to the weighting scheme with an experimental instability factor, P, was used in the final stages of refinement ($P = 0.06$).[33] Non-hydrogen atoms were refined anisotropically except for some carbon atoms that were refined isotropically (see Table IV). Hydrogen atoms were not located. The relatively high shift to error ratio is probably due to thermal motion in the *t*-Bu groups. The maximum peak in the final difference Fourier map was 0.65 eÅ^{-3} and it was located 1.19 Å from C(20). Scattering factors were taken from ref 34. The correct absolute configuration for **2** was determined by anomolous dispersion techniques.

4: Crystals of **4** were grown from hexane solutions (-20 °C) and mounted in thin-walled glass capillaries under nitrogen. Unit cell parameters were obtained by carefully centering 25 reflections having 2θ values between 20.0° and 28.0°. The monoclinic space group $P2_1/c$ (No. 14) was uniquely determined by systematic absences ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$). Data were collected in the $+h,+k,\pm l$ quadrant. Details of the crystal data parameters and other relevant information are collected in Table I. The data were corrected for Lorentz and polarization effects. No absorption correction was made since none was deemed necessary. A 25% decay of the standard reflections occurred after 3500 reflections so a new crystal was mounted and data collection was resumed. This crystal also had a 25% decay of standards over the course of data collection and an anisotropic decay correction was applied. The observed structure factors of equivalent reflections were averaged. The structure was solved by direct methods (MULTAN) followed by successive cycles of difference Fourier maps followed by refinement. A non-Poisson contribution weighting scheme with $P = 0.06$ was used in the final stages of refinement. The Rh, Fe, P, and Na atoms were refined anisotropically and the remaining atoms isotropically. Hydrogen atoms were not located. The maximum peak in the final difference Fourier map had a height of 0.69 eÅ^{-3} and was located 1.15 Å from C(11).

(33) P is used in the calculation of $\sigma(I)$ to downweight intense reflections in the least-squares refinement. The function minimized was $\sum\omega(|F_o| - |F_c|)^2$ where $\omega = 4(F_o)^2/[\sum(F_o)^2]^2$, where $[\sum(F_o)^2]^2 = [S^2(C + R^2B) + (P(F_o)^2)^2]/Lp^2$, where S is the scan rate, C is the total integrated peak count, R is the ratio of scan time to background counting time, B is the total background count, and Lp is the Lorentz-polarization factor.

(34) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4.

Acknowledgment. We thank the National Science Foundation (Grants CHE 85-17759 and CHE84-02135), the Robert A. Welch Foundation (F-816), and the Texas Advanced Technology Research Program for support. R.A.J. thanks the Alfred P. Sloan Foundation for a fellowship (1985-1987).

Supplementary Material Available: Complete tables of bond lengths, angles, and thermal parameters for **2** and **4** and a view of the unit cell of **4** (10 pages); observed and calculated structure factor tables for **2** and **4** (34 pages). Ordering information is given on any current masthead page.

Substituent Effects on η^2-Coordinated Arene Complexes of Pentaammineosmium(II)

W. Dean Harman, Mikiya Sekine, and Henry Taube*

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. *Received November 19, 1987*

Abstract: Pentaammineosmium(II) reacts with substituted benzenes to yield complexes in which the arene is coordinated η^2 to the osmium. The surprising stability of these complexes is attributed to the high tendency of this metal center to back-bond. Unlike cationic η^6-arene complexes, both electron-donating and -withdrawing substituents on the ring stabilize the Os(II) with respect to arene dissociation. By oxidizing these compounds electrochemically, the stabilities of the Os(III)-arene analogues have also been investigated. For these complexes in which the back-bonding interaction has been diminished, electron-withdrawing substituents are found to destabilize the complex. Also attributable to π back-bonding are the relatively slow rates of tautomerization found in the osmium(II)-arene species.

The chemistry of arenes with transition-metal centers has developed considerably over the last two decades.[1a-c] Though a wealth of complexes have been studied in which the metal coordinates η^6 to the aromatic ligand, far less is known about the lower coordination modes. Recently, particular interest has been given to η^2-coordinated arenes because of their suspected role as intermediates in C-H activation,[2a-e,33] yet only a handful of these species have been isolated. Typically, η^2-arene complexes are unstable with respect to dissociation or deprotonation of the aromatic ligand. Their instability can in part be attributed to the loss of resonance energy experienced upon coordination.[1d]

Our interest in the reactivity of pentaammineosmium(II) with unsaturated ligands has recently led to the discovery of a stable η^2 complex of benzene.[3] This species, $[Os(NH_3)_5(\eta^2\text{-}C_6H_6)]^{2+}$ (**1**), is resistant to deprotonation, is stable as a triflate salt for months, and persists, even in aqueous solution, for many hours at room temperature. We felt pentaammineosmium(II) would lend itself nicely to a systematic study of this unusual mode of arene bonding, allowing us to explore the effect of a substituent on the coordination position and stability of the π-bound species. By exploitation of the facile one-electron oxidation of these materials, the study has been extended to η^2-coordinated arene complexes of Os(III) as well.

Experimental Section

Reagents: TMB = 1,2,3,4-tetramethylbenzene; Otf = $CF_3SO_3^-$; DMPP = 2,2-dimethylpropiophenone; DME = 1,2-dimethoxyethane; DMA = *N*,*N*-dimethylacetamide; TBB = *tert*-butylbenzene; NMP = *N*-methylpyrrolidinone; isn = isonicotinamide; py = pyridine.

Infrared spectra were recorded on an IBM 98 FTIR spectrometer and ^{13}C and ^1H NMR spectra on a Varian XL-400 spectrometer.[4] Electrochemical experiments were performed under argon with a PAR model 173 potentiostat driven by a PAR Model 175 universal programmer. Cyclic voltammograms were recorded from +1.0 to -1.5 V (NHE) with a Pt^0 working electrode (1 mm^2), a Pt^0 counter electrode, and a reference cell consisting of a Au^0 button in a DME solution containing $FeCp_2$

(1) (a) Silverthorn, W. E. *Adv. Organomet. Chem.* **1975**, *13*, 47. (b) Gastinger, R. G.; Klabunde, K. J. *Transition Met. Chem.* **1979**, *4*, 1. (c) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J. *Chem. Rev.* **1982**, *82*, 499. (d) Brauer, D. J.; Krüger, C. *Inorg. Chem.* **1977**, *16*, 884.

(2) (a) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 305. (b) Sweet, J. R.; Graham, W. A. G. *Organometallics* **1982**, *2*, 135. (c) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 4240. (d) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650. (e) Chatt, J.; Davidson, J. M. *J. Chem. Soc.* **1965**, 843.

(3) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 1883.

(4) All ^1H NMR spectra are presented in ppm shift from tetramethylsilane.

