Organoiron-mediated dendrimer syntheses with 1→3 connectivity and applications

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1. Introduction

The discovery of ferrocene[1–5] initiated considerable organometallic,[5] and in particular π-organo-iron chemistry.[5–7] Among the prolific pioneering works in organometallic chemistry, the synthesis of π-arene complexes of iron and other transition metals was of particular interest, because of the perspective of modifying the properties of the arene ligand.[5,8] The most useful families in terms of arene synthesis turned out be the robust 18-electron complexes of the [Cr(η^6-arene(CO)$_3$)],[9–11] [Mn(η^6-arene)(CO)$_3$]$^+$,[12,13] [Fe(η^6-arene)(η^5-C$_5$H$_5$)]$^+$,[14,15] and [Ru(η^6-arene)(η^5-C$_5$H$_5$)]$^+$[16,17] families. The relative strengths of activation of the 12-electron activating groups were found to follow their electron-withdrawing properties:[18]

$$Cr(CO)_3 < MCp^+ < [Mn(CO)_3]^+ \text{ with } Cp = \eta^5 - C_5H_5; M = Fe \text{ or } Ru$$
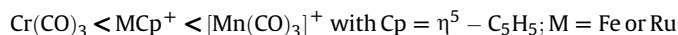
The use of all these 12-electron activating groups in aromatic synthesis has been reviewed,[9–22] including FeCp$^+$.[14] In the present review, we focus on the arene reactivity in the complexes [Fe(η^6-arene)(η^5-C$_5$H$_5$)]$^+$ and their use in dendrimer synthesis for which we specifically illustrate 1→3 connectivity developed in our laboratory including various applications.

2. Arene 'Umpolung' in the complexes [Fe(η^6-arene)-(η^5-C$_5$H$_5$)]$^+$

The complexes [Fe^{II}(η^6-arene)(η^5-C$_5$H$_5$)]$^+$[X] X$^-$=BF$_4^-$ or PF$_6^-$] have been known for half a century,[23] and their chemistry was first developed by the groups of Nesmeyanov, especially following the

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very useful synthesis by Cp/arene exchange starting from ferrocene in the presence of $AlCl_3$ and Al (Scheme 1).[24,25]
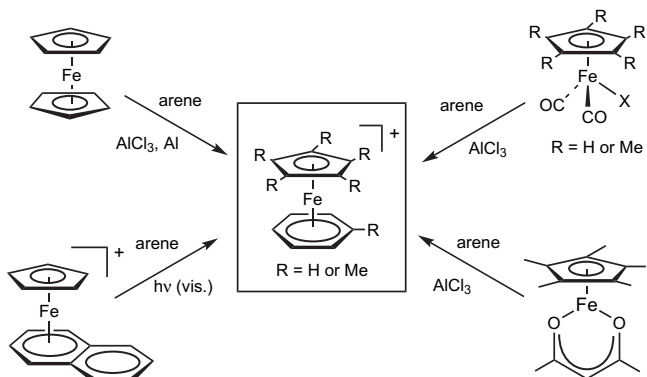

Scheme 1. Modes of synthesis of the complexes $[Fe(\eta^5-C_5R_5)(\eta^6-arene)]^+$, R=H or Me, usually isolated as their PF_6 salts. The most common synthesis is the ligand exchange reaction from ferrocene, also applicable to 1,1'-disubstituted ferrocenes and to monoacylferrocenes.

The properties of these complexes are briefly summarized in Schemes 2 and 3 for the representative toluene and chlorobenzene complexes, respectively. From these general schemes, it can be observed that (i) a complete 'Umpolung' is involved in the chemistry of the arene ligands, and (ii) the organometallic chemistry of the arene complexes is very rich and multiple use can lead to unusual structures.[5,14] In particular, the activation by the cationic 12-electron CpFe$^+$ group results in the lowering of the pK_a in DMSO of the polymethylbenzenes, from 42 to 28 for instance for hexamethylbenzene.[26,27] The interest in such an increase of the acidity of the benzylic protons was first realized thirty years ago when the yellow toluene complex was deprotonated by t-BuOK in THF to a deep-red cyclohexadienylmethylene complex **1** (Scheme 4),

especially because deprotonation could be followed by alkylation with MeI and various electrophiles to form C–C and C–element bonds.[28–30] Moreover, deprotonation could also be obtained upon reaction of O_2 or air with the corresponding neutral 19-electron Fe^I complexes (for instance **2**, R=Me) that resulted from single electron reduction of $[Fe^{II}(\eta^6-ArMe)(\eta^5-C_5H_5)]^+[X]$ (Scheme 5).[31–35] This reaction of O_2 with the Fe^I complexes in THF was totally inhibited by $Na^+PF_6^-$,[36,37] which confirmed the role of the deprotonation intermediate superoxide radical anion in the ion pair $[Fe^{II}(\eta^6-arene)(\eta^5-C_5H_5),O_2^-]$ formed by electron transfer between Fe^I and O_2.[38,39] The role of O_2 or air acting as a base (via O_2^-), in the presence of the electron donor Fe^I, was recently exploited to deprotonate functional imidazolium salts to useful N-heterocyclic carbenes.[40]

3. Use of the enhanced acidity the benzylic protons of polymethylarenes in the complexes $[Fe(\eta^6-arene)(\eta^5-C_5H_5)]^+$ for one-pot synthesis of dendritic cores and dendrons

Simple one-pot procedures were disclosed to polyfunctionalize the polymethylbenzenes using KOH and allyl bromide in tetrahydrofuranne (THF) or 1,2-dimethoxyethane (DME) under ambient conditions (Scheme 6).[41,42] Deprotonation of a methyl group by KOH is followed by allylation in situ, regenerating the cationic $[Fe(\eta^6-arene)(\eta^5-C_5H_5)]^+$ structure the acidity of which allows the continuation the reaction with other deprotonation-allylation sequences in one-pot procedures. The allylated benzylic carbon in the functionalized $[Fe(\eta^6-arene)(\eta^5-C_5H_5)]^+$ is slightly less acidic than the initial polymethylbenzene complex, but it is acidic enough to be deprotonated again and allylated. With the hexamethylbenzene complex **3**, however, perallylation can be stopped after the first allylation, because of the steric bulk, and the hexabutenyl star complex obtained can be easily isolated after 24 h. The second allylation is much slower than the first, but, after three weeks, the dodeca–allylated complex could be synthesized. [29] With durene, the octa-allylation is easy in two days.[43] With
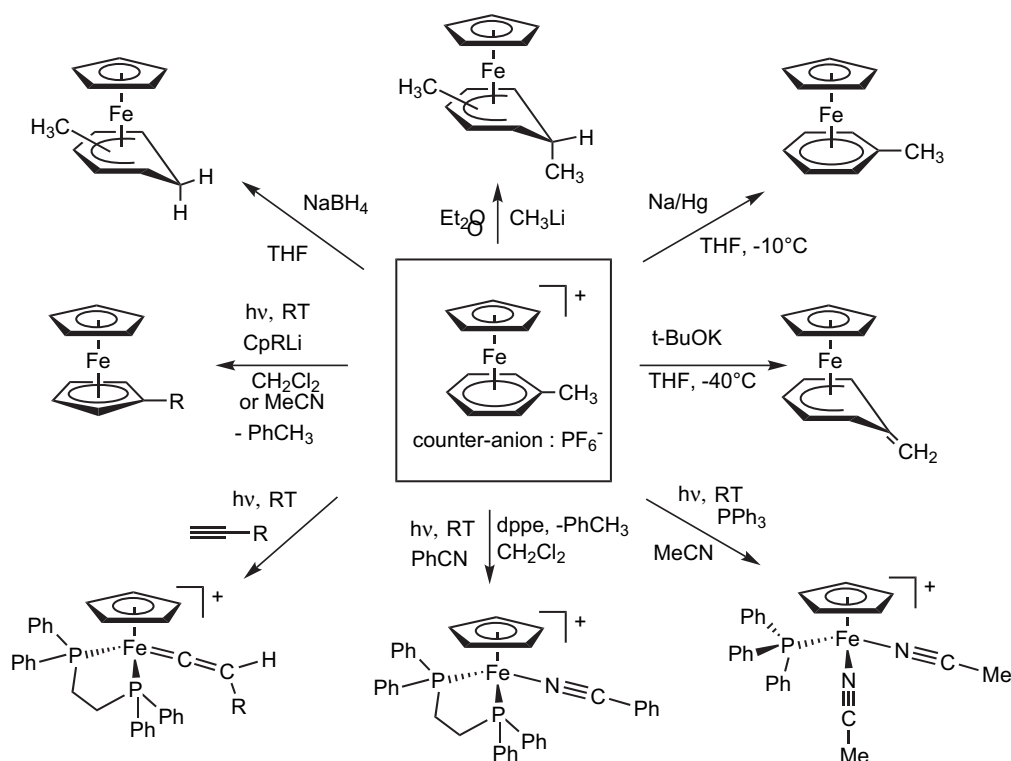
Scheme 2. Reactions of the toluene complex $[Fe(\eta^5-C_5H_5)(\eta^6-PhMe)][PF_6]$.
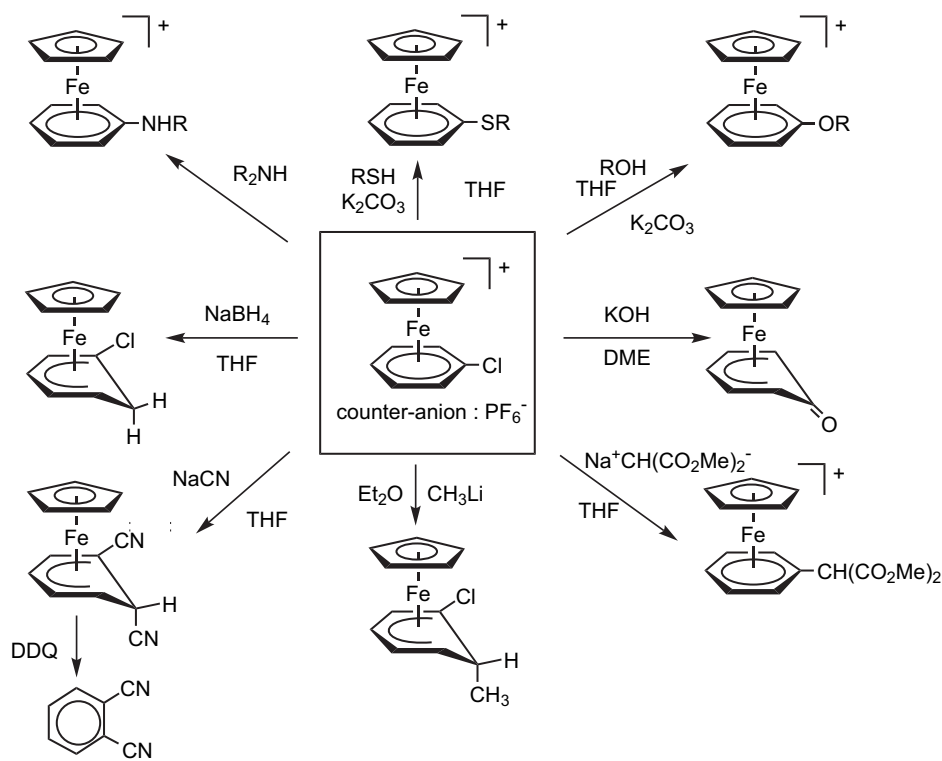
Scheme 3. Reactions of the chlorobenzene complex [Fe(η^5-C$_5$H$_5$)(η^6-PhCl)][PF$_6$].
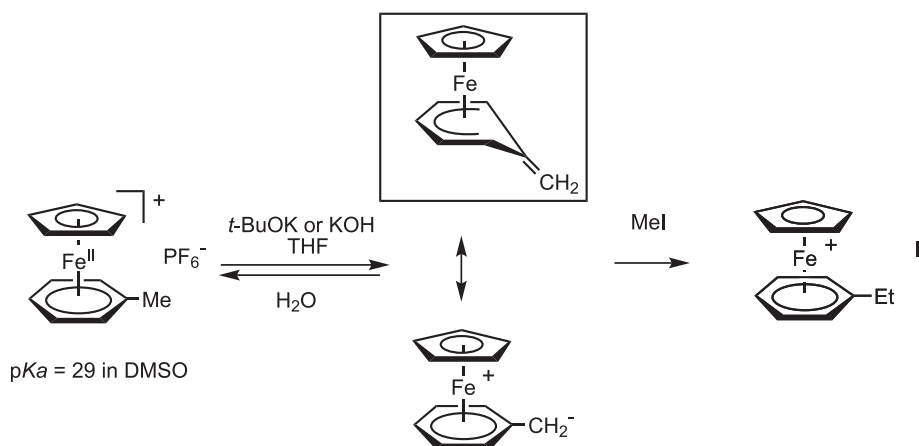
Scheme 4. Deprotonation of [Fe(η^5-C$_5$H$_5$)(η^6-PhMe)][PF$_6$] followed by methylation. The X-ray crystal structure of the dark-red product resulting from deprotonation of [Fe(η^5-C$_5$H$_5$)(η^6-C$_6$Me$_6$)][PF$_6$] shows a structure close to the framed structure, although the reactivity is best explained by the zwitterionic mesomer structure.

