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Nano-Scale Metallodendritic Complexes in Electron-Transfer Processes and Catalysis

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Summary: Nano-sized metallodendrimers in which the equivalent metal fragments are located at the periphery can be assembled covalently, by H-bonding (supramolecular) or onto dendronized nanoparticles. They can be used as electron-reservoirs, i.e. molecular batteries, redox catalysts and sensors for the recognition of biologically relevant anions. They can also be deposited on metal surfaces or electrodes, which optimizes their use as recoverable sensors.

Keywords: catalysis; dendrimers, nanocomposites; sensors; transition metal chemistry

Content

Introduction

Metallodendrimers [1-10] with redox stability are electron-reservoir systems that should prove useful as molecular batteries, catalysts and sensors. With a low polydispersity, their molecular definition is much more precise than that of organometallic polymers, yet they can be very large. Moreover, their use in molecular electronics is promising in the context of nano-technology.

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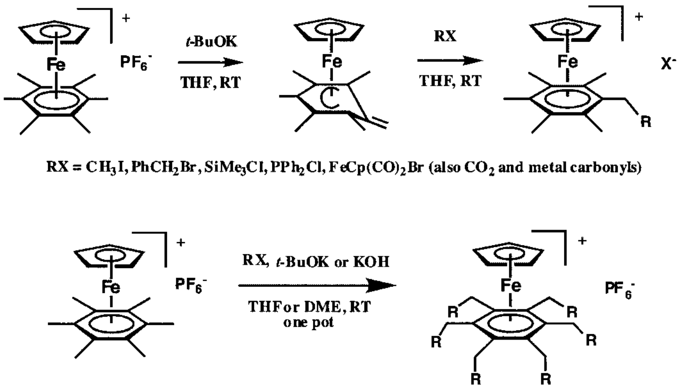
Ferrocenyl dendrimers are now a well-spread field of dendrimer research to which we have contributed.[11-14] In this chapter, we review our strategy as well as electron-transfer processes in other metallodendrimers involving monomeric electron-reservoir iron-sandwich complexes.

Organo-Iron Syntheses of Dendritic Cores, Dendrons and Large Dendrimers

In the robust, very easily accessible cationic complexes [FeCp(arene)][PF_6)], the benzylic protons are more acidic than in the free arene because of the electron-withdrawing character of the 12-electron $CpFe^+$ moiety. For instance, [FeCp(C_6Me_6)][PF_6)] is more acidic by 15 p*K*a units (p*K*a = 28 in DMSO) than in the corresponding free arene (p*K*a = 43 in DMSO). As a result, these complexes are much more easily deprotonated than the free arene. [15,16] This key proton-reservoir property led us to synthesize stars and dendrimers in an easy way. [15] Indeed, reaction of [FeCp(C_6Me_6)][PF_6)],[17-19] with excess KOH (or *t*-BuOK) in THF or DME and excess methyl iodide, alkyl iodide, allyl bromide or benzylbromide result in the one-pot hexasubstitution (Scheme 1a).[20-22] With allyl bromide (or iodide) in DME, the hexaallylated complex has also been easily isolated and its X-ray crystal structure determined. With alkyliodides, the reaction using *t*-BuOK only leads to dehalogenation of the alkyl iodide giving the terminal olefin. Thus, one must use KOH, and the reactions with various alkyl iodides (even long-chain ones) were shown to work very well with this reagent to give the hexaalkylated Fe^{II}-centered complexes. The hexa-alkylation was also performed with alkyl iodides containing functional groups at the alkyl chain termini. [23] For instance, 1-ferrocenylbutyliodide reacts nicely to give the hexaferrocene star containing the $CpFe^+$ center.[24] The reaction with excess benzylbromide, [20,24] *p*-alkoxybenzylbromide [24] or *p*-bromobenzylbromide [24] only gives the hexabenzylated, hexa-*p*-alkoxybenzylated or hexa *p*-bromobenzylated complex as the ultimate reaction product. Cleavage of the methyl group in the *p*.methoxybenzyl derivatives synthesized in this way yields the hexaphenolate stars that could be combined with halogen containing organometallic compounds.[24b,c]



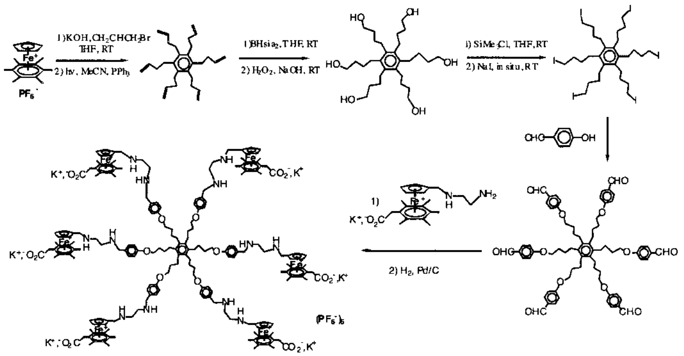
$RX = CH_3I, PhCH_2Br, SiMe_3Cl, PPh_2Cl, FeCp(CO)_2Br$ (also CO_2 and metal carbonyls)

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

Scheme 1: Deprotonation of $[FeCp(\eta^6\text{-}C_6Me_6)][PF_6]$ followed by reactions with electrophiles (top) and one-pot hexafunctionalization of this complex under ambient conditions (bottom). The top reaction illustrates the mechanism of the bottom one.

It is remarkable that the allyl group (as allyl bromide or iodide) is the only one leading to complete double branching of the C_6Me_6 complex. $CpFe^+$-induced dodecaallylation of C_6Me_6 indeed gives the extremely bulky dodeca-allylation product [26] that can be reached when the reaction is prolonged for two weeks at 40°C. The chains are blocked in a directionality that cannot convert into its enantiomer and makes the metal complex chiral. Both the hexa- and dodeca-allylation reactions are well controlled.

