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Coordination Chemistry Reviews 233–234 (2002) 223–235

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CHEMISTRY REVIEWS

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Designing dendritic polymers containing phosphorus donor ligands and their corresponding transition metal complexes

Mohua Dasgupta, M. Brad Peori, Ashok K. Kakkar *

Department of Chemistry, McGill University, 801 Sherbrooke St. West, Montreal, Quebec, Canada H3A 2K6

Received 19 November 2001; accepted 24 May 2002

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Abstract

Dendritic polymers, especially those incorporating donor ligand sites in their backbone, constitute an intriguing class of macromolecules that offers opportunities in building smart catalytic materials. Their synthesis using easily accessible reagents and high-yield methodologies has been a subject of intense investigation, and still remains a topical area of research. The availability of such materials in large quantities can help one explore their physical characteristics in detail, which can lead to tailor-made systems with manipulated properties. A survey of recent efforts devoted to the synthesis of dendritic macromolecules containing mainly phosphorus based donor ligands and their corresponding transition metal fragments, is reported. An attempt is also made to evaluate the applications of these organometallic dendrimers in catalysis.

Keywords: Dendritic polymers; Phosphorus donor ligands; Transition metal complexes

1. Introduction

There has been considerable interest in the development of new materials for supported metal catalysis that offer the potential for the design of efficient catalytic systems with an advantageous combination of specific properties of homogeneous and heterogeneous phases. Such systems will retain the catalyst's activity and selectivity while facilitating its removal from the reaction products [1]. Much of the effort in this area has been directed at tethering organometallic fragments to inorganic oxide (silica) [2] or organic polymers [3]. One of the disadvantages of anchoring homogeneous catalysts to such supports is the difficulty in determining the accurate amount and location of the metal sites. Dendritic polymers, often referred to as dendrimers and hyperbranched polymers, offer an alternative and viable approach to address some of these issues [4]. Dendrimers possess a precise molecular architecture, predetermined chemical composition and the ability, due to their large (nanoscopic) size and relative rigidity, to be removed from solvent streams by crystallization or ultrafiltration methods, and recycled [5]. In a divergent mode, these tree-like molecules evolve from a controlled

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* Corresponding author. Tel.: +1-514-398-6912; fax: +1-514-398-3797

E-mail address: ashok.kakkar@mcgill.ca (A.K. Kakkar).

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PII: S0010-8545(02)00200-X

repetitive growth starting from a polyfunctional core. From the core, two or more identical branches emanate, each branch containing further sites at the end. With each successive generation, a ball-like structure evolves until further growth is limited by surface congestion. Monodispersity, uniform branching, and radial symmetry typically characterize dendrimers [6,7], whereas hyperbranched polymers tend to be polydisperse, irregularly branched, and asymmetric [8]. The contrasting synthetic approaches used to generate dendritic polymers, namely the uncontrolled, single-step growth of hyperbranched polymers versus the controlled, iterative growth of dendrimers, are responsible for the structural attributes distinguishing these two types of macromolecules [6–8]. However, both subclasses of dendritic polymers share certain structural features, such as the tendency to adopt globular conformations at high molecular weights, and an abundance of functional groups within their branched frameworks [7,8]. In dendrimers these moieties may be located at the dendrimer periphery or within [6,7,9], while hyperbranched polymers generally contain functional groups throughout their dendritic infrastructure [8,10]. The structural similarities and differences between dendrimers and hyperbranched polymers greatly influence their physical properties, and consequently their suitability for potential applications [6–10].

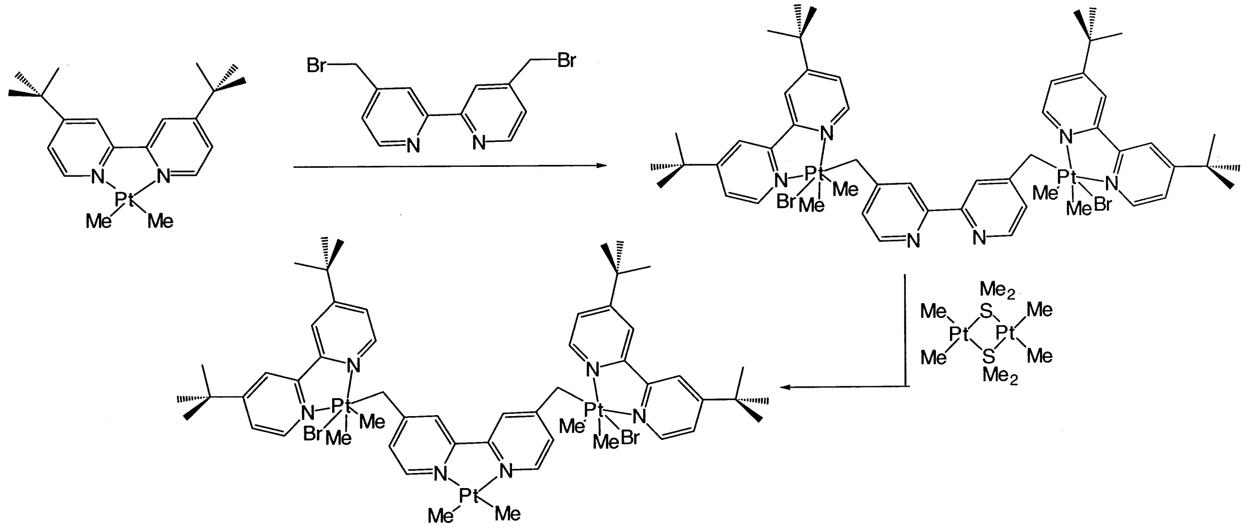
The introduction of transition metals on the surface or within dendrimers has been a recent trend, particularly towards desired applications in a variety of areas. The incorporation of metal complexes in dendritic materials is done either by surface modification in which the mode of attachment is at the periphery of the arboral, or by incorporation of the transition metals within the dendritic infrastructure, which is a much more arduous task [11]. However, metallodendrimers containing luminescent and redox-active transition metal centers in every generation have been prepared using sequential reaction of the metal centers and the protection/deprotection of the ligands [12]. Puddephatt's group has reported building dendrimers by oxidative addition to Pt^{II} complexes in a convergent synthetic approach [13]. They prepared a dendritic wedge by oxidative addition of the C–Br bonds of 4,4′-bis(bromomethyl)-2,2′-bipyridine to the square planar Pt(II) complex, $[PtMe_2(bu_2\text{-bpy})]$ (bu_2-bpy = 4,4′di-*tert*-butyl-2,2′-bipyridine) leading to a complex with two Pt(IV) centers and a bipyridine unit with free nitrogen sites. The latter was then used for a ligand displacement reaction with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ to give the triplatinum dendron which contains a Pt(II) site that can be subsequently reacted in a similar manner to give the desired dendritic wedge (Scheme 1). The dendritic wedge was finally coupled to the 1,2,4,5-tetrakis(bromomethyl)benzene core resulting in the organometallic dendrimer containing 28 platinum based moieties (Scheme 2).

Periphery functionalized silicon dendrimers with 12 arylnickel(II) centers capable of catalyzing the Kharasch addition of perhaloalkanes to olefins, were reported by van Koten's group [14]. They anchored up to 12 pincer type NCN–Ni(II) complexes to the periphery of soluble carbosilane dendrimers (Scheme 3). The catalytic activity of the resulting organometallic dendrimer was determined to be slightly lower than that of the monomeric compound. An investigation of this behavior suggested that the lower rates were due to high local concentration of nickel centers, as evidenced by molecular modeling studies [14b]. The local concentration resulted in an interaction between neighboring Ni(II) and Ni(III) sites formed during the catalytic reaction. This catalyst deactivation due to steric congestion was relieved by synthesizing starburst carbosilane dendrimer which had four well spaced pincer type NCN–NI(II) centers (Scheme 3). The catalytic activity of this organometallic starburst dendrimer was found to be higher than that of above mentioned organometallic dendrimer [14b]. Similar functionalization at the periphery was used to prepare dendrimers containing eight zirconocene centers capable of catalyzing olefin polymerizations [15].

