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Organometallic dendrimers with transition metals

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Abstract

Dendrimers are a novel class of macromolecules whose hyperbranched symmetrical architectures and special properties fascinate scientists from a wide range of disciplines. One of the most active current areas of research in the chemistry of dendrimers is the incorporation of metal centres into such structures, thus resulting in well-defined molecules with new advantageous properties. This review summarises our contributions in the developing field of organo-transition metal dendrimers, together with relevant works of expert groups on this field. Throughout the article, the synthetic aspects are especially emphasised. Likewise, the electrochemical behaviour exhibited by new families of organometallic dendrimers and some of their relevant applications are highlighted here.

Keywords: Dendrimers; Metallodendrimers; Organometallics; Transition metals; Metallocenes; Electrochemistry

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1. Introduction

Dendrimers (from the Greek word for tree, δενδρον = dendron), also known as arborols, cascade molecules, or starburst polymers, constitute a new class of highly branched three-dimensional macromolecules which are constructed from a multifunctional central core and expand to a periphery that becomes more dense with increasing generation number, and which exhibit a unique combination of chemical and physical properties [1–9]. The design and synthesis of these tree-like well-defined molecules is a field which is undergoing dramatic growth and has generated enthusiastic studies at the frontiers of organic, inorganic, supramolecular and polymer chemistry. Since the pioneering pivotal works of Vögtle [10], Denkewalter [11], Newkome [12] and Tomalia [13], the synthetic research on dendritic macromolecules has generally been centred on the creation of purely organic, and more recently also inorganic dendrimers, with high molecular weights, and as many generations as possible. In the last years the trends in the research on dendrimers have changed, and the emphasis has been focused mainly in the modification of the properties of dendritic molecules by the introduction of reactive functional groups at the interior or on the outer dendrimer surface.

More recently, attention has shifted towards the construction of dendrimers containing metal centres [1,7,14–22]. The interest in developing these materials resulted from the fact that the introduction of metals into dendritic structures allows access to highly ordered materials with attractive magnetic, electronic, and photo-optical properties.

In particular, the incorporation of organo-transition metal entities on the surface or within dendritic structures represents a stimulating challenging target in both organometallics and dendrimers research, because this opens the way to new nanostructured organometallic macromolecules of desired nuclearity and possessing new topologies [22]. Interestingly, the σ- or π-character of the metal–carbon bond in the organometallics, as well as the flexible coordination of transition metals and their variety of stable oxidation states, will have a significant influence on the reactivity of the dendrimer, and provide a unique opportunity for tailoring organometallic dendrimers to achieve desirable properties. Thus, by choosing the appropriate core and building blocks, dendritic macromolecules having organometallic entities in precise positions and numbers can be designed and constructed for specific applications (for example, as novel dendritic catalysts, in multi-electron redox and photocatalytic processes, as molecular sensors, and others). In addition, organo-transition metal dendritic macromolecules offer attractive advantages over their polymeric counterparts since they possess a precisely defined three-dimensional molecular architecture, and because of the potential to fully control their chemical constitution.

The main goal of this review is to summarise our contributions in the young and rapidly growing field of organo-transition metal dendrimers. The review also intends to highlight recent contributions of expert groups on this area, reported as far as the summer of 1998. The content has been organised into two main sections according to the synthetic approach and to the nature of the dendritic structure. As we will see below, two main strategies have been employed for the construction of such structures. Firstly, functionalization of preformed dendrimers with reactive organometallic moieties has proven to be an excellent method for preparing new well-defined organometallic macromolecules. This is clearly illustrated by a variety of silicon-, nitrogen-, and phosphorus-based organo-transition metal dendrimers. In this regard, we describe some synthetic efforts we have made toward a variety of organometallic dendrimers accessible by this approach, constructed from tetraallylsilane, cyclotetrasiloxane and diaminobutane cores, and in addition, the redox properties exhibited by several families of peripherally functionalized ferrocene and cobaltocenium dendrimers have been examined. The second approach is based on synthetic routes which start with key organometallic entities, from which several authors, including our own research group, have developed convergent and divergent growth strategies for the construction of very notable dendritic organometallic structures. Finally, remarkable organo-transition metal dendrimers exhibiting catalytic properties are described.

2. Functionalization of dendritic structures with organometallic moieties

2.1. Silicon-based organometallic dendrimers

2.1.1. Ferrocenyl dendrimers

Our research in the chemistry of dendrimers was initiated in 1993, and specifically, ferrocenyl-containing dendrimers constructed from organosilicon frameworks represented our first target organometallic dendritic molecules [23]. Our interest in preparing such systems stems from our investigations on silicon-based ferrocenyl multimetallic compounds and polymers, and in particular, from our efforts to understand the relationship between the structure and the redox properties of ferrocene siloxane materials [24–26]. Due to its high thermal stability and its interesting chemical and physical properties, ferrocene has become a versatile building block for the synthesis of materials with tailor-made properties [27,28]. Thus, ferrocene-based polymers have attracted great interest for the chemical modification of electrodes, as electrode mediators, and as materials for the construction of liquid crystals, electronic devices and non-linear optical (NLO) systems.

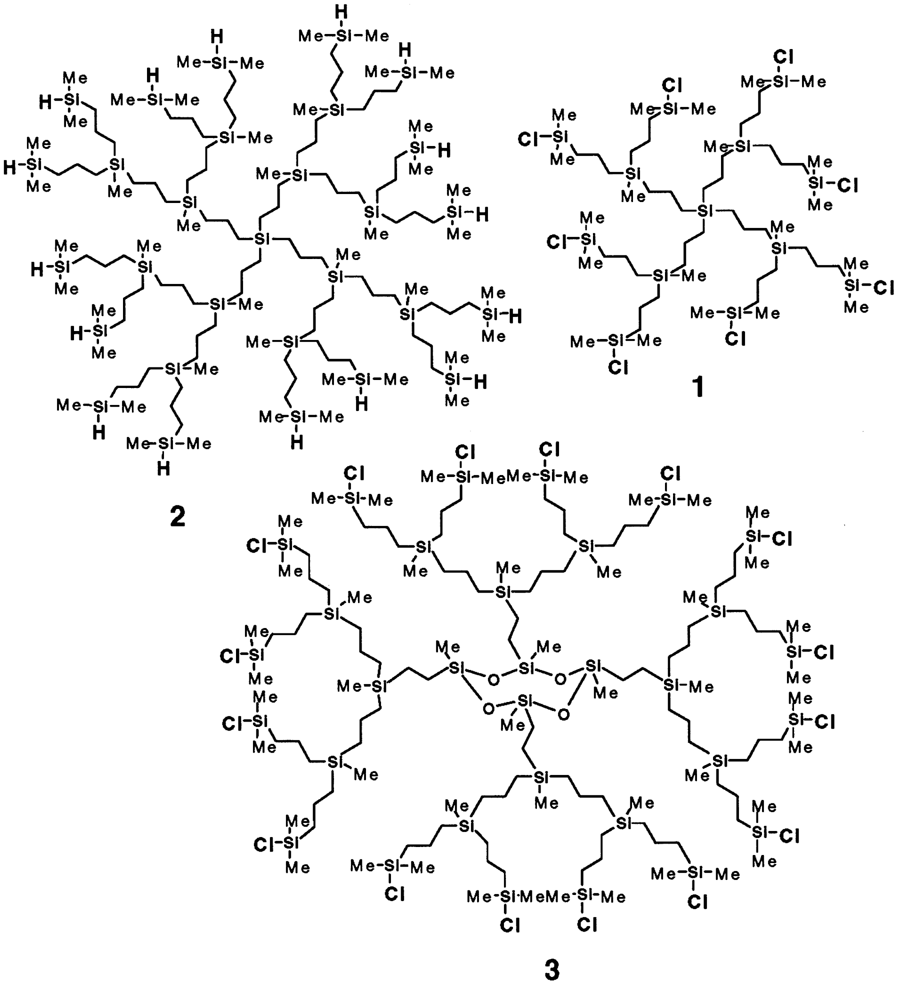
The same reasons for the interest in incorporating ferrocene units into polymers also provided motivation for the synthesis of ferrocene-containing dendrimers of well-defined sizes and perfectly branched structures. An attractive additional reason is that such macromolecules raise the possibility of combining the unique and valuable redox properties associated with the ferrocene nucleus with the highly structured macromolecular chemistry. This may provide access to materials of nanoscopic-size possessing unusual symmetrical architectures, as well as specific physical and chemical properties, which would be expected to differ from those of the ferrocene-based materials prepared to date.

Our initial approach to the construction of ferrocenyl dendritic structures focused on reactions that exploit the reactivity of organosilicon dendrimers functionalized at their surfaces with Si–Cl and Si–H sites, toward suitable reactive ferrocenyl monomers. The divergent synthetic route to the key silicon-based dendrimers selected as frameworks starts with tetraallylsilane and tetramethylcyclotetrasiloxane, as four-directional centres of branching, and involves the repetition of hydrosilylation and alkenylation reactions as growing steps [22,23,32,33]. This procedure follows approximately the valuable methodology developed by van der Made et al. [29], Roovers et al. [30] and Seyferth et al. [31] for the synthesis of carbosilane dendrimers. Using this synthetic approach we have prepared four different families of silicon-based dendritic molecules containing four, eight and 16 reactive Si-H and Si–Cl functional groups, located at the periphery. Some representative examples are dendrimers **1**–**3**, which are illustrated in Scheme 1.

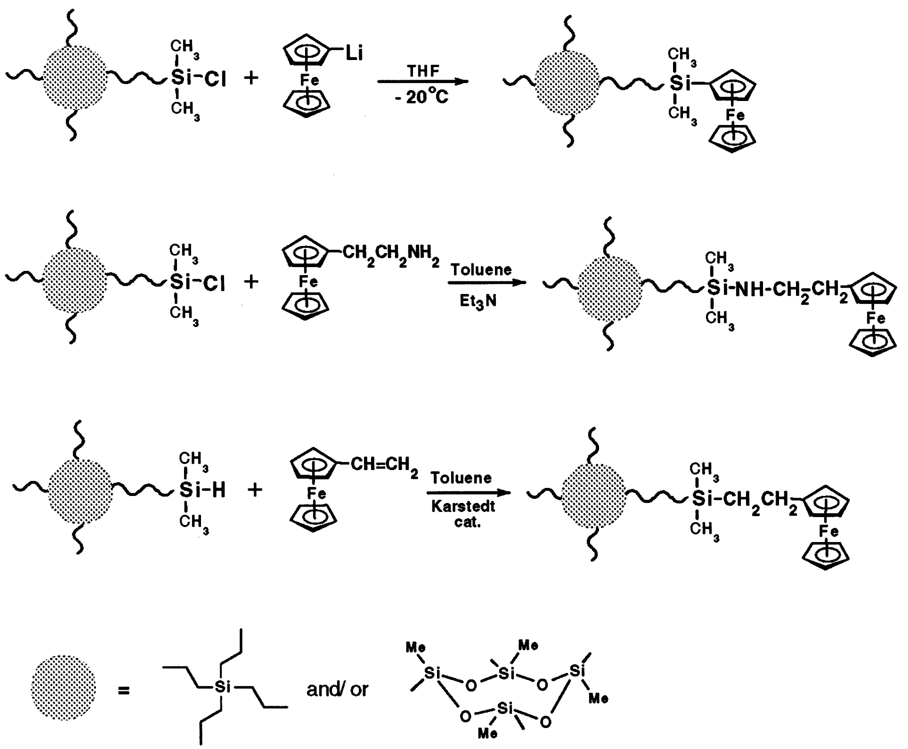
Three different synthetic routes have been developed for the incorporation of ferrocenyl moieties onto organosilicon dendritic cores, which are schematically summarised in Scheme 2, in which only one of the branches of the dendrimer, containing a peripheral functional group, is shown. The first method involved reactions of the Si–Cl functionalized dendrimers with monolithioferrocene, $(\eta^5\text{-}C_5H_4Li)Fe(\eta^5\text{-}C_5H_5)$, in THF at low temperature [22,23,32,33]. These reactions afforded the first, second and third generations of dendritic macromolecules **4**–**9**, shown in Scheme 3, which possess four, eight and 16 peripheral ferrocenyl moieties, directly bonded to the external silicon atoms of the organosilicon dendritic framework.

On the other hand, the high reactivity of the Si–Cl bonds toward the amine groups, also allowed facile organometallic functionalization of the surface of dendrimers. In this synthesis the key organometallic monomer was (β-aminoethyl)ferrocene, $(\eta^5\text{-}C_5H_4CH_2CH_2NH_2)Fe(\eta^5\text{-}C_5H_5)$, which was selected because the amino reactive group is two methylene units removed from the ferrocene nucleus (Scheme 2). This fact is of critical importance because minimises steric and electronic effects due to the organometallic moiety, and likewise, the instability found in α-functional ferrocene derivatives, due to the α-ferrocenyl carbonium ion stability is removed. Treatment of the Si–Cl functionalized dendrimers with the appropriate mole ratios of (β-aminoethyl)ferrocene in toluene, at reflux temperature, and in the presence of triethylamine as the acid acceptor, yielded the desired macromolecules **10–12**, which remarkably possess four, eight, and 16 Si–NH linked ethylferrocenyl moieties, attached to the surface of the dendritic structure [22,32] (Scheme 4).

A third type of reaction was attempted on the dendritic surface, which involves the use of silicon hydride-terminated dendrimers. This strategy is based in our earliest synthetic efforts focused toward the incorporation of ferrocenyl moieties into polyfunctional siloxane frameworks, via hydrosilylation reactions of vinylferrocene ($(\eta^5\text{-}C_5H_4CH{=}CH_2)Fe(\eta^5\text{-}C_5H_5)$), with the SiH-containing 1,3,5,7-tetramethyl-cyclotetrasiloxane and octakis(hydrodimethylsiloxy)octa-silsesquioxane,



Scheme 1. Examples of peripherally functionalized organosilicon dendrimers.

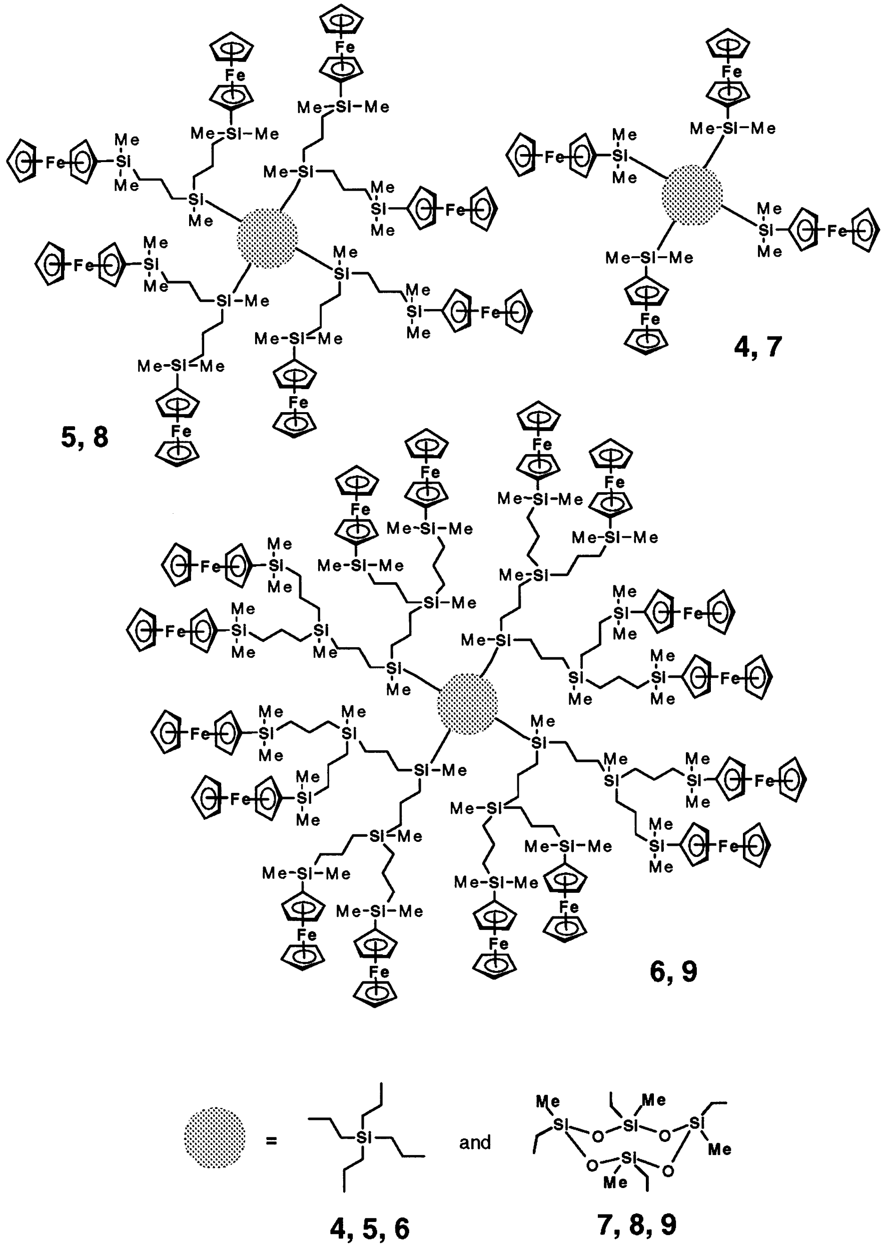


Scheme 2. Schematic representation for the functionalization of silicon-based dendrimers using ferrocenyl moieties.

