Dearomatization of Anilines by Coordination to Pentaammineosmium(II)

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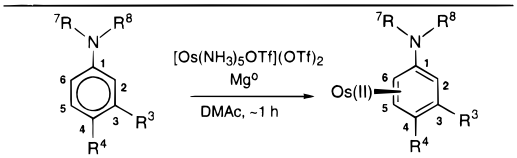
η^2-Aniline complexes of the π-base pentaammineosmium(II) are synthesized with a variety of different aniline ligands in good yield. Once synthesized, these complexes display ligand-based reactivity with a variety of electrophiles. Reaction with trifluoromethanesulfonic (triflic) acid produces 2*H*- and 4*H*-anilinium complexes, species resulting from protonation *on the ring*. The regioselectivity of protonation depends on a variety of factors, including the aniline substitution pattern, temperature, and solvent. In addition, the η^2-aniline complexes undergo regiospecific, chemospecific, and stereospecific reactions with carbon electrophiles such as Michael acceptors, acetals, and ketals. The resulting anilinium complexes are stabilized by a strong metal-to-ligand back-bonding interaction. As a result, these 4*H*-anilinium complexes may be functionalized further by their reaction with nucleophiles and complete dearomatization of the aniline ligand is thus achieved. The resulting allylamine and imine complexes are oxidatively removed from the metal center to provide organic allyl amine and cyclohexenone products in moderate yield. This methodology is complementary to that based on η^6-complexation of an electron-deficient metal center to the aniline.

Introduction

The high stability and availability of anilines make them useful as building blocks in the synthesis of functionalized alicyclic compounds. The amino group can be preserved and incorporated into a heterocyclic or alkaloidal ring system or used for the introduction of other functional groups or carbon−carbon bonds. Yet, surprisingly few reactions involving the dearomatization of anilines have been documented.[1] In preliminary accounts,[2] we have reported that dihapto coordination of aniline by the π-base pentaammineosmium(II) activates the arene toward electrophilic addition at C(4) and subsequently leads to its dearomatization and reductive functionalization. The reactivity of η^2-aniline complexes of pentaammineosmium(II) toward electrophiles has now been thoroughly investigated, and the results are presented herein.

Table 1. Synthesis and Numbering Scheme of η^2-Pentaammineosmium(II) Anilines 1−7 (Os(II) = $[Os(NH_3)_5](OTf)_2$)[5]



Complex	R^3	R^4	R^7	R^8	Yield (%)[a]
1	H	H	H	H	63
2	H	H	H	Et	94
3	H	H	Me	Me	88
4	H	Me	Me	Me	88
5	Me	H	Me	Me	93
6	H	H	H	TBS	67
7	H	H	H	Ac	95

[a]This value represents the yield of crude material, which was used without further purification.

Results

Preparation of η^2-Aniline Complexes of Pentaammineosmium(II). The aniline complexes of pentaammineosmium(II) are readily prepared from $[Os(NH_3)_5OTf](OTf)_2$ and an excess of the desired ligand by a slight modification of the literature preparation, as described in the Experimental Section (Table 1).[3] Upon precipitation from methylene chloride, the complexes are isolated as yellow-orange solids in good yield (Table 1). The aniline complex (**1**) exists primarily as its *N*-bound form (η^1) in weakly-coordinating solvents such as acetonitrile.[4] However, its 5,6-η^2 linkage isomer may be isolated by precipitation from a DMSO solution[4] and used in reactions that are fast relative to its isomerization to the η^1 form (*vide infra*). Complexes **1**−**7** have been characterized by ^{1}H and ^{13}C NMR and cyclic voltammetry. A ^{1}H NMR spectrum of any of these compounds at 20 °C typically shows several resolved resonances which have been shifted upfield relative to

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1995.

(1) Using catalytic hydrogenation (Rylander, P. N. In *Catalytic Hydrogenation in Organic Synthesis*; Academic Press: New York, 1979, p 186), anilines have been converted to bicyclic ring systems via intermediate aminocyclohexanes: (a) Snieckus, V. A.; Onouchi, T.; Boekelheide, V. *J. Org. Chem.* **1972**, *37*, 2845. (b) Fraser, R. R.; Swingle, R. B. *Can. J. Chem.* **1970**, *48*, 2065. Using Birch reduction, anilines have been selectively transformed into conjugated enamines that are subsequently used in carbon−carbon bond forming reactions: (c) Millward, B. B. *J. Chem. Soc.* **1960**, 26. (d) Birch, A. J.; Hutchinson, E. G.; Subba Rao, G. *J. Chem. Soc., Chem. Commun.* **1970**, 657.

(2) Portions of this work have been previously communicated: (a) Kopach, M. E.; Gonzalez, J.; Harman, W. D. *J. Am. Chem. Soc.* **1991**, *113*, 8972. (b) Gonzalez, J.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1993**, *115*, 8857.

(3) Harman, W. D.; Schaefer, W. P.; Taube, H. *J. Am. Chem. Soc.* **1990**, *112*, 2682.

(4) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 5403.

(5) Throughout this document, the pentaammineosmium(II) moiety and triflate counterions ($[Os(NH_3)_5](OTf)_2$) are abbreviated as Os(II) for clarity.

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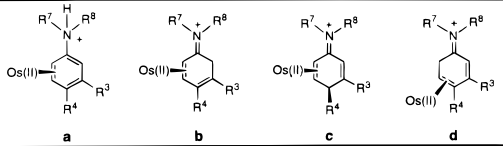
Table 2. Distribution of η^2-Anilinium Isomers



a b c d

Base[a]	R^3	R^4	R^7	R^8	Solvent	T(°C)	a[b]	b	c	d
3	H	H	Me	Me	MeCN	-40	>95			
2	H	H	H	Et	MeCN	-40		>95	-	-
1[c]	H	H	H	H	MeOH	20		-	>95	-
2	H	H	H	Et	MeOH	20		15	85	-
3	H	H	Me	Me	MeOH	20		20	40	40
4	H	Me	Me	Me	MeOH	20		>95	-	-
5	Me	H	Me	Me	MeOH	20		-	67	33

[a] Starting aniline complexes. [b] The numbers in these columns, determined by ^{1}H NMR integrations, represent the *relative amounts* of the various isomers. [c] The protonated complex **1c** was generated from **6** by desilylation.

those of the uncoordinated ligand, as well as two broad *cis*- and *trans*-ammine resonances spaced ~1 ppm apart. Cyclic voltammograms for **1**−**7** show an electrochemically reversible but chemically irreversible oxidation with $E_{p,a} \sim 0.30$ V (100 mV s^{-1}/CH_3CN/TBAH). The complexes are often contaminated with trace amounts (typically 5−10%) of a binuclear impurity that does not interfere with subsequent reactions. Although the aniline complexes are sufficiently stable to allow their use in acetonitrile solution, they will undergo substitution in this solvent with a half-life of hours to days at room temperature, depending on how sterically congested the aniline ligand is. The only case where the complexation procedure failed in our hands to deliver a clean product was for L = *N*,*N*-dimethyl-*o*-toluidine, where the desired mononuclear complex was always isolated with approximately equal amounts of two isomers of the binuclear complex $[\{(Os(NH_3)_5\}_2(\eta^2{:}\eta^2\text{-}\mu\text{-(L)}]^{4+}$.

Protonation of the η^2-Pentaammineosmium(II) Aniline Complexes. Treatment of the *N*,*N*-dimethylaniline complex (**3**) with trifluoromethanesulfonic (triflic) acid in acetonitrile at −40 °C followed by precipitation in ether affords the product of *N*-protonation (**3a**) (Table 2). This anilinium complex has the spectroscopic features (acetone-d_6; 300 MHz, 20 °C) common to other moderately fluxional η^2-arene complexes of pentaammineosmium(II). These include severely broadened ring proton resonances at 7.4 and 5.5 ppm, NH and N−CH_3 peaks at 9.2 and 3.4 ppm, respectively, and quadrupole-broadened ammine resonances at 3.6 and 4.9 ppm, values downfield from those of the conjugate base (**3**). When the *N*,*N*-dimethyl-*p*-toluidine complex (**4**) is dissolved in methanol with 1 equiv of triflic acid, the solution changes color from amber to pink. Upon addition to ether, a complex is precipitated whose ^{1}H and ^{13}C NMR and cyclic voltammetric data are consistent with an anilinium species where protonation has occurred at C(2) (**4b**, Table 2). Of particular note, the ^{1}H NMR spectrum for **4b** shows two broad doublets at 2.75 and 1.48 ppm with a geminal coupling constant of 25.8 Hz. In addition, a ^{13}C NMR spectrum of **4b** shows an iminium carbon C(1) at 192.6 ppm and a methylene signal (confirmed by a DEPT experiment) at 22.4 ppm. Cyclic voltammetric data for **4b** indicate an osmium(II) species bound to a highly electron-deficient olefin, showing an oxidation wave at $E_{p,a} = 1.31$ V (NHE) (cf. $[Os(NH_3)_5(2,3\text{-}\eta^2\text{-2-cyclohexen-1-one})]^{2+}$, $E_{1/2} = 0.92$)[6] and a reduction wave at $E_{p,c} = -1.11$ V. ^{1}H and ^{13}C NMR data for these and other anilinium isomers are presented in Table 3.

Table 3. Selected ^{1}H and ^{13}C NMR Data in ppm for Isomers of η^2-Anilinium Complexes in CD_3CN Solution

complex	C1	H6/C6	H5/C5	H4/C4	H3/C3	H2/C2
2b	196.0	4.99 (d)	5.58 (m)	6.63 (m)	5.83 (m)	2.66, 1.38
		55.1	54.2	130.3	123.1	31.0
3b	193.3	*a*	5.73 (m)	*a*	5.82 (m)	*a*, 1.45 (d)
		55.8	44.1	129.8	120.3	30.8
4b	192.6	5.58 (m)	5.27 (m)		5.58 (m)	2.76, 1.48
		45.0	59.0	137.8	114.1	33.5
1c	184.3	4.74 (d)	5.12 (m)	2.61 (br s)	7.13 (m)	6.44 (d)
		45.1	53.6	31.8	154.7	122.0
2c	181.2	4.66 (d)	4.99 (m)	2.70 (br s)	7.17 (m)	6.58 (d)
		52.3	46.2	31.8	155.7	118.0
3c	180.8	4.58 (d)	4.94 (m)	3.02 (br s)	7.02 (m)	6.61 (d)
		53.9	42.4	33.4	152.0	118.8
5c	180.8	4.87 (d)	5.07 (dd)	2.88, 2.80		6.46 (s)
		41.6	53.9	35.8	166.4	117.2
3d	172.9	2.71 (br s)	5.13	4.99	8.01 (dd)	6.64 (d)
		34.0	44.8	44.7	169.4	111.2
5d	184.6	2.67, 2.59	4.75 (d)	4.75 (d)		6.51 (s)
		34.4	47.6	46.8	171.1	110.6

[a] This resonance was not observed due to overlap with neighboring peaks.

The regioselectivity of protonation is dependent upon the reaction conditions. Under equilibrating conditions (methanol, 20 °C), the *N*-ethylaniline complex (**2**) is protonated with triflic acid to give a 15:85 mixture of *ortho*- and *para*-protonated isomers **2b**,**c**, respectively. However, when the same complex is protonated under kinetically-controlled reaction conditions (CH_3CN, −40 °C), only **2b** is isolated. When this isomer is allowed to stand in acetonitrile at room temperature, it slowly (~12 h) converts to the ratio of isomers observed upon protonation in methanol. In methanol, isolated **2b** rapidly changes its color from red to purple, and the same 15:85 equilibrium mixture of **2b**,**c** is formed. Equilibrium is reached rapidly under these conditions, resulting in no further change after 5 min. Furthermore, H(2) and H(4) undergo deuterium exchange when the isomerization is performed in CD_3OD. In the case of the aniline complex (**1**), attempted protonation of either the η^1- or η^2-form results in oxidation side reactions. However, exposure of the *N*-TBS−aniline complex (**6**) to acidic (HOTf) methanol results in cleavage of the TBS group, affording the *p*-protonated aniline complex (**1c**).

The regioselectivity of protonation for the aniline complexes is also dependent upon the substitution pattern of the aniline ring. For instance, whereas the *N*,*N*-dimethyl-*p*-toluidine complex (**4**) is exclusively protonated at the *ortho*-carbon (**4b**), the *N*-ethylaniline complex (**2**) protonates under equilibrating conditions predominantly *para* to the nitrogen (Table 2). In addition to these isomers, the *N*,*N*-dimethyl-*m*-toluidine (**5**) and *N*,*N*-dimethylaniline (**3**) complexes give rise to a 6*H*-anilinium species with the metal occupying the C(4)−C(5) double bond. Spectroscopic features for this form include low-field ^{13}C resonances corresponding to

(6) The reported value of 0.72 V was determined in acetone/NaOTf. In acetonitrile/TBAH, III/II reduction potentials for pentaammineosmium complexes typically are 200 mV positive of those reported for acetone/NaOTf.[3]

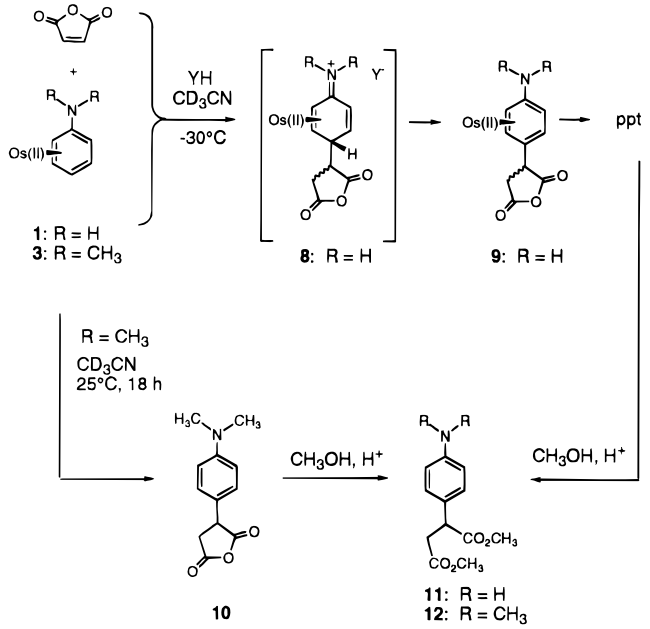


Figure 1. 1,4-Conjugate additions of aniline complexes to maleic anhydride.

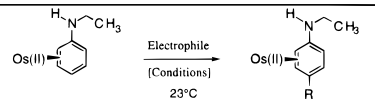
C(3) and proton signals characteristic of a diastereotopic methylene group (J = 27 Hz).

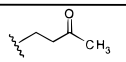
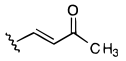
The aniline complexes are similar in basicity to their corresponding organic ligands. For instance, when the protonated *N*,*N*-dimethyl-*p*-toluidine complex (**4b**) is dissolved in CD_3CN with 1 equiv of uncomplexed *N*,*N*-dimethyl-*p*-toluidine, the ^{1}H NMR spectrum reveals an equal mixture of both the protonated and free-base complexes, as well as protonated and free *N*,*N*-dimethyl-*p*-toluidine. The pK_a (H_2O) of this ligand has been reported to be 5.5.[7]

Chemoselective Electrophilic Substitution Reactions of η^2-Pentaammineosmium(II) Aniline Complexes. As part of a general survey of electrophilic reactivity of η^2-arene complexes, the reactivity of the aniline complexes **1**−**4** toward maleic anhydride was explored.[2a] When a solution of the aniline complex (**1**) is treated with an excess of maleic anhydride at −30 °C in CD_3CN, the ^{1}H NMR spectrum reveals the formation of a transient ($t_{1/2} \sim$ 2 h) species (**8**) bearing a conjugated iminium functional group (*vide infra*) (Figure 1). Intermediate **8** converts over the course of several hours at −30 °C to a *p*-substituted aniline complex (**9**), which in turn forms an intractable precipitate. In the case of the *N*,*N*-dimethylaniline complex (**3**), the corresponding intermediates undergo substitution with the solvent over the course of hours (25 °C), liberating the anhydride (**10**) in 25−30% yield. Treatment of the precipitate from **9** or the anhydride (**10**) with methanol and acid affords the corresponding succinate esters **11** and **12** in 20−30% yield. The overall yield of **12** is nearly doubled to 48−50% if a catalytic amount of triflic acid (e.g. 10−30 mol %) is used in the reaction of **3** with maleic anhydride.

