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Novel Cyclization Reactions for η^2-Furan Complexes

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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 2-alkylated furans. Electrophilic addition to C(3) results in an unstable reaction intermediate, a 4,5-η^2-3*H*-furanium species, that leads to several novel cyclization reactions with tethered nucleophiles to form new heterocycles. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

For the past decade, our research group has been interested in the ability of π-basic transition metals to dearomatize aromatic molecules.[1] More specifically, we have utilized transition-metal fragments that have the ability to form stable complexes with aromatic molecules in which the aromatic ring is bound through only two carbons. As a result, the uncoordinated portion of the aromatic system becomes susceptible to chemical transformations not accessible for the aromatic precursor. In this regard, the term *dearomatize* takes on a dual meaning. The transition metal (or dearomatization agent) diminishes the aromaticity of arenes and aromatic heterocycles merely upon forming complexes with these compounds. In a broader sense of this term, however, when these complexes are incorporated into a synthetic strategy, dearomatized organic products can often be obtained from aromatic precursors.[2]

The present study involves the activation of furan, and in particular, the use of this heterocycle in the formation of new heterocyclic ring systems. 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.[3] In past studies, we have observed that coordination of furan by pentaammineosmium(II) at C(4) and C(5) blocks α-electrophilic addition and, as a result of donation of π electron density from the metal, activates the heterocycle toward electrophilic addition at the uncoordinated β-carbon.[4] Electrophilic addition at C(3) of a furan ligand results in a 4,5-η^2-3*H*-furanium intermediate that can, in turn, undergo deprotonation at C(3), nucleophilic addition at C(2), or nucleophilic substitution at C(5). Our strategy for the present study was to generate new heterocyclic cores by combing the elements of (i) electrophilic addition at C(3) and (ii) nucleophilic addition at C(5) by a tethered heteroatom. Fig. 1 illustrates this basic approach.

Results and Discussion

Furan complexes of pentaammineosmium(II) ($[Os(NH_3)_5(\eta^2\text{-L})](OTf)_2$ where L=furan (**1**), 2-methylfuran (**2**), 2-(hydroxymethyl)furan (**3**), 3-(2-furyl)-propan-1-ol (**4**) were prepared in high yield by the reduction of $Os(NH_3)_5(OTf)_3$[5] with activated magnesium in the presence of the furan

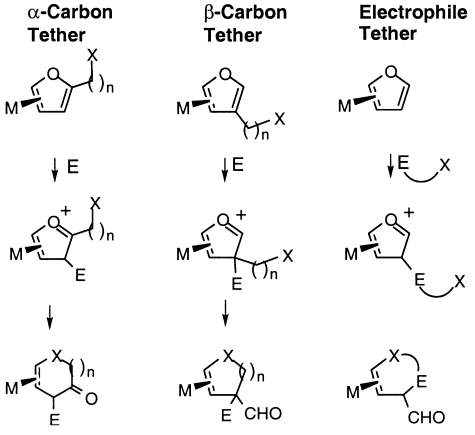

Figure 1.

Keywords: osmium and compounds; furans; cyclization reactions; pyrans.
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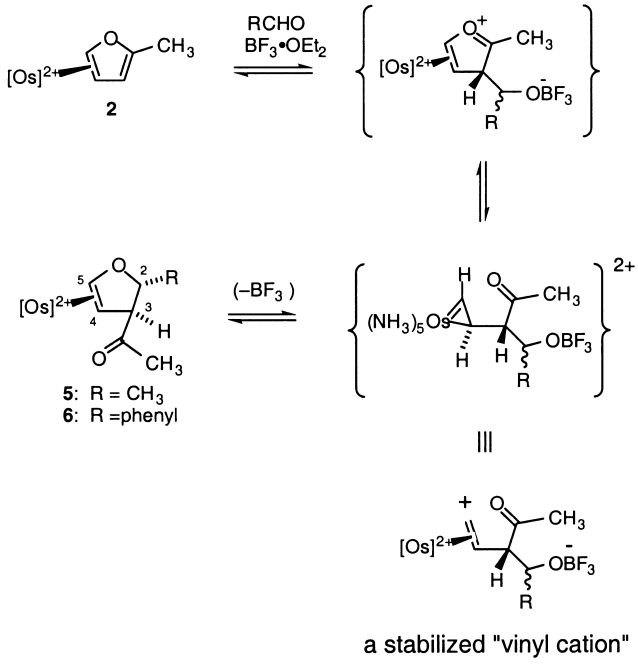


Figure 2.

ligand. An early example of a dihapto-coordinated furan complex undergoing a cyclization reaction involved its reaction with aldehydes.[6] In the presence of a Lewis acid, aldehydes react with the 2-methylfuran complex, $[Os(NH_3)_5(2\text{-methylfuran})]^{2+}$ (**2**), to form 3-acetylated-2,3-dihydrofuran complexes. Interestingly, the aldehyde is incorporated in the heterocyclic ring of the product (**5**, **6**; Fig. 2). In these reactions, electrophilic addition at C(3) results in cleavage of the C(5)–O bond, and the resulting 'vinyl cation' (formally a metallacyclopropene)[7] is intercepted by the alkoxide derived from the aldol process. Note that this reaction is an example of the 'Electrophile Tether' strategy outlined in Fig. 1. As a result of the rotation on the C(3)–C(4) bond that is required to form the new heterocycle, the acetal group in the product is oriented *syn* to the metal. In contrast, the stereochemistry at the α-carbon is derived from the initial aldol reaction, a reversible process. Thus, these complexes (**5**, **6**) adapt a stereochemistry that orients the α substituent away from the metal (Fig. 2).

Cyclization reactions of furans with α-carbon tethered nucleophiles

In the above examples the nucleophilic heteroatom used to form the new heterocycle was derived from the aldehyde electrophile. But it is also possible to carry out this type of ring closure with an alcohol tethered to the furan ring. For example, treatment of **3** with a catalytic amount of HOTf or $BF_3{\cdot}OEt_2$ at low temperature yields the dihapto-coordinate pyranone complex, **7**, as the major product (Fig. 3). The ^{13}C NMR and DEPT data indicate that the complex **7** has two methine groups, two methylene groups, and a quaternary carbon at 214.4 ppm. Judging from ^1H and ^{13}C NMR chemical shifts of the two methine groups, their resonances are assigned to the coordinated olefin. ^1H-^1H coupling data show that the two most upfield protons belong to one

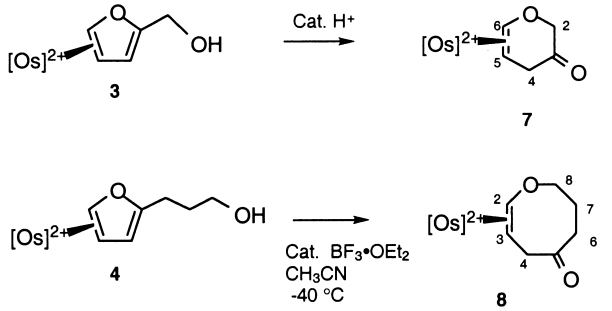


Figure 3.

methylene group and couple with the coordinated β-carbon at 3.4 ppm. The protons on another methylene group only couple with each other (17.3 Hz). A complete analysis confirms the assignment of **7** as being the 5,6-η^2-4*H*-pyran-3-one complex. Note that the principal driving force of this reaction is the conversion within the uncoordinated portion of the organic ligand of a vinyl ether and alcohol to a ketone and ether. In a manner analogous to the formation of **7** from **3**, the furan complex **4** isomerizes into a single 7,8-η^2-3,4-dihydro-2*H*,6*H*-oxocin-5-one complex, **8**, whose ^{13}C NMR spectrum features a carbonyl signal at 218 ppm (Fig. 3).

Interestingly, if the furan complex **3** is treated with a stoichiometric amount of HOTf at ambient temperature, followed by quenching with base (DIEA) in CH_2Cl_2, an entirely different product results (**9**). The ^1H and ^{13}C NMR spectra of **9** feature the characteristic chemical shifts of both an aldehyde group (9.74/206.4 ppm) and a ketone group (216.2 ppm). In addition, the ^{13}C NMR spectrum also shows the resonances of two methine groups (DEPT) at 59.0 and 54.6 ppm. The chemical shifts of the *cis*/*trans* ammines present in ^1H NMR spectrum (acetonitrile-d_3) are at 4.73 and 3.49 ppm, respectively, indicating complexation to an electron-deficient olefin.[8] Taken together, these observations indicate the formation of the pentaammineosmium(II) complex of 4-oxo-2-pentenal. When an NMR sample of either **3** or **9** was treated with concentrated HOTf, ^1H NMR spectra indicate that both reactions produce a common species **10**, which can be isolated by precipitation in a mixture of CH_2Cl_2 and Et_2O. However, **10** slowly undergoes decomposition in acetonitrile. The full NMR spectroscopic characterization of **9** was accomplished in a mixture of acetonitrile-d_3 and HOTf. The ^1H NMR spectrum of **10** shows a set of *cis*- and *trans*-ammine resonances at 3.80 and 5.00 ppm respectively, which is the characteristic feature for an η^3-allyl species of pentaammineosmium(II).[9] ^{13}C and DEPT data show that the most downfield methine is at 124.0 ppm, which is much closer to a value expected for an electron deficient acetal carbon resonance than it is to the aldehyde carbon resonance of **9**. Based on these observations, the 2H-furanium complex **10** is proposed along with a plausible mechanism for the isomerization from **3** to **7** to **9** in Fig. 4.