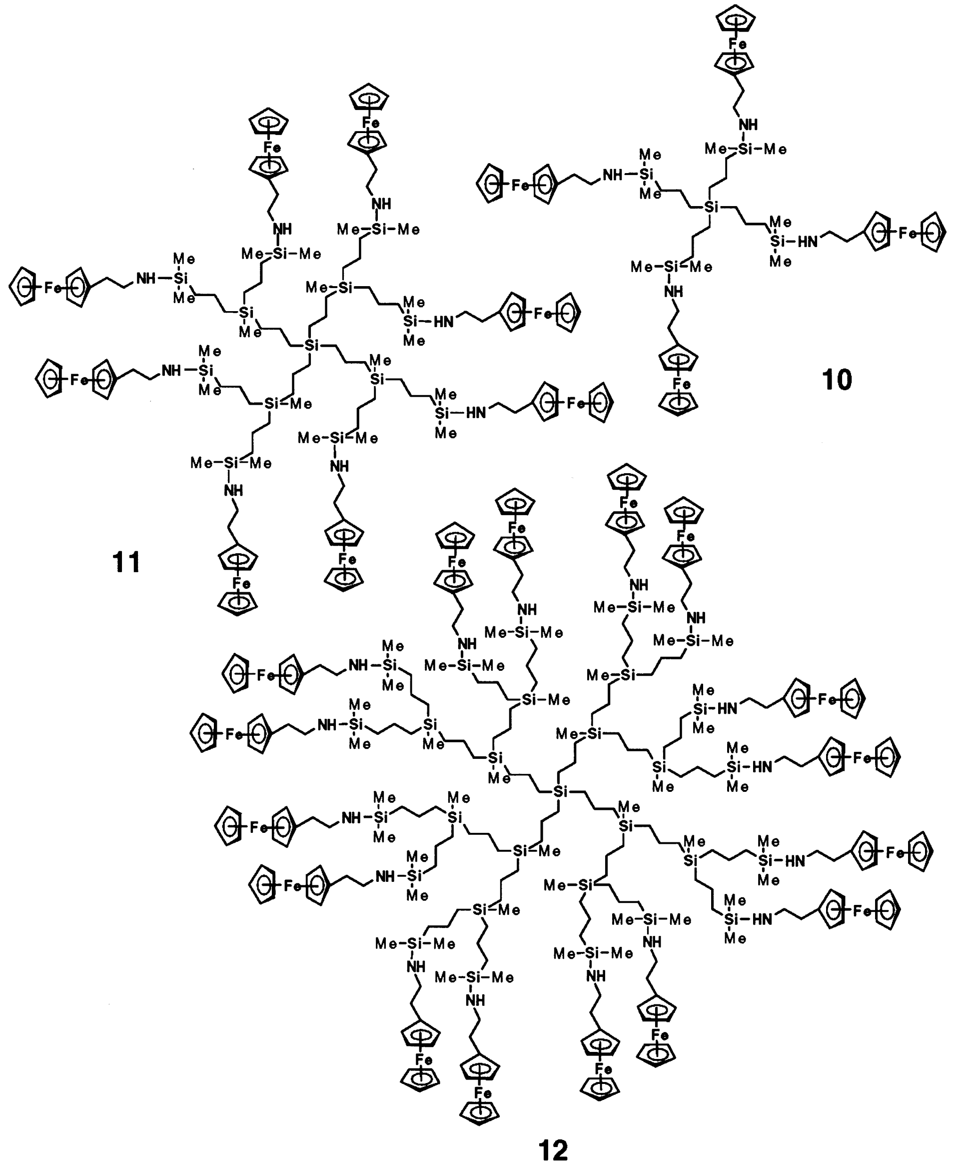
which successfully provide multimetallic redox-active molecules such as **13** and **14** (Scheme 5) [24,26]. In view of these results, the hydrosilylation reactions of Si–H peripherally functionalized dendrimers with the appropriate equivalents of vinylferrocene, in the presence of catalytic amounts of Karstedt catalyst (bis(divinyltetramethyldisiloxane)platinum(0)), in toluene as solvent, were investigated [23] (Scheme 2). These reactions cleanly afforded the novel ferrocene dendrimers **15**–**17**, in which the external silicon atoms of the dendritic core units are attached to ferrocenyl moieties through a two-methylene flexible spacer (Scheme 6).

It is noteworthy to mention that the chemistry necessary to perform the syntheses described above appeared to be well in hand and suitable for incorporation of organo-transition metal units into dendrimeric structures. Likewise, the synthetic routes we have employed are of potentially broad applicability for designing novel organo-transition metal dendrimers, because permit structural variation in the starting organosilicon frameworks (by changing the nature and multiplicity of the initiator core, the degree of branching, and the length of the branches), as well as variation of the organometallic functionality.

The structures of the novel ferrocenyl dendrimers were straightforwardly established by a variety of spectroscopic and analytical techniques including NMR and IR spectroscopies, FAB MS, MALDI-TOF MS, molecular weight determination



Scheme 3. Dendrimers containing ferrocenyl units directly bonded to an external silicon atom.



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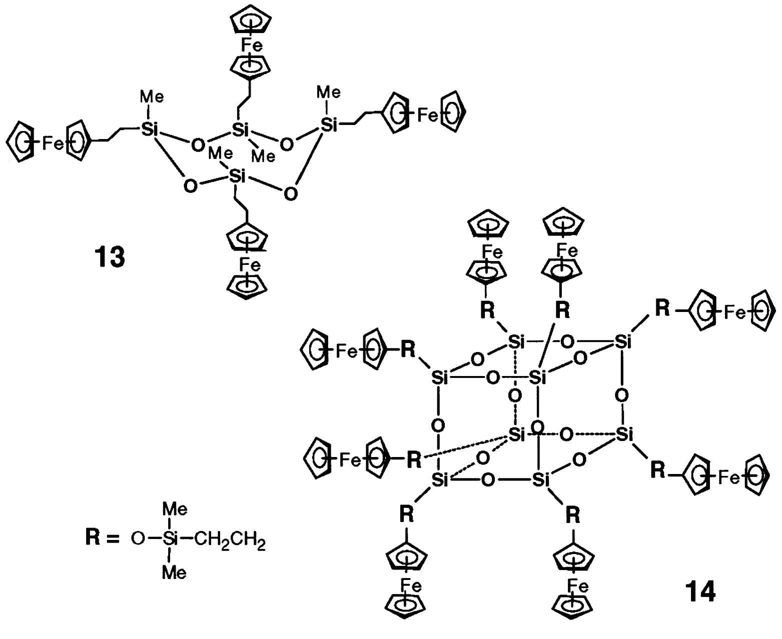
Scheme 4. Dendrimers containing Si–NH linked ferrocenyl moieties on the surface.

(VPO), as well as elemental analysis. It is interesting to note that the high symmetry of these dendrimers has made NMR spectroscopy a useful technique for their characterisation, and ^{1}H-, ^{13}C- and ^{29}Si-NMR spectra have provided confirming evidence for the complete functionalization of the peripheral sites in the organosilicon dendritic cores with ferrocenyl moieties. Thus for example, in the ^{29}Si-NMR spectra of dendrimers **5** (Fig. 1(A)) and **16** (Fig. 1(B)) the corresponding peaks appear clearly separated and can be easily assigned on the basis of the peak intensities, although the chemical environments around the three different silicon atoms are very similar.

Attempts to isolate the ferrocenyl dendrimers described above in a crystalline form suitable for X-ray structural determination have so far been unsuccessful. For this reason, we have used computer-generated molecular models in order to gain further information about the nature of the three-dimensional structures of these dendritic materials. Fig. 2 illustrates two energy-minimised structures determined from CAChe™ molecular mechanic calculations of two ferrocenyl dendrimers grown from silicon-containing cores of different constitution. From these studies we have measured approximate diameters of 2, 3 and 4 nm for the first, second and third generation dendrimers, respectively.

2.1.1.1. Electrochemical properties. The incorporation of redox-active organometallic units at well-defined locations within dendrimeric structures is an especially challenging objective, because such molecules are good candidates to play a key role as multielectron-transfer mediators in electrocatalytic processes of biological and industrial importance. In particular, the ferrocene moiety is an attractive organometallic redox centre to integrate into dendritic structures, not only because it is electrochemically well behaved in most common solvents undergoing a reversible one-electron oxidation, but in addition such electron removal commonly does not involve fragmentation of the original molecular framework.



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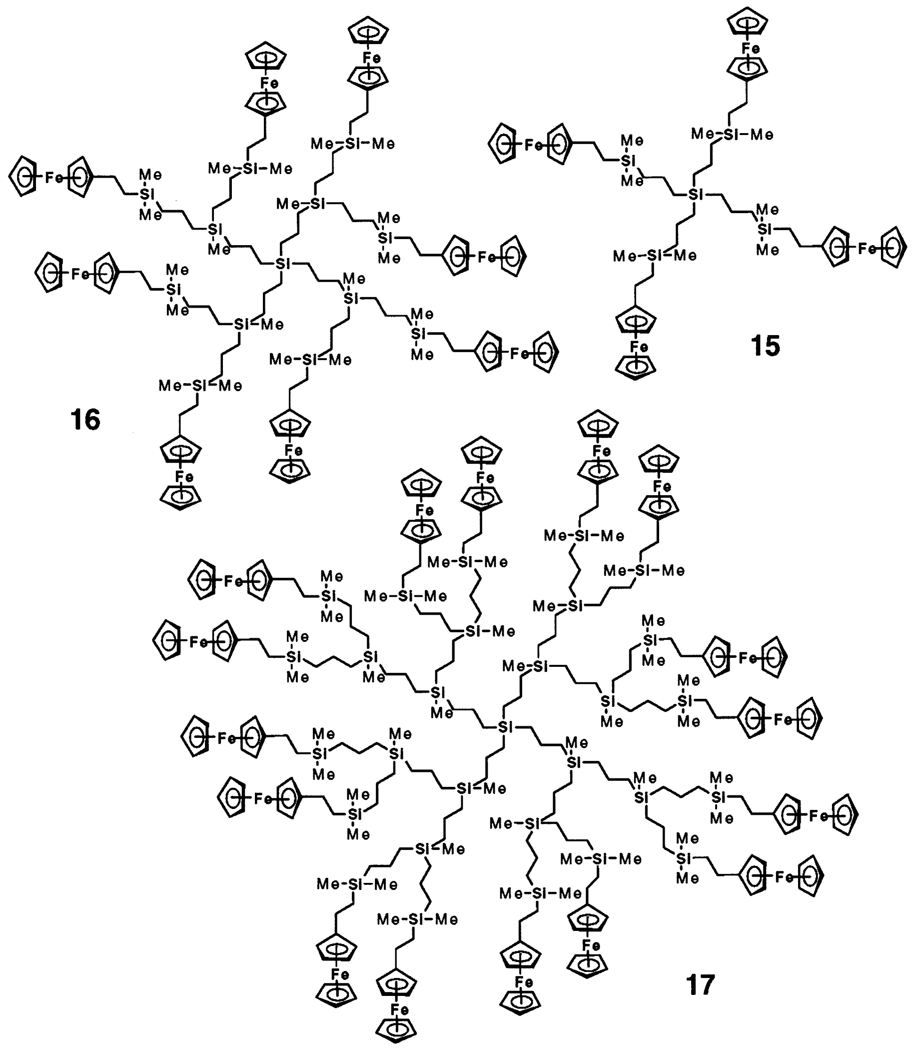
Scheme 5. Cyclosiloxane- and silsesquioxane-based polyferrocenyl molecules.



Scheme 6. Organometallic dendrimers in which the peripheral ferrocenyl groups are attached to the silicon-based framework through a two methylene spacer.

The redox behaviour in solution of the peripherally functionalized ferrocenyl dendritic macromolecules described above has been studied by cyclic voltammetry, differential pulse voltammetry and bulk coulometry [23,32–34]. Cyclic voltammograms show a single reversible oxidation process, at potentials that are a function of the electron-donating ability of the different substituents attached to the cyclopentadienyl rings (see for example Fig. 3(A)). Likewise, in the differential pulse voltammograms only one oxidation wave is observed (Fig. 3(B)). In addition, careful coulometry measurements result in the removal of the expected number of electrons for all the peripheral ferrocenyl groups. These results clearly show that the reversible oxidation wave observed corresponds to a simultaneous multielectron transfer at the same potential, of four, eight or 16 electrons, depending on the dendrimer. Therefore, the multiple ferrocenyl moieties in each dendrimer are independent non-interacting redox-centres.

The most noteworthy aspect of the redox behaviour of the synthesized ferrocenyl silicon-based dendritic macromolecules, having a predetermined number of non-interacting redox centres, is their ability to modify electrode surfaces. In this way, for the first time, electrode surfaces have been successfully modified with films of dendrimers containing reversible four-, eight- and 16-electron redox systems, resulting in detectable electroactive materials persistently attached to the electrode surfaces [34]. The voltammetric response of an electrodeposited film of dendrimer **5** in CH_2Cl_2 solution is shown in Fig. 3(C) as a representative example. A well defined, symmetrical oxidation-reduction wave is observed, which is characteristic of surface-immobilised reversible redox couples, with the expected linear relationship of peak current with potential sweep rate v [35,36].

Ferrocenyl dendrimers also afford electroactive films on indium tin oxide (ITO) electrodes in the same manner as described above. UV-vis spectroelectrochemical measurements of this modified electrodes on oxidation show changes characteristic for the formation of ferrocenium cations, as evidenced by the apparition of an absorption band centred at 600 nm, which agrees with that observed for the corresponding cationic dendrimers obtained by chemical oxidation with $NOPF_6$ [22,34].

2.1.1.2. Electrochemical applications. The molecular recognition of anionic guest species by positively charged or neutral receptors constitutes a relatively new area

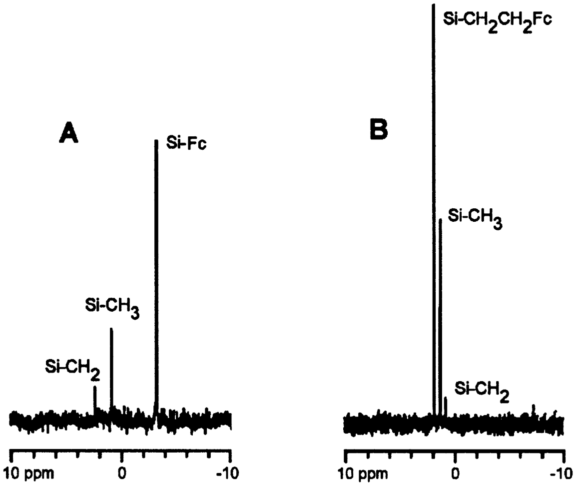


Fig. 1. $^{29}Si\{^1H\}$-NMR spectra at 59.3 MHz in $CDCl_3$, of the octaferrocenyl dendrimers **5** (A) and **16** (B); (adapted from Ref. [22]).

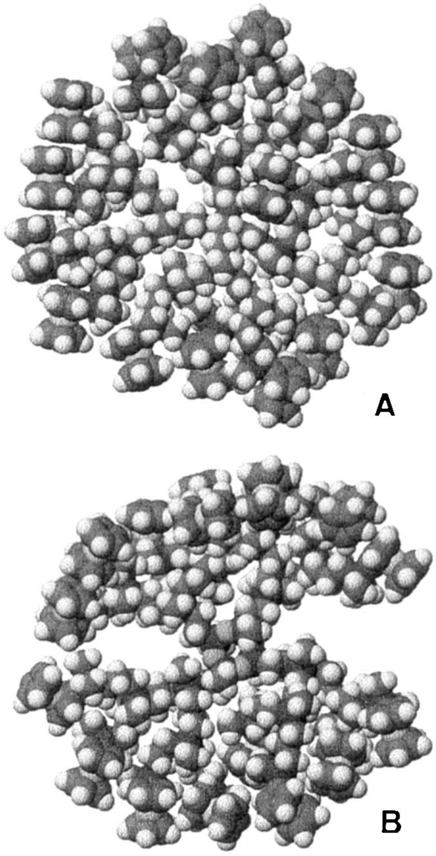


Fig. 2. Computer-generated structures of dendrimers **6** (A) and **9** (B).

of research of growing interest [37] due to the key roles that anions play in biological and chemical processes, as well as the importance of developing novel sensors for environmentally important anions such as nitrate and phosphate. Redox-responsive receptor molecules are able to selectively bind and recognise electrochemically guest species through the perturbation of the redox system provoked by the host–guest interactions.

A key feature concerning ferrocenyl dendrimers **10**–**12** is the presence of multiple Si–NH groups as well as characteristic internal cavities. Thus, these dendrimers can coordinate anion guest species via the cooperative forces of favourable hydrogen bonding interactions in the neutral state and electrostatic attractions after the electrochemical oxidation of the ferrocenyl moieties in the receptor [22,38]. Cyclic voltammograms of dendrimer **11** in CH_2Cl_2 solution, show significant anion induced cathodic perturbations of the oxidation potential of the ferrocene couple. To establish the selectivity of the receptor in the electrochemical recognition, competition experiments were carried out. The results obtained indicated that the dendrimer displays the selectivity trend $H_2PO_4^- > HSO_4^- > Cl^- > Br^-$. It is noteworthy that these dendrimers exhibit selective preferences for the large and tetrahedral anions $H_2PO_4^-$ and HSO_4^-, which could be related to the presence of cavities in the receptor with complementary dimensions to these anions. In addition, it is interesting to note that the voltammetric response of electrodes derivatized with electroactive films of dendrimer **11** is sensitive to the presence and concentration of anions [38].

On the other hand, over the last few years amperometric enzyme electrodes with electroactive species acting as mediators replacing the natural electron acceptor, dissolved oxygen, have been developed. Monomeric mediators such as ferrocene were initially used as electron-shuttling redox couples. The solubility of the oxidised form would inevitably be a source of long-term instability, due to loss of ferroce-

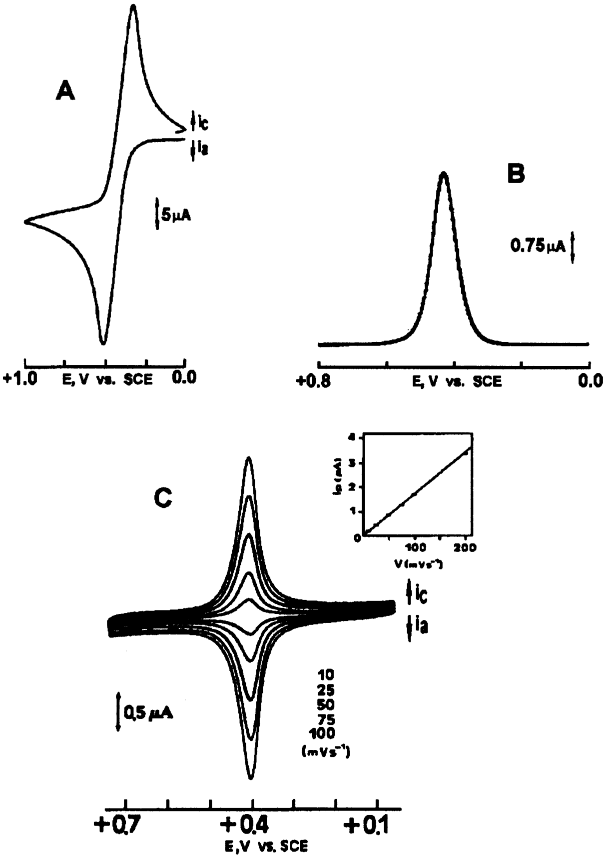


Fig. 3. (A) Cyclic voltammogram measured in $CH_2Cl_2 | 0.1$ M Bu_4NPF_6, at a Pt disk-electrode of dendrimer **5**, (B) differential pulse voltammogram of **5** in $CH_2Cl_2 + CH_3CN$ (14:1), 0.1 M Bu_4NPF_6 solution, (C) cyclic voltammograms of a platinum disk-electrode modified with dendrimer **5** measured in 0.1 M $Bu_4NPF_6 + CH_2Cl_2$. Inset: plot of peak current vs. sweep rate; (adapted from Ref. [34]).

nium ions that can diffuse away from the electrode surface. Increasing the molecular weight of the mediator should significantly decrease this possible loss.

