# Formation of Charge-transfer Complexes Between Bis(arene)iron(II) Salts and Electron-rich Aromatic Compounds

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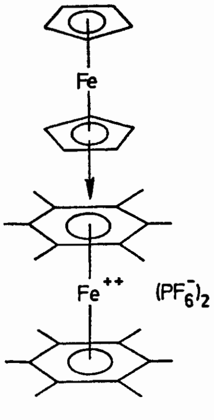
*Summary* Bis(arene)iron(II) salts (arene = hexamethylbenzene, durene) react with aromatic compounds having electron-donating properties to give 1:1 charge-transfer complexes which may be used to separate some closely related compounds.

ELECTROPHILIC compounds such as tetracyanoethylene and polynitrobenzenes are known to react with electron-donating aromatic compounds to form stable 1:1 molecular complexes.[1] Since many organic compounds having electron-releasing substituents behave as electrophiles when complexed to a transition metal cation [2] we examined the reactions of nucleophilic reagents with several cationic transition-metal complexes containing arenes.



(I)

We now report that bis(hexamethylbenzene)iron(II) hexafluorophosphate reacts with a wide variety of aromatic compounds to form coloured, stable 1:1 charge-transfer complexes with the donor molecules benzene, naphthalene, phenanthrene, anthracene, benzo[*b*]thiophen, indole, aniline, *NN*-dimethylaniline, *m*-chloroaniline, *p*-bromoaniline, *p*-phenylenediamine, hydroquinone, pyridine, furan, and ferrocene.† In a typical preparation pure crystals of the 1:1 molecular complex precipitated when acetone solutions of the arene-iron salt and the donor (D) were mixed. Bis(durene)iron(II) hexafluorophosphate gave similar results with many of the donor compounds listed above. However, (arene)manganesetricarbonyl cations (arene = mesitylene, hexamethylbenzene) which closely resemble bis(arene)iron(II) cations in their reactions with nucleophiles to form cyclohexadienyl adducts, showed no tendency to form similar charge-transfer complexes with the donor species mentioned.

The molecular complexes described are stable only in the solid state. When dissolved in polar solvents, an equilibrium mixture‡ is obtained which consists almost entirely of starting materials. Thus the n.m.r. spectrum of (ferrocene)bis(hexamethylbenzene)iron(II) hexafluorophosphate in $(CD_3)_2CO$ consists of only two singlets (rel. area 5:18) corresponding to the ferrocenyl protons and the methyl protons of the complexed hexamethylbenzene respectively, neither absorption being shifted from its literature value. The colours of the individual complexes are highly dependent on the electron density in the donor molecule as well as in the complexed arene, as expected, ranging from pink (D = benzene), to purple (D = *NN*-dimethylaniline), to blue (D = *p*-phenylenediamine) as the electron-donating ability of D is increased. Also, the colours of the bis(arene)iron(II) hexafluorophosphate adducts with ferrocene vary from brick-red (arene = hexamethylbenzene) to dark green (arene = durene) indicating varying degrees of charge transfer as substituents on the arene ring are changed.

In all cases, complex formation was completely reversible and both starting materials could be recovered quantitatively by dissolution of the 1:1 complexes in acetone or acetonitrile followed by precipitation of the arene-iron salt with ether. The donor compound could then be isolated from the filtered solution, usually simply by evaporation. Since the solubility of these complexes in acetone varies considerably and is greatly influenced by substitutents on the aromatic portion of the donor molecule, we have been able to use these complexes to effect simple separations of some closely related compounds. For example, phenanthrene was separated from anthracene by virtue of the differing solubility products of their complexes, and *NN*-dimethylaniline could be quantitatively removed from solutions of 2,6-dimethylaniline since the ring methyl groups in the latter compound inhibit complex formation.

The complexes containing ferrocene are particularly interesting since they should have the structure (I) by analogy with the known ferrocene adduct of tetracyanoethylene.[3] Such an unusual stacking of rings has not been reported previously. A crystal structure determination is in progress.

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† All compounds gave satisfactory microanalysis.

‡ Supported by u.v.–visible spectral data which will be discussed in detail elsewhere.

[1] See, for example, C. K. Prout and J. D. Wright, *Angew. Chem. Internat. Edn.*, 1968, **7**, 659.

[2] D. Jones, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1962, 4458; J. F. Helling and D. M. Braitsch, *J. Amer. Chem. Soc.*, 1970, **92**, 7207.

[3] E. Adman, M. Rosenblum, S. Sullivan, and T. N. Margulis, *J. Amer. Chem. Soc.*, 1967, **89**, 4540.