Chem. Rev. **1999,** *99,* 1689–1746

Suprasupermolecules with Novel Properties: Metallodendrimers

George R. Newkome,* Enfei He, and Charles N. Moorefield

Center for Molecular Design and Recognition, Department of Chemistry, 4202 East Fowler Avenue, University of South Florida, Tampa, Florida 33620-5250

Received October 6, 1998 (Revised Manuscript Received March 22, 1999)

Contents

I. Introduction

Since the mid-1980s, interest in highly branched and regularly repeating molecular architectures, now commonly referred to as *dendrimers*, has emerged to become a key element in the research efforts of scientists worldwide. Numerous reasons for the rapid emergence of these (macro)molecular curiosities can be cited, for instance, unprecedented control over structural unit positioning, a general ease of construction, well-behaved solubility features that facilitate characterization, and the overwhelming abundance of documented proof that such species can, in fact, be constructed for utilitarian as well as aesthetic purposes. However, it is important to note that with the advent of more recent mass spectroscopy techniques, absolute purity and perfect branching are, in many cases, difficult to obtain. But perhaps one of the most important attributes of dendritic chemistry, which tends to propagate this new polymeric regime, is its vast potential to easily integrate into, and meld with, more mature chemistries.

It is the ease of integration of dendritic chemistry that provides the basis for this review. More specifically, the unification of organometallic and dendritic arenas is herein examined from the relatively new perspective of *metallodendrimers*.

The advent of dendritic chemistry is founded in the efforts of many researchers, such as Flory,[1−4] who published theoretical and experimental evidence for the existence of branched-chain, 'three-dimensional' macromolecules, as well as Webster and Kim,[5] specifically Kim[6] who patented in 1987 the first intentional preparation of a *hyperbranched* polymer, to mention but a couple examples. More extensive monographs of the historical development of this field, prior to 1985, are available.[7]

Vögtle's[8] seminal work, published in 1978 and entitled "Cascade and Nonskid-Chain-Like Syntheses of Cavity Topologies", set the stage for the elaboration of simple repetitive transformations to that of modern dendrimer chemistry. In general, dendrimers are globular, highly branched, fractal-like polymers of "well-defined" three-dimensional shape, size, and molecular weight that are constructed via iterative, or stepwise, procedures. The distinction between dendrimers and hyperbranched polymers is that the hyperbranched polymers are prepared via a one-step or single-pot process and possess greater molecular weight distributions or polydispersities. The term *dendrimer*, coined by Tomalia[9] from the Greek term dendro for tree-like, is synonymous with both arborol[10] founded in the Latin term arbor for tree, and cascade[8] referring to successive stages, which also defines the nomenclature family name.[11−13] Dendrimers can be tailored to possess uniform or discrete functionality and possess tunable internal packing densities, void volumes, surface moieties, molecular mass, solvent-dependent size, and branching dimensions.

Many applications have been claimed for this new type of polymer. They are currently being investigated for use as biomimetic catalysts,[14] building blocks for fabrication of designed materials,[15] molecular carriers for chemical catalysts,[16] and potential vehicles for delivery of drugs and immunogens.[17−19]

Synthetic methodologies used for the construction of these branched macromolecules rely on two approaches (Scheme 1) described as *divergent* and *convergent* or a combination of the two. Both key methods usually employ complementary protection and deprotection steps. The divergent method[9,10] can be envisioned by considering the sequential addition of the repeating units (*building blocks*, *monomers*, or *dendrons*) to a starting unit or *core*, thus forming *layers* or *generations* of repeat units within the superstructure. This protocol was independently developed by Tomalia and Newkome. In 1985, Tomalia et al.[9] reported the preparation of Starburst *p*oly*am*ido*am*ine (PAMAM) dendrimers that were constructed through the purported 10th generation

---

* To whom correspondence should be addressed. E-mail: gnewkome@research.usf.edu; URL: www.dendrimers.com.

10.1021/cr9800659 CCC: $35.00

George R. Newkome, after receiving his Ph.D. in organic chemistry from Kent State University, completed a postdoctoral fellowship at Princeton University, which served to confirm his choice of a career in academia. He then joined the faculty at Louisiana State University, ultimately becoming involved in the Center for Energy Studies as Executive Director and Professor. In 1986, he moved his research program to the University of South Florida, where he serves as Vice President for Research and Distinguished Research Professor. Dr. Newkome received the Medallist Award from the Florida Academy of Sciences and the Florida Section Award of the American Chemical Society as the most outstanding chemist of the year. He has published over 310 papers in international journals and numerous books and recently held visiting appointments at the University of Bordeaux and Louis Pasteur Institute. Although his interests are in the areas of organic and inorganic chemistry, architectural design in nature, and environmental issues, Dr. Newkome is also creator and host of a weekly PBS TV show, “Beyond Science”, which takes an innovative approach to how technology applies to humanitarian needs.

Enfei He completed his B.S. in applied chemistry at Shanghai Jiao Tong University in 1988. He then worked five years in electrochemistry and environmental chemistry in government-owned companies in Shanghai, China. In 1993, he worked for W. R. Grace & Co., Grace China Ltd., as an engineer in polymer chemistry. He earned his Ph.D. in chemistry with Professor George R. Newkome at the University of South Florida in Tampa in 1998. His graduate research involved the development of supramolecular metallomacromolecules. During his graduate study, he received an honor from the Consulate General of the Peoples Republic of China at Houston in 1997 and a Tharpe Publication award from USF in 1998. Dr. He is currently a Postdoctoral Research Associate with Dr. Blake R. Peterson studying medicinal chemistry and chemical biology at the Pennsylvania State University at University Park.

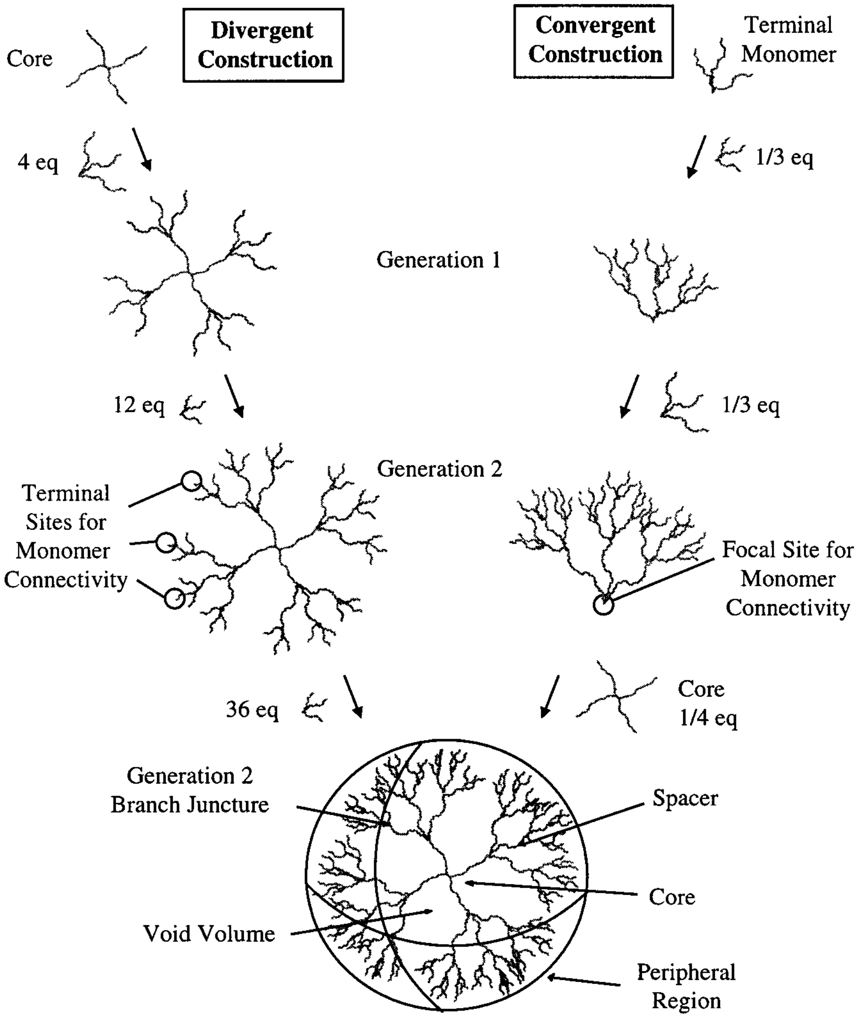
while Newkome et al.[10] reported the synthesis of tree-like arborols via the sequential addition of two different 1→3 branched monomers.

A notable, and general, difference between these two divergent methods is rooted in the formation and introduction of the branching centers of the growing molecule or polymer. Tomalia’s procedure produces branching centers *during* dendritic construction at the periphery of the growing polymer via attachment of *linear* (AB-type) monomers to a dendritic surface. The use of linear monomers for dendrimer synthesis is also the basis of DSM’s commercial Astramol dendrimer preparation[20−22] as well as that of Vögtle’s original method.[8] In contrast, Newkome’s protocol approached dendrimer synthesis from a *modular* perspective whereby monomers, possessing *C*-based, 1→3 branching sites, were *preconstructed* for subsequent attachment to a molecular surface.[23] Similarities between the two divergent synthetic methods include the requirement of completing an exponentially increasing number of transformations for *perfect* growth (however, this can lead to branch defects when viewed from a statistical consideration)[24,25] and ease of purification from the perspective of removal of small molecule reactants, or contaminants, from large species (i.e., the dendrimers).

Charles N. Moorefield received both his B.S. in chemistry and his M.S. in industrial chemistry from the University of Central Florida. Upon completion of two years of graduate study at Louisiana State University, he transferred to the University of South Florida to continue working with Professor George R. Newkome, where he received his Ph.D. in 1991. During his graduate career, he earned several academic honors, a graduate fellowship, and the Outstanding Doctoral Student Award presented by the USF Sigma Xi Research Society. After completing a postdoctoral appointment, he accepted a research faculty position at the Center for Molecular Design and Recognition in the University of South Florida. Interest in novel molecular architectures has led to the award of numerous patents in the area of dendritic chemistry.

In an eloquent extension of this branched monomer procedure, the convergent method[26] essentially constructs dendritic architectures starting from the *periphery* and progressing inward. Thus, multifunctional, large, dendritic *wedges* are produced that possess single functional moieties termed *focal* groups that are the site of *wedge* attachment to another monomer for continued growth or to a *core* for final dendrimer assembly (Scheme 1). This procedure was initially pioneered by Fréchet et al.[27] and was followed, shortly thereafter, by Miller and Neenan.[28] Notable attributes of the convergent protocol include a small number of required transformations per dendron for sequential *tier* construction (e.g., two reactions for AB_2-type monomers). This statistically minimizes defects, although hindered reactivity of focal groups due to the juxtaposed branching for larger wedges can lead to diminished yields, but purification can be improved due to the size differences in the final product(s).

Scheme 1. Representative 'Divergent' and 'Convergent' Protocols for Dendrimer Construction with Common Terminology



Due primarily to steric hindrance, access to certain dendritic architectures has only been accomplished via a combination of these methods. Thus, final attachment of a convergently prepared wedge can be facilitated by the use of divergently synthesized, extended dendrons possessing less congested terminal groups.

The merger of supramolecular chemistry, defined as "chemistry beyond the molecule" by Lehn,[29−32] and the chemistry of dendrimers leads directly to "suprasupermolecular" chemistry[33] and the creation of the metallodendritic regime. Incorporation of metal ions to the framework was initiated by Balzani's[34−36] and Newkome's[37] research groups in the early 1990s, either by the use of metal branching centers or by internal metal complexation or encapsulation at specific binding site(s), respectively. Commonly, metals have served as *branching centers*, *building block connectors*, which include core as well as monomer connection, *terminal groups*, and *structural auxiliaries*, whereby metals are introduced to a framework after dendritic construction (Figure 1). The later category allows for *site-specific* versus *random* inclusion. These main categories shall serve as the basis for metallodendrimer classification in this review.

Metallodendrimers are suprasupermolecular species possessing novel physical, optical, electrochemical, photochemical, biological, and catalytic properties. Although they have been discussed to some degree in recent literature,[38,39,39−50,50−57,57−61] this review attempts to address the chemistry of these new materials, as well as selected multibranched, metal-based molecules, that are not strictly within the dendritic arena (i.e., construction with only 2−3 repetitive reaction sequences). It is hoped that the reader will gain a greater appreciation for metallodendritic chemistry, as well as dendritic chemistry in general, upon exposure to the molecular diversity that is conveyed in this review.

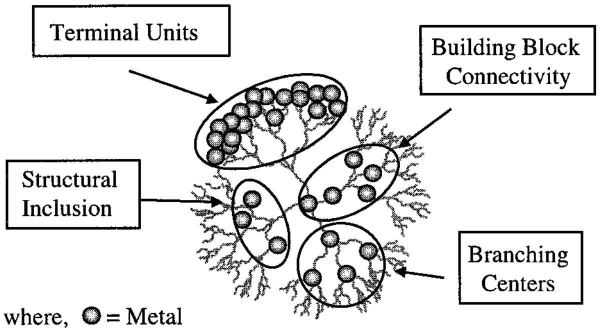
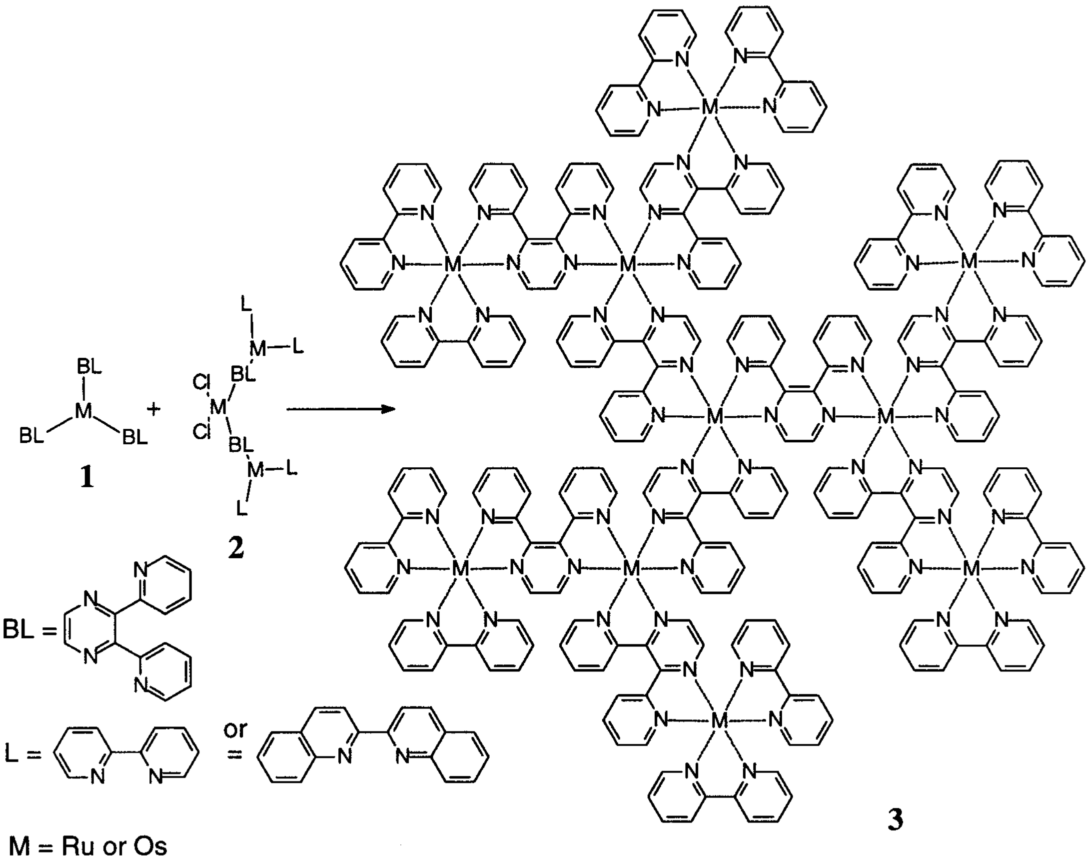


Figure 1. Potential uses and positioning of metals within dendritic architectures.

Scheme 2. Balzani's Pyridyl-Based Metallodendrimers



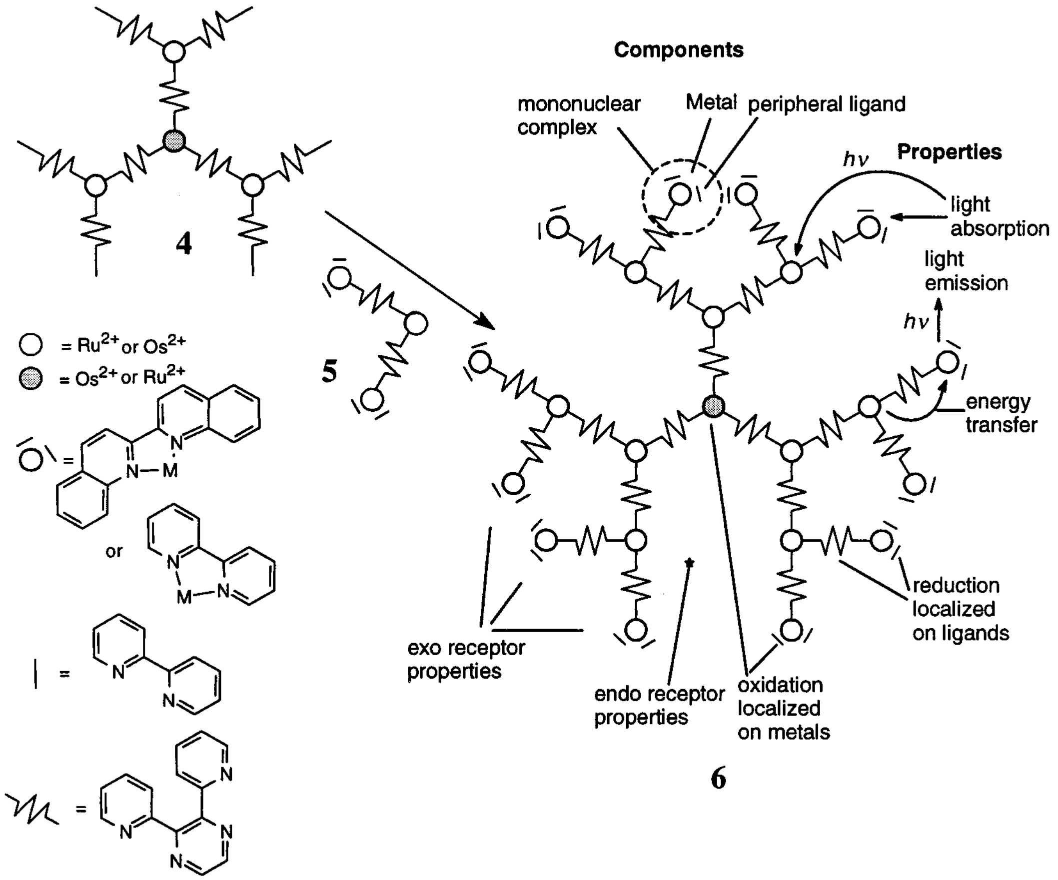
II. Metals as Branching Centers

The first synthesis of metallodendrimers possessing homo- and heterometallic branching centers (ruthenium and osmium) was reported by Balzani et al.[34−36] (Scheme 2). Decanuclear polypyridine complex **3** was prepared from a trigonal core, M(BL)$_3^{2+}$ (**1**), containing a metal coordinated to three 2,4-bis(2-pyridyl)pyrazine (BL) ligands[62] and the preconstructed building block Ru[(BL)M(L)$_2$]$_2$Cl(PF$_6$)$_4$ (**2**), where L is either bipyridine (bpy) or biquinoline (biq).[63] Assembly was accomplished via treatment of the 1→2 branched building block **2** with the core M(BL)$_3$ (**1**) [MeOH/H$_2$O/(CH$_2$OH)$_2$/AgNO$_3$]. Balzani et al. further reported the examination of analogous metallodendrimers derived from transition-metal complexes[64−66] and subsequently studied their luminescence properties, electrochemical and redox behavior, intercomponent energy, and electron-transfer ability. Pure Ru-containing complexes exhibit luminescence bands at ca. 770 nm, whereas all the Ru/Os mixed-metal complexes display the bands in the 850−1000 nm spectral region, which was assigned to triplet metal-to-ligand charge-transfer levels localized on the Os-possessing components. Also, for the Ru/Os mixed-metal constructs, only an Os-based luminescence is observed. The electrochemical results indicate that each redox step in these metal complexes is essentially localized on a specific ligand. Assignment of the redox sites has been proposed, and their mutual interactions have been discussed.[65]

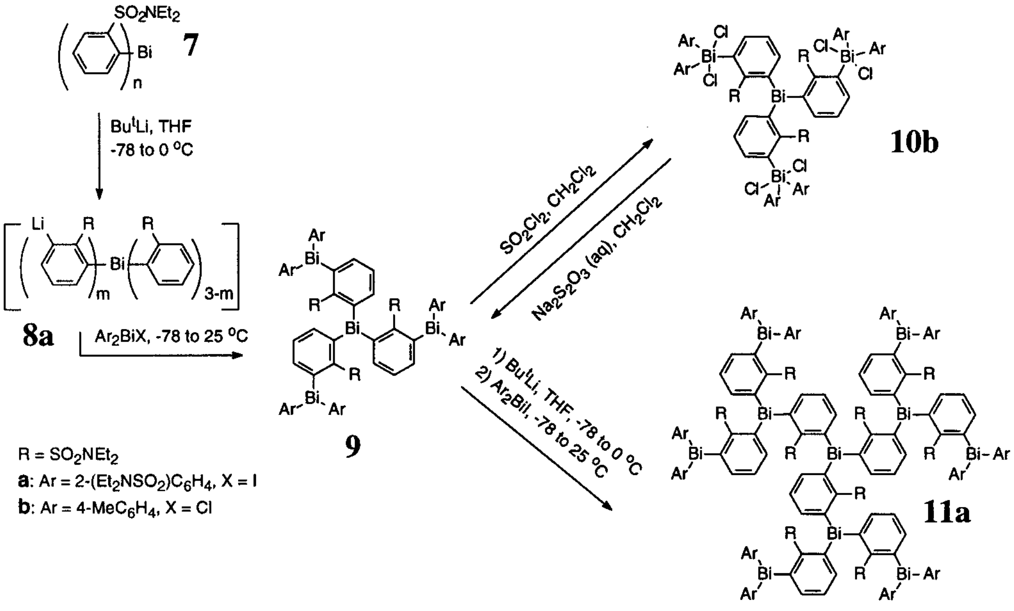
This synthetic strategy developed by Balzani's group allows the preparation of dendrimers possessing two or more different metals and/or ligands. Each dendrimer can be viewed as an ordered ensemble of weakly interacting [M(L)$_n$(BL)$_{3-n}$]$^{2+}$ units (M = Ru(II) or Os(II); L = bpy or biq; BL = 2,3- or 2,5-dpp; n = 0 or 2). Absorption bands and the electrochemical properties of each unit are only slightly perturbed in the assembled structure, so that the absorption spectrum and redox pattern of a dendrimer resemble the "sum" of the spectra and redox patterns of the constituent units. Electronic interactions, however, are sufficiently strong to allow very fast (exoergonic) energy transfer between nearby units. Thus, with an instilled maximized degree of control of the electrochemical behavior, light absorption properties, and direction of energy transfer, these dendrimers have been proposed to be ideal for light-harvesting devices.[67,68]

Campagna, Denti, Balzani and co-workers[69,70] have pursued the preparation of higher generations of this series (Scheme 3). The largest member (e.g., **6** possessing 22 metal centers) was prepared by treatment of the tetraRu(II) core **4** with the triRu(II) dendron **5**. These metallodendrimers exhibit[69] strong absorption in the UV−vis spectral region, a moderate red luminescence as well as a number of metal-based oxidation and ligand-based reduction processes. For instance, **6** has an UV absorption maximum at 542 nm with $\epsilon = 2.02 \times 10^5$ (M^{-1} cm^{-1}), a luminescence band at 786 nm ($\tau = 45$ ns), and a peak at +1.52 V (vs SCE) corresponding to the simultaneous oxidation of the 12 weakly interacting metals. The absorption spectra, luminescence properties, and electrochemical behavior of the various generations of these metal-

Scheme 3. Representative Ru- and Os-Containing Macromolecule Possessing 22 Branching Metal Centers



Scheme 4. Suzuki's Bi-Branched Macromolecules

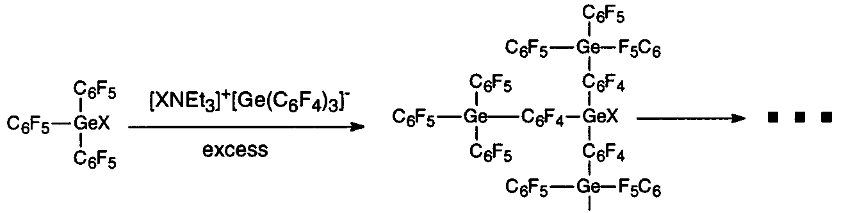


lodendrimers have been reported.[70] Some electrochemical interactions between neighboring units were observed; however, as previously noted, each metal-based building block in the polymetallic dendrimers possessed its own absorption properties.

The first synthesis of "dendritic bismuthanes", reported by Suzuki and co-workers[71] (Scheme 4), utilized directed tris-ortholithiation of tris[2-(diethylaminosulfonyl)phenyl]bismuthane (**7**) with *tert*-butyllithium, followed by treatment with 3 equiv of bis[2-(diethylaminosulfonyl)phenyl]bismuth iodide (**8a**) to give the symmetrically branched Bi_4—bismuthane **9** as the main product. Similarly, tetraBi **9** was converted, in a one-pot procedure, to Bi_{10}—bismuthane **11a**. Treatment of tetraBi **9** with SO_2Cl_2 gave the corresponding chloride **10b**, which could be transformed to the reduced form **9** using $Na_2S_2O_3$.

Bochkarev et al.[72] constructed hyperbranched, Ge-branched macromolecules via polymerization of tris(pentafluorophenyl)germanium anions (Scheme 5).

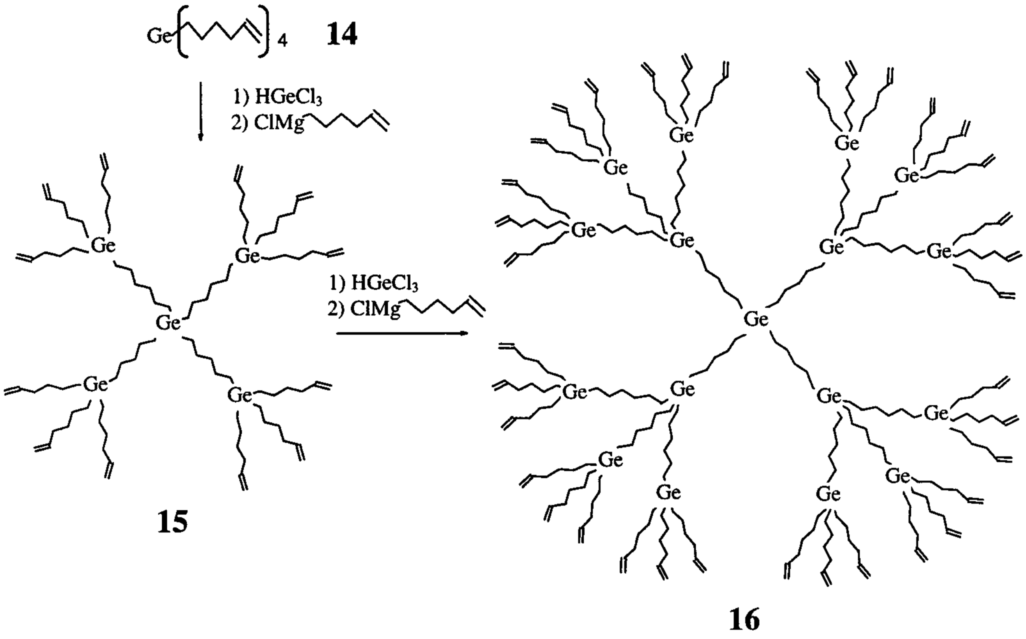
Scheme 5. Hyperbranched Constuction of Ge-Based Metallodendrimers

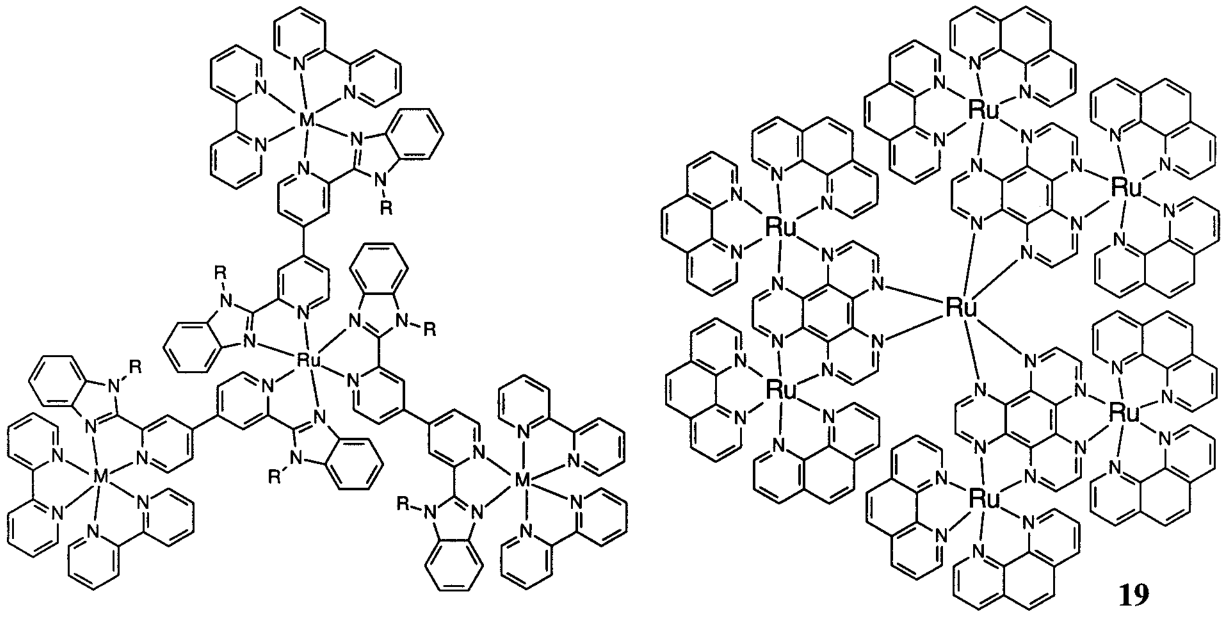


12

13

Scheme 6. Mazerolles's Ge-Branched, Alkyl-Based Metallodendrimers

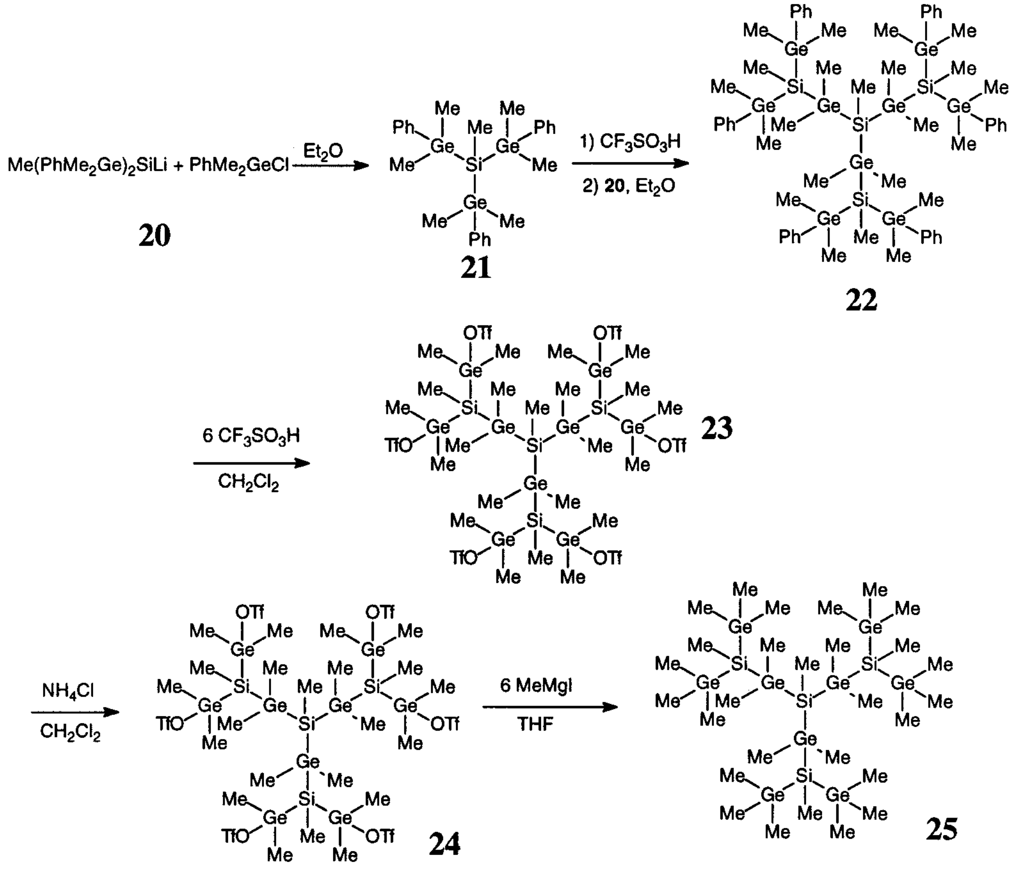




17 R = H, CH_3, M = Ru, $8ClO_4^-$
18 R = H, M = Os, $8ClO_4^-$

Figure 2. Branched Ru-based architectures constructed using heterocyclic ligands.

Scheme 7. Hybrid, Metallodendrimers Possessing Ge-Based Monomer Connectivity and Si-Based Branching Centers



Building block connectivity was accomplished via Ge substitution of the *para*-fluoro substituents in monomers, such as **12**, affording the hyperbranched dendritic polymers (e.g., **13**). Molecular weights in the range from 100 000 to 170 000 amu were determined.

Mazerolles and co-workers[73] reported the synthesis of Ge-branched, alkane-based, metallodendrimers (Scheme 6). The first-generation dodecaalkene **15** was synthesized via both convergent and divergent methods starting from the tetravalent core **14**; however, the second-generation, 36-alkene **16** was only successfully obtained by a divergent approach. Purification of these metallomacromolecules proved arduous via silica-based column chromatography due to the inability to remove the trace impurities formed during construction; $CoCl_2$- and $NiCl_2$-impregnated silica afforded improved results. These authors further noted that differentiation of generations one and two via IR and NMR was not feasible. Mass spectrometric analysis was facilitated by terminal functionalization using methyl thioglycolate, notably yielding lipophilic interiors and hydrophilic shells.

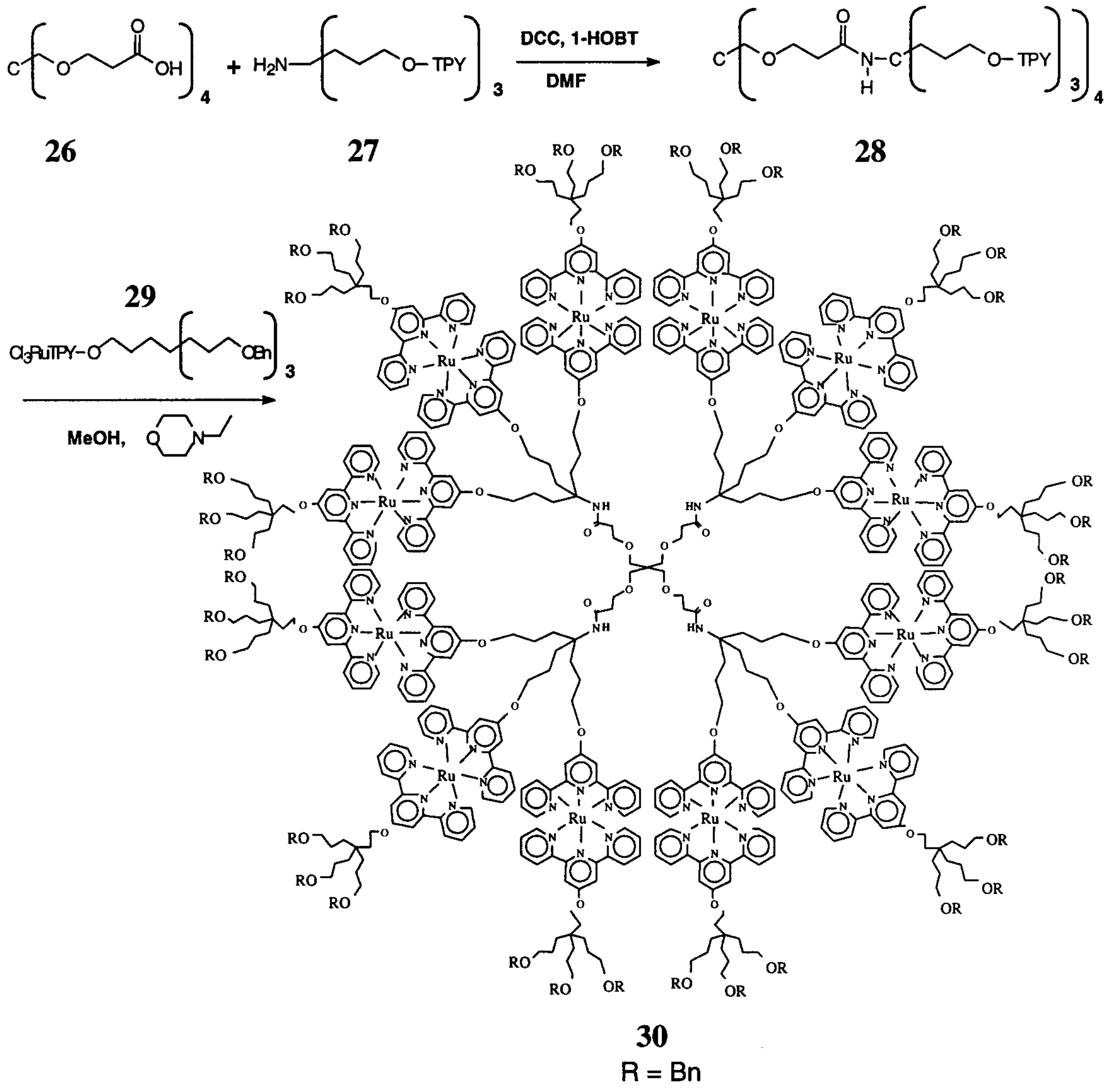
Metals serving as branching centers are also well-known in small yet nondendritic architectures. A couple of notable examples are herein described based on their potential to be incorporated into the dendritic regime.

Arakawa, Haga et al.[74] prepared a tetraRu(II) complex (**17**; Figure 2) that was characterized by analysis of multiply charged ions generated by electrospray ionization mass spectrometry. Later, they[75] studied the proton-induced switching of electron-transfer pathways in the analogous monoRu(II)−triOs(II) complex **18**. Mesmaeker et al.[76] reported the synthesis and electrospray mass spectrometric characterization of a larger heptaRu(II) construct **19**. The mass spectra exhibited four sets of peaks attributed to 3−6 charges. A key building block included the planar, trisligating chelate 1,4,5,8,9,12-hexaazatriphenylene (HAT).

III. Metals as Building Block Connectors

Nanjo and Sekiguchi[77] reported the synthesis of metallodendrimers possessing alternating Si-branching centers and Ge-branched chain connectors (Scheme 7). Employing divergent construction, the reaction of chlorodimethylphenylgermane with lithiosilane monomer **20** gave tris(dimethylphenylgermyl)methylsilane (**21**) as the initial core. Phenyl cleavage via treatment with trifluoromethanesulfonic acid and subsequent reaction with the silane monomer (**20**) afforded (12%) the first-generation hexaphenyl, nonagermane **22**. Sequential reaction of dendritic hybrid **22** with triflic acid, $NH_4^+Cl^-$, and CH_3MgI gave the corresponding hexatriflate **23**, hexachloride **24**, and hexamethyl species **25**, respectively. The molecular structure of **25** was confirmed by X-ray diffraction, while its UV spectrum in 3-methylpentane at 300 K exhibited an absorption (271 nm (ϵ = 5.07 × 10^4 M^{-1} cm^{-1})) attributed to the $\sigma-\sigma^*$ band of the Si−Ge chains.

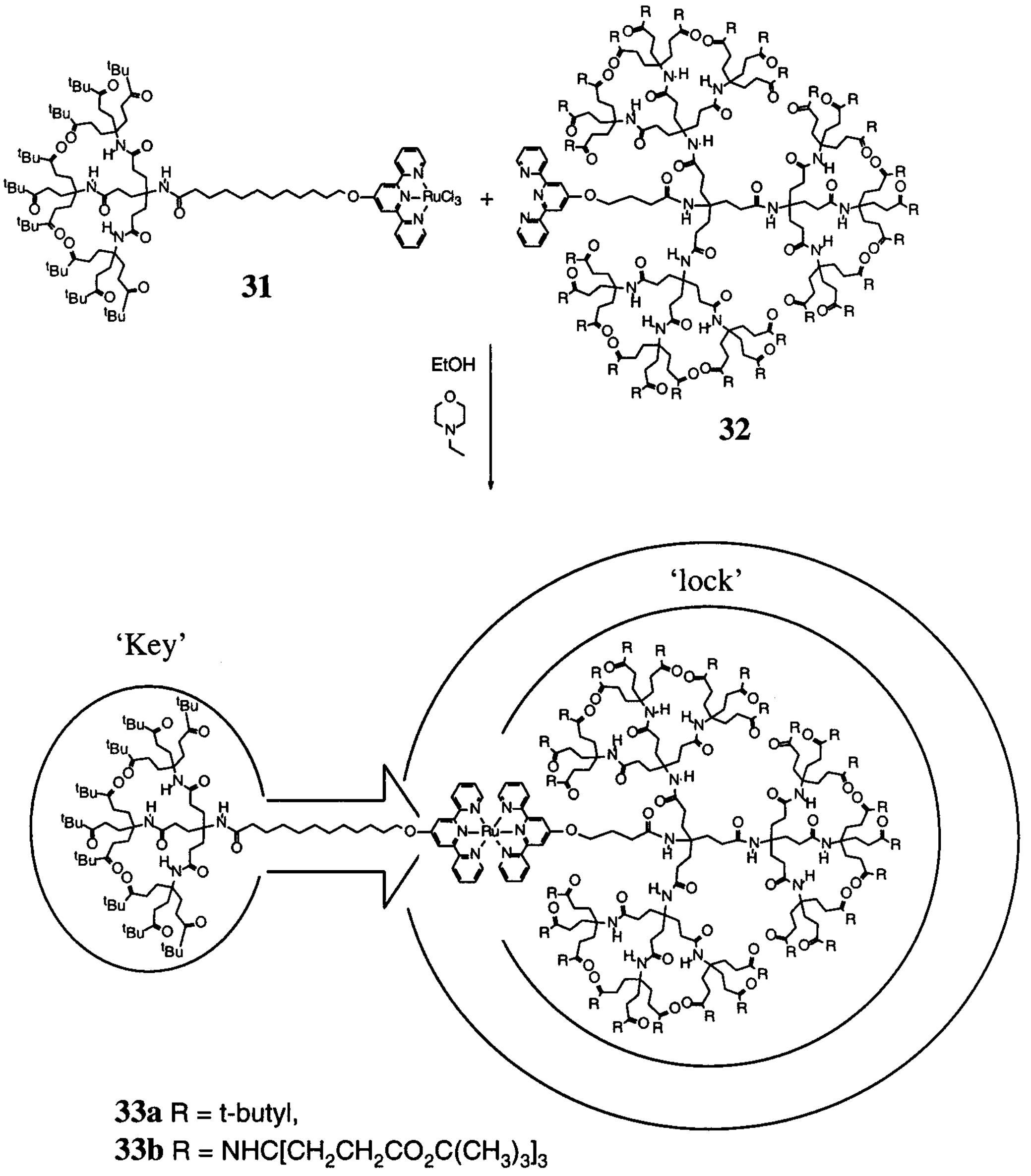
Scheme 8. Synthesis of a Dodecaruthenium Metallodendrimer Employing Metal-Mediated Chain Connectivity



Tridentate 2,2′:6′,2″-terpyridine (tpy)[78] is a strong transition-metal binding ligand[79] used to facilitate and control the assembly of molecular architectures. Newkome et al.[80] first reported the preparation of dendrimers incorporating convenient ligand—metal—ligand (herein denoted via —⟨*M*⟩—; in which ‘⟩—’ ≡ 4′-tpy) connectivity for building block attachment (Scheme 8). Metallodendrimer **30** possesses 12 pseudooctahederal Ru(II) centers,[81,82] whereby each metal center is coordinated by two orthogonal 4′-substituted 2,2′:6′,2″-terpyridines. Construction was achieved by coupling tetracarboxylic acid[83] **26** with aminotristerpyridine **27** (accessed via base-promoted alkoxylation of 4′-chloroterpyridine[84] with the corresponding aminotriol) to give dodecaterpyridine **28**. Next, reaction of polyterpyridine **28** with 12 equiv of the paramagnetic Ru(III) adduct **29** (prepared from the corresponding monohydroxytrisbenzyl ether[37]), under reductive conditions, gave the desired diamagnetic polybenzyl ether terminated metallodendrimer **30**.