Cyclizations of furans with electrophile-tethered nucleophiles: incorporation of acetonitrile

Previously, we reported the formation of vinylacetimidate and vinylacetamide complexes from vinyl ether precursors

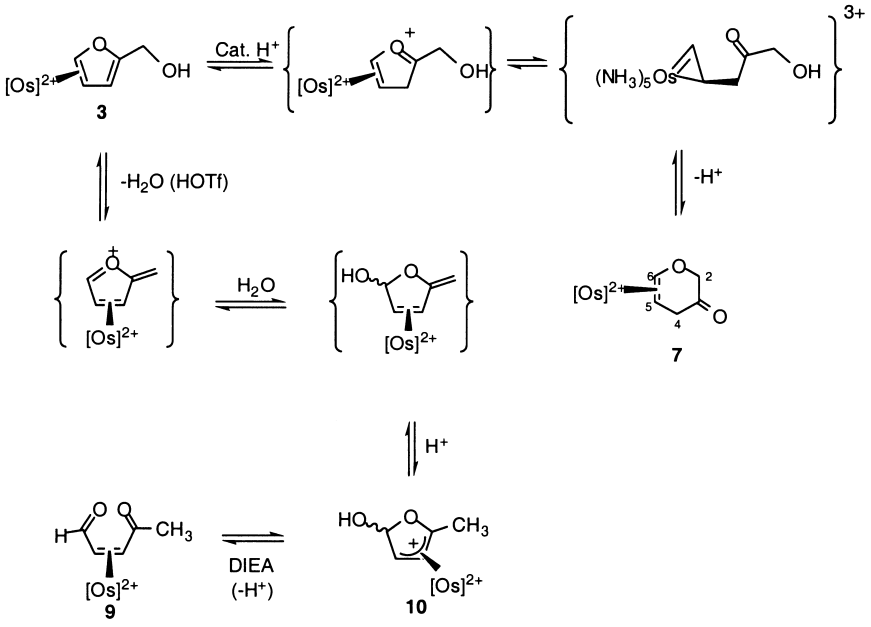


Figure 4.

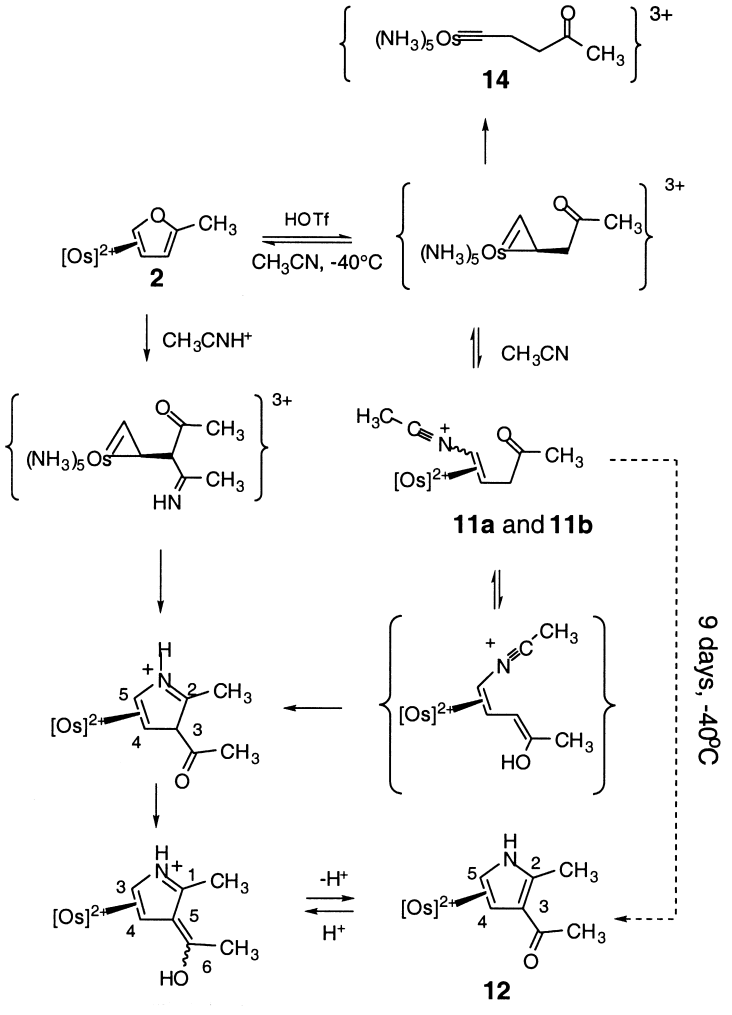


Figure 5.

and acetonitrile.[7] We have found that similar reactions occur with furan derivatives and acetonitrile. For example, when an acetonitrile solution of the 2-methylfuran complex **2** is treated with triflic acid (HOTf, 3–8 equiv.) at −40°C, the η^2-*N*-vinylacetonitrilium complexes **11a,b** are generated immediately. If the solution of **11a,b** is allowed to stand at −40°C for 9 days, treatment with pyridine followed by addition of CH_2Cl_2 leads to the isolation of a new osmium complex **12**. The ^{1}H NMR spectrum of **12** features a broad singlet at 7.87 ppm for the proton on the nitrogen and two downfield ring protons which couple with each other (J=3.9 Hz). The ^{13}C NMR, DEPT and HETCOR data indicate that the complex **12** has two methines, two methyl groups and three quaternary carbons, including a carbonyl at 195 ppm. The data for **12** indicate the formation of a 4,5-η^2-2,3-disubstituted pyrrole complex. If the reaction is repeated without quenching with pyridine, the isolated product is a mixture of two diastereomeric 3,4-η^2-2-azafulvenium complexes **13a,b**, along with a small amount of a carbyne complex, **14**, previously reported.[4] The ^{1}H and ^{13}C NMR spectroscopic data of complexes **12** and **13a,b** are consistent with those for analogous pyrrole and azafulvenium complexes previously synthesized.[10] Treatment of **13a,b** with pyridine (CH_3CN, 22°C) results in the formation of **12** as the sole product. The production of **12** from acetonitrile is analogous to that observed for the reaction of **2** with aldehydes, the product being formed via an electrophilic addition to the uncoordinated β-carbon and a nucleophilic addition of the heteroatom. Note, however, that mechanistically the formation of **12** may differ from that of **5** and **6**. In the formation of the 3-acylated pyrrole complex **12** (Fig. 5), it is possible that the initial event is protonation at the β-carbon followed by nitrile addition to form **11**. Subsequent addition of the enol of **11** to the nitrilium carbon would generate a 3H-pyrrolium precursor to **13a** and **13b**. However, there is likely to be sufficient strain in the transition state for the addition of the enol to the nitrilium ion such that this route seems unlikely. A more plausible scenario would be that **11** reverts to **2** which then reacts at the β-carbon with the acetonitrilium ion. Subsequent ring-opening and C–N ring-closure would result in the same 3H-pyrrolium complex as hypothesized above.

We have reported previously that treatment of **2** with acidic methanol followed by base prior to precipitation generates a mixture of two sets of diastereomeric vinyl ether complexes, (**15a,b** and **16a,b**), which together function as surrogates of **2** under many reaction conditions.[4] In a variation of the synthesis of 2-azafulvenium complexes **13a,b**, a mixture of **15a,b** and **16a,b**, was dissolved in acetonitrile and treated with TBSOTf and allowed to stand at −40°C for 5 days. Treatment with pyridine and precipitation with CH_2Cl_2 yielded products **17a,b** as a mixture of two diastereomers of the 3,4-η^2-1,6-dimethyl-6-methoxy-2-azafulvenium complex (Fig. 6). The ^{1}H and ^{13}C NMR spectra of **17a,b** resemble those of **13a,b** except that the hydroxy signals of **13a,b** are replaced by the methoxy signals of **17a,b**.

In an interesting variation of the pyrrole formation above, when the 3-(2-furyl)-propan-1-ol complex **4** was combined with acetonitrile and $BF_3{\cdot}OEt_2$ (−40°C), the alcohol side chain reacts with the azafulvenium intermediate (see **13** in Fig. 5) to form the biheterocyclic species **18** as a single diastereomer (Fig. 6).

