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Organometallic and related metal-containing dendrimers

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Reports of the synthesis of new dendrimers containing organometallic fragments have increased dramatically over the past few years and examples of dendrimers containing many different metals are now known. This article highlights some of the the ways in which transition metals and their ligand systems have been incorporated into the growing number of dendrimers. Some structural details and properties of metal-containing dendrimers are described, and their applications are also discussed. The cover illustration shows Table Mountain, South Africa and a fourth generation ruthenium dendritic wedge.

Introduction

Nature has the ability to manipulate and control the structures of molecules in three dimensions. The rising demand for materials with improved and novel properties has now changed the emphasis in polymer research to new classes of materials with highly controlled molecular architectures.[1,2] New families of highly branched three-dimensional molecules, termed dendrimers, arborals or starburst polymers, have recently been prepared and have sparked great interest. Several review articles have appeared recently.[1] One of the driving forces in the study of these highly branched macromolecules has been the anticipation that these new materials will have fundamentally different properties when compared to more traditional linear polymers. While the majority of dendrimers prepared so far have been purely organic in nature, there is growing interest in the synthesis of dendrimers containing transition metals. The metal centres can be incorporated at the core, throughout the structure, or at the periphery of a dendrimer and may give compounds with novel or unusual properties. Such compounds are new materials and may have important applications, including uses as molecular devices, as antennas for harvesting light or as catalysts. Exploration of the synthesis, properties, structures and applications of these new materials is both challenging and exciting. Over the past six years, we have developed a methodology for synthesizing dendrimers containing covalent metal–carbon sigma bonds. To date, we have concentrated on compounds containing Ru–C and Fe–C bonds but we are currently investigating the synthesis of many other organometallic systems. In the following pages, we describe some of our work along with that of others in the field. Dendrimers are discussed according to the mode of bonding between the metal and dendrimer.

Dendrimers with M–C σ bonds

The first transition metal alkyl compound was prepared by Pope and Peachey in 1907[3] and today alkyl compounds of nearly every transition metal are known.[4] A driving force for this development has been in part due to the important applications of the alkyl species in catalytic reactions of industrial importance, for example titanium and zirconium catalysts for the polymerization of alkenes, as well as cobalt and rhodium catalysts in hydroformylation and hydrogenation reactions.[5] Our research group has worked on transition metal alkyl and functionalized alkyl compounds for many years.[4] From our studies on haloalkyl compounds,[6] we have developed methods for the preparation of organometallic dendrimers containing metal–carbon sigma bonds.[7] We applied the convergent methodology developed by Hawker and Fréchet[2] and used 3,5-dihydroxybenzyl alcohol as the monomer unit.[7] The advantage of using the convergent approach is that it allows for precise control over the number and placement of functional groups at the surface of the final dendrimer. The reactions are carried out in a stepwise fashion and the dendritic wedges were isolated, purified and characterized after each step. Since the products are all highly soluble, in spite of the large number of metals present, the reactions could be monitored by NMR spectroscopy, so that defects in branching of the wedges could be detected prior to complexation with a core molecule. Our first attempts to build dendrimers were with functionalized iron complexes of the type $Cp(CO)_2Fe(CH_2)_3Br$.[6] Although the reaction with 3,5-dihydroxybenzyl alcohol yielded the expected binulcear complex (see Scheme 1), conversion of the benzyl alcohol to the benzyl bromide gave a low yield, which we attributed to the instability of the iron-alkyl bond of the benzyl bromide. Iron dendrimers containing Cp (Cp = η^5-C_5H_5) acyl and Cp* (Cp* = η^5-C_5Me_5) monomer units have since been prepared and will be reported in further publications.[8]

We explored the reactions of $Cp(CO)_2RuR$ derivatives, *e.g.* $Cp(CO)_2Ru(CH_2)_5Ru(CO)_2Cp$ or $Cp(CO)_2RuR$ (R = alkyl) with PPh_3 and showed that no reaction occurred in refluxing THF over 25 h, forcing conditions (refluxing xylene, 140 °C) being necessary to get the reaction to go at all.[9] This suggested to us that the ligand system around the metal in these $Cp(CO)_2RuR$ derivatives was both thermodynamically stable and kinetically relatively inert. It was for this reason that we turned our attention to building up organometallic dendrimers with ruthenium–carbon sigma bonds. Thus, the reaction of 3,5-dihydroxybenzyl alcohol with $Cp(CO)_2Ru(CH_2)_3Br$ was investigated and we obtained the expected benzyl alcohol (see Scheme 1). This and higher generation dendritic wedges could

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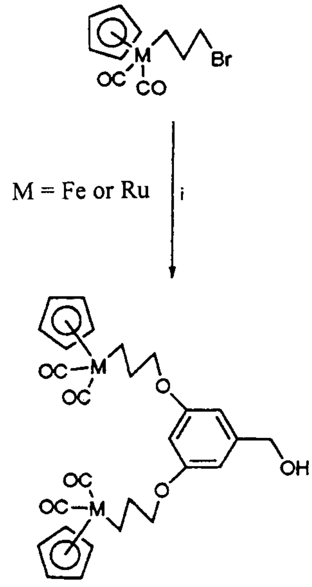
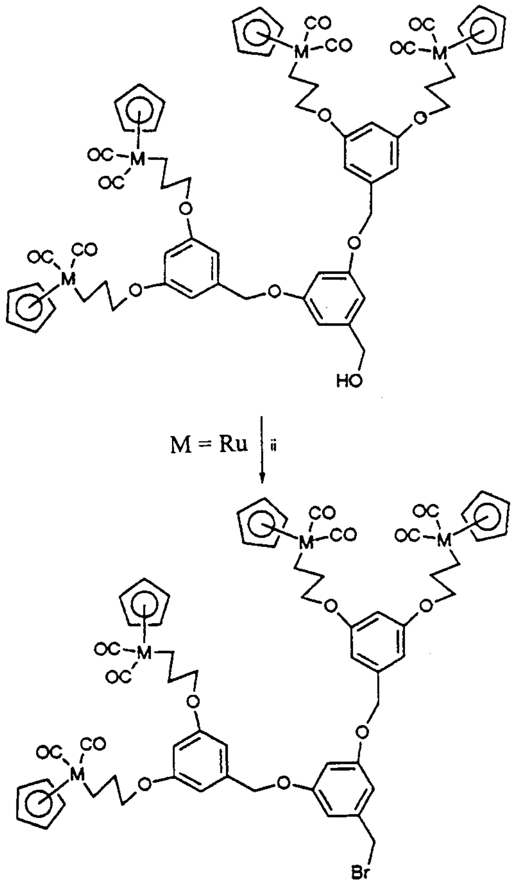
Meredith A. Hearshaw (née Timme) was born in Cape Town, South Africa and obtained her BSc (Hons) degree in 1993 in the First Class. She is currently completing her PhD degree on the synthesis, structure and chemistry of organometallic dendrimers under the supervision of Professors John Moss and Mino Caira at the University of Cape Town.



