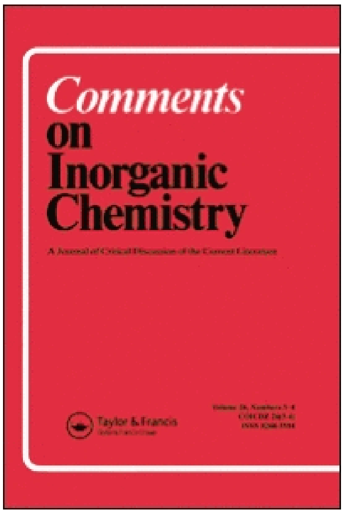

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Nitrile Hydrolysis Promoted by Rhenium(III) Metal-Metal Bonded Systems

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Nitrile Hydrolysis Promoted by Rhenium(III) Metal-Metal Bonded Systems

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The ability to hydrolyze nitriles to form coordinated amidate ligands has recently been demonstrated using Re_2(III, III) and Re_3(III, III, III) reagents such as $[N(C_4H_9)_4]_2[Re_2Cl_8]$ and $Re_3(\mu\text{-}Cl)_3Cl_6$. Products containing a single amidate $[N(C_4H_9)_4][Re_2Cl_6(\mu\text{-}C_6H_5C(O)NH)]$, *cis*-amidates $[N(C_4H_9)_4][Re_2Cl_5(\mu\text{-}CH_3C(O)NH)(\mu\text{-}CH_3C(OH)N)]$, and a diamidate $[N(C_4H_9)_4]_2[Re_2Cl_6\cdot C_3H_7NO)_2(1,4\text{-}(C(O)NH)_2C_6H_4)]$ have been isolated. The significance of nitrile hydrolysis reactions, proposed reaction mechanism, and potential applications of this type of reaction are reviewed.

Keywords: *nitrile hydrolysis; dirhenium; small molecule activation*

INTRODUCTION

The partial and complete hydrolysis of nitriles to amides and carboxylates respectively are processes that have been studied for many years,

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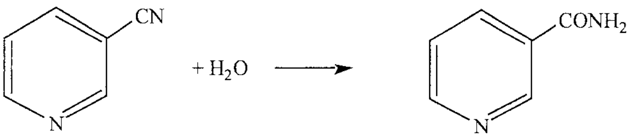
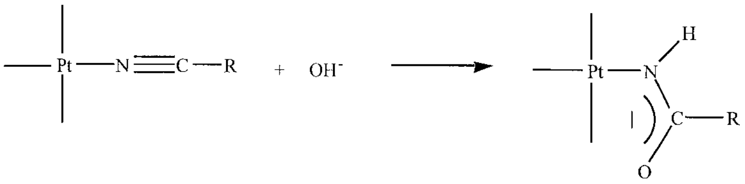
demonstrating the importance of the reaction in organic chemistry.[1–8] However, the conversion of the amide to the carboxylic acid is faster than the preceding conversion of the nitrile to the amide, making the isolation of the pure amide intermediate difficult. While milder reaction conditions are required to isolate the intermediate amide, the conversion of nitriles to carboxylates in bulk organic syntheses is typically performed under harsh reaction conditions.

$$\mathrm{R{-}C{\equiv}N} \longrightarrow \mathrm{R{-}CONH_2} \longrightarrow \mathrm{R{-}COOH}$$

In order to minimize the conversion of amide to carboxylic acid, the Nitto Chemical Company in Japan produces acrylamide (6,000 tons) by the large-scale use of biocatalytic nitrile hydrolysis.[2,5] To eliminate the formation of nicotinic acid in the synthesis of the vitamin nicotinamide, an animal feed supplement, the use of *Rhodococcus Rhodochrous* J1 cells in the synthesis of this commercially important amide is being developed for the reaction shown below.[2,9] However, a restriction of biocatalysis is the substrate specificity of the enzyme activity. For example, nitrile hydratase from *P. chloroaphis* B23 hydrolyzes acrylonitrile efficiently, but has no activity towards benzonitrile.[2] In order to hydrolyze benzonitrile or other aromatic nitriles, *Rhodococcus Rhodochrous* Jl cells are used.[2,6,9]



The hydrolysis of nitriles is not limited to the nitrile hydratase, a metalloenzyme. When the transition metal complex *trans*-$[\mathrm{PtCl_2(NCCH_3)_2}]$ in $\mathrm{CH_2Cl_2}$ is reacted with KOH, a monodentate bisamide species, *trans*-$[\mathrm{PtCl_2(CH_3C(OH)NH)_2}]$ is synthesized.[10] The amide is coordinated to the Pt center through the nitrogen atom as shown in Scheme 1 and the process eliminates the use of a biocatalyst and stops the reaction at the amide product.[10] With the potential to limit the hydrolysis of nitriles to the formation of amides by the use of relatively mild reaction conditions through the coordination of the nitrogen atom to a transition metal center, complexes with a number of metal centers[11,12] such as Pt,[10,13–23] Pd,[15,24–26] Rh,[27] Ir,[27] Ru,[28] Cu,[29,30] Ni,[29,31–33] Co,[33–45] Fe,[5,46–54] Mo,[55,56] and Re[57–61] have been investigated. The formation of amides from hydrolysis[2,29,45,62] or nucleophilic attack by base[22,33,34,38–40] of a nitrile coordinated to a single transition metal center is a well-established synthetic strategy. Aside from the relevance of this research to organic synthesis, enzymatic hydrolysis mechanisms of nitriles are under investigation with the goal of understanding the chemo-, regio-, and stereo-selectivity of these reactions performed under mild conditions.[2,5–7,35,54,63–65]



SCHEME 1 The amide coordination through the nitrogen atom in *trans*-[$PtCl_2(CH_3C(OH)NH)_2$]

COBALT AND IRON COMPLEXES

In nitrile hydratase, both a single Fe(III) center with mixed nitrogen and sulfur containing ligands[5,46–54] and a Co(III) center with mixed sulfur, oxygen, and nitrogen containing ligands[33–45] have been proposed as models of the active site of the metalloenzyme. Cobalt complexes have been widely studied as artificial enzymes due to their proven ability to form amides from coordinated nitriles.[35] For [(cyclen)$Co(CO)_3$][ClO_4], where catalysis is observed under neutral pH conditions, studies have shown the diaqua complex [(cyclen)$Co(OH_2)_2]^{3+}$ forms prior to the coordination of benzonitrile. Subsequent hydrolysis of the nitrile results in the formation of a benzamidate intermediate coordinated to the metal center as a bidentate anionic ligand.[35,45] More recent synthetic attempts to mimic the active site of both cobalt and iron[48] containing nitrile hydratase have focused on nitrogen and sulfur donor centers, FeN_3S_2[46,47,51,52,54,66] and

