Theoretical Study of the Nature of the (η^5-Cyclopentadienyl)dicarbonyliron–Arene Bond. Significance of the π Interaction

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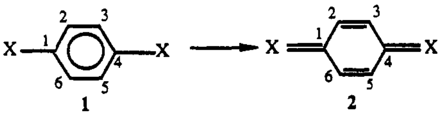
The substituent–arene orbital interactions in 1,4-$C_6H_4Fp_2$, where Fp = (η^5-C_5H_5)Fe$(CO)_2$, are compared with the interactions in the series $C_6H_4X_2$, X = BH_2, NH_2, CH_2 and O, by using unparameterized Fenske–Hall molecular orbital calculations. Analysis of the MOs, the Mulliken populations of the fragments, and the overlap populations provides an understanding of the extent and nature of the relative σ and π interactions between the arene and the various substituents. In our fragment analysis the interactions of the main-group fragments are compared easily with the interactions of the transition-metal fragment. Although it has been suggested that 1,4-$C_6H_4Fp_2$ has a significant contribution from a quinone-like resonance structure, our study of the bonding reveals very little π character in the Fe–arene bonds.

Introduction

In recent work Hunter and co-workers describe organometallic complexes such as 1,4-$C_6H_4Fp_2$ and (η^6-1,4-$C_6H_4Fp_2$)Cr$(CO)_3$ where Fp = (η^5-C_5H_5)Fe$(CO)_2$ as having contributions from both phenylene, 1, and quinone, 2, like resonance structures.[1-7] The phenylene form results in similar bond order between all the carbons in the arene and single bonds between the arene and the substituent. Contribution from 2 suggests partial double bonds between the ipso carbon on benzene and X (X = Fp for the complex above) as well as weaker bonds between carbon atoms one and two and stronger bonds between carbon atoms two and three.



Hunter suggests that several experimental observations including bond lengths, ^{13}C NMR spectra, IR spectra, and electrochemical studies[1] support the importance of a contribution from quinoidal-type resonance for X = Fp. The length of Fe–C(sp^2) bonds averages 2.015 Å in (η^6-1,3,5-$C_6H_3Fp_3$)Cr$(CO)_3$.[4,6] As Hunter points out, this value is typical of formal single bonds in many Fe–C(sp^2) complexes (1.94–2.03 Å) but also approaches the length of double Fe–C(sp^2) bonds in some cationic carbene complexes (1.91–2.00 Å).[8]

The NMR data show a ^{13}C shift for the ipso carbon in 1,4-$C_6H_4Fp_2$ about 5 ppm smaller than expected. If this is due to an increase in the para substituent constant from −6 to −11,[3] synergic conjugation produces a quinoidal contribution to the bonding interaction,[9] indicating a π-donor is opposite to a π-acceptor. But changes in total electron density due to Fp may sensitize the ipso carbon, causing anomalous chemical shifts. The $^1J_{CH}$ coupling constant in 1,4-$C_6H_4(Fp)_2$ of 154 Hz[3] is at the low end of the range typical for a double C–C bond (156–187 Hz)[9] while $^1J_{CH}$ = 173.2 Hz for (η^6-1,4-$C_6H_4Fp_2$)Cr$(CO)_3$. However, citing this as direct evidence for double bond character between carbons two and three and indirect evidence for double bond character in the Fe–C bond ignores the possibility of σ donation alone shifting charge to the ipso carbon from the iron.

The difference in the decrease observed in the carbonyl stretching frequencies, 2014 cm^{-1} for 1,4-$C_6H_4Fp_2$ and 2030 cm^{-1} for (η^6-1,4-$C_6H_4Fp_2$)Cr$(CO)_3$, is cited as evidence for the transfer of electron density from Fp to Cr in (η^6-1,4-$C_6H_4Fp_2$)Cr$(CO)_3$. However, σ bonds alone may transfer sufficient density. Hunter's investigation of the stretching frequencies of related compounds in which H in the arene was replaced by F or Cl showed that the replacement of Cl with F produced a further decrease in the CO stretching frequency.[7] Thus, removing electron density from a σ bonding orbital must have decreased the bond order and caused the lower frequency.

