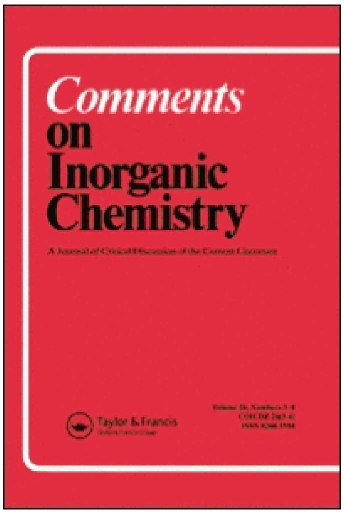

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How to Design Organometallic "Electron-Reservoirs"

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How to Design Organometallic "Electron-Reservoirs"

Two essential facets of transition metal organometallic compounds are (i) their ability to undergo transformations of organic and inorganic species at the metal and (ii) the ease of redox changes induced by the metal. This Comment indicates the potential of this second aspect and how organometallics may be designed and used to promote electron transfer (ET). Inexpensive, easily available organometallic electron-reservoirs can conveniently effect a variety of stoichiometric and catalytic ET processes. The salt effect and the activation of dioxygen are especially under our scrutiny in stoichiometric reactions. Catalytic ET involves redox catalysis of electrochemical reactions (the catalyst lowers the overpotential) and electrocatalysis of organometallic reactions (ligand substitution, decomplexation, isomerization, chelation, insertion). These processes can be effected using (instead of an electrode) iron sandwich compounds: the electron-deficient ferricinium Cp_2Fe^+ (17 valence electrons) for oxidations and the electron-reservoir compound $CpFe^IC_6Me_6$ (19 valence electrons) for reductions.

I. INTRODUCTION

The concept of the "organometallic electron-reservoir" appeared as soon as it was realized that organometallic compounds are able to store energy in the form of one or several electrons.[1] However, the property is restricted to the classes of compounds that can withstand single or multiple redox changes without molecular disruption.[2] The well-known redox properties of metal ions in water have found application *inter alia* in inorganic and organic redox synthesis.[3] On the other hand, the more recent bioinorganic chemistry of metal ions has stimulated a great deal of interest for the design of biomimetic models.[4] As occurs in these areas, organometallic compounds can be submitted to redox changes which are

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largely modulated by the ligands.[5] The stabilization and use of the molecular structures in these various redox states is the main focus of this Comment. The structural changes occurring by oxidation or reduction of organometallic complexes have recently received a great deal of attention and have been elegantly examined using electrochemistry and x-ray crystal structures.[5] However, we are concentrating here on compounds showing a minimum structural change, i.e., no reorganization of the complex geometry, and only small variations of metal–ligand bonds imposed by the removal of an electron from a bonding orbital or addition of an electron to an antibonding orbital. Large structural changes upon such redox variations can be prevented if the orbitals affected by electron addition or removal are delocalized over an extended framework (thermodynamic stabilization). When a metal or a cluster of metals is located at the center of a bulky molecular architecture, redox changes will leave the geometry essentially unchanged if the orbitals involved in the redox variation are highly metal based. In this way, the periphery of the molecular structure, i.e., the ligands, bear little spin density, which brings about kinetic stabilization. This notion parallels the steric stabilization of organic radicals. The extensive use of such stabilized systems is possible if they are easily accessible and handled.[1] Various applications of organometallic reservoirs include stoichiometric electron-transfer (ET) processes, activation of small molecules, study of the reactivity of ion pairs and salt effects. Catalytic applications are redox catalysis of electrochemical reactions and electrocatalysis, a technique that does not require electrochemical preparative techniques. On the contrary, the availability of a library of readily available electron-reservoirs having a range of redox potentials could ideally allow us to avoid electrochemical routes in organometallic reactions involving ET. Although electron-reservoirs were initially designed to store and subsequently release electrons, we will also consider the parallel strategy applied to oxidizing species.

II. TRANSITION METAL SANDWICHES AS ELECTRON-RESERVOIRS

Extensive electronic delocalization is provided by the conjugated planar Π ring systems[6]; in this way, the number of valence electrons on the central transition metal can vary widely around 18, the valence electron number frequently required for stabilization with various geometries of monometallic transition metal complexes. Neutral metallocenes are known to be thermally stable for Cr, Mn, Fe, Co and Ni (15 to 20 valence electrons).[5,7] However, only the Fe and Co metallocenes are used as redox reagents since others are considered difficult to handle due to air-sensitivity. Ferrocene (like several other metallocenes) is known to give a four-member redox series. The latter extends from the 16-electron dication (reversibly generated electrochemically only in liquid SO_2)[8] to the 19-electron anion (reversibly generated only at -30 °C in DME).[9]

$$Cp_2Fe^{++} \rightleftharpoons Cp_2Fe^{+} \rightleftharpoons Cp_2Fe \rightleftharpoons Cp_2Fe^{-} \ (Cp = \eta^5\text{-}C_5H_5)$$

$$16e^- \quad -2\,V \quad 17e^- \quad 0.5\,V \quad 18e^- \quad -2.8\,V \quad 19e^-$$

$$\text{vs SCE} \qquad \text{vs SCE} \qquad \text{vs SCE} \quad Cp = \eta^5\text{-}C_5H_5$$

The reversible ferricinium–ferrocene redox pair was recognized as soon as ferrocene was discovered.[10] It is useful for the derivation of electrodes[11] and ferricinium is now largely used as a one-electron oxidant in organometallic chemistry.[5] It is conveniently synthesized by oxidation of ferrocene with concentrated sulfuric acid followed by metathesis with aqueous HPF_6 and recrystallization from ethanol.[12]

Cobaltocene (Cp_2Co), a stable 19-electron sandwich, forms a useful reversible redox couple ($E^0 \simeq 1$ V vs SCE) with its robust 18-electron cobalticinium cation (Cp_2Co^+).[13] Thus cobaltocene is often used as a one-electron reducing agent.

