# Dissociative Nucleophilic Substitution of $\eta^2$-Olefin Complexes via a Novel $\eta^2$-Vinyl Cation Intermediate

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**Abstract:** A series of $\eta^2$-$[Os(NH_3)_5(\text{vinyl ether})]^{2+}$ complexes have been prepared by three independent methods that involve direct coordination of a vinyl ether, alcohol addition to an $\eta^2$-alkyne complex, or nucleophilic substitution of an $\eta^2$-vinyl ether species. In the presence of an acid catalyst, the vinyl ether ligand undergoes a novel acid-catalyzed substitution reaction at the α-carbon with a broad range of nucleophiles that includes alcohols, amines, carboxylates, hydrides, silylated enols, nitriles, phosphines, and dialkyl sulfides. These reactions appear to proceed through an elimination−addition process where the first step is loss of an alcohol to form an $\eta^2$-vinyl cation intermediate. In cases where the α-carbon bears an alkyl group, an $\eta^2$-vinyl cation species can be isolated and characterized. For example, protonation of $[Os(NH_3)_5(\eta^2\text{-2-methoxypropene})]^{2+}$ (**3**) in neat HOTf allows the characterization of the substitution reaction intermediate $\eta^2$-$[Os(NH_3)_5(C_3H_5)]^{3+}$ (**32**), formally a metallocyclopropene that behaves chemically like a vinyl cation. In contrast, when the α-carbon of the vinyl ether bears a hydrogen such as with $[Os(NH_3)_5(\eta^2\text{-ethoxyethene})]^{2+}$ (**1**), the hypothetical vinyl cation intermediate, in absence of a suitable nucleophile, undergoes an intramolecular 1,2-hydrogen shift to yield the Fischer carbyne $[(NH_3)_5Os{\equiv}CCH_3]^{3+}$ (**33**). Examples of nucleophilic substitution reactions for other types of $\eta^2$-$[Os(NH_3)_5(\text{olefin})]^{n+}$ complexes are also demonstrated.

## Introduction

Nucleophilic substitution at a vinylic carbon is considerably more difficult to carry out than is the corresponding reaction for a saturated system.[1] However, coordination of the olefin to an electron-withdrawing transition metal (e.g., $PdCl_2$, $[FeCp(CO)_2]^+$) activates it toward nucleophilic addition, and this principle is the bedrock for some of the most useful organometallic processes in organic synthesis.[2] In contrast, the chemistry of olefins coordinated to an electron-rich transition metal is less understood. In this paper, we describe our findings concerning the nucleophilic substitution of olefins bound to the $\pi$-base pentaammineosmium(II), a system showing an unusual ability to activate various unsaturated ligands toward reactions with electrophiles.[3] Whereas nucleophilic substitution for $\eta^2$-olefin complexes is typically initiated by nucleophilic attack (path A, Figure 1), we find that substitution for the pentaammine(olefin)osmium system proceeds through the electrophile-induced removal of the leaving group (e.g., alkoxide or carboxylate) followed by nucleophilic addition to a vinyl cation intermediate (path B, Figure 1).

## Results

**Syntheses of Vinyl Ether Complexes.** Complexes of the form $[Os(NH_3)_5(\eta^2\text{-vinyl ether})]$ $(OTf)_2$ can be synthesized through three independent synthetic routes (Figure 2). Analogous to that reported for the synthesis of $\eta^2$-furan and dihydrofuran complexes, $[Os(NH_3)_5(OTf)]^{2+}$ may be reduced (Zn/Hg or $Mg^0$) in the presence of an excess of vinyl ether in the appropriate solvent to generate the vinyl ether complex directly.[4] Using this method, pentaammineosmium(II) complexes of ethoxyethene (**1**), 2-methoxypropene (**3**), 3,4-2*H*-dihydropyran (**4**), and 1-ethoxypropene (*cis*, **7a**; *trans*, **7b**) were prepared with yields ranging from 70% to 95%. In the latter case, the ligand is commercially available as a mixture of *cis* and *trans* isomers in a 2:1 ratio, and after complexation and isolation this diastereomeric ratio was identical ($^1$H NMR). Accordingly, the stereochemistry for **7a** and **7b** has been assigned as *cis* and *trans*, respectively, consistent with the original isomeric composition of the ligand. The ruthenium analog of **1**, $[Ru(NH_3)_5(\eta^2\text{-(ethoxyethene)}](OTf)_2$ (**8**), was synthesized in ∼70% yield by a procedure similar to that used for the osmium compound **1**.

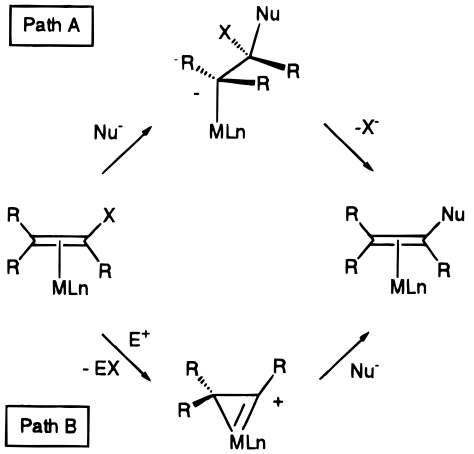


**Figure 1.** Complementary approaches to nucleophilic substitution for an $\eta^2$-coordinated olefin.

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1996.

(1) Patai, S. *The Chemistry of Alkenes*; John Wiley & Sons: London, 1964; Chapter 8.

(2) For the general chemistry of transition metal−olefin complexes, see: (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; Chapters 7−9, 16, 17. (b) Crabtree, R. H. *The Organometallics Chemistry of the Transition Metals*; John Wiley & Sons: New York, 1994; Chapters 5, 6, 11, 14. (c) Pearson A. J. *Metallo-Organic Chemistry*; John Wily & Sons: New York, 1985; Chapter 5.

(3) (a) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 1883. (b) Kopach, M. E.; Harman, W. D. *J. Am. Chem. Soc.* **1994**, *116*, 6581. (c) Hodges, L. M.; Gonzalez, J.; Koontz, J. I.; Myers, W. H.; Harman, W. D. *J. Org. Chem.* **1995**, *60*, 2125. (d) Gonzalez, J.; Koontz, J. I.; Myers, W. H.; Hodges, L. M.; Sabat, M.; Nilsson, K. R.; Neely, L. K.; Harman, W. D. *J. Am. Chem. Soc.* **1995**, *117*, 3405. (e) Spera, M. E.; Harman, W. D. *Organometallics* **1995**, *14*, 1559.

(4) Harman, W. D.; Hasegawa, T.; Taube, H. *Inorg. Chem.* **1991**, *113*, 453.

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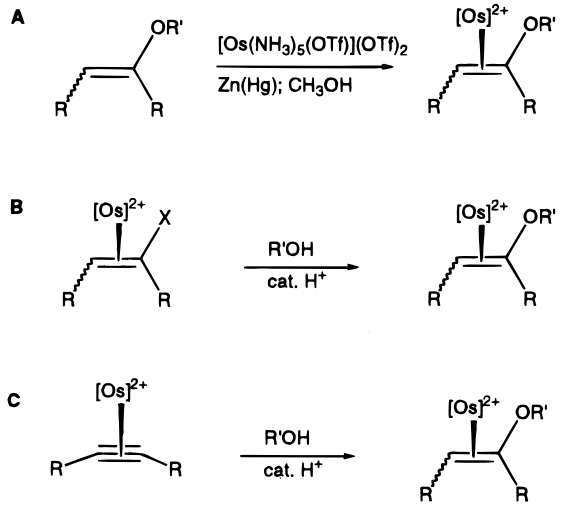



**Figure 2.** Methods for the synthesis of $\eta^2$-pentaammineosmium(II) vinyl ethers ($[Os]^{2+} = [Os(NH_3)_5](OTf)_2$).

An alternative method to prepare $\eta^2$-vinyl ether complexes is the nucleophilic substitution of $\eta^2$-pentaammmine(olefin)-osmium complexes (described herein). For example, when the complex $[Os(NH_3)_5(\eta^2\text{-ethoxyethene})]^{2+}$ (**1**) is dissolved in methanol and treated with a catalytic amount of HOTf, $[Os(NH_3)_5(\eta^2\text{-methoxyethene})](OTf)_2$ (**2**) is recovered in analytically pure form. $^1$H and $^{13}$C NMR spectra of **2** closely resemble those of **1** except that the ethoxy signals have been replaced with a methoxy resonance. Finally, as has been previously reported, alkyne complexes may undergo addition of alcohols to form $\eta^2$-vinyl ether complexes.[5] For example, the 2-butyne complex $[Os(NH_3)_5(CH_3CCCH_3)]^{2+}$ readily forms the $\eta^2$-*cis*-2-methoxybut-2-ene complex when allowed to stand in methanol. In an interesting variation of this reaction, when $\{Os(NH_3)_5\}^{2+}$ is generated in the presence of 3-butyn-1-ol and methanol, a mixture of two products is isolated in a 3:2 ratio. A $^1$H NMR spectrum of the major product shows a methoxy resonance, and a pair of olefinic protons, whose small coupling constant ($J = 2.7$ Hz) indicates their geminal relationship. A quaternary $^{13}$C resonance at 91.4 ppm and a methylene signal at 38.0 ppm confirm the assignment of **9** as an $\eta^2$-3-methoxy-3-buten-1-ol species (Figure 3), a product (**9**) resulting from protonation of the alkyne at C(4) followed by addition of methoxide at C(2). The minor product **10** was determined not to be a regioisomer of **9**, but rather the Fischer carbene shown in Figure 3, a product resulting from C(3) protonation of the 2-butyne ligand. In addition to the above general methods, organic transformations on the uncoordinated portion of $\eta^2$-furan complexes have led to a wide range of cyclic vinyl ether complexes of pentaammineosmium(II).[6]

A single crystal of compound **1** was structurally analyzed using X-ray diffraction.[7] Due to extensive internal disorder in the crystal, the optimized structural parameters calculated are not meaningful; however, the $\eta^2$-binding mode of the vinyl ether was unambiguously determined. In addition, the methylene

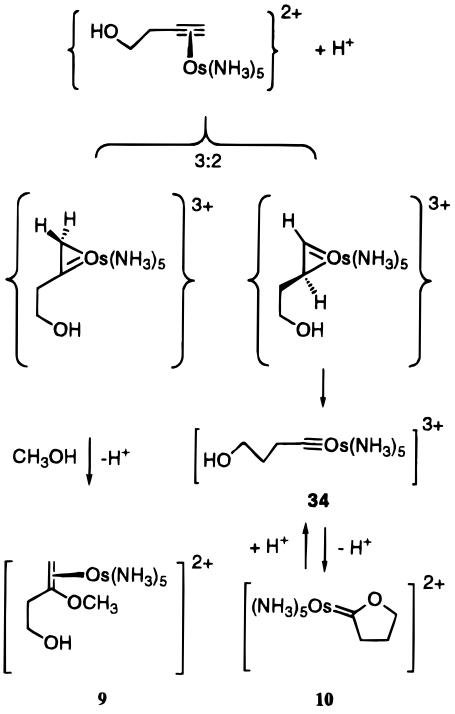



**Figure 3.** Reaction of the 3-butyn-1-ol complex of pentaammineosmium(II) (prepared *in situ)* in the presence of acid.

carbon of the ethoxy group lies well outside the plane formed by the oxygen and vinyl carbons, a geometric arrangement that rules out any significant $\pi$ interaction between the oxygen and the vinyl group. Spectroscopic data for the $\eta^2$-vinyl ether complexes show $^1$H and $^{13}$C resonances of the coordinated vinyl group shifted significantly upfield as is typical for $\eta^2$-olefin complexes. In general, the *trans* vicinal coupling constants for the vinyl protons sharply decrease ($J_{trans} = \sim 6-9$ Hz) upon coordination relative to the free ligand (12−15 Hz) while *cis* coupling constants suffer only a modest decrease. In the case of complexes **1**, **2**, and **7a**,**b**, *trans* vicinal coupling constants are especially low ($J_{trans} = \sim 6$ Hz).[8] In contrast to the open-chain $\eta^2$-vinyl ether complexes, the five-membered cyclic vinyl ether complexes **5** and **6** actually show a slight *increase* in the *cis* coupling constant upon coordination. As a result, vicinal coupling constants or chemical shifts are so similar for different diastereomers that these data are no longer reliable indicators of stereochemistry. However, careful comparison with known systems (e.g., **7a** and **7b**; *vide infra*) allows assignment in many cases (Tables 1 and 2).

**Nucleophilic Substitution Reactions of $\eta^2$-Vinyl Ether Complexes.** The $\eta^2$-vinyl ether complexes of pentaammineosmium(II) are inert to nucleophiles such as $NaOCH_3$ and $NBu_4BH_4$ under basic conditions. However, addition of a catalytic amount of Lewis or Brönsted acid activates these complexes toward nucleophilic substitution and these reactions are summarized in Figure 4.

**Oxygen and Sulfur Nucleophiles.** When the ethyl vinyl ether complex **1** in methanol is treated with catalytic HOTf, facile exchange of the ethoxy group for a methoxy group occurs. Addition of a mixture of $CH_2Cl_2$ and $Et_2O$ precipitates the methyl vinyl ether complex **2** as a single product (72%). $^1$H and $^{13}$C NMR data for all of the $\eta^2$-vinyl ether complexes discussed herein are reported in Tables 1 and 2.[9] When the 2:1 mixture of *cis*- and *trans*-1-ethoxypropene complexes **7a** and **7b** is treated with catalytic acid (HOTf, 0.5 equiv, 0.05 M)

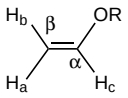
(5) Harman, W. D.; Dobson, J. C.; Taube, H. *J. Am. Chem. Soc.* **1989**, *111*, 3061.

(6) (a) Chen, H.; Hodges, L. M.; Liu, R.; Stevens, W. C.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1994**, *116*, 5499. (b) Liu, R.; Chen, H.; Harman, W. D. *Organometallics* **1995**, *14*, 2861.

(7) Crystallographic data for $C_6H_{23}F_9N_5O_7S_2Os$: $M_r = 702.6$, monoclinic, space group *C*2/*c* (no. 15), $a = 21.719$ Å, $b = 7.917(4)$ Å, $c = 28.746$ Å, $\beta = 104.86°$, $V = 4777(3)$ Å$^3$, $Z = 8$, $d_{calcd} = 1.95$ g cm$^{-3}$, $T = -100$ °C. The structure was solved by direct methods and refined to an *R* of 0.054 ($R_w = 0.067$) for 1967 absorption-corrected reflections with $I > 3\sigma(I)$. Unresolvable disorder of the organic ligand prevented any detailed analysis of its geometry.

(8) (a) Culter, A.; Raghu, S.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *108*, 93. (b) Thyret, H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 520.

