Protonation of Unactivated Aromatic Hydrocarbons on Osmium(II): Stabilization of Arenium Cations via Unprecedented η^2- and η^3-Coordination

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Received September 19, 1996[⊗]

Abstract: Complexes of the form [Os(NH$_3$)$_5$(L)](OTf)$_2$ (where L = an unactivated arene or polyaromatic hydrocarbon) are readily protonated by triflic acid (HOTf) to generate stable arenium, naphthalenium, and anthracenium cations. A series of substituted anisole complexes were also investigated. The metal stabilizes the hydrocarbon arenium system, in most cases, by coordinating the organic ligand in an η^3 fashion. Where L = *m*-xylene, however, NMR data strongly suggest that the arenium ion is essentially dihapto-coordinated, where an allyl cation fragment remains uncoordinated. For the corresponding anisolium systems, NMR data indicate η^2-coordination. It is likely that η^2 and η^3 geometries represent limiting cases for a continuum of distorted allyl (pseudo-allyl) complexes. The pK_a values determined for these complexes are dramatically higher than those of the free arenium cations.

Introduction

Electrophilic aromatic substitutions are among the most widely used and well-studied reactions in organic chemistry.[1] Manipulating the chemical nature of the common intermediate to these reactions, the arenium ion (i.e., the cyclohexadienyl cation), has a direct bearing on rate and product distribution of both addition and substitution reactions for aromatic systems. Arenium ions have been generated under extreme conditions and directly observed,[2−4] and numerous cyclohexadienyl anion systems have been generated on transition metals from arene precursors by the addition of nucleophiles.[5,6] Cooper et al. have shown that the isoelectronic complexes Cr(CO)$_3$(η^4-benzene)$^{2-}$ [7] and Mn(CO)$_3$(η^4-benzene)$^-$ [8] oxidatively react with a proton to form cyclohexadienyl species; however, examples of arenium complexes formed *directly from the protonation* of an arene ligand are rare. In a recent study by Ashby et al.,[9] convincing evidence was presented that the protonation of [Mo(TRIPOD)-(η^6-benzene)] (TRIPOD = tris[(diphenylphosphino)methyl]-ethane) to form the corresponding metal hydride occurs through the direct *exo* protonation of the ligated benzene, but the elusive arenium intermediate was never observed.

The pentaammineosmium(II) system is known to activate phenols,[10] anilines,[11] and anisoles[12,13] toward electrophilic addition and substitution reactions by binding the aromatic ligand in an η^2 fashion, a process that partially localizes the π system. In these examples, protonation at C(4) results in the formation of a heterotriene system that is stabilized by the donation of π-electron density from the osmium. However, unactivated aromatic hydrocarbons do not have an external electron donor available and, consequently, cannot support electrophilic addition in this manner.
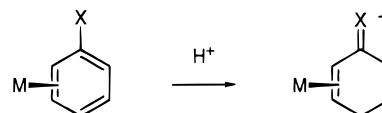
Conjugated diene complexes of the pentaammineosmium-(II) system readily undergo protonation to form π-allyl complexes,[14] and we questioned whether through such η^3-coordination the osmium alone could stabilize an arenium system. Herein we report our findings regarding the protonation of benzene, alkylated benzenes, and polyaromatic hydrocarbons bound to osmium(II) along with a companion study of the protonation of complexed anisoles.
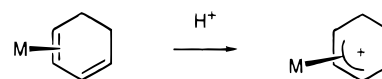
Results

The one-electron reduction of Os(NH$_3$)$_5$(OTf)$_3$ in the presence of various arenes provides complexes of the form [Os(NH$_3$)$_5$-(η^2-L)](OTf)$_2$ (L = benzene (**1**), toluene (**2**), *o*-xylene (**3**), *m*-xylene (**4**), *p*-xylene (**5**), naphthalene (**6**), and anthracene (**7**)) in nearly quantitative yield. The metal is highly fluxional in these complexes at 20 °C, and ^{1}H NMR spectra recorded in CD$_3$CN at 300 MHz are significantly broadened. ^{1}H and ^{13}C NMR spectra recorded at low temperature (−40 °C; CD$_3$CN) indicate that while many positions in the ring are kinetically accessible, the metal has a clear preference to be away from

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

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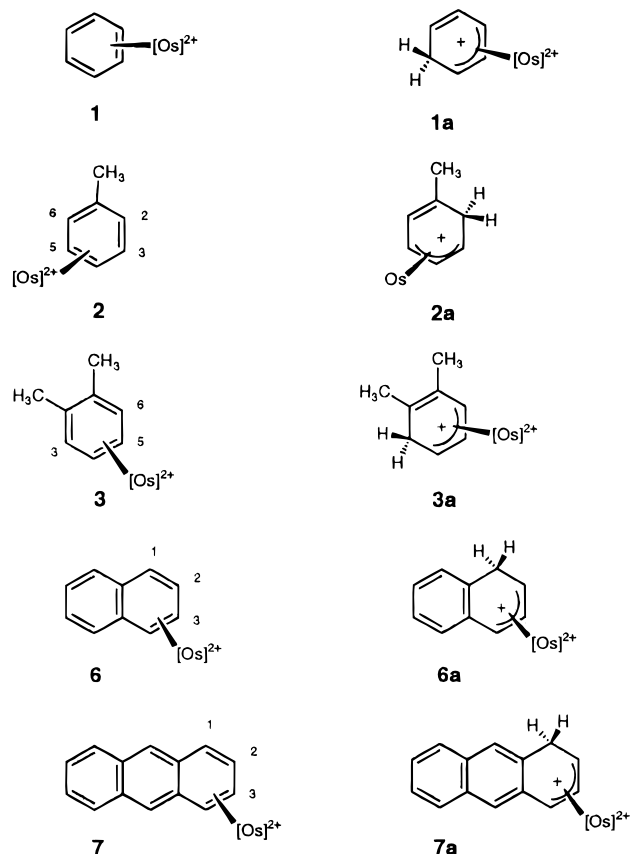(12) Kopach, M. E.; Harman, W. D. *J. Am. Chem. Soc.* **1994**, *59*, 6506.

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Figure 1. η^2-Arene complexes of pentaammineosmium(II) ([Os]$^{2+}$) and their η^3-arenium conjugate acids.

Figure 2. Two isomers of η^3-*p*-xylenium complex and the free energy of their isomerization.

alkyl substituents. Therefore, at −40 °C, the toluene complex is present as a 3:2 mixture of 4,5-η^2 and 5,6-η^2 isomers. The *o*- and *m*-xylene complexes occur solely as their 4,5-η^2 isomers, and for the *p*-xylene complex, the 5,6-η^2 form is heavily favored. In contrast to their arene analogs **1**−**5**, both the anthracene (**7**) and naphthalene (**6**) complexes have ^{1}H NMR spectra showing well-resolved resonances at 20 °C that indicate 3,4-η^2 coordination.