[Fe(η^6-mesitylene)(η^5-C$_5$H$_5$)][PF$_6$], **4**, nona-allylation is achieved in three days under ambient conditions,[44] and this latter reaction is the most useful for dendrimer syntheses, because it quantitatively provides a remarkable pre-dendritic iron complex **5** on a large scale. The CpFe$^+$-induced polylallylation reactions can be followed by photolytic decomplexation using visible light from a 100-watt desk lamp (Scheme 7).[45–49]

The polyallylation of methylarenes can be applied to the p-ethoxytoluene complex, **6**,[50] obtained by facile nucleophilic substitution of chloride by ethoxy in ethanol in the presence of potassium carbonate at 60 °C (Scheme 8).[51] Thus, reaction of [Fe(η^6-p-ethoxytoluene)(η^5-C$_5$H$_5$)][PF$_6$] with t-BuOK and allyl bromide in THF leads to the triple allylation of the methyl group, as described above. In the same pot, the CpFe$^+$-induced heterolytic cleavage of the C–O bond and decomplexation are also obtained. The C–O bond cleavage by t-BuOK is facilitated upon heterogeneous

activation by KPF$_6$ formed in situ or by other simple salts (such as NaCl). The latter step, decomplexation, results from electron transfer from t-BuOK to the bulky cationic iron complex **7**. It is characterized by a color change from dark yellow to purple, the color of the unstable 19-electron Fe^I complex [Fe(η^6-p-HOC$_6$H$_4$-C(allyl)$_3$)(η^5-C$_5$H$_5$)] the instability of which is due to the presence of the juxta-cyclic heteroatom.[52–54] Overall, the very useful dendron p.HOC$_6$H$_4$C(allyl)$_3$, **8**, is synthesized in this way after 8 steps in the same pot. Note that, in this reaction, t-BuOK successively plays the role of base, nucleophile and electron-transfer reagent (Scheme 8).

The polyallylarene derivatives can also be synthesized by purely organic routes using multiple reactions, but the yields are only very low to modest, whereas the organoiron syntheses are facile, quantitative and the complex [Fe(η^6-arene)(η^5-C$_5$H$_5$)][PF$_6$] is recycled. The organic synthesis of the dendron can also be achieved over a series of organic reactions, but it is costly, requires multiple
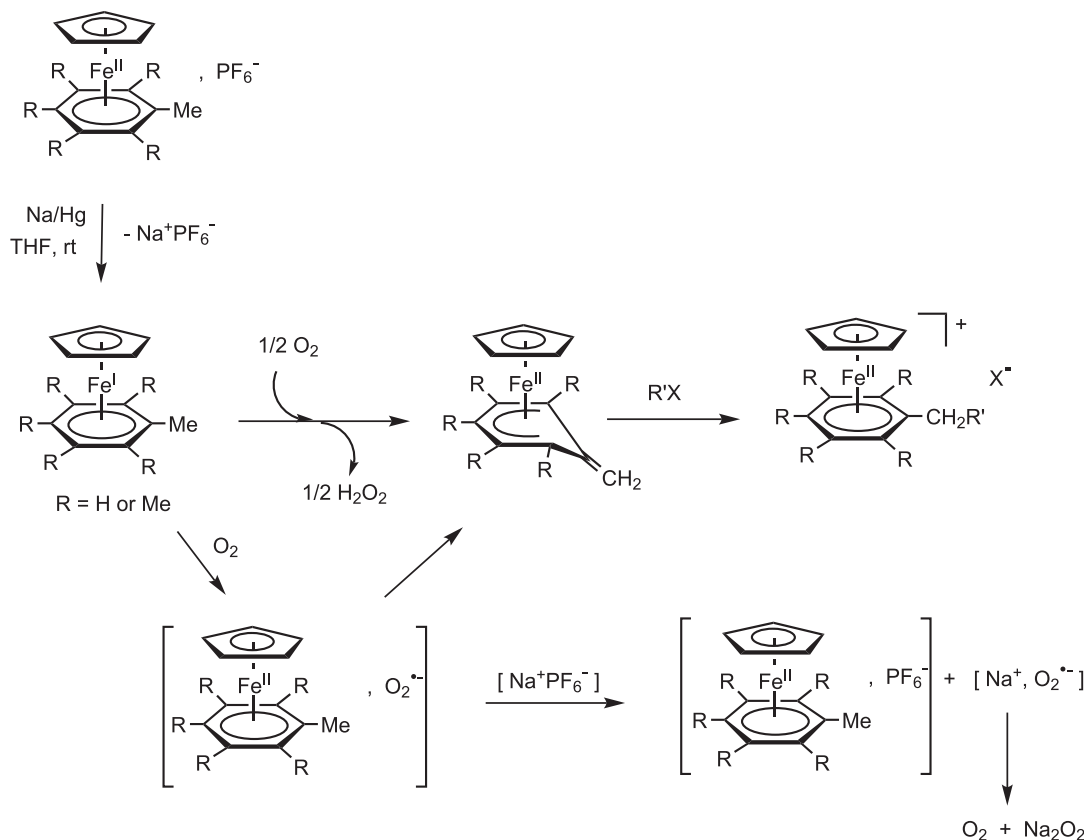
Scheme 5. Synthesis and reactivity with O₂ of the 19-electron complex [Feᴵ(η⁵-C₅H₅)(η⁶-C₆Me₆)] including a dramatic salt effect.
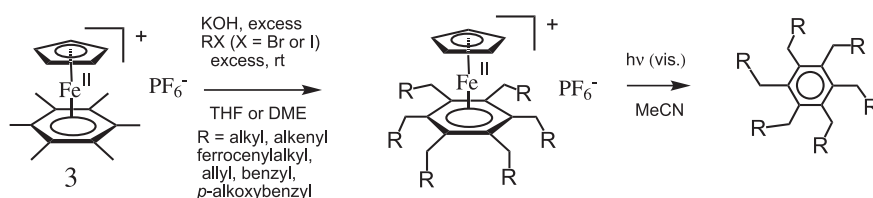
Scheme 6. CpFe⁺-induced hexa-alkylation and hexafunctionalization of C₆Me₆.
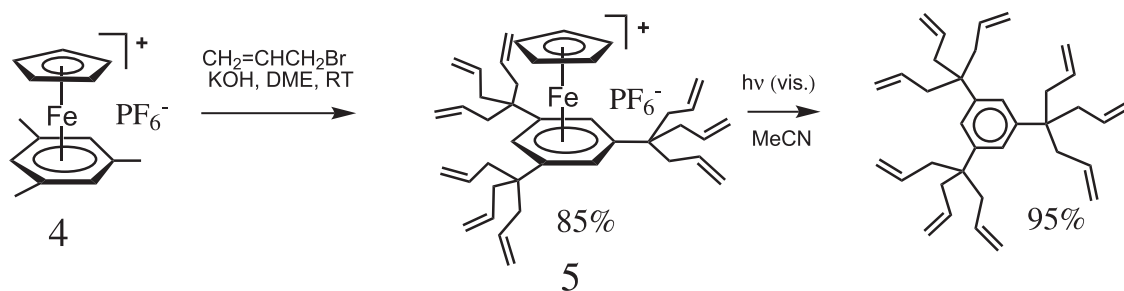
Scheme 7. CpFe⁺-induced nona-allylation of mesitylene.

synthesis and can sometimes fail if great care is not involved.[55] Overall, the organo-iron syntheses are much preferred.