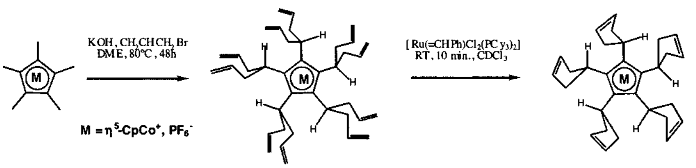
Alkynyl halides cannot be used in the $CpFe^+$-induced hexafunctionalization reaction, but alkynyl substituents can be introduced from the hexa-alkene derivative by bromination followed by dehydrohalogenation of the dodecabromo compound.[27] The hexa-alkene is also an excellent starting point for further syntheses, especially using hydroelementation reactions. Hydrosilylation reactions catalyzed by Speir's reagent led to long-chain hexasilanes [28] and hydrometallations were also achieved using $[ZrCp_2(H)(Cl)]$.[29] The hexa-zirconium compound obtained is an intermediate for the synthesis of the hexa-iodo derivative.[29] One of most useful



Scheme 2: CpFe$^+$-induced hexa-allylation of C_6Me_6 and subsequent hexafunctionalization of the aromatic stars with the heterodifunctional, water soluble organometallic redox catalyst (bottom) for the cathodic reduction of nitrates and nitrites to ammonia in water).

hydroelementation reactions of the hexabutenyl derivatives is the hydroboration leading to the hexaborane. The latter is oxidized to the hexa-ol using H_2O_2 under basic condition.[21] This chemistry can be carried out on the iron complex or alternatively on the free hexa-alkene which may be liberated from the metal by photolysis in CH_2Cl_2 or MeCN using visible light.[20] The polyol stars and dendrimers can be transformed into mesilates and iodo derivatives that are useful for further functionalization. The hexa-ol is indeed the best source of hexa-iodo derivative either using HI in acetic acid or even better by trimethylsilylation using $SiMe_3Cl$ followed by iodination using NaI.[30] Williamson coupling reactions between the hexa-ol and 4-bromomethylpyridine or -polypyridine led to hexa-pyridine and hexa-polypyridine and to their ruthenium complexes (31,32). This hexa-iodo star was condensed with *p*-hydroxybenzaldehyde to give an hexa-benzaldehyde star, which could further react with substrates bearing a primary amino group. Indeed, this reaction yielded a water-soluble hexametallic redox catalysts which was active in the electroreduction of nitrate and nitrite to ammonia in basic aqueous solution, *vide infra*.[33-35]

If the hexafunctionalization of hexamethylbenzene leads to stars, the octafunctionalization of durene leads to dendritic cores. The first of these octa-alkylation reactions was reported as early as 1982, and led to a primitive dendritic core containing a metal-sandwich unit.[20] Thus, as the hexafunctionalization, this reaction is very specific. Two hydrogen atoms of each methyl group are now replaced by two methyl, allyl or benzyl groups.[26] Applications to the synthesis of dendrimers containing 8 [36] or 24 redox-active groups has recently been reported. Double branching, *i.e.* replacement of two out of three hydrogen atoms by two groups on each methyl substituent of an aromatic ligand coordinated to an activating cationic group CpM^+ in an 18-electron complex is also easily obtained in the pentamethylcyclopentadienyl ligand (in pentamethyl cobaltocenium [37] and in penta- [38] and decamethylrhodocenium [39]). The interconversion of the two directionalities of decafunctionalized ligands coordinated to $CpCo^+$ or $CpRh^+$ whose could be observed by ^1H NMR for the decaisopropyl- and decaisopentyl cyclopentadienyl cobalt and rhodium complexes [37-39] (Scheme 3).

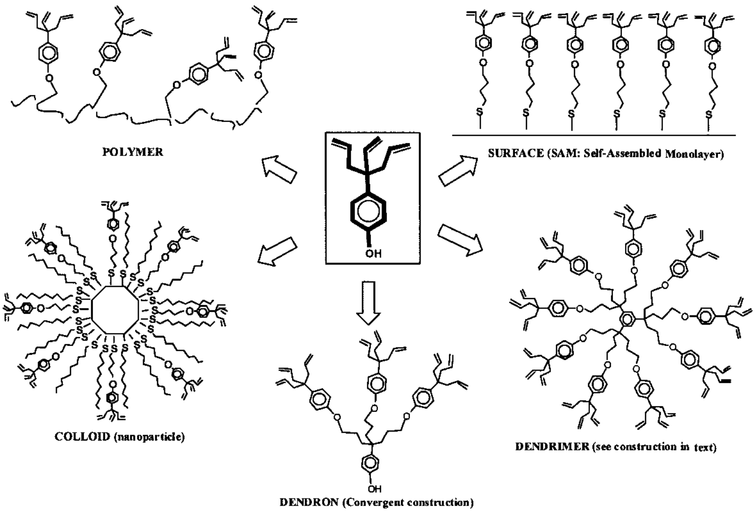


Scheme 3: Deca-allylation of 1,2,3,4,5-pentamethylcobaltocenium in a one-pot reaction consisting in 10 deprotonation-allylation sequences (steric constraints inhibit further reaction, and the 10 groups introduced are self-organized according to a single directionality) and follow-up RCM of the deca-allylated complex.

In all the above examples, the polybranching reaction of arene ligands was limited by the steric bulk. In the toluene and mesitylene ligands, the deprotonation-allylation reactions are no longer restricted by the neighborhood of other alkyl groups. All the benzylic protons, *i.e.* three per benzylic carbon, can be replaced by methyl or allyl groups in the one-pot iterative methylation or allylation reactions.[30] Thus, the toluene complex can be triallylated and the resulting tripod can be disymetrized by stoichiometric [40] or catalytic reaction [41] with transition metals shown in Scheme 18. The metathesis reaction, in particular, is complete in 5 min. at room temperature using the first-generation Grubb's catalyst $[Ru(=CHPh)Cl_2(PCy_2)_2]$ [2] with many polyallylated complexes $[FeCp(arene)]^+$ described above as well as to the decaallylated cobalt complex.[41] The reaction is very selective and terminal double bonds remain unreacted using this catalyst at room temperature.

The mesitylene complex can be nonaallylated, these reactions being carried out smoothly at room temperature in the presence of excess KOH and allyl bromide. The nonaallyl complex was photolyzed using visible light to remove the metal group $CpFe^+$, then hydroborated using 9-BBN, and the nonaborane was oxidized using H_2O_2/OH^- to the nona-ol.[30]

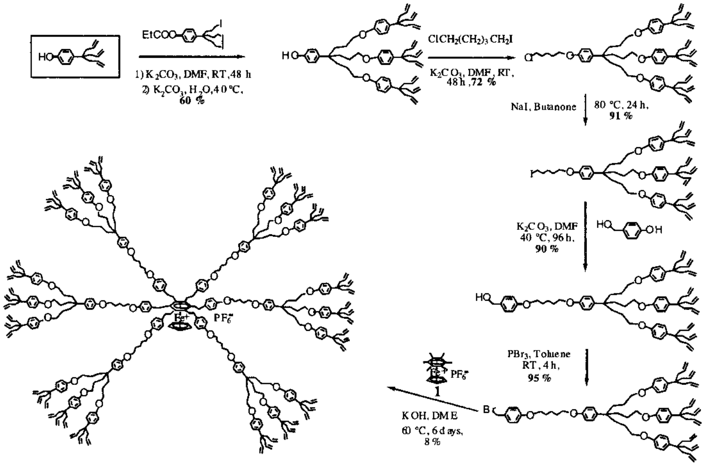
The triple branching reaction being very straightforward, we sought a more sophisticated version compatible with a functional group in the para position of the tripod in order to open the access to a functional dendron. Serendipitously, we found that KOH or *t*-BuOK easily cleaved the iron complexes of aromatic ethers under very mild conditions. The activating $CpFe^+$ group again induces this reaction, which is very general for a variety of aromatic ether complexes (42,43).



