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Metallocenyl Dendrimers and Their Applications in Molecular Electronics, Sensing, and Catalysis

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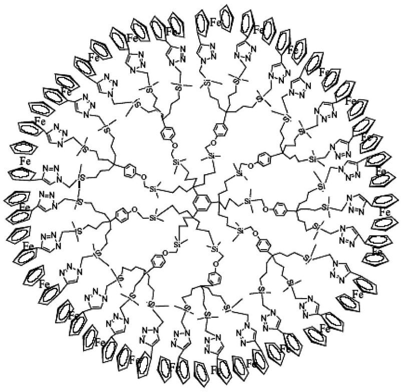

We have investigated the movement of electrons around the peripheries of dendrimers and between their redox termini and electrodes through studies of the electrochemistry of dendrimers presenting metallocenes (and other transition metal sandwich complexes) as terminal groups. Because these compounds can be stabilized in both their oxidized and their reduced forms, their electrochemical and chemical redox processes proceed without decomposition (chemical reversibility). Most interestingly, electrochemical studies reveal that electron transfer within the dendrimers and between the dendrimers and electrodes are both very fast processes when the branches are flexible (electrochemical reversibility).

When the dendrimer branches are sufficiently long, the redox events at the many termini of the metallodendrimer are independent, appearing as a single wave in the cyclic voltammogram, because of very weak electrostatic effects. As a result, these metallodendrimers have applications in the molecular recognition, sensing, and titration of anions (e.g., ATP^{2-}) and cations (e.g., transition metal complexes). When the recognition properties are coupled with catalysis, the metallodendrimers function in an enzyme-like manner. For example, Pd^{II} can be recognized and titrated using the dendrimer's terminal redox centers and internal coordinate ligands. Redox control over the number of Pd^{II} species located within a dendrimer allows us to predetermine the number of metal atoms that end up in the form of a dendrimer-encapsulated Pd nanoparticle (PdNP).

For hydrogenation of olefins, the efficiency (turnover frequency, TOF) and stability (turnover number, TON) depend on the size of the dendrimer-encapsulated PdNP catalysts, similar to the behavior of polymer-supported PdNP catalysts, suggesting a classic mechanism in which all of the steps proceed on the PdNP surface. On the other hand, Miyaura−Suzuki carbon−carbon bond-forming reactions catalyzed by dendrimer-encapsulated PdNPs proceed with TOFs and TONs that do not depend on the size of the PdNPs. Moreover these catalysts are more efficient when employed in lower (down to "homeopathic") amounts, presumably because of a leaching mechanism whereby Pd atoms escape from the PdNP surface subsequent to oxidative addition of the aryl halide. Under these conditions, the "mother" PdNPs have greater difficulty quenching the extremely active leached Pd atoms because of their low concentration.

Although dendrimers presenting catalysts at their branch termini can be recovered and reused readily, their inner-sphere components can lead to steric inhibition of substrate approach. In contrast, star-shaped catalysts do not suffer from such steric problems, as has been demonstrated for water-soluble dendrimers bearing cationic iron-sandwich termini, which are redox catalysts of cathodic nitrate and nitrite reduction in water.

Introduction

Metallodendrimers[1,2] are a well-recognized class of precise macromolecules that should find multiple applications in molecular electronics,[3−6] energy conversion,[4] sensing,[7−10] and catalysis.[10−13] Few metallodendrimer families present redox stability and have been investigated from the viewpoint of their electron-transfer properties, however. They include dendrimers containing metallocenes,[7,8] ruthenium polypyridine,[3,4] and metal-cluster units.[1,2,5] We will restrict this Account to metal-

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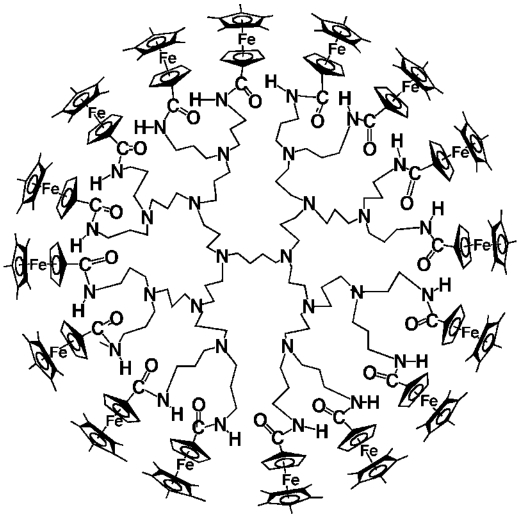
locenyl dendrimers[7] that have been the subject of our attention with emphasis on their applications.

Dendrimer Design for Molecular Electronics

Star compounds and dendrimers were synthesized with metal-sandwich units located either at the center or at the periphery or even both.[14–23] The redox activity of each redox center showed reversibility and the possibility to isolate at least two redox forms by multiple electron-transfer reactions. Early examples included the first dendrimers terminated by ferrocenyl (Scheme 1),[17,18] cobaltocenyl (eq 1),[21,22] and [FeCp(η^6-arene)]$^+$ (eq 2)[16,21] units. More extended dendrimer architectures were disclosed by one-pot CpFe$^+$-induced synthesis of a triallyl phenol dendron and subsequent 1→3 connectivity[24] of dendrimer growth therewith containing 3^{n+2} terminal branches with generation numbers n up to 9,[25–27] far beyond the de Gennes dense-packing limit.[28] Ferrocenyl units were then introduced either in a divergent way by hydrosilylation of the polyolefin dendrimers (only up to $n = 3$) using ferrocenyldimethylsilane (Schemes 2 and 3)[29] or in a convergent way using the same direct hydrosilylation of the unprotected dendron followed by convergent synthesis of the nonasilylferrocenyldendron and condensation onto aromatic (**1**), polypropylene imine (PPI, **2** and **3**), octahedral inorganic cluster (**4**), or nanoparticle (NP, **5**) cores.[30–33] Casado and Alonso et al. have also synthesized interesting and useful series of metallocenyl dendrimers since the mid-1990s.[7,34]



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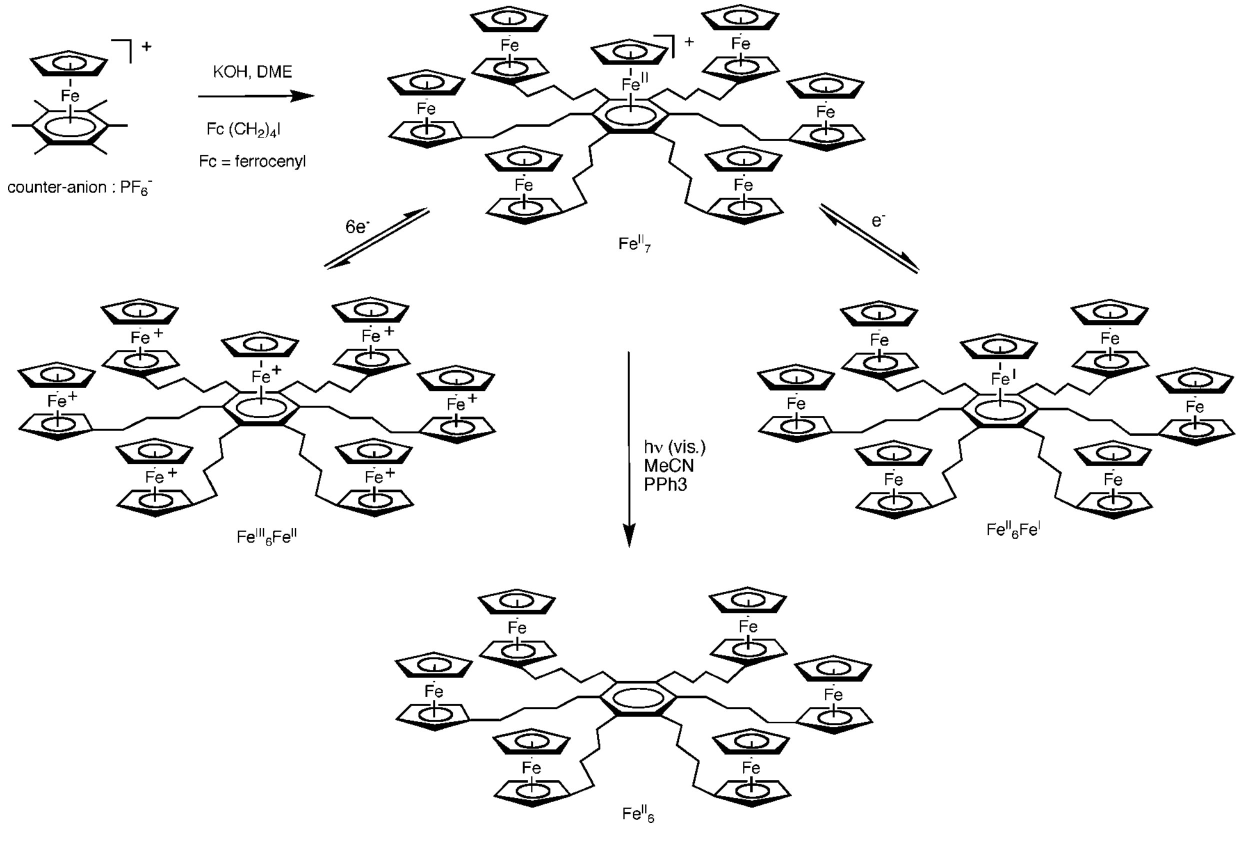
The electrochemical reversibility[35] (very fast electron transfer between the redox termini and the electrode) of dendrimers terminated by ferrocenyl, cobaltocenyl, and [FeCp(η^6-arene)]$^+$ groups is remarkable. Electron transfer between a remote redox center and the electrode would be expected to

