β-Electrophilic Additions of Pentaammineosmium(II) η²-Pyrrole Complexes

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The reactivity of a series of pyrrole complexes of the form $[Os(NH_3)_5(4,5\text{-}\eta^2\text{-L})]^{2+}(OTf)_2$ (L = pyrrole and alkylated pyrroles) is surveyed with various electrophiles. The pyrrole ligand undergoes alkylation or acylation with a wide variety of electrophiles (e.g., acids, alkyl triflates, anhydrides, aldehydes, ketones, and Michael acceptors) predominately at the β-position. Depending on reaction conditions, the resulting products are either β-substituted 1*H*-pyrrole or 3*H*-pyrrolium complexes, the latter of which resist rearomatization due to the electron-donating properties of the metal. In all cases observed, the initial addition of the electrophile occurs on the ring face *anti* to osmium coordination. The osmium(II)–4,5-η²-pyrrole complexes are each in dynamic equilibrium with a minor isomer where the metal binds across C(3) and C(4). In this form, the uncoordinated portion of the pyrrole ring resembles an azomethine ylide, which can undergo a 1,3-dipolar cycloaddition reaction with certain electrophiles. The resulting 7-azanorbornene complexes may be ring-opened with Lewis acids to generate α-substituted 2*H*-pyrrolium complexes. As with the 3*H*-pyrrolium species, the 2*H*-pyrrolium complexes are stabilized by metal coordination and thereby resist rearomatization. The selectivity between Michael addition and dipolar cycloaddition depends on the pyrrole, electrophile, solvent, temperature, the presence of Lewis acids, and in some cases, concentration. The iminium carbon of both 2*H*- and 3*H*-pyrrolium tautomers is considerably less electrophilic than its organic analogs, but readily undergoes borohydride reduction to form complexes of 3- and 2-pyrrolines, respectively. When pyrrole complexes are combined with alkyne Michael acceptors, the intermediate enolate can be trapped by the iminium carbon of the 3*H*-pyrrolium species in DMSO to form a metalated cyclobutene derivative. Decomplexation of most pyrrole and 3-pyrroline derivatives can be accomplished in good yield either by heating or by oxidation of the metal (Ce^{IV} or DDQ). Complexes of 2-pyrrolines are considerably more difficult to remove from the metal; however, quaternization or acylation of the nitrogen facilitates their decomplexation.

Introduction

The pyrrole nucleus is an integral part of many natural products, being found in chlorophylls, bile pigments, porphyrins, antibiotics, and polymer systems. Given that pyrroles are nitrogen heterocycles in which all of the carbons are unsaturated, they represent valuable synthetic precursors to other aromatic heterocycles, cyclic alkaloids, and other biologically active compounds. Unfortunately, the synthetic utility of a pyrrole is often limited by its tendency to undergo electrophilic addition or substitution at the α-positions rather than at the biologically more significant β-positions, or to polymerize in the presence of electrophiles.[2] At present, three primary methods are available to synthesize β-substituted pyrroles from a pyrrolic precursor:[3] (a) placement of a removable electron-withdrawing group at the α-position, which directs electrophilic addition to the β-position on the opposite side of the ring, (b) isomerization of an α-substituted pyrrole to the corresponding β-substituted isomer, and (c) placement of a bulky substituent on the nitrogen to direct electrophilic addition away from the α-position.

In an alternative approach, η²-coordination of a pyrrole serves to dearomatize the ring in both a structural and electronic sense, significantly altering the reactivity of the heterocycle.[4] Using the pentaammineosmium(II) moiety, coordination across C(4) and C(5) renders the remaining portion of the ring chemically similar to an enamine, now susceptible to electrophilic addition at the β-carbon, C(3). In our previous study, the fundamental characteristics of η²-pyrrole and η²-pyrrolium complexes were first characterized (classes **I**–**VI**, Figure 1).[4c] Furthermore, a preliminary report of electrophilic addition at C(3) of pyrrole complexes has appeared.[4d,e] The following constitutes an in-depth study of the scope of the β-electrophilic addition reaction for η²-pyrrole complexes, emphasizing common carbon electrophiles. In the course of this investigation, several new classes of pyrrole and pyrrolium isomers were encountered that were not observed in our earlier studies (classes **VII**–**XIII**, Figure 1), and their spectroscopic features and reactivity patterns are also included. A complete listing of all complexes reported herein may be found in Table 1, organized according to their structure class.

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(1) Alfred P. Sloan Research Fellow (1994–6); NSF Young Investigator (1993–8); Camille and Henry Dreyfus Teacher-Scholar (1992–95).

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(3) Bray, B. L.; Mathies, P. H.; Naef, R.; Solas, D. R.; Tidwell, T. T.; Artis, D. R.; Muchowski, J. M. *J. Org. Chem.* **1990**, *55*, 6317 and references therein. For a review of β-substituted pyrrole syntheses, see: Anderson, H. J.; Loader, C. E. *Synthesis* **1985**, 353 and references therein.

(4) (a) Cordone, R.; Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1989**, *111*, 5969. (b) Myers, W. H.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1991**, *113*, 6682., (c) Myers, W. H.; Koontz, J. I.; Harman, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 5684. (d) Hodges, L. M.; Gonzalez, J.; Koontz, J. I.; Myers, W. M.; Harman, W. D. *J. Org. Chem.* **1993**, *58*, 4788. (e) Hodges, L. M.; Moody, M. W.; Harman, W. D. *J. Am. Chem. Soc.* **1994**, *116*, 7931.

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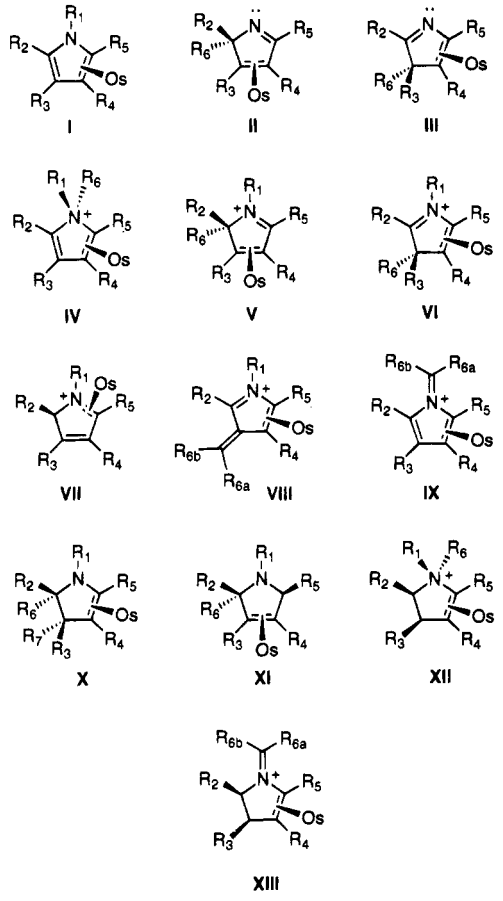


Figure 1. Class key for η^2-pyrrole derivatives.

Results

Complexes of the form $[Os(NH_3)_5(4,5\text{-}\eta^2\text{-pyrrole})](OTf)_2$[5] are synthesized from various pyrroles in 85–95% yield by reducing the precursor $[Os(NH_3)_5OTf](OTf)_2$ in the presence of ~10 equiv of the pyrrole ligand in DMAc or in a cosolvent mixture of DMAc and DME.[4] While the neutral 1*H*-tautomer predominates for all complexes synthesized, the possibility for formation of the 2*H*- or 3*H*-pyrrole tautomer exists when the nitrogen is unsubstituted. For example, when the 2,5-dimethylpyrrole complex **3** is dissolved in protic solvents, a significant amount of another compound (**13**) is observed in solution. When **3** is dissolved in water, an equilibrium ratio of 9:1 is established favoring this new product. In a solution of water in acetone (7 M H_2O), the observed ratio is 1:1. Given the sensitivity of the equilibrium of this reaction to the concentration of water, the new product was initially assigned to be the product of hydration of the double bond.[4c] However, further characterization of this compound by ^{13}C NMR in D_2O[6] shows a quaternary signal at 175.78 ppm, a value inconsistent with the originally assigned structure. After a thorough spectroscopic analysis,[7] we now believe this compound to be the 3*H*-tautomer shown in Figure 2. The analogous 3*H*-(2-ethylpyrrole) complex **14**, present in D_2O as a 9:2 ratio with the 1*H*-tautomer, has been similarly characterized by ^1H and ^{13}C NMR (Figure 2).[8]

Protonations of β-Substituted Pyrroles. As previously described, protonation of neutral pyrrole complexes free of substituents at either C(3) or C(4) occurs exclusively at C(3) on the ring face opposite the metal to give a 3*H*-pyrrolium adduct. Addition of weak base to the 3*H*-pyrrolium tautomers resulting from the 1-methylpyrrole (**2**) or 2,5-dimethylpyrrole (**3**) complexes generates the thermodynamically favored 2*H*-pyrrolium tautomers **8** and **9**, respectively.[4c] In the course of our investigation, several new aspects concerning the protonation and tautomerization of η^2-pyrroles were revealed for the special case where the pyrrole ligand has a single β-substituent. A summary of these findings follows.

A solution of the 3-methylpyrrole complex **6a** (CD_3CN; 44.5 mg, 0.068 mmol) was added to neat HOTf (13.5 mg, 0.090 mmol), and the resulting solution was monitored by ^1H NMR. A spectrum taken after 10 min shows an approximate 2:3:3:3 ratio of four different pyrrolium tautomers, identified as adducts **6b–d** and **6f** (Figure 3). Protonation at C(3) on the ring face opposite to metal coordination produces the 3*H*-pyrrolium tautomer with the methyl at C(3) *syn* with respect to the osmium (**6c**). This product is characterized (^1H NMR, CD_3CN) by the presence of a triplet at 4.35 ppm (J = 5.1 Hz) for the *anti* H(4),[9] which is coupled to both H(5) and H(3).[10] Also present for **6c** is a doublet (7.5 Hz) at 1.30 ppm corresponding to the methyl group bound to C(3), as well as signals for H(5) and the iminium proton [H(2)] at 6.43 and 8.91 ppm, respectively. Isomerization of the metal in complex **6a** to the more substituted double bond of the ring followed by protonation of the unsubstituted β-carbon gives tautomer **6d**.[11] This product is characterized (^1H NMR) by singlets at 6.40 and 1.51 ppm for H(5) and the C(4)-methyl, respectively. Isomerization of the metal in **6a** to the 3,4-position allows for protonation at the α-carbon [C(2)], giving the 2*H*-pyrrolium tautomer **6f**. This tautomer, characterized by its ^1H and ^{13}C NMR spectra, shows a singlet for the iminium proton [H(5)] at 9.14 ppm (CD_3CN) as well as a ^{13}C resonance at 190 ppm, peaks which are diagnostic for the 2*H*-pyrrolium species.[12] Also present are singlets at 5.44 ppm for H(4) and 1.71 ppm for the C(3)-methyl group. Irradiation of H(5) gives a 4.7% NOE enhancement of H(4), establishing **6f** as the isomer in which the methyl group is adjacent to protonated α-carbon, C(2).

A fourth product is also present after the initial protonation, which quickly disappears over time in solution, and is not present in material isolated by precipitation with Et_2O. Present in its ^1H NMR spectrum are signals consistent with an intact β-substituted 1*H*-

(5) In this paper, we will show the osmium coordinated to the 4,5 position of the pyrrole ring by convention in order to utilize standard pyrrole nomenclature.

(6) ^1H NMR data for **13** (3:1 H_2O/D_2O): δ 4.35 (br s, 3H), 3.80 (d, 1H), 3.23 (br s, 12H), 2.78 (dd, 1H), 2.24 (d, 1H), 2.08 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (3:1 H_2O/D_2O) δ 175.78 (C), 83.95 (C), 46.81, 45.39 (CH and CH_2), 18.07 (CH_3), 17.64 (CH_3).

(7) DEPT data of **13** recorded in acetone-d_6 solution which was 8 M in H_2O shows a quaternary peak at 169.67 ppm for the imine carbon [C(2)], along with one CH_2 resonance at 43.27 ppm for C(3).

(8) ^1H NMR data for **14** (3:1 H_2O/D_2O): δ 5.96 (d, 1H), 4.43 (br s, 3H), 4.10 (dd, 1H), 3.24 (br s, 12H), 2.69 (dd, 1H), 2.40 (m, 2H), 2.22 (d, 1H), 1.10 (t, 3H); ^{13}C NMR (3:1 H_2O/D_2O) δ 183.43, 81.96, 45.50, 43.77, 26.53, 11.67.

(9) While this resonance is partially overlapped by the *trans*-NH_3 resonance in CD_3CN, it is clearly resolved in acetone-d_6.

(10) When H(3) is *syn* with respect to the osmium, no coupling to H(4) is observed. See reference 4c.

(11) Note that even though the metal has isomerized to the opposite side of the pyrrole ring, the carbons to which the metal is coordinated are still numbered C(4)–C(5).

(12) The ^1H NMR resonance for the iminium proton for 2*H*-pyrrolium complexes appears ~0.3–0.5 ppm downfield from the corresponding proton resonance for 3*H*-pyrrolium complexes in identical solvents; similarly, the ^{13}C NMR resonance for the iminium carbon is ~15 ppm downfield from that of 3*H*-pyrrolium complexes. See Table 5.

Table 1. Compound Identification Key

class	cpd	R_1	R_2	R_3	R_4	R_5	R_6
I	**1**	H	H	H	H	H	
I	**2**	Me	H	H	H	H	
I	**3**	H	Me	H	H	Me	
I	**4**	H	Et	H	H	H	
I	**5a**	Me	H	Me	H	H	
VI	**5c**	Me	H	Me	H	H	H
VI	**5d**	Me	H	H	Me	H	H
VI	**5e**	Me	H	H	H	H	Me
V	**5f**	Me	H	Me	H	H	H
I	**6a**	H	H	Me	H	H	
IV	**6b**	H	H	Me	H	H	H
VI	**6c**	H	H	Me	H	H	H
VI	**6d**	H	H	H	Me	H	H
VI	**6e**	H	H	H	H	H	Me
V	**6f**	H	H	Me	H	H	H
VII	**6g**	H	H	Me	H	H	H
II	**7**		Me	H	H	Me	H
V	**8**	Me	H	H	H	H	H
V	**9**	H	Me	H	H	Me	H
VI	**10**	Me	H	H	H	H	H
VI	**11**	H	Me	H	H	Me	H
VI	**12**	H	Et	H	H	H	H
III	**13**		Me	H	H	Me	H
III	**14**		Et	H	H	H	H
I	**15**	Me	H	Ac	H	H	
I	**16**	H	H	$[C(Me)=NHMe]^+$	H	H	
I	**17**	Me	H	$[C(Me)=NHMe]^+$	H	H	
VI	**18**	H	H	H	H	H	$C(Me)_2OTBS$
VI	**19**	Me	H	H	H	H	$C(Me)_2OTBS$
VI	**20**	H	Me	H	H	Me	$C(Me)_2OTBS$
III	**21**		Me	H	H	Me	$C(Me)_2OTBS$
VI	**22**	Me	H	H	H	H	CH(Ph)(OTBS)
VI	**23**	Me	H	H	H	H	CH(Ph)(OMe)
VIII	**24**	Me	H	H	H	H	R_{6a}, R_{6b} = Me
IX	**25**		H	Me	H	H	R_{6a}, R_{6b} = Me
I	**26**	$(CH_2)_2C(O)Me$	H	$(CH_2)_2C(O)Me$	H	H	
I	**27a**	Me	H	$(CH_2)_2C(O)Me$	H	H	
IV	**27b**	Me	H	$(CH_2)_2C(O)Me$	H	H	H
VI	**27c**	Me	H	$(CH_2)_2C(O)Me$	H	H	H
VI	**27e**	Me	H	H	H	H	$(CH_2)_2C(O)Me$
V	**27f**	Me	H	$(CH_2)_2C(O)Me$	H	H	H
II	**29**	H	Me	H	H	Me	$(CH_2)_2C(O)Me$
III	**30**	H	Me	H	H	Me	$(CH_2)_2C(O)Me$
I	**31**	Me	H	$(CH_2)_2CHO$	H	H	
I	**32**	Me	H	CH=CHC(O)Me	H	H	
X	**33**	Me	H	H	H	H	*a*
I	**34**	Me	H	$C(CO_2Me)$=CH-CO_2Me	H	H	
X	**35**	Me	H	H	H	H	*b*
I	**36**	H	H	CH=CHC(O)Me	H	H	
VI	**38**	H	Me	H	H	Me	$(CH_2)_2CO_2Me$
VI	**39**	Me	H	H	H	H	$(CH_2)_2CO_2Me$
VI	**40**	H	Et	H	H	H	$(CH_2)_2CO_2Me$
VI	**41**	Me	H	H	H	H	$CH(Me)CH_2$-CO_2Me
VI	**42**	H	H	Me	H	H	$(CH_2)_2CO_2Me$
I	**43a**	Me	H	$(CH_2)_2CO_2Me$	H	H	
VI	**43c**	Me	H	$(CH_2)_2CO_2Me$	H	H	H
VI	**43d**	Me	H	H	$(CH_2)_2CO_2Me$	H	H
VI	**43e**[c]	Me	H	H	H	H	$(CH_2)_2CO_2Me$
V	**46**	H	Me	H	H	Me	$(CH_2)_2CO_2Me$
V	**47**	Me	H	H	H	H	$(CH_2)_2CO_2Me$
II	**48**		Me	H	H	Me	$(CH_2)_2CO_2Me$
X	**49**	Me	H	H	H	H	R_6, R_7 = H
XII	**50**	R_{1a}, R_{1b} = Me	H	H	H	H	
X	**51**	H	Me	H	H	Me	R_6, R_7 = H
X	**52**	Ac	Me	H	H	Me	R_6, R_7 = H
XIII	**53**		Me	H	H	Me	R_{6a} = OH, R_{6b} = Me
XI	**54**	Me	H	H	H	H	H
XI	**55**	H	Me	H	H	Me	H
XI	**56**	H	Me	H	H	Me	$(CH_2)_2CO_2Me$

[a] R_6, R_7 = −C[C(O)Me]=CH− (cyclobutene derivative). [b] R_6, R_7 = $-C(CO_2Me)=C(CO_2Me)-$ (cyclobutene derivative). [c] Note that **43e** and **39** are the same compounds.

pyrrole ring along with a set of *cis*- and *trans*-ammines slightly downfield from those of a neutral 1*H*-pyrrole complex (e.g., **6a**). On the basis of this data, this product has been tentatively assigned as the *N*-protonated 1*H*-pyrrolium tautomer **6b**. The C(3)-epimer of **6c**, the *anti*-alkylated isomer **6e**, is only found to be present in small amounts (~10%), and the intensity of its signals do not change significantly over time.[13]

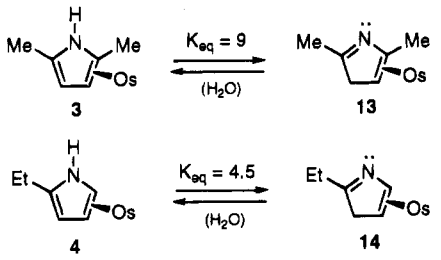


Figure 2. Formation of the 3*H*-tautomer of the 2,5-dimethylpyrrole and 2-ethylpyrrole complexes.

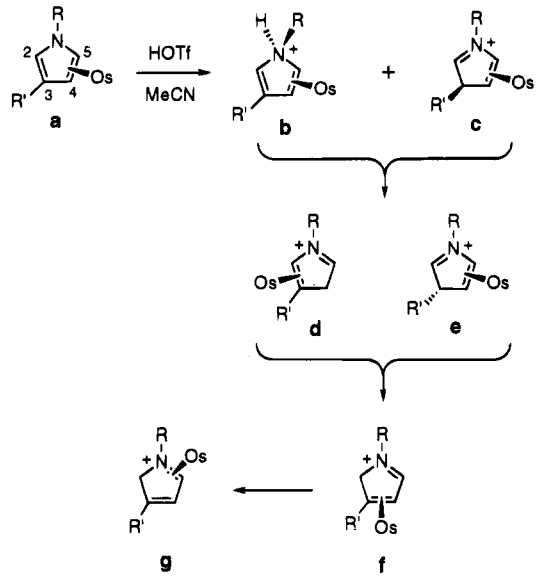


Figure 3. Various pyrrolium tautomers derived from protonation of β-substituted pyrrole complexes.

The original ratio of tautomers **6b**–**f** changes over time in the acidic CD_3CN solution. After approximately 4 h, the only observed products to be present are **6d** and **6f** in a 1:2 ratio. However, after 30 h, the presence of yet another product (**6g**) is detected. This material, formed directly from the α-protonated tautomer **6f**, appears to be the product of a linkage isomerization where the osmium shifts from *3,4*-η^2 to *1,5*-η^2 (Figure 3). In a separate experiment, protonation of **6a** (HOTf) is carried out in acetonitrile, and the product mixture is precipitated by addition of Et_2O. Although the initial product ratio showed approximately a 9:14:22:1:54 ratio of tautomers **6b**–**f**, conversion to a 4:1 mixture of **6f** and **6g** had occurred after standing in the solid state for 1 week. After standing for 3 months in the solid state, the ratio of **6f** and **6g** was 1:1.[14] Analysis by ^1H and ^{13}C NMR, as well as DEPT and NOE, confirms the assignment of **6f** and **6g** as being the 2*H*-pyrrolium tautomers shown in Figure 3. In dramatic contrast to the result observed in acetonitrile, protonation of **6a** in methanol leads to immediate oxidation of the metal. A cyclic voltammogram for the new product shows a reversible III/II reduction wave at −0.30 V (NHE), and a ^1H NMR spectrum shows no features related to the new species in a standard ppm range for diamagnetic materials.

(13) The presence of **6e** is supported by a doublet (7.5 Hz) at 1.60 ppm [C(3)-methyl] and a doublet at 8.82 ppm [H(2)], which are comparable to the analogous protons for the fully characterized 1,3-dimethyl analog **5e**. See reference 4c.

(14) This linkage isomerization is considerably faster in either acetone or acetonitrile solution, and can be accelerated by gentle heating.

Addition of base (Proton Sponge, 1 equiv, CD_3CN) to **6g** results in a deep green solution whose ^1H NMR spectrum indicates the formation of a new diamagnetic species. This new product has *cis*- and *trans*-ammine signals at 3.20 and 3.91 ppm[15] (CD_3CN), respectively, as well as those corresponding to ring protons (8.42, 6.03 ppm), and a methyl group (1.75 ppm). A cyclic voltammogram shows an irreversible II/III oxidation wave ($E_{p,a}$ = −0.24 V).[16] Taken together, these data are consistent with this species being the *N*-bound 2*H*-pyrrole derivative [$Os(NH_3)_5$(1-η^1-2*H*-3-methylpyrrole)].