Scheme 4: Example of the linkage of the phenoltriallyl dendron to various nanostructures.

Since this cleavage reaction is carried out with the same reagent and solvent as the one used in the trialkylation reaction (ideally *t*-BuOK in THF), we have attempted to perform both reactions in a well-defined order (triallylation before ether cleavage) in a one-pot reaction. Indeed, this works out well and the $CpFe^{II}$ complex of the phenol tripod was made in 50% yield in this way. This complex can be photolyzed in the usual way using visible light, which yields the free phenol tripod. However, we have also further investigated the possibility to obtain the cleavage of the arene ligand *in situ* at the end of the phenol tripod construction; *t*-BuOK is a reductant when it cannot perform other reactions. Since the two important reactions are over, then comes the third role of *t*-BuOK: single-electron reductant. Reasoning in this way turned out to be correct: the cleavage of the arene intervenes rapidly at the 19-electron stage because 19-electron complexes of this kind are not stable with an heteroatom located in exocyclic position (most probably because the heteroatom coordinates to the metal from the labile 19-electron structure). After optimizing the reaction conditions, a 50%-yield of free phenol dendron from the ethoxytoluene complex could be reproducibly obtained,[44,45] and this reaction is now currently used in our laboratory to synthesize this very useful dendron as a starting material.

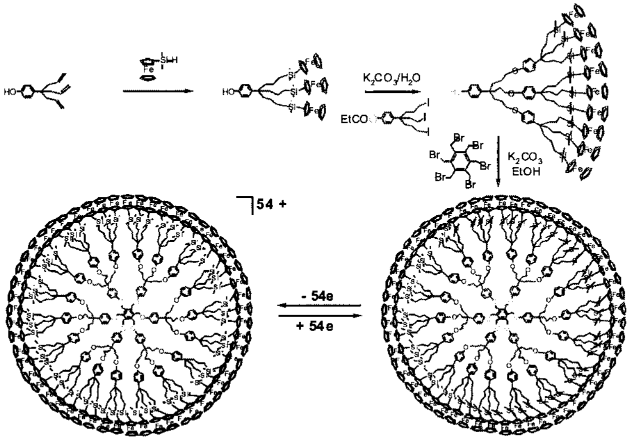
This phenoltriallyl dendron has been functionalized at both the phenolic and allylic positions. For instance, the dendron can be bound, after suitable molecular engineering, to the branches of a phenolic-protected dendron (convergent construction) onto stars and dendritic cores (divergent construction), nonaparticles, surfaces and polymers. An example is provided by the $CpFe^+$-induced hexafunctionalization by a phenol-nonaallyl dendron (prepared according to such a convergent synthesis) that was functionalized in phenolic position by a tail terminated by a benzylbromide group. This type of strategy allows direct access to large dendrimers by simply using the $CpFe^+$-induced hexafunctionalization reaction that gives hexa-branch stars with linear organic halides.



Scheme 5: $CpFe^+$-induced hexabenzylation of C_6Me_6 applied to direct convergent dendrimer synthesis of a 54-allyl dendrimer.

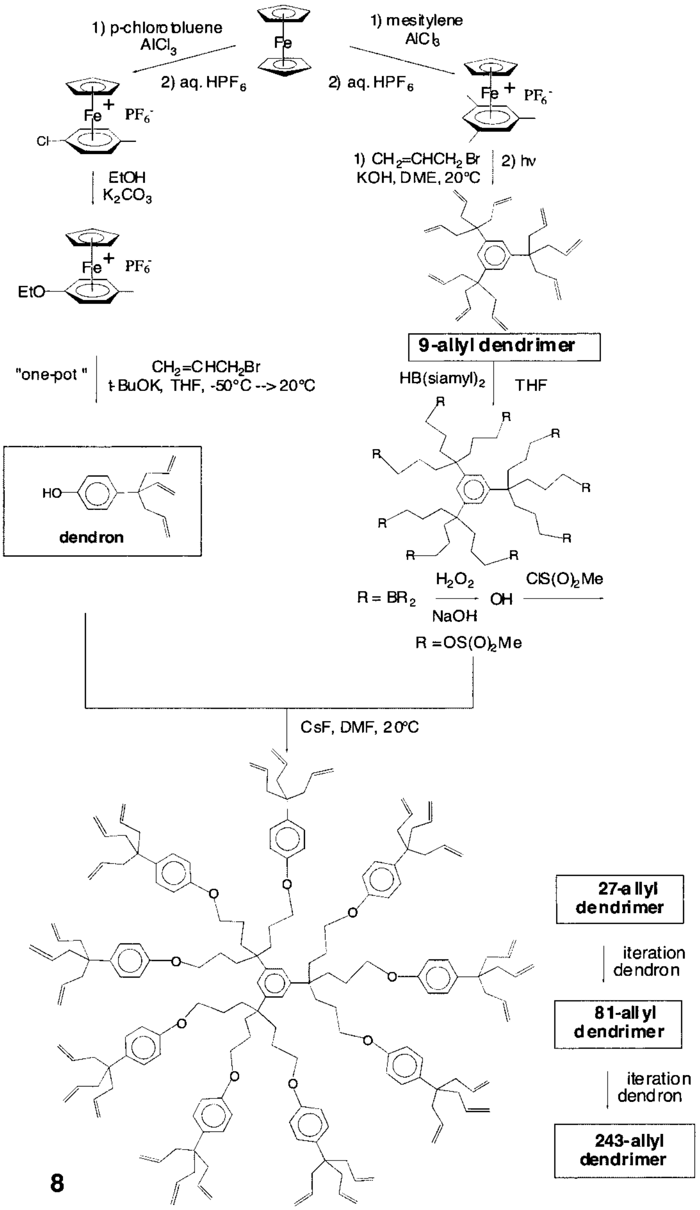
Decoration of Dendrimers with Redox-Active Groups: Towards Molecular Batteries

The functionalization of the three allyl chains of the phenol dendron could be achieved by hydrosilylation reaction catalyzed by the Karsted catalyst.[46] Indeed, it is very interesting that there is no need to protect the phenol group before performing these reactions. For instance, catalyzed hydrosilylation using ferrocenyldimethylsilane gives a high yield of the triferrocenyl dendron $HO\textit{p}\text{-}C_6H_4C(CH_2CH_2CH_2SiMe_2Fc)_3$ that is easily purified by column chromatography.[46,47] Protection of the phenol dendron using propionyliodide gave the phenolate ester which was hydroborated. Oxidation of the triborane using H_2O_2/OH^- gave the triol, then reaction with $SiMe_3Cl$ gave the tris-silyl derivative. Reaction with NaI yielded the tri-iodo compound, and reaction with the tri-ferrocenyl dendron provided the nona-ferrocenyl dendron that was deprotected using K_2CO_3 in DMF. The nona-ferrocenyl dendron was allowed to react with hexakis(bromomethyl)benzene, which gave the 54-ferrocenyl dendrimer. This convergent synthesis is clean and the 54-ferrocenyl dendrimer gave correct analytical data, although a mass spectrum could not be obtained (Scheme 6).This approach is somewhat limited, however, since



Scheme 6: Convergent synthesis of a redox-robust 54-silylferrocenyl dendrimer.

larger dendrons, which one would like to synthesize in this way, cannot be made because dehydrohalogenation becomes faster than nucleophilic substitution of the iodo by phenolate for bulkier higher generations of dendrons. Although this problem might be overcome by modifying the iodo branch in such a way that there would be no hydrogens in β positions, the condensation of higher dendrons onto a core would become tedious or impossible for steric reasons. This well known inconvenient is intrinsic to the convergent dendritic synthesis. On the other hand, divergent syntheses are not marred by such a problem since additional generations and terminal groups are added at the periphery of the dendrimer. The limit is that indicated by De Gennes, *i. e.* the steric congestion encountered at a generation where the peripheral branches can no longer by divided. Another obvious limit intervenes if the molecular objects added onto the termini of the branches are large and interfere with one another. We have developed a divergent synthesis of polyallyl dendrimers indicated on *Scheme 20* whereby each generation consists in hydroboration, oxidation of the borane to the alcohol, formation of the mesylate, and reaction of the phenol dendron with the mesylate. This strategy has allowed us to synthesize dendrimers of generation 0, 1, 2 and 3 with respectively 9 (G_0), 27 (G_1), 81 (G_2) and 243 branches (G_3) (Scheme 7 and Chart 1).



Scheme 7: Strategy for the construction of large dendrimers starting from ferrocene.

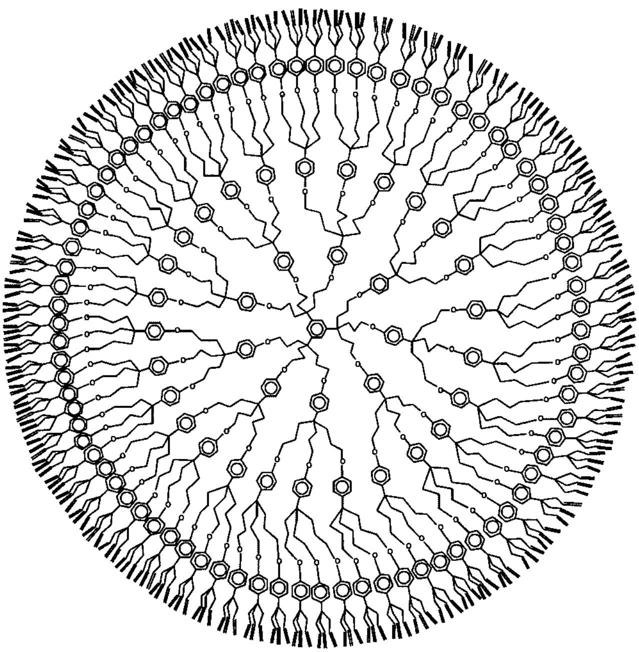
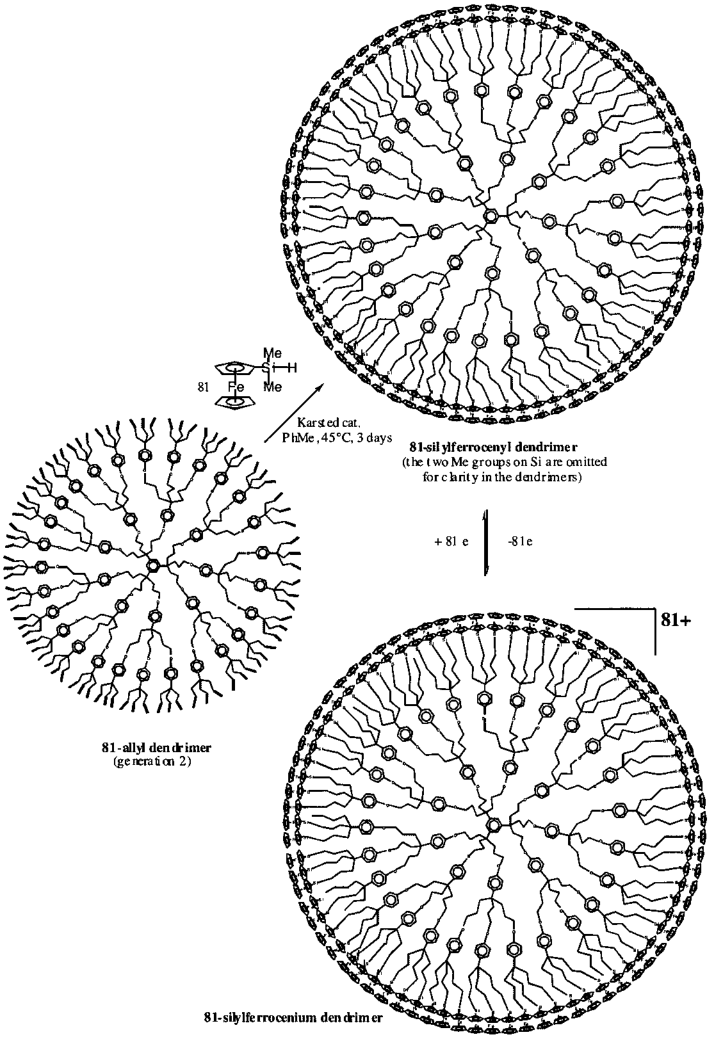


Chart 1: 243-allyl dendrimer (3rd generation, see the construction on Scheme 7).