Electrochemical experiments on (η^6-1,4-$C_6H_4Fp_2$)Cr$(CO)_3$ and similar complexes give evidence that electron density is transferred from Fe to Cr. This evidence suggests that an electron is being removed from a HOMO which has significant Cr character[1] and indicates that Cr withdraws electron density but does not give conclusive evidence for dimetalloquinone character in 1,4-$C_6H_4Fp_2$. Again, σ donation alone may transfer the electron density.

Quantum mechanical calculations in this paper determine whether significant contribution from a quinoidal resonance form for 1,4-$C_6H_4Fp_2$ exists. The specific effect on the bonding in the molecular orbitals and the π-donor/π-acceptor properties are considered. In order to determine the importance of these contributions, a series of molecular orbital calculations were performed on para-substituted benzenes with X = BH_2 (π-acceptor), X =

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NH_2 (π-donor), X = CH_2 and O (both π-acceptors and π-donors), and X = Fp. Comparison of bonding in the simpler main-group substituents with the transition metal provides a basis for explaining the bonding of Fp to the benzene ring.

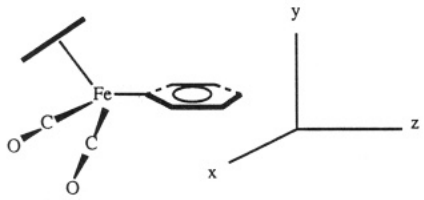
Methods

The Fenske–Hall[10] program was used to perform parameter-free approximate molecular orbital calculations on 1,4-$C_6H_4X_2$ where X = NH_2, CH_2, BH_2, O, and Fp using the Department of Chemistry's VAX11/780 computer.

The results on these $C_6H_4X_2$ molecules were expressed in the molecular orbitals of the fragments C_6H_4 and X. The basis sets were based on the numerical Xα atomic orbital program written by Herman and Skillman[11] together with the Xα-to-Slater basis program written by Bursten and Fenske.[12] Nontransition-metal atoms assumed ground-state atomic configurations, while a d^7s^0 cationic configuration was used for Fe. The exponents for the valence s and p orbitals of Fe were interpolated from values that minimized the difference between the experimental and theoretical ionization energies. The principal valence orbitals (d for Fe and p for the other atoms) were fit to the double-ζ analytical Slater type orbitals using the numerical Xα atomic orbitals. Single-ζ functions represent all the other orbitals, and 1.20 was the orbital exponent used for hydrogen.

Gross populations and overlap populations and individual atomic charges were determined by Mulliken's method of population analysis,[13] which is incorporated into the Fenske–Hall program.

In the calculations, the geometry of the fragment substituents was idealized to C_{2v} for all X except for Fp, where the symmetry was C_s. The combination of the three molecular fragments as X + C_6H_4 + X → $C_6H_4X_2$ resulted in D_{2h} symmetry except where X = Fp. For this case, the symmetry was C_{2h}. Consistent with experimental data,[2,4,6] the orientation chosen for the calculation of X = Fp was such that the mirror plane of the Fp was perpendicular to the C_6H_4, **3**, plane. Average bond lengths were taken from an experimentally determined geometry.[6] The bond lengths for X = CH_2 and BH_2 were estimated from similar compounds,[14a] while those for X = NH_2 and O were taken from experimental data.[14] All C–C bond lengths in the $C_6H_4X_2$ ring were equal to those of free benzene, so that a comparison of Mulliken populations would reflect the electronic effect of X only.



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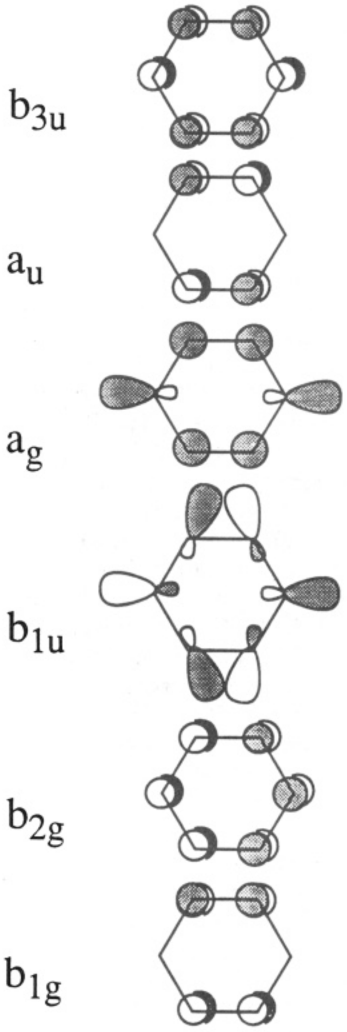
Results and Discussion

