# Dearomatization of Furan: Elementary Transformations of $\eta^2$-Coordinated Furan Complexes of Pentaammineosmium(II)

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**Abstract:** A series of complexes has been prepared of the form $[Os(NH_3)_5(4,5\text{-}\eta^2\text{-L})]^{2+}$ where L = furan and various alkylated furans. These heterocycle complexes were surveyed for their reactivity with various electrophiles (e.g., acids, silyl triflate, *N*-methylacetonitrilium triflate, acetals, aldehydes, and Michael acceptors). Electrophilic addition to C(3) results in an unstable reaction intermediate, a 4,5-$\eta^2$-3*H*-furanium species, that leads to complexes of 4,5-$\eta^2$-3-substituted furans, 2,3-dihydrofurans, C(5)-substituted 2-oxoalkenes, cyclic vinyl ethers, or osmium carbyne complexes. The specific reactivity displayed by the $\eta^2$-furan complexes strongly depends on the presence and location of alkyl substituents and their ability to stabilize $\eta^2$-vinyl cation intermediates resulting from C(5)−O bond cleavage. In all cases investigated, the addition of an electrophile at C3 occurs anti to osmium coordination.

## Introduction

In the past 20 years, there has been steady growth in the use of heteroaromatic systems in organic synthesis.[1] Among the simple heteroaromatic systems, furans have been by far the most heavily exploited. Because furans provide up to four unsaturated carbons and are readily derivatized through the electrophilic substitution and Diels−Alder reactions, they represent valuable synthetic intermediates for the preparation of natural products, pharmaceuticals, and flavor or fragrance compounds.[2] However, the synthetic utility of furans is limited by their great tendency to undergo electrophilic substitution at the α-position or to polymerize in the presence of electrophiles. As a result, many biologically significant $\beta$-substituted furan compounds are obtained only by "indirect" methods involving the ring closure of the corresponding open-chain derivatives, which are typically not readily available.[3] In a limited number of cases, furans undergo 2,5-difunctionalization initiated by electrophilic addition, but vicinal addition reactions for furans are practically unknown.[4]

The overwhelming tendency of furans to undergo α-electrophilic substitution has been attributed to the greater thermodynamic stability of the 2*H*-furanium ion compared to its 3*H*-furanium isomer, coupled with a strong driving force for the furanium ion to rearomatize. Thus, strategies to enhance the synthetic utility of furans involve blocking reactivity at the α-carbons or inhibiting the rearomatization of furanium ions. Synthetic methods that achieve this, such as the [2 + 2] photocycloaddition of furan and aldehydes, have become useful tools for the synthesis of carbohydrate-based natural products.[5]

In a preliminary paper from our laboratories,[6] we reported that coordination of furan by pentaammineosmium(II) at C(4) and C(5) blocks α-electrophilic addition and, as a result of donation of $\pi$-electron density from the metal, activates the heterocycle toward electrophilic addition at the uncoordinated $\beta$-carbon. Electrophilic addition at C(3) of a furan ligand was postulated to result in a 4,5-$\eta^2$-3*H*-furanium intermediate that could, in turn, undergo deprotonation at C(3) or nucleophilic addition at C(2) as has been observed with analogous pyrrole complexes.[7] However, in addition to these reactions, nucleophilic addition at C(5) and rearrangement of the 4,5-$\eta^2$-3*H*-furanium intermediate to a carbyne were also observed,[6,8] processes which are not identified for the nitrogen analogs.[7] In the following paper, we seek to understand what factors influence this complex reaction manifold (Scheme 1).

## Results

**Syntheses and Properties of $\eta^2$-Furan Complexes.** Furan complexes of pentaammineosmium(II) are readily prepared from the reduction of $[Os(NH_3)_5(OTf)](OTf)_2$ (Zn/Hg or $Mg^0$) in the presence of an excess of the corresponding furan ligand to generate compounds $[Os(NH_3)_5(L)](OTf)_2$,[9] where L = furan

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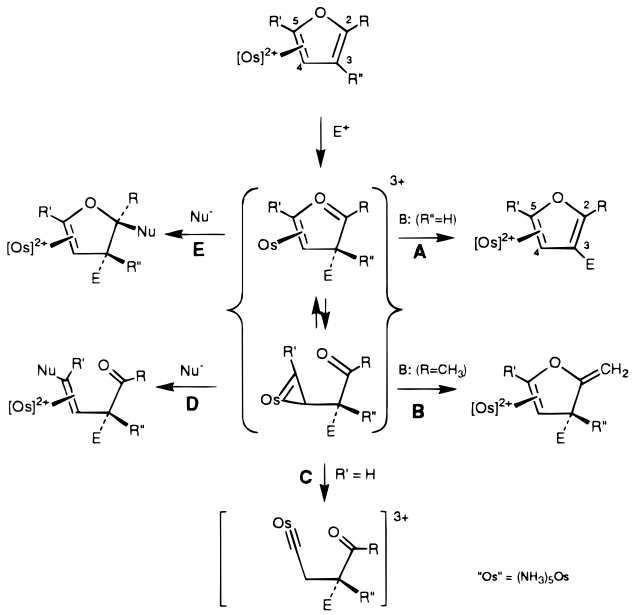
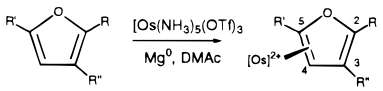
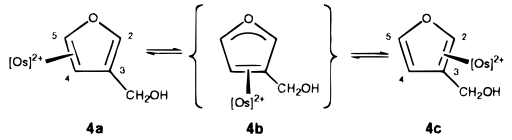
**Scheme 1.** Reaction Pathways of an $\eta^2$-3*H*-Furanium Complex




(**1**), 2-methylfuran (**2**), 2,5-dimethylfuran (**3**), and 3-furanmethanol (**4**). With the exception of 3-furanmethanol, complexation




of these ligands yields only one regioisomer in which the metal is bound in an $\eta^2$-fashion at C(4) and C(5). The reaction of 3-furanmethanol with $[Os(NH_3)_5]^{2+}$ initially yields a mixture of two regioisomers (**4a** and **4c**) in a ratio of ~1:1. Over time in acetonitrile, a linkage isomerization occurs ($t_{1/2} \approx 10$ h) with **4a** being the final product. Proton NMR spectra of the furan




complexes show well-resolved resonances and a slight *increase* in the $J_{4,5}$ *cis*-coupling constant (~3.3 Hz), compared to that of the uncoordinated ligand. Their $^{13}$C NMR spectra feature two vinyl carbon signals shifted well upfield relative to corresponding signals of the uncoordinated ligand. NMR data ($^1$H, $^{13}$C) for selected furan complexes are shown in Table 1.

Unlike $\eta^2$-pyrrole complexes of pentaammineosmium(II),[10] $^1$H NMR spectra of furan complexes show no evidence of a rapid linkage isomerization at room temperature. When **1** is heated to 130 °C in DMF-$d_7$, irradiation of the H(4) resonance results in partial spin saturation of the H(3) signal, indicating that osmium undergoes the expected $\eta^2$-4,5 ↔ $\eta^2$-2,3 shift but only at forcing conditions. In the same experiment, a small amount of free ligand is detected by $^1$H NMR after 30 min at 130 °C. In order to probe the kinetic aspects of coordination for the asymmetric alkyl substituted furans, a competition experiment was carried out where $[Os(NH_3)_5(OTf)](OTf)_2$ was reduced in the presence of a 1:1:1 mixture of furan, 2-methylfuran, and 2,5-dimethylfuran. The isolated reaction mixture was shown by $^1$H NMR to be close to a 1:1:1 ratio of **1**, **2**, and **3**. This outcome indicates that the binding rates for methylated and nonmethylated sites in furans are very similar. Given that the 2-methylfuran complex **2** is isolated as a single isomer and that the typical reaction time is ~10 min, the 2,3-$\eta^2$ to 4,5-$\eta^2$ isomerization for this complex must have a half-life of less than 0.03 h at 20 °C in order for the former isomer to be undetectable in an $^1$H NMR spectrum of **2**. Thus, the much slower isomerization rate observed for the 3-furanmethanol complex **4** is significant. Were a linkage isomerization mechanism for furan complexes **1**−**4** to involve an $\eta^1$-furan (i.e., oxygen bound) intermediate, the isomerization rate would be expected to increase upon alkylation at C(3) while alkylation at C(2) should decrease the 2,3-$\eta^2$ to 4,5-$\eta^2$ isomerization. The experimental observation of the reverse situation suggests that a 3,4-$\eta^2$ isomer (e.g., **4b**) is more likely to be the intermediate, a species similar to that previously invoked for the pyrrole analog.[11]

**C(3) Electrophilic Substitution.** Furan complexes **1** and **2** are unreactive toward acetic anhydride in acetonitrile at 22 °C, and direct acylations of **1** and **2** using acetic acid with 4-(*N*,*N*-dimethylamino)pyridine (DMAP) or $BF_3$·OEt or using a mixture of triflic anhydride and acetic acid also failed to give expected reactions.[12] However, as we have reported, treatment of **1** with *N*-methylacetonitrilium triflate in acetonitrile produces the iminium-substituted furan complex **5** (Scheme 2).[6] Similarly, when a stoichiometric amount of *N*-methylacetonitrilium triflate in acetonitrile is combined with **2**, the corresponding $\eta^2$-iminium-substituted complex **6** is isolated in good yield. Compounds **5** and **6** each are hydrolyzed by water to give the corresponding $\eta^2$-4-acetylfuran complexes **7** and **8** at ambient temperature (Scheme 2).[13]

If this reaction is carried out in acetonitrile-$d_3$ and monitored by $^1$H NMR (22 °C, 1.5 equiv *N*-methylacetonitrilium triflate), $^1$H NMR spectra reveal that at short reaction times, an intermediate species (**6b**) is present. The complex **6b** was cleanly prepared by the combination of **2** with *N*-methylacetonitrilium triflate in acetonitrile (22 °C, 10 min), followed by direct precipitation of the reaction solution in $CH_2Cl_2$ without prior treatment with pyridine. Complex **6b** rearranges to **6a** very slowly in solution in $CH_3CN$, and adding either acid ($H^+$) or pyridine accelerates the isomerization process significantly. Combustion analysis indicates that **6b** is a constitutional isomer of **6a**, and comprehensive spectroscopic analysis ($^1$H, $^{13}$C, DEPT, HETCOR) reveals that **6b** is the compound shown in Scheme 2, the product of deprotonation at the C(2) methyl substituent.

Although several attempts to alkylate furan complexes **1** and **2** with methyl triflate failed, vinylation of **2** at the uncoordinated $\beta$-position was achieved through a conjugate addition reaction. For example, when the methylfuran species **2** is combined with *trans*-4-methoxy-3-buten-2-one and a Lewis acid, the $\beta$-sub-

(9) The ring positions in these and other complexes reported herein are numbered as would be the corresponding free ligand. This numbering scheme is a change from the scheme used by us in earlier reports dealing with this chemistry. See refs 6 and 8a.

(10) Myers, W. H.; Koontz, J. I.; Harman, W. D. *J. Am. Chem. Soc*. **1992**, *114*, 5684.

(11) Cordone, R.; Harman, W. D.; Taube, H. *J. Am. Chem. Soc*. **1989**, *111*, 5969.

(12) Reaction of these furan complexes with a mixture of acetic acid and triflic acid at 22 °C gave evidence of carbyne complex formation. Reaction with acetic anhydride or with acetic anhyride and DMAP gave no reaction.

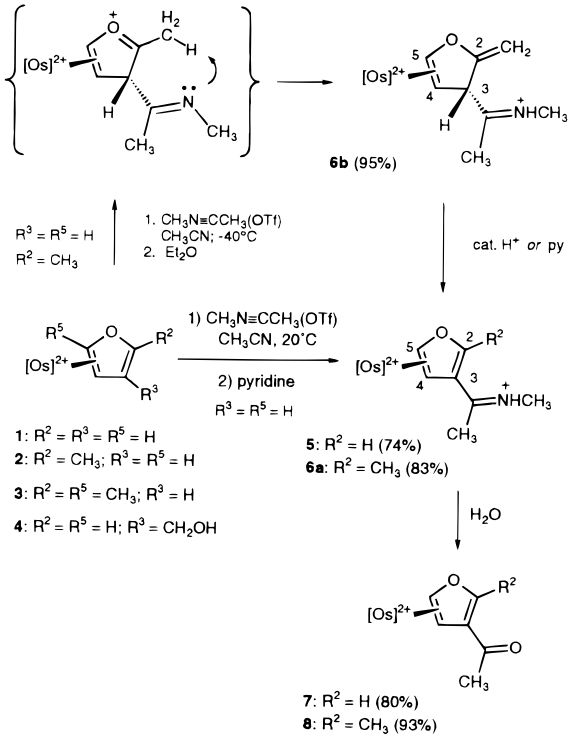
(13) In contact with water, the iminium salts are hydrolyzed more or less rapidly. The rate of hydrolysis of **5** and **6** ($t_{1/2}$ = ~3 days for **5**) is close to that of some iminium salts containing heterocyclic substituents. See: Böhme, H.; Auterhoff, G. *Chem. Ber*. **1971**, *104*, 2013.

**Table 1.** Selected $^1$H and $^{13}$C NMR Data for $\eta^2$-Complexes of Furan and Furan Derivatives

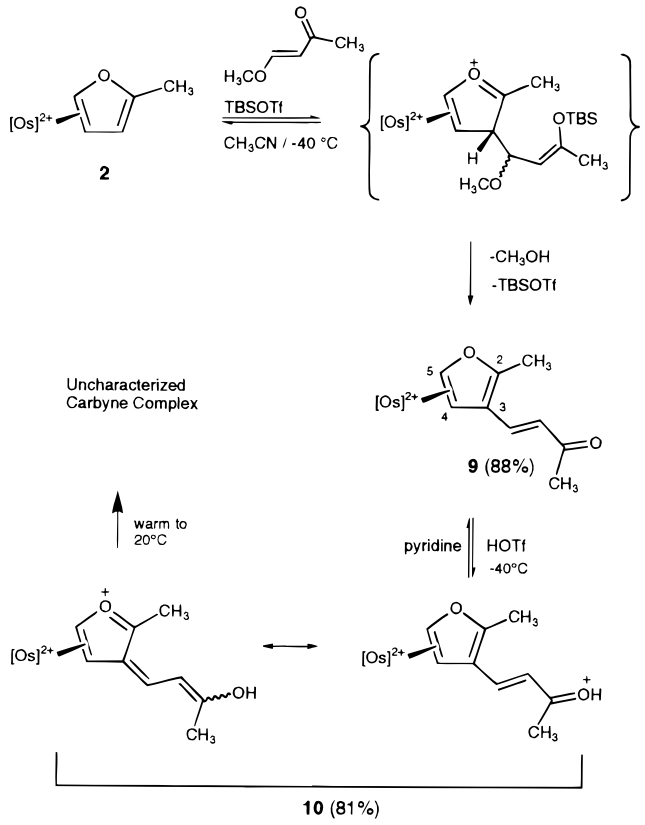
| | $\delta$ ppm ($^1$H) | | | | | $\delta$ ppm ($^{13}$C) | |
|---|---|---|---|---|---|---|---|
| cmpd | c-$NH_3$ | t-$NH_3$ | H(4) | H(5) | $J_{4,5}$ | C(4) | C(5) |
| **1**[a] | 3.46 | 4.70 | 5.09 | 7.45 | 3.3 | 49.0 | 98.6 |
| **2**[a] | 3.46 | 4.63 | 5.00 | 7.38 | 3.6 | 50.4 | 97.8 |
| **3**[a] | 3.50 | 4.65 | 4.80 | | | 51.8 | 98.8 |
| **4a**[b] | 2.96 | 4.10 | 4.76 | 7.29 | 3.3 | 51.0 | 100.4 |
| **4c**[b] | 3.08 | 4.10 | | 7.25 | | 55.6 (C(3)) | 97.7 (C(2)) |
| **5**[b] | 3.16 | 4.33 | 5.13 | 7.71 | 3.3 | 37.9 | 102.8 |
| **7**[b] | 3.00 | 4.16 | 5.17 | 7.47 | 3.5 | 45.6 | 101.8 |
| **8**[b] | 3.04 | 4.09 | 5.18 | 7.23 | | 48.4 | 97.8 |
| **9**[b] | 3.02 | 4.13 | 5.06 | 7.28 | 3.6 | 44.7 | 97.3 |
| furan[c] | | | 6.44 | 7.54 | 1.4 | 110.3 | 143.4 |
| 2-methylfuran[c] | | | 6.27 | 7.33 | 1.2 | 111.2 | 141.7 |
| 2,5-dimethylfuran[c] | | | 5.86 | | | 106.9 | 150.7 |

[a] Recorded in acetone-$d_6$. [b] Recorded in acetonitrile-$d_3$. [c] Recorded in $CDCl_3$.

