Dearomatization of Naphthalene: Novel Stereoselective Cyclization Reactions Promoted by Osmium(II)

Mark D. Winemiller and W. Dean Harman*

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

Received October 25, 1999

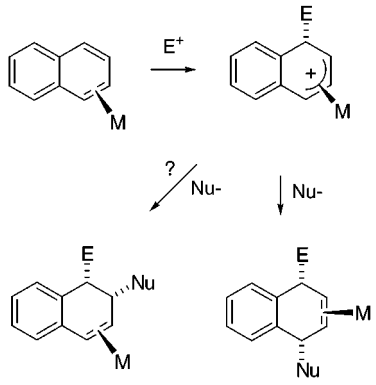
A series of Michael acceptors has been combined with the Os(II) η^2-naphthalene complex (**1**) to form stable 1*H*-naphthalenium species. Under acidic conditions, these complexes undergo ring closure at C2 to form the phenanthrenone core. In contrast, the corresponding 1-methylnaphthalene complex (**15**) upon addition of MVK at C8 undergoes ring closure at C5 to form a bridged tricyclic complex (**18**). Michael addition of MVK to the naphthalene complex (**1**) followed by deprotonation, an inter-ring linkage isomerization, and ring closure forms a 9-methylphenalene complex (**21**). In all cases, the organic cyclization products may be decomplexed by heating with silver triflate and isolated in moderate yield.

Introduction

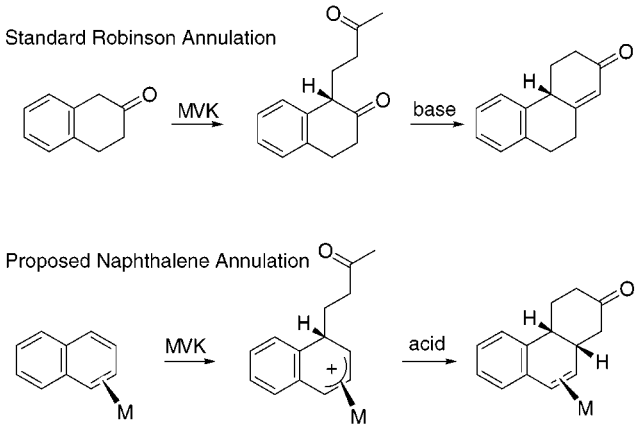
Hydrophenanthrenones have served as important intermediates in the synthesis of a broad range of steroids, steroidal alkaloids, diterpenes, and triterpenes.[1] Accordingly, their synthesis has been the subject of numerous studies.[1−6] One of the classical methods for the preparation of a tetrahydrophenanthren-2-one ring system is based on a Robinson annulation of 2-tetralones with methyl vinyl ketone (MVK) or other Michael acceptors.[7,8] Yet, we are aware of no route to this tricyclic system starting from simple naphthalenes. Given the diversity and availability to the synthetic chemist of these bicyclic aromatic molecules, a direct route from naphthalenes to phenanthrenones is potentially useful. Thus, we set out to develop such a method by exploiting the recent finding in our laboratories that coordination of naphthalene by the π base $[Os(NH_3)_5]^{2+}$ activates the coordinated ring toward the addition of electrophiles.[9] The resulting 1*H*-naphthalenium system is highly stabilized by the π-donating osmium(II) fragment when compared to organic arenium species, yet this system is electrophilic enough to readily undergo addition reactions with mild nucleophiles. Using this approach, we have recently synthesized numerous 1,4-dihydronaphthalenes (Scheme 1).[9]

The purpose of the present study was to develop an annulation procedure for naphthalenes and α,β-unsaturated ketones (Scheme 2) similar to the Robinson annulation of tetralones. The basic conditions required for the standard Robinson (Michael−Aldol) sequence are not compatible with the osmium approach due to the high acidity of the 1*H*-naphthalenium species.[10] Therefore, the ultimate success of the proposed reaction sequence (Scheme 2) depended on the ability of the naphthalenium intermediate to undergo intramolecular addition with an enol under the acidic conditions required to inhibit the competitive deprotonation at C1.

Scheme 1



Scheme 2



Results

As reported previously,[9] when the naphthalene complex **1** is combined with the Michael acceptor MVK in

(1) Schultz, A. G.; Wang, A. *J. Org. Chem.* **1996**, *61*, 4857−4859.
(2) Majetich, G.; Liu, S.; Siesel, D. *Tetrahedron Lett.* **1995**, *36*, 4749−4752.
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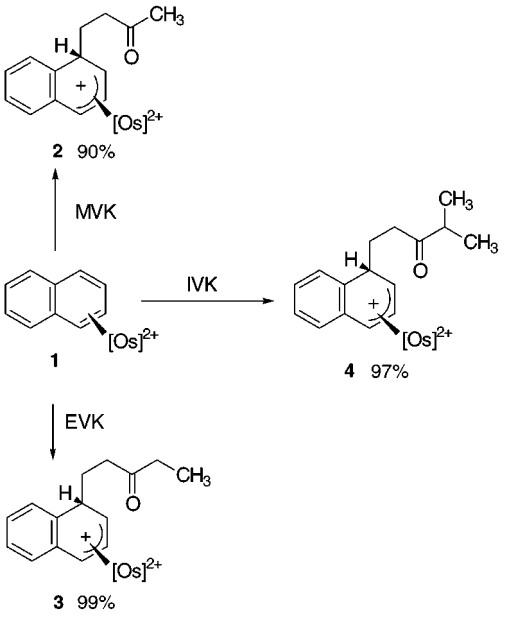
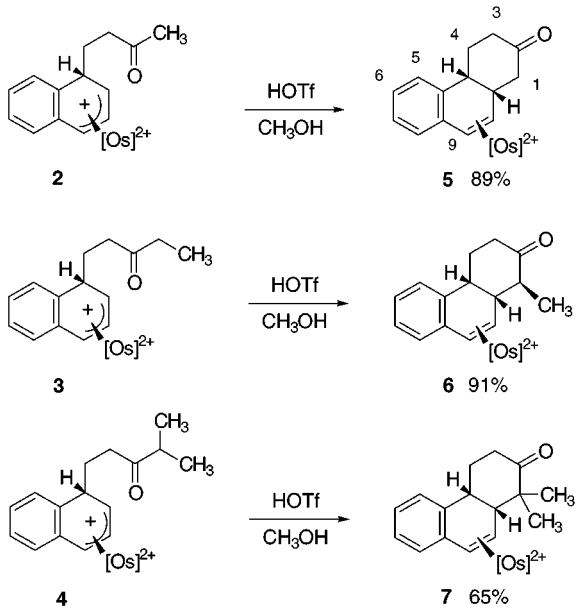
10.1021/jo9916737 CCC: $19.00
Published on Web 02/08/2000

Scheme 3



Scheme 4



the presence of triflic acid (HOTf), a conjugate addition reaction generates the naphthalenium complex **2** in a 90% yield (Scheme 3). In a similar procedure, ethyl vinyl ketone (EVK) and isopropyl vinyl ketone (IVK) may be combined with the naphthalene complex **1** to form naphthalenium complexes **3** and **4**, and these products may be isolated as triflate salts in yields >95%. Naphthalenium complexes **3** and **4** have features in their proton spectra nearly identical with that of the naphthalenium complex **2**.

