

Allyl Complexes of Pentaammineosmium

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Treatment of $[\text{Os}(\text{NH}_3)_5(\text{C}_3\text{H}_5)_2\text{O}](\text{OTf})_2$ in methanol with triflic acid produces $[\text{Os}(\text{NH}_3)_5(\eta^3\text{-C}_3\text{H}_5)](\text{OTf})_3$ in good yield. The cation in solution was characterized by ^1H NMR spectroscopy. In cyclic voltammetry, no redox activity is revealed within the solvent window, +1.5 to -1.5 V vs NHE. The complex readily undergoes addition at a terminal carbon by a variety of neutral and negatively charged nucleophiles. Complexes of cyclic allyls are generated when either the complex of anisole or of 1,4-dimethoxybenzene is hydrogenated in acidic methanol. As is true of the benzene analogue, hydrogenation does not proceed beyond two molecules of H_2 /molecule of ligand. In the reduction of the complex of 1,4-dimethoxybenzene, elimination of methanol leads to the η^2 -benzene complex as the reaction product. A proton is eliminated from $[\text{Os}(\text{NH}_3)_5(\eta^3\text{-C}_6\text{H}_9)]^{3+}$, yielding $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-1,3-cyclohexadiene})]^{2+}$, and the reaction is governed by an equilibrium quotient of 0.3 M in methanol. This equilibrium quotient, together with that for the addition of CH_3O^- to coordinated allyl, leads to an estimate of 2×10^{15} for the equilibrium quotient for elimination of CH_3OH from $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-3-methoxycyclohexene})]^{2+}$, to be compared to ca. 0.1 for the free organic ligand. The comparison shows that the affinity of $[\text{Os}(\text{NH}_3)_5]^{2+}$ for the carbon/carbon double bond in a conjugated diene is very much greater than for the carbon/carbon double bond of 3-methoxycyclohexene.

In the course of investigating the regiochemistry of the hydrogenation of η^2 -coordinated arenes,¹ we observed that reduction of the anisole complex of pentaammineosmium(II) in strongly acidic CH_3OH leads to the formation of the osmium(IV) cycloallyl complex² $[\text{Os}(\text{NH}_3)_5(\eta^3\text{-C}_6\text{H}_9)]^{3+}$, in high yield. This has motivated the work reported in this paper, undertaken to extend the descriptive chemistry of the allyl complexes of the pentaammineosmium moiety. Apart from that already noted, there is not literature precedent for these compositions. An allyl complex is encountered in the hydrogenation of the 1,4-dimethoxybenzene complex of $[\text{Os}(\text{NH}_3)_5]^{2+}$, as well as in the example already cited. To facilitate the interpretation of the rather complex chemistry encountered with the cyclic ligands, we undertook the investigation also of a complex of simpler composition, namely of $[\text{Os}(\text{NH}_3)_5(\eta^3\text{-C}_3\text{H}_5)]^{2+}$.

Experimental Section

Reagents. $\text{Os}(\text{NH}_3)_5(\text{OTf})_3$ was synthesized as described by Lay et al.³ Acetone was purified by vacuum distillation over B_2O_3 ,⁴ dimethoxyethane (DME) by distillation over Na, and CH_3OH by distillation over $\text{Mg}(\text{OCH}_3)_2$ (prepared in situ from Mg and I_2 under argon).⁵ Anhydrous ether and dichloromethane were purchased from Aldrich (Sure/Seal bottles) and used without further purification. Granular Zn/Hg amalgam was prepared from 30-mesh granular Zn that was washed with 3 M HCl(aq) and then treated with a saturated HgCl_2 (aq) solution for 20 min. $\text{Na}(\text{HC}(\text{COOCH}_3)_2)$ was synthesized from dimethyl malonate and NaOCH_3 in methanol. The addition of ether resulted in a precipitation of the final product. Solvents were deoxygenated by purging with argon, and reactions were carried out under an argon atmosphere in a Vacuum Atmospheres Corp. glovebox.

Osmium Compounds. The preparations of $[\text{Os}(\text{NH}_3)_5(2,3\text{-}\eta^2\text{-anisole})](\text{OTf})_2$ (1), $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-3-methoxycyclohexene})](\text{OTf})_2$ (2), $[\text{Os}(\text{NH}_3)_5(2,3\text{-}\eta^2\text{-1,4-dimethoxybenzene})](\text{OTf})_2$ (3), $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-3,6-dimethoxycyclohexene})](\text{OTf})_2$ (4), and $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-C}_6\text{H}_6)](\text{OTf})_2$ (5) have been described in refs 6, 1, 1, 1, and 7, respectively.

The pentaammineosmium compounds dealt with in the following have not hitherto been prepared.