More recently, this strategy of —⟨*Ru*⟩— connectivity has been applied to the development of metal complexes capable of connecting multiple, preconstructed branched polymers, thereby resulting in the precise creation of dendritic assemblies or networks.[85,86] Each component of the resultant construct can be fully characterized. Thus, bis-dendrimer **33** was subsequently prepared (Scheme 9) via the formation of a single —⟨*Ru*⟩— connection of two independently constructed dendrons (i.e., **31** and **32**). These two, coupled dendrons were designed to loosely mimic a “key” and “lock” based on the proximity of the incorporated terpyridine units to the core branch junctures. Preconstructed dendron synthesis was facilitated by 4′-chloroterpyridine alkoxylation using the appropriate ω-hydroxycarboxylic acid to provide the requisite functionalized cores. Generational, amide-based dendrimer construction was then accomplished via iterative DCC coupling and ester deprotection using $H_2NC(CH_2CH_2CO_2t\text{-bu})_3$, “Be-

Scheme 9. Newkome's 'Key' and 'Lock' Metallodendrimer Assemblies



33a R = t-butyl,
33b R = $NHC[CH_2CH_2CO_2C(CH_3)_3]_3$

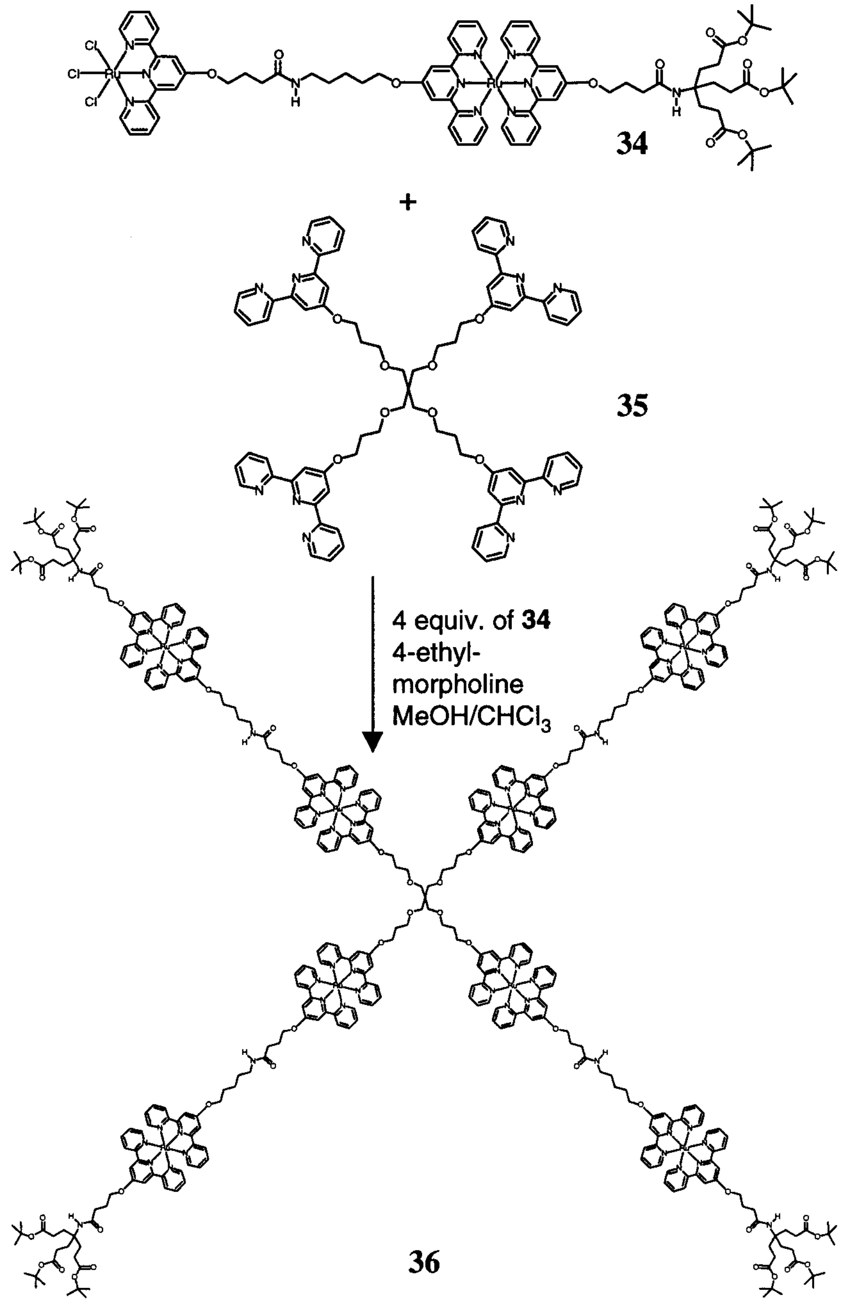
hera's amine".[87,88] Cyclic voltammetry experiments conducted on the series of lock and key complexes revealed electrochemically reversible redox behavior in the cases of connected lower generation components; however, irreversible behavior was observed for complexes comprised of third generation or greater locks and second generations or greater keys. This was postulated to result for slowed electron transfer due to branch chain steric hindrance.

Newkome and He[89] have expanded the $-\langle Ru\rangle-$ single connectivity to include the incorporation of linearly connected complexes (i.e., $-\langle Ru\rangle-(x)-\langle Ru\rangle-$) in each arm of a tetrahedral, metallodendrimer "hypercore" (Scheme 10). Construction of the octaRu(II) core **36** was predicated on reaction of the two complementary fragments, the paramagnetic Ru(III) triester **34** and the tetraterpyridyl ether **35**. Key transformations for fragment synthesis included the treatment of 4′-chloroterpyridine with the potassium alkoxide of either 4-hydroxybutyric acid, 5-aminopentanol, or a tetrahydroxy-terminated core derived from reduction of the corresponding tetracarboxylic acid[90] (**26**; Scheme 8). Characterization of the +16 charged cationic metallocore **36** included UV–vis spectra that revealed an 8-fold adsorbence increase when compared to the spectra of a single Ru(II) terpyridine-based complex.

Newkome and He[91] further exploited the $-\langle Ru\rangle-$ connectivity to examine the potential to create new metallodendrimer architectures comprised of more than two preconstructed branched macromolecules (Scheme 11). On the basis of the instilled tetrahedral architectures of dendrimers prepared with saturated, sp^3-based, *C*-foundations, nanoscale dendritic networks were obtained possessing nanoscopic *methane-based* geometries.

Complementary components, used for network assembly, were prepared starting with acylation of amine **38** (**38a** and **38b**; synthesized via treatment

Scheme 10. Newkome and He's Metallodendrimer Hypercore

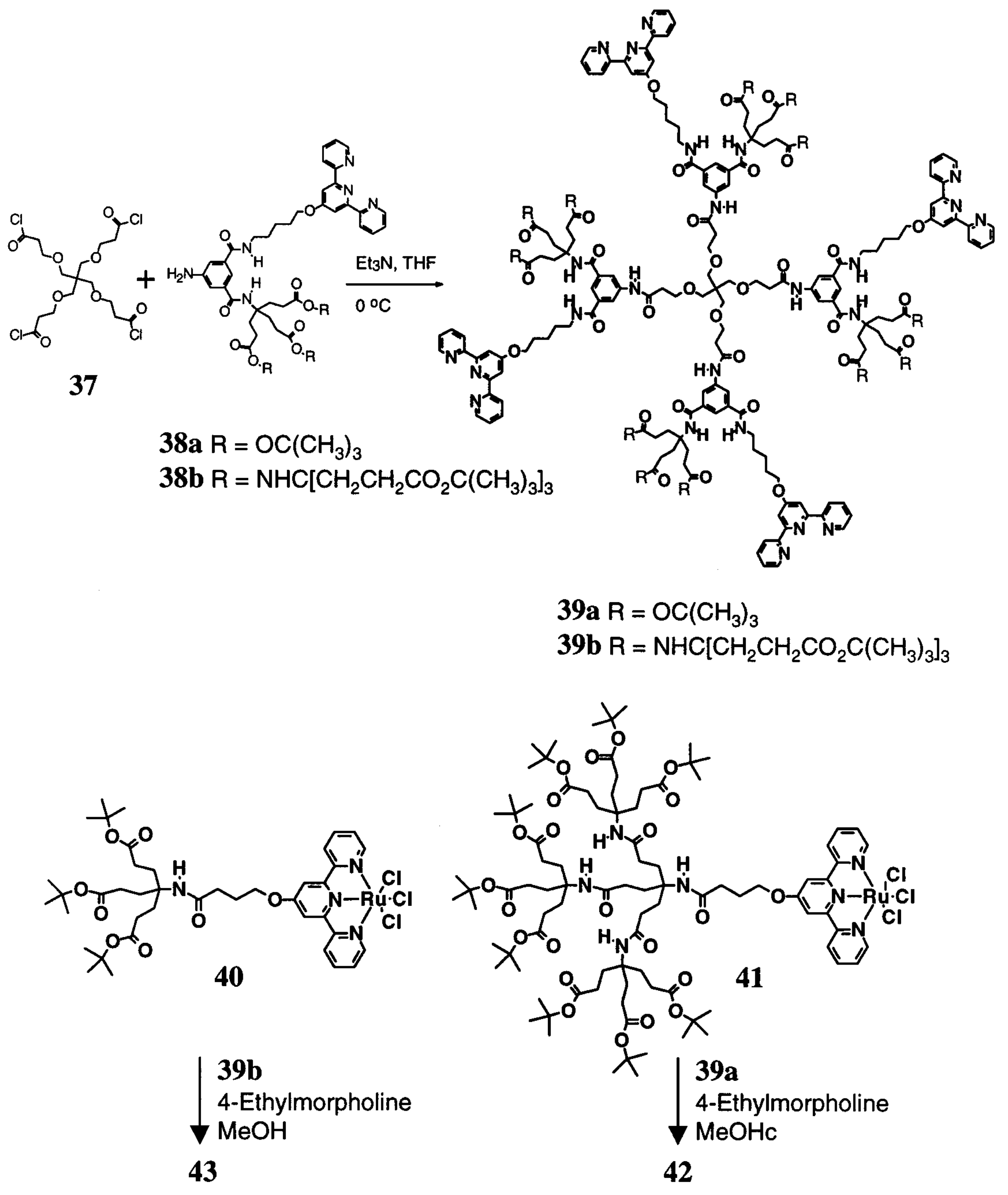


of 5-nitroisophthalic acid monoacid halide with the aminotriester, Behera's amine, followed by the DCC coupling of an aminoterpyridine) with tetraacyl halide **37** (accessed by $SOCl_2$ reaction with tetraacid **26**), affording the first- and second-generation "*carbon*" fragment **39** (**39a** and **39b**). The "*hydrogen-type*" components **40** and **41** were synthesized as described for the lock and key assemblies in Scheme 9. Final network construction was achieved by treatment of the tetraterpyridyl cores **39** (**39a** and **39b**) with 4 equiv each of the first- and second-generation monoterpyridylRu(III) dendrons to yield the tetraRu(II) metallodendrimers **42** and **43** (Figure 3).

Notably, the mixing of first- and second-generation components has led to the creation of the first dendritic constitutional isomers. Each isomer possesses a nominal molecular weight of 12 526 amu and displays nearly identical IR, UV, NMR, and MALDI-TOF spectra. In addition, other physical properties such as decomposition temperature and solubilities are similar. In contrast, electrochemical studies suggest that the internal densities and void regions differ. The cyclic voltammograms exhibit a single, quasi-reversible pattern for the Ru metals of isomer **42** and two waves for the metallic centers of isomer **43**. This suggests that the internal dendritic scaffolding of these metallodendrimers, as well as others, can be tailored to facilitate, or negate, internal electrochemical communication.[92]

Constable and co-workers developed a number of metal chelating agents useful as bridging ligands[93] that have subsequently been incorporated into met-

Scheme 11. Complementary Dendritic Components Metal-Based, Dendritic Network Construction



allosupramolecules (Figure 4). Constable and Harverson[94] reported a convergent strategy for the construction of $-\langle Ru \rangle-$ based, branched macromolecule **44**. Arm construction involved, as the key transformation, terpyridine precursor oxyanion displacement of a chloroterpyridyl substituent resulting in back-to-back terpyridine connectivity. The resulting linear arms were then attached to the benzene core. Adsorption of nonaRu **44** to silica–titania surfaces, as studied by optical waveguide lightmode spectroscopy[95] (OWLS), revealed that the deposition mode strongly depends on the bulk concentration. A similar approach allowed the convergent synthesis[96] of an octadecanuclear complex **45**. Constable, Housecroft, and co-workers[97] also developed another first-generation, "high-nuclearity" metallodendrimer **46** possessing terminal carborane moieties employing pentaerythritol as the four-directional core.

In a later report,[98] Constable et al. treated nucleophile **47** with bis(bromomethyl)benzene to give bromide **48** possessing an electrophilic site away from the metal, which was subsequently reacted with 4,4′-dihydroxy-2,2′-bipyridine (Scheme 12). The resulting product **49** is a dinuclear complex possessing two terpyridyl Ru(II) moieties linked by an uncomplexed bipyridine ligand. Coordination to transition metals, such as Fe(II) and Co(II), afforded the desired heptanuclear metallomacromolecule **50**.

Other polypyridinyl-based molecules are also known in the literature, e.g., hexakis(4-pyridinyl)benzene,[99] 1,3,5-tris(4′-terpyridinyl)benzene,[100] poly(4-vinylpyridino)benzenes, and poly(4-ethylpyridino)benzenes,[101]

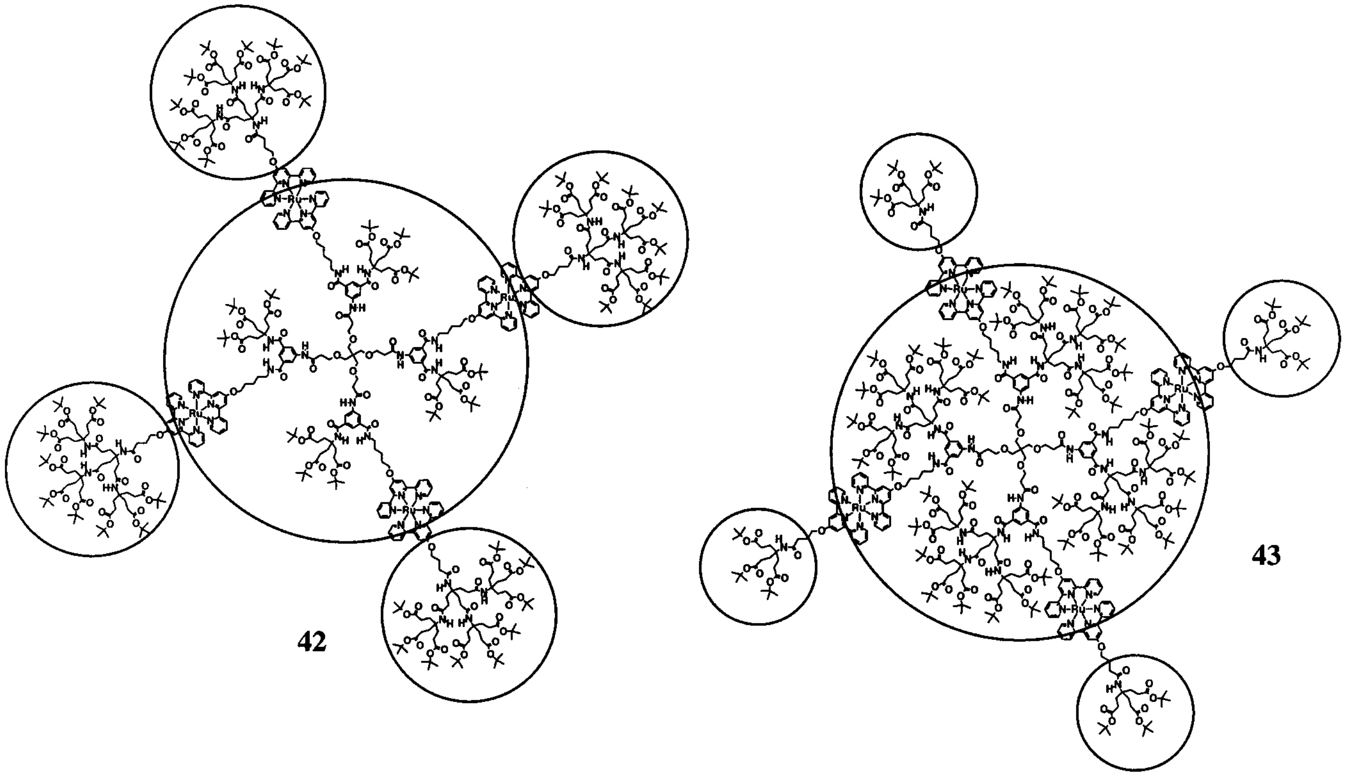


Figure 3. Isomeric, metallodendritic networks.

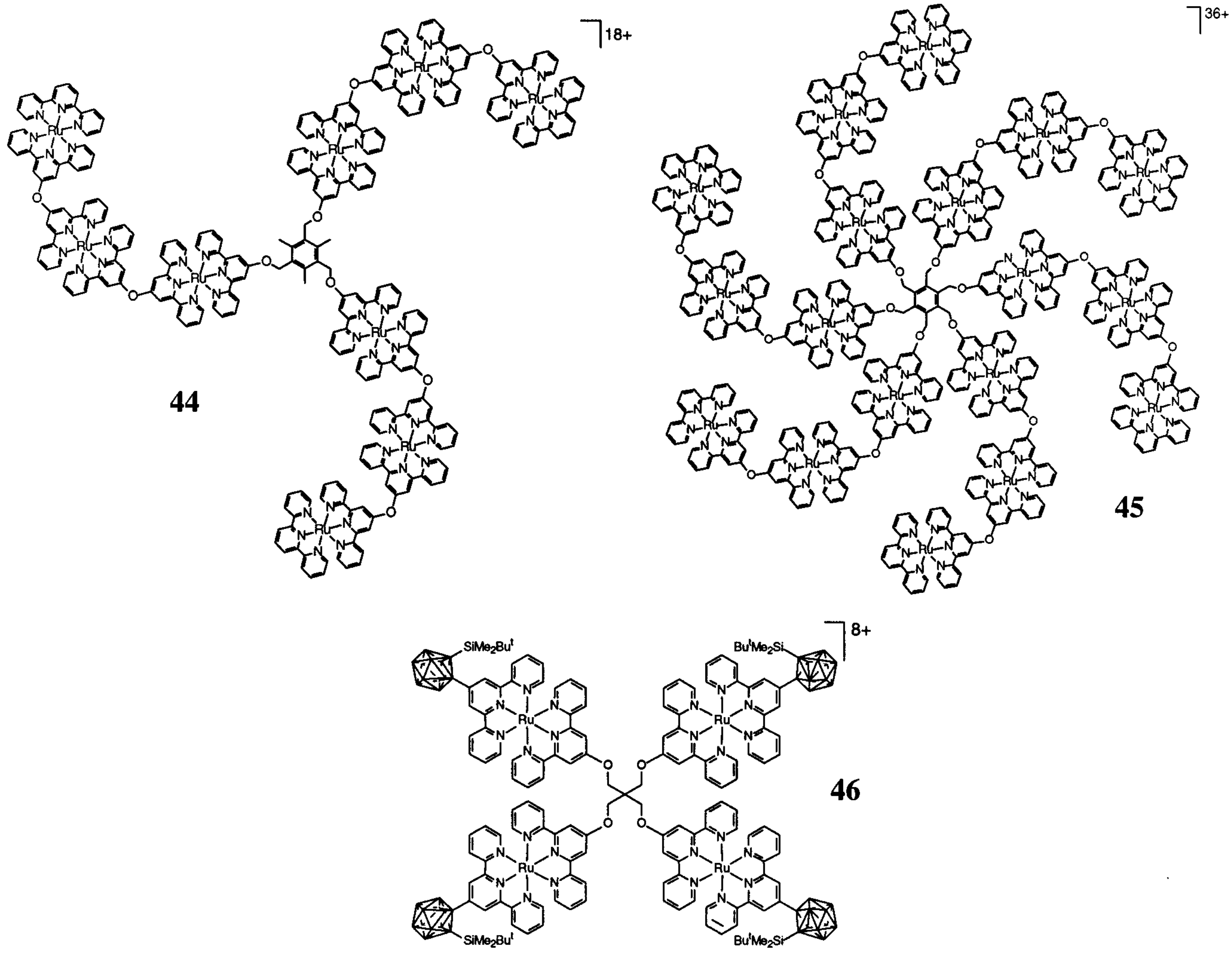
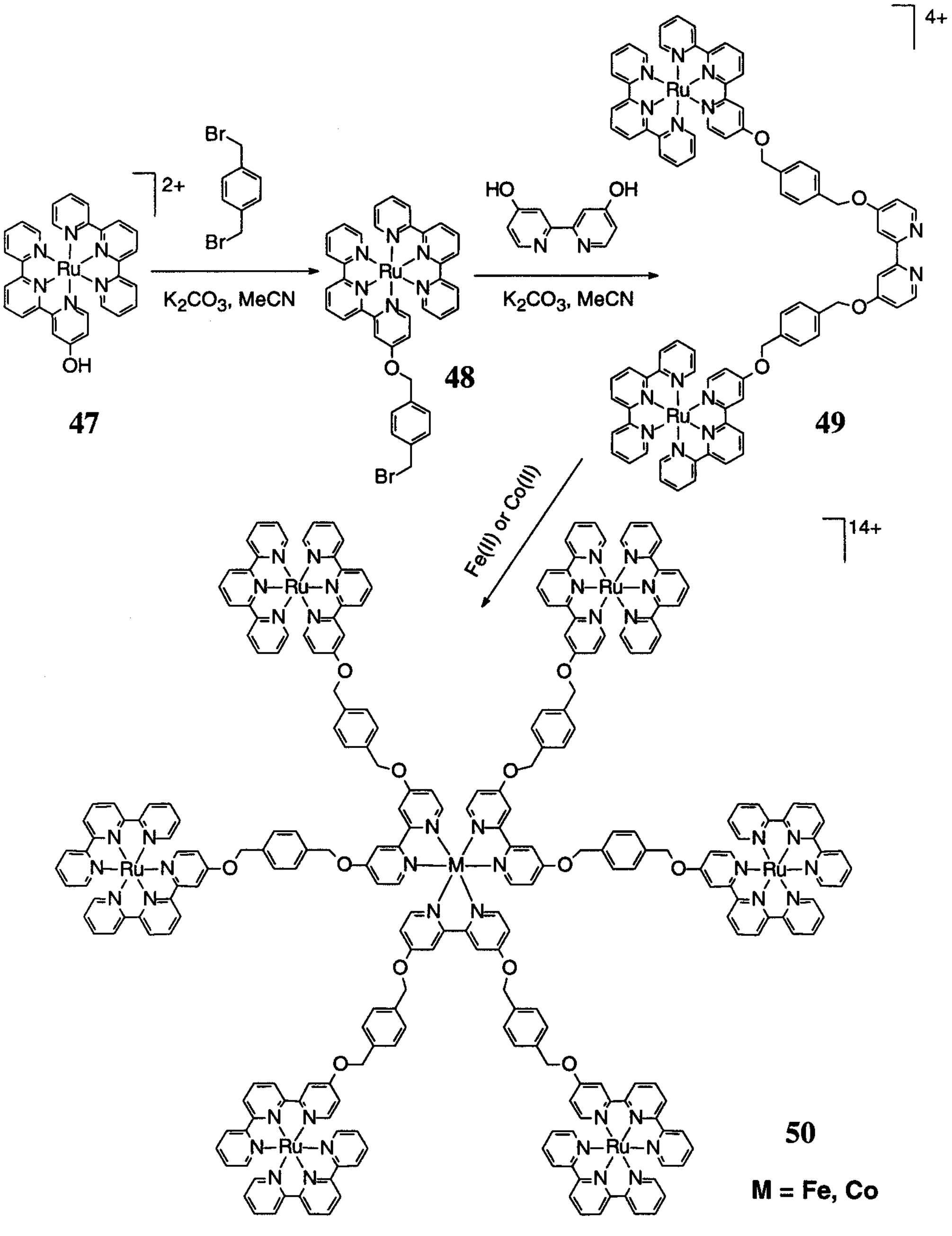


Figure 4. Ru−terpyridyl-based architectures.

Scheme 12. Construction of a Heptanuclear, Mixed-Metal Complex



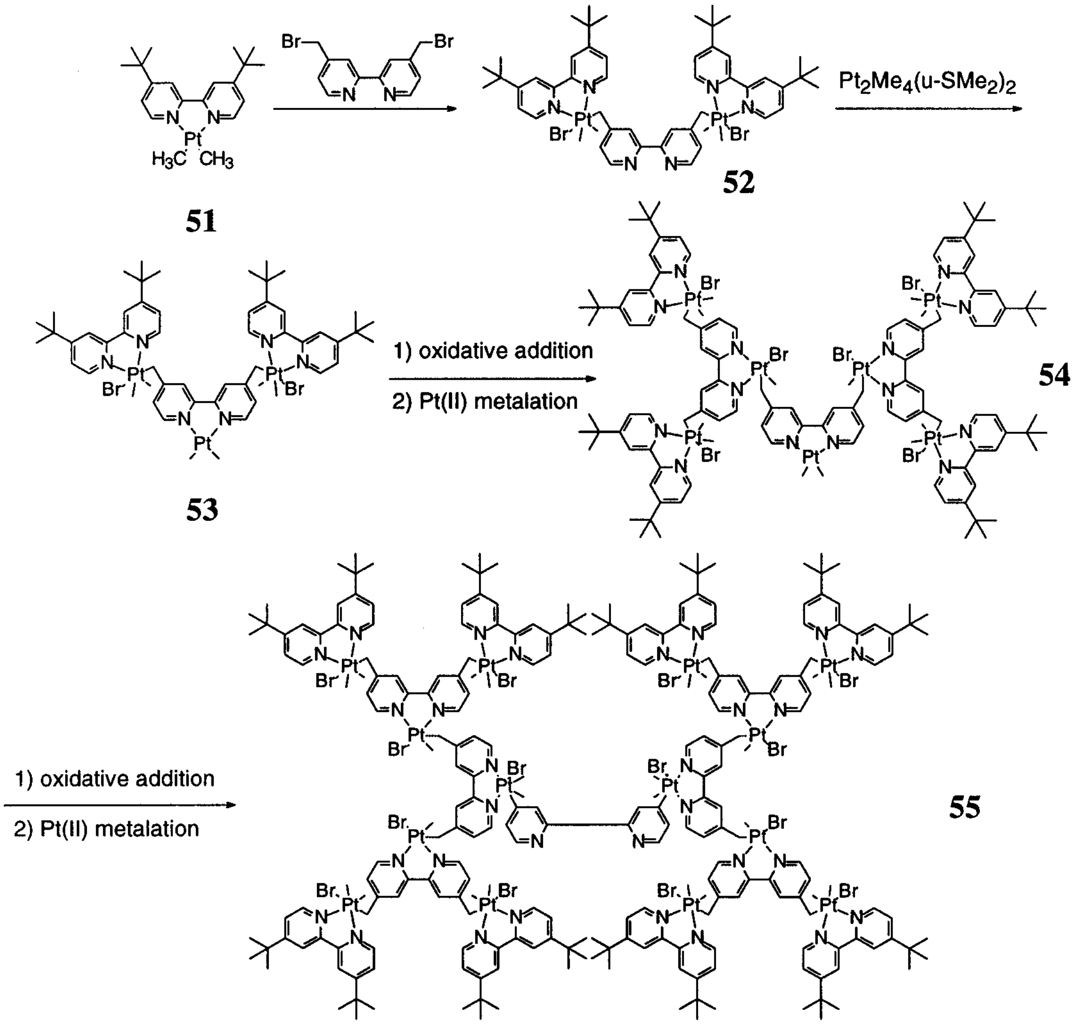
which could lead to the synthesis of large metallodendrimers.

Achar and Puddephatt[102] created a series of convergently prepared organoplatinum dendrimers (Scheme 13) using two repeating reactions: (1) oxidative addition of $PtMe_2(t\text{-}Bu_2bpy)$ via CH_2Br insertion generating stable Pt(IV) centers and (2) SMe_2 ligand displacement from $Pt_2Me_4(\mu\text{-}SMe_2)_2$ by a free bipyridine. Thus, treatment of 2 equiv of $PtMe_2(t\text{-}Bu_2bpy)$ (**51**) with 1 equiv of 4,4′-bis(bromomethyl)-2,2′-bipyridine afforded the first-generation **52**, which was subsequently treated with the platinum dimethyl sulfide complex to afford the mixed-valence, trisplatinum complex **53**. Oxidative addition and Pt(IV) metalation of **53** gave the heptaplatinum **54**. Repetition of the same synthetic sequence afforded the third-generation **55** with 14 platinum metal centers. Later, the authors created the fourth-generation metallodendrimer with 28 platinum centers.[103]

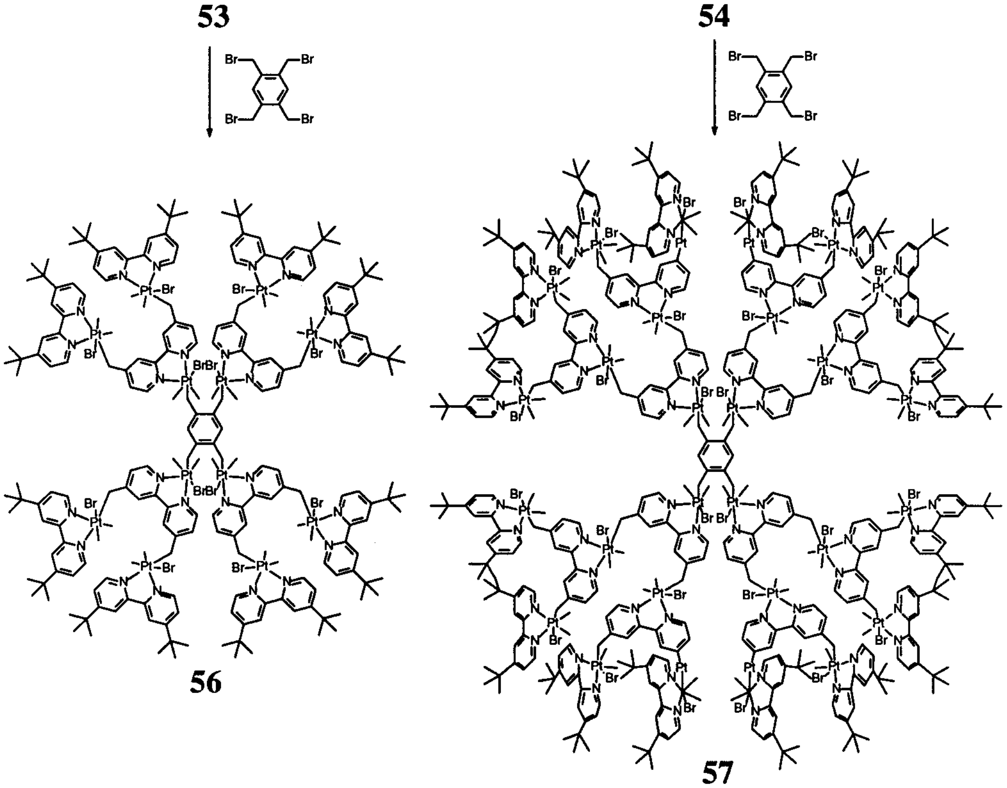
Puddephatt et al.[104] also reported oxidative addition reactions of 4 equiv of each Pt-complex precursors, **53** and **54**, to 1,2,4,5-tetrakis(bromomethyl)benzene (Scheme 14) to form Pt-containing metallodendrimers possessing 12 (**56**) and 28 (**57**) metal centers, respectively. The authors[105] also reported the preparation of oligomers and a polymer containing organoplatinum centers.

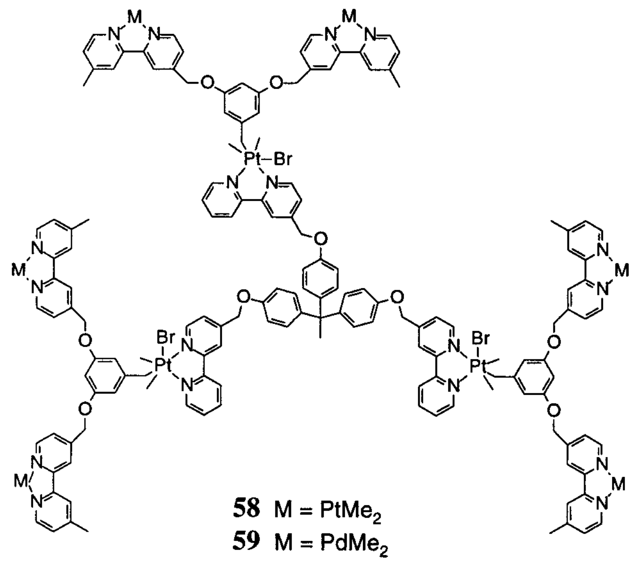
Recently, Liu and Puddephatt[106] explored routes to the synthesis of Pt/Pd-containing dendrimers using their oxidation−addition procedure. Although synthesis of the desired metallodendrimer was not successful, the building blocks could be very useful in future approaches. Nevertheless, these authors[107] successfully developed a divergent route to Pt- and

Scheme 13. Convergent Approach to Organo-Pt Metallodendrimers



Scheme 14. Pt Dendrimers Possessing up to 22 Metal Centers





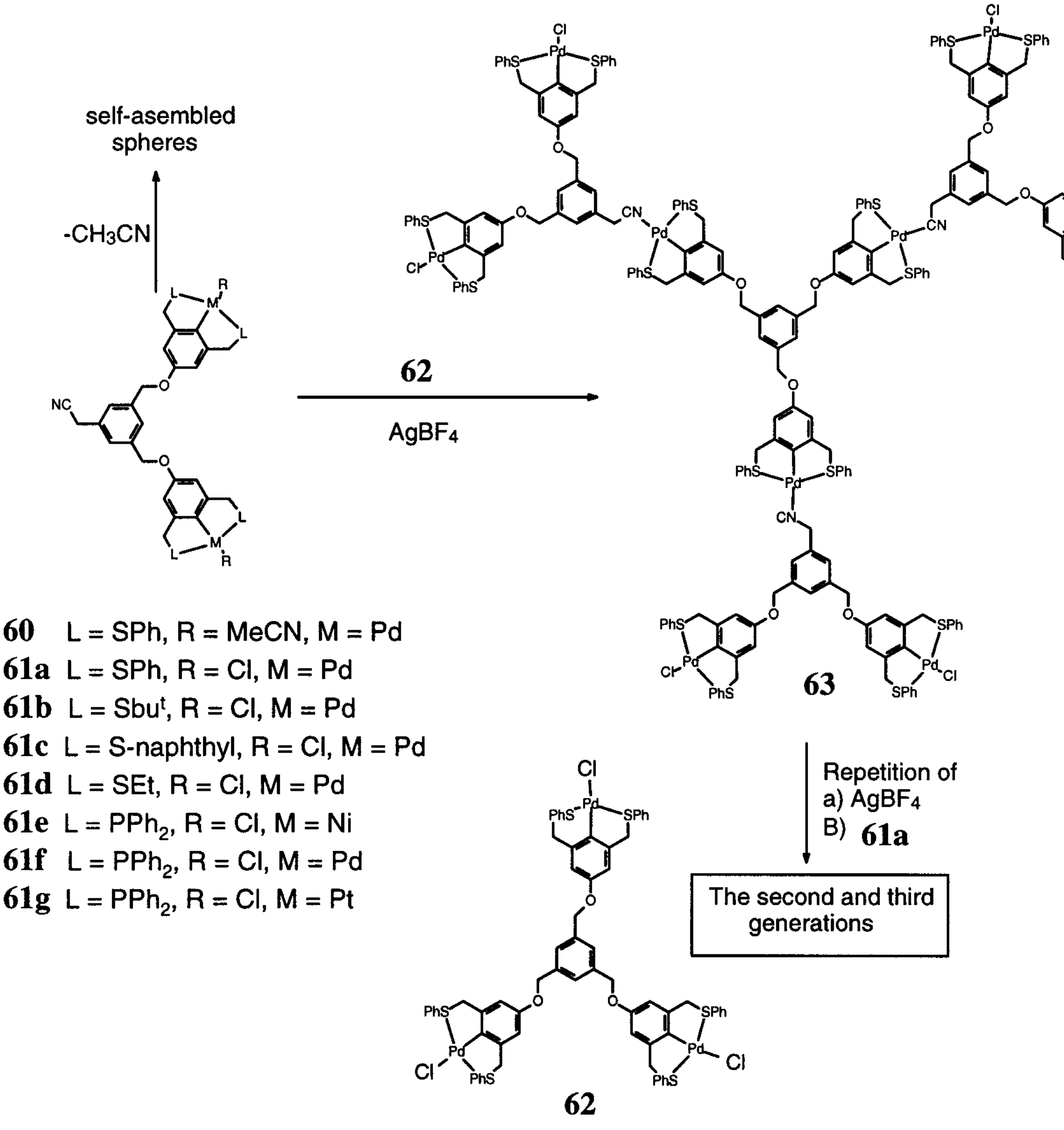
58 M = $PtMe_2$
59 M = $PdMe_2$

Figure 5. Puddephatt's metallodendrimers possessing Pt and Pd metal centers.

Pt/Pd-containing dendrimers (**58** and **59**) comprised of inner generation layers possessing platinum metal centers while outer layers possessed either platinum or palladium complexes (Figure 5).

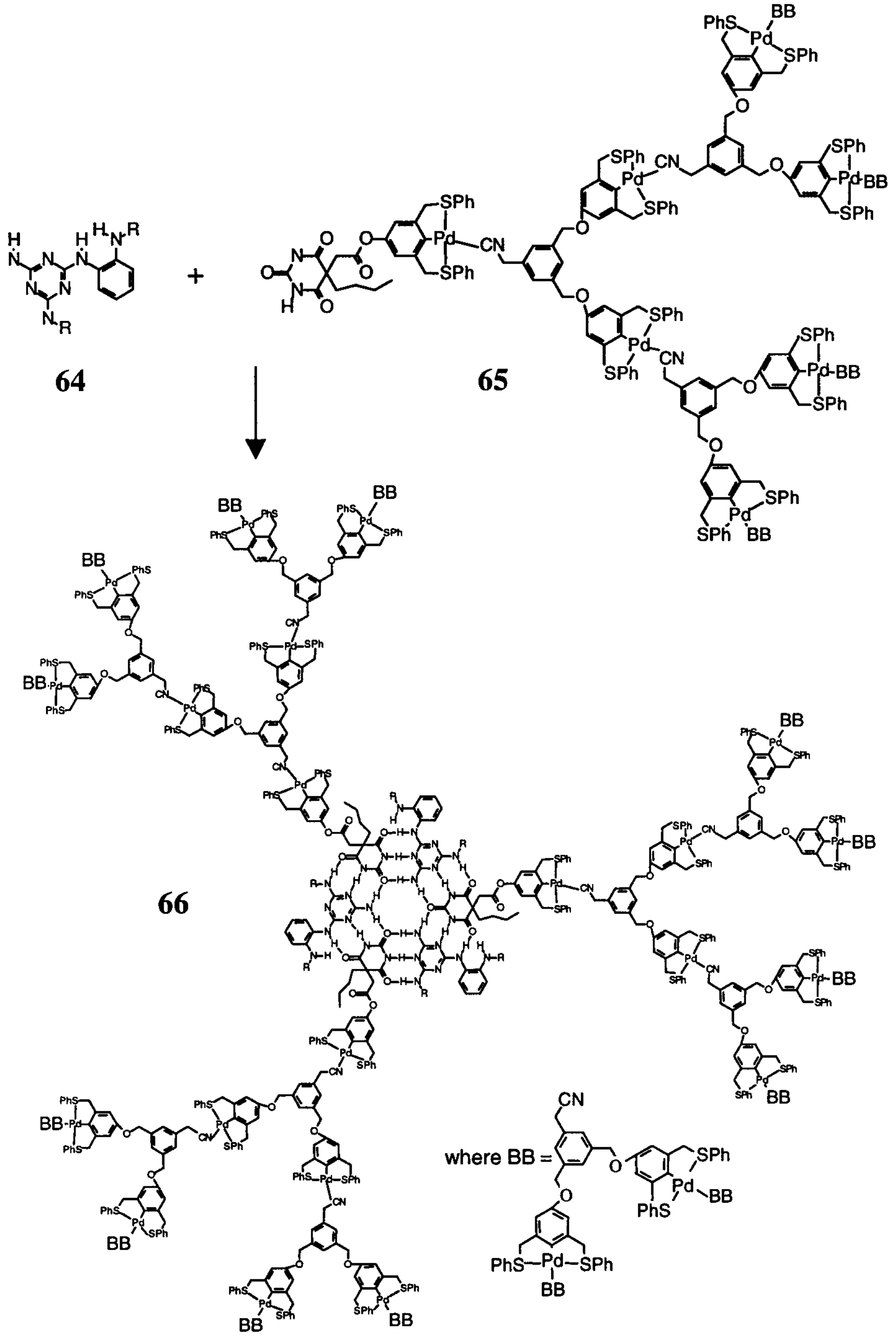
Reinhoudt and co-workers[108,109] reported the assembly of hyperbranched dendrimers via the polymerization of AB_2 monomer **60**. Polymerization was induced by acetonitrile ligand displacement promoted by heating under low pressure, allowing benzylnitrile coordination, leading to "self-assembled metallospheres". In an effort to control the density of the self-assembled polymeric spheres, building blocks **61a**–**g** possessing different ligating groups (*S*-*tert*-butyl, *S*-naphthyl, *S*-ethyl,[110] and *P*-$Ph_2$111) as well as different metals (e.g., Ni(II) and Pt(II)) were synthesized. Reinhoudt et al.[14,112] also developed Pd-containing dendrimers up to the third generation with 47 palladium metal connectors through a controlled divergent approach (Scheme 15). Assembly relies on a kinetically inert tridentate (S–C–S) palladium complex that is labile toward substitution, when the "external" ligand is a nitrile group. The first-generation metallodendrimer **63** was assembled via the addition of a mixture of trispalladium chloride **62** and $AgBF_4$ to bispalladium chloride **61a**. By repetition of the same procedure, second- and third-generation

Scheme 15. Reinhoudt's Hyperbranched Metallospheres and Pd Macromolecules



60 L = SPh, R = MeCN, M = Pd
61a L = SPh, R = Cl, M = Pd
61b L = Sbu^t, R = Cl, M = Pd
61c L = S-naphthyl, R = Cl, M = Pd
61d L = SEt, R = Cl, M = Pd
61e L = PPh_2, R = Cl, M = Ni
61f L = PPh_2, R = Cl, M = Pd
61g L = PPh_2, R = Cl, M = Pt

Scheme 16. Self-Assembly of “Rosettes” via H Bonding

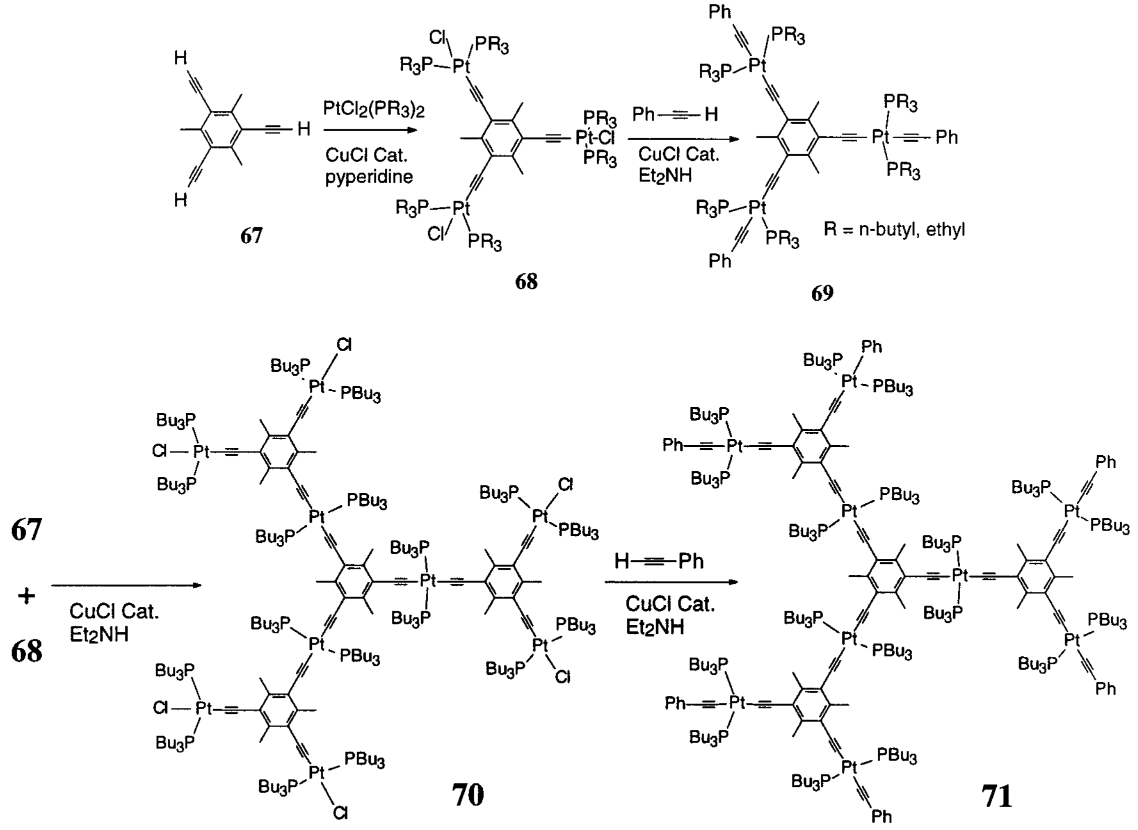


metallodendrimers were prepared and characterized by NMR and MALDI-TOF mass spectrometry.