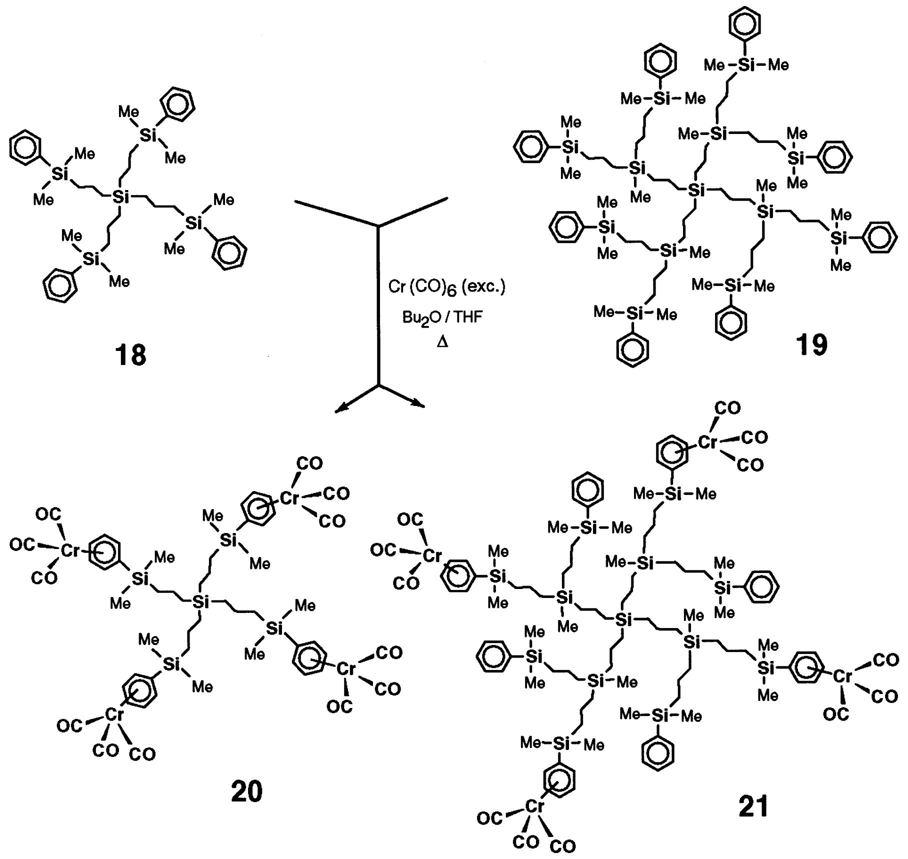
Potentially, our ferrocene-containing dendritic macromolecules with relatively high molecular weights and in which the ferrocenyl units are at the end of long flexible silicon-containing branches can serve to electrically connect the enzyme, facilitating a flow of electrons from the enzyme to the electrode. For this reason, in order to test the ability of ferrocenyl dendrimers **4**, **5**, **15** and **16** to act as electron mediating species, a study of the efficiency of dendrimer | glucose-oxidase | carbon paste electrodes was undertaken [22,39]. Dependence of the glucose response on the dendrimer structure has been examined and the results clearly suggest that the flexibility of the dendritic mediator is an important factor in the ability to facilitate the interaction between the mediating species and the flavin adenine dinucleotide (FAD) redox centres of glucose oxidase. In addition, it has been observed that for sensors based in ferrocenyl dendrimers of the higher generations the mediating ability is enhanced. Studies of comparison with monomeric and polymeric mediators show that the sensors based on the octanuclear ferrocenyl dendrimers **5** and **16** display a similar response to glucose as sensors based on monomeric ferrocene mediators and in addition, they show a better operational stability because their oxidised forms are less soluble than those of the freely diffusing mediators. Furthermore, ferrocenyl dendrimers-based sensors exhibit a higher sensitivity than ferrocene-modified polymers mediated electrodes.

2.1.2. Carbonyl-containing dendrimers

In order to search new synthetic strategies to build up novel families of organometallic dendritic macromolecules, we explored pathways that allow the efficient π-coordination of transition metals to terminal arene ligands on organosilicon dendrimers. Particularly, we focused on polynuclear chromium carbonyl derivatives in which $Cr(CO)_3$ moieties are π-bound to peripheral arene rings directly attached to organosilicon dendritic core units. Our interest in these systems derives from our earlier investigations of a series of chromium tricarbonyl mono-, di- and polymetallic compounds containing reactive organosilane groups on the arene rings [40].

The key silicon-based dendrimers **18** and **19** functionalized at the periphery with aromatic rings (Scheme 7), were prepared following a divergent approach starting with tetraallylsilane as four-directional, tetrahedral centre of branching [41]. Subsequently the incorporation of $Cr(CO)_3$ moieties into the organosilicon dendritic polyfunctional core **18** involved thermal replacement of CO from chromium hexacarbonyl by the peripheral phenyl groups in the dendrimer, in the donor solvent medium of dibutylether/tetrahydrofurane (9/1) at 140°C, affording the first generation tetrametallic dendrimer **20**. In contrast, functionalization of the eight phenyl-terminated dendrimer arms of **19** with $Cr(CO)_3$ units afforded the partially metalated organosilicon dendrimer **21** as the major reaction product.

The high symmetry of the tetranuclear molecule **20** makes structural verification by NMR spectroscopy very simple. For example, in its ^1H-NMR spectrum (Fig. 4(B)) the complete η^6-coordination of the $Cr(CO)_3$ moieties to the four phenyl rings



Scheme 7. Phenyl-terminated dendrimers and functionalization with $Cr(CO)_3$ units.

in the dendritic silicon core was evidenced by the total absence of resonances in the range 7.37–7.53 ppm, in which the arene ligand resonances of the non-coordinated organosilicon dendrimer **18** are observed (see Fig. 4(A)). The integration of resonances confirms the tetrafunctionalization. Further evidence for the dendritic structures was also provided by ^{13}C- and ^{29}Si-NMR spectroscopy, FAB mass spectrometry and elemental analysis. In addition, cyclic voltammetric studies of these metallodendrimers showed one reversible oxidation wave at $E_{1/2} = +0.8$ V versus SCE, which formally corresponds to the oxidation of the zero valent chromium centres to the chromium(I) oxidation state. Thus, the peripheral tricarbonyl chromium moieties are independent, non-interacting redox centres and are oxidizable at the same potential.

Within organometallic chemistry, cyclopentadiene is perhaps the most important and widely used ligand. Indeed, cyclopentadienyl derivatives, π- or σ-bonded to the central atom, are known for all transition metals. For this reason we thought that a stimulating challenge in the synthetic research on organometallic dendrimers would be the incorporation of the cyclopentadienyl ligand into well defined dendritic structures, because it offers an enhanced variability in the designed generation of novel families of highly structured organometallic macromolecules.

To pursue this aim, the reaction of the sodium cyclopentadienide anion with a tetrafunctionalized Si–Cl dendrimer in THF solution was performed, affording successfully the desired cyclopentadienyl-functionalized organosilicon dendrimer **22** shown in Scheme 8 [42]. The coordinating ability of these surface located cyclopentadienyl ligands was assessed via the reaction with octacarbonyldicobalt. Treatment of **22** with $Co_2(CO)_8$ in CH_2Cl_2 at reflux temperature, and in the presence of 1,3-cyclohexadiene, afforded the desired brown-red derivative **23**. Support of the η^5-coordination of the cyclopentadienyl ligands to the $Co(CO)_2$ moieties included the characteristic transformations of the cyclopentadienyl ring resonances in the ^{1}H- and ^{13}C-NMR spectra, as well as the presence of the two typical ν(C≡O) bands in the IR spectrum of **23**, which are in accord with the proposed structure.

Likewise, an additional evaluation of the functionalization of the surface groups of the SiCl-terminated dendrimer was effected by its treatment with a THF solution of the carbonyl anion, $Na^+[\eta^5\text{-}C_5H_5Fe(CO)_2]^-$, affording the tetranuclear dendrimer **24**, which contains silicon-iron σ-bonds at the periphery.

On the other hand, the reactivity of octacarbonyldicobalt toward Si–H functionalized organosilicon derivatives also offered a good chance to gain an easy synthetic access to a novel tetrametallic dendrimer **25**, which bears the organometallic

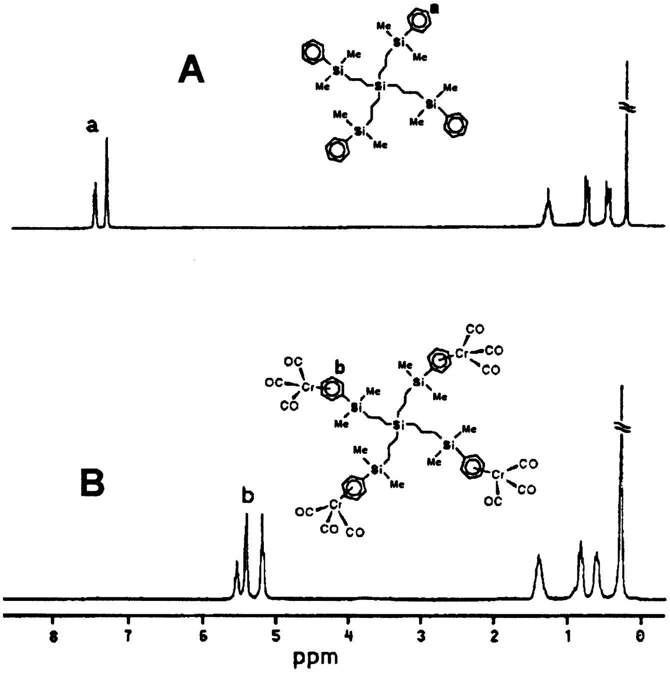
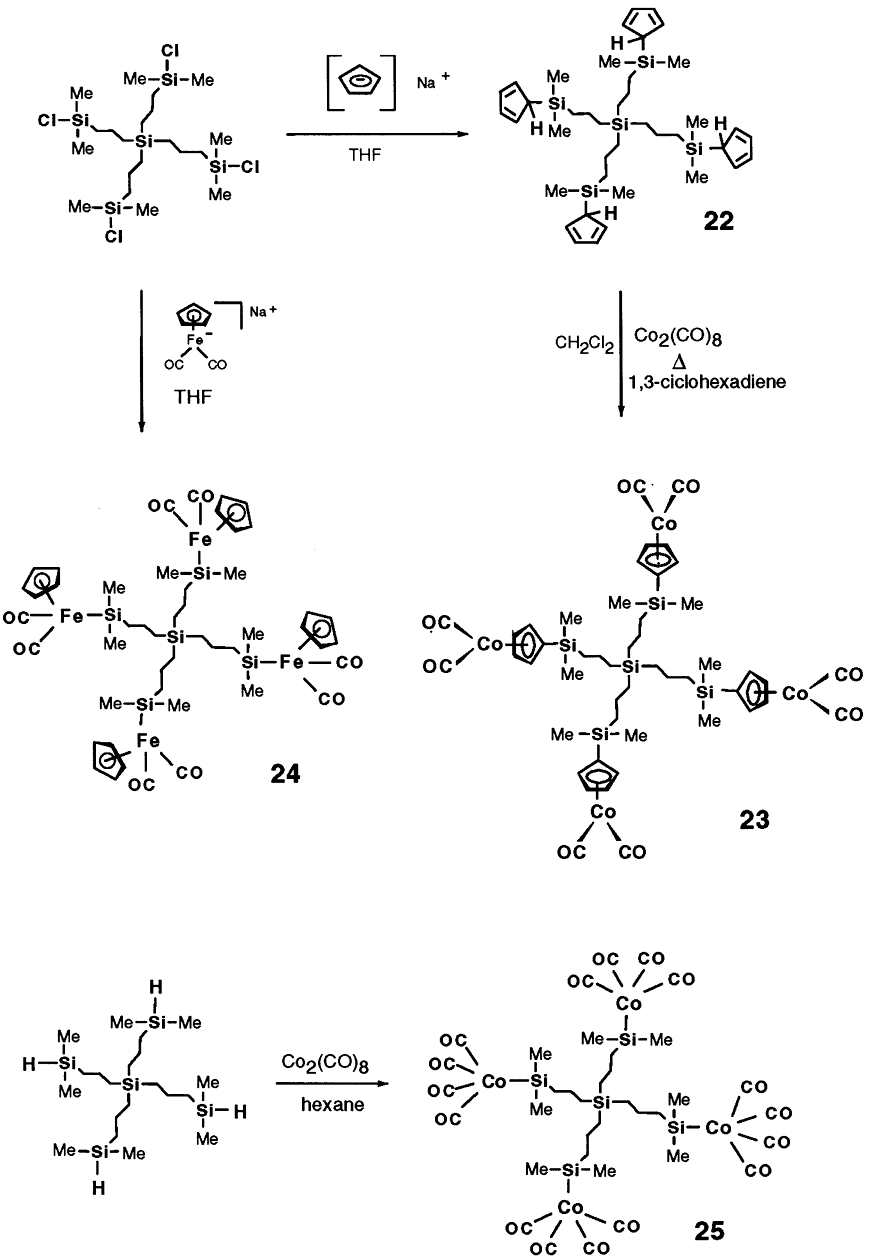


Fig. 4. ^{1}H-NMR (360 MHz in $CDCl_3$) spectra of dendrimers **18** (A) and **20** (B); (adapted from Ref. [41]).

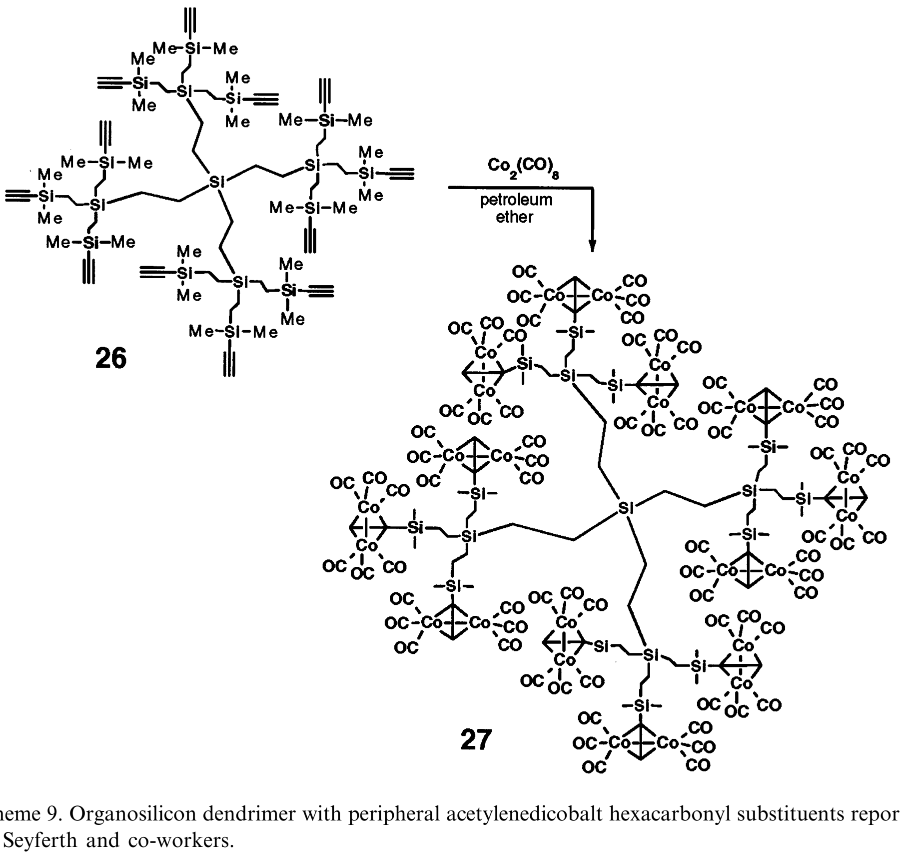


Scheme 8. Organometallic dendrimers with peripheral Si–cyclopentadienyl, Si–Co and Si–Fe σ–bonds.

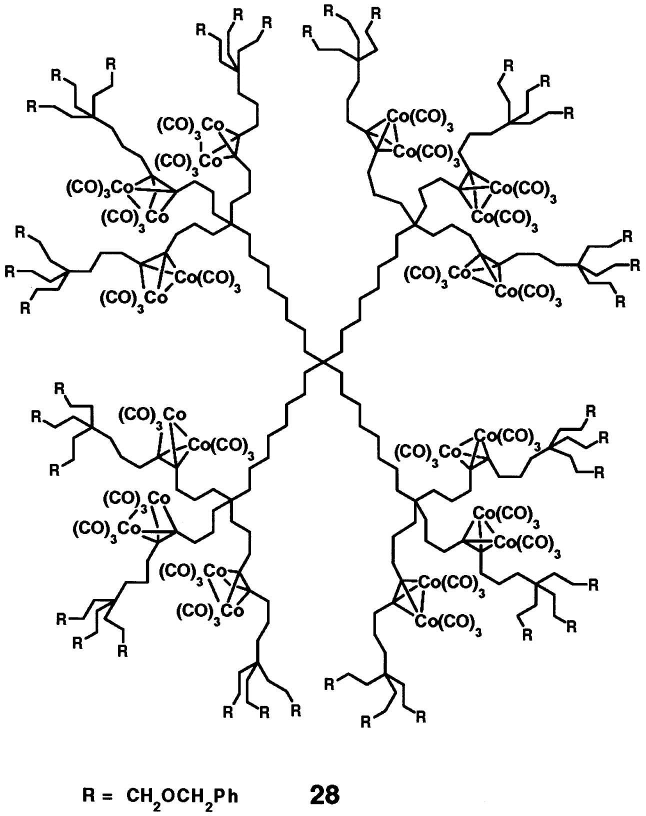
moieties directly attached to the dendritic framework through silicon–metal σ-bonds (Scheme 8) [42].

Seyferth et al. [43] reported the construction of silicon-based dendrimers bearing peripheral ethynyl substituents of the type exemplified by **26** (Scheme 9). The reaction of these dendrimers with $Co_2(CO)_8$ affords the first- and second-generation dendrimers functionalized with acetylenedicobalt hexacarbonyl units such as **27**. The structure of the first generation cobalt-containing dendrimer was determined by X-ray diffraction studies.

Although it is not an example of silicon-based dendrimers, it should be mentioned here that Newkome and Moorefield had previously used this same reaction of polyalkynes with $Co_2(CO)_8$ to introduce metal centres at specific sites within the interior of dendritic structures. In particular, by using polyalkyne precursors to unimolecular micelles (called Micellanes™ due to the topological resemblance to globular micelles), they prepared hydrocarbon-based carbonyl-containing dendrimers such as **28** possessing 24 internal metal centres (Scheme 10), which have been termed Cobaltomicellanes™ [44].



Scheme 9. Organosilicon dendrimer with peripheral acetylenedicobalt hexacarbonyl substituents reported by Seyferth and co-workers.



