Syntheses, Characterizations, and Stereoelectronic Stabilization of Organometallic Electron Reservoirs: The 19-Electron d^7 Redox Catalysts η^5-$C_5R_5Fe^I$-η^6-$C_6R'_6$[1]

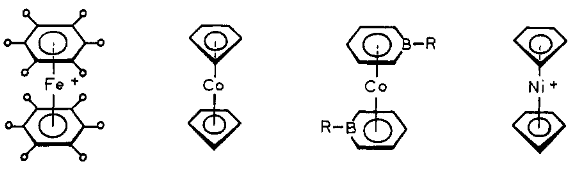
Jean-René Hamon,[2a,3a] **Didier Astruc,***[2b,3a] **and Pascal Michaud**[3a,b]

Contribution from the Laboratoire de Chimie des Organométalliques, Université de Rennes, 35042 Rennes Cedex, and Groupe de Physique et Chimie du Solide, Université du Maine, 72017 Le Mans Cedex, France. *Received May 19, 1980*

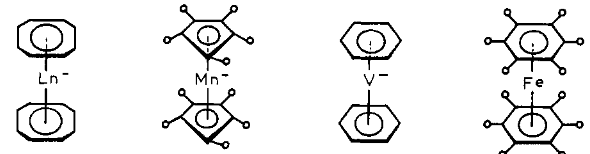
Abstract: The stabilization of electron-rich neutral sandwiches has been investigated to provide suitable reagents for catalytic and stoichiometric electron-transfer processes of synthetic and mechanistic interest. The neutral η^5-CpFe-η^6-arene series is sterically stabilized by peralkylation of the arene and electronically destabilized by peralkylation of Cp. The dark forest green complexes η^5-CpFe-η^6-C_6Me_6 (**1**), η^5-CpFe-η^6-C_6Et_6 (**2**) and η^5-C_5Me_5Fe-η^6-C_6Me_6 (**3**) ($E_{1/2} = -1.8$ to -1.9 V vs. SCE in aqueous LiOH (0.1 N)) are synthetized with good yields by Na/Hg reduction of their cationic precursors in DME at 20 °C, crystallized, and characterized by elemental analyses, optical, EPR, NMR, and Mössbauer spectroscopies, and magnetic susceptibility ($\mu = 1.70$–$1.84\ \mu_B$). Both stable and unstable η^5-CpFe-η^6-arene are d^7 19-electron complexes of Fe(I) (^2E). The near degenerate HOMO e^*_1 is approximately three-fourths metal based (contrary to recent predictions) and has slightly more Cp than benzene character. The rhombic distortion due to the single occupancy of e^*_1 is static up to 20–30 K and nearly fully dynamic at 293 K (e^*_1 splitting = 100–140 cm^{-1}). $CpFe^IC_6H_{6-n}Me_n$ (**5**, $1 \leq n \leq 5$) dimerize thermally (−20 °C) through the arene ring in the condensed state more rapidly than $CpFeC_6H_6$ (**4**). This process follows an intramolecular electron transfer from Fe(I) to an arene C. The favorable influence of Me groups cannot be taken into account by an electronic effect in the ground state but can be taken into account by lowering the transition state. This is best observed with $C_5Me_5Fe^IC_6H_6$ (**6**) (stable in DME at −20 °C) which cannot be obtained in the condensed state (contrary to **1**–**5**) since removing the solvent gives the orange dimer (η^5-$C_5Me_5Fe^{II}$-η^5-C_6H_6-$)_2$ even at −80 °C. Electron reservoirs are the reduced forms of totally reversible redox systems having very negative redox potentials. Therefore the stable $C_5R_5Fe^IC_6R'_6$ (e.g., with R′ = Me or Et) corresponds well to this definition insofar as they are efficient redox catalysts and are among the most electron-rich neutral species known to date.

Although much work has been carried out on the electrochemistry of organometallic complexes[4] and metallocenes,[5] few electron-rich metal sandwiches have so far been isolated.[6] It is however of major interest to bring about ready syntheses of electron-rich complexes which can be isolated in both reduced and oxidized forms. Useful applications are expected if the redox potential of such a system is very negative and if the reduced form is not sensitive to decomplexation or dimerization. Then it can be called, in our sense, an "electron reservoir". The expected properties are the ability of these systems (a) to render feasible studies of stoichiometric electron-transfer reactions with substrates having various redox potentials and (b) to behave catalytically in electron-transfer processes. Although clusters and metal chelates also present interesting redox properties, changes in oxidation levels involve orbitals of high metal character for the clusters[7] and of high ligand character for chelates.[8] Thus, highly reduced species of this type often have high spin density on the periphery inducing decomposition. On this basis, clusters and chelates are unsuitable as starting points for the synthesis of electron reservoirs. Furthermore, many transition-metal sandwiches can also be discounted. No sandwich compound with more

Scheme I



d^7 sandwiches



Ln.Ce,Pr,Nd,Sm,Tb.

electron-rich sandwiches

o—:CH_3

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[1] Organometallic Electron Reservoirs. 3: part 1, ref 17; part 2, ref 21.

[2] (a) D.G.R.S.T. Fellow 1979–1981. (b) C.N.R.S. Fellow 1978–1982.

[3] (a) Laboratoire de Chimie des Organométalliques, ERA CNRS No. 477. (b) Laboratoire de Spectrométrie Mössbauer, ERA CNRS No. 482.

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Scheme II

$$[C_5Me_5Fe(CO)_2]_2 \xrightarrow{Br_2} C_5Me_5Fe(CO)_2Br \xrightarrow[AlCl_3]{arene} C_5Me_5Fe^+(arene)$$

arene = C_6H_6,[27] C_6Me_6

than 18 electrons is known for second- and third-row transition metals. Attempts to prepare a 19-electron species give rise to dimers,[9] and the expected 20-electron complexes turned out to follow the 18-electron count, due to partial decoordination.[10] By contrast, several examples of metal sandwiches with more than 18 electrons are known for the first-row transition metals, but curiously, they have low redox potentials ($E°$): Cp_2Ni/Cp_2Ni^+ (20 e^-/19 e^-),[5b,d] $(C_6Me_6)_2Fe^+/(C_6Me_6)_2Fe^{2+}$ [11] and $(C_5H_5BR)_2Co/(C_5H_5BR)_2Co^+$mtc[12] (19 e^-/18 e^-) have $E°$'s in the range −0.4 to −0.6 V vs. SCE. The 18 e^-/19 e^- system Cp_2Co/Cp_2Co^+ [13] has a somewhat more negative $E°$ (−1 V vs. SCE), but its reaction with O_2 is a coupling that gives the peroxide (CpCo-η^4-Cp–O–)$_2$.[14] The stability of the first-row transition-metal sandwiches which violate the 18-electron rule arises because they often have largely metal-based HOMO's.[15] Note, however, that, for instance, $CpCrC_7H_7^-\cdot$ was shown by EPR to have C_7H_7-based spin density[16] and could therefore not be isolated. Interesting examples of isolated electron-rich metal sandwiches are the bis(cyclooctatetraenyl) lanthanides,[6a,b] the bis(benzene)vanadium anion,[6c] the recently reported bis(pentamethylcyclopentadienyl)manganese anion,[6d,e] and the 20-electron complex bis(hexamethylbenzene)iron.[16] Only the latter bears more than 18 electrons, and the class of highly reduced metal sandwiches does not necessarily correspond to a more than 18-electron count (Scheme I).

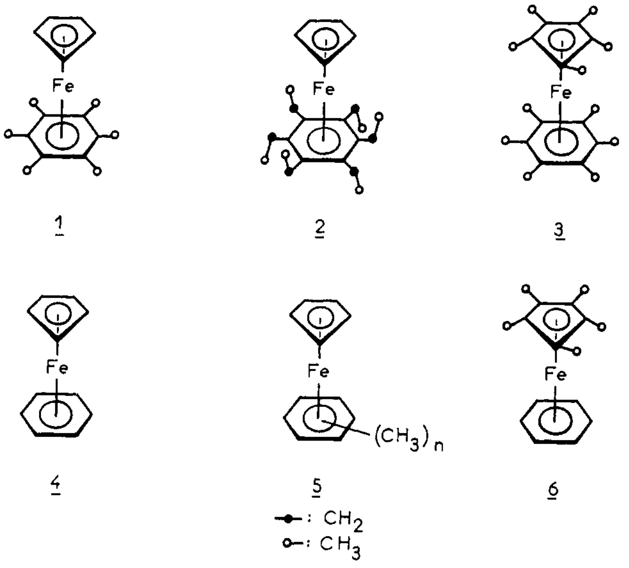
We are reporting here the syntheses, stabilization, and full characterization of a series of 19-electron mixed sandwiches of the general formula $C_5R_5FeC_6R'_6$. These sandwiches are electron rich and undergo interesting stoichiometric and catalytic electron transfer reactions such as the activation of O_2[17] via $O_2^-\cdot$ and the catalytic electroreduction $NO_3^- \rightarrow NH_3$.[18] Russian authors have reported $CpFeC_6H_6$[19] and some of its analogues,[20] but their unstabilities presumably precluded elemental and extensive spectral analyses.