$[\text{Os}(\text{NH}_3)_5(\eta^2\text{-C}_3\text{H}_5)_2\text{O}](\text{OTf})_2$ (6). The mixture consisting of 10 mL of methanol, 1.1 g of $[\text{Os}(\text{NH}_3)_5(\text{OTf})](\text{OTf})_2$, 2 mL of allyl ether, and 8 g of zinc amalgam was prepared and was stirred for 5 min to effect the reduction of Os(III) to Os(II). At the end of this time the yellow color of the liquid deepened. The liquid was separated by filtration through a frit of porosity 4-5.5 μm . Ether was added to the liquid, producing a solid that was used without further purification.

^1H NMR (acetone- d_6): δ 5.95 (m, 1 H), 5.19 (t of q, 1 H), 4.72 (b, 3 H, trans- NH_3), 4.58 (dd, 1 H), 4.02 (d of t, 2 H), 3.7 (m, 2 H), 3.70 (b, 12 H, cis- NH_3) (in CD_3CN , the 3.7 signals are resolved, making it possible to assign relative abundance, but other signals are formed to overlap), 3.55 (m, 1 H), 3.45 (t, 1 H), 3.22 (d, 1 H).

$[\text{Os}(\text{NH}_3)_5(\eta^3\text{-C}_3\text{H}_5)](\text{OTf})_3$ (7). To ca. 10 mL of CH_3OH was added 1.1 g of 6 and a solution prepared by mixing 1 mL of HOTf and 1 mL

of CH_3OH (owing to the heat developed the mixing must be done slowly and cautiously). After about 30 min a yellow solid separated. This was redissolved by adding CH_3OH (ca. 8 mL), and after 20 min ether (ca. 100 mL) was added. A yellow solid precipitated, which was collected on a frit and washed with ether. Yield based on 6 was about 91%.

^1H NMR (acetone- d_6): δ 6.23 (b, 3 H, trans- NH_3), 5.60 (d, 2 H, syn, $J_{\text{syn,cent}} = 5.2$ Hz), 5.53 (m, 1 H, cent), 4.90 (b, 12 H, cis- NH_3), 4.66 (d, 2 H, anti, $J_{\text{anti,cent}} = 9.2$ Hz). ^1H NMR (acetonitrile- d_3): 5.3 (b, 3 H, trans- NH_3), 5.20 (d, 2 H, anti, $J_{\text{anti,anti}} = 6.0$ Hz), 5.04 (m, 1 H, cent), 4.28 (d, 2 H, syn, $J_{\text{syn,cent}} = 9.6$ Hz), 4.0 (b, 12 H, cis- NH_3).

Anal. Calcd for $\text{C}_6\text{H}_{20}\text{N}_5\text{OsS}_3\text{F}_9\text{O}_9$: C, 9.44; H, 2.64; N, 9.17. Found: C, 9.79; H, 2.72; N, 8.97.

$[\text{Os}(\text{NH}_3)_5(\eta^2\text{-CH}_2=\text{CH}-\text{CH}_2-\text{CH}(\text{CO}_2\text{CH}_3)_2)](\text{OTf})_2$ (8). A solution containing 0.10 g of 7 in 2 mL of cooled acetone (ca. -30°C) was mixed with one containing 20 mg of sodium dimethyl malonate in 1 mL of acetone. After 2 min ether was added to produce a precipitate. Yield: 40%.

^1H NMR (acetone- d_6): δ 4.74 (b, 3 H, trans- NH_3), 3.70 (6 H, CH_3), 3.62 (t, 1 H, a), 3.60 (12 H, cis- NH_3), ~ 3.4 (m, 1 H, b), 3.21 (d, 1 H, c), 3.18 (d, 1 H, d), 2.28 (m, 1 H, e), 1.60 (m, 1 H, f). ^1H NMR (acetonitrile- d_3): δ 4.03 (b, 3 H, trans- NH_3), 3.71 (s, 3 H, CH_3), 3.70 (s, 3 H, CH_3), 3.60 (dd, 1 H, a), ~ 3.2 (m, 2 H, b, c), 2.99 (d, 1 H, d), 2.93 (b, 12 H, cis- NH_3), 2.12 (ddd, 1 H, e), 1.45 (ddd, 1 H, f). $J_{\text{af}} = 7.2$ Hz, $J_{\text{ad}} = 9.6$ Hz, $J_{\text{ef}} = 13$ Hz, $J_{\text{ae}} = 7.6$ Hz, and $J_{\text{bc}} = 2.0$ Hz.

$[\text{Os}(\text{NH}_3)_5(\eta^2\text{-CH}_2=\text{CH}-\text{CH}_2\text{NC}_5\text{H}_5)](\text{OTf})_3$ (9). Compound 7 (0.10 g) was treated with pyridine (13.5 μL , 10% in excess of Os) dissolved in 2 mL of CH_3CN . After 10 min the solution had changed from light to orange yellow. At this point it was filtered. Ether (ca. 100 mL) was added, which resulted in the formation of an orange-yellow solid. This was collected on a frit and was washed with ether. Yield: 48%.