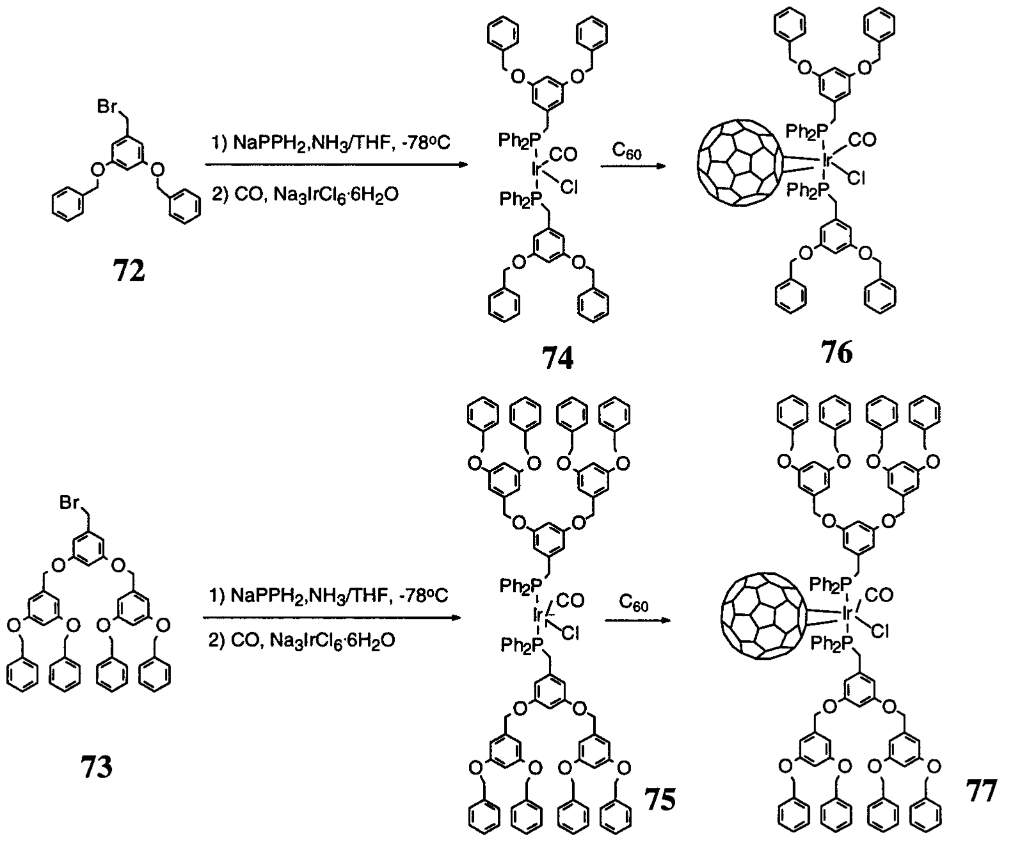
Van Veggel, Reinhoudt et al.[113] developed a synthesis of metallodendrimers via the combination of coordination chemistry and H-bonding (Scheme 16). “Rosettes” were constructed via addition of *N*-octadecanyl-*N*′-(2-*N*-tBoc-amino)phenylmelamine (**64**) to the metallodendrimers G_{1-3} (**65**) to afford up to the third generation of H bonding and mixed-metal dendrimer **66**.

Takahashi et al.[114] reported Pt-containing metallodendrimers with a backbone composed of platinum–acetylide units (Scheme 17). Similar metal–acetylide units with iridium and rhodium have been previously reported by Tykwinski and Stang,[115] while related organoplatinum dendrimers have also appeared.[116] The treatment of 1,3,5-triethynyl-2,4,6-trimethylbenzene (**67**) with dichlorobis(tri-*n*-butylphosphine)platinum or dichlorobis(triethylphosphine)platinum in the presence of a CuCl catalyst in piperidine afforded trinuclear complex **68**, which was subsequently treated with phenylacetylene to give the first-generation metallodendrimer **69**. Via a convergent approach, the larger dendrimer **70** was synthesized by coupling of **67** with **68**, which then was converted to the second generation phenyl-terminated metallodendrimer **71**. The structures were supported by IR, ^{1}H NMR, and combustion analysis.

Scheme 17. Metallodendrimers Possessing Pt Atoms in the Backbone

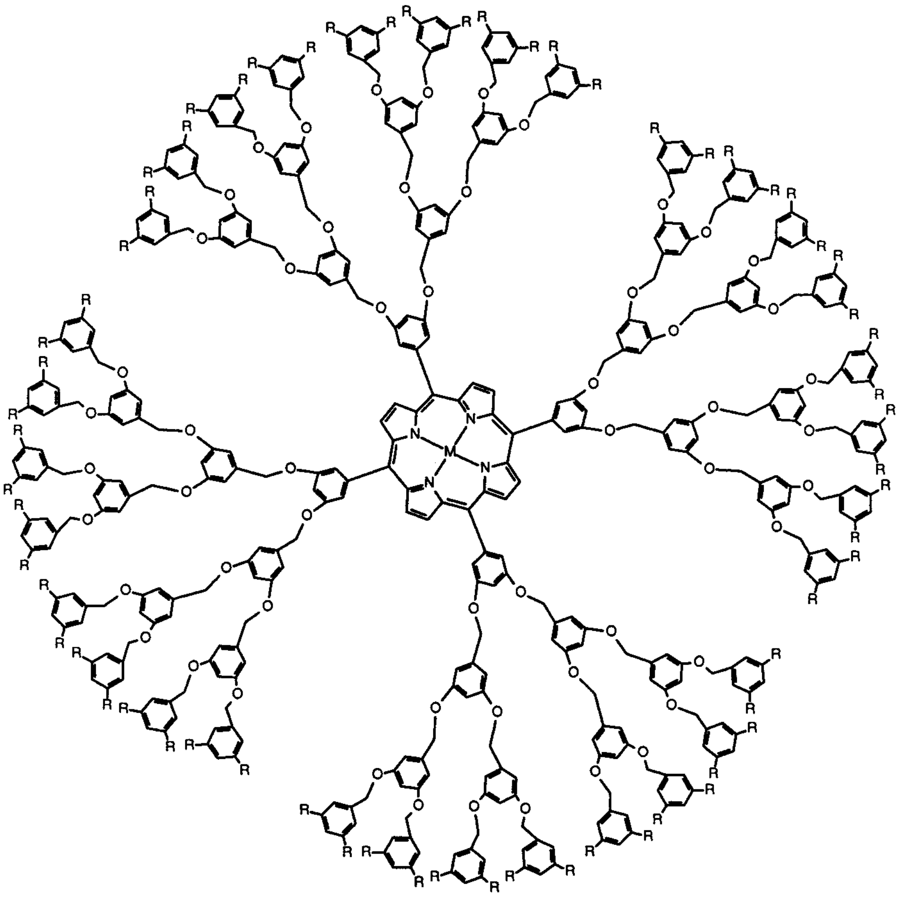


Scheme 18. *trans*-Ir Core Moieties Exhibit Reversible C_{60} Binding



IV. Metals as Cores

Catalano and Parodi[117] have reported the reversible C_{60} binding to metallodendrimer core complexes (i.e., $Ir(CO)Cl(PPh_2R)_2$; Scheme 18). Dendritic wedges possessing focal phosphine ligands were constructed via treatment of the Fréchet-type dendritic fragments[27] 3,5-bis(benzyloxy)benzyl bromide (**72**) and



78 M = Zn^{2+}, R = OMe
79 M = Zn^{2+}, R = $OCH_2Ar(OMe)_2$
80 M = Fe^{2+}, R = $OCH_2Ar(OMe)_2$
81 M = Zn^{2+}, R = $OCH_2Ar(CO_2K)$

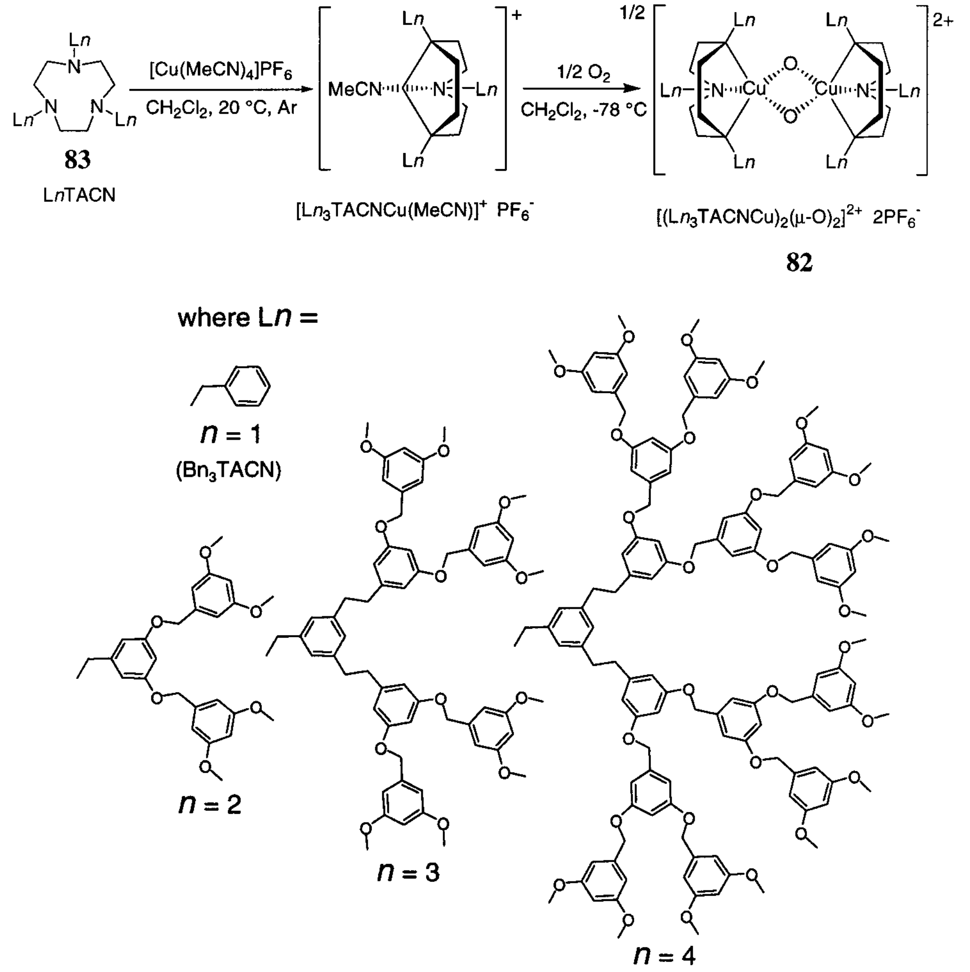
Figure 6. Porphyrin-containing metallodendrimers possessing novel biological properties.

3,5-bis[(3,5-bis(benzyloxy)benzyl)oxy]benzyl bromide (**73**) with $NaPPh_2$. Under reductive conditions (CO), addition of $Na_3IrCl_6{\cdot}6H_2O$ to the diphenylphosphine-based wedges yielded complexes **74** (cis and trans) and **75** (trans only). Each was subsequently bound to C_{60} to afford metallodendrimers **76** and **77**. Both *trans*-**74** and -**75** exhibited thermally reversible binding with C_{60}. Thermodynamic data on the reversible binding were obtained in chlorobenzene by line-width analysis of the $^{31}P\{^1H\}$ NMR spectra. Activation parameters, such as $\Delta G_{265}{}^{\ddagger}$, $\Delta H_{265}{}^{\ddagger}$, and $\Delta S_{265}{}^{\ddagger}$ and the thermodynamic quantities $\Delta G_{265}{}^{\circ}$, $\Delta H_{265}{}^{\circ}$, and $\Delta S_{265}{}^{\circ}$ for **76** and **77** were calculated. Similar rates of reaction with O_2 for both **76** and **77** indicate that the bulkiness of the dendritic branches, in these cases, does not significantly perturb the metal center.

Inoue et al.[118] reported a dendritic 'caged' porphyrin−zinc complex with photochemical functionality (Figure 6). Metallodendrimers up to the fourth-generation **78** were synthesized employing Fréchet's established convergent method.[27] Fluorescence quenching studies using the fourth-generation metallodendrimer revealed that access to the porphyrin core by small-sized quenchers (i.e., vitamin K_3) was facile while larger quenchers (i.e., the first-generation dendrimer) were denied approach. The authors thus suggested the dendritic branches in higher tiers behaved as "shielding barriers" to the metal core although they acted as a trap for small molecules.[119]

Jiang and Aida[120] synthesized similar Fe-containing porphyrin metallodendrimers up to the fourth generation (**80**; Figure 6) that mimic the biological functions of hemoproteins. This dendritic iron porphyrin complex displays reversible dioxygen-binding activity, whereby the O_2 adduct has a lifetime of several months even in the presence of water and a half-life of 50 h upon exposure to carbon monoxide. Aida and co-workers[121] also prepared fifth-generation zinc porphyrin metallodendrimer **79** that was subsequently used as a spectroscopic probe. At the fifth-generation stage, the λ_{max} of the Soret band (ca. $\lambda_{max} = 0.7$ nm) became solvent independent, suggesting that the metallocore was almost completely shielded by the dendritic surroundings. Recently, Aida et al.[122] modified the same zinc porphyrin metallodendrimers (e.g., **81**) with carboxylate groups on the surface. Using higher generations of dendrimers, the addition of methyl viologen (MV^{2+}) or the more negatively charged naphthalenesulfonate did not show notice-

Scheme 19. Self-Assembly of a Copper Ligating Dendrimer to Mimic a Non-Heme Metalloprotein



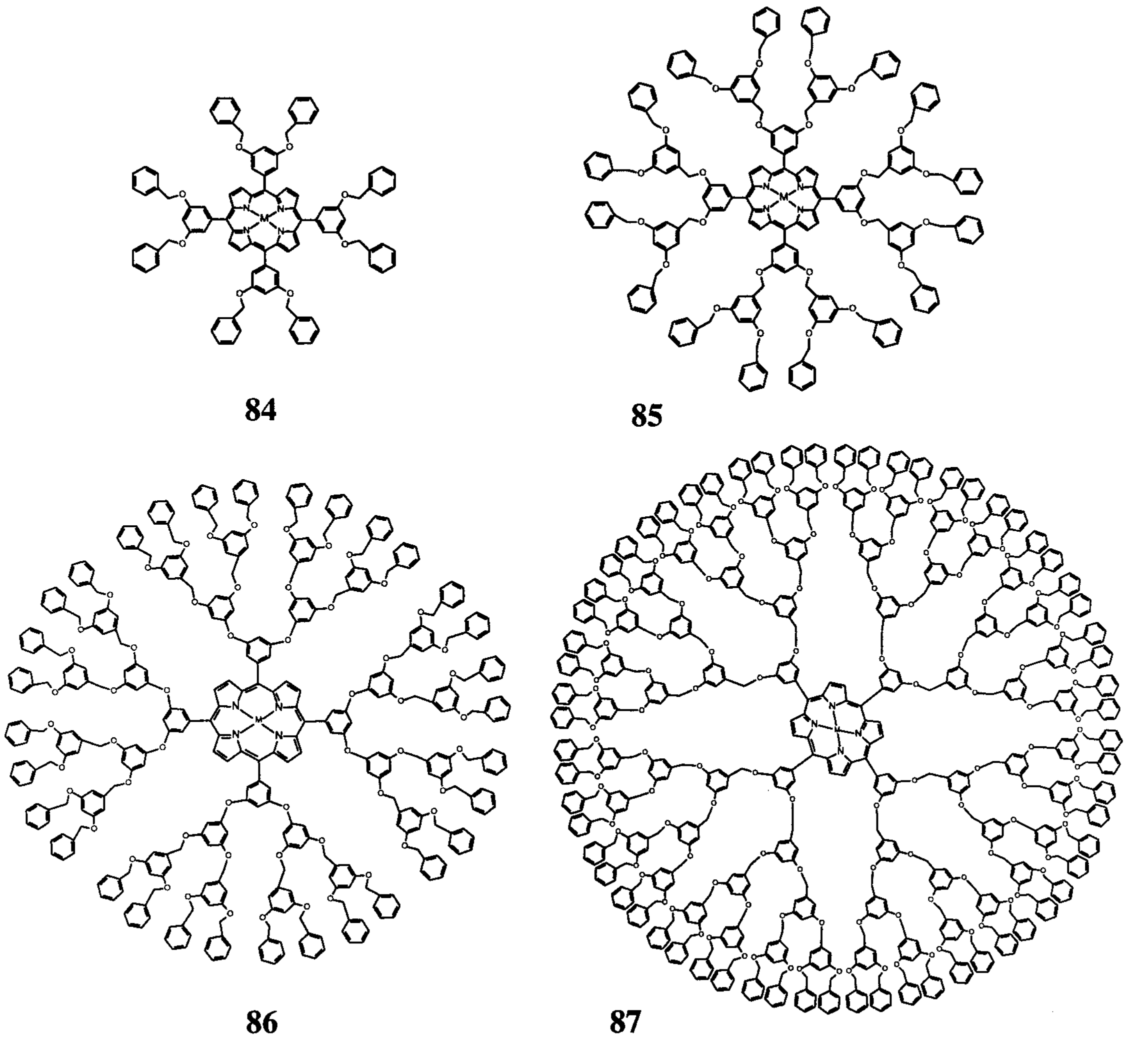
able solvatochromic changes, while a significant change was observed with the first generation. This result, again, illustrates the shielding effect of the large dendritic shell, which correlates with their earlier results.[118]

Aida and Enomoto[123] have reported the "oxygen promoted" self-assembly of copper-ligating dendrimers for the examination of dendritic effects on a non-heme metalloprotein mimic (e.g., **82**; Scheme 19). Construction of the "copper-ligating" metallodendrimers was achieved via attachment of methyl-terminated, Fréchet-type dendrons to the cyclic triamine (1,4,7-triazacyclononane) via amine displacement of benzyl bromide focal groups (**83**), followed by treatment with [Cu(MeCN)$_4$]PF$_6$ and O$_2$ to give the bis(μ-oxo)-bridged dicopper core moiety. Oxidative decomposition studies on each member of the series suggested a greater stability for the higher generation metallodendrimer based on entropy loss for the reaction. Steric effects were postulated to account for the phenomenon.

Fréchet and co-workers[124,125] prepared zinc porphyrin metallodendrimers up to the fourth generation (**87**; Figure 7). They concluded that the dendritic shell did not significantly affect the electrochemical or photophysical nature of the metalloporphyrin core. However, even with smaller generations of dendrimers (**84**, **85**, or **86**), the rate of interfacial electron transfer is noticeably reduced, presumably due to the decreasing proximity of the porphyrin core to the electrode surface in cyclic voltammetry experiments. No noticeable hindrance to penetration of the dendritic shell, by small molecules, was observed, which is in accord with Inoue's and Aida's observations.[118] Only the fourth-generation metallodendrimer **87** showed a 33% rate enhancement of the viologen fluorescence quenching of the zinc porphyrin. Suslick et al.[126,127] reported the "shape-selective control of ligation" of dendritic metalloporphyrins.

Moore, Suslick, and co-workers[128,129] recently synthesized Mn-containing metallodendrimers as selective oxidation catalysts (Figure 8). Four ester-based dendritic building blocks were appended to the meta-positions of the 5,10,15,20-tetrakis(3′,5′-hydroxyphenyl)porphinatomanganese(III) chloride to obtain the second and third generations of metallodendrimers **88** and **89**. Both dendrimers have been examined as regioselective oxidation catalysts for both intra- and intermolecular cases. Epoxidation of nonconjugated dienes and of 1:1 mixtures of various alkenes possessing different shapes and sizes was examined. The dendritic catalysts showed superior regioselectivity at the less hindered double bond positions when compared to the corresponding parent, 5,10,15,20-tetrakis(3′,5′-hydroxyphenyl)porphinatomanganese(III) cation.

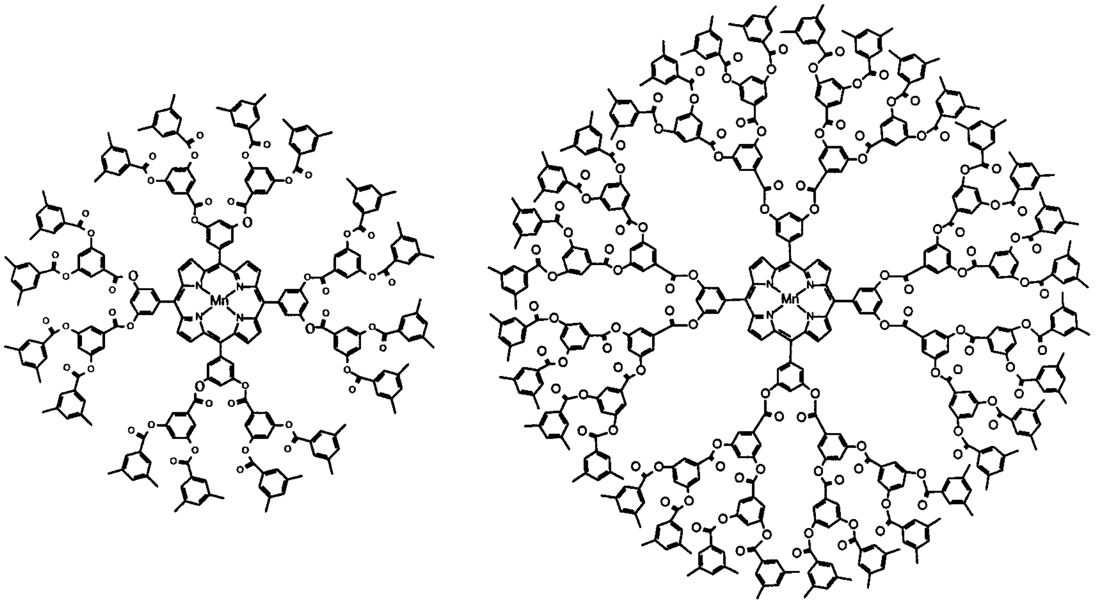
Diederich et al.[130] synthesized zinc porphyrin metallodendrimers (e.g., **90** and **91**) through a divergent



84 **85**

86 **87**

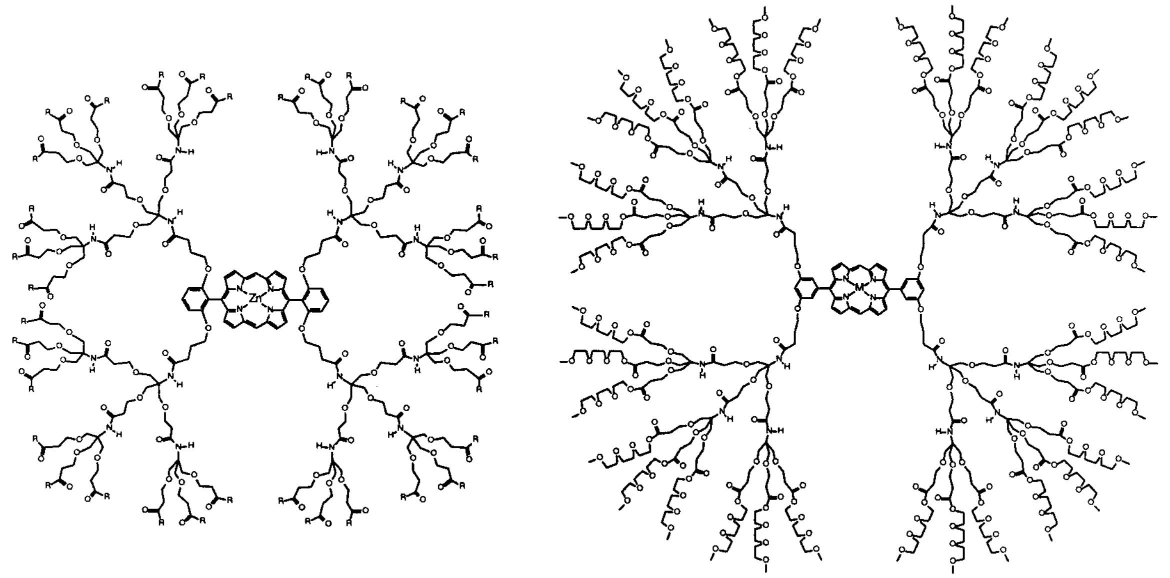
Figure 7. Fréchet's zinc porphyrin macromolecules.



88 **89**

Figure 8. Moore's and Suslick's Mn-based metallodendrimers constructed as selective oxidation catalysts.

strategy, employing a 1→3 C-branched amino triester building block,[131] to construct the dendritic shell (Figure 9). Those molecules were regarded as models for electron-transfer proteins such as cytochrome *c*, in which the dendritic polypeptide branches can affect the metalloporphyrin core redox potential. The

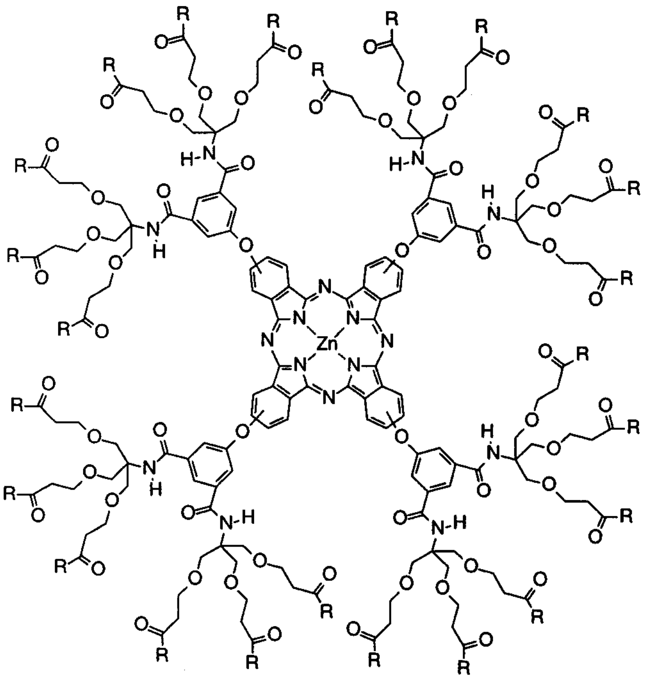


90 R = OCH_3
91 R = $NHC(CH_2OCH_2CH_2CO_2CH_3)_3$
92 M = Zn, Fe

Figure 9. Diederich's porphyrin-containing metallodendrimers possessing novel electrochemical and biological properties.

first reduction potential of the zinc porphyrin unit becomes more negative with increasing dendrimer generation by 90−300 mV, which can be explained by the increasing electron-rich microenvironment around the porphyrin core. Meanwhile, the first oxidation potential becomes less positive by up to 300 mV than the tetraester porphyrin core alone. Both reduction and oxidation processes become totally irreversible at the third generation (**91**).

Diederich, Gross, and co-workers[132,133] later synthesized similar Fe(II) porphyrin metallodendrimers (e.g., **92**; Figure 9) with triethylene glycol monomethyl ether groups on the surface, facilitating solubility in solvents with polarity ranges from nonpolar (*p*-xylene) to polar (H_2O). The electrochemical studies indicate that solvent polarity strongly affects the redox potential of electrochemical reactions that occur at the heme metal center. In organic solvents, such as CH_2Cl_2, the iron porphyrins in both the first and second generations are exposed to similar microenvironments, so that similar potentials for the Fe^{III}/Fe^{II} couple are measured. In water, however, the loosely packed first generation does not impede aqueous solvation of the iron porphyrin whereas the more densely packed dendritic shell of metallodendrimer **92** significantly reduces contact between the heme and external H_2O molecules, destabilizing the oxidized form while increasing the charged state and shifting the redox potential to a more positive value. The large potential shift in water is comparable to the difference observed between cytochrome *c* and a cytochrome *c* heme model possessing a more open structure.



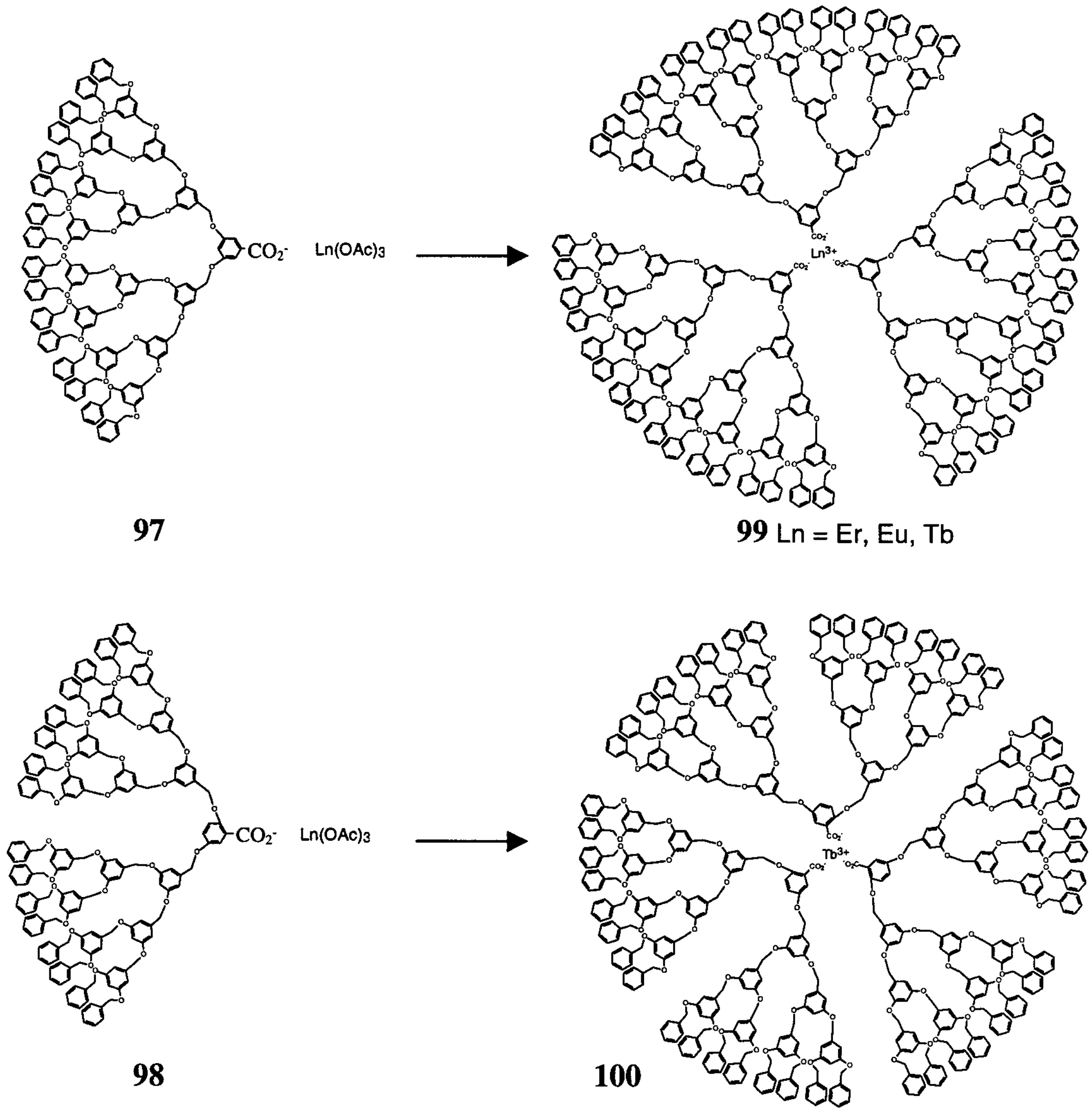
93 R = OEt
94 R = OLi
95 R = $NHC(CH_2OCH_2CH_2CO_2Et)_3$
96 R = $NHC(CH_2OCH_2CH_2CO_2Li)_3$

Figure 10. Divergently constructed of phthalocyanine-based metallodendrimers.

Collman, Diederich et al.[134] reported the dioxygen and carbon monoxide binding behavior of the same Fe(II) porphyrin metallodendrimers (e.g., **92**). Remarkably, the O_2 affinities of the dendritic porphyrins are about 1500 times greater than that of T-state hemoglobins. The CO affinities of the dendritic porphyrins are lower than those of the 'picket fence' model but are close to the value of hemoglobin in the T-state.

Kimura, Shirai, and co-workers[135] synthesized zinc phthalocyanine metallodendrimers, based on a divergent-growth strategy using a 1→3 C-branched amino ester[136] (Figure 10). The UV−vis spectra of

Scheme 20. Kawa and Fréchet's Lanthanide-Containing Metallodendrimers



97

99 Ln = Er, Eu, Tb

98

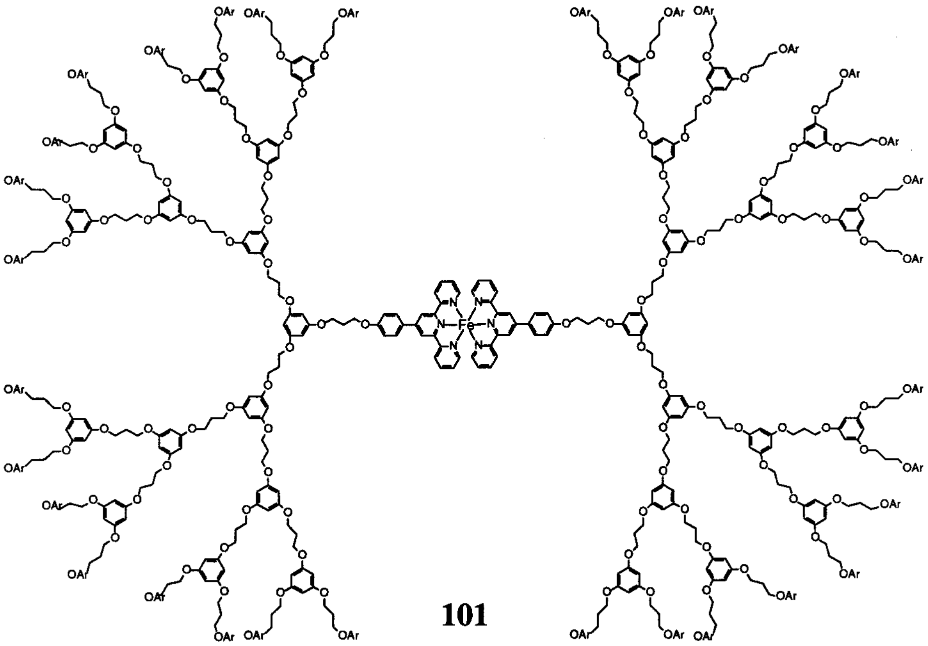
100

lipophilic metallodendrimers **93** and **95** in CHCl$_3$ showed a sharp signal at 621 nm ($\epsilon = 2.95 \times 10^5$ dm^3 mol^{-1} cm^{-1}) with a shoulder at 621 nm and are not influenced by the generations of dendrimers. However, the spectra of hydrophilic metallodendrimers **94** and **96** are quite different, owing to the nonaggregation of zinc phthalocyanine of **96** presumably because of the bulky dendritic branches. The higher generation **96** also displayed a strong fluorescence peak at 674 nm in aqueous media, while lower generations do not fluoresce due to zinc phthalocyanine aggregation.

Kawa and Fréchet[137] reported lanthanide-containing metallodendrimers (Scheme 20) up to the fourth generation (**99** and **100**) via the self-assembly of three polybenzyl ether dendrons (e.g., **97** and **98**) by carboxylate anion coordination to a central trivalent cation (Er^{3+}, Tb^{3+}, Eu^{3+}). The luminescence properties of these novel metallodendrimers, measured in both solution and bulk, were enhanced as the size of the dendritic surroundings increased. This was attributed to both a large "antenna effect" from the nonconjugated phenyl benzyl ether dendritic cluster and a shielding effect derived from site isolation of the lanthanide cations, thus preventing their interaction and decreasing the rate of self-quenching.

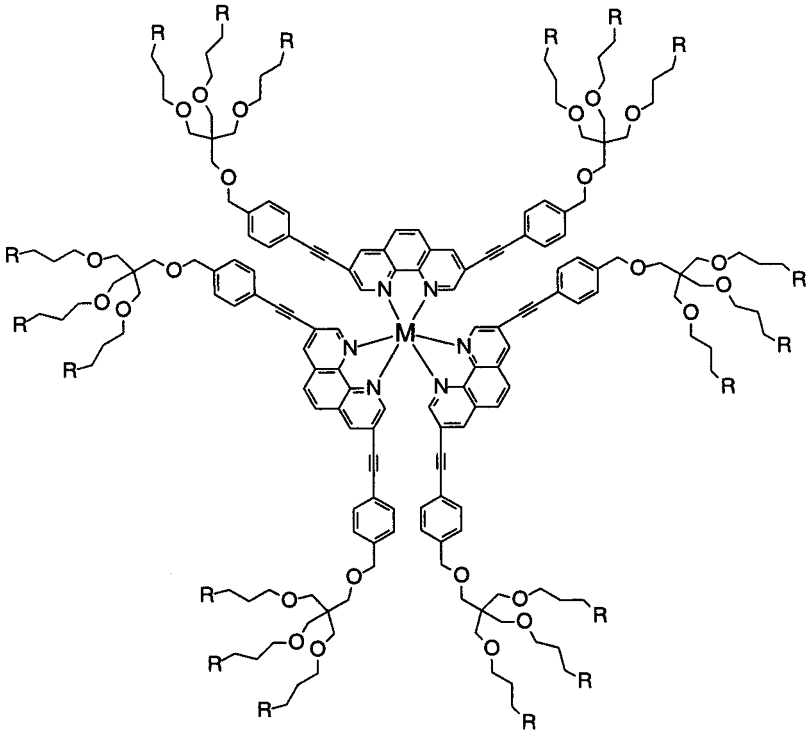
Chow et al.[138,139] reported the synthesis and characterization of $-\langle Fe \rangle-$ metallodendrimers up to the fourth generation (**101**; Figure 11) using benzyl ether-based dendritic building blocks possessing propylene spacer moieties.[140,141] Cyclic voltammetry revealed similar behavior to that reported by Newkome,[86] whereby the reversibility of the metal redox centers decreases when the generation increases. These results were rationalized by the steric hindrance caused by the bulky dendritic shell, thus isolating the redox center from the electrode surface.

Bidentate ligands, such as bipyridine and 1,10-phenanthroline, are powerful metal chelating agents[142] and have been widely used in the construction of metallodendrimers (see section II. Metals as Branching Centers). Several examples are given here using bidentate ligands as the dendritic core. Tzalis and Tor[143] synthesized the metallodendrimers **102** by incorporating Cu$^+$ and Fe^{2+} ions within symmetrically substituted 1,10-phenanthroline ligands. Branching was effected using pentaerythritol-based building blocks (Figure 12). All structures were subjected to



101

Figure 11. Chow's Fe(II)−terpyridyl core assemblies.



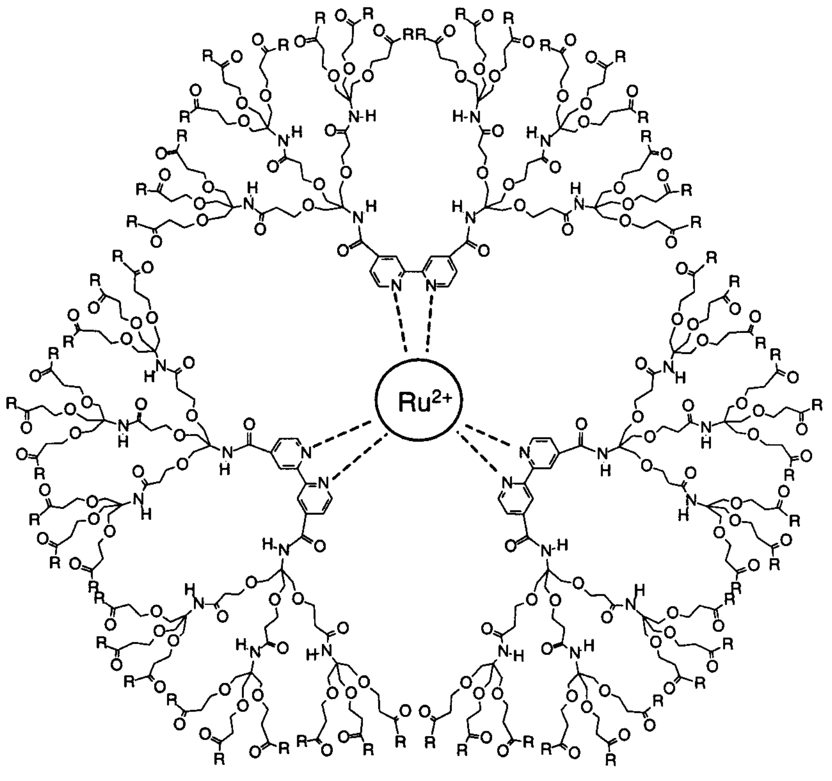
102 R = OH, M = Cu$^+$, Fe^{2+}

Figure 12. Tzalis and Tor's Cu- and Fe-containing complexes.

ESI-MS revealing mono- or double-charged molecular peaks.

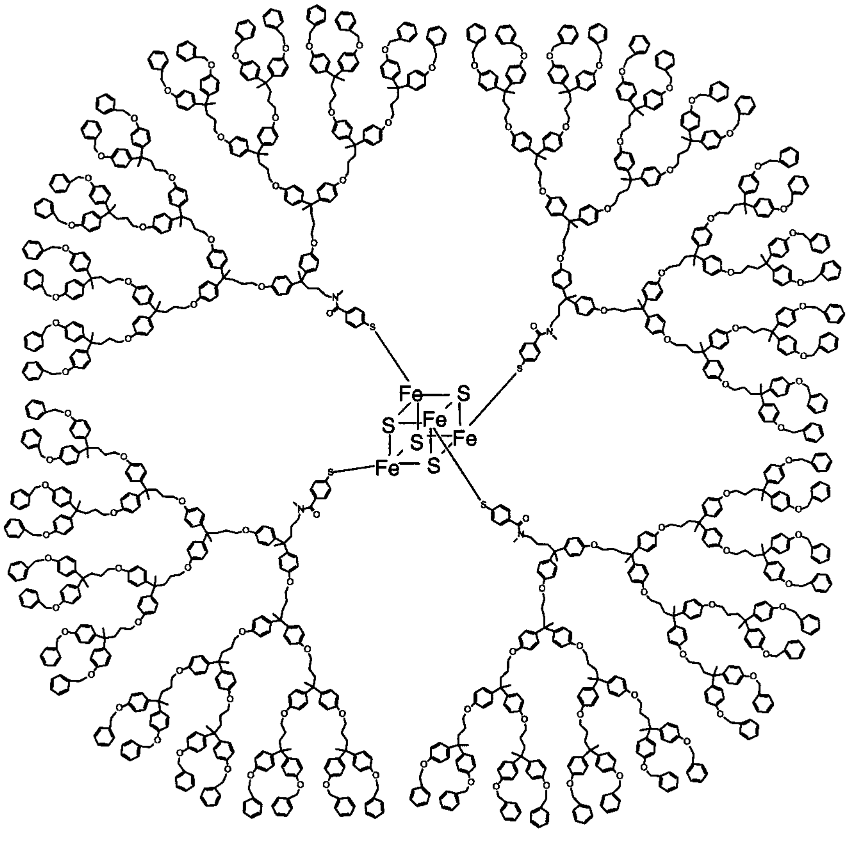
Vögtle, Balzani et al.[144] reported metallodendrimers constructed up to the third generation with a [Ru(bpy)$_3$]$^{2+}$ complex as its core (**103**; Figure 13) with the largest generation possessing 54 peripheral methyl ester groups. Branching was instilled using an amino triester monomer prepared via methyl acrylate addition to "tris".[136] The larger metallomacromolecule exhibited a more intense emission spectrum and a longer excited-state lifetime than the parent Ru(II) cation in aerated solutions. This was rationalized by considering the shielding effect of the dendritic scaffolding. Notably, the third-generation metallodendrimer **103** has an excited-state lifetime longer than 1 μs. The quenching constant of the luminescent Ru(II)−bipyridine MLCT level decreases as the generation of the metallodendrimers increases until the third generation when it reaches a value of one-twelfth of the original Ru(II)−bipyridine core.

Gorman et al.[145] reported the synthesis of novel Fe−S cluster-based metallodendrimers up to the fourth generation (Figure 14). Focally substituted thiol-based dendrons[146] were treated with 0.25 equiv



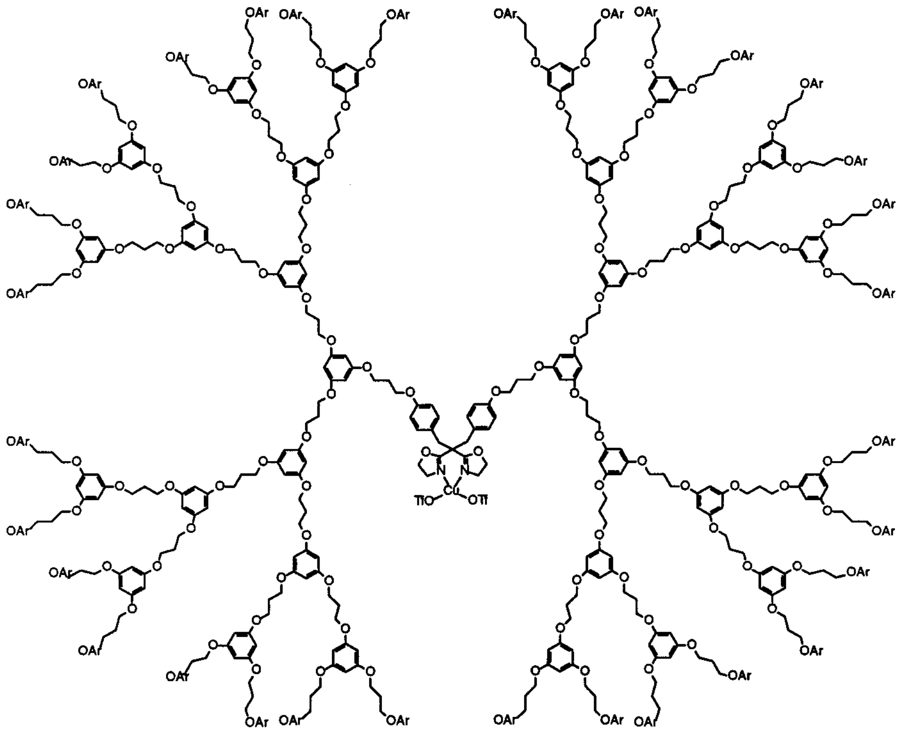
103 R =OMe

Figure 13. Vögtle's and Balzani's metallodendrimers possessing a Ru(II) bipyridine complex at the core.



