

Electron and Proton Reservoir Complexes: Thermodynamic Basis for C–H Activation and Applications in Redox and Dendrimer Chemistry

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ABSTRACT

This Account focuses on fundamental aspects and applications of the concept of “electron and proton reservoirs”. Permethylated electron reservoir iron sandwich complexes, which were known to be excellent reducing agents in their neutral 19e Fe^I form, have recently been shown to be stable strong oxidants in their dicationic 17e Fe^{III} form. Thermodynamic, mechanistic, and synthetic aspects of the redox chemistry of these and related organoiron complexes are summarized. Proton reservoir properties of these complexes are due to enhanced acidity in their cationic form and result in an original type of activation: perfunctionalization leading to dendritic cores and useful metallodendrimers of variable topology.

Electron and proton transfers play a key role in supramolecular chemistry,¹ biochemistry,² and molecular activation.^{3–9} They are also intimately connected as, for instance, in the redox processes of the organic heterocycles of NADH, FADH₂, and NADPH involved in respiration and photosynthesis.³ Thus, redox systems which are reversible in any sense are essential for natural and unnatural processes because, by definition, there is no breakdown of the molecular entities upon redox change other than the removal or addition of electrons and protons. Some monoelectronic systems with mild potentials, mostly inorganic, are very well known for their ability to withstand the redox change in biological processes³ (mediators: cytochromes and iron–sulfur proteins), molecular materials⁹ (conductors and superconductors, mixed-valence compounds for nonlinear optics, molecular ferromagnetism), catalysis^{5,7} (Wacker-type processes⁴), and light emission or absorption (sensitizers such as [Ru(bpy)₃]²⁺ involved in light–energy conversion²). Although the above examples indicate that stable redox systems can be found in various areas of molecular chemistry, the vast majority of oxidation and reduction processes of molecular compounds show a lack of reversibility or a limited reversibility even on the short electrochemical time scales.⁸ The reason for this is that, most of the time, an electron is removed from a bonding orbital upon oxidation

and added into an antibonding orbital upon reduction, which leads to violation of the rare gas “rule” (octet or 18-electron) and is a strong destabilizing factor. Only delocalized systems with degenerate orbitals and low-lying antibonding orbitals are suitable for a redox change without dramatic consequence for the molecular integrity, and such redox systems are useful redox reagents (Scheme 1). Twenty years ago, we introduced the name and concept of “electron reservoir” for stable, very electron-rich permethylated sandwiches such as [Fe^I(η⁵-C₅R₅)(η⁶-C₆Me₆)] {R = H (**1a**) or Me (**1b**)}, i.e., compounds with 19 valence electrons on the transition element located at the heart of the molecular structure and well protected from the outside by the shell of the permethylated rings.¹⁰ These compounds are the most electron-rich compounds known with ionization potentials as low as that of potassium metal and can reduce a large variety of substrates. For instance, with O₂, the generation, spectroscopic characterization, and reactivity and inhibition of superoxide radical anion O₂^{•-} were shown.¹¹ In this Account, I would like to give a unifying view of the electron and proton reservoir iron–aromatic sandwich complexes including a recently established thermodynamic basis and synthetic applications.

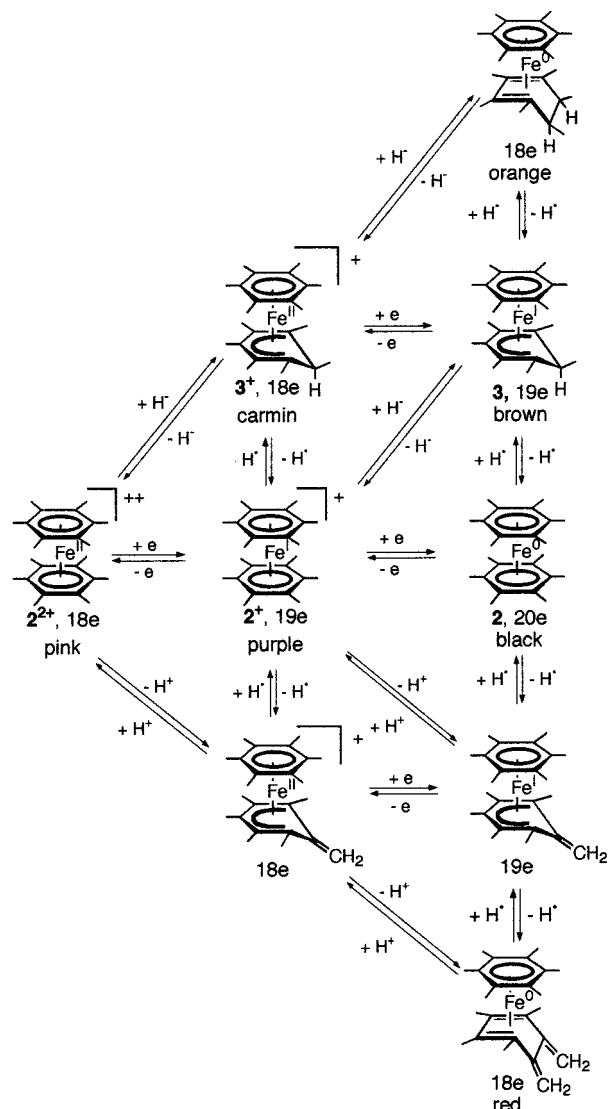
The First Triad of Stable 17-, 18-, and 19-Electron Complexes

The yellow 18e complexes **1**⁺ as well as a large number of iron complexes with other arene ligands, whose reduction to the neutral forest-green 19e complexes was known, could be oxidized in SO₂ in a single-electron wave at very positive potentials ranging from 0.9 to 1.7 V vs Cp₂Fe^{0/+} (Cp = η⁵-C₅H₅). Furthermore, **1b**⁺ as well as the analogous iron complexes of durene and pentamethylbenzene could be oxidized by SbCl₅ or SbF₅ in SO₂ to the stable purple 17e dications obtained as SbCl₆⁻ or SbF₆⁻ salts which were recrystallized from SO₂ (Scheme 2).

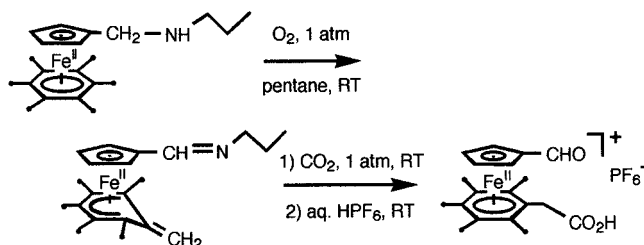
The electronic structure of these 17e cations was examined using the DFT method, UV–visible, ESR, and Mössbauer spectroscopy and magnetic susceptibility measurements and was shown to be close to that of ferricinium, i.e., ²E₂ corresponding to the metallic (a₁)²(e₂)³ electron configuration. This means that a single positive charge shifts the potential toward anodic values by about 1.7 V, the potential of the parent redox system [FeCp(η⁶-C₆H₆)]^{+/2+} vs Cp₂Fe^{0/+}. It was also possible to oxidize the 19e complex **1b** directly to the 17e complex **1b**[SbCl₆]₂, a potential jump of 3 V! This is the first case for which both monoelectronic oxidation and reduction give stable 17e and 19e complexes, respectively. The 17e Fe^{III} complex **1**²⁺ is, indeed, the most powerful stable organometallic oxidant.¹² *The electron reservoir principle now applies on both oxidation and reduction sides.* One may compare this triad to the bis-arene series [Fe(η⁶-C₆Me₆)₂]^{0/+ / 2+} (**2**^{0/+ / 2+}, Scheme 3) This extension with mechanistic considerations is the subject of the following section.

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Scheme 3. Example of Diagram Illustrating the Combinatorial View of Electron, Proton, H-Atom, and Hydride Transfers in Permethylated Late Transition-Metal Sandwich Complexes



Scheme 4



to 20e) led to the requirement of a thermodynamic basis in one of these families in order to facilitate their understanding.

Thermodynamics of C–H Activation in the 16–20-Electron Isostructural Complexes $[\text{Fe}^x(\eta^5\text{-C}_5\text{R}_5)(\eta^6\text{-arene})]$ ($x = 0\text{--}4$; $\text{R} = \text{H}$ or Me)

To start, we measured the potentials of the reversible (or partly reversible) oxidation and two reductions of the 18e

complexes $[\text{M}^{\text{II}}(\eta^5\text{-C}_5\text{R}_5)(\eta^6\text{-arene})][\text{PF}_6]$ ($\text{R} = \text{H}$ or Me , $\text{M} = \text{Fe}$ or Ru) for a variety of arenes. The determination of the peak potentials of the irreversible oxidation and reduction of the complexes $[\text{Fe}^{\text{II}}(\eta^5\text{-C}_5\text{R}_5)(\eta^6\text{-C}_6\text{Me}_5\text{CH}_2)]$ (**4a**, $\text{R} = \text{H}$; **4b**, $\text{R} = \text{Me}$), resulting from the deprotonation of **1**, was also carried out. In this case, it was necessary to correct these values with the potential shifts provoked by the irreversible follow-up reactions according to Parker et al. in order to estimate the E° values.²² The accuracy on E° is now weaker than in the reversible cases. Then, we measured the $\text{p}K_{\text{a}}$ of these cations²¹ by the direct method used inter alia by the groups of Norton,²³ Tilset,²⁴ and Theopold²⁵ to investigate the acidity of transition-metal hydrides. It consists of the addition of a known quantity of base with strength similar to that of the compound under investigation to a solution of this compound, and the position of this equilibrium is spectroscopically determined (using ^1H NMR or UV–vis in the present case). Knowing the position of this equilibrium, one may calculate the $\text{p}K_{\text{a}}$ of the analyte from the $\text{p}K_{\text{a}}$ of the base used (Scheme 6).