The reactions of other aniline complexes with maleic anhydride were also investigated. The *N*-ethylaniline complex (**2**) reacts in a manner similar to **1**, forming an arene intermediate analogous to **9** which was observed by ^{1}H NMR. In contrast, the *N*,*N*-dimethyl-*p*-toluidine complex (**4**) affords only the solvent substitution product, $[Os(NH_3)_5(CH_3CN)](OTf)_2$,[8] after standing for 12 h at room temperature (25 °C).

Table 4. Electrophilic Substitution Reactions of the *N*-Ethylaniline Complex (2)



#	Electrophile	Solvent	R	Yield (%)
13	MVK	MeOH		94
14	3-butyn-2-one	MeOH		89
15	Ac_2O, DMAP	CH_3CN/DMSO		87

In a control experiment, *N*,*N*-dimethylaniline does not react with maleic anhydride in CD_3CN at room temperature after several weeks. An orange color results from the formation of a charge transfer complex,[9] but no reaction could be observed by ^{1}H NMR. Aniline itself undergoes a fast and virtually quantitative *N*-acylation in acetonitrile, as has been observed in other solvents.[10]

The reactivity of a wide range of α,β-unsaturated carbonyl compounds toward the *N*,*N*-dimethylaniline complex (**3**) was investigated. For the less reactive electrophiles (e.g. acrylonitrile, diethyl maleate, α-methylene-γ-butyrolactone), no reaction takes place, and eventually the complex undergoes ligand exchange with CH_3CN to yield the unreacted aniline ligand and the Os(II)−acetonitrile complex. For the more reactive electrophiles (e.g. tetracyanoethylene, 1,2-bis(phenylsulfonyl)ethylene, and *N*-phenyltriazolinedione), uncharacterizable mixtures are formed. Similar results are obtained under a variety of reaction conditions (i.e. different solvents, concentrations, temperatures, and use of lithium or zinc salts as Lewis acids).

The *N*,*N*-dimethylaniline and *N*-ethylaniline complexes do not react with methyl vinyl ketone (MVK) in acetonitrile solution. However, when *methanol* is used as the solvent, a reaction does take place. When the *N*-ethylaniline complex (**2**) is placed in methanol with 1 equiv of MVK, the solution darkens over a period of ∼0.5 h. After addition to ether, a complex is isolated whose spectral and cyclic voltammetric data indicate the clean formation of a *para*-substituted aniline complex (**13**, Table 4). The ^{1}H NMR spectrum for this complex shows four doublets in the region from δ 4.75 to 6.10 which are indicative of *para* substitution. In addition, the ^{13}C NMR spectrum shows a resonance for a quaternary carbon at 211.0 ppm, which is assigned to the carbonyl carbon on the oxobutyl group, as well as another quaternary carbon resonance at 133.3 ppm (C(4)). Cyclic voltammetric data are consistent with an η^2-aniline complex, displaying an oxidation wave at $E_{p,a}$ = 0.30 V. A similar reaction takes place for the *N*,*N*-

(7) Aufauvre, F.; Dantonnet, M.; Dondon, M. L. *Bull. Soc. Chim. Fr.* **1965**, *12*, 3566.

(8) Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 2439.

(9) Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* **1953**, *75*, 3776.

(10) Cava, M. P.; Deana, A. A.; Muth, K.; Mitchell, M. J. *Org. Syn. Coll. Vol. V* **1973**, 944.

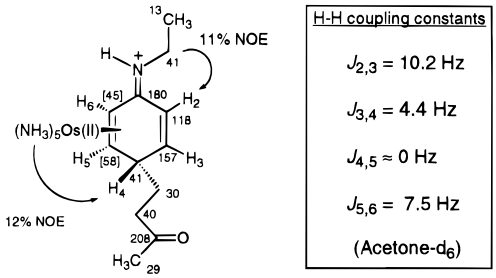


Figure 2. Diagnostic NMR data for the 5,6-η^2-anilinium complex **17**.

dimethylaniline complex (**3**), but at a somewhat slower rate. Repeating the reaction with an excess of Michael acceptor does not compromise the yield or purity of this reaction and does not result in multiple alkylations. Although this Michael addition will proceed with other activated electrophiles such as 3-butyn-2-one to afford **14**, less reactive acceptors (e.g. methyl acrylate and acrylonitrile) still fail to react under these reaction conditions.

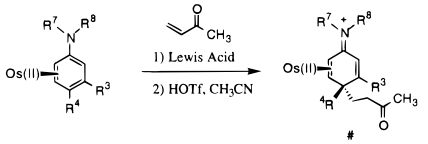
In addition to alkylation in methanol, the *N*-ethylaniline complex (**2**) reacts with acetic anhydride/DMAP in an CH_3CN/DMSO solvent mixture to afford, after precipitation, an aniline complex that has been acylated on the ring at the *para* position (**15**). No minor products resulting from nitrogen acylation are observed. Compound **15** has an orange color and displays many of the other spectroscopic characteristics of a disubstituted η^2-aniline complex. The presence of an electron-withdrawing group on the ring causes a shift of the oxidation potential to $E_{p,a} = 0.52$ V. This shift in potential is also observed for the reaction product of the *N*-ethylaniline complex and 3-butyn-2-one (**14**) and presumably results from the conjugation afforded by the vinylogous carbonyl group.

The corresponding organic ligands may be obtained by heating the arene complexes at 70 °C in a coordinating solvent such as acetonitrile. For example, when compound **13** is heated in CD_3CN, 4-(4-(ethylamino)-phenyl)-2-butanone (**16**) is liberated in 74% isolated yield.

Acid-Promoted Electrophilic Additions of η^2-Pentaammineosmium(II) Complexes. The *N*-ethylaniline complex (**2**) is unreactive toward MVK in acetonitrile solution. However, when a stoichiometric amount of $BF_3{\cdot}OEt_2$ is added to an acetonitrile solution of the *N*-ethylaniline complex (**2**) and MVK, an immediate color change from amber to purple occurs. After treatment with triflic acid (anion metathesis)[11] and precipitation from ether, a purple solid is isolated whose ^{1}H NMR, ^{13}C NMR, and cyclic voltammetric data are consistent with a 4*H*-anilinium complex (**17**, Figure 2). This addition reaction may also be promoted by the use of 1 equiv of HOTf. When the *N*-ethylaniline complex (**2**) is protonated and dissolved in methanol with 1 equiv of MVK for ~0.5 h, compound **17** is isolated upon precipitation with ether.

The ^{1}H NMR of **17** shows a downfield shift (~0.5 ppm relative to the starting material) in the *cis*- and *trans*-ammine resonances, as well as a new singlet at 2.10 ppm attributed to the oxobutyl group (Figure 2). The conjugated iminium functionality in **17** appears in the ^{1}H NMR spectrum as peaks at 6.8 and 7.1 ppm. The corresponding ^{13}C NMR resonances at 180 (C), 157 (CH), and 118 (CH) are also highly diagnostic for this fragment. A 12% NOE enhancement of H(4) upon irradiation of the *cis* ammines is consistent with the *anti* stereochemistry. The absence of coupling between H(4) and H(5) suggests an H(4)−C(4)−C(5)−H(5) dihedral angle approaching 90°, also consistent with *anti* stereochemistry of addition.[12] In all cases encountered, 4*H*- and 2*H*-anilinium complexes derived from *N*-ethylaniline are formed as single stereoisomers with respect to the C=N bond. Judging from NOE data for compound **17**, the ethyl group of this species is away from the side of the ring that is coordinated, and this orientation is likely preferred in other 4*H*-anilinium species as well. The addition of MVK to afford compound **17** can be generalized to most other aniline complexes including the case where C(4) is alkylated (i.e. **20**), and these reactions are summarized in Table 5.

Table 5. Michael Addition of η^2-Aniline Complexes to Methyl Vinyl Ketone



#	R^3	R^4	R^7	R^8	L. Acid	Solvent	T(°C)	Yld(%)
17	H	H	H	Et	$BF_3{\cdot}OEt_2$	CH_3CN	20	89
"	"	"	"	"	H^+	MeOH	20	84
19	H	H	Me	Me	$BF_3{\cdot}OEt_2$	CH_3CN	20	89
20	H	Me	Me	Me	$BF_3{\cdot}OEt_2$	CH_3CN	-40	98
21[a]	H	H	-	Ac	H^+	CH_3CN	-40	69
22	H	H	H	H	H^+	MeOH	20	86

[a] In this case the reaction mixture was neutralized with base prior to workup. This complex is actually the corresponding *N*-acylimine (R^7 = lone pair), since the iminium complex is unstable (*vide infra*).

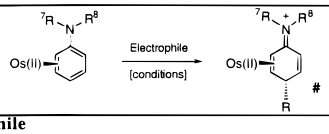
This alkylation reaction is general for an electronically- and structurally-diverse range of electrophiles including α,β-unsaturated esters and nitriles (Table 6). The reaction between the *N*-ethylaniline complex and acrolein takes place in water to afford the 4*H*-anilinium product (**23**). The use of water prevents competing acetal formation in the product which is observed when methanol is used as the reaction medium. In cases where a second stereogenic center (exogenous to the aniline ring) is created in the alkylation process, no significant stereoselectivity is observed at this center (compounds **26**, **27**, **29**, and **30**; Table 6). The fumarate adduct (**30**) was characterized further by conversion to the organic succinate ester (**12**) by rearomatization and decomplexation (Hünig's base, heat, CH_3CN).

These electrophilic addition reactions of the aniline complexes are also promoted by TBSOTf. In cases where the electrophile is an α,β-unsaturated ester, the initial product of the reaction is a silyl ketene acetal which is hydrolyzed by addition of water before isolation of the complex.[2b] In the case of methyl pentadienoate (methyl butadiene-1-carboxylate), addition occurs in a 1,6-fashion, affording the silyl ketene acetal (**31**) as an

(11) The putative counterion formed in the reactions with BF_3 is $[BF_3OH]^-$, presumably generated from trace amounts of water in the reagents.

(12) This negligible coupling between H4 and H5 has also been observed in *anti*-substituted pentaammineosmium(II) complexes of 2,5-cyclohexadienones.[2a,33]

Table 6. Scope of Electrophilic Additions for Aniline Complexes 2 and 3



#	Electrophile (Conditions)[a]	R^7	R^8	R	isomers[b]	Yield(%)[c]
23	acrolein (**D**)	H	Et	$-CH_2CH_2CHO$	-	81
24	methyl acrylate (**B**)	H	Et	$-CH_2CH_2CO_2Me$	-	86
25	acrylonitrile (**A**)	H	Et	$-CH_2CH_2CN$	-	95
26	2-cyclopenten-1-one (**A, B, C**)	H	Et		4:1 (**C**)	77 (**C**)
27	benzaldehyde dimethylacetal (**A**)	H	Et		1:1	53
28	2,2-dimethoxypropane (**A**)	H	Et	$-C(CH_3)_2OMe$	-	82
29	2-cyclohexen-1-one (**A**)	Me	Me		6:1	80
30	dimethyl fumarate (**A**)	Me	Me		2:1	63

[a]Conditions: **A**: 1) TBSOTf, CH_3CN, 20°C; 2) H_2O. **B**: Same as **A**, but at -40°C. **C**: 1) HOTf (1 equiv), 2) CH_3OH, 20°C. **D**: Same as **C**, but using water as the solvent. [b]Isomer ratio for the stereogenic center located in R. This ratio is based on the relative heights of ^{13}C NMR resonances and is thus approximate. [c] Unoptimized yields.

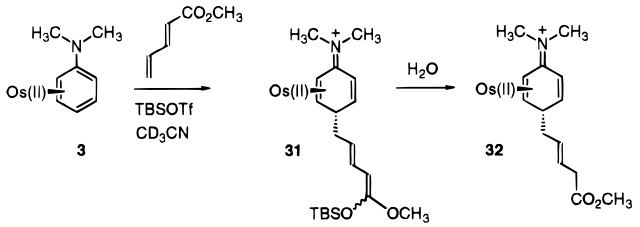


Figure 3. TBSOTf-promoted Michael addition of **3** to methyl pentadienoate.

8:1 mixture of isomers. A coupling constant of 15 Hz indicates the internal double bond has *trans* stereochemistry. Protonation of the silyl ketene acetal by water occurs at the α-position, affording the 4*H*-anilinium complex (**32**) (Figure 3).[13] When the iminium−ketene acetal (**31**) is treated with the lithium salt of a halide (F^-, Cl^-, or I^-), it undergoes a facile retro-Michael reaction, and when it is treated with a softer (tertiary amine) base, it undergoes deprotonation at C(4) and rearomatization.

The alkylation is highly sensitive to steric effects: no reaction is observed for acceptors bearing a methyl group at the *β*-position (i.e. methyl crotonate, 3-methyl-2-cyclopenten-1-one, 3-methyl-2-cyclohexen-1-one). Similarly, the C(4)-hindered *N*,*N*-dimethyl-*p*-toluidine complex (**4**) is resistant to alkylation with most mono-activated Michael acceptors other than MVK.

(13) Both *δ*-nucleophilic attack and α-protonation of the enolate are expected, on the basis of literature precedents: Cain, D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, U.K., 1991; Vol. 3, p 50.

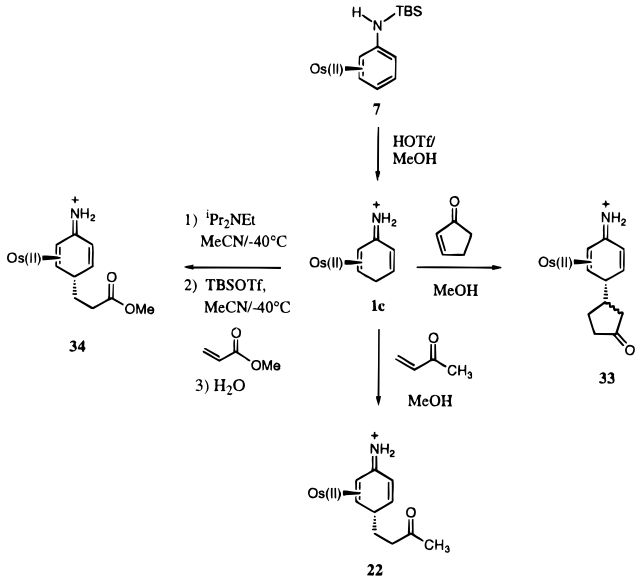


Figure 4. Alkylation reactions of the aniline (**1**) and 4*H*-anilinium (**1c**) complexes.

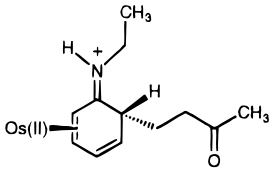
These alkylation reactions are not limited to the use of α,*β*-unsaturated carbonyl compounds. Acetals and ketals react to form 4*H*-anilinium complexes in good yield, although aldehydes and ketones do not react with the complexes. In the reaction of benzaldehyde dimethyl acetal with the *N*-ethylaniline complex (**2**), the product **27** is isolated as a 1:1 mixture of diastereomers about the benzylic carbon.

The parent aniline complex (**1**) reacts with methyl vinyl ketone to give a complex mixture of products under a variety of conditions. However, when a solution of the protonated aniline complex (**1c**) in methanol is treated with 1 equiv of MVK and the reaction mixture diluted with ether after ∼0.5 h, a purple solid is isolated whose spectral and cyclic voltammetric data are consistent with a 4*H*-anilinium complex (**22**, Figure 4). The protonated aniline complex will also react under these conditions with 2-cyclopenten-1-one to afford the 4*H*-anilinium complex (**33**), as a ∼4:1 mixture of diastereomers.

The η^2-aniline complex (**1**) may be generated *in situ* in acetonitrile solution by deprotonation of **1c** with 1 equiv of Hünig's base at low temperature (−40 °C). Since isomerization to the η^1-form is slow at this temperature, fast alkylation reactions can occur selectively. This is illustrated for the TBSOTf-promoted addition of **1** to methyl acrylate, affording anilinium complex **34** (Figure 4).

