Asymmetric Induction in η^2-Arene Complexes of Pentaammineosmium(II)

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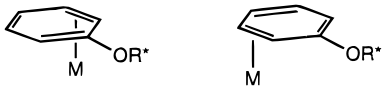
Abstract: A series of η^2-arene complexes (**2a**−**i**) of the form $[Os(NH_3)_5(ArOCHR^1CH_3)]^{2+}$ was prepared in which the alkoxy substituent R^1 bears a potential hydrogen bond acceptor. Using an ester or amide group as the hydrogen bond acceptor, a two-point interaction was achieved between the pentaammineosmium system and the organic ligand. For these complexes, a single coordination diastereomer was observed. For compound **2a**, evidence for hydrogen bonding between the carbonyl oxygen and the pentaammineosmium fragment was obtained through ^{1}H NMR studies and by a comparison of the rate of arene displacement for **2a** compared to that of the parent complex $[Os(NH_3)_5(anisole)]^{2+}$. Complex **2a** undergoes stereospecific protonation to form a 4*H*-anisolium product **3a**. Complex **3a** undergoes nucleophilic addition of a silylketene acetal at C3 to generate an alkoxydiene complex (**4**) as a single diastereomer. Hydrolysis of **4** removes the chiral auxiliary, and subsequent oxidative decomplexation yields a cyclohexenone with a new stereogenic center.

Introduction

A diverse number of methods are available to the synthetic chemist for the conversion of an arene into a functionalized alicyclic ring system containing stereogenic centers. However, few of these methods achieve a high degree of stereocontrol. Examples of asymmetric dearomatization of arenes include reductive alkylation,[1] nucleophilic addition to oxazoline-substituted naphthalenes,[2] nucleophilic addition to η^6-arene complexes of chromium[3,4] and manganese,[5] and enzymatic dihydroxylation.[6] Recently, we have shown that dihapto coordination of an arene by pentaammineosmium(II) dearomatizes the aromatic ligand, rendering it highly susceptible to electrophilic addition reactions.[7−10] Although an η^2-arene complex bearing a single arene substituent is chiral, a facile linkage isomerization process can result in rapid racemization of the two enantiomeric species.[7] Thus, although the reaction of η^2-arenes with electrophiles and the subsequent reactions of the arenium products with nucleophiles are highly regio- and stereospecific, organic products have been formed previously in racemic form.[8−10] Desiring a means to introduce asymmetry into the η^2-dearomatization methodology without corrupting the integrity of the pentaammine ligand set,[11] we sought coordination of an anisole derivative bearing a removable stereogenic center that would discriminate for a single coordination diastereomer.



Coordination Diastereomers

Results and Discussion

Our strategy for designing an asymmetric arene ligand relied on three key observations from previous studies. In η^2-anisole complexes of pentaammineosmium(II), the 5,6-η^2 isomer is heavily favored over its 3,4-η^2 counterpart.[7] The methoxy carbon of anisole for these complexes is oriented such that it lies in the arene plane and points *away* from the metal.[12] Finally, the ammonium-like ligands of η^2-arene complexes are mildly acidic and readily hydrogen bond with H-bond acceptor groups (e.g., alcohols, ethers, carbonyl groups).[9] We reasoned that, by replacing the methyl group of anisole with a stereogenic carbon bearing a hydrogen acceptor group (R^1) and a sterically encumbering methyl group, an unfavorable interaction between the methyl and the uncoordinated ortho hydrogen of the anisole would be established. Thus, one of the two expected coordination diastereomers would be destabilized (Figure 1).

A series of chiral alkoxyarene ligands (**1a**−**h**) were synthesized by routine organic reactions as shown in Scheme 1. Using previously established methods,[12] the reduction of $Os(NH_3)_5(OTf)_3$ in the presence of each of these ligands afforded complexes **2a**−**h** in yields ranging from 76 to 97% (Figure 2). Complex **2i** was prepared by treating complex **2f** with TBSOTf and pyridine at −40 °C. All complexes were characterized primarily by comparison of their ^{1}H NMR and electrochemical data with those of the parent anisole complex, $[Os(NH_3)_5(anisole)]^{2+}$, or with an appropriately substituted anisole analogue (e.g., *p*-methylanisole).[12]

The parent anisole complex undergoes a 5,6-η^2 to 2,3-η^2 linkage isomerization with a specific rate of about 1 s^{-1} at 20 °C;[7] thus, NMR spectra of complexes **2a**−**i** should reflect

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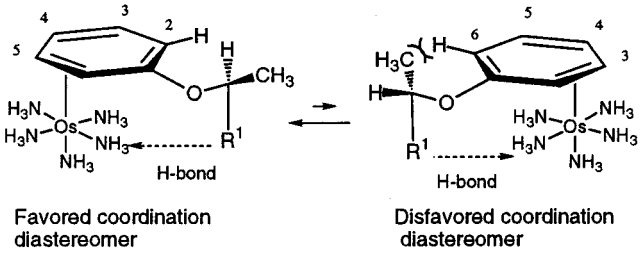


Figure 1. Favored and disfavored coordination diastereomers.