Arene and Substituent Fragment Orbitals. The important valence molecular orbitals of the C_6H_4 fragment are depicted in **4**. The lowest energy orbitals, b_{2g} and b_{1g}, are derived from the highest filled π orbitals of benzene (e_{1g} in D_{6h}). They are doubly occupied and have one node perpendicular to the plane of the molecule. When the one and four substituents are π-acceptors, they accept π electron density from b_{2g}, which is antibonding between carbons 2 and 3. This transfer lessens the antibonding between carbons 2 and 3 and increases the bond strength between them.

The next two orbitals in **4**, b_{1u} and a_g, are σ orbitals which are the out-of-phase and in-phase combinations of the singly occupied carbon sp orbitals. Electron density changes in these orbitals reflect σ donation or acceptance of X in $C_6H_4X_2$.



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The highest energy orbitals in **4**, a_u and b_{3u}, are derived from the empty π^* orbitals of benzene (e_{2u} in D_{6h}). These each have two nodes perpendicular to the plane of the molecule. When the one and four substituents are π-donors, they donate electron density to b_{3u}, which is bonding between carbons 2 and 3. This transfer also increases the bond strength between carbons 2 and 3.

Among the simplest substituents which have donor and acceptor character are the fragments AH_2 where A = B, N, and C. The symmetry-adapted fragment molecular orbitals (FMOs) of the substituents labeled according to D_{2h} symmetry are depicted in **5**. For the substituent AH_2 each H is bonded to A by a two-electron σ bond. These

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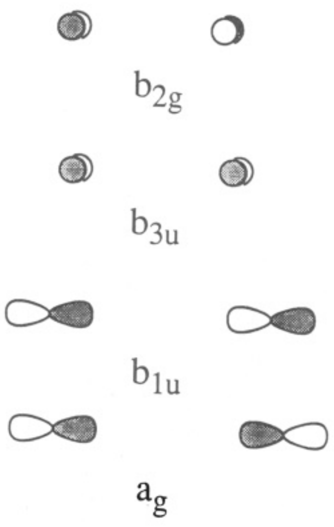

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substituents have singly occupied a_g and b_{1u} σ orbitals which are either σ-acceptors or σ-donors depending on the electronegativity of A. The π orbitals, b_{3u} and b_{2g}, have zero, one, or two electrons for BH_2, CH_2, or NH_2, respectively. Thus BH_2 will be a strong π-acceptor, and NH_2 will be a strong π-donor. CH_2 will both accept electron density from the filled b_{2g} in C_6H_4 and donate electron density to the empty b_{3u} in C_6H_4.

π-Acceptor. The combination of 4 and 5 yields Figure 1 for X = BH_2. The orbital energies of C_6H_4 compose the left side of the MO diagram, while the orbital energies of the substituents compose the right side of the MO diagram. (Not all of the MOs for $C_6H_4X_2$ appear in the figure; only those frontier orbitals resulting from the interaction of the orbitals of 4 and 5 are shown.) The Mulliken population for each FMO is shown beneath the orbital and is the total amount of electron density that each FMO has after interaction with the FMOs in the other fragment. The changes in Mulliken populations of the π and σ orbitals give the amount of π and σ donation or acceptance which takes place when fragments join to make a molecule. The empty b_{2g} orbital of BH_2 increases in population as it accepts density from the filled b_{2g} orbital in C_6H_4 whose population decreases. These orbitals interact to form an orbital directly above the LUMO and an orbital directly below the second highest occupied molecular orbital (SHOMO). Removing electron density from the b_{2g} orbital in the C_6H_4 fragment creates acceptor-type quinone character in $C_6H_4X_2$.

Although BH_2 accepts π density, it donates σ density when the principal C–B bonds form. The a_g and b_{1u} orbitals of BH_2 lose population to the a_g and b_{1u} orbitals of C_6H_4 when they interact to form the SHOMO and an MO two orbitals below the SHOMO (the two C–B bonding MOs).

