Methanol Addition to Dihapto-Coordinated Rhenium Complexes of Furan

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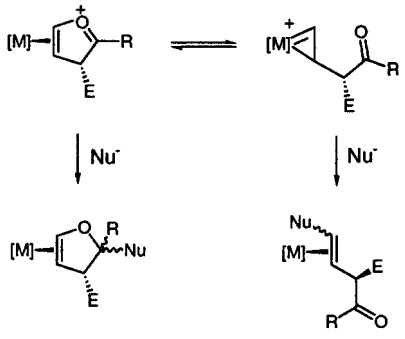
Abstract: The complexes [TpRe(CO)(L)(4,5-η^2-furan)], present as diastereomeric mixtures (L = ^{t}BuNC (**1A**, **1B**), PMe_3 (**2A**, **2B**), pyridine (**3A**, **3B**), or 1-methylimidazole (**4A**, **4B**)), undergo acid-catalyzed methanol addition in CH_2Cl_2 at −40 °C, resulting in the syntheses of dihapto-coordinated 2-methoxy-2,3-dihydrofuran complexes. In all cases, two diastereomers resulted, one in which the oxygen of the dihydrofuran is oriented toward the L ligand (**5A**, **6A**, **7A**, and **8A**), and one in which the oxygen is oriented away from the L ligand (**5B**, **6B**, **7B**, and **8B**). In all cases, the methoxy group adds stereoselectively, *anti* to the metal fragment. In addition, the ^{t}BuNC complex **1** yields a dihapto-coordinated vinyl ether (**5C**) that results from ring opening of the protonated furan ligand. In no case does the diastereomeric ratio of products correlate with that of the starting material.

Introduction

It is well-known that furans readily react with electrophiles at the 2-position.[1,2] In addition to 2-substituted furans, electrophilic attack at the 2-position can lead to open chain dicarbonyl compounds, 2,5-dihydrofurans, and polymers. In contrast to these usual reactivity patterns, when furan is η^2-coordinated to the pentaammineosmium(II) fragment (abbreviated [Os]),[3] the uncoordinated portion behaves chemically like a vinyl ether, reacting primarily through electrophilic addition at the 3-position. The resulting 3*H*-furanium system readily reacts with nucleophiles at either C2 or C5, allowing the syntheses of a variety of dihydrofuran and open chain vinyl ether complexes.[4−6] However, little is known about what factors control this regiochemistry.



A significant drawback to the [Os] fragment is the inability to modify the ligand set to modulate the reactivity of the heterocyclic ligand.[7,8] In addition, the pentaammineosmium(II) fragment is achiral, and therefore it is not possible to control the absolute stereochemistry of ligand-centered organic transformations. Our group has recently developed a series of electron-rich Re(I) fragments capable of binding a wide variety of aromatic molecules in dihapto fashion.[9] Complexes of the type [TpRe(CO)(L)(η^2-furan)], where Tp = hydridotris(pyrazolyl)borate and L = *tert*-butylisonitrile (^{t}BuNC), PMe_3, pyridine (py), or 1-methylimidazole (MeIm), not only are thermally stable but also allow us to adjust the electron density of the metal center, thereby influencing the π-back-bonding interaction with the ligand.

In this study, we have comprehensively investigated the addition of MeOH as an example of the tandem addition of an electrophile and a nucleophile to an η^2-furan ligand. Our primary concern is how various properties of the metal system affect the reaction rate, regiochemistry, and stereochemistry of this elementary reaction sequence not commonly observed for this heterocycle.

Results

A family of furan complexes of the form [TpRe(CO)(L)(η^2-furan)], where Tp = hydridotris(pyrazolyl)borate and L = ^{t}BuNC (**1**), PMe_3 (**2**), py (**3**), or MeIm (**4**), were prepared by established methods.[9] At −40 °C in CH_2Cl_2, using approximately 40 equiv of methanol (∼2 M) and 2−5 equiv of HOTf to promote the reaction, the addition of methanol to furan readily takes place to generate complexes of the form [TpRe(CO)(L)-(4,5-η^2-2β-methoxy-2,3-dihydrofuran)]. In all cases, two diastereomers are isolated, one in which the oxygen of the dihydrofuran ligand is oriented toward the L ligand (**A**) and one in which the oxygen of the dihydrofuran ligand is oriented away from the L ligand (**B**) (Scheme 1). The aliphatic portion

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(7) Orth, S. D.; Barrera, J.; Rowe, S. M.; Helberg, L. E.; Harman, W. D. *Inorg. Chim. Acta* **1998**, *270*, 337.
(8) Barrera, J.; Orth, S. D.; Harman, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 7316.
(9) Meiere, S. H.; Brooks, B. C.; Gunnoe, T. B.; Carrig, E. H.; Sabat, M.; Harman, W. D. *Organometallics* **2001**, *20*, 3661.

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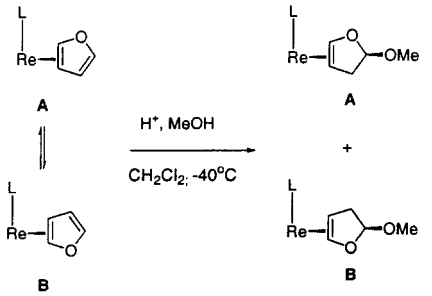
Table 1. Chemical Shifts of the Bound 2-methoxy-2,3-dihydrofuran Ligands

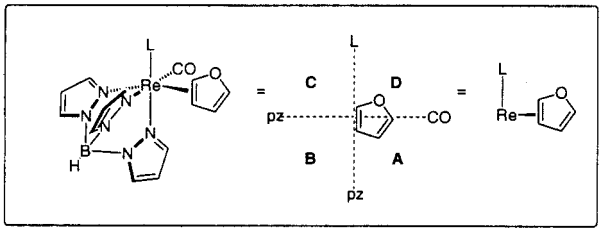
	^{1}H NMR chemical shifts δ^a				^{13}C NMR chemical shifts δ^a			
	diastereomer **A**		diastereomer **B**		diastereomer **A**		diastereomer **B**	
L ligand	α-bound	β-bound	α-bound	β-bound	α-bound	β-bound	α-bound	β-bound
^{t}BuNC	6.66	2.15	5.37	3.61	108.9	42.9	108.7	44.0
PMe_3	6.35	1.86	4.94	3.02	97.6	39.7	99.8	37.3
pyridine	6.3[b]	2.56	5.54	3.1[b]	105.9	44.9	106.2	46.7
1-methylimidazole	6.15	2.31	5.38	2.81	109.2	43.8	105.1	45.0

[a] All chemical shifts were determined in CD_3CN. [b] These chemical shifts were unable to be determined exactly since they were obscured by other peaks in the ^{1}H NMR spectrum.

Scheme 1. Structures, Relative Ligand Orientations, and Abbreviated Notations for the Parent Furan Complexes Used and the Dihydrofuran Complexes Synthesized, as Well as the Quadrant Designation Used Throughout the Paper



	A:B		A:B
1: L=^{t}BuNC	1:2.2	**5**: L=^{t}BuNC	1:2
2: L=PMe_3	1:2.1	**6**: L=PMe_3	2:1
3: L=pyridine	1:1.6	**7**: L=pyridine	1:1
4: L=1-methylimidazole	1.3:1	**8**: L=1-methylimidazole	1:3



of the dihydrofuran ligand lies over the Re−CO bond axis (quadrants A and D).[10,11] Under similar conditions (∼2 M MeOH and 100−250 mM acid), the half-lives for addition correlate with the reduction potential and CO stretching frequency of the complexes. The reaction of the most electron-deficient complex, the isonitrile derivative (**1**; $\nu_{CO} = 1846$ cm^{-1}, $E_{p,a} = 0.47$ V (NHE, 100 mV/s)) has a half-life of approximately 1200 min, while that of the phosphine complex (**2**; 1826 cm^{-1}, 0.30 V) is approximately 70 min. Methanol addition to the pyridine complex (**3**; 1810 cm^{-1}, 0.16 V) has a half-life of approximately 4 min, while addition to the most electron-rich complex, the 1-methylimidazole species (**4**; 1798 cm^{-1}, −0.02 V) has a half-life of approximately 1 min, although significant decomposition occurs before the reaction reaches completion. Methanol addition to **4** can be accomplished, albeit in low yield (10%), using a weaker acid (trifluoroacetic acid) in methylene chloride for a longer reaction period.

