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Pentaammineruthenium(II) and Pentaammineosmium(II) Complexes of Olefins and Linear Dienes Related to 1,3-Butadiene

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$[M(NH_3)_5(olefin)]^{2+}$ complexes, M = Ru^{II} and Os^{II}, have been prepared for the olefin series isobutylene, propene, 1,3-butadiene, 1,4-pentadiene, and 1,5-hexadiene. These complexes have been characterized by ^1H NMR spectroscopy and differential-pulse voltammetry. Protons directly attached to the coordinated olefin moiety exhibit upfield ^1H shifts of 1.5–2.5 ppm vs the free ligand for Ru^{II}. The Os^{II} derivatives are shifted an additional 15% upfield. The $E_{1/2}$ values of the Ru$^{III/II}$ complexes are 0.65–0.88 V more positive of the $(NH_3)_5RuOH_2^{3+/2+}$ couple; the Os$^{III/II}$ couples are shifted ca. 1.1 V relative to $(NH_3)_5OsOH_2^{3+/2+}$. Both the upfield ^1H NMR shifts of coordinated olefin protons and $E_{1/2}$ values implicate very strong back-donation from Ru^{II}, and even more for the Os^{II} species, into the π^* ligand orbitals. With the conjugated 1,3-butadiene ligand, the inner hydrogen H_c of the uncoordinated olefinic unit, adjacent to the coordinated olefin, is also shielded by 0.78 ppm for the Ru^{II} complex and 0.98 ppm for the Os^{II} complex. This suggests substantial back-bonding influences are transmitted as much as two or three bonds away from the coordinated olefin. The binuclear 1,3-butadiene-bridged complexes $A_5Ru(1,3\text{-butadiene})RuA_5^{4+}$, $A_5Os(1,3\text{-butadiene})OsA_5^{4+}$, and $A_5Os(1,3\text{-butadiene})RuA_5^{4+}$ (A = NH$_3$ or ND$_3$) have been prepared. The mixed-metal (Os^{II}, Ru^{II}) ions's ^1H shifts are observed upfield of the (Ru^{II}, Ru^{II}) binuclear ion and downfield of the (Os^{II}, Os^{II}) analogue. The ^1H resonance positions in the binuclear ions are further upfield of the related mononuclear $A_5Ru(1,3\text{-butadiene})^{2+}$ and $A_5Os(1,3\text{-butadiene})^{2+}$ complexes. The uncoordinated olefinic unit of the 1,3-butadiene mononuclear complexes remains susceptible to electrophilic addition of Br$_2$ but is inert to H$_2$; the coordinated olefins are inert to both reagents.

Introduction

π-Base behavior of the $(NH_3)_5Ru^{II}$ and $(NH_3)_5Os^{II}$ moieties toward π-acceptor ligands such as pyridines and pyrazines has been extensively studied.[1] Other π-acceptor ligands such as olefins, acetylenes, and CO have been much less studied as π-acids toward $(NH_3)_5Ru^{II}$,[2] yet these molecules are of greater general interest to the subject of catalysis. Ludi et al. have investigated a series of unsaturated hydrocarbons as ligands for $(NH_3)_5Ru^{2+}$ by ^1H NMR and electrochemical methods.[2] The dimethyl acetylenedicarboxylate, dmad, and the CO complexes are among those recently examined by spectral and surface science techniques.[3,4] The ESCA study of a series of $(NH_3)_5RuL^{2+}$ complexes has shown that dmad is about 83% as good of a π-acceptor as CO.[4] This is in keeping with the observation that the $E_{1/2}$ values for the $(NH_3)_5RuL^{3+/2+}$ couples vary from 0.6 to 1.35 V more positive for olefin and acetylene complexes compared to NH$_3$ as the sixth ligand.[2-4] This shows a very strong stabilization of the Ru^{II} center by unsaturated hydrocarbons acting as π-acceptors to an even greater extent than N-heterocycles such as pyridine and pyrazine.[4,5] $(NH_3)_5Ru^{II}$ is well-known to decarbonylate formic acid.[6] The $(NH_3)_5Os^{II}$ chromophore forms π-bonded complexes with acetone[7] and benzene[8] bonded in an η_2 manner. It is capable of decarbonylating aldehydes and amides at or above room temperature.[7] Both species exhibit capacities to catalyze chemical conversions at unsaturated carbon centers. Donation of dπ electron density from Ru^{II} or Os^{II} into π^* orbitals of olefins should increase shielding of olefinic protons. Coordination of olefins should be evidenced by an upfield shift in the ligand ^1H NMR resonances. Olefinic complexes of $(NH_3)_5Ru^{2+}$ do experience a 1–2 ppm upfield shift relative to the free ligand.[2,3] The influence of dπ donation to acetylenes results in a downfield shift of acetylenic protons as the π-system becomes more alkene-like in nature.[3]

The coordination of conjugated olefins to transition-metal centers has been an active area of research.[9] Typically, this type of complex employs a metal in a low oxidation state with strong π-acid ligands also present in the coordination sphere. No report of a 1,3-diene complex with A_5Ru^{II} or A_5Os^{II} has yet been published. These complexes differ from most other olefin complexes in that the ammonia ligands do not compete for π-interactions.