Phosphorus based donor ligands have been extensively utilized in the design of transition metal homogeneous catalysts, and are expected to play a pivotal role in heterogenizing these complexes on key supports [1c,2,9c,16]. This review is intended to condense and bring into focus efforts of our group and others in the design of dendritic supramolecular structures containing such donor sites, and their ligation to transition metals leading to organometallic dendritic polymers. This is still a growing area and the emphasis is placed on their synthesis while highlighting any catalytic applications that have been explored. Two general methodologies have emerged over the years, and as pointed out above, include functionalization of pre-formed dendrimers with donor sites on the periphery or distribution of such donor moieties continuously throughout the backbone. An advantageous choice of one over the other in the design of smart catalysts remains a debatable issue.

2. Phosphorus containing dendrimers

One of the earliest examples of phosphorus containing dendrimers can be traced back to 1990, when a core of $P(C_6H_4\text{-}p\text{-}CH_2OCH_3)_3$ was prepared from PCl_3 and $BrMg\text{–}C_6H_4\text{–}CH_2OCH_3$. The phosphorus center was quaternized by its reaction with CH_3I or $C_6H_5CH_2Br$, and then used to build dendrimers containing up to 40 cationic phosphorus centers [17]. Since the phosphorus centers in these dendrimers were quaternized, they were

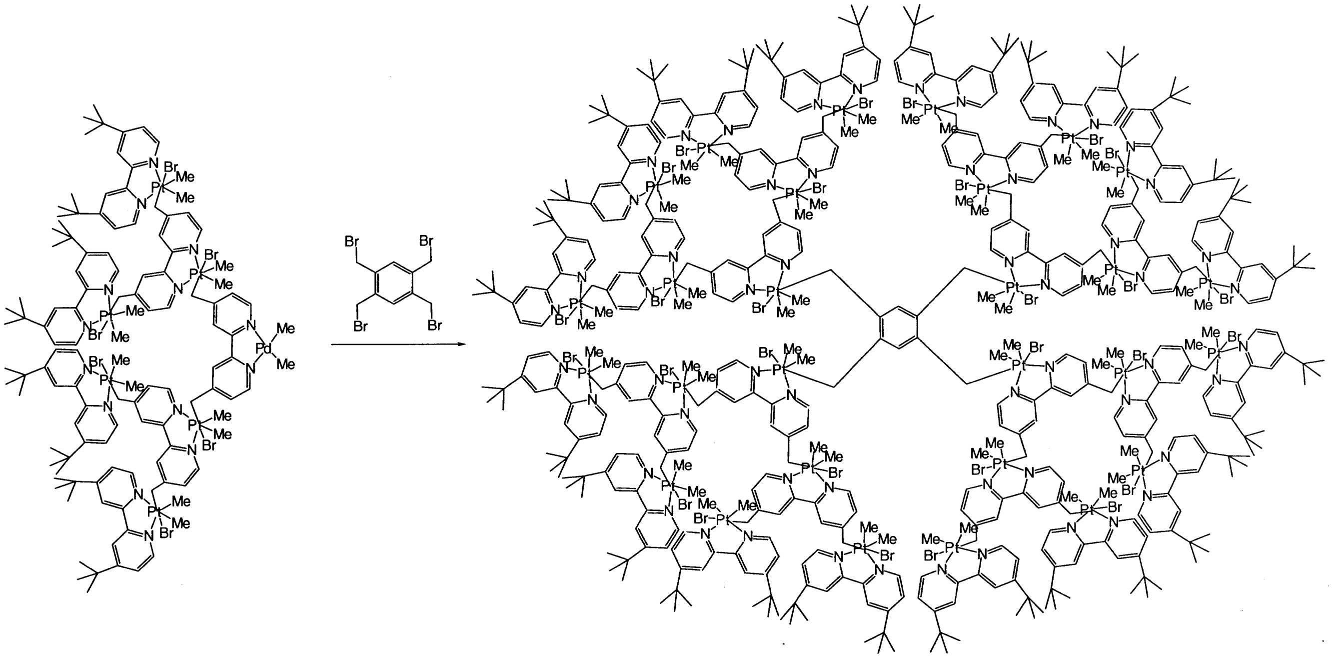


Scheme 1. Synthesis of a platinum-bipyridyl dendritic wedge [13].

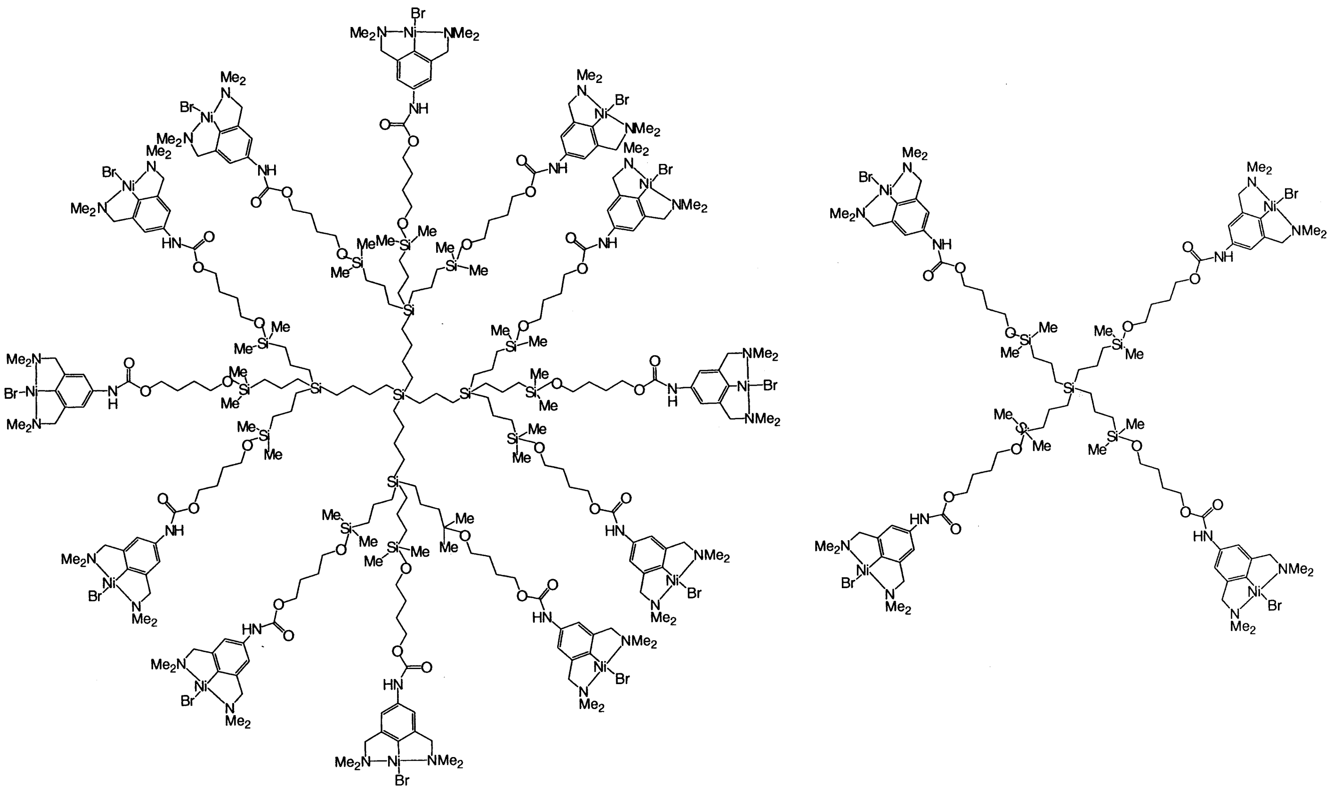
unsuitable to bind any metal centers. The same group later prepared similar phosphonium dendrimers in which the core P(V) centers could be reduced to P(III), and the latter was bonded to Au(I)Cl (Scheme 4) [18]. Their work showed that dendrimers containing phosphorus in the backbone can be prepared, even though very few actual metal anchoring sites (phosphines) were present in these dendrimers.

