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The Regio- and Stereospecific Selective Hydrogenation of η^2-Coordinated Arenes

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Abstract: Several η^2-bound arene complexes of pentaammineosmium(II) have been selectively hydrogenated to alkene products in the presence of a heterogeneous catalyst (Pd, Rh). In all cases the coordinated osmium was shown both to activate the arene ligand toward catalytic hydrogenation and to protect the alkene product toward further reduction. Hydrogenation can be achieved both regio- and stereoselectivity and is shown to occur exclusively anti to the metal center. The structure of the 3-methoxycyclohexene complex $[Os(NH_3)_5(\eta^2-C_7H_{12}O)](OTf)_2$ has been determined. The hydrogenation of η^2-bound anisole or 1,4-dimethoxybenzene is not concerted; the semihydrogenation product, a vinyl ether, rapidly hydrolyzes in acid medium to form a cyclohexenone complex.

The catalytic hydrogenation of arene molecules is considerably more difficult than for simple olefins owing to the inherent stability of aromatic systems.[1] The product of arene hydrogenation is typically a saturated hydrocarbon; though cyclic olefins are undoubtedly intermediates in this process, their rapid reduction usually precludes their isolation in high yield.[2] Recently, we reported that in the presence of a heterogeneous catalyst, the η^2-coordinated benzene complex $[Os(NH_3)_5(\eta^2-C_6H_6)]^{2+}$ undergoes a facile hydrogenation to the cyclohexene analogue.[3] η^2 metal coordination was found both to *activate* the benzene ligand toward reduction and to *protect* the resulting olefin product.

In an earlier study, several substituted benzenes were investigated[4] as ligands for pentaammineosmium(II). Relative to other η^2-bound arene species reported, these osmium complexes offer a high degree of kinetic stability, lasting from hours to weeks in solution at ambient temperatures. Equally significant is the observation that the metal center shows a high degree of regioselectivity, and often a single isomeric form dominates as product. Although in many cases tautomerization is detected in these complexes, the corresponding activation barrier is comparatively large, with values ranging from 12 to 17 kcal/mol at 20 °C. In light of these findings, it seemed plausible that this regiospecific coordination could lead to regioselective reactivity (e.g., hydrogenation) at the bound arene.

Experimental Section

Infrared spectra were recorded on an IBM 98 FTIR spectrometer and ^{13}C and ^{1}H NMR spectra on a Varian XL-400 spectrometer. Electrochemical experiments were performed under argon with a PAR Model 173 potentiostat driven by a PAR Model 175 universal programmer. Cyclic voltammograms were recorded in a standard three-electrode cell[5] from +1.0 to −1.5 V with a Pt^0 working electrode. The reference was calibrated with the ferrocene/ferrocenium couple ($E_{1/2}$ = 0.55 V; NHE) in situ. The peak-to-peak separation for this couple was between 60 and 80 mV for all cyclic voltammograms reported. All potentials are reported vs the normal hydrogen electrode. The hydrogenation apparatus used consisted of a 15-cm Schlenk tube fitted with a rubber balloon. For all hydrogenations, a slurry of the heterogeneous catalyst (5% Pd^0/C or 5% Rh^0/C) and solvent was treated with hydrogen for a period of 1 h prior to the addition of the osmium–arene complex.

Reagents. $[Os(NH_3)_5(OTf)](OTf)_2$ (OTf = $CF_3SO_3^-$) was synthesized as described by Lay et al.[6] Acetone was purified by vacuum distillation over B_2O_3,[7] and MeOH was purified by distillation over $Mg(OMe)_2$ prepared in situ from Mg^0 and I_2 under argon.[8] 1,2-Dimethoxyethane (DME) was dried over Na^0 and distilled after 24 h. NaOTf was prepared by the neutralization of HOTF by Na_2CO_3 and was recrystallized twice from acetone and ether. Magnesium turnings were cleaned in a DME solution of iodine for 1 h followed by copious washing with DME and Et_2O. Amalgamated zinc granules (Zn/Hg) were prepared by treating granular Zn^0 (30 mesh) with 3 M HCl(aq) (15 min) followed by a saturated $HgCl_2$(aq) solution (15 min). The amalgam was then thoroughly washed with water, acetone, and ether. Anisole was distilled over CaH_2 after 2 days of stirring, and 1,4-dimethoxybenzene was recrystallized from petroleum ether. Anhydrous ether and CH_2Cl_2 were purchased from Aldrich and used without further purification. Otherwise, reagents were used as supplied. All solvents were deoxygenated by purging with argon, and reactions were carried out under an argon atmosphere in a Vacuum Atmospheres Corp. glovebox.