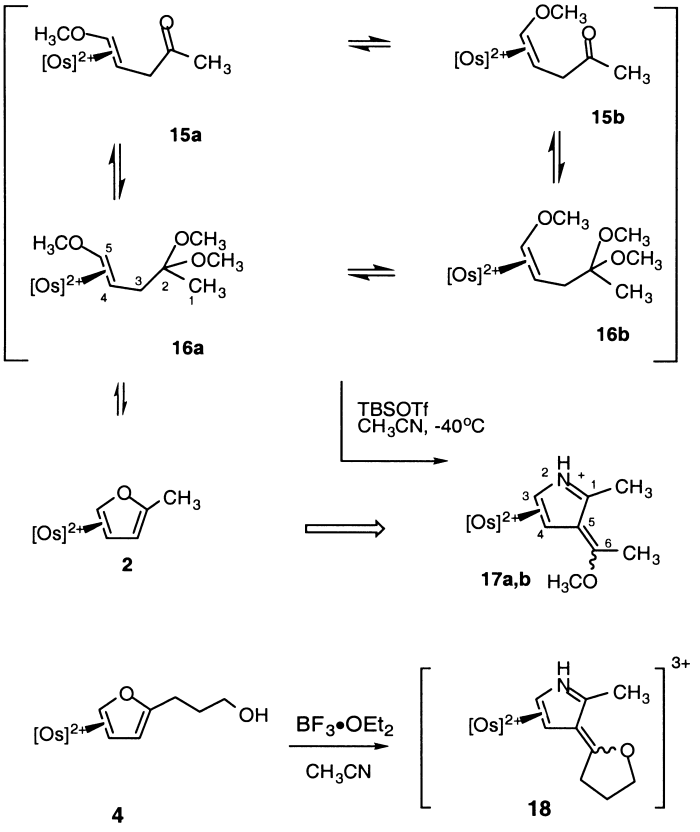


Figure 6.

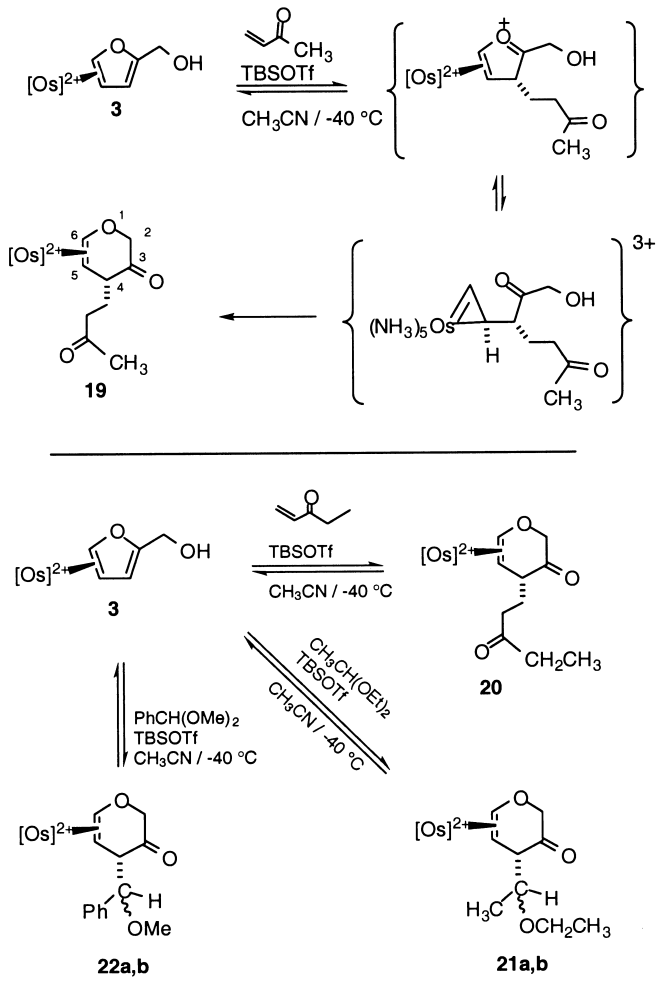
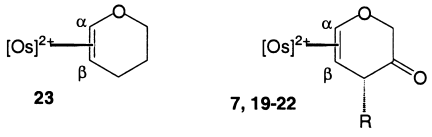


Figure 7.

The cyclizations of furyl alcohols outlined in the above sections are all initiated with protonation of the uncoordinated β-carbon of the furan ring. Similar reaction patterns emerge when these furan complexes are combined with carbon electrophiles. Using conditions similar to those that form the 5,6-η^2-4*H*-pyran-3-one complex **7** (Fig. 3), we were able to prepare 4-alkylated derivatives of **7** from the reactions of the 2-furanmethanol complex **3** with carbon electrophiles. For example, when **3** is combined with methyl vinyl ketone and TBSOTf in acetonitrile, and the solution is

Table 1. NMR data for selected 5,6-η^2-2*H*-pyran-3(4*H*)-one complexes



Compound	–R	^{1}H δ^a (ppm)			$J\alpha,\beta$ (Hz)	^{13}C δ^a (ppm)	
		Hα	Hβ	*trans*/*cis*-NH_3		Cα	Cβ
23	–	6.06	3.35	4.03:3.02	6.0	89.9	40.0
7[b,c]	–H	6.17	–	4.61:3.49	5.2	89.2	35.6
19	$-CH_2CH_2C(=O)CH_3$	6.12	3.12	4.22:3.25	4.4	89.2	40.1
20	$-CH_2CH_2C(=O)CH_2CH_3$	6.12	3.18	4.23:3.25	4.5	89.2	40.1
21a	$-CH(OC_2H_5)CH_3$	6.00	3.41	4.12:3.23	4.8	89.1	37.6
21b[c]	$-CH(OC_2H_5)CH_3$	6.13	–	4.13:3.17	5.2	90.2	34.5
22a	$-CH(OCH_3)C_6H_5$	6.08	3.52	4.21:3.25	5.2	89.3	37.7
22b	$-CH(OCH_3)C_6H_5$	6.03	3.51	4.21:3.21	5.2	89.9	34.7

[a] Recorded in acetonitrile-d_3 as a triflate salt at 22°C unless otherwise noted.
[b] Recorded in acetonitrile-d_3/DMF-d_7.
[c] Hβ overlaps with *cis*-ammines.

allowed to stand 17 h at −40°C, quenching with pyridine and adding a mixture of Et_2O and CH_2Cl_2 precipitates **19** as a single product. A complete analysis of ^1H and ^{13}C NMR data indicates that **19** is a 4-(3′-oxobutyl)-4*H*-pyran-3-one complex, generated from the Michael addition of MVK at C(3) of **3** followed by the intramolecular nucleophilic addition of the exocyclic hydroxy group at C(5) (Fig. 7). The isolation of only one diastereomer indicates that the Michael addition at C(3) occurs stereoselectively from the *exo*-face of the ring as has been observed for other electrophilic additions of furan complexes.[4] Similarly, the 2-furanmethanol complex **3** reacts with ethyl vinyl ketone, acetaldehyde diethyl acetal and benzaldehyde dimethyl acetal to produce the corresponding dihydropyran-3-one complexes **20**, **21a,b** and **22a,b** respectively. The reaction of **3** with an acetal produces two diastereomers as a result of the additional stereogenic center created away from the ring. The ^1H and ^{13}C NMR data are summarized in Table 1 along with data for the parent 3,4-dihydro-2*H*-pyran, **23**.

This novel rearrangement reaction of the 2-furanmethanol complex **3** is limited by the aforementioned competing isomerization of **3** to the 4*H*-pyran-3-one complex **7** and the reactions caused by the elimination of the hydroxy group on the side chain of **3**. For example, when **3** is combined with diethoxymethane in the presence of TBSOTf in acetonitrile (−40°C, 24 h), a complicated mixture results which contains the dihydropyran-5-one complex **7** and the 4-oxo-2-pentenal complex **9** as the two major products. Similar results were also found in the reactions of **3** with 3-penten-2-one, *N*-phenyl maleimide, and benzaldehyde. In some cases, what appears to be a binuclear osmium species is also formed as one of the major products. The ^1H NMR spectrum of this material shows two sets of