Protonation of the 1,3-dimethylpyrrole complex **5a** gives similar results to **6a.** Protonation in acetonitrile followed by precipitation in Et_2O gives the 3*H*-pyrrolium adduct **5c** as the major product, where protonation occurs at C(3) *anti* to the metal. In addition, approximately 20–25% of the reaction mixture is in the form of 2*H*-pyrrolium tautomer **5f**. When allowed to stand in neutral CD_3CN solution, **5c** slowly epimerizes at C(3) to form **5e** with little change in the amount of **5f** present.[17] However, the reaction mixture converts exclusively to **5f** within 24 h in methanol solution; this transformation also occurs in the solid state over a period of a few weeks. Treatment of **5a** with acidic methanol does not oxidize the metal as in the case of 3-methylpyrrole, but gives the 3*H*-pyrrolium tautomer **5d** in which the metal has moved to the more hindered double bond of the pyrrole ring prior to protonation at the unhindered β-position.[4c] In a separate experiment, the 2*H*-pyrrolium adduct **5f** can also be synthesized directly from **5a** by treatment with a 1:6 molar ratio of anilinium triflate/aniline in methanol for 24 h, conditions identical to those used to generate the 2*H*-pyrrolium tautomers of the 1-methylpyrrole (**8**) and 2,5-dimethylpyrrole complexes (**9**). NOE data for **5f** are consistent with the methyl group being adjacent to the protonated α-carbon, analogous to the 3-methyl analog **6f**.

Protonation of the 1-methyl-3-(3-oxobutyl)pyrrole complex **27a** (*vide infra*) with triflic acid in acetonitrile gives the *syn*-alkylated adduct **27c** in high yield (Figure 4) along with a small amount of what appears to be the *N*-protonated isomer (**27b**).[18] In acidic acetonitrile solution, this product isomerizes over several hours to the more stable *anti* tautomer **27e** with formation of a small amount of the corresponding 2*H*-tautomer (**27f**). In the solid state, **27c** converts to the 2*H*-pyrrolium tautomer **27f** over a period of several days. Interestingly, when freshly prepared **27c** is isolated and then dissolved in CD_3CN, the product undergoes a rearrangement sequence involving deprotonation of the pyrrole, isomerization of the osmium to the more hindered double bond of the ring, and finally, a proton-induced intramolecular aldol reaction.[19] The resulting tetrahydrocyclopenta[*c*]-pyrrolium adduct, **27d**, whose structure is consistent with

(15) The separation of the *cis*- and *trans*-ammines for π-bound $Os^{II}(NH_3)_5$ complexes has been observed to be at least 1 ppm for all complexes characterized; the close separation of the ammines in this product strongly suggests that it is not π-bound, but rather, η^1-bound to the ligand. Harman, W. D. Ph. D. dissertation, Stanford University, 1987.

(16) The reduction potental of the olive-green *N*-bound $Os^{II}(NH_3)_5$-(η^1-pyridine) complex in 0.1 M HCl (aq) is −0.39 V. Sen, J.; Taube, H. *Acta Chem. Scan. A* **1979**, *33*, 125. In DME (0.5 M NaOTf), the potential is −0.45 V. Cordone, R. Ph. D. dissertation, Stanford University, 1988.

(17) The direct syntheses and NMR data for **5d** and **5e** have been previously reported (reference 4c).

(18) Partial characterization of **27b**: ^1H NMR (CD_3CN) δ 5.97 (s, 1H), 5.90 (d, 1H), 4.90 (d, 1H), 3.79 (s, 3H), 3.3 (br s, 12H).

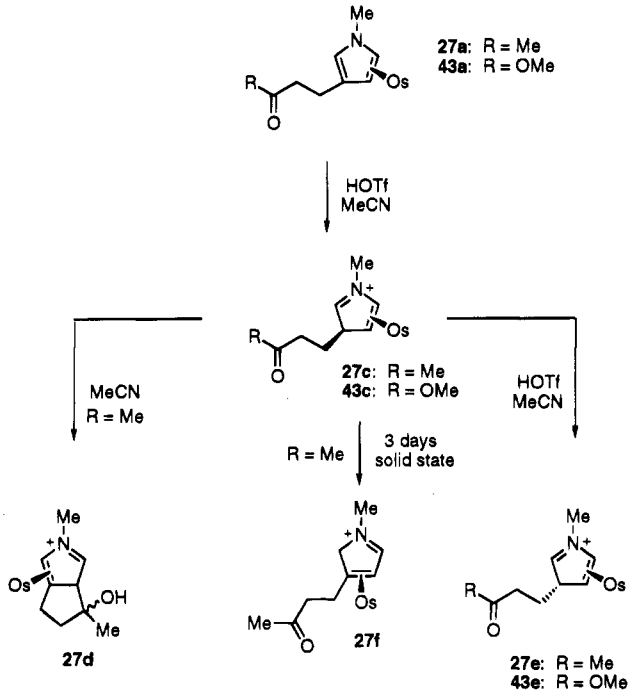
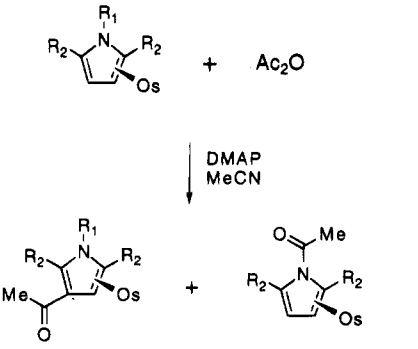


Figure 4. Protonation of the 1-methyl-3-(3-oxobutyl)pyrrole and 3-(2-carbomethoxyethyl)-1-methylpyrrole complexes.

^{1}H and ^{13}C NMR, DEPT, and HETCOR data, is observed as a 5:2 ratio of diastereomers (Figure 4).[20]

The 3-[2-(carbomethoxy)ethyl]-1-methylpyrrole complex **43a** gives exclusively the *syn*-regioisomer **43c** upon protonation in acetonitrile, subsequently converting over a period of hours to the *anti* isomer (**43e** = **39**, *vide infra*) (Figure 4). As in the case of the 1,3-dimethyl adduct, protonation in methanol gives the isomerized 3*H*-pyrrolium tautomer **43d**. When isolated **43d** is placed in neutral acetonitrile solution, this product also converts exclusively to **43e**.

Acylation and Imination. The 1-methylpyrrole complex **2** is unreactive toward acetic anhydride in acetonitrile at room temperature; however, addition of 1 equiv of DMAP gives clean acylation at the β-position within 10 min to give the 3-acetyl-1-methylpyrrole complex **15** (Figure 5). This compound shows signals in the ^{1}H NMR spectrum (acetone-d_6) characteristic of a neutral, β-substituted pyrrole coordinated by osmium: two doublets at 6.49 and 5.78 ppm for H(5) and H(4), respectively, and a singlet at 7.59 ppm for H(2), shifted downfield due to conjugation with the acetyl group. To exchange residual acetate counterion[21] for triflate, the product was treated with excess HOTf in methanol, isolated, and subsequently treated with base (DBU, acetonitrile solution) to regenerate **15** as analytically pure material.[22] Under these acylation reaction conditions, the parent pyrrole complex (**1**) and 2,5-dimethylpyrrole complex **3** undergo predominately *N*-acylation (Figure 5).



St. Mat.	R(1)	R(2)	β-acylation	N-acylation
1	H	H	0	100
2	Me	H	100 (15)	0
3	H	Me	30	70

Figure 5. Acylation of various pyrrole complexes with acetic anhydride/DMAP.

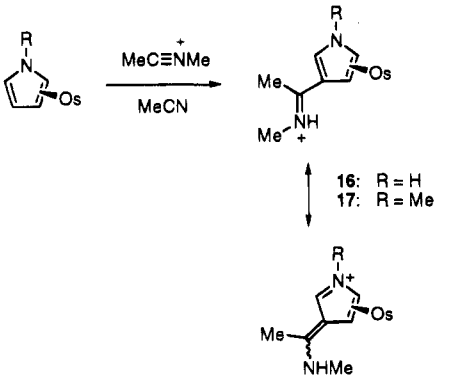


Figure 6. Imination of various pyrrole complexes with *N*-methylacetonitrilium triflate.

Treatment of either the pyrrole (**1**) or 1-methylpyrrole (**2**) complexes with methylacetonitrilium triflate in acetonitrile gives the iminium-substituted 1*H*-pyrrole complexes **16** and **17**, respectively (Figure 6).[4c,23] The presence of the conjugated iminium functionality is assigned from ^{1}H and ^{13}C NMR data, which indicate a neutral 1*H*-pyrrole nucleus substituted at the β-position by an electron-withdrawing group containing an NH proton. Furthermore, anion methathesis with $NaBPh_4$ gives a complex with three anions (^{1}H NMR), consistent with a monocationic pyrrole ligand. Cyclic voltammetric data shows an irreversible oxidation wave ($E_{p,a}$ = +0.75 V), also indicative of a strong electron withdrawing group at the β-position. This complex is resistant to deprotonation with Proton Sponge (pK_a = 12.4), and to hydrolysis under either acidic or basic conditions. Reaction of the 2,5-dimethylpyrrole complex **3** under the same reaction conditions or at reduced temperature (−50 °C) gives a complex mixture of products. In contrast with the reactivity observed with acetic anhydride, electrophilic addition at the nitrogen does not occur to a significant degree with the pyrrole complex **1**.

Aldol Reactions. Aldol reactions at C(3), promoted by either Lewis or Brönsted acids, have led to several

(19) Presumably, deprotonation of **27c** at C(3) (pK_a ~6) occurs first, followed by isomerization of the metal. This proton subsequently serves as a Lewis acid to promote the aldol reaction to form **27d**.

(20) This compound is synthesized on a preparative scale by addition of a methanolic triflic acid solution to a methanol solution of **27a** followed by precipitation with Et_2O. See Experimental Section.

(21) Acetate anion, a byproduct from the use of acetic anhydride, is incorportated into the osmium complex as a counterion in preference to triflate. Protonation with excess triflic acid results in the conversion of acetate to acetic acid and allows the complexes to be isolated as homogeneous triflate salts.

(22) Protonation of **15** occurs on the carbonyl oxygen of the acetyl group and generates a 6-hydroxy-2-azafulvenium complex similar to **24** (*vide infra*). Hodges, L. M.; Moody, M. W.; Spera, M. L.; Harman, W. D. Manuscript in preparation.

(23) Compounds **16** and **17** can also be described as 6-(methylamino)-2-azafulvenium complexes.

different η^2-pyrrole derivatives.[4e] Mukaiyama-type aldol reactions can be carried out with ketones and certain aldehydes using *tert*-butyldimethylsilyl triflate (TBSOTf) (Figure 7). Reaction of the pyrrole (**1**), 1-methylpyrrole (**2**), or 2,5-dimethylpyrrole (**3**) complexes with excess acetone in the presence of TBSOTf (in CH_3CN) results in the formation of the silylated 3*H*-pyrrolium aldol adducts **18**–**20** (Figure 7). These compounds have not been isolated, but have been characterized spectroscopically (CD_3CN) and subsequently carried on to other products. Addition of the amidine base DBU to **19** effects the elimination of TBSOH and the subsequent deprotonation of a methyl substituent to give a substituted β-vinylpyrrole complex.[24] Reprotonation of the isolated β-vinylpyrrole complex (HOTf, CH_3OH) cleanly generates the 2-azafulvenium complex **24**.[25] In the case of the 2,5-dimethyl analog **20**, addition of base (DBU) results in deprotonation at the nitrogen, giving the TBS-substituted 3*H*-neutral tautomer **21** in good yield. Reaction of **2** with benzaldehyde in the presence of 1 equiv TBSOTf (acetonitrile) followed by precipitation with hexanes gives the TBS-substituted aldol adduct **22** in good yield as a 1:1 ratio of diastereomers.

In addition to aldehydes and ketones, electrophilic additions can also be achieved with acetals (Figure 7). Reaction of the 1-methylpyrrole complex **2** with benzaldehyde dimethyl acetal in the presence of 1 equiv TBSOTf gives complex **23** in excellent yield as a 1:1 ratio of diastereomers.

Ketones can react at nitrogen if the β-position away from metal coordination is substituted. Protonation of the 3-methylpyrrole complex **6a** in the presence of acetone results in loss of water and formation of a purple solution of the 5-azafulvenium complex **25**, which is isolated by precipitation with Et_2O (Figure 7). Unlike its 2-azafulvenium counterpart **24**, complex **25** is unstable in water. When **25** is dissolved in D_2O, acetone is liberated, and only paramagnetic byproducts are formed.

β-Alkylations. The alkylation of the 1-methylpyrrole complex **2** using methyl triflate in DME followed by base has been reported and gives a 4:1 ratio of the 1,3-dimethylpyrrole (**5a**) and 1,1-dimethyl-1*H*-pyrrolium complexes, which can be separated using ion-exchange chromatography.[4c] While this method serves as a good pathway to 1,3-dialkylated pyrrole complexes, the analogous reaction with either the pyrrole (**1**) or 2,5-dimethylpyrrole (**3**) complexes gives alkylation at the nitrogen rather than at the β-position to produce the 1-methyl-3*H*-pyrrolium (**10**) or 1,2,5-trimethyl-3*H*-pyrrolium complexes, respectively.

Alkylation at the β-position can also be achieved through conjugate addition to Michael acceptors. Reaction of the 1-methylpyrrole complex **2** with 1 equiv of methyl vinyl ketone (MVK) in methanol gives the β-alkylated 1*H*-pyrrole species, **27a**, in 93% yield (Figure 8).[4d] Reaction of pyrrole complex (**1**) with 2 equiv of MVK gives the corresponding 1,3-dialkylated 1*H*-pyrrole complex **26**.

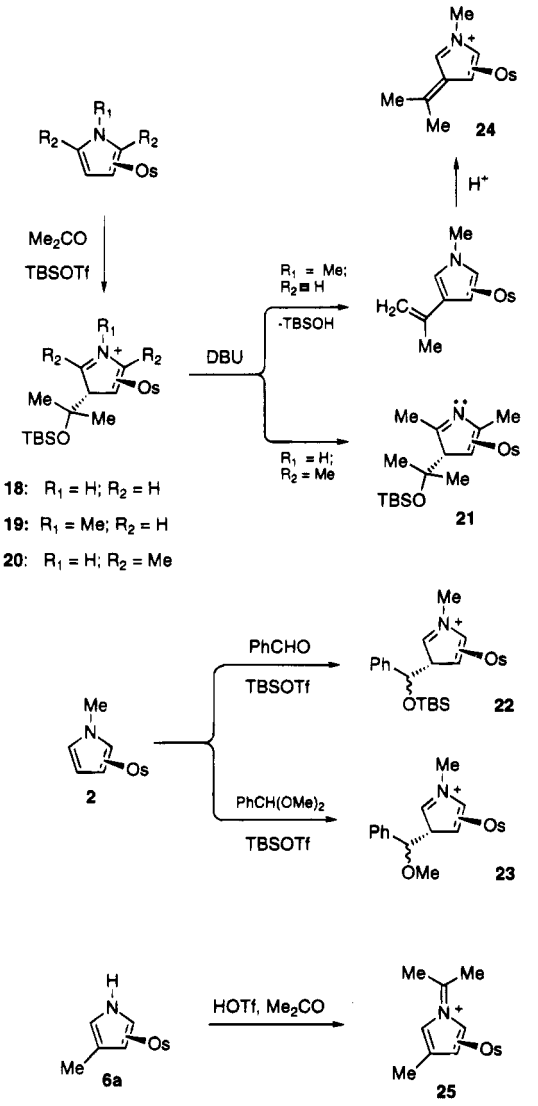


Figure 7. Aldol reactions of various pyrrole complexes.

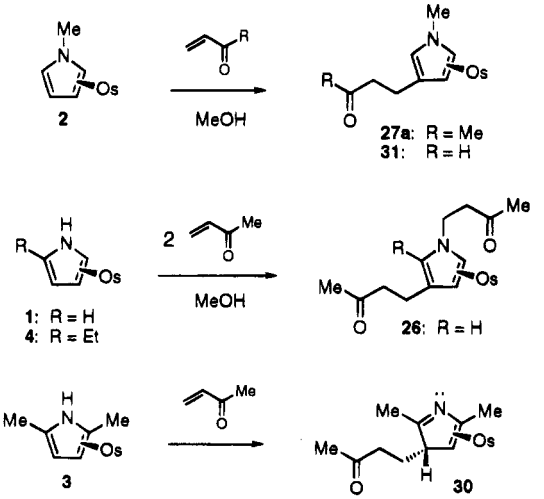


Figure 8. Michael addition of various pyrrole complexes with methyl vinyl ketone (MVK).

When only 1 equiv of MVK is used with **1**, a 50% yield of **26** is generated, with the remainder being starting material. The 2,5-dimethylpyrrole complex **3** reacts with MVK in acetonitrile to give a 1:1 ratio of the neutral β-alkylated 3*H*-tautomer **30** along with a second alky-

(24) The elimination of TBSOH from **19** results in the direct formation of the 2-azafulvenium adduct **24**; however, this product deprotonates to give the β-vinylpyrrole complex in the presence of DBU, and therefore is not isolated at this step. The synthesis, characterization, and reactivity of β-vinylpyrrole complexes are the focus of a separate study. See ref 4e.

(25) Both azafulvenium complexes **24** and **25** (*vide infra*) are named in the Experimental Section using nomenclature consistent with uncomplexed azafulvenes and azafulveniums; however, for clarity, they are numbered based on their pyrrole precursors in the tables in the Results section.

lated product (*vide infra*). As is observed with the pyrrole complex, reaction of the 2-ethylpyrrole complex **4** with 2 equiv of MVK (CH_3OH) gives the 1,3-dialkylated adduct analogous to **26**.[26] Similar results are obtained with α,β-unsaturated aldehydes. When **2** is combined with acrolein in methanol, monoalkylated complex **31** is obtained in high yield, a product of clean 1,4 addition.[27]

Electrophilic additions with activated alkynes also occur rapidly with the η^2-pyrrole complexes. In methanol solution, the pyrrole (**1**) and 1-methylpyrrole (**2**) complexes undergo conjugate addition cleanly at C(3) with 3-butyn-2-one to give the β-enone-substituted pyrrole complexes **36** and **32**, respectively, in >80% yield (Figure 9). In both cases, *trans*-stereochemistry is assigned from the coupling constants (J = 15.3 Hz) of the vinyl protons on the side chain. In contrast to what is observed with the electrophile MVK, **1** only undergoes monoaddition with 3-butyn-2-one, even in the presence of excess electrophile. In DMSO solution, reaction of the alkyne with **2** gives a new product, **33**, whose ^1H and ^{13}C NMR spectra indicate an α,β-disubstituted enone and an osmium-coordinated 2-pyrroline fragment. These data, along with HETCOR (300 MHz) and $^1H-^{13}C$ long range correlation spectroscopy (500 MHz) data, confirm that **33** is the [3.2.0]azabicycloheptadiene shown in Figure 9, a product resulting from a Michael–Mannich reaction sequence.[28] When this product is treated with a protic solvent or undried reagent grade acetone, a retro-Mannich reaction rapidly ensues, generating **32** quantitatively.

In contrast to what is observed in methanol, the parent pyrrole complex **1** reacts with 3-butyn-2-one in DMSO with 1:2 stoichiometry, even when only 1 equiv of the alkyne is added. The new product (**37**, 89% yield), isolated as an 85:15 ratio of diastereomers, shows several spectroscopic features consistent with both a 2-pyrroline and an α,β-disubstituted enone. However, the presence of an additional allylic alcohol group and the absence of a NH signal led us to propose the tricyclic compound **37** shown in Figure 9, whose structure is consistent with DEPT, COSY, and HETCOR data. The analogous reaction with the 2,5-dimethylpyrrole complex **3** in DMSO gives a mixture of products. In methanol, treatment of **3** with 3-butyn-2-one results in oxidation of the metal.

The reaction of the doubly activated dimethylacetylenedicarboxylate (DMAD) with **2** in DMSO cleanly generates the cyclobutene derivative **35**. While **35** is less sensitive to the retro-Mannich reaction than the acetyl derivative **33**, ring-opening can be achieved in methanol ($t_{1/2}$ < 0.5 h, 25 °C) to give **34** as one isomer (de > 95%).[29] Attempts to generate **34** directly by the reaction of **2** and DMAD in methanol result in a complex mixture of unidentified products.

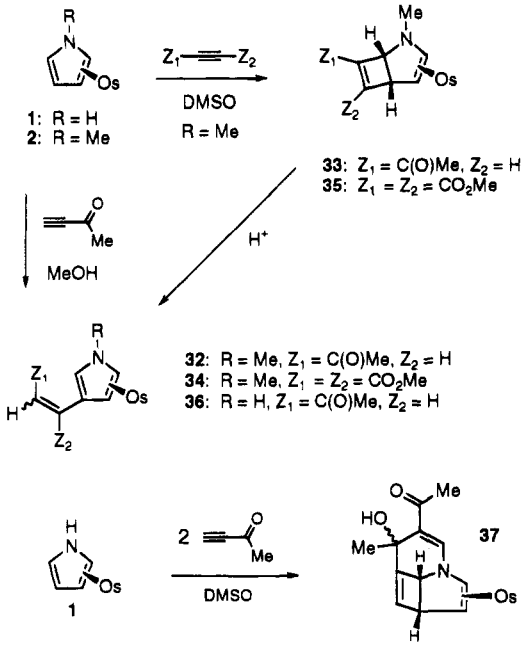
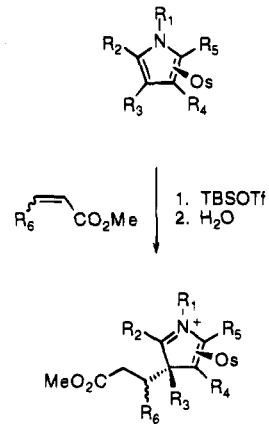


Figure 9. Michael addition of various pyrrole complexes with activated alkynes.



Cpd	R_1	R_2	R_3	R_4	R_5	R_6
38	H	Me	H	H	Me	H
39	Me	H	H	H	H	H
40	H	Et	H	H	H	H
41	Me	H	H	H	H	Me
42	H	H	Me	H	H	H

Figure 10. Lewis acid-promoted Michael additions of various pyrrole complexes.

Compared to MVK or 3-butyn-2-one, methyl acrylate is slower to react at room temperature with any of the pyrrole complexes studied; however, activation of the electrophile using a suitable Lewis acid produces clean alkylation at C(3). Reaction of the 1-methylpyrrole (**2**) or 2,5-dimethylpyrrole (**3**) complexes with methyl acrylate in the presence of 1 equiv of TBSOTf followed by hydrolysis of the intermediate silyl ketene acetals gives the β-alkylated, 3*H*-pyrrolium adducts **39** and **38**, respectively (Figure 10).[4d] While the parent pyrrole complex **1** undergoes this reaction, the resulting product is contaminated with significant amounts of a paramagnetic Os(III) material. The presence of a substituent at C(2) of the pyrrole ring or on the double bond of the electro-

(26) Note that β-alkylation occurs from the more hindered side of the pyrrole ring. Partial characterization: ^1H NMR (acetone-d_6) δ 6.48 (d, J = 4.2 Hz, 1H), 5.28 (d, J = 4.5 Hz, 1H), 4.56 (br s, 3H), 4.02 (m, 2H), 2.72 (m, 2H), 2.38 (m, 1H), 2.12 (s, 3H), 2.11 (s, 3H), 1.04 (t, 3H); ^{13}C NMR (acetone-d_6) δ 208.82 (C), 207.35 (C), 137.36 (C), 117.93 (C), 79.61 (CH), 54.51 (C), 43.70, 43.37, 42.75 (CH_2), 29.63 (CH_3), 29.33 (CH_3), 21.44 (CH_2), 17.25 (CH_2), 16.00 (CH_3).