Scheme III

$$CpFe^+(arene)X^- \xrightarrow[DME,\ 25\ °C]{Na/Hg} CpFe^I(arene)$$

$X^- = BF_4^-$ or PF_6^-

Scheme IV



A preliminary account of this work has appeared,[21] and the crystal structure of $CpFe^IC_6Me_6$ confirms that it is a 19-electron complex, both rings being planar and parallel[21,22] (thus CpFe(arene) = η^5-C_5H_5Fe-η^6-arene throughout this paper).

Results

Cationic Precursors. $CpFe^+C_6H_n(CH_3)_{6-n}X^-$ ($X^- = BF_4^-$ or PF_6^-, n = 0–6) have been synthetized by ligand exchange between ferrocene and the arene,[23] the yield being essentially quantitative if the reaction is carried out in the presence of water.[24] The new complex $CpFeC_6(C_2H_5)_6{}^+PF_6^-$ can also be synthetized according to this procedure in 44% yield after reaction overnight at 72 °C in heptane.

Although a plethora of CpFe+(arene) complexes have been reported,[23,26] no example with the ligand C_5Me_5 is known, presumably because decamethylferrocene is inert toward the lig-

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(25) Similar dealkylation was already reported to occur in the course of ligand exchange between ruthenocene and hexamethylbenzene.[24c] $C_6(C_2H_5)_6$ is much more sensitive to this side reaction than $C_6(CH_3)_6$, however.

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and-exchange reaction. We have synthetized the complexes $C_5Me_5Fe^+(arene)PF_6^-$ by the route outlined in Scheme II.

For the latter step, the solid reactants (with C_6Me_6) must be homogeneously mixed in an inert atmosphere and the reaction carried out in the melt at 125 °C since higher temperatures induce dealkylation of the arene.[25]

19-Electron Complexes (Scheme IV). When the arene is hexasubstituted, we find that Na/Hg reductions of the yellow cations $CpFe^+(arene)$ or $C_5Me_5Fe^+(arene)$ to the neutral green species (Scheme III) can be carried out at ambient temperature since these 19-electron sandwiches are thermally stable. The best solvent is dimethoxyethane. In this manner, the neutral complexes $CpFeC_6Me_6$, $CpFeC_6Et_6$, and $C_5Me_5FeC_6Me_6$ are isolated in nearly quantitative yields and recrystallized from pentane or sublimed.

We have also examined the syntheses of the whole series of 19-electron species $CpFeC_6H_nMe_{6-n}$, with n = 0–6 (Scheme IV). Only $CpFeC_6Me_6$ is stable in the solid state. All the series can be synthetized at −20 °C in DME, and the neutral complexes are not too unstable even at room temperature in this solvent, whereas they dimerize at a higher rate in the solid state (n = 1–5), mainly for n = 2, 3, and 4 (10 min at −20 °C). Thus the electronic effect of the methyl groups favors the dimerization occurring in the condensed state. On the other hand the steric effect of these methyl groups inhibits the dimerization as their number becomes close to 6. $CpFeC_6H_5CH_3$ and $CpFeC_6H(CH_3)_5$ dimerize only at −10 °C in 5–10 min and thus could be characterized as Fe(I) sandwiches by Mössbauer spectroscopy as the thermally stable analogues. The dimerization of $CpFeC_6H_6$ proceeds at a lower rate;[28,29] some disproportionation into ferrocene and metallic iron is also observed.[19] Overall, the highest rate of dimerization is observed for $C_5Me_5FeC_6H_6$. Although we could characterize it by the Mössbauer spectrum of the green frozen DME solution, all attempts to remove the solvent led to dimerization in the solid state even at −80 °C. This d^7 complex is stable in DME below −10 °C and dimerizes (50%) in 10 min in this solvent at 20 °C. Remarkably this is the only compound in the whole series for which the green solid 19-electron complex could not be obtained. The dimers are orange crystalline d^6 Fe(II) complexes (CpFe-η^5-cyclohexadienyl)$_2$ which are well characterized by NMR.[28] In their mass spectra, the molecular peaks are those of the monomers since easy splitting of the dimers occurs in the mass spectrometer. Thus the observation of the molecular peaks in the mass spectra is not specific to the monomers.

The 19-electron complexes react slowly with water, giving H_2 and the 18-electron cations. They are extremely air sensitive even at a temperature as low as −78 °C; these reactions will be described elsewhere. The complexes $CpFe^IC_6R_6$ are stable in hydrocarbon solvents and ethers but decompose immediately in CH_3CN at 20 °C to give ferrocene and the arene. Contrary to the d^6 $CpFe^+(arene)$ salts,[57,77–79] the neutral d^7 complexes $CpFeC_6R_6$ (R = alkyl) are inert to UV irradiation (pentane, 240 nm).

Electrochemical and Spectroscopic Data

The thermally stable complexes **1–3** have been characterized by elemental analysis, mass spectra, infrared spectra, EPR, ^1H and ^{13}C NMR, magnetic susceptibility, redox potentials, and visible and Mössbauer spectra. Studies of crystal structures of **1** at 205 and 298 K are in progress.[22]

We have also characterized the thermally unstable complexes $CpFeC_6H_6$, $CpFeC_6H_5Me$, $CpFeC_6HMe_5$, and $C_5Me_5FeC_6H_6$ as Fe(I) species by means of Mössbauer spectroscopy.

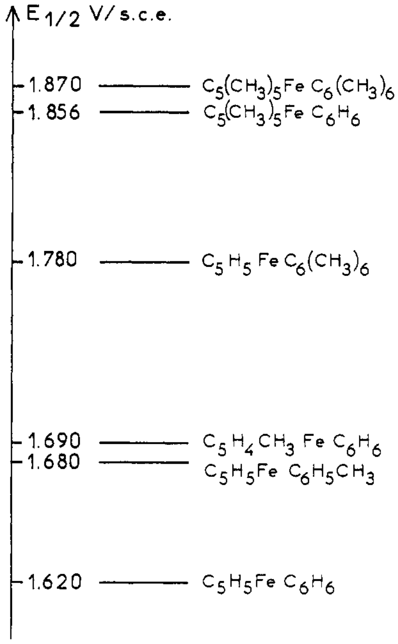

Figure 1. Polarographic $E_{1/2}$ values for the electroreduction d^6 $CpFe^+(arene)PF_6^- \rightleftharpoons d^7$ CpFe(arene) in aqueous LiOH (0.1 N). See also ref 29b.

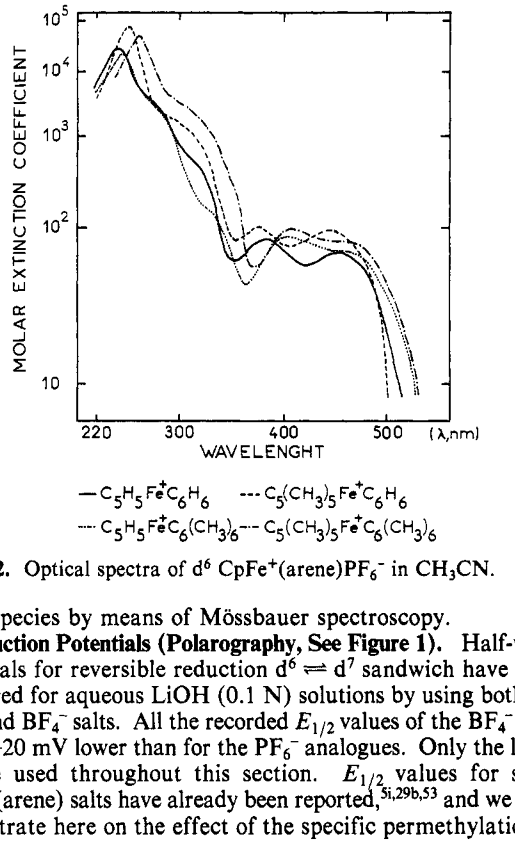

Figure 2. Optical spectra of d^6 $CpFe^+(arene)PF_6^-$ in CH_3CN.

Reduction Potentials (Polarography, See Figure 1). Half-wave potentials for reversible reduction $d^6 \rightleftharpoons d^7$ sandwich have been measured for aqueous LiOH (0.1 N) solutions by using both the PF_6^- and BF_4^- salts. All the recorded $E_{1/2}$ values of the BF_4^- salts are 10–20 mV lower than for the PF_6^- analogues. Only the latter will be used throughout this section. $E_{1/2}$ values for some $CpFe^+(arene)$ salts have already been reported,[5i,29b,53] and we shall concentrate here on the effect of the specific permethylation of Cp and arene ligands.

(1) Referring to $CpFe^+C_6H_6PF_6^-$ (−1.62 V vs. SCE), the permethylation of Cp shifts $E_{1/2}$ significantly more (5 Me, 236 mV) than the permethylation of benzene (6 Me, 160 mV), although both effects are of the same order of magnitude.