The directional diastereomers derived from **2** and **4** (**6A** and **6B**, and **8A** and **8B**) could be separated by preparatory thin-layer chromatography (silica gel). Those derived from **1** and **3** (**5A** and **5B**, and **7A** and **7B**) could not be separated by this method despite repeated attempts.

Proton and carbon 1D and proton 2D NMR spectra are consistent with the proposed structures for all of the complexes. For the PMe_3 complexes **6A** and **6B,** the phosphorus coupling constant for the bound methine group closer to the phosphorus is 15−16 Hz for both C and H. In contrast, J_{PH} and J_{PC} of the bound methine group oriented away from the phosphine were much lower (2−4 Hz in the ^{1}H NMR spectrum and not observable in the ^{13}C spectrum).[9−11]

Of note, while the ^{13}C NMR chemical shifts of the bound dihydrofuran ligands seem relatively insensitive to changes in stereochemistry, the ^{1}H NMR chemical shifts vary considerably between the **A** and **B** diastereomers (Table 1). This variation is attributed to the anisotropy of the pyrazole ring *trans* to the L ligand. Interestingly, the shielding effect of this ring is similar for both diastereomers of a given complex, and therefore the *difference* of the chemical shifts for the bound protons is roughly the same for both diastereomers. For example, in **6A** the chemical shift of the α-bound proton is 6.35 ppm, and in **6B** the same proton is at 4.94 ppm, a difference of approximately 1.4 ppm. In **6A**, the chemical shift of the β-bound proton is 1.86 ppm, and in **6B**, the same proton is at 3.02 ppm, a difference of approximately 1.2 ppm. After the relative orientations of **6A** and **6B** were determined by this analysis (aided by phosphorus coupling in the ^{1}H and ^{13}C NMR spectra), the similarities of the chemical shifts for the methanol addition products **5A**, **5B**, **7A**, **7B**, **8A**, and **8B** to either **6A** or **6B**, as well as 2D NMR data, allowed facile determination of the relative ligand orientations (Table 1). For all of the dihydrofuran and furan complexes, the diastereomer with the larger $\Delta\delta$ value in the ^{1}H NMR is the diastereomer in which the oxygen is oriented toward the L ligand.

The coordinated vinyl ethers have C≡O stretching frequencies 7−10 cm^{-1} lower than those of their parent furan complexes, consistent with the vinyl ethers being better σ donors and worse π acceptors than the furans. Conversely, the $E_{p,a}$ values were all ∼100−200 mV higher for the coordinated vinyl ethers than for the parent furan complexes (Table 2). The lower reduction potentials for the furan systems compared to their nonaromatic counterparts is likely a reflection of the increase in aromatic stability experienced by the furan ligand upon oxidation of the metal (note that the values reported in Table 2 are $E_{p,a}$ values; thus, it is possible that this trend may not hold for $E°$).

The ^{1}H NMR spectra of **6B**, **7B**, and **8B** indicate fluxionality at room temperature. Upon cooling of NMR samples of these complexes to −15 °C or lower, a spectrum indicative of only one complex appears, consistent with the structures presented. Fluxionality at ambient temperature is possible due to large chemical shift differences along with very unequal populations of two rotamers[12−14] which are related by a 180° rotation about

(10) Gunnoe, T. B.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 6499.

(11) Gunnoe, T. B.; Sabat, M.; Harman, W. D. *Organometallics* **2000**, *19*, 728.

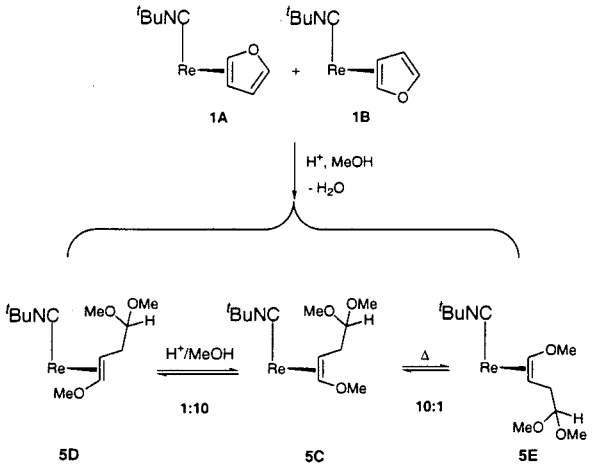
(12) Anet, F. A. L.; Basus, V. J. *J. Magn. Reson.* **1978**, *32*, 339.

Table 2. Electrochemical and Infrared Spectroscopic Data of Parent Furan and Dihydrofuran Complexes

L ligand	ν_{CO} of furan complex[a]	$E_{p,a}$ of furan complex[b,d]	ν_{CO} of dihydrofuran complex[a]	$E_{p,a}$ of dihydrofuran complex[b]
^{t}BuNC	1846	0.47	1839	0.57
PMe_3	1826	0.30	1816/1817[c]	0.52/0.42[c]
pyridine	1810	0.16	1802	0.27
1-methylimidazole	1798	−0.02	1794/1793[c]	0.15

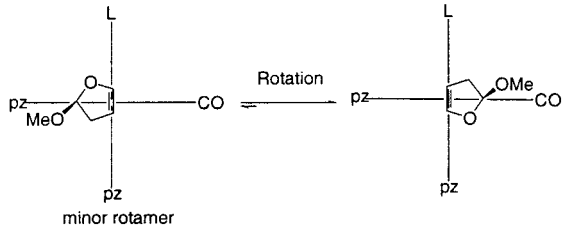
[a] CO stretching frequencies are reported in wavenumbers (cm^{-1}). [b] $E_{p,a}$ values are reported in volts (V) recorded at 100 mV/s, and referenced to NHE. [c] In these cases, different data were observed for each diastereomer (**A** and **B**), and both are reported. [d] Electrochemistry data recorded in DMA (*N*,*N*-dimethylacetamide) for these complexes.

Scheme 2. Synthesis of Complexes **5C**, **5D**, and **5E**[a] and Their Isomerizations



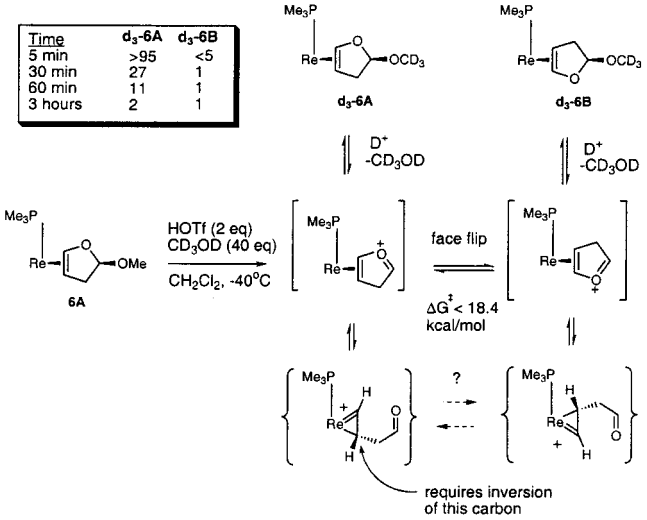
[a] **5A** and **5B** not shown.

the metal−olefin bond. Other work in our group[15] has shown that quadrant C (Scheme 1) is the most sterically congested of the four possible quadrants. This is due to the proton of the pyrazole ring *trans* to the CO interfering with the bound proton or alkyl group in this region. It then seems counterintuitive that **6B**, **7B**, or **8B** would rotate, since rotation places an oxygen and partially the substituents of C2 in quadrant C. Molecular modeling (MM2) studies, however, show that the dihydrofuran ring can pucker in such a way as to place the proton at C2 that is *syn* to the metal relatively far away from this pyrazole proton, thus avoiding steric congestion. Interestingly, the similar complex **5B** was static in ambient solution by ^{1}H NMR.



