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Small Molecule Activation of Nitriles Coordinated to the $[Re_6Se_8]^{2+}$ Core: Formation of Oxazine, Oxazoline and Carboxamide Complexes

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Abstract

Novel oxazine, oxazoline and carboxamide cluster complexes were prepared when different nucleophilic oxygen species reacted with nitriles coordinated to the Lewis acidic $[Re_6Se_8]^{2+}$ cluster core. Reaction of $ICH_2CH_2O^-$ (generated *in situ*) with $[Re_6Se_8(PEt_3)_5(NCR)]A_2$ (**1**A_2 (R = Me) and **2**A_2 (R = Ph) where A = BF_4^-), leads to the formation of $[Re_6Se_8(PEt_3)_5(2\text{-methyloxazoline})]^{2+}$ (**3**$^{2+}$) and $[Re_6Se_8(PEt_3)_5(2\text{-phenyloxazoline})]^{2+}$ (**4**$^{2+}$). Similarly, reaction of $BrCH_2CH_2CH_2O^-$ with the same nitrile complexes, **1**A_2 and **2**A_2 (where A = BF_4^- or SbF_6^-) leads to the corresponding oxazine complexes, $[Re_6Se_8(PEt_3)_5(2\text{-methyloxazine})]^{2+}$ (**5**$^{2+}$) and $[Re_6Se_8(PEt_3)_5(2\text{-phenyloxazine})]^{2+}$ (**6**$^{2+}$). In addition, reaction of **2**$(BF_4)_2$ with KOH leads to the formation of the carboxamide complex, $[Re_6Se_8(PEt_3)_5(\text{phenylcarboxamide})](BF_4)$ (**7**(BF_4)). The neutral oxazine and oxazoline ligands can be removed using either heat or UV irradiation; UV irradiation was found to be more efficient at ligand removal as indicated by the shorter reaction times. The relative coordination strength of the neutral N-donor ligands was determined by these reaction times. X-ray structure determinations of **5**$(BF_4)_2$ and **7**(BF_4) are also reported.

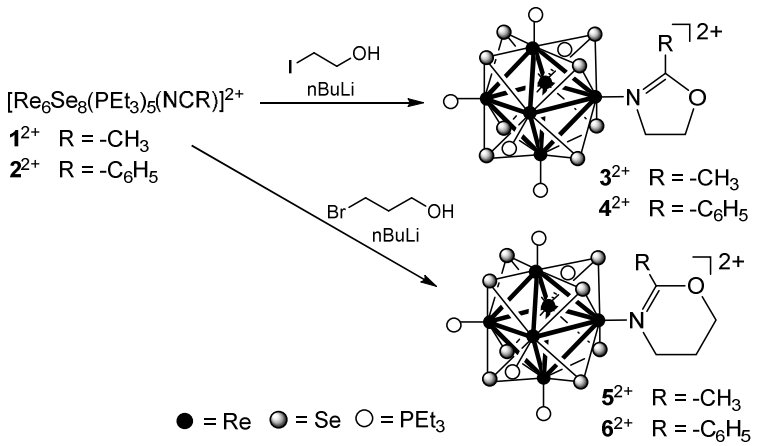
Introduction

Hexanuclear clusters containing the $[Mo_6X_8]^{4+}$ or the $[Re_6Q_8]^{2+}$ (X = halogen and Q = chalcogen) core have drawn attention over the past 20 years. Their unique structural characteristics and photoluminescent properties have led researchers to explore how these clusters can be utilized in various applications such as photocatalysis, liquid crystals, and functional hybrid materials.[1-3]

However, the Lewis acidic nature of these hexanuclear clusters is starting to attract more attention. Reports of both molybdenum chloride and rhenium chalcogenide clusters influencing the reactivity of coordinated ligands have appeared in the literature.[4-8] It is thought that having multiple transition metal ions bonded together in one cluster core leads to the enhanced Lewis acidity of these clusters compared to their single metal analogs. For example, phosphine ligands coordinated to the $[Mo_6Cl_8]^{4+}$ core are oxidized in the presence of trimethylamine-N-oxide (Me_3NO).[8] Typically, Me_3NO does not oxidize trialkylphosphines (free or coordinated).[9] Nitrile ligands coordinated to the $[Re_6Se_8]^{2+}$ undergo a [2+3] cycloaddition with azide to form tetrazolate complexes, i.e. $[Re_6Se_8(PEt_3)_5(1,5\text{-methyltetrazolato})]^{+}$ is formed within minutes at room temperature when $[Re_6Se_8(PEt_3)_5(NCCH_3)]^{2+}$ is reacted with NaN_3 at room temperature.[4] Zheng and coworkers have studied reactions of nitrile activation by the $[Re_6Se_8]^{2+}$cluster core as well.[5-7] Their reports include studies of simple alcohols, ammonia, and organic azides (RN_3) reacting with $[Re_6Se_8(PEt_3)_5(NCCH_3)]^{2+}$ to form imino esters, amidine and imino complexes, respectively.[5-7] These findings are significant, because methanol, ammonia and organic azides are much less nucleophilic than the azide ion, confirming the strong Lewis acid nature of the $[Re_6Se_8]^{2+}$ core. Activation of nitrile ligands via coordination to a transition metal center is not new, although it is notable that only select transition metals facilitate similar reactions. For example, up until the 2007 reports of nitrile activation by rhenium chalcogenide clusters,[4a,5] the majority of the reports of coordinated nitriles reacting with free alcohols involved Pt(II), Ni(II) and Cu(II) metal centers. The only report of rhenium nitrile activation was with a high oxidation state Re(IV) complex, $[ReCl_4(MeCN)_2]$.[10,11]

After our discovery that these clusters facilitate the formation of different tetrazolate and triazolate rings, we became interested in other important heterocyclic systems, specifically oxazine and

oxazoline rings. Oxazine and oxazoline moieties have important applications in polymers, pharmaceutical agents, and in fuel cells.[12,13] The reaction of free nitriles with alcohols can be achieved via the Pinner reaction, which utilizes a large excess of HCl. While transition metals can facilitate this reaction, the types of metals that can be used are limited, with most of the examples in the literature utilizing Pt(II) and Ni(II). Here we expand on the scope of $[Re_6Se_8]^{2+}$ based small molecule activation by utilizing nucleophilic oxygen donor species (haloalcohols and hydroxide) to form oxazine, oxazoline (Scheme 1) and carboxamide containing clusters. Carboxamide ligands are strongly electron donating and transition metal complexes containing these ligands have also been