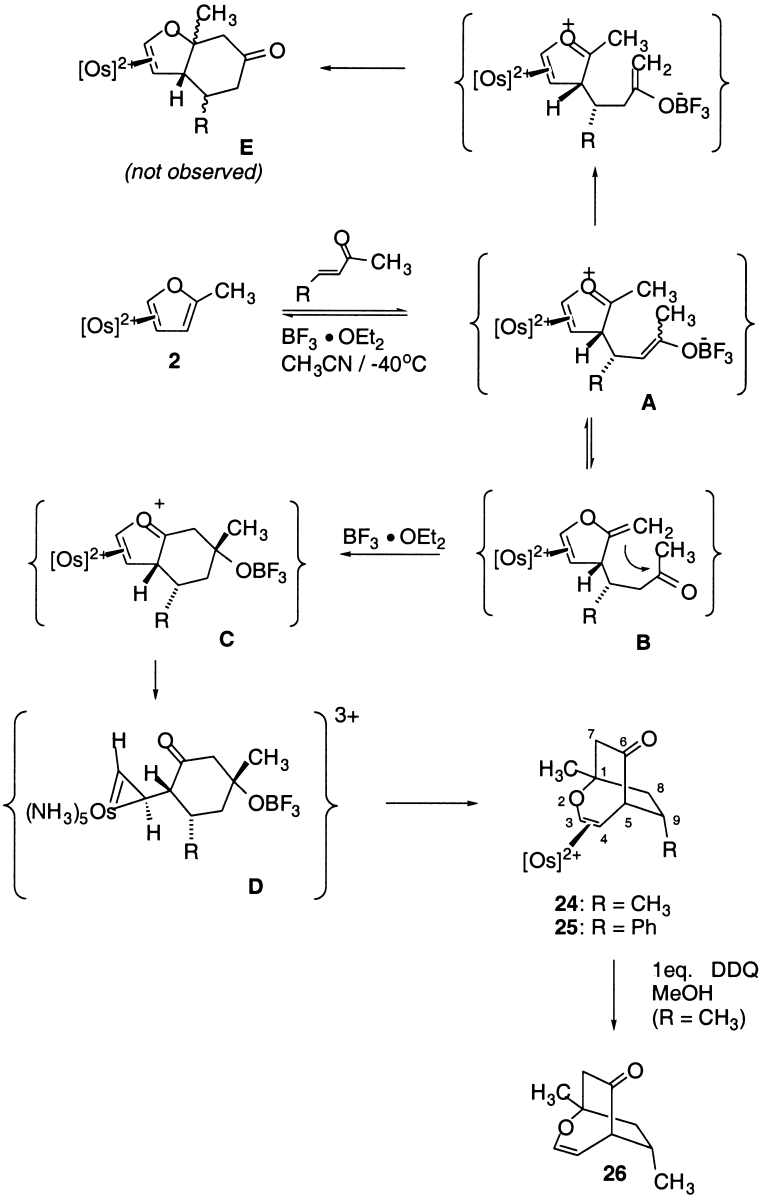


Figure 8.

trans/*cis* ammine signals at equal intensity, and one set is consistant with an η^3-allyl complex.

Formation of a [3.2.2]-oxabicyclic ring system from 2-methylfuran

In an earlier report, we described the reaction of the 2-methylfuran complex, **2**, with 2 equiv. of methyl vinyl ketone, which gave the benzofuran skeleton via an initial electrophilic attack on C(3) of the coordinated furan ring.[4] Surprisingly, the reaction of **2** with 3-penten-2-one under otherwise identical reaction conditions produces an entirely different type of osmium complex **24**. Combustion analysis indicates that **24** is a 1:1 adduct of **2** with 3-penten-2-one. The ^{13}C NMR and DEPT data for **24** indicate the presence of two methyl groups, two methylenes, four methines, and two quaternary carbons, including a carbonyl at 222.2 ppm as expected for the tetrahydrobenzofuranone complex **E** in Fig. 8. However, ^{1}H and ^{13}C NMR data for the corresponding vinyl group of **24** differ from those for a typical η^2-dihydrofuran species. This disparity called into question our initial assignment of **24**, and ultimately, HMBC experiments were carried out that confirmed the structure of **24** as a pentaammineosmium(II) complex of 1,9-dimethyl-2-oxabicyclo[3.2.2]non-3-en-6-one.[11] A plausible mechanism is outlined in Fig. 8. Initially, BF_3 promotes a Michael addition at the unbound β-carbon of the furan. The resulting boron-enolate (**A**) then deprotonates the C(2) methyl group to form the vinyl ether intermediate (**B**) that subsequently undergoes an intramolecular aldol reaction generating a 3*H*-furanium ion (**C**). This species ring-opens to the metallacyclopropene intermediate (**D**) that subsequently undergoes an intramolecular addition with the BF_3-alkoxide to form **24** (Fig. 8) in 92% yield. The results from 1D NOE and NOESY experiments provide additional support for the stereochemistry of **24** shown in Fig. 8. In particular, irradiation of the *cis*-NH_3 resonance causes NOE enhancements of H(3), H(4), H(5), and $H(7)_{endo}$ (2.22 ppm). The molecular model of the structure for **24** shows that the $H(7)_{endo}$ is in the vicinity of the metal moiety. Irradiation of the methyl resonance (doublet at 1.25 ppm) causes NOE enhancements of H(3) (3%) and H(4) (3%), an observation that indicates the methyl group on C(9) is on the *exo*-face of the ring with respect to the metal moiety. A similar reaction of **2** with *trans*-phenyl-3-buten-2-one generates compound **25**, the phenyl analog of **24**, which is fully characterized by ^{1}H and ^{13}C NMR spectroscopy. The bicyclic oxepin **24** is integral to the core of the Seiricardines, compounds which are moderate fungal growth inhibitors.[12]

Decomplexation of vinyl ethers

Vinyl ethers such as those prepared in this work can be decomplexed via a procedure in which the metal is oxidized to osmium(III). Oxidants that have given encouraging results include silver triflate, CAN, and DDQ. However, yields vary considerably (10–80%) depending on the reaction conditions and nature of the organic product.[4] The bicyclic-[3.2.2]-nonenone ligand **26** can be liberated from the complex **24** by use of 1 equiv. DDQ, albeit in low yield. When **24** was treated with DDQ in CH_3OH, followed by moderate heating (50°C) for 4 h, compound **26** was isolated along with two other uncharacterized organic compounds. After chromatography, **26** was isolated separately in 12% yield.

Summary

Complexation of furan by the π base pentaammineosmium(II) significantly alters the reactivity of this heterocycle. Several novel cyclization reactions have been demonstrated for furan through the combination of electrophilic addition to the uncoordinated β-carbon followed by nucleophilic addition at the bound α-carbon.

Experimental

General Procedures

Infrared spectra were recorded on a Mattson Cygnus 100 FTIR spectrometer. Routine ^{1}H and ^{13}C NMR spectra were recorded on a General Electric QE-300 or GN-300 spectrometer at 20–23°C unless otherwise noted (^{1}H and ^{13}C NMR spectra were obtained at 300 and 75 MHz, respectively). Carbon multiplicities, if provided, are supported by DEPT and/or HETCOR data. Chemical shifts are reported in ppm and are referenced to residual proton-containing solvent (δ acetone-d_5=2.04; δ acetonitrile-d_2=1.93; δ methanol-d_3=3.30). Electrochemical experiments were performed under nitrogen using a PAR model 362 potentiostat driven by a PAR model 175 universal progammer. Cyclic voltammograms were recorded (Kipp & Zonen BD90 XY recorder) in a standard three-electrode cell from +1.8 to −1.8 V with a glassy carbon electrode. All potentials are reported versus NHE and, unless otherwise noted, were determined in acetonitrile (~0.5 M TBAH) using ferrocene ($E_{1/2}$=+0.55 V) or colbaltocenium hexafluorophosphate ($E_{1/2}$=−0.78 V) in situ as a calibration standard. The peak-to-peak separation ($E_{p,a}$–$E_{p,c}$) was between 80–100 mV for all reversible couples unless otherwise noted. This work was carried out under a nitrogen atmosphere in a Vacuum Atmospheres Co. glove box, separate boxes being used for aqueous and non-aqueous reactions. When necessary, the complexes were purified by: (a) redissolving in acetone or acetonitrile and reprecipitation; (b) ion-exchange chromatography using Sephadex SP C-25 resin with aqueous NaCl as the mobile phase. Salts purified by ionic-exchange chromatography were precipitated as their tetraphenylborate salts by adding an excess of aqueous $NaBPh_4$. Elemental analyses were obtained in house on a Perkin–Elmer PE-2400 Series II CHN analyzer. Two-dimensional NMR spectra of **24** (HETCOR and HMBC) were recorded on a General Electric Omega-500 spectrometer.

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 vacuum distillation. All distillations were performed under nitrogen. Methylene chloride was refluxed over P_2O_5 for at least 8 h 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.[5] but can also be purchased from Aldrich. Magnesium powder (Aldrich, 50 mesh) was activated by treating with iodine in DME under nitrogen, stirring for 1 h, filtering, and washing with DMAc, acetone and diethyl ether. Other solid reagents were used as received. Liquid reagents were used as received except that they were deoxygenated prior to use. 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 used. Synthesis of compounds **5**, **6**, **11**, and **14–16**, and **23** have been previously reported.[4,6] 3-(2′-furyl)-propanol was prepared from 2-furanacrylic acid by reducing the latter to the alcohol with LAH followed by selective hydrogenation (Lindlars catalyst).

$[Os(NH_3)5(4,5\text{-}\eta^2\text{-Furan})](OTf)_2$ [1]. The synthesis and characterization of this compound have been previously reported (Ref. 6; compound **1**) ^{1}H NMR (acetonitrile-d_3): δ 7.25 (d, J=3.3 Hz, 1H, H-C5), 6.90 (d, J=2.7 Hz, 1H, H-C2), 6.05 (t, J=2.4 Hz, 1H, H-C3), 4.85 (t, J=2.7 Hz, 1H, H-C4), 4.02 (br s, 3H, *trans*-NH_3), 2.85 (br s, 12H, *cis*-NH_3). ^{13}C NMR (acetone-d_6): δ 142.7 (C2), 112.0 (C3), 98.6 (C5), 49.0 (C4). CV (CH_3CN, TBAH, 100 mV/s): $E_{p,a}$=0.67 V (NHE).

