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Mechanism for the Activation of Carbon Monoxide via Oxorhenium Complexes

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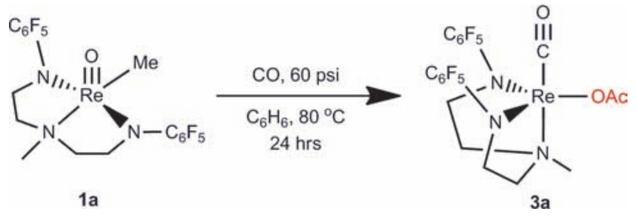
S *Supporting Information*

ABSTRACT: Activation of CO by the rhenium(V) oxo complex [(DAAm)Re(O)(CH_3)] (**1**) [DAAm = *N,N*-bis(2-arylaminoethyl)methylamine; aryl = C_6F_5, Mes] resulted in the isolation of the rhenium(III) acetate complex [(DAAm)Re(O_2CCH_3)(CO)] (**3**). The mechanistic details of this reaction were explored experimentally. The novel oxorhenium(V) acyl intermediate [(DAAm)Re(O)(C(O)CH_3)] (**2**) was isolated, and its reactivity with CO was investigated. An unprecedented mechanism is proposed: CO is activated by the metal oxo complex **1** and inserted into the rhenium−methyl bond to yield acyl complex **2**, after which subsequent migration of the acyl ligand to the metal oxo ligand yields acetate complex **3**. X-ray crystal structures of **2** and **3** are reported.

The ability to utilize CO as a C_1 source is attractive, especially as natural gas reserves are diminished and the need for alternative fuels is apparent.[1] Currently the major industrial source of CO is syngas, which is primarily used to produce CH_3OH. The subsequent carbonylation of CH_3OH yields acetic acid. A catalytic method for the synthesis of acetic acid and other C_{n+} oxygenates directly from syngas without the synthesis of methanol as an intermediate is highly desirable. However, despite tremendous research effort, the development of a homogeneous catalytic system has not been achieved.[2] We are pursuing a novel catalytic system for syngas conversion that involves three critical steps: (1) reduction of a CO ligand with H_2 to produce an alkyl, (2) C−C bond formation, and (3) C−O bond formation to produce C_{n+} oxygenates. In this paper, we demonstrate that two of these critical steps can be achieved (C−C and C−O bond formation) using a high-valent metal oxo complex.

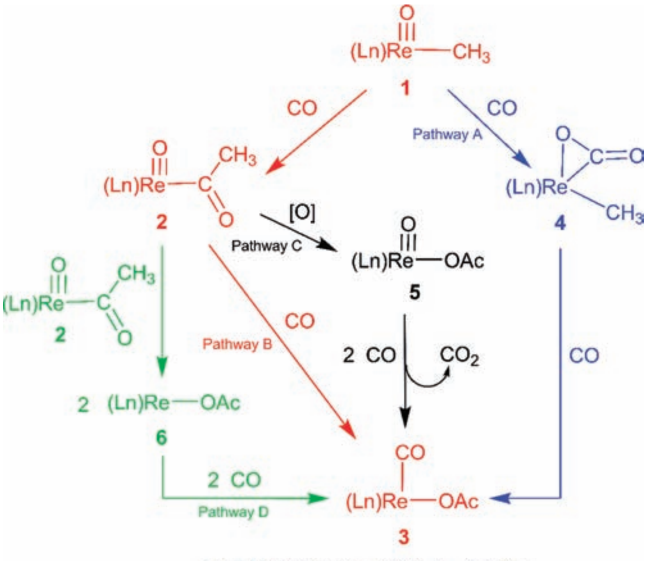
Addition of CO to [(DAAm)Re(O)(CH_3)] (**1a**)[3] [DAAm = *N,N*-bis(2-arylaminoethyl)methylamine; aryl = C_6F_5] in benzene (60 psi, 80 °C) resulted in the formation of [(DAAm)Re(O_2CCH_3)(CO)] (**3a**), as identified by ^{1}H NMR and FTIR spectroscopies (Scheme 1). Similarly, treatment of **1b** (aryl = Mes) with CO resulted in the formation of [(DAAm)Re(O_2CCH_3)(CO)] (**3b**) [Scheme S3 in the Supporting Information (SI)].

