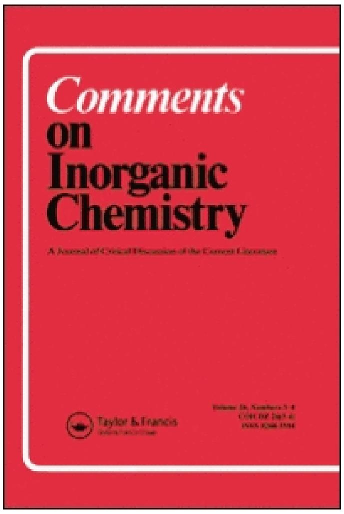

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NEW DIRECTIONS OF CLUSTER CHEMISTRY - THE STORY OF THE $[Re_6(\mu_3\text{-}Se)_8]^2$ CLUSTERS

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NEW DIRECTIONS OF CLUSTER CHEMISTRY – THE STORY OF THE $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ CLUSTERS

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Transition metal clusters are a unique class of chemical substances. Not only do they have well-defined molecular structures, they also exhibit interesting and potentially useful properties that are inherent to metal-metal bonded species. In this *Comment* our recent results in developing synthetic methodologies necessary to bring a cluster system out of the limited sphere of fundamental cluster chemistry and into general synthetic applicability are summarized. Specifically, we have explored the uses of site-differentiated cluster complexes, featuring the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ core, as stereospecific building blocks for supramolecular construction. A great variety of cluster-supported molecular and supramolecular architectures have been realized, some of which display rather interesting electronic and spectroscopic properties. Following a distinctly different line of research, we have also pursued the activation of nitriles toward nucleophilic attack, as a result of their prior coordination to the Lewis acidic rhenium sites of the cluster. The isolation and characterization of imino ester complexes proved that the cluster core acts as a powerful Lewis acid catalyst. Subsequent photocleavage in the presence of nitriles, regenerating the procatalytic solvate, marks the completion of one cycle of a potentially photocatalytic process. It is not unreasonable to imagine applying cluster-based Lewis acid activation to a range of substrates beyond nitriles and alcohols. The work therefore marks the beginning of what promises to be an exciting new chapter in cluster chemistry.

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INTRODUCTION

A quiet revolution has been developing slowly over the last half decade in the world of transition metal cluster chemistry.[1] So subtle has been its emergence that even the key players may not realize what they have started. Yet a close examination of the literature reveals that researchers are beginning to prepare, study, and utilize molecular clusters in ways never before contemplated, nor perhaps even considered possible. Catalyzed by the stunning growth of supramolecular chemistry, and to some degree by widespread interest in nanoscience, the changes are fundamental – they challenge us to think about clusters in contexts radically different from their traditional inorganic niche. Not only have we begun to think about new roles for clusters, but recent research suggests that we might begin to redefine what the cluster is, at least in the synthetic arena. To clarify, it is important to emphasize that this discussion is restricted to the cluster as defined by Cotton: "a finite group of metal atoms that are held together mainly or at least to a significant extent, by bonds directly between metal atoms, even though some non-metal atoms may also be intimately associated with the cluster."[2] Our new view of clusters does not, of course, alter this basic definition. Indeed, the large size (relative to mononuclear complexes) and the subtleties of metal-metal bonding are the very foundation upon which this revolution is built. The purpose of this *Comment* is to survey some highlights of our own synthetic manipulations of the $[Re_6(\mu_3\text{-Se})_8]^{2+}$ cluster (Fig. 1)[3] in the context of the "cluster revolution."

Closed polyhedral clusters of varying composition and geometry have fascinated inorganic chemists since the 1950's. Their topologies, chemistries, and physical properties have been an endless source of fundamental research.[4] The study of the three dimensional arrangement of atoms has been instrumental in our understanding of the very nature of the chemical bond – advancing the concept of electron delocalization, creating electron counting rules, and establishing the notion of multicenter bonding. Even though much is known about the basic nature of clusters, a great deal remains to be discovered. Hence the major emphasis of cluster research has traditionally been on simple preparation and extensive exploration of the structure/property relationship in a given cluster

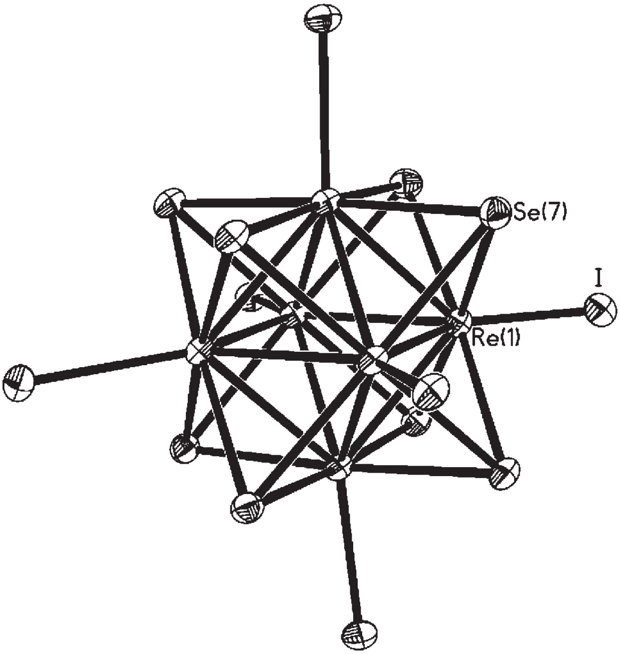


Figure 1. The structure of the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ cluster shown with terminal iodo ligands.

species. This is particularly true of the transition metal clusters. Although clusters of most transition elements are known in a vast array of nuclearities, compositions, and geometries, the bulk of synthetic research has served primarily as a means of manipulating chemically addressable variables to probe some cluster core property. The result in cluster research remains focused inward (core-based) and may appear somewhat esoteric to the chemist-at-large. However, the large size and intrinsically interesting and potentially useful properties of transition metal clusters suggest a vast, virtually untapped pool of synthetic targets that would interest a much broader audience. This observation defines the cluster revolution, *i.e.*, *the cluster revolution is the drive to take cluster chemistry beyond fundamental research and explore its potential in the general chemical and materials science fields.*

Our own efforts have focused on demonstrating the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ cluster core's utility as a highly generalized synthon for use in a variety of applications and a standard bearer for the cluster revolution.[5] To our knowledge, no other cluster system offers the combined set of properties that make the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ core ideally suited to this role. Most important of the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ cluster's attributes is its facile and high yielding preparation as the organically soluble $[n\text{-}Bu_4N]_3[Re^{III}{}_5Re^{IV}(\mu_3\text{-}Se)_8I_6]$ salt.[6] Many isostructural systems across the *d*-block do not share this luxury. In addition to its ready synthesis, the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ core is air-stable and structurally robust under most solution-phase conditions. Even when undergoing the *ca.* 1V Re^{III}-Re^{IV} redox couple the core remains intact, as suggested by the isolation of the one-electron oxidized halide complex mentioned above. As well as being structurally sound, the cluster core only allows ligand-exchange reactions to occur at the Re^{III} apices under normal conditions. This fact, combined with the kinetic inertness of the Re^{III} sites, allows fine control over the substitution chemistry.[7,8] By carefully controlling the ligand-exchange reaction conditions, one can easily prepare a range of isomers and optimize the reaction to enhance the yield of a single one. When the incoming ligand is an inert phosphine, the reaction site becomes protected, only allowing further substitutions to occur at the remaining Re^{III} apices. The protection process is referred to as "site differentiation" and is a powerful tool for fixing the stereochemistry of the cluster. The ability to fix the cluster stereochemistry turns the site-differentiated species into prefabricated building blocks with shapes commensurate with their stereochemistry. Key stereospecific isomers **(1–3)** of the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ clusters are collected in Fig. 2.[7] As well as being more stereochemically versatile than a typical mononuclear complex, the cluster core is significantly larger with Re-Re bond lengths averaging about 2.6 Å. Consequently, any molecule or material based on the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ core instead of a single-metal ion will be "cluster-expanded." Such expansion is ideal for the construction of porous solids and large host species.