π-Donor. In contrast to the substituent BH_2, NH_2 is a π-donor and a σ-acceptor. In similar fashion to Figure 1, the combination of 4 and 5 yields Figure 2 for X = NH_2. The filled b_{3u} orbital of NH_2 decreases in population as it donates electron density to the empty b_{3u} orbital of C_6H_4. This interaction forms the SHOMO and an orbital one level above the LUMO. Adding electron density to b_{3u} in the C_6H_4 fragment creates donor-type quinone character in C_6H_4.

The NH_2 substituent accepts σ density when the principal C–N bonds form. The a_g and b_{1u} orbitals of NH_2 gain Mulliken population from the a_g and b_{1u} orbitals of C_6H_4 when they interact to form a_g and b_{1u} bonding MOs, which lie several orbital levels below the HOMO.

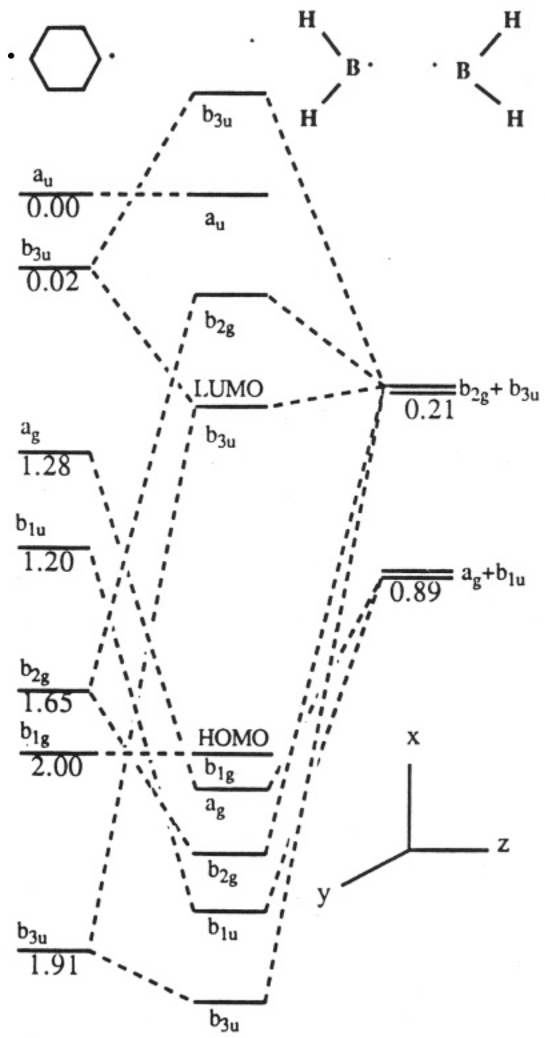


Figure 1. Partial molecular orbital diagram of 1,4-$C_6H_4(BH_2)_2$ showing the acceptor nature of the π bonding in BH_2 to the arene, as well as the σ bonding. Mulliken gross populations are listed with the orbitals.

Donor–Acceptor Synergism. Possessing both the qualities of BH_2 and NH_2 is CH_2. A pair of these substituents has one π electron in the b_{2g} and b_{3u} orbitals and is both a π-acceptor and a π-donor. In similar fashion to Figures 1 and 2, the combination of 4 and 5 yields Figure 3 for X = CH_2. The half-filled b_{2g} orbital of CH_2 increases in population as it accepts electron density from the filled b_{2g} orbital in C_6H_4. This interaction forms the LUMO and an orbital two orbitals below the HOMO. The half-filled b_{3u} orbital of CH_2 decreases in population as it donates electron density to the empty b_{3u} orbital in the C_6H_4 fragment. These transfers of electron density provide both acceptor and donor quinone character.

The CH_2 substituent shows little change in σ density when the principle C–C bonds form. The a_g and b_{1u} orbitals of CH_2 remain nearly the same in population when they interact with the a_g and b_{1u} orbitals of C_6H_4 forming the a_g and b_{1u} orbitals of $C_6H_4(CH_2)_2$ several levels below the HOMO.