**Scheme 2.** Imination of Various $\eta^2$-Furan Complexes with *N*-Methylacetonitrilium Triflate




**Scheme 3.** An Example of $\beta$-Vinylation of the Methylfuran Complex **2**




stituted furan complex **9** is formed (Scheme 3).[14] NMR data ($^1$H, $^{13}$C, and DEPT) for **9** indicate that this product is a 2,3-disubstituted $\eta^2$-furan complex with a conjugated carbonyl and four methine groups. Judging from their large coupling constant ($J$ = 15.6 Hz), the uncoordinated vinyl protons are likely in a trans configuration as shown in Scheme 3. Protonation of **9** in acetonitrile at −40 °C produces a new species (**10**) in good yield. The $^1$H NMR spectrum for **10** is identical to that of **9** except that all the signals are shifted downfield by 0.2−1.1 ppm. Other $^1$H NMR data indicate that **10** is not stable at room temperature in acetone-$d_6$, but rather transforms within 2 h into a product whose $^1$H NMR spectrum displays resonances consistent with the *cis*- and *trans*-ammines of an osmium carbyne complex. Combustion analysis following the synthesis of **10** at −40 °C confirms that **10** is the adduct of 1 equiv of HOTf to **9**. Taken together, **10** is assigned to be the conjugate acid of **9**, where protonation has occurred at the ketone oxygen (Scheme 3).

(14) Compound **9** can also be generated from the reaction of 3-butyn-2-one with **2** (−40 °C, acetonitrile, TBSOTf).

**C(3)−C(2) Vicinal Difunctionalization.** The parent furan complex **1** reacts with benzaldehyde dimethyl acetal in the presence of $BF_3$·$OEt_2$ to give a mixture of two diastereomers of complexed 3-(1-methoxybenzyl)-2-methoxy-2,3-dihydrofuran (**11a** and **11b**).[6,8a] In a similar manner, **1** reacts with methyl vinyl ketone in methanol to provide the addition product, a complex of 2-methoxy-3-(3-oxobutyl)-2,3-dihydrofuran (**12**) (Scheme 4).[6] For the 2-methylfuran analog (**2**), treatment with these carbon electrophiles results in cleavage of the C(5)−O bond (*vide infra*). However, vicinal difunctionalization of **2** can be achieved using a proton as the electrophile. For example, when a solution of **2** is treated with an excess of HOTf (−40 °C) followed by methyl trimethylsilyl dimethyl ketene acetal, the dihydrofuran complex **13** is cleanly isolated. Similarly, when ((trimethylsilyl)oxy)propene is used as the nucleophile, the 4,5-$\eta^2$-2,3-dihydro-2-methyl-2-(2-oxopropyl)furan complex **14** is obtained (yield 98%). NOE data indicate the stereochemistry of **13** and **14** shown in Scheme 4 where nucleophilic

**Scheme 4.** Vicinal Difunctionalization of Furan Complex **1** and Methylfuran Complex **2**

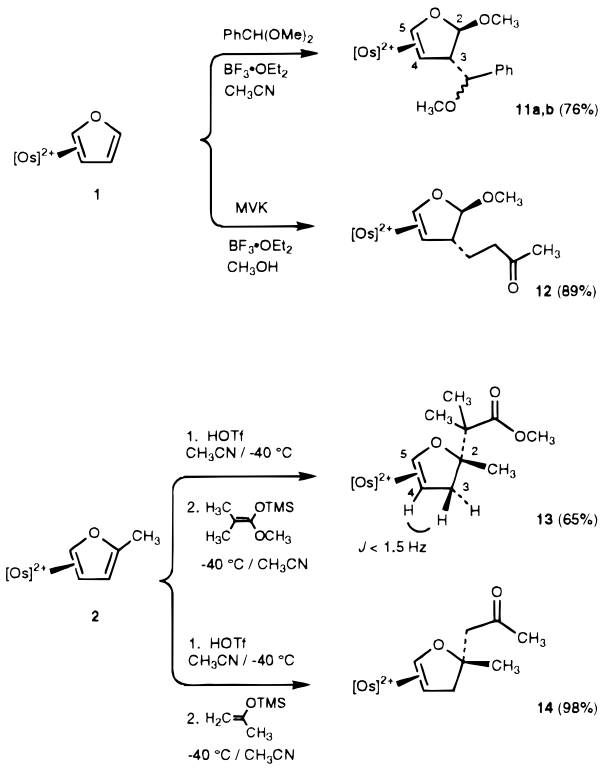



**Table 2.** Selected $^{13}$C Data for 4,5-$\eta^2$-2,3-Dihydrofuran Complexes

| cmpd | C(5) | $\delta$ ppm[a] C(4) | C(3) |
|---|---|---|---|
| **15** | 95.4 | 37.6 | 30.1 |
| **11a** | 96.4 | 39.0 | ~56 |
| **11b** | 96.4 | 40.6 | ~56 |
| **12** | 95.8 | 41.6 | 48.6 |
| **13** | 98.2 | 42.8 | 38.3 |
| **14** | 95.8 | 41.7 | 41.0 |
| **16a** | 94.0 (C(2)) | 48.6 (C(3)) | 48.8 |
| **16b** | 97.0 (C(2)) | 47.7 (C(3)) | 48.6 (C(4a)) |
| **22** | 96.6 | 37.9 | 67.1 |
| **23** | 96.7 | 37.4 | 69.6 |
| **31** | 95.0 | 36.7 | 52.4 |
| 2,3-dihydrofuran | 146.7 | 100.5 | 29.8 |

[a] Recorded in acetonitrile-$d_3$.

addition at C(2) occurs anti to the osmium. Attempts to repeat these reactions with **1** resulted in a complicated product mixture.

For the $\eta^2$-dihydrofuran complexes described herein, $^{13}$C resonances of the coordinated vinyl group are shifted significantly upfield in comparison to corresponding signals in uncoordinated 2,3-hydrofuran, as was observed in our earlier work[8b] and as shown in Table 2. For comparison we have included data for the parent 2,3-$\eta^2$-4,5-dihydrofuran−osmium-(II) complex (**15**).[8b] While the proton signals from the coordinated vinyl group in these complexes all have coupling constants, $J_{H(4)\text{-}H(5)}$, in the range of 4.0 ± 0.3 Hz, the two methylene protons on C(3) differ significantly in their coupling constants with H−C(4), depending on whether the proton is syn ($J_{H(3)\alpha-H(4)} < 1.5$ Hz) or anti to the osmium ($J_{H(3)\beta\text{-}H(4)} = 4$ to 6 Hz; Table 3).[15] Most dihydrofuran complexes show a reversible couple with $E_{1/2}$ in the range of 0.6−0.8 V(NHE).

When either furan complex **1** or **2** is combined with an excess (5−20 equiv) of methyl vinyl ketone ($CD_3CN$, −40 °C) followed by either a Lewis acid or HOTf, an initial Michael addition at C(3) occurs. A second Michael addition and an intramolecular nucleophilic attack at C(2) follow to generate the benzofuran skeleton (Scheme 5). While this [2 + 2 + 2] Michael−Michael−ring closure sequence (MIMIRC) for the parent complex **1** results in multiple stereoisomers, that for **2** results in only two diastereoisomers, **16a** and **16b**, in a nearly 1:1 ratio (Scheme 5).

Combustion analysis of the product mixture confirms that 2 equiv of methyl vinyl ketone are incorporated in the structure of **16a** and **16b**. The absence of significant coupling between H(3) and H(4) in either diastereomer indicates that the initial electrophilic attack at C(3) by the first equivalent of methyl vinyl ketone is from the face anti to the osmium; NOE data indicate that the final nucleophilic addition of the enolate to C(2) also occurs from this face for both isomers. Exposure of the mixture of **16a** and **16b** to a one-electron oxidant (2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in DMF at −40 °C) generates the two hexahydrobenzofurans **17a** and **17b** in 87% isolated yield.

**C(3)−C(5) Tandem Difunctionalization.** Previously, we disclosed that triflic acid catalyzes a ring opening of the $\eta^2$-furan complex **1** in $CH_3OH$ to give the trans and cis diastereomers of the 4-methoxy-3-butenal dimethyl acetal complex (**18a**, **18b**).[6] Continuing this investigation, when a solution of the 2-methyl furan complex **2** is treated with HOTf in methanol under similar conditions, the resulting product is a 5:3 ratio of two stereoisomers (**19a** and **19b**) shown by $^{13}$C and $^1$H NMR to be the trans- and cis-5-methoxy-4-penten-2-one complexes. If in the above reaction, prior to precipitation, the reaction solution is neutralized with *i*-$Pr_2EtN$ (Hünig's base), the isolated product mixture is more complex, including **19a**, **19b**, and new products **20a** and **20b** determined to be the corresponding acetals of **19a** and **19b** (Scheme 6).

When the reaction is repeated in $CD_3OD$ (complex at $[Os]^{2+}$ = 0.10 M, [DOTf] = 0.01 M, 22 °C) and monitored by $^1$H NMR spectroscopy for a period of 6 days, it is found that two of the four products, **19a** and **20a**, are formed at a significantly faster rate than their counterparts **19b** and **20b**. When the reaction conditions are adjusted, either **19a** or **20a** can be isolated in large excess over the other three vinyl ether complexes (Scheme 6). Through the comparison of coupling constants with known vinyl ether analogs,[8b] **19a** and **20a**, the kinetic products of the ring-opening reaction, are assigned to be trans isomers.[16]

Spectroscopic data for the above experiment show that from the beginning of the reaction, one of the two diastereotopic C(3) methylene protons of **19a**-$d_4$ and **20a**-$d_{10}$ is fully deuterated while the other, along with the ketone methyl group and the vinyl protons, appears at full strength.[17] In the latter stages of this reaction, spectroscopic data shows that the other C(3) proton

(15) A similar coupling situation was also observed in 4,5-$\eta^2$-3*H*-pyrrolium systems. See: ref 7a.

(16) Monitoring the reaction solution in this manner disclosed that although **19a** is formed first, **20a** appears very soon thereafter, with **19b** and **20b** forming later, eventually producing a 1:1:1:1 mixture of these four complexes. The equilibria involved in this process are quenched if acid is not present; therefore, adding base locks in the product mixture. However, adding a precipitation solvent ($Et_2O$) *without quenching with base* allows the equilibria to continue during precipitation, so that only **19a** or **19b** or both are found in the precipitated solid. If more that 0.1 equiv of acid is used, the equilibria are established more quickly (still eventually giving a 1:1:1:1 ratio of these complexes); with 0.5 equiv of acid, the 1:1:1:1 mixture forms immediately. On standing, new signals are seen, consistent with the formation of carbyne product(s).

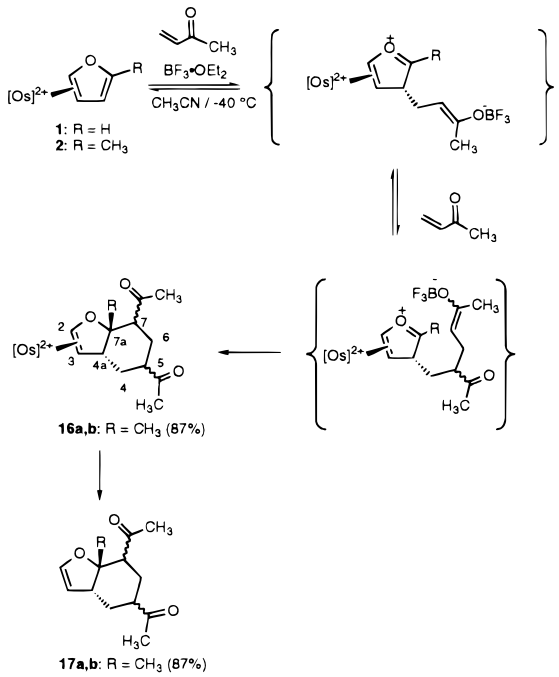
(17) The proton on C(3) which is fully deuterated (in both **19a**-$d_4$ and **20a**-$d_{10}$) is the proton with the *larger* coupling to the proton on C(4), 9.6 Hz for **19a** and 13.5 Hz for **20a**. The proton which remains on C(3) in **19a**-$d_4$ and **20a**-$d_{10}$ features a *small* coupling constant to the proton on C(4), 3.6 and 1.2 Hz, respectively.

**Table 3.** Selected $^1$H NMR Data for 4,5-$\eta^2$-2,3-Dihydrofuran Complexes

| | $\delta$ ppm[a] | | | | | | J (Hz) | | |
|---|---|---|---|---|---|---|---|---|---|
| cmpd | t-$NH_3$ | c-$NH_3$ | H(5) | H(4) | H(3α) | H(3$\beta$) | $J_{4,5}$ | $J_{3\alpha,4}$ | $J_{3\beta,4}$ |
| **15** | 3.99 | 3.04 | 6.11 | 3.48 | 2.70 | 1.81 | 3.9 | <1.5[b] | 4.2 |
| **11a** | 3.94 | 2.93 | 6.28 | 3.19 | 2.26 | | 3.9 | <1.5[b] | |
| **11b** | 3.97 | 2.99 | 6.28 | 3.83 | 2.26 | | 3.9 | <1.5[b] | |
| **12** | 4.03 | 3.09 | 6.26 | 3.39 | 1.88 | | 4.2 | <1.5[b] | |
| **13** | 3.99 | 3.06 | 6.34 | 3.62 | 3.22 | 1.37 | 3.9 | <1.5[b] | 6.6 |
| **14** | 4.05 | 3.07 | 6.51 | 3.97 | 2.60 | 1.41 | 3.9 | <1.5[b] | 6.0 |
| **16a** | 4.05 | 3.08 | 6.55 (C(2)) | 3.66 (C(3)) | 1.88 (C(4a)) | | | | |
| **16b** | 3.99 | 3.03 | 6.50 (C(2)) | 3.46 (C(3)) | 2.01 (C(4a)) | | 3.9 | <1.5[b] | |
| **22** | 3.98 | 3.12 | 6.18 | 3.66 | | 3.96 | 4.2 | | 4.2 |
| **23** | 4.05 | 3.21 | 6.39 | 3.79 | | 4.31 | 4.2 | | 4.2 |
| **31** | 4.21 | 3.25 | 6.70 | 4.01 | 4.23 | | 3.9 | <1.5[b] | |
| 2,3-dihydro furan | | | 6.32 | 4.95 | 2.56 | | 2.7 | 2.7 | |

[a] Recorded in acetonitrile-$d_3$. [b] Coupling not observed, $J$ < 1.5 Hz.

