ORGANOMETALLICS

Effect of the Ancillary Ligand on the Mechanism for CO Migratory Insertion in High-Valent Oxorhenium Complexes

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S Supporting Information

ABSTRACT: Several oxorhenium complexes bearing an SSS pincer ligand were isolated and characterized, and their reactivity with carbon monoxide was explored. The corresponding oxorhenium(V) acyl derivatives were also isolated and characterized. Carbonylation reactions required high pressures (400 psi) and temperatures (50 °C). The mechanism for carbonylation was explored with DFT (M06) calculations and revealed that the most likely mechanism for carbonylation involved stepwise formation of CO adducts followed by migration of the carbonyl ligand to the alkyl/aryl groups.

INTRODUCTION

The insertion of carbon monoxide into metal ligand bonds, carbonylation, is one of the most well-known migratory insertion reactions. Examples of insertion of carbon monoxide into metal ligand bonds are known for most transition metals,¹ and the insertion of carbon monoxide into metal alkyl and aryl bonds to generate metal acyl complexes and intermediates is generally proposed as the carbon-carbon bond forming step. Important, large-scale, industrial processes that utilize this process include the carbonylation of methanol to generate acetic acid in the Monsanto Acetic Acid Process,² BP's Cativa Process,³ and Eastman Chemical's Acetic Anhydride Process.⁴ Hydroformylation utilizes the migratory insertion of carbon monoxide in a reaction with olefin and molecular hydrogen to produce aldehydes.⁵ Because of the utility of carbonylation as a source for new C–C bond forming reactions, the design of new catalysts capable of these reactions is critical.

General mechanisms for the carbonylation of metal alkyl and aryl complexes are depicted in Scheme 1.6 The primary difference between the two mechanisms has been elucidated by isotopic labeling.⁷ In the direct CO insertion mechanism the acyl ligand is formed by an intermolecular attack of CO on a metal carbonyl complex. In contrast, in the classic CO "migratory insertion" mechanism, the acyl ligand is formed from intramolecular migration of an alkyl/aryl ligand to an adjacent CO ligand or the insertion of a CO ligand into an adjacent alkyl/aryl. The exact nature of the migrating group (CO vs alkyl/aryl) has been the subject of many mechanistic studies.8 Generally, these reactions have been shown to proceed via alkyl/aryl migrations rather than CO insertions.^{1,7,8c,9} However, Wojcicki and co-workers have shown with [CpFe-(CO)(Me)(L) (L = chiral phosphine) that the mechanism for CO insertion switches from alkyl/aryl migration to CO







insertion when the solvent is changed from nitromethane to HMPA (hexamethylphosphoramide).

In recent years, we have investigated carbonylation reactions with oxorhenium(V) complexes that contain tridentate diamidoamine DAAm (DAAm = N_1N -bis(2-arylaminoethyl)methylamine; $aryl = C_6 F_5$, Mes) and diamidopyridine DAP $(DAP = 2,6-bis((mesitylamino)methyl)pyridine).^{10}$ From mechanistic, kinetic, and computational studies it was shown that the most likely mechanism for the insertion of CO was a direct insertion mechanism and not the typical two-step intramolecular mechanism (see Scheme 1).

The mechanism for CO insertion is affected by the strong trans influence of the axial oxo ligand in these square pyramidal oxorhenium(V) complexes. As an illustration, calculated structures for the complex $MeRe(CO)_5$ and MeRe(O)

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 $(CO)_{4}$, where one CO ligand has been replaced with an oxo ligand, are depicted in Figure 1. The *trans* influence of the oxo



Figure 1. Optimized (M06) structures for $MeRe(CO)_5$ (left) and MeRe(O) (CO)₄ (right). Bond lengths are in angstroms, Å. Calculations were performed in the gas phase with the 6-31G(d,p) basis set on the C, H, and O atoms and the SDD basis set augmented with an f polarization function on Re.