Complementing the cluster core's excellent synthetic characteristics are its interesting physical properties. As already mentioned, the cluster

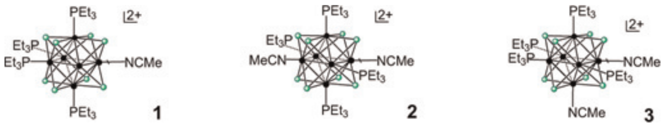


Figure 2. The chemical structures of three key stereospecific isomers of the hexanuclear rhenium cluster.

undergoes a number of reversible and quasi-reversible redox processes that are heavily influenced by the apical ligand environment.[1b] Also influenced by the ligands is the strong, broad luminescence the cluster exhibits.[9,10] Photo- and redox activity of this type suggests the cluster might act as a signal transducer of binding events in a variety of host-guest chemistry scenarios. Finally, it has been shown recently that despite the inertness of the Re^{III} apices,[11] ligands may be photolyzed from cluster.[9a] The implications for synthetic photochemistry are clear and completely unexplored.

To demonstrate the general utility of the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ cluster system, we channeled our effort into two main areas: 1) Construction of molecular and supramolecular cluster arrays, capitalizing on the cluster's stereochemistry to direct the self-assembly process; and 2) initial development of a novel "photocatalytic" cycle for the preparation of nitrile derivatives.

MOLECULAR CLUSTER ARRAYS

Novel molecules containing multiple identical redox centers have attracted much recent interest. The goals are not only to develop synthetic methodology, but also to gain electronic understanding of their possibly unique properties and to exploit these systems for practical applications.[12]

Realizing the potential of the cluster to assemble molecules featuring multiple redox centers, we proposed the synthesis of the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ cluster-supported molecular arrays (Fig. 3).[7c,13] The synthesis is a traditional ligand-exchange reaction, which we refer to as "cluster condensation," as the cluster array condenses from the starting solvate $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(MeCN)](SbF_6)_2$ (**1**) and appropriately selected multitopic ligands with concomitant expulsion of the acetonitrile molecules.

Interestingly, for each of the cluster arrays non-interaction between the clusters has been inferred from the observation of only a single redox wave at a potential that is essentially identical to that of a monocluster. Coulometry confirmed the electron counts, with the overlay of the cyclic voltammograms (Fig. 4) revealing qualitatively a nice correlation between the number of clusters and the number of electrons involved in the redox event.[14] Perhaps the cluster is predominantly capable of sustaining the charge associated with the oxidized state, without substantially polarizing neighboring clusters even when conjugated linking

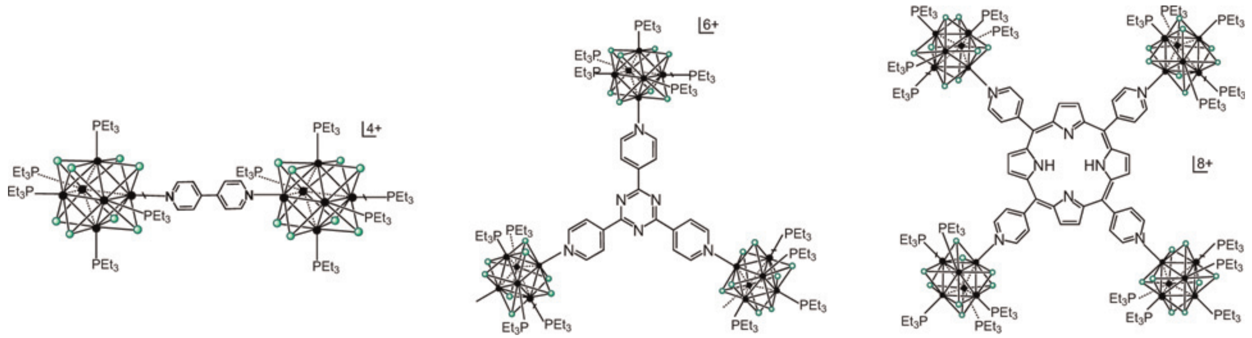


Figure 3. The chemical structures of three molecular cluster arrays bridged by multitopic ligands.

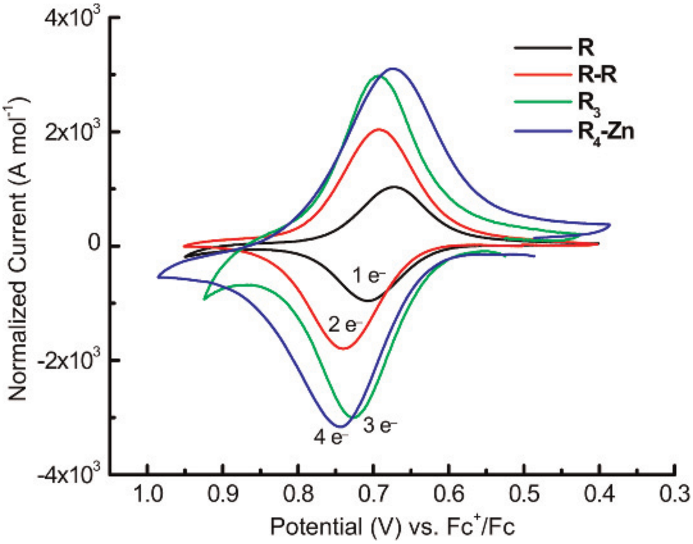
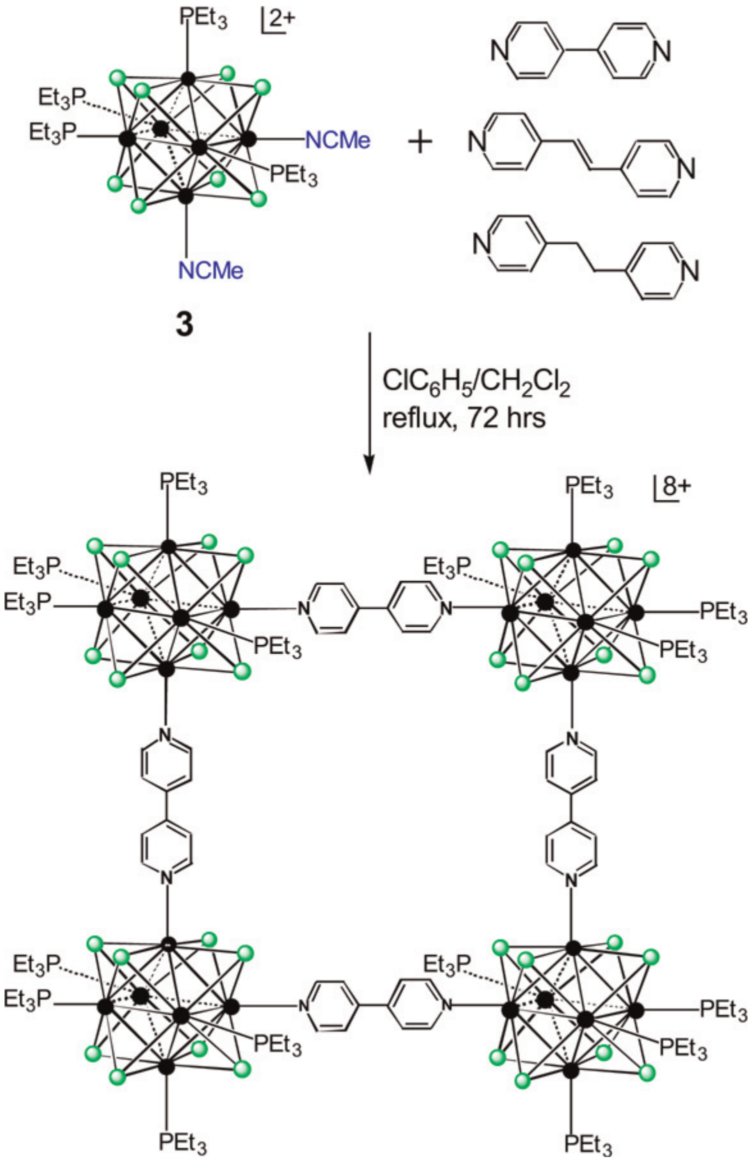