Quinone itself (X = O, which is isoelectronic with CH_2) has similar shifts of electron density. Since O is more electronegative, it accepts more σ density into its a_g and

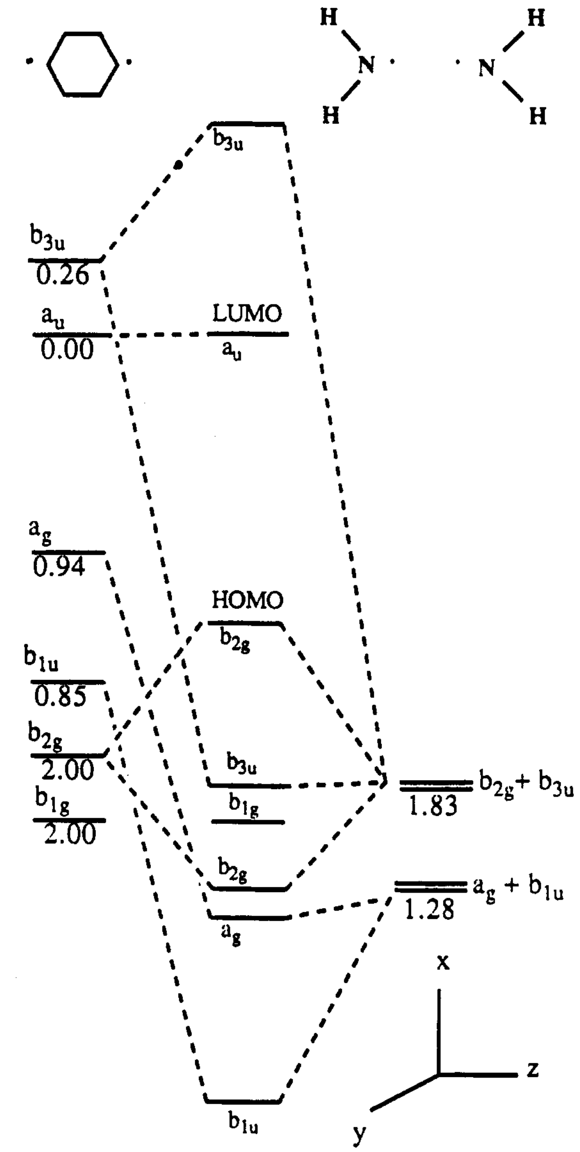


Figure 2. Partial molecular orbital diagram of 1,4-$C_6H_4(NH_2)_2$ showing the donor nature of the π bonding in NH_2 to the arene, as well as the σ bonding.

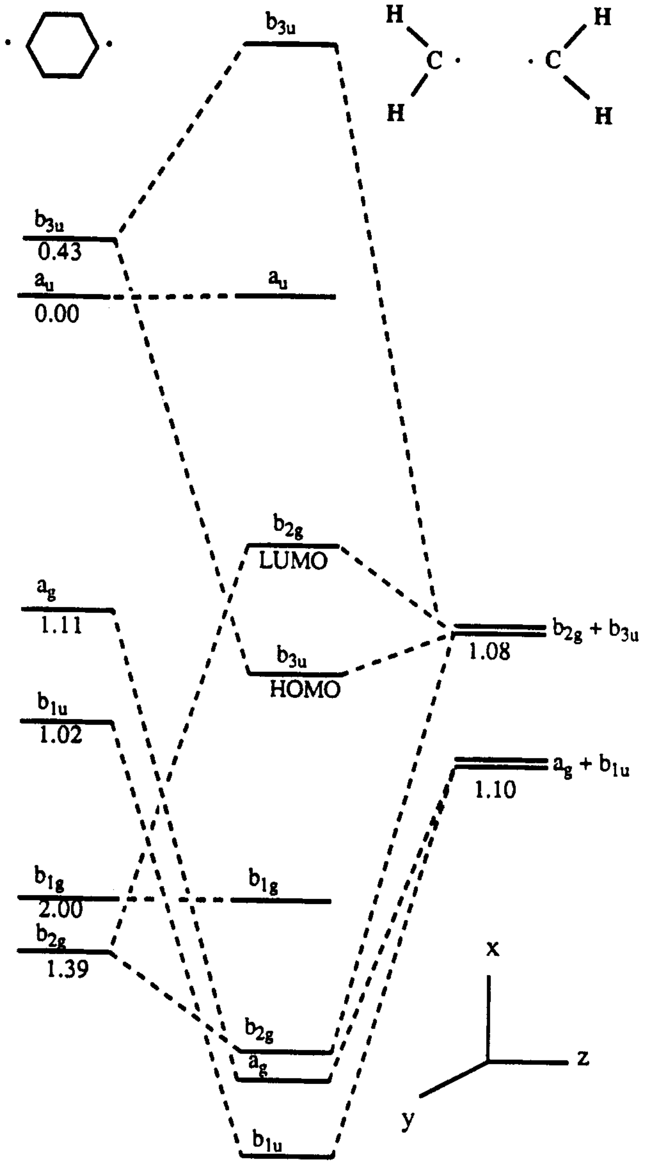
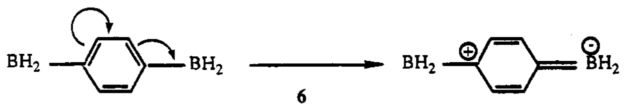