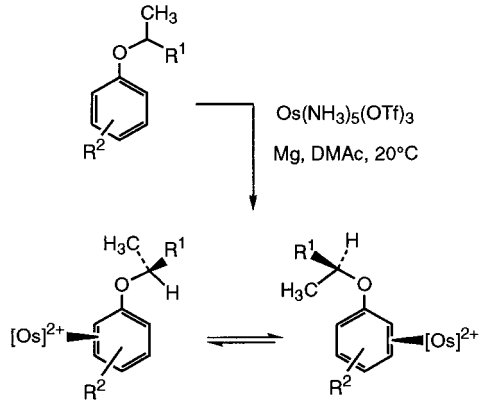
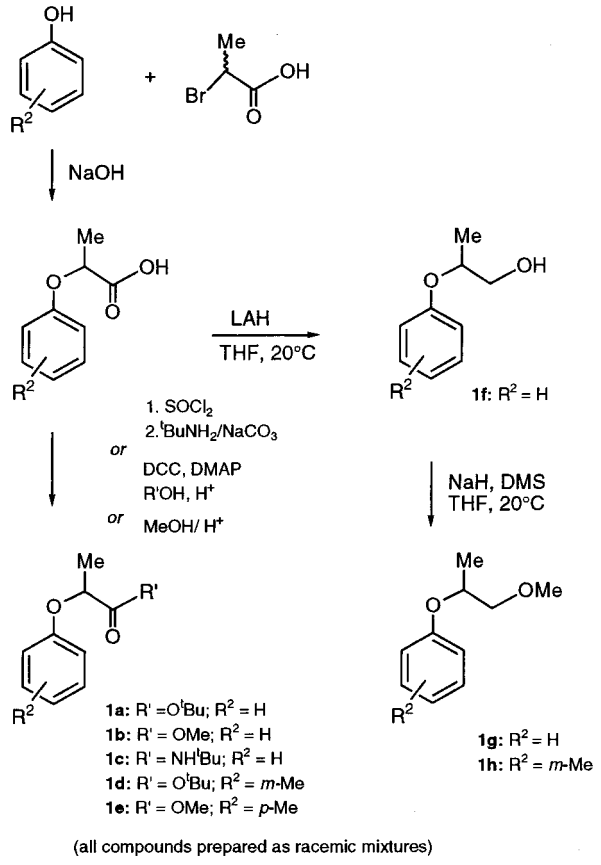


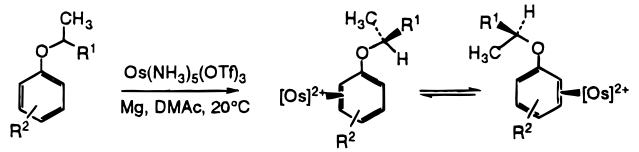
Figure 2. Complexation by Os^{II} of an alkoxybenzene bearing a stereogenic carbon.

Scheme 1. Synthesis of Asymmetric Anisole Derivatives



thermodynamic distributions of diastereomers. For complexes **2a**−**e**, all of which bear a carbonyl substituent (R^1), only one coordination diastereomer could be detected by ^{1}H NMR. ^{1}H NMR spectra for these complexes exhibit a single set of well-resolved ring resonances in the range of 5−7 ppm with the two most upfield resonances belonging to the ring protons (5 and 6) of the bound carbons. A ^{1}H NMR spectrum of complex **2a** shows a set of five intercoupled ring protons and a single set of signals corresponding to *t*-Bu, CH_3, and $OCHR^1$ groups. A proton-decoupled ^{13}C NMR spectrum of **2a** shows 13 carbon resonances in agreement with the assigned structure (Figure 1), including six appropriately positioned ring carbon signals and a carbonyl carbon at 174.0 ppm. A cyclic voltammogram of complex **2a** (CH_3CN, TBAH; 100 mV/s) features a chemically irreversible anodic wave at $E_{p,a} = 0.60$ V (NHE) and a reversible couple corresponding to the Os^{III} acetonitrile complex (−0.10 V, NHE) upon reversing the scan, a feature not present for the bulk solution. The purity of complex **2a** was determined to be >98% based on microanalytical, NMR, and electrochemical data. Through the close examination of ^{1}H and ^{13}C NMR data in acetone, we estimate that for **2a** the single observed diastereomeric complex is favored by >12:1 over its unobserved coordination isomer. Similar data were obtained for complexes **2b**−**e**. Lower limits for the diastereomer ratio differ slightly in Table 1 due to differences in the quality of available NMR data. Note that stereoselectivity is maintained for the carbonyl-bearing arene complexes **2a**−**e**, regardless of the size of the alkoxy group of the ester (*t*-Bu vs methyl; complexes **2a**,**b**) or the polarity of the carbonyl (amide vs esters **2c** and **2a**). Furthermore, alkyl substituents on the arene do not appear to compromise the selectivity of complexation, as can be seen in the comparison of *m*-methyl (**2d**) and *p*-methyl (**2e**) substituted arene complexes with **2a**.

Table 1. Yield and de Data for Asymmetric Arene Complexes



compd	R^2	R^1	yield (%)	de (%)[a]
2a	H	COO^tBu	95	>85
2b	H	COOMe	97	>80
2c	H	$CONH^tBu$	92	>90
2d	*m*-Me	COO^tBu	92	>90
2e	*p*-Me	COOMe	93	>90
2f	H	CH_2OH	85	50
2g	H	CH_2OMe	95	50
2h	*m*-Me	CH_2OMe	92	50
2i	H	CH_2OTBS	76	20

[a] Acetone-d_6 solvent, 20 °C.

In contrast to the those complexes bearing a carbonyl donor group, mixtures of coordination diastereomers are observed for complexes **2f**−**i** in acetone. For example, complex **2g**, shown by microanalytical and electrochemical data to be >95% pure, gives a ^{1}H NMR spectrum with two partially overlapping sets of ring proton signals. In particular, signals corresponding to the protons attached to the coordinated ortho carbons for these isomers are well-separated and appear as two doublets in a ratio of 3:1. In addition, ^{13}C NMR data for **2g** support a 3:1 assignment. Of note, some of the signals in the ^{1}H NMR spectrum of **2g** at 20 °C are significantly broadened compared to those in complex **2a**. The broadness of these signals indicates of a dynamic interconversion of the coordination diastereomers occurring on the order of seconds at 20 °C, a process similar to that documented for the parent anisole complex.[7] Further supporting this interpretation, the alcohol and methyl ether complexes **2f,g** were observed to show partial spin saturation exchange between major and minor coordination diastereomers

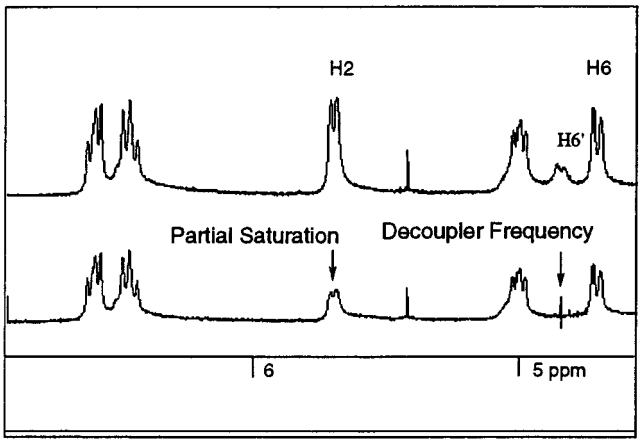


Figure 3. Homonuclear decoupling experiment of **2g** indicating spin-saturation exchange.

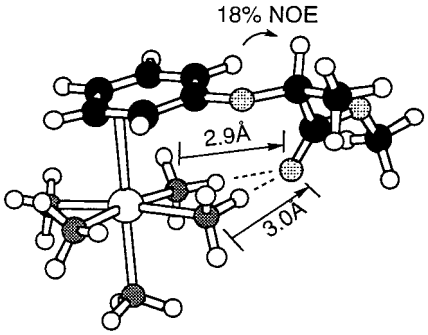


Figure 4. Molecular model of **2b** showing intramolecular hydrogen-bonding interaction.

(Figure 3). The stereoselectivities and yields of all complexes **2a**−**i** are compiled in Table 1.

Examination of complex **2a** in different deuterated solvents along with decoupling and NOE difference spectra reveals information about the factors affecting the coordination diastereoselectivity. Decoupling experiments indicate that, in contrast to the parent anisole complex, spin saturation is not exchanged between the ortho protons of C6 and C2 nor between the meta protons of C5 and C3. Note that the migration of osmium from the 5,6-η^2 to the 2,3-η^2 coordination positions would lead to formation of a diastereomer in the case of **2a**, whereas for anisole these two isomers are chemically equivalent. NOE difference spectra of compound **2a** showed a pronounced (18%) enhancement between the ortho proton H2 (see Figure 1) and the methine proton of the stereogenic carbon. These data coupled with molecular modeling data (MM2; Figure 4) indicate that that the methine proton is oriented toward the uncoordinated ortho proton for the favored coordination diastereomer. In solvents known to disrupt H-bonds such as DMF-d_7 or DMSO-d_6, the diastereoselectivity of **2a** was significantly compromised, changing from >12:1 to 9:1. Decoupling experiments in DMF-d_7 indicate partial spin saturation exchange betweeen correlated protons (e.g., H2) of the major and minor isomers. This observation confirms that the minor species is indeed a coordination diastereomer of the major one and supports the hypothesis that hydrogen bonding between the carbonyl group and the ammine ligands is an essential feature of high stereospecificity for these systems. Samples of both **2a** and the parent anisole complex were dissolved in CD_3CN, and these solutions were monitered over a period of 2 weeks by proton NMR. Contrary to what would be expected if the primary interaction between the alkyl substituent and the arene

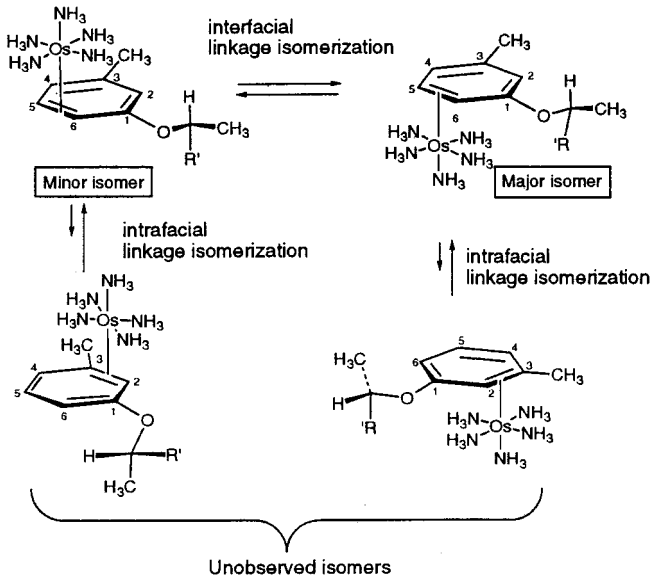


Figure 5. Dynamic processes for the η^2-3-methylanisole derivatives **2d**,**h**.

or metal sytem were steric in nature, the asymmetric complex **2a** was found to be twice (half-life of 4 days) as stable as its anisole counterpart with regard to displacement of the arene ligand by acetonitrile.