SCHEME 1. Synthesis and Electron-Transfer Reactions of Polyiron Complexes



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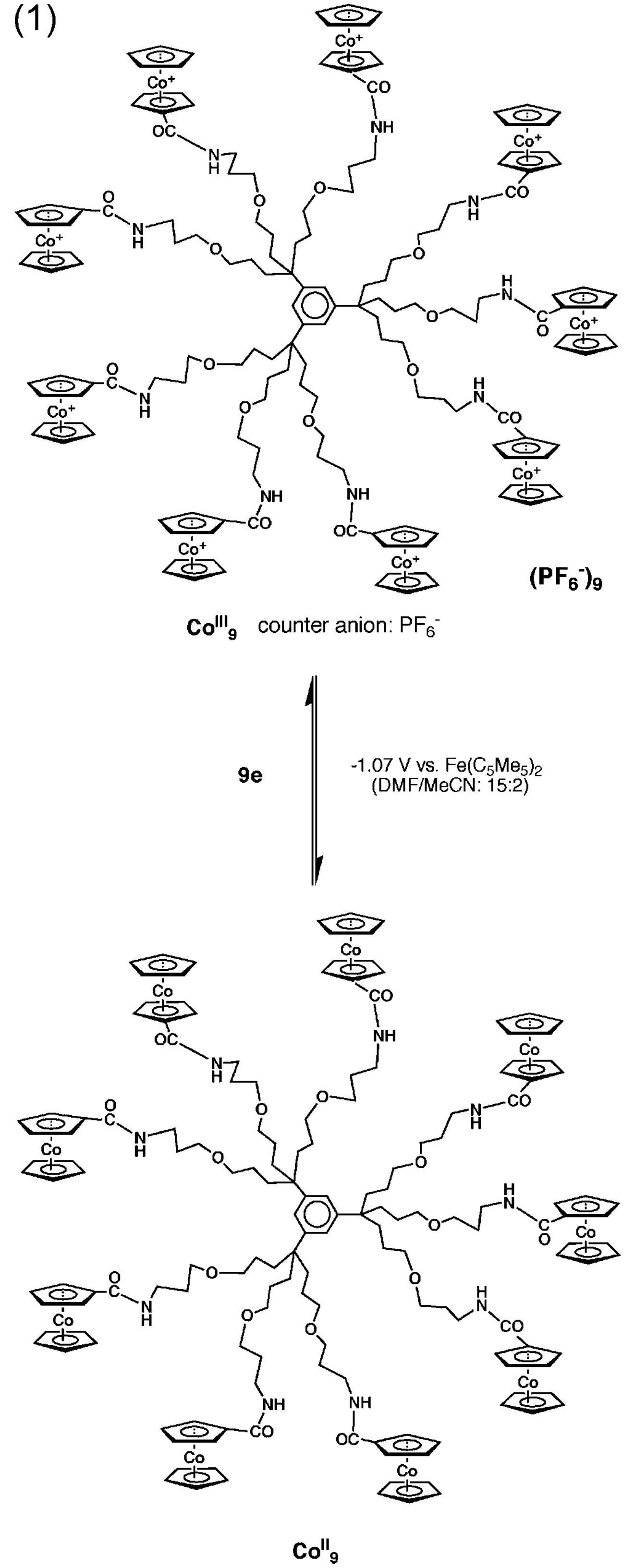

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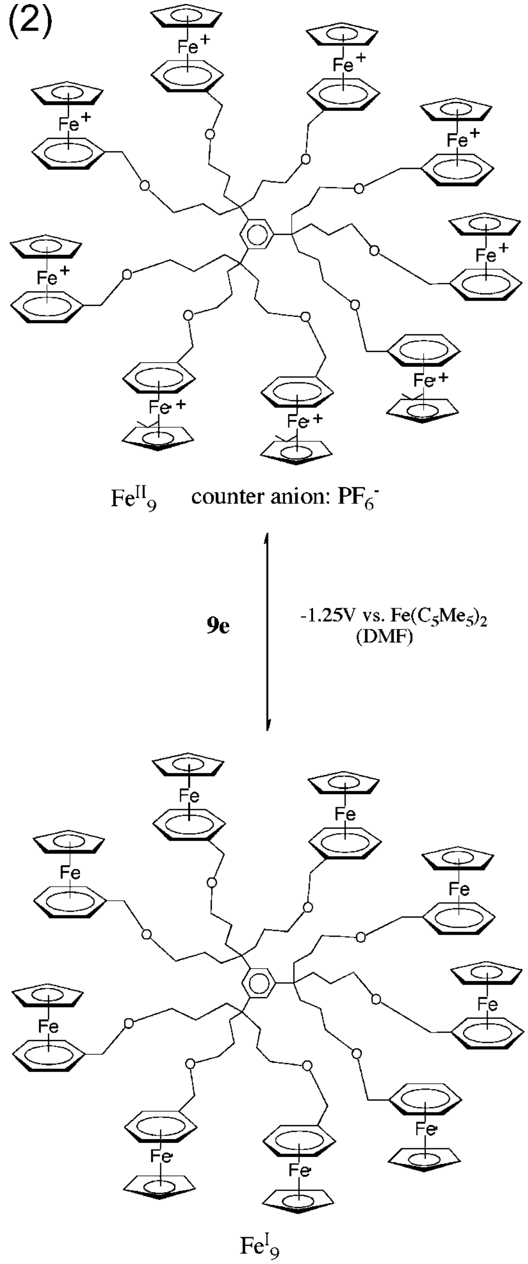
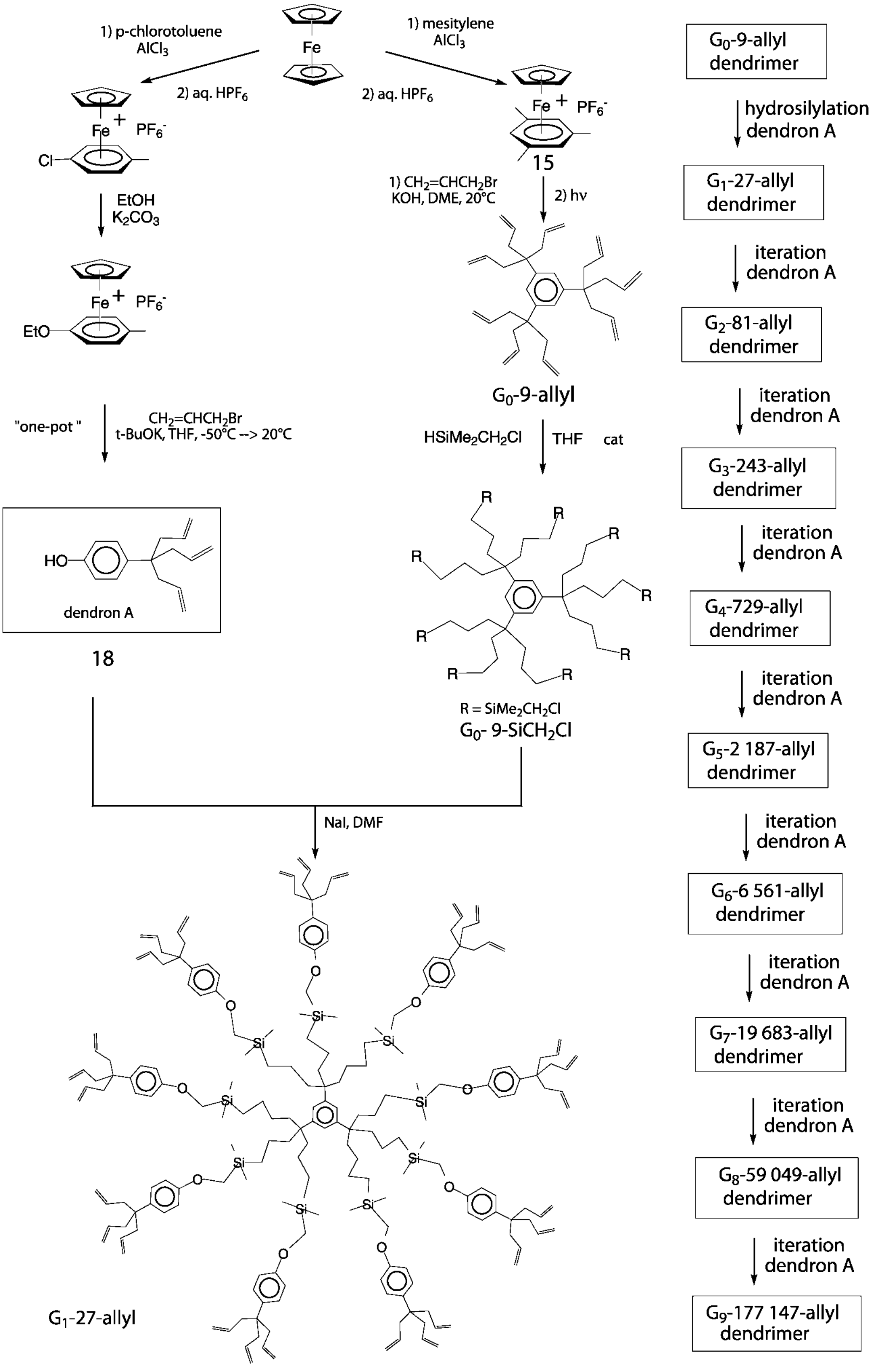