Aside from **5A** and **5B** (in a 1:2 ratio), the reaction of the isonitrile−furan complex **1** yields an additional product in which the 3*H*-furanium species resulting from protonation reacts with methanol at the *bound carbon* C5 to generate a vinyl ether complex (**5C**), isolated as a dimethyl acetal (Scheme 2). The methoxy group of the vinyl ether in **5C** was found to be oriented *cis* to the alkyl portion, as evidenced by an 8.5% NOE enhancement between the protons on the coordinated double bond. Allowing this reaction to run for longer periods increases

Scheme 3. Mechanism of the Conversion of **6A** to d_3-**6A** and d_3-**6B**



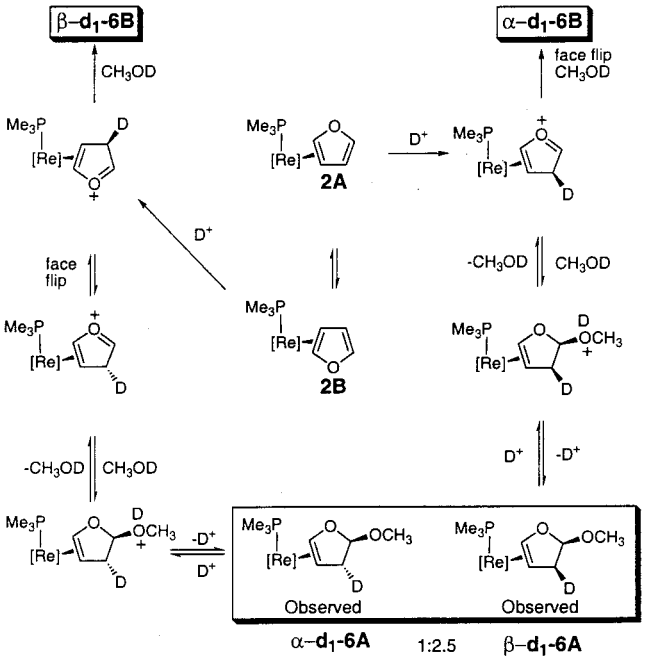
the ratio of **5C** to **5A** and **5B**, as do higher concentrations of acid (∼700 mM). When the reaction is allowed to proceed for even longer times (>5 days), additional coordinated vinyl ethers are observed. In a separate experiment, when a purified sample of the *cis*-vinyl ether complex **5C** (vide supra) is allowed to stand in a solution of $MeOH/CH_2Cl_2$ with HOTf, an equilibrium is established between **5C** and its *trans* isomer **5D** as a 10:1 ratio. In contrast, when a solution of **5C** is heated (80 °C) in the absence of acid, yet another isomer (**5E**) is formed. Although the large equilibrium ratio of **5C** to **5E** (10:1) and difficulties separating the various vinyl ethers prevented us from absolutely confirming the identity of **5E**, ^{1}H NMR data are most consistent with it being a *cis*-vinyl ether complex with the methoxy group oriented toward the isonitrile ligand. In other words, an interfacial linkage isomer of **5C** has occurred.

Methanol addition to pyridine complex **3** was complete within 20 min under the conditions used, giving a ratio of **7A** to **7B** of 1:1 (Scheme 1). These same conditions caused decomposition of 1-methylimidazole complex **4**, although methanol addition to this complex could be effected with CF_3COOH. The equilibrium ratio of **8A** to **8B** is 1:3.

Treatment of phosphine complex **6A** with HOTf (∼100 mM) and CD_3OD (∼2000 mM) in CH_2Cl_2 at −40 °C for 3 h results in the formation of d_3-**6A** and d_3-**6B** in a ratio of 2:1 (Scheme 3). The ^{1}H NMR spectrum of this mixture shows complete exchange of $-OCH_3$ by $-OCD_3$, but no incorporation of deuterium at either C3 proton. This indicates that any deprotonation of the 3*H*-furanium complex under these reaction conditions is orders of magnitude slower than alkoxy exchange. Allowing this reaction to proceed for only 5 min generates only d_3-**6A**, which indicates that methoxy exchange is also much faster than face flipping of the oxonium ligand. However, after the reaction proceeds for 30 min, this ratio is approximately

(13) Okazawa, N.; Sorensen, T. S. *Can J. Chem.* **1978**, *56*, 2737.
(14) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982.
(15) Meiere, S. H.; Harman, W. D. *Organometallics* **2001**, in press.

Scheme 4. Synthesis of C3-Deuterated Epimers **α-*d*$_1$-6A** and ***β*-*d*$_1$-6A**[a]



[a] Deuterated epimers of the type **6B** were not isolated.

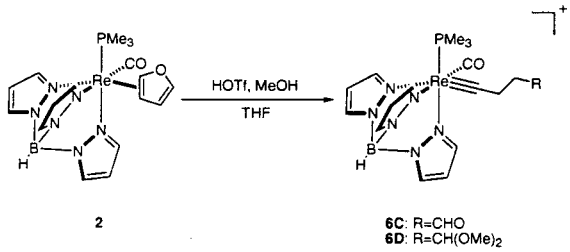
27:1, and after 60 min, it is approximately 11:1. These data allow the determination of an upper limit of $\Delta G^{\ddagger} < 18.4$ kcal/mol at −40 °C for face flipping of the oxonium ligand of **2** *provided that this isomerization does not occur via a metallocyclopropene intermediate*.[16] One-dimensional NOE experiments with ***d*$_3$-6A** show an 8.4% enhancement between the acetal proton (C2) and the proton at C3 *syn* to the Re, confirming that the methoxy group is oriented *anti* to the metal center (the other proton chemical shifts and coupling constants remain unchanged).

To directly deuterate the furan ring, the PMe_3 complex **2** was combined with DOTf and CH_3OD at −40 °C. Complex **6A** was isolated from the reaction mixture using preparatory thin-layer chromatography and analyzed by ^{1}H NMR. This purified sample of **6A** contained two C3-monodeuterated epimers of **6A** (***β*-*d*$_1$-6A** and **α-*d*$_1$-6A**) in a 2.5:1 ratio (β/α) (Scheme 4). The acetal protons (C2) appear at δ 5.09 ppm in the ^{1}H NMR spectrum, appearing as two separate doublets, with $J = 5.9$ Hz when the deuterium is *anti* to rhenium, and $J = 3.7$ Hz when the deuterium is *syn* to rhenium. At the same time, no dideuterated or nondeuterated compounds were isolated. This experiment shows that while the initial protonation at C3 is completely irreversible under these reaction conditions, diastereomer **6A** can be prepared from either of the diastereomers of the furan complex precursor, with **2A** leading exclusively to ***β*-*d*$_1$-6A** and **2B** leading exclusively to **α-*d*$_1$-6A**. (Note that, in Scheme 4, even though the concentration of **2B** is always greater than **2A**, the majority of this material develops into a form of **6B** rather than **α-*d*$_1$-6A**.) Monitoring the synthesis of **6A** and **6B** from **2** shows that the ratio of **6A** to **6B** remains 2:1 for up to 17 h, and the ratio of **2A** to **2B** remains 1:2.1 (the same as its initial diastereomeric ratio).[10]

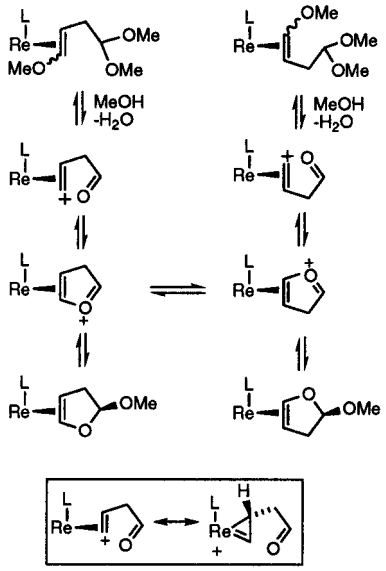
If the low-temperature reaction conditions used to synthesize PMe_3 complexes **6A** and **6B** are employed at room temperature (in THF instead of CH_2Cl_2), oxidation of the metal by triflic acid yields the ring-opened Re(V) carbyne. Both the aldehyde

(16) Espenson, J. H. *Kinetics of Complex Reactions--Reversible and Concurrent Reactions*; McGraw-Hill: New York, 1981; pp 42−45.