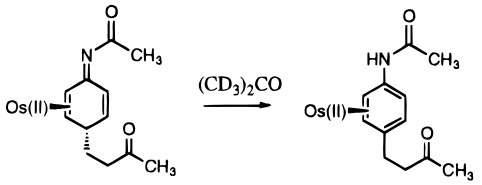
Virtually all reactions reported above occur with high regioselectivity to form 4*H*-anilinium products. Our attempts to effect an intermolecular addition at the 2 position have been for the most part unsuccessful. However, for the reaction of the *N*-ethylaniline complex (**2**) and methyl vinyl ketone, if TBSOTf is used as the promoting agent (at room temperature or at −40 °C), a 1:1 mixture of two compounds is isolated. One is the 4*H*-anilinium complex (**17**) identified earlier when $BF_3{\cdot}OEt_2$ was used as the promoter. The other product, **18**, features an iminium carbon at 198 ppm, a value significantly downfield of that for **17**, and a set of ^{13}C and ^1H NMR resonances indicative of an uncoordinated double bond that is *not* in conjugation with the iminium group. On the basis of the comparison of NMR data

for **18** and the 2*H*-anilinium compounds (**2**−**4b**), we assign **18** as the 2*H*-anilinium species shown. All our attempts to increase the ratio of **18** to **17** were unsuccessful.



18

In addition to anilines, the acetanilide complex **7** undergoes the alkylation reaction with MVK. When a solution of **7** and 1 equiv of MVK in acetonitrile is cooled to −40 °C and treated with 1 equiv of triflic acid, the amber solution changes color to a deep blue-green. A blue solid is isolated upon addition of ether. This material decomposes to a mixture of unidentified products in CD_3CN solution. However, if the blue solid is treated with 1 equiv of $^iPr_2NEt$ at −40 °C, the solution turns from blue back to amber, and a solid is isolated whose ^1H NMR, ^{13}C NMR, and cyclic voltammetric data are consistent with the acylated imine complex (**21**). The new material contains a quaternary center at δ 209.8 for the oxobutyl carbonyl group, as well as a quaternary center at δ 187.8 which is assigned to the imine carbon C(1). Over time, an acetone-d_6 solution of **21** rearomatizes to form **21a**.



21 **21a**

Nucleophilic Additions to Anilinium Complexes. The reaction of the *N*,*N*-dimethylaniline complex (**3**) with α-methylene-γ-butyrolactone and TBSOTf in CD_3CN affords a mixture of iminium species in combination with several other products. However, the reaction takes a different course in the presence of a tertiary amine base. When an excess of this Michael acceptor and TBSOTf are added to a solution of **3** and Hünig's base, the color of the mixture changes instantly from brown-orange to black. As the solution is allowed to stand for 15−20 min at room temperature, the color gradually changes to a clear brown. Dropwise addition of the solution to methylene chloride affords a tan precipitate, containing as the major product the spirolactone (**35**), a product of a MIchael−MIchael Ring Closure (MIMIRC) reaction. The spirolactone (**35**) may be recrystallized from acetone, affording bright yellow crystals in 48−52% overall yield from **3** (Figure 5).[2b]

When the reaction that forms **35** is repeated at low temperature (−30 °C) using only 1 equiv of α-methylene-γ-butyrolactone and TBSOTf in CD_3CN, a ∼50:50 mixture of unreacted *N*,*N*-dimethylaniline complex (**3**) and MIMIRC product (**35**) is obtained. However, when the procedure is repeated using 2 equiv of the Michael acceptor in *tetraglyme*, and the reaction worked up after complex **3** is consumed (the temperature was slowly raised from −20 to 20 °C over 15 min), the intermediate silyl ketene acetal (**36**) is observed as a 50:50 mixture with **35**.

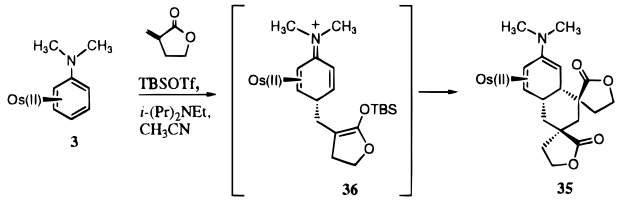


Figure 5. Michael−Michael ring closure reaction of **3** with α-methylene-γ-butyrolactone.

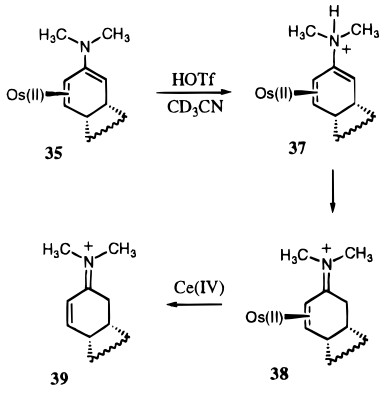


Figure 6. Protonation/decomplexation sequence for the tetracyclic enamine **35**.

The protonation of **35** with triflic acid was studied by ^1H NMR in CD_3CN. The data suggest the kinetic product is an *N*-protonated species (**37**) that converts over time ($t_{1/2}$ ∼ 1 h) to the iminium complex (**38**). Oxidation of **38** affords the corresponding organic product **39**, which was characterized by ^1H NMR (Figure 6). Attempts to alkylate the enamine functionality in **35** with methyl triflate resulted only in protonation.

Following the observation of this Michael−Michael ring closure reaction, a variety of experiments were conducted to explore the scope of this reaction with other Michael acceptors. When the conditions used in the synthesis of **35** are employed with methyl acrylate, competing deprotonation at C(4) and decomplexation affords the rearomatized material, methyl 3-(*p*-(dimethylamino)phenyl)propionate.[2b] Furthermore, the silyl ketene acetal intermediates do not undergo cyclization with excess quantities of other Michael acceptors. Similar attempts to effect a crossed MIMIRC reaction using the methyl acrylate-derived silyl ketene acetal and α-methylene-γ-butyrolactone lead to protonation of the silyl ketene acetal and polymerization of the acceptor.

Hydride Reductions of η^2-Pentaammineosmium(II) 4*H*-Anilinium Complexes. The 4*H*-anilinium complex (**25**) may be reduced to iminium (**40**) and allylamine (**41a**,**b**) complexes, depending on the reaction conditions (Figure 7). For instance, when **25** is dissolved in methanol and added to $NaBH_4$, the reaction mixture evolves gas and changes in color from purple to gold. Addition of triflic acid and precipitation from ether/CH_2Cl_2 affords a 4:1 ratio of products **41a**,**b**. The milder reducing agent Bu_4NBH_4 under these conditions similarly affords a 5:1 mixture of **41a**,**b**. However, the reduction occurs with greater stereoselection using the latter reagent in methanol−acetonitrile solution at −40 °C, affording **41a** in combination with only traces (<5%) of the other isomer.

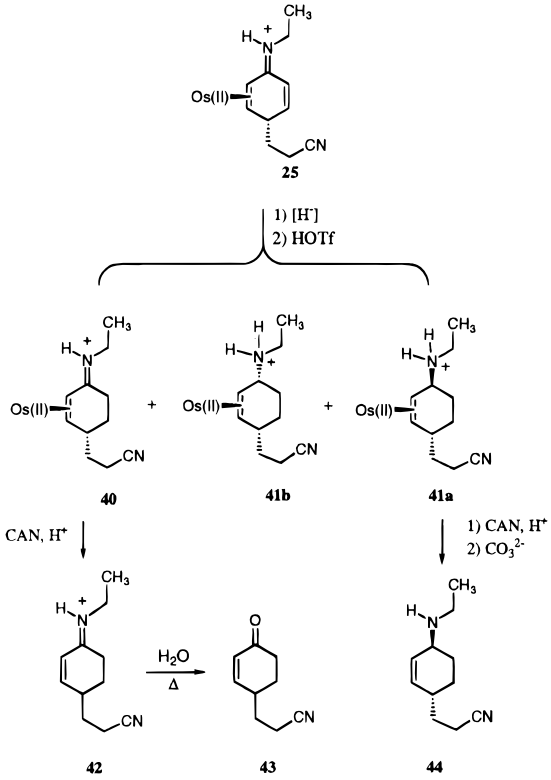


Figure 7. Dearomatization of the anilinium complex **25**.

Table 7. Product Distribution for Hydride Additions to the Anilinium Complex 25

reagent[a]	*T* (°C)	solvent	yld (%)	**40**	**41a**	**41b**
$NaBH_4$	20	MeOH	*b*		80	20
Bu_4NBH_4	−40	MeOH/MeCN	95		>95	
Li−9BBNH	−40	tetraglyme/THF	67	90	10	
H_2, Pd/C	20	MeOH	87	>95		

[a] The reaction mixtures were treated with triflic acid prior to workup. [b] These products are contaminated with NaOTf.

When **25** is treated with lithium 9-BBN-H in a tetraglyme/THF solution at −40 °C, the reduction may be stopped after the addition of 1 mol of hydride, affording an ~9:1 mixture of complexes **40** and **41** after an acidic workup. Reduction of the 2,3-double bond in the 4*H*-anilinium complexes may be achieved more selectively by hydrogenation with 50 mol % of 10% Pd/C in methanol, with a typical reaction time of several hours. The pink solid isolated upon precipitation from ether shows a peak in the ^{13}C NMR spectrum at δ 197.0 (C1), as well as an oxidation wave in the cyclic voltammogram at $E_{p,a}$ = 1.23 V, corresponding to the iminium species (**40**). A summary of the product distribution as a function of reducing agent is shown in Table 7. The organic ligands may be liberated from the complexes via a one-electron oxidation using CAN or DDQ. For example, when complex **40** is dissolved in a CD_3CN/D_2O mixture and a D_2O solution of CAN is added, the organic conjugated iminium species (**42**) is liberated in 56% yield by ^1H NMR integration. This compound undergoes hydrolysis to the enone (**43**) after standing in solution overnight at 55 °C. Similarly, when the allylamine complex (**41a**) in CD_3OD/D_2O solution is treated with 1 equiv of DDQ, the organic allylamine (**44**·HOTf) is liberated in 86% yield by ^1H NMR (Figure 7). The organic products **43** and **44** are isolated in 46% and 60% yields, respectively, following chromatographic purification.

Discussion

Synthetic Considerations. In contrast to the vast number of reports and reviews that have appeared concerning the activation of benzenes, haloarenes, and phenyl ethers by organometallic means,[14] the activation of anilines is relatively unexplored. Accounts concerning organometallic chemistry of anilines have mostly dealt with either complex formation[15] or nucleophilic substitution[16] on the aromatic ring. In contrast to the chemistry of η^6-aniline compounds, the η^2-aniline complexes **1**−**7** undergo Lewis- or Brønsted-acid-catalyzed, C(4)-selective alkylations with a vareity of carbon-based *electrophiles* (Tables 5 and 6). Under appropriate reaction conditions, alkylations occur with excellent regiochemical control to give stable 4*H*-anilinium complexes. This holds true even in the case of the *N*,*N*-dimethyl-*p*-toluidine complex (**4**), where alkylation occurs at the more hindered *ipso* (C4) carbon, and the reaction results in the formation of a quaternary center (**19**). These reactions are highly stereoselective, with electrophilic addition reliably occurring on the face of the ring *anti* to that of metal coordination. Furthermore, the reactions are chemoselective in that electrophilic addition occurs on the ring carbon rather than the nitrogen. The treatment of the *protonated* aniline complex (**1c**) with MVK results in a C4-selective alkylation to generate the dearomatized iminium complex (**22**, Figure 4), whereas free aniline affords only the *N*-alkylation product under similar reaction conditions.[17]

The reactivity of the η^2-aniline complexes of pentaammineosmium(II) is complementary to that observed for η^6-anilines bound to electron-deficient metal centers such as $\{Cr(CO)_3\}$,[18] $\{Mn(CO)_3\}^+$,[19] and $\{FeCp\}^+$.[20] Although aniline complexes of these systems have yet to be used in a dearomatization process, a few examples of ring nucleophilic addition followed by rearomatization exist. In the example shown in Figure 8, coordination of *N*,*N*-dimethylaniline by chromium tricarbonyl activates the arene ligand toward nucleophilic attack *meta* to the amino group.[21,22] In contrast, in the osmium(II) complexes, the aniline ligand is activated toward electrophilic attack *para* to the amino group. η^6-Coordination by $Cr(CO)_3$ also promotes the deprotonation of *N*,*N*-dimethylaniline by *n*-butyllithium, but methylation of the resulting aryl anion and photodecomplexation results in a mixture of regioisomeric toluidines (19% *ortho*, 20% *para*, 61% *meta*).[23] Protecting the nitrogen of

(14) Semmelhack, M. F. *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, U.K., 1991; Vol. 2, p 517.
(15) Mahaffy, C. A. L. *Synth. React. Inorg. Met.-Org. Chem.* **1985**, *15*, 945−950. Baldoli, C.; DelButtero, P.; Maiorana, S. *Tetrahedron Lett.* **1992**, *33*, 4049−52.
(16) (a) Ohlsson, B.; Ullenius, C. *J. Organomet. Chem.* **1988**, *350*, 35. (b) Ohlsson, B.; Ullenius, C.; Jagner, S.; Grivet, C.; Wenger, E.; Kundig, E. P. *J. Organomet. Chem.* **1989**, *365*, 243.
(17) Tamura, S.; Takiguchi, C.; Sakai, K. *J. Pharm. Soc. Jpn.* **1956**, *76*, 915; *Chem. Abstr.* **1956**, *51*, 2782i.
(18) Semmelhack, M. F. *Pure Appl. Chem.* **1981**, *53*, 2379.
(19) Walker, P. J. C.; Mawby, R. J. *Inorg. Chim. Acta* **1973**, *7*, 621.
(20) Astruc, D. *Tetrahedron*, **1983**, *39*, 4027.
(21) Semmelhack, M. F.; Clark, G. R.; Farina, R.; Saeman, M. *J. Am. Chem. Soc.* **1979**, *101*, 217.
(22) This form of activation and regiochemistry is general for η^6-arene complexes in which the metal center is $Cr(CO)_3$. For a review of transition-metal-mediated dearomatization, see ref 14.
(23) Card, R. J.; Trahanovsky, W. W. *J. Org. Chem.* **1980**, *45*, 2560.

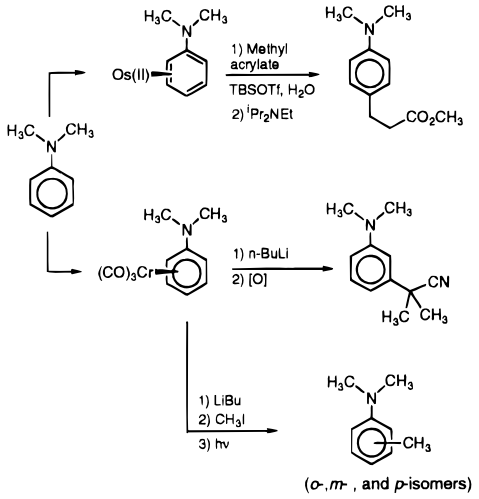


Figure 8. Complementary methods of ring alkylation for *N*,*N*-dimethylaniline.

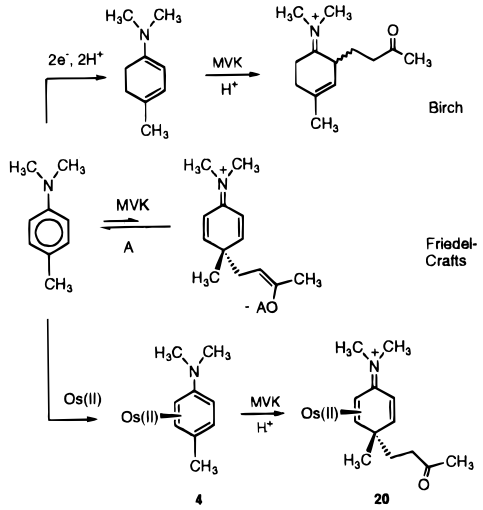


Figure 9. Comparison of conjugate addition reaction for an enamine, an aniline, and an η^2-aniline complex (**4**).

N-methylaniline a with Boc group leads to regiospecific *ortho* lithiation.[24] In contrast to the electron-withdrawing chromium tricarbonyl group, the pentaammineosmium(II) moiety stabilizes the 4*H*-anilinium intermediates resulting from the initial electrophilic attack at C(4) (e.g. compounds **19**−**34**). The metal−arenium back-bonding interaction is substantial. This is demonstrated by the observations that the iminium carbon is resistant to hydrolysis (e.g. aqueous solution, 70 °C) or reduction by tetrabutylammonium cyanoborohydride, and rearomatization does not occur without addition of a moderate base ($pK_b < 9$). The latter is a key feature of the osmium(II) system as subsequent nucleophilic addition to a 4*H*-anilinium complex can occur at C(3), resulting in a vicinal difunctionalization of the 3,4-double bond and dearomatization of the aniline. This is illustrated in the synthesis of the MIMIRC compound **35** and the iminium complex (**40**) (Figures 5 and 7).

