

Dendritic Coordination Compounds

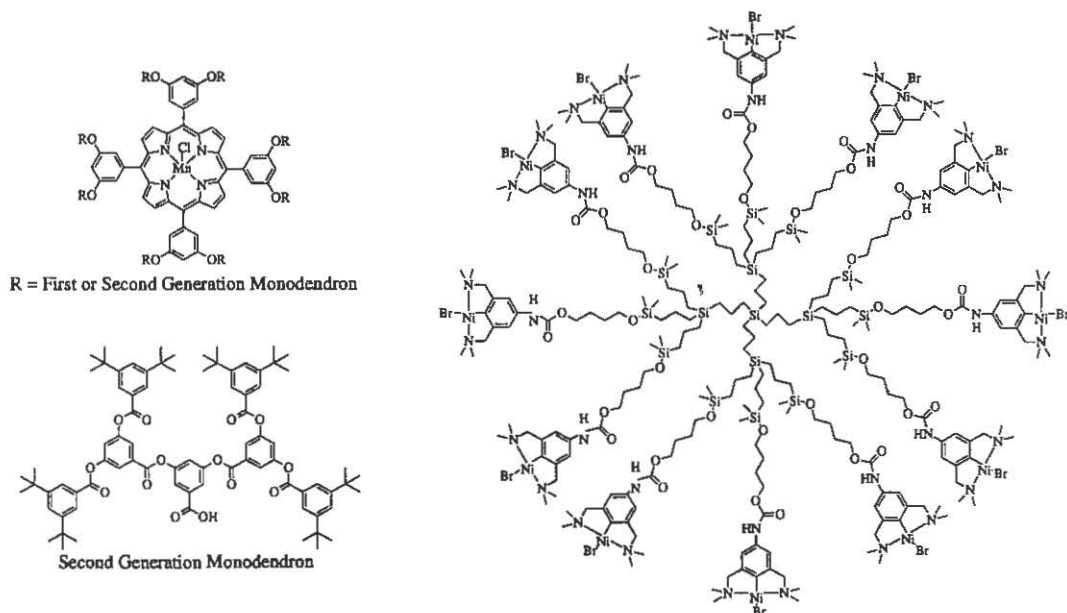
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Since the first report in 1978 of the highly branched class of molecules now known as dendrimers, there has been a rising interest in developing the chemistry of these massive species. The majority of the initial work was focused on carbon-based systems that form linkages via organic mechanisms, often involving ether bonds and peptide bonds.¹ Parallel with the development of organic dendrimers and industrial interest in them, research efforts have turned to dendrimers that contain metal centers.^{2,3}

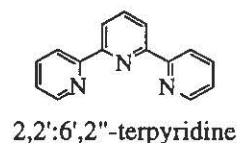
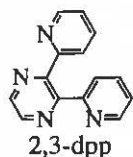
There are three basic classes of metallodendrimers, depending on the location of the metal within the dendrimer. Dendrimers with metals only at the core of the molecule⁴ and dendrimers with metals bound to the peripheral generation⁵ comprise two of these classes. One example compound from both of these classes is shown below. The third class is based



upon synthetic strategies that create dendrimers with metal centers in every generation. It has been proposed that these novel dendritic coordination compounds might exhibit photo-physical, electrochemical, or catalytic properties advantageous for molecular devices.⁶ Interesting challenges, such as insolubility and multiple diastereomer formation, arise in the syntheses of these types of dendrimers.⁷

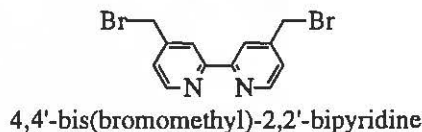
The synthesis of dendrimers requires high yield reactions for the joining of successive generations, otherwise the synthesis is impractical for creation of large generation molecules. Dendrimers of coordination complexes are designed by using ligands which can provide the control necessary for the synthesis. Recent research has led to methodologies that are simple and versatile.⁸⁻¹¹

One important concept in designing dendritic coordination compounds is the strategy described as "complexes as metals / complexes as ligands." Complexes with labile ligands are considered to function as metals while complexes with non-coordinated ligand sites function as ligands. Early work in this area utilized the bridging ligand 2,3-bis-(2-pyridyl)pyrazine (2,3-dpp). The 2,3-dpp ligand, when protected by a methyl group, can be used in octahedral

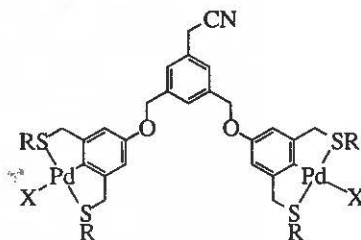


ruthenium and osmium compounds to allow for a higher level of synthetic control in the divergent formation of successive generations.¹² The ligand 2,2':6',2''-terpyridine has also been used to create numerous dendrimers.¹³ Octadecanuclear dendrimers¹⁴ and chiral heptanuclear dendrimers¹⁵ have been developed by using convergent and divergent strategies, as well as an *in situ* formation of an ether linkage between terpyridine ligands.

The oxidative addition of primary alkyl halides to platinum(II) centers is the basis for a new strategy leading to the formation of organoplatinum dendrimers.¹⁶ In this approach, diimine ligands with two pendant alkyl bromide groups (see figure below) are used in a convergent synthesis to produce dendrimers containing up to twenty-eight platinum atoms.¹⁷ Attempts to form mixed-metal dendrimers with palladium and platinum have revealed that palladium(IV) centers are not stable within the inner generations of the dendrimer.¹⁸



A divergent synthesis to form dendrimers of palladium(II) has been developed.¹⁹ The monomer in this system incorporates square planar palladium centers with one labile ligand (see figure below). After the loss of the labile ligand, a nitrile group from another monomer can bind to form a new generation. Dendrimers of up to three generations have been made by this one-pot process.²⁰ Reversible self-assembly of the monomer units to form hyperbranched organopalladium spheres has been observed in which the average sphere diameter is controlled by changing the size of the monomer or the counterion.²¹



The field of metallodendrimers, specifically those formed by iterative metal coordination reactions, is just beginning to be investigated. The success seen to date and the implications for remarkable applications in nanoscale technology²² will no doubt continue to drive interest in researching the chemistry of dendritic coordination compounds.

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