The MALDI TOF mass spectrum of the 27-allyl dendrimer only shows the molecular peak with only traces of side product. That of the 81-allyl shows a dominant molecular peak, but also important side products resulting from incomplete branching. That of the 243-allyl could not be obtained possibly signifying that this dendrimer is polydisperse (correct ^1H and ^{13}C NMR spectra were obtained, however, indicating that the ultimate reactions had proceeded to completion). This dendrimer was soluble which indicated that this generation is not the last one, which might be reached. Larger dendrimers have recently been synthesized using a slightly diferent strategy. The ferrocenylsilylation of all these polyallyl dendrimers was carried out using ferrocenyldimethylsilane in ether or toluene and was catalyzed by the Karsted catalyst [48,49] at 40-45°C. The reactions were complete after two or three days except for the ferrocenylsilylation of 243-allyl that required a reaction time of one weeks indicating some degree of steric congestion (Scheme 8).



Scheme 8: Ferrocenylsilylation of the polyallyl dendrimers synthesized. Example of the 2nd generation 81-allyl dendrimer.

The ^1H and ^{13}C spectra indicated the absence of regioisomer. The solubility in pentane decreased from good for the 9-Fc dendrimer to low for the 27-Fc dendrimer and nil for the superior dendrimers, but the solubility in ether remained good for all the ferrocenyl dendrimers. Likewise, the retention times on plate or column chromatography increased with generation and no migration was observed for the "243-Fc" dendrimer. The silane use here, $HSi(Fc)Me_2Cl$, reported by Pannel and Sharma,[50] was already used by Jutzi [51] to synthesize the decaferrocenyl dendrimer $[Fe(CCH_2CH_2SiMe_2Fc)_{10}]$ (with Fc = ferrocenyl) from deca-allylferrocene.

The cyclic voltammetry of all the ferrocenyl dendrimers on Pt anode shows that all the ferrocenyl centers are equivalent and only one wave was observed. It was possible to avoid adsorption using even CH_2Cl_2 for the small ferrocenyl dendrimers, but it was required to use MeCN for the medium size ones (27-Fc, 54-Fc and 81-Fc). Finally, adsorption was not avoided even with MeCN for the "243-Fc" dendrimer. From the intensity of the wave, the number of ferrocenyl units could be estimated using the Anson-Bard equation,[52] and the number found were within 5% of the branch numbers except for the "243-Fc"dendrimer, for which the experimental number was too high (250) because of the adsorption.

The first polyferrocenium dendrimers reported by our group in 1994 and characterized *inter alia* by Mössbauer spectroscopy (a "quantitative" technique) were mixed valence Fe^{II}/Fe^{III} complexes.[23] Since then, we have been seeking to synthesize larger ferrocenyldendrimers, which could also withstand oxidation to their ferrocenium analogues. The syntheses of amidoferrocene dendrimers were reported five years ago simultaneously by our group [11,53] and the Madrid group using different cores.[54,55] In our reports, we were able to show the use of these metallodendrimers as redox sensors for the recognition of oxo-anions, with remarkable positive dendritic effects when the generation increased. The amidoferrocenyl dendrimers are not the best candidates for a stable redox activity on the synthetic scale, however, and thus even less so for molecular batteries. Indeed, although they give fully reversible cyclic voltammetry waves, it is known that ferrocenium derivatives bearing an electron-withdrawing substituent are at least fragile, if stable at all. This inconvenient is probably enhanced in the dendritic structures because of the steric effect which forces ferrocenium groups to encounter one another more easily than as monomers. Thus, we have oxidized our silylferrocenyl dendrimers using [NO][PF_6] in CH_2Cl_2 and obtained stable polyferrocenium dendrimers as dark-blue precipitates, as expected from the known characteristic color of ferrocenium itself. These polyferrocenium dendrimers were reduced back to soluble orange polyferrocenyl dendrimers using decamethylferrocene as the reductant.[56] No decomposition was observed either in the oxidation or in the reduction reactions which were very clean, and this redox cycle could be achieved in quantitative yield even with the "243-ferrocenyl" dendrimer. The zero-field Mössbauer spectrum of the 243-ferrocenium dendrimer (Figure 1) showed a single line corresponding to the expected spectrum known for ferrocenium itself,[57] confirming its electronic structure. Thus, these polyferrocenyl dendrimers are molecular batteries, which could be used, in specific devices. Indeed, as large as they may be, they transfer a very large number of electrons rapidly and "simultaneously" with the electrode. By "simultaneously", we mean that, visually, the cyclic voltammogram looks as if it were that of a monoelectronic wave. One must question the notion of the isopotential for the many ferrocenyl units at the periphery of a dendrimer. In theory, all the standard potentials of the n ferrocenyl units of a single dendrimer are distinct even if all of them are equivalent and independent. This situation arises since the charge of the overall dendrimer molecule increases by one unit of charge every time one of its ferrocenyl units is oxidized to ferrocenium. The next single-electron oxidation is more difficult than the preceding one since, the dendritic molecule having one more unit of positive charge, it is more difficult to oxidize because of the increased electrostatic factor. Thus, the potentials of the n redox units are statistically distributed around an average standard potential centered at the average potential (Gaussian distribution).[52] In practice, the situation is complicated by the fact that the dendritic molecule, as large as it may be, is rotating much more rapidly than the usual electrochemical time scales.[58,59] Under these conditions, all the potentials are probably averaged. The fast rotation is also responsible for the fact that all the ferrocenyl units come close to the electrode within the electrochemical time scale. Consequently, there is no slowing down of the electron transfer due to long distance from the electrode even in large dendrimers. Indeed, the waves of the ferrocenyl dendrimers always appear fully electrochemically reversible indicating fast electron transfer.

The ferrocenyl dendrimers also adsorb readily on electrodes, a phenomenon already well known with various kinds of polymers.[60] When polymers contain redox centers, the adsorbed polymer have long been shown to disclose a redox wave for which the cathodic and anodic waves are located at exactly the same potential and the intensity of each wave is proportional to scan rate. Continuous cycling shows the stability of the adsorption of the electrode modified in this way. The ferrocenyl dendrimers described show this phenomenon as expected. The stability of the electrode modified by soaking the Pt electrode in a CH_2Cl_2 solution containing the ferrocenyl dendrimer and cyclic scanning between the ferrocenyl and ferrocenium regions is all the better as the ferrocenyl dendrimer is larger. For instance, in the case of the 9-ferrocenyl dendrimer, scanning twenty times is necessary before obtaining a constant intensity, and this intensity is weak. With the 27-, 54-, 81-, and 243-ferrocenyl dendrimers, only approximately ten cyclic scans are necessary before obtaining a constant wave, and the intensity is much larger. When such derivatized electrodes are washed with CH_2Cl_2 and re-used with a fresh, dendrimer-free CH_2Cl_2 solution, the cyclic voltammogram is obtained with $\Delta E_p = 0$. Other characteristic features are the linear relationship between the intensity and scan rate and the constant stability after cycling many times with no sign of diminished intensity (Figure 1).