Although the aniline complexes described in this study exist as an equilibrium mixture of linkage isomers,[25] the preferred form involves coordination at C(5) and C(6).[4] Thus, the unbound portion of the aniline ligand resembles a linearly conjugated dienamine, and as such might be expected to show chemical reactivity similar to an organic dienamine. In Figure 9, the reactions of 5,6-dihydro-*N*,*N*-dimethyl-*p*-toluidine (obtained from the arene by Birch reduction)[26] and 5,6-η^2-pentaammineosmium(II) *N*,*N*-dimethyl-*p*-toluidine (**4**) toward MVK are contrasted. From a synthetic perspective, the two dearomatization processes offer complementary regiochemical control as the dienamine system undergoes electrophilic addition specifically at the α carbon,[27] whereas the osmium(II) aniline complexes show a *para* selectivity reminiscent of that observed under Friedel−Crafts conditions (i.e. electrophilic addition to an aniline). For the latter reaction, the observed selectivity for C(4) addition has been attributed to the magnitude of the HOMO coefficients, which are significantly larger at C(4) than at C(2),[28] and this may be the case for the osmium systems as well. For example, extended Hückel calculations performed on a CaChe system in our laboratories indicate that, for the aniline complex **1**, the highest energy occupied *ring-centered* MO has its largest coefficient at C(4).[29] For *p*-substituted anilines such as *N*,*N*-dimethyl-*p*-toluidine, an *ipso* alkylation at C(4) would be greatly disfavored since it disrupts the aromatic nature of the ring. However, in the case of the corresponding osmium(II) complex (e.g. **4**), the resulting dearomatized iminium product is stabilized by back-bonding to the point that *para* addition is observed even though this carbon is more substituted than is C(2). Finally, we note that whereas the Friedel−Crafts alkylation of an aniline is often plagued by low yields resulting from multiple electrophilic substitutions, the stabilization of the 4*H*-anilinium ligand by osmium effectively eliminates formation of unwanted multiple alkylation products.

Perhaps the most dramatic testimony to osmium(II) altering the reactivity of the aniline ring system is the reaction between the aniline complex (**1**) and maleic anhydride where osmium coordination promotes a C(4)-selective conjugate addition. When this reaction is observed by ^1H NMR, no evidence of *N*- or *C*-acylation (i.e. signals corresponding to a maleate group) is observed (Figure 1). In contrast, the reaction of aniline itself with maleic anhydride affords the *N*-acylated product.[17] In cases where the aniline nitrogen is protected, either by an acetyl group[30] or by methyl groups (*N*,*N*-dimethylaniline),[31] the dominant reaction with maleic anhydride under Lewis-acidic conditions is *acylation* at C(4).

Fundamental Considerations. First, we consider the favored position of the osmium within the arene

(24) Uemura, M.; Hayashi, Y.; Hayashi, Y. *Tetrahedron Asymmetry* **1994**, *5*, 1427.
(25) Harman, W. D. Ph.D. Dissertation, Stanford University, 1987.
(26) See ref 1d (the kinetic 1,4-diene isomerizes under the Birch reduction reaction conditions).
(27) The mechanistic relevance of this comparison must be interpreted with caution in the absence of a control experiment, since the reaction conditions were different (refluxing dioxane for the organic compound vs $BF_3{\cdot}OEt_2$ at −40 °C for compound **4**).
(28) Klopman, G. *Chemical Reactivity and Reaction Paths*; Wiley: New York, 1974; p 81. Extended Hückel calculations performed on a CAChe system in our laboratories show that *N*,*N*-dimethyl-*p*-toluidine has a larger HOMO coefficient at C(4) than at C(2), whereas, for the corresponding 5,6-dihydro compound, the electron density is more evenly distributed between these two reactive centers.
(29) Coefficients for the highest energy occupied molecular orbital *that is ring-centered* (no. 38) for compound **1**: C(4), 0.482; C(2), 0.389.
(30) Bianchi, M.; Butti, A.; Christidis, Y.; Perronnet, J.; Barzaghi, F.; Cesana, R.; Nencioni, A. *Eur. J. Med. Chem.* **1988**, *23*, 45.
(31) (a) Koga, W. *Nippon Kagaku Zasshi* **1956**, *77*, 1276. (b) Webster, V. S.; Kamstra, L. D. *Proc. S. Dakota Acad. Sci.* **1951**, *30*, 40.

ring. Anilines, like their phenol and anisole counterparts, are preferentially coordinated at C(5) and C(6). In no case has an alternate ring-bound arene isomer been detected.[32] In addition, these complexes are usually static on the NMR time scale (300 MHz, 20 °C) and are stable in acetonitrile solution for several days. In contrast, monosubstututed hydrocarbon complexes of pentaammineosmium(II) (e.g. toluene) are highly fluxional at 20 °C, typically show little preference for 4,5-η^2- and 5,6-η^2 forms, and undergo arene displacement by acetonitrile over a period of hours.[25] Both the preference for the 5,6-η^2 isomer and the much slower rates of tautomerization and substitution for anilines can be attributed to a significant π-interaction of the electron-releasing substituent with the *uncoordinated portion of the aromatic ligand* (i.e. C(2)−C(4)). In cases where this π-interaction is disrupted by placing an electron-withdrawing group on the heteroatom (i.e. acetanilide), rates of both isomerization and solvent substitution are increased. As mentioned earlier, of the complexes **1**−**7**, only for the aniline complex (**1**) is the nitrogen-bound isomer ever observed.

In principle, the ring-bound aniline isomer of **1** could undergo an intramolecular proton transfer thereby generating a 4*H*-aniline (i.e. a cyclohexadienone imine) species, but no such osmium species has ever been detected. However, for the case of the acetanilide complex (**7**), a neutral 4*H*-acetanilide isomer has been generated from the sequence of alkylation (MVK) and subsequent imine deprotonation to form **21**. Over time, however, this species yields to its thermodynamically preferred aromatic isomer (**21a**). In contrast, anilinium salts that are coordinated by pentaammineosmium(II) exist solely as their dearomatized 2*H*- and 4*H*-iminium isomers. Presumably the more electron-deficient nature of the C(1) substituent increases the π-acid character of the 4*H*-arene isomer and stabilizes the electron-rich metal. Thus, the latter species is increasingly favored over its aromatic isomer. This relationship is summarized in Figure 10, where the corresponding phenol and phenolium systems are shown for comparison.

The effect of η^2-coordination on the dienone-phenol equilibrium has been studied for a number of pentaammineosmium(II)−phenol complexes.[33] In the case of the phenol complexes, isomerization is fast in acid, so thermodynamic products are isolated following metal coordination. In the case of the aniline complexes described here, however, isomerization is sufficiently slow that under appropriate conditions either kinetic or thermodynamic products of protonation may be observed. For example, when the *N*,*N*-dimethylaniline complex (**3**) is treated with triflic acid at −40 °C in acetonitrile solution, the initial product formed is predominantly *N*-protonated (e.g. **3a**, Table 2). This *N*-protonated anilinium complex isomerizes quickly to a mixture of 2*H*- and 4*H*-anilinium species (**3b**,**c**) at room temperature in acetonitrile solution. Equilibration is sufficiently fast in methanol so that no further changes in the product distribution are observed after 5 min. A similar result is observed for the *N*-ethylaniline complex (**2**), except in this case only the 2*H*-anilinium complex (**2b**) is observed as the kinetic

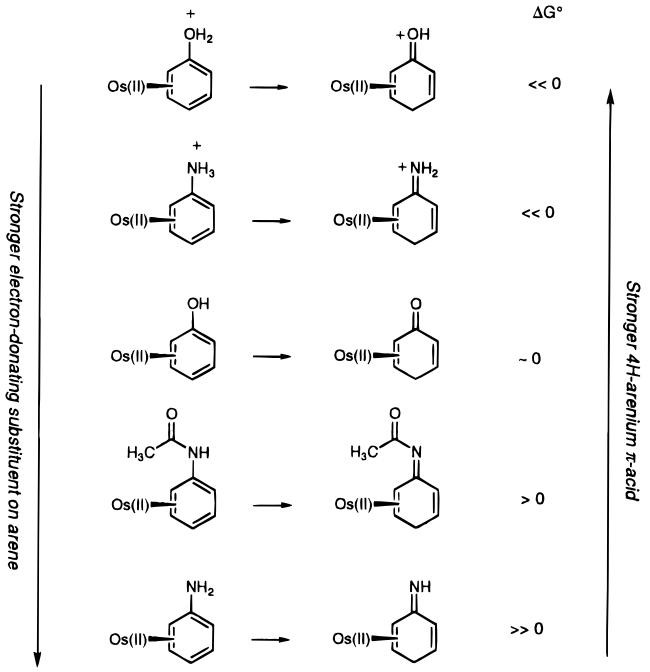


Figure 10. Comparison of thermodynamic relationships for various osmium(II)−arene/arenium complexes and their 4*H*-arene/arenium isomers.

product. In cases where C(4) is not alkylated, the equilibrium distributions favor the 4*H*-anilinium tautomers over their 2*H*-counterparts (**c**, Table 2). In the case of the former isomers, note that the uncomplexed olefin is adjacent to the iminium group. In a similar finding, the 4*H*-phenol complex of osmium(II) is thermodynamically more stable than its 2*H*-isomer.[30]

Where C(4) of aniline is alkylated, protonation at C(4) would force this substituent into an unfavorable steric interaction with the pentaammineosmium moiety, and as a consequence, 4-alkylated, 4*H*-anilinium complexes where the 4-methine proton is *anti* to the osmium have not been observed. In contrast, 4*H*-anilinium complexes containing a 4-methine proton *syn* to the osmium, such as those generated from C(4) alkylation, are readily formed (*vide supra*). In fact, the latter complexes are expected to be *kinetically* stabilized relative to the parent 4*H*-anilinium species in that the C(4)-substituent hinders deprotonation at C(4). A similar effect has been observed for 4-substituted, 4*H*-phenol complexes of osmium(II).[34]

Under equilibrating conditions, the *N*-ethylaniline complex (**2**) exists as a mixture of 4*H*- and 2*H*-anilinium isomers indicating that these two forms of anilinium are practically isoergic at 20 °C provided that neither C(2) or C(4) bear substituents. Further, the pK_a (aq) of the 2*H*-anilinium complex derived from *N*,*N*-dimethyl-*p*-toluidine (**4b**) was determined to be approximately equal to that of the conjugate acid of *N*,*N*-dimethyl-*p*-toluidine (pK_a = 5.5). Finally, the reduction potentials for the aniline complex ($E_{1/2}$ = 0.30 V)[35] and its 4*H*-anilinium isomer ($E_{1/2}$ ~ 1.18 V)[36] have been directly measured or can be estimated from analogous systems. In Figure 11, this information is combined to give an estimate of

(32) This statement holds for anisoles, phenols, and anilines without other π donor substituents.

(33) Kopach, M. E.; Hipple, W. G.; Harman, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 1736.

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

(35) Previously, $E_{1/2}$ = 0.16 V (NHE) was determined for compound **1** in *N*-methylpyrrolidinone.[4] Correcting for solvent,[25] $E_{1/2}$ ~ 0.30 V in CH_3CN. Note that, for the *N*-ethylaniline analog **2**, $E_{p,a}$ = 0.36 V.

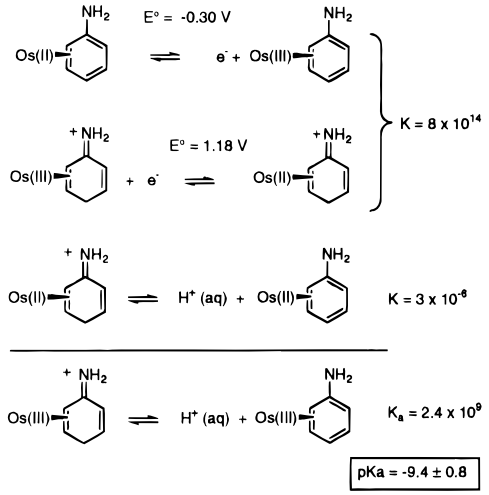


Figure 11. Determination of the acidity of an osmium(III) η^2-anilinium complex.

the acidity of the corresponding osmium(III) 5,6-η^2-4*H*-anilinium species. A p$K_a = -9.4 \pm 0.8$ for $[Os(NH_3)_5$-(4H-anilinium)$]^{3+}$ indicates that *the acidity increases by over 14 orders of magnitude as a result of a one-electron oxidation of the metal.* Although the increase in overall charge of the complex is expected to render the ligand more acidic, this dramatic increase in acidity upon oxidation of the 4*H*-anilinium complex testifies to the degree that the osmium(II) interacts with the π^* system of the conjugated iminium ligand. Thus, we conclude that it is not the act of η^2-coordination that biases an arene toward electrophilic addition. Rather the increased π-acidity of the 4*H*-anilinium or other localized π system stabilizes the electron-rich osmium(II) complex and this strong π interaction biases the equilibrium away from the aromatic isomer upon coordination.

Conclusions

η^2-Complexation by pentaammineosmium(II) not only activates anilines toward C(4)-selective electrophilic additions but greatly stabilizes the resulting dieniminium intermediates through a strong π-back-bonding interaction. Consequently, nucleophilic addition at C(3) becomes possible. The metal sets the stereochemistry of both addition reactions, directing both electrophile (C(4)) and nucleophile (C(3)) *anti* to the face of metal coordination. This reaction sequence is a dearomatization strategy that is complementary to existing methods in both regiochemistry and types of bonds formed.

Experimental Section

General Methods. Infrared spectra were recorded on a Mattson Cygnus 100 FTIR spectrometer. Electronic spectra were recorded on an HP 8452A diode array spectrophotometer and were obtained in acetonitrile solution unless otherwise specified. ^{1}H and ^{13}C NMR spectra were recorded on a General Electric QE-300 or GN-300 spectrometer and were recorded at 23 °C unless otherwise noted. Chemical shifts are reported in ppm relative to solvent ($\delta(CDCl_3) = 7.26$; δ(acetone-d_5) = 2.04; δ(acetonitrile-d_2) = 1.93; δ(DMSO-d_5) = 2.49; δ(methanol-d_3) = 3.30). 2D-NMR experiments (DEPT, COSY, NOESY, HETCOR) were recorded on a General Electric GN-300 spectrometer. ^{13}C multiplicities are supported by DEPT data.

Electrochemical experiments were performed under nitrogen using a PAR Model 362 potentiostat driven by a PAR Model 175 universal programmer. Cyclic voltammograms were recorded (Kipp & Zonen BD90 XY recorder) in a standard three-electrode cell[37] from +1.7 to −1.7 V with a glassy carbon electrode. All potentials are reported vs NHE and, unless otherwise noted, were determined in acetonitrile (~0.5 M TBAH) at 100 mV/s using ferrocene ($E_{1/2} = 0.55$ V) or colbaltocenium hexafluorophosphate ($E_{1/2} = -0.78$ V) *in situ* as a calibration standard. The peak-to-peak separation ($E_{p,a} - E_{p,c}$) was between 80 and 100 mV for all reversible couples unless otherwise noted.

This work was carried out under a nitrogen atmosphere in a Vacuum Atmospheres Co. glovebox, except for the isolation of organic products. Preparative GC was performed on a GOWMAC-350 gas chromatograph using a 5% OV17 on 80/100 mesh GaschromQ, $^1/_4$ in. × 6 ft nickel column (Alltech), at 65 cc/min and 182 °C unless noted otherwise. Elemental analyses were obtained on a Perkin-Elmer PE-2400 Series II CHN analyzer.

The osmium complexes reported herein were used without further purification with the exception of compound **35**, which crystallized from acetone. In a number of cases, it has not been possible to obtain satisfactory elemental analyses, owing to difficulties in the purification of the complexes.