The 18-electron $M(arene)_2$ (Cr,Mo,W) and isoelectronic MCp(CHT) (CHT = cycloheptatrienyl) also form reversible redox couples with their 17-electron cation, the redox potential of which widely vary with the ring substituents.[14] These well-known systems have not been used in this way, however. Similarly, $V(C_6H_6)_2$ is known in three forms (16 to 18 electrons).[15]

The permethylation of sandwich rings greatly aids in the stabilization of various oxidation states, expanding the variety of redox reagents now available. Permethylmanganocene[16] is isolable in three oxidation states, among which is the extremely reducing 18-electron anion.

$$\underset{16e^-}{\mathrm{Cp_2^*Mn^+}} \xrightleftharpoons{-0.56} \underset{17e^-}{\mathrm{Cp_2^*Mn}} \xrightleftharpoons{-2.50} \underset{18e^-}{\mathrm{Cp_2^*Mn^-}}$$

$$(\mathrm{Cp^*} = \eta^5\text{-}\mathrm{C_5Me_5}, \text{ potentials in V vs SCE})$$

Permethylnickelocene is also stable in three oxidation states as the isoelectronic bis(hexamethylbenzene) (HBM) iron sandwich.[5a]

$$\mathrm{NiCp_2^{*++}} \xrightleftharpoons{+0.35} \mathrm{NiCp_2^{*+}} \xrightleftharpoons{-0.7} \mathrm{NiCp_2^*}$$

$$\mathrm{Fe(HMB)_2^{++}} \xrightleftharpoons{-0.5} \mathrm{Fe(HMB)_2^+} \xrightleftharpoons{-1.45} \mathrm{Fe(HMB)_2}$$

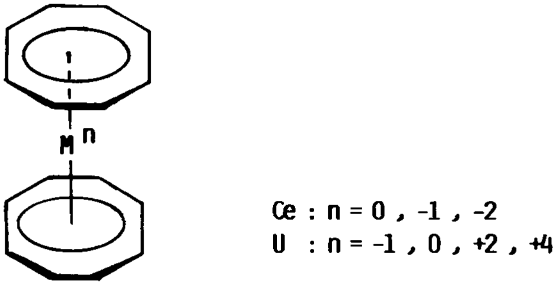
The 18-electron mixed sandwich $(\mathrm{CpFearene})^+$ series is known for many arenes,[17] but the neutral 19-electron Fe(I) form is only stable if the arene is peralkylated[18,19] or sufficiently bulky such as in 1,3,5-*tris* tertiobutylbenzene or pentaethylbenzene.[17b] Thus a number of 19-electron compounds are known with very negative redox potentials and extremely low ionization potentials (4.2–4.7 eV) as measured by He(I) photoelectron spectroscopy.[20]

These findings led to their use as electron-reservoir compounds because they are inexpensive, readily made, strong reducing agents.[1] The redox potential desired can be modulated by a large choice of arene substituents (see the scale in Fig. 1). The electrochemistry,[21] x-ray crystal structures,[18,19] paramagnetic NMR,[22] EPR,[23] He(I) photoelectron[20] and Mössbauer[24] spectroscopies and theoretical calculations[25] indicate that the singly occupied, antibonding *Fe(HMB)* level has a large metal character (~80%), consistent with the stability. When two identical units are linked by a fulvalene ligand, the binuclear mixed valence $\mathrm{Fe^IFe^{II}}$ 37-electron cation $(\mathrm{Fe_2\mu_2,\eta^{10}\text{-}Fv(C_6R_6)_2{}^+}$, Fv = fulvalene, R = H or $\mathrm{CH_3}$) is delocalized on the Mössbauer time scale whereas the $\mathrm{Fe^IFe^I}$ 38-electron complex has two unpaired electrons.[26] Again, the binuclear system has stable reduced states (37- and 38-valence electrons) when the arene ligand is HMB, which makes a series of three stable oxidation states, unlike biferrocene for which only the neutral and monocationic forms are isolable.[27] On the contrary, the dication of biferrocenylene ($\mathrm{Fe_2Fv^{++}}$) is a stable diamagnetic compound and $\mathrm{Fe_2Fv}$ has three stable redox states.[28]

Cp Fe napht	$CpCO_2H$ Fe HMB	Cp Fe C_6H_6	Cp Fe $Bu^t_3C_6H_3$	Cp Fe HMB	Cp-Cp Fe Fe HMB Cp	$CpCO_2^-$ Fe HMB	Cp Fe C_6Et_6	Cp-Cp Fe Fe HMB HMB	C_5Me_5 Fe HMB	C_5Me_5 Fe C_5Et_5H
-1.07	-1.27	-1.36	-1.50	-1.52	-1.58	-1.67	-1.75	-1.76	-1.80	-1.85
Cp Fe^+ napht	$CpCO_2H$ Fe^+ HMB	Cp Fe^+ C_6H_6	Cp Fe^+ $Bu^t_3C_6H_3$	Cp Fe^+ HMB	Cp-Cp Fe^+Fe HMB Cp	$CpCO_2^-$ Fe^+ HMB	Cp Fe^+ C_6Et_6	$Cp-Cp^+$ Fe Fe HMB HMB	C_5Me_5 Fe HMB	C_5Me_5 Fe^+ C_5Et_5H

→ V. vs s.c.e.

FIGURE 1 Reversible Fe^{II}/Fe^{I} systems classified by increasing $|E_0|$ values (DMF, 0.1 M $Bu^n_4NPF_6$, 25°C) determined by cyclic voltammetry on a Hg cathode of the d^6Fe^{II} cationic sandwiches (below the axis); the d^7, 19-electron Fe^I forms are located above the axis.