ligand is clearly evident, as the rhenium–carbonyl bond *trans* to the oxo ligand is significantly lengthened compared to the analogous bond in MeRe(CO)₅ (2.12 vs 2.02 Å). In comparison, the carbonyl ligand *trans* to the methyl ligand (another strong *trans* influence ligand) is barely changed in both structures. In carbonylation reactions with metal oxo complexes, the weakening of a ligand *trans* to the oxo ligand lends to the instability of the resultant carbonyl and consequently a direct insertion mechanism. These types of mechanisms have been observed for oxorhenium(V) DAAm and DAP complexes.^{10,11}

Many factors affect the rates and migratory aptitudes of insertion reactions of CO. The effects of an entering ligand on the rate of migratory insertion have been highlighted in many studies.¹² However, reports on the effect of ancillary ligands on the rates of migratory insertion in transition metal complexes are somewhat limited.¹³

In this article, we examine the effect of the ancillary ligand on the mechanism for migratory insertion in high-valent oxorhenium species by synthesizing a series of oxorhenium complexes that contain SSS (SSS = 2-mercaptoethylsulfide) chelating ligands. Unlike the DAAm and DAP analogues, these ligands are not expected to be electron rich, and as a result, the CO adducts in Figure 1a may be stabilized because of the increased Lewis acidity at the metal center. Support for experimental data is provided by DFT (M06) calculations.

RESULTS AND DISCUSSION

Synthesis of SSS Alkyl and Aryl Complexes. A series of oxorhenium alkyl and aryl complexes bearing a tridentate SSS framework were successfully synthesized and isolated in good yields via transmetalation of the Re–X (X = Br) precursors with the corresponding transmetalating reagent (R_2Zn or RMgBr) (Chart 1). The known (SSS)Re(O)(Me) complex was made from the methyltrioxorhenium starting material as previously reported.¹⁴

All new SSS rhenium complexes (2-4) were fully characterized using ¹H NMR, ¹³C NMR, and IR spectroscopies. By ¹H NMR each complex exhibits four distinct multiplets each integrating to two protons. The four multiplets correspond to four diastereotopic protons of the ethylene backbone. All SSS Chart 1. (SSS)Re(O) Alkyl, Aryl, and Benzyl Complexes Utilized in This Study



complexes also exhibit a distinct Re=O stretch in the FT/IR spectrum at 963-972 cm⁻¹.

X-ray Crystal Structure of 1, 2, 3, and 4. X-ray quality crystals of 2, 3, and 4 were obtained by vapor diffusion of pentane into a concentrated solution of methylene chloride (Figure 2). The geometry around rhenium is best described as distorted square pyramidal, with the oxo ligand occupying the axial position. A comparison of the bond lengths and angles in the three structures is depicted in Table 1. Bond lengths and angles for all three structures are remarkably similar. The sp²-hybridized Re–C bond in 3 is slightly shorter than the corresponding sp³ Re–C bonds in 1, 2, and 4 as expected (entry 1).

Reactivity of Complexes 1–4 with CO. The addition of CO (400 psi) to complexes 1, 2, and 3 in toluene at 50 °C from 3 to 8 h resulted in the corresponding acyl derivatives (Scheme 2). The formation of the acyl derivatives 6-8 required harsher reaction conditions than the analogous DAAm and DAP complexes. In addition to 6-8, in all cases, the reaction with CO also led to the bimetallic [((SSS)Re(CO)₃)Re(CO)(SSS)], 9, which was isolated as a side-product.¹⁵

