of **3** (2.05 g; 3.87 mmol) in dry THF (75 mL) was added dropwise to a solution of $Me_3SiOReO_3$ (1.25 g; 3.87 mmol) also in the same solvent (50 mL). The mixture was stirred at room temperature for 10 h before the solvent was removed in vacuo to yield a brown crystalline solid. Recrystallization from toluene–CH_2Cl_2 gave pure **4** (yield 2.70 g, 81%; mp 160–162 °C). Anal. Calcd for $C_{32}H_{42}NAsO_4PReSi_2$: C, 45.65; H, 4.92; N, 1.64. Found: C, 45.49; H, 4.91; N, 1.62%. MS (EI, *m/z*) 852 (M^+). MW: calcd, 852.20; found (dibromomethane), 870. IR (Nujol, cm^{-1}): 1260 (s, br), 1225 (s), 1115 (m), 960 (m, br), 895 (s), 780 (m), 750 (m, br), 685 (m), 505 (m). ^{31}P NMR (161.98 MHz in $CDCl_3$, ppm vs 85% H_3PO_4) $\sigma(P)$ 38.98 (s). ^{29}Si NMR (INEPT; 79.5 MHz, in $CDCl_3$, ppm vs Me_4Si): δ 18.17 (s), 8.25 (s). ^1H NMR ($CDCl_3$, ppm): phenyl rings, δ 7.36, 7.55, 7.70 (m, 20 H); $AsCH_2CH_2P$, δ 2.20 (m, 2 H), 2.61 (m, 2 H); $-OSi(CH_3)_3$, δ 0.16 (s, 18 H).

Reaction of 1 with Re_2O_7. A solution of **1** (3.01 g; 6.30 mmol) in dry THF (50 mL) was added dropwise to a suspension of Re_2O_7 (1.55 g; 3.19 mmol) also in THF (75 mL). The mixture when stirred at room temperature for 24 h turned into a clear, dark brown solution. The solution was then concentrated (~50 mL) in vacuo, and an aliquot of this solution was investigated by ^{31}P NMR spectroscopy (161.98 MHz, $CDCl_3$ lock, ppm vs 85% H_3PO_4). **5**: $\sigma(P_A)$ 72.47, $\sigma(P_X)$ 10.20 ($^2J_{P_AP_X}$ = 23.56 Hz). **2**: $\sigma(P^{III})$ 25.40, $\sigma(P^V)$ 36.97 ($^2J_{PP}$ = 13.80 Hz). Ratio of **5**:**2** from the relative integrations: 2:3.

The remainder of the concentrated solution obtained above (consisting of the mixture of **5** and **2**) was treated with a solution of $(Me_3Si)_2O$ (0.58 g; 3.00 mmol) in THF (20 mL) at room temperature. The mixture was stirred for 6 h before the solvent was removed in vacuo to yield a brown crystalline solid. Recrystallization from THF gave pure **2** (yield 74%). The physical constants and the spectroscopic parameters of this product were the same as listed for **2** above.

Synthesis of the Triphenylphosphine Oxide Adduct of 2. A solution of **2** (1.17 g; 1.47 mmol) in dry CH_2Cl_2 (50 mL) was added dropwise to a solution of Ph_3PO (0.41 g; 1.47 mmol) also in CH_2Cl_2 (25 mL). The reaction mixture, which changed its color from dark brown to pale yellow during the course of this addition, was stirred at room temperature for 2 h before the solvent was removed in vacuo to yield a pale yellow solid **10** (yield 1.46 g, 93%; mp 190–192 °C dec). Anal. Calcd for $C_{49}H_{55}NP_3O_5Si_2Re$: C, 54.85; H, 5.13; N, 1.30. Found: C, 54.78; H, 5.09; N, 1.29. ^{31}P NMR (161.98 MHz in $CDCl_3$, ppm vs 85% H_3PO_4): $\sigma(P^V)$ 37.49, $\sigma(P^{III})$ −28.50 ($^2J_{PP}$ = 61.55 Hz); $\sigma(P^V)(Ph_3P(O))$ 35.40. ^1H NMR ($CDCl_3$, ppm): phenyl rings, δ 7.40, 7.62, 7.70 (m, 35 H); PCH_2P, δ 3.80 (dd, 2 H; $^2J_{HP^V}$ = 13.15 Hz; $^2J_{HP^{III}}$ = 1.15 Hz); $OSi(CH_3)_3$, δ 0.12 (s, 18 H).

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Pentaammineruthenium(II), Pentaammineosmium(II), and (*N*-(Hydroxyethyl)ethylenediaminetriacetato)ruthenate(II) Complexes of Styrenes

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$[M(NH_3)_5(styrene)^{2+}]$ and $[M(NH_3)_5(olefin)^{2+}]$ (M = Ru^{II}, Os^{II}) and the related $Ru(hedta)(styrene)^-$ and $Ru(hedta)(olefin)^-$ complexes have been prepared and characterized by ^1H and ^{13}C NMR spectroscopy and by cyclic voltammetry and differential-pulse polarography. Complexes in these series include styrene, 4-vinylbenzoic acid, dimethyl acetylenedicarboxylate (DMAD), 1,3-cyclohexadiene, and 3-cyclohexene-1,1-dimethanol (CHDM). Preferential coordination of the metal centers to the exo vinylic substituent of the styrenes rather than η^2 ring coordination was observed. The chemical shifts and electrochemical behavior were found to be similar to those of linear olefin analogues such as propylene and 1,3-butadiene. ^1H NMR upfield shifts of protons of the coordinated vinylic group of styrene are virtually the same as those of the $M(NH_3)_5(1,3\text{-butadiene})^{2+}$ analogues; the greater effect of Os^{II} vs Ru^{II} is maintained. $E_{1/2}$ values for the styrene complexes were found to be 0.98 V for $(NH_3)_5Ru(styrene)^{2+}$, 0.49 V for $(NH_3)_5Os(styrene)^{2+}$ and 0.64 V for $(hedta)Ru(styrene)^-$ complexes, again similar to those for linear olefin analogues. $E_{1/2}$ values for substituted styrenes with para substituents $-CO_2H$ and $-CO_2^-$ were virtually the same (±0.02 V) as those for the parent styrene complexes. A plot of $\Delta E_{1/2} = (E_{1/2}[Ru(NH_3)_5L] - E_{1/2}[Ru(hedta)L])$ vs the π-acceptor power of L (ESCA scale) was shown to be linear with a slope of 0.325 ± 0.073 V and an intercept of 0.106 ± 0.044 V, including points for L = H_2O, CH_3CN, py, pz, olefins, styrenes, CO, and CH_3pz^+. DMAD was shown to deviate from the line, which is attributed to the π-donor character of the second π lone pair available with acetylenes. The ammine environment is better than $hedta^{3-}$ in stabilizing Ru^{II} complexes with strong π-acceptor ligands. The ^{13}C NMR spectra reveal an opposite influence of the coordination of $Ru(NH_3)_5^{2+}$ and $Os(NH_3)_5^{2+}$ moieties. The aromatic carbon attached to the vinylic substituent shifts downfield 12 ppm for Ru^{II} and upfield 8 ppm for Os^{II}. A greater involvement of the ring carbon in a "allylic-like" coordination to $(NH_3)_5Os^{2+}$ is suggested by this result.

Introduction

We recently have begun a series of studies to examine the coordination chemistry of olefins and acetylenes toward the π-base $(NH_3)_5Ru^{II}$ and $(NH_3)_5Os^{II}$ moieties.[1-3] This work is of general interest as the $(NH_3)_5M^{II}$ chromophore (M^{II} = Ru^{II}, Os^{II}) has been shown to catalyze chemical changes at unsaturated carbon centers such as decarbonylations of aldehydes,[4,8,14] amides,[4] and formic acid.[5] We have examined the coordination of dimethyl acetylenedicarboxylate (DMAD) to $(NH_3)_5Ru^{II}$ by X-ray diffraction and spectral, electrochemical, and surface science techniques.[1,2] These studies have shown that DMAD is about 83% as good a π-acceptor ligand as CO toward $(NH_3)_5Ru^{II}$ and that the acetylenes and olefins are better π-acceptors than the N-heterocyclic pyridines and pyrazines.[2] The latter N-bases have been extensively studied in their complexes of $(NH_3)_5Ru^{II}$ and $(NH_3)_5Os^{II}$, largely because the N-heterocyclic complexes of these metal centers exhibit convenient MLCT transitions in the visible

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region.[6] The observation that olefins and acetylenes are intermediate between CO and the N-heterocycles in forming π-back-bonds with these ligands prompted our recent study of the coordination of olefins and linear dienes to $(NH_3)_5Ru^{II}$ and $(NH_3)_5Os^{II}$.[3] The $(NH_3)_5M^{II}(1,3\text{-butadiene})^{2+}$ ($M^{II} = Ru^{II}, Os^{II}$) complexes proved to be particularly interesting. These complexes exhibit significant 1–2 ppm upfield shifts of ^1H resonances and 40–80 ppm upfield shifts of ^{13}C resonances for the coordinated olefinic unit. The pendant olefin moiety was much less perturbed except for the proton on the third carbon of the 1,3-butadiene chain. This position was also shifted upfield, but at ca. 40% percent of the influence received for protons of the coordinated olefin. These results suggest that the π-back-bonding from Ru^{II} or Os^{II} extends beyond the intimate coordination position through the $2\pi^*_u$ molecular orbital of 1,3-butadiene.[3] This prompted an interest as to whether such an influence is general, as in the styrene system.