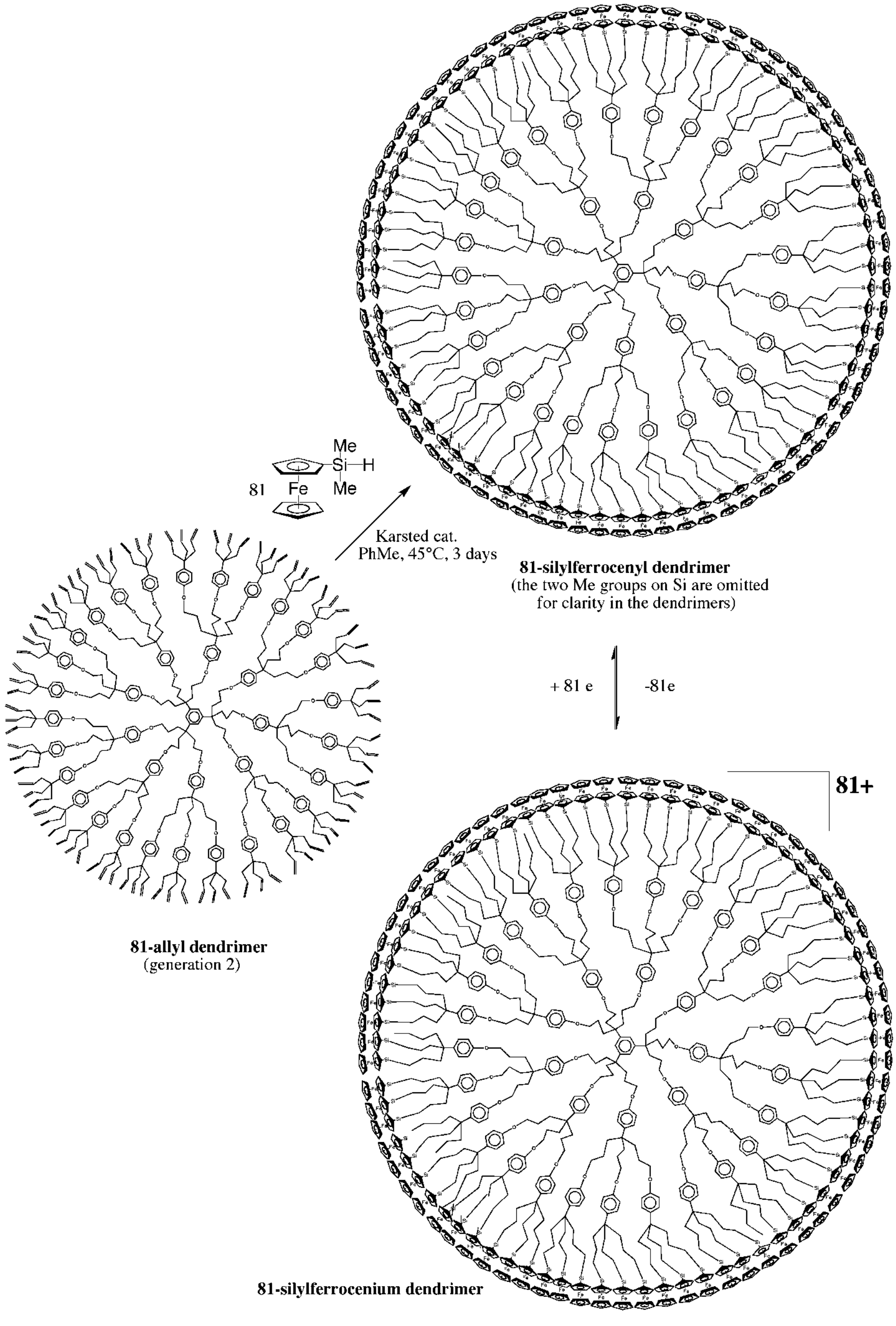
be slow because of the distance problem if the remote redox center is isolated, that is, not surrounded by other identical redox centers. Several reasons are invoked to rationalize fast electron transfer in ferrocenyl-terminated dendrimers, however. First, the time scale of the standard electrochemical experiment (usually around 0.1 s) is larger than the rotation rate of the dendrimer. Thus, all the redox centers have time to come close to the electrode within this electrochemical time scale.[36] Then, even if the intramolecular distance between two redox centers is large (most often more than ten bonds), through-space electron hoping is optimized when the flexible dendritic tethers bring two redox center at the minimum distance between them in a very fast dynamic process. This stepwise electron transfer among the redox centers between the remote ones and the ones that are located near the electrode also brings the electron or electron hole to the electrode

SCHEME 2. Synthesis of Dendrimers Containing a Theoretical Number of 3^{n+2} Terminal Branches



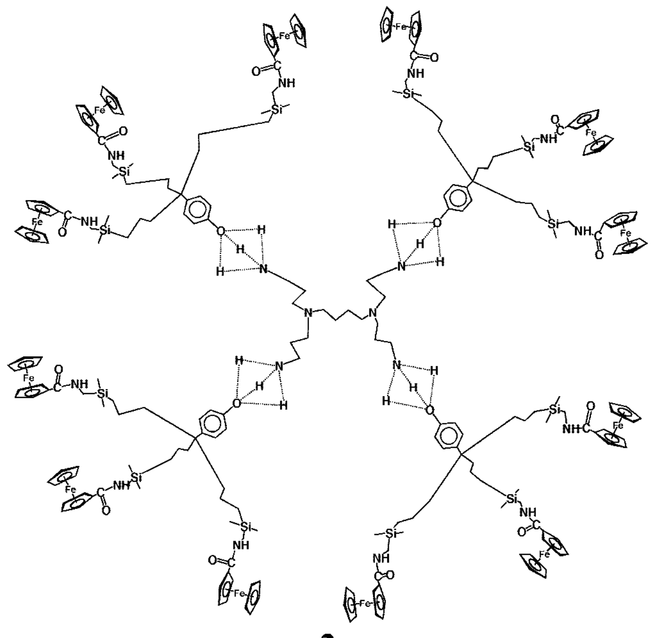
faster than the standard electrochemical time scale. A precise analysis of this later mechanism has been proposed by Amatore et al. for dendrimers terminated by $[Ru(terpy)_2]^{2+}$, based on the measured electron hopping rate constant using

SCHEME 3. Synthesis and Electron-Transfer Reaction of an 81-Ferrocenyl Dendrimer



ultramicroelectrodes and on a Smoluchowski-type model developed to take into account viscosity effects during the displacement of the $Ru^{II}/Ru^{III}(tpy)_2$ redox centers around their equilibrium positions.[37,38]

In addition, these metallocenyl dendrimers also exhibit chemical reversibility (both redox forms involved in the redox process are stable). Only one reversible redox wave is observed upon electrochemical redox change for all these dendrimers, because the terminal redox centers are located many bonds apart from one another, rendering the electrostatic factor so minute that it is not observable. Thus the formal redox potentials of the redox systems are distributed statistically along this redox curve as shown by Bard and Anson with ferrocenyl polymers,[39] and this curve appears identical to a clean single-electron wave if the solvent is chosen appropriately. The number of electrons that is theoretically equal to the number of redox units contained in the dendrimer can be determined using an internal reference such as decamethylferrocene, however. The resulting numbers are satisfactory as expected within a reasonable approximation on