Treatment of a solution of the benzene complex **1** with HOTf (0.5 M) in CD$_3$CN at −40 °C results in an immediate color change that indicates the formation of a new species (**1a**). ^{1}H and ^{13}C NMR spectra at this temperature show well-resolved signals *upfield* from those of the unbound ligand while the *cis*- and *trans*-ammine signals appear approximately 1 ppm downfield from the parent complex **1**. Diastereotopic methylene protons at 1.35 and 1.10 ppm ($J = 26$ Hz), three ^{13}C resonances in the range of 75−85 ppm, and two (uncoordinated) olefinic ^{13}C resonances indicate that the metal is binding the arenium system in an η^3 fashion analogous to the π-allyl system.[14] The benzenium complex **1a** is stable for several hours at −40 °C but quickly decomposes at −30 °C or above. Treatment of **1a** with Hünig's base (−40 °C) restores compound **1**. When a sample of **1** is treated with DOTf at −40 °C in CD$_3$CN, complex **1a**−d_1 is generated, with an ^{1}H NMR spectrum similar to that of its protonated analog **1a** except that only one methylene signal (1.29 ppm, 1H) is present as a broad singlet. Irradiation of the *cis*-ammine signal in **1a**-d_1 indicates a 6% NOE with the remaining methylene proton, a observation that, taken with other spectral data, indicates an *exo* protonation of the arene ring. Similar to the formation of the benzenium system **1a**, arenium complexes are formed from the protonation of toluene **2a** and *o*-xylene **3a**, and the structures for these (Figure 1) have been assigned on the basis of ^{1}H NMR, ^{13}C NMR, NOE, and COSY data. For example, data for the toluenium complex **2a** include
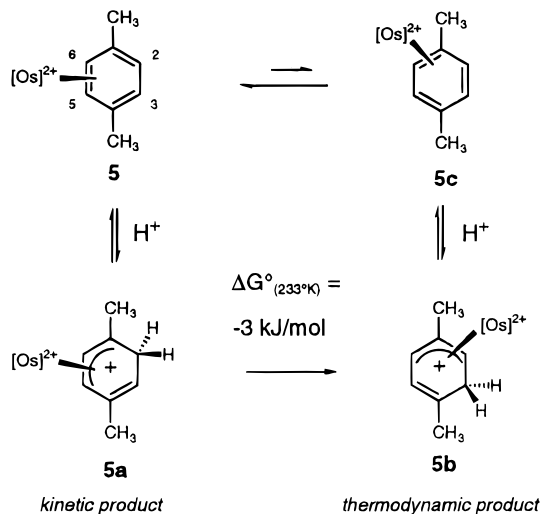
a proton signal at 6.19 ppm that is attached to an unbound olefinic methine carbon (HETCOR) resonating at 120.8 ppm. This proton couples with one of the protons of the allyl system (5.1 Hz), confirming the assignment of **2a** as that shown in Figure 1. In both cases, a *single* isomer is recovered (>95%) where the alkyl substituent(s) occupies a position on the isolated double bond.

When subjected to triflic acid concentrations similar to those reported for **1a**, the *p*-xylene complex **5** shows virtually no reaction. Increasing the acid concentration to 2 M generates a new species (**5b**) and trace amounts of another species (**5a**), whose signals rapidly diminish over a 15-min period. ^{1}H and ^{13}C NMR spectra of **5b** are similar to those of the other η^3-arenium species. One quaternary and two methine carbons from 77 to 86 ppm, representing the sites of metal coordination, a methylene carbon at 35.7 ppm, and two free olefinic carbons indicate a substituted η^3-arenium isomer. NOE interactions are observed between the *cis*-ammines and one methyl group, and between a methylene proton and the other methyl group, observations that confirm the structural isomer shown in Figure 2.

When a solution of **5** is combined with HOTf (2.0 M) in CD$_3$CN/CD$_2$Cl$_2$ at −75 °C, complex **5a** is formed exclusively. Like **5b**, this species also shows two methine and one quaternary allyl ^{13}C NMR resonances as well as one sp^3 methylene and two free olefinic carbons. When the solution of **5a** is allowed to warm slowly to −40 °C, signals for **5a** are first replaced by those of starting material **5** but then convert to those of **5b**. Returning the temperature to −75 °C does not effect any further changes.

Characterization of an η^2-Arenium Complex. When **4** is treated with HOTf (0.5 M) in CD$_3$CN at −40 °C, a deep green solution forms. A ^{1}H NMR spectrum of the new complex **4a** is unremarkable in that olefinic methine and diastereotopic methylene protons ($J = 28$ Hz) appear at chemical shifts similar to those for other arenium species (*vide supra*). However, the ^{13}C NMR spectrum of **4a** reveals only *two* upfield signals at 70.8 and 61.1 ppm and *three* low-field resonances, two of which (191.0 and 170.4 ppm) are features similar to those of *organic* arenium ions.[3] Finally, treatment of a solution of **4a** with a tertiary amine base (−40 °C) regenerates **4** quantitatively. Remarkably, unlike the other arenium species, **4a** is stable in solution at temperatures as high as 20 °C ($t_{1/2} = 0.5$ h). On the basis of the above observations, as well as DEPT, HETCOR, COSY, and NOE data, **4a** is assigned as the η^2-arenium species shown in Figure 3.
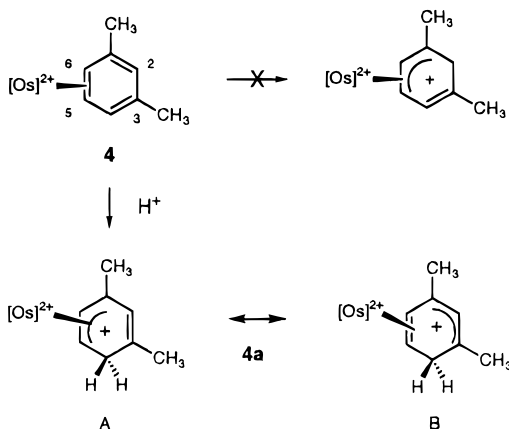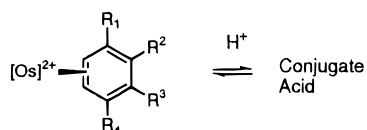
Figure 3. Formation of an η^2-arenium complex from *m*-xylene and several possible mechanisms.

Table 1. pK_a(H$_2$O) Data for η^2- and η^3-Arenium Complexes

acid	R^1	R^2	R^3	R^4	p$K_a{}^a$
1a	H	H	H	H	−8.9
2a	CH$_3$	H	H	H	−6.6
3a	CH$_3$	CH$_3$	H	H	−6.5
4a	CH$_3$	H	CH$_3$	H	−6.9
5a	CH$_3$	H	H	CH$_3$	−8.1
5b	CH$_3$	H	H	CH$_3$	−8.7^b
6a		naphthalene			−8.2
7a		anthracene			−8.0

^{a} pK_a values are estimated as pK_a = pK_1 − 10.1 (see text), where the estimated error of K_1 is ± 0.5 (see text). ^{b} This value was measured at −75 °C.

η^3-Naphthalenium and η^3-Anthracenium Complexes. Compared to the benzenium system, the naphthalenium (**6a**) and anthracenium (**7a**) complexes are more stable and can be easily characterized at 20 °C. These complexes are stable in solution for up to 3 h in HOTf (1.5 M, CD$_3$CN) and display ^{1}H NMR spectra similar to those of the arenium complexes. These features are bound ring protons shifted upfield of the free aromatic ligand and ammine signals shifted downfield. Both naphthalene and anthracene complexes are protonated at C(1) exclusively.

Determination of pK_a Values. The pK_a(H$_2$O) values for the various arenium complexes were estimated by equilibrating the parent complexes with their corresponding arenium complexes in acidic CD$_3$CN (pK_a = −10.1) at −40 °C, where K_1 is defined for the equilibrium

$$M(ArH_2)^+ + CH_3CN \rightleftharpoons CH_3CNH^+ + M(ArH)$$
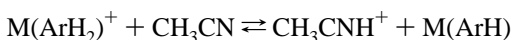
Values for pK_a(H$_2$O) were estimated for each compound by subtracting −10.1 from pK_1, and these results are listed in Table 1. For the naphthalene system **6/6a**, lowering the temperature resulted in a systematic increase in the pK_a of the naphthalenium complex. However, a plot of ln K vs $1/T$ fails to give a straight line, suggesting a significant temperature dependence of ΔH and ΔS. In the case of the *p*-xylene system **5a/5b/5**, it was possible to measure acid dissociation equilibria for both arenium isomers (each at different temperatures).