Scheme 1 *Reagents and conditions:* i, 3,5-dihydroxybenzyl alcohol, K_2CO_3, 18-crown-6, reflux, acetone, 48 h.



Scheme 2 *Reagents and conditions:* ii, CBr_4, PPh_3, room temp., 20 min.

be converted to the corresponding benzyl bromides in good yield (see Scheme 2).[7] These ruthenium-based dendritic wedges were sufficiently stable to withstand the vigorous conditions required for their synthesis and thus it was possible to build up large dendritic wedges, and organometallic dendrimers, containing Ru–C sigma bonds. For these ruthenium complexes, the reactions of the organometallic wedges behaved similarly to the analogous organic reactions, although the yields tended to be slightly lower. The ruthenium dendrimers described above are highly soluble in common polar organic solvents and have been characterized by conventional spectroscopic (NMR, IR, MS) and analytical techniques.[7] Since the first publication in 1993, our group has made organometallic dendrimers of high purity up to the fourth generation containing 48 metal atoms and with a molecular mass of over 18 000.[7]

We have thus shown that with the correct choice of metal and ligand system, it is possible to build up very large organometallic molecules. We are currently working on dendrimers of a range of other metals, including those containing iron, cobalt, rhenium, chromium and tungsten, as well as investigating the properties and applications of some of these dendrimers.[10]

It has been shown that oxidative addition of primary alkyl or benzyl halides, RX to $[PtMe_2(NN)]$ gives $[PtXMe_2R(NN)]$ (where NN represents a diimine ligand such as 2,2′-bipyridine) and these complexes can be prepared in essentially quantitative yields.[11] The oxidative addition reactions occur in high yield but the ability to grow large oligomers is limited since the solubility decreases with chain length. This strategy was adapted to prepare star-shaped multinuclear organoplatinum complexes.[12] The oxidative addition reactions occur with a colour change from orange–red of platinum(II) to the pale yellow of platinum(IV) and hence the reactions were easily monitored by visible spectroscopy.[12] The reaction cycles were repeated until NMR spectroscopy showed that the products contained defects. The limit to growth appears to occur after formation of the Pt_{14} dendrimer, shown in Fig. 1. Growth beyond this to give the Pt_{30} dendrimer failed.[11] The limit to growth can be understood in terms of steric hindrance. The synthesis of larger platinum dendrimers was achieved by modification of the ligand. The key reagent for this work is the tetrafunctional core, 1,2,4,5-tetrakis(bromomethyl)benzene which could react with four organoplatinum(II) centres by oxidative addition of the C–Br bonds. In this approach, larger fragments are built first and then coupled to a polyfunctional core.[12] The solubility of the complexes was enhanced by the addition of the *tert*-butyl groups and the solubility of the products was found to increase with increased branching.

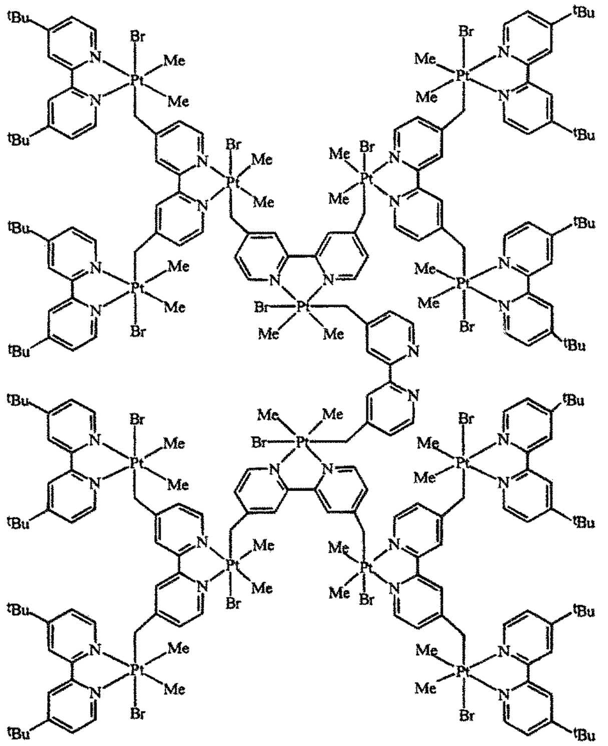


Fig. 1 The pale yellow Pt_{14} dendrimer.[11] Reprinted with permission from *Organometallics*, 1996, **15**, 43, copyright (1996) American Chemical Society.

Recent work of the Puddephatt group has focussed on multinuclear organopalladium complexes and heterobimetallic palladium–platinum complexes. The authors wanted to see if the oxidative addition reactions used previously could be employed. They found that incorporation of palladium in the structures is limited by the tendency of organopalladium(IV) complexes to undergo reductive elimination or alkyl halide transfer reactions. Some model complexes have been sucessfully synthesized.[13]

A sucessful route to multinuclear platinum complexes involves oxidative addition of an alkyl halide to platinum(II) providing the branching step, while ligand substitution by the bipyridine group provides a means of regenerating a reactive platinum(II) centre for the next growth cycle.[13]

Dendrimers with M–C π bonds

Ferrocene-based dendrimers

The majority of iron dendrimers reported to date have involved ferrocene derivatives. Perhaps the most obvious reason for this is that ferrocene chemistry is well established and documented and the compounds are stable. The construction of well defined dendrimers possessing redox-active organometallic units linked together in close proximity, so that there can be electronic communication between the metal sites in the dendritic structure, is a challenging target.[14] The dendrimer shown in Fig. 2 is the first example of an organometallic molecule to display electronic interaction between the transition metal atoms in the dendritic structure.[14]