Complex 4 did not result in any isolable acyl derivative and decomposed even under milder reaction conditions (15-300 psi, 25–80 °C, 2–16 h) evident by the loss of protons for the SSS framework by ¹H NMR spectroscopy. Even though this complex was observed to react with CO by ¹H NMR spectroscopy, rapid decomposition of the new rhenium species was observed. Complexes 6-8 were characterized by ¹H and ¹³C NMR and FTIR spectroscopies, as well as elemental analyses. The FTIR spectra for all complexes exhibit a strong C-O stretch for the acyl group from 1602 to 1631 cm⁻¹ Similarly, other CO stretches for acyl complexes have been reported in the literature. For example, Bergman and coworkers have reported that $[CpRe(CO)_2(COCH_3)(CH_3)]$ has an IR stretching frequency of 1630 cm^{-1.16} Filippou and coworkers reported an IR stretching frequency of 1618 cm⁻¹ for the complex [CpRe(CO)₂C(O)Ph(Br)].^{17'} Hoffman and coworkers reported IR stretching frequencies of 1505 cm⁻¹ for $[\operatorname{Re}(O)(C(O)R)R_2(PMe_3)]$ (R = CH_2SiMe_3).¹⁸ The corresponding DAAm analogue of 6 exhibits a CO stretch 1587 cm⁻¹, and the DAP analogue exhibits a CO stretch of 1599 cm⁻¹. The DAP analogue of 8 exhibits a CO stretch at 1592 cm⁻¹. These data suggest the SSS ligand, in general, results in rhenium complexes that are less electron rich than the corresponding DAAm and DAP analogues.

X-ray Crystal Structure of 6. X-ray quality crystals of 6 were obtained via the slow diffusion of pentane into a concentrated solution of the rhenium compound in methylene chloride (Figure 3). The geometry around the metal center can be described as distorted square pyramidal with the terminal oxo ligand in the apical position. The rhenium carbon bond length decreases from 2.16 Å in 1 to 2.08 Å in 6. This bond length is approximately 0.05 Å longer than the analogous DAAm complex [DAAmRe(O)(C(O)CH₃)] and 0.04 Å longer



Figure 2. X-ray crystal structures of **2**, **3**, and **4**. Thermal ellipsoids are at 50% probability. Selected bond lengths (Å) and angles (deg). **2**: Re1–O1, 1.6901(15); Re1–C5, 2.157(2); Re1–S2, 2.3498(6); Re1–S1, 2.291(5); Re1–S3, 2.2890(5); S2–Re1–C5, 149.33(6); O1–Re1–C5, 101.16(9); S1–Re1–S3, 127.138(19). **3**: Re1–O1, 1.6831(14); Re1–C5, 2.1101(17); Re1–S2, 2.3461(4); Re1–S1, 2.2803(4); Re1–S3, 2.2886(4); S2–Re1–C5, 150.36(5); O1–Re1–C5, 101.81(7); S1–Re1–S3, 127.852(17). **4**: Re1–O1, 1.6861(15); Re1–C5, 2.1694(19); Re1–S2, 2.3360(5); Re1–S1, 2.2878(5); Re1–S3, 2.2901(5); S2–Re1–C5, 149.99(5); O1–Re1–C5, 102.10(8); S1–Re1–S3, 127.730(19).

Table 1. Selected Bond Lengths and Angles for 1-4

entry	bond (Å)	1 ¹⁴	2	3	4
1	Re-C	2.16	2.16	2.11	2.17
2	Re-S ₂	2.34	2.35	2.35	2.34
3	Re-S ₁	2.28	2.29	2.29	2.29
	angle (deg)				
4	O-Re-S ₁	115	116	115	115
5	O-Re-S ₃	NA	116	117	117
5	S ₁ -Re-S ₃	129	128	128	128
6	C-Re-S ₂	147	149	150	150

Scheme 2. Synthesis of Complexes 6-8



Figure 3. X-ray crystal structure of **6**. Ellipsoids are at 50% probability. Selected bond lengths (Å): Re1–O1, 1.691(2); Re–S1, 2.3327(6); Re–S2, 2.2920(5); Re–C, 2.077(3); O–Re–C, 104.63(11); S2–Re–O, 114.759(14).

than the corresponding DAP complex $[(DAP)Re(O)(C(O)-(CH_3)]]$. These differences, though small, appear to reflect increased electron density on rhenium in proceeding from SSS to DAP to DAAm ancillary ligands and consequently increased back-bonding from the metal center to the acyl CO π^* orbital. Thus, the data appear to suggest that the SSS ligand is the least electron donating ligand in the series.