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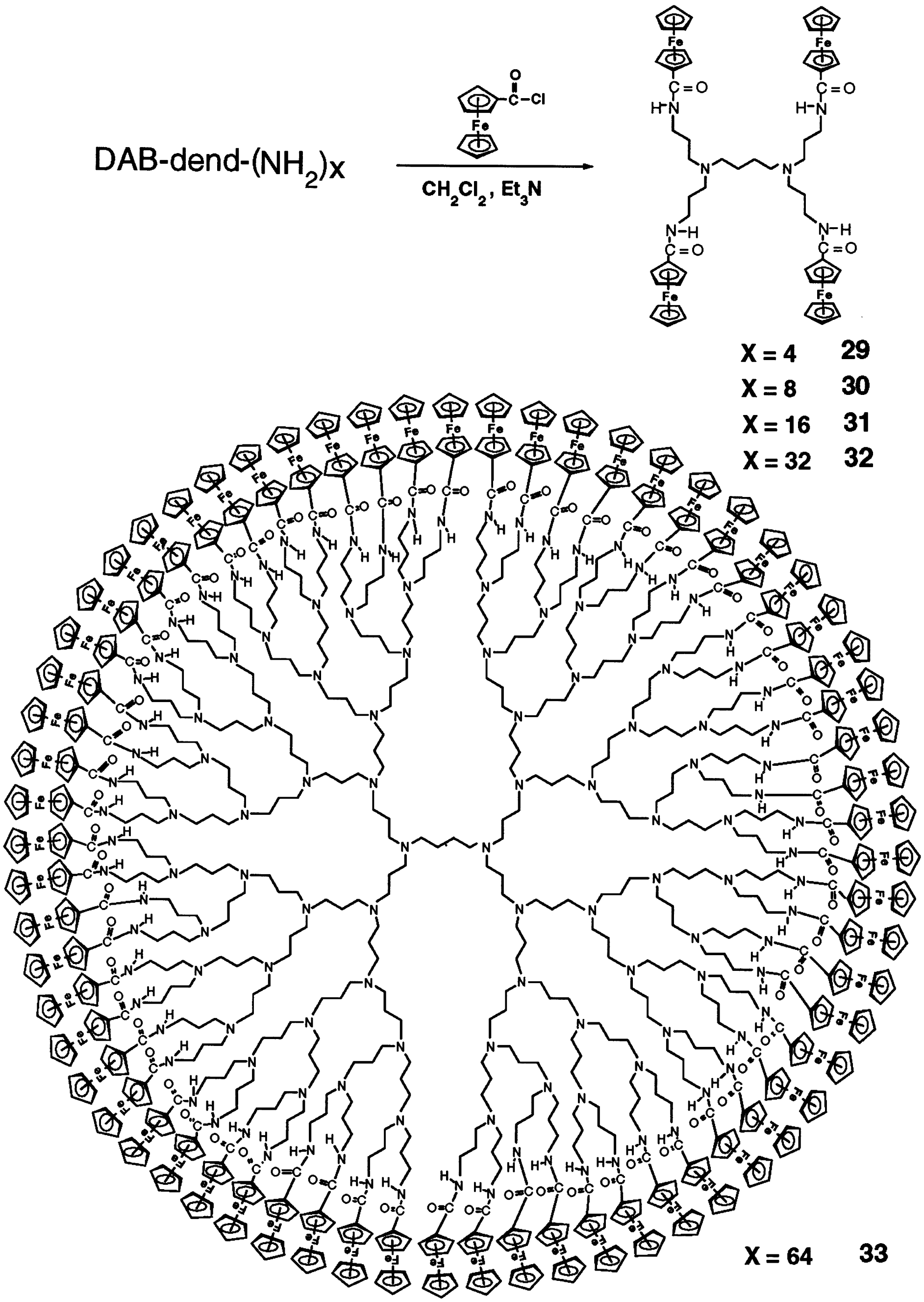
Scheme 10. Hydrocarbon-based dendrimer with internal acetylenedicobalt hexacarbonyl units prepared by Newkome et al..

2.2. Nitrogen-based organometallic dendrimers

An attractive synthetic target in the chemistry of dendrimers is the construction of very large dendrimeric molecules. For this reason, in order to achieve a higher degree of organometallic functionalization in dendritic structures, we have used commercially available dendrimers DAB-dend-$(NH_2)_x$ ($x = 4$, 8, 16, 32, and 64), containing nitrogen as branching point and possessing $(CH_2)_3$ spacer moieties, which have been constructed divergently up to the fifth generation, starting from 1,4-diaminobutane (DAB) as the dendritic core. Thus, the presence of NH_2 terminal groups in these poly(propylene imine) dendritic molecules has allowed the surface of dendrimers to be covered with up to 64 peripheral ferrocenyl moieties, via condensation reactions with 1-chlorocarbonylferrocene, as shown in Scheme 11 [45]. The structures of the new peripherally functionalized ferrocenyl dendrimers DAB-dend-$(NHCOFc)_x$ (Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$, $x = 4$, 8, 16, 32, and 64, **29**–**33**) have been established on the basis of ^{1}H-, ^{13}C-NMR and IR spectroscopy,



X = 4 **29**
X = 8 **30**
X = 16 **31**
X = 32 **32**

X = 64 **33**

Scheme 11. Functionalization of DAB-based poly(propylene imine) dendrimers with up to 64 ferrocenyl moieties.

mass spectrometry (FAB and MALDI-TOF MS), and elemental microanalysis. The transition from a small organometallic molecule to a polymer-like structure, on going from the first to the fifth generation, was clearly evident by the peak broadness in the ^{1}H NMR spectra (Fig. 5). Likewise, it is interesting to note that the chemical shifts of the protons corresponding to the amide spacer groups residing on the surface of the poly(propylene imine) dendrimers vary in a generation-dependent manner. This observation is consistent with the participation of NH and C=O groups in hydrogen bonds. This NH...O hydrogen-bonding effect is

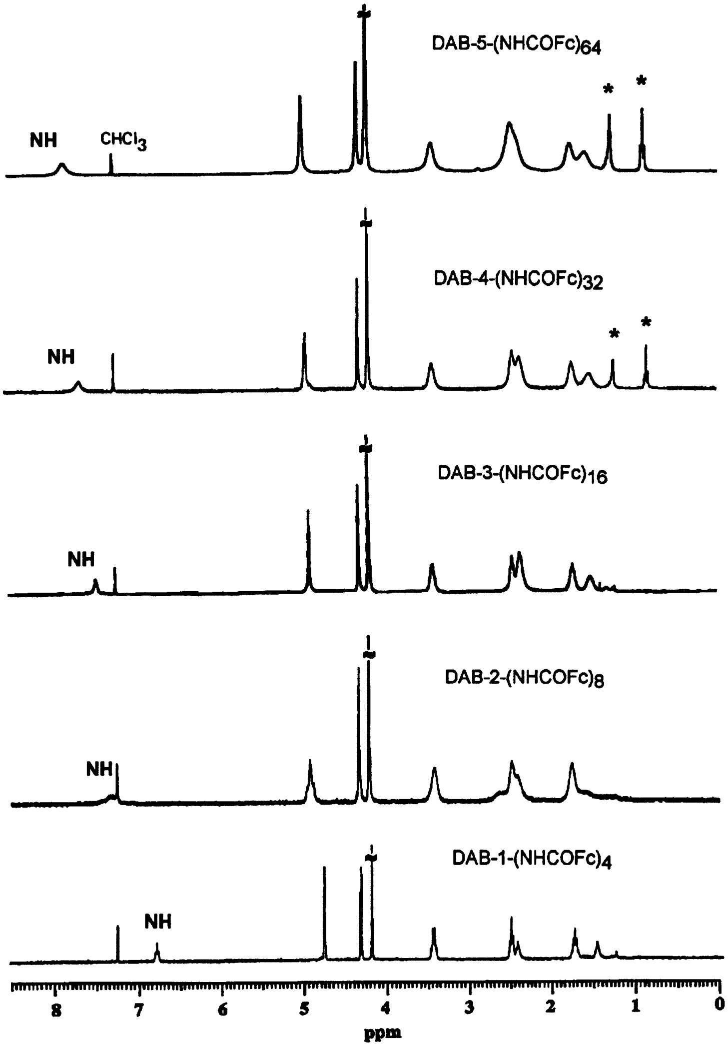


Fig. 5. ^{1}H-NMR (300 MHz, $CDCl_3$) spectra of dendrimers **29**–**33**, * occluded hexane; (adapted from Ref. [45]).

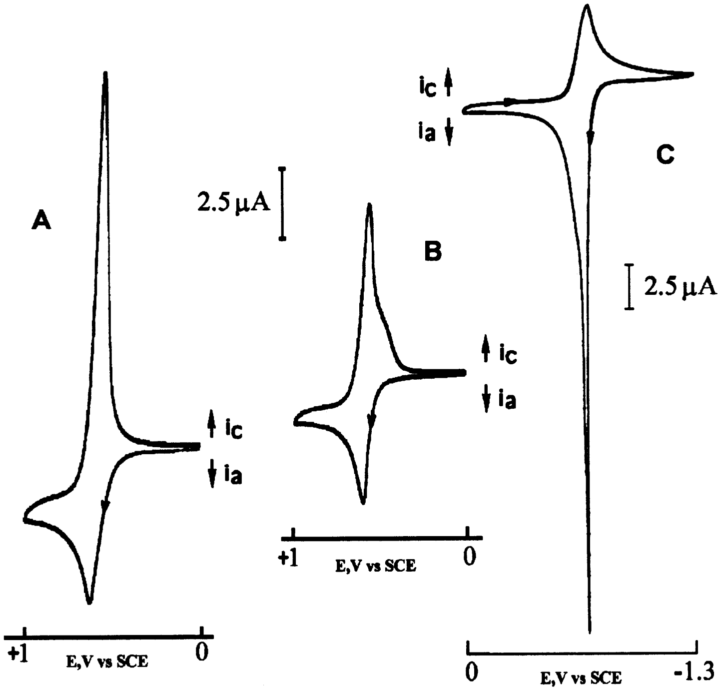


Fig. 6. Cyclic voltammograms of (A) dendrimer **30** (in CH_2Cl_2), (B) dendrimer **33** (in CH_2Cl_2), (C) dendrimer **34** (in CH_3CN). Supporting electrolyte: 0.1 M Bu_4NPF_6, Pt disk electrode, scan rate 100 mV s^{-1}; (adapted from Ref. [45]).

reasonably larger in the higher generations because the presence of bulky molecular skeletons, in which the peripheral ferrocenyl moieties on adjacent dendritic branches are in close contact, leads to a greater number of NH...O intramolecular hydrogen bonds.

Solution cyclic voltammetric studies of these functionalized poly(propylene imine) dendrimers showed a single oxidation wave, indicating that all the ferrocenyl redox centres attached to the dendritic surface are electrochemically independent. Thus, the organometallic dendrimers exchange all the electrons simultaneously at the same potential. In addition, it is worth noting that the redox behaviour of the ferrocenyl dendrimers in CH_2Cl_2 or THF solvents is marked by changes in solubility with the change in the oxidation state of the ferrocene units on the dendritic surface. Whereas the anodic wave has a typical diffusional shape, in contrast, a sharp cathodic stripping peak was observed (Figs. 6(A and B)), which indicates the precipitation of the dendrimers onto the electrode upon oxidation. In addition, for all dendrimers upon continuous scanning in either CH_2Cl_2 or THF, there is an increase in the peak current with successive scans, which indicates that the formation of an electroactive film occurs on the electrode surface. These oxidative precipitation effects have allowed the modification of electrode surfaces with films of these dendrimers.

Likewise, we have studied the thermodynamics and kinetics of adsorption of the redox-active ferrocenyl dendrimers using electrochemical and electrochemical quartz crystal microbalance (EQCM) techniques [46]. These studies show that the oxidised form of the dendrimers deposits onto the Pt electrode, likely due to the low solubility of the salts of oxidised dendrimers, whereas the reduced form of the dendrimers easily redissolves except for the first monolayer, which appears to be strongly adsorbed. Further, the mass transfer process during the redox reaction of the adsorbed dendrimers in CH_3CN solution was found to be of the anion exchange type. In addition, it was determined that the anions (ClO_4^-) are accompanied by solvent molecules (CH_3CN), whose numbers appear to depend on the charge density (density of ferrocenyl groups) of each dendrimer.

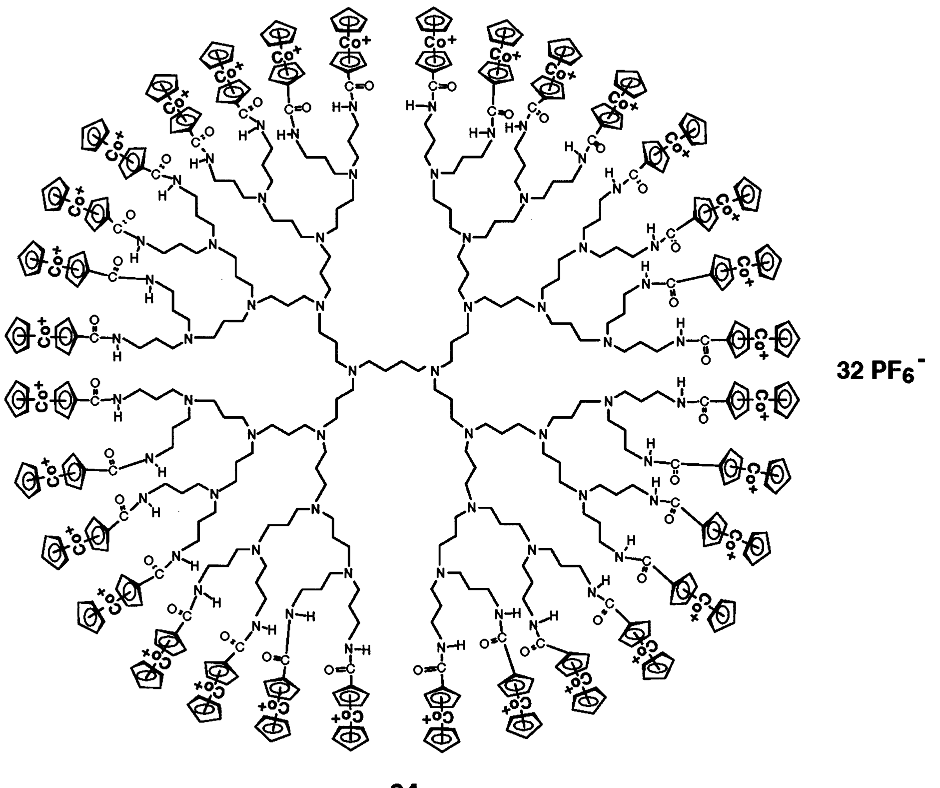
On the other hand, we have been able to obtain molecularly resolved images of the dendrimer with 64 peripheral ferrocenyl units adsorbed onto a Pt (111) single crystal electrode, using tapping mode atomic force microscopy (TMAFM) [46]. The analysis of these images suggests that the apparent size of the adsorbed dendrimer is significantly larger than the calculated value. We believe that this is due, in part, to a convolution of the tip profile and the sample as well as to a flattening of the dendrimer upon adsorption.

The synthetic strategy involving condensation reactions of DAB-based polyamino dendrimers has been extended to the construction of new cationic dendrimers having 4, 8, 16 and 32 peripheral cobaltocenium units [47]. Dendrimer **34** shown in Scheme 12, is the largest molecule of this family prepared so far. These metallodendrimers have been fully characterised by IR and ^1H- and ^{13}C-NMR spectroscopies, FAB and electrospray mass spectrometry. Likewise, their electrochemical behaviour has been studied both in aqueous and acetonitrile solution. All cobaltocenium dendrimers exhibit similar cyclic voltammograms as that of dendrimer **34** shown in Fig. 6(C). Thus, as it can be observed, the voltammetric response is characterised by an extremely sharp anodic peak which indicates that the electrogenerated neutral cobaltocene dendrimer precipitates on the electrode surface.

A key feature of both ferrocene and cobaltocenium functionalized poly(propylene imine) dendrimers is their ability to act as multisite, redox active guests for inclusion complexation by β-cyclodextrins (β-CD), giving rise to high molecular weight, supramolecular species. Thus, in the case of the ferrocenyl dendrimers, electrochemical and spectroscopic data along with the competitive binding experiments indicate that the aqueous solubility of these hydrophobic dendritic molecules results from the inclusion complexation of the ferrocenyl moieties in the dendrimers by the CD hosts in the solution [48]. The enhancement in solubility decreases with increasing dendrimer generation, since more ferrocenyl moieties are packed on the surface of the guest and therefore the individual complexation events become sterically hindered. In contrast, cyclic voltammetric studies show that while the positively charged cobaltocenium-containing dendrimers are not complexed by β-cyclodextrin in aqueous media, their electrochemical reduction triggers their binding interactions with β-CD hosts [47]. The formation of these multisite inclusion complexes affords a very interesting example of electrochemical activation of molecular recognition forces.

Astruc et al. have also reported stable polycationic metallodendrimers which were prepared from condensation reactions of a nona-amine and chlorocarbonyl cyclopentadienyl–metal sandwiches of iron and cobalt [49]. Following a similar synthetic approach, they have synthesized another family of dendritic molecules containing peripheral amide-linked ferrocenyl units, such as dendrimer **35** (Scheme 13) and its less branched analogues [50]. These metallodendrimers have been used as supramolecular redox sensors for the recognition of inorganic anions. Interestingly, cyclic voltammetric studies show that the ability of these dendrimers to achieve a better sensing and recognition of anions increases, as the dendritic generation becomes higher.

More recently Kaifer and Cardona have reported a series of novel, asymmetric redox-active dendrimers of different sizes containing a single amide-linked ferrocenyl moiety, such as **36** and **37** (Scheme 14) [51]. These organometallic dendritic molecules have been prepared by condensation reaction of 1-chlorocarbonylferrocene with Behera's amine type dendritic molecules [52]. For these dendrimers the measured heterogeneous electron transfer rate constant values (k°), as well as the



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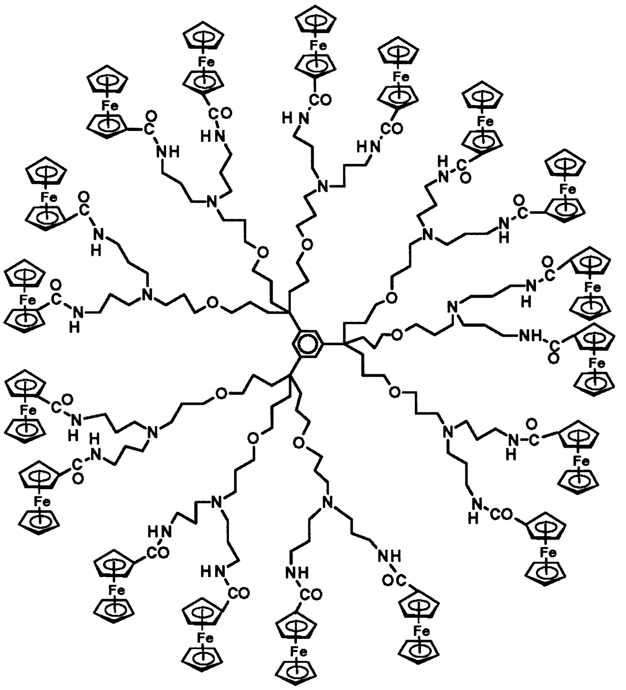
Scheme 12. A DAB-based poly(propylene imine) dendrimer containing 32 cobaltocenium units at the surface.



