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Organometallic Electron-Reservoir Complexes. Concepts and Applications

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The 19-electron complexes $[\mathrm{Fe^I}(\eta^5\text{-}C_5R_5)(\eta^6\text{-arene})]$ (R = H, arene = C_6Me_6, 1,3,5-tBu$_3$C$_6$H$_3$; R = Me, arene = C_6Me_6, C_6Et_5H) are thermally stable and serve as strong single-electron reductant in a variety of stoichiometric and catalytic electron-transfer processes that are detailed in this review (prototype: $[\mathrm{Fe^I}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$). They are electron-reservoirs because their redox potential is very negative and they form a redox system for which both redox forms are stable. In this sense, they are Green redox reagents, since the oxidized form is recovered after use and is even frequently catalytically used. Symmetrically, the 17-electron complex $[\mathrm{Fe^{III}}(\eta^5\text{-}C_5R_5)(\eta^6\text{-}C_6Me_6)][SbCl_6]_2$, the strongest organometallic single-electron oxidant with a redox potential 1 V more positive than that of its isoelectronic ferrocenium analog, is a reservoir of electron hole.

Introduction

The notion of electron reservoir is reminiscent to Nature whereby many transformations require redox enzymes as catalysts.[1] In materials chemistry, single electron transfer also is a key reaction to dope conducting materials such as conducting polymers.[2] In molecular chemistry, single electron transfer onto a molecule is often encountered when the antibonding level of the LUMO is not too high in energy such as in cases of orbital degeneracy due to molecular symmetry (polyaromatics, C_{60}, transition-metal sandwich complexes), or a positive charge in organic (trityl cation, ammoniums, phosphoniums, etc.) and organometallic cations.[3] Likewise, single-electron oxidation is readily observed in electron-rich molecules such as tetrathia-, selena-, and tellura-fulvalene precursors of conducting and superconducting materials.[4] In organometallic complexes such as the prototype ferrocene, an electron is removed preferentially from a non-bonding orbital.[5] Indeed, redox changes are especially frequent in transition-metal chemistry,[6,7] including organometallic mechanisms[8,9] due to the ability of transition-metal ions to change their redox states.

Redox reagents have been known and used for a long time,[10] but the concept of electron reservoir is relatively more recent. In 1979, we introduced this concept by defining an electron reservoir as a redox system for which both redox forms are robust and the reduced form is electron-rich enough to reduce a large variety of substrates. In modern time when ecology becomes more and more important, this concept appears useful in the sense that it opens the route to the recovery of the oxidized form of a redox reagent that has been used in its reduced form. The electron-reservoir system can thus be considered to be a Green redox system.[11]

The Electron-Reservoir Complexes $[\mathrm{Fe^I}(\eta^5\text{-}C_5H_5)(\eta^6\text{-arene})]$ and Their Electronic Structure

The electron-reservoir behavior was revealed by the chemical and physical properties of the 19-electron complex $[\mathrm{Fe^I}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$ whose X-ray crystal structure confirmed the sandwich geometry with parallel rings.[12] The related 18-electron cation is isolobal to ferrocene, thermally stable up to 250 °C and stable in concentrated sulfuric acid under ambient conditions. It is reduced to the neutral form at −2 V vs. FcH$^+$/FcH, (FcH = ferrocene).[12] The 19-electron iron(I) complex that is shown below, is conveniently prepared from its cationic precursor in THF or dimethoxyethane using Na/Hg at 20 °C. It sublimes at 80 °C, is stable up to 100 °C, and its ionization potential is close to that of potassium metal.[13] It can reduce CO_2 to oxalate in organic solvents, and many other substrates are also reduced.[14] The family of complexes $[\mathrm{FeCp}(\eta^6\text{-arene})][PF_6]$ (Cp = η^5-C_5H_5) is very broad, because many compounds of this series are directly accessible upon reaction of ferrocene and the arene in the presence of aluminum chloride. Oxidation of the monocations to the 17e dications is difficult but was successfully achieved on a preparative scale when the rings are permethylated (Scheme 1) and the electronic structures of the four oxidation states observable by cyclic voltammetry are shown on Scheme 2.

The acido-basic and redox properties of the sandwich system could be investigated using redox potentials determined by cyclic voltammetry, pK_a value of the cation determined by the direct ^{1}H NMR method and Breslow-type thermodynamic cycles (Scheme 3). Concerning the Fe^{IV} species, its redox potential was evaluated by comparison with that of the dication resulting from the anodic oxidation of ferrocene.

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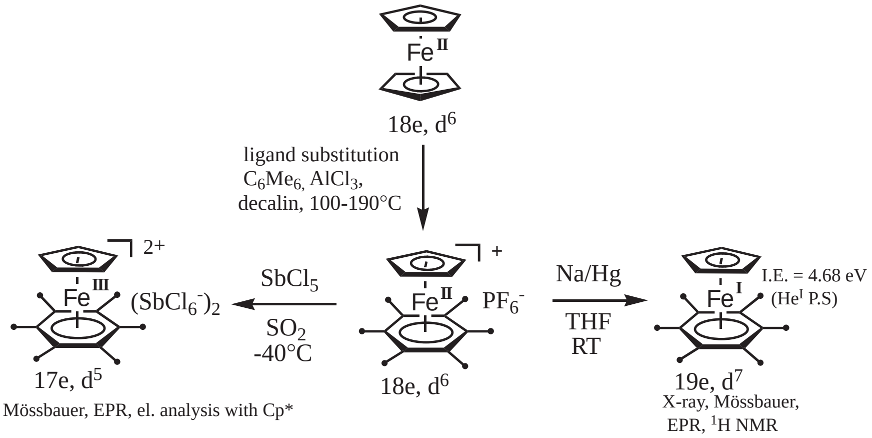
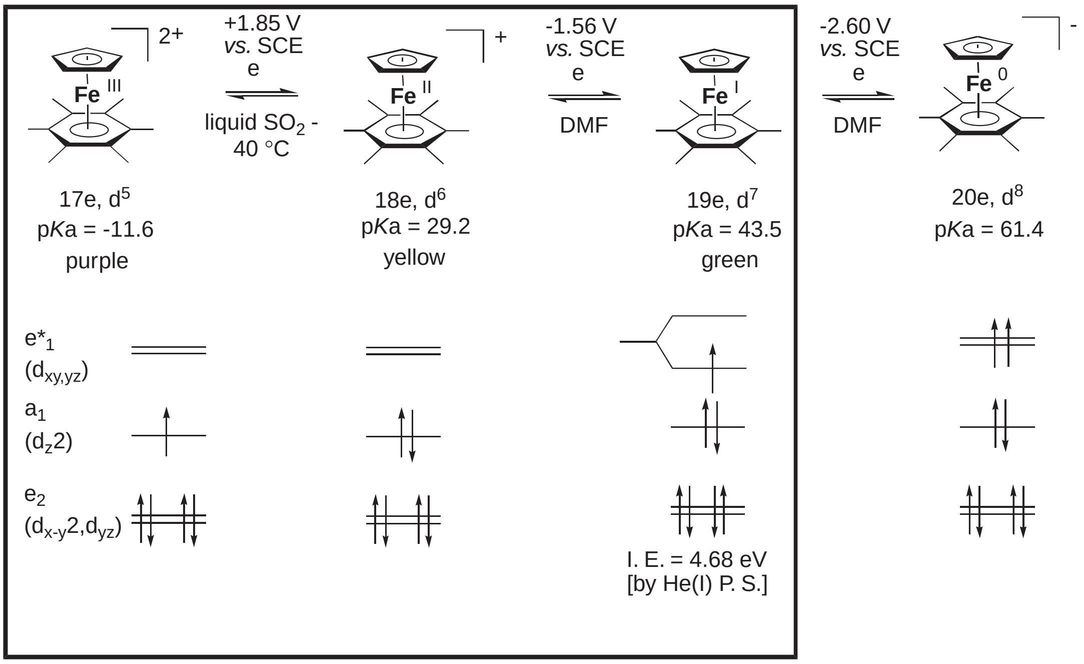
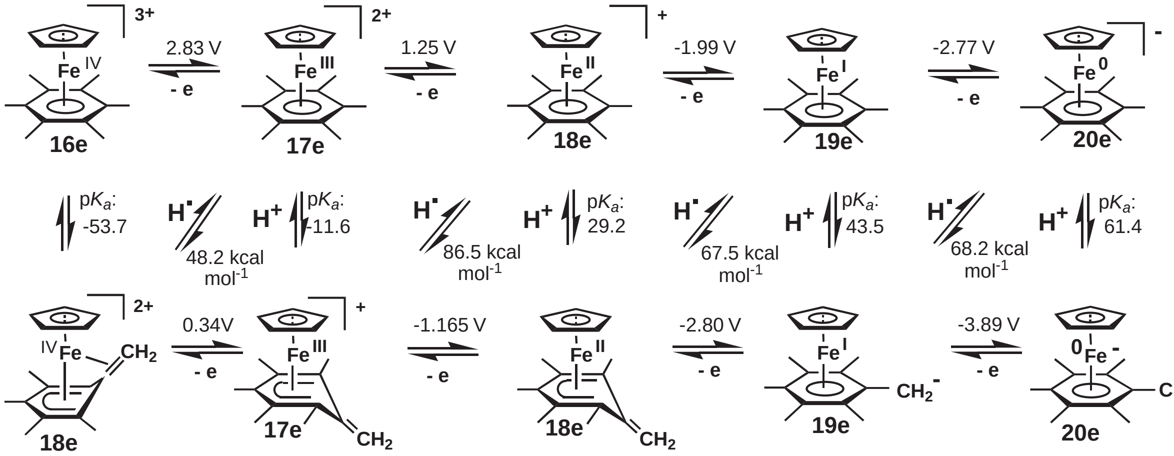