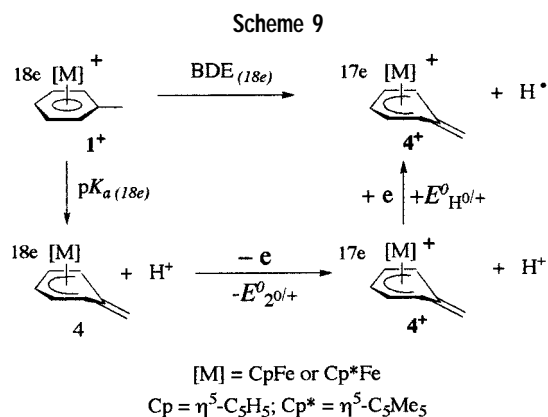
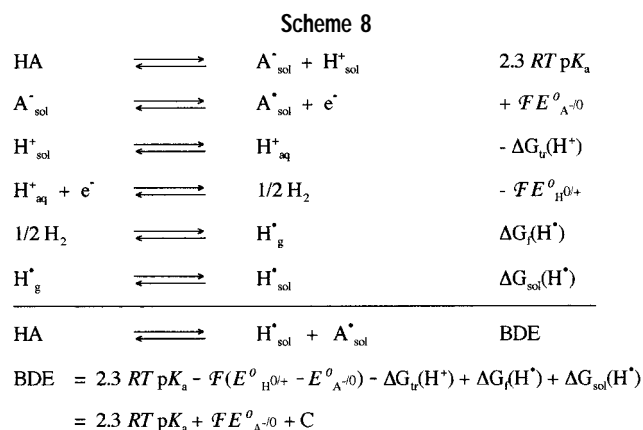
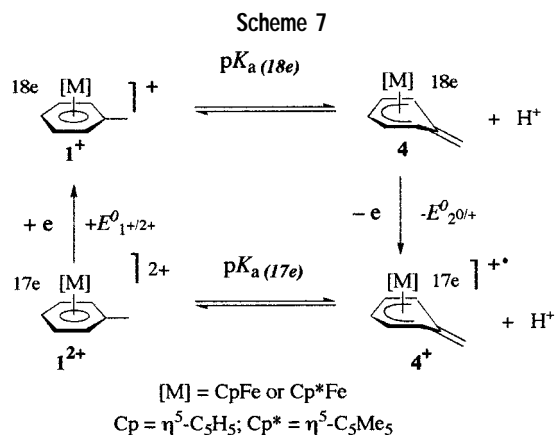
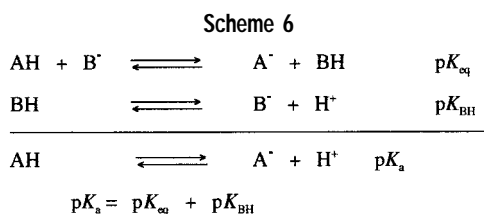
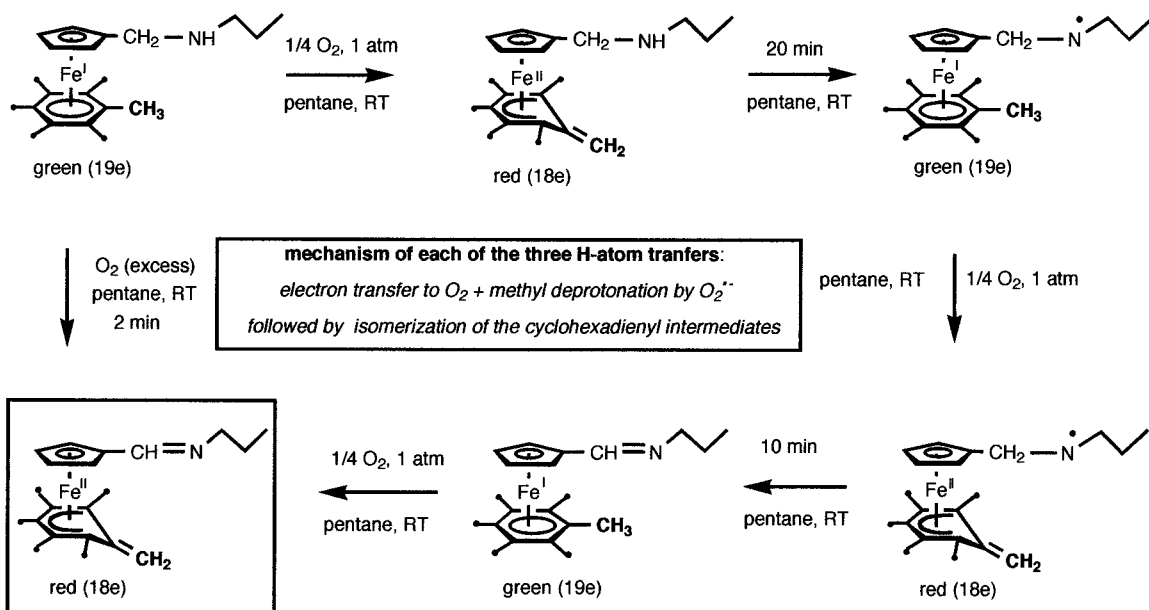
Using other methods, the groups of Terrier²⁶ and Bordwell²⁷ measured the $\text{p}K_{\text{a}}$ of the diphenylmethane and fluorene iron complexes, respectively, which are much more acidic than **1**⁺. With $\text{p}K_{\text{a}}$ and E° values in hand, it is possible to estimate other thermodynamic values such as the C–H bond energy and the $\text{p}K_{\text{a}}$ of other isostructural oxidation states with the help of thermodynamic diagrams. Such thermodynamic cycles were first introduced by Breslow and Balasubramanian²⁸ in the late 1960s and then used by many others.^{22–31} Thus, the $\text{p}K_{\text{a}}$ of the 17e complexes **1**²⁺ can be calculated in this way using those of the 18e complexes **1**⁺ and the oxidation potentials of **1** and their deprotonated species **4** (Scheme 7). For instance,

$$\begin{aligned} \text{p}K_{\text{a}}(\mathbf{1a}^{2+}) &= \text{p}K_{\text{a}}(\mathbf{1a}^+) - F(E_{\mathbf{1a}^{+/2+}}^{\circ} - E_{\mathbf{4a}^{0/+}}^{\circ})/2.303RT \\ &= \text{p}K_{\text{a}}(\mathbf{1a}^+) - 16.89(E_{\mathbf{1a}^{+/2+}}^{\circ} - E_{\mathbf{4a}^{0/+}}^{\circ}) \\ &= 29.2 - 16.89(1.165 + 1.250) = -11.6 \end{aligned}$$

Likewise, the $\text{p}K_{\text{a}}$ of the 19e complex **1** can be calculated using those of the 18e complexes and the reduction potentials of **1**⁺ and **4**. Since second-oxidation and second-reduction potentials are sometimes accessible or can be estimated, it is possible to extend this type of cycle to the estimation of the $\text{p}K_{\text{a}}$ values of the 16e and 20e species with some approximation.

The calculation of the element–hydrogen bond dissociation energies (BDEs) has also been achieved using other thermodynamic cycles, which required measurement of the $\text{p}K_{\text{a}}$ of the acid AH and the oxidation potential of the conjugate base A[−] and estimation of the solvation, transfer, and formation energies of the hydrogen radical and the proton (Scheme 8).

A value of $73.5 \pm 1 \text{ kcal}\cdot\text{mol}^{-1}$ for the constant C has been determined by Parker et al.²² for DMSO as the solvent and $\text{FeCp}_2^{0/+}$ as the reference, and we used this value and these conditions. Parker and Tilset have introduced cycles based on isodesmic reactions²² and calculated many M–H

Scheme 5. Proposed Mechanisms of the Reaction of Scheme 3, a Triple H-Atom Abstraction (via Electron Transfer) by O₂ in a 19e Fe^I Complex


BDEs of metal hydrides using this technique.^{22,24,29–31} The BDEs of transition metal–fluorene complexes have also recently been determined.²⁷ Application of the technique of Scheme 6 to the 18e complexes **1**⁺ to calculate the benzylic C–H BDE is shown in Scheme 9. For instance,

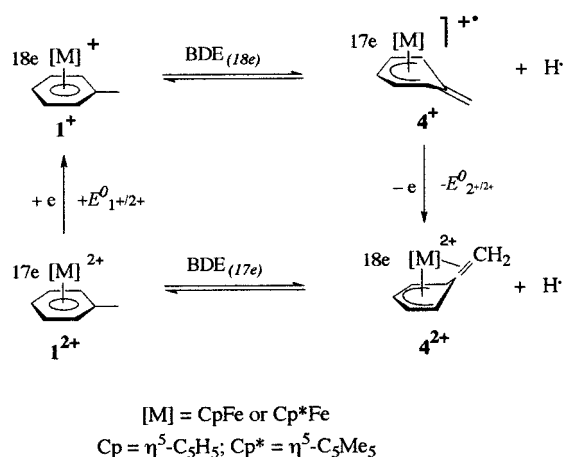
$$\begin{aligned} \text{BDE}(\mathbf{1a}^+) &= 2.3RT \text{p}K_{\text{a}} + FE^{\circ}_{\text{A}^-/\text{A}^{\bullet}} + C \\ &= 1.365 \text{p}K_{\text{a}}(\mathbf{1a}^+) + 23.06E^{\circ}_{\text{4a}^0/\text{4a}^0/+} + 73.5 \text{ kcal/mol} \\ &= 1.365(29.2) + 23.06(-1.165) + 73.5 = 86.5 \text{ kcal/mol} \end{aligned}$$

