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Alcohol Addition to Acetonitrile Activated by the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ Cluster Core

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The addition of methanol and ethanol to the previously reported cluster solvates $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(MeCN)](SbF_6)_2$ and *trans*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(CH_3CN)_2][SbF_6]_2$ afforded three cluster complexes with imino ester ligands: $\{Re_6(\mu_3\text{-}Se)_8(PEt_3)_5[HN{=}C(OCH_3)(CH_3)]\}(SbF_6)_2$, $\{Re_6(\mu_3\text{-}Se)_8(PEt_3)_5[HN{=}C(OCH_2CH_3)(CH_3)]\}\{SbF_6\}_2$, and *trans*-$\{Re_6(\mu_3\text{-}Se)_8(PEt_3)_4[HN{=}C(OCH_3)(CH_3)]_2\}\{SbF_6\}_2$. In all cases, predominant formation of the *Z* isomers was observed.

Keen experimental and theoretical efforts are currently focused on the face-capped octahedral clusters $[Re_6(\mu_3\text{-}Q)_8]^{2+}$ (Q = S, Se, Te).[1] These cluster species, particularly those of the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ core, have proven to be quite amenable to synthetic manipulation[2−4] and exhibit interesting electrochemistry and photophysical properties.[5] Consequently, a host of derivatives, monoclusters, and multicluster arrays with intriguing properties have rapidly appeared in the literature.[1a−h,2−4]

Prominent among the unique spectroscopic features of these derivatives are the substantial downfield chemical shifts in the ^1H NMR spectra of the bound ligands versus their free ligand counterparts.[1e,3] This serves as a hallmark of coordination to a strong Lewis acid, which, it is presumed, significantly activates an otherwise inert ligand to further transformation. New chemistry may be discovered, and the development of novel catalysis schemes may be possible as a result. However, the reactivity of the ligands bound to these clusters has not yet been explored, thus providing impetus for our efforts described herein.

Our initial attempts have been focused on the nucleophilic addition to the nitrile molecule(s) bound to the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ core. Cluster solvates of the general formula $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_{6-n}(MeCN)_n][SbF_6]_2$ [$n = 1$, 2 (cis and trans), 6][3] can be readily prepared, and their synthetic utility in constructing other cluster derivatives, including multicluster arrays, has been demonstrated.[1e,3] Substantial downfield chemical shifts of up to 1 ppm have been shown for the cluster-bound nitrile ligand(s). We note that nitrile hydrolysis promoted by di-, tri-, and tetranuclear Re clusters has recently been reported, but surprisingly alcohol addition to the same cluster-bound nitriles was not observed, even when alcohols were used as the bulk solvent.[6] On the other hand, nucleophilic addition with alcohol to metal-activated organonitrile is well established in mono- and dinuclear systems of many other metal elements, affording derivatives with imino ester ligands.[7] However, catalytic generation of free imino esters—valuable intermediates in synthetic organic chemistry[8]—is rare.[9] These intriguing results prompted us to study the reactivity of the nitrile ligand(s) bound to the hexanuclear Re cluster core.

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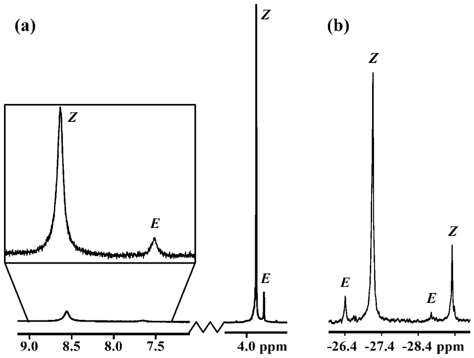

Figure 1. (a) ^1H (partial showing of the resonances of the imino methyl ester ligand) and (b) ^{31}P NMR spectra of $\{Re_6(\mu_3\text{-}Se)_8(PEt_3)_5[HN{=}C(OCH_3)(CH_3)]\}\{SbF_6\}_2$ showing the signals attributable to both the *Z* and *E* isomers.

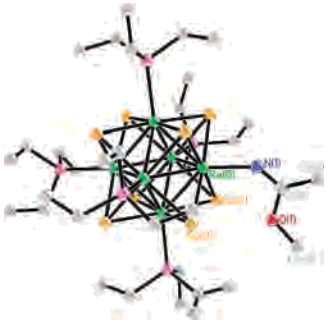

Figure 2. ORTEP view (25% ellipsoids) of the cationic cluster of **2** with partial atomic labeling. H atoms are omitted for clarity. Color scheme: C, gray; N, blue; P, purple; Re, green; Se, yellow.

