Reaction of Ferrocene with Polyaromatic Molecules. π-Arene Bis((π-cyclopentadienyl)iron) Dications. I. Molecular Structure

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Abstract: A general procedure is described whereby (π-cyclopentadienyl)iron moieties can be π bonded to polyaromatic systems, including fused molecules. Disubstitution by (π-cp)Fe is found to be possible for some 15 polyaromatic molecules, while higher substitutions are not possible. Carbon-13 and proton nmr are used to ascertain the molecule structure of the (π-cp)Fe-substituted polyaromatic molecules. The ^{13}C resonance of a (π-cp)Fe-substituted arene carbon is shown to be shifted ~40 ppm upfield from the ^{13}C resonance for the free arene carbon. A similar upfield shift is seen for the coordinated cyclopentadienyl ring. An intensification of quaternary ^{13}C resonances in concentrated sulfuric acid, over what is seen in organic solvents, is attributed to paramagnetic impurities resulting from a slow decomposition of the compounds in concentrated sulfuric acid.

Biscyclopentadienyl and bisbenzenoid transition metal "sandwich" compounds have been reported for many elements. The first transition metal "sandwich" complex in which both a *pentahapto*cyclopentadienyl and a *hexahapto*benzenoid ring are coordinated to the metal was reported by Coffield, *et al.*,[1] in 1957. They prepared the iodide salt of h^6-mesitylene-h^5-cyclopentadienyliron(II) by treatment of h^5-cyclopentadienyliron(II)dicarbonyl chloride with aluminum chloride in refluxing mesitylene; hydrolysis, followed by treatment of the aqueous layer with potassium iodide, gave the final product. Green, Pratt, and Wilkinson prepared the h^6-benzene analog in 1960.[2]

In 1963 Nesmeyanov, *et al.*,[3,4] reported that the h^6-benzene-h^5-cyclopentadienyliron cation could be readily prepared by the reaction of ferrocene and benzene in the presence of aluminum chloride and aluminum powder. In later reports[5-8] these same workers were able to replace benzene with other arenes. It was found that electron-donating substituents on either the arene or the cyclopentadienyl rings facilitated the ring-substitution reaction, while electron accepting substituents hindered it. The various h^6-arene h^5-cyclopentadienyliron cations were found to have interesting properties. Although they formally contain Fe(II) and as such are isoelectronic with ferrocene, they are extremely stable toward oxidation.[9] In fact, it is possible to oxidize substituents on the rings without oxidizing the metal.[10] In contrast to ferrocene, the h^6-arene h^5-cyclopenta-

dienyliron(II) cations are very stable in concentrated acid solutions and exhibit little tendency toward electrophilic substitution. However, nucleophiles react with the cations fairly readily. For example, h^6-chlorobenzene-h^5-cyclopentadienyliron cation readily exchanges chloride for RO⁻ (R = alkyl and phenyl), RS⁻ (R = alkyl and phenyl), NH_2^-, NHR⁻, and CN⁻.[7,8,10,11] For a review of this work, see ref 12.

When polyaromatics such as biphenyl, naphthalene, and fluorene were used in the ferrocene cyclopentadienyl ring-replacement reaction, Nesmeyanov, *et al.*,[6] found that only one of the rings took part in the ligand exchange with ferrocene. The reactant ratios were ferrocene–AlCl₃–Al powder–arene = 1:2:1:excess. Reaction times were 3–5 hr. In the early phases of this work Sutherland, *et al.*,[13] reported the synthesis of three π-arene bis((π-cyclopentadienyl)iron) dications. Their approach was to react the PF₆⁻ salts of the h^6-arene h^5-cyclopentadienyliron *monocations* (where arene = biphenyl, diphenylmethane, and fluorene) with excess ferrocene to substitute the remaining aromatic rings. The reaction mixture contained both monocation and dication salts, and the latter was purified by fractional crystallization. Hexafluorophosphate salts of the following three dications were prepared (the numbering is used in the description of ^{13}C resonances).

Ia, n = 0
b, n = 1

II
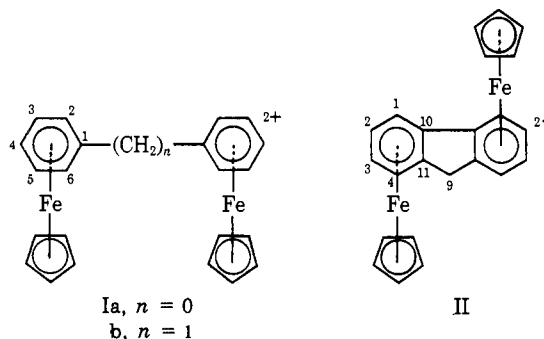
In this paper we report a direct and simplified syn-

