Electrophilic Addition to η^2-Aldehyde Complexes of Pentaammineosmium(II): The Formation of Fischer Carbyne Complexes via η^2-Aldehydium Intermediates

Michael L. Spera, Huiyuan Chen, Marcus W. Moody, Maria M. Hill, and W. Dean Harman*

Contribution from the Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

Received August 8, 1997[⊗]

Abstract: A series of η^2-aldehyde complexes of pentaammineosmium(II) of the form $[Os(NH_3)_5(L)](OTf)_2$ (L = formaldehyde (**1**), acetaldehyde (**2**), trimethylacetaldehyde (**3**), benzaldehyde (**4**), and crotonaldehyde (**5**), OTf = trifluoromethanesulfonate) are prepared and characterized. Treatment of these η^2-bound aldehyde complexes with CH_3OTf affords Fischer carbyne complexes **14**−**18** with typical yields ranging from 25−92%. Protonation (HOTf/MeCN) or methylation (MeOTf/DME) of many of these aldehyde complexes afford *O*-protonated or *O*-methylated η^2-aldehydium intermediates, respectively, which over time convert to the corresponding carbyne complex. The chemistry of olefin-coordinated α,β-unsaturated aldehyde complexes is also explored.

Introduction

The Fischer−Tropsch process, in which CO and H_2 (i.e., syngas) are converted to a mixture of hydrocarbons and alcohols by a heterogeneous transition metal catalyst, represents a synthetic source of hydrocarbon-based fuels, and as such has been the focus of intense investigation.[1] The Fischer−Tropsch process suffers from a low selectivity for gasoline-range hydrocarbons but could be improved with a better understanding of the complex mechanisms operating at the catalytic surface. Numerous mechanisms have been postulated, and some are supported by the observation of surface reaction intermediates.[1] Homogeneous solution models of these intermediates include aldehyde, formyl, carbyne, hydroxycarbene, hydroxymethylene, and carbonyl complexes (Figure 1), and all have been explored for their possible link to the Fischer−Tropsch process.[1]

Thus, aldehyde complexes and those reactions which link these species to other proposed intermediates of the Fischer−Tropsch process have been the subject of numerous investigations.[2] While nucleophiles generally add to the carbonyl carbon of η^1-aldehyde complexes,[3] electrophilic addition can occur in η^2-aldehyde complexes either at the carbonyl oxygen[4] or the carbon.[5] Significantly, several groups have observed cleavage of the metal−oxygen bond upon treatment of an η^2-formaldehyde complex with an electrophile. For example, Roper *et al.* have obtained hydroxy- and methoxymethylosmium complexes upon treatment of $Os(CO)_2(PPh_3)_2(\eta^2\text{-}CH_2O)$ with acid or MeOTf,[4b,e] and Head has observed a similar reaction with $Pt(PR_3)_2(\eta^2\text{-}CH_2O)$.[4d] Our interest in the ability of the π-base pentaammineosmium(II) to activate various unsaturated organic ligands toward electrophilic addition[6] led us to explore this theme with aldehydes. Herein we report a general route for the efficient formation of Fischer carbyne complexes directly from aldehyde precursors (Scheme 1).

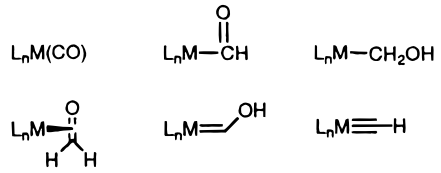


Figure 1. Organometallic models of species implicated in heterogeneous Fischer−Tropsch chemistry.

Results

Synthesis of η^2-Aldehyde Complexes. Carbonyl coordinated η^2-aldehyde complexes **1**−**5** are prepared in high yield (77−93% isolated yield) by reducing a methanol solution of $[Os(NH_3)_5OTf](OTf)_2$ with zinc amalgam in the presence of an excess (∼10 equiv) of the desired aldehyde.[7] The resulting complexes are isolated as their triflate salts and are characterized by ^{1}H NMR and ^{13}C NMR spectroscopy, as well as cyclic voltammetry (CV). A portion of each isolated complex was recrystallized prior to combustion microanalysis (see Supporting Information). For all cases examined, the ^{1}H NMR spectra (CD_3CN, δ vs TMS) of η^2-aldehyde complexes exhibit widely

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1997.

(1) For reviews of the Fischer−Tropsch reaction, see (a) Wender, I. *Fuel Processing Technol.* **1996**, *48*, 189. (b) Herrmann, W. A. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: Weinheim, 1996; Vol 2, Chapter 3.1.8. (c) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479.

(2) For reviews of transition metal aldehyde complexes, see: (a) Delbecq, F.; Sautet, P. *J. Am. Chem. Soc.* **1992**, *114*, 2446. (b) Huang, Y.-H.; Gladysz, J. A. *J. Chem. Ed.* **1988**, *60*, 298.

(3) (a) Klein, D. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 8710. (b) Garner, C. M.; Méndez, N. Q.; Kowalczyk, J. J.; Fernández, J. M.; Emerson, K.; Larsen, R. D.; Gladysz, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 5146. (c) Buhro, W. E.; Georgiou, S.; Fernández, J. M.; Patton, A. M.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1986**, *5*, 956.

(4) (a) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1986**, *5*, 2425. (b) Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Organomet. Chem.* **1982**, *231*, 335. (c) Gambarotta, S.; Floriani, C. *J. Am. Chem. Soc.* **1982**, *104*, 2019. (d) Head, R. A. *J. Chem. Soc., Dalton Trans.* **1982**, 1637. (e) Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 503.

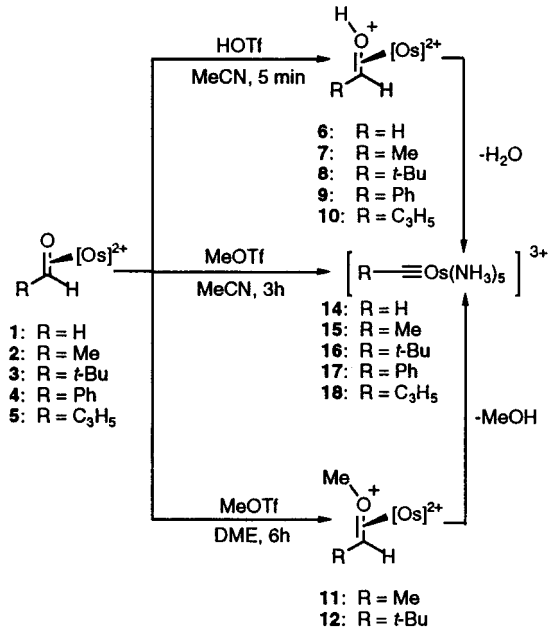
(5) Thiyagarajan, B.; Kerr, M. E.; Bollinger, J. C.; Young, V. G., Jr.; Bruno, J. W. *Organometallics* **1997**, *16*, 1331.