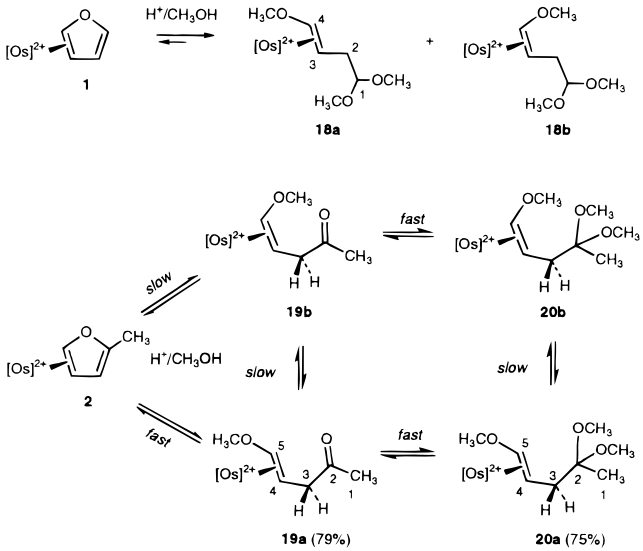
**Scheme 5.** Michael−Michael−Aldol Ring Closure Reaction of the Methylfuran Complex **2**




and the protons on the ketone methyl group are deuterated at about the same rate. In a parallel experiment, a mixture of fully protonated **19a** and **19b** was dissolved in acidic methanol-$d_4$, where protons of methylene and of ketone methyl were found to exchange with deuterium at about the same rate to generate **19a**-$d_8$ and **19b**-$d_8$. Considering the high stereoselectivity of the initial deuteration in the first reaction, it is likely that it is protonation at C(3) that induces ring opening rather than at oxygen. On the basis of the related studies in pyrrole and arene systems,[18] it is likely that this protonation occurs from the side of the furan ring anti to osmium.

Interestingly, the $\eta^2$-vinyl ether complexes **19a**, **19b** or **20a**, **20b** were found to function as surrogates of $\eta^2$-2-methylfuran complex **2** under the reaction conditions mentioned above. For example, when these complexes are treated at −40 °C with an excess of triflic acid in acetonitrile followed by pyridine, complex **2** is the major product. If treatment of triflic acid with a mixture of **19a**, **19b** and **20a**, **20b** in acetonitrile at −40 °C is followed by the addition of methyl trimethylsilyl dimethyl ketene acetal, **13** is isolated by precipitation in a mixture of $Et_2O$ and $CH_2Cl_2$.

**Scheme 6.** Acid-Catalyzed Alcoholysis of Furan Complexes **1** and **2**



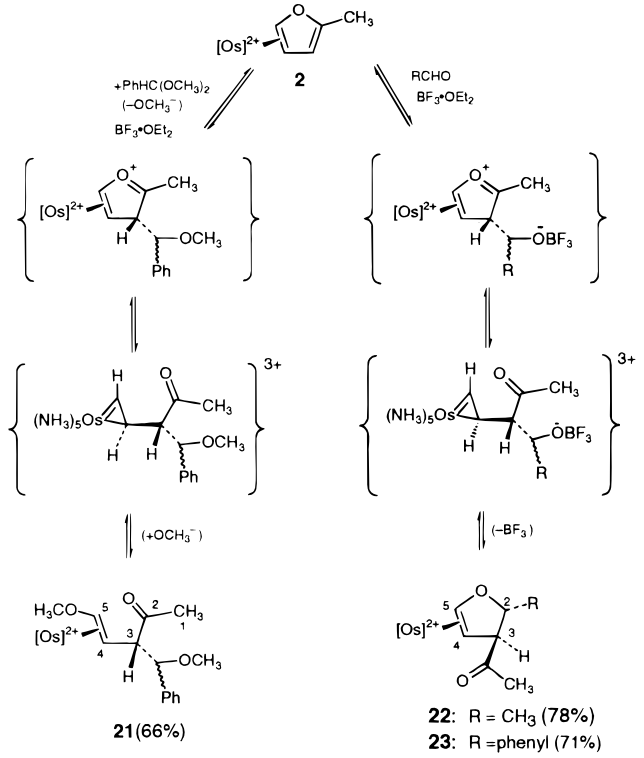

We have previously reported that when an acetal is combined with the $\eta^2$-2-methylfuran complex **2**, 3-alkylated 5-methoxy-4-penten-2-one complexes are formed.[8a] For example, when a sample of **2** is combined with benzaldehyde dimethyl acetal in the presence of $BF_3$•$OEt_2$ (0.5−1.0 equiv of Lewis acid, −40 °C), vinyl ether complex **21** is isolated as a single product. NOE data support the trans stereochemistry which is depicted in Scheme 7. Further, we reported that aldehydes react with **2** at C(3) in the presence of a Lewis acid. In this case, however, in the absence of an alcoholic solvent, an intramolecular nucleophilic addition at C(5) occurs to give $\eta^2$-3-acetylated 2,3-dihydrofuran complexes (e.g., **22** and **23** shown in Scheme 7).[8a]

In a process similar to the formation of **19**, complex **2** is treated with an excess of HOTf in acetonitrile-$d_3$ at −40 °C. $^1$H NMR data show the formation of two diastereoisomers **24a**-$d_3$ and **24b**-$d_3$ in a 1:1 ratio.[19] Attempts to isolate products from this mixture failed, but **24a**-$d_3$ and **24b**-$d_3$ were characterized *in situ* by $^1$H, $^{13}$C, and DEPT. These data indicate that **24a**-$d_3$ and **24b**-$d_3$ possess two methines, one methylene, one methyl, and an unconjugated carbonyl group for each diaste-

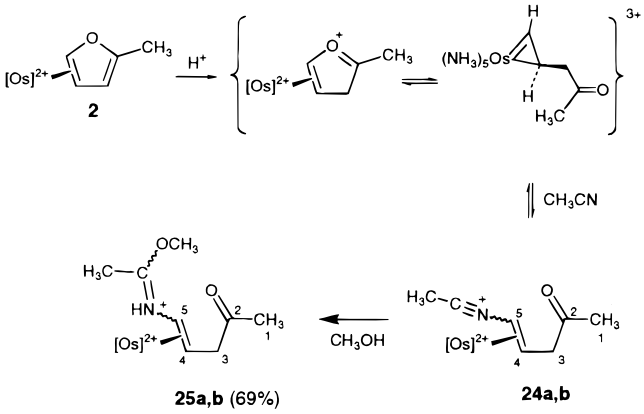
(18) (a) Winemiller, M. D.; Kopach, M. E.; Harman, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 2096. (b) Myers, W. H.; Koontz, J. I.; Harman, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 5684.

(19) An NMR sample of **1** (0.11 M) in acetonitrile-$d_3$ was treated with triflic acid (0.46 M) at −30 °C; $^1$H NMR shows the formation of a complicated reaction mixture. The sample freezes at temperatures lower than −30 °C.

**Scheme 7.** Nucleophilic Substitution of Furan Complexes at C(5) Initiated by Electrophilic Addition



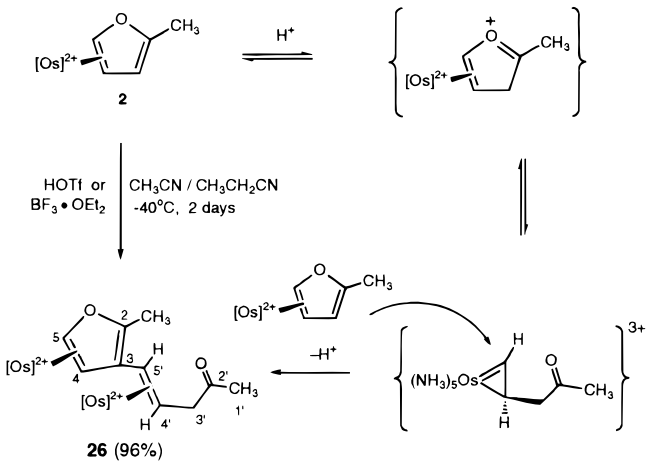

**Scheme 8.** Formation of *N*-Vinylacetonitrilium and *N*-Vinylimidate Complexes Initiated by Electrophilic Addition at C(3)




reomer. The unusual coupling constant of the two vinyl protons ($J$ = 6.8 Hz) and the $^{13}$C chemical shifts of the coordinated vinyl carbons (49 ppm for the α-carbon and 39 ppm for the $\beta$-carbon) indicate that **24a**-$d_3$ and **24b**-$d_3$ are different from the reported dihapto-coordinated vinyl ether complexes of pentaammineosmium.[8b] Considering the ability of acetonitrile to act as a nucleophile, **24a**-$d_3$ and **24b**-$d_3$ are likely to be $\eta^2$-*N*-vinylacetonitrilium complexes. A similar species has been invoked as an intermediate in the formation of $\eta^2$-vinylimidate complexes.[8b] Consistent with this hypothesis, when a solution of **24a** and **24b** is generated in the presence of methanol, two diastereomeric vinyl imidate complexes **25a** and **25b** are formed (Scheme 8).

An acetonitrile/propionitrile solution of the methylfuran complex **2** is treated with ~0.3 equiv of HOTf or $BF_3$•$OEt_2$, and the solution is allowed to stand at −40 °C for 48 h. After the reaction is quenched with pyridine and the product is precipitated in $CH_2Cl_2$, compound **26** is isolated in analytically

**Scheme 9.** Acid-Catalyzed Dimerization of 4,5-$\eta^2$-2-Methylfuran Complex **2**




pure form. The $^1$H NMR spectrum of **26** features *two sets* of *cis*- and *trans*-ammine resonances of equal intensity, while $^{13}$C and HETCOR data indicate that **26** contains twice the number of carbons and protons as those of **2**. These observations as well as microanalytical data support the assignment of **26** as a dimer of **2**. The structure of **26** includes an α,$\beta$-disubstituted $\eta^2$-furan fragment as confirmed by the characteristic resonances for the coordinated vinyl protons (6.82, 3.92 ppm, $J$ = 3.0 Hz) in $^1$H NMR and the coordinated vinyl carbons (95.4, 46.1 ppm) in the $^{13}$C NMR spectrum. A $^{13}$C resonance at 217.5 ppm suggests that one of the two furan complexes participating in the reaction has undergone nucleophilic substitution at C(5). The $^{13}$C NMR data of **26** also shows two methine signals at 48.5 and 42.3 ppm which are within range of the coordinated vinyl carbon signals for an $\eta^2$-alkene.[20] Taken together, **26** is assigned to be {[Os(NH$_3$)$_5$]$_2$(4,5-$\eta^2$-:4′,5′-$\eta^2$-$\mu$-3-(2′-oxo-4′-pentenyl)-2-methylfuran)}(OTf)$_4$ (Scheme 9).

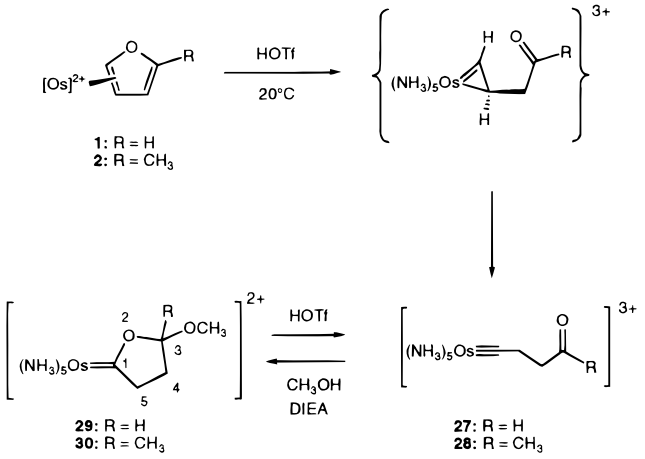
**Carbyne and Carbene Complexes.** Simple $\eta^2$-vinyl ether complexes of pentaammineosmium(II) containing an α-proton react in neat HOTf at 20 °C to form osmium carbyne complexes.[8b] Similarly, complexes **1** and **2** form carbyne complexes **27**[6] and **28** in acidic (HOTf) solutions of methanol, DMF, acetonitrile, and acetone. In contrast, for the $\eta^2$-2,5-dimethylfuran complex **3** where C(2) is methylated, a carbyne is not formed under otherwise identical reaction conditions.[21] Spectroscopic data for **27** or **28** include a *cis*-ammine resonance *downfield* from that of the *trans*-ammine and a downfield $^{13}$C signal at ~300 ppm.[22] The osmium carbyne complexes **27** and **28** are stable in acidic solution for days. However, when the carbyne complex **27** is dissolved in methanol in the presence of *N*,*N*-disopropylethylamine (DIEA), the acetal carbene species **29** is formed. $^1$H and $^{13}$C NMR data led us to assign **29** as [(NH$_3$)$_5$Os(3-methoxy-2-oxacyclopentylidene)]$^{2+}$, a compound whose features include closely spaced *cis*- and *trans*-ammine resonances and a carbene signal at 254.9 ppm in the $^{13}$C

(20) Spera, M. L.; Chin, R. M.; Winemiller, M. D.; Lopez, K. W.; Sabat, M.; Harman, W. D. *Organometallics* **1996**, *15*, 5447.

(21) Exposure of **3** to HOTf in DMAc shows no reaction for a week. When **3** was treated with a stoichiometric amount of acid in acetonitrile, the corresponding 4,5-$\eta^2$-3-(iminiumacetyl)−2,5-dimethylfuran complex formed.

(22) A 1D NOE experiment with **27** (acetone-$d_6$) shows that irradiation of the downfield $CH_2$ signal (3.36 ppm) causes a 16% enhancement on the aldehyde proton signal, while irradiation of the other $CH_2$ signal (2.27 ppm) cuases essentially no NOE enhancement on the aldehyde proton signal. Assuming that the two methylene groups of **27** are in staggered conformation, the methylene at 3.36 ppm is assigned to be α to Os≡C.

**Scheme 10.** The Formation of Pentaammineosmium Carbyne and Carbene Complexes




spectrum.[23] In addition, $^{13}$C NMR and DEPT data indicate that **29** also has a methyl (OMe), one methine, and two methylene groups. In the samer manner, $[(NH_3)_5Os$(3-methoxy-3-methyl-2-oxacyclopentylidene)$]^{2+}$ carbene complex **30** is produced from the reaction of methanol with **2** in the presence of DIEA. Treatment of **29** or **30** with a stoichiometric amount of acid in methanol or acetonitrile fully recovers the carbyne complex **27** or **28** (Scheme 10).