0002-7863/88/1510-5725$01.50/0 © 1988 American Chemical Society

Table I. ^{1}H NMR Data for Selected $[Os(NH_3)_5(\eta^2\text{-Arene})]^{2+}$ Complexes[a]

arene	isomer	T, °C	H_α	H_β	H_γ	cis-NH_3	trans-NH_3	other
C_6H_6		−87	5.22	7.25	6.55	3.51	4.80	
		24		6.45 (b)		3.47	4.75	
$PhCH_3$	2,3-η^2, 3,4-η^2	−45		unassigned		3.62	4.80	2.22 (s)
						3.70	4.88	2.39 (s)
p-$C_6H_4(CH_3)_2$		20	5.38 (b)		6.27 (b)	3.58	4.75	2.32 (s, 6 H)
		55	20	6.5 (vb)		3.45	4.75	2.32 (s)
				6.5, 6.2, 6.1 (b)		3.43	4.70	2.35 (s, 3 H)
$PhCH(CH_3)_2$	3,4-η^2	20	5.42 (t)	6.3, 6.8 (b)		3.43	4.70	1.21 (s, 6 H), 2.90 (m, 1 H)
$PhC(CH_3)_3$	3,4-η^2	20	5.21 (t)	6.3, 7.0 (b)		3.45	4.70	1.25 (s, 9 H)
TMB	5,6-η^2	20	5.42 (s)			3.55	4.75	2.36 (s, 6 H), 2.12 (s, 6 H)
PhCOPh		20				3.83	5.00	7.75 (d, 2 H), 7.60 (t, 2 H), 7.52 (t, 1 H)
	2,3-η^2	−80	5.75 (d)	7.75 (m)	7.15 (d)	3.75	4.87	as above
			5.50 (m)		6.62 (t)			
$PhCOC(CH_3)_3$		20		6.90 (b, 1 H)		3.71	4.87	1.29 (s, 9 H)
	2,3-η^2	−83	5.46 (d)	7.59 (m)	7.65 (d)	3.71	4.97	1.24 (s, 9 H)
			5.33 (m)		6.56 (t)			
	3,4-η^2	−83	5.40 (t)	8.42 (d)	6.91 (d)	3.61	4.80	1.35 (s, 9 H)
			5.33 (m)	7.33 (m)				
$PhCF_3$		52	5.74 (b, 2 H)	7.2, 6.4 (b)		3.63	4.90	
	3,4-η^2	−89	5.33 (t)	7.77 (d)	6.57 (d)	3.58	4.86	
			5.22 (m)	7.49 (m)				
PhPh		20		7.1 (b, 1 H)		3.55	4.73	7.28 (t, 1 H), 7.40 (t, 2 H), 7.60 (d, 2 H)
	3,4-η^2	−62	5.39 (b)	7.61 (b)	6.96 (b)	3.61	4.91	as above
			5.35 (b)	7.47 (b)				
$PhN(CH_3)_2$	2,3-η^2	20	5.38 (b)	6.62 (b)	5.60 (b)	3.57	4.70	2.88 (6 H)
			5.35 (b)		6.50 (b)			
		−80	5.17 (d)	6.49 (m)	5.40 (d)	3.61	4.81	2.92 (s, 3 H)
			5.20 (m)		6.33 (t)			2.55 (s, 3 H)
$PhNH_2$	2,3-η^2	20	5.10 (d)	6.4 (m)	5.58 (d)	3.58	4.75	4.98 (b, 2 H)
			5.32 (t)		6.4 (m)			
$PhOCH_3$	2,3-η^2	20	5.06 (d)	6.72 (m)	6.48 (t)	3.48	4.72	3.70 (s, 3 H)
			5.35 (t)		5.72 (d)			

[a] All spectra reported in ppm shift from TMS in acetone-d_6. Integrations are reported as number of protons per pentaammineosmium(II) unit.

separated from the main cell by Vycor frit. The reference was calibrated with the ferrocene/ferrocenium couple ($E^\circ \equiv 0.55$ V; NHE) kept in situ. The peak-to-peak separation for this couple was about 60 mV for all cyclic voltammograms reported. All potentials are reported vs the normal hydrogen electrode. Cyclic voltammograms taken at fast scan rates (1.0–500 V s^{-1}) were recorded on a Tektronix single-beam storage oscilloscope.

Line-shape analyses of NMR spectra were performed with a version of DNMR4 (available through the QCPE program) following conventional procedures. MNDO (modified neglect of diatomic overlap) calculations, which are described by Dewer and Thiel,[5] were carried out with the QCPE program No. 353 as outlined by Pople and Gordon,[6] assuming both fixed and optimized geometries.

Reagents. $[Os(NH_3)_5(Otf)](Otf)_2$ was synthesized as described by Lay et al.[7] Acetone was purified by vacuum distillation over B_2O_3,[8] Et_2O and DME were purified by distillation over NaK alloy, and MeOH was purified by distillation over $Mg(OMe)_2$ prepared in situ from Mg^0 and I_2 under argon.[9] DMA was dried over BaO, then refluxed for 24 h, and distilled from triphenylsilyl chloride.[9] The resulting material was then refluxed with CaH_2 for 24 h and distilled to remove traces of HCl. Benzonitrile and acetonitrile were distilled from CaH_2.[9] NaOtf was recrystallized from acetone and ether. Magnesium turnings were cleaned in a DME solution of iodine for 1 h followed by copious washing with DME and Et_2O. Benzene, toluene, TMB, TBB, and cumene were stirred over Na^0 for 24 h and then vacuum distilled. Anisole and aniline were distilled over CaH_2. 2,2-Dimethylpropiophenone (DMPP) and α,α,α-trifluorotoluene were distilled over P_2O_5. All other reagents were used as supplied. All solvents were deoxygenated by purging with argon, and reactions were carried out under argon atmosphere in a Vacuum Atmospheres Corp. glovebox.

Preparations. The synthesis and characterization of $[Os(NH_3)_5(\eta^2\text{-}C_6H_6)](Otf)_2$[3] (**1**) and $[Os(NH_3)_5(\eta^2\text{-TMB})](Otf)_2$[10] (**13**) have been previously described as have the complexes $[Os(NH_3)_5(\eta^2\text{-DMPP})](Otf)_2$ (**5**) and $[Os(NH_3)_5(\eta^2\text{-PhCOPh})](Otf)_2$ (**6**).[11] All of the complexes reported herein are found to be >90% pure on the basis of cyclic voltammetry and ^{1}H NMR. Attempts to obtain acceptable microanalyses were hampered by small amounts (5–10%) of binuclear impurities analogous to the complex $[(Os(NH_3)_5)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_6)]^{4+}$. Their formation is minimized by keeping the ligand in high concentration. ^{1}H NMR data for $[Os(NH_3)_5(\eta^2\text{-arene})]^{2+}$ are summarized in Table I. Typical yields range from 70 to 90%.

$[Os(NH_3)_5(2,3\text{-}\eta^2\text{-PhOCH}_3)](Otf)_2$ (2). $Os(NH_3)_5(Otf)_3$ (400 mg) was dissolved in a cosolvent mixture of 0.5 mL of DMA and 5 mL of DME. To this solution were added 3 mL of anisole and 1.5 g of activated magnesium. The mixture was stirred for 45 min and then filtered to remove traces of magnesium. When the filtrate was slowly added to 100 mL of CH_2Cl_2, a precipitate formed, which was collected, washed with CH_2Cl_2 and Et_2O, and dried under vacuum.

$[Os(NH_3)_5(N\text{-PhNH}_2)](Otf)_2$ (3a). $Os(NH_3)_5(Otf)_3$ (200 mg) was dissolved in a cosolvent mixture of 0.5 mL of DMA and 5.0 mL of DME. Freshly distilled aniline (3.0 mL) and 1.5 g of activated magnesium were added, and the reaction mixture was stirred for 3 h. During the course of the reduction period, a yellow solid precipitated, which was filtered and washed with 3 mL of acetone. The resulting solid was then dissolved in 50 mL of acetone and again filtered to achieve separation from the unreacted magnesium. Treating the filtrate with ether caused precipitation of a pale yellow solid, which was filtered, copiously washed with ether, and dried under vacuum. The product was recrystallized from acetone and ether.