CoN_3S_2 systems,[41,42] with evidence to support intermolecular attack of cobalt-bound hydroxide at a CoN_3S_2 core to result in the hydrolysis of nitriles.[41]

DIPALLADIUM COMPLEXES

Although a single metal center is present in nitrile hydratase, bimetallic or polymetallic active sites are often found in hydrolytic enzymes, like urease, phosphatases, and esterases.[54,63–65,67] The commonly accepted rationale, termed "two-metal-mechanism" by Steitz and Steitz,[68] is that the transfer of positive charge from one metal center enhances the electrophilicity of the bound substrate, while the second metal ion facilitates the deprotonation of the coordinated water, yielding a bound hydroxide that serves as an intramolecular nucleophile.

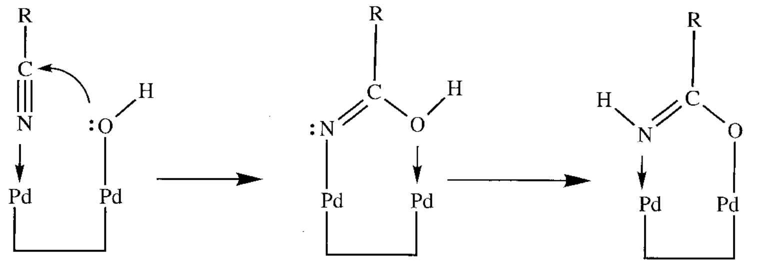
Shown in Scheme 2, a bimetallic pathway or "two-metal-mechanism" was proposed for the dipalladium(II, II) complexes containing thiolate-hinged ligands prepared by McKenzie and Robson.[25,26] Coordination of the nitrile to a single Pd center, with coordination of OH^- on the adjacent metal center, leads to a concerted formation of the amide. Unlike mononuclear Pt systems,[10,15,17,19–21] the hydration of acrylonitrile to acrylamide at the Pd_2(II, II) core is acid catalyzed, and performed in water/acetonitrile mixtures.[26]

RHENIUM COMPLEXES

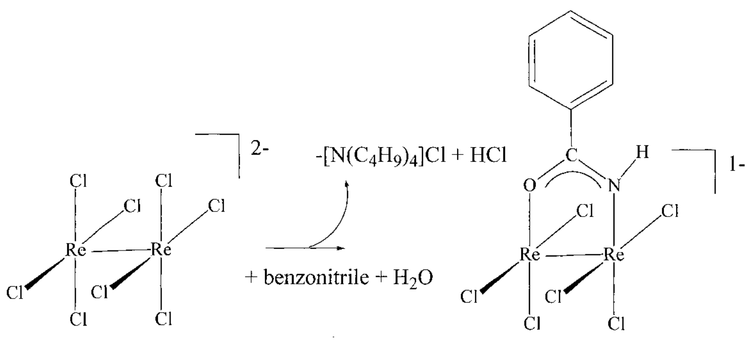
Reactions of $[N(C_4H_9)_4]_2[Re_2Cl_8]$ with benzonitrile

Dirhenium (III, III) and dirhenium (II, II) species have a diverse reactivity due to their high electron-density, $\sigma^2\pi^4\delta^2$ and $\sigma^2\pi^4\delta^2\delta^{*2}$ respectively, which allows them to coordinate and activate a variety of unsaturated organic substrates.[57–60,69–76] In our studies of the reactivity of $[N(C_4H_9)_4]_2[Re_2Cl_8]$ with benzonitrile, we observed the formation of benzamidate from benzonitrile at a Re_2(III, III) core, the first nitrile hydrolysis observed in an anionic bimetallic system containing a metal-metal multiple bond.[57] The reaction is shown in Scheme 3.

The bridging benzamidate, $(\mu\text{-}C_6H_5C(O)NH)^-$, is produced from the hydrolysis of benzonitrile coordinated to $Re_2Cl_8^{2-}$ without oxidation of



SCHEME 2 The bimetallic pathway for nitrile hydrolysis in dipalladium(II, II) complexes containing thiolate-hinged ligands

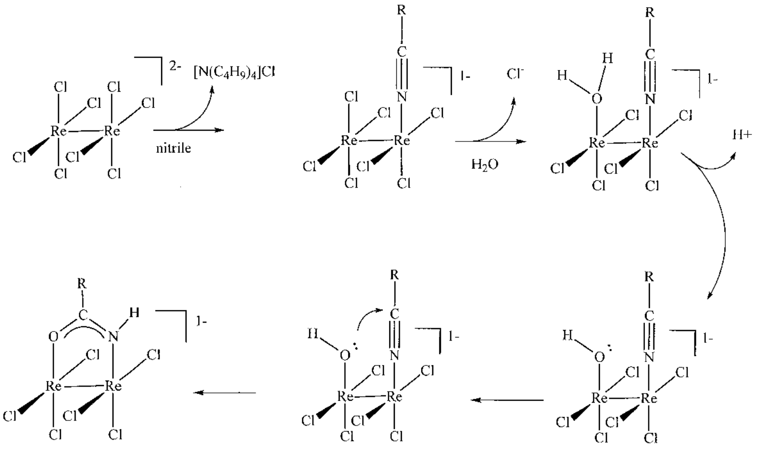


SCHEME 3 The reaction of $[N(C_4H_9)_4]_2[Re_2Cl_8]$ with benzonitrile

the transition metal core to result in $[N(C_4H_9)_4][Re_2Cl_6(\mu\text{-}C_6H_5C(O)NH)]$. To determine the oxygen source, ^1H NMR spectra were obtained for both the benzonitrile and ethanol used in the reactions. The spectra indicated the presence of 3 % water in the benzonitrile. Since the reactions were performed under an argon atmosphere, O_2 was eliminated as the source of the oxygen in the benzamidate. Therefore, hydrolysis of the nitrile occurs due to the presence of water in the reaction mixture, as proposed for water/acetonitrile solvent mixtures in the dipalladium systems.[26]

Reaction Mechanism

Shown in Scheme 4, the proposed reaction mechanism for the hydrolysis of a nitrile to the amidate at the Re_2(III, III) core is analogous to the dipalladium system.[26] Coordination of the nitrile results in a more electrophilic C ≡ N bond due to the positive charge of the adjacent Re(III) and facilitates the nucleophilic attack of the OH^- or H_2O coordinated at the other Re(III) center. The reaction is shown as the attack of the lone pair of electrons on a coordinated hydroxide since OH^- is a stronger nucleophile than H_2O. However, neither coordination of the nucleophile to the second Re(III) center nor deprotonation of the water upon coordination[24] are required for the reaction to proceed. Subsequent proton migration results in $[N(C_4H_9)_4][Re_2Cl_6(\mu\text{-}C_6H_5C(O)NH)]$.[57]



SCHEME 4 The reaction pathway for the hydrolysis of nitriles upon coordination to $[N(C_4H_9)_4]_2[Re_2Cl_8]$

Studies of the reactivity of a related Mo_2(II, II) cationic system, $[Mo_2(CH_3CN)_8(ax\text{-}CH_3CN)][BF_4]_4$, with water and the chelating phosphine dppe $[Ph_2PCH_2CH_2PPh_2]$ led to the synthesis of $[Mo_2(\mu\text{-}CH_3C(NH)O)_2(CH_3CN)_4][BF_4]_2$ and demonstrated the reaction occurs in dinuclear systems that contain a coordinated nitrile in the starting material. In the Mo_2(II, II) cationic system, the oxidation state of the dimolybdenum core is retained.[56] If dppe is eliminated from the reaction mixture and $[Mo_2(CH_3CN)_8(ax\text{-}CHCN)_2][BF_4]_4$[77] is used as the starting material, the reaction results in the synthesis of $[Mo_2(\mu\text{-}CH_3C(NH)O)(CH_3CN)_6][BF_4]_3$ to confirm the sensitivity of the reaction to the conditions as outlined in the following section.[55,56]

Reactions of $[N(C_4H_9)_4]_2[Re_2Cl_8]$ with other nitriles

Contrasting the hydrolysis of a single benzonitrile to result in the formation of $[N(C_4H_9)_4][Re_2Cl_6(\mu\text{-}C_6H_5C(O)NH)]$, the hydrolysis of the acetonitrile results in the synthesis of $[N(C_4H_9)_4][Re_2Cl_5(\mu\text{-}CH_3C(O)NH)(\mu\text{-}CH_3C(OH)N)]$.[58] The reaction to synthesize the complex with two coordinated *cis*-amidate ligands is performed in a 30:1 ethanol:acetonitrile solvent mixture stirred for 24 hours.[58] The Re_2(III, III) core is retained in $[N(C_4H_9)_4][Re_2Cl_5(\mu\text{-}CH_3C(O)NH)(\mu\text{-}CH_3C(OH)N)]$ and unlike $[N(C_4H_9)_4][Re_2Cl_6(\mu\text{-}C_6H_5C(O)NH)]$ contains a weakly coordinated axial chloride [Cl(5)] as shown in Figure 1. Extended arrays of repeating Re-Re-Cl units are formed as shown in Figure 2; zig-zagging along the crystallographic *c* axis by approximately 129° between the linked Re-Re-Cl units and nearly linear with a torsion angle of less than 5° when viewed along the *a* axis.

Although our initial studies were performed in ethanol solvent systems,[57,58] Treichel has synthesized a complex with a single amidate ligand, $[N(C_4H_9)_4][Re_2Cl_6(\mu\text{-}CH_3C(O)NH)]$, from $[N(C_4H_9)_4]_2[Re_2Cl_8]$ in acetonitrile using $AgBF_4$ in a 1:2 $[N(C_4H_9)_4]_2[Re_2Cl_8]$:$AgBF_4$ ratio.[59] The use of less than two equivalents of the silver salt in the reaction results in diminished yields, less than the optimal 21%, and supports the proposed reaction mechanism in which both OH^- or H_2O and CH_3CN are coordinated at the Re_2(III, III) core.[58,59]

The ability to form conjugated systems containing multiple metal-metal bonds has been confirmed,[78–88] and the potential to form extended systems based on the $[N(C_4H_9)_4][Re_2Cl_5(\mu\text{-}CH_3C(O)NH)(\mu\text{-}CH_3C(OH)N)]$[58] building block through linkage of the dirhenium core *via* weak axial chlorides demonstrated. With the ability to hydrolyze nitriles to amides, the potential exists to link two or more of the Re_2(III, III) units by the use of an arene bearing two nitrile functionalities. Using ethanol as the solvent system, McGaff reacted

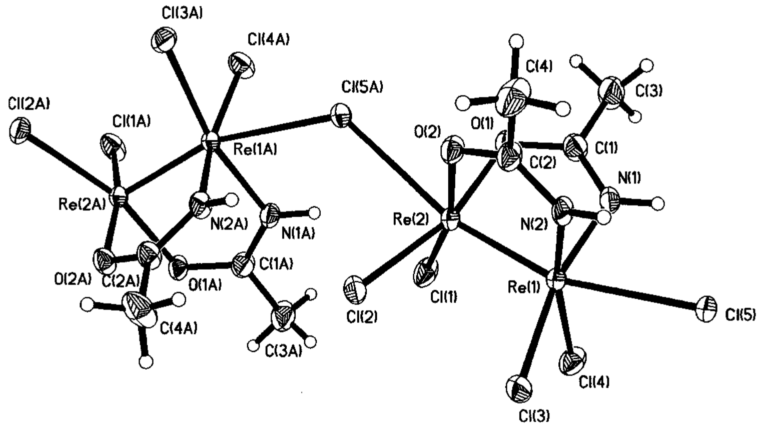


FIGURE 1 ORTEP diagram of $[N(C_4H_9)_4][Re_2Cl_5(\mu\text{-}CH_3C(O)NH)(\mu\text{-}CH_3C(OH)N)]$ with thermal ellipsoids at 30% probability level. The cation $N(C_4H_9)_4$ has been removed for clarity

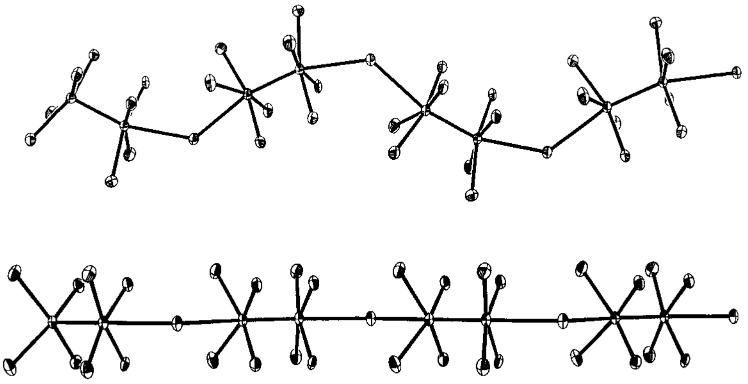
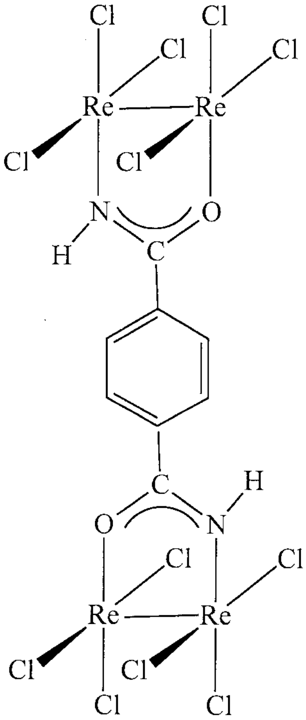


FIGURE 2 Extended arrays of repeating Re-Re-Cl units in $[N(C_4H_9)_4][Re_2Cl_5(\mu\text{-}CH_3C(O)NH)(\mu\text{-}CH_3C(OH)N)]$ with thermal ellipsoids at 30% probability level. The cation $N(C_4H_9)_4$ and carbon and hydrogen atoms have been removed for clarity. Zig-zagging chains are shown at the top of the figure as viewed along the crystallographic *c* axis and nearly linear chains viewed along the *a* axis are shown at the bottom of the figure

$[N(C_4H_9)_4]_2[Re_2Cl_8]$ with 1,4-$(CN)_2C_6H_4$ (2:1 ratio) at elevated temperatures in the presence of water.[60] Although produced in low yield (23.5%), the Re_2(III, III) core is linked by 1,4-$(C(O)NH)_2C_6H_4^{2-}$ as shown in Scheme 5[60] and utilizes the hydrolysis reaction to link the Re_2(III, III) cores with an unsaturated organic ligand.[58]



SCHEME 5 The Re_2(III, III) core linked by 1,4-$(C(O)NH)_2C_6H_4^{2-}$

Reactions $[N(C_4H_9)_4][Re_2Cl_6(\mu\text{-}C_6H_5C(O)NH)]$ and $[N(C_4H_9)_4][Re_2Cl_5(\mu\text{-}CH_3C(O)NH)(\mu\text{-}CH_3C(OH)N)]$ with dppm

Reactivity studies of $[N(C_4H_9)_4][Re_2Cl_6(\mu\text{-}C_6H_5C(O)NH)]$ and $[N(C_4H_9)_4][Re_2Cl_5(\mu\text{-}CH_3C(O)NH)(\mu\text{-}CH_3C(OH)N)]$ with dppm $[(C_6H_5)_2PCH_2P(C_6H_5)_2]$ result in a one-electron reduction to form

$Re_2Cl_4(\mu\text{-dppm})_2(\mu\text{-}C_6H_5C(O)NH)$ and $Re_2Cl_4(\mu\text{-dppm})_2(\mu\text{-}CH_3C(O)NH)$ respectively, Re_2(III, II) systems with the bridging phosphines in a *trans* geometry.[57,58] Note that $Re_2Cl_4(dppm)_2(\mu\text{-}CH_3C(O)NH)$ forms with the loss of $(CH_3C(OH)N)^-$ from the starting material $[N(C_4H_9)_4][Re_2Cl_5(\mu\text{-}CH_3C(O)NH)(\mu\text{-}CH_3C(OH)N)]$.[58] In the analogous $[Mo_2(\mu\text{-}CH_3C(NH)O)(CH_3CN)_6][BF_4]_3$ system, the reaction of the dimolybdenum complex with dppm retains the Mo_2(II, II) core to form $[Mo_2(\mu\text{-}CH_3C(NH)O)((\mu\text{-dppm})_2(CH_3CN)_2][BF_4]_3$.[55] The reduction of the Re_2(III, III) core by a phosphine ligand is not unusual, as demonstrated by the synthesis of $Re_2Cl_4(\mu\text{-dppm})_2$ from $Re_2Cl_6(P\text{-}n\text{-}Bu_3)_2$, a two-electron reduction.[89,90] Magnetic susceptibility studies performed on $Re_2Cl_4(\mu\text{-dppm})_2(\mu\text{-}C_6H_5C(O)NH)$ (1.45 B. M) and $Re_2Cl_4(dppm)_2(\mu\text{-}CH_3C(O)NH)$ (1.34 B. M) confirmed the paramagnetic Re_2(III, II) systems with one unpaired electron.[91]

Reactions of $Re_3(\mu\text{-}Cl)_3$ with acetonitrile

In work related to the study of the reactivity of $[N(C_4H_9)_4]_2[Re_2Cl_8]$ with a variety of nitriles, a series of trinuclear Re(III) compounds, such as $Re_3(\mu\text{-}Cl)_3Cl_6$ and $Cs_3Re_3(\mu\text{-}Cl)_3Cl_9$,[92] were reacted with acetonitrile under a variety of conditions.[59] While earlier studies of the reactivity of $Re_3(\mu\text{-}Cl)_3Cl_6$ with acetonitrile and benzonitrile resulted in the formation of $Re_3Cl_9(CH_3CN)_3$ and $Re_3Cl_9(C_6H_5CN)_3$ as dark purple powders,[93] the addition of $[N(C_4H_9)_4]Cl$, and deionized water to the reaction mixture allows the formation of the trinuclear compound $[N(C_4H_9)_4][Re_3Cl_8(\mu\text{-}1,2\text{-}CH_3C(O)NH)(\mu\text{-}2,3\text{-}CH_3C(O)NH)]$ as shown in Equation 1.[59] As in the synthesis of $[N(C_4H_9)_4][Re_2Cl_5(\mu\text{-}CH_3C(O)NH)(\mu\text{-}CH_3C(OH)N)]$ and $[N(C_4H_9)_4][Re_2Cl_6(\mu\text{-}C_6H_5C(O)NH)]$, the use of $AgBF_4$ does not appear to be required for the reaction to occur.[59] Studies of the trinuclear systems confirmed the production of HCl in the reaction as shown previously in Scheme 3.[59]

$$Re_3Cl_9(CH_3CN)_3 + 2H_2O + [N(C_4H_9)_4]Cl \longrightarrow$$

$$[N(C_4H_9)_4][Re_3Cl_8(\mu\text{-}1,2\text{-}HNCOCH_3)(\mu\text{-}2,3\text{-}HNCOCH_3)] + CH_3CN + 2HCl$$