(2) The shift observed upon methylation is not proportional to the number of methyl groups added.

(a) Addition of only one Me on either ring already shifts the $E_{1/2}$ values of $CpFe^+C_6H_6$ by 60–70 mV.

(b) Permethylation of the benzene ring in $C_5Me_5Fe^+C_6H_6$ only shifts the $E_{1/2}$ values by 14 mV and permethylation of Cp in $CpFe^+C_6Me_6$ only shifts the $E_{1/2}$ values by 90 mV.

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(27) With $CpFe(CO)_2Br$, a similar route afforded the first synthesis of $CpFe^+C_6H_6$ (Coffield, T. H.; Sandel, V.; Closson, R. D. *J. Am. Chem. Soc.* **1957**, *79*, 5826). However a complicated mixture arises from this reaction because of side reactivity of the Cp group (Singer, H.; personal communication). With the use of C_5Me_5 this side reactivity is avoided.

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(29) In aqueous alcohol media $CpFe^I(arene)$ (arene : $PhMe_n$, $1 \leq n \leq 5$) are decomplexed when they are soluble whereas they dimerize when they are not, but $CpFe^IC_6H_6$ (Cp = C_5H_5 or C_5H_4Me) are decomplexed whether they are soluble or not: (a) Moinet, C.; Roman, E.; Astruc, D. *J. Organomet. Chem.* **1977**, *128*, C45–C48. (b) *J. Electroanal. Chem. Interfac. Electrochem.*, in press.

Table I. Optical Data for $CpFe^+(arene)PF_6^-$ in CH_3CN^a [λ, nm (ε, L mol^{-1} cm^{-1})]

$CpFe^+C_6H_6$ (4^+)	$C_5Me_5Fe^+C_6H_6$ (6^+)	$CpFe^+C_6Me_6$ (1^+)	$C_5Me_5Fe^+C_6Me_6$ (3^+)
239 (12 900)	252 (25 000)	244 (12 100)	258 (20 200)
261 (2600)	275 (1800)	264 (2400)	282 (2500)
312 (245)	315 (1000)	323 (160)	325 (500)
381^b (80)	375 (101)	403^c (85)	406 (99)
450 (61)	444 (95)	455 (66)	456 (77)

^{a} See also ref 73 for 1^+ and 4^+. ^{b} λ = 365 nm in THF. ^{c} λ = 380 nm in THF.

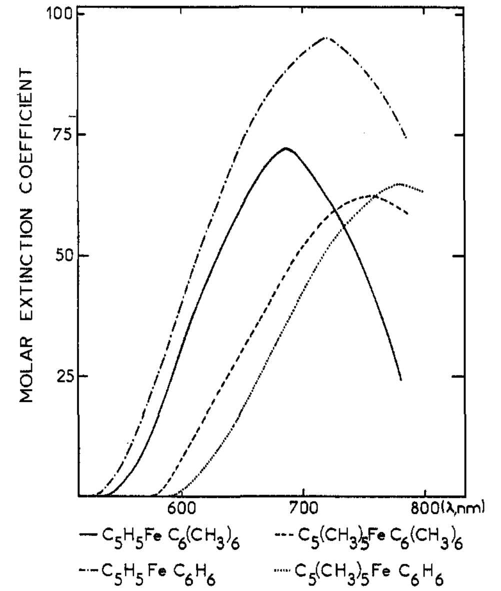

Figure 3. Optical spectra of d^7 CpFe(arene) in DME in the visible region.

Optical Spectra. d^6 Cationic Sandwiches (Figure 2). Permethylation of C_6H_6 has more influence than that of Cp on the e_2 (d_{xy}, $d_{x^2-y^2}$) MO because the $e_2(C_6H_6)$ level is closer than the e_2(Cp) level. This is clear for the band at 381 nm which is blue-shifted by 6 nm for **6** and red-shifted by 22 nm for **1**, consistently with the $e_2 \rightarrow a_2$ transition assignment.

Similarly, the quadrupole splitting of the Mössbauer doublet increases much more upon permethylation of C_6H_6 (by ≃0.4 mm s^{-1}) than upon permethylation of Cp (by ≃0.1 mm s^{-1}). This increase of the electric field gradient V_{zz} corresponds to an increase of the positive contribution $V_{zz}(e_{2g}) = {}^4/_7\langle r^{-3}\rangle$ of the d_{xy,x^2-y^2} orbitals due to a lesser delocalization of these orbitals into the ligands (less covalency).[70]

These observations are consistent with the optical data obtained by Hendrickson et al.[73] with $CpFe^+$(arene) sandwiches showing that the variation of the arene strongly perturbs the e_2 MO and not the e^*_1 LUMO.

Among the five bands recorded for these d^6 cations, the only one which is solvent dependent is the one located at 312 nm, previously assigned to a d–d transition.[73] Therefore there must be some mixing with a charge-transfer band. Since permethylation of benzene shifts this band toward red to a much larger extent than permethylation of Cp, it may be assigned to a benzene → metal transition. Finally the high-intensity bands at 239 and 261 nm were previously assigned to an intraligand $\pi \rightarrow \pi^*$ transition involving the arene.[73] These bands are shifted much more (13–14 nm) upon permethylation of Cp than upon permethylation of benzene (3–5 nm); thus this attribution must be reconsidered.

d^7 Neutral Sandwiches (Figure 3). The spectra of the extremely air-sensitive 19-electron Fe(I) series were recorded with DME solutions. A broad, low-intensity band is found specifically for this series around 700 nm, which corresponds to the dark green color of these complexes. This band is strongly shifted upon specific permethylation of either ligand. Permethylation of Cp induces a red shift from 720 nm for **4** to 782 nm for **6** whereas permethylation of benzene induces a blue shift to 684 nm for **1**. Since it is excluded that such an effect could be caused by d–d transitions, we assign this band to a spin-forbidden metal → ligand $e^*_1 \rightarrow e^*_2$ (benzene) transition. There may also be some mixing with d–d transitions (a weak shoulder is observed). The present assignment is consistent with the change in energy levels of the ligand's orbitals upon permethylation[75] (see Discussion and Figure 5). Permethylation of Cp raises e_1(Cp), which brings this orbital energy level closer to that of the d set and thus increases the covalency. The corresponding antibonding e^*_1 MO is subsequently higher in energy, whereas the e^*_2 benzene orbital level is unchanged, which decreases the energy of the transition. Permethylation of benzene substantially raises its e^*_2 level (more than that of the largely metal-based e^*_1); therefore, the transition energy is increased. One may be tempted to extend this assignment to the purple 19-electron $(C_6Me_6)_2Fe^+$ complex (560 nm). Both MO calculations[55b] and UV data[73] have pointed to a decreased interaction between the e_1 metal and ring orbitals for the 18-electron $(C_6Me_6)_2Fe^+$ complex in comparison to $FeCp_2$ and to the $CpFe^+$(arene) series. If one admits that relaxation of the orbitals, due to the presence of the nineteenth electron in e^*_1, does not change this effect, then e^*_1 is lower in $(C_6Me_6)_2Fe^+$, which is consistent with the $e^*_1 \rightarrow e^*_2$ transition following a blue shift in comparison with the case for the $CpFe^I$(arene) series.

In the UV region, it is impossible to distinguish the bands of the $CpFe^I$(arene) complexes from the intense ones of their oxidation products (of the $CpFe^{II}$ cyclohexadienyl type) which cannot be rigorously excluded at concentrations below 10^{-4} mol L^{-1} due to the extreme sensitivity of the $CpFe^I$(arene) complexes toward O_2.

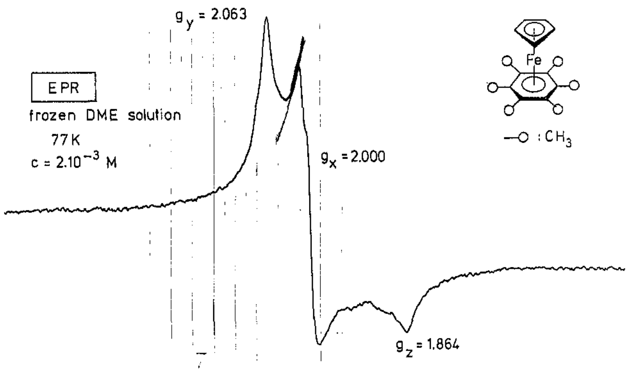

Figure 4. EPR spectrum of $CpFeC_6Me_6$.