DuBois's group has employed free-radical addition of diethylvinylphosphonate to a primary phosphine, followed by $LiAlH_4$ reduction to prepare dendrimers containing up to 15 phosphorus units in the backbone [19]. The latter were then used to react with $[Pd(CH_3CN)_4](BF_4)_2$ to create square planar palladium centers that could catalyze electrochemical reduction of CO_2 to CO (Scheme 5). However, Pd–Pd bond formation was observed during the electrochemical reductions which led to the deactivation of the catalyst. To circumvent this problem a better spatial separation of the palladium centers was proposed.

The concept of functionalization of the commercially available dendrimers was used by Schmidbaur's group to introduce phosphines on the periphery [20]. They used β-(diphenylphosphino)propionic acid as a coupling agent to bind diphenylphosphines to third and fourth generation dendrimer, diaminobutane-poly(trimethyle-



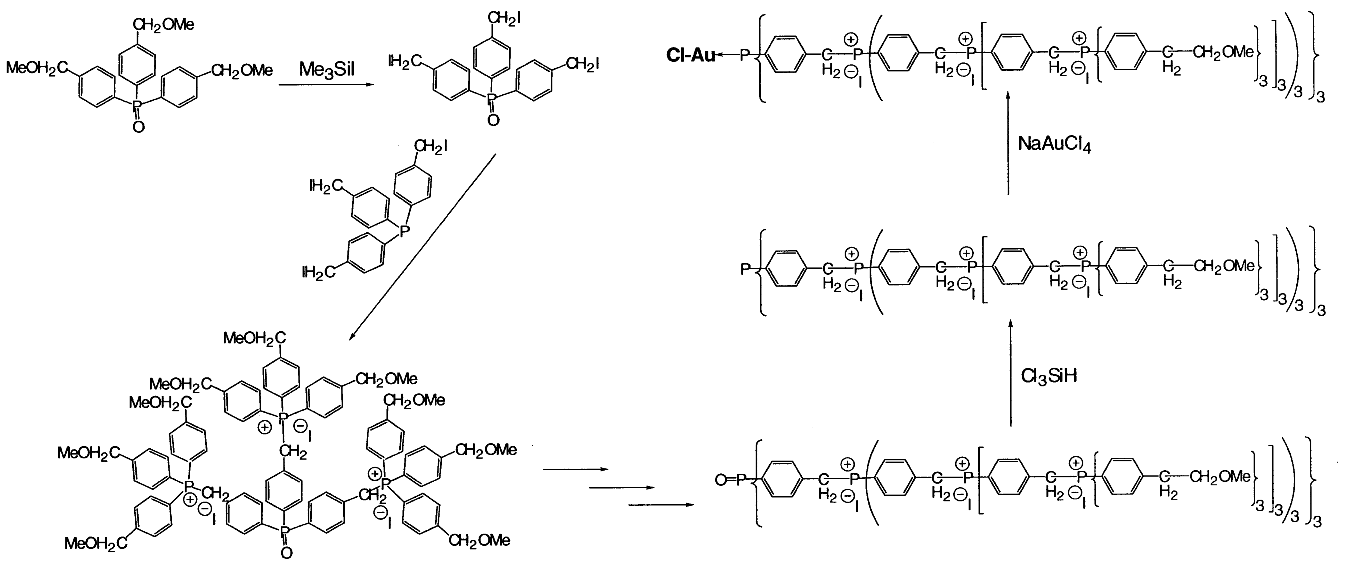
Scheme 2. Coupling of platinum-bipyridyl dendron to a tetrafunctional core [13].



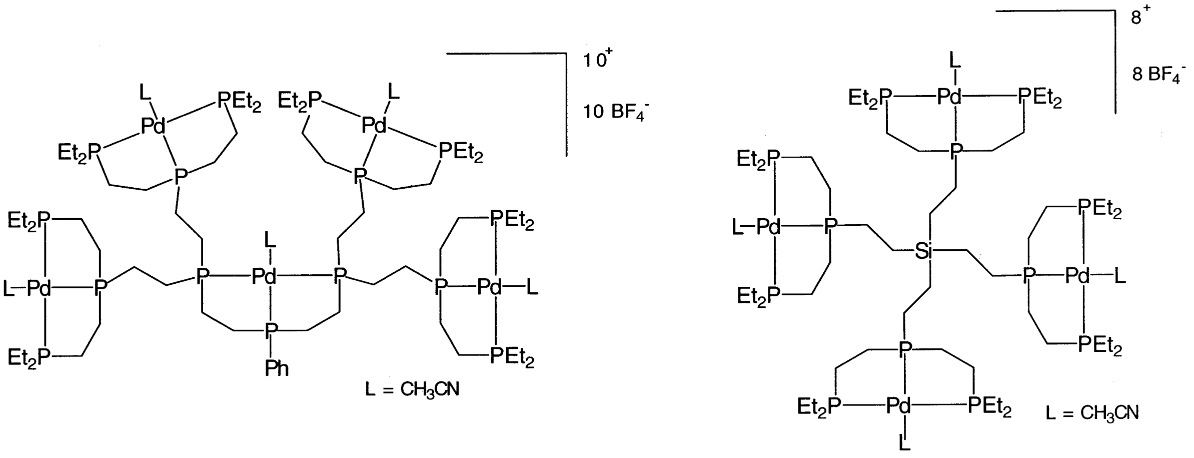
Scheme 3. Carbosilane based nicket(II) dendrimers [14].

neamine), leading to 16 or 32 phosphines at the terminus. The latter were then coupled to gold by reacting the dendritic compounds with Me_2SAuCl.

Similarly functionalized dendrimers containing phosphine ligands on the periphery were prepared by Reetz et al. by a double phosphinomethylation of the terminal primary amino groups of the commercially available 1,4-diaminobutane based dendrimer [21]. The group prepared a dendrimer containing eight bidentate phosphine end groups (Scheme 6) that were reacted with a variety of metal complexes including $[PdCl_2(C_6H_5CN)_2]$, $Ir(1,5\text{-cyclooctadiene})_2BF_4$ and $Rh(1,5\text{-cyclooctadiene})_2BF_4$. The palladium bound dendrimer was used as a catalyst for Heck reaction using bromobenzene and styrene as substrates, leading to the formation of stilbene. The organometallic dendrimer was recovered



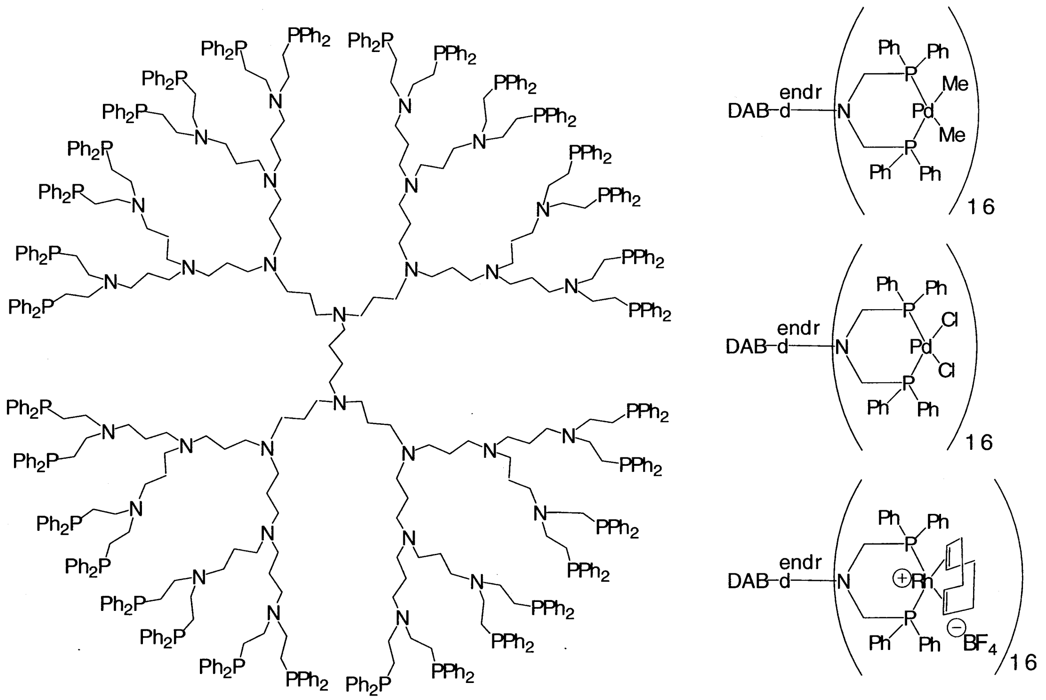
Scheme 4. Synthesis of phosphonium based metallodendrimers [18].



