Characterization and Isomerization of η^2-Naphthalene and η^2-Phenanthrene Complexes of Pentaammineosmium(II)

Mark D. Winemiller, Beth A. Kelsch, Michal Sabat, and W. Dean Harman*

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901[⊗]

Received March 24, 1997

A series of substituted-naphthalene complexes have been synthesized of the form $[Os(NH_3)_5(\eta^2\text{-L})](OTf)_2$ (where L = 1-methylnaphthalene, 2-methylnaphthalene, 2-methoxynaphthalene, 2-hydroxynaphthalene, 1-methoxynaphthalene, 1-hydroxynaphthalene, 1-acetonaphthone, 2-acetonaphthone, and phenanthrene), with two or more linkage isomers identified for several of these complexes. The ratio of these isomers changes over time in solution (acetone-d_6) and eventually reaches dynamic equilibrium. The final equilibrium ratios and the associated specific rates are reported. In several cases, protonation of an isomer mixture generates a single naphthalenium species, which upon deprotonation provides the original η^2-naphthalene complex as a single set of ring isomers.

Introduction

Electrophilic aromatic substitutions are among the most widely used and well-studied reactions in organic chemistry.[1] Our interest in the ability of the pentaammineosmium(II) system to enhance this reaction[2,3] and to promote sequential electrophile/nucleophile addition reactions with arenes[4,5] has led us to consider the possibility of such transformations with polyaromatic hydrocarbons. For naphthalene, we have recently shown that complexation at C1 and C2 by pentaammineosmium(II) greatly enhances the basicity at C4 of the hydrocarbon,[6] and preliminary data indicate that carbon electrophiles also readily add to this position. For the parent naphthalene, the choice of coordination is unambiguous, as is the position of electrophilic addition. With substituted naphthalenes, however, multiple coordination sites are possible. Our intention in this study is to explore the kinetic and thermodynamic regioselectivity of η^2-coordination for a series of monosubstituted naphthalene complexes and to draw from these observations a set of guidelines for the selective preparation of individual isomers.

Experimental Section

General Procedure for the Preparation of η^2-Naphthalene Complexes. Activated magnesium (788 mg) was added to a solution of $[Os(NH_3)_5(OTf)](OTf)_2$[7] (462 mg, 0.64 mmol) in *N*,*N*-dimethylacetamide (DMAc; (1.36 g) and an excess of ligand (10−20 equiv). The heterogeneous mixture was stirred for 0.5 h. The reaction mixture was filtered through a fritted glass funnel into stirred CH_2Cl_2 (150 mL), and the resulting solid was filtered and washed with CH_2Cl_2 and then ether to yield the pentaammineosmium(II) complexes in 80−90% yield. Characterization data for selected compounds follow. Complete characterization data may be found in the Supporting Information.

$[Os(NH_3)_5((3,4\text{-}\eta^2)\text{-1-methylnaphthalene})](OTf)_2$ (1A). ^{1}H NMR (300 MHz, acetone-d_6): δ 7.74 (m, 1H), 7.63 (m, 1H), 7.38−7.30 (m, 3H), 5.40 (d, 1H, J = 7.8 Hz), 5.16 (dd, 1H, J = 7.8, 5.1 Hz), 4.80 (br s, 3H), 3.41 (br s, 12H), 2.42 (s, 3H). ^{13}C NMR (75 MHz, acetone-d_6): δ 144.00 (C), 134.52 (CH), 134.44 (C), 132.49 (C), 127.72 (CH), 127.26 (CH), 125.78, (CH), 124.43 (CH), 56.89 (CH), 55.44 (CH), 19.23 (CH_3).

$[Os(NH_3)_5((5,6\text{-}\eta^2)\text{-1-methylnaphthalene})](OTf)_2$ (1B). ^{1}H NMR (300 MHz, acetone-d_6): δ 7.55 (d, 1H, J = 7.2 Hz), 7.35 (dd, 1H, J = 9.0, 5.1 Hz), 7.20−7.09 (m, 3H), 5.40 (d, 1H, J = 7.5 Hz), 5.22 (dd, 1H, J = 7.5, 5.1 Hz), 4.81 (br s, 3H), 3.41 (br s, 12H), 2.46 (s, 3H). ^{13}C NMR (75 MHz, acetone-d_6): δ 143.51 (C), 136.34 (CH), 134.36 (C), 129.98 (C), 127.44 (CH), 127.26, (CH), 125.45 (CH), 118.42 (CH), 58.19 (CH), 55.80 (CH), 19.74 (CH_3). Cyclic voltammetry: $E_{p,a}$ = 0.60 V. Anal. Calcd for $C_{13}H_{25}N_5O_6S_2F_6Os$: C, 21.82; H, 3.52; N, 9.79. Found: C, 21.43; H, 3.27; N, 9.68.

$[Os(NH_3)_5((3,4\text{-}\eta^2)\text{-2-methoxynaphthalene})](OTf)_2$ (3A). ^{1}H NMR (300 MHz, acetone-d_6): δ 7.61 (d, 1H, J = 7.2 Hz), 7.35 (d, 1H, J = 7.8 Hz), 7.18 (dd, 1H, J = 7.2 Hz), 7.11 (dd, 1H, J = 7.2 Hz), 6.15 (d, 1H, J = 1.8 Hz), 5.48 (d, 1H, J = 8.1 Hz), 5.03 (dd, 1H, J = 8.1, 1.8 Hz), 4.84, (br s, 3H), 3.84 (s, 3H), 3.47 (br s, 12H). ^{13}C NMR (75 MHz, acetone-d_6): δ 167.43 (C), 138.21 (C), 137.75 (C), 126.49 (CH), 126.09 (CH), 125.99 (CH), 124.77 (CH), 92.62 (CH), 56.56 (CH), 55.36 (CH), 50.93 (CH_3). Cyclic voltammetry: $E_{p,a}$ = 0.62 V. Anal Calcd for $C_{13}H_{25}N_5O_7S_2F_6Os$: C, 21.34; H, 3.44; N, 9.57. Found: C, 20.95; H, 3.55; N, 9.66.

$[Os(NH_3)_5((7,8\text{-}\eta^2)\text{-2-methoxynaphthalene})](OTf)_2$ (3B′) and $[Os(NH_3)_5((5,6\text{-}\eta^2)\text{-2-methoxynaphthalene})](OTf)_2$ (3B). ^{1}H NMR (300 MHz, acetone-d_6): δ 7.64−7.59 (m, 1H), 7.38−7.27 (m, 1H), 7.20−7.07 (m, 4H), 7.03−6.82 (m, 4H), 5.39 (d, 1H, J = 7.5 Hz), 5.38 (d, 1H, J = 7.2 Hz), 5.20 (dd, 1H, J = 7.2, 5.7 Hz), 5.16 (dd, 1H, J = 7.2, 5.4 Hz), 4.85 (br s, 6H), 3.85 (s, 3H), 3.81 (s, 3H), 3.48 (br s, 24H).