## Discussion

Whereas organic furans are valuable synthons that are widely used in organic synthesis,[1,24] transition metal complexes of furans are practically unknown.[25] The first furan $\pi$-complex, $[Cp^*Ru(\eta^5\text{-}C_4H_4O)]Cl$ (where $Cp^* =$ pentamethylcyclopentadienyl), was reported in 1988 and was only observed in solution.[26] To date, pentaammineosmium(II) is the only metal center reported to form a thermally stable dihapto-coordinate complex with furan. The ease of formation and remarkably high kinetic stability of these complexes make them ideally suited for an investigation of how dihapto-coordination affects the reactivity of a furan.[27]

Since furan is an electron-rich and aromatic heterocycle, its chemistry is dominated by electrophilic substitution at the α-carbons. In contrast, both structural and chemical evidence indicate that the complexation of furan at C(4) and C(5) dearomatizes the ligand, an action that results in the uncoordinated portion of the ring resembling a vinyl ether. Thus, the addition of electrophiles to a 4,5-$\eta^2$-furan complex would be expected to occur either at oxygen or at the uncoordinated $\beta$-carbon, C(3). Although preliminary experiments with trimethylsilyl triflate (TMSOTf) indicate that oxophilic electrophiles may in certain cases directly attack the oxygen,[28] addition of carbon electrophiles is observed exclusively at C(3); examples of this include Michael acceptors, aldehydes, acetals, and *N*-methylacetonitrilium triflate.

Owing to its more electronegative heteroatom, the 4,5-$\eta^2$-3*H*-furanium species resulting from C(3) electrophilic addition is much less stable than its 3*H*-pyrrolium analog. Correspondingly, the chemistry of the former system is considerably more diverse. Whereas 3*H*-pyrrolium complexes of pentaammineosmium(II) are mostly limited to deprotonation at C(3) or nucleophilic addition at C(2), the furanium counterpart, in addition to these reactions, readily undergoes cleavage of the carbon−heteroatom bond or deprotonation external to the ring (Scheme 1). Significantly, electrophilic addition to $\eta^2$-furan occurs exclusively from the ring face opposite to osmium coordination. As a result, 4,5-$\eta^2$-furanium complexes are kinetically protected against rearomatization because the pentaammineosmium(II) moiety blocks access to the acidic $sp^3$ methine proton at C(3). A similar feature has been identified in osmium(II)−pyrrole and −arene systems.[29] As a result, sequential electrophile−nucleophile addition reactions are much more accessible for $\eta^2$-furan complexes than for the organic heterocycles where electrophilic substitution dominates.

In a number of cases, an electrophile−nucleophile tandem addition to furan complexes **1** and **2** has led to difunctionalized 4,5-$\eta^2$-2,3-dihydrofuran species. This is in stark contrast to the chemical behavior of organic furans, which seldom undergo difunctionalization involving the 2,3-double bond of the ring.[4] In contrast to the well-defined exo stereochemistry of electrophilic addition, both exo and endo nucleophilic additions have been observed at C(2). For those reactions involving carbon nucleophiles, exo addition has been observed exclusively. However, when the nucleophile is an alcohol, under acidic reaction conditions, the C(2) addition is likely to be reversible. Therefore, the stereochemistry is thought to be controlled by thermodynamic rather than kinetic factors. For a methoxy substituent, a hydrogen-bond between the oxygen and the acidic ammine ligands is likely to be a significant factor in the expressed preference for an endo orientation.

The 3,5-difunctionalization of organic (i.e., uncomplexed) furans is also uncommon, but the alcoholysis of uncomplexed furans has been documented. Nucleophilic addition of an alcohol to an initially formed 3*H*-furanium, gives rise to an open-chain 1,4-dicarbonyl compound or derivative.[30] However, this reaction sequence is not known for carbon electrophiles. In a similar manner, the alcoholysis of 4,5-$\eta^2$-furan complexes results in the formation of vinyl ether derivatives of the corresponding 1,4-dicarbonyl compounds (e.g., **18**−**20**). As is the case for pentaammineosmium(II) complexes of simple vinyl ethers, the reaction of furan complexes **1** or **2** with methanol proceeds through initial protonation at C(3) followed by nucleophilic substitution at C(5), and this reaction is thought to occur through a dihapto-coordinated vinyl cation (i.e., a metallacyclopropene) intermediate.[6,8b] Although our attempts to isolate and characterize these $\eta^2$-vinyl cation species for the furan system have not been successful, their existence is evident from the broad range of nucleophiles which participate in nucleophilic substitution at C(5) of furan. Further evidence for the production of $\eta^2$-vinyl cation species is found in the formation of osmium carbyne complexes from these furan complexes analogous to those found for simple vinyl ether complexes.[8b] For the reaction of **2** with

(23) Hodges, L. M.; Sabat, M.; Harman, W. D. *Inorg. Chem.* **1993**, *32*, 371.

(24) (a) Alvarez, J. R.; Cuza, D.; Montero, L. A.; Isoba, R. *J. Mol. Struct. (THEOCHEM)* **1990**, 361. (b) Alvarez, J. R.; Cuza, D.; Montero, L. A. *J. Mol. Struct. (THEOCHEM)* **1992**, 243.

(25) For general reviews on organometallic complexes of five-membered monoheterocycles, see: (a) Sadimenko, A. P.; Garnovskii, A. D.; Retta, N. *Coord. Chem. Rev.* **1993**, *126*, 237. (b) Kershner, D. L.; Basolo, F. *Coord. Chem. Rev.* **1987**, *79*, 279.

(26) Chaudret, B.; Jalon, F. A. *J. Chem. Soc., Chem. Commun.* **1988**, 711.

(27) $\eta^2$-Pyrrole complexes undergo substitution with acetonitrile at 50 °C with a substitution half-life on 22 min. Comparatively, the substitution half-life of furan complexes is much longer.

(28) Chen, H.; Harman, W. D. Unpublished results.

(29) The representative reports on various aromatic ligands are as follows: (a) (Arenes) Kopach, M. E.; Harman, W. D. *J. Am. Chem. Soc.* **1994**, *116*, 6581. (b) (Pyrroles) Hodges, L. M.; Gonzalez, J.; Koontz, J. I.; Myers, W. H.; Harman, W. D. *J. Org. Chem.* **1995**, *60*, 2125.

(30) (a) Nowlin, G. *J. Am. Chem. Soc.* **1950**, *72*, 5754. (b) Scott, L. T.; Naples, J. O. *Synthesis* **1973**, 209.

methanol, although the alcohol molecule may in principle approach either side of the $\eta^2$-vinyl cation, the kinetic product is found to be the trans isomer (e.g., the formation of **19a** and **20a** at −40 °C), an observation which suggests that this nucleophilic substitution occurs through a dissociative mechanism analogous to that invoked for vinyl ethers.

As with open-chain $\eta^2$-vinyl ether complexes, treatment of **19a**, **19b** or **20a**, **20b** with an acid would be expected to form the $[Os(NH_3)_5(4,5\text{-}\eta^2\text{-}(4\text{-penten-1-yl-2-one}))]^{3+}$ (*vinyl cation*) resulting from the proton-induced removal of the methoxy group on C(5). Indirect evidence for the conversion of $[Os(NH_3)_5(4,5\text{-}\eta^2\text{-}(4\text{-penten-1-yl-2-one}))]^{3+}$ back to 4,5-$\eta^2$-3*H*-2-methylfuranium is found in this observation of the formation of **13** from the vinyl ether complexes **19** and **20**. The high stereoselectivity at C(2) in the product **13** suggests a reaction course involving an exo-specific nucleophilic addition of the methyl trimethylsilyl dimethyl ketene acetal to C(2) of the 3*H*-furanium species.

Thus, the key to controlling the outcome of organic reactions with $\eta^2$-furan complexes lies in the understanding of the factors which influence the chemoselectivity of the 3*H*-furanium intermediate (Scheme 1). The following discussion summarizes these factors. In the absence of any nucleophile, the 3*H*-furanium is in equilibrium with its metallacyclopropene isomer, and the latter will ultimately undergo a hydride shift to form a Fischer carbyne complex provided that C(5) of the initial furan bears a proton (Scheme 1, path C). If the 3*H*-furanium species is formed with an electron-withdrawing group on C(3), then the acidity at C(3) is sufficient that deprotonation is spontaneous, even under acidic conditions, and C(3) electrophilic substitution is likely to occur (path A). In the presence of a nonbasic nucleophile, a competition will exist between addition at C(5) and C(2) (paths D and E, respectively). Factors which influence this selectivity might include the nature of the nucleophile as well as reaction time and temperature. But most apparent in our studies is that this reaction manifold is highly sensitive to the substituent at C(2) of the original furan. As a general rule, for cases where the reactivity of furan complexes **1** and **2** could be compared directly, a methyl group at the 2-position tends to promote C(5) additions whereas the absence of this group favors C(2) addition. For example, under otherwise identical conditions, addition of an acetal to methylfuran **2** results in a ring-opened product (path D),[8a] whereas for the parent, only the dihydrofuran is observed (path E).[6] But this trend is not universally observed (e.g., Scheme 4). There are several reasons which may account for the differences seen between 2-methylfuran and furan. An alkyl group at C(2) should significantly affect the equilibrium between the 4,5-$\eta^2$-3*H*-furanium species and its oxoalkylmetallacyclopropene isomer as a result of stabilizing the 3*H*-furanium at C(2) or the carbonyl of the metallacyclopropene isomer relative to their unsubstituted forms (Scheme 1), but it is not obvious in which direction this equilibrium will be shifted. Addition at C(5) is likely a direct product of the metallacyclopropene isomer, and this notion along with experimental observations described above would suggest that alkylation might shift the equilibrium toward the carbonyl of the metallacyclopropene.[8b] However, an alkyl group at C(2) should have a steric effect as well, also making addition to C(5) more attractive. Further studies are needed to understand and control this complex reaction manifold. Note, however, that despite the diverse range of chemical transformations that the 3*H*-furanium species has been observed to participate in, the chemo- and stereoselectivity for the individual reactions reported is extraordinarily high.

## Summary

Coordination of the electron-rich pentaammineosmium(II) moiety to a furan dramatically alters the structural and chemical nature of the ligand. The resulting complexed ligands readily undergo a variety of electrophilic addition reactions featuring two reactive species, the open-chain $\eta^2$-vinyl cation species and $\eta^2$-3*H*-furanium species which appear to be interchangeable. The former species is susceptible to the nucleophilic addition at C(5), producing acyclic or cyclic $\eta^2$-olefin complexes; the latter species is susceptible to nucleophilic addition at C(2) or deprotonation at C(3), producing a variety of $\eta^2$-furan and $\eta^2$-2,3-dihydrofuran derivatives. Decomplexation of osmium from such products is achieved with appropriate one-electron oxidizing agents, and the free ligands so released may be purified via normal organic workup. When the coordinated α-carbon of the furan complexes bears a hydrogen, reaction with acid may produce carbyne complexes. Given the high degree of chemo-, regio-, and stereoselectivity of the reactions of $\eta^2$-furans, this dearomatization methodology holds promise as a new synthetic tool for organic synthesis.

## Experimental Section

**Abbreviations.** OTf = $CF_3SO_3^-$; DMAc = *N*,*N*-dimethylacetamide; DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone; DIEA = *N*,*N*-diisopropylethylamine.

**General.** This work was carried out under a nitrogen atmosphere in a Vacuum Atmospheres Company glovebox, separate boxes being used for aqueous and nonaqueous reactions. When necessary, osmium complexes were purified by (a) redissolving in acetone or acetonitrile and reprecipitating or (b) ion-exchange chromatography using Sephadex SP C-25 resin with aqueous NaCl as the mobile phase, in which case the purified salts were precipitated as the tetraphenylborate salt by adding an excess of aqueous $NaBPh_4$. Routine $^1H$ and $^{13}C$ NMR spectra (obtained at 300 and 75 MHz, respectively) were recorded on a General Electric QE-300 or GN-300 spectrometer at 20 °C unless otherwise noted. Carbon multiplicities, if provided, are supported by DEPT and/or HETCOR data. Chemical shifts are reported in ppm and are referenced to tetramethylsilane. Electrochemical experiments were performed under nitrogen using a PAR model 362 potentiostat driven by a PAR model 175 universal programmer. Cyclic voltammograms were recorded in a standard three-electrode cell from +1.8 to −1.8 V with a glassy carbon electrode.[31] All potentials are reported vs NHE and, unless otherwise noted, were determined in acetonitrile (∼0.5 M TBAH) at 100 mV/s using ferrocene ($E_{1/2}$ = +0.55 V(NHE)) or colbaltocenium hexafluorophosphate ($E_{1/2}$ = −0.78 V(NHE)) *in situ* as a calibration standard. The peak-to-peak separation ($E_{p,a} - E_{p,c}$) was 100 mV or less for all reversible couples, unless otherwise noted. Elemental analyses were obtained on a Perkin-Elmer PE-2400 Series II CHN analyzer.

**Solvents.** All solvents were deoxygenated by purging with nitrogen for at least 15 min; deuterated solvents were deoxygenated either by repeated freeze−pump−thaw cycles or by vacuum distillation. All distillations were performed under nitrogen. Methylene chloride was refluxed over $P_2O_5$ for at least 8 h and distilled. Diethyl ether was refluxed for at least 8 h over sodium/benzophenone and distilled. Methanol was refluxed over $Mg(OMe)_2$, prepared *in situ* from magnesium activated by $I_2$, and distilled. Acetonitrile and propionitrile were refluxed over $CaH_2$ and distilled. Aldrich anhydrous grade DMAc and DME were used without further purification, except that they were deoxygenated prior to use.

**Reagents.** $[Os(NH_3)_5(OTf)](OTf)_2$ was synthesized as described by Lay et al.[32] Magnesium powder (Aldrich, 50 mesh) was activated by treating the powder with iodine in DME under nitrogen, stirring the

(31) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; John Wiley & Sons: New York, 1980.

(32) (a) Lay, P. A.; Magnuson, R. H.; Taube, H. *Inorg. Chem.* **1989**, *28*, 3001. (b) Lay, P. A.; Magnuson, R. H.; Taube, H. *Inorg. Synth.* **1986**, *24*, 269.

solution for 1 h, filtering the solution, and washing the solid powder with DMAc, acetone, and diethyl ether. Dihydrofuran and 2-methoxypropene were purified by distillation from $CaH_2$. Acetonitrile-$d_3$ (Cambridge Isotope Labs) was distilled from $CaH_2$. Acetone-$d_6$ and DMSO-$d_6$ were used as received, except that they were deoxygenated prior to use.

***N*-Methylacetonitrilium Triflate** was synthesized by a procedure described in the literature.[33]

**Complexes.** The synthesis and characterization of the furan complexes $[Os(NH_3)_5(4,5\text{-}\eta^2\text{-furan})](OTf)_2$ (**1**) and $[Os(NH_3)_4(4,5\text{-}\eta^2\text{-2-methylfuran})](OTf)_2$ (**2**) have been previously reported, as have several $\eta^2$-furan, $\eta^2$-dihydrofuran, and $\eta^2$-vinyl ether complexes and related osmium carbyne complexes.[6,8] Consequently, for these compounds only a limited set of characterization data are provided and are marked with an asterisk (*) in the Experimental Section.