Similarly, this cycle could be also carried out for the estimation of the benzylic C–H BDE in the 17e complexes

1²⁺, the 19e complexes **1**, and the 20e complexes **1**⁻, or, more practically, the C–H BDE in the next oxidation state can be deduced from the C–H BDE of the known oxidation state and the redox potentials involving these two states, as shown in Scheme 10 for the 17e species **1**²⁺. For instance,

$$\begin{aligned} \text{BDE}(\mathbf{1a}^{2+}) &= \text{BDE}(\mathbf{1a}^+) - 23.06(E^{\circ}_{\text{1a}^+/2+} - E^{\circ}_{\text{4a}^+/2+}) \\ &= 86.5 - 23.06(1.25 - 0.34) = 65.5 \text{ kcal/mol} \end{aligned}$$

Scheme 10



An overall picture of the thermodynamic data is shown in the case of 1a^+ and related species in Scheme 11.

The conclusions of this first thermodynamic study in molecular chemistry spanning several oxidation states are the following:

(1) Coordination of the arene by CpM^+ and Cp^*M^+ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) in the 18e complex increases its acidity by 14 and 12 $\text{p}K_{\text{a}}$ units, respectively (analogous Fe and Ru complexes have about the same $\text{p}K_{\text{a}}$), so these monocationic sandwich complexes can be reversibly deprotonated by *t*-BuOK. On the other hand, the benzylic C–H BDE in these 18e complexes is not significantly different from that found in the free arene.

(2) In the neutral 19e iron complexes, the reverse situation is found: the acidity is about the same as that in the free arene, but the C–H BDE is lower by 21 $\text{kcal}\cdot\text{mol}^{-1}$ than that in the 18e complexes or in the free arene because the loss of a H atom leads to a stable 18e species.

(3) In the anionic 20e iron species, the acidity decreases by 18 $\text{p}K_{\text{a}}$ units compared to that of the 19e species or the free arene because of the negative charge. The benzylic C–H BDE is as low as that in the 19e complex for the same reason; i.e. there is one less electron in an anti-

bonding orbital after the homolytic cleavage of a benzylic C–H bond.

(4) The acidity of the dicationic 17e iron complex is considerably increased (40 $\text{p}K_{\text{a}}$ units lower) compared to that of the 18e complex and even more compared to that of the free ligand (53 $\text{p}K_{\text{a}}$ units). The benzylic C–H BDE is the weakest in the whole series, which may appear surprising because homolytic cleavage of a benzylic C–H bond should lead to the very unfavorable 16e metal configuration. Coordination of the exocyclic double bond to the free metal site as shown in the proposed structure (reminiscent of a ferrocenyl carbonium cation) would bring back its valence electron count to 18, and this could explain its stability and the observation of low BDEs.

(5) The tricationic 16e species would have a $\text{p}K_{\text{a}}$ 95 units lower than that of the free arene and 114 $\text{p}K_{\text{a}}$ units lower than that of the 20e species (although neither the 16e nor the 20e species has been isolated).²¹

Synthetic Applications of the Electron and Proton Reservoir Complexes

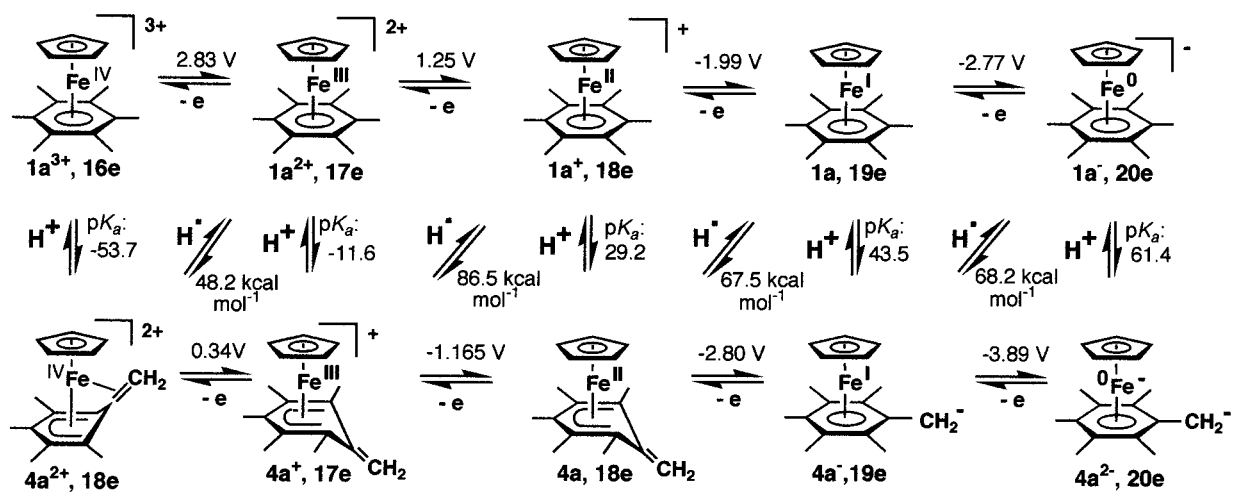
Applications of $[\text{Fe}^I(\eta^5\text{-C}_5\text{R}_5)(\eta^6\text{-arene})]$ ($\text{R} = \text{H}$ or Me) as Electron Reservoirs. The prototype of stable 19e complexes 1a is most often used, but solubilization in water by introduction of a carboxylate substituent or variation of the redox potential by changing the number of methyl groups on the Cp and arene ligands can be affected at will. Since these applications have already been reviewed,⁹ only the main types of properties of the electron reservoir Fe^I complexes are summarized here.

Stoichiometric monoelectronic reductants: many acceptors have been reduced (O_2 , C_{60} , C_{60}^- , C_{60}^{2-} ,³² TCNQ, TCNQ^- , inorganic and organometallic cations, and many neutral organic compounds such as aldehydes, ketones, and phenazine).

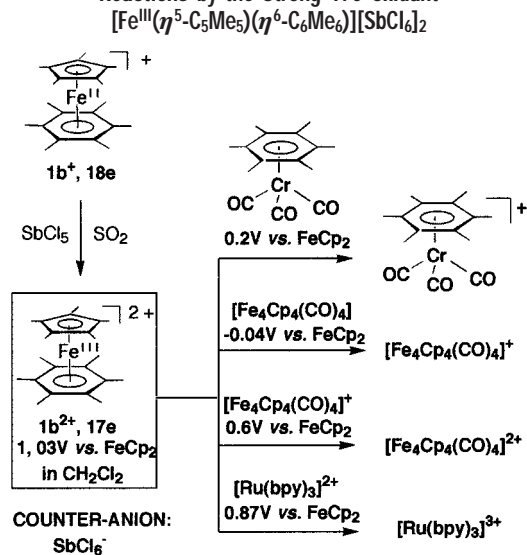
Redox mediators or catalysts (cathodic reduction of nitrite and nitrate to ammonia in water).²⁰

Electrocatalysts (initiators of electron-transfer chain-catalyzed reactions such as chelation and substitution of

Scheme 11



Scheme 12. Examples of Exergonic Mono-electronic Oxidation Reactions by the Strong 17e Oxidant



arene or CO by P donors in mono-, di-, and polynuclear complexes).^{33,34}

Dendritic redox sensors for the recognition of small inorganic anions (*vide infra*): Cl^- , Br^- , H_2PO_4^- , HSO_4^- .^{35,36}

References for the determination of redox potentials by cyclic voltammetry. Unlike in ferrocene, the redox-active metal centers is shielded from the outside by the shell of permethylated ligands in $[\text{Fe}^{\text{I}}(\eta^5\text{-C}_5\text{R}_5)(\eta^6\text{-C}_6\text{R}_6)]$, $[\text{Fe}^{\text{II}}(\eta^5\text{-C}_5\text{R}_5)_2]$, and $[\text{Co}^{\text{II}}(\eta^5\text{-C}_5\text{R}_5)_2]$, which were found to be more reliable than ferrocene as references.³⁷

Applications of $[\text{Fe}^{\text{III}}(\eta^5\text{-C}_5\text{R}_5)(\eta^6\text{-C}_6\text{Me}_6)]^{2+}$ $\{\text{R} = \text{H}$ ($\mathbf{1a}^{2+}$) or Me ($\mathbf{1b}^{2+}$) $\}$ as Single-Electron Oxidants. Being a strong mono-electronic oxidant with a redox potential about 1 V higher than that of ferrocene, $\mathbf{1b}^{2+}[\text{SbCl}_6]_2$ can oxidize a large number of substrates. Representative examples are shown in Scheme 12.¹²

In principle, $\mathbf{1a}^{2+}$ or $\mathbf{1b}^{2+}$ can play the same role in oxidation as $\mathbf{1}$ in reduction above. For instance, $\mathbf{1a}^{2+}$ is a good redox catalyst for the useful ring-opening oxidation of furfural in SO_2 at -40°C on a Pt anode (rate constant, $k = 115 \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$).¹²

Synthetic Applications of the Complexes $[\text{FeCp}(\eta^6\text{-arene})][\text{PF}_6]$ as Proton Reservoirs. The reaction between an 18e cationic complex $[\text{MCp}(\eta^6\text{-C}_6\text{Me}_6)][\text{PF}_6]$ ($\text{M} = \text{Fe}$ or Ru) and excess base and organic halide leads to the replacement of six protons by six branches in a one-pot reaction (Scheme 13).^{10,38–42}

This CpM^+ -induced hexaalkylation, hexaaalkylation or hexabenzoylation of C_6Me_6 consists of a series of deprotonation/C–C bond formation sequences.

