C_5R_5–Iron Complexes (R = H or Me) of Polyaromatic Hydrocarbons: Stabilization of the Monoreduced State and Large Variation of Spin Distribution as a Function of the Ligand Structures

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Several new polyaromatic iron complexes have been synthesized with C_5H_5 or C_5Me_5 ligands and the synthesis of others is much improved using molten components; cyclic voltammetry shows a considerable stabilization of the Fe^I state by permethylation of the C_5H_5 ligand, and a wide range of spin distribution on the polyaromatic ligand: biphenyl $\sim$ triphenylene $\leqslant$ naphthalene $<$ phenanthrene $<$ pyrene $<$ perylene $\leqslant$ corronene, is found for the C_5H_5 complexes only.

Polyaromatic substrates are of importance in geochemistry,[1] cancer studies,[2] spectroscopy of stars,[3] material science[4] (liquid crystals, semiconductors, photochromes, and fluorescent and luminescent agents), and graph theory,[5] among other areas, yet very few transition metal complexes are known, essentially only with $Cr(CO)_3$[6] and $(C_5H_5)Fe^+$.[7—10] We report here the synthesis of a series of $(C_5Me_5)Fe^+$ polyaromatic complexes and propose an improved synthetic method of the C_5H_5 complexes in the melt. We have recorded cyclic voltammograms for both series (C_5H_5 and C_5Me_5) of

Table 1. Synthetic data for $[\mathrm{Fe^{II}}(C_5R_5)(\text{polyaromatic})]^+$ $[PF_6]^-$ complexes (R = H or Me), first reduction potentials, and spin density on the polyaromatic ligands in the mono-reduced complexes.

	Synthesis		First reduction potential			
			Iron complex		Rev.	
	Ref.	This work, % yield	Ref.	This work[a]	i_a/i_c[b]	d[c] on Ar
$[\mathrm{Fe^{II}}(C_5H_5)(\text{benzene})]^+$ (**1**)	7		20, 24	−1.36	0.8	10—15% [14–19]
$[\mathrm{Fe^{II}}(C_5H_5)(\text{biphenyl})]^+$ (**2**)	7,8		20	−1.27	0.8	10—30%
$[\mathrm{Fe^{II}}(C_5H_5)(\text{naphthalene})]^+$ (**3**)	7,8,9a	—[d]	20	−1.00	0.9	15—35%
$[\mathrm{Fe^{II}}(C_5H_5)(\text{phenanthrene})]^+$ (**4**)	7,8,9e	62	20	−1.07	0.83	40—60%
$[\mathrm{Fe^{II}}(C_5H_5)(\text{triphenylene})]^+$ (**5**)	—	74		−1.14	0.77	10—30%
$[\mathrm{Fe^{II}}(C_5H_5)(\text{pyrene})]^+$ (**6**)	8,9f	74		−1.10	0[e]	55—75%
$[\mathrm{Fe^{II}}(C_5H_5)(\text{perylene})]^+$ (**7**)	—	10		−0.8	0.73	70—90%
$[\mathrm{Fe^{II}}(C_5H_5)(\text{coronene})]^+$ (**8**)	25	8		−1.07	0[e]	80—100%
$[\mathrm{Fe^{II}}(C_5Me_5)(\text{benzene})]^+$ (**9**)	13	63		−1.64	0.9	
$[\mathrm{Fe^{II}}(C_5Me_5)(\text{biphenyl})]^+$ (**10**)	—	90		−1.57	0.96	15—30%
$[\mathrm{Fe^{II}}(C_5Me_5)(\text{naphthalene})]^+$ (**11**)	10	—[d]		−1.28	1	15—30%
$[\mathrm{Fe^{II}}(C_5Me_5)(\text{phenanthrene})]^+$ (**12**)	—	7[f]		−1.36	0.75	15—30%
$[\mathrm{Fe^{II}}(C_5Me_5)(\text{triphenylene})]^+$ (**13**)	—	9[f]		−1.43	0.95	15—30%
$[\mathrm{Fe^{II}}(C_5Me_5)(\text{pyrene})]^+$ (**14**)	—	7[f]		−1.32	0.85	15—30%