Compared to the carbonyl-bearing complexes, the alcohol derivative (**2f**) shows very low selectivity (de ~ 50%). When the alcohol is converted to the bulkier silyl ether (**2i**) the diastereoselectivity suffers (de ~ 20%). One possible explanation is that the alcohol still forms a hydrogen bond with the ammine ligands, but for the bulkier TBS analogue, hydrogen bonding is diminished to an extent that there is virtually no differentiation between coordination isomers. It is conceivable that the superior selectivity found for the amide and ester derivatives is a result of the an additional hydrogen-bonding site offered by these functional groups. But if this were true, one would expect to see a substantial lowering in diastereoselectivity when the methoxy group of **2b** is replaced with the *t*-Bu group of **2a**, yet this is not observed. An alternative explanation is that the hydrogen bonding with the ammine ligands, which is largely a product of dipole−dipole interactions, is stronger in the case of the amides or esters as a result of their larger dipole moments.[13] However, from an examination of an extensive compilation of experimental data,[13] it is difficult to draw general conclusions about the relative H-bonding acceptor properties of ethers vs esters or amides.

The appearance of a single diastereomer for the 3-methylated compound **2d** deserves special comment in that this is the only case for complexes **2a**−**e**, in which an *intrafacial* linkage isomerization from 5,6-η^2 to 2,3-η^2 would produce a constitutional isomer rather than a diastereomer. Thus, unlike **2a**, an *intrafacial* isomerization mechanism cannot equilibrate the two 5,6-η^2 coordination isomers. Even more remarkable is the comparison of the alcohol **2f** with its *m*-methyl substituted derivative **2h**. In both cases the diastereomeric ratio is 3:1, and these observations suggest that a thermodynamic equilibrium has been reached in both cases. To equilibrate isomers of a 5,6-η^2-3-methylanisole complex, the metal must undergo an *interfacial* isomerization whereby it moves from one face of the arene to the other (Figure 5). This type of isomerization

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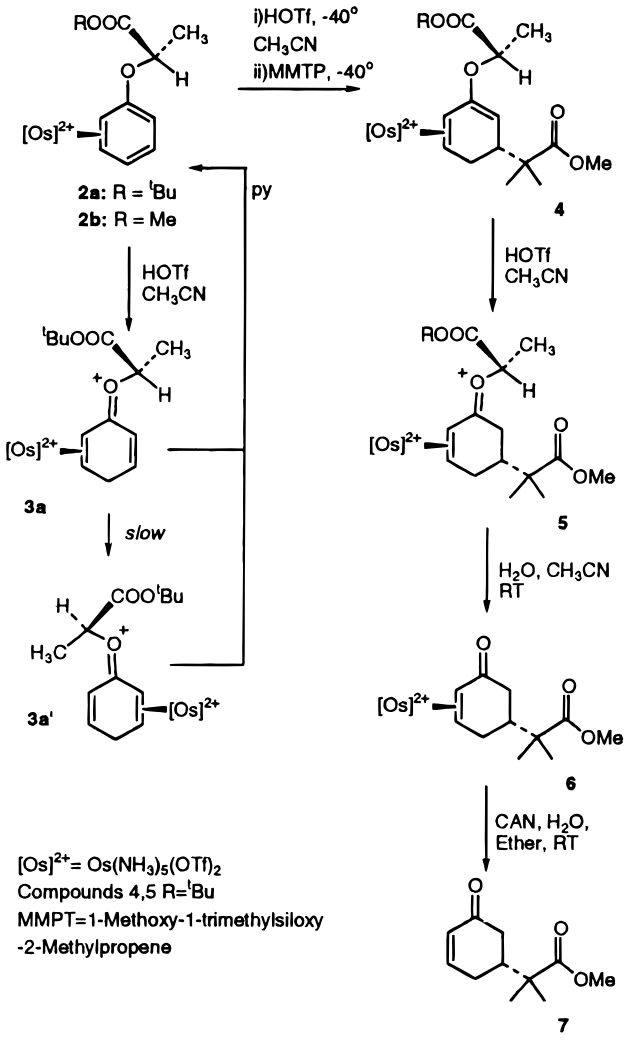
Scheme 2. Asymmetric Induction for an η^2-Anisole Complex



has not previously been documented for η^2-arene coordination complexes, but such a process could occur through an aryl hydride intermediate as has been proposed in a rhodium system by Jones et al.[14] Alternatively, it is possible that the interfacial isomerization occurs via an intermediate wherein the metal is coordinated through the aryl oxygen. We note that an *intermolecular* isomerization mechanism may be ruled out given the high thermal stability of the complex $[Os(NH_3)_5(\eta^2\text{-acetone})]^{2+}$. Regardless of which mechanism is operative, the asymmetric substituent in these arene complexes has revealed new information concerning the dynamics of linkage isomerizations of η^2-arene systems.

With this information, we initiated a preliminary investigation of the reactivity of complexes **2a**,**b** with electrophile and nucleophile (Scheme 2). The treatment of complex **2a** with triflic acid in CD_3CN (−40 °C) results in a color change from yellow to deep blue. The ^{1}H NMR (−40 °C) of the protonated species **3a** is similar to that of the parent 4*H*-anisolium species[8] and features a diastereotopic methylene group at 2.34 and 1.10 ppm, as well as two ring protons at 7.62 and 6.45 ppm corresponding to H3 and H2. Monitoring a solution of **3a** over a period of hours reveals the formation of a second species (**3a′**) assigned to a linkage diastereomer of **3a** (Scheme 2). The rate of production of this second isomer increased with increased concentration of triflic acid, and the equilibrium ratio was determined to be 1:1 at −40 °C. Interestingly, when a 1:1 mixture of **3a**/**3a′** was treated with pyridine and precipitated from solution, the product was shown by ^{1}H NMR to be exclusively complex **2a**, appearing as a single diastereomer. The apparently low thermodynamic diastereoselectivity for the 4*H*-oxonium species **3a** could be explained on the basis of disruption of the hydrogen bonding between donor group and ammine ligand by acid. The possibility of epimerization of the chiral center was ruled out by treating a sample of **2a** with triflic acid-d_1. Under identical reaction conditions to those which formed the diastereomeric mixture of **3a**, no deuterium incorporation took place at the epimerizable stereogenic sp^3 methine carbon.