$[Os(NH_3)_5(4,5\text{-}\eta^2\text{-2-Methylfuran})](OTf)_2$ [2]. The synthesis and characterization of this compound have been previously reported (Ref. 6; compound **2**) ^{1}H NMR (acetone-d_6): δ 7.38 (d, J=3.6 Hz, 1H, H-C5), 5.81 (d, J=1.5 Hz, 1H, H-C3), 5.00 (dd, J=3.6, 1.5 Hz, 1H, H-C4), 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): δ 153.1 (C2), 107.2 (C3), 97.8 (C5), 50.4 (C4) 13.1 (CH_3). CV (CH_3CN, TBAH, 100 mV/s): $E_{p,a}$=0.60 V(NHE). Anal. Calcd for $C_7H_{21}O_7N_5S_2OsF_6$: C, 12.83; H, 3.23; N, 10.68. Found: C, 12.51; H, 3.19; N, 10.57.

$[Os(NH_3)_5(4,5\text{-}\eta^2\text{-2-Hydroxymethylfuran})](OTf)_2$ [3]. To a solution of $[Os(NH_3)_5(OTf)](OTf)_2$ (796 mg, 1.10 mmol) in methanol (5.0 g), was added 2-furanmethanol (3.78 g, 38.5 mmol), and then Zn/Hg (4.99 g). After being stirred for 12 min, the slurry was filtered through a fine frit into a flask containing a mixture of CH_2Cl_2 (600 mL) and Et_2O (200 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: 593 mg, (0.883 mmol, 80%). ^{1}H NMR (acetonitrile-d_3): δ 7.24 (d, J=3.7 Hz, 1H, H-C5), 6.01 (d, J=2.2 Hz, 1H, H-C3), 4.83 (dd, J=3.7, 2.2 Hz, 1H, H-C4), 4.13 (d, J=1.5 Hz, 2H, CH_2), 4.05 (br s, 3H, *trans*-NH_3), 2.96 (br s, 12H, *cis*-NH_3). ^{13}C NMR (acetonitrile-d_3): δ 156.2 (C2), 110.5 (C3), 98.3 (C5), 57.9 (CH_2), 49.9 (C4). CV (CH_3CN, TBAH, 100 mV/s): $E_{p,a}$=0.65 V(NHE). Anal. Calcd for $C_7H_{21}O_7N_5S_2OsF_6$: C, 12.52; H, 3.15; N, 10.43. Found: C, 12.63; H, 3.40; N, 10.36.

$[Os(NH_3)_5(4,5\text{-}\eta^2\text{-2-(3′-Hydroxypropyl)furan})](OTf)_2$ [4]. A methanol (800 mg) solution of $[Os(NH_3)_5(OTf)](OTf)_2$ (134 mg, 0.186 mmol) was prepared. A methanol (617 mg) solution of 3-(2′-furyl)-propanol (92.7 mg, 0.735 mmol) was also prepared, to which Zn(Hg) (679 mg) was added. The osmium(III) solution was added dropwise into the slurry containing the ligand and Zn(Hg) over a period of 2 min with stirring. The reaction mixture was stirred for 20 additional minutes and then added to a mixture of CH_2Cl_2 and Et_2O, which produced a pale yellow precipitate. The pale yellow precipitate was collected, washed with CH_2Cl_2 and Et_2O and dried in vacuo. Yield of a pale yellow solid: 117 mg, (0.168 mmol, 90%). ^{1}H NMR (acetonitrile-d_3): δ 7.20 (d, J=3.2 Hz, 1H, H-C5), 5.75 (d, J=2.2 Hz, 1H, H-C3), 4.81 (dd, J=3.2, 2.2 Hz, 1H, H-C4), 4.09 (br s, 3H, *trans*-NH_3), 3.79 (br s, 1H, OH), 3.54 (t, J=6.5 Hz, 2H, CH_2), 2.97 (br s, 12H, *cis*-NH_3), 2.34 (t, J=7.3 Hz, 2H, CH_2), 1.71 (m, 2H, CH_2). ^{13}C NMR (acetonitrile-d_3): δ 158.2 (C2), 106.6 (C3), 97.8 (C5), 62.3 (CH_2), 50.9 (C4), 31.3 (CH_2), 25.5 (CH_2). Anal. Calcd for $C_9H_{25}O_8N_5S_2OsF_6$: C, 15.45; H, 3.06; N, 10.01. Found: C, 13.39; H, 3.41; N, 9.38.

$[Os(NH_3)_5(5,6\text{-}\eta^2\text{-2}H\text{-Pyran-3(4}H\text{)-one})](OTf)_2$ [7]. A solution of **3** (59.8 mg, 0.0890 mmol) in acetonitrile (620 mg) was prepared and cooled to −40°C. To this was added an acetonitrile solution of $BF_3{\cdot}OEt_2$ (7.5 mg, 0.0528 mmol). After standing at −40°C for 16 h, pyridine (34.2 mg, 0.432 mmol) was added to quench the solution. 20 min later, the solution was added into a mixture of CH_2Cl_2 and Et_2O (70 mL, 6:1), producing a brown precipitate, which was collected, washed with CH_2Cl_2 and Et_2O, and dried in vacuo. Yield of tan solid: 50.3 mg (0.075 mmol, 89%). ^{1}H NMR shows that the product mixture contains **7** as the major product with ~20% **9**. ^{1}H NMR (acetonitrile-d_3/DMF-d_7) δ 6.18 (d, J=5.2 Hz, 1H, H-C6), 4.61 (br s, 3H, *cis*-NH_3), 4.06 (d, J=17.3 Hz, 1H, H-C2), 3.85 (d, J=17.3 Hz, 1H, H-C2), H-C5 overlap with *cis*-NH_3, 2.96 (dd, J=17.5, 7.3 Hz, 1H, H-C4), 2.15 (dd, J=17.5, 5.1 Hz, 1H, H-C4). ^{13}C NMR (acetonitrile-d_3/DMF-d_7): δ 214.4 (C3), 89.2 (C6), 72.2 (C2), 40.8 (C4), 35.6 (C5).

$[Os(NH_3)_5(7,8\text{-}\eta^2\text{-3,4-Dihydro-2}H\text{,6}H\text{-oxocin-5-one})](OTf)_2$ [8]. A solution of **4** (62.9 mg, 0.0899 mmol) in acetonitrile (1.23 g) was prepared and cooled to −45°C. A solution of $BF_3{\cdot}OEt_2$ (8.7 mg, 0.062 mmol) in acetonitrile (500 mg) was also prepared, and cooled to −45°C, which was added to the solution of **4**. The reaction solution was allowed to stand at −45°C for 9 h, and then quenched with pyridine (25 mg, 0.316 mmol). The reaction mixture was added into a mixture of Et_2O (80 mL) and CH_2Cl_2 (20 mL), producing a yellow precipitate, which was filtered, washed with Et_2O and CH_2Cl_2. Yield of a brown solid: 51.4 mg (0.0737 mmol, 82%). ^{1}H NMR (acetone-d_6) δ 6.26 (d, J=4.0 Hz, H-C8), 4.59 (br s, 3H, *trans*-NH_3), 3.70 (m, 2H, CH_2, H-C2), 3.64 (br s, 12H, *cis*-NH_3), 2.91 (m, 1H, H-C7), 1.78–2.82 (m, 6H, 3 CH_2). ^{13}C NMR (D_2O/acetonitrile-d_3): δ 217.6, 86.2, 61.8, 41.7, 39.2, 34.8, 26.8. Anal. Calcd for $C_9H_{25}N_5O_8S_2OsF_6$: C, 15.45; H, 3.60; N, 10.01. Found: C, 14.15; H, 3.35; N, 10.32.

$[Os(NH_3)_5(2,3\text{-}\eta^2\text{-4-Oxa-2-pentenal})](OTf)_2$ [9]. An acetonitrile (754 mg) solution of **3** (82.2 mg, 0.122 mmol) was

prepared, and H_2O (18.2 mg, 1.01 mmol) then triflic acid (155 mg, 1.03 mmol) were added. After 1 min, the solution was treated with DIEA (200 mg, 1.55 mmol). The reaction mixture was added into a mixture of CH_2Cl_2 (100 mL) and Et_2O (25 mL), producing an orange precipitate, which was collected, washed with CH_2Cl_2 and Et_2O, and dried in vacuo. Yield of the orange solid: 61.0 mg (0.0908 mmol, 74%). ^{1}H NMR (acetonitrile-d_3): δ 9.74 (d, J=7.3 Hz, 1H, COH), 5.32 (d, J=8.46 Hz, 1H, H-C3), 4.78 (d, J=7.26, 8.46, 1H, H-C2), 4.73 (br s, 3H, *trans*-NH_3), 3.49 (br s, 12H, *cis*-NH_3). 2.36 (s, 3H, CH_3). ^{13}C NMR (acetonitrile-d_3): δ 216.2 (C=O), 206.4 (CH=O), 59.0 (CH), 54.6 (CH), 35.6 (CH_3).