Figure 4. Normalized cyclic voltammograms (1 mV/s) for representative monomers to tetramers.

groups exist. However, the cluster is not entirely efficient in doing this, and the additive effect due to the oxidation of multiple cluster units may still result in substantial polarization of neighboring moieties, as is revealed in the dendritic arrays composed of seven $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ clusters.[15]

The cluster's ability to dictate the product geometry is best demonstrated with the formation of the first cluster-supported molecular squares.[16] This synthesis is similarly based upon ligand exchange between the cluster solvate *cis*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(MeCN)_2](SbF_6)_2$ (**3**) and pyridyl-based ditopic ligands (Scheme 1). Although we were unable to obtain single crystal structural data, the identity of the squares was established by other spectroscopic evidence. The use of the *cis*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(MeCN)_2](SbF_6)_2$ building block as the sole structural determinant was thus demonstrated. Combined with the cluster arrays in Fig. 3, we also demonstrated that the cluster condensation reaction is a viable route to molecular cluster arrays using a variety of bridging ligands, confirming the structural tunability in the cluster system. By changing the ligands used to tie the clusters together in the host framework, we could prepare hosts with varying sizes and chemical affinities.



Scheme 1. Synthesis of cluster-supported molecular squares by cluster condensation.

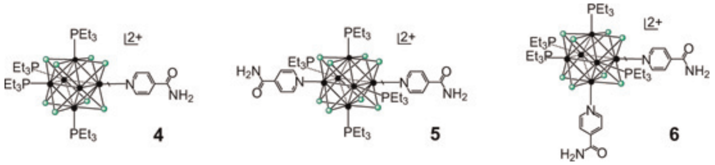
Given the strong Lewis acidity of the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ core, these cluster-based hosts might be good activators of electron rich guests.

The rapid, likely concerted self-assembly process, combined with preset *cis*-coordination, serves as a powerful kinetic tool for forming square-shaped macrocycles. Later experiments with *fac*-$[Re_6(\mu_3\text{-}Se)_8(PPh_3)_3(MeCN)_3](SbF_6)_2$ and *cis*-$[Re_6(\mu_3\text{-}Se)_8(PPh_3)_4(MeCN)_2](SbF_6)_2$ indicated that the cluster condensation route had limitations, however.[14] When the number of concerted condensation/solvent expulsion reactions necessary to form the target increases, uncontrolled oligomerization dominated the cyclization process. Likewise, depending on the electronic structure of the site-protecting ligands, the exchange kinetics of the solvent ligands for the bridging ligands may be slowed sufficiently to allow polymerization to dominate cyclization in what would appear to be a standard square reaction. These observations led us to pursue non-covalent (supramolecular) routes to cluster assemblies to allow us to extend the cluster's geometric control to higher dimensions.

SUPRAMOLECULAR CLUSTER ARRAYS

Hydrogen bonding offers an ideal means of creating arrays of clusters. The main advantage of the hydrogen bond is its inherent directional and selective binding. Directional hydrogen bonding is usually achieved by choosing strong hydrogen bond donor-acceptor (DA) pairs such as amides or carboxylic acids and arranging them in molecules such that the hydrogen-bond donors (and acceptors) extend along one or more independent axes or in symmetrically significant directions (e.g. displaced 60° from one another for a hexagonal array). Provided the DA interactions are significantly stronger than other possible interactions with solvent or counterions, the final aggregate will exhibit hydrogen bonding only in the directions dictated by their placement in the starting monomer. A naked metal ion has effectively spherical symmetry and, therefore, requires careful choice of ligands to impart any vectorial quality to the metal-ligand bond.

To demonstrate the enhanced structure directing properties of site-differentiated clusters in hydrogen-bonded assemblies, we prepared a series of cluster derivatives that used one, two, and three hydrogen-bonding capable isonicotinamide ligands (Fig. 5).[17] Isonicotinamide was chosen as the amide-amide homotopic hydrogen bond is one of the strongest neutral hydrogen bonds and therefore, one of the most



4 5 6

Figure 5. The chemical structures of three cluster complexes featuring hydrogen bonding capable ligand(s).

predictable. This series was designed to increase the dimensionality and geometric complexity of the assemblies in a controlled way, going from "zero-dimensional" hydrogen-bonded dimers to one-dimensional chains and potentially to three-dimensional cubic structures.

The monoisonicotinamide complex **4** features an isonicotinamide ligand bound to the non-phosphine protected Re site via the pyridyl nitrogen. Each cluster engages in self-complementary amide-amide hydrogen bonding to a cluster in a neighboring cell, generating a hydrogen-bonded dimer in the solid-state (not shown).

Compound **5**, the *trans*-bis(isonicotinamide) derivative of the cluster features two symmetry-related isonicotinamide ligands bound to the Re centers via the pyridyl nitrogen. The amide groups undergo conventional N–H…O hydrogen bonding with the ligand of a neighboring cluster complex, generating infinite chains featuring the cluster units and the pair-wise cluster-linking hydrogen bonds (a, Fig. 6).

Compound **6**, *cis*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(\text{isonicotinamide})_2]^{2+}$, also features one-dimensional infinite chains of clusters in the solid state, which display a zigzag topology due to *cis*-displacement of the isonicotinamide ligands (b, Fig. 6). This zigzag arrangement results in the chains fitting together to form sheets of chains. The lamellae are apparently stabilized by hydrophobic interdigitation of the phosphine groups between layers. The formation of a hydrogen-bonded square was not realized, probably due to the otherwise thermodynamically disfavored porous structure and packing thereof.

Using *fac*-$[Re_6(\mu_3\text{-}Se)_8(PPh_3)_3(\text{isonicotinamide})_3](SbF_6)_2$ (**7**)[18], attempts have also been made to generate a discrete, hydrogen-bonded cluster cube, featuring eight corner-occupying cluster units and twelve edges of paired hydrogen bonds. Instead of a cube, however, the cluster complexes form three-dimensional channels by packing such that the isonicotinamide cluster faces form the inner walls of the channels (Fig. 7).