DFT Calculations. Recently, possible mechanisms for the insertion of CO into oxorhenium(V) complexes with DAAm and DAP ancillary ligands were examined by our group.^{10,11} The most likely mechanism for the migratory insertion of these complexes is a direct insertion mechanism and not the

commonly proposed two-step mechanism that involves the formation of CO adducts (Scheme 1). In order to examine the effect of the ancillary ligand on the mechanism for the insertion of CO into rhenium alkyl/aryl bonds with SSS ligands, a computational study was pursued.

For the calculations in this article, structures were optimized in the gas phase with the $M06^{19}$ functional as implemented by Gaussian 09 with the 6-31G(d,p)²⁰ basis set on C, H, S, and O and the Stuttgart–Dresden²¹ basis set and relativistic effective core potential (RECP) combination (SDD) on Re with an additional f polarization function.²² Energetics were calculated with the 6-311++G(d,p)²³ basis set for C, H, S, and O atoms and the same basis set and RECP on Re as above. Reported energies utilized analytical frequencies and the zero-point corrections from the gas phase calculations and included solvation energies, which were computed using the SMD²⁴ model with benzene as the solvent. Throughout the article solvent-corrected free energies are reported without parentheses and gas phase values are reported with parentheses.

Three possible pathways were considered for the approach of CO to the metal center (Figure 4.) Because complex 1 is five



Figure 4. Computationally considered pathways for CO insertion.

coordinate, the trajectories considered were approaching (a) syn to the rhenium-methyl bond (pathway A), (b) syn to the rhenium-sulfido bond (pathway B), and finally (c) *trans* to the terminal oxo ligand (pathway C).

Pathway A. Attack of CO Syn to the Rhenium–Methyl Bond. The approach of CO syn to the rhenium–methyl bond results in the CO adduct 10. The geometry at the rhenium center in 10 is best described as distorted octahedral, where the oxo–rhenium–carbonyl bond angle is 87.2° , the oxo–rhenium–methyl bond angle is 147.4° , and the rhenium–methyl bond is elongated (2.35 Å) compared to the rhenium–methyl bond length in 1 (2.14 Å). The elongation of the rhenium–methyl bond in 10 is likely due to the *trans* influence of the terminal oxo ligand. The formation of 10 is endergonic

overall ($\Delta G^{\circ} = 17.4 \text{ kcal/mol}$), and the activation barrier for its formation is 33.7 kcal/mol.



Migration of the methyl group to CO results in **6syn**. The overall transformation from **10** to **6syn** proceeds with a barrier of 17.7 kcal/mol and is exergonic ($\Delta G^{\circ} = -5.4$ kcal/mol). Complex **6syn** isomerizes to the experimentally observed product **6** (Scheme 4). Isomerization is exergonic overall ($\Delta G^{\circ} = -7.5$ kcal/mol) and proceeds with a barrier of 5.5 kcal/mol.

Scheme 4. Isomerization Pathway from 6syn to 6



The large barrier for the addition of CO to 1 via TS1 ($\Delta G^{\ddagger}_{298} = 33.7$ kcal/mol) makes pathway A unlikely for the formation of **6**.

Pathway B. Addition of CO Syn to the Rhenium– Sulfido Bond. The approach of CO syn to the rhenium– sulfido bond of 1 resulted in the formation of the CO adduct 11, which is endergonic overall ($\Delta G^{\circ} = 9.3 \text{ kcal/mol}$). Adduct 11 has both the CO and methyl ligands in the equatorial plane, and the SSS is now arranged around rhenium in a facial orientation. Complex 11 is structurally similar to 10 and is also best described as a distorted octahedron around rhenium with an oxo-rhenium–carbonyl bond angle of 87.1°. The formation of 11 is more favorable than the formation of 10 by 8.1 kcal/ mol and proceeds with a lower barrier ($\Delta G^{\ddagger}_{298} = 16.9 \text{ kcal/}$ mol). The increased stabilization of 11 may be due to the orientation of the sulfur ligand *trans* to the terminal oxo ligand, whereas 10 has two strong *trans* influence ligands (methyl and oxo) approximately 180° from each another.

From 11, methyl migration occurs to afford the acyl product 12. The formation of 12 from 1 is unfavorable overall ($\Delta G^{\circ} =$ 37.7 kcal/mol) and proceeds with a large activation barrier, **TS5** ($\Delta G^{\dagger}_{298} =$ 49.4 kcal/mol). In addition, pathway B does not lead to the experimentally observed product and is thermodynamically and kinetically unfavorable.

Pathway C. Attack of CO *Trans* to the Oxo Ligand. Finally, the approach of CO *trans* to the terminal oxo ligand was considered (Scheme 6). Initial addition of CO *trans*

Scheme 5. Pathway B



proceeds with an activation barrier of 12.7 kcal/mol, is endergonic overall ($\Delta G^{\circ} = 12.2 \text{ kcal/mol}$), and results in the CO adduct 13. The rhenium–carbonyl bond in 13 is weak (2.46 Å). Of the more than 20 000 rhenium–carbonyl bonds reported in the Cambridge Structural Database the average is 1.93(5) Å (see Supporting Information), and only two complexes with comparable bond lengths have been reported. Complex 13 is then transformed into CO adduct 14. The transformation from 1 to 14 is endergonic ($\Delta G^{\circ} = 21.6 \text{ kcal/}$ mol) and proceeds with a barrier of 23.0 kcal/mol. The major structural features for 13 and 14 are summarized in Table 2.

In proceeding from 13 to 14 the oxo-rhenium-carbonyl bond angle is decreased from 172° in 13 to 140° in 14 (entry 4), the rhenium-carbonyl bond (2.04 Å) is significantly shorter (entry 3), and the rhenium-methyl bond is increased significantly from 2.15 Å in 13 to 2.26 Å in 14 (entry 2).

Carbon-carbon bond formation occurs from 14 to 6 with an overall barrier of 21.9 kcal/mol. Thus, the barrier for this elementary step (TS8, 14 to 6) is essentially barrierless (0.3 kcal/mol). These data suggest that the most likely pathway for the formation of 6 is pathway C, which results in the formation of unstable CO adducts (13 and 14) before proceeding to product.

Pathway C thus describes the stepwise insertion of CO into the rhenium–methyl bond of **1**. There have been several mechanistic studies aimed at clarifying the exact nature of the migrating group (CO insertion versus alkyl/aryl migration) in metal–alkyl/aryl carbonylation reactions.^{1,7,8c,9,25} Generally, it has been established that alkyl/aryl migration is the dominant mechanism compared to CO insertion. However, based on the geometry of the acyl product **6** (acyl ligand *cis* to oxo) and the vibrational analysis of **TS8** it is evident that the mechanism here involves CO insertion. Thus, pathway C is a rare example where a CO ligand migrates to an alkyl ligand.

More importantly, because the ancillary SSS chelating ligand is not very donating, the effect on the mechanism for insertion is (a) CO adducts are slightly stabilized relative to the DAAm and DAP analogues, where a direct CO insertion mechanism was observed, and (b) the reduced electron density at rhenium results in harsher conditions (400 psi CO, 50 °C) for carbonylation when this ligand is employed compared to the corresponding DAAm and DAP complexes. The computational data for the three calculated pathways are summarized in Figure 5.

CONCLUSIONS

The effect of the ancillary ligand on the mechanism for migratory insertion of CO in high-valent oxorhenium species has been clarified by synthesizing a series of oxorhenium complexes that contain SSS (SSS = 2-mercaptoethylsulfide) chelating ligands. Unlike the DAAm and DAP analogues, SSS ligands result in complexes that are less electron rich at rhenium. As a result, CO adducts are slightly stabilized because of the stronger electrostatic interaction between the CO ligand, which acts as a σ donor, and the Lewis acidic metal center. Consequently, CO adducts are intermediates on the potential energy surface.