Finally, in an attempt to show how an asymmetric arene substituent could influence the stereochemistry of a carbon−carbon bond forming reaction of the arene, we combined complex **2a** with triflic acid at −40 °C to generate the 4*H*-anisolium species **3a**, then treated this species in situ with 1-methoxy-2-methyl-1-(trimethylsiloxy)propene (MMTP). The nucleophilic addition product **4** was isolated as a single diastereomer (de > 90%). The enol ether complex **4** when treated with triflic acid at −40 °C forms the cyclohexenonium complex **5**, which was characterized primarily by a comparison of ^{1}H and ^{13}C NMR data with the *O*-methyl analogue.[15] Hydrolysis of oxonium **5** with water leads to the formation of enone complex **6**, which judging from ^{13}C and^{1}H NMR data is identical to that prepared from anisole. Oxidative decomplexation of the metal center (CAN) gave the free cyclohexenone **7** (Scheme 2) bearing a new stereogenic center.[16]

The present study shows that a remote stereogenic center in the alkyl substituent of a phenyl ether can profoundly influence the chirality of a newly formed stereogenic center located four bonds away *without* directly interacting with the chemical reagent (e.g., MMTP). In separate studies, we have shown that η^2-anisole complexes of pentaammineosmium(II) can participate in tandem electrophile−nucleophile addition reactions,[15,19] Diels−Alder reactions,[17,19] and intramolecular aldol cyclizations,[18,19] all of which create new stereogenic centers with high stereocontrol relative to that of metal coordination. Thus, in principle, a single enantiomer of an anisole bearing a remote chiral auxiliary may be used to set the absolute stereochemistry of multiple ring carbons for a broad array of reactions. Once used, the auxiliary may be discarded or recycled (Scheme 2). Of particular significance, the auxiliary functions by interacting with the metal center rather than the various organic reagents. Thus the chiral auxiliary should in principle deliver the same degree of stereocontrol for any organic reaction than can be accomplished with anisole using this dearomatization methodology. Efforts are currently underway to apply this novel methodology to more complex organic systems.

Experimental Section

General Procedure. All phenols used in this work were obtained from commercial sources and used without further purification. Organic solvents were dried prior to use using standard procedures. Organic ligands were purified by chromatography over silica gel and used for complexation. All complexation reactions were performed under

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nitrogen atmosphere in Vacuum Atmospheres Co. glovebox equipped with electronic balance. Solvents utilized inside the glovebox were purged with nitrogen prior to use. The deuterated solvents for NMR spectroscopy (acetone-d_6, acetonitrile-d_3, DMF-d_7) were first stirred with calcium hydride and then distilled under nitrogen. Chemical shifts are reported in parts per million (δ) and are referenced to tetramethylsilane (TMS) using residual protonated solvent. Distortionless enhancement polarization transfer (DEPT), NOE, and decoupling studies were performed on GN-300 instrument with routine parameters. Carbon multiplicities were assigned by DEPT experiments. In some of complexes the triflate carbon were very weak and could not be detected. Cyclic voltammograms were recorded under nitrogen using a standard three-electrode cell from 1.8 to −1.8 V with a glassy carbon working electrode. All electrochemical data were obtained in CH_3CN using n-Bu_4NPF_6 as electrolyte with a scan rate of 100 mV/s. Potentials were referenced to NHE using an internal standard of cobaltocenium hexafluorophosphate [$E_{1/2}$ = −0.78 V (NHE)]. Elemental analyses were obtained on a Perkin-Elmer PE−2400 series II CHN analyzer.

General Procedure for the Preparation of Complexes 2a−h. Activated magnesium granules (20 equiv) were added to a mixture of the organic ligand (**1a−h,** 2 mmol, 10 equiv), $Os(NH_3)_5(OTf)_3$ (0.2 mmol), and DMAc (0.5 g). The mixture was stirred for 1 h, during which time the solid dissolved and color changed to deep red. The mixture was then diluted with acetonitrile and filtered through a frit to remove magnesium powder. The red filtrate was added to ether/methylene chloride (1:1) (200 mL), and the resulting yellow solid was filtered, washed with methylene chloride followed by ether, and dried in vacuo. On the basis of ^{1}H and ^{13}C data, compounds (or diastereomeric mixtures) **2a−h** are >95% pure.

Complex 2a: 95%; CV (CH_3CN, TBAH, 100 mV/s) E_{pa} = 0.6 V (NHE), ^{1}H NMR (Acetone-d_6) δ 6.74 (brd, J = 5.2, 1H, CH), 6.37 (t, J = 7.2, 1H, CH), 5.46 (d, J = 5.8, 1H, CH), 5.32 (q, J = 5.2, 1H, CH), 5.03 (d, J = 8.0, 1H, CH), 4.76 (brs, 3H, *trans*-NH_3), 4.66 (q, J = 6.8, 1H, OCH), 3.44 (bs, 12H, *cis*-NH_3), 1.54 (d, J = 6.4, 3H, CH_3), 1.44 (s, 9H, *t*-Bu). ^{13}C NMR (acetone-d_6) δ 173.98 (CO), 167.84 (O−C═), 126.33 (CH), 124.02 (CF_3), 121.66 (CH), 119.80 (CF_3), 94.12 (CH), 83.74 (O−C), 72.06 (CH), 62.21 (O−CH), 55.44 (CH), 28.00 (CH_3)$_3$, 18.54 (CH_3). Anal. Calcd for $C_{15}H_{33}N_5O_9F_6S_2Os$: C, 22.64; H, 4.18; N, 8.80. Found: C, 22.97; H, 4.18; N, 8.49.