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Scheme 13. Dendrimer with peripheral amide-linked ferrocenyl units reported by Astruc et al.

apparent diffusion coefficients (D_o), and the half-wave potentials ($E_{1/2}$) for ferrocene oxidation decrease with increasing generation, thus revealing that the dendritic mass has a considerable effect on the thermodinamics and kinetics of the electron transfer reactions of the ferrocene centre. These dendrimers are of interest, since they may exhibit orientation-dependent rates of electron transfer, due to the asymmetric and partially buried location of the redox centre, which is reminiscent of that generally found in numerous redox proteins.

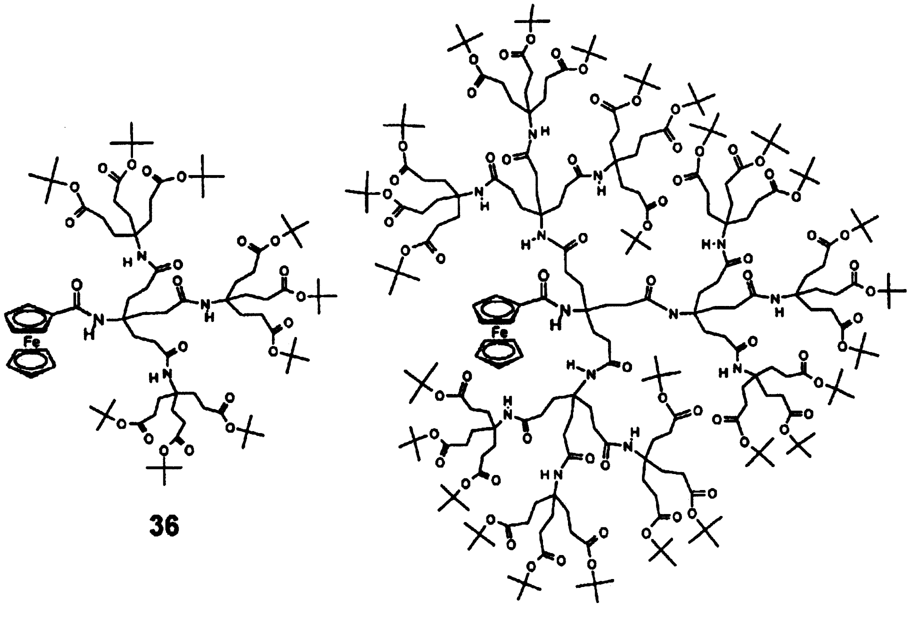
Very recently, Welton et al. have functionalised poly(amido)amine (PAMAM) dendrimers with dithiocarbamate groups which were then reacted with ruthenium derivatives to form novel organometallic dendrimers such as **38** (Scheme 15) [53].

2.3. Phosphorus-based organometallic dendrimers

Majoral and co-workers have reported the surface functionalization of large neutral phosphorus-containing dendrimers with organometallic moieties. The dendritic structures, in which the core and subsequent branching points are pentavalent phosphorus atoms, have been constructed divergently up to the tenth generation [54]. The remarkable synthesis of these phosphorus dendrimers starts with $P(S)Cl_3$ which was reacted with the sodium salt of 4-hydroxybenzaldehyde to give the trialdehyde shown in Scheme 16. Subsequent treatment with the hydrazine derivative $H_2NNMeP(S)Cl_2$ affords the first generation dendrimer **39** possessing six P–Cl bonds. Higher generations such as dendrimer **40** have been constructed by repetition of these two steps. It is interesting to note that the only by-products in these syntheses are sodium chloride and water. ^{31}P-NMR was found to be a useful tool to follow the construction of these dendrimers since all phosphorus atoms are distinguishable at each generation by their chemical shifts and by the intensities of the different signals. In addition, a rich surface chemistry has been developed for these phosphorus-based dendrimers. Thus, the periphery of these dendrimeric molecules has been subsequently functionalized with different groups such as aminoacids, crown ethers, amines and phosphines. In particular the excellent coordinating ability of the phosphino-terminated phosphorus-based dendrimers has been used to cover the dendritic surface with various low oxidation state organo-transition metal moieties (see for example dendrimers **41**–**46** in Scheme 16), as well as with a series of Pd, Pt, Rh and Ru complexes [55,56].

3. Dendrimers constructed from organometallic entities

A wide variety of organic and inorganic dendrimers have been successfully prepared by using either divergent [10–13] or convergent [57,58] synthetic ap-



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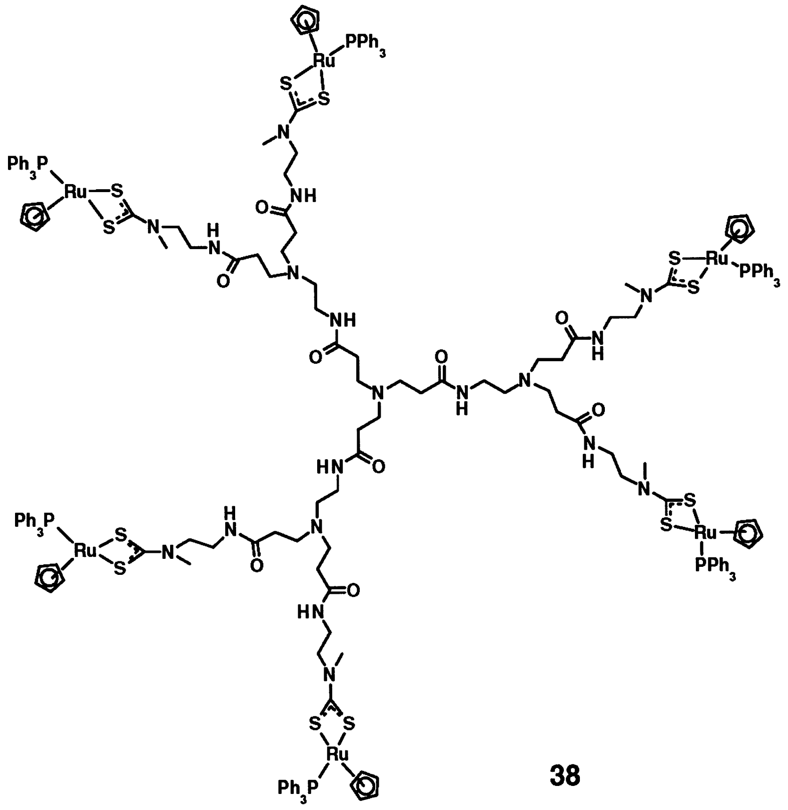
Scheme 14. Asymmetric organometallic dendrimers reported by Kaifer and Cardona.



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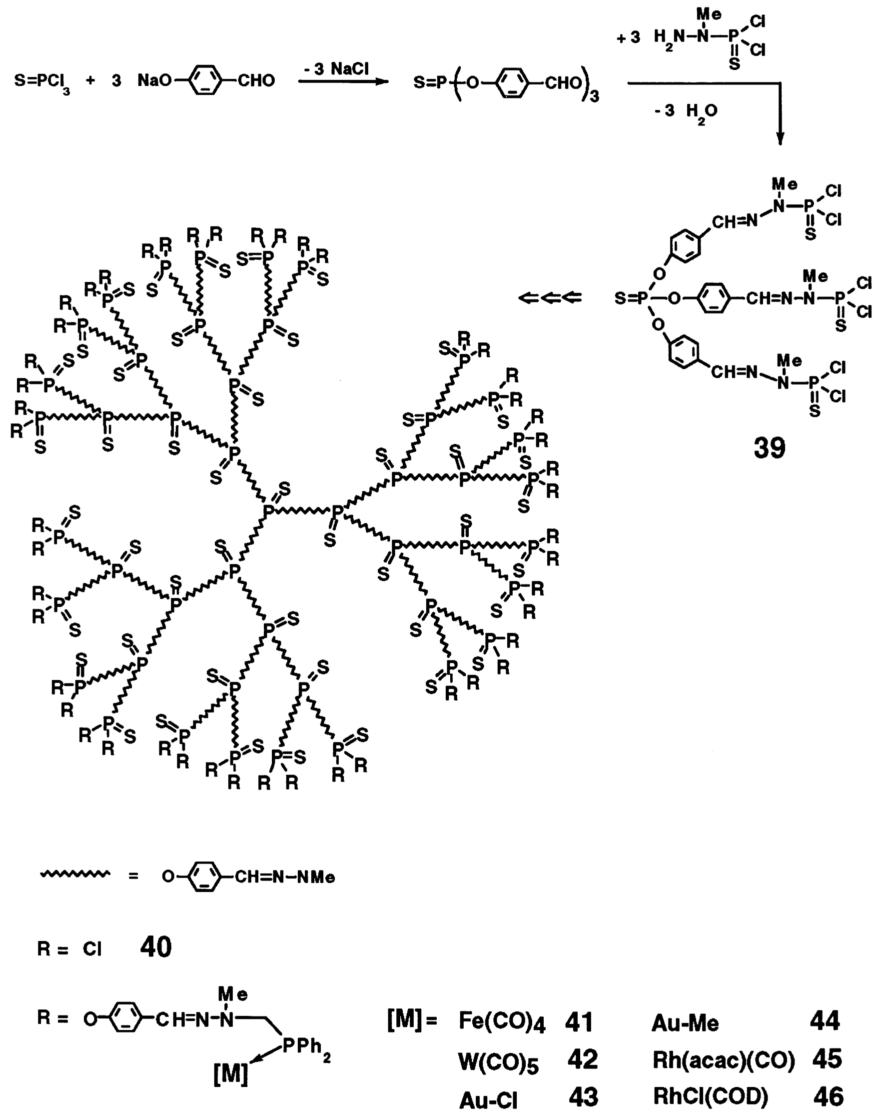
Scheme 15. Welton's dithiocarbamate-functionalized dendrimers as ligands for metal complexes.

proaches. In a similar way, a variety of organo-transition metal dendrimers have been constructed by first preparing suitable organometallic moieties, from which the build-up of the structure was accomplished following also either divergent or convergent growth synthetic strategies. For instance, a divergent approach to organometallic dendrimers involves growth from a polyfunctional organometallic initiator core, where branching outward is accomplished via an increasing number of terminal branches transformations. Without doubt, the main disadvantage of such divergent growth to organometallic dendrimers derives from the fact that a progressively large number of organometallic monomers have to react successfully with the reactive functional groups of the dendrimer surface. Therefore, as a result of the steric hindrance imposed by the steric-demanding organometallic units, at higher generation numbers it becomes extremely difficult to complete the reaction of all the external functionalities of the dendrimer. For this reason, a critical aspect in the divergent strategy is the choice of a suitable organometallic initiator core, in which an appropriate number of reactive sites are conveniently placed, in order to assure that complete functionalization of the branches is accomplished easily, and in relatively high yields. In the alternative convergent approach, the construction of organometallic dendrimers starts at what will ultimately become the outer surface of the dendrimer, and progresses inward. Thus, this approach first requires the synthesis of conveniently functionalized, progressively larger, organometallic dendritic wedges or dendrons in order to be subsequently attached around a polyfunctional central core, resulting in the final organometallic dendrimer. A key



Scheme 16. Majoral's synthesis of phosphorus-based dendrimers and functionalization with organometallic moieties.

requirement of the convergent approach is that the organometallic moiety is stable to the reaction conditions of the stepwise synthesis, since it is introduced at the beginning of the preparation of dendrimers. One attractive advantage of the convergent construction is that by coupling organometallic wedges of different nature to the same core molecule, segment-block or layer-block organo-transition heterometallic dendritic macromolecules may be constructed.

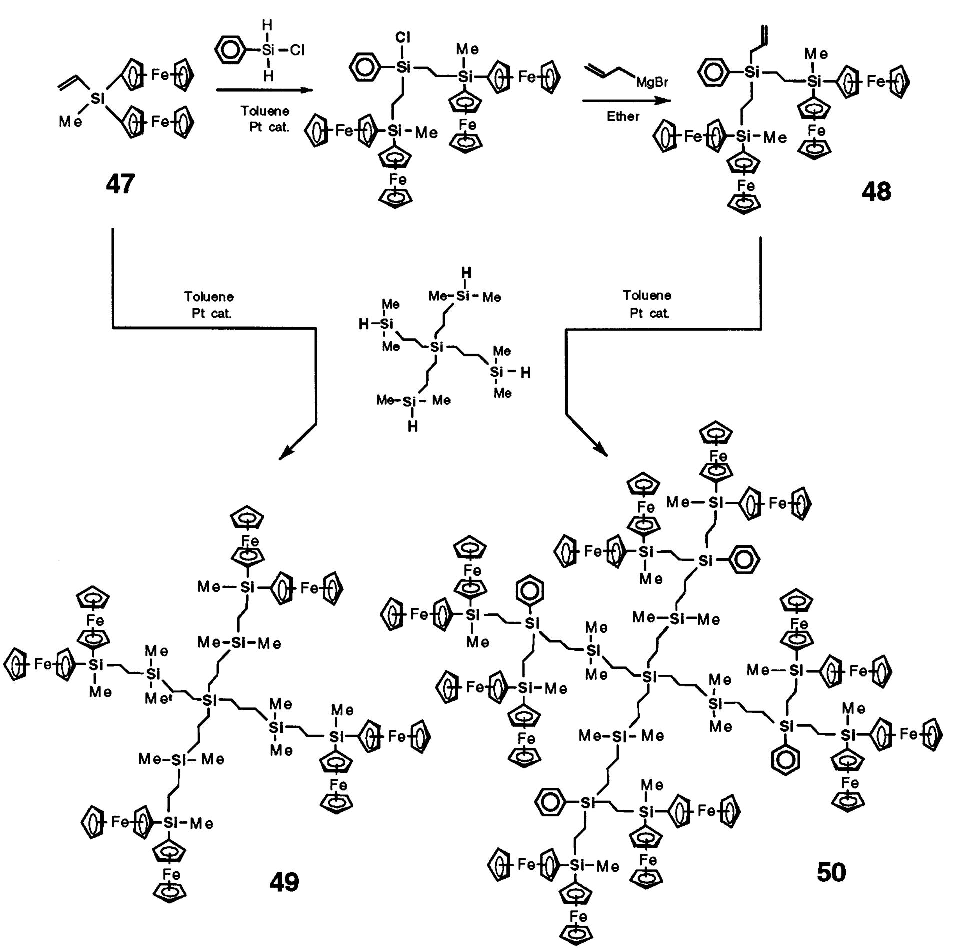
3.1. Convergent approach

In our quest of new series of transition-metal dendritic molecules exhibiting predetermined redox patterns, a challenging synthetic target was the construction of dendrimers possessing redox-active organometallic units linked together in close proximity so that there is electronic communication between the metal sites in the dendritic structure. This would provide access to new multimetallic dendrimers with appreciable electron mobility and consequently with interesting electrical, redox, optical and magnetic properties.

To pursue this aim, following a convergent approach, we have constructed the first and second generations of dendrons and dendrimers possessing ferrocenyl units electronically communicated [59]. The key dendritic wedge for the synthesis of the new dendrimers is the silicon-bridged biferrocene **47** (Scheme 17), which is prepared by the salt elimination reaction of ferrocenyllithium with vinylmethyldichlorosilane, and has been characterised by X-ray studies. Further growth of this first-generation dendron was achieved by hydrosilylation and alkenylation reaction steps affording the desired larger dendron **48**, carrying four ferrocenyl units. The availability of the free carbon–carbon double bonds at the focal point of the dendritic wedges **47** and **48** enables the incorporation of interacting organometallic redox centres in dendritic structures through hydrosilylation reactions with Si–H polyfunctionalized cores, thus following a convergent approach. In this way we have prepared dendrimers **49** and **50** (Scheme 17) containing eight and 16 ferrocenyl moieties on the dendritic surface, respectively. To our knowledge these are the first examples of organometallic dendritic molecules displaying metal–metal interactions in the dendritic structure.

Undoubtedly, the most notable feature of the redox behaviour of the ferrocenyl dendritic structures **47**–**50** is the presence of two well separated and reversible oxidation waves of equal intensity in their cyclic voltammograms (Fig. 7(A)). Likewise, differential pulse voltammetry (DPV) measurements for **47**–**50**, exhibit two separated oxidation waves of the same area (Fig. 7(B)).

The electrochemical behaviour observed for these dendritic molecules can be explained by the existence of significant interactions between the two ferrocenyl units which are linked together by the bridging silicon atom. The first oxidation occurs in the dendritic wedges at non-adjacent ferrocene sites, which makes the subsequent removal of electrons from the remaining ferrocenyl centres, neighbouring those already oxidised, more difficult. The wave splitting ($\Delta E = {}^{2}E_{1/2} - {}^{1}E_{1/2}$) provides information about the degree of interaction between the metal centres. From ΔE, which varies from 190 mV to 160 mV, the comproportionation constant



Scheme 17. Convergent construction of dendrimers with electronically communicated ferrocenyl moieties.

K_c relative to the equilibrium Fe(II)–Fe(II) + Fe(III)–Fe(III) $\rightleftarrows$ 2Fe(II)–Fe(III) was calculated, resulting in values of $K_c = 1630$ to 507, which indicate that the partially oxidised dendritic molecules **47**–**50**, can be classified as class II mixed-valence species according to the Robin–Day classification [60].

Molecules **49** and **50** have been used successfully to prepare dendrimer-modified electrode surfaces. The voltammetric response of an electrodeposited film of dendrimer **49** is shown in Fig. 7(C). Two successive well-defined, reversible oxidation-reduction waves are observed, with formal potential values of $^{1}E_{1/2} = 0.40$ and $^{2}E_{1/2} = 0.55$ V versus SCE. A linear relationship of peak current with potential sweep rate, v, was observed, and the potential difference between the cathodic and anodic peak is smaller than 10 mV at scan rates of 0.1 V s^{-1} or less. These voltammetric features unequivocally indicate the surface-confined nature of the electroactive dendrimer film.