Preparations. $[Os(NH_3)_5(1,2-\eta^2\text{-naphthalene})](OTf)_2$ (**1**) was prepared by use of established synthetic procedures for pentaammineosmium(II) complexes.[6] A solution of $Os(NH_3)_5(OTf)_3$ (280 mg), DME (8 mL), *N,N*-dimethylacetamide (DMA) (2 mL), and naphthalene ($C_{10}H_8$) (2.5 g) was treated with 1.5 g of activated magnesium turnings. After a 1-h reduction period, the yellow solution was filtered with a fine frit, and the filtrate was slowly *added to* CH_2Cl_2 (150 mL). The yellow precipitate that formed was collected, washed with CH_2Cl_2 and Et_2O, and dried under vacuum. Typical yield: 85–90%.

Characterization of **1**: Anal. Calcd for $C_{12}H_{23}OsS_2F_6O_6N_5$: C, 20.54; H, 3.30; N, 9.98. Found: C, 20.82; H, 3.30; N, 9.72. ^1H NMR (acetone-d_6): 7.70 (d, 1 H), 7.48 (d, 1 H), 7.3 (m, 3 H), 7.02 (d, 1 H), 5.42 (d, 1 H), 5.23 (d of d, 1 H) ppm. Cyclic voltammetry (acetone, NaOTf, 100 mV/s): $E_{1/2}$ = 0.41 V.

$[Os(NH_3)_5(3,4-\eta^2\text{-1,2-dihydronaphthalene})](OTf)_2$ (2). Methanol (5 mL) and 5% Pd^0/C (132 mg) were slurried under 1 atm of hydrogen for a period of 1 h. After this prereduction of the catalyst, 73 mg of the naphthalene complex (**1**) was added, and the mixture was stirred under hydrogen (1 atm) for 18 h.[9] The reduced solution was filtered with a fine frit, evaporated to about 0.5 mL, and treated with ether (15 mL). The resulting precipitate was collected, washed with ether, and dried under vacuum. The major product (>85%) is characterized as a complex of 1,2-dihydronaphthalene. A minor product is detected which does not appear to alter the elemental analysis. This material is likely to be the 1,4-dihydronaphthalene isomer of **2**.[10]

Anal. Calcd for $C_{12}H_{25}OsS_2F_6O_6N_5$: C, 20.48; H, 3.58; N, 9.95. Found: C, 20.35; H, 3.71; N, 9.83. ^1H NMR (acetone-d_6): 7.35 (d, 1 H), 7.1 (m, 3 H), 4.83 (br, 3 H), 4.55 (d, 1 H), 4.07 (m, 1 H), 3.60 (br, 12 H), 2.95 (m, 1 H), 2.60 (m, 1 H), 2.20 (m, 1 H), 1.65 (m, 1 H) ppm. Cyclic voltammetry (acetone, NaOTf, 100 mV/s): $E_{1/2}$ = 0.50 V.

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(1) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; Benjamin Cummings: Menlo Park, 1972.

(2) Augustine, R. L. *Catalytic Hydrogenation*; Marcel Dekker: New York, 1965.

(3) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 7906.

(4) Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 5725.

(5) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980.

(6) Lay, P.; Magnuson, R.; Sen, J.; Taube, H. *J. Am. Chem. Soc.* **1982**, *104*, 7658.

(7) Burfield, D. R.; Smithers, R. H. *J. Org. Chem.* **1978**, *43*, 3966.

(8) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Oxford University Press: New York, 1980.

(9) The rate of hydrogenation is extremely sensitive to impurities in solution which may poison the catalyst. As a result, hydrogenation times may vary considerably.

(10) ^1H NMR data (acetone-d_6) for the minor hydrogenation product include three equal-intensity peaks at 3.90 (m), 4.20 (d), and 3.15 (m) ppm. The aromatic and ammine regions are obscured by the dominant product.

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[Os(NH$_3$)$_5$(2,3-η^2-PhOCH$_3$)](OTf)$_2$ (3) was characterized earlier.[4] A solution of $Os(NH_3)_5(OTf)_3$ (500 mg), anisole (2.0 mL), and methanol (10 mL) was treated with granular Zn/Hg amalgam (3 g) for 10 min. The deep yellow solution was filtered, and to the filtrate 100 mL of ether was added slowly. The resulting precipitate was collected, washed with ether, and dried under vacuum. Yield: 79%. The purity of **3** was estimated to be >95%, judging from cyclic voltammetric and ^{1}H NMR data.