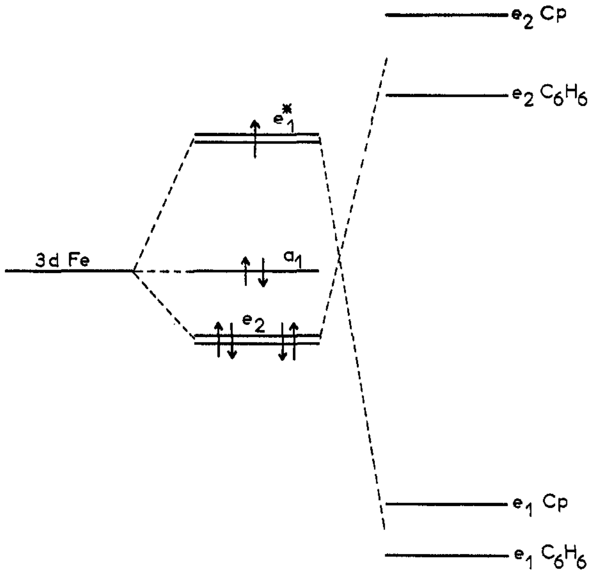

Figure 5. Molecular orbital diagram (d set) for d^7 $CpFeC_6H_6$. Note that ring levels are raised upon permethylation.

EPR (Figure 4) and Magnetic Susceptibility. The EPR of the 19-electron complexes of hexaalkylbenzene **1**–**3** have been recorded

Table II. Spectroscopic Data for the 19-Electron Fe(I) Sandwiches[a]

entry		magnetic susceptibility χ	EPR[b] g values	optical data[c]		Mössbauer parameters[d]		
				λ, nm[a]	ε, L mol^{-1} cm^{-1}	temp, K	QS, mm s^{-1}	IS, mm s^{-1}
1	$CpFeC_6Me_6$	1.84	1.864	684	68	293	0.50	0.74
			2.000	770 (s)	34	4.2	1.54	0.90
			2.063			1^+ 293	2.00	0.45
						77	2.00	0.56
2	$CpFeC_6Et_6$	1.73	1.896	684	68	293	0.50	0.75
			2.003	770 (s)	25	4.2	1.52	0.90
			2.059			2^+ 293	4.92	0.44
						77	1.92	0.55
3	$C_5Me_5FeC_6Me_6$	1.85	1.912	760	63	293	0.52	0.75
			2.002			4.2	1.50	0.90
			2.062			3^+ 293	1.80	0.47
						77	1.80	0.58
4	$CpFeC_6H_6$		2.00, 1.85[20a]	720	95	260	0.95	0.87
				768 (s)	86	4.2	1.20	0.92
			2.26, 2.006[20d]			4^+ 273	1.64	0.41
						77	1.64	0.52
6	$C_5Me_5FeC_6H_6$			782	65	77[b]	0.82	0.73
						6^+ 293	1.40	0.45
						77	1.40	0.55
			1.865	580	604	293	0.66	0.77
7	$(C_6Me_6)_2Fe^+PF_6^-$	1.89[16a]	1.996	478[16a]	416	4.2	1.70	0.91
			2.086[76]			dication		
						293	2.14	0.51
						77	2.14	0.62

[a] s = shoulder. [b] Frozen DME solution. [c] DME solution. [d] Fitted parameters (±0.01 mm s^{-1}).

in frozen dimethoxyethane only below 170 K and show three g values close to 2 very similar to those of $Fe(C_6Me_6)_2^+$ reported by Brintzinger[30] and those of $NiCp_2^+$ reported by Ammeter.[31] Powdered samples do not show any spectrum above 30 K.[32] The fast spin-lattice relaxation precluding observation of a signal at room temperature is typical for d^7 metallocenes with a singly occupied doubly degenerate e^*_{1g} level.[34] Thus the host lattice effect splits the near degeneracy of e^*_1, giving rise to a rhombic distortion (3 g values being observed).[32] That these 3 g values are close to 2 means, according to the calculations of Ammeter, that the dynamic Jahn-Teller coupling is large.[32,35] Since no coupling with the nucleus can be observed contrary to the situation encountered in cobaltocene,[31,33] only the product $kV = 0.1$ of the covalent factor k by the vibronic coupling term V can be reached but neither of them separately. Labeling with ^{57}Fe must therefore be envisaged.

The magnetic susceptibility measurements using the Gouy method on the thermally stable solids **1**–**3** indicate a Curie-Weiss behavior ($\chi^m = C/T - \Theta$) in every case, in the range 77–273 K. The moments found are close ($\mu_{eff} = 1.70$–1.84 μB) to the spin-only value for $S = {}^1/_2$, 1.73 μB, showing that the spin-orbit contributions to the moment generally observed in orbitally degenerate metallocenes[36] are small in this case.

Paramagnetic NMR. In the proton spectrum of $CpFeC_6Me_6$, the Me group shows a sharp singlet at −2.15 ppm whereas the Cp protons are found at 35.01 ppm. Remarkably neither of these values indicate a large downfield shift. NMR data for paramagnetic metallocenes[37–39] and bis(arene)metal sandwiches have been reported and analyzed. Anderson and Drago[40] concluded that little spin density was localized on the ligand in the d^7 sandwich $Fe(C_6Me_6)_2^+$. Since both σ- and π-delocalization mechanisms are expected to give downfield shifts for the methyl groups of arene ligands, no net spin is delocalized onto these methyls and the nineteenth electron is in a molecular orbital of high metal character as for $Fe(C_6Me_6)_2^+$. Moreover the observation of a sharp resonance is consistent with a dynamic Jahn-Teller distortion for both $Fe(C_6Me_6)_2^+$ and $CpFeC_6Me_6$. Similar conclusions are drawn from the ^{13}C spectrum (ring carbons, 449 and 584 ppm; CH_3, −35.9 ppm).[41]

Mössbauer Spectroscopy. There are no reports of a Mössbauer spectroscopic study of organometallic iron(I) sandwiches.[42,43] The parameters observed at 293 K are very different from those of the Fe(II) precursors and are specific for the Fe(I) series (IS = 0.73–0.75 mm s^{-1}; QS = 0.5–0.6 mm s^{-1}). Since the monoelectronic 3d function is ≃2 mm s^{-1} for a degenerate e^*_{1g} MO,[44] the difference between the QS value of the Fe(I) sandwiches and those of their Fe(II) cationic precursors gives an opportunity of calculating 1.3–1.5/2 = 65–75% metal character for the antibonding HOMO e^*_{1g} of the nineteenth electron. This calculation[46] is only approximate, however, as it does not take into account the relaxation of the other filled orbitals.[45]

The QS values vary with temperature and reach a limiting the same of 1.5 mm^{-1} at 4 K for the stable Fe(I) complexes **1**–**3**. Despite its thermal unstability, $CpFeC_6H_6$ could be examined by Mössbauer spectroscopy in the solid state. Its spectra show slightly lower QS values (0.4 mm^{-1} at 293 K, 1.2 mm^{-1} at 4 K) and the

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(30) Brintzinger, H.; Palmer, H.; Sands, R. A. *J. Am. Chem. Soc.* **1966**, *88*, 623.

(31) Ammeter, J. H.; Ostwald, N.; Bücher, R. *Helv. Chim. Acta* **1975**, *58*, 671–682.

(32) Ammeter, J. H.; personal communication.

(33) Ammeter, J. H.; Swalen, J. D. *J. Chem. Phys.* **1972**, *57*, 678–698.

(34) Warren, K. D. *Struct. Bonding (Berlin)* **1976**, *27*, 45–159.

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(37) Fritz, H. P.; Keller, H. J.; Schwarzhans, K. E. *J. Organomet. Chem.* **1967**, *7*, 105–111.

(38) Köhler, F. H. *J. Organomet. Chem.* **1976**, *110*, 235–236.

(39) Rettig, M. F.; Drago, R. S. *J. Am. Chem. Soc.* **1969**, *91*, 1361–1370, 3432–3441.

(40) Anderson, S. E.; Drago, R. S. *J. Am. Chem. Soc.* **1969**, *91*, 3656–3658; *Ibid.* **1970**, *92*, 4244–4254.

(41) Cozak, D.; Beauchamp, A. L.; Hamon, J.-R.; Astruc, D., work in progress.

(42) For rare known examples of Fe(I) complexes, see: (a) Murdock, H. D.; Lucken, E. A. C. *Helv. Chim. Acta* **1964**, *47*, 1517–1524; (b) Mutterties, E. L.; Sosinsky, B. A.; Zamaraev, K. I. *J. Am. Chem. Soc.* **1975**, *97*, 5299–5300; (c) Rakowski, M. C.; Busch, D. H. *Ibid.* **1975**, *97*, 2570–2571; (d) Gargano, M.; Giannocarro, P.; Rossi, M.; Vasapello, G.; Sacco, A. *J. Chem. Soc., Dalton Trans.* **1975**, 9–12.

(43) For preliminary accounts of this Mössbauer study, see: ref 21; (a) Mariot, J.-P.; Astruc, D.; Batail, P.; Varret, F. "Mössbauer Discussion Group of the Chemical Society"; London, Nov 23 1978; Abstr p 1–2; (b) Michaud, P.; Mariot, J.-P.; Varret, F.; Hamon, J.-R.; Althoff, G.; Astruc, D. *Ibid.* Canterbury, 1979, Abstr p 1–2; International Conference Mössbauer Spectroscopy"; Porto-Roz, Sept 1979; *J. Phys. C* **1980**, *1*, 319–320.

(44) Varret, F. *J. Phys. C* **1976**, *6*, 437–456.