4. Dendrimer construction using the dendritic cores and the dendron bricks

The nona-allyl dendritic core (G0) is regiospecifically hydroborated using disiamyl borane or 9-BBN or hydrosilylated using a Karsted catalyst and dimethylchloromethylsilane. The hydoboration can be followed by oxidation to the nona-alcohol, and then nucleophilic substitution of the corresponding mesylate by the phenolate dendron leads to the 27-olefin dendrimer of the first generation (G1). This sequence can be repeated to synthesize the 81-allyl dendrimer G2, the MALDI TOF mass spectrum of which showed the presence of the molecular peak, and then the 243-allyl dendrimer G2, that is, quite impure due to the difficulty in
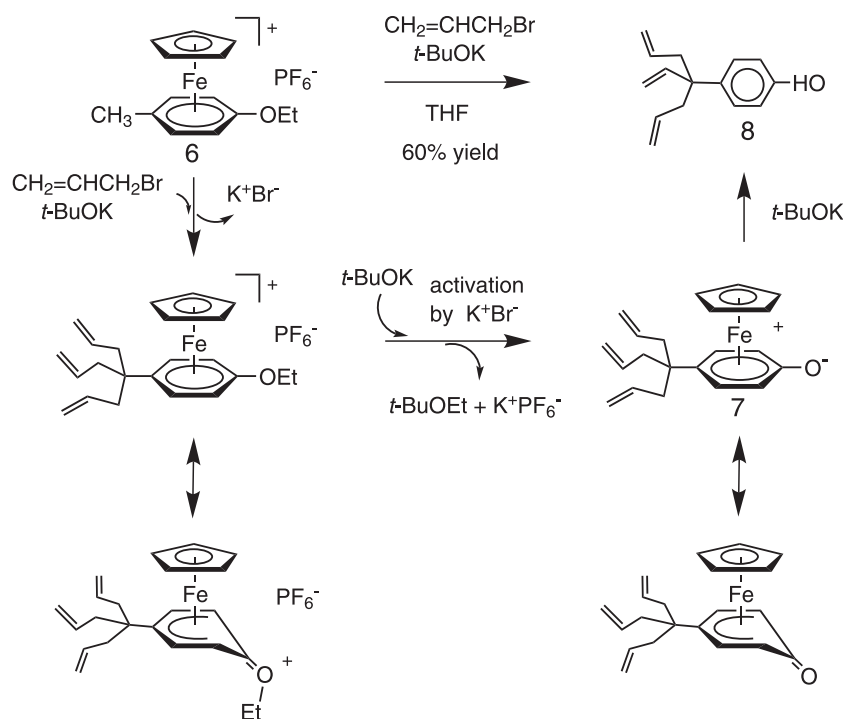
Scheme 8. One-pot, eight-step synthesis of the phenoltriallyl dendron p.HOC$_6$H$_4$C(CH$_2$CH=CH$_2$)$_3$ from [Fe(η^5-C$_5$H$_5$)(η^6-p.EtOC$_6$H$_4$CH$_3$)][PF$_6$], and its mechanism involving the multiple roles of t-BuOK.

completing the hydroboration with such bulky boranes at this stage (Scheme 9).[50] On the other hand, the hydrosilylation using chloro dimethylsilane or chloromethyldimethylsilane is not marred by this problem, because these silanes are small.[56,57] Thus, iteration of the sequence consisting of hydrosilylation with chloro methyldimethylsilane[58,59] followed by nucleophilic substitution of chloride by iodide and of iodide by the phenolate dendron could be pursued until the Ninth generation that contains a theoretical number of 177,147 (i. e. 3^{11}) allyl branches (Scheme 10). After each reaction, completion was checked by ^{1}H, ^{13}C and ^{29}Si NMR until G9. The dendrimers are very soluble in CDCl$_3$, even up to G9, and the NMR spectra clearly show the peripheral dendrimer groups (the inside groups being too few to observe, especially with a growth involving $1 \rightarrow 3$ connectivity). The MALDI TOF mass spectrum of the 81-allyl dendrimer (G2) shows the largely dominant molecular peak and a tiny signal corresponding to the lack of a phenoltriallyl dendron. Lack of dendrons rapidly increases with generation increase, however, as known for divergent dendritic constructions. Thus, the low amount of defects that are not detected at the NMR accuracy is sufficient for growing the number of defects with generation increase.[59] The dense-packing limit predicted by de Gennes[60] is around 6000 termini, corresponding to G6 (3^8=6 561 termini). At this generation, the level of defects is estimated to be 5% of the number of termini. Despite these defects, this dense-packing limit is very largely overtaken, which, we believe, is due to the fact that the termini backfold toward the dendrimer center to fill the cavities. This means that the de Gennes dense-packing limit would only be valid if a particular reason is responsible for retaining the termini at the dendrimer periphery, such as H-bonding (Tomalia's PAMAM dendrimers[61–64]) or rigid tethers (Moore's[65,66] and Müllen's[67–69] polyarene dendrimers or Balzani's polypyridine-ruthenium dendrimers[70–73]). Indeed, other theoretical studies have shown that backfolding must proceed beyond a certain generation in order to share the bulk between the dendrimer periphery and the dendrimer interior.[74–77] The present polyallyl dendrimers have small CH$_2$ termini and flexible branches that can backfold toward the dendrimer center. Thus, beyond the
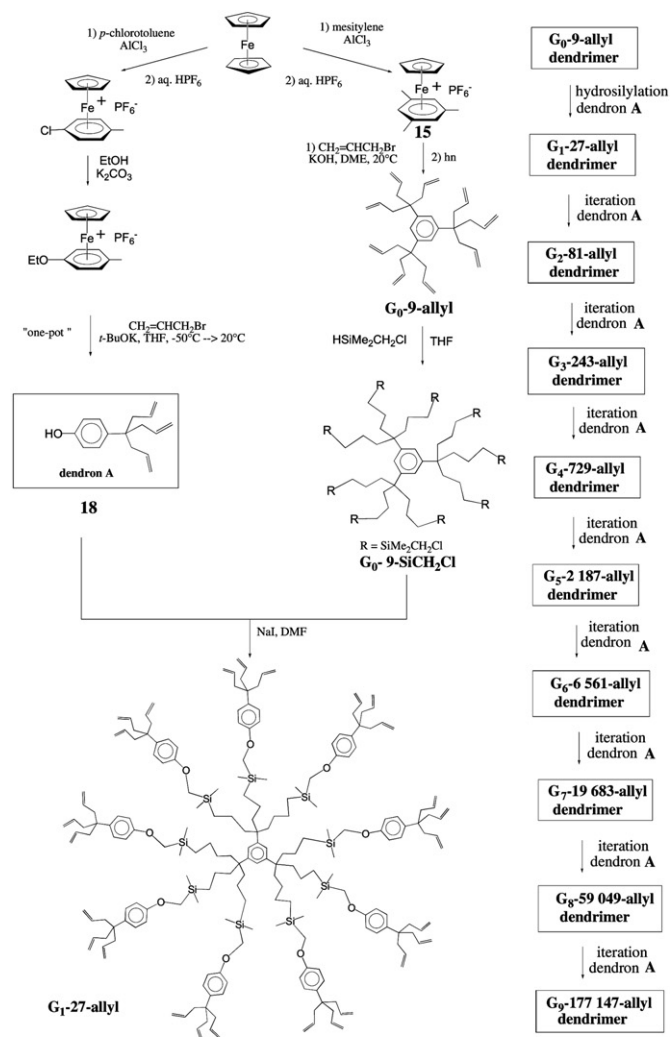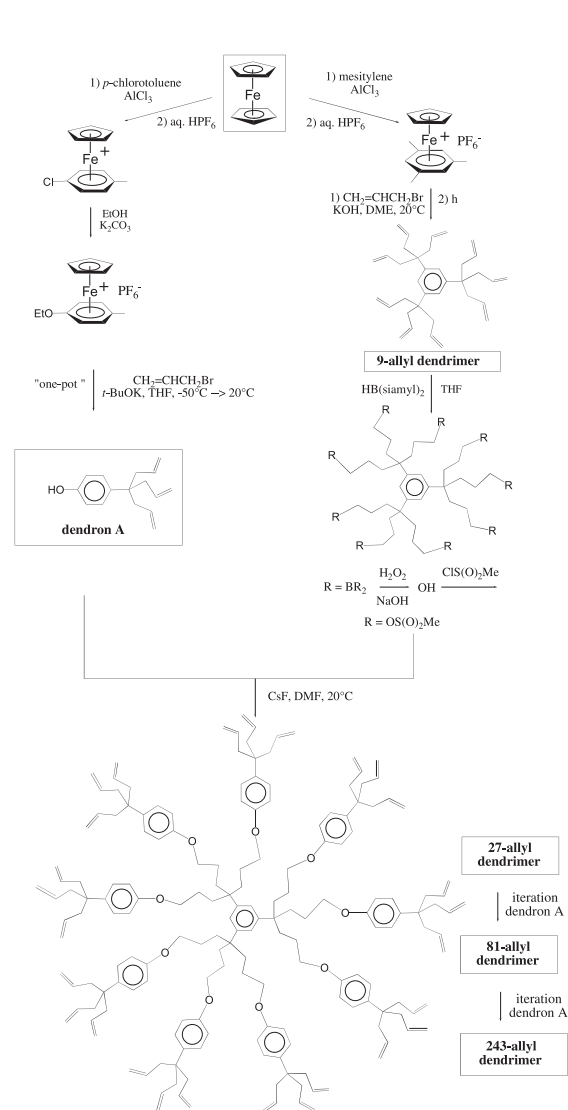
dense-packing limit, the dendrimer construction largely proceeds inside the dendrimers, which explains why the reactions become slower and slower as the generation increases. It is the volume, rather than the surface, that limits the dendrimer construction.[59]