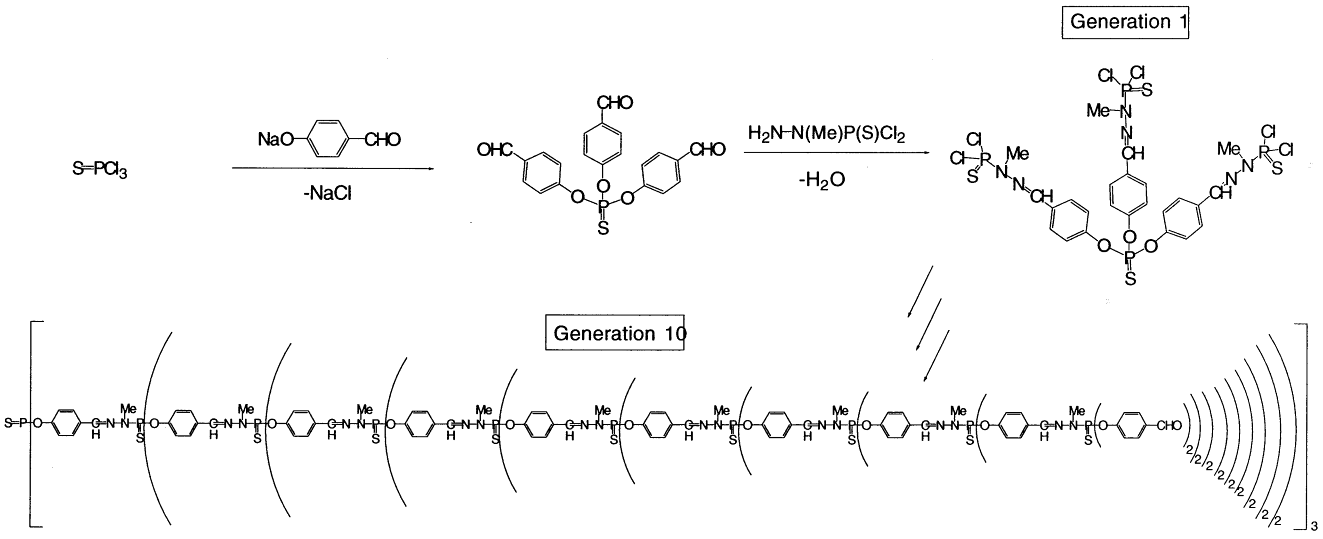
Scheme 5. Palladium dendrimers capable of reducing CO_2 to CO [19].

from the reaction mixture, and recycled with retention of its original catalytic activity. They noted that the catalytic activity of the dendrimer was in fact higher than the corresponding monomeric complex. The Rh-bound dendrimer was found to be active in hydroformylation of 1-octene. The phosphine dendrimers were also used to prepare bimetallic complexes by first reacting the dendrimer with 50% molar concentration of $[Pd(CH_3)_2(tmeda)]$, and then with $[Ni(CH_3)_2(tmeda)]$.

The most notable contribution to the dendrimers containing phosphorus in the backbone has been made by the group of Majoral and Caminade [9d,22]. The synthesis of large phosphorus containing dendrimers is achieved by first reacting $(S)PCl_3$ with the sodium salt of 4-hydrobenzaldehyde to give the trialdehyde. Alternate additions of hydrazine derivative $H_2NNMeP(S)Cl_2$ and hydroxybenzaldehyde sodium salt afforded up to 10th generation dendrimer (Scheme 7). The peripheries of some of these dendrimers with a P(V) backbone could be functionalized with phosphines. To achieve this, aldehyde terminal groups were treated with methylhydrazine, followed by reaction with $HOCH_2PPh_2$. Using this approach, they prepared up to 10th generation dendrimers containing 3000 donor phosphorus groups



Scheme 6. Periphery functionalized DAB dendrimers [21].



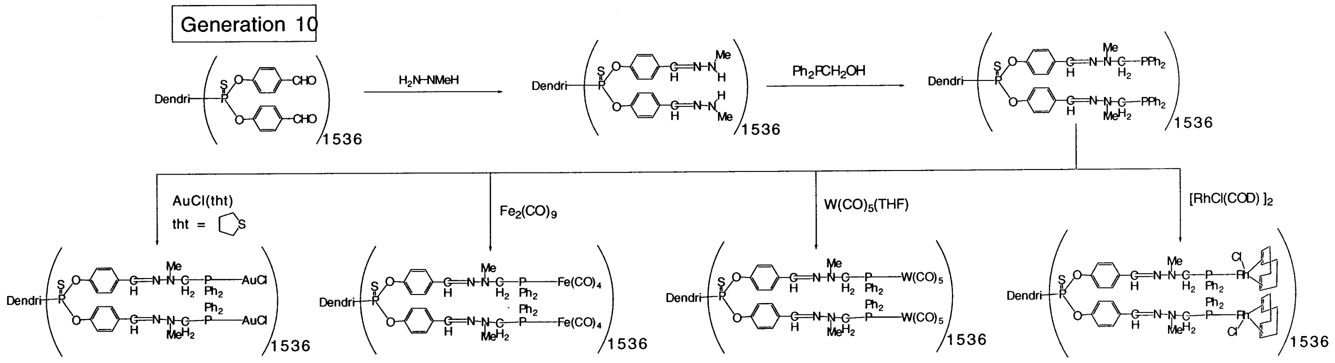
Scheme 7. Synthesis of P(V) Dendrimers [9d, 22].

on the outside [22]. These dendrimers were then coupled with a variety of metal centers including $Fe(CO)_4$, $W(CO)_5$ and Au–Cl (Scheme 8).