The first convergent approach to organometallic dendritic macromolecules was reported in 1993 by Moss and Liao [61], resulting in dendrimers that contain ruthenium-carbon σ-bonds on the molecule surface. In their strategy they have followed the same convergent methodology developed by Fréchet and Hawker [57] for the synthesis of polyethereal dendrimers. The selected organometallic functionalized monomer was the bromoalkyl ruthenium derivative (η^5-C_5H_5)Ru-$(CO)_2\{(CH_2)_3Br\}$ and the initial organic dendritic building block was 3,5-dihydroxybenzyl alcohol (see Scheme 18). The construction of the organometallic dendron required two synthetic transformations. Firstly, selective alkylations of the phenolic hydroxyl groups in the presence of potassium carbonate and 18-crown-6, afforded the ether dimetallic derivative **51**. This first generation benzyl alcohol was converted to the benzyl bromide **52** by treatment with an excess of PPh_3 and CBr_4. This dendritic wedge **52** was attached to a three-directional trisphenolic core affording the hexametallic dendritic system **53**. Similarly, by reacting a second generation benzyl bromide dendritic fragment with the same trihydroxy core, dendrimer **54** with twelve dicarbonylcyclopentadienyl ruthenium moieties was prepared. More recently [62], this stepwise convergent synthetic methodology has been extended to higher generations and thus, a large dendrimer containing 48

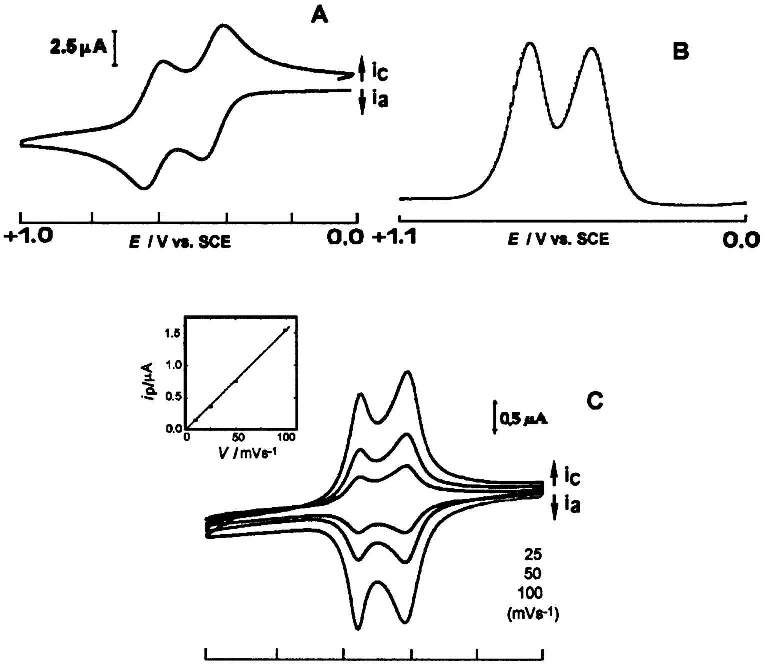
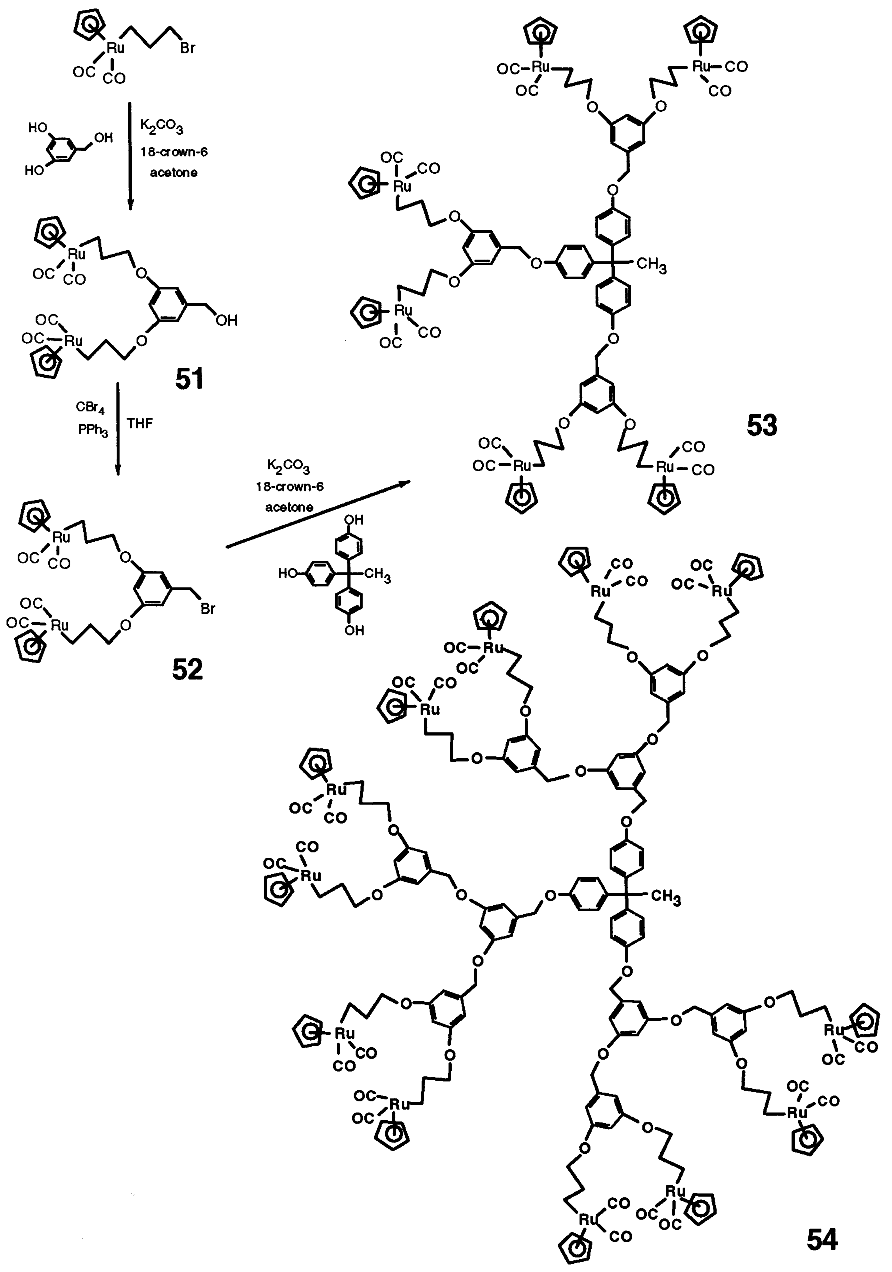


Fig. 7. Cyclic voltammogram (scan rate 100 mV s^{-1}) (A) and DPV (B) of **49** in $CH_2Cl_2 + CH_3CN$ (5:1 by volume). Supporting electrolyte: 0.1 M Bu_4NPF_6, Pt-disk electrode. (C) Voltammetric response of a Pt-disk electrode modified with dendrimer **49**, measured in CH_2Cl_2 + 0.1 M Bu_4NPF_6; (Adapted from Ref. [59]).

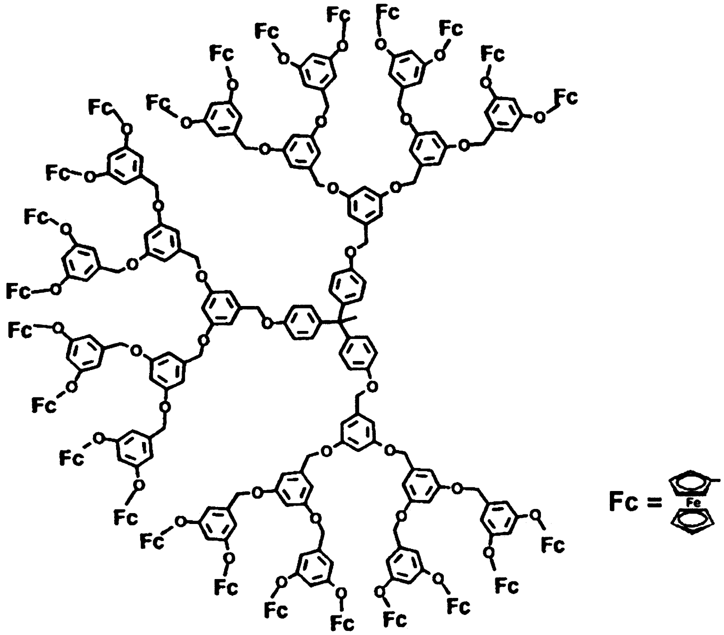


Scheme 18. Moss's convergent construction of dendrimers containing ruthenium carbon σ-bonds.

organoruthenium functional groups exclusively attached at the periphery of a poly(benzyl phenyl ether) dendritic structure has been prepared.

In another example of this strategy Shu et al. placed the ferrocenyl unit at the peripheries of a series of Fréchet-type poly(aryl ether) dendrimers [63]. In this way, dendrimer **55** was prepared (Scheme 19), as were its lower generation analogues. Cyclic and normal pulse voltammetric studies indicated that the peripheral ferrocenyl moieties are non-interacting redox centres.

A completely different convergent approach was reported by Puddephatt et al. for the synthesis of organoplatinum dendrimers [64]. These dendritic complexes were constructed employing as alternating growing steps the two reactions shown in Scheme 20. First, oxidative addition of the C–Br bonds of the trifunctional 4,4′-bis(bromomethyl)-2,2′-bipyridine to the square-planar platinum(II) centres of $[PtMe_2(bu_2bpy)]$ ($bu_2bpy = 4,4'$-di-*tert*-butyl-2,2′-bipyridine) gave the binuclear complex **56**, which contains two stable platinum(IV) centres. Second, displacement of SMe_2 ligands from $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ by the free bipyridine group of **56** gave the trinuclear derivative **57**. After repetition of these alternating synthesis steps, dendrimer **58** was obtained, in which steric hindrance at the reaction centre precludes further growth to a dendrimer of higher nuclearity. A modification of this method by using oxidative addition of 1,2,4,5-tetrakis(bromomethyl)benzene to a heptanuclear precursor with dimethylplatinum(II) centres, allowed the synthesis of an organometallic dendrimer containing 28 platinum atoms.



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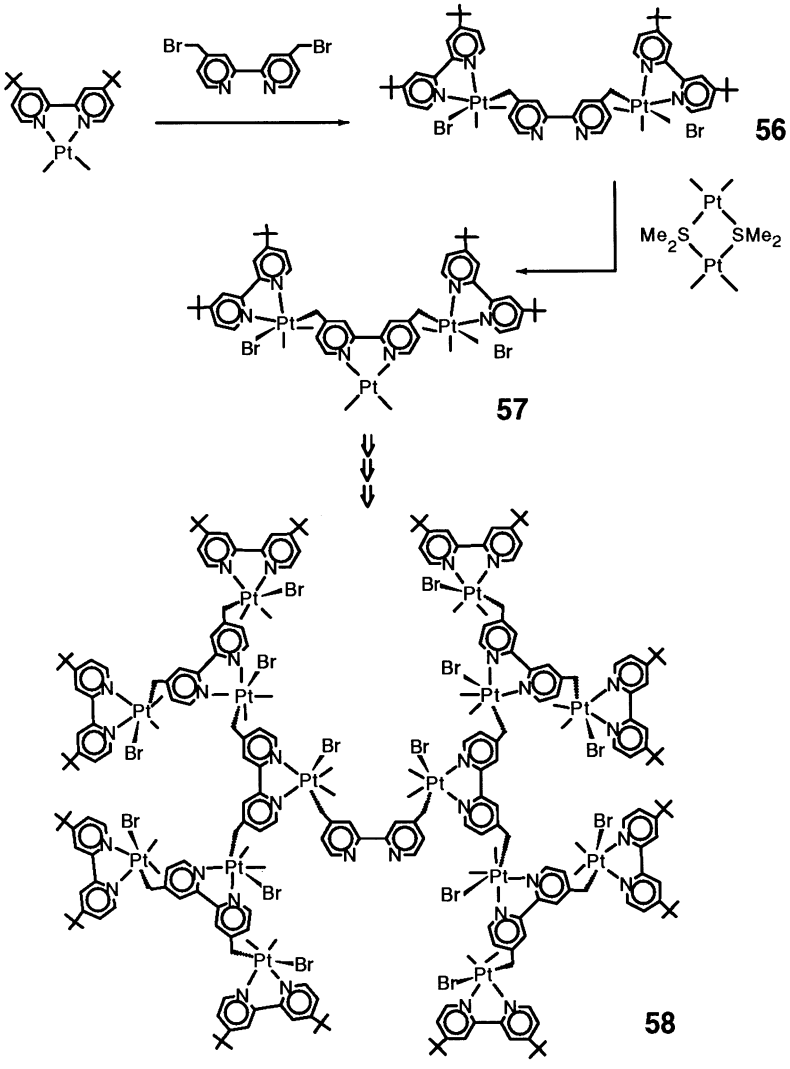
Scheme 19. A ferrocenyl dendrimer reported by Shu et al.



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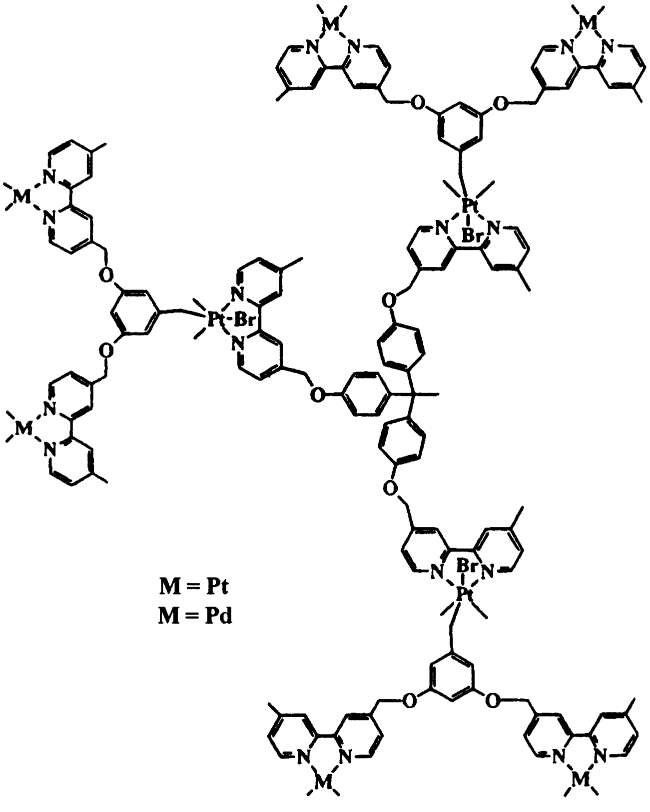
Scheme 20. Synthesis of organoplatinum dendrimers reported by Puddephatt et al.

In a related work, this group also used the oxidative addition as key reaction step for the divergent construction of new organometallic dendrimers such as **59** (Scheme 21) which contain organoplatinum(IV) centres in each inner generation layer and either platinum(II) or palladium(II) centres in the outermost layer [65].

Using a similar convergent strategy, Catalano et al. prepared heterometallic dendrimers containing organoplatinum(IV) and ferrocene units (Scheme 22) [66]. The starting organometallic molecule in this synthesis was the α-diimine bpy-Fc_2 **60**, which was converted in the heterometallic trinuclear derivative **61** by reaction with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$. Reaction of **61** with a series of bromomethylbenzenes yields new heterometallic dendrimers of the type exemplified by **62**, in which the pendant ferrocenyl units are non-interacting.

This same group has also reported new (benzyloxy)benzyl dendrimer-containing phosphine derivatives of *trans*-Ir(CO)Cl(PPh$_2$R)$_2$ which have been attached to C$_{60}$ in an oxidative-addition fashion, as illustrated by **63** (Scheme 23) [67]. IR and ^{31}P{^{1}H}-NMR studies have shown the reversible binding of these Vaska type complexes to fullerene.

On the other hand, Van Koten et al. have prepared dendrimers functionalized with square planar platinum(II) metal centres [68]. The synthesis follows the convergent methodology developed by Miller et al. for the construction of purely organic dendrimers based on symmetrically substituted benzenetricarboxylic acid esters [69]. The synthesis starts with the organometallic complex **64** (Scheme 24) possessing a *tert*-butyldimethylsilyl ether protecting group, which can be removed by treatment with tetrabutylammonium fluoride and water to afford the corresponding (*p*-hydroxylaryldiamine)platinum complex **65**. Subsequent treatment with



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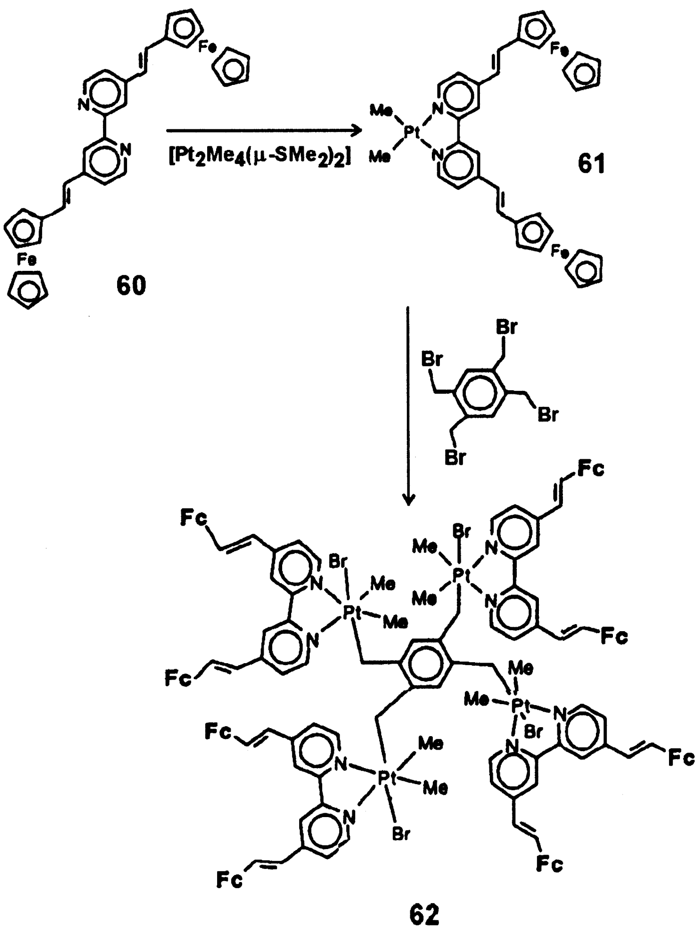
Scheme 21. Organoplatinum dendrimer constructed by Puddephatt et al. following a divergent route.



Scheme 22. Convergent synthesis of heterometallic dendrimers reported by Catalano et al.

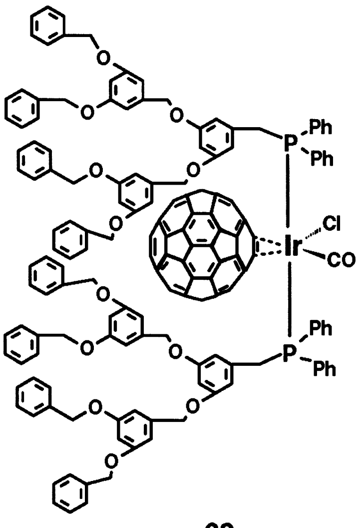
1,3,5-tris(chlorocarbonyl)benzene yields the desired trimetallic derivative **66**. In a similar way, the hexametallic molecule **67** was prepared. Dendrimer **67** is interesting since reversibly binds SO_2 and therefore can be potentially used as a molecular sensor for this gas.