Styrene complexes of $(NH_3)_5Ru^{II}$ and $(NH_3)_5Os^{II}$ have now been prepared and examined by NMR and electrochemical techniques. This is the primary subject of this report. Of related interest to our studies are those reported by Harman and Taube concerning the coordination of benzene and 3,4,5,6-tetramethylbenzene (TMB) to $(NH_3)_5Os^{II}$.[7,8] More recently these workers have prepared η^2,η^2-heterobinuclear ions of $(NH_3)_5Ru^{2+}$ and $(NH_3)_5Os^{2+}$ bridged by benzene and naphthalene.[31,32] These complexes have been found to have benzene, naphthalene, and TMB coordinated in an η^2 manner.[7,8,31,32] The $(NH_3)_5Os(TMB)^{2+}$ complex is particularly useful to synthesize other π-acceptor complexes of $(NH_3)_5Os^{II}$ by displacement of TMB in the absence of water.[7] We have recently shown that $(NH_3)_5Ru^{2+}$, $(NH_3)_5Os^{2+}$, and $Ru^{II}(hedta)^-$ will coordinate in the η^2 mode with 1,3-dimethyluracil[34] and pyrimidine nucleosides[35] with disruption of the aromaticity of the heterocyclic ring. In the styrene complexes of this present report the $Ru^{II}(NH_3)_5^{2+}$, $Os^{II}(NH_3)_5^{2+}$, and $Ru^{II}(hedta)^-$ centers have a choice between coordination at the vinylic region or η^2 on the benzene ring. The results show preferential attachment to the olefin substituent. However ^{13}C data implicate a greater interaction between the Os^{II} center and the carbon of the benzene ring that carries the vinyl substituent than is observed for the Ru^{II} analogue.

Experimental Section

Preparation of Complexes. Styrene (Aldrich) was distilled under reduced pressure immediately prior to use. *cis*-Stilbene, 4-vinylpyridine, 4-vinylbenzoic acid, dimethyl acetylenedicarboxylate (DMAD), and 3-cyclohexene-1,1-dimethanol (CHDM) (Aldrich) were used without further purification.

$[Ru(NH_3)_5Cl]Cl_2$ was prepared from $[Ru(NH_3)_6]Cl_3$ (Strem) according to the method of Creutz and Taube.[8,10]

$[Os(NH_3)_5N_2]Cl_2$ was prepared from $(NH_4)_2[OsCl_6]$ (Strem) according to literature methods and stored in vacuo.[11]

$[Os(NH_3)_5(tfms)](tfms)_2$ was prepared from $[Os(NH_3)_5N_2]Cl_2$ according to literature methods and stored over $CaCl_2$ at ambient temperature and pressure.[12]

$[Ru(ND_3)_5(styrene)]^{2+}$ was prepared by reaction of $[Ru(NH_3)_5Cl]Cl_2$ in D_2O with Zn/Hg present as the reducing agent under an inert atmosphere of argon.[3] In a typical experiment, ca. 8 mg of $[Ru(NH_3)_5Cl]Cl_2$ was added to 1.50 mL of D_2O. The sample was purged with Ar for 30 min, with Zn/Hg present. Approximately 0.25 mL of the appropriate olefin was added. The solution was further purged slowly with Ar for 30 min. The vessel was sealed and vigorously stirred for 8 h. Excess ligand was removed by an Ar purge at the termination of the reaction.

$[Ru(NH_3)_5(styrene)](PF_6)_2$ was isolated under Ar by Zn/Hg reduction of 0.50 g of $(NH_3)_5RuCl_3$ in 25.0 mL of H_2O in a 50.0-mL round-bottom flask sealed with a rubber septum. The reactant solution was purged with Ar for 1 h by using syringe techniques. Then 1.50 mL of styrene was added with a syringe. The solution was stirred under Ar over the Zn/Hg chips for 14 h. The solution was filtered through a Kimwipe plus in a dropper pipet to remove partiulate Zn/Hg, and the solution was then purged of excess styrene by means of a rigorous Ar stream inside a sealed round-bottom flask. Solid $[(NH_3)_5Ru(styrene)](PF_6)_2$ was precipitated by addition of saturated NH_4PF_6. The crystals appeared yellow-orange when wet and yellow when dry. The elemental analysis was obtained from Galbraith Laboratories as follows (found, calcd): C, 16.3, 16.5; H, 3.99, 3.96; N, 12.2, 12.1; Ru, 15.3, 17.4.

The solid was redissolved in D_2O, and the ^1H NMR spectrum was obtained; this matched the spectrum of $Ru(ND_3)_5(styrene)^{2+}$ prepared in homogeneous solution except for the presence of two additional resonances of the NH_3 ligands in the ratio of 1:4 for trans and cis ammonias (see text).

$[Ru(NH_3)_5(3\text{-cyclohexene-1,1-dimethanol})]$ was prepared by a similar reduction of $[Ru(NH_3)_5Cl]Cl_2$ in Ar purged H_2O over Zn/Hg. Appropriate weights of Ru^{II} salt and 3-cyclohexene-1,1-dimethanol were dissolved to prepare a 2.7×10^{-3} M Ru^{II} solution with a ligand:Ru^{II} ratio of 1.6. The solution was maintained under constant Ar bubbling over Zn/Hg and protected from room light with Al foil. After 4.0 h, the cyclic voltammogram and differential-pulse voltammograms were obtained at pH = 3.91, which revealed 46% of the $(NH_3)_5RuOH_2^{2+}$ complex ($E_{1/2} \simeq 0.04$ V) and 54% of $(NH_3)_5Ru(CHDM)^{2+}$ ($E_{1/2} \simeq 0.84$v). After 15 h, the sample showed evidence for the formation of $(NH_3)_4Ru(OH_2)_2^{2+}$ with loss of NH_3 from $(NH_3)_5RuOH_2^{2+}$ (pH = 7.06) by an increasing amount of a species with a slightly lower $E_{1/2}$ value. The total amount uncomplexed Ru^{II} was reduced to ca. 37% while the olefin complex region accounted for the remaining Ru^{II} (~63%). Evidence for both $(NH_3)_5Ru(CHDM)^{2+}$ and $(NH_3)_4Ru(CHDM)(H_2O)^{2+}$ was observed as a shift in the potential toward lower values (ca. 0.74 V) for the $(NH_3)_4Ru(CHDM)(H_2O)^{2+}$ species.

$[Os(ND_3)_5(styrene)]^{2+}$ was prepared in a manner analogous to that for the Ru^{II} complexes.[3] In a typical experiment, ca. 10 mg of $[Os(NH_3)_5(tfms)](tfms)_2$ was dissolved in 1.00 mL of D_2O. Zn/Hg was employed as the reducing agent. (Gulens et al.[13] and Taube[14] have recognized the instability of the A_5Os^{II} center (A = NH_3) toward oxidation by protic solvents; thus, the Os^{II} complexes in H_2O on D_2O were only generated in the presence of coordinating olefin with excess reducing agent also present (Zn/Hg).) After the initial 45-min Ar purge (with olefin present), the system was sealed for 12 h. Excess ligand was removed by an Ar purge after 12 h.

$[Os(NH_3)_5(styrene)](PF_6)_2$ was prepared by following the same procedure as given for the Ru^{II} analogue except that 0.20 g of $[Os(NH_3)_5(tfms)](tfms)_2$ was used in 1.50 mL of H_2O, flushed over Zn/Hg for 30 min. Reaction time was also 14 h, with stirring, after adding 1.50 mL of styrene into the reaction mixture. NH_4PF_6 was added to precipitate the $[Os(NH_3)_5(styrene)](PF_6)_2$.