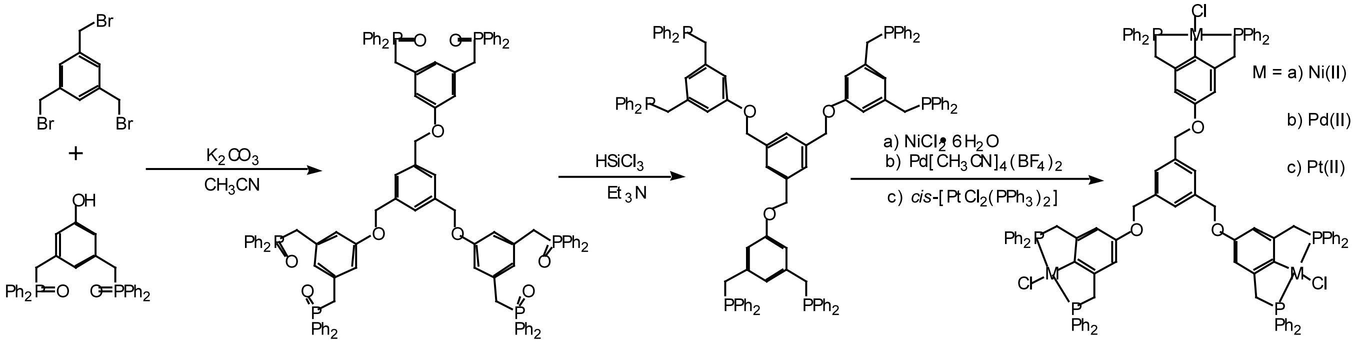
Phosphorus containing pincer type small dendrimers have been synthesized by coupling 3,5-bis[(diphenylphosphenyl)methyl]phenol with α,α′,α″-tribromomesitylene under basic (K_2CO_3) conditions [23]. The P=O units on the first generation dendrimer were reduced using a trichlorosilane and triethylamine mixture. This resulted in poor yields and a difficulty in purification of the products. However, the desired compound containing bidentate phosphines at the periphery was then reacted with $NiCl_2{\cdot}6H_2O$, $Pd[CH_3CN]_4(BF_4)_2$ or *cis*-$[PtCl_2(PPh_3)_2]$ in a cyclometallation reaction to yield the corresponding metallo-dendrimers (Scheme 9).

Carbosilane dendrimers offer a combination of useful properties such as inertness, solubility and a rigid framework [24]. The peripheries of these dendrimers can be functionalized with phosphine donor groups that can bind transition metal complexes. Van Leeuwen's group used such a carbosilane dendrimer that had double bonds at the periphery. The latter were hydrosilylated with chlorodimethylsilane or dichloromethylsilane, and upon further reaction with lithium methyldiphenylphosphine–TMEDA, diphenylphosphine groups were introduced on the peripheral layer. The functionalized carbosilane dendrimers containing up to 36 monodentate phosphine units or 12 bidentate phosphines were obtained as waxy solids with more than 95% purity [25]. The phosphines were then reacted with $[\eta^3\text{-}C_3H_7)PdCl]_2$ to form allyl–palladium complexes (Scheme 10). The latter were employed as catalysts for the allylic alkylation of allyl trifluoroacetate and sodium diethyl methylmalonate. These metallo-dendrimers were also used in continuous flow process using a membrane reactor.

Rossell's group has also used carbosilane dendrimers to anchor phosphine groups on the periphery. The Si–Cl end groups on the carbosilane dendrimer were reacted with $LiCH_2PPh_2$ leading to grafted PPh_2 end groups. These were then treated with AuCl(tetrahydrothiophene) to anchor AuCl moieties on the surface.



Scheme 8. Anchoring of transition metals to P(V) dendrimers [22].

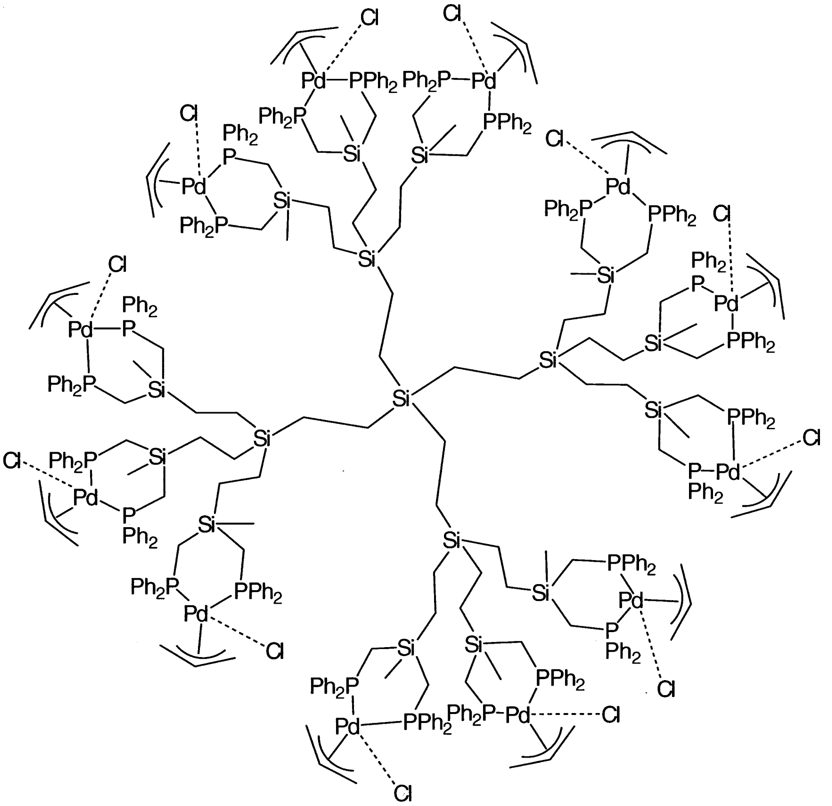


Scheme 9. Synthesis of pincer type metallodendrimer [23].

The chloride groups on the latter could then be reacted with $(PPh_2)_4[Fe_3(CO)_{11}]$ to introduce iron cluster anions on to the dendrimer [26]. These dendrimers were found to be insoluble, and to enhance their solubility they recently [27] enlarged the dendrimer framework.

van Koten's group has recently developed a route to lithiate the outskirts of carbosilane dendrimers which can then be used to introduce a variety of functional groups including diphenylphosphine [28]. This is an excellent route to prepare functionalized carbosilane dendrimers. One such organophosphine functionalized dendrimer was used to anchor a Ru(II) complex upon reaction with a N_2-bridged binuclear complex, $[\{RuCl_2(\eta^3\text{-NN'N})\}_2(\mu\text{-}N_2)]$ [29].

Our group has been involved in the design of new materials that could be prepared using commercially available or easily accessible reagents [2,30]. We have developed a simple methodology to prepare a variety of such supramolecular structures including dendrimers containing donor sites distributed throughout their backbone. It typically employs acid–base hydrolysis of an aminosilane with a desired molecule containing terminal OH groups under ambient conditions [31]. This approach has allowed us to prepare P(III) containing dendritic polymers that could be subsequently used to bind transition metal complexes, or to prepare organometallic dendrimers in which a Rh-bound complex is used for dendrimer growth and thereby, embedded throughout the cascade. The elegance of this



Scheme 10. Carbosilane based metallodendrimer [25].

simple synthetic methodology lies in ease of synthesis, and high yield reactions.

The divergent build-up of dendrimers containing P(III) donor sites in the backbone [32], required a controlled addition of tri(hydroxypropyl)phosphine to a solution of 3 equivalents of bis(dimethylamino)dimethylsilane, leading to the formation of the silylamine adduct. The latter was subsequently added to a solution of 3 equivalents of tri(hydroxypropyl)phosphine, resulting in the synthesis of the first generation dendrimer (referred to as $\mathbf{P_4}$) with terminal hydroxyl groups which could then be used to continue dendrimer growth [32]. By a repetitive reaction sequence of $(CH_3)_2Si(NMe_2)_2$ and $P[(CH_2)_3OH]_3$ we have prepared second ($\mathbf{P_{10}}$), third ($\mathbf{P_{22}}$) and fourth ($\mathbf{P_{46}}$) generations of such dendrimers. These phosphorus containing dendrimers were found to be soluble or miscible in a wide range of solvents including THF, diethylether, dimethylsulfoxide, chloroform and toluene. The latter was very useful in their characterization by ^{1}H-NMR, $^{31}P\{^1H\}$-NMR, $^{29}Si\{^1H\}$-NMR, and FTIR. For example, the ^{1}H-NMR spectrum of $\mathbf{P_4}$ showed a noticeable downfield resonance shift attributable to the methylene protons bound to oxygen from those of tris(hydroxypropyl)phosphine ($\mathbf{P_1}$), and the signals in the ^{1}H-NMR spectrum showed some broadening on increasing size. $^{31}P\{^1H\}$-NMR spectral data for these dendrimers was also highly characteristic, and indicated that the phosphines in each generation were chemical shift distinct. For example, with the evolution of dendritic structure, a new peak appeared for the phosphorus groups in each generation. FTIR spectra of these phosphorus containing dendrimers in the solid state (KBr pellet) showed stretching frequencies for Si–O (~ 1088 cm^{-1}), $Si-CH_3$ (~ 1258 cm^{-1}), and H_2C-OH (~ 3350 cm^{-1}). The peak intensities of the hydroxyl groups were reduced in comparison to the alkyl vibrations with the growth of each generation.

The above phosphine dendrimers were easily linked to Rh(I) centers via a bridge-splitting reaction [33] with μ-chloro-(1,5-cyclooctadiene)rhodium (I) dimer, $[(\mu\text{-}Cl)(1,5\text{-}C_8H_{12})Rh]_2$ resulting in the functionalization of the dendrimer bound phosphine with the rhodium complex (Scheme 11). The latter was indicated by a downfield shift in the cyclooctadiene peaks upon binding of Rh to the phosphine in the ^{1}H-NMR spectra, and by the presence of doublets in the $^{31}P\{^1H\}$-NMR spectrum due to Rh–P coupling.

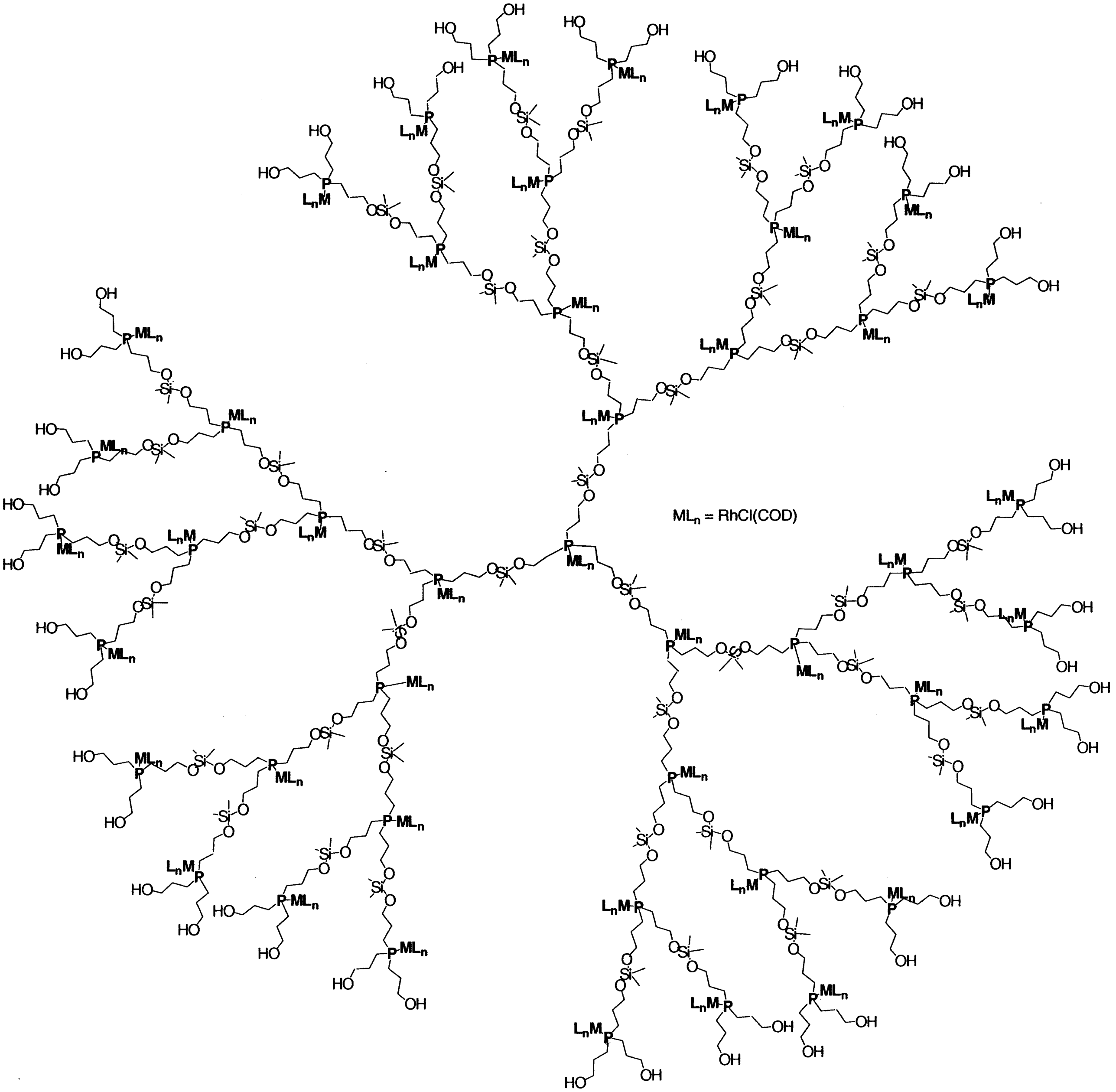
The organometallic dendrimers in which each phosphine is bonded to Rh(I) centers can also be prepared by a similar divergent synthetic methodology, by first preparing the complex, $Rh(1,5\text{-}C_8H_{12})(Cl)P\{(CH_2)_3OH\}_3$ ($\mathbf{Rh_1}$) that is used as the core, and also a repeat unit. A similar approach to that mentioned above for organo-phosphine dendrimers, involved a careful treatment of $Rh(1,5\text{-}C_8H_{12})(Cl)P\{(CH_2)_3OH\}_3$ with 3 equivalents of $(CH_3)_2Si(NMe_2)_2$, followed by addition to 3 equivalents of $\mathbf{Rh_1}$, resulting in the formation of first generation dendrimer containing four rhodium centers ($\mathbf{Rh_4}$). The process was repeated leading to the synthesis of higher generation dendrimers containing up to 46 rhodium centers (Scheme 11). These Rh(I) containing dendrimers were also characterized by ^{1}H-, $^{31}P\{^1H\}$-NMR, MALDI-TOF mass spectrometric and elemental microanalyses. The $^{31}P\{^1H\}$-NMR spectrum indicated the presence of a doublet for the bound **Rh** center, and with the growth of each generation, a new Rh–P doublet emerged. Molecular masses determined from MALDI-TOF MS spectra for $\mathbf{Rh_{22}}$ and $\mathbf{Rh_{46}}$ showed peaks related to the required molecular weight plus lithium ions, complexation which takes place inside the mass spectrometer generating the multiply charged anions necessary for detection and determination of molecular weights.

The organo-rhodium dendrimers were found to be active catalysts for olefin hydrogenation. The catalytic activity of these Rh(I) dendrimers was found to be similar to that of the monomeric complex, however, the turnover frequencies decreased upon growth of the Rh(I) cascade. The similarity in reaction magnitude is expected, however the catalytic selectivities may show differences since the Rh(I) sites are present throughout the dendrimer. The dendritic catalyst was found to be stable and could be reused with only a 5% decrease in conversion.