Scheme 1

found to have important biological activity.[14]

One of the most important applications of Lewis acids is to facilitate organic transformations. Notable advantages of using hexanuclear cluster complexes for such transformations is that they are often both air and water stable. The key step in developing these clusters as catalysts, is proving that the transformed substrate can be removed from the metal cluster followed by regeneration of the starting nitrile cluster complex. Notably, we report the first example of the coordinated

benzonitrile ligand being transformed into a heterocyclic ring (the 2-phenyloxazine ring) which is subsequently removed under ambient conditions, demonstrating the potential of these clusters as Lewis acid catalysts. We also tested the removal of the neutral oxazine and oxazoline ligands using heat and light; the relative ligand strengths of these rings can be deduced from these studies.

Synthesis and Characterization

The preparation of the oxazine and oxazoline cluster complexes was achieved via reaction of the nitrile cluster complex, **1**A_2 or **2**A_2 (A = BF_4^- or SbF_6^-) with a mixture of the corresponding haloalcohol (2-iodo-1-ethanol or 3-bromo-1-propanol) and *n*-BuLi in chlorobenzene. Typically, a slight excess of haloalcohol was used along with enough base to generate slightly more than one equivalent of the alkoxide. The most likely mechanism for ring formation is alkoxide attack of the coordinated nitrile followed by subsequent cyclization and loss of halide, with the precipitation of LiI or LiBr being one of the driving forces. When **1**$(BF_4)_2$ or **2**$(BF_4)_2$ was utilized as the starting nitrile for the preparation of compounds $\mathbf{3}^{2+}$ - $\mathbf{6}^{2+}$, the products often contained mixed counter ions (i.e., BF_4^- and halide, *vide infra*), which adversely affected our CHN data. In order to circumvent this issue, we prepared complexes containing tetraphenylborate (obtained via metathesis) or, in the preparation of $\mathbf{6}^{2+}$, hexafluoroantimonate. The carboxamide complex ($\mathbf{7}^{+}$) was generated via reaction of an aqueous solution of KOH with **2**$(BF_4)_2$. All complexes were characterized via NMR spectroscopy, elemental analysis and MS.

In our initial studies, the isolation of $\mathbf{6}^{2+}$ eluded us. Work up of the reaction mixture between $\mathbf{2}^{2+}$ and 3-Br-1-propanol led to a mixture of $[Re_6Se_8(PEt_3)_5L]^{n+}$ containing products as determined by ^{31}P NMR spectroscopy (we are still working to determine the identity of these compounds).

However, ^{1}H NMR spectroscopy of the filtrate revealed the presence of *free* 2-phenyloxazine. Since free benzonitrile does not react with 3-Br-1-propanol, we determined that the coordinated nitrile underwent reaction prior to being substituted. After conducting ligand removal studies on complexes $\mathbf{3}^{2+}$, $\mathbf{4}^{2+}$, and $\mathbf{5}^{2+}$ (*vide infra*), it occurred to us that ambient light might have affected our ability to isolate $\mathbf{6}^{2+}$. Therefore, we recently went back and repeated the reaction of $\mathbf{2}(SbF_6)_2$ with 3-Br-1-propanol, this time in the absence of light, and we found that $\mathbf{6}(SbF_6)_2$ was isolable. As observed with the other heterocyclic rings, the proton resonances of the coordinated ring are clearly distinguishable from the free ligand.

Zheng and coworkers report that imino ester ligands were formed when $\mathbf{1}(SbF_6)_2$ was stirred in neat MeOH (at room temperature) or neat EtOH (under reflux).[5] We did not observe a reaction when $\mathbf{1}(SbF_6)_2$ was combined with 3-bromo-1-propanol in chlorobenzene in the absence of base. However, after heating this reaction mixture at reflux overnight we observed that the nitrile complex had been cleanly converted to what we believe to be the imino ester complex, $[Re_6Se_8(PEt_3)_5(NH{=}C(OCH_2CH_2CH_2Br)(CH_3)](SbF_6)_2$. Notably, subsequent addition of *n*-BuLi did not lead to oxazine ring formation. This is likely due to steric factors which would hinder *n*-BuLi from being able to remove the –NH proton. Therefore, in order for ring formation to occur it was necessary for us to deprotonate the haloalcohol prior to reaction with the nitrile complex.

Compounds were characterized by ^{1}H, and $^{31}P\{^{1}H\}$ NMR spectroscopy, elemental analysis and ESI mass spectrometry. The only ion observed in the MS of $\mathbf{6}(SbF_6)_2$ was that of $[Re_6Se_8(PEt_3)_5]^{2+}$, indicating loss of the weakly coordinated 2-phenyloxazine ligand during ionization. In addition, we were able to obtain single crystals of $\mathbf{5}(BF_4)_2$ and $\mathbf{7}(BF_4)$. Complex $\mathbf{5}(BF_4)_2$ crystallizes via vapor diffusion using a mixture of acetone and diethyl ether. One half of the cation and one anion are