[Os(NH$_3$)$_5$(η^2-3-methoxycyclohexene)](OTf)$_2$ (4). Methanol (10 mL) containing 5% Rh^0/C (220 mg) was slurried under 1 atm of hydrogen for a period of 1 h. After prereduction of the catalyst, 100 mg of the anisole complex (**3**) was added, and the mixture was stirred under hydrogen (1 atm) for 2.5 h.[9] The reduced solution was filtered with a fine frit, evaporated to about 0.5 mL, and treated with ether (15 mL). The resulting precipitate was collected, washed with ether, and dried under vacuum. Typical yield: 60–75%. Crystals of **4** were grown from an acetone/ether solution. The compound **4**-d_4 was prepared by substituting deuterium gas and CD_3OD for hydrogen and methanol, respectively.

4: Anal. Calcd for $C_9H_{27}OsS_2F_6O_7N_5\cdot{}^1/_2C_3H_6O$: C, 17.65; H, 4.23; N, 9.80. Found: C, 17.56; H, 4.03; N, 9.81. ^{1}H NMR (acetone-d_6): 4.96 (q, 1 H), 4.70 (b, 3 H), 3.86 (d of t, 1 H), 3.78 (d of d, 1 H), 3.66 (br, 12 H), 3.40 (s, 3 H), 2.70 (m, 1 H), 1.96 (m, 1 H), 1.63 (m, 1 H), 1.50 (m, 2 H), 1.20 (m, 1 H), $E_{1/2}$ (acetone, NaOTf, 100 mV/s) = 0.44 V. **4**-d_4: ^{1}H NMR (acetone-d_6): 4.96 (<0.05 H), 4.70 (br, 3 H), 3.86 (1 H), 3.78 (1 H), 3.66 (br, 12 H), 3.40 (s, 3 H), 2.70 (<0.05 H), 1.96 (<0.1 H), 1.63 (1 H), 1.50 (1 H), 1.20 (1 H) ppm.

[Os(NH$_3$)$_5$(2,3-η^2-2-cyclohexen-1-one)](OTf)$_2$ (5). The olefin isomer can be obtained in high yield (>80%) from the hydrogenation of the anisole complex **3**: a 1 M H$_2$O mixture of methanol (10 mL), 5% Rh^0/C (132 mg), and trace amounts of HOTf was slurried under 1 atm of hydrogen for a period of 1 h. After this prereduction of the catalyst, 75 mg of the anisole complex (**1**) was added, and the mixture was stirred under hydrogen (1 atm) for 3 h.[9] The reduced solution was filtered through a fine frit, evaporated to about 0.5 mL, and treated with ether (15 mL). The resulting precipitate was collected, washed with ether, and dried under vacuum. ^{1}H NMR (acetone-d_6): 5.10 (br, 3 H), 4.63 (t of d, 1 H), 4.14 (d, 1 H), 3.82 (br, 12 H), 3.00 (m, 1 H), 2.30 (m, 1 H), 1.93 (m, 2 H), 1.80 (m, 2 H) ppm. Cyclic voltammetry (acetone, NaOTf, 100 mV/s): $E_{1/2}$ = 0.72 V. IR (acetone glaze): a ν(C–O) was not observed over the range 1800–1640 cm^{-1}.

The complex **5**-d_3 was obtained as a byproduct of the preparation of **4**-d_4 in reagent grade CD_3OD (which we believe to contain traces of water). ^{1}H NMR (acetone-d_6): 5.10 (br, 3 H), 4.63 (1 H), 4.14 (1 H), 3.82 (br, 12 H), 3.00 (<0.05 H), 2.30 (<0.05 H), 1.93 (1 H), 1.80 (2 H) ppm.

[Os(NH$_3$)$_5$(2-cyclohexene-1-one)](OTf)$_2$ (Mixture of Isomers 5 and 6). $Os(NH_3)_5(OTf)_3$ (320 mg), DMA (1.0 mL), and 2-cyclohexen-1-one (1.0 mL) were dissolved in DME (15 mL), and the solution was treated with 1.5 g of activated magnesium turnings. After 2 h the orange solution was filtered through a fine frit, and the filtrate was added slowly to 100 mL of CH_2Cl_2. The resulting precipitate was collected, washed with CH_2Cl_2 and Et_2O, and dried under vacuum. ^{1}H NMR and CV data indicate a 1:1 mixture of the η^2-ketone (**6**) and η^2-alkene (**5**) isomers. Anal. Calcd for $C_8H_{23}OsS_2F_6O_7N_5$: C, 15.71; H, 3.74; N, 10.18. Found: C, 15.69; H, 3.74; N, 10.62. Partial characterization of the η^2-ketone isomer **6**: ^{1}H NMR (acetone-d_6): 6.23 (d of t, 1 H, =CH), 5.53 (br, 3 H, t-NH$_3$), 5.02 (d of t, 1 H, =CH), 4.02 (br, 12 H, NH$_3$) ppm (aliphatic resonances not characterized).