Scheme 1. Synthesis of 3a



A mechanism for the formation of **3** from **1** can be invoked in which initial attack of CO at the rhenium oxo would yield CO_2 intermediate **4**.[4] Subsequent migration of the methyl group to the CO_2 ligand would yield complex **3** (Scheme 2, pathway A).

Scheme 2. Possible Mechanisms for the Activation of CO via Oxorhenium Complexes



Ln = DAAm; aryl = (a) C_6F_5, (b) Mes

Three alternative mechanisms can also be proposed. These mechanisms first proceed via migratory insertion of CO into the rhenium−methyl bond of **1** yield oxorhenium(V) acyl intermediate **2**. Upon addition of CO to **2**, migration of the acyl ligand from the rhenium metal center to the terminal oxo ligand to yield **3** could occur (pathway B). The Re−acyl bond in **2** could also be oxidized, resulting in oxorhenium acetate complex **5**, and subsequent reduction of this complex with CO would yield **3** (pathway C). Lastly, the formation of **3** could result from intermolecular transfer of the acyl ligands from two molecules of **2** to form **6** followed by addition of CO to yield **3** (pathway D). In any of these pathways, the metal center is reduced from Re(V)

Received: June 13, 2011
Published: August 02, 2011

dx.doi.org/10.1021/ja205477w | *J. Am. Chem. Soc.* 2011, 133, 13288–13291

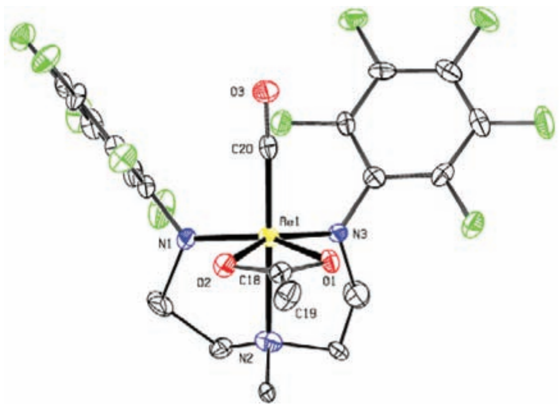


Figure 1. Thermal ellipsoid plot of complex **3a**. Thermal ellipsoids are at 50%. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Re1−C20, 1.872(6); Re1−N1, 1.922(4); Re1−N2, 2.240(4); Re1−N3, 1.929(4); N1−Re1−N3, 108.71(16); N1−Re1−C18, 122.15(17); N3−Re1−C18, 126.14(17); N1−Re1−C20, 96.10(2); N2−Re1−C20, 174.20(2); N3−Re1−C20, 95.60(2).

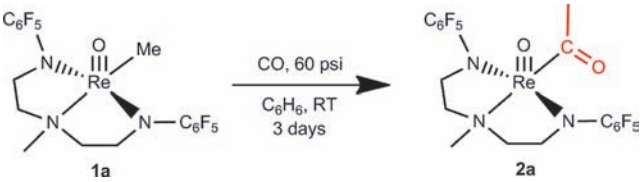
to Re(III) by two electrons and CO is oxidized to acetate. Pathway B would define a new mechanism for the conversion of a transition-metal acyl complex to an acetate complex. The formation of **3** from **1** is also an illustration of two of the critical steps leading toward the production of C_{2+} oxygenates from CO, namely, the C−C and C−O bond-formation steps. Efforts to probe the viability of these pathways are described below. Specifically, we examined experimentally the intimate mechanism for the activation of CO by metal oxo complexes.

X-ray-quality crystals of **3a** were obtained by slow diffusion of pentane into a concentrated methylene chloride solution of the complex at room temperature. The geometry at rhenium in **3a** (Figure 1) is best described as a distorted trigonal bipyramid, where the carbonyl ligand and the amine nitrogen occupy the axial sites and the amido nitrogens and the acetate carbon lie in the equatorial plane (N1−Re1−N3, 108.71°; N1−Re1−C18, 122.15°; N3−Re1−C18, 126.14°; N2−Re1−C20, 174.2°). This bonding description accounts for the diamagnetism observed for **3a**. Furthermore, the geometry of **3a** is similar to that of the analogous complex [(DAAm)Re(Cl)(CO)], which was synthesized in our lab, suggesting that the acetate ligand is best viewed as occupying one site in the equatorial plane of a trigonal bipyramid. The FTIR spectrum of **3a** exhibited carbonyl stretches at 1876 and 1868 cm^{-1}. These two bands were tentatively attributed to two isomeric forms of **3a**. The ^1H NMR spectrum of **3a** displayed the average peak resonances for the equilibrium. Cooling a CD_2Cl_2 sample of **3a** to −60 °C did not result in decoalescence of the resonances (Figure S2), suggesting that the barrier for the interconversion of the two isomers is low and thus easily accessible on the NMR time scale at room temperature.

The addition of CO to **1a** in benzene at room temperature resulted in the isolation of complex **2a**, as identified by ^1H NMR and FTIR spectroscopies (Scheme 3). Similarly, complex **2b** was synthesized from **1b** under analogous conditions (Scheme S4). Complex **2** is only the third example of a complex containing both an oxo ligand and an acyl ligand.[5]

The ^1H NMR spectrum revealed the presence of two isomers in a ratio of 4:1. Similarly, two FTIR acyl stretching frequencies (1587 and 1575 cm^{-1}) were observed for **2a**. These two isomers have been assigned as having anti and syn orientations of the acyl ligand with respect to the rhenium oxo ligand (Scheme 4).

Scheme 3. Synthesis of 2a



Scheme 4. Anti and Syn Isomers of 2a (Ancillary Ligands Have Been Removed for Clarity)

Ln = DAAm; aryl = C_6F_5

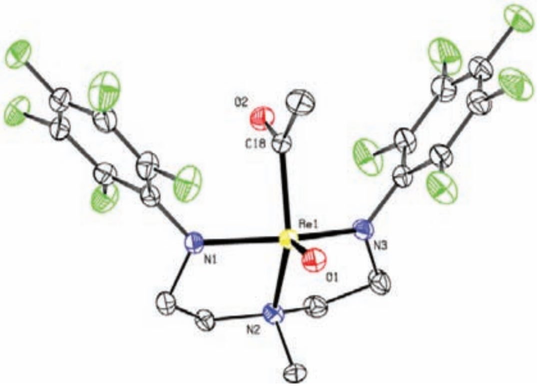
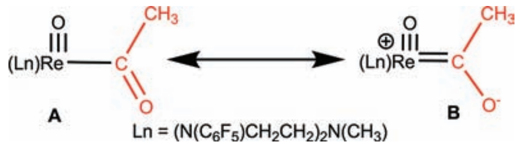


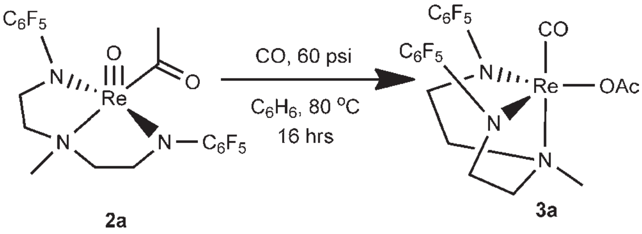
Figure 2. Thermal ellipsoid plot of **2a**. Thermal ellipsoids are at 50%. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Re1−O1, 1.687(2); Re1−N1, 1.983(3); Re1−N2, 2.164(3); Re1−N3, 1.974(3); Re1−C18, 2.026(3); C18−O2, 1.234(4); N1−Re1−N3, 139.65(12); N1−Re1−N2, 77.91(11); O1−Re1−N1, 110.13(11); O1−Re1−N2, 117.32(11); O1−Re1−N3, 109.50(12), O1−Re1−C18, 106.78(13); N1−Re1−C18, 88.14(12); N2−Re1−C18, 135.89(11).