Figure 3. Partial molecular orbital diagram of 1,4-$C_6H_4(CH_2)_2$ showing both the acceptor and donor nature of the π bonding in CH_2 to the arene.

b_{1u} orbitals. For quinone-type resonance character to contribute strongly, the 1,4-substituents must have both π-donor and π-acceptor character. When a substituent is only an acceptor, such as BH_2, a resonance form has a negative charge on boron and a positive charge on the carbon opposite, **6**. The "double bond" results from the transfer of electrons from the carbon ring to boron. The opposite situation occurs when the ligand is only a donor, such as NH_2. Here, one ligand acquires a negative charge, and the other forms a "double bond" with the C_6H_4, **7**. However, when $C_6H_4X_2$ has one donor and one acceptor or when a ligand acts as both a donor and an acceptor, X = CH_2, the contribution from **2** is enhanced, **8** and **9**, respectively. Can we apply one of these descriptions to the effects of the substituent Fp?



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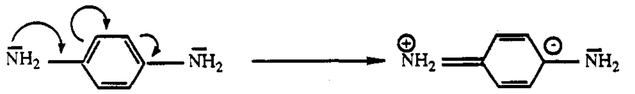

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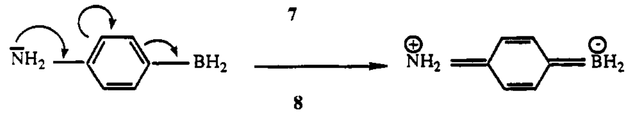

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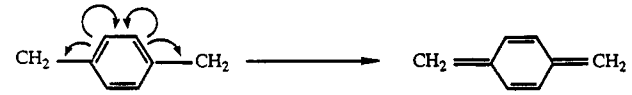

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Transition-Metal Case. The main component of the frontier orbitals of Fp (FeCp(CO)$_2$$^•$, a neutral d^7 fragment) comes from the d orbitals of Fe. The energies of these orbitals compose the right side of Figure 4. The two lowest energy orbitals on Figure 4, 13a′ and 10a″, are formed from about 10% d and 90% Cp carbon orbitals (main components of Fe–Cp "π" bond). The next three higher energy orbitals on each Fp are formed almost entirely from Fe d orbitals; these are the t_{2g}-like orbitals of the octahedral-like fragment. The 14a′ is formed of $d_{x^2-y^2}$ mixed with some d_{z^2}. It is the lowest energy t_{2g}-like orbital because it is the only one being stabilized by back-bonding to both carbonyls. The 11a″ is formed of d_{xz}, and the 15a′