(27) No evidence of 1,2-addition for this reaction is observed; a similar observation is made with η^2-aniline complexes. Kolis, S. P.; Harman, W. D. Manuscript in preparation.

(28) The analogous cycloaddition reaction with methyl propiolate or DMAD occurs with acyclic enamines. See: (a) Brannock, K. C.; Burpitt, R. D.; Goodlett, V. W.; Thweatt, J. G. *J. Org. Chem.* **1963**, *28*, 1464. (b) Brannock, K. C.; Burpitt, R. D.; Goodlett, V. W.; Thweatt, J. G. *J. Org. Chem.* **1964**, *29*, 818.

(29) Although compound **34** is stereochemically pure, the stereochemistry at the double bond is currently unknown.

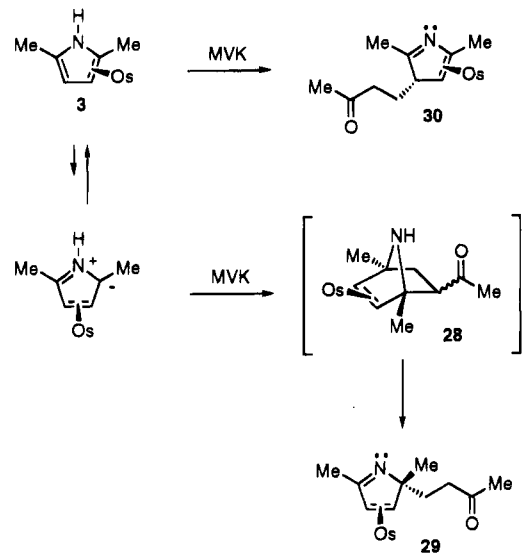


Figure 11. Conjugate addition/dipolar cycloaddition reaction manifold for the 2,5-dimethylpyrrole complex **3** and MVK.

phile appears to have little effect on this reaction. Reaction of the 2-ethylpyrrole complex **4** with methyl acrylate gives a single product with alkylation occurring on the more hindered side of the ring to give the 2,3-disubstituted 3*H*-pyrrolium adduct **40** (80% yield). The reaction of **2** with methyl crotonate gives the expected conjugate addition product **41** as a 4:1 ratio of diastereomers.[4d] Even in the case of the 3-methylpyrrole complex **6a**, monoalkylation at the *hindered* β-position occurs exclusively to give adduct **42** in good yield.[4d] NOE experiments[30] for **42** are consistent with the methyl group at C(3) being *syn* to the pentaammineosmium group, with addition of the electrophile occurring *anti* to the metal. Upon addition of amine base (Proton Sponge, *i*-PrEt$_2$N), the 1-methyl analog **39** deprotonates at C(3) to give the 1*H*-tautomer **43a**; the 2,5-dimethylpyrrolium adduct **38** deprotonates at nitrogen, giving the corresponding neutral 3*H*-tautomer.

1,3-Dipolar Cycloaddition. When the 2,5-dimethylpyrrole complex **3** (0.13 mmol) is combined with 1 equiv MVK in acetonitrile (439 mg), two products, **29** and **30**, are isolated as a 1:1 mixture after several hours. Compound **30** is readily identified as the β-alkylated 3*H*-pyrrole complex (*vide supra*). When the reaction is repeated in CD_3CN and monitored over time, a new species in addition to **30** is formed at early reaction times and eventually converts ($t_{1/2}$ ~1 h) to compound **29** (Figure 11). This new material (**28**)[31] has been characterized as a 7-azabicyclo[2.2.1]heptene complex, the product resulting from a 1,3-dipolar cycloaddition of the 2,5-dimethylpyrrole complex **3** and MVK.[32] Compound **29**, resulting from a retro-Mannich reaction of **28** followed by proton transfer, is characterized by ^{1}H and ^{13}C NMR, as well as DEPT and HETCOR data, to be an α-alkylated 2*H*-pyrrole complex containing a pendant 3-oxobutyl group.

The conjugate addition/cycloaddition manifold is highly influenced by the pyrrole complex, electrophile, solvent, temperature, and in some cases, concentration. To explore the solvent dependence of these reactions, the dimethylpyrrole complex **3** was combined with MVK in different solvents and the ratio of compounds **29**:**30** measured by ^{1}H NMR (Table 2). A solution which was 0.23−0.32 M in **3** with 1−2 equiv of MVK was monitored in various solvents at 25 °C (Table 2). For polar aprotic solvents such as acetonitrile, acetone, or DMF, an approximate 1:1 ratio of the two products was obtained. In DMSO, there was a marked enhancement of the cycloaddition reaction, especially under dilute conditions (*vide infra*). In protic solvents such as methanol or water, the formation of conjugate addition products was favored.

Table 2. Solvent, Temperature, and Concentration Dependence of the Reaction between the 2,5-Dimethylpyrrole Complex 3 and MVK

entry	solvent	[3], M	MVK, equiv	temp, °C	product ratio 3H[a]:2H[b]
a	MeCN	0.32	2.0	50	50:50
b	MeCN	0.33	1.1	25	50:50
c	MeCN	0.32	2.0	−10	80:20
d	MeOH	0.32	2.0	50	75:25
e	MeOH	0.23	1.3	25	75:25
f	MeOH	0.32	2.0	−10	90:10
g	MeOH	0.32	1.7	−50	98:2
h	H_2O	0.020	1.2	25	89:11
i	H_2O	0.30	1.0	25	91:9
j	Me_2CO	0.16	1.1	25	40:60
k	Me_2CO	0.33	1.1	25	50:50
l	DMF	0.26	1.0	25	50:50
m	DMSO	0.59	1.2	25	45:55
n	DMSO	0.40	1.1	25	40:60
o	DMSO	0.25	2.2	25	33:67
p	DMSO	0.057	1.2	25	18:82
q	DMSO	0.035	1.4	25	11:89

[a] 3H = {4β,5β-η^2-[Os(NH$_3$)$_5$]-2,5-dimethyl-3α-(3-oxobutyl)-3*H*-pyrrole}OTf$_2$ [**30**]. [b] 2H = {3β,4β-η^2-[Os(NH$_3$)$_5$]-2β,5-dimethyl-2α-(3-oxobutyl)-2*H*-pyrrole}OTf$_2$ [**29**].

The effect of temperature on the selectivity of the above reaction was investigated in both methanol and acetonitrile (entries a−g, Table 2). In both solvents, a significant preference for conjugate addition was observed at reduced temperatures, although the selectivity was more pronounced in methanol, where a 50:1 ratio of **30** to **29** was obtained at −50 °C. In either solvent, running the reaction at a higher temperature (50 °C) had no effect on the reaction selectivity.

In a few cases, the selectivity of the reaction has a pronounced dependence on concentration of the osmium complex. In DMSO, running the reaction under dilute (0.035 M) conditions resulted in an 8:1 ratio of cycloaddition to conjugate addition products. Increasing the concentration of the reaction steadily erodes the selectivity to where it almost becomes 1:1 at 0.59 M (entries m−p). In water, this concentration dependence was barely discernible; varying the concentration of **3** from 0.30 to 0.020 M only changed the ratio of **29** to **30** from 10:1 to 8:1.

While activated ketones react primarily at the β-carbon with complexes of pyrrole (**1**) or 1-methylpyrrole (**2**) and at least partially with the 2,5-dimethylpyrrole complex (**3**), esters such as dimethyl fumarate or methyl acrylate show a considerably stronger preference for dipolar cycloaddition. When either **2** or **3** is combined with methyl acrylate in DMAc, the exclusive products are the

(30) Irradiation of the *cis*-ammine (3.96 ppm, acetone-d_6) results in a 4.5% NOE enhancement of the methyl signal (1.51 ppm) and no enhancement of the CH_2 resonances (2.54 ppm).

(31) Partial characterization of **28**: ^{1}H NMR (CD_3CN) δ 4.03 (br s, 3H), 3.4 (br s, 12H), 2.06 (s, 3H), 1.35 (s, 3H), 1.24 (s, 3H).

(32) Pyrrole complexes, such as **2** or **3**, undergo dipolar cycloadditions with a wide range of α,β-unsaturated carbonyl compounds. See reference 4a and Gonzalez, J.; Koontz, J. I.; Hodges, L. M.; Nilsson, K. R.; Neely, L. K.; Myers, W. H.; Sabat, M.; Harman, W. D. *J. Am Chem. Soc.* **1995**, in press.

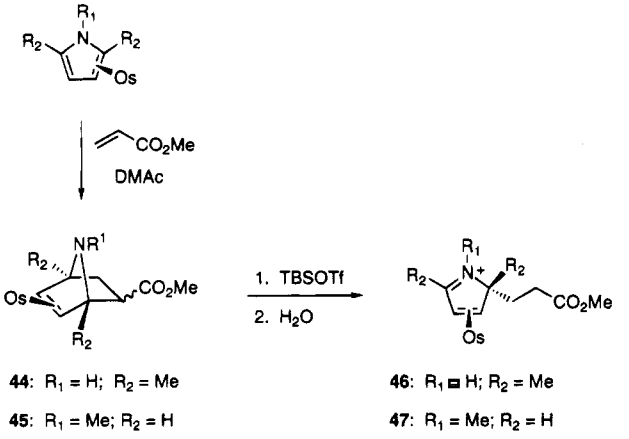


Figure 12. Lewis acid-promoted ring opening of 7-azabicyclo-[2.2.1]heptene complexes.

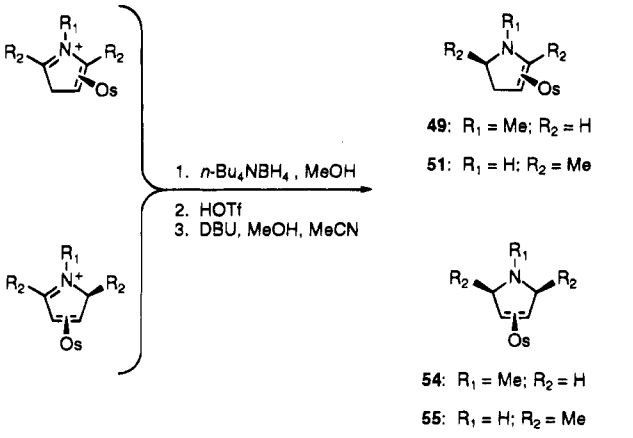


Figure 13. Reduction of 3*H*- and 2*H*-pyrrolium complexes with tetra-*n*-butylammonium borohydride (TBAB).

7-azanorbornene complexes **45** and **44**, respectively (80–95% yield) (Figure 12). When treated with a Lewis acid, these cycloadducts undergo a retro-Mannich reaction to give α-substituted 2*H*-pyrrolium complexes **47** and **46**, respectively (Figure 12).[4d] Thus, when the cycloadduct **44** derived from **3** and methyl acrylate is treated with TBSOTf in acetonitrile followed by water, the α-substituted 2,5-dimethyl-2*H*-pyrrolium complex **46** can be isolated in excellent yield. Similarly, ring opening of the cycloadduct **45** derived from the **2** and methyl acrylate gives the 1-methyl-2*H*-pyrrolium analog **47** in excellent yield.

Nucleophilic Addition. Both 2*H*- and 3*H*-pyrrolium tautomers are susceptible to nucleophilic addition at the iminium carbon. Dihapto-coordinated 2- and 3-pyrroline complexes, as well as protonated and alkylated derivatives, can be synthesized from η^2-pyrrole complexes by a formal reduction of either the C(2)–C(3) or C(2)–C(5) system (Figure 13). Hydride reduction of the 2*H*- or 3*H*-pyrrolium tautomers of 1-methylpyrrole (**8**, **10**) or 2,5-dimethylpyrrole (**9**, **11**) can be accomplished with either sodium borohydride or tetrabutylammonium borohydride (TBAB) in either methanol or methanol/acetonitrile solution.[33] The corresponding 2-pyrroline (**49**, **51**) and 3-pyrroline (**54**, **55**) complexes are formed in good yield after workup (Figure 13). Furthermore, the 2-pyrroline complexes can be synthesized from their 1*H*-pyrrole precursors in a one-pot reaction sequence. ^1H and ^{13}C NMR data, NOE experiments,[34] and proton coupling data are consistent with both protonation and hydride addition occurring *anti* to the metal.

The intermolecular addition of carbon nucleophiles to the η^2-pyrrolium complexes has also shown promise. Preliminary results indicate that cyanide ion adds to the α-carbon of 2*H*-pyrrolium complexes, as well as 3*H*-pyrrolium derivatives in cases where the acidic C(3)-proton is *syn* to the metal. In contrast, treatment of the 3*H*-pyrrolium species **10** with cyanide, which possesses an acidic C(3)-proton in an *anti* orientation, results in a significant amount of deprotonation. Additional studies are currently in progress to further determine the scope of intermolecular nucleophilic additions to η^2-pyrrolium complexes.

(33) The use of $NaBH_4$ gives NaOTf as a byproduct, which is difficult to remove from the pyrroline complexes; thus, the use of TBAB is preferred.

(34) Irridation of the *cis*-ammine of the symmetric 2,5-dimethyl-3-pyrroline complex **55** results in a 3.0% NOE enhancement of the C(2)- and C(5)-methyl resonances.

Table 3. Electrochemical and Yield Data for Various Osmium Complexes[a]

class	complex	$E_{p,a}$	yield[b]	class	complex	$E_{p,a}$	yield
–	$Os^{II}A_5CO$[c]	0.75[d]		VI	**11**	1.09[e]	89
–	$Os^{II}A_6$[f]	-0.78[d]		VI	**22**	1.41	89
I	**3**[g]	0.05	>95	VI	**23**	1.43	94
I	**6a**	0.13	92	VI	**27d**	1.37	88
I	**15**	0.47	>90	VI	**38**	1.33	93
I	**16**[h]	0.75	79	VI	**39**	≈1.3	97
I	**17**	0.78	88	VI	**40**	1.43	80
I	**26**	0.17	84	VI	**41**	1.34	72
I	**27a**	0.17	90	VI	**42**	1.33	65
I	**31**	0.19	91	VII	**6g**	1.63	–
I	**32**	0.39	93	VIII	**24**	1.21	79
I	**34**	0.51	84	IX	**25**	1.35	88
I	**36**	0.35	84	X	**35**	0.51	72
I	**43a**	0.18	51	X	**37**	0.74	89
II	**7**[g]	0.84	82	X	**49**	0.03	80
II	**48**	0.91	62	X	**51**	0.29	90
III	**21**	0.68	71	X	**52**	0.84	*i*
V	**9**[g]	1.34	92	XI	**50**	1.35	50
V	**27f**	1.37	–	XII	**54**	0.66	83
V	**46**	1.38	96	XII	**55**	0.71	74
V	**47**	1.40	87	XII	**56**	0.72	*j*
				XIII	**53**	1.21	71

[a] All scans recorded on triflate salts in acetonitrile (TBAH electrolyte); all potentials are given in volts vs NHE. [b] Yields reported are overall isolated yields from starting pyrrole complexes (e.g. **1**–**6a**); yields given for **3** and **6a** are from the starting ligand. [c] (a) Allen, A. D.; Stevens, J. R. *Can. J. Chem.* **1972**, *50*, 3093. (b) Harman, W. Dean, Ph.D. Dissertation, Stanford University, 1987. [d] Reversible couple; value given is $E_{1/2}$. [e] First wave; a second irreversible wave is present at +1.35 V. See footnote g. [f] Harman, W. D.; Taube, H. *Inorg. Chem.* **1988**, *27*, 3261. [g] Myers, W. H.; Koontz, J. I.; Harman, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 5684. [h] Recorded as tetraphenylborate (BPh_4) salt. [i] Not reported due to acetate anion contamination; see overall yield for **53**. [j] Not reported due to NaOTf contamination.

Cyclic Voltammetry. Electrochemical data for selected pyrrole complexes are shown in Table 3. As reported previously,[4c] all oxidation waves are believed to result from the one-electron oxidation of osmium(II), as seen previously in other pentaammineosmium(II) systems.[35] Consistent with our prior observations, 1*H*-pyrrole complexes and their alkylated analogs show irreversible oxidation waves between 0.0 and +0.2 V; the presence of electron-withdrawing groups at the 3-position shifts this potential positive by 200–600 mV, depending on the substituent. The 2*H*- and 3*H*-pyrrole complexes have potentials in the range of +0.7 to +0.9 V, consider-

(35) Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 5725.

Table 4. Electronic Data for Various η^2-Pyrrole Complexes

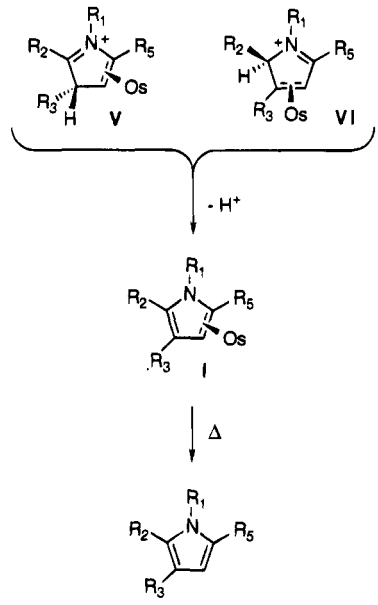
class	cpd	color	λ, nm (log ϵ)[a]
I	**2**	light yellow	200 (4.08), 242 (3.74), 300 (3.34)
I	**3**	light yellow	206 (3.96), 304 (3.27)
I	**6a**	light yellow[b]	200 (3.99), 242 (3.75), 294 (3.28)
I	**15**	golden yellow	222 (4.07), 288 (3.58), 348 (3.73)
II	**7**	tan	200 (3.78), 222 (3.81), 272 (3.47)
III	**21**	yellow	198 (3.87), 234 (3.70), 320 (2.67)
V	**9**	purple-red	196 (3.83), 230 (3.79), 286 (3.60), 488 (2.44)
VI	**10**	light orange	196 (3.76), 230 (3.64), 268 (3.40), 464 (2.22)
VII	**6g**	golden brown	196 (3.83), 240 (3.86), 312 (3.46), 416 (3.09)
VIII	**24**	turqoise	198 (3.90), 244 (3.88), 352 (3.66), 592 (2.54)
IX	**25**	lavender	198 (3.95), 218 (3.93), 258 (3.59), 328 (3.72), 522 (2.63)
X	**49**[c]	off-white	204 (3.84)
XI	**55**[c]	off-white	200 (3.89), 246 (3.35)

[a] All spectra obtained in acetonitrile solution unless otherwise noted; wavelengths (λ) are given in nm, and extinction coefficients (ϵ) are in L mol^{-1} cm^{-1}. [b] This compound in crude form often has an olive green appearance due to an impurity. [c] Recorded in methanol.

ably positive of their 1*H*-counterparts. In contrast to the complexes of neutral organic ligands, 3*H*-, 2*H*-, and 1*H*-pyrrolium analogs, including the azafulvenium complexes, show potentials $\geq +1.2$ V. Complexes of 2-pyrrolines show reduction potentials in the range of 0.0 to +0.3 V, similar to those of the 1*H*-pyrrole complexes, while 3-pyrroline complexes are more resistant to oxidation, having potentials ranging from +0.65 to +0.75 V.

UV-Visible Spectra. UV-visible data for selected pyrrole and pyrrolium complexes are given in Table 4. 1*H*-Pyrrole complexes (**2**, **3**, **6a**) show one large $\pi-\pi^*$ absorption at approximately 200–210 nm (log ϵ = 3.9–4.1) and two smaller absorptions at approximately 240–250 nm (log ϵ = 3.7) and 300 nm (log ϵ = 3.3). The latter two bands for the 3-acetyl derivative **15** are shifted approximately 40–50 nm to lower energy. Neutral 2*H*- and 3*H*-pyrrole tautomers (**7**, **21**) have similar features to the 1*H*-pyrroles. The 2*H*-pyrrolium species **9** shows a different spectrum, having three distinct bands between 200 and 300 nm with λ_{max} occurring at approximately 230 nm (log ϵ = 3.8) and a low intensity band at 488 nm (log ϵ = 2.44), responsible for the purple appearance. The 3*H*-pyrrolium species **10** shows three broad bands at 196 nm (log ϵ = 3.76), 230 nm (log ϵ = 3.64), and 268 nm (log ϵ = 3.40), as well as a very broad absorption (~460 nm, log ϵ ~2.2) in the visible region, giving it a light orange color. In addition to absorbances at 198 nm and 244 nm, the azafulvenium complex **24** has low energy absorptions at 352 nm (log ϵ = 3.66) and 592 nm (log ϵ = 2.54), giving rise to a turquoise color. The 5-azafulvenium complex **25** has absorptions at 198 and 218 nm as well as lower energy absorptions at 258 nm (log ϵ = 3.59) and 328 nm (log ϵ = 3.72). Also present is a weak absorption at 522 nm (log ϵ = 2.63), giving this compound a lavender appearance. In contrast to the unsaturated analogs, the off-white pyrroline complexes **49** and **51** have a relatively simple electronic spectrum (methanol solution) with no significant absorptions beyond 250 nm.

Decomplexation. 1*H*-Pyrrole and -pyrrolium complexes capable of rearomatization can usually be decomplexed simply by moderate heating under anaerobic conditions (Figure 14). For example, 3-acetyl-1-methylpyrrole (**57**) can be generated cleanly from the corresponding η^2-complex **15** in 80% yield (NMR) by heating a CD_3CN/D_2O solution at 95 °C for 50 min. Other 1*H*-pyrrole complexes (e.g., **27a** and **43a**) can be decomplexed (80 °C, ca. 1 h, CH_3CN) to give 1-methyl-3-(3-oxobutyl)-pyrrole (**58**) and 3-[2-(carbomethoxy)ethyl]-1-methylpyrrole (**59**), respectively, in 75–95% yield (Figure 14).[4d] In the case of the 2,5-dimethyl-3*H*-pyrrolium adduct **38**, prior deprotonation is not necessary; heating **38** (80 °C, CH_3CN) gives **60** directly in 95% isolated yield. Finally, the α-substituted pyrrole **62** can be synthesized by deprotonation of the 2*H*-pyrrolium adduct **47** (*i*-Pr_2EtN, CH_3CN), followed by heating (100 °C, 75 min, CH_3CN) (55% isolated yield from **47** after chromatography, 48% overall yield from **2**).



St. Mat.	Cls	R_1	R_2	R_3	R_5	Pdt	Yld[1]
15	I	Me	H	Ac	H	57	80
27a	I	Me	H	$(CH_2)_2C(O)Me$	H	58	>95 [77]
38	VI	H	Me	$(CH_2)_2CO_2Me$	Me	60	[95]
39	VI	Me	H	$(CH_2)_2CO_2Me$	H	59	75
47	V	Me	$(CH_2)_2CO_2Me$	H	H	62	[55]

(1) Percentages given are NMR yields; numbers in brackets are isolated yields.

Figure 14. Decomplexation of η^2-pyrrolium and pyrrole complexes to give 1*H*-pyrroles.