The dendrimers are also characterized by size exclusion chromatography up to G5 with very low polydispersity (between 1.00 and 1.02), by HRTEM up to G9 (G9-SiCH$_2$I termini with the heavy I atoms) and atomic force microscopy (AFM) in the condensed phase on HOPG support, that shows the steady growth from G0 to G9, reaching a 25-nm thickness for the flattened dendrimers.[59]

5. Functionalizations of the dendrimers for applications

The applications of dendrimers[78–80] are in materials sciences,[81–89] light harvesting,[90–95] catalysis,[96–102] and nanomedicine.[103–111] For these applications, it is necessary to specifically engineer the dendrimer construction, and in particular to functionalize the dendrimer periphery and the focal points of the dendrons. Dendrimer chemistry is now a mature field of science that has been considerably developed from the synthetic point of view and toward these potential applications. For instance, peripheral functionalization appeared to be crucial for guest encapsulation and function of dendrimers as *exo*-receptors for the recognition of anions, in view of their use as anion sensors.[112–114] Functionalization of olefin-terminated dendrimers is essential for the present strategy involving polyallylation of the polymethylbenzene cores.

The nonol **G$_0$-9-ol** synthesized from the nona-allylarene core **9** led to a nona-amine **10** by a Michael reaction with acrylonitrile followed by reduction of the nona-nitrile using BH$_3$:Me$_2$S, which allowed functionalization with organometallic groups by reaction with the corresponding acyl chlorides (Scheme 11). Thus, amidometallocene-terminated dendrimers with ferrocenyl, colbaltocenyl and [CpFe$^+$(arene)]$^+$ groups that were made in this way were the first dendritic oxo-anion sensors, and this redox sensing was shown to improve upon increasing the dendrimer generation, especially in the case of the ferrocenyl dendrimers, indicating a 'positive dendritic effect'.[115–118]

Scheme 9. Overall construction of 27-allyl, 81-allyl and 243-allyl dendrimers using the hydroboration procedure.

Scheme 10. Overall construction of dendrimers containing a theoretical number of 3^{n+2} allyl tethers using the hydrosilylation procedure (n=generation number).

Another nona-alcohol core synthesized from the nona-ally-benzene core was converted into a nona-iodo, and then to a nona-(tris-hexyl)ammonium dendrimer. The iodide counteranions were then replaced by three peroxophosphotungstate trianions for the
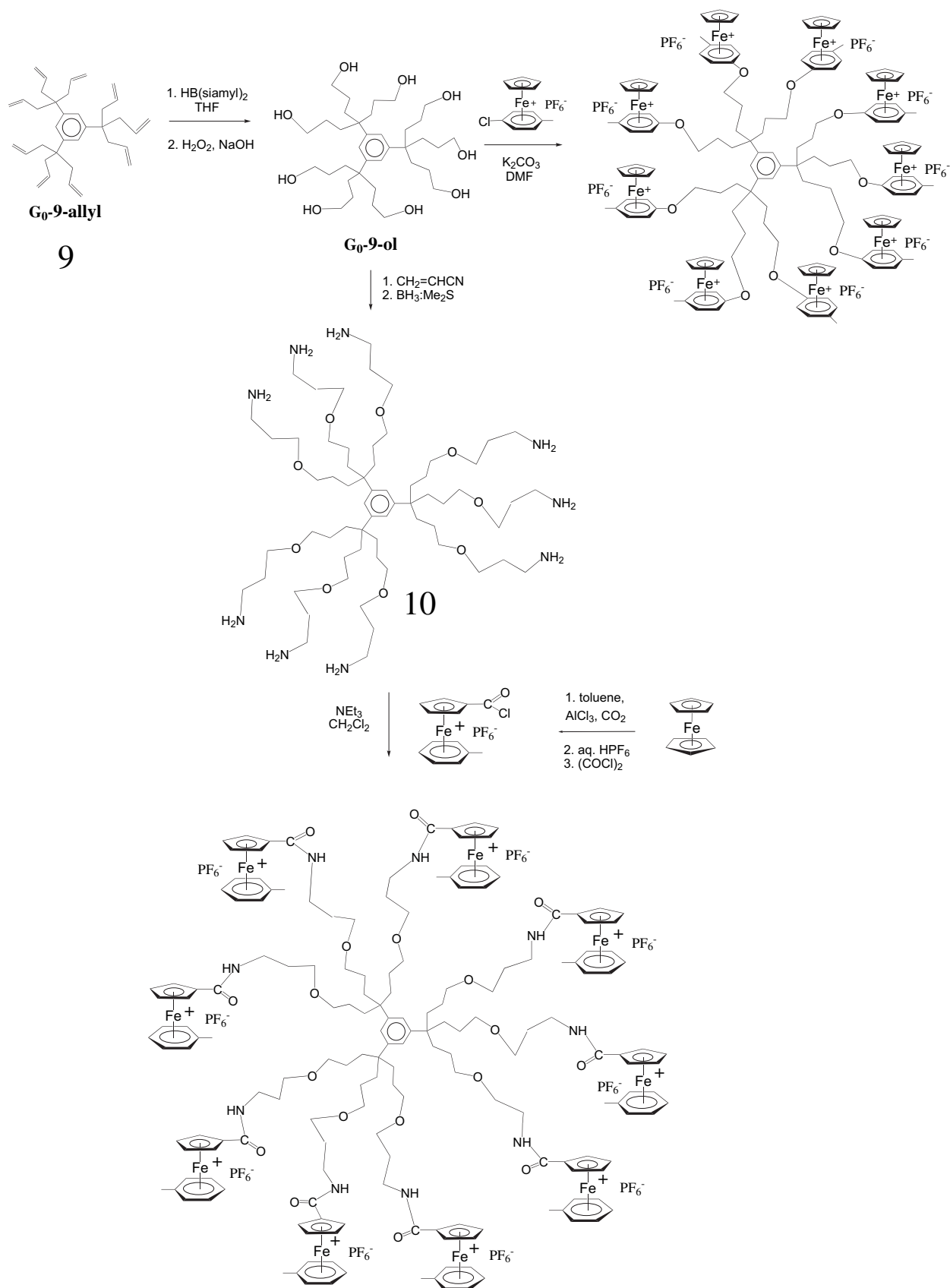
Scheme 11. Synthesis and reactions of a G0-9-ol dendritic core.
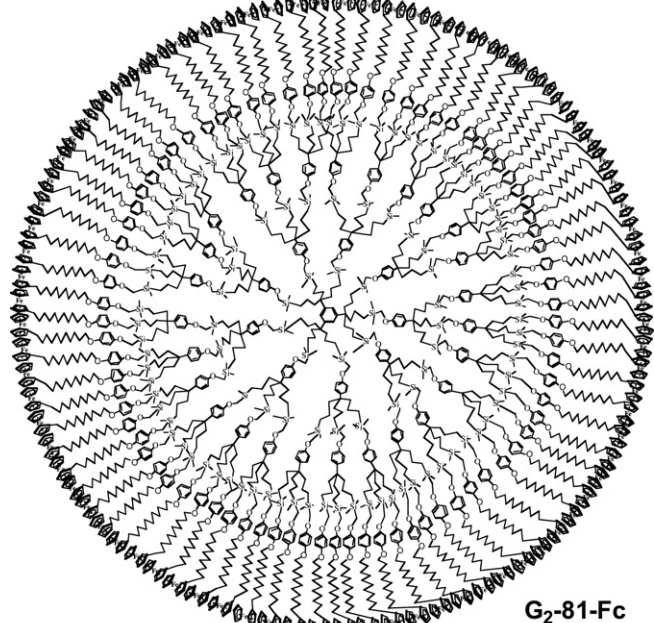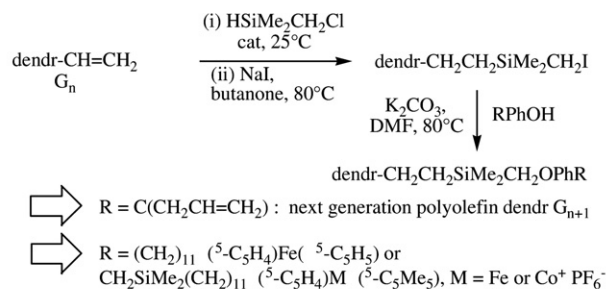
Scheme 12. Tether lengthening for the functionalization of giant dendrimers with redox-robust metallocenyl groups.

encapsulation of these anions into this 27-hexyl dendrimer. The goal was the protection of these anions that are good epoxidation and oxidation catalysts, but could not be recycled when the counteranion was linear, contrary to the dendritic anions that can be recycled and stored for months between re-uses. This strategy was also applied to related fully polyoxometalate (POM)-centered dendrimers.[119–122]