(1) T. H. Coffield, V. Sandel, and R. D. Closson, *J. Amer. Chem. Soc.*, 79, 5826 (1957).
(2) M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc. A*, 989 (1960).
(3) A. N. Nesmeyanov, N. A. Vol'kenau, and I. N. Bolesova, *Dokl. Akad. Nauk SSSR*, 149, 615 (1963).
(4) A. N. Nesmeyanov, N. A. Vol'kenau, and I. N. Bolesova, *Tetrahedron Lett.*, 1725 (1963).
(5) A. N. Nesmeyanov, N. A. Vol'kenau, and I. N. Bolesova, *Dokl. Akad. Nauk SSSR*, 160, 1327 (1965).
(6) A. N. Nesmeyanov, N. A. Vol'kenau, and I. N. Bolesova, *Dokl. Akad. Nauk SSSR*, 166, 607 (1966).
(7) A. N. Nesmeyanov, N. A. Vol'kenau, E. I. Sirotkina, and V. V. Deryabin, *Dokl. Akad. Nauk SSSR*, 177, 1110 (1967).
(8) E. I. Sirotkina, A. N. Nesmeyanov, and N. A. Vol'kenau, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1524 (1969).
(9) A. N. Neseyanov, N. A. Vol'kenau, and E. I. Sirotkina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1170 (1967).
(10) A. N. Nesmeyanov, N. A. Vol'kenau, and I. N. Bolesova, *Dokl. Akad. Nauk SSSR*, 175, 606 (1967).

(11) A. N. Nesmeyanov, N. A. Vol'kenau, and L. S. Isaeva, *Dokl. Akad. Nauk SSSR*, 176, 106 (1967).
(12) A. N. Nesmeyanov, *Advan. Organometal. Chem.*, 10, 44 (1972).
(13) C. C. Lee, R. G. Sutherland, and B. J. Thomson, *J. Chem. Soc., Chem. Commun.*, 907 (1972).
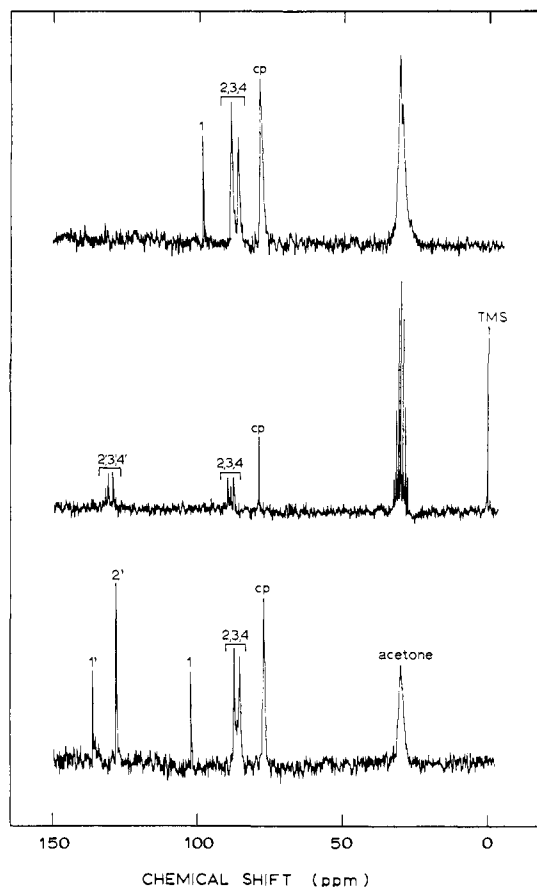
Figure 1. Proton-decoupled carbon-13 nmr spectra for (π-cp)Fe-substituted arenes: top [biphenyl((π-cp)Fe)$_2$]$^{2+}$ dissolved in concentrated D$_2$SO$_4$; middle, [biphenyl((π-cp)Fe)]$^+$ dissolved in (CD$_3$)$_2$CO; bottom, [p-terphenyl((π-cp)Fe)$_2$]$^{2+}$ dissolved in concentrated D$_2$SO$_4$.

thetic approach giving the above three dications as well as a manifold of other dications resultant from h^5-cyclopentadienyliron disubstitution on various polyaromatic molecules (*e.g.*, anthracene, pyrene, and phenanthrene). Carbon-13 and proton nmr data will be presented to characterize the molecular structure of the various compounds. In a later paper in this series, polarographic, infrared, electronic absorption, and ^{57}Fe Mössbauer spectroscopic data will be used to characterize the electronic structure of these interesting molecules.