Ce : n = 0 , -1 , -2

U : n = -1 , 0 , +2 , +4

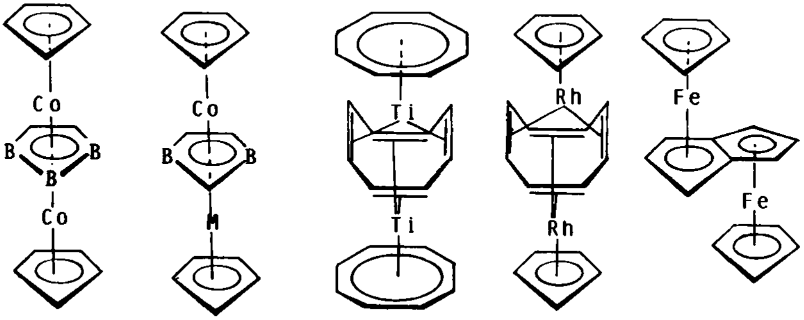
FIGURE 2

$$\underset{36e^-}{\mathrm{Fe_2Fv_2^{+\,+}}} \overset{+0.2}{\rightleftharpoons} \underset{37e^-}{\mathrm{FeFv_2^{+}}} \overset{+0.8}{\rightleftharpoons} \underset{38e^-}{\mathrm{FeFv_2}}$$

$$\underset{38e^-}{\mathrm{Fe_2Fv(HMB)_2^{+\,+}}} \overset{-1.3}{\rightleftharpoons} \underset{37e^-}{\mathrm{Fe_2Fv(HMB)_2^{+}}} \overset{-1.75}{\rightleftharpoons} \underset{38e^-}{\mathrm{Fe_2Fv(HMB)_2}}$$

$$\mathrm{Fv} = \mu_{2,}\eta^{10}\text{-}\mathrm{C_{10}H_8}\text{(fulvalene)}$$

There are several other mixed transition metal sandwiches giving isolable cations, especially with the iron triad metals.[5] Bis cyclooctatetraenyl lanthanides and actinides form an outstanding class of sandwiches undergoing redox changes without dramatic geometric variation.[29] However, despite these syntheses, electrochemical studies are scarce (Fig. 2).



M=Fe, Co, Ni

FIGURE 3

Triple decker sandwiches,[30] stable in the 30- and 34-electron configurations, are delocalized systems bearing multiple variations of their redox states. Multiple deckers,[31] now available, are even more promising and their design is part of a strategy aimed at the achievement of organometallic conductors (Fig. 3).

III. MULTIPLE FUNCTIONS OF ELECTRON-RESERVOIR COMPOUNDS

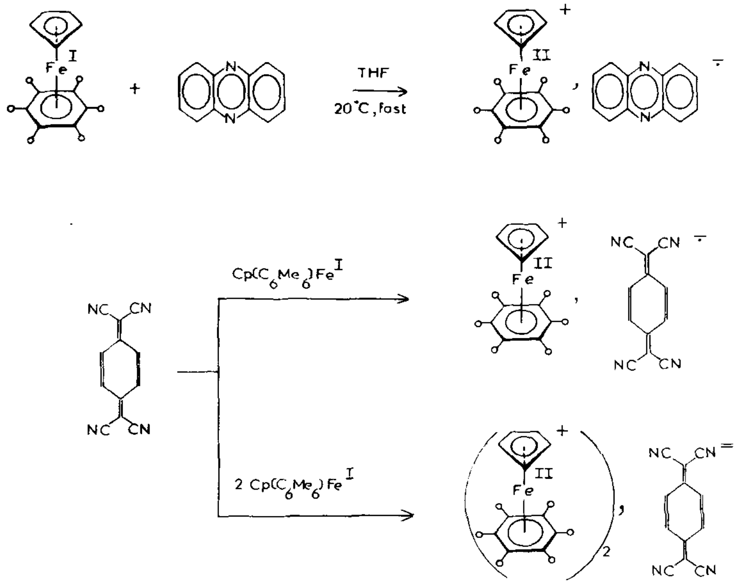
1. *Stoichiometric ET Cage Reactions and Salt Effects*

(a) *Reduction of Substrates which Are Reversibly Reduced.* Organic, inorganic and organometallic substrates which give stable radical anions can be reduced by an electron reservoir only if the reduction potential of the substrate is lower than the oxidation potential of the electron reservoir, provided there is no cage reaction.

Thus FeCpHMB, **1**, reduces phenazine, tetracyanoquinodimethane (TCNQ),[32] giving the salts FeCpHMB$^+$, substrate$^-$. Similarly, TCNQ$^-$ and 17-electron and 18-electron organometallic cations can be reduced (Scheme 1).[33]

The reduction of the majority of organometallic cations is indeed feasible. One reason is that many of them have a reduction potential lower than that of **1**. Hexafluorophosphate salts of 17-electron organometallic cations are conveniently reduced to their neutral 18-electron isostructural form. The PF_6^- salt of the organometallic electron-reservoir cation precipitates from the solution and can thus be removed in this way and recycled. Na/Hg reduction of 17-electron organo-iron cations generally gives poor yields of their 18-electron counterpart whereas **1** gives excellent yields. This is also the case for the reduction of some 18-electron cations to stable 19-electron compounds. For instance, the Na/Hg reduction of $\mathbf{4}^+PF_6^-$ gives poor yields and mixtures whereas reduction with a stoichiometric amount of **1** gives the pure 19-electron compound **4** in high yield (Scheme 2).

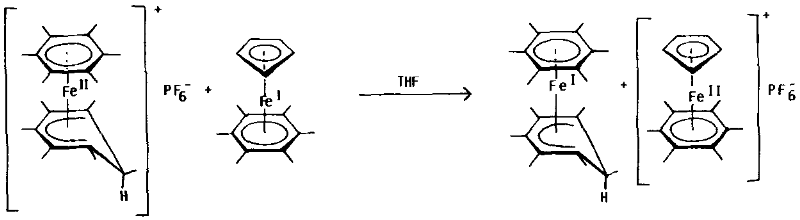
(b) *Irreversible Reduction of Substrates which Have a More Negative Reduction Potential Than the Electron-Reservoir Complex.* The reduction of polyaromatics such as naphtalene, anthracene,



SCHEME 1

etc., which have a reduction potential more negative than that of **1**, is not possible because their reduction is reversible.[32] This is not the case if the reduced substrate is not thermodynamically stable or is reactive under the reaction conditions. For instance, acridine[32] is reduced although its reduction potential (-1.65 V vs SCE) is more negative than that of **1**. Indeed the reaction is driven by the cage deprotonation of $\mathbf{1}^+$.