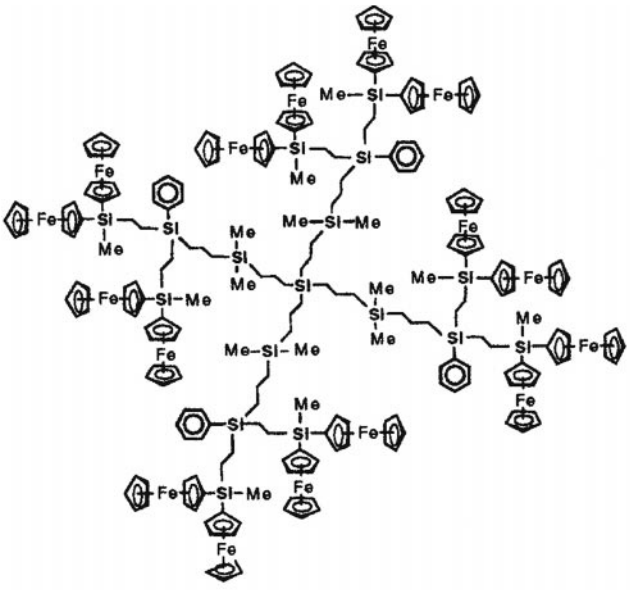


Fig. 2 A second generation silicon based dendrimer with ferrocenyl surface groups.[14] Reprinted with permission from *J. Am. Chem. Soc.*, 1997, **119**, 7613, copyright (1997) American Chemical Society.

Polymers containing ferrocene units are useful as redox catalysts for the modification of electrodes, and as biosensors.[15] $[FeCp(arene)]^+$ can serve as an excellent starting core for dendrimers since polyalkylation, polyallylation and polybenzylation of polymethyl arenes leads to various topologies.[15] The reaction of $[FeCp(C_6Me_6)]PF_6$ with excess base and an alkyl halide results in selective hexasubstitution [eqn. (1)].

$$[FeCp(C_6Me_6)]PF_6 \xrightarrow[\text{RI (R = ferrocenylalkyl)}]{\text{KOR}' \text{ (R}' = \text{H, Bu}^t)} [FeCp\{C_6(CH_2R)_6\}]PF_6 \quad (1)$$

Cyclic voltammetry experiments showed that all six ferrocene units are electrochemically equivalent. The central cationic unit showed no influence on the oxidation process as the six outer ferrocene groups were oxidized at the same potential. The $CpFe^+$-induced hexaferrocenylalkylation of C_6Me_6 opens the route to isolable mixed-valence star-shaped molecules with independent redox centres and leads to a fully reversible six-electron redox system which may be useful for multielectron redox catalysis.[15] The multinuclear compounds have dendritic cores with organometallic surface groups.

One may also think of dendrimers as multisite guests for chemical interactions of any nature due to the regular placement of repeating residues on the dendrimer surface.[16] Ferrocenyl-functionalized amino dendrimers have been shown to include well known molecular hosts, specifically the cyclodextrins. The dendrimer serves as a three-dimensional template to organize the cyclodextrin receptors at the periphery of the dendritic structure, giving rise to large supramolecular assemblies.[16] The number of ferrocene units that can be included by the bulky cyclodextrin host is limited by the steric congestion on the surface of the dendrimer.

Fig. 3 shows the first heterometallic dendrimer containing different transition metals in different layers.[17] This dendrimer features platinum(IV) units arranged in a concentric fashion around a central organic unit, with ferrocenyl groups as the surface functional groups. In this approach, dendritic arms containing one platinum and two ferrocenyl moieties were built first and then attached to a polyfunctional core *via* a convergent synthesis (Fig. 3).[17] The inclusion of redox-active centres into the dendrimers allows their composition to be determined by cyclic voltammetry. This alternative method of characterization may prove useful for other redox-active dendrimers.

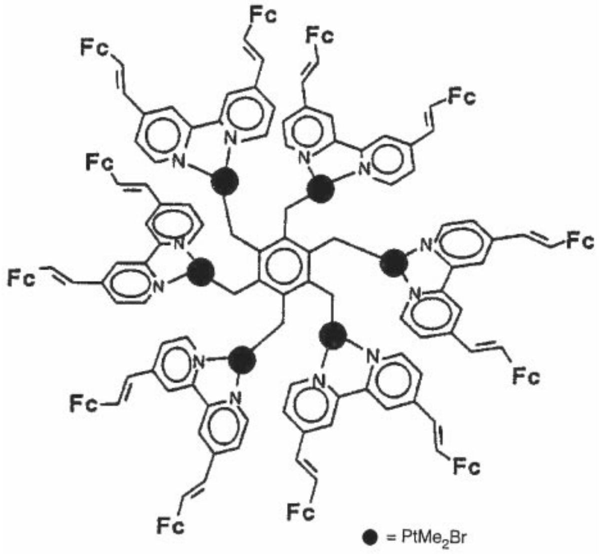


Fig. 3 A heterometallic dendrimer containing six platinum and twelve ferrocenyl centres.[17] Reprinted with permission from *Inorg. Chem.*, 1997, **36**, 2314, copyright (1997) American Chemical Society.

Until recently, molecular recognition using dendrimer-based sensors was unknown. Some amido-ferrocenyl dendrimers have been synthesized and have been shown to be excellent redox sensors for the recognition of small inorganic anions such as Cl^-, NO_3^- and HSO_4^- (Fig. 4).[18] Cyclic voltamograms of these ferrocenyl dendrimers all show a single anodic reversible wave, indicating that all the iron(II)/iron(III) redox centres are independent and equivalent.[18] The dendrimers ability to sense and recognize the anions by cyclic voltammetry as the dendritic generation increases was found to be maximum for the generation (18 ferrocene groups) preceeding steric surface saturation (36 ferrocene groups). As the dendritic generation becomes higher, the ferrocenyl termini of the different dendritic branches become closer to one another, making the surface hole for the penetration of the anion smaller. Since the anions are small, the greatest effect and selectivity is found for the highest generation that is soluble because it forms the best open cavities. In comparison, endoreceptors also favour anion inclusion with open cavities where size compatibility is important.[18]

One potential role for a dendrimer is as an encapsulating shell around small molecules within it, or around the core of the