crystallographically unique. The final model contains well-separated cations and anions. The crystal structure can be solved in $P2_1/c$ with $Z = 2$. The X-ray structure of **5**$(BF_4)_2$ warrants some comment. The structure reported here can be refined with the formulation $[Re_6Se_8(PEt_3)_6](BF_4)_2$ for a final R_1 of ca. 3.5%. A solvated form of that species, namely $[Re_6Se_8(PEt_3)_6](BF_4)_2 \cdot 2CHCl_3$,[15] has been previously reported, with significantly different unit cell parameters. Initially, then, it was believed that this structure may just be a solvent-free crystal of $[Re_6Se_8(PEt_3)_6](BF_4)_2$. Spectroscopically, however, **5**$(BF_4)_2$ is distinct from $[Re_6Se_8(PEt_3)_6](BF_4)_2$. Specifically, the $^{31}P\{^1H\}$ NMR spectrum of the crystals is distinctive for a 5:1 PEt_3:oxazine. There is some evidence of disorder in the BF_4^- anion and, more importantly, in the cation. Minor ring density is evident in the difference map at all three crystallographically-unique PEt_3 sites. Free-refinement of the occupancy of the oxazine ring and PEt_3 leads to chemically-unsatisfactory results, but occupancies of ca. 80-86% for the three PEt_3 moieties. One of the three sites shows only marginal density for the oxazine, and modeling of that site was abandoned. Attempting to model only one site also leads to chemically-unreasonable results. Final occupancies were fixed at PEt_3:L ratios of 80/20, 70/30, and 100/0 and oxazine rings were constrained with typical reported bond lengths and angles based on values in over 2000 oxazine-containing structures[16] for a final R_1 of 3.24%. The oxazine was only modeled in one possible configuration for each site, leading to larger displacement ellipsoids and residual shifts in the final refinement, but no further modeling was done, given such limited electron density. The highest probability $\mathbf{5}^{2+}$ cation is shown in Figure 1; see Figure S13 in the online Supporting Information (or the CIF) for the more complete model. The $[Re_6Se_8]^{2+}$ core has similar metrics to previously reported species: Re–Re distances are in the range 2.6405(4) - 2.6498(4) Å, Re–Se distances are in the range of 2.5105(6) – 2.5258(6) Å, and Re–P distances are in the range 2.4491(19) – 2.4701(16) Å. The Re–N distance is 2.32(2) Å in the larger electron density model and 2.52(2) Å in the other site.

Complex **7**BF_4 crystallizes from a saturated acetone solution layered with toluene with the formulation $[Re_6Se_8(PEt_3)_5(NHCOC_6H_5)](BF_4)\cdot 2(C_7H_8)$ in space group $I2/a$ with $Z = 8$. The structure contains an entirely crystallographically unique cation and BF_4^- anion as well as two unique toluene molecules of crystallization, all of which are well-separated. The ORTEP diagram of $\mathbf{7}^+$ is shown in Figure 2. There is no evidence of hydrogen bonding or π-stacking in the structure. The structure of **7**BF_4 contains a fairly typical $[Re_6Se_8]^{2+}$ core, with five PEt_3 bound to Re atoms via phosphorus atoms. The sixth rhenium atom is coordinated to the nitrogen of the phenylcarboxamide ligand. Re–Re distances are in the range 2.6301(5) - 2.6477(5) Å, Re–Se distances are in the range of 2.5105(7) – 2.5270(8) Å, and Re–P distances are in the range 2.465(2) – 2.482(2) Å. The Re–N distance is 2.089(6) Å.

Ligand Removal studies

In the interest of testing for catalytic reactivity, we conducted studies to see if the newly formed heterocyclic rings could be removed from the cluster core using either heat or light. Ligand loss would open up a coordination site, which could lead to the regeneration of the starting nitrile complex and, therefore, a catalytic process. We began our studies with **4**$(BF_4)_2$ which was isolated from the reaction of **1**$(BF_4)_2$ with 2-iodo-1-ethanol and *n*-BuLi. Approximately 5 mg of **4**$(BF_4)_2$ was dissolved in CD_3CN in a quartz NMR tube and, after obtaining a spectrum at t = 0, the solution was subsequently irradiated with UV light[17] and monitored via both ^1H and ^{31}P NMR spectroscopy at different time intervals. Initially, the ^1H NMR spectrum shows the methylene resonances assigned to the coordinated phenyloxazoline ring, appearing at δ4.53 and 4.27 ppm (Figure 3a). After 30 minutes of photolysis, the methylene resonances for the coordinated ring have been reduced by more than half (approximately 40% remains) and new resonances at δ4.40 and 3.98

ppm (Figure 3b), assigned to the free phenyloxazoline ring, are now apparent. The ^{31}P NMR spectral data show that during the same time period, approximately half of the starting phenyloxazoline complex (**4**$^{2+}$) is converted primarily to $[Re_6Se_8(PEt_3)_5I]^+$ (δ -29.13 and -31.53 ppm) although some $[Re_6Se_8(PEt_3)_5(NCCD_3)]^{2+}$ (δ -24.78 and -28.89 ppm) is also been generated (Figure 4). The presence of $[Re_6Se_8(PEt_3)_5I]^+$ was initially surprising and we deduced that **4**$^{2+}$, which was prepared from **1**$(BF_4)_2$, must have precipitated out as a mixture of anions, BF_4^- and I^- (the iodide ion is a byproduct of the cyclization of the starting haloalcohol). We observed the formation of $[Re_6Se_8(PEt_3)_5I]^+$ in the photolysis of the methyloxazoline complex as well. Therefore, we tried to prepare one of the oxazoline complexes with the tetraphenylborate anion. We were successful in preparing **3**$(BPh_4)_2$ (which was used for the full characterization of this complex) where the integration of the ^{1}H NMR spectrum of **3**$(BPh_4)_2$ confirms a cluster:anion ratio of 1:2; as does the elemental analysis data. Confident that this solid was free of halide ions we repeated photolysis now using **3**$(BPh_4)_2$. However, we found that the decomposition products from the light sensitive tetraphenylborate anion react with the cluster, causing it to decompose as well. Therefore, we were unable to conduct photolysis studies on any of the BPh_4^- containing complexes.

Holm and coworkers reported that ligand substitution of terminal solvate ligands coordinated to the $[Re_6Se_8]^{2+}$ core proceeds via a dissociative mechanism;[18] therefore, we proposed that the identity of the anions should not impact the rate of heterocyclic ring substitution. To test this theory, we monitored the thermolysis of two methyloxazine complexes, **5**A_2, with different counterions (one had mixed counterions, tetrafluoroborate and halide, the other had exclusively hexafluoroantimonate) and confirmed that there was no significant difference in the overall rate of ligand removal. We concluded that the counterion did not influence the relative rates of heterocyclic ring substitution (only the ratio of products formed, i.e. nitrile:halide); therefore, we

utilized the complexes we had available, that is $\mathbf{3}^{2+}$, $\mathbf{4}^{2+}$ and $\mathbf{5}^{2+}$ with a mixture of BF_4^- and halide counterions, for our photolysis and thermolysis studies.