$[Os(NH_3)_5((3,4\text{-}\eta^2)\text{-2-hydroxynaphthalene})](OTf)_2$ (4A). ^{1}H NMR (500 MHz, acetone-d_6): δ 8.90 (br s, 1H), 7.59 (d, 1H, J = 7.5 Hz), 7.22 (d, 1H, J = 7.5 Hz), 7.06 (m, 2H), 6.16 (s, 1H), 5.49 (d, 1H, J = 8.0 Hz), 5.05 (d, 1H, J = 8.0 Hz), 4.84 (br s, 3H), 3.48 (br s, 12H). ^{13}C NMR (75 MHz, acetone-d_6):

[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1997.

(1) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry Part A: Structure and Mechanism*; Plenum Press: New York, 1990.
(2) Kolis, S. P.; Kopach, M. E.; Liu, R.; Harman, W. D. *J. Org. Chem.* **1997**, *62*, 130.
(3) Kopach, M. E.; Gonzalez, J.; Harman, W. D. *J. Am. Chem. Soc.* **1991**, *113*, 8972.
(4) Gonzalez, J.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1993**, *115*, 8857.
(5) Kolis, S. P.; Gonzalez, J.; Bright, L. M.; Harman, W. D. *Organometallics* **1996**, *15*, 245.
(6) Winemiller, M. D.; Kopach, M. E.; Harman, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 2096.
(7) Lay, P. A.; Magnuson, R. H.; Taube, H. *Inorg. Synth.* **1986**, *24*, 269.

S0276-7333(97)00244-6 CCC: $14.00

δ 165.06 (C), 138.05 (C), 133.71 (C), 126.90 (CH), 126.33 (CH), 125.46 (CH), 124.47 (CH), 95.36 (CH), 57.71 (CH), 51.26 (CH). Cyclic voltammetry: $E_{p,a} = 0.63$ V. Anal. Calcd for $C_{12}H_{23}N_5O_7S_2F_6Os$: C, 20.08; H, 3.23; N, 9.76. Found: C, 19.84; H, 2.91; N, 9.51.

[Os(NH$_3$)$_5$((3,4-η^2)-1*H*-naphth-2-one](OTf)$_2$ (4K). ^{1}H NMR (500 MHz, acetone-d_6): δ 7.48 (m, 1H), 7.26 (m, 1H), 7.13 (m, 2H), 5.59 (d, 1H, $J = 7.5$ Hz), 5.19 (br s, 3H), 4.81 (d, 1H, $J = 7.5$ Hz), 3.69 (br s, 12H), 3.06 (d, 1H, $J = 24$ Hz), 2.49 (d, 1H, $J = 24$ Hz). ^{13}C NMR (75 MHz, acetone-d_6): δ 210.33 (C), 139.61 (C), 131.04 (C), 129.81 (CH), 128.50 (CH), 127.11 (CH), 126.76 (CH), 54.62 (CH), 52.27 (CH), 42.07 (CH_2). Cyclic voltammetry: $E_{1/2} = 0.88$ V.

[Os(NH$_3$)$_5$((2,3-η^2)-4*H*-naphth-1-one)](OTf)$_2$(6K). ^{1}HNMR (300 MHz, CD_3CN): δ 7.90 (d, 1H, $J = 7.5$ Hz), 7.48 (m, 1H), 7.33 (m, 2H), 4.61 (m, 1H), 4.38 (br s, 3H), 4.33 (d, 1H, $J = 7.5$ Hz), 3.76 (dd, 1H, $J = 21.6$, 4.8 Hz), 3.17 (d, 1H, $J = 21.9$ Hz), 3.02 (br s, 12H). ^{13}C NMR (75 MHz, CD_3CN): δ 199.6 (C), 141.5 (C), 134.0 (CH), 133.2 (C), 129.8 (CH), 127.7 (CH), 127.0 (CH), 53.9 (CH), 51.9 (CH), 31.2 (CH_2).

[Os(NH$_3$)$_5$((3,4-η^2)-1-acetonaphthone)](OTf)$_2$ (7A). ^{1}H NMR (300 MHz, acetone-d_6): δ 8.53 (d, 1H, $J = 7.2$ Hz), 8.39 (d, 1H, $J = 5.4$ Hz), 7.76 (dd, 1H, $J = 7.5$, 1.5 Hz), 7.35 (m, 1H), 7.27 (m, 1H), 5.69 (d, 1H, $J = 7.2$ Hz), 5.39 (dd, 1H, $J = 7.2$, 5.4 Hz), 4.99 (br s, 3H), 3.61 (br s, 12H), 2.51 (s, 3H). ^{13}C NMR (75 MHz, CD_3CN): δ 200.89 (C), 148.19 (CH), 142.91 (C), 128.37 (CH), 128.07 (C), 127.65 (CH), 127.30 (CH), 126.57 (CH), 123.70 (C), 58.81 (CH), 52.69 (CH), 29.28 (CH_3). Cyclic voltammetry: $E_{p,a} = 0.77$ V. Anal. Calcd for $C_{60}H_{65}N_5OB_2Os$: C, 66.48; H, 6.04; N, 6.46. Found: C, 66.69; H, 6.14; N, 6.97.

[Os(NH$_3$)$_5$(η^2(*C,O*)-1-acetonaphthone)](OTf)$_2$ (7K), [Os(NH$_3$)$_5$((7,8-η^2)-1-acetonaphthone)](OTf)$_2$ (7B′), and [Os(NH$_3$)$_5$((5,6-η^2)-1-acetonaphthone)](OTf)$_2$ (7B). ^{1}H NMR (300 MHz, acetone-d_6): δ 8.03 (d, 1H, $J = 7.2$ Hz), 7.91 (d, 1H, $J = 7.5$ Hz), 7.85 (m, 1H), 7.80 (d, 1H, $J = 7.8$ Hz), 7.72 (m, 1H), 7.67 (d, 1H, $J = 7.5$ Hz), 7.61 (d, 1H, $J = 9.0$ Hz), 7.53 (m, 1H), 7.44−7.23 (m, 8H), 7.05 (d, 1H, $J = 9.0$ Hz), 5.91 (d, 1H, $J = 7.5$ Hz), 5.59 (br s, 3H), 5.46 d, 1H, $J = 7.2$ Hz), 5.29 (dd, 1H, $J = 7.8$, 5.1 Hz), 5.24 (dd, 1H, $J = 7.8$, 4.8 Hz), 4.89 (br s, 6H), 3.96 (br s, 12H), 3.48 (br s, 24H), 2.68 (s, 3H), 2.60 (s, 3H), 2.10 (s, 3H).

[Os(NH$_3$)$_5$((1,2-η^2)-phenanthrene)](OTf)$_2$ (9A) and [Os(NH$_3$)$_5$((3,4-η^2-phenanthrene)](OTf)$_2$ (9A′). ^{1}H NMR (300 MHz, acetone-d_6): δ 8.85 (d, 1H, $J = 8.1$ Hz), 8.45 (d, 1H, $J = 8.4$ Hz), 7.96−7.88 (m, 4H), 7.75 (d, 1H, $J = 7.2$ Hz), 7.69 (d, 1H, $J = 8.1$ Hz), 7.62−7.52 (m, 6H), 7.48 (d, 1H, $J = 7.2$ Hz), 7.14 (d, 1H, $J = 9.3$ Hz), 6.50 (d, 1H, $J = 7.5$ Hz), 5.67 (d, 1H, $J = 7.5$ Hz), 5.51 (m, 1H), 5.43 (m, 1H), 4.83 (br s, 3H), 4.75 (br s, 3H), 3.49 (br s, 24H). Cyclic voltammetry: $E_{p,a} = 0.47$ V.

[Os(NH$_3$)$_5$((9,10-η^2)-phenanthrene)](OTf)$_2$ (9B). ^{1}H NMR (300 MHz, acetone-d_6): δ 8.32 (d, 2H, $J = 8.1$, 1.8 Hz), 7.75 (d, 2H, $J = 7.2$, 1.8 Hz), 7.44−7.33 (m, 4H), 5.45 (s, 2H), 4.86 (br s, 3H), 3.35 (br s, 12H). ^{13}C NMR (75 MHz, acetone-d_6): δ 143.05 (C), 129.25 (C), 129.10 (CH), 127.73 (CH), 126.32 (CH), 123.77 (CH), 53.59 (CH). Cyclic voltammetry: $E_{1/2} = 0.70$ V. Anal. Calcd for $C_{16}H_{25}N_5O_6S_2F_6Os$: C, 25.56; H, 3.35; N, 9.32. Found: C, 25.01; H, 3.32; N, 9.38.

[Os(NH$_3$)$_5$((5,6,7-η^3)-8H-1-methylnaphthalenium)](OTf)$_3$ (1BH). Complex **1BH** was prepared from the *in situ* protonation of **1** (63 mg, 0.088 mmol), with HOTf, (233 mg, 1.55 mmol) in 555 mg of CD_3CN. ^{1}H NMR (300 MHz, CD_3CN): δ 7.48 (d, 1H, $J = 6.9$ Hz), 7.35 (dd, 1H, $J = 7.8$, 7.5 Hz), 7.24 (d, 1H, $J = 7.8$ Hz), 6.43 (dd, 1H, $J = 6.0$, 2.7 Hz), 6.22 (dd, 1H, $J = 6.3$, 2.4 Hz), 5.36 (dd, 1H, $J = 6.3$, 6.0 Hz), 5.04 (br s, 3H), 3.72 (br s, 12H), 2.23 (s, 3H), 2.23 (dd, 1H, $J = 24$, 2.4 Hz), 1.96 (dd, 1H, $J = 24$, 2.4 Hz). ^{13}C NMR (75 MHz, CD_3CN): δ 139.19 (C), 133.49 (CH), 131.43 (C), 130.75 (CH), 129.94 (C), 128.80 (CH), 86.91 (CH), 83.04 (CH), 75.46 (CH), 29.07 (CH_2), 18.60 (CH_3).

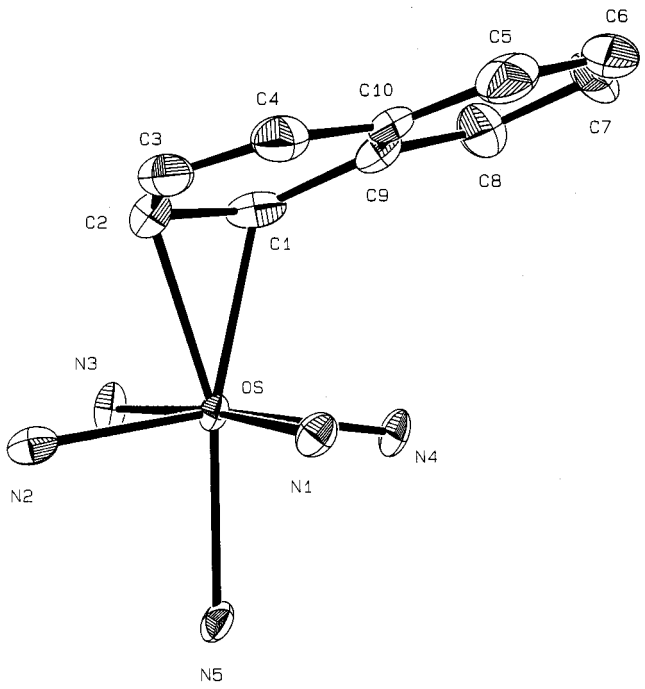

Figure 1. ORTEP drawing of the complex [Os(NH$_3$)$_5$(naphthalene)]$^{2+}$ showing an increase and decrease in the aromatic character of the uncoordinated and coordinated rings, respectively. Bond distances and angles: C1−C2, 1.40(2) Å; C2−C3, 1.45(2) Å; C3−C4, 1.35(2) Å; C5−C6, 1.38(2) Å; C6−C7, 1.38(2) Å; C7−C8, 1.39(2) Å; C8−C9, 1.38(2) Å; C9−C10, 1.39(2) Å; Os−C1, 2.18(1) Å; Os−C2, 2.19(1) Å; C2−C3−C4, 120(1)°; Os−C1−C2, 71.4(6)°.

Results

The one-electron reduction of $Os(NH_3)_5(OTf)_3$ in the presence of various substituted polycyclic aromatic hydrocarbons provides complexes of the form [Os(NH$_3$)$_5$(η^2-L)](OTf)$_2$ (where L = 1-methylnaphthalene (**1**), 2-methylnaphthalene (**2**), 2-methoxynaphthalene (**3**), 2-hydroxynaphthalene (**4**), 1-methoxynaphthalene (**5**), 1-hydroxynaphthalene (**6**), 1-acetonaphthone (**7**), 2-acetonaphthone (**8**), and phenanthrene (**9**)) in good yields. These complexes exhibit ^{1}H NMR spectra (300 MHz) showing well-resolved resonances at 23 °C. The parent complex [Os(NH$_3$)$_5$(η^2-naphthalene)](OTf)$_2$ was also synthesized by established procedures,[8] and its structure was determined using X-ray diffraction. An ORTEP drawing of the corresponding cation (Figure 1) confirms that the metal is η^2-coordinated at C1 and C2 with the metal-ligand bond oriented approximately perpendicular to the plane of the naphthalene. The C1−C2 bond length has been elongated from 1.37 to 1.40(2) Å upon coordination, indicating loss of double-bond character, while the C3−C4 bond length has been marginally reduced to 1.35(2) Å. In contrast, the uncoordinated ring shows distortions upon complexation, indicating an *increase* in aromatic character. In particular, the C6−C7 bond length has been reduced from 1.45 to 1.38(2) Å, a value within experimental error for the C−C bond length of benzene.

Characterization of Substituted η^2-Naphthalene Complexes. ^{1}H NMR data for naphthalene complexes **1**−**8** and phenanthrene **9** indicate that, in general, kinetic binding selectivities are poor; often the product

(8) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 7555.

isolated from the above complexation procedure contains three or more isomers. In acetone-d_6 solution at 26 °C, the ratio of intraannular isomers remains constant over a period of days. The half-life of this isomerization at 26 °C is on the order of seconds to minutes, and dynamic equilibrium is established during the complexation procedure (<1 h). In contrast, interannular isomerizations are slow, taking hours to days to reach equilibrium at 26 °C. Using this as a guideline, mixtures of isomers are assigned where possible from ^{1}H, ^{13}C, COSY, and {^{13}C} DEPT data.

In several cases, complex spectra of isomeric mixtures of the naphthalene complexes are simplified by briefly exposing the sample to a catalytic amount of acid (~0.05 M HOTf; CH_3CN). Under these conditions, equilibrium mixtures are obtained that are identical with those obtained when the sample is allowed to stand for 1 week or more in solution. The outcome is very different when the naphthalene sample is treated with a much higher concentration of triflic acid (>1 M) followed by an excess of Hünig's base (DIEA). Under these conditions, the system is arrested far from equilibrium where, in some cases, a single isomer dominates. Related studies with arene and aromatic heterocycle complexes of pentaammineosmium(II) have determined that the metal generally avoids binding substituted carbons. Thus, for 1- or 2-monosubstituted naphthalene complexes, in which four different binding sites are possible that maintain full aromaticity in the uncoordinated ring, only three ring-bound isomers are ever observed. We assume that the missing isomer is the 1,2-η^2 form.

Treatment of a solution of the 1-methylnaphthalene complex (**1A**,**B**; Figure 2) with HOTf (1.5 M in CH_3CN at −40 °C) followed by deprotonation with DIEA (−40 °C), gives the single isomer **1B**. A ^{1}H NMR spectrum of this complex shows two bound (5.40 and 5.22 ppm) and five unbound methine protons and cis and trans ammine signals typical of η^2-arene complexes of pentaammineosmium(II).[8] The ^{13}C NMR spectrum closely matches that of the previously reported η^2-naphthalene complex, with bound carbon resonances at 58.2 and 55.8 ppm.[6] When a solution of isomer **1B** is observed using ^{1}H NMR (acetone-d_6) over several days, signals for the second isomer **1A** gradually appear with a specific rate of $(2.8 \pm 0.5) \times 10^{-6}$ s^{-1} (26 °C). Characteristic ^{1}H and ^{13}C NMR spectral data for **1A** include proton resonances at 5.40 and 5.16 ppm and ^{13}C features at 56.9 and 55.4 ppm. After 7 days, an equilibrium ratio for **1A**:**1B** of approximately 5:4 is established, and no further change is seen after 23 days. When a fresh solution containing only **1B** is prepared and treated with a catalytic amount of HOTf (0.5 equiv; 0.05 M) in CH_3CN, ^{1}H NMR data indicate that the system immediately establishes the same equilibrium ratio as that obtained in acetone-d_6 after 30 days. Given that the two isomers are slow to reach equilibrium in the absence of acid, they are assigned to different rings in the two most unhindered positions (3,4-η^2 and 5,6-η^2). These two isomers are not distinguishable without taking into account their relationship to the compound **1BH** *(vide infra)*.

In a procedure identical with that used for the 1-methylnaphthalene complex, the three-component mixture of 2-methylnaphthalene complexes (**2A**,**B**,**B′**; Figure 3) can be treated with an excess of HOTf in CH_3CN at −40 °C and then deprotonated (DIEA) to give

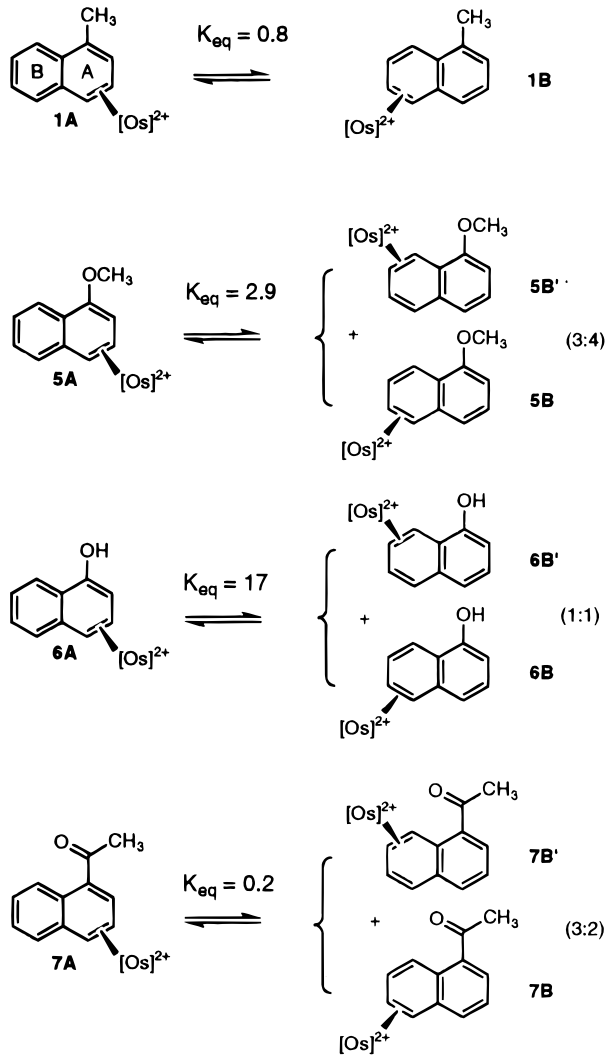

Figure 2. Equilibria of linkage isomers for 1-substituted naphthalene complexes of pentaammineosmium(II).

a 1:1 ratio of the two isomers **2B**,**B′** in a proportion identical with that always observed for the three-component mixture. On this basis, **2B** and **2B′** are assigned as intraannular isomers. Again, spectral features of each isomer are similar to those of the parent naphthalene complex. When a solution of **2B** and **2B′** is observed over 1 week using ^{1}H NMR (acetone-d_6), the A-ring isomer **2A** grows in with a specific rate of $(1.1 \pm 0.5) \times 10^{-6}$ s^{-1} (26 °C). The equilibrium ratio at the end of this period is approximately 1:3.3 in favor of the B-ring isomers. This ratio was also obtained by treating an acetonitrile solution of **2B** and **2B′** with a trace amount of HOTf. A distinction between the two B-ring isomers has not been made.