[Os(NH$_3$)$_5$(2,3-η^2-1,4-dimethoxybenzene)](OTf)$_2$ (7) was prepared in DME by using established procedures for pentaammineosmium(II) complexes.[11] A solution of $Os(NH_3)_5(OTf)_3$ (1.00 g), DME (10 mL), *N*,*N*-dimethylacetamide (DMA) (1.0 mL), and 1,4-dimethoxybenzene (2.5 g) was treated with 3 g of activated magnesium turnings. After a 2-h reduction period, the yellow solution was filtered through a fine frit, and the filtrate was slowly *added to* CH_2Cl_2 (250 mL). The yellow precipitate that formed was collected, washed with CH_2Cl_2 and Et_2O, and dried under vacuum. Yield: 805 mg (82%). Anal. Calcd for $C_{10}H_{25}Os_1S_2F_6O_8N_5$: C, 16.88; H, 3.54; N, 9.84; S, 9.01. Found: C, 16.50; H, 3.43; N, 9.99; S, 8.84. ^{1}H NMR (acetone-d_6): 5.50 (s, 2 H), 5.14 (s, 2 H), 4.70 (br, 3 H), 3.65 (s, 6 H), 3.50 (b, 12 H) ppm. Cyclic voltammetry (CH_3CN, TBAH, 100 mV/s): $E_{p,a}$ = 0.47 V.

[Os(NH$_3$)$_5$(η^2-3,6-dimethoxycyclohexene)](OTf)$_2$ (8). Methanol (5 mL) and 5% Rh^0/C (220 mg) were slurried under 1 atm of hydrogen for a period of 20 min. After this prereduction of the catalyst, 100 mg of the dimethoxybenzene complex (**7**) was added, and the mixture was stirred under hydrogen (1 atm) for 18 h.[10] The reduced solution was filtered through a fine frit, evaporated to about 0.5 mL, and treated with ether (15 mL). The resulting precipitate was collected, washed with ether, and dried under vacuum. In the preparation of the complex **8**-d_4, deuterium and CD_3OD were substituted for hydrogen and methanol, respectively.

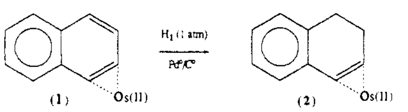

Figure 1. Selective hydrogenation of the η^2-coordinated naphthalene complex **1** (Os(II) = Os^{II}(NH$_3$)$_5$).

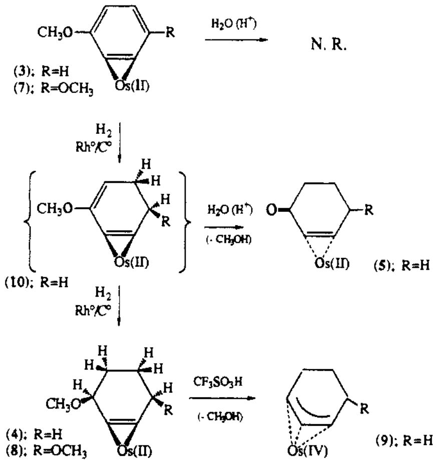

Figure 2. Chemistry associated with the hydrogenation of the η^2-bound methoxybenzene complexes **3** and **7**. (Os(IV) = Os^{IV}(NH$_3$)$_5$; Os(II) = Os^{II}(NH$_3$)$_5$).

Anal. Calcd for $C_{10}H_{29}OsS_2F_6O_8N_5$: C, 16.78; H, 4.08; N, 9.79; S, 8.96. Found: C, 16.57; H, 3.96; N, 9.97; S, 8.92. ^{1}H NMR (acetone-d_6): 4.78 (H$_a$, m, 2 H), 4.70 (H$_b$, br, 3 H), 3.96 (H$_c$, d of d, 2 H), 3.80 (H$_d$, br, 12 H), 3.38 (H$_e$, s, 6 H), 1.76 (H$_f$, m, 2 H), 1.55 (H$_g$, m, 2 H) ppm. NOE (resonance irradiated, 3.80 ppm): H$_a$, 0.81%; H$_e$, 4.5%; H$_f$, 0.58%; H$_g$, 1.43%. Cyclic voltammetry (CH_3CN, TBAH, 100 mV/s): $E_{1/2}$ = 0.69 V. **8**-d_4: ^{1}H NMR (acetone-d_6): 4.78 (<0.05 H), 4.70 (br, 3 H), 3.96 (s, 2 H), 3.80 (br, 12 H), 3.38 (s, ≈4 H), 1.76 (<0.05 H), 1.55 (s, ≈1 H) ppm.