Under these conditions, one may note that the argument of the fast rotation of the dendritic molecule to bring all the redox centers in turn close to the electrode does not hold for modified electrodes. Some redox centers must be close to the electrode and some must be far. It is probable that a hoping mechanism in the solid state is responsible for fast electron transfer and for averaging all the potentials of the different ferrocenyl groups of a single dendritic molecule around a mean value. The proximity of the ferrocenyl groups at the periphery of the dendrimer is a key factor allowing this hoping to occur since it is known that electron transfer with redox sites which are remote or buried inside a molecular framework is slow, if at all observable.[61-67]

CYCLIC VOLTAMMETRY OF THE 243-FERROCENYL DENDRIMER

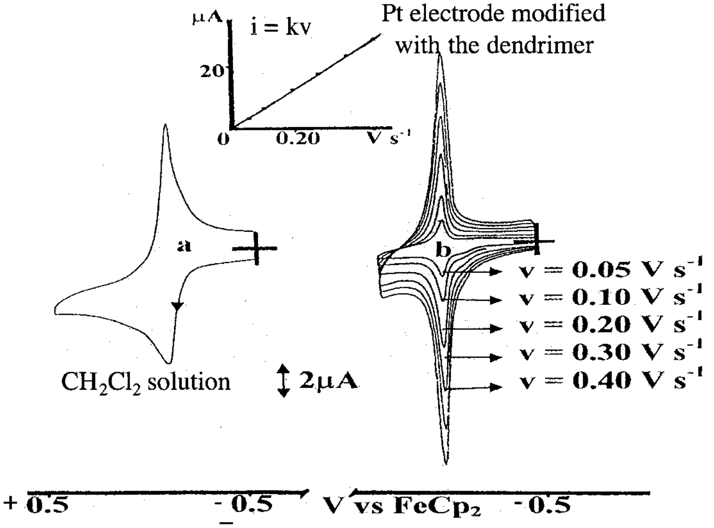
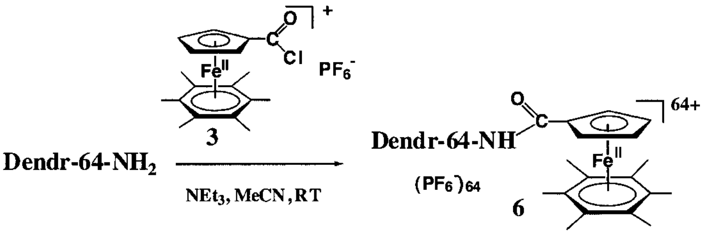


Figure 1: Cyclic voltammogram of the 243-ferrocenyl dendrimer (“243-Fc”) in CH_2Cl_2 solution containing 0.1M $[n\text{-}Bu_4N][PF_6]$: a) in solution (10-4 M) at 100 mV. s-1 on Pt anode; b) Pt anode modified with “243-Fc” at various scan rates, dendrimer-free clear CH_2Cl_2 solution (inset: intensity as a function of scan rate: the linearity shows the expected behavior of a modified electrode with a fully adsorbed dendrimer).

Ferrocenes and ferrocenyl dendrimers are poor reductants. On the other hand, the complexes $[Fe(\eta^5\text{-}C_5R_5)(\eta^6\text{-}C_6Me_6)]^{2+/+/0}$ (R = H or Me) have been shown to be efficient for various stoichiometric and catalytic electron-transfer reactions.[16,68] The covalent linkage of this sandwich complex to the Cp ligand by means of a chlorocarbonyl substituent leads, upon reaction with dendritic polyamines, to soluble Fe^{II} metallodendrimers. Moreover, these Fe^{II} metallodendrimers can be reduced to Fe^{I} by $[Fe^{I}Cp(\eta^6\text{-}C_6Me_6)]$, **1**. Reduction of the monomeric model $[Fe^{II}(\eta^5\text{-}C_5H_4CONH\text{-}n\text{-}Pr)(\eta^6\text{-}C_6Me_6)][PF_6]$ by Na/Hg in THF (RT) gives the deep-blue-green, thermally stable 19-electron complex $[Fe^{I}(\eta^5\text{-}C_5H_4CONH\text{-}n\text{-}Pr)(\eta^6\text{-}C_6Me_6)]$ that shows the classic rhombic distorsion of the Fe^{I} sandwich family, observable by EPR in frozen THF at 77K (3 g values around 2).[69] Given this stability, we carried out the same reaction of $[Fe^{II}(\eta^5\text{-}C_5H_4COCl)(\eta^6\text{-}$

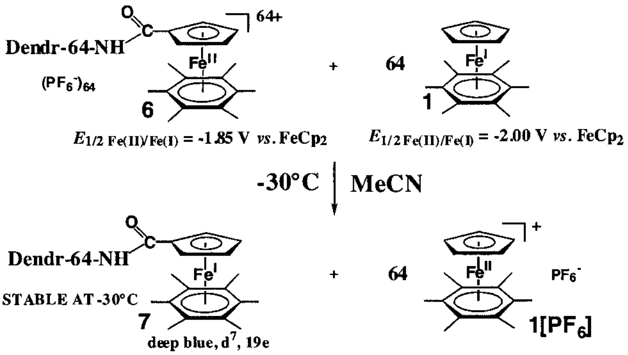
$C_6Me_6)][PF_6]$ with the commercial polypropyleneimine dendrimer of generation 5 (64 amino termini) in $MeCN/CH_2Cl_2$: 2/1 in the presence of NEt_3. The polycationic metallodendrimer DAB *dendr*-64--NHCOCpFe^{II}(η^6-C_6Me_6), was obtained as the PF_6^- salt, soluble in MeCN and DMF (Equation 1).