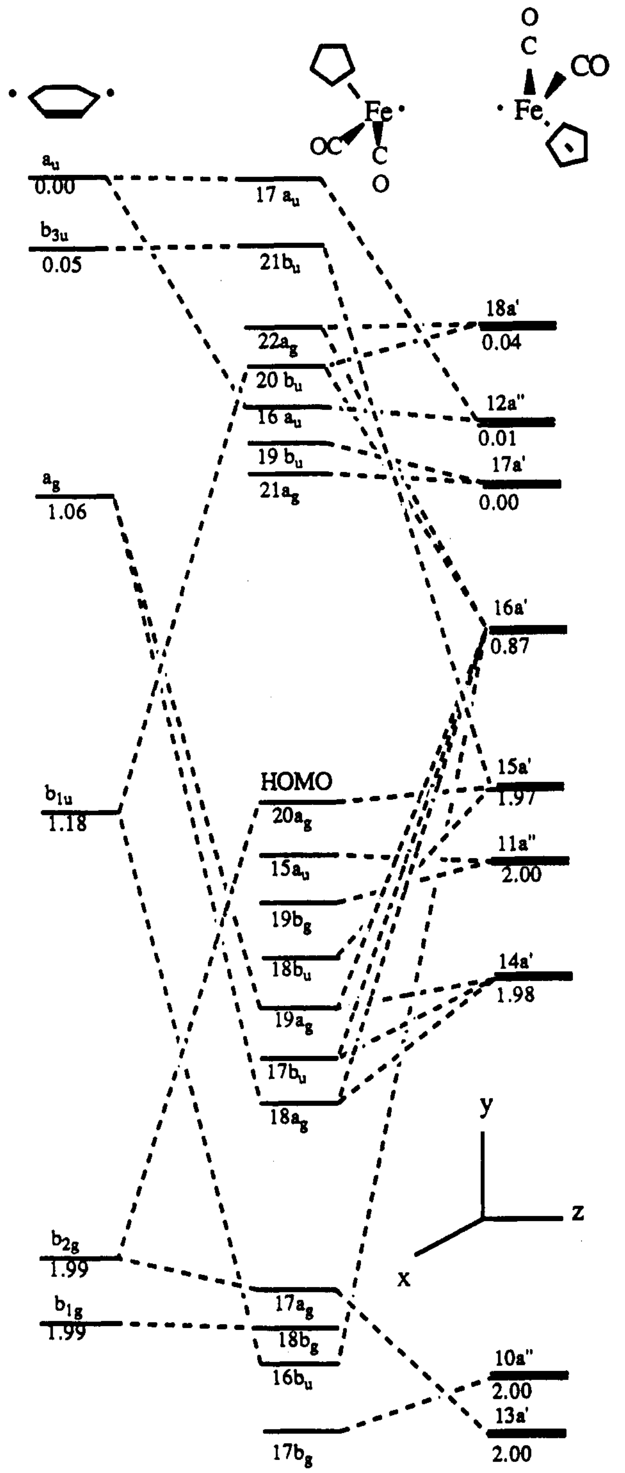

Figure 4. Partial molecular orbital diagram of 1,4-$C_6H_4Fp_2$ showing the lack of either acceptor or donor π bonding of Fp to the arene. Only σ bonding orbitals change significantly in Mulliken population.

Table I. π **Mulliken Populations of Orbitals in** $C_6H_4X_2$

	X				
	BH_2	NH_2	CH_2	O	Fp
b_{3u}	0.02	0.26	0.43	0.31	0.05
b_{2g}	1.65	2.00	1.39	1.30	2.00

Table II. σ **Mulliken Populations of Orbitals in** $C_6H_4X_2$

	X				
	BH_2	NH_2	CH_2	O	Fp
a_g	1.28	0.94	1.11	0.90	1.06
b_{1u}	1.20	0.85	1.02	0.82	1.18

is formed of d_{yz}. Since these orbitals are approximately the same energy, only a small difference will exist in the electronic energy of the MOs for orientation of the C_6H_4 parallel or perpendicular to pseudomirror plane of Fp. The orientation expected here is contrary to expectations based on extended Hückel (EH) calculations done earlier on similar systems.[15] The EH results suggested 11a″ would be above the 15a′; with our order the orientation for the best Fe to ipso C donation is the same as that observed in the crystal structure.[6] The single occupied HOMO is oriented to participate in σ bonding with the ipso carbon of the C_6H_4 and is composed of Fe d_{z^2} and p_z. The three orbitals highest in energy in Figure 4 are the empty antibonding orbitals of Fp.

In similar fashion to the other molecules, the combination of 4 and the FMOs of Fp yields the MOs in the center of Figure 4. The Mulliken populations of b_{2g} and b_{3u}, the π orbitals of C_6H_4, do not change significantly when they interact to form the MOs of $C_6H_4Fp_2$. The b_{2g} of C_6H_4 contributes to the MO $17a_g$ and the HOMO $20a_g$. Since the populations of the FMOs remain constant, in neither interaction does electron density flow from the b_{2g} to a FMO of Fp, and so no decrease in the antibonding between carbons 2 and 3 occurs. Fp then is not an acceptor substituent and does not create acceptor-type quinone character. The b_{3u} of C_6H_4 interacts with Fp 15a′ to create the MO $21b_u$. No significant amount of density is added to the b_{3u} and so the bonding between carbons 2 and 3 is not strengthened much by this weak transfer. Fp then is not a strong donor-type substituent and creates little donor-type quinone character, a conclusion that is contrary to previous notions that the frontier orbitals of Fp interacted strongly with the π^* orbitals of benzene.[1-7] No other significant changes occur in the π orbitals which enhance the contribution to a quinone-like resonance form. Since Fp creates little of either type of quinone character, $C_6H_4Fp_2$ cannot be considered to have significant quinone-like resonance character.