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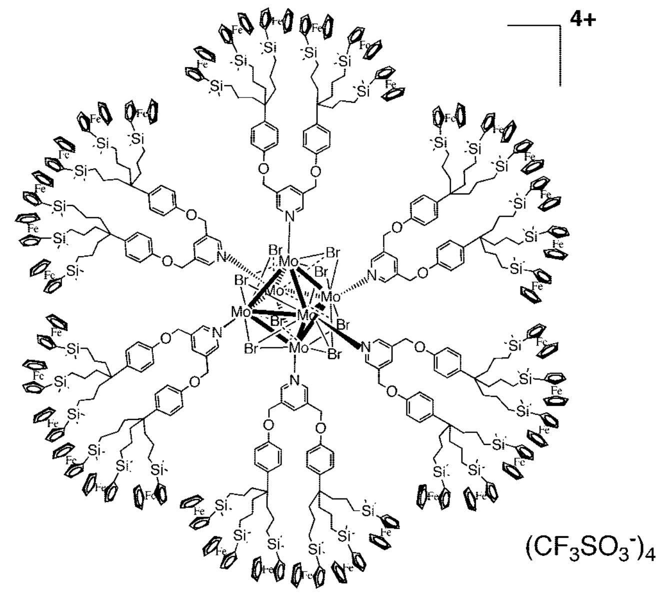

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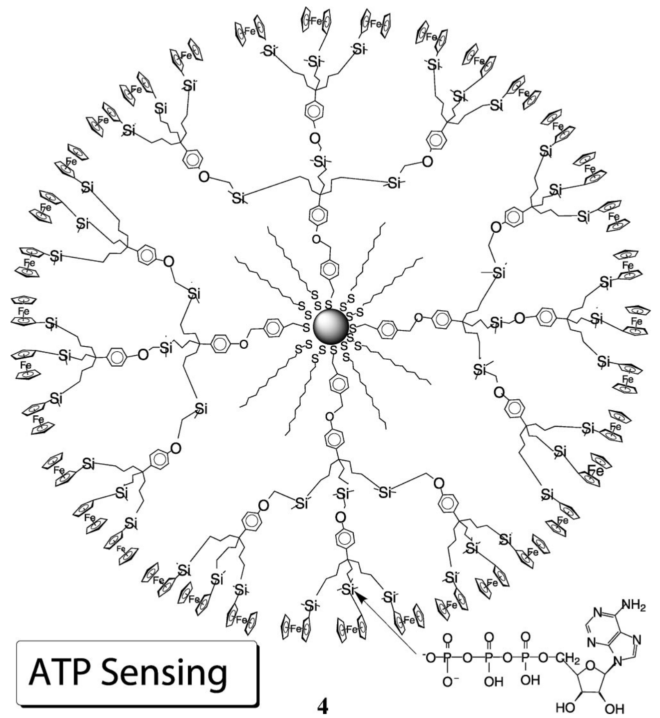

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the order of 5−10% if the dendrimer is not too large. When the dendrimer contains more than, for example, 50−100 metallocene units, depending strongly on the solvent, adsorption is observed, which yields results in excess for the determination of this electron number.[36,39] Coulometry is then an alternative method to verify the number of electrons engaged in the redox process.

On the other hand, in iron-sandwich-centered dendrimers, the reversible cyclovoltammetry wave is only observed if the dendrimer is small. When it becomes larger, electron transfer between a buried redox center and the electrode is unfavorable, because its rate drops exponentially with the electron-transfer distance. Such systems have been carefully examined in particular with Fe_4S_4 cluster-centered dendrimers by Gorman who has also studied the influence of various parameters on the electron-transfer rates.[5,36,40]

Application of the Redox Reversibility of Metallocenyl-Terminated Dendrimers to Anion Recognition and Sensing

We have taken advantage of the simplicity of the electrochemical technique with metallocenyl dendrimers showing both electrochemical and chemical reversibilities of a single cyclic voltammetry wave to use these dendrimers as exoreceptors. Endoreceptors (crown ethers, cryptands, cyclophanes, calixarenes, polypods) containing a redox systems have been shown, especially by Beer's group,[41,42] to be excellent anion sensors. Exoreceptors are attractive because they mimic viruses by their peripheral surface. It was also of interest to investigate how guests of potential medicinal interest might interact with the dendrimer surface and what kind of dendrimer effect might result. It was necessary to design metallocenyl-terminated dendrimers containing a group that would interact through a supramolecular bond (hydrogen bond, hypervalence, coordination) with the species to be recognized. This group had to be located near the redox group to sufficiently perturb the redox system upon interaction with the guest species.

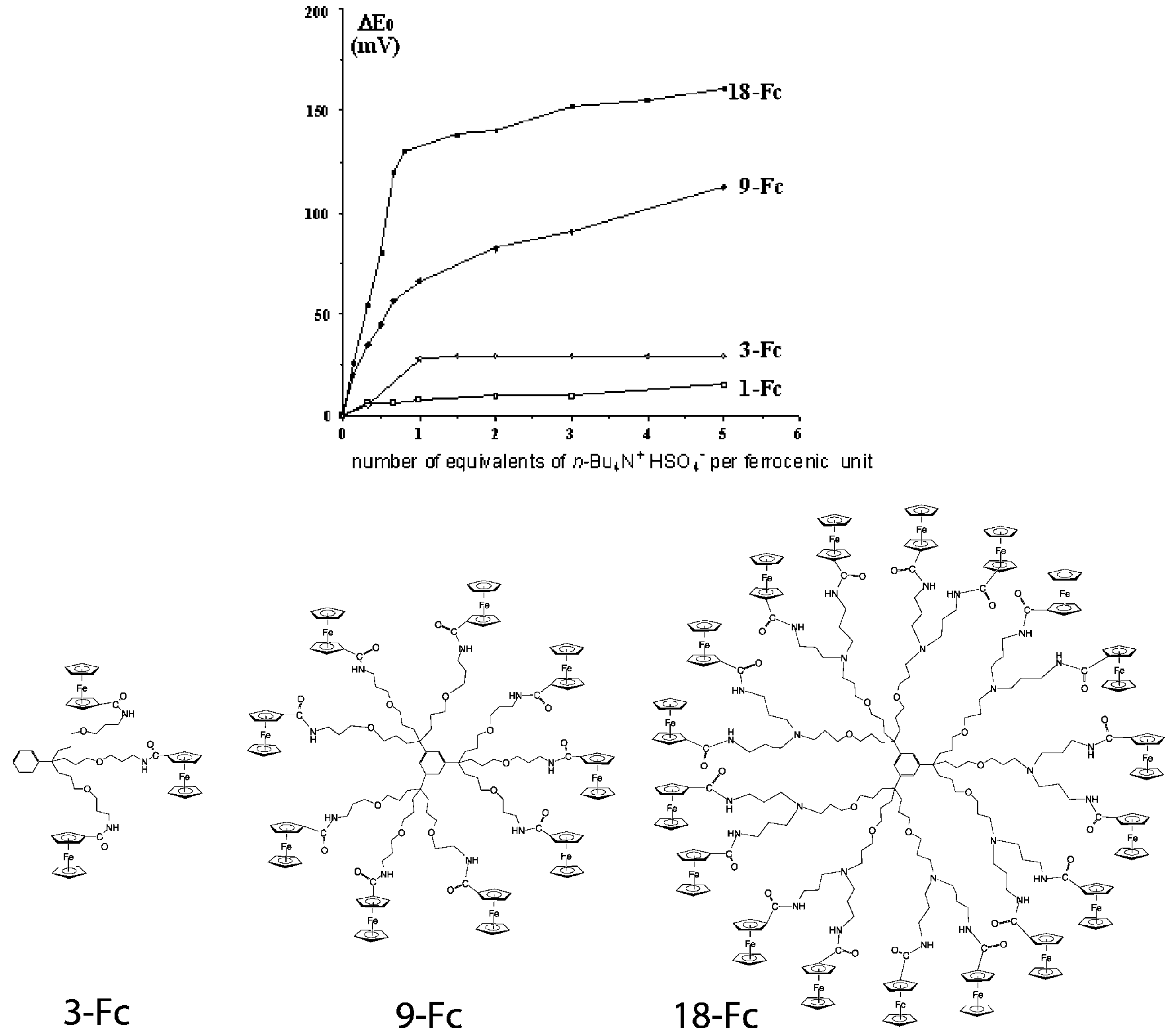
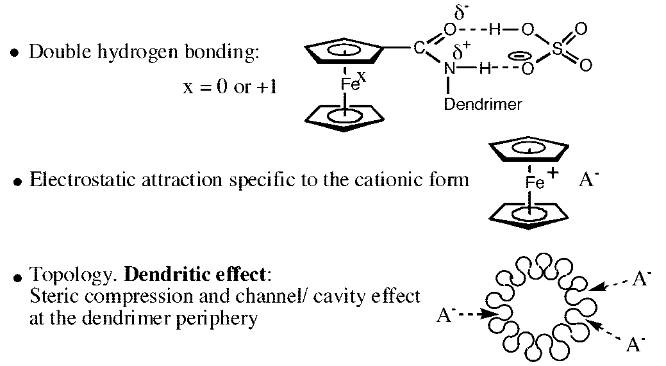


FIGURE 1. Variation ΔE° of the redox potential of the ferrocenyl system upon addition of [n-Bu_4N][HSO_4] to mono- (1-Fc), tri- (3-Fc), nona- (9-Fc), and octadeca-amidoferrocenyl (18-Fc) derivatives (1-Fc = [$FeCp(\eta^5$-$C_5H_4CONHCH_2CH_2OPh)$]).

