Inorganic Chemistry
COMMUNICATION
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Investigation of Mixed Oxidation State Cyanide-Bridged Re^VOxo ($acac_2en$/pn) and Re^I(bipy)$(CO)_3$ Complexes

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S *Supporting Information*

ABSTRACT: A series of cyanide-bridged complexes that combine a low-valent photoacceptor rhenium(I) metal center with an electroactive midvalent rhenium(V) complex were prepared. The synthesis involved the preparation of novel asymmetric rhenium(V) oxo compounds, *cis*-$Re^VO(CN)(acac_2en)$ (**1**) and *cis*-$Re^VO(CN)(acac_2pn)$ (**2**), formed by reacting *trans*-$[Re^VO(OH_2)(acac_2en)]Cl$ or *trans*-$Re^VO(acac_2pn)Cl$ with $[NBu_4][CN]$. The μ-bridged cyanide mixed-oxidation Re^V−Re^I complexes were prepared by incubating the asymmetric complexes, **1** or **2**, with *fac*-$[Re^I(bipy)(CO)_3][OTf]$ to yield *cis*-$[Re^VO(acac_2en)$-(μ-CN-1κC:2κN)-*fac*-$Re^I(bipy)(CO)_3][PF_6]$ (**3**) and [*cis*-$Re^VO(acac_2pn)$(μ-CN-1κC:2κN)-*fac*-$Re^I(bipy)(CO)_3$]-$[PF_6]$ (**4**), respectively.

The design of metal complexes for electron-transfer properties has evolved considerably from the $Ru(NH_3)_5$ pyrazine dimer reported by Creutz−Taube[1] to more complicated asymmetric bimetallic systems that incorporate a variety of symmetric and asymmetric bridging organic ligands.[2] Utilizing the inherent characteristics of metals, complexes, and particular oxidation states, the application of multimetallic complexes has gained considerable attention in recent years. Multimetallic complexes vary from systems containing two or more different metal centers to systems containing two of the same metal in different oxidation states. These investigations have expanded the underlying scientific principles of electron transfer and have led to advances in applications in molecular wires/switches, solution-phase sensors, semiconductors, and biomimetic models.[3−5]

Several variations of metal−metal-bridged compounds with different aromatic bridging ligands have been investigated for their role in generating electrical potentials. $Ru(bipy)_3^{2+/3+}$ represents a substantial portion of the investigated compounds because of the photoabsorption capabilities of the $Ru^{II/III}$ redox couple.[6,7] $Re^I(CO)_3(bipy)Cl$ has also been suggested as an alternate because of its similar photon absorption properties.[8] Although a few rhenium compounds containing bridging cyanides have been reported, the oxidation state has been limited to symmetric low-valent centers (Re^I−Re^I).[9] Midvalent rhenium(V) oxo complexes with $Re^{V/IV}$ and $Re^{V/VI}$ redox couples have been shown to exhibit interesting electrochemistry; however, they have not previously been coupled to a photoelectron donor system.[10] Therefore, we examined the combination of the photoabsorption properties of the $Re^I(bipy)(CO)_3OTf$ moiety with a midvalent, diamagnetic, rhenium(V) center to evaluate a redox-active complex for electron transfer by preparing the first Re^I−Re^V cyano-bridged complexes and exploring their properties.

