Activation of Styrenes toward Diels−Alder Cycloadditions by Osmium(II): Synthesis of Stereodefined Decalin Ring Systems

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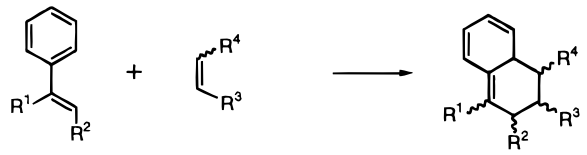
Received October 24, 1997

Abstract: The complex $[Os(NH_3)_5(\eta^2\text{-anisole})]^{2+}$ reacts with acetals or Michael acceptors to form 4-methoxystyrene complexes that are exclusively coordinated at the arene (η^2). These styrene complexes are active dienes and readily participate in Diels−Alder reactions with electron-deficient olefins to form tetrahydronaphthalene complexes. The cycloadducts are formed typically as single diastereomers and are valuable as precursors to functionalized tetralins and decalins.

Introduction

Because of their widespread occurrence in terpenes, steroids, and other natural products, decalins remain popular targets for synthetic chemists. The Diels−Alder cycloaddition of a styrene and olefin is an attractive strategy for decalin formation, as the bicyclic system would be formed with up to four new stereogenic centers. However, styrenes more commonly participate in [2 + 2] cycloadditions[1,2] or as *dienophiles* in [4 + 2] cycloaddition reactions.[3] Although styrenes can participate as



dienes in Diels−Alder reactions,[4,5] the associated loss of aromatic character requires either extremely reactive dienophiles or harsh reaction conditions that are incompatible with most functional groups. Furthermore, the products of the cycloaddition reaction are prone to rearomatization, a process that often destroys one or more of the newly created stereocenters. In addition, these cycloadducts are often more reactive as dienes than are their styrene precursors and can participate in subsequent chemistry that is often undesirable.[6,7]

The dearomatization agent pentaammineosmium(II) is known to activate arenes toward electrophilic additions through its ability to partially localize the arene π system. We reasoned that if the aromatic portion of a styrene could be selectively coordinated, then perhaps the synthesis of functionalized decalin ring systems by a Diels−Alder route could be readily achieved. Herein we describe our results regarding the [4 + 2] cycloaddition reactions of *p*-methoxystyrene complexes of pentaammineosmium(II).

Experimental Details

Abbreviations: CAN = ceric ammonium nitrate; DIEA = diisopropylethylamine; DMF = *N*,*N*-dimethylformamide; NMM = *N*-methylmaleimide; OTf = trifluoromethanesulfonate; TBAC = tetrabutylammonium cyanoborohydride; TBAH = tetrabutylammonium hexafluorophosphate; [Os] = $[Os(NH_3)_5]^{2+}$.

All reactions were performed under nitrogen. Acetonitrile and CD_3CN were distilled from CaH_2 before use. All other solvents and reagents were used as received without further purification.

^1H and ^{13}C NMR spectra were obtained on 300 MHz spectrometers. The ^{13}C resonances for $CF_3SO_3^-$ ions are very weak and are not listed. Electrochemical experiments were performed using a PAR model 362 potentiostat driven by a PAR model 175 Universal Programmer. All cyclic voltammograms were recorded at 100 mV/s, and potentials are reported versus NHE. Mass spectra (GCMS) were obtained with a HP 5972 Series mass selective detector. Elemental analyses were obtained on a Perkin-Elmer PE-2400 Series II CHN analyzer. For a more detailed description of experimental procedures, see ref 8.

$[Os(NH_3)_5(2,3\text{-}\eta^2\text{-}4\text{-}(1\text{-ethoxyethane})anisole)](OTf)_2$ (2). Complex **1** (522 mg, 0.77 mmol)[9] was dissolved in CH_3CN (6.0 g), and acetaldehyde diethyl acetal (95 mg, 0.77 mmol) was added. In a separate vial, HOTf (347 mg, 2.3 mmol) was dissolved in CH_3CN (753 mg), and the two solutions were cooled to −40 °C and combined. The reaction solution immediately turned purple. After ∼20 min, cold (−40 °C) pyridine (1.04 g, 13.16 mmol) was added, and the solution color changed to amber. After ∼10 min, the solution was added to ∼200 mL of a 1:1 ether/CH_2Cl_2 solution, and the resulting precipitate was filtered, rinsed with CH_2Cl_2 and ether, and dried in vacuo. The product (**2**, 549 mg, 94%) was isolated as a yellow powder. ^1H NMR revealed a 9:1 ratio of diastereomers. ^1H NMR (acetone-d_6): (major isomer) δ 6.53 (dd, J = 8.4, 2.1 Hz, 1H), 5.53 (dd, J = 8.4, 2.1 Hz, 1H), 5.47 (dd, J = 8.4, 2.1 Hz, 1H), 5.09 (dd, J = 8.4, 2.1 Hz, 1H), 4.71 (br s, 3H), 4.30 (q, J = 6.6 Hz, 1H), 3.69 (s, 3H), 3.55 (br s, 12H), 3.40−3.70 (m, 2H), 1.43 (d, J = 6.6 Hz, 3H), 1.21 (t, J = 7.2 Hz, 3H). ^{13}C NMR (acetone-d_6): δ 170.8 (C), 139.9 (C), 121.0 (CH), 93.2 (CH), 80.5 (CH), 64.3 (CH_2), 58.5 (CH), 56.7 (CH), 55.4(CH_3), 19.2 (CH_3), 15.6 (CH_3). CV (CH_3CN; TBAH): $E_{1/2}$ = 0.40 V.

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S0002-7863(97)03700-1 CCC: $15.00
Published on Web 03/03/1998

[Os(NH$_3$)$_5$(2,3-η^2-4-(1-hydroxyethyl)anisole](OTf)$_2$ (3). This complex was synthesized using the procedure employed for the synthesis of complex **1**.[9] The product (**3**) was isolated as a yellow solid (95%) in a 3:1 ratio of diastereomers. ^{1}H NMR (acetone-d_6; major isomer only): δ 6.46 (dd, J = 7.2, 1.6 Hz, 1H), 5.51 (d, J = 7.2 Hz, 1H), 5.07 (m, 2H), 4.86 (br s, 4H), 3.68 (s, 3H), 3.58 (br s, 12H), 1.44 (d, J = 6.6 Hz, 3H), OH not observed. ^{13}C NMR (CD$_3$CN): δ 168.8 (C), 139.8 (C), 119.1 (CH), 94.12 (CH), 72.2 (CH), 59.1 (CH), 57.2 (CH), 56.0 (CH$_3$), 23.2 (CH$_3$). Anal. Calcd for $C_{11}H_{27}N_5O_8S_2F_6Os$: C, 18.20; H, 3.75; N: 9.65. Found: C, 18.16; H, 3.99; N, 9.39. CV (CH$_3$CN; TBAH): $E_{1/2}$ = 0.52 V.

***p*-Quinone Methide Complex 4.** Complex **2** was dissolved in CD$_3$CN in an NMR tube and cooled to −40 °C. A triflic acid solution (CD$_3$CN) maintained at −40 °C was added, and the reaction solution immediately turned green. ^{1}H NMR data reported for the 1:1 mixture of isomers. ^{1}H NMR (CD$_3$CN; −40 °C): δ 8.30 (d (×2), 2H), 7.80 (d, 1H), 7.50 (d, 1H), 6.80 (q (×2), 2H), 6.45 (d, 1H), 6.39 (d, 1H), 5.91 (d, 1H), 5.88 (d, 1H), 5.09 (br s, 3H), 5.06 (br s, 3H), 4.25 (s, 6H), 3.70−3.67 (br s, 24 H), 1.66 (d, 3H), 1.50 (d, 3H).

[Os(NH$_3$)$_5$(2,3-η^2-4-(1-*N*-pyridiniumethyl)anisole)](OTf)$_3$ (5). Complex **2** (226 mg, 0.30 mmol) was dissolved in CH$_3$CN (2 g). The reaction mixture was cooled to −40 °C, and upon addition of HOTf (60 mg, 0.40 mmol) in CH$_3$CN (350 mg), the solution changed from amber to dark green. After ∼20 min, cold pyridine (956 mg, 12.1 mmol, −40 °C) was added causing the solution to turn from dark green to light orange. Addition of reaction mixture to a stirring solution of 1:1 Et$_2$O/CH$_2$Cl$_2$ (∼100-mL) resulted in the precipitation of compound **5** (230 mg, 80%) as an orange solid in a 10:1 diastereomeric ratio. ^{1}H NMR (CD$_3$CN; major isomer): δ 8.74 (m, 2H), 8.46 (m, 1H), 7.99 (m, 2H), 6.99 (d, J = 7.2 Hz, 1H), 5.78 (d, J = 6.9 Hz, 1H), 5.72 (d, J = 7.2 Hz, 1H), 4.77 (m, 1H), 4.60 (d, J = 7.2 Hz, 1H), 4.22 (br s, 3H), 3.70 (s, 3H), 3.02 (br s, 12H), 1.83 (d, J = 7.2 Hz, 3H). ^{13}C NMR (CD$_3$CN): δ 171.1 (C), 143.1 (2 × CH), 132.0 (C), 128.3 (2 × CH), 125.0 (CH), 121.8 (CH), 91.2 (CH), 71.5 (CH), 57.3 (CH), 55.4 (CH), 53.8 (CH$_3$), 19.9 (CH$_3$). CV (CH$_3$CN; TBAH): $E_{1/2}$ = 0.60 V.

[Os(NH$_3$)$_5$(2,3-η^2-4-methoxystyrene)](OTf)$_2$ (6). Complex **2** (549 mg, 0.73 mmol) was dissolved in CH$_3$CN (7.0 g), and in a separate vial, HOTf (217 mg, 1.44 mmol) was dissolved in CH$_3$CN (807 mg). The two solutions were cooled to −40 °C, and an immediate color change from amber to green was observed upon mixing. After ∼20 min, cold (−40 °C) pyridine (983 mg, 12.44 mmol) was added, and the solution changed from green to amber. The solution was added to 100 mL of stirring ether, and the ether was decanted off the resulting oil. The residue was dissolved in CH$_3$CN (∼6 g), and diisopropylethylamine (944 mg, 7.32 mmol) was added; the reaction solution changed from amber to purple red. The reaction mixture was precipitated into ∼200 mL of a 1:1 Et$_2$O/CH$_2$Cl$_2$ solution, and the resulting solid was filtered, rinsed, and dried in vacuo (**6**, 456 mg, 88%).

Alternate Synthesis of 6. Complex **3** (727 mg, 1.00 mmol) was dissolved in CH$_3$CN (8.00 g). The solution was cooled to −40 °C, and triflic acid (303 mg, 2.00 mmol) was added. The reaction solution changed from amber to green. After ∼20 min, cold (−40 °C) pyridine (956 mg, 12.1 mmol) was added, and the solution returned to amber. The solution was added to ∼100 mL of stirring ether, and the ether was decanted off the resulting oil. The residue was dissolved in CH$_3$CN (∼10 g), and diisopropylethylamine (1.30 g, 10.1 mmol) was added. The reaction solution changed from amber to purple red. The solution was precipitated into ∼300 mL of a 1:1 Et$_2$O/CH$_2$Cl$_2$ solution, and the resulting solid was collected by filtration, rinsed, and dried in vacuo (**6**, 594 mg, 84%). ^{1}H NMR (acetone-d_6): δ 6.60 (dd, J = 17.7, 11.1 Hz, 1H), 6.39 (dd, J = 6.9, 1.2 Hz, 1H), 5.71 (dd, J = 8.7, 1.2 Hz, 1H), 5.61 (dd, J = 17.7, 1.2 Hz, 1H), 5.38 (dd, J = 6.9, 1.2 Hz, 1H), 4.99 (dd, J = 8.4, 1.2 Hz, 1H), 4.73 (d, J = 11.1 Hz, 1H), 4.59 (br s, 3H), 3.57 (s, 3H), 3.42 (br s, 12H). ^{13}C NMR (acetone-d_6): δ 170.7 (C), 141.3 (CH), 124.1 (CH), 124.0 (C), 110.4 (CH$_2$), 93.6 (CH), 56.1 (CH), 55.8 (CH), 55.4 (CH$_3$). Anal. Calcd. for $C_{11}H_{25}N_5O_7S_2F_6Os$: C, 18.67; H, 3.56; N, 9.89. Found: C, 18.44; H, 3.62; N: 10.13. CV (CH$_3$CN; TBAH): $E_{1/2}$ = 0.62 V.

[Os(NH$_3$)$_5$(2,3-η^2-4-methoxyphenylethene)](OTf)$_2$ (6v). This compound was synthesized by dissolving complex **6** in CD$_3$CN in an NMR tube and heating the solution at 60 °C for ∼1 h. ^{1}H NMR (CD$_3$CN): δ 7.01 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 4.39 (dd, J = 9.9, 8.7 Hz, 1H), 4.15 (br s, 3H), 4.03 (dd, J = 9.9 Hz, 1.8 Hz, 1H), 3.74 (s, 3H), 3.32 (dd, J = 8.7 Hz, 1.8 Hz, 1H), 2.88 (br s, 12H).

[Os(NH$_3$)$_5$(2,3-η^2-4-(1-methoxycyclopentyl)anisole)](OTf)$_2$ (7). The anisole complex **1** (310 mg, 0.45 mmol) was dissolved in CH$_3$CN (5.0 g), and 1,1-dimethoxycyclopentane (131 mg, 1.00 mmol) was added. In a separate vial, HOTf (209 mg, 1.40 mmol) was dissolved in CH$_3$CN (1.00 g), and the two solutions were cooled to −40 °C and combined. The reaction solution immediately changed from brown to purple. After ∼25 min, cold (−40 °C) pyridine (1.0 g, 12.7 mmol) was added to the reaction mixture, and the solution changed from purple to brown. After ∼5 min, the solution was added to ∼200 mL of a stirring 1:1 Et$_2$O/CH$_2$Cl$_2$ solution, and the resulting slurry was filtered. The solid was rinsed with CH$_2$Cl$_2$ followed by an ether rinse and dried in vacuo to yield the product (**5**, 322 mg, 92%) as a yellow powder. ^{1}H NMR (acetone-d_6): δ 6.71 (dd, J = 7.5, 1.8 Hz, 1H), 5.60 (dd, J = 7.5, 1.8 Hz, 1H), 5.50 (dd, J = 8.7, 1.8 Hz, 1H), 5.08 (dd, J = 8.7, 1.8 Hz, 1H), 4.68 (br s, 3H), 3.70 (s, 3H), 3.57 (br s, 12H), 2.96 (s, 3H), 1.75 (m, 8H). CV (CH$_3$CN; TBAH): $E_{1/2}$ = 0.60 V. Batches of this material often contain the elimination product **9** as an impurity.

***p*-Quinone Methide Complex 8.** Complex **7** (7 mg, 0.01 mmol) was dissolved in CD$_3$CN (400 mg), and triflic acid (5 mg, 0.03 mmol) was added. The solution was transferred to an NMR tube and characterization data was recorded in situ. ^{1}H NMR (CD$_3$CN): δ 7.93 (dd, J = 9.6, 1.8 Hz, 1H), 6.59 (d, J = 6.9 Hz, 1H), 6.36 (d, J = 9.9 Hz, 1H), 5.80 (dd, J = 6.9, 1.8 Hz, 1H), 4.91 (br s, 3H), 4.26 (s, 3H), 3.58 (br s, 12H), 2.31−2.44 (m, 1H), 2.12−2.23 (m, 3H), 1.77−2.07 (m, 4H). ^{13}C NMR (CD$_3$CN): δ 199.4 (C), 177.5 (C), 152.6 (CH), 138.0 (C), 113.0 (CH), 62.1 (CH$_3$), 57.1 (CH), 54.6 (CH), 38.6 (CH$_2$), 37.1 (CH$_2$), 26.6 (CH$_2$), 26.3 (CH$_2$).

[Os(NH$_3$)$_5$(2,3-η^2-4-(1-cyclopentenyl)anisole)](OTf)$_2$ (9). Complex **7** (780 mg, 1.00 mmol) was dissolved in CH$_3$CN (9.0 g), and in a separate test tube, triflic acid (304 mg, 2.01 mmol) was dissolved in CH$_3$CN (509 mg). The two solutions were cooled to −40 °C and combined, and the solution changed from yellow to gold. After ∼20 min, cold (−40 °C) diisopropylethylamine (334 mg, 2.6 mmol) in CH$_3$CN (501.0 mg) was added, and the solution was shaken. After ∼15 min, the solution was precipitated into a 1:1 Et$_2$O/CH$_2$Cl$_2$ solution (300 mL), and the resulting slurry was filtered. The solid was rinsed with CH$_2$Cl$_2$ and then Et$_2$O and dried *in vacuo* to yield the product (**9**, 683 mg, 91%) as a yellow solid. ^{1}H NMR (CD$_3$CN): δ 6.28 (d, J = 7.2 Hz, 1H), 6.16 (br s, 1H), 5.60 (dd, J = 7.2 1.5 Hz, 1H), 5.56 (d, J = 8.4 Hz, 1H), 4.85 (dd, J = 8.4, 1.5 Hz, 1H), 4.09 (br s, 3H), 3.66 (s, 3H), 2.94 (br s, 12H), 2.51 (m, 4H), 2.00 (m, 2H). ^{13}C NMR (CD$_3$CN): δ 168.9 (C), 146.1 (C), 134.0 (C), 125.4 (CH), 119.4 (CH), 93.6 (CH), 58.2 (CH), 56.1 (CH), 55.8 (CH$_3$), 34.1 (CH$_2$), 33.8 (CH$_2$), 24.2 (CH$_2$). CV (CH$_3$CN; TBAH): $E_{1/2}$ = 0.52 V.

[Os(NH$_3$)$_5$(6,7-η^2-2-aza-8-methoxy-2-methyl-3a,4,9a,9b-tetrahydro-2*H*-benz[*e*]inden-1,3-dione)](OTf)$_2$ (10). Complex **6** (637 mg, 0.90 mmol) was dissolved in CH$_3$CN (5.78 g), and *N*-methylmaleimide (495 mg, 4.5 mmol) dissolved in CH$_3$CN (1.00 g) was added. The solution was allowed to stand for ∼1 h and was then precipitated into ∼300 mL of stirring Et$_2$O/CH$_2$Cl$_2$ (1:1), and the resulting slurry was filtered. The solid was rinsed with ether and dried in vacuo to yield the product (**10**, 727 mg, 99%) as a tan solid. ^{1}H NMR (CD$_3$CN): δ 5.75−5.85 (m, 1H), 4.93 (br s, 3H), 4.89 (m, 1H), 4.32 (d, J = 7.8 Hz, 1H), 4.18 (d, J = 7.8 Hz, 1H), 3.68 (s, 3H), 3.59 (br s, 12H), 3.22 (dd, J = 7.8, 7.2 Hz, 1H), 3.03 (dd, J = 7.8, 7.2 Hz, 1H), 2.79 (s, 3H), 2.68 (dd, J = 14.4 Hz, 7.2 Hz, 1H), 2.35−2.45 (m, 1H), 2.10−2.25 (m, 1H). ^{13}C NMR (CD$_3$CN): δ 180.0 (C), 176.9 (C), 158.6 (C), 145.2 (C), 118.8 (CH), 87,7 (CH), 54.6 (CH$_3$), 49.1 (CH), 46.1 (CH), 44.0 (CH), 38.5 (CH), 36.6 (CH), 25.1 (CH$_2$), 24.4 (CH$_3$). CV (CH$_3$CN; TBAH): $E_{1/2}$ = 0.73 V.

[Os(NH$_3$)$_5$(3,4-η^2-8-formyl-2-methoxy-6,7,8,8a-tetrahydronaphthalene)](OTf)$_2$ (11). Acrolein (34 mg, 0.61 mmol) was dissolved in CH$_3$CN (354 mg) containing LiOTf (67 mg, 0.43 mmol), and this solution was added to complex **6** (39 mg, 0.05 mmol). The solution was allowed to stir for ∼12 h and then added to stirring Et$_2$O (∼50 mL). The resulting precipitate was filtered and rinsed with ether. Drying

in vacuo yields the product (**11**, 37 mg, 97%). ^{1}H NMR (CD_3CN): δ 9.79 (s, 1H), 5.56 (q, J = 3.3 Hz, 1H), 4.57 (br s, 1H), 4.30 (br s, 3H), 4.08 (d, J = 8.1 Hz, 1H), 3.86 (d, J = 8.1 Hz, 1H), 3.55 (s, 3H), 3.02 (br s, 12H), 2.47−2.50 (m, 1H), 2.06−2.16 (m, 4H), 1.66−1.73 (m, 1H). ^{13}C NMR (CD_3CN): δ 206.8 (CH), 160.0 (C), 141.2 (C), 123.2 (CH), 89.2 (CH), 54.9 (CH_3), 53.7 (CH), 50.0 (CH), 43.2 (CH), 35.9 (CH), 23.1 (CH_2), 22.7 (CH_2). Anal. Calcd for $C_{14}H_{29}N_5O_8S_2F_6Os$: C, 22.02; H, 3.83; N, 9.17. Found: C, 21.98; H, 4.15; N, 9.10.

[Os(NH$_3$)$_5$(3,4-η^2-8-acetyl-2-methoxy-3-phenyl-6,7,8,8a-tetrahydronaphthalene)](OTf)$_2$ (12). Complex **6** (46 mg, 0.07 mmol) was dissolved in CH_3CN (1.6 g), and *trans*-4-phenyl-3-buten-2-one (331 mg, 2.26 mmol, −40 °C) was added. The solution was cooled to −40 °C, and cold BF_3·OEt_2 (10 mg, 0.07 mmol) was added. The reaction solution was allowed to stand for ∼45 min at −40 °C, and cold pyridine (200 mg, 2.53 mmol) was then added. The solution was precipitated into ∼100 mL of stirring ether, and the resulting slurry was filtered and dried in vacuo. The product (**12**, 43 mg, 77%) was isolated as a tan brown powder. ^{1}H NMR (CD_3CN): δ 7.20−7.35 (m, 5H), 5.81−5.90 (m, 1H), 4.37 (s, 1H), 4.29 (br s, 3H), 4.22 (d, J = 7.8 Hz, 1H), 3.92 (d, J = 7.8 Hz, 1H), 3.47 (s, 3H), 3.00−3.15 (m, 1H), 2.99 (br s, 12H), 2.80−2.90 (m, 1H), 2.50−2.65 (m, 1H), 2.27−2.29 (m, 1H), 2.12 (s, 3H), 1.90−2.10 (m, 1H). ^{13}C NMR (CD_3CN): δ 210.2 (C), 159.6 (C), 146.7 (C), 141.9 (C), 129.5 (CH), 128.0 (CH), 127.2 (CH), 123.1 (CH), 90.1 (CH), 61.3 (CH), 55.4 (CH_3), 52.5 (CH), 44.0 (CH), 40.9 (CH), 34.9 (CH), 31.1 (CH_2), 30.6 (CH_3).

[Os(NH$_3$)$_5$(6,7-η^2-8-methoxy-2,3,3a,4,9a,9b-hexahydrobenz[*e*]inden-1-one)](OTf)$_2$ (13). A mixture of complex **6** (270 mg, 0.38 mmol), freshly distilled cyclopentenone (631 mg, 7.70 mmol), and water (600 mg) was stirred at 20 °C for 24 h. The volatiles were removed under reduced pressure, and the resulting residue was dissolved in CH_3CN and precipitated from Et_2O/CH_2Cl_2 (1:1, 350 mL). The dark solid obtained after filtration and washing with CH_2Cl_2 was dried in vacuo to yield a 3:1 mixture of cycloadduct **13** and **6v**, the vinyl-bound isomer of **6**. Adjusted yield of **13**: (283 mg, 71%). ^{1}H NMR (CD_3CN): δ 5.60−5.70 (m, 1H), 4.59−4.62 (m, 1H), 4.31 (br s, 3H), 4.00 (d, J = 7.8 Hz, 1H), 3.86 (d, J = 7.8 Hz, 1H), 3.74 (s, 3H), 3.55 (br s, 12H), 2.62−2.74 (m, 1H), 2.45−2.53 (m, 1H), 2.35−2.45 (m, 1H), 2.00−2.13 (m, 5H), 1.62−1.74 (m, 1H). ^{13}C NMR (CD_3CN): δ 219.0 (C), 157.5 (C), 143.2 (C), 122.3 (CH), 91.7 (CH), 55.2 (CH_3), 53.8 (CH), 52.0 (CH), 44.4 (CH), 38.4 (CH_2), 36.6 (CH), 33.3 (CH), 30.4 (CH_2), 29.4 (CH_2).

[Os(NH$_3$)$_5$(8,9-η^2-4,5-(*N*-methylsuccinimido)-7-methoxy-2,3,3a,4,5,-5a-hexahydrobenz[*e*]indene)](OTf)$_2$ (14). Complex **9** (129 mg, 0.17 mmol) was dissolved in CH_3CN (1.00 g), and to this mixture, a solution of *N*-methylmaleimide (188 mg, 1.70 mmol) in CH_3CN (600 mg) was added. After standing for 18.5 h, the reaction solution was added to ∼200 mL of stirring Et_2O, and the resulting slurry was filtered. The solid was rinsed with Et_2O and dried in vacuo to yield the product (**14**, 148 mg, 98%) as a yellow solid. ^{1}H NMR (acetone-d_6): δ 4.86 (br s, 4H), 4.61 (d, J = 7.8 Hz, 1H), 4.20 (d, J = 7.8 Hz, 1H), 3.67 (br s, 15H), 3.16 (m, 1H), 3.05 (t, J = 7.8 Hz, 1H), 2.92 (m, 1H), 2.77−2.85 (m, 1H), 2.74 (s, 3H), 2.62 (m, 1H), 2.42−2.50 (m, 2H), 1.91 (m, 1H), 1.68 (m, 1H), 1.53 (m, 1H). ^{13}C NMR (acetone-d_6): δ 178.2 (C), 176.7 (C), 158.3 (C), 139.7 (C), 132.7 (C), 90.2 (CH), 54.6 (CH_3), 50.0 (CH), 47.8 (CH), 44.7 (CH), 41.0 (CH), 40.8 (CH), 37.8 (CH), 31.0 (CH), 28.1 (CH_2), 27.5 (CH_2), 24.3 (CH_3). Anal. Calcd for $C_{19}H_{34}N_6O_9S_2F_6Os$: C, 26.57; H, 3.99; N, 9.79. Found: C, 26.27; H, 4.12; N, 9.82.

[Os(NH$_3$)$_5$(8,9-η^2-5-formyl-7-methoxy-2,3,3a,4,5,5a-hexahydrobenz[*e*] indene)](OTf)$_2$ (15). Complex **9** (202 mg, 0.27 mmol) was dissolved in a solvent mixture of H_2O (393 mg) and DMF (884 mg). To this solution was added acrolein (677 mg, 12.1 mmol). The solution was allowed to stand for ∼18 h, after which time the solvent was evaporated. The residue was redissolved in acetone, and the resulting solution was precipitated into ∼200 mL of stirring Et_2O. The slurry was filtered, and the filter cake was rinsed with Et_2O and dried. The product (**15**, 173 mg) was isolated in 80% yield. ^{1}H NMR (CD_3CN): δ 9.53 (d, J = 0.9 Hz, 1H), 4.61 (dd, J = 3.3, 1.2 Hz, 1H), 4.38 (d, J = 8.1 Hz, 1H), 4.29 (br s, 3H), 3.93 (d, J = 8.1 Hz, 1H), 3.55 (s, 3H), 3.09 (br s, 12H), 2.47−2.64 (m, 1H), 2.32−2.37 (m, 1H), 2.17−2.29 (m, 1H), 1.54−1.71 (m, 7H), 1.25−1.37 (m, 1H). ^{13}C NMR (CD_3CN): δ 206.3 (C), 159.6 (C), 143.7 (C), 131.2 (C), 89.5 (CH), 55.2 (CH_3), 53.1 (CH), 49.6 (CH), 43.7 (CH), 39.0 (CH), 37.3 (CH), 34.4 (CH_2), 30.7 (CH_2), 26.7 (CH_2), 25.9 (CH_2). CV (CH_3CN, TBAH, 100 mV/s): $E_{1/2}$ = 0.75 V.

[Os(NH$_3$)$_5$(8,9-η^2-5-chloro-5-cyano-7-methoxy-2,3,3a,4,5,5a-benz[*e*]indene)](OTf)$_2$ (16). Complex **9** (317 mg, 0.42 mmol) was dissolved in a solvent mixture of H_2O (660 mg) and DMF (1.21 g), and to this solution was added 2-chloroacrylonitrile (1.46 g, 16.6 mmol). After standing for ∼17 h, the solvent was evaporated. The residue was redissolved in acetone, and the resulting solution was precipitated into ∼200 mL of stirring Et_2O. The filter cake was rinsed with Et_2O and dried, and the product (**16**, 291 mg) was isolated in 83% yield. ^{1}H NMR (CD_3CN): δ 4.84 (s, 1H), 4.42 (d, J = 8.1 Hz, 1H), 4.32 (br s, 3H), 4.02 (d, J = 8.1 Hz, 1H), 3.61 (s, 3H), 3.09 (br s, 12H). ^{13}C NMR (acetone-d_6/DMF-d_7): δ 140.8 (C), 129.8 (C), 123.5 (C), 119.5 (C), 119.3 (C), 84.1 (CH), 54.7 (CH_3), 48.1 (CH), 46.5 (CH), 42.9 (CH), 41.4 (CH_2), 39.7 (CH), 33.6 (CH_2), 29.8 (CH_2), 24.3 (CH_2). CV (CH_3CN, TBAH, 100 mV/s): $E_{1/2}$ = 0.82 V.

[Os(NH$_3$)$_5$(6,7-η^2-2-aza-8-methoxy-4-acetyl-3a,4,9a,9b-tetrahydro-2*H*-benz[*e*]inden-1,3-dione)(OTf)$_2$ (18). Complex **17** (230 mg, 0.31 mmol)[9] was dissolved in water (5.7 g) and NMM (347 mg, 3.13 mmol) dissolved in CH_3CN (1.5 g). The two solutions were combined and allowed to stir for ∼14.5 h. The reaction mixture was diluted then with acetone (∼10 mL). The solvent was removed in vacuo at room temperature, the resulting residue was redissolved in acetone, and the solution was added *slowly* to ∼200 mL of stirring ether. The resulting slurry was filtered; the solid was rinsed with ether and dried to yield a yellow powder (**18**, 218 mg, 82%). ^{1}H NMR (acetone-d_6): δ 6.26 (m, 1H), 4.96 (br s, 3H), 4.90 (d, J = 3.0 Hz, 1H), 4.33 (d, J = 7.8 Hz, 1H), 4.21 (d, J = 7.8 Hz, 1H), 3.84 (dd, J = 8.4, 5.4 Hz, 1H), 3.68 (s, 3H), 3.59 (br s, 12H), 3.35−3.42 (m, 1H), 3.26−3.32 (m, 1H), 2.75 (s, 3H), 2.35 (s, 3H), 2.29 (m, 1H). ^{13}C NMR (acetone-d_6): δ 204.0 (C), 178.7 (C), 176.7 (C), 159.4 (C), 145.1 (C), 117.0 (CH), 89.7 (CH), 55.4 (CH_3), 49.7 (CH), 49.2 (CH), 47.3 (CH), 44.7 (CH), 42.0 (CH), 38.3 (CH), 28.8 (CH_3), 25.2 (CH_3).

[Os(NH$_3$)$_5$(6,7-η^2-(methyl 2-aza-8-methoxy-2-methyl-3a,9,9a,9b-tetrahydro2*H*,4*H*-benz[*e*]inden-1,3,8-trionium)](OTf)$_3$ (19). Complex **10** (618 mg, 0.76 mmol) was dissolved in CH_3CN (7.20 g), and HOTf (142 mg, 0.95 mmol) was added. After ∼ 5 min, the reaction mixture was precipitated into ∼100 mL of stirring Et_2O, and the resulting slurry was filtered. The filter cake was rinsed with ether and dried, and the product (**19**, 715 mg, 97%) was isolated as a purple solid. ^{1}H NMR (CD_3CN): δ 6.32 (d, J = 6.6 Hz, 1H), 6.05−6.10 (m, 1H), 5.35 (d, J = 6.6 Hz, 1H), 5.18 (br s, 3H), 4.42 (s, 3H), 3.91 (d, J = 22.8 Hz, 1H), 3.68 (br s, 12H), 3.10−3.23 (m, 2H), 2.82 (s, 3H), 2.63 (dd, J = 14.7, 8.4 Hz, 1H), 2.50−2.60 (m, 1H), 2.37−2.45 (m, 1H), 2.18 (dd, J = 22.8, 11.1 Hz, 1H). ^{13}C NMR (CD_3CN): δ 208.8 (C), 178.8 (C), 178.7 (C), 137.6 (C), 126.8 (CH), 62.7 (CH_3), 61.7 (CH), 52.3 (CH), 45.1 (CH), 37.4 (CH), 29.7 (CH & CH_2), 24.9 (CH_2), 23.9 (CH_3). CV (CH_3CN; TBAH): $E_{1/2}$ = 0.82 V.

[Os(NH$_3$)$_5$(6,7-η^2-2-aza-2-methyl-3a,9,9a,9b-tetrahydro-2*H*,4*H*-benz[*e*]inden-1,3,8-trione)](OTf)$_2$ (20). Complex **19** (530 mg, 0.53 mmol) was dissolved in CH_3CN (5.5 g), and water (109 mg, 6.1 mmol) was added. The solution was allowed to stir for ∼1.5 h and was then precipitated into ∼300 mL of stirring Et_2O. The resulting slurry was filtered. The solid was rinsed with ether and dried in vacuo to yield complex **20** (415 mg, 94%). ^{1}H NMR (DMF-d_7): δ 5.80 (m, 1H), 5.41 (br s, 3H), 4.81 (d, J = 7.6 Hz, 1H), 4.27 (d, J = 7.6 Hz, 1H), 3.85 (br s, 12H), 3.21 (m, 4H), 2.85 (s, 3H), 2.45 (m, 2H), 2.24 (m, 1H). ^{13}C NMR (DMF-d_7): 209.38(C), 180.77 (C), 179.97 (C), 144.58 (C), 119.05 (CH), 56.24 (CH), 51.76 (CH), 46.84 (CH), 40.81 (CH), 37.42 (CH), 32.88 (CH_2), 26.29 (CH_2), 25.03 (CH_3).

2-Aza-2-methyl-3a,9,9a,9b-tetrahydro-2*H*,4*H*-benz[*e*]inden-1,3,8-trione (21). Complex **20** (208 mg, 0.26 mmol) was dissolved in water EtOAc (∼5 mL) layered with EtOAc (∼5 mL). CAN (346 mg, 0.63 mmol) dissolved in water (∼3.0 mL) was added, and the mixture was allowed to stir at room temperature for ∼1.5 h. The mixture was then filtered through a bed of silica gel, and the silica gel bed was washed with additional EtOAc. The combined filtrates were separated, washed with saturated brine, dried over Na_2SO_4, and concentrated under reduced

pressure to yield a crude solid. Column chromatography (SiO_2, 3:1; petroleum ether/EtOAc) yielded the product (**22**, 27 mg, 46%). ^{1}H NMR ($CDCl_3$): δ 6.91 (d, J = 10.2 Hz, 1H), 6.14−6.20 (m, 1H), 5.93 (d, J = 10.2 Hz, 1H), 3.60 (dd, J = 17.7, 8.4 Hz, 1H), 3.22 (q, J = 7.2 Hz, 1H), 3.17 (t, J = 7.2 Hz, 1H), 3.00−3.10 (m, 1H), 2.92 (s, 3H), 2.91 (dd, J = 16.2, 7.2 Hz, 1H), 2.81 (dd, J = 17.4, 9.0 Hz, 1H), 2.28−2.39 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 198.1 (C), 178.9 (C), 177.3 (C), 143.7 (CH), 135.8 (C), 131.0 (CH), 126.6 (CH), 42.9 (CH), 39.7 (CH), 37.7 (CH_2), 32.1 (CH), 25.4 (CH_2), 25.0 (CH_3). GCMS (*m*/*z*): 231.

[Os(NH$_3$)$_5$(6,7-η^2-2-aza-8-methoxy-2-methyl-3a,4,8,9,9a,9b-hexahydro-2*H*-benz[*e*]inden-1,3-dione)](OTf)$_2$ (22). Complex **19** (706 mg, 0.73 mmol) was dissolved in CH_3CN (7.70 g), and a solution of TBAC (247 mg, 0.87 mmol) dissolved in CH_3CN (1.01 g) was added. The solution immediately changed color from purple to brown. After ∼20 min, the reaction solution was precipitated into ∼200 mL of a stirring 1:1 Et_2O/CH_2Cl_2 solution, and the slurry was filtered. The filter cake was rinsed with CH_2Cl_2 followed by Et_2O and dried, and the product (**22**, 531 mg) was isolated in 89% yield. ^{1}H NMR (CD_3CN): δ 5.64 (m, 1H), 5.21 (m, 1H), 4.16 (br s, 3H), 3.88 (d, J = 9.0 Hz, 1H), 3.76 (dd, J = 9.0, 4.5 Hz, 1H), 3.40 (s, 3H), 3.11 (br s, 13H), 2.82 (s, 3H), 2.55 (m, 3H), 2.19−2.28 (m, 2H), 1.24 (m, 1H). ^{13}C NMR (CD_3CN): δ 179.7 (C), 178.4 (C), 144.0 (C), 117.9 (CH), 81.0 (CH), 55.6 (CH_3), 51.0 (CH), 46.6 (CH), 45.3 (CH), 39.7 (CH), 31.3 (CH), 27.7 (CH_2), 24.4 (CH_2), 23.7 (CH_3). CV (CH_3CN; TBAH): $E_{1/2}$ = 0.70 V.

2-Aza-8-methoxy-2-methyl-3a,4,8,9,9a,9b-hexahydro-2*H*-benz[*e*]-inden-1,3-dione (23). Complex **22** (308 mg, 0.38 mmol) was dissolved in acetonitrile (1.0 g), and diethyl ether (2.5 g) was added. CAN (210 mg, 0.38 mmol) in water (∼3 mL) was added, and the mixture was stirred at 25 °C for 0.5 h. The mixture was diluted with water and ether and separated. The organic layer was washed with $NaHCO_3$ followed by brine and dried over Na_2SO_4. Concentration under reduced pressure gave a dark residue. Preparative TLC (SiO_2, 4:1; petroleum ether/EtOAc) yielded the product **23** (12 mg, 35%). ^{1}H NMR ($CDCl_3$): δ 6.16 (d, J = 9.6 Hz, 1H), 5.95 (dd, J = 9.6 Hz, 5.2 Hz, 1H), 5.73 (m, 1H), 3.92 (m, 1H), 3.36 (s, 3H), 3.15 (m, 2H), 2.90 (s, 3H), 2.80 (m, 2H), 2.25 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 179.4 (C), 178.1 (C), 137.0 (C), 130.6 (CH), 126.7 (CH), 123.5 (CH), 72.0 (CH), 56.3 (CH_3), 42.8 (CH_3), 40.4 (CH), 29.3 (CH), 28.2 (CH_2), 24.9 (CH), 24.2 (CH_2). GCMS (*m*/*z*): 247.

[Os(NH$_3$)$_5$(7,8-η^2-2-aza-2-methyl-3a,4,6,9,9a,9b-hexahydro-2*H*-benz[*e*]inden-1,3-dione)](OTf)$_2$ (24). Complex **22** (649 mg, 0.79 mmol) was dissolved in CH_3CN (3.6 g) and cooled to −40 °C. A cold solution of HOTf (−40 °C) (302 mg, 2.01 mmol) in CH_3CN (4.5 g) was added to the solution of **22**. After 20 min, a cold solution of TBAC (590 mg, 2.09 mmol) in CH_3CN (1.8 g) was added. The reaction mixture was allowed to stand for 1 h at −40 °C followed by warming to 20 °C. Precipitation of the reaction mixture in CH_2Cl_2/ether (1:1, 400 mL) gave a red solid that was filtered and dried in vacuo (**24**, 602.3 mg, 96%). ^{1}H NMR ($CDCl_3$, partial characterization): δ 5.55 (bs, 1H), 4.61 (bs, 3H), 3.57 (bs, 12H), 2.95 (m, 3H), 2.79 (s, 3H), 2.51 (dd, 1H), 1.96 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 180.5 (C), 179.7 (C), 143.5 (C), 120.7 (CH), 50.6 (CH), 46.0 (CH), 44.49 (CH), 41.4 (C), 34.4 (CH), 32.7 (CH), 24.7 (CH_2), 24.3 (CH_2), 13.8 (CH_3). CV (CH_3CN; TBAH): $E_{1/2}$ = 0.63 V.

2-Aza-2-methyl-3a,4,6,9,9a,9b-hexahydro-2*H*-benz[*e*]inden-1,3-dione (25). Complex **24** (358 mg, 0.453 mmol) was dissolved in acetone (3.6 g), and AgOTf (177 mg, 0.689 mmol) was added to this solution. The solution was then heated at 70 °C for 3 h. The reaction mixture was allowed to cool to 20 °C, diluted with EtOAc, and filtered through a bed of silica gel. The filtrate was put under vacuum to remove the volatiles, and the crude product was purified with chromatography (SiO_2) using hexanes/EtOAc (8:2) to afford compound **25** (33.3 mg, 33%). ^{1}H NMR ($CDCl_3$): 5.82 (m, 2H), 5.53 (m, 1H), 3.07 (m, 1H), 2.98 (d, J = 7.3 Hz, 1H), 2.92 (s, 3H), 2.64 (m, 4H), 2.39 (m, 1H), 2.16 (m, 1H), 1.25 (dd, J = 7.0, 8.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 179.6 (C), 178.7 (C), 139.2 (C), 128.0 (CH), 126.3 (CH), 117.8 (CH), 42.9 (CH), 39.6 (CH), 34.6 (CH), 32.1 (CH), 26.4 (CH_2), 24.6 (CH_2), 23.6 (CH_3). GCMS (*m*/*z*): 217.

2-Aza-2-methyl-8-methoxynaphalene-1,3-dione (26) and 2-Aza-5-hydroxy-8-methoxy-2-methyl-3a,4,5,9b-tetrahydro-2*H*-benz[*e*]inden-1,3-dione (27). A solution of complex **10** (209.5 mg, 0.26 mmol) in CH_3CN (3.0 g) and alumina (2.5 g) were placed in pressure tube, and AgOTf (100.6 g, 0.391 mmol) was added. The pressure tube was sealed and heated on oil bath at 65 °C for 1.5 h. The mixture was then cooled and filtered through a bed of alumina on a frit. The bed was washed with acetone, and the volatiles of the filtrate were evaporated in vacuo. The crude material was purified by column chromatography over silica gel (7:3 hexanes/EtOAc) to isolate aromatic compound **26** (first fraction 11.0 mg, 18%) and compound **27** (second fraction 22.0 mg, 33%). Compound **26**: ^{1}H NMR ($CDCl_3$) 8.23 (d, J = 2.4, 1H), 8.07 (d, J = 8.0, 1H), 7.83 (d, J = 9.0, 1H), 7.72 (d, J = 8.2, 1H), 7.28 (dd, J = 2.4, 9.2, 1H), 4.00 (s, 3H), 3.22 (s, 3H); GCMS (*m*/*z*) 241. Compound **27**: ^{1}H NMR ($CDCl_3$) 7.12 (d, J = 8.2 Hz, 1H), 7.11 (d, J = 2.6 Hz, 1H), 6.81 (dd, J = 2.6, 8.3 Hz, 1H), 4.84 (bs, 1H), 4.03 (d, J = 9.2 Hz, 1H), 3.84 (s, 3H), 3.20 (bt, J = 9.4 Hz, 1H), 2.96 (s, 3H), 2.77 (ddd, J = 1.8, 2.1, 14.3 Hz, 1H), 1.90 (ddd, J = 1.7, 7.8, 9.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 180. 9 (C), 177.4 (C), 160.0 (C), 131.1 (C), 130.2 (C), 129.0 (CH), 115.8 (CH), 113.5 (CH), 67.6 (CH), 55.4 (CH_3), 43.4 (CH), 35.9 (CH), 30.9 (CH_2), 25.3 (CH_3); GCMS ($M - H_2O$)$^+$ 243.

[Os(NH$_3$)$_5$(6,7-η^2-2,3,3a,9,9a,9b-hexahydro-4*H*-benz[*e*]inden-1,8-dione (28). Complex **13** (315 mg, mmol) was dissolved in an acetonitrile/water mixture (95:5, 3.1 g), and triflic acid (31.0 mg) was added. The mixture was stirred for 1 h, and the product was precipitated from stirring Et_2O/CH_2Cl_2 (3:2, ∼200 mL). The product was filtered, washed, and dried to give **28** (283 mg, 91%). ^{1}H NMR ($CDCl_3$): 6.06 (m, 1H), 5.10 (br s, 3H), 4.63 (d, J = 7.8 Hz, 1H), 4.47 (d, J = 7.8, 1H), 3.78 (br s, 12H), 2.94 (m, 2H), 2.50 (m, 1H), 2.30 (dd, J = 9.0, 18.0, 1H), 2.04 (m, 6H), 1.57 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 216.7 (C), 214.8 (C), 141.1 (C), 125.0 (CH), 58.0 (CH), 56.7 (CH), 48.9 (CH), 43.9 (CH_2), 38.2 (CH), 37.8 (CH_2), 33.7 (CH), 33.2 (CH_2), 27.5 (CH_2).

2,3,3a,9,9a,9b-Hexahydro-4*H*-benz[*e*]inden-1,8-dione (29). Complex **28** (277.0 mg, 0.357 mmol) was dissolved in a biphasic mixture of water, acetone, and diethyl ether (2:1:3, ∼5 mL). CAN (378 mg, 0.69 mmol) dissolved in water (∼2.0 mL) was added, and the mixture was allowed to stir for ∼0.5 h. The mixture was then separated, and the aqueous layer was extracted twice with ether (5 mL × 2). The ether layer was washed with $NaHCO_3$ (aqueous) and brine and then dried over Na_2SO_4 and concentrated under reduced pressure to yield a crude oily material. Purification of the oil using preparative TLC (SiO_2, 85:15; hexanes/EtOAc) yielded the pure product (**29**, 23.7 mg, 44% (adjusted taking into account complex **6v**)). ^{1}H NMR ($CDCl_3$): δ 7.05 (d, J = 9.6 Hz, 1H), 6.10−6.18 (m, 1H), 5.91 (d, J = 9.6 Hz, 1H), 3.38 (dd, J = 16.1, 5.4 Hz, 1H), 2.77−2.90 (m, 1H), 2.55−2.70 (m, 1H), 2.38−2.50 (m, 1H), 2.10−2.30 (m, 3H), 1.75−1.90 (m, 2H), 1.50−1.70 (m, 12H). ^{13}C NMR ($CDCl_3$) δ 216.2 (C), 198.4 (C), 146.8 (CH), 135.1 (C), 133.8 (CH), 126.6 (CH), 55.6 (CH), 41.8 (CH), 37.5 (CH,-CH_2), 35.6 (CH), 32.6 (CH_2), 27.2 (CH_2). Anal. Calcd. for $C_{13}H_{12}O_2$: C, 77.20; H, 7.22. Found: C, 77.06; H, 7.22. GCMS (M^+): 202.

Results

Direct complexation of styrene derivatives by pentaammineosmium(II) is not a useful synthetic procedure for forming η^2-arene complexes because of the generally poor kinetic regioselectivity encountered.[10] For example, when complexation of styrene is carried out under standard conditions,[9] a 3:2 ratio of vinyl-bound to arene-bound complexes is isolated. However, using one of the two procedures shown in Figure 1, the *p*-vinylanisole complex **6** is synthesized solely as its arene-bound isomer. Following a procedure previously described,[9] complex **2** is prepared as a 9:1 mixture of diastereomers by the aldol condensation of the parent anisole pentaammineosmium(II) complex (**1**) with acetaldehyde diethyl acetal. Alternatively,

(10) Spera, M. L. Unpublished results. (Direct complexation of styrene) Elliott, M. G.; Zhang, S.; Shepherd, R. E. *Inorg. Chem.* **1989**, *28*, 3036.

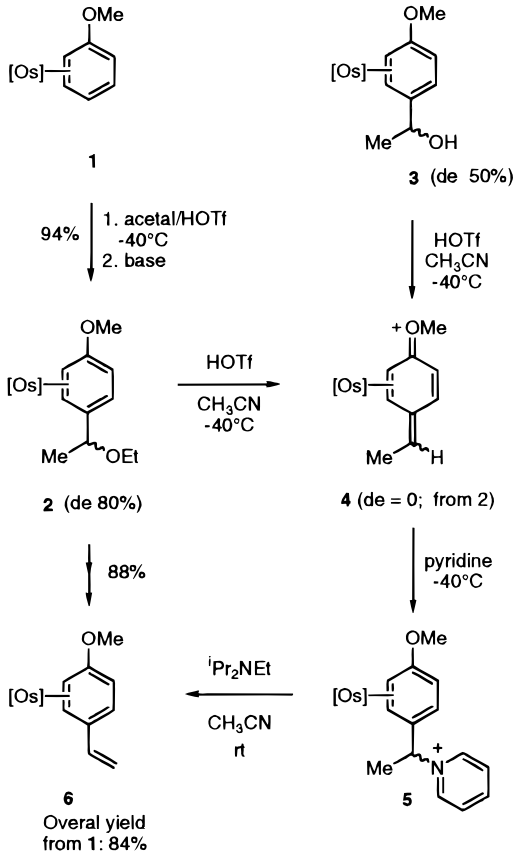


Figure 1.

complex **3** is prepared as a 3:1 equilibrium mixture of diastereomers by the direct complexation of 4-methoxy-α-methylbenzyl alcohol to the pentaammineosmium(II) metal center. Both **2** and **3** are converted to the *p*-quinone methide complex **4** by treatment with trifluoromethanesulfonic (triflic) acid in acetonitrile at −40 °C. Although this complex decomposes in solution at 25 °C, it is quite stable in acidic solution at −40 °C. ^{1}H NMR data in CD_3CN (−40 °C) reveal that complex **4** is formed from **2** as a 1:1 mixture of diastereomers differing at the exocyclic double bond. Spectroscopic features include four doublets and a quartet in the range of 5−8 ppm, a methoxy singlet (4.25 ppm), and a methyl doublet (∼1.66, 1.50 ppm) for each isomer.

Complex **4** is highly electrophilic and reacts with a variety of mild nucleophiles to regenerate substituted arenepentaammineosmium(II) complexes. For example, when **4** is generated (−40 °C) and treated with pyridine (1.5−2.0 equiv), complex **5** is formed as a 10:1 equilibrium mixture of diastereomers. Combining pyridinium **5** with a tertiary amine base (^{i}Pr$_2$NEt, 10 equiv, 25 °C) yields the *p*-vinylanisole complex **6** which is isolated as a triflate salt by precipitation into an Et_2O/CH_2Cl_2 mixture. Complex **6**, which is also conveniently synthesized directly from **2** (88%), shows the spectral characteristics of a para-substituted 5,6-η^2-anisole complex of pentaammineosmium(II), including broad cis/trans ammine signals spaced ∼1 ppm apart and coordinated and uncoordinated arene protons in the range from 5 to 7 ppm. In addition, new signals appear in the alkenyl region at δ 6.60, 5.61, and 4.73 ppm corresponding to the vinyl group.

Over a period of days, an isomerization occurs in which the pentaammineosmium(II) metal center migrates to the pendant double bond (**6v**). This process is analogous to that observed for β-vinylpyrrole complexes of pentaammineosmium(II).[11] This process of metal migration occurs both in the solid state and in solution (CD_3CN, 25 °C) and is accelerated by gentle heating (CD_3CN, 50 °C) or by treatment with strong oxidants or Lewis acids (vide infra). Despite this, however, the triflate salt of **6** may be stored at room temperature for ∼12 h or at −40 °C for months without any observable isomerization of the metal center to the pendant double bond.

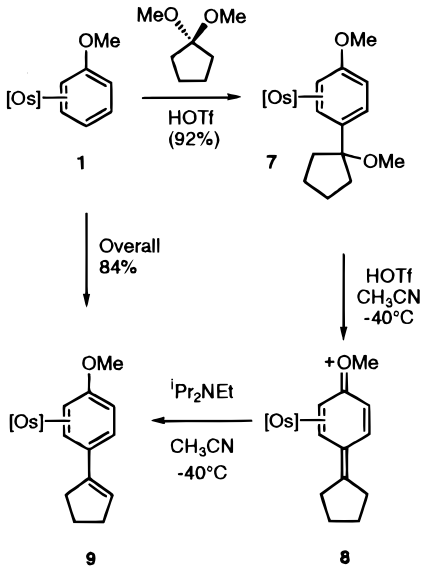
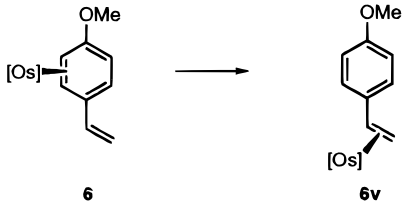


Figure 2.



In addition to the parent vinyl anisole complex **6**, *p*-vinylanisole complexes that contain substituents on the pendant double bond are also synthesized in a straightforward manner (Figure 2). As previously reported,[9] anisole complex **1** reacts with 1,1-dimethoxycyclopentane to afford aldol complex **7**. Protonation of complex **7** with triflic acid similar to the procedure for the synthesis of **6** results in the formation of the *p*-quinone methide derivative **8**, which is considerably more stable than its less substituted counterpart (**4**). Complex **8** is observable by NMR spectroscopy at 20 °C in CD_3CN. Spectral features of **8** include four doublets in the ^{1}H NMR at δ 7.93, 6.59, 6.36, and 5.80 and ^{13}C NMR resonances at δ 199.4, 177.5, and 152.6 for the oxonium C(1) carbon and the uncoordinated carbons at the β and δ positions, respectively. Direct addition of ^{i}Pr$_2$NEt to **8** at −40 °C results in the formation of compound **9**, a *p*-cyclopentenylanisole complex of pentaammineosmium(II). Complex **9** can also be synthesized directly from **7** without isolation of intermediates in 91% yield. Migration of the osmium metal center to the pendent double bond of the cyclopentenyl ring is considerably slower than for the parent complex **6.**

[4 + 2] Cycloaddition Reactions. When the vinylanisole complex **6** is combined with *N*-methylmaleimide (NMM, 5−10

(11) Hodges, L. M.; Moody, M. W.; Harman, W. D. *J. Am. Chem. Soc.* **1994**, *116*, 7931−7932.

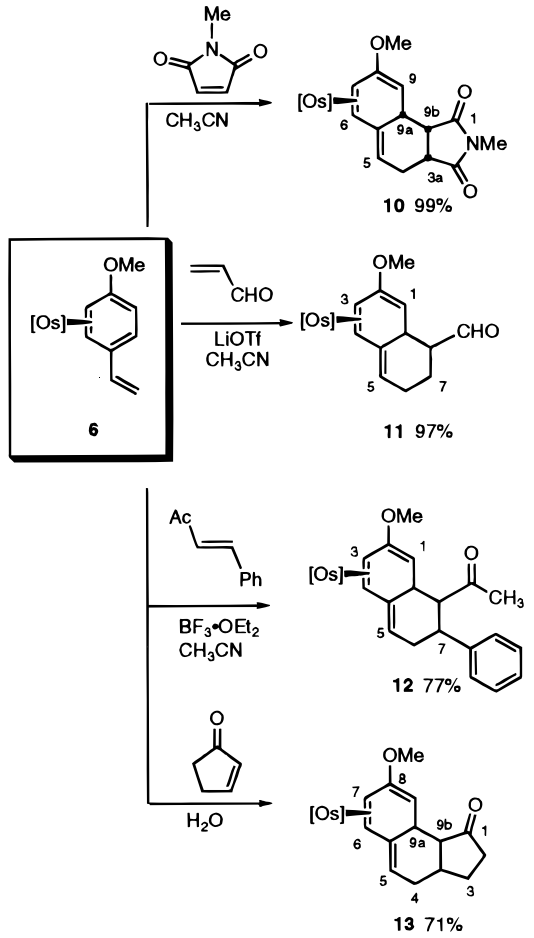


Figure 3.

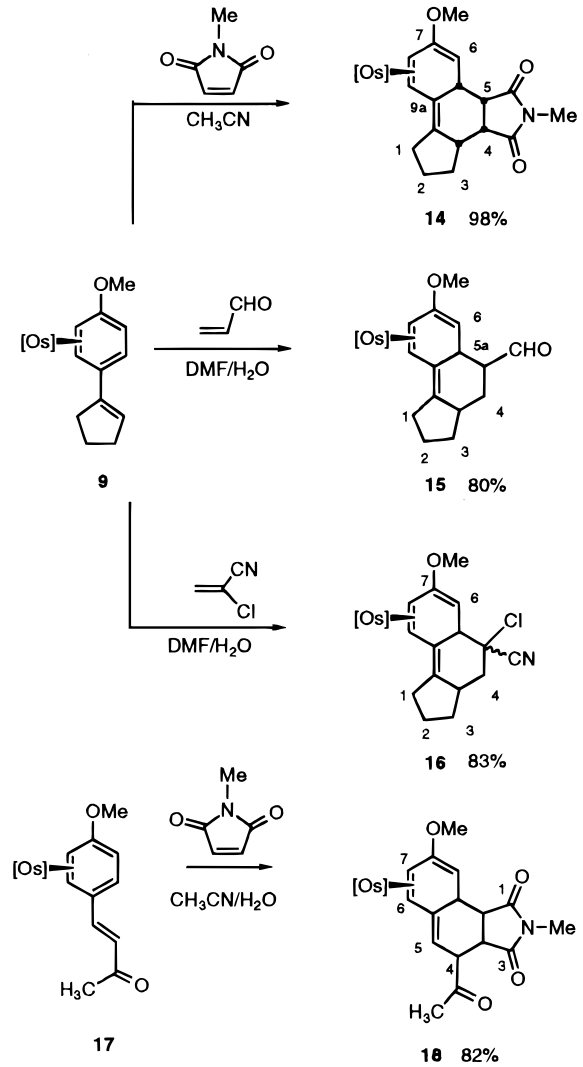


Figure 4.

equiv) in acetonitrile, a cycloaddition takes place over a period of ~1 h to generate complex **10** (Figure 3). The cycloaddition is shown to be >95% regioselective by ^{1}H and ^{13}C NMR, forming only the *external* cycloadduct. Spectral features of **10** which support this assignment include resonances in the ^{1}H NMR spectrum at δ 5.70 and 4.89 corresponding to the olefinic methine group at C(5) and the vinyl ether proton at C(1). In addition, a cyclic voltammogram of complex **10** is consistent with an alkene complex of pentaammineosmium(II), showing a reversible wave at $E_{1/2} = 0.73$ V (NHE). Although doubly activated dienophiles such as maleimides and maleic anhydride react with complex **6** in acetonitrile at 20 °C, less reactive dienophiles such as acrolein, methyl vinyl ketone (MVK), 2-cyclopenten-1-one, and methyl acrylate fail to participate in the [4 + 2] cycloaddition under these conditions. Instead, migration or oxidation of the metal center is observed. The decreased reactivity of these dienophiles is circumvented by the use of mild Lewis acids or aqueous solvent (Figure 3). For example, when complex **6** is combined with acrolein (12 equiv) in a 1.0 M LiOTf/CH_3CN solution, the cycloaddition occurs over a period of 12 h to yield complex **11** as a single diastereomer (97% yield; >95% diastereomeric excess (de)).

Ketone dienophiles such as MVK, 3-penten-2-one, and *trans*-4-phenyl-3-buten-2-one require the use of a stronger Lewis acid (BF_3·OEt_2), and therefore, these reactions must be performed at low temperature (−40 °C) to prevent metal migration (vide supra). For example, *trans*-4-phenyl-3-buten-2-one reacts with **6** in acetonitrile with BF_3·OEt_2 to form **12**. The reaction is stereo- and regioselective, as only a single diastereomer is observed. The exact stereochemistry for product **12** has not been assigned. Even under these Lewis acidic conditions, the dienophiles 2-cyclopenten-1-one and methyl acrylate fail to react. The beneficial effect of water as a solvent in Diels−Alder reactions has been well-documented,[12,13] and the sluggish reactivity of the aforementioned dienophiles is overcome by performing the reaction in water. As an example, the cycloaddition between **6** and 2-cyclopenten-1-one is complete after standing for ~24 h in aqueous solution to yield **13** with excellent regio- and stereocontrol (de >95). For some of the reactions described in Figures 3 and 4, cycloaddition is partially preempted by migration of the osmium from the arene to the vinyl group. Yields reported in Figure 3 are adjusted to account for this, reflecting only the yield of the cycloadduct component. ^{1}H NMR and electrochemical data unambiguously determine the relative amounts of cycloadduct compared to **6v**. Separation of these product mixtures proved difficult, but satisfactory combustion analysis was obtained where possible.

The cyclopentenyl anisole complex **9** reacts in a manner analogous to that of **6** to generate the tricyclic BCD fragment integral to steroids (Figure 4). Although the rates of cycloaddition are somewhat slower due to the more hindered nature of **9**, so is the rate of metal migration. After ~18 h at 20 °C, a solution of **9** and NMM yields the cycloadduct complex **14** in near quantitative yield (de>95%). Reactions of **9** with the less

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activated dienophiles acrolein and 2-chloroacrylonitrile in a H_2O/DMF cosolvent form cycloadducts **15** and **16** with both good yield and excellent stereocontrol.

Previously, we have reported that the anisole complex **1** undergoes Michael additions with an assortment of α,β-unsaturated carbonyl compounds. When 3-butyn-2-one is combined with **1**, the *p*-(2-oxo-3-butenyl)anisole complex **17** is formed in 98% yield.[9] As would be expected by orbital energy matching arguments, the more electron-deficient styrene complex **17** is less reactive toward cycloadditions and reacts only with highly electron-deficient dienophiles. Thus, the reaction of NMM with **17** produced the β-acetylated decalin **18** in 82% yield.

All of the cycloadducts presented in Figures 3 and 4 are isolated as single diastereomers (de > 95%). For two of these products, both 1D and 2D NOE experiments have been carried out to assign stereochemistry. The cycloadduct **10**, formed as a single stereoisomer (>95% de), gives NOE data indicating that the cis ammine protons are in close proximity to H9a (8.1%), and that H9b is close to both H3a (3.8%) and H9a (4.9%) in the decalin product. This is in agreement with a cycloadduct formed by the approach of the dienophile from the uncoordinated face of the arene in an orientation consistent with the Alder rule, forming an endo cycloadduct. For the cyclopentenyl derivative **14**, a NOESY experiment shows positive NOE among the cis ammines, H5a, H5, H4, and H3a, data again consistent with an endo cycloadduct where addition has occurred anti to the osmium. Overlap of proton resonances prevents a confirmation of stereochemistry in other cases. Given the universally high stereoselectivity for the cycloadducts shown in Figures 3 and 4 and the NOE data described, it is likely that the stereochemistry for all cycloadducts is that due to an endo cycloaddition opposite to the osmium. This stereochemical generalization has been previously observed for cycloaddition reactions of β-vinylpyrrole complexes of pentaammineosmium-(II).[14]

Once synthesized, cycloadducts **10**−**16** can be further transformed and decomplexed to yield a variety of organic products (Figure 5). The cycloadduct **10** formed from the methoxystyrene complex **6** and NMM is taken as an example. Protonation of complex **10** with triflic acid in acetonitrile at 20 °C results in the formation of the dienonium pentaammineosmium(II) complex **19**. Key spectral data for **19** include a ^{13}C NMR resonance at 209 ppm a typical of C═O. While complex **19** is stable for hours in dry acetonitrile, addition of water rapidly hydrolyzes this material to form **20**, a dienone complex of pentaammineosmium(II). Subsequent treatment of this product with CAN in a Et_2O/H_2O biphasic mixture produces the free dienone **21** in 41% overall yield from the styrene complex **6** after chromatography. Alternatively, complex **19** can react with a nucleophile at the oxonium carbon in a stereoselective manner. For example, addition of TBAC to **19** results in a 1,2-reduction of the dienonium species to generate the methoxydiene complex **22** as a single diastereomer. Oxidation of **22** by AgOTf liberates the organic ligand **23** in 35% yield after chromatography (overall 28% from **6**). Alternatively, the methoxydiene **22** may be treated with acid at −40 °C to generate an η^3-trienium complex (not isolated) that undergoes nucleophilic addition at C6. In the example shown in Figure 5, reaction with TBAC yields the diene complex **24**. Subsequent treatment of this product with AgOTf generates the free diene **25** in 25% overall yield from **6**. Finally, when the cycloadduct **10** is directly subjected to oxidative conditions (AgOTf), the benzyl alcohol **27** is recovered as the major product. Although the dienes **21**, **23**, and **25** are produced in only modest yields, it is important to note that majority of product loss for a given reaction sequence comes from purification and isolation of the organic ligand. This is largely due to the highly reactive nature of the diene products which are prone to decomposition, especially in their concentrated forms. These free ligands are susceptible to polymerization both in solution as well as in pure form. Indeed, our characterization and assessment of the purity for these compounds often relied on ^1H, ^{13}C, DEPT, and GCMS data without the aid of combustion analysis data, although we were able to obtain satisfactory analysis for the diendione **29**, an analogue