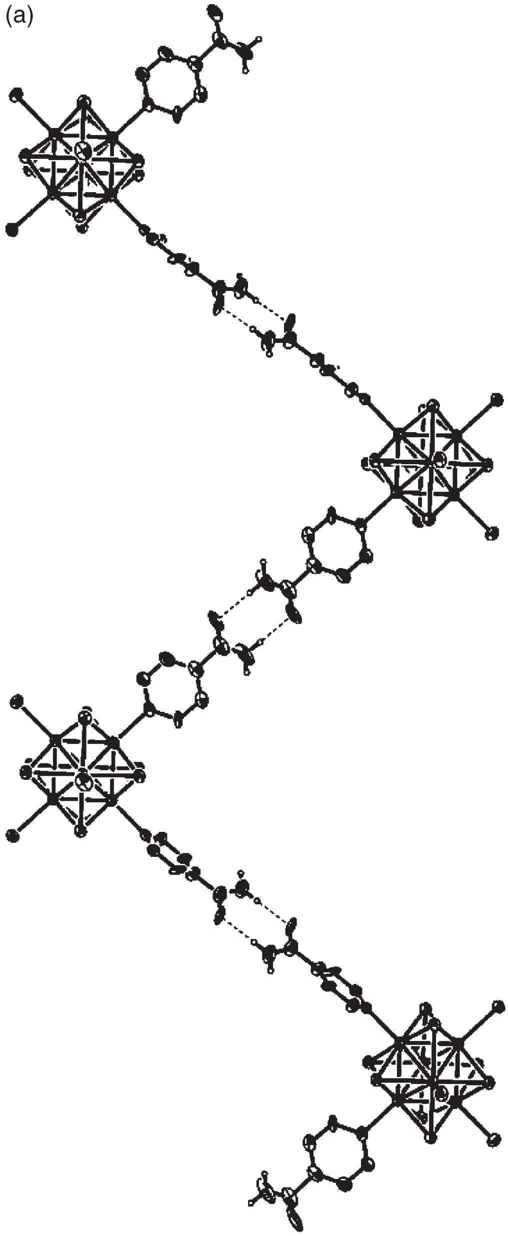


Figure 6. The structures of the hydrogen-bonded linear polymer (**5**, (a)), and zigzag polymer (**6**, (b)). Atoms rendered at the 50% probability level. The aliphatic portion of the phosphine ligands have been removed for clarity.

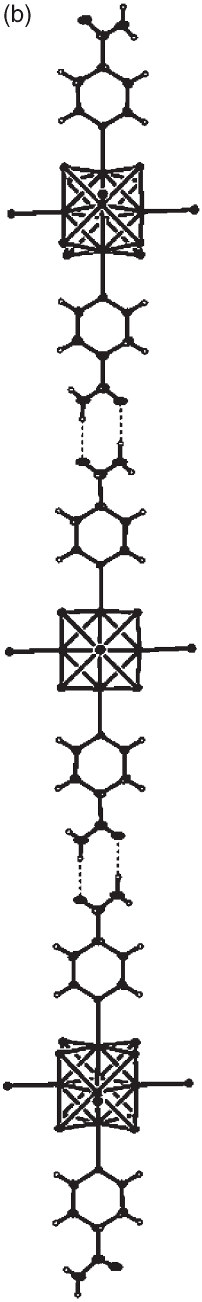


Figure 6. Continued.

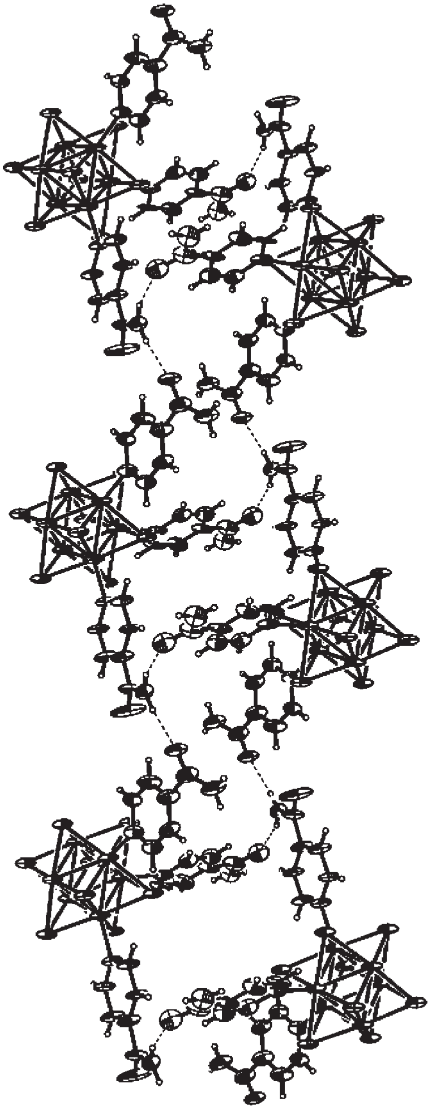


Figure 7. The hydrogen bonded channel of **7** shown side-on. Atoms rendered at the 50% probability level. Phenyl groups are excluded for clarity.

The channels are stitched together by weaker, non-complementary hydrogen bonds from the "equatorial" amides in adjacent clusters along the channel axis (Fig. 7). The very bulky and hydrophobic PPh_3 cluster faces form the outer walls. The structure may be stabilized by the clear separation of the relatively polar hydrogen bonding faces from the hydrophobic PPh_3, which subsequently engage in extensive π-π interactions with neighboring channels.

The purpose of this part of the project was to demonstrate the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ cluster core's capacity to not only support hydrogen-bonded arrays, but to direct their geometry and dimensionality. Use of the specific cluster stereoisomers $[Re_6(\mu_3\text{-}Se)_8](PEt_3)_5]^{2+}$, *trans*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4]^{2+}$, *cis*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4]^{2+}$, and *fac*-$[Re_6(\mu_3\text{-}Se)_8(PPh_3)_3]^{2+}$ in the "aufbau" synthesis of arrays **4–7** succeeded in large part in this endeavor, and provided useful guidance for future studies. With **4** and **5**, the targeted zero-dimensional dimer and one-dimensional polymer were realized, respectively; in both cases the cluster geometry exerts the dominant influence on the bulk structure. While the discrete hydrogen bonded square and cube were not realized with arrays **6** and **7**, the local cluster geometry was still expressed in the extended chains and channel structures observed in the solid state. These latter results are not too surprising considering that both targeted structures would involve large void volumes that directly contradict the principle of close packing. Still, **6** and **7** provide useful clues for obtaining the desired structure in future work.

Using cluster ligands to direct secondary metal ion coordination represents the second half of our noncovalent cluster assembly paradigm. Although some argue that this is not a true supramolecular interaction as many metal-ligand bonds clearly have large amounts of covalent character,[19] the interaction has been included in supramolecular literature since the advent of the field.[20]

Like the hydrogen bond-supported cluster assemblies, the metal-mediated assemblies are based on the creation of easily synthesized and purified monocluster building blocks. Even though the additional step of adding the secondary metal ion to a solution containing the cluster ligands is necessary, slow crystallization from the liquor increases the likelihood of realizing thermodynamically stable (not kinetically trapped) products as single crystal samples. Despite the lack of inherent directionality, transition metal ions do exhibit at least local geometric preferences and often have bond strengths approaching that of a covalent bond. Thus, with judicious choice of ligand set, the desired directionality and predictability of self-assembly may be realized with transition metals.