**Furan Complexes. *$[Os(NH_3)_5(4,5\text{-}\eta^2\text{-furan})](OTf)_2$ (1).**[11] $^1$H NMR (acetonitrile-$d_3$): $\delta$ 7.25 (d, $J$ = 3.0 Hz, 1H, H-C(5)), 6.90 (d, $J$ = 2.6 Hz, 1H, H-C(2)), 6.05 (t, $J$ = 2.6 Hz, 1H, H-C(3)), 4.85 (t, $J$ = 2.0 Hz, 1H, H-C(4)), 4.02 (br s, 3H, *trans*-$NH_3$), 2.85 (br s, 12H, *cis*-$NH_3$). $^{13}$C NMR (acetone-$d_6$): $\delta$ 142.7 (C(2)), 112.0 (C(3)), 98.6 (C(5)), 49.0 (C(4)). CV: $E_{p,a}$ = 0.67 V(NHE).

***$[Os(NH_3)_5(4,5\text{-}\eta^2\text{-2-methylfuran})](OTf)_2$ (2).**[8a] $^1$H NMR (acetone-$d_6$): $\delta$ 7.38 (d, $J$ = 3.6 Hz, 1H, H-C(5)), 5.81 (d, $J$ = 1.5 Hz, 1H, H-C(3)), 5.00 (dd, $J$ = 3.6, 1.5 Hz, 1H, H-C(4)), 4.63 (br s, 3H, *trans*-$NH_3$), 3.46 (br s, 12H, *cis*-$NH_3$), 1.97 (s, 3H, $CH_3$). $^{13}$C NMR (acetone-$d_6$): $\delta$ 153.1 (C(2)), 107.2 (C(3)), 97.8 (C(5)), 50.4 (C(4)), 13.1 ($CH_3$). CV: $E_{p,a}$ = 0.60 V(NHE).

***$[Os(NH_3)_5(4,5\text{-}\eta^2\text{-2,5-dimethylfuran})](OTf)_2$ (3).**[8a] Activated $Mg^0$ (2.40 g, 98.8 mmol) was added to a solution of $[Os(NH_3)_5(OTf)](OTf)_2$ (1.55 g, 2.14 mmol) and 2,5-dimethylfuran (10.69 g, 111 mmol) dissolved in DMAc (3.33 g). The slurry was stirred for 137 min and then filtered through a fine porosity frit into a mixture of $CH_2Cl_2$ (600 mL) and $Et_2O$ (150 mL), producing a yellow precipitate, which was filtered, washed with $Et_2O$ and $CH_2Cl_2$, and dried *in vacuo*. Yield of yellow powder: 1.21 g (1.81 mmol, 85%). $^1$H NMR (acetone-$d_6$): $\delta$ 5.80 (d, $J$ = 2.1 Hz, 1H, H-C(3)), 4.80 (d, $J$ = 2.1 Hz, 1H, H-C(4)), 4.65 (br s, 3H, *trans*-$NH_3$), 1.99 (s, 1H, $CH_3$-C(2)), 3.50 (br s, 12H, *cis*-$NH_3$), 1.73 (s, 3H, $CH_3$-C(5)). $^{13}$C NMR (acetone-$d_6$): $\delta$ 152.1 (C(2)), 107.7 (C(3)), 98.8 (C(5)), 51.8 (C(4)), 18.7 ($CH_3$), 13.1 ($CH_3$). CV: $E_{p,a}$ = 0.57 V(NHE). Anal. Calcd for $C_8H_{23}O_7N_5S_2OsF_6$: C, 14.35; H, 3.46; N, 10.46. Found: C, 14.38; H, 3.55; N, 10.46.

**$[Os(NH_3)_5(4,5\text{-}\eta^2\text{-3-(hydroxylmethylene)furan})](OTf)_2$ (4a) and $[Os(NH_3)_5(2,3\text{-}\eta^2\text{-3-(hydroxymethylene)furan})](OTf)_2$ (4c).** $[Os(NH_3)_5(OTf)](OTf)_2$ (559 mg, 0.774 mmol) was dissolved in methanol (2.40 g) with stirring. 3-Furanmethanol (2.55 g, 26.0 mmol) was added to the solution, followed by Zn/Hg (1.75 g). After 30 min of stirring, the slurry was filtered through a fine porosity frit into a mixture of $Et_2O$ (400 mL) and $CH_2Cl_2$ (100 mL) producing a light yellow precipitate, which was collected, washed with $CH_2Cl_2$ and $Et_2O$, and dried *in vacuo*. Yield of light yellow powder: 423 mg (0.76 mmol, 81%). The solid appeared by $^1$H NMR to be a mixture of **4a** and **4c** in 1:1 ratio. Anal. Calcd for $C_7H_{21}O_7N_5S_2OsF_6$: C, 12.52; H, 3.15; N, 10.43. Found: C, 12.78; H, 3.13; N, 10.57.

The mixture (98.0 mg, 0.146 mmol) of **4a** and **4c** in 1:1 ratio was dissolved in acetonitrile (0.4 mL). After 3 days, the solution was added to a mixture of $Et_2O$ (70 mL) and $CH_2Cl_2$ (5 mL), giving a light yellow precipitate, which was collected, washed with $CH_2Cl_2$ and $Et_2O$, and dried *in vacuo*. Yield of light yellow powder: 75 mg, 77%. The solid appeared by $^1$H NMR to be exlusively **4a**.

**4a.** $^1$H NMR (acetonitrile-$d_3$): $\delta$ 7.29 (d, $J$ = 3.3 Hz, 1H, H-C(5)), 6.84 (s, 1H, H-C(2)), 4.76 (d, $J$ = 3.3 Hz, 1H, H-C(4)), 4.35 (d, $J$ = 3.0 Hz, 2H, $CH_2$), 4.10 (br s, 3H, *trans*-$NH_3$), 3.77 (t, $J$ = 3.0 Hz, 1H, OH), 2.96 (br s, 12H, *cis*-$NH_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 140.4 (C(2)), 126.2 (C(3)), 100.4 (C(5)), 56.8 ($CH_2$) 51.0 (C(4)). CV: $E_{p,a}$ = 0.70 V(NHE).

**4c.** $^1$H NMR (acetonitrile-$d_3$): $\delta$ 7.25 (s, 1H, H-C2), 6.76 (d, $J$ = 1.4 Hz, 1H, H-C(5)), 5.99 (d, $J$ = 1.4 Hz, 1H, H-C(4)), 4.28 (d,d $J$ = 11.7, 3.6 Hz, 1H, $CH_2$), 4.10 (br s, 3H, *trans*-$NH_3$), 3.69 (dd, $J$ = 11.7, 3.6 Hz, 1H, $CH_2$), 3.61 (t, $J$ = 3.6 Hz, 1H, OH) 3.08 (br s, 12H, *cis*-$NH_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 143.1 (C(5)), 126.2 (C(4)), 97.7 (C(2)), 64.1 ($CH_2$), 55.6 (C(3)).

**$[Os(NH_3)_5(4,5\text{-}\eta^2\text{-3-(}N\text{-methyliminiumacetyl)furan})](OTf)_3$ (5).**[6] A solution of *N*-methylacetonitrilium triflate (100 mg, 0.478 mmol) in acetonitrile (598 mg) was prepared and added to a solution of **1** (125 mg, 0.195 mmol) in acetonitrile (3.02 g). The reaction mixture was stirred for 80 min and treated with pyridine (120 mg, 1.52 mmol). After 15 min, the reaction mixture was added to $CH_2Cl_2$ (150 mL) with stirring, giving an orange precipitate which was filtered, washed with $CH_2Cl_2$ and $Et_2O$, $Et_2O$, and dried *in vacuo*. Yield of tan solid: 122 mg (0.143 mmol, 74%). $^1$H NMR (acetonitrile-$d_3$) $\delta$ 10.0 (br s, 1H, NH), 8.17 (s, 1H, H-C(2)), 7.71 (d, $J$ = 3.3 Hz, 1H, H-C(5)), 5.13 (d, $J$ = 3.3 Hz, 1H, H-C(4)), 4.33 (br s, 3H, *trans*-$NH_3$), 3.26 (s, 3H, $NCH_3$), 3.16 (br s, 12H, *cis*-$NH_3$), 2.43 (s, 3H, $CH_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 176.5 (C═N), 163.5 (C(2)), 125.5 (C(3)), 102.8 (C(5)), 37.9 (C(4)), 33.4 ($NCH_3$), 17.6 ($CH_3$). CV: $E_{p,a}$ = 1.16 V(NHE). Anal. Calcd for $C_{10}H_{25}N_6O_{10}S_3OsF_9$: C, 14.19; H, 2.98; N, 9.93. Found: C, 14.84; H, 2.76; N, 10.13.

**$[Os(NH_3)_5(4,5\text{-}\eta^2\text{-3-(}N\text{-methyliminiumacetyl)-2-methylfuran})](OTf)_3$ (6a).** A solution of methylacetonitrilium triflate (34 mg, 0.164 mmol) in acetonitrile (0.5 g) was prepared and added to a solution of **2** (85 mg, 0.130 mmol) in acetonitrile (1 g). The reaction mixture was stirred for 7 min and then treated with pyridine (51 mg, 0.64 mmol). After 10 min, the reaction mixture was added to a mixture of $Et_2O$ (140 mL) and $CH_2Cl_2$ (20 mL) with stirring, giving an orange yellow precipitate which was filtered, washed with $CH_2Cl_2$ and $Et_2O$, and dried *in vacuo*. Yield of tan solid: 93 mg (0.108 mmol, 83%). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 9.00 (br s, 1H, NH), 7.47 (d, $J$ = 3.9 Hz, 1H, H-C(5)), 5.11 (d, $J$ = 3.9 Hz, 1H, H-C(4)), 4.27 (br s, 3H, *trans*-$NH_3$), 3.26 (s, 3H, $NCH_3$), 3.14 (br s, 12H, *cis*-$NH_3$), 2.50 (s, 3H, $CH_3$), 2.49 (s, 3H, $CH_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 176.9 (C═N), 174.7 (C(2)), 120.3 (C(3)), 98.7 (C(5)), 40.6 (C(4)), 33.4 ($NCH_3$), 18.8 ($CH_3$), 17.9 ($CH_3$). CV: $E_{p,a}$ = 1.06 V(NHE). Anal. Calcd for $C_{11}H_{27}N_6O_{10}S_3OsF_9$: C, 15.35; H, 3.16; N, 9.76. Found: C, 14.93; H, 3.08; N. 9.70.

**$[Os(NH_3)_5(4\alpha,5\alpha\text{-}\eta^2\text{-}3\beta\text{-(N-methyliminiumacetyl)-2-}exo\text{-vinyl-2,3-dihydrofuran})](OTf)_2$ (6b).** A solution of *N*-methylacetonitrilium triflate (36.7 mg, 0.179 mmol) in acetonitrile (0.538 g) was prepared and added to a solution of **2** (91.4 mg, 0.139 mmol) in acetonitrile (0.885 g). The reaction mixture was stirred for 7 min at 22 °C and then added to stirring $CH_2Cl_2$ (100 mL), giving a yellow precipitate which was filtered, washed with $CH_2Cl_2$ and $Et_2O$, and dried *in vacuo*. Yield of yellow solid: 114 mg (0.132 mmol, 95%). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 11.2 (br s, 1H, NH), 6.70 (d, $J$ = 3.9 Hz, 1H, H-C(5)), 4.46 (s, 1H, $CH_2$), 4.28 (s, 1H, H-C(3)), 4.21 (br s, 3H, *trans*-$NH_3$), 4.12 (s, 1H, $CH_2$), 4.01 (d, $J$ = 3.9 Hz, 1H, H-C(4)), 3.46 (d, $J$ = 5.1 Hz, 3H, $NCH_3$), 3.25 (br s, 12H, *cis*-$NH_3$), 2.54 (s, 3H, $Ch_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 191.3 (q), 159.4 (C(2)), 95.0 (C(5)), 89.7 ($CH_2$), 52.4 (C(3)), 36.7 (C(4)), 35.1 (N-$CH_3$), 21.5 ($CH_3$). Anal. Calcd for $C_{11}H_{27}N_6O_{10}S_3OsF_9$: C, 15.35; H, 3.16; N, 9.76. Found: C, 15.21; H, 3.46; N, 10.04. CV: $E_{1/2}$ = +1.03 V(NHE); $E_{p,c}$ = −1.39 V(NHE).

**$[Os(NH_3)_5(4,5\text{-}\eta^2\text{-3-acetylfuran})](OTf)_2$ (7).** A sample of **1** (130 mg, 0.203 mmol) was treated with methylacetonitrilium triflate and then pyridine in acetonitrile to give **5** (130 mg, 74%). After standing for 2 weeks, a sample of this product (71 mg) was dissolved in a mixture of acetonitrile (1.43 g) and water (0.495 mg), and the resulting solution was allowed to stand. After 11 days, the solvent of the reaction mixture was removed by rotary evaporation, and the resulting solid was dissolved in acetone (990 mg). This solution was added to $CH_2Cl_2$ (100 mL), giving a brown precipitate, which was filtered, washed with $CH_2Cl_2$ and $Et_2O$, and dried *in vacuo*. The yield of light brown solid was 60 mg (0.088 mmol, ca. 80% from **5**). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 7.74 (s, 1H, H-C(2)), 7.47 (d, $J$ = 3.6 Hz, 1H, H-C(5)), 5.17 (d, $J$ = 3.6 Hz, 1H, H-C(4)), 4.16 (br s, 3H, *trans*-$NH_3$), 3.00 (br s, 12H, *cis*-$NH_3$), 2.27 (s, 3H, $CH_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 196.8 (C═O), 154.6 (C(2)), 131.6 (C(3)), 101.8 (C(5)), 45.6 (C(4)), 27.0 ($CH_3$). CV: $E_{p,a}$ = 0.86 V(NHE). Anal. Calcd for $C_8H_{21}N_5O_8S_2OsF_6$: C, 14.06; H, 3.10; N, 10.26. Found: C, 14.46; H, 2.82; N, 9.98.

**$[Os(NH_3)_5(4,5\text{-}\eta^2\text{-3-acetyl-2-methylfuran})](OTf)_2$ (8).** The complex **6a** (93.3 mg, 0.109 mmol) was dissolved in $H_2O$ (1.15 g). After 10 days, the solvent of the reaction mixture was removed by rotary

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evaporation, and the resulting solid was dissolved in acetone (843 mg). This solution was added to $CH_2Cl_2$ (100 mL) giving a tan precipitate, which was filtered, washed with $CH_2Cl_2$ and $Et_2O$, and dried *in vacuo*. Yield of light brown solid: 70.9 mg (0.101 mmol, 93%). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 7.23 (d, $J$ = 3.9 Hz, 1H, H-C(5)), 5.18 (d, $J$ = 3.9 Hz, 1H, H-C(4)), 4.09 (br s, 3H, *trans*-$NH_3$) 3.04 (br s, 3H, *cis*-$NH_3$), 2.40 (s, 3H, $CH_3$), 2.36 (s, 3H, $CH_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 197.4 (C═O), 164.3 (C(2)), 126.6 (C(3)), 97.8 (C(5)), 48.4 (C(4)), 29.3 ($CH_3$), 15.3 ($CH_3$). Anal. Calcd for $C_9H_{23}N_5O_8S_2OsF_6$: C, 15.49; H, 3.32; N, 10.04. Found: C, 15.13; H, 3.30; N, 9.86.