104

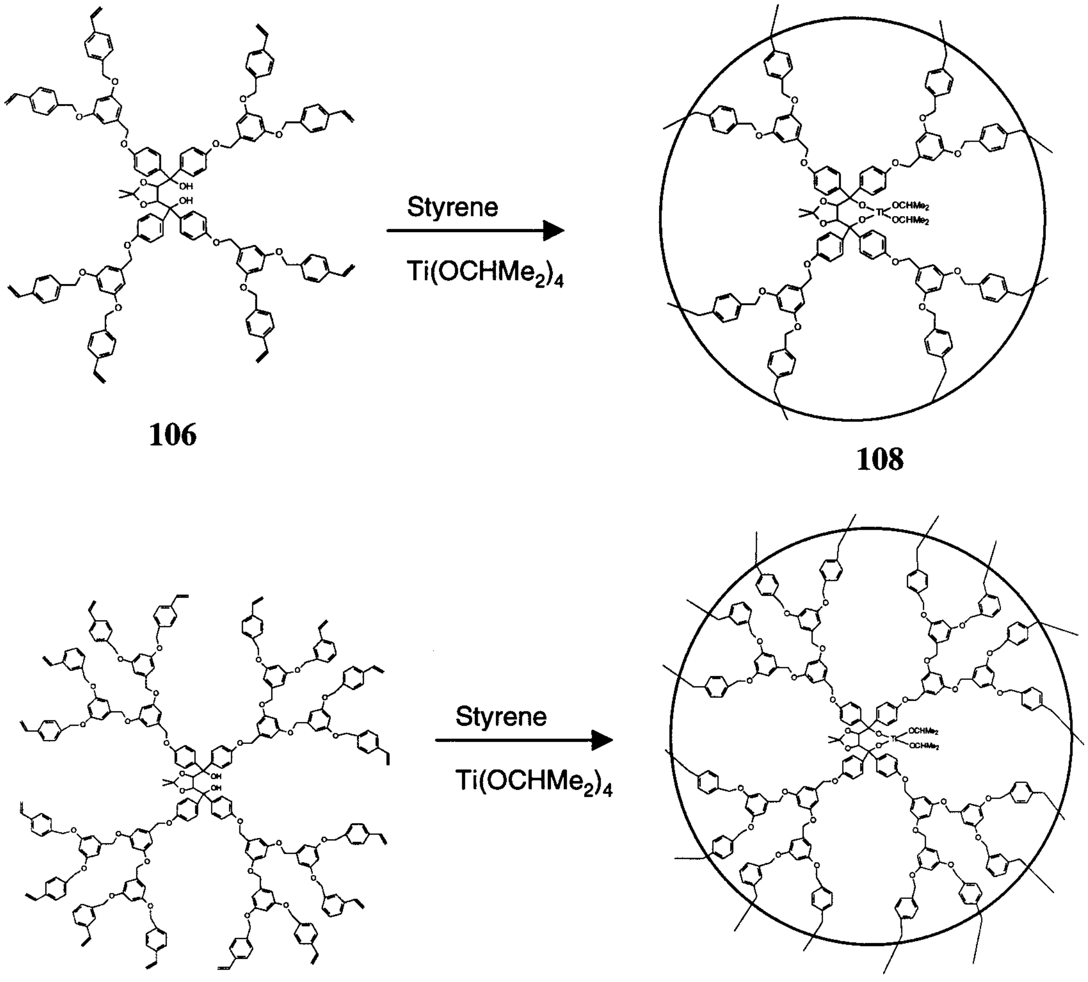
Figure 14. Gorman's novel Fe-containing metallodendrimers.



105

Figure 15. Chow's Cu-coordinating macromolecular catalyst for Diels–Alder reactions.

Scheme 21. Seebach's Novel Ti-Containing Polymer Cross-Linkers



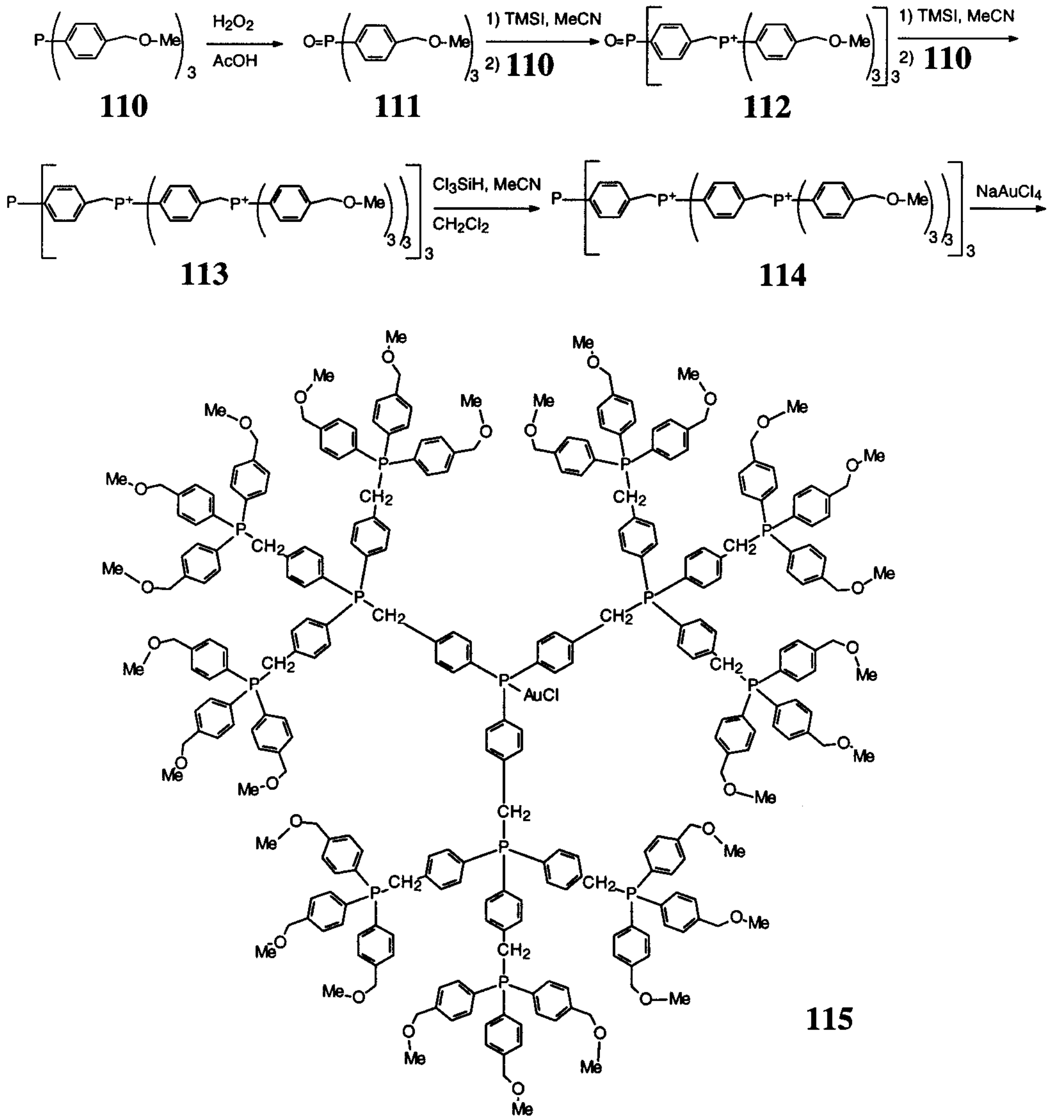
106

108

107

109

Scheme 22. Engel's Phosphonium Metallodendrimer with Au Attached to the Phosphorus Core

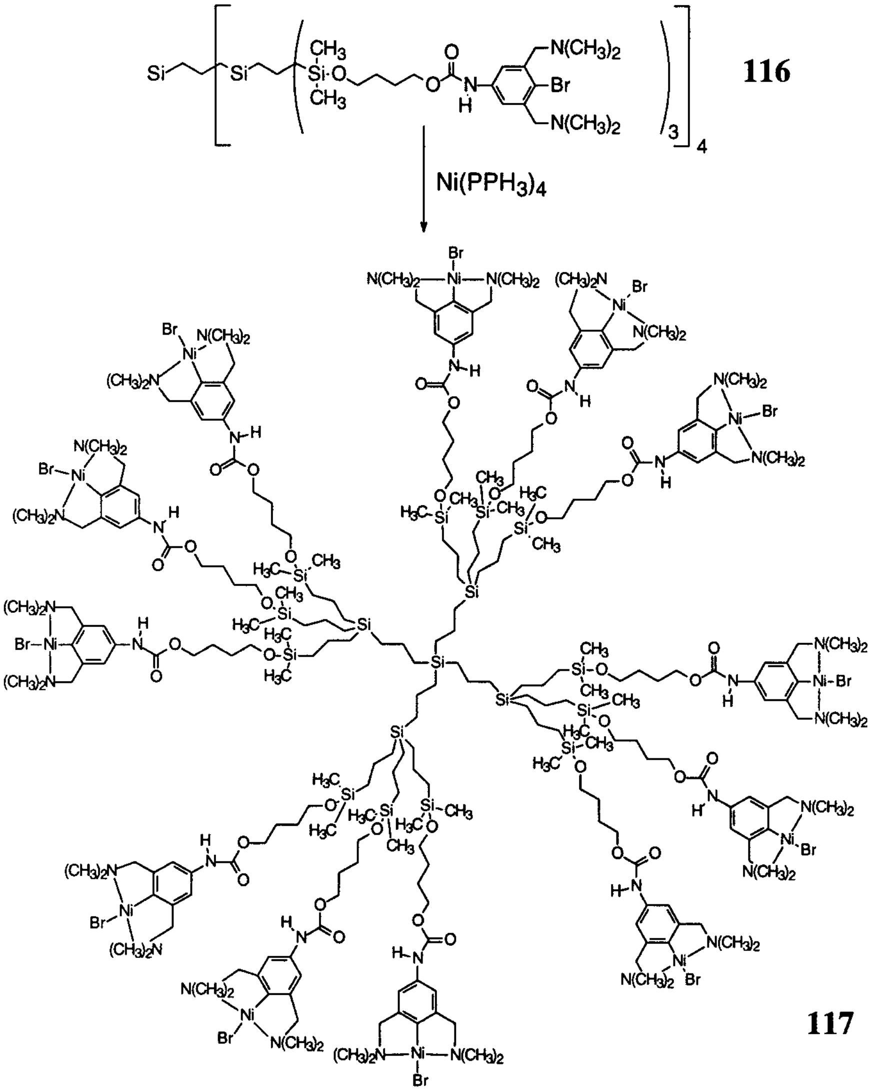


of (n-Bu$_4$N)$_2$[Fe$_4$S$_4$(S-*t*-Bu)] to give the desired product in high yield (e.g., **104**). Cyclic voltammetry experiments exhibited an increasingly negative reduction potential of the one-electron reduction of the metal center as the dendrimer generation increased. The largest molecule **104** also displayed an irreversible oxidation wave. These observations were rationalized by considering the increased steric hindrance of the dendritic shell that would render the redox centers, both kinetically and thermodynamically, more difficult to reduce and oxidize. The molecular weights of these metallomacromolecules were determined by vapor phase osmometry (VPO), which provided data similar to calculated values. The paramagnetic FeS core has been used as a NMR probe to study the conformation of these metallodendrimers.[147] The T_1 relaxation time of the protons in these dendrimers was found to be shorter than that of protons in a similar dendrimer possessing a diamagnetic (tetraphenylmethane) core.

Chow and Mak[148,149] prepared metallodendrimers up to the fourth generation containing bis(oxazoline)-copper(II) **105** and reported their evaluation as catalysts for the Diels–Alder reaction between cyclopentadiene and crotonyl imide (Figure 15). The synthetic details are analogous to their previously described examples whereby phenolic-based dendrons are prepared convergently.[141,150] The binding constant ($K_c = k_1/k_{-1}$) of the bis(oxazoline)copper(II)–dienophile complex decreases from 9.8 [G$_1$·Cu(OTf)$_2$] to 5.7 M^{-1} [G$_3$·Cu(Otf)$_2$]. While, the Diels–Alder reaction constant (k_2) remains almost constant (3.3 × 10^3 M^{-1} s^{-1}) for the first- and second-generation catalysts, it decreases suddenly at the third generation (1.9 × 10^3 M^{-1} s^{-1}). These observations were attributed to the loosely packed branches that have little effect upon the metal catalytic center, while increased steric hindrance caused by the larger dendritic and more densely packed shell impedes both the reactivity and binding profiles of the central metal.

Seebach et al.[151] developed novel dendritic styryl α,α,α′,α′-tetraaryl-1,3-dioxolane-4,5-dimethanols (TADDOLs) to serve as polymer cross-linkers that incorporate titanium metal in the core upon copolymerization with styrene (Scheme 21). The dioxolane core moiety was tetrasubstituted with styryl-terminated dendrons prepared from 1→2 aryl-branched building blocks via the Fréchet convergent protocol[27] to afford the first and second generations of dendrimers **106** and **107**. Both dendrimers were copolymerized sepa-

Scheme 23. van Koten's Ni-Terminated Macromolecular Catalysts for the Kharasch Addition of Polyhalogenoalkanes to C−C Double Bonds



116

117

rately with styrene to give beads ranging in size from 100 to 600 μm. Treatment of these dried beads with $Ti(OCHMe_2)_4$ in toluene gave the Ti-loaded copolymers **108** and **109**. Both dendritic copolymers exhibited similar catalytic activity for the Et_2Zn addition to PhCHO as the nondendritic Ti−TADOLates.

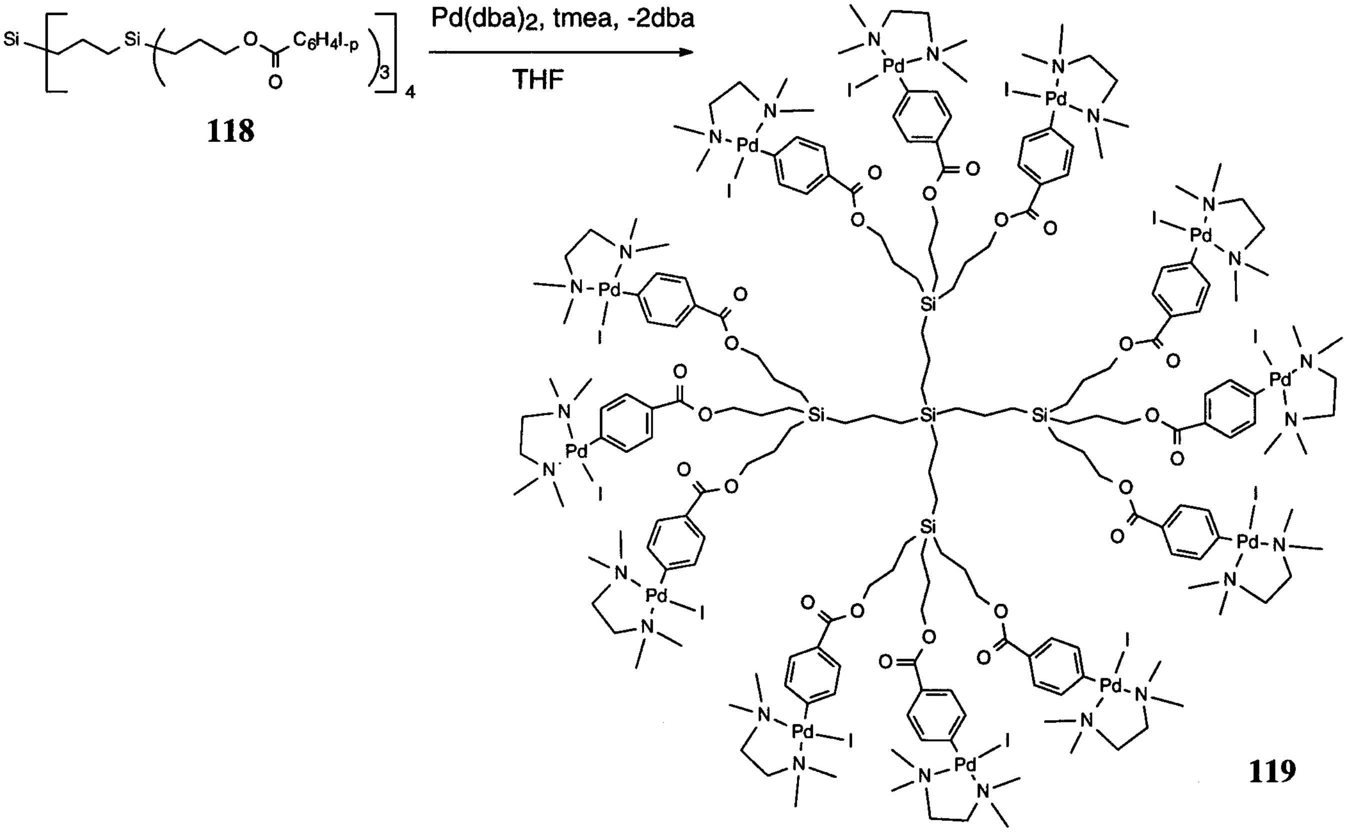
Engel et al.[152] reported a metallodendrimer with gold chloride attached to a trivalent phosphine core (Scheme 22). Oxidation of tris(*p*-methoxymethyl)-phenylphosphine[153] (**110**) (H_2O_2/acetic acid) gave the corresponding phosphine oxide **111**, which was treated with trimethylsilyl iodide (TMSI) in MeCN, followed by **110**, to afford the first-generation phosphonium dendrimer **112**; repetition afforded *P*-oxide **113**, which was then reduced by Cl_3SiH to afford the trivalent *P*-containing dendrimer **114**. The treatment of **114** with $NaAuCl_4$ gave the corresponding Au-containing macromolecule **115**.

V. Metals as Termination Groups (Surface Functionalization)

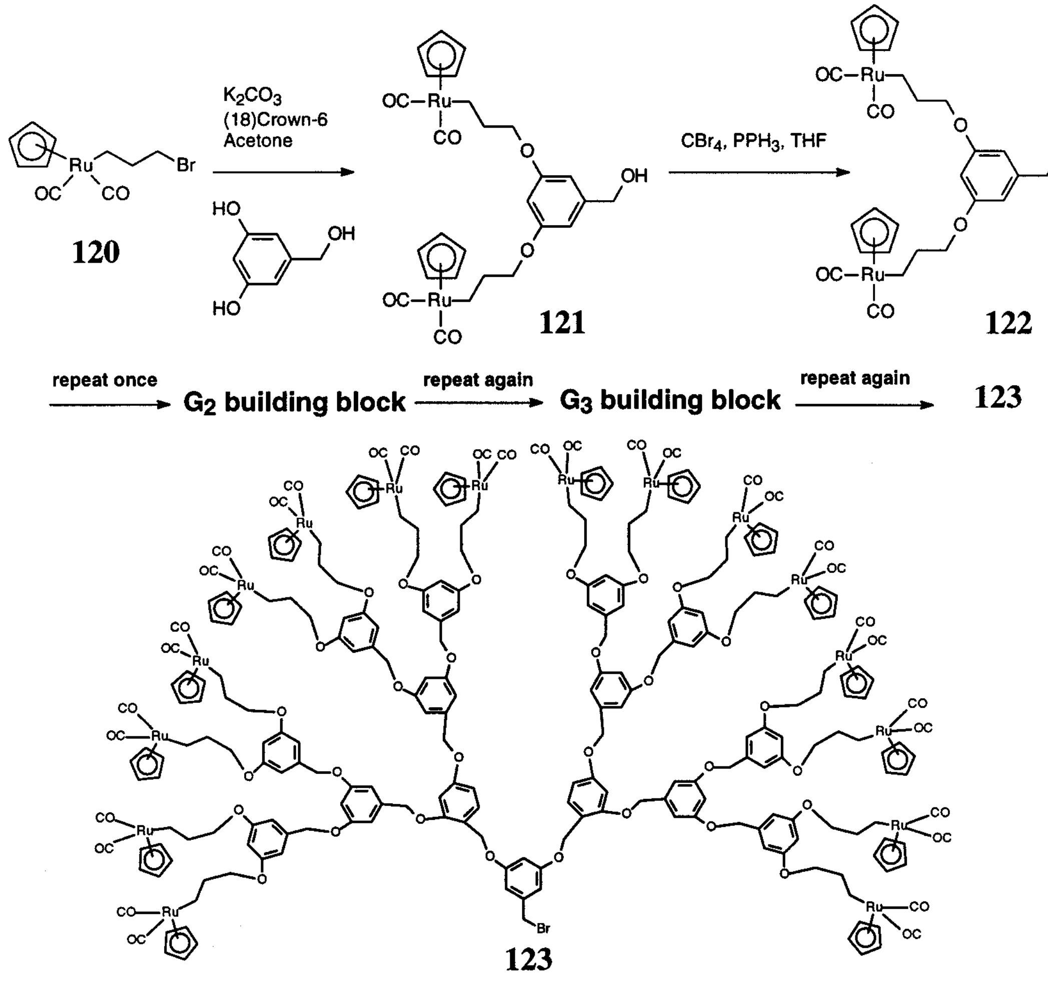
van Koten et al.[16] developed novel Ni-containing metallodendrimers up to the second generation to serve as homogeneous catalysts for the Kharasch addition[154] of polyhalogenoalkanes to simple C=C double bonds (Scheme 23). Dodecaarylbromide **116** was functionalized at the periphery via oxidative addition with $Ni(PPh_3)_4$ to afford the second-generation metallodendrimer **117**. Catalytic activity of both the first- and second-tier poly-Ni dendrimers displayed comparable kinetic data to that observed for the monomeric organometallic complex. A notable advantage of these metallodendritic catalysts is their facile removal from the reaction mixture, providing a recyclable property to the "dendrocatalyst." The authors also reported the attachment of similar nickel complexes to the polysiloxane polymers,[155] silica surfaces,[156] and amino acid-based dendritic macromolecules.[157]

van Koten et al.[158] prepared a small metallodendrimer possessing 12 peripheral palladium metal centers (Scheme 24) attached to a silicon-based framework; useful synthetic procedures to the incorporation of lithiated-surface derivatives have appeared.[159] Dodecaaryliodo-terminated dendrimer **118** was treated with palladium dibenzylideneacetone $[Pd(dba)_2]$ and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) to yield metallodendrimer **119**. This is the first example of Pd metals σ-bonded to a dendritic scaffolding.

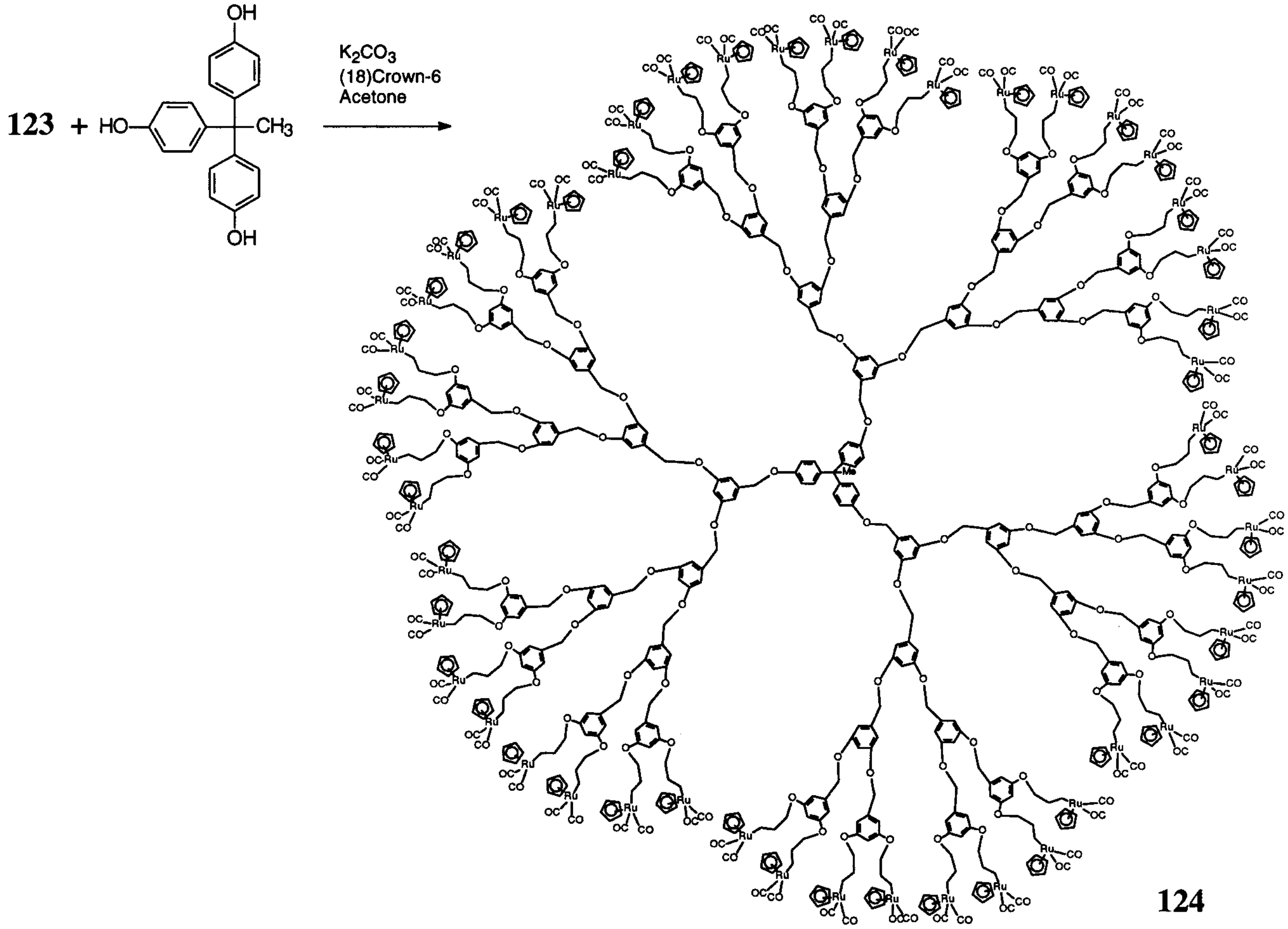
Scheme 24. Metallomacromolecule with Pd σ-Bonded to the Surface



Scheme 25. Convergent Construction of Building Blocks Possessing 16 Ru Metal Centers on the Periphery

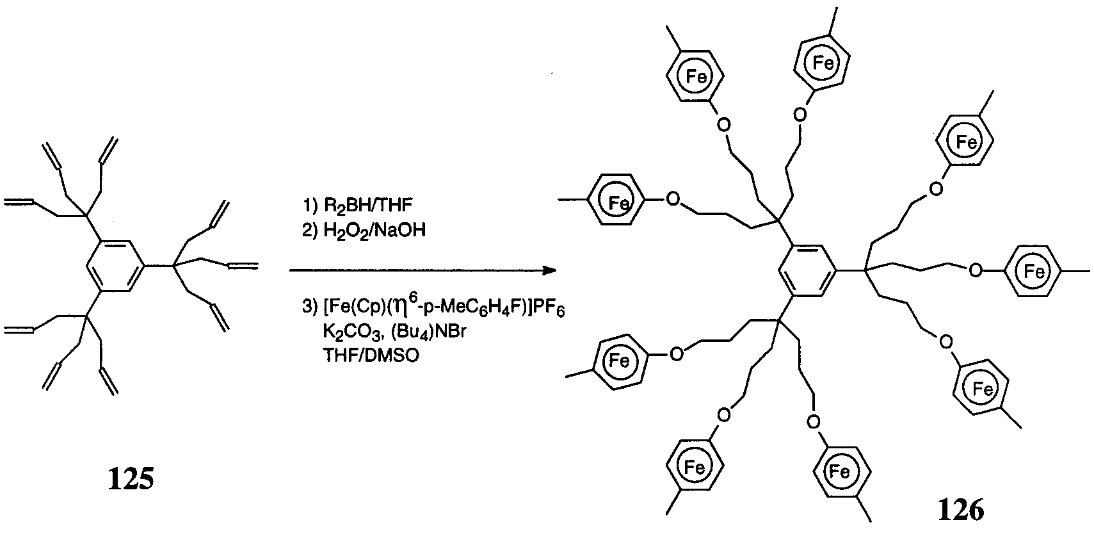


Scheme 26. Liao and Moss's Ru-Capped Metallodendrimer



124

Scheme 27. Astruc's Branched Iron Sandwich



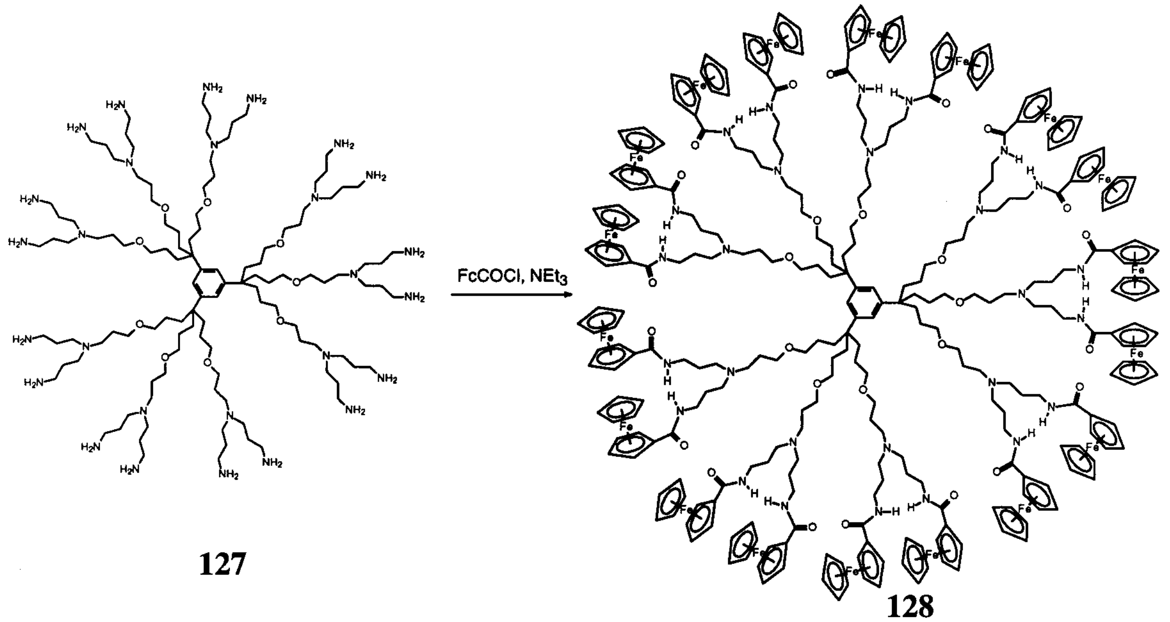
125

126

Liao and Moss[160] prepared metallodendrimers up to the fourth generation[161,162] containing 48 peripheral ruthenium metals on a dendritic framework that were constructed by Fréchet's convergent synthetic method.[27] Preparation of the first-generation metallodendritic building blocks **121** and **122** began via the reaction of (η^5-C_5H_5)Ru(CO_2)[(CH_2)$_3$Br] (**120**) and 3,5-dihydroxybenzyl alcohol (Scheme 25). Transformation of the focal hydroxyl moiety to the corresponding bromide permitted iterative access to produce the fourth-generation wedge **123** with 16 ruthenium metal centers. Three equivalents of each generation dendron were assembled via the nucleophilic substitution reaction with 1,1,1-tris(4′-hydroxyphenyl)ethane to afford the corresponding larger metallodendrimers (e.g., **124**; Scheme 26), whose characterization included standard spectroscopic methods and elemental analysis as well as thermal properties, such as glass transition temperatures (T_g).

Astruc and co-workers[163,164] developed a strategy for the construction of metallodendrimers possessing

Scheme 28. Amidoferrocene-Terminated Dendrimer with 18 Metals on the Surface

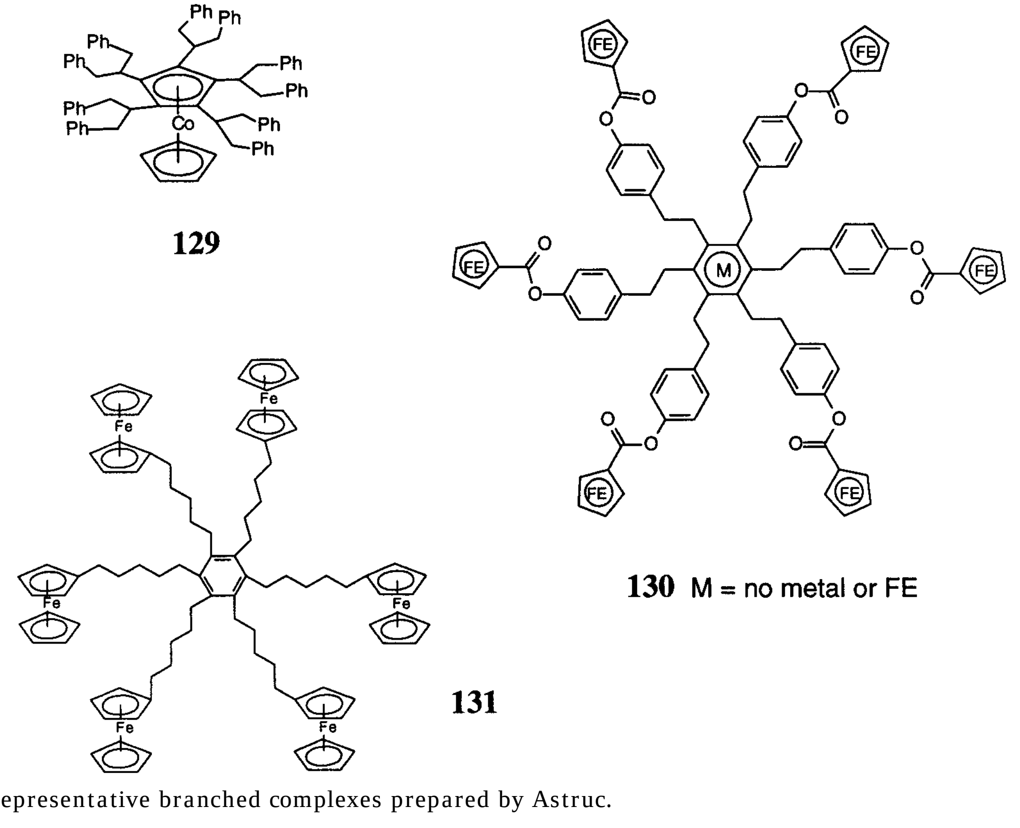


127

128

iron sandwich complexes on the periphery (Scheme 27). Nonaene **125** (prepared via exhaustive addition of allyl bromide to an iron-activated mesitylene complex) was hydroborated, oxidized with H_2O_2, and treated with $[FeCp(\eta^6\text{-}p\text{-}MeC_6H_4F)]PF_6$ to give the metallodendrimer **126**. More recently, Astruc et al.[165] synthesized amido–ferrocene dendrimers with up to 18 ferrocenes on the surface (Scheme 28). The amino dendrimer **127** was treated with FcCOCl (Fc = ferrocenyl) and triethylamine to give 18-ferrocenyl-containing metallodendrimer **128**. Similarly, 36- and 72-amine-terminated dendrimers were converted to metallodendrimers that were found to be insoluble in all solvents used. It was speculated that for these constructs, peripheral steric hindrance reaches a limiting, *dense-packed* point between the 18- and 36-ferrocenyl metallodendrimers. $\Delta E°$ values were found to increase with each generation, and all the Fe^{II}/Fe^{III} redox centers behaved independently. These authors also reported several syntheses of other branched macromolecules, such as **129**,[166] **130**,[167] and **131**[168] (Figure 16). Chiral ferrocenyl *P,P* or *P,L* ligands bound to the dendrimer's surface have also been prepared.[169]

Moors and Vögtle[170] prepared hexaamine dendron **132** that was treated with 2-hydroxybenzaldehyde to



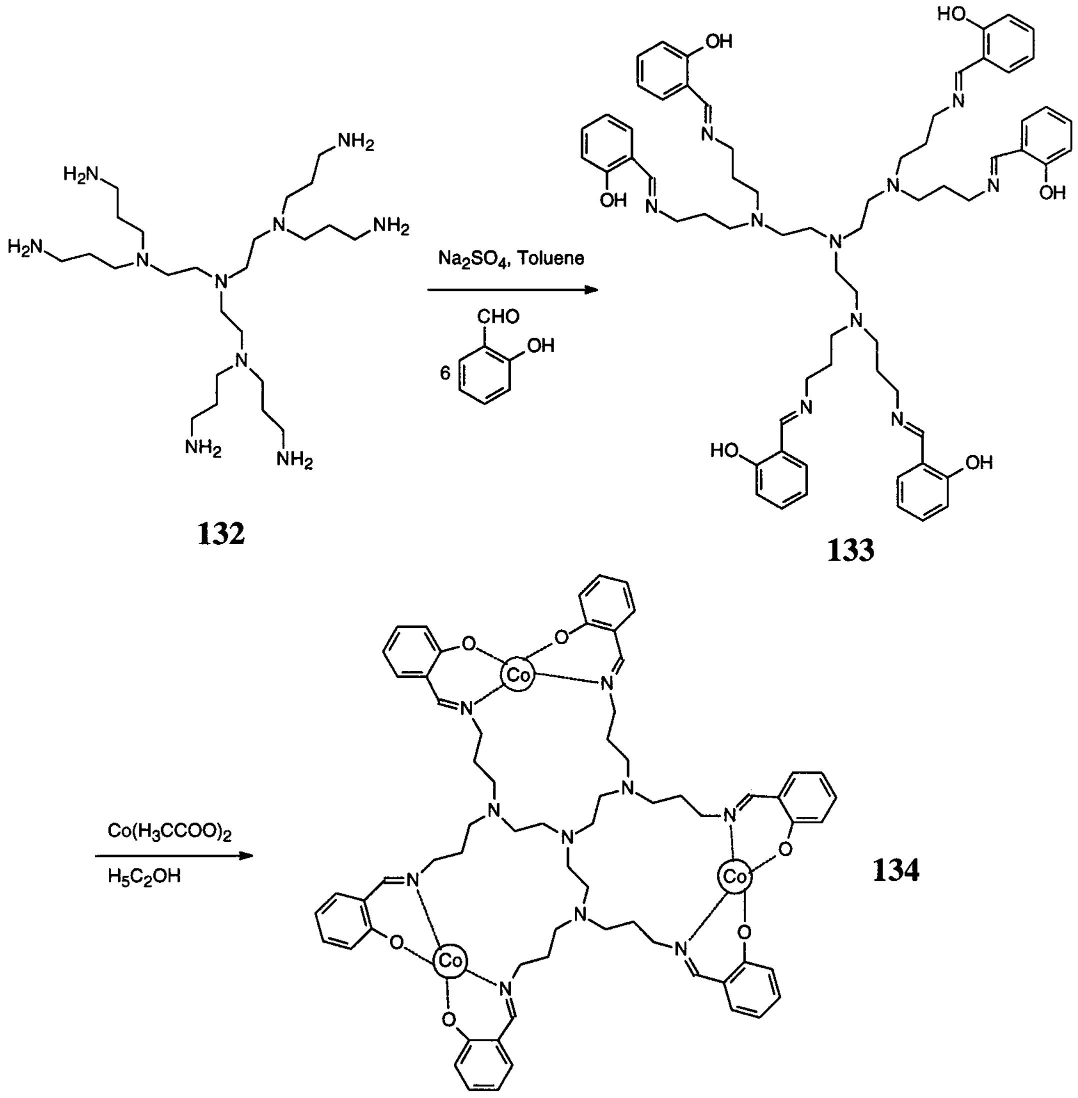
129

130 M = no metal or FE

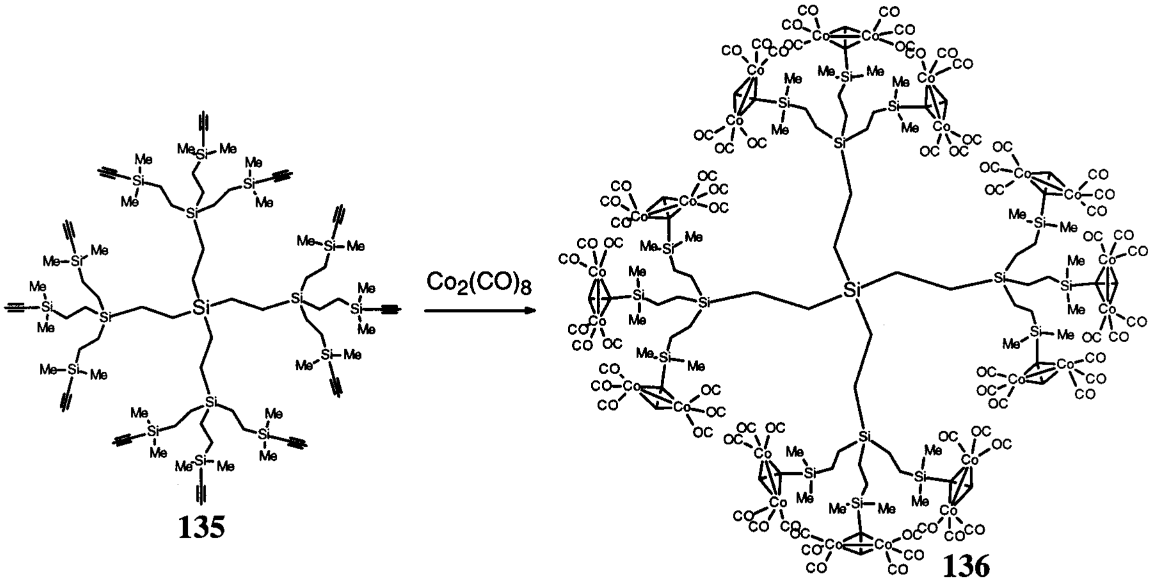
131

Figure 16. Representative branched complexes prepared by Astruc.

Scheme 29. Moor's and Vögtle's Polycobalt Complex

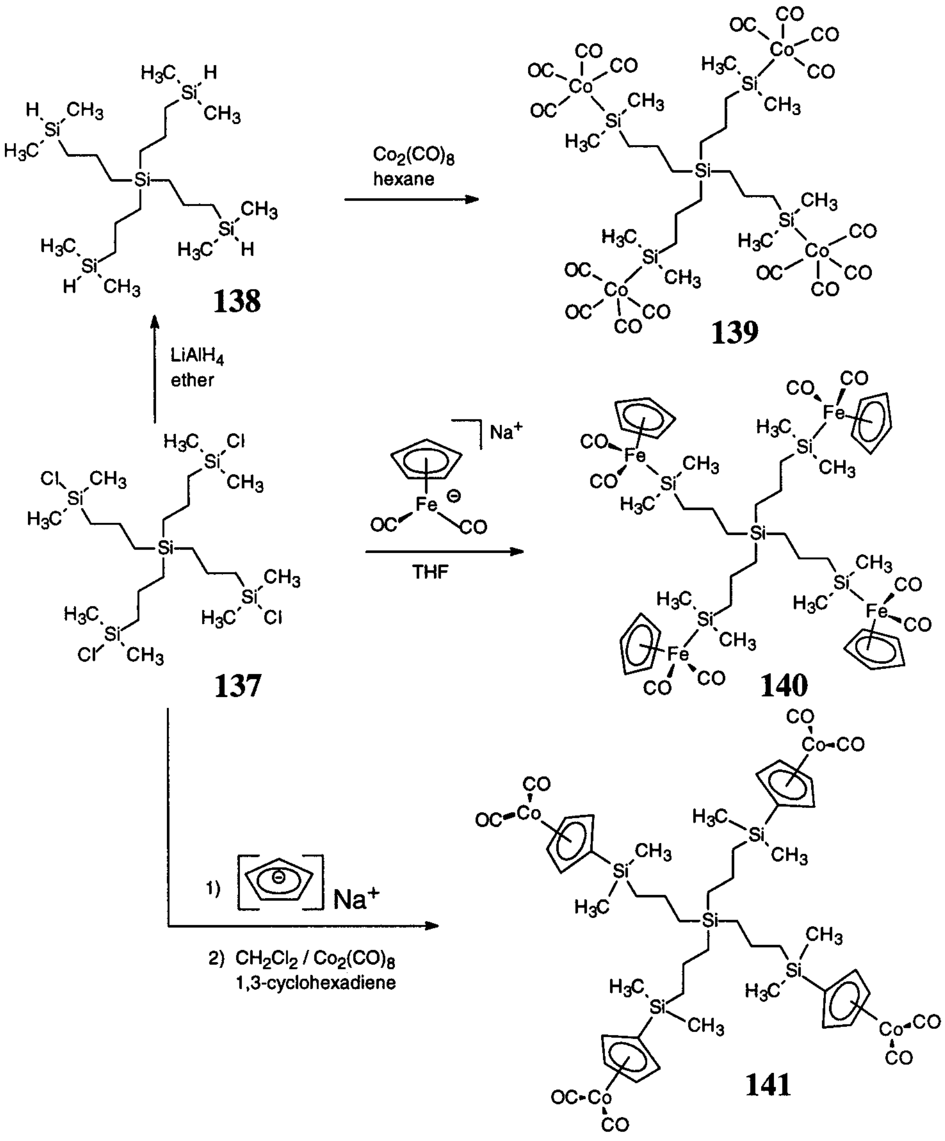


Scheme 30. Seyferth's Co-Capped Dendrimers Prepared from Alkyne-Terminated Carbosilanes



give the corresponding hexaimine **133** (Scheme 29). Reaction of hexaimine **133** with Co(II) acetate afforded the tricobalt complex **134** in quantitative yield. Seyferth et al.[171] also reported Co-capped metallodendrimers up to second generation (**136**). Formation of the terminal bisCo complexes was effected via treatment of the alkyne moieties on the carbosilane dendrimer **135** with $Co_2(CO)_8$ (Scheme 30).

Scheme 31. Silane-Based Branched Molecules Used for "Scaffolding" of Ferrocenyl Units



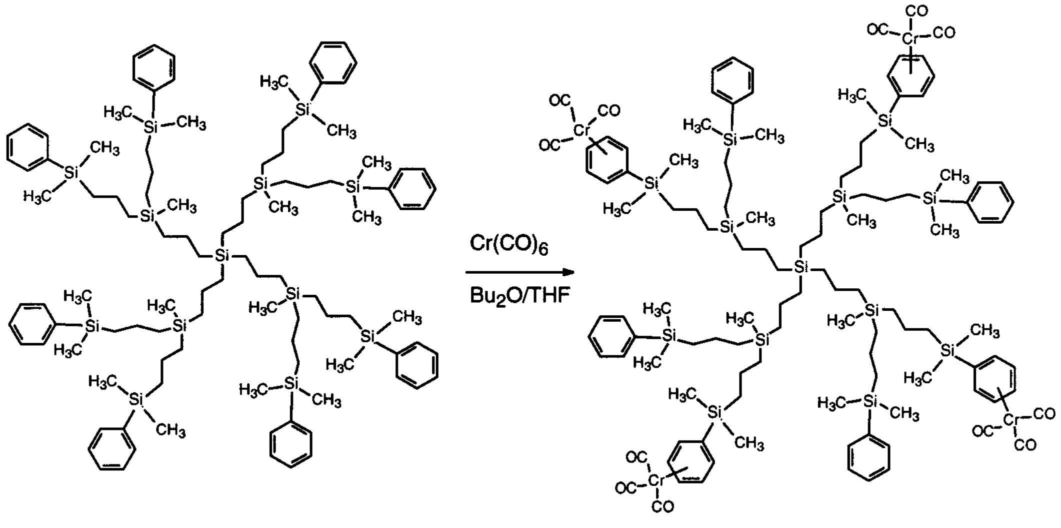
Morán et al. made numerous contributions to the literature via preparation of Co-, Cr-, and ferrocene-containing metallodendrimers, as well as hyperbranched[172] polymers. Cuadrado, Morán, and coworkers[173] functionalized the surface of carbosilane dendrimers with cobalt or iron–cobalt mixed complexes (Scheme 31). Tetrachlorosilane core **137** was treated with $Na[\eta^5\text{-}C_5H_5Fe(CO)_2]$ to give the small Fe-containing dendrimer **140**, whereas treatment with sodium cyclopentadienide, followed by $Co_2(CO)_8$, gave the cobaltocene-terminated construct **141**. Reduction of the Si–Cl moieties on core **137** afforded carbosilane **138** that was further treated with $Co_2(CO)_8$ to generate the Co-terminated dendrimer **139**. These unique materials could provide new possibilities in catalysis, multielectron redox, and photochemical processes.

Morán et al.[174,175] modified the termini of phenylsilane dendrimers with chromium carbonyl complexes (Scheme 32). The zero-generation phenylsilane dendrimer (not shown) was treated with excess $Cr(CO)_6$ to afford the tetra-$Cr(CO)_3$ complex, whereas the first-generation, octaphenyl construct **142** afforded only partially metalated metallodendrimers (e.g., **143**). The *Si*-based infrastructures were prepared via Pt-mediated hydrosilylation of the tetraallylsilane core using $HSiMe_3$, followed by treatment with allylmagnesium bromide, to give the desired polyalkene.

Employing similar *Si*-based architectures, the Morán and Cuadrado research team[176] has created a series of ferrocenyl-terminated metallodendrimers (Scheme 33). The treatment of octachlorosilane **144** with $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2NH_2)$ or $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4Li)$ afforded the corresponding **145** and **146**, respectively. Electrochemical studies of the polyferrocenes revealed an eight-electron oxidation process, while the zero-generation analogue, possessing only four ferrocenyl units, showed a four-electron oxidation process; it was concluded that the ferrocenyl moieties were essentially *noninteracting* redox centers.

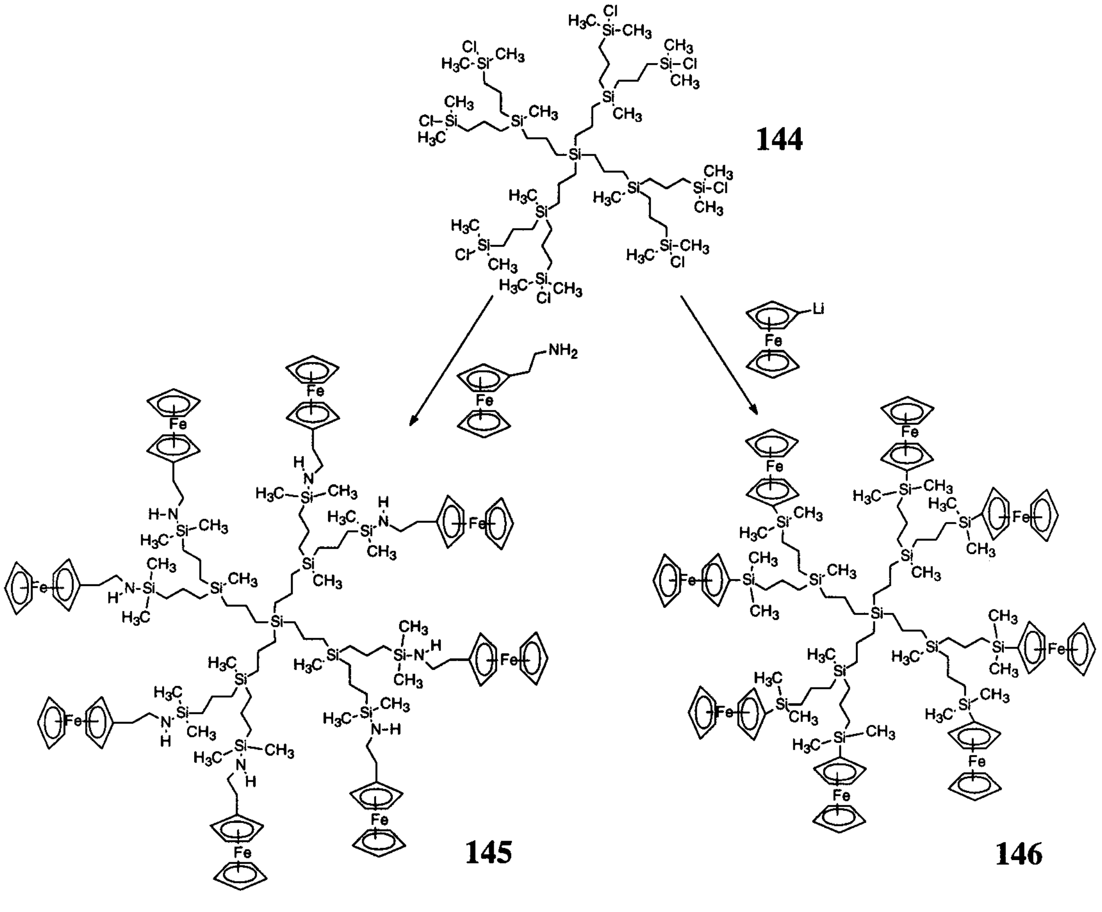
Reductive substitution of octachlorosilane **144** afforded hydrosilane **147**, which was subsequently

Scheme 32. Morán and Cuadrado's Cr-Containing Macromolecules



142 **143**

Scheme 33. Ferrocenyl-Terminated Complexes Built onto Functionalized Carbosilanes

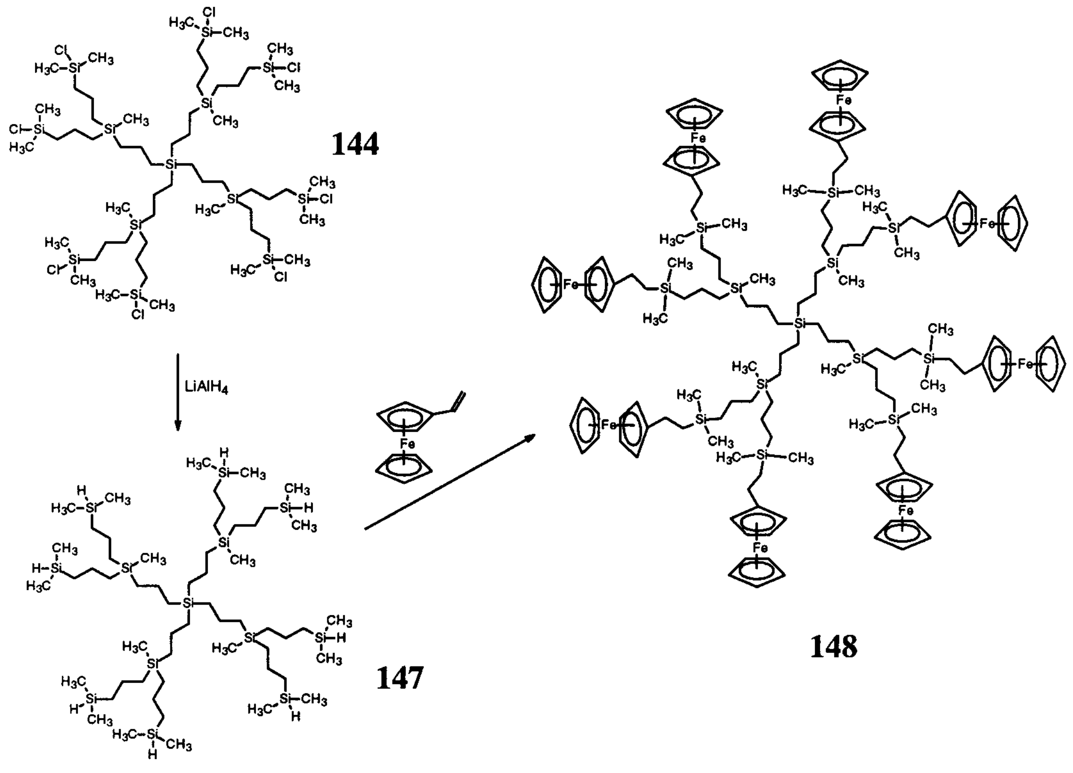


144

145 **146**

treated with (η^5-C_5H_5)Fe(η^5-$C_5H_4CH{=}CH_2$) in the presence of the Karstedt catalyst[177] to give metallodendrimer[178,179] **148** (Scheme 34). Losada et al.[180] reported the novel application of these metallodendrimers (e.g., **146** and **148**) as mediators in amperometric biosensors by modification of carbon paste electrodes via dendrimer incorporation. Electrochemical data suggest that ferrocene **148** possesses better mediating capabilities than ferrocene **146**. It was reasoned that chain length and spacing between ferrocenes play an important role in the ability to facilitate electron transfer from the reduced enzyme. A smaller energy barrier to bond rotation for longer, less rigid ferrocene connectors makes the interaction between the dendritic redox centers and enzyme surfaces more efficient.

Scheme 34. Cuadrado and Morán's Mediators for Amperometric Biosensors



Cuadrado et al.[92] observed the electronic interactions between the transition-metal centers for surface-functionalized metallodendrimers (e.g., **149**; Figure 17) that were synthesized via a convergent method.[181,182] The dendritic wedges as well as the corresponding metallodendrimers exhibit two well-separated and reversible oxidation waves of equal intensity in cyclic voltammetry experiments. This behavior is in agreement with that observed for two ferrocenyl units linked together by a bridging silicon atom.[183] It was postulated that the first oxidation occurs on nonadjacent ferrocene centers, making the adjacent ferrocenyl centers more difficult to oxidize. Thus, there is an 'electronic communication' between the *Si*-bridged ferrocenyl centers. This result is in accord with that observed for some Ru-containing metallodendrimers.[91]

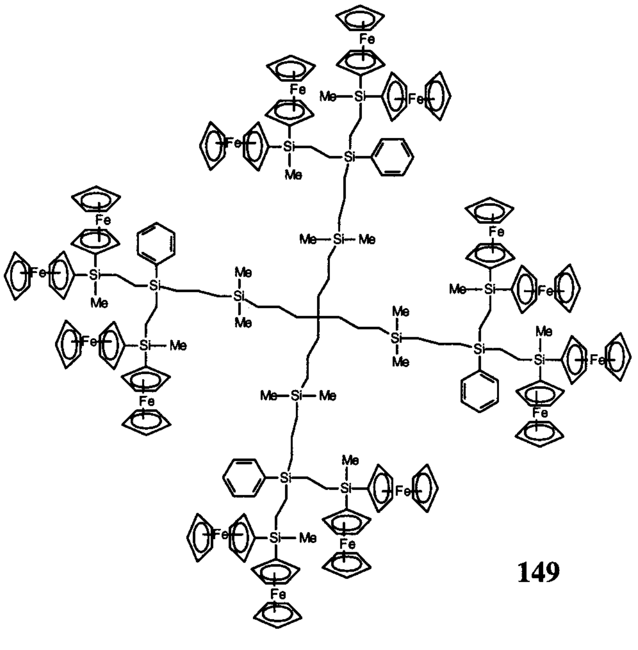
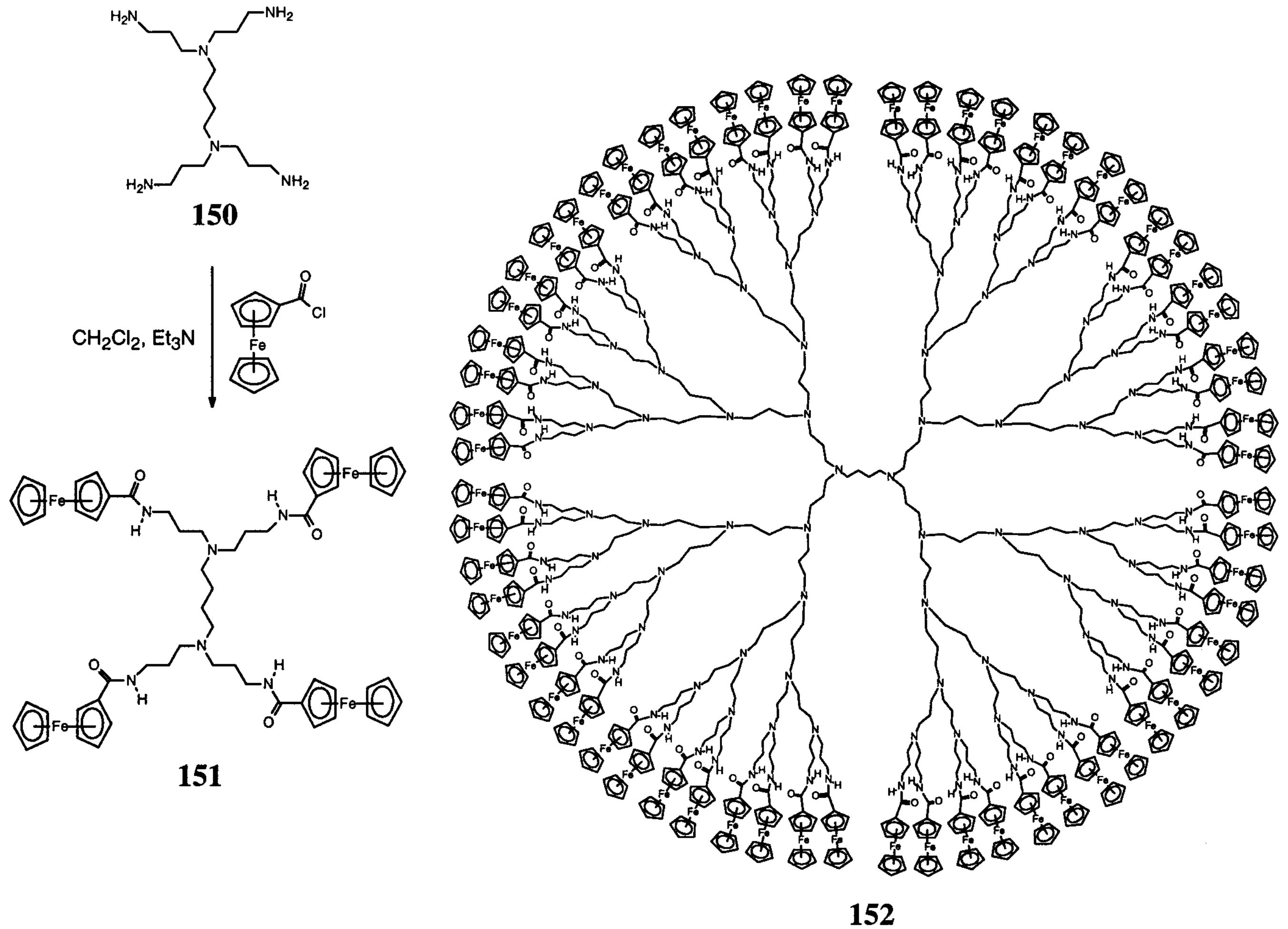


Figure 17. Cuadrado's ferrocenyl complexes exhibiting electronic interaction between bridged transition-metal centers.

Cuadrado, Morán, and co-workers[184] reported new ferrocenylmetallodendrimers based on commercially available Astramol poly(propyleneimine) dendrimer frameworks (Scheme 35). Construction of the series through the fifth generation relied on treatment of the requisite polyamine (e.g., **150**) with (η^5-C_5H_5)Fe(η^5-C_5H_4COCl) to afford the corresponding polyferrocene (e.g., **151** and **152**). Each member of the series exhibits a single, reversible oxidation process, suggesting all of the metal centers in a single molecule are electrochemically equivalent. These redox-active cascades have been investigated to determine their thermodynamics and kinetics of adsorption on a platinum electrode surface by Abruña et al.[185] Rate constants for the kinetics of absorption were observed to be largely dependent on generation and less dependent on the concentration.

Similar metallodendrimers, up to the third generation, have been used to form large supramolecular polycomplexes via coordination of cyclodextrin moieties on ferrocenium termini by Kaifer et al.[186] A later report by Kaifer, Morán, Cuadrado, and co-workers[187] described the terminal functionalization of the Astramol dendrimers, through generation four, to yield a series of polycobaltocene macromolecules (e.g., **153**; Figure 18). β-Cyclodextrin derivatives were shown to facilitate aqueous solubilization of the reduced [Cp_2-

Scheme 35. Cuadrado and Morán's Metallodendrimer Possessing 64 Amide-Linked Ferrocenyl Metal Centers on the Surface



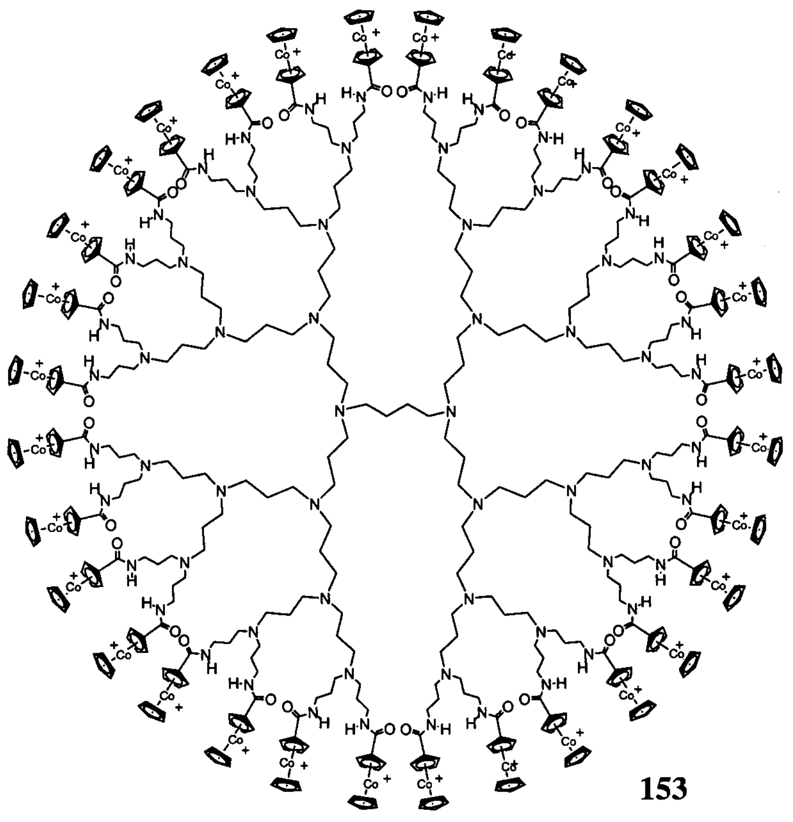
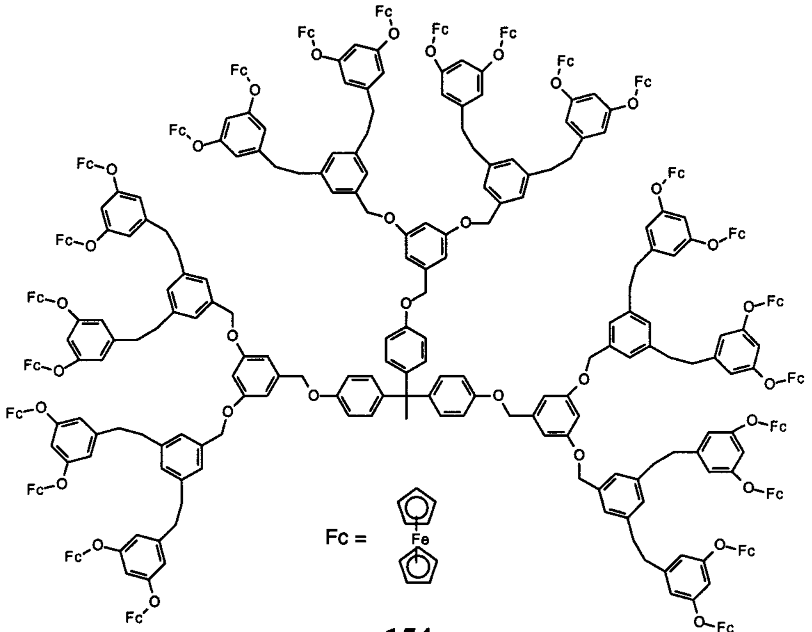

153

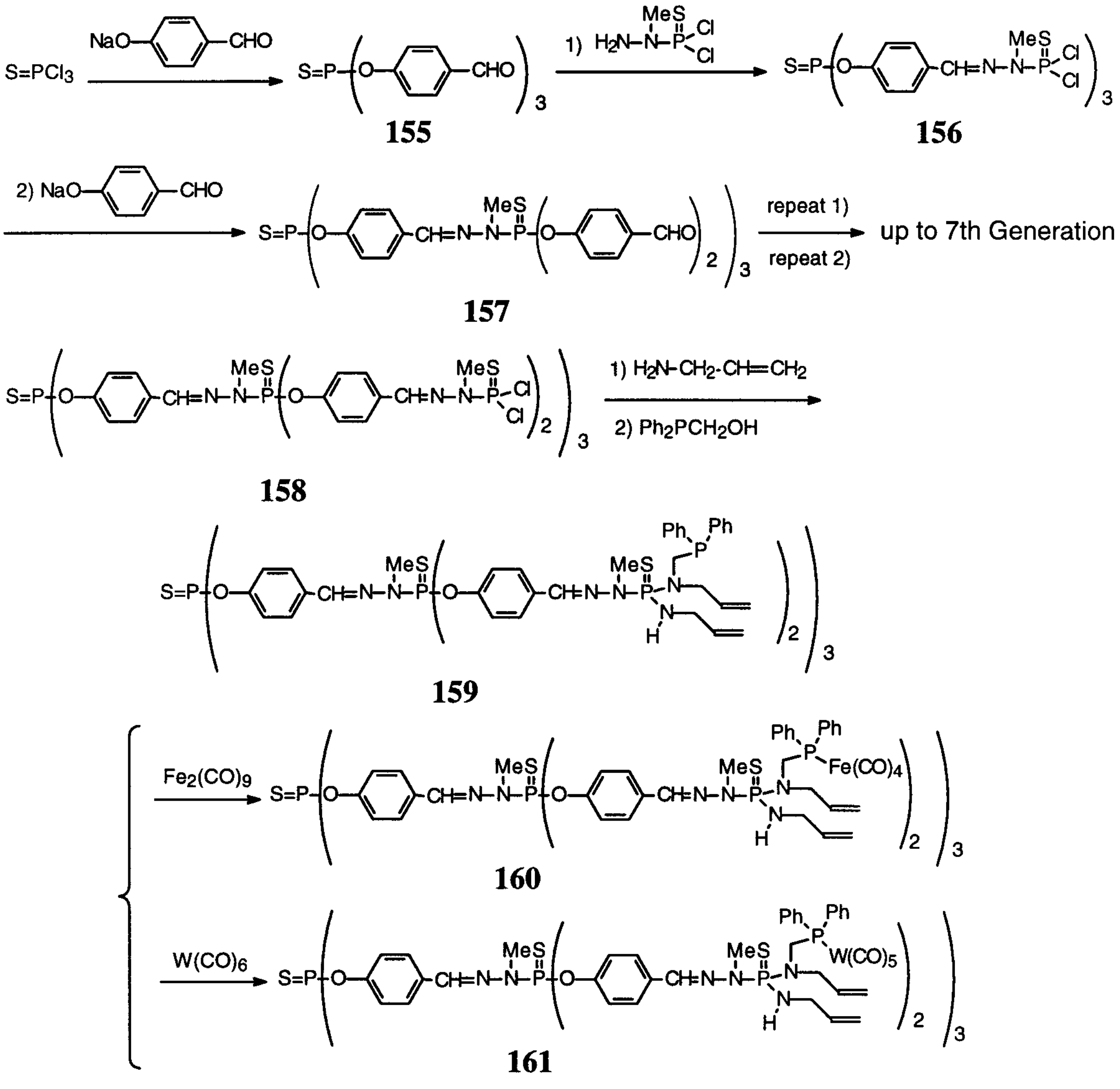
Figure 18. Polycobaltocene dendrimer that has been shown to coordinate β-cyclodextrin.

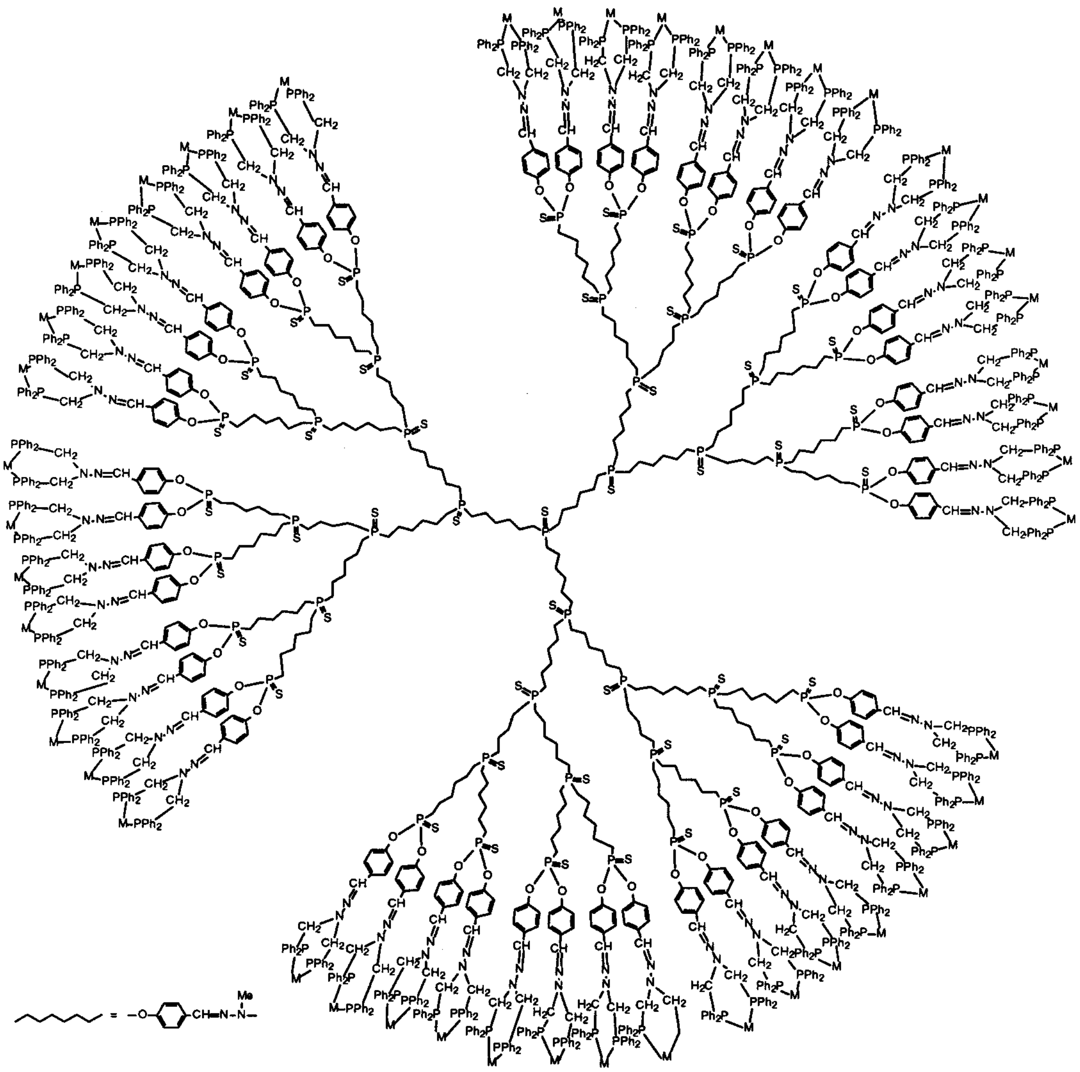


154

Figure 19. Ferrocene-terminated, Frechet-type dendrimer prepared by Shu and Shen.

Scheme 36. Construction of Phosphorus-Containing Metallodendrimers and Surface Functionalization with W and Fe Metal Complexes





162 M = no metal
163 M = PtR_2
164 M = PdR_2
165 M = RhR_2

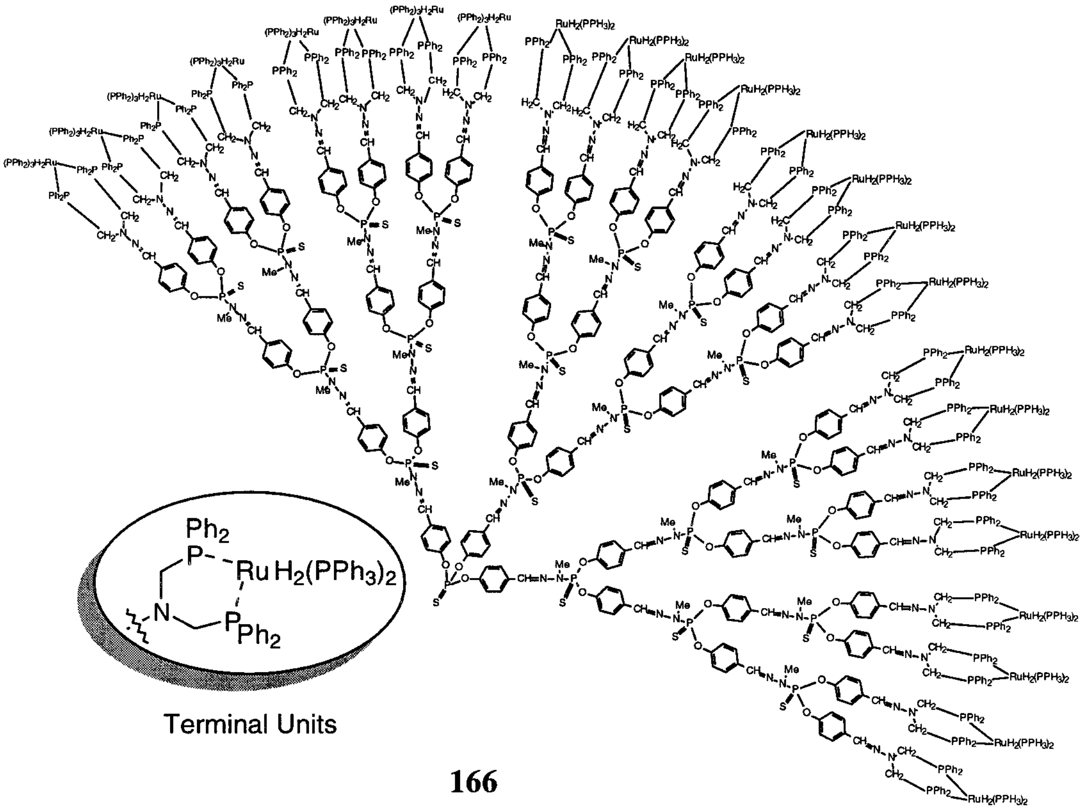
Figure 20. Highly branched macromolecules possessing Pt, Pd, and Rh metal complexes.

Co(0)] form via termini encapsulation; an overview of the molecular recognition and redox chemistry has recently appeared.[188]

Shu and Shen[189] reported the preparation of ferrocene-coated metallodendrimers up to the third generation (e.g., **154**) based on a convergent approach[27] (Figure 19). The peripheral metal centers were shown to be electrochemically equivalent, which is consistent with other examples of ferrocene-containing metallodendrimers.

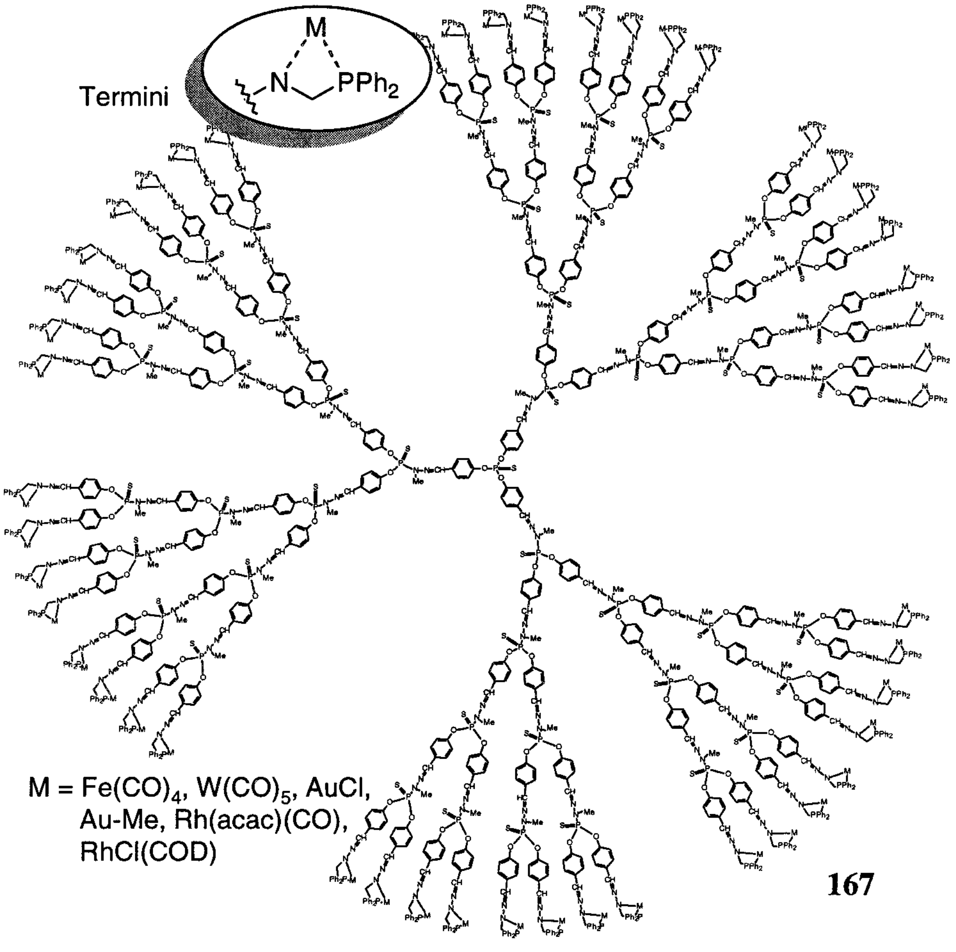
Majoral et al.[45] synthesized a variety of *P*-based macromolecules (e.g., phosphate-, phosphite-, ylide-, and phosphonate-terminated;[190] amino acid-terminated;[191] bowl-shaped dendrimers[192] and others[193]).[194] These authors functionalized their macromolecular cascades with numerous transition metals, such as iron and tungsten[195] (Scheme 36). The divergent approach to their high-generation, P-branched dendrimers relies on a two-step procedure for tier construction. Beginning with the trifunctional core $P(S)Cl_3$, trialdehyde **155** was prepared via chloride displacement by reaction with $NaOC_6H_4CHO$. Subsequent condensation of the aldehyde moieties with $H_2NN(CH_3)P(S)Cl_2$ generated the polyimine **156**, which could then be treated with additional $NaOC_6H_4$-CHO monomer to yield the hexaaldehyde **157**. Purification of these dendritic structures is facilitated by only having to remove the trivial byproducts of NaCl and H_2O. The entire series of $-P(S)Cl_2$-terminated dendrimers (e.g., **158**) was treated with H_2NCH_2-$CH{=}CH_2$ followed by Ph_2PCH_2OH to generate the phosphino−alkene-terminated cascades (e.g., **159**). Polyalkene **159** was then converted to the hexaFe-$(CO)_3$ complex **160** or the hexa$W(CO)_3$ **161** by treatment with $Fe_2(CO)_9$ or $W(CO)_5$, respectively.

Caminade, Majoral, Chaudret, and co-workers[196] also functionalized the surface of their P-branched dendrimers with platinum, palladium, and rhodium transition metals (Figure 20). Polycomplexes **163**, **164**, and **165** were prepared by treatment of the



166

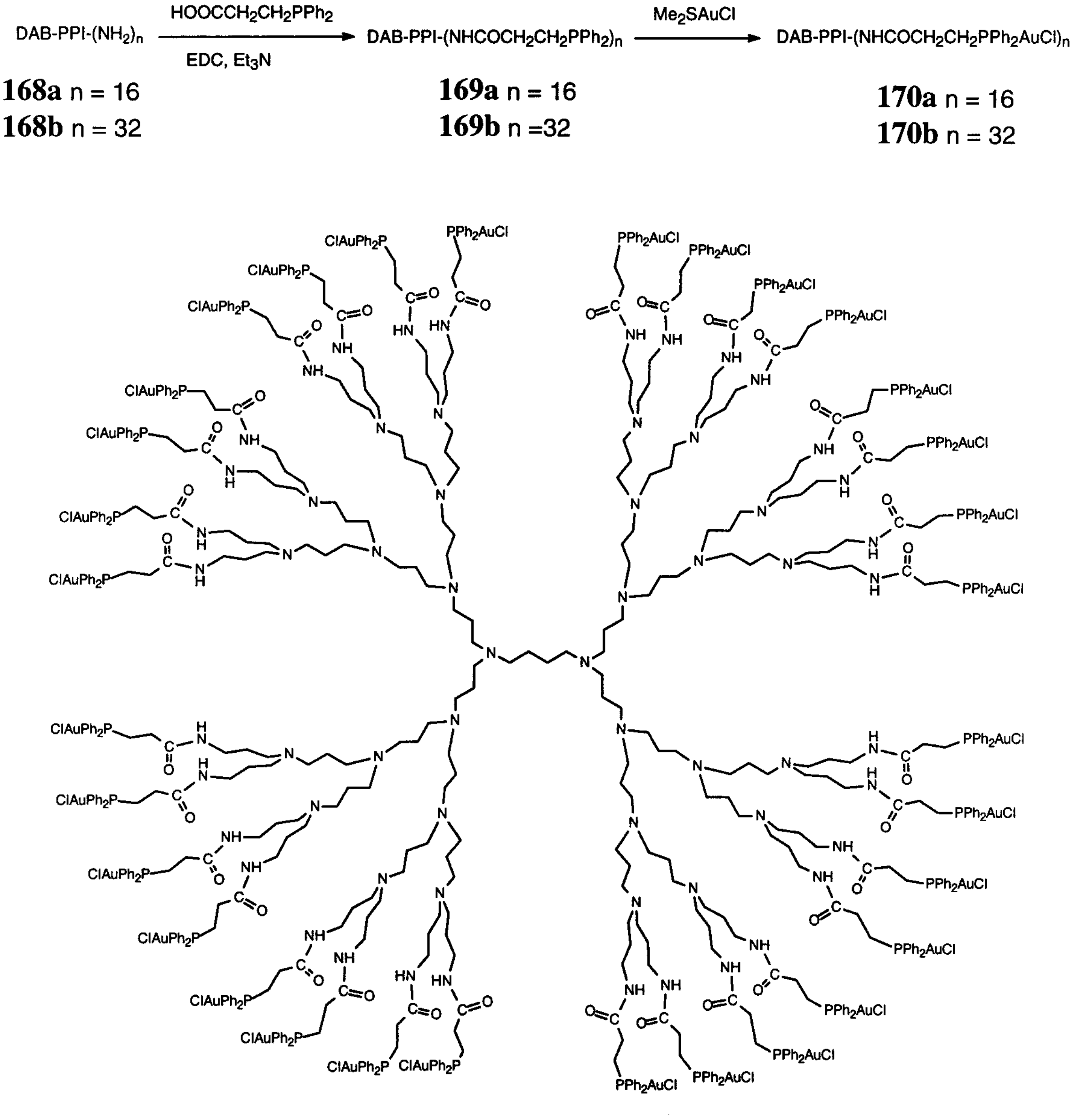
Figure 21. Surface modification with Ru complexes.



167

Figure 22. Surface functionalization with Fe, W, Au, and Rh complexes.

Scheme 37. Schmidbaur's Gold-Surfaced Metallodendrimers



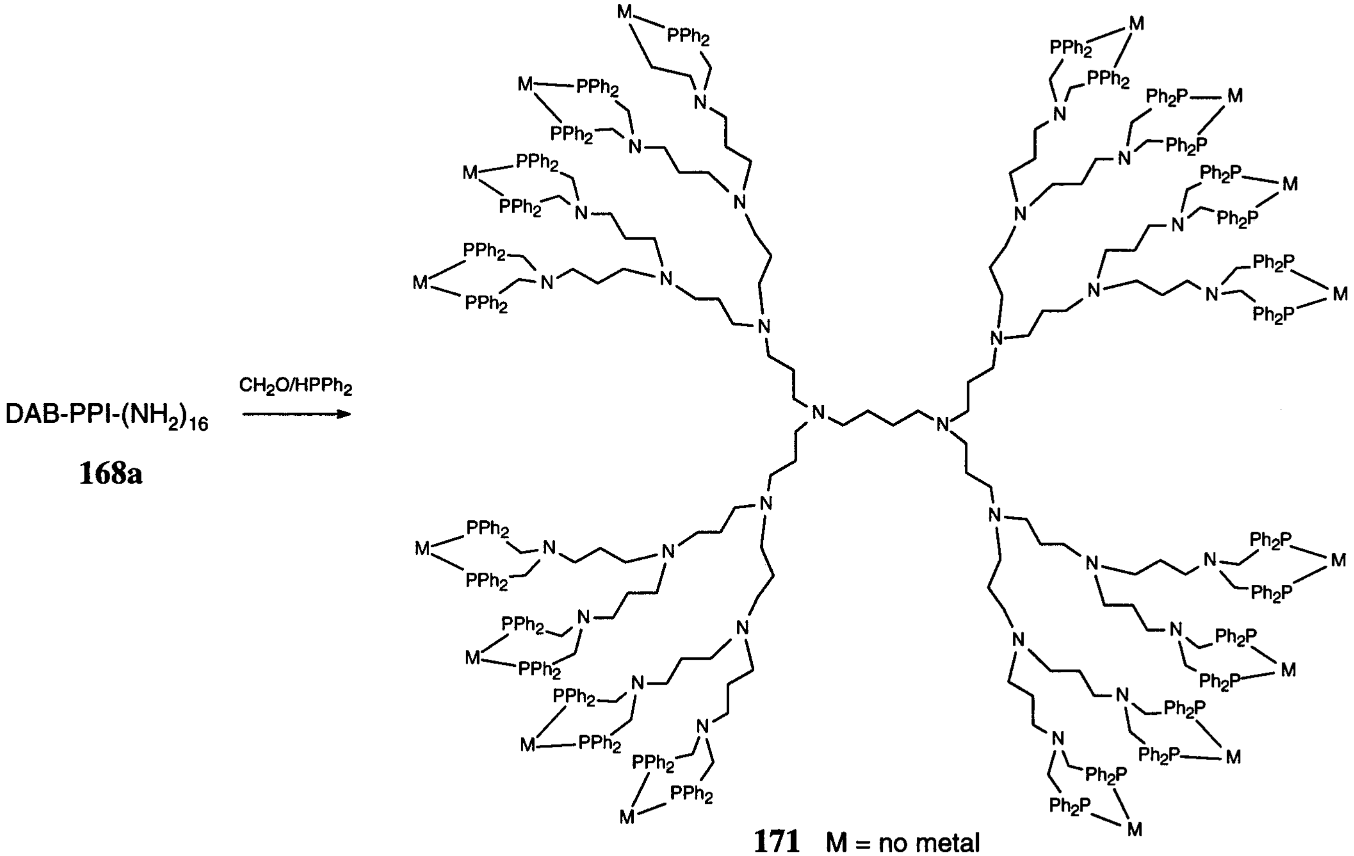
170b

diphenylphosphino-capped dendrimer **162** with requisite $PtX_2(COD)$, $PdX_2(COD)$, and Rh(acac)(COD) reagents, respectively. Majoral, Chaudret et al.[197] also modified the surface of the same *P*-dendrimers with ruthenium moieties (Figure 21). The metallodendrimer **166** was prepared by treatment of the third-generation *P*-dendrimer with $RuH_2(PPh_3)_4$. Notably, the new complexes exist as a mixture of different stereoisomers with the coordination ligands arranged differently in the space. The authors[198] widely applied the surface functionalization to a variety of metals (Figure 22). Metallodendrimers (e.g., **167**) possessing iron, tungsten, gold, and rhodium were realized for the fifth, fourth, tenth, and sixth generations, respectively.

