine uppermost filled molecular orbitals.

B or the p-C atom of the ring, the overlaps of its d orbitals with the corresponding ligand orbitals decrease. The curve for the d_{yz}–π_2^- interaction is less concave than the curve for the d_{xz}–π_3^- interaction because the Fe atom slides in the nodal plane of π_2 but is perpendicular to the nodal plane of π_3. Overlap between d_{xy} and π_4^- is the most sensitive to slippage apparently because orbital π_4^- (analogous to π_4) has a nodal plane perpendicular to the direction of slippage, as well as one (through the B and p-C atoms) in the direction of slippage. Overlaps between the iron 4p orbitals and the in-phase ("+") combinations of the ring orbitals show similar variations, but these interactions are weaker than the interactions whose overlaps are shown in Figure 4a because the 4p level has relatively high energy. Nevertheless, 4p orbitals do contribute to metal–ligand bonding, as Figures 2 and 3 and Table I show.

The sum of four important overlaps involving iron d orbitals reaches a maximum for $S = 1.6$ Å, as Figure 4b shows. The total energy (sum of eigenvalues) of the nine uppermost filled molecular orbitals, among them all those that correspond to the important overlaps, reaches a minimum for the same degree of slippage, as Figure 4c shows. The criteria of maximum overlap and of minimum orbital energy both lead to the same prediction of slippage in the C_{2h} (**7**) and C_{2v} (**8**) rotamers of (BBz)₂Fe, namely, that S should be about 1.60 Å in each of them. The values found in two (BBz)₂Co "sandwiches" with different substituents at the B atoms are close to the predicted value: 1.59 and 1.64 Å.[23] However, this agreement between the calculated structure of (BBz)₂Fe and the observed structure of (BBz)₂Co should not be overemphasized because the Co compound contains an additional electron in the yz^* molecular orbital.

Rotation of the Borabenzene Rings. Rotamers **7**, **8**, and **9** of (BBz)₂Fe are best compared with one another by considering rotation of a BBz⁻ ring with respect to the (BBz)Fe⁺ fragment. Having examined bonding abilities of both these units, we are now prepared to consider how their mutual position affects their interactions.

Table IV. Overlaps in the Principal π and δ Interactions between $(C_5H_6B)Fe^+$ and $C_5H_6B^-$ in Three Conformations of $(C_5H_6B)_2Fe$

(BBz)Fe⁺	trans (C_{2h})				cis (C_{2v})				general (C_1)			
	π_2	π_3	π_4	π_5	π_2	π_3	π_4	π_5	π_2	π_3	π_4	π_5
π^*_{xz}		0.247				0.256			0.259			
π^*_{yz}	0.239				0.239					0.230		
δ_{xy}				0.100				0.099				0.098
$\delta_{x^2-y^2}$			0.110				0.119				0.106	

The weak σ interaction between π_1 and an 4s–4p$_z$ hybrid of Fe is practically insensitive to rotation because the corresponding molecular orbital is nearly cylindrical. It is the π and δ interactions that in principle are affected by intramolecular roation, and we will discuss them in some detail.

As Table I shows, the vacant orbitals π^*_{yz} and π^*_{xz} differ slightly in their compositions. Since π^*_{xz} has slightly more 4p character than π^*_{yz} does, π^*_{xz} overlaps slightly better than π^*_{yz} with a given orbital (π_2 or π_3) of the BBz⁻ ring. As Figure 1 shows, the borabenzene orbitals π_2 and π_3 also have somewhat different compositions. Since π_2 is more symmetrical than π_3, π_2 overlaps slightly better than π_3 with a given orbital (π^*_{yz} or π^*_{xz}) of the (BBz)Fe⁺ fragment. In conformations 7 and 8, the mirror planes of the individual BBz⁻ rings coincide with each other, so that the pairs of interacting orbitals in both conformations are the same: π^*_{yz} with π_2 and π^*_{xz} with π_3. In the conformation 9 the mirror planes of the rings are perpendicular to each other, so that π^*_{yz} interacts with π_3 and π^*_{xz} with π_2. The δ interactions involve the same orbital pairs in all three conformations: d_{xy} with π_4 and $d_{x^2-y^2}$ with π_5. All these π and δ overlaps are listed in Table IV. Although orbital π_3 is very polarized and other borabenzene orbitals are somewhat polarized, their overlaps with the (BBz)Fe⁺ orbitals in the trans conformation 7 differ only slightly from these overlaps in the cis conformation 8. This is so because the frontier orbitals ($\delta_{x^2-y^2}$, δ_{xy}, π^*_{yz}, and π^*_{xz}) of (BBz)Fe⁺ are not tilted; we already explained this absence of tilt. In the conformation designated C_1 (9), one π overlap (π^*_{xz}–π_2) is maximized and the other (π^*_{yz}–π_3) is minimized, as Table IV shows.