Results and Discussion

An excess of ferrocene reacts in the presence of AlCl$_3$ and Al with the following polyaromatic molecules: biphenyl, diphenylmethane, fluorene, 9,10-dihydroanthracene, 1,2:4,5-dibenzo-1,4-cycloheptadiene, 3,3',-4,4'-tetramethylbiphenyl, p-terphenyl, anthracene, phenanthrene, pyrene, chrysene, β-phenylnaphthalene, and 1,2:5,6-dibenzanthracene. Two h^5-cyclopentadienyliron(II) moieties π bond to each of the above arenes to give dications which are isolated as yellow PF$_6^-$ salts. Very good analytical data (C, H, and Fe) were obtained for all compounds.

There are two basic questions relating to the molecular structure of the above bis(h^5-cyclopentadienyliron-(II)) substituted arenes. For the arenes that have more than two six-membered rings, the h^5-cyclopentadienyliron substitution pattern needs to be determined.

Also, many of the polyaromatic molecules studied in this work are fused systems, which leads to the possibility of having different disubstitution patterns. Both (h^5-C$_5$H$_5$)Fe moieties could be substituted on the same side of the fused polyaromatic or on opposite sides.

Sutherland, *et al.*,[13] prepared two dications for which neither of the above questions needed to be broached. Biphenyl and diphenylmethane were disubstituted to give the dications Ia and Ib. There are, obviously, only two six-membered aromatic rings in each of these, and because there is relatively free rotation of the two benzene moieties in solution the molecular structure of the two dications is determined, providing the *hexahapto*benzenoid character is accepted. A carbon-13 nmr spectrum (all ^{13}C spectra in this paper are proton decoupled) of the PF$_6^-$ salt of the biphenyl dication was obtained to check this last point; the spectrum is reproduced in Figure 1 and the spectral features are summarized in Table I.[14] To properly identify the various ^{13}C peaks it was necessary to first secure the ^{13}C spectra of some related molecules, to which we now turn.

Relative to tetramethylsilane (TMS), the free benzene ^{13}C resonance occurs 128.5 ppm downfield, and free cyclopentadienyl occurs 103 ppm downfield.[15] Two nonsolvent ^{13}C resonances are seen in the spectrum of h^6-benzene-h^5-cyclopentadienyliron(II) cation (see Table I[14]). In CD$_3$CN solvent the benzene resonance is at 88.4 ppm and the cyclopentadienyl resonance at 76.8 ppm (all shifts relative to TMS). Coordination of either benzene or cyclopentadienyl to a transition metal leads to large upfield shifts in respect to the free ligands ($\sim$40 ppm for the benzene ring). Carbon-13 data have been reported[16] for several organometallic molecules having either a h^6-benzenoid or a h^5-cyclopentadiene and generally the coordinated arene resonance is at appreciably higher field than the free arene. It is not simply the charge on the h^6-benzene-h^5-cyclopentadienyliron cation that causes the large upfield shift, because many of the molecules that are reported to have large upfield shifts are uncharged, *e.g.*, (CO)$_2$(h^5-C$_5$H$_5$)-FeX (X = Cl, Br, I, CN), where δ 85.6, 85.4, 84.8, and 85.9 ppm peaks are found, respectively.[16] There are also a few charged molecules with large upfield cyclopentadienyl ring shifts, *e.g.*, [(CO)(h-C$_5$H$_5$)Fe(CN)$_2$]$^-$ where the h-C$_5$H$_5$ resonance is found at δ 82.6 ppm. The upfield shift has been attributed to changes in hybridization of the cyclopentadienyl ring associated with the use of cyclopentadienyl ring π orbitals to σ bond with the metal d orbitals.

The upfield shift has proved to be a very useful tool in the work reported in this paper. This is the case because rings that are *not* (cyclopentadienyl)iron substituted, although they are in close proximity or bonded to a (cp)Fe-substituted ring, do not experience large upfield shifts. For example, biphenyl can be monosubstituted with a single (cp)Fe moiety to give cation III. The ^{13}C spectrum of cation III dissolved in (CD$_3$)$_2$CO, reproduced in Figure 1 (middle), shows seven nonsolvent resonances. There is a cyclopenta-

(14) See paragraph at end of paper regarding supplementary material.
(15) G. C. Levy and G. L. Gordon, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley, New York, N. Y., 1972.
(16) B. E. Mann, *Chem. Commun.*, 976 (1971); L. F. Farnell, E. W. Randall, and E. Rosenberg, *ibid.*, 1078 (1971).

III
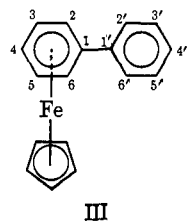
dienyl resonance at δ 78.6 ppm and two groups of three peaks, one group at high field (δ ~88 ppm) and the other at low field (δ ~130 ppm). The high-field group of three is assignable to carbons 2, 3, and 4 in III, while the low-field group is assignable to "unsubstituted" carbons 2', 3', and 4'. The resonances for the quaternary carbons (1 and 1') were not detectable, most likely due to the absence of a nuclear Overhauser effect. The important point is that the ^{13}C resonances for the unsubstituted phenyl ring fall very close to that for free benzene.