Complex 2b: 97%; CV (CH_3CN, TBAH, 100 mV/s) E_{pa} = 0.70 V (NHE), ^{1}H NMR (acetone-d_6) δ 6.77 (dd, J = 5.2,8.4, 1H, CH), 6.36 (t, J = 7.6, 1H, CH), 5.46 (dd, J = 1.8,6.8, 1H, CH), 5.35 (dd, J = 5.6,8.5, 1H, CH), 5.05 (dd, J = 1.6,8.4,1H, CH), 4.85 (q, J = 6.8,1H, OCH), 4.80 (brs, 3H, *trans*-NH_3), 3.57 (s, 3H, $COOCH_3$), 3.47 (bs, 12H, *cis*-NH_3), 1.58 (d, J = 6.4, 3H, CH_3). ^{13}C NMR (acetone-d_6) δ 174.73 (CO), 167.64 (O−C═), 126.48 (CH), 123.90 (CF_3), 121.77 (CH), 119.67 (CF_3), 94.26 (CH), 71.55 (CH_3), 62.25 (O−CH), 55.55 (CH), 53.28 (CH), 18.70 (CH_3). Anal. Calcd. for $C_{12}H_{27}N_5O_9F_6S_2Os$: C, 19.12; H, 3.61; N, 9.29. Found: C, 19.02; H, 3.79; N, 9.09.

Complex 2c: 92%; CV (CH_3CN, TBAH, 100 mV/s) E_{pa} = 0.62 V (NHE), ^{1}H NMR (acetone-d_6) δ 7.61 (bs, 1H, NHCO), 6.69 (dd, J = 5.2, 8.6, 1H, CH), 6.35 (t, J = 7.0, 1H, CH), 5.51 (dd, J = 1.6,6.6, 1H, CH), 5.27 (dd, J = 5.2, 8.2, 1H, CH), 4.93 (dd, J = 1.6, 8.2, 1H, CH), 4.78 (brs, 3H, *trans*-NH_3), 4.70 (q, J = 6.7, 1H, OCH), 3.47 (bs, 12H, *cis*-NH_3), 1.46 (d, J = 6.6, 3H, CH_3), 1.27 (s, 9H, *t*-Bu). ^{13}C NMR (acetone-d_6) δ 173.63 (CO), 168.00 (O−C═), 125.50 (CH), 123.99 (CF_3), 121.90 (CH), 119.65 (CF_3), 94.40 (CH), 72.83 (C), 62.02 (O−CH), 55.32 (CH), 52.03 (CH), 28.71 (CH_3)$_3$, 19.69 (CH_3).

Complex 2d: 92%; CV (CH_3CN, TBAH, 100 mV/s) E_{pa} = 0.48 V (NHE), ^{1}H NMR (acetone-d_6) δ 6.52 (bd, J = 4.8, 1H, CH), 5.37 (s, 1H, CH), 5.25 (dd, J = 5.2,8.4, 1H, CH), 4.95 (dd, J = 1.6,8.0, 1H, CH), 4.76 (brs, 3H, *trans*-NH_3), 4.69 (q, J = 6.8, 1H, OCH), 3.46 (bs, 12H, *cis*-NH_3), 2.15 (s, 3H, CH_3), 1.54 (d, J = 6.8, 3H, CH_3), 1.45 (s, 9H, *t*-Bu). ^{13}C NMR (acetone-d_6) δ 174.05 (CO), 167.93 (O−C═), 131.23 (C), 123.98 (CF_3), 122.56 (CH), 119.74 (CF_3), 97.21 (CH), 83.75 (C), 72.16 (CH), 62.12 (O−CH), 53.72 (CH), 28.04 (CH_3)$_3$, 21.50 (CH_3), 18.53 (CH_3). Anal. Calcd. for $C_{16}H_{35}N_5O_9F_6S_2Os$: C, 23.73; H, 4.36; N, 8.65. Found: C, 23.37; H, 4.15; N, 8.49.

Complex 2e: 93%; CV (CH_3CN, TBAH, 100 mV/s) 0.52 V (NHE), ^{1}H NMR (acetone-d_6) δ 6.14 (brd, J = 6.8, 1H, CH), 5.39 (bd, J = 8.2, 1H, CH), 5.27 (dd, J = 1.8,6.9, 1H, CH), 5.13 (dd, J = 2.1,8.2, 1H, CH), 4.81 (brs, 3H, *trans*-NH_3), 4.75 (q, J = 6.8, 1H, OCH), 3.74 (s, 3H, OCH_3) 3.54 (bs, 12H, *cis*-NH_3), 2.29 (s, 3H, CH_3), 1.55 (d, J = 6.8, 3H, CH_3). ^{13}C NMR (acetone-d_6) δ 174.82 (CO), 165.10 (O−C═), 137.71 (C), 124.03 (CF_3), 119.78 (CF_3), 117.99 (CH), 94.10 (CH), 71.68 (C), 64.48 (O−CH), 56.28 (CH), 53.22 (CH), 23.85 (CH_3), 18.78 (CH_3).