The ^1H and ^{31}P NMR spectral data from all of the thermolysis and photolysis studies can be found in the supporting information. Of note is that in some cases, such as in the photolysis of the phenyloxazoline ring, the nitrile complex, $[Re_6Se_8(PEt_3)_5(NCCD_3)]^{2+}$ (Figure S3) is formed initially and then converted to the halide complex, $[Re_6Se_8(PEt_3)_5I]^+$. It is not surprising that the nitrile coordinates first as the nitrile solvent is in much higher concentration; however, the ultimate conversion of the nitrile complex to the halide complex indicates that coordination of the halide ion is thermodynamically favored. We tested for catalysis, even though we were concerned that halide coordination could hinder the catalytic cycle. Specifically, we added $\mathbf{1}(BF_4)_2$ to a solution of 3-bromo-1-propanol and *n*-BuLi in pure acetonitrile-d_3, exposed it to UV light and monitored the reaction via ^1H NMR spectroscopy. Over time, we observed the formation of only one equivalent of free 2-methyloxazine and $[Re_6Se_8(PEt_3)_5Br]^+$. Attempts at removing the halide ligand and regenerating the starting nitrile complex through the addition of thallium(I) and silver(I) salts also proved ineffective. Therefore, although these clusters facilitate ring formation and photolysis and thermolysis can be used to successfully remove the oxazine and oxazoline rings from the cluster core, catalytic activity is not viable due to the coordination of the halide byproduct.

We found it instructive to compare the spectral data for the photolysis and thermolysis of complexes $\mathbf{3}^{2+}$, $\mathbf{4}^{2+}$ and $\mathbf{5}^{2+}$ to determine the relative ligand strengths of the newly formed heterocyclic rings. Examining the photolysis data, substitution of the phenyloxazoline ring was complete in ~2 hours (Figures 3 and 4), as was the substitution of the methyloxazine (Figures S5 and S6) while less than half of methyloxazoline was substituted within ~5 hours (Figures S1 and S2). Examining the data

from our thermolysis studies, we observed that the phenyloxazoline ring was removed in ~4 hours (Figures S9 and S10), whereas at 4.5 hours only 55% of the methyloxazine ligand had been removed (Figures S11 and S12). Notably, the methyloxazoline ligand showed no signs of substitution, even after heating for 24 hours (Figures S7 and S8). Combining this data with what we know about the phenyloxazine ring, which was removed with exposure to ambient light, we ranked these heterocyclic rings in terms of increasing ligand strength: phenyloxazine < phenyloxazoline < methyloxazine < methyloxazoline. Methyl substituents are more strongly electron donating when compared to phenyl substituents. More strongly donating substituents at the 2 position on these rings likely increases the Lewis basicity of the N-donor atom, making the methyloxazoline and methyloxazine the two most strongly coordinating ligands. In addition to electronic effects, there are also steric considerations. The fact that the methyloxazoline and phenyloxazoline rings are more strongly coordinating compared to their respective oxazine rings, is most likely a steric effect. The five membered oxazoline ring reduces steric hindrance between the substituent at the 2 position and the cluster core. In the space filling diagram of $\mathbf{5}^{2+}$ (Figure S15) one can see how the six membered oxazine ring forces the methyl group into close proximity with the cluster core. A phenyl substituent in the same location would have even greater steric hindrance. Therefore, it is not surprising that the phenyloxazine cluster is the most weakly coordinating.

Zheng and coworkers reported that photolysis could be used to remove the coordinated imino ester in $[Re_6Se_8(PEt_3)_5(HN{=}C(OCH_3)(CH_3)]^{2+}$ in CH_3CN, where complete conversion was achieved in 48 hours.[5] However, catalytic production of the imino esters was not shown. In other examples of cluster activation of small molecules, removal of the transformed ligand is achieved only after the introduction of additional reagents, which interfere with the catalytic process. For example, free amidine ligands (generated from the reaction of ammonia with coordinated nitriles) can be

generated only after the addition of trifluoroacetic acid.[6] Our findings are significant in that we report the first example of a transformed ligand (phenyloxazine) that can be substituted in ambient light at room temperature. The other heterocyclic rings generated here, can be substituted at room temperature after exposure to UV-light, where substitution occurs in less than 24 hours. In addition, our findings indicate that photolysis is more efficient than thermolysis. Although others have reported the use of heat and light to facilitate terminal ligand substitution at rhenium chalcogenide cluster cores,[5,18,19] our results provide the first direct comparison of photochemical vs thermal ligand substitution of the $[Re_6Se_8]^{2+}$ cluster core. Facile photochemical ligand substitution is an attractive feature of these cluster complexes, as one can envision the development of a catalytic process, whereby the starting complex is regenerated via exposure to UV-light, without the need of additional reagents. Currently, we are looking into other applications of photochemically induced cluster based ligand substitution processes.

Conclusion

Here we report the synthesis and isolation of the first rhenium complexes to contain oxazine, oxazoline and carboxamide ligands. These studies provide another example of how the rhenium selenide cluster core activates nitriles to react with nucleophilic species, specifically alkoxides and hydroxide. Oxazine and oxazoline rings have a wide variety of applications, most importantly in the pharmaceutical industry; therefore, it is of interest that these rings can be easily removed using photolysis. Data for the phenyloxzaoline and methyloxazoline cluster complexes indicate that UV-irradiation is more efficient than heating for ligand removal. Although we do observe formation of some of the nitrile complex in these ligand removal studies, it appears as though halide ultimately interferes with the possibility of a catalytic process. Other methods of eliminating the halide, which should then enable catalysis, are currently underway.

Experimental

General Methods and Materials

The nitrile complexes used, **1**A_2 and **2**A_2 (A = BF_4^- or SbF_6^-), were prepared according to previously published procedures.[15,4b] *n*-Butyllithium (1.6 or 2.5 M in hexanes) and all other reagents and solvents were used as received. All reactions were carried out under an inert atmosphere, and the synthesis of **6**$(SbF_6)_2$ was conducted in the dark. All cluster products are stable in the presence of both O_2 and water; therefore, they were handled in air. NMR data was collected using a Bruker Avance III (400 MHz or 500 MHz) spectrometer. Elemental analysis were conducted by the Microanalysis Laboratory at the University of Illinois, Urbana; mass spectral data was obtained at the Mass Spectrometry Laboratory at the University of Illinois, Urbana.