Results

Pentaammineosmium(II) binds naphthalene across C$_1$ and C$_2$. Hydrogenation of the resulting complex (**1**) at 1 atm in the presence of a heterogeneous Pd^0 catalyst results in two new species. The dominant product (>85%) (**2**) displays four unique aliphatic resonances in the ^{1}H NMR, an outcome that is consistent with the product being both partially hydrogenated and asymmetric. Four aromatic resonances (7.1–7.4 ppm) and two coordinated-olefin resonances (4.55, 4.07 ppm) indicate that further reduction of the naphthalene ligand has been successfully avoided. As with all the hydrogenation products reported, the 3+/2+ reduction potential and large separation of ^{1}H ammine resonances are consistent with a reduction product in which the metal is coordinated η^2 to the organic ligand.[12] Taken together, the electrochemical and ^{1}H NMR data provide convincing evidence that **2** is a 1,2-dihydronaphthalene complex coordinated through the vinyl group (Figure 1). Although the minor product has not been positively identified, we believe it is the 1,4-dihydronaphthalene isomer of **2**.

Anisole forms a complex (**3**) with pentaammineosmium(II) in which the metal selectively coordinates the 2,3 position of the organic ligand.[4] Hydrogenation of **3** proceeds smoothly with Rh^0 over a period of 2.5 h.[13] The new species isolated, **4**, displays six aliphatic resonances ranging from 1.20 to 2.70 ppm and one at 4.96 ppm, corresponding to the proton geminal to the methoxy

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(11) Harman, W. D.; Taube, H. *Inorg. Chem.* **1987**, *26*, 2917.

(12) Reduction potentials for simple olefin–pentaammineosmium(II) complexes typically range from 0.3 to 0.6 V (NHE). The separation between trans and cis ammine resonances is >1 ppm for all known cases of pentaammineosmium(II) with π-bound ligands. See: Harman, W. D. Ph.D. Dissertation, Stanford University, 1987.

(13) Although Pd^0 has also been used successfully as the hydrogenation catalyst for the anisole complex, reduction occurs somewhat sluggishly.

(14) Crystals of **4** were obtained by the method of vapor diffusion.

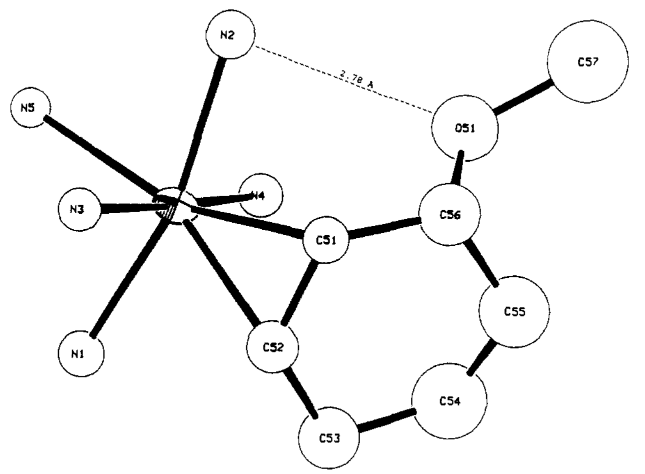

Figure 3. ORTEP diagram for the cation $[Os(NH_3)_5(\eta^2\text{-3-methoxycyclohexene})]^{2+}$.

group. The latter proton couples with two other aliphatic resonances (1.20, 1.96 ppm) and one bound-olefin proton (3.78 ppm), thus confirming that the anisole ligand of **3** has been regiospecifically reduced to 3-methoxycyclohexene (Figure 2). The complex $[Os(NH_3)_5(\eta^2\text{-}C_6H_9OCH_3)](OTf)_2$ (**4**) shows a single methoxy peak, which suggests that this species is present as a single stereoisomer in solution.

Crystals of **4** were grown over a period of 1 week from acetone and ether[14] and their structure was determined. Two independent osmium cations are located and have similar geometries; the methoxy group is found to be syn to the coordinated osmium for both (Figure 3). Osmium–nitrogen distances average 2.167 (32) Å; the nitrogen atoms are approximately octahedrally coordinated to the osmium, with the C=C group filling the sixth site. Nitrogen atoms cis to the C=C group and in the Os–C=C plane are bent away from the carbon atoms by 6–8°. The organic ligands are roughly similar. At Os1, the Os–C distances are both 2.14 (3) Å and the C=C distance is 1.44 Å. The remaining C–C distances average 1.50 (4) Å. The C–C–C angles at the double bond are 120 (2) and 124 (3)°; the remaining four angles average 117 (3)°, larger than expected. For the second cation, as a result of internal disorder in the crystal, several of the values found for bond distances and angles are unreasonable; however, the rough geometry is identical with that of the cation previously described. The triflate anions have distances and angles that approximate those expected, but disorder prevents an accurate determination of their atomic positions. Information regarding the crystal structure determination is given in the supplementary material.