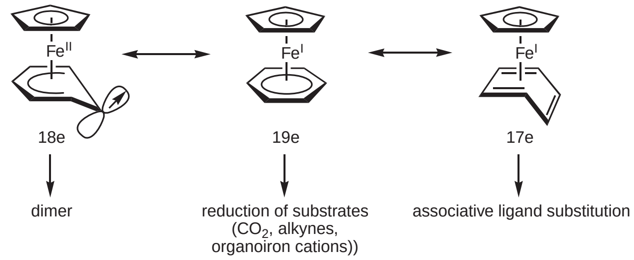
Scheme 1. Synthesis, single-electron reduction, and single-electron oxidation of the 18e complex $[Fe^{II}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)][PF_6]$.



Scheme 2. Electronic structures of the four oxidation states that are accessible by cyclic voltammetry from the 18e precursor complex $[Fe^{II}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)][PF_6]$.



Scheme 3. Thermodynamic diagrams providing thermodynamic values interconnecting five oxidation states starting $[Fe^{II}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)][PF_6]$ (see text).



Scheme 4. The three mesomeric forms of the so-called 19e complex $[Fe^{I}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]$ that take its account the structure–reactivity relationship.

All the monocationic 18e complexes can be preparatively reduced to the forest-green 19-electron neutral species that rapidly decomposes or dimerizes below room temperature.[15] Reduction must be carried out at low temperature using Na/Hg or $LiAlH_4$ in order to study the Fe^{I} species in solution. The benzene complex itself is modesty stable at 0 °C and spontaneously dimerizes at room temperature, which was disclosed by Nesmeyanov's group. More recent DFT calculation are in accord with Mössbauer data showing that the extra (19th) electron is essentially metal-based. Reactivities studies indicate that 17e, 18e, and 19e mesomeric forms are involved with a single potential well. Structure–reactivity relationship of this so-called 19e complexis best represented as follows in Scheme 4.

The only 19-electron compounds of the family that are stable at 20 °C for long periods of time are those of C_6Me_6, C_6Et_6, and 1,3,5-C_6H_3t-Bu_3.[16] The complexes $[Fe^{I}(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6Me_6)]$ and $[Fe^{I}(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6Et_5)]$ are the most electron rich of the series with ionization potential measured by in He(I) photoelectron spectroscopy even lower than that of potassium metal, and they are thermally stable at room temperature.[17] The Mössbauer spectra have a low quadruple splitting that vary with temperature due to the thermal population of the upper Kramer's doublet. Indeed, these complexes are Jahn–Teller active due to the presence of a single electron in the doubly degenerate antibonding e^*_1 orbital. This Jahn–Teller activity is also reflected in the EPR spectra showing the rhombic distortion with 3 g values close to 2.[18] The value of QS (0.5 $mm\,s^{-1}$ at 20 °C) is in accord with an 80% iron-based antibonding orbital. Molecular orbital calculations including DFT confirm that the antibonding orbital is 80% metal based, whereas it is only 50% in the isolobal cobaltocene complex. What is more intriguing in the Mössbauer spectrum of the complex $[Fe^{I}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$ is the splitting into two doublets below a second-order phase transition. This results from the coupling between the electronic structure and the lattice, which is confirmed by the absence of this phenomenon when the spectra are recorded in frozen solutions.

In summary of the electronic structure determination using a variety of techniques, it appears that the extra electron is located on the metal at the core of the molecular architecture. Thus, it is encapsulated inside the reservoir and protected against side reactions with outer substrates.[19]

Stoichiometric Electron-Transfer Reactions of Electron-Reservoir Complexes

Electron-transfer processes using electron-reservoir complexes can be achieved when the thermodynamics is favorable according to the Weller equation[20] that takes into account both the thermodynamic potential of the donor and acceptor substrates and the electrostatic factor (Eqs. 1 and 2):

$$\begin{aligned}\Delta G^\circ\ (\mathrm{kcal\,mol^{-1}}) &= 23.06[(E^\circ{}_D - E^\circ{}_A) \\ &\quad + (Z_A - Z_D - 1)e^2 f/ed] \qquad (1)\\ &= 23.06[E^\circ{}_D - E^\circ{}_A] \\ &\quad + 331.2[(Z_A - Z_D - 1)(f/ed). \qquad (2)\end{aligned}$$

If the monocations are reduced by neutral electron-reservoir complexes, this electrostatic factor is nil, and the thermodynamics is then only governed by the redox potentials of the donor and acceptor (simplified Weller equation, Eq. 3).

$$\Delta G^\circ\ (\mathrm{kcal\,mol^{-1}}) = 23.06[E^\circ{}_D - E^\circ{}_A]. \qquad (3)$$

If the reaction is carried out in a solvent of low dielectric constant or if the radiuses of the donor and acceptor are small, the electrostatic factor can be large, especially if the charges of the donor and acceptor are very different.

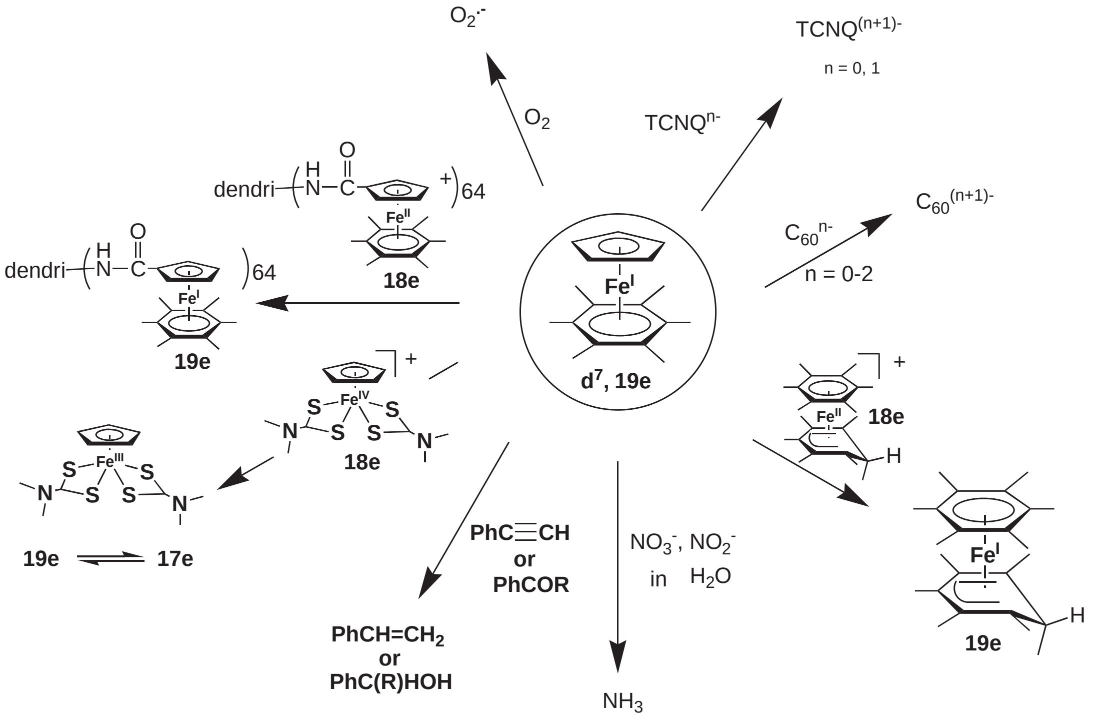
Examples of such reactions (most reactions of Scheme 5) are electron transfers from the iron(I) electron-reservoir complex and oxidants whose reduction potential is lower than that of the reductant.[21]

With C_{60}, monoelectronic reductions are well known from electrochemical studies (Scheme 6)[22] and can be carried out stepwise till the hexa-anion without breakdown on the electrochemical time scale. Strong chemical reductants such as alkali metals, however, can reduce C_{60} till the trianion only given the two extreme values of the last reduction potentials. Moreover, the cesium salt of $C_{60}{}^{3-}$ was shown to be a superconductor.[23] Reduction of C_{60} by $[Fe^{I}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$ gives the mono-, di-, or trianion of C_{60} depending on the stoichiometry. In the salt of the trianion, the lattice is determined by the large organoiron cation rather than by the anion, however. Thus, its physical properties are only those of a paramagnetic species. When the iron(I) complex is located at the periphery of dendrimers, electron transfer to C_{60} is obtained likewise, for instance to give $C_{60}{}^{\bullet-}$ with the suitable stoichiometry of reactants (Scheme 7).