The solid was dissolved in D_2O in order to obtain the ^1H NMR spectrum. This spectrum matched the one obtained by synthesis in D_2O, which shows that the NH_3 protons rapidly exchange with D_2O for this Os^{II} complex. Analytical data obtained from Galbraith are as follows (found, calcd): H, 2.8, 3.4; N, 11.5, 10.5; F, 34.1, 34.1. The carbon analysis was not good for the Os^{II} complex; therefore, varification of the substance was made on the basis of the fluorine determination.

$Na[Ru(hedta)(H_2O)]\cdot 4H_2O$ was prepared by modifications of the procedure of Shimizu for the Na[Ru(edta)] salt.[15] The composition of the isolated $Na[Ru(hedta)(H_2O)]\cdot 4H_2O$ solid was determined by titration with 2-methylpyrazine as reported elsewhere.[16] The $Ru^{II}(hedta)(H_2O)^-$ ion was further reduced over Zn/Hg for 3 h to assure the absence of any Ru^{III} complex. The reduced Ru^{II} complex was combined with each of the following ligands and stirred under Ar for the specified reaction times before carrying out analysis of the resultant solutions using cyclic voltammetry and differential-pulse polarography: 1,3-cyclohexadiene (60 h); styrene (24 h); 4-vinylbenzoic acid (20 h); 3-cyclohexene-1,1-dimethanol (4.0 h); dimethyl acetylenedicarboxylate (4.0 h).

Instrumentation. Electrochemical studies were performed on an IBM 225 electrochemical analyzer operating in the cyclic voltammetry and differential-pulse modes. A glassy-carbon working electrode, sodium chloride saturated calomel electrode (SSCE) as reference, and a Pt-wire auxilliary electrode were employed. The electrolyte solution was 0.10 M NaCl; T = 22 °C. Suitable standard one-electron waves were obtained by using $[Ru(NH_3)_6]Cl_3$ for calibration purposes; details have been given elsewhere.[33] An electrochemically reversible wave for $Ru(NH_3)_6^{2+/3+}$ with a cyclic voltammetric peak-to-peak separation of 69 mV and a differential pulse wave of 90 mV at half-height with $E_{1/2} = 0.072$ V was obtained at sweep rates of 50 (CV) and 40 mV/s (DPP). Presence of styrene in the electrochemical cell with $Ru(NH_3)_6^{3+}$ was shown to cause coverage of the glassy-carbon electrode and a reduction of electrochemical current. Purging the cell with Ar for a long period would reverse the coverage of the electrode by removal of styrene from the cell due to its volatility.

^1H and ^{13}C nuclear magnetic resonances were recorded on a Bruker AF300 NMR spectrometer at a magnetic field strength of 70.46 kG. ^1H

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Table I. ^1H NMR Resonances for Styrene and 1,3-Butadiene Complexes of A_5Ru^{2+} and A_5Os^{2+} ($A = NH_3$)[a]

complex	δ, ppm (Δδ,[c] ppm) $H_{a'}$	$H_{b'}$	$H_{c'}$	H_{Ph}
$[A_5Ru(styrene)]^{2+}$	3.53 (1.79)	4.18 (1.69)	4.56 (2.25)	7.23–7.41
$[A_5Os(styrene)]^{2+}$	3.41 (1.91)	4.16 (1.71)	4.43 (2.38)	7.15–7.39
styrene	5.32	5.87	6.81	7.36–7.54
1,3-butadiene	5.16	5.29	6.42	
$[A_5Ru(1,3\text{-butadiene})]^{2+}$ [b]	3.39 (1.77)	3.56 (1.73)	3.98 (2.44)	
$[A_5Os(1,3\text{-butadiene})]^{2+}$ [b]	3.23 (1.93)	3.40 (1.89)	3.81 (2.61)	

[a] All data collected in D_2O at 25 °C with NaTMPS as reference. [b] Reference 3. [c] $\Delta\delta = (\delta_{ligand} - \delta_{complex})$.

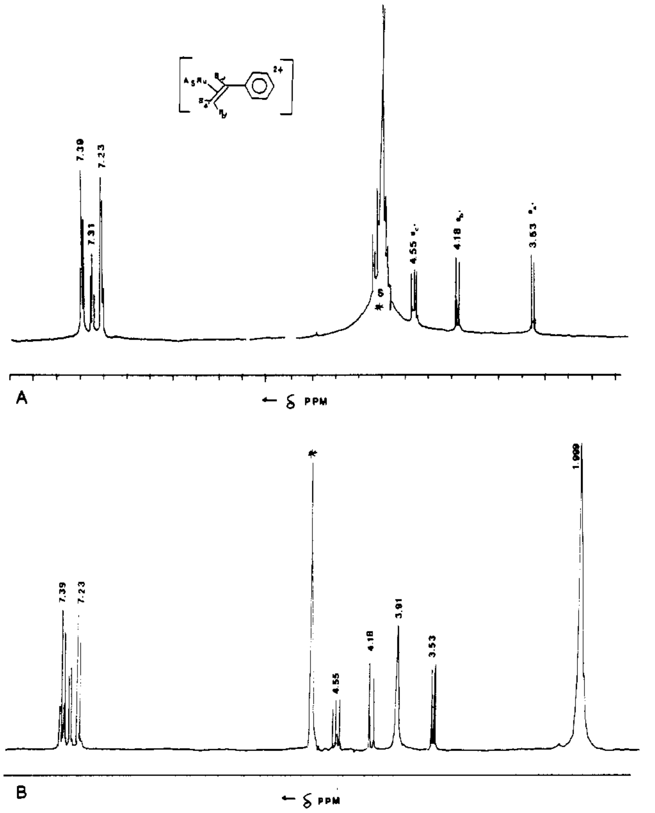


Figure 1. ^1H NMR spectra: (A) $(ND_3)_5Ru(styrene)^{2+}$ in D_2O at 25 °C (* = HOD resonance); (B) $(NH_3)_5Ru(styrene)^{2+}$ analogue.

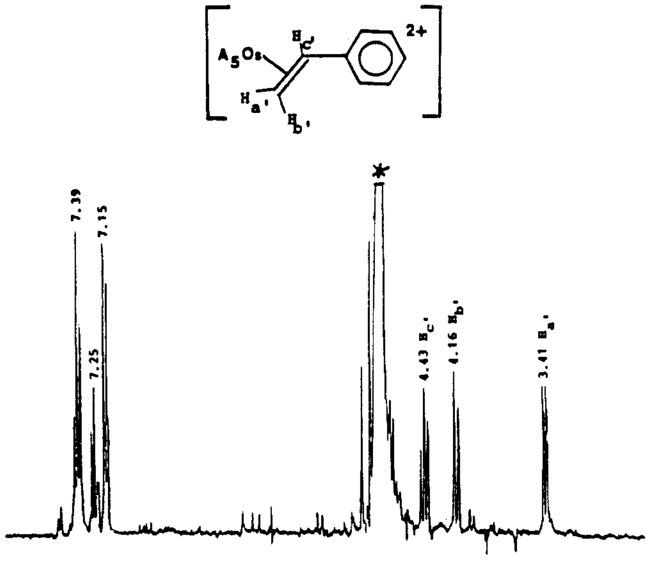


Figure 2. ^1H NMR spectrum of $(ND_3)_5Os(styrene)^{2+}$ in D_2O at 25 °C. * = HOD resonance.

NMR spectra employed a radio frequency of 300.13 MHz; ^{13}C NMR spectra employed a radio frequency of 75.46 MHz. All spectra were recorded with D_2O as solvent and NaTMPS as reference (0.00 ppm) for ^1H NMR spectra and *p*-dioxane as reference (66.5 ppm) for ^{13}C NMR spectra. ^{13}C NMR spectra were decoupled by using 1-W broad-band decoupling power.

Table II. ^{13}C NMR Resonances for A_5Ru^{2+} and A_5Os^{2+} Complexes of Styrene

complex	δ,[a] ppm $C_{1'}$	$C_{2'}$	$C_{3'}$
styrene	112.0	135.5	138.0
$(NH_3)_5Ru(styrene)^{2+}$	25.9	81.5	150.3
$(NH_3)_5Os(styrene)^{2+}$	36.6	81.1	129.8

[a] Resonances measured in D_2O at 25 °C with *p*-dioxane as internal reference (66.5 ppm).