2H-Furanium complex [10]. An acetonitrile (623 mg) solution of **3** (50.9 mg, 0.0856 mmol) was prepared. To it added was triflic acid (36.7 mg, 0.245 mmol). After 15 min, the reaction solution was added to CH_2Cl_2 (80 mL), producing a black precipitate which was collected, washed with CH_2Cl_2 and Et_2O, and dried in vacuo. Yield of the black solid was 53.2 mg (0.0648 mmol, 76%). ^{1}H NMR (acetonitrile-d_3/HOTf): δ 6.22 (d, J=4.9 Hz, 1H, CH), 6.22 (d, J=2.9 Hz, 1H, CH), 5.91 (dd, J=4.9, 2.9 Hz, 1H, CH), 5.00 (br s, 3H, *trans*-NH_3), 3.79 (br s, 12H, *cis*-NH_3). 2.29 (s, 3H, CH_3). ^{13}C NMR (acetonitrile-d_3/HOTf): δ 223.5 (q), 124.0 (CH), 59.0 (CH), 57.4 (CH), 24.2 (CH_3).

[Os(NH_3)$_5$(4,5-η^2-3-Acetyl-2-methylpyrrole)](OTf)$_2$ [12]. η^2-Methylfuran complex **2** (86.8 mg, 0.132 mmol) was dissolved in acetonitrile (1.72 g) and cooled to −40°C. To it added was an acetonitrile (716 mg) solution of HOTf (133 mg, 0.886 mmol) at −40°C. The solution was allowed to stand at −40°C for 9 days, and then was quenched with pyridine (150 mg, 1.89 mmol). The reaction mixture was added into CH_2Cl_2 (120 mL), producing an orange precipitate, which was collected, washed with CH_2Cl_2, and dried in vacuo. Yield of the orange solid: 81.7 mg. ^{1}H NMR spectrum shows that the product is a mixture of **12** and **2** in a 3:1 ratio. ^{1}H NMR (acetonitrile-d_3): δ 7.87 (br s, 1H, N–H), 6.12 (d, J=3.9 Hz, 1H, H-C5), 5.52 (d, J=3.9 Hz, 1H, H-C4), 3.99 (br s, 3H, *trans*-NH_3), 2.99 (br s, 12H, *cis*-NH_3), 2.39 (s, 3H, CH_3), 2.25 (s, 3H, CH_3). ^{13}C NMR (acetonitrile-d_3): δ 194.6 (q), 149.9 (q), 121. 1(q), 70.1 (CH), 54.4 (CH), 28.6 (CH_3), 14.9 (CH_3).

[Os(NH_3)$_5$(3,4-η^2-1,6-Dimethyl-6-hydroxy-2-azafulvenium)](OTf)$_3$ [13a] and [13b]. η^2-Methylfuran complex **2** (72.4 mg, 0.110 mmol) was dissolved in acetonitrile (1.72 g) and cooled to −40°C. To it added was an acetonitrile (716 mg) solution of HOTf (118 mg, 0.786 mmol) at −40°C. The solution was allowed to stand at −40°C for 50 h, and then added into CH_2Cl_2 (100 mL), producing a peach precipitate, which was collected, washed with CH_2Cl_2, and dried in vacuo. Yield of the orange solid: 84.6 mg. (0.100 mmol, 90%). The ^{1}H NMR spectrum shows that the product is a mixture of two diastereomers **13a** and **13b** in a 3:2 ratio along with ~10% of carbyne complex **14**.

[13a]. *(major isomer):* ^{1}H NMR (acetonitrile-d_3): δ 10.6 (br s, 1H), 10.6 (s, 1H), 6.36 (d, J=4.9 Hz, 1H, CH), 5.75 (d, J=4.9 Hz, 1H, CH), 4.30 (br s, 3H, *trans*-NH_3), 3.15 (br s, 12H, *cis*-NH_3), 2.52 (s, 3H, CH_3). 2.29 (s, 3H, CH_3). ^{13}C NMR (acetonitrile-d_3): δ 177.4 (q) 169.0 (q), 122.8 (q), 67.3 (CH), 45.4 (CH), 22.4 (CH_3), 17.6 (CH_3).

[13b] *(minor isomer):* ^{1}H NMR (acetonitrile-d_3): δ 10.5 (br s, 1H), 10.4 (s, 1H), 6.36 (d, J=4.4 Hz, 1H, CH), 5.38 (d, J=4.4 Hz, 1H, CH), 4.32 (br s, 3H, *trans*-NH_3), 3.15 (br s, 12H, *cis*-NH_3), 2.51 (s, 3H, CH_3). 2.38 (s, 3H, CH_3). ^{13}C NMR (acetonitrile-d_3): δ 177.3 (q) 168.5 (q), 117.5 (q), 67.5 (CH), 46.0 (CH), 23.0 (CH_3), 18.3 (CH_3).

[Os(NH_3)$_5$(3,4-η^2-1,6-Dimethyl-6-methoxy-2-azafulvenium](OTf)$_3$ [17a] and [17b]. A mixture of **15a**, **15b**, **16a** and **16b** (45.6 mg) was dissolved in acetonitrile (~400 mg) and cooled to −40°C. The solution was added to an acetonitrile solution of TBSOTf (20.1 mg, 0.076 mmol) at −40°C. After five and a half days at −40°C, the solution was treated with pyridine (70 mg, 0.885 mmol) and then added to a mixture of CH_2Cl_2 (5 mL) and Et_2O (40 mL), producing a peach solid, which was collected, washed with CH_2Cl_2 and Et_2O, and dried in vacuo. Yield of the peach solid 46.0 mg.

[17a] *(major isomer):* ^{1}H NMR (acetone-d_6): δ 11.20 (br s, 1H, H–N), 6.74 (d, J=4.4 Hz, 1H, CH), 5.84 (d, J=4.4 Hz, 1H, CH), 5.03 (br s, 3H, *trans*-NH_3), 4.13 (s, 3H, CH_3), 3.75 (br s, 12H, *cis*-NH_3), 2.59 (s, 3H, CH_3). 2.56 (s, 3H, CH_3). ^{13}C NMR (acetone-d_6): δ 178.2 (q) 167.5 (q), 124.9 (q), 67.3 (CH), 58.4 (OCH_3), 45.5 (CH), 19.0 (CH_3), 17.5 (CH_3).

[17b] *(minor isomer):* ^{1}H NMR (acetone-d_6): δ 11.02 (br s, 1H, H–N), 6.74 (d, J=4.4 Hz, 1H, CH), 6.09 (d, J=4.4 Hz, 1H, CH), 4.99 (br s, 3H, *trans*-NH_3), 4.11 (s, 3H, CH_3), 3.75 (br s, 12H, *cis*-NH_3), 2.74 (s, 3H, CH_3). 2.39 (s, 3H, CH_3). ^{13}C NMR (acetone-d_6): δ 178.1 (q) 167.6 (q), 122.0 (q), 67.2 (CH), 57.8 (OCH_3), 44.8 (CH), 18.3 (CH_3), 17.8 (CH_3).

[Os(NH_3)$_5$(3,4-η^2-1-Methyl-6-(1-oxa-cyclobutyl)-2-azafulvenium] (OTf)$_3$ [18]. A solution of **4** (51.6 mg, 0.0738 mmol) in acetonitrile (1.55 g) was prepared. To it added was a solution of $BF_3{\cdot}OEt_2$ (18.9 mg, 0.133 mol) in acetonitrile (300 mg). After 23 h, the reaction mixture was quenched with pyridine (30 mg, 0.380 mmol). The reaction mixture was added into CH_2Cl_2, producing a brown precipitate, which was collected, washed with Et_2O and CH_2Cl_2, and dried in vacuo. Yield of the dark brown solid: 42.1 mg (0.0482 mmol, 65%). ^{1}H and ^{13}C NMR spectra show the formation of only one diastereomer. ^{1}H NMR (acetonitrile-d_3/D_2O): δ 6.25 (d, J=4.4 Hz, 1H, CH), 5.55 (d, J=4.8 Hz, 1H, CH), 4.58 (m, 2H, CH_2), 4.45 (br s, 3H, trans-NH_3), 3.23 (br s, 12H, *cis*-NH_3), 2.86 (t, J=8.1 Hz, 2H, CH_2), 2.43 (s, 3H, CH_3), 2.27 (m, 2H, CH_2). ^{13}C NMR (acetonitrile-d_3/D_2O): δ 182.3 (q), 169.3 (q), 118.5 (q), 77.7 (CH_2), 68.2 (CH), 45.6 (CH), 34.3 (CH_2), 24.6 (CH_2), 16.9 (CH_3).