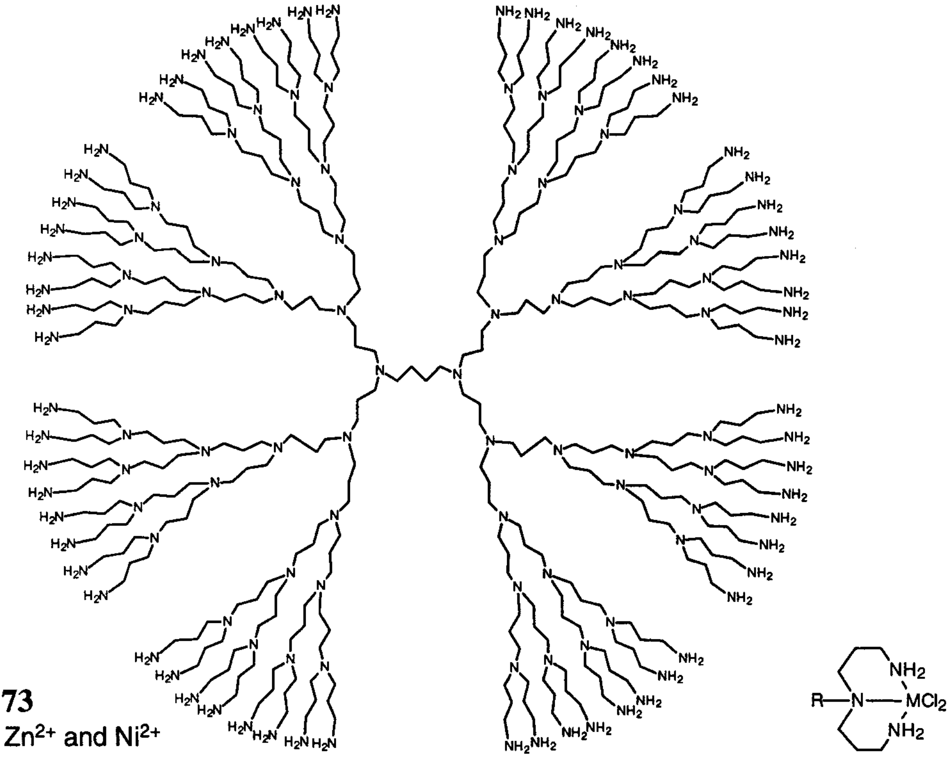
Schmidbaur and co-workers[199,200] reported Au-containing metallodendrimers based on amino-terminated cascades (Scheme 37). The third- and fourth-generation diaminobutane–poly(trimethyleneamine)s ($DAB-PPI-(NH_2)_n$, $n = 16$ or 32) **168a**,**b** were treated with *β*-(diphenylphosphino)propionic acid ($HOOCCH_2CH_2PPh_2$) to give the diphenylphosphino-terminated dendrimers **169a**,**b**, whose subsequent treatment with $(Me_2S)AuCl$ afforded the corresponding Au-substituted dendrimers **170a**,**b**.

Several other research groups also utilized the same diaminobutane–poly(trimethyleneamine) ($DAB-PPI-(NH_2)_n$) to functionalize the surface. Reetz et al.[201] started with the third-generation dendrimer **168a**, which was treated with Ph_2PCH_2OH to afford phosphino-terminated dendrimer **171** (Scheme 38), which was then converted to the related metallodendrimers **172a**–**e** by treatment with $[PdCl_2(PhCN)_2]$, $[Pd(CH_3)_2(tmeda)]$, $[Ir(cod)_2BF_4]$, $[Rh(cod)_2BF_4]$, and a 50:50 mixture of $[Pd(CH_3)_2(tmeda)]$ and $[Ni(CH_3)_2(tmeda)]$, respectively. The catalytic activity of **172a** was tested in the Heck reaction of bromobenzene and styrene for the formation of stilbene. The conversion

Scheme 38. Reetz's Pd, Ir, Rh, and Ni Complexes Based on DAB–PPI–$(NH_2)_n$

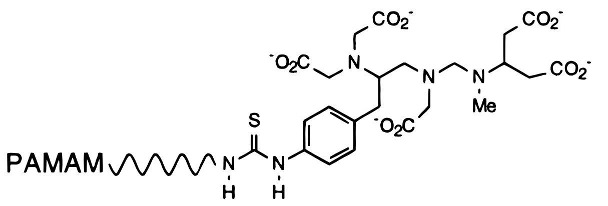


171 M = no metal
172a M = $Pd(Cl)_2$
172b M = $Pd(CH_3)_2$
172c M = $Ir(cod)_2$
172d M = $Rh(cod)_2$
172e M = $Pd(CH_3)_2$ and $Ni(CH_3)_2$



173
M = Cu^{2+}, Zn^{2+} and Ni^{2+}

Figure 23. Cu, Zn, and Ni complexes on amino-terminated dendrimer surface.



174 2th generation, 92% substituted, 11-12 sites Gd(III) complexed

175 6th generation, 88% subsituted, 170-192 sites Gd(III) complexed

Figure 24. Gd-coordinating PAMAM dendrimers used as MRI contrast agents.

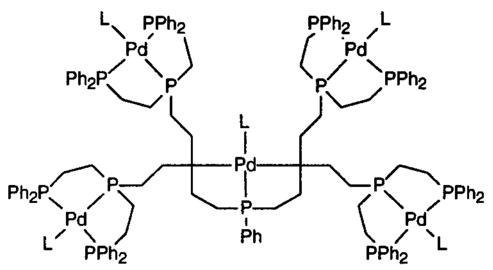
rate to stilbene was 89%, and 1,1-diphenylethylene (11%) was the byproduct. This macromolecular catalyst showed a significantly higher activity than the parent material [RN(CH_2PPh_2)$_2$Pd(CH_3)$_2$] possessing typical turnover numbers (TON) of 50 versus 16 for the mononuclear complex. When the *recycled* dendrimer catalyst **172a** was reused at a later time for the same reaction, it displayed comparable catalytic activity.

Meijer and co-workers[202] treated the same diaminobutane–poly(trimethyleneamine) dendrimers **173** (up to the fifth generation) with $NiCl_2$, $CuCl_2$, and $ZnCl_2$ (Figure 23). These complexes were studied by various spectroscopic methods, thereby aiding in structure conformation. For example, ^{1}H NMR studies with the Zn(II) complexes indicate that metal binding occurs exclusively at the surface via the terminal primary amines and the outermost tertiary amines. This, combined with the symmetry of the spectra during titration experiments, provides strong support for the purity of these materials. Also, extinction coefficients of the fully Cu(II)-complexed dendrimers increased linearly progressing from low to high generations.

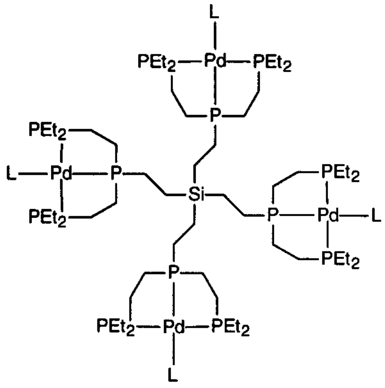
Wiener et al.[203] prepared PAMAM-based[9] Gd-coordinating metallodendrimers that were used as magnetic resonance imaging (MRI) contrast agents (Figure 24). Second- and sixth-generation PAMAM dendrimers were treated with diethylenetriaminepentaacetic acid followed by Gd(III) complexation to give partially complexed **174** and **175**, respectively. Their applications to medical imaging have recently been reviewed.[19]

DuBois et al.[204] reported Pd-containing metallomacromolecules (e.g., **176** and **177**; Figure 25) that catalyze the electrochemical reduction of CO_2 to CO. Beer et al.[205] constructed dodecaferrocene **178** for the study of multiple redox centers (Figure 26). Deschenaux et al.[206] prepared a "ferrocene-containing liquid-crystalline" dendrimer **179** (Figure 27) that was shown to exhibit a 'broad enantiotropic smectic A phase' along with suitable thermal properties. The mesogenic group was comprised of a cholesterol-substituted ferrocene that was anchored to a small aryl-based dendrimer.

A series of branched metal complexes of alkyne-bridged α-amino acids has been reported by Beck et al.[207] The series included mono- to hexaPt complexes using di-, tri-, tetra-, and hexaethynyl phenylalanines as ligating moieties. The small, rigid, phenylacetylene-supporting structures were constructed via Heck-type acetylene–aryl iodide coupling reactions. Similar ferrocenyl Schiff base complexes were also prepared along with their unbranched analogues. Representative examples (i.e., **180** and **181**) are shown in Figure 28.

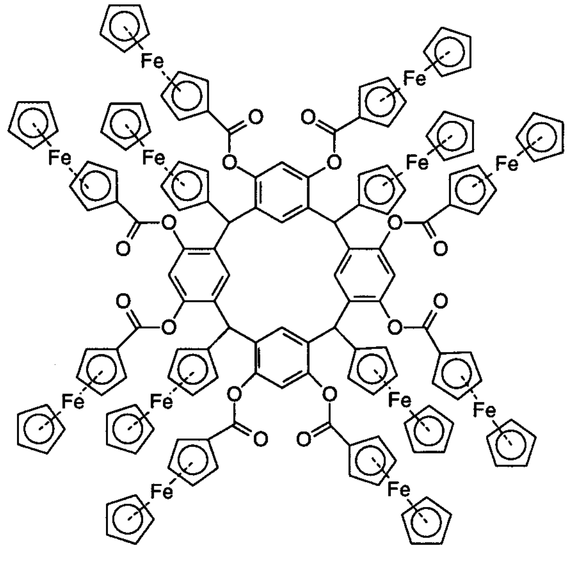


176
L = MeCN or PEt_3



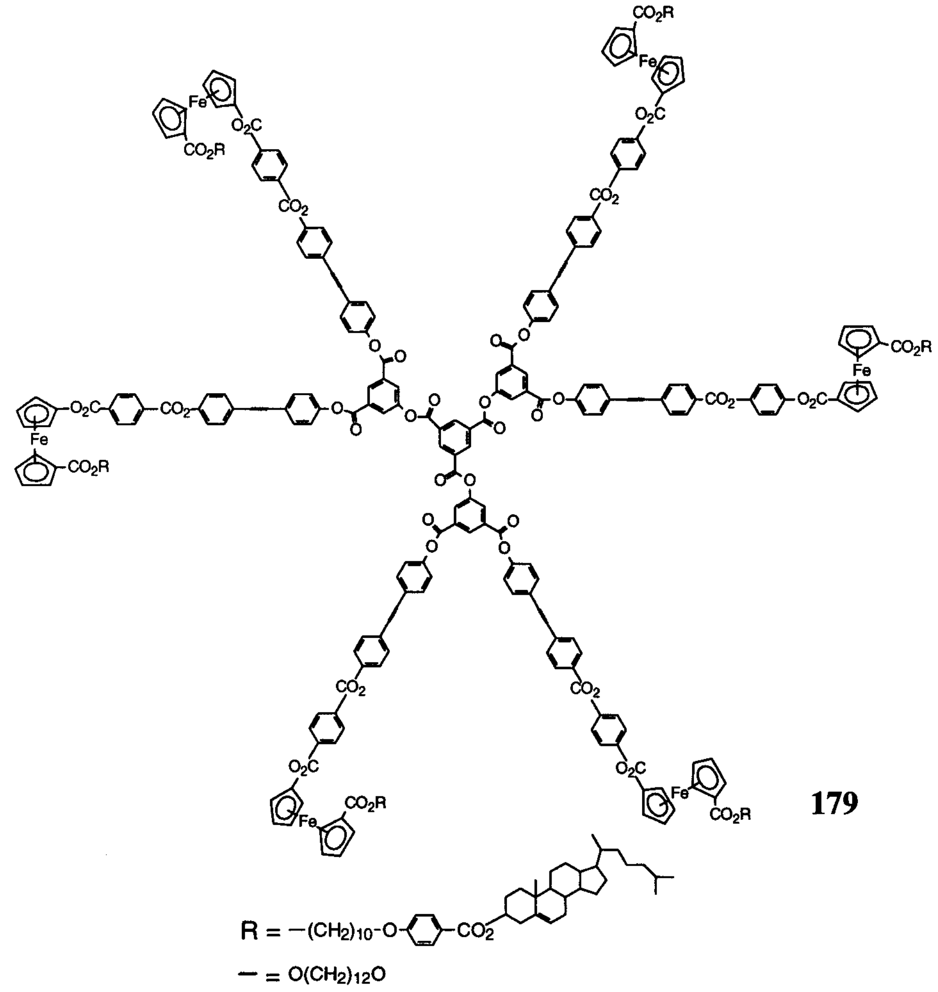
177
L = MeCN or PEt_3

Figure 25. DuBois's Pd complexes used as catalysts for electrochemical reduction of CO_2 to CO.



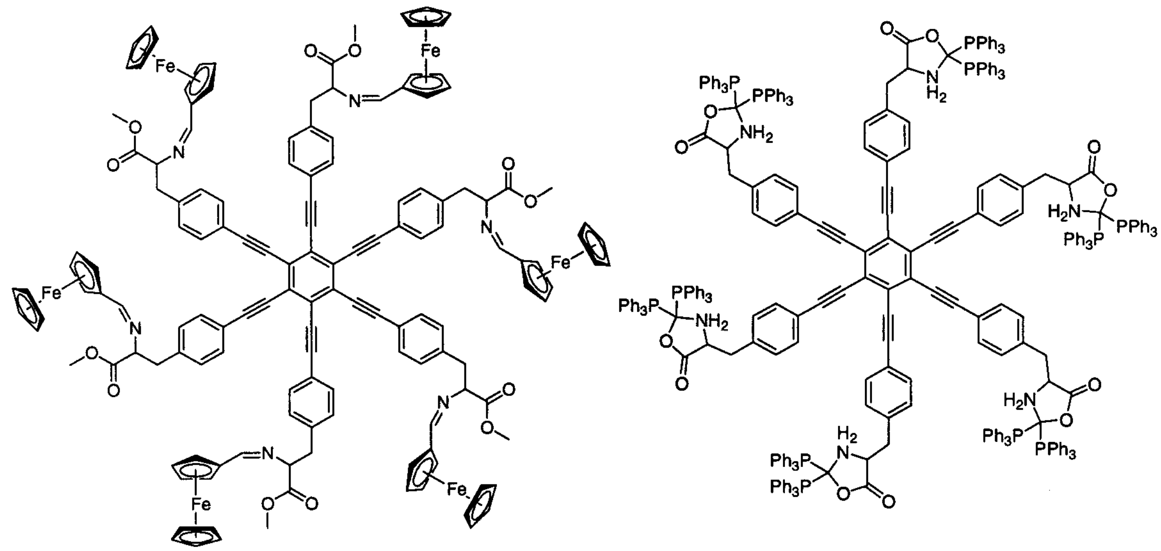
178

Figure 26. Beer's rigid dodecaferrocene.



179

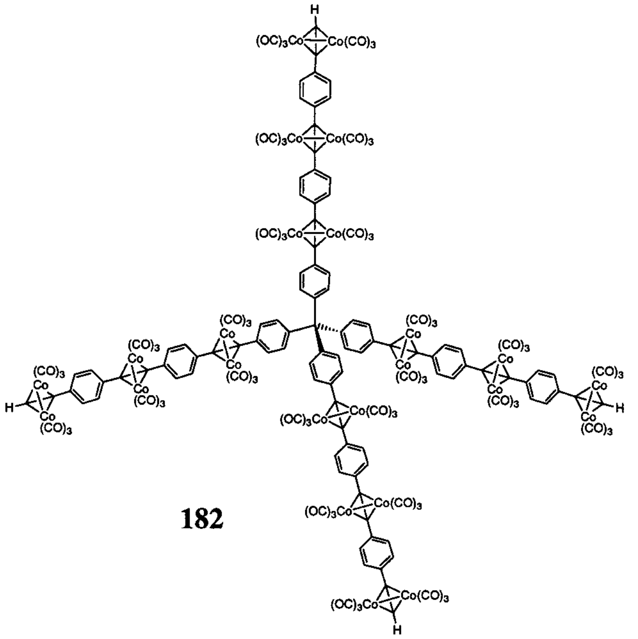
Figure 27. Deschenaux's ferrocene-containing, liquid-crystalline macromolecules.



180 **181**

Figure 28. Metalated, phenylacetylene-bridged amino acids.

Constable, Housecroft, and co-workers[208] reported the synthesis of a tetrahedral polyphenylacetylene using tetraphenylmethane as the core (Figure 29). Treatment of the acetylene moieties with dicobalt octacarbonyl (Co_2CO_8) afforded the corresponding dicobalt hexacarbonyl polycomplex **182**, which was pur-



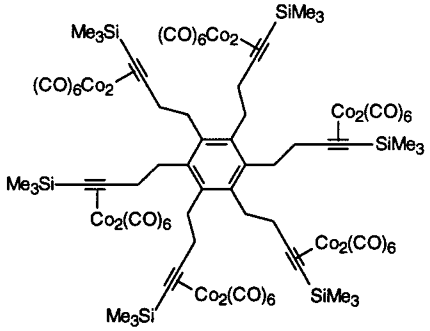
182

Figure 29. Tetrahedral array of phenylacetylenecobalt complexes.

sued as a potential precursor to the formation of metal oxide nanospheres possessing exact dimensions.

VI. Metals as Structural Auxiliaries

A. Site-Specific Inclusion



185

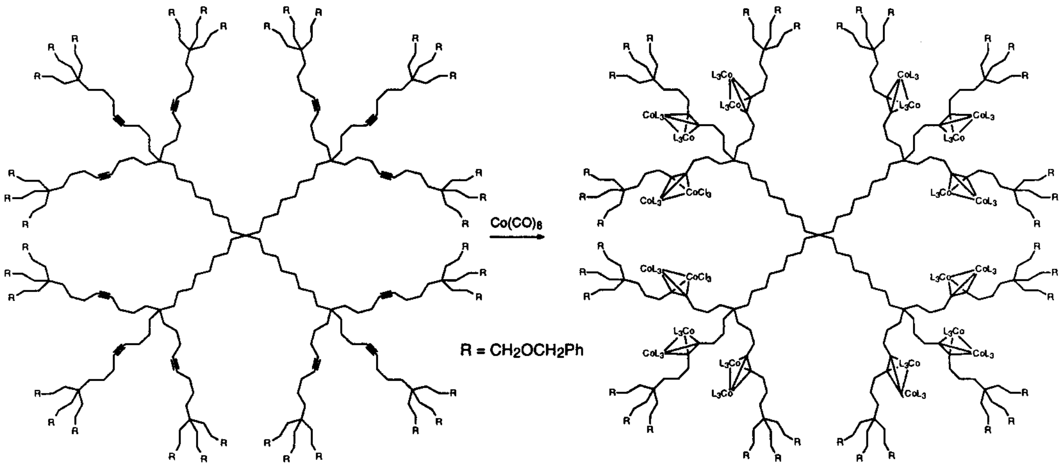
Figure 30. Astruc's Co-containing hexasubstituted benzene.

The first organometallic dendrimer possessing a site-specific attachment of a metal center within the structure was reported by Newkome et al.[209] During the construction of an all-carbon unimolecular micelle,[37] the intermediate dodecaalkyne **183** was treated with dicobalt octacarbonyl to afford the corresponding cobalt-containing cascade **184** that was termed a 'cobaltomicellane' (Scheme 39). In an analogous synthesis, Astruc et al.[210] prepared a first-generation cobalt complex (**185**) from its hexaalkyne precursor (Figure 30). The potential to perform reactions on a branched framework[211] was thus realized along with precedent to construct ligating sites directly or inherently within a highly branched framework.[212,213]

Newkome et al.[214] reported a series of macromolecules possessing multiple piperazine moieties inside the dendritic framework (Scheme 40). Treatment of tetraacid chloride **186** with 4 equiv of the extended monomer **187** gave the first-generation dendrimer **188**, which was then converted to the second-generation **189** by treatment of formic acid, followed by a DCC coupling reaction with Behera's amine.[88] Both **188** and **189** were treated with $Pd(MeCN)_2Cl_2$ and $CuCl_2$ to afford the first- and second-generation metallodendrimers **190** and **191**, respectively. Complexation with Cu was followed via ^1H NMR titration.[212,213,215,216]

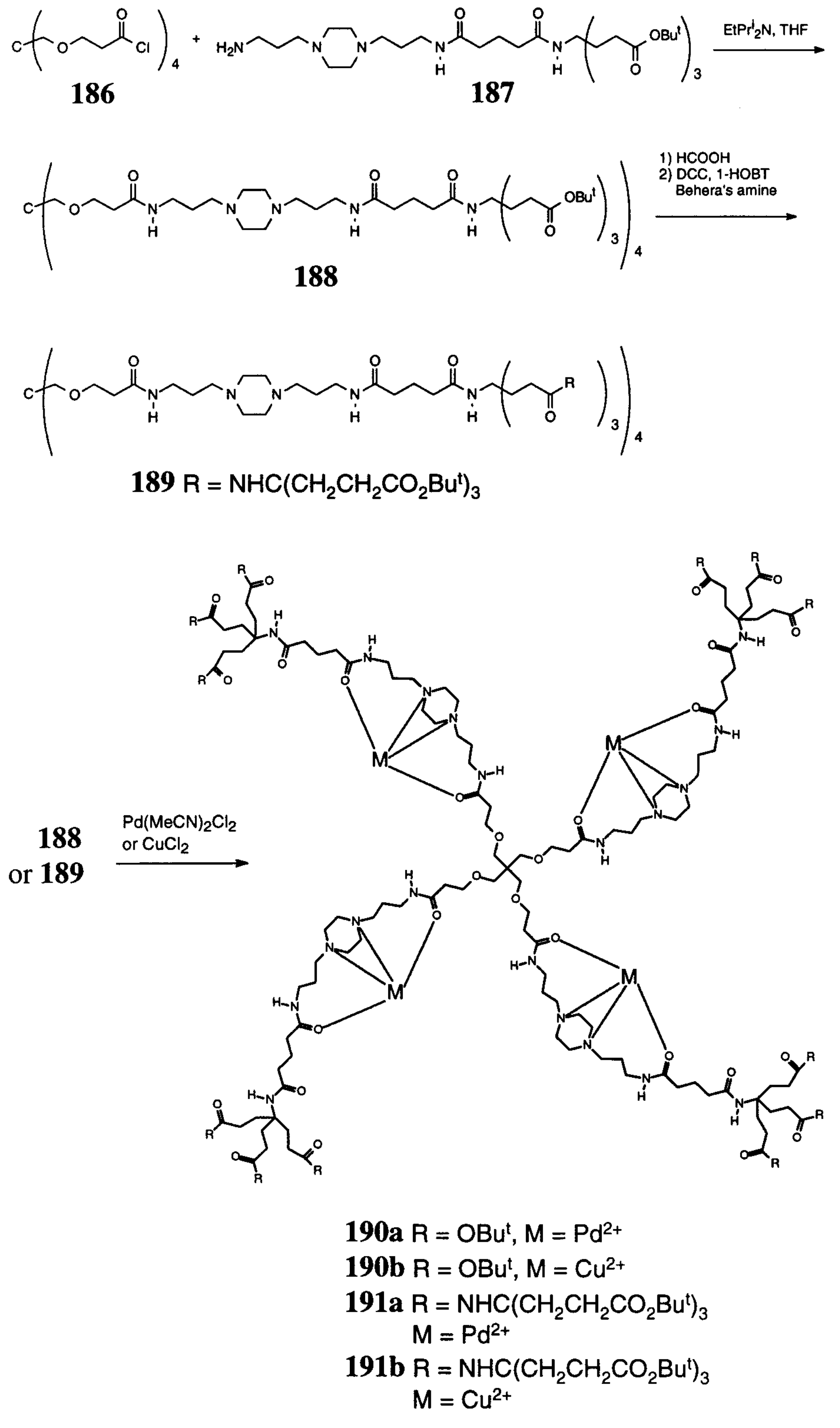
Ming and Newkome et al.[88,217] utilized Co(II) as a paramagnetic ^1H NMR probe to investigate the internal cavities of dendrimers possessing specifically located binding sites (Figure 31). Addition of less than 0.25 equiv of Co(II) to the diaminopyridinyl-containing macromolecules **192a**,**b**[218] formed a 1:1 Co(II):dendrimer complex. Using EXSY, TOSY, and COSY techniques, it was observed that protons close to the paramagnetic complex exhibited hyperfine-shifted signals and possessed shortened relaxation times (T_1

Scheme 39. Metallodendrimers Prepared via Site-Specific Attachment of Cobalt Metal Centers



183 **184**

Scheme 40. Site-Specific Inclusion of Pd– and Co–Piperazine Complexes



186 **187**

188

189 R = NHC($CH_2CH_2CO_2Bu^t$)$_3$

188 or **189**

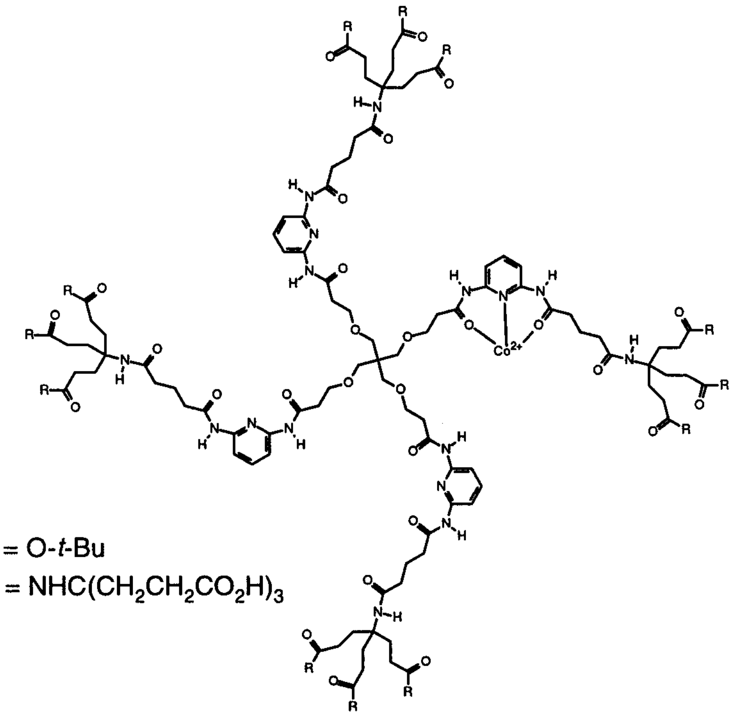
190a R = OBu^t, M = Pd^{2+}
190b R = OBu^t, M = Cu^{2+}
191a R = NHC($CH_2CH_2CO_2Bu^t$)$_3$
M = Pd^{2+}
191b R = NHC($CH_2CH_2CO_2Bu^t$)$_3$
M = Cu^{2+}

and T_2). Analysis of the data thus provided information pertaining to the geometry of the inner dendritic region.

Dendrimers with four internal bipyridine subunits at precise locations within the dendritic superstructure have recently been reported;[219] their subsequent transformation to [Ru(bpy′)(bpy)$_2$]$^{2+}$ complexes was straightforward.

B. Random Metal Inclusion

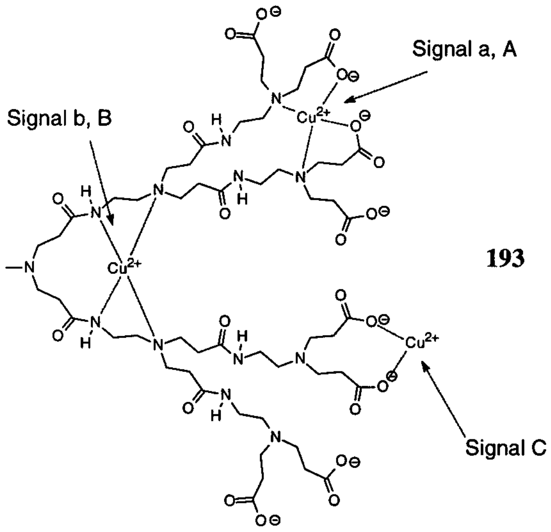
Ottaviani et al.[220] characterized the metallomacromolecules with copper(II) complexes randomly located in 'half generations' (carboxylate-terminated) of PAMAM dendrimers (e.g., **193**) in aqueous solution using the electron paramagnetic resonance (EPR) technique (Figure 32). EPR spectra exhibited three



192a R = O-*t*-Bu

192b R = NHC$(CH_2CH_2CO_2H)_3$

Figure 31. Co(II) has been employed as a paramagnetic, metal-ion structural probe.



193

Figure 32. Half-generation PAMAM dendrimers possessing Cu complexes dispersed throughout the branched framework.

types of signals indicating three distinct types of metal complexes. Coordination sites were determined to be comprised of carboxylate−amine, amido−amine, and bis-carboxylate ligand groups. More recently, Ottaviani et al.[221] characterized the 'full generation' (amino-terminated) series of PAMAM dendrimers with the copper(II) complexes (e.g., **194**) by EPR spectroscopy (Figure 33). One to four different types of signals were observed depending on the generations and the pH value of the solution. At pH = 4−5, the EPR spectra showed all four signals (A−D) at low generation while signal D disappeared at higher generations; at pH ≥ 6, only signal B appeared in the Cu(II) solution.

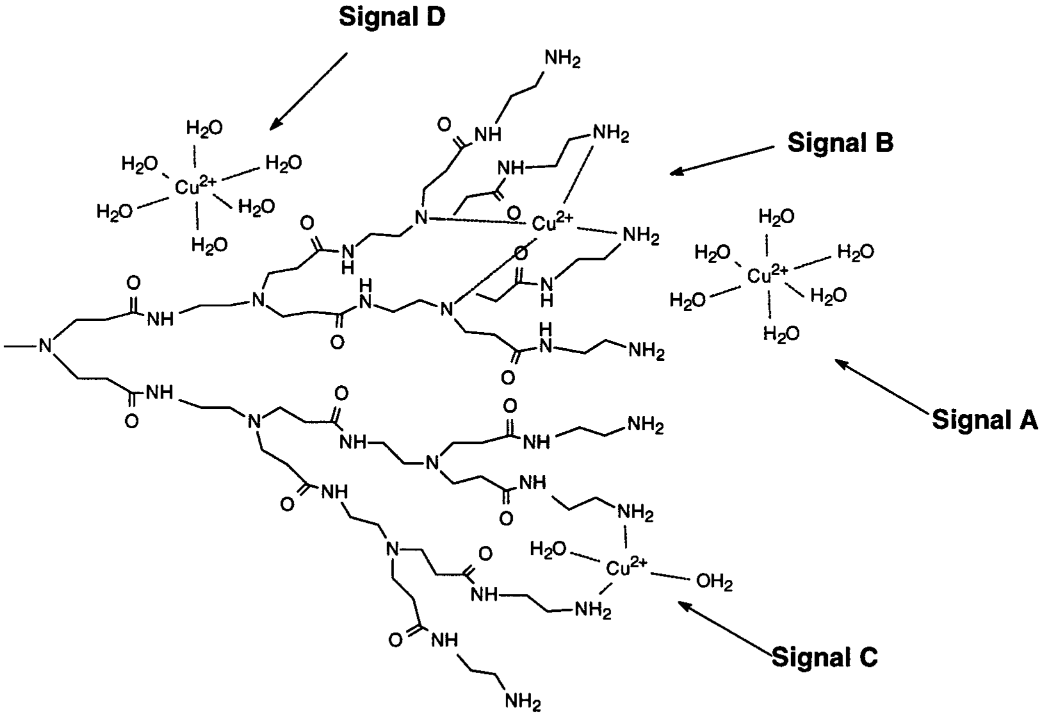
Yang et al.[222] reported several metallomacromolecules with Cu(II) complexes randomly encapsulated in the framework (Scheme 41). Polythioether **195** coordinates one Cu^{2+} ion to give **197**; while polysulfoxide **196** coordinates two Cu^{2+} ions to give complex **198**.

Balogh and Tomalia[223] recently prepared stable metallic copper(II) PAMAM complexes **199** and copper(0) PAMAM composites **200** (Scheme 42). A fourth- or fifth-generation PAMAM dendrimer was added to a copper(II) acetate solution to give approximately 15−32 possible copper(II) complex sites within the dendrimers as detected by spectrophotometric titration. Dropwise addition of an aqueous hydrazine solution afforded the reduced copper(0) dendrimer nanocomposites. Display of a strong UV−vis absorption at very short wavelengths (250, 310, 350 nm) suggested the presence of individual copper atoms or very small copper domains. This is the first example of dendrimer-stabilized metal colloids within the protected binding regime of the internal domain and could have far reaching ramifications in many areas including the crafting of new molecular electronic devices. Crooks et al.[224−226] reported the preparation of similar materials.

VII. Other Branched Architectures

Metallodendrimers possessing porphyrin cores have been discussed (see section III); however, there are several reports in the literature whereby porphyrin−metal complexes comprise the entire structure. Essentially the porphyrin complexes are used as building blocks for unique branched architectures. We herein describe selected examples.

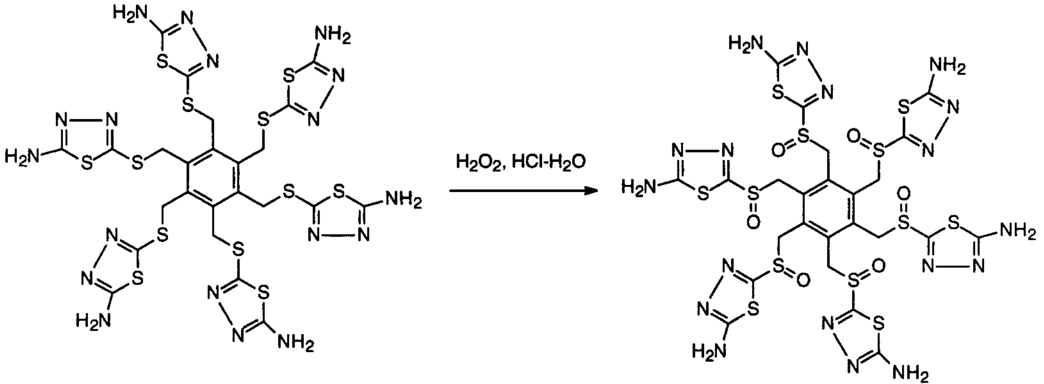
Alessio and Marzilli et al.[227] prepared a polyporphyrin **201** possessing a Zn−porphyrin complex core



194

Figure 33. Full-generation PAMAM dendrimers with randomly coordinated Cu complexes.

Scheme 41. Yang's Polythioether and Polysulfoxide Branched Molecules Exhibit Cu Coordination



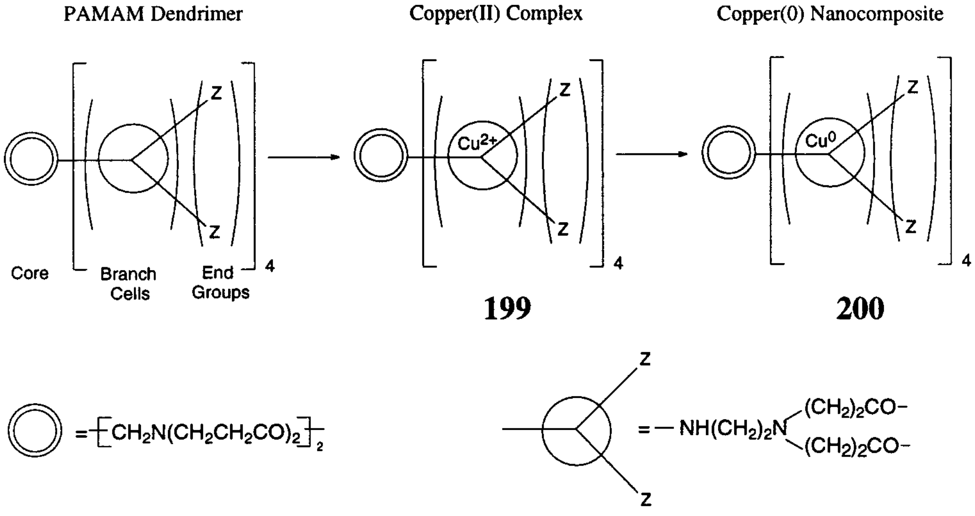
195

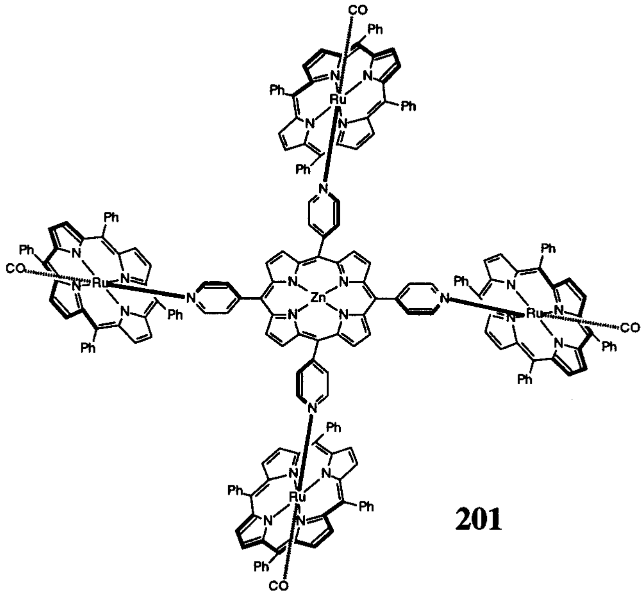
197: 195 ·$CuCl_2$

196

198: 196 ·Cu_2Cl_4

Scheme 42. PAMAM-Based Copper(II) Complexes and Copper(0) Nanocomposites





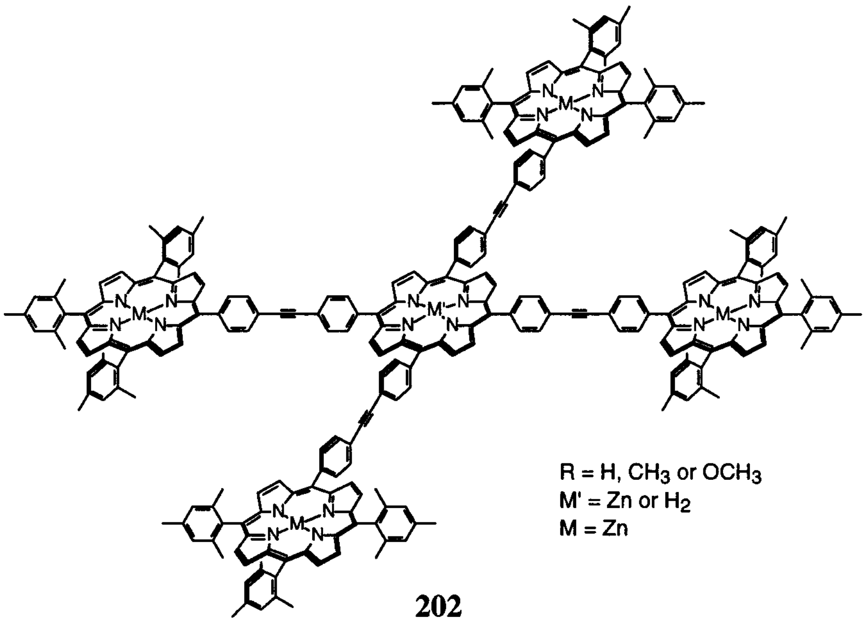
201

Figure 34. Pyridyl-coordinated pentaporphyrin.

surrounded by four pyridine-coordinated Ru−porphyrin complexes (Figure 34). Lindsey et al.[228,229] prepared planar, four-directional complexes (e.g., **202**) to be employed as light-harvesting arrays (Figure 35). Lindsey et al.[230] also constructed linear, two directional, multiporphyrin arrays that were investigated as photonic wires.

Officer and Burrell et al.[231] developed a unique, branched porphyrin-containing macromolecule (Scheme 43) employing a convergent approach. The Ni- and Zn-containing complex **204** was prepared via Lindsey-type conditions[232] whereby cyclization of 4 equiv of **203** was accomplished via treatment with trifluoroacetic acid, followed by reaction with *o*-chloranil. Metal complexation with $Zn(OAc)_2$ afforded monoporphyrin **204**.

Sanders et al.[233] reported the construction of metalloporphyrin dendrimers (Figure 36) using readily accessible porphyrin building blocks such as monoalkyne **205** and bis-alkyne tetraester **206**. The dendritic assembly was accomplished convergently; monoalkyne

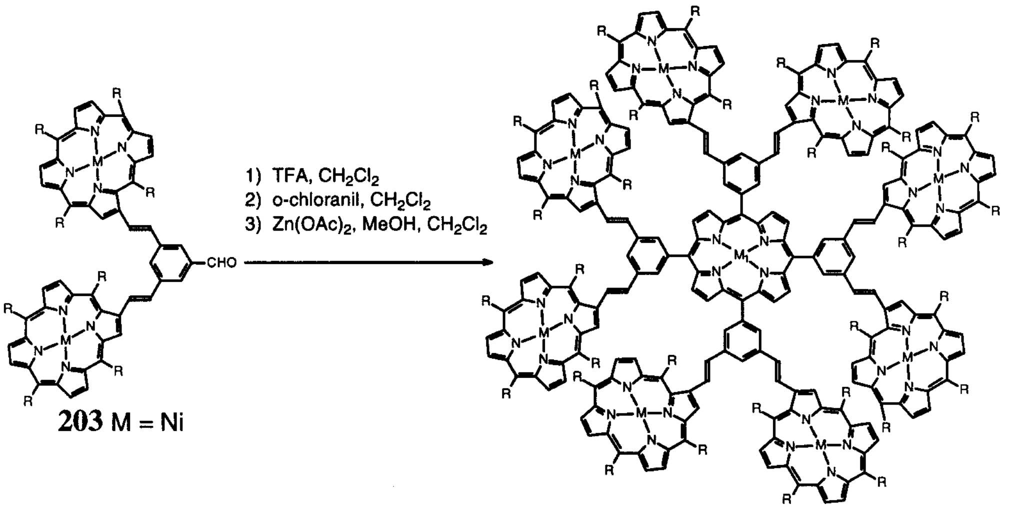


R = H, CH_3 or OCH_3
M' = Zn or H_2
M = Zn

202

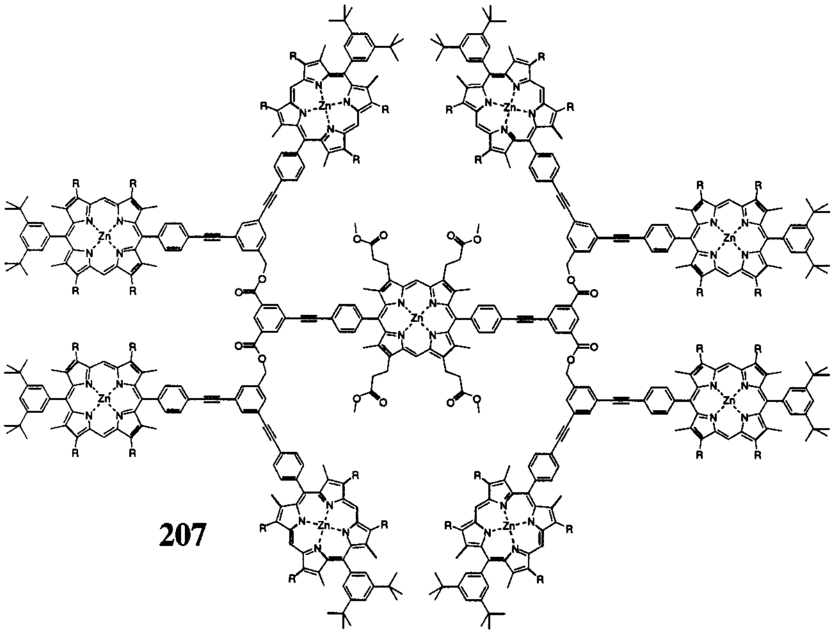
Figure 35. Lindsey's light-harvesting arrays.

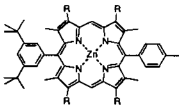
Scheme 43. Officer's and Burrell's Branched Metal−Porphyrin Complexes

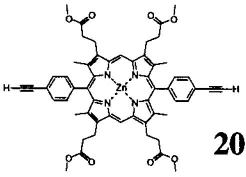


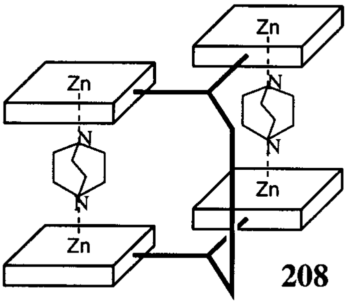
203 M = Ni

204 M = Ni, M_1 = Zn, R = $C_6H_3Me_2$


207


205


206



208

Figure 36. Dendritic metalloporphyrins that exhibit controlled folding.