From the comparisons of *overlaps* in Table IV we conclude that $(BBz)_2Fe$ does not greatly prefer any of the three conformations, but one may expect the cis structure 8 to be slightly more stable than the other two. In contrast, summed *energies* of the important molecular orbitals in the three conformations indicate that $(BBz)_2Fe$ has a small preference for the trans structure 7 and that the other two conformations have nearly the same energies, about 8 kcal mol⁻¹ above that of the trans structure. Although the similarity between the conformations of $(BBz)_2Fe$ and $(BBz)_2Co$ is not necessarily the proof of the correctness of these calculations, we note that two $(BBz)_2Co$ "sandwiches" whose structures are known indeed adopt the trans conformation 7 in their crystals.[23] The NMR spectra of several $(BBz)_2Fe$ "sandwiches"[6,9] do not permit conclusions about conformations because the spectra were recorded at one temperature and because the two ligands in each "sandwich" were equally substituted. To study conformations of $(BBz)_2M$ complexes by variable-temperature NMR spectroscopy, one would have to chose carefully the nature and positions of the substituents in the borabenzene rings.

In our earlier studies of transition-metal carbene,[17] carbyne,[17] and vinyl[21] complexes we noticed that, in the absence of steric crowding, the optimal orientations of the ligands with respect to the metal fragments are those that

minimize orbital energies and not necessarily maximize attractive overlaps in the dominant metal–ligand interactions. In this study we find that $(BBz)_2Fe$ apparently prefers the conformation for which the overlaps in the attractive metal–ligand π interactions seem not to attain their very maxima. This apparent discrepancy between the criteria of maximum overlap and minimum orbital energy points at the importance of noncovalent intramolecular interactions, some of which are taken into account in our calculations (vide supra). These forces are neither specific nor directional, and the small preference for the trans conformation cannot be attributed to any particular interaction. The centrosymmetric distribution of charges would make the structure 7 nonpolar as a whole, which may be its advantage over structures 8 and 9. Intermolecular interactions, caused by packing in crystals or solvation in solutions, may also affect conformational preferences; they may even dictate conformations of compounds whose intramolecular interactions change little from one molecule to another.

Electronic Structure of $(BBz)_2Co$. This paramagnetic molecule has 19 valence electrons, so that the formal oxidation state of Co is +2 and its formal configuration d⁷. Our calculations show that the nature and sequence of its moleucular orbitals are quite similar to those for diamagnetic $(BBz)_2Fe$, shown in Figure 3. The unpaired electron occupies the π-antibonding combination of d_{yz} with π_2⁻, whose predominant character is d_{yz}. The lowest unoccupied molecular orbital is a π-antibonding combination of d_{xz} with π_3⁻, mainly d_{xz} in character. The energy gap between these two molecular orbitals is small, about 0.6 eV. These finding agree with the results from INDO calculations[11,12] to show that molecular orbitals of $(BBz)_2M$ corresponding to the e_1 level of metallocenes or bis(arene) complexes are split little; this splitting is not large enough to cause the lower of the two "e_1" orbitals to become lower in energy than the d_{z^2} orbital.[10] The similarity between the sequences of molecular orbitals in $(BBz)_2Fe$ and $(BBz)_2Co$ justifies qualitative use of molecular orbital diagrams in predicting electronic structures of oxidized and reduced forms of a molecule or ion for which a calculation has been carried out.

Reactivity of Borabenzene Ligand. Little is known about reactions of borabenzene ligands in "sandwich" complexes. The rings in $(BBz)_2Fe$ undergo electrophilic substitution (proton exchange and acetylation) at the α-C atoms[5-7] and nucleophilic substitution (displacement of hydride by carbanion) at the B atom.[5] To the extent that these reactions are kinetically controlled, their regioselectivity should depend upon the electronic structure of the "sandwich" molecule.

Most theorists agree that atomic charges calculated by Mulliken population analysis may not be true in the absolute sense but that their qualitative pattern in a given molecule is realistic.[38] The calculations on $(BBz)_2Fe$ show

(38) Schaefer, H. F. "The Electronic Structure of Atoms and Molecules"; Addison-Wesley: Reading, MA, 1972; p 384.

that α-C is the most negative carbon atom, more negative than β-C and γ-C atoms, in accord with the classical view of resonance structure for borabenzene anion. This might explain why α-C is much more reactive than β-C or γ-C atoms toward electrophiles. The electrophilic substitutions seem to be charge controlled. Others[39,40] and we[16,21] have suggested that electrophilic attacks at some other organometallic compounds as well are essentially charge controlled.