[Os(NH_3)$_5$(5,6-η^2-4-(3′-Oxo-butyl)-2*H*-pyran-3(4H)-one](OTf)$_2$ [19]. Methyl vinyl ketone (23.2 mg, 0.331 mmol) and **3** (120.2 mg, 0.179 mmol) were dissolved in acetonitrile (1.5 g) and cooled to −40°C. A solution of TBDMSOTf (9.2 mg, 0.0348 mmol) in acetonitrile (200 mg) was also prepared and cooled to −40°C, which was added to the solution of **3**. The reaction solution was allowed to stand at −40°C for 9 h, and then quenched with

pyridine (30 mg, 0.379 mmol). The reaction mixture was added to a mixture of Et_2O (125 mL) and CH_2Cl_2 (25 mL), precipitating a green solid, which was filtered, washed with Et_2O and dried in vacuo. Yield: 102.3 mg (0.138 mmol, 77%). ^1H NMR (acetonitrile-d_3): δ 6.11 (d, J=4.4 Hz, 1H, H-C6), 4.22 (br s, 3H, *trans*-NH_3), 4.18 (d, J=17.2 Hz, 1H, H-C2), 3.89 (d, J=17.2 Hz, 1H, H-C2), 3.25 (br s, 12H, *cis*-NH_3), 3.20 (overlap with *cis*-NH_3, 1H, H-C5). 2.63–2.73 (m, 2H, CH_2), 2.13 (m, 1H, H-C4), 2.07 (s, 3H, CH_3), 1.91 (m, 1H, CH_2), 1.68 (m, 1H, CH_2). ^{13}C NMR (acetonitrile-d_3): δ 215.6 (q), 212.5 (q), 89.2 (C6), 72.7 (C2), 47.9 (C4), 42.3 (CH_2), 40.1 (C5), 30.1 (CH_3), 23.5 (CH_2). Anal. Calcd for $C_{11}H_{27}N_5O_9S_2OsF_6$: C, 17.81; H, 3.67; N, 9.44. Found: C, 18.84; H, 3.42; N, 9.37.

[Os(NH$_3$)$_5$(5α,6α-η^2-4β-(3′-Oxo-pentyl)-2*H*-pyran-3(4H)-one)](OTf)$_2$ [20]. Ethyl vinyl ketone (16.7 mg, 0.199 mmol) and **3** (83.5 mg, 0.124 mmol) were dissolved in acetonitrile (1.0 g) and cooled to −40°C. A solution of TBDMSOTf (6.8 mg, 0.025 mmol) in acetonitrile (200 mg) was also prepared and cooled to −40°C, which was added to the solution of **3**. The reaction solution was allowed to stand at −40°C for 20 h, and then quenched with pyridine (39.9 mg, 0.504 mmol). The reaction mixture was added to CH_2Cl_2 (100 mL), precipitating a green solid, which was filtered, washed with Et_2O and dried in vacuo. Yield: 71.3 mg (0.094 mmol, 69%). ^1H NMR (acetonitrile-d_3): δ 6.12 (d, J=4.5 Hz, 1H, H-C6), 4.23 (br s, 3H, *trans*-NH_3), 4.18 (d, J=15.7 Hz, 1H, H-C2), 3.89 (d, J=15.7 Hz, 1H, H-C2), 3.25 (br s, 12H, *cis*-NH_3), 3.18 (overlap with *cis*-NH_3, 1H, H-C5), 2.68 (m, 2H, CH_2), 2.40 (q, J=7.3 Hz, 2H, CH_2), 2.08, (m, 1H, CH, H-C4), 1.81 (m, 1H, CH_2), 1.68 (m, 1H, CH_2), 0.95 (t, J=7.3 Hz, 3H, CH_3). ^{13}C NMR (acetonitrile-d_3): δ 215.6 (q), 215.1 (q), 89.2 (C6), 72.7 (C2), 48.0 (C4), 41.0 (CH_2), 40.1 (C5), 36.3 (CH_2), 23.5 (CH_3), 23.5 (CH_2). Anal. Calcd for $C_{12}H_{29}N_5O_9S_2OsF_6$: C, 19.07; H, 3.87; N, 9.27. Found: C, 18.27; H, 3.84; N, 9.44.

[Os(NH$_3$)$_5$(5α,6α-η^2-4β-(1′-Ethoxyethyl)-2*H*-pyran-3(4H)-one)](OTf)$_2$ [21a] and [21b]. Acetaldehyde diethyl acetal (164.8 mg, 1.39 mmol) and **3** (101.4 mg, 0.151 mmol) were dissolved in acetonitrile (1.2 g) and cooled to −40°C. A solution of TBDMSOTf (9.8 mg, 0.0371 mmol) in acetonitrile (200 mg) was also prepared and cooled to −40°C, which was added to the solution of **3**. The reaction solution was allowed to stand at −40°C for 4 h, and then quenched with pyridine (40 mg, 0.50 mmol). The reaction mixture was added to a mixture of Et_2O (80 mL) and CH_2Cl_2 (80 mL), precipitating a tan solid, which was filtered, washed with Et_2O and dried in vacuo. Yield of the tan solid: 77.4 mg (0.104 mmol, 69%). The solid appears by ^1H NMR to be a mixture of two diastereomers **21a** and **21b** in a 5:4 ratio. Anal. Calcd for $C_{11}H_{29}N_5O_9S_2OsF_6$: C, 17.77; H, 3.93; N, 9.42. Found: C, 17.83; H, 3.77; N, 9.76.

[21a] *(major isomer):* ^1H NMR (acetonitrile-d3): δ 6.00 (d, J=4.8 Hz, 1H, H-C6), 4.13 (br s, 3H, *trans*-NH_3), 4.07 (d, J=17.3 Hz, 1H, H-C2), 3.83 (d, 1H, J=17.3 Hz, H-C2), 3.7 (overlap with other peaks, 2H, OCH_2), 3.68 (m, 1H, CH), 3.41 (overlap, 1H, H-C5), 3.23 (br s, 12H, *cis*-NH_3), 2.12 (dd, J=9.3, 5.6 Hz, 1H, H-C4), 1.48–1.13 (6H, 2 CH_3). ^{13}C NMR (acetonitrile-d_3): δ 213.9 (C3), 89.1 (C6), 74.8 (CH), 73.1 (C2), 65.0 (CH_2), 55.9 (C4), 37.6 (C5), 20.0 (CH_3), 15.6 (CH_3).

[21b] *(minor isomer):* ^1H NMR (acetonitrile-d_3): δ 6.13 (d, J=5.2 Hz, 1H, H-C6), 4.20 (d, J=17.3 Hz, 1H, H-C2), 4.2 (m, overlap with H-C2, 1H, CH), 4.13 (br s, 3H, *trans*-NH_3), 3.87 (d, 1H, J=17.3 Hz, H-C2), 3.55–3.80 (overlap 3H, OCH_2 and H-C5), 3.17 (br s, 12H, *cis*-NH_3), 2.45 (t, J=3.2 Hz, 1H, H-C4), 1.15–1.12 (overlap, 6H, 2 CH_3). ^{13}C NMR (acetonitrile-d_3): δ 213.6 (C3), 90.1 (C6), 73.6 (CH), 72.9 (C2), 64.9 (CH_2), 54.8 (C4), 34.5 (C5), 15.6 (CH_3), 15.0 (CH_3).

[Os(NH$_3$)$_5$(5α,6α-η^2-4β-(1′-Methoxy-1′-phenyl-methyl)-2*H*-pyran-3(4H)-one)](OTf)$_2$ [22a] and [22b]. Benzaldehyde dimethyl acetal (105 mg, 0.690 mmol) and **3** (77.5 mg, 0.115 mmol) were dissolved in acetonitrile (1.0 g) and cooled to −40°C. A solution of TBDMSOTf (17.4 mg, 0.0658 mmol) in acetonitrile (187 mg) was also prepared and cooled to −40°C, which was added to the solution of **50**. The reaction solution was allowed to stand at −40°C for 4 h, and then quenched with pyridine (37 mg, 0.48 mmol). The reaction mixture was added to a mixture of Et_2O (80 mL) and CH_2Cl_2 (20 mL), precipitating a green solid, which was filtered, washed with Et_2O and dried in vacuo. Yield of the green solid: 55.8 mg (0.0704 mmol, 61%). The solid appears by ^1H NMR to be a mixture of two diastereomers **22a** and **22b** in a 2:1 ratio. Anal. Calcd for $C_{15}H_{29}N_5O_9S_2OsF_6$: C, 22.76; H, 3.69; N, 8.85. Found: C, 23.10; H, 3.69; N, 8.93.

[22a] *(major isomer):* ^1H NMR (acetonitrile-d_3): δ 7.28–8.72 (m, 5H, H-phenyl), 6.08 (d, J=5.2 Hz, 1H, H-C6), 4.55 (d, J=9.3 Hz, 1H, CH), 4.21 (br s, 3H, *trans*-NH_3), 4.13 (d, J=17.3 Hz, 1H, H-C2), 3.88 (d, 1H, J=17.3 Hz, H-C2), 3.52 (t, J=5.44, H-C5), 3.25 (br s, 12H, *cis*-NH_3), 3.15 (s, 3H, OCH_3), 2.67 (dd, J=8.1, 5.6 Hz, 1H, H-C4). ^{13}C NMR (acetonitrile-d_3): δ 212.1 (C3), 141.6 (q), 128.9–129.5 (5 CH, phenyl carbons), 89.3 (C6), 83.2 (CH), 72.8 (C2), 56.5 (CH_3), 55.9 (C4), 37.7 (C5).