Table III. $E_{1/2}$ Values of $(NH_3)_5RuL^{3+/2+}$ and $Ru(hedta)^{0/-}$ Complexes[a]

L	$E_{1/2}$, V $RuA_5L^{3+/2+}$	$Ru(hedta)L^{0/-}$	ref
styrene	0.98	0.64	*a*
4-vinylbenzoic acid	1.01 (pH = 2.20)	0.64 (pH = 2.01)	*a*
4-vinylbenzoate	1.02 (pH = 8.10)	0.62 (pH = 7.14)	*a*
1,3-butadiene	0.94	(0.59)[b]	3, *a*
CHDM	0.84	0.45	*a*
CO	1.40	0.99	20, *a*
DMAD	1.00	0.88	1, *a*
pyrazine	0.490	0.262	21, *a*
pyrimidine	0.40	0.172	22, *a*
pyridine	0.305	0.10[c]	21a, 15c
H_2O	0.051	0.00	21, *a*

[a] This work unless specified. [b] Value for the pentadentate $edta^{4-}$ complex; usually the $E_{1/2}$ values of the $edta^{4-}$ complex is ca. 0.04 V more negative of the corresponding value for the $hedta^{3-}$ complex. [c] Value for the 1,3-cyclohexadiene complex.

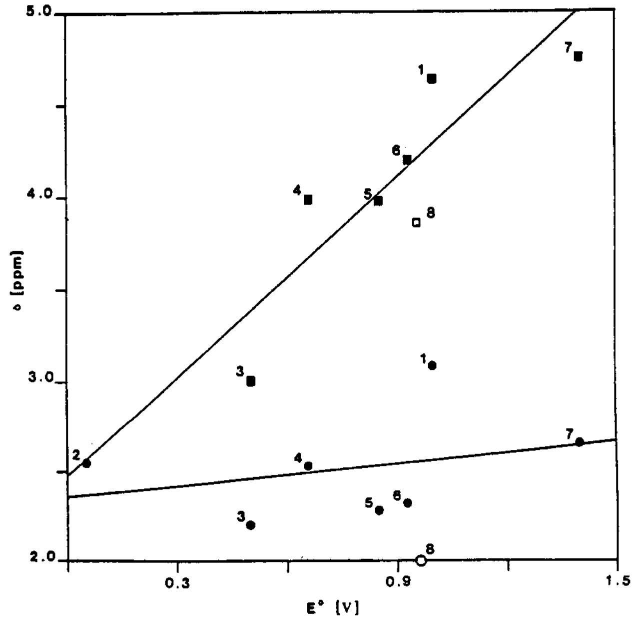


Figure 3. ^1H NMR shifts of cis and trans NH_3 resonances in $(NH_3)_5RuL^{2+}$ complexes: (●) cis; (■) trans. Key: 1, dmad; 2, NH_3; 3, $S(CH_3)_2$; 4, C_2H_2; 5, C_4H_8 (isobutene); 6, C_2H_4; 7, $C_4H_4O_4$ (fumaric acid); 8, C_7H_8 (styrene).

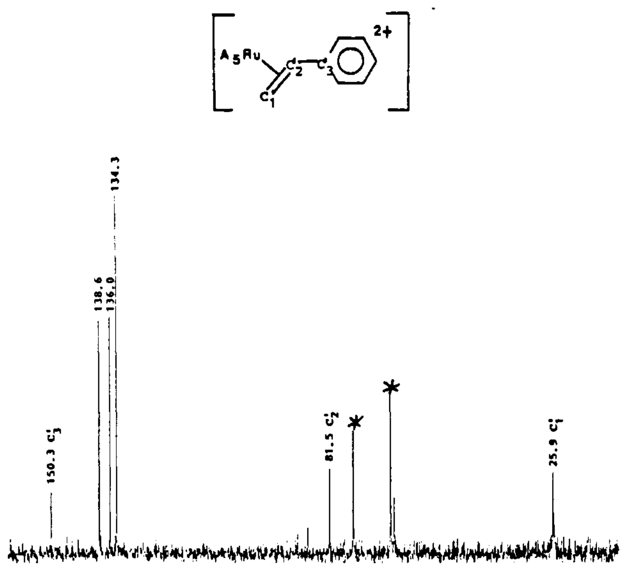


Figure 4. ^{13}C NMR spectrum of $(NH_3)_5Ru(styrene)^{2+}$ in D_2O at 25 °C. * = impurity and *p*-dioxane reference.

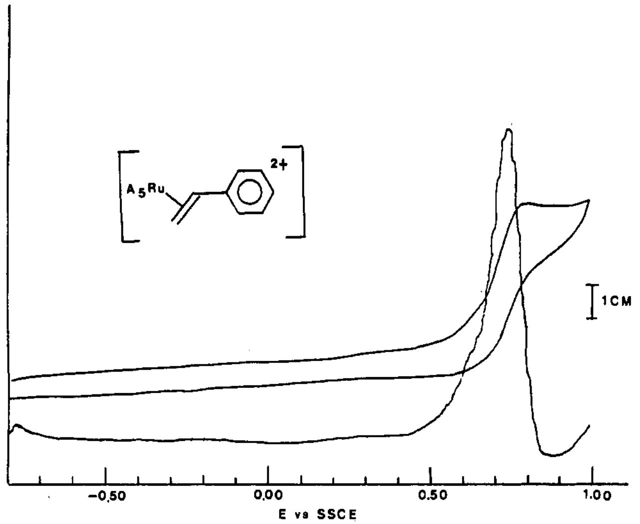


Figure 5. Cyclic voltammogram and differential-pulse polarogram of $(NH_3)_5Ru(styrene)^{2+}$ in 0.10 M NaCl. Conditions: SSCE reference; [complex] = 4.05×10^{-3} M; T = 25 °C; 50 mV/s sweep and current = 10 μA/cm at glassy-carbon working electrode for CV; 40 mV/s sweep and current = 0.10 μA/cm for DPP.

Results

Spectroscopic and electrochemical data obtained in these studies are presented in Tables I–III and Figures 1–9, introduced at the appropriate places in the following section.

Discussion

^1H NMR Spectra of Ru^{II}(styrene) and Os^{II}(styrene) Complexes. Figure 1A shows the ^1H NMR spectrum of $[(ND_3)_5Ru(styrene)]^{2+}$ in D_2O. The $H_{a'}$, $H_{b'}$, and $H_{c'}$ styrene vinylic resonances are assigned on the spectrum. No attempt was made to assign the individual phenyl resonances. Figure 1B shows the ^1H NMR spectrum of the $[(NH_3)_5Ru(styrene)]^{2+}$ cation. The cis ammonias appear at δ 1.99 and the trans NH_3 at δ 3.90. Figure 2 shows the ^1H NMR spectrum of $[A_5Os(styrene)]^{2+}$ in D_2O at 25 °C. As in the other olefin complexes,[3] the resonances for the Os^{II} species are more upfield than those for the Ru^{II} complex. Table I summarizes the ^1H NMR spectral data for styrene, 1,3-butadiene, and their respective $(NH_3)_5Ru^{2+}$ and $(NH_3)_5Os^{2+}$ complexes.

The chemical shifts of the ammonia ^1H resonances in $(NH_3)_5RuL^{2+}$ complexes are known to follow a linear relationship for trans NH_3 with the reduction potential of the $(NH_3)_5RuL^{3+/2+}$ complex.[33] The chemical shift of the cis-NH_3 groups are nearly independent of the nature of L.[33] However, the δ values for the cis-NH_3 groups show rather wide scatter as a function of L. The δ value of the trans-NH_3 group of the $(NH_3)_5Ru(styrene)^{2+}$ complex is 3.90 ppm. This agrees well with the known correlation (Figure 3). The cis-NH_3 ligands are more upfield than with any previously reported olefinic ligand. A reasonable explanation for the styrene influence on the cis-NH_3 groups is that, with rotation of the Ru^{II}–olefinic bond, the aromatic phenyl ring is passed over the NH_3 positions. This gives a ring current for the aromatic ring above the NH_3 hydrogens, which are also averaged by rotations, and the resultant chemical shift is upfield of a saturated substituent's influence such as observed with propylene. The exchange of the coordinated NH_3 hydrogens with D_2O in the solvent is surprisingly slow. After 7 days the signal of the trans NH_3 is completely removed while 17.6% of the cis-NH_3 signal is still observed.