Data suggest that the most likely mechanistic pathway results in the formation of two distinct CO adducts before proceeding to product. Thus, the most likely pathway with SSS ligands describes the stepwise insertion of CO into the rhenium– methyl bond of 1 rather than the concerted direct CO insertion observed for DAAm and DAP complexes.^{10,11}

Scheme 6. Pathway C







^{*a*}Structures were optimized in the gas phase with the 6-31G* basis set²⁶ on C, H, S, and O and the SDD basis set and effective core potential on Re. The basis set on Re was augmented with a single f polarization function. Hydrogens have been omitted for clarity.

On the basis of the geometry of the acyl product and the vibrational analysis of carbon–carbon bond forming step, it is evident that the mechanism here involves CO insertion. Thus, the calculated mechanism with SSS ligands is a rare example of CO insertion rather than alkyl/aryl migration.

The differences between the mechanistic pathways are summarized in Scheme 7. These results have important implications for the design of catalysts for efficient carbonylation reactions and suggest that the employment of an oxo ligand as well as donating ancillary ligands on a transition metal center may result in lower barriers for carbon–carbon bond formation. The enhanced reactivity stems from the strong *trans* influence of the oxo ligand, which has the effect of destabilizing CO adducts prior to migratory insertion.

EXPERIMENTAL SECTION

Complex 1¹⁴ and (SSS)Re(O)Br²⁷ were synthesized as previously reported. All other reagents were purchased from commercial resources and used as received. ¹H and ¹³C NMR spectra were obtained on 300 or 400 MHz Varian Mercury spectrometers at room temperature. Chemical shifts are listed in parts per million (ppm) and referenced to their residual protons or carbons of the deuterated solvents, respectively. All deuterated solvents were obtained from Cambridge Isotopes Laboratory. All reactions were run open to air unless otherwise noted. FTIR spectra were obtained on a JASCO FT/ IR-4100 instrument in KBr thin films. High-pressure reactions were performed in a stainless steel Parr 4590 micro bench top reactor. Elemental analyses were performed by Atlantic Micro Laboratories, Inc.

(SSS)Re(O)Et, 2. In a 25.0 mL scintillation vial (SSS)Re(O)Br (0.691 mmol, 300 mg) was dissolved in ~15.0 mL of THF. (Et)₂Zn (1.38 mL of a 1.0 M solution in ether) was added to a stirred reaction mixture, and the resulting dark brown solution was allowed to stir for 1 h at room temperature. Solvent was removed *in vacuo*, and the residual brown residue was dissolved in a minimal amount of methylene chloride. Addition of excess pentanes resulted in a dark precipitate. Filtration afforded a pale yellow-orange powder (0.345 mmol, 132 mg, 50% yield). ¹H NMR (CD₂Cl₂) δ : 4.14 (m, 2H), 3.94 (m, 2H), 3.83 (q, *J* = 7.4 Hz, 2H), 3.00 (m, 2H), 2.28 (t, *J* = 7.4 Hz, 3H), 1.79 (m, 2H). ¹³C NMR (CD₂Cl₂) δ : 49.3, 44.2, 24.3, 24.1. Anal. (C₆H₁₃S₃ORe) Calcd: C 18.79; S 25.08; H 3.42. Found: C 18.90; S 24.91; H 3.46.

(SSS)Re(O)Ph, 3. In a 25.0 mL scintillation vial, (SSS)Re(O)Br (0.691 mmol, 300 mg) and Zn₂Ph (1.38 mmol, 303 mg) were dissolved in ~15 mL of THF in a nitrogen-filled glovebox. The reaction was stirred for 0.5 h at room temperature. The resulting mixture was extracted with CH₂Cl₂ (25.0 mL × 3) and washed with a saturated NaCl solution (50.0 mL × 3). The organic layer was dried over NaSO₄ and filtered. The filtrate was reduced *in vacuo* to afford the concentrated product. Excess pentanes (~50.0 mL) were added to afford the product as a red powder (0.506 mmol, 219 mg), 73% yield. ¹H NMR (CD₃CN) δ : 7.2 (d, *J* = 7.4 Hz, 2H), 7.1 (dd, *J* = 6.9, 1.4 Hz, 2H), 7.0 (t, *J* = 6.6 Hz, 1H), 4.3 (m, 2H), 4.1 (m, 2H), 3.1 (m, 2H), 2.1 (m, 2H). ¹³C NMR (CD₂Cl₂) δ : 138.2, 128.1, 124.9, 48.4, 44.7. Anal. (C₁₀H₁₃S₃ORe) Calcd: C 27.83; S 22.28; H 3.04. Found: C 27.96; S 22.56; H 3.00.

(SSS)Re(O)Bn, 4. In a 25 mL scintillation vial, (SSS)Re(O)Br (300 mg, 0.691 mmol) was dissolved in 10.0 mL of dry CH2Cl2 in a nitrogen-filled glovebox. BnZnBr (5.5 mL of a 0.5 M solution in THF) was added. The reaction mixture was stirred at room temperature for 0.5 h. The product was extracted with CH_2Cl_2 (25.0 mL \times 3) and washed with a saturated NaCl solution (25.0 mL \times 3). The organic layer was dried with NaSO4 and filtered, and the filtrate was reduced in vacuo. To the concentrated solution, excess hexanes were added (50.0 mL) to afford a gray precipitate. The precipitate was filtered and dried to afford product (0.202 mmol, 88.5 mg), 44% yield. ¹H NMR $(CD_{2}Cl_{2})$ δ : 7.3 (m, 4H), 7.0 (m, 1H), 5.0 (s, 2H, benzylic), 4.1 (m, 2H), 4.0 (m, 2H), 3.0 (m, 2H), 1.9 (m, 2H). $^{13}\mathrm{C}$ NMR (CD_2Cl_2) $\delta:$ 130.1, 127.5, 124.6, 49.7, 44.5, 33.2. Anal. (C₁₁H₁₅S₃ORe·CH₂Cl₂) Calcd: C 27.17; H 3.23; S 18.13. Found: C 27.82; H 3.10; S 20.13. Despite several attempts satisfactory elemental analysis could not be obtained for this molecule. NMR spectra are provided in the Supporting Information.

General Procedure for Complexes 6–8. In a 25 mL glass liner, **6–8** and a stir bar were added and dissolved in 15 mL of toluene. The glass liner was added to a Parr reactor and allowed to stir. The reactor was pressurized with carbon monoxide (400 psi) and heated to 50 °C for 3–7 h. The reactor was then cooled to room temperature and depressurized. The reaction mixture was concentrated under reduced pressure and filtered over Celite. To the resulting filtrate were added excess pentanes to afford an orange precipitate. Filtration of the precipitate gave a pale orange powder.



Reaction Coordinate

Figure 5. Computational pathways for the migratory insertion of CO in (SSS)Re(O)Me. Structures were optimized with Gaussian 09 in the gas phase with the M06 functional and employed the SDD basis set on Re with an added f polarization function and the 6-31G(d,p) basis set on all other atoms. Energetics were calculated with the 6-311++G(d,p) basis set for C, H, N, O, and F atoms and the SDD basis set with an added f polarization function on Re as implemented in Gaussian 09. Reported energies utilized analytical frequencies and the zero-point corrections from the gas phase calculations and included solvation corrections, which were computed using the SMD model as implemented in Gaussian 09.