When the naphthalenium complex **2** was dissolved in acidic MeOH (0.88 M HOTf) and allowed to stand for 3 days, the anticipated cyclization reaction occurred forming complex **5** in 89% yield (Scheme 4). Complex **5** shows two resonances that appear in the ^{1}H NMR spectrum (CD_3CN) at 4.41 and 3.62 ppm and correspond to the protons of the bound olefin. Significantly, these protons have a greater separation in chemical shift than is characteristically observed for 1,4 dihydronaphthalene

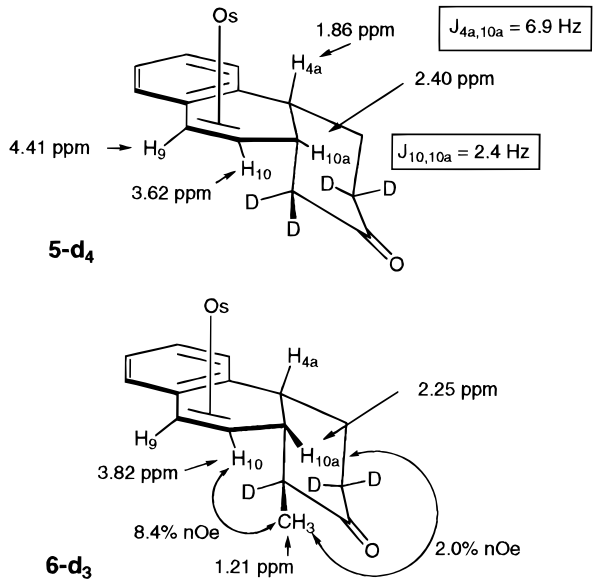


Figure 1.

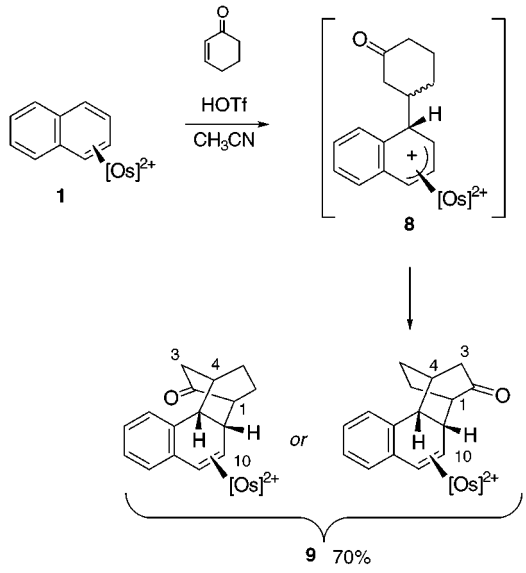
complexes, and the proton α to the remaining aromatic ring (H9) is shifted more downfield than is the case for the 1,4-disubstituted analogues.[9] The ^{13}C NMR spectrum of **5** (CD_3CN) features a carbonyl peak at 211.3 ppm and three methylene peaks at 47.5, 27.8, and 27.9 ppm (DEPT). These observations confirm that the product **5** results from a nucleophilic attack by the external tethered enol. A cyclic voltammogram of complex **5** indicates a chemically reversible oxidation at 0.74 V (NHE, ν = 100 mV/s). This value is slightly greater than those potentials observed for the 1,4-naphthalene addition products,[9] where values typically range between 0.68 and 0.70 V.

The cis ring stereochemistry of **5**, shown in Figure 1, was confirmed by NMR studies carried out after exchanging the protons α to the carbonyl group with deuterium (DOTf, CH_3OD). A COSY spectrum was then used to establish connectivities of the remaining protons. The bound olefin proton H10 at 3.62 ppm couples (J = 2.4 Hz) to the proton at 2.40 ppm (H10a; Scheme 4). When H10 is irradiated, the doublet at 4.41 ppm (H9) collapses to a singlet and the multiplet for H10a collapses to a doublet (J = 6.9 Hz). The latter splitting arises from the coupling of H10a to H4a. This coupling constant of 6.9 Hz confirms a cis ring juncture.[11] A coupling constant of about 16 Hz would be expected between the bridgehead protons if complex **5** contained a trans ring juncture.

The organic ligand of **3** cyclizes under less acidic conditions than are required to close the ring for **2**. Thus, a methanolic solution of **3** and 0.34 M HOTf generates the tricyclic compound **6** in 91% yield after 3 days (Scheme 4). Complex **6** has spectroscopic features similar to those of **5** and closes stereoselectively with the methyl group adopting an exo orientation on the cyclohexanone ring. This stereochemistry was confirmed by a NOESY and a COSY experiment on the deuterated derivative of complex **6** (**6**-d_3; Figure 1). According to COSY data, H10 (3.82 ppm) couples with the bridgehead proton H10a (2.25 ppm), and a NOESY spectrum of the complex

(11) Rabideau, P. W. *The Conformational Analysis of Cyclohexenes, Cyclohexadienes, and Related Hydroaromatic Compounds*; VCH Publishers: New York, NY, 1989.

Scheme 5



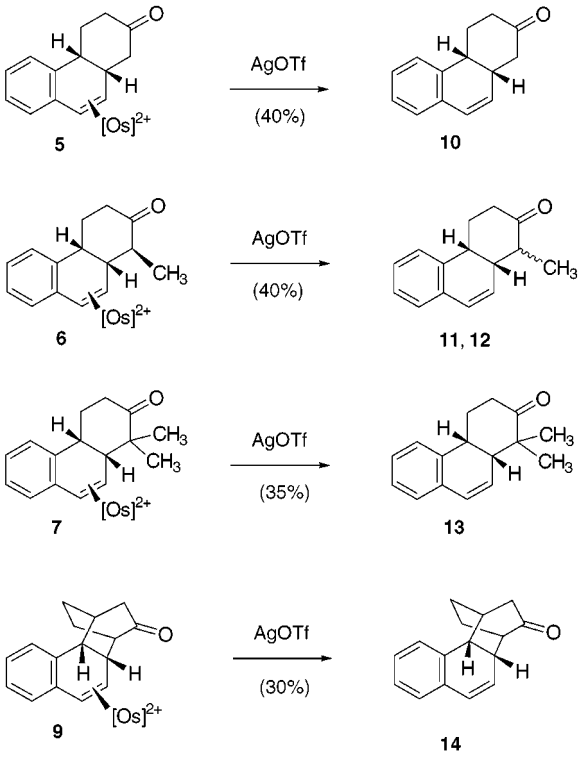
reveals an interaction of the latter proton with the cis ammine protons of the pentaammineosmium(II) fragment. Also significant, H10 and H10a show an 8.4% and 2.0% NOE enhancement, respectively, when the methyl group at 1.21 ppm is irradiated. The closure of naphthalenium **4** requires a much higher concentration of acid (2.62 M) than do the other ring closures. This higher concentration of acid caused complications with the precipitation of **7**, which was isolated in only 65% yield.

When the naphthalene complex **1** is treated with 2-cyclohexen-1-one and HOTf in CH_3CN, the putative naphthalenium species **8** (Scheme 5) directly closed to form the cyclization product **9** (70%). This complex also has spectroscopic features indicative of a single stereoisomer of a phenanthren-2-one complex. Two doublets in the ^{1}H NMR spectrum at 4.56 and 3.81 ppm confirm the presence of a 1,2-dihydronaphthalene complex. The presence of three methylene signals at 39.1, 23.9, and 22.7 ppm, along with a carbonyl at 215.1 ppm and four methine signals in the ^{13}C NMR spectrum, confirm the assignment. While it seems reasonable to assume that complex **9** is also a product of a syn tandem addition, the stereochemistry at the bridgehead carbon C4 has not been determined. The configuration at C4 should uniquely determine the stereochemistry at C1, and therefore either of the two diastereomers shown for complex **9** would be consistent with the known data for this compound (Scheme 5).

The tetrahydrophenanthrenone ligands of complexes **5**, **6**, **7**, and **9** were all decomplexed in the same manner using AgOTf and heat (80 °C). Individual yields for decomplexation varied from 30 to 40% with the overall yield for molecules **10**−**13** being between 22% and 36% for the entire process starting from naphthalene. Molecule **14** was generated in a three-step process in an overall 21% yield. Under the reaction conditions required for decomplexation, the tetrahydromethylphenanthrenone ligand of complex **6** underwent partial isomerization (presumably epimerization at C1).

Phenanthrenones **10**−**14** (Scheme 6) have been characterized by a combination of ^{13}C and ^{1}H NMR, GCMS (low resolution), and combustion analysis where possible. In their concentrated forms, these materials readily

Scheme 6



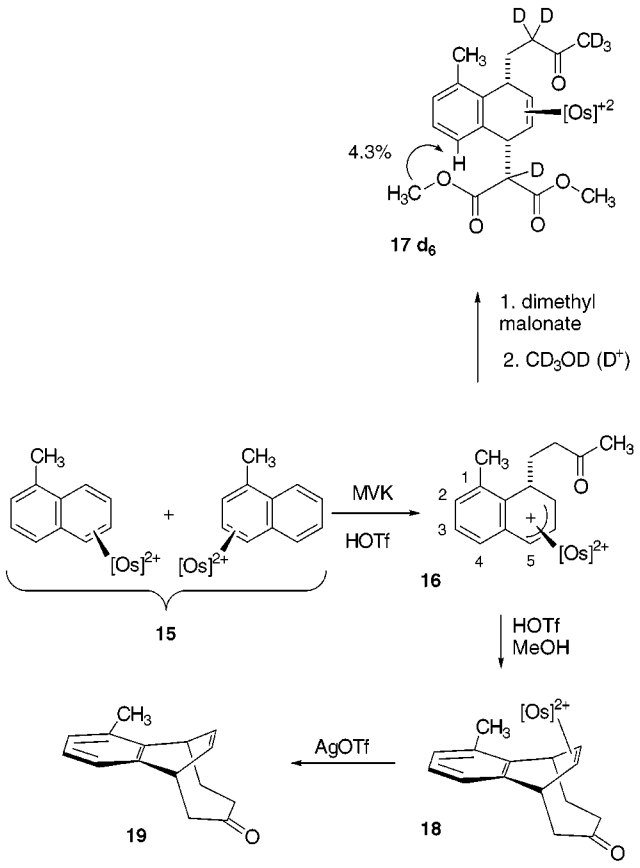
decompose, probably through polymerization. Compounds **10**−**14** exhibit spectroscopic features consistent with other 1,2-dihydronaphthalenes reported in the literature.[11] All these compounds have vinyl proton resonances in the range of 6.6 ppm to 5.5 ppm, with the difference between proton signals in the range of 0.6−0.7 ppm. ^{13}C NMR and DEPT data reveal the correct number of methine and methylene groups for **10**−**14**, and all carbonyl resonances appear in the range of 211−221 ppm.

Where possible, the assignments of the ring stereochemistry for **10**−**14** were made on the basis of NOE and ^{1}H−^{1}H coupling data. Because 1,2-dihydronaphthalenes have been shown to exist in puckered conformations,[11] the differences in bridgehead coupling constants for trans and cis ring junctions are well pronounced. J_{trans} values in such systems have been experimentally determined to be on the order of 16 Hz, whereas the J_{cis} value has been shown to be between 6.0 and 7.0 Hz.[11] In addition, phenanthrenone **10** exhibits a vinyl-H1 coupling constant of 2.4 Hz, which fits well with the published value of 2.0 Hz for cis ring systems.[11]

In an attempt to explore the regiochemistry of the naphthalene annulation procedure for substituted naphthalenes, 1-methylnaphthalene was complexed according to the published procedure.[12] In this case, complexation results in a mixture of two isomers of **15** where the metal is bound across either C3,C4 or C5,C6.[12] However, when the isomeric mixture of **15** was treated with MVK and HOTf in CH_3CN under conditions similar to those used to convert complex **1** to **2**, a *single* naphthalenium complex **16** was formed (Scheme 7). The ^{1}H NMR spectrum of complex **16** shows cis and trans ammine resonances shifted downfield from those of the naphtha-

(12) Winemiller, M. D.; Kelsch, B. A.; Sabat, M.; Harman, W. D. *Organometallics* **1997**, *16*, 3672.

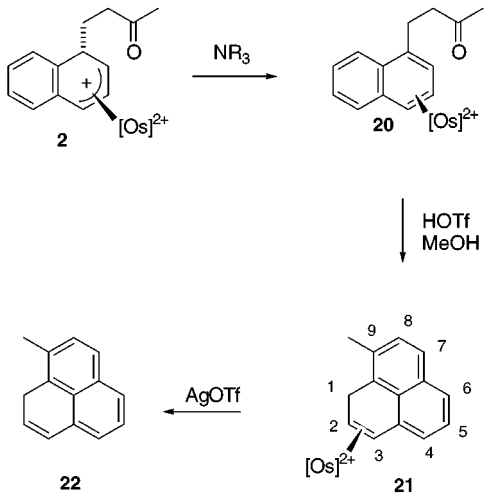
Scheme 7



lene complex (**1**) and a set of three allyl signals at 6.39, 6.07, and 5.49 ppm, similar to those seen in complexes **2**−**4**. To confirm that **16** was the result of a Michael addition to C8 rather than C5, this material was combined with the nucleophile dimethyl malonate and an amine base to yield the putative 5,8-dihydronaphthalene product **17** (Scheme 7). This compound was then partially deuterated by dissolving it in a mixture of CD_3OD and DOTf and then precipitating the product from ether (**17**-d_6). Upon irradiation of the methoxy singlet at 3.76 ppm, a 4.3% enhancement of the doublet at 6.85 was observed (H4). No NOE enhancement was seen between the methoxy (3.76 ppm) and the methyl (2.29 ppm) signals of **17**.

When the methylnaphthalenium complex **16** was dissolved in acidic MeOH (0.13 M) and allowed to stand for 3 days, a product was isolated (**18**) whose NMR features indicated a 1,4-dihydronaphthalene complex (i.e., product of a 5,8-tandem addition to 1-methylnaphthalene).[9] This outcome was in stark contrast to that observed for the naphthalenium complexes **2**−**4**. Proton resonances for **18** corresponding to the bound olefin site (H6, H7) are present at 3.74 and 3.52 ppm, whereas the other phenanthrenone complexes reported herein have α proton signals shifted below 4.0 ppm. Decomplexation with AgOTf results in compound **19** (Scheme 7) isolated in a 40% yield (35% from 1-methylnaphthalene). The ^{1}H NMR spectrum of compound **19** shows vinyl proton signals at 6.23 and 6.16 ppm consistent with other 1,4-dihydronaphthalenes.[11] The ^{13}C NMR spectrum confirms that, like **10**−**13**, compound **19** also contains a carbonyl (212.1 ppm) and three methylene groups (DEPT; 56.3, 38.3, and 25.7 ppm).

Scheme 8



In an attempt to activate both rings of naphthalene with a single metal, the naphthalenium complex **2** was rearomatized to form the substituted naphthalene system **20** (80%; Scheme 8) by treating the former compound with diisopropylethylamine (DIEA) in CH_3CN. Our hope was that, upon rearomatization, the metal would migrate to the unsubstituted ring, undergo protonation to form the naphthalenium system, and cyclize with the pendent enol of the complimentary ring. Exposure of **20** to acid induced a rapid inter-ring isomerization, but the resulting complex underwent an *electrophilic* cyclization reaction with the pendent ketone group followed by elimination of water (i.e., an Aldol-like condensation reaction). A ^{13}C NMR spectrum of the resulting compound (**21**) displayed only four peaks in the spectrum below 50 ppm. The peaks at 49.9, 47.3, 30.2, and 19.5 ppm were those expected for two bound carbons, a methyl, and a methylene. In addition, proton and carbon data indicated the presence of an uncoordinated naphthalene-type ring system. Thus, we tentatively assign **21** as the 9-methylphenalene complex shown in Scheme 8. Although mass recovery was almost quantitative, cyclic voltammetry experiments on product **21** revealed that partial oxidation of Os^{II} had occurred, creating a complex mixture that included the paramagnetic complex $[(Os(NH_3)_5(CH_3CN)]^{3+}$. Thus, an exact yield for **21** was difficult to determine. Nonetheless, product **21** was oxidized in a H_2O/ether solution with AgOTf to give a hydrocarbon product (**22**) in an isolated overall yield of 20% from naphthalene. ^{1}H and ^{13}C NMR and DEPT data for **22** closely matched that of the parent phenalene,[13−17] with the exception that compound **22** has one less methine group, has a methyl group, and has an additional quaternary carbon. Although spectral data may be consistent with other methylphenalene isomers as well, we have assigned **22** as 9-methylphenalene. Pioneering work by Boekelheide and co-workers showed that other methylphenalene isomers readily convert to 9-methylphenalene, even under mild conditions.[15,16]

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(14) Boudjouk, P.; Johnson, P. D. *J. Org. Chem.* **1978**, *43*, 3979−3980.
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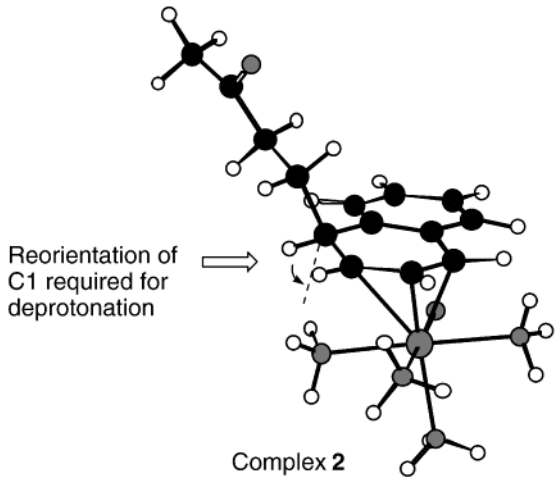
(17) Meltzheim, B.; Kilway, K.; Lignell, M.; Waegell, B.; Tort, F. *Bull. Soc. Chim. Fr.* **1996**, *133*, 979−985.

Discussion

Procedures that generate functionalized dihydronaphthalenes directly from their aromatic precursors have become valuable tools to the synthetic chemist, due to the availability and stability of naphthalene and substituted naphthalenes.[18] In addition to the Birch reduction,[19] more recently developed methods for the dearomatization of naphthalene to dihydronaphthalenes are based on the addition of nucleophiles to electron-deficient naphthalene systems.[20,21] The reaction sequence presented here is similar in nature to the classical Robinson annulation (see Scheme 2), except that, rather than a ketone, the electrophilic carbon in the ring formation step is a terminus of an osmium-stabilized allyl cation. Remarkably, even though methanol is sufficiently basic to quantitatively deprotonate the naphthalenium system,[10] enol addition preempts this rearomatization. The slow rate of deprotonation can be explained largely through stereoelectronic factors of naphthalenium complexes such as **2**. As seen below, the acidic H1 proton is trapped between the pentaammineosmium moiety and the oxobutyl group hindering access by a potential base. In order for deprotonation to occur, this proton needs to draw in closer to the osmium in order to bring the C−H bond into the proper alignment with the p orbitals of the allyl system. In this pseudoaxial position, the approach by a base is even more sterically hindered by the pentaammineosmium fragment. Thus, the metal plays the role of kinetically as well as thermodynamically stabilizing the naphthalenium system.



In general, nucleophiles preferentially add to the 4-position of a 1*H*-naphthalenium system.[12] Hypothetically, for the allylic system of a 1*H*-naphthalenium complex, the metal has a predisposition toward binding across C2 and C3, thereby allowing for partial delocalization of the positive charge into the remaining aromatic ring.[9] Thus, for the intramolecular examples shown in Scheme 4, the minimization of entropy losses associated with forming a six-membered ring in a chair conformation is normally enough to overcome the electronic bias for addition at C4.

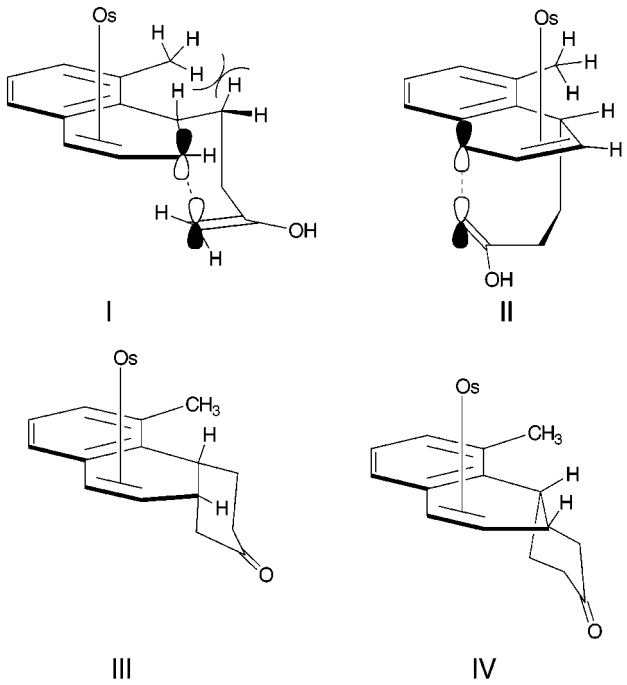


Figure 2.

For the naphthalene complex **15**, the steric interaction of the C1 methyl group and the pentaammineosmium moiety is sufficient to inhibit the formation of the 7,8-η^2 isomer. Thus, electrophilic addition of MVK is directed by the metal to occur specifically at C8 (Scheme 7), with the osmium also enforcing addition anti to the metal. Were the alkyl chain of **16** to adopt the equatorial orientation required to form a chair transition state for cyclization at C7, severe $A^{(1,3)}$ strain would develop between the methyl group at C1 and the alkyl chain (structure I in Figure 2). This steric interaction effectively prevents approach of the enol to C7, and the fused ring system fails to form. Rather, the alkyl chain of **16** favors an axial alignment (Figure 2, structure II) that makes formation of the eight-membered ring at C5 (i.e., the bridged ring system) kinetically favored. However, the phenanthrenone isomer of **18** is likely to be favored *thermodynamically* over its bridged counterpart: While conformation III (Figure 2) would be highly destabilized by a peri interaction with the C1 methyl group, conformation IV is not affected by the methyl group at C1. The [6.4.0]bicyclododecane ring is present in numerous natural product classes including the neolemnane family of sesquiterpenoids and the taxanes.[22−26] Ozonolysis of the double bond of compounds such as **19** would, in principle, produce highly functionalized synthons to compounds containing the ubiquitous [6.4.0] bicyclododecane ring system.

The osmium-promoted preparation of 9-methylphenalene from naphthalene and MVK represents a novel example of a single transition metal activating two

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(22) Petasis, N. A.; Patane, M. A. *Tetrahedron* **1992**, *48*, 5757−5821.
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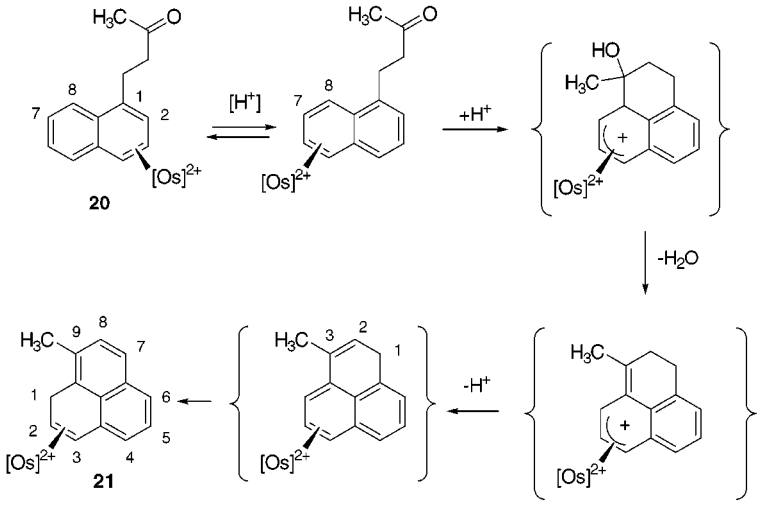
(24) Dowd, P.; Zhang, W. *Tetrahedron Lett.* **1996**, *37*, 957−960.
(25) Magnus, P.; Diorazio, L.; Donohoe, T.; Giles, M.; Pye, P.; Tarrant, J.; Thom, S. *Tetrahedron* **1996**, *52*, 14147−14176.
(26) Galatsis, P.; Manwell, J. J. *Tetrahedron* **1995**, *51*, 665−678.

Scheme 9



separate rings in a polyaromatic hydrocarbon system. A plausible mechanism for this reaction is outlined in Scheme 9. Electrophilic addition of MVK followed by deprotonation results in a 1-oxobutylated naphthalene complex **20**. Upon addition of acid, rapid inter-ring isomerization to 5,6-η^2 occurs followed by an aldol condensation at C8. The resulting phenalenium system is expected to readily deprotonate at the bridgehead methine to give the 3-phenalene complex. Finally, either a series of two 1,3-hydride shifts or intermolecular proton or hydride transfer[17] would result in the 9-methylphenalene isomer. Of note, the electrophilic ring closure employed above is similar in concept to a reaction sequence reported by Kise et al.[27] using nonconjugated aromatic ketones.

Conclusion

A convenient method for forming the phenanthren-2-one nucleus in moderate yields from naphthalene has been developed. In addition to the high degree of functionalization possible for the newly formed A ring of the phenanthrenone, the olefin that remains in the 9,10 position allows for the further modification of the molecule on the B ring. Alternatively, a 9-methylphenalene was prepared from naphthalene and MVK by a subtle modification of those reaction conditions used to create the phenanthrene system, and a novel bridged ring system was formed when C1 of the naphthalene precursor was methylated. In all, three fundamentally new and potentially useful cyclization reactions have been demonstrated starting from a simple naphthalene and an enone.

Experimental Section

Chemical shifts are reported in ppm relative to TMS (δ CD_3CN = 1.93, acetone-d_6 = 2.04, $CDCl_3$ = 7.26, CD_3OD = 3.30). ^{13}C NMR assignments are supported by DEPT data. Electrochemical experiments were performed under nitrogen using a PAR model 362 potentiostat driven by a PAR model 175 universal programmer. Cyclic voltammograms were recorded (Kipp & Zonen BD90 XY recorder) in a standard three-electrode cell, 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. Most of this work was carried out under a nitrogen atmosphere in a Vacuum Atmospheres Co. glovebox.

Solvents. Acetonitrile-d_3 was refluxed over CaH_2 and distilled under argon. Acetone-d_6 was used as received except that it was deoxygenated prior to use. Methanol-d_4 was received in sealed ampules and was used without any further purification, as was chloroform-*d*.

Reagents. The precursor, $[Os(NH_3)_5OTf](OTf)_2$, was synthesized as described by Lay *et al*.[28] Methyl vinyl ketone, ethyl vinyl ketone, and isopropyl vinyl ketone were distilled under vacuum. All other reagents were used as received. Complexes **1**[29] and **15**[12] were previously reported.

$[Os(NH_3)_5(2,3,4\text{-}\eta^3\text{-}[1\text{-}(3\text{-oxobutyl})\text{-}1H\text{-naphthalenium})]](OTf)_3$ (2). To a stirring solution of **1** (535 mg, 0.76 mmol) in 3.52 g of CH_3CN was added dropwise a solution of MVK (70 mg, 1.00 mmol), in 530 mg of CH_3CN, followed by HOTf (126 mg, 0.84 mmol) in 500 mg of CH_3CN. The solution was stirred rapidly for 15 min, and then, to ensure completion, a solution of MVK (methy vinyl ketone; 39 mg, 0.56 mmol) in 500 mg of CH_3CN was added, followed by a solution of HOTf (31 mg, 0.21 mmol) in 500 mg of CH_3CN. Stirring was continued for an additional 15 min, and the product precipitated upon addition of diethyl ether to yield **2**, 633 mg (0.69 mmol, 90%): ^1H NMR (300 MHz, CD_3CN) δ 7.57 (d, J = 6.3 Hz, 1H), 7.35 (m, 3H), 6.42 (dd, J = 5.7, 1.8 Hz, 1H), 6.04 (m, 1H), 5.50 (t, J = 6.6 Hz, 1H), 5.27 (br, s, 3H), 3.85 (br, s, 12H), 2.65−2.20 (m, 5H), 2.05 (s, 3H). ^{13}C NMR (75 MHz, acetone-d_6) δ 207.3 (CO), 135.1 (C), 132.7 (C), 131.7 (CH), 130.7 (CH), 129.8 (CH), 128.2 (CH), 84.6 (CH), 83.4 (CH), 75.6 (CH), 39.0 (CH), 38.9 (CH_2), 29.5 (CH_3), 28.5 (CH_2). Anal. Calcd for $C_{17}H_{30}N_5O_{10}S_3F_9Os$: C, 22.15; H, 3.28; N, 7.60. Found: C, 21.76; H, 3.26; N, 7.75.