^1H NMR (acetone- d_6): δ 9.32 (d, 2 H, a), 8.75 (t, 1 H, b), 8.29 (t, 2 H, c), 5.19 (dd, 1 H, d), 4.89 (b, 3 H, trans- NH_3), 4.52 (t, 1 H, e), 4.26 (m, 1 H, f), 4.00 (dd, 1 H, g), 3.86 (b, 12 H, cis- NH_3), 3.45 (d, 1 H, h). $J_{\text{ac}} = 6.8$ Hz, $J_{\text{bc}} = 6.8$ Hz, $J_{\text{ab}} = 1.2$ Hz, $J_{\text{de}} = 13$ Hz, $J_{\text{df}} = 3.2$ Hz, $J_{\text{ef}} = 11$ Hz, $J_{\text{gh}} = 1.2$ Hz, $J_{\text{fg}} = 8.8$ Hz, and $J_{\text{fh}} = 8.0$ Hz. ^1H NMR (acetonitrile- d_3): δ 8.90 (d, 2 H, a), 8.52 (t, 1 H, b), 8.07 (t, 2 H, c), 4.72 (dd, 1 H, d), 4.22 (b, 3 H, trans- NH_3), 4.02 (t, 1 H, e), 3.80 (m, 1 H, f), 3.59 (dd, 1 H, g), 3.20 (d, 1 H, h), 3.17 (b, 12 H, cis- NH_3). $J_{\text{ac}} = 7.2$ Hz, $J_{\text{bc}} = 7.2$ Hz, $J_{\text{ab}} = 1.2$ Hz, $J_{\text{de}} = 13$ Hz, $J_{\text{df}} = 2.8$ Hz, $J_{\text{ef}} = 12$ Hz, $J_{\text{gh}} = 1.4$ Hz, $J_{\text{fg}} = 8.8$ Hz, and $J_{\text{fh}} = 8.8$ Hz.

Anal. Calcd for $\text{C}_{11}\text{H}_{25}\text{N}_6\text{OsS}_3\text{F}_9\text{O}_9$: C, 15.68; H, 2.99; N, 9.47. Found: C, 15.15; H, 2.87; N, 9.65.

$[\text{Os}(\text{NH}_3)_5(\eta^2\text{-CH}_2=\text{CH}-\text{CH}_2\text{OCH}_3)](\text{OTf})_2$ (10). The reaction solution was prepared by adding 90 mg of 7 and 5 drops of *tert*-butylamine to 2 mL of MeOH. At the end of 20 min ether was added, which resulted in the precipitation of colorless crystals from the liquid, which was pale yellow. Yield: 60%.

- (1) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1990**, *112*, 2682.
- (2) In this paper we follow the convention of assigning to the metal in the $[\text{Os}(\text{NH}_3)_5(\eta^3\text{-allyl})]^{3+}$ complexes the oxidation state 4+.
- (3) Lay, P.; Magnuson, R. H.; Taube, H. *J. Am. Chem. Soc.* **1982**, *104*, 7658.
- (4) Burfield, D. R.; Smithers, R. H. *J. Org. Chem.* **1978**, *43* (20), 3966.
- (5) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Oxford: England, 1980.
- (6) Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 5725.
- (7) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 1883.

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¹H NMR (acetone-*d*₆): δ 4.71 (b, 3 H, trans-NH₃), 4.56 (m, 1 H), 3.74 (m, 2 H), 3.65 (b, 12 H, cis-NH₃), 3.45 (t, 1 H), 3.32 (s, 3 H), 3.20 (d, 1 H). ¹H NMR (acetonitrile-*d*₃): δ 4.37 (dd, 1 H), 4.03 (b, 3 H, trans-NH₃), 3.54 (m, 1 H), 3.29 (s, 3 H), 3.26 (dd, 1 H), 3.14 (d, 1 H), 3.04 (b, 12 H, cis-NH₃), 2.98 (d, 1 H).

Anal. Calcd for C₆H₂₃N₅OsO₇S₂F₆: C, 11.16; H, 3.59; N, 10.85. Found: C, 11.54; H, 3.54; N, 10.36.

[Os(NH₃)₅(η²-H₂C=CH-CH₂-PPh₃)](OTf)₃ (**11**). The reaction mixture consisted of 2 mL of CH₃CN, 0.12 g of **7**, and 0.40 g of PPh₃. After 3 h, it was filtered and ether (ca. 100 mL) was added to cause precipitation. The solid was collected on a frit and was washed with 50 mL of ether. Yield: 71%.