This proton transfer is also the driving force for the reduction of aldehydes and ketones to alcohols by **1** although the radical



SCHEME 2

anions of these organic substrates are produced at more negative potentials than that of $1 \rightleftharpoons 1^+$ (*vide infra*)[34]

$$1 + RR'CO \rightleftharpoons 1^+,RR'CO^{-\cdot} \xrightarrow{H^+} RR'\dot{C}OH \longrightarrow \text{alcohols}$$

The catalytic reduction of NO_3^- to NH_3 on a mercury cathode in water (*vide infra*)[35] starts by an ET from **1** although the reduction of NO_3^- on Hg presumably occurs at a potential 0.5 V more negative than that of $\mathbf{1}^+$. The otherwise unfavorable reduction $1 + NO_3^- \rightarrow 1^+,NO_3^{=\cdot}$ is driven by the protonation of $NO_3^{=\cdot}$ in the cage by $\mathbf{1}^+$ or by the aqueous solvent.

An extreme case is the reduction of CO_2 in a few minutes in THF at room temperature.[36] The difference between the reduction potentials of $\mathbf{1}^+$ and that of CO_2 reaches ca. 0.7 V but the radical anion $CO_2^{-\cdot}$ reacts rapidly[37] and irreversibly, which drives CO_2 reduction. The stability of organometallic electron-reservoir compounds in this reaction in a wide range of solvents and experimental conditions merits a search of the selectivity of the carbon–carbon bond formation (α) for this cheap, low energy, C_1 molecule.

$$\mathbf{1} + {}^{13}CO_2 \rightarrow \mathbf{1}^+ + \alpha\,{}^{13}C_2O_4^{=} + \beta CO_3^{=}$$

(c) *Cage Reactions*. The reaction between a neutral donor and a neutral acceptor provides an ion pair. If the acceptor is large and delocalized (low-lying LUMO, on an extended Π system), such as TCNQ, the ion pair precipitates and can be isolated (see Section III.1.a). If, on the other hand, the acceptor is small and gives a reactive anion, a fast cage reaction between the cationic form of the electron-reservoir and the reactive anion may occur. Depending on the goal, one may wish to induce or to avoid such cage reactions but, in any case, their study is necessary. The ET to dioxygen has been the subject of great attention since the toxicity of superoxide anion O_2^- became known[38]; in this case, the search of the cage reactions of O_2^- is desirable. Dioxygen reacts at −80°C with **1**, removing one H atom.[39] However, the mechanism is not a direct H atom abstraction and O_2^- was well characterized by EPR in the course of these reactions.[40] The intermediacy of superoxide, resulting from ET from **1** to O_2, is consistent with the one-volt difference between the two reversible systems **1**/**1**$^+$ and O_2/O_2^-, a tremendous driving force. The outer-sphere mechanism for ET from **1** to O_2 is confirmed by the fact that $Fe^IC_5Me_5(HMB)$, **2**, reacts faster than **1** with O_2; **2** is more bulky than **1** and has a more negative redox potential. The second step of the reaction of **1** (or **2**) with O_2 is a deprotonation of **1**$^+$ (or **2**$^+$) at a benzylic position by O_2^-, driven by the fast disproportionation of HO_2. Indeed **1**$^+PF_6^-$ can be deprotonated not only using t-BuOK in THF or NaOH in ethanol, but also by KO_2 in DMSO or with a stoichiometric amount of 18 crown-6 in THF. Consistently, O_2 reacts with $Fe^ICp(C_6Me_5NH_2)$, giving selectively $Fe^{II}Cp(\eta^5\text{-}C_6Me_5NH)$,[41] the more acidic N-H hydrogen atom being removed. When there are no benzylic hydrogens, O_2^- can add to the benzene ring as a nucleophile to generate an intermediate peroxy radical $Fe^{II}Cp(\eta^5\text{-}C_6H_6OO\cdot)$ which couples with another $Fe^ICp(C_6H_6)$ molecule giving the peroxo dimer $(Fe^{II}Cp\ \eta^5\text{-}C_6H_5O\text{-})_2$ (Schemes 3 and 4).[42,43]

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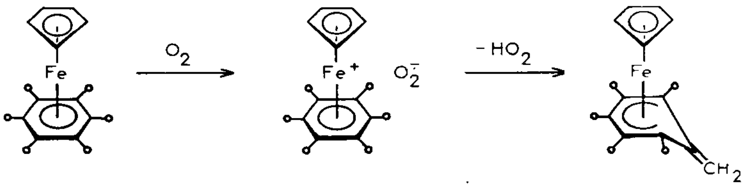
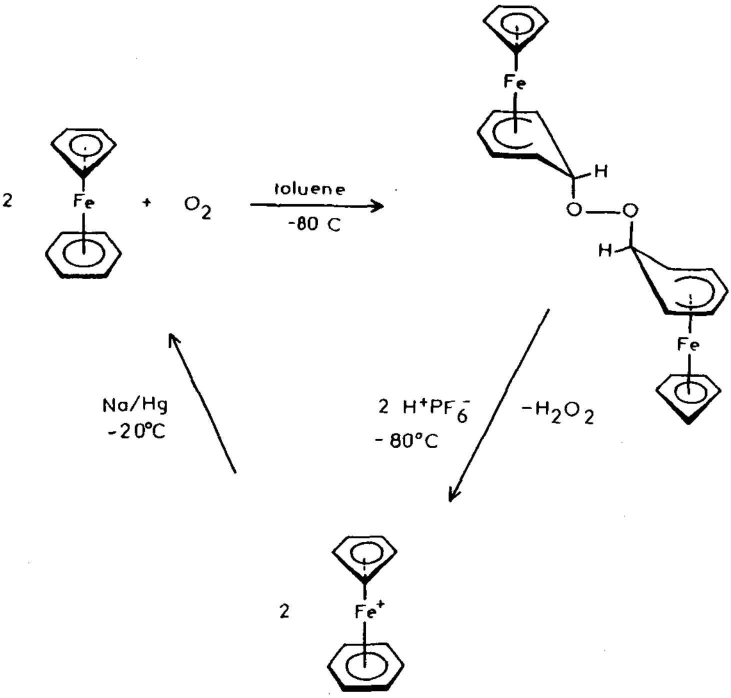
Besides allowing a study of the cage reaction of O_2^-, another interesting feature of this reaction is that it easily provides an "activated form" of the electron-reservoir compound **1** in high yield upon simple contact with air. This aerobically activated form can cleanly react with a variety of electrophiles to make carbon–carbon bonds as well as bonds between carbon and many elements (halogens, Si, P, transition metals) (Scheme 5).[40,44]