Anisole Protonations. The one-electron reduction of Os-(NH$_3$)$_5$(OTf)$_3$ in the presence of various anisole ligands provides
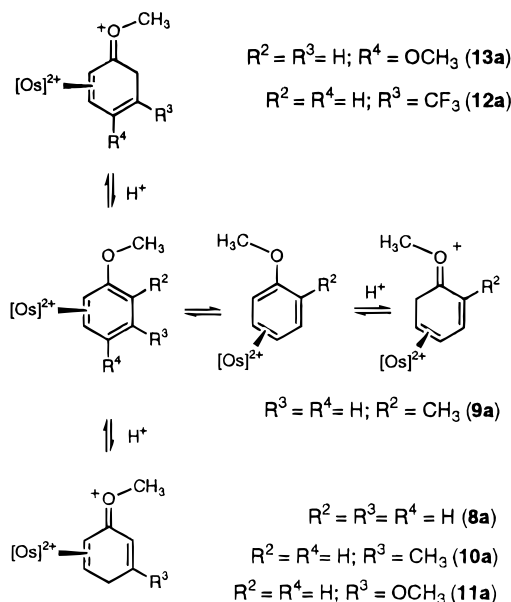

Figure 4. Protonation of various η^2-anisole complexes resulting in 2*H*-, 4*H*- and 6*H*-anisolium species.

complexes of the form [Os(NH$_3$)$_5$(η^2-L)](OTf)$_2$ (L = anisole (**8**), 2-methylanisole (**9**), 3-methylanisole (**10**), 3-methoxyanisole (**11**), α,α,α-trifluoro-3-methylanisole (**12**), and 4-methoxyanisole (**13**)). In all cases the metal preferentially binds the unsubstituted *ortho* and *meta* carbons (i.e., 5,6-η^2), and with the exception of the 2-substituted anisole complex **9**, all systems appear static at 20 °C in a 300 MHz ^{1}H NMR spectrum. In the case of complex **9**, ^{1}H NMR data recorded at −40 °C were required to confirm 5,6-η^2-coordination. In acidic (DOTf) CD$_3$-OD, several of the η^2-anisole complexes undergo deuterium exchange at the *ortho* (H(2), H(6)) and *para* (H(4)) positions, but in no case was exchange of the *meta* protons (H(3) or H(5)) detected. When a solution of the anisole complex **8** (0.02 M) in CD$_3$CN is cooled to −40 °C and treated with HOTf (~0.2 M; −40 °C), the reaction solution changes from yellow to deep blue. A ^{1}H NMR spectrum taken after 5 min at −40 °C reveals the formation of a single compound (**8a**) whose ^{1}H NMR, ^{13}C NMR, and DEPT data indicate that **8a** is a pentaamminosmium(II) complex of an η^2-4*H*-anisolium cation (see Figure 4).[12] Decomposition occurs as the solution of **8a** is warmed to 20 °C, and a ^{1}H NMR spectrum of the reaction solution reveals the absence of any diamagnetic metal salts and a 1:1 ratio of *benzene* and anisole. Even at −40 °C with an excess of acid, decomposition occurs if the concentration of acid becomes too low or if the addition sequence is altered. The addition of a weak base to a solution of **8a** (−40 °C) rapidly deprotonates C(4) to quantitatively regenerate **1**. To probe the stereoselectively of protonation, a solution of **1** (0.02 M) was treated with DOTf at −40 °C (~0.2 M). A ^{1}H NMR spectrum revealed the formation of a product (**8a-d_1**) similar to **8a**, with the exception that only one aliphatic resonance (H(4)) was present. The absence of coupling between H(4) and H(5) and a substantial NOE between H(4) (1.46 ppm) and the *cis*-ammines (9.7%) indicate that deuteration occurs stereoselectively, *anti* to the metal center, as is the case with the unactivated hydrocarbon complexes.

Substituents on the anisole ring strongly influence the regioselectivity of protonation (Figure 4) and the acidity of the corresponding products. When the 3-methoxyanisole complex **11** is treated with 1 equiv of HOTf at 20 °C, the solution quickly darkens to deep blue. After 1 min, addition to ether affords a dark blue solid in quantitative yield. The resulting η^2-anisolium

complex **11a** has ^1H and ^{13}C NMR data similar to those of complex **8a** but is stable in solution for several hours at room temperature ($t_{1/2} \approx 12$ h). In contrast, when a solution of the 3-(trifluoromethyl)anisole complex **12** is treated with HOTf (1 equiv, approximately 0.05 M) in CD_3CN (20 °C), mostly starting material is observed, even if the temperature is lowered to −40 °C. ^1H NMR spectra at −40 °C reveal approximately 20% conversion to a new material (**12a**) with *cis-* and *trans*-ammine signals that are well downfield from those of complex **12**. Warming the reaction mixture to room temperature causes a color change, and a ^1H NMR spectrum (CD_3CN) reveals only complex **12**. Returning the solution to −40 °C regenerates approximately 20% of the protonated material **12a**, confirming that the system is in dynamic equilibrium. At higher concentrations of acid, **12a** becomes the dominant product, a compound whose spectral features differ significantly from the 4*H*-anisolium species observed previously. On the basis of ^1H and ^{13}C NMR, DEPT, and $^1H/^1H$ coupling data, **12a** is assigned to the 5,6-η^2-2*H*-anisolium complex shown in Figure 4. Similarly, addition of HOTf to a solution of the 1,4-dimethoxybenzene complex **13** at −40 °C also gives a η^2-2*H*-anisolium complex (**13a**).[15] Treatment of either **12** or **13** with DOTf forms **12a** or **13a**, respectively, each present in solution as a single stereoisomer. $^1H/^1H$ coupling and NOE data show the deuterium to be oriented *exo* to metal coordination. Finally, like the CF_3 analog **12**, the 2-methylanisole complex **9** protonates in acetonitrile only under high concentrations of HOTf (0.7 M). In this case, however, ^1H NMR data are inconsistent with either a 2,3-η^2-2*H*- or a 4*H*-anisolium product. Rather, proton data closely resemble those obtained for the species [Os(NH₃)₅(4,5-η^2-6*H*-N,N-dimethylanilinium]$^{+3,9}$ and **9a** is assigned to be a product of C(6) protonation for the 4,5-η^2 linkage isomer of **9** (see Figure 4).

The acidity of the anisolium system **8a** was estimated in CD_3CN solution by a method similar to that described for the hydrocarbon analogs, where pK_1 was determined to be 4.1 ± 0.5 and $pK_a(H_2O)$ was estimated as −6. Although pK_a values for other 4*H*-anisolium complexes were not precisely determined, useful estimates of acidities at −40 °C were obtained from bracketing experiments in acetonitrile. For example, since the η^2-anisolium complex of 3-methoxyanisole **11a** deprotonates in the presence of 1 equiv of pyridine ($pK_a = 5.3$), but does not deprotonate in the presence of 1 equiv of N,N-dimethylacetamide ($pK_a = 3$), a pK_a of 4 ± 1 is assigned. In contrast, for both 2-methylanisole and 3-(triflouromethyl)anisole complexes, only partial protonation occurs in an acetonitrile solution with 1 equiv of HOTf (approximately 0.05 M), an observation that indicates a pK_a of −8 ± 1. Table 2 summarizes these findings along with the corresponding data for the N,N-dimethylaniline complex.[11]

Discussion

Previous reports of protonation of organometallic complexes $L_3M(\eta^6$-arene) have focused mainly on the formation of metal hydrides and the participation of these species in the electrophilic substitution of an aromatic ligand.[16,17] The present study appears to be the first report of a bound arene undergoing *direct*

Table 2. Approximate pK_a Data for η^2-Arenium Complexes

acid	X	R^2	R^3	$pK_a(H_2O)$
8a	OCH_3	H	H	−6.0
9a	OCH_3	CH_3	H	−8 ± 1[a]
10a	OCH_3	H	CH_3	0 ± 2[a]
11a	OCH_3	H	OCH_3	4 ± 1[a]
12a	OCH_3	H	CF_3	−8 ± 1[a]
15a	$N(CH_3)_2$	H	H	5.5[b]