Attempts to hydrogenate the anisole complex (**3**) in reagent grade methanol resulted in the formation of **4** as the major product, but significant amounts (20–40%) of a new material, **5**, were also detected (Figure 2). Only after distillation of the solvent was **4** obtained in quantitative yield. When **3** was hydrogenated in an acidic methanol solution that was 1 M in H_2O, complex **5** comprised over 80% of the isolated reduction product. ^1H NMR revealed both aliphatic and bound-olefinic resonances but no methoxy signal. Speculating that **5** was a hydrolysis product of a vinyl ether intermediate, we attempted a preparation of a pentaammineosmium(II) complex of 2-cyclohexen-1-one using established synthetic procedures.[15] The isolated solid was shown by NMR and CV to be a mixture of **5** and its isomer, **6**, in which the osmium is bound η^2 to the carbonyl fragment. Ammine resonances corresponding to **6** appear at 5.53 (3 H) and 4.02 (12 H) ppm, virtually identical in position with those reported for the acetone analogue.[16] Upon heating (12 min at 75 °C), an acetonitrile-d_3 solution of this mixture changed from orange to yellow, and ^1H NMR spectra indicate that the η^2-ketone species (**6**) rearranges (>95%) to its olefin isomer, **5** (Figure 4).[17] A cyclic voltammogram of this species shows a reversible couple at 0.72 V, slightly positive to values observed for typical olefin complexes of pentaammineosmium(II).[12] Homonuclear decoupling confirms our interpretation of **5** as being a 2-cyclohexen-1-one complex in which the osmium engages the olefin (Figure 2).

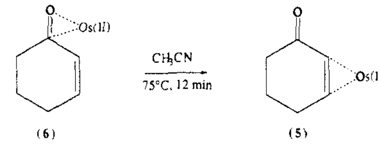

Figure 4. Linkage isomerization observed for the complex $[Os(NH_3)_5(\eta^2\text{-2-cyclohexen-1-one})](OTf)_2$.

When the hydrogenation of the anisole complex (**3**) is repeated under a deuterium atmosphere in CD_3OD the isolated product is found to have deuterium incorporated at four positions. Most notably, the resonance assigned to the proton geminal to the methoxy group is absent in the 3-methoxycyclohexene product (**4**-d_4). In addition to **4**-d_4, the isolated reaction mixture contained about 50% of the cyclohexenone species, **5**-d_3. Isotopic scrambling was not observed for either product.

When **3** is hydrogenated in strongly acidified methanol, the yield of the allyl ether product is greatly reduced, and the major product of the reaction under these conditions is the Os(IV)–η^3-allyl complex **9**.[18]

Hydrogenations of the anisole complex (**3**) performed in ethanol solvent or with Pd^0/C catalyst (in place of Rh^0/C) were moderately successful but required longer reaction times and afforded lower yields.

The hydrogenation of coordinated 1,4-dimethoxybenzene parallels that observed for anisole. For the complex $[Os(NH_3)_5(\eta^2\text{-}C_6H_8(OCH_3)_2)](OTf)_2$ (**7**), ^1H NMR data reveal that the metal coordinates the organic ligand at the 2,3 position; the presence of only two arene resonances (5.50, 5.14 ppm) indicates that the complex has mirror symmetry. When a methanol solution of **7** is stirred under 1 atm of hydrogen for 18 h in the presence of Rh^0, a new pentaammineosmium(II) complex (**8**) is formed in which the mirror symmetry of the organic ligand has been conserved. Aliphatic resonances that integrate to two protons each appear at 1.76 and 1.55 ppm. A signal at 4.78 ppm corresponds to the protons geminal to the methoxy groups, and a doublet of doublets at 3.96 ppm is attributed to the coordinated olefin site. On the basis of these data as well as the electrochemical evidence, the organic ligand of **8** is assigned as 3,6-dimethoxycyclohexene (Figure 2). When this experiment is repeated in CD_3OD under D_2, two singlets belonging to ring protons (1.55 and 3.96 ppm) remain in the NMR spectrum.