X-ray-quality crystals were obtained by slow diffusion of pentane into a concentrated methylene chloride solution of **2a**, allowing the crystallographic characterization of the anti isomer (Figure 2). The geometry at rhenium in **2a** is best described as a distorted square pyramid with the oxo ligand (O1) in the apical position. The Re−O1 bond length (1.69 Å) is consistent with that of a Re−O multiple bond.[6] The Re$-C_{\text{acyl}}$ bond length in **2a** (2.040 Å) is short relative to those in similar reported rhenium acyl complexes. For example, the rhenium(III) acyl complex $[CpRe(CO)_2(COCH_3)(CH_3)]$ reported by Bergman and coworkers[7] has a Re$-C_{\text{acyl}}$ bond length of 2.192 Å, which is 0.152 Å longer than that in **2a**. In addition, the C$-O_{\text{acyl}}$ bond length in $[CpRe(CO)_2(COCH_3)(CH_3)]$ (1.189 Å) is shorter than that in **2a** (1.229 Å). The longer Re$-C_{\text{acyl}}$ bond and shorter C$-O_{\text{acyl}}$ bond in $[CpRe(CO)_2(COCH_3)(CH_3)]$ can be attributed to the presence of multiple π-accepting ligands that deplete the metal center of electron density and result in less π back-donation to the acyl ligand. Conversely, the electron-donating DAAm ligand

Scheme 5. Bonding Character of the Re$-$C$_{acyl}$ Bond in 2a (Ancillary Ligands Have Been Removed for Clarity)



Scheme 6. Synthesis of 3a from 2a



provides electron density to the metal center, resulting in more π back-donation to the acyl ligand. This is also supported by the fact that the average C═O acyl stretching frequency for **2a** (1582 cm^{-1}) is lower than that in [CpRe(CO)$_2$(COCH$_3$)(CH$_3$)] (1630 cm^{-1}).

FTIR absorption bands in the range 1558$-$1496 cm^{-1} for complexes of the type [(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(COR)] were observed by Gladysz and co-workers.[8] For R = CH(CH$_3$)CH$_2$C$_6$H$_5$, the Re$-$C$_{acyl}$ bond length (2.081 Å) and the C$-$O$_{acyl}$ bond length (1.252 Å) are comparable to those for **2a**.[8] The short Re$-$C$_{acyl}$ bond length was attributed to contributions from a carbene-like resonance structure in which metal$-$carbon multiple bonding is significant.[8] The bonding in **2a** may be described similarly (Scheme 5).

Metal$-$carbon multiple bonding accounts for the presence of the two isomers observed in the ^{1}H NMR and FTIR spectra of **2a**. Line broadening of the isomer resonances was not observed by ^{1}H NMR spectroscopy when a CD$_3$CN sample of **2a** was heated to 75 °C (Figure S9).[8]

The reaction of **2a** with CO was investigated. Addition of CO to **2a** in benzene (60 psi, 80 °C) yielded **3a** in ~60% isolated yield (Scheme 6). This result is consistent with the hypothesis that **2a** is an intermediate in the formation of **3a**. In an attempt to monitor the formation of other possible intermediates, the addition of CO to **1a** in CD$_2$Cl$_2$ at room temperature was monitored over time using ^{1}H NMR spectroscopy (Figure 3). Decay of **1a** occurred along with the formation of **2a**. Once a significant amount of **2a** had been formed, **2a** was consumed as **3a** was formed. *This result does not support the mechanism involving direct attack of CO at the rhenium oxo (pathway A).*

In order to test the possibility that complex **3** may result from oxidation of the Re$-$acyl bond in **2** by adventitious oxidant followed by reduction with CO (pathway C), complex **5a** was isolated and characterized and its reactivity with CO investigated. Complex **5** was not reduced by CO under identical reaction conditions, even in the presence of PPh$_3$ (see the SI). *This suggests that pathway C does not occur under these conditions.*

^{13}C labeling studies were also performed to determine whether the acetate ligand in **3a** originates from the acyl ligand in **2a**. The ^{13}C-labeled acyl complex **2a*** was isolated and characterized by ^{1}H NMR and FTIR spectroscopies (see the SI). The addition of ^{12}CO to **2a*** was then investigated. In pathway B, the migration of the acyl ligand to the rhenium oxo should result in incorporation of the ^{13}C label only at the acetate carbon in **3a***, with the carbonyl carbon in **3a*** remaining unlabeled (Scheme 7).