Using also 1,3,5-tris(chlorocarbonyl)benzene as core molecule as well as a ferrocene-based cholesterol dendron, Deschenaux and co-workers have prepared the thermotropic dendritic molecule **68** (Scheme 25), which constitutes the first example of organometallic liquid-crystalline dendrimers [70]. The novel dendrimer exhibits a broad enantiotropic smectic A phase as well as a good thermal stability.

3.2. Divergent approach

In our quest for new series of dendritic macromolecules possessing ferrocenyl moieties at predetermined sites into organosilicon frameworks, our group also prepared, following a divergent approach, the first generation of a novel family of organometallic dendrimers using a ferrocenyl derivative as two-directional starting core, as it is shown in Scheme 26 [71]. The key organometallic monomer in this synthesis is the divinyl-functionalyzed ferrocene **69**, which constitutes a valuable starting core molecule for the construction of dendrimers. Thus hydrosilylation reaction of **69** with methyldichlorosilane and methyldiphenylsilane afforded molecules **70** and **71**, respectively. Further reaction of **70** with ferrocenyllithium led to the first generation dendrimer **72** possessing a central ferrocene and four outer interacting redox active ferrocenyl units. Likewise, thermal treatment of **71** with an excess of $Cr(CO)_6$ yielded the heterometallic pentanuclear molecule **73**. All new molecules have been characterised by IR and multinuclear NMR spectroscopies, elemental analysis, FAB mass spectrometry, and electrochemical techniques.

Astruc et al. were the first to report the divergent construction of organometallic molecular trees [72,73]. A representative example of the remarkable synthetic strategy followed for the synthesis of multimetallic molecules is illustrated in Scheme 27 [73]. The growing step is based on the fact that the π-complexation of aromatic compounds by electron-withdrawing cationic organo-transition metal fragments, enhances the acidity of methyl substituents in polymethyl hydrocarbon ligands, facilitating nucleophilic reactions. In this way, polyfunctionalization of methylated aromatics via their $(\eta^5\text{-}C_5H_5)M^+$ (M = Fe, Co) complexes has been successfully achieved. In the synthesis shown in Scheme 27, the starting



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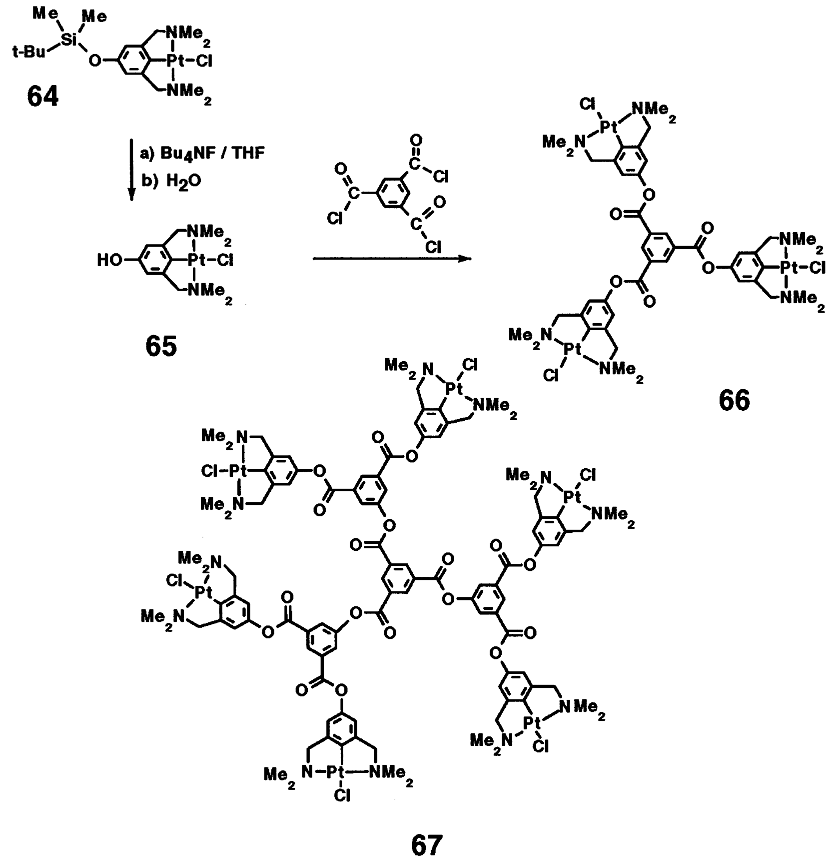
Scheme 23. C_{60} has been reversibly bound to a dendritic Vaska-type complex.



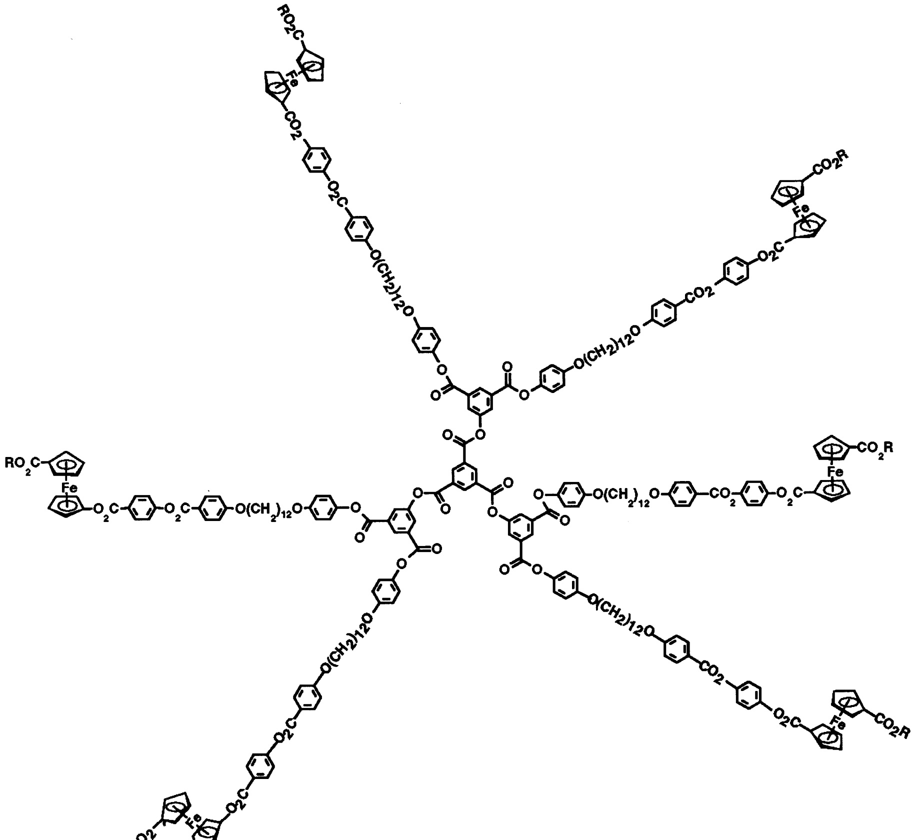
Scheme 24. Van Koten's synthesis of organoplatinum dendrimers containing aryldiamine ligands.

organometallic core molecule was the mesitylene derivative **74** in which each methyl group was converted into a substituent with three allyl functionalized branches by one-pot nonaallylation with allyl bromide and KOH in dimethoxyethane. Clean demetalation of the resulting nonaolefin iron complex **75** by visible-light photolysis afforded the nonaallyl **76**, whose crystal structure was established by X-ray analysis. Regiospecific hydroboration, followed by alkaline oxidation afforded the nonaol **77**. Subsequently, the attachment of external organometallic units to this core molecule was accomplished by reaction of **77** with $[(\eta^6\text{-}p\text{-MeC}_6H_4F)Fe(\eta^5\text{-}C_5H_5)]PF_6$ affording the nonairon molecular tree **78**. Examination of the electrochemical properties showed that **78** has a reversible reduction wave corresponding to the Fe^{II} (18 e^-)/Fe^{I} (19 e^-) system, and that 8 ± 1 electrons per molecule are transferred in the process.

Likewise, following the polysequential synthetic strategy involving organoiron mediated reactions, closely related star-shaped hexa- and heptanuclear iron sandwich molecules have been also synthesized [74–76]. Interestingly, the organometallic star molecule **79** (Scheme 28) catalyses the cathodic reduction of nitrates and nitrites to ammonia [76].

In a related work, Jutzi et al. have synthesized decaallylferrocene **80** (Scheme 29) [77], which potentially provides access to new dendritic molecules. Thus, as a first approach in this context, the star-like organometallic molecule **81** has been prepared by using a hydrosilylation reaction of **80** with dimethylsilyl ferrocene.

On the other hand, Reinhoudt et al. reported interesting examples of metallodendrimers constructed by self-assembly [78,79]. This approach employs as key organometallic derivative the bis(palladium complex) **82** (Scheme 30). Gently



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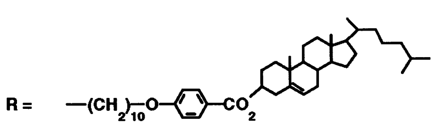
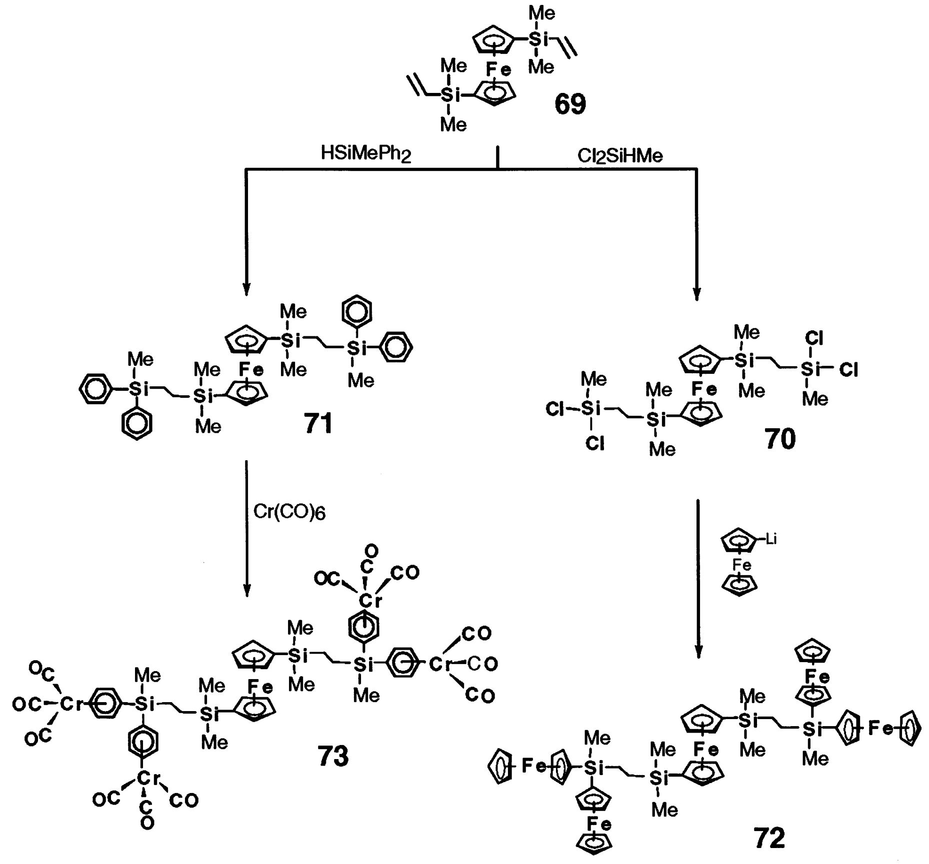


Scheme 25. A ferrocene-containing liquid crystal dendrimer synthesized by Deschenaux et al.



Scheme 26. Ferrocene as two-directional core for the synthesis of homo and heterometallic molecules.

heating of **82** in vacuum induces the substitution of the labile acetonitrile molecules for cyanomethyl groups through an uncontrolled polymerisation, which leads to self-assembled organopalladium spheres. Atomic force microscopy (AFM), and transmission electron microscopy (TEM) studies indicate that these aggregates of about 200 nm diameter exhibit a globular shape.

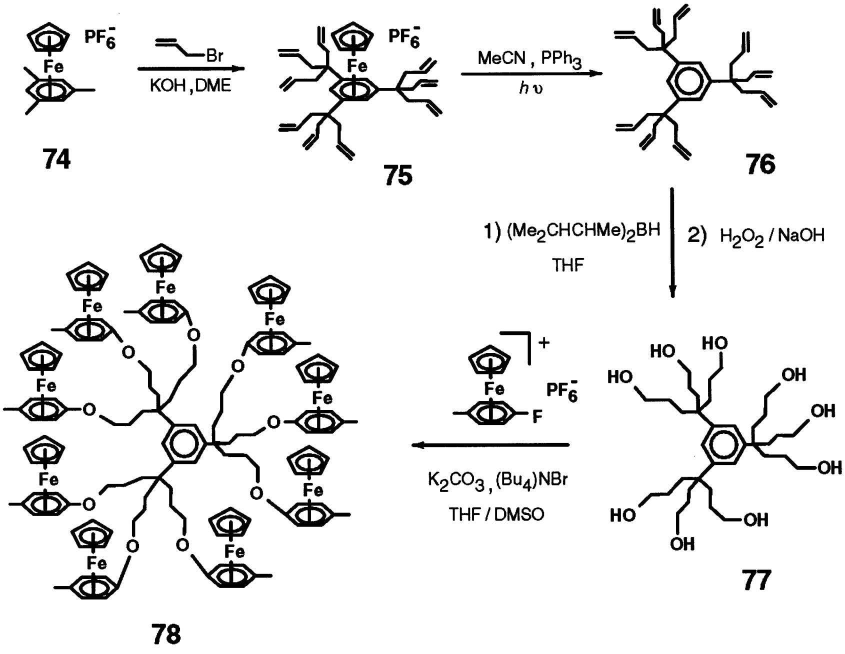
More recently, the same group has also described a controlled assembly strategy for the synthesis of metallodendrimers consisting in iterative protecting-deprotecting steps [80]. Key molecules in this approach, such as the tris(palladium chloride) **83**, contain kinetically inert tridentate ligands in square planar palladium complexes, in which the fourth position is protected by a strongly coordinating Cl^- anion. Likewise, the starting building block bis(palladium chloride) **84** also contains a labile coordinating cyano group. Replacement of the Cl^- anion in **83** by a non-coordinating BF_4^- ion and subsequent reaction with **84** affords the dendritic palladium complex **85** (Scheme 30). Further iteration of these steps has provided access up to the third generation dendrimer. Similar building blocks containing

Ni(II) and Pt(II) centres have been also synthesized which can be used for the controlled assembly of homo and heteromultinuclear metallodendrimers [81].

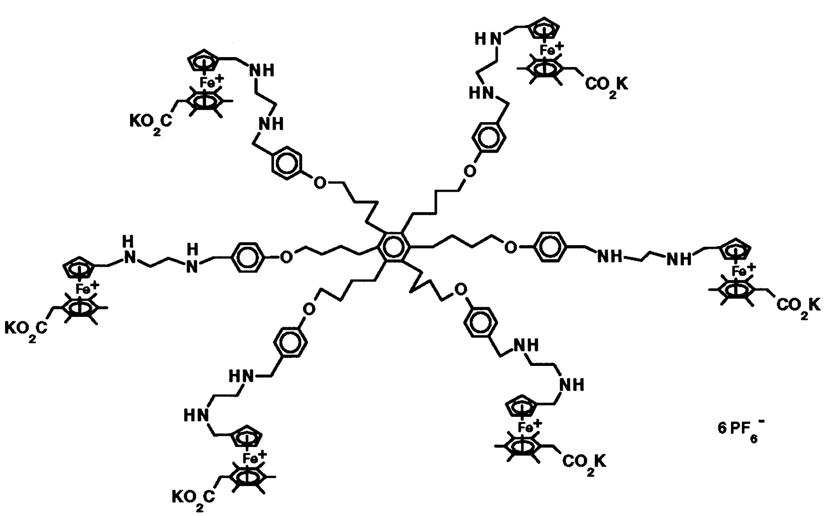
Independently, Takahashi et al. [82,83] and Leininger et al. [84] have employed a divergent methodology for the construction of a number of organo-platinum dendrimers in which alkynylarenes are used as linking groups between the metal atoms. Representative examples of such structures are metallodendrimers **86** and **87**. These molecules have been prepared by reaction of the appropriate triethynylbenzene with dihalobis(trialkylphosphine)platinum complexes in the presence of a cuprous halide catalyst and an amine base as it is illustrated in Scheme 31. The molecular structures of some of the trinuclear organoplatinum dendrimers have been determined by X-ray diffraction studies.

4. Catalytically active organo-transition metal dendrimers

Organometallic dendrimers have a key role to play in the future research in the field of catalysis. The combination of the unique structural features of the dendrimer architecture with the rich catalytic chemistry exhibited by organo-transition metal complexes, may allow the designed generation of novel efficient catalysts with highly controlled structures and precisely placed catalytic centres. Likewise, as a result of the high degree of branching, large dendrimers adopt a globular shape,



Scheme 27. Astruc's approach to the synthesis of a nonairon molecular tree.



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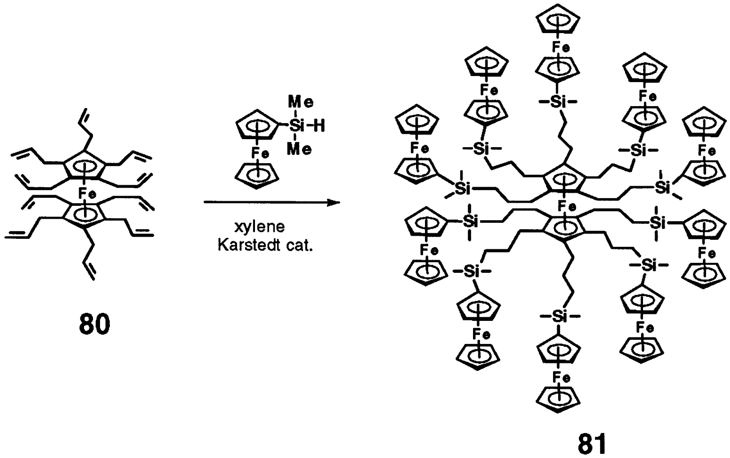
Scheme 28. Polycationic star shaped iron molecule reported by Astruc et al.

which assures the accessibility of all the catalytically active centres to the reactive substrate. These new dendrimeric catalytic systems not only would be expected to retain the advantages of homogeneous catalysts (high activity and selectivity), but in addition, due to their nanoscopic size, would be easily separated from the resulting reaction-products mixtures by nanofiltration methods.