Liberation of the organic ligand in 3-pyrroline complexes can be accomplished in good yield either by Ce^{IV} oxidation or by heating under anaerobic conditions. For example, isolation of the substituted pyrrolizinone **63** is accomplished by first reducing **46** ($NaBH_4$, MeOH) to give the 3-pyrroline complex **56**. Subsequent heating (9:1 CH_3CN/DMSO, 110 °C, 4 h) of complex **56** yields the free 3-pyrroline, which ring closes during aqueous workup to give the pyrrolizinone **63** in 65% overall yield (de > 90%) (Figure 15).[4d] The direct oxidation of **46** with $Ce^{IV}(NH_4)_2(NO_3)_6$ in acidic CD_3CN (~0.22 M HOTf) results in approximately 70% NMR yield of the demetalated 2*H*-pyrrolium species.[36]

While 3-pyrrolines are readily decomplexed, 2-pyrrolines present a problem due to their inherent nucleophilicity and/or tendency to polymerize. Treatment of the 1-methyl-2-pyrroline complex **49** with $Ce(NH_4)_2(NO_3)_6$ under neutral conditions or in acidic acetonitrile fails to

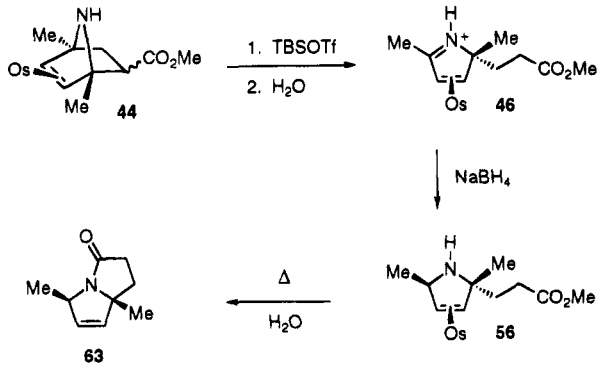


Figure 15. Decomplexation of a 3-pyrroline complex to give a substituted pyrrolizinone.

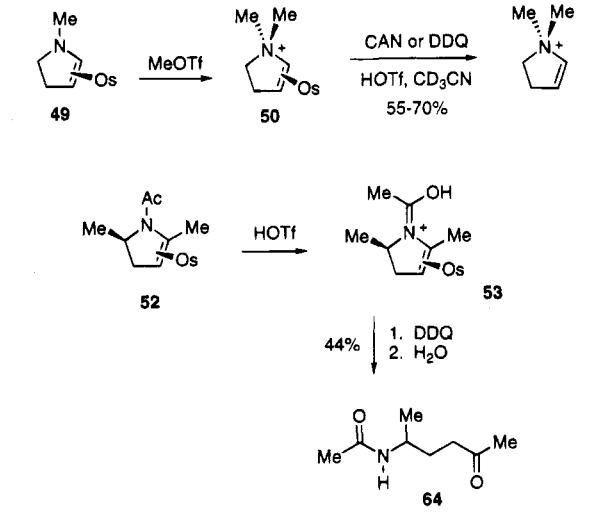


Figure 16. Decomplexation of 2-pyrroline complexes.

give a detectable amount of organic products. Treatment of the *N*-BF_3 derivative[37] with Ce^{IV} yields similar results. However, when the nitrogen is first quaternized using CH_3OTf (**50**), oxidation with 1.0 equiv of either Ce^{IV} (70%) or DDQ (55%) in HOTf/CD_3CN solution cleanly gives the vinylammonium product shown in Figure 16.[38] An alternative method to remove an organic fragment from 2-pyrroline complexes can be used when the nitrogen is unsubstituted. Acylation of the 2,5-dimethyl-2-pyrroline complex **51** with Ac_2O/pyridine gives the *N*-acetyl derivative **52**, which can be protonated (HOTf, CH_3OH) on the carbonyl oxygen to give **53** (87% yield from **51**, de = 80%). Without prior protonation, oxidation again fails to liberate any organic product.[39] Treatment of **53** with 1 equiv DDQ in acidic acetonitrile followed by addition of water decomplexes the ligand, which subsequently hydrolyzes and ring opens to give amide **64** in 44% NMR yield as shown in Figure 16.[40] Attempts to decomplex **52** or **53** using Ce^{IV} have led to recovery of either starting material or intractable product mixtures.

Discussion

The pentaammineosmium(II) moiety is unparalleled in its ability to form stable η^2-coordination complexes with aromatic molecules.[4,41] The η^2-pyrrole and η^2-pyrrolium complexes reported herein, as well as their derivatives, derive their stability from a substantial metal-to-ligand backbonding interaction, and such complexes are presently unknown for other transition metals. Their ease of formation, high kinetic stability, and simplicity of ancillary ligands make these η^2-pyrrole and η^2-pyrrolium species ideally suited for an investigation of how dihaptocoordination affects the reactivity of a pyrrole.

With osmium(II) binding pyrrole across C(4) and C(5), the uncoordinated portion of the ring both structurally and chemically resembles an enamine. Thus, addition of electrophiles to a *4,5*-η^2-pyrrole complex would be expected to occur either at the nitrogen or the β-carbon, C(3).[42] In general, for cases where the nitrogen is alkylated (e.g., the 1-methylpyrrole complex **2**), electrophilic addition is observed predominantly at C(3). Examples include the electrophiles methyl acrylate (TBSOTf-promoted), methyl vinyl ketone, 3-butyn-2-one, DMAD, acetic anhydride (DMAP-catalyzed), methylacetonitrilium triflate, acetone (TBSOTf-promoted), benzaldehyde (TBSOTf-promoted), benzaldehyde dimethyl acetal (TBSOTf-promoted), triflic acid, and methyl triflate. For the last example, *N*-methylation competes with electrophilic addition at the β-carbon to a minor extent (1:4).[4c] For all other electrophiles examined, electrophilic addition occurs at the β-carbon exclusively for the 1-methylpyrrole complex **2**. The 3*H*-pyrrolium products are unusually stable to rearomatization, requiring a moderate base to effect deprotonation at C(3).[43] As a result, multiple alkylation of the pyrrole carbons is virtually never observed.

When the pyrrole nitrogen is unsubstituted, *N*-addition becomes the primary reaction for "hard" electrophiles. Thus, methylation or acylation occurs predominantly at the nitrogen for both the pyrrole (**1**) or 2,5-dimethylpyrrole (**3**) complexes. In contrast, when "softer" electrophiles such as methylacetonitrilium triflate, MVK, 3-butyn-2-one, α,β-unsaturated esters (TBSOTf-promoted), aldehydes, and ketones (TBSOTf-promoted) are used, electrophilic addition occurs preferentially at C(3), even for the pyrrole complex **1**. In the case of the nitrilium additions, the final products after rearomatization are 1*H*-pyrrole complexes with a protonated imine substituent on C(3). These compounds (**16**, **17**), which formally

(36) ^1H NMR (CD_3CN, 0.22 M HOTf) δ 11.9 (br s, 1H), 7.84 (dd, J = 5.4, 1.5 Hz, 1H), 6.78 (dd, J = 5.4, 1.5 Hz, 1H), 3.55 (s, 3H), 2.67 (s, 3H), 2.34 (t, J = 5.4 Hz, 2H), 2.17 (t, J = 5.1 Hz, 2H), 1.59 (s, 3H); ^{13}C NMR (CD_3CN (0.22 M HOTf)) δ 185.89, 173.85, 166.29, 128.53, 80.17, 52.52, 30.47, 29.09, 20.19, 18.03.

(37) Prepared in 82% yield from **49** by treatment with $BF_3{\cdot}Et_2O$ (CH_3CN solvent): ^1H NMR (CD_3CN) δ 5.23 (d, J = 4.8 Hz, 1H), 4.22 (br s, 3H), 4.15 (t, J = 5.1 Hz, 1H), 3.23 (br s, 12H), 3.10 (s, 3H), 2.73 (m, 2H), 2.17 (m, 2H).

(38) ^1H NMR (CD_3CN) δ 6.22 (m, 2H), 3.82 (dd, J = 7.5, 7.2 Hz, 1H), 3.18 (s, 6H), 2.90 (t, J = 6.9 Hz, 2H).

(39) DDQ is not a strong enough oxidant ($E_{1/2}$ = 0.75 V) to oxidize the metal in complex **52** ($E_{p,a}$ = 0.84 V). However, under acidic conditions (5 equiv of HOTf, CH_3CN), DDQ becomes a sufficiently strong oxidant to oxidize **53** ($E_{p,a}$ = 1.21 V) and liberate the organic ligand.

(40) This compound has been previously reported: (a) Becker, J. Y.; Byrd, L. R.; Miller, L. L. *J. Am. Chem. Soc.* **1974**, *96*, 4718. (b) Becker, J. Y.; Byrd, L. R.; Miller, L. L.; So, Y. *J. Am. Chem. Soc.* **1975**, *97*, 853. Spectral data presented in reference a for the title compound matches the observed data for **64**; however, in reference b, NMR data for the same compound was inadvertently switched with that of a different structural isomer.

(41) (a) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 1883. (b) Kopach, M. E.; Gonzalez, J.; Harman, W. D. *J. Am. Chem. Soc.* **1991**, *113*, 8972. (c) Cordone, R.; Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1989**, *111*, 2896. (d) Gonzalez, J.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1993**, *115*, 8857. (e) Kopach, M. E.; Harman, W. D.; Hipple, W. G. *J. Am. Chem. Soc.* **1992**, *114*, 1736.

(42) Alt, G. H.; Cook, A. G., in *Enamines: Synthesis, Structure, and Reactions*; Cook, A. G., Ed., Marcel Dekker, Inc.: New York, 1988, p 181.

(43) The pK_a of η^2-pyrrolium complexes ranges approximately from 5.5 to 8. See reference 4c.

are conjugate acids of vinylogous amidines, are characteristically resistant to deprotonation ($13 < pK_a < 17$) and hydrolysis, being stable to both aqueous acid and mild base.

The *4,5-*η^2 ↔ *2,3-*η^2 linkage isomerization occurs with specific rates ranging from 10^3 to 1 s^{-1} for these η^2-pyrrole complexes at 20 °C.[4a,c] Thus, at ambient temperatures, an equilibrium is established where the metal preferentially occupies the least hindered side of the heterocycle, away from any alkyl substituents. As a consequence, the *more hindered* β-carbon is most prone to electrophilic addition. Osmium(II) complexes of either 2-ethyl- (**4**) or 3-methylpyrrole (**6a**) undergo conjugate addition with methyl acrylate at C(3) exclusively (acetonitrile solvent, 1 equiv of TBSOTf), even for the latter case where this carbon is the only one that is substituted.

While both activated olefins and alkynes react cleanly with the η^2-pyrrole complexes, the latter Michael acceptors show a distinct difference in reactivity. When an η^2-pyrrole complex is treated with 3-butyn-2-one in a protic solvent, a single Michael addition occurs at C(3) regardless of the substitution on nitrogen or the excess of alkyne. In contrast to MVK, the alkyne gives rise to an enone substituent, deactivating the pyrrole ring toward additional electrophilic addition. Furthermore, when this reaction is carried out in DMSO with either 3-butyn-2-one or DMAD, the enolate resulting from conjugate addition attacks the adjacent electrophilic α-carbon, thereby forming a stable cyclobutene ring (Figure 9).

The chemoselectivity observed for the osmium(II)-η^2-pyrrole complexes is in marked contrast to that seen for the organic heterocycle. Pyrroles undergo electrophilic addition preferentially at the α carbon unless these positions are sterically hindered.[1,44] In cases where, for steric reasons, the β-carbons are more reactive, electrophilic substitution is expected to occur at the less hindered β-carbon. A second significant difference between the reactivity of the pyrrole complexes and that of their organic counterparts is the tendency of the latter to undergo multiple alkylations. Alkylation of a pyrrole renders the heterocycle more electron-rich than its precursor, and hence, more reactive to additional alkylation. As an example, a control reaction in which 1-methylpyrrole was combined with 1.0 equiv each of methyl acrylate and TBSOTf gives a reaction mixture containing at least four different alkylated products along with starting material. Under these same conditions, the corresponding osmium(II) complex gives only one product (**39**), monoalkylated at the β carbon. Only in cases where the nitrogen is unsubstituted are double alkylations occasionally observed (e.g., **26**) and then only in the case when the initial electrophilic addition produces a product more electron-rich than the starting material.

As Taube, *et al.*, first observed, η^2-pyrrole complexes are also susceptible to 1,3-dipolar cycloaddition reactions with suitable dipolarophiles.[4a] Since electron-deficient olefins can participate in either cycloaddition at both α-carbons or conjugate addition at the β-carbon, one

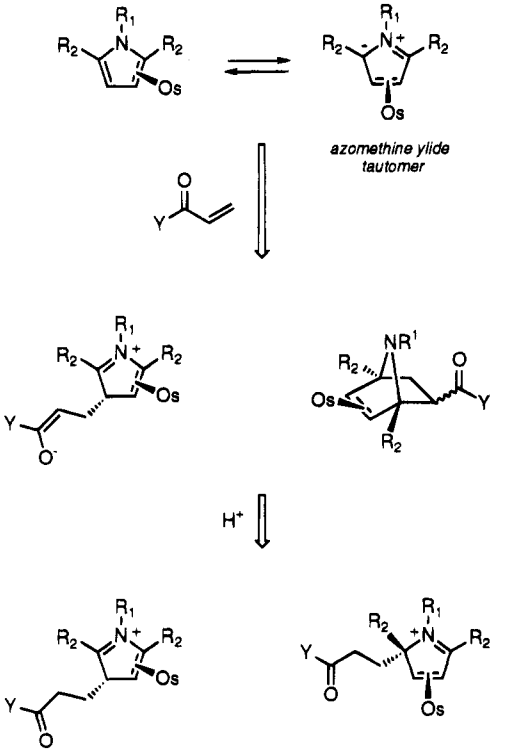


Figure 17. Conjugate addition vs cycloaddition/ring opening reaction manifold for η^2-pyrrole complexes.

aspect of this study has focused on the factors that influence this reaction manifold. The key for determining the course of a reaction between the olefin and an η^2-pyrrole complex is the coordination site of the metal at the time of electrophilic attack (Figure 17). Although the intermediate azomethine ylide, where the osmium is coordinated *3,4-*η^2, is sufficiently less stable than the *4,5-*η^2 analog as to not be detectable by NMR, it is clearly the more reactive tautomer toward certain electophiles. Thus, certain reagents such as maleate or fumarate esters show a definite preference toward cycloaddition with all η^2-pyrrole complexes, where the pyrrole is symmetrically substituted. For the asymmetrically substituted pyrrole complexes examined, *3,4-*η^2 coordination is further destabilized relative to *4,5-*η^2 binding, and the rate of cycloaddition becomes insignificant. In contrast, for the 2,5-dimethylpyrrole complex **3**, the methyl substituents decrease the stability of the *2,3-*η^2 and *4,5-*η^2 isomers. As a result, the relative population of the *3,4-*η^2 form is increased relative to that for the unsubstituted pyrrole complex **1** to the point that cycloaddition becomes the dominant pathway, even for dipolarophiles as mild as methyl acrylate or acrylonitrile.[32]

To the extent that the enolate resulting from conjugate addition at the β-carbon can be stabilized, the rate of this reaction is enhanced. Thus, MVK reacts with the 2,5-dimethylpyrrole complex **3** to form a considerable amount of β-alkylation product, whereas only cycloaddition is observed for methyl acrylate (Figures 11 and 12). Similarly, the reaction of MVK with 1-methylpyrrole complex **2** gives a conjugate addition product exclusively. The use of a Lewis acid or protic solvent also enhances the reactivity at the β-position relative to cycloaddition. While methyl acrylate forms a cycloadduct with the 2,5-dimethylpyrrole complex **3** in the absence of external Lewis acids, the addition of TBSOTf to the reaction mixture results in exclusive conjugate addition.

(44) In a control reaction, 2,5-dimethylpyrrole was treated with 1 equiv of methyl acrylate in the presence of 1 equiv of TBSOTf (CD_3CN or C_6D_6 solvent). The product mixture is a 1:2:1 ratio of starting pyrrole, **60**, and 3,4-bis(2-carbomethoxyethyl)-2,5-dimethylpyrrole (**61**), products which can be separated by either column chromatography or preparative TLC (7:3 petroleum ether/ethyl acetate mobile phase). The analagous reaction with uncomplexed 1-methylpyrrole gives a complex mixture of more than four alkylated products.

Lowering the temperature of the reaction with MVK and **3** enhances the ratio of conjugate addition to cycloaddition in both methanol and acetonitrile. In contrast, raising the temperature from 20 to 50 °C does not have any noticeable effect on the ratio of products. Conceivably, at low enough temperatures, the rate of conversion to the azomethine ylide intermediate is slowed to the point that this step becomes rate-limiting for the cycloaddition pathway (Figure 11). However, for **3**, the specific rate of *4,5*-$\eta^2 \rightarrow$ *2,3*-η^2 tautomerization is >300 s^{-1} at 20 °C,[4b] and it is highly unlikely that lowering the temperature by 30 °C would cause the specific rate to fall below the rate of cycloaddition, which has an experimental half-life of several hours at the lower temperature.[45]

The cycloaddition/Michael addition manifold can also be influenced by concentration of osmium. By lowering the concentration of **3** from 0.59 to 0.035 M, cycloaddition becomes favored over conjugate addition by 8:1 (Table 2, entries m–q). Possibly, this effect is due to the $[Os(NH_3)_5]^{2+}$ moiety itself acting as a mild Lewis acid through its acidic ammine ligands, an effect similar to that seen with protic solvents. Were this the case, the concentration dependence should be most dramatic in nonacidic solvents such as DMSO, and this is what we observe. By comparison, in protic solvents, the interactions of the ammine ligands with the electrophile are diminished by the competing solvent interactions, and the concentration of the osmium complex has an almost negligible effect on the selectivity of the reaction (Table 2, entries h and i).

The 7-azanorbornene cycloadducts formed from η^2-pyrrole complexes are susceptible to an acid-promoted retro-Mannich reaction where the final product is a 2*H*-pyrrolium species. In this regard, the cycloaddition/retro-Mannich sequence is synthetically equivalent to a controlled Michael addition at the α-carbon C(2), the complementary reaction to β-addition. The vulnerability of the 7-azanorbornene complexes towards ring-opening depends primarily on the stability of the resulting enolate. Most susceptible to the retro-Mannich reaction are those cycloadducts derived from α,β-unsaturated ketones (e.g., MVK), followed by maleic anhydride, maleimides, and maleate esters. In the case of MVK, we find that spontaneous decomposition occurs in solution, even in the absence of external acid. A similar decomposition occurs for the 2,5-dimethylpyrrole/maleic anhydride cycloadduct, though at a somewhat slower rate.[46] For the corresponding cycloadduct derived from methyl acrylate, however, even prolonged exposure to triflic acid in acetonitrile fails to open the azanorbornene ring system at room temperature. In this case, 1 equiv of TBSOTf is required for efficient conversion to the 2*H*-pyrrolium species (Figure 12).

In addition to the role the metal plays in promoting electrophilic additions at the β-position of an η^2-pyrrole complex, the metal acts to stabilize the resulting 3*H*-pyrrolium species, preventing its rearomatization or polymerization (*vide supra*). Like their η^2-pyrrole precursors, the η^2-bound 1*H*-, 2*H*-, and 3*H*-pyrrolium complexes (classes **IV**, **V**, and **VI** in Figure 1) have not been observed for other transition metals, and thus deserve further comment. Although several of the classes of pyrrolium species shown in Figure 1 have been investigated in detail in our initial work,[4c] β-substituted pyrroles offer access to several types of η^2-pyrrolium complexes whose formation and reactivity have not been previously observed. For instance, the 3-methylpyrrole pyrrole complex **6a** can be protonated at nitrogen to give a 1*H*-pyrrolium species of the type **IV** (Figure 1) that is stable enough to characterize by ^1H NMR. Without β-substitution, protonation at C(3) is the dominant reaction pathway, even under seemingly irreversible conditions (excess HOTf/CH_3CN). For β-substituted pyrrole complexes, protonation at C(3) occurs most readily *from the ring face and side opposite to that of metal coordination*, i.e., at the β-substituted carbon (structure **c** in Figure 3).[47] As a result, the β-substituent, now on an sp^3 carbon, is forced into the ammine ligands, creating a significant steric interaction. This destabilizing effect makes form **c** inherently unstable with respect to formation of two other 3*H*-pyrrolium species (structures **d** and **e** in Figure 3). However, as observed in our initial study,[4c] the 3*H*-pyrrolium species are also unstable, and even in the solid state, convert to the corresponding *3,4*-η^2-2*H*-pyrrolium complex (class **V**, Figure 1). With a β-substituent, this form also has a significant steric interaction between the substituent and the ammine ligands; consequently, the 3-methyl analog **6f** undergoes another linkage isomerization, this time from the olefinic to the iminium π bond to form **6g** (class **VII**, Figure 1). Thus, given the ease of isomerization of these pyrrolium complexes, the metal is not necessarily restricted to the least hindered binding site provided that an alternative coordination site provides a more stable product. For example, protonation of the conjugate addition product of MVK and the 1-methylpyrrole complex **27a** in methanol results in an intramolecular aldol reaction to give the tetrahydrocyclopenta[*c*]pyrrolium system (**27d**).[48] Note that in this example, the osmium must first isomerize to the more-hindered side of the pyrrole in order for the carbonyl to gain access to the appropriate β-carbon (Figure 4). Curiously, unlike **6a**, the 2-ethylpyrrole complex **4** does not give oxidized byproducts when protonated in methanol solution and fails to isomerize to the 2*H*-pyrrolium tautomer under standard reaction conditions.[4c]

The 2*H*- and 3*H*-pyrrolium species generated from electrophilc addition are moderately electrophilic at the α carbon. The metal stabilizes the iminium carbon considerably through π back-bonding to the point that these complexes resist hydrolysis, even in aqueous solution. Although *intramolecular* examples of nucleophilic addition have been observed with alkyne Michael acceptors in DMSO, our preliminary attempts to introduce carbon substitutents at the α-carbon of the pyrrole ring via *intermolecular* addition of nucleophiles have resulted in either recovery of starting material or deprotonation. However, the addition of cyanide ion has been accomplished in selected cases. The 2*H*-pyrrolium tautomer of the 1-methylpyrrole complex (**8**), which is

(45) For the complex $[Os(NH_3)_5(benzene)]^{2+}$, dropping the temperature from 20 °C to −3.0 °C, results in a decrease in the specific rate of tautomerization from 1×10^4 to 9×10^2 s^{-1}. See: (a) Harman, W. D.; Sekine, M. Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 5725. (b) Harman, W. D. Ph. D. dissertation, Stanford University, 1987.

(46) Partial characterization of the cycloadduct between 2,5-dimethylpyrrole complex and maleic anhydride (2:1 ratio of isomers; major isomer): ^1H NMR (CD_3CN) δ 4.07 (br s, 3H), 3.37 (br s, 12H), 1.48 (s, 6H). The remaining 2 ring proton resonances are partially obscured by the *cis*-NH_3 protons and are observed in the range of 3.31–3.44 ppm.

(47) Note that this gives the C(3) epimer of that formed upon introduction of the substituent via electrophilic addition.