With the above foundation we are now in a position to analyze the ^{13}C spectrum (see Figure 1 and Table I[14]) for (cp)Fe-disubstituted biphenyl, that is, dication Ia. The spectrum reproduced in Figure 1 (top) is for a concentrated D$_2$SO$_4$ solution of dication Ia. One cyclopentadienyl (δ 79.4 ppm) and three biphenyl (δ 87.3, 89.5, and 99.3 ppm) peaks are seen. The δ 99.3 ppm peak is assigned to the one quaternary-type carbon in dication Ia by comparison with the reported spectrum of free biphenyl. The δ 87.3 ppm peak is assigned to the ortho carbons (carbons 2 and 6 as numbered in Table I[14]) while the more intense δ 89.5 ppm peak is assigned to both the meta and para (carbons 3, 4, and 5) carbons. These last assignments are made mainly on the basis that the δ 89.5 ppm peak is appreciably more intense than the δ 87.3 ppm peak. In the case of free biphenyl there is a reversal in the intensities of these two peak systems with the ortho and para carbons having resonances at *higher* field that are almost degenerate (chemical shift difference = 0.1 ppm) and the meta carbon with a lower field shift (by ~0.7 ppm). In the case of the substituted biphenyl the separation between the two peak systems is larger (2.2 ppm vs. 0.7 ppm) and apparently this is a result of each ortho carbon being shielded to a *small* degree by the positively charged cp(Fe) moiety on the other biphenyl ring. In summary, the ^{13}C spectrum of dication Ia does substantiate the hexahapto character of each of the biphenyl rings.

The relatively intense peak for the quaternary carbons of dication Ia also bears comment. As indicated in Table I,[14] the CD$_3$CN spectrum of dication Ia shows one cp peak at δ 79.3 ppm and only *two* biphenyl peaks at δ 88.0 and 89.6 ppm. It is clear that changing the solvent from concentrated D$_2$SO$_4$ to CD$_3$CN dramatically alters the intensity of the low-field δ 99.3 ppm biphenyl peak. It is our experience with these substituted arenes that quaternary carbon resonances are generally more intense for concentrated D$_2$SO$_4$ solutions than for CD$_3$CN or (CD$_3$)$_2$CO solutions. This effect could be due to the greater viscosity of concentrated D$_2$SO$_4$ solutions modifying the overall tumbling and internal rotational rates of the molecules. A more probable explanation is found in the possibility that there are paramagnetic impurities present, impurities resultant from decomposition in the concentrated D$_2$SO$_4$. In fact, monitoring the proton nmr of concentrated H$_2$SO$_4$

solutions of [(h^6-C$_6$H$_6$)(h^5-C$_5$H$_5$)Fe]$^+$ does show the appearance of additional peaks growing in slowly over a period of 24–48 hr. The presence of trace paramagnetic material has been reported to eliminate nuclear Overhauser effects by modulating the populations in the various spin states.[17-19] Concentrated D$_2$SO$_4$ solutions were used for many of our complexes for solubility reasons.

Finally, as a dramatic example of the intensification of quaternary resonances in concentrated D$_2$SO$_4$ solutions of these arene (cyclopentadienyl)iron systems, the ^{13}C spectrum (CH$_3$ resonances not shown) of 3,3',4,4'-tetramethylbiphenylbis((cyclopentadienyl)iron) dication is reproduced in Figure 2.[14] The broad high-field resonance at δ 79.5 ppm is due to the cp carbons. In addition, there are three relatively intense peaks assignable, by comparison with the free 3,3',4,4'-tetramethylbiphenyl spectrum (see Table I[14]), to the three types of quaternary carbon atoms. The three weaker peaks are associated with the three types of nonquaternary carbon atoms. The molecular structure of this dication, however, is still not totally established for there are two possible isomeric forms (IV and V). With the present

IV   V
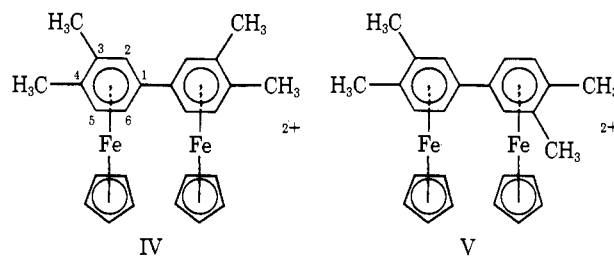
understanding of the ferrocene ring replacement reaction it is difficult to rationalize why only one of these isomers would be formed. Perhaps ^{13}C spectroscopy is not sensitive enough to detect the presence of both isomers. Nevertheless, the 3,3',4,4'-tetramethylbiphenylbis((cyclopentadienyl)iron) hexafluorophosphate ^{13}C spectrum reproduced in Figure 2[14] does demonstrate the point that the nonquaternary carbon resonances are apparently broadened, seemingly leading to an intensification of the quaternary resonances. In agreement with the above proposal, we have found that shorter spectrum running time for this sample in D$_2$SO$_4$ does give a spectrum with quaternary and nonquaternary resonances of comparable intensities. Even further, most all of the compounds dissolved in CD$_3$CN and run for long periods (2–2.5 hr) of time do give spectra, *vide infra*, with relatively intense quaternary resonances. This effect has, in fact, turned out to be useful in assigning peaks.