(6) For recent examples of electrophilic additions to η^2-pentaammineosmium(II) complexes, see: (a) Kolis, S. P.; Gonzalez, J.; Bright, L. M.; Harman, W. D. *Organometallics* **1996**, *15*, 245. (b) Spera, M. L.; Harman, W. D. *Organometallics* **1995**, *14*, 1559. (c) Hodges, L. M.; Gonzalez, J.; Koontz, J. I.; Myers, W. H.; Harman, W. D. *J. Org. Chem.* **1995**, *60*, 2125.

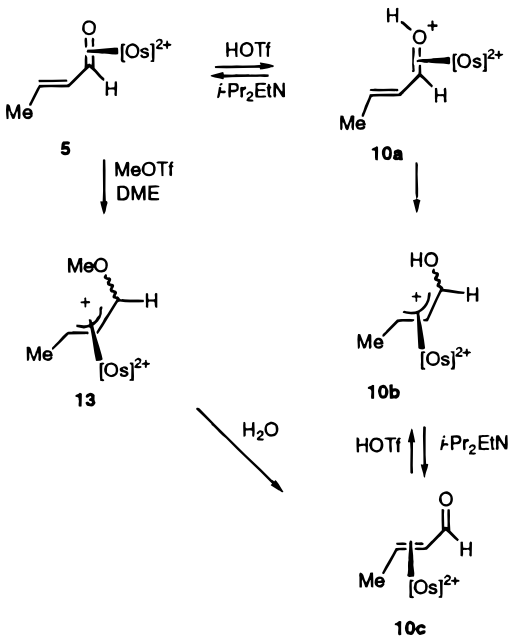
(7) (a) A solution of gaseous formaldehyde in methanol is prepared by the thermal decomposition of paraformaldehyde. (b) The synthesis and characterization of the acetaldehyde complex has been previously reported. See Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 2439.

S0002-7863(97)02766-2 CCC: $14.00

Scheme 1



Scheme 2



separated *cis/trans* ammine resonances at ~3.3/4.9 ppm and a resonance between ~5 and 6 ppm assigned as the coordinated aldehyde proton. ^{13}C NMR data (CD_3CN) show a substantial (~130 ppm) upfield shift of the coordinated aldehyde carbon to *ca.* 70−80 ppm. For aldehyde complexes **1**−**5**, the cyclic voltammogram (CH_3CN/*n*-Bu_4NPF_6/100 mV/s) exhibits an irreversible oxidation wave with $E_{p,a}$ between 0.59 and 0.73 V (NHE); on the return scan, an irreversible reduction wave appears with $E_{p,c}$ between −0.10 and −0.45 V (NHE). As is observed for other η^2-aldehyde complexes,[8] the infrared absorption corresponding to the aldehyde C−O stretch (KBr) is not found in the normal range of carbonyls (near 1700 cm^{-1}). As reported previously for acetaldehyde, these aldehyde complexes decompose over time in the solid state or in a heated solution or slurry (100 °C) to form the complex $[Os(NH_3)_5(CO)]^{2+}$.[7] Roper and Head have both observed similar thermal decomposition of η^2-formaldehyde complexes to metal carbonyl complexes.[4b,d,e]

In cases where an alternative site of metal coordination is available (i.e., benzaldehyde, crotonaldehyde), the complexation procedure still produces the carbonyl-bound isomer (>90%) even after short reduction times (<10 min). For benzaldehyde, the minor isomer is thought to be an arene−aldehyde binuclear species based on the presence of both bound arene and aldehyde signals. With crotonaldehyde, the minor product formed is the olefin-bound isomer **10c** (*vide infra*). Isomerization of **10c** to the carbonyl-bound isomer **5** is not observed when a CD_3CN solution of **10c** is maintained at 80 °C for several hours, nor is complex **5** observed to undergo isomerization to the olefin complex **10c** under similar conditions (Scheme 2).

Protonation. Treatment of each aldehyde complex with 1.1 equiv of triflic acid (CH_3CN, 22 °C) and precipitation into diethyl ether affords the complexes **6**−**10** (85−93%, Scheme 1). Proton NMR data are consistent with *O*-protonated aldehyde complexes (i.e., aldehydium complexes). These aldehydium complexes are characterized by a ~1.5 ppm downfield shift of the *cis*/*trans*-ammine resonances relative to the starting material and a ~1 ppm downfield shift of the aldehydic proton resonance. In contrast, the ^{13}C NMR spectrum (CD_3CN) for these complexes exhibits a 10−15 ppm *upfield* shift for the coordinated carbonyl carbon relative to those observed for the unprotonated complexes. These data are consistent with a species in which the aldehyde remains coordinated to the osmium(II) metal center in an η^2-manner. If the aldehyde complexes are exposed to triflic acid (neat or MeCN solution) for long reaction times (>1 h), only the carbyne complexes **14**−**18** are isolated (*vide infra*).[9] The *O*-protonated aldehydium complexes are readily deprotonated by bases as weak as PPh_3 to quantitatively regenerate aldehyde complexes **1**−**5**.

Methylation. Both the acetaldehyde and trimethylacetaldehyde complexes **2** and **3** react cleanly with methyl triflate in dimethoxyethane (DME), affording the highly reactive *O*-methylated aldehydium species **11** and **12** (Scheme 1). For example, when the trimethylacetaldehyde complex **3** is added to a solution of methyl triflate in DME and the resulting slurry is stirred for 3 h, complex **12** (along with ~20% of carbyne complex **16**) is isolated whose ^{1}H NMR spectral features are similar to those of **8** with the addition of a methoxy resonance at 4.00 ppm. The aldehyde proton resonates ~0.3 ppm further downfield (7.2 ppm) than its protonated analog (6.89 ppm), as do the *cis*- and *trans*-ammine resonances ($\Delta\delta$ ~0.3 ppm). Poor solubility of these materials in common NMR solvents (i.e., CD_3CN, DMSO-d_6, etc.) has frustrated our efforts to characterize these compounds by ^{13}C NMR spectroscopy. For the benzaldehyde complex **4**, carbyne formation occurs so rapidly as to preclude the observance of any aldehydium intermediate.[10] The formaldehyde complex **1** decomposes to uncharacterized products when treated under similar conditions. Finally, the crotonaldehyde complex **5** reacts with methyl triflate to form two diastereomers of the methoxyallyl species **13** as is described below (Scheme 2).