Solvents. All solvents were deoxygenated by purging with nitrogen for at least 20 min; deuterated solvents were deoxygenated either by repeated freeze−pump−thaw cycles or vacuum distillation. All distillations were performed under nitrogen. Methylene chloride was refluxed over P_2O_5 for at least 8 h and distilled. Methanol was refluxed over $Mg(OMe)_2$ prepared *in situ* from magnesium activated by I_2 and distilled. Acetonitrile was 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. Acetonitrile-d_3 (Cambridge Isotope Labs) was distilled from CaH_2. Acetone-d_6 and DMSO-d_6 were used as received except that they were deoxygenated prior to use.

Reagents. The precursor, $[Os(NH_3)_5OTf](OTf)_2$, was synthesized as described by Lay *et al.*[38] Magnesium powder (Aldrich, 50 mesh) was activated by treating with iodine in DME under nitrogen, stirring for 1 h, and washing with DMAc, acetone, and diethyl ether. The anilines and acetanilide were obtained from commercial sources (Aldrich, Lancaster, and Pfaltz and Bauer), with the exception of *N*-TBS−aniline.[39] The anilines were distilled from CaH_2 under reduced pressure. All other liquid reagents were used as received except that they were deoxygenated by repeated freeze−pump−thaw cycles prior to use.

General Procedure for the Preparation of η^2-Pentaammineosmium(II) Aniline Complexes. To a solution of $[Os(NH_3)_5OTf](OTf)_2$ (2.07 g, 2.90 mmol) in DMAc (2 mL) and an excess of the desired aniline ligand (≥10 equiv) was added activated magnesium (1 g), and the heterogeneous mixture was stirred for ~1.25 h. The resulting mixture was diluted with DME (2 mL) and filtered through a fritted glass funnel into stirring CH_2Cl_2 (300 mL). The resulting yellow to orange-red slurry was filtered through a fritted glass funnel, and the filter cakes were washed with CH_2Cl_2 (10 mL) and ether (10 mL). The solid was dried either *in vacuo* or under nitrogen, affording the pentaammineosmium(II) aniline com-

(36) Compound **34**, a 4-alkylated 4*H*-anilinium complex, has a chemically reversible oxidation with $E_{1/2} = 1.18$ V in CH_3CN at 100 mV/s. The corresponding value for the parent 4*H*-anilinium analog is estimated to be the same (Figure 11).

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

(38) (a) Lay, P.; Magnuson, R.; Sen, J.; Taube, H. *J. Am. Chem. Soc.* **1982**, *104*, 7658. (b) Lay, P. A.; Magnuson, R. H.; Taube, H. *Inorg. Synth.* **1986**, *24*, 269.

(39) Obtained in 93% yield from aniline (Calverly, M. J. *Synth. Commun.* **1983**, *13*, 601): bp 63−64 °C/0.15 Torr; lit bp 113−114 °C/10 Torr.

plexes in >90% yield. Most of the aniline complexes prepared this way contain ~5−10% of a binuclear impurity that is not removed.

General Procedure for the Protonation of η^2-Pentaammineosmium(II) Aniline Complexes. To a solution of an aniline complex (0.1 mmol) in acetonitrile or methanol (400 mg) was added triflic acid (18 mg, 0.12 mmol), resulting in a rapid color change from orange to deep purple, red, or brown. This solution was added dropwise to stirring ether (50 mL), the resulting purple or pink slurry filtered, and the solid washed with ether and dried *in vacuo*, affording the anilinium complex in >90% yield.

{5,6-η^2-[Os(NH$_3$)$_5$](*N*-ethylaniline)}(OTf)$_2$ (2): ^{1}H NMR (CD$_3$CN) δ 6.38 (t, J = 7.5 Hz, 1H), 6.21 (dd, J = 7.5 Hz, 6 Hz, 1H), 5.20 (d, J = 6 Hz, 1H), 4.98 (t, J = 6 Hz, 1H), 4.65 (br s, m overlap, 2H), 4.08 (br s, 3H), 2.96 (br s, m overlap, 14 H), 1.18 (t, J = 7 Hz, 3H); ^{13}C NMR (CD$_3$CN) δ 158.0 (C), 124.5 (CH), 121.5 (q, J = 317 Hz, $CF_3SO_3^-$), 117.5 (CH), 92.1 (CH), 63.0 (CH), 55.9 (CH), 38.6 (CH$_2$), 14.2 (CH$_3$); $E_{p,a}$ = 0.36 V. Anal. Calcd for $C_{10}H_{26}N_6O_6S_2F_6Os$: C, 17.29; H, 3.75; N, 12.10. Found: C, 16.90; H, 3.83; N, 11.94.

{5,6-η^2-[Os(NH$_3$)$_5$](*N*,*N*-dimethylaniline)}(OTf)$_2$ (3). This is prepared by a modification of a reported procedure:[4] A mixture of [Os(NH$_3$)$_5$OTf](OTf)$_2$ (2.89 g, 4.0 mmol), *N*,*N*-dimethylacetamide (3 g), *N*,*N*-dimethylaniline (4 g), and magnesium (1g) was stirred for 1.5 h. The slurry was filtered into 2:1 methylene chloride/ether (300 mL), the precipitate filtered, the cake washed with methylene chloride (2 × 15 mL) and ether (1 × 15 mL), and the solid dried over nigrogen, affording 2.532 g (91%).

{5,6-η^2-[Os(NH$_3$)$_5$](*N*,*N*-dimethyl-*p*-toluidine)}(OTf)$_2$ (4): ^{1}H NMR (CD$_3$CN) δ 6.17 (d, J = 5.2 Hz, 1H), 5.30 (d, J = 5.2 Hz, 1H), 5.08 (m, 2H), 4.05 (br s, 3H), 3.06 (br s, 12H), 2.66 (s, 6H), 2.22 (s, 3H); ^{13}C NMR (CD$_3$CN) δ 157.1 (C), 133.8 (C), 121.1 (q, $CF_3SO_3^-$), 119.4 (CH), 99.1 (CH), 64.6 (CH), 52.1 (CH), 40.2 (CH$_3$), 23.0 (CH$_3$); $E_{p,a}$ = 0.32 V. Anal. Calcd for $C_{11}H_{26}N_6O_6S_2F_6Os$: C, 18.62; H, 3.95; N, 11.85. Found: C, 18.32; H, 4.07; N, 11.64.

{5,6-η^2-[Os(NH$_3$)$_5$](*N*,*N*-dimethyl-*m*-toluidine)}(OTf)$_2$ (5): ^{1}H NMR (acetone-d_6) δ 6.35 (s, 1H), 5.48 (s, 1H), 5.23 (m, 2H), 4.62 (br s, 3H), 3.47 (br s, 12H), 2.83 (s, 6H), 2.19 (s, 3H); ^{13}C NMR (acetone-d_6) δ 159.8 (C), 131.9 (C), 119.1 (CH), 100.9 (CH), 62.3 (CH), 46.7 (CH), 40.2 (CH$_3$), 21.0 (CH$_3$); $E_{p,a}$ = 0.30 V.

{5,6-η^2-[Os(NH$_3$)$_5$](*N*-(*tert*-butyldimethylsilyl)aniline)}(OTf)$_2$ (6): ^{1}H NMR (CD$_3$CN, −40 °C) δ 6.24 (m, 2H), 5.48 (d, J = 5.7 Hz, 1H), 4.92 (m, 1H), 4.74 (d, J = 7.5 Hz, 1H), 4.02 (br s, 3H), 3.68 (br s, 1H), 2.89 (br s, 12H), 0.92 (s, 9H), 0.19 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (acetone-d_6) δ 157.8 (C), 123.6 (CH), 119.5 (CH), 96.7 (CH), 63.5 (CH), 58.7 (CH), 26.1 (CH$_3$), 17.9 (C), −4.9 (CH$_3$), −5.1 (CH$_3$); $E_{p,a}$ = 0.38 V.

{5,6-η^2-[Os(NH$_3$)$_5$](acetanilide)}(OTf)$_2$ (7): ^{1}H NMR (acetone-d_6, −40 °C) δ 9.25 (br s, 1H), 7.04 (d, J = 7.2 Hz, 1H), 6.90 (dd, J = 8.1 Hz, 5.1 Hz, 1H), 6.42 (t, J = 7.2 Hz, 1H), 5.32 (t, J = 7.2 Hz, 1H), 5.25 (d, J = 7.8 Hz, 1H), 4.88 (br s, 3H), 3.55 (brs, 12H), 2.01 (s, 3H); ^{13}C NMR (acetone-d_6, −40 °C) δ 168.6 (C), 147.0 (C), 128.3 (CH), 120.7 (CH), 104.0 (CH), 60.8 (CH), 54.6 (CH), 23.3 (CH$_3$); $E_{p,a}$ = 0.52 V.

Reaction of 1 with Maleic Anhydride. The aniline complex (**1**) (10 mg, 0.015 mmol) was dissolved in CD$_3$CN (0.4 g) containing cyclohexane (a trace amount) to serve as a relative integration standard. The solution was transferred immediately to an NMR tube and cooled to −30 °C in a cold bath inside a glovebox. After several minutes, solid maleic anhydride (10 mg, 0.1 mmol) was added and the mixture shaken. The NMR tube and cold bath were removed from the glovebox, the sample was transferred directly to a ^{1}H NMR probe precooled to −30 °C, and data were collected at regular intervals at this temperature. The peaks for the starting complex were replaced after 30 min by a series of peaks correponding to the zwitterionic intermediate **8**. Parital data: ^{1}H NMR (CD$_3$CN) δ 6.75 (dd, J = 9.5, 3.5 Hz, 1H), 6.45 (d, J = 9.5 Hz, 1H), 5.80 (d, J = 6.5 Hz, 1H), 4.65 (br s, m, overlap, 4H), 3.30 (br s, 12H), 2.60 (dd, J = 19.3, 6.4 Hz, 1H). Some resonances were concealed by overlap with either solvents or ammine peaks. As the reaction of the aniline complex (**1**) was nearing completion, a new set of resonances was visible in the baseline. Gradually, these peaks, corresponding to the arene intermediate (**9**), grew in intensity as those for the iminium intermediate (**8**) disappeared ($t_{1/2} \approx$ 2 h). Partial data for **9**: ^{1}H NMR (CD$_3$CN) δ 6.41 (d, J = 6 Hz, 1H), 5.32 (d, J = 6 Hz, 1H), 5.08 (d, J = 6 Hz, 1H), 4.85 (d, J = 6 Hz, 1H), 4.2−4.1 (br s, dd overlap, 4H), 3.45 (dd, J = 18, 9 Hz, 1H), 3.2 (br s, 16 H). As the reaction mixture was warmed to room temperature, the peaks for compound **9** diminished in intensity relative to those of the solvent and integration standard and a crystalline precipitate formed. This precipitate was converted to the diester (**10**) as described below.

(4-(Dimethylamino)phenyl)succinic Anhydride (10). A solution of maleic anhydride (10 mg, 0.1 mmol) in CD$_3$CN was added to **2** (70 mg, 0.1 mmol), and the color changed from light to dark brown. After 10−20 min the ^{1}H NMR spectrum appeared to be complex, showing a mixture of several products. The presence of doublets at δ 5.5, 6.18, and 6.40 with a coupling constant of ~6 Hz tentatively suggests one of the intermediates may be a *p*-disubstituted 5,6-η^2-aniline complex. As the reaction mixture was allowed to stand at room temperature, these intermediates disappeared and a new product was formed over the course of 1 day. An infrared spectrum of the solution revealed bands at 1861 and 1788 cm^{-1}, suggesting the presence of a substituted succinic anhydride.[40] The yield of **10** was estimated to be about 30% using cyclohexane as an internal NMR standard. Dilution of the reaction mixture with ether, filtration of the precipitate, and evaporation of the filtrate afforded the title compound (6 mg, 27%): ^{1}H NMR δ 7.10 (d, J = 8.7 Hz, 2H), 6.71 (d, J = 8.7 Hz, 2H), 4.23 (dd, J = 10.2, 6.4 Hz, 1 H), 3.40 (dd, J = 19.0 Hz, 10.2 Hz, 1H), 3.06 (dd, J = 19.0, 6.4 Hz, 1H), 2.96 (s, 6 H); ^{13}C NMR δ 172.7, 170.4, 151.0, 128.4, 122.1, 113.3, 46.3, 40.8, 37.3; IR (CD$_3$CN) 1861, 1788 cm^{-1}. This compound was found to be highly moisture-sensitive. Outside of the glovebox it rapidly hydrolyzed to the acid, as suggested by IR: 3600−2400 (br), 1695 (s) cm^{-1}.

Dimethyl (4-Aminophenyl)succinate (11). To a mixture of **1** (67 mg, 0.1 mmol) and maleic anhydride (11 mg, 0.11 mmol) was added CD$_3$CN (0.4 g). After 10 min the short-lived complex **7** could be observed by ^{1}H NMR before precipitation of a solid occurred. The resulting mixture was treated with methanol (5 mL) and H_2SO_4 (0.1 g) and refluxed on the benchtop for 1 h. The reaction mixture was diluted with aqueous 10% Na_2CO_3 (40 mL) and extracted with methylene chloride (2 × 40 mL). The extract was dried over $MgSO_4$ and evaporated, yielding the crude product as an oil (27 mg). This was chromatographed on silica gel using methylene chloride as the eluent, affording 5 mg (21%) of pure **11**: R_f = 0.35 (CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 7.05 (d, J = 8.4 Hz, 2H), 6.62 (d, J = 8.4 Hz, 2H), 3.96 (dd, J = 10.5, 5.4 Hz, 1H), 3.67 (s, 6H), 3.16 (dd, J = 16.8, 10.5 Hz, 1H), 2.62 (dd, J = 16.8, 5.4 Hz, 1H), 1.6 (br s, 2H); GC/MS m/z 237 (M^+).

Dimethyl (4-(Dimethylamino)phenyl)succinate (12). This compound was prepared by treating the isolated anhydride (**10**) with methanol and acid. It was also obtained directly from the reaction mixture containing **10**: A solution of maleic anhydride (76 mg, 0.77 mmol) and triflic acid (21 mg, 0.14 mmol) in acetonitrile (3 mL) was added to a solution of **2** (487 mg, 0.7 mmol) in acetonitrile (2 mL). The mixture, which turned black instantly, was allowed to stand for 13 h (not optimized). The solution was removed from the glovebox, the acetonitrile was removed *in vacuo*, and the residue was

(40) Succinic anhydride is reported to have C=O stretching bands at 1865 and 1782 cm^{-1} (Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; Wiley: New York, 1981; p 121).

refluxed in methanol (15 g) and 50% BF_3·MeOH (1.9 g) for 3 h. The mixture was partitioned between methylene chloride (50 mL) and 10% Na_2CO_3 (50 mL), and the aqueous layer was extracted with methylene chloride (2 × 50 mL). The combined extracts were dried over anhydrous $MgSO_4$ and the solvent evaporated, affording compound **12** (94 mg; 50%; >90% pure by ^{1}HNMR). The product obtained from several runs was combined and chromatographed on silica gel using methylene chloride as the eluent (R_f = 0.5), and this material was recrystallized from pentane, affording the product in 30% overall yield: mp 73−74 °C; ^{1}H NMR ($CDCl_3$) δ 7.13 (d, J = 8.6 Hz, 2 H), 6.67 (d, J = 8.6 Hz, 2 H), 3.99 (dd, J = 10.1 Hz, 5.2 Hz, 1 H), 3.663 (s, 3 H), 3.66 (s, 3H), 3.15 (dd, J = 16.9 Hz, 10.2 Hz, 1 H), 2.93 (s, 6 H), 2.63 (dd, J = 16.9 Hz, 5.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 174.4, 172.7, 150.4, 125.6, 113.1, 52.6, 52.2, 46.5, 40.9, 38.2; GC/MS m/z 265 (M^+). Anal. Calcd for $C_{14}H_{19}NO_4$: C, 63.38; H, 7.22; N, 5.28. Found: C, 62.84; H, 7.08; N, 5.16.

Reaction of 2 with Maleic Anhydride. Maleic anhydride and the *N*-ethylaniline complex **2** reacted in CD_3CN to yield a short-lived complex before an intractable precipitate was formed. Partial NMR data after 10 min: ^{1}H NMR (CD_3CN) δ 6.50 (d, J = 6 Hz, 1H), 5.10 (d, J = 6 Hz, 1H), 5.0 (d, J = 6 Hz, 1H), 4.74 (d, J = 6 Hz, 1H), 4.12 (dd, J = 18, 10 Hz, 1H), 4.08 (br s, 3H), 3.5 (dd, J = 18, 10 Hz, 1H), 3.08 (br s, 12H), 1.2 (t, J = 7 Hz, 3H). The other resonances overlap with ammine peaks of minor products around 3 ppm.