SCHEME 3

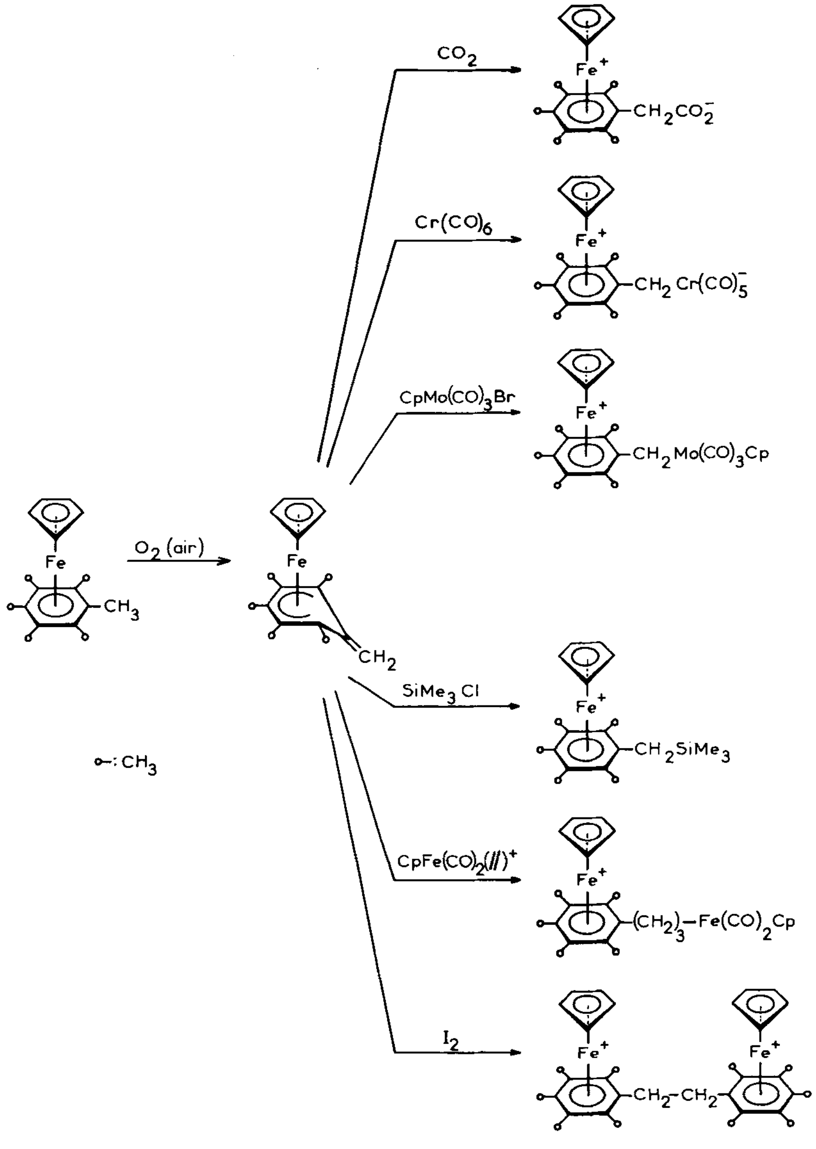


SCHEME 4

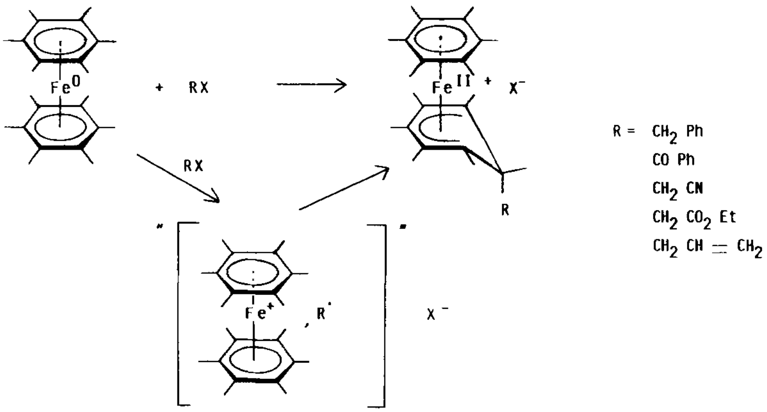
Using a similar strategy, the 20-electron organo-iron electron-reservoir $Fe(HMB)_2$ reacts with O_2 to give an Fe^O o-xylylene complex as a result of double H atom abstraction from two ortho methyls of a single HMB ligand.[45] A number of other 19-electron Fe(I) compounds also react similarly with O_2 leading to significant aromatic functionalization after electrophilic attack.[43]

Not only O_2 but also functional organic halides RX give synthetically useful cage reactions with $Fe(HMB)_2$. Electron transfer to RX leaves a 19-electron cation and $RX^{-\cdot}$, or rather $R^\cdot$ and X^-. Coupling between the 19-electron organometallic and the organic radicals occurs within the cage to make a carbon–carbon bond which, again, functionalizes the aromatic and further leads to new organic compounds (Scheme 6).[45(a),46]

In the case of a similar reaction with Fe(I), half of the starting material is lost since both the coupling product and the cation are


Fe
CH$_3$
O$_2$ (air)
Fe
CH$_2$
o–: CH$_3$
CO$_2$
Fe$^+$
CH$_2$CO$_2^-$
Cr(CO)$_6$
Fe$^+$
CH$_2$ Cr(CO)$_5^-$
CpMo(CO)$_3$Br
Fe$^+$
CH$_2$Mo(CO)$_3$Cp
SiMe$_3$ Cl
Fe$^+$
CH$_2$SiMe$_3$
CpFe(CO)$_2$(//)$^+$
Fe$^+$
(CH$_2$)$_3$–Fe(CO)$_2$Cp
I$_2$
Fe$^+$
Fe$^+$
CH$_2$–CH$_2$