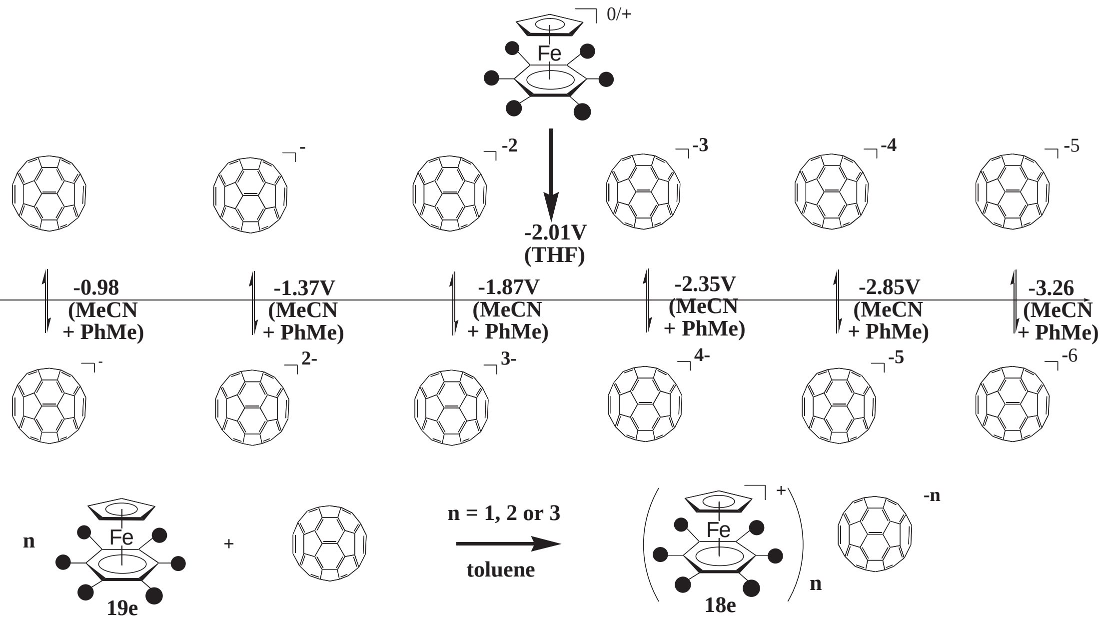
When the reduced form of the oxidant is not stable (Scheme 5, cases of $CO_2{}^{\bullet-}$ and $NO_3{}^{\bullet-}$), it is possible that electron transfer occurs with a reductant whose redox potential is more negative than that of the electron-reservoir complex, because the electron-transfer reaction is shifted towards product formation (all the more as the decomposition of the reduced form of the oxidant is faster). This is the case for CO_2 whose radical anion dimerizes very fast to the oxalate dianion in toluene and of $NO_3{}^-$ whose reduction can then be made catalytic (vide infra).[14,24]

Electron Transfer to Dioxygen: Chemistry of Superoxide Radical Anion and Its Inhibition by a Sodium Salt

The reaction of forest-green $[Fe^{I}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$ with dioxygen in various solvents (pentane, THF) corresponds to an overall hydrogen atom abstraction on a benzylic group to give a high yield of the deep red methylene cyclohexadienyl complex. At −78 °C, 1/2 mol H_2O_2 is formed from 1/2 mol O_2, whereas at room temperature, only 1/4 mol O_2 is con-



Scheme 5. Examples of electron-transfer reactions of the prototypal electron-reservoir complex $[\mathrm{Fe^I}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$.

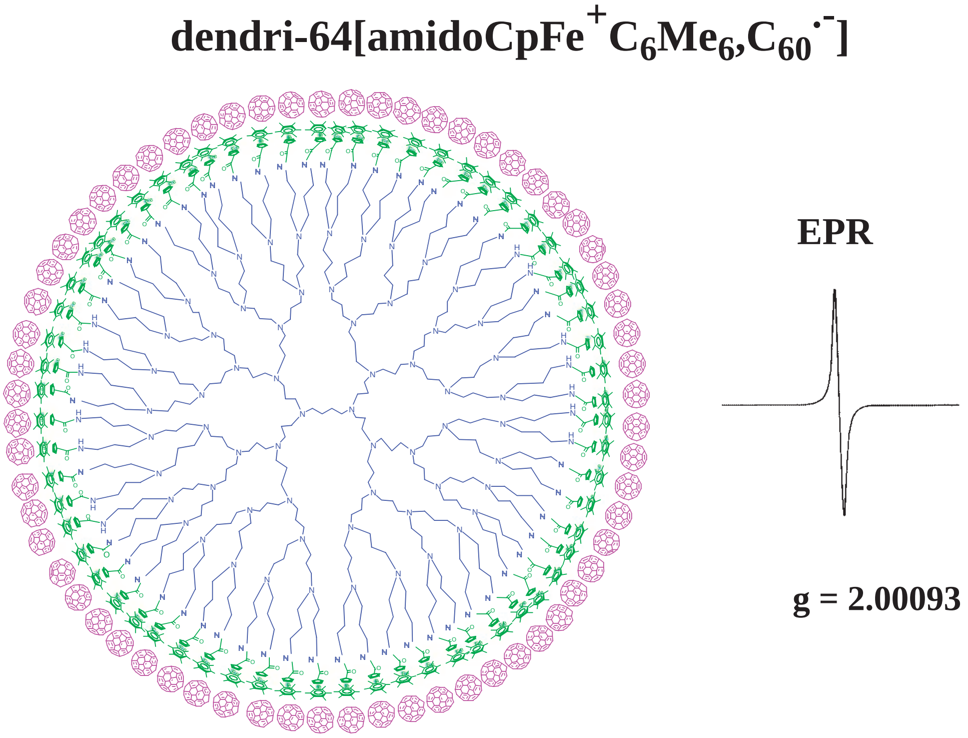


Scheme 6. Reduction of C_{60} by $[\mathrm{Fe^I}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$ to the mono-, di-, or trianion depending on the stoichiometry. For the redox potential values of C_{60}, see Echegoyen's Ref. 22.

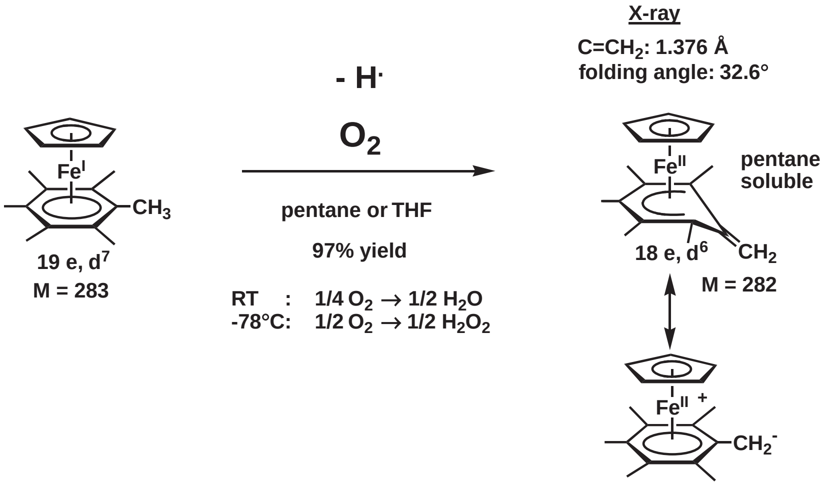
sumed, giving 1/2 mol H_2O (thus the O–O bond in dioxygen is cleaved, Scheme 8.[25]

The other 19e complexes $[\mathrm{Fe^I}Cp(\eta^6\text{-arene})]$ and $[\mathrm{Fe^I}Cp^*\text{-}(\eta^6\text{-arene})]$ bearing at least one hydrogen atom in benzylic position react in the same way, but when no benzylic hydrogen is present on the arene ring, formation of a peroxocyclohexadienyl dimer is observed. Hydrogen atom abstraction on the Cp* ligand is never observed.