{5,6-η^2-[Os(NH$_3$)$_5$](4-(2-oxobutyl)-*N*-ethylaniline)}(OTf)$_2$ (13). The *N*-ethylaniline complex (285 mg, 0.41 mmol) was dissolved in methanol (915 mg), and methyl vinyl ketone (38 mg, 0.54 mmol) was added. After 1 h, the dark solution was diluted with acetonitrile (0.5 mL) and added dropwise to ether (50 mL) with stirring. The resulting tan solid was filtered out, washed with ether, and dried *in vacuo*, affording **13** as a tan solid (294 mg, 94%): ^{1}H NMR (CD_3CN) δ 6.09 (d, J = 6.9 Hz, 1H), 5.09 (d, J = 7.8 Hz, 1H), 5.03 (d, J = 6.9 Hz, 1H), 4.75 (d, J = 7.8 Hz, 1 H), 4.45 (m, 1H), 4.19 (br s, 3H), 3.14 (br s, 14 H), 2.80 (m, 4H), 2.11 (s, 3H), 1.16 (t, J = 7.2 Hz, 3H); ^{13}C NMR (CD_3CN) δ 211.0 (C), 155.8 (C), 133.3 (C), 117.8 (CH), 92.0 (CH), 63.9 (CH), 56.7 (CH), 42.7 (CH_2), 38.9 (CH_2), 30.2 (CH_2), 30.2 (CH_3), 14.0 (CH_3); $E_{p,a}$ = 0.30 V.

{5,6-η^2-[Os(NH$_3$)$_5$](4-(*trans*-3-oxo-1-butenyl)-*N*-ethylaniline)}(OTf)$_2$ (14). The *N*-ethylaniline complex (**2**, 102 mg, 0.15 mmol) was dissolved in methanol (598 mg), and the solution was cooled to −40 °C. After 20 min, 3-butyn-2-one (34 mg, 0.50 mmol) was added, and the reaction was allowed to stand at −40 °C overnight. The solution was diluted with acetonitrile (∼0.5 mL) and added to ether (50 mL). The slurry was filtered, and the solid was rinsed with ether and dried *in vacuo*, affording **14** as a brick red powder (101 mg, 89%): ^{1}H NMR (CD_3CN) δ 7.56 (d, J = 15.3 Hz, 1H), 6.68 (d, J = 7.5 Hz, 1H), 6.50 (d, J = 15.6 Hz, 1H), 5.71 (m, 1H), 5.59 (d, J = 7.8 Hz, 1H), 5.33 (d, J = 7.2 Hz, 1H), 4.76 (d, J = 7.5 Hz, 1H), 4.19 (br s, 3H), 3.08 (br s, 14H), 2.20 (s, 3H); ^{13}C NMR (CD_3CN) δ 198.4 (C), 164.7(C), 149.0 (CH), 137.6 (CH), 125.6 (C), 117.3 (CH), 93.0 (CH), 56.2 (CH), 53.7 (CH), 38.7 (CH_2), 27.5 (CH_3), 14.0 (CH_3); $E_{p,a}$ = 0.46 V.

{5,6-η^2-[Os(NH$_3$)$_5$](4-acetyl-*N*-ethylaniline)](OTf)$_2$ (15). The *N*-ethylaniline complex (**2**, 501 mg, 0.70 mmol) was dissolved in acetonitrile (2 g) and DMSO (181 mg). A solution of acetic anhydride (96 mg, 0.90 mmol) and 4-(dimethylamino)-pyridine (160 mg, 1.3 mmol) in CH_3CN (1 g) was added and the mixture allowed to stir overnight. The solution was added to 1:1 CH_2Cl_2/ether (200 mL), and the resulting orange slurry was filtered. The filter cake was washed with CH_2Cl_2 and ether and dried *in vacuo*, affording **15** as an orange solid (461 mg, 87%): ^{1}H NMR (acetone-d_6) δ 7.42 (d, J = 7.8 Hz, 1H), 6.50 (m, 1H), 6.01 (d, J = 8.1 Hz, 1H), 5.27 (d, J = 7.2 Hz, 1H), 4.95 (d, J = 8.1 Hz, 1H), 4.77 (br s, 3H), 3.62 (br s, 12H), 3.16 (m, 2H), 2.27 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H); ^{13}C NMR (acetone-d_6) δ 197.5 (C), 167.4 (C), 136.9 (CH), 126.4 (C), 89.8 (CH), 56.3 (CH), 52.9 (CH), 38.2 (CH_2), 24.4 (CH_3), 13.8 (CH_3); $E_{p,a}$ = 0.52 V. Anal. Calcd for $C_{12}H_{28}N_6O_7S_2F_6Os$: C, 19.54; H, 3.80; N, 11.40. Found: C, 19.12; H, 4.13; N, 11.59.

4-(4-(Ethylamino)phenyl)-2-butanone (16). A solution of compound **13** (715 mg, 0.94 mmol) in acetonitrile (4.5 g) was heated in an oil bath at 65 °C for 3 h. The solution was diluted with 10% Na_2CO_3 (30 mL) and extracted with CH_2Cl_2 (2 × 30 mL). The organic layer was dried (Na_2SO_4), concentrated to ∼3 mL, filtered through a plug of basic alumina, and evaporated, affording the product as an oil (133 mg, 74%): ^{1}H NMR ($CDCl_3$) δ 7.02 (d, J = 8.4 Hz, 2H), 6.57 (d, J = 8.4 Hz, 2H), 3.50 (br s, 1H), 3.15 (q, J = 7.2 Hz, 2H), 2.77 (m, 4H), 2.14 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 208.4 (C), 146.6 (C), 129.2 (C), 128.8 (CH), 112.7 (CH), 45.5 (CH_2), 38.6 (CH_2), 30.1 (CH_3), 30.0 (CH_2), 14.9 (CH_3). A sample of analytically pure material was obtained by preparative GC (t_R = 6.0 min, using conditions described in the general section but at 187 °C). Anal. Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.08; H, 9.28; N, 7.30.

{5β,6β-η^2-[Os(NH$_3$)$_5$](4α-(3-oxobutyl)-*N*-ethyl-2,5-cyclohexadien-1-iminium)}(OTf)$_3$ (17). A solution of the *N*-ethylaniline complex (70 mg, 0.10 mmol) and MVK (8 mg, 0.11 mmol) in CH_3CN (254 mg) was treated with BF_3·OEt_2 (17 mg, 0.12 mmol) resulting in a color change from amber to purple. This solution was treated with excess triflic acid (23 mg, 0.15 mmol), and added to ether (50 mL). The resulting purple suspension was filtered, and the filter cake was rinsed with ether and dried *in vacuo*, affording **17** as a purple solid (84 mg, 89%): ^{1}H NMR (acetone-d_6) δ 10.31 (br s, 1H), 7.27 (dd, J = 10.2, 4.4 Hz, 1H), 6.78 (d, J = 10.2 Hz, 1H), 5.29 (br s, 4H), 4.95 (d, J = 7.5 Hz, 1H), 3.84 (br s, 12H), 3.70 (q, J = 7.2 Hz, 2H), 2.95 (m, 1H), 2.70 (m, 2H), 2.20 (m, 2H), 2.10 (s, 3H), 1.36 (t, J = 7.2 Hz, 3H); ^{13}C NMR (acetone-d_6) δ 207.8 (C), 180.3 (C), 157.2 (CH), 117.8 (CH), 57.7 (CH), 45.1 (CH), 41.1 (CH_2), 40.6 (CH), 39.5 (CH_2), 29.8 (CH_2), 29.3 (CH_3), 13.0 (CH_3); $E_{p,a}$ = 1.27 V, $E_{p,c}$ = −0.99 V.

{5β,6β-η^2-[Os(NH$_3$)$_5$](2α-(3-oxobutyl)-*N*-ethyl-3,5-cyclohexadien-1-iminium)}(OTf)$_3$ (18). A solution of the *N*-ethylaniline complex (73 mg, 0.11 mmol) and MVK (9 mg, 0.12 mmol) in CH_3CN (400 mg) was treated with a solution of TBSOTf (37 mg, 0.14 mmol) in CH_3CN (241 mg). After 5 min the solution was treated with one drop of water and then added to ether (50 mL). The resulting solid was filtered out, washed with ether, and dried *in vacuo*, affording a 1:1 mixture of **17** and **18** as a purple solid. Data for **18**: ^{13}C NMR (acetone-d_6) δ 206.9 (C), 198.0 (C, C1), 131.3 (CH), 121.3 (CH), 50.2 (CH), 43.5 (CH_2), 42.7 (CH), 37.9 (CH), 37.5 (CH_2), 28.6 (CH_3), 24.6 (CH_2), 13.6 (CH_3).

{5β,6β-η^2-[Os(NH$_3$)$_5$](4α-(3-oxobutyl)-*N*,*N*-dimethyl-2,5-cyclohexadien-1-iminium)}(OTf)$_3$ (19). To a solution of the *N*,*N*-dimethylaniline complex (**3**, 69 mg, 0.10 mmol) and methyl vinyl ketone (8 mg, 0.12 mmol) in acetonitrile (209 mg) was added BF_3·OEt_2 (16 mg, 0.11 mmol), resulting in a color change from amber to purple. After 5 min, triflic acid (17 mg, 0.11 mmol) was added, and the mixture was added to ether (50 mL) with stirring. The resulting purple suspension was filtered, and the solid was rinsed with ether and dried *in vacuo*, affording **19** as a purple solid (81 mg, 89%): ^{1}H NMR (acetone-d_6) δ 7.15 (dd, J = 10.2 Hz, 4.8 Hz, 1H), 6.82 (d, J = 10.2 Hz, 1H), 5.45 (d, J = 6.6 Hz, 1H), 5.38 (d, J = 8.1 Hz, 1H), 5.29 (br s, 3H), 3.96 (br s, 12H), 3.74 (s, 3H), 3.54 (s, 3H), 2.96 (m, 1H), 2.66 (m, 2H), 2.10 (s, 3H); ^{13}C NMR (acetone-d_6) δ 207.9 (C), 180.3 (C), 154.3 (CH), 120.1 (CH), 60.0 (CH), 43.9 (CH_3), 43.4 (CH_3), 41.6 (CH), 39.8 (CH), 30.6 (CH_2), 29.4 (CH_2); $E_{p,a}$ = 1.27 V, $E_{p,c}$ = −1.03 V. Anal. Calcd for $C_{15}H_{33}N_6O_{10}S_3F_9Os$: C, 19.69; H, 3.39; N, 9.19. Found: C, 19.27; H, 3.66; N, 8.91.

{5β,6β-η^2-[Os(NH$_3$)$_5$](4α-(3-oxobutyl)-4β-methyl-*N*,*N*-dimethyl-2,5-cyclohexadien-1-iminium)}(OTf)$_3$ (20). The *N*,*N*-dimethyl-*p*-toluidine complex (144 mg, 0.20 mmol) was dissolved in cold (−40 °C) acetonitrile (1 g), and MVK (18 mg, 0.26 mmol) was added. After 20 min, a solution of BF_3·OEt_2 (35.0 mg, 0.25 mmol) in acetonitrile (0.5 g) was added,

resulting in a color change from amber to purple. After 5 min, triflic acid (49 mg, 0.33 mmol) in acetonitrile (0.2 g) was added, and the mixture was added to ether (150 mL) while stirring. The slurry was filtered, and the resulting solid was washed with ether and dried *in vacuo*. The product **20** was isolated as a purple solid (181 mg, 98%): ^{1}H NMR (CD_3CN) δ 6.81 (d, J = 10.2 Hz, 1H), 6.51 (d, J = 10.2 Hz, 1H), 5.10 (d, J = 7.5 Hz, 1H), 5.02 (d, J = 7.5 Hz, 1H), 4.61 (br s, 3H), 3.54 (s, 3H), 3.45 (br s, 12H), 3.39 (s, 3H), 2.42 (m, 2H), 2.08 (s, 3H), 1.99 (m, 2H), 1.20 (s, 3H); ^{13}C NMR (CD_3CN) δ 209.0 (C), 178.9 (C), 159.4 (CH), 120.3 (CH), 61.1 (CH), 44.7 (CH_3), 44.1 (CH_3), 43.4 (C), 42.2 (CH), 40.2 (CH_2), 39.0 (CH_2), 29.9 (CH_3), 22.8 (CH_3); $E_{p,a}$ = 1.17 V, $E_{p,c}$ = −0.95 V; Anal. Calc'd for $C_{16}H_{35}N_6O_{10}S_3F_9Os$: C, 20.69; H, 3.77; N, 9.05. Found: C, 20.94; H, 3.88; N, 8.71.

{5β,6β-η^2-[Os(NH$_3$)$_5$](4α-(3-oxobutyl)-*N*-acyl-2,5-cyclohexadien-1-imine)}(OTf)$_3$ (21). The acetanilide complex (72 mg, 0.10 mmol) was dissolved in acetonitrile (322 mg), and methyl vinyl ketone (11 mg, 0.15 mmol) was added. The solution was cooled to −40 °C and a cold solution of triflic acid (18 mg, 0.12 mmol) in acetonitrile (196 mg) was added, resulting in an immediate color change to blue-green. After 0.5 h, a solution of Hünig's base (16 mg, 0.12 mmol) in acetonitrile (198 mg) was added, resulting in a color change from blue to amber. The solution was added to ether (∼50 mL), and the resulting precipitate was filtered out, washed with ether, and dried *in vacuo*, affording **21** as an amber solid (64 mg, 69%): ^{1}H NMR (CD_3CN) δ 6.46 (dd, J = 9.6 Hz, 3.9 Hz, 1H), 5.99 (d, J = 9.9 Hz, 1H), 4.42 (br s, 3H), 4.17 (d, J = 8.1 Hz, 1H), 4.07 (d, J = 8.1 Hz, 1H), 3.21 (br s, 12H), 2.60 (m, 1H), 2.43 (m, 2H), 2.16 (s, 3H), 2.11 (s, 3H), 2.05 (m, 2H); ^{13}C NMR (CD_3CN) δ 209.8 (C), 187.8 (C), 168.7 (C), 147.4 (CH), 125.3 (CH), 55.5 (CH), 48.3 (CH), 40.1 (CH_2), 38.8 (CH), 31.5 (CH_2), 30.0 (CH_3), 26.1 (CH_3); $E_{p,a}$ = 0.95 V.

{5β,6β-η^2-[Os(NH$_3$)$_5$](4α-(3-oxobutyl)-2,5-cyclohexadien-1-iminium)}(OTf)$_3$ (22). To a solution of the protonated aniline complex **1c** (81 mg, 0.10 mmol) in methanol (302 mg) was added methyl vinyl ketone (8 mg, 0.12 mmol). The solution was allowed to stand at room temperature for 1 h, diluted with acetonitrile (1 mL), and added to ether (50 mL) while stirring. The slurry was filtered, and the resulting solid was rinsed with ether and dried *in vacuo*, affording **22** as a purple solid (76 mg, 86%): ^{1}H NMR (acetone-d_6) δ 10.06 (br s, 1H), 10.02 (br s, 1H), 7.20 (dd, J = 9 Hz, 3.9 Hz, 1H), 6.57 (d, J = 9.6 Hz, 1H), 5.44 (d, J = 7.5 Hz, 1H), 5.37 (br s, 3H), 5.07 (d, J = 7.2 Hz, 1H), 3.93 (br s, 12H), 2.89 (m, 1H), 2.71 (m, 2H), 2.23 (m, 2H), 2.11 (s, 3H); ^{13}C NMR (acetone-d_6) δ 207.6 (C), 182.9 (C), 155.7 (CH), 121.4 (CH), 58.5 (CH), 43.9 (CH), 40.0 (CH_2), 39.2 (CH), 29.1 (CH_2), 29.1 (CH_3); $E_{p,a}$ = 1.30 V, $E_{p,c}$ = −0.95 V.

{5β,6β-η^2-[Os(NH$_3$)$_5$](4α-(3-oxopropyl)-*N*-ethyl-2,5-cyclohexadien-1-iminium)}(OTf)$_3$ (23). The protonated *N*-ethylaniline complex (**2**, 95.4 mg) was dissolved in water (332 mg), and acrolein (8 mg) was added. The solution was allowed to stand for 0.5 h, and the solvent was evaporated. The residue was dissolved in acetone, and the solution was added to ether (50 mL). The resulting slurry was filtered, and the filter cake was washed with ether and dried *in vacuo*, affording **23** as a purple solid in 81% yield: ^{1}H NMR (acetone-d_6) δ 10.35 (br s, 1H), 9.76 (s, 1H), 7.28 (dd, J = 10.2 Hz, 4.2 Hz, 1H), 6.81 (d, J = 10.2 Hz, 1H), 5.31 (br s, 4H), 4.97 (d, J = 7.8 Hz, 1H), 3.86 (br s, 12H), 3.67 (q, J = 7.2 Hz, 2H), 3.04 (m, 1H), 2.70 (m, 2H), 2.31 (m, 2H), 1.37 (t, J = 7.2 Hz, 3H); ^{13}C NMR (acetone-d_6) δ 201.9 (CH), 180.5 (C), 156.8 (CH), 118.3 (CH), 57.5 (CH), 45.2 (CH), 41.3 (CH_2), 40.5 (CH), 40.2 (CH_2), 28.0 (CH_2), 13.1 (CH_3); $E_{p,a}$ = 1.27 V, $E_{p,c}$ = −1.03 V.

{5β,6β-η^2-[Os(NH$_3$)$_5$](4α-(2-carbomethoxyethyl)-*N*-ethyl-2,5-cyclohexadien-1-iminium)}(OTf)$_3$ (24). Methyl acrylate (14 mg, 0.16 mmol) was added to a solution of the *N*-ethylaniline complex (100 mg, 0.14 mmol) in CH_3CN (198 mg), and the resulting mixture was cooled to −40 °C. TBSOTf (47 mg, 0.18 mmole) was added, causing a change in color from amber to purple. The solution was allowed to stand at −40 °C for ∼5 min and treated with 1 drop of water. The solution was added to ether (75 mL), and the resulting purple suspension was filtered. The filter cake was rinsed with ether and dried *in vacuo*, affording **24** as a purple solid (112 mg, 86%): ^{1}H NMR (acetone-d_6) δ 10.36 (br s, 1H), 7.26 (dd, J = 10.2, 4.5 Hz, 1H), 6.80 (d, J = 10.2 Hz, 1H), 5.31 (br s, 4H), 4.96 (d, J = 7.8 Hz, 1H), 3.86 (br s, 12H,), 3.69 (q, J = 7.2 Hz, 2H), 3.62 (s, 3H), 3.05 (m, 1H), 2.51 (m, 2H), 2.29 (m, 2H), 1.36 (t, J = 7.2 Hz, 3H); ^{13}C NMR (acetone-d_6) δ 180.5 (C), 173.4 (C), 156.7 (CH), 118.2 (CH), 57.3 (CH), 51.3 (CH_3), 45.2 (CH), 41.4 (CH_2), 40.6 (CH), 30.8 (CH_2), 30.4 (CH_2), 13.1 (CH_3); Anal. Calcd for $C_{15}H_{33}N_6O_{11}S_3F_9Os$: C, 19.35; H, 3.55; N, 9.03. Found: C, 19.07; H, 3.66; N, 8.77.

{5β,6β-η^2-[Os(NH$_3$)$_5$](4α-(2-cyanoethyl)-*N*-ethyl-2,5-cyclohexadien-1-iminium)}(OTf)$_3$ (25). The *N*-ethylaniline complex (502 mg, 0.72 mmol) was dissolved in CH_3CN (2 g), and acrylonitrile (48 mg, 0.91 mmol) was added. Upon the addition of TBSOTf (227 mg, 0.86 mmol) the solution changed in color from amber to purple. After ∼5 min, the reaction was treated with one drop of water and the solution added to ether (150 mL) with stirring. The resulting purple suspension was filtered, and the filter cake washed with ether and dried *in vacuo*. The product **25** was isolated as a purple solid (605 mg, 94%): ^{1}H NMR (acetone-d_6) δ 10.38 (br s, 1H), 7.29 (dd, J = 10.2 Hz, 4.2 Hz, 1H), 6.84 (d, J = 10.2 Hz, 1H), 5.31 (br s, 4H), 4.48 (d, J = 7.5 Hz, 1H), 3.86 (br s, 12H), 3.70 (q, J = 7.2 Hz, 2H), 3.09 (m, 1H), 2.69 (m, 2H), 2.36 (m, 2H), 1.36 (t, J = 7.2 Hz, 3H); ^{13}C NMR (acetone-d_6) δ 180.0 (C), 155.0 (CH), 118.8 (CH), 55.9 (CH), 44.8 (CH), 41.2 (CH_2), 40.0 (CH), 30.8 (CH_2), 12.8 (CH_2), 11.7 (CH_3); $E_{p,a}$ = 1.25 V, $E_{p,c}$ = 1.11 V, $E_{p,c}$ = −1.01 V. Anal. Calcd for $C_{14}H_{30}N_7O_9S_3F_9Os$: C, 18.73; H, 3.34; N, 10.93. Found: C, 18.73; H, 3.38; N, 10.61.

{5β,6β-η^2-[Os(NH$_3$)$_5$](4α-(3-oxocyclopentyl)-*N*-ethyl-2,5-cyclohexadien-1-iminium)}(OTf)$_3$ (26). The protonated *N*-ethylaniline complex (**2b** + **2c**, 84 mg, 0.10 mmol) was dissolved in methanol (150 mg), and 2-cyclopenten-1-one (10 mg, 0.12 mmol) was added. The reaction was allowed to stand for ∼1 h and was then diluted with acetonitrile and added to ether (50 mL) with stirring. The purple suspension was filtered, and the solid was rinsed with ether and dried *in vacuo*. The product **26** is isolated as a purple solid (72 mg, 77%): ^{1}H NMR (acetone-d_6) δ 10.41 (br s, 1H), 7.31 (dd, J = 10.2 Hz, 4.7 Hz, 1H), 6.87 (d, J = 10.2 Hz, 1H), 5.40 (d, J = 7.5 Hz, 1H), 5.35 (br s, 3H), 5.00 (d, J = 7.5 Hz, 1H), 3.88 (br s, 12H), 3.72 (q, J = 7.2 Hz, 2H), 3.16 (m, 1H), 2.75 (m, 1H), 2.21 (m, 6H), 1.36 (t, J = 7.2 Hz, 3H); ^{13}C NMR (acetone-d_6) δ 216.4 (C), 180.5 (C), 155.6 (CH), 119.3 (CH), 56.1 (CH), 45.6 (CH), 45.1 (CH), 42.9 (CH), 41.8 (CH_2), 41.6 (CH_2), 38.3 (CH_2), 27.3 (CH_2), 13.3 (CH_3); $E_{1/2}$ = 1.12 V; $E_{p,c}$ = −1.01 V.

{5β,6β-η^2-[Os(NH$_3$)$_5$](4α-(methoxybenzyl)-*N*-ethyl-2,5-cyclohexadien-1-iminium)}(OTf)$_3$ (27). The *N*-ethylaniline complex (**2**, 70 mg, 0.1 mmol) was dissolved in acetonitrile (263 mg), and benzaldehyde dimethyl acetal (19 mg, 0.12 mmol) was added. A solution of $BF_3{\cdot}OEt_2$ (17 mg, 0.12 mmol) in acetonitrile (200 mg) was added, resulting in a color change from amber to purple. The solution was added to ether (50 mL) with stirring, and the resulting purple suspension was filtered. The solid was washed with ether and dried *in vacuo*, affording compound **27** as a purple solid (51 mg, 53%): ^{1}H NMR (acetone-d_6) δ 10.24, 10.10 (br s, 1H), 7.20−7.60 (m, 5H), 7.04, 6.95 (dd, J = 10.2, 4.8 Hz, 1H), 6.74, 6.69 (d, J = 10.2 Hz, 1H), 5.51 (m, 2H), 5.30 (br s, 6H), 4.94 (d, J = 4.2 Hz, 1H), 4.77 (d, J = 6.3 Hz, 1H), 4.85, 4.68 (d, J = 7.8 Hz, 1H), 3.84 (br s, 24H), 3.56, 3.45 (q, J = 7.2 Hz, 2H), 3.33, 3.32 (s, 3H), 1.24, 1.18 (t, J = 7.2 Hz, 3H); ^{13}C NMR (acetone-d_6) δ 180.9 (C), 180.6 (C), 153.2 (CH), 152.8 (CH), 139.0 (C), 138.2 (C), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 127.9 (CH), 120.2 (CH), 120.1 (CH), 86.5 (CH), 84.8 (CH), 57.3 (CH_3), 57.0 (CH_3), 55.3 (CH), 55.0 (CH), 49.2 (CH), 48.6 (CH), 46.6 (CH), 46.0 (CH), 41.3 (CH_2), 13.3 (CH_3) (resonances for the phenyl and ethyl groups are partially overlapping).

{5*β*,6*β*-η^2-[Os(NH$_3$)$_5$](4α-(1-methyl-1-methoxyethyl)-*N*-ethyl-2,5-cyclohexadien-1-iminium)}(OTf)$_3$ (28). A solution of the *N*-ethylaniline complex (**2**, 69 mg, 0.10 mmol) in acetonitrile (248 mg) was treated with 2,2-dimethoxypropane (13 mg, 0.12 mmol). A solution of TBSOTf (35 mg, 0.13 mmol) in acetonitrile (200 mg) was added, resulting in a color change to brown. The solution was added to ether (50 mL), and the resulting solid was filtered out and dried *in vacuo*, affording 75 mg (82%) of **28** as a purple solid: ^{1}H NMR (acetone-d_6): δ 10.39 (br s, 1H), 7.27 (dd, J = 10.2 Hz, 4.8 Hz, 1H), 6.89 (d, J = 10.2 Hz, 1H), 5.48 (d, J = 6.6 Hz, 1H), 5.33 (br s, 3H), 5.01 (d, J = 7.8 Hz, 1H), 3.85 (br s, 12H), 3.73 (q, J = 7.2 Hz, 2H), 3.32 (s, 3H), 3.02 (m, 1H), 1.36 (m, 9H); ^{13}C NMR (acetone-d_6) δ 180.5 (C), 154.4 (CH), 119.8 (CH), 77.2 (C), 55.1 (CH), 51.5 (CH,), 49.3 (CH$_3$), 46.1 (CH), 41.4 (CH$_2$), 22.8 (CH$_3$), 21.4 (CH$_3$), 13.2 (CH$_3$); $E_{p,a}$ = 1.23 V, $E_{p,c}$ = −1.03 V. Anal. Calcd for $C_{15}H_{35}N_6O_{10}S_3F_9Os$: C, 19.65; H, 3.82; N, 9.17. Found: C, 19.56; H, 3.80; N, 8.99.

{5*β*,6*β*-η^2-[Os(NH$_3$)$_5$](4α-(3′-oxocyclohexano)-*N*,*N*-dimethyl-2,5-cyclohexadien-1-iminium)}(OTf)$_3$ (29). To a solution of complex **3** (140 mg, 0.2 mmol) in CD$_3$CN (0.4 g) was added 2-cyclohexen-1-one (24 mg, 0.25 mmol) and a solution of TBSOTf (52 mg, 0.2 mmol) in CD$_3$CN (0.1 g). The mixture, which turned dark purple instantly, was analyzed by NMR. The proton spectrum was broadened, but the ^{13}C NMR spectrum suggested the presence of an iminium and silyl enol ether resonances. Partial data (downfield region): δ 180.0, 154.4, 153.5, 121.1, 104.4. To the solution was added water (∼20 mg), resulting in the appearance of another set of resonances corresponding to the ketone. Partial data (downfield region): δ 211.7, 179.9, 151.8, 122.1. The solution was added to ether (20 mL), affording a purple solid (150 mg, 80%). This consists of a 6:1 ratio of diastereomers. Data for major isomer: ^{13}C NMR (DMSO-d_6) δ 211.2 (C), 179.6 (C), 150.4 (CH), 122.2 (CH), 56.8 (CH), 44.7 (CH, CH$_2$ overlap), 44.3 (CH$_3$), 43.8 (CH), 43.7 (CH$_3$), 41.6 (CH, CH$_2$ overlap), 29.0 (CH$_2$), 25.6 (CH$_2$).

{5*β*,6*β*-η^2-[Os(NH$_3$)$_5$](4α-[1′,2′-bis(carbomethoxy)ethyl]-*N*,*N*-dimethyl-2,5-cyclohexadien-1-iminium)}(OTf)$_3$ (30). To a solution of complex **3** (140 mg, 0.2 mmol) in CD$_3$CN (0.4 g) was added dimethyl fumarate (20 mg, 0.2 mmol) and TBSOTf (53 mg, 0.2 mmol). After 5 min the reaction was quenched with water (20 mg, ∼1 mmol), affording a dark purple solution. Analysis by ^{1}H NMR revealed complete conversion to the title product. The solution was added to ether (20 mL), affording a purple solid (125 mg, 63%). The compound was formed as a ∼2:1 ratio of diastereomers. Data for both isomers: ^{13}C NMR (CD$_3$CN) δ 179.8 (C), 173.3 (C), 172.5 (C), 150.9 (CH), 150.1 (CH), 122.4 (CH), 122.4 (CH), 56.8 (CH), 56.6 (CH), 52.8 (CH$_3$), 52.4 (CH$_3$), 52.0 (CH$_3$), 46.0 (CH), 44.4 (CH, CH$_3$ overlap), 43.9 (CH$_3$), 42.1 (CH), 41.7 (CH), 41.5 (CH), 41.4 (CH), 32.3 (CH$_2$), 32.0 (CH$_2$). This compound was further characterized by its clean conversion the the succinate ester **12** in 60% yield by heating in the presence of Hünig's base.

{5*β*,6*β*-η^2-[Os(NH$_3$)$_5$](4α-(5′-[((1,1-dimethylethyl)dimethylsilyl)oxy]-2,4-pentadienyl)-*N*,*N*-dimethyl-2,5-cyclohexadien-1-iminium)}(OTf)$_3$ (31). To a solution of **3** (139 mg, 0.2 mmol) and methyl pentadienoate (22 mg, 0.2 mmol) in CD$_3$CN (0.2 g) was added a solution of TBSOTf (53 mg, 0.2 mmol) in CD$_3$CN (0.2 g). The mixture turned purple instantly (the reaction was complete in <5 min). The solution was analyzed by NMR: ^{1}H NMR (CD$_3$CN) δ 6.9 (dd, J = 10.3, 5 Hz, 1H), 6.52 (d, J = 10.3 Hz, 1H), 6.10 (dd, J = 15.2, 10 Hz, 1H), 5.20 (dt, overlapped, J = 15.2, 7.5 Hz, 1H), 5.0 (d, J = 8 Hz, 1H), 4.84 (d, J = 8 Hz, 1H), 4.6 (br s, 3H), 4.48 (d, J = 10 Hz, 1H), 3.52 (s, 3H), 3.45 (s, 3H), 3.35 (br s, 12H), 3.31 (s, 3H), 2.6 (m, 3H), 0.92 (s, 9H), 0.14 (s, 6H); ^{13}C NMR (CD$_3$CN) δ 180.6 (C), 158.2 (C), 154.3 (CH), 129.7 (CH), 121.0 (q, $CF_3SO_3^-$), 120.3 (CH), 118.6 (CH), 79.7 (CH), 60.3 (CH), 55.1 (CH$_3$), 44.2 (CH$_3$); 43.6 (CH$_3$), 42.3 (CH), 41.8 (CH), 39.7 (CH$_2$), 25.9 (CH$_3$), 18.2 (C), −4.6 (CH$_3$). This compound was stable for hours in solution but could not be isolated.