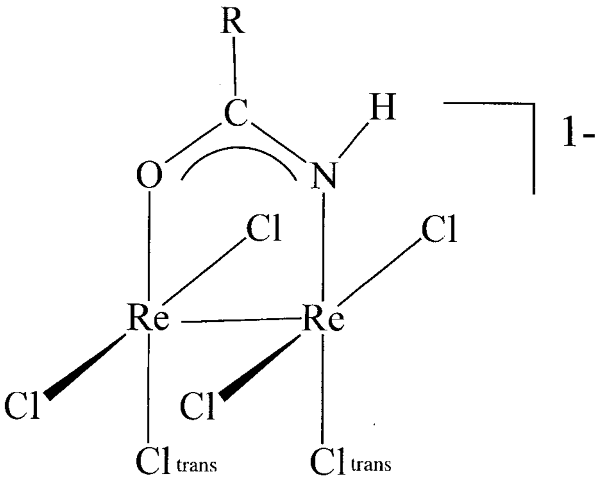
Examination of the redox chemistry of the $[Re_3(\mu\text{-}Cl)_3]^{9+}$ core afforded the first trinuclear systems with mixed oxidation states, Re_3(II, III, III), that hydrolyze coordinated nitriles.[61] Recent studies by Neuman confirm the trinuclear compound $[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_7(H_2O)_2]$ with a Re_3^{8+} core reacts with acetonitrile to form a mixture of $[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_7(CH_3CN)_2]$ and $[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_6\ (CH_3CN)_2(\mu\text{-}1,2\text{-}CH_3C(O)NH)]$. Subsequent exposure of the $[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_7(CH_3CN)_2]$: $[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_6(CH_3CN)_2(\mu\text{-}1,2\text{-}CH_3C(O)NH)]$ mixture dissolved in acetonitrile to dry oxygen provides a synthetic pathway to the Re_3^{9+} core, $[(C_6H_5)_4P]_2\ [Re_3(\mu\text{-}Cl)_3Cl_7(\mu\text{-}1,2\text{-}CH_3C(O)NH)]$.[61]

Structures

The classic salt $[N(C_4H_9)_4]_2[Re_2Cl_8]$ with a $\sigma^2\pi^4\delta^2$ electron configuration has a Re-Re bond distance of 2.222(2) Å.[94] Although bond distances are not necessarily correlated to bond order,[95] the comparison of bond distances and angles in the Re_2(III, III) and Re_3(III, III, III)$(\mu\text{-}Cl)_3$ complexes prepared to date along with spectroscopic properties provides insight into systematic trends developed in this new series of compounds. Using the data provided in Table I with a standard labeling scheme shown in Scheme 6, the Re-Re bond lengths of $[N(C_4H_9)_4]$ $[Re_2Cl_6(\mu\text{-}C_6H_5C(O)NH)]$ [**1**],[57] $[N(C_4H_9)_4][Re_2Cl_5(\mu\text{-}CH_3C(O)NH)(\mu\text{-}CH_3C(OH)N)]_2$ [**2**],[58] $[N(C_4H_9)_4][Re_2Cl_6(\mu\text{-}CH_3C(O)NH)]$ [**3**],[59] and $[N(C_4H_9)_4]_2[Re_4Cl_{12}(\mu\text{-}1,4\text{-}(C(O)NH)_2C_6H_4)]$ [**4**][60] fall within the expected range for quadruply bonded dirhenium species.[94,95] The structures of **2** and **4** both contain axially coordinated ligands, the anion Cl in **2** and dimethylformamide in **4**, that result in the longer Re-Re bond distances.[58,60] The axial chloride ligand bonded to Re(la) in **2**, shown previously in Figure 1, also interacts with the Re(2) atom on the adjacent dinuclear core with a Re(2)-Cl(5a) distance of 2.854 Å to form an extended chain. In compound **4**, the Re-O bond distance for the oxygen atom of the axially coordinated dimethylformamide solvent is 2.412(8) Å. Hydrogen bonding between the N-*H* of the amide and a chloride on the adjacent dirhenium core is also observed. The structures of **1**, shown in Figure 3, and **3** are similar with minimal changes in the structure resulting from the change in the coordinated amide ligand.[57,59] The Re(1)-Cl(2) bond distance in **1** is slightly longer than the Re(1)-Cl(3) bond distance as a result of the weak interaction between Cl(2) and Re(1A), 2.833 Å, a trend also observed in **3** (2.3858(9) and 2.8084(9) Å). In both **1** and **3**, the amide ligands adopt the *trans*-configuration to minimize steric interactions.