Scheme 5. Oxidation of Complex **2** to **6C** and **6D** by Triflic Acid



Scheme 6. Equilibration of Rhenium−Furanium Complexes with Their Ring-Opened Forms



(**6C**) and the dimethyl acetal (**6D**) forms can be isolated (Scheme 5). Spectroscopic features of **6C** and **6D** include ^{13}C carbyne resonances at 308 and 310 ppm,[17] respectively, features that are in agreement with what is observed for the osmium analogue (296.7 ppm).[4]

Discussion

The η^2-furan complex of pentaammineosmium(II) undergoes reaction with methanol in the presence of triflic acid to give exclusively *cis*- and *trans*-vinyl ether complexes analogous to those observed with the isonitrile system (**5C**−**E**).[4] 2-Methoxy-2,3-dihydrofuran complexes such as those resulting from the phosphine, pyridine, and imidazole systems were never observed with pentaammineosmium(II). However, when the osmium−furan system was alkylated at C3 with either an acetal or a Michael acceptor, methoxide added to C2, resulting in a 2-methoxy-3-alkyl-2,3-dihydrofuran complex. This difference in reactivity can possibly be attributed to an inductive effect of the alkyl group at C3 stabilizing the reputed 3*H*-furanium intermediate via extended hyperconjugation.[18] Increasing the electron density of the metal apparently has the same effect. Replacing the isonitrile ligand of **1** with phosphine, pyridine, or imidazole increases the reducing power of the metal and the back-bonding interaction, and thereby stabilizes the 3*H*-furanium species such that only methoxydihydrofuran products are observed for these systems (Scheme 6). Interestingly, under the experimental conditions used in the preparation of the isonitrile

(17) Edwards, D. S.; Biondi, L. V.; Ziller, J. W.; Churchill, M. R.; Schrock, R. R. *Organometallics* **1983**, *2*, 1505.

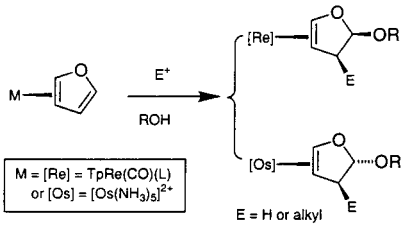
(18) Gonikberg, E. M.; le Noble, W. J. *J. Org. Chem.* **1995**, *60*, 7751.

complexes **5A**−**E**, the methoxydihydrofuran species (**5A** and **5B)** are observed at early stages of the reaction, but these eventually give way to vinyl ether products **(5C**−**E**). Thus, in the case of L being an isonitrile, the ring-opened vinyl ether complexes are thermodynamically favored over their dihydrofuran counterparts in a 2 M solution of MeOH. This is likely to be the case for the other rhenium systems as well; however, either decomposition to carbynes (e.g., **6C**) or oxidation of the metal preempts their formation. Thus, it appears that the more electron-rich metal systems ({TpRe(CO)(PMe_3)}, {TpRe(CO)(py)}, and {TpRe(CO)(MeIm)}) serve to stabilize the 3*H*-furanium intermediate sufficiently such that nucleophilic addition can take place at C2 in preference to C5, even though the latter reaction is thermodynamically favored. We note that the above discussion does not take into account the concentration of water, an important component of the 3*H*-furanium/metallocyclopropene equilibrium. The concentration of water in these experiments is difficult to ascertain, given that it is in lower concentration than the triflic acid and is likely to be intimately involved with solvated protons. Attempts to standardize the concentration of water by having it present in excess of the acid resulted in complicated mixtures of unidentified products.

The conversion of diastereomer **6B** from **6A** under acidic conditions likely occurs at the oxonium stage (Scheme 3). In the absence of acid, both **6A** and **6B** are stable in d_3-acetonitrile at room temperature under nitrogen for days, indicating either that face flip isomerization is too slow to observe or that having the methoxy group oriented *syn* to the metal is thermodynamically disfavored. Under acidic conditions, it is conceivable that **6A** could face flip to form the disfavored linkage isomer and then epimerize at C2 (via a 3*H*-oxonium) to form **6B**. However, independent measurements of the complex [TpRe(CO)(PMe_3)(4,5-η^2-2,3-dihydrofuran)] indicate that the rate of face-flipping (25.6 kcal/mol at 25 °C) is considerably slower than what is observed for **6A** → **6B** even in the presence of acid.[19] The absence of deuterium incorporation at C3 indicates that the furan ligand is irreversibly protonated under the reaction conditions used, which allows us to rule out any isomerization mechanism that incorporates an η^2-furan. While it is conceivable that furan may be protonated *syn* to the metal, as has been observed for some transition-metal arene complexes,[20] this is inconsistent with the results obtained using various [Os] systems.[3] Access to a hypothetical vinylidine intermediate via deprotonation at C5 can be ruled out, as there is no incorporation of deuterium at this position when **6A** is subjected to DOTf/CH_3OD.[21]

The upper limit of $\Delta G^{\ddagger} < 18.4$ kcal/mol (−40 °C) for the interfacial migration (face flip) of the oxonium ligand for the PMe_3 complex is very close to that of the parent furan complex. Previous spin saturation studies[19] have determined a face-flipping barrier of 19.0 kcal/mol for [TpRe(CO)(PMe_3)(4,5-η^2-furan)] at 50 °C. For comparison, the face-flipping barrier of [TpRe(CO)(PMe_3)(4,5-η^2-2,3-dihydrofuran)] is 25.6 kcal/mol at 25 °C, and that of [TpRe(CO)(PMe_3)(3,4-η^2-2β,5β-dideutero-2,5-dihydrofuran)] is 30.3 kcal/mol at 75 °C.[19] The oxonium ligand is sufficiently conjugated so that the upper limit of its barrier is within the error of the furan complex. In contrast, the observations that vinyl ether **5C** does not undergo conversion to **5E**, even in the presence of 175 mM triflic acid, but does so (partially) upon heating at 80 °C suggests that face-flipping does not occur readily for metallacyclopropenium intermediates. It is not possible to verify this theory without data pertaining to the equilibrium of **5C** or **5D** and acid with the reputed metallocyclopropene intermediate.

Scheme 7. Contrast between Tandem Electrophile/Alkoxide Additions to [$Os(NH_3)_5(\eta^2$-furan)]$^{2+}$ and the Rhenium Complexes Used in the Present Study



The addition of methoxide occurred *anti* to the metal fragment in all cases. Note that this is in contrast to methoxide addition to the [Os] system, in which methoxide adds to an oxonium such that it is *syn* to the metal.[4,22] This *syn* addition of methoxide, which has been shown to be a thermodynamic preference, is thought to be due to a hydrogen-bonding interaction between the methoxide and the moderately acidic ammine ligand protons. For rhenium, this hydrogen-bonding interaction is not possible, due to the absence of Lewis basic sites. Thus, the stereochemistry of methanol addition to a furan ligand can be controlled by varying the coordinating metal. In principle, this observation means that the tandem addition of an alkyl group to C3 and an alkoxide to C2 could be accomplished with complete stereocontrol (Scheme 7).