$E_{1/2} = -0.58$ V (acetone/NaOtf). ^{1}H NMR (acetone-d_6): 7.32 (t, 2 H), 7.02 (t, 1 H), 7.05 (d, 2 H), 7.04 (b, 2 H), 3.78 (b, 12 H), 3.90 (b, 3 H).

$[Os(NH_3)_5(2,3\text{-}\eta^2\text{-PhNH}_2)](Otf)_2$ (3b). The arene isomer of the aniline complex was generated in solution through the slow conversion of (**3a**) in either DMSO or acetone. In DMSO the isomerization is virtually complete after 9 h. In acetone an equilibrium is reached after 3 h in which approximately 35% of $[Os(NH_3)_5(PhNH_2)]^{2+}$ is in its π-bound form.

$[Os(NH_3)_5(2,3\text{-}\eta^2\text{-PhN(CH}_3)_2)](Otf)_2$ (4). $Os(NH_3)_5(Otf)_3$ (200 mg) was dissolved in a cosolvent mixture of 0.5 mL of DMA and 10 mL of

(5) Dewer, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.
(6) Pople, J. A.; Gordon, M. *J. Am. Chem. Soc.* **1967**, *89*, 4253. Also, see: Fletcher, R.; Powell, M. J. D. *Comput. J.* **1963**, *6*, 163. Davidson, W. C. *Comput. J.* **1968**, *10*, 406.
(7) Lay, P.; Magnuson, R.; Sen, J.; Taube, H. *J. Am. Chem.* Soc. **1982**, *104*, 7658.
(8) Burfield, D. R.; Smithers, R. H. *J. Org. Chem.* **1978**, *43*, 3966.
(9) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Oxford: New York, 1980.
(10) Harman, W. D.; Taube, H. *Inorg. Chem.* **1987**, *26*, 2917.
(11) Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 2439. Also, see: Harman, W. D.; Fairlie, D. P.; Taube, H. *J. Am. Chem. Soc.* **1986**, *108*, 8223.

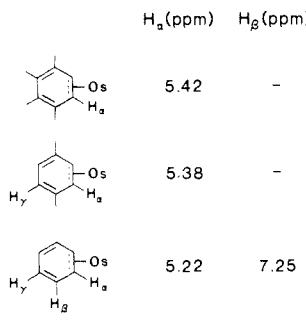

Figure 1. Representative ^1H NMR chemical shifts for α, β, and γ ring protons of $[Os(NH_3)_5(\eta^2\text{-arene})]^{2+}$ complexes.

DME. To this solution were added 1 mL of *N,N*-dimethylaniline and 1.5 g of activated magnesium. The mixture was stirred for 40 min and then filtered to remove traces of magnesium. The filtrate was slowly added to 100 mL of CH_2Cl_2, and the resulting precipitate was filtered, washed with CH_2Cl_2 and Et_2O, and dried under vacuum.

$[Os(NH_3)_5(3,4\text{-}\eta^2\text{-}PhCF_3)](Otf)_2$ (7). $Os(NH_3)_5(Otf)_3$ (200 mg) was dissolved in a cosolvent mixture of 0.5 mL of DMA and 10 mL of DME. To this solution were added 1 mL of α,α,α-trifluorotoluene and 1.5 g of activated magnesium. The mixture was stirred for 40 min and then filtered to remove pieces of magnesium. The brownish red filtrate is then slowly added to 100 mL of CH_2Cl_2. The resulting precipitate was filtered, washed with CH_2Cl_2 and Et_2O, and dried under vacuum.

$[Os(NH_3)_5(3,4\text{-}\eta^2\text{-}(Ph\text{-}Ph))](Otf)_2$ (8). $Os(NH_3)_5(Otf)_3$ (200 mg) was dissolved in a cosolvent mixture of 0.5 mL of DMA and 10 mL of DME. To this solution were added 1 g of biphenyl and 1.5 g of activated magnesium. The mixture was stirred for 45 min and then filtered to remove the magnesium. The red filtrate was then slowly added to 100 mL of CH_2Cl_2. The orange solid that formed was filtered, washed with CH_2Cl_2 and Et_2O, and dried under vacuum.

General Preparation of $[Os(NH_3)_5(\eta^2\text{-Ar})](Otf)_2$: Ar = Toluene (9), Cumene (10), *tert*-Butylbenzene (11), *p*-Xylene (12). In a typical preparation, 300 mg of $Os(NH_3)_5(Otf)_3$ was dissolved in a cosolvent mixture of 0.5 mL of DMA and 20 mL of DME. Activated magnesium (2.0 g) and 2.0 mL of the corresponding aromatic hydrocarbon were added, and the solution was stirred for 1 h and then filtered. The addition of the filtrate to 150 mL of CH_2Cl_2 resulted in a precipitate, which was collected, washed with CH_2Cl_2 and Et_2O, and dried under vacuum. Attempts to utilize this procedure with halobenzenes or nitrobenzene resulted in intractable mixtures.

Results

Structural Assignment. As we have previously reported,[3] the NMR spectrum of $[Os(NH_3)_5(\eta^2\text{-}C_6H_6)]^{2+}$ (**1**) at room temperature reveals a single, broadened arene resonance at 6.45 ppm. When **1** is cooled to −87 °C, however, this feature resolves into three well-defined signals at 7.25, 6.55, and 5.22 ppm. The majority of the analogous substituted benzene complexes display fluxional behavior similar to that of **1**, which can be frozen out at easily accessible temperatures (−85 to +25 °C). Homonuclear decoupled NMR spectra provide a convenient method of structural assignment. Typically, the temperature is adjusted in order to observe spin saturation exchange between tautomerically equivalent ring protons upon irradiation. This information together with chemical shift and homonuclear decoupling data provides a conclusive structural assignment.

When the arene protons for these η^2 species are compared, it is useful to classify them according to their proximity to the metal. Hence, the ring positions α, β, and γ are defined (Figure 1), where α refers to the sites closest to coordination. NMR spectra were recorded for a series of aliphatically substituted benzene complexes in which the proton assignments were unambiguous due to the symmetry of the ligand. As seen in Figure 1, η^2-complexation shifts the α protons upfield by about 2 ppm from the free-ligand resonance, an effect that is common to all the pentaammineosmium(II)–arene species. The shift observed for α protons is similar to that in olefin complexes; the cation $[Os(NH_3)_5CH_2CH_2]^{2+}$ displays an ethylene resonance 2.1 ppm upfield from that of the free ligand.[12]

(12) Harman, W. D. Ph.D. Thesis, Stanford University, 1987.

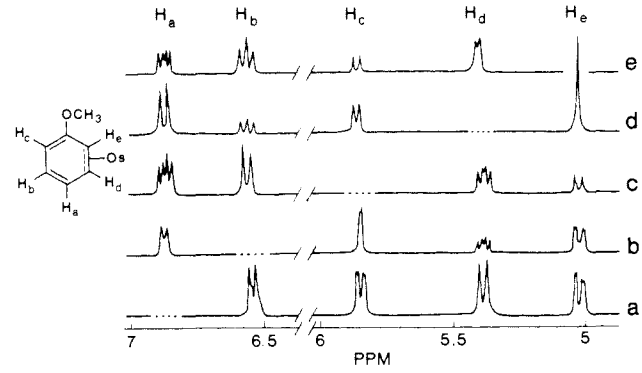

Figure 2. Homonuclear decoupling data for $[Os(NH_3)_5(\eta^2\text{-}CH_3OPh)]^{2+}$ in acetone-d_6.

Table II. Thermodynamic Tautomerization Parameters for Selected $[Os(NH_3)_5(\eta^2\text{-Arene})]^{2+}$ Complexes

arene	major isomer	minor isomer[a]	ΔG,[b] kcal/mol	T, °C
$PhOCH_3$	2,3-η^2	(3,4-η^2)	>2.5	20
$PhNH_2$	2,3-η^2	(3,4-η^2)	>1.8	20
$PhN(CH_3)_2$	2,3-η^2	(3,4-η^2)	>1.8	20
PhCOPh	2,3-η^2	(3,4-η^2)	1.0	−80
$PhCOC(CH_3)_3$	2,3-η^2	3,4-η^2	0.5	−80
$PhCH_3$	3,4-η^2	2,3-η^2	≈0	−45
$PhCF_3$	3,4-η^2	(2,3-η^2)		
PhPh	3,4-η^2	(2,3-η^2)		
$PhC(CH_3)_3$	3,4-η^2	(2,3-η^2)	>1.8	20

[a] Parentheses indicate minor isomer has not been postively identified. [b] ΔG refers to the difference in free energy between the major isomer and the (minor) isomer, which is closest in energy to the former.

Structural Assignment of $[Os(NH_3)_5(2,3\text{-}\eta^2\text{-}PhOCH_3)]^{2+}$. As an example of how the various η^2-arene isomers were identified by ^1H NMR, the relevant data are discussed in detail for the complex **2**. The NMR spectrum of this material shows broad ammine proton resonances at 3.27 and 4.51 ppm. The relatively large separation of these peaks is indicative of a pentaammineosmium(II) species hosting a π-bound ligand.[12] Five well-resolved ring proton resonances from 5–7 ppm indicate that the molecule does not tautomerize on the time scale of the NMR measurement. The corresponding homonuclear decoupling experiment is shown in Figure 2. Inspection of the data suggests that the ring protons have the vicinal ordering H_e–H_d–H_a–H_b–H_c, with H_c and H_e ortho to the methoxy group. The high-field chemical shifts of H_e and H_d indicate that these are α protons and, hence, metal coordination must occur at the 2,3-η^2-position of the ring. This assignment is further supported by the observed spin-saturation exchange[13] between the proton pairs H_e–H_c and H_d–H_b. For monosubstituted benzene complexes, a tautomerization symmetric to the substituent bond vector would equate both the ortho and meta proton pairs. For **2** this implies that the metal migrates between the 2,3-η^2- and chemically equivalent 5,6-η^2-position on the time scale of proton relaxation, T_1. An evaluation of this value for the ring protons[14] leads to a specific rate of 8.6×10^{-1} s^{-1} for this tautomerization at room temperature.[13] ($\Delta G^{\ddagger} = 17.2 \pm 0.1$ kcal/mol.) When the sample is cooled to −20 °C, homonuclear decoupling data no longer indicate spin-saturation exchange. By analogous reasoning, structures have been assigned to other η^2-arene complexes and are reported in Table II.

Tautomerization Processes. (a) $[Os(NH_3)_5(PhOCH_3)]^{2+}$: A 2,3-$\eta^2$ ⇄ 5,6-η^2 Exchange. When NMR spectra of **2** are taken at higher temperatures, the rate of exchange is increased enough so that the fluxional behavior is detected by direct measurement of the NMR spectrum. This results in both a severe broadening

(13) Sandström, J. *Dynamic NMR Spectroscopy*; Academic: London, 1982; p 53.

(14) T_1 values from 1.8 to 2.5 s^{-1} for the ring protons of the complexes investigated (see Table III). These values were measured with standard software supplied by Varian for the XL-400 spectrometer.

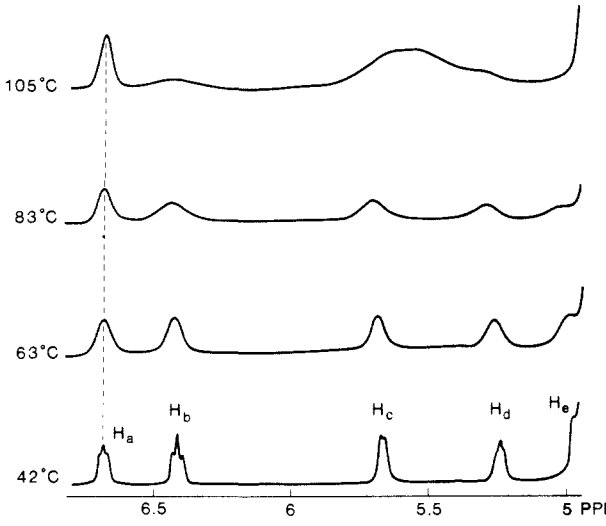

Figure 3. Variable-temperature ^{1}H NMR data for $[Os(NH_3)_5(\eta^2\text{-}CH_3OPh)]^{2+}$ in acetone-d_6.

and shifting of the rapidly exchanging ortho and meta resonances. In contrast, the chemical shift for the para proton remains constant with temperature, and this resonance broadens only slightly. Figure 3 shows NMR spectra for a sample of $[Os(NH_3)_5(2,3\text{-}\eta^2\text{-}PhOCH_3)](Otf)_2$ in DMF-d_7 from 42 to 105 °C.

If the various η^2 tautomers of **2** are in thermal equilibrium,[15] the free energy of isomerization can be obtained from the ratio of these species. At 25 °C, no other tautomer is detected by NMR, which places a lower limit of 2.5 kcal/mol on the stabilization of the 2,3-η^2 (or 5,6-η^2) species to other kinetically accessible forms. The invariance of the para proton resonance with temperature indicates that, even at 105 °C, the dominant isomer of **2** features coordination at the 2,3-η^2-position.

(b) $[Os(NH_3)_5(PhCF_3)]^{2+}$: A 3,4-$\eta^2$ ⇌ 4,5-η^2 Exchange. At −41 °C the only detectable isomer of **7** is one in which osmium is bound in the 3,4-η^2-position. Upon heating, the two ortho protons at 7.82 and 6.61 ppm coalesce into a single resonance at 7.19 ppm. The meta protons behave in a similar manner. The para proton remains relatively constant throughout the warming process, however, indicating tautomerization, which is dominated by a 3,4-η^2 ⇌ 4,5-η^2 exchange. Coalescence of the meta protons occurs close to 10 °C, which corresponds to a specific rate of 10^3 s^{-1} ($\Delta G^\ddagger$ = 12.5 ± 0.5 kcal/mol) for this process.

At 52 °C the para proton resonance has actually shifted downfield 0.36 ppm from the static value of 5.38 ppm recorded at −41 °C. Presumably, this is an indication of a limited population of another isomer at the higher temperature.[16]

(c) $[Os(NH_3)_5(DMPP)]^{2+}$: A 2,3-η^2 ⇌ 3,4-η^2 Isomerization. When a solution of **5** is cooled to −83 °C, homonuclear decoupled NMR spectra reveal that the 2,3-η^2- and 3,4-η^2-tautomers are present in an equilibrium ratio of 4:3, respectively. When it is warmed to 55 °C, the four ortho protons of these two isomers coalesce to a single resonance corresponding to their weighted average. The meta protons behave in a similar fashion. Unlike the first two examples, the chemical shift of the para proton at fast exchange does not resemble that of either the 2,3-η^2- or the 3,4-η^2-isomer (7.59 and 5.40 ppm, respectively) but rather their weighted average. Thus, at 24 °C, a single peak integrating to one proton per metal center is present at 6.90 ppm. At this temperature, although the ortho and meta protons of the dominant isomers are unresolved, the para protons have coalesced. This provides a lower limit for the rate of 2,3-η^2 ⇌ 3,4-η^2 isomerization by treating the para protons of the 2,3-η^2- and 3,4-η^2-isomers as an AB two-site exchange.[17] At 24 °C, a lower limit of 2 × 10^3 s^{-1} ($\Delta G^\ddagger$ < 13.2 kcal/mol) is calculated for this isomerization by approximating the forward and back rates as equal.

When methods similar to those used in the preceding examples are used, thermodynamic and kinetic parameters have been estimated for other arene–pentaammineosmium(II) complexes, and the results are summarized in Tables II and III.

Replacement of Arene on Os(II). A 2.5 mM solution of **1** is prepared with an excess of a substituting ligand (Table IV). The rate of benzene displacement is measured by cyclic voltammetry or ^{1}H NMR. In all cases the observed decay of **1** is overall first order and shows a 1:1 correspondence with the appearance of the substituted pentaammineosmium(II) product:

$$[Os(NH_3)_5(\eta^2\text{-}C_6H_6)]^{2+} + L \rightarrow [Os(NH_3)_5L]^{2+} + C_6H_6$$

This stoichiometry is confirmed in several deuteriated solvents where ^{1}H NMR spectra indicate that the formation of $[Os(NH_3)_5(solvent)]^{2+}$ is accompanied by that of free benzene. The specific rates of substitution for **1** under a variety of reaction conditions are reported in Table IV.

The substitution rates of other arene complexes have also been measured by ^{1}H NMR in acetone-d_6. In these experiments, the reaction is assumed to be overall first order, and the specific rates reported in Table V have been calculated accordingly.

Oxidation and the Rate of Substitution on Os(III). Figure 4 shows a cyclic voltammogram of **1** in CH_3CN. The first positive

Table III. Activation Parameters of Tautomerization for Selected $[Os(NH_3)_5(\eta^2\text{-Arene})]^{2+}$ Complexes

arene	tautomerization	k,[d] s^{-1}	$\Delta G^\ddagger$, kcal/mol
PhH	1,2-η^2 ⇌ 2,3-η^2	1 × 10^4 [a]	11.8 ± 0.1
$PhOCH_3$	2,3-η^2 ⇌ 5,6-η^2	9 × 10^{-1} [b]	17.2 ± 0.1
$PhN(CH_3)_2$	2,3-η^2 ⇌ 5,6-η^2	3[b]	16.4 ± 0.1
$p\text{-}C_6H_4(CH_3)_2$	2,3-η^2 ⇌ 5,6-η^2	7 × 10^1 [a]	14.7 ± 0.1
$PhCF_3$	3,4-η^2 ⇌ 4,5-η^2	3 × 10^3 [c]	12.5 ± 0.5
$PhCOC(CH_3)_3$	2,3-η^2 ⇌ 3,4-η^2	>1 × 10^3 [c]	<13.2

[a] Rate determined through band-shape analysis. [b] Rate determined through spin-saturation exchange. [c] Rate determined through coalescence expression. [d] All rates measured at 20 ± 2 °C.

Table IV. Arene Ligand Substitution Rates for $[Os(NH_3)_5(\eta^2\text{-}C_6H_6)]^{2+}$

ligand (L)	[L], M	k,[b] s^{-1}
$(CH_3)_2CO$	1.0[a]	5.8 × 10^{-6}
py	1.0[a]	1.2 × 10^{-5}
isn	0.1[a]	7.1 × 10^{-6}
CH_3CN	1.0[a]	1.8 × 10^{-5}
CH_3CN	0.5[a]	1.7 × 10^{-5}
$(CD_3)_2CO$	neat[c]	1.8 × 10^{-5}
CD_3CN	neat[c]	3.5 × 10^{-5}
$CH_3COPh\text{-}d_8$	neat[c]	2.5 × 10^{-6}

[a] DME solution with 10% DMA added to enhance solubility of $[Os(NH_3)_5(\eta^2\text{-}C_6H_6)](Otf)_2$. Rate measured by cyclic voltammetry. [b] All rates determined ±10% at 25 ± 3 °C. [c] Rate measured by ^{1}H NMR.

Table V. Arene Ligand Substitution Rates for Various $[Os(NH_3)_5(\eta^2\text{-Arene})]^{2+}$ Complexes

arene[a]	k,[b] 10^{-6} s^{-1}
$PhCF_3$	1.1
$PhOCH_3$	1.3
PhCOPh	<2
$PhN(CH_3)_2$	2.7
$PhC(CH_3)_3$	11
PhH	18
$p\text{-}C_6H_4(CH_3)_2$	48
TMB	380

[a] Measured in neat acetone-d_6. [b] All rates measured ±25% at 25 ± 3 °C.

(15) This assumption seems reasonable upon consideration of the activation data reported in Table III for both **2** and other complexes. The 2,3-η^2 ⇌ 5,6-η^2 exchange has a specific rate of 9 × 10^{-1} s^{-1} and would most likely occur through either a 1,2-η^2- or 3,4-η^2-intermediate.

(16) E.g., the 2,3-η^2-isomer.

(17) Reference 13, p 84.

(18) Scan rate 200 mV/s. Acetonitrile solution saturated with NaOtf.

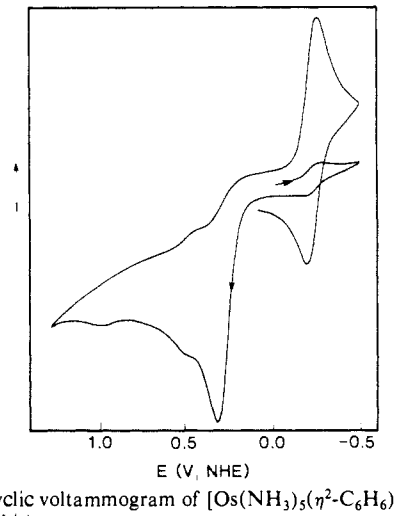

Figure 4. Cyclic voltammogram of $[Os(NH_3)_5(\eta^2\text{-}C_6H_6)]^{2+}$ in CH_3CN (v = 200 mV/s).

scan shows a sharp, chemically irreversible oxidation wave at +0.31 V corresponding to the one-electron oxidation of $[Os(NH_3)_5(\eta^2\text{-}C_6H_6)]^{2+}$. The return scan and the second forward scan produce a reversible couple at −0.22 V, indicating that the oxidation product $[Os(NH_3)_5(\eta^2\text{-}C_6H_6)]^{3+}$ rapidly substitutes to yield $[Os(NH_3)_5CH_3CN]^{3+}$:[11]

$$[Os(NH_3)_5(C_6H_6)]^{2+} - e^- \xrightarrow{E} [Os(NH_3)_5(C_6H_6)]^{3+} \xrightarrow[CH_3CN]{k_s} [Os(NH_3)_5CH_3CN]^{3+}$$

Cyclic voltammograms recorded from 50–500 mV/s show the expected scan rate dependence of $E_{p,a}$ for an E_rC_i reaction in the limit of purely kinetic control.[19] Cyclic voltammograms of **1** in an NMP solution saturated with TBAH were taken at 5 and 50 V/s. At the latter scan rate the oxidation of $[Os(NH_3)_5(\eta^2\text{-}C_6H_6)]^{2+}$ becomes chemically reversible. When the method of Nicholson and Shain is used,[20] the specific rate of benzene substitution on pentaammineosmium(III) (k_s) is determined to be $(3.5 \pm 0.3) \times 10^2$ s^{-1}. At low scan rates (50–500 mV/s), the substitution reaction following the oxidation of **1** has the effect of displacing the oxidation wave to negative values from the formal reduction potential.[19] When a correction for this effect is made, a formal potential of 0.15 ± 0.01 V is calculated for the reduction of $[Os(NH_3)_5(\eta^2\text{-}C_6H_6)]^{3+}$.

As with **1** cyclic voltammograms of the substituted benzene complexes indicate that their oxidation to Os(III) is followed by a rapid chemical reaction. In addition to arene substitution, many of these species undergo intramolecular isomerization to coordinate through the substituent of the aromatic ring. Thus, Os(III) complexes of aniline and *N,N*-dimethylaniline readily form nitrogen-bound species with pentaamineosmium(III),[21] whereas anisole[12] and phenone[11] ligands coordinate through the oxygen. The specific rates of substitution (k_s) and isomerization (k_i) for these Os(III) complexes are reported in Table VI.

Evidence for the Formation of $[Os(NH_3)_5(\eta^2\text{-mesitylene})]^{2+}$. Though attempts to isolate a mesitylene complex of pentaamineosmium(II) have been unsuccessful, cyclic voltammetric data suggest that complexation does occur. A DME solution of $Os(NH_3)_5(Otf)_3$ saturated with NaOtf shows a reversible redox couple with $E_{1/2}$ = −0.75 V (100 mV/s), corresponding to $[Os(NH_3)_5(DME)]^{3+/2+}$. When this solution is brought to 1 M in mesitylene, the oxidation wave vanishes and a new chemically irreversible peak at +0.17 V is observed. This feature, which is absent prior to the cathodic scan, appears at a potential consistent with those reported for the η^2-arene complexes in Table VI and is considered to be evidence for an analogous species.

(19) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods Fundamentals and Applications*; Wiley: New York, 1980; pp 452 and 222.
(20) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.
(21) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.*, in press.

Table VI. Reduction Potentials and Os(III)–Arene Substitution Rates for Selected $[Os(NH_3)_5(\eta^2\text{-Arene})]^{3+}$ Complexes

ligand	$E_{1/2}$,[a] V	k_s,[b] 10^2 s^{-1}	k_i, 10^2 s^{-1}	η^1 bond
benzene	0.15 ± 0.02	3.5 ± 0.3		
aniline	−0.02 ± 0.02	$\ll k_i$	4.5 ± 0.3	Os–N
$PhNH(CH_3)_2$	0.01 ± 0.02	$\ll k_i$	0.6 ± 0.1	Os–N
anisole	0.16 ± 0.02	3.2 ± 0.3	3.2 ± 0.3	Os–O
$PhC(CH_3)_3$	0.13 ± 0.02	3.0 ± 0.3		
$PhCF_3$	0.39 ± 0.05	60 ± 30		
$PhCOC(CH_3)_3$	0.22 ± 0.03			Os–O

[a] Vs NHE in NMP saturated with NaOtf.

Discussion

I. Relative Stabilities of η^2-Arene Isomers. Both steric and electronic effects must be considered in an attempt to understand how substituents affect the coordination position of the metal center. Of the substituents studied, the purely electronic effects are expected to be the least for alkyl radicals and, thus, the corresponding complexes are the best suited to reveal the steric component in determining the position of ligation. That these electronic effects are small is suggested by the fact that the 2,3-η^2- and 3,4-η^2-isomers for the toluene complex (**9**) are equally abundant at −45 °C. Although the NMR spectral assignments are incomplete, it is certain that both isomers show methyl resonances similar to that of the free ligand (2.35 ppm), indicating that coordination adjacent to the methyl group does not occur. The failure to find evidence for such a species is attributable to repulsion by the methyl group of the bulky pentaammine moiety in the 1,2-position. This effect is even more clearly demonstrated by the observations made with *p*-xylene as the ligand, where, to the limits of detection, the NMR spectrum can be fully accounted for by assuming only 2,3-ligation. Given the sensitivity of the method, we can conclude that a 1,2-isomer would comprise less than 5% of the total and therefore that $\Delta G^\ddagger$ for the 2,3-$\eta^2 \rightarrow$ 1,2-η^2 conversion is in excess of 1.8 kcal/mol at 25 °C. Still further evidence for the steric effect of a methyl group comes from the comparison of mesitylene and 1,2,3,4-tetramethylbenzene as ligands: although it can be generated and detected electrochemically, attempts to isolate a stable mesitylene complex have been unsuccessful presumably due to the high lability of the arene. In contrast, a stable complex of 1,2,3,4-tetramethylbenzene (**13**) has been isolated and characterized without difficulty. In the case of the isopropyl (**10**) or *tert*-butyl (**11**) substituents, steric effects apparently extend to the 2,3-positions as well, the only detectable isomer in solution being the 3,4-η^2-species. Hence, for aliphatically substituted benzene complexes, the metal coordination site can successfully be accounted for through purely steric arguments.

The arene complexes derived from the isostructural ligands *N,N*-dimethylaniline (**4**) and cumene (**10**) have little in common. At room temperature the dominant isomer of **10** exhibits coordination at the 3,4-η^2-position and is fluxional at room temperature ($\Delta G^\ddagger \approx$ 10–12 kcal/mol). In acetone, this complex undergoes substitution with a half-life on the order of hours. In contrast, **4** is static at room temperature, exists primarily as the 2,3-η^2-isomer, and substitutes with acetone over a period of several days. Thus, it is apparent that steric effects alone cannot account for the differing behavior of these complexes. Attempting to account for the electronic effects of a substituent with regard to the relative isomer stability, one must consider not only the factors influencing metal–ligand bond strength but also the effects that are inherent to the stability of the organic ligand. With regard to the former point, the affinity of pentaammineosmium(II) for π acids has been well documented,[11,12,22] and it seems reasonable to assume that the primary stabilization in the η^2-arene complexes arises from π back-bonding. In an effort to understand the dominant coordination site through the consideration of the antibonding orbitals, a series of MNDO calculations were performed that describe the full set of molecular orbitals for the free ligand (supplementary material). However, our attempts to correlate the metal bonding site with the coefficients of the LUMO for the free arene were

(22) Taube, H. *Pure Appl. Chem.* **1979**, *51*, 901.

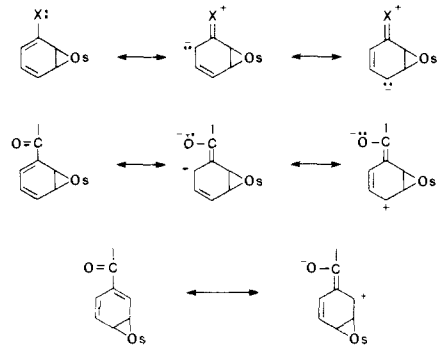

Figure 5. Resonance structures of η^2-bound substituted benzene ligands.

unsuccessful. Efforts to account for the ligation site solely through consideration of the σ-donating ability of the arene also failed.

As an alternative approach, we considered the stability of the "diene fragment" resulting from η^2 coordination (Figure 5). Crystallographic evidence for other η^2-bound arene species[23] supports this description, revealing alternating short and long C–C bonds in the ring. If the metal–olefin interaction is assumed to be equal for the 2,3-η^2- and 3,4-η^2-isomers of a monosubstituted benzene complex, the relative stability of these species would correspond to that of the resulting one- or two-substituted diene, respectively. Both qualitative evidence and theoretical considerations indicate that linear is more effective than cross conjugation.[24] By this argument, regardless of the nature of the conjugated substituent, the 2,3-η^2-species would always be electronically favored relative to its 3,4-isomer, which is contrary to observation. No single factor among those considered appears to be dominant in determining the relative isomer stabilities for these η^2-bound arene systems, a not surprising outcome when it is recognized that isomerization energies are typically less than a few kilocalories per mole, absent steric factors. A complete analysis would also have to take into account hydrogen bonding[25] between the substituent and the ammine protons. Crystal structure determinations would dirctly address this point.