Positive Dendritic Effects in Anion Recognition, Sensing, and Titration

Anion sensing is of crucial importance due to the presence of anions in biological systems and as waste in the environment. The first attempt used amidoferrocenyl-terminated dendrimers for the recognition of the oxo-anions $H_2PO_4^-$ and HSO_4^-.[19,20] Such dendrimers with 3, 9, and 18 amidoferrocene termini were compared with a nondendritic monoamidoferrocene analogue. Figure 1 shows that this monomeric amidoferrocene hardly provokes any change of the ferrocenyl redox potential upon addition of the n-Bu_4N^+ salt of HSO_4^- in CH_2Cl_2, whereas the dendrimers do. The shift of this redox potential of the Fe^{III}/Fe^{II} system is all the larger as the dendrimer contains more amidoferrocene termini. The best result is obtained with the largest dendrimer containing 18 amidoferrocenyl termini. Thus the dendritic effect is positive; that is, the effect is all the larger as the dendrimer generation increases. The synergistic addition of the hydrogen bonding between the amido group and the anion and the electrostatic effect resulting from the interaction between the ferrocenium form generated at the anode and the anion is not sufficient to provoke a significant change of redox potential, but the additional topological effect of the dendrimer is crucial as shown by the positive dendritic effect (Chart 1). The break in the titration curves is marked for a one-to-one interaction (one amidoferrocene branch per HSO_4^- unit). A variation of potential upon anion addition signifies that the interaction is of the weak type according to the Echegoyen–

CHART 1. Factors Responsible for the Recognition of Oxoanions

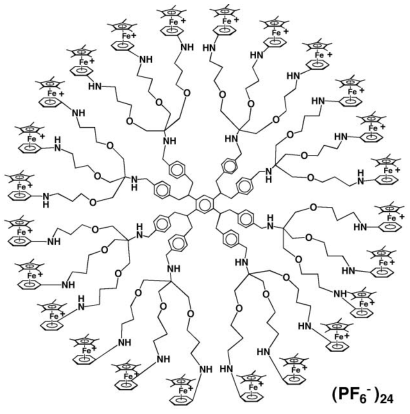


- Double hydrogen bonding: x = 0 or +1
- Electrostatic attraction specific to the cationic form
- Topology. **Dendritic effect**: Steric compression and channel/ cavity effect at the dendrimer periphery

Kaifer model,[43] whereas the appearance of a new wave at the expense of the decrease of the initial wave observed with $H_2PO_4^-$ is the sign of an interaction of the strong type according to this model. In the case of the weak interaction, the variation of redox potential of the initial wave allows determination of the apparent association constant K_+ between the oxidized ferrocenium form and the ferrocenium$-HSO_4^-$ anion complex according to $E°_{free}$ - $E°_{bound} = \Delta E°(V) = 0.059 \log cK_+$ at 25 °C, yielding $K_+ = 544 \pm 50$, 8500 ± 500, and $61\,000 \pm 3000$ for 3-Fc, 9-Fc, and 18-Fc, respectively, where $E°_{bound}$ is the redox potential obtained after addition of 1 equiv of anion per ferrocenyl branch, and *c* is the anion concentration. In the case of the strong interaction with $H_2PO_4^-$, the ratio K_+/K_0 is accessible: $\Delta E°(V) = 0.059 \log K_+/K_0$. Determination of K_0 by ^{1}H NMR (using the shift of the NH signal) gives, for instance, for 9-Fc, $K_+ = (2.2 \pm 0.2) \times 10^5$ in CH_2Cl_2. The nature of the solvent is also crucial; for instance, in DMF, recognition and titration are only possible in the amidoferrocenyl dendrimers in which the free Cp rings of the amidoferrocenyl groups are permethylated ([Fe(η^5-C_5Me_5)(η^5-C_5H_4CONH-dendr)], Chart 1).[44,45]

Selectivity in Anion Sensing Using Metallocenyl Dendrimers

Another dendritic effect is observed on the selectivity of anion recognition. Whereas the amidoferrocenyl dendrimers recognize the oxoanions as above but not the halides, dendrimers terminated with $[Fe(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_5NH\text{-dendr})]^+$ recognize chloride and bromide but not the oxoanions. For bromide, a positive dendritic effect is observed as usual with a one-to-one interaction between Br^- and an iron-sandwich branch, whereas with the chloride anion the 24-Fe dendrimer shows



24-FeAr
5

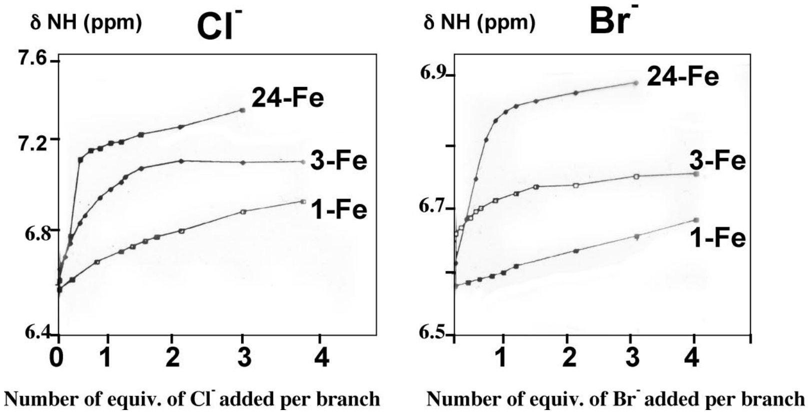


FIGURE 2. ^{1}H NMR variation of δ_{NH} for the mono- (1-Fe), tri- (3-Fe), and 24-Fe dendrimer **5** upon addition of *n*-Bu_4NCl or *n*-Bu_4NBr.

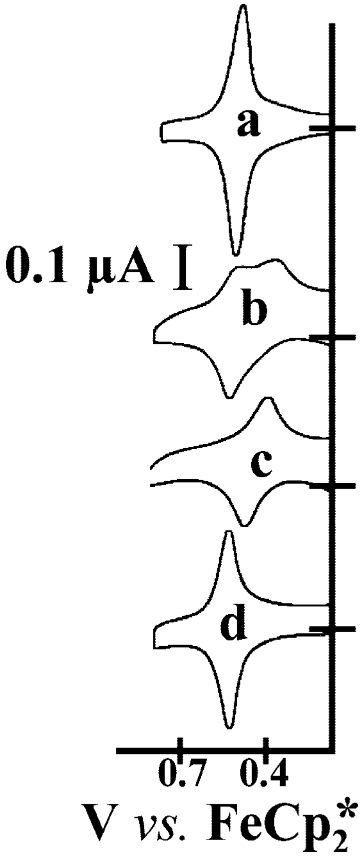


FIGURE 3. Recognition of ATP^{2-} by AuNP-cored dendrimer **5**: modified Pt electrode (a) alone, (b) during the course of titration, (c) with excess $[n\text{-}Bu_4N]_2[ATP]$, and (d) after washing off $[n\text{-}Bu_4N]_2[ATP]$.

strong recognition for only one Br^- per tripodal unit (i.e., 8 Br^- per 24-Fe dendrimer, Figure 2). This recognition is effective by variation of the ^1H NMR shift of the NH proton signal upon addition of the halide anion.[23] This type of analysis as well as cyclic voltammetry analysis of the Co^{III}/Co^{II} wave were also productive with a nona-amidocobalticinium dendrimer for the recognition of the anions HSO_4^-, $H_2PO_4^-$, and Cl^-, provoking, for instance, the appearance of a new cyclic voltammetry wave with a redox potential variation of 270, 205, and 60 mV, respectively, on Pt anode upon addition of 1 equiv of anion per cobaltocenyl branch in CH_3CN/DMF (2:15).[22] In all these studies with the ferrocenyl and cobaltocenyl dendrimers, the recognition of the strongly interacting anions is selective. For instance, recognition of $H_2PO_4^-$ can be carried out in a mixture of various anions such as HSO_4^- and halides.