$[Re_6Se_8(PEt_3)_5(2\text{-methyloxazoline})](BPh_4)_2$ $(3(BPh_4)_2)$

n-Butyllithium (82 μL of 1.6 M, 0.13 mmol) and 2-iodo-1-ethanol (26 μL, 0.33 mmol) were added to a mixture of chlorobenzene (22 mL) and acetonitrile (1 mL) and allowed to stir for a few minutes at 0˚C before adding **1**$(BF_4)_2$ (150.8 mg, 0.053 mmol). The mixture was stirred at 0˚C for 1 h and then stirred at room temperature for another hour. The orange slurry was filtered through Celite to remove the $LiI_{(s)}$ byproduct, and the filtrate was reduced to dryness. The resulting oil was dissolved in a minimal amount of CH_2Cl_2 and precipitated out of Et_2O to afford a solid (115.3 mg). Next, a metathesis reaction was performed by dissolving this solid in 250 mL of absolute EtOH, and then slowly adding a solution of $NaBPh_4$ (409.3 mg dissolved in 5 mL of 95% of EtOH) to form a precipitate. The solid was collected, washed with 95% ethanol and dried (125 mg, 77%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): 0.95 (9H, m, -$PCH_2C\underline{H}_3$), 1.05 (36H, m, -$PCH_2C\underline{H}_3$), 1.95 (6H, m, -$PC\underline{H}_2CH_3$), 2.08 (27H, m, -$PC\underline{H}_2CH_3$ and -$C\underline{H}_3$), 3.48 (4H, m, -O-$C\underline{H}_2$-and N-$C\underline{H}_2$-), 6.85 (8H, t, -$C_6\underline{H}_5$), 7.01 (16H, m, -$C_6\underline{H}_5$), and 7.40 (16H, m, -$C_6\underline{H}_5$). ^{31}P $\{^1$H$\}$ NMR (202.5 MHz, $CDCl_3$, ppm):

-26.78 (s), -28.48(s). MS (ESI (+)): 1211.6 ($[Re_6Se_8(PEt_3)_5$(2-methyloxazoline)$]^{2+}$). Anal. Calcd for $C_{82}H_{122}NOP_5B_2Re_6Se_8 \cdot 2H_2O$: C, 31.78; H, 4.10; N, 0.45. Found: C, 30.71; H, 3.70; N, 0.41. (An independent sample of $[Re_6Se_8(PEt_3)_5$(2-methyloxazoline)$](SbF_6)_2$ was also analyzed, Anal. Calcd for $C_{34}H_{82}NOP_5Re_6Se_8Sb_2F_{12}$: C, 14.10; H, 2.85; N, 0.48. Found: C, 13.97; H, 2.67; N, 0.47.)

$[Re_6Se_8(PEt_3)_5$(2-phenyloxazoline)$](BF_4)_2$ ($4(BF_4)_2$)

This procedure is similar to that described for the preparation of **3**$(BPh_4)_2$ except that the entire reaction was done at room temperature as the reaction mixture stirred for 48 h, during which time an orange solid precipitated out. The resulting slurry was filtered through Celite to trap the orange solid, which was subsequently removed via washing the Celite with CH_2Cl_2. After reducing the solvent, the resulting oil was dissolved in CH_2Cl_2, passed down Celite to remove residual LiI and precipitated out of Et_2O. Starting with 203 mg of **2**$(BF_4)_2$ (0.078 mmol), 131 mg (63%) of crude product was obtained. This product was clean by ^1H and ^{31}P NMR spectroscopy; however, the product had to be recrystallized multiple times (vapor diffusion using CH_2Cl_2:Et_2O) in order to obtain acceptable EA data. ^1H NMR (400 MHz, $CDCl_3$, ppm): 1.08 (45H, m, -$PCH_2C\underline{H}_3$, 2.11 (30H, m, -$PC\underline{H}_2CH_3$), 4.48 (2H, t, -N-$\underline{CH}_2$-), 4.74 (2H, t, -O-$\underline{CH}_2$-), 7.49 (3H, m, -$C_6\underline{H}_5$), 7.56 (2H, m, -$C_6\underline{H}_5$). ^{31}P {^1H} NMR (162 MHz, $CDCl_3$, ppm): -27.23 (s), -29.82 (s). MS (ESI(+)): *m/z* 1244.6 ($[Re_6Se_8(PEt_3)_5$(2-phenyloxazoline)$]^{2+}$). Anal. Calcd for $C_{39}H_{84}NOP_5B_2F_8Re_6Se_8$: C, 17.61; H, 3.18; N, 0.53. Found: C, 17.29; H 2.83; N, 0.51.

$[Re_6Se_8(PEt_3)_5$(2-methyloxazine)$](BPh_4)_2$ ($5(BPh_4)_2$). This procedure is also similar to that described for the preparation of **3**$(BPh_4)_2$ except that 3-bromo-1-propanol was used instead of 2-iodo-1-ethanol, and the crude product was purified via column chromatography (silica gel, 50:50 NO_2CH_3:CH_2Cl_2 on silica gel) prior to metathesis. Starting with 152.9 mg of **1**$(SbF_6)_2$, 93.8 mg of

product was obtained (57%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): 0.94 (9H, m, -$PCH_2C\underline{H}_3$), 1.04 (36H, m, -$PCH_2C\underline{H}_3$), 1.32 (2H, m, -$CH_2C\underline{H}_2CH_2$-), 1.94 (6H, m, -$PC\underline{H}_2CH_3$), 2.06 (24H, m, -$PC\underline{H}_2CH_3$), 2.18 (3H, s, -$C\underline{H}_3$), 3.40 (2H, t, -N-$C\underline{H}_2$-), 3.78 (2H, t, -O-$C\underline{H}_2$-), 6.86 (8H, m, -$C_6\underline{H}_5$), 7.02 (16H, m, -$C_6\underline{H}_5$) and 7.38 (16H, m, -$C_6\underline{H}_5$). ^{31}P {^{1}H} NMR (202.5 MHz, $CDCl_3$, ppm): -27.15(s), -29.25(s). MS (ESI(+)): m/z 1220.9 ($[Re_6Se_8(PEt_3)_5(2\text{-methyloxazine})]^{2+}$). Anal. Calcd for $C_{83}H_{124}NOP_5B_2Re_6Se_8$: C, 32.40; H, 4.06; N, 0.46. Found: C, 32.29; H, 4.00; N, 0.53.