II. Lability of the Arene Ligand. As we have previously reported,[3] over a period of hours the complex $[Os(NH_3)_5(\eta^2\text{-}C_6H_6)]^{2+}$ suffers arene displacement by a variety of ligands. The measurements reported in Table IV indicate that the corresponding rate is virtually independent of either solvent or incoming ligand, implying a substitution mechanism that is largely dissociative. If it is assumed the same mechanism holds for other arene complexes, a comparison of substitution rates under identical conditions would provide an indication of relative stabilities for these complexes. In Table V such data are reported for a series of arene complexes in acetone. The addition of methyl groups to benzene increases the rate in which the arene complex substitutes. The species derived from 1,2,3,4-tetramethylbenzene (**13**) reacts at a rate that is 20 times faster than that of the parent complex (**1**). Dines et al.[26] have shown for a series of monosubstituted benzene adducts of Cu^+ that their stability is predominantly dictated by the geometry and size of the ring substituents, and this is clearly a major factor in the pentaammineosmium(II) species as well.

By comparison of substitution rates in a common solvent for various η^2-bound monosubstituted benzene species, the stabilizing effect of a substituent can be estimated. In contrast to η^6-coordinated arene complexes,[27] which are typically destabilized by electron-withdrawing substituents, the data in Table V indicate that both electron-withdrawing and electron-donating groups

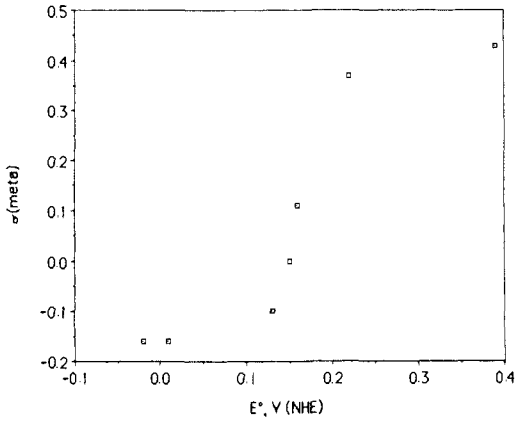

Figure 6. Correlation between the arene Hammett substituent constant and the III/II reduction potential for several $[Os(NH_3)_5(\eta^2\text{-arene})]^{3+}$ complexes.

stabilize the η^2 complex with respect to substitution. This outcome can be understood by considering the duality of the Os(II)–arene bond. Although the back-bonding interaction may be dominant, the dipositive metal ion acting as a Lewis acid also makes an important contribution. As MNDO calculations indicate, an electron-donating substituent on benzene interacts primarily with one of the π orbitals, raising its energy. This is expected to result in a stabilization of the metal–arene σ bond. A conjugated electron-withdrawing group, on the other hand, interacts primarily with a π^* orbital, lowering its energy. This would have the effect of stabilizing the π back-bond while leaving the σ bond virtually unaffected.

A significant contrast in behavior is seen when the labilities of the corresponding Os(III) complexes are considered. Here, the back-bonding interaction is greatly diminished relative to the divalent form, and, hence, the metal–arene bond is expected to be primarily a Lewis acid–base interaction. The stability is therefore expected to be a reflection of the basicity of the arene. The substitution rates for the osmium(III)–arene species support this notion (Table VI); relative to **1**, complexes containing electron-donating substituents are slower to dissociate whereas electron-withdrawing substituents appear to increase this rate. Cationic η^6-arene complexes show a similar substituent dependence.[27] The electrophilic metal centers in these species are stabilized by electron-releasing groups on the arene and destabilized by electron-withdrawing substituents.

This interpretation is further supported by comparison of the redox potentials for the corresponding (η^2-arene)pentaammineosmium species. As shown in Table VI, there is a general trend of increased stability for Os(III) over Os(II) as the substituent is changed from electron withdrawing to donating. Previously, several authors have noted the relationship between this parameter and π acidity for a variety of pentaammineruthenium(III) complexes.[28] The effect of a substituent on the reduction potential is best demonstrated by the correlation of $E°$ and σ_m, the Hammett constant,[29] which has been widely used to quantify the effect of a substituent on an aromatic ring (Figure 6).

It should be noted that, because the time scale of tautomerization is much faster than that for either substitution or cyclic voltammetry, it is impossible to differentiate the behaviors of the various tautomeric forms. For the purposes of these measurements, each of the osmium(II)–arene complexes acts as a single substance.

III. Tautomerization Rates. A striking difference between the (arene)pentaammineosmium(II) complexes and other species featuring an η^2-bound arene is in their rate of isomerization or exchange. Typically, measurement of the specific rate for these

(23) Browning, J.; Penfold, B. R. *J. Cryst. Mol. Struct.* **1974**, *4*, 335. Cobbledick, R. E.; Einstein, F. W. B. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 1849. Also, see: References 1c and 34.

(24) Streitwieser, A.; Heathcock, C. H. *Introduction to Organic Chemistry*; Macmillan: New York, 1976; pp 560–1. Fleming I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: London, 1982.

(25) Vinogradov, S. N.; Linnell, R. H. *Hydrogen Bonding*; Van Nostrand Reinhold: New York, 1971.

(26) Dines, M. B.; Bird, P. H. *Chem. Commun.* **1973**, 12.

(27) Reference 1a, p 56. Reference 1b, pp 9 and 10.

(28) Lehmann, H.; Schenk, K. J.; Chapuis, G.; Ludi, A. *J. Am. Chem. Soc.* **1979**, *101*, 6197.

(29) Since the coordination position in the electroactive species has not been established, σ_m is arbitrarily chosen over σ_p because the meta position is common to both 2,3-η^2- and 3,4-η^2-isomers. Also, see: Reference 28, p 947–9.

Table VII. Selected ^{1}H NMR Data for Various $[Os(NH_3)_5(\eta^2\text{-Arene})]^{2+}$ Complexes Reported as Their Difference from the Corresponding Free Ligand Value[a]

arene	isomer	H_α shift, ppm	H_β shift, ppm	H_γ shift, ppm
C_6H_6		−2.1	−0.1	−0.8
p-$C_6H_4(CH_3)_2$	2,3-η^2	−1.7		−0.8
PhPh	3,4-η^2	−2.0 (m)	−0.0 (m)	−0.7 (o)
		−1.9 (p)	−0.0 (o)	
$PhOCH_3$	2,3-η^2	−2.0 (m)	−0.2 (p)	−1.2 (o)
		−1.9 (o)		−0.8 (m)
$PhN(CH_3)_2$	2,3-η^2	−2.1 (m)	−0.2 (p)	−1.1 (o)
		−1.9 (o)		−0.8 (m)
$PhCOC(CH_3)_3$	2,3-η^2	−2.1 (m)	−0.1 (p)	−0.0 (o)
		−2.2 (o)		−0.9 (m)
$PhCOC(CH_3)_3$	3,4-η^2	−2.2 (m)	+0.7 (o)	−0.8 (o)
		−2.1 (p)	−0.2 (m)	
PhCOPh	2,3-η^2	−2.0 (o)	+0.1 (p)	−0.6 (o)
		−2.0 (m)		−0.9 (m)
$PhCF_3$	3,4-η^2	−2.3 (p)	+0.1 (o)	−1.1 (o)
		−2.3 (m)	−0.1 (m)	

[a] All spectra recorded in acetone-d_6.

tautomerizations is inaccessible by NMR techniques, even at low temperature, whereas, for the Os(II) complexes, room-temperature exchange is as slow as 1 s^{-1} (Table III). A popular mechanism proposed for tautomerization or "ring whizzing" in these complexes incorporates an arenium intermediate,[30] analogous to that postulated for electrophilic substitution of organic arenes. Unlike the other metal centers that have been reported to form stable η^2-arene complexes, pentaammineosmium(II) has saturated auxiliary ligands, which are unable to compete with the aromatic ligand for π electron density. As with other pentaammineosmium(II) species containing unsaturated ligands,[11,12,22] the dominant interaction is thought to be metal back-bonding. Relative to η^2 coordination, an arenium species would allow considerably less metal π overlap with the antibonding orbitals of the ligand; the slow tautomerization rates observed may be a reflection of this loss.