[a] pK_a estimated by bracketing experiments in aceonitrile at −40 °C. [b] pK_a estimated from equilibration with amine base in acetonitrile at 20 °C.

protonation to generate stable arenium species, although we note that both chromium− and manganese−η^4-arene complexes have been shown to react with protons via a hydride intermediate to give stable cyclohexadienyl systems.[7,8] The dihapto-coordinated pentaammineosmium(II) fragment is fundamentally different from most metal systems that coordinate arenes in an η^6 fashion (e.g., $Cr(CO)_3$, $Mn(CO)_3^+$) in that the osmium activates the ligand toward *electrophilic* rather than nucleophilic addition. As a consequence, the η^2-arene complex behaves chemically like an η^2-diene complex of osmium(II), directly reacting with protons to form π-allyl complexes.[14] The difference in the acidities of the η^2-benzenium ($pK_a = -8.9$) and η^2-cyclohexadienium ($pK_a = -1.7$) complexes[14] of pentaammineosmium-(II) is only about 7 pK_a units. Estimating the pK_a of **1a** at 25 °C to be equal to that measured at −40 °C,[18] the energy difference for eq 1 is only about 40 kJ/mol. The difference in free energy for an analogous organic reaction (eq 2) is over 3 times as great. This striking difference in energy between eqs 1 and 2 can largely be attributed to the role the metal plays in dearomatizing the arene in compound **1**.

$$\Delta G° = -40 \text{ kJ/mol} \quad (1)$$

$$\Delta G° = -143 \text{ kJ/mol} \quad (2)$$
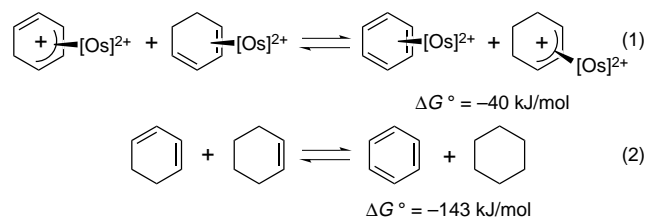
Surprisingly, the pK_a values for the benzenium, naphthalenium, and anthracenium complexes at −40 °C (see Table 1) vary by less that one pK_a unit. This is a stark contrast to the difference in acidity between free benzenium and anthracenium ions ($\Delta pK_a = 13$).[19] Apparently, the aromatic stabilization in the benzene, naphthalene, and anthracene complexes is disrupted to such a degree that these hydrocarbons protonate with almost equal facility.

The ease with which the metal can adjust its coordination site (e.g., for benzene $k \sim 10^4$ s^{-1} at 20 °C)[20] and the tendency of the metal to avoid alkyl substituents result in an unusually high regioselectivity of protonation for unactivated hydrocarbons that is often counter to that observed for uncomplexed arenes. Whereas the methyl group of toluene directs protonation *para*

(15) Experiments attempting to protonate the 4-methylanisole and 3,4-dimethylanisole complexes at subambient temperatures resulted in poorly resolved ^1H NMR spectra that were also consistent with η^2-2*H*-anisolium species, but our efforts to characterize these species were hampered by their instability.

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(17) Davison, A.; McFarlane, W.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, 3653.

(18) The value of pK_1 for the naphthalenium complex **6a** varies with temperature from 1.9 (−40 °C) to 2.1 (20 °C).

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

to the alkyl substituent (*para/ortho* ratio 1.6),[19] in the corresponding complex (i.e., **2**), the methyl group directs the *metal* away from it, and consequently, protonation occurs at the *ortho* carbon exclusively. For the *o*-xylene complex **3**, the metal prefers the 4,5-η^2 position, away from the methyl groups, but protonation at one of the alkylated sites would force a methyl group into an *endo* orientation that would sterically interfere with the metal system. Thus, protonation occurs only at C(3) to give **3a** (see Figure 1). For the corresponding organic *o*-xylene, protonation is favored at C(4) with only moderate selectivity.[19]

Protonation of the *m*- and *p*-xylene complexes occurs with the same site preference as is observed for the free ligands, but for the former case, the preference for C(4) is more pronounced than that for the uncoordinated arene where the ratio of C(4)/C(2) protonation is only 1.6. Protonation of the *5,6-η^2-m*-xylene complex **4** can occur at C(2) or C(4), but only the latter process places methyl groups at the most electronegative carbons. For this arenium system, η^3-coordination would set up a steric interaction between the ammine ligands and the C(1) methyl group. Consequently, complex **4a** is most stable with the osmium remaining η^2-coordinated, where only metal π-backbonding and methyl hyperconjugation stabilize the allyl cation fragment. Although the striking differences in ^{13}C data between **4a** and the other arenium complexes compel us to assign **4a** as η^2-coordinated, the η^3 and η^2 representations (A and B in Figure 3) are most likely not discrete constitutional isomers, but rather two limiting resonance structures of a distorted allyl or "pseudoallyl" system (Figure 3).[21,22]

As a result of the opposing methyl groups of *p*-xylene, the osmium in complex **5** cannot adapt an η^3 orientation upon protonation without a steric interaction with one of these substituents. On the other hand, formation of a 5,6-η^2-arenium species analogous to **4a** would result in an *endo*-oriented methyl group, an outcome that is also sterically undesireable. Consequently, the *p*-xylene complex **5** is more difficult to protonate *in a kinetic sense* than is the benzene analog (see Table 1). At −75 °C, the metal heavily favors the 5,6-η^2 position, causing protonation to occur at C(2) to avoid creating an *endo*-oriented methyl substituent. However, at −40 °C, the broadened ^{1}H NMR spectrum of **5** indicates that the metal has access to other positions in the ring. To form arenium **5b**, the metal can move to the 1,6-η^2 position (**5c**) and then protonate at C(3). Alternatively, **5b** might form directly from **5a**, either by a 1,2-hydrogen shift[2] or by a linkage isomerization (see Figure 2). By combining the K_a values for each of these isomers with the assumption that K_a for **5a** at −75 °C is similar to that at −40 °C, we estimate the free energy of isomerization for **5a** to **5b** to be approximately 3 ± 1 kJ/mol (see Figure 2).

Naphthalene preferentially protonates at C(1), as does the corresponding complex **6**. However, whereas free anthracene favors protonation in the internal ring at C(9), compound **7** preferentially protonates at C(1), leaving the aromatic B and C rings intact. Other η^2-complexes of anthracene have been reported,[23,24] and like these systems, the metal in **7** adopts a coordination site (3,4-η^2) that minimizes the disruption to the π-system. Thus, protonation occurs at the A ring exclusively.