Variation of the Nature of the Dendritic Core and Supramolecular Binding Modes to Metallocenyl Dendrons

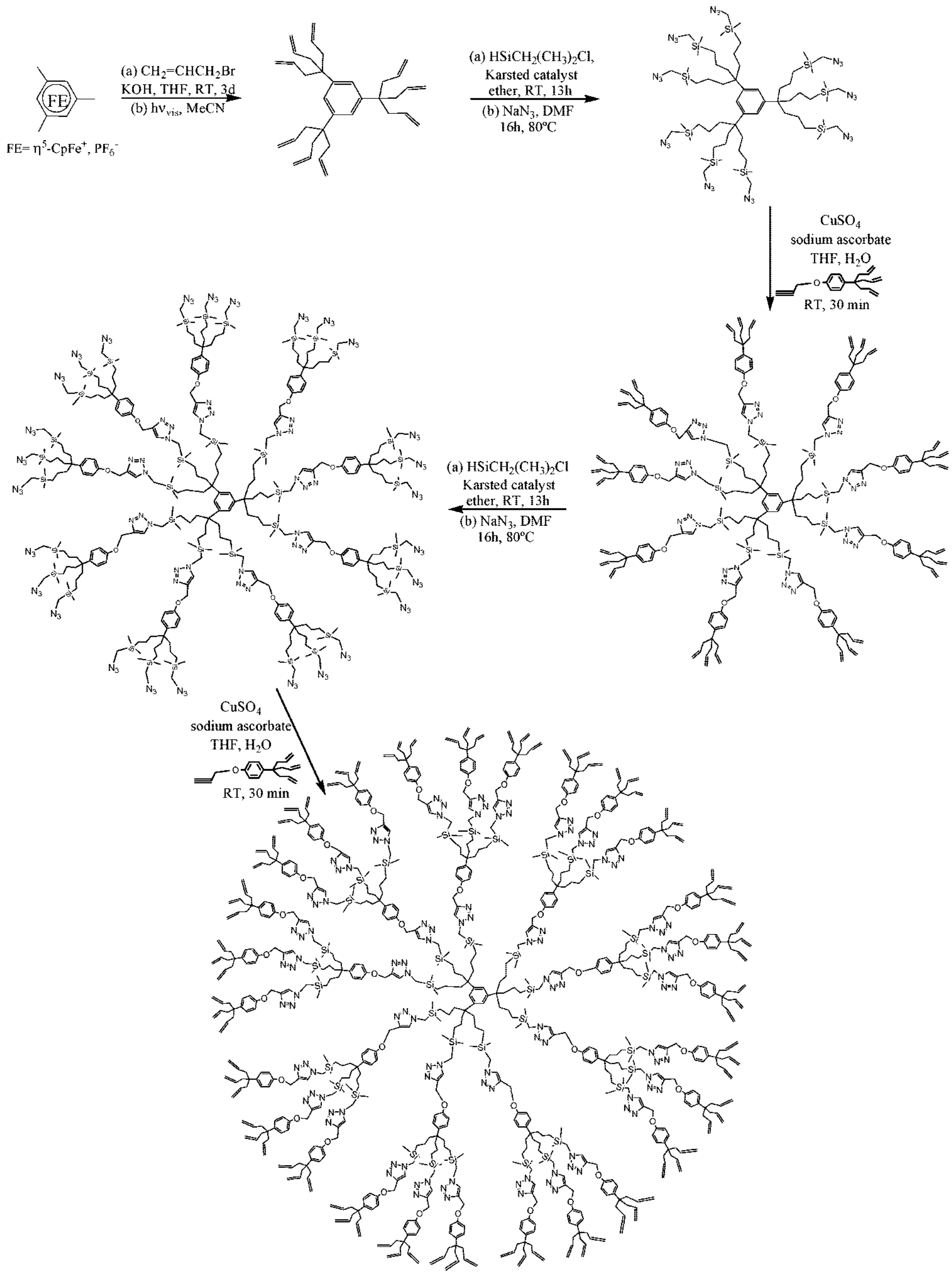
It is possible to assemble commercial PPI dendritic core with triferrocenyl dendrons containing a phenol focal group forming a triple hydrogen bonding with primary amino termini of the cores in **3** as shown by ^1H NMR.[32] This procedure avoids dendrimer synthesis yet allows recording of cyclic voltammograms of the H-bonded dendrimer that is reversibly formed during the electrochemical time scale of the experiment (of the order of 0.1 s). Recognition of $H_2PO_4^-$ proceeds as with covalent dendrimers with a dramatic drop of the intensity of the cyclic voltammetry wave at the equivalent point. This drop is proposed to be due to the formation of a large supramolecular assembly with the oxoanion at the equivalence point provoking a drop of the diffusion coefficient.[46]

Other ferrocenyl dendrimers were assembled by coordination of ferrocenyl dendrons to inorganic cores that are either octahedral Mo_6 clusters connected at their six apical positions to ferrocenyl dendrons containing a phenol focal point in **4**[47] or AuNPs connected to a variable number of ferrocenyl dendrons containing a thiol-terminated focal point in **5**.[48] The number of ferrocenyl dendrons is fixed in the synthesis by the proportion of gold and thiol amounts. The thiols that provide the thiolate ligands at the AuNP surface can be chosen as pure dendrons or mixtures of dodecanethiol[49] and thiol dendrons.[50,51] The ferrocenyl dendrons connected to these inorganic cores contain dimethylsilyl groups for which the silicon atom is directly linked to a cyclopentadienyl ligand in the ferrocenyl termini. This silicon atom is oxophilic and potentially hypervalent, which is responsible for the interaction with an oxygen atom of the oxoanions $H_2PO_4^-$ and adenosyltriphosphate (ATP^{2-}), a DNA fragment. Recognition of these two anions by cyclic voltammetry on Pt anode proceeds with strong interaction, provoking the appearance of a new wave upon addition of a $n\text{-}Bu_4N^+$ salt of one of these anions in CH_2Cl_2.

Derivatized Pt Electrodes with Large AuNP-Cored Ferrocenyl Dendrimers As Recyclable ATP^{2-} Sensors

One advantage of large ferrocenyl dendrimers is that they benefit from the positive dendritic effect that is systematically observed for anion recognition, which optimizes sensing. Another advantage concerns the fabrication of modified electrodes.[52,53] Adsorption of dendrimers onto Pt anodes[54] is indeed all the easier because they are larger.[43] Upon scanning around the ferrocene potential region, small dendrimers are rapidly disconnected, whereas large ones form very stable modified electrodes. An especially practical way to assemble large ferrocenyl dendrimers is that using AuNPs as templating cores, which allows connecting up to around 200

SCHEME 4. Synthesis of "Click" Dendrimers



ferrocenyl centers. Perfectly stable modified electrodes herewith are formed upon scanning about 50 times around the ferrocene potential region. Recognition and sensing of ATP^{2-} is characterized by the appearance of a new wave that progressively replaces the original wave upon addition of the ATP^{2-} salt in CH_2Cl_2. After disappearance of the original wave, the electrode is washed using CH_2Cl_2 to remove the ATP^{2-}, and the original wave of the modified electrode is recovered, which allows starting a new recognition experiment. Whereas most electrochemical sensors are not recyclable, these ones are (Figure 3).[33]

Design of "Click" Ferrocenyl Dendrimers That Recognize Both Oxoanions and Transition-Metal Cations

The outstanding properties of enzymes combine molecular recognition and catalysis. Although dendrimers are not enzyme models,[55] they possess some features resembling those of biomolecules, that is, size and topology.[56] Thus, one may imagine designed dendrimers that would have both recognition and catalysis properties. One way to approach this concept is to introduce an intradendritic ligand that would recognize and bind catalyti-