Direct Formation of Carbyne Complexes. While the isolated aldehydium products resulting from protonation of **1**−**5** lead to carbyne complexes, these methods often result in impure products. This problem is circumvented by dissolving the η^2-aldehyde complexes in MeCN with methyl triflate and allowing

(8) The C−O stretch for the η^2-coordinated carbonyl has been reported for **2** as 1074 cm−1, but it is obscured by N−H bending and triflate absorptions and has not been confirmed. See ref 7b.

(9) The facile conversion from oxonium to carbyne has hampered accurate measurement of the pK_a of the aldehyde complexes.

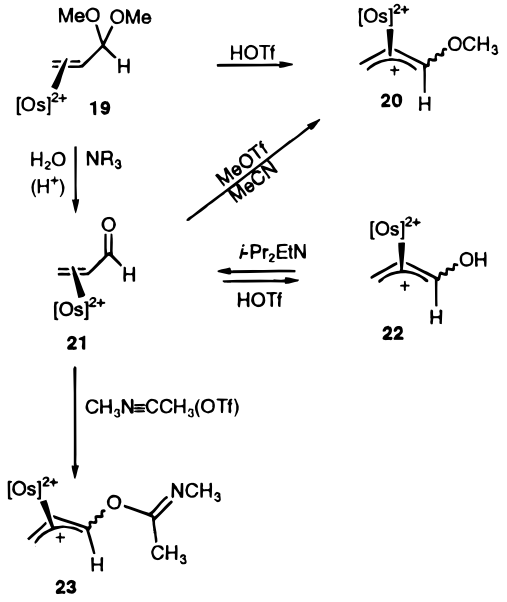
(10) This compound has been previously reported by another synthetic route. See Hodges, L. M.; Sabat, M.; Harman, W. D. *Inorg. Chem.* **1993**, *32*, 371.

the solution to stand for several hours. Over time, the corresponding Fischer carbyne complexes **14**−**18** crystallize from solution (yield: 10−92%, Scheme 1). Recrystallization of the product from acetone/methylene chloride affords the analytically pure carbyne complexes. Characteristic ^{1}H and ^{13}C NMR (CD_3CN, 5% DMSO-d_6) resonances and electrochemical data for these products include *cis*- and *trans*-ammine resonances near 5.0 (12H) and 3.5 (3H) ppm which are *reversed* from their normal relative positions, a carbyne ^{13}C resonance near 275 ppm, and an irreversible reduction wave near $E_{p,c} = -0.9$ V (NHE). These data are consistent with those reported previously for two other pentaammineosmium(VI) carbyne complexes $[Os(NH_3)_5(\equiv L)]^{3+}$ (L = CMe, CPh) prepared by other less general methods.[7,11] Note that while the parent carbyne complex **14**, $[Os(NH_3)_5(\equiv CH)]^{3+}$, derived from the formaldehyde complex **1** cannot be prepared via protonation in MeCN or methylation in DME, it is formed in low yield (∼10%) by the MeOTf/MeCN route. However, this complex rapidly decomposes in either solution or solid state to unidentified products and has been only partially characterized.

α,β-Unsaturated Aldehyde Complexes. Protonation of the *C,O*-η^2-crotonaldehyde complex **5** initially forms the η^2-aldehydium complex **10a**, whose coordinated carbonyl resonance at 74.4 ppm is in good agreement with those observed for protonated aldehyde complexes **7**−**9**. Rather than convert to the corresponding carbyne, the η^2-aldehydium species **10a** derived from crotonaldehyde undergoes a linkage isomerization to afford the hydroxyallyl complex **10b** (Scheme 2). ^{13}C NMR data for this compound show two diagnostic allyl methine signals at 80.0 and 69.7 ppm[12] and a downfield methine signal at 162.7 ppm that corresponds to the hydroxy-substituted carbon.[13] When **10b** is treated with *i*-Pr_2NEt (1.5 equiv) in MeCN and precipitated with CH_2Cl_2, complex **10c**, the olefin-bound isomer of **5,** is isolated in 78% yield. Diagnostic NMR data for **10c** include a ^{1}H resonance at 8.54 ppm and a ^{13}C resonance at 202.9 corresponding to the uncoordinated aldehyde moiety, as well as two methine carbon resonances (60.97 and 53.63 ppm) corresponding to the coordinated olefin. The cyclic voltammogram of **10c** exhibits a reversible oxidation wave at 0.91 V, similar to that observed for the olefin-bound η^2-2-cyclohexen-1-one analog.[14] Finally, complex **10c** may be treated with triflic acid in CD_3CN to regenerate the hydroxyallyl **10b**. When the crotonaldehyde complex **5** is treated with MeOTf in DME, the methoxyallyl complex **13** is formed as a 2:1 mixture of diastereomers (Scheme 2). While both diastereomers are readily characterized by ^{1}H NMR spectroscopy, the major diastereomer **13a** is considerably more soluble in CD_3CN and is characterizable by ^{13}C NMR spectroscopy. When the methoxyallyl complex **13** is exposed to water, hydrolysis to the olefin-bound crotonaldehyde complex **10c** is rapid.

Because of our inability to prepare the η^2-acrolein complex directly from acrolein,[15] we instead prepared the *C,C*-η^2-acrolein complex in two steps from the corresponding acetal (Scheme 3). Reducing $[Os(NH_3)_5OTf](OTf)_2$ in the presence of acrolein dimethyl acetal (Zn/Hg, MeOH) affords the acrolein dimethyl acetal complex **19** in good yield. The ^{13}C NMR (CD_3CN) spectrum of **19** exhibits two methine resonances (112.3, 48.3 ppm), a methylene resonance (39.9 ppm), and two methoxy resonances (55.5, 53.5 ppm). Treatment of **19** with 1 equiv of triflic acid in acetonitrile (−40 °C) yields the methoxyallyl complex **20**, as a 2:1 mixture of diastereomers (**20a** and **20b**). When the acetal complex **19** is hydrolyzed with acidic (HOTf) water followed by treatment with base (*i*-Pr_2NEt), the olefin bound η^2-acrolein complex **21** can be cleanly isolated by precipitation into CH_2Cl_2. Diagnostic spectral features for **21** include an aldehyde carbonyl resonance (203.0 ppm) and two coordinated vinyl carbon resonances (58.2 and 45.4 ppm). This complex, like the crotonaldehyde analog, is thermally stable (80 °C, CD_3CN) for several hours and does not isomerize to the *C,O*-bound aldehyde complex.