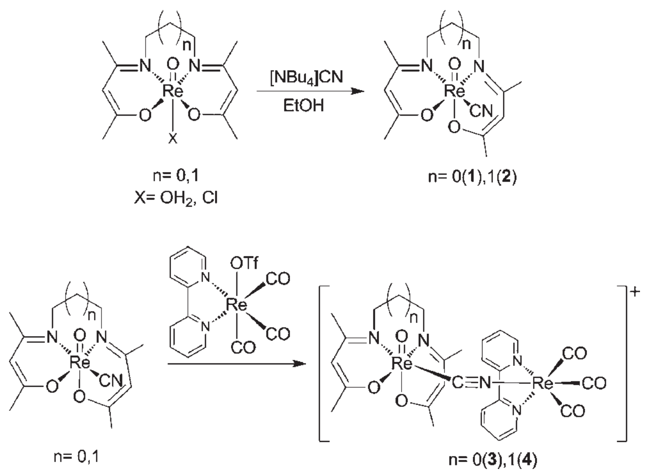
The preparation of the asymmetric cyanide complexes initially followed the previously reported method,[11] which involved the addition of a single equivalent of $[NBu_4][CN]$ to the symmetric trans ($[Re^VO(acac_2pn)Cl]$ and $[Re^VO(acac_2en)OH_2][Cl]$) compounds in a refluxed ethanol solution in a N_2 atmosphere. The reported procedure worked successfully for *cis*-$[Re^VO(acac_2pn)]CN]$ (**2**) but was unsuccessful for *cis*-$[Re^VO(acac_2en)]CN]$ (**1**). It was thought that **1** could not be formed because only the μ-O-$[Re_2^VO_3(acac_2en)_2]$ dimer was observed.[11] It was our hypothesis that dimer formation occurred by proton abstraction of a coordinated water or trace water by the cyanide anion, which led to a competing reaction of HCN(g) formation and the hydroxide moiety. To alleviate the loss of CN^- from the reaction vessel and shift the equilibrium toward the formation of **1**, *trans*-$[Re^VO(OH_2)(acac_2en)]Cl$ was reacted with $[NBu_4][CN]$ (3 equiv) in a sealed vial to successfully prepare **1** in high yield (92%). The ^1H NMR spectrum of **1** shows two singlets (5.43 and 6.06 ppm) that correspond to the inequivalent acac CH protons. The four methyl groups of the acac substrate are also inequivalent, with the furthest downfield resonance occurring at 2.88 ppm. As expected, the en backbone is twisted out of the equatorial plane. Because of the asymmetric nature of **1**, four inequivelent proton resonances for the ethylene backbone can be detected at 5.10, 4.01, 3.73, and 3.45 ppm, respectively.

Reacting equimolar equivalents of **1** and *fac*-$[Re^I(bipy)(CO)_3)][OTf]$ overnight at ambient temperature produced [*cis*-$Re^VO(acac_2en)$(μ-CN-1κC:2κN)-*fac*-$Re^I(bipy)(CO)_3][PF_6]$ (**3**; Scheme 1) in modest yield (54%). Observation of the reaction by ^1H NMR indicated a large upfield shift in the methyne resonances to 5.55 and 5.40 ppm, in addition to the bipyridyl resonances, which are observed from 8.94 to 7.58 ppm. The methyl resonances, on the acac moiety, have also shifted upfield to 2.71, 2.37, 2.15, and 1.75 ppm. Similarly, the reaction between equimolar equivalents of **2** and *fac*-$[Re^I(bipy)(CO)_3]$-[OTf] produced **4** in good yield (74%). The appearance of the bipyridyl resonances (8.94−7.81 ppm) along with shifts in the methyne proton resonances (5.46 and 5.41 ppm) indicates the formation of **4**.

Received: March 10, 2011
Published: May 02, 2011

dx.doi.org/10.1021/ic2005002 | *Inorg. Chem.* 2011, 50, 4686–4688

Scheme 1. Synthesis of *cis*-Re^{V}oxo(CN)($acac_2$en/pn) and the Asymmetric μ-CN-Bridged Complexes



Complexes **1**−**4** are dark green and deep brown in color and were investigated in the UV−visible region. A color change was observed in the conversion of the asymmetric **1** and **2** to the bridged complexes of **3** and **4**. The complexes turned from deep brown of **1** to red/brown of **3** and from dark green of **2** to blue/green of **4**. The low-energy, Laporte-forbidden, d−d transitions observed in the asymmetric complexes **1** and **2** (555 and 614 nm; ε = 100 and 200 M^{-1} cm^{-1}) are blue-shifted in the μ-CN-bridged complexes **3** and **4** (531 and 610 nm, ε = 100 and 200 M^{-1} cm^{-1}), indicating a change in the electron density (Figure S3). Unfortunately, extension of the UV spectrum into the near-IR region did not show an intervalence charge-transfer band for either of the bridged compounds. Exchange of the solvents only reproduced the absorbance observed. The absence of the intervalence charge-transfer band is likely attributed to the lack of symmetry of the individual compounds (minimal orbital mixing) coupled with the diamagnetic nature of each metal center to produce viable orbitals accessible for electron transfer. These data suggest that complexes **3** and **4** behave as weakly coupled independent complexes according to predictions by Marcus[12] and Hush.[13]

Complexes **1**, **3**, and **4** were additionally characterized by IR spectroscopy. The stretching frequencies of the cyanide moiety for **1** and **2** (2122 and 2125 cm^{-1}) red shift upon end-on metal coordination in complexes **3** (2152 cm^{-1}) and **4** (2153 cm^{-1}), as reported by both Darensbourg et al. and Kettle et al.[4,14] As expected, two CO stretches were observed for complexes **3** (2024 and 1916 cm^{-1}) and **4** (2019 and 1895 cm^{-1}), as well as the Re═O stretch in the generally accepted region (910−965 cm^{-1}).[11,15−17] Electrospray mass spectroscopy for compound **1** indicates m/z 449.3 for M^+. The M^+ parent cation of the μ-cyano-bridged complexes **3** and **4** was observed at m/z 876.3 and 890.6, respectively. This result was slightly unexpected because asymmetric fragmentation of dimetallic compounds with only a single bridging cyanide ligand is frequently observed.

