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# Routes to Metallodendrimers of the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ Core-Containing Clusters

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Received April 1, 2002

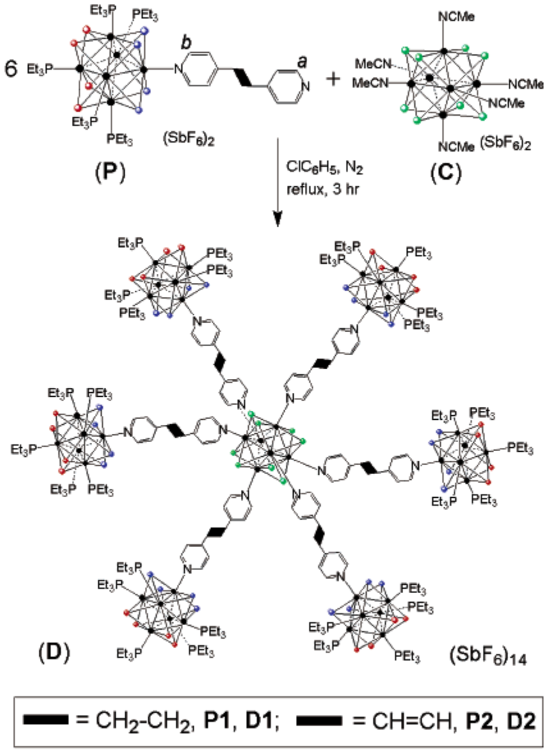
The preparation and property investigation of dendrimers constitute one of the most exciting frontiers of current chemical research.[1] The focus has shifted from mere construction of molecules with dendritic architecture to creation of materials with interesting properties and potentially important applications.[2] Metallodendrimers (dendrimers containing metal element(s) in the framework) have been contrived in this context, with the hope of integrating the unique electronic, magnetic, or catalytic properties of metals with the nanoscopic dimension of dendrimers.[3] Utilizing transition metal ions in conjunction with polydendate ligands, a great variety of metallodendrimers have been prepared, whereby the metal−ligand dative bonding serves to drive and direct the assembly of dendrimers.[3] We envision an analogous yet probably more intriguing class of metallodendrimers with the use of metal clusters in place of single metal ions. The accessible multiple metal sites of a cluster allow for structurally unique disposal of dendritic ligands. More importantly, the inherent metal−metal or metal−ligand interactions provide an opportunity for interesting and possibly useful physical and chemical properties. Thus, the study of cluster-based metallodendrimers is expected to offer many fascinating research problems with potentially important consequences.

The first cluster-supported metallodendrimers featuring a central $[Fe_4S_4]^{2+}$ cluster were reported by Gorman and co-workers.[4] It has been demonstrated that the dendritic ligands regulate both the kinetics and potential of the cluster-centered redox processes. Our own efforts in this vein resulted in the first metallodendrimers centered on the octahedral $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ cluster core.[5] These novel metallodendrimers exhibit intriguing photophysical properties that are profoundly affected by the dendritic ligands. Gorman et al have subsequently reported analogous dendrimers supported by the $[Mo_6(\mu_3\text{-}Cl)_8]^{4+}$ core.[6] Other examples of cluster-containing dendrimers include those featuring peripheral or branching metal carbonyl clusters polyoxometalates.[7]

Respectable progress notwithstanding, bona fide cluster dendrimers, characterized by the presence of cluster building blocks at the core, within the branching units, and on the periphery of the dendrimer, are not yet known. We present here the first examples of such dendritic assemblies built on the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ clusters.[8] Specifically, two first-generation metallodendrimers, each featuring a central $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ core surrounded by six units of $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(\mathbf{L})]^{2+}$ (1,2-bis(4-pyridyl)ethane, **L1**; (*E*)-1,2-bis(4-pyridyl)ethene, **L2**), have been realized; the dipyridyl-based ligands serve to bridge the central and the peripheral clusters.

The synthesis of the heptacluster dendrimers is set out in Scheme 1. Making use of the reactivity difference between the substitutionally inert phosphines and the easily displaced nitrile ligands,[9] the reaction of $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(MeCN)](SbF_6)_2$[10] with an excess of **L1** and **L2** produced respectively site-differentiated cluster derivatives, $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(\mathbf{L1})](SbF_6)_2$ (**P1**) and $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(\mathbf{L2})](SbF_6)_2$ (**P2**), each bearing an accessible pyridyl N atom capable of further metal coordination. Subsequent reactions of **P1** and **P2** with the fully solvated cluster complex, $[Re_6(\mu_3\text{-}Se)_8(MeCN)_6](SbF_6)_2$ (**C**),[10] afforded the targeted dendrimers, **D1** and **D2**, respectively.

***Scheme 1***



Both **D1** and **D2** are readily soluble in $CH_2Cl_2$, $CH_3CN$, and other common polar organic solvents. Single crystals of these compounds have so far eluded us, but microanalysis (CHN) is in agreement with the stoichiometry of the targeted dendrimers.[11] Furthermore, several lines of spectroscopic evidence convergently support the proposed molecular structure and stereochemistry. Upon the formation of **D1**, for example, the $^1H$ NMR resonance of the coordinated nitriles of **C** disappears, indicating that all the bonded solvent molecules are displaced. The signal at 9.55 ppm is attributed to the α-H atoms (**A**, Figure 1) of the pyridyl moiety bound to the central cluster core; the corresponding resonance in **P1** appears at 8.55 ppm, and is no longer present. Accompanying are the less dramatic changes of the chemical shifts of the other aromatic H atoms. The simplicity of the $^1H$ NMR spectrum is consistent with the symmetric structure of **D1**, wherein all the bridging ligands are equivalent. The proposed dendritic structure is further supported by the unsophisticated $^{31}P$ NMR spectrum (**B**, Figure 1), which