$[Re_6Se_8(PEt_3)_5(2\text{-phenyloxazine})](SbF_6)_2$ ($6(SbF_6)_2$). This procedure is similar to that described for the preparation of **5**$(BPh_4)_2$ except that all solutions were kept in the dark and metathesis was not necessary. The crude product was purified using column chromatography (50:50 CH_2Cl_2: NO_2CH_3) then precipitated out of Et_2O. Starting with 102.7 mg (0.0352 mmol) of **2**$(SbF_6)_2$, 47.9 mg of product was isolated (49% yield). MS (ESI(+)): m/z 1169.7 ($[Re_6Se_8(PEt_3)_5]^{2+}$). ^{1}H NMR (500 MHz, CD_2Cl_2, ppm): 1.03 (9H, m, -$PCH_2\underline{CH}_3$), 1.11 (36H, m, -$PCH_2\underline{CH}_3$), 2.04 (8H, m, -$P\underline{CH}_2CH_3$), 2.10 (22H, m, -$P\underline{CH}_2CH_3$), 2.21 (3H, m, -CH_2-$\underline{CH}_2$-CH_2-), 4.03 (2H, t, - N-$\underline{CH}_2$-), 4.46 (2H, t, -O-$\underline{CH}_2$-), 7.38 (2H, dd, -$C_6\underline{H}_5$), 7.46 (1H, tt, -$C_6\underline{H}_5$), 7.52 (2H, tt, -$C_6\underline{H}_5$). ^{31}P {^{1}H} NMR (202.5 MHz, CD_2Cl_2, ppm): -26.39 (s), -30.30 (s). Anal. Calcd for $C_{40}H_{86}NOP_5Sb_2F_{12}Re_6Se_8 \cdot H_2O$: C, 16.07; H, 2.97; N, 0.47. Found C, 15.73; H, 2.69; N, 0.30.

$[Re_6Se_8(PEt_3)_5(\text{phenylcarboxamide})]BF_4$ ($7BF_4$). To a solution containing 256 mg (0.098 mmol) of **2**$(BF_4)_2$ dissolved in 10 mL of acetone, 4.9 mL of ~0.40 M solution of KOH was added. The solution was stirred at room temperature for 30 min, then filtered through Celite and stripped dry. The resulting oily residue was dissolved in 1.5 mL of acetone, reduced to dryness and precipitated using a mixture of acetone and toluene. Column chromatography (silica gel, 2:1 CH_2Cl_2:MeCN) was used to elute an impurity; pure MeCN was used to elute the product. This band

was reduced to dryness, and the product reprecipitated using a mixture of acetone and toluene. Crystals were obtained *via* vapor diffusion out of the same solvent mixture (187 mg, 75% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): 1.10 (45H, m, -$PCH_2C\underline{H}_3$, 2.11 (30H, m, -$PC\underline{H}_2CH_3$), 6.25 (1H, s, -N$\underline{H}$), 7.29 (3H, m, -$C_6\underline{H}_5$), 7.64 (3H, m, -$C_6\underline{H}_5$). ^{31}P {^{1}H} NMR (202 MHz, $CDCl_3$, ppm): -30.57. MS (ESI(+)): *m/z* 2461.0 ($[Re_6Se_8(PEt_3)_5$(phenylcarboxamide)$]^+$). Anal. Calcd for $C_{37}H_{81}NOP_5BF_4Re_6Se_8$: C, 17.45; H, 3.21; N, 0.55. Found: C, 17.80; H 2.99; N, 0.60.

X-ray crystallographic data collection and refinement.

By omitting the metathesis step, **5**$(BF_4)_2$ was synthesized from **1**$(BF_4)_2$. Single crystals of **5**$(BF_4)_2$ were obtained via vapor diffusion (using acetone and Et_2O). Single crystals of **7**BF_4 were also obtained via the vapor diffusion using acetone and toluene. Intensity data for a single crystal were collected on a Bruker SMART Apex 2 (**5**$(BF_4)_2$) or D8 (**7**BF_4) diffractometer equipped with a CCD area detector using graphite monochromated Mo Kα radiation at -92 and -100 °C, respectively. Data were reduced and corrected for absorption using the SAINT+ Software Suite[20] or using measure crystal faces (SADABS),[21] respectively. Structure solutions were obtained by direct methods and were refined on F^2 with the use of full-matrix least squares techniques.[22,23] Hydrogen atoms were placed in geometrically idealized positions using a riding model. The carboxamide complex, **7**(BF_4), refines routinely with well-separated cation and anion along with two toluene molecules. As described in detail earlier, complex **5**$(BF_4)_2$ contains a disordered oxazine over all three crystallographically equivalent positions and was modeled accordingly. There is also some disorder in the tetrafluoroborate anion. Selected crystallographic details are shown in Table 1. More extensive crystallographic details are included in Supporting Information.

Ligand Removal Studies

Approximately 5 mg of **3**A_2, **4**A_2, **5**A_2 (where the anions were often mixed (*vide supra*) and A = halide and/or BF_4^-) was dissolved in 0.5 mL of CD_3CN. The solution was transferred to a Wilmad LPV NNR tube containing a Teflon stopcock, the stopcock was closed, and either submerged in a 100 ˚C oil bath or irradiated with a Hg/Xe lamp (200 W, 280 – 400 nm). Quartz NMR tubes were used for the UV irradiation studies. ^{1}H and ^{31}P $\{^1$H$\}$ NMR data was recorded at different time intervals to monitor the progress of the reaction.

Supporting information. ^{1}H and ^{31}P NMR spectral data obtained from the photolysis and thermolysis studies of **3**$^{2+}$, **4**$^{2+}$ and **5**$^{2+}$, displacement ellipsoid plots of **5**$(BF_4)_2$ and **7**BF_4, the space filling diagram of **5**$^{2+}$ and the UV-visible spectrum of **5**$^{2+}$. CCDC-1812815 (**5**$(BF_4)_2$) and 1812816 (**7**BF_4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Conflicts of Interest. There are no conflicts of interest to declare.