Complex 2f: 85%; CV (CH_3CN, TBAH, 100 mV/s) E_{pa} = 0.63 V (NHE), ^{1}H NMR (acetone-d_6, major isomer) δ 6.67 (d, J = 8.4, 1H, CH), 6.41 (t, J = 7.6, 1H, CH), 5.75 (d, J = 6.4, 1H, CH), 5.29 (d, J = 8.2, 1H, CH), 4.99 (d, J = 8.0, 1H, CH), 4.67 (brs, 3H, *trans*-NH_3), 4.46 (m, 1H, OCH), 3.43 (m, 14H, *cis*-NH_3 + CH_2), 1.25 (d, J = 6.0, 3H, CH_3).

Complex 2g: 95%; CV (CH_3CN, TBAH, 100 mV/s) E_{pa} = 0.51 V (NHE), ^{1}H NMR (acetone-d_6, major isomer) δ 6.69 (dd, J = 5.2,8.4, 1H, CH), 6.42 (t, J = 7.2, 1H, CH), 5.76 (d, J = 6.4, 1H, CH), 5.30 (bt, J = 7.6, 1H, CH), 4.99 (d, J = 8.0, 1H, CH), 4.70 (brs, 3H, *trans*-NH_3), 4.54 (m, 1H, OCH), 3.43 (bs, 14H, *cis*-NH_3 and CH_2), 3.33 (s, 3H, OCH_3), 1.27 (d, J = 6.4, 3H, CH_3). ^{13}C NMR (acetone-d_6) δ 167.92 (O−C═), 125.02 (CH), 123.97 (CF_3), 122.48 (CH), 119.73 (CF_3), 94.31 (CH), 76.24 (OCH_3), 72.19 (OCH_2), 62.68 (O−CH), 59.06 (CH), 56.67 (CH), 16.22 (CH_3). Anal. Calcd. for $C_{12}H_{29}N_5O_8F_6S_2Os$: C, 19.48; H, 3.95; N, 9.46. Found: C, 19.55; H, 4.00; N, 9.33.

Complex 2h: 92%; CV (CH_3CN, TBAH, 100 mV/s) E_{pa} = 0.50 V (NHE), ^{1}H NMR (acetone-d_6, major isomer) δ 6.45 (brd, J = 4.8, 1H, CH), 5.68 (s, 1H, CH), 5.20 (bd, J = 8.4, 1H, CH), 4.89 (d, J = 8.1, 1H, CH), 4.64 (brs, 3H, *trans*-NH_3), 4.55 (m, 1H, OCH), 3.53 (m, 2H, CH_2), 3.39 (bs, 12H, *cis*-NH_3), 3.31 (s, 3H, OCH_3) 2.16 (s, 3H, CH_3), 1.26 (d, J = 6.2, 3H, CH_3).

Complex 2i: 76%; ^{1}H NMR (acetone-d_6, major isomer) δ 6.69 (bt, J = 5.2,8.4, 1H, CH), 6.45 (d, J = 8.0, 1H, CH), 5.76 (d, J = 6.4, 1H, CH), 5.33 (bt, J = 4.4, 1H, CH), 5.05 (d, J = 8.0, 1H, CH), 4.68 (brs, 3H, *trans*-NH_3), 4.41 (m, 1H, OCH), 3.68 (m, 2H, CH_2), 3.45 (bs, 12H, *cis*-NH_3), 1.28 (d, J = 6.0, 3H, CH_3), 0.89 (s, 9H, *t*-Bu), 0.08 (s, 6H, CH_3).

Complex 3a: A solution of complex **2a** (11.2 mg, 0.014 mmol) in CD_3CN (0.32 g) in an NMR tube was cooled to −40 °C, and a cold solution of TfOH (8.5 mg, 0.056 mmol, −40 °C) in CD_3CN (0.27 g) was added. An immediate change from orange to purple was observed: ^{1}H NMR (acetonitrile-d_3) δ 7.62 (bd, J = 5.2, 1H, CH), 6.45 (d, J = 7.4, 1H, CH), 5.88 (t, J = 7.2, 1H, CH), 5.45 (q, J = 6.8, 1H, CH), 5.20 (bd, J = 5.4, 1H, CH), 4.80 (brs, 3H, *trans*-NH_3), 3.61 (bs, 12H, *cis*-NH_3), 2.34 (d, J = 25.4, 1H, CH_2), 1.69 (d, J = 6.9, 3H, CH_3), 1.46 (s, 9H, *t*-Bu), 1.10 (d, J = 25.4, 1H, CH_2).