(45) The problem of the relaxation was first taken into account for ferrocene from a theoretical standpoint by: Coutière, M.-M.; Demuynk, J.; Veillard, A. *Theor. Chim. Acta* **1972**, *27*, 281–287.

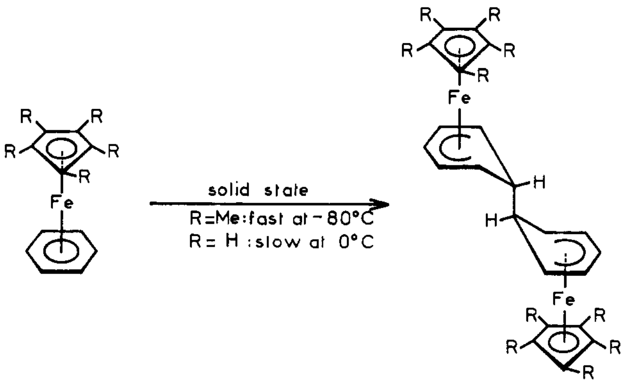
difference between the QS values of the Fe(I) and Fe(II) sandwiches is also lower. Mössbauer spectroscopy was also a useful tool to characterize the Fe(I) sandwiches $CpFeC_6H_5Me$ and $CpFeC_6HMe_5$ in the solid state and $C_5Me_5FeC_6H_6$ in frozen DME solution. The parameters are the same as for the stable analogues with a similar electronic structure. Isomer shifts are constant along the Fe(I) series, and the difference between the values of the Fe(I) and Fe(II) sandwiches is 3 times larger (0.3 mm s^{-1}) than between those of Cp_2Fe and Cp_2Fe^+ (0.1 mm s^{-1}).[46] This is in agreement with a large metal character for e^*_1. The temperature dependance of QS for all the Fe(I) complexes is sensitive to substituents. It is connected to the rhombic distorsion becoming fully dynamic as the temperature is raised.[47] The thermal population of the lower Kramers' doublet corresponds to a splitting of e^*_1 which is reduced to 100–140 cm^{-1} by the dynamic Jahn–Teller effect.

We also find that the 19-electron d^7 complex $(C_6Me_6)_2Fe^+PF_6^+$ presents the same behavior as the d^7 CpFe(arene) series, e.g., parameters in the same range and temperature dependence of QS indicating similar electronic structure and Jahn–Teller activity.[43b]

Discussion

The CpFe(arene) series provides great possibilities for syntheses since many arenes and polyarenes[49] are complexable in this fashion. In particular functional substituents[48] may be introduced to the Cp or arene ring of $CpFe^+$(arene) by oxidation,[50] nucleophilic substitution,[51] or benzylic activation.[52] Moreover we have brought about a satisfactory route to $C_5Me_5Fe^+$(arene) complexes. These features are also useful from a practical standpoint. For example, a convenient introduction of a carboxylate group[18a] affords water-soluble redox catalysts in this series. The electroreduction of the cations $CpFe^+$(arene) to the neutral species has been shown to be highly reversible;[53] therefore, the isolation of these latter complexes was brought about. However, not unexpectedly,[37,54] $CpFeC_6H_6$ was found[19] to be thermally unstable. That only two EPR *g* values were observed by Nesmeyanov et al.[20a] is in conflict with the expected distortion of a d^7 system and may be attributed to experimental difficulties related to this unstability. From the QS values found in the Mössbauer spectra, we deduce that $CpFeC_6H_6$ is d^7 as well as thermally stable analogues $CpFe^I$(hexaalkylbenzene).

Scheme V



The molecular orbital ordering for the late transition-metal metallocenes and bis(arene) has been established[55] and is in agreement with our findings. The order is e_2 (d_{xy}, $d_{x^2-y^2}$) < a_1 (d_{z^2}) < e^*_1 (d_{xz}, d_{yz}). See Figure 5.

The antibonding e^*_{1g} orbital lies well above the nonbonding a_{1g} orbital. According to INDO SCF calculation of Warren[56] on $CpFeC_6H_6$, the benzene e_2 level lies on the same level or slightly under this e^*_1 level so that the spin would be localized on the benzene ligand and the complex would be d^6 instead of d^7.

Ligand Character in the e^*_1 Level. Our Mössbauer, EPR, and NMR data indicate that the e^*_1 HOMO of the 19-electron Fe(I) complexes has a high metal character. This is in accord with semiempirical extended Hückel calculations (in conflict with Warren's predictions[56]). Although e^*_1 is the more covalent of the three sets of d orbitals (from semiempirical calculations and optical data) in the d^6 as well as in the d^7 sandwiches, the optical and Mössbauer spectra also indicate that e^*_1 is much less sensitive to benzene substituents than the e_2 MO. A probable explanation for this apparent contradiction is that there is more Cp than benzene character in e^*_1, and we shall now put forward supporting evidence for this statement.

The shifts of $E_{1/2}$ observed upon specific permethylation are a direct consequence of the covalency, e.g., of the ligand character in this orbital.[66] The ligand orbital of e_1 symmetry which mixes with the metal $d_{xz,yz}$ orbital to provide the (e_1, e^*_1) set lies far below the metal d level. Therefore any effect increasing the e_1 ligand level will improve the mixing with d(xz,yz), thus increasing the ligand character in e^*_1 while increasing its energy level. These effects are (a) the reduction of the size of the ring ($C_6H_6 \rightarrow C_5H_5$) and (b) the addition of methyl groups. From these arguments, it should follow that e^*_1 would have more Cp than benzene character.

Vlček's theory[59] allows estimating the ligand and metal "eigenvectors" in the LUMO using the $E_{1/2}$ values of the free ligand(s) and of the complex. This theory was used by Gubin et al. to calculate 20% of benzene character in the LUMO of the $CpFe^+$(arene) series.[60] However this estimate was based on

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(46) (a) Collins, R. L. *J. Chem. Phys.* **1965**, *42*, 1072–1080; (b) Greenwood, N. N.; Gibb, T. C. "Mössbauer Spectroscopy"; Chapman and Hall: London, 1971; p 234.

(47) With **1**, a splitting of the quadrupole doublet is observed at 77 K. This is best explained in terms of two sites with different asymmetries of the external potential, due to a peculiar packing arrangement. These solid-state interactions will be described in detail. Mössbauer and EPR studies in various host lattices and in various aromatic and aliphatic frozen solvents with natural abundance and ^{57}Fe-enriched mono- and polycrystalline samples are in progress.[43]

(48) Arenes bearing alkyl, phenyl, methoxy, and amino groups have been complexed. With functional groups bearing CO, the complexation is inhibited. However the introduction of such a function is feasible after complexation.[26a]

(49) (a) Morrison, W. H.; Ho, E. Y.; Hendrikson, D. N. *J. Am. Chem. Soc.* **1974**, *96*, 3603–3608. (b) Sutherland, R. G.; Chen, S. C.; Pannekoek, W. J.; Lee, C. C. *J. Organomet. Chem.* **1975**, *101*, 221–229. (c) Lee, C. C.; Demchuk, K. J.; Pannekoek, W. J.; Sutherland, R. G. *Ibid.* **1978**, *162*, 253–269. (d) Sutherland, R. G.; Pannekoek, W. J.; Lee, C. C. *Can. J. Chem.* **1978**, *56*, 1782–1787. (e) Lee, C. C.; Demchuk, K. J.; Sutherland, R. G. *Ibid.* **1979**, *57*, 933–936. (f) Schmitt, G.; Keim, W.; Fleischhauer, J.; Walbergs, U. *J. Organomet. Chem.* **1978**, *152*, 315–327.

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(51) (a) Nesmeyanov, A. N.; Vol'kenau, N. A.; Bolesova, I. N. *Dokl. Akad. Nauk SSSR* **1967**, *175*, 606–609. (b) Nesmeyanov, A. N.; Vol'kenau, N. A.; Isaeva, L. S. *Ibid.* **1967**, *176*, 106–109. (c) Khand, I. U.; Pauson, P. L.; Watts, E. W. *J. Chem. Soc. C* **1969**, 2024–2030. (d) Helling, J. F.; Hendrikson, W. A. *J. Organomet. Chem.* **1977**, *141*, 99–105, **1979**, *168*, 87–95. (e) A great number of arene syntheses have been performed using such reactions in (arene)Cr(CO)$_3$ series: Semmelhack, M. F. *Ann. N.Y. Acad. Sci.* **1977**, *295*, 36–51 and references cited therein.

(52) See: ref 17; also (a) Jaouen, G.; Meyer, A.; Simonneaux, G. *J. Chem. Soc., Chem. Commun.* **1975**, 813–814; (b) Simmoneaux, G.; Jaouen, G. *Tetrahedron* **1979**, *35*, 2249–2254; (c) Lee, C. C.; Steele, B. R.; Demchuk, K. J.; Sutherland, R. G. *Can. J. Chem.* **1979**, *57*, 946–948; *J. Organomet. Chem.* **1979**, *181*, 411–424; (d) Johnson, J. W.; Treichel, P. M. *J. Chem. Soc., Chem. Commun.* **1976**, 688–689; (e) *J. Am. Chem. Soc.* **1977**, *99*, 1427–1436.