Functionalizaton of olefin-terminated dendrimers by hydrosilylation reactions using chlorosilanes has been achieved in particular in van Leeuwen's divergent dendrimer synthesis[123] and using chloromethyldimethylsilane by Seyferth, both with $1\rightarrow2$ connectivity.[58] Chlorodimethylsilane could also be used for a direct one-pot iterative dendrimer synthesis with $1\rightarrow3$-connectivity up to G3-243-allyl.[124] The $1\rightarrow3$ connectivity has appeared at the pioneering stage of dendrimer chemistry when 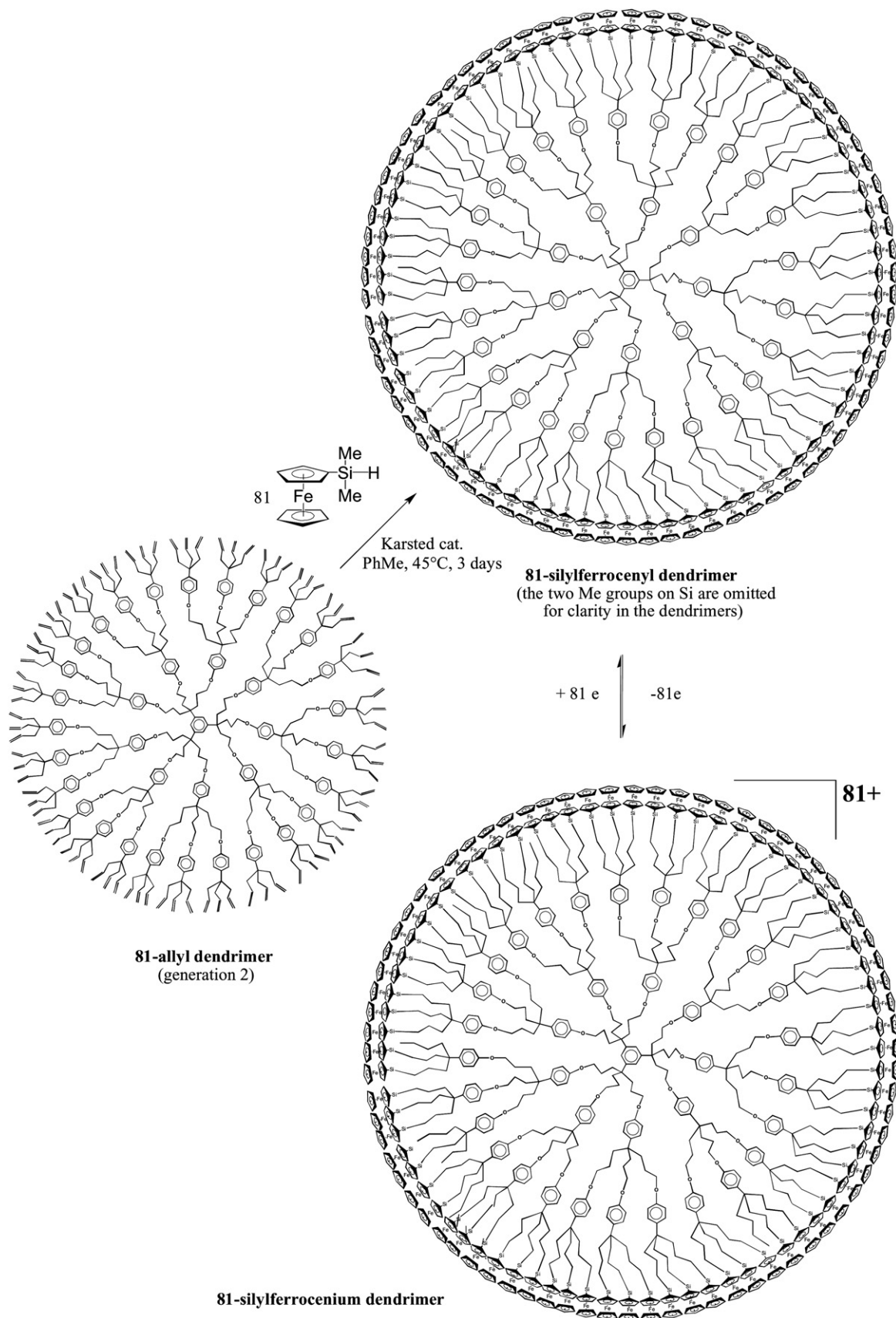Newkome reported in 1985 his arborols containing 27 alcohol termini and the concept of dendritic molecular micelles with important applications in supramolecular chemistry.[125–131]

With hydrosilylation using chloromethyldimethylsilane, the advantage is that the chloromethylsilyl group is hydrolytically stable, unlike the chlorosilyl group, and thus the chloromethylsilyl-terminated dendrimers can be easily handled and stored in air. For suitable follow-up reactions, chloride substitution by iodide or azide can be very easily carried out upon refluxing for a few hours in butanone or DMF in the presence of NaI or NaN_3. Nucleophilic substitution of iodide by phenolate (Williamson reaction) is a useful means of introducing functional groups located in the para position of the phenol substrate. For instance, arylcarboxylate-terminated dendrimers were synthesized and used for the recognition of acetylcholine and other cations in water.[132,133] Phenols containing long tethers were synthesized with ferrocenyl, pentamethylferrocenyl, and pentamethylcobaltocenium termini and linked to dendrimers in this way in order to avoid steric bulk at the dendrimer periphery (Scheme 12).[134] The reduction of the azido group by PPh_3 and H_2O at the dendrimer termini yields the amino-terminated dendrimers that reacted with protected esters containing redox-robust tetra-iron clusters for excellent ATP redox recognition.[135]

Azidomethyl-terminated dendrimers undergo Cu^I-catalyzed 'click' reactions with a variety of terminal alkynes including
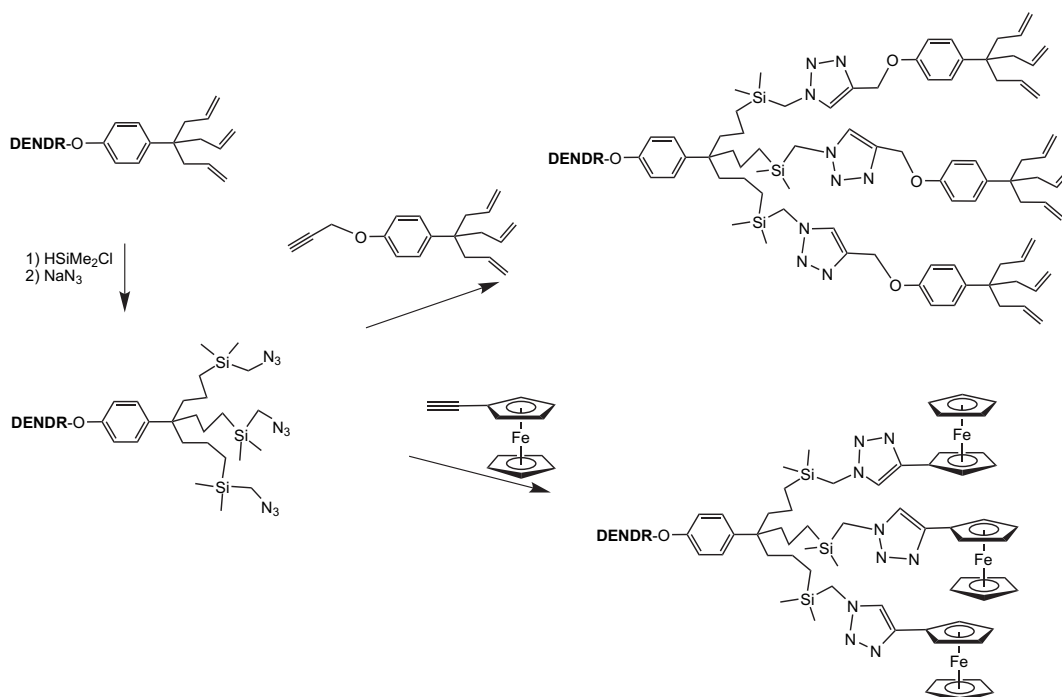
Scheme 13. 'Click' reactions between azido-terminated dendrimers and ethynylferrocene for functionalization or dendrons bearing a terminal alkyne at the focal point for generation increase.

81-silylferrocenyl dendrimer
(the two Me groups on Si are omitted
for clarity in the dendrimers)

Karsted cat.
PhMe, 45°C, 3 days

+ 81 e   -81e

81+

81-allyl dendrimer
(generation 2)