TABLE I Selected bond lengths (Å) and angles (°) for $[N(C_4H_9)_4][Re_2Cl_6(\mu\text{-}C_6H_5C(O)NH)]$ [**1**], $[N(C_4H_9)_4][Re_2Cl_5(\mu\text{-}CH_3C(O)NH)(\mu\text{-}CH_3C(OH)N)]$ [**2**], $[N(C_4H_9)_4][Re_2Cl_6(\mu\text{-}CH_3C(O)NH)]$ [**3**], and $[N(C_4H_9)_4]_2[Re_4Cl_{12}(\mu\text{-}1,4\text{-}(C(O)NH)_2C_6H_4)$ [**4**]

	[1]$\cdot 0.5CH_2Cl_2$	***[2]***$\cdot 3CH_2Cl_2$	***[3]***	***[4]***$\cdot 2OC(H)N(CH_3)_2$
Re-Re	2.2209(5)	2.2395(5)	2.2222(2)	2.2317(7)
Re-O	2.009(6)	2.012(6)	2.027(2)	2.032(9)
Re-N	2.044(7)	2.038(8)	2.052(3)	2.02(1)
Re-$Cl_{eq(O)}$	$2.322(3)_{trans}$	$2.332(3)_{trans}$	$2.3209(9)_{trans}$	$2.324(4)_{trans}$
	2.310(3)	$2.331(2)_{trans}$	2.3146(10)	$2.343(3)_{trans}$
	2.306(3)		2.3092(9)	2.355(3)
Re-$Cl_{eq(N)}$	$2.334(2)_{trans}$	$2.369(2)_{trans}$	$2.3537(8)_{trans}$	$2.339(4)_{trans}$
	2.332(2)	$2.351(8)_{trans}$	2.3356(9)	2.317(3)
	2.375(2)		2.3858(9)	2.311(3)
Re-Cl_{ax}		2.707(2)		
O-C	1.302(11)	1.291(11)	1.291(4)	1.28(1)
		1.297(11)		
N-C	1.315(11)	1.297(12)	1.299(4)	1.33(1)
		1.300(12)		
Re-Re-O	92.7(2)	92.37(17)	92.67(7)	90.8(2)
		92.44(18)		
Re-Re-N	88.1(2)	87.3(2)	87.38(9)	88.2(3)
		87.4(2)		
Re-Re-$Cl_{eq(O)}$	$103.86(8)_{trans}$	$102.01(6)_{trans}$	$103.58(3)_{trans}$	$102.(9)_{trans}$
	106.17(7)	$103.22(6)_{trans}$	106.21(3)	99.06(9)
	106.61(7)		106.33(3)	100.05(7)
Re-Re-$Cl_{eq(N)}$	$105.37(7)_{trans}$	105.58(6)	$105.03(2)_{trans}$	$106.36(9)_{trans}$
	100.07(6)	104.57(6)	99.29(2)	105.67(7)
	101.39(6)		101.00(3)	105.75(8)
Re-Re-Cl_{ax}		166.29(5)		



SCHEME 6 A standard labeling scheme shown for $[N(C_4H_9)_4][Re_2Cl_6(\mu\text{-}RC(O)NH)]$ complexes

Re-Re bond lengths of 2.3129(7) Å for $Re_2Cl_4(\mu\text{-}dppm)_2(\mu\text{-}C_6H_5C(O)NH)$[57] and 2.3011(3) Å for $Re_2Cl_4(dppm)_2(\mu\text{-}CH_3C(O)NH)$[95] are observed for these Re_2(III, II) species, where Re-Re bond distances of 2.20 to 2.30 Å are typical. As shown in Figure 4 containing the core structure of $Re_2Cl_4(dppm)_2(\mu\text{-}CH_3C(O)NH)$, two axially coordinated chlorides are present in these systems, and the Re-Re bond length in systems with axial halides is usually longer than the Re-Re bond length in Re_2(III, II) systems without axial chlorides. Weakening of the Re-Re σ bond results from the axially coordinated ligand, as in the case of the Re_2(III, III) system $Re_2((p\text{-}CH_3C_6H_4)NC(H)N((p\text{-}CH_3C_6H_4))_4(OMe)_2$ (Re-Re bond distance of 2.3047 Å) containing axially coordinated methoxy groups.[95,96]

In order to compare the trinuclear systems, a common labeling scheme was designed to allow the comparison of bond distances and angles for $[N(C_4H_9)_4][Re_3Cl_8(\mu\text{-}1,2\text{-}CH_3C(O)NH)(\mu\text{-}2,3\text{-}CH_3C(O)NH)]$ [**5**],[59] $[N(C_4H_9)_4]_2[Re_3Cl_{10}(\mu\text{-}1,2\text{-}CH_3C(O)NH)]$ [**6**],[59] $[N(C_4H_9)_4]_2[Re_3Cl_8(\mu\text{-}1,2\text{-}CH_3C(O)NH)(OH)_2]$ [**7**],[59] $[N(C_4H_9)_4]_2[Re_3$

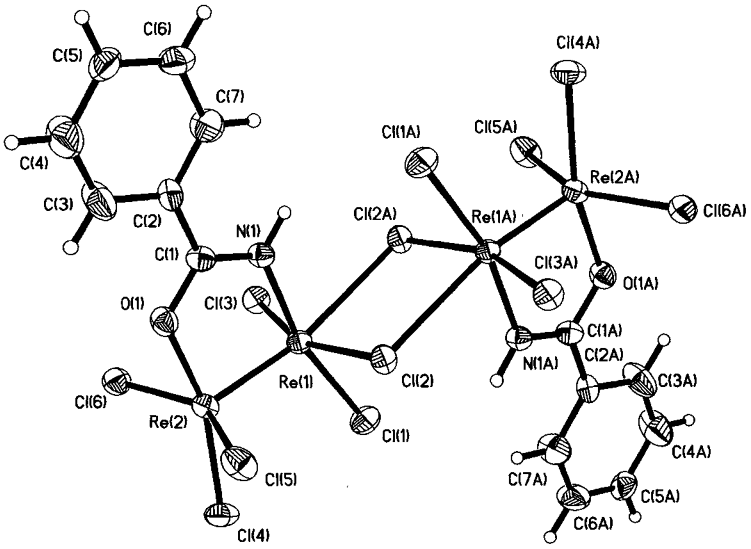


FIGURE 3 ORTEP diagram of $[N(C_4H_9)_4][Re_2Cl_6(\mu\text{-}C_6H_5C(O)NH)]$ with thermal ellipsoids at 30% probability level. The cation $N(C_4H_9)_4$ has been removed for clarity