SCHEME 5



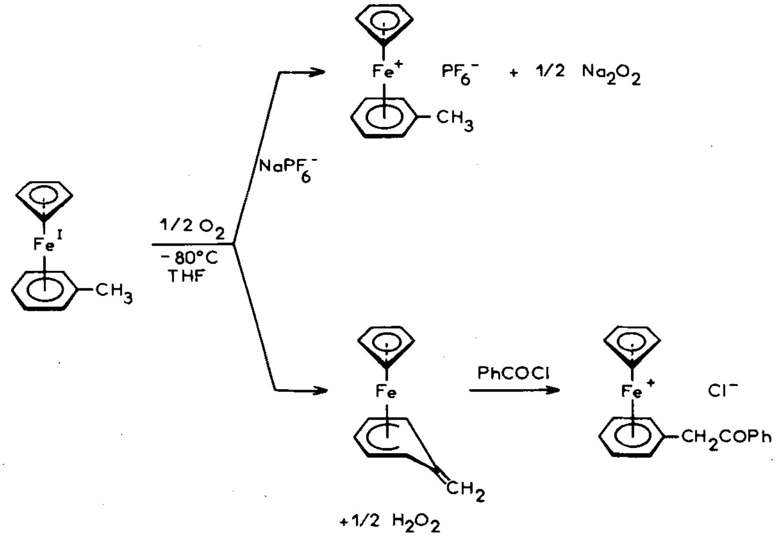
SCHEME 6

formed in stoichiometric amounts.[47] The radical cannot couple in the cage since iron, in the cation, has only 18 valence electrons. Thus, synthetic strategies should avoid coupling reactions with 19-electron complexes and switch to another type of activation using the salt effect (*vide infra*, carbonyl compounds).

(d) *Salt Effect* (Ref. 48). Reactions occurring in caged ion pairs subsequent to ET between the neutral electron-reservoir and a neutral acceptor can be inhibited by another salt present in stoichiometric amount in THF solution. The two soluble salts are tight caged ion pairs in this solvent, but ion exchange proceeds very fast even at low temperature to reach the equilibrium depending *inter alia* on the relative sizes of the ions.[49] It is well known that the ion pairs are energetically favored when the sizes of the cation and anion are comparable (i.e., both are small or large).

$$\mathrm{R} + \mathrm{A} \longrightarrow [\mathrm{R}^+,\mathrm{A}^-] \underset{\mathrm{THF}}{\overset{\mathrm{M}^+\mathrm{X}^-}{\rightleftharpoons}} [\mathrm{R}^+\mathrm{X}^-] + [\mathrm{M}^+,\mathrm{A}^-]$$

Thus if the acceptor is small, it forms a more stable caged ion pair with a small cation such as Na^+ than with the large electron-reservoir sandwich cation. The effect is more marked if the counter



SCHEME 7

anion is large (larger than the acceptor). Thus, if a suitable salt is added, fast equilibrium will inhibit the cage reaction of the electron-reservoir with the acceptor. This is exactly the case when a stoichiometric amount of $Na^+PF_6^-$ is added to a THF solution of $CpFe^I$ arene before reaction with O_2. The cage reaction (deprotonation of benzylic H or nucleophilic attack) is totally inhibited (Scheme 7).[43] When a larger cation than Na^+ or a smaller anion than PF_6^- is used, the salt effect is not longer quantitative and its magnitude is consistent with the relative size as described above. It is thus interesting that not only the superoxide dismutase enzymes and transition metal ions can catalyze the disproportionation of superoxide, but also simple Na^+ salts.

The reaction of $CpFe^I$ HMB with organic carbonyl compounds RCOR′ (R = H, alkyl) give coupling product η^4-RCOR′-$C_5H_5Fe^0$HMB, but reduction of the organic compound to alcohols occurs in the presence of $Na^+PF_6^-$ in stoichiometric amounts.[34] At this time, the acceptor is relatively large and the partition is not in favor of ion pair metathesis, but the fast reactions of the radical anion shift the equilibrium.

$$\mathrm{CpFe^{I}C_6Me_6 + RCOR' \longrightarrow [CpFe^{II}C_6Me_6^{+}, RCOR^{-\cdot}]}$$

$$\xrightleftharpoons[\mathrm{THF}]{[\mathrm{Na^{+}PF_6^{-}}]} \mathrm{CpFe^{II}C_6Me_6^{+}, PF_6^{-} + RCOR^{-\cdot}, Na^{+}}$$

$$\Big\downarrow \begin{array}{l}\text{protonation}\\ \text{reduction}\end{array}$$

$$\mathrm{RCHOHR'}$$

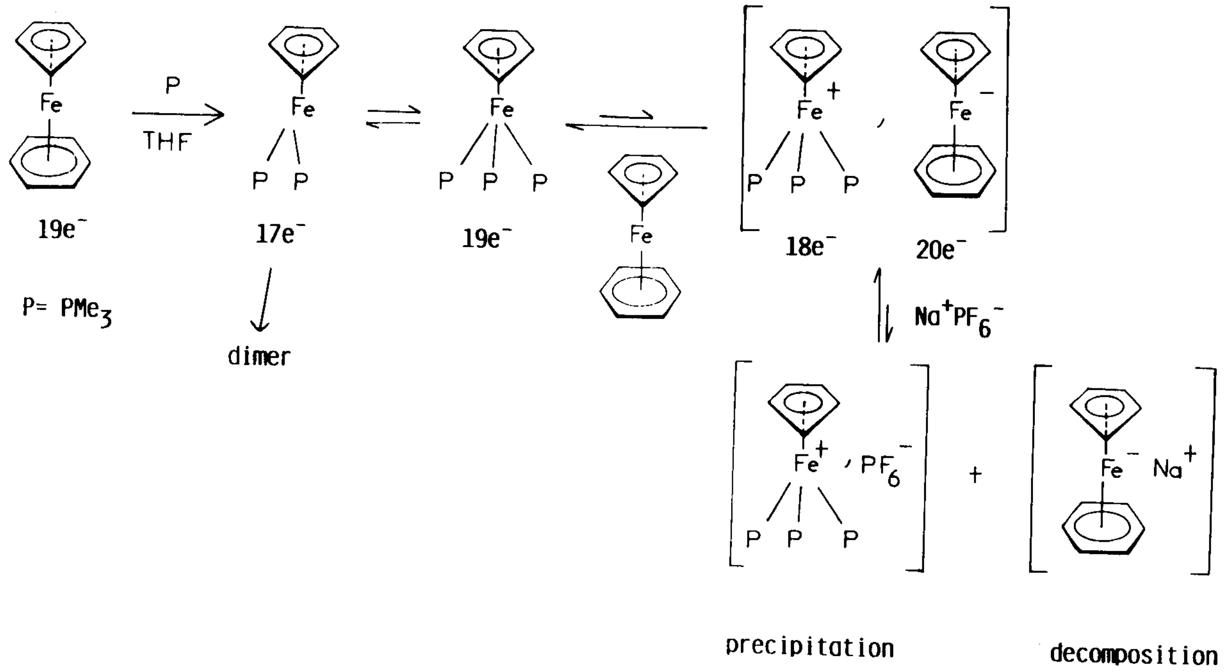
Similar reactions of $\mathrm{CpFe^{I}C_6H_6}$ with P donor ligands[34] lead to the dimer (coupling of the 17-electron species $\mathrm{CpFe^{I}P_2}$) only in the absence of a salt such as $\mathrm{NaPF_6^{-}}$. In the presence of a stoichiometric amount of $\mathrm{Na^{+}PF_6^{-}}$, the cation $\mathrm{CpFe^{+}P_3}$ are formed in 50% yield. This oxidation $\mathrm{Fe^{I} \rightarrow Fe^{II}}$ in the absence of any oxidant is in fact a disproportionation induced by the salt effect. The 19-electron species $\mathrm{CpFe^{I}P_3}$ reduces $\mathrm{CpFe^{I}C_6H_6}$ to $\mathrm{(CpFeC_6H_6)^{-}}$ although the redox potential is not favorable. The reaction is driven by the instability of the 20-electron salt $\mathrm{(CpFeC_6H_6)^{-}Na^{+}}$.