[a] E_p values determined by cyclic voltammetry (DMF, 0.1 M $\mathrm{Bu^n{}_4N^+}$ PF_6^-, Hg cathode, −30 °C) *vs.* standard calomel electrode (S.C.E.) using ferrocene as internal reference. [b] The ratio i_a/i_c indicates chemical reversibility (values from this work) for a scan rate of 0.3 V s^{-1}. [c] d = spin density on the polyaromatic ligand in the monoreduced state, (see text). Differences ΔE are extracted from the same literature reference for each pair of free polyaromatic compound; there are many reports[23] and the values of difference ΔE taken to calculate d are average values, but the variation of differences are small: pyrene–perylene, 0.41 V; pyrene–phenanthrene, 0.34 V; phenanthrene–perylene, 0.72 V; naphthalene–pyrene, 0.43 V; naphthalene–perylene, 0.83 V; triphenylene–perylene, 0.72 V; triphenylene–pyrene, 0.36 V. [d] Kindly provided by Dr. V. Guerchais. [e] Some degree of reversibility appears only at temperatures lower than −30 °C, *e.g.* ~30% at −60 °C on Pt. Thermodynamic potentials are thus always accessible. One only needs the chemical process C (following the electron transfer E) to be not too fast in order to obtain correct values of thermodynamic potentials. [f] Unoptimized yield (only one synthesis on a 1 or 2 mmol scale).

polyaromatic iron complexes and find that (i) using 'Vlček's theory,'[11] large variations of spin density on the polyaromatic ligand in the monoreduced complexes are found only for the C_5H_5 series; (ii) the reversibility of the first one-electron reduction is considerably increased in the C_5Me_5 series and truly 19-electron complexes are stabilized with C_5Me_5.

Since the first report of an iron–polyaromatic complex,[7] $[\mathrm{Fe^{II}}(C_5H_5)(\eta^6\text{-naphthalene})]^+$ BF_4^-, by Nesmeyanov, three groups[8—10] have published a number of $[\mathrm{Fe^{II}}(C_5H_5)(\eta^6\text{-polyaromatic})]^+$ PF_6^- compounds. Anthracene has been found to be completely hydrogenated in the 9,10-positions in its (C_5H_5)Fe complex[9] whereas hydrogenation essentially occurs on the outer ring in C_5Me_5 analogues.[10] Hydrogenation was also reported for phenanthrene and pyrene[9] during the complexation [$(C_5H_5)_2$Fe, $AlCl_3$, Al] but we find that this is not the case. In addition we find that complexation of polyaromatic compounds by $(C_5H_5)Fe^+$ proceeds best in the melt at 120—140 °C, leading to much higher yields and cleaner reactions than in solution (the alkanes used as solvents most often contain aromatic components such as tetralin *etc.*, which presumably contributed to the erroneous reports mentioned above). We also made the new perylene complex which appears to be extremely light sensitive (Table 1). Its *X*-ray crystal[12] structure will be reported elsewhere.

Since we found that aromatic compounds (C_6H_6 or C_6Me_6) are conveniently complexed by $(C_5Me_5)Fe^+$ using $[\mathrm{Fe^{II}}(C_5Me_5)(CO)_2]_2$ + $AlCl_3$[13] at 100—110 °C, we have reported $(C_5Me_5)Fe^+$–naphthalene and derivatives,[10] although these latter reactions gave low yields. We now find that other polyaromatic compounds can similarly be complexed by $(C_5Me_5)Fe^+$, but without hydrogenation (except perylene). The new orange, crystalline complexes of phenanthrene, pyrene, triphenylene, and biphenyl are obtained in modest yields (Table 1) and are not light sensitive, contrary to all C_5H_5 analogues.† Comparison of cyclic voltammograms shows that the first one-electron reduction is much more chemically reversible with C_5Me_5 compounds than with the C_5H_5 analogues. This trend is especially marked with large polyaromatic compounds for which one-electron reduction of C_5H_5 compounds is highly irreversible in dimethylformamide (DMF) (Table 1).