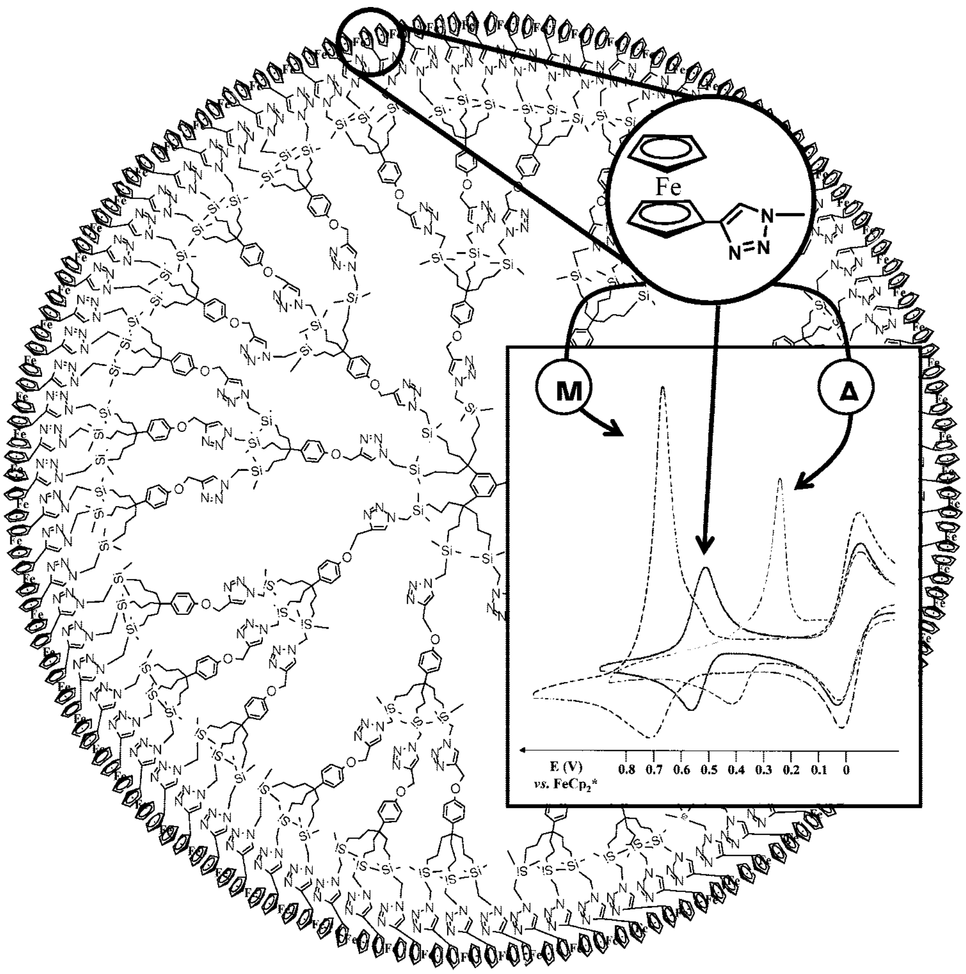


FIGURE 4. Cyclic voltammetry: recognition of both oxoanions and transition-metal cationic acetonitrile complexes by a "click" ferrocenyl dendrimer.

cally active transition-metal species. We have chosen the 1,2,3-triazolyl ligand, because it can smoothly bind transition metals and can be easily, selectively, and catalytically formed by reaction between a terminal alkyne and an azide, a process that has recently been improved and rendered popular by Sharpless under the heading of "click chemistry". This Huisgen -type cycloaddition reaction is now indeed catalyzed by Cu^I in an aqueous solvent under mild conditions.[57,58] Thus, three generations of ferrocenyl "click" dendrimers containing 3^{n+2} terminal ferrocenyl tethers ($n = 0-2$) were synthesized by reaction of azido-terminated dendrimers and dendronic alkynes, the construction being terminated by a "click" reaction with ferrocenylacetylene to introduce ferrocenyl termini. A stoichiometric amount of Cu(I) was required in the absence of added ligand, because the metal ions are trapped inside the dendrimer (Scheme 4 and eq 3).[59,60] A tripodally ligated Cu(I) catalyst designed by Vincent could also be efficiently used, however.[61] Catalytically efficient and recyclable dendrimers have been largely studied, and various locations of metal ions have been used (periphery, core, branch point, interstitial).[10–13] Various metals have been introduced in the dendritic interiors of commercial PAMAM and PPI dendrimers, and in particular, the catalytic activity of dendrimer-encapsulated PdNPs formed by NaBH$_4$ reduction of Pd^{II} dendritic complexes has been largely investigated by Crooks' group among others.[62–64] We reasoned that the recognition and titration of various transition metal ions by smoothly coordinating ferrocenyl triazolyl dendrimers, in particular, Pd^{II}, would allow a precise count of dendrimer-encapsulated metal ions. Indeed, a one-to-one interaction was shown by cyclic voltammetry between the dendritic triazolyl ligands and Cu^I, Cu^{II}, Pd^{II}, and Pt^{II}. Monometallic (nonden-

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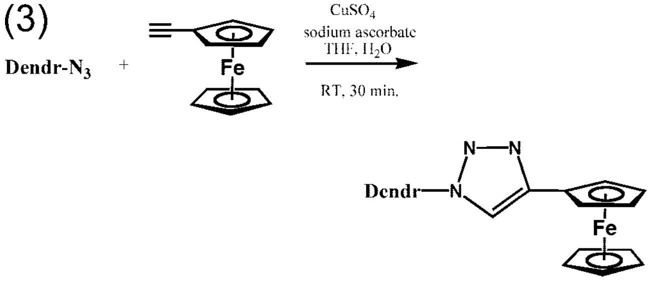
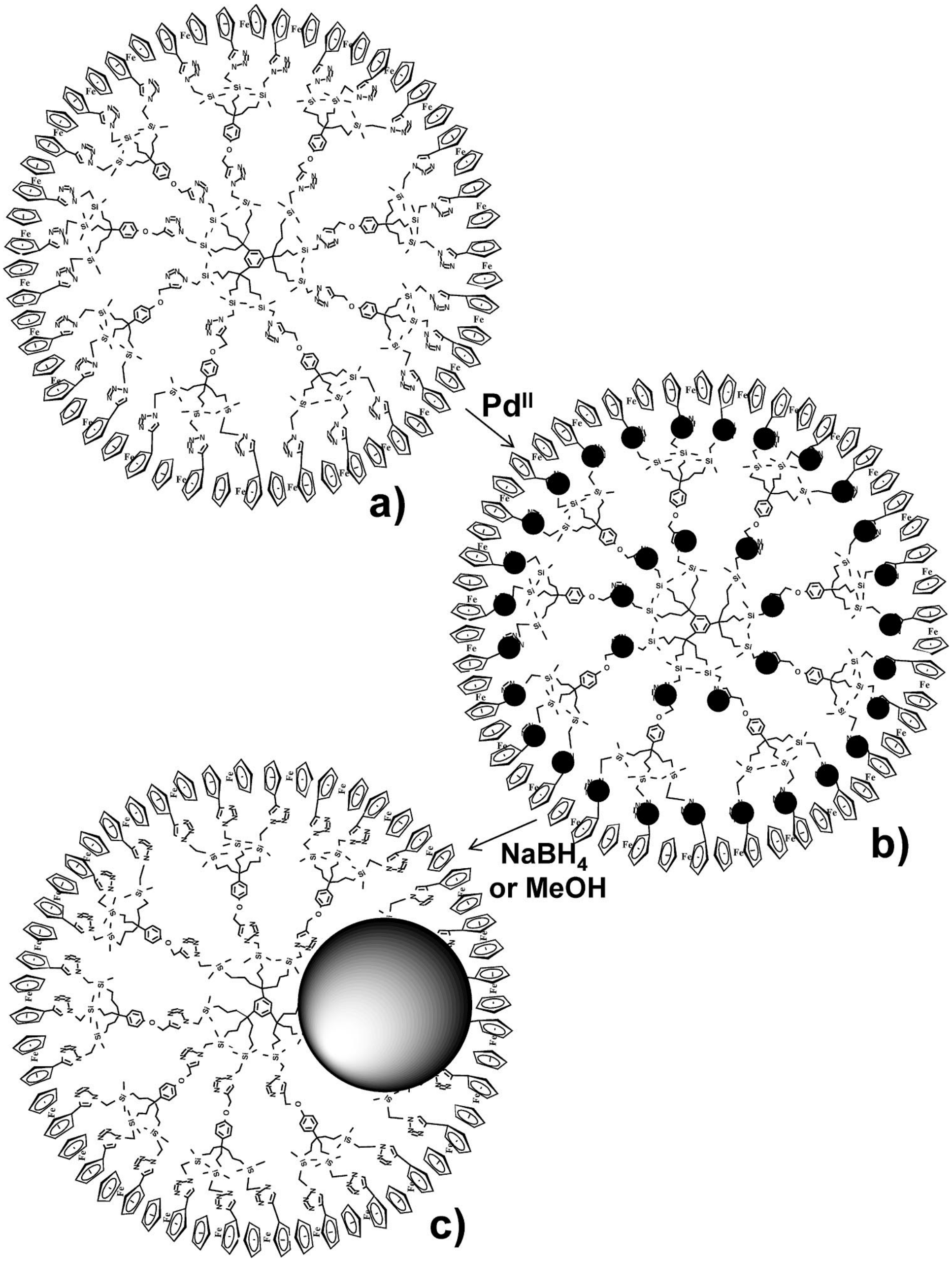