When these reactions are carried out in an EPR tube at −90 °C, the EPR spectrum of the frozen solution shows the known temperature-dependent spectrum of superoxide radical anion, consistent with the fact that the potentials of the $[\mathrm{Fe^I}Cp(\eta^6\text{-arene})]/[\mathrm{Fe^{II}}Cp(\eta^6\text{-arene})]^+$ and $O_2/O_2^{\bullet-}$ redox couples have a difference of 1 V. Thus, the exergonicity of the electron transfer from the iron(I) complex to O_2 is about 23 kcal mol^{-1}. As a consequence, electron transfer must be very fast, according to Marcus theory.[26] The ion pair generated in a cage is a contact ion pair in these solvent of low dielectric



Scheme 7. Reduction of C_{60} to its mono-anion using dendrimer-supported 19e complex $[Fe^{I}(\eta^5\text{-dendr-NHCO-}C_5H_4)(\eta^6\text{-}C_6Me_6)]$ in MeCN a −30 °C. The ESR spectrum of the insoluble reaction product shows the same ESR as that of $C_{60}^{\bullet -}$ and its Mössbauer spectrum is identical to that of $[Fe^{II}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)][PF_6]$.



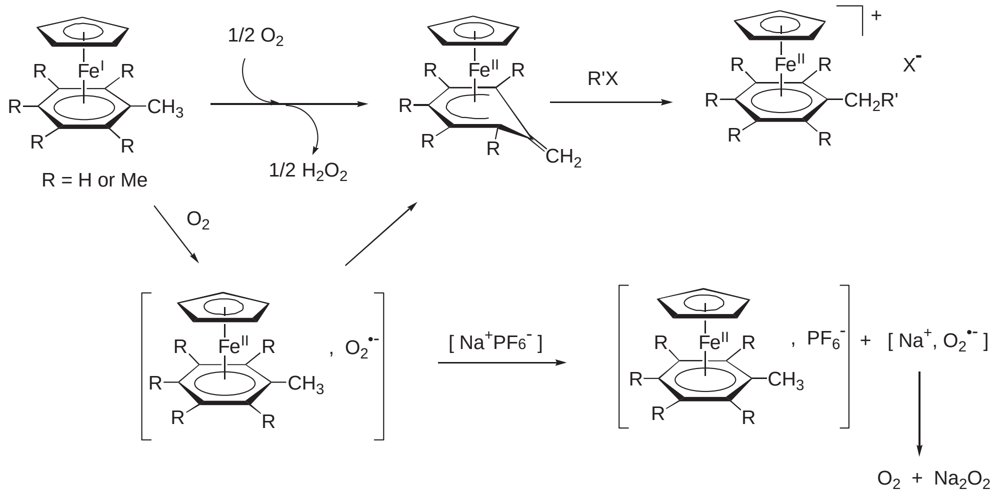
Scheme 8. Reaction of the 19e complex $[Fe^{I}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$ with O_2.

constant,[27] and deprotonation of a methyl group in the intermediate cation is driven by the fast dismutation of HO_2.[28] The possibility of this deprotonation can be checked by the reaction of $[Fe^{II}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)][PF_6]$ with KO_2 + 18-crown-6 in THF that also yields the deprotonated complex.

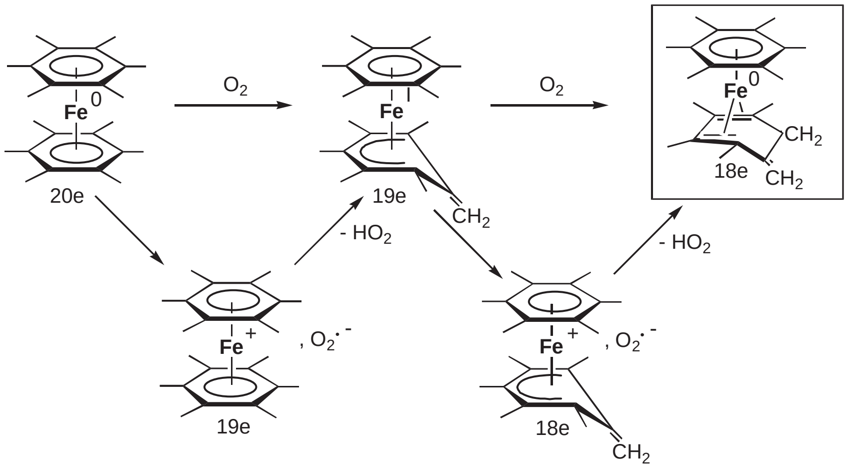
A spectacular experiment is that involving the same reaction in THF in the presence of one equiv of $Na^+PF_6^-$. No deprotonated complex is formed, and the reaction yields a colorless solution and a precipitate containing $[Fe^{II}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)][PF_6]$ and Na_2O_2.[29] This dramatic salt effect, quantitative when $NaPF_6$ is used, is observed in both situations where an H atom is present in benzylic position (H atom abstraction by O_2) or when it is not (formation of the peroxo dimer). This inhibition of the superoxide chemistry by a simple Na^+ salt is reminiscent to that of superoxide dismutase enzymes,[30] although we are far from biological systems.

In summary, the reactivity of the ion pair containing superoxide in a few seconds at −78 °C and its total inhibition by a Na^+ salt are very impressive, especially taking into account the fact that superoxide in commonly generated in vivo by single-electron reduction of dioxygen (Scheme 9).

The principle of the overall removal of a hydrogen atom in benzylic position by the electron-transfer/proton-transfer mechanism could be generalized to other classes of electron-



Scheme 9. Mechanism of the reaction of the 19e complex $[Fe^{I}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$ with O_2 involving the electron-transfer pathway followed by deprotonation within the caged superoxide ion pair. The spectacular (quantitative) salt effect of $NaPF_6$ in THF is fully consistent with this mechanism.



Scheme 10. Double H-atom abstraction by O_2 in the 20e complex $[Fe^{0}(C_6Me_6)_2]$ according to the electron-transfer/proton-transfer mechanism analogous to that shown with the 19e complex $[Fe^{I}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$ in Schemes 7 and 8. Compare the mechanism with Scheme 9.

$$[Fe^{I}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)] + \tfrac{1}{4}\,O_2 \rightarrow [Fe^{II}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_5CH_2)]$$

$$[Fe^{I}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)] + RX \rightarrow [Fe^{II}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_5CH_2R)][X]$$

$$RX = CH_3I,\ SiMe_3Cl,\ Mn(CO)Br,\ CpFe(CO)_2Cl,\ CO_2,\ CS_2$$

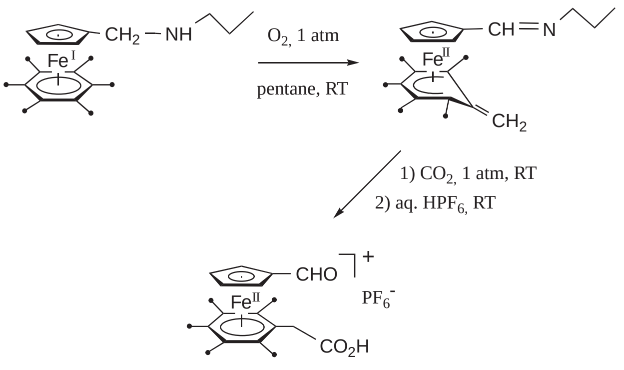
Scheme 11. Functionalization of the iron–arene sandwich in benzylic position by C–H activation upon contact of the 19e complex with air and benzylic C–R bond formation upon subsequent contact of the activated intermediate complex with an electrophile RX (both reactions are fast upon contact under ambient conditions).

rich neutral 19e or 20e complexes.[31,32] Indeed for instance, the reaction of O_2 or air with the 20e complex $[Fe(\eta^6\text{-}C_6Me_6)_2]$ (Scheme 10) proceeds with double H-atom abstraction to yield an iron(0)–orthoquinodimethane complex.[32]

Synthetic Applications of the Reaction of the Electron-Reservoir Complexes with O_2 or Air in Organoiron Chemistry and Molecular Engineering

Synthetic applications of the reaction of the electron-reservoir complex $[Fe^{I}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$ with O_2 are provided by the reactions with electrophiles subsequent to contact of the electron-reservoir complex with air.[25] Thus functionalization of the sandwich iron complexes in benzylic position with a variety of elements is straightforward under ambient conditions (Scheme 11).

The 19e Fe^{I} complex of C_6Me_6 in which the Cp ring bears an amino-alkyl group reacts with 3/4 equiv. of O_2 to give overall three H-atom abstraction (Scheme 12), and the mechanism was shown to proceed similarly by a series of electron transfer–deprotonation sequences (Scheme 13). Reaction of the imine product with CO_2 and acid yields the sandwich containing both the aldehyde function on the Cp ligand and the carboxylic acid function on the arene ligand. The aldehyde group allows linking the sandwich to an hexa-amine star to yield an hexa-sandwich star containing carboxylic acid functional groups that solubilize the hexairon complex in alkaline water.[33] This molecular engineering is useful, because the systems $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]^{+/0}$ and derivatives are redox catalysts (vide infra).