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17. The UV-vis spectrum of **5**$(SbF_6)_2$ can be found in the supporting information (Figure S16). UV light (200 – 400 nm) was utilized because the absorption bands for these compounds are primarily in the UV region of the spectrum. Photolysis studies of **5**$(SbF_6)_2$ were conducted using UV (200 – 400 nm) as well as visible (515 – 750 nm) light; approximately 95% of the oxazine ligand is removed after 3 hours of irradiation with UV light, whereas no more than 5% is removed when exposed to visible light.
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Table 1. Crystallographic Parameters for complexes **5**$(BF_4)_2$ and **7**BF_4.

Complex	**5**$(BF_4)_2$	**7**BF_4
Empirical Formula	$C_{35}H_{84}B_2F_8NOP_5Re_6Se_8$	$C_{51}H_{97}BF_4NOP_5Re_6Se_8$
Moiety Formula	$C_{35}H_{84}NOP_5Re_6Se_8$, $2BF_4$	$C_{37}H_{81}NOP_5Re_6Se_8$, BF_4, 2 C_7H_8
Formula Weight	2612.38	2730.83
Temperature, K	181(2)	173(2)
λ (Å)	0.71073	0.71073
Crystal System	Monoclinic	Monoclinic
Space Group	$P2_1/c$	$I2/a$
a (Å)	12.0673(13)	29.181(3)
b (Å)	20.309(2)	13.3905(16)
c (Å)	12.8377(14)	37.295(4)
β (°)	94.218(1)	97.3133(15)
V (Å^3)	3137.7(6)	14454(3)
Z	2	8
D_{calcd} (Mg m^{-3})	2.765	2.510
μ(mm^{-1})	16.347	14.193
F(000)	2376	10 048
Total Reflections	7 374	16 609
Unique Reflections	5 856	11 475
Final *R* indices R_1[a] and wR_2[b] [$I>2\sigma(I)$]:	0.0324, 0.0760	0.0299, 0.0634

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]\}^{1/2}$; w=1/[$\sigma^2(F_o^2)$+$(XP)^2$+$YP$] where P=($F_o^2$+2$F_c^2$)/3; **5**$(BF_4)_2$: X=0.0333 Y=8.8287; **7**BF_4: X= 0.0288, Y=161.0870.

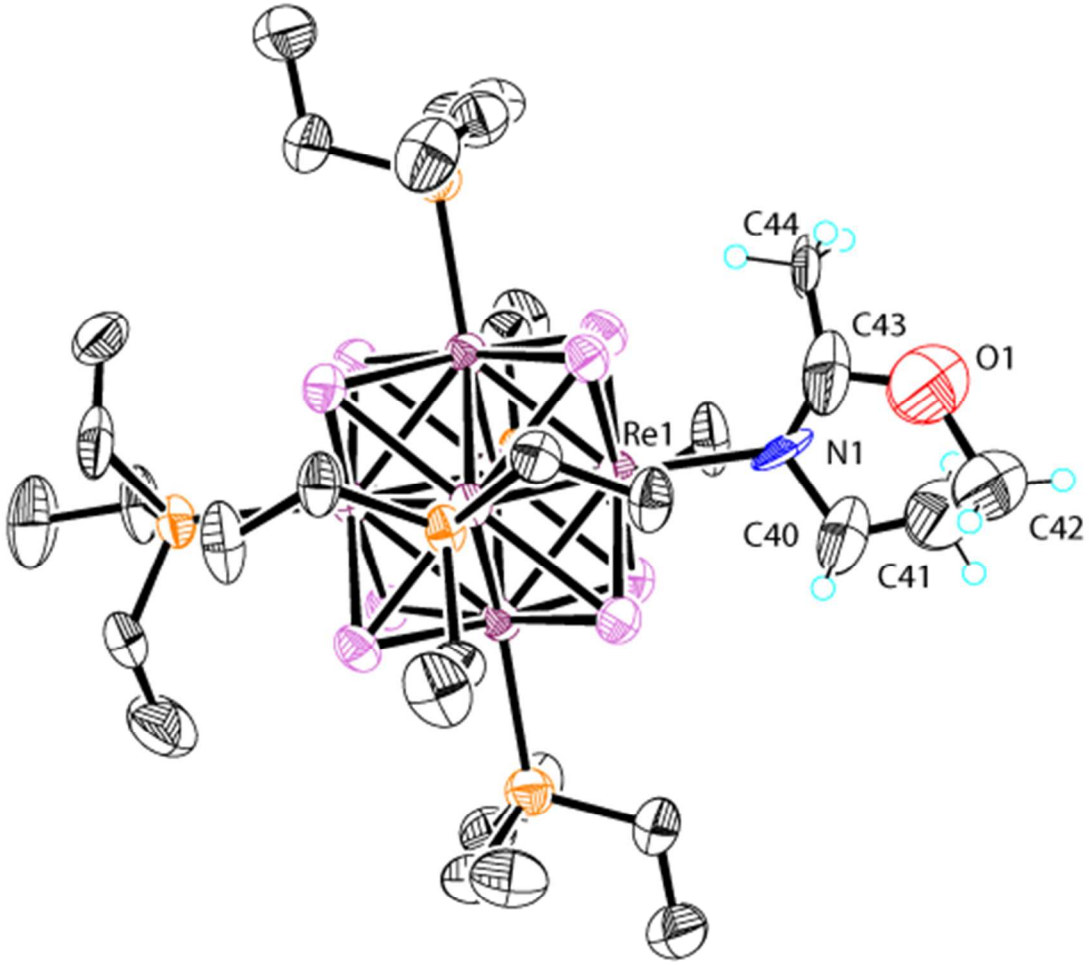

Figure 1. Displacement ellipsoid plot (50%) of the highest probability density of $[Re_6Se_8(PEt_3)_5(2\text{-methyloxazine})]^{2+}$ cation (i.e., $\mathbf{5}^{2+}$). Disorder has been removed for clarity. Hydrogen atoms have also been omitted for clarity, except for those on the oxazine ring. See text and Supporting Information (Figure S13) for details.