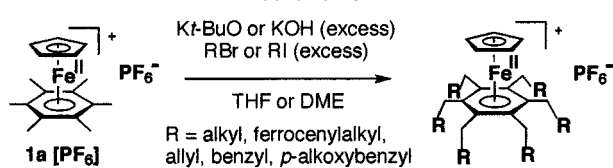
The deprotonation of the organometallic cation is a reversible process considering its $\text{p}K_a$ and that of the base respectively, but the reaction is shifted toward the alkylation reaction products because the alkylation steps are irreversible. The first deprotonation of the yellow salt of the 18e organoiron cation gives a deep-red 18e cyclohexadienyl complex, as shown in Scheme 11. Recovery of the aromatic structure of the ligand and of the yellow color is accomplished by the alkylation step. Thus, a new sequence can start again, and so on until the steric limit is reached. This complex is a reservoir of six protons in the hexafunctionalization reaction. Visually, the reaction is “oscillatory” between yellow and red in terms of color changes. For instance, the hexamethylation of $\mathbf{1a}^+$ with CH_3I and $t\text{-BuOK}$ spontaneously occurs in 1 min altogether, and the rapid sequences can be visually followed. Although the reactions are stoichiometric, the metal center is firmly held to activate the aromatic ligand during all the sequences. One can compare this process with catalysis, each sequence being the equivalent of a catalytic cycle. Synthetic applications are shown in Schemes 14 and 15.^{43–45}

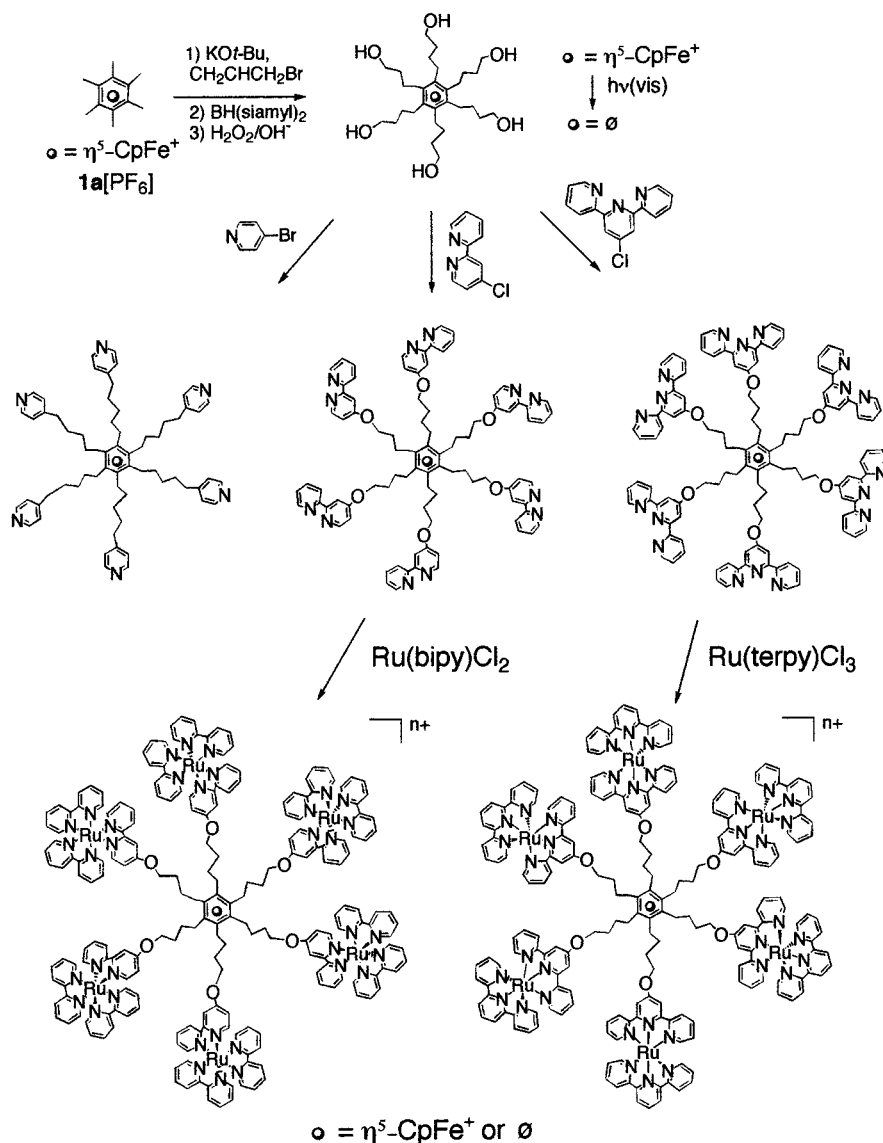
With allyl bromide, the perallylation of the hexamethylbenzene ligand can be continued until dodecaalkylation involving 12 sequences (24 reactions altogether), in which $[\text{FeCp}(\text{C}_6\text{Me}_6)][\text{PF}_6]$ is a reservoir of 12 protons. The resulting dodecaalkylated complex and closely related ones can be considered as the first organometallic dendrimers.⁴⁶ Since only one face of the ligand bears a metal center, the molecule is chiral because no free rotation of the chains is possible. The directionality of the chains (responsible for the chirality⁴⁷) is generated by self-assembly of the chains during the iron-induced perallylation reaction (Scheme 16).

With a five-membered ring as a ligand, i.e., with $\text{C}_5\text{-Me}_5$, there is more space around the ligand (angle with the centroid, 72°) than with a six-membered ring (60°), so rotation of the doubly alkylated chains can be induced thermally and monitored by ^1H NMR. Although the methyl groups of the C_5Me_5 ligands are less acidic than those of $\mathbf{1a}^+$, double alkylation,⁴⁸ allylation, and benzylation⁴⁹ of each methyl group can proceed in the 18e complexes $[\text{MCp}^*\text{Cp}][\text{PF}_6]$ ($\text{M} = \text{Co}$ or Rh) (Scheme 17), whereas only dodecaalkylation is possible in $\mathbf{1a}^+$. These double-branching reactions providing directional ligands are one-pot syntheses of chiral dendritic cores, avoiding the tedious isolation–purification–repetition procedure commonly used in dendrimer chemistry.^{50,51}

Attempted permethylation of the 18e complex $[\text{CoCp}^*_2][\text{PF}_6]$ ($\mathbf{5}^+$) failed because of steric problems even under forcing conditions, but that of the Rh analogue $\mathbf{6}^+$ was successful since the larger radius of rhodium induces a larger inter-ring distance in $\mathbf{6}^+$ than in $\mathbf{5}^+$, which circumvents the bulk problem.⁵² Thus, $\mathbf{6}^+$ is a reservoir of 20 protons. In the course of this reaction, self-organization induces an opposite directionality of the two rings, only one diastereoisomer being obtained. The ability of the second-row transition-metal permethylated sandwich com-

Scheme 13



Scheme 14. Star-Shaped Molecular Architectures Generated by Hexafunctionalization of $[\text{Fe}^{\text{II}}\text{Cp}(\eta^6\text{-C}_6\text{Me}_6)][\text{PF}_6]$ 

plex to undergo permethylation or perfunctionalization while first-row metal complex does not because of steric constraints is, in fact, a quite general feature, as we could recently show with $[\text{MCp}^*(\eta^6\text{-C}_6\text{Me}_6)]^+$ ($\text{M} = \text{Ru}$ vs Fe).⁵³