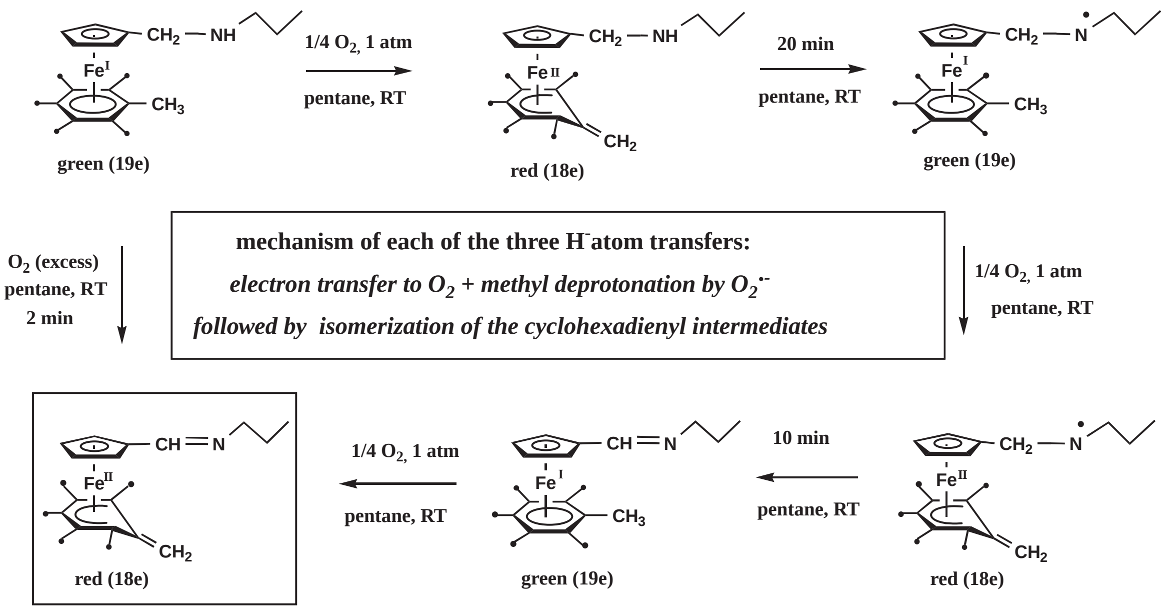


Scheme 12. Reaction of the aminoalkylcyclopentadienyl 19e complex with O_2 or air consuming $\frac{3}{4}O_2$ and preceded with triple overall atom abstraction. See the mechanism in Scheme 13.

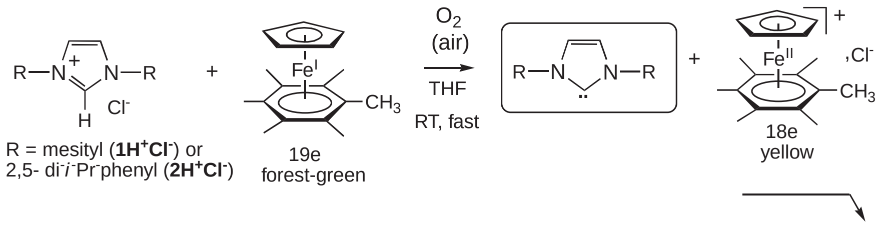
How to Deprotonate a Weak Acid Using an Electron-Reservoir Complex and Air: Example of the Generation of *N*-Heterocyclic Carbenes from Imidazolium Salts

In principle, the deprotonation of imidazolium salts[34] to *N*-heterocyclic carbenes is easy using *t*-BuO^-K^+ in simple cases. These carbenes are famous since their introduction in catalysis by Herrmann[35] and are used in olefin metathesis catalysts[36–39] and Pd C–C coupling catalysts.[40] They are versatile, however,[41] and reaction of *t*-BuO^-K^+ with silyl-substituted *N*-heterocyclic carbenes forms a colored charge-transfer complex resulting from the oxophilicity of the Si atom, and deprotonation does not proceeds cleanly. On the other hand, in the presence of the electron-reservoir complex $[Fe^I(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$ and air, deprotonation of parent and silyl-substituted imidazolium salts to *N*-heterocyclic carbenes proceeds easily and is fast (Scheme 14).

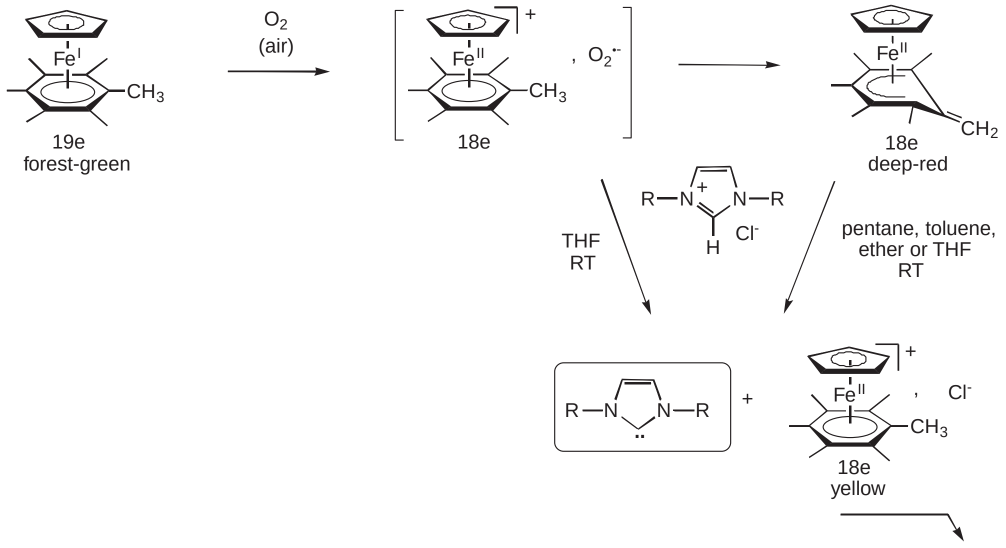
The mechanism involves electron transfer from the electron-



Scheme 13. Mechanism of triple H-atom abstraction by O_2 or air from $[Fe^I(\eta^5\text{-}PrNHCH_2C_5H_5)(\eta^6\text{-}C_6Me_6)]$ (Scheme 12). Compare with Scheme 9.



Scheme 14. Deprotonation of the weak acid imidazolium using the prototypal electron-reservoir complex $[Fe^I(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$ and air under ambient conditions.



Scheme 15. Mechanism of the deprotonation of the weak acid imidazolium using the prototypal electron-reservoir complex $[Fe^{I}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$ and air via superoxide anion in various solvents. Two proposed paths following electron transfer from Fe^{I} to O_2 involve direct deprotonation by superoxide ion or via the intermediacy of the 18e complex $[Fe^{II}(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_6Me_5CH_2)]$.

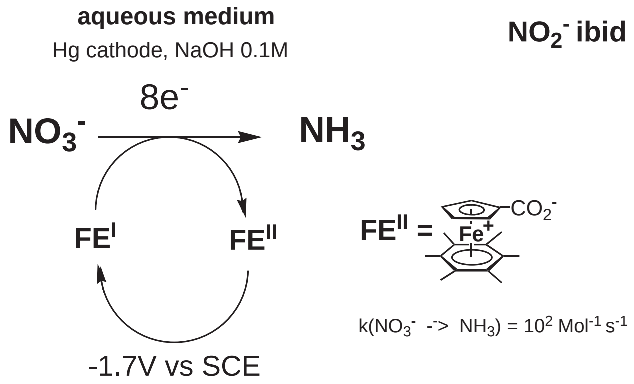
reservoir complex and O_2 forming superoxide radical anion. The latter either directly deprotonates the imidazolium salt or deprotonation occurs via the iron sandwich complex. In principle, this system could also work with other weak acids (Scheme 15).[42]

Electron-Reservoir Complexes as Redox Catalysts

Redox catalysts facilitate reduction or oxidation processes that are thermodynamically favorable (exergonic), but suffer from kinetic limitations due to extensive structural reorganization. They also facilitate endergonic electron transfers for which the product is reactive enough to shift the redox process. The two extreme mechanisms by which redox catalysts work are outer-sphere electron transfer and inner-sphere electron transfer. In the first case, they are rather called mediators, whereas in the latter case, they are called redox catalysts.[43] The mechanism (outer sphere vs. inner sphere) is not always clear, especially because mechanisms that are intermediate between these two situations can be envisaged. Thus, the word redox catalyst is generally used for these families of catalysts.