(SSS)Re(O)C(O)CH₃, 6. Compound 1 (300 mg, 0.813 mmol) was reacted with CO for 7 h. Isolated amount: 129 mg, 0.325 mmol, 40% yield. ¹H NMR (CDCl₃) δ : 4.3 (m, 2H) 3.9 (m, 2H), 3.0 (m, 5H) 2.1 (m, 2H). ¹³C NMR (CDCl₃) δ : 245.0, 52.2, 46.3, 43.0. IR (FTIR, KBr

pellet, cm⁻¹): ν (C–O_{acyl}) 1620(s); ν (Re–O) 968 (s). Anal. (C₆H₁₁S₃O₂Re) Calcd: C 18.13; S 24.19; H 2.79. Found: C 18.35; S 24.49; H 2.75.

(SSS)Re(O)C(O)CH₂CH₃, 7. Compound 2 (152 mg, 0.395 mmol) was reacted with CO for 7 h. Isolated amount: 51.8 mg, 0.126 mmol, 31% yield. ¹H NMR (CDCl₃) δ : 4.3 (m, 2H) 3.9 (m, 2H) 3.3 (q, *J* = 7.7 Hz, 2H) 3.1 (m, 2H) 2.0 (m, 2H) 1.4 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (CDCl₃) δ : 248.2, 47.8, 44.6, 24.9, 25.1. Anal. (C₇H₁₃S₃O₂Re·(0.5)CH₂Cl₂) Calcd: C 19.84; H 3.11. Found: C 19.84; H 3.20. IR (FTIR, KBr pellet, cm⁻¹): ν (C–O_{acyl}) 1631(s).

[((SSS)Re(CO)₃)Re(CO)(SSS)], 9. Complex 1 (300 mg, 0.813 mmol) was added to a 25.0 mL glass liner with a stir bar and dissolved in toluene (\sim 15.0 mL). The glass vial was added to a Parr reactor, pressurized with carbon monoxide (800 psi), and heated to 80 °C for 16 h. The reaction mixture was cooled to room temperature and depressurized, and the solvent was evaporated *in vacuo*. The resulting red powder was collected in 26% yield (83.5 mg, 0.106 mmol). FTIR

(KBr pellet, cm⁻¹): ν (C–O) 2012 (bs); 1939 (bm); 1871(bm). UV– vis: λ_{max} 557 nm, 0.05 M in CH₂Cl₂. Anal. (C₁₂H₁₆S₆O₄Re₂) Calcd: C 18.24; S 24.38; H 2.04. Found: C 18.42; S 24.37; H 2.05.

Computational Methods. Computations were performed on clusters provided by NC State Office of Information Technology High Performance Computing. Theoretical calculations have been carried out using the Gaussian 09²⁸ implementation of the M06¹⁹ density functional theory. All geometry optimizations were carried out in the gas phase using tight convergence criteria ("opt = tight") and pruned ultrafine grids ("Int = ultrafine"). The basis set for rhenium was the small-core $(311111,22111,411) \rightarrow [6s5p3d]$ Stuttgart–Dresden basis set and RECP combination (SDD)²⁹ with an additional f polarization function.³⁰ The 6-31G(d,p) basis set was used for all other atoms.² Cartesian d functions were used throughout; that is, there are six angular basis functions per d function. All structures were fully optimized and analytical frequency calculations were performed on all structures to ensure either a zeroth-order saddle point (a local minimum) or a first-order saddle point (transition state: TS) was achieved. The minimum associated with each transition state was determined by animation of the imaginary frequency and, if necessary, with intrinsic reaction coordinate calculations.

Energetics were calculated at 298.15 K with the $6-311++G(d,p)^{23}$ basis set for C, H, N, O, and F atoms and the SDD basis set with an added f polarization function on Re. Reported energies utilized analytical frequencies and the zero-point corrections from the gas phase optimized geometries and included solvation corrections that were computed using the SMD model,²⁴ with benzene as the solvent as implemented in Gaussian 09.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.6b00570.

X-ray experimental data for **2**, **3**, **4**, **6**, and **7**; full Gaussian reference (PDF)

Text file of all computed molecule Cartesian coordinates in a format for convenient visualization (XYZ) Crystallographic data (CIF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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