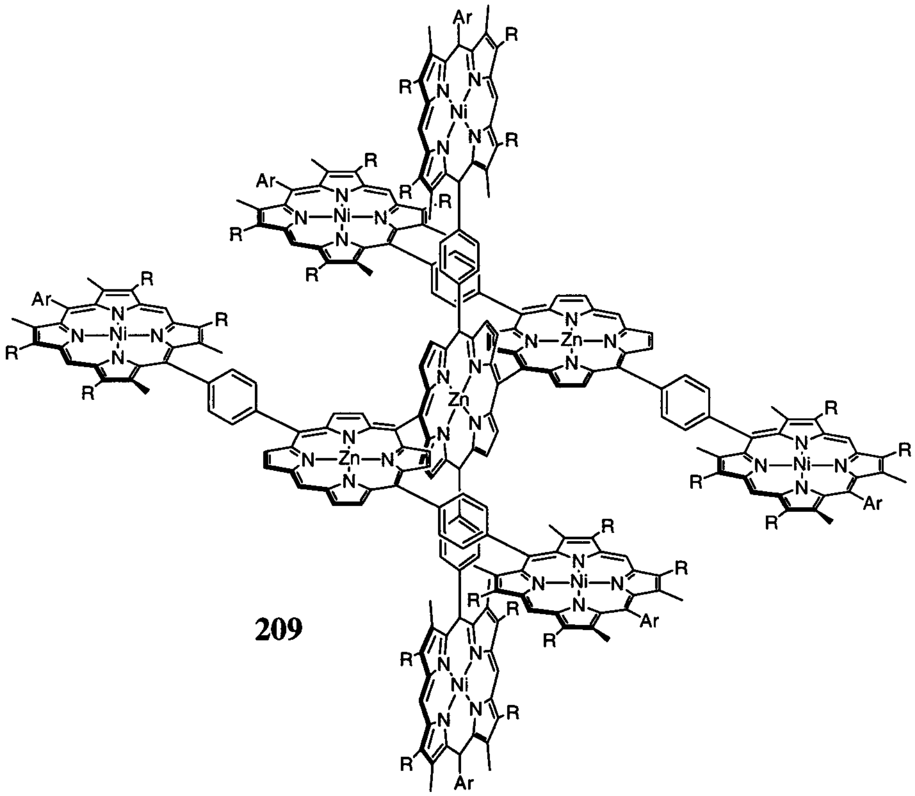
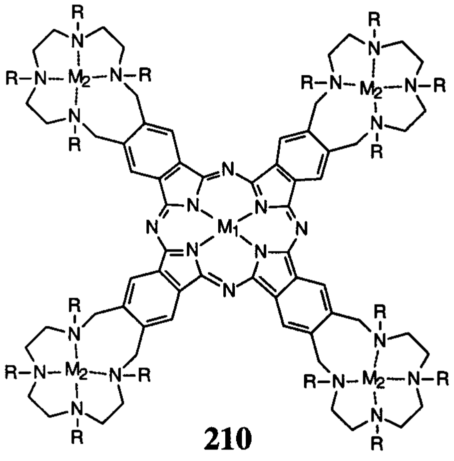

209

Figure 37. Osuka's "Windmill-like" light-harvesting porphyrin arrays.

coupling with 3,5-diiodobenzyl alcohol afforded the bis-porphyrin wedge possessing a benzyl hydroxy focal group. Subsequently, the focal group was coupled to 5-iodoisophthalic acid via Mitsunobu conditions (Ph_3P/DIAD) to form a tetraporphyrin wedge, which was then reacted with bis-alkyne **206** to provide the desired metallodendrimer **207**. Pertinent features of these novel constructs include the incorporation complementary rigid and flexible connectors that function cooperatively to allow folding of the paddle-like arms (**208**) in the presence of a bifunctional ligand such as 1,4-diazabicyclo[2.2.2]octane (DABCO).



210

R = H, Ts
M_1 = Cu, Ni, Co and Sn
M_2 = Ni or no metal

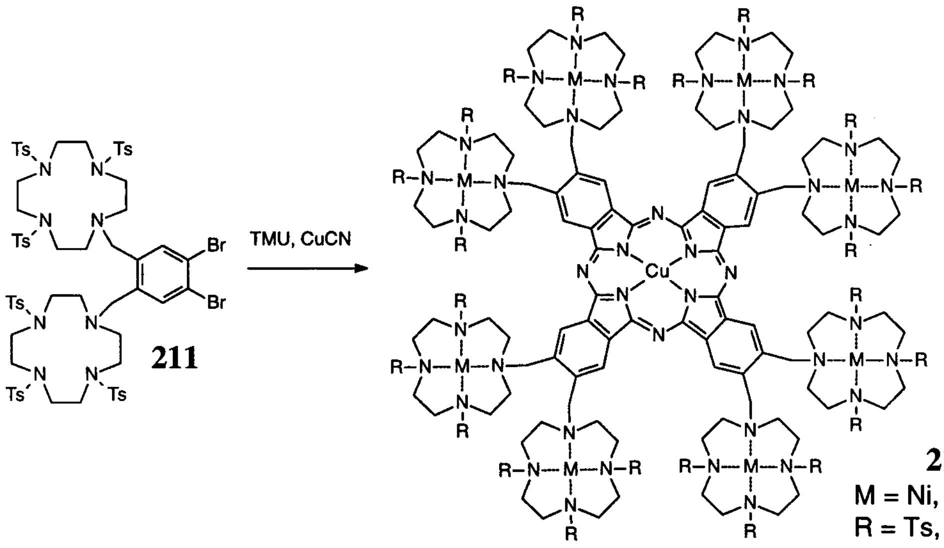
Figure 38. Bekaroglu's phthalocyanine-based poly(aza-crown ethers) complexes.

Osuka et al.[234] reported the preparation novel polymetalloporphyrin architectures described as "windmill-like" light-harvesting antenna complexes (e.g., **209**; Figure 37). Linear porphyrin arrays were constructed via classic condensation reactions, while the *meso,meso*-linked Zn-porphyrins were connected via Lindsay conditions ($AgPF_6/MeCN/CHCl_3$).

Bekaroglu et al.[235,236] synthesized phthalocyanine-based complexes (e.g., **210**) containing metals, such as Cu, Ni, Co, and Sn (Figure 38), that were coordinated by four benzo-connected, tetraazacrown ether moieties. Later, Agar et al.[237] elaborated the aza-crown ether periphery (Scheme 44). The octaazacrown **212** was prepared by treatment of dibromide building block **211** with tetramethylurea (TMU) in the presence of CuCN. These metal complexes were observed to be thermally stable to 210 °C.

Jutzi and co-workers[238] reported the preparation of a polyferrocene-branched construct resembling a "ferrocene−crowned-ferrocene" (Scheme 45). Undecaferrocene **214** was prepared by hydrosilylation of

Scheme 44. Agar's Phthalocyanine-Centered Poly(azacrown ether)

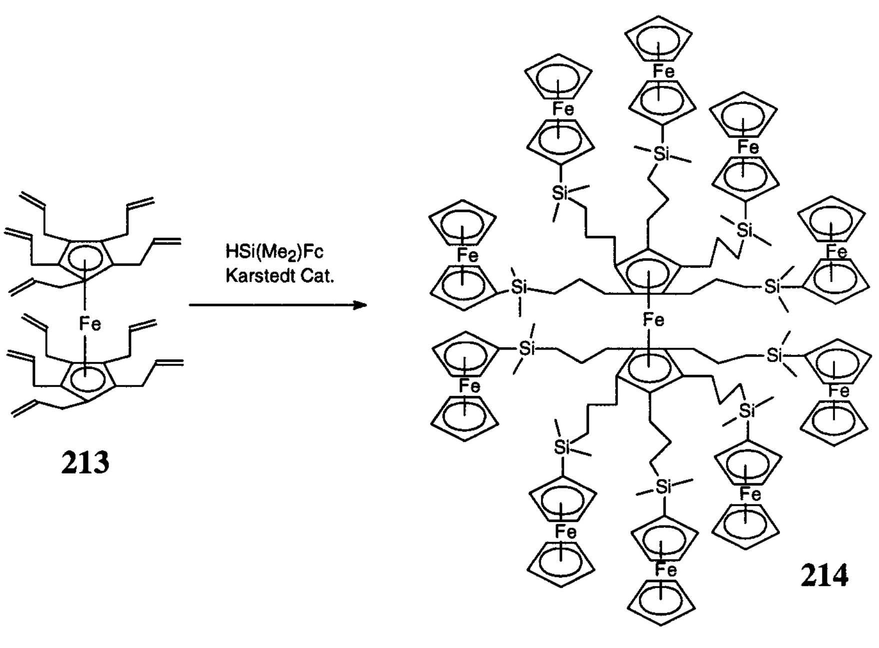


211

212

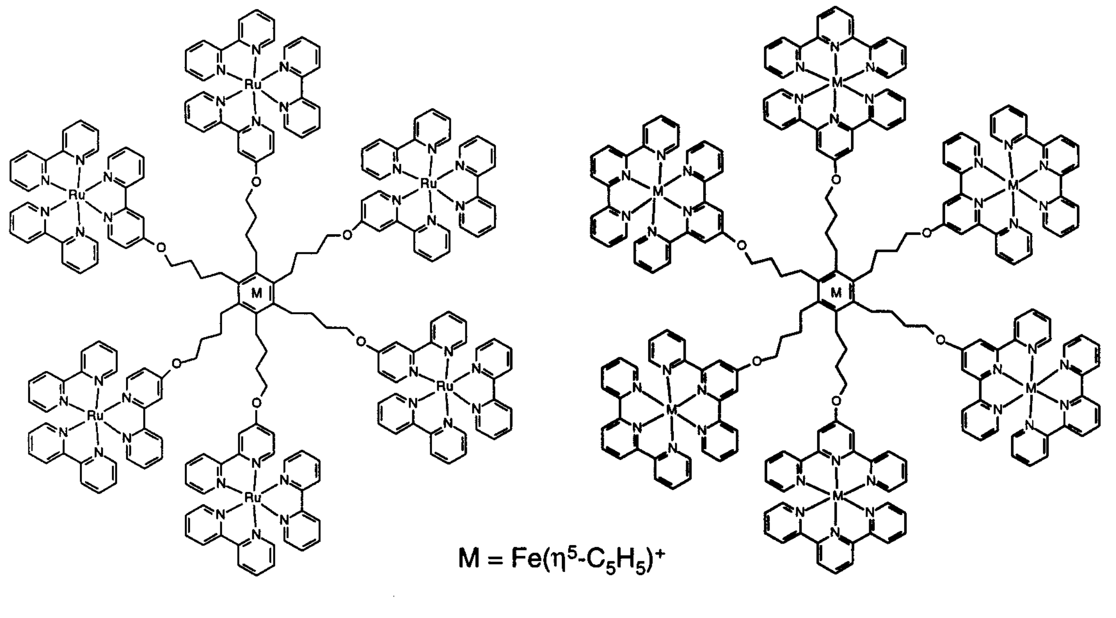
M = Ni, Cu, Co, Zn
R = Ts, H

Scheme 45. Jutzi's Polyferrocene



213

214

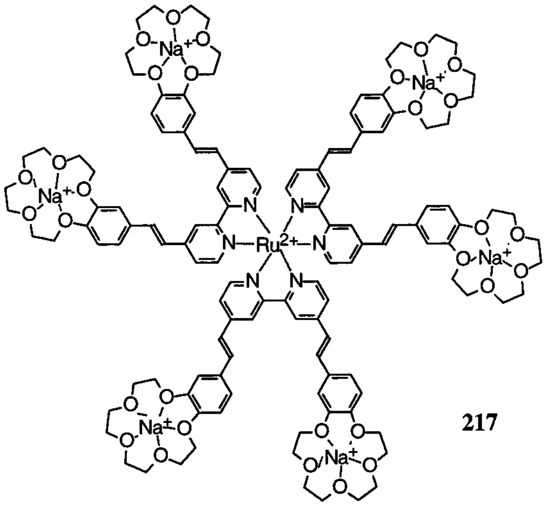


215 **216**

Figure 39. Marvaud's and Astruc's macromolecules possessing metal–arene cores and Ru or Fe complexes at the periphery.

pentaalkene core **213** with [(η^5-C_5H_5)Fe(η^5-C_5H_4Si-(Me_2)H)]. Cyclic voltammetry of the core revealed a reversible oxidation process at 0.144 V, while that of polyferrocene **214** exhibited a more negative potential at −0.163 V. Both of these $E_{1/2}$ values are more negative than that of unsubstituted ferrocene (0.337 V). This was rationalized by both the steric effects as well as the smaller inductive effect exerted by the allyl groups when compared to that of the methyl groups.

Marvaud and Astruc[239] constructed iron and ruthenium hybrid architectures as well as an iron-based analogue (e.g., **215** and **216**) possessing peripheral ruthenium–bipyridine or iron–terpyridine complexes and metal arene cores (Figure 39). Beer et al.[240] constructed hexacrown ether **217** employing a ruthenium–bipyridine-based core for the coordination of Na^+ ions. (Figure 40).



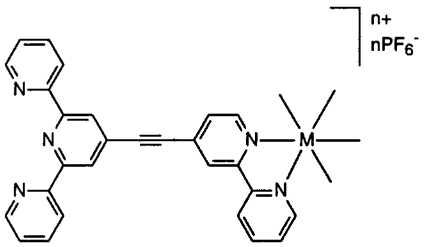
217

Figure 40. Beer's branched molecule possessing a ruthenium–bipyridine complex core and a polysodium surface.

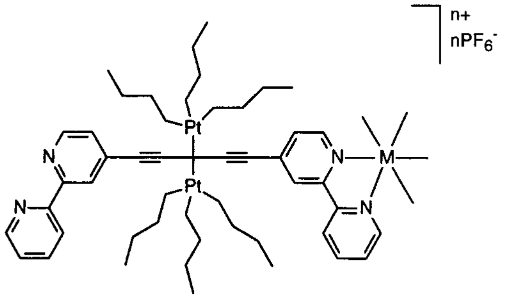
Ziessel et al.[241] prepared several interesting multiple transition-metal-containing architectures (Figure 41). Reaction of complexes **218a**–**c** and **219a**–**c** with $FeSO_4$ afforded the rigid-rod trinuclear complexes **220a**–**c** and the branched construct **221a**–**c**, respectively. The violet complexes **220a**–**c** exhibited a charge-transfer absorption band at 589 nm. The MLCT of fragment Fe(bpy)$_3$ in **221a**–**c** showed an absorption band at about 530 nm. The electronic absorption and luminescence spectra showed a number of similar features and general trends. All complexes exhibited π–π^* absorption (high-energy band) and charge-transfer transitions (low-energy band). The photophysical results based on fluorescence quenching and lifetime measurements indicated that a simple alkyne spacer allows better electronic communication than a platinum–alkyne spacer.

Ziessel et al.[242] also prepared several Ru-, Pt-, Os-, Fe-, Zn-, and Co-containing metallomolecules (e.g., **222**) as photoactive molecular-scale wires (Figure 42). Notably, the Pt(II) unit in the center has a dramatic effect on the electronic properties of the bridge. Rates of intramolecular triplet energy transfer were determined to be 3000-fold faster in the absence of the Pt(II) unit.

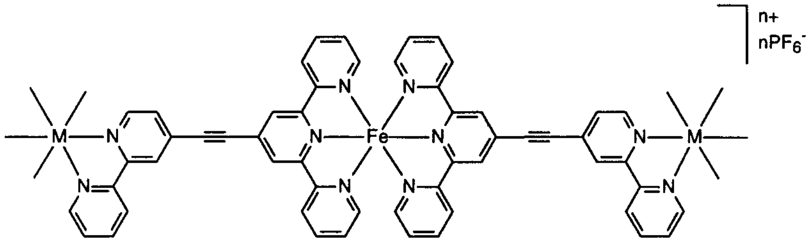
Catalano et al.[243] constructed unusual polyferrocene-possessing platinum complexes as building block connectors (Scheme 46). 1,2,3,4,5,6-Hexakis(bromomethyl)benzene (**223**) was treated with the heterometallic complex PtMe$_2${bpy[(η^5-C_5H_5)Fe(η^5-C_5H_5)]$_2$} (**224**) to afford the dodecaferrocene **225**. Notable aspects of the resultant architecture include a planar, hexa-branched core, platinum–bipyridine 1→2 branching, and a "shell of unsaturation" created by 12 alkene moieties positioned equidistant from the molecular core.



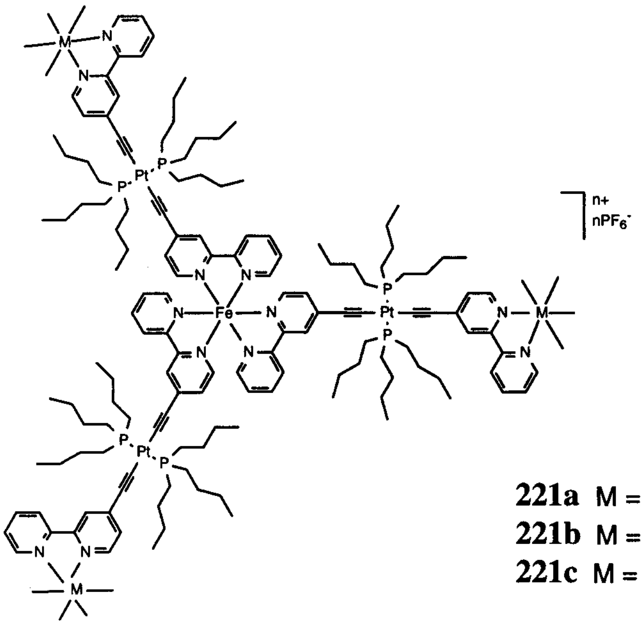
218a M = Ru(bpy)$_2$, n =2
218b M = Os(bpy)$_2$, n = 2
218c M = Re(CO)$_3$, n = 0



219a M = Ru(bpy)$_2$, n =2
219b M = Os(bpy)$_2$, n = 2
219c M = Re(CO)$_3$, n = 0

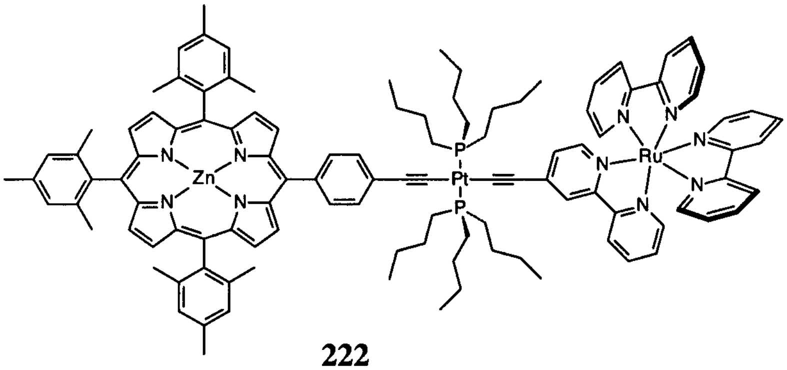


220a M = Ru(bpy)$_2$, n =6
220b M = Os(bpy)$_2$, n = 6
220c M = Re(CO)$_3$, n = 2



221a M = Ru(bpy)$_2$, n =8
221b M = Os(bpy)$_2$, n = 8
221c M = Re(CO)$_3$, n = 2

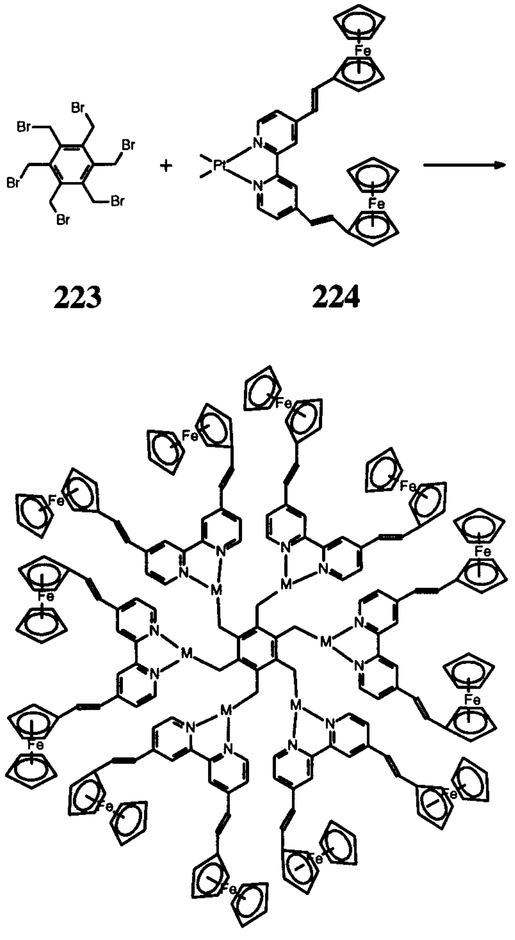
Figure 41. Ziessel's novel metalloconstructs for studying photophysical properties.



222

Figure 42. Ziessel's metallohybrids used for photoactive molecular-scale wires.

Scheme 46. Catalano's Poly(ferroceneplatinum) Hybrid Macromolecule



223 **224**

225

M = $PtMe_2Br$

VIII. Conclusions

In conclusion, the preceding examples of metallodendrimers and metal-based (macro)molecules have presented a case for the continued investigation of these unique architectural constructs. The use and incorporation of metals within the confines of the dendritic regime have already led to the synthesis of important new materials, such as potential drug carriers,[17,244] enzyme mimics,[245,246] MRI contrast agents,[247] and biocatalysts.[248] Thus, the systematic integration of dendrimer chemistry with the well-established, traditional areas of study has, at a relatively early stage, played a role in the development of useful molecular composites. As forward progress proceeds unabated, the development of suprasupermolecules will undoubtedly continue to produce lasting effects on many areas of chemistry and, maybe more importantly, material science well into the next millenium. The melding of dendritic methods to that of rich disciplines, such as transition-metal chemistry, has not only created a new field of study, but it has forever changed the way in which we view, conceive, plan, and bring to fruition the construction of macromolecular assemblies.

IX. Appendix

Rapid advances in the area of metallodendrimers have afforded numerous reports during manuscript production. Other pertinent reviews[249−252] and papers[253−272] have since been published (please see references for details).

X. Acknowledgments

We gratefully acknowledge the funding provided by National Science Foundation (DMR-96-22609) and the Office of Naval Research (N00014-99-1-0082).

XI. References

(1) 1) Flory, P. J. Molecular Size Distribution in Three-Dimensional Polymers. III. Tetrafunctional Branching Units. *J. Am. Chem. Soc.* **1941**, *63*, 3096−3100.

(2) Flory, P. J. Molecular Size Distribution in Three-Dimensional Polymers. I. Gelation. *J. Am. Chem. Soc.* **1941**, *63*, 3083−3090.

(3) Flory, P. J. Molecular Size Distribution in Three-Dimensional Polymers. II. Trifunctional Branching Units. *J. Am. Chem. Soc.* **1941**, *63*, 3091−3096.

(4) Flory, P. J. Molecular Size Distribution in Three-Dimensional Polymers. IV. Branched Polymers Containing A-R-Bf-1 Type Units. *J. Am. Chem. Soc.* **1952**, *74*, 2718−2723.

(5) Kim, Y. H.; Webster, O. W. Hyperbranched Polyphenylenes. *Polym. Prepr.* **1988**, *29*, 310−311.

(6) Kim, Y. H. Hyperbranched Polymers 10 Years After. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1685−1698.

(7) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendritic Molecules: Concepts, Syntheses, Perspective*; VCH: Weinheim, Germany, 1996.

(8) Buhleier, E.; Wehner, W.; Vögtle, F. “Cascade” and “Nonskid-Chain-Like” Syntheses of Molecular Cavity Topologies. *Synthesis* **1978**, 155−158.

(9) Tomalia, D. A.; Baker, H.; Dewald, J. R.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. A New Class of Polymers: Starburst-Dendritic Macromolecules. *Polym. J. (Tokyo)* **1985**, *17*, 117−132.

(10) Newkome, G. R.; Yao, Z.; Baker, G. R.; Gupta, V. K. Cascade Molecules: A New Approach to Micelles. A [27]-Arborol. *J. Org. Chem.* **1985**, *50*, 2003−2004.

(11) Baker, G. R.; Young, J. K. A Systematic Nomenclature for Cascade (Dendritic) Polymers. In *Advances in Dendritic Macromolecules*; JAI: Greenwich, CT, 1994; Chapter 5, pp 169−186.

(12) Newkome, G. R.; Baker, G. R.; Young, J. K.; Traynham, J. G. A Systematic Nomenclature for Cascade Polymers. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 641−651.

(13) Newkome, G. R.; Baker, G. R. Macromolecular Nomenclature Note No. 7. *Polym. Prepr.* **1994**, *35*, 6−9.

(14) Huck, W. T. S.; Prins, L. J.; Fokkens, R. H.; Nibbering, N. M. M.; van Veggel, F. C. J. M.; Reinhoudt, D. N. Convergent and Divergent Noncovalent Synthesis of Metallodendrimers. *J. Am. Chem. Soc.* **1998**, *120*, 6240−6246.

(15) Mongin, O.; Gossauer, A. Tripodaphyrins, a New Class of Porphine Derivatives Designed for Nanofabrication. *Tetrahedron Lett.* **1996**, *37*, 3825−3828.

(16) Knapen, J. W. J.; van der Made, A. W.; de Wilde, J. C.; van Leeuwen, P. W. W. N. M.; Wijkens, P.; Grove, D. M.; van Koten, G. Homogeneous Catalysts Based on Silane Dendrimers Functionalized with Arylnickel(II) Complexes. *Nature* **1994**, *372*, 659−663.

(17) Duncan, R.; Kopecek, J. Soluble Synthetic Polymers as Potential Drug Carriers. *Adv. Polym. Sci.* **1984**, *57*, 51−101.

(18) Peppas, N. A.; Nagai, T.; Miyajima, M. Prospects of Using Star Polymers and Dendrimers in Drug Delivery and Other Pharmaceutical Application. *Pharm. Tech. Jpn.* **1994**, *10*, 611−617.

(19) Bieniarz, C. Dendrimers: Applications to Pharmaceutical and Medicinal Chemistry. In *Encyclopedia of Pharmaceutical Technology*; Marcel Dekker: New York, 1999; pp 55−89.

(20) de Brabander-van den Berg, E. M. M.; Meijer, E. W. Poly-(Propylene Imine) Dendrimers: Large Scale Synthesis via Heterogeneously Catalyzed Hydrogenation. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1308−1311.

(21) Meijer, E. W.; Bosman, H. J. M.; Vandenbooren, F. H. A. M. J.; de Brabander-van den Berg, E. M. M.; Castelijns, A. M. C. F.; De Man, H. C. J.; Reintjens, R. W. E. C.; Stoelwinder, C. J.; Nijenhuis, A. J. Dendritic Macromolecules and the Preparation Thereof. U.S. Pat. 5,530,092, 1996.

(22) Meijer, E. W.; Bosman, H. J. M.; Vandenbooren, F. H. A. M. J.; de Brabander-van den Berg, E. M. M.; Castelijns, A. M. C. F.; De Man, H. C. J.; Reintjens, R. W. E. C.; Stoelwinder, C. J.; Nijenhuis, A. J. Dendritic Macromolecules and the Preparation Thereof. U.S. Pat. 5,610,268, 1997.

(23) Newkome, G. R.; Moorefield, C. N.; Baker, G. R. Building Blocks for Dendritic Macromolecules. *Aldrichim. Acta* **1992**, *25*, 31–38.

(24) Newkome, G. R.; Weis, C. D.; Moorefield, C. N.; Weis, I. Detection and Functionalization of Dendrimers Possessing Free Carboxylic Acid Moieties. *Macromolecules* **1997**, *30*, 2300–2304.

(25) Hummelen, J. C.; van Dongen, J. L. J.; Meijer, E. W. Electrospray Mass Spectrometry of Poly(Propylene Imine) Dendrimers–The Issue of Dendritic Purity or Polydispersity. *Chem. Eur. J.* **1997**, *3*, 1489–1493.

(26) Hawker, C.; Fréchet, J. M. J. A New Convergent Approach to Monodisperse Dendritic Macromolecules. *J. Chem. Soc., Chem. Commun.* **1990**, 1010–1013.

(27) Hawker, C. J.; Fréchet, J. M. J. Preparation of Polymers with Controlled Molecular Architecture. A New Convergent Approach to Dendritic Macromolecules. *J. Am. Chem. Soc.* **1990**, *112*, 7638–7647.

(28) Miller, T. M.; Neenan, T. X. Convergent Synthesis of Monodisperse Dendrimers Based upon 1,3,5-Trisubstituted Benzenes. *Chem. Mater.* **1990**, *2*, 346–349.

(29) Lehn, J.-M. Supramolecular Chemistry–Scope and Perspectives. Molecules, Supermolecules, and Molecular Devices (Nobel Lecture). *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89–112.

(30) Lehn, J.-M. Perspectives in Supramolecular Chemistry–From Molecular Recognition toward Molecular Information Processing and Self-Organization. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304–1319.

(31) Jiang, H.; Kakkar, A. K. Soluble High-T_g Polymers for Second-Order Nonlinear Optics from an Unusual Mix of Imide and Siloxane Linkages in the Backbone. *Macromolecules* **1998**, *31*, 4170–4176.

(32) Kelch, S.; Rehahn, M. Soluble Ruthenium(II) Coordination Polymers Bearing Bulky Side Groups. *Macromolecules* **1998**, *31*, 4102–4106.

(33) Newkome, G. R. Suprasupermolecular Chemistry: The Chemistry within the Dendrimer. *Pure Appl. Chem.* **1999**, in press.

(34) Denti, G.; Serroni, S.; Campagna, S.; Ricevuto, V.; Balzani, V. Directional Energy Transfer in a Luminescent Tetranuclear Ru(II) Polypyridine Complex that Contains Two Different Types of Bridging Ligands. *Inorg. Chim. Acta* **1991**, *182*, 127–129.

(35) Campagna, S.; Denti, G.; Serroni, S.; Ciano, M.; Juris, A.; Balzani, V. A Tridecanuclear Ruthenium(II)-Polypyridine Supramolecular Species: Synthesis, Absorption and Luminescence Properties, and Electrochemical Oxidation. *Inorg. Chem.* **1992**, *31*, 2982–2984.

(36) Denti, G.; Campagna, S.; Serroni, S.; Ciano, M.; Balzani, V. Decanuclear Homo- and Heterometallic Polypyridine Complexes: Syntheses, Absorption Spectra, Luminescence, Electrochemical Oxidation, and Intercomponent Energy Transfer. *J. Am. Chem. Soc.* **1992**, *114*, 2944–2950.

(37) Newkome, G. R.; Moorefield, C. N.; Baker, G. R.; Johnson, A. L.; Behera, R. K. Alkane Cascade Polymers Possessing Micellar Topology: Micellanoic Acid Derivatives. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1176–1178.

(38) Archut, A.; Fischer, M.; Issberner, J.; Vögtle, F. Dendrimere: Hochverzweigte Moleküe Mit Neuen Eigenschaften. *GIT Labor-Fachz.* **1997**, *41*, 198–202.

(39) Ardoin, N.; Astruc, D. Molecular Trees: From Syntheses Towards Applications. *Bull. Soc. Chim. Fr.* **1995**, *132*, 875–909.

(40) Bosman, A. W.; Janssen, H. M.; Meijer, E. W. About Dendrimers. *Chem. Rev.* **1999**, *99*, 0000.

(41) Chow, H.-F.; Mong, T. K. K.; Nongrum, M. F.; Wan, C.-W. The Synthesis and Properties of Novel Functional Dendritic Molecules. *Tetrahedron* **1998**, *54*, 8543–8660.

(42) Fréchet, J. M. J. Functional Polymers and Dendrimers: Reactivity, Molecular Architecture, and Interfacial Energy. *Science* **1994**, *263*, 1710–1715.

(43) Gorman, C. Metallodendrimers: Structural Diversity and Functional Behavior. *Adv. Mater. (Weinheim, Fed. Repub. Ger.)* **1998**, *10*, 295–309.

(44) Issberner, J.; Moors, R.; Vögtle, F. Dendrimers: From Generations and Functional Groups to Functions. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2413–2420.

(45) Majoral, J.-P.; Caminade, A.-M. Divergent Approaches to Phosphorus-Containing Dendrimers and Their Functionalization. In *Topics in Current Chemistry*; Springer-Verlag: Berlin, 1998; Chapter 3, pp 79–124.

(46) *Advances in Dendritic Macromolecules*; Newkome, G. R., Ed.; JAI: Greenwich, CT, 1994; Vol. 1, pp 1–198.

(47) *Advances in Dendritic Macromolecules*; Newkome, G. R., Ed.; JAI: Greenwich, CT, 1995; pp 1–204.

(48) *Advances in Dendritic Macromolecules*; Newkome, G. R., Ed.; JAI: Greenwich, CT, 1996; Vol. 3, pp 1–201.

(49) *Advances in Dendritic Macromolecules*; Newkome, G. R., Ed.; JAI: Greenwich, CT, 1999; Vol. 4, pp 1–201.

(50) Newkome, G. R.; Moorefield, C. N. Dendrimers. In *Comprehensive Supramolecular Chemistry*; Pergamon: New York, 1996; Chapter 25, pp 777–832.

(51) Schlüter, A.-D. Dendrimers with Polymeric Core: Towards Nanocylinders. In *Topics in Current Chemistry*; Vögtle, F., Ed.; Springer-Verlag: Berlin, 1998; Chapter 5, pp 165–191.

(52) Seebach, D.; Rheiner, P. B.; Greiveldinger, G.; Butz, T.; Sellner, H. Chiral Dendrimers. In *Topics in Current Chemistry*; Vögtle, F., Ed.; Springer-Verlag: Berlin, 1998; Chapter 4, pp 125–164.

(53) Smith, D. K.; Diederich, F. Functional Dendrimers: Unique Biological Mimics. *Chem. Eur. J.* **1998**, *4*, 1353–1361.

(54) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III Starburst Dendrimers: Molecular-Level Control of Size, Shape, Surface Chemistry, Topology and Flexibility in the Conversion of Atoms to Macroscopic Materials. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138–175.

(55) Vögtle, F.; Plevoets, M.; Nachtsheim, G.; Wörsdörfer, U. Monofunctionalized Dendrons of Different Generations–As Reagents for the Introduction of Dendritic Substituents. *J. Prakt. Chem.* **1998**, *340*, 112–121.

(56) Venturi, M.; Serroni, S.; Juris, A.; Campagna, S.; Balzani, V. Electrochemical and Photochemical Properties of Metal-Containing Dendrimers. In *Topics in Current Chemistry*; Vögtle, F., Ed.; Springer-Verlag: Berlin, 1998; Chapter 6, pp 193–228.

(57) Zeng, F.; Zimmerman, S. C. Dendrimers in Supramolecular Chemistry: From Molecular Recognition to Self-Assembly. *Chem. Rev.* **1997**, *97*, 1681–1712.

(58) Narayanan, V. V.; Newkome, G. R. Supramolecular Chemistry within Dendritic Structures. In *Topics in Current Chemistry*; Vögtle, F., Ed.; Springer-Verlag: Berlin/Heidelberg, 1998; Chapter 2, pp 19–77.

(59) Trollsås, M.; Hedrick, J. L. Hyperbranched Poly(ϵ-Caprolactone) Derived from Intrinsically Branched AB$_2$ Macromonomers. *Macromolecules* **1998**, *31*, 4390–4395.

(60) Boulas, P. L.; Gómez-Kaifer, M.; Echegoyen, L. Electrochemistry of Supramolecular Systems. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 216–247.

(61) Matthews, O. A.; Shipway, A. N.; Stoddart, J. F. Dendrimers–Branching Out from Curiosities into New Technologies. *Prog. Polym. Sci.* **1998**, *23*, 1–56.

(62) Campagna, S.; Denti, G.; Sabatino, L.; Serroni, S.; Ciano, M.; Balzani, V. A New Hetero-Tetrametallic Complex of Ruthenium and Osmium: Absorption Spectrum, Luminescence Properties, and Electrochemical Behaviour. *J. Chem. Soc., Chem. Commun.* **1989**, 1500–1501.

(63) Campagna, S.; Denti, G.; Serroni, S.; Ciano, M.; Balzani, V. Hexanuclear Homo- and Heterobridged Ruthenium(II) Polypyridine Complexes: Syntheses, Absorption Spectra, Luminescence Properties, and Electrochemical Behavior. *Inorg. Chem.* **1991**, *30*, 3728–3732.

(64) Belser, P.; von Zelewsky, A.; Frank, M.; Seel, C.; Vögtle, F.; De Cola, L.; Barigelletti, F.; Balzani, V. Supramolecular Ru and/or Os Complexes of Tris(Bipyridine) Bridging Ligands. Syntheses, Absorption Spectra, Luminescence Properties, Electrochemical Behavior, Intercomponent Energy, and Electron Transfer. *J. Am. Chem. Soc.* **1993**, *115*, 4076–4086.

(65) Roffia, S.; Marcaccio, M.; Paradisi, C.; Paolucci, F.; Balzani, V.; Denti, G.; Serroni, S.; Campagna, S. Electrochemical Reduction of (2,2′-Bipyridine)- and Bis((2-Pyridyl)pyrazine)Ruthenium(II) Complexes Used as Building Blocks for Supramolecular Species. Redox Series Made of 8, 10, and 12 Redox Steps. *Inorg. Chem.* **1993**, *32*, 3003–3009.

(66) Juris, A.; Balzani, V.; Campagna, S.; Denti, G.; Serroni, S.; Frei, G.; Güdel, H. U. Near-Infrared Luminescence of Supramolecular Species Consisting of Osmium(II)- and/or Ruthenium(II)-Polypyridine Complexes. *Inorg. Chem.* **1994**, *33*, 1491–1496.

(67) Chen, C.-D.; Huang, J.-W.; Leung, M.; Li, H. *S,S*-Dimethyl Dithiocarbonate: A Novel Carbonyl Dication Synthon in the Synthesis of Ketones. *Tetrahedron* **1998**, *54*, 9067–9078.

(68) Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. Designing Dendrimers Based on Transition-Metal Complexes. Light-Harvesting Properties and Predetermined Redox Patterns. *Acc. Chem. Res.* **1998**, *31*, 26–34.

(69) Campagna, S.; Denti, G.; Serroni, S.; Juris, A.; Venturi, M.; Ricevuto, V.; Balzani, V. Dendrimers of Nanometer Size Based on Metal Complexes: Luminescent and Redox-Active Polynuclear Metal Complexes Containing Up to Twenty-Two Metal Centers. *Chem. Eur. J.* **1995**, *1*, 211–221.

(70) Serroni, S.; Juris, A.; Venturi, M.; Campagna, S.; Resino, I. R.; Denti, G.; Credi, A.; Balzani, V. Polynuclear Metal Complexes of Nanometre Size. A Versatile Synthetic Strategy Leading to Luminescence and Redox-Active Dendrimers Made of an Osium(II)-Based Core and Ruthenium(II)-Based Units in the Branches. *J. Mater. Chem.* **1997**, *7*, 1227–1236.

(71) Suzuki, H.; Kurata, H.; Matano, Y. First Synthesis and Properties of Dendritic Bi$_n$-Bismuthanes. *Chem. Commun.* **1997**, 2295–2296.

(72) Bochkarev, M. N.; Cilkin, V. B.; Mayorova, L. P.; Razuvaev, G. A.; Cemchkov, U. D.; Sherstyanux, V. E. Polyphenylenegermane–A New Type of Polymeric Material. *Metalloorg. Khim.* **1988**, *1*, 196–200.

(73) Huc, V.; Boussaguet, P.; Mazerolles, P. Organogermanium Dendrimers. *J. Organomet. Chem.* **1996**, *521*, 253–260.

(74) Arakawa, R.; Matsuo, T.; Nozaki, K.; Ohno, T.; Haga, M. Analysis of Multiply Charged Ions of Ruthenium(II) Tetranuclear Complexes by Electrospray Ionization Mass Spectrometry. *Inorg. Chem.* **1995**, *34*, 2464–2467.

(75) Haga, M.-A.; Ali, M. M.; Arakawa, R. Proton-Induced Switching of Electron Tranfer Pathways in Dendrimer-Type Tetranuclear RuOs$_3$ Complexes. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 76–78.

(76) Moucheron, C.; Kirsch-De Mesmaeker, A.; Dupont-Gervais, A.; Leize, E.; Van Dorsselaer, A. Synthesis and Characterization by Electrospray Mass Spectrometry of a Novel Dendritic Heptanuclear Complex of Ruthenium(II). *J. Am. Chem. Soc.* **1996**, *118*, 12834–12835.

(77) Nanjo, M.; Sekiguchi, A. Group-14-Element-Based Hybrid Dendrimers. Synthesis and Characterization of Dendrimers with Alternating Si and Ge Atoms in the Chains. *Organometallics* **1998**, *17*, 492–494.

(78) Moss, J. R.; Stipkala, J. M.; Yang, J. C.; Bignozzi, C. A.; Meyer, G. J.; Meyer, T. J.; Wen, X.; Linton, R. W. Sensitization of Nanocrystalline TiO$_2$ by Electropolymerized Thin Films. *Chem. Mater.* **1998**, *10*, 1748–1750.

(79) Collin, J.-P.; Heitz, V.; Sauvage, J.-P. A Porphyrin Rigidly Linked to One or Two Terpyridine Chelates Used as Assembling Subunits. *Tetrahedron Lett.* **1991**, *32*, 5977–5980.

(80) Newkome, G. R.; Cardullo, F.; Constable, E. C.; Moorefield, C. N.; Thompson, A. M. W. C. Metallomicellanols: Incorporation of Ruthenium(II)-2,2′:6′,2″-Terpyridine Triads into Cascade Polymers. *J. Chem. Soc., Chem. Commun.* **1993**, 925–927.

(81) Sauvage, J.-P.; Collin, J.-P.; Chambron, J. C.; Guillerez, S.; Coudret, C.; Balzani, V.; Barigelletti, F.; De Cola, L.; Flamigni, L. Ruthenium(II) and Osmium(II) Bis(Terpyridine) Complexes in Covalently-Linked Multicomponent Sysytems: Synthesis, Electrochemical Behavior, Absorption Spectra, and Photochemical and Photophysical Properties. *Chem. Rev.* **1994**, *94*, 993–1019.

(82) Seddon, K. R. Ruthenium: "A Dance to the Music of Time". *Platinum Met. Rev.* **1996**, *40*, 128–134.

(83) Newkome, G. R.; Young, J. K.; Baker, G. R.; Potter, R. L.; Audoly, L.; Cooper, D.; Weis, C. D.; Morris, K. F.; Johnson, C. S., Jr. Cascade Polymers: pH Dependence of Hydrodynamic Radii of Acid Terminated Dendrimers. *Macromolecules* **1993**, *26*, 2394–2396.

(84) Constable, E. C.; Ward, M. D. Synthesis and Co–Ordination Behaviour of 6′,6″-Bis(2-Pyridyl)-2,2′:4,4″:2″,2‴-quaterpyridine; 'Back-to-Back' 2,2′:6′,2″-Terpyridine. *J. Chem. Soc., Dalton Trans.* **1990**, 1405–1409.

(85) Newkome, G. R.; Moorefield, C. N.; Güther, R.; Baker, G. R. Novel Building Blocks for Incorporation of Molecular Recognition Sites within Cascade Polymeric Architectures. *Polym. Prepr.* **1995**, *36*, 609–610.

(86) Newkome, G. R.; Güther, R.; Moorefield, C. N.; Cardullo, F.; Echegoyen, L.; Pérez-Cordero, E.; Luftmann, H. Routes to Dendritic Networks: Bis-Dendrimers by Coupling of Cascade Macromolecules through Metal Centers. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2023–2026.

(87) Newkome, G. R.; Behera, R. K.; Moorefield, C. N.; Baker, G. R. Cascade Polymers: Syntheses and Characterization of One-Directional Arborols Based on Adamantane. *J. Org. Chem.* **1991**, *56*, 7162–7167.

(88) Newkome, G. R.; Weis, C. D. Di-*tert*-Butyl 4-[2-(*tert*-Butoxycarbonyl)ethyl]-4-aminoheptanedicarboxylate. *Org. Prep. Proc. Int.* **1996**, *28*, 485–488.

(89) Newkome, G. R.; He, E. Nanometric Dendritic Macromolecules: Stepwise Assembly by Double (2,2′:6′,2″-Terpyridine)Ruthenium(II) Connectivity. *J. Mater. Chem.* **1997**, *7*, 1237–1244.

(90) Newkome, G. R.; Weis, C. D. 6,6-Bis(Carboxy-2-oxabutyl)-4,8-dioxaundecane-1,11-dicarboxylic Acid. *Org. Prep. Proc. Int.* **1996**, *28*, 242–246.

(91) Newkome, G. R.; He, E.; Godínez, L. A. Construction of Dendritic Assemblies: A Tailored Approach to Isomeric Metallomacromolecules by Means of Bis(2,2′:6′,2″-Terpyridine)Ruthenium(II) Connectivity. *Macromolecules* **1998**, *31*, 4382–4386.

(92) Cuadrado, I.; Casado, C. M.; Alonso, B.; Morán, M.; Losada, J.; Belsky, V. Dendrimers Containing Organometallic Moieties Electronically Communicated. *J. Am. Chem. Soc.* **1997**, *119*, 7613–7614.

(93) Balzani, V.; Gómez-Lopez, M.; Stoddart, J. F. Molecular Machines. *Acc. Chem. Res.* **1998**, *31*, 405–414.

(94) Constable, E. C.; Harverson, P. A New Convergent Strategy for High-Nuclearity Metallodendrimers. *Chem. Commun.* **1996**, 33–34.

(95) Constable, E. C.; Harrverson, P.; Ramsden, J. J. Adsorption of Ruthenadendrimers to Silica–Titania Surfaces Studied by Optical Waveguide Lightmode Spectroscopy (OWLS). *Chem. Commun.* **1997**, 1683–1684.

(96) Constable, E. C.; Harverson, P. Convergent Synthesis of an Octadecaruthenium Metallodendrimer. *Inorg. Chim. Acta* **1996**, *252*, 9–11.

(97) Constable, E. C. Metallodendrimers: Metal Ions as Supramolecular Glue. *Chem. Commun.* **1997**, 1073–1080.

(98) Constable, E. C.; Harverson, P.; Oberholzer, M. Convergent and Divergent Approaches to Metallocentric Metallodendrimers. *Chem. Commun.* **1996**, 1821–1822.