{5*β*,6*β*-η^2-[Os(NH$_3$)$_5$](4α-(4′-(carbomethoxy)-2′-butenyl)-*N*,*N*-dimethyl-2,5-cyclohexadien-1-iminium)}(OTf)$_3$ (32). The solution containing the corresponding silyl ketene acetal (**31**) (prepared from 0.2 mmol of **3**) was quenched with ∼35−40 mg (∼2 mmol, excess) of water and then added dropwise to ether (50 mL) with stirring, and the purple precipitate was filtered through a fine-porosity fritted glass funnel and washed with ether (20 mL), affording 139 mg (73%): ^{1}H NMR (CD$_3$CN) δ 6.91 (dd, J = 10, 4 Hz, 1H), 6.55 (d, J = 10 Hz, 1H), 5.55 (AB quartet, J = 5.5 Hz, 2H), 5.05 (d, J = 8 Hz, 1H), 4.87 (d, J = 8 Hz, 1H), 4.63 (br s, 3H), 3.61 (s, 3H), 3.46 (s, 3H), 3.37 (br s, 12H), 3.34 (s, 3H), 3.0 (d, J = 5.3 Hz, 2H), 2.7 (m, 1H), 2.5 (m, 2H); ^{13}C NMR (CD$_3$CN) δ 180.1 (C), 172.8 (C), 154.2 (CH), 129.9 (CH), 126.8 (CH), 121.1 (q, $CF_3SO_3^-$), 120.3 (CH), 59.8 (CH), 51.9 (CH$_3$), 44.2 (CH$_3$), 43.7 (CH$_3$), 41.8 (CH), 40.8 (CH), 38.3 (CH$_2$), 37.4 (CH$_2$). (Assignments are supported by DEPT and HETCOR.)

{5*β*,6*β*-[Os(NH$_3$)$_5$](4α-(3-oxocyclopentyl)-η^2-2,5-cyclohexadien-1-iminium)}(OTf)$_3$ (33). The protonated aniline complex (**1c**, 83 mg, 0.10 mmol) was dissolved in methanol (201 mg), and 2-cyclopenten-1-one (11 mg, 0.14 mmol) was added. The solution was allowed to stand for 1 h, diluted with acetonitrile (1 mL), and added to ether (50 mL) while stirring. The resulting purple suspension was filtered and the solid washed with ether and dried *in vacuo*. The product **33** was isolated as a purple solid (75 mg, 83%): ^{1}H NMR (acetone-d_6) δ 10.12 (br s, 1H), 10.08 (br s, 1H), 7.25 (dd, J = 9.9 Hz, 3.3 Hz, 1H), 6.66 (d, J = 9.9 Hz, 1H), 5.56 (d, J = 7.3 Hz, 1H), 5.42 (br s, 3H), 5.13 (d, J = 7.3 Hz, 1H), 3.96 (br s, 12H), 3.33 (m, 2H), 3.07 (m, 1H), 2.76 (m, 1H), 2.18 (m, 4H); ^{13}C NMR (acetone-d_6) δ 216.6 (C), 182.8 (C), 154.2 (CH), 123.3 (CH), 56.9 (CH), 44.6 (CH), 44.3 (CH), 42.2 (CH), 41.6 (CH$_2$), 38.1 (CH$_2$), 27.0 (CH$_2$).

{5*β*,6*β*-η^2-[Os(NH$_3$)$_5$](4α-(2-(carbomethoxy)ethyl)-2,5-cyclohexadien-1-iminium)}(OTf)$_3$ (34). The protonated aniline complex (**1c**, 61 mg, 0.07 mmol) was dissolved in CH$_3$CN (289 mg), and methyl acrylate (7 mg, 0.09 mmol) was added. The solution was cooled to −40 °C and treated with a cold (−40 °C) solution of Hünig's base (11 mg, 0.08 mmol) in CH$_3$CN (200 mg) resulting in a color change from purple to red. After ∼1 min, *tert*-butyldimethylsilyl triflate (20 mg, 0.08 mmol) in CH$_3$CN (197 mg) was added, resulting in a color change from red to purple. After 10 min, one drop of water was added and the mixture added to ether (50 mL). The resulting suspension was filtered and the solid washed with CH$_2$Cl$_2$ and Et$_2$O and dried *in vacuo*, affording compound **34** (47 mg, 75%) as a purple solid: ^{1}H NMR (acetone-d_6) δ 10.10 (br s, 1H), 10.04 (br s, 1H), 7.21 (dd, J = 9.9 Hz, 3.3 Hz, 1H), 6.61 (d, J = 9.9 Hz, 1H), 5.48 (d, J = 7.5 Hz, 1H), , 5.40 (br s, 3H), 5.12 (d, J = 7.5 Hz, 1H), 3.96 (br s, 12H), 3.63 (s, 3H), 2.99 (m, 1H), 2.52 (m, 2H), 2.36 (m, 2H); ^{13}C NMR (acetone-d_6) δ 181.3 (C), 173.4 (C), 155.5 (CH), 122.1 (CH), 58.4 (CH), 51.3 (CH$_3$), 44.2 (CH), 40.3 (CH), 30.5 (CH$_2$), 30.3 (CH$_2$); $E_{1/2}$ = 1.18 V; $E_{p,c}$ = −0.95 V.

Reaction of 3 with α-Methylene-γ-butyrolactone in Tetraglyme. The *N*,*N*-dimethylaniline complex **3** (278 mg, 0.4 mmol) and Hünig's base (206 mg, 1.6 mmol) were dissolved in tetraglyme (5 g), and the mixture was cooled to −20 °C. To this mixture was added a cold solution of α-methylene-γ-butyrolactone (83 mg, 0.85 mmol) and TBSOTf (211 mg, 0.8 mmol) in tetraglyme (1 g), causing the formation of a dark purple color. The progress of the reaction was monitored by CV as the mixture was gradually allowed to warm. The starting complex, **3**, was consumed in 15 min. The solution was added to ether (50 mL), affording 328 mg of a tan-purple solid, consisting of a 1:1 mixture of silyl ketene acetal **36** and MIMIRC compound **35** by ^{1}H NMR. Partial data for compound **36**: ^{1}H NMR (CD$_3$CN) δ 6.98 (dd, J = 9.6, 5.5 Hz, 1H), 6.50 (d, J = 9.6 Hz, 1H), 4.84 (AB quartet, J = 7.2 Hz, 2H), 4.55

(br s, 3H), 3.54 (br s), 0.95 (s, 9H), 0.18 (s, 6H). Some of the other resonances overlap with those of **35** and are not listed.

When the reaction was repeated using a 50% excess (3 equiv) of electrophile (same concentration of complex **2**) and allowed to stand for a longer period (1 h) under otherwise identical conditions, the ratio of MIMIRC compound **35** to silyl ketene acetal **36** was about 95:5.

Protonation of Compound 21. Recrystallized **35** (45 mg, 0.05 mmol) was slurried in acetonitrile (0.5 g) and treated with excess triflic acid (45 mg, 0.3 mmol). The solid dissolves to form a blush-colored solution. After 5 min, the mixture was added to ether, affording 42 mg (81%) of a yellow-tan colored solid. Analysis by proton and carbon NMR revealed the presence of an intermediate, tentatively identified as the *N*-protonated species **37**, which converts to the red *C*-protonated complex **38** with a half life of approx 1 h. Partial data for **37**: ^{1}H NMR (CD_3CN) δ 8.75 (br s, 1H), 5.92 (s, 1H); ^{13}C NMR (CD_3CN) δ 180.3, 179.6, 147.8, 112.6, 65.8, 65.3, 47.1, 44.0, 41.6, 39.8, 37.7, 37.0, 34.9, 33.5, 33.3, 33.1.

The *C*-protonated complex **38** could be prepared more directly using methanol as the solvent: Recrystallized **35** (178 mg, 0.2 mmol) was slurried in methanol (1 g) and treated with a solution of triflic acid (38 mg, 0.25 mmol) in methanol (0.5 g). The solid dissolved to form a deep red solution. Addition to ether (50 mL) afforded **38** as a pink solid (192 mg, 92%): ^{1}H NMR (CD_3CN) δ 4.91 (dd, J = 8.1, 1.8 Hz, 1H), 4.78 (d, J = 8.1 Hz, 1H), 4.60 (br s, 3H), 4.4−4.2 (m, 4H), 3.66 (br s, 12H), 3.41 (s, 3H), 3.25 (s, m, overlap, 4H), 2.4−2.1 (m, overlap, 8H), 1.67 (d, J = 15.6 Hz, 1H), 1.45 (t, J = 15.6 Hz, 1H), 0.92 (m, 1H); ^{13}C NMR (acetone-d_6) δ 193.9 (C), 180.7 (C), 179.9 (C), 65.7 (CH_2), 65.5 (CH), 65.3 (CH_2), 44.77 (CH_3), 44.73 (CH_3), 44.0 (C), 42.4 (C), 39.5 (CH_2), 37.0 (CH), 36.5 (CH_2), 35.7 (CH_2), 33.3 (CH), 32.6 (CH_2), 30.3 (CH), 27.9 (CH_2). Anal. Calcd for $C_{21}H_{39}F_9N_6O_{13}OsS_3$: C, 24.23; H, 3.78; N, 8.07. Found: C, 23.52; H, 4.30; N, 7.70. This compound was further characterized by conversion to the corresponding organic allylamine[2b] and also to the iminium compound, as described below.

A sample of complex **38** (25 mg, 0.024 mmol) was treated with a solution of CAN (16 mg, 0.029 mmol) in CD_3CN (0.4 g) containing triflic acid (19 mg, 0.125 mmol) (to help dissolve the CAN). Analysis by ^{1}H NMR revealed conversion to the organic iminium product **39**. Partial data: ^{1}H NMR (CD_3CN) δ 7.41 (dd, J = 10.4, 2.4 Hz, 1H), 6.81 (d, J = 10.4 Hz, 1H), 3.48 (s, 3H), 3.46 (s, 3H).

{5*β*,6*β*-η^2-[Os(NH$_3$)$_5$](4α-(2-cyanoethyl)-*N*-ethyl-2-cyclohexen-1-iminium)}(OTf)$_3$ (40). Compound **25** (462 mg, 0.52 mmol) was dissolved in methanol (6 g), and the solution was added to Pd/C (284 mg, 50 mol % Pd) and then stirred under an atmosphere of H_2 for 4 h. The reaction mixture was filtered through Celite, and the filter cake was rinsed with acetone (∼10 mL). The filtrate was concentrated under reduced pressure and then added to ether (50 mL) with stirring. The resulting slurry was filtered and rinsed with ether and then dried *in vacuo*, affording compound **40** (407 mg, 87%): ^{1}H NMR (acetone-d_6) δ 5.38 (br s, 3H), 5.31 (d, J = 7.8 Hz, 1H), 4.90 (d, J = 7.8 Hz, 1H), 4.04 (br s, 12H), 3.60 (m, 2H), 3.00 (m, 1H), 2.63 (m, 2H), 1.98 (m, 4H), 1.37 (t, J = 7.8 Hz, 3H); ^{13}C NMR (acetone-d_6) δ 197.0 (C), 120.3 (C), 60.7 (CH), 44.6 (CH), 42.3 (CH_2), 34.8 (CH), 34.6 (CH_2), 27.2 (CH_2), 25.3 (CH_2), 14.8 (CH_2), 12.4 (CH_3); $E_{p,a}$ = 1.23 V.

{5*β*,6*β*-η^2-[Os(NH$_3$)$_5$](4-(2-cyanoethyl)-*N*-ethyl-2-cyclohexen-1-amine)}(OTf)$_2$HOTf (41). A solution of iminium complex **25** (419 mg, 0.47 mmol) in methanol (-2 g) was cooled to −40 °C and treated with a cold (−40 °C) solution of Bu_4NBH_4 (143 mg, 0.56 mmol) in acetonitrile (503 mg). After the solution was allowed to stand at −40 °C overnight (∼14 h), triflic acid (282 mg, 1.88 mmol) was added. The mixture was added to 1:1 ether/CH_2Cl_2 (300 mL), and the tan slurry was filtered. The product was isolated as an off-white powder (401 mg, 95%): ^{1}H NMR (d_6-acetone) δ 4.94 (br s, 3H), 4.74 (m, 1H), 3.84 (br s, 15H), 3.52 (m, 1H), 2.92 (m, 1H), 2.54 (m, 2H), 2.16 (m, 5H), 1.81 (m, 1H), 1.40 (t, J = 7.2 Hz, 3H), 1.12 (m, 1H); ^{13}C NMR (CD_3CN/DMSO-d_6) δ 121.6 (C), 65.5 (CH), 53.6 (CH), 42.3 (CH), 41.7 (CH_2), 36.7 (CH_2), 35.8 (CH), 29.1(CH_2), 23.1(CH_2), 14.1(CH_2), 10.9 (CH_3); $E_{p,a}$ = 0.95 V, $E_{p,c}$ = −0.29 V, $E_{p,c}$ = −0.57 V.

4-(2-Cyanoethyl)-2-cyclohexen-1-one (43). A solution of complex **40** (535 mg, 0.59 mmol) in acetonitrile (3.98 g) and water (1.00 g) was treated with a solution of CAN (387 mg, 0.71 mmol) in acetonitrile (1.67 g) and water (0.326 g). The resulting mixture was allowed to stand at 60 °C for ∼12 h. The solvent was evaporated and the residue dissolved in 10% aqueous HCl (30 mL). This was extracted with methylene chloride (2 × 30 mL), and the extract was dried (Na_2SO_4) and evaporated, affording a dark residue (80 mg). The crude material was dissolved in methylene chloride (∼1−2 mL) and filtered through a plug of basic alumina in a pipet. The solvent was evaporated, affording a yellowish oil (40 mg, 46%): ^{1}H NMR ($CDCl_3$) δ 6.79 (dd, J = 10.2, 1.2 Hz, 1H), 6.04 (dd, J = 10.2, 2.4 Hz, 1H), 2.34−2.64 (m, 6H), 2.18 (m, 1H), 1.95 (m, 1H), 1.75 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 198.7 (C), 151.6 (CH), 130.1 (CH), 118.8 (C), 36.4 (CH_2), 34.8 (CH), 29.9 (CH_2), 27.8 (CH_2), 14.8 (CH_2). An analytically pure sample was obtained by preparative GC (t_R = 4.2 min, using the conditions described in the general section). Anal. Calcd for $C_9H_{11}NO$: C, 72.48; H, 7.38; N, 9.40. Found: C, 72.61; H, 7.42; N, 9.62.

***trans*-*N*-Ethyl-4-(2-cyanoethyl)-2-cyclohexen-1-amine (44).**[41] A solution of complex **41** (490 mg, 0.54 mmol) in CH_3CN (5.44 g) was treated with triflic acid (245 mg, 1.63 mmol) and DDQ (146 mg, 0.64 mmol), in that order. The resulting heterogeneous mixture was removed from the box and the acetonitrile removed *in vacuo*. The residue was dissolved in 10% aqueous Na_2CO_3 (50 mL) and extracted with methylene chloride (3 × 50 mL). The organic phase was dried over Na_2SO_4 and evaporated, affording 95 mg of a brown residue. This material was chromatographed on basic alumina (1 × 9 cm column) using ether. The Dragendorff-positive[42] fraction was collected and evaporated, affording an oil (58 mg, 60%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.76 (ddd, J = 10.3 Hz, 3.5 Hz, 2.5 Hz, 1H), 5.56 (ddd, J = 10.3 Hz, 3.5 Hz, 2.5 Hz, 1H), 3.18 (m, $w_{h/2}$ = 19.5 Hz, 1H), 2.72 (q, J = 7.3 Hz, 2H), 2.38 (m, 2H), 2.05 (m, $w_{h/2}$ = 19.5 Hz 1H, H4), 1.91 (m, 1H), 1.73 (m, 1H), 1.63 (m, 1H), 1.27 (m, 2H), 1.13 (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 131.7 (CH), 130.5 (CH), 119.7 (C), 53.6 (CH), 40.9 (CH_2), 34.7 (CH), 31.4 (CH_2), 29.5 (CH_2), 27.1 (CH_2), 15.6 (CH_3), 14.5 (CH_2). An analytically-pure sample was obtained by preparative GC (t_R = 3.1 min using conditions described in the general section). Anal. Calcd for $C_{11}H_{18}N_2$: C, 74.16; H, 10.11; N, 15.73. Found: C, 73.73; H, 10.02; N, 15.57.

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(41) Assignment of *trans* stereochemistry is based on the widths in Hz of the multiplets corresponding to H(1) and H(4). The value of $w_{h/2}$ of about 20 Hz suggests these two methine resonances are axial when the cyclohexene ring is in a chair conformation (Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*; Pergamon Press: New York, 1969; p 288). H-(1) and H(4) were assigned using COSY and HETCOR experiments.

(42) This amine stains red on TLC with Dragendorff's reagent: Touchstone, J. C.; Dobbins, M. F. *Practice of Thin Layer Chromatography*; Wiley & Sons: New York, 1978.