Herein the synthesis and characterization of three new $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ cluster complexes featuring imino ester ligands derived from alcohol addition to cluster-bound acetonitrile molecule(s) are reported (see the Supporting Information for experimental details). Stimulated by the recent discovery of the photolability of certain $[Re_6(\mu_3\text{-}Q)_8]^{2+}$ cluster complexes,[5g] we have also carried out preliminary photolytic studies for one of these imino ester complexes, with the hope of finding ways to liberate the imino ester ligand while regenerating the potentially precatalytic nitrile complex.

The previously reported cluster solvate $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(MeCN)][SbF_6]_2$ (**1**)[3] was dissolved in neat methanol. The resulting orange-yellow solution was stirred at room temperature for 12 h, producing in quantitative yield the corresponding imino methyl ester complex $\{Re_6(\mu_3\text{-}Se)_8(PEt_3)_5[HN{=}C(OCH_3)(CH_3)]\}\{SbF_6\}_2$ [**2**$(SbF_6)_2$]. Its ^1H NMR spectrum (Figure 1a) in a CD_3CN solution features a mixture of the *E* an *Z* isomers with broad singlets at 8.57 and 7.65 ppm (−NH; *Z*/*E*, respectively), sharp singlets at 3.88 and 3.78 ppm (−OMe; *Z*/*E*, respectively), and a singlet at 2.43 ppm (not shown) attributable to the original nitrile methyl; this peak is upfield-shifted upon the addition of methanol from its initial position at 2.79 ppm. The chemical shift values overall agree with those reported for similar mononuclear imino ester complexes of strong Lewis acid centers;[10] the predominance of the *Z* isomer, corresponding to the trans addition of an alcohol to the nitrile triple bond, is suggested. This is surprising because in previous studies the products are often either solely the *E* isomer or an equilibrium mixture of both.[7] Furthermore, facile interconversion between the *Z* and *E* isomers subsequent to the addition and purification is common, especially when a base, believed to function as a catalyst, is present.[7]

The ^{31}P NMR spectrum (Figure 1b) also exhibits major resonances due to the *Z* isomer at −27.2 and −29.3 ppm, shifted slightly upfield from those of **1**[3] but maintaining the 4:1 relative integration mandated by the stereochemistry of the pentaphosphine-substituted complex. Meanwhile, small but identifiable peaks attributable to the *E* isomer are shown at −26.5 and −28.8 ppm. Barring any other workup, the ratio of the isomers remains constant at approximately 94.45% *Z* and 5.55% *E*, as calculated from the integration of the $-OCH_3$ peaks in the ^1H NMR spectrum. The two distinct sets of signals in both the ^1H and ^{31}P NMR spectra remain unchanged in a standing solution of the product mixture, suggesting that under ambient conditions interconversion of the isomers does not occur on the NMR time scale.

Isolation of the *Z* isomer from the product mixture was achieved by anion exchange with $NaBPh_4$, followed by recrystallization from methanol. Its *Z* configuration is inferred from a comparison of its straightforward ^1H NMR spectrum with those of reported *Z*-configured imino ester complexes. As expected, isomerization to the *E* form or an equilibrium mixture of both was not observed in a standing solution of the *Z* isomer.

The structure of the cationic cluster of **2**$(BPh_4)_2$, established by single-crystal X-ray diffraction, is clearly shown in Figure 2. The core appears unaffected by the ligand transformation, with bond lengths and angles varying insignificantly relative to **1**. The Re−N bond length is normal, but other metric parameters concerning the coordinated imino ester clearly manifest the anticipated consequences of the transformation from the nitrile to the imino ester. The C(31)−N(1) bond length of 1.232(3) Å is consistent with an imine (N=C) moiety, whereas the counterpart in **1** is 1.091(3) Å, typical of a coordinated nitrile. The Re(6)−N(1)−C(31) angle is reduced significantly to 137.3(2)° relative to **1** [173(1)°]. The angles about C(31) [N(1)−C(31)−C(32), 125.9(3)°; C(32)−C(31)−O(1), 119.2(2)°; N(1)−C(31)−O(1), 114.9(3)°] are all close to the expected values for sp^2 hybridization.

A careful examination of the crystal structure of **2** reveals interesting Se···O(OMe) distances: Both Se(2)···O(1) (3.291 Å) and Se(3)···O(1) (3.322 Å) fall into the range of the reported Se···O distance when hydrogen bonding involving Se is observed.[11] Experimental and theoretical studies have shown that intramolecular OH···Se hydrogen bonding is as strong as OH···O and OH···S hydrogen bonding and has significant implications in the conformational stabilization of many Se-containing organic molecules.[12] Considering the

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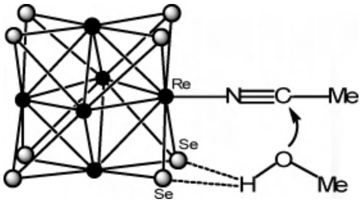