Complexation of 2-methoxynaphthalene provides an initial mixture of three isomers (**3A**,**B**,**B′**; see Figure 3). However, when this mixture is allowed to reach dynamic equilibrium over the course of 1 week, NMR data reveal that the single isomer **3A** dominates. This material is formed from the mixture of B-ring isomers with a specific rate of $(3.7 \pm 0.5) \times 10^{-6}$ s^{-1} (26 °C). As described earlier, the ratio of intraannular isomers (**3B**,**B′**) remains in a constant ratio (3:1) for the duration of the observation period, and no isomer other than **3A** was detectable at equilibrium. Among the spectral features of **3A** is a doublet at 6.1 ppm (H1), a chemical shift that is considerably upfield from the other unbound

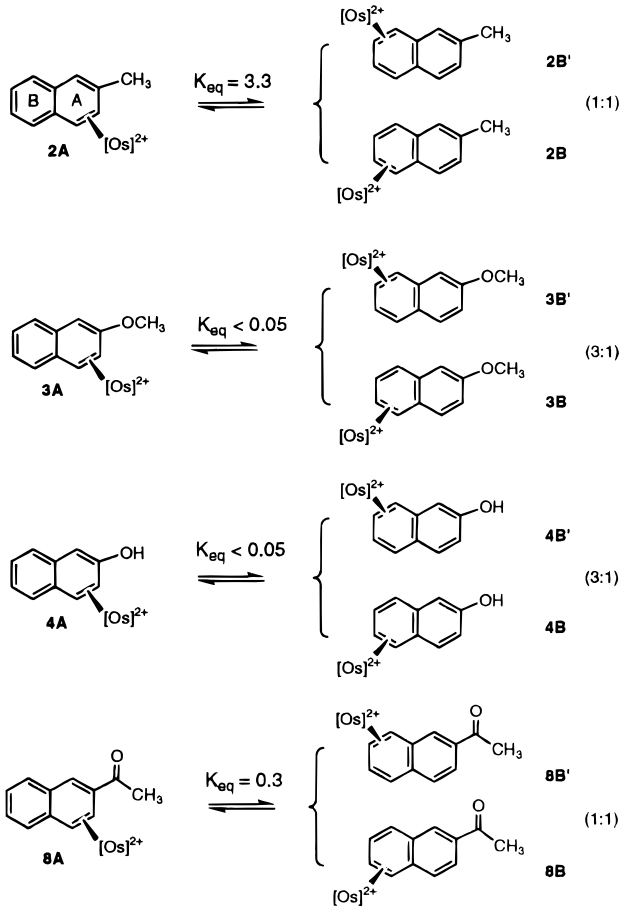

Figure 3. Equilibria of linkage isomers for 2-substituted naphthalene complexes of pentaammineosmium(II).

(aromatic) protons and is in line with that observed for H2 of the complex $[Os(NH_3)_5((5,6\text{-}\eta^2)\text{-anisole})]^{2+}$.[2] The weak splitting observed (1.8 Hz) arises from "W" coupling with H8.

The 2-hydroxynaphthalene system behaves much like its 2-methoxynaphthalene counterpart, and isomers can be conveniently assigned by comparison of ^1H and ^{13}C NMR data. However, an additional isomer, **4K**, is also present at equilibrium. Observation of the initial mixture (^1H NMR; acetone-d_6) over 1 week shows that the B-ring isomers convert to the A-ring isomers **4A** and **4K** with a specific rate of $(4.8 \pm 0.5) \times 10^{-6}$ s^{-1} (26°C). At equilibrium, only the A-ring isomers are observed. Isomer **4K**, which constitutes ~40% of the equilibrium mixture, has ^1H and ^{13}C NMR spectra and electrochemical data that differ significantly from those of typical naphthalene complexes. Diastereotopic methylene resonances at 3.06 and 2.49 ppm (J = 24 Hz) and a carbonyl signal at 210.3 ppm confirm that **4K** is the enone isomer shown in Figure 4, analogous to the 2,5-cyclohexadienone complexes prepared from phenol.[9]

The three isomers of the 1-methoxynaphthalene complex **5** were never isolated as single products. However, after initial complexation, the metal was observed, using ^1H NMR (acetone-d_6), to move *away* from the substituted A-ring with a specific rate of $(1.3 \pm 0.5) \times 10^{-6}$ m^{-1} s^{-1}. The equilibrium ratio was approximately 2.9:1 in favor of the B-ring isomers (**5B**,**B′**). A ^1H NMR spectrum of the mixture of isomers

(9) Kopach, M. E.; Harman, W. D.; Hipple, W. G. *J. Am. Chem. Soc.* **1992**, *114*, 1737.

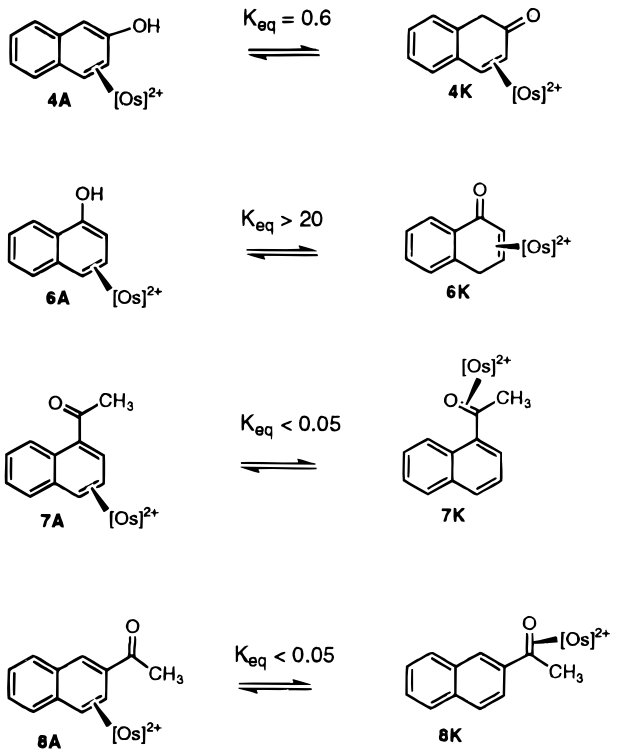

Figure 4. Linkage isomers of 2-hydroxy-, 1-hydroxy, 1-acetyl-, and 2-acetylnaphthalene complexes.