Diene, naphthalene, and anthracene complexes of pentaammineosmium(II) unambiguously protonate at the β position to

form π-allyl species, but for arene systems, a second mechanism is possible whereby protonation occurs at the δ carbon. The protonation of the *m*-xylene complex **4** to form the η^2-arenium species **4a** appears to be an example of such a protonation (see Figure 3), but without a comprehensive series of labeling or kinetics experiments, it is difficult to differentiate between β addition and δ addition. Given the ability of the metal to undergo linkage isomerizations and the precedence of 1,2-hydrogen shifts in the corresponding organic systems,[17] several equally plausible mechanisms can be envisioned for the formation of arenium complexes **1a**−**5a**.
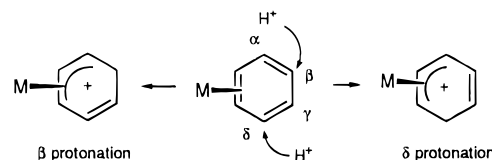
As we have described previously,[9,11] protonation of arene complexes bearing a heteroatom donor results in η^2-heterotriene complexes. Although it is plausible that these complexes, like their hydrocarbon analogs, have significant allyl character, ^{13}C NMR data for complexes **9**−**13** corresponding to C(1) (197−216 ppm) are most consistent with an uncoordinated carbonyl group.[25] Crystallographic studies have previously shown that electron-donating groups at a terminal position of a π-allyl complex result in a lengthening of the bond between the terminal carbon and metal.[21,22] Apparently, the propensity of pentaammineosmium(II) to back-bond through η^2-coordination enhances this distortion to the point that the ligand becomes effectively dihapto-coordinated.
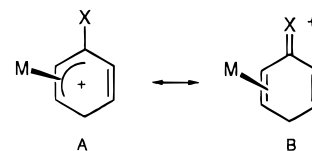
For organic anisoles and phenols, the strong *para*-directing ability of the heteroatom substituent causes protonation to occur either *para* to or on the donor atom.[19] Although protonation at the heteroatom has never been seen with the corresponding osmium complexes, a number of the anisole species (i.e., **8**, **10**, **11**) selectively protonate at C(4). Substituents located at C(3) are in conjugation with the oxonium system resulting from protonation at C(4). As expected, this position greatly influences the favored protonation site. When a methoxy or methyl group is present at this position, the basicity of the corresponding anisole complex is significantly enhanced. On the other hand, when a CF$_3$ group is placed in this position, the destabilizing nature of two withdrawing groups in conjugation causes C(2) protonation to dominate.

Another exception to the general rule of C(4) protonation of anisole is found for the 2-methylanisole complex **9**. For the oxygen to participate as a π donor, the methoxy group must lie in the plane of the arene. The methyl group at the 2-position forces the methoxy substituent to point toward C(6), causing a steric interaction with the pentaammineosmium group (see Figure 4). To minimize this interaction, the metal shifts to the 4,5-position and, consequently, protonation occurs at C(6). The regiospecific protonation for this osmium complex is again

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(25) Typical ^{13}C resonances for the carbonyl of a *C,C*-dihapto-coordinated enone complex of pentaammineosmium(II) are in the range of 200−210 ppm, while for the trihapto-coordinate acrolienium complex, the most downfield carbon is 160 ppm. See: Chen, H. C. Ph.D. Dissertation, University of Virginia, 1996.

vastly different from what is seen with organic anisoles (2,6-dimethylanisole is a much weaker carbon base than anisole for similar reasons).[19]

Concluding Remarks

The coordination of a π base to an aromatic hydrocarbon markedly enhances the basicity of the arene to the point that stable η^2- and η^3-arenium species may be characterized in solution under mild conditions. The metal also profoundly enhances the regioselectivity of protonation. An in depth understanding of the protonation of unactivated η^2-arene complexes will facilitate development of electrophile-initiated sequential addition reactions for unactivated arenes, a methodology that is complementary to the nucleophile-initiated sequential additions developed previously.[5,26]

Experimental Section

General Procedures. ^{1}H and ^{13}C NMR spectra were recorded on a General Electric GN-300 spectrometer at −40 °C unless otherwise noted. Chemical shifts are reported in parts per million relative to solvent (δ(CD$_3$CN) = 1.93, δ(acetone-d_6) = 2.04). 2D-NMR experiments (DEPT, NOE) were recorded on a General Electric GN-300 spectrometer as well. ^{13}C multiplicities are supported by DEPT data.

Electrochemical experiments were performed under nitrogen using a PAR Model 362 potentiostat driven by a PAT Model 175 universal programmer. Cyclic voltammograms were recorded (Kipp & Zonen BD90 XY recorder) in a standard three-electrode cell, 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 (about 0.5 M TBAH) at 100 mV/s using cobaltocene ($E_{1/2}$ = −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. The work was carried out under a nitrogen atmosphere in a Vacuum Atmospheres Co. glovebox.

Solvents. Methylene chloride-d_2 and acetonitrile-d_3 (Cambridge Isotope Labs) were refluxed over CaH$_2$ and distilled under argon. Acetone-d_6 (Cambridge Isotope Labs) was used as received except that it was deoxygenated prior to use.

Reagents. The precursor [Os(NH$_3$)$_5$OTf](OTf)$_2$ was synthesized as described by Lay *et al.*[27] 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 benzenes, naphthalene, and anthracene were obtained from commercial sources (Aldrich and Lancaster) and used without further purification. Penta-ammineosmium(II) complexes of benzene,[28] 1,4-dimethoxybenzene, anisole, naphthalene,[29] *N,N*-dimethylaniline,[11] and toluene[20] have been previously reported.

General Procedure for the Preparation of the η^2-Pentaammine-osmium(II)−Arene Complexes. To a solution of [Os(NH$_3$)$_5$OTf]-(OTf)$_2$ (462 mg, 0.64 mmol) in DMAc (1.36g) and an excess of ligand (10−20 equiv) was added activated magnesium (788 mg), and the heterogeneous mixture was stirred for 0.5 h. The reaction mixture was filtered through a fritted glass funnel into stirring CH$_2$Cl$_2$ (150 mL), and the resulting solid was filtered and washed with CH$_2$Cl$_2$ and then ether to yield pentaammineosmium(II)−arene complexes in 80−90% yield.

[Os(NH$_3$)$_5$(2,3,4-η^3-1*H*-benzenium)](OTf)$_3$ (1a). The complex [Os-(NH$_3$)$_5$(1,2-η^2-(benzene))](OTf)$_2$ (36.4 mg, 0.056 mmol) was dissolved in a solution of HOTf (50.4 mg, 0.336 mmol) and 456 mg of CD$_3$CN that had been cooled to −40 °C. ^{1}H NMR (300 MHz, CD$_3$CN; −40 °C): δ 6.50 (br t, *J* = 7.5, 6.6 Hz, 1H), 6.19 (br d, *J* = 8.7 Hz, 1H), 5.95−6.10 (m, 2H), 4.98 (t, *J* = 6.0 Hz, 1H), 4.84 (br s, 3H), 3.78 (br s, 12H), 1.35 (br d, *J* = 26.4 Hz, 1H), 1.10 (br d, *J* = 26.4, 1H). ^{13}C

NMR (75 MHz, CD$_3$CN): δ 134.55 (CH), 125.82 (CH), 82.13 (CH), 81.90 (CH), 74.98 (CH), 30.54 (CH$_2$).

[Os(NH$_3$)$_5$(4,5,6-η^3-(2-methyl-1*H*−benzenium))](OTf)$_3$ (2a). The complex [Os(NH$_3$)$_5$(3,4-η^2-(1-methylbenzene))](OTf)$_2$ (39.1 mg, 0.059 mmol) was dissolved in a solution of HOTf (46.3 mg, 0.309 mmol) and 536 mg of CD$_3$CN that had been cooled to −40 °C. ^{1}H NMR (300 MHz, CD$_3$CN; −40 °C): δ 6.19 (d, 1H, *J* = 5.1), 5.99 (m, 1H), 5.92 (m, 1H), 5.06 (t, 1H, *J* = 6.3 Hz), 4.95 (br s, 3H), 3.81 (br s, 12H), 1.92 (s, 3H), 1.18 (m, 2H). ^{13}C NMR (75 MHz, CD$_3$CN): δ 146.52 (C), 120.82 (CH), 88.11 (CH), 78.90 (CH), 74.34 (CH), 34.76 (CH$_2$), 22.14 (CH$_3$).

[Os(NH$_3$)$_5$(4,5-η^2-(1,2-dimethylbenzene))](OTf)$_2$ (3). ^{1}H NMR (300 MHz, CD$_3$CN; −40 °C): δ 6.83 (br, s, 2H), 4.83 (br s, 2H), 4.00 (br, s, 3H), 2.80 (br s, 12H), 2.12 (s, 6H). ^{13}C NMR (75 MHz, CD$_3$-CN): δ 133.70 (CH), 131.37 (C), 61.83 (CH), 19.71 (CH$_3$). CV (CH$_3$-CN; TBAH; 100 mV/s): $E_{p,a}$ = +0.40 V (NHE).

[Os(NH$_3$)$_5$(4,5,6-η^3-(2,3-dimethyl-1*H*-benzenium))](OTf)$_3$ (3a). The complex [Os(NH$_3$)$_5$(4,5-η^2-(1,2-dimethylbenzene))](OTf)$_2$ (44.6 mg, 0.066 mmol) was dissolved in a solution of HOTf (50.3 mg, 0.335 mmol) and 514 mg of CD$_3$CN that had been cooled to −40 °C. ^{1}H NMR (300 MHz, CD$_3$CN; −40 °C): δ 5.89 (d, 2H, *J* = 6.0 Hz), 5.03 (t, 1H, *J* = 6.0 Hz), 4.97 (br s, 3H), 3.83 (br s, 12H), 1.94 (s, 3H), 1.91 (s, 3H), 1.34 (m, 2H). ^{13}C NMR (75 MHz, CD$_3$CN): δ 137.84 (C), 126.72 (C), 92.58 (CH), 78.88 (CH), 74.51 (CH), 35.49 (CH$_2$), 19.34 (CH$_3$), 18.52 (CH$_3$).

[Os(NH$_3$)$_5$(4,5-η^2-(1,3-dimethylbenzene))](OTf)$_2$ (4). ^{1}H NMR (300 MHz, CD$_3$CN; −40 °C): δ 6.59 (d, *J* = 4.2 Hz, 1H), 6.26 (s, 1H), 4.96 (m, 1H), 4.87 (d, *J* = 7.5 Hz, 1H), 4.04 (br s, 3H), 2.86 (br s, 12H), 2.27 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (75 MHz, CD$_3$CN): δ 147.78 (C), 131.76 (C), 128.13 (CH), 121.59 (CH), 63.52 (CH), 62.57 (CH), 24.41 (CH$_3$), 20.96 (CH$_3$). CV (CH$_3$CN; TBAH; 100 mV/s): $E_{p,a}$ = +0.44 V (NHE).

[Os(NH$_3$)$_5$(5,6-η^2-(2,4-dimethyl-1*H*-benzenium))](OTf)$_3$ (4a). The complex [Os(NH$_3$)$_5$(4,5-η^2-(1,3-dimethylbenzene))](OTf)$_2$ (42.4 mg, 0.062 mmol) was dissolved in a solution of HOTf (46.6 mg, 0.311 mmol) and 506 mg of CD$_3$CN that had been cooled to −40 °C. ^{1}H NMR (300 MHz, CD$_3$CN; −40 °C): δ 6.73 (dd, 1H, *J* = 6.0,6.9 Hz), 6.52 (s, 1H), 6.00 (d, 1H, *J* = 6.0), 5.10 (br s, 3H), 3.97 (br s, 12H), 2.29 (s, 3H), 2.06 (d, 1H, *J* = 28.2 Hz), 1.85 (s, 3H), 0.58 (dd, 1H, *J* = 28.2, 6.9). ^{13}C NMR (75 MHz, CD$_3$CN): δ 190.97 (C), 170.35 (C), 128.86 (CH), 70.81 (CH), 61.09 (CH), 41.32 (CH$_2$), 29.02 (CH$_3$), 24.82 (CH$_3$).

[Os(NH$_3$)$_5$(5,6-η^2-(1,4-dimethylbenzene))](OTf)$_2$ (5). ^{1}H NMR (300 MHz, CD$_3$CN; −40 °C): δ 6.16 (s, 2H), 5.04 (s, 2H), 4.07 (br s, 3H), 2.94 (br s, 12H), 2.19 (s, 3H). ^{13}C NMR (75 MHz, CD$_3$CN): δ 143.57 (C), 119.23 (CH), 65.77 (CH), 24.26 (CH$_3$). CV (CH$_3$CN; TBAH; 100 mV/s): $E_{p,a}$ = +0.39 V (NHE).

[Os(NH$_3$)$_5$(2,3,4-η^3-(2,5-dimethyl-1*H*-benzenium))](OTf)$_3$ (5a). The complex [Os(NH$_3$)$_5$(5,6-η^2-(1,4-dimethylbenzene))](OTf)$_2$ (21.5 mg, 0.032 mmol) was dissolved in a solution of HOTf (170.4 mg, 1.14 mmol) and a mixture of 289 mg of CD$_3$CN and 318 mg of CD$_2$Cl$_2$ that had been cooled to −80 °C. Spectra were then recorded at −75 °C. ^{1}H NMR (300 MHz, CD$_3$CN): δ 5.88 (d, *J* = 5.4 Hz, 1H), 5.53 (s, 1H), 5.41 (d, *J* = 6.3 Hz, 1H), 4.96 (br s, 3H), 3.81 (br s, 12H), 1.87 (s, 3H), 1.81 (s, 3H), 0.98 (d, *J* = 28.5 Hz, 1H), 0.74 (d, *J* = 28.5 Hz, 1H). ^{13}C NMR (75 MHz, CD$_3$CN/CD$_2$Cl$_2$): δ 142.72 (C), 124.16 (CH), 78.33 (C), 76.44 (CH), 71.21 (CH), 37.58 (CH$_2$), 24.14 (CH$_3$), 23.79 (CH$_3$).

[Os(NH$_3$)$_5$(4,5,6-η^3-(2,5-dimethyl-1*H*-benzenium))](OTf)$_3$ (5b). The complex [Os(NH$_3$)$_5$(5,6-η^2-(1,4-dimethylbenzene))](OTf)$_2$ (43.3 mg, 0.064 mmol) was dissolved in a solution of HOTf (294.0 mg, 1.96 mmol) and 512 mg of CD$_3$CN that had been cooled to −40 °C. ^{1}H NMR (300 MHz, CD$_3$CN; −40 °C): δ 6.17 (d, *J* = 5.4 Hz, 1H), 5.46 (m, 2H), 4.78 (br s, 3H), 3.69 (br s, 12H), 2.16 (s, 3H), 1.86 (s, 3H), 1.28 (m, 2H). ^{13}C NMR (75 MHz, CD$_3$CN): δ 144.93 (C), 121.79 (CH), 86.54 (C), 81.59 (CH), 77.24 (CH), 35.69 (CH$_2$), 21.84 (CH$_3$), 14.92 (CH$_3$).

[Os(NH$_3$)$_5$(2,3,4-η^3-1*H*-napthalenium)](OTf)$_3$ (6a). The complex [Os(NH$_3$)$_5$(1,2-η^2-(naphthalene))](OTf)$_2$ (43.4 mg, 0.062 mmol) was dissolved in a solution of HOTf (62.6 mg, 0.42 mmol) and 513 mg of CD$_3$CN that had been cooled to −40 °C. ^{1}H NMR (300 MHz, CD$_3$-CN): δ 7.55 (d, *J* = 7.8 Hz, 1H), 7.39 (td, *J* = 6.9, 1.2 Hz, 1H), 7.32

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(td, $J = 7.8$, 1.8 Hz, 1H), 7.24 (d, $J = 7.5$, 1H), 6.42 (dd, $J = 6.0$, 2.4 Hz, 1H), 6.15 (m, 1H), 5.36 (q, $J = 6.0$ Hz, 1H), 5.00 (br s, 3H), 3.20 (br s, 12H), 2.32 (dd, $J = 23.8$, 1.2 Hz, 1H), 2.15 (dd, $J = 23.8$, 1.2 Hz, 1H). ^{13}C NMR (75 MHz, CD$_3$CN): δ 132.12 (CH), 131.13 (CH), 131.80 (C), 130.90 (C), 130.16 (CH), 128.28 (CH), 83.13 (CH), 82.74 (CH), 74.83 (CH), 29.59 (CH$_2$).

[Os(NH$_3$)$_5$(1,2-η^2-anthracene)](OTf)$_2$ (7). ^{1}H NMR (300 MHz, CD$_3$CN): δ 8.02 (s, 1H), 7.93−7.88 (m, 3H), 7.46 (m, 2H), 7.09 (m, 2H), 5.22 (d, $J = 7.2$ Hz, 1H), 4.97 (m, 1H), 4.26 (br s, 3H), 2.94 (br s 12H). ^{13}C NMR (75 MHz, CD$_3$CN): δ 141.34 (C), 136.13 (CH), 133.66 (C), 132.78 (C), 131.30 (C), 128.44 (CH), 127.93 (CH), 126.65 (CH), 126.22 (CH), 125.97 (CH), 124.87 (CH), 122.88 (CH), 54.83 (CH), 52.80 (CH). CV (CH$_3$CN; TBAH; 100 mV/s): $E_{1/2} = +0.66$V (NHE).

[Os(NH$_3$)$_5$(2,3,4-η^3-1H-anthracenium)](OTf)$_3$ (7a). The complex [Os(NH$_3$)$_5$(1,2-η^2-anthracene)](OTf)$_2$ (42.6 mg, 0.057 mmol) was dissolved in a solution of HOTf (68.8 mg, 0.46 mmol) and 521 mg of CD$_3$CN that had been cooled to −40 °C. ^{1}H NMR (300 MHz, CD$_3$-CN): δ 7.99 (s, 1H), 7.92 (dd, $J = 6.3$, 3.0 Hz, 1H), 7.83 (d, $J = 7.8$ Hz, 1H), 7.66 (s, 1H), 7.54 (m, 2H), 6.48 (d, $J = 6.3$ Hz, 1H), 6.05 (m, 1H), 5.39 ("t", $J = 6.3$ Hz, 1H), 5.03 (br, s, 3H), 3.70 (br, s, 12H), 2.71 (d, $J = 23.4$ Hz, 1H), 2.42, (d, $J = 23.4$ Hz, 1H). ^{13}C NMR (75 MHz, CD$_3$CN): δ 134.53 (C), 132.38 (C), 132.22 (CH), 130.07 (C), 129.19 (CH), 128.80 (CH), 128.67 (CH), 127.82 (CH), 127.32 (CH), 126.67 (C), 83.52 (CH), 82.59 (CH), 75.41 (CH), 28.91 (CH$_2$).

[Os(NH$_3$)$_5$(5,6-η^2-4H-anisolium)](OTf)$_3$ (8a). η^2-Anisole **1** (25 mg, 0.036 mmol) was dissolved in CD$_3$CN (400 mg) and cooled to −40 °C. Cold HOTf (15 mg, 0.100 mmol) was added, imparting a dark blue color. After 5 min at −40 °C, an ^{1}H NMR spectrum was recorded. ^{1}H NMR (CD$_3$CN; −40 °C): δ 7.75 (dd, 1H, $J = 10.2$, 3.9 Hz), 6.65 (d, 1H, $J = 10.2$ Hz), 5.72 (t, 1H, $J = 7.2$ Hz), 5.12 (d, 1H, $J = 7.2$ Hz), 4.70 (br s, 3H), 4.31 (s, 3H), 3.41 (br s, 12H), 2.55 (dd, 1H, $J = 28.2$, 3.9 Hz), 1.46 (dd, 1H, $J = 28.2$, 7.2 Hz). ^{13}C NMR (CD$_3$CN; −40 °C): δ 201.7 (CO), 165.1 (CH), 118.2 (CH), 62.5 (CH$_3$), 56.0 (CH), 52.0 (CH), 35.0 (CH$_2$).

Os(NH$_3$)$_5$(5,6-η^2-(4H-anisolium-d_1))](OTf)$_3$ (8a-d_1). This compound was prepared as above substituting DOTf for HOTf. ^{1}H NMR (CD$_3$CN; −40 °C): δ 7.71 (br d, 1H, $J = 9.60$ Hz), 6.73 (d, 1H, $J = 9.60$ Hz), 5.73 (d, 1H, $J = 6.6$ Hz), 5.12 (d, 1H, $J = 6.6$ Hz), 4.76 (br s, 3H), 4.30 (s, 3H), 3.45 (br s, 12H), 2.51 (s, 1H). 1D NOE (CD$_3$-CN; −40 °C): H$_4$, *cis*-NH$_3$ (10%).

[Os(NH$_3$)$_5$(5,6-η^2-(2-methylanisole))](OTf)$_2$ (9). ^{1}H NMR (CD$_3$-CN; −40 °C): δ 6.85 (t, 1H, $J = 6.3$ Hz), 6.13 (d, 1H, $J = 8.3$ Hz), 4.92 (t, 1H, $J = 6.0$ Hz), 4.72 (d, 1H, $J = 6.0$ Hz), 3.97 (br s, 3H), 3.61 (s, 3H), 2.77 (br s, 12H), 2.02 (s, 3H). ^{13}C NMR (CD$_3$CN; −40 °C): δ 154.4 (C), 135.5 (CH), 125.7 (CH), 103.8(C), 61.3(CH), 56.6-(CH), 54.0(CH$_3$), 16.2(CH$_3$). CV: $E_{p,a} = 0.45$ V. Anal. Calcd for C$_{56}$H$_{65}$ON$_5$B$_2$Os·H$_2$O : C, 63.82; H, 6.41; N, 6.61. Found: C, 63.70; H, 6.42; N, 6.51.

[Os(NH$_3$)$_5$(4,5-η^2-(2-methyl-6H-anisolium))](OTf)$_3$ (9a). The complex [Os(NH$_3$)$_5$(5,6-η^2-(2-methylanisole))](OTf)$_2$ (13.8 mg, 0.020 mmol) was dissolved in a solution of HOTf (459.6 mg, 3.064 mmol) and 508 mg of CD$_3$CN that had been cooled to −40 °C. ^{1}H NMR (CD$_3$CN; −40 °C): δ 8.53 (d, $J = 5.7$ Hz, 1H), 5.45 (m, 2H), 4.56 (br s, 3H), 4.15 (s, 3H), 3.43 (br s, 12H), 2.35 (br d, 1H, $J = 30.0$ Hz), 2.13 (s, 3H), 1.25 (br d, 1H, $J = 30.0$ Hz). ^{13}C NMR (CD$_3$CN; −40 °C): δ 197.65 (C), 189.17 (C), 166.83 (CH), 61.62 (CH$_3$), 52.80 (CH), 49.42 (CH), 37.86 (CH$_2$), 14.66 (CH$_3$).

[Os(NH$_3$)$_5$(5,6-η^2-3-methylanisole)](OTf)$_2$ (10). ^{1}H NMR (CD$_3$CN): δ 6.31 (d, 1H, $J = 8.1$ Hz), 5.60 (s, 1H), 5.00 (t, 1H), 4.74-(d, 1H, $J = 8.1$ Hz) 4.05 (br s, 3H), 3.65 (s, 3H), 2.90 (br s, 12H), 2.18 (s, 3H). ^{13}C NMR (CD$_3$CN): δ 168.5 (C), 132.0 (C), 120.2 (CH), 96.4 (CH), 62.0 (CH), 54.8 (CH$_3$), 54.1 (CH), 20.5 (CH$_3$). CV: $E_{p,a}$ = 0.35 V. Anal. Calcd for C$_{10}$H$_{25}$N$_5$O$_7$S$_2$F$_6$Os: C, 17.27; H, 3.62; N, 10.00. Found: C, 17.52; H, 3.58; N, 9.64.