Scheme 3



The η^2-acrolein complex **21** undergoes protonation at oxygen to afford the hydroxyallyl complex **22** whose NMR spectral features are almost identical to those of the crotonaldehyde analog **10b**. Complex **21** also undergoes *O*-methylation in the presence of methyl triflate. When a solution of **21** in CD_3CN is treated with methyl triflate and the reaction is monitored by ^{1}H NMR spectroscopy, a mixture of **20a** and a new compound **23**-d_3 is observed after 3 h. No evidence of carbyne formation is observed. When **21** is treated with methylacetonitrilium triflate in acetonitrile, complex **23** is the sole product. ^{1}H NMR data for **23** feature the signals for three vinyl protons and *cis*- and *trans*-ammine resonances which resemble those of the methylated product **20a**. Besides these resonances, the ^{1}H NMR spectrum of **23** includes a methyl signal at 2.26 ppm, which is absent in the ^{1}H NMR spectrum of **20a** and the complex **23**-d_3 prepared from methyl triflate and acetonitrile-d_3 *(vide supra*). These observations have lead us to tentatively assign **23** as the imidate-substituted allyl complex shown in Scheme 3. Complexes **20a**,**b** and **22** are stable in the solid state and in acetonitrile solution; however, in methanol or DMAc, they gradually decompose to unidentified products.

Acidity of η^2-Acrolein Complex. The ^{1}H NMR spectrum of a mixture of the acrolein complex **21** and its protonated form **22** in CD_3CN is an average spectrum of the two complexes due to the establishment of a rapid equilibrium between them. In order to determine the pK_a of the coordinated acrolein, the diphenylamine/diphenylammonium couple can be used to measure their equilibrium with **21** and **22** (Figure 2). When an NMR tube is charged with the acrolein complex **21** (4.8 mg,

(11) (a) Chen, H.; Harman, W. D. *J. Am. Chem. Soc.* **1996**, *118*, 5672. (b) Chen, H.; Hodges, L. M.; Liu, R.; Stevens, W. C., Jr.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1994**, *116*, 5499.

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

(13) We have observed uncoordinated oxonium carbons in this range. See: (a) Kolis, S. P.; Kopach, M. E.; Liu, R.; Harman, W. D. *J. Org. Chem.* **1997**, *62*, 130. (b) Kopach, M. E.; Gonzalez, J.; Harman, W. D. *J. Am. Chem. Soc.* **1991**, *113*, 8972.

(14) Kopach, M. E.; Harman, W. D. *J. Am. Chem. Soc.* **1994**, *116*, 6581.

(15) The reduction of the Os(III) precursor in the presence of acrolein results in an unidentified paramagnetic product.

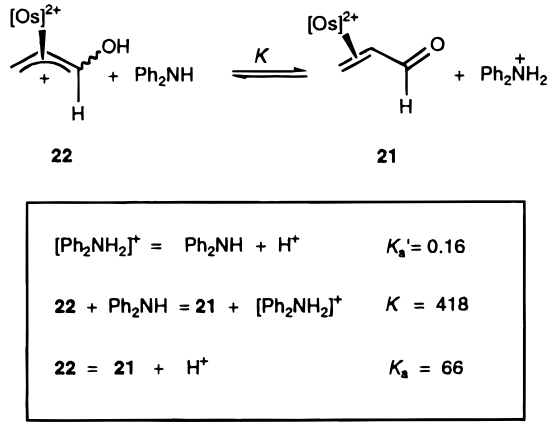


Figure 2. pK_a determination of protonated η^2-*C,C*-acrolein complex **22**. $[Os]^{2+}$ = the cation $[(NH_3)_5Os]^{2+}$. Triflate counteranions omitted for clarity.

7.6 mmol), diphenylammonium triflate (14.1 mg, 44.2 mmol), and acetonitrile-d_3 (583 mg), the equilibrium shown in Figure 2 is established in less than 1 min. Equilibrium concentrations for **22**, diphenylamine, **21**, and diphenylammonium are 1.21, 1.21, 9.80, and 62.5 (10^{-3} M), respectively, which yield an equilibrium constant $K = 418$. Taking the K_a' of diphenylamine ion as 0.16, the acid−base equilibrium of the **22** and **21** couple can be determined as p$K_a = -1.8$.

Discussion

Aldehyde Coordination. In contrast to other d^6 transition metal systems in which an equilibrium between η^1- and η^2-coordination is observed,[16] pentaammineosmium(II) coordinates the aldehyde carbonyl in aliphatic, aromatic, and α,β-unsaturated aldehydes predominantly in a dihapto fashion. Upon oxidation to Os^{III}, the metal center becomes a much weaker π-base and coordination of an aldehyde occurs η^1 solely through the oxygen.[7b] For crotonaldehyde and acrolein, coordination can occur through either the olefin or carbonyl moieties. Gladysz has shown that for the system $[CpRe(NO)(PPh_3)]^+$ there is a kinetic preference for the carbonyl of α,β-unsaturated aldehydes (i.e., acrolein and crotonaldehyde) and a thermodynamic preference for the olefin.[17] By analogy, the olefin isomer **10c** is likely to be thermodynamically more stable than the carbonyl isomer (i.e. **5**) for osmium as well, but this hypothesis has not been confirmed. It is only through the indirect sequence of protonation of **5** and deprotonation of **10b** that such an isomerization has been achieved for the pentaammineosmium(II) system.

Formation of η^2-Aldehydium Complexes. Complexes **6**−**12** may be described by several different resonance forms, with limiting resonance structures being an osmium(II) η^2-aldehydium species (Figure 3, structure I) and an osmium(IV) η^1-hydroxymethyl species (structure III). ^{1}H NMR data for the *cis* and *trans* ammines for these complexes closely resemble those of other pentaammineosmium(II) complexes of η^2-bound cationic ligands (i.e., allyl, arenium, and pyrrolium complexes), and both ^{1}H and ^{13}C NMR data for the organic ligand are very close to those of neutral aldehyde and ketone complexes. Thus, we have chosen to describe these species as osmium(II) complexes of stabilized aldehydium ligands (structure I). We note, however, that protonation or methylation of the η^2-aldehyde moderately shifts the bound carbonyl carbon upfield relative to the coordinated aldehyde, and this shift indicates at least partial sp^3 character for this carbon.