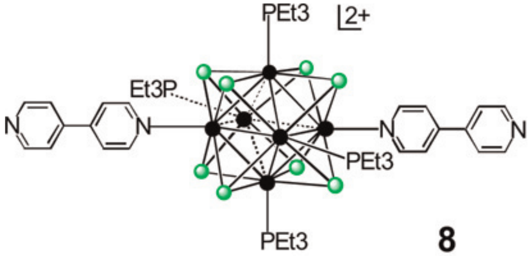
The "metal complexes-as-ligands" approach[21] offers two distinct advantages over traditional organic ligands. The first and most obvious is the fact that the complex ligand will bring its own physicochemical properties to the ensemble, significantly easing the challenge of creating heterometallic and/or mixed redox state materials. Second, the geometric preferences of a given complex ligand allow the realization of building blocks with shapes not trivially nor cheaply generated with purely organic molecules. Relative to traditional coordination polymers and oligomers, more sophisticated structures may be anticipated.

With the demonstration of the aufbau synthesis of hydrogen-bonded arrays directed and supported by the $[Re_6(\mu_3\text{-Se})_8]^{2+}$ cluster stereoisomers, we were confident that the cluster core would be ideal in the role of "cluster complex-as-ligand." Although the coordination to a naked metal ion sacrifices some of the directionality and predictability of a hydrogen-bonded linkage, the large size and rigid displacement of cluster-supported ligands are likely to ameliorate some of the potentially complicating factors associated with self-assembly (e.g. packing forces, ligand flexibility).

Relevant to our research is the recent work of the groups of Fedorov[22] and Long.[23] Both of these groups have focused on using the $[Re_6(\mu_3\text{-Se})_8]^{2+}$ cluster core to create analogues of the well-known Prussian blue phases. By replacing the hexacyano complex of iron with the persubstituted $[Re_6(\mu_3\text{-Se})_8(CN)_6]^{4-}$ tetraanion, the two groups independently synthesized cluster-expanded Prussian blues. The Long group is actively pursuing applications in chemical sensing, as these arrays exhibit dramatic color change in the presence of specific solvent vapors.

Our efforts focused on two distinct supramolecular motifs (Fig. 8). The first, intended as a proof of concept, was a series of linear coordination polymers based on *trans*-$[Re_6(\mu_3\text{-Se})_8(PEt_3)_4(4,4'\text{-dipyridyl})_2](SbF_6)_2$ (**8**, Fig. 8).[24] The secondary metal ions, Co^{2+}, Zn^{2+}, and Cd^{2+} were chosen to represent both open and closed shell ions and to establish what role orbital and electronic factors might play in the final assembly.

As a representative, the crystal structure of the coordination polymer formed between the complex ligand **8** and $Cd(NO_3)_2$ is depicted in Fig. 9. It is a linear polymer with a repeat unit consisting of a single *trans*-$[Re_6(\mu_3\text{-Se})_8(PEt_3)_4(4,4'\text{-dipyridyl})_2]$ unit bound to a Cd^{2+} ion via the open nitrogen of a single 4,4′-dipyridyl ligand. The cadmium is bound



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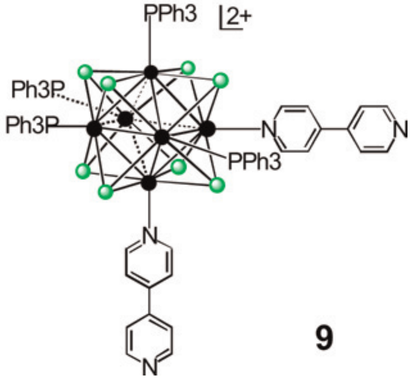


9

Figure 8. The chemical structures of two cluster complex ligands, **8** and **9**.

to a second pyridyl nitrogen from the next repeat unit. The $N_{pyridyl}$-M^{2+}-$N_{pyridyl}$ coordination mode is *trans*. Charge is balanced by a single SbF_6^- counterion and three nitrato ligands bound to the cadmium ion. The polymer formed by this repeat unit has significant curvature between the Re atom coordinated to one end of the 4,4′-dipyridyl ligand and the Cd^{2+} unit at the other—a result of the summation of small shifts from linearity at each individual bond between the two metals. The curvature results in the polymers forming sinusoidal chains of modest amplitude and the chains form a lamellar structure in the solid state with each layer composed of parallel polymer chains.

Probably due to the extended rigid structure, the highly crystalline compound was insoluble in dichloromethane, in stark contrast to the starting cluster complex **8**. But it was readily soluble in water and common polar organic solvents such as alcohol, MeCN, DMF, and DMSO, and the extended structure was presumably disrupted in these solvents.

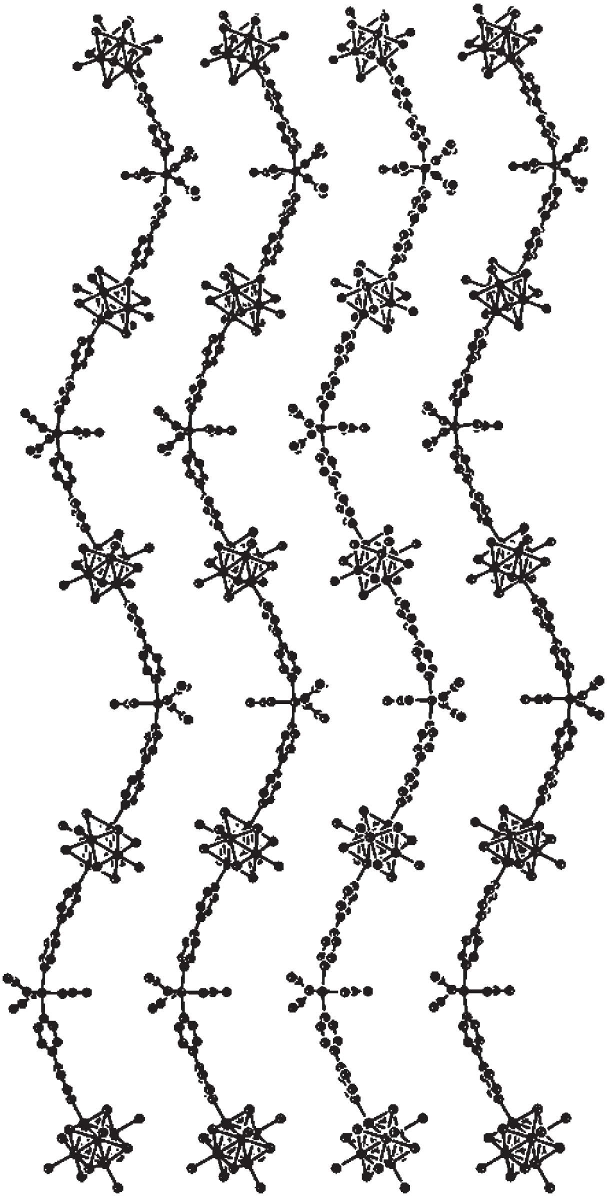


Figure 9. The sinusoidal coordination polymer mediated by Cd^{2+}. The aliphatic portion of the phosphine ligands have been removed for clarity.