**Table 1.** $^1$H NMR Data for Selected Vinyl Ether Complexes and Their Organic Ligands[a]

| | | δ (ppm) | | | | | |
|---|---|---|---|---|---|---|---|
| | |  | | | | | |
| compound | *trans*-$NH_3$/*cis*-$NH_3$ | $H_a$ | $H_b$ | $H_c$ | $J_{a,b}$ (Hz) | $J_{a,c}$ (Hz) | $J_{b,c}$ (Hz) |
| $[Os(NH_3)_5$(ethoxyethene)$]^{2+}$ **(1)** | 4.08/3.00 | 2.85 | 3.06 | 5.70 | 2.4 | 4.8 | 6.3 |
| $[Os(NH_3)_5$(methoxyethene)$]^{2+}$ **(2)** | 4.07/3.00 | 2.84 | 3.09 | 5.69 | 2.5 | 5.1 | 6.3 |
| $[Os(NH_3)_5$(2-methoxypropene)$]^{2+}$ **(3)** | 4.07/3.03 | 2.91 | 3.25 | | 2.0 | | |
| $[Os(NH_3)_5$(4,5-6*H*-dihydropyran)$]^{2+}$ **(4)** | 4.03/3.02 | 3.35 | | 6.05 | | 6.0 | |
| $[Os(NH_3)_5$(4,5-dihydrofuran)$]^{2+}$ **(5)** | 4.02/3.02 | 3.49 | | 6.10 | | 3.6 | |
| $[Os(NH_3)_5$(furan)$]^{2+}$ **(6)** | 4.02/2.85 | 4.85 | | 7.24 | | 3.3 | |
| $[Os(NH_3)_5$(*cis*-1-ethoxypropene)$]^{2+}$ **(7a)** | 3.99/2.97 | 3.44 | | 5.52 | | 5.2 | |
| $[Os(NH_3)_5$(*trans*-1-ethoxypropene)$]^{2+}$ **(7b)** | 3.99/2.97 | | 3.12 | 5.63 | | | 6.0 |
| $[Ru(NH_3)_5$(ethoxyethene)$]^{2+}$ **(8)** | 3.57/1.82 | 2.84 | 3.08 | 5.89 | 2.4 | 5.1 | 8.7 |
| ethoxyethene | | 3.94 | 4.16 | 6.46 | 1.5 | 6.9 | 14.4 |
| 2-methoxypropene | | 3.85 | 3.87 | | 1.8 | | |
| 3,4-2*H*-dihydropyran | | 4.59 | | 6.27 | | 6.0 | |
| 1,2-dihydrofuran | | 4.95 | | 6.32 | | 2.7 | |
| furan | | 6.44 | | 7.54 | | 1.4 | |
| *cis*-1-ethoxypropene | | 4.27 | | 5.93 | | 6.7 | |
| *trans*-1-ethoxypropene | | | 4.71 | 6.17 | | | 12.8 |

[a] Recorded in acetonitrile-$d_3$ solution at 22 °C unless otherwise noted. Complexes **1**−**8** are triflate salts ($OTf^-$).

**Table 2.** $^{13}$C NMR and Electrochemical Data for Selected Vinyl Ether Complexes and Their Organic Ligands

| | $\delta_C$ of complex (ppm) | | $\delta_C$ of free ligands (ppm) | | reduction potential | |
|---|---|---|---|---|---|---|
| compound | Cα | C$\beta$ | Cα | C$\beta$ | $E_{p,a}$ (V) | $E_{1/2}$ (V) |
| $[Os(NH_3)_5$(ethoxyethene)$]^{2+}$ **(1)** | 93.30 | 33.05 | 152.80 | 86.75 | | 0.67 |
| $[Os(NH_3)_5$(2-methoxypropene)$]^{2+}$ **(3)** | 94.95 | 35.63 | 161.63 | 81.36 | | 0.63 |
| $[Os(NH_3)_5$(4,5-6*H*-dihydropyran)$]^{2+}$ **(4)** | 89.92 | 40.00 | 145.00 | 101.57 | | 0.49 |
| $[Os(NH_3)_5$(4,5-dihydrofuran)$]^{2+}$ **(5)** | 95.44 | 37.64 | 147.74 | 100.46 | | 0.63 |
| $[Os(NH_3)_5$(furan)$]^{2+}$ **(6)** | 98.64 | 48.96 | 143.44 | 110.26 | 0.67 | |
| $[Os(NH_3)_5$(*cis*-1-ethoxypropene)$]^{2+}$ **(7a)** | 92.84 | 38.55 | 146.56 | 100.82 | | 0.66 |
| $[Os(NH_3)_5$(*trans*-1-ethoxypropene)$]^{2+}$ **(7b)** | 95.24 | 39.75 | 147.57 | 98.84 | | 0.66 |
| $[Ru(NH_3)_5$(ethoxyethene)$]^{2+}$ **(8)** | 112.65 | 49.85 | 152.80 | 86.75 | 1.14 | |

[a] The data for the complexes and their ligands are recorded in acetonitrile-$d_3$ solution at 22 °C. [b] Recorded by cyclic voltammetry in acetonitrile/∼0.5 M TBAH, 100 mV/s, NHE.

in ethanol, the two diastereomers rapidly interconvert, resulting in a 1:1 equilibrium mixture. Treatment of either the 2:1 or the 1:1 mixture of **7a** and **7b** with HOTf (0.5 equiv, 0.05 M) in methanol (2 h, 22 °C) results in a 1:1 mixture of *cis*- and *trans*-$\eta^2$-1-methoxypropene complexes **12a** and **12b**. Next, this reaction is repeated using a 1:1 mixture of **7a** and **7b** (32.4 mg, 0.049 mmol) with a lower concentration of a Lewis acid ($BF_3$·$OEt_2$, 0.01 M), and monitored by $^1$H NMR (methanol-$d_4$). After 10 min, an absorption spectrum shows approximately a 0:0.6:1.0:0.4 ratio of the four vinyl ether complexes **7b**, **7a**, **12b**, and **12a** involved in the reaction. Comparison of the following spectra taken over a period of 2 h shows that while nucleophilic substitution of the *trans* isomer **7b** and formation of the *trans* isomer **12b** is essentially complete in 10 min, complete consumption of the *cis* isomer **7a** takes roughly 1 h ($k_{trans}/k_{cis}$ > 5), and during this period the *cis* product **12a** is formed. In a separate series of experiments, the reaction of the $\eta^2$-dihydrofuran complex **5** with methanol was monitored in methanol-$d_4$ over a period of 1 week (0.3 equiv of HOTf, ∼22 °C). A comparison of the spectra indicates that, after 9 h, 90% of the starting material is converted to a 1:2 thermodynamic mixture of **13a** and **13b**, two new vinyl ether species spectroscopically characterized as *cis*- and *trans*-4-methoxy-3-buten-1-ol complexes, respectively. Treatment of this reaction mixture with ether resulted in precipitation of a solid that was collected and dried *in vacuo* (70% recovery). Spectroscopic analysis reveals that the isolated product was the dihydrofuran starting material **5** exclusively! If, prior to precipitation, the acid in solution was neutralized with Hünig's base, the isolated product mixture was a 1:2 ratio of **13a** and **13b** ($^1$H NMR spectra in $CD_3CN$), identical to that seen in acidic methanol-$d_4$ solution. Finally, when this reaction was repeated at −40 °C for 3 days, then quenched with base, and precipitated with $Et_2O$, the *sole* product isolated (62%) was the *trans i*somer **13b**.

The reaction of the ethoxyethene complex **1** with water in acidic solution results in the formation of the $\eta^2$-vinyl alcohol complex **11**, and this cation is precipitated out of the reaction solution as the tetraphenylborate salt. Three vinyl protons of **11** show a clear ABX coupling pattern, but the α-proton also weakly couples to the hydroxyl proton at 3.83 ppm ($J$ = 3.9 Hz). $^{13}$C NMR data for **11** show two olefinic (coordinated) resonances at 88.4 and 32.3 ppm, values similar to those observed for the vinyl ether **1**. We note here that spectroscopic data for this $\eta^2$-enol complex (**11**) differ significantly from those of other late transition metal cationic complexes. $^1$H NMR data for the latter compounds (e.g., $[FeCp(CO)_2(\eta^2$-ethenol$)]^+$) typically show a broadened hydroxyl proton and an $A_2X$ splitting pattern for the vinyl protons, due to a rapid acid−base equilibrium between the vinyl alcohol and its $\beta$-oxoalkyl isomer.[10]

When **1** is combined with *tert*-butyldimethylsilyl triflate

(9) The assignments of the coordinated carbons α or $\beta$ to the oxygenated substituent were determined through DEPT experiments, and the assignments for the respective protons were confirmed by proton−proton decoupling and HETCOR procedures.

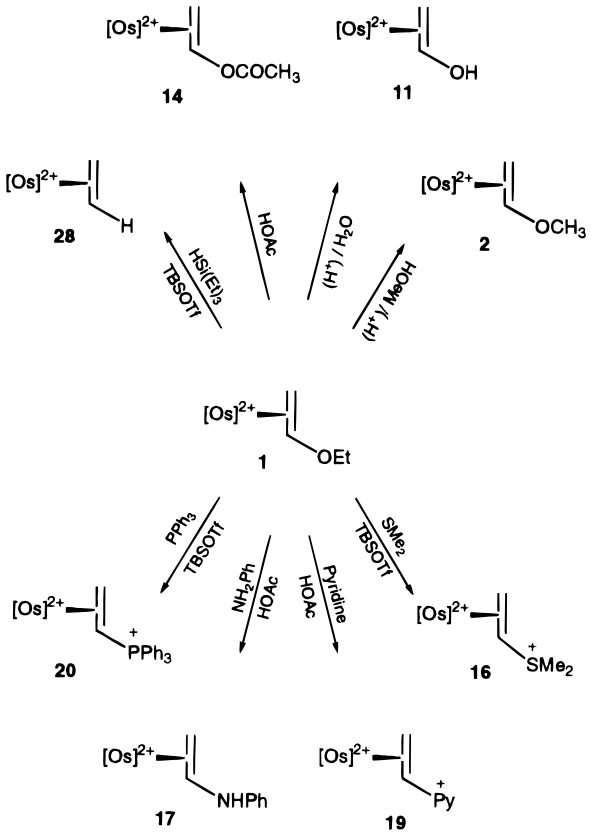



**Figure 4.** Representative acid-catalyzed nucleophilic substitution reactions for the $\eta^2$-vinyl ether complex **1**.

(TBSOTf) (1 equiv, 22 °C, $CH_3CN$) in the presence of excess ammonium acetate, no reaction occurs. However, if the complex **1** is dissolved in acetic acid and allowed to stand (40 min), addition of a mixture of $CH_2Cl_2$ and $Et_2O$ quantitatively precipitates a new olefin complex (**14**, 92%). Relevant NMR data for **14** include a methyl proton resonance at 1.98 ppm and carbonyl $^{13}C$ signal at 174.1 ppm. Complete spectroscopic and combustion analysis reveals that the complex **14** is the $\eta^2$-carbomethoxyethene complex of pentaammineosmium(II). Repeating the reaction in acetic acid for the 2-methoxypropene complex **3** gives a similar outcome, the $\eta^2$-isopropenyl acetate species **15**.

Treatment of the vinyl ether complex **1** with a stoichiometric amount of TBSOTf in the presence of dimethyl sulfide also results in a facile nucleophilic substitution reaction. A $^1H$ NMR spectrum of the product $\eta^2$-vinyldimethylsulfonium complex **16** features *trans*- and *cis*-ammine resonances that are shifted *downfield* relative to those of more typical olefin complexes of pentaammineosmium(II). Two well-resolved methyl signals ($^1H$ and $^{13}C$ NMR) indicate a relatively high inversion barrier (>10 kcal/mol) for the pyramidal sulfonium center.[11] Over the course of 10−15 days, the complex **16** decomposes in $CH_3CN$ solution, yielding only paramagnetic compounds; however, it is stable for months when kept in the solid state at −20 °C.

**Nitrogen and Phosphorus Nucleophiles.** Dissolving vinyl ether complex **1** or **3** in a mixture of acetic acid and aniline (30 min) followed by precipitation with $CH_2Cl_2$ and $Et_2O$ produces the $\eta^2$-enamine complexes **17** and **18**, respectively. Repeating this reaction with pyridine as the nucleophile affords the corresponding vinylpyridinium complex **19** (*vide infra*).[12] When triphenylphosphine is combined with a Lewis acid and the vinyl ether complex **1** or **3** in acetonitrile, the corresponding $\eta^2$-vinyltriphenylphosphonium complexes **20** and **21** are formed in good yield.

When complex **1** is treated with 1 equiv of HOTf in acetonitrile, a new species (**22**) is recovered, which gives a $^1H$ NMR spectrum similar to that of **1**, but with a new methyl resonance at 2.38 ppm and a broad singlet at 9.57 ppm. Signals for the vinyl protons and *cis/trans*-ammines are shifted downfield by 0.2−0.8 ppm relative to those of starting material **1**. A complete spectroscopic analysis reveals the structure of the organic ligand as protonated acetimidate (Figure 5). When this reaction is repeated in $CD_3CN$, the product **22**-$d_3$ has a $^1H$ NMR spectrum that is missing only the methyl signal at 2.38 ppm relative to that of **22**, an observation verifying the incorporation of acetonitrile in the product. Irradiation of the methyl signal at 2.38 ppm for **22** causes a 9% NOE enhancement of the NH feature, indicating that the ligand is exclusively in its *Z*-form.[13]

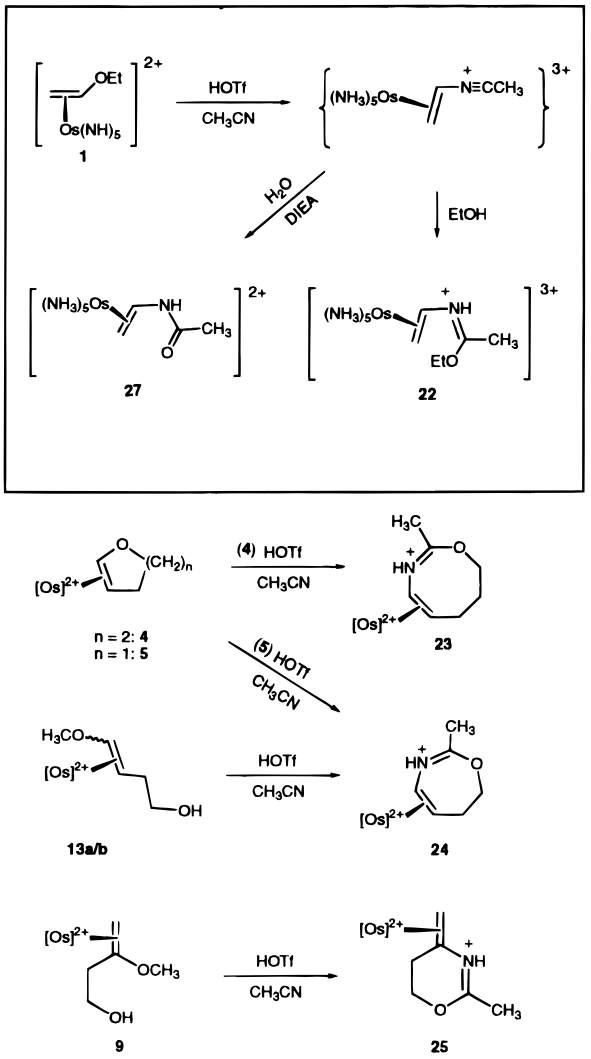



**Figure 5.** Formation of vinylacetimidate and vinylacetamide complexes from vinyl ether precursors and acetonitrile.

(10) Milstein, D. In *The Chemistry of Enols*; Rappoport, Z. V. I., Ed.; J. Wiley & Sons: New York, 1990; Chapter 12.