**[Os(NH$_3$)$_5$(4,5-$\eta^2$-3-(*trans*-3-oxo-1-butenyl)-2-methylfuran)](OTf)$_2$ (9).** A solution of **2** (75 mg, 0.114 mmol) in acetonitrile (667 mg) and a solution of *trans*-4-methoxy-3-buten-2-one (739 mg, 7.39 mmol) in acetonitrile (723 mg) were prepared and cooled to −40 °C. A solution of TBSOTf (49 mg, 0.189 mmol) in acetonitrile (460 mg) was also cooled to −40 °C and added to the solution of 4-*trans*-4-methoxy-3-buten-2-one. After 10 min at −40 °C, this mixture was added to the solution of **2**. The reaction mixture was allowed to stir for 27 h and then treated with DIEA (87 mg, 0.670 mmol). The product was precipitated with a mixture of $Et_2O$ (20 mL) and $CH_2Cl_2$ (60 mL) and collected. Yield of greenish yellow solid: 72 mg (0.100 mmol, 88%). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 7.61 (d, $J$ = 15.6 Hz, 1H, CH), 7.28 (d, $J$ = 3.6 Hz, 1H, H-C(5)), 6.40 (d, $J$ = 15.6 Hz, 1H, CH), 5.06 (d, $J$ = 3.6 Hz, 1H, H-C(4)), 4.13 (br s, 3H, *trans*-$NH_3$), 3.02 (br s, 12H, *cis*-$NH_3$), 2.25 (s, 3H, $CH_3$), 2.19 (s, 3H, $CH_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 199.1 (C═O), 161.8 (C(2)), 138.1 (CH), 123.2 (CH), 121.5 (C(3)), 97.3 (C(5)), 44.7 (C(4)), 27.5 ($CH_3$), 12.0 ($CH_3$). CV: $E_{1/2}$ = 0.70 V(NHE). The compound was purified by ion-exchange chromatography and isolated as its tetraphenylborate trihydrate salt. Anal. Calcd for $C_{57}H_{65}N_5O_2B_2Os\cdot 3H_2O$: C, 61.23; H, 6.40; N, 6.26. Found: C, 61.48; H, 6.52; N, 6.53.

**[(NH$_3$)$_5$Os(4,5-$\eta^2$-3-(*trans*-3-hydroxonium-1-butenyl)-2-methylfuran)](OTf)$_3$ (10).** The complex **9** (44 mg, 0.0611 mmol) was dissolved in acetonitrile (767 mg) and cooled to −40 °C. Triflic acid (36 mg, 0.243 mmol) was added to the solution of **9** under −40 °C, producing a dark red solution. After 10 min at −40 °C, the solution was added to a mixture of $CH_2Cl_2$ (20 mL) and $Et_2O$ (10 mL) (at −40 to −20 °C), producing a brown precipitate, which was filtered, washed with $CH_2Cl_2$ and $Et_2O$, and dried *in vacuo*. Yield: 43 mg (0.050 mmol, 81%). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 8.81 (d, $J$ = 13.8 Hz, 1H, CH), 7.84 (d, $J$ = 3.6 Hz, 1H, H-(C(5)), 6.84 (d, $J$ = 13.8 Hz, 1H, CH), 5.35 (d, $J$ = 3.6 Hz, 1H, H-C(4)), 4.32 (br s, 3H, *trans*-$NH_3$), 3.21 (br s, 12H, *cis*-$NH_3$), 2.62 (s, 3H, $CH_3$), 2.48 (s, 3H, $CH_3$). Anal. Calcd for $C_{12}H_{26}O_{11}N_5S_3OsF_6$: C, 16.50; H, 3.00; N, 8.02. Found: C, 16.83; H, 3.32; H, 8.38.

***[Os(NH$_3$)$_5$(4,5-$\eta^2$-3-(1-methoxybenzyl)-2-methoxy-2,3-dihydrofuran)](OTf)$_2$ (11a** and **11b).**[6] For **11a**: $^1$H NMR (acetonitrile-$d_3$): $\delta$ 7.29−7.25 (m, 5H, $C_6H_5$), 6.28 (d, $J$ = 3.9 Hz, 1H, H-C(5)), 5.31 (d, $J$ = 3.0 Hz, 1H, H-C(2)), 4.28 (d, $J$ = 8.4 Hz, 1H, H-CPh), 3.94 (br s, 3H, *trans*-$NH_3$), 3.24 (s, 3H, $OCH_3$), 3.20 (s, 3H, $OCH_3$), 3.19 (d, $J$ = 3.9 Hz, 1H, H-C(4)), 2.93 (br s, 12H, *cis*-$NH_3$), 2.28−2.25 (m, 1H, H-C(3)). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 141.3 (1C, Ph), 129.4−128.2 (CH, 5C, Ph), 113.6 (C(2)), 96.4 (C(5)), 86.5 (CH, C-Ph), 57.2−56.5 (3C, $OCH_3$, $OCH_3$, C(3)), 39.0 (C(4)).

**11b.** $^1$H NMR (acetonitrile-$d_3$): $\delta$ 7.29−7.25 (m, 5H, $C_6H_5$), 6.28 (d, $J$ = 3.9 Hz, 1H, H-C(5)), 5.02 (d, $J$ = 4.2 Hz, 1H, H-C(2)), 4.31 (d, $J$ = 8.4 Hz, 1H, H-CPh), 3.97 (br s, 3H, *trans*-$NH_3$), 3.83 (d, $J$ = 3.9 Hz, 1H, H-C(4)), 3.19 (s, 3H, $OCH_3$), 2.99 (s, 3H, $OCH_3$), 2.99 (br s, 12H, *cis*-$NH_3$), 2.28−2.25 (m, 1H, H-C(3)). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 140.4 (1C, Ph), 129.4−128.2 (CH, 5C, Ph), 113.4 (C(2)), 96.4 (C(5)), 86.2 (CH, C-Ph), 57.2−128.6 (3C, $OCH_3$, $OCH_3$, C3), 40.6 (C4).

***[Os(NH$_3$)$_5$(4α,5α-$\eta^2$-3$\beta$-(3-oxobutyl)-2α-methoxy-2,3-dihydrofuran)](OTf)$_2$ (12).**[6] $^1$H NMR (acetonitrile-$d_3$): $\delta$ 6.26 (d, $J$ = 4.2 Hz, 1H, H-C(5)), 4.93 (d, $J$ = 2.1 Hz, 1H, H-C(2)), 4.03 (br s, 3 H, *trans*-$NH_3$), 3.39 (d, $J$ = 4.2 Hz, 1H, H-C(4)), 3.23 (s, 3H, $OCH_3$), 3.09 (br s, 12H, *cis*-$NH_3$), 2.57 (t, $J$ = 7.8 Hz, 2H, $CH_2$), 2.11 (s, 3H, $CH_3$), 1.88 (m, 1H, H-C(3)), 1.85 (m, 2H, $CH_2$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 209.6 (C═O), 116.1 (C(2)), 95.8 (C(5)), 56.9 ($OCH_3$), 48.6 (C(3)), 41.7 ($CH_2$), 41.6 (C(4)), 30.2 ($CH_3$), 30.1 ($CH_2$). Anal. Calcd for $C_{11}H_{29}N_5O_9S_2OsF_6$: C, 17.77; H, 3.93; N, 9.42. Found: C, 18.15; H, 4.18; N, 9.43.

**[Os(NH$_3$)$_5$(4α,5α-$\eta^2$-2$\beta$-(2-oxo-1,1′-dimethyl-2-methoxyethyl)-2α-methyl-2,3-dihydrofuran)](OTf)$_2$ (13).** Solutions of **2** (95 mg, 0.145 mmol) in a mixture of acetonitrile (2.92 g) and propionitrile (1.48 g), of triflic acid (27 mg, 0.179 mmol) in acetonitrile, and of methyl trimethylsilyl dimethyl ketene acetal (135 mg, 0.776 mmol) in acetonitrile were prepared separately and cooled to −40 °C. The triflic acid solution was added to the solution of complex **2**, and 30 s later, the ketene acetal solution was also added. After 10 min, the reaction mixture was treated with pyridine (53 mg, 0.670 mmol); after an additional 6 min, the reaction mixture was added to a mixture of $Et_2O$ (80 mL) and $CH_2Cl_2$ (20 mL), producing a tan precipitate, which was filtered through a medium-porosity frit. The solid was washed with $Et_2O$ and $CH_2Cl_2$ and dried *in vacuo*. Yield of tan solid: 72 mg (0.095 mmol, 65%). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 6.34 (d, $J$ = 3.9 Hz, 1H, H-C(5)), 3.99 (br s, 3H, *trans*-$NH_3$), 3.64 (s, 3H, $OCH_3$), 3.63 (m, overlap with $CH_3O$, 1H, H-C(4)), 3.21 (dd, $J$ = 15.0, 6.5 Hz, 1H, H-C(3)), 3.06 (br s, 12H, *cis*-$NH_3$), 1.37 (d, $J$ = 15.0 Hz, 1H, H-C(3)), 1.31 (s, 3H, $CH_3$), 1.17 (s, 3H, $CH_3$), 1.09 (s, 3H, $CH_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 177.7 (C═O), 98.2 (C(5)), 96.6 (C(2)), 52.6 ($CH_3$), 51.2 (C), 42.8 (C(4)), 38.3 (C(3)), 22.6 ($CH_3$), 21.8 ($CH_3$), 21.6 ($CH_3$). CV: $E_{1/2}$ = 0.69 V(NHE). Anal. Calcd for $C_{12}H_{31}N_5O_9S_2OsF_6$: C, 19.20; H, 4.12; N, 9.24. Found: C, 18.98; H, 4.37; N, 9.62.

**[Os(NH$_3$)$_5$(4α,5α-$\eta^2$-2$\beta$-(2-oxopropyl)-2α-methyl-2,3-dihydrofuran)](OTf)$_2$ (14).** Solutions of **2** (70 mg, 0.107 mmol) in a mixture of acetonitrile (1.37 g) and propionitrile (0.15 g), of triflic acid (57 mg, 0.378 mmol) in acetonitrile (0.30 g), and of ((trimethylsilyloxy)propene (132 mg, 1.01 mmol) in acetonitrile (0.21 g) were prepared separately and cooled to −45 °C. The triflic acid solution was added to the solution of **2**, and 5 min later, the ((trimethylsilyl)oxy)propene solution was also added. After an additional 5 min, the reaction mixture was treated with pyridine (43 mg, 0.34 mmol). The reaction mixture was added to a mixture of $Et_2O$ (40 mL) and hexane (40 mL), producing a tan precipitate, which was filtered through a medium-porosity frit. The solid was washed with $Et_2O$ and $CH_2Cl_2$ and dried *in vacuo*. Yield of tan solid: 75 mg (0.105 mmol, 98%). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 6.51 (d, $J$ = 3.9 Hz, 1H, H-C(5)), 4.05 (br s, 3H, *trans*-$NH_3$), 3.97 (dd, $J$ = 8.7, 3.9 Hz, 1H, H-C(4)), 3.00 (d, $J$ = 14.1 Hz, 1H, $CH_2$), 3.07 (br s, 12H, *cis*-$NH_3$), 2.61 (d, $J$ = 14.1 Hz, 1H, $CH_2$), 2.58 (dd, $J$ = 14.4, 6.0 Hz, 1H, H-C(3)), 2.19 (s, 3H, $CH_3$), 1.40 (d, $J$ = 14.4 Hz, 1H, H-C(3)), 1.18 (s, 3H, $CH_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 209.0 (q), 95.8 (CH), 92.8 (q), 53.2 ($CH_2$), 42.7 (CH), 41.0 ($CH_2$), 32.3 ($CH_3$), 23.5 ($CH_3$). CV: $E_{1/2}$ = 0.74 V(NHE). The compound was purified by ion-exchange chromatography and isolated as its tetraphenylborate dihydrate salt. Anal. Calcd for $C_{56}H_{67}N_5O_2B_2Os\cdot 2H_2O$: C, 61.71; H, 6.56; N, 6.43. Found: C, 62.14; H, 6.70; N, 6.39.

***[Os(NH$_3$)$_5$(4,5-$\eta^2$-2,3-dihydrofuran)](OTf)$_2$ (15).**[6,8b] $^1$H NMR (acetonitrile-$d_3$): $\delta$ 6.11 (d, $J$ = 3.9 Hz, 1H, H-C(5)), 4.02 (dt, $J$ = 9.6, 4.2 Hz, 1H, H-C(2)), 3.99 (br s, 3H, *trans*-$NH_3$), 3.48 (t, $J$ = 4.2 Hz, 1H, H-C(4)), 3.02 (br s, 12H, *cis*-$NH_3$), 2.97 (q, $J$ = 9.0 Hz, 1H, H-C(2)), 2.75−2.62 (m, 1H, H-C(3)), 1.81 (ddd, $J$ = 13.5, 8.4, 4.2 Hz, 1H, H-C(3)). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 95.4 (C(5)), 69.4 (C(2)), 37.6 (C(4)), 30.1 (C(3)). CV: $E_{1/2}$ = 0.63 V(NHE).

**[Os(NH$_3$)$_5$(2α,3α-$\eta^2$-5,7-diacetyl-7aα-methyl-4,4aα,5,6,7,7aα-hexahydrobenzofuran)](OTf)$_2$ (16a** and **16b).** Methyl vinyl ketone (6.70 g, 95.6 mmol) and **2** (433 mg, 0.661 mmol) were dissolved in acetonitrile (5.49 g), and the solution was cooled to −40 °C. $BF_3\cdot OEt_2$ (92 mg, 0.648 mmol) was added to the reaction solution, which was allowed to stir at −40 °C for 1 h. The reaction was then quenched with pyridine (249 mg, 3.15 mmol). After 10 min, the reaction solution was added to $CH_2Cl_2$ (40 mL), producing a tan precipitate which was filtered, washed with $Et_2O$ and $CH_2Cl_2$, and dried *in vacuo*. Yield of tan solid: 456 mg (0.573 mmol, 87%). The solid appeared by $^1$H NMR to be a mixture of two diastereomers **16a** and **16b** in a 1:0.9 ratio. CV: $E_{1/2}$ = 0.75 V(NHE). Anal. Calcd for $C_{15}H_{33}O_9N_5S_2OsF_6$: C, 22.64; H, 4.18; N, 8.80. Found: C, 22.26; H, 4.15; N, 9.08.

**16a (major isomer).** $^1$H NMR (acetonitrile-$d_3$): $\delta$ 6.55 (d, $J$ = 3.9 Hz, 1H, H-C(2)), 4.05 (br s, 3H, *trans*-$NH_3$), 3.66 (d, $J$ = 3.9 Hz, 1H, H-C(3)), 3.58 (dd, $J$ = 10.5, 7.8 Hz, 1H, CH), 3.08 (br s, 12H, *cis*-

$NH_3$), 2.48 (m, 1H, CH), 2.27 (m, 1H, $CH_2$), 2.27 (s, 3H, $CH_3$), 2.16 (s, 3H, $CH_3$), 1.88 (m, 1H, H-C(4a)), 1.83 (m, 1H, $CH_2$), 1.75−1.71 (m, 2H, $CH_2$), 0.99 (s, 3H, $CH_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 211.8 (C═O), 211.4 (C═O), 94.7 (C(7a)), 94.0 (C(2)), 49.5 (CH), 48.8 (C(4a)), 48.6 (C(3)), 44.8 (CH), 30.7 ($CH_2$), 25.5 ($CH_2$), 33.2 ($CH_3$), 28.4 ($CH_3$), 20.4 ($CH_3$).