¹H NMR (acetone-*d*₆): 8.00 (m, 9 H), 7.80 (b, 12 H, cis-NH₃), 4.92 (b, 3 H, trans-NH₃), 4.21 (t of d, 2 H), 3.31 (m, 3 H). ¹H NMR (acetonitrile-*d*₃/acetone-*d*₆ 1:1 v/v): δ 7.93 (m, 9 H), 7.76 (m, 6 H), 4.66 (b, 3 H, trans-NH₃), 3.93 (t, 1 H), 3.67 (m, 1 H), 3.50 (b, 12 H, cis-NH₃), 3.22 (d, 1 H), 3.12 (d, 1 H), 3.05 (q, 1 H).

Anal. Calcd for C₂₄H₃₅N₅OsS₃F₉O₉P: C, 28.1; H, 3.44; N, 6.83. Found: C, 27.58; H, 3.39; N, 6.68.

[Os(NH₃)₅(η²-1,3-cyclohexadiene)](OTf)₂ (**12**). Amalgamated zinc (3 g) was added to a methanol solution that contained [Os(NH₃)₅(OTf)₃] (200 mg, 0.28 mmol) and 0.5 mL of 1,3-cyclohexadiene. After 5 min the solution was filtered through a fine (porosity = 4–5.5 μm) frit and the filtrate was added slowly to ether (ca. 100 mL). The resulting yellow precipitate was collected, washed with ether, and dried under vacuum. Yield: 70%.

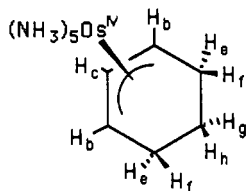
¹H NMR (acetone-*d*₆): 6.32 (m, 1 H), 5.89 (m, 1 H), 4.79 (b, 3 H, trans-NH₃), 4.10 (m, 1 H), 3.82 (m, 1 H), 3.62 (b, 12 H, cis-NH₃), 2.80 (m, 1 H), 2.00 (m, 1 H), 1.87 (m, 1 H), 1.05 (m, 1 H).

[Os(NH₃)₅(η³-C₆H₅)](OTf)₃ (**13**). **Method 1**. A solution comprised of 48 mg of HOTf dissolved in 0.5 mL of CH₃OH was added slowly to another that contained 80 mg of **12** dissolved in 1.5 mL of CH₃OH. After 10 min this solution was added to 40 mL of ether. A fine yellow powder precipitates, which after 30 min was collected by filtration, washed with ether, and then dried under vacuum. **Method 2**. The mixture of HOTf (90 mL) and methanol (200 mL) was added slowly to a solution of 40 mg of **2** dissolved in 1.5 mL of CH₃OH. On cooling of the solution to -27 °C, a fine powder precipitated, which was collected on a fine frit, washed with ether, and dried under vacuum. Yield: 71%.

¹H NMR (acetone-*d*₆): δ 6.05 (b, 3 H, trans-NH₃), 6.05 (m, 2 H, b), 5.68 (t, 1 H, c), 4.76 (b, 12 H, cis-NH₃), 2.96 (m, 2 H, e), 2.10 (m, 2 H, f), 1.60 (m, 1 H, g), 0.7 (m, 1 H, h). NOE (resonance irradiated: 4.76 ppm): H_c, 24%; H_e, 3.8%; H_f, 15%; H_g, 3.5%; H_h, 13%. ¹H NMR (acetonitrile-*d*₃): δ 5.63 (m, 2 H), 5.20 (b, 3 H), 5.17 (t, 1 H), 3.92 (b, 12 H), 2.84 (m, 2 H), 1.69 (2 H), 1.60 (1 H), 0.18 (m, 1 H).

Anal. Calcd for C₁₀H₂₈N₅OsS₃F₉O₁₀: C, 14.37; H, 3.38; N, 8.38. Found: C, 14.08; H, 3.16; N, 8.53.

The proton positions for the above NMR spectral assignments are shown as follows:



Instrumentation. ¹H NMR spectra were obtained on Varian XL-400 (400 MHz) and Gemini (200 MHz) spectrometers. Electrochemical experiments were performed under argon by using a PAR Model 173 potentiostat driven by a PAR Model 175 universal programmer. Cyclic voltammograms were recorded with a Pt⁰ working electrode (1 mm²), a Pt⁰ counter electrode, and a reference that was calibrated with the ferrocene/ferrocenium couple (*E*⁰ = 0.55 V; NHE) in situ. All potentials are reported vs the NHE. The hydrogenation apparatus used consisted of a 15-cm Schlenk tube fitted with a rubber balloon.¹ Microanalyses were performed by Berkeley Microanalytical Laboratory, Berkeley, CA.

Results

Because of the simplicity of composition, the observations made with the three-carbon allyl complex [Os(NH₃)₅(η³-C₃H₅)]³⁺ are dealt with first.