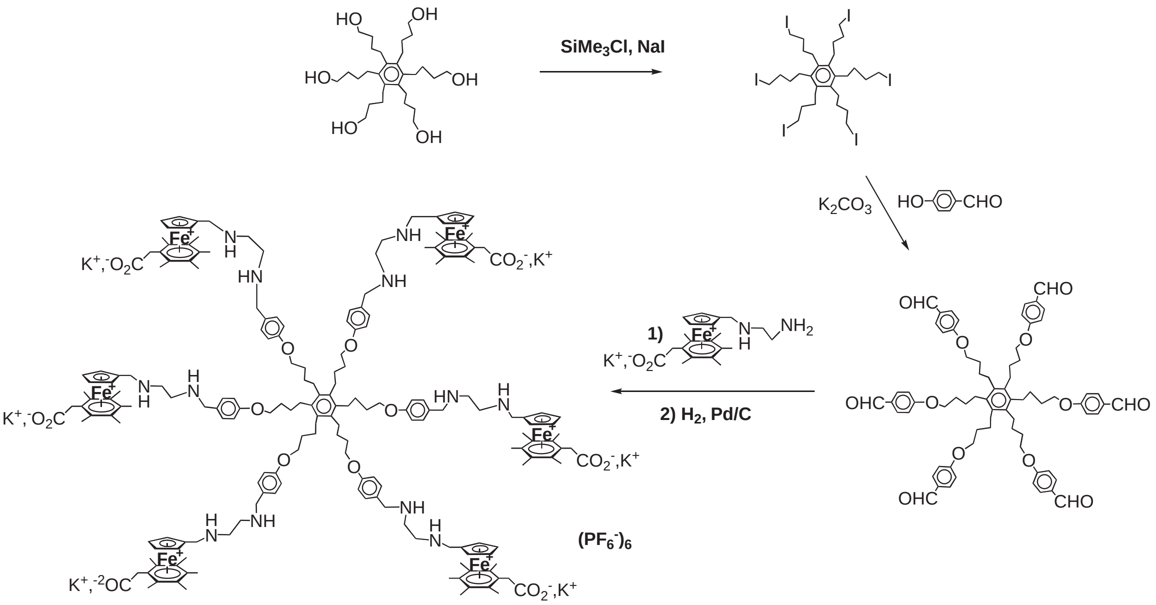
Redox catalysts are important in biological processes for which coupling between several redox catalysts (including mediators and true redox catalysts) are required in complex fundamental processes such as respiration, nitrogen fixation, etc. They are also designed for chemical processes (for instance Cu^{I}/Cu^{II} in the Wacker process), photochemical processes (water splitting), and electrochemical processes (fuel cells).[44]

The electron-reservoir complexes $[Fe^{I}(\eta^5\text{-}C_5H_4R)(\eta^6\text{-}C_6Me_6)]$ ($R = H$ or CO_2H) and derivatives are redox catalysts for nitrate and nitrite cathodic reduction in water using an Hg cathode in alkali aqueous solution. These oxo-anions are not reducible (electroactive) in water at basic pH, and it is water that is reduced to dihydrogen at very negative potentials around −2 V vs. SCE. In the presence of the $Fe^{I}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$ catalyst, however, these nitrogen oxides are reduced to ammonia. In the absence of a nitrate or nitrite, the redox catalysts slowly catalyze water reduction to dihydrogen. Catalysis of nitrogen oxide reduction to ammonia works whether the reduced form of the catalyst is water-soluble or not (i.e. homogeneously or heterogeneously). When a carboxylic group is present on the Cp ring of the catalyst, the catalyst becomes soluble in alkaline water in both the Fe^{II} and Fe^{I} forms, which gives access to the kinetics of redox catalysis. The rate constant is then directly accessible from the ratio of current intensities for the $Fe^{II/I}$ reduction in the voltammogram measured in the presence and absence of nitrate or nitrite (Scheme 16).[45–47]



Scheme 16. Redox catalysis of the cathodic reduction of nitrate and nitrite in water on a Hg cathode. These anions are not electroactive in the absence of catalyst in basic aqueous medium (water is then reduced to H_2). The organoiron electron-reservoir redox catalyst is fully stable upon cycling in water.

It was also possible to derivatize redox catalysts onto hexafunctional star-shaped cores using the aerobic activation of alkylamino–$CpFe(\eta^6\text{-}C_6Me_6)^+$ delineated above (Scheme 17). Introduction of catalysts at the termini of dendrimers is a useful strategy allowing to recover and re-use the catalyst.[48,49] Indeed, large molecules are easy to separate from reaction media by precipitation or ultra-centrifugation, contrary to small



Scheme 17. Synthesis of a star-shaped water-soluble electron-reservoir redox catalyst. No kinetic loss is observed compared to the monoiron complex, and stability upon cycling is retained. The function of such dendrimer-type catalysis is the recovery of the catalyst due to its large size. The star shape avoid kinetic drop observed with bulky dendritic cores inhibiting access of the substrate to the metal center.

monometallic complexes. One problem, however, is that metal sites are not so easily accessible at the termini of dendritic branches because of steric inhibition that slows down reaction rates. Therefore, we have proposed that it is best to use stars rather than dendrimers for this kind of strategy whereby the catalyst is located at the termini of the tethers.[50] Thus, the hexairon redox catalysts were found to be about as efficient as mononuclear catalysts, whereas introduction of bulk around the iron sandwich by hexasubstitution of the arene ring slowed down the redox catalysis of nitrate and nitrite reduction. This indicates that there is some inner-sphere component in the electron-transfer step between the 19-electron complex and nitrate or nitrite. Although the low-oxidation state of Fe^I is not favorable for binding an oxygen atom of these nitrogen oxides, decoordination of an arene double bond to generate a 17-electron Fe^I species that would weakly bind an oxygen atom to facilitate electron transfer is probable given the kinetic data (Scheme 18).[47]

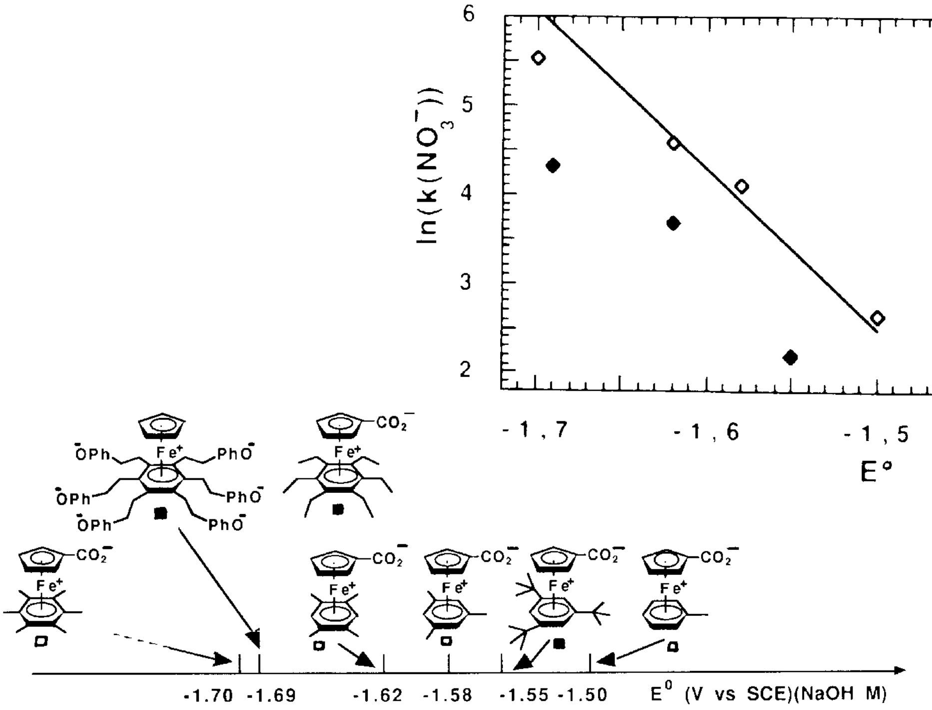
In summary, mono- and star-shaped hexanuclear iron-sandwich electron-reservoir systems bearing the water-solubilizing carboxylate group catalyze cathodic nitrate and nitrite reduction to ammonia on Hg cathode in alkaline water. Kinetic data show that location of the iron catalyst at the termini of the star core is favorable to avoid steric inhibition of the inner-sphere mechanism of redox catalysis.

$[Fe^I(\eta^5\text{-}C_5R_5)(\eta^6\text{-}C_6Me_6)]$ (R = H or Me) as Selective Electrocatalysts: Initiation of Electron-Transfer-Chain Catalysis in Di- and Polynuclear Complexes and Dendritic Clusters

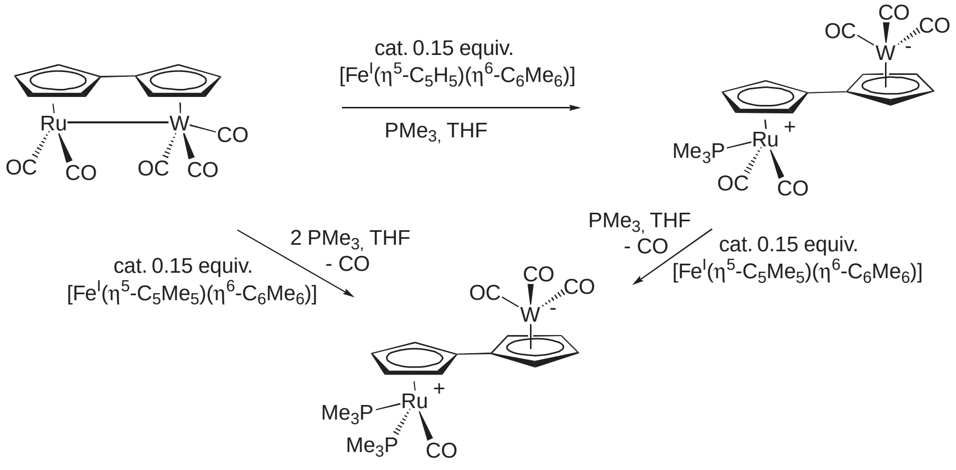
Electron-transfer-chain catalysis, introduced first by Taube and Rich with inorganic complexes,[51] has been much studied and applied to organotransition-metal synthesis in the early 1980s.[52–54] The electron-reservoir complexes $[Fe^I(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$ and derivatives are excellent initiators when initiation must be carried out by a reductant, i.e. when the product is more electron rich than the starting complex in order to design an exergonic cross electron-transfer step in the catalytic chain. For instance substitution of the toluene ligand by three phosphanes can be achieved in a few seconds at room temperature by adding 1% of $[Fe^I(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$ in THF.[55]

In fulvalene dimetal carbonyl complexes, ETC-induced introduction of PMe_3 leads to the zwitterionic-monosubstituted complex in the presence of a catalytic amount of $[Fe^I(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$. Introduction of the second phosphane involving carbonyl substitution does not proceed, however. Substitution of CO by the second PMe_3 ligand can be only achieved using the more powerful reductant $[Fe^I(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6Me_6)]$ as a catalyst (Scheme 19).[56]

In the cluster $[Ru_3(CO)_{12}]$, substitution of carbonyl by phosphane ligands leads to mixtures when it is carried out thermally. Using ETC catalysis, CO substitution by phosphanes was shown by Bruce's group to be very selective and clean.[57] Subsequently, this synthetic strategy was pursued in a dendrimer series. Therefore, dendritic phosphines containing 32 diphenylalkyl phosphine termini were synthesized and showed a single ^{31}P NMR signal signifying the equivalence of the phosphorus atoms around the dendrimer. ETC catalysis was initiated by 1% $[Fe^I(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$ and carried out using a stoichiometric dendritic phosphine/cluster ratio in order to perform single CO substitution by a dendritic phosphine tether. The resulting product showed a single ^{31}P NMR signal indicating that the 32-phosphine dendrimer has bound 32 $Ru_3(CO)_{11}$ cluster units. A similar procedure was applied to the next generation of dendrimer containing 64 phoshine termini.[58] The overall reaction and its proposed mechanism are shown in Schemes 20 and 21.



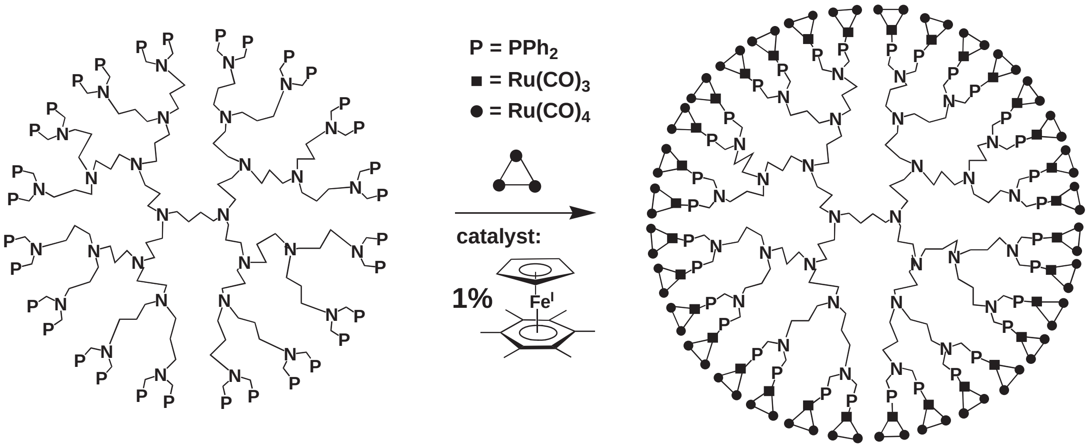
Scheme 18. Kinetics of the redox catalysis of nitrate cathodic reduction (ln of rate constant k of the mediation step: $Fe^{I} + NO_3^- \rightarrow Fe^{II} + \ldots$) in water as a function of the driving force E of the redox catalyst. Note the kinetic drop with the redox catalysts containing a bulky arene ligand that inhibits the approach of nitrate to iron center. This effect shows the inner-sphere component of the electron-transfer mechanism. Non-bulky catalysts are on the straight line. The star-shape catalyst of Scheme 17 nearly falls on this straight line.



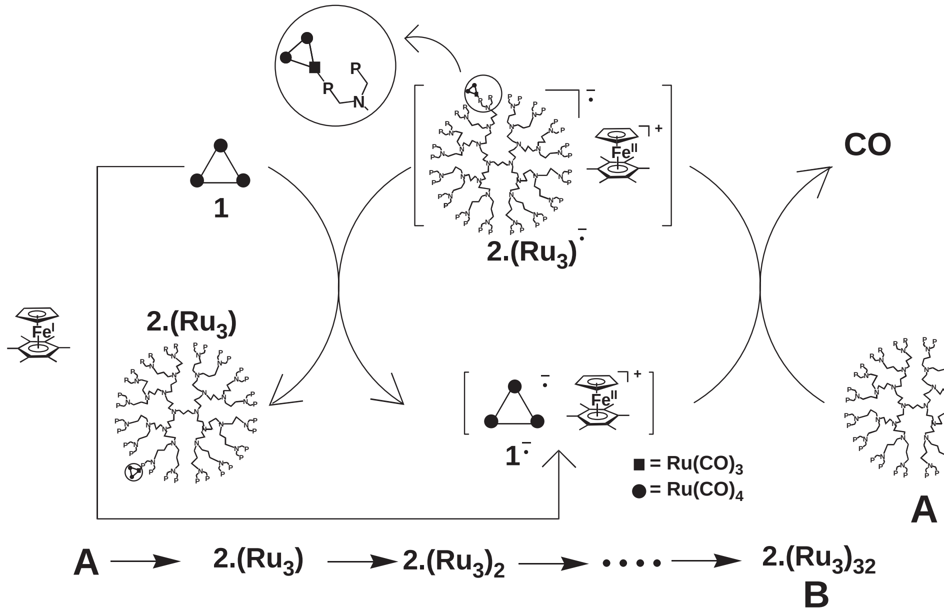
Scheme 19. Electrocatalytic (electron-transfer-chain-catalyzed or ETC-catalyzed) phosphine addition and electron transfer from Ru to W catalyzed by $[Fe^{I}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$. This catalyst is too weak, however, to catalyze CO substitution by PMe_3 in the zwitterionic complex (top right). The stronger catalyst $[Fe^{I}(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6Me_6)]$ can catalyze this reaction (its more negative redox potential is due to the five methyl groups on the Cp* ligand).

Reservoir of Electron Hole: The 17-Electron Complex $[Fe^{III}(\eta^5\text{-}C_5R_5)(\eta^6\text{-}C_6Me_6)][SbCl_6]_2$, the Strongest Known Organometallic Oxidant

Oxidation of the yellow 18-electron complex $[Fe^{II}(\eta^5\text{-}C_5R_5)(\eta^6\text{-}C_6Me_6)][PF_6]$ by $SbCl_6$ in liquid SO_2 yields the purple 17-electron complex $[Fe^{III}(\eta^5\text{-}C_5R_5)(\eta^6\text{-}C_6Me_6)][SbCl_6]_2$, isoelectronic to ferrocenium, that is stable in dry air. The electrochemical oxidation of the monocationic 18-electron complexes $[FeCp(\eta^6\text{-arene})][PF_6]$ in liquid SO_2 shows a reversible monoelectronic wave around +2 V vs. SCE, but the 17-electron dicationic complexes are not isolable. The full steric protection of the iron(III) center that bears the electron hole in the dication insures stability of the complex with 11 methyl groups. The redox potential of this Fe^{II}/Fe^{III} system is 1.4 V vs. SCE, i.e. 1 V lower than that of ferrocenium. This large difference of redox potential for two isoelectronic redox systems involving the same oxidation states with the same the sand-



Scheme 20. Substitution of CO by a phosphine tether of the dendrimer in $[Ru_3(CO)_{12}]$ represented by a triangle on the arrow. ^{31}P NMR shows a single peak for the dendritic reaction product matching a model reaction. This ETC reaction is catalyzed cleanly by $[Fe^{I}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$.



