Activation of Benzylic Carbons in η^2-Arene Complexes: A Novel and Efficient Synthesis of Functionalized Decalins

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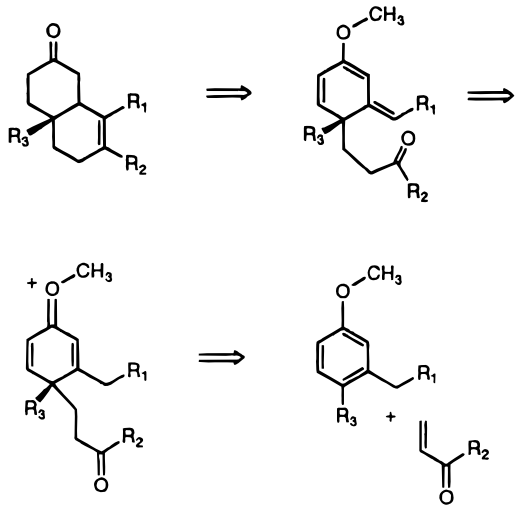
Abstract: 3-Alkylated anisole complexes of pentaammineosmium(II) are treated with methyl vinyl ketone and triflic acid to form 4*H*-anisolium Michael adducts. These compounds deprotonate regioselectively at the benzylic position adjacent to C3 and then undergo an aldol cyclization with the pendant carbonyl to form the decalin core. Reduction of the dienonium product can be directed in a 1,4 fashion to generate a trans decalin or in a 1,2 fashion to provide a methoxydiene complex that serves as a precursor to other functionalized decalins.

Introduction

It is well established that an electron-withdrawing transition metal coordinated to an arene activates benzylic positions.[1,2] The electrophilic metal center is typically coordinated to the arene in an η^6 fashion and stabilizes the anion resulting from benzylic deprotonation such that it may be combined with a suitable electrophile to generate highly substituted arenes. Our interest in the ability of pentaammineosmium(II) to bind arenes in an η^2 fashion and subsequently activate them toward electrophilic addition reactions[3−5] led us to question whether an η^2-arenium system resulting from electrophilic addition might be stable enough that deprotonation at the benzylic position could successfully compete with rearomatization. Such a reaction sequence would be complementary to η^6-arene chemistry and would constitute a new method for the activation of benzylic carbons. In the following account we explore this reaction sequence using 3-alkylated anisole complexes of osmium(II) in an intramolecular aldol reaction sequence to form functionalized decalins (Scheme 1).

Scheme 1. Michael-Aldol Cyclization with an Arene: A Retrosynthetic Analysis



Results

Arene complexes of pentaammineosmium(II) undergo addition reactions with a variety of electrophiles to give stable 4*H*-arenium complexes.[4] Of the different arenium species that we have studied,[3−5] 4*H*-anisolium complexes are the most electron-deficient and thus are most likely to undergo deprotonation at a benzylic position.[4] Through the introduction of an α,β-unsaturated ketone to C4 of a 3-alkylated anisole, we hoped to both generate the anisolium species and use the tethered ketone as an electrophile in an intramolecular aldol reaction. Unlike their C4-protonated counterparts, 4,4-dialkylated anisolium complexes can be isolated and characterized at room temperature.[4] Thus, our first attempt was to use the complex of 3,4-dimethylanisole (**1**) where the resulting 4*H*-anisolium could not be rearomatized by simple deprotonation. Accordingly, when the 3,4-dimethyl anisole complex (**1**) and MVK are combined with triflic acid in acetonitrile (−40 °C), a brilliant purple color develops. The anisolium complex **2** is isolated (96%) upon precipitation from diethyl ether. Key spectroscopic features of **2** include broad *cis*- and *trans*-ammine resonances located approximately 1 ppm apart as well as two carbonyl resonances near 200 ppm in the ^{13}C NMR spectrum.

When the anisolium complex **2** is treated with the weak base dimethylacetamide (DMA) in CD_3CN, an intramolecular aldol reaction occurs between the methyl group at C3 and the C4 side chain carbonyl (Scheme 2). The reaction is complete in approximately 15 min at 20 °C, and the final product is isolated as a 7:1 mixture of C7 epimers in 96% yield. As the reaction occurs, it is possible to monitor the conversion of **2** to **4a** (the major diastereomer) by watching the disappearance of the three methyl group signals at 2.44, 2.09, and 1.23 ppm. These three signals are replaced by the emergence of only two new

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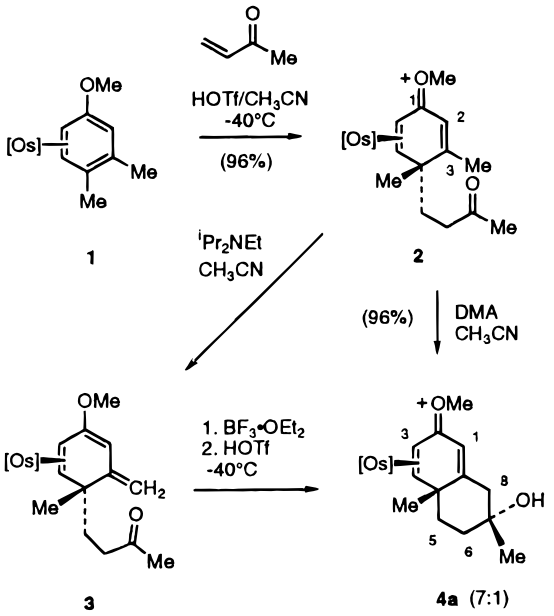
Scheme 2. Osmium(II)-Promoted Synthesis of a Decalin Ring System from 3,4-Dimethylanisole and MVK



methyl groups at 1.37 and 1.28 ppm. ^{1}H and ^{13}C NMR and DEPT data confirm that **4a** is the decalin complex shown in Scheme 2.

Amine bases such as ^{i}Pr$_2$NEt (Hünig's base) or pyridine stoichiometrically deprotonate C3 to generate the methoxytriene intermediate **3** (Scheme 2). This material is differentiated from **2** by a lack of a methyl signal near δ 2.4 in the ^{1}H NMR spectrum and the presence of an olefinic methylene group at δ 107 ppm in the ^{13}C NMR spectrum (DEPT). When complex **3** is treated with a Lewis acid such as boron trifluoride etherate (BF_3•OEt_2) followed by triflic acid, the aldol product **4** is again formed as a 7:1 C7 epimeric mixture.

More highly substituted anisole complexes also participate in the Michael addition/aldol reaction sequence. The 6-methoxy-1,2,3,4-tetrahydronaphthalene complex **5** reacts with MVK under reaction conditions similar to those for the preparation of **2** (Scheme 3). However, when the resulting anisolium species **6** is combined with DMA, the aldol reaction which generates **7** does not go to completion, but rather reaches dynamic equilibrium as a 1:1 mixture of complexes **6** and **7**. Thus, it is necessary to drive the reaction to completion using an oxophilic electrophile. The conjugated vinyl ether complex **8** is generated under basic conditions by treatment of **7** with pyridine. Subsequent treatment of **8** with *tert*-butyldimethylsilyl triflate (TBSOTf) promotes the aldol reaction which is followed by a spontaneous elimination of TBSOH to form complex **9** in good yield (82%). The 4*H*-anisolium complex **9** is surprisingly resistant to hydrolysis, but dissolution in water and heating at 80 °C for a period of ∼1 h results in the conversion to the dienone complex. This product is oxidized by treatment with ceric ammonium nitrate (CAN) to release the tricyclic dienone (**10**) in 25% yield.

The 3-methylanisole complex **11** undergoes a Michael addition with MVK to form what we assume to be the 4*H*-anisolium **12** (not characterized). Unlike the 4-alkylanisolium intermediates **2** and **6**, 4*H*-anisolium intermediates such as **12** are not stable at 20 °C and must be manipulated at low temperature. To determine the feasibility of using these materials in the intramolecular aldol process, the regioselectivity for the deprotonation of 4*H*-anisolium complex **12** was exam-

Scheme 3. Osmium(II)-Promoted Michael-Aldol Reaction Sequence Starting with a Tetralin Complex

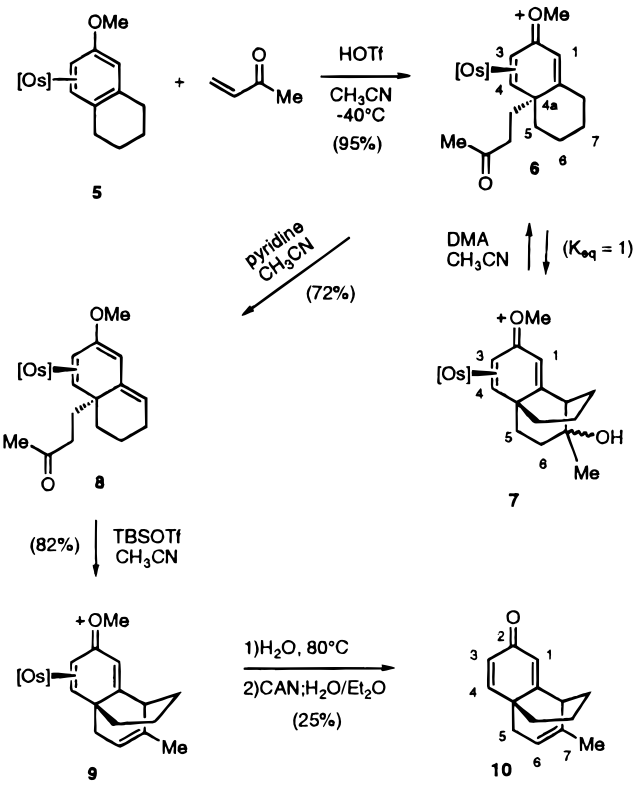
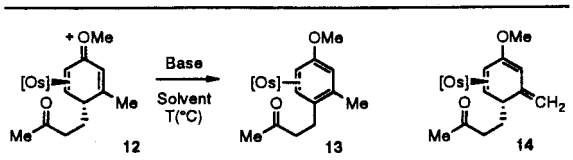


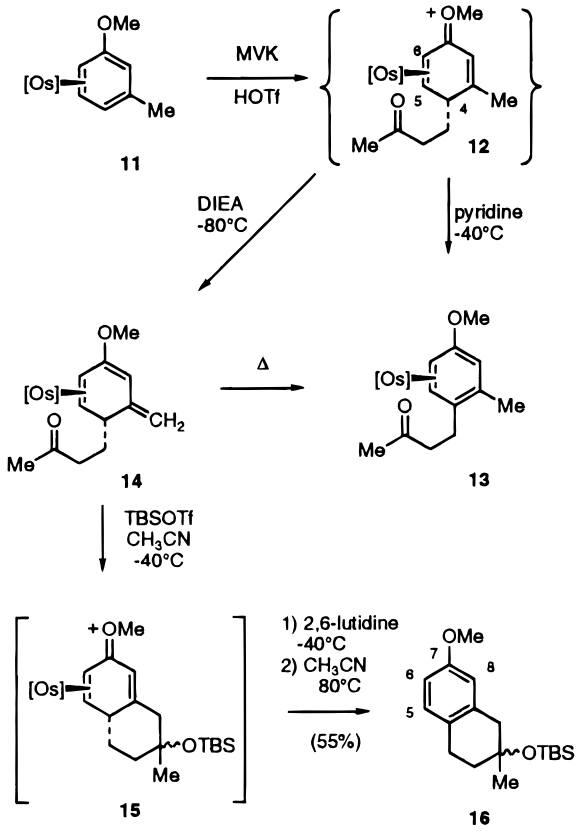
Table 1. Deprotonation of Anisolium Complex **12**



Entry	Base	Solvent	T(°C)	Ratio (13:14)
1	pyridine	MeCN	-40	>95:5
2	2,6-lutidine	MeCN	-40	>95:5
3	2,6-di^{t}Bu pyridine	MeCN	-40	>95:5
4	^{i}Pr$_2$NEt	MeCN	-40	1:7
5	^{i}Pr$_2$NEt	MeCN/EtCN	-80	1:12
6	DBU	MeCN	-40	1:3

ined with a variety of different bases at both −40 and −80 °C. The results are presented in Table 1. Treatment of **12** with any of the weak pyridine-derived bases (entries 1−3) results in regioselective deprotonation at C4 to generate the arene complex **13** as the only product (^{1}H NMR). However, the stronger tertiary amine bases in Table 1 (^{i}Pr$_2$NEt and DBU) favor deprotonation at the C3 methyl group. Lowering the temperature further promotes deprotonation of the C3 methyl group until this reaction is nearly quantitative. A 12:1 mixture (^{1}H NMR) of complexes **14**:**13** is isolated from the reaction medium by precipitation into ether/CH_2Cl_2. In the absence of an external acid, complex **14** is stable in solution (CD_3CN) for an extended period of time, but addition of excess acid to a solution of **14** quantitatively regenerates complex **12**. However, when **14** is combined with an equivalent of TBSOTf at −40 °C in CH_3-CN, an aldol reaction occurs with the pendant ketone to generate the 4*H*-anisolium complex **15** (Scheme 4). Treatment of complex **15** with 2,6-lutidine and warming to ∼80 °C in

Scheme 4. Michael-Aldol Cyclization Using a Complex of 3-Methylanisole



acetonitrile generates the free organic tetralin derivative **16** in a 55% yield.