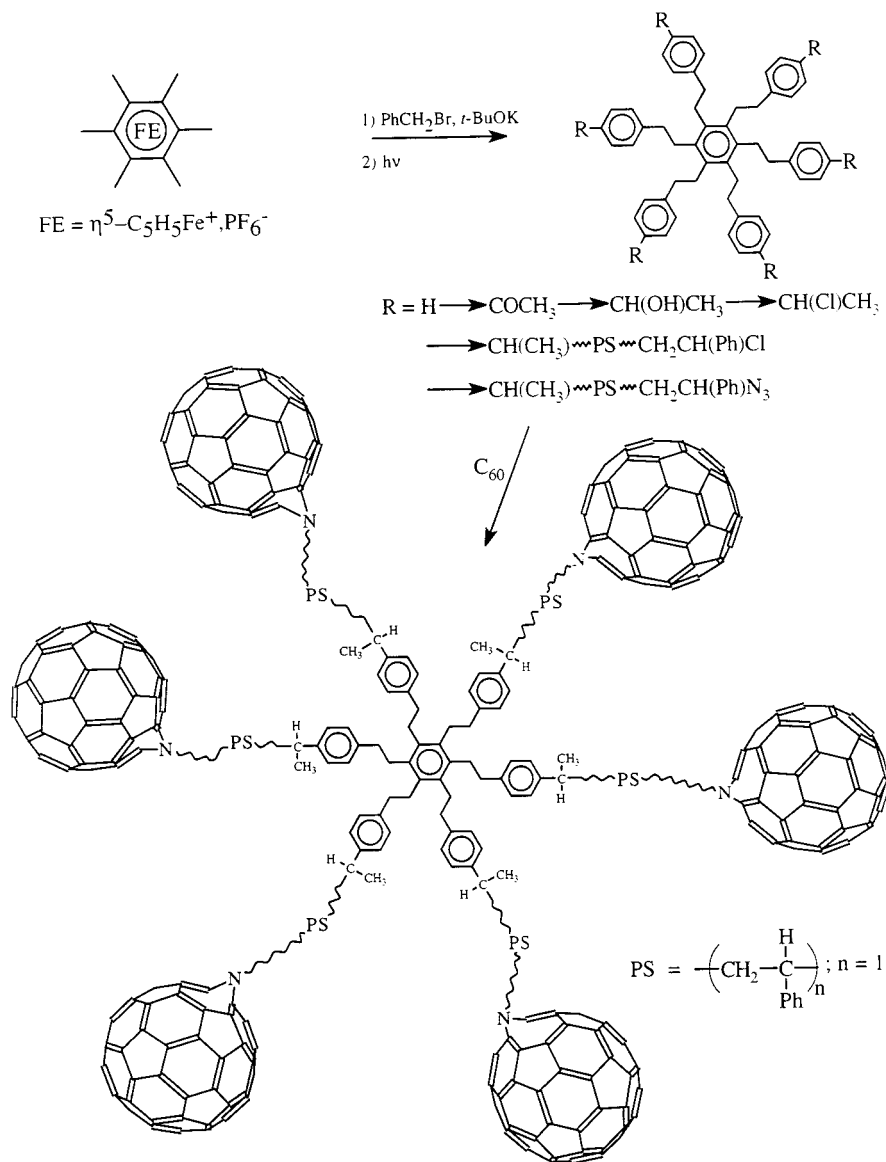
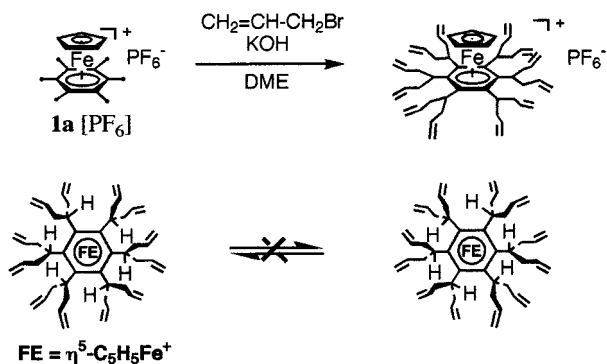
The double branching is also very easy for some 18e CpFe^+ complexes of polymethylaromatics such as *o*-xylene and durene, in which each methyl group has one methyl and one hydrogen neighbor on the benzene ring. These facile reactions are accessible for benzylation and allylation⁴⁶ and are thus suitable for immediate application in synthesis. Indeed, polyallyl cores can be easily transformed into poly-primary alcohols by regioselective hydroboration using disiamylborane and oxidation using $\text{H}_2\text{O}_2/\text{OH}^-$ (Scheme 14),^{38,43,44} and polybenzyl cores can be regioselectively acylated (Scheme 15)⁴⁵ and chlorocarbonylated in para positions (Scheme 18).³⁶

An example of an application is represented in Scheme 18, where the octabenylation and subsequent chlorocarbonylation reactions are used to introduce 24 amidofer-

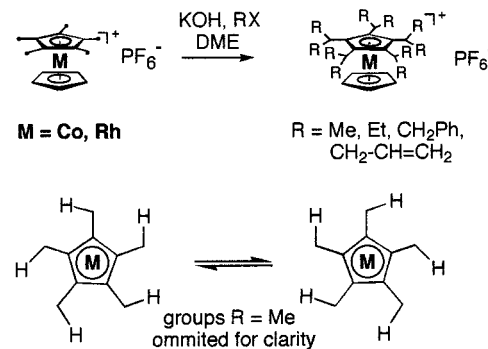
rocene and 24 $[\text{Cp}^*\text{Fe}(\eta^6\text{-N-anilino-})]$ termini on the branches of dendrimers.

The former dendrimer is useful as a sensor for the recognition of the H_2PO_4^- and HSO_4^- anions (but not the halides) using electrochemistry, which takes advantage of the difference in the interactions of the anion with the amido group (presumably by double H-bonding) between the weakly bonded ferrocene form and the strongly bound ferricinium form.³⁵ The latter dendrimer nicely and very selectively recognizes the chloride and bromide anions (but not the above oxoanions) through a single H-bonding interaction in the branches.⁵⁵ In both cases, dramatic dendritic effects were found; i.e., the recognition by tripods with the same branches is, by comparison with these dendrimers, weak.

The complex $[\text{FeCp}(\eta^6\text{-mesitylene})]^+$ is a reservoir of nine protons since nine allyl group can be introduced. This nonallylation is facile and useful. It led to the discovery of another early organometallic dendrimer,^{54–57}

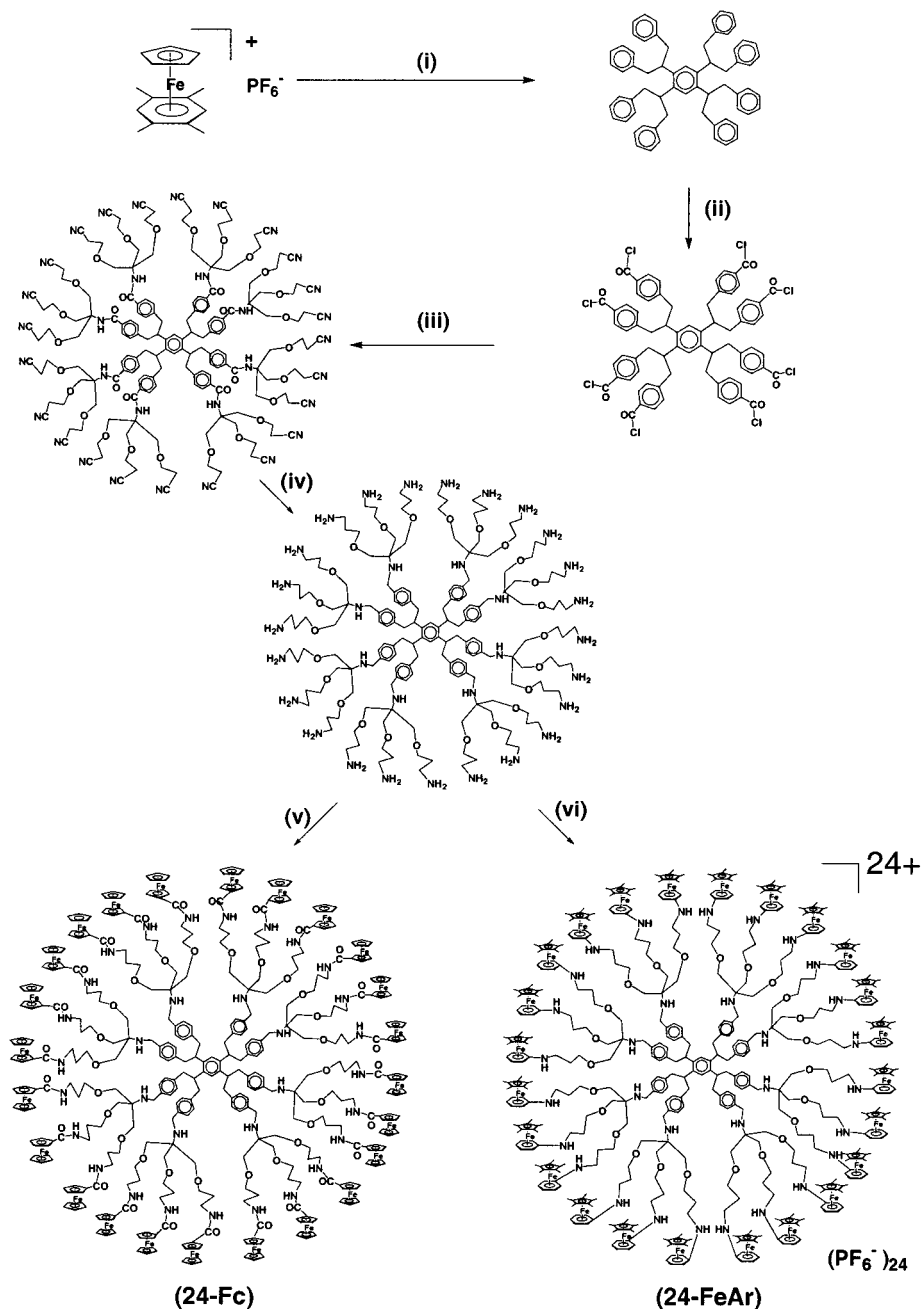
Scheme 15. C₆₀-Terminated Star-Shaped Polystyrene Polymer Generated by Hexabenzylation of [Fe^{II}Cp(η⁶-C₆Me₆)] [PF₆]Scheme 16. Self-Organization of a Directionally Rigid, Chiral Dendritic Core Generated by Dodecaallylation of [Fe^{II}Cp(η⁶-C₆Me₆)] [PF₆] as a Reservoir of 12 Protons

a nona-[FeCp(η⁶-arene)]⁺ complex (Scheme 19).⁵⁸ Nonaferrocene³⁵ and nonacobalticinium⁵⁹ dendrimers derived from the nonaallyl core were also efficient for the recognition of oxoanions with strong dendritic effects.^{35,60} Fur-

Scheme 17. Chiral, Metallocene-Centered Dendritic Cores Generated from [Co^{III}Cp* Cp] [PF₆] as a Reservoir of 10 Protons

$M = Co, \Delta G^\ddagger = 71.13 \text{ kJ}\cdot\text{mol}^{-1} (17.0 \pm 0.2 \text{ kcal}\cdot\text{mol}^{-1})$
 $Rh, \Delta G^\ddagger = 70.21 \text{ kJ}\cdot\text{mol}^{-1} (16.8 \pm 0.2 \text{ kcal}\cdot\text{mol}^{-1})$

thermore, this nonaallyl dendrimer served as a core for the divergent synthesis of 27-, 81-, and 243-allyl dendrim-

Scheme 18. Dendritic Multielectron Reservoirs Active in Sensing Anions and Generated from $[\text{Fe}^{\text{II}}\text{Cp}(\eta^6\text{-durene})][\text{PF}_6]_2^a$ 

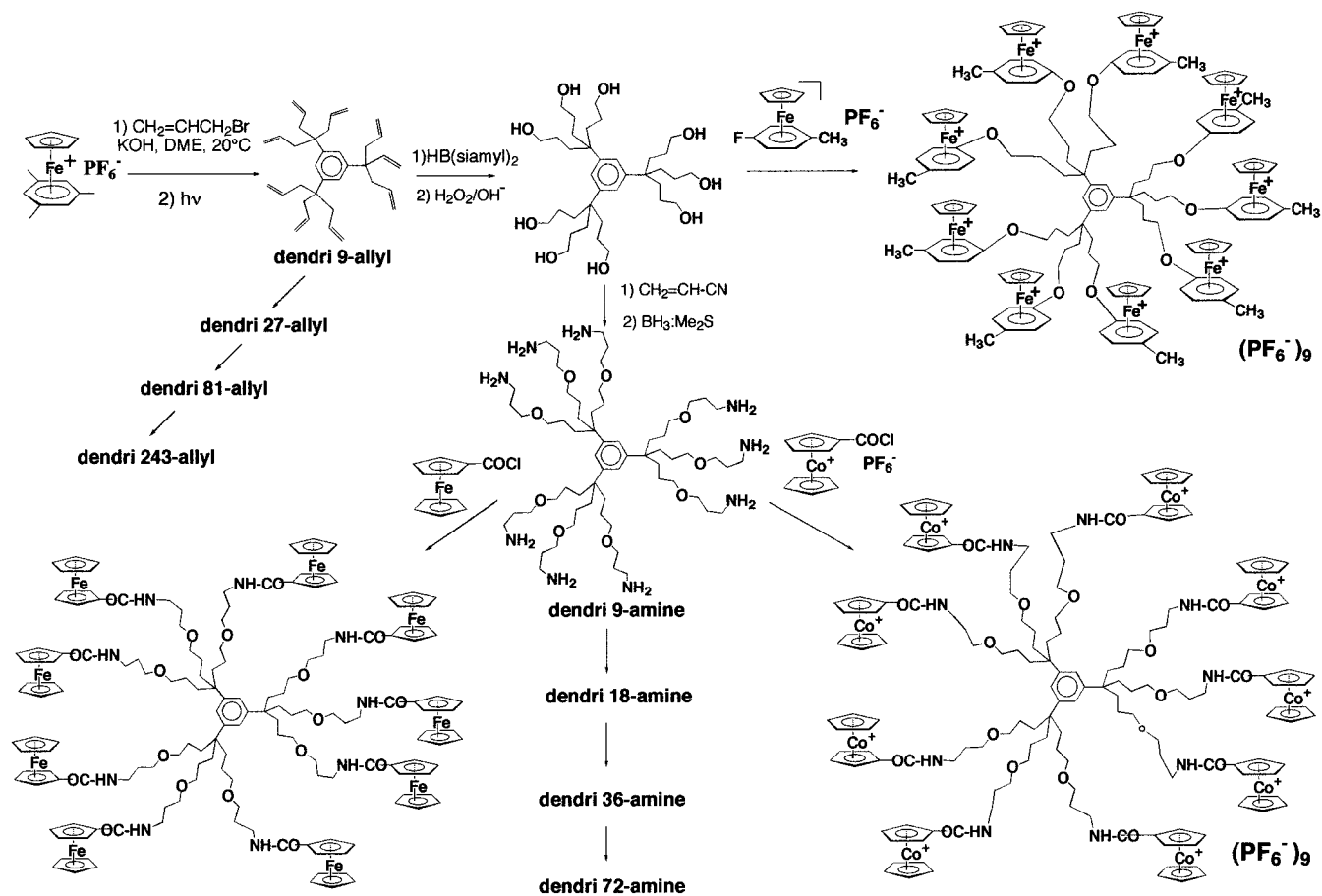
^a Conditions: (i) PhCH_2Br , KOH , DME , 2 d, room temperature; (ii) $(\text{COCl})_2$, AlCl_3 , CH_2Cl_2 , 15°C , 1 h; (iii) $\text{NH}_2\text{C}(\text{CH}_2\text{OCH}_2\text{CH}_2\text{CN})_3$, NEt_3 , CH_2Cl_2 , 3 d, room temperature; (iv) $\text{BH}_3\text{-Me}_2\text{S}$, THF , room temperature, 1 d; (v) $[\text{Fe}(\text{Cp})(\text{C}_5\text{H}_4\text{COCl})]$, **6**, CH_2Cl_2 , 4 d; (vi) $[\text{FeCp}^*(\eta^6\text{-C}_6\text{H}_5\text{F})]^+\text{PF}_6^-$, **8**, CH_2Cl_2 , room temperature, 15 d.

ers using the dendron $p\text{-OHC}_6\text{H}_4\text{C}(\text{CH}_2\text{CH}=\text{CH}_2)_3$ in reactions with the polyomesylates; i.e., dendritic syntheses that occur in this way are fast.⁶¹

Conclusion and Perspectives

Our delineation of the concept of “electron reservoir” in 1979 has led us to a number of areas where applications are involved: stoichiometric, chain, and catalytic reactions in organic, inorganic, and organometallic chemistry. Some of these electron-transfer reactions, such as those involving dioxygen, were of interest for mimicking the reactivity of superoxide radical anions in biology, and also provided the basis for very mild yet powerful C–H activation

systems of great synthetic utility. Other SET reactions of the electron reservoir complexes were useful in materials sciences, such as those using C_{60} and TCNQ and their mono- and polyanions. Recently, we have synthesized dicationic 17e complexes which are strong oxidants with functions comparable to those of electron reservoirs on the oxidation side. The variety of oxidation states and valence electron numbers involved in electron-, proton-, hydrogen-atom-, and hydride-transfer chemistry led us to examine diagrams organized in a combinatorial way in order to illustrate the mechanistic possibilities implicated in the many particle-transfer reactions. A systematic thermodynamic investigation of the C–H activation pro-

Scheme 19. Generation of Dendritic Architectures Based on $[\text{Fe}^{\text{II}}\text{Cp}(\eta^6\text{-Mesitylene})][\text{PF}_6]_a$ 

^a The dendritic growth of the polyamines (9 → 18 → etc.) follows Vögtle's strategy,^{35,51} and that of the polyolefins (9 → 27 → etc.) is achieved by branching a tripod dendron (see text).⁶¹

cesses in these various oxidation states highlights the strong influences of the charge and coordination on the acidity and BDE, respectively. Among all the particle transfer reactions, the proton reservoir properties of the cationic organotransition-metal sandwich complexes bearing polymethylated ligands were synthetically powerful because they rapidly generated diverse topologies for star and dendritic cores that allow the construction of nano-sized molecules. The evolving fascinating domain of dendrimers has applications in molecular recognition when dendritic effects are disclosed and in catalysis when no steric inhibition problem at the bulky dendritic surface intervenes. Thus, the new directions are now in nanosciences, where the concept of electron reservoir is also very useful and powerful. For instance, the metallodendrimers illustrated in this Account have reversible redox centers and show a unique reversible wave in cyclic voltammetry.^{35,36,59} We are now examining dendrimers^{36,61} surrounded by electron reservoir units which are huge reservoirs of electrons⁵⁸ for which two redox forms can be isolated⁴¹ with the transfer of a large number of electrons between the "red" and "ox" forms. This principle should be extended to a variety of nanoscale assemblies and find use in catalysis,^{54,62} molecular recognition,^{1,62,63} molecular electronics,^{1,2,8} biotechnologies,⁶⁴ and lithography.⁶⁵

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References

- (1) Lehn, J.-M. *Supramolecular Chemistry. Concepts and Perspectives*; VCH: Weinheim, 1995.
- (2) Balzani, V.; Scandola, F. *Supramolecular Chemistry*; Ellis Horwood: New York, 1991.
- (3) Bertini, I.; Gray, H. B.; Lippard, S. J.; Valentine, J. S. *Bioinorganic Chemistry*; University Science Books: Mill Valley, CA, 1994.
- (4) Taube, H. *Electron-Transfer of Complex Ions in Solutions*; Academic Press: New York, 1970.
- (5) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978.
- (6) Marcus, R. A.; Sutin, N. Electron Transfers in Chemistry and Biology. *Biochim. Biophys. Acta* **1985**, *811*, 265–322.
- (7) *Paramagnetic Species in Activation, Selectivity and Catalysis*; Chanon, M., Juliard, M., Poite, J. C., Eds.; Kluwer: Dordrecht, 1988.
- (8) *Electron and Proton Transfer in Chemistry and Biology*; Müller, A., Ratajczak, H., Junge, W., Diemann, E., Eds.; Elsevier: Amsterdam, 1992.
- (9) Astruc, D. *Electron Transfer and Radical Processes in Transition Metal Chemistry*; VCH: New York, 1995.