showed bound protons spread over a slightly larger range (5.1−6.0 ppm) than any previous complex reported above, with all other signals in the normally observed range. At all times, the ratio of **5B′** to **5B** was 3:4, although these two isomers were never differentiated. The 1-hydroxynaphthalene complex (**6**; see Figure 2) behaved almost identically with its 1-methoxynaphthalene counterpart. A-ring to B-ring isomerization occurred with a specific rate of $(5.7 \pm 0.5) \times 10^{-6}$ s^{-1}, and equilibrium was established as a 17:1 ratio favoring the B-ring isomers. In contrast to the 2-hydroxynaphthalene system, an enone isomer for the 1-hydroxynaphthalene system **6** was not formed under the neutral conditions even after standing in acetonitrile solution for 1 month. However, on a reviewer's suggestion we tried to generate an enone isomer using base as a catalyst. When the 1-hydroxynaphthalene complex **6** is allowed to stand in a 0.08 M solution of DIEA in CD_3CN, the new isomer **6K** (see Figure 4) slowly forms. The ^{13}C NMR spectra of this new complex has signals at 53.9 and 51.9 ppm corresponding to the two bound methine carbons, a ketone signal at 199.6 ppm, and a methylene resonance at 31.2 ppm. The ^1H NMR spectrum of **6K** shows diastereotopic methylene signals at 3.76 and 3.17 ppm with a coupling constant of 21.6 Hz. This isomerization also takes place in CD_3OD, with deuterium exchange at both the ortho and para positions. The complex **6K** is assigned as the 4*H*-naphth-1-one isomer, on the basis of a carbonyl stretch absorption in the IR spectrum at ~1650 cm^{-1} and a III/II reduction potential of 0.92 V. For a hypothetical 2*H*-naphth-1-one isomer, the carbonyl would not be in conjugation with the electron-donating osmium group and thus would be expected to have a C═O absorption close to 1700 cm^{-1} and an $E_{1/2}$ value close to that of the styrene complex (0.71 V). Even though 2,3-η^2 coordination is not favorable for η^2-naphthalene complexes (*vide*

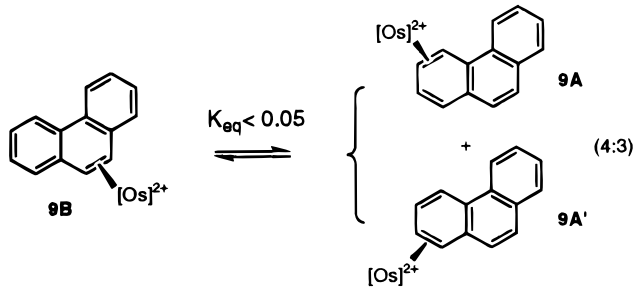

Figure 5. Phenanthrene complex linkage isomers.

infra), tautomerization to **6K** results in a π-acid ligand (i.e. (*2,3*-η^2)-4*H*-naphth-1-one) that is superior to a styrene (i.e. (*3,4*-η^2)-2*H*-naphth-1-one).

After complexation, both the 1-acetonaphthone (**7**) and 2-acetonaphthone (**8**) complexes are isolated as a mixture of four isomers. As judged from a comparison of the NMR data for complexes **7** and **8** with those obtained for η^2-ketone complexes of pentaammineosmium(II),[10] one of the isomers in each case is the η^2 ketone **7K** or **8K** (see Figure 4). Once again, over time, an *interannular* isomerization is observed with a specific rate of $(2.7 \pm 0.5) \times 10^{-6}$ s^{-1} for system **7** and $(6.1 \pm 0.5) \times 10^{-7}$ s^{-1} for **8**. The final interannular equilibrium ratios (η^2-ketone isomers excluded) are about 5:1 for **7** and 3:1 for **8**, favoring the A ring.

When phenanthrene was complexed with osmium(II), a mixture of three isomers was initially observed (**9A**,**A′**,**B**; Figure 5). Interestingly, the metal shows a slight kinetic preference for the outer rings (~60/40) despite the increased loss of aromatic character expected for this isomer.[11] However, after 1 week in acetone-d_6, the metal moves completely to the 9,10 position (**9B**), with a specific rate of $(7.0 \pm 0.5) \times 10^{-6}$ s^{-1}. Treatment of the original mixture of isomers with HOTf results in a rapid conversion of the A-ring isomers to **9B**. Even when high concentrations of acid and low temperatures (1.5 M of HOTf in CD_3CN at −40 °C) are used, no phenanthrenium species were observed (*vide infra*).

Characterization of Substituted η^3-Naphthalenium Complexes. As previously mentioned, treatment of the methyl-substituted naphthalene complexes with acid quickly establishes equilibrium conditions, but if the isomeric mixtures are treated with an excess of acid (1.5 M of HOTf in CD_3CN) followed by base, a single set of ring isomers often results. Direct observation using ^{1}H NMR reveals that, upon the addition of acid, distinct naphthalenium species are generated at 26 °C analogous to that observed for the parent naphthalene complex.[6] These highly acidic complexes decompose over a period of hours at this temperature, but at −40 °C, the naphthalenium products are stable indefinitely and can be easily characterized spectroscopically.

When the isomers of the 1-methylnaphthalene complex **1** are treated with 1.5 M HOTf in CD_3CN, the ^{1}H NMR spectrum shows cis and trans ammine signals shifted downfield from their precursor to 3.72 and 5.04 ppm, respectively. Three allylic proton signals at 6.43, 6.22, and 5.37 ppm and corresponding carbon resonances at 86.9, 83.0, and 75.5 ppm indicate η^3 coordination in **1BH** (Figure 6), and a methylene carbon at 29.1 ppm confirms that protonation does not occur at the substituted carbon. Interestingly, only one 1-methylnaphthalenium isomer is detected.

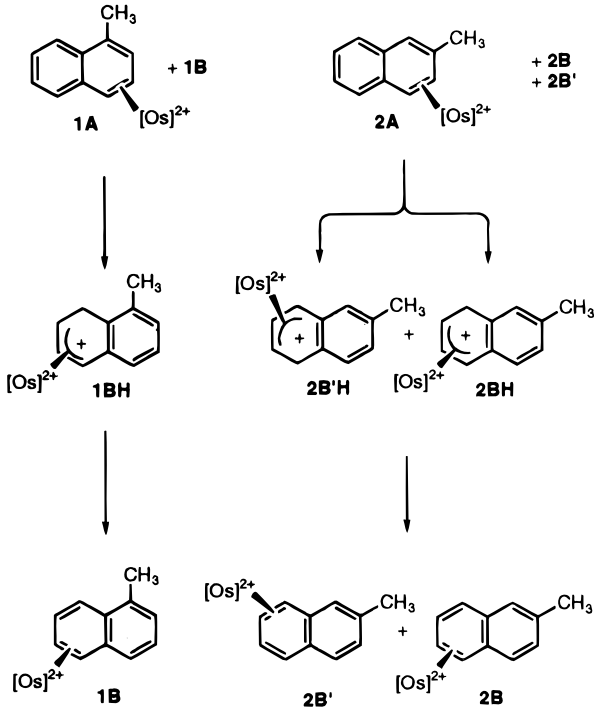

Figure 6. Preparation of a single set of ring isomers.