$[Os(NH_3)_5(2,3,4\text{-}\eta^3\text{-}[1\text{-}(3\text{-oxopentyl})\text{-}1H\text{-naphthalenium})]](OTf)_3$ (3). To a stirring solution of **1** (423 mg, 0.60 mmol) in a solution of EVK (ethyl vinyl ketone; 74.6 mg, 0.89 mmol) in 2.75 g of CH_3CN was added dropwise a solution of HOTf (137.5 mg, 0.92 mmol) in 2.66 g of CH_3CN. The solution was stirred rapidly for 15 min, and then, to ensure completion, a solution of EVK (72.5 mg, 0.86 mmol) in 2.75 g of CH_3CN was added, followed by HOTf (59.6 mg, 0.40 mmol). Stirring was continued for an additional 15 min, and the product precipitated upon addition of diethyl ether to yield **3**, 559 mg (0.60 mmol, 99%): ^1H NMR (300 MHz, CD_3CN) δ 7.58 (d, J = 6.3 Hz, 1H), 7.34 (m, 3H), 6.42 (dd, J = 6.3, 2.1 Hz, 1H), 6.05 (m, 1H), 5.52 (t,

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J = 6.3 Hz, 1H), 5.30 (br, s, 3H), 3.89 (br, s, 12H), 2.65−2.20 (overlapping signals, 7H), 0.93 (m, 3H).

[Os(NH$_3$)$_5$(2,3,4-η^3-[1-(4-methyl-3-oxopentyl)-1*H*-naphthalenium)]](OTf)$_3$ (4). To a stirring solution of **1** (158 mg, 0.23 mmol) in a solution of IVK (isopropyl vinyl ketone; 27.1 mg, 0.28 mmol) in 1.16 g of CH_3CN was added dropwise a solution of HOTf (41.1 mg, 0.27 mmol) in 500 mg of CH_3CN. The solution was stirred rapidly for 15 minutes, and then, to ensure completion, a solution of IVK (24.9 mg, 0.26 mmol) in 500 mg of CH_3CN was added, followed by HOTf (15.6 mg, 0.10 mmol). Stirring was continued for an additional 15 min and the product precipitated upon addition diethyl ether to yield **4**, 207 mg (0.22 mmol, 97%): ^{1}H NMR (300 MHz, CD_3CN) δ 7.58 (d, J = 6.3 Hz, 1H), 7.34 (m, 3H), 6.42 (dd, J = 6.3, 2.4 Hz, 1H), 6.06 (m, 1H), 5.53 (t, J = 6.3 Hz, 1H), 5.30 (br, s, 3H), 3.89 (br, s, 12H), 2.65−2.20 (overlapping signals, 6H), 1.01 (d, J = 6.9 Hz, 3H), 0.97 (d, J = 6.9 Hz, 3H).

[Os(NH$_3$)$_5$[9,10-η^2-(3,4,4a,10a-tetrahydro-1*H*-phenanthren-2-one)]](OTf)$_2$ (5). The complex **2** (94 mg, 0.10 mmol) was dissolved in a solution that consisted of HOTf (84 mg, 0.56 mmol) in 504 mg of MeOH. The solution was then allowed to stand for 3 days at room temperature and the product precipitated upon addition of diethyl ether to yield 70 mg of **5** (0.09 mmol, 89%): ^{1}H NMR (300 MHz, CD_3CN) δ 7.25 (m, 4H), 4.41 (d, J = 8.4 Hz, 1H), 4.13 (br, s, 3H), 3.62 (dd, J = 8.4, 2.4 Hz, 1H), 2.96 (br s, 12H), 2.69 (m, 2H), 2.44−2.40 (m, 2H), 2.22 (m, 2H); ^{13}C NMR (75 MHz, CD_3CN) δ 211.3 (CO), 141.7 (C), 133.5 (C), 128.2 (CH), 127.6 (CH), 127.3 (CH), 126.1 (CH), 53.7 (CH), 47.5 (CH_2), 46.8 (CH), 42.1 (CH), 37.8 (CH_2), 35.1 (CH), 27.9 (CH_2); CV (CH_3CN, TBAH, 50 mV/s) $E_{1/2}$ = +0.74 V (NHE). Anal. Calcd for $C_{16}H_{29}O_7N_5F_6S_2Os$: C, 24.90; H, 3.79, N, 9.07. Found: C, 24.44; H, 3.89; N, 8.81.

[Os(NH$_3$)$_5$[9,10-η^2-(3,4,4a,10a-tetrahydro-1-methylphenanthren-2-one)]](OTf)$_2$ (6). The complex **3** (554.8 mg, 0.59 mmol) was dissolved in a solution that consisted of HOTf (467 mg, 3.11 mmol) in 7.12 g of MeOH. The solution was then allowed to stand for 3 days at room temperature, and the product was precipitated by first adding the MeOH solution to 200 mL of rapidly stirring CH_2Cl_2 and then adding 300 mL of diethyl ether to the CH_2Cl_2 to yield 425 mg of **6** (0.54 mmol, 91%): ^{1}H NMR (300 MHz, CD_3CN) δ 7.41 (m, 1H), 7.26 (m, 3H), 4.42 (d, J = 8.4 Hz, 1H), 4.15 (br, s, 3H), 3.82 (dd, J = 8.4, 2.7 Hz, 1H), 2.96 (br s, 12H), 2.60 (m, 2H), 2.30 (overlapping signals, 4H), 1.78 (m, 1H), 1.22 (d, 3H).

[Os(NH$_3$)$_5$[9,10-η^2-(3,4,4a,10a-tetrahydro-1,1-dimethylphenanthren-2-one)]](OTf)$_2$ (7). The complex **4** (647.5 mg, 0.68 mmol) was dissolved in a solution that consisted of HOTf (4.55 g, 30.3 mmol) in 9.23 g of MeOH. The solution was then allowed to stand for 3 days at room temperature and the product precipitated upon addition of a 4:1 ether/CH_2Cl_2 solution to yield 347 mg of **7** (0.44 mmol, 65%): ^{1}H NMR (300 MHz, CD_3CN) δ 7.40 (m, 1H), 7.20 (m, 3H), 4.60 (d, J = 8.4 Hz, 1H), 4.20 (br, s, 3H), 3.80 (dd, J = 8.4, 2.4 Hz, 1H), 2.98 (br s, 12H), 2.60 (m, 2H), 2.20 (m, 2H), 2.05 (m, 2H), 1.10 (s, 3H), 0.80 (s, 3H).

[Os(NH$_3$)$_5$[9,10-η^2-(3,4,4a,10a-tetrahydro-1,4-ethanophenanthren-2-one]](OTf)$_2$ (9). To a stirring solution of **1** (500 mg, 0.71 mmol) dissolved in a solution of 2-cyclohexen-1-one (355.6 mg, 3.70 mmol) in 2.37 g of CH_3CN was added dropwise a solution of HOTf (129.5 mg, 0.86 mmol) in 2.40 g of CH_3CN. The solution was stirred rapidly for 1 h, and then, to ensure completion, a solution of 2-cyclohexen-1-one (351.0 mg, 3.66 mmol) in 2.41 g of CH_3CN was added, followed by HOTf (19.1 mg, 0.72 mmol) in 2.23 g of CH_3CN. Stirring was continued for an additional 1 h, and the solution was precipitated in diethyl ether to yield 399 mg of **9** (0.50 mmol, 70%): ^{1}H NMR (300 MHz, acetone-d_6) δ 7.22 (d, J = 7.5 Hz, 1H), 7.14 (m, 2H), 7.04 (m, 1H), 4.78 (br s, 3H), 4.56 (d, J = 8.4 Hz, 1H), 3.81 (d, J = 8.4 Hz, 1H), 3.46 (br s, 12H), 2.50−1.69 (10H); ^{13}C NMR (75 MHz, acetone-d_6) δ 215.1 (CO), 140.0 (C), 133.4 (C), 128.5 (CH), 126.5 (CH), 124.7 (CH), 124.6 (CH), 52.7 (CH), 48.7 (CH), 46.2 (CH), 39.1 (CH_2), 38.4 (2xCH), 37.4 (CH), 23.9 (CH_2), 22.7 (CH_2).

3,4,4a,10a-Tetrahydro-1*H*-phenanthren-2-one (10). The complex **5** (348 mg, 0.45 mmol) was dissolved in 5.0 g of acetone and stirred rapidly while AgOTf (236.4 mg, 0.92 mmol) was added. The solution was stirred for an additional 30 min and then transferred to a pressure tube and heated at 80 °C for another 30 min. The solution was cooled and added to 200 mL of stirring ether. The resulting precipitate was filtered off, and the ether was removed. Chromatography of the oily product on silica gel (5% ether/pet ether) resulted in 35.8 mg of **10** (0.18 mmol, 40%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (m, 3H), 7.14 (m, 1H), 6.50 (dd, J = 9.6, 1.8 Hz, 1H), 5.82 (dd, J = 9.6, 2.4 Hz, 1H), 3.17 (m, 2H), 2.64 (m, 1H), 2.38 (m, 4H), 2.0 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 220.7 (CO), 137.4 (C), 132.8 (C), 130.1 (CH), 128.1 (CH), 127.7 (CH), 127.0 (CH), 126.8 (CH), 126.5 (CH), 44.3 (CH_2), 40.1 (CH_2), 38.1 (CH), 37.9 (CH), 28.6 (CH_2). Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.64; H, 7.64.

3,4,4a,10a-Tetrahydro-1-methylphenanthren-2-one (11 and 12). The complex **6** (611.6 mg, 0.78 mmol) was dissolved in 7.5 g of acetone and stirred rapidly while AgOTf (488.0 mg, 1.90 mmol) was added. The solution was stirred for an additional 30 min and then transferred to a pressure tube and heated at 80 °C for another 30 min. The solution was cooled and added to 300 mL of stirring ether. The resulting precipitate was filtered off, and the ether was removed. Chromatography of the oily product on silica gel (5% ether/hexanes) resulted in 66.1 mg of **11** and **12** (0.31 mmol, 40%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (m, 2H), 7.18 (m, 6H), 6.52 (d, J = 9.6 Hz, 1H), 6.48 (dd, J = 9.6, 2.4 Hz, 1H), 6.02 (dd, J = 9.6, 5.1 Hz, 1H), 5.79 (d, J = 9.6 Hz, 1H), 3.28 (q, J = 5.1 Hz, 1H), 3.17 (m, 2H), 2.92 (m, 1H), 2.45 (m, 7H), 2.07 (m, 2H), 1.86 (m, 1H), 1.16 (d, J = 6.9 Hz, 3H), 1.10 (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.8 (CO), 212.2 (CO), 139.4 (C), 135.9 (C), 133.8 (C), 132.9 (C), 130.5 (CH), 128.4 (CH), 127.9 (CH), 127.7 (CH), 127.6 (CH), 127.1 (CH), 127.0 (CH), 126.9 (CH), 126.8 (CH), 126.6 (CH), 125.3 (CH), 125.1 (CH), 46.2 (CH_2), 45.5 (CH_2), 44.5 (CH), 44.3 (CH), 41.7 (CH), 41.1 (CH), 37.4 (CH), 36.1 (CH), 30.4 (CH_2), 27.5 (CH_2), 13.1 (CH_3), 11.3 (CH_3). Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.43; H, 8.44.

3,4,4a,10a-Tetrahydro-1,1-dimethyl-phenanthren-2-one (13). The complex **7** (288.0 mg, 0.30 mmol) was dissolved in 3.5 g of acetone and stirred rapidly while AgOTf (165.8 mg, 0.64 mmol) was added. The solution was stirred for an additional 30 min and then transferred to a pressure tube and heated at 80 °C for another 30 min. The solution was cooled and added to 200 mL of stirring ether. The resulting precipitate was filtered off, and the ether was removed. Chromatography of the oily product on silica gel (5% ether/petroleum ether) resulted in 23.0 mg of **13** (0.11 mmol, 35%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (m, 3H), 7.12 (m, 1H), 6.55 (dd, J = 9.9, 2.4 Hz, 1H), 5.93 (dd, J = 9.6, 1.8 Hz, 1H), 3.46 (m, 1H), 2.76 (m, 1H), 2.33 (m, 1H) 1.92 (m, 1H), 1.42 (s, 3H), 1.17 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.3 (CO), 138.9 (C), 132.9 (C), 128.7 (CH), 127.6 (CH), 126.9 (CH), 126.6 (2xCH), 126.3 (CH), 48.8 (CH_2), 47.1 (C), 37.1 (CH), 36.2 (CH), 29.1 (CH_2), 26.4 (CH_3), 21.8 (CH_3). Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 85.34; H, 8.56.

3,4,4a,10a-Tetrahydro-1,4-ethanophenanthren-2-one (14). The complex **9** (540.4 mg, 0.68 mmol) was dissolved in 6.1 g of acetone and stirred rapidly while AgOTf (358.4 mg, 1.39 mmol) was added. The solution was stirred for an additional 30 min and then transferred to a pressure tube and heated at 80 °C for another 30 min. The solution was cooled and added to 300 mL of stirring ether. The resulting precipitate was filtered off, and the ether was removed. Chromatography of the oily product on silica gel (5% ether/pet ether) resulted in 50.0 mg of **14** (0.20 mmol, 30%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 (m, 3H), 6.96 (m, 1H), 6.26 (dd, J = 9.6, 2.4 Hz, 1H), 5.51 (dd, J = 9.6, 3.0 Hz, 1H), 3.48 (m, 1H), 3.30 (m, 1H) 2.30 (m, 1H), 2.37 (m, 2H), 2.08 (m, 2H), 1.71 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 216.3 (CO), 135.4 (C), 131.8 (C), 128.6 (CH), 128.4 (CH), 128.2 (CH), 127.8 (CH), 126.8 (C_H), 126.5 (CH), 48.3 (CH), 40.5 (CH2), 38.7 (CH), 37.7 (CH), 37.2 (CH), 26.2 (CH2), 23.6 (CH2). Anal. Calcd for $C_{16}H_{16}O$: C, 86.19; H, 7.84. Found: C, 85.68; H, 7.19.

[Os(NH$_3$)5(5,6,7-η^3-[1-methyl-8-(3-oxobutyl)-8*H*-naphthalenium)]](OTf)$_3$ (16). To a stirring solution of **15** (776.7 mg, 1.09 mmol) in MVK (155.0 mg, 2.21 mmol) and 4.40 g of CH_3CN was added dropwise a solution of HOTf (187.6 mg, 1.25 mmol) in 2.20 g of CH_3CN. The solution was stirred rapidly for 15 min, and then, to ensure completion, a solution of MVK (151.1 mg, 2.16 mmol) in 2.20 g of CH_3CN was added, followed by HOTf (67.7 mg, 0.45 mmol). Stirring was continued for an additional 15 min, and the solution was precipitated in diethyl ether to yield 1.01 g of **16** (1.08 mmol, 99%): ^{1}H NMR (300 MHz, CD_3CN) δ 7.41 (d, J = 6.6 Hz, 1H), 7.30 (t, J = 7.8 Hz, 1H), 7.15 (d, J = 7.8 Hz, 1H), 6.39 (dd, J = 6.0, 2.1 Hz, 1H), 6.07 (m, 1H), 5.49 (t, J = 6.0 Hz, 1H), 5.27 (br s, 3H), 3.80 (br s, 12H), 2.65−2.20 (m, 5H), 2.28 (s, 3H), 2.04 (s, 3H).