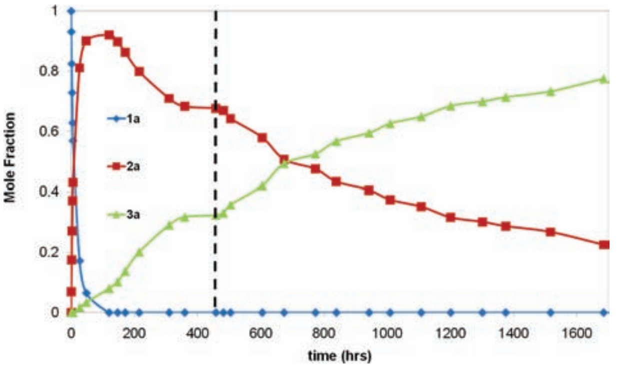
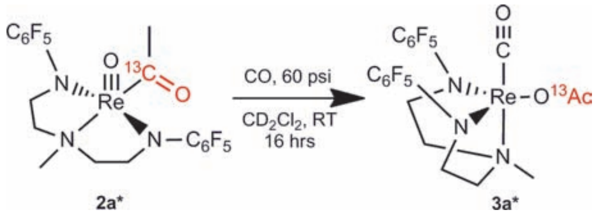


Figure 3. Time profile for the addition of CO (60 psi) to **1a** (9.2 mg, 0.14 mmol) in CD$_2$Cl$_2$ at room temperature. The reaction was monitored in a J. Young NMR tube by ^{1}H NMR spectroscopy with a hexamethylcyclotrisiloxane internal standard. At 458 h, the reaction was repressurized with CO.

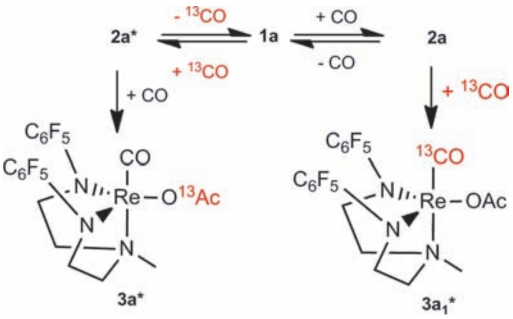
Scheme 7. Incorporation of the ^{13}C Label into 3a*, Representative of Migration of the Acyl Ligand to the Oxo Ligand (Pathway B)



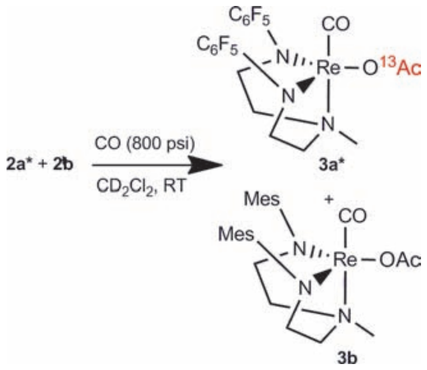
The addition of CO to **2a*** was monitored at room temperature (CD$_2$Cl$_2$, 60 psi). Under these reaction conditions, absorbances for the carbonyl ligand were observed only at 1876 and 1869 cm^{-1}, indicating the formation of **3a***. Similarly, the acetate methyl protons were observed as a doublet (J = 6.3 Hz), indicative of coupling to a ^{13}C-labeled acetate carbon. *These results unambiguously suggest that the carbon in the acetate ligand originates from the acyl ligand, in support of pathway B.* Under these reaction conditions, attack of CO at the terminal oxo (pathway A) is not viable, as this would require decarbonylation of **2a** to produce **1a** prior to attack at the oxo.