Structural characterization of compound **1** was afforded through X-ray-quality crystals grown from the slow diffusion of hexane into chloroform. Compound **1** crystallizes in the monoclinic space group $P2(1)/n$ (Figure S1). The rhenium(V) center possesses a pseudooctahedral coordination geometry.

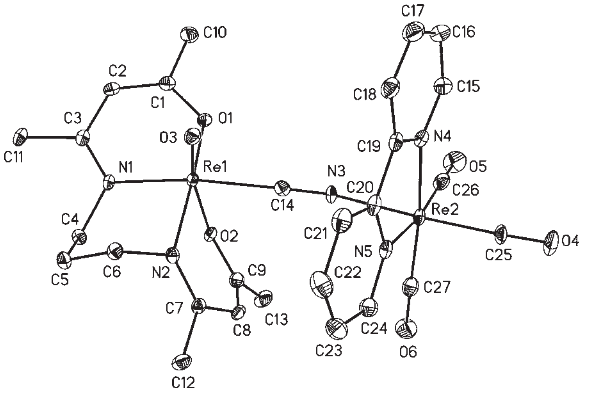


Figure 1. X-ray structure of **3** with 30% thermal ellipsoids. Selected bond distances (Å) and angles (deg): O1−Re1 2.035(2), Re1−O2 2.046(2), Re1−O3 1.687(3), Re1−N2 2.073(3), Re1−N1 2.080(3), Re1−C14 2.112(4), Re2−N3 2.123(3), Re2−C25 1.914(4), Re2−C26 1.931(4), Re2−C27 1.920(5), N3−C14 1.143(5); O1−Re1−N2 167.84(11), O1−Re1−N1 87.67(11), N1−Re1−C14 166.26(13), Re1−C14−N3 177.0(3), Re2−N3−C14 166.8(3), C25−Re2−N3 173.37(15).

The cyanide moiety is positioned cis to the oxo functionality, while the acac moieties are oriented trans to the oxo ligand and trans to the amine en backbone. Additionally, the cyanide ligand is positioned trans to the acac amine rather than trans to the oxo moiety because of the better σ-donating abilities of the amine functionality. The cyanide ligand has little back-bonding character, as evidenced from the Re1−C17 and C17−N18 distances of 2.121(3) and 1.152(4) Å. However, the Re1−N7 distance (2.063(3) Å) is significantly affected by the trans cyanide substituent when compared to the Re1−N10 distance of 2.034(3) Å, which is trans to the acac oxygen.

Complex **3** crystallizes in the monoclinic space group $P2(1)/c$ with one cation and one PF_6 anion in the asymmetric unit. The Re1 center shows the same cis pseudooctahedral coordination geometry as that found in compounds **1** and **2**, as shown in Figure 1. The bridging cyanide is coordinated to the $Re^{I}(CO)_3$(bipy) portion of the molecule in an end-on fashion through the nitrogen, creating the dimetallic complex **3**. The cyano group bridging the rhenium centers is slightly bent from linearity, as evidenced by the bond angles about C14 and N3 (Re1−C14−N3 177.0(3)° and Re2−N3−C14 166.8(3)°). Additionally, bond distances Re1−C14 (2.112(4) Å) and N3−Re2 (2.123(3) Å) are in the range typical of single bonds. The C14−N3 distance (1.143(5) Å) more closely resembles that of a triple bond, as was usually found for cyanide ligands bridging two metal centers.[4,18,19]