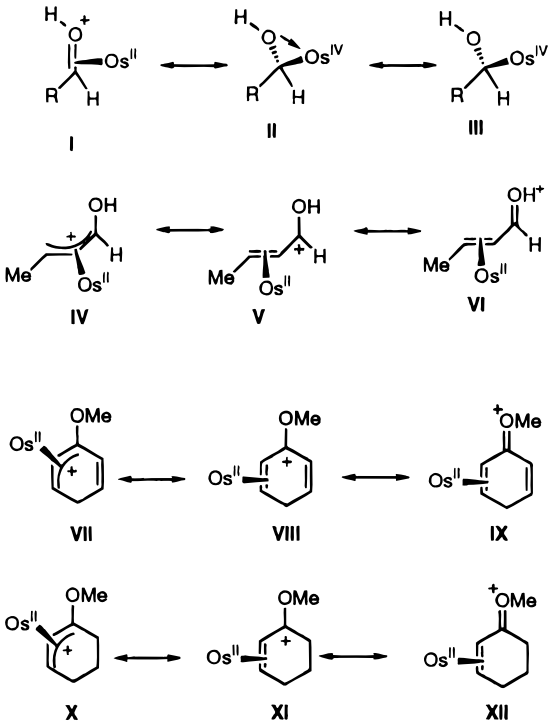


Figure 3. Comparison of resonance structures for aldehydium and anisolium species.

Hydroxy- or alkoxymethyl complexes[4] have been prepared by the reaction of η^2-aldehyde complexes with electrophiles as well as by other methods. For example, Thorn and Calabrese report the formation of an η^1-hydroxymethylene complex of iridium via the protonation of the formyl hydride complex $[Ir(PPh_3)_4(H)(CHO)]PF_6$ with HBF_4.[18] These hydroxy and alkoxymethyl complexes have been structurally characterized in both η^1 (carbon) and η^2 forms. Buchwald *et al.* have prepared examples of η^2-coordinated alkoxymethylene complexes of zirconium in which a weak but significant (i.e., ∼2.20 Å) Zr−O bonding interaction is observed.[19] In a related study, Erker *et al*. have found that for the metallocene system $Cp_2M(CH_2OCH_3)$, the alkoxymethyl ligand is coordinated η^1 when M = Ti (Ti-O 3.118 Å), and is *C,O*-η^2 coordinated for M = Zr.[20] While X-ray crystallographic analyses of these complexes strongly support their description as alkoxymethylene complexes, Erker *et al.* have suggested the existence of significant oxonium character in the oxygen of similar metallaoxirane complexes.[21]

Mechanism of Carbyne Formation. The osmium methodology described herein represents a *general* route to the synthesis of Fischer carbynes[22] whose functionality at the carbyne carbon is controlled by the choice of aldehyde precursor. The pentaammine system is interesting in that the metal retains a true octahedral environment and aside from the carbyne ligand,

(16) (a) Méndez, N. Q.; Seyler, J. W.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 2323. (b) Powell, D. W.; Lay, P. A. *Inorg. Chem.* **1992**, *31*, 3542. See also ref 7.

(17) Wang, Y.; Agbossou, F.; Dalton, D. M.; Liu, Y.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 2699. An $\eta^2-\eta^1$ linkage isomerization is also discussed.

(18) Thorn, D. L.; Calabrese, J. C. *J. Organomet. Chem.* **1984**, *272*, 283.

(19) (a) Buchwald, S. L.; Nielsen, R. B.; Dewan, J. C. *Organometallics* **1989**, *8*, 1593. (b) Buchwald, S. L.; Nielsen, R. B.; Dewan, J. C. *Organometallics* **1988**, *7*, 2324.

(20) Erker, G.; Schlund, R.; Krüger, C. *J. Organomet. Chem.* **1988**, *338*, C4.

(21) Erker, G.; Schlund, R.; Krüger, C. *J. Chem. Soc., Chem. Commun.* **1986**, 1403.

(22) For a reveiw of other methods of carbyne and alkylidyne formation, see Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley and Sons Inc.: New York, 1988.

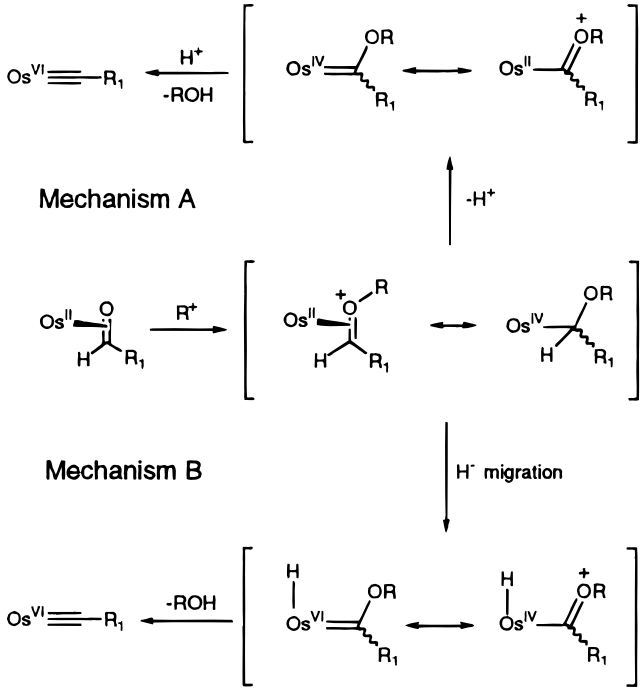


Figure 4. Possible mechanisms for the conversion of η^2-aldehdye complexes to osmium(VI) carbyne species.

possesses a relatively simple ligand set (i.e., the ammines) which does not interfere with spectroscopic characterization.[23] Thus, these complexes bridge both classical coordination chemistry and synthetic organometallic chemistry. Previously, we have reported the formation of pentaammineosmium carbynes *from* methoxycarbene complexes.[10] Thus, an attractive mechanism of carbyne formation from an aldehyde precursor would involve a Fischer carbene intermediate (Figure 4). We hoped to trap such a carbene species via treatment of *O*-methylated aldehydium complexes **11** and **12** with base (*i*-Pr_2NEt or 2,6-di-*tert*-butylpyridine). However, we have been unsuccessful in observing the expected pentaammine−carbene intermediate. Moreover, we have found that acid does not appear to inhibit the transformation of aldehydium to carbyne. For example, carbyne **15** is formed when the acetaldehyde complex **2** is dissolved in neat HOTf and allowed to stand for 3 h.

Based on these observations, an alternative mechanism is presented in Figure 4. Hydride *migration* would afford an intermediate alkoxycarbene hydrido complex which could eliminate either methanol or water (depending on the electrophile used) to afford the final carbyne product. Roper has proposed a similar mechanism for the electrophile-initiated transformation of an η^2-formaldehyde complex to a hydroxymethylene complex in which an initial hydride migration from the aldehyde to the metal generates an osmium formyl hydride complex; however, no carbyne formation is reported.[4b] The key difference in mechanisms A and B in Figure 4 is that there is no dissociation of a proton in the latter reaction, an important consideration in light of the facile carbyne formation observed under acidic conditions (neat HOTf).