Decarbonylation of **2a** did not occur at room temperature, but heating **2a** in the absence of CO (80 °C) led to the formation of **1a**. When ^{12}CO was added to **2a*** in benzene-d_6 at 60 psi CO and 80 °C, absorbances for the CO ligand were observed at 1876 and 1869 cm^{-1}, which are indicative of **3a***. In addition, an absorbance at 1825 cm^{-1} was also observed, which is indicative of a ^{13}C-labeled carbonyl ligand. This result suggests that scrambling of the ^{13}C label occurred under these reaction conditions. The observed scrambling of the ^{13}C label at elevated temperatures results from decarbonylation of **2a*** according to Scheme 8. Decarbonylation to give **1a** results in a mixture of free ^{13}CO and ^{12}CO, which is available for addition to **1a**. At room temperature, however, the decarbonylation pathway is either not favored or slower than the migration of the acyl ligand to the rhenium oxo ligand. These results suggest that CO attack at the oxo ligand (pathway A) is not the lowest-energy pathway for the formation of **3**.

Scheme 8. Decarbonylation Pathway by Which Heating 2a* Yields Acetate Complexes 3a* and 3a$_1$*



Scheme 9. Addition of CO to 2a* and 2b



The formation of **3** via intermolecular transfer of the acyl ligands from two molecules of **2** (pathway D) was investigated by the addition of CO to a 1:1 mixture of **2a*** and **2b** (Scheme 9). After 16 h, only **3a*** and **3b** were observed, indicating that no crossover had occurred. *This implies that the intermolecular pathway (pathway D) is not viable under these reaction conditions.*

Pathway B appears to be the only pathway among those considered that is supported by all of the available data. The observed migration of the acyl ligand to the oxo ligand represents an unprecedented mechanism for acetate complex formation and is only the second thermal example of the migration of a ligand from the metal center to a terminal oxo ligand.[9] Addition of CO to **2a** depletes the metal center of electron density. As a result, the oxo ligand becomes electrophilic and is subject to intramolecular nucleophilic attack from the acyl σ bond. In the absence of CO, migration of the acyl ligand to the oxo ligand is not observed.

To summarize, the activation of CO by **1** was investigated and found to result in the synthesis of rhenium(III) acetate complex **3**. Four mechanisms for the formation of **3** were considered; an unprecedented mechanism for CO activation via metal oxo complexes that involves insertion of CO into the rhenium–methyl bond to yield **2** followed by migration of the acyl ligand to the terminal oxo to yield **3** is the only mechanism supported by all of the available data. The major evidence for this mechanism is the following: (a) the proposed intermediate **2** was isolated; (b) complex **2** is converted to **3** under the reaction conditions; (c) when the time course of the reaction was followed, it was observed that **2** accumulated and was consumed as expected; and (d) labeling studies showed that the acyl carbon in **2** is the acetate carbon in **3** and that scrambling does not occur at room temperature.

The observed reaction ultimately involves two key steps required for the selective conversion of CO to C_{2+} oxygenates: C–C bond formation and, observed here for the first time, C–O bond formation in the form of an acyl migration. Oxo ligands usually stabilize high-valent transition-metal complexes and as a result are typically inert. Thus, the apparent activation of the Re≡O bond is novel. Current efforts in our laboratories are aimed at developing these reactions for the design of homogeneous catalysts for syngas activation. In addition, the mechanistic details of both steps are currently being explored computationally.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Crystallographic data (CIF) for **2a**, **2b**, **3a**, and **3b**; NMR spectra of **2a** and **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

The authors acknowledge funding by North Carolina State University and by the National Science Foundation via the CAREER Award (CHE-0955636). Also, the Department of Chemistry of North Carolina State University and the State of North Carolina are acknowledged for funding the purchase of the Apex2 diffractometer. The authors thank Dr. Hanna Gracz for assistance with the 2D NMR experiments.

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■ NOTE ADDED AFTER ASAP PUBLICATION

Scheme 2 was replaced and reposted August 10, 2011.