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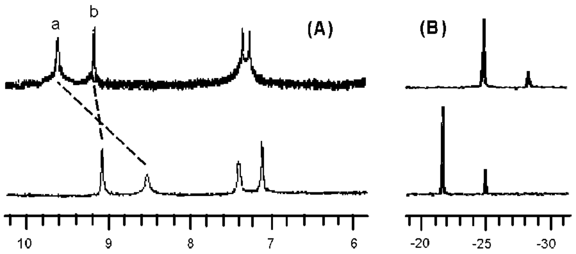

***Figure 1.*** (A) $^1$H NMR (aromatic resonances only) spectra of **P1** (lower) and **D1**. (B) $^{31}$P NMR spectra of **P1** (lower) and **D1**.

clearly shows one common chemical environment for the dendritic branching units.

The most convincing supporting evidence is provided by the comparative $^{77}$Se NMR studies of **C**, **P1**, and **D1** (Figure 2). As suggested by the top spectrum, the Se atoms of **D1** are present in three distinct chemical environments, which is indicated in Figure 1 with different colors. The relative signal intensity indicates a ratio of 3:3:1 for the different types of Se; such a ratio is mandated by, and thus in agreement with, the formulation of the heptacluster dendrimer. The signal at $-249$ ppm is a new feature when the spectrum is compared with that of **P1**, and is ascribed to the Se atoms associated with the central cluster core. This resonance is shifted downfield by 35 ppm from its equivalent at $-284$ ppm of parent **C**. The $^{77}$Se resonances of the peripheral clusters remain essentially unchanged, likely because the local structural alteration upon dendrimer formation is minimal. The use of $^{77}$Se NMR has been instrumental for the characterization of many Se-containing compounds, but has hitherto not been applied to the present and now intensively studied $[Re_6(\mu_3\text{-Se})_8]^{2+}$ clusters.[12] Our work thus presents the very first example of using $^{77}$Se NMR as a unique and definitive characterization tool for the structural determination of these fascinating multicluster arrays. This technique is especially valuable when the product identity cannot be unambiguously established by other characterization means such as mass spectrometry.[13]

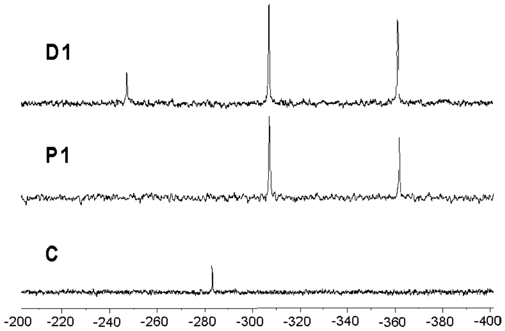

***Figure 2.*** $^{77}$Se NMR spectra of **D1**, **P1**, and **C**.

Cyclic and differential pulse voltammetric experiments of **D1** reveal two oxidation processes, the first being at $E_{1/2} = 1.26$ V (vs SCE) and chemically reversible, while the second is at 1.91 V but irreversible (see Supporting Information). The ratio of 1:6 of the number of electrons involved suggests that the first oxidation originates from the central cluster, while the oxidation at the higher potential is due to simultaneous oxidation of the surrounding clusters. The redox events are positively shifted from those of the anionic and neutral cluster analogues, a likely consequence of positive charge buildup. That the oxidation of the central cluster "camouflaged" by six cationic clusters actually occurs at a lower potential, as compared with the peripheral clusters, is intriguing, which merits further investigation.

In summary, we have presented the synthesis and characterization of the first bona fide dendrimers of metal clusters, wherein the $[Re_6(\mu_3\text{-Se})_8]^{2+}$ building components are situated at the focal point, within the branch, and on the periphery of the dendritic structure. The identity and stereochemistry of the metallodendrimers have been established, with the most convincing evidence furnished by a unique $^{77}$Se NMR spectroscopic study. Preliminary electrochemical studies suggest very interesting electronic properties of these novel metallodendrimers. A more detailed investigation of these properties and the preparation of higher generation cluster dendrimers are underway.

**Acknowledgment.** Support from Research Corporation and the University of Arizona is acknowledged. We thank Prof. N. R. Armstrong for use of the electrochemistry instrument, Dr. N. Jacobsen for help with the $^{77}$Se NMR experiments, and Prof. J. R. Long and Mr. E. G. Tulsky (Berkeley) for EI-MS analysis.

**Supporting Information Available:** Synthesis and characterization of **P1**, **P2**, **D1**, and **D2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) **D1**: Anal. Calcd for $C_{252}H_{522}N_{12}F_{84}P_{30}Re_{42}Sb_{14}Se_{56}$: C, 14.99; H, 2.61; N, 0.83. Found: C, 15.19; H, 2.66; N, 0.94. **D2**: Anal. Calcd for $C_{252}H_{510}N_{12}F_{84}P_{30}Re_{42}Sb_{14}Se_{56}$: C, 15.00; H, 2.55; N, 0.83. Found: C, 15.33; H, 2.67; N, 1.02.

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(13) FT-ICR ESI mass spectral studies of **D1** and **D2** were inconclusive; the major peaks correspond to +2 charged monocluster fragments. The high molecular weights (**D1**, 20,192.90 amu; **D2**, 20,180.84 amu) and the highly ionic nature (+14) of these compounds are probably responsible for the inability to observe the parent ions. Similar difficulty has been previously experienced with the square-shaped tetracluster arrays.[9c]

JA026377H