Treatment of the yellow η²-allyl ether compound previously stated (**6**) with a methanol solution of HOTf results in the formation of a lemon yellow solid, the microanalysis of which is consistent with the formula proposed for the three-carbon allyl

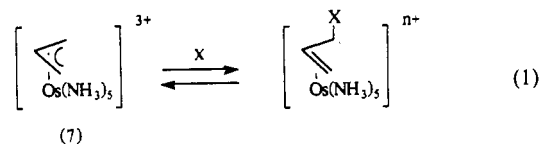
Table I. Reduction Potentials^a of [(NH₃)₅OsL]^{3+/2+}

ligand, L	<i>E</i> _{p.c.} , V	<i>E</i> _{p.a.}	<i>E</i> _{1/2} , V	conditns ^b
C ₃ H ₂ C ₃ H ₅ N	0.89	0.99	0.95	
C ₃ H ₄ P(C ₆ H ₅) ₃	0.83	0.91	0.87	10 mV/s
C ₃ H ₅ OCH ₃	0.64	0.74	0.69	
C ₃ H ₅ CH(COOCH ₃) ₂	0.62	0.73	0.67	
	0.64	0.70	0.67	10 mV/s
C ₆ H ₆	0.62	0.71	0.67	
C ₆ H ₅ OCH ₃	0.60	0.69	0.65	AN-3.0 N TBAH
<i>p</i> -C ₆ H ₄ (OCH ₃) ₂	(-0.15)	(0.50)		
<i>p</i> -C ₆ H ₄ (OCH ₃) ₂	0.65	0.75	0.70	AN-2.0 N TBAH

^aVs NHE as triflate salts. ^bUnless otherwise specified, 1.0 N TBAH in acetonitrile (AN) with scan rate at 100 mV/s.

complex **7**. A ¹H NMR spectrum of **7** in acetonitrile reveals quadrupole-broadened cis- and trans-ammine resonances at 4.00 (12 H) and 5.30 (3 H) ppm, signals, which as a result of the high cationic charge, are slightly downfield of the pentaammine-osmium(II) complexes that have been reported.⁹ In addition, three well-defined resonances occur at 5.20 (2 H, d, *J* = 6.0 Hz), 5.04 (1 H, m), and 4.28 (2 H, d, *J* = 9.6 Hz) ppm. With the exception of the last value these chemical shifts and splitting patterns are consistent with other η³-allyl complexes reported.¹⁰ The signal at 4.28 ppm is somewhat downfield from those reported for anti protons, and we attribute this to the high charge of the osmium. Homonuclear coupling of either the syn (5.20) or anti (4.28 ppm) protons fails to manifest spin saturation exchange, a result which indicates that the rate of isomerization to a hypothetical η¹ intermediate is much less than 1 s⁻¹ at 20 °C. Electrochemical measurements on **7** in CH₃CN reveal no redox activity over the range of -1.5 to +1.5 V.

The reactions of the parent allyl complex **7** with a variety of nucleophiles were explored. In each case nucleophilic attack is observed to occur at a terminal carbon, so that an osmium(II) complex of a terminal olefin substituted at the C₃ position is formed:



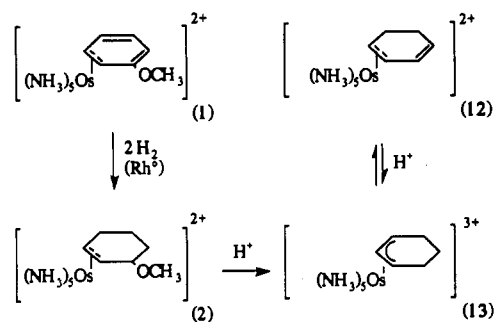
For a reaction mixture that is ca. 50 mM each in osmium and nucleophile, the reaction is complete in a matter of minutes, except for the case of triphenylphosphine where the reaction time is somewhat longer.

The product olefin complexes of the form [Os(NH₃)₅(H₂CCHCH₂X)](OTf)_{*n*}, where when X = -CH(COOCH₃)₂ (**8**), *n* = 2; when X = -NC₅H₅ (**9**), *n* = 3; when X = -OCH₃ (**10**), *n* = 2; and when X = -PPh₃ (**11**), *n* = 3, give ¹H NMR and electrochemical data in good agreement with that of the parent ethylene complex [Os(NH₃)₅(CH₂CH₂)](OTf)₂. NMR spectra in acetone show quadrupole-broadened cis- and trans-ammine resonances over the ranges 3.60–3.86 and 4.71–4.89 ppm, respectively; terminal olefin signals, the assignment of which are confirmed by homonuclear decoupling and chemical shift data, are found from 3.18 to 4.00 ppm. For the ethylene complex, resonances occur in acetone at 3.58 (12 H), 4.78 (3 H), and 3.22 (4 H) ppm.¹¹ The methylene protons are well resolved.