81-silylferrocenium dendrimer

Scheme 14. Ferrocenylsilylation of an 81-allyl dendrimer using ferrocenyldimethylsilane.
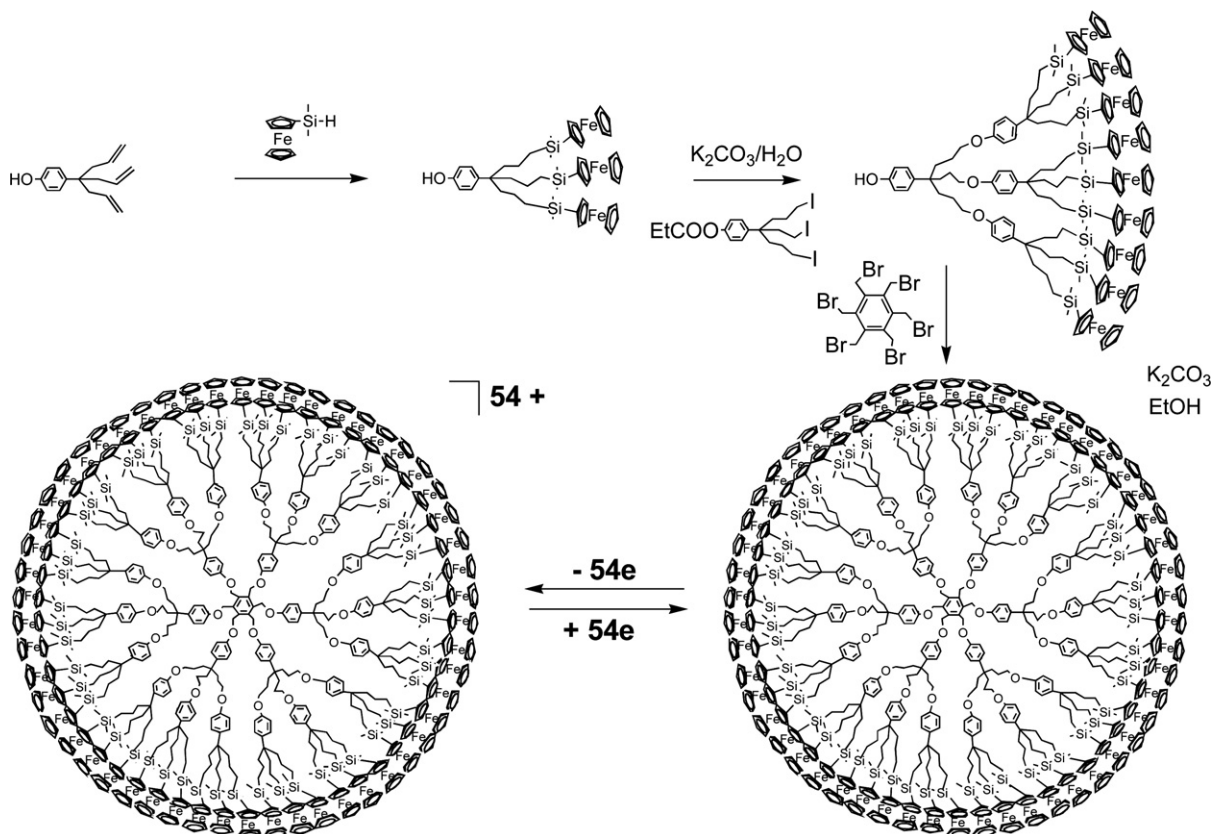
Scheme 15. Synthesis of a 54-ferrocenyl dendrimer including functionalization of a core with nonaferrocenyl dendrons.
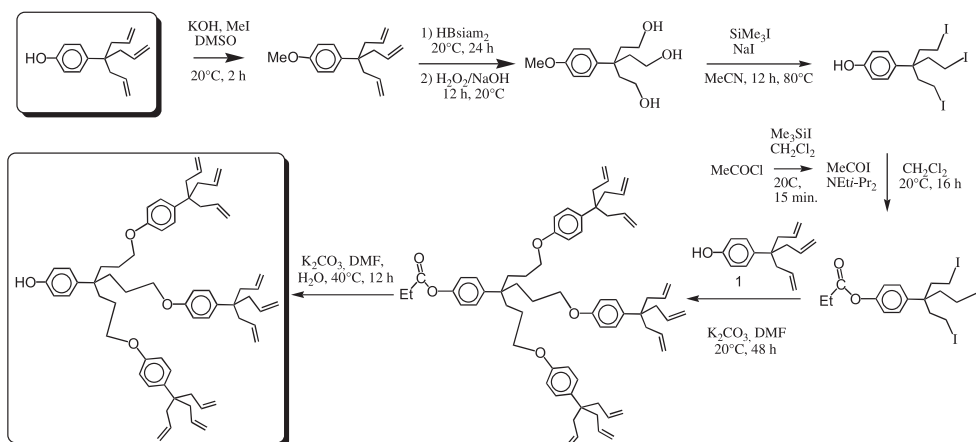
Scheme 16. Convergent dendron synthesis using a protection-deprotection procedure. This method was pursued up to the synthesis of a 27-allyl phenol dendron. An analogous strategy was engaged using hydrosilylation.

ethynylferrocene, phenylacetylene, and ethynylsulfonate, yielding ferrocenyltriazolyl- and other substituted triazolyl-terminated dendrimers (Scheme 13).[136,137] With the triazolylferrocenyl termini, these dendrimers can recognize and sense both oxo-anions and transition-metal cations. Indeed, transition-metal cations such as Pd^{II}, Pt^{II}, Cu^{I}, and Cu^{II} coordinate to the triazolyl nitrogen ligand of these triazolyl-terminated dendrimers, which can be monitored by cyclic voltammetry in the case of the ferrocenyltriazolyl-terminated dendrimers of generation 0–2 using the single reversible ferrocenyl wave, that is, shifted anodically upon complexation. The oxo-anions such as ATP can also be recognized and titrated using these ferrocenyltriazolyl-terminated dendrimers, because the single reversible ferrocenyl wave is now shifted cathodically.[136]

Complexation of these dendrimers by Pd^{II} can be followed by reduction to Pd^0 that form nanoparticles (PdNPs) inside or outside the dendrimer framework depending on the dendrimer generation.[138,139] This strategy affords PdNPs of predetermined and precise size, and catalysis using these PdNPs of varying sizes provides a useful insight into the catalysis mechanisms. For instance, styrene hydrogenation proceeds all the better as the PdNPs are smaller,[138] as known previously with polymer-stabilized PdNPs[140–144] and PAMAM-dendrimer-encapsulated Pd nanoparticles.[89] On the other hand, the Suzuki cross-coupling reaction between iodobenzene and phenylboronic acid proceeds at ambient temperature independently of the dendrimer-stabilized PdNPs used and all the better as the PdNPs are used at lower concentrations down to
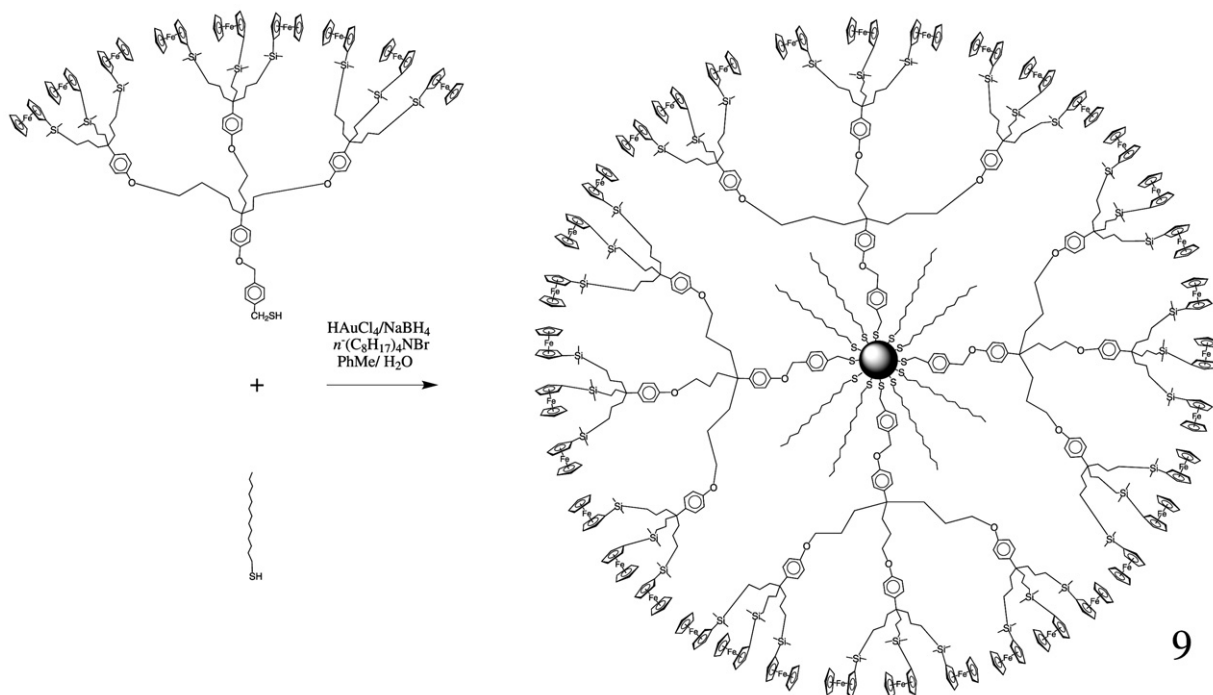
Scheme 17. Synthesis of gold-nanoparticle-cored functional dendrimers using ferrocenyl-terminated dendrons containing a thiol at the focal point.
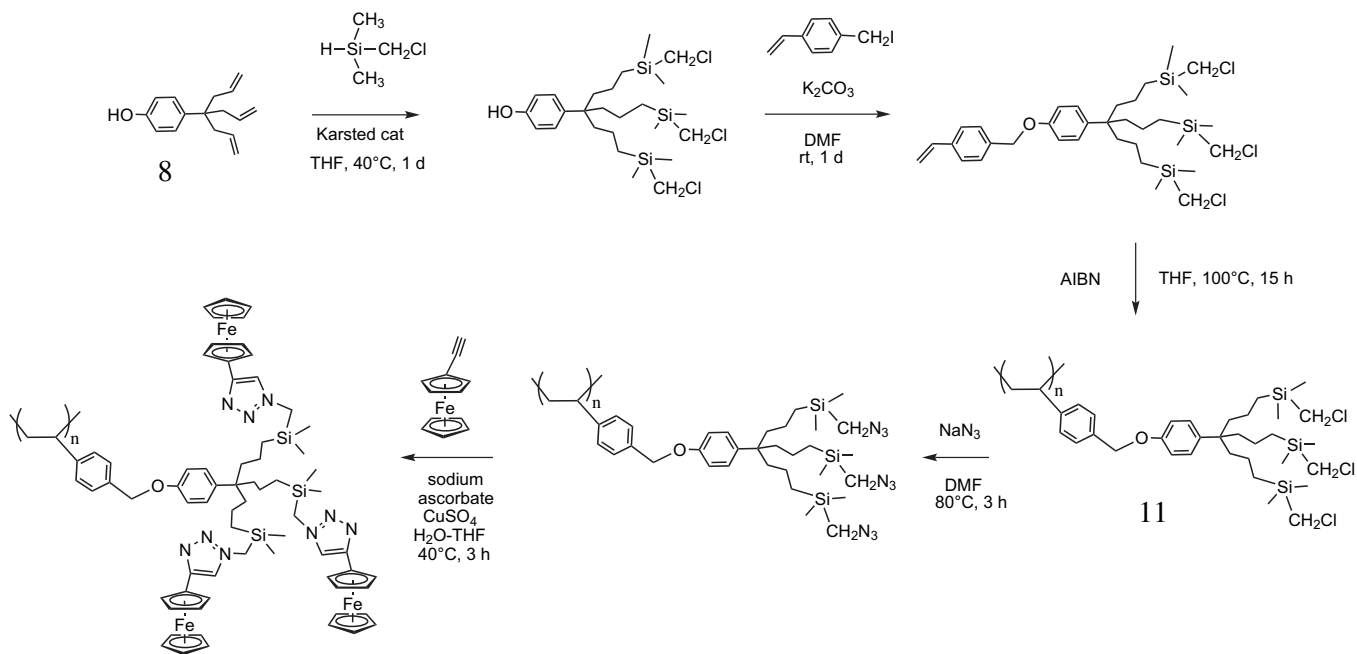
Scheme 18. Radical polymerization of a dendron-containing styrene monomer for the synthesis of a ferrocenyl dendronized polymer.