Synthesis of the 1,3-butadiene complexes of A_5Ru^{II} and A_5Os^{II} would be of considerable interest in regard to the study of the activation of olefins by metal centers. Such complexes impact on many areas of coordination chemistry and catalysis of which polymerization, hydroformylation, and hydrogenation are only a few examples.

Coordination of one π-system in a conjugated diene such as butadiene may affect the more remote hydrogens through the π-system in a much more profound way than remote hydrogens are affected in a monoene such as isobutylene. 1,3-Butadiene is a logical choice for 1,3-olefin studies because it is frequently used in many synthetic reactions.

Olefin-bridged binuclear ions related to the Creutz–Taube ion are another class of compounds where dienes may produce some interesting results.[10] Typical bridges between two metal centers in this class of compounds are pyridines, pyrazine,[10] N$_2$,[11] and cyanogen.[12] Diene bridging between metal centers has never been investigated and could lead to a series of binuclear ions where the interaction between metal centers can be weak (class I type ion),[13]

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Table I. ^1H NMR Data for Ruthenium Complexes[a]

complex	δ H_a	H_b	H_c	$H_{a'}$	$H_{b'}$	$H_{c'}$	H_d	$J_{a'c'}$, Hz	$J_{b'c'}$, Hz
$[Ru(ND_3)_5(isobutylene)]^{2+}$				3.14			1.3 (CH_3)		
$[Ru(ND_3)_5(propene)]^{2+}$				3.12 s	3.15 d	3.73 m	1.40 d (CH_3)	0	5.22
$[Ru(ND_3)_5(1,3\text{-butadiene})]^{2+}$	5.19 d	5.35 d	5.58 m	3.39 d	3.56 d	3.98 m		8.22	11.73
$[Ru(ND_3)_5(1,4\text{-pentadiene})]^{2+}$	5.09 d	5.22 d	6.12 m	3.18 d	3.22 d	3.68 m	2.48 m, 1.91 m	2.31	0
$[Ru(ND_3)_5(1,4\text{-hexadiene})]^{2+}$	5.50 d	5.12 d	6.00 m	3.20 m	3.20 m	3.73 m	2.40, 1.86, 1.09[b] 2.17, 2.08, 1.41[c]		

[a] All data collected with D_2O as solvent at 25.0 °C. H_a, H_b, H_c, $H_{a'}$, $H_{b'}$, $H_{c'}$, and H_d are assigned according to Chart I. [b] Major component, 63%; splittings are complicated but suggest overlapped triplets. [c] Minor component, 37%.

or stronger (class II type ion),[14] or even fully delocalized (class III),[8] based on the overlap between π-systems in the derivatized diene. The series of complexes of A_5Ru^{II}–L, where L = 1,3-butadiene, 1,4-pentadiene, and 1,5-hexadiene, have been synthesized and characterized in this report. Addition of an equivalent amount of A_5Ru^{II}–OH_2 or A_5Os^{II}–OH_2 to these complexes has yielded the binuclear diene-bridged ions of the general type $[A_5M^{II}\text{–diene–}M'^{II}A_5]^{4+}$, where M, M′ = Ru, Os.

The nonconjugated diene complexes (L = 1,4-pentadiene, 1,5-hexadiene) have been prepared to see how the remote π-system is affected when not in direct communication, i.e. conjugation, with the coordinated π-system.

NMR spectroscopy is the chief means of identifying and categorizing these olefin/diene complexes of A_5Ru^{II}/A_5Os^{II}. Because UV–visible spectrophotometry has proven ineffectual as a probe of π-acceptor ability in unsaturated hydrocarbons,[2] electrochemical means have been employed to evaluate the relative π-acceptor ability of the various olefins/dienes as evidenced by the magnitude of the shift in the $E_{1/2}$ of the $A_5Ru^{3+/2+}$ or $A_5Os^{3+/2+}$ couple.

Experimental Section

Preparation of Complexes. $Ru(NH_3)_5OH_2^{2+}$ was prepared from $[Ru(NH_3)_5Cl]Cl_2$ by reduction over Zn/Hg under an argon atmosphere according to the method of Creutz and Taube.[10] $Ru(ND_3)_5OD_2^{2+}$ was prepared by the reduction of $[Ru(NH_3)_5Cl]Cl_2$ with Zn/Hg under an argon atmosphere with D_2O as solvent. These reagents were used immediately as described below to prepare other derivatives.