The molecular structure of (cp)Fe-disubstituted *p*-terphenyl is evident from its ^{13}C spectrum, see Figure 1 (bottom). A comparison with the spectrum of the biphenyl dication Ia clearly points to the structure VI. The alternative structure VII would have a much more complicated ^{13}C spectrum. Peak assignments are indicated in Figure 1 and are given in Table I.[14]

Ferrocene reacts with either fluorene, or 9,10-dihydroanthracene, or 1,2:4,5-dibenzo-1,4-cycloheptadiene to

(17) G. N. La Mar, *J. Amer. Chem. Soc.*, **93**, 1040 (1971); *Chem. Phys. Lett.*, **10**, 230 (1971).

(18) R. Freeman, K. G. R. Pachler, and G. N. La Mar, *J. Chem. Phys.*, **55**, 4586 (1971).

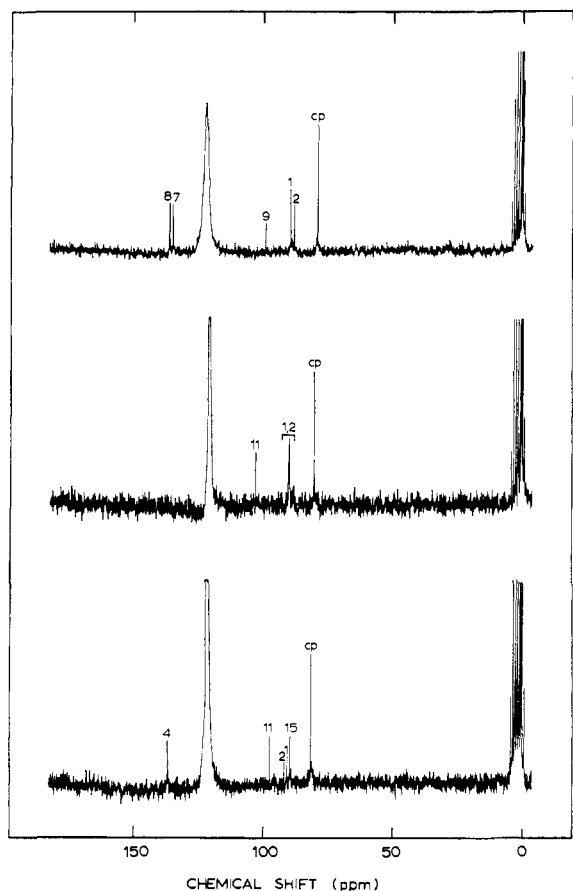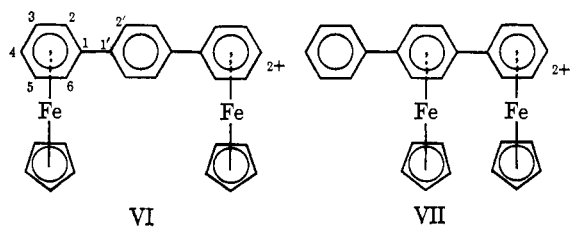(19) D. F. S. Natusch, *J. Amer. Chem. Soc.*, **93**, 2566 (1971).

Figure 4. Proton-decoupled carbon-13 nmr spectra for three (π-cp)Fe-substituted arenes dissolved in CD₃CN: top, [naphthalene((π-cp)Fe)]⁺; middle, [anthracene((π-cp)Fe)₂]²⁺; bottom, [pyrene((π-cp)Fe)₂]²⁺.

VI   VII

give a yellow PF₆⁻ salt of a (cp)Fe-disubstituted dication. The two benzene rings in these molecules are bound into a relatively rigid configuration. Proton nmr (60 and 220 MHz) spectra were taken for concentrated D₂SO₄ and acetonitrile solutions of each dication and it was concluded that the dications resultant from fluorene and 9,10-dihydroanthracene have the structures II and VIII, respectively. Thus, the proton nmr spec-

VIII   IX
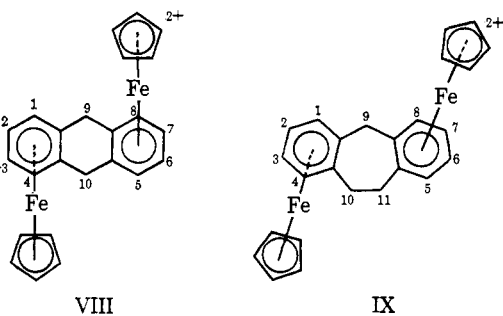
trum of dication VIII shows only a *single* CH₂ resonance

(2.0 ppm downfield of TMS). If both of the cyclopentadienyl moieties were substituted on the same side of the 9,10-dihydroanthracene plane, then two CH₂ resonances would be seen. Carbon-13 nmr data were obtained for the fluorene system, dication II, dissolved in D₂SO₄ (see Table I[14]). The requisite seven resonances were seen; one cp resonance at δ 79.5 ppm, two quaternary fluorene resonances at δ 101.5 and 106.7 ppm, and four nonquaternary fluorene resonances (δ 81.8, 86.8, 87.6, and 87.9), which we have not attempted to assign. The resonance for the saturated carbon number 7 was *not* located. From the observations on the fluorene and 9,10-dihydroanthracene dications, the structure of the 1,2:4,5-dibenzo-1,4-cycloheptadiene dication would be best formulated as IX. Much to our amazement we found, however, that the ¹³C and ¹H nmr data for this compound clearly point to the presence of an equimolar mixture of both the trans isomer IX and the cis isomer where the two (π-cp)Fe moieties are π bonded on the same side of the arene. Thus, the ¹H nmr shows *two* almost equal area cyclopentadienyl resonances and a very complicated pattern for the –CH₂– protons. The ¹³C spectrum for the mixture (see Figure 3)[14] is dramatic proof of what we are proposing. There are *two* cyclopentadienyl resonances, *each* isomer has two –CH₂– resonances (δ ~30.8 and 37.9 ppm) of 2:1 relative intensity, and *each* isomer has two quaternary resonances. Finally, thin-layer chromatography using nitromethane and silica gel gives a separation of the two isomers.

Nonrigid polyaromatics and rigid polyaromatics with intervening saturated centers have been treated. The question at hand is what type of substitution and configuration pattern will develop for fused polyaromatics. Their rigidity is certainly not unique, but presumably there is more interaction between the various aromatic centers by virtue of the fusing or sharing of carbon atoms between the aromatic rings. The simplest fused aromatic molecule is naphthalene, which we have found only binds one (cp)Fe moiety. Various reaction conditions were tried; the reaction time and relative amounts of reactants and solvent for refluxing the reactants (*e.g.*, cyclohexane and decalin) were varied, nevertheless, only monosubstitution was found. Apparently, monosubstitution leaves the other fused ring with a decreased basicity. It should be noted that, unlike the other materials, the PF₆⁻ salt of the π-naphthalene(π-cyclopentadienyl)iron(II) cation is orange colored. A carbon-13 nmr spectrum was obtained for a CD₃CN solution of the naphthalene compound and it is reproduced in Figure 4. Six nonsolvent peaks are discernible. The cyclopentadienyl resonance is found at δ 77.3 ppm, see Table II.[14] The pattern of the other five resonances is such as to indicate the molecular structure is that depicted for cation X. Thus, there are

X
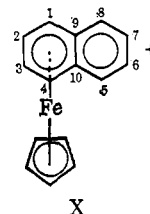
two low-field peaks (δ 133.1 and 131.8 ppm) assignable to the two different types of carbon atoms of the "un-

substituted ring." Even though there is a fusing between the two halves of the naphthalene moiety, the carbon resonances for the unsubstituted ring again fall very close to those for the free arene. The peak at δ 96.9 ppm is due to the two equivalent quaternary carbon atoms, while the two peaks at δ 87.7 and 86.1 ppm are associated with the two different types of substituted ring carbon atoms.

Anthracene binds two (cp)Fe moieties to give a yellow PF_6^- salt, the ^{13}C spectrum of a CD_3CN solution of this salt is reproduced in Figure 4. This spectrum presents a problem. The simplicity of the spectrum points to the symmetric structure XI. The trans con-