Conclusion

Methanol adds to η^2-coordinated furan complexes **1**−**4** in a manner which differs from both the traditional organic reaction (i.e., uncoordinated furan) and addition to the pentaammineosmium(II)−η^2-furan system. Reaction with the rhenium furans results in two diastereomers of η^2-coordinated 2-methoxy-2,3-dihydrofurans. These dihydrofuran complexes have methoxy groups oriented *anti* to the rhenium fragments, and differ only in the orientations of the dihydrofuran ligand relative to the asymmetric rhenium system. The isonitrile analogue **1** was also found to generate vinyl ether complexes at longer reaction times, the product of C−O bond cleavage within the furan ring. The half-lives for the addition of methanol to **1**−**4** correlate with the relative electron density at the metal center. This observation suggests that these new rhenium analogues to the pentaammineosmium(II)−furan system are likely to show further enhanced reactivity with carbon electrophiles at the β-carbon of furan and thereby create new avenues for the functionalization of this ubiquitous heterocycle.

Experimental Section

General Procedures. All reactions were performed in a Vacuum Atmospheres Co. glovebox. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova-300, Varian Inova-500, or GN-300 spectrometer at room temperature unless otherwise noted. Low-temperature experiments were performed on a Varian Inova-500 spectrometer or GN-300 spectrometer operating at either −15 or −40 °C. Chemical shifts are reported in parts per million relative to TMS (tetramethylsilane) using residual protonated solvent (acetonitrile-d_2, δ 1.94 ppm) as an internal standard. Two-dimensional NMR experiments (gDQCOSY, gHSQC, NOE) were recorded on a Varian Inova-300 or Varian Inova-500 spectrometer. Electrochemical experiments were performed under nitrogen using a PAR model 362 potentiostat driven by a PAR model

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(20) Kowalski, A. S.; Ashby, M. T. *J. Am. Chem. Soc.* **1995**, *117*, 12639.

(21) Frohnapfel, D. S.; Templeton, J. L. *Coord. Chem. Rev.* **2000**, *206*−*207*, 199.

(22) Chen, H. C. Ph.D. Thesis, University of Virginia, Charlottesville, VA, 1997.

175 universal programmer. Cyclic voltammograms were recorded (Kipp & Zonen BD90 XY recorder) in a standard three-electrode cell from +1.7 to −1.7 V utilizing a glassy carbon electrode. All potentials are reported versus NHE and, unless otherwise noted, were determined in CH_3CN (~0.5 M TBAH) at a scan rate of 100 mV/s using colbaltocenium hexafluorophosphate ($E_{1/2} = -0.78$ V) in situ as a calibration standard. Infrared spectra were recorded on a MIDAC Prospect (model PRS) spectrometer as a glaze using a horizontal attenuated total reflectance accessory (HATR, Pike Industries). Elemental analyses were obtained on a Perkin-Elmer PE-2400 Series II CHN analyzer.

Solvents and Reagents. All solvents were purified via distillation under nitrogen or passage through an activated alumina column under inert atmosphere and degassed prior to use.[23] Methanol was refluxed over $Mg(OMe)_2$ (prepared in situ from magnesium activated by I_2) and distilled. Acetonitrile was refluxed over CaH_2 and distilled. Acetonitrile-d_3 (Cambridge Isotope Laboratories) was also distilled over CaH_2 under an inert atmosphere prior to use. Preparatory TLC plates were obtained from Analtech, Inc. The syntheses of complexes **1**−**4** were accomplished in good yield using previously published procedures.[9,10] See the text for identification of the diastereomers.

[TpRe(CO)(ᵗBuNC)(4,5-η^2-2β -methoxy-2,3-dihydrofuran)] (5A and 5B) and [TpRe(CO)(ᵗBuNC)(1,2-η_2-1,4,4-trimethoxybut-1-ene)] (5C, 5D, and 5E). In a glovebox, **1** (0.104 g, 0.180 mmol), methanol (0.219 g, 6.85 mmol, 38.0 equiv), and approximately 2.5 g of CH_2Cl_2 were combined in a test tube and cooled to −40 °C. Separately, a solution of triflic acid (0.107 g, 0.710 mmol, 3.94 equiv) in approximately 1.25 g of CH_2Cl_2 was also cooled to −40 °C. The triflic acid solution was added to the metal complex, and the resulting mixture was allowed to stand at −40 °C for approximately 48 h. The solution was quenched via the addition of approximately 90 mg of cold pyridine and then filtered through a small deactivated alumina column (activity grade V). Most of the solvent was removed via nitrogen purge under vacuum. The sample was removed from the glovebox, dissolved in acetonitrile, and chromatographed on a preparatory TLC plate (1000 μm) using an eluent of 1:4 ethyl acetate/hexanes. The desired bands were cut out, extracted with acetone, and rotary evaporated to dryness. Three different complexes were isolated.

Isomers A and B. Yield: 0.043 g (39%) of a 1:2 mixture of **5A**/**5B**.

Isomer A. ^{1}H NMR (CD_3CN): δ 8.25 (d, $J = 2.0$ Hz, 1H, TpH), 7.97 (d, $J = 2.4$ Hz, 1H, TpH), 7.77 (dd, $J = 2.4$, 0.7 Hz, 1H, TpH), 7.71 (dd, $J = 2.4$, 0.7 Hz, 1H, TpH), 7.68 (dd, $J = 2.4$, 0.7 Hz, 1H, TpH), 7.42 (d, $J = 2.2$ Hz, 1H, TpH), 6.66 (dd, $J = 4.5$, 1.0 Hz, 1H, HC5), 6.33 (t, $J = 2.2$ Hz, 1H, TpH), 6.27 (t, $J = 2.2$ Hz, 1H, TpH), 6.19 (t, $J = 2.2$ Hz, 1H, TpH), 5.13 (dd, $J = 6.0$, 4.4 Hz, 1H, HC2), 3.36 (s, 3H, OCH_3), 3.35 (ddd, $J = 13.8$, 5.4, 4.4 Hz, 1H, HC3), 3.16 (m, 1H, HC3), 2.15 (m, 1H, HC4), 1.50 (s, 9H, ᵗBu) ppm. ^{13}C NMR (CD_3CN): δ 146.5, 143.9, 141.6, 136.7, 136.5, 136.2 (Tp 3- and 5-positions), 108.9 (C5), 107.5, 107.1, 106.8 (Tp 4-position), 100.8 (C2), 56.5 (C_q), 55.4 (OMe), 43.0 (C4), 41.5 (C3), 31.8 (ᵗBu) ppm (C≡O and C≡N not seen).

Isomer B. ^{1}H NMR (CD_3CN): δ 8.37 (d, $J = 2.0$ Hz, 1H, TpH), 7.91 (d, $J = 2.0$ Hz, 1H, TpH), 7.79 (dd, $J = 2.4$, 0.9 Hz, 1H, TpH), 7.73 (d, $J = 2.4$, 0.9 Hz, 1H, TpH), 7.69 (dd, $J = 2.4$, 0.7 Hz, 1H, TpH), 7.40 (d, $J = 2.0$ Hz, 1H, TpH), 6.34 (d, $J = 2.2$ Hz, 1H, TpH), 6.26 (d, $J = 2.2$ Hz, 1H, TpH), 6.17 (d, $J = 2.2$ Hz, 1H, TpH), 5.37 (dd, $J = 4.4$, 1.3 Hz, 1H, HC5), 5.06 (dd, $J = 6.2$, 3.3 Hz, 1H, HC2), 3.61 (ddd, $J = 6.0$, 4.4, 0.7 Hz, 1H, HC4), 3.33 (s, 3H, OCH_3), 3.21 (ddd, $J = 14.5$, 6.0, 3.3 Hz, 1H, HC3), 2.92 (dddd, $J = 14.5$, 6.4, 1.7, 0.9 Hz, 1H, HC3), 1.51 (s, 9H, ᵗBu) ppm. ^{13}C NMR (CD_3CN): δ 200.2 (C≡O), 160.1 (C≡N), 146.1, 144.7, 141.6, 136.9, 136.2 (two resonances) (Tp 3- and 5-positions), 108.7 (C5), 107.5, 107.1, 106.7 (Tp 4-position), 100.7 (C2), 58.8 (C_q), 55.0 (OMe), 44.0 (C4), 43.4 (C3), 31.8 (ᵗBu) ppm.

Data for Both Isomers A and B. $E_{p,a} = 0.57$ V (NHE). IR (HATR): 1839 (ν_{CO}), 2065 (ν_{CN}), 2104 (ν_{CN}), 2482 (ν_{BH}) cm^{-1}. Anal. Calcd for $C_{20}H_{27}N_7BO_3Re$: C, 39.35; H, 4.46; N, 16.06. Found: C, 39.49; H, 4.33; N, 16.57.

(23) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

Isomer C. Yield: 0.035 g (29.4%). ^{1}H NMR (CD_3CN): δ 8.32 (d, $J = 1.7$ Hz, 1H, TpH), 7.93 (d, $J = 1.7$ Hz, 1H, TpH), 7.79 (dd, $J = 2.4$, 0.7 Hz, 1H, TpH), 7.72 (dd, $J = 2.4$, 0.7 Hz, 1H,TpH), 7.70 (dd, $J = 2.4$, 0.7 Hz, 1H, TpH), 7.42 (d, $J = 2.0$ Hz, 1H, TpH), 6.30 (d, $J = 2.4$ Hz, 1H, TpH), 6.26 (d, $J = 2.0$ Hz, 1H, TpH), 6.17 (d, $J = 2.4$ Hz, 1H, TpH), 4.46 (dd, $J = 7.6$, 4.2 Hz, 1H, HC4), 4.40 (d, $J = 6.4$ Hz, 1H, HC1), 3.52 (s, 3H, vinyl OMe), 3.37 (s, 3H, acetal OMe), 3.32 (s, 3H, acetal OMe), 2.75 (ddd, $J = 9.7$, 6.3, 2.4 Hz, 1H, HC2), 2.11 (m, 2H, CH_2), 1.47 (s, 9H, ᵗBu) ppm. ^{13}C NMR (CD_3CN): δ 146.1, 144.0, 142.0, 136.6, 136.4, 136.1 (Tp 3- and 5-positions), 108.9 (C4), 107.3, 106.9, 106.6 (Tp 4-position), 101.2 (C1), 63.0 (OMe), 53.6 (OMe), 53.4 (OMe), 43.1 (C2), 36.1 (C3), 31.7 (ᵗBu) ppm (C≡O, C≡N, and *C*(CH_3)$_3$ not seen). $E_{p,a} = 0.45$ V (NHE). IR (HATR): 1846 (ν_{CO}), 2065 (ν_{CN}), 2101 (ν_{CN}), 2481 (ν_{BH}) cm^{-1}. Anal. Calcd for $C_{22}H_{33}N_7BO_4Re$: C, 40.25; H, 5.07, N, 14.93. Found: C, 39.97; H, 5.03; N, 14.95.

Isomer D (Selected Data). ^{1}H NMR (CD_3CN): δ 5.55 (d, $J = 6.8$ Hz, 1H, HC1), 4.36 (dd, $J = 6.5$, 4.9 Hz, 1H, HC4), 3.24 (s, 3H, OMe), 3.22 (s, 3H, OMe), 3.20 (s, 3H, OMe), 3.04 (ddd, $J = 11.2$, 7.0, 3.1 Hz, 1H, HC2), 1.46 (s, 9H, ᵗBu) ppm.

Isomer E (Selected Data). ^{1}H NMR (CD_3CN): δ 5.75 (d, $J = 6.4$ Hz, 1H, HC1), 4.39 (dd, $J = 5.3$, 4.8 Hz, 1H, HC4), 3.68 (s, 3H, vinyl OMe), 3.29 (s, 3H, OMe), 3.19 (s, 3H, OMe), 2.30 (m, 2H, CH_2), 1.42 (s, 9H, ᵗBu), 1.31 (d, $J = 5.5$ Hz, 1H, HC2) ppm.

[TpRe(CO)(PMe_3)(4,5-η^2-2β-methoxy-2,3-dihydrofuran)] (6A and 6B). In a glovebox, **2** (0.104 g, 0.181 mmol), methanol (0.198 g, 6.19 mmol, 34.2 equiv), and approximately 2.5 g of CH_2Cl_2 were combined in a test tube and cooled to −40 °C. Separately, a solution of triflic acid (0.051 g, 0.337 mmol, 1.86 equiv) in approximately 1.25 g of CH_2Cl_2 was also cooled to −40 °C. The triflic acid solution was added to the metal complex solution, and the resulting mixture was allowed to stand at −40 °C for approximately 20 h. The solution was quenched via the addition of approximately 40 mg of cold pyridine and then filtered through a small deactivated alumina column (activity grade V). Most of the solvent was removed via nitrogen purge under vacuum. The sample was removed from the glovebox, dissolved in acetonitrile, and chromatographed on a preparatory TLC plate (1000 μm) using an eluent of 2:3 ether/hexanes. The desired bands were cut out, extracted with approximately 40 mL of ether, and rotary evaporated to dryness. Yield: 0.043 g (39%) of a 2:1 ratio of **6A**/**6B**.

Isomer A. ^{1}H NMR (CD_3CN): δ 8.22 (d, $J = 1.8$ Hz, 1H, TpH), 8.01 (d, $J = 2.0$ Hz, 1H, TpH), 7.76 (d, $J = 2.6$ Hz, 1H, TpH), 7.72 (d, $J = 2.4$ Hz, 1H, TpH), 7.64 (d, $J = 2.4$ Hz, 1H, TpH), 7.38 (d, $J = 2.2$ Hz, 1H, TpH), 6.35 (ddd, $J = 15.8$, 5.3, 0.7 Hz, 1H, HC5), 6.26 (t, $J = 2.2$ Hz, 1H, TpH), 6.22 (t, $J = 2.2$ Hz, 2H, TpH), 5.09 (dd, $J = 5.9$, 3.5 Hz, 1H, HC2), 3.36 (dd, $J = 13.8$, 5.9 Hz, 1H, HC3), 3.32 (s, 3H, OCH_3), 3.12 (ddd, $J = 14.0$, 5.9, 3.5 Hz, 1H, HC3), 1.86 (ddd, $J = 5.9$, 5.8, 2.6 Hz, 1H, HC4), 1.36 (d, $J_{PH} = 9.0$ Hz, 9H, $P(CH_3)_3$) ppm. ^{13}C NMR (CD_3CN): δ 200.0 (CO), 148.6, 143.7, 141.4, 137.1, 136.8, 135.9 (six Tp resonances, 3- and 5-positions), 109.0 (C2), 107.2, 106.7, 106.6 (three Tp resonances, 4-position), 97.6 (d, $J_{PC} = 15.1$ Hz, C5), 54.9 (OCH_3), 43.7 (C3), 39.8 (C4), 16.8 (d, $J_{PC} = 32.0$ Hz, $P(CH_3)_3$) ppm. $E_{p,a} = 0.42$ V (NHE). IR (HATR): 1816 (ν_{CO}), 2480 (ν_{BH}) cm^{-1}.

Isomer B. ^{1}H NMR (CD_3CN, −40 °C): δ 8.35 (d, $J = 1.7$ Hz, 1H, TpH), 7.96 (d, $J = 1.7$ Hz, 1H, TpH), 7.81 (d, $J = 2.4$ Hz, 1H, TpH), 7.75 (d, $J = 2.4$ Hz, 1H, TpH), 7.70 (d, $J = 2.4$ Hz, 1H, TpH), 7.29 (d, $J = 2.0$ Hz, 1H, TpH), 6.28 (t, $J = 2.0$ Hz, 1H, TpH), 6.25 (t, $J = 2.4$ Hz, 1H, TpH), 6.19 (t, $J = 2.0$ Hz, 1H, TpH), 5.03 (dd, $J = 6.0$, 3.0 Hz, 1H, HC2), 4.94 (dd, $J = 4.3$, 4.3 Hz, 1H, HC5), 3.29 (s, 3H, OCH_3), 3.23 (ddd, 1H, $J = 13.8$, 6.4, 3.0, Hz, HC3), 3.02 (m, 1H, HC4), 2.93 (dd, $J = 14.1$, 6.4 Hz, 1H, HC3), 1.23 (d, $J = 8.7$ Hz, 9H, $P(CH_3)_3$) ppm. ^{13}C NMR (CD_3CN, −40 °C): δ 146.9, 144.0, 140.6, 136.8, 136.6, 135.7 (six Tp resonances, 3- and 5-positions), 108.4 (C2), 107.1, 106.4, 106.3 (three Tp resonances, 4-position), 99.9 (C5), 54.8 (OCH_3), 44.6 (C3), 37.3 (d, $J_{PC} = 12.4$ Hz, C4), 16.1 (d, $J_{PC} = 32.0$ Hz, $P(CH_3)_3$) ppm (C≡O not seen). $E_{p,a} = 0.52$ V (NHE). IR (HATR): 1817 (ν_{CO}), 2483 (ν_{BH}) cm^{-1}. Anal. Calcd for $C_{18}H_{27}O_3N_6BPRe$: C, 35.83; H, 4.51; N, 13.93. Found: C, 36.11; H, 4.60; N, 13.96.

[Tp(CO)(PMe_3)Re≡CCH$_2$CH$_2$C(O)H](OTf) (6C). Complex **2** (0.063 g, 0.111 mmol) and methanol (0.480 g, 15.00 mmol, 135.2 equiv)

were dissolved in approximately 2 g of THF. To this mixture was added triflic acid (0.072 g, 0.48 mmol, 4.3 equiv). After the solution was allowed to stand for 45 min, sufficient polyvinylpyridine/polystyrene copolymer (10% pyridine) was added to quench all of the acid. The supernatant was decanted, and the residual polymer was washed with THF. The THF portions were combined, and the solvent was removed under vacuum, resulting in an oil. The sample was precipitated by dissolution in a minimal volume of CH_2Cl_2 followed by addition into approximately 50 mL of diethyl ether. The orange powder was washed with approximately 30 mL of diethyl ether. Yield: 0.037 g (47%). ^{1}H NMR (CD_3CN): δ 9.72 (s, 1H, CHO), 8.10 (d, J = 2.2 Hz, 1H, TpH), 8.05 (d, J = 2.4, 1H, TpH), 7.98 (d, J = 2.4 Hz, 1H, TpH), 7.91 (d, J = 2.0 Hz, 1H, TpH), 7.84 (d, J = 2.2 Hz, 1H, TpH), 7.81 (d, J = 2.4 Hz, TpH), 6.50 (t, J = 2.4 Hz, 1H, TpH), 6.38 (t, J = 2.2 Hz, 1H, TpH), 6.38 (t, J = 2.2 Hz, 1H, TpH), 2.97 (dd, J = 6.5, 3.3 Hz, 1H, CH_2), 2.95 (d, J = 6.2 Hz, 1H, CH_2), 2.84 (ddd, J = 6.4, 6.4, 3.3 Hz, 1H, CH_2), 2.83 (ddd, J = 7.0, 6.4, 3.3 Hz, 1H, CH_2), 1.69 (d, J = 10.3 Hz, 9H, $P(CH_3)_3$) ppm. ^{13}C NMR (CD_3CN): δ 308.2 (d, J_{PC} = 12.2 Hz, Re≡C), 206.3 (C≡O), 200.7 (C═O), 147.8, 147.2, 145.4, 138.8 (2C), 137.7 (six Tp resonances, 3- and 5-positions), 108.4, 108.3, 108.1 (three Tp resonances, 4-position), 45.4 (CH_2), 38.6 (CH_2), 17.8 ppm (d, J = 36.6 Hz, $P(CH_3)_3$). $E_{p,c}$ = −1.25 V (NHE). IR (HATR): 1727 ($\nu_{C=O}$), 1996 ($\nu_{C\equiv O}$), 2517 (ν_{BH}) cm^{-1}. Anal. Calcd for $C_{18}H_{24}O_5N_6F_3BPSRe$: C, 29.97; H, 3.35; N, 11.65. Found: C, 30.28; H, 3.13; N, 11.48.

[Tp(CO)(PMe$_3$)Re≡CCH$_2$CH$_2$C(OMe)$_2$H](OTf) (6D). Complex **2** (0.057 g, 0.099 mmol) and methanol (0.304 g, 9.49 mmol, 95.8 equiv) were dissolved in approximately 2 g of THF. To this mixture was added triflic acid (0.054 g, 0.36 mmol, 3.6 equiv). After the solution was allowed to stand for 20 min, sufficient polyvinylpyridine/polystyrene copolymer (10% pyridine) was added to quench all of the acid. The supernatant was decanted, and the residual polymer was washed with THF. The THF portions were combined, and the solvent was removed under vacuum, resulting in an oil. The sample was precipitated by dissolution in a minimal volume of CH_2Cl_2 followed by addition into approximately 50 mL of diethyl ether. The orange powder was washed with approximately 30 mL of diethyl ether. Yield: 0.020 g (28%). ^{1}H NMR (CD_3CN): δ 8.10 (d, J = 2.0 Hz, 2H, TpH), 7.98 (dd, J = 2.4, 0.4 Hz, 1H, TpH), 7.91 (d, J = 2.2 Hz, 1H, TpH), 7.85 (d, J = 2.2 Hz, 1H, TpH), 7.82 (ddd, J = 2.4, 1.1, 0.7 Hz, 1H, TpH), 6.50 (t, J = 2.4 Hz, 1H, TpH), 6.38 (t, J = 2.2 Hz, 2H, TpH), 4.32 (t, J = 5.3 Hz, 1H, acetal), 3.21 (s, 3H, OMe), 3.21 (s, 3H, OMe), 2.70 (dt, J = 7.3, 3.3 Hz, 2H, CH_2), 2.00 (dt, J = 7.0, 5.3 Hz, 2H, CH_2), 1.68 (d, J = 10.3 Hz, 9H, $P(CH_3)_3$) ppm. ^{13}C NMR (CD_3CN): δ 310.5 (d, J_{PC} = 9.8 Hz, Re≡C), 206.3 (C≡O), 147.8, 147.1, 145.4, 138.8, 138.7, 137.7 (six Tp resonances, 3- and 5-positions), 108.4, 108.2, 108.1 (three Tp resonances, 4-position), 104.2 (acetal), 54.3 (OMe), 54.1 (OMe), 48.0 (CH_2), 28.4 (CH_2), 17.9 (d, J = 39.0 Hz, $P(CH_3)_3$) ppm. $E_{p,c}$ = −1.15 V (NHE). IR (HATR): 1991 (ν_{CO}), 2517 (ν_{BH}) cm^{-1}.

[TpRe(CO)(pyridine)(4,5-η^2-2β-methoxy-2,3-dihydrofuran)] (7A and 7B). In a glovebox, **3** (0.098 g, 0.171 mmol) and methanol (0.204 g, 6.38 mmol, 37.3 equiv) were dissolved in approximately 2.5 g of CH_2Cl_2 and cooled to −40 °C. A solution of cold triflic acid (0.096 g, 0.639 mmol, 3.7 equiv) in approximately 1.25 g of CH_2Cl_2 was added to the rhenium solution, and the resulting mixture was allowed to stand for 20 min. Cold pyridine (70 mg) was added, and the solution was filtered through a small deactivated alumina (activity grade V) plug. The solvent was removed via nitrogen purge under vacuum, and the resulting oil was redissolved in a minimal amount of CH_3CN. The sample was removed from the glovebox, and chromatography was accomplished using a preparatory TLC plate (silica) and an eluent of 60% ethyl acetate in hexanes. The desired band was cut out and extracted with acetone, and the resulting solution was rotary evaporated to dryness. Two diastereomers were observed by ^{1}H NMR analysis (1:1 ratio), but attempts to separate these diastereomers failed. Yield: 0.026 g (25%).