The isomers of the 2-methylnaphthalene complex **2** give two different napthalenium upon protonation with excess acid (**2B′H**, **2BH**). Again, proton and carbon data confirm the presence of two chemically similar η^3-naphthalenium species in approximately a 1:1 ratio. Neither the sp^3 ring carbon nor the allyl carbons are substituted. Thus, **2BH** and **2B′H** are both isomers in which the metal coordinates the unsubstituted B-ring (see Figure 6).

Protonation of the 2-methoxynaphthalene system **3** and the 1-acetylnaphthalene system **7** also delivers stable conjugate acids, but in these cases, ^{1}H and ^{13}C data indicate that the metal adopts an η^2 orientation. In the former case, protonation of **3** at 26 °C generates complex **3AH**, a material with spectral features that include a downfield carbonyl signal at 211.7 ppm and a methylene carbon at 35.8 ppm. These are features similar to those of the 2*H*-anisolium species prepared from 4-methoxyanisole.[6] Conversely, complex **7AH** shows two bound olefin signals at 63.4 and 59.7 ppm, a proton signal at 8.9 ppm corresponding to H2, and downfield signals at 172.4 and 197.9 ppm corresponding to C2 and the carbonyl, respectively. Were the isomers **7AH** and **3AH** bound in an η^3 fashion, the carbonyl signal would appear upfield by 30 ppm or more.[6] As with system **1**, only one naphthalenium system is detectable by ^{1}H NMR (Figure 7).

Discussion

The regiospecific coordination observed for η^2-arene complexes of pentaammineosmium(II) has led to regiospecific electrophilic addition reactions, especially those in which the arene bears a donor group.[2−4] For most arene complexes, the ring-bound linkage isomers

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

(11) Chin, R. M.; Dong, L.; Duckett, S. B.; Partridge, M. G.; Jones, W. D.; Perutz, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 7685.

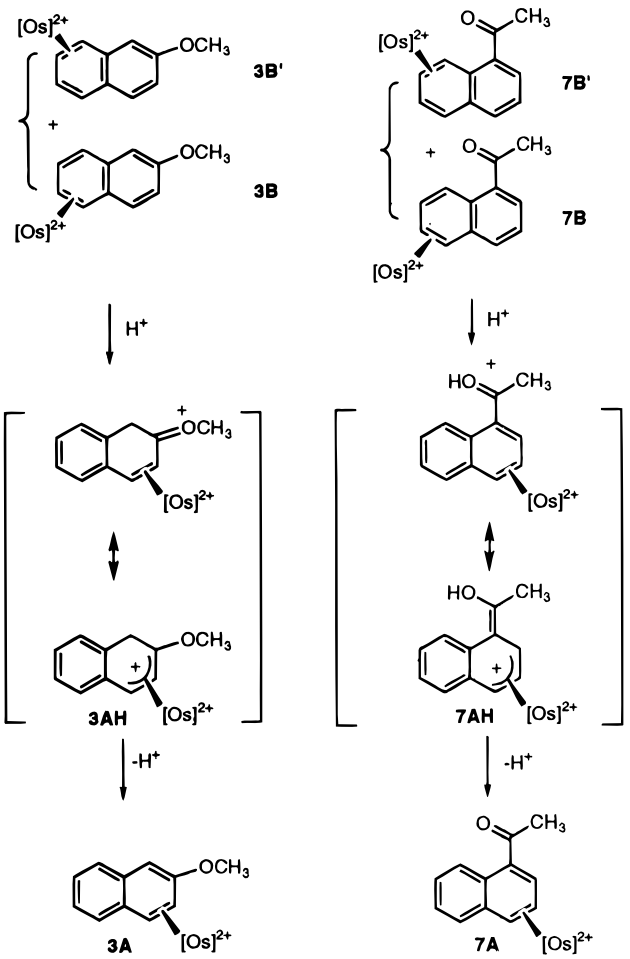

Figure 7. Conjugate acids of 2-methoxynaphthalene and 1-acetylnaphthalene complexes.

Table 1. Summary of Kinetic and Thermodynamic Data for Interannular Linkage Isomerizations

ligand (complex)	isomerization[a]	k^b (10^{-6} s^{-1})	kinetic isomer[c]	thermodynamic isomer[d]
1-Me-np (**1**)[f]	B → **A**	2.8 ± 0.5	B	A, B
2-Me-np (**2**)	**B** → A	1.1 ± 0.5	B	A, B
2-MeO-np (**3**)	B → **A**	3.7 ± 0.5	A	A
2-HO-np (**4**)	B → **A**	4.8 ± 0.5	A	A
1-HO-np (**6**)	A → **B**	5.7 ± 0.5	*e*	A, B
1- Ac-np (**7**)	**A** → B	2.7 ± 0.5	A	A, B
2-Ac-np (**8**)	**A** → B	0.6 ± 0.05	A, B	A, B
Phen (**9**)	A → **B**	7.0 ± 0.5	B	B

[a] A and B refer to coordination at the substituted and unsubstituted rings, respectively. Bold indicates thermodynamically favored isomer. [b] Specific rates determined for stated isomerization at 26 ± 1 °C. [c] Initial product formed from protonation/deprotonation sequence (recorded if >10% of total). [d] Product observed at equilibrium (recorded if >10% of total). [e] Decomposition upon exposure to acid. [f] np = naphthalene.

are in dynamic equilibrium at 26 °C, and the factors that influence coordination selectivity have been documented.[12] With η^2-naphthalene complexes, however, a significant kinetic barrier exists between rings. Specific rates for interannular isomerizations at 26 °C fall in the range of $(0.5-6.0) \times 10^{-6}$ s^{-1} (Table 1). Thus, the mixture of interannular isomers formed from the complexation of a substituted naphthalene is likely to yield a mixture of electrophilic addition products. Therefore, to conduct ligand-centered reactions with high regiocontrol, it becomes essential to be able to prepare single-ring isomers of η^2-naphthalene complexes.

Although η^2-naphthalene complexes have been observed for several transition metals, including ruthenium,[13] rhodium,[11] and nickel,[14] the only study of substituted naphthalenes has been that carried out by Jones *et al.*[11] In two separate studies,[11,14] the thermodynamically favored coordination site for a polyaromatic hydrocarbon was shown to be at the most *localized* double bond, which for naphthalene is C1−C2. Stated differently, the metal will preferentially bind at a position that causes a minimum disruption to the π system of the aromatic ligand. In the case of 2-hydroxy-, 2-methoxy-, and 2-acetylnaphthalenes, coordination at the 3,4-position allows for a π interaction of the substituent with the uncoordinated B-ring. For the corresponding 1-substituted naphthalene systems, however, coordination across C3 and C4 would effectively isolate the substituent from overlap with the B-ring. Consequently, for the 1-hydroxy and 1-methoxynaphthalene systems (**5** and **6**) the B-ring isomers are significantly favored, whereas for the 2-substituted analogs, the A-ring is favored. However, note that *both* the 1- and 2-acetylnaphthalene systems show a modest preference for coordination of the substituted A-ring. The preferred binding site for **7** contradicts the general pattern. This can be understood by considering the ability of the acetyl group to enhance the π-acid character of the ligand when the metal binds the 3,4 position (*vide infra*).