(11) Theoretical calculations and experimental findings (synthesis of optically active sulfonium salt, and their crystal structure data) both confirm a pyramidal conformation for sulfonium salt. The barrier for inversion is calculated to be 24 kcal/mol with d orbitals and 13.5 kcal/mol without d orbitals. See: (a) Simonetta, M.; Gavezzotti, A. In *The Chemistry of the Sulphonium Group*; Stirling, C. J. M., Ed.; J. Wiley & Sons: New York, 1981; Part 1, Chapter 1, pp 1−14. (b) Andersen, K. K. *Ibid.*; Chapter 10.

(12) This method of preparation for the vinylpyridinium complex **19** was found to be inferior to that reported in the Experimental Section.

(13) Fodor, G.; Phillips, B. A. In *The Chemistry of Amidines and Imidates*; Patai, S., Ed.; J. Wiley & Sons: New York, 1975; Chapter 2, pp 132−138.

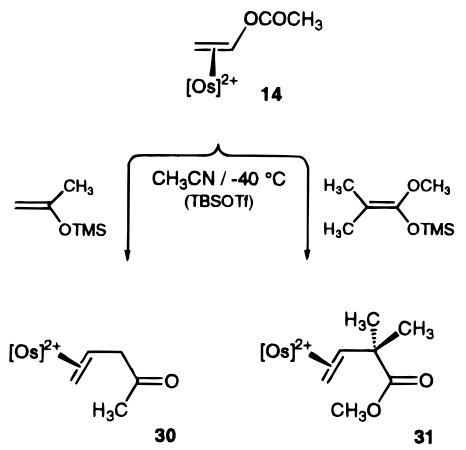



**Figure 6.** Reactions of the $\eta^2$-vinyl acetate complex **14** with carbon nucleophiles.

A similar nucleophilic substitution is postulated for the reaction of 2,3-$\eta^2$-6*H*-4,5-dihydropyran (**4**), and complexes of 2,3-dihydrofuran (**5**) and 3,4-$\eta^2$-1-hydroxy-3-methoxy-3-buten-1-ol (**9**). In these cases, $\eta^2$-cyclic imidate complexes **23**, **24**, and **25** are formed according to Figure 5. These products are characterized by $^1$H and $^{13}$C NMR, DEPT, and HETCOR, and their spectroscopic data are consistent with those of known organic imidates. Finally, when a mixture of **13a** and **13b** is treated with 1 equiv of HOTf in $CH_3CN$, the cyclic imidate **24** is the only product isolated.

In a variation of the imidate reaction above, an acetonitrile solution of **1** was treated with 1 equiv of triflic acid and an excess of water. The resulting compound, a protonated vinylacetamide (**26**), is then deprotonated (Hünig's base) to yield the corresponding $\eta^2$-*N*-vinylacetamide complex **27** in overall 81% yield.

**Hydride Nucleophiles.** Although $\eta^2$-vinyl ether complexes of pentaammineosmim(II) fail to react with $Et_3SiH$ or $Bu_4NBH_4$ in $CH_3CN$ alone, when the vinyl ether complex **1** is combined with a mixture of triethylsilane and TMSOTf, nucleophilic substitution readily occurs. The product obtained is identical to the $\eta^2$-ethylene complex **28**, previously prepared by direct reduction of $[Os(NH_3)_5(OTf)](OTf)_2$ in DME solution saturated with ethylene.[14] However, both the purity and yield of the ethylene complex **28** are significantly improved by this new procedure. $[Os(NH_3)_5(\eta^2\text{-propene})](OTf)_2$ (**29**) is prepared by a similar reaction starting from compound **3**. Spectra for compound **29** are consistent with those previously reported by Shepherd et al.[15]

**Carbon Nucleophiles.** When **1** or **3** is combined with a Lewis acid and carbon nucleophile such as a silyloxy or alkoxy vinyl ether, only intractable mixtures or starting materials are obtained. However, the addition of carbon nucleophilies was ultimately achieved by utilizing olefin complexes with better leaving groups. When the $\eta^2$-carbomethoxyethene complex **14** is combined with 2-(trimethylsiloxy)propene or methyl trimethylsilyl ketene dimethyl acetal (1.0−2.0 equiv, $CH_3CN$) and a catalytic amount of a Lewis acid (TMSOTf, 0.1−0.5 equiv, −40 °C), nucleophilic substitution readily occurs at the coordinated α-carbon to generate alkyl-substituted ethylene complexes **30** and **31**, respectively (Figure 6).

Osmium(II) complexes of vinylsulfonium (**16**) and vinyl acetate (**14**) were found to be particularly useful as synthons to other substituted olefins. In acetonitrile solution, compound **16** rapidly reacts with methanol to form the $\eta^2$-methyl vinyl ether complex **2**. The $\eta^2$-vinyl acetate complex **14**, although stable in methanol alone, rapidly reacts with the addition of acid, generating **2** and acetic acid as the only products. The $\eta^2$-vinyldimethylsulfonium complex readily reacts with pyridine to give $\eta^2$-*N*-vinylpyridinium complex **19** as a single product. In contrast to the above results, when the $\eta^2$-vinylphosphonium complex **20** was combined with excess methanol in acetonitrile, and kept at 60−70 °C for 12 h, no reaction occurred. Similarly, under all the reaction conditions tried, the amine group of $\eta^2$-*N*-vinylphenylamine complex **17** does not exchange with methanol. $^1$H and $^{13}$C NMR data for the $[Os(NH_3)_5(\eta^2\text{-olefin})]^{n+}$ complexes reported herein are collected for comparison in Tables 3 and 4. Proton and carbon assignments have been made, where possible using $^1$H/$^1$H coupling, DEPT, and HETCOR data.

**Isolation and Characterization of Vinyl Cation.** Protonation of the vinyl ether complex **3** with a stoichiometric amount of HOTf in acetonitrile, either at room temperature or at −40 °C, produces a dark peach solution. The product **32**, precipitated as its triflate salt by a mixture of $Et_2O$ and $CH_2Cl_2$, shows a pair of broadened resonances at 4.35 (3H) and 4.11 (12H) ppm ($CD_3CN$) corresponding to the *trans*- and *cis*-ammines, signals that are shifted unusually far downfield and appear unusually close together relative to those of simple olefin complexes.[16] In addition to these signals, two slightly broadened singlets are present in the $^1$H NMR spectrum at 3.12 ppm (2H) and 2.37 ppm (3H). The same product can also be generated from **3** and neat triflic acid and isolated by precipitation in $Et_2O$. The low solubility of **32** and its highly reactive nature prevented the convenient characterization by $^{13}$C NMR in acetonitrile, acetone, or DMF. Thus, triflic acid-*d*, was used as the solvent for $^{13}$C NMR and 2D NMR characterization of **32** (Figure 7). Addition of **3** (48.7 mg) to a sample of triflic acid-*d* (725 mg) rapidly shows the dark peach color earlier observed in acetonitrile. Comparison of the $^1$H NMR spectrum of the reaction mixture with that of methanol in triflic acid confirmed that methanol is produced as a byproduct. DEPT and HETCOR data confirm that the ligand in **32** contains one methyl group, one methylene group, and a downfield quaternary carbon (299.9 ppm). These data are most consistent with a dihapto-coordinated isopropenyl cation resulting from the loss of methanol from protonated **3** (Figure 8). When a solution of **32** in acetonitrile is treated with a nucleophile (e.g., methanol or aniline), the corresponding addition product (i.e., **3** or **18**) rapidly forms in good purity. When a solution of **32** is allowed to stand in triflic acid-*d*, for a 2-day period, the methyl group partially undergoes deuterium exchange (∼50%) while the methylene group remains fully intact.

**Formation of Osmium Carbynes.** Despite the similarities between the vinyl ether complexes **1** and **3**, protonation of these complexes in neat HOTf has an entirely different outcome. Spectroscopic data for the new material **33** include a *cis*-ammine resonance *downfield* of the *trans*-ammine signal, and a $^{13}$C resonance at 296.1 ppm, features that are diagnostic for a pentaammineosmium carbyne complex (Figure 8).[6a,17] Taken together with the appearence of a single methyl group (DEPT), compound **33** is unambiguously assigned as $[Os(NH_3)_5(\equiv CCH_3)](OTf)_3$.[18] In order to gain some insight into the mechanism of carbyne formation, complex **1** was treated with DOTf and then

(14) Harman, W. D. Ph.D. Dissertation, Stanford University, Stanford, CA, 1987.

(15) Elliott, M. G.; Shepherd, R. E. *Inorg. Chem.* **1988**, *27*, 3332.

(16) $\pi$-bound olefin, ketone, and iminium complexes of pentaammineosmium(II) in every case documented show *cis*- and *trans*-ammine resonances separated by >1 ppm.

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

(18) Carbyne **33** can also be generated from the protonation of the $\eta^2$−vinylacetate complex **14** with neat HOTf.

**Table 3.** $^1$H NMR Data for Various Dihapto-Coordinated Olefin Complexes of Pentaammineosmium(II)

| | | $\delta^b$ (ppm) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| compd | α-substituent | $H_a$[a] | $H_b$[a] | $H_c$ | *trans*-$NH_3$ | *cis*-$NH_3$ | $J_{a,b}$ (Hz) | $J_{a,c}$ (Hz) | $J_{b,c}$ (Hz) |
| **28** | H | | 3.01 | | 4.11 | 2.95 | | | |
| **29** | $CH_3$ | 2.81 | 3.06 | 3.34 | 4.01 | 2.93 | ~0 | 9.0 | 9.0 |
| **31** | $C(CH_3)_2COCH_3$ | 2.95 | 3.42 | 3.57 | 4.06 | 3.10 | 1.5 | 9.0 | 10.2 |
| **1** | $OCH_2CH_3$ | 2.85 | 3.07 | 5.70 | 4.08 | 3.00 | 2.4 | 4.8 | 6.3 |
| **11**[c] | OH | 2.76 | 2.99 | 5.93 | 3.70 | 2.78 | 2.9 | 5.2 | 6.9 |
| **14** | $OOCCH_3$ | 3.20 | 3.39 | 6.92 | 4.16 | 3.11 | 3.3 | 5.9 | 5.9 |
| **17** | NHPh | 3.12 | 3.17 | 5.30 | 4.04 | 3.06 | 2.0 | 8.2 | 6.7 |
| **27** | $NHCOCH_3$ | 3.05 | 3.25 | 5.98 | 4.03 | 3.19 | 2.1 | 7.2 | 7.2 |
| **22** | $HN{=}C(OEt)(CH_3)$ | 3.49 | 3.86 | 5.90 | 4.30 | 3.21 | 3.6 | 6.9 | 7.2 |
| **19** | pyridine | 4.04 | 4.94 | 6.56 | 4.48 | 3.26 | 5.4 | 7.2 | 7.4 |
| **20**[d] | $PPh_3$ | 4.75 | 4.81 | 5.08 | 5.08 | 3.71 | | | |
| **16** | $S(CH_3)_2$ | 3.95 | 4.15 | 4.73 | 4.51 | 3.40 | 3.9 | 7.8 | 7.8 |

[a] $H_a$ and $H_b$ are located on the $\beta$-carbon; however, their geometrical orientation is unknown. [b] Recorded in acetonitrile-$d_3$ solution as a triflate salt ($OTf^-$), at 22 °C unless otherwise noted. [c] **11** as a $BPh_4^-$ salt. [d] Due to the overlap of peaks, coupling constants are not available.

**Table 4.** $^{13}$C NMR and Electrochemical Data for Various Dihapto-Coordinated Olefin Complexes of Pentaammineosmium(II)

| | | $\delta$ (ppm) | | reduction potential | |
|---|---|---|---|---|---|
| compd | α-substituent | Cα (CH) | Cβ ($CH_2$) | $E_{p,a}$ (V) | $E_{1/2}$ (V) |
| **28** | H | 41.79 | | | 0.65 |
| **29** | $CH_3$ | 47.33 | 43.04 | | 0.58 |
| **31** | $C(CH_3)_2COCH_3$ | 56.45 | 38.77 | | 0.76 |
| **1** | $OCH_2CH_3$ | 93.30 | 33.05 | | 0.67 |
| **11**[d] | OH | 88.49 | 32.35 | | 0.65 |
| **14** | $OOCCH_3$ | 87.08 | 31.34 | | 0.86 |
| **17**[b] | NHPh | 65.18 | 36.02 | | 0.36 |
| **27** | $NHCOCH_3$ | 60.91 | 32.85 | | 0.67 |
| **22** | $HN{=}C(OEt)(CH_3)$ | 57.84 | 33.80 | | 1.03 |
| **19** | pyridine | 70.25 | 30.49 | | 1.28 |
| **20**[b] | $PPh_3$ | 17.49 (d) | 39.40 | 1.45 | |
| **16** | $S(CH_3)_2$ | 48.77 | 38.47 | | 1.32 |

[a] Recorded in acetonitrile-$d_3$ as a triflate salt, at 22 °C unless otherwise noted. [b] In acetone-$d_6$. [c] Recorded in acetonitrile/~0.5 M TBAH, NHE. [d] Compound **11** is isolated as the $BPh_4^-$ salt.

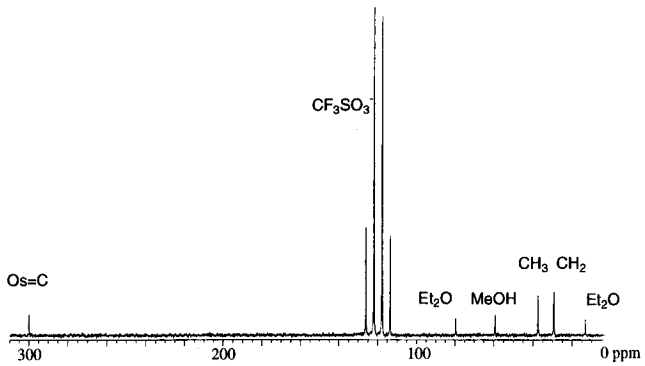



**Figure 7.** $^{13}$C NMR spectrum of the dihapto-coordinated isopropenyl cation−pentaammineosmium **32** in neat triflic acid-$d_1$.

isolated ($Et_2O$ and $CH_2Cl_2$). Judging from the integration of the methyl signal in the $^1$H NMR spectrum and the H−C coupling pattern of the methyl group in a proton-coupled $^{13}$C NMR spectrum of **33**,[19] the carbyne complex was recovered in its fully protonated form. In contrast to the vinyl cation **32**, the carbyne complex **33** shows no H/D scrambling in a triflic acid-$d_1$ solution.

As mentioned previously, when $\{Os(NH_3)_5\}^{2+}$ is generated in the presence of 3-butyn-1-ol and methanol, a mixture of two products is isolated in a 3:2 ratio (Figure 3). The minor component **10** shows an overlap of the *cis*- and *trans*-ammine proton resonances and a $^{13}$C resonance at 256.5 ppm, spectral

(19) $^{13}$C−$^1$H coupling constants of complex **33** are as follows: $^1J_{CH}$ = 134.5 Hz and $^2J_{CH}$ = 7.9 Hz.

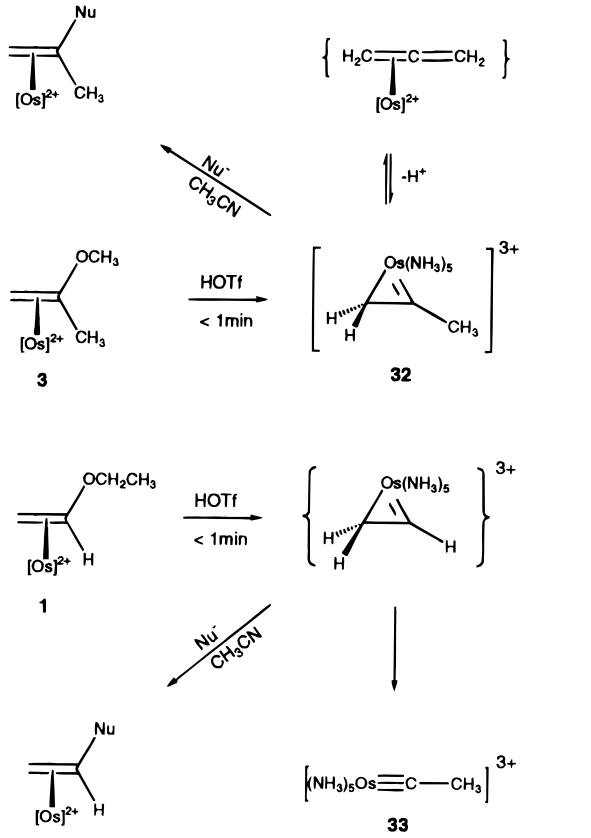



**Figure 8.** A comparison of reaction patterns for a vinyl ether complex with and without alkylation at the α-carbon.

features that are most consistent with the assignment of **10** as the Fischer carbene shown in Figure 3. Previously, we have observed that protonation of methoxycarbene complexes of pentaammineosmium results in formation of carbynes, and true to form, protonation of the mixture of the vinyl ether **9** and carbene **10** prepared from 3-butyn-1-ol (*vide supra*) results in the formation of carbyne complex **34** (via **10**) along with the cyclic imidate **25** (via **9**). Alternatively, protonation of the $\eta^2$-dihydrofuran complex **5** in HOTf or DME (2 M LiOTf) generates the corresponding carbyne complex **34**, but attempts to isolate **34** in analytically pure form were unsuccessful. Structural assignments of all carbene and carbyne complexes of pentaammineosmium(II) in this paper are made on the basis of a comparison of spectral data with previously reported pentaamminesosmium carbene and carbyne complexes.[17]

The ruthenium analog **8** of the ethoxyethene complex **1** behaves quite differently from its congener in acidic methanol.

A methanolic solution of **8** containing acid (HOTf, 0.30 M) was allowed to stand for 5 days, then the solution was added to a mixture of $CH_2Cl_2$ and $Et_2O$, and the precipitated salts were isolated. According to $^1H$ and $^{13}C$ NMR spectra ($CD_3CN$), the product mixture contains starting material and a new compound also containing ethoxyethene but shows no *trans*-ammine signal in the $^1H$ NMR. Incorporation of methanol was ruled out given the absence of a detectable methyl signal. Over time the product mixture slowly decomposes and free ethoxyethene is released.

## Discussion

**Features of Nucleophilic Substitution.** Nucleophilic addition and substitution reactions of olefins bound to cationic transition-metal complexes, particularly $Pd^{II}$,[20] $Pt^{II}$,[21] and $Fe^{II}$,[22] have been extensively studied and in many cases sucessfully applied to organic synthesis.[2a] The characteristic feature for these systems is the ability of the transition metal to activate the coordinated olefin toward nucleophilic addition and to stabilize the resulting carbanion through a $\sigma$ metal−alkyl bond that can be further elaborated. In the present study, the transition metal center is acting in a complimentary sense. Despite its divalent character, the pentaammineosmium(II) system acts as an electron donor through a substantial interaction with the olefin $\pi^*$ orbital. In the case of a vinyl ether or vinyl ester complex, for example, coordination by osmium(II) facilitates the loss of the oxygen substituent through the stabilization of the resulting vinyl cation. When the α-carbon contains an alkyl substituent (e.g., **32**), this intermediate can be isolated.

The fundamental difference in the vinyl ether substitution reactions observed for the pentaammineosmium(II) system and other cationic metal centers is that the substitution is electrophile-initiated. Whereas most nucleophilic substitutions of cationic transition metal olefin complexes (e.g., Fe(II) and Pt(II)) occur by addition−elimination processes,[23] the osmium(II) olefin system functions by an elimination−addition process. In the case of the acid-catalyzed isomerization and substitution reaction of the ethoxypropene complexes **7a** and **7b**, a dissociative substitution mechanism would explain the following experimental observations. Starting from a 1:1 equilibrated mixture of **7a** and **7b** in acidic methanol, the *trans* substitution product **12b** is formed much earlier than is the *cis* form **12a**. Inspection of molecular models reveals that the approach of a nucleophile (i.e., methanol) *trans* to the methyl substituent of the $\beta$-carbon for a hypothetical vinyl cation should be favored by steric arguments (Figure 9). When a 2:1 mixture of **7a** and **7b** is treated with an acid solution containing triphenylphosphine, where the nucleophile adds *irreversibly* to the olefin, the only product isolated is the *trans* isomer of $[Os(NH_3)_5(\eta^2$-1-propenyltriphenylphosphonium)$]^{3+}$, a vinylphosphonium complex analogous to **20**.[24] Further evidence comes from the equilibrium ratio of **7a** and **7b** which is 1:1 in ethanol. Assuming a dissociative mechanism where $k_{trans} > k_{cis}$ (*vide supra*) for loss of ethanol, the *addition of ethanol* to the vinyl cation *trans* to the methyl group must be more facile than that for the *cis* form in order to be consistent with the equilibrium

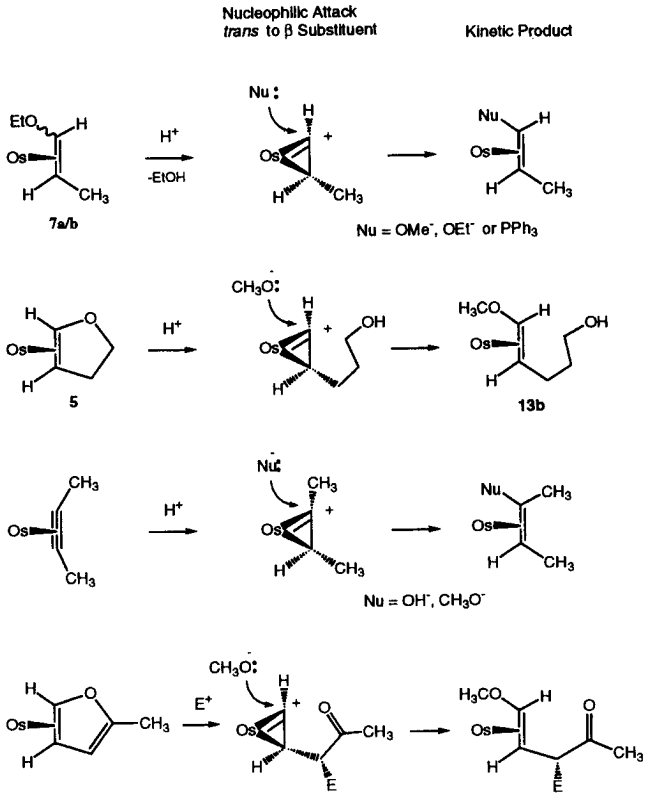



**Figure 9.** Stereochemistry of nucleophilic substitution of a vinyl ether or addition to an alkyne coordinated to pentammineosmium(II), and a comparison of the intermediate vinyl cation species.

data. This preference for addition to the vinyl cation *trans* to the $\beta$-carbon alkyl group is also seen for the dihydrofuran complex **5** where the kinetic isomer is **13b**, the *trans* isomer of the $\eta^2$-4-methoxy-3-buten-1-ol complex. Related to this is work concerning the electrophilic addition of $[Os(NH_3)_5(2,3\text{-}\eta^2$-(5-methylfuran))$]^{2+}$,[25] where we have observed that, upon electrophilic addition at C(4), the C(5)−O bond severs and methanol adds to C(2). The stereochemistry of the initial product (−40 °C) is once again *trans*. A final example can be found in the addition of methanol or water to the 2-butyne complex of pentaammineosmium(II).[5] Here, under acidic conditions, the addition of the nucelophile to the bound alkyne initially gives only substituted *cis*-2-butenes. In light of the present study, the addition is thought to be initiated by protonation of the alkyne ligand, resulting in a vinyl cation analogous to **32** (see Figure 9).[26] Subsequent addition of methanol or water *trans* to the $\beta$-carbon substituent of the vinyl cation leads to the *cis*-butene isomer. We note that, in the case of the enol, the thermodynamically favored isomer is formed from *cis* addition

(20) (a) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic: New York, 1985. (b) Hegedus, L. S. *Comprehensive Organic Synthesis*; Pergamon: Oxford, U.K., 1992; Vol. 4, Chapter 3.

(21) (a) Panunzi, A.; DeRenzi, A.; Palumbo, R.; Paiaro, G. *J. Am. Chem. Soc.* **1969**, *91*, 3879. (b) Panunzi, A.; DeRenzi, A.; Paiaro, G. *J. Am. Chem. Soc.* **1970**, *92*, 3488.

(22) (a) Lennon, P.; Madhavarao, M.; Rosan, A. M.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *108*, 93. (b) Lennon, P.; Rosan, A. M.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 8426.

(23) (a) Chang, T. C. T.; Rosenblum, M.; Samuels, S. B. *J. Am. Chem. Soc.* **1980**, *102*, 5930. (b) Marsi, M.; Rosenblum, M. *J. Am. Chem. Soc.* **1984**, *106*, 7264.

(24) Characterization of $[Os(NH_3)_5(\eta^2$-1-propenyltriphenylphosphonium)](OTf)$_3$. $^1H$ NMR (acetonitrile-$d_3$): $\delta$ 7.92−7.68 (m, 15 H, overlap of H-Ph), 4.68 (d, $J$ = 11.7 Hz, 2H, overlap of two olefinic protons), 4.42 (br s, 3H, *trans*-$NH_3$), 3.07 (br s, 12H, *cis*-$NH_3$), 1.73 (s, 3H, $CH_3$). $^{13}C$ NMR (acetonitrile-$d_3$): $\delta$ 135.89 (s, CH, *p*-C on Ph), 134.34 (d, $J_{PC}$ = 9.7 Hz, CH, *o*-C on Ph), 131.65 (d, $J_{PC}$ = 12.2 Hz, CH, *m*-C on Ph), 123.12 (d, $J_{PC}$ = 83.0 Hz, q, *ipso*-C on Ph), 46.81 (CH), 20.68 (d, $J_{PC}$ = 72.0 Hz, CH), 18.81 ($CH_3$). $^1H$ NMR (acetonitrile-$d_3$, −40 °C): $\delta$ 7.92−7.68 (m, 15 H, overlap of H-Ph), 4.71 (t, $J$ = 10.7 Hz, 1H, CH), 4.56 (m, 1H, CH), 4.38 (br s, 3H, *trans*-$NH_3$), 3.00 (br s, 12H, *cis*-$NH_3$), 1.68 (d, $J$ = 5.6 Hz, 3H, $CH_3$). Stereochemical assignment is made on the basis of the large vicinal coupling constant ($J_{HH}$ = 10.7 Hz).

(25) Chen, H.; Liu, R.; Harman, W. D. Manuscript in preparation.

(26) Protonation of the 2-butyne complex in absence of a nucleophile generates a vinyl cation analogous to **32**. Chen, H.; Harman, W. D. Unpublished results. Characterization of $[Os(NH_3)_5(\eta^2$-C(CH$_3$)CH(CH$_3$))](OTf)$_3$. $^1H$ NMR (acetonitrile-$d_3$/HOTf, ratio 5:1): $\delta$ 4.61 (br s, 3H, *trans*-$NH_3$), 4.29 (br s, 12H, *cis*-$NH_3$), 3.98 (m, 1H, CH), 2.36 (s, 3H, $CH_3$), 1.84 (d, $J$ = 6.8 Hz, 3H, $CH_3$). $^{13}C$ NMR (HOTf, with $CD_2Cl_2$ as internal reference): $\delta$ 299.40 (q), 44.02 (CH), 37.47 ($CH_3$), 10.92 ($CH_3$).

of the nucleophile (i.e., water). In the above cases, the stereochemistry of the kinetic products was self-consistent but was *independent* of the stereochemistry of the reactants. The isolation (triflate salt) and characterization of **32** as an $\eta^2$-vinyl cation species, in the context of the above observations, provides supporting evidence that the substitution process is dissociative in nature, especially when one considers the broad range of mild nucleophiles (silyl enol ethers, pyridine, dimethyl sulfide, phosphines, nitriles), which add on similar time scales. Finally, when equal amounts of the methoxyethene (**2**) and methoxypropene (**3**) complexes were dissolved in $CD_3OD$ and treated with acid (0.019 M HOTf, 22 °C), the more substituted propene complex underwent methoxide substitution at a rate that was >100-fold that of the ethene analog. Were these substitution reactions primarily associative, the relative rate of the less substituted olefin **2** would be expected to be significantly *faster* than that of the more hindered **3**. This result too is readily explained by a dissociative mechanism, where the extra methyl group on **3** stabilizes the vinyl cation intermediate.

The formation of the $\eta^2$-imidate salts **22**−**25** (Figure 5) from acetonitrile and various vinyl ether complexes provides an interesting example of vinyl substitution followed by nitrilium electrophilic addition that represents a net insertion of the nitrile into the vinyl ether C−O linkage. True to theme, the insertion reaction is thought to be initiated by the proton-assisted loss of alcohol to generate the corresponding vinyl cation. Addition of acetonitrile to the vinyl cation activates the nitrile carbon toward electrophilic addition by an alcohol, completing the formation of the vinyl imidate salt. This reaction is conceptually similar to the Pinner reaction or its modification by Borch that forms imidates from nitrilium salts and alcohols.[27] In order to verify that the acetonitrilium ion itself was not an active participant in this reaction, methylnitrilium triflate was combined with the vinyl ether **1** in absence of any alcohol, but under otherwise identical reaction conditions. Over a similar reaction period, no reaction was observed.

Of the known examples of transition metal complexes bearing vinyl ligands, most have the vinyl group attached through a single $\sigma$ bond ($\eta^1$). Few $\eta^2$-vinyl complexes are known to date, and these have been limited to earlier transition metals (e.g., Mo, W, or Re),[28] these species having been investigated for their possible role in insertion, oligomerization, and cocyclization reactions of alkynes. Rearrangements of $\eta^2$-vinyl species to carbyne, carbene, allene, and $\eta^3$-allyl complexes have also been demonstrated.[28] However, surprisingly little is known about their reactivity toward nucleophiles and electrophiles. Among the few well-studied $\eta^2$-vinyl complexes, *trans*-[ReCl{$\eta^2$-C($CH_2$Ph)$CH_2$}(dppe)$_2$][$BF_4$][29] and [Mo{$\eta^2$-C(R)CHPh}-{P($OMe$)$_3$}$_2$($\eta^5$-$C_5H_5$)][30] are useful comparisons for the osmium species **32**. Like these $\eta^2$-vinyl complexes of rhenium(III) and molybdenum(II), a resonance far downfield (299.8 ppm) is observed in the $^{13}$C NMR spectrum for the osmium(IV) species **32** (DOTf, 22 °C), characteristic of a carbon−metal multiple bond. The methylene resonance for **32** (29.2 ppm) is also in good agreement with the corresponding values for the Re and Mo systems. Finally, the chemical shifts of the *cis*- and *trans*-ammines are relatively close to each other, similar to those of pentaammineosmium carbene complexes.[17] On these grounds it would seem reasonable to describe **32** as a form of metallocyclopropene ($\eta^2$-vinyl) similar to the rhenium and molybdenum systems. Although the $\eta^2$-vinyl complexes of molybdenum(0), rhenium(I), and osmium(II) are likely to be structurally as well as spectroscopically similar, their chemical behavior is very different. The reaction between the weak acid $C_6F_5SH$ and [Mo{$\eta^2$-C(R)CHPh}{P($OMe$)$_3$}$_2$($\eta^5$-$C_5H_5$)] reveals that the vinyl ligand in this species behaves chemically as a vinyl anion; i.e., the α-carbon behaves like an alkylidine.[31] In contrast, the vinyl ligand of pentaammineosmium complex **32** functions as a vinyl cation; i.e., the α-carbon acts like a Fischer carbene (Figure 8).[32]

**Formation of Osmium Carbynes.** Over the last decade, several $\eta^2$-vinyl complexes of molybdenum and tungsten have been reported to undergo a 1,2 migration of hydrogen or trimethylsilyl to form carbyne complexes.[33] A similar transformation is invoked for the protonation of the vinyl ether complex **1** by HOTf (Figure 9) to form carbyne **33**. An $\eta^2$-vinyl cation intermediate analogous to [Os($NH_3$)$_5$($C_2H_5$)]$^{3+}$ (**32**) is expected to be the direct product of protonation, and this species proceeds through a 1,2-hydrogen shift to give the carbyne **33**. The isomerization of the $\eta^2$-vinyl cation [Os($NH_3$)$_5$-($C_2H_3$)]$^{3+}$ to [Os($NH_3$)$_5$(≡$CCH_3$)]$^{3+}$ can occur in principle by either an intra- or intermolecular process. The observation that compound **1** dissolved in neat DOTf results in a carbyne without any detectable incorporation of deuterium clearly indicates that the intramolecular mechanism is the only one operative under the stated reaction conditions. All attempts to deuterate the methyl group of the carbyne **33** or directly generate a vinylidine species by treating **33** with base have been unsuccessful.

In the case of the vinyl cation **32**, conversion to a carbyne would involve a 1,2-alkyl shift, a process expected to have a much higher kinetic barrier. In addition, the methyl group is able to stabilize the electrophilic α-carbon more effectively than a hydrogen through hyperconjugation; thus, carbyne complexes are not generated from vinyl ethers in cases where the α-carbon is alkylated. However, in contrast to the carbyne, the methyl group of the vinyl cation **32** is readily deuterated. Presumably this reaction occurs via an $\eta^2$-allene intermediate (Figure 9),[34] a species similar to that serving as the precursor to the $\eta^2$-vinyl species [ReCl{$\eta^2$-C($CH_2$Ph)$CH_2$}(dppe)$_2$][$BF_4$].[29]

**Conclusions.** Coordination of the electron-rich pentaammineosmium(II) moiety to a vinyl ether dramatically alters the structural and chemical nature of the ligand. These species readily undergo a vinylic substitution reaction, passing through a dihapto-coordinated vinyl cation intermediate. Using this method, a wide range of dihapto-coordinated pentaammineosmium(II) olefin complexes were synthesized from vinyl ether precursors. When the α-carbon of the vinyl ether is alkylated, the vinyl cation intermediate is stabilized to the point that it may be isolated as its triflate salt and characterized in acetonitrile or triflic acid solution. When the α-carbon bears only a

(27) (a) Neilson, D. G. In *The Chemistry of Amidines and Imidates*; Patai, S., Ed.; J. Wiley & Sons: New York, 1975; Chapter 9, pp 389−412. (b) Borch, R. F. *J. Org. Chem.* **1969**, *34*, 627.

(28) (a) Green, M. *J. Organomet. Chem.* **1986**, *300*, 93 and references within. (b) Pombeiro, A. J. L. *J. Organomet. Chem.* **1988**, *358*, 273 and references within.

(29) Pombeiro, A. J. L.; Hughes, D. L.; Richards, R. L.; Silvestre, J.; Hoffmann, R. *J. Chem. Soc., Chem. Commun.* **1986**, 1125.

(30) Allen, S. R.; Beevor, R. G.; Green, M.; Norman, N. C.; Orpen, A. G.; William, I. D. *J. Chem. Soc., Dalton Trans.* **1985**, *103*, 1267.

(31) Green, M.; Norman, N. C.; Orpen, A. G. *J. Am. Chem. Soc.* **1981**, *103*, 1267.

(32) Prior to publication of this paper a study by Green et al. appeared demonstrating hydride addition to a rhenium $\eta^2$-vinyl cation complex. See: Carfagna, C.; Carr, N.; Deeth, R. J.; Dossett, S. J.; Green, M.; Mahon, M. F.; Vaughan, C. *J. Chem. Soc., Dalton. Trans.* **1996**, 415.

(33) (a) For a review of the formation of carbyne complexes involving α,β-migration of hydrogen in a vinyl ligand, see: Mayr, A.; Hoffmeister, H. *Adv. Organomet. Chem.* **1991**, *32*, 251. (b) Bottrill, M.; Green, M. *J. Am. Chem. Soc.* **1977**, *99*, 5795. (c) Allen, S. R.; Beevor, R. G.; Green, M.; Orpen, A. G.; Paddick, K. E.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1987**, 591. (d) Atagi, L. M.; Mayer, J. M. *Polyhedron* **1995**, *14* (1), 113.

(34) Our attempts to generate an $\eta^2$-allene from **33** resulted in intractable mixtures.

hydrogen, a 1,2-hydrogen shift occurs in absence of nucleophiles, resulting in a pentaammineosmium(II) carbyne. Thus, for nucleophilic substitution a reaction pattern common to $sp^3$ carbons is imparted on vinylic systems through coordination to an electron-rich transition metal.

## Experimental Section

**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 parts per million and are referenced to residual proton-containing solvent ($\delta$(acetone-$d_5$) = 2.04; $\delta$(acetonitrile-$d_2$) = 1.93; $\delta$(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[35] from +1.8 to −1.8 V with a glassy carbon electrode. All potentials are reported vs 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 and 100 mV for all reversible couples unless otherwise noted. This work was carried out under a nitrogen atmosphere in a Vacuum Atmospheres Co. glovebox, separate boxes being used for aqueous and nonaqueous reactions. When necessary, the complexes were purified by (a) redissolving in acetone or acetonitrile and reprecipitation or (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.

**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. 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.[36] 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. Dihydrofuran and 2-methoxypropene were purified by distillation from $CaH_2$. All the other liquid reagents were used as received except that they were deoxygenated prior to use.

***N*-Methylacetonitrilium Triflate.** A modification of the reported procedure was used:[37] In a drybox, methyl triflate (837 mg, 5.10 mmol) was dissolved in acetonitrile (518 mg), and the reaction mixture was heated in an oil bath at 65−75 °C for 30 min. The reaction mixture was cooled to room temperature and then added dropwise to the chilled $CH_2Cl_2$, giving a yellow precipitate. The precipitate was filtered and washed with benzene. The yellow product was purified by repeated dissolving in acetonitrile and precipitating with $CH_2Cl_2$ to give a pale yellow powder. Yield: 680 mg (3.32 mmol, 66%).

**Complexes.** The synthesis and characterization of the furan complex $[Os(NH_3)_5(\eta^2\text{-furan})](OTf)_2$ (**6**) have been previously reported.[6a]

**$[Os(NH_3)_5(\eta^2\text{-ethoxyethene})](OTf)_2$ (1).** $[Os(NH_3)_5(OTf)](OTf)_2$ (1.32 g, 1.83 mmol) was dissolved in methanol (6.92 g), and this solution was added to a methanol (6.10 g) suspension of ethoxyethene (5.22 g, 72.4 mmol) and Zn/Hg (9.4 g). The slurry was stirred (22 °C) for 15 min and then filtered into a stirred mixture of $Et_2O$ (600 mL) and $CH_2Cl_2$ (200 mL), giving a light yellow precipitate. The precipitate was collected by filtration, washed with $CH_2Cl_2$ and $Et_2O$, and dried *in vacuo*. Yield: 1.07 g (1.66 mmol, 91%). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 5.70 (dd, $J$ = 6.3, 4.8 Hz, 1H, CH), 4.08 (br s, 3H, *trans*-$NH_3$), 3.69 (m, 2H, $CH_2$), 3.06 (dd, $J$ = 6.3, 2.4 Hz, 1H, $CH_2$), 3.00 (br s, 12H, *cis*-$NH_3$), 2.85 (dd, $J$ = 4.8, 2.4 Hz, 1H, $CH_2$), 1.13 (t, $J$ = 6.9 Hz, 3H, $CH_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 93.30 (CH), 71.00 ($CH_2$), 33.05 ($CH_2$), 15.57 ($CH_3$). CV ($CH_3CN$, TBAH, 100 mV/s): $E_{1/2}$ = 0.67 V (NHE). Anal. Calcd for $C_6H_{23}O_7N_5S_2OsF_6$: C, 11.16; H, 3.59; N, 10.85. Found: C, 10.90; H, 3.51; N, 10.50.

**$[Os(NH_3)_5(2,3\text{-}\eta^2\text{-methoxyethene})](OTf)_2$ (2).** A solution of **1** (55.7 mg, 0.0863 mmol) in methanol (398 mg) was added to a methanolic solution of HOTf (3.2 mg, 0.0216 mmol). After 1 h, the reaction mixture was added to $Et_2O$ (50 mL), giving a light yellow precipitate that was filtered, washed with $Et_2O$ and $CH_2Cl_2$, and dried *in vacuo*. Yield: 39.3 mg (0.0622 mmol, 72%). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 5.69 (dd, $J$ = 6.3, 5.1 Hz, 1H, CH), 4.07 (br s, 3H, *trans*-$NH_3$), 3.52 (s, 3H, $CH_3$), 3.09 (dd, $J$ = 6.3, 2.7 Hz, 1H, $CH_2$), 3.00 (br s, 12H, *cis*-$NH_3$), 2.84 (dd, $J$ = 5.1, 2.7 Hz, 1H, $CH_2$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 95.26 (CH), 63.18 ($CH_3$), 33.40 ($CH_2$). CV ($CH_3CN$, TBAH, 100 mV/s): $E_{1/2}$ = 0.67 V (NHE). Anal. Calcd for $C_5H_{21}O_7N_5S_2OsF_6$: C, 9.51; H, 3.35; N, 11.09. Found: C, 9.92; H, 3.42; N, 10.99.

**$[Os(NH_3)_5(2,3\text{-}\eta^2\text{-2-methoxypropene})](OTf)_2$ (3).** 2-Methoxypropene (4.15 g, 57.6 mmol) was dissolved in DME (3.76 g) and cooled to −20 °C. A solution of $[Os(NH_3)_5(OTf)](OTf)_2$ (827 mg, 1.14 mmol) in DMAc (896 mg) was added dropwise to the chilled ligand solution with $Mg^0$ (2.56 g, 0.107 mmol) present. The slurry was stirred for 30 min (22 °C) and was filtered into a mixture of $Et_2O$ (400 mL) and $CH_2Cl_2$ (400 mL). The resulting tan precipitate was filtered, washed with $Et_2O$, and dried *in vacuo*. Yield: 599 mg (0.927 mmol, 81%). **3** may also be prepared by reducing $[Os(NH_3)_5(OTf)](OTf)_2$ with Zn/Hg in methanol. $^1$H NMR (acetonitrile-$d_3$): $\delta$ 4.07 (br s, 3H, *trans*-$NH_3$), 3.48 (s, 3H, $OCH_3$), 3.26 (d, $J$ = 2.1 Hz, 1H, H-C3), 3.03 (br s, 12H, *cis*-$NH_3$), 2.91 (d, $J$ = 2.1 Hz, 1H, H-C3), 1.49 (s, 3H, $CH_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 94.95 (q), 59.29 ($OCH_3$), 35.63 ($CH_2$), 18.62 ($CH_3$). CV ($CH_3CN$, TBAH, 100 mV/s): $E_{1/2}$ = 0.61 V (NHE). Anal. Calcd for $C_6H_{23}O_7N_5S_2OsF_6$: C, 11.16; H, 3.59; N, 10.85. Found: C, 10.94; H, 3.42; N, 10.99.

**$[Os(NH_3)_5(2,3\text{-}\eta^2\text{-6}H\text{-4,5-dihydropyran})](OTf)_2$ (4).** $Mg^0$ (0.67 g, 28 mmol) was added to a solution of $[Os(NH_3)_5(OTf)](OTf)_2$ (332 mg, 0.460 mmol), 3,4-2*H*-dihydropyran (0.913 g, 10.6 mmol), DMAc (1.31 g), and DME (2.36 g), and the slurry was stirred for 2 h. The reaction mixture was filtered into $Et_2O$ (300 mL), and the product filtered, washed with $Et_2O$, and dried *in vacuo*. Yield: 216.4 mg (0.329 mmol, 72%). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 6.06 (d, $J$ = 6.0 Hz, 1H, H-C2), 4.03 (br s, 3H, *trans*-$NH_3$), 3.69 (dt, $J$ = 6.6, 2.4 Hz, 1H, H-C6), 3.55 (td, $J$ = 10.8, 2.4 Hz, 1H, H-C6), 3.35 (t, $J$ = 6.0 Hz, 1H, H-C3), 3.02 (br s, 12H, *cis*-$NH_3$), 2.80 (m, 1H, H-C4), 1.57 (m, 1H, H-C5), 1.51 (m, 1H, H-C4), 1.13 (m, 1H, H-C5). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 89.92 (C2), 66.10 (C6), 40.0 (C3), 24.95 (C5), 23.46 (C4). CV ($CH_3CN$, TBAH, 100 mV/s): $E_{1/2}$ = 0.49 V (NHE). Anal. Calcd for $C_7H_{23}O_7N_5S_2OsF_6$: C, 12.79; H, 3.53; N, 10.65. Found: C, 13.10; H, 3.64; N, 10.31.

**$[Os(NH_3)_5(2,3\text{-}\eta^2\text{-4,5-dihydrofuran})](OTf)_2$ (5).** The synthesis of **5** by direct hydrogenation of $[Os(NH_3)_5(2,3\text{-}\eta^2\text{-furan})](OTf)_2$ and its full characterization have been reported.[6a] In an alternative method, $[Os(NH_3)_5(OTf)](OTf)_2$ (1.04 g, 1.44 mmol) was dissolved in methanol (6.83 g), and the solution was added dropwise to a slurry of dihydrofuran (5.44 g, 77.6 mmol), Zn/Hg (11.4 g), and methanol (6.12 g). After being stirred for 9 min, the reaction mixture was filtered. The filtrate was concentrated and then added to a mixture of $CH_2Cl_2$ (500 mL) and $Et_2O$ (550 mL), producing a light orange precipitate that was collected, washed with $CH_2Cl_2$ and $Et_2O$, and dried *in vacuo*. Yield: 846 mg (1.31 mmol, 91%). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 6.11 (d, $J$ = 3.9 Hz, 1H, H-C2), 4.02 (dt, $J$ = 9.6, 4.2 Hz, 1H, H-C5), 3.99 (br s, 3H, *trans*-$NH_3$), 3.48 (t, $J$ = 4.2 Hz, 1H, H-C3), 3.02 (br s, 12H, *cis*-$NH_3$), 2.97 (q, $J$ = 9.0 Hz, 1H, H-C5), 2.75−2.62 (m, 1H, H-C4), 1.81 (ddd, $J$ = 13.5, 8.4, 4.5 Hz, 1H, H-C4). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 95.43 (C2), 69.39 (C5), 37.64 (C3), 30.05 (C4). CV ($CH_3CN$,

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

(36) (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.

(37) Booth, B. L.; Jibodu, K. O.; Proenca, M. F. *J. Chem. Soc., Chem. Commun.* **1980**, 1151.

TBAH, 100 mV/s): $E_{1/2}$ = 0.63 V (NHE). Anal. Calcd for $C_6H_{21}O_7N_5S_2OsF_6$: C, 11.20; H, 3.29; N, 10.88. Found: C, 11.52; H, 3.37; N, 11.22.

**[Os(NH$_3$)$_5$(2,3-$\eta^2$-furan)](OTf)$_2$ (6).**[6a] $^1$H NMR (acetonitrile-$d_3$): $\delta$ 7.25 (d, $J$ = 3.3 Hz, 1H, H-C2), 6.90 (d, $J$ = 2.7 Hz, 1H, H-C5), 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 (acetonitrile-$d_3$): $\delta$ 142.69 (C5), 111.96 (C4), 98.64 (C2), 48.96 (C3).

**[Os(NH$_3$)$_5$(*cis*-$\eta^2$-1-ethoxypropene)](OTf)$_2$ (7a) and [Os(NH$_3$)$_5$(*trans*-$\eta^2$-1-ethoxypropene)](OTf)$_2$ (7b).** [Os(NH$_3$)$_5$(OTf)](OTf)$_2$ (426 mg, 0.589 mmol) was dissolved in methanol (4.10 g) and added to a methanol (1.55 g) suspension of 1-ethoxypropene (2.75 g, 31.9 mmol) and Zn/Hg (3.4 g). The slurry was stirred for 15 min and then filtered into a stirred mixture of Et$_2$O (250 mL) and CH$_2$Cl$_2$ (50 mL), giving a light yellow precipitate. The precipitate was collected by filtration, washed with CH$_2$Cl$_2$ and Et$_2$O and dried *in vacuo*. Yield: 359 mg (0.544 mmol, 92%). The solid appeared by $^1$H NMR to be in a 2:1 ratio. CV (CH$_3$CN, TBAH, 100 mV/s): $E_{1/2}$ = 0.66 V (NHE). Anal. Calcd for $C_7H_{25}N_5O_7S_2OsF_6$: C, 12.75 H, 3.82; N, 10.62. Found: C, 12.56; H, 3.91; N, 10.60.

**7a (Major Isomer).** $^1$H NMR (acetonitrile-$d_3$): $\delta$ 5.53 (d, $J$ = 5.2 Hz, 1H), 3.99 (br s, 3H, *trans*-NH$_3$), 3.72 (m, 2H, CH$_2$), 3.44 (m, 1H, CH), 2.97 (br s, 12H, *cis*-NH$_3$), 1.20 (d, $J$ = 6.9 Hz, 3H, CH$_3$), 1.16 (t, $J$ = 6.7 Hz, 3H, CH$_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 92.84 (CH), 69.10 (CH$_2$), 38.55 (CH), 15.65 (CH$_3$), 10.94 (CH$_3$).

**7b (Minor Isomer).** $^1$H NMR (acetonitrile-$d_3$): $\delta$ 5.64 (d, $J$ = 6.0 Hz, 1H), 3.99 (br s, 3H, *trans*-NH$_3$), 3.70 (q, $J$ = 7.2 Hz, 2H, CH$_2$), 3.12 (m, 1H, CH), 2.97 (br s, 12H, *cis*-NH$_3$), 1.25 (d, $J$ = 6.0 Hz, 3H, CH$_3$), 1.16 (t, $J$ = 6.7 Hz, 3H, CH$_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 95.26 (CH), 70.81 (CH$_2$), 39.75 (CH), 15.66 (CH$_3$), 14.06 (CH$_3$).

**[Ru(NH$_3$)$_5$($\eta^2$-ethoxyethene)](OTf)$_2$ (8).** A solution of ethoxyethene (1.64 g, 22.7 mmol) was prepared in acetone (1.18 g) and cooled to −20 °C. [Ru(NH$_3$)$_5$(OTf)](OTf)$_2$ (827 mg, 0.352 mmol) was dissolved in acetone (1.10 g), and the solution added dropwise into the chilled ligand solution along with Zn/Hg (8.5 g). The slurry was stirred for 20 min (22 °C), and then filtered into a mixture of Et$_2$O (300 mL) and CH$_2$Cl$_2$ (200 mL). The white precipitate was filtered, washed with Et$_2$O and CH$_2$Cl$_2$, and dried *in vacuo*. Yield: 135 mg (0.243 mmol, 69%). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 5.89 (dd, $J$ = 8.7, 5.1 Hz, 1H, CH), 3.81 (m, 2H, CH$_2$), 3.57 (br s, 3H, *trans*-NH$_3$), 3.08 (dd, $J$ = 8.7, 2.2 Hz, 1H, CH$_2$), 2.84 (dd, $J$ = 5.1, 2.2 Hz, 1H, CH$_2$), 1.82 (br s, 12H, *cis*-NH$_3$), 1.20 (t, $J$ = 6.9 Hz, 3H, CH$_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 112.65 (CH), 70.73 (OCH$_2$), 49.85 (CH$_2$), 15.32 (CH$_3$). CV (CH$_3$CN, TBAH, 100 mV/s): $E_{p,a}$ = 1.14 V (NHE). Anal. Calcd for $C_6H_{25}N_5O_7S_2RuF_6$: C, 12.95; H, 4.17; N, 12.59. Found: C 13.30; H 4.33; N 12.73.

**[Os(NH$_3$)$_5$(3,4-$\eta^2$-3-methoxy-3-buten-1-ol)](OTf)$_2$ (9) and [Os(NH$_3$)$_5$(2-oxacyclopentylidene)](OTf)$_2$ (10).** [Os(NH$_3$)$_5$(OTf)](OTf)$_2$ (107 mg, 0.148 mmol) was dissolved in methanol (1.45 g), and then 3-butyn-1-ol (413 mg, 5.89 mmol) and Zn/Hg (797 mg) were added. After stirring (5 min), the slurry was filtered into CH$_2$Cl$_2$ (200 mL), producing an orange yellow precipitate that was collected, washed with CH$_2$Cl$_2$ and Et$_2$O, and dried *in vacuo*. Yield: 70 mg. The solid appeared by $^1$H NMR to be a mixture of **9** and **10** in a 3:2 ratio.

**9.** $^1$H NMR (acetonitrile-$d_3$): $\delta$ 4.04 (br s, 3H, *trans*-NH$_3$), 3.89 (m, 2H, H-C1), 3.45 (s, 3H, OCH$_3$), 3.23 (d, $J$ = 2.7 Hz, 1H, H-C4), 3.20 (br s, 12H, *cis*-NH$_3$), 2.86 (d, $J$ = 2.7 Hz, 1H, H-C4), 2.76 (q, $J$ = 15 Hz, 1H, H-C2), 1.40 (ddd, $J$ = 15.6, 9.6, 4.5 Hz, H-C2), OH(?). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 91.3 (C3), 59.6 (OCH$_3$), 58.0 (C1), 38.0 (C4), 38.0 (C2).

**10.** $^1$H NMR (acetonitrile-$d_3$): $\delta$ 4.39 (t, $J$ = 7.5 Hz, 2H, H-C3), 3.18 (br s, 15H, *trans*- and *cis*-NH$_3$), 2.04 (quintet, $J$ = 7.5 Hz, 2H, H-C4), 1.49 (t, $J$ = 7.5 Hz, 2H, H-C4). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 256.5 (Os=C), 77.9 (C3), 53.0 (C5), 24.6 (C4).

**[Os(NH$_3$)$_5$($\eta^2$-hydroxyethene)](BPh$_4$)$_2$ (11).** To a solution of **1** (55.5 mg, 0.0860 mmol) in H$_2$O (654 mg) was added a solution of HOTf (8.6 mg, 0.0573 mmol) in H$_2$O (110 mg). After 10 min, a saturated aqueous solution of NaBPh$_4$ was added to the reaction mixture, giving a white precipitate. The solid was collected, washed with H$_2$O, and dried *in vacuo*. Yield: 65.2 mg (0.0674 mmol, 78%). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 7.29 (br s, 16H, H-Ph), 7.01 (t, $J$ = 7.2 Hz, 16H, H-Ph), 6.86 (t, $J$ = 7.2 Hz, 8H, H-Ph), 5.93 (m, 1H, H-C1), 3.83 (d, $J$ = 4.0 Hz, 1H, OH), 3.70 (br s, 3H, *trans*-NH$_3$), 2.99 (dd, $J$ = 6.9, 2.9 Hz, 1H, H-C2), 2.78 (br s, 12H, *cis*-NH$_3$), 2.76 (dd, $J$ = 5.2, 2.9 Hz, 1H, H-C2). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 165.08 (m, $J_{B-C}$ = 50.6 Hz, Ph), 136.69 (Ph), 126.64 (Ph), 122.8 (Ph), 88.49 (C1), 32.35 (C2). Anal. Calcd for $C_{50}H_{59}ON_5B_2Os\cdot{}^1/_2H_2O$: C, 62.11; H, 6.26; N, 7.24. Found: C, 61.86; H, 6.42; N, 7.70.

**[Os(NH$_3$)$_5$(*cis*-$\eta^2$-1-methoxypropene)](OTf)$_2$ (12a) and [Os(NH$_3$)$_5$(*trans*-$\eta^2$-1-methoxypropene)](OTf)$_2$ (12b).** A solution of triflic acid (10.4 mg, 0.0693 mmol) in methanol was added to a solution of a 2:1 mixture of complexes **7a** and **7b** (67.2 mg, 0.102 mmol). After 4 h, the solution was added to Et$_2$O (60 mL), producing a light yellow precipitate that was filtered, washed with Et$_2$O and CH$_2$Cl$_2$, and dried *in vacuo*. Yield: 42.2 mg (0.0653 mmol, 64%). The solid appeared by $^1$H NMR to be a mixture of two isomers **12a** and **12b** in a 1:1 ratio. Anal. Calcd for $C_6H_{23}N_5O_7S_2OsF_6$: C, 11.16; H, 3.59; N, 10.85. Found: C, 11.58; H, 3.84; N, 10.70.

**12a.** $^1$H NMR (acetonitrile-$d_3$): $\delta$ 5.48 (d, $J$ = 5.4 Hz, 1H), 4.00 (br s, 3H, *trans*-NH$_3$), 3.54 (s, 3H, OCH$_3$), 3.45 (m, 1H, CH), 2.98 (br s, 12H, *cis*-NH$_3$), 1.16 (d, $J$ = 6.9 Hz, CH$_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 94.41 (CH), 60.92 (OCH$_3$), 38.34 (CH), 10.70 (CH3).

**12b.** $^1$H NMR (acetonitrile-$d_3$): $\delta$ 5.65 (d, $J$ = 5.7 Hz, 1H), 3.99 (br s, 3H, *trans*-NH$_3$), 3.54 (s, 3H, CH$_3$), 3.13 (m, 1H, CH), 2.97 (br s, 12H, *cis*-NH$_3$), 1.27 (t, $J$ = 6.7 Hz, 3H, CH$_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 97.00 (CH), 63.07 (CH$_3$), 39.22 (CH), 14.24 (CH$_3$).

**[Os(NH$_3$)$_5$(*cis*-3,4-$\eta^2$-4-methoxy-3-buten-1-ol)](OTf)$_2$ (13a) and [Os(NH$_3$)$_5$(*trans*-3,4-$\eta^2$-4-methoxy-3-buten-1-ol)](OTf)$_2$ (13b).** A solution of triflic acid (8.2 mg, 0.055 mmol) in methanol (200 mg) was added to a solution of **5** (121 mg, 0.188 mmol) in methanol (611 mg). After 9 h, *N*,*N*-diisopropylethylamine (12.9 mg, 0.100 mmol) was added to the reaction mixture. After 5 min, the reaction mixture was added to Et$_2$O (120 mL), producing a tan precipitate that was filtered, washed with Et$_2$O and CH$_2$Cl$_2$, and dried *in vacuo*. Yield: 89.1 mg. The solid appeared by $^1$H NMR to be a mixture of two isomers and starting material in a 6:3:1 ratio. CV (CH$_3$CN, TBAH, 100 mV/s): $E_{p,a}$ = 0.78 V (NHE).

**13a (Minor Isomer).** $^1$H NMR (acetonitrile-$d_3$): $\delta$ 5.44 (d, $J$ = 5.4 Hz, 1H, H-C4), 4.03 (br s, 3 H, *trans*-NH$_3$), 3.80 (m, 2H, H-C1), 3.56 (s, 3H, OCH$_3$), 3.06 (m, 1H, overlap with *cis*-NH$_3$, H-C3), 3.06 (br s, 12H, *cis*-NH$_3$), 2.03 (m, 1H, H-C2), 1.38 (m, 1H, H-C2). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 93.58 (C4), 62.73 (C1), 60.72 (OCH$_3$), 38.73 (C3), 29.23 (C2).

**13b (Major Isomer).** $^1$H NMR (acetonitrile-$d_3$): $\delta$ 5.70 (d, $J$ = 6.0 Hz, 1H, H-C4), 3.74 (m, 2H, H-C1), 4.07 (br s, 3H, *trans*-NH$_3$), 3.53 (s, 3H, OCH$_3$), 3.41 (m, 1H, H-C3), 3.07 (br s, 12 H, *cis*-NH$_3$), 1.42 (m, 1H, H-C2), 1.19 (m, 1H, H-C2). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 95.77 (C4), 62.19 (OCH$_3$), 62.19 (C1), 40.13 (C3), 32.42 (C2).

When the reaction is run at −40 °C, and 3 days later worked up under the same conditions, the recovered product is exclusively **13b** in a yield of 62%. Anal. Calcd for $C_7H_{25}O_8N_5S_2OsF_6$: C, 12.45; H, 3.73; N, 10.37. Found: C, 12.47; H, 3.77; N, 10.25.

**[Os(NH$_3$)$_5$($\eta^2$-carbomethoxyethene)](OTf)$_2$ (14).** The ethoxyethene complex **1** (116 mg, 0.179 mmol) was dissolved in acetic acid (1.09 g) at 22°C. After 50 min, this solution was added to a mixture of Et$_2$O (60 mL) and CH$_2$Cl$_2$ (60 mL), producing a pale yellow precipitate. This solid was filtered, washed with Et$_2$O and CH$_2$Cl$_2$, and dried *in vacuo*. Yield: 109 mg (0.165 mmol, 92%). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 6.92 (t, $J$ = 5.9 Hz, 1H, CH), 4.16 (br s, 3H, *trans*-NH$_3$), 3.39 (dd, $J$ = 5.9, 3.3Hz, 1H, CH$_2$), 3.19 (dd, $J$ = 5.9, 3.3 Hz, 1H, CH$_2$), 3.11 (br s, 12H, *cis*-NH$_3$), 1.99 (s, 3H, CH$_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 174.07 (q), 87.08 (CH), 31.34 (CH$_2$), 21.23 (CH$_3$). Anal. Calcd for $C_6H_{21}O_8N_5S_2OsF_6$: C, 10.93; H, 3.21; N, 10.62. Found: C, 10.79; H, 3.23; N, 10.56.