[22b] *(minor isomer):* ^1H NMR (acetonitrile-d_3): δ 7.28–8.72 (m, 5H, H-phenyl), 6.03 (d, J=5.2 Hz, 1H, H-C6), 5.13 (d, J=9.3 Hz, 1H, CH), 4.21 (br s, 3H, *trans*-NH_3), 4.05 (d, J=17.3 Hz, 1H, H-C2), 3.61 (d, 1H, J=17.3 Hz, H-C2), 3.51 (t, J=5.44, H-C5), 3.31 (s, 3H, OCH_3), 3.21 (br s, 12H, *cis*-NH_3), 2.77 (t, J=4.4 Hz, 1H, H-C4). ^{13}C NMR (acetonitrile-d3): δ 212.3 (C3), 143.9 (q), 128.9–129.5 (5 CH, phenyl carbons), 89.8 (C6), 81.1 (C2), 72.8 (CH_2), 57.3 (CH_3), 57.3 (C4), 34.7 (C5).

[Os(NH$_3$)$_5$(3,4-η^2-2-Oxa-bicyclo-[3.2.2]-1,9-dimethylnon-3-en-6-one)](OTf)$_2$ [24]. The osmium complex **2** (169 mg, 0.258 mmol) was dissolved in 3-penten-2-one (1.56 g, 18.6 mmol) and acetonitrile (2.6 g), then cooled to −40°C. A solution of $BF_3{\cdot}EtO_2$ (37.0 mg, 0.258 mmol) in acetonitrile (300 mg) was also cooled to −40°C and added to the solution of **2**. After 18 h, the reaction mixture was treated with pyridine (143 mg, 1.80 mmol) at −40°C. After 10 min, the reaction solution was added to a mixture of Et_2O (25 mL) and CH_2Cl_2 (75 mL), producing a peach precipitate, which was filtered, washed with CH_2Cl_2 and Et_2O, and dried in vacuo. Yield: 176 mg (0.238 mmol,

92%). ^{1}H NMR (acetonitrile-d_3): δ 5.86 (d, *J*=5.4 Hz, 1H, H-C3), 3.98 (br s, 3H, *trans*-NH3), 3.83 (t, *J*=5.4 Hz, 1H, H-C4), 3.03 (br s, 12H, *cis*-NH3), 2.58 (d, *J*=5.4 Hz, 1H, H-C5), 2.49 (d, *J*=17.7 Hz, 1H, H-C7), 2.28 (m, 1H, H-C8), 2.22 (d, *J*=17.7 Hz, 1H, H-C7), 2.13 (m, 1H, H-C9), 2.06 (m, 1H, H-C8), 1.26 (s, 3H, CH_3-C7), 1.25 (d, *J*=7.2 Hz, 3H, CH_3-C9). ^{13}C NMR (D_2O): δ 222.2 (C═O), 82.6 (C3), 77.0 (C1), 55.1 (C4), 50.8 (C7), 41.6 (C5), 39.1 (C8), 31.1 (C9), 28.2 (CH_3-C1), 17.7 (CH_3-C9). CV (CH_3CN, TBAH, 100 mV/s): $E_{p,a}$=0.86 V (NHE). Anal. cacld for $C_{12}H_{29}O_8N_5S_2OsF_6$: C, 19.49; H, 3.95; N, 9.47. Found, C, 19.51; H, 4.02; N, 9.80.

[Os(NH$_3$)$_5$(2(3-η^2-2-Oxa-bicyclo-[3.2.2]-1β-methyl-9β-phenylnon-3-en-6-one)](OTf)$_2$ [25]. The osmium complex **2** (162 mg, 0.247 mmol) was dissolved in a mixture of *trans*-4-phenyl-3-buten-2-one (1.93 g, 13.2 mmol), acetonitrile (3.0 g), and propionitrile (1 g), and the solution was cooled to −45°C. A solution of $F_3{\cdot}EtO_2$ (35.0 mg, 0.247 mmol) in acetonitrile (300 mg) was also cooled to −45°C and added to the solution of **2**. The reaction mixture was allowed to stand at −45°C for 24 h, then treated with pyridine (97.6 mg, 1.07 mmol). After 10 min, the reaction solution was added to Et_2O (150 ml), producing a greenish yellow precipitate, which was filtered, washed with Et_2O and CH_2Cl_2 and dried in vacuo. Yield of a green solid: 176 mg (0.219 mmol, 89%). ^{1}H NMR (acetonitrile-d_3): δ 7.20–7.60 (m, 5 H, C_6H_5), 6.01 (d, *J*=5.7 Hz, 1H, H-C3), 4.00 (br s, 3 H, *trans*-NH_3), 3.50–3.65 (m, 1H, H-C4), 3.02 (br s, 12H, *cis*-NH_3), 3.00–3.20 (m, 2H, H-C7), 2.80–3.00 (m, 1H, H-C5), 2.00–2.40 (m, 3H, H-C8, H-C9), 1.37 (s, 3H, CH_3-C1). ^{13}C NMR (acetonitrile-d_3): δ 218.4 (C═O), 141.7 (Ph, q), 129.5 (Ph, CH), 129.3 (Ph, CH), 127.6 (Ph, CH), 83.5 (C3), 75.9 (C1), 56.2 (C4), 51.2 (C7), 43.0 (C5), 41.9 (C9), 36.6 (C8), 29.1 (C1-CH_3). CV (CH_3CN, TBAH, 100 mV/s): $E_{p,a}$=0.85 V (NHE). The compound was purified by ion-exchange chromatography and isolated as its tetraphenylborate tetrahydrate salt. Anal. cacld for $C_{63}H_{71}N_5O_2B_2Os{\cdot}4H_2O$: C, 62.32; H, 6.56; N, 5.77. Found: C, 62.42; H, 6.40; N, 5.72.

2-Oxa-bicyclo-[3.2.2]-1α,9α-dimethylnon-3-en-6-one [26]. The complex **24** (150 mg, 0.203 mmol) was dissolved in methanol (~5 ml). To this was added DDQ (47 mg, 0.207 mmol). After 5 min, the reaction mixture was diluted with saturated $NaHCO_3$ solution (50 mL) and extracted with Et_2O (2×40 mL). The combined extracts were evaporated to dryness to give a yellow residue which was purified by column chromatography (SiO_2, hexane/ether=10:1). Yield: 4.0 mg, (0.024 mmol, 12%). ^{1}H NMR (benzene-d_6): δ 5.93 (d, *J*=7.2 Hz, 1H, H-C3), 4.19 (dd, *J*=7.2, 9.0 Hz, 1H, H-C4), 2.74 (dd, *J*=2.7, 18.9 Hz, 1H, H-C7), 2.45 (d, *J*=9.0 Hz, 1H, H-C5), 2.08 (d, *J*=18.9 Hz, 1H, H-C7), 1.53-1.62 (m, 1H, H-C9), 1.32–1.44 (m, 1H, H-C8), 1.10–1.28 (m, 1H, H-C8), 0.91 (s, 3H, CH_3-C1), 0.80 (d, *J*=6.6 Hz, 3H, CH_3-C9). ^{13}C NMR (benzene-d_6): δ 203.1 (C═O),144.7 (C3), 95.0 (C4), 77.1 (C1), 53.0 (C5), 49.8 (C7), 41.7 (C8), 33.5 (C9), 28.9 (CH_3-C1), 18.6 (CH_3-C9).

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References

1. Harman, W. D. *Chem. Rev.* **1997**, *97*, 1953.
2. Mander, L. N. *Synlett* **1991**, 134.
3. Joule, J. A.; Mills, K.; Smith, G. F. *Heterocyclic Chemistry*, 3rd ed.; Chapman & Hill: London, 1995.
4. Chen, H.; Liu, R.; Myers, W. H.; Harman, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 509.
5. Lay, P. A.; Magnuson, R. H.; Taube, H. *Inorg. Synth.* **1986**, *24*, 269.
6. Liu, R.; Chen, H.; Harman, W. D. *Organometallics* **1995**, *14*, 2861.
7. Chen, H.; Harman, W. D. *J. Am. Chem. Soc.* **1996**, *118*, 5672.
8. Kopach, M. E.; Harman, W. D.; Hipple, W. G. *J. Am. Chem. Soc.* **1992**, *114*, 1737.
9. Harman, W. D.; Hasegawa, T.; Taube, H. *Inorg. Chem.* **1991**, *30*, 453.
10. Hodges, L. M.; Spera, M. L.; Moody, M.; Harman, W. D. *J. Am. Chem. Soc.* **1996**, *118*, 7117.
11. Chen, H. *Activation of Olefins and Dearomatization of Furans with Pentaammineosmium(II)*, University of Virginia, 1997.
12. Evidente, A.; Motta, A.; Sparapano, L. *Phytochemistry* **1993**, *33*, 69.