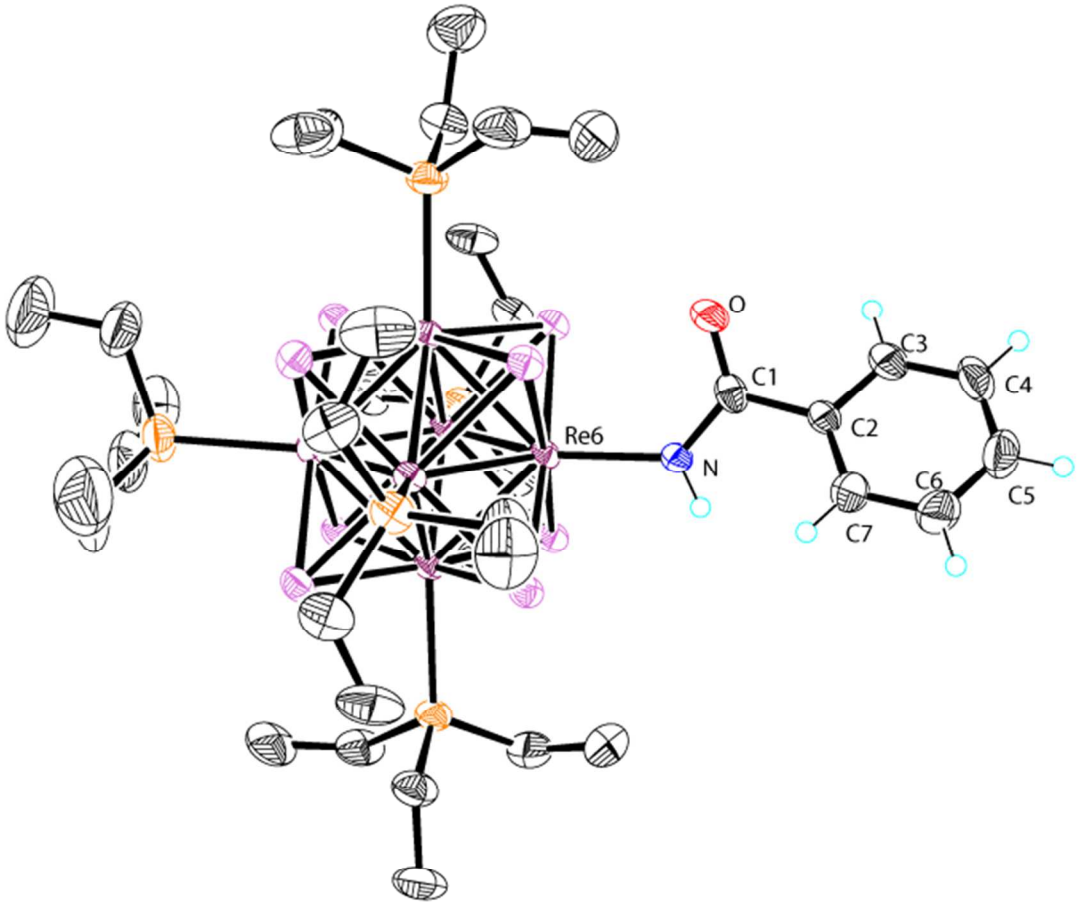

Figure 2. Displacement ellipsoid plot (50%) of the $[Re_6Se_8(PEt_3)_5(\text{phenylcarboxamide})]^+$ cation (i.e., $\mathbf{7}^+$). Hydrogen atoms have been omitted for clarity, except for those on the phenylcarboxamide.

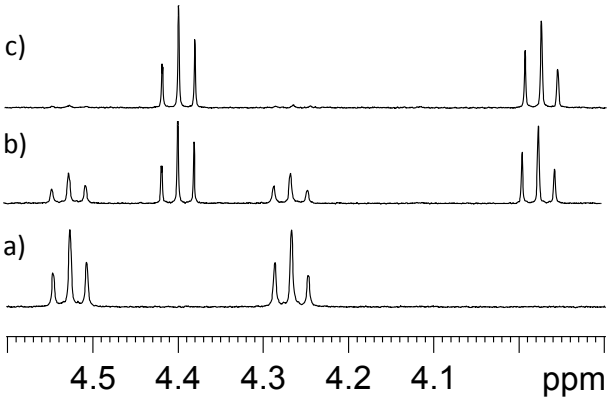

Figure 3. 500 MHz ^{1}H NMR spectral data of the room temperature UV-irradiation of $\mathbf{4}^{2+}$ in CD_3CN, samples taken at a) $t = 0$, b) $t = 0.5$ hour and c) $t = 2$ hours.

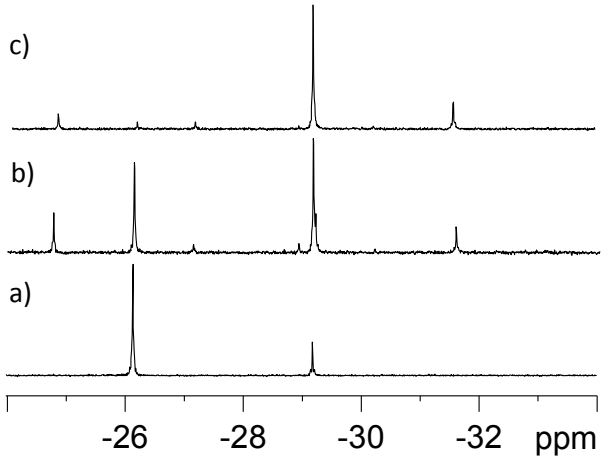

Figure 4. 202.4 MHz ^{1}H NMR spectral data of the room temperature UV-irradiation of $\mathbf{4}^{2+}$ in CD_3CN, samples taken at a) $t = 0$, b) $t = 0.5$ hour and c) $t = 2$ hours.

Table of Contents

Small Molecule Activation of Nitriles Coordinated to the $[Re_6Se_8]^{2+}$ Core: Formation of Carboxamide, Oxazine and Oxazoline Complexes

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Lewis acidic properties of the rhenium selenide core lead to the formation of cluster complexes containing novel heterocyclic rings.