(48) The *syn*-alkylated adduct **27c** undergoes conversion to **27d** in acetonitrile solution.

kinetically difficult to deprotonate,[4c] undergoes clean nucleophilic addition with cyanide; however, the corresponding 3*H*-tautomer **10**, possessing an unhindered acidic proton at C(3), undergoes 30% deprotonation under the same reaction conditions. In contrast, deprotonation at C(3) is not competitive when this proton is hindered, as is the case for 3-(2-carbomethoxyethyl)-1-methyl-3*H*-pyrrolium complex **39**. Hydridic nucleophiles can be added readily without such complications, providing a high-yielding route to 3- and 2-pyrrolines. As observed for electrophilic addition, hydride reduction occurs stereoselectively with reagent attack occurring from the ring-face opposite to that of osmium coordination. This stereocontrol is highlighted in the reaction sequence illustrated in Figure 14 where dipolar cycloaddition, retro-Mannich, hydride reduction, and cyclocondensation reactions are combined to generate a single diastereomer (de > 90%) of a pyrrolizinone (**63**) possessing an angular methyl group (overall yield of isolated organic product: 65%).[4d]

In conclusion, *4,5*-η^2-coordinated pyrrole complexes undergo a variety of electrophilic addition reactions to give β-substituted pyrrole or 3*H*-pyrrolium complexes. Furthermore, reactions with α,β-unsaturated carbonyl compounds give rise to 1,3-dipolar cycloaddition adducts that can ring-open to an α-substituted pyrrole or 2*H*-pyrrolium species with the osmium coordinating the 3,4-position. The 2*H*- or 3*H*-pyrrolium complexes are greatly stabilized by metal coordination and can be reduced at the α carbon to stereoselectively generate 2- or 3-pyrrolines. With the exception of 2-pyrrolines, heating the complex or oxidation of the metal center successfully removes the osmium, and the organic ligand may be isolated. The ability of an η^2-coordinated metal to activate pyrrole, stabilize the resulting pyrrolium ions, and direct the corresponding regio- and stereochemistry make *dearomatization* agents such as $[Os(NH_3)_5]^{2+}$, and those reagents to follow, potentially exciting new tools for the synthesis of organic molecules.

Experimental Section

General. Infared spectra were recorded on a Mattson Cygnus 100 FTIR spectrometer. Electronic spectra were recorded on an HP 8452A diode array spectrophotometer in acetonitrile solution unless otherwise specified. Routine ^1H and ^{13}C NMR spectra were recorded on a General Electric QE-300 or GN-300 spectrometer at 23 °C (room temperature) unless otherwise noted. Unless otherwise noted, ^1H and ^{13}C spectra were obtained at 300 and 75 MHz, respectively. Carbon multiplicities, if provided, are supported by DEPT and/or HETCOR data. Chemical shifts are reported in ppm and are referenced to residual protonated solvent (δ $CHCl_3$ = 7.26; δ acetone-d_5 = 2.04; δ acetonitrile-d_2 = 1.93; δ DMSO-d_5 = 2.49; δ methanol-d_3 = 3.30). Two-dimensional NMR spectra (e.g., DEPT, COSY, NOESY, HETCOR) were recorded on a General Electric GN-300 spectrometer. 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[49] 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 80−100 mV for all reversible couples unless otherwise noted. This work was carried out under a nitrogen atmosphere in a Vacuum Atmospheres Co. glove box, separate boxes being used for aqueous and nonaqueous reactions. When necessary, pyrrole complexes were purified by ion-exchange chromatography using Sephadex SP C-25 resin with aqueous NaCl as the mobile phase. The purified complexes were precipitated as the tetraphenylborate salts by adding an excess of aqueous $NaBPh_4$. Elemental analyses were either obtained in-house on a Perkin-Elmer PE-2400 Series II CHN analyzer or performed by Galbraith Laboratories, Inc.; all experimental values obtained are within 0.40% of theoretical values unless otherwise indicated.

Solvents. All solvents were deoxygenated by purging with nitrogen for at least 15 min; deuterated solvents were deoxygenated either by repeated freeze-pump-thaw cycles or vacuum distillation. All distillations were performed under nitrogen. Benzene and hexanes were refluxed over sodium/benzophenone and distilled. Methylene chloride was refluxed over either CaH_2 or P_2O_5 for at least 8 h and distilled. Diethyl ether was refluxed for at least 8 h over sodium/benzophenone and distilled. Methanol was refluxed over $Mg(OMe)_2$ prepared *in situ* from magnesium activated by I_2 and distilled. Acetonitrile and propionitrile were refluxed over CaH_2 and distilled. Aldrich anhydrous grade DMAc and DME were used without further purification, except that they were deoxygenated prior to use. Acetone was used as received, except that it was deoxygenated prior to use. Deuterated solvents were obtained from Cambridge Isotopes, with the exception of D_2O and DMF-d_7 (Aldrich), and were purified in the following manner: Deuterochloroform was distilled from P_2O_5. Acetonitrile-d_3 was distilled from CaH_2. Acetone-d_6, methanol-d_4, D_2O, DMF-d_7, and DMSO-d_6 were used as received except that they were deoxygenated prior to use.

Reagents. $[Os(NH_3)_5OTf](OTf)_2$ was synthesized as described by Lay et al.[50] Magnesium powder (Aldrich, 50 mesh) was activated by treating with iodine in DME under nitrogen, stirring for 1 hour, filtering, and washing with DMAc, acetone, and Et_2O. Pyrrole ligands were distilled from CaH_2, with the exception of 3-methylpyrrole, which was used as received from Sigma. All other liquid reagents were used as received except that they were deoxygenated by repeated freeze-pump-thaw cycles prior to use.

***N*-Methylacetonitrilium Triflate.** A modification of the reported procedure[51] was used: In a drybox, methyl triflate (4.12 g, 25.1 mmol) and acetonitrile (1.31 g, 31.2 mmol) were dissolved in 2.0 g of benzene and the reaction mixture heated in an oil bath at 75 °C for 20 min to give a yellow oil. The reaction mixture was cooled to 0 °C and then allowed to slowly warm to room temperature, 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 white fluffy solid. Yield: 2.91 g (14.2 mmol, 57%).

Complexes. The synthesis and characterization of the starting pyrrole complexes $[Os^{II}(NH_3)_5(L)](OTf)_2$ (L = pyrrole, alkylated pyrroles) as well as their neutral and protonated tautomers (compounds **1-12**, Figure 1 and Table 1) have been previously reported,[4] with the exception of the 3-methylpyrrole complex **6a** and the complexed 3*H*-tautomers of 2,5-dimethylpyrrole (**13**) and 2-ethylpyrrole (**14**), which are reported herein. Furthermore, several compounds (**19**, **24**, **27a**, **38**, **39**, **41**, **42**, **44**−**47**, **57**,[52] and **58**−**63**) have been previously reported[4] and are marked with an asterisk (*) in the Experimental Section; consequently, only NMR data is given for many of these compounds. A complete key of compound numbers and their respective classes (**I**−**XIII**, Figure 1) is given in Table 1, and a partial listing of ^1H and ^{13}C data for

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

(50) (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.

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

(52) Anderson, H. J.; Loader, C. E.; Foster, A. *Can. J. Chem.* **1980**, *58*, 2527.

selected complexes is given in Table 5. A representative synthesis of the 1-methylpyrrole complex (**2**) is also reported herein for the convenience of the reader.

{4,5-η^2-[Os(NH$_3$)$_5$]-1-Methylpyrrole}(OTf)$_2$ [2]*. [Os(NH$_3$)$_5$OTf](OTf)$_2$ (3.53 g, 4.88 mmol) was dissolved in DMAc (4.48 g), and 1-methylpyrrole (4.30 g, 53.0 mmol) was added. Activated magnesium powder (2.5 g) was added, and the slurry was stirred for 55 min. The reaction mixture was diluted with 20 mL of DME, transferred into a 150 mL fine porosity frit, and then filtered into 325 mL of stirred CH_2Cl_2, giving a yellow precipitate. The precipitate was collected by filtration, washed with CH_2Cl_2 and Et_2O, and dried *in vacuo*. Yield of light yellow powder: 3.03 g (4.63 mmol, 95%).

Tautomeric 1,3-Dimethylpyrrolium Complexes[53] [5c, 5f]. A solution of the 1,3-dimethylpyrrole complex **5a**[54] (80.7 mg, 0.121 mmol) in acetonitrile (560 mg) was prepared and added to a solution of HOTf (31 mg, 0.207 mmol) in acetonitrile (550 mg), giving a red solution. After 10 min, the reaction mixture was added to 50 mL of Et_2O, giving a light pink precipitate, which was filtered, washed with Et_2O, and dried *in vacuo*. Yield of pink powder: 68 mg (0.083 mmol, 69%). (See main text for details of tautomer distribution and isolation). Partial spectroscopic characterization of the resulting tautomers is as follows:[55]

{4β,5β-η^2-[Os(NH$_3$)$_5$]-1,3β-Dimethyl-3*H*-pyrrolium}(OTf)$_3$ [5c]: ^{1}H NMR (CD_3CN) δ 8.67 (s, 1H), 6.31 (d, J = 4.8 Hz, 1H), 4.67 (t, J = 5.1 Hz, 1H), 4.43 (br s, 3H), 3.73 (s, 3H), 3.32 (br s, 3H), 1.24 (d, J = 7.5 Hz, 3H).

{3,4-η^2-[Os(NH$_3$)$_5$]-1,3-Dimethyl-2*H*-pyrrolium}(OTf)$_3$ [5f]: ^{1}H NMR (CD_3CN) δ 9.04 (s, 1H), 5.32 (s, 3H), 4.58 (br s, 3H), 3.49 (s, 3H), 3.40 (br s, 12H), 1.67 (s, 3H).

{4,5-η^2-[Os(NH$_3$)$_5$]-3-Methylpyrrole}(OTf)$_2$ [6a]. [Os(NH$_3$)$_5$OTf](OTf)$_2$ (0.900 g, 1.25 mmol) and 3-methylpyrrole (1.0 g, 12 mmol) were dissolved in DMAc (2.6 g). Activated Mg° (1.3 g) was added, and the slurry was stirred for 55 min. The reaction mixture was diluted with 5 mL of DME and filtered into 300 mL of stirred CH_2Cl_2, giving a green precipitate which was filtered, washed with CH_2Cl_2 and Et_2O, and dried *in vacuo*. Yield of olive green powder: 0.750 g (1.15 mmol, 92%); ^{1}H NMR (acetone-d_6) δ 6.96 (br s, 1H, NH), 6.60 (d, J = 3.3 Hz, 1H), 6.47 (s, 1H), 5.21 (d, J = 3.9 Hz, 1H), 4.45 (br s, 3H), 3.32 (br s, 12H), 2.17 (s, 3H); ^{13}C NMR (acetone-d_6) δ 121.76, 117.13, 77.74, 59.17, 13.48. Anal. ($C_7H_{22}N_6O_6S_2F_6Os$): C, H, N (calcd 12.84, found 12.29).

Tautomeric 3-Methylpyrrolium Complexes 6b–g. A solution of **6a** (44.5 mg, 0.068 mmol) was prepared in CD_3CN and added to neat HOTf (13.5 mg, 0.090 mmol, 1.3 equiv), giving a red solution. The initial product ratio was determined by ^{1}H NMR within 10 min of initiation of the reaction. (See main text for details of tautomer distribution and isolation.) Spectroscopic characterization of the resulting tautomers is as follows:

{4,5-η^2-[Os(NH$_3$)$_5$]-3-Methyl-1*H*-pyrrolium}(OTf)$_3$ [6b]: ^{1}H NMR (CD_3CN) δ 6.00 (s, 1H), 5.95 (t, 1H), 4.90 (d, J = 4.5 Hz, 1H), 4.4 (br s, 3H), 3.2 (br s, 12H), 1.97 (d, J = 1.2 Hz, 3H). The protons on the nitrogen are unassigned.

{4β,5β-η^2-[Os(NH$_3$)$_5$]-3β-Methyl-3*H*-pyrrolium}(OTf)$_3$ [6c]: ^{1}H NMR (CD_3CN) δ 8.91 (d, J = 5.4 Hz, 1H), 6.43 (d, J = 4.8 Hz, 1H), 4.43 (br s, 3H), 4.36 (t, 1H, partially obscured), 3.26 (br s, 12H), 1.30 (d, J = 7.5 Hz, 3H).

{4,5-η^2-[Os(NH$_3$)$_5$]-4-Methyl-3*H*-pyrrolium}(OTf)$_3$ [6d]: ^{1}H NMR (CD_3CN) δ 8.65 (d, J = 5.7 Hz, 1H), 6.40 (s, 1H), 4.42 (br s, 3H), 3.21 (br s, 12H), 2.93 (d, J = 25.8 Hz, 1H), 2.28 (d, J = 26.1 Hz, 1H), 1.51 (s, 3H).

{3,4-η^2-[Os(NH$_3$)$_5$]-3-Methyl-2*H*-pyrrolium}(OTf)$_3$ [6f]: ^{1}H NMR (CD_3CN) δ 10.56 (br s, 1H), 9.14 (d, J = 4.2 Hz, 1H), 5.44 (s, 1H), 4.63 (br s, 3H), 3.40 (br s, 12H), 3.44 (d, 1H, overlap), 2.86 (d, J = 19.8 Hz, 1H), 1.71 (s, 3H); ^{13}C NMR (CD_3CN) δ 190.23 (CH), 64.83 (CH_2), 60.62 (C), 54.04 (CH), 12.97 (CH_3).

{1,5-η^2-[Os(NH$_3$)$_5$]-3-Methyl-2*H*-pyrrolium}(OTf)$_3$ [6g]:[56] ^{1}H NMR (acetone-d_6)[57] δ 8.85 (br s, 1H), 7.17 (d, J = 4.8 Hz, 1H), 6.57 (s, 1H), 5.83 (br s, 3H), 4.32 (br s, 12H), 3.53 (br s, 2H), 1.96 (s, 3H); ^{13}C NMR (acetone-d_6) δ 140.25 (C), 126.12 (CH), 66.00 (CH), 59.71 (CH_2), 17.97 (CH_3). Anal. ($C_8H_{23}N_6O_9S_3F_9Os$): C, H, N.

{4,5-η^2-[Os(NH$_3$)$_5$]-3-Acetyl-1-methylpyrrole}(OTf)$_2$ [15]. A solution of **2** (405 mg, 0.618 mmol) and DMAP (89 mg, 0.73 mmol) was prepared in acetonitrile (2.12 g). The yellow solution was then added to acetic anhydride (85 mg, 0.83 mmol). After 15 min, the dark yellow solution was added to 110 mL of stirred CH_2Cl_2, giving a golden precipitate which was filtered, washed with CH_2Cl_2 and Et_2O, and dried *in vacuo*. Yield of yellow powder: 388 mg (0.556 mmol, 90%); ^{1}H NMR (acetone-d_6) δ 7.59 (s, 1H), 6.49 (d, J = 4.2 Hz, 1H), 5.78 (d, J = 4.5 Hz, 1H), 4.72 (br s, 3H), 3.65 (s, 3H), 3.59 (br s, 12H), 2.14 (s, 3H); ^{13}C NMR (acetone-d_6) δ 192.63, 141.51, 123.48, 77.62, 52.79, 37.14, 25.28. Crude **15** was purified by first protonating with excess HOTf in methanol, isolating the resulting 2-azafulvenium complex, and subsequently deprotonating with DBU (acetonitrile solvent); the final product was precipitated by addition to CH_2Cl_2, filtered, washed with CH_2Cl_2 and Et_2O, and dried *in vacuo*.[58] Anal. ($C_9H_{24}N_6O_7S_2F_6Os$): C, H, N.

{3,4-η^2-[Os(NH$_3$)$_5$]-6-Methyl-6-(methylamino)-2-azafulvenium}(OTf)$_3$ [16]. A solution of **1** (125 mg, 0.19 mmol) in acetonitrile (2.5 g) was added to dry methylacetonitrilium triflate (49 mg, 0.24 mmol) giving a dark solution which was allowed to react for 20 min. Proton Sponge (419 mg, 1.96 mmol) was then added, giving a dark red-orange solution. After 10 min, the reaction mixture was added to 35 mL of CH_2Cl_2, giving an orange precipitate which was filtered, washed with CH_2Cl_2 and Et_2O, and dried *in vacuo*. Yield of orange powder: 127 mg (0.15 mmol, 79%); ^{1}H NMR (acetone-d_6) δ 9.90 (br s, 1H), 9.31 (br s, 1H), 8.24 (s, 1H), 6.81 (d, J = 4.5 Hz, 1H), 5.71 (d, J = 4.5 Hz, 1H), 4.92 (br s, 3H), 3.64 (br s, 12H), 3.16 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (acetone-d_6) δ 169.96, 146.89, 118.17, 71.98, 44.61, 31.36, 16.36. A sample of this compound was purified by ion-exchange chromatography and precipitated as its tetraphenylborate (BPh_4) salt. Anal. ($C_{79}H_{86}N_7B_3Os\cdot 3H_2O$): C, H, N.

{3,4-η^2-[Os(NH$_3$)$_5$]-2,6-Dimethyl-6-(methylamino)-2-azafulvenium}(OTf)$_3$ [17]. A solution of **2** (156 mg, 0.238 mmol) in acetonitrile (1.0 g) was prepared and added to a solution of methylacetonitrilium triflate (57 mg, 0.28 mmol) in acetonitrile (185 mg), giving a dark solution which was allowed to react for 20 min. Proton sponge (550 mg, 2.57 mmol) was then added, giving a dark red-orange solution. After 10 min, the reaction mixture was added to 50 mL of CH_2Cl_2, giving an orange precipitate which was filtered, washed with CH_2Cl_2 and Et_2O, and dried *in vacuo*. Yield of orange powder: 180 mg (0.209 mmol, 88%); ^{1}H NMR (acetone-d_6) δ 9.04 (br s, 1H), 8.18 (s, 1H), 6.73 (d, J = 4.8 Hz, 1H), 5.76 (d, J = 4.5 Hz, 1H), 4.89 (br s, 3H), 3.81 (s, 3H), 3.66 (br s, 12H), 3.12 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (acetone-d_6) δ 168.57, 148.81, 116.72, 75.92, 45.91, 38.06, 31.05, 16.26. A sample of this compound was purified by ion-exchange chromatography and precipitated as its tetraphenylborate (BPh_4) salt. Anal. ($C_{80}H_{88}N_7B_3Os\cdot H_2O$): C, H, N.

{4β,5β-η^2-[Os(NH$_3$)$_5$]-3α-[2-(*tert*-Butyldimethylsiloxy)-2-propyl]-3*H*-pyrrolium}(OTf)$_3$ [18]. A solution of pyrrole complex **1** (102 mg, 0.160 mmol) and acetone (~20 mg) was

(53) Complexes **5d** and **5e** have been reported previously; see reference 4c.

(54) Present in a 4:1 ratio with the 1,1-dimethyl-1*H*-pyrrolium complex when prepared according to literature methods (reference 4c).

(55) Complete ^{1}H NMR data for the tautomers originating from either **5a** or **6a** are given only when assignments are unambiguous; due to overlapping signals from the *cis*-NH_3 resonances and from the other tautomers present in solution, a complete listing of resonances for ring protons are not reported for every tautomer.

(56) Alternatively, this complex can be named as {1,2-η^2-[Os(NH$_3$)$_5$]-4-methyl-5*H*-pyrrolium}(OTf)$_3$.

(57) This complex was identified in CD_3CN solution during the described reaction; however, full spectroscopic characterization (e.g. ^{13}C NMR, NOE) was perfomed separately in acetone-d_6 solution on isolated material.

(58) Alternatively, the tetraphenylborate (BPh_4) salt could be synthesized by dissolving **15** (ca. 50 mg) in 0.5 mL of water and adding excess $NaBPh_4$ (aq). The resulting precipitate was isolated by filtration, washed with water, and dried *in vacuo*. Anal. ($C_{55}H_{64}N_6OB_2Os\cdot 3H_2O$): C, H, N.

Table 5. ^{1}H and ^{13}C NMR Data[a] for Selected η^2-Pyrrole Complexes

class	cpd	R_1	R_2	R_3	R_5	R_6	sol[b]	N-CH_3	H(2)	H(3)	H(4)	H(5)	C(2)	C(3)	C(4)	C(5)
I	**1**	H	H	H	H		a	–	6.81	5.68	5.37	6.69	126.44	105.25	57.42	75.81
I	**2**	Me	H	H	H		a	3.59	6.61	5.4–5.6	5.4–5.6	6.61	129.78	104.38	58.20	80.60
I	**3**[c]	H	Me	H	Me		a	–	–	5.36	4.93	–	135.05	101.42	58.06	74.79
I	**4**	H	Et	H	H		a	–	–	5.44	5.24	6.57	144.25	100.81	57.83	75.19
I	**5a**[d]	Me	H	Me	H		a	3.54	6.29	–	5.25	6.44	125.92	117.33	59.68	83.87
I	**6a**	H	H	Me	H		a	–	6.47	–	5.21	6.59	121.76	117.13	59.17	77.73
I	**15**	Me	H	Ac	H		a	3.65	7.59	–	5.78	6.49	141.51	123.48	52.79	77.62
I	**16**	H	H	$[C(Me)=NHMe]^+$	H		a	–	8.24	–	5.71	6.81	146.89	118.17	44.61	71.98
I	**27a**	Me	H	$(CH_2)_2C(O)Me$	H		a/c[e]	3.48	6.33	–	5.33	6.54	125.61	121.00	57.25	82.11
I	**31**	Me	H	$(CH_2)_2CHO$	H		a	3.50	6.33	–	5.36	6.56	125.45	121.35	57.94	82.98
I	**32**	Me	H	CH=CHC(O)Me	H		a	3.66	7.16	–	5.82	6.61	141.51	120.58	51.25	78.34
I	**34**	Me	H	$C(CO_2Me)=CHCO_2Me$	H		a	3.59	6.95	–	5.77	6.61	137.17	117.25	50.6	77.43
I	**36**	H	H	CH=CHC(O)Me	H		a	–	7.25	–	5.71	6.70	142.11	121.32	49.83	73.64
I	**43a**	Me	H	$(CH_2)_2CO_2Me$	H		a	3.51	6.35	–	5.37	6.56	124.81	120.96	57.60	82.41
II	**7**		Me	H	Me	H	a	–	4.12	5.02	5.27	–	58.88	60.27	69.76	186.3
II	**29**		Me	H	Me	$(CH_2)_2C(O)Me$	e	–	–	4.15	4.56	–	75.64	57.58	63.71	178.82
II	**48**		Me	H	Me	$(CH_2)_2CO_2Me$	a	–	–	4.60	5.04	–	76.77	59.85	66.14	179.51
III	**13**		Me	H	Me	H	d	–	–	2.78, 2.24	3.80	–	175.78	46.81	45.39	83.95
III	**14**		Et	H	H	H	d	–	–	2.69, 2.22	4.10	5.96	183.43	45.50	43.77	81.96
III	**21**		Me	H	Me	$C(Me)_2OTBS$	a	–	–	2.63	3.78	–	170.72	71.85	48.46	74.92
III	**30**		Me	H	Me	$(CH_2)_2C(O)Me$	d	–	–	*f*	3.55	–	176.40	57.34	50.28	82.25
V	**8**	Me	H	H	H	H	a	3.73	3.60	5.72	5.72	9.60	65.41	51.81	54.46	191.40
V	**9**	H	Me	H	Me	H	a	–	4.1	5.57	5.72	–	66.85	53.72	57.22	201.44
V	**6f**	H	H	Me	H	H	a	–	3.93, 3.08	–	5.85	9.52	64.83	60.62	54.04	190.23
V	**27f**	Me	H	$(CH_2)_2C(O)Me$	H	H	b	3.51	3.54, 3.09	–	5.27	8.94	67.61	65.52	51.29	191.57
V	**46**	H	Me	H	Me	$(CH_2)_2CO_2Me$	a	–	–	5.44	5.73	–	75.67	61.65	51.86	200.72
V	**47**	Me	H	H	H	$(CH_2)_2CO_2Me$	a	3.66	3.76	5.60	5.71	9.60	75.97	59.00	50.23	191.48
VI	**10**	Me	H	H	H	H	a	4.09	9.09	3.21, 2.91	5.11	6.76	173.99	43.03	42.89	76.31
VI	**11**	H	Me	H	Me	H	a	–	–	3.21, 3.05	4.71	–	187.1	46.2	42.1	74.3
VI	**12**	H	Et	H	H	H	a	–	–	3.37, 3.03	4.98	6.64	193.27	44.28	41.60	71.25
VI	**19**	Me	H	H	H	$C(Me)_2OTBS$	b	3.83	8.73	2.79	4.72	6.34	174.66	67.88	47.04	75.15
VI	**22**[g]	Me	H	H	H	CH(Ph)OTBS	a	4.14, 4.00	9.22, 9.06	3.69, 3.50	5.16	6.85, 6.36	173.45, 172.87	64.06, 63.57	47.05, 45.02	75.3–73.5
VI	**23**[g]	Me	H	H	H	CH(Ph)OMe	a	4.10, 3.98	9.06, 8.93	3.65, 3.55	5.20, 5.05	6.77, 6.47	172.40, 172.29	61.60, 61.21	46.09, 45.93	74.58, 74.34
VI	**27c**	Me	H	$(CH_2)_2C(O)Me$	H	H	b	3.73	8.64	3.16	4.75	6.36	178.03	56.12	~42	76.51
VI	**27e**	Me	H	H	H	$(CH_2)_2C(O)Me$	b	3.77	8.60	3.49	4.63	6.27	175.41	53.96	49.45	74.51
VI	**38**	H	Me	H	Me	$(CH_2)_2CO_2Me$	a	–	–	3.3	4.64	–	187.21	55.91	46.65	72.32
VI	**39**	Me	H	H	H	$(CH_2)_2CO_2Me$	a	4.06	9.08	3.28	5.04	6.73	174.66	53.43	48.53	74.40
VI	**40**	H	Et	H	H	$(CH_2)_2CO_2Me$	a	–	–	3.4	4.91	6.64	193.62	54.60	46.52	69.56
VI	**41**	Me	H	H	H	$CH(Me)CH_2CO_2Me$	a	4.05	9.08	3.22	5.07	6.73	173.96	59.00	46.76	74.36
VI	**42**	H	H	Me	H	$(CH_2)_2CO_2Me$	a	–	9.29	–	4.90	6.85	181.68	58.65	48.49	70.35
VII	**6g**	H	H	Me	H	H	a	–	3.53	–	6.57	7.17	59.71	140.25	126.12	66.00
VIII	**24**	Me	H	H	H	$R_{6a} = R_{6b} = Me$	a	4.10	9.10	–	6.22	7.14	156.20	141.64	42.04	73.77
IX	**25**		H	Me	H	$R_{6a} = R_{6b} = Me$	a	–	7.24	–	6.04	7.46	119.38	153.64	49.10	63.85