(53) (a) Astruc, D.; Dabard, R.; Laviron, E. "Proceedings of Fourth International Conference on Organometallic Chemistry"; Bristol, Sept 1969; Abstr B2; *C.R. Hebd. Seances Acad. Sci., Ser. C* **1969**, *269*, 608–6. (b) Nesmeyanov, A. N.; Denisovitch, L. I.; Gubin, S. P.; Vol'kenau, N. A.; Sirotkina, E. I.; Bolesova, I. N. *J. Organomet. Chem.* **1969**, *20*, 169–176.

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(55) (a) Prins, R. *Mol. Phys.* **1970**, *19*, 603–620. (b) Anderson, S. E.; Drago, R. S. *Inorg. Chem.* **1972**, *11*, 1564–1572. (c) Anderson, S. E.; Rai, R. *Chem. Phys.* **1970**, *92*, 4831.

(56) Clark, D. W.; Warren, K. D. *J. Organomet. Chem.* **1978**, *152*, C60–C62.

(57) For example, 1^+OH^-[17] is quantitatively decomplexed after 1 min to C_6Me_6, CpH, and $Fe(OH)_2$ by UV irradiation (240 nm) of an aqueous solution. It was suggested by Russian authors that $CpFe^IC_6H_6$ is an intermediate in the photodecomplexation of $CpFe^+C_6H_6$, following a solvent to metal charge transfer.[78,79] Since **1** is stable both under UV irradiation and in aqueous LiOH,[18,29] this mechanism is not valid (but rather e_2 (d_{xy}, $d_{x^2-y^2}$) $\rightarrow$ e^*_2 (arene) MLCT).

(58) (a) Marcus, R. A.; Sutin, N. *Inorg. Chem.* **1975**, *14*, 213–219. (b) Kochi, J. K. *Acc. Chem. Res.* **1974**, *7*, 351–360.

(59) Vlček, A. A. *Z. Anorg. Allg. Chem.* **1960**, *304*, 109–115.

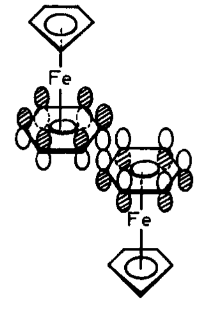
complexes of polyarenes,[61] and we now believe[32] that, in contrast to the 19-electron d^7 $C_5R_5Fe^IC_6R_6$ series, CpFe(polyarene) are d^5 rather than d^7. Indeed it is impossible to estimate the covalency of ligands such as $C_5H_5^-$, $C_5Me_5^-$, and C_6Me_6, e.g., their eigenvectors in the LUMO of CpFe$^+$(arene) series using Vlček's theory, because the half-wave potentials of these ligands are unknown. Neither is it strictly possible to use the comparison between the shifts of $E_{1/2}$ recorded upon substitution of Cp and benzene. However one may assume that the overall ligand character in e^*_1 is small (≃0.2) and that the Cp and benzene character are of the same order of magnitude. On the basis of the shifts of $E_{1/2}$ observed upon specific permethylation of Cp and benzene on one hand and secondly of the fact that the level of e_1(Cp) is higher than that of $e_1(C_6H_6)$, it is probable that the covalency of Cp is superior to that of benzene. This latter distinction might no longer be valid for $CpFe^+C_6Me_6$ since permethylation of benzene raises its e_1 level. Indeed X-ray studies have shown that the metal–Cp distance is 0.12 Å longer in $CpFe^IC_6Me_6$ than in the 18-electron complexes, whereas the metal–arene distance is only 0.04 Å longer.[67] Thus there is more Cp than benzene character in e^*_1 in **1** also, although the benzene character in e^*_1 must be larger than in the unsubstituted parent complex. That the 3d (*xz*, *yz*) metal orbitals are delocalized to a larger extent onto the Cp e_1 orbitals than onto the benzene e_1 orbitals is thus presumably the result of geometrical factors. Consistently there is also more delocalization in the e^*_{1g} LUMO in ferrocene[74] than in $(C_6Me_6)_2Fe^{2+}$.[73] The finding that e^*_1 has more Cp than benzene character will be most useful in the following discussion concerning the stereoelectronic stabilization of the CpFe^I(arene) sandwiches.

Stereoelectronic Stabilization–Destablization. Besides sensitivity to air and coordinating solvents, $CpFeC_6H_6$ is not thermally stable.[19] In pentane, or (more rapidly) in the solid state, it dimerizes through the benzene ring at ambient temperature, accordint to Scheme V.

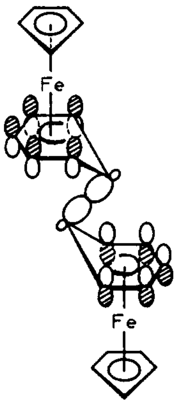
Since there is more spin density on the Cp than on the benzene ring, dimerization should occur through a Cp carbon if spin density on carbons in the ground state was the dominant factor (vide infra). Now permethylation of the Cp does lead to a much increased ability to dimerize. However this substitution substantially raises the e_1(Cp) level, giving more Cp covalency in e^*_{1g} for **6**. This is compensated by a smaller metal character in the HOMO, but the spin density on the benzene ring is the same in **6** and in the parent complex **4**.[75] Thus here again the enhanced ability to dimerize cannot be explained in terms of changes in spin densities on the benzene ligands of the two Fe(I) complexes **4** and **6** in the ground state. Remarkably, this permethylation of Cp introduces a pure electronic effect since the dimerization site is far from Cp (or C_5Me_5). Thus we have to consider electronic effects in the transition state of the dimerization pathway. This transition state is not easy to locate but may be estimated between A and B.

Why permethylation of Cp lowers the transition-state energy remains an open question. The presence of Me groups on the benzene ligand also increases the rate of dimerization although to a lesser extent (contrary to **6**, the Fe(I) monomers can be isolated at low temperature). The maximum effect is obtained with 2, 3, and 4 Me. Steric and electronic effects are combined in this latter series, but the electronic effects play the same part as with Cp substitution (vide supra).

It is noteworthy that $CpFeC_6R_6$ (R = Me or Et) do not dimerize whatever be the temperature (they can be sublimed at 70–80 °C) in spite of a spin density on Cp larger than on C_6H_6 in $C_5Me_5FeC_6H_6$. One concludes that the transition state leading to dimerization through the Cp ligand has much higher energy than the one providing dimerization through the benzene ligand. Indeed the η^4-C_5H_5R ligand is much less common than the η^5-C_6H_6R ligands. Also note that dimerization through Cp would lead to a formally d^8 Fe(0) complex whereas dimerization through C_6H_6 gives the d^6 Fe(II) configuration which is favored in these series. Rhodocene exists as a dimer and so do $Re(C_6Me_6)_2$ and $Tc(C_6Me_6)_2$. There would presumably be a too large spin density on the rings for the HOMO of the second- and third-row 19-electron sandwiches. This provides the driving force for dimerization through Cp or even through C_6Me_6 in spite of the permethylation of the benzene ring, whereas such a steric effect precisely prevents it in the CpFe^I(arene) series. Similarly cobaltocene and nickelocene exist as monomers, whereas their second- and third-row counterparts do not. In this respect, the spin density on the ligands in the ground state is all important if this spin density is very large (second and third row) but not if it is small (first row).



A



B

Jahn–Teller Effect. The relatively narrow peaks observed in NMR, the similarity of the EPR spectra with those of $Fe(C_6Me_6)_2^+$ and $NiCp_2^+$, and the fact that the QS values no longer depend on temperature at 293 K are all consistent with a dynamic rhombic Jahn–Teller effect at ambient temperature. Ammeter has shown that the Jahn–Teller effect was fully dynamic for the d^7 system Cp_2Co and $NiCp_2^+$, the distortion parameter being a fraction of a vibrational quantum of the reactive coupling mode.[35]

That the magnetic moments are very close to the spin-only values, indicating low spin–orbit coupling contribution, is consistent with a large distortion parameter (e.g., ≃2000 cm^{-1}) as assumed from the kV product, which is close to the 0.4 value calculated for $NiCp_2^+$ and $Fe(C_6Me_6)_2^+$. On the other hand Raymond et al. have found by an x-ray investigation a static distorsion at 293 K in the d^5 complex decamethylmanganocene.[62] From the Mössbauer data obtained for the $C_5H_5FeC_6R'_6$ series it appears that the distortion static only up to 20–30 K (no dependence on temperature) and then progressively becomes dynamic. However the situation may be different for dilute samples which therefore need to be examined by both EPR and Mössbauer spectroscopies. It can already be stated that great similarities are observed among the Jahn–Teller behavior of the d^7 sandwiches as noted from EPR and paramagnetic NMR[63] data.