Electrochemical investigation of complexes **1**−**4** through cyclic voltammetry yielded an interesting comparison between the monomeric compounds (**1** and **2**) and the cyano-bridged complexes (**3** and **4**). Analysis was carried out in acetonitrile at a 100 mV/s scan rate with ferrocene (0.615 V) as the reference. The monomers **1** and **2** were found to have pseudoreversible $Re^{V/VI}$ couple potentials at $E_{1/2}$ of 1.335 and 1.365 V, respectively. The $E_{1/2}$ potentials of **1** and **2** are slightly higher than those observed for analogous symmetric Schiff base $Re^{V}O(acac_2en/pn)$ monomer and μ-oxo dimer complexes.[17] The observed differences may be related to the structural conformations and the impact of the trans effect by rhenium oxo on ligand dissociation in the symmetric and asymmetric complexes. The $Re^{V/IV}$ redox couples appear to be quasi-reversible in both **1** and **2** with $E_{1/2}$ values of −1.014 and −1.099 V, respectively. For comparison, $[Re^{I}(bipy)(CO)_3][OTf]$ was also examined and the four

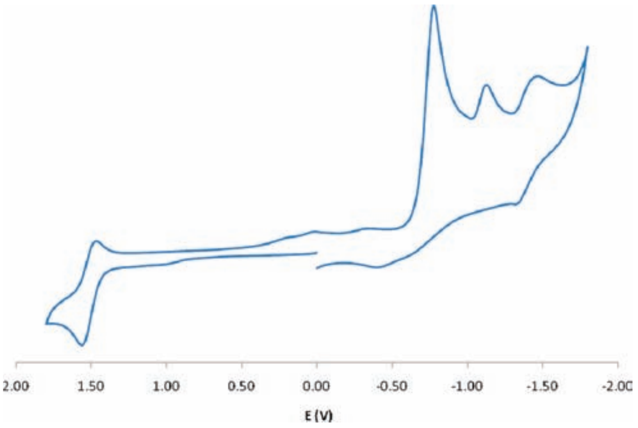


Figure 2. Cyclic voltammagram of **4** performed in acetonitrile with scan rates of 100 mV/s using a platinum working electrode, a platinum wire auxiliary electrode, and a Ag/Ag^+ reference electrode.

reduction potentials (E_{pc} = −0.341, −0.678, −1.032, and −1.315 V) observed were consistent with the literature.[20−23]

The bridging complexes **3** and **4** yielded a composite voltammogram indicative of both the Re^V and Re^I complexes. The $Re^{V/VI}$ redox couples of both **3** ($E_{1/2}$ = 1.590 V) and **4** ($E_{1/2}$ = 1.520 V) remained pseudoreversible, but the $E_{1/2}$ values were slightly more positive (anodic), indicating that they were more difficult to oxidize than those of **1** and **2** (Figure 2). The observed differences are most likely due to electronic changes in the π-back-bonding of the CN moiety with the addition of the rhenium(I) complex. The reductive portion of the voltammogram (−0.5 to −1.5 V) proved to be quite challenging to interpret for the bridging complexes because of overlap of the rhenium(V) and rhenium(I) complexes and the quasi-reversible nature of the $Re^{V/IV}$ redox couple. In this portion of the voltammogram, only three predominant E_{pc} peaks were observed. A comparison of the reduction potentials (E_{pc} (V) = −1.048 and −1.576 (**3**) and −1.102 and −1.415 (**4**)) for the nitrogen-bound cyano $[Re^I(NC)(bipy)(CO)_3]$ portion of the complex shows a modest shift, to a more negative potential (cathodic), and is in agreement with the reduction potential of the analogous carbon-bound cyano complex $[Re^I(CN)(bipy)(CO)_3]$ ($E_{1/2}$ = −1.125 V),[20] whereas the $Re^{V/IV}$ couple appears to be shifted positively (anodic; E_{pc} (V) = −0.882 (**3**) and −0.745 (**4**)) relative to the monomer.

In conclusion, we report a new synthetic route to produce asymmetric *cis*-$Re^VO(acac_2en)(CN)$ complexes in good yields that minimize the μ-oxo dimer side products. When these rhenium(V) complexes were reacted with $[Re^I(bipy)(CO)_3][OTf]$, unique asymmetric mixed-oxidation-state (Re^I−Re^V) cyanide-bridged complexes were isolated as different types of complexes that have not previously been examined. The initial studies of the bridging complexes indicate fusion of the two complexes through a bridging cyanide, which impacts the electronics of both individual complexes. However, the complexity of the electron shuttling between the Re^I−Re^V systems requires further investigation and electronic tuning of the ligands but does offer some promise.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. X-ray structural information for **1** and **4** in CIF format, full syntheses, characterization of the compounds, X-ray crystallographic experimental details, and bond angles and distances. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

The work was funded by the Department of Energy Radiochemistry Education Award Program DEFG20705ID14692I-DNE006) and the Washington State University Start Up fund. B.T. thanks the NSF-EPSCoR program and the M. J. Murdock Charitable Trust.

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