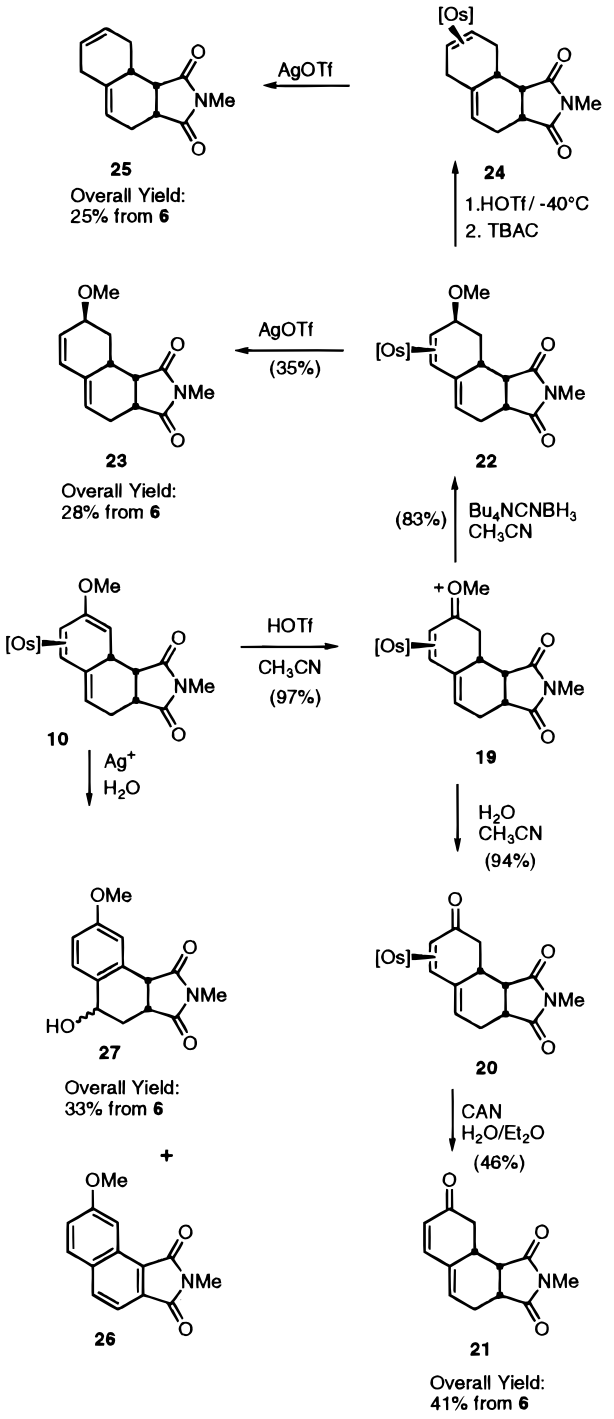

Figure 5.

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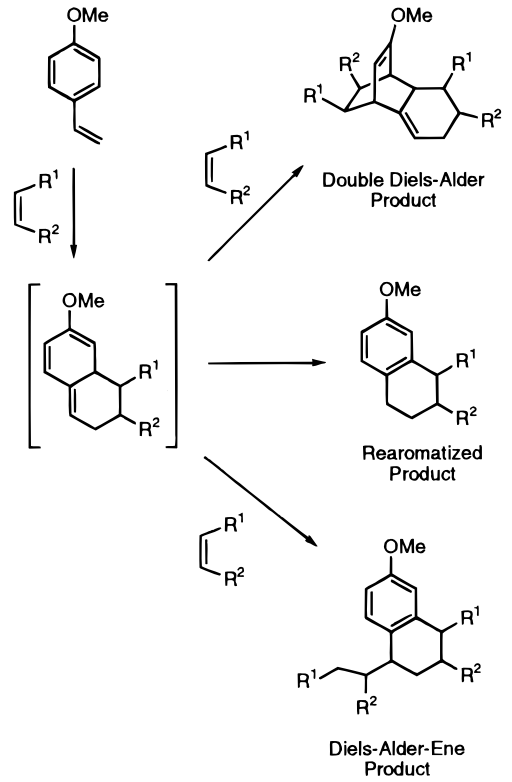
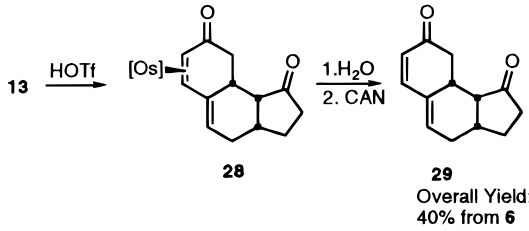


Figure 6.

of **21** prepared from **6** and cyclopentenone via dienonium complex **28** in the similar reaction sequence.



Discussion

The [4 + 2] cycloaddition between styrenes and dienophiles has been well documented, but the loss of aromaticity that occurs when styrene participates as a diene requires conditions that severely limit the utility of this reaction. With maleic anhydride and *p*-benzoquinone, the harsh reaction conditions required for styrene to participate cause degradation of the final product and yields are typically very poor.[15] With more reactive dienophiles, secondary reactions diminish or completely preclude the isolation of 1:1 Diels−Alder adducts (Figure 6).[15] In these instances, double Diels−Alder reactions forming Wagner−Jauregg adducts are usually the predominant product, but Diels−Alder-ene reactions and rearomatization have also been observed. In addition, the aromatic products resulting from the latter reaction often have synthetic value.[16−18]

Compared to its unsubstituted parent, 4-methoxystyrene tends to more often react to form double Diels−Alder adducts with highly reactive dienophiles. 4-Methoxystyrene was shown to react with tetracyanoethylene in a [2 + 2] cycloaddition to form phenyl-substituted cyclobutanes. In their study using time-resolved absorption spectrometry, Nakahara and co-workers determined that this product is formed through a reversible [4 + 2] cycloaddition.[19,20] This mode of reactivity for styrenes with electron-releasing substituents has also been observed by Huisgen et al. where bis(trifluoromethyl)-1,1-dicyanoethylene was combined with styrenes possessing electron-releasing substituents (R = OMe, SMe) to form only [2 + 2] cycloadducts even though this potent dienophile reacted with less activated styrenes to form stable [4 + 2] cycloadducts.[21]

Transition metals play an important role in the stabilization of reactive intermediates, and the reactivity of an organic molecule may be dramatically altered by coordination to a transition metal center. The Diels−Alder reaction has received extensive attention in this regard, and the use of stoichiometric transition metal complexes in cycloaddition reactions has been reviewed.[22,23] The diene component has been modified by η^1-coordination to electron-rich metal centers such as cobalt,[24] iron,[25−32] manganese,[33] and molybdenum.[34,35] The activation may involve direct attachment to the π system or at an allylic position. In addition, strategies have been developed employing derivitization of the dienophile with an electron-withdrawing metal center. Most commonly this approach takes the form of carbene complexes of the group 6 metal carbonyls,[36−38] but other approaches have been developed.[39,40] None of these approaches, however, has involved increasing the reactivity of the diene or stabilizing the reaction products through η^2-coordination, nor have these strategies been applied to styrene.

The pentaammineosmium(II) metal center selectively binds and dearomatizes a variety of arenes and heterocycles. This metal center has been shown to promote [4 + 2] cycloadditions between anisole and maleimides to form bicyclooctadienes,[41] as well as promoting [3 + 2] cycloadditions between pyrroles

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and dipolarophiles to form the 7-azanorbornane nucleus.[42,43] More recently, a variety of substituted indoles have been prepared through the cycloaddition of β-vinylpyrrole complexes of osmium(II).[13] The readily prepared methoxystyrene complexes of pentaammineosmium(II) participate in cycloaddition reactions with a diverse range of dienophiles. Even relatively unreactive dienophiles such as 2-cyclopenten-1-one participate in the reaction, and under the mild reaction conditions required, reagents as sensitive as α,β-unsaturated aldehydes give clean reaction products. Such reactions are unprecedented for the uncoordinated styrenes.

The pentaammineosmium(II) unit plays a variety of roles in the cycloaddition process. Foremost, it alters the chemical behavior of arenes allowing for the facile formation of styrenes from anisole and acetals or Michael acceptors. Second, osmium promotes the regioselective addition of the styrene and dienophile. Through π-back-bonding and localization of the aromatic π system, the metal activates the methoxystyrene ligand to a degree that is unparalleled by organic analogues. Reactions occur exclusively to form external cycloadducts, with the favored polarity of the dienophile readily predicted by frontier molecular orbital theory. We have not detected any formation of internal cycloaddition products in these reactions. The stereochemistry is also directed by the metal center. Addition of the dienophile to the arene nucleus must take place from the face of the molecule opposite to that of metal coordination. The pentaammineosmium(II) metal center is also responsible for *stabilizing* the resulting cycloadduct and preventing its methoxytriene fragment from participating in further reactions with the dienophile. Through coordination, the metal effectively disrupts the triene system, making further cycloadditions unfavorable. Since the metal remains coordinated to the triene product, subsequent derivitization is possible that takes advantage of the activating and stereodirecting properties of the metal. Up to five of the six carbons of the original arene (anisole) are capable of modification. Finally, the metal stabilizes the reactive alicyclic diene derivatives prepared from their cycloadduct precursors (e.g., **21**, **23**, and **25**) such that they may be isolated and later released in a controlled manner using a one-electron oxidant.

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Concluding Remarks

The versatile dearomatization agent pentaammineosmium(II) is useful for promoting regio- and stereoselective cycloaddition reactions with 4-methoxystyrenes. The reactions occur with a wide variety of dienophiles under mild conditions and in excellent yield. These cycloadduct complexes may then be used in further ligand-centered transformations to generate highly functionalized decalin or tetralin systems.

Acknowledgment is made to the National Science Foundation (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, and to Dr. Jeffrey Ellena for assistance with 2D and 500 MHz NMR experiments.

JA973700L