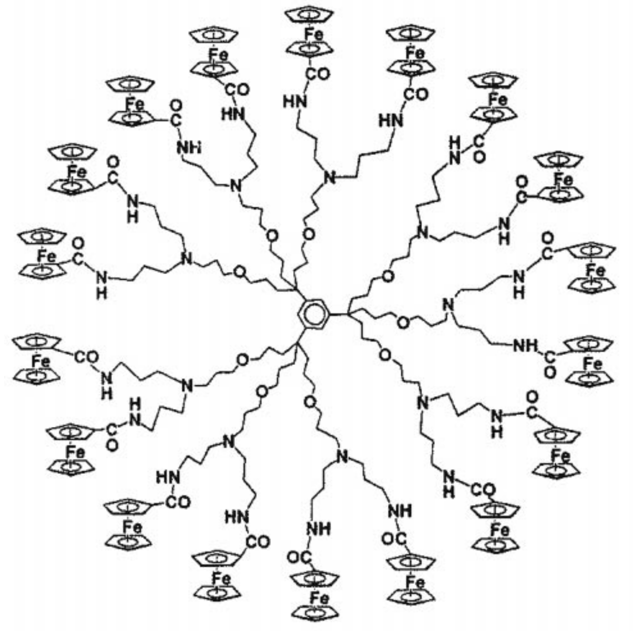


Fig. 4 An amidoferrocenyl dendrimer which acts as a redox sensor for the recognition of small inorganic anions.[18] Reprinted with permission from *J. Am. Chem. Soc.*, 1997, **119**, 2588, copyright (1997) American Chemical Society.

dendrimer itself. Dendritic encapsulation offers a means of preventing facile electron transfer between closely spaced molecules which would result in loss of stored information.[19] One such application is as a molecular switch, in which an electroactive group can be held alternately in one of two binary states (corresponding to ‘on’ or ‘off’).[19] A third generation dendrimer with an electroactive core is shown in Fig. 5. The core of one such dendrimer is an $Fe_4S_4(SR)_4^{2-}$ unit such as that found in some iron–sulfur proteins and is capable of existing in two stable redox states. Cyclic voltammetry experiments showed that as the number of branches in the dendrimer ligands around this core increased, the kinetic facility of electron transfer to and from the core decreased.[19]

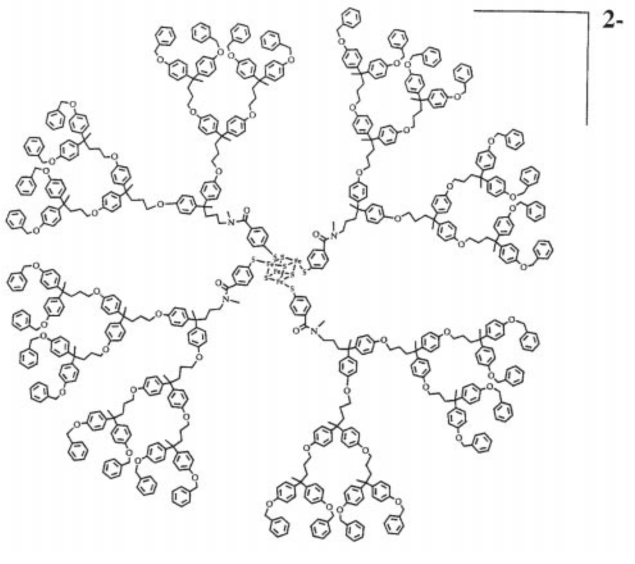


Fig. 5 An electroactive third generation encapsulated dendrimer.[19] Reprinted with permission from *Adv. Mater.*, 1997, **9**, 1117, copyright (1997) Wiley-VCH.

From the number of ferrocene-containing dendrimers synthesized, it is evident that the ferrocene group is useful in the construction of dendrimers. The dendrimers prepared can be relatively easily characterized and their properties investigated by electrochemical methods.

Metal arene complexation

π-Complexation of transition metals to terminal arene ligands is another method of dendrimer modification. First and second generation organosilicon dendrimers have been prepared with aromatic rings on the periphery.[20] These surface-located arene rings were then π-coordinated to $Cr(CO)_3$ groups to give a new family of organometallic dendritic macromolecules containing η^6-arene coordinated $Cr(CO)_3$ groups at the periphery of the organosilicon dendritic cores; the tetranuclear compound is shown in Fig. 6. Attempts to prepare the octachromium macromolecules failed probably due to the forcing reaction conditions which caused decomposition. The silicon dendrimers were prepared following a divergent approach which involved hydrosilylation and allylation as a means of growth.[20] These authors anticipate that the ability of the transition metals to π-complex to the peripheral aromatic rings of the novel silicon-based dendrimers should also be possible and will provide increased versatility for the design and synthesis of new families of dendritic macromolecules with different organotransition metal groups.[20]

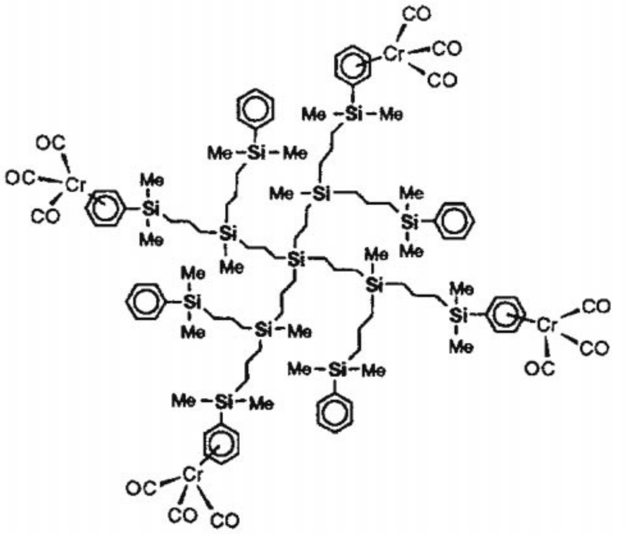


Fig. 6 The tetranuclear $Cr(CO)_3$ dendrimer.[20] Reprinted from *J. Organomet. Chem.*, 1996, **509**, 109, copyright (1996), with permission from Elsevier Science.