The $(NH_3)_5Os(styrene)^{2+}$ complex, isolated as its PF_6^- salt, rapidly exchanges the NH_3 protons with D_2O. These resonances

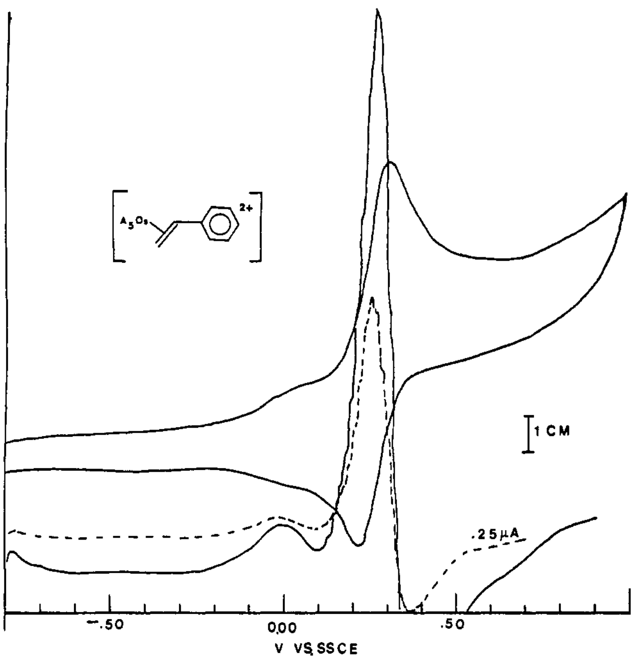


Figure 6. Cyclic voltammogram and differential-pulse polarogram of $(NH_3)_5Os(styrene)^{2+}$ in 0.10 M NaCl. Conditions: T = 25 °C, SSCE reference, [complex] = 4.06×10^{-3} M; 50 mV/s sweep and current = 10 μA/cm for CV; 40 mV/s sweep and current = 0.10 μA/cm for DPP.

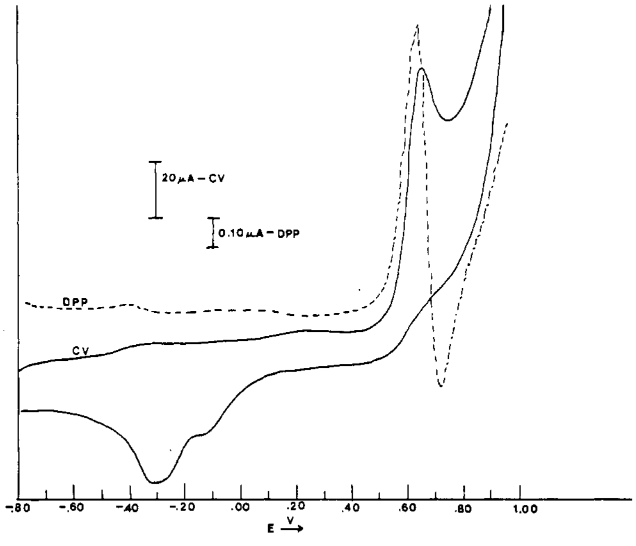


Figure 7. Cyclic voltammogram and differential-pulse polarogram of $Ru(hedta)(DMAD)^-$ after 2.0 h of reaction. Conditions: [complex] = 3.33×10^{-3} M; other settings as in Figure 5; DPP at 40 mV/s, 20-mV step.

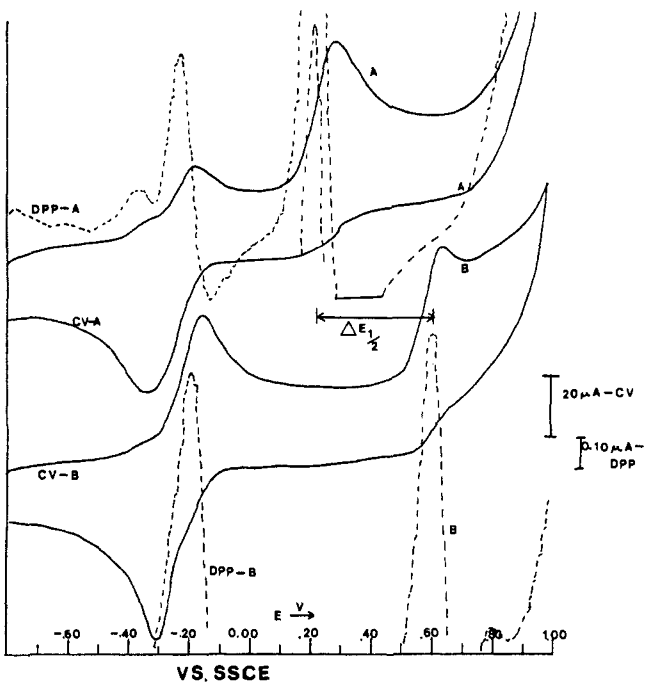


Figure 8. Cyclic voltammograms and differential-pulse polarograms of Ru(hedta)(CHDM)$^-$ and (NH$_3$)Ru(CHDM)$^{2+}$ after 5.0 h of reaction. (A) [Ru(hedta)(CHDM)$^-$] = 3.33 × 10^{-3} M; other settings as in Figure 6. (B) [(NH$_3$)$_5$Ru(CHDM)$^{2+}$] = 2.73 × 10^{-3} M; μ = 0.10 M (NaCl) for each solution.

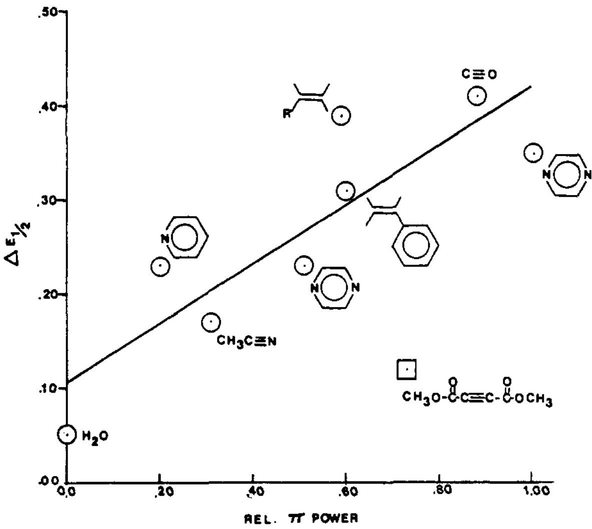


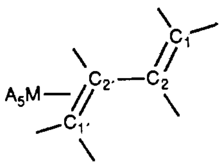
Figure 9. Difference in standard potentials of the (NH$_3$)$_5$RuL$^{3+/2+}$ and (hedta)RuL$^{0/-}$ couples vs π-acceptor power of ligands (L).

were not observed for either A$_5$Os(styrene)$^{2+}$ prepared in D$_2$O or from H$_2$O as a PF$_6^-$ salt.

No evidence is found for η^2-type coordination of the metal center to the phenyl ring of styrene.[4,7,8,31] Coordination at the exo vinyl group of styrene avoids the disruption of the aromaticity of the phenyl ring[31,32] as well as providing a less hindered olefin donor (one substituent instead of two on the aromatic site). The H$_{a'}$, H$_{b'}$, and H$_{c'}$ resonance of the styrene complexes follow the same pattern as for the other olefin complexes.[3] The $\Delta\delta$ values of the same magnitude for the styrene complexes as with the other olefins (cf. Table I). The styrene complexes do not possess an H$_c$ resonance on the ring attachment carbon for comparison with the $\Delta\delta$ value of the equivalent position in 1,3-butadiene.

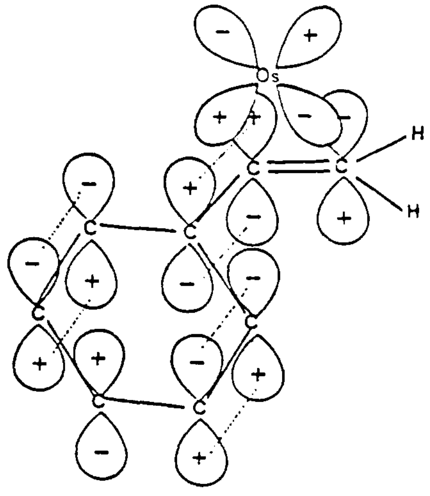
^{13}C NMR Spectra of Ru^{II}(styrene) and Os^{II}(styrene) Complexes. ^{13}C NMR spectra of the A$_5$Ru^{2+} and A$_5$Os^{2+} (A = NH$_3$) ions and their complexes with styrene and 1,3-butadiene were recorded by using D$_2$O as solvent and *p*-dioxane as the internal reference. Figure 4 presents the ^{13}C NMR spectrum of [A$_5$Ru(styrene)]$^{2+}$. Only the C$_{3'}$ resonance was assigned of the four phenyl resonances. As C$_{3'}$ is the only phenyl carbon to be devoid of a proton, it is expected to have the lowest intensity of these resonances. C$_{3'}$ also bears a vinyl substituent, which should make it resonate further downfield than the other phenyl carbons. Table II shows the ^{13}C NMR frequencies for the C$_{1'}$, C$_{2'}$, and C$_{3'}$ carbons of styrene, [A$_5$Os(styrene)]$^{2+}$, and [A$_5$Ru(styrene)]$^{2+}$. The effect of coordination on the olefin is quite dramatic. As seen in the ^{1}H NMR spectra, coordination and the resultant rehybridization produce large upfield shifts in the ^{13}C resonances. For C$_{1'}$, A$_5$Ru^{II} has produced an upfield shift of ~80 ppm. The effect of coordination on C$_{3'}$ is rather unexpected. A$_5$Ru^{II} shifts this resonance downfield by ~12 ppm, while A$_5$Os^{II} shifts this resonance upfield by ~8 ppm. The case of one metal center of the Ru^{II} and Os^{II} pair producing an upfield shift while the other produces a downfield shift has not been observed in the ^{1}H NMR data for other olefin complexes. It is possible that this difference reflects rehybridization effects at C$_{3'}$ upon coordination.