$Cl_9(H_2O)(\mu\text{-}1,2\text{-}CH_3C(O)NH)]$ [**8**],[59] and $[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_7(\mu\text{-}1,2\text{-}CH_3C(O)NH)]$ [**9**].[61] The compound $[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_6(CH_3CN)_2(\mu\text{-}1,2\text{-}CH_3C(O)NH)]$ was not included in the comparison since the crystals are a 50:50 mixture of $[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_7(CH_3CN)_2]$ and $[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_6(CH_3CN)_2(\mu\text{-}1,2\text{-}CH_3C(O)NH)]$ to result in an average of bond distances and angles of the two complexes.[61] Shown in Scheme 7, the trinuclear core is labeled with positions A, B, and C occupied by the ligands listed in Table II. If complexes **6** and **9** are perceived as the base structure with positions A, B, and C occupied by a chloride, then the distance between Re_1 and Re_2 bridged by $(CH_3C(O)NH)^-$ is the shortest Re-Re bond distance. However, there is surprisingly little variation in the Re-Re bond distances and angles within the compounds studied to date. In fact, one of the largest deviations in Re-Re and Re-Cl bond distances occurs between the crystal structures of compound **6** and **9** that vary only in the lattice solvent CH_3CN present in **9**. With the lengthening of the Re-Re bond

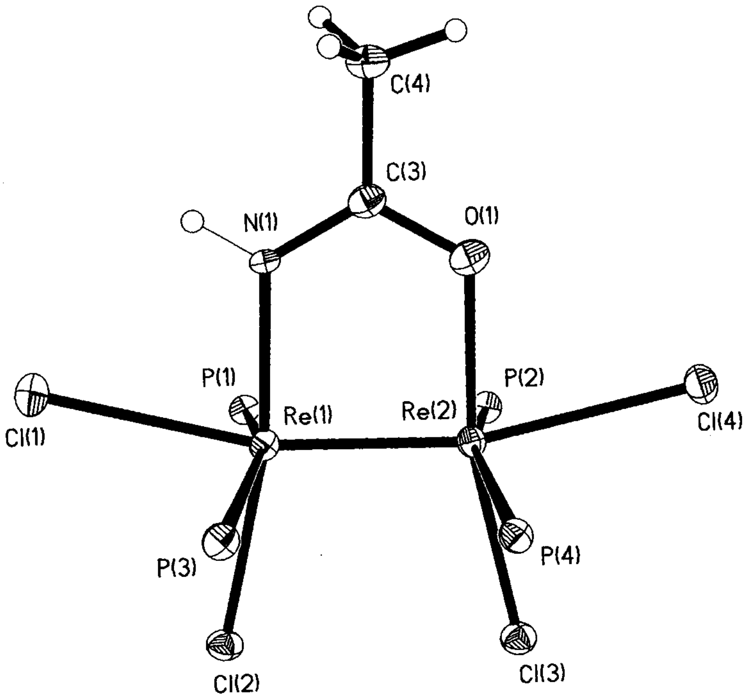
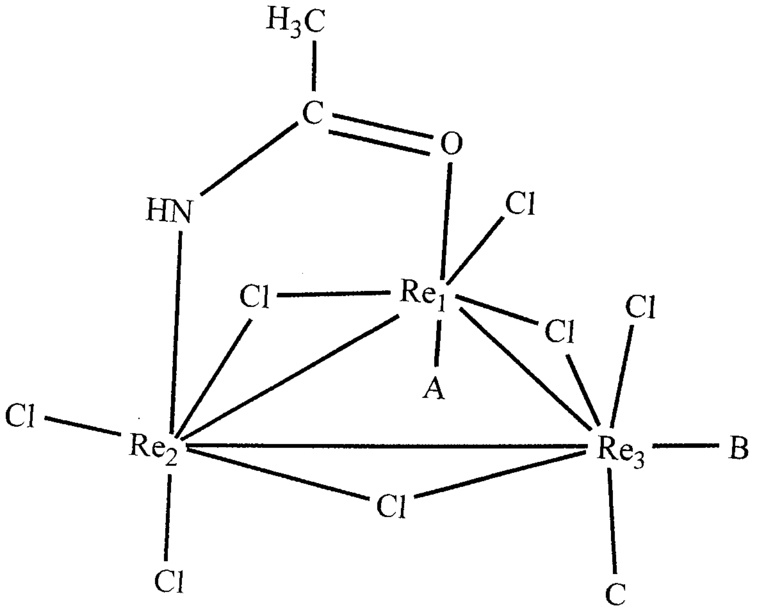


FIGURE 4 ORTEP diagram of the $Re_2Cl_4P_4(\mu\text{-}CH_3C(O)NH)$ core structure of $Re_2Cl_4(dppm)_2(\mu\text{-}CH_3C(O)NH)$ with thermal ellipsoids at 30% probability level

distances in **5–9** as compared to **1–4** by approximately 0.2 Å, the Re-Re-N and Re-Re-O bond angles become more acute by approximately 1 to 4° respectively with minimal changes in the Re-O and Re-N bond distances.

Spectroscopy

A distinct characteristic of both the trinuclear and dinuclear systems is the ^{1}H NMR spectroscopy; specifically the observation of the N-*H* peak. ^{1}H NMR spectra of $[N(C_4H_9)_4][Re_2Cl_5(\mu\text{-}CH_3C(O)NH)(\mu\text{-}CH_3C$



SCHEME 7 A standard labeling scheme for trinuclear $Re_3(\mu\text{-}Cl)_3$ complexes with bridging amidate ligands

(OH)N)] (10.67 ppm),[58] $[N(C_4H_9)_4][Re_2Cl_6(\mu\text{-}C_6H_5C(O)NH)]$ (11.34 ppm),[57] $[Mo_2(\mu\text{-}CH_3C(NH)O)(CH_3CN)_6][BF_4]_3$ (10.78 ppm),[55] $[Mo_2(\mu\text{-}CH_3C(NH)O)((\mu\text{-}dppm)_2(CH_3CN)_2][BF_4]_3$ (12.68 ppm),[55] and $[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_7(\mu\text{-}1,2\text{-}CH_3C(O)NH)]$ (9.390 ppm)[61] indicate the sensitivity of the N-*H* peak to the formal oxidation state of the transition metal core and the ligand environment. Although the N-*H* peak was not observed in $[N(C_4H_9)_4][Re_2Cl_6(\mu\text{-}CH_3C(O)NH)]$, a comparison of the $CH_3C(O)NH$ chemical shift, $[N(C_4H_9)_4][Re_2Cl_6(\mu\text{-}CH_3C(O)NH)]$ at 3.05 ppm[59] and $[Mo_2(\mu\text{-}CH_3C(NH)O)(CH_3CN)_6][BF_4]_3$ at 3.03 ppm[55] versus $[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_7(\mu\text{-}1,2\text{-}CH_3C(O)NH)]$ at 2.641 ppm, confirms a downfield chemical shift with an increasing bond order due to diamagnetic anisotropy, the secondary magnetic field created by the metal-metal multiple bond.