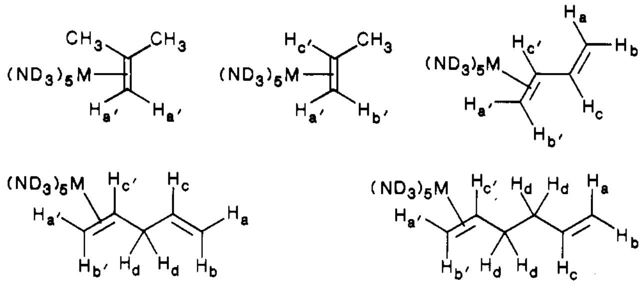
$[Ru(NH_3)_5(olefin)]Cl_2$ and $[Ru(ND_3)_5(olefin)]Cl_2$ were prepared by reaction of the olefin with $Ru(NH_3)_5OH_2^{2+}$ or $Ru(ND_3)_5OD_2^{2+}$ in H_2O or D_2O, respectively, with Zn/Hg present as a reducing agent, under an inert atmosphere of Ar. In a typical experiment ca. 8 mg of $[Ru(NH_3)_5Cl]Cl_2$ was added to 1.50 mL of either D_2O or H_2O. The sample was purged with Ar continuously to provide stirring over the Zn/Hg chips. After 30 min was allowed for reduction, the desired olefin was vigorously bubbled through the solution for 30 min; the system was then sealed for 8 h to allow for complete reaction. In the cases of 1,5-hexadiene and 1,4-pentadiene, which are liquids, 0.75 mL of the olefin was added to the 1.50-mL Ru^{II} solution under Ar and mixed vigorously for 8 h in a sealed 10-mL pear-shaped flask. Excess ligand was then removed by a vigorous Ar purge. The resulting complexes could be handled without rigorous protection from air.

$[(Ru(NH_3)_5)_2(1,3\text{-butadiene})]^{4+}$ and its deuteriated analogue were prepared by the reaction of $[Ru(NH_3)_5(butadiene)]^{2+}$ or $[Ru(ND_3)_5(butadiene)]^{2+}$ (1×10^{-2} M) with 1 equiv of $[Ru(NH_3)_5Cl]Cl_2$ under an inert atmosphere of Ar with Zn/Hg present. Reaction time was typically 12 h.

$[Os(NH_3)_5tfms](tfms)_2$ was prepared according to the method of Taube et al.[13] and stored over $CaCl_2$ at ambient temperature and pressure ($tfms^- = CF_3SO_3^-$).

$[Os(NH_3)_5OH_2]^{2+}$ and $[Os(ND_3)_5OD_2]^{2+}$ were prepared in the same manner as their Ru analogues by using $[Os(NH_3)_5tfms](tfms)_2$ as starting material. The presence of Zn/Hg and the olefin ligand is essential for formation of the desired $(NH_3)_5OsL^{2+}$ derivatives as described below.[19d]

Chart I. M = Ru^{II}, Os^{II}



$[Os(NH_3)_5(olefin)]^{2+}$ and $[Os(ND_3)_5(olefin)]^{2+}$ were prepared by the same method used for their Ru analogues. In a typical experiment, ca. 10 mg of $[Os(NH_3)_5tfms](tfms)_2$ in 1.00 mL of D_2O or H_2O over Zn/Hg was employed. After an initial 30-min purge with Ar, the olefin was vigorously bubbled through the solution for 40 min, and then the system was sealed for 12 h. Unlike the Ru analogues, these compounds were much more air-sensitive and required an inert Ar atmosphere at all times.

$[Os(NH_3)_5(1,3\text{-butadiene})Os(NH_3)_5]^{4+}$ and its deuteriated analogue were prepared by the reaction of $[Os(NH_3)_5(butadiene)]^{2+}$ or $[Os(ND_3)_5(butadiene)]^{2+}$ (1.2×10^{-2} M) with 1 equiv of $[Os(NH_3)_5tfms](tfms)_2$ under an inert atmosphere of Ar with Zn/Hg present.[13c,19d] Reaction time was typically 14 h.

$[Os(ND_3)_5(1,3\text{-butadiene})Ru(ND_3)_5]^{4+}$ was prepared by the reaction of $[Os(ND_3)_5(butadiene)]^{2+}$ (1×10^{-2} M) with 1 equiv of $[Ru(ND_3)_5OD_2]^{2+}$ in D_2O under an argon atmosphere with Zn/Hg present. The reaction time was 16 h.

Early attempts to isolate the Ru or Os olefin complexes either by precipitation as the PF_6^- salts or by addition of acetone or ethanol to their aqueous solutions led to a low yield of this product that IR and NMR data showed to be of dubious purity. Consequently, olefin complexes to be studied by NMR were prepared directly in D_2O at a metal concentration of $\sim 10^{-2}$ M and filtered into Ar-flushed NMR tubes prior to use. Samples to be analyzed electrochemically were prepared in 0.1 M NaCl in Ar-purged H_2O with a metal complex concentration of $\sim 10^{-3}$ M.

Instrumentation. UV–visible spectra were recorded on a Varian Cary 118C spectrophotometer in standard quartz cells. IