

Organoiron activation combined with electron- and proton transfer: implications in biology, organic synthesis, catalysis and nanosciences

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Abstract

This *Account* summarizes the results obtained in our research group on the intra- and intermolecular organoiron activation of substrates by combining the coordination of arenes by $\text{CpFe}^{+/0}$ and electron and/or proton transfer. The concepts involved are those of electron and proton reservoirs, activation of O_2 by single electron transfer in solution, mimic and inhibition of the reactivity of superoxide radical anion, materials synthesis (for instance fullerene anions), electronic communication between two metals connected by a hydrocarbon bridge, activation of arene ligands for multiple functionalization, giant dendrimer synthesis and electron transfer in catalysis (redox and electron-transfer-chain).

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1. Introduction

Iron chemistry occupies a central place in bioinorganic chemistry, catalysis and materials science. Its role in inorganic chemistry has also been a key one since the end of the XIX century with the finding of iron pentacarbonyl, and especially since the discovery of ferrocene and its π -structure in the middle of the XX century [1–5]. Iron being also the most common and cheapest metal, efficient chemistry using iron, exemplified very early with the Haber–Bosch and Fischer–Tropsch processes, is likely to find wide-spread use and applications. In the present *Account*, I wish to briefly illustrate some aspects of our research in the last 25 years on the connection between organoiron

chemistry and electron and proton transfer (Scheme 1). I will tentatively indicate how it led to implications in biology, organic synthesis, catalysis and nanosciences. The following Scheme 1 illustrates the basic concepts, simple reactions and key thermodynamic data that have guided our research in organometallic chemistry.

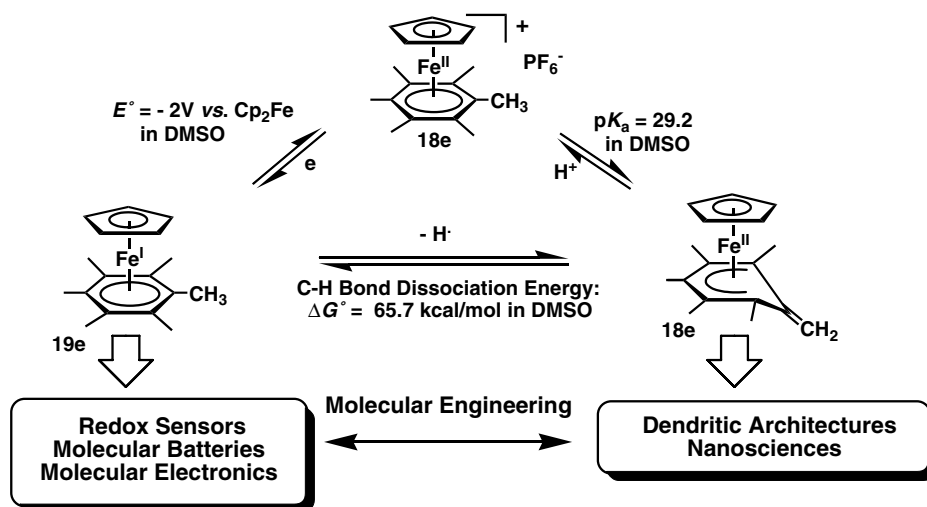
2. Electron-reservoir complexes, electron-transfer and organoiron activation: concepts and relevance to biology, organic synthesis, catalysis and molecular materials

2.1. Syntheses of electron reservoir complexes

The key compound in the beginning of our studies was the yellow complex $[\text{FeCp}(\eta^6\text{-C}_6\text{Me}_6)][\text{PF}_6]$, $\mathbf{1}^+[\text{PF}_6^-]$, stable in concentrated sulphuric acid, and easily accessible in large quantities from ferrocene and the arene using the useful ligand substitution reaction

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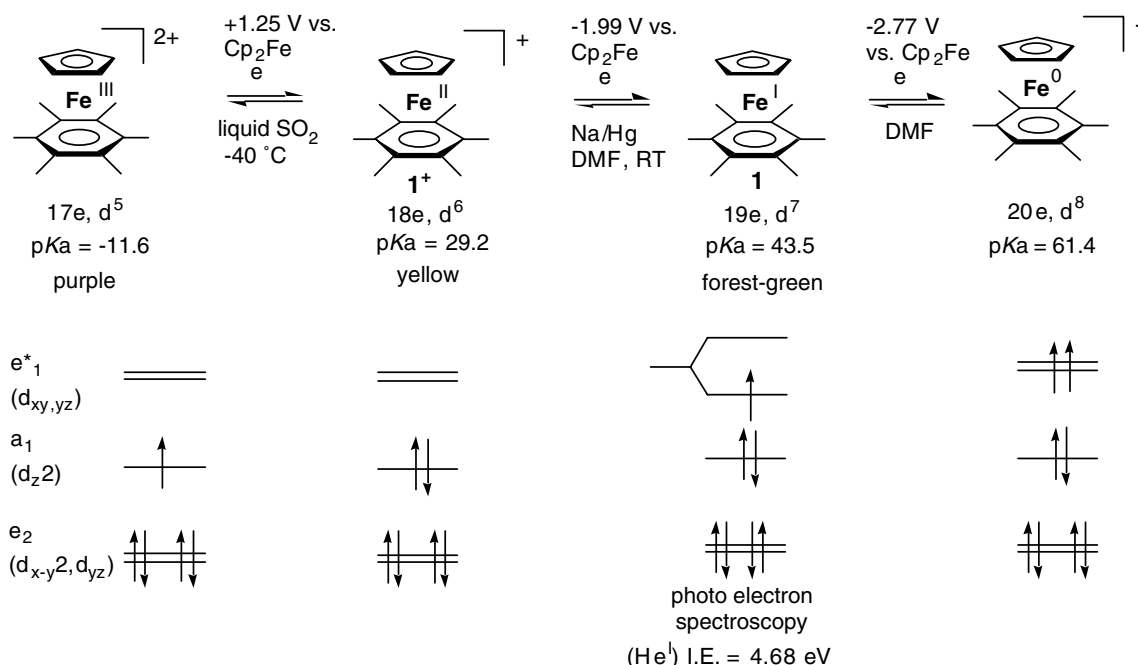
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Scheme 1. Electron- and proton-reservoir properties of the prototypical cationic iron-sandwich complex $1^+PF_6^-$.

reported by the Nesmeyanov group [6]. The cyclic voltammetry of $1^+[PF_6^-]$ shows two one-electron cathodic waves at -1.99 and -2.77 V vs. ferrocene in DMF [7,8]; later we found that a reversible anodic wave could be observed in liquid SO_2 at 1.25 V vs. ferrocene [8]. Both the forest-green one-electron reduction (using Na/Hg in DME at RT) [7] and the purple one-electron oxidation (using $SbCl_5$ in SO_2 or MeCN) [8] products were isolated in the $[Fe(\eta^5-C_5R_5)(\eta^6-C_6Me_6)]^{0/+1/+2}$ series ($1^{0/+1/+2}$; R = H; $2^{0/+1/+2}$; R = CH_3) (Scheme 2).

The 19-electron series is stable with both Cp and Cp^* and these 19-electron Fe^I complexes have the lowest re-

ported values of ionization potentials disclosed by He(I) photoelectron spectroscopy [7d]. Consequently, they are the most electron-rich neutral compounds known, and we called them electron-reservoir systems [7]. The 17-electron dication $[FeCp\eta^6-C_6Me_6]^{2+}$ also is the strongest organometallic oxidant known so far [8]. Both these 17- and 19-electron complexes are very useful one-electron transfer reagents, and have extensively been used as such [7,10,11]. In these compounds, the redox centers is buried, thus protected inside the molecular frame, which explains their stability despite their odd-electron numbers. Yet, although the orbital of the 19 electron



Scheme 2. Electron-reservoir complexes: the three first forms are isolable, and the fourth one (20e) is observed by cyclic voltammetry.

is largely metal based (about 80%), the structures of 19-electron radicals oscillate between 19-electron, 18-electron-radical and 17-electron (fast interconversion or average structure), these forms being either tautomers or mesomers depending on the cases [9].

2.2. Generation of reactive superoxide radical anion and inhibition of its reactivity: implication in biology

Among the many electron-transfer reaction achieved with these electron-reservoir complexes, let us only mention the reduction of two mono-element inorganic compounds: O_2 and C_{60} , because they are connected respectively with biology and materials science. The reaction of $[FeCp(\eta^6-C_6Me_6)]$ (**1**) in pentane or THF, with O_2 is fast, from forest green to deep red, consumes 1/4 mol O_2 , and 1/4 mol H_2O is produced at 20 °C. At -80 °C, 1/2 mol O_2 is consumed, and 1/2 H_2O_2 is formed. In all cases, the deep-red reaction product **3** results from the lost of one H atom. With **2**, the reaction is regioselective and gives only the Fe^{II} cyclohexadienyl complex, not the Fe^0 fulvene isomer. When the reaction is carried out in an EPR tube, the known temperature-dependent EPR spectrum of superoxide radical anion is seen at the interphase of color change. Indeed, the electron transfer from **1** to O_2 is exergonic by almost 1 V. When the same reaction in THF is carried out in the presence of one equiv. $NaPF_6$, however, it gives a completely different compound: a yellow precipitate of $1^+[PF_6^-]$ is formed, which was taken into account by the ion pair exchange (Scheme 3).

The superoxide salt KO_2 can also deprotonate $1^+[PF_6^-]$ in the same way, consistent with a deprotonation of 1^+ by O_2^- in the reaction of **1** with O_2 . The compound **3** reacts smoothly with many electrophiles under ambient conditions to functionalize the arene ligand as

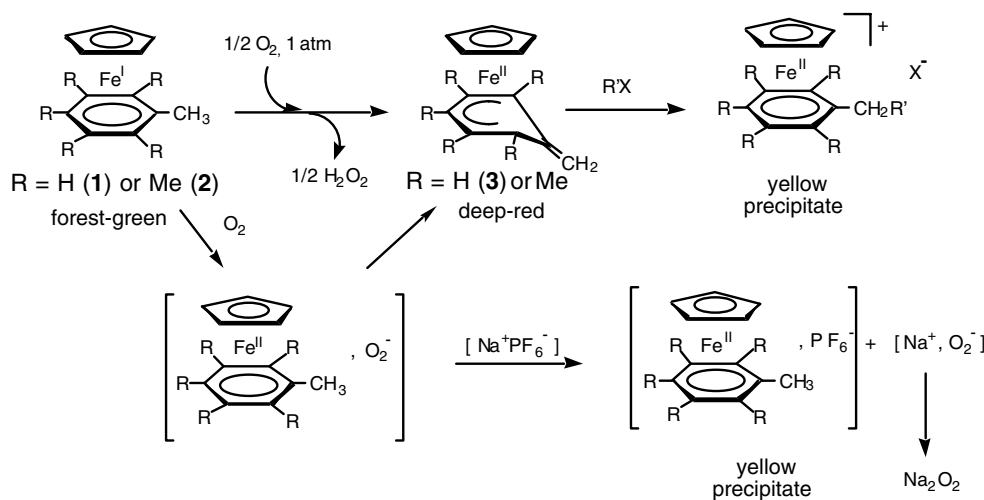
shown in Scheme 2, which also makes the C–H activation of **1** by O_2 a useful process in aromatic synthesis [12].

Thus, the electron-reservoir complexes such as **1** and **2** can generate superoxide radical anion in pentane, THF or DMSO, and the subsequent reactivity of superoxide is very interesting. It reacts as a base in the ion pair to deprotonate the organoiron cation, a process that is seemingly not favored viewing the low pK_a value of HO_2 (4.8), but strongly driven by the very fast follow-up disproportionation of HO_2^{\cdot} to O_2 and H_2O_2 . Furthermore, this remarkable reactivity of superoxide radical anion in the ion pair is totally inhibited by a simple sodium salt.

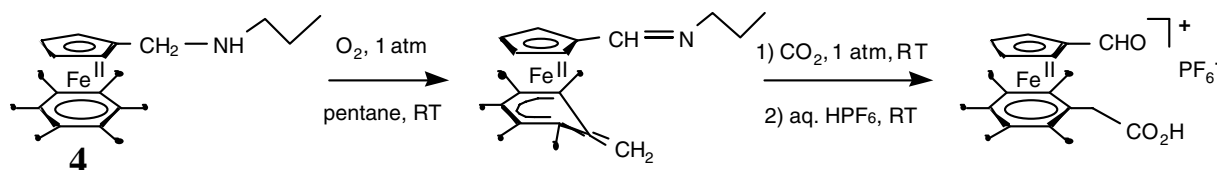
Later, the reaction of functional 19-electron complexes such as **4** with O_2 was shown to lead to the loss of three hydrogen atoms, leading to the functionalization of the sandwich complex (Scheme 4) [10].

The sequence consisting in electron-transfer followed by proton transfer is involved three consecutive times in this case, and the intermediates could be found accordingly. When the arene ligand in **1** lacks benzylic hydrogen atoms, for instance, with $[Fe^I Cp(\eta^6-C_6H_6)]$, superoxide in the cage acts as a nucleophile onto the electron-poor arene ligand giving first a peroxocyclohexadienyl radical complex that couples to the starting complex to give an orange peroxy dimer. This formation is also inhibited by the presence of one equiv. $NaPF_6$ [12d].

The single electron transfer to O_2 is of great interest in the biological context because of the damages caused by superoxide radical anion in vivo. Superoxide radical anion can be stable in the solid state as KO_2 , because it is then strongly engaged in electrostatic forces in the lattice. The studies described above clearly show that it becomes extremely reactive (down to -80 °C!) when it is



Scheme 3. Reaction of the 19e complex **1** with O_2 in pentane or THF proceeding by electron transfer followed by proton transfer, its use for benzylic functionalization and its complete inhibition using one equiv. $NaPF_6$.



Scheme 4. triple activation by O_2 (two C–H bonds and one N–H bond) proceeding sequentially by electron transfer followed by proton transfer for heterobifunctionalization.

generated in solution in ion pairs resulting from the reaction between O_2 and a single-electron reductant. Despite the fast reactions that we have observed, it is also remarkable that these reactions are totally inhibited by $NaPF_6$ that thus plays the same role here as superoxide dismutase enzymes in biology. In other studies, this salt effect can even be catalytic in sodium salt [9b]. The organometallic conditions are far from biologic ones, but the dramatic reactivity found here by simple electron transfer to O_2 and its impressive inhibition may be somewhat relevant to what may happen in cells when the efficiency of superoxide dismutase enzymes is diminished upon ageing. It is indeed known that superoxide radical anion is responsible for a number of ageing illnesses attributed to radicals, although the exact secondary mechanisms are still obscure [13].

2.3. Stoichiometric electron transfer from electron-reservoir complexes to C_{60} : fullerene materials

With C_{60} , reduction can proceed up to the trianion of C_{60} , and **1** and its derivatives are the only series of neutral compounds that can do it. For instance, cobaltocene can only reduce C_{60} to the monoanion. Thus, depending on the stoichiometry of the reaction, **1** can form the salts of the mono-, di- or tri-anion. The implication in materials science resulted from the finding that some alkali

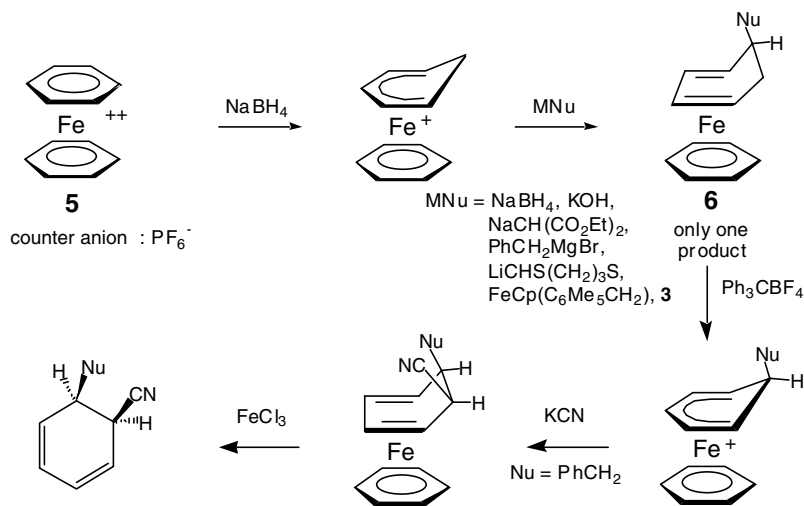
salts of C_{60} are superconductors but, in the present case, the lattice is governed by the counter cation, unlike in the alkali C_{60} salts [14].

2.4. Stoichiometric electron-transfer reaction combined with organoiron activation: application to organic synthesis

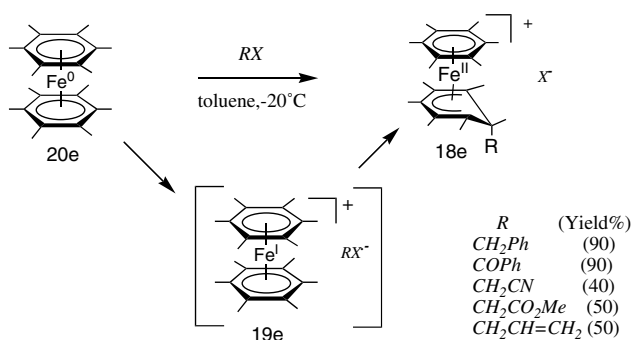
The combination of organoiron activation and electron transfer was also found useful for arene activation. For instance, regio- and stereospecific sequential double nucleophilic addition onto coordinated benzene in **5** was obtained subsequent to hydride abstraction from **6** via an electron-transfer mechanism when direct hydride abstraction would fail for steric reasons in the related isolobal iron carbonyl series (Scheme 5) [15]. In another strategy, electron transfer from the 20-electron complex **7** to organic halides provided 19-electron analogues that coupled with the resulting organic radicals to give **8** (Scheme 6) [16].

2.5. Catalytic electron-transfer using electron-reservoir complexes: application to inorganic and organometallic synthesis and to polymer chemistry

The robustness of the electron-reservoir complexes under both oxidation states Fe^{II} and Fe^I is very useful



Scheme 5. Double functionalization of benzene in **5** to form cis-1,2-heterodisubstituted cyclohexadienes: hydride deprotection in **6** before the second nucleophilic addition sequentially proceeds by electron transfer followed by H-atom transfer.



Scheme 6. Functionalization of the arene ligand proceeds by electron transfer to RX followed by coupling of the organic radical R' with the organoiron 19e radical in the radical cage.

for catalysis without fatigue. Two types of catalysis were envisaged: electron-transfer-chain catalysis and redox catalysis. Thus, the electron-reservoir complexes **1** and **2** are excellent catalytic initiators for electron-transfer reactions [17] that are very clean under these conditions. For instance, Vollhard's fulvalene dimetallic compounds such as **9** undergo the formation of zwitterions using **1** or **2** as a catalyst depending on the driving force required (Scheme 7).

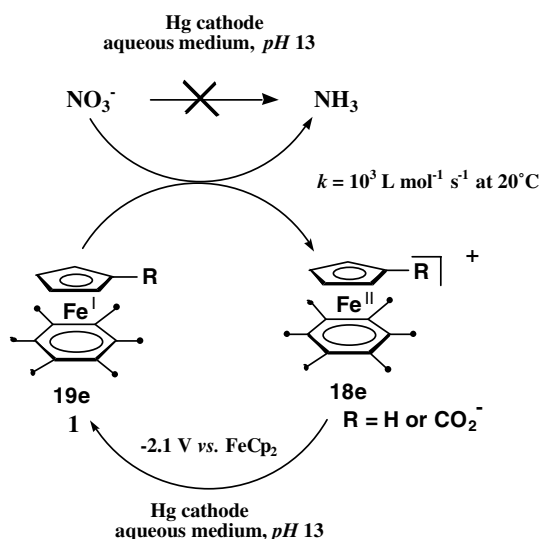
In another example that works remarkably well, **1** (1%) catalyzes CO substitution by a phosphine ligand in the clusters [Ru₃(CO)₁₂], [Fe₃(CO)₁₂] and [RCCO₃(CO)₁₂] [11,18].

Moreover, it was shown that the coupling between electron-transfer-chain catalysis using an iron-sandwich catalyst and polymerization of alkynes according to the square Chauvin-Katz mechanism using a W(0) catalyst could be efficient [18]. The electron-reservoir complexes are also redox catalysts, and are especially useful even in water when they are appropriately functionalized. Thus, the cathodic reduction of nitrate and nitrite to ammonia is not possible in water using a mercury cathode, but it

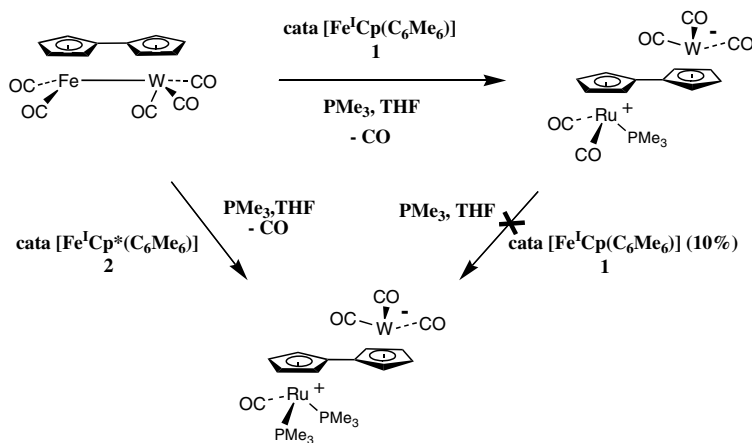
becomes possible by using a catalyst such as **1**. This system is homogeneous when **1** is functionalized by a solubilizing carboxylate group on the Cp ligand (Scheme 8) [10,18].

2.6. Hydrocarbon-bridged bimetallic electron-reservoir complexes and investigation of the electronic communication between the two metals: towards molecular electronics

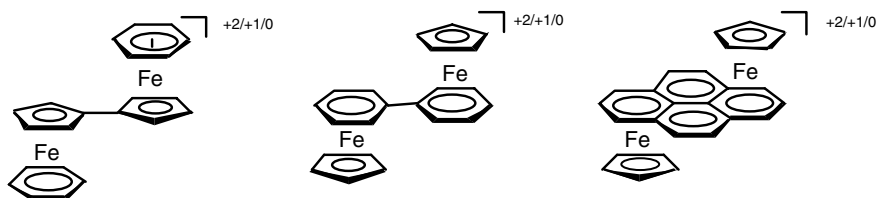
Bimetallic electron reservoir complexes of the same series as **1** were shown to exhibit five oxidation states (including mixed valence states) that are easily accessible in cyclic voltammetry. The electronic communication or coupling between the two metal centers across the fulvalene or polyaromatic ligand that bridges these two iron



Scheme 8. Cathodic reduction of NO₃⁻ and NO₂⁻ to NH₃ in water catalyzed by the iron-sandwich complexes.



Scheme 7. The number of phosphine ligands added onto the ruthenium center of **9** along the intramolecular electron transfer between the two metals to form zwitterionic fulvalene complexes depends on the reducing power (driving force) of the Fe^I electron-transfer-chain catalyst (**1** vs. **2**).



Scheme 9. Prototypes of hydrocarbon-bridged di-iron complexes whose electrochemical and spectroscopic studies of mixed valences are informative on the electronic communication between the two metals across the bridging ligand.

centers could be investigated in particular by Mössbauer and infrared spectroscopies and theoretical calculations. It was shown to depend on the nature of the ancillary ligand, and the mixed-valence states were found delocalized even on the infrared timescale. Combined crystal-structure determinations and cyclic voltammetry data indicated for the first time that a two-electron transfer proceeds by structural re-organization in the course of the second electron transfer that has an energy equal to or larger than that of the electrostatic factor (Scheme 9) [19].

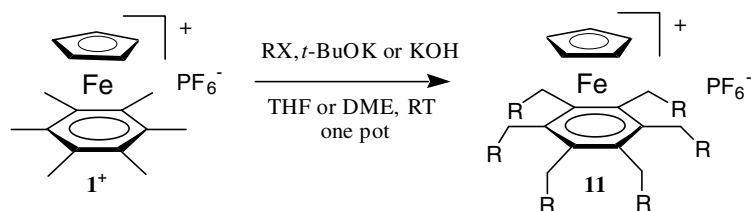
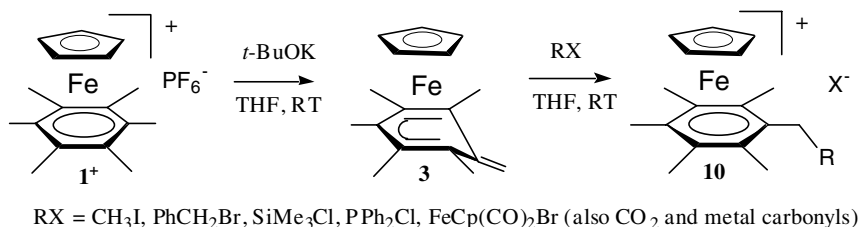
3. Proton transfer, proton reservoirs and organoiron activation: Application to the construction of giant dendrimers

3.1. Proton-reservoir complexes and arene multifunctionalization

In the reaction of O_2 with **1** above, the ion pair reaction of superoxide is a deprotonation reaction whenever a benzylic proton is present on the arene ligand. Thus, we investigated the pK_a of 1^+ , 2^+ and other salts of the

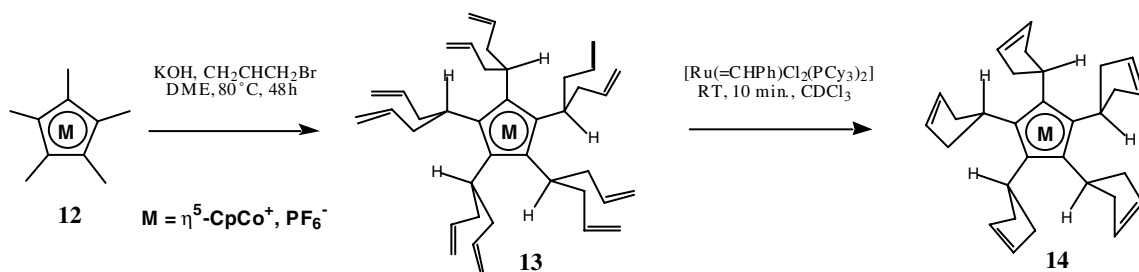
series by 1H NMR using the direct method, and found pK_a values (28.2 in DMSO for **1PF₆**) compatible with the deprotonation by various bases including *t*-BuOK. Indeed, the deprotonation of **1PF₆** by *t*-BuOK gives **3** [12a]. Since the reaction of **3** with electrophiles gives back the cationic sandwich structure with a functional benzylic carbon in **10**, we investigated the one-pot reaction using excess *t*-BuOK and CH_3I [7a] or $PhCH_2Br$ [20]. Hexaalkylation was obtained selectively in this way, giving **11**. The reaction was extended to allylbromide [21], but could not work with longer alkyl halides, because the dehydrohalogenation of the halides was faster than the organometallic reaction. Thus, we switched to KOH that allowed avoiding to be marred by this latter problem, and the peralkylation could be extended to functional alkyl iodides, also yielding **11** (Scheme 10).

With bulky alkyl iodides, the best yields are obtained at room temperature after prolonged reaction times in order to inhibit decomplexation. These reactions can be carried out on any scale, since they are eventually easily monitored by 1H NMR [9b]. The reaction with allylbromide is especially fruitful, because at this time double branching can be achieved with the durene complex.

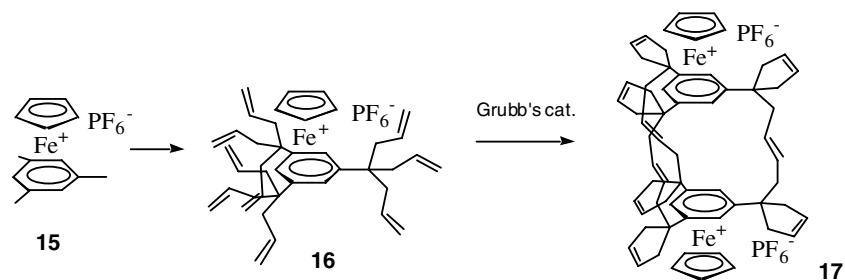


R = CH_3 , $(CH_2)_nCH_3$, $(CH_2)_4Fc$ (X = I), CH_2Ph , $p-CH_2PhOR'$, $CH_2CH=CH_2$ (X = Br)

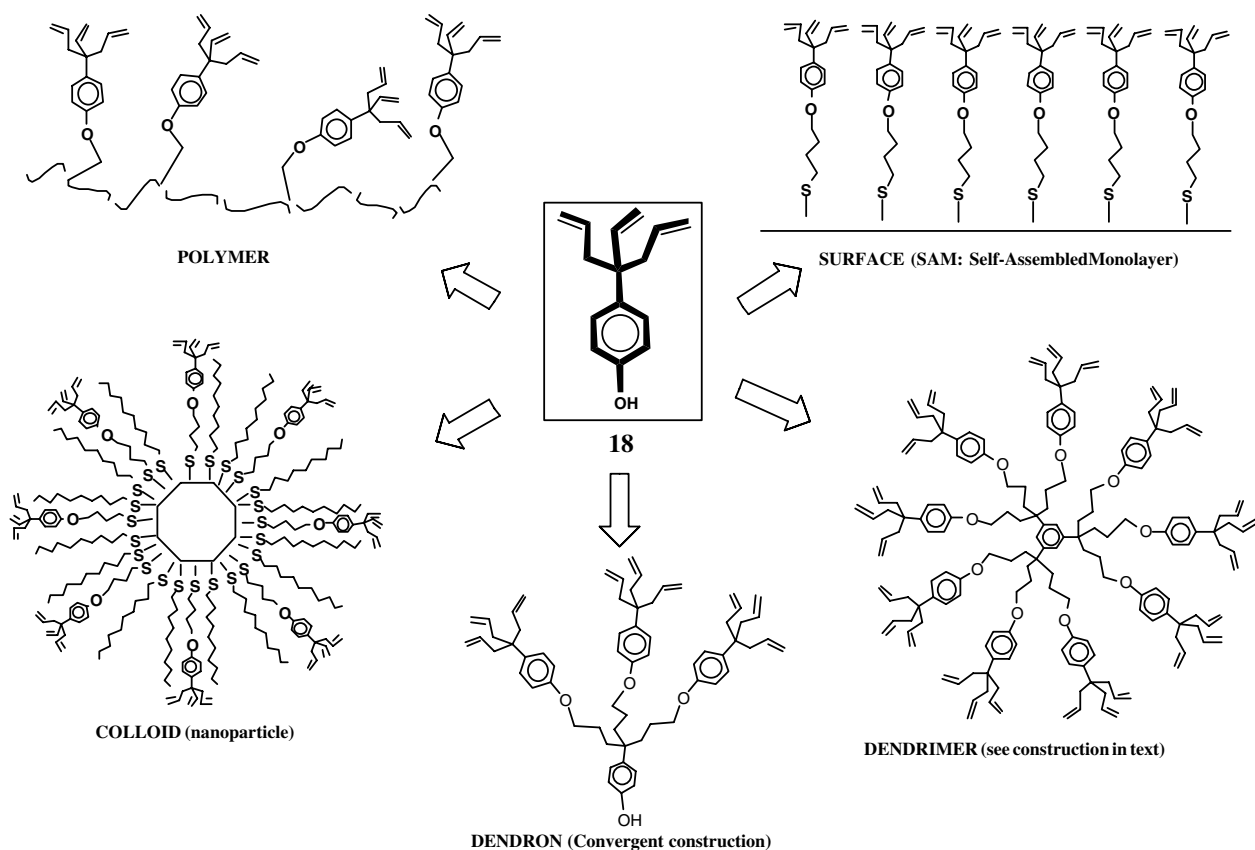
Scheme 10. Activation of hexamethylbenzene in the proton-reservoir complex **1PF₆**.



Scheme 11. CoCp^+ - or RhCp^+ -induced deca-allylation of the Cp^* ligand in pentamethylmetallocenium, coupled with RCM. Note the directionality of the ligands in the products.



Scheme 12. CpFe^+ -induced nona-allylation of mesitylene using $\text{KOH} +$ allyl bromide in THF at RT followed by olefin metathesis using the second generation Grubb's catalyst.



Scheme 13. Functionalization of various structures with a phenol dendronic brick towards nanodevices.

temperature as monitored by ^1H NMR. The deca-allylated complex **13** can be submitted to RCM metathesis, and the reaction proceeds at room temperature in a few minutes using Grubbs' catalyst to give **14** (Scheme 11) [22d,22e].

With $[\text{CoCp}_2^*]\text{PF}_6$, the reaction with CH_3I cannot be completed for steric reasons. However, with $[\text{RhCp}_2^*]\text{PF}_6$ in which the rings are located further apart, $[\text{Rh}(\text{C}_5\text{iPr}_5)_2]$ forms with opposite directionalities on the two rings, a nice example of specific self-assembly [22c]. In this case, the permethylation reaction leads to the formation of 20 C–C bonds in a single complex.

Perhaps the easiest, most useful and most common reaction in our laboratory (vide infra) is that involving the mesitylene complex $[\text{FeCp}(\eta^6\text{-1,3,5-Me}_3\text{-C}_6\text{H}_3)]$ $[\text{PF}_6]$ (**15**) with allylbromide giving the nona-allylated complex **16** in the presence of either KOH or *t*-BuOK. The reaction does not suffer from steric constraints given the location of the methyl groups about the arene ring and easily proceeds to completion to form the nine C–C bonds in high yield under ambient conditions [21c]. Coupling this reaction with alkene metathesis leads to the formation of a bimetallic capsule **17** after triple RCM metathesis on each ring and triple cross metathesis linking the two arenes (Scheme 12) [23].

In conclusion, the cationic organometallic complexes bearing methylated or permethylated ligands such as Cp, Cp^* , C_6Me_6 , mesitylene, durene, etc. are proton res-

ervoirs in which a specific number of benzylic protons can be replaced by benzyl-, *p*-bromobenzyl-, functional alkyl- or allyl groups.

3.2. From C–H activation in mononuclear proton-reservoir complexes to giant dendrimers and nanodevices

Another challenge using the above proton-reservoir complexes was the perfunctionalization using functional aromatics to synthesize a dendron. This was achieved in the case of *p*-chlorotoluene. Its CpFe^+ complex is easily converted to the *p*-ethoxytoluene analog in large scale by reaction with ethanol using K_2CO_3 . Further reaction with *t*-BuOK and allylbromide directly gives the organic dendron $p\text{-ClC}_6\text{H}_4\text{C}(\text{CH}_2\text{CH}=\text{CH}_2)_3$. This one-pot reaction involves eight steps and three roles of *t*-BuOK: first the three deprotonation–allylation sequences followed by the CpFe^+ -activated nucleophilic cleavage of the C–O bond, and finally electron transfer to Fe^{II} giving the unstable Fe^{I} complex that provides the final decomplexation product. The dendron can be attached to dendrimers covalently [24] or by hydrogen bonding [25] to more dendrons (convergent synthesis), surfaces and electrodes, polymers and nanoparticles either as such or with a decoration of the three branches [26] (Scheme 13).

For instance, hydrosilylation with chloromethyldimethylsilane of the nonaolefin derivative obtained by

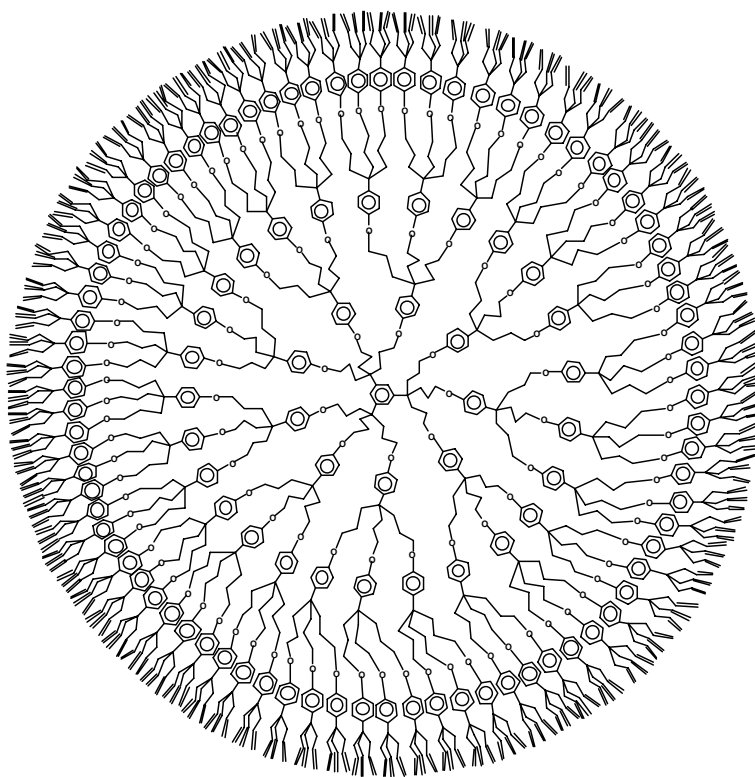
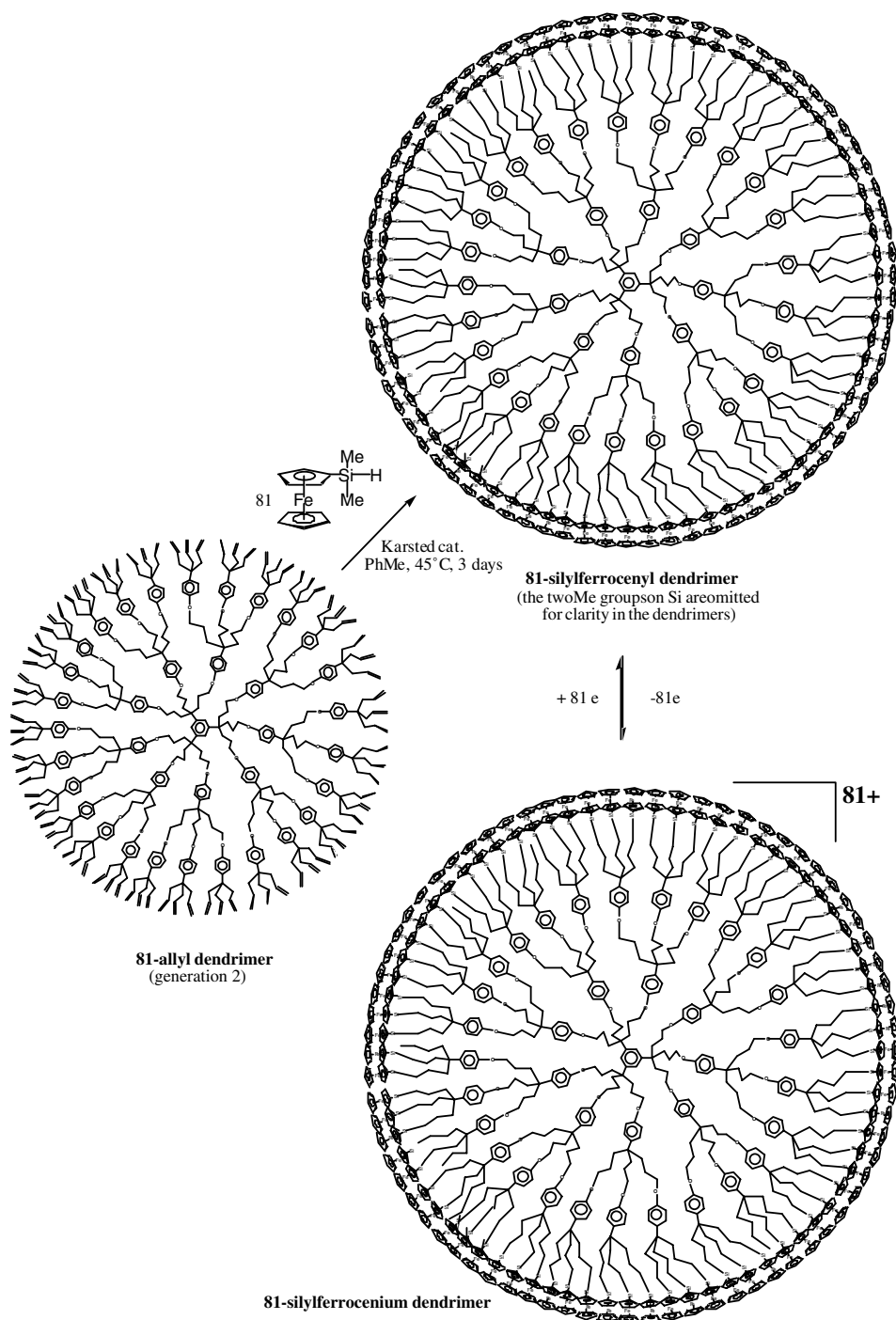


Chart 1. Third generation 243-allyl dendrimer whose molecular peak is observed in the MALDI TOF mass spectrum (35,640 for 35,660 Da) together with major defects at lower mass.

nonaallylation gives a nona-chloromethylsilane whose reaction with the phenol dendron yields a 27-allyl dendrimer. These two steps allow growing from the zeroth generation to the first one, and can proceed up to the ninth generation (Scheme 14). These reactions are easily followed by ^1H , ^{13}C and ^{29}Si NMR so that completion is insured before extraction. The molecular peaks in the

MALDI TOF mass spectra can be observed up to the third generation (243 branches, Chart 1). The other techniques of characterization were size exclusion chromatography up to the five generation (polydispersity between 1.00 and 1.02), HRTEM (that requires the presence of heavy elements) and AFM that showed the steady increase of the heights of the dendrimers. Given



Scheme 15. Synthesis of a molecular battery by functionalization of a dendrimer with 81 ferrocenyl groups. Oxidation of the ferrocenyl dendrimer to the blue ferricinium dendrimer using NOPF_6 and reduction of the ferricinium dendrimer with decamethylferrocene can be repeated many times without decomposition.

the level of defects observed, we estimated that the largest dendrimers have $>10^5$ branches out of a theoretical number of 177,147 branches (molecular weight $>26 \times 10^6$ Da, Scheme 14) [24b].

The previous largest dendrimers known had sizes (around 6000 branches) in agreement with the de Gennes dense-packing limit indicating that it is not possible to continue dividing the branches regularly beyond this limit because of the steric congestion at the periphery [27]. Our synthesis, the first one far beyond this limit, can be taken into account by a dynamic view, i.e. the fact that the termini of the branches avoid the steric congestion by turning inside the dendrimer towards the core. Under these conditions, the internal dendritic cavities are filled, and the limit to the dendrimer construction lies more in the volume than the surface at the periphery. It should be noted that the ability for the termini to turn toward the dendritic core is due to their non-polar character and their small size. Functional groups may form hydrogen bonds with neighbors inhibiting the turn of the branch termini towards the center, and this ability must also rapidly decrease while increasing the size of the termini.

4. Prospects from organoiron chemistry to nanosciences

To conclude, dendritic, nanoparticles and surface nanocomponents now lead us towards four directions that have been made possible using the molecular tools described in this Account:

(i) *Nanocatalysis* for green chemistry with recoverable and re-usable dendritic catalysts [28–30]. Progress has already been made in redox catalyzed nitrate reduction [10], ROMP [29], oxidation using polyoxometalates [28b] and Pd-catalyzed C–C coupling reactions [28c]. A preliminary conclusion is that small dendrimers are more efficient than large ones (negative dendritic effects) and even that stars are more appropriate than dendrimers that are sterically congested at the periphery with the large catalytic groups.

(ii) *Nanosensors* for the recognition and titration of inorganic anions and ATP (a DNA fragment). Dendrimers decorated with amido-, amino- or silyl-ferrocenyl groups can selectively recognize electrochemically these anions and behave as exo-receptors with dramatically positive dendritic effect. Moreover, dendrimers, for instance nanoparticle-centered ones are all the better adsorbed on electrodes as they are larger and can function as re-usable sensors [25].

(iii) *Molecular nanoelectronics* by linking solid-state components with nanosized dendrimers covered with redox centers among which electrons hop (Scheme 15). The goal is to make nanodevices such as molecular batteries, diodes and transistors.

(iv) *Physical properties*: the functionalization of dendrimers and nanoparticles with molecular compounds for optical, magnetic and electrical properties.

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