- (10) Astruc, D.; Hamon, J.-R.; Althoff, G.; Román, E.; Batail, P.; Michaud, P.; Mariot, J.-P.; Varret, F.; Cozak, D. Design, Stabilization and Efficiency of Organometallic "Electron Reservoirs". 19-Electron Sandwichs $\eta^5\text{-C}_5\text{R}_5\text{Fe}(\eta^6\text{-C}_6\text{R}_6)$, a Key Class Active in Redox Catalysis. *J. Am. Chem. Soc.* **1979**, *101*, 5445–5447.
- (11) Astruc, D. Organonion Electron Reservoir Complexes. *Acc. Chem. Res.* **1986**, *19*, 377–383.
- (12) Ruiz, J.; Ogliaro, F.; Saillard, J.-Y.; Halet, J.-F.; Varret, F.; Astruc, D. First 17–18–19-Electron Triads of Isostructural Organometallic Complexes. The 17-Electron Complexes $[\text{Fe}(\text{C}_5\text{R}_5)(\text{arene})]^{2+}$ (R = H or Me), a Novel Family of Strong Oxidants: Isolation, Characterization, Electronic Structure, and Redox Properties. *J. Am. Chem. Soc.* **1998**, *120*, 11693–11705.
- (13) Michaud, P.; Mariot, J.-P.; Varret, F.; Astruc, D. Improved Syntheses and Electronic Structures of the 19- and 20-Electron Complexes $[\text{Fe}(\eta^6\text{-C}_6\text{Me}_6)_2]^{n+}$ (n = 1, 0). *J. Chem. Soc., Chem. Commun.* **1982**, 1383–1384.
- (14) Michaud, P.; Astruc, D.; Ammeter, J. H. Electron-Transfer Pathways in the Reduction of d^6 and d^7 Organo-Iron Cations by LiAlH_4 and NaBH_4 . *J. Am. Chem. Soc.* **1982**, *104*, 3755–3757.
- (15) Mandon, D.; Astruc, D. Activation of a Single Aromatic Ligand in $[\text{Fe}(\eta^6\text{-C}_6\text{Me}_6)](\text{PF}_6)_2$: Bifunctionalization via Protection by Hydride. *Organometallics* **1990**, *9*, 341–346.
- (16) Astruc, D.; Mandon, D.; Madonik, A. M.; Michaud, P.; Ardoin, N.; Varret, F. Electron-Transfer Chemistry of the 20-Electron Complex $[\text{Fe}^0(\text{C}_6\text{Me}_6)_2]$ and of the 19-Electron Complex $[\text{Fe}(\text{C}_6\text{Me}_6)(\eta^5\text{-C}_6\text{-Me}_6\text{H})]$. Mild Activation by O_2 via Superoxide Ion and Functionalization of the Exocyclic Methylene in the Resulting Complexes $[\text{Fe}^0(\text{C}_6\text{Me}_6)(\eta^4\text{-Polyene})]$. *Organometallics* **1990**, *9*, 2155–2164.
- (17) Astruc, D.; Michaud, P.; Madonik, A.; Saillard, J.-Y.; Hoffmann, R. The Regiospecific Reaction of Nucleophiles with the $(\eta^5\text{-Cyclohexadienyl})(\eta^6\text{-Benzene})$ Iron (II) Cation: A Frontier Orbital Controlled Route to Synthetically Useful $(\eta^4\text{-Cyclohexadiene})(\eta^6\text{-Benzene})$ Iron (0) Derivatives. *Nouv. J. Chim.* **1985**, *9*, 41–50.
- (18) Mandon, D.; Toupet, L.; Astruc, D. Electron-Transfer Pathways in the Hydride Abstraction by Ph_3C^+ from Exo-Substituted Cyclohexadiene Fe(0) Complexes: A Key in the Synthesis of Heterobifunctional Cyclohexadienes from Benzene. *J. Am. Chem. Soc.* **1986**, *108*, 1320–1321.
- (19) Mandon, D.; Astruc, D. Nucleophilic Attack on the Cyclohexadienyl Ligand: From Mono to Heterobifunctional Cyclohexadiene Iron Complexes and the Role of the Electron-Transfer Pathway in Hydride Abstraction. *Organometallics* **1989**, *8*, 2372–2377.
- (20) Rigaut, S.; Delville, M.-H.; Astruc, D. Triple C–H/N–H Activation by O_2 for Molecular Engineering: Heterobifunctionalization of the 19-Electron Redox Catalysts $[\text{Fe}(\text{Cp}(\text{arene}))]$. *J. Am. Chem. Soc.* **1997**, *119*, 11132–11133.
- (21) Trujillo, H. A.; Casado, C. M.; Ruiz, J.; Astruc, D. Thermodynamics of C–H Activation in Multiple Oxidation States: Compared Benzylic C–H Acidities and C–H Bond Dissociation Energies in the Isostructural 16 to 20-Electron Complexes $[\text{Fe}^x(\eta^5\text{-C}_5\text{R}_5)(\eta^6\text{-arene})]^{n+}$, x = 0–IV, R = H or Me; n = –1 to + 3. *J. Am. Chem. Soc.* **1999**, *121*, 5674–5686.
- (22) Parker, V.; Handoo, K. L.; Roness, F.; Tilset, M. Electrode Potentials and the Thermodynamics of Isodesmic Reactions. *J. Am. Chem. Soc.* **1991**, *113*, 7493.
- (23) Moore, E. J.; Sullivan, J. M.; Norton, J. R. Kinetics and Thermodynamic Acidity of Hydrido Transition-Metal Carbonyl Complexes. *J. Am. Chem. Soc.* **1986**, *108*, 2257–2263.
- (24) Tilset, M.; Parker, V. D. Solution Homolytic Bond Dissociation Energies of Organotransition-Metal Hydrides. *J. Am. Chem. Soc.* **1989**, *111*, 6711.
- (25) Protasiewicz, J. D.; Theopold, K. H. A Direct Comparison of the Rates of Degenerate Transfer of Electrons, Protons, Hydrogen Atoms between Metal Complexes. *J. Am. Chem. Soc.* **1993**, *115*, 5559.
- (26) Terrier, F.; Vichard, D.; Chatrousse, A. P.; Top, S.; McGlinchey, M. J. Ionization of $(\eta^6\text{-Diphenylmethane})(\eta^5\text{-cyclopentadienyl})$ Iron Cations in H_2O – Me_2SO Mixtures: A Kinetic, NMR, and EHMO Study. *Organometallics* **1994**, *13*, 690–697.
- (27) Zhang, X.-M.; Bordwell, F. G. Effects of π -Coordinated Transition-Metal Groups on Fluorene Acidities and Homolytic Bond Dissociation Enthalpies. *Organometallics* **1994**, *13*, 2920.
- (28) Breslow, R.; Balasubramanian, K. The pK_a of Triphenylcyclopropane. Electrochemical Determination of an Inaccessible Equilibrium Constant. *J. Am. Chem. Soc.* **1969**, *91*, 5182.
- (29) Wayner, D. D. M.; Parker, V. D. Bond Energies in Solution from Electrode Potentials and Thermodynamic Cycles. A Simplified and General Approach. *Acc. Chem. Res.* **1993**, *26*, 287–294.
- (30) Tilset, M. One-Electron Oxidation of Cyclopentadienylchromium Carbonyl Hydrides: Thermodynamics of Oxidative Addition of Metal–Hydrogen Bonds toward Homolytic and Heterolytic Cleavage. *J. Am. Chem. Soc.* **1992**, *114*, 2740.
- (31) Tilset, M.; Hamon, J.-R.; Hamon, P. Relative Bond M–X Bond Dissociation Energies in 16, 17 and 18e Organo-Transition Metal Complexes (X = Halide, H). *Chem. Commun.* **1998**, 765–766.
- (32) Bossard, C.; Rigaut, S.; Astruc, D.; Delville, M.-H.; Félix, G.; Février-Bouvier, A.; Amiel, J.; Flandrois, S.; Delhaès, P. One-, Two- and Three-Electron Reduction of C_{60} Using the Electron-Reservoir Complex $[\text{Fe}(\text{Cp}(\text{C}_6\text{Me}_6))]$. *J. Chem. Soc., Chem. Commun.* **1993**, 333–334.
- (33) Brown, D. S.; Delville, M.-H.; Vollhardt, K. P. C.; Astruc, D. Use of the Electron-Reservoir $[\text{Fe}(\text{Cp}(\text{arene}))]$ Sandwiches as Efficient and Selective Electrocatalysts: Syntheses of Homo- and Heterodinuclear Zwitterionic Transition-Metal Fulvalene Complexes. *Organometallics* **1996**, *15*, 2360–2372.
- (34) Alonso, E.; Ruiz, J.; Astruc, D. The Use of the Electron-Reservoir Complexes $[\text{Fe}(\text{I})(\text{Cp}(\text{arene}))]$ for the Electrocatalytic Synthesis of Redox-Reversible Metal–Carbonyl Clusters Containing Ferrocenyldiphenylphosphine. *J. Cluster Sci.* **1998**, *9*, 271–287.
- (35) Valério, C.; Fillaut, J.-L.; Ruiz, J.; Guittard, J.; Blais, J.-C.; Astruc, D. The Dendritic Effect in Molecular Recognition: Ferrocene Dendrimers and their Use as Supramolecular Redox Sensors for the Recognition of Small Inorganic Anions. *J. Am. Chem. Soc.* **1997**, *119*, 2588–2589.
- (36) Valério, C.; Alonso, E.; Ruiz, J.; Blais, J.-C.; Astruc, D. A Polycationic Metalloendramer with 24 $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^6\text{-N-Alkyl-aniline})]^+$ Termini which Recognizes Chloride and Bromide Anions. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1747–1751.
- (37) Ruiz, J.; Astruc, D. Permethylyated Electron-Reservoir Sandwich Complexes as References for the Determination of Redox Potentials. Suggestion of a New Redox Scale. *C. R. Acad. Sci. Paris, t. 1, Sér. II c* **1998**, 21–27.
- (38) Moulines, F.; Astruc, D. Tentacled Iron Sandwichs. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1347–1349.
- (39) Fillaut, J.-L.; Astruc, D. Tentacled Aromatics: from Central-Ring to Outer-Ring Iron Sandwich Complexes. *J. Chem. Soc., Chem. Commun.* **1993**, 1320–1322.
- (40) Fillaut, J.-L.; Boese, R.; Astruc, D. Tentacled Sandwichs: Iron-Mediated Hexa-*p*-Alkoxybenzylation of Hexamethylbenzene and X-ray Crystal Structure of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\text{C}_6(\text{CH}_2\text{CH}_2\text{-}i\text{-p-ETOC}_6\text{H}_4)_6]^{2+}\text{PF}_6^-$. *Synlett* **1992**, 55–56.
- (41) Fillaut, J.-L.; Linares, J.; Astruc, D. Single-Step Six-Electron Transfer in a Heptanuclear Complex: Isolation of Both Redox Forms. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2460–2462.
- (42) Fillaut, J.-L.; Astruc, D. Polyalkoxybenzylation of $[\text{Fe}(\text{Cp}(\text{arene}))]^+$ Complexes and Polyfunctionalization of the Tentacles with Iron Sandwich Redox Centers. *New J. Chem.* **1996**, *20*, 945–957.
- (43) Moulines, F.; Djakovitch, L.; Fillaut, J.-L.; Astruc, D. Hexahydrozirconation versus Hexahydroboration Routes to Hexaoido Tentacled Aromatic Iron Sandwichs. *Synlett* **1992**, 57–58.
- (44) Marvaud, V.; Astruc, D.; Leize, E.; Van Dorsselaer, A.; Guittard, J.; Blais, J.-C. Synthesis and Mass Spectral Characterization of Iron-Centered Hexa-Polypyridine Stars and Their Hexa-Ruthenium Complexes. *New J. Chem.* **1997**, *21*, 1309–1319.
- (45) Cloutet, E.; Gnanou, Y.; Fillaut, J.-L.; Astruc, D. C_{60} End-Capped Polystyrene Stars. *J. Chem. Soc., Chem. Commun.* **1996**, 1565–1566.
- (46) Moulines, F.; Gloaguen, B.; Astruc, D. One-Pot Multifunctionalization of Polymethyl Hydrocarbon π -Ligands. Maximum space Occupancy by Double Branching and Formation of Arborols. *Angew. Chem., Int. Ed. Engl.* **1992**, *28*, 458–460.
- (47) Siegel, J.; Gutiérrez, A.; Scheizer, W. B.; Ermer, O.; Mislou, K. Static and Dynamic Stereochemistry of Hexaisopropylbenzene. *J. Am. Chem. Soc.* **1986**, *108*, 1569–1575.
- (48) Gloaguen, B.; Astruc, D. Chiral Pentaisopropyl- and Pentaisopentyl Complexes: One-Pot Synthesis by Formation of Ten Carbon–Carbon Bonds from Pentamethylcobalticinium. *J. Am. Chem. Soc.* **1990**, *112*, 4607–4609.
- (49) Buchholz, D.; Gloaguen, B.; Fillaut, J.-L.; Cotrait, M.; Astruc, D. Mono- and Bis(pentaisopropylcyclopentadienyl) Cobalt and Rhodium Sandwich Complexes and Other Decabranching Cyclopentadienyl Complexes. *Chem. Eur. J.* **1995**, *1*, 374–381.
- (50) Tomalia, D. A.; Naylor, A. N.; Goddard, W. A., III Starburst Dendrimers: Molecular-Level Control of Size, Shape, Surface Chemistry, Topology and Flexibility in the Conversion of Atoms to Macroscopic Materials. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138.
- (51) Newkome, G. R.; Moorefield, C. N.; Vogtle, F. *Dendritic Molecules: Concepts, Syntheses and Perspectives*; VCH: New York, 1996.
- (52) Buchholz, D.; Astruc, D. The First Decaisopropylmetallocene: Synthesis of $[\text{Rh}(\text{C}_5\text{IPr}_5)_2][\text{PF}_6]$ by One-Pot Formation of 20 Carbon–Carbon Bonds from $[\text{Rh}(\text{C}_5\text{Me}_5)_2][\text{PF}_6]$. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1637–1639.
- (53) Ruiz, J.; Astruc, D. Regioselective Permethylation, Perallylation and Perbenzylation of the Arene Ligand in $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\eta^6\text{-C}_6\text{-Me}_6)][\text{PF}_6]$. *C. R. Acad. Sci. Paris, t. 2, Sér. II c* **1999**, 205–208.