^{13}C results for the A$_5$Ru^{II} and A$_5$Os^{II} complexes of 1,3-butadiene indicate that the carbons directly coordinated to the metal (C$_{1'}$, C$_{2'}$) are shielded upon coordination for either Ru^{II} or Os^{II}:[2]



This is analogous to the results for the styrene complexes. The C$_2$ resonance in 1,3-butadiene is shifted slightly downfield upon coordination, while the C$_1$ resonance is shifted slightly upfield. These shifts observed for C$_1$ and C$_2$ in 1,3-butadiene are most likely due to some rehybridization effects upon coordination.[3] This is the same effect observed for the C$_{3'}$ resonance (like C$_2$ in 1,3-butadiene) in [A$_5$Ru(styrene)]$^{2+}$. The C$_{3'}$ resonance in the [A$_5$Os(styrene)]$^{2+}$ complex has the unusual value. From Table II, it can be seen that the C$_{2'}$ resonances for the A$_5$Ru^{II} and A$_5$Os^{II} complexes are virtually identical. Further, the C$_{1'}$ resonance for the [A$_5$Os(styrene)]$^{2+}$ complex is *downfield* of that for the ruthenium analogue. These results are inconsistent with the ^{1}H NMR results where osmium coordination *always* results in a greater *upfield* shift of the NMR resonances.

It is doubtful that rehybridization effects alone can account for the shift differences between the ^{13}C NMR and ^{1}H NMR spectra. An alternate explanation can be offered that implies some allylic-like bonding in the [A$_5$Os(styrene)]$^{2+}$ complex:



Some overlap between C$_{2'}$, C$_{3'}$, and the dπ orbital of Os(II) would account for the shielding of C$_{3'}$ and also explain the smaller than expected upfield shifts in the C$_{1'}$ and C$_{2'}$ frequencies. The [A$_5$Ru(styrene)]$^{2+}$ complex does not experience this allylic interaction as the dπ orbitals of ruthenium would be smaller than those of osmium. Thus, (NH$_3$)$_5$Ru(styrene)$^{2+}$ exhibits only the π-base effects toward the exo vinyl substituent as observed for the other Ru^{II}–olefin complexes.[3]

The A_5Ru^{2+} and A_5Os^{2+} complexes of 1,3-butadiene do not show any allylic-type interaction as 1,3-butadiene is known to be virtually nonconjugated.[17] This free rotation about the C_2–$C_{2'}$ bond prevents any overlap of the $d\pi$ orbitals of the metal with the C_2 carbon.

Electrochemical Studies of Ru^{II}(styrene) and Os^{II}(styrene) Complexes. Figures 5 and 6 show the cyclic voltammograms of $[A_5Ru(styrene)]^{2+}$ and $[A_5Os(styrene)]^{2+}$, respectively. The ruthenium complex exhibits a quasi-reversible $Ru^{3+/2+}$ redox couple at +0.98 V vs NHE. The osmium complex exhibits reversible redox behavior with an $Os^{3+/2+}$ potential of +0.49 V vs NHE. These values are similar to those for other olefin complexes.[31] For example the $(NH_3)_5Ru(olefin)^{3+/2+}$ half-wave potentials of 1,3-butadiene, 1,4-pentadiene, and ethylene are 0.94, 0.93, and 0.93 V, respectively.[3] The $(NH_3)_5Os(olefin)^{3+/2+}$ waves of propylene, 1,3-butadiene, and ethylene are 0.35,[3] 0.44,[3] and 0.40 V,[7,8] respectively. Unlike Ru^{III}, Os^{III} still exhibits some π-donor character.[18] The more reversible wave for the Os system reflects the increased stability of the Os^{III}–styrene species relative to that of the Ru^{III}–styrene species. A 4.05×10^{-3} M solution of $[(NH_3)_5Ru(styrene)]^{2+}$ and 4.06×10^{-3} M solution of $[(NH_3)_5Os(styrene)]^{2+}$ may be compared in Figures 5 and 6. Both complexes exhibit DPP waves in the oxidation scan at 40 mV/s of identical areas (17.20 cm^2 for Ru^{II} and 17.25 cm^2 for Os^{II}). Both complexes have DPP waves of 90-mV width at half-height for a theoretically quasi-reversible wave. However, the Ru^{II} complex lacks the reduction wave in the CV curve (Figure 5) while the Os^{II} displays this feature. The wave for the Ru^{II} oxidation implies an EC-type complex in which a quasi-reversible electrochemical oxidation is followed by a rapid chemical reaction (aquation) that prevents detection of the reduction cycle of the CV wave. Studies at more rapid scan rates (50 mV/s up to 1400 mV/s) showed that the Os^{II} complex becomes increasingly irreversible at more rapid scanning. The CV peak-to-peak separation increased from 79 mV (a quasi-reversible, 1e wave) at a sweep of 50 mV/s to 195 mV at 300 mV/s and 510 mV at 1400 mV/s. The position of the CV oxidation peak potential shifted 100 mV more positive in comparing 50 vs 500 mV/s sweeps. Similarly, the oxidation peak potential shifts more positive by 90 mV in comparing sweeps at 50 vs 500 mV/s in the CV of the $[(NH_3)_5Ru^{II}(styrene)]^{2+}$ complex, but the reverse reduction wave was not detected at the more rapid sweeps. On the basis of the time to scan between the onset of the oxidation wave and the return to the region anticipated for the reduction peak potential, it is estimated that the aquation rate constant of $[(NH_3)_5Ru^{III}(styrene)]^{3+}$ is much greater than 7 s^{-1}. The identical peak areas for the Ru^{II} and Os^{II} DPP waves, together with nearly reversible one-electron behavior of the Os^{II} complex at a sweep of 40 mV/s, implies that the Ru complexes also carry out one-electron oxidations at the glassy-carbon surface. The DPP peak potential is the best available estimate of the effective $E_{1/2}$ value for the Ru^{II} complex given the nature of the EC steps in the oxidation process.

A pink species is detectable by eye upon oxidation of the Os^{II} styrene complex with chemical oxidants such as H_2O_2. No new $Os^{II/III}$ waves are detected for the solution having the pink complex if the sample is scanned immediately. We infer the pink species is the Os^{III}–styrene derivative. Under similar conditions, the Ru^{III}–olefin complexes rapidly dissociate, and no colored complex is detectable. A diminished amplitude of the reduction wave in the cyclic voltammograms of the Ru olefin complexes and appearance of the aqua complex indicates dissociation of the Ru^{III}–olefin unit.

Coordination of 4-vinylbenzoic acid to A_5Ru^{II} proceeds smoothly at the vinyl olefin system. This complex exhibits an $E_{1/2}$ of +1.01 V vs NHE that is virtually invariant with pH. Apparently, substitution on the phenyl ring is not important to the chemistry at the metal–olefin site. Attempts were made to coordinate the vinyl group of 4-vinylpyridine to the A_5Ru^{II} subunit. Even at low pH, where the pyridine nitrogen is fully protonated, the Ru^{II} center slowly coordinates to the pyridyl nitrogen and not to the vinyl group. The kinetic course of this process may proceed through olefin coordination followed by a rapid linkage isomerism to the pyridine nitrogen. However, no intermediate was detectable by means of electrochemical studies of visible spectroscopy. The $E_{1/2}$ values of olefin vs pyridine bound $(NH_3)_5Ru^{2+}$ are so different, ~0.95 V vs 0.30V, that either species would be readily detected in the presence of a reasonable fraction of the other ($\leqslant$5% by our techniques). The unusually slow substitution rate of typical olefins and styrenes on the $(NH_3)_5Ru^{2+}$ and $(NH_3)_5Os^{2+}$ appears to be related to solvation factors of the olefin moiety compared to more easily solvated entering ligands such as pyridines and other H-bonding ligands (see below).