Dendrimers with tertiary phosphine ligands

Chemical functionality can be used as a means to control the ‘placement’ of the metal atom. Tertiary phosphines are known to bind to almost all transition metals of the periodic table.[21] It is thus not surprising to find a number of papers where a variety of metals, including palladium, rhodium and iridium, have been included in dendrimers *via* coordination of the metal to the surface phosphines. Thus, phosphorus-containing dendrimers up to the tenth generation and posessing either aldehyde groups or P–Cl bonds on the surfaces have been synthesized.[22] These terminal functions were reacted in order to anchor diphosphino groups on the surface of the dendrimer. The ability of the higher generation dendrimers to act as ligands towards palladium, platinum and rhodium complexes was then investigated. It was found that the end groups $\{–CH{=}NN(CH_2PPh_2)_2\}$ remained available for complexation with the metals and these new dendrimers may be of use as catalysts.[22]

Similarly, reactions of phosphorus dendrimers with ruthenium polyhydrides were investigated.[23] The new dendrimers have characteristic spectroscopic properties, in particular their ^{31}P and ^1H NMR spectra. Preliminary catalytic tests indicate good activity of these compounds for ketone hydrogenation.[23] The excellent coordinating ability of phosphorus to transition metals has been used to synthesize many novel organometallic dendrimers and a number of these examples are discussed in the ‘Dendrimers as catalysts’ section.

Dendrimers with nitrogen donor ligands

Coordination centres in every layer

Dendrimers with coordination centres in every layer were constructed using transition metal coordination complexes as building blocks for branching or bridging to yield polynuclear compounds which behave as supramolecular systems.[24] The synthetic procedure is based on a protection/deprotection procedure in which a complex with free chelating sites is used as a ligand, and those with labile ligands play the role of metals (‘complexes-as-ligands/complexes-as-metals’ synthetic strategy).[25] This procedure allows the construction of large polynuclear metal complexes *via* metal–ligand coordination bonds. One of the advantages of this approach is that it is possible to introduce the desired building blocks at each stage of the synthesis. Dendrimers containing units of different chemical nature can exhibit valuable properties with specific functions, *e.g.* gradients for photoinduced directional energy and electron transfer, and sites for multi-electron transfer catalysis (see Fig. 7).[25]

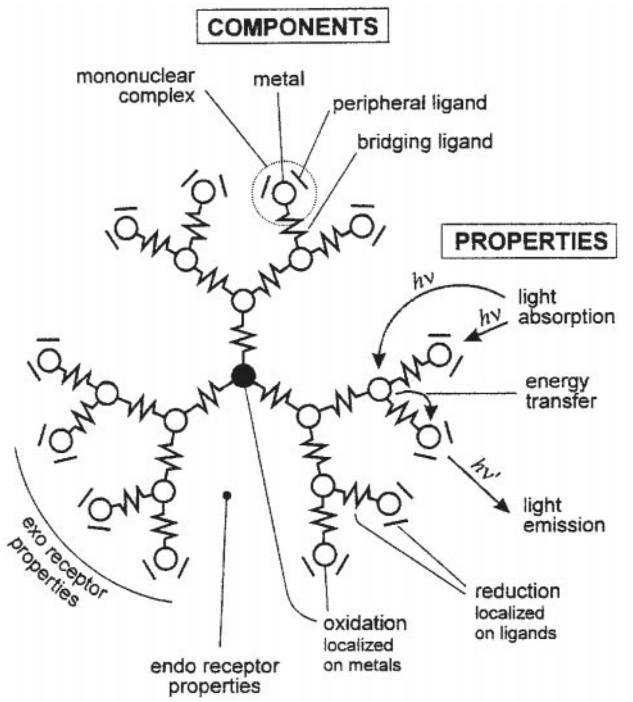


Fig. 7 Schematic representation of a luminescent and redox-active docosanuclear dendrimer with some of the properties indicated.[25] Reprinted with permission from *J. Mater. Chem.*, 1997, **7**, 1227, copyright (1997) The Royal Society of Chemistry.

Because of their remarkable photophysical and electrochemical properties, ruthenium(II)– and osmium(II)–polypyridine complexes[25,26] are ideal components to synthesize luminescent and redox-active oligonuclear species where energy and electron transfer can be driven by light.[26] A great number of compounds have been synthesized using the 2,3- and 2,5-bis(2-pyridyl)pyrazine (2,3- and 2,5-dpp) bridging ligands, and the 2,2′-bipyridine (bpy) and 2,2′-biquinoline (biq) terminal ligands.[26]

The complexes studied contain several chromophoric units in addition to a large number of redox-active centres. Studies carried out on these complexes show the oxidation behaviour to exhibit a selectivity based on the nature of the metal ion and its position in the supramolecular array, thus offering a means of fingerprinting the compounds. Because of the presence of both interacting and non-interacting redox centres, these complexes are good candidates for multielectron-transfer catalysts.[26] The dendrimers reported also display luminescence in solution at room temperature.[25]

2,2′:6′,2″-Terpyridine as a ligand

The coordination of appropriate organic molecules containing multiple metal-binding sites to metal ions provides a versatile alternative to carbon–carbon or carbon–heteroatom bond formation for the construction of dendrimers.[27,28] 2,2′:6′,2″-Terpyridine (terpy), has been reported by a number of authors as a successful connecting ligand to combine preconstructed metal–ligand fragments.[29] Such connectivity permitted the analysis of the final product by electrochemical methods. It had previously been shown that benzylic halides react smoothly with the triruthenium nucleophile, [(terpy)Ru(botpy)Ru(botpy)Ru(HOtpy)][PF_6]$_6$, [botpy = bis(4′-(2,2′:6′,2″-terpyridinyl) ether, HOtpy = 2,2′:6′,2″-terpyridin-4′(1′*H*)-one].The reaction of 1 equiv. of hexakis(bromomethyl) benzene with 6 equiv. of [(terpy)Ru(botpy)Ru(botpy)Ru(HOtpy)][PF_6]$_6$ gave the octadecaruthenium complex (Fig 8).[27] MALDI TOF mass spectrometry provided a convenient and rapid method for the determination of the nuclearity.[27]