Complex 4: Cold solutions (−40 °C) of complex **2a** (240.7 mg, 0.303 mmol) in CH_3CN (2.99 g) and TfOH (95.3 mg, 0.635 mmol) in CH_3CN (1.0 g) were mixed. The resulting mixture immediately turned deep purple. After 5 min (−40 °C), a cold solution of 1-methoxy-2-methyl-1-(trimethylsiloxy)propene (MMTP, 153.1 mg, 0.879 mmol) in CH_3CN (0.75 g) was added. The reaction mixture was kept at −40 °C for 3 h and then quenched with 2,6-lutidine (250 mg, 2.33 mmol). The light orange solution was allowed to warm to room temperature. Precipitation of the salt in ether (100 mL) gave a yellow oil. Reprecipitation of this oil from CH_3CN using a 3:1 ether:hexanes (100 mL) mixture gave the yellow solid **4** (183.3 mg, 68%): CV (CH_3CN, TBAH, 100 mV/s) E_{pa} = 0.70 V (NHE); ^{1}H NMR (acetone-d_6) δ 4.82 (brs, 3H, *trans*-NH_3), 4.50 (q, 1H, J = 6.5, OCH), 4.17 (d, J = 2.4, 1H, CH), 3.98 (d, 1H, J = 8.4, CH), 3.89 (m, 1H, CH), 3.62 (bs, 12H, NH_3 × 4), 3.61 (s, 3H, COOMe), 2.65 (m, 1H), 1.96 (m, 2H), 1.44 (s, 9H, *t*-Bu), 1.43 (d, J = 6.5, 3H, CH_3), 1.10 (s, 6H, CH_3 × 2); ^{13}C NMR (acetone-d_6) δ 178.18 (CO), 174.06 (CO), 160.67 (O−C═), 89.72 (CH), 83.33 (C), 71.20 (CH), 52.01 (CH_3), 48.02 (C), 46.73 (CH), 43.56 (CH), 40.95 (CH), 28.09 (CH_3)$_3$, 26.70 (CH_2), 21.75 (CH_3), 18.49 (CH_3).

Complex 5: A cold solution (−40 °C) of complex **4** (227.1 mg, 0.253 mmol) in CH_3CN (0.81 g) was mixed with a cold solution of TfOH (58.8 mg, 0.392 mmol) in CH_3CN, and a color change from orange to purple was observed. The reaction mixture was allowed to warm to 20 °C after 10 min at −40 °C and was added to ether (150 mL). The precipitate was filtered, washed with ether, and dried in vacuo to yield **5** (230 mg, 87%): ^{1}H NMR (acetonitrile-d_3) δ 5.88 (m, 1H, CH), 5.62 (q, 1H, J = 6.9, OCH), 5.21 (d, J = 7.2, 1H, CH), 5.07 (bs, 3H, trans −NH_3), 3.92 (bs, 12H, NH_3 × 4), 3.65 (s, 3H,

COOMe), 2.89 (m, 1H), 2.17 (dd, 1H, $J = 21.0, 10.2$, CH_2), 1.88 (m, 1H), 1.76 (m, 1H), 1.74 (d, 3H, $J = 6.9$, CH_3), 1.63 (bs, 6H, $CH_3 \times 2$), 1.16 (s, 9H, *t*-Bu), 0.92 (m, 1H); ^{13}C NMR (acetone-d_6) δ 201.24 (CO), 177.40 (CO), 170.87 (O−C═), 78.69 (CH), 66.27 (C), 61.57 (CH), 57.00 (CH), 52.85 (CH_3), 45.58 (C), 38.22 (CH), 31.02 (CH_2), 26.41 (CH_2), 23.29 (CH_3), 22.81 (CH_3), 17.40 (CH_3), 15.63 (CH_3).

Complex 6: Complex **5** (218.8 mg, 0.209 mmol) was dissolved in CH_3CN (3.0 g), and two drops of water were added. An immediate color change to orange was observed. The mixutre was further stirred for 30 min. Addition of this mixture to ether (100 mL) formed an off-white precipitate. Filteration followed by washing with ether and drying gave complex **6** (151.2 mg, 94%): CV (CH_3CN, TBAH, 100 mV/s) $E_{pa} = 0.95$ V (NHE); ^{1}H NMR (acetonitrile-d_3) δ 4.65 (bs, 3H, *trans*-NH_3), 3.95 (m, 1H), 3.85 (d, 1H, $J = 7.5$, CH), 3.51 (s, 3H, OMe), 3.35 (bs, 12H, *cis*-$NH_3 \times 4$), 2.61 (m, 1H), 2.05−1.75 (m, 3H), 1.40 (m, 1H), 1.12 (s, 3H, CH_3), 1.10 (s, 3H, CH_3); ^{13}C NMR (acetone-d_6) δ 214.23 (CO), 177.92 (CO), 161.47 (C), 52.52 (CH_3), 51.60 (CH), 50.03 (CH), 45.78 (C), 45.21 (C), 38.12 (CH), 26.71 (CH_2), 23.29 ($CH_3 \times 2$).

5-(2-Methyl-2-(carbomethoxy)ethyl)-2-cyclohexen-1-one (**7**). Complex **6** (191.3 mg, 0.248 mmol) was dissolved in water (5.0 mL), and ether (5.0 mL) was added. To this biphasic mixture was added a solution of CAN (cerric ammonium nitrate, 275.5 mg, 0.514 mmol) in water (0.5 mL), and the mixture was stirred for 30 min. Ether (10 mL) was added, and the organic layer was separated and washed with dilute $NaHCO_3$ (aq), water, and brine. The organic layer was dried over Na_2SO_4 and evaporated under reduced pressure to yield a compound **7** as a transparent oil (33.7 mg, 71%): ^{1}H NMR (chloroform-*d*) δ 6.96 (m, 1H, CH), 5.98 (d, 1H, $J = 9.6$, CH), 3.64 (s, 3H, OMe), 2.41−2.00 (m, 5H), 1.15 (s, 3H), 1.13 (s, 3H, CH_3); ^{13}C NMR (chloroform-*d*) δ 199.01 (CO), 176.52 (COO), 149.47 (CH), 128.92 (CH), 51.42 (CH_3), 44.32 (C), 41.8 (CH), 39.32 (CH_2), 27.04 (CH_2), 21.89 (CH_3), 21.43 (CH_3). These data match those previously reported. See ref 16.

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Supporting Information Available: Experimental details and spectra for **2a**−**i**, **3**−**5**, and **7** (16 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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