Allyl Character of α,β-Unsaturated Aldehydium Complexes. The olefin bound α,β-unsaturated aldehyde complexes exhibit reactivity similar to η^2-diene complexes of pentaammineosmium(II) in that they react with electrophiles at the terminal position (Figure 5) and as such may be considered heterodienes. Olah *et al.* have found that upon protonation in super-acid media,

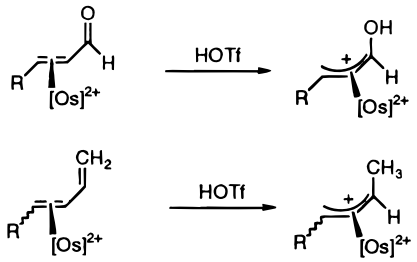


Figure 5. Comparison of the reactions of an η^2-α,β-unsaturated aldehyde and an η^2-diene with an electrophile.

α,β-unsaturated aldehydes exhibit downfield shifts of the carbonyl carbons (C1, ∼14−20 ppm) and terminal olefin carbons (C3, ∼39−49 ppm), while the central olefinic carbon is shifted slightly upfield (C2, ∼1−3 ppm) relative to the unprotonated aldehyde.[24] Strikingly different spectroscopic changes are observed with the α,β-unsaturated aldehyde complexes. Upon protonation, there is a significant (∼40 ppm) *upfield* shift of the carbonyl carbon relative to that in the unprotonated uncoordinated aldehyde. For example, ^{13}C NMR spectra of **20** or **22** show that C(3) is shifted downfield by only 7 ppm while C(1) is shifted upfield by 38 ppm. These observations suggest a significant contribution from resonance structure IV in Figure 3 and indicate that the osmium has a significant bonding interaction with C(1) in the protonated form.

It is interesting to compare these results to those obtained from protonation of η^2-anisole complexes.[25] As with the simpler heterodienes, the 4*H*-anisolium complex may be understood by considering resonance structures VII−IX in Figure 3. For 4*H*-anisolium complexes, ^{13}C NMR signals corresponding to C(1) are typically in the range of 200−215 ppm and are most consistent with an η^2-structure shown in resonance structure IX. Preliminary studies indicate that even the 2,3-dihydro-4*H*-anisolium analog (resonance structure X−XII) has a C(1) resonance near 200 ppm,[26] and this observation suggests that α,β-unsaturated aldehydes may be unique in forming η^3-type structures with pentaammineosmium(II) upon *O*-protonation. Apparently, α,β-unsaturated ketonium carbonyls are sufficiently stabilized by hyperconjugation that η^2-coordination dominates (structure XII).

Concluding Remarks. We have demonstrated the novel conversion of an η^2-aldehyde complex directly into a Fischer carbyne and in the process have synthesized an intermediate best characterized as an η^2-aldehydium complex. This new route to Fischer carbyne complexes of pentaammineosmium allows for the rapid and general preparation of carbynes and carbenes for a structurally simple coordination environment.

Experimental Section

General. All ^{1}H NMR spectra were recorded at 300 MHz and are referenced versus TMS using residual CD_2HCN, acetone-d_5, or $CHCl_3$ as an internal standard. All ^{13}C NMR spectra were recorded at 75 MHz and are referenced versus TMS using the same internal standards. The ^{13}C NMR (CD_3CN) resonance for the triflate anion (∼122 ppm, q, J = 316 Hz) is not always observed due to its low intensity and is not reported. All cyclic voltammograms were recorded in CH_3CN using tetra-*n*-butylammonium hexafluorophosphate as electrolyte with a scan rate of 100 mV/s and are referenced to the normal hydrogen electrode (NHE) using the internal standards ferrocene ($E_{1/2}$ = 0.55 V) or cobaltocenium hexafluorophosphate ($E_{1/2}$ = −0.78 V). Aldehyde

(23) Trammell, S.; Sullivan, B. P.; Hodges, L. M.; Harman, W. D.; Thorp, H. H.; Smith, S. R. *Inorg. Chem.* **1995**, *34*, 2791.

(24) Olah, G. A.; Halpern, Y.; Mo, Y. K.; Liang, G. *J. Am. Chem. Soc.* **1972**, *94*, 3554.

(25) Winemiller, M. D.; Kopach, M. E.; Harman, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 2096.

(26) Kopach, M. E.; Kolis, S. P.; Liu, R.; Harman, W. D. Manuscript in preparation.

ligands were used as purchased after deoxygenation. $[Os(NH_3)_5OTf](OTf)_2$ was synthesized as described by Lay, *et al.*[27] All reactions were performed under nitrogen in a glovebox (Vacuum Atmospheres Co.) equipped with an electronic balance. All reported yields are crude isolated yields and in all cases are >95% pure by ^{1}H NMR spectroscopy and electrochemistry. For some complexes recrystallization was performed in order to obtain satisfactory combustion microanalysis.

Synthesis of η^2-Aldehyde Complexes. The synthesis of the formaldehyde complex **1** is given as a representative example and includes the preparation of methanolic formaldehyde. All other aldehyde complexes are prepared in a manner similar to **1** using the appropriate aldehyde in a 10-fold excess to the osmium(III) precursor.

$[Os(NH_3)_5(\eta^2$-Formaldehyde$](OTf)_2$ (1). Preparation of methanolic formaldehyde: A 100 mL three-necked round-bottom flask fitted with a thermometer and a gas T-adapter connected to a nitrogen flow was charged with 5.82 g of paraformaldehyde. A nitrogen outlet was connected via glass tubing to a 100 mL two-necked round-bottom receiving flask fitted with a bubbler and nitrogen outlet feeding into a mineral oil bubbler. Methanol (50 mL) was added to the receiving flask, and the system was purged with nitrogen for 20 min. The paraformaldehyde was heated under a slow nitrogen flow at approximately 150 °C (internal) while the gaseous formaldehyde evolved was bubbled into the methanol.

Synthesis of Formaldehyde Complex (1). To a solution of methanolic formaldehyde (1.32 g) was added zinc amalgam (699 mg), and the slurry was stirred vigorously while solid $[Os(NH_3)_5OTf](OTf)_2$ (421 mg, 0.586 mmol) was slowly added over a period of 5 min. Stirring was continued for 30 min after which time the resulting red solution was filtered into 75 mL of stirring diethyl ether. The red-orange precipitate was filtered, washed with diethyl ether (2 × 10 mL), and dried *in vacuo*, affording 270 mg (0.448 mmol) of a red-orange solid, 77%. ^{1}H (CD_3CN) δ 5.19 (br s, 3H), 4.86 (s, 2H), 3.58 (br s, 12H). ^{13}C NMR (CD_3CN) δ 75.51 (CH_2). CV (CH_3CN/*n*-Bu_4NPF_6/-100 mV/s): $E_{p,a} = 0.71$ V (NHE). The product was recrystallized from methanol/ether. Anal. Calcd for $C_3H_{17}N_5O_7F_6S_2Os\cdot 0.5CH_3OH$: C, 6.79; H, 3.09; N, 11.30. Found: C, 6.56; H, 2.69; N, 11.14.