Concluding Remarks. One of the main practical features is that localization of the spin density essentially on the metal prevents decomposition or dimerization of the sandwich and stabilizes a d^7 complex. The localization of the nineteenth electron on the metal seems quite general and specific over the series of 19-electron complexes $(C_6Me_6)_2Fe^+$, Cp_2Co, C_2Ni^+, and $(C_5H_5BR)_2Co$ as was shown by Ammeter's results[31] and can be checked by considering the thermal stability of these species. However, among this d^7 series of sandwiches, the CpFe^I(arene) complexes are the

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(60) For example, reported $E_{1/2}$ values[53b] for benzene, biphenyl, and their CpFe$^+$ complexes are respectively (vs. SCE) −3.4, −2.70, −1.45, and −1.30 V. This theory provides 3.4 − 2.7/1.45 − 1.30 ≃ 20% arene character for the LUMO of the cationic complexes.

(61) The Russian authors' estimation[53b,60] is based on $E_{1/2}$ values of benzene, fluorene, naphthalene, phenanthrene, and their CpFe$^+$ complexes. Only the results obtained with naphthalene give an arene character in the LUMO at variance with 20%. However, it has been shown since that what was believed to be (CpFe(phenanthrene))$^+$ is in fact partly hydrogenated, phenanthrene being more susceptible than naphthalene to hydrogenation during the synthesis of the CpFe$^+$(arene) complex.[49e]

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only ones having very negative redox potentials, which confer specific properties, as for instance the redox catalysis of the aqueous electroreduction of NO_3^- to NH_3[18].

The $CpFe^I$(arene) series are also unique among the 19-electron sandwiches of the first row for their strong tendency to dimerize, although their HOMO is essentially based on the metal. We have shown that electronic effects can facilitate this dimerization by lowering the transition-state energy, whereas steric effect can inhibit it, contrary to the second- and third-row series. Note that the dimerization is formally an intramolecular electron transfer Fe(I) $\rightarrow$ C(arene) as, presumably, in other decomposition processes. The driving force for such specific metal to arene electron transfers may well be the lower energy of arene orbitals as compared to Cp ones.

The large synthetic possibilities of CpFe(arene) design have afforded (i) stabilization and (ii) water-soluble redox catalysts as well as pentane-soluble electron-rich species. In both polar and nonpolar solvents, electron-transfer processes[58] can now be provided for mechanistic and synthetic purposes, as exemplified by the dramatic activation of C–H bond upon short contact with O_2 or air.[17]

Indeed, the recent photoelectron spectroscopy data obtained by Green[80] indicate that the thermally stable complexes **1**, **2**, and **3** are among the most electron-rich neutral species characterized to date, having ionization potentials close to that of potassium metal. In this respect, as well as for the reasons summarized above, we believe they specially deserve the term "electron reservoirs".

Experimental Section

General Data. Reagent grade tetrahydrofuran and 1,2-dimethoxyethane were predried on Na foil and distilled from sodium benzophenone ketyl under nitrogen just before use. Benzene and toluene were distilled and stored under nitrogen. Reagent grade pentane and hexane were degassed with nitrogen before use. 1,2,3,4,5-Pentamethylcyclopentadiene was prepared according to the method of Bercaw et al.[64] All other chemicals were used as received. All manipulations were done by Schlenk technique in a nitrogen-filled Vacuum Atmosphere Drylab or in glovebags. Infrared spectra were recorded with a Pye Unicam SP 1100 infrared spectrophotometer which was calibrated with polystyrene. Samples were prepared between KBr disks in Nujol. Proton-decoupled ^{13}C NMR spectra were obtained at 25 MHz in the pulsed Fourier transform mode with a Varian H-100 spectrometer. ^1H NMR spectra were obtained with a Varian EM 360 spectrometer. All chemical shifts are reported in parts per million (δ) with reference to tetramethylsilane and were measured relative to the solvent or Me_4Si. The usual δ convention for diamagnetic molecules with positive values increasing downfield was also used for paramagnetic complexes (Dr. D. Cozak). Bulk magnetic susceptibility measurements were made on a Bruker Magnet MB4 magnetometer. Polarographic measurements were made on PO4 Radiometer polarograph. Half-wave potentials were recorded with reference to SCE in LiOH (0.1 N). Concentrations were 5×10^{-4} M. A 1% gelatin solution was added (to remove adsorbtion peaks) until $E_{1/2}$ values remain unchanged. Mass spectra were recorded by Dr. P. Guénot at the Center of Physical Measurements of Rennes by using a Varian MAT 311 spectrometer. Ultraviolet spectra were recorded with a Beckman DB spectrophotometer. EPR spectra were recorded at Grenoble (CENG) by using a Varian E 112 spectrometer. Mössbauer spectra were recorded with a 25-mCi ^{57}Co source on Rh, using a symmetric triangular sweep mode. Thermally unstable 19-electron complexes were quickly transfered from the Schlenk tube to the Mössbauer cell by using a glovebag under argon which is cooled by passing through a plastic tube at −196 °C. Mössbauer spectra were fitted by J. P. Mariot. Elemental analyses were performed by the Center of Microanalyses of the CNRS at Lyon-Villeurbanne.

Preparations. (1) $CpFe^+C_6(C_2H_5)_6PF_6^-$. Ferrocene (2.8 g, 15 mmol), $C_6(C_2H_5)_6$ (4.9 g, 20 mmol), aluminum chloride (8 g, 60 mmol), Al powder (0.4 g, 15 mmol), and H_2O (0.27 g, 15 mmol) are mixed under N_2 and heated at 72 °C for 12 h in 50 mL of heptane. After hydrolysis at 0 °C, aqueous NH_3 is added to the aqueous layer to remove Al^{3+}, and then aqueous HPF_6 (11 mmol) is added to the filtrate to precipitate the desired salt. Reprecipitation by addition of excess ether to a CH_2Cl_2 solution provides 3.7 g (48.7% yield) of powdered salt found pure by ^1H NMR. Recrystallization from hot ethanol gives 3.4 g (44% yield) of yellow flakes after the solution was cooled and left standing overnight at −21 °C (mp 260 °C dec): IR 432 (w), 482 (w), 565 (w), 745 (w), 855 (s), 972 (m), 1045 (s), 1258 (s), 2285 (m), 2940 (w) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 4.91 (Cp, 5 H), 3.14 (q, CH_2, 12 H), 1.42 (t, CH_3, 18 H); ^{13}C NMR (CD_3CN) δ 105.4 (C_6 ring), 78.2 (Cp), 23.8 (CH_2), 16.3 (CH_3).

Anal. Calcd for $C_{23}H_{35}FePF_6$: C, 53.92; H, 6.88; Fe, 10.90. Found: C, 53.94; H, 6.89; Fe, 11.09.

(2) $C_5(CH_3)_5Fe(CO)_2Br$. To 15 g (30.4 mmol) of $[C_5Me_5Fe(CO)_2]_2$ (prepared according to the procedure of King and Bisnette[65]) in 500 mL of CH_2Cl_2 at 20 °C was added a solution of Br_2 (4.9 g, 30.4 mmol) in 10 mL of CH_2Cl_2 dropwise. The reaction was monitored by TLC (hexane/ether, 9/1). A 99% sample of crude compound is obtained after filtration and removal of the solvent in vacuo. Recrystallization from hexane gives 18.75 g (95%) of red-purple needles; mp 139 °C; IR 550 (w), 580 (m), 620 (w), 1040 (w), 1400 (m), 1990 (s), 2060 (s), 2950 (m) cm^{-1}; ^1H NMR (CD_3CODC_3) δ 1.86 (CH_3); ^{13}C NMR (CD_3CN) δ 215.7 (CO), 97.5 (C_5Me_5), 10.0 (CH_3).

Anal. Calcd for $C_{12}H_{15}FeBr$: C, 44.07; H, 4.62; Fe, 17.08; Br, 24.43. Found: C, 44.14; H, 4.47; Fe, 17.24; Br, 24.34.

(3) $C_5Me_5Fe^+C_6H_6PF_6^-$. $C_5Me_5Fe(CO)_2Br$ (5.52 g, 16.8 mmol) and $AlCl_3$ (9.65 g, 72.3 mmol) were stirred under N_2 in refluxing benzene (50 mL) for 12 h. Then the reaction mixture was hydrolyzed with 100 mL of ice water. Al^{3+} was removed from the aqueous phase as in 1, and the salt was isolated by precipitation after metathesis with HPF_6. Reprecipitation as in 1 gives 4.44 g (63.% yield) of powder, found pure by ^1H NMR. Recrystallization from hot ethanol provides 4.0 g (57% yield) of canary yellow needles: mp $\simeq$307 °C dec; IR 435 (w), 475 (w), 565 (m), 855 (s), 885 (w), 1045 (w), 3120 (w) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 610 (6 H, C_6H_6) and 2.04 (15 H, CH_3); ^{13}C NMR (CD_3CN) δ 92.3 (C_6H_6), 90.4 (C_5Me_5), 10.2 (CH_3).

Anal. Calcd for $C_{16}H_{21}FePF_6$: C, 46.39; H, 5.11; Fe, 13.48. Found: C, 46.56; H, 4.93; Fe, 13.49.