One-electron reduction of $[\mathrm{Fe^{II}}(C_5H_5)(\eta^6\text{-arene})]^+$ complexes (arene = monoaromatic) is known to give $\mathrm{Fe^I}$ compounds having a largely metal based $e^*{}_1$ HOMO.[14] Mössbauer studies[15], *X*-ray crystal structures,[16] He I photoelectron spectroscopy,[17] ^1H and ^{13}C paramagnetic n.m.r.,[18] e.s.r.,[19] and electrochemical studies[13,20] all confirm this statement, also in agreement with EHT SCC and X α calculations.[21] Vlček's theory[11] can be used to calculate the ligand character d in the HOMO if the reduction potentials ($E_{\frac{1}{2}}$) are known for two closely related ligands L_1 and L_2 and their complexes ML_1 and ML_2 [equation (1)].

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† Analytical data including ^1H and ^{13}C n.m.r. spectra of the cations showing their structures will be reported in the full paper.

$$d = \frac{E_{\frac{1}{2}}(\mathrm{ML_1}) - E_{\frac{1}{2}}(\mathrm{ML_2})}{E_{\frac{1}{2}}(\mathrm{L_1}) - E_{\frac{1}{2}}(\mathrm{L_2})} \qquad (1)$$

Gubin used this theory[20] for complexes $[\mathrm{Fe^{II}}(\mathrm{C_5H_5})(\mathrm{arene})]^+$ of simple arenes but the deduced value of 20% would only be valid if complexes of similar d values are considered. INDO calculations by Clack and Warren[22] predicted the instability of $[\mathrm{Fe^I}(\mathrm{C_5H_5})(\eta^6\text{-}\mathrm{C_6H_6})]$ based on the fact that the HOMO is an e_2 ligand-based orbital rather than the metal-based e^*_1. Although this was not confirmed for the C_6H_6 ligand, it could well become true when the enlargement of the aromatic delocalization lowers the level of the e_2 orbital. Re-using more confidently Vlček's equation indicates a wide range of spin density as a function of the polyaromatic size and structure in the C_5H_5 series (Table 1). The e.s.r. spectra of $\mathrm{Fe^I}$ complexes of naphthalene, phenanthrene, triphenylene, and biphenyl, [generated from the $\mathrm{Fe^{II}}$ cationic complexes (Table 1) and $\mathrm{LiAlH_4}$ at −80 °C in tetrahydrofuran (THF)] show the usual three g values close to 2 indicating a singly occupied doubly degenerate e^*_1 state as for $[\mathrm{Fe^I}(\mathrm{C_5H_5})(\mathrm{C_6H_6})]$ and related metal centred radicals. On the other hand, the e.s.r. spectra of the monoreduced complexes of perylene and coronene show only one signal around 2, a new trend not observed before, which could be attributable to $(\mathrm{C_5H_5})\mathrm{Fe^{II}}$ complexes of polyaromatic radical anions. Note that these complexes are the ones which have a spin density on the polyaromatic component significantly higher than on Fe from our present data using Vlček's equation. On the other hand, Table 1 also shows that C_5Me_5 complexes always have a reduced spin density (15—30%) on the polyaromatic ligand. Thus the monoreduced C_5Me_5 compounds are all true 19-electron complexes with an essentially metal-based e_1^* HOMO, which provides kinetic stability (*cf.* concept of electron reservoir[14,16]). This finding should open the route to the isolation of stable $\mathrm{Fe^I}$ polyaromatic complexes, also possibly with more than one metal. We are currently working along these lines in order to search for polyaromatic polymetal compounds with unusual physical properties.

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