Differential-pulse studies of $(NH_3)_5Ru(CHDM)^{2+}$ revealed an $E_{1/2}$ value of 0.84 V. This complex is similar to the propylene (0.83 V) and isobutylene (0.85 V) olefin complexes characterized previously.[3] The influence of a saturated substituent on raising the absolute energies of both the π and the complementary π^* molecular orbitals and the influence on the decreasing back-donation and the lowering of the $E_{1/2}$ values for the respective complexes were described elsewhere.[3] The trend is clearly observed for the CHDM ligand.

We examined the rate of addition of CHDM to $(NH_3)_5RuOH_2^{2+}$ by following complexation with time via cyclic voltammetry. In this case, the entering olefin substrate is quite water soluble. Its rate constant for addition is ca. 0.02 M^{-1} s^{-1} at 22 °C. This is lower by a factor of 3.5 compared to 0.07 M^{-1} s^{-1} for a typical neutral ligand such as pyridine.[19] The less soluble styrenes and linear olefins are more likely to have even a greater degree of solvent ordering around them than would the CHDM ligand. The methanolic substituents of CHDM makes a more favorable encounter–complex interaction with $(NH_3)_5MOH_2^{2+}$ (M^{II} = Ru^{II}, Os^{II}) than for the styrenes and linear olefins. Therefore, the rate of addition of CHDM is most probably at the higher limit for the olefins as a group. This explains the relatively long times required for syntheses of the $(NH_3)_5M^{II}(olefin)^{2+}$ or $(NH_3)_5M(styrene)^{2+}$ complexes (see Experimental Section). Displacement of the cage solvent molecules about the olefin region should retard the addition to the five-coordinate $M(NH_3)_5^{2+}$ species. Then the loss of solvent from $M(NH_3)_5^{2+}$ may no longer be rate determining. The slower addition to olefins may then allow for even very low concentrations of the deprotonated pyridine unit to compete effectively with the vinylpyridine case.

Olefin Complexes of $Ru(hedta)^-$. The styrene, 4-vinylbenzoic acid, 1,3-cyclohexadiene, CHDM, and DMAD complexes of $Ru^{II}(hedta)^-$ were prepared as in the Experimental Section. Coordination occurs at the olefin moiety in each case; see Scheme I.

Assignment of coordination at the olefinic site is made on the basis of quasi-reversible cyclic voltammetric waves at 0.64 V for the styrene complex, 0.64 V for the 4-vinylbenzoic acid complex at pH = 2.01 and 0.62 V for the 4-vinylbenzoate complex at pH = 7.14, and 0.59 V for the 1,3-cyclohexadiene complex. Even at reaction times of 24 h for the styrene complex, 20 h for the 4-vinylbenzoic acid complex, and 60 h for the 1,3-cyclohexadiene, a residual amount of the $Ru^{II}(hedta)(H_2O)^-$ complex is detectable by CV or DPP (15%, 22%, 8%, respectively) at ca. 0.00 V vs NHE.

The $Ru(hedta)(DMAD)^-$ complex was nearly fully formed, according to DPP, after 2.0 h of reaction time. The species is an orange complex at pH = 5.42 with an $E_{1/2}$ value of 0.88 V. The cyclic voltammogram shows a poorly reversible wave at 50 mV/s sweep from −0.56 to +1.24 V vs NHE (Figure 7). On the reduction scan, the appearance of the reduction wave of $Ru^{III}(hedta)(H_2O)$ is clearly detected. The voltammogram shows that the $Ru^{III}(hedta)(DMAD)$ complex rapidly aquates after oxidation ($k \simeq 0.35$ s^{-1}).

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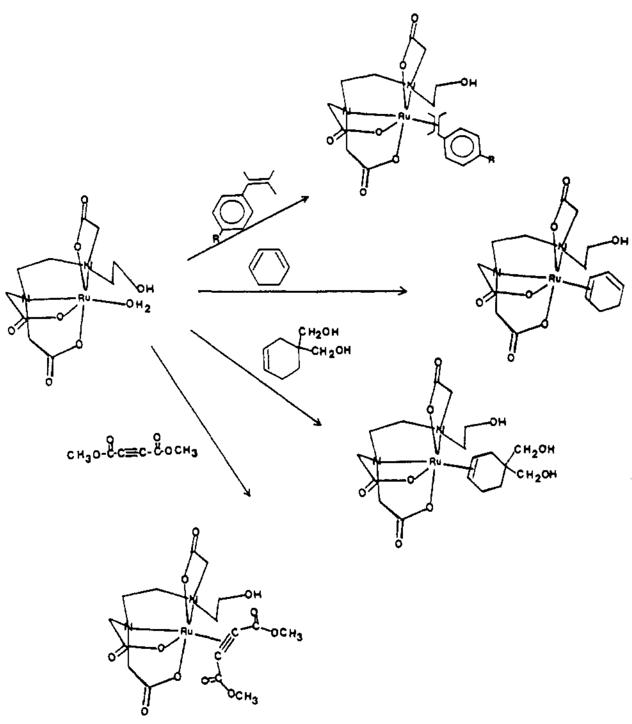
Scheme I



The $Ru^{II}(hedta)(CHDM)^-$ complex appears to be colorless to very pale yellow (similar to the $Ru(hedta)(H_2O)^-$ complex). Its cyclic voltammetric behavior is shown in Figure 8A at 5 h of reaction time. The DDP curve shows 25.8% of the Ru^{II} is present as $Ru(hedta)(CHDM)^-$ complex at 5.0 h, pH = 6.23, $\mu = 0.10$ M (NaCl). The DPP technique allows assignment of $E_{1/2}$ for the $Ru(hedta)(CHDM)^{0/-}$ couple as 0.45 V vs NHE. From the total ligand concentration of 3.91×10^{-3} M and the total $Ru^{II}(hedta)^-$ concentration of 3.33×10^{-3} M, an association constant for $Ru(hedta)(CHDM)^-$ may be calculated as 2.03×10^3 M^{-1} based on the amount of $Ru(hedta)(H_2O)^-$ and $Ru(hedta)(CHDM)^-$ at equilibrium. This value is of particular interest in regards to a similar determination of $(1.96 \pm 0.07) \times 10^3$ M^{-1} for the association constant of the η^2-coordinated 1,3-dimethyluracil complex under identical conditions ($\mu = 0.10$ M (NaCl), $T = 25.0$ °C), which will be described elsewhere.[36] Repetitive sweeps of the cyclic voltammogram at 50 and 200 mV/s showed loss of signal amplitude for $Ru(hedta)(CHDM)^{0/-}$ and growth of the $Ru(hedta)(H_2O)^{0/-}$ wave. Therefore, aquation of the $Ru^{III}(hedta)(CHDM)$ complex also occurs rapidly as for the DMAD analogue. The $Ru(NH_3)_5(CHDM)^{2+}$ complex was prepared; the CV and DPP spectra at 5.0 h of reaction time are shown in Figure 8B for comparison.

A comparison between the $E_{1/2}$ values commonly observed for $Ru(NH_3)_5L^{3+/2+}$ and $Ru(hedta)L^{0/-}$ complexes are shown in Table III. A linear relationship between the $E_{1/2}$ value of the $(NH_3)_5RuL^{3+/2+}$ couple and the π-acceptor ability, calibrated via the energy difference for the C 1s and Ru $3d_{5/2}$ ESCA photoemission lines, has been shown previously.[2] When the difference in half-wave potentials between the $(NH_3)_5RuL^{3+/2+}$ and $Ru(hedta)L^{0/-}$ couples are plotted vs the relative π-acceptor strength[2] calibrated against methylpyrazinium, the data show a linear relationship with a slope of 0.325 ± 0.073 V and an intercept of 0.106 ± 0.044 V (Figure 9). The influence of various factors such as changes in the extent of solvation, ion-pairing, etc. in solution cause deviations from the idealized $\Delta E_{1/2}$ vs relative π-power of as much as 0.06 V for mildly deviant points. However, the DMAD ligand is strikingly off the line while the linear olefins and styrene complexes contribute to the linearity. The lower $E_{1/2}$ value for the $Ru(hedta)L^{0/-}$ complexes compared to the $Ru(NH_3)_5L^{3+/2+}$ analogues is explained by the stabilization of the Ru^{III} complexes by the anionic carboxylate donors of the $hedta^{3-}$ ligand more than the ammonias of the $(NH_3)_5$ ligand set. This is most certainly due to the charge and π-donor character of the carboxylate moiety.