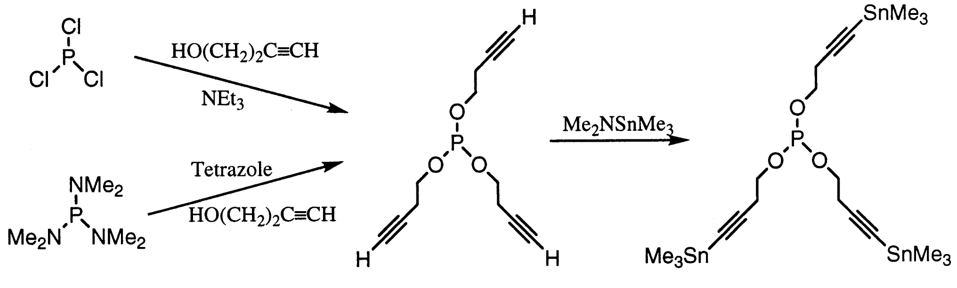
We have also prepared P(III) compounds which have three terminal alkynyl units per phosphorus center, $P[O(CH_2)_2C{\equiv}CH]_3$. The synthesis of the latter was achieved by reacting PCl_3 with $HO(CH_2)_2C{\equiv}CH$ in the presence of excess base (e.g. triethylamine) to neutralize HCl released during the reaction [34]. An alternative route to this compound involved the tetrazole mediated coupling of hexamethylphosphorus triamide, $P[N(CH_3)_2]_3$ with 3 equivalents of terminal alkynyl alcohol. The latter are useful starting materials for making dendritic polymers. The terminal alkynyl units in $P[O(CH_2)_2C{\equiv}CH]_3$ were metallated by reacting it with Me_2NSnMe_3 to give $P[O(CH_2)_2C{\equiv}CSnMe_3]_3$ (Scheme 12). The latter could then be reacted with molecules containing terminal Cl groups ($ClENMe_2$) and the reaction sequence repeated to make dendritic polymers.

3. Phosphorus containing hyperbranched polymers

The two-step divergent synthetic route to phosphorus(III) containing dendrimers described above relied on the controlled combination of reactants in relevant steps to perpetuate dendritic growth. In the first step of this methodology, dropwise addition ensured that $(CH_3)_2Si(NMe_2)_2$ remained in excess of OH-terminated



Scheme 11. Phosphine bound rhodium dendrimer [32].



Scheme 12. Phosphorus based cores with terminal alkyne units.

phosphine, thereby encouraging the reaction of one amine group per silicon atom with hydroxyl moieties. Similarly, dropwise addition in the second step made certain that $P[(CH_2)_3OH]_3$ was in excess of amine-bearing intermediates to favor the coupling of one hydroxyl group per phosphorus atom with amine groups. Thus, controlled combination allowed us to dictate the layer-by-layer construction of organophosphine dendrimers, and minimize the insertion of structural defects into dendritic backbones.

We were intrigued to know if the uncontrolled combination of reactants would also lead to highly branched macromolecules. This led to the exploration of a one-pot synthesis of hyperbranched polymers containing P(III) units distributed throughout the backbone by random condensation of 2 molar equivalents of $P[(CH_2)_3OH]_3$ with 3 equivalents of $(CH_3)_2Si(NMe_2)_2$ in THF [34]. This ratio of reactants ensures that for every hydroxyl functionality a complementary amine group is present, thereby potentially inducing hyperbranched growth. It was hoped that these hyperbranched polymers would architecturally resemble phosphorus(III) containing dendrimers derived from the same monomeric units, albeit with the structural imperfections commonly characterizing dendritic polymers prepared using one-step synthesis.

A white, viscous liquid, was typically afforded from this reaction and the ^{1}H-NMR spectrum consistently pointed to the presence of one compound, as evidenced by the single peak in the Si–CH_3 region of the spectrum. The broadness of CH_2 multiplets in the above spectrum indicated that this compound was polymeric in nature. $^{31}P\{^{1}H\}$-NMR spectrum exhibited three singlets, suggesting a hyperbranched structure of the product. If the above reaction had led to a linear growth by uncontrolled polymerization of $P[(CH_2)_3OH]_3$ and $(CH_3)_2Si(NMe_2)_2$, a single broad phosphorus resonance would have appeared in the $^{31}P\{^{1}H\}$-NMR spectrum. The MALDI-TOF mass spectrum of the polymer contained a major peak that corresponded to the mass of the first-generation dendrimer $\mathbf{P_4}$, and a minor peak close to the mass of P_{10}. The phosphorus containing hyperbranched polymer was reacted with $[(\mu\text{-Cl})(1,5\text{-}C_8H_{12})Rh]_2$ in THF at room temperature, and the $^{31}P\{^{1}H\}$-NMR of the resulting compound showed doublets due to Rh–P coupling, and contained no peaks that could be assigned to residual free phosphines. Its MALDI-TOF mass spectrum corresponded with the mass of the metallated dendritic polymer-$\mathbf{Rh_4}$.

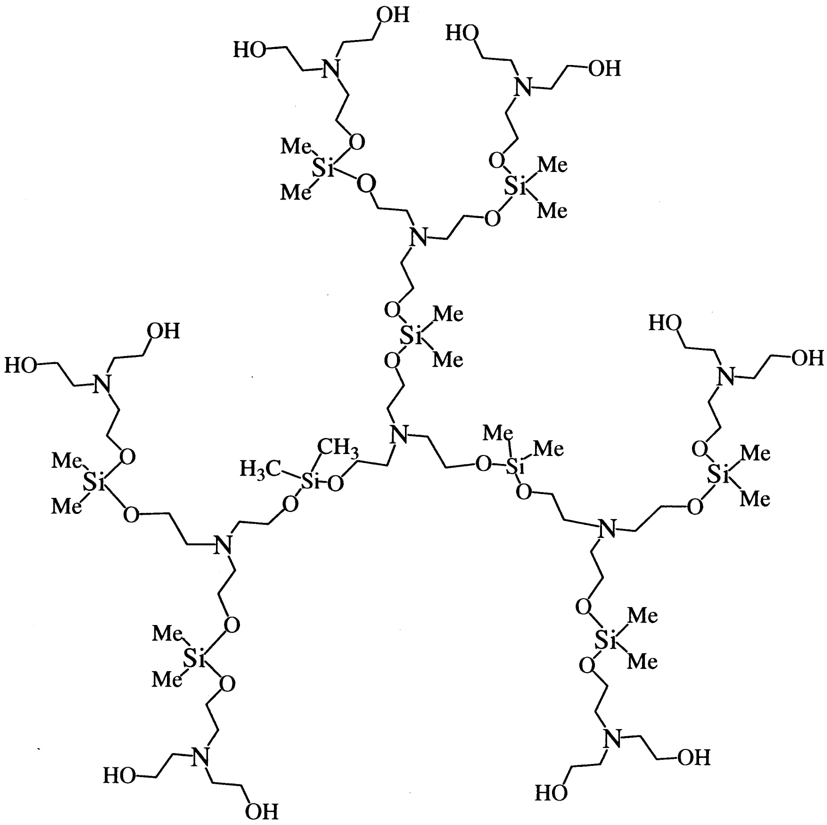
4. Nitrogen containing dendrimers

In an attempt to evaluate the versatility of our acid–base hydrolytic approach, we have explored the use of other core materials for the synthesis of dendrimers. An obvious choice was triethanolamine monomer which resembled in its composition with the monomer used earlier for the synthesis of phosphorus containing dendritic polymers. Triethanolamine reacted, as expected, quantitatively with 3 equivalents of trimethylsilylamine yielding the model compound, $N[(CH_2)_2OSiMe_3]_3$. The synthesis of nitrogen-dendrimers was then carried out by following a similar two-step procedure that was used for the phosphorus dendrimers. A solution of $N[(CH_2)_2OH]_3$ in acetone was added to a solution of 3 equivalents of $Me_2Si(NMe_2)_2$ in acetone, under controlled conditions, and the resulting mixture was then added to a solution of 3 equivalents of $N[(CH_2)_2OH]_3$. Purification of the product by vacuum distillation afforded a yellow viscous liquid that was characterized as the first generation nitrogen dendrimer ($\mathbf{N_4}$) [34]. An extension of this methodology led to the careful addition of $\mathbf{N_4}$ to a concentrated acetone solution of $Me_2Si(NMe_2)_2$, followed by the addition of the resulting mixture to 6 equivalents of $N[(CH_2)_2OH]_3$. The product was purified by vacuum distillation, and characterized by ^{1}H-NMR, MALDI-TOF MS and elemental analysis to be the second generation nitrogen dendrimer ($\mathbf{N_{10}}$) (Scheme 13). The isolation of these nitrogen containing dendrimers demonstrates the versatility of the acid–base hydrolysis synthetic approach.