Thermodynamic binding selectivities for alkylated naphthalene complexes are governed primarily by steric interactions. The 1-methylnaphthalene system is the only example studied in which only one B-ring isomer is detectable at equilibrium. Apparently, the bulky pentaammineosmium group, when bound at C7 and C8, interferes with the C1 substituent to the point that this isomer becomes energetically unfavorable relative to the other two isomers (**1A** and **1B**). A similar steric interaction is responsible for the unusual fluxional and chemical behavior of the 2-methylanisole complex of pentaammineosmium(II).[2]

Although a π donor in the 2-position of naphthalene gives rise to regiospecific binding, in general, the thermodynamic binding selectivity for η^2-naphthalene complexes is unacceptably low. However, the regioselectivity is markedly enhanced for the conjugate acids of these systems. A recent study on the protonation of alkylated benzenes[6] identifies several features that contribute to the instability of η^3-arenium complexes. Alkylation at the terminal position of the bound allyl fragment or at the sp^3 ring carbon (*syn* to the metal) is not well tolerated by the metal. Thus, *for 1-or 2-alkylated naphthalene complexes, the most stable allyl system will always be formed in the unsubstituted B ring.* Given that the rate of interannular isomerization can be accelerated by a Brønsted acid, systems **1** and **2** can be prepared exclusively as their B-ring isomers by a sequence of acid followed by base (see Table 1). Furthermore, with an acetyl substituent at C1 (e.g., **7**) or a π donor group at C2 (e.g., **3** and **4**), a proton can augment the π-acid character of the organic ligand when the metal binds C3 and C4 (see Figure 7). Note that in

(12) Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 5725.
(13) Tagge, C. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 6908.
(14) Brauer, D. J.; Krüger, C. *Inorg. Chem.* **1977**, *16*, 884.

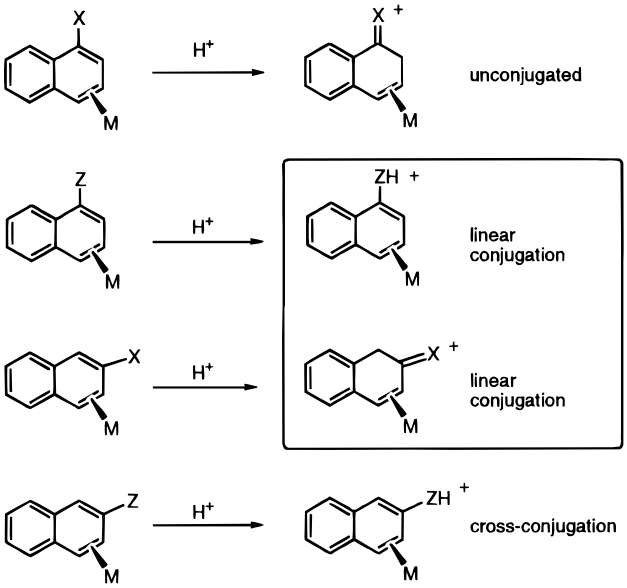

Figure 8. Linear vs cross-conjugation for conjugate acids of substituted naphthalene complexes.

both the case of **7AH** and **3AH** the metal is effectively coordinated to a highly activated (i.e., electron-deficient) olefin fragment. Thus, A-ring isomers may be selectively prepared for naphthalenes bearing a π donor group at C2 or a π accepting group at C1 through a protonation/deprotonation sequence (see Table 1). For the reverse situation in which a donor group is at C1 (e.g., **5**) or a withdrawing group is at C2 (e.g., **8**), the metal cannot adopt a position in either ring where it can effectively stabilize the protonated ligand. In this case the bound carbons would be in cross-conjugation with the withdrawing group (Figure 8). Thus, the binding selectivity for the 2-acetylnaphthalene system **8** does not improve upon protonation (HOTf in CH_3CN) and, in the case of the 1-methoxynaphthalene system, decomposition occurs upon exposure to acid, yielding the free ligand naphthalene and $[Os(NH_3)_5(CH_3CN)](OTf)_3$.

Finally, we note that the equilibrium between the naphthalene isomers **7** and **8** and their carbonyl-bound isomers greatly favors the ring-bound isomers. Although η^2-aldehyde and -ketone complexes are not common, a greater number of transition metals have been reported to form such complexes than to form stable η^2-arene species.[10,15] The observation that the ketone-naphthalene equilibrium favors the ring for the 1-acetyl and 2-acetylnaphthalene systems indicates that η^2-coordination complexes of naphthalenes or other polyaromatic hydrocarbons may be more favorable than is suggested by their infrequent occurrence in the literature.

Conclusions

Pentaammineosmium(II) forms unusually stable complexes with naphthalene that do not show any signs of substitution by solvent over several days. When the naphthalene bears an A ring substituent at the C1 or C2 position, three isomers (3,4-η^2; 5,6-η^2; 7,8-η^2) are generally observed, but in varying ratios depending on the nature of the substituent. Among these, the two B-ring isomers rapidly interconvert, whereas the interannular isomerization occurs over a period of days. Although both kinetic and thermodynamic binding selectivities are generally poor, in many cases a single set of ring isomers may be obtained through a protonation/deprotonation sequence. Unlike the complexes of the neutral ligands, the naphthalenium species are often formed with high selectivity for a particular ring. It appears that an alkyl substituent leads to only B-ring naphthalenium complexes, whereas an electron donor at the C2 position or an electron-withdrawing group at the C1 position leads to A-ring naphthaleniums. Given these observations, it may ultimately be possible to carry out highly regioselective electrophilic additions of naphthalenes promoted by π bases such as pentaammineosmium(II).

Acknowledgment is made to the Camille and Henry Dreyfus Foundation, the National Science Foundation (Grant No. CHE-9509883 and the NYI program), the Alfred P. Sloan Foundation, and Colonial Metals Inc. (Elkton, MD; OsO_4) for their generous support of this work. Special thanks are due to Dr. Jeffrey Ellena for assistance in some aspects of NMR data that were collected.

Supporting Information Available: Text giving full experimental procedures and characterizations for all compounds described in this account and tables giving X-ray crystal structure data for $[Os(NH_3)_5(naphthalene)]^{2+}$ (12 pages). Ordering information is given on any current masthead page.

OM9702441

(15) Harman, W. D.; Fairlie, D. P.; Taube, H. *J. Am. Chem. Soc.* **1986**, *108*, 8223 and references therein.