[Os(NH$_3$)$_5$(5,6-η^2-(3-methyl-4H-anisolium))](OTf)$_3$ (10a). ^{1}H NMR

(4:1 CD$_3$CN/CD$_2$Cl$_2$; −50 °C): δ 6.64 (br s, 1H), 5.70 (m, 1H), 5.09 (m, 1H), 4.84 (br s, 3H), 4.20 (s, 3H), 3.48 (br s, 12 H), 2.68 (br d, 1H, $J = 27.0$ Hz), 2.41 (s, 3H), 1.80 (br d, 1H, $J = 27.0$ Hz). ^{13}C NMR (4:1 CD$_3$CN/CD$_2$Cl$_2$; −50 °C): δ 202.6 (CO), 183.8 (C), 115.6 (CH), 62.5 (CH$_3$), 54.0 (CH), 53.0 (CH), 50.2 (CH$_2$), 25.0 (CH$_3$).

[Os(NH$_3$)$_5$(5,6-η^2-(1,3-dimethoxybenzene))](OTf)$_2$ (11). ^{1}H NMR (CD$_3$CN): δ 5.69 (d, 1H, $J = 7.2$ Hz), 5.54 (s, 1H), 5.06 (dd, 1H, $J = 8.1$, 7.2 Hz), 4.65 (d, 1H, $J = 8.1$ Hz), 4.12 (br s, 3H), 3.68 (s, 3H), 3.63 (s, 3H), 2.90 (br s, 12 H). ^{13}C NMR (CD$_3$CN): δ 170.4 (C), 155.8 (C), 93.4 (CH), 90.1 (CH), 66.7 (CH), 55.1 (CH), 54.3 (CH$_3$), 50.6 (CH$_3$). CV: $E_{p,a} = 0.37$ V. Anal. Calcd for C$_{10}$H$_{25}$O$_8$N$_5$S$_2$F$_6$Os : C, 16.88; H, 3.54; N, 9.84. Found: C, 16.42; H, 3.72; N, 9.94.

[Os(NH$_3$)$_5$(5,6-η^2-(3-methoxy-4H-anisolium))](OTf)$_3$ (11a). ^{1}H NMR (CD$_3$CN): δ 6.05 (s, 1H), 5.18 (t, 1H, $J = 7.5$, 7.2 Hz), 4.95 (d, 1H, $J = 7.5$ Hz), 4.74 (br s, 3H), 4.24 (s, 3H), 4.10 (s, 3H), 3.38 (br s, 12H), 2.70 (d, 1H, $J = 24.9$ Hz), 2.52 (dd, 1H, $J = 24,9$, 7.2 Hz). ^{13}C NMR (CD$_3$CN): δ 205.7 (CO), 193.5 (C), 93.6 (CH), 61.8 (CH$_3$), 60.2 (CH$_3$), 48.0 (CH), 45.5 (CH), 35.6 (CH$_2$). CV: $E_{p,a} = 1.25$ V. Anal. Calcd for C$_{11}$H$_{26}$O$_{11}$N$_5$S$_3$F$_9$Os: C, 15.33; H, 3.04; N, 8.13. Found: C, 15.07; H, 3.23; N, 8.30.

[Os(NH$_3$)$_5$(5,6-η^2-(3-methoxy-4H-anisolium)-d_1)](OTf)$_2$ (11a-d_1). ^{1}H NMR (CD$_3$CN): δ 6.03 (s, 1H), 5.15 (d, 1H, $J = 7.5$), 4.92 (d, 1H, $J = 7.5$ Hz), 4.66 (br s, 3H), 4.22 (s, 3H), 4.09 (s, 3H), 3.30 (br s, 12 H), 2.64 (s, 1H). ^{13}C NMR (CD$_3$CN): δ 205.3 (CO), 193.2 (C), 93.2 (CH), 61.3 (CH$_3$), 59.8 (CH$_3$), 47.6 (CH), 45.0 (CH), 34.8 (t, CD$_2$).

[Os(NH$_3$)$_5$(5,6-η^2-(3-(trifluoromethyl)anisole))](OTf)$_2$ (12). ^{1}H NMR (CD$_3$CN): δ 7.16 (d, 1H, $J = 5.1$ Hz), 5.76 (s, 1H), 5.09 (t, 1H, $J = 7.8$, 5.1 Hz), 4.23 (br s, 3H), 3.75 (s, 3H), 2.97 (br s, 12H). ^{13}C NMR (CD$_3$CN): δ 170.3 (C), 127.2 (CH), 124.7(q, $J = 300$ Hz), 122.9 (C), 87.9 (CH), 57.3 (CH), 55.43 (CH$_3$), 55.36 (CH). CV: $E_{p,a} = +0.70$ V. Anal. Calcd for C$_{10}$H$_{22}$N$_5$O$_7$S$_2$F$_9$Os: C, 16.02; H, 2.96; N, 9.34. Found: C, 15.71; H, 2.96; N, 9.36.

[Os(NH$_3$)$_5$(5,6-η^2-(3-(trifluoromethyl)-2H-anisolium))](OTf)$_3$ (12a). ^{1}H NMR (CD$_3$CN; −38 °C): δ 7.52 (m, 1H), 6.53 (m, 1H), 5.88 (m, 1H), 5.00 (br s, 3H), 4.36 (s, 3H), 3.67 (br s, 12H), 2.08 (d, 1H, $J = 27.9$ Hz), 0.75 (d, 1H, $J = 27.9$ Hz). ^{13}C NMR (CD$_3$CN; −38 °C): δ 215.1 (CO), 137.7 (C), 117.0 (CH), 64.8 (CH$_3$), 53.5 (CH), 53.4 (CH), 30.8 (CH$_2$), (CF$_3$ not observed).

[Os(NH$_3$)$_5$(5,6-η^2-(3-(trifluoromethyl)-6H-anisolium-d_1))](OTf)$_3$ (12a-d_1). ^{1}H NMR (CD$_3$CN; −40 °C): δ 7.50 (d, 1H, $J = 4.5$ Hz), 6.54 (t, 1H, $J = 5.4$, 4.8 Hz), 5.89 (d, 1H, $J = 6.0$ Hz), 5.07 (br s, 3H), 4.36 (s, 3H), 3.70 (br s, 12H), 2.36 (s, 1H). NOE: H(2), *cis*-NH$_3$ (3%).

[Os(NH$_3$)$_5$(5,6-η^2-(4-methoxy-6H-anisolium))](OTf)$_2$ (13a). ^{1}H NMR (CD$_3$CN; −38 °C): δ 6.10 (d, 1H, $J = 6.6$ Hz), 5.67 (d, 1H, $J = 6.6$ Hz), 5.07 (br s, 3H), 4.60 (s, 1H), 4.26 (s, 3H), 3.68 (br s, 12 H), 3.57 (s, 3H), 2.15 (d, 1H, $J = 29.4$ Hz), 0.88 (dd, 1H, $J = 29.4$, 1.2 Hz). ^{13}C NMR (CD$_3$CN; −38 °C): δ 216.8 (CO), 158.5 (C), 84.0 (CH), 63.7 (CH$_3$), 56.2 (CH), 55.6 (CH$_3$), 53.5 (CH), 31.7 (CH$_2$).

[Os(NH$_3$)$_5$(5,6-η^2-(4H-phenolium))](OTf)$_3$ (14a). ^{1}H NMR (CD$_3$-CN; −40 °C): δ 7.97 (br s, 1H), 7.51 (br d, 1H, $J = 8.1$ Hz), 6.54 (d, 1H, $J = 8.1$ Hz), 5.70 (t, 1H, $J = 6.9$ Hz), 5.05 (d, 1H, $J = 6.9$ Hz), 4.72 (br s, 3H), 3.44 (br s, 12H), 2.45 (dd, 1H, $J = 27.6$, 3.9 Hz), 1.55 (dd, 1H, $J = 27.6$, 6.9 Hz). ^{13}C NMR (CD$_3$CN; −40 °C): δ 198.3 (C), 161.3 (CH), 122.6 (CH), 56.7 (CH), 51.9 (CH), 34.2 (CH$_2$).