1 ppm (TON: 540,000).[145] This 'homeopathic' mechanism[146–148] is proposed to result from the fact that catalytically very active Pd atoms escape from the PdNPs,[145] even at room temperature, but are all the better annihilated by the mother PdNPs as the PdNP concentration is higher.

'Click' reactions between analogous azido-terminated G0-G2 dendrimers and a Percec-type[149,150] dendron functionalized with propargyltetraethylene glycol at the focal point and triethylene glycol units on the three terminal tethers of the dendron yielded

water-soluble polyethylene glycol dendrimers containing triazolyl and PEG ligands that could bind Au^{III} for further reduction to dendrimer-stabilized gold nanoparticles (AuNPs).[151] 'Click' reactions with the same dendron were used to functionalize AuNPs containing azido termini, yielding water-soluble AuNPs.[152]

Inverse 'click' reactions, i.e., between azidomethyferrocene and dendrimer cores decorated with alkynyl-terminated Percec-type dendrons, also yielded triazolyl-containing dendrimers up to G3-243-ferrocenyl that disclosed oxo-anion-recognition properties, in
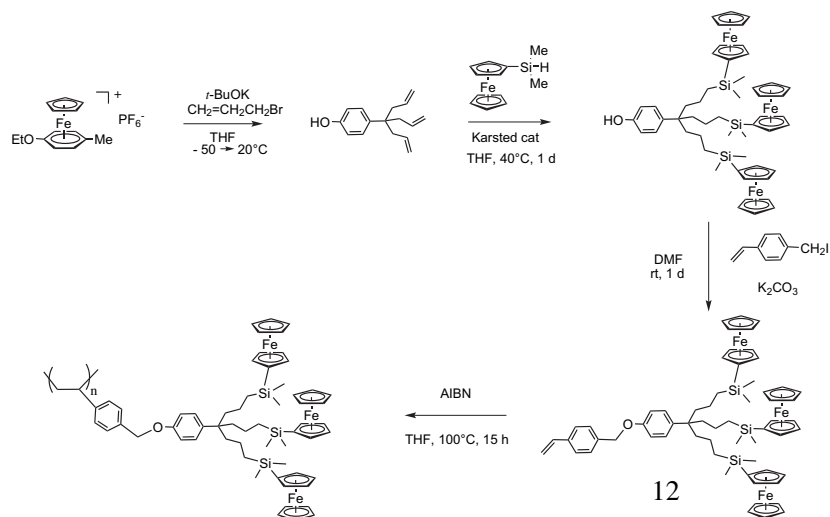
Scheme 19. Radical polymerization of a styrene derivative containing a triferrocenyl dendron for the synthesis of a ferrocenyl dendronized polymer.
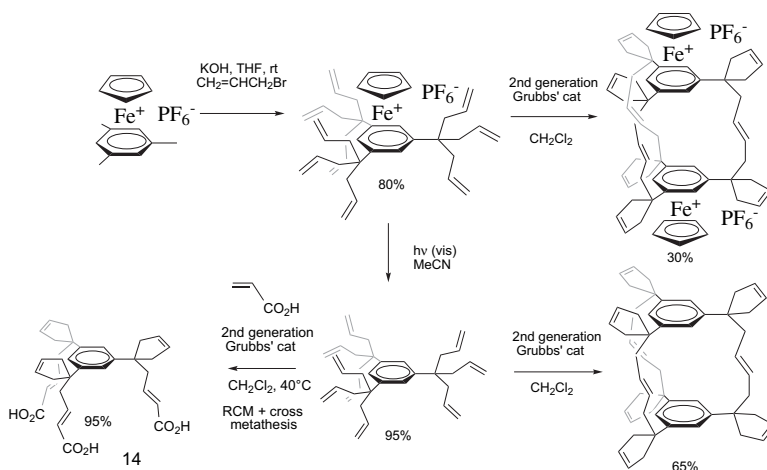
Scheme 20. Metathesis reactions of the nona-allyl benzene core and its CpFe$^+$ complex. Note the complete reaction change under identical conditions in the presence of acrylic acid.
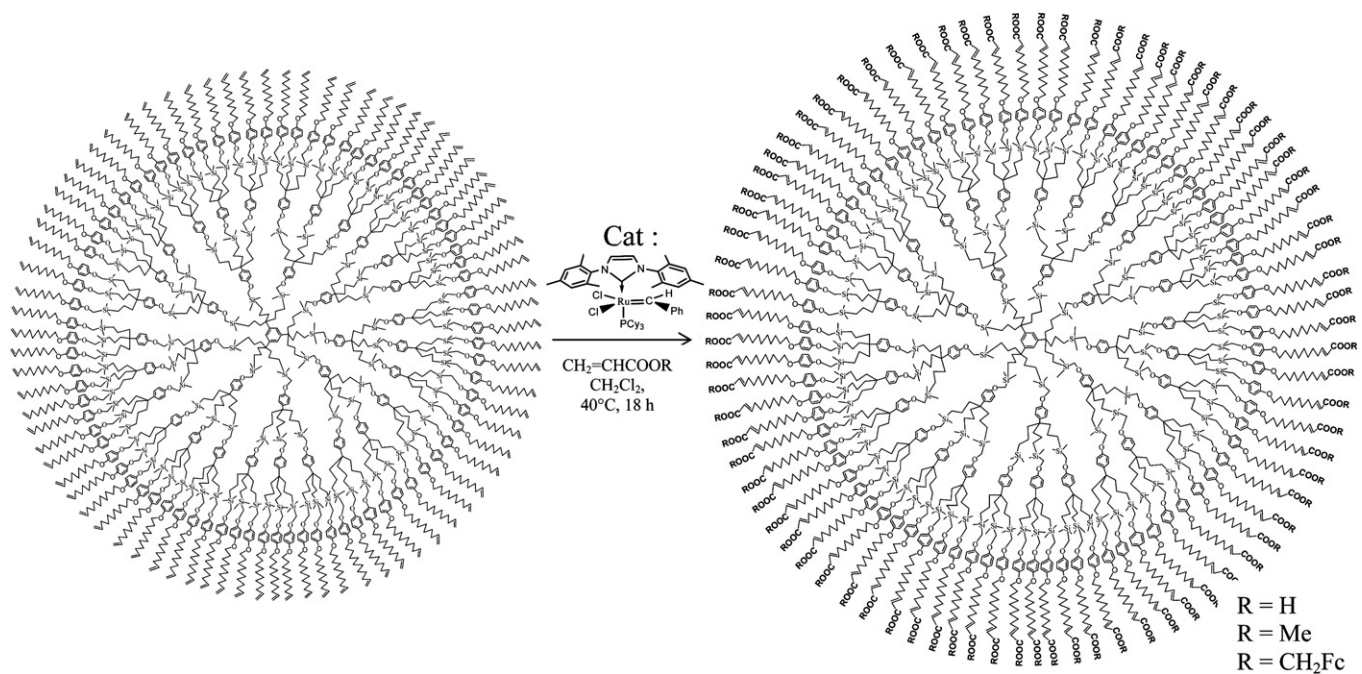
Scheme 21. Functionalization of the terminal tethers of a polyolefin dendrimer by regio- and stereoselective cross metathesis with acrylic acid using Grubbs' second-generation catalysts.
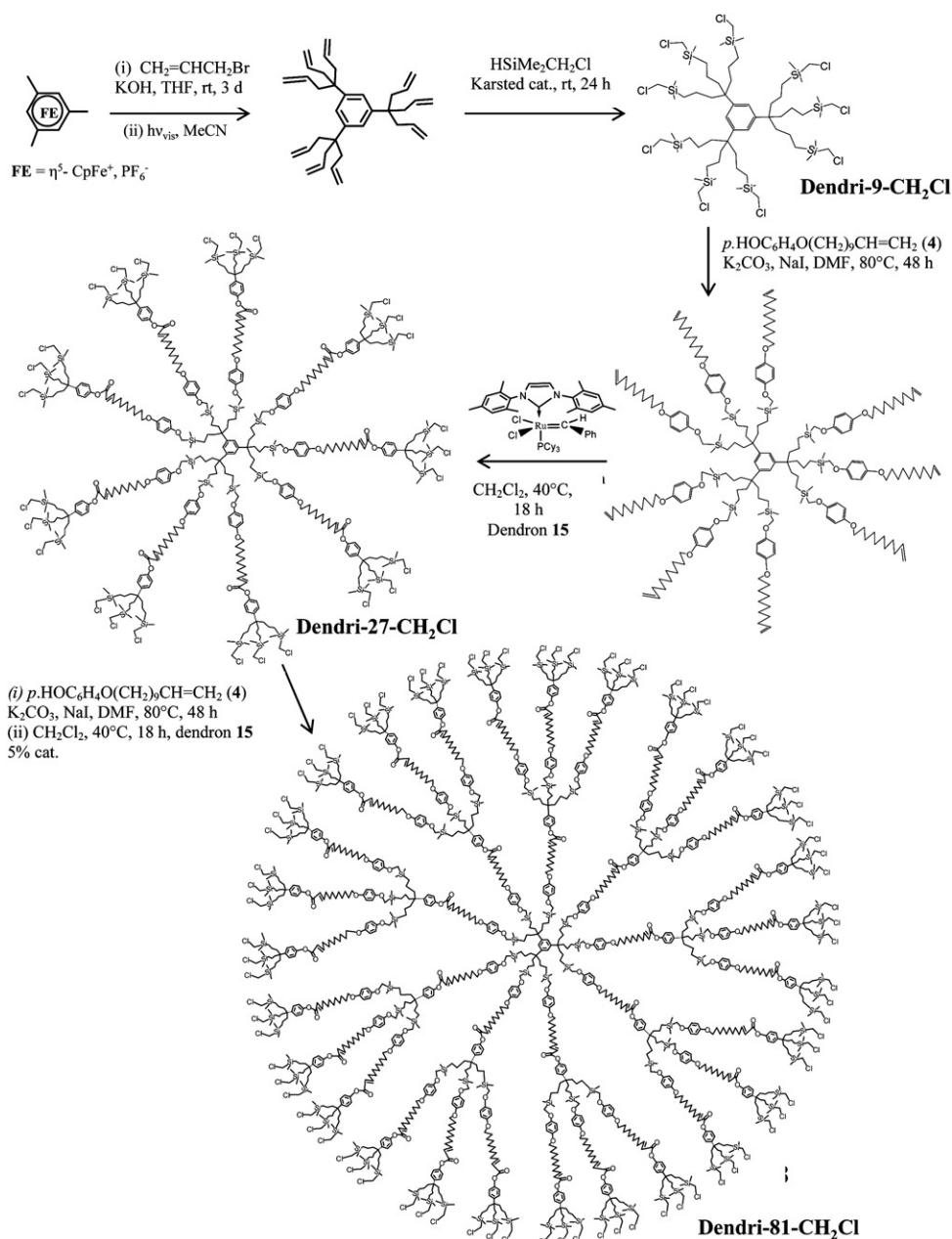
Scheme 22. Dendrimer growth from one generation to the next by cross metathesis with a dendronic acrylate using Grubbs' second-generation catalyst.