Figure 3. Proposed bifurcated hydrogen bonding involving the methanol OH group and two Se atoms of the cluster at the initial stage of the nucleophilic addition.

unexpected predominance of the *Z* isomer and the salient structural features observed, it may not be entirely unreasonable to hypothesize that a bifurcated hydrogen bonding (Figure 3) involving the methanol OH group and the two Se atoms of the cluster core forms at the initial stage of the nucleophilic addition, while a second molecule of alcohol helps stabilize the increasing electron density on the N atom. Such stereospecific organization of the substrates, leading ultimately to the *Z* isomer, is completely different from the previously proposed four- or six-membered ring transition state.[13]

The reaction of **1** with ethanol and that of *trans*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(CH_3CN)_2][SbF_6]_2$ (**3**)[3] with methanol afforded the corresponding imino ester complexes, $\{Re_6(\mu_3\text{-}Se)_8(PEt_3)_5[HN{=}C(OCH_2CH_3)(CH_3)]\}\{SbF_6\}_2$ (**4**) and *trans*-$\{Re_6(\mu_3\text{-}Se)_8(PEt_3)_4[HN{=}C(OCH_3)(CH_3)]_2\}\{SbF_6\}_2$ (**5**), respectively, both predominantly in the *Z* form. Crystallographic studies unambiguously established the *Z* configuration of the ligands in both complexes (Supporting Information). Similar to the case of **2**, the shortest Se···O distances in these two new complexes are also in the range suitable for intramolecular OH···Se hydrogen bonding.

The predominance of the *Z* isomer in the product mixture in both cases was also revealed by NMR results (Supporting Information). Although the bis(acetonitrile) complex **3** reacts with methanol as facilely as its mono(acetonitrile) analogue **1**, the reaction between ethanol and **1** requires reflux of the reaction mixture for an extended period of time. This disparity in reactivity of different alcohols suggests that the steric bulk of the nucleophile is critically important in such reactions. Corroborating evidence is provided in the observation of no reaction when isopropyl alcohol is utilized.

It remains to be seen, regardless of the configuration of the complex, whether the newly formed ligands(s) can be released from the cluster core and whether the potentially precatalytic acetonitrile complexes can be regenerated. The documented difficulty in liberating imino ester ligands from their metal complexes originates from their enhanced coordinating ability to soft metal centers with respect to their nitrile parents.[7]

At first glance, these cluster compounds offer no obvious benefit over previously reported imino ester complexes in terms of ligand expulsion because the cluster system is known to be inert to ligand exchange at ambient temperature.[14] Fortuitously, recent photophysical studies have shown that the cluster is labile in the excited state, indicating a possible route to photochemically generating a variety of interesting species.[5g]

We thus carried out a photolytic study of $\mathbf{2}(SbF_6)_2$, whereby an acetonitrile solution of $\mathbf{2}(SbF_6)_2$ was subjected to UV irradiation. NMR spectra (^1H and ^{31}P) were obtained every 12 h of irradiation to monitor the reaction progress. The progressive spectra show a smooth consumption of the starting imino ester complexes and simultaneous emergence of signals due to **1** (Supporting Information). Complete conversion of the original product mixture of $\mathbf{2}(SbF_6)_2$ (both *Z* and *E* isomers) into **1** was accomplished after ca. 48 h. However, diethyl ether extracts of the photolysis product(s) did not contain enough material for reliable NMR characterization of the liberated imino methyl ester. Therefore, we can only conclude that the starting nitrile complex was regenerated; no definitive conclusion can be drawn as to whether the imino ester ligand was released in its free form.

In summary, it has been found that alcohol addition to $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ cluster-activated nitrile affords the corresponding imino ester complex primarily in the *Z* configuration and, to a much lesser extent, in the *E* configuration. Though unexpected, the observation may be rationalized by invoking a bifurcated hydrogen-bonding mode involving the alcohol OH group and the Se atoms of the cluster at the onset of the reaction. Increasing the steric bulk of the incoming alcohol impedes its addition to the cluster-bound acetonitrile molecule but does not significantly alter the *Z*/*E* ratio once the reaction is made complete by increasing the temperature and extending the reaction time.

In summary, this work offers a new route to metal-mediated organonitrile additions with a significant degree of stereochemical control of the addition products. Although the product complex is consumed and a complete regeneration of the starting nitrile complex achieved via photolysis in the presence of acetonitrile, definitive evidence in support of the release of free imino ester has yet to be gathered. Nevertheless, given the known versatility of coordination chemistry of these clusters, one may imagine applying cluster-based Lewis acid activation to a range of substrates beyond nitriles and possibly developing new catalytic schemes. This work therefore marks the beginning of what promises to be an exciting new direction in cluster chemistry.

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Supporting Information Available: Crystallographic data of **2**, **4**, and **5** in CIF format and details of syntheses and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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