Others[40–43] and we[19–21] have also suggested that nucleophilic attacks at various organometallic complexes are frontier controlled. This notion has recently been extended by a proposal that coordinated olefin is activated toward nucleophilic attack by slippage of the metal fragment attached to it.[44] Our calculations on (BBz)$_2$Fe indicate that nucleophilic attack at boron may well be assisted by slippage of the borabenzene ring. Drawings 10 and 11 shown schematically the composition of the vacant molecular

$s = 1.4$ Å $s = 2.0$ Å

10   11
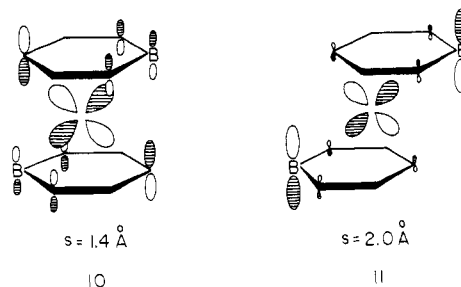
orbital designated xz^* in *trans*-(BBz)$_2$Fe when the Fe atom is nearly above the center of each ring ($S = 1.4$ Å) and when it is much nearer to the p-C than to the B atom ($S = 2.0$ Å). As the BBz$^-$ rings slip and the B atoms get farther from the Fe atom, the lobes of this frontier orbital decline at the p-C atoms and grow at the B atoms. According to our calculations (see Figure 4c), the high-lying, filled molecular orbitals of (BBz)$_2$Fe would be raised in energy by a total of about 10 kcal mol^{-1} as the rings slip from 10 to 11. Since this gain in energy is rather small, the substrate molecule is likely to "afford" it in the course of its reaction with an incoming nucleophile.

Registry No. (BBz)Fe$^+$, 86563-66-8; BB$_z^-$, 55926-39-1; (BB$_Z$)$_2$Fe, 68344-23-0; (BB$_Z$)$_2$Co, 68378-62-1.

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Amphoteric Ligands. 4. Reactions of HMn(CO)₅ with (Aluminoamino)phosphine Ligands. Structure of (CO)₃Mn[CHOAl(CH₃)₂N(C(CH₃)₃)P(C₆H₅)₂]⁻ [P(C₆H₅)₂N(C(CH₃)₃)Al(HCH₂)(CH₃)]

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The amphoteric ligands Ph$_2$PN-*t*-BuAlR$_2$ (**1a**, R = Et; **1b**, R = Me) react with HMn(CO)$_5$ to give (CO)$_4$Mn(CHOAlR$_2$N-*t*-BuPPh$_2$) (**2**), a product resulting from net migration of hydrogen from Mn to CO. However, NMR studies indicate that direct migration is not occurring. Instead, proton transfer from Mn to P is the initial process observed. From the reaction of CpMo(CO)$_3$H with **1b** it is possible to isolate an analogue to the proposed proton-transfer intermediate [CpMo(CO)$_3$][AlMe$_2$N-*t*-BuPPh$_2$H]. Complexes **2** react with a second equivalent of **1**; for R = Me the product was characterized by X-ray crystallography as

(CO)₃Mn(CHOAlMe₂N-*t*-BuPPh₂)(PPh₂N-*t*-BuAl(HCH₂)(CH₃))
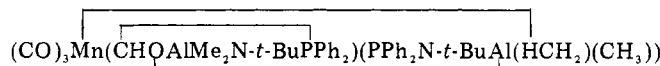
in which a C–H bond from an Al–Me group is acting as one of the ligands to Mn. Crystal data: orthorhombic; space group *Pbca*; $a = 18.063$ (7) Å, $b = 18.446$ (8) Å, $c = 25.003$ (7) Å; $Z = 8$; final $R = 0.053$ for 1808 reflections used.

Introduction

Migration step 1 has been widely considered a key element in homogeneous hydrogenation of carbon monoxide.[1]

(1)
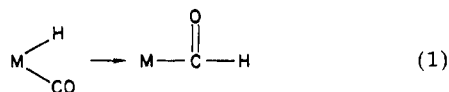
However, unequivocal evidence for this transformation in model studies has proven elusive. The intermediacy of a

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