SCHEME 5. Synthesis of "Click"-Ferrocenyl Dendrimer-Encapsulated PdNPs



dritic) ferrocenyltriazolyl ligand could not recognize these metal ions, which were recognized by these dendrimers all the more easily as the dendrimer generation increased (positive dendritic effect). The electron-withdrawing properties of these metal cations (introduced as their tetrakis acetonitrile complexes) decreased the electron density on the ferrocenyl center, which shifted the CV wave to more positive potential values. On the other hand, oxoanions such as $H_2PO_4^-$ and ATP^{2-} were also recognized by these dendrimers, because the electron-releasing properties of these anions shifted the ferrocenyl CV wave to less positive potential values (Figure 4).[59]

Very Efficient and Selective Hydrogenation Catalysis by Precise Ferrocenyl Dendrimer-Stabilized Pd Nanoparticles under Ambient Conditions

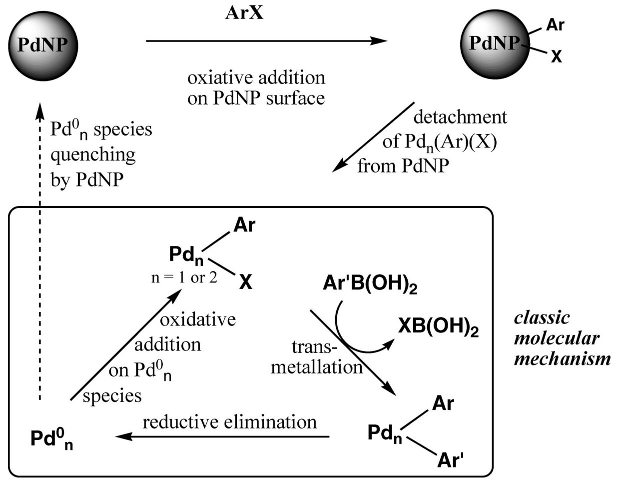
The recognition and titration of $Pd(OAc)_2$ by three generations of triazolylferrocenyl dendrimers allowed determination of the number of Pd^{II} species coordinated to the intradendritic triazolyl ligands, which corresponded to a one-to-one coordination per ligand. Reduction of G_1 and G_2 using $NaBH_4$ or methanol produced PdNPs whose sizes, determined by TEM, matched those determined by electrochemical titration of the

Pd^{II} precursors.[65] On the other hand, the PdNPs formed from the zeroth generation (9-Fc) were large, because such small dendrimers cannot encapsulate NPs but instead stabilize PdNPs at their periphery. Thus, the smallest PdNPs were those formed from the G_1 27-Fc dendrimer containing 36 triazolyl rings and encapsulating PdNPs that contained 36 Pd atoms (Scheme 5). Selective hydrogenation of dienes to monoenes was readily achieved under ambient conditions for small dienes, but large steroidal dienes remained unreacted, in accord with their lack of ability to reach the PdNP surface. The hydrogenation rates (TOFs) and TONs were all the larger as the PdNPs were smaller, as expected from previous results with polymer-stabilized PdNPs according to a mechanism that involves all the mechanistic steps of the hydrogenation on the PdNP surface.[60,65]

Homeopathic Catalysis of Suzuki C−C Coupling by "Click" Ferrocenyl Dendrimer-Stabilized PdNPs under Ambient Conditions and Evidence for a Leaching Mechanism

Contrary to hydrogenation catalysis, which proceeds at the PdNP surface and therefore depends on the PdNP size, catalysis of Miyaura−Suzuki coupling[66] between PhI and $PhB(OH)_2$ proceeds at room temperature without significant dependence on the PdNP size or whether its stabilization is intra- or interdendritic. This indicates that the dendrimer is not involved in the rate-limiting step of the reaction. Not only do the dendrimer-stabilized PdNPs work identically whatever their size, but the TONs regularly increase upon decreasing the amount of catalyst from 1% down to 1 ppm or upon dilution of the reaction solution. Thus, the efficiency of the catalyst is remarkable at "homeopathic" amounts (54% yield with 1 ppm equivalent of Pd atom, that is, TON = 540 000), whereas a quantitative yield is not even reached (75% yield) with 1% equivalent of Pd atom.[67] The "homeopathic" catalysis was already observed for the Heck reaction at 150 °C and was rationalized by de Vries according to a leaching mechanism involving detachment of Pd atoms from the PdNP subsequent to oxidative addition of the organic halide PhI on the PdNP surface.[68,69] If such a mechanism is reasonable at such high temperature due to decomposition of the Pd catalyst to naked PdNPs, it may look unexpected for a room-temperature reaction. The ease of the room-temperature mechanism must be due, however, to the lack of ligands on the dendrimer-stabilized PdNPs that therefore can easily undergo oxidative addition of PhI at their surface, which provokes the leaching of Pd atoms. These isolated Pd atoms must be extraordinarily reactive in solution, because they do not bear ligands other than the very weakly coordinating solvent molecules. The limitation of their efficiency is trapping by their mother NP. This inhibiting trapping mechanism is all the less efficient as the catalyst is more dilute, however. It is not efficient under extremely diluted solutions, whereas it strongly inhibits catalysis at relatively high concentrations. It is likely that this concept can be extended to various other PdNP-catalyzed C−C bond formation reactions (Scheme 6).[70]

SCHEME 6. Leaching Mechanism in the "Homeopathic" Catalysis of Suzuki C−C Coupling at Ambient Temperature between PhI and $PhB(OH)_2$ by "Click" Ferrocenyl Dendrimer-Stabilized PdNPs

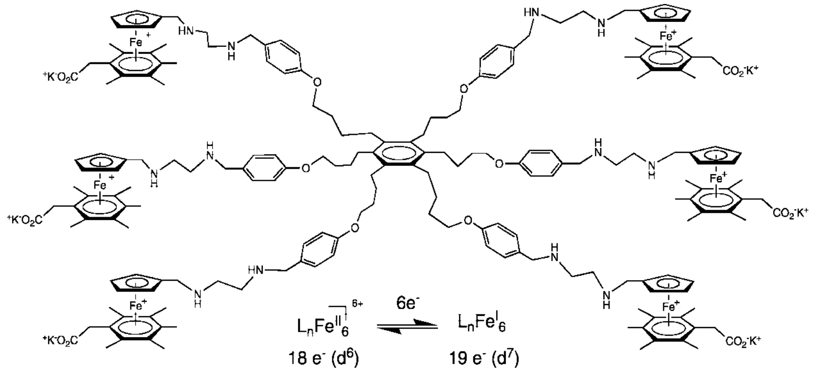


Functional [FeCp(η^6-arene)]$^+$ Sandwich-Terminated Stars As Redox Catalysts: Stars Better than Dendrimers for Catalysis

Let us finally consider iron-sandwich-terminated star-shaped compounds that are good examples of the topological optimization of this type of nanosized catalyst. The complexes $[Fe(\eta^5\text{-}C_5H_4R)(\eta^6\text{-} C_6Me_6)]^{+/0}$ (R = H or CO_2^-) are stable redox catalysts for the cathodic reduction of nitrates and nitrites in water.[71] Star complexes terminated by such stable redox catalysts such as **6** have been shown to catalyze these cathodic reactions without kinetic loss compared with monometallic systems.[72,73] On the other hand, star complexes with alkyl chains on the benzene ligand, that is, in which the catalyst is at the core center, react 1−2 orders of magnitudes more slowly. This is an indication that steric constraints may cause kinetic limitations, when an inner-sphere component is involved in the reaction of the catalyst. Similar kinetic limitations were usually disclosed in other catalyst-terminated dendrimers.[74]

Conclusion and Outlook

Redox-robust metallocenyl-terminated dendrimers have useful molecular electronic properties including very fast elec-



6

tron transfer with electrodes, independence of the redox centers, and increasing adsorption ability as their size increases. Applications are (i) anion exoreceptors with dendritic effects whose selectivity vary with the metallocenyl dendrimer structure, size, and terminal groups and (ii) catalysts whereby recognition and titration of transition-metal ions allow preparation of precise NPs of various size for optimization and mechanistic determination. "Homeopathic" catalysis using ligandless dendrimer-stabilized NPs shows considerable promise for green chemistry, whereas leaching of catalyst-terminated dendrimers may turn out to be a major problem for industrial applications. Other applications of metallocenyl dendrimers have appeared in materials science,[1,2,7–10] in particular, as liquid crystals,[75] and metallocene dendrimers also show promise compared with ferrocene-containing polymers.[76]

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Cátia Ornelas studied at the University of Madeira, Portugal including her Master degree with Professor João Rodrigues before her Ph.D. in Bordeaux with Professor Didier Astruc on metallodendrimer chemistry. She is presently a postdoctoral fellow at New York University. Her interests are in supramolecular organometallic chemistry, sensing, and catalysis.

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FOOTNOTES

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