**16b (minor isomer).** $^1$H NMR (acetonitrile-$d_3$): $\delta$ 6.50 (d, $J$ = 3.9 Hz, 1H, H-C(2)), 3.99 (br s , 3H, *trans*-$NH_3$), 3.46 (d, $J$ = 3.9 Hz, 1H, H-C(3)), 3.03 (br s, 12H, *cis*-$NH_3$), 2.74 (m, 1H, $CH_2$), 2.69 (m, 1H, CH), 2.41 (dd, $J$ = 9.6, 4.2 Hz, 1H, CH), 2.35 (m, 1H, $CH_2$), 2.26 (s, 3H, $CH_3$), 2.19 (s, 3H, $CH_3$), 2.01 (m, 1H, H-C(4a)), 2.00 (m, 1H, $CH_2$), 1.94 (m, 1H, $CH_2$), 1.25 (s, 3H, $CH_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 211.4 (C═O), 210.8 (C═O), 97.0 (C(2)), 93.3 (C(7a)), 57.8 (CH), 48.6 (C(4a)), 47.7 (C(3)), 45.1 (CH), 30.6 ($CH_2$), 28.3 ($CH_2$), 25.8 ($CH_3$), 24.4 ($CH_3$), 24.1 ($CH_3$).

**5,7-Diacetyl-7aα-methyl-4,4aα,5,6,7,7aα-hexahydrobenzofuran (17a) and (17b).** A solution of a mixture of **16a** and **16b** (98 mg, 0.124 mmol, 1:0.9 ratio) in DMF (800 mg) was prepared and added to a solution of DDQ (30 mg, 0.134 mmol) in DMF (300 mg). After 4 min, the reaction mixture was added to $Et_2O$ (50 mL), and the resulting slurry was filtered. The filtrate was washed with a saturated aqueous $NaNCO_3$ solution (3 × 50 mL). The solvent was evaporated, and a pale yellow crystalline solid was obtained. Yield: 24 mg (0.108 mmol, 87%). The solid appeared by $^1$H NMR to be a mixture of two diastereomers **17a** and **17b** in a 1:0.9 ratio. Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.89; H, 7.32; N, 0.0. Found: C, 70.47; H, 8.60; N, 0.26.

**17a (major isomer).** $^1$H NMR (benzene-$d_6$): $\delta$ 6.01 (dd, $J$ = 2.4, 1.8 Hz, 1H, H-C(2)), 4.54 (t, $J$ = 2.7 Hz, 1H, H-C(3)), 2.81 (dd, $J$ = 12.9, 4.5 Hz, 1H, H-C(7)), 2.20 (s, 3H, $CH_3$), 2.04 (m, 1H, H-C(5)), 1.92 (dddd, $J$ = 15, 5.4, 4.8, 2.7 Hz, 1H, H-C(4a)), 1.88 (m, 1H, $CH_2$), 1.65 (m, 1H, $CH_2$), 1.64 (s, 3H, $CH_3$), 1.35 (m, 1H, $CH_2$), 1.20 (dd, $J$ = 13.5, 11.7 Hz, 1H, $CH_2$), 1.07 (s, 3H, $CH_3$). $^{13}$C NMR (benzene-$d_6$): $\delta$ 208.3 (q), 207.7 (q), 144.4 (CH, C(2)), 103.6 (CH, C(3)), 86.6 (q, C(7a)), 50.2 (CH, C(7)), 49.2 (CH, C(5)), 43.4 (CH, C(4a)), 31.6 ($CH_3$), 28.9 ($CH_2$), 27.7 ($CH_3$), 22.2 ($CH_3$), 22.0 ($CH_2$).

**17b (minor isomer).** $^1$H NMR (benzene-$d_6$): $\delta$ 5.91 (d, $J$ = 2.7 Hz, 1H, H-C(2)), 4.71 (t, $J$ = 2.7 Hz, 1H, H-C(3)), 2.18 (dd, $J$ = 12.6, 3.6 Hz, 1H, H-C(7)), 2.05 (s, 3H, $CH_3$), 1.94 (dddd, $J$ = 8.7, 6.6, 2.4, 1.2 Hz, 1H, H-C(4a)), 1.67 (s, 3H, $CH_3$), 1.67 (m, 1H, $CH_2$), 1.52 (m, 1H, H-C(5)), 1.46 (m, 1H, $CH_2$), 1.42 (overlap, 1H, $CH_2$), 1.20 (s, 3H, $CH_3$), 1.15 (m, 1H, $CH_2$). $^{13}$C NMR (benzene-$d_6$): $\delta$ 207.9 (q), 207.6 (q), 144.3 (CH, C(2)), 106.9 (CH, C(3)), 83.8 (q, C(7a)), 57.4 (CH, C(7)), 46.9 (CH, C(4a)), 46.1 (CH, C(5)), 31.7 ($CH_2$), 28.7 ($CH_3$), 27.4 ($CH_3$), 25.9 ($CH_2$), 25.5 ($CH_3$).

***[Os(NH$_3$)$_5$(*trans*-3,4-$\eta^2$-4-methoxy-3-butenal dimethyl acetal)](OTf)$_2$ (18a) and [Os(NH$_3$)$_5$(*cis*-3,4-$\eta^2$-4-methoxy-3-butenal dimethyl acetal)] (OTf)$_2$ (18b).**[6] **18a (major isomer).** $^1$H NMR (acetonitrile-$d_3$): $\delta$ 5.70 (d, $J$ = 5.7 Hz, 1H, H(C(4)), 4.54 (t, $J$ = 5.4 Hz, 1H, H-C(1)). 4.05 (br s, 3H, *trans*-$NH_3$), 3.55 (s, 3H, $OCH_3$), 3.43 (m, 1H, H-C(3)), 3.34 (s, 3H, $OCH_3$), 3.32 (s, 3H, $OCH_3$), 3.03 (br s, 12H, *cis*-$NH_3$), 1.51 (ddd, $J$ = 16, 5.4, 3.6 Hz, 1H, H-C(2)), 1.22 (ddd, $J$ = 16, 10.5, 5.4 Hz, 1H, H-C(2)). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 107.3 (C(1)), 96.7 (C(4)), 63.1 ($OCH_3$), 53.7 ($OCH_3$), 53.6 ($OCH_3$), 39.3 (C(3)), 34.0 (C(2)).

**18b (minor isomer).** $^1$H NMR (acetonitrile-$d_3$): $\delta$ 5.44 (d, $J$ = 5.4 Hz, 1H, H-C(4)), 4.50 (dd, $J$ = 6.0, 4.2 Hz, 1H, H-C(1)), 4.01 (br s, 3H, *trans*-$NH_3$), 3.56 (s, 3H, $OCH_3$), 3.38 (s, 3H, $OCH_3$), 3.36 (s, 3H, $OCH_3$), 3.14 (m, 1H, H-C(3)), 3.03 (br s, 12H, *cis*-$NH_3$), 2.03 (ddd, $J$ = 14.7, 7.8, 4.2 Hz, 1H, H-C(2)), 1.44 (ddd, $J$ = 14.7, 6.0, 4.5 Hz, 1H, H-(C(2)). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 107.1 (C(1)), 94.7 (C(4)), 61.7 ($OCH_3$), 54.9 ($OCH_3$), 54.5 ($OCH_3$), 36.6 (C(3)), 31.5 (C(2)).

**[Os(NH$_3$)$_5$(*trans*-4,5-$\eta^2$-5-methoxy-4-penten-2-one)](OTf)$_2$ (19a), [Os(NH$_3$)$_5$(*cis*-4,5-$\eta^2$-5-methoxy-4-penten-2one)](OTf)$_2$ (19b), [Os(NH$_3$)$_5$(*trans*-4,5-$\eta^2$-5-methoxy-4-penten-2-one dimethyl acetal)](OTf)$_2$ (20a), and [Os(NH$_3$)$_5$(*cis*-4,5-$\eta^2$-5-methoxy-4-penten-2-one dimethyl acetal)](OTf)$_2$ (20b).** A solution of triflic acid (5 mg, 0.031 mmol) in methanol (128 mg) was added to a solution of **2** (84 mg, 0.127 mmol) in methanol (526 mg). After 14 h, the reaction mixture was treated with DIEA (11 mg, 0.0853 mmol) and then added to $Et_2O$, producing a pale yellow solid, which was filtered, washed with $Et_2O$ and $CH_2Cl_2$, and dried *in vacuo*. Yield of pale yellow solid: 57 mg. The solid appeared by $^1$H NMR to be a mixture of four compounds **19a**, **19b**, **20a**, and **20b** in a 1.0:0.9:0.6:0.25 ratio.

**19a.** $^1$H NMR (acetonitrile-$d_3$): $\delta$ 5.70 (d, $J$ = 5.7 Hz, 1H, H-C(5)), 4.10 (br s, 3H, *trans*-$NH_3$), 3.64 (ddd, $J$ = 9.6, 5.7, 3.6 Hz, 1H, H-C(4)), 3.55 (s, 3H, $OCH_3$), 3.08 (br s, 12H, *cis*-$NH_3$), 2.39 (dd, $J$ = 16.5, 9.6 Hz, 1H, H-C(3)), 2.18 (s, 3H, $CH_3$), 2.14 (dd, $J$ = 16.5, 3.6 Hz, 1H, H-C(3)). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 210.4 (C(2)), 96.0 (C(5)), 63.1 ($OCH_3$), 45.0 (C(4)), 37.8 (C(3)), 30.0 ($CH_3$).

**19b.** $^1$H NMR (acetonitrile-$d_3$): $\delta$ 5.54 (d, $J$ = 5.4 Hz, 1H, H-C(5)), (ddd, $J$ = 8.7, 5.4, 3.9 Hz, 1H, H-C(4)), 4.05 (br s, 3H, *trans*-$NH_3$), 3.48 (s, 3H, $OCH_3$), 3.04 (br s, 12H, *cis*-$NH_3$), 2.96 (dd, $J$ = 18.3, 8.7 Hz, 1H, H-C(3)), 2.42 (dd, $J$ = 18.3, 3.9 Hz, 1H, H-C(3)), 2.18 (s, 3H, $CH_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 211.1 (C(2)), 94.0 (C(5)), 61.7 ($OCH_3$), 42.3 (C(4)), 35.8 (C(3)), 29.8 ($CH_3$).

**20a.** $^1$H NMR (acetonitrile-$d_3$): $\delta$ 5.75 (d, $J$ = 5.7 Hz, 1H, H-C(5)), 4.06 (br s, 3H, *trans*-$NH_3$), 3.58 (s, 3H, $OCH_3$), 3.40 (ddd, $J$ = 13.5, 5.7, 1.2 Hz, 1H, H-C(4)), 3.17 (s, 3H, $OCH_3$), 3.16 (s, 3H, $OCH_3$), 3.05 (br s, 12H, *cis*-$NH_3$), 1.42 (dd, $J$ = 10.8, 1.2 Hz, 1H, H-C(3)), 1.24 (dd, $J$ = 13.5, 10.8 Hz, 1H, H-C(3)). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 102.8 (C(2)), 97.9 (C(5)), 62.9 ($OCH_3$), 48.6 (2$OCH_3$), 39.3 (C(4)), 38.1 (C(3)), 21.7 ($CH_3$).

**20b.** $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 102.8 (C(2)), 95.3 (C(5)), 62 ($OCH_3$), 48.9 (2$OCH_3$), 37.1 (C(4)), 35.3 (C(3)), 21.8 ($CH_3$). Due to the excessive overlap of proton resonances, $^1$H NMR of **20b** could not be assigned.

**[Os(NH$_3$)$_5$(*trans*-4,5-$\eta^2$-5-methoxy-4-penten-2-one)](OTf)$_2$ (19a).** $BF_3$·$OEt_2$ (6 mg, 0.04 mmol) was dissolved in methanol (200 mg) and cooled to −40 °C. The solution of $BF_3$·$OEt_2$ in methanol was added to the cold solution of **2** (74 mg, 0.11 mmol) in methanol (800 mg). After 2 days at −40 °C, the solution was directly added to $Et_2O$ (100 mL), producing a pale yellow solid, which was filtered, washed with $Et_2O$ and $CH_2Cl_2$, and dried *in vacuo*. The yield of pale yellow solid was 61 mg (0.09 mmol, 79%). The solid appeared by $^1$H NMR to be a mixture of the same two isomers **19a** and **19b** in 12:1 ratio. CV: $E_{p,a}$ = 0.78 V(NHE). Anal. Calcd for $C_8H_{25}O_8N_5S_2OsF_6$: C, 13.97; H, 3.66; N, 10.19. Found: C, 13.47; H, 3.34; N, 10.02.

**[Os(NH$_3$)$_5$(*trans*-4,5-$\eta^2$-5-methoxy-4-penten-2-one dimethyl ketal)](OTf)$_2$ (20a).** Triflic acid (5 mg, 0.03 mmol) was dissolved in methanol (343 mg), cooled to −40 °C and added to a cold solution of **2** (100 mg, 0.15 mmol) in methanol (1.18 g). After 2 days, the solution was treated with DIEA (18 mg, 0.136 mmol) at −40 °C. After 20 min, the reaction mixture was directly added to a mixture of $Et_2O$ (100 mL) and $CH_2Cl_2$ (10 mL), producing a tan solid, which was filtered, washed with $Et_2O$ and $CH_2Cl_2$, and dried *in vacuo*. Yield of tan solid: 84 mg (0.11 mmol, 75%). The solid appeared by $^1$H NMR to be only one single diastereoisomer **20a**. CV: $E_{p,a}$ = 0.80 V(NHE). Anal. Calcd for $C_{10}H_{31}O_9N_5S_2OsF_6$: C, 16.37; H, 4.26; N, 9.55. Found: C, 15.85; H, 4.22; N, 9.59.

***[Os(NH$_3$)$_5$(*trans*-4,5-$\eta^2$-3-((methoxyphenyl)methyl)-5-methoxy-4-penten-2-one)](OTf)$_2$ (21).**[8a] $^1$H NMR (acetonitrile-$d_3$): $\delta$ 7.20−7.50 (m, 5H, Ph), 5.78 (d, $J$ = 6.0 Hz, 1H, H-C(5)), 4.61 (d, $J$ = 10.5 Hz, 1H, H-C-Ph), 4.13 (br s, 3H, *trans*-$NH_3$), 3.82 (dd, $J$ = 6.0, 4.2 Hz, 1H, H-C(4)), 3.55 (s, 3H, $OCH_3$), 3.22 (br s, 12H, *cis*-$NH_3$), 3.19 (s, 3H, $OCH_3$), 2.39 (dd, $J$ = 10.5, 4.2 Hz, 1H, H-(C(3)), 1.99 (s, 3H, $CH_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 208.5 (C═O), 139.4 (Ph, q), 129.8 (Ph), 129.6 (Ph), 129.4 (Ph), 95.1 (C(5)), 84.7 (CPh), 64.0 (C(4)), 62.7 ($OCH_3$), 56.6 ($OCH_3$), 40.0 (C(3)), 28.8 ($CH_3$). CV: $E_{p,a}$ = 0.97 V(NHE).