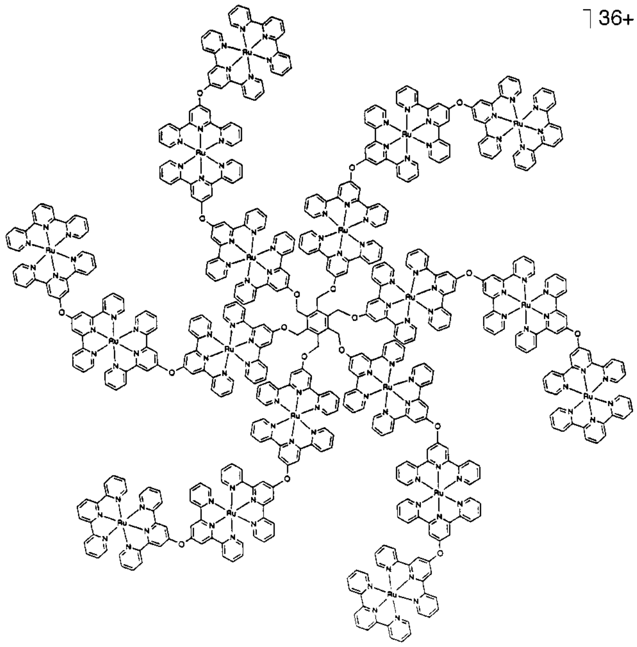
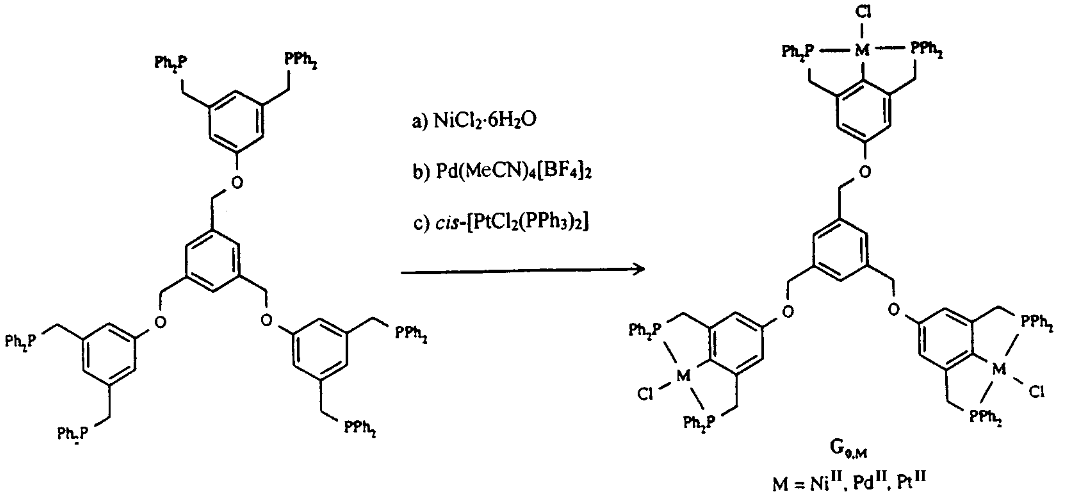


Fig. 8 An octadecaruthenium metallodendrimer.[27] Reprinted from *Inorg. Chim. Acta*, 1996, **252**, 9, copyright (1996), with permission from Elsevier Science.

The construction of this new type of double-tiered metallodendrimer illustrates the importance of stepwise construction by means of controlled metal complexation.[29] This approach also provides versatile methodology for the synthesis of specifically assembled metallodendrimers and related polymers using a combination of the convergent and divergent approaches.[29]

Pincer-type complexes

There is considerable interest in the synthesis of well defined structures of nanometer dimensions.[30] Nanostructures can be developed in an efficient way through non-covalent interactions, *e.g.* H-bonds as opposed to covalent bonds which require multistep syntheses.[30] The early work was carried out using building blocks containing kinetically inert SCS Pd-pincer complexes, coupled *via* branched spacers. The complexes are labile when the fourth ligand is nitrile but not chloride. The coordination of the nitrile ligand to coordinatively unsaturated palladium centres was exploited to assemble the dendrimer building blocks *via* non-covalent interactions. Changing from SCS to PCP ligands made it possible to introduce a variety of transition metals.[31] Ligands derived from the coupling of 3,5-bis[(diphenylphosphino)methyl]phenoxy



Scheme 3 Reprinted with permission from *Organometallics*, 1997, **16**, 4287, copyright (1997) American Chemical Society.

groups to bi- and tri-functional spacers have been cyclometalated with $[Pd(MeCN)_4][BF_4]_2$, *cis*-$[PtCl_2(PPh_3)_2]$ or $NiCl_2 \cdot 6H_2O$ and the resulting cationic complexes converted to neutral complexes. These resulting pincer complexes were then used as building blocks for the controlled assembly of homo- and hetero-multinuclear dendrimers (see Scheme 3).[31] ^{31}P NMR spectroscopy was successfully used as a diagnostic tool for the assembly process as the chemical shift values are very sensitive towards small changes in the microenvironment around the metal centre.

Polynuclear gold(I) complexes

Very little is known about the surface coordinating properties of dendrimers.[32] A few papers on surface-complexing properties of polynuclear gold(I) complexes have been reported[32,33] Dendritic polyamines have been functionalized with terminal diphenylphosphino groups which are ideal for surface complexation of transition metals in low oxidation states and a tailor made ‘spacer’ bearing a group suitable for coupling.[32] A fourth generation polynuclear gold(I) complex with 32 terminal chloro(diphenylphosphino)gold(I) groups is shown in Fig. 9.[32]

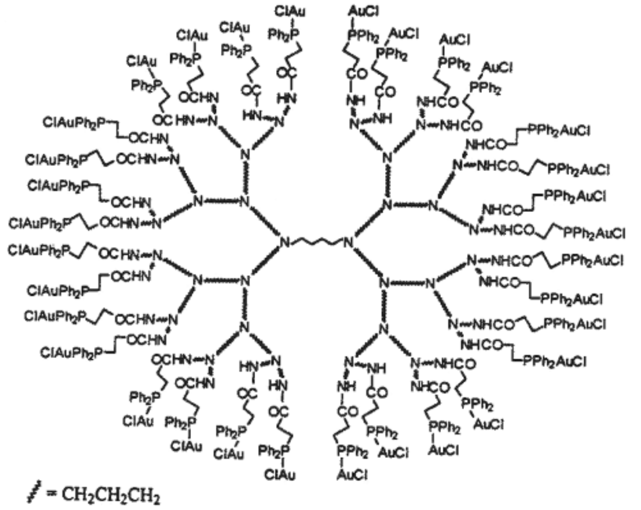


Fig. 9 A polynuclear gold(I) complex with 32 terminal chloro(diphenylphosphino)gold(I) groups.[32] Reprinted with permission from *Inorg. Chem.*, 1996, **35**, 637, copyright (1996) American Chemical Society.