$$\mathrm{CpFeC_6H_6} \xrightleftharpoons{\substack{-2.2\,\mathrm{V}\\ \mathrm{vs\,SCE}}} \mathrm{CpFeC_6H_6^{-}}; \qquad \mathrm{CpFe^{+}P_3} \underset{\mathrm{P\,=\,PMe_3}}{\xrightleftharpoons{\substack{\sim-2\,\mathrm{V}\\ \mathrm{vs\,SCE}}}} \mathrm{CpFeP_3}$$

On the other hand, the salt $\mathrm{[(CpFeC_6H_6)^{-}, (CpFeP_3)^{+}]}$ is sufficiently stabilized to decompose more slowly than the dimerization of $\mathrm{CpFeP_2}$ in the absence of a salt effect (Scheme 8).

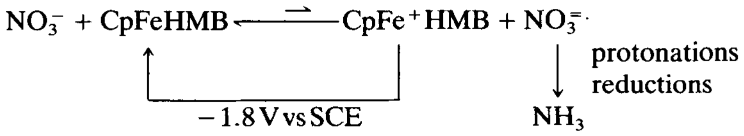
2. Redox Catalysis

Redox catalysts are stable redox systems which can lower the overpotential for the electrolysis of a substrate on a given electrode.[50] They are especially useful when the overpotential is large (mercury cathode), making the electrolysis impossible under the working conditions. This is the case for the cathodic reduction of $\mathrm{NO_3^{-}}$ to $\mathrm{NH_3}$ on Hg in basic aqueous media. The overpotential for the cathodic reduction of $\mathrm{NO_3^{-}}$ is so large that it is not electroactive. However, addition of a catalytic amount of $\mathrm{CpFe^{+}HMB}$


Fe
P
THF
19e$^-$
P= PMe$_3$
Fe
P P
17e$^-$
dimer
Fe
P P P
19e$^-$
Fe
Fe$^+$
P P P
18e$^-$
Fe$^-$
20e$^-$
Na$^+$PF$_6^-$
Fe$^+$, PF$_6^-$
P P P
+
Fe$^-$ Na$^+$
precipitation
decomposition

SCHEME 8

PF_6^-, or better, of $CpCO_2^-Fe^+HMB$ (soluble in both the oxidized and reduced forms) provides rapid electroreduction to NH_3 ($k \sim 10^2$ mol^{-1} L s^{-1}).[35]



3. Electrocatalysis

An electrocatalyst induces a reaction which does not necessarily involve an overall redox change, contrary to the redox catalyst.[51] Electrocatalysis can be performed using an electrode providing a catalytic amount of electrons, or using an electron-reservoir compound as the catalyst.[52] In organometallic chemistry, mainly ligand exchange reactions have been performed. As redox catalysts, electrocatalysts can be either reducing or oxidizing agents, depending on the reactant and substrate of the reaction. The principle, first found by Kornblum,[53] was extended synthetically by Bunnet[54] in the nucleophilic substitution of aromatic compounds ($S_{RN}1$ mechanism). Reviews are available,[55] some by Chanon, embracing both organic and inorganic chemistry. Here we will emphasize examples of organometallic reactions.[56,66]

(a) *Electrocatalytic Exchange of Two-Electron Ligands.* Anodic oxidation of 18-electron complexes such as $MeCpMn(CO)_2CH_3CN$ (~0.2 V vs SCE, CH_3CN, Pt) leads to 17-electron cations which react rapidly with phosphines whereas the 18-electron compound is rather inert.[57] After ligand exchange between CH_3CN and the phosphine in the 17-electron cation, the new 17-electron cation containing the phosphine ligand oxidizes the starting 18-electron compound because its potential is more positive (~0.7 V vs SCE, CH_3CN, Pt for PPh_3). The reaction continues and is thus catalytic in the amount of electricity or of oxidant which is consumed.

$$\underset{\mathbf{5}}{MeCp(CO)_2\,(CH_3CN)} \xrightarrow[PPh_3]{\text{catalyst:ox.}} \underset{\mathbf{6}}{CeCpMn(CO)_2\,PPh_3} + CH_3CN$$

$$\mathbf{5} \xrightarrow{-e^-} \mathbf{5}^+ \xrightarrow{PPh_3} \mathbf{6}^+ \xrightarrow{\mathbf{5}} \mathbf{5}^+ + \mathbf{6} \rightarrow \text{etc.}$$