***[Os(NH$_3$)$_5$(4α,5α-$\eta^2$-3α-acetyl-2$\beta$-methyl-2,3-dihydrofuran)](OTf)$_2$ (22).**[8a] $^1$H NMR (acetonitrile-$d_3$): $\delta$ 6.18 (d, $J$ = 4.2 Hz, 1H, H-C(5)), 3.96 (dd, $J$ = 10.5, 4.2 Hz, 1H, H-C(3)), 3.2−3.4 (m, 1H, H-C(2)), 3.98 (br s, 3H, *trans*-$NH_3$), 3.66 (t, $J$ = 4.2 Hz, 1H, H-C(4)), 3.12 (br s, 12H, *cis*-$NH_3$), 2.31 (s, 3H, $COCH_3$), 1.22 (d, $J$ = 5.7 Hz, 3H, $CH_3$-C(2)). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 215.4 (C═O), 96.6 (C(5)), 77.2 (C(2)), 67.1 (C(3)), 37.9 (C(4)), 32.5 ($CH_3$), 22.2 ($CH_3$). CV: $E_{p,a}$ = 0.76 V(NHE).

***[Os(NH$_3$)$_5$(4α,5α-$\eta^2$-3α-acetyl-2$\beta$-phenyl-2,3-dihydrofuran)](OTf)$_2$ (23).**[8a] $^1$H NMR (acetonitrile-$d_3$): $\delta$ 7.30−7.40 (m, 5H, Ph), 6.39 (d, $J$ = 4.2 Hz, 1H, H-C(5)), 4.31 (dd, $J$ = 10.5, 4.2 Hz, 1H, H-C(3)), 4.17 (d, $J$ = 10.5 Hz, 1H, H-C(2)), 4.05 (br s, 3H, *trans*-

$NH_3$), 3.79 (t, $J$ = 4.2 Hz, 1H, H-C(4)), 3.21 (br s, 12H, *cis*-$NH_3$), 2.10 (s, 3H, $COCH_3$). $^{13}C$ NMR (acetonitrile-$d_3$): $\delta$ 214.7 (C═O), 142.5 (Ph, C), 129.4 (Ph, CH), 129.0 (Ph, CH), 127.4 (Ph, CH), 96.7 (C(5)), 82.3 (C(2)), 69.6 (C(3)), 37.4 (C(4)), 32.5 ($CH_3$). CV: $E_{p,a}$ = 0.76 V(NHE).

**[Os(NH$_3$)$_5$(4,5-$\eta^2$-*N*-(2-oxa-4-pentenyl)acetonitrilium)](OTf)$_3$-$d_3$ (24a-$d_3$) and (24b-$d_3$).** A solution of the complex **2** (49 mg, 0.075 mmol) in acetonitrile-$d_3$ (350 mg) and a solution of triflic acid (89 mg 0.594 mmol) in acetonitrile-$d_3$ (150 mg) were prepared separately and cooled −40 °C. The two solutions were mixed together, producing a green solution, which was kept below −40 °C and checked by both $^1H$ and $^{13}C$ NMR. $^1H$ and $^{13}C$ NMR revealed formation of an approximately 1:1 ratio of two diastereoisomers **24a**-$d_3$ and **24b**-$d_3$. Compound **24a**-$d_3$ is slightly the major isomer. The quaternary carbon and methyl-$d_3$ of the nitrile groups incorporated in **24a**-$d_3$ and **24b**-$d_3$ are not assigned.

**24a-$d_3$.** $^1H$ NMR (acetonitrile-$d_3$, −40 °C): $\delta$ 5.61 (d, $J$ = 6.8 Hz, 1H, CH), 4.37 (br s, 3H *trans*-$NH_3$), 4.30 (m, 1H, CH), 3.08 (m, 1H, $CH_2$), 3.19 (br s, 12H, *cis*-$NH_3$), 2.70 (m, 1H, $CH_2$), 2.59 (s, 3H, $CH_3$). $^{13}C$ NMR (acetonitrile-$d_3$, −40 °C): $\delta$ 222.0 (C═O), 49.5 (CH), 45.2 ($CH_2$), 38.3 (CH), 29.7 ($CH_3$).

**24b-$d_3$.** $^1H$ NMR (acetonitrile-$d_3$, −40 °C): $\delta$ 5.59 (d, $J$ = 6.8 Hz, 1H, CH), 4.82 (m, 1H, CH), 4.43 (br s, 3H *trans*-$NH_3$), 3.08 (m, 1H, $CH_2$), 3.25 (br s, 12H, *cis*-$NH_3$), 2.53 (m, 1H, $CH_2$), 2.63 (s, 3H, $CH_3$). $^{13}C$ NMR (acetonitrile-$d_3$, −40 °C): $\delta$ 224.9 (C═O), 49.5 (CH), 46.0 ($CH_2$), 39.4 (CH), 29.6 ($CH_3$).

**[Os(NH$_3$)$_5$(methyl 4,5-$\eta^2$-*N*-(2-oxo-4-pentenyl)acetimidate)(HOTf)](OTf)$_2$ (25a) and (25b).** The complex **2** (54 mg, 0.0824 mmol) was dissolved in a mixture of methanol (30 mg, 0.930 mmol) and acetonitrile (520 mg) and cooled to −40 °C. Triflic acid (122.4 mg, 0.813 mmol) was dissolved in acetonitrile (237 mg) and cooled to −40 °C. The cold triflic acid solution was added to the solution of **2**, producing a dark brown solution. After the reaction mixture was stayed at −40 °C for 24 h, an excess of pyridine (134 mg, 1.69 mmol) was added. After 5 min, the solution was added to a stirring mixture of 1:1 $Et_2O/CH_2Cl_2$ solution. The resulting slurry was filtered, and the solid was washed with $Et_2O$ and $CH_2Cl_2$ and dried *in vacuo*. Yield of a light orange yellow solid: 50 mg (0.057 mmol, 69%). $^1H$ NMR revealed an approximately 1:1 ratio of two diastereomers. Characterization data follows, reported for both diastereomers together. $^1H$ NMR (DMF-$d_7$): $\delta$ 6.03, 5.91 (d, $J$ = 7.3 Hz, 1H, CH), 4.91, 4.89 (br s, 3H, *trans*-$NH_3$), 4.16, 4.12 (s, 3H, $OCH_3$), 3.81, 3.77 (br s, 12H, *cis*-$NH_3$), 4.39, 3.95 (m, 1H, CH), 2.99 (m, 2H, $CH_2$), 2.75 (m, overlap with $CH_3$, 1H, $CH_2$), 2.37 (m, overlap with $CH_3$, 1H, $CH_2$), 2.73, 2.56 (s, 3H, $CH_3$), 2.41, 2.35 (s, 3H, $CH_3$). $^{13}C$ NMR (DMF-$d_7$): $\delta$ 209.1, 208.6 (C═O), 176.6, 175.2 (C═N), 60.3, 60.0 ($OCH_3$), 58.8, 56.8 (CH), 45.6, 43.8 ($CH_2$), 38.3, 36.6 (CH), 29.6, 29.3 ($CH_3$), 17.9, 17.8 ($CH_3$). The crude product was dissolved in acetone and precipitated by addition to $CH_2Cl_2$. The resulting slurry was filtered, and the solid was washed and dried *in vacuo*. Purification yield: 93%. Anal. Calcd for $C_{11}H_{29}O_{11}N_6S_3OsF_9$: C, 14.41; H, 3.63; N, 10.05. Found: C, 15.04; H, 3.33; N, 9.56.

**{[Os(NH$_3$)$_5$]$_2$(4,5-$\eta^2$-:4′,5′-$\eta^2$-$\mu$-3-(2′-oxo-4′-pentenyl)-2-methylfuran)}(OTf)$_4$ (26).** The complex **2** (40 mg, 0.0602 mmol) was dissolved in acetonitrile (0.81 g) and propionitrile (0.30 g) and cooled to −40 °C, to which triflic acid (3 mg, 0.023 mmol) was added. After 2 days below −40 °C, pyridine (38 mg, 0.480 mmol) was added into the reaction solution. After 15 min, the solution was poured into $CH_2Cl_2$ (70 mL), producing a gray precipitate, which was filtered, washed with $CH_2Cl_2$ and $Et_2O$, and dried *in vacuo*. Yield of the gray solid: 38 mg (0.029 mmol, 96%). $^1H$ NMR ($D_2O$): $\delta$ 6.82 (d, $J$ = 3.0 Hz, 1H, H-C(5)), 4.41 (br s, 3H, *trans*-$NH_3$), 4.37 (br s, 3H, *trans*-$NH_3$), 4.01 (d, $J$ = 9.3 Hz, 1H, H-C(5′), 3.92 (d, $J$ = 3.0 Hz, 1H, H-C(4)), 3.76 (t, $J$ = 9.3 Hz, 1H, H-C(4′), 3.31 (br s, 12H, *cis*-$NH_3$), 3.20 (br s, 12H, *cis*-$NH_3$), 2.93 (d, $J$ = 18.6 Hz, 1H, H-C(3′), 2.26 (dd, $J$ = 18.6, 9.3 Hz, 1H, H-C(3′), 2.11 (s, 3H, $CH_3$), 1.94 (s, 3H, $CH_3$). $^{13}C$ NMR ($D_2O$): $\delta$ 217.5 (C═O), 147.4 (C(2)), 123.6 (C(3)), 95.4 (C(5)), 48.5 (C(5′), 47.8 (C(3′), 46.1 (C(4)), 42.3 (C(4′), 29.6 ($CH_3$), 11.6 ($CH_3$). Anal. Calcd for $C_{14}H_{42}N_{10}O_{14}S_4OsF_{12}$: C, 12.82; H, 3.23; N, 10.68. Found: C, 12.97; H, 3.53; H, 10.70.

***[Os(NH$_3$)$_5$(≡CCH$_2$CH$_2$CHO)](OTf)$_3$ (27).**[6] $^1H$ NMR (acetonitrile-$d_3$): $\delta$ 9.74 (s, 1H, CHO), 4.64 (br s, 12H, *cis*-$NH_3$), 3.19 (br s, 3H, *trans*-$NH_3$), 3.19 (t, $J$ = 6.3 Hz, 3H, $CH_2$), 2.51 (t, $J$ = 6.3 Hz, 3H, $CH_2$). $^{13}C$ NMR (acetonitrile-$d_3$): $\delta$ 296.7 (Os≡C), 202.5 (CO), 47.8 ($CH_2$), 36.9 ($CH_2$). CV ($CH_3CN$, TBAH, 100 mV/s): $E_{p,c}$ = −0.82 V(NHE).

**[Os(NH$_3$)$_5$(≡CCH$_2$CH$_2$COCH$_3$)](OTf)$_3$ (28).** Triflic acid (538 mg, 3.58 mmol) was added to a solution of **2** (223 mg, 0.340 mmol) in methanol (3.1 g). After 40 min, the reaction mixture was added to $CH_2Cl_2$ (150 mL), giving a tan precipitate which was filtered, washed with $CH_2Cl_2$ and $Et_2O$, and dried *in vacuo*. Yield of brown powder: 225 mg (0.279 mmol, 82%). $^1H$ NMR (acetonitrile-$d_3$): $\delta$ 4.62 (br s, 12H, *cis*-$NH_3$), 3.16 (br s, 3H, *trans*-$NH_3$), 3.14 (t, $J$ = 6.0 Hz, 3H, $CH_2$), 2.45 (t, $J$ = 6.0 Hz, 3H, $CH_2$), 2.21 (s, 3H, $CH_3$). $^{13}C$ NMR (acetonitrile-$d_3$): $\delta$ 297.3 (Os≡C), 209.4 (C═O), 49.2 ($CH_2$), 37.2 ($CH_2$), 29.4 ($CH_3$). CV ($CH_3CN$, TBAH, 100 mV/s): $E_{p,c}$ = −0.87 V(NHE). Anal. Calcd for $C_7H_{20}O_{10}N_5S_3OsF_9$: C, 11.93; H, 2.75; N, 8.69. Found: C, 12.06; H, 2.67; N, 9.12.

**[Os(NH$_3$)$_5$(3-methoxy-2-oxacyclopentylidene)](OTf)$_2$ (29).** The carbyne complex **27** (51.6 mg, 0.0652 mmol) was dissolved in a solution of DIEA (8.9 mg, 0.0688 mmol) in methanol (382 mg). After 20 min, the reaction solution was added to $CH_2Cl_2$ (40 mL) producing a peach solid, which was filtered, washed with $CH_2Cl_2$, and dried *in vacuo*. Yield of peach solid: 30.9 mg (0.0458 mmol, 70%). $^1H$ NMR (acetonitrile-$d_3$): $\delta$ 5.59 (dd, $J$ = 5.7, 4.2 Hz, 1H, H-C(3)), 3.48 (s, 3H, $OCH_3$), 3.28 (br s, 15H, *trans*- and *cis*-$NH_3$). 2.11 (m, 1H, H-C(4)), 1.90 (m, 1H, H-C(4)), 1.63 (ddd, $J$ = 18.3, 9.6, 4.2 Hz, 1H, H-C(5)), 1.15 (dt, $J$ = 18.3, 8.7 Hz, 1H, H-C(5)). $^{13}C$ NMR (acetonitrile-$d_3$): $\delta$ 254.9 (Os═C(1)), 112.6 (C(3)), 56.4 ($OCH_3$), 51.3 (C(5)), 30.7 (C(4)). CV: $E_{1/2}$ = 0.54 V(NHE). Anal. Calcd for $C_7H_{23}O_8N_5S_2OsF_6{\cdot}CH_3OH$: C, 13.62; H, 3.86; N, 9.92. Found: C, 14.35; H, 3.37; N, 10.38.

**[Os(NH$_3$)$_5$(3-methoxy-3-methyl-2-oxacyclopentylidene)](OTf)$_2$ (30).** The carbyne complex **28** (59.0 mg, 0.0732 mmol) was dissolved in a solution of DIEA (14.4 mg, 0.111 mmol) in methanol (396 mg). After 14 min, the reaction solution was added to a mixture of $CH_2Cl_2$ (25 mL) and $Et_2O$ (25 mL) producing a peach-yellow solid, which was filtered, washed wiht $CH_2Cl_2$ and $Et_2O$, and dried *in vacuo*. Yield of peach-yellow solid: 42.8 mg, (0.0622 mmol, 85%). $^1H$ NMR (acetonitrile-$d_3$): $\delta$ 3.29 (s, 3H, $OCH_3$), 3.25 (br s, 15H, *trans*- and *cis*-$NH_3$), 2.16 (ddd, $J$ = 15.9, 9.0, 3.9 Hz, 1H, H-C(4)), 1.92 (m, overlap with solvent peak, 1H, H-C(4)), 1.73 (ddd, $J$ = 18.0, 9.0, 3.9 Hz, 1H, H-C(5)), 1.58 (s, 3 H, $CH_3$), 1.27 (ddd, $J$ = 18.0, 9.0, 8.1 Hz, 1H, H-C(5)). $^{13}C$ NMR (acetonitrile-$d_3$): $\delta$ 254.9 (OS═C(1)), 119.0 (C(3)), 53.0 ($OCH_3$), 50.5 (C(5)), 34.8 (C(4)), 23.5 ($CH_3$). CV: $E_{1/2}$ = 0.57 V(NHE). Anal. Calcd for $C_8H_{25}O_8N_5S_2OsF_6{\cdot}CH_3OH$: C, 15.02; N, 4.06; N, 9.73. Found: C, 15.56; H, 3.53; N, 9.99.

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