Once synthesized, intramolecular aldol adduct **4** is further derivatized via functionalization with hydride reducing agents. The regioselectivity of reduction for compound **4** is dependent upon the hydride reducing agent used as well as the reaction temperature (Scheme 5). When complex **4** is treated with 1 equiv of Bu_4NCNBH_3 at 20 °C the solution changes from purple to light brown. Addition of methanol followed by precipitation into an ether/CH_2Cl_2 mixture results in the isolation of compound **17**, in which the hydride reduction has occurred regioselectively in a 1,4-manner. Complex **17** contains many distinguishing features, including diagnostic resonances for the C(2) vinyl ether group. The *cis*- and *trans*-ammine resonances and the cyclic voltammogram for **17** ($E_{1/2}$ = 0.75 V, NHE) are consistent with values typically observed for diene complexes of pentaammineosmium(II).[6] The product complex is again isolated as a 7:1 mixture (^{1}H NMR) of diastereomers (C7 epimers). However, the reduction at the bridgehead position is entirely stereoselective (vide infra).

The vinyl ether functionality of complex **17** is easily protonated with triflic acid in acetonitrile at room temperature to generate the enonium complex **18**. Concurrent with protonation, elimination of the tertiary hydroxy group of **17** occurs and a new double bond is formed in the product. The double bond elimination is not completely regioselective, and a 7:1 mixture (**18a**:**18b**) of isomeric decalins is formed. Compound **18** is prone to form an oil when precipitating solvents such as ether are added to the reaction mixture, and this significantly compromises the isolated yield. Therefore we developed a procedure for the direct transformation of **17** into an enone

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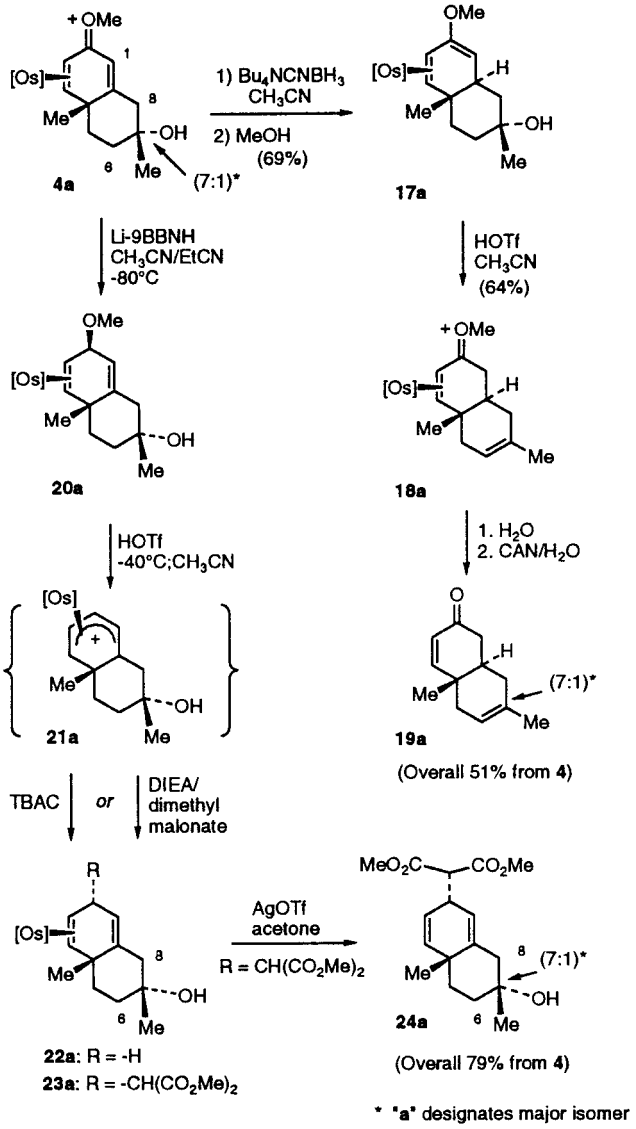
Scheme 5. Elaboration of the Methoxytetralinium Complex **4a**



product. Protonation of complex **17** in acetonitrile followed by addition of water to this mixture results in the rapid hydrolysis of the oxonium functionality to produce an enone complex of pentaammineosmium(II). Direct addition of CAN in water results in oxidation of the metal center and the release of the isomeric mixture of enones **19a** and **19b**. The two organic enones are difficult to separate using conventional chromatographic techniques, but a ^{1}H−^{1}H COSY experiment (500 MHz, $CDCl_3$) allows identification of the major constitutional isomer as compound **19a**. In addition, confirmation of the trans ring fusion was obtained by comparison with literature values for the bridgehead methyl group in similar naphthalen-2-one systems.[7]

By changing the reducing agent and reaction conditions it is possible to alter the regioselectivity of the hydride addition. When complex **4** is combined with lithium-9-boratobicyclo-[3.3.1]nonane hydride (Li9BBNH) in a 1:1 acetonitrile/propionitrile mixture at −80 °C, the solution changes color from purple to light brown. Precipitation into ether results in the isolation of complex **20**, a 1,4-diene complex of pentaammineosmium(II). Although complex **20** displays electrochemical

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data and *cis*- and *trans*-ammine resonances similar to those of 1,3-diene complex **17**, there are pronounced differences in the ^{1}H NMR and ^{13}C NMR spectra of both. Complex **20** contains resonances at δ 5.62 and 5.29−5.32 corresponding to the uncoordinated olefinic proton and the allylic methine proton, respectively. In addition, the ^{13}C NMR spectrum shows a typical olefinic pattern with a methine resonance at 121 ppm and a quaternary olefinic resonance at 144 ppm.

Decomplexation of the methoxydiene ligand of **20** with silver triflate in acetone does not proceed cleanly, and a complex mixture of organic products is isolated. However, when complex **20** is protonated at −40 °C with triflic acid in acetonitrile, the solution darkens, indicating the formation of what we presume is the arenium species **21**. This complex is analogous to that formed from protonation of η^2-benzene complexes.[8] Addition of a nucleophile such as Bu_4NCNBH_3 or dimethyl malonate/DIEA results in the formation of the 1,4-diene complexes **22** and **23**, (both formed as 7:1 C7 epimeric mixtures). When silver triflate is added to an acetone solution of complex **23**, oxidation takes place to liberate the organic compound **24** in an *overall yield* of 79% from **4** (>93% average per step).

A crystal of **24a** (major diastereomer) suitable for X-ray structure determination was grown by vapor diffusion (EtOAc/hexanes). The ORTEP diagram (Supporting Information) confirms several stereochemical issues. The anti disposition of the methyl group at C4a and the malonate group at C2 demonstrate clearly that all electrophilic and nucleophilic additions occur on the face of the ring that is opposite that of metal coordination. In addition, given the high percentage of mass recovered after recrystallization, the major isomer of **24** (i.e., **24a**) has the hydroxy group at C7 on the same face of the ring system as the malonate ester (or anti to the osmium in complex **12**). By inference, the same orientation of the C7 hydroxy group is assumed to hold for **4a, 17a,** and **20a**−**23a.**

Discussion

Pioneering studies by Semmelhack et al. of complexed arene cyclization reactions utilized an α-cyano anion. Using a deprotonation/electrophilic addition/nucleophilic addition sequence with (anisole)$Cr(CO)_3$ various tetralin derivatives were prepared.[9] Recent variations on this theme have achieved the cyclization while dearomatizing the complexed arene. Schmalz et al. have reported an intramolecular radical addition to a chromium tricarbonyl tetralin complex using SmI_2 to provide hydrophenalene derivatives.[10] Cyclization reactions taking advantage of an activated benzylic position of an arene complex have been carried out by Meyer and Jaouen to synthesize a variety of benzobicyclic ring systems.[11,12] In this synthetic sequence, the ability of the chromium tricarbonyl fragment to increase the acidity of benzylic protons was used to generate benzylic nucleophiles that closed rings in an aldol fashion.[2] However, this methodology has not been widely developed, possibly due to the fact that bases that are normally used to deprotonate the benzylic positions of (arene)$Cr(CO)_3$ complexes are basic enough to deprotonate positions α to carbonyl groups.[11,12]

The osmium(II)-promoted ring closures presented herein differ from those of η^6-arenes in two fundamental aspects. Because the metal is electron-donating rather than accepting, activation of the benzylic position is promoted by electrophilic addition rather than direct deprotonation. Given that an *arenium* rather than an arene ligand is deprotonated at the benzylic position, bases required to deprotonate the benzylic position are extremely mild (e.g., DMA) and cyclizations are performed under *acidic* rather than basic reaction conditions. Furthermore, since the product of the cyclization is an η^2-4*H*-anisolium system, the metal may be used to promote subsequent reactions at other carbons of the arene precursor prior to decomplexation of the organic ligand. As demonstrated herein and in previous studies,[3,4,13−15] the metal strictly defines the stereochemistry for the majority of these transformations.

The aldol reaction is a common method for forming rings in organic synthesis. Examples that are most relevant to the osmium-promoted cyclization presented herein include the acid mediated ring closure of a suitably functionalized 2-cyclohexen-1-one to generate a tetrahydronaphthalenone[16] and the ring closure of a dienol derived from α-ionone to form bicyclic retenoic acid derivatives.[17]

The osmium-promoted intramolecular aldol reaction may be achieved even when C4 of the arene precursor contains a proton. Given the high acidity of this proton for anisolium complexes (e.g., **12**; $pK_a(H_2O)$ = (0 to −6),[8] it is remarkable that a selectivity as high as 12:1 can be achieved for deprotonation at the benzylic position. Thus, an additional feature of the pentaammineosmium system is that the C4 proton is shielded on the top face of the molecule by the pentaammineosmium-(II) metal center while it is blocked on the lower face by the butanone chain. Thus the most kinetically accessible protons are those on the C3 methyl group. When a strong base is used, deprotonation at the C3 methyl group provides the desired methoxytriene product. Although deprotonation most likely occurs at the benzylic position, with the weaker pyridine bases (see Table 1), the resulting pyridinium conjugate acid is strong enough to reprotonate the *exo*-methylene group and eventually the arenium **12** undergoes C4 deprotonation.

Concluding Remarks

A novel method for the synthesis of functionalized decalins has been presented which takes advantage of the dearomatizing properties of pentaammineosmium(II). Michael additions with various 3-alkylated anisole complexes result in stabilized 4*H*-arenium systems that may be deprotonated at the C3 benzylic position in order to achieve cyclization with the pendant carbonyl. In addition to promoting the cyclization, the metal center governs the stereochemistry of subsequent hydride reductions of the resulting tetrahydronaphthalonium system.

Experimental Section

Abbreviations: DDQ = 2,3-dichloro-5,6-dicyanobenzoquinone; DME = 1,2-dimethoxyethane; DMA = *N*,*N*-dimethylacetamide; TBAC = tetra-*n*-butylammonium cyanoborohydride; TBS = *tert*-butyldim-

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ethylsilyl; $OTf^- = CF_3SO_3^-$ (triflate); TBAH = tetra-*n*-butylammonium hexafluorophosphate; MVK = methyl vinyl ketone. CAN = $Ce(NO_3)_6(NH_4)_2$.

[Os(NH$_3$)$_5$(5,6-η^2-3-methylidine-1-methoxy-4-methyl-4-(3-oxobutyl)-1,5-cyclohexadiene)](OTf)$_2$ (3). Compound **2** (198 mg, 0.21 mmol) was dissolved in CH_3CN (800 mg), and diisopropylethylamine (35 mg, 0.27 mmol) was added, causing an instant color change to light yellow. Precipitation into a 1:1 mixture of ether/CH_2Cl_2 (300 mL) gave a light yellow solid which was collected, washed with CH_2Cl_2 (~1 mL) and ether (~1 mL), and dried in vacuo (151 mg, 92%). ^{1}H NMR (CD_3CN): δ 5.12 (s, 1H), 4.64 (s, 1H), 4.58 (s, 1H), 4.41 (br s, 3H), 3.94 (d, J = 8.7 Hz, 1H), 3.89 (d, J = 8.4 Hz, 1H), 3.58 (s, 3H), 3.15 (br s, 12H), 2.43 (m, 2H), 2.06 (s, 3H), 1.81 (t, J = 7.8 Hz, 2H), 1.20 (s, 3H); ^{13}C NMR δ 209.8 (C), 165.1 (C), 150.3 (C), 107.0 (CH_2), 94.7 (CH), 56.4 (CH), 55.6 (CH_3), 45.5 (C), 44.7 (CH), 42.1 (CH_2), 39.2 (CH_2), 30.0 (CH_3), 22.8 (CH_3).

[Os(NH$_3$)$_5$)(3,4-η^2-(methyl 7,4a-dimethyl-7-hydroxy-5,6,7,8-tetrahydro-4a*H*-naphthal-2-onium))](OTf)$_3$ (4). Complex **2** (890 mg, 0.96 mmol) was dissolved in CH_3CN (7.1 g), and dimethylacetamide (94 mg, 1.10 mmol) was added. After ~15 min, the solution was added to ~300 mL of stirring ether, the resulting slurry was filtered, and the solid was dried in vacuo. The product (**4a** + **4b**) was isolated as a purple solid (856 mg, 0.92 mmol, 96%). ^{1}H NMR (major isomer **4a**) (CD_3CN): δ 6.57 (s, 1H), 5.69 (d, J = 7.5 Hz, 1H), 5.32 (d, J = 7.5 Hz, 1H), 4.85 (br s, 3H), 4.31 (s, 3H), 3.68 (br s, 12H), 3.01 (m, 1H), 2.61 (d, J = 11.7 Hz, 1H), 2.18 (d, J = 9.9 Hz, 1H), 2.05 (d, J = 5.1 Hz, 1H), 1.80 (m, 1H), 1.37 (s, 3H), 1.32 (m, 1H), 1.28 (s, 3H), 1.16 (m, 1H). ^{13}C NMR δ 196.4 (C), 195.0 (C), 114.9 (CH), 80.1 (C), 67.0 (CH), 62.5 (CH_3), 50.2 (CH), 50.1 (CH_2), 49.1 (C), 44.1 (CH_2), 35.2 (CH_2), 30.6 (CH_3), 18.4 (CH_3); Anal. Calcd for $C_{16}H_{33}N_5O_{11}S_3F_9Os$: C, 20.69; H, 3.58; N, 7.54. Found: C, 20.21; H, 3.85; N, 7.76.

[Os(NH$_3$)$_5$(3,4-η^2-(methyl 4a-(3-oxobutyl)-5,6,7,8-tetrahydro-4a*H*-naphthal-2-onium)](OTf)$_3$ (6). Complex **5** (218 mg, 0.30 mmol) was dissolved in CH_3CN (1.60 g), and methyl vinyl ketone (25 mg, 0.36 mmol) was added. The reaction mixture was cooled to −40 °C, and HOTf (50 mg, 0.33 mmol) in CH_3CN (370 mg) was added, imparting a purple color to the reaction mixture. After ~0.5 h, addition to ether (100 mL) caused the precipitation of a lavender solid which was collected, washed with ether, and dried in vacuo (260 mg, 95%). ^{1}H NMR (CD_3CN): δ 6.62 (s, 1H), 5.59 (d, J = 7.2 Hz, 1H), 5.42 (d, J = 7.2 Hz, 1H), 5.00 (br s, 3H), 4.33 (s, 3H), 3.66 (br s, 12H), 2.80−2.90 (m, 2H), 2.00−2.50 (m, 6H), 2.09 (s, 3H), 1.65−1.85 (m, 2H), 1.00−1.30 (m, 2H). ^{13}C NMR δ 207.6 (C), 197.3 (C), 190.5 (C), 115.2 (CH), 64.1 (CH), 62.3 (CH_3), 50.9 (CH), 49.7 (C), 36.7 (CH_2), 34.9 (CH_2), 34.6 (CH_2), 33.4 (CH_2), 29.3 (CH_3), 26.4 (CH_2), 20.4 (CH_2)

Complex (7). Compound **6** (25 mg, 0.03 mmol) was dissolved in CD_3CN (400 mg), and DMA (4 mg, 0.05 mmol) in CD_3CN (100 mg) was added. Conversion to the aldol adduct **7** was monitored by ^{1}H NMR. After ~12 h, ^{1}H NMR revealed a 1:1 ratio of **6**:**7** where the latter compound is a 1:1 mixture of diastereomers. Partial characterization: ^{1}H NMR (CD_3CN): δ 6.68 (br s, 2H), 5.80 (br d, J = 7.2 Hz, 2H), 5.35 (m, 2H), 4.85 (br s, 6H), 4.31 (s, 3H), 4.30 (s, 3H), 3.73 (br s, 24H), 1.38 (s, 3H), 1.37 (s, 3H).

[Os(NH$_3$)$_5$(3,4-η^2-2-methoxy-4a-(3-oxobutyl)-4a,5,6,7-tetrahydronaphthalene)](OTf)$_2$ (8). Compound **6** (376 mg, 0.39 mmol) was dissolved in CH_3CN (5.00 g) and pyridine (246 mg, 3.11 mmol) was added, causing the reaction mixture to change in color from purple to brown. Addition of the reaction solution to a 1:1 mixture of ether and CH_2Cl_2 (~150 mL) caused the precipitation of a yellow solid which was rinsed with CH_2Cl_2 (~3 mL) and ether (~3 mL), collected, and dried in vacuo (225 mg, 72%). ^{1}H NMR (CD_3CN): δ 5.10 (t, J = 3.9 Hz, 1H), 4.96 (s, 1H), 4.14 (br s, 3H), 3.94 (d, J = 8.7 Hz, 1H), 3.86 (d, J = 8.7 Hz, 1H), 3.54 (s, 3H), 3.17 (br s, 12H), 2.65 (m, 2H), 2.00−2.20 (m, 3H), 2.08 (s, 3H), 1.70−1.90 (m, 3H), 1.65 (m, 1H), 1.22 (m, 1H). ^{13}C NMR δ 209.2 (C), 162.1 (C), 140.2 (C), 119.6 (CH), 94.0 (CH), 54.5 (CH_3), 52.6 (CH), 44.5 (CH), 42.2 (C), 38.6 (CH_2), 38.2 (CH_2), 31.1 (CH_2), 29.2 (CH_3), 24.6 (CH_2), 18.4 (CH_2).

Complex 9. Complex **8** (325 mg, 0.28 mmol) was dissolved in CH_3CN (2.1 g), and TBSOTf (94 mg, 0.36 mmol) was added, imparting a purple color to the reaction mixture. After ~1.5 h, addition of the reaction solution to ether (~200 mL) caused the precipitation of a purple solid. The solid was collected, rinsed with ether, and dried in vacuo (212 mg, 82%). ^{1}H NMR (CD_3CN): δ 6.66 (d, J = 7.5 Hz, 1H), 5.70 (d, J = 7.5 Hz, 1H), 5.41 (m, 1H), 5.20 (dd, J = 7.2 Hz, 1.8 Hz, 1H), 4.80 (br s, 3H), 4.30 (s, 3H), 3.60 (br s, 12H), 3.38−3.41 (m, 1H), 2.76−2.87 (m, 2H), 1.80−2.10 (m, 2H), 1.50−1.78(m, 4H). ^{13}C NMR δ 199.2 (C), 198.0 (C), 137.1 (C), 125.6 (CH), 110.7 (CH), 66.7 (CH), 62.9 (CH_3), 50.4 (CH), 49.7 (CH), 49.1 (CH_2), 48.8 (C), 38.3 (CH_2), 28.5 (CH_2), 20.8 (CH_3), 18.4 (CH_2).

Compound 10. Complex **9** (606 mg, 0.65 mmol) was dissolved in water (7.5 mL), and the solution was transferred to a pressure tube. The tube was removed from the glovebox, placed in an oil bath, and maintained at 80 °C for ~1 h. After this time, the tube was returned to the glovebox and allowed to cool. Ether (~5 mL) was layered on top of the aqueous solution, and then CAN (714 mg, 1.31 mmol) dissolved in water (2.5 mL) was added. The heterogeneous mixture was allowed to stir for ~1 h, and the aqueous phase was separated. The organic layer was diluted with 25 mL of ether and was then washed with 2 × 25 mL of $NaHCO_3$ (saturated), 2 × 25 mL of water, and 2 × 25 mL of brine. The aqueous layers were then separated and washed with 1 × 10 mL of ether. The organic layers were combined and dried (Na_2SO_4), and the solvent was removed in vacuo. Chromatography on SiO_2 (9:1 petroleum ether/ethyl acetate) resulted in the isolation of **10** (33 mg, 25%) as a white solid. ^{1}H NMR ($CDCl_3$): δ 6.80 (d, J = 9.9 Hz, 1H), 6.17 (s, 1H), 6.15 (d, J = 9.9 Hz, 1H), 5.54 (br s, 1H), 2.96 (br s, 1H), 2.29−2.35 (m, 1H), 2.13−2.19 (m, 1H), 1.77−1.96 (m, 3H), 1.72 (s, 3H), 1.51−1.61 (m, 2H), 1.24−1.34 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 187.3 (C), 168.5 (C), 155.6 (CH), 134.3 (C), 126.7 (CH), 121.9 (CH), 120.5 (CH), 46.6 (CH), 42.1 (CH_2), 40.7 (C), 39.0 (CH_2), 30.7 (CH_2), 21.5 (CH_3), 18.3 (CH_2). Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 84.03; H, 8.24.

[Os(NH$_3$)$_5$(5,6-η^2-4-(3-oxobutyl)-3-methylanisole)](OTf)$_2$ (13). Complex **11** (70 mg, 0.10) was dissolved in CH_3CN (514 mg), and MVK (9 mg, 0.13) was added. The solution was cooled to −40 °C, and pre-cooled HOTf (20 mg, 0.13 mmol) in CH_3CN (204 mg) was added. The reaction mixture immediately turned purple upon addition of HOTf. After ~20 min, 2,6-di-*tert*-butylpyridine (204 mg, 1.07 mmol) in CH_3CN (206 mg) was added, and the solution was allowed to stand until the purple color changed to brown (2.2 h). The solution was added to a 1:1 solution of CH_2Cl_2/Et_2O (100 mL), and the resulting slurry was filtered. The product was collected, rinsed with CH_2Cl_2 (~3 mL) and Et_2O (~3 mL), and dried in vacuo (**13**, 66 mg, 86%). ^{1}H NMR (CD_3CN): δ 5.48 (s, 1H), 5.15 (d, J = 8.1 Hz, 1H), 4.82 (d, J = 8.1 Hz, 1H), 4.07 (br s, 3H), 3.62 (s, 3H), 2.93 (br s, 12H), 2.51 (m, 2H), 2.13 (s, 3H), 2.09 (s, 3H), 2.01 (m, 2H).

[Os(NH$_3$)$_5$(5,6-η^2-3-methylidine-4-(3-oxobutyl)-1,5-cyclohexadiene)](OTf)$_2$ (14). Complex **11** (355 mg, 0.51 mmol) was dissolved in CH_3CN (2.0 g), MVK (49 mg, 0.69 mmol) was added, and the solution was cooled to −40 °C. Precooled HOTf (122 mg, 0.81 mmol) in CH_3CN (1.0 g) was added, imparting a purple color to the reaction mixture. After ~0.5 h, a cold solution of diisopropylethylamine (698 mg, 5.4 mmol) was added, and the reaction mixture changed color to brown. After ~10 min, addition to ether/CH_2Cl_2 (200 mL) caused the precipitation of a yellow solid (273 mg, 70%) which was collected, rinsed with CH_2Cl_2 and ether, and dried in vacuo. ^{1}H NMR (CD_3CN): δ 5.21 (s, 1H), 4.67 (s, 1H), 4.41 (s, 1H), 4.14 (br s, 3H), 3.79 (s, 2H), 3.59 (s, 3H), 3.01 (br s, 12H), 2.49−2.60 (m, 3H), 2.09 (s, 3H), 1.70−1.85 (m, 2H)

2-Methyl-2-(*tert*-butyldimethylsiloxy)-7-methoxy-1,2,3,4-tetrahydronaphthalene (16). Complex **14** (418 mg, 0.55 mmol) was dissolved in CH_3CN (1.5 g), and the solution was cooled to −40 °C. Precooled TBSOTf (187 mg, 0.71 mmol) in CH_3CN (503 mg) was added, and the color of the solution rapidly changed from brown to purple. After ~25 min, precooled pyridine (1.0 g) was added, and the solution was transferred to a pressure tube. The solution was heated overnight (~12 h) in an oil bath maintained at 85 °C. After cooling to room temperature, the solution was added to ~100 mL of stirring ether, and the resulting slurry was filtered. The organic phase was rinsed with 2 × 25 mL of $NaHCO_3$ (saturated), 2 × 25 mL of water, and 2 × 25 mL of brine, and the aqueous extracts were in turn washed with 1 × 10 mL of ether. The organic layers were combined, dried (Na_2SO_4), and the solvent was removed in vacuo. Chromatography on SiO_2 (hexanes)

yielded the product (**16**, 85 mg, 55%) as a clear liquid. ^{1}H NMR ($CDCl_3$): δ 6.69 (d, J = 7.8 Hz, 1H), 6.37 (dd, J = 7.8 Hz, 2.4 Hz, 1H), 6.25 (d, J = 2.4 Hz, 1H), 3.47 (s, 3H), 2.55−2.68 (m, 1H), 2.49 (d, J = 8.1 Hz, 1H), 2.31−2.42 (m, 2H), 1.52−1.60 (m, 1H), 1.34−1.43 (m, 1H), 1.02 (s, 3H), 0.47 (s, 9H), −0.20 (s, 3H), −0.32 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 157.5 (C), 136.8 (C), 129.4 (CH), 128.0 (C), 114.0 (CH), 111.9 (CH), 71.9 (C), 55.4 (CH_3), 44.8 (CH_2), 37.6 (CH_2), 29.2 (CH_3), 26.4 (CH_2), 26.0 (CH_3), 18.3 (C), −1.7 (CH_3), −2.0 (CH_3). Anal. Calcd for $C_{18}H_{30}O_2Si$: C, 70.53; H, 9.87. Found: C, 70.67; H, 10.19.

[Os(NH$_3$)$_5$(3,4-η^2-4a,7-dimethyl-7-hydroxy-4a,5,6,7,8,8a-hexahydronaphthalene)](OTf)$_2$ (17). Complex **4** (453 mg, 0.49 mmol) was dissolved in CH_3CN (3.5 g), and a solution of Bu_4NCNBH_3 (169 mg, 0.60 mmol in CH_3CN, 1.0 g) was added. After ∼10 min, the purple color changed to brown, and MeOH (505 mg) was added. The solution was allowed to stand for ∼1.5 h and was then added to a 1:1 solution of CH_2Cl_2/Et_2O (200 mL). The resulting slurry was filtered. The product was collected, rinsed with CH_2Cl_2 (3 mL) and ether (∼3 mL), and dried in vacuo (**17**, 265 mg, 69%). The product was isolated as a 7:1 mixture of diastereomers. Characterization reported for major diastereomer (**17a**) only. ^{1}H NMR (CD_3CN): δ 4.38 (br s, 1H), 4.12 (br s, 3H), 3.67 (m, 2H), 3.57 (s, 3H), 3.15 (br s, 12H), 2.43 (s, 1H), 1.52−1.76 (m, 5H), 1.34−1.46 (m, 2H), 1.11 (s, 3H), 1.07 (s, 3H). ^{13}C NMR (CD_3CN): δ 159.8 (C), 93.4 (CH), 69.6 (C), 59.5 (CH), 55.1 (CH_3), 44.9 (CH), 42.1 (C), 40.8 (CH_2), 38.0 (CH), 36.1 (CH_2), 35.2 (CH_2), 31.2 (CH_3), 23.2 (CH_3). Electrochemistry (CH_3CN, 100 mV/s): $E_{1/2}$ = 0.75 V.

[Os(NH$_3$)$_5$(3,4-η^2-4a,7-dimethyl-4a,5,8,8a-tetrahydro-1*H*-naphthal-2-onium)](OTf)$_3$ (18a) and [Os(NH$_3$)$_5$(3,4-η^2-4a,7-dimethyl-4a,5,6,-8a-tetrahydro-1*H*-naphthal-2-onium)](OTf)$_3$ (18b). Complex **17** (515 mg, 0.66 mmol) was dissolved in CH_3CN (1.2 g), and HOTf (199 mg, 1.33 mmol) was added. The solution immediately darkened, and after ∼1 h, the solution was added to ether (150 mL). The resulting slurry was filtered, and the product was collected, rinsed with ether (∼10 mL), and dried in vacuo (**18**, 395 mg, 64%). Characterization is reported for major diastereomer (**18a**) only. ^{1}H NMR (CD_3CN): δ 5.77 (d, J = 7.5 Hz, 1H), 5.42−5.44 (m, 1H), 5.20 (d, J = 7.5 Hz, 1H), 4.94 (br s, 3H), 4.28 (s, 3H), 3.84 (br s, 12H), 3.05−3.12 (m, 1H), 2.20−2.35 (m, 2H), 2.03−2.08 (m, 2H), 1.67 (s, 3H), 1.20 (s, 3H), 1.08−1.13 (m, 2H). ^{13}C NMR (CD_3CN): δ 217.3 (C), 131.4 (C), 122.1 (CH), 71.7.(CH), 64.6 (CH_3), 54.5 (CH), 43.9 (CH_2), 40.9 (C), 35.2 (CH_2), 33.7 (CH), 32.7 (CH_2), 23.7 (CH_3), 23.6 (CH_3).

4a,7-Dimethyl-4a,5,8,8a-tetrahydro-1*H*-naphthal-2-one (19a) and 4a,7-Dimethyl-4a,5,6,8a-tetrahydro-1*H*-naphthal-2-one (19b). Complex **18** (255 mg, 0.33 mmol) was dissolved in CH_3CN (2.0 g), and HOTf (107 mg, 0.71 mmol) was added. After ∼0.5 h, water (1.1 g) was added, and the solution was allowed to stand for ∼1 h. Ether (5 mL) was added to the solution, and the heterogeneous mixture was treated with CAN (363 mg, 0.66 mmol) dissolved in water (1.3 g). The heterogeneous mixture was allowed to stir for ∼1 h, and the solution was removed from the glovebox and the aqueous layer separated off. The organic phase was diluted with ether (25 mL) and washed with 2 × 25 mL of $NaHCO_3$ (saturated), 2 × 25 mL of water, and 2 × 25 mL of brine. The aqueous layers were then separated and washed with 1 × 10 mL of ether. The organic layers were combined and dried (Na_2SO_4), and the solvent was removed in vacuo. Chromatography on SiO_2 (9:1 petroleum ether/ether) resulted in the isolation of **19a**,**b** (42 mg, 75% from **17**) as a clear liquid. ^{1}H NMR (**19a**) ($CDCl_3$, 500 MHz): δ 6.79 (d, J = 10.0 Hz, 1H), 5.86 (d, J = 10.0 Hz, 1H), 5.38 (m, 1H), 2.35 (d, J = 6.0 Hz, 1H), 2.34 (d, J = 10.0 Hz, 1H), 2.04−2.07 (m, 1H), 2.02−2.06 (m, 2H), 1.68−1.70 (m, 2H), 1.66 (s, 3H), 1.15 (s, 3H). ^{13}C NMR for major isomer ($CDCl_3$): δ 200.3 (C), 161.2 (CH), 131.5 (C), 127.5 (CH), 118.9 (CH), 41.6 (CH_2), 38.4 (CH), 35.2 (CH_2), 34.6 (C), 33.8 (CH_2), 25.9 (CH_3), 23.6 (CH_3). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.86; H, 9.47. ^{1}H NMR (**19b**). Not all peaks could be assigned due to overlapping resonances in the spectrum. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.54 (d, J = 10.0 Hz, 1H), 5.18 (m, 1H), 2.64 (dd, J = 16.5 Hz, 5.0 Hz, 1H), 2.50 (d, J = 5.0 Hz, 1H), 2.28−2.30 (m, 1H), 2.25−2.27 (m, 1H), 2.21 (dd, J = 16.5 Hz, 7.5 Hz, 1H), 1.63 (s, 3H), 1.49−1.53 (m, 1H), 1.16 (s, 3H).

[Os(NH$_3$)$_5$(3,4-η^2-4a,7-dimethyl-7-hydroxy-2-methoxy-2,4a,5,6,7,8-hexaahydronaphthalene)](OTf)$_2$ (20). Complex **4** (509 mg, 0.55 mmol) was dissolved in CH_3CN (3.5 g) and EtCN (3.5 g), and cooled to −80 °C. Precooled 1.0 M Li-9BBNH dissolved in THF (611 mg, 0.56 mmol) was added, immediately discharging the purple color to a light yellow. After ∼0.5 h, the solution was added to ether (100 mL), and the resulting slurry was filtered. The solid was collected, rinsed with ether (∼3 mL), and dried in vacuo (**20**, 395 mg, 96%). ^{1}H NMR **(20)** (CD_3CN): δ 5.62 (d, J = 2.1 Hz, 1H), 5.29−5.32 (m, 1H), 4.00 (br s, 3H), 3.87−3.92 (m, 1H), 3.63 (d, J = 5.4 Hz, 1H), 3.42 (s, 3H), 3.22 (br s, 12H), 2.53 (d, J = 12.9 Hz, 1H), 2.14 (d, J = 12.9 Hz, 1H), 1.72−1.83 (m, 2H), 1.54−1.63 (m, 1H), 1.43−1.48 (m, 1H), 1.18 (s, 3H), 0.98 (s, 3H). ^{13}C NMR (CD_3CN): δ 144.3 (C), 120.8 (CH), 82.0 (CH), 72.3 (C), 59.1 (CH), 57.1 (CH_3), 46.1 (CH_2), 45.8 (CH), 43.1 (CH_2), 40.9 (C), 36.1 (CH_2), 30.4 (CH_3), 21.1 (CH_3). This complex was recrystallized from methanol/ether via vapor diffusion to yield material suitable for analysis. Anal. Calcd for $C_{15}H_{35}N_5O_8S_2F_6Os$: C, 23.05; H, 4.51; N, 8.96. Found: C, 23.02; H, 4.51; N, 8.51.