Van Koten et al. [85] reported in 1994 interesting silane-based dendrimers bearing catalytically active aryl-nickel sites precisely ordered onto the periphery of the dendritic framework. The synthesis of these organometallic dendritic molecules



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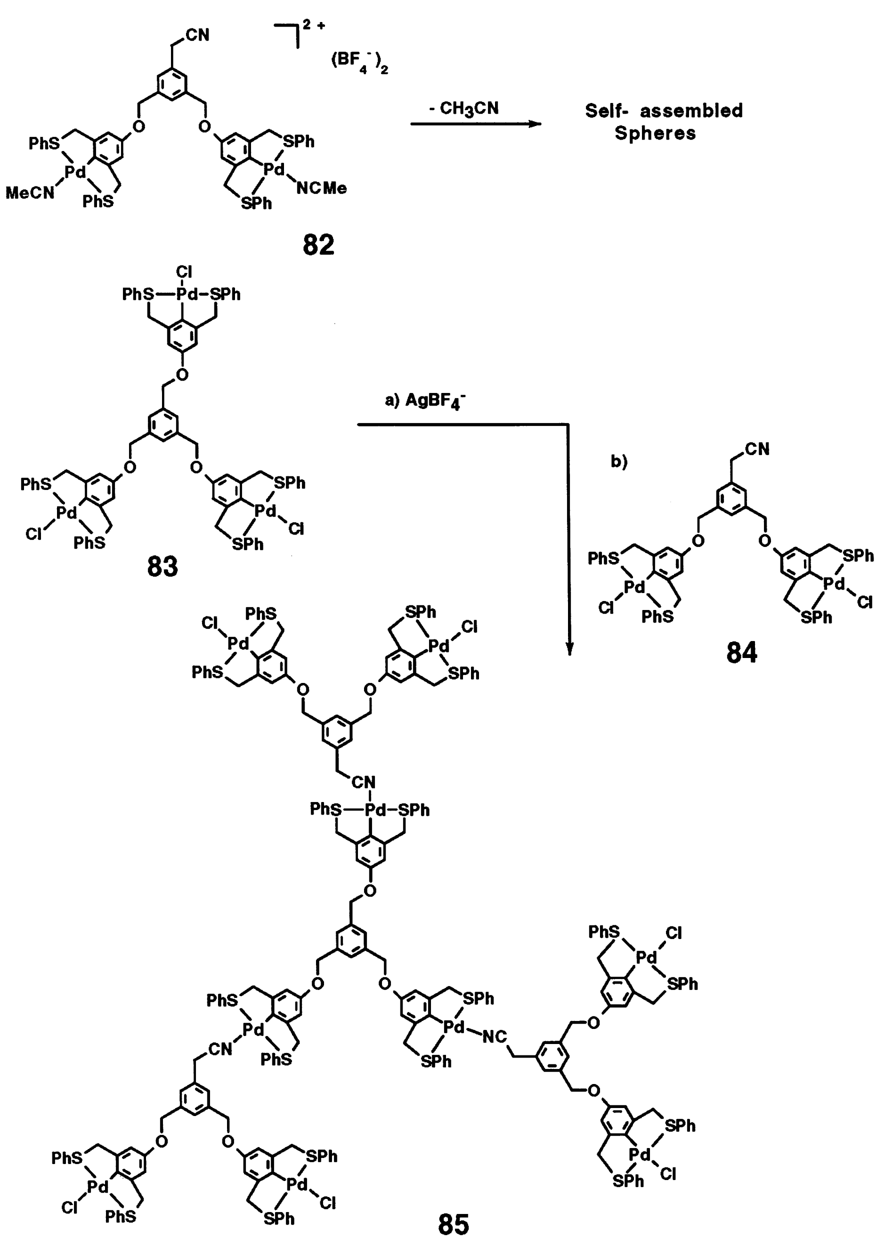
Scheme 29. Jutzi's synthesis of decaferrocenyl ferrocene.



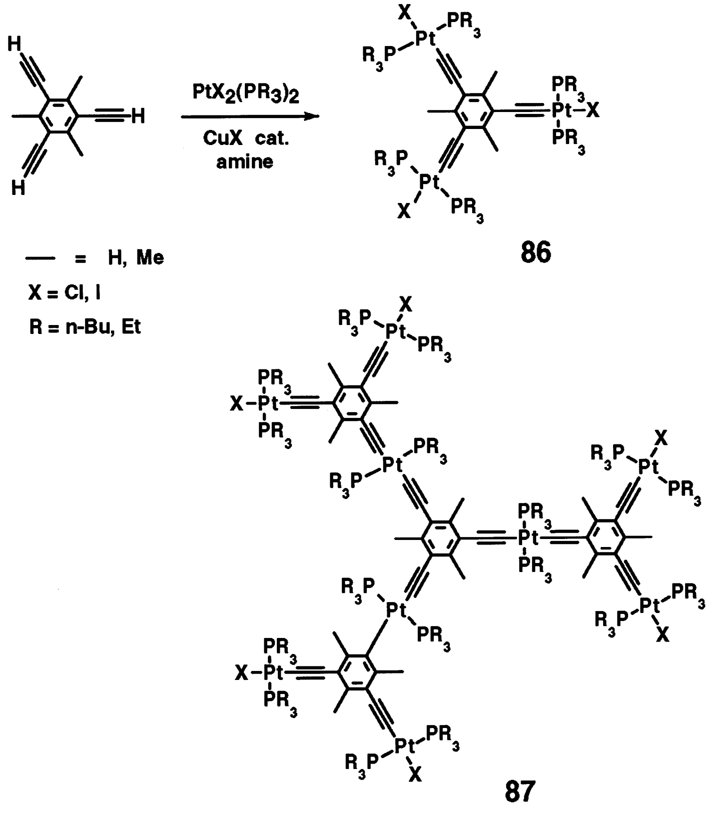
Scheme 30. Uncontrolled and controlled assembly of organopalladium dendrimers reported by Reinhoudt et al.

involved the use of the polyfunctionalized chlorocarbosilane dendrimers such as **88**, and a diamino aryl bromide moiety as the precursor entity for the organometallic catalytic centre (see Scheme 32), yielding the aryl bromide substituted system **89**.

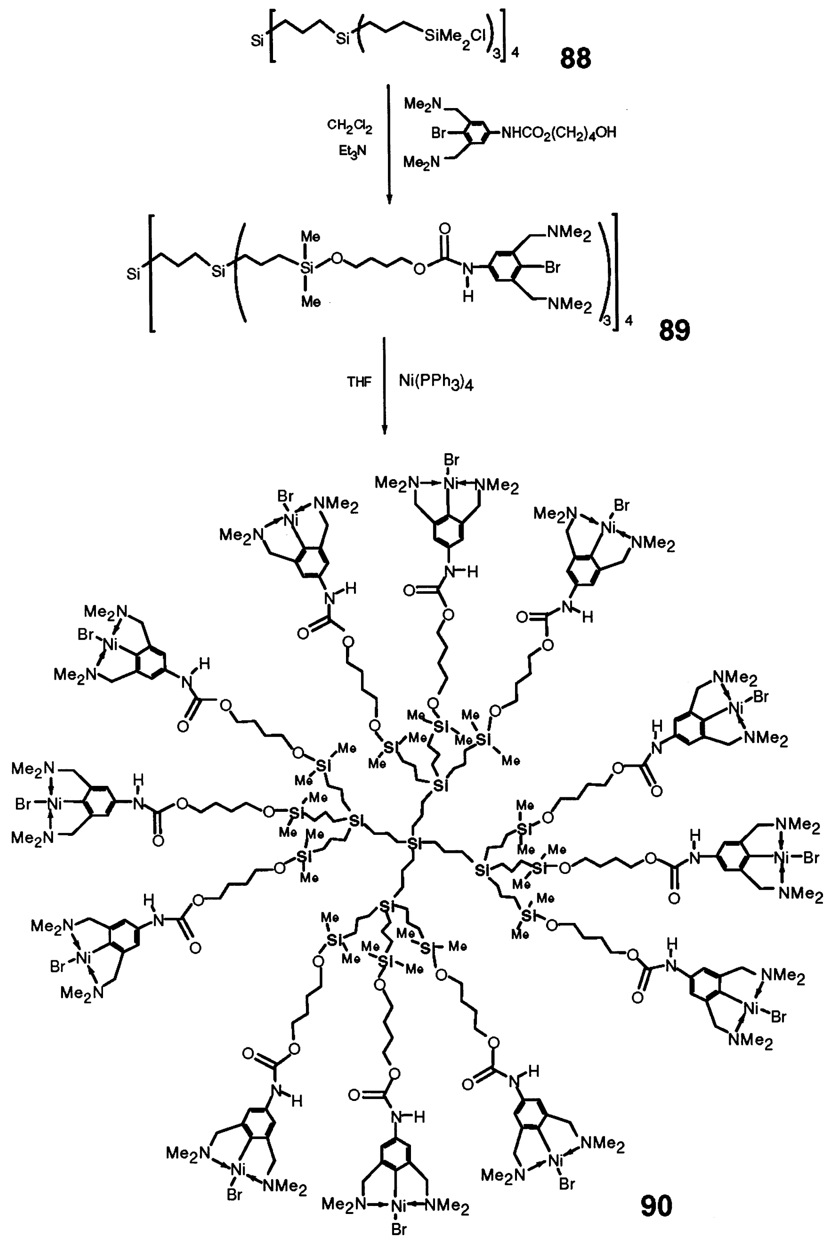
This dendrimer was subsequently reacted with the zerovalent nickel derivative $Ni(PPh_3)_4$, in order to obtain the oxidative addition product **90**, with twelve discrete metal sites. The most notable feature of these new dendrimeric organometallic molecules is their ability to act successfully as effective homogeneous catalysts for the Kharasch addition reaction of polyhalogenoalkanes to olefinic C=C double bonds. Likewise, the nanoscopic size of these first examples of soluble dendritic catalysts allows the separation of such macromolecules from the solution of the products by ultrafiltration methods.

More recently this group also reported related silicon-based dendrimers containing organopalladium moieties bonded directly to the dendritic surface exclusively via a Pd–C σ-bond. These palladium functionalized dendrimers have been prepared via the insertion of palladium(0) into carbon–iodine bonds of carbosilane dendrimers containing peripheral iodoarene groups [86].

Another interesting silane-based organophosphine dendrimer containing palladium which exhibits electrocatalytic activity was reported by DuBois et al. [87]. The synthesis is illustrated in Scheme 33, and was accomplished by free-radical addition of bis[(diethylphosphino)ethyl]phosphine to tetravinylsilane, to yield dendrimer **91**



Scheme 31. Divergent construction of organoplatinum dendrimers containing alkynyl-aryl backbones.



88

89

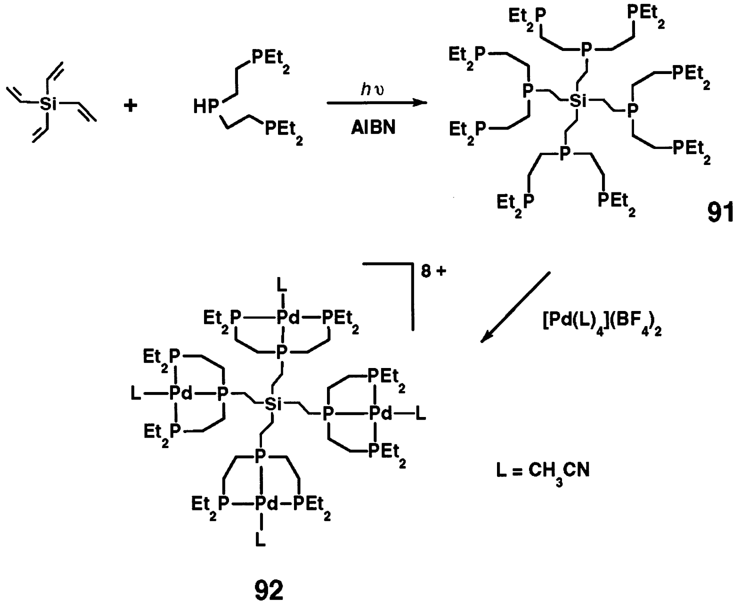
90

Scheme 32. Van Koten's construction of a dendrimer functionalized with arylnickel(II) catalytically active sites.

possessing twelve phosphorus atoms at the periphery. Metalation of this dendrimer by reaction with $[Pd(CH_3CN)_4](BF_4)_2$ gives the dendritic macromolecule **92**, which contains four well-separated palladium complexes bound to a central silicon atom. Electrochemical studies showed that this metalated dendrimer catalyses the electrochemical reduction of CO_2 to CO. Interestingly, on the basis of the comparison of the catalytic activity for electrochemical reduction of CO_2 exhibited by **92**, with that observed for related palladium organophosphine dendrimers without organosilicon frameworks, the authors noted relationships between catalytic properties and dendrimer structure.

Reetz et al. have modified the diaminobutane-based poly(propylene imine) dendrimer DAB-dend-$(NH_2)_{16}$ by double phosphinomethylation of the 16 primary amino terminal groups with Ph_2PCH_2OH [88]. This reaction affords a dendritic molecule containing 16 bidentate phosphorus ligands on the outer surface, which was used to prepare homo and heterometallic dendrimers such as **93**, **94** and **95** (Scheme 34). Some of these dendritic diphosphane metal complexes have been successfully used in catalysis. Thus for example, the palladium-containing dendrimer **93** exhibits a significantly higher catalytic activity in the Heck reaction of bromobenzene and styrene with formation of stilbene, than that of the corresponding monomeric parent compound.

On the other hand, Brunner has reported a new class of catalytically active organometallic dendrimers such as **96** shown in Scheme 35, containing a metal atom in the centre [89]. These dendrimers are constructed from expanded, dendrimeric phosphorus ligands, which he has called dendrizymes since reactions are



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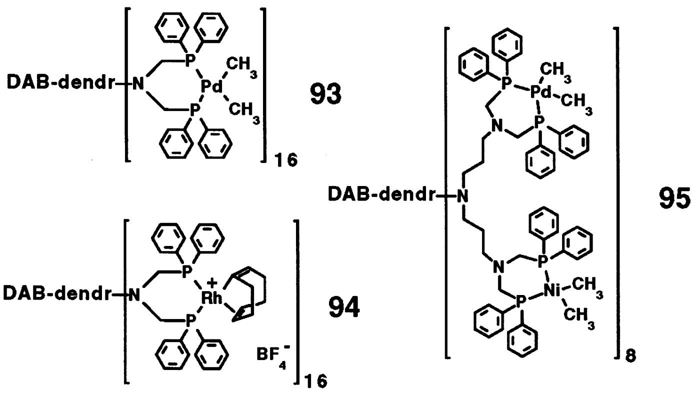
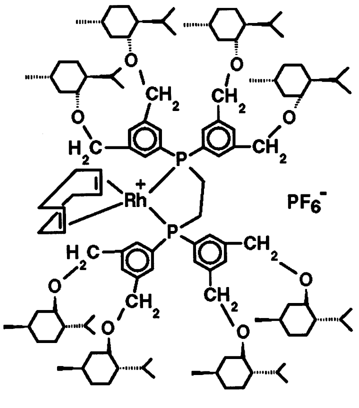
Scheme 33. DuBois's synthesis of a palladium containing dendrimer capable of reducing CO_2 to CO.



Scheme 34. Homo and heterometallic dendritic diphosphane molecules reported by Reetz et al.

supposed to take place in the same way as in the pocket of an enzyme. Their catalytic activity in hydrogenation reactions was studied.

Very recently, Togni et al. have prepared dendrimers such as **97** (Scheme 36), containing chiral ferrocenyl diphosphines, which have demonstrated to be effective in highly enantioselective hydrogenation reactions [90]. Such catalytic system bound at the periphery of dendrimers display very similar activity and selectivity features as the unsubstituted monomeric units. In addition, due to their nanoscopic size, these materials can be easily removed by commercial nanofiltration membranes.



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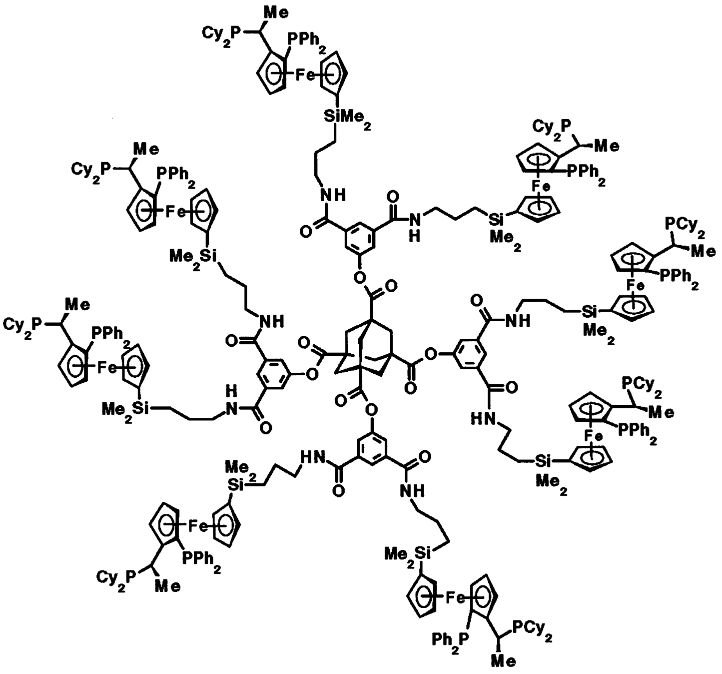
Scheme 35. A catalytically active dendrimer reported by Brunner.



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Scheme 36. A ferrocenyl dendrimer used for asymmetric catalysis reported by Togni and Pugin.

5. Conclusions

The research on dendrimers is currently undergoing an exponential growth. The dendritic molecules described above have been reported in the course of the last six years, and constitute an important advance for both fields organometallics and dendrimers. Organometallic dendrimers combine the unique feature of the dendrimer architecture with the rich chemistry exhibited by organo-transition metal complexes and have already demonstrated to be useful for a range of interesting applications such as dendrimeric catalysts, as electron-transfer mediators in redox catalysis, molecular recognition, and electrochemical biosensors, as dendritic liquid crystalline materials, as well as guest templates for multisite inclusion complexation. Moreover, the opportunities for future progress are almost unlimited considering the diversity of synthetic routes, numerous variations in the topologies of the dendrimers, along with the rich variety and the large number of organo-transition metal complexes and possible combinations of these that can be incorporated into dendritic structures.

In summary, the continuous development of synthetic strategies for the construction of new families of such organometallic dendrimers, which will play a key role in the future research of organometallic chemistry, supramolecular chemistry and material science, appears to be very promising.

Acknowledgements

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