Scheme 21. ETC mechanistic cycle for the catalyzed CO substitution by a dendritic phosphine tether in $[Ru_3(CO)_{12}]$ using the catalyst $[Fe^{I}(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$.

wich structure is only due to the charge difference that is responsible for the difference of electrostatic effect.[59]

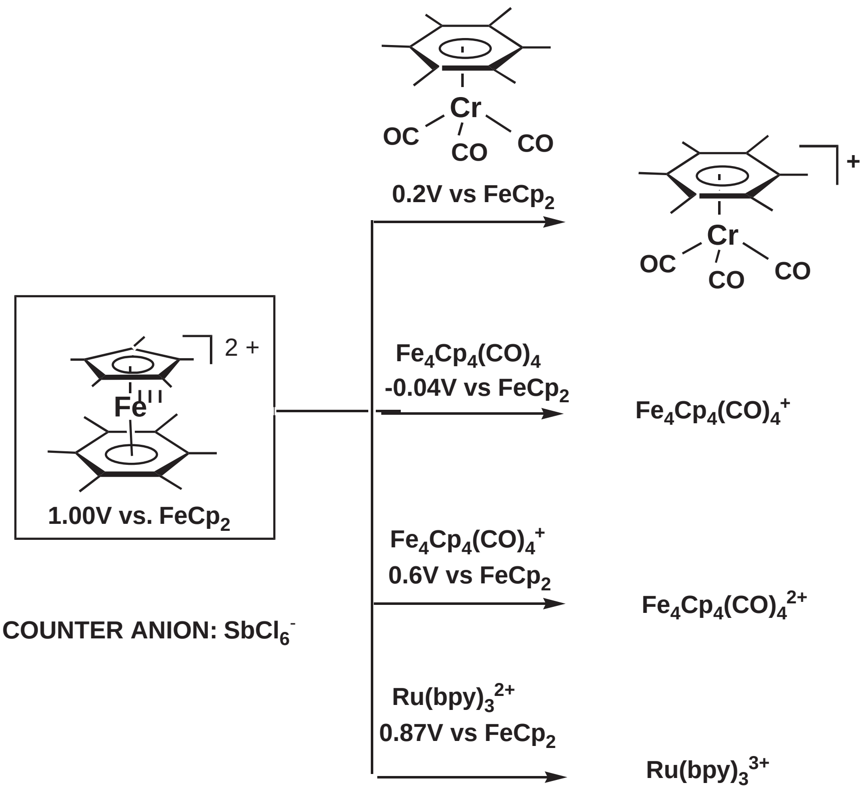
The complex $[Fe^{III}(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6Me_6)][SbCl_6]_2$ is a redox catalyst for the oxidation of furfural (Scheme 22). It can also oxidize $[Cr(\eta^6\text{-}C_6H_6)(CO)_3]$ to the cation and the monocationic complex $[FeCp(CO)]_4[PF_6]$ to the isostructural dication.[59]

References for the Determination of Electrochemical Redox Potentials

Although ferrocene has been proposed by the IUPAC to serve as a reference, its potential varies within 0.5 V with the nature of the solvent and supporting electrolyte because of possible interactions between nucleophiles and the iron center in the ferrocenium form. On the other hand, permethylated iron and cobalt complexes has been shown to be reliable, their potential being not solvent dependent. Thus, decamethylferrocene,[60] decamethylcobaltocene, and $[Fe^{I}(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6Me_6)]$[61] form a set of three good references that cover the redox scale. Potentials determined vs. ferrocene can now be easily calculated vs. any of these three reference compounds using published potential tables.[61]

Concluding Remarks and Prospects

The family of 19-electron Fe^{I} complexes $[Fe^{I}(\eta^5\text{-}C_5R_5)(\eta^6\text{-}C_6Me_6)]$ (R = H or Me) are electron-reservoir complexes that are extremely useful single-electron-transfer reagents. They can reduce a large variety of substrates stoichiometrically or catalytically, because their redox potentials are very negative. These electron-transfer reactions are clean, because the oxidized form of the electron-reservoir system is very stable and precipitates from the reaction mixture.



Scheme 22. Single-electron oxidation of inorganic and organometallic substrates using the strong oxidant [$\mathrm{Fe^{III}}(\eta^5\text{-}\mathrm{C_5Me_5})(\eta^6\text{-}\mathrm{C_6Me_6})][\mathrm{SbCl_6}]_2$, a 17e complex (isoelectronic to ferrocenium) that is a reservoir of electron hole.

It is also possible to choose the working potential of the electron reservoir in a range of potentials by selecting the appropriate number of methyl substituents on the rings. If the number of methyl substituents on the arene ring is lower than 6, the electron-reservoir system must be handled at −10 °C in order to avoid its decomposition or dimerization. Alternatively, [$\mathrm{Fe^{I}}(\eta^5\text{-}\mathrm{C_5H_5})(1,3,5\text{-}t\mathrm{Bu_3C_6H_3})$], thermally stable at room temperature, can be used. The parent complex [$\mathrm{Fe^{I}}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^6\text{-}\mathrm{C_6H_6})$],[15] whose potential is 0.5 V more negative than that of cobaltocene can be used at 0 °C in solution, but its isolation and storage in the solid state requires to work at −10 °C.

The use of the complex [$\mathrm{Fe^{I}}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^6\text{-}\mathrm{C_6Me_6})$] is routine and standard,[62] because it does not decompose below 100 °C, and its synthesis is facile (under rigorously inert atmosphere). It can be stored for a long time and its multiple uses have been described in this review. If a more powerful neutral reductant is needed, the analog [$\mathrm{Fe^{I}}(\eta^5\text{-}\mathrm{C_5Me_5})(\eta^6\text{-}\mathrm{C_6Me_6})$] is useful, with a redox potential 0.35 V more negative than that of its Cp analog. These electron-reservoir complexes can be used inter alia in pentane, ether, THF, DME, benzene, and toluene solution at room temperature for the thermally stable $\mathrm{Fe^{I}}$ complexes or below for the others. The use in MeCN is possible for [$\mathrm{Fe^{I}}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^6\text{-}\mathrm{C_6Me_6})$] at −30 °C. At room temperature, reaction with MeCN leads to slow decomposition.

So far, the use of these $\mathrm{Fe^{I}}$ electron-reservoir complexes has been more extensive in inorganic and organometallic synthesis, and under exploited in organic synthesis where Kagan's reagent $\mathrm{SmI_2}$ has proved to be a very valuable reductant[63] working by an inner-sphere mechanism.

Electron transfer from [$\mathrm{Fe^{I}}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^6\text{-}\mathrm{C_6H_6})$] to $\mathrm{O_2}$, exergonic by 1 V, is an important case because of the cytotoxicity of superoxide radical anion and its cage reactions that can be used in synthesis. The dramatic reactivity of superoxide has been shown (−78 °C, only a few seconds) as well as its inhibition by $\mathrm{Na^+}$. A general, simple application of the reaction of [$\mathrm{Fe^{I}}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^6\text{-}\mathrm{C_6H_6})$] with air via superoxide is the recent deprotonation of weak bases, exemplified with the formation of functional *N*-heterocyclic carbene ligands.

A challenging goal is to fabricate molecular nanobatteries using stable $\mathrm{Fe^{I}}$ complexes, possibly by branching stable $\mathrm{Fe^{I}}$ complexes to dendritic nanoarchitectures. Difficulties resided so far in handling functional cationic precursors in branching reactions. On the contrary, dendrimers terminated with ferrocene tethers are more easily accessible,[64] but they are poor reductants and cannot be considered as electron-reservoir systems.

The concept of electron reservoir has been extended to reservoirs of electron holes using the same family of complexes. Symmetrical use has been shown with the stable 17-electron complex [$\mathrm{Fe^{III}}(\eta^5\text{-}\mathrm{C_5R_5})(\eta^6\text{-}\mathrm{C_6Me_6})][\mathrm{SbCl_6}]_2$, a very strong but thermally stable monoelectronic oxidant. Prospects in electron-reservoir system now reside in the disclosure, characterization and introduction into devices of dendritic and polymeric stable complexes for which two oxidation states are also stable.

It is a pleasure to acknowledge here the contribution of the many students, post-docs and colleagues cited in the references who have contributed to bring ideas and efforts in the research area of electron-reservoir complexes and their applications and must be warmly thanked therefore. Financial support from the Institut Universitaire de France (IUF), the University Bordeaux I, the Centre National de la Recherche Scientifique (CNRS), the Agence Nationale de la Recherche (ANR) and the Ministère de la Recherche et de la Technologie (MRT) are gratefully acknowledged.

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