**[Os(NH$_3$)$_5$($\eta^2$-2-carbomethoxypropene)](OTf)$_2$ (15).** The 2-methoxypropene complex **3** (46.6 mg, 0.0722 mmol) was dissolved in acetic acid (1.35 g, 22 °C), and after 1 h, the solution was added to a mixture of Et$_2$O (35 mL) and CH$_2$Cl$_2$ (35 mL), producing a pale yellow precipitate. This solid was filtered, washed with Et$_2$O and CH$_2$Cl$_2$, and dried *in vacuo*. Yield: 42.2 mg (0.0626 mmol, 88%). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 4.11 (br s, 3H, *trans*-NH$_3$), 3.42 (d, $J$ = 5.7 Hz, 1 H, CH$_2$), 3.30 (d, $J$ = 5.7 Hz, 1H, CH$_2$), 3.10 (br s, 12H, *cis*-NH$_3$), 1.91 (s, 3H, CH$_3$), 1.56 (s, 3H, CH$_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 172.11 (q), 90.84 (q), 38.08 (CH$_2$), 21.46 (CH$_3$), 21.19 (CH$_3$). CV

($CH_3CN$, TBAH, 100 mV/s): $E_{1/2} = 0.86$ V (NHE). Anal. Calcd for $C_7H_{23}O_8N_5S_2OsF_6$: C, 12.48; H, 3.44; N, 10.40. Found: C, 12.38; H, 3.35; N, 10.49.

**[Os(NH$_3$)$_5$($\eta^2$-vinyldimethylsulfonium)](OTf)$_3$ (16).** A solution of complex **1** (116 mg, 0.180 mmol) in acetonitrile (500 mg) was combined with methyl sulfide (93.2 mg), followed by TMSOTf (69.5 mg, 0.263 mmol). After 10 min, the yellow reaction mixture was added to $Et_2O$, giving a precipitate that was filtered, washed with $Et_2O$ and $CH_2Cl_2$, and dried *in vacuo*. Yield: 140 mg (0.173 mmol, 96%). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 4.73 (t, $J = 7.8$ Hz, 1H, H-C1), 4.51 (br s, 3H, *trans*-$NH_3$), 4.15 (dd, $J = 7.8$, 3.9 Hz, 1H, H-C2), 3.94 (dd, $J = 7.8$, 3.9 Hz, H-C2), 3.40 (br s, 12H, *cis*-$NH_3$), 3.06 (s, 3H, $CH_3$), 2.92 (s, 3H, $CH_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 48.77 (C1), 38.47 (C2), 33.81 ($CH_3$), 27.99 ($CH_3$). Anal. Calcd for $C_7H_{24}O_9N_5S_4OsF_9$: C, 10.36; H, 2.98; N, 8.63. Found: C, 10.72; H, 3.12; N, 8.62.

**[Os(NH$_3$)$_5$($\eta^2$-1-(*N*-phenylamino)ethene)](OTf)$_2$ (17).** Complex **1** (34.4 mg, 0.0533 mmol) was dissolved in a mixture of acetic acid (400 mg) and aniline (200 mg). After 3 h, the reaction mixture was precipitated in a mixture of $Et_2O$ (35 mL) and hexane (35 mL), giving a tan precipitate that was filtered, washed with $Et_2O$ and $CH_2Cl_2$, and dried *in vacuo*. Yield: 30.5 mg (0.0440 mmol, 83%). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 7.16 (dd, $J = 8.1$, 7.2 Hz, 2H, H-Ph), 6.87 (d, $J = 8.1$ Hz, 2H, H-Ph), 6.67 (t, $J = 7.2$ Hz, 1H, H-Ph), 5.30 (dd, $J = 8.2$, 6.7 Hz, 1H, H-C1), 4.03 (br s, 3H, *trans*-$NH_3$), 3.16 (dd, $J = 6.7$, 2.0 Hz, 1H, H-C2), 3.13 (dd, $J = 8.2$, 2.0 Hz, 1H, H-C2), 3.06 (br s, 12H, *cis*-$NH_3$). $^1$H NMR (acetone-$d_6$): $\delta$ 7.08 (dd, $J = 8.1$, 7.5 Hz, 2H, H-Ph), 6.90 (d, $J = 8.1$ Hz, 2H, H-Ph), 6.57 (t, $J = 7.5$ Hz, 1H, H-Ph), 5.57 (dd, $J = 7.8$, 6.9 Hz, 1H, H-C1), 4.69 (br s, 3H, *trans*-$NH_3$), 3.68 (br s, 12H, *cis*-$NH_3$), 3.38 (dd, $J = 6.9$, 1.8 Hz, 1H, H-C2), 3.36 (dd, $J = 7.8$, 1.8 Hz, 1H, H-C2). $^{13}$C NMR (acetone-$d_6$): $\delta$ 151.02 (Ph), 129.66 (Ph), 117.58 (Ph), 113.93 (Ph), 65.18 (C1), 36.02 (C2). The crude product was redissolved in acetonitrile and treated with 2 equiv of *N*,*N*-diisopropylethylamine. After 5 min, the solution was reprecipitated to give a clean product. Anal. Calcd for $C_{10}H_{24}O_6N_6S_2OsF_6$: C, 17.34; H, 3.49; N, 12.13. Found: C, 17.23; H, 3.76; N, 11.74.

**[Os(NH$_3$)$_5$($\eta^2$-2-(*N*-phenylamino)propene)](OTf)$_2$ (18).** Complex **3** (52.7 mg, 0.0816 mmol) was dissolved in a mixture of acetic acid (727 mg) and aniline (345 mg, 22 °C). After 2 h, the reaction mixture was added to a mixture of $Et_2O$ (45 mL) and hexane (15 mL), giving a light yellow precipitate. The solid was filtered, washed with $Et_2O$ and $CH_2Cl_2$, and dried *in vacuo*. Yield: 49.3 mg (0.0698 mmol, 86%). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 7.16 (dd, $J = 7.5$, 7.2 Hz, 2H, H-Ph), 6.98 (d, $J = 7.5$ Hz, 2H, H-Ph), 6.67 (t, $J = 7.2$ Hz, 1H, H-Ph), 4.20 (br s, 3H, *trans*-$NH_3$), 3.59 (d, $J = 1.2$ Hz, 2H, $CH_2$), 3.18 (br s, 12H, *cis*-$NH_3$), 1.45 (s, 3H, $CH_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 150.09 (Ph), 129.90 (Ph), 118.9 (Ph), 115.5 (Ph), 64.70 (C1), 47.98 (C2), 22.06 ($CH_3$). The product was redissolved in acetone, treated with *N*,*N*-diisopropylethylamine, and then reprecipitated in the mixture of $Et_2O$ and hexane. Yield: 70%. Anal. Calcd for $C_{11}H_{26}O_6N_6S_2OsF_6$: C, 18.70; H, 3.71; N, 11.89. Found: C, 18.50; H, 3.78; N, 11.99.

**[Os(NH$_3$)$_5$($\eta^2$-*N*-vinylpyridinium)](OTf)$_3$ (19).** A solution of **16** (35.3 mg, 0.0435 mmol) in acetonitrile (1 g) was treated with pyridine (15 mg, 0.19 mmol). After 5 min, the reaction solution was added to a mixture of $Et_2O$ (40 mL) and $CH_2Cl_2$ (10 mL), giving a peach precipitate that was filtered, washed with $Et_2O$ and $CH_2Cl_2$, and dried *in vacuo*. Yield: 31.0 mg (0.0374 mmol, 86%). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 8.71 (d, $J = 5.8$ Hz, 2H, *o*-H on py), 8.46 (t, $J = 6.9$ Hz, 1H, *p*-H on py), 7.94 (t, $J = 7.0$ Hz, 2H, *m*-H on py), 6.56 (t, $J = 7.4$ Hz, 1H, CH), 4.94 (dd, $J = 7.4$, 5.4 Hz, 1H, $CH_2$), 4.48 (br s, 3H, *trans*-$NH_3$), 4.04 (dd, $J = 7.4$, 5.4 Hz, 1H, $CH_2$), 3.26 (br s, 12H, *cis*-$NH_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 144.24 (CH), 140.90 (CH), 130.49 (CH), 70.25 (CH), 30.49 ($CH_2$). Anal. Calcd for $C_{10}H_{23}O_9N_6S_3OsF_9$: C, 14.49; H, 2.80; N, 10.14. Found: C, 14.21; H, 2.83; N, 9.98.

**[Os(NH$_3$)$_5$($\eta^2$-vinyltriphenylphosphonium)](OTf)$_3$ (20).** A solution of complex **1** (41.5 mg, 0.0643 mmol) in acetonitrile (500 mg) was treated with triphenylphosphine (43.1 mg, 0.164 mmol), followed by $BF_3{\cdot}OEt_2$ (18.4 mg, 0.130 mmol). After 2 days, the orange reaction solution was added to $Et_2O$, giving an orange solid that was filtered, washed with $Et_2O$, and dried *in vacuo*. Yield: 53.4 mg (0.0528 mmol, 82%). $^1$H NMR (acetone-$d_6$): $\delta$ 8.15 (dd, $J = 11.7$, 7.5 Hz, 6H, H-Ph), 7.88 (dd, $J = 7.5$, 6.6 Hz, 3H, H-Ph), 7.77 (m, 6H, H-Ph), 5.08 (br s, 3H, *trans*-$NH_3$), 5.08 (m, overlap with *trans*-$NH_3$, 1H, H-C1), 4.84 (m, 1H, H-C2), 4.73 (m, 1H, H-C2), 3.71 (br s, 12H, *cis*-$NH_3$). $^{13}$C NMR (acetone-$d_6$): $\delta$ 135.57 (s, CH, *p*-C on Ph), 134.68 (d, $J_{PC} = 7.4$ Hz, CH, *o*-C on Ph), 131.44 (d, $J_{PC} = 11.1$ Hz, CH, *m*-C on Ph), 123.09 (d, $J_{PC} = 79.0$ Hz, q, *ipso*-C on Ph), 39.40 ($CH_2$), 17.49 (d, $J_{PC} = 69.5$ Hz, CH). Anal. Calcd for $C_{23}H_{33}O_9N_5S_3OsF_9$: C, 27.30; H, 3.29; N, 6.92. Found: C, 27.30; H, 3.67; N, 7.44.

**[Os(NH$_3$)$_5$($\eta^2$-isopropenyltriphenylphosphonium)](OTf)$_3$ (21).** A solution of complex **3** (40.8 mg, 0.0632 mmol) in acetonitrile (400 mg) was treated with triphenylphosphine (33.0 mg, 0.125 mmol), followed by $BF_3{\cdot}OEt_2$ (16.0 mg, 0.112 mmol). After 1 h, the reaction was added to $Et_2O$ (70 mL), giving a yellow precipitate that was filtered, washed with $Et_2O$, and dried *in vacuo*. Yield: 44.2 mg (0.0443 mmol, 70%). $^1$H NMR (acetone-$d_6$): $\delta$ 8.07 (dd, $J = 10.8$, 8.7 Hz, 6H, H-Ph), 7.91 (dd, $J = 7.5$, 6.9 Hz, 3H, H-Ph), 7.80 (m, 6H, H-Ph), 5.36 (dd, $J = 17.4$, 2.7 Hz, 1H, H-C2), 5.06 (br s, 3H, *trans*-$NH_3$), 4.88 (dd, $J = 15.9$, 2.7 Hz, 1H, H-C2), 3.76 (br s, 12H, *cis*-$NH_3$), 1.96 (d, $J = 14.7$ Hz, 3H, $CH_3$). $^{13}$C NMR (acetone-$d_6$): $\delta$ 135.61 (s, CH, *p*-C on Ph), 135.37 (d, $J_{PC} = 8.9$ Hz, CH, *o*-C on Ph), 131.47 (d, $J_{PC} = 12.1$ Hz, CH, *m*-C on Ph), 121.77 (d, $J_{PC} = 79.5$ Hz, q, *ipso*-C on Ph), 53.26 ($CH_2$), 25.35 (d, $J_{PC} = 12.5$ Hz, $CH_3$), 23.75 (d, $J_{PC} = 54.1$ Hz, q).

**[Os(NH$_3$)$_5$(ethyl $\eta^2$-*N*-vinylacetimidate)·(HOTf)](OTf)$_2$ (22).** A solution of **1** (53.4 mg, 0.0827 mmol) in acetonitrile (661 mg) was added to a solution of HOTf (29.0 mg, 0.166 mmol) in acetonitrile (120 mg). After 10 min, the yellow reaction mixture was added to a mixture of $Et_2O$ (60 mL) and $CH_2Cl_2$ (30 mL), giving a yellow precipitate that was filtered, washed with $CH_2Cl_2$ and $Et_2O$, and dried *in vacuo*. Yield: 62.0 mg (0.0740 mmol, 90%). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 9.57 (br s, 1 H, H-N), 5.90 (dd, $J = 7.2$, 6.9 Hz, 1H, CH), 4.30 (br s, 3H, *trans*-$NH_3$), 4.57 (q, $J = 6.9$ Hz, 2H, $CH_2$), 3.87 (dd, $J = 7.2$, 3.6 Hz, 1H, $CH_2$), 3.50 (dd, $J = 6.9$, 3.6 Hz, 1H, $CH_2$), 3.21 (br s, 12 H, *cis*-$NH_3$), 2.38 (s, 3H, $CH_3$), 1.49 (t, $J = 6.9$ Hz, 3H, $CH_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 176.17 (q), 71.98 ($OCH_2$), 57.84 (CH), 33.80 ($CH_2$), 18.97 ($CH_3$), 15.57 ($CH_3$). Anal. Calcd for $C_9H_{27}N_6O_{10}S_3OsF_9$: C, 12.92; H, 3.25; N, 10.04. Found: C, 12.62; H, 3.28; N, 10.13.

**[Os(NH$_3$)$_5$(4,5-$\eta^2$-7,8-dihydro-2-methyl-6*H*-1,3-oxazocine)·HOTf)](OTf)$_2$ (23).** A solution of **4** (89.4 mg, 0.136 mmol) in acetonitrile (2.30 g) was treated with HOTf (134 mg, 0.893 mmol). After 10 min, the reaction mixture was added to $CH_2Cl_2$ (100 mL), giving an orange yellow precipitate that was filtered, washed with $CH_2Cl_2$ and $Et_2O$, and dried *in vacuo*. Yield: 99.2 mg (0.117 mmol, 86%). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 8.79 (br s, 1H, H-N), 5.72 (td, $J = 12.0$, 0.9 Hz, 1H, H-C8), 5.62 (d, $J = 6.9$ Hz, 1H, H-C4), 4.60 (dd, $J = 12.0$, 4.5 Hz, 1H, H-C8), 4.30 (br s, 3H, *trans*-$NH_3$), 3.69 (ddd, $J = 12.0$, 6.9, 2.7 Hz, 1H, H-C5), 3.25 (br s, 12H, *cis*-$NH_3$), 2.36 (s, 3H, $CH_3$), 2.31 (overlap with $CH_3$, 1H, H-C7), 1.88 (m, 1H, H-C6), 1.79 (m, 1H, H-C7), 1.41 (m, 1H, H-C6). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 177.70 (C2), 74.57 (C8), 58.70 (C4), 46.14 (C5), 28.37 (C7), 23.25 (C6), 23.30 ($CH_3$). Anal. Calcd for $C_{10}H_{27}N_6O_{10}S_3OsF_9$: C, 14.15; H, 3.21; N, 9.90. Found: C 13.90; H 2.83; N 9.09.