Isomer A. ^{1}H NMR (CD_3CN): δ 8.3−6.8 (m, 11H, Tp 3- and 5-positions and pyridine), 6.4−6.0 (m, 3H, Tp 4-position), 6.3 (m, 1H, HC5), 5.42 (dd, J = 6.2, 3.5 Hz, 1H, HC2), 3.52 (dd, J = 13.7, 6.0 Hz, 1H, HC3), 3.37 (s, 3H, OCH_3), 3.29 (ddd, J = 14.0, 6.6, 3.5 Hz, 1H, HC3), 2.56 (dd, J = 5.3, 5.3 Hz, 1H, HC4) ppm. ^{13}C NMR (CD_3CN, −20 °C): δ 146−135 (11C, Tp 3- and 5-positions and pyridine resonances), 108−106 (3C, Tp 4-position), 108.5 (C2), 105.9 (C5), 54.9 (OCH_3), 44.9 (C4), 43.2 (C3) ppm.

Isomer B. ^{1}H NMR (CD_3CN, −40 °C): δ 8.3−6.8 (m, 11H, Tp 3- and 5-positions and pyridine), 6.4−6.0 (m, 3H, Tp 4-position), 5.54 (d, J = 4.4 Hz, 1H, HC5), 5.35 (m, HC2), 3.34 (s, 3H, OCH_3), 3.4−3.0 ppm (2 × HC3 and HC4). ^{13}C NMR (CD_3CN, −20 °C): δ 146−135 (11C, Tp 3- and 5-positions and pyridine), 108−106 (3C, Tp 4-position), 108.9 (C2), 106.2 (C5), 55.1 (OCH_3), 46.7 (C4), 42.2 (C3) ppm. [Note: Due to the small chemical shift differences between the OCH_3 resonances and the resonances for C2 of **7A** and **7B**, the assignments above are not 100% certain.] $E_{p,a}$ = 0.27 (Re(I/II)), 1.31 (Re(II/III)) V (NHE). IR (HATR): 1802 (ν_{CO}), 2481 (ν_{BH}) cm^{-1}. Anal. Calcd for $C_{20}H_{23}O_3N_7BRe$: C, 39.61; H, 3.82; N, 16.17. Found: C, 39.99; H, 3.42; N, 15.92.

[TpRe(CO)(1-methylimidazole)(4,5-η^2-2β-methoxy-2,3-dihydrofuran)] (8A and 8B). In a glovebox, **4** (0.080 g, 0.139 mmol) and methanol (0.335 g, 10.5 mmol, 75.3 equiv) were dissolved in approximately 2.5 g of CH_2Cl_2 and cooled to −40 °C. A solution of cold trifluoroacetic acid (0.040 g, 0.348 mmol, 2.5 equiv) in approximately 1.25 g of CH_2Cl_2 was added to the rhenium solution, and the resulting mixture was allowed to stand for 8.5 h. Cold pyridine (30 mg) was added, and the solution was filtered through a small deactivated alumina (activity grade V) plug. The solvent was removed via nitrogen purge under vacuum, and the resulting oil was redissolved in a minimal amount of CH_3CN. Chromatography was accomplished using a preparatory TLC plate (silica) and an eluent of ethyl acetate. The desired bands were cut out and extracted with acetone followed by removal of the solvent. Two diastereomers were isolated in a 1:3 ratio (**8A**/**8B**). Yield: 0.008 g (8.9%).

Isomer A. ^{1}H NMR (CD_3CN): δ 8.09 (d, J = 2.0 Hz, 1H, TpH), 7.78 (dd, J = 2.2, 0.7 Hz, 1H, TpH), 7.72 (dd, J = 2.4, 0.7 Hz, 2H, TpH), 7.52 (s, br, 1H, ImH), 7.29 (d, J = 2.0 Hz, 1H, TpH), 7.27 (d, J = 2.2 Hz, 1H, TpH), 6.84 (t, J = 1.6 Hz, 1H, ImH), 6.64 (t, J = 2.2 Hz, 1H, ImH), 6.35 (t, J = 1.3 Hz, 1H, TpH), 6.25 (t, J = 2.2 Hz, 1H, TpH), 6.15 (dd, J = 5.0, 0.9 Hz, 1H, HC5), 6.14 (t, J = 2.2 Hz, 1H, TpH), 5.34 (dd, J = 6.0, 3.3 Hz, 1H, HC2), 3.65 (s, 3H, NCH_3), 3.45 (dd, J = 13.8, 6.0 Hz, 1H, HC3), 3.34 (s, 3H, OCH_3), 3.22 (ddd, J = 13.8, 6.4, 3.3 Hz, 1H, HC3), 2.31 (dd, J = 5.3, 5.3 Hz, 1H, HC4) ppm. ^{13}C NMR (CD_3CN): δ 144.5, 144.4, 142.0, 140.9, 136.5, 136.5 (Tp 3- and 5-positions), 135.5, 132.0, 122.0 (Im), 109.2 (C5), 107.1 (2C), 106.9, 106.7 (Tp 4-position and C2), 54.6 (OMe), 43.8 (C4), 43.6 (C3), 34.6 (NMe) ppm (C≡O not seen). $E_{p,a}$ = 0.15 (Re(I/II)), 1.25 (Re(II/III)) V (NHE). IR (HATR): 1794 (ν_{CO}), 2483 (ν_{BH}) cm^{-1}.

Isomer B. ^{1}H NMR (CD_3CN, −20 °C): δ 8.19 (d, J = 1.3 Hz, 1H, TpH), 7.81 (d, J = 2.3 Hz, 1H, TpH), 7.73 (m, 2H, 2 TpH), 7.71 (s, 1H, ImH), 7.41 (d, J = 1.9 Hz, 1H, TpH), 7.31 (d, J = 1.6 Hz, 1H, TpH), 6.90 (br t, J = 1.3 Hz, 1H, ImH), 6.52 (s, 1H, ImH), 6.27 (t, J = 1.9 Hz, 1H, TpH), 6.24 (t, J = 2.2 Hz, 1H, TpH), 6.12 (t, J = 2.3 Hz, 1H, TpH), 5.38 (d, J = 4.8 Hz, 1H, HC5), 5.29 (dd, J = 6.1, 3.5 Hz, 1H, HC2), 3.64 (s, 3H, NCH_3), 3.40 (m, 1H, HC3), 3.32 (s, 3H, OCH_3), 3.18 (ddd, J = 16.2, 6.1, 4.0 Hz, HC3), 2.81 (dd, J = 5.1, 5.1 Hz, 1H, HC4) ppm. ^{13}C NMR (CD_3CN, −20 °C): δ 144.8, 143.2, 141.5, 140.2, 136.6, 135.9 (Tp 3- and 5-positions), 135.4, 130.9, 122.3 (Im), 108.6 (C2), 106.8, 106.6, 106.5 (Tp 4-position), 105.1 (C5), 55.0 (OCH_3), 45.0 (C4), 43.5 (C3), 34.5 (NMe) ppm (C≡O not seen). $E_{p,a}$ = 0.15 (Re(I/II)), 1.21 (Re(II/III)) V (NHE). IR (HATR): 1793 (ν_{CO}), 2485 (ν_{BH})cm^{-1}. We were unable to obtain combustion analysis for these diastereomers due to their low yield combined with oxygen sensitivity.

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