particular because Pt electrodes were easily modified with these giant metallodendrimers.[153] An analogous strategy was used to decorate these dendrimers with sugar units using 2′-azidoethyl-2,3,4-tris-O-acetyl-β-D-xylopyranoside up to G3-243-xylopyrano-side, reaching a diameter of 7 to 8 nm in water solution as determined by DOSY NMR and dynamic light scattering.[154]

Regioselective hydrosilylation not only allows dendrimers to be grown from one generation to the next, but it also allows the decoration of dendrimers, for instance by ferrocenylsilylation of poly-olefin dendrimers (Scheme 14). Hydrosilylation of phenoltriallyl dendrons does not require protection, which allows the synthesis of phenoltriferrocenyl or nonaferrocenyl dendrons that can be condensed onto dendritic cores (Scheme 15). On the other hand, the convergent synthesis of 9-allyl or 27-allyl dendrons using either hydroboration or hydosilylation first requires protection of the phenol function at the dendron focal point, as shown in Scheme 16. Phenol dendrons decorated with ferrocenylsilyl groups were indeed

attached to various generations of dendritic cores, and the silylfer-rocenyl-terminated dendrimers were found to be oxo-anion sensors (Scheme 15). This strategy was extended to AuNP-cored dendrimers. The tris- and nona-ferrocenylphenol dendrons were functionalized at the focal point with an alkylthiol tether in order to bind the AuNP core (Scheme 17). Alternatively, convergent synthesis of nonaferrocenyl phenol dendrons was carried out before functionalization with the alkylthiol tether and binding to the AuNP.[155–158] Likewise, triferrocenyl- and nonaferrocenyl-phenolate dendrons were coordinated to Mo₆ clusters upon substitution of the six terminal chloro cluster ligands by the phenolates, yielding Mo₆-cluster-centered silylferrocenyl-terminated dendrimers.[159–162]

Ferrocenyl dendronized polymers could be synthesized by AIBN-induced radical polymerization of a styrene monomer containing either a triferrocenyl-phenolate dendron or a tri(chloromethyl)-phenolate dendron that has been introduced by Williamson reaction with the iodomethyl *para* substituent of the styrene monomer. The
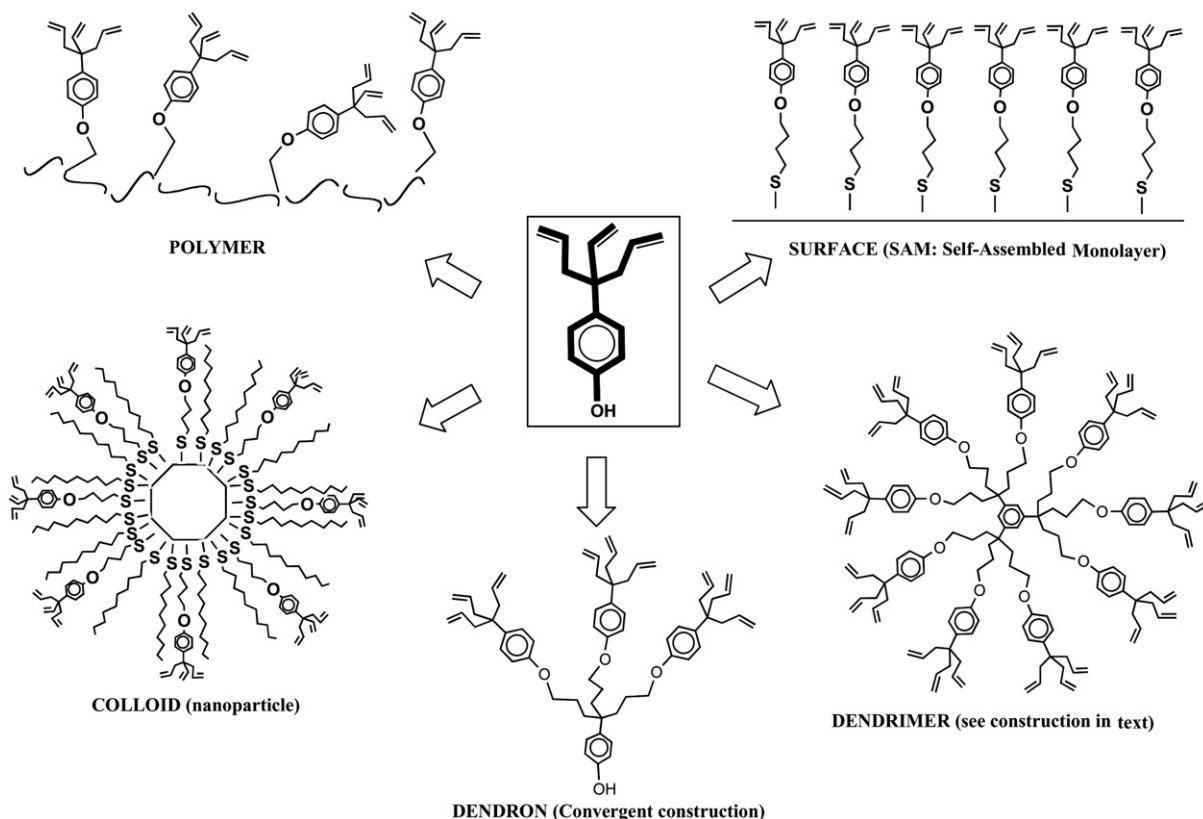
Scheme 23. Uses of the phenoltriallyl dendron including the introduction of the 1→3 connectivity into molecular architectures and nanomaterials.

polymer **11** containing the tri(chloromethyl)phenolate dendron was further functionalized by substitution of chloride by azide followed by a successful 'click' reaction with ethynylferrocene.[163] Alternatively, AIBN-induced radical polymerization of the *para*-substituted styrene derivative **12** containing the triferrocenyl dendron could be followed by substitution of chloride by iodide followed by substitution by the triferrocenylphenolate (Schemes 18 and 19).[163]

Application of Grubbs' metathesis catalysts[164–167] to poly-allylbenzenes yielded bi- and polycyclic compounds.[168] In particular, the nona-allyl benzene core and its CpFe$^+$ complex produced organic and organo-iron cages resulting from triple ring-closing metathesis (RCM) followed by triple cross metathesis between two molecules,[169] but if the reaction was carried out in the presence of acrylic acid, cross coupling gave the tris-acid **12** (Scheme 20).[170] Using a tether-lengthening strategy, RCM could be avoided, and only cross metathesis proceeded on the nine olefin-terminated tethers with acrylic acid, giving the nona-*trans*-acrylic acid selectively, a reaction that also worked identically with the G1-27-long olefin and G2-81-long olefin-terminated dendrimers (Scheme 21).[170,171] Water-soluble dendrimers could be made in this way. Moreover, the cross-metathesis reaction could be extended to dendronic acrylates containing three chloromethyl branches, precursors of long olefin tethers, which provided a novel type of divergent dendrimer construction using cross metathesis (Scheme 22).[171]

Finally, another application of these functionalization reactions[172] concerns the robustness of the late transition-metal redox systems that could be applied to the design of dendritic molecular batteries.[173–175]

6. Conclusions and outlook

In conclusion, the 1→3 connectivity starting from mesitylene and *p*-ethoxytoluene upon facile CpFe$^+$-induced triallylation of the benzylic methyl groups of simple arene substrates produced elemental bricks for very efficient constructions of dendrimers. A strength of 1→3 connectivity, pioneered by Newkome, is that the dendrimer size grows much more rapidly than with the 1→2 connectivity, [176] and in a well-controlled manner. The phenoltriallyl dendron can introduce the →3 connectivity into a variety of molecular architectures and practical devices (Scheme 23). These nano-objects also include giant organic and organometallic dendrimers, cluster- and nanoparticle-cored dendrimers and dendronized polymers. The dendrimers contain a theoretical number of 3^n terminal allyl tethers that were suitably functionalized. Specific applications range from sensing and nanomaterials to catalysis and nanomedicine with, most recently, water-soluble dendrimers that are very promising.[151,152] Indeed, their encapsulation properties are remarkable and currently under scrutiny and use in our laboratory.

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Biographical sketch
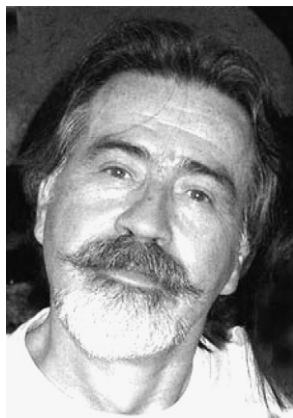
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