That the $\Delta E_{1/2}$ values increase with the π-acceptor power of the ligand implies that the σ donation from NH_3 is better than that from the carboxylates in the $hedta^{3-}$ environment. Therefore, the Ru^{II} complexes of $hedta^{3-}$ are less able to have the $hedta^{3-}$ ligand compensate for the π-accepting ligands. As a consequence, the Ru^{II} oxidation state is less favored compared to the Ru^{III} state for the $hedta^{3-}$ series compared to the pentaammines. The one ligand that counters this trend is the DMAD ligand. In this case, the orthogonal filled π orbital of DMAD the correct symmetry to π bond to the ruthenium center at the same time the ligand π accepts from the Ru^{II} $d\pi$ orbitals and as the ligand σ donates from the other filled π orbital. The disparity between $(NH_3)_5Ru^{II}$ and $(hedta)Ru^{II}$ donors toward a π-acceptor ligand is thus *self-compensated* for DMAD on binding to the $(hedta)Ru^{II}$ moiety. This leads to a smaller than predicted $\Delta E_{1/2}$ value. Note that the normal olefins and styrene, which do not have a π "lone pair" orthogonal to the bonding region, behave normally in $\Delta E_{1/2}$ vs π-acceptor power. Therefore, we attribute the anamolous behavior of DMAD to its ability to enter into a synergistic π effect with π-donating metal centers, much in the fashion commonly attributed to increased σ donation of olefins, CO, etc. induced by π-back-bonding metal centers. The same π orbital of DMAD can serve as a π donor toward Ru^{III}; the ability of Ru^{III} to accept π density from π-donating ligands has been documented with the π-donating imidazole ligands.[12d,23-28] However, when the π-donated lone pair resides on a heteroatom that has a higher electronegativity than that for the carbons of the acetylenic bond, the degree of π donation is thought to be smaller and to have a less dramatic influence on the standard $Ru^{III/II}$ reduction potentials.[28]

An interesting feature of the styrene and 4-vinylbenzoic acid or 4-vinylbenzoato complexes is that the $E_{1/2}$ value is rather independent of the nature of the substituent of the 4-position of the aromatic ring of the styrene. For example $E_{1/2}$ of the $(NH_3)_5RuL$ complex for styrene differs from that for the 4-vinylbenzoic acid complex by only 0.06 V. The corresponding $Ru(hedta)L$ complexes have the same $E_{1/2}$ value (0.64 V). Furthermore, deprotonation of the para carboxylic acid moiety changes the potential by only 0.01 or 0.02 V. The insensitivity of the $E_{1/2}$ value of the styrene or para-substituted analogues stresses the relatively decoupled olefin moiety from the inductive effects produced by substituents on the aromatic ring.

An opposite effect has been observed in the epoxidation of styrene substrates ($RPhCH{=}CH_2$) by Fe-oxo porphyrins.[29] Variation in the rate of epoxidation with the Hammett σ^+ for various R substituents on the substituted styrene argues for a tunable electron density in the olefin region of the various styrenes. The epoxidations were carried out in methylene chloride while our electrochemical data were obtained in aqueous solution. Solvation may influence the allowable rotational structures and indirectly influence the coupling between the vinylic unit and the aromatic ring. Therefore opposite effects may be observed depending on solvation. Also the Ru-oxo porphyrins epoxidize styrenes with little dependence on the R substituents.[30]

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Summary

The styrene complexes of $M(NH_3)_5^{2+}$ (M^{II} = R^{II}, Os^{II}) and $Ru^{II}(hedta)^-$ have been shown to exhibit the same effects on the ^1H and ^{13}C NMR spectra as their linear olefin counterparts. The magnitudes of the upfield shifts for the protons in the coordinating olefin region are virtually the same for the respective Ru^{II} and Os^{II} complexes. The $E_{1/2}$ values of related members are nearly identical with those of linear olefins and diene cases where conjugation is small. Therefore the exo olefinic region is the preferential site of addition for A_5Ru^{2+}, A_5Os^{2+}, or $Ru^{II}(hedta)^-$; almost no influence on the electrochemical potential is observed by a change in the para substituent of the aromatic ring from –H to –COOH or $-CO_2^-$. This provides additional evidence for insulation of the olefin moiety of styrene from the phenyl ring. The A_5Os^{2+} case does exhibit evidence through its altered ^{13}C NMR spectrum of the carbon attached to the vinylic substituent for a greater interaction with Os^{II} in its $(NH_3)_5Os(styrene)^{2+}$ complex than for $(NH_3)_5Ru(styrene)^{2+}$. This has been tentatively expressed as a "more allylic-like" coordination of A_5Os^{2+} to styrene. The pentaamine environment was shown to be more able to compensate the ruthenium center compared to a polyamino polycarboxylate environment ($hedta^{3-}$) upon demand of a π-acceptor ligand. This is shown by an increase in $\Delta E_{1/2}$ as a function of the relative π-acceptor power of ligands as calibrated by the ESCA studies of Shepherd et al.[2] In this manner linear olefins, cyclic nonconjugated olefins, and styrenes are found to be normal π-acceptors. However acetylenes, with the DMAD complex used as a representative case, show high capacity as a π acceptor, but upon electronic demand, as in the $Ru(hedta)(DMAD)^-$ complex, the same group can synergistically π donate. This makes the $E_{1/2}$ value of $Ru(hedta)(DMAD)^-$ much closer to the $(NH_3)_5Ru(DMAD)^{2+}$ value even though DMAD is a strong π acceptor on the ESCA scale.

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Energy Factors Governing the Partial Irreversibility of Lithium Intercalation in Layered Trichalcogenides MX_3 (M = Ti, Zr, Hf; X = S, Se) and the Structural Changes in the Intercalated Species Li_3MX_3

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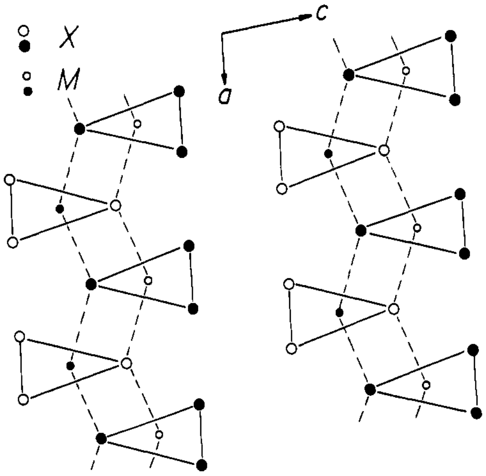
The two-step mechanism proposed to explain the results of electrochemical intercalation of layered trichalcogenides MX_3 (M = Ti, Zr, Hf; X = S, Se) cannot explain the results of chemical intercalation. Thus, we propose a one-step mechanism for chemical intercalation in which each metal of MX_3 is affected by three lithium atoms at a time and analyze the merits of the one- and two-step mechanisms. State correlation diagrams show that the one- and two-step mechanisms are symmetry-allowed and symmetry-forbidden, respectively. This conclusion is supported by tight-binding band electronic structure calculations on the model ZrS_5 chain. The cell parameter changes from *a*, *b*, and *c* in MX_3 to approximately $2a + 1$, *b*, and $c + 0.3$ in Li_3MX_3 are explained by considering how the X–X bond breaking affects the interchain X···X and M···X interactions.

Layered transition-metal trichalcogenides MX_3 (M = Ti, Zr, Hf; X = S, Se)[1] consist of MX_3 slabs held together by van der Waals forces as schematically shown in **1** and **2**. Each MX_3 slab is made up of trigonal-prismatic MX_3 chains in such a way that two rectangular faces of an MX_6 prism are capped by X atoms of neighboring MX_3 chains. As a result, each metal atom M is coordinated to eight X atoms as shown in **3a**. Layered tri-



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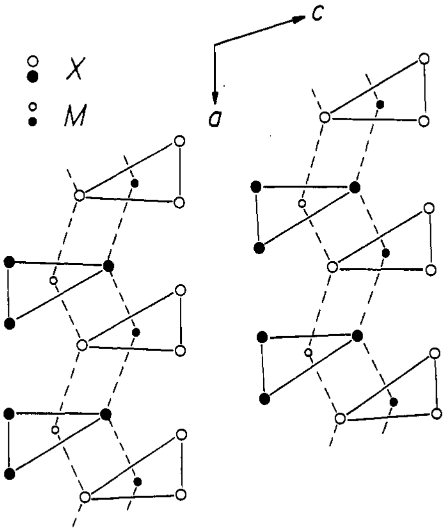

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