However, the Mulliken populations of the σ bonding orbitals in C_6H_4 do change significantly as the HOMO of Fp, 16a′, interacts with a_g and b_{1u} of C_6H_4 to form the principal C–Fe σ bonds which are dominated by the contributions of MOs $19a_g$ and $16b_u$. The antibonding combination of b_{1u} and 16a′ forms the MO $20b_u$ which also has some Fp 18a′. The 18a′ gains a slight amount of population because of the mixing with the b_{1u}. However, this gain is offset by the loss of electron density in 16a′. Thus, the total Fe–C σ bond is polarized toward the carbon.

Analysis of Trends in Mulliken Population Changes. Tables I and II summarize the Mulliken populations of the important π and σ orbitals of C_6H_4 on addition of the various substituents. For X = NH_2, a π-donor, electron density is donated into b_{3u}, and for X = BH_2, a π-acceptor, electron density is accepted from b_{1u}. However, the π populations change most for X = O and CH_2, while for Fp the π populations hardly change at all. This lack of change indicates lack of π bonding. The Mulliken populations for σ FMOs a_g and b_{1u} on C_6H_4 show the flow of electron density in σ bonding. For X = Fp, Fe transfers electron density to C_6H_4 via the σ bonds.

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Table III. Net Overlap Populations in $C_6H_4X_2$

	X				
	BH_2	NH_2	CH_2	O	Fp
σ 1–2	0.80	0.81	0.81	0.81	0.82
σ 2–3	0.79	0.78	0.79	0.78	0.84
π 1–2	0.23	0.26	0.15	0.16	0.34
π 2–3	0.30	0.27	0.38	0.37	0.34

Overlap Populations. The overlap populations listed in Table III provide another way to analyze the bonding between the carbons. By summing the contributions of the overlap populations from the 2s, $2p_x$, and $2p_z$ of adjacent carbons, the total σ overlap population was obtained. Total π overlap population for the carbons is isolated in the $2p_y$. As expected, when X = CH_2, the π overlap of carbons 2 and 3 is the greatest, and the overlap between carbons 1 and 2 is the smallest. This large difference in overlap population reflects the strong quinone-like character.

For X = Fp, the π overlap population is the same for carbons 1 and 2 as for carbons 2 and 3. This lack of difference in overlap population indicates little change in double bond character between the carbons. The Fps neither accept nor donate π density from or into the ispo carbons. Thus little double bonding occurs between iron and the ipso carbon. However, the σ overlap population in $C_6H_4X_2$ is at least as great when X = Fp as it is for any other substituent and the difference is nearly as large and in the opposite direction. For the main-group substituents, σ and π effects oppose one another, and the π effect dominates. However, for X = Fp the σ differences are larger than the π differences and these σ differences could produce some quinone-like character in the C_6 ring.

Conclusion. The iron–arene bond is mainly σ in character and polarized toward its ipso carbon, resulting in some ionic contributions to the bonding. Effects in the NMR and IR indicating possible contribution from a quinoidal-type resonance can be explained by changes in the σ charge distribution.

Other calculations, where a $Cr(CO)_3$ was added in an η^6 fashion to 1,4-$C_6H_4Fp_2$ and C_6H_4, show that the only significant change in the Mulliken populations of the Fp orbitals occurs in the iron–arene σ donor orbital. Furthermore, the changes in π FMOs of the C_6H_4 fragment of 1,4-$C_6H_4Fp_2$ were changes which occurred on addition of $Cr(CO)_3$ to C_6H_4 alone. The changes in the Fp ν_{CO} stretching frequencies and in the ^{13}C NMR when $Cr(CO)_3$ is added to 1,4-$C_6H_4Fp_2$ must be attributed to changes in the σ bonding.

From the analysis of these comparative calculations, the best description of the Fp–C bonding in the para-substituted benzene is that Fp is an excellent σ-donor, with only a weak π-donor component in the bonding.

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