- (54) Newkome, G. R.; He, E.; Moorefield, C. N. Suprasuper molecules with Novel Properties: Metallo dendrimers. *Chem. Rev.* **1999**, *99*, 1689–1746.
- (55) Casado, C. M.; Cuadrado, I.; Morán, M.; Alonso, B.; García, B.; Gonzalès, B.; Losada, J. Redox-Active Ferrocenyl Dendrimers and Polymers in Solution and Immobilized on Electrode Surfaces. *Coord. Chem. Rev.* **1999**, *185–186*, 53–79.
- (56) Majoral, J.-P.; Caminade, A.-M. Dendrimers Containing Heteroatoms (Si, P, B, Ge or Bi). *Chem. Rev.* **1999**, *99*, 845–880.
- (57) Hearnshaw, M. A.; Moss, J. R. Organometallic and Related Metal-Containing Dendrimers. *Chem. Commun.* **1999**, 1–8.
- (58) Moulines, F.; Djakovitch, L.; Boese, R.; Gloaguen, B.; Thiel, W.; Fillaut, J.-L.; Delville, M.-H.; Astruc, D. Organometallic Molecular Trees as Multi-electron and Proton Reservoirs: CpFe⁺ Induced Nona-Allylation of Mesitylene and Phase-Transfer Catalyzed Synthesis of a Redox-Active Nonairon Complex. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1075–1077.
- (59) Alonso, E.; Valério, C.; Ruiz, J.; Astruc, D. Polycationic Metallo-dendrimers with Cobalticinium and [FeCp(arene)]⁺ termini. *New J. Chem.* **1997**, *21*, 1139–1141.
- (60) Valério, C.; Ruiz, J.; Fillaut, J.-L.; Astruc, D. Dendritic Effect in the Recognition of Small Inorganic Anions Using a Polycationic Nonairon Cobalticinium Dendrimer. *C. R. Acad. Sci. Paris, t. 2, Sér. II c* **1999**, 79–83.
- (61) Sartor, V.; Djakovitch, L.; Fillaut, J.-L.; Moulines, F.; Neveu, F.; Marvaud, V.; Guittard, J.; Blais, J.-C.; Astruc, D. Organoiron Route to a New Dendron for Fast Dendritic Syntheses using Divergent and Convergent Methods. *J. Am. Chem. Soc.* **1999**, *121*, 2929–2930.
- (62) Bosman, A. W.; Janssen, H. M.; Meijers, E. W. About Dendrimers: Structure, Physical Properties, and Applications. *Chem. Rev.* **1999**, *99*, 1665–1688.
- (63) Beer, P. D. Transition-Metal Receptor Systems for the Selective Recognition of Anion Sensing of Anionic Guest Species. *Acc. Chem. Res.* **1998**, *31*, 71–80.
- (64) Ewing, A. G.; Strein, T. G.; Lau, Y. Y. Analytical Chemistry in Microenvironments: Single Nerve Cells. *Acc. Chem. Res.* **1992**, *25*, 440–447.
- (65) Xia, Y.; Rogers, J. A.; Paul, K. E.; Whitesides, G. M. Unconventional Methods for Fabricating and Patterning Nanostructures. *Chem. Rev.* **1999**, *99*, 1823–1848.

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