Even if the anodic oxidation of **5** is reversible, the cathodic wave disappears upon addition of PPh_3 and a new oxidation wave (that of **6**) appears at a more positive potential in the cyclic voltammogram. The kinetics and mechanisms of these ligand exchange processes have been carefully examined by Kochi and Amatore using computer simulated cyclic voltammetry.[57] Such electrocatalytic ligand exchange can also be effected using cathodic reduction[58] or an electron-reservoir compound if the entering ligand is now more basic than the leaving one. For instance, carbonyls have been replaced by P donor ligands in this way in mono- and polynuclear complexes.[58]

(b) *Electrocatalytic Decomplexation.* We have found that catalytic amounts of current (cathodic reduction on Hg in EtOH) are able to decompose $(\mathrm{CpFe^{II}arene})^+$ if the arene ligand is not peralkylated.[59]

$$\underset{\mathbf{7}^+}{(\mathrm{CpFe^{II}arene})^+} \xrightarrow[\mathrm{EtOH}]{\text{catalyst:red}} \mathrm{CpH} + \text{arene}$$

$$+\ \mathrm{Fe^{II}}\ (30\%\ \text{of cathodic current},\ -1.8\ \text{V vs SCE at 20 °C})$$

$$\mathbf{7}^+ \xrightarrow{e^-} \mathbf{7} \xrightarrow[-\text{arene}]{\mathrm{EtOH}} \underset{\mathbf{8}}{\mathrm{CpFe^{I}(EtOH)}_n}$$

$$\mathbf{8} \xrightarrow{\mathbf{7}^+} \mathbf{8}^+ + \mathbf{7}\ \text{etc.}$$

$$\mathbf{8}^+ \xrightarrow[-\mathrm{EtO}^-]{\mathrm{EtOH}} \mathrm{CpH} + \mathrm{Fe^{II}} + \text{arene}$$

In the presence of a phosphite P, $\mathrm{CpFe^+P_3}$ is isolated.[60]

(c) *Electrocatalytic Chelation* (Ref. 61). The dialkyldithiocarbamate ligands (dtc) are chelated in $\mathrm{CpFe(CO)_2dtc}$ complexes using catalytic amounts of ferricinium as the oxidant[61] whereas the thermal reaction is difficult.[62]

$$\mathrm{CpFe(CO)_2(\eta^1\text{-}dtc)} \xrightarrow[-\mathrm{CO}]{\text{catalyst:ox.}} \mathrm{CpFe(CO)(\eta^2\text{-}dtc)}$$

$$\mathbf{9} \qquad\qquad \text{fast} \qquad\qquad \mathbf{10}$$

$$\mathbf{9} \xrightarrow[-\mathrm{Cp_2Fe}]{\mathrm{Cp_2Fe^+}} \mathbf{9}^+ \xrightarrow{-\mathrm{CO}} \mathbf{10}^+ \xrightarrow{\mathbf{g}} \mathbf{10} + \mathbf{9}^+ \text{ etc.}$$

In the presence of a *stoichiometric* amount of ferricinium, a stable 17-electron chelate complex is obtained if the reaction is performed in the presence of PPh_3.

$$\mathbf{9} \xrightarrow[\mathrm{PPh_3}]{\text{stoich. ox.}} \underset{\mathbf{11}^+}{[\mathrm{CpFe(\eta^2\text{-}dtc)PPh_3}]^+} + 2\,\mathrm{CO}$$

11$^+$ can be reduced to **11** cleanly using the electron-reservoir complex **1** (cf. Section II.1.a).

(d) *Electrocatalytic Isomerization* (Ref. 63). *Trans* ⇄ *cis* isomerization of octahedral dicarbene metal tetra carbonyls of Mo and W were among the first examples of electrocatalytic organometallic reactions via 17-electron cations. The coulometry effected at −7 °C consumed 10% of anodic current to transform all the *trans* isomer into the *cis* isomer.

(e) *Electrocatalytic Migratory Insertion* (Ref. 64). Catalytic amounts of ferricinium are able to induce fast CO insertion into the iron–methyl bond of $CpFe(CO)_2Me$ under a CO atmosphere.[64]

$$\mathrm{CpFe(CO)_2Me} \xrightarrow[\mathrm{CH_2Cl_2,0^\circ C}]{\text{catalyst:ox.}} \mathrm{CpFe(CO)_2\ (\eta^1\text{-}COMe)}$$

$$\mathbf{12} \qquad\qquad \text{fast,1 atm CO} \qquad\qquad \mathbf{13}$$

The process is feasible because **13** is oxidized at a more positive potential than **12**, so that **13**$^+$ can oxidize **12**, thus affording a catalytic chain.

$$\mathbf{12} \xrightarrow{\text{ox.}} \mathbf{12}^+ \xrightarrow{\mathrm{CO}} \mathbf{13}^+ \xrightarrow{\mathbf{12}} \mathbf{13} + \mathbf{12}^+ \rightarrow \text{etc.}$$

IV. CONCLUSION AND OUTLOOK

Organometallic electron-reservoir complexes ($Fe^{I}Cp$ arene) can cleanly reduce nearly all organometallic cations in outer-sphere single-electron transfer processes under various conditions. They can be stabilized under ambient conditions by peralkylation of the arene; they can be functionalized at the Cp ligand or at the benzylic position by mild carbon–carbon bond formation using CO_2, which affords *inter alia* solubilization of both redox forms in water. They are also available with a large number of aromatics,[17] which provides an extensive modulation of the redox potential. The design of such tools affords a number of stoichiometric and catalytic functions as ET reagents. The study of caged ion pairs generated from these electron-reservoir compounds and of the salt effect on their reactivity is of major interest in order to disclose the intimate conditions that allow the activation of small organic and inorganic molecules.

Analogously, ferricinium can oxidize many neutral organometallic compounds and can effect a similar function, although the use of more strongly oxidizing agents is often necessary.[65] Both the stable 19-electron and 17-electron iron sandwiches can function as redox catalysts or electrocatalysts in a number of processes including most classical organometallic reactions. Systems with the CpFe arene and the ferrocene units linked have recently been isolated under three stable redox forms $Fe^{II}Fe^{III}$, $Fe^{II}Fe^{II}$ and $Fe^{II}Fe^{I}$ and should show ambivalent catalytic properties.[65] The recently developed electrocatalytic synthesis of clusters substituted by several P donor ligands[58] can be recognized as an interactive strategy leading to novel organometallic electron-reservoirs which is now also attracting our attention.[66]

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