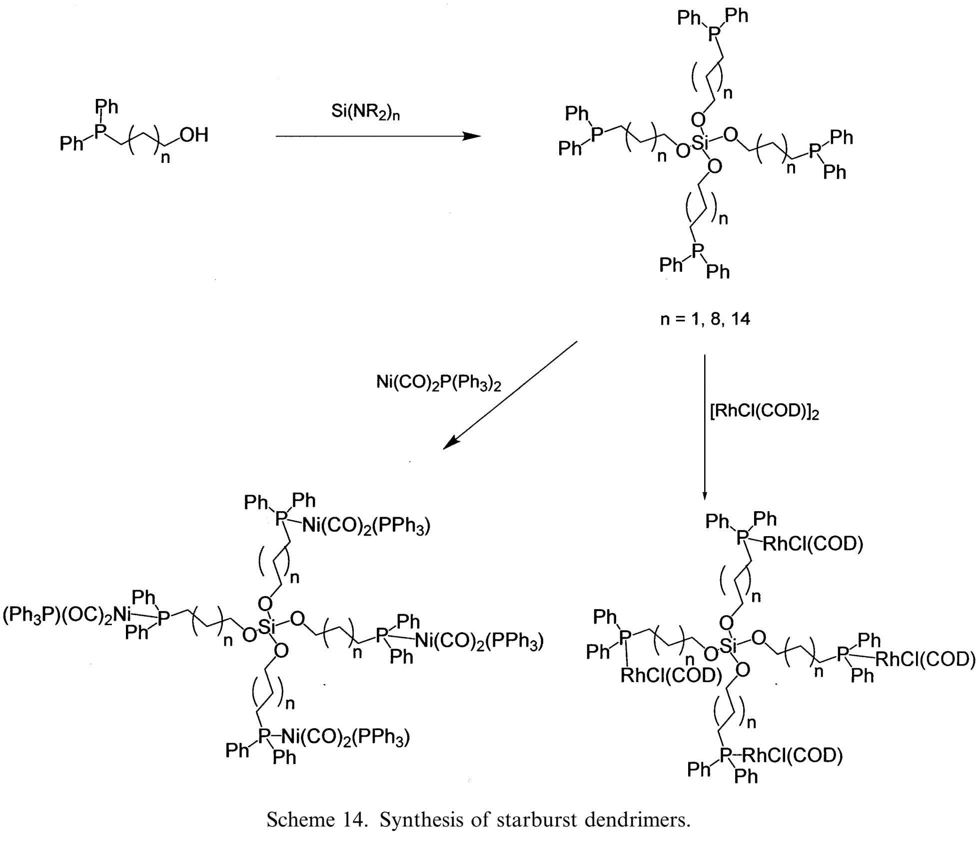
5. Phosphorus containing starburst dendrimers

The design of novel catalytic systems sometimes necessitates a closer look at the overall structure of the carriers of active metal centers. An investigation of the catalytic activity of the organometallic dendrimers by several groups has generally led to a conclusion that performance of these systems decreases with an increase in surface congestion due to extensive branching of the dendritic structure [9]. Perhaps the interactions between neighboring metal centers in these congested molecules contributes significantly to the lower rates of catalysis with an increasing number of generations [35]. Structures such as starburst dendrimers offer to address some of these issues [14]. They have less surface congestion due to more open structure emanating from the core, and are more flexible. The combination of these useful architecture attributes may lead to a greater access of substrates to the active catalytic sites in these dendrimers, and thus a decrease in catalyst deactivation due to interaction of neighbors.

Using our acid–base hydrolytic chemistry we have prepared starburst dendrimers containing terminal phosphine units which can bind transition metal centers [36]. The synthesis of these compounds was achieved by reacting an appropriate aminosilane $Me_nSi(NR_2)_{4-n}$ with OH terminated phosphines $HO(CH_2)_nPPh_2$ ($n = 3$,



Scheme 13. 'N$_{10}$' dendrimer.



Scheme 14. Synthesis of starburst dendrimers.

10, 16). For example, a solution of 4 equivalents of $HO(CH_2)_{16}PPh_2$ was added to 1 equivalent of $ClSi(NEt_2)_3$ in benzene, and the reaction mixture was heated to ~60 °C over a period of 48 h. It led to the preparation of the starburst phosphine core $Si[O(CH_2)_{16}PPh_2]_4$. The terminal phosphine units in $Si[O(CH_2)_nPPh_2]_4$, $MeSi[O(CH_2)_nPPh_2]_3$ and $Me_2Si[O(CH_2)_nPPh_2]_2$ ($n = 3$, 10 and 16) were then used to anchor Ni(0) metal centers by reacting them with 4, 3 and 2 equivalents of $Ni(CO)_2(PPh_3)_2$, respectively, in a ligand displacement reaction. It led to the formation of the first generation starburst organometallic dendrimers, $Si[O(CH_2)_nPPh_2Ni(CO)_2(PPh_3)]_4$, and $MeSi[O(CH_2)_nPPh_2Ni(CO)_2(PPh_3)]_3$.

The above mentioned phosphorus starburst dendrimers were also used to prepare the first-generation Rh(I) bound dendrimers. In a typical reaction, the polyphosphine core was treated with $[(\mu\text{-Cl})(1,5\text{-}C_8H_{12})Rh]_2$ dimer in THF at room temperature. A bridge-splitting reaction led to the preparation of Rh(I) bound complexes, $Si[O(CH_2)_nPPh_2RhCl(1,5\text{-COD})]_4$, and $MeSi[O(CH_2)_nPPh_2RhCl(1,5\text{-COD})]_3$ ($n = 3$, 10, 16) (Scheme 14).

6. Conclusions

Phosphorus bound organometallic dendrimers offer tremendous potential in heterogenizing homogeneous catalysis, and these compounds are now becoming available in large quantities so that their full characterization to shed light on structure–property relationships could be attempted. The focus of this review has been in building organometallic dendrimers for applications in catalysis, and the latter study would help in the future design of efficient supported metal catalysts with desired activity and selectivity in key organic transformations. One of the pertinent issues related to catalysis is the location of metallic sites in organometallic dendrimers. It needs to be established if it is advantageous to have active sites distributed throughout the backbone or periphery functionalization is sufficient or of more value. This will need a careful evaluation using dendrimers with similar backbone structures to eliminate other contributing factors. The organophosphine dendrimers developed in our laboratory offer promise in which the internal structure could be built without the metal, and further generations could be added using monomers that already contain bound metallic centers.

It is also essential to establish the influence of the structure of organometallic dendrimers on their catalytic activity. This is expected to be an important and key factor in understanding their behavior, and in building catalysts by molecular design. Dendrimers are generally assigned a spherical structure, and it is considered to be a feature that differentiates them from linear polymers. The pertinent question to consider is what role, if any, is played by this globular shape. It is important to compare their catalytic activity with hyperbranched polymers that have a non-spherical and non-linear structure. Synthesis of phosphorus based ligands that offer a unique opportunity in controlling the structure that evolves in a step-by-step divergent build-up or a convergent synthesis of dendrimers, will be useful in addressing this issue. We have recently focused our efforts in this direction by developing tripodal polyphosphorus ligands in which the phosphorus atom at the core plays a significant role in determining the final structure of the dendrimer [37].

Recycling of the catalyst is another important variable in the design of new venues for supporting transition metal complexes. This area is still in its infancy stage when we consider the available data on organometallic dendrimers used in catalysis. It needs to be explored further using full characterization of the dendrimers before and after catalysis. Availability of better characterization methods will help establish the structure of the organometallic species in the catalytic cycle, and will go a long way in the future design of catalytic dendrimers.

Acknowledgements

We thank NSERC (Canada) and FCAR (Quebec, Canada) for continued financial support.

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