XI
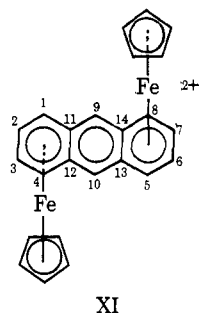
figuration for the (cp)Fe moieties is most probable, based on the above observations, but has not been established for XI. The peaks at δ 78.4 and 100.4 ppm account for the cp and quaternary carbons, respectively, and two closely spaced intermediate-field peaks (δ 88.0 and 87.8 ppm) account for the two types of non-quaternary substituted ring carbon atoms. The problem is found in identifying the 9,10-anthracene carbon resonance, which should have occurred at $\sim$130 ppm. Initially it was thought that the broad low-field CD_3CN solvent peak at δ 118.2 ppm had obscured this particular anthracene peak, but this did not prove to be the case, for a ^{13}C spectrum of a concentrated D_2SO_4 solution did not show a peak at this field position. Perhaps the missing resonance is accidentally degenerate with one of the other resonances or possibly the 9,10-anthracene carbon atoms have unusual spin–lattice relaxation times. Neither of these explanations seems probable. It is possible that the 9,10 carbon atoms are no longer very "aromatic" and the missing peak has moved a considerable distance upfield. Inspection of the resonance forms of free anthracene shows that in order for the outside six-membered rings to have a six-electron π system to bond to each iron(II), it is necessary that a considerable amount of the π-electron density of the central "ring" be drained. This situation is not to be found in the other fused arenes that are considered below. In spite of the problem with the ^{13}C spectrum of the anthracene system, proton nmr data (concentrated H_2SO_4 solution at 60 MHz) do substantiate the above proposed structure XI. The proton spectrum is very simple to analyze. In addition to a single cyclopentadienyl resonance, there are three other resonances. Two are found at a lower field than the cp (93 and 95 Hz downfield), these are most likely the peaks for the anthracene protons 1–8. The third resonance is found at *higher* (32 Hz) field than the cp resonance and this is the signal for the anthracene 9,10 protons. All three peaks are fairly sharp indicating little in the way of structure.

Carbon-13 nmr spectra were also obtained for the

(cp)Fe-disubstituted pyrene, phenanthrene, chrysene, and β-phenylnaphthalene dications. Even though these spectra are somewhat complicated, peak assignments (see Table II[14]) were possible to the extent of locating the number and type of resonances required for a given structure of each dication. Structural formulas XI–XIV depict the structures of these four dications as

XII   XIII

XIV   XV
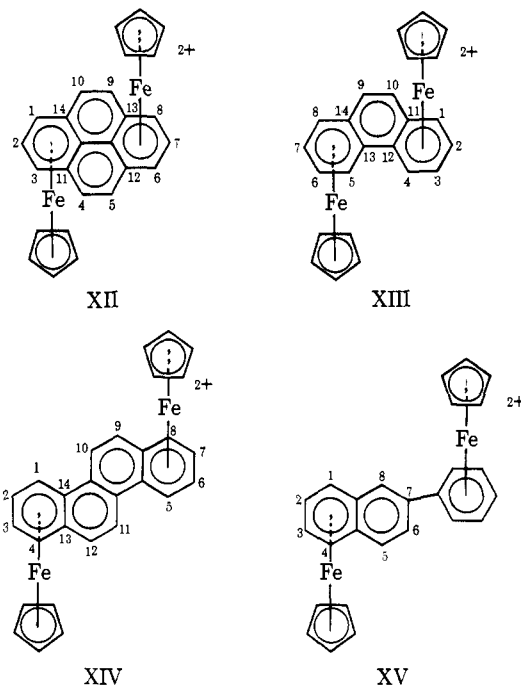
inferred from the ^{13}C data. Perusal of Table II[14] shows that, as above, the carbon atoms that are not bonded to an iron atom have resonances at $\delta \simeq$130 ppm. This feature was used in assigning dication XV as the structure of the β-phenylnaphthalene compound. Table II[14] shows that this compound has 14 non-cyclopentadienyl resonances with four resonances in the nonsubstituted region. Only structure XV has a *quaternary* carbon in the nonsubstituted region and this is what is observed. Changes in relative peak position and intensity between the free and coordinated polyaromatic molecule are evident. It should prove interesting to determine spin–lattice relaxation times and nuclear Overhauser enhancement ratios for many of the above molecules. The solubility of the salts will have to be appreciably increased (change PF_6^- to BF_4^-) in order to do this and the impurity problem overcome.

There are still many unanswered questions concerning the above synthetic endeavors. In particular, it is somewhat puzzling that p-terphenyl did not, under the conditions of excess ferrocene, yield any (cp)Fe trisubstituted product. Perhaps the formation of such a product with these two arenes is sterically unfavorable or our product work-up is such as to not yield the trisubstituted material, although the residue was extracted and yielded no product. Other polyaromatic systems were reacted with excess ferrocene in an attempt to prepare trisubstituted materials. Triphenylmethane, triphenylene, and 1,2:5,6-dibenzanthracene were tried, but only disubstituted compounds resulted. On some occasions the analytical work indicated the possibility of having a small amount of trisubstituted product present. Only with tetraphenylporphine were we able to obtain a product with more than two (cp)Fe groups

substituted. The properties of this last compound will be reported in a later paper.

Experimental Section

Compound Preparation. All analyses were performed by the microanalytical laboratory of the University of Illinois' School of Chemical Sciences. All reactants were reagent grade or purchased from commercial sources.

The π-arene mono((π-cyclopentadienyl)iron) hexafluorophosphate salts were prepared by the method described for the benzene derivative.[20] The π-arene bis((π-cyclopentadienyl)iron) hexafluorophosphate salts studied in this work were prepared by the following procedure. A Schlenk flask (250 ml) is flushed thoroughly with nitrogen. Then under a continuous stream of nitrogen, 5.58 g (0.030 mol) of ferrocene, 20.0 g (0.15 mol) of anhydrous aluminum chloride, 1.35 g (0.050 mol) of aluminum powder, 50.0 ml of cyclohexane (or decalin), and 0.0015 mol of the arene compound to be exchanged were added to the flask. The reaction mixture is then heated under reflux, with rapid stirring, in a nitrogen atmosphere, for 12–16 hr (overnight). Then the reaction flask was cooled to room temperature and placed in an ice bath, and the reaction mixture (still under N_2) was slowly hydrolyzed with 50 ml of ice–water. The mixture was filtered, and the aqueous layer was separated after washing with several 30-ml portions of cyclohexane. The aqueous layer, which is air stable, was then filtered into a concentrated aqueous solution of ammonium hexafluorophosphate (2 g in a few ml) to isolate the desired compound. The precipitated material was filtered to give a solid which was quite frequently yellow in color. A greenish coloration indicates impurities. Two solids (naphthalene and chrysene) were orange colored. The yields were generally 35–50% based on the arene. The compounds were recrystallized either from a warm acetone–water solution (do not heat excessively), or by dissolving the solid in acetonitrile and then adding anhydrous ether. They were then dried for at least 24 hr *in vacuo* over P_2O_5.

Physical Measurements. All proton nmr spectra were obtained with either Varian 60- or 220-MHz spectrometers at ambient probe temperatures. Carbon-13 nmr spectra were obtained on a Varian Model XL-100-15 spectrometer with a 15-in. magnet and at a frequency of 25.5 MHz. A Digit Lab FTS-NMR/3 Model Fourier transform system was used. For many samples D_2SO_4 (for locking purposes) was used as a solvent and acetone was used as an internal standard. Other samples were run in CD_3CN with TMS internal standard. Data collection took from 1 to 1.5 hr for each ^{13}C run. All ^{13}C spectra were run in the proton-decoupled mode with a 1.5-kHz noise bandwidth. Pulse conditions were nominally, width, 15 μsec; acquisition time, 1.5 sec; and delay, 0.025.

Supplementary Material. Tables I and II and Figures 2 and 3 will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 $\times$ 148 mm, 24$\times$ reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-3603.

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Hydration of Carboxamides. Evaluation of the Free Energy Change for Addition of Water to Acetamide and Formamide Derivatives

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Abstract: The method employed for estimating the free energy of formation of ortho acids from the free energy of formation of ortho esters was extended to estimate the free energy of formation of ortho acid monoamides $(RC(OH)_2NR'_2)$ from the free energies of formation of amide dimethyl acetals. The heat of formation of liquid $RC(OCH_3)_2N(CH_3)_2$ was determined calorimetrically by measuring the heat of hydrolysis in aqueous base. This permitted calculation of the required free energies of formation in aqueous solution. The free energies for addition of water (standard state, the pure liquid) to N,N-dimethylformamide and N,N-dimethylacetamide (standard states, 1 M solutions with an infinitely dilute reference state) are respectively $+19.3$ and $+19.6$ kcal/mol. These results permit construction of more detailed reaction coordinate diagrams for amide hydrolysis and ester aminolysis than has previously been possible.

Recently it has been shown[1] that the equilibrium constant for reaction 1 is only slightly dependent

$$ROH + CH_3OH = ROCH_3 + H_2O \qquad (1)$$

on the nature of R and that for a given number of substituents on the carbon bearing the hydroxyl it is essentially constant. This fact was used to evaluate the free energies of formation in aqueous solution of orthoformic and orthoacetic acids from the free energies of formation of the corresponding trimethyl esters. This approach has now been extended to estimate the free energies of formation of species $RC(OH)(OCH_3)N(CH_3)_2$ and $RC(OH)_2N(CH_3)_2$, which are the intermediates in the aminolysis of the methyl ester and the hydrolysis of the amide. In order to do this it was necessary to determine the heats of formation of the corresponding amide dimethyl acetals, which could be done by measuring the heats of hydrolysis in aqueous base. With the equilibrium constants for formation of the tetrahedral intermediates, the results of earlier kinetic investigations of amide hydrolysis[2] and ester

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