- (9) Ammine resonances compared in acetonitrile and in acetone for a variety of complexes of the type [Os(NH₃)₅(η²-L)](OTf)₂, where L = ketone, arene; also nitrile, pyridinium salts, etc. (a) L = ketone: Harman, W. D.; Fairlie, D. P.; Taube, H. *J. Am. Chem. Soc.* **1986**, *108*, 8223. (b) L = benzene: Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 1883.
- (10) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; p 175.
- (11) (a) Harman, W. D. Ph.D. Thesis, Stanford University, 1987. (b) The term equilibrium *quotient* rather than equilibrium *constant* is used, since the latter should be expressed in terms of activities. The refinements that this would call for were not carried out in this work.

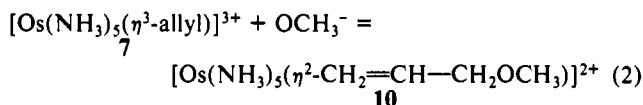
(8) The symbols used to identify the salts are used also for the cations.

Scheme I



Cyclic voltammograms of all the olefin products give reversible couples at 100 mV/s with $E_{1/2}$ values ranging from 0.67 to 0.95 V (Table I). For the couple $[\text{Os}(\text{NH}_3)_5(\text{C}_2\text{H}_4)]^{3+/2+}$, $E_{1/2}$ in DME is measured as 0.40 V; with correction for solvent change applied, this becomes 0.47 V in acetonitrile.^{11a} As is expected, complexes with cationic ligands (formed from pyridine (9) and triphenylphosphine (11)) are the most difficult to oxidize.

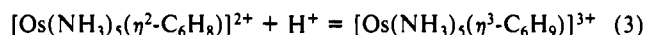
It was of interest, for purpose to be dealt with later, to determine the equilibrium quotient^{11b} K_2 for the reaction



This was done by measuring the relative intensities of the ^1H NMR resonances for the two osmium species as a function of the concentration of OCH_3^- in CD_3OD . A value of $5 \pm 1.5 \text{ M}^{-1}$ (at $20.0 \pm 0.3 \text{ }^\circ\text{C}$) was obtained for K_2 as a result of four experiments with $[\text{OCH}_3^-]$ at 0.0091, 0.12, 0.32, and 0.90 M and total $[\text{Os}(\text{NH}_3)_5] = 0.22 \text{ M}$ (except in the first experiment, in which it was 0.0032 M). The scatter proved to be greater than we can account for, but there is no trend in the values with the concentration of the base. Equilibration appears to be complete by the time the measurements are made, that is, in ca. 15 min.

Hydrogenation of the anisole complex (1) affords¹ the 3-methoxycyclohexene complex (2). When this allylic ether species in methanol is treated with acid, the final concentration being 0.34 M, a yellow crystalline product (13) precipitates from solution. ^1H NMR spectroscopy reveals trans- and cis-ammine resonances at 6.05 and 4.76 ppm, respectively, similar to those found for the parent C_3 allyl species (7) in acetone. Homonuclear decoupling experiments performed on the six ligand resonances lead to a conclusive assignment of 13 as a symmetrical allylic species. As is the case for the other $\text{Os}(\text{IV})$ -allyl complexes dealt with in this paper, species 13 does not show electrochemical activity within the solvent window, -1.5 to $+1.5 \text{ V}$ (NHE). As is the case for allyl complexes of other metal centers,¹² 13 can also be generated by protonation of a 1,3-diene precursor (12) (Scheme I). When a methanol solution of the cyclohexadiene complex $[\text{Os}(\text{NH}_3)_5(\text{C}_6\text{H}_8)](\text{OTf})_2$ (12) is treated with a high concentration of triflic acid ($>0.1 \text{ M}$ in final solution), the allylic species 13 is generated in quantitative yield.

A series of experiments was performed to determine the equilibrium quotient for the reaction



In CD_3OD , at $20 \pm 2 \text{ }^\circ\text{C}$, with $[\text{Os}(\text{II})]$ at 1.4×10^{-2} and $0.99 \times 10^{-2} \text{ M}$ and $[\text{HOTf}]$ at 0.33, 1.1×10^{-1} , and $4.5 \times 10^{-2} \text{ M}$, by comparison of the ^1H NMR absorption intensities, K_3 values of 3.4 and 3.1 M^{-1} , respectively, were determined. At these concentrations of acid, equilibration takes place in a matter of hours.

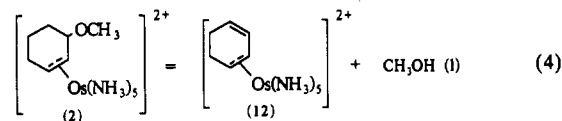
Allyl formation is observed also for the dimethoxycyclohexene analogue (4). Treatment of this material with 1 equiv of acid results in an allyl species (14) analogous to 13. Although this material has not been isolated in pure form, ^1H NMR data on

a solution in acetone- d_6 support its characterization as a salt of $[\text{Os}(\text{NH}_3)_5(\eta^3\text{-C}_6\text{H}_8\text{OCH}_3)]^{3+}$: trans- and cis-ammine resonances at 6.01 and 4.93 ppm are too far downfield for the complex to be a typical pentaammineosmium(II) species. Eight ligand resonances show the asymmetry of the molecule, and a sharp singlet at 3.45 ppm confirms the presence of a single methoxy group.