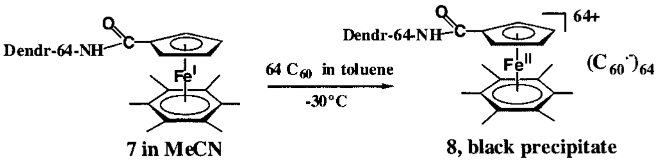
Equation 1: Covalent linkage of the complex [FeCpCOCl(η^6-C_6Me_6)][PF_6] to the DSM polyamine dendrimer of generation 5 (64 branches). Example of the 64-NH_2 dendrimer (generation 5).

This dendritic complex was characterized by ^1H and ^{13}C NMR and IR spectroscopies and cyclovoltammetry (a single reversible wave in DMF, at $E_{1/2}$ = -1.84 V *vs.* $FeCp_2^{0/+}$; ΔE = 70 mV). Attempts to reduce it with the classic reductants that reduce monomeric complexes [Fe^{II}(η^5-Cp)(η^6-arene)][PF_6] such as Na sand, Na/Hg or $LiAlH_4$ in THF or DME failed due to the insolubility of both the metallodendrimer and the reductant in the required solvents. The only successful reductant was the parent 19-electron complex [Fe^{I}Cp(η^6-C_6Me_6)] [70,71] (in pentane or THF) that reduced the metallodendrimer in MeCN at –30°C to the neutral, deep-green-blue 19-electron Fe^I dendrimer **6** in a few minutes (Equation 2).[72]

The exoergonicity of this electron-transfer reaction is 0.16 V, which is due to the electron-withdrawing effect of the juxta-cyclic carbonyl group on the Cp ring that lowers the reduction potential of the metallodendrimer as compared to that [Fe^{I}Cp(η^6-C_6Me_6)]. Although the Fe^I dendrimer decomposes a 0°C, it was also characterized by its EPR spectrum at 10 K confirming, as the deep-blue-green color, the Fe^I -sandwich structure analogous to that of the monomeric model.



Equation 2: Exergonic reduction of the cationic Fe^{II} dendritic sandwich groups by the parent 19-electron complex $[FeICp(\eta^6\text{-}C_6Me_6)]$ to the Fe^I dendrimer complex.



Equation 3: Dendr-64-NHCOCpFe$(C_6Me_6)^{64+}$, 64 $C_{60}^{\bullet-}$ resulting from the reaction of the 64-Fe^I dendrimer with C_{60} in MeCN/toluene at –30°C yielding the 64-Fe^{II}-C_{60} - dendrimer with EPR spectrum (bottom, right) in MeCN at 10K and Mössbauer spectrum at 77K (bottom, left) of the latter.

Contrary to the case of $[Fe^ICp(\eta^6\text{-}C_6Me_6)]$,[69] however, it was not possible to record the EPR spectrum of the solution of the Fe^I dendrimer above 10 K. This is presumably due to the intramolecular relaxation among the peripheral Fe^I sandwich units. The intermolecular version of this relaxation effect is known to preclude observation of the spectrum of monomeric Fe^I sandwich complexes in the solid state above 4K and in solution above 77K.[69] This acetonitrile solution of the 64-Fe^I dendrimer was used for the reaction with C_{60}, the stoichiometry being Fe^I/C_{60}: 1/1 (64 C_{60}*per* dendrimer). Upon reaction with a toluene solution of C_{60}, the deep-blue-green color of the Fe^I dendrimer disappeared, leaving a yellow solution that contained $[Fe^{II}Cp(\eta^6\text{-}C_6Me_6)][PF_6]$ and a black precipitate (Equation 3). Tentative extraction of this precipitate with toluene yielded a colorless solution, which indicated that no C_{60} was present. The Mössbauer spectra of this black solid at 298K discloses parameters that show the presence of an Fe^{II} sandwich complex of the same family as $[Fe^{II}Cp(\eta^6\text{-}C_6Me_6)]^+$.[69-71] Its EPR spectrum recorded at 77 K shows the same EPR spectrum as that of $[Fe^{II}Cp(\eta^6\text{-}C_6Me_6)]^+$ C_{60}.[73] It could thus be concluded that C_{60} had been reduced to its monoanion, as designed for a process that is exergonic by 0.9 V (74). The $[\text{dendr-}Fe^{II}]^+$ C_{60}^- units being very large, they must be located at the dendrimer periphery, presumably with rather tight ion pairs although the number of fullerene layers and overall molecular size are unknown (Figure 2).

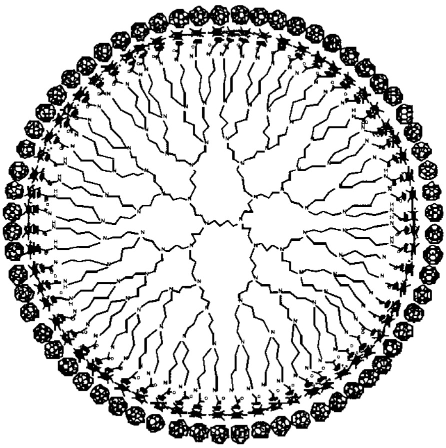
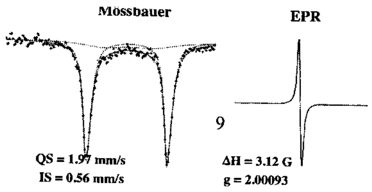
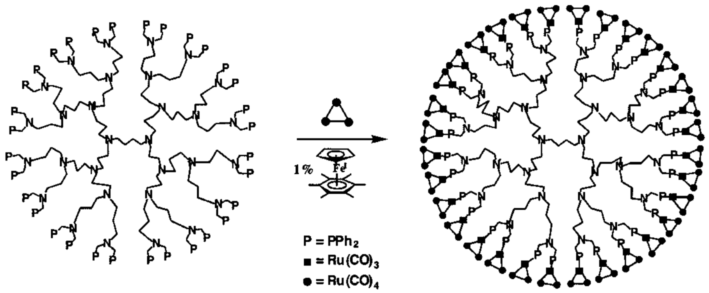


Figure 2 : Dendr-$[NHCOCp\text{-}Fe^{II}C_6Me_6]_{64}[C60]64$ (top) ; Mössbauer (left, bottom) and EPR (right, bottom) spectra.