$[Os(NH_3)_5(\eta^2$-Acetaldehyde·HOTf$](OTf)_2$ (7). To a solution of **2** (180 mg, 0.291 mmol) in 2.28 g MeCN was added HOTf (64 mg, 0.427 mmol). After 1 min, the deep red solution was added to 50 mL of diethyl ether. The solid was filtered, washed with ether (2 × 10 mL), and dried *in vacuo*, affording 199 mg (0.259 mmol) of **7** as a light pink solid, 89%. This product contains up to 15% of **15** as an impurity; the reported yield is a crude mass yield. ^{1}H NMR (CD_3CN) δ 6.58 (q, $J = 5.1$ Hz, 1H), 5.52 (br s, 3H), 4.07 (br s, 12H), 1.83 (d, $J = 5.1$ Hz, 1H). OH resonance not observed. ^{13}C NMR (CD_3CN) δ 72.52 (CH), 18.22 (CH_3).

$[Os(NH_3)_5(C,O$-η^2-Crotonaldehyde·HOTf$)](OTf)_2$ (10a). To a solution of **5** (182 mg, 0.283 mmol) in 1.00 g of MeCN was added HOTf (55 mg, 0.368 mmol). After 5 min, the deep red solution was added to 50 mL of diethyl ether, and the precipitate was filtered, washed with ether (2 × 10 mL), and dried *in vacuo*, affording 189 mg (0.238 mmol) of **10a** as a rose powder, 85%. ^{1}H NMR (CD_3CN) δ 6.80 (d, $J = 8.8$ Hz, 1H), 6.8 (m, 1H), 5.56 (br s, 3H), 5.48 (m, 1H), 4.00 (br s, 12H), 1.85 (d, $J = 5.9$ Hz, 1H). OH resonance not observed. ^{13}C NMR (CD_3CN) δ 139.26 (CH), 128.26 (CH), 74.44 (CH), 19.12 (CH_3).

$[Os(NH_3)_5(\eta^3$-Crotonaldehyde·HOTf$](OTf)_2$ (10b). A solution of **10a** (178 mg, 0.224 mmol) in 1.06 mg of MeCN was allowed to stand at 22°C for 5 h and then added to 50 mL of ether. The product was filtered, washed with ether, and dried *in vacuo*, affording 158 mg (0.199 mmol) of the hydroxyallyl complex as a brown powder, 89%. ^{1}H NMR (CD_3CN) δ 6.94 (d, $J = 8.8$ Hz, 1H), 5.59 (m, 1H), 5.09 (br s, 3H), 4.98 (m, 1H), 3.91 (br s, 12H), 1.88 (d, $J = 6.6$ Hz, 1H). OH resonance not observed. ^{13}C NMR (CD_3CN) δ 162.74 (CH), 80.00 (CH), 69.67 (CH), 13.91 (CH_3). Anal. Calcd for $C_7H_{22}N_5O_9F_9S_3Os\cdot 0.5$MeCN: C, 11.80; H, 2.91; N, 9.46. Found: C, 11.56; 3.25; N, 9.06.

$[Os(NH_3)_5(C,C$-η^2-Crotonaldehyde$)](OTf)_2$ (10c). To a solution of **5** (89 mg, 0.138 mmol) in 622 mg of CD_3CN was added HOTf (28 mg, 0.186 mmol), causing an immediate color change to deep red (compound **10a**). The sample was monitored by ^{1}H NMR spectroscopy until the signals for **10a** were replaced by those of **10b** (approximately 5 h). *i*-Pr_2NEt (28 mg, 0.217 mmol) was added and the reaction mixture allowed to stand for 5 min. The solution was added to 50 mL of CH_2Cl_2, and the precipitate was filtered, washed with CH_2Cl_2 (1 × 10 mL) and ether (1 × 10 mL), and dried *in vacuo*, affording 69 mg (0.107 mmol) of the olefin complex as a tan powder, 78%. ^{1}H NMR (CD_3CN) δ 8.54 (d, $J = 7.3$ Hz, 1H), 4.83 (m, buried, 1H), 4.42 (br s, 3H), 4.13 (m, 1H), 3.22 (br s, 12H), 1.54 (d, $J = 5.9$ Hz, 3H). ^{13}C NMR (CD_3CN) δ 202.89 (CH), 60.97 (CH), 53.63 (CH), 16.14 (CH_3). CV (CH_3CN/*n*-Bu_4NPF_6/100 mV/s): $E_{1/2} = 0.91$ V (NHE). Anal. Calcd for $C_6H_{21}N_5O_7F_6S_2Os$: C, 11.20; H, 3.29; N, 10.88. Found: C, 11.20; H, 3.45; N, 10.68.

$[Os(NH_3)_5(\eta^2$-Trimethylacetaldehyde·MeOTf$)](OTf)_2$ (12). To a solution of MeOTf (108 mg, 0.656 mmol) in 1.72 g of DME was added **3** (144 mg, 0.219 mmol), and the slurry was stirred for 2 h. The slurry was added to 50 mL of diethyl ether, and the product was filtered, washed with ether (2 × 10 mL), and dried *in vacuo*, affording 162 mg of crude aldehydium complex. This product contained ~20% of the carbyne complex **16** as an impurity. ^{1}H NMR (CD_3CN) δ 6.89 (s, 1H), 5.77 (br s, 3H), 4.52 (br s, 12H), 4.00 (s, 3H), 1.26 (s, 9H).