[Os(NH$_3$)$_5$(3,4-η^2-4a,7-dimethyl-7-hydroxy-2,4a,5,6,7,8-hexahydronaphthalene)](OTf)$_2$ (22). Complex **20** (79 mg, 0.10 mmol) was dissolved in CH_3CN (404 mg), and the soltution was cooled to −40 °C. Cold triflic acid (18 mg, 0.12 mmol) in CH_3CN (203 mg) was added, and the solution darkened in color. After ∼20 min, TBAC (57 mg, 0.20 mmol) dissolved in CH_3CN (400 mg) was added, and the solution lightened. After ∼1 h, the solution was precipitated into ∼50 mL of a 1:1 ether/CH_2Cl_2 solution, and the slurry is filtered. The resulting solid was filtered, rinsed with CH_2Cl_2 then ether, and the product was isolated as a white powder (**22**, 56 mg, 74%). ^{1}H NMR (**22**) (CD_3CN): δ 5.35 (br s, 1H), 3.95 (br s, 3H), 3.58−3.63 (m, 1H), 3.39−3.44 (m, 1H), 3.04 (br s, 12H), 2.54 (d, J = 12.9 Hz, 1H), 1.84 (dd, J = 12.9 Hz, 3.9 Hz, 1H), 1.72 (dd, J = 12.6 Hz, 2.1 Hz, 1H), 1.44−1.58 (m, 2H), 0.93−1.20 (m, 4H), 1.15 (s, 3H), 0.98 (s, 3H). ^{13}C NMR (CD_3CN) δ 140.6 (C), 122.8 (CH), 71.4 (C), 58.0 (CH), 47.3 (CH), 46.3 (CH_2), 43.2 (CH_2), 40.2 (C), 36.4 (CH_2), 30.2 (CH_3), 28.8 (CH_2), 21.1 (CH_3).

[**Os(NH$_3$)$_5$(3,4-η^2-4a,7-dimethyl-2-(dimethylmalonyl)-7-hydroxy-2,4a,5,6,7,8-hexahydronaphthalene)](OTf)$_2$ (23).** Complex **20** (266 mg, 0.34 mmol) was dissolved in CH_3CN (2.0 g), and the solution was cooled to −40 °C. Cold triflic acid (105 mg, 0.7 mmol) dissolved in CH_3CN (1.0 g) was added, and the solution darkened. After ∼20 min, cold dimethyl malonate (494 mg, 3.63 mmol) and DIEA (116 mg, 0.90 mmol) dissolved in CH_3CN (1.4 g) was added and the solution immediately lightened. After ∼1.5 h, the solution was precipitated into ∼200 mL of an ether/CH_2Cl_2 solution, and the resulting slurry was filtered. The solid was washed with CH_2Cl_2 then ether, and the product (**23**, 234 mg, 78%) was isolated as a white solid. Product isolated as an ∼7:1 mixture of diastereomers, characterization reported for major diastereomer (**23**) only. ^{1}H NMR (acetone-d_6): δ 5.26 (d, J = 2.1 Hz, 1H), 4.60 (br s, 3H), 3.75 (s, 3H), 3.74 (s, 3H), 3.73 (br s, 14H), 2.94−2.98 (m, 1H), 2.66 (d, J = 11.7 Hz, 1H), 1.65−1.95 (m, 4H), 1.40−1.55 (m, 1H), 1.10−1.20 (m, 2H), 1.17 (br s, 6H). ^{13}C NMR (acetone-d_6) δ 170.8 (C), 170.7 (C), 144.7 (C), 123.7 (CH), 71.7 (C), 61.1 (CH), 56.8 (CH), 53.7 (CH_3), 53.5 (CH_3), 48.2 (CH), 47.1 (CH_2), 44.8 (CH_2), 41.1 (C), 40.6 (CH), 37.1 (CH_2), 30.5 (CH_3), 21.6 (CH_3). Electrochemistry (TBAH, CH_3CN, 100 mV/s): $E_{p,a}$ = 0.82 V.

4a,7-Dimethyl-2-(dimethylmalonyl)-7-hydroxy-2,4a,5,6,7,8-hexahydronaphthalene (24). Complex **20** (256 mg, 0.33 mmol) was dissolved in CH_3CN (1.6 g), and the solution was cooled to −40 °C. Cold triflic acid (101 mg, 0.67 mmol) dissolved in CH_3CN (817 mg) was added, and the solution was allowed to stand at −40 °C for ∼20 min. After this time, a cold solution consisting of dimethyl malonate (518 mg, 3.81 mmol) and diisopropylethylamine (111 mg, 0.86 mmol) in CH_3CN (417 mg) was added, and the solution color immediately lightened. After ∼1 h, AgOTf (176 mg, 0.69 mmol) dissolved in acetone (1.0 g) was added, and the solution immediately became heterogeneous. The solution was allowed to warm to room temperature over the course of ∼1 h and was then added to ∼50 mL of stirring ether. The slurry was filtered, and the organic phase was washed with 2 × 25 mL of 10% NaOH (aq), 2 × 25 mL of water, 2 × 25 mL of 10% HCl (aq) and 2 × 25 mL of brine. The organic phase was separated off and dried (Na_2SO_4) and the solvent removed in vacuo. Chromatography of the

residue (4:1 hexanes/EtOAc, SiO_2) resulted in the isolation of **24** (83 mg, 82%) as a white powder. ^{1}H NMR (**24**) ($CDCl_3$): δ 5.52 (m, 2H), 5.41 (m, 1H), 3.69 (s, 6H), 3.00 (m, 1H), 2.46 (d, J = 12.6 Hz, 1H), 1.95 (dd, J = 13.2 Hz, 2.4 Hz, 1H), 1.65 (dd, J = 13.2 Hz, 5.1 Hz, 1H), 1.49−1.57 (m, 2H), 1.39−1.46 (m, 1H), 1.22 (s, 3H), 1.09 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 168.8 (C), 168.5 (C), 140.5 (C), 138.2 (CH), 121.6 (CH), 121.2 (CH), 56.3 (CH), 52.8 (CH_3), 52.7 (CH_3), 46.1 (CH_2), 37.1 (CH), 36.4 (CH_2), 35.8 (C), 35.2 (CH_2), 29.4 (CH_3), 24.1 (CH_3), 21.4 (C). This sample was recrystallized from ethyl acetate/hexanes to generate a crystal suitable for X-ray structure analysis and elemental analysis. Anal. Calcd for $C_{17}H_{24}O_5$: C, 66.21; H, 7.84. Found: C, 66.11; H, 7.97.

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Supporting Information Available: ORTEP diagram and tables of crystallographic data and collection parameters, atomic positional parameters, complete bond distances and angles, and anisotropic temperature factors for **24** as well as complete experimental details (16 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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