However, the hybrid polymer can be re-generated upon ether vapor diffusion to these solutions. And this dissolution and recrystallization process provided a convenient means of purification.

Analogous coordination polymers were obtained with other secondary metal ions, save some variations in the details of the solid state structure. These polymers are aesthetically pleasing supramolecules and serve as excellent proofs-of-concept for the utility of cluster-expanded "big bpy" ligands. However, as our goal is the creation of *rationally designed* host compounds, it is clear that greater control over the geometry and dimension of the assembly is required.

To this end, the second cluster ligand was devised.[25] By reacting *cis*-$[Re_6(\mu_3\text{-Se})_8(PPh_3)_4(MeCN)_2](SbF_6)_2$ with an excess of 4,4′-dipyridyl, the desired cluster ligand, *cis*-$[Re_6(\mu_3\text{-Se})_8(PPh_3)_4(4,4'\text{-dipyridyl})_2](SbF_6)_2$ (**9**, Fig. 8), was prepared. There is an enforced right angle between the two dipyridyl ligands, each with one of its N atoms coordinated to the cluster, leaving the other available for further metal coordination. We hoped to realize a very large molecular square with the cluster forming the corners. Of course, several other structures were possible and perhaps more likely when considered from a crystal energetics perspective.

Upon vapor diffusion of ether, a mixture of **9** and $Cd(NO_3)_2 \cdot 4H_2O$ produced a highly crystalline solid **10**, formulated as $[\{Re_6(\mu_3\text{-Se})_8(PPh_3)_4(4,4'\text{-dipyridyl})_2\}_2\{Cd(NO_3)_2\}](SbF_6)_4 \cdot 21C_4H_{10}O \cdot 21CH_2Cl_2$. Its solid-state structure is shown in Fig. 10, displaying a one-dimensional chain

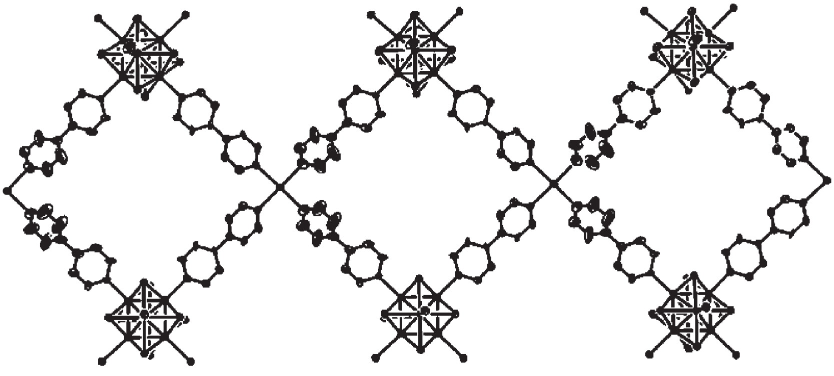


Figure 10. The fused square structure of **10**. The phenyl portion of the phosphine ligands have been removed for clarity.

of corner-sharing squares. Each shared corner is a single octahedrally coordinated Cd^{2+} ion, bound in the equatorial plane by four pyridyl nitrogens and axially by two NO_3^- ligands. The unshared corners are formed by the *cis*-$[Re_6(\mu_3\text{-}Se)_8(PPh_3)_4]$ cluster units.

Interestingly, the cluster/Cd^{2+} ratio significantly affected the outcome of the assembly. Using a large excess of the Cd^{2+} salt, compound **11**, formulated as $\{[Re_6(\mu_3\text{-}Se)_8(PPh_3)_4(4,4'\text{-dipyridyl})_2]\ [Cd(NO_3)_3]\}(NO_3) \cdot 2C_4H_{10}O \cdot CH_2Cl_2$, was isolated quantitatively. Its solid-state structure is a one-dimensional zigzag chain, featuring repeating units of $\{[Re_6(\mu_3\text{-}Se)_8(PPh_3)_4(4,4'\text{-dipyridyl})_2][Cd(NO_3)_3]\}^-$ (Fig. 11). This single-chain coordination polymer may be regarded as derived from **10**–the fused-square coordination polymer – by formally zipping through the middle of the squares.

The cluster complex ligand is clearly a true structure director. The rigid geometry of the *cis*-$[Re_6(\mu_3\text{-}Se)_8(PPh_3)_4(4,4'\text{-dipyridyl})_2]^{2+}$ ligand limits the number of possible architectures that may be generated. The formation of the extended structure is nevertheless dependent as well on the coordination of the secondary metal ions. Conceivably it is the ***balance*** between the thermodynamic forces of the close packing of the polymeric chains and the coordination of Cd^{2+} that is ultimately responsible for the formation of a particular structure.

Utilizing both hydrogen bonding and metal coordination as supramolecular forces to mediate the assembly of the cluster arrays described here, we have established that the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ clusters are indeed superior building blocks for supramolecular construction. The complete set of building blocks available from the cluster basis, combined with the adaptability to any assembly mode, will no doubt make the task of uncovering these secrets considerably easier.

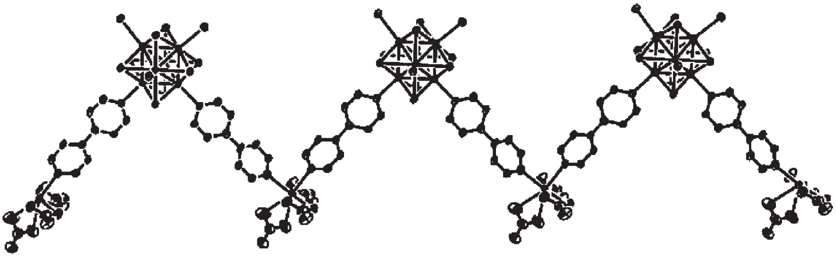


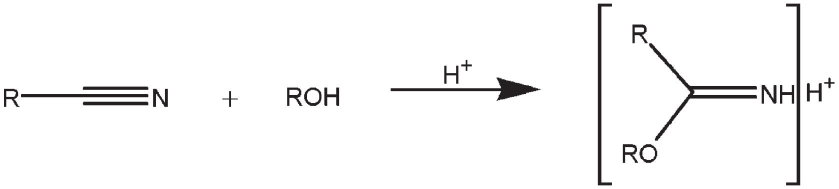
Figure 11. The *cis*-, *cis*-(*cis*- at both cadmium and cluster sites) zigzag chain observed for **11**.

CLUSTER-MEDIATED AND PHOTO-ASSISTED PINNER REACTIONS

Throughout the period of this research project, we have had occasion to consider the fundamental nature of the cluster core. Despite the fact that the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ cluster core is electron precise, it is an early transition metal cluster. Consequently, the Re^{III} apices "desire" electron density and are extremely strong Lewis acid sites. This is most noticeable in the ^{1}H NMR spectra of the solvates and pyridine derivatives, all of which feature strong downfield shifts relative to the free ligands.[7,16] In certain experiments involving the acetonitrile solvates $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_{6\text{-}n}(MeCN)_n]^{2+}$, workup using alcohols resulted in spectra that revealed not only the solvate but some unexpected signals. Aware that the coordinated nitrile was likely activated toward nucleophilic attack, we surmised that the new species were the result of limited alcoholysis of the nitrile ligand(s). Still, quantities were minute – the new products were treated as impurities and removed. More importantly, the cluster was known to be inert to ligand exchange, making the removal of any modified ligands for further analysis difficult. Because of the issue with cluster inertness, further research in this vein was deemed futile.