Many of the complexes reported in Table III display specific rates of tautomerization on the order of 10^3 s^{-1}, similar to that reported for **1**. In contrast are those that show a distinct preference for coordination at the 2,3-η^2-position. For these complexes, the 2,3-$\eta^2 \rightleftarrows$ 5,6-η^2 exchange is typically several orders of magnitude slower than that for benzene, corresponding to an increase of 4–5 kcal/mol for $\Delta G^\ddagger$. Presumably, a mechanism for this exchange includes the higher energy 3,4-η^2-isomer as an intermediate. Thus, the high-tautomerization barriers reported probably reflect the difference in energy between these two isomers.

Enhanced Substituent Conjugation. In Table VII proton resonances for several monosubstituted benzene complexes are reported as their differences from those of the corresponding free-ligand values. A high correlation exists for α protons of the different complexes; these resonances are found about 2 ppm lower than their free-ligand values and typically show upfield shifts within 0.2 ppm of that reported for **1**. There is also good agreement for the β and γ proton shifts *except* when the hydrogen is in an ortho position to the substituent. Relative to the unconjugated meta positions, the ortho γ proton of a 2,3-η^2-isomer is often shifted significantly upfield for the arenes with an electron-donating group or downfield for those cases in which an electron-withdrawing group is present. For a 3,4-η^2-isomer, the ortho β proton shows this behavior. Since the resonances in Table VII are reported relative to their free-ligand values, this suggests that the conjugated substituent has an enhanced interaction with the unsaturated ring when coordinated to Os(II). This effect can be rationalized by considering possible resonance structures of the resulting substituted diene system (Figure 5). When the arene double bonds are localized, η^2 coordination of osmium(II) apparently results in an increased interaction between the substituent and the *single conjugated* ortho position. Although less pronounced, these effects are also present for the para protons of 2,3-η^2-isomers. If the NMR data are an indication of increased electron density at an ortho position relative to the free ligand, complexes of electron-donating substituents may show an enhanced reactivity at this site toward electrophilic species, such as Friedel–Crafts reagents.

Coordination of a Second Metal Center. Crystallographic evidence for other η^2-arene complexes indicates that coordination disrupts the aromaticity of the ligand.[23] An interesting manifestation of this phenomenon is the tendency for the pentaammineosmium(II) complexes to form binuclear species. In an earlier publication[3] we reported that **1** was inherently unstable with respect to condensation:

$$2[Os(NH_3)_5(\eta^2\text{-}C_6H_6)]^{2+} \rightarrow [(Os(NH_3)_5)_2(\eta^2\text{:}\eta^2\text{-}\mu\text{-}C_6H_6)]^{4+} + C_6H_6$$

Unlike its forebear, this binuclear benzene complex shows virtually no substitution in acetone even after 1 week. On comparison of this material to **1**, it is seen that auxiliary coordination *stabilizes* the Os(II)–benzene bond even though statistical or electrostatic arguments would contradict this observation. Analogous binuclear materials with other ligands have been isolated as byproducts in the present work and are reported for at least one other metal system.[31] The remarkable stability of these complexes, relative to their mononuclear precursors, can be understood by considering the π localization found in the latter. Compared to the free arene, the diene-like fragment of the mononuclear species serves as a better ligand for an additional metal since the aromaticity has already been disrupted. This is further illustrated by considering the stability of the mixed-valence complex $[(Os(NH_3)_5)_2(C_6H_6)]^{5+}$. Contrary to electrostatic arguments, this species shows no detectable substitution after 0.5 h, reflecting a specific rate of dissociation that is at least 6 orders of magnitude slower than for $[Os(NH_3)_5(\eta^2\text{-}C_6H_6)]^{3+}$. This can be usefully compared to the limiting case of $[Os(NH_3)_5(CH_2CH_2)]^{3+}$, in which the ligand is truly olefinic; here, no substitution is detected in acetone, even after 24 h.[32]

The activation of an arene C–H bond has often been associated with an η^2-coordinated intermediate, and this has been verified in several cases.[2a–d] Although substituted benzenes coordinated to pentaammineosmium(II) appear, upon cursory inspection, to resist formation of an aryl complex, Cordone et al.[33] have observed this process, over time, for π-bound nitrogen heterocycles. Further investigation of the chemistry for these aromatic osmium(II) π complexes is certain to provide a better understanding of this activation process.

Acknowledgment. We gratefully acknowledge Rossella Cordone for her insight and helpful suggestions. Support of this work by National Science Foundation Grants CHE85-11658 and CHE84-14329 (400-MHz NMR) and National Institutes of Health Grant GM13638-20 is also gratefully acknowledged.

Registry No. 2, 115289-80-0; **3a**, 115245-78-8; **3b**, 115245-76-6; **4**, 115289-81-1; **7**, 115289-83-3; **8**, 115289-85-5; **9**, 115289-87-7; **10**, 115289-89-9; **11**, 115289-91-3; **12**, 115289-93-5; $[Os(NH_3)_5(\eta^2\text{-}C_6H_6)]^{2+}$, 107202-74-4; $[Os(NH_3)_5(3,4\text{-}\eta^2\text{-}PhCH_3)]^{2+}$, 115289-75-3; $[Os(NH_3)_5(5,6\text{-}\eta^2\text{-}TMB)]^{2+}$, 109242-79-7; $[Os(NH_3)_5(2,3\text{-}\eta^2\text{-}PhCOPh)]^{2+}$, 113161-71-0; $[Os(NH_3)_5(2,3\text{-}\eta^2\text{-}PhCOC(CH_3)_3)]^{2+}$, 115289-76-4; $[Os(NH_3)_5(3,4\text{-}\eta^2\text{-}PhCOC(CH_3)_3)]^{2+}$, 115289-77-5; $[Os(NH_3)_5(2,3\text{-}\eta^2\text{-}PhOPh)]^{2+}$, 115289-78-6; $[Os(NH_3)_5(Otf)](Otf)_2$, 83781-30-0; anisole, 100-66-3; aniline, 62-53-3; *N*,*N*-dimethylaniline, 121-69-7; α,α,α-trifluorotoluene, 98-08-8; biphenyl, 92-52-4; toluene, 108-88-3; cumene, 98-82-8; *tert*-butylbenzene, 98-06-6; *p*-xylene, 106-42-3.

Supplementary Material Available: Listings of MNDO calculations for several monosubstituted benzene complexes (4 pages). Ordering information is given on any current masthead page.

(30) See: References 2a, 2b, and 3. Also, see: Cotton, F. A. *Acc. Chem. Res.* **1968**, *1*, 257.

(31) van der Heijden, H.; Orpen, A. G.; Pasman, P. *Chem. Commun.* **1985**, 1576.

(32) Harman, W. D., unpublished results.

(33) Cordone, R.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 8101.