[Os(NH$_3$)$_5$[6,7-η^2-(1-methyl-4-(2′-dimethyl malonate)-8-(3′-oxobutyl)-5,8-dihydronaphthalene)]](OTf)$_2$ (17-d_6). Complex **16** (284.9 mg, 0.30 mmol) was dissolved in 1.37 g of CH_3CN and cooled to −40 °C and then added to a solution of dimethyl malonate (207.5 mg, 1.57 mmol) and diisopropyl ethylamine (72.9 mg, 0.60 mmol) in 1.10 g of CH_3CN. The solution was precipitated into 200 mL of 1:1 ether/CH_2Cl_2 to yield 182.6 mg of **17** (0.19 mmol, 65%). Complex **17** (148.8 mg, 0.16 mmol) was then dissolved in a solution of DOTf (156.6 mg, 1.04 mmol) in 1.0 g of CD_3OD and allowed to stand for 10 min. It was then precipitated into ether to yield 142.9 mg of **17**-d_6 (0.15 mmol, 95%): ^{1}H NMR (300 MHz, CD_3CN) δ 7.04 (m, 2H), 6.84 (d, J = 6.9 Hz, 1H), 3.97 (br s, 3H), 3.88 (d, J = 9.9 Hz, 1H), 3.76 (s, 3H), 3.69 (d, J = 9.9 Hz, 1H), 3.67 (dd, J = 9.0, 1.5 Hz, 1H), 3.5 (m, 1H), 3.47 (s, 3H), 2.73 (br s, 12H), 2.29 (s, 3H), 2.30 (m, 1H), 1.31 (m, 1H).

[Os(NH$_3$)$_5$[11,12-η^2-(1-Methyl-5,10-ethenobenzocyclooctan-7-one)](OTf)$_2$ (18). The complex **16** (691.2 mg, 0.74 mmol) was dissolved in a solution that consisted of HOTf (219.3 mg, 1.46 mmol), in 8.7 g of MeOH. The solution was then allowed to stand for 3 days at room temperature, and the product was precipitated in ether to yield 531 mg of **18**, (0.68 mmol, 91%): ^{1}H NMR (300 MHz, CD_3CN) δ 7.10−6.99 (m, 3H), 3.90 (br s, 3H), 3.74 (d, J = 8.7, 1.8 Hz, 1H), 3.52 (dd, J = 8.7, 1.8 Hz, 1H), 3.27 (m, 1H), 3.0−1.8 (m, 7H), 2.68 (br s, 12H), 2.28 (s, 3H).

1-Methyl-5,10-ethenobenzocyclooctan-7-one (19). The complex **18** (586.8 mg, 0.75 mmol) was dissolved in 5 mL of H_2O containing HOTf (185.1 mg, 1.23 mmol), and then 5 mL of diethyl ether was added and the solution stirred rapidly while AgOTf (282.0 mg, 1.10 mmol) was added. The solution was stirred for an additional 30 min and then transferred to a pressure tube and heated at 80 °C for another 30 min. The solution was cooled, and the ether was removed. The H_2O was extracted twice with ether, the extracts were combined, and the ether was removed. Chromatography of the oily product on silica gel (10% EtOAc/pet ether) gave 43.1 mg of **19** (0.20 mmol, 31%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (m, 3H), 6.23 (dd, J = 9.2, 5.4 Hz, 1H), 6.16 (dd, J = 9.2, 6.0 Hz, 1H), 3.94 (m, 1H), 3.72 (m, 1H), 2.89 (m, 2H), 2·34 (s, 3H), 2.15 (m, 1H), 1.96 (m, 1H), 1.81 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.1 (CO), 140.0 (C), 137.0 (C), 134.1 (C), 132.0 (CH), 130.7 (CH), 128.7 (CH), 126.5 (CH), 124.9 (CH), 56.3 (CH_2), 38.3 (CH_2), 38.0 (CH), 35.9 (CH), 25.7 (CH_2), 18.8 (CH_3). Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.89; H, 8.14.

[Os(NH$_3$)$_5$(3,4-η^2-1-(3-oxobutyl)naphthalene)](OTf)$_2$ (20). A solution of **2** (799.8 mg, 0.87 mmol) was dissolved in 3.0 g of CH_3CN and added to a stirring solution of diisopropyl ethylamine (336.0 mg, 2.60 mmol) in 1.0 g of CH_3CN. The solution was precipitated in CH_2Cl_2 to yield 538.9 mg of **20** (0.70 mmol, 80%): ^{1}H NMR (300 MHz, CD_3CN) δ 7.7−7.5 (m, 2H), 7.5−7.0 (m, 2H), 6.92 (d, J = 5.4 Hz, 1H), 5.09 (d, J = 8.1 Hz, 1H), 4.88 (dd, overlapped, J = 5.4, 2.1 Hz, 1H), 4.11 (br, s, 3H), 3.1−2.9 (m, 4H), 2.79 (br, s, 12H), 2.14 (s, 3H). Anal. Calcd for $C_{16}H_{29}O_7N_5F_6S_2Os$: C, 24.90; H, 3.79; N, 9.07. Found: C, 24.58; H, 3.66; N, 8.74.

[Os(NH$_3$)$_5$(9-methylphenalene)](OTf)$_2$ (21). Partial characterization: ^{1}H NMR (300 MHz, CD_3CN) δ 7.6 (m, 2H), 7.25 (m, 2H), 7.18 (d, 1H), 4.62 (d, 1H, 8.7 Hz), 4.32 (m, 1H), 4.12 (b, 3H), 3.0−3.2 (2H), 2.82 (b, 12H), 2.38 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ: 130.2, 128.0, 127.2, 127.6, 126.3, 125.8, 123.8, 122.5, 119.5, 115.5, 49.9 (CH), 47.3 (CH), 30.2 (CH_3), and 19.5 (CH_2).

9-Methylphenalene (22). The complex **21** (664.4 mg, 0.88 mmol) was dissolved in 5 mL of H_2O, and then 1 g of K_2CO_3 was added along with 5 mL of diethyl ether. The mixture was stirred rapidly while AgOTf (465.3 mg, 1.81 mmol) was added. The solution was stirred for an additional 30 min and then transferred to a pressure tube and heated at 80 °C for another 30 min. The solution was cooled, the ether was removed, and the remaining H_2O was extracted twice with ether. The extracts were combined, and the ether was removed. Chromatography of the oily product on Florisil with pentane gave 31.7 mg of **22** (0.18 mmol, 20%): ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.54 (m, 1H), 7.30 (m, 3H), 7.01 (d, J = 7.2 Hz, 1H), 6.67 (dt, J = 9.9, 2.1 Hz, 1H), 6.17 (dt, J = 9.9, 4.2 Hz, 1H), 3.82 (m, 2H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.3 (C), 131.9 (C), 131.3 (C), 130.9 (C), 129.0 (C), 128.9 (CH), 127.8 (CH), 127.7 (CH), 126.6 (CH), 125.2 (CH), 124.9 (CH), 122.1 (CH), 30.7 (CH_3), 19.6 (CH_2).

Acknowledgment is made to the Camille and Henry Dreyfus Foundation, the National Science Foundation (CHE-9807375 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 is also given to Dr. Jeffrey Ellena for assistance in all aspects of NMR data that were collected.

JO9916737