However, recent work by Holm and colleagues dramatically changed the situation.[9,11] They had been studying the effects of the terminal ligands on cluster luminescence when a pronounced solvent effect was discovered.[9] In the absence of coordinating media, it was found that excited state lifetimes and quantum yields were significantly attenuated. In a coordinating solvent, lifetimes were restored along with increased quantum yields. The group concluded that this evidence was consistent with excited-state dissociation of the apical ligands. In another study, Holm and Gray quantified the ground state ligand exchange kinetics and conclusively demonstrated that the cluster is inert in the ground state and that the previously observed ligand exchange could only be the result of photoexpulsion.[11] Now the way was clear to a whole new chapter of very promising synthetic chemistry.

In light of Holm's findings and our own observation of nucleophilic additions to the acetonitrile cluster solvates, we began to look more closely at nitrile chemistry. The study of nitrile hydrolysis to yield amides is a mature field; the reaction is known in biology through the action of the nitrile hydratases.[26] More interesting from both a fundamental and application standpoint are the analogous alcoholysis reactions. The

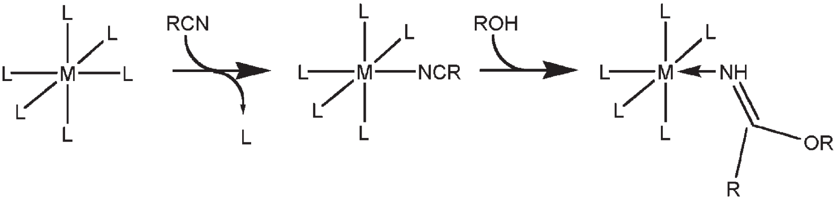


Scheme 2. The acid-catalyzed Pinner reaction, affording the unstable iminium cation.

process of nucleophilic addition of alcohols to the nitrile carbon is known in organic synthesis as the Pinner reaction (Scheme 2).[27] Because the HN=C(OR)R′ fragment cannot tautomerize like the hydrolytic intermediate HN=C(OH)R, the isolated product is the reactive imino ester. The imino esters are desirable intermediates in polymer and peptide syntheses but are usually prepared as the iminium hydrochloride. The iminium hydrochloride often requires neutralization to be accessible, and the process can easily destroy the imino ester by hydrolysis to the more stable amide.

Consequently, a vast amount of literature exists on the use of Lewis acid catalysis (both transition metal and main group elements) to generate the neutral imino ester directly.[28] This method is based on the two-step process shown in Scheme 3. The first step entails the coordination of the free nitrile to the catalyst via the nitrogen lone pair. The Lewis acid then polarizes the C–N triple bond, shifting electron density away from the nitrile carbon nucleus. This lowers the activation barrier to nucleophilic attack at the nitrile carbon; subsequent addition of the alcohol generally proceeds to generate the coordinated imino ester.

The challenge lies in the implicit step of releasing the imino ester. Transition metal complexes, particularly the stronger Lewis acids of



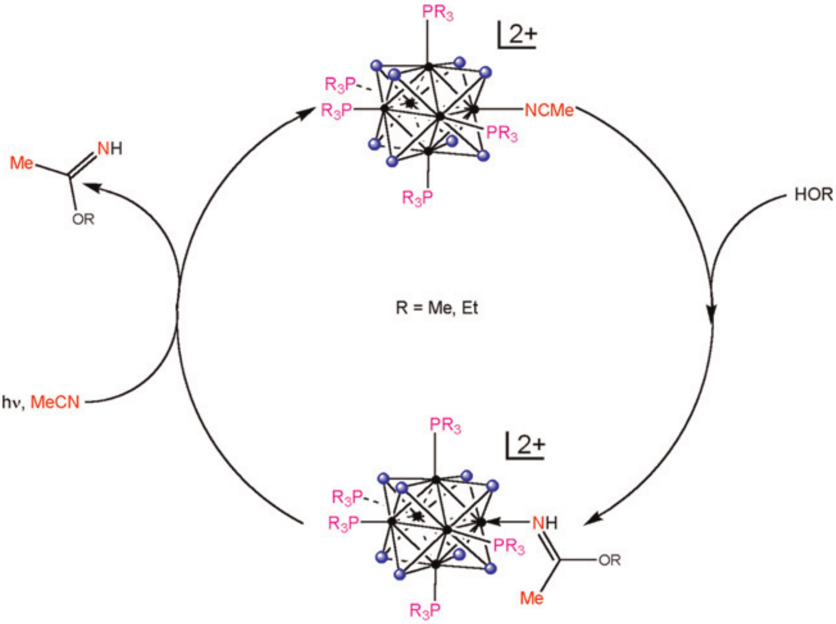
Scheme 3. The metal-mediated Pinner reaction, yielding the generally inert imino ester complex.

the early series, tend to make decomplexation very difficult or impossible. The first reason for this is the Lewis acid strength itself. The more activating the complex, the more tightly bound the substrate. Worse, imino ester nitrogens are more basic than nitrile nitrogens. Once converted to the imino ester, the ligand is even less labile than the activated nitrile. The second barrier to release often comes from the formation of a chelate complex. The oxygen atom of the imino ester bears lone pairs that readily coordinate to available sites on the complex. Naturally, the chelate effect virtually prohibits release of the imino ester, save by complete decomposition of the complex. There are means of surmounting these two obstacles, but they require particularly careful catalyst design and control of conditions. The work of Pombeiro, Kukushkin, and colleagues is some of the most thorough and well developed in this area.[29] The collaborative effort has developed processes based on Pt(II/IV) complexes, which do release free imino esters and related compounds. Still, their "pop-the-cork" strategy relies on the introduction of strong chelating ligands to displace the imino esters, limiting the turnover number to one. As might be expected, catalytic generation of imino esters is rarer still. To the best of our knowledge, only one study demonstrated catalytic generation of free imino esters, and these were from "preactivated" halonitriles such as $NC(CCl_2H)$.[30]

Our review of metal-mediated Pinner chemistry clearly revealed a challenge that the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ cluster core might easily address. Although only circumstantial evidence suggested that the alcohol addition reaction could work, the cluster's strong Lewis acidity made success seem highly probable. More importantly, the cluster's newfound photolability promised to overcome issues regarding the release of the addition product. With the ultimate goal of creating a (photo)catalytic cycle, we proposed the photoassisted Pinner reaction shown in Scheme 4.

Experimentally, the monoacetonitrile cluster solvate $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(MeCN)][SbF_6]_2$ (**1**) was treated with methanol. The reaction proceeded smoothly and the corresponding methoxy imino ester complex $\{Re_6(\mu_3\text{-}Se)_8(PEt_3)_5[HN{=}C(OCH_3)(CH_3)]\}(SbF_6)_2$ (**12**) was obtained in excellent yields at ambient temperature.

Spectroscopic evidence supported the formation of the imino ester complex. Its identity was further confirmed by single-crystal diffraction. The structure is shown in Fig. 12. The cluster core appears unaffected by the addition reaction, with bond lengths and angles of the core varying insignificantly relative to other clusters. Although the Re-N bond length



Scheme 4. Proposed photocatalytic generation of free imino esters using a cluster based Lewis acid catalyst.

is also unremarkable, other metric parameters concerning the coordinated imino ester ligands clearly manifest the anticipated consequence of the nitrile-to-imino ester transformation.