X-Ray crystallography was carried out on the smaller mono- and di-nuclear gold(I) complexes. Intermolecular NH···O hydrogen bonds direct the aggregation of the molecules in the solid state to give chainlike structures. These multinuclear gold(I) complexes[32] represent a new type of metal-containing polymer with a well defined, probably spherical structure and having dendrimer molecules as supporting matrices. They have potential applications in catalysis, biochemical diagnostics and imaging.[32]

Seventh generation phosphorus-containing dendrimers containing reactive functional groups also allowed the complexation of gold derivatives.[33] These appear to be the largest polyphosphine complexes ever prepared, with 3072 $CH_2PPh_2(AuCl)$ end groups.[33]

Main group dendrimers

Much attention has been focussed on main-group-element-based dendrimers, in particular on those based on silicon because of their optical properties and importance in surface functionalization.[34] We will only mention here the recently prepared germanium/silicon dendrimers[35] in this article. The most direct method of preparation would have involved sucessive alkenylations and hydrogermylations, starting with $GeCl_4$. However allylic germanium derivatives are very sensitive to electrophilic reagents. To avoid difficulties associated with undesirable by-products and to diminish the steric strain resulting from the accumulation of branched chains, six-membered ω-ethylenic chains, which are more stable than α- or β-ethylenic chains, were used. Bis(dimethylphenylgermyl)-(methyl) silyllithium was used as the building agent. Using this method, second generation dendrimers having a molecular weight of 5590 were synthesized.[35] Very recently, some dendritic molecules with alternating silicon and germanium atoms along the dendritic backbone, including the molecular structure of a first-generation hybrid permethylated dendrimer, have also been reported.[34]

Structural details and properties of dendrimers

There has been much controversy over the exact shape of dendrimers in solution and many conflicting results have been obtained. The first attempts to calculate dendritic structures were by de Gennes and Hervet.[36] They showed the chain ends to be on the periphery and found a density minimum at the core and a density maximum at the surface. In contrast, Lescanec and Muthukumar allowed the inward folding of chain ends in their calculations which resulted in a density maximum between the dense core and the periphery.[37] Other solution studies showed dendrimers to have low intrinsic viscosities that decreased as the molecular weight increased. They concluded that dendrimers posess globular shapes and lack intermolecular entanglements.[38]

Monte Carlo calculations by Mansfield and Klushin found the chain ends to be distributed throughout the structure, and in close proximity to the core and revealed a density maximum between the centre of mass and the periphery.[39]

Our investigations of Fréchet type poly(benzylphenyl ether) dendrimers functionalized with arene tricarbonylchromium(0) groups showed a transition from an extended to a globular structure as the generation number increased.[40] Solvent accessible surface calculations showed more backfolding to occur as the dendrimer became larger. Although the chain ends were found in all regions of the dendrimer to some extent, most were still located on the periphery of the molecule or in a solvent accessible area for those dendrimers studied. Recent rotational-echo double-resonance NMR experimnets by Wooley *et al.* used experimental constraints on molecular dynamics simulations for the prediction of dendritic structure.[41]

Generally speaking, lower generation dendrimers tend to exist in relatively open forms, but as sucessive layers are added, dendrimers adopt a spherical three-dimensional structure. Solution state properties of dendrimers are generally consistent with a globular shape with the chain ends accessible to the surface, but the precise shape and chain end locations remain uncertain.

Applications of dendrimers as catalysts

One of the most important and exciting uses of dendrimers is expected to be in the field of catalysis. There is great scope for the development of new materials that combine the advantages and minimise the disadvantages associated with heterogeneous and homogeneous catalysts.[42] One approach to such materials is to anchor homogeneous catalysts to polymer supports. Such polysiloxane polymers containing a catalytically active nickel(II) centre have been prepared.[43] However, the disadvantages encountered when anchoring catalytically active metal sites to polymers include the difficulty of accurate control of the number and location of these sites.[42] An ideal polymeric catalyst should be a soluble, multifunctional macromolecule, favouring configurations in which all active sites would be exposed towards the reaction mixture so that they are easily accessible to migrating reactants. Owing to their expected spherical nature, dendritic catalysts are expected to retain the benefits of homogeneous catalysts, such as faster kinetics and accessibility of metal sites but should be easily recoverable from a product-containing solution because of their large size. Ultrafiltration techniques could be used as a means of separation.

The most well known example of a dendrimer used as a catalyst was published in 1994.[42] Zero and first generation polysilane dendrimers were functionalized with diamino arylnickel(II) complexes on their periphery, the metal centre being fixed by a metal–carbon sigma bond to the ligand system (Fig. 10). These dendrimers have been successfully used as homogeneous catalysts for the Kharasch addition of polyhalogenoalkanes to an alkenic C═C double bond. Under mild reaction conditions (room temperature, CH_2Cl_2 as solvent) using methyl methacrylate as substrate and CCl_4 as reagent, the catalytic activity of these zero and first generation dendrimers, as shown by kinetic data, is 20 and 30 % respectively less than the monomeric compound.[42] Molecular models of these dendrimers such as that in Fig. 10, show the nickel sites to be well separated from one another at the end of long flexible branches and consequently the accessibility of the catalytically active nickel centres should be similar to the monomeric model compounds synthesized previously. All the characteristics found for the monomeric model are retained in the dendrimer catalyst system. These new dendrimers represent nanoscopic catalysts with physical characteristics such as size, solubility and dispersity of catalytic sites that are very precisely defined, so affording these molecules advantageous properties for physical separation and catalyst recycling.[42]