X	**33**	Me	H	H	H	*h*		3.0	3.60	4.42	67.79	46.80	40.69	80.26
X	**35**	Me	H	H	H	*i*		3.17	4.03	4.74	66.46	47.89	40.09	79.80
X	**49**	Me	H	H	H			2.74, 1.71	3.80	5.12	59.58	29.84	41.38	83.62
X	**51**	H	Me	H	Me			2.79, 1.10	3.74	–	62.97	37.59	44.50	78.65
X	**52**	Ac	Me	H	Me			3.20, 1.71	4.01	–	61.48	37.85	46.95	75.31
XI	**54**	Me	H	H	H			3.88	3.88	3.30	61.34	52.28	52.28	61.34
XI	**55**	H	Me	H	Me			3.87	3.87	4.44	60.83	57.18	57.18	60.83
XI	**56**[d]	H	Me	H	Me	$(CH_2)_2CO_2Me$		3.88	3.88	4.65	65.37	57.21	56.03	61.46
XII	**50**	Me	H	H	H	Me		2.44, 2.30	4.01	5.54	62.88	28.95	45.16	82.76
XIII	**53**		Me	H	Me	R_{6a} = OH; R_{6b} = Me		3.66, 2.08	4.55	–	64.72	37.71	50.00	74.84

X	**33**	Me	H	H	H	*h*		3.99	3.0		3.60	4.42	67.79	46.80	40.69	80.26
X	**35**	Me	H	H	H	*i*		4.09	3.17		4.03	4.74	66.46	47.89	40.09	79.80
X	**49**	Me	H	H	H			2.81, 2.74	2.74, 1.71		3.80	5.12	59.58	29.84	41.38	83.62
X	**51**	H	Me	H	Me			4.30	2.79, 1.10		3.74	–	62.97	37.59	44.50	78.65
X	**52**	Ac	Me	H	Me			4.74	3.20, 1.71		4.01	–	61.48	37.85	46.95	75.31
XI	**54**	Me	H	H	H			3.30	3.88		3.88	3.30	61.34	52.28	52.28	61.34
XI	**55**	H	Me	H	Me			4.44	3.87		3.87	4.44	60.83	57.18	57.18	60.83
XI	**56**[d]	H	Me	H	Me	$(CH_2)_2CO_2Me$		–	3.88		3.88	4.65	65.37	57.21	56.03	61.46
XII	**50**	Me	H	H	H	Me		3.08	2.44, 2.30		4.01	5.54	62.88	28.95	45.16	82.76
XIII	**53**		Me	H	Me	R_{6a} = OH; R_{6b} = Me		5.20	3.66, 2.08		4.55	–	64.72	37.71	50.00	74.84

[a] All spectra recorded as triflate salts at room temperature (22 °C) unless otherwise noted. [b] Solvent key: a = acetone-d_6; b = CD_3CN; c = D_2O; d = 4:1 H_2O/D_2O; e = DMSO-d_6; f = 95% CD_3CN/5% DMSO-d_6. [c] Recorded at −10 °C. [d] Recorded as the tetraphenylborate (BPh_4) salt. [e] ^1H NMR data recorded in acetone-d_6; ^{13}C NMR data recorded in D_2O. [f] Not reported due to overlap with other resonances. [g] Data reported for both diastereomers (1:1 ratio). [h] R_6, R_7 = −C[C(O)Me]=CH− (cyclobutene). [i] R_6, R_7 = −C(CO_2Me)=C(CO_2Me)− (cyclobutene). [j] ^1H NMR data recorded in CD_3CN; ^{13}C NMR recorded in DMSO-d_6. [k] ^1H NMR data recorded in acetone-d_6; ^{13}C NMR recorded in 95% CD_3CN/5% DMSO-d_6.

prepared in CD_3CN (550 mg). TBSOTf (42.3 mg, 0.160 mmol) was added dropwise followed by swirling to give a red solution. NMR analysis showed a clean spectrum of **18**, which was characterized spectroscopically, but not isolated: ^1H NMR (CD_3CN) δ 8.88 (s, 1H), 6.41 (d, J = 4.2 Hz, 1H), 4.64 (d, J = 4.5 Hz, 1H), 4.53 (br s, 3H), 3.26 (br s, 12H), 2.83 (s, 1H), 1.60 (s, 3H), 1.44 (s, 3H), 0.86 (s, 9H), 0.14 (s, 6H); ^{13}C NMR (CD_3CN) δ 176.61, 74.85, 70.50, 68.43, 45.49, 30.28, 28.22, 26.12, 18.62, −2.04.

{4β,5β-η^2-[Os(NH_3)$_5$]-3α-[2-(*tert*-Butyldimethylsiloxy)-2-propyl]-1-methyl-3*H*-pyrrolium}(OTf)$_3$ [19]*. Complex **19** was generated in CD_3CN solution using a procedure parallel to that used to prepare **18**, except that **2** was substituted for **1**: ^1H NMR (CD_3CN) δ 8.71 (s, 1H), 6.30 (d, J = 4.5 Hz, 1H), 4.69 (d, J = 4.5 Hz, 1H), 4.50 (br s, 3H), 3.82 (s, 3H), 3.27 (br s, 12H), 2.76 (s, 1H), 1.57 (s, 3H), 1.44 (s, 3H), 0.87 (s, 9H), 0.15 (s, 6H); ^{13}C NMR (CD_3CN) δ 174.66 (CH), 75.15 (C, CH, overlap), 67.88 (CH), 47.04 (CH), 42.58 (CH_3), 30.03 (CH_3), 28.26 (CH_3), 26.09 ((CH_3)$_3$), 18.50 (C), −2.05 (CH_3)$_2$.

{4β,5β-η^2-[Os(NH_3)$_5$]-3α-[2-(*tert*-Butyldimethylsiloxy)-2-propyl]-2,5-dimethyl-3*H*-pyrrole}(OTf)$_2$ [21]. A solution of 2,5-dimethylpyrrole complex (**3**) (299 mg, 0.448 mmol) and acetone (55.6 mg, 0.960 mmol) was prepared in acetonitrile (1.4 g). TBSOTf (146 mg, 0.553 mmol) was added dropwise with swirling, giving a red solution of **20**, which was not isolated. After 5 min, DBU (113 mg, 0.744 mmol) was added dropwise with swirling, giving a dark golden yellow solution that produced a significant amount of yellow precipitate over 15−20 min. After 20 min, the reaction mixture was added to 75 mL of stirred CH_2Cl_2, precipitating the remaining product, which was filtered, washed with CH_2Cl_2 and Et_2O, and dried *in vacuo*. Yield of golden yellow powder: 269 mg (0.320 mmol, 71%); ^1H NMR (acetone-d_6) δ 4.71 (br s, 3H), 3.78 (s, 1H), 3.54 (br s, 12H), 2.63 (s, 1H), 2.18 (s, 3H), 1.66 (s, 3H), 1.51 (s, 3H), 1.24 (s, 3H), 0.91 (s, 9H), 0.20 (s, 3H), 0.16 (s, 3H); ^{13}C NMR (acetone-d_6) δ 170.72, 83.77, 74.92, 71.85, 48.46, 30.15, 26.16, 25.49, 20.40, 18.57, 18.45, −1.77, −1.81. Anal. ($C_{17}H_{44}N_6O_7SiS_2F_6Os$): C, H, N.

{4β,5β-η^2-[Os(NH_3)$_5$]-3α-[1-(*tert*-Butyldimethylsiloxy)-benzyl]-1-methyl-3*H*-pyrrolium}(OTf)$_3$ [22]. A solution of 1-methylpyrrole complex (**2**) (153 mg, 0.234 mmol) in acetonitrile (400 mg) was prepared, and benzaldehyde (34.2 mg, 0.322 mmol) was added. TBSOTf (78.5 mg, 0.297 mmol) was added dropwise, giving a red solution which was allowed to stand for 5 min. The reaction mixture was added to stirrred hexanes (30 mL), giving an oil. The hexanes were decanted, and 40 mL of Et_2O was added. The mixture was stirred for 10 min, giving a solid precipitate. The precipitate was filtered, washed with Et_2O, and dried *in vacuo*. Yield of pink powder: 206 mg (0.201 mmol, 89%); ^1H NMR (acetone-d_6); (1:1 ratio of diasteromers) δ 9.22 (s, 1H), 9.06 (s, 1H), 7.6−7.3 (m, 10H), 6.85 (d, J = 3.9 Hz, 1H), 6.36 (d, J = 3.9 Hz, 1H), 5.76 (d, J = 5.1 Hz, 1H), 5.67 (d, J = 3.6 Hz, 1H), 5.16 (br s, 8H), 4.14 (s, 3H), 4.00 (s, 3H), 3.96 (br s, 12H), 3.90 (br s, 12H), 3.69 (d, J = 4.2 Hz, 1H), 3.50 (br s, 1H), 0.93 (s, 9H), 0.92 (s, 9H), 0.20 (s, 3H), 0.16 (s, 3H), −0.10 (s, 3H), −0.16 (s, 3H); ^{13}C NMR (acetone-d_6) δ 173.45, 172.87, 142.64, 140.77, 128.89, 128.58, 128.47, 128.43, 127.25, 126.73, 75.26, 74.78, 74.48, 73.48, 64.06, 63.57, 47.05, 45.02, 41.98, 41.84, 25.76, 25.66, 18.12, 18.02, −5.06, −5.10, −5.40. Anal. ($C_{21}H_{43}N_6O_{10}S_3F_9SiOs$): H, N, C (calcd 24.78, found 22.24).[59]

{4β,5β-η^2-[Os(NH_3)$_5$]-3α-(1-Methoxybenzyl)-1-methyl-3*H*-pyrrolium}(OTf)$_3$ [23]. A solution of 1-methylpyrrole complex **2** (178 mg, 0.272 mmol) in acetonitrile (950 mg) was prepared, and benzaldehyde dimethyl acetal (49.1 mg, 0.323 mmol) was added. TBSOTf (79 mg, 0.30 mmol) was added dropwise, giving a light pink solution. After 5 min, the reaction mixture was added to 40 mL of stirrred Et_2O, giving a pink precipitate, which was filtered, washed with Et_2O, and dried *in vacuo*. Yield of pink powder: 237 mg (0.256 mmol, 94%); ^1H NMR (acetone-d_6, 1:1 ratio of diastereomers) δ 9.06 (s, 1H), 8.93 (s, 1H), 7.55−7.38 (m, 10H total, Ph), 6.77 (d, J

(59) Although the elemental analysis data for carbon is outside the acceptable range, the material is pure by both ^1H and ^{13}C NMR; cyclic voltammetry is also consistent with the given structure.

= 4.5 Hz, 1H), 6.47 (d, J = 4.2 Hz, 1H), 5.20 (d, J = 4.8 Hz, 1H), 5.05 (d, J = 4.8 Hz, 1H), 5.16 (br s, 3H), 5.14 (br s, 3H), 4.97 (d, J = 6.0 Hz, 1H), 4.94 (d, J = 6.6 Hz, 1H), 4.10 (s, 3H), 3.98 (s, 3H), 3.91 (br s, 24H total), 3.65 (d, J = 6.6 Hz, 1H), 3.55 (d, J = 5.1 Hz, 1H), 3.37 (s, 3H), 3.32 (s, 3H); ^{13}C NMR (acetone-d_6) δ 172.40, 172.29, 138.72, 137.92, 128.9–127.3 (6 carbons), 82.17, 81.17, 74.58, 74.34, 61.60, 61.21, 56.75, 56.51, 46.09, 45.93, 41.74, 41.60. Anal. ($C_{16}H_{31}N_6O_{10}S_3F_9Os$): H, N, C (calcd 20.78, found 20.37).

{3,4-η^2-[Os(NH$_3$)$_5$]-2,6,6-Trimethyl-2-azafulvenium}-(OTf)$_3$ [24]*: ^{1}H NMR (acetone-d_6) δ 9.10 (s, 1H), 7.14 (d, J = 4.2 Hz, 1H), 6.22 (d, J = 4.2 Hz, 1H), 5.19 (br s, 3H), 4.10 (s, 3H), 3.97 (br s, 12H), 2.08 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (acetone-d_6) δ 160.44, 156.20, 141.64, 73.77, 42.04, 40.29, 25.15, 24.15.

{1,2-η^2-[Os(NH$_3$)$_5$]-3,6,6-Trimethyl-5-azafulvenium}-(OTf)$_3$ [25]. A solution of **5a** (76.2 mg, 0.116 mmol) in acetone (474 mg) was prepared and added to a solution of HOTf (25.6 mg, 0.171 mmol) in acetonitrile (340 mg), giving a yellow-orange solution that slowly turned purple over 10–15 min. After 20 min, the reaction mixture was added to 40 mL of stirred Et_2O, giving a lavender precipitate, which was filtered, washed with Et_2O, and dried *in vacuo*. Yield of lavender powder: 86.5 mg (0.102 mmol, 88%); ^{1}H NMR (acetone-d_6) δ 7.46 (d, J = 4.2 Hz, 1H), 7.24 (s, 1H), 6.04 (d, J = 4.2 Hz, 1H), 5.29 (br s, 3H), 4.06 (br s, 12H), 2.62 (s, 3H), 2.32 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (acetone-d_6) δ 175.01, 153.64, 119.38, 63.85, 49.10, 26.51, 25.76, 14.31. Anal. ($C_{11}H_{27}N_6O_9S_3F_9Os$): H, N, C (calcd 15.64, found 14.90).

{4,5-η^2-[Os(NH$_3$)$_5$]-1,3-Bis(3-oxobutyl)pyrrole}(OTf)$_2$ [26]. A solution of **1** (152 mg, 0.238 mmol) in methanol (450 mg) was prepared, and MVK (39.6 mg, 0.565 mmol) was added. The reaction mixture was allowed to stand for 2 h, over which time the solution turned dark yellow. The reaction mixture was added to 40 mL of stirrred Et_2O, giving a tan precipitate, which was filtered, washed with Et_2O, and dried *in vacuo*. Yield of tan powder: 157 mg (0.201 mmol, 84%); ^{1}H NMR (acetone-d_6) δ 6.57 (d, J = 3.6 Hz, 1H), 6.30 (s, 1H), 5.30 (d, J = 3.9 Hz, 1H), 4.50 (br s, 3H), 3.88 (m, 2H), 3.38 (br s, 12H), 2.9–2.6 (m, 6H), 2.12 (s, 6H); ^{13}C NMR (acetone-d_6) δ 209.18 (C), 207.94 (C), 122.74 (C), 122.68 (CH), 82.22 (CH), 56.66 (CH), 45.39 (CH_2), 43.34 (CH_2), 42.83 (CH_2), 29.78 (CH_3), 29.49 (CH_3), 22.57 (CH_2). Anal. ($C_{14}H_{32}N_6O_8S_2F_6Os$): C, H, N.

{4,5-η^2-[Os(NH$_3$)$_5$]-1-Methyl-3-(3-oxobutyl)pyrrole}-(OTf)$_2$ [27a]*: ^{1}H NMR (acetone-d_6) δ 6.54 (d, J = 3.9 Hz, 1H), 6.30 (s, 1H), 5.33 (d, J = 3.9 Hz, 1H), 4.50 (br s, 3H), 3.48 (s, 3H), 3.42 (br s, 12H), 2.79 (m, 4H), 2.12 (s, 3H); ^{13}C NMR (D_2O) δ 216.87, 125.61, 121.00, 82.11, 57.25, 43.34, 36.93, 29.94.

{4β,5β-η^2-[Os(NH$_3$)$_5$]-1-Methyl-3β-(3-oxobutyl)-3*H*-pyrrolium}(OTf)$_3$ [27c]. A solution of **27a** (81.8 mg, 0.113 mmol) in acetonitrile (380 mg) was added to a solution of HOTf (24.1 mg, 0.161 mmol) in acetonitrile (340 mg), giving a light red solution. After 5 min, the reaction mixture was added to 50 mL of Et_2O, giving a pink precipitate, which was filtered, washed with Et_2O, and dried *in vacuo*. Yield of pink powder: 83.8 mg (0.0958 mmol, 85%); ^{1}H NMR (CD_3CN) δ 8.64 (s, 1H), 6.36 (d, J = 4.5 Hz), 4.75 (dd, J = 5.1, 4.8 Hz), 4.47 (br s, 3H), 3.73 (s, 3H), 3.42 (br s, 12H), 3.16 (d, J = 4.8 Hz, 1H), 2.83 (m, 2H), 2.15 (s, 3H), 2.08 (m, 1H), 1.33 (m, 1H); ^{13}C NMR (CD_3CN) δ 210.82, 178.03, 76.51, 56.12, 43.94, 42.39, 41.78, 30.08, 20.55.

{3,3a-η^2-[Os(NH$_3$)$_5$]-2,6-Dimethyl-6-hydroxy-4,5,6,6a-tetrahydrocyclopenta[c]pyrrolium}(OTf)$_3$ [27d]. A *freshly prepared sample* of **27c** (ca. 50 mg) was dissolved in CD_3CN and the solution monitored by ^{1}H NMR. After approximately 3 h, complete conversion of **27c** to **27d** (5:2 ratio of diastereomers) was observed.

An alternate method of preparation is as follows: A solution of the 1-methylpyrrole complex (**2**, 300 mg, 0.458 mmmol) in methanol (0.75 g) was prepared, and MVK (39 mg, 0.55 mmol) was added. After 45 min, a solution of HOTf (84 mg, 0.56 mmol) in 0.25 g of methanol was added, giving a red solution of **27d**. After 15–20 min, the reaction mixture was added to 40 mL of stirred Et_2O, giving an orange-red precipitate, which was filtered, washed with Et_2O, and dried *in vacuo*. Yield of orange-red powder: 351 mg (0.401 mmol, 88%) (the diastereomeric ratio does not significantly differ from that observed in the former procedure); ^{1}H NMR (CD_3CN) δ 8.60 (s, 1H), 6.35 (s, 1H), 4.48 (br s, 3H), 3.82 (s, 3H), 3.30 (br s, 12H), 3.16 (s, 1H), 2.28 (m, 1H), 2.07 (m, 2H), 1.77 (m, 1H), 1.62 (s, 3H), (O*H* resonance not assigned); ^{13}C NMR (CD_3CN) δ 172.31 (CH), 81.91 (C), 75.84 (CH), 69.79 (CH), 58.13 (C), 44.43 (CH_2), 42.72 (CH_3), 29.57 (CH_2), 27.06 (CH_3). Anal. ($C_{12}H_{29}N_6O_{10}S_3F_9Os$): C, H, N.

{4β,5β-η^2-[Os(NH$_3$)$_5$]-1-Methyl-3α-(3-oxobutyl)-3*H*-pyrrolium}(OTf)$_3$ [27e]. A solution of **27a** (46.3 mg, 0.0639 mmol) in CD_3CN (430 mg) with toluene as an integration standard was prepared and added to neat HOTf (13.1 mg, 0.0873 mmol, 1.4 equiv), giving a light pink solution, which was monitored by NMR. Initial spectra (10 min after initiation of the reaction) showed approximately an 80:8:12 ratio of **27c** to **27e** to **27b**. Over a period of 6 h, all of **27b** disappeared and the ratio of **27e** to **27c** had become 87:13 and a small amount (13%) of **27f** was present: ^{1}H NMR (**27e**) (CD_3CN) δ 8.60 (s, 1H), 6.27 (d, J = 4.2 Hz, 1H), 4.63 (d, J = 4.5 Hz, 1H), 4.49 (br s, 3H), 3.78 (s, 3H), 3.29 (br s, 12H), 2.75 (m, 2H), 2.15 (s, 3H), 2.10 (m, 2H) (H(3) was not assigned for this tautomer due to overlap with other resonances); ^{13}C NMR (CD_3CN) δ 209.37, 175.41, 74.51, 53.96, 49.45, 42.58, 40.48, 30.15, 24.10.