With the imino ester complex of the cluster in hand, it remained to complete the second half of the catalytic cycle shown in Scheme 4. To this end, an acetonitrile solution of the imino ester cluster complex was subjected to UV irradiation and the photolysis was monitored by NMR spectroscopy in order to follow the reaction progress. Both the ^{1}H and $^{[31]}$P NMR spectra showed a smooth consumption of the starting imino ester complexes and simultaneous emergence of signals attributed to the regeneration of the starting nitrile complex. Extracts of the photolysis product(s) did not contain enough material for reliable NMR characterization, but were sufficient for GC-MS analysis. An early eluting fraction ionized to yield a base peak that matched the molecular ion of the free methyl imino ester (m/z 73 amu) and a second peak corresponding to acetamide (m/z 59 amu), the very stable hydrolysis product of the imino ester.

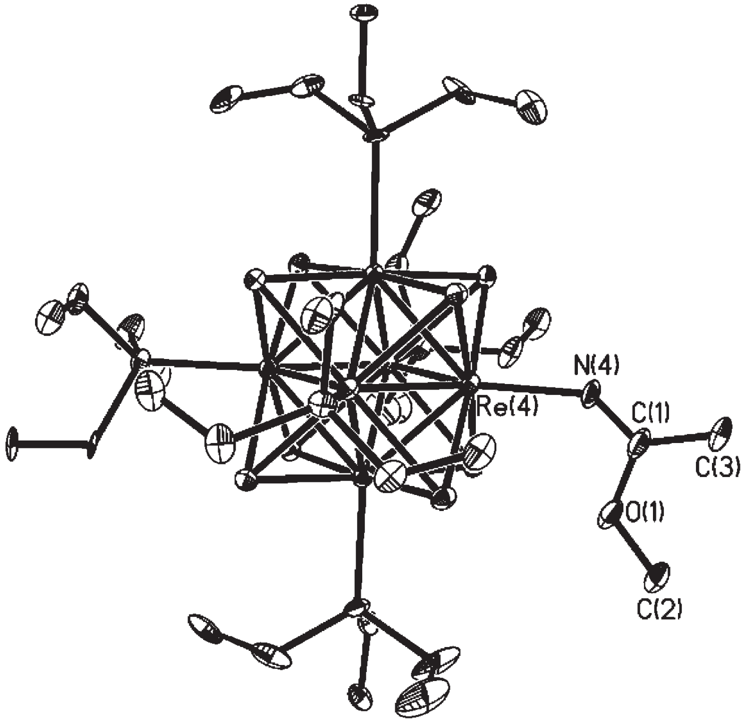


Figure 12. The crystal structure of the cluster complex (**12**) with a methyl imino ester ligand of the. Atoms are rendered at 50% probability; anions and H-atoms have been removed for clarity.

We have thus successfully completed each step in a novel, cluster-based photocatalytic cycle. Although currently stoichiometric, these early results demonstrate the feasibility of such a cycle, which may become catalytic in the starting nitrile complex upon optimization of conditions. More generally, this work offers a new route to metal-mediated organonitrile additions with a built-in means to avoid the typical inertness of the resultant imino ester complexes. Given the known versatility of the Re^{III} coordination chemistry in these cluster systems, it is not unreasonable to imagine applying cluster-based Lewis acid activation to a range of substrates beyond nitriles. Our work therefore marks the beginning of what promises to be an exciting new chapter in the remarkable chemistry of the $[Re_6(\mu_3\text{-Se})_8]^{2+}$ clusters.

CONCLUSIONS

The purpose of our studies was to demonstrate the general synthetic utility of the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ cluster core. This was to be accomplished by developing and executing synthetic strategies and methods to address two current themes in chemistry at large: supramolecular construction and catalysis. Of course, the project could only approach specific areas within these two large fields. With regard to supramolecular construction, we sought to demonstrate that the stereochemistry of the site-differentiated cluster derivatives $[Re_6(\mu_3\text{-}Se)_8(PR_3)_{6-n}(L)_n]^{2+}$ could dictate the structural outcome of self-assembly processes. The catalytic problem we pursued was the activation of nitriles to nucleophilic attack by the strongly Lewis acidic rhenium sites of the cluster. The prospect of a catalytic cycle was only recently made possible by the discovery of the cluster core's excited state photolability.

In both areas, the principal focus was on the isolation and structural characterization of the targeted molecules. Since the efforts were intended to prove the general utility of the cluster core in synthesis, preparative methods needed to be developed. However, this is merely the first step in practical development. It is therefore important to consider future directions for the research and suggest experiments to further our understanding of the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ core's chemistry.

With regard to the supramolecular aspects of the cluster system, the potential for future experimentation is truly limited only by imagination. As has been demonstrated, the combination of readily controlled cluster stereochemistry and carefully selected ligands and linking modes, virtually any structural motif may be realized. However, simply generating novel structure by blind empiricism is not necessarily a useful scientific pursuit. In light of the current status of the supramolecular endeavors, there are two fundamental and practical directions the research must take.

The first is the development of a reliable method to control the "tertiary structure" of the final products. The primary (cluster stereochemistry) and secondary (cluster linkage mode) structure was demonstrated. However, realization of the tertiary structure was often hindered by the multitude of competing forces involved in the self assembly process. One of the most promising methods for controlling the assembly process is the use of templates, or "innocent guests," which may be removed upon isolation of the host compounds. This may be accomplished in a number of ways, such as the use of linking moieties that feature functionalities designed to interact weakly with the templates, for example. Another means of controlling the tertiary assembly might be the employment of other even more labile solvates; the problems we faced with slow cyclization might be avoided by replacing the acetonitrile solvates with the more labile solvates such as those of alcohols. In this way, the extremely rapid ligand exchange reaction should favor cyclized products.

The second critical direction the supramolecular studies must follow is the characterization of the materials functions. Of course, this depends to some degree on the success of the further development of the synthetic chemistry, since most of the complexes prepared in the present project were proofs-of-concept. Once better control over tertiary structure is achieved, quantification of structural robustness and strength and extent of host-guest interactions needs to be performed. Also, in order to address possible applications as catalysts or molecular sensors, the bulk physical properties of the materials should be characterized. Of particular interest are guest diffusion rates and binding constants, as well as photo- and redox shifts observed upon guest incorporation.

The catalytic work is a purely chemical endeavor and the work is clearly only the first brief glance at what promises to be a very fruitful research project. The most obvious focus for the immediate future is a more thorough investigation of the nuances of the already executed research. For example, it is necessary to fully describe the actual Lewis acid catalytic rate enhancement for the alcohol addition reaction in the context of other known systems. It would be desirable to determine how general the chemistry is, i.e., establish what types of bonds may or may not be formed and to explore the use of more than one Re^{III} site.

To summarize, none of the work we and others have done with the remarkable $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ cluster might appear revolutionary. However, we have been able to capitalize on the cluster's unique properties and execute research that would not be possible with any other single chemical system, cluster or otherwise. Hopefully, some aspect of this research will catch the eye of a non-cluster chemist who will truly bring the system out into full view and fulfill the purpose of the cluster revolution.

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