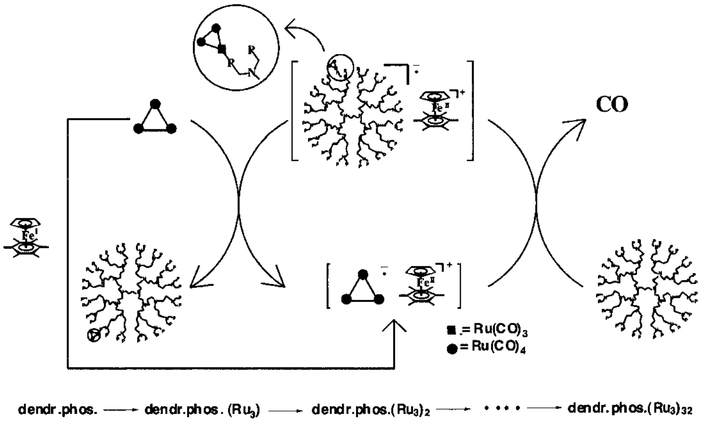
Decoration of Dendrimers with Ruthenium Clusters: Towards Dendritic Catalysts

The clean introduction of clusters onto the termini of polyphosphine dendrimers is a real challenge because of the current interest of dendritic clusters in catalysis and the mixtures usually obtained in thermal reactions of $[Ru_3(CO)_{12}]$ with phosphines. The diphosphine $CH_3(CH_2)_2N(CH_2PPh_2)_2$ (abbreviated P-P below) was used as a simple, model ligand. The reaction between P-P and $[Ru_3(CO)_{12}]$ [75] (molar ratio: 1/1.05) in the presence of 0.1 equiv. $[Fe^ICp(\eta^6\text{-}C_6Me_6)]$ in THF at 20°C led to the complete disappearance of $[Ru_3(CO)_{12}]$ in a few minutes and the appearance of a mixture of chelate $[\text{P-P. } Ru_3(CO)_{10}]$, monodentate $[\text{P-P. } Ru_3(CO)_{11}]$ and bis-cluster $[\text{P-P. } \{Ru_3(CO)_{11}\}_2]$. These reactions were reported by Bruce with simple diphosphines.[76] On the other hand, the reaction of P-P with $[Ru_3(CO)_{12}]$ in excess (1/4) and only 0.01 equiv. $[Fe^ICp(\eta^6\text{-}C_6Me_6)]$ in THF at 20°C led, in 20 minutes, to the formation of the air-stable, light-sensitive bis-cluster $[\text{P-P. } \{Ru_3(CO)_{11}\}_2]$ as the only reaction product. Given the simplicity of the above characterization of the reaction product by ^{31}P NMR and the excellent selectivity of this model reaction when excess $[Ru_3(CO)_{12}]$ was used, the same reaction between Reetz's dendritic phosphines,[77a] derived from DSM's dendritic amines,[77b] and $[Ru_3(CO)_{12}]$ could be more confidently envisaged. This reaction, catalyzed by 1% equiv. $[Fe^ICp(\eta^6\text{-}C_6Me_6)]$ was carried out in THF at 20°C. The dendrimer-cluster assembly was obtained in 50% yield. This shows the selectivity and completion of the coordination of each of the 32 phosphino



Scheme 9: Electron-Transfer-Chain catalyzed ligand substitution of one Ru-coordinated CO by a dendritic phosphine termini in Reetz's 32-phosphine dendrimer under ambiant conditions leading to the 32-$Ru_3(CO)_{11}$ dendrimer-cluster.

ETC mechanism [78-80] proceeds for the introduction of the 32 cluster fragments in the dendrimer for ligation of the first $Ru_3(CO)_{11}$ fragment to the dendritic phosphine. Then, this first complex [dendriphosphine.$Ru_3(CO)_{11}$] would undergo the same ETC cycle as [$Ru_3(CO)_{12}$] initially does to generate the bis-cluster complex [dendriphosphine.$\{Ru_3(CO)_{11}\}_2$], and so on (Scheme 10).



Scheme 10: Electron-Transfer-Chain mechanism for the synthesis of the 96-Ru dendrimer-cluster complex.

Finally, the 64-branch phosphine DAB-*dendr*-G4-$[N(CH_2PPh_2)_2]_{32}$ analogously reacts with [$Ru_3(CO)_{12}$] and 1% [$Fe^ICp(\eta^6\text{-}C_6Me_6)$] (20°C, THF, 20 min.) to give the dark-red 192-Ru dendrimer. Characterization of the purity of these dendrimer-cluster assemblies is conveniently monitored by ^{31}P NMR. This application should find extension to other metal-carbonyl clusters and other families of phosphine dendrimers.

Dendritic Catalysts and Sensors

It is of interest to compare the efficiency of homologous metallo-stars and metallo-dendrimers in catalysis and sensing. Recently, we were able to compare the rate of the redox catalyzed cathodic reduction of nitrate and nitrite to ammonia using metallo-stars and cyclic voltammetry. It was found that the metallo-stars in which the catalytic metal centers were located at the periphery of the metallo-stars showed about the same rate of reduction of the nitrogen oxides NO_2^- and NO_3^- by the 19-electron form of the catalysts as mononuclear complexes with the same driving force. On the other hand, those containing the redox-active site at the center of the dendritic- or star core showed rates that were at least an order of magnitude lower.[81]

In another example using dendritic ruthenium carbene dendrimers for the living ROMP of norbornene, it was found that the most efficient dendrimer was that of first generation (4 arms) whereas the efficiency decreased as the generation increased. This finding is due to the increasing steric bulk around the ruthenium-carbene centers that increases with the dendrimer generation.[82] This type of steric congestion is not found is metallostars. Thus, first-generation dendrimers (which are in fact stars rather than dendrimers) are best for catalytic activity as long as they are large enough to be removed by ultra-filtration or centrifugation.[8-10]

For dendritic amido- or silylferrocene nano-sensors, stars show some activity, but dendrimers are far better, and their efficiency increases as the dendritic generation increases. In this case, the steric bulk at the dendrimer periphery provides narrow channels that are desired and ideal with an optimized topology in view of efficient recognition.[83-85]

Outlook

Very large dendrimers [86] have been synthesized and functionalized with transition metal fragments including ferrocenyl and other metal-sandwich type complexes that include a supramolecular function (amide, silicon center).[87].Their large size is a very important parameter for improved adsorption on metal surfaces and electrodes. It is also essentiel to have in hands nano-sized, well defined macromolecules for integration in devices as nano-wires. For instance, comparison of surfaces and electrodes modified with several layers and average-size metallodendrimers with those modified with giant metallodendrimers should provide insight into the mechanism of electron-hoping in the solid (compare intramolecular vs. intermolecular hoping). It is also essential to control reactions such as those involving metal-ligand bond formation at the nanoscale. The behavior of nano-catalysts is highlighted in this review and different topologies have been compared in term of efficiency. These studies are needed in order to make progress in green catalysis.[88] Applications of these fundamental studies are awaited in the fields of catalysts, sensors and nano-devices.

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