{3,4-η^2-[Os(NH$_3$)$_5$]-1-Methyl-3-(3-oxobutyl)-2*H*-pyrrolium}(OTf)$_3$ [27f]. An isolated sample of **27c** was allowed to sit in the solid state undisturbed for 3 days; an NMR sample prepared after this time showed the major product to be **27f**: ^{1}H NMR (CD_3CN) δ 8.94 (s, 1H), 5.27 (s, 1H), 4.62 (br s, 3H), 3.51 (s, 3H), 3.48 (br s, 12H), 3.54 (d, J = 20.4 Hz, 1H), 3.09 (d, J = 20.4 Hz, 1H), 2.79 (m, 2H), 2.18 (m, 1H), 2.09 (s, 3H), 1.81 (m, 1H); ^{13}C NMR (CD_3CN) δ 211.06 (C), 191.57 (CH), 67.61 (CH_2), 65.52 (C), 51.29 (CH), 43.38 (CH_2), 39.69 (CH_3), 30.33 (CH_3), 26.11 (CH_2).

{3β,4β-η^2-[Os(NH$_3$)$_5$]-2β,5-Dimethyl-2α-(3-oxobutyl)-2*H*-pyrrole}(OTf)$_2$ [29]. A solution of **3** (76.9 mg, 0.115 mmol) in DMSO-d_6 (551 mg) was prepared and added to methyl vinyl ketone (MVK) (18.8 mg, 0.268 mmol) and the reaction monitored by ^{1}H NMR. After approximately 2 h, no further change was noted in the products being formed; an approximate 9:4 ratio of **29** to **30** was observed: ^{1}H NMR[60] (DMSO-d_6) δ 4.45 (br s, 3H), 4.54 (d, J = 4.5 Hz, 1H), 4.13 (d, J = 4.5 Hz, 1H), 3.32 (br s, 12H) 2.5 (m, 1H), 2.35 (m, 1H), 2.06 (s, 3H), 1.82 (s, 3H), 1.8 (m, 2H), 0.83 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 208.68 (C), 178.82 (C), 75.64 (C), 63.71 (CH), 57.58 (CH), 38.81 (CH_2), 37.70 (CH_2), 29.74 (CH_3), 20.55 (CH_3), 19.72 (CH_3).

{4β,5β-η^2-[Os(NH$_3$)$_5$]-2,5-Dimethyl-3α-(3-oxobutyl)-3*H*-pyrrole}(OTf)$_2$ [30]. A solution of **3** (59.0 mg, 0.088 mmol) was prepared in a mixture of H_2O (360 mg) and D_2O (95 mg).[61] This solution was then added to methyl vinyl ketone (MVK) (5.8 mg, 0.083 mmol) and the solution monitored by ^{1}H NMR. After approximately 20 min, the reaction appeared to be complete. The major product was **30** along with a small amount of what is assigned to be **29** (9:1 ratio): ^{1}H NMR (4:1 H_2O/D_2O) δ 4.42 (br s, 3H), 3.55 (s, 1H), 3.23 (br s, 12H), 2.3–2.7 (m, 4H), 2.20 (s, 3H), 1.97 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (4:1 H_2O/D_2O) δ 216.40, 176.40, 82.25, 57.34, 50.28, 39.62, 29.91, 24.27, 17.74, 16.12. Anal. (isolated mixture of **29** and **30**) ($C_{12}H_{30}N_6O_7S_2F_6Os$): H, C (calcd 19.51, found 20.0), N (calcd 11.38, found 10.89).

{4,5-η^2-[Os(NH$_3$)$_5$]-1-Methyl-3-(3-oxopropyl)pyrrole}-(OTf)$_2$ [31]. Compound **31** was prepared using a procedure similar to that used for the synthesis of **27a** except that acrolein was used instead of methyl vinyl ketone (see ref 4d). Yield: 91%. ^{1}H NMR (acetone-d_6) δ 9.78 (s, 1H), 6.56 (d, J = 3.9 Hz, 1H), 6.33 (s, 1H), 5.36 (d, J = 3.9 Hz, 1H), 4.50 (br s, 3H), 3.50 (s, 3H), 3.43 (br s, 12H), 2.7–2.9 (m, 4H); ^{13}C NMR (acetone-d_6) δ 203.41, 125.45, 121.35, 82.98, 57.94, 43.86, 37.21, 21.49.

(60) Major product (**29**); assignments made by DEPT and HETCOR data.

(61) The reaction was run in H_2O to prevent deuteration of the β-positions of the pyrrole ring which would make the final ^{1}H and ^{13}C NMR assignments ambiguous. D_2O was added to provide a lock signal for the spectrometer.

{4,5-η^2-[Os(NH$_3$)$_5$]-1-Methyl-3-(3-oxo-*trans*-1-butenyl)-pyrrole}(OTf)$_2$ [32]. A solution of **2** (201 mg, 0.307 mmol) in methanol (450 mg) was prepared and added to a solution of 3-butyn-2-one (29 mg, 0.43 mmol) in methanol. The reaction mixture turned dark red-orange over a period of 5 min. After approximately 15 min, the reaction mixture was added to 80 mL of stirred Et_2O, giving an intense red-orange precipitate which was filtered, washed with Et_2O, and dried *in vacuo*. Yield of orange powder: 207 mg (0.286 mmol, 93%); ^{1}H NMR (acetone-d_6) δ 7.67 (d, J = 15.3 Hz, 1H), 7.16 (s, 1H), 6.61 (d, J = 4.2 Hz, 1H), 6.44 (d, J = 15.3 Hz, 1H), 5.82 (d, J = 4.2 Hz), 4.69 (br s, 3H), 3.66 (s, 3H), 3.60 (br s, 12H), 2.09 (s, 3H); ^{13}C NMR (acetone-d_6) δ 196.57, 141.51, 140.23, 120.58, 116.81, 78.34, 51.25, 37.06, 26.83. Anal. ($C_{11}H_{26}N_6O_7S_2F_6Os$): C, H, N.

{3,4-η^2-[Os(NH$_3$)$_5$]-2-Methyl-2-azabicyclo[3.2.0]-7-acetyl-3,6-heptadiene}(OTf)$_2$ [33]. A solution of **2** (48.4 mg, 0.0739 mmol) in DMSO-d_6 (467 mg) was prepared and added to 3-butyn-2-one (4.8 mg, 0.071 mmol), and the reaction monitored by ^{1}H NMR. After 4 h, the reaction was complete, and **33** was characterized spectroscopically in DMSO-d_6 solution. Structure assignment is based on ^{1}H, and ^{13}C NMR, HETCOR, and 500 MHz ^{1}H–^{13}C long range correlation spectroscopy data. ^{1}H NMR (DMSO-d_6) δ 7.42 (s, 1H), 4.43 (d, J = 4.8 Hz, 1H), 4.28 (br s, 3H), 3.99 (s, 1H), 3.60 (d, J = 4.8 Hz, 1H), 3.28 (br s, 12H), 3.0 (1H) (proton buried under *cis*-ammine), 2.56 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 193.77 (C), 155.26 (CH), 147.59 (C), 80.26 (CH), 67.79 (CH), 46.80 (CH), 41.57 (CH_3), 40.69 (CH), 24.73 (CH_3).

{4,5-η^2-[Os(NH$_3$)$_5$]-3-(1,2-dicarbomethoxyethenyl)-1-methylpyrrole}(OTf)$_2$ [34]. A sample of **35** (49.4 mg, 0.0620 mmol) was dissolved in methanol (310 mg), and the solution was allowed to stand. After 75 min, the reaction mixture was added to 15 mL of Et_2O, giving a red-orange tacky precipitate. The Et_2O was decanted, and the solid was dissolved in acetone followed by reprecipitation with 15 mL of Et_2O. The precipitate was filtered, washed with Et_2O, and dried *in vacuo*. Yield of red-orange powder: 41.4 mg (0.0520 mmol, 84%); ^{1}H NMR (acetone-d_6) δ 6.95 (s, 1H), 6.61 (d, J = 4.2 Hz, 1H), 6.00 (s, 1H), 5.77 (d, J = 4.2 Hz, 1H), 4.68 (br s, 3H), 3.78 (s, 3H), 3.67 (s, 3H), 3.60 (br s, 12H), 3.59 (s, 3H); ^{13}C NMR (acetone-d_6) δ 169.76, 166.75, 147.77, 137.17, 117.25, 101.54, 77.43, 51.93, 50.59, 50.32, 37.04.

{3,4-η^2-[Os(NH$_3$)$_5$]-2-methyl-2-azabicyclo[3.2.0]-6,7-dicarbomethoxy-3,6-heptadiene}(OTf)$_2$ [35]. A solution of DMAD (45.8 mg, 0.322 mmol) in DMSO (775 mg) was prepared and added directly to dry **2** (177 mg, 0.271 mmol) to give a reddish-orange solution. After 25 min, the reaction mixture was added to a 2:1 mixture of Et_2O/CH_2Cl_2 (45 mL) to give an oily precipitate which was redissolved in acetone and reprecipitated with Et_2O. The orange precipitate was filtered, washed with Et_2O, and dried *in vacuo*. Yield of orange powder: 156 mg (0.196 mmol, 72%); ^{1}H NMR (acetone-d_6) δ 5.00 (d, J = 4.8 Hz, 1H), 4.66 (br s, 3H), 4.24 (d, J = 3.3 Hz, 1H), 4.20 (d, J = 4.8 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.66 (br s, 12H), 3.46 (d, J = 3.3 Hz, 1H), 2.79 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 161.67 (2 carbons), 149.29, 142.11, 79.80, 66.46, 51.91, 51.85, 47.89, 40.09, 39.58. Anal. (mixture of **35** and **34**) ($C_{13}H_{28}N_6O_{10}S_2F_6Os$): C, H, N (calcd 10.55, found 10.12).

{4,5-η^2-[Os(NH$_3$)$_5$]-3-(3-Oxo-*trans*-1-butenyl)pyrrole}-(OTf)$_2$ [36]. Compound **36** was prepared using a procedure similar to that used for the synthesis of **32** except that **1** was used instead of **2**. Yield: 84%. ^{1}H NMR (acetone-d_6) δ 8.44 (br s, 1H, NH), 7.71 (d, J = 15.6 Hz, 1H), 7.25 (s, 1H), 6.70 (d, J = 4.2 Hz, 1H), 6.43 (d, J = 15.6 Hz, 1H), 5.71 (d, J = 4.2 Hz, 1H), 4.68 (br s, 3H), 3.53 (br s, 12H), 2.10 (s, 3H); ^{13}C NMR (acetone-d_6) δ 197.12, 142.11, 137.77, 121.32, 117.17, 73.64, 49.83, 26.49.

Tricyclic Compound [37]. A solution of **1** (129 mg, 0.202 mmol) in DMSO was prepared, and 3-butyn-2-one (39.0 mg, 0.573 mmol) was added, giving a dark orange solution. After 2.5 h, the reaction mixture was diluted with an equal volume of acetone and added to 30 mL of Et_2O to give an oily precipitate. The Et_2O was decanted, and the crude product purified by repeatedly dissolving in acetone and reprecipitation with Et_2O to give a golden brown precipitate, which was filtered, washed with Et_2O, and dried *in vacuo*. Yield of golden-brown solid: 140 mg (0.180 mmol, 89%); ^{1}H NMR (DMSO-d_6) δ 7.71 (s, 1H), 6.08 (d, J = 2.4 Hz, 1H), 5.21 (d, J = 4.5 Hz, 1H), 4.38 (br s, 3H), 3.30–3.42 (m, 3H), 3.38 (br s, 12H), 2.11 (s, 3H), 1.56 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 194.80 (C), 153.71 (C), 153.46 (CH), 130.48 (CH), 123.68 (C), 78.56 (CH), 64.07 (C), 58.17 (CH), 48.92 (CH), 37.73 (CH), 25.98 (CH_3), 23.57 (CH_3). Anal. ($C_{14}H_{28}N_6O_8S_2F_6Os$): C, H, N (calcd 10.82, found 10.24).

Michael Additions with Methyl Acrylate/TBSOTf. The procedure for preparation of β-substituted 3*H*-pyrrolium Michael adducts from the starting pyrrole complexes using methyl acrylate/TBSOTf is general, and with the exception of the 2-ethyl derivative **40**, gives rise to compounds which have been previously reported.[4d] A representative procedure for the preparation of **38** from the 2,5-dimethylpyrrole complex **3** is presented below and is followed by a complete listing of NMR data for all compounds reported herein:

{4β,5β-η^2-[Os(NH$_3$)$_5$]-3α-(2-Carbomethoxyethyl)-2,5-dimethyl-3*H*-pyrrolium}(OTf)$_3$ [38]*. A solution of **3** (505 mg, 0.755 mmol) in acetonitrile (2.5 g) was prepared and added to methyl acrylate (66 mg, 0.77 mmol). TBSOTf (209 mg, 0.791 mmol) dissolved in 550 mg of acetonitrile was added, giving a dark red solution. After 2 min, water (0.1 g) was added with swirling. After 3 min, the reaction mixture was added to 100 mL of stirrred Et_2O to give an orange precipitate, which was filtered, washed with Et_2O, and dried *in vacuo*. Yield of an orange powder: 633 mg (0.699 mmol, 93%); ^{1}H NMR (acetone-d_6) δ 12.5 (br s, 1H), 5.09 (br s, 3H), 4.64 (s, 1H), 3.83 (br s, 12H), 3.66 (s, 3H), 3.3 (br s, 1H), 2.54 (s, 3H), 2.25–2.4 (m, 4H), 1.84 (s, 3H); ^{13}C NMR (acetone-d_6) δ 187.21 (C), 172.96 (C), 72.32 (C), 55.91 (CH), 51.31 (CH_3), 46.65 (CH), 29.95 (CH_2), 24.99 (CH_2), 16.19 (CH_3), 16.05 (CH_3). Anal. ($C_{13}H_{31}N_6O_{11}S_3F_9Os$): C, H, N.

{4β,5β-η^2-[Os(NH$_3$)$_5$]-3α-(2-Carbomethoxyethyl)-1-methyl-3*H*-pyrrolium}(OTf)$_3$ [39]*: ^{1}H NMR (acetone-d_6) δ 9.08 (s, 1H), 6.73 (d, J = 3.6 Hz, 1H), 5.14 (br s, 3H), 5.04 (d, J = 3.9 Hz, 1H), 4.06 (s, 3H), 3.91 (br s, 12H), 3.65 (s, 3H), 3.28 (s, 1H), 2.71 (dd, 2H), 2.38 (m, 2H); ^{13}C NMR (acetone-d_6) δ 174.66 (CH), 173.25 (C), 74.40 (CH), 53.43 (CH), 51.45 (CH_3), 48.53 (CH), 41.87 (CH_3), 30.83 (CH_2), 24.93 (CH_2).

{4β,5β-η^2-[Os(NH$_3$)$_5$]-3α-(2-Carbomethoxyethyl)-2-ethyl-3*H*-pyrrolium}(OTf)$_3$ [40]: ^{1}H NMR (acetone-d_6) δ 12.6 (br s, 1H), 6.64 (d, J = 4.5 Hz, 1H), 5.12 (br s, 3H), 4.91 (d, J = 4.5 Hz, 1H), 3.85 (br s, 12H), 3.66 (s, 3H), 3.4 (br s, 1H), 2.65–3.05 (m, 5H), 2.18 (m, 1H), 1.34 (t, 3H); ^{13}C NMR (acetone-d_6) δ 193.62 (C), 173.21 (C), 69.56 (CH), 54.60 (CH), 51.59 (CH_3), 46.52 (CH), 30.35 (CH_2), 25.39 (CH_2), 24.95 (CH_2), 9.66 (CH_3). Anal. ($C_{13}H_{31}N_6O_{11}S_3F_9Os$): H, N, C (calcd 17.26, found 16.58).

{4β,5β-η^2-[Os(NH$_3$)$_5$]-3α-(2-Carbomethoxy-1-methylethyl)-1-methyl-3*H*-pyrrolium](OTf)$_3$ [41]*: ^{1}H NMR (acetone-d_6)[62] δ 9.08 (s, 1H), 6.73 (d, J = 3.9 Hz, 1H), 5.11 (br s, 3H), 5.07 (d, J = 3.9 Hz, 1H), 4.05 (s, 3H), 3.87 (br s, 12H), 3.65 (s, 3H); 3.22 (s, 1H), 2.8 (m, 2H), 2.6 (m, 1H), 1.21 (d, J = 6.6 Hz, 3H); ^{13}C NMR (acetone-d_6) δ 173.96 (CH), 172.44 (C), 74.36 (CH), 59.00 (CH), 51.10 (CH_3), 46.76 (CH), 41.46 (CH_3), 37.73 (CH_2), 31.11 (CH), 16.75 (CH_3).

{4β,5β-η^2-[Os(NH$_3$)$_5$]-3α-(2-Carbomethoxyethyl)-3β-methyl-3*H*-pyrrolium}(OTf)$_3$ [42]*: ^{1}H NMR (acetone-d_6) δ 12.68 (br s, 1H), 9.29 (s, 1H), 6.85 (d, J = 4.5 Hz, 1H), 5.07 (br s, 3H), 4.90 (d, J = 4.5 Hz, 1H), 3.96 (br s, 12H), 3.64 (s, 3H), 2.63 (m, 2H), 2.54 (m, 2H), 1.51 (s, 3H); ^{13}C NMR (acetone-d_6) δ 181.68, 173.19, 70.35, 58.65, 51.53, 48.49, 33.91, 28.81, 17.10.

{4,5-η^2-[Os(NH$_3$)$_5$]-3-(2-Carbomethoxyethyl)-1-methylpyrrole}(OTf)$_2$ [43a]. A solution of **39** (273 mg, 0.306 mmol) in acetonitrile (700 mg) was prepared, and diisopropylethylamine (46 mg, 0.36 mmol) was added, giving a golden solution. After 5 min, the reaction mixture was added to 40 mL of stirred CH_2Cl_2, giving an oily precipitate. The oil was dissolved in acetone and precipitated with Et_2O, giving a tan precipitate, which was filtered, washed with Et_2O, and dried *in vacuo*. Yield of tan powder: 107 mg. Yield from **2**: 51%. ^{1}H NMR (acetone-d_6) δ 6.55 (d, J = 3.6 Hz, 1H), 6.34 (s, 1H),

(62) Major stereoisomer; 4:1 ratio of diastereomers observed.

5.36 (d, J = 3.9 Hz, 1H), 4.52 (br s, 3H), 3.61 (s, 3H), 3.50 (s, 3H), 3.45 (br s, 12H), 2.62 (m, 4H); ^{13}C NMR (acetone-d_6) δ 174.22, 124.81, 120.96, 82.41, 57.60, 51.21, 36.75, 33.65, 23.81. Anal. ($C_{11}H_{28}N_6O_8S_2F_6Os$): C, H, N (calcd 11.35, found 10.92).

{4β,5β-η^2-[Os(NH$_3$)$_5$]-3β-(2-Carbomethoxyethyl)-1-methyl-3*H*-pyrrolium}(OTf)$_3$ [43c]. A solution of HOTf (4.8 mg, 0.032 mmol) in CD_3CN (400 mg) was prepared and added to **43a** (22.0 mg, 0.0297 mmol), giving a light red solution which was monitored by ^{1}H NMR. After 10 min, the major product was observed to be **43c**, which completely converted to **39** within 12 h (**39** = **43e**): ^{1}H NMR (CD_3CN) (**43c**) δ 8.76 (s, 1H), 6.35 (d, J = 4.5 Hz, 1H), 4.73 (t, J = 4.8 Hz, 1H), 4.46 (br s, 3H), 3.74 (s, 3H), 3.67 (s, 3H), 3.38 (br s, 12H), 2.64 (dd, J = 6.6 Hz, 2H), 2.17 (m, 1H), 1.42 (m, 1H). (H(3) is obscured and thus not assigned).

{4,5-η^2-[Os(NH$_3$)$_5$]-4-(2-Carbomethoxyethyl)-1-methyl-3*H*-pyrrolium}(OTf)$_3$ [43d]. A solution of HOTf (12.4 mg, 0.0827 mmol) was dissolved in methanol (270 mg) and added to dry **43a** (43.2 mg, 0.060 mmol), giving a red-orange solution. After 3 min, Et_2O was added to the reaction mixture, giving a pink precipitate, which was filtered, washed with Et_2O, and dried *in vacuo*. Yield of light pink powder: 41.0 mg (0.046 mmol, 77%); ^{1}H NMR of the product showed a 2:1:1 ratio of **43d** to **43c** to **39**. ^{1}H NMR (CD_3CN) (**43d**) δ 8.47 (s, 1H), 6.34 (s, 1H), 4.46 (br s, 3H), 3.75 (s, 3H), 3.65 (s, 3H), 2.87 (m, 2H), 2.78 (m, 2H), 2.17 (m, 1H), 1.61 (m, 1H).

{3β,4β-η^2-[Os(NH$_3$)$_5$]-2α-(2-Carbomethoxyethyl)-2β,5-dimethyl-2*H*-pyrrolium}(OTf)$_3$ [46]*. To a solution of 2,3-*exo*-η^2-Os(NH$_3$)$_5$-1,4-dimethyl-5-*exo*-carbomethoxy-7-azabicyclo-[2.2.1]hept-2-ene (OTf)$_2$ (**44**)[4d] (333 mg, 0.441 mmol) in acetonitrile (655 mg) was added TBSOTf (130 mg, 0.492 mmol) in acetonitrile, giving a red solution. After 2 min, H_2O (21 mg) was added, and the mixture was swirled. The reaction mixture was then added to 90 mL of stirred Et_2O, giving a red-purple precipitate, which was filtered, washed with Et_2O, and dried *in vacuo*. Yield of pink-red powder: 391 mg (0.432 mmol, 98%); ^{1}H NMR (acetone-d_6) δ 11.5 (br s, 1H), 5.73 (d, J = 4.8 Hz, 1H), 5.44 (d, J = 4.8 Hz, 1H), 5.24 (br s, 3H), 4.15 (br s, 12H), 3.63 (s, 3H), 2.57 (s, 3H), 2.48 (m, 4H), 1.48 (s, 3H); ^{13}C NMR (acetone-d_6) δ 200.72, 172.94, 75.67, 61.65, 51.86, 51.49, 36.39, 28.99, 18.82, 18.67. Anal. ($C_{13}H_{31}N_6O_{11}S_3F_9Os$): C, H, N.

{3β,4β-η^2-[Os(NH$_3$)$_5$]-2α-(2-Carbomethoxyethyl)-1-methyl-2*H*-pyrrolium}(OTf)$_3$ [47]*. Compound **47** was prepared using a procedure parallel to the synthesis of **46**, except that 2,3-*exo*-η^2-Os(NH$_3$)$_5$-5-*exo*-carbomethoxy-7-methyl-7-azabicyclo-[2.2.1]hept-2-ene (OTf)$_2$ (**45**)[4d] was used as the starting material: ^{1}H NMR (acetone-d_6) δ 9.60 (s, 1H), 5.71 (br d, 1H), 5.60 (d, J = 5.4 Hz, 1H), 5.37 (br s, 3H), 4.09 (br s, 12H), 3.66 (s, 3H), 3.76 (s, 1H), 3.65 (s, 3H), 2.75 (m, 1H), 2.58 (m, 2H), 2.32 (m, 1H); ^{13}C NMR (acetone-d_6) δ 191.48, 173.05, 75.97, 59.00, 51.69, 50.23, 37.00, 28.21, 24.88.