TABLE II Selected bond lengths (Å) and angles (°) for $[N(C_4H_9)_4][Re_3Cl_8(\mu\text{-}1,2\text{-}CH_3C(O)NH)(\mu\text{-}2,3\text{-}CH_3C(O)NH)]$ **[5]**, $[N(C_4H_9)_4]_2[Re_3Cl_{10}(\mu\text{-}1,2\text{-}CH_3C(O)NH)]$ [**6**], $[N(C_4H_9)_4]_2[Re_3Cl_8(\mu\text{-}1,2\text{-}CH_3C(O)NH)(OH)_2]$ [**7**], $[N(C_4H_9)_4]_2[Re_3Cl_9(H_2O)(\mu\text{-}1,2\text{-}CH_3C(O)NH)]$ **[8]**, and $[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_7(\mu\text{-}1,2\text{-}CH_3C(O)NH)]$ [**9**]

	[5]·*2.5*($C_4H_{10}O$)	***[6]***	***[7]***·*1.7*($C_4H_{10}O$)	***[8]***·C_3H_6O	***[9]***·CH_3CN
	A = O; $CH_3C(O)NH$	A = Cl	A = Cl,	A = Cl	A = Cl
	B = Cl	B = Cl	B = OH^-	B = H_2O	B = Cl
	C = N; $CH_3C(O)NH$	C = Cl	C = OH^-	C = Cl	C = Cl
Re_1-Re_2	2.4437(3)	2.4702(5)	2.4667(8)	2.4551(15)	2.4460(3)
Re_1-Re_3	2.4511(3)	2.5062(5)	2.4531(9)	2.4558(14)	2.4525(3)
Re_2-Re_3	2.4608(3)	2.4798(5)	2.4625(8)	2.4490(13)	2.4695(3)
Re_2-N	2.061(4)	2.073(8)	2.054(10)	2.05(2)	2.030(4)
Re_1-O	2.008(4)	2.040(6)	2.029(11)	2.01(2)	2.046(3)
Re_2-Cl_{ax}	2.4579(13)	2.519(2)	2.473(4)	2.444(7)	2.4812(16)
Re_2-Cl_{trans}	2.3264(15)	2.333(3)	2.340(4)	2.322(8)	2.2946(16)
Re_1-Re_2-N	84.79(12)	86.7(2)	87.0(3)	86.1(6)	86.27(13)
Re_2-Re_1-O	89.71(11)	88.4(2)	87.7(3)	88.2(5)	87.83(11)

For the quadruply bonded species, the δ to δ^* transition is observed in the UV-vis spectroscopy. In comparison to the parent compound $[N(C_4H_9)_4]_2[Re_2Cl_8]$ with a δ to δ^* transition between 680 – 690 nm depending on the solvent,[97] the transition in the amidate series $[N(C_4H_9)_4][Re_2Cl_5(\mu\text{-}CH_3C(O)NH)(\mu\text{-}CH_3C(OH)N)]$ (602 nm), $[N(C_4H_9)_4]$ $[Re_2Cl_6(\mu\text{-}C_6H_5C(O)NH)]$ (614 nm), $[N(C_4H_9)_4][Re_2Cl_6(\mu\text{-}CH_3C(O)NH)]$ (651 nm),[59] and $[N(C_4H_9)_4]_2[Re_4Cl_{12}(\mu\text{-}1,4\text{-}(C(O)NH)_2C_6H_4)]$ (666 nm)[60] is observed at higher energy. The trend to higher energy is to be expected since the δ to δ^* transition for the formamidinate and carboxylate complexes $Re_2Cl_2(\mu\text{-form})_4$, $Re_2Cl_4(\mu\text{-}O_2CR)_2$, and $Re_2Cl_2(\mu\text{-}O_2CR)_4$ fall in the general ranges of 386 – 418 nm,[98] 633 – 635 nm,[99] and 495 – 560 nm,[100] respectively.

CONCLUSIONS

Our investigation of the reactivity of $[N(C_4H_9)_4]_2[Re_2Cl_8]$ with C_6H_5CN marks the first use of a multiply bonded dirhenium species to synthesize coordinated amidate ligands from nitriles.[57] Since the initial study, the research has been extended to include the synthesis of new materials in the form of linear arrays of the Re_2(III, III) core linked by axial halides[58] and disubstituted amidate ligands, $1,4\text{-}(C(O)NH)_2C_6H_4$.[60] Nitrile hydrolysis studies with metal-metal bonded systems have been expanded to include both anionic and cationic systems, and all of the complexes, Re_2(III, III),[57–60] Mo_2(II, II),[55,56] and $Re_3(\mu\text{-}Cl)_3$,[59,61] contain two transition metal centers in close proximity coordinated by reasonably labile ligands. Since the hydrolysis of the nitrile is independent of the metal-metal bond order, oxidation state of the transition metal center, and nature of the transition metal, other dinuclear or trinuclear transition metal compounds may exhibit similar reactivities under the appropriate reaction conditions.

With the dirhenium systems, we will be able to pursue the bulk synthesis of the amides under mild reaction conditions using $[N(C_4H_9)_4]_2[Re_2Cl_8]$ once a methodology to remove the coordinated amidate ligand is developed. Critical experiments toward this goal have already been performed. For example, the addition of a silver salt, while not required, appears to expedite the hydrolysis of the nitrile. The dissociation of the coordinated amidate ligand can be achieved with the addition of a chelating phosphine, as in the case of the synthesis of $Re_2Cl_4(dppm)_2(\mu\text{-}CH_3C(O)NH)$ from $[N(C_4H_9)_4][Re_2Cl_5(\mu\text{-}CH_3C(O)NH)(\mu\text{-}CH_3C(OH)N)]$.[58] Therefore, the potential applications of Re_2(III, III) and $Re_3(\mu\text{-}Cl)_3$ promoted nitrile hydrolysis include both the construction of extended arrays linked by transition metal centers through the amidate ligands and, as an enzyme mimic for the catalytic hydrolysis of nitriles to yield an amide under mild reaction conditions. We are currently investigating both avenues of research in our laboratory.

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