**[Os(NH$_3$)$_5$(4,5-$\eta^2$-6,7-dihydro-2-methyl-6*H*-1,3-oxazepine)·(HOTf)](OTf)$_2$ (24).** A solution of **5** (84.1 mg, 0.131mmol) in acetonitrile (660 mg) was treated with HOTf (47.5 mg, 0.317 mmol). After 10 min, the reaction mixture was added to $CH_2Cl_2$ (100 mL), giving an orange yellow precipitate that was filtered, washed with $CH_2Cl_2$ and $Et_2O$, and dried *in vacuo*. Yield of yellow powder: 94.0 mg (0.113 mmol, 86%). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 9.59 (br s, 1H, H-N), 5.57 (d, $J = 6.9$ Hz, H-C4), 5.03 (m, 1H, H-C7), 4.97 (m, 1H, H-C7), 4.32 (br s, 3H, *trans*-$NH_3$), 4.09 (q, $J = 7.5$ Hz, H-C5), 3.25 (br s, 12H, *cis*-$NH_3$), 2.58 (m, 1H, H-C6), 2.34 (s, 3H, $CH_3$), 1.94 (m, 1H, H-C6). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 173.64 (C2), 78.32 (C7), 58.97 (C4), 45.25 (C5), 31.57 (C6), 23.40 ($CH_3$). Anal. Calcd for $C_9H_{25}N_6O_{10}S_3OsF_9$: C, 12.95; H, 3.02; N, 10.07. Found: C, 13.08; H, 3.12; N, 9.83.

**[Os(NH$_3$)$_5$(6-methyl-3,4-dihydro-5-oxa-2-pyridone methide)·(HOTf)](OTf)$_2$ (25) and [(NH$_3$)$_5$Os≡CCH$_2$CH$_2$CH$_2$OH](OTf)$_3$ (34).** An orange solution of the mixture of **9** and **10** (53.6 mg) in acetonitrile (853 mg) was treated with HOTf (22.2 mg, 0.148 mmol) in acetonitrile (210 mg), giving a yellow solution. After 5 min, the reaction mixture was added to a mixture of $Et_2O$ (35 mL) and $CH_2Cl_2$ (35 mL), producing a yellow precipitate that was filtered, washed with $Et_2O$ and $CH_2Cl_2$,

and dried *in vacuo*. Yield: 54.3 mg. The solid appeared by $^1$H NMR to be a mixture of two products, **25** and **34**, with the same ratio as that of the mixture of starting complexes **9** and **10**.

**25.** $^1$H NMR (acetonitrile-$d_3$): $\delta$ 8.58 (br s, 1H, H-N), 4.91 (dt, $J$ = 11.1, 3.9 Hz, 1H), 4.59 (td, $J$ = 11.1, 2.7 Hz, 1H), 4.37 (br s, 3H, *trans*-$NH_3$), 3.97 (d, $J$ = 3.0 Hz, 1H), 3.60 (d, $J$ = 3.0 Hz, 1H), 3.33 (br s, 12H, *cis*-$NH_3$), 2.30 (s, 3H, $CH_3$), 2.26 (ddd, $J$ = 14.1, 11.1, 3.9 Hz, 1H), 1.85 (overlap with solvent peak, 1H). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 175.16 (q), 72.65 ($CH_2$), 60.65 (q), 37.67 ($CH_2$), 29.25 ($CH_2$), 21.01 ($CH_3$).

**34.** $^1$H NMR (acetonitrile-$d_3$): $\delta$ 4.73 (br s, 12H, *cis*-$NH_3$), 3.67 (t, $J$ = 4.8 Hz, 2H), 3.34 (br s, 3H, *trans*-$NH_3$), 2.62 (t, $J$ = 6.0 Hz, 2H), 2.10 (m, 2H). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 302.18 (Os≡C), 61.52 ($CH_2$), 53.99 ($CH_2$), 26.39 ($CH_2$).

**$[Os(NH_3)_5(\eta^2$-*N*-vinylacetamide)·(HOTf)$](OTf)_2$ (26) and $[Os(NH_3)_5(\eta^2$-*N*-vinylacetiamide$](OTf)_2$ (27).** A solution of complex **1** (76.6 mg, 0.119 mmol) in acetonitile (726 mg) was treated with $H_2O$ (42.9 mg, 2.38 mmol), and then HOTf (34.1 mg, 0.227 mmol), giving a bright yellow solution. After 15 min, the solution was added to $Et_2O$ with stirring, giving a yellow precipitate that was filtered, washed with $Et_2O$ and $CH_2Cl_2$, and dried *in vacuo*. Yield of orange yellow solid **26**: 76.4 mg (0.0944 mmol).

An orange solution of **26** (50.0 mg) in acetone (500 mg) was treated with DIEA (20 mg, 0.15 mmol). After 1 min, the solution was precipitated in a mixture of $Et_2O$ (25 mL) and $CH_2Cl_2$ (25 mL), giving a light yellow precipitate, **27**. Yield: 41.5 mg (0.0630 mmol, 81% from **1**).

**26.** $^1$H NMR (acetonitrile-$d_3$): $\delta$ 13.22 (br s, 1H, OH), 8.42 (br d, $J$ = 7.5 Hz, 1H, H-N), 5.93 (q, $J$ = 7.5 Hz, 1 H, CH), 4.18 (br s, 3H, *trans*-$NH_3$), 3.61 (dd, $J$ = 7.5, 2.7 Hz, 1H, $CH_2$), 3.28 (dd, $J$ = 7.5, 2.7 Hz, 1H, $CH_2$), 3.19 (br s, 12H, *cis*-$NH_3$), 2.16 (s, 3H, $CH_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 175.24 (q), 56.24 (CH), 33.19 ($CH_2$), 21.47 ($CH_3$).

**27.** $^1$H NMR (acetonitrile-$d_3$): $\delta$ 6.95 (br d, $J$ = 7.2 Hz, 1H, H-N), 5.94 (q, $J$ = 7.5 Hz, 1 H, CH), 4.03 (br s, 3H, *trans*-$NH_3$), 3.25 (dd, $J$ = 7.2, 2.7 Hz, 1H, $CH_2$), 3.05 (dd, $J$ = 7.2, 2.7 Hz, 1H, $CH_2$), 3.19 (br s, 12H, *cis*-$NH_3$), 1.86 (s, 3H, $CH_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 173.90 (q), 60.91 (CH), 32.85 ($CH_2$), 23.16 ($CH_3$). CV ($CH_3CN$, TBAH, 100 mV/s): $E_{1/2}$ = 0.67 V (NHE). Anal. Calcd for $C_6H_{22}O_7N_6S_2OsF_6$: C, 10.94; H, 3.37; N, 12.76. Found: C, 11.34; H, 3.26; N, 12.55.

**$[Os(NH_3)_5(\eta^2$-ethylene$)](OTf)_2$ (28).**[14] A solution of complex **1** (81.2 mg, 0.126 mmol) in acetonitrile (721 mg) was treated with triethylsilane (24.1 mg, 0.184 mmol), followed by TMS(OTf) (11.9 mg, 0.0450 mmol). After 1 h, the yellow reaction mixture was added to $Et_2O$ (100 mL), giving a white precipitate that was filtered, washed with $Et_2O$ and $CH_2Cl_2$, and dried *in vacuo*. Yield: 69.7 mg, (0.116 mmol, 92%). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 4.11 (br s, 3H, *trans*-$NH_3$), 3.01 (s, 4H, ethylene), 2.95 (br s, 12H, *cis*-$NH_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 41.79. CV ($CH_3CN$, TBAH, 100 mV/s): $E_{1/2}$ = 0.65 V (NHE). The complex was purified by ion-exchange chromatography and isolated as its tetraphenylborate trihydrate salt. Anal. Calcd for $C_{50}H_{59}N_5B_2Os·3H_2O$: C, 60.30; H, 6.58; N, 7.44. Found: C, 60.68; H, 6.63; N, 7.12.

**$[Os(NH_3)_5(\eta^2$-propene$)](OTf)_2$ (29).**[15] A solution of **3** (55.7 mg, 0.0863 mmol) in acetonitrile (567 mg) was treated with triethylsilane (20.7 mg, 0.178 mmol), followed by TMS(OTf) (7.3 mg, 0.0276 mmol). After 30 min, the reaction mixture was added to $Et_2O$ (80 mL), giving a white precipitate that was filtered, washed with $Et_2O$ and $CH_2Cl_2$, and dried *in vacuo*. Yield: 48.9 mg (0.0794 mmol, 92%). $^1$H NMR ($D_2O$): $\delta$ 4.22 (br s, 3H, *trans*-$NH_3$), 3.25 (m, 1H, CH), 3.14 (br s, 12H, *cis*-$NH_3$), 2.86 (d, $J$ = 7.2 Hz, 1H, $CH_2$), 2.83 (d, $J$ = 5.1 Hz, 1H, $CH_2$), 1.23 (d, 3H, $CH_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 47.33 (CH), 43.04 ($CH_2$), 15.88 ($CH_3$). CV ($CH_3CN$, TBAH, 100 mV/s): $E_{1/2}$ = 0.58 V (NHE). Anal. Calcd for $C_5H_{21}O_6N_5S_2OsF_6$: C, 9.76; H, 3.43; N, 11.34. Found: C, 9.74; H, 3.25; N, 11.56.

**$[Os(NH_3)_5(4,5$-$\eta^2$-4-penten-2-one$)](OTf)_2$ (30).** A solution of **14** (48.2 mg, 0.0730 mmol) and 2-[(trimethylsilyl)oxy]propene (12.5 mg, 0.0960 mmol) in acetonitrile (0.76 g) and a solution of TMSOTf (9.6 mg, 0.0363 mmol) in acetonitrile (0.78 g) were prepared. After cooling, these solutions were mixed and allowed to stand at −40 °C. After 10 h, the solution was added to a mixture of $Et_2O$ (35 mL) and $CH_2Cl_2$ (35 mL), giving a light yellow precipitate that was filtered, washed with $Et_2O$ and $CH_2Cl_2$, and dried *in vacuo*. Yield: 41.7 mg (0.0634 mmol, 87%). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 4.12 (br s, 3H, *trans*-$NH_3$), 3.51 (m, 1H, H-C4), 3.08 (m, overlap with *cis*-$NH_3$, 2H, H-C5), 3.02 (br s, 12H, *cis*-$NH_3$), 2.54 (dd, $J$ = 15.6, 3.0 Hz, 1H, H-C3), 2.26 (dd, $J$ = 15.6, 9.3 Hz, 1H, H-C3), 2.17 (s, 3H, $CH_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 211.21 (C2), 47.12 (C3), 44.95 (C4), 42.20 (C5), 27.98 (C1). Anal. Calcd for $C_7H_{23}O_7N_5S_2OsF_6$: C, 12.78; H, 3.53; N, 10.65. Found: C, 12.63; H, 3.38; N, 10.27.

**$[Os(NH_3)_5$(methyl 3,4-$\eta^2$-2,2-dimethyl-3-butenoate$)](OTf)_2$ (31).** A solution of **14** (48.7 mg, 0.0738 mmol) and methyl trimethylsilyl ketene dimethyl acetal (17.5 mg, 0.100 mmol) in acetonitrile (0.89 g) was prepared, and cooled to −40 °C. A solution of TMSOTf (10.7 mg, 0.0404 mmol) in acetonitrile (0.78 g) was also cooled to −40 °C, and then added to the reaction mixture. After 12 h, the solution was treated with pyridine (17 mg, 0.215 mmol) and then directly added to a mixture of $Et_2O$ (30 mL), $CH_2Cl_2$ (20 mL), and hexane (20 mL). After being stirred for 10 min, a light orange precipitate formed that was filtered, washed with $Et_2O$ and $CH_2Cl_2$, and dried *in vacuo*. Yield: 43.1 mg (0.0614 mmol, 83%). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 4.06 (br s, 3H, *trans*-$NH_3$), 3.66 (s, 3H, $OCH_3$), 3.57 (dd, $J$ = 10.2, 9.0 Hz, 1H, H-C3), 3.42 (dd, $J$ = 10.2, 1.5 Hz, 1H, H-C4), 3.10 (br s, 12H, *cis*-$NH_3$), 2.85 (dd, $J$ = 9.0, 1.5 Hz, 1H, H-C4), 1.46 (s, 3H, $CH_3$), 1.07 (s, 3H, $CH_3$). $^{13}$C NMR (acetonitrile-$d_3$): $\delta$ 180.85 (C1), 56.45 (C3), 52.82 ($OCH_3$), 47.30 (C2), 38.77 (C4), 32.10 ($CH_3$), 25.21 ($CH_3$). Anal. Calcd for $C_9H_{27}O_8N_5S_2OsF_6$: C, 15.41; H, 3.88; N, 9.98. Found: C, 15.49; H, 3.80; N, 9.63.

**$[Os(NH_3)_5(\eta^2$-$C_3H_5)](OTf)_3$ (32).** A solution of **3** (107.1, 0.166 mmol) in acetonitrile (0.90 g) was cooled to −40 °C and treated with a solution of HOTf (78.9 mg, 0.526 mmol). After 8 min, the peach solution was added to a mixture of $Et_2O$ (80 mL) and $CH_2Cl_2$ (20 mL), producing a dark peach precipitate that was filtered, washed with $Et_2O$ and $CH_2Cl_2$, and dried *in vacuo*. Yield: 100 mg (0.131 mmol, 79%). $^1$H NMR (acetonitrile-$d_3$/triflic acid, ratio ≅ 5:1): $\delta$ 4.35 (br s, 3H, *trans*-$NH_3$), 4.11 (br s, 12H, *cis*-$NH_3$), 3.12 (br s, 2H, $CH_2$), 2.37 (br s, 3H, $CH_3$). $^{13}$C NMR (DOTf, with $CD_2Cl_2$ as internal reference): $\delta$ 299.85 (q), 37.24 ($CH_3$), 29.19 ($CH_2$); $^{13}$C NMR (acetonitrile-$d_3$/triflic acid, ratio ≅ 5:1): $\delta$ 36.41 ($CH_3$), 27.60 ($CH_2$) (quartenary carbon not identified).

**$[Os(NH_3)_5(\equiv CCH_3)](OTf)_3$ (33).** Complex **1** (81.1 mg, 0.126 mmol) was ground into a fine powder, and dissolved in HOTf (1.77 g). After 20 min, the solution was added to $Et_2O$ (100 mL), producing a fine light brown precipitate that was filtered, washed with $Et_2O$ and $CH_2Cl_2$, and dried *in vacuo*. The crude product (116 mg) was dissolved in acetone (1.5 g), and then reprecipitated with a mixture of $Et_2O$ (80 mL) and $CH_2Cl_2$ (40 mL). The precipitate was collected, washed with $Et_2O$ and $CH_2Cl_2$, and dried *in vacuo*. Yield of tan solid: 78.6 mg (0.104 mmol, 83%). $^1$H NMR (acetone-$d_6$): $\delta$ 5.32 (br s, 12H, *cis*-$NH_3$), 3.78 (br s, 3H, *trans*-$NH_3$), 2.10 (s, 3H, $CH_3$). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 4.58 (br s, 12H, *cis*-$NH_3$), 3.12 (br s, 3H, *trans*-$NH_3$), 2.09 (s, 3H, $CH_3$). $^{13}$C NMR (acetone-$d_6$): $\delta$ 296.07 (q), 41.71 ($CH_3$). CV ($CH_3CN$, TBAH, 100 mV/s): $E_{p,c}$ = −1.25 V (NHE). Anal. Calcd for $C_5H_{18}O_9N_5S_3OsF_9$: C, 8.01; H, 2.42; N, 9.34. Found: C, 8.75; H, 2.54; N, 8.89.

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