The excellent coordinating ability of phosphines has been used to prepare novel organometallic dendrimers. It has previously been shown that mononuclear [Pd(triphosphine)(MeCN)][BF_4]$_2$ complexes will catalyse the electrochemical reduction of CO_2 to CO.[44] The presence of a triphosphine ligand in these catalysts suggests that dendrimers containing this unit may also catalyse the reduction. Two approaches have been used to synthesize such dendrimers, the first involving sequential addition of diethyl vinylphosphonate to primary phosphines followed by reduction with lithium aluminium hydride; the second approach using the addition of bis[(diethylphosphino)ethyl]phosphine to tetravinylsilane. Small dendrimers containing 12 or 15 phosphorus atoms metallated with [Pd(MeCN)$_4$][BF_4]$_2$ have now been shown to exhibit catalytic activity for the electrochemical reduction of CO_2. These results demonstrate the feasibility of performing catalytic reactions using metallated organophosphine dendrimers.[44]

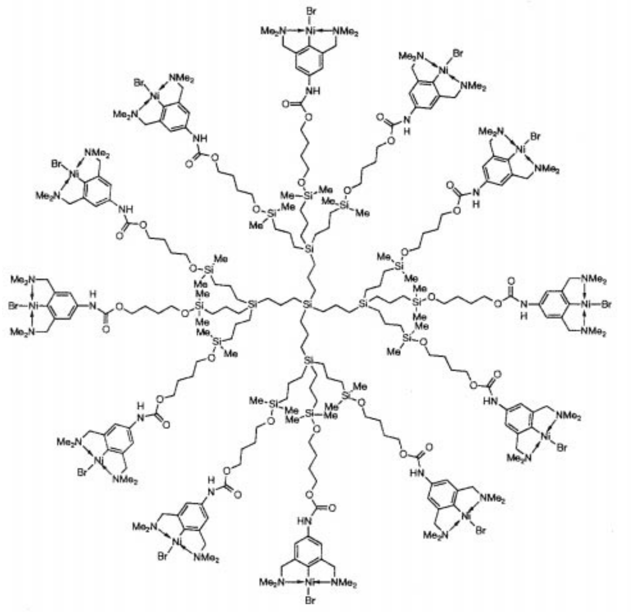


Fig. 10 Schematic structure of the first generation poylsilane dendrimer functionalized with catalytically active diamino arylnickel(II) complexes on the periphery.[42] reprinted with permission from *Nature*, 1994, **372**, 659, copyright (1994) Macmillan Magazines Ltd.

Dendritic diphosphines synthesized from polyamino dendrimers by double phosphinomethylation of each of the primary amino end-groups provides the possibility of specific complexation with a variety of transition metals including iridium, palladium and rhodium (Fig. 11).[45] The metal-containing dendrimers were successfully used to catalyse the Heck reaction of bromobenzene and styrene to form stilbene. The reaction mixture was analysed by gas chromatography.[45] In previous examples of catalysis with dendritic metal complexes, the catalytic activity was shown to be slightly or significantly lower than that of the corresponding monomeric parent compounds.

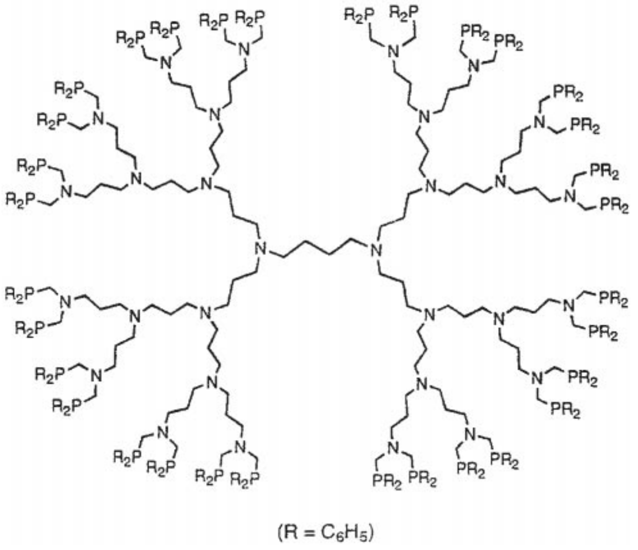


Fig. 11 The phosphinomethylated dendrimer with sixteen bidentate ligands on the outer surface provides the possibility of complexation with many transition metals.[39] Reprinted with permission from *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1526, copyright (1997) Wiley-VCH.

This system, however, showed a significantly higher activity, which is attributable to the higher thermal stability of the dendritic complexes. The strategy developed here for the synthesis of dendritic diphosphines opens up a general method for preparing transition metal-containing dendrimers for use in catalysis.[45]

Most of the optically active chelating phosphines used in enantioselective transition metal catalysis involve a chiral skeleton bearing two diphenylphosphino groups.[46] The chiral information is transferred from the ligand to the catalytically active centre *via* the arrangement of the phenyl rings of the diphenylphosphino groups.[46] Owing to the limited size of the diphenylphosphino groups, the idea of using larger phosphines represents a promising new approach.[46] The expanded phosphines should contain a chelate skeleton, *e.g.* the PCH_2CH_2P grouping, and several layers of branching units built up with optically active groups attached to the phosphorus atoms.[46] Owing to the space-filling nature of the expanded ligands, the chiral information should be forced towards the pocket of the catalyst, in which the enantioselective reaction takes place. Because the catalytic reaction takes place at the core of the dendrimer, the system resembles the prosthetic group of an enzyme. For this reason, these molecules have been termed 'dendrizymes'.

Conclusions and future developments

An exciting future is forseen for dendrimers, and transition-metal-containing dendrimers in particular. Already the rapidly growing increase in the number of publications is an indication that dendrimers represent a new and important class of compounds. It has been demonstrated in the examples above that it is possible to synthesize mono- and multi-metallic molecules with desirable characteristics and properties by careful choice of metal and ligand systems. Little work on the solid-state structures of dendrimers has thus far been carried out, presumably because of the difficulty of crystallising them. For this reason, molecular modelling is expected to play a key role in providing some of the answers concerning structures and also properties. Dendrimer research has already shifted from a purely synthetic orientation towards investigating the novel properties and exploring the potential applications of these molecules, in particular catalysis. Already we have seen their novel applications as encapsulation reagents, artificial gene-transfer materials, as building blocks for the self-assembly of larger nanostructures and in chiral recognition. Important applications will likely emerge in the next few years in a diversity of fields. New synthetic methods will continue to be important until dendrimers can be produced cheaply and easily on an industrial scale.

Only time will unveil the full range of applications of these large and beautiful molecules.

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