(4) $C_5Me_5Fe^+C_6Me_6PF_6^-$. $C_5Me_5Fe(CO)_2Br$ (1.37 g, 4.2 mmol), $AlCl_3$ (2.4 g, 18 mmol), and C_6Me_6 (3.89 g, 24 mmol) were mixed in a glovebag under N_2. The reaction mixture was melted and heated at 115 °C for 12 h under stirring and N_2 atmosphere. After the solution was cooled down, workup proceeds as above, yielding 0.806 g (38.6% yield) of powder found pure by ^1H NMR. Recrystallization from ethanol gives 0.708 g (34% yield) of yellow needles: mp 323 °C dec; IR 430 (w), 453 (w), 565 (m), 855 (s), 885 (w), 1038 (m), 2990 (w) cm^{-1}; ^1H NMR

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(74) That the e^*_{1g} LUMO is so much destabilized in ferrocene (due to the covalency of $3d_{xz,yz}$ orbital with the Cp e_1 orbitals) is part of the reason why it is so difficult to reach the d^7 19-electron complex Cp_2Fe^-. The monoelectronic electroreduction of ferrocene (−2.93 V vs. SCE, reversible at −35 °C in DME) was only recently, but elegantly characterized. Mugnier, Y.; Moise, C.; Tirouflet, J.; Laviron, E. *J. Organomet. Chem.* **1980**, *186*, C49–C52.

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(CD$_3$COCD$_3$) δ 2.30 (18 H, C$_6$Me$_6$) and 1.70 (15 H, C$_5$Me$_5$); ^{13}C NMR (CD$_3$CN) δ 98.35 (C$_6$Me$_6$); 87.0 (C$_5$Me$_5$), 15.6 (C$_6$Me$_6$), 8.5 (C$_5$Me$_5$).

Anal. Calcd for C$_{22}$H$_{33}$FePF$_6$: C, 53.02; H, 6.67; Fe, 11.20. Found: C, 52.92; H, 6.64; Fe, 11.12.

(5) CpFeC$_6$Me$_6$. A 2.2-g sample of CpFe$^+$C$_6$Me$_6$PF$_6^-$ (5 mmol) in 30 mL of dimethoxyethane is stirred with 35 g of Na/Hg amalgam (1%, 15 mmol) for 30 min at ambient temperature under N$_2$. Then DME is removed in vacuo, and the residue is extracted and recrystallized from pentane. Standing overnight at −40 °C affords dark forest green, air-sensitive crystals of **1** (1.28 g, 90% yield): sublimation 70 °C at 0.2 × 10^{-3} mmHg; mass spectrum M$^+$ calcd 283.115, found 283.115; ^{1}H NMR (C$_6$D$_5$CD$_3$) δ 35.01 (C$_5$H$_5$, line width at half-height = 330 Hz), −2.15 (C$_6$Me$_6$, linewidth at half-height = 140 Hz); ^{13}C NMR (C$_6$D$_5$CD$_3$) δ 44 9 and 584 (ring C), −35.9 (CH$_3$); IR (pentane) 785 (w), 823 (s), 1040 (s), 1120 (s), 1285 (s) cm^{-1}.

Anal. Calcd for C$_{17}$H$_{23}$Fe: C, 72.09; H, 8.22; Fe, 20.57. Found: C, 71.81; H, 8.23; Fe, 20.55.

(6) CpFeC$_6$(C$_2$H$_5$)$_6$. An identical procedure applied to 1.37 g (2.67 mmol) of CpFe$^+$C$_6$(C$_2$H$_5$)$_6$PF$_6^-$ gives 0.387 g (1.05 mmol, 40% yield) of **2** as dark forest green, air-sensitive crystals after recrystallization from pentane and 2 days of standing at −21 °C: sublimation 49 °C at 0.7 mmHg; mass spectrum M$^+$ calcd 367.209, found 367.209; IR (pentane) 790 (m), 828 (s), 1040 (s), 1077 (w), 1120 (s), 1285 (s) cm^{-1}.

Anal. Calcd for C$_{23}$H$_{35}$Fe: C, 75.20; H, 9.60; Fe, 15.20. Found: C, 75.13; H, 9.55; Fe, 15.08.

(7) C$_5$Me$_5$FeC$_6$Me$_6$. Similarly 5.02 g of C$_5$Me$_5$Fe$^+$C$_6$Me$_6$PF$_6^-$ (10.08 mmol) gives 1.424 g (4.03 mmol, 40% yield) of **3** as deep ivory-green crystals after recrystallization overnight from pentane at −21 °C: sublimation 103 °C at 5 mmHg; mass spectrum M$^+$ calcd 353.193, found 353.193; IR (pentane) 830 (s), 1044 (w), 1102 (s), 1285 (s) cm^{-1}.

Anal. Calcd for C$_{22}$H$_{33}$Fe: C, 74.78; H, 9.41; Fe, 15.80. Found: C, 74.82; H, 9.42; Fe, 15.69.

(8) Isolation, Characterization, and Dimerization of CpFeC$_6$H$_n$Me$_{6-n}$. (a) n = 6. The Na/Hg reduction of CpFe$^+$C$_6$H$_6$BF$_4^-$ (1.5 g, 5.26 mmol) was carried out at −20 °C for 1 h in 30 mL of dimethoxyethane under N$_2$. After removal of the solvent in vacuo, the residue was extrated with a minimum (2 × 5 mL) of toluene at −20 °C and filtered. Cold pentane (50 mL) was added, and the solution was cooled down to −78 °C, which provides 0.83 g (4.16 mmol) of dark green microcrystalline **4** (79% yield). Fast transfer to a Mössbauer cell in a glovebag which is cooled to ≃−10 °C by flushing N$_2$ through a plastic tubing at −196 °C afforded an observation of a clean Mössbauer spectrum of solid CpFeC$_6$H$_6$.

(b) n = 1 and 5. CpFeC$_6$H$_5$Me and CpFeC$_6$HMe$_5$ were obtained with a similar procedure; since they were much more soluble in pentane than the parent complex **4**, they were extracted from this solvent. After removal of the solvent and transfer to suitable cells, the Mössbauer spectra were observed as above. The rate of dimerization is greater than for CpFeC$_6$H$_6$, the transformation of the green monomer to the red dimers being complete in 10 min at −10 °C.

(c) n = 2, 3, and 4. Similarly the green solid monomers CpFe(p-xylene), CpFe(mesitylene), CpFe(durene), and CpFe(isodurene) were isolated in the solid state after reduction of the cations, extraction with pentane, filtration, and removal of the pentane in vacuo, all these operations being carried out at temperatures not higher than −20 °C. Transformations to bright orange dimers in the solid state were complete in 10 min at −20 °C. The monomers were stable in pentane for more than 1 h at 0 °C, as for n = 1, 5, and 6. The solid dimers were identified by comparison with authentic samples by ^{1}H NMR, molecular weight determination in benzene, and mass spectra (M/2)$^+$.

(9) Attempts to Isolate C$_5$Me$_5$FeC$_6$H$_6$ in the Solid State, Characterization in Frozen DME Solution and Dimerization. A 3-g sample of C$_5$Me$_5$Fe$^+$C$_6$H$_6$PF$_6^-$ (7.3 mmol) was stirred in 30 mL of DME with 50 g of Na/Hg amalgam (1%, 22 mmol) at −20 °C for 1 h. DME was removed in vacuo from the deep ivory-green solution. Upon saturation, a red solid always crystallizes from the ivory-green solution whatever be the temperature (this experiment was repeated about 10 times). After removal of all the solvent at −80 °C, only red microcrystals were obtained (if a DME solution is warmed to room temperature, the red dimer begins to appear only after ≃20 min as a precipitate and the overall transformation takes about 1 h). The weak pentane-soluble red solid is extracted (under N$_2$) with a minimum (30 mL) of toluene. Filtration, addition of 150 mL of pentane, and slow cooling down to −78 °C provide bright orange flakes (0.4 g, 0.74 mmol, 20.5% yield): mp 103 °C; mass spectrum calcd for (M/2)$^+$ 269.099, found 269.099; ^{1}H NMR (C$_6$D$_6$) δ 1.60 (s, 15 H, CH$_3$), 1.60–1.80 (m, 3, η^5-C$_6$H$_6$), 3.60 (m, 2), 5.12 (m, 1); ^{13}C NMR (CDCl$_3$) δ 10.5 (5 CH$_3$), 91.4 (5 C$_{Cp}$), 43.4 (sp^3 C$_{C_6H_6}$), 32.9 (2 C ortho), 81.5 (2 C meta), 80.9 (1 C para).

Anal. Calcd for C$_{32}$H$_{42}$Fe$_2$: C, 71.39; H, 7.86; Fe, 20.74. Found: C, 71.19; H, 8.31; Fe, 20.50.

A cold, deep ivory-green, concentrated DME solution was transferred into a Mössbauer cell in a glovebag at ≃−10 °C, which afforded the Mössbauer spectra of a frozen DME solution of C$_5$Me$_5$FeC$_6$H$_6$ as a monomer.

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