A 30-mg sample of the triflate salt of 14 was dissolved in 1 mL of CH_3OH containing 8 drops of neat HOTf. After 2 h, the yellow solution had turned orange, and the addition of ether resulted in a fine precipitate. ^1H NMR and cyclovoltammetric data confirm that the solid contains only the salt of the benzene complex 5. When a solution of 14 in acetone- d_6 is allowed to stand overnight, all of the original peaks vanish and new ones grow in corresponding to the formation of C_6H_6 (7.31 ppm) and methanol (3.30 ppm). The benzene complex has been shown in other work^{9b} to dissociate in acetone to yield free benzene.

The observations made on the allyl complex are quite straightforward and in line with those reported for the allyl complexes of other metal centers. Those made with the cyclic ligands have at least this element of novelty: they owe much to the unique capacity that $\text{Os}(\text{NH}_3)_5^{2+}$ displays for robust attachment to arenes, thereby altering the reactivity of the arene. In the work reported in ref 1, it was shown that when H_2O is present in the reaction mixture, hydrogenation of anisole is interrupted after a single molecule of H_2 has added to each molecule of the complex, and the end product is $\text{Os}(\text{NH}_3)_5(2,3\text{-}\eta^2\text{-cyclohexene-1-one})$. When, as in this work, the solvent is neutral and dry, and a second molecule of H_2 adds, this takes place without a change in coordination site.

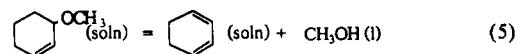
Not common, we believe, is the facile conversion of the allyl to the cyclohexadiene complex by proton loss (reverse of reaction 3). Having determined the equilibrium quotient for this reaction, we became interested in learning the stability of the species 12 in methanol in relation to species 2, as represented by eq 4.



The experiments that led to the determination of the equilibrium quotient for reaction 3 were done in CD_3OD as solvent. The fact that we saw no hint of species 2 in the equilibrium mixture suggested that the equilibrium quotient governing reaction 4 (K_4 is so large as to be beyond the reach of direct determination. We therefore undertook the estimation of K_4 by an indirect route. We assume the equilibrium quotient for reaction 2 (K_2), which we have measured as $5 \pm 1.5 \text{ M}^{-1}$, to be the same as it is for the corresponding reaction of OCH_3^- with the cyclic allylic species, where because of deprotonation, it cannot be measured directly. When this value is multiplied by K_3 and the value of the dissociation constant¹³ for liquid CH_3OH this corresponds (4×10^{-17})—to adding the associated reactions—the reciprocal of K_4 is obtained, and K_4 ($\equiv [\text{12}]/[\text{2}]$) is calculated as 2×10^{15} .

It should be noted that an important contribution to the driving force for reaction 4 is the great affinity of CH_3O^- for H^+ . Were these components, each at standard state concentration, to act as independent reagents, the adduct complex 2 becomes somewhat (by a factor of ca. 5) more stable than the diene complex 12. Thus, it is quite possible that H^+ and PPh_3 , which have a low affinity for each other, will convert the $\text{Os}(\text{II})$ -bound diene to the adduct.

As far as we have been able to ascertain, there is no direct measurement of the corresponding equilibrium quotient for the free ligand (see reaction 5). An estimate was made, by use of

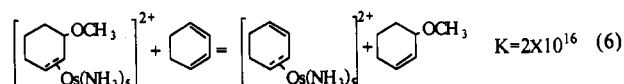


group thermodynamic properties as tabulated by Benson.¹⁴ For

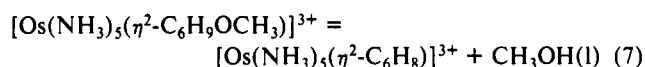
(12) Reference 10, p 181.

(13) King, E. J. *Physical Chemistry of Organic Solvent Systems*; Covington, A. K., Dickinson, T., Eds.; Plenum Press: London and New York, 1973; p 391.

the conversion of 3-methoxycyclohexene to cyclohexadiene and methanol, all species in the gas phase, ΔG° at 20 °C is calculated as 2.1 kcal. We assume that ΔG° for transferring the two cyclic molecules to the liquid phase, CH₃OH, is the same, and then, on inclusion of ΔG° for converting CH₃OH(g) to CH₃OH(l), the equilibrium quotient [cyclohexene]/[3-methoxycyclohexene] for reaction 5 is calculated as 0.1. Even with allowance for an error of 10² in the estimation of K_5 , the comparison of K_4 with K_5 shows a profound effect of Os(NH₃)₅²⁺ in promoting the conversion of 3-methoxycyclohexene to the conjugated diene. Stated in another way, the addition of reaction 4 to the reverse of reaction 5 results in reaction 6 (methanolic solution) governed by an equilibrium