An NOE experiment was performed so as to establish the stereochemistry of **8**. An acetone-d_6 solution of this material was selectively irradiated at the frequency corresponding to the cis ammines (Figure 5). Although the NOE signals reported are weak, they fully support a model for **8** in which the hydrogens delivered to the coordinated arene are located anti to the osmium metal center.

As with anisole, the hydrogenation of the 1,4-dimethoxybenzene complex, **7**, in the presence of water and acid results in the hydrolysis of the vinyl ether intermediate **10** shown in Figure 2. The 4-methoxy-2-cyclohexen-1-one complex $[Os(NH_3)_5(C_7H_{10}O)](OTf)_2$ was not isolated but was positively identified in solution by cyclic voltammetry and ^1H NMR.[19]

Discussion

A variety of arenes have been investigated as ligands on pentaammineosmium(II),[4] including polycyclic hydrocarbons, me-

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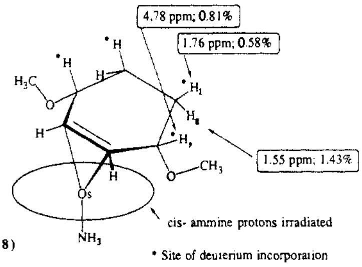
(15) See ref 11 and Experimental Section.

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

(17) Solvent substitution of the ketone-bound cyclohexenone ligand is a competitive process to ketone–olefin isomerization.

(18) Details of this reaction and other pentaammineosmium(IV)–allyl chemistry will be reported separately. ^1H NMR data for $[Os(NH_3)_5(\eta^3\text{-}C_6H_9)](OTf)_3$ (**9**) (acetone-d_6): 6.05 (m, 5 H), 5.68 (t, 1 H), 4.76 (br, 12 H), 2.96 (m 2 H), 2.10 (m, 2 H), 1.60 (m, 1 H), 0.7 (m, 1 H) ppm.

(19) Characteristic peaks for this complex include the olefinic resonances 4.27 (d, 1 H) and 4.75 (d of d, 1 H) ppm, a methoxy resonance at 3.44 ppm, and several aliphatic resonances.



(8)

Figure 5. Stereochemical assignment for the cation $[Os(NH_3)_5(\eta^2\text{-}3,6\text{-dimethoxycyclohexene})][OTf)_2$ as determined by an NOE experiment.

thoxybenzenes, anilines, phenones, diphenylacetylene, and phenol. Of these ligands, we limited our initial study to hydrocarbons (naphthalene and benzene[3]) and methoxybenzenes; the latter were chosen because they form osmium(II) complexes with high barriers to ring tautomerization, have relatively long substitution half-lives, and were judged as inert to competing reactions.

Pentaammineosmium(II) binds naphthalene across C_3 and C_4,[20] an action that results in a *localized* C_1–C_2 double bond. In contrast to the delocalized π system defined by C_5–C_{10}, this bond shows enhanced reactivity toward hydrogenation. True to expectation, the major product in the reduction of the naphthalene complex is a 1,2-dihydronaphthalene species. Parallel to what we reported earlier for benzene,[3] free naphthalene is not hydrogenated under the present reaction conditions.[1]

Both anisole[4] and 1,4-dimethoxybenzene form complexes with pentaammineosmium(II) in which bonding is thermodynamically favored at the *2,3* position (Figure 2). The anisole complex (**3**) differs from the other arene complexes investigated in this study in that it readily tautomerizes to the η^2-*3,4* isomer ($k \approx 1\ s^{-1}$ at 20 °C). With either ligand, however, the only detectable cyclohexane product corresponds to the precursor in which the metal occupies the thermodynamically favored site; as is the case with naphthalene, hydrogenation of these substituted benzene complexes affords regiospecific products.

Isotopic hydrogenation experiments for the complex $[Os(NH_3)_5(\eta^2\text{-}C_6H_6)]^{2+}$ reveal that the hydrogen is delivered S-cis to the benzene in the presence of a heterogeneous catalyst.[3] Analogous experiments reported herein for 1,4-dimethoxybenzene are in agreement with this result; ^{1}H NMR data reveal that the dimethoxycyclohexene product **8**-d_4 maintains mirror symmetry and hence must result from 2 equiv of hydrogen adding to the same side of the ring of **7**. The shifts observed in the NOE experiment (see Figure 5) show that these protons reside anti to the osmium system in the final product. Similar conclusions can be drawn from the crystal structure of the anisole reduction product (**4**): although the lower symmetry of 3-methoxycyclohexene precluded a complete stereochemical assignment, the structural feature that the methoxy group is on the same side of the ring as the osmium is established (Figure 3) so that the hydrogen geminal to the methoxy group points away from the metal center. It remains unclear, however, whether **4** and **8** represent the *immediate* reduction products or products of an isomerization in which the metal inverts across the double bond.[21] The most convincing evidence that this type of isomerization does *not* readily occur is provided from our earlier report of the hydrogenation of the benzene complex:[3] after many hours in solution under conditions similar to those reported here, the deuterated cyclohexene reduction product exists as a single isotopomer (Figure 6). Finally, a crystal structure of the binuclear benzene complex $[\{Os(NH_3)_5\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_6H_6)](OTf)_4$ reveals that both faces of the organic ligand are sterically encumbered by the metallopentaammine fragments; this compound fails to undergo hydrogenation under similar conditions.[3,22] Taken together, we feel that the data presented provide a solid argument that hydrogenation occurs exclusively anti to metal coordination for these complexes.