(99) Boury, B.; Corriu, R. J. P.; Nuñez, R. Hybrid Xerogels from Dendrimers and Arborols. *Chem. Mater.* **1998**, *10*, 1795–1804.

(100) Constable, E. C.; Thompson, A. M. W. C. A New Ligand for the Self-Assembly of Starburst Coordination Oligomers and Polymers. *J. Chem. Soc., Chem. Commun.* **1992**, 617–619.

(101) Amoroso, A. J.; Thompson, A. M. W. C.; Maher, J. P.; McCleverty, J. A.; Ward, M. D. Di-, Tri-, and Tetranucleating Pyridyl Ligands which Facilitate Multicenter Magnetic Exchange between Paramagnetic Molybdenum Centers. *Inorg. Chem.* **1995**, *34*, 4828–4835.

(102) Achar, S.; Puddephatt, R. J. Organoplatinum Dendrimers Formed by Oxidative Addition. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 847–849.

(103) Achar, S.; Vittal, J. J.; Puddephatt, R. J. Organoplatinum Dendrimers. *Organometallics* **1996**, *15*, 43–50.

(104) Achar, S.; Puddephatt, R. J. Large Dendrimeric Organoplatinum Complexes. *J. Chem. Soc., Chem. Commun.* **1994**, 1895–1896.

(105) Achar, S.; Puddephatt, R. J. Chains and Stars in Organoplatinum Oligomers. *Organometallics* **1995**, *14*, 1681–1687.

(106) Liu, G.-X.; Puddephatt, R. J. Model Reactions for the Synthesis of Organometallic Dendrimers Containing Platinum and Palladium. *Inorg. Chim. Acta* **1996**, *251*, 319–323.

(107) Liu, G.-X.; Puddephatt, R. J. Divergent Route to Organoplatinum or Platinum–Palladium Dendrimers. *Organometallics* **1996**, *15*, 5257–5259.

(108) Huck, W. T. S.; van Veggel, F. C. J. M.; Kropman, B. L.; Blank, D. H. A.; Keim, E. G.; Smithers, M. M. A.; Reinhoudt, D. N. Large Self-Assembled Organopalladium Spheres. *J. Am. Chem. Soc.* **1995**, *117*, 8293–8294.

(109) Huck, W. T. S.; Snellink-Ruël, B. H.; Lichtenbelt, J. W.; van Veggel, F. C. J. M.; Reinhoudt, D. N. Self-Assembly of Hyperbranched Spheres; Correlation between Monomeric Synthon and Sphere Size. *Chem. Commun.* **1997**, 9–10.

(110) Huck, W. T. S.; van Veggel, F. C. J. M.; Reinhoudt, D. N. Self-Assembly of Hyperbranched Spheres. *J. Mater. Chem.* **1997**, *7*, 1213–1219.

(111) Huck, W. T. S.; Snellink-Ruel, B.; van Veggel, F. C. J. M.; Reinhoudt, D. N. New Building Blocks for the Noncovalent Assembly of Homo- and Hetero-Multinuclear Metallodendrimers. *Organometallics* **1997**, *16*, 4287–4291.

(112) Huck, W. T. S.; van Veggel, F. C. J. M.; Reinhoudt, D. N. Controlled Assembly of Nanosized Metallodendrimers. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1213–1215.

(113) Huck, W. T. S.; Hulst, R.; Timmerman, P.; van Veggel, F. C. J. M.; Reinhoudt, D. N. Noncovalent Synthesis of Nanostructures: Combining Coordination Chemistry and Hydrogen Bonding. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1006–1008.

(114) Ohshiro, N.; Takei, F.; Onitsuka, K.; Takahashi, S. Synthesis of a Novel Organometallic Dendrimer with a Backbone Composed of Platinum-Acetylide Units. *Chem. Lett.* **1996**, 871–872.

(115) Tykwinski, R. R.; Stang, P. J. Preparation of Rigid-Rod, Di- and Trimetallic, σ-Acetylide Complexes of Iridium(III) and Rhodium(III) via Alkynyl(Phenyl)Iodonium Chemistry. *Organometallics* **1994**, *13*, 3203–3208.

(116) Leininger, S.; Stang, P. J.; Huang, S. Synthesis and Characterization of Organoplatinum Dendrimers with 1,3,5-Triethynylbenzene Building Blocks. *Organometallics* **1998**, *17*, 3981–3987.

(117) Catalano, V. J.; Parodi, N. Reversible C$_{60}$ Binding to Dendrimer-Containing Ir(CO)Cl(PPh$_2$R)$_2$ Complexes. *Inorg. Chem.* **1997**, *36*, 537–541.

(118) Jin, R.-H.; Aida, T.; Inoue, S. 'Caged' Porphyrin: The First Dendritic Molecule Having a Core Photochemical Functionality. *J. Chem. Soc., Chem. Commun.* **1993**, 1260–1262.

(119) Jansen, J. F. G. A.; Meijer, E. W.; de Brabander-van den Berg, E. M. M. The Dendritic Box: Shape-Selective Liberation of Encapsulated Guests. *J. Am. Chem. Soc.* **1995**, *117*, 4417–4418.

(120) Jiang, D.-L.; Aida, T. A Dendritic Iron Porphyrin as a Novel Haemoprotein Mimic: Effects of the Dendrimer Cage on Dioxygen-Binding Activity. *Chem. Commun.* **1996**, 1523–1524.

(121) Tomoyose, Y.; Jiang, D.-L.; Jin, R.-H.; Aida, T.; Yamashita, T.; Horie, K.; Yashima, E.; Okamoto, Y. Aryl Ether Dendrimers with an Interior Metalloporphyrin Functionality as a Spectroscopic Probe: Interpenetrating Interaction with Dendritic Imidazoles. *Macromolecules* **1996**, *29*, 5236–5238.

(122) Sadamoto, R.; Tomioka, N.; Aida, T. Photoinduced Electron-Transfer Reactions through Dendrimer Architecture. *J. Am. Chem. Soc.* **1996**, *118*, 3978–3979.

(123) Enomoto, M.; Aida, T. Self-Assembly of a Copper-Ligating Dendrimer that Provides a New Non-Heme Metalloprotein Mimic: "Dendrimer Effects" on Stability of the Bis(μ-Oxo)-Dicopper(III) Core. *J. Am. Chem. Soc.* **1999**, *121*, 874−875.
(124) Pollak, K. W.; Leon, J. W.; Fréchet, J. M. J. Dendritic Porphyrins by the Convergent Growth Approach: Their Preparation and Their Properties. *Polym. Mater. Sci. Eng.* **1995**, *73*, 333−334.
(125) Pollak, K. W.; Leon, J. W.; Fréchet, J. M. J.; Maskus, M.; Abruña, H. D. Effects of Dendrimer Generation on Site Isolation of Core Moieties: Electrochemical and Fluoresence Quenching Studies with Metallporphyrin Core Dendrimers. *Chem. Mater.* **1998**, *10*, 30−38.
(126) Bhyrappa, P.; Vaijayanthimala, G.; Suslick, K. S. Shape-Selective Ligation to Dendrimer-Metalloporphyrins. *J. Am. Chem. Soc.* **1999**, *121*, 262−263.
(127) Suslick, K. S.; Bhyrappa, P. Dendrimer Metalloporphyrins as Shape Selective Oxidation Catalysts. *J. Inorg. Biochem.* **1997**, 234.
(128) Bhyrappa, P.; Young, J. K.; Moore, J. S.; Suslick, K. S. Dendrimer-Metalloporphyrins: Synthesis and Catalysis. *J. Am. Chem. Soc.* **1996**, *118*, 5708−5711.
(129) Bhyrappa, P.; Young, J. K.; Moore, J. S.; Suslick, K. S. Shape Selective Epoxidation of Alkenes by Metalloporphyrin Dendrimers. *J. Mol. Catal. A: Chem.* **1996**, *113*, 109−116.
(130) Dandliker, P. J.; Diederich, F.; Gross, M.; Knobler, C. B.; Louati, A.; Sanford, E. M. Dendritic Porphyrins: Modulating Redox Potentials of Electroactive Chromophores with Pendant Multifunctionality. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1739−1742.
(131) Newkome, G. R.; Lin, X.; Weis, C. D. Polytryptophane Terminated Dendritic Macromolecules. *Tetrahedron: Asymmetry* **1991**, *2*, 957−960.
(132) Dandliker, P. J.; Diederich, F.; Gisselbrecht, J.-P.; Louati, A.; Gross, M. Water-Soluble Dendritic Iron Porphyrins: Synthetic Models of Globular Heme Proteins. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2725−2728.
(133) Dandliker, P. J.; Diederich, F.; Zingg, A.; Gisselbrecht, J.-P.; Gross, M.; Louati, A.; Sanford, E. Dendrimers with Porphyrin Cores: Synthetic Models for Globular Heme Proteins. *Helv. Chim. Acta* **1997**, *80*, 1773−1801.
(134) Collman, J. P.; Fu, L.; Zingg, A.; Diederich, F. Dioxygen and Carbon Monoxide Binding in Dendritic Iron(II)Porphyrins. *Chem. Commun.* **1997**, 193−194.
(135) Kimura, M.; Nakada, K.; Yamaguchi, Y.; Hanabusa, K.; Shirai, H.; Kobayashi, N. Dendritic Metallophthalocyanines: Synthesis and Characterization of a Zinc(II) Phthalocyanine$[8]^3$-Arborol. *Chem. Commun.* **1997**, 1215−1216.
(136) Newkome, G. R.; Lin, X. Symmetrical, Four-Directional, Poly-(Ether-Amide) Cascade Polymers. *Macromolecules* **1991**, *24*, 1443−1444.
(137) Kawa, M.; Fréchet, J. M. J. Self-Assembed Lanthanide-Cored Dendrimer Complexes: Enhancement of the Luminescence Properties of Lanthanide Ions through Site-Isolation and Antenna Effects. *Chem. Mater.* **1998**, *10*, 286−296.
(138) Lau, R. L.; Chan, T.-W. D.; Chan, I. Y. K.; Chow, H.-F. Fourier Transform Ion Cyclotron Resonance Studies of Terpyridine-Based Polyether Dendrimers and Their Iron(II) Metallocomplexes by Liquid Secondary Ion Mass Spectrometry. *Eur. Mass Spectrom.* **1995**, *1*, 371−380.
(139) Chow, H.-F.; Chan, I. Y. K.; Chan, D. T.; Kwok, R. W. Dendritic Models of Redox Proteins: X-ray Photoelectron Spectroscopy and Cyclic Voltammetry Studies of Dendritic Bis(Terpyridine) Iron-(II) Complexes. *Chem. Eur. J.* **1996**, *2*, 1085−1091.
(140) Chow, H.-F.; Chan, I. Y. K.; Mak, C. C. Facile Construction of Acid−Base and Redox Stable Polyether-Based Dendritic Fragments. *Tetrahedron Lett.* **1995**, *36*, 8633−8636.
(141) Chow, H.-F.; Chan, I. Y. K.; Mak, C. C.; Ng, M.-K. Synthesis and Properties of a New Class of Polyether Dendritic Fragments: Useful Building Blocks for Functional Dendrimers. *Tetrahedron* **1996**, *52*, 4277−4290.
(142) Tomasik, P.; Ratajewicz, Z. *Pyridine Metal Complexes*; Newkome, G. R., Strekowski, L., Eds.; John Wiley & Sons: New York, 1985; Vol. 14, Part 6, A−C.
(143) Tzalis, D.; Tor, Y. Toward Self-Assembling Dendrimers: Metal Complexation Induces the Assembly of Hyperbranched Structures. *Tetrahedron Lett.* **1996**, *37*, 8293−8296.
(144) Issberner, J.; Vögtle, F.; De Cola, L.; Balzani, V. Dendritic Bipyridine Ligands and Their Tris(Bipyridine)Ruthenium(II) Chelates−Syntheses, Absorption Spectra, and Photophysical Properties. *Chem. Eur. J.* **1997**, *3*, 706−712.
(145) Gorman, C. B.; Parkhurst, B. L.; Su, W. Y.; Chen, K.-Y. Encapsulated Electroactive Molecule Based upon an Inorganic Cluster Surrounded by Dendron Ligands. *J. Am. Chem. Soc.* **1997**, *119*, 1141−1142.
(146) Chen, K.-Y.; Gorman, C. B. Synthesis of a Series of Focally-Substituted Organothiol Dendrons. *J. Org. Chem.* **1996**, *61*, 9229−9235.
(147) Gorman, C. B.; Hager, M. W.; Parkhurst, B. L.; Smith, J. C. Use of a Paramagnetic Core to Affect Longitudinal Nuclear Relaxation in Dendrimers−A Tool for Probing Dendrimer Conformation. *Macromolecules* **1998**, *31*, 815−822.
(148) Chow, H.-F.; Mak, C. C. Dendritic Bis(Oxazoline)Copper(II) Catalysts. 2. Synthesis, Reactivity, and Substrate Selectivity. *J. Org. Chem.* **1997**, *62*, 5116−5127.
(149) Mak, C. C.; Chow, H.-F. Dendritic Catalysts: Reactivity and Mechanism of the Dendritic Bis(Oxazoline)Metal Complex Catalyzed Diels−Alder Reaction. *Macromolecules* **1997**, *30*, 1228−1230.
(150) Chow, H.-F.; Mak, C. C. Facile Preparation of Optically Active Dendritic Fragments Containing Multiple Tartrate-Derived Chiral Units. *Tetrahedron Lett.* **1996**, *37*, 5935−5938.
(151) Rheiner, P. B.; Sellner, H.; Seebach, D. Dendritic Styryl TADDOLs as Novel Polymer Cross-Linkers: First Application in an Enantioselective Et_2Zn Addition Mediated by a Polymer-Incorporated Titanate. *Helv. Chim. Acta* **1997**, *80*, 2027−2032.
(152) Engel, R.; Rengan, K.; Chan, C. S. New Cascade Molecules Centered about Phosphorus. *Heteroat. Chem.* **1993**, *4*, 181−184.
(153) Rengan, K.; Engel, R. The Synthesis of Phosphonium Cascade Molecules. *J. Chem. Soc., Perkin Trans. 1* **1991**, 987−990.
(154) Gossage, R. A.; de Kuil, L. A.; van Koten, G. Diaminoarylnickel-(II) "Pincer" Complexes: Mechanistic Considerations in the Kharasch Addition Reaction, Controlled Polymerization, and Dendrimeric Transition Metal Catalysts. *Acc. Chem. Res.* **1998**, *31*, 423−431.
(155) Lee, J.-D.; Vrana, L. M.; Bullock, E. R.; Brewer, K. J. A Tridentate-Bridged Ruthenium−Rhodium Complex as a Stereochemically Defined Light-Absorber-Electron-Acceptor Dyad. *Inorg. Chem.* **1998**, *37*, 3575−3580.
(156) van Koten, G.; Grove, D. M. Advances in Catalysis with Organonickel(II) Complexes Anchored to Dendrimers and Polymers. *Polym. Mater. Sci. Eng.* **1995**, *73*, 228−229.
(157) Gossage, R. A.; Jastrzebski, J. T. B. H.; van Ameijde, J.; Mulders, S. J. E.; Brouwer, A. J.; Liskamp, R. M. J.; van Koten, G. Synthesis and Catalytic Application of Amino Acid Based Dendritic Macromolecules. *Tetrahedron Lett.* **1999**, *40*, 1413−1416.
(158) Hoare, J. L.; Lorenz, K.; Hovestad, N. J.; Smeets, W. J. J.; Spek, A. L.; Canty, A. J.; Frey, H.; van Koten, G. Organopalladium-Functionalized Dendrimers: Insertion of Palladium(0) into Peripheral Carbon−Iodine Bonds of Carbosilane Dendrimers Derived from Polyols. Crystal Structure of $Si\{(CH_2)_3O_2CC_6H_4I\text{-}4\}_4$. *Organometallics* **1997**, *16*, 4167−4173.
(159) Kleij, A. W.; Kleijn, H.; Jastrzebski, J. T. B. H.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. Dendritic Carbosilanes Containing Silicon-Bonded $1\text{-}[C_6H_2(CH_2NMe_2)_2\text{-}3,5\text{-}Li\text{-}4]$ or $1\text{-}[C_6H_3(CH_2NMe_2)\text{-}4\text{-}Li\text{-}3]$ Mono- and Bis(Amino)Aryllithium End Groups: Structure of $\{[CH_2SiMe_2C_6H_3(CH_2NMe_2)\text{-}4\text{-}Li\text{-}3]_2\}_2$. *Organometallics* **1999**, *18*, 268−276.
(160) Liao, Y.-H.; Moss, J. R. Ruthenium-Containing Organometallic Dendrimers. *J. Chem. Soc., Chem. Commun.* **1993**, 1774−1777.
(161) Liao, Y.-H.; Moss, J. R. Synthesis of Very Large Organoruthenium Dendrimers. *Organometallics* **1995**, *14*, 2130−2132.
(162) Liao, Y.-H.; Moss, J. R. Organoruthenium Dendrimers. *Organometallics* **1996**, *15*, 4307−4316.
(163) Moulines, F.; Djakovitch, L.; Boese, R.; Gloaguen, B.; Theil, W.; Fillaut, J.-L.; Delville, M.-H.; Astruc, D. Organometallic Molecular Trees as Multielectron and Multiproton Reservoirs: $CpFe^+$-Induced Nonallylation of Mesitylene and Phase-Transfer-Catalyzed Synthesis of a Redox-Active Nonairon Complex. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1075−1077.
(164) Cloutet, E.; Fillaut, J.-L.; Gnanou, Y.; Astruc, D. Hexaarm Star-Shaped Polystyrenes by Core-First Method. *J. Chem. Soc., Chem. Commun.* **1994**, 2433−2434.
(165) Valério, C.; Fillaut, J.-L.; Ruiz, J.; Guittard, J.; Blais, J.-C.; Astruc, D. The Dendritic Effect in Molecular Recognition: Ferrocene Dendrimers and Their Use as Supramolecular Redox Sensors for the Recognition of Small Inorganic Anions. *J. Am. Chem. Soc.* **1997**, *119*, 2588−2589.
(166) Moulines, F.; Gloaguen, B.; Astruc, D. One-Pot Multifunctionalization of Polymethyl Hydrocarbon π Ligands. Maximum Space Occupancy by Double Branching and Formation of Arboroles. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 458−460.
(167) Fillaut, J.-L.; Astruc, D. Tentacled Aromatics: From Central-Ring to Outer-Ring Iron Sandwich Complexes. *J. Chem. Soc., Chem. Commun.* **1993**, 1320−1322.
(168) Fillaut, J.-L.; Linares, J.; Astruc, D. Single-Step Six-Electron Transfer in a Heptanuclear Complex: Isolation of Both Redox Forms. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2460−2462.
(169) Köllner, C.; Togni, A.; Weber, I. Chiral Ferrocenyl PP or PN Ligands Bound on Dendrimers. *Chimia* **1998**, *52*, 459.
(170) Moors, R.; Vögtle, F. Dendrimere Polyamine. *Chem. Ber.* **1993**, *126*, 2133-2135.
(171) Seyferth, D.; Kugita, T.; Rheingold, A. L.; Yap, G. P. A. Preparation of Carbosilane Dendrimers with Peripheral Acetylenedicobalt Hexacarbonyl Substituents. *Organometallics* **1995**, *14*, 5362−5366.

(172) Ishow, E.; Gourdon, A.; Launay, J.-P.; Lecante, P.; Verelst, M.; Chiorboli, C.; Scandola, F.; Bignozzi, C.-A. Tetranuclear Tetrapyrido[3,2-a:2′,3′-c:3″,2″-h:2‴,3‴-j]Phenazineruthenium Complex: Synthesis, Wide-Angle X-ray Scattering, and Photophysical Studies. *Inorg. Chem.* **1998**, *37*, 3603−3609.

(173) Cuadrado, I.; Morán, M.; Moya, A.; Casado, C. M.; Barranco, M.; Alonso, B. Organometallic Silicon-Based Dendrimers with Peripheral Si−Cyclopentadienyl, Si−Co and Si−Fe σ-Bonds. *Inorg. Chim. Acta* **1996**, *251*, 5−7.

(174) Lobete, F.; Cuadrado, I.; Casado, C. M.; Alonso, B.; Morán, M.; Losada, J. Silicon-Based Organometallic Dendritic Macromolecules Containing {η^6-(Organosilyl)Arene}Chromium Tricarbonyl Moieties. *J. Organomet. Chem.* **1996**, *509*, 109−113.

(175) Hofkens, J.; Verheijen, W.; Shukla, R.; Dehaen, W.; De Schryver, F. C. Detection of a Single Dendrimer Macromolecule with a Fluorescent Dihydropyrrolopyrrolrdione (DPP) Core Embedded in a Thin Polystyrene Polymer Film. *Macromolecules* **1998**, *31*, 4493−4497.

(176) Alonso, B.; Cuadrado, I.; Morán, M.; Losada, J. Organometallic Silicon Dendrimers. *J. Chem. Soc., Chem. Commun.* **1994**, 2575−2576.

(177) Karstedt, B. D. Platinum Complexes of Unsaturated Siloxanes and Platinum Containing Organopolysiloxanes. U.S. Pat. 3,775,452, 1973.

(178) Uppuluri, S.; Keinath, S. E.; Tomalia, D. A.; Dvornic, P. Rheology of Dendrimers. I. Newtonian Flow Behavior of Medium and Highly Concentrated Solutions of Polyamidoamine (PAMAM) Dendrimers in Ethylenediamine (EDA) Solvent. *Macromolecules* **1998**, *31*, 4498−4510.

(179) Beijer, F. H.; Sijbesma, R. P.; Kooijman, H.; Spek, A. L.; Meijer, E. W. Strong Dimerization of Ureidopyrimidones via Quadruple Hydrogen Bonding. *J. Am. Chem. Soc.* **1998**, *120*, 6761−6769.

(180) Losada, J.; Cuadrado, I.; Morán, M.; Casado, C. M.; Alonso, B.; Barranco, M. Ferrocenyl Silicon-Based Dendrimers as Mediators in Amperometric Biosensors. *Anal. Chim. Acta* **1997**, *338*, 191−198.

(181) Zhou, L.-L.; Roovers, J. Synthesis of Novel Carbosilane Dendritic Macromolecules. *Macromolecules* **1993**, *26*, 963−968.

(182) Seyferth, D.; Son, D. Y.; Rheingold, A. L.; Ostrander, R. L. Synthesis of an Organosilicon Dendrimer Containing 324 Si−H Bonds. *Organometallics* **1994**, *13*, 2682−2690.

(183) Lüning, U.; Kühl, C. Heterodimers for Molecular Recognition by Fourfold Hydrogen Bonds. *Tetrahedron Lett.* **1998**, *39*, 5735−5738.

(184) Cuadrado, I.; Morán, M.; Casado, C. M.; Alonso, B.; Lobete, F.; Garcia, B.; Ibisate, M.; Losada, J. Ferrocenyl-Functionalized Poly(Propylenimine) Dendrimers. *Organometallics* **1996**, *15*, 5278−5280.

(185) Takada, K.; Díaz, D. J.; Abruña, H. D.; Cuadrado, I.; Casado, C.; Alonso, B.; Morán, M.; Losada, J. Redox-Active Ferrocenyl Dendrimers: Thermodynamics and Kinetics of Adsorption, in-Situ Electrochemical Quartz Crystal Microbalance Study of the Redox Process and Tapping Mode AFM Imaging. *J. Am. Chem. Soc.* **1997**, *119*, 10763−16773.

(186) Castro, R.; Cuadrado, I.; Alonso, B.; Casado, C. M.; Morán, M.; Kaifer, A. E. Multisite Inclusion Complexation of Redox Active Dendrimer Guests. *J. Am. Chem. Soc.* **1997**, *119*, 5760−5761.

(187) González, B.; Casado, C. M.; Alonso, B.; Cuadrado, I.; Morán, M.; Wang, Y.; Kaifer, A. E. Synthesis, Electrochemistry and Cyclodextrin Binding of Novel Cobaltocenium-Functionalized Dendrimers. *Chem. Commun.* **1998**, 2569−2570.

(188) Kaifer, A. E. Interplay between Molecular Recognition and Redox Chemistry. *Acc. Chem. Res.* **1999**, *32*, 62−71.

(189) Shu, C.-F.; Shen, H.-M. Organometallic Ferrocenyl Dendrimers: Synthesis, Characterization and Redox Properties. *J. Mater. Chem.* **1997**, *7*, 47−52.

(190) Prévôté, D.; Caminade, A.-M.; Majoral, J.-P. Phosphate-, Phosphite-, Ylide-, and Phosphonate-Terminated Dendrimers. *J. Org. Chem.* **1997**, *62*, 4834−4841.

(191) Prévôté, D.; Le Roy-Gourvennec, S.; Caminade, A.-M.; Masson, S.; Majoral, J.-P. Application of the Horner−Wadsworth−Emmons Reaction to the Functionalization of Dendrimers: Synthesis of Amino Acid Terminated Dendrimers. *Synthesis* **1997**, 1199−1207.

(192) Launay, N.; Caminade, A.-M.; Majoral, J.-P. Synthesis of Bowl-Shaped Dendrimers from Generation 1 to Generation 8. *J. Organomet. Chem.* **1997**, *529*, 51−58.

(193) Larré, C.; Caminade, A.-M.; Majoral, J.-P. Chemoselective Polyalkylations of Phosphorus-Containing Dendrimers. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 596−598.

(194) Launay, N.; Caminade, A.-M.; Majoral, J.-P. Synthesis and Reactivity of Unusual Phosphorus Dendrimers. A Useful Divergent Growth Approach Up to the Seventh Generation. *J. Am. Chem. Soc.* **1995**, *117*, 3282−3283.

(195) Slany, M.; Caminade, A.-M.; Majoral, J.-P. Specific Functionalization on the Surface of Dendrimers. *Tetrahedron Lett.* **1996**, *37*, 9053−9056.

(196) Bardaji, M.; Kustos, M.; Caminade, A.-M.; Majoral, J.-P.; Chaudret, B. Phosphorus-Containing Dendrimers as Multidentate Ligands: Palladium, Platinum, and Rhodium Complexes. *Organometallics* **1997**, *16*, 403−410.

(197) Bardaji, M.; Caminade, A.-M.; Majoral, J.-P.; Chaudret, B. Ruthenium Hydride and Dihydrogen Complexes with Dendritic Multidentate Ligands. *Organometallics* **1997**, *16*, 3489−3497.

(198) Slany, M.; Bardaji, M.; Caminade, A.-M.; Chaudret, B.; Majoral, J.-P. Versatile Complexation Ability of Very Large Phosphino-Terminated Dendrimers. *Inorg. Chem.* **1997**, *36*, 1939−1945.

(199) Lange, P.; Schier, A.; Schmidbaur, H. Mono-, Di- and Trinuclear Gold(I) Complexes of New Phosphino-Substituted Amides: Initial Steps to Chlorogold(I) Diphenylphosphino-Terminated Dendrimers. *Inorg. Chim. Acta* **1995**, *235*, 263−272.

(200) Lange, P.; Schier, A.; Schmidbaur, H. Dendrimer-Based Multinuclear Gold(I) Complexes. *Inorg. Chem.* **1996**, *35*, 637−642.

(201) Reetz, M. T.; Lohmer, G.; Schwickardi, R. Synthesis and Catalytic Activity of Dendritic Diphosphane Metal Complexes. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1526−1529.

(202) Bosman, A. W.; Schenning, A. P. H. J.; Janssen, R. A. J.; Meijer, E. W. Well-Defined Metallodendrimers by Site-Specific Complexation. *Chem. Ber. /Recl.* **1997**, *130*, 725−728.

(203) Wiener, E. C.; Brechbiel, M. W.; Brothers, H.; Magin, R. L.; Gansow, O. A.; Tomalia, D. A.; Lauterbur, P. C. Dendrimer-Based Metal Chelates: A New Class of Magnetic Resonance Imaging Contrast Agents. *Magn. Reson. Med.* **1994**, *31*, 1−8.

(204) Miedaner, A.; Curtis, C. J.; Barkley, R. M.; DuBois, D. L. Electrochemical Reduction of CO_2 Catalyzed by Small Organophosphine Dendrimers Containing Palladium. *Inorg. Chem.* **1994**, *33*, 5482−5490.

(205) Nierengarten, J.-F.; Schall, C.; Nicoud, J.-F.; Heinrich, B.; Guillon, D. Amphiphilic Cyclic Fullerene Bisadducts: Synthesis and Langmuir Films at the Air−Water Interface. *Tetrahedron Lett.* **1998**, *39*, 5747−5750.

(206) Deschenaux, R.; Serrano, E.; Levelut, A. M. Ferrocene-Containing Liquid-Crystalline Dendrimers: a Novel Family of Mesomorphic Macromolecules. *Chem. Commun.* **1997**, 1577−1578.

(207) Kayser, B.; Altman, J.; Nöth, H.; Knizek, J.; Beck, W. Metal Complexes of Alkyne-Bridged α-Amino Acids. *Eur. J. Inorg. Chem.* **1998**, *1791*, 1−1798.

(208) Constable, E. C.; Housecroft, C. E.; Johnson, L. A. Dicobalt Cluster-Functionalized 2,2′:6′,2″-Terpyridine Ligands: Ruthenium(II) Complexes with Covalently Linked $C_2Co_2(CO)_6$ Units. *Inorg. Chem. Commun.* **1998**, *1*, 68−70.

(209) Newkome, G. R.; Moorefield, C. N. Chemistry within a Unimolecular Micelle: Metallomicellanoic Acids. *Polym. Prepr.* **1993**, *34*, 75−76.

(210) Marx, H.-W.; Moulines, F.; Wagner, T.; Astruc, D. Hexakis(but-3-ynyl)Benzene. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1701−1704.

(211) Newkome, G. R.; Moorefield, C. N. Metallo- and Metalloido-Micellane Derivatives: Incorporation of Metals and Nonmetals within Unimolecular Superstructures. In *International Symposium on New Macromolecular Architectures and Supramolecular Polymers*; Hüthig & Wepf Verlag: Basel, 1994; pp 63−71.

(212) Newkome, G. R. and Moorefield, C. N. Metallospheres and Superclusters. U.S. Pat. 5,516,810, 1996.

(213) Newkome, G. R. and Moorefield, C. N. Metallospheres and Superclusters. U.S. Pat. 5,376,690, 1994.

(214) Newkome, G. R.; Gross, J.; Moorefield, C. N.; Woosley, B. D. Approaches Towards Specifically Functionalized Cascade Macromolecules: Dendrimers with Incorporated Metal Binding Sites and Their Palladium(II) and Copper(II) Complexes. *Chem. Commun.* **1997**, 515−516.

(215) Newkome, G. R.; Moorefield, C. N. Metallospheres and Superclusters. U.S. Pat. 5,422,379, 1995.

(216) Newkome, G. R.; Moorefield, C. N. Metallospheres and Superclusters. U.S. Pat. 5,585,457, 1996.

(217) Epperson, J.; Ming, L.-J.; Woosley, B. D.; Baker, G. R.; Newkome, G. R. Analyzing the Infrastructure of Dendritic Macromolecules Using a Paramagnetic Metal Ion NMR Probe. *Inorg. Chem.* **1999**, submitted for publication.

(218) Newkome, G. R.; Woosley, B. D.; He, E.; Moorefield, C. N.; Güther, R.; Baker, G. R.; Escamilla, G. H.; Merrill, J.; Luftmann, H. Supramolecular Chemistry of Flexible, Dendritic-Based Structures Employing Molecular Recognition. *Chem. Commun.* **1996**, 2737−2738.

(219) Newkome, G. R.; Patri, A. K.; Godínez, L. A. Design, Syntheses, Complexation, and Electrochemistry of Polynuclear Metallodendrimers Possessing Internal Metal Binding Loci. *Chem. Eur. J.* **1999**, *5*, 2069−2075.

(220) Ottaviani, M. F.; Bossmann, S.; Turro, N. J.; Tomalia, D. A. Characterization of Starburst Dendrimers by the EPR Technique. 1. Copper Complexes in Water Solution. *J. Am. Chem. Soc.* **1994**, *116*, 661−671.

(221) Ottaviani, M. F.; Montalti, F.; Turro, N. J.; Tomalia, D. A. Characterization of Starburst Dendrimers by the EPR Technique. Copper(II) Ions Binding Full-Generation Dendrimers. *J. Phys. Chem. B* **1997**, *101*, 158−166.

(222) Yang, C.; Chen, X. M.; Lu, X. Q.; Zhou, Q. H.; Yang, Y. S. First Metal-Encapsulating Star Polysulfoxide Incorporating 2-Amino-1,3,4-thiadizole. *Chem. Commun.* **1997**, 2041−2042.

(223) Balogh, L.; Tomalia, D. A. Poly(Amidoamine) Dendrimer-Templated Nanocomposites. 1. Synthesis of Zerovalent Copper Nanoclusters. *J. Am. Chem. Soc.* **1998**, *120*, 7355−7356.

(224) Zhao, M.; Sun, L.; Crooks, R. M. Preparation of Cu Nanoclusters within Dendrimer Templates. *J. Am. Chem. Soc.* **1998**, *120*, 4877−4878.

(225) Zhao, M.; Sun, L.; Crooks, R. M. Dendrimer-Encapsulated Transition Metal Nanocluster: Synthesis, Characterization, and Applications to Catalysts. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1999**, *40*, 400−401.

(226) Zhao, M.; Crooks, R. M. Homogeneous Hydrogenation Catalysis with Monodisperse, Dendrimer-Encapsulated Pd and Pt Nanoparticles. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 364−366.

(227) Weider, S.; Pikramenou, Z. Photoactive Ruthenium(II) Cyclodextrins Responsive to Guest Binding. *Chem. Commun.* **1998**, 1473−1474.

(228) McCubbin, Q. J.; Stoddart, J. F.; Welton, T.; White, A. J. P.; Williams, D. J. Dithiocarbamate-Functionalized Dendrimers as Ligands for Metal Complexes. *Inorg. Chem.* **1998**, *37*, 3753−3758.

(229) Archut, A.; Issberner, J.; Vögtle, F. Dendrimers, Arborols, and Cascade Molecules: Breakthrough into Generations of New Materials. In *Organic Synthesis Highlights III*; Wiley-VCH: Weinheim, 1998; pp 391−405.

(230) Hsiao, J. S.; Krueger, B. P.; Wagner, R. W.; Johnson, T. E.; Delaney, J. K.; Mauzerall, D. C.; Fleming, G. R.; Lindsey, J. S.; Bocian, D. F.; Donohoe, R. J. Soluble Synthetic Multiporphyrin Arrays. 2. Photodynamics of Energy-Transfer Processes. *J. Am. Chem. Soc.* **1996**, *118*, 11181−11193.

(231) Officer, D. L.; Burrell, A. K.; Reid, D. C. Building Large Porphyrin Arrays: Pentamers and Nonamers. *Chem. Commun.* **1996**, 1657−1658.

(232) Matyjaszewski, K.; Gaynor, S. G.; Kulfan, A.; Podwika, M. Preparation of Hyperbranched Polyacrylates by Atom Transfer Radical Polymerization. 1. Acrylate AB* Monomers in "Living" Radical Polymerization. *Macromolecules* **1997**, *30*, 5192−5194.

(233) Mak, C. C.; Bampos, N.; Sanders, J. K. M. Metalloporphyrin Dendrimers with Folding Arms. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3020−3023.

(234) Nakano, A.; Osuka, A.; Yamazaki, I.; Yamazaki, T.; Nishimura, Y. Windmill-Like Porphyrin Arrays as Potent Light-Harvesting Antenna Complexes. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3023−3026.

(235) Koçak, M.; Cihan, A.; Okur, A. Ì.; Bekaroglu, Ö. Synthesis and Characterization of Novel Phthalocyanines Substituted with Four Tetraaza Macrocycles. *J. Chem. Soc., Chem. Commun.* **1991**, 577−578.

(236) Kocak, M.; Gürek, A.; Gül, A.; Bekaroglu, Ö. Synthesis and Characterization of Phthalocyanines Containing Four 14-Membered Tetraaza Macrocycles. *Chem. Ber.* **1994**, *127*, 355−358.

(237) Agar, E.; Bati, B.; Erdem, E.; Özdemir, M. Synthesis and Characterization of a Novel Phthalocyaninate Substituted with Eight Tetraazamacrocycles and Its Nonanuclear Complexes. *J. Chem. Res., Synop.* **1995**, 16−17.

(238) Jutzi, P.; Batz, C.; Neumann, B.; Stammler, H.-G. Maximum Functionalization of Metallocenes: Decaallylferrocene and Derivatives. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2118−2120.

(239) Marvaud, V.; Astruc, D. Fe(H^5-C$_5$H$_5$)$^+$ Initiated Construction of Hexaruthenium-Polypyridine Complexes. *Chem. Commun.* **1997**, 773−774.

(240) Beer, P. D.; Kocian, O.; Mortimer, R. J.; Ridgway, C. Syntheses, Coordination, Spectroscopy and Electropolymerization Studies of New Alkynyl and Vinyl Linked Benzo- and Aza-Crown Ether−Bipyridyl Ruthenium(II) Complexes. Spectrochemical Recognition of Group IA/IIA Metal Cations. *J. Chem. Soc., Chem. Commun.* **1991**, 1460−1463.

(241) Saji, T.; Aoyagui, S. Polarographic Studies on Bipyridine Complexes. I Correlation between Reduction Potentials of Iron(II), Ruthenium(II) and Osium(II) Complexes and Those of Free Ligands. *Electroanal. Chem. Interfac. Electrochem.* **1975**, *58*, 401−410.

(242) Elliott, C. M.; Hershenhart, E. J. Electrochemical and Spectral Investigations of Ring-Substituted Bipyridine Complexes of Ruthenium. *J. Am. Chem. Soc.* **1982**, *104*, 7519−7526.

(243) Achar, S.; Immoos, C. E.; Hill, M. G.; Catalano, V. J. Synthesis, Characterization, and Electrochemistry of Heterometallic Dendrimers. *Inorg. Chem.* **1997**, *36*, 2314−2320.

(244) Akiyoshi, K. Cascade Polymers as Drug Carriers. *Kagaku (Kyoto)* **1994**, *49*, 442.

(245) Anderson, H. L.; Sanders, J. K. M. Enzyme Mimics Based on Cyclic Porphyrin Oligomers: Strategy, Design and Exploratory Synthesis. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2223−2229.

(246) Brady, P. A.; Levy, E. G. Enzyme Mimics. *Chem. Ind. (London)* **1995**, 18−21.

(247) Tóth, E.; Pubanz, D.; Vauthey, S.; Helm, L.; Merbach, A. E. The Role of Water Exchange in Attaining Maximum Relaxivities for Dendrimeric MRI Contrast Agents. *Chem. Eur. J.* **1996**, *2*, 1607−1615.

(248) Kokufuta, E. Novel Applications for Stimulus-Sensitive Polymer Gels in the Preparation of Functional Immobilized Biocatalysts. *Adv. Polym. Sci.* **1993**, *110*, 157−177.

(249) Schlenk, C.; Frey, H. Carbosilane Dendrimers−Synthesis, Functionalization, Application. *Monatsh. Chem.* **1999**, *130*, 3−14.

(250) Fischer, M.; Vögtle, F. Dendrimers: From Design to Application−A Progress report. *Angew. Chem. Int. Ed.* **1999**, *38*, 885−905.

(251) Majoral, J.-P.; Caminade, A.-M. Dendrimers Containing Heteroatoms (Si, P, B, Ge, or Bi). *Chem. Rev.* **1999**, *99*, 845−880.

(252) Hearshaw, M. A.; Moss, J. R. Organometallic and Related Metal-Containing Dendrimers. *Chem. Commun.* **1999**, 1−8. Hearshaw, M. A.; Hutton, A. T.; Moss, J. R.; Naidoo, K. J. Organometallic Dendrimers: Synthesis, Structural Aspects, and Applications in Catalysis. *Advances in Dendritic Macromolecules*; Newkome, G. R., Ed.; JAI Press Inc.: Stamford, CT, 1999; Vol. 4, pp 1−60.

(253) Storrier, G. D.; Takada, K.; Abruña, H. D. Synthesis, Characterization, Electrochemistry, and EQCM Studies of Polyamidoamine Dendrimers Surface-Functionalized with Polypyridyl Metal Complexes. *Langmuir* **1999**, *15*, 872−884.

(254) Köllner, C.; Pugin, B.; Togni, A. Dendrimers Containing Chiral Ferrocenyl Diphosphine Ligands for Asymmetric Catalysis. *J. Am. Chem. Soc.* **1999**, *120*, 10274−10275.

(255) Kim, C.; Jung, I. Preparation of Dendritic Carbosilanes with Peripheral Ethynyldicobalt Hexacarbonyl Tetrahedron C$_2$Co$_2$. *Inorg. Chem. Commun.* **1999**, *1*, 427−430.

(256) Bourque, S. C.; Maltais, F.; Xiao, W.-J.; Tardif, O.; Alper, H.; Arya, P.; Manzer, L. E. Hydroformylation Reactions with Rhodium-Complexed Dendrimers on Silica. *J. Am. Chem. Soc.* **1999**, *121*, 3035−3038.

(257) Wang, R.; Zheng, Z. Dendrimers Supported by the [Re$_6$Se$_8$]$^{2+}$ Metal Cluster Core. *J. Am. Chem. Soc.* **1999**, *121*, 3549−3550.

(258) Morgan, D. R.; Stejskal, E. O.; Andrady, A. L. ^{129}Xe NMR Investigation of the Free Volume in Dendritic and Cross-Linked Polymers. *Macromolecules* **1999**, *32*, 1897−1903.

(259) Ziegler, J.; Chang, R. T.; Wright, D. W. Multiple-Antigenic Peptides of Histidine-Rich Protein II of *Plasmodium falciparum*: Dendrimeric Biomineralization Templates. *J. Am. Chem. Soc.* **1999**, *121*, 2395−2400.

(260) McAlvin, J. E.; Fraser, C. L. Metal-Centered Star Block Copolymers: Amphiphilic Iron Tris(bipyridine)-Centered Polyoxazolines and Their Chemical Fragmentation to Bipyridine-Centered BAB Triblock Copolymers. *Macromolecules* **1999**, *32*, 1341−1347.

(261) Petrucci-Samija, M.; Guillemette, V.; Dasgupta, M.; Kakkar, A. K. A New Divergent Route to the Synthesis of Organophosphine and Metallodendrimers via Simple Acid-Base Hydrolytic Chemistry. *J. Am. Chem. Soc.* **1999**, *121*, 1968−1969.

(262) Campagna, S.; Serroni, S.; Bodige, S.; MacDonnell, F. M. Adsorption Spectra, Photophysical Properties, and Redox Behavior of Stereochemically Pure Dendritic Ruthenium(II) Tetramers and Related Dinuclear and Mononuclear Complexes. *Inorg. Chem.* **1999**, *38*, 692−701.

(263) Zhao, M.; Crooks, R. M. Homogeneous Hydrogenation Catalysis with Monodisperse, Dendrimer-Encapsulated Pd and Pt Nanoparticles. *Angew. Chem. Int. Ed.* **1999**, *38*, 364−366.

(264) Bo, Z.; Zhang, L.; Zhao, B.; Zhang, X.; Shen, J.; Höppener, S.; Chi, L.; Fuchs, H. Self-assembled Mono-layers of Dendron-thiol on Solid Substarate. *Chem. Lett.* **1998**, 1197−1198.

(265) Zhao, M.; Sun, L.; Crooks, R. M. Dendrimer-encapsulated transition metal nanocluster: synthesis, characterization, and applications to catalysts. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1999**, *40*, 400−401.

(266) Miura, N.; Dubin, P. L.; Moorefield, C. N.; Newkome, G. R. Complex formation by electrostatic interaction between carboxyl-terminated dendrimers and oppositely charged polyelectrolytes. *Langmuir* **1999**, in press.

(267) Gossage, R. A.; Jastrzebski, J. T. B. H.; van Ameijde, J.; Mulders, S. J. E.; Brouwer, A. J.; Liskamp, R. M. J.; van Koten, G. Synthesis and Catalytic Application of Amino Acid Based Dendritic Macromolecules. *Tetrahedron Lett.* **1999**, *40*, 1413−1416.

(268) Enomoto, M.; Aida, T. Self-Assembly of a Copper-Ligating Dendrimer that Provides a New Non-Heme Metalloprotein Mimic: "Dendrimer Effects" on Stability of the Bis(oxo)dicopper(III) Core. *J. Am. Chem. Soc.* **1999**, *121*, 874−875.

(269) Kleij, A. W.; Kleijn, H.; Jastrzebski, J. T. B. H.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. Dendritic Carbosilanes Containing Silicon-Bonded 1-[$C_6H_2(CH_2NMe_2)_2$-3,5-Li-4] or 1-[$C_6H_3(CH_2NMe_2)$-4-Li-3] Mono- and Bis(amino)aryllithium End Groups: Structure of {[$CH_2SiMe_2C_6H_3(CH_2NMe_2)$-4-Li-3]$_2$}$_2$. *Organometallics* **1999**, *18*, 268−276.

(270) Naidoo, K. J.; Hughes, S. J.; Moss, J. R. Computational Investigations into the Potential Use of Poly(benzyl phenyl ether) Dendrimers as Supports for Organometallic Catalysts. *Macromolecules* **1999**, *32*, 331−341.

(271) Schubert, U. S.; Weidl, C. H.; Moorefield, C. N.; Baker, G. R.; Newkome, G. R. Design, Synthesis and First Metal Complexes of Dendritic 5,5″-Disubstituted-2,2′:6′,2″-Terpyridine. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1999**, in press.

(272) Cadierno, V.; Igau, A.; Donnadieu, B.; Caminade, A.-M.; Majoral, J.-P. Dendrimers Containing Zwitterionic [Phosphonium Anionic Zirconocene(IV)] Complexes. *Organometallics* **1999**, *18*, 1580−1582.

CR9800659