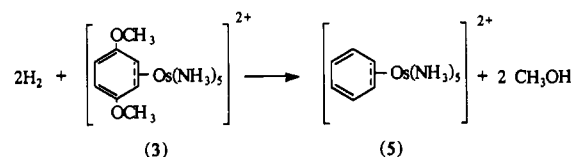
quotient of 2×10^{16} . Thus, we see an enormous increase in the affinity of Os(NH₃)₅²⁺ for the ligand when 3-methoxycyclohexene is converted to cyclohexadiene by elimination of CH₃OH. The effect can in part be attributed to the greater back-bonding interaction with the conjugated diene compared to the lone double bond, combined with a stronger σ interaction for the diene. The equilibrium quotient for reaction 4 when combined with the measured values of $E_{1/2}$ for the Os(III)/Os(II) couples for cyclohexadiene and allyl ether complexes makes possible for calculation of the equilibrium quotient for reaction 7.



Since the potentials for the two couples (Table I) are virtually the same (0.67 and 0.65 V), K_7 is almost the same as K_4 . That K_7 is also very large is at first sight surprising; it is less so when the relative tendencies of the two ligands for σ -bond formation

are compared. A measure of the relative tendency is provided by a comparison¹⁵ of ground-state ionization potentials, which show that the work of removing an electron from butadiene is ca. 22 kcal less than it is for ethylene. An additional factor is the residual tendency of [Os(NH₃)₅]³⁺, as a third-row transition metal, to engage in back-bonding interactions. Qualitative rationalizations of this kind however do not account for the fact that the equilibrium quotients in the two cases are so nearly alike.

Changes in driving force are frequently reflected in rates of reaction, and this is the case in the system under discussion. The coordinated allyl ether in the presence of acid is converted to the allyl-cyclohexadiene equilibrium mixture at room temperature within minutes. The conditions reported¹⁶ for the analogous conversion of the free allyl ether are as follows: solvent, triethylene glycol containing 10% by volume of 85% H₃PO₄; temperature, 150–160 °C; reaction time, 1–2 h. The observations made on the partial hydrogenation of 1,4-dimethoxybenzene shows that coordination of the ligand greatly facilitates the reaction



Hydrogenation under the same conditions, absent η^2 coordination to a metal center, can reasonably be expected to yield either dimethoxy- or dihydroxycyclohexane. While little can be said on the basis of our experience on the relative rates of hydrogenation in the two cases, an effect of the metal ion in redirecting the course of the hydrogenation reaction is revealed.

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Solvent Effects on the Reactivity of Vanadium(II)

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Absorption spectra of V(II), covering a range wide enough to encompass the expected three absorption bands arising from d–d transitions, were registered in nine solvents. The source of V(II) in most cases was V(DME)₂(O₃SCF₃)₂ (DME is 1,2-dimethoxyethane), but in some cases V(II) was generated by reducing V(O₃SCF₃)₃ with Zn/Hg. Only in the case of the weakly nucleophilic solvent CH₂Cl₂ is there evidence that the DME introduced with the solid affects the spectrum. Striking changes are registered in passing from a solvent such as H₂O to solvents, the molecules of which have π -acid character. In the case of acetone, pyridine, and acetonitrile, strong MLCT absorption sets in, accompanied by hypochromic shifts of those d–d transitions that are not obscured by the charge-transfer bands. Thus the long-wavelength bands ν_1 , which measured 10Dq, for H₂O, acetone, CH₃CN, and pyridine appear at 843, 820, 614, and 490 nm respectively. There are, as well, marked increases in the intensities of the d–d absorptions for the last three solvents, compared to that for H₂O. The reactivity of V(II) to epoxides and to O₂ is a sensitive function of the nature of the solvent. In some solvents, with either kind of oxidant, [VOV]⁴⁺ is the first observable vanadium-containing product. In certain solvents, on continued oxygenation, VO²⁺ is formed, and there is evidence that V(V) can also be produced. In the case of epoxides, the gross features of the differences in rate can be understood in terms of the accessibility of a normal coordination position on V(II) to the epoxides. When O₂ reacts, substitution in a normal coordination site is not necessarily a prerequisite to reaction.

Introduction

Oxygen atom transfer reactions involving transition-metal centers are important in industrial and biological chemistry. Current concern^{1,2} at a basic level with the nature of such processes

is leading to an improved understanding of how the properties of the metal center and of the auxiliary ligand environment affect the reactivity of the metal–oxo bond.

Until recently oxygen atom transfer from metal to substrate has received most of the attention, perhaps in part because of the

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