{3β,4β-η^2-[Os(NH$_3$)$_5$]-2α-(2-Carbomethoxyethyl)-2β,5-dimethyl-2*H*-pyrrole}(OTf)$_2$ [48]. To a solution of **44** (241 mg, 0.319 mmol) in acetonitrile (0.89 g) was added TBSOTf (92.7 mg, 0.351 mmol) in acetonitrile, giving a red-purple solution of **46**. After 5 min, H_2O (2 drops) was added, followed by DBU (79.2 mg, 0.520 mmol), giving a golden brown solution upon swirling. After 5 min, the reaction mixture was added to 50 mL of stirred CH_2Cl_2, giving an oily precipitate, which was isolated, redissolved in acetone, and reprecipitated with Et_2O. The resulting precipitate was filtered, washed with Et_2O, and dried *in vacuo*. Yield of yellow-tan powder: 155 mg (0.205 mmol, 64%); ^{1}H NMR (acetone-d_6) δ 5.04 (d, J = 4.8 Hz, 1H), 4.87 (br s, 3H), 4.60 (d, J = 4.8 Hz, 1H), 3.73 (br s, 12H), 3.59 (s, 3H), 2.07–2.42 (m, 4H), 2.00 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (acetone-d_6) δ 179.51, 174.25, 76.77, 66.14, 59.85, 51.24, 39.53, 29.5, 20.77, 19.86. Anal. ($C_{12}H_{30}N_6O_8S_2F_6Os$): C, H, N.

{4,5-η^2-[Os(NH$_3$)$_5$]-1-Methyl-2-pyrroline}(OTf)$_2$ [49]. In a 50 mL Erlenmeyer flask, a solution of 1-methylpyrrole complex **2** (526 mg, 0.803 mmol) in methanol was prepared, and to it was added a solution of HOTf (161 mg, 1.07 mmol) in methanol (800 mg), giving a red solution of **10**. Solid TBAB (426 mg, 1.66 mmol) was then added, resulting in gas evolution and a tan-brown solution. After 5 min, a solution of HOTf (146 mg) in methanol (800 mg) was then added. After 10 min, the reaction mixture was added to 125 mL of a stirred solution of Et_2O/CH_2Cl_2 (3:1), giving a white precipitate, which was filtered, washed with CH_2Cl_2 and Et_2O, and dried *in vacuo*. Crude yield of white powder [*N*-protonated **49**]: 559 mg (0.693 mmol, 86%).

A solution of the above material in a cosolvent mixure of acetonitrile (1.72 g) and methanol (0.37 g) was prepared, and DBU (124 mg, 0.815 mmol) was added dropwise. After 5 min, the reaction mixture was added to 100 mL of stirred CH_2Cl_2, giving a white coagulated precipitate, which was filtered, washed with CH_2Cl_2 and Et_2O, and dried *in vacuo*. Yield of 2-pyrroline **49** (off-white powder): 420 mg (0.639 mmol; 92% last step, 80% overall): ^{1}H NMR (acetone-d_6) δ 5.12 (d, J = 4.8 Hz, 1H), 4.61 (br s, 3H), 3.80 (dd, J = 5.1, 4.8 Hz, 1H), 3.63 (br s, 12H), 2.81 (m, 1H), 2.74 (m, 2H), 2.63 (s, 3H), 1.71 (m, 1H); ^{13}C NMR (CD_3CN, 5% DMSO-d_6) δ 83.62 (CH), 59.58 (CH_2), 45.04 (CH_3), 41.38 (CH), 29.84 (CH_2). Anal. ($C_7H_{24}N_6O_6S_2F_6Os$): C, H, N.

{4,5-η^2-[Os(NH$_3$)$_5$]-1,1-Dimethyl-2-pyrrolinium}(OTf)$_3$ [50]. A solution of **49** (84.6 mg, 0.129 mmol) in acetonitrile (785 mg) was prepared, and MeOTf (43.6 mg, 0.266 mmol) was added dropwise, producing a significant amount of white precipitate over 5–10 min. The precipitate was filtered, washed with Et_2O, and dried *in vacuo*. Yield of white powder: 67.1 mg (0.082 mmol, 63%); ^{1}H NMR (CD_3CN, 5% DMSO-d_6) δ 5.54 (d, J = 4.5 Hz, 1H), 4.47 (br s, 3H), 4.01 (t, J = 4.5 Hz, 1H), 3.44 (br s, 12H), 3.29 (s, 3H), 3.00 (s, 3H), 3.2–3.0 (m, 2H), 2.44 (m, 1H), 2.30 (m, 1H); ^{13}C NMR (CD_3CN, 5% DMSO-d_6) δ 82.76, 62.88, 56.67, 51.58, 45.16, 28.95. Anal. ($C_9H_{27}N_6O_9S_3F_9Os$): C, H, N.

{4,5-η^2-[Os(NH$_3$)$_5$]-2,5-Dimethyl-2-pyrroline}(OTf)$_2$ [51]. A solution of **3** (1.499 g, 2.242 mmol) in methanol (5.5 g) was prepared in a 50 mL Erlenmeyer flask, and to it was added a solution of HOTf (375 mg, 2.50 mmol) in methanol (2.6 g), giving a red solution of **11**. A solution of TBAB (723 mg, 2.81 mmol) in acetonitrile (2.42 g) was added, giving gas evolution and a dark golden-yellow solution. After 5 min, a solution of HOTf (875 mg) in 2.75 g of methanol was added, giving a slightly dark golden-yellow solution. After 5 min, the reaction mixture was added to 200 mL of 3:1 cosolvent mixture of Et_2O/CH_2Cl_2, giving a white precipitate, which was filtered, washed with Et_2O, and dried *in vacuo*.

All of the above product was dissolved in a cosolvent mixture of acetonitrile (2.82 g) and methanol (2.42 g), and DBU (448 mg, 2.94 mmol) was added dropwise. After 10 min, the reaction mixture was added to 150 mL of stirred CH_2Cl_2, giving a tan precipitate, which was filtered, washed with CH_2Cl_2 and Et_2O, and dried *in vacuo*. Yield of tan powder: 1.360 g (2.028 mmol, 90%); ^{1}H NMR (acetone-d_6) δ 4.59 (br s, 3H), 4.30 (m, 1H), 3.74 (m, 1H), 2.79 (m, 1H), 2.48 (d, J = 5.1 Hz, 1H (NH)), 1.73 (s, 3H), 1.10 (m, 1H), 0.96 (d, J = 6.0 Hz, 3H); ^{13}C NMR (acetone-d_6) δ 78.65, 62.97, 44.50, 37.59, 20.37, 19.18. Anal. ($C_8H_{26}N_6O_6S_2F_6Os$): C, H, N.

{4,5-η^2-[Os(NH$_3$)$_5$]-1-Acetyl-2,5-dimethyl-2-pyrroline}(OTf)$_2$ [52]. A solution of **51** (213 mg, 0.317 mmol) in acetonitrile (500 mg) was prepared, and to it was added pyridine (42 mg, 0.53 mmol) followed by acetic anhydride (98 mg, 0.96 mmol). The reaction was allowed to stand for 1 h and then added to 50 mL of stirred CH_2Cl_2, giving a light brown precipitate, which was filtered. All of this material was dissolved in ca. 2 mL of acetone and added to 75 mL of stirred Et_2O, giving an off-white solid, which was filtered, washed with Et_2O, and dried *in vacuo*. Yield of off white solid: 155 mg;[63] ^{1}H NMR (acetone-d_6) δ 4.74 (m, 1H), 4.69 (br s, 3H), 4.01 (dd, J = 6.9, 1.5 Hz, 1H), 3.76 (br s, 12H), 3.20 (m, 1H), 2.07 (s, 3H), 1.71 (m, 1H), 1.64 (s, 3H), 1.32 (d, J = 6.0 Hz, 3H); ^{13}C NMR (acetone-d_6) δ 171.86, 75.31, 61.48, 46.95, 37.85, 23.96, 19.98, 19.41.

{(*Z*)-1β,2β-η^2-[Os(NH$_3$)$_5$]-3,4α-Dihydro-1,4β,6-trimethyl-6-hydroxy-5-azafulvenium}(OTf)$_3$ [53]. A solution of **51**

(63) The yield was not calculated due to the partial anion exchange from triflate to acetate arising from acetic anhydride (see preparation of **15**). Complete anion exchange to give analytically pure material was achieved by protonation with excess HOTf (methanol solvent) to give **53** (71% from **3**).

(686 mg, 1.02 mmol) in acetonitrile (910 mg) was prepared, and to it was added pyridine (176 mg, 2.23 mmol), followed by acetic anhydride (212 mg, 2.08 mmol). The reaction was stirred for 1 h, at which time partial precipitation of the product **52** had occurred. The reaction mixture was then transferred to 50 mL of stirred CH_2Cl_2, giving a light brown precipitate, which was filtered, washed with CH_2Cl_2, and partially dried.

All of the above product was dissolved in 2 g of methanol, and 450 mg of HOTf (3.00 mmol) was added dropwise to give a golden brown solution. After 5 min, the reaction mixture was added to 100 mL of stirred Et_2O, giving a light tan precipitate, which was filtered, washed with Et_2O, and dried *in vacuo*. Yield of light tan powder: 770 mg (0.892 mmol, 87%); ^{1}H NMR (acetone-d_6) δ 5.23 (m, 1H), 4.95 (br s, 3H), 4.58 (d, J = 6.6 Hz, 1H), 3.89 (br s, 12H), 3.67 (m, 1H), 2.66 (s, 3H), 2.10 (m, 1H), 1.91 (s, 3H), 1.49 (d, J = 6.6 Hz, 3H), (O*H* resonance not assigned); ^{13}C NMR (acetone-d_6) δ 173.47, 74.84, 64.72, 50.00, 37.71, 21.34, 20.33, 18.92. Anal. ($C_{11}H_{29}N_6O_{10}S_3F_9Os$): C, H, N.

{4,5-η^2-[Os(NH$_3$)$_5$]-1-Methyl-3-pyrroline}(OTf)$_2$ [54]. A purple solution of α-protonated 1-methylpyrrole complex **8** (175 mg, 0.217 mmol) in methanol (0.7 g) was prepared, and to it was added a solution of TBAB (69.3 mg, 0.269 mmol) in acetonitrile (0.53 g), giving gas evolution and a dark yellow solution. After 10 min, a solution of HOTf (131 mg, 0.873 mmol) in 0.3 g of methanol was added. After 5 min, the reaction mixture was added to 50 mL of a 3:1 mixture of Et_2O/CH_2Cl_2, giving a tan precipiate, which was filtered, washed with Et_2O, and dried *in vacuo*.

All of the above material was dissolved in a cosolvent mixture of acetonitrile (565 mg) and methanol (315 mg), and DBU (47.2 mg, 0.310 mmol) was added to give a dark golden solution. After 5 min, the reaction mixture was added to 75 mL of stirrred CH_2Cl_2, giving a dark tan precipiate, which was filtered, washed with CH_2Cl_2 and Et_2O, and dried *in vacuo*. Yield of tan powder: 119 mg (0.181 mmol, 83%); ^{1}H NMR (acetone-d_6) δ 4.62 (br s, 3H), 3.88 (s, 2H), 3.76 (br s, 12H), 3.29 (m, 4H), 2.29 (s, 3H); ^{13}C NMR (acetone-d_6) δ 61.34, 52.28, 41.18. Anal. ($C_7H_{24}N_6O_6S_2F_6Os$): H, C (calcd 12.80, found 13.46), N (calcd 12.80, found 12.23).

{4,5-η^2-[Os(NH$_3$)$_5$]-2,5-Dimethyl-3-pyrroline}(OTf)$_2$ [55]. A slurry of red-purple α-protonated 2,5-dimethylpyrrole complex **9** (252 mg, 0.308 mmol) in 1.5 g of acetonitrile was prepared, and a solution of TBAB (97.3 mg, 0.378 mmol) in acetonitrile (500 mg) was added, giving no apparent reaction. Approximately 500 mg of methanol was then added, giving gas evolution and a golden yellow solution over 1−2 min. After 5 min, HOTf (59 mg, 0.393 mmol) was added dropwise, giving a slighly darker golden yellow solution. After 5 additional min, the reaction mixture was added to 50 mL of a 4:1 mixture of Et_2O/CH_2Cl_2, giving a white precipitate, which was filtered, washed with Et_2O, and dried *in vacuo*.

N-Protonated **55** (isolated above) (197 mg, 0.240 mmol) was dissolved in 1.5 g of a 1:2 mixture of methanol/acetonitrile. DBU (63 mg, 0.41 mmol) was added dropwise to give a dark golden solution. After 5 min, the reaction mixture was added to 75 mL of stirred CH_2Cl_2 to give a light pink precipitate, which was filtered, washed with CH_2Cl_2 and Et_2O, and dried *in vacuo*. Yield of light pink powder: 145 mg (0.215 mmol, 74% from **9**): ^{1}H NMR (acetone-d_6) δ 4.48 (br s, 3H), 4.44 (m, 2H), 3.87 (s, 2H), 3.8 (vbr s, 12H), 2.49 (br t, 1H, NH), 1.09 (d, J = 6.6 Hz, 6H); ^{13}C NMR (acetone-d_6) δ 60.83 (CH), 57.18 (CH), 18.00 (CH_3). Anal. ($C_8H_{26}N_6O_6S_2F_6Os$): C, H, N.

{3β,4β-η^2-[Os(NH$_3$)$_5$]-2α-(2-Carbomethoxyethyl)-2β,5β-dimethyl-3-pyrroline}(OTf)$_2$ [56]. To a dark red solution of **46** (1.59 g, 1.76 mmol) in methanol (5.69 g) in a 50 mL Erlenmeyer flask was slowly added 178 mg (4.69 mmol) dry $NaBH_4$ with stirring. After 1−2 min, a tan precipitate started to form. After 2 min of additional stirring, a solution of HOTf (277 mg, 1.85 mmol) in acetone (750 mg) was added, followed, after several more minutes of stirring, by a solution of Proton Sponge (766 mg, 3.58 mmol) in acetone (1.7 g). The resulting tan slurry was added to 120 mL of stirred CH_2Cl_2. The precipitate was filtered, washed with CH_2Cl_2 and Et_2O, and dried *in vacuo*. The yield of the crude product, contaminated with NaOTf, was 1.52 g (off-white powder): ^{1}H NMR (acetone-d_6−5% DMSO-d_6) δ 4.58 (m, 1H), 4.40 (br s, 3H), 4.13 (br s, 12H), 3.77 (m, 2H), 3.62 (s, 3H), 2.46 (m, 2H), 2.18 (d, J = 4.8 Hz, 1H, NH), 1.99 (m, 2H), 0.99 (d, J = 6.6 Hz, 3H), 0.95 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 174.18, 64.64, 58.71, 56.74, 53.38, 48.67, 35.83, 29.85, 22.20, 17.76.

The presence of sodium triflate did not appear to affect the subsequent steps in the synthesis. However, the complex was purified for elemental analysis by precipitation as its tetraphenylborate salt from an aqueous solution of $NaBPh_4$. Anal. ($C_{58}H_{72}N_6O_2B_2Os\cdot 1.5\ H_2O$): C, H, N.

3-Acetyl-1-methylpyrrole [57]*. A solution of **15** (~25 mg) in CD_3CN with 1 drop D_2O along with *tert*-butylbenzene as an integration standard was prepared. A ^{1}H NMR spectrum was taken, and the solution was heated under anaerobic conditions for 50 min at 95−100 °C. A subsequent ^{1}H NMR spectrum showed an 80% NMR yield of **57**: ^{1}H NMR (isolated material, $CDCl_3$) δ 7.22 (m, 1H), 6.57 (m, 2H), 3.68 (s, 3H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 193.20, 126.70, 125.99, 123.21, 109.26, 36.45, 26.90.

3-(3-Oxobutyl)-1-methylpyrrole [58]*. A solution of **27a** (380 mg, 0.524 mmol) in 1.48 g of acetonitrile was prepared, and the solution was heated inside the dry box at 75 °C for 40 min. The reaction mixture was added to Et_2O, and the precipitate was filtered. The filtrate was evaporated to dryness, yielding **58** as a yellow oil. Yield: 61.1 mg (0.404 mmol, 77%). A similar experiment was carried out in >90% NMR yield in CD_3CN with an integration standard. Compound **58** was purified by preparative GC (20% DC-710 on chromosorb P (80/100 mesh), 8 ft × 1/4 in. column, T = 200 °C, t_r = 9.4 min): ^{1}H NMR ($CDCl_3$) δ 6.50 (m, 1H), 6.39 (br s, 1H), 5.95 (br s, 1H), 3.59 (s, 3H), 2.71 (m, 4H), 2.14 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 208.95, 122.85, 121.59, 119.23, 107.95, 45.34, 35.98, 29.98, 21.30. Anal. ($C_9H_{13}NO$): H, N, C (calcd 71.49, found 70.82).

3-(2-Carbomethoxyethyl)-1-methylpyrrole [59]*. Compound **59** was prepared in 75% NMR yield from **39** and isolated following a procedure similar to that of **58**. Compound **59** was purified by preparative GC (20% DC-710 on chromosorb P (80/100 mesh), 8 ft × 1/4 in. column, T = 200 °C, t_r = 10.3 min): ^{1}H NMR ($CDCl_3$) δ 6.50 (t, J = 2.1 Hz, 1H), 6.40 (br s, 1H), 5.96 (br s, 1H), 3.67 (s, 3H), 3.59 (s, 3H), 2.79 (dd, J = 8.1, 7.2 Hz, 2H), 2.56 (dd, J = 8.1, 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 173.83, 122.53, 121.54, 119.14, 107.88, 51.39, 35.92, 35.78, 22.38. Anal. ($C_9H_{13}NO_2$): H, N, C (calcd 64.65, found 64.08).

3-(2-Carbomethoxyethyl)-2,5-dimethylpyrrole [60]*. A solution of **38** (905 mg, 1.00 mmol) in dry acetonitrile (8.4 g) was transferrred to a 25-mL round-bottomed flask fitted with a condenser. The solution was heated without stirring in the absence of oxygen for 3 h at approximately 83 °C, giving a white crystalline precipitate suspended in a dark orange-brown solution. After the reaction mixture had cooled, it was added to 200 mL of Et_2O while stirring, which precipitated the osmium salts. The slurry was filtered and the filtrate evaporated to dryness, giving a yellow oil. Yield: 175 mg (0.966 mmol, 96%); ^{1}H NMR ($CDCl_3$) δ 7.42 (br s, 1H), 5.65 (br s, 1H), 3.68 (s, 3H), 2.68 (dd, J = 8.1, 7.2 Hz, 2H), 2.51 (dd, J = 8.1, 7.2 Hz, 2H), 2.20 (s, 3H), 2.15 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 174.05, 125.16, 121.95, 117.50, 105.95, 51.47, 35.78, 21.39, 12.89, 10.79. Anal. ($C_{10}H_{15}NO_2$): C, H, N.

3,4-Bis(2-carbomethoxyethyl)-2,5-dimethylpyrrole [61]*. A solution of 2,5-dimethylpyrrole (108 mg, 1.13 mmol) and methyl acrylate (95 mg, 1.10 mmol) in dry benzene-d_6 was prepared, and TBSOTf (278 mg, 1.05 mmol) was added dropwise, resulting in the formation of a light yellow solution which gradually turned orange. The reaction mixture was diluted with 50 mL of Et_2O, and the solution was extracted three times with 50 mL of 10% (aq) K_2CO_3. The organic layer was dried over anhydrous K_2CO_3 and evaporated to give 225 mg of a colorless oil. Analysis by ^{1}H NMR indicated a 1:2:1 mixture of 2,5-dimethylpyrrole, **60** and **61**, which were separated by silica gel chromatography (7:3 petroleum ether/ethyl acetate). (This reaction was also carried out in dry acetonitrile and the same ratio of products were observed.) The title compound (R_f = 0.23) had the following properties: ^{1}H NMR ($CDCl_3$) δ 7.33 (br s, 1H), 3.67 (s, 6H), 2.69 (m, 4H), 2.45 (m,

4H), 2.14 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 173.76, 121.58, 116.82, 51.49, 35.88, 19.96, 11.03. Anal. ($C_{14}H_{21}NO_4$): C, H, N.

2-(2-Carbomethoxyethyl)-1-methylpyrrole [62]*. A purple solution of **47** (560 mg, 0.629 mmol) was prepared in acetonitrile (3.58 g). Diisopropylethylamine (102 mg, 0.789 mmol) was added, and the reaction mixture added to an Ace pressure tube. The reaction mixture was heated to 95–100 °C for 75 min, giving a light brown solution. The reaction mixture was added to 75 mL of stirred Et_2O, giving a light tan precipitate, which was filtered off and discarded. The filtrate was evaporated to give crude **62**, which was purified by preparative TLC (6:1 $CHCl_3$/EtOAc mobile phase, $R_f = 0.65$) to give a colorless oil (58 mg, 0.35 mmol, 55%), which was further purified by preparatory GC as described for **58** and **59** (t_r = 10 min): ^1H NMR ($CDCl_3$) δ 6.58 (dd, J = 2.4, 2.1 Hz, 1H), 6.07 (dd, J = 3.6, 3.0 Hz, 1H), 5.90 (d, J = 3.6 Hz, 1H), 3.72 (s, 3H), 3.57 (s, 3H), 2.91 (m, 2H), 2.69 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 173.19, 131.29, 121.40, 106.57, 105.28, 51.61, 33.43, 33.06, 21.48. Anal. ($C_9H_{13}NO_2$): C, H, N.

5β,7aβ-Dimethyl-1,2,5,7a-tetrahydro-3*H*-pyrrolizin-3-one [63]*: ^1H NMR ($CDCl_3$) δ 5.83 (dd, J = 6.6, 1.8 Hz, 1H), 5.71 (dd, J = 6.6, 1.8 Hz, 1H), 4.62 (qdd, J = 6.6, 1.8, 1.8 Hz, 1H), 2.81 (m, 1H), 2.29 (m, 1H), 2.04 (m, 2H), 1.36 (s, 3H), 1.24 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 177.92, 134.53, 131.71, 73.45, 57.38, 35.87, 33.15, 27.71, 21.50. Anal. ($C_9H_{13}NO$): C, H, N.

***N*-(1-Methyl-4-oxopentyl)acetamide[40] [64].** A solution of **53** (149 mg, 0.209 mmol) was prepared in acetonitrile (1 g), and excess HOTf (144 mg, 0.959 mmol, 4.6 equiv) was added dropwise. A solution of DDQ (48.9 mg, 0.215 mmol) in acetonitrile (1.2 g) was prepared and slowly added to the osmium solution, giving a dark yellow reaction mixture.

The reaction mixture was treated with H_2O (1 mL) and partitioned between 30 mL each of saturated $NaHCO_3$ (aq) and CH_2Cl_2, and the organic layer was separated. The aqueous layer was extracted with 3 × 25 mL portions of CH_2Cl_2, and the organic layers were combined and back-extracted once with 40 mL of saturated $NaHCO_3$ (aq). The organic solution was dried (K_2CO_3) and evaporated to give 12 mg (0.074 mmol, 36%) of crude **64**. (In a separate experiment, the decomplexation was accomplished in 44% NMR yield): ^1H NMR ($CDCl_3$) δ 5.60 (br s, 1H), 3.91 (m, 1H), 2.49 (m, 2H), 2.12 (s, 3H), 1.91 (s, 3H), 1.68 (q, J = 6.9 Hz, 2H), 1.11 (d, J = 6.3 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 208.98, 169.60, 45.23, 40.49, 30.26, 30.06, 23.43, 21.27; IR (salt plate) (cm^{-1}) 3287, 3075, 2970, 1717, 1653.

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