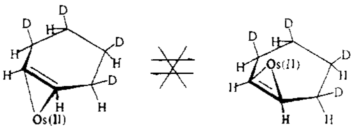


Figure 6. Noninterconverting stereoisomers of the cation $[Os(NH_3)_5(\eta^2\text{-cyclohexene})](OTf)_2$.

Although hydrogenation of the substituted benzene complexes **3** and **7** occurs on one face of the arene, this process is clearly not concerted. Both of these complexes can be semihydrogenated and the resulting vinyl ether intermediates hydrolyzed. Cyclic voltammograms of aliquots removed from hydrogenations of the anisole complex **3** after short reduction times (5–15 min) reveal the presence of a transient species ($E_{1/2} \approx 0.5$ V), which, though never successfully isolated, is thought to be the methoxy diene intermediate (**10**) shown in Figure 2.[23] If our assignment is correct, the diene–monoene reduction of this species occurs at a rate comparable to arene–diene hydrogenation, an observation that is in marked contrast to that reported for uncoordinated arenes.[2]

Optimizing reaction conditions for the hydrolysis of the 2-methoxy-1,3-cyclohexadiene intermediate[24] shown in Figure 2 affords >80% of the cyclohexen-1-one complex, **5**, which is stable to further reduction under the reported conditions. In contrast, a solution of **1** in 1 M HTFA (TFA = trifluoroacetate) shows no detectable hydrolysis after 1 h. If the assumption is made that the methoxy diene intermediate is the direct precursor to **5**, the observations indicate that primary hydrogenation of the anisole complex **3** at the C_4–C_5 π bond occurs at least 4 times faster than at the C_1–C_6 bond of the anisole ligand;[24] the reduction of anisole at the latter position would result in an unconjugated methoxy group resistant to subsequent hydrolysis.

The absence of a ν(C–O) in the IR spectrum of the olefin-bound 2-cyclohexen-1-one (**5**) deserves some comment. As described earlier, **5** can be generated directly from coordination of the organic ligand. In addition, preliminary results indicate that the pentaammineosmium(II) complex of phenol can be hydrogenated to form **5** in high yield. Finally, the one-electron oxidation of an acetone-d_6 solution of **5** liberates 2-cyclohexen-1-one. In view of these facts, it seems unlikely that our assignment of **5** is misguided. Osmium(II) with saturated auxiliary ligands is an exceptionally π-basic metal. Partial occupation of the LUMO for 2-cyclohexen-1-one would result in a reduction of the C–O bond order, an effect that could account for a bathochromic shift of the C–O band to below 1640 cm^{-1} where it would be obscured by N–H deformations.

Conclusion

The present study demonstrates the potential utility of transition metals to activate aromatic systems through η^2 coordination: both regio- and stereoselective partial hydrogenation of bound arenes has been achieved in high yield.

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Supplementary Material Available: A description of the crystal structure data collection and refinement, and tables of crystallographic data, atomic parameters, anisotropic thermal parameters, and complete bond distances and angles for **4** (11 pages); a listing of observed and calculated structure factors for **4** (20 pages). Ordering information is given on any current masthead page.

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(20) Identical with bonding across C_1 and C_2. The "3,4-" representation is chosen to conserve the carbon numbering scheme of the metallodihydronaphthalene precursor.

(21) A strong hydrogen bond between the methoxy oxygen and an ammonia proton in **4** (O–N distance = 2.78 Å) suggests that the structure shown in Figure 3 represents the thermodynamically favored stereoisomer.

(22) Harman, W. D.; Taube, H.; Gebhard, M., submitted for publication.

(23) $E_{1/2}$ = 0.65 V (CH_3CN/TBAH, NHE) recorded for the pentaammineosmium(II) complex of cyclohexadiene.

(24) The carbon numbering scheme for all organic ligands is identical with the IUPAC convention for the uncoordinated molecule.