$[MeC{\equiv}Os(NH_3)_5](OTf)_3$ (15). Preparation from MeOTf/DME: To a solution of MeOTf (126 mg, 0.772 mmol) in 3.6 g of DME was added **2** (119 mg, 0.193 mmol), and the resulting slurry was vigorously stirred for 10 h after which the slurry was added to 50 mL of diethyl ether. The precipitate was filtered, washed with ether (2 × 10mL), and dried *in vacuo*, affording 114 mg (0.153 mmol) of the carbyne as a yellow powder, 80%. The ^{1}H NMR spectrum (acetone-d_6) of **15** is identical to that reported by Chen *et al.*[11a]

$[t$-BuC$\equiv$Os$(NH_3)_5](OTf)_3$ (16). Preparation from MeOTf/MeCN: To a solution of MeOTf (286 mg, 1.74 mmol) in 1.95 g of MeCN was added **3** (230 mg, 0.349 mmol), and the reaction mixture was allowed to stand for 3 h. The orange precipitate was filtered, washed with several drops of MeCN, followed by ether (2 × 10 mL), and dried *in vacuo*, affording 202 mg (0.260 mmol) of a yellow-orange powder, 75%. ^{1}H NMR (CD_3CN) δ 4.91 (br s, 12H), 3.20 (br s, 3H), 1.37 (s, 9H). ^{13}C NMR (CD_3CN/5% DMSO-d_6) δ 298.25 (C), 59.20 (C), 23.11 (CH_3 × 3). CV (CH_3CN/*n*-Bu_4NPF_6/100 mV/s): $E_{p,c} = -0.89$ V (NHE). Anal. Calcd for $C_8H_{24}N_5O_9F_9S_3Os$: C, 12.14; H, 3.06; N, 8.85. Found: C, 12.30; H, 3.20; N, 8.80.

$[Os(NH_3)_5(\eta^3$-(Crotonaldehyde·$CH_3OTf))](OTf)_2$ (20). Complex **19** (107 mg, 0.158 mmol) was dissolved in acetonitrile and cooled to −40 °C. To this solution was added HOTf (56 mg, 0.374 mmol). After 5 min, the solution was added to CH_2Cl_2, producing a brown solid. The precipitate was filtered, washed with Et_2O and CH_2Cl_2, and dried *in vacuo*, affording 113 mg (0.143 mmol) of the title compound as a 2:1 mixture of diastereomers, 90%. Major diastereomer **20a**: ^{1}H NMR (CD_3CN) δ 6.93 (d, $J = 9.5$ Hz, 1H), 5.38 (dd, $J = 6.6$, 1.6 Hz, 1H), 5.23 (br s, 3H), 5.15 (dd, $J = 9.3$, 1.6 Hz, 1H), 5.06 (ddd, $J = 9.5$, 9.3, 6.6 Hz, 1H), 4.25 (s, 3H), 3.97 (br s, 12H). ^{13}C NMR (CD_3CN) δ 166.31 (CH), 67.79 (CH_3), 66.87 (CH), 52.65 (CH_2). Minor diastereomer **20b**: ^{1}H NMR (CD_3CN) δ 7.11 (d, $J = 9.5$ Hz, 1H), 5.31 (dd, $J = 5.1$, 2.2 Hz, 1H), 5.17 (br s, 3H), 5.1 (overlap with the peaks of **20a**, 1H), 4.97 (m, overlap with the peak of **20a**, 1H), 4.25 (s, 3H), 3.85 (br s, 12H). ^{13}C NMR (CD_3CN) δ 165.47 (CH), 67.79 (CH_3), 66.87 (CH), 52.65 (CH_2). Anal. Calcd for $C_7H_{22}N_5O_{10}F_9S_3Os$: C, 10.59; H, 2.79; N, 8.82. Found: C, 10.36; H, 2.50; N, 8.78.

$[Os(NH_3)_5(C,C$-η^2-Acrolein$)](OTf)_2$ (21). Complex **19** (234 mg, 0.346 mmol) was dissolved in a mixture of acetonitrile (950 mg) and HOTf (74 mg, 0.495 mmol). To this solution was added H_2O (40 mg, 2.2 mmol). After 5 min, the solution was added to Et_2O (50 mL), affording an orange solid. The precipitate was filtered, washed with Et_2O and CH_2Cl_2, (2 × 10 mL each), and dried *in vacuo*. The crude product of **21** (containing some **22**) was dissolved in acetonitrile and treated with *i*-Pr_2NEt. After 5 min, the solution was added to CH_2Cl_2 (100 mL). The precipitate was filtered, washed with Et_2O and CH_2Cl_2, and dried *in vacuo*, affording 199 mg (0.315 mmol) of an orange solid, 91%. ^{1}H NMR (CD_3CN) δ 8.64 (d, $J = 7.3$ Hz, 1H), 4.49 (br s, 3H), 4.47 (dd, $J = 9.3$, 2.0 Hz, 1H), 4.18 (q, $J = 8.3$ Hz, 1H), 4.03 (dd, $J = 7.7$, 2.0 Hz, 1H), 3.27 (br s, 12H). ^{13}C NMR (CD_3CN) δ 203.00 (CH), 58.16 (CH), 45.38 (CH_2).

(27) (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. For an improved detailed procedure for the synthesis of this reagent, see: Gonzalez, J., Ph.D. Dissertation, Department of Chemistry, University of Virginia, May, 1995. This compound is currently available from Aldrich.

[Os(NH$_3$)$_5$(*C,C*-η^3-(Acrolein·HOTf))](OTf)$_2$ (22). Crude **21** (210 mg) was dissolved in acetonitrile and treated with triflic acid (74 mg, 0.95 mmol). After 5 min, the solution was added to stirred Et_2O (120 mL), producing a purple precipitate. The precipitate was filtered, washed with Et_2O and CH_2Cl_2 (2 × 10mL each), and dried *in vacuo*, affording 223 mg (0.286 mmol) of a brown solid, 83%. ^{1}H NMR (CD_3CN) δ 7.10 (d, J = 9.3 Hz, 1H), 5.34 (dd, J = 6.9, 2.0 Hz, 1H), 5.15 (dd, J = 8.9, 2.0 Hz, 1H), 5.13 (br s, 3H), 5.02 (ddd, J = 9.3, 8.9, 6.9 Hz), 3.81 (br s, 12H). OH resonance not observed. ^{13}C NMR (CD_3CN) δ 164.59 (CH), 65.61 (CH), 51.14 (CH_2). Anal. Calcd for $C_6H_{20}N_5O_{10}F_9S_3Os$: C, 9.24; H, 2.59; N, 8.98. Found: C, 9.97; H, 2.51; N, 9.58.

[Os(NH$_3$)$_5$(*C,C*-η^3-(Acrolein·[CH$_3$NCCH$_3$](OTf))](OTf)$_2$ (23). ^{1}H NMR (CD_3CN) δ 7.76 (d, J = 11.2 Hz, 1H), 5.87 (d, J = 5.01 Hz, 1H), 5.80 (d, J = 8.1 Hz, 1H), 5.25 (m, 1H, CH), 5.12 (br s, 3H), 4.02 (br s, 3H), 3.44 (s, 3H, CH_3), 2.46 (s, 3H, CH_3). NH resonance is not observed.

Acknowledgment is made to the National Science Foundation (NSF Young Investigator program) and the A. P. Sloan Foundation for their generous support of this work.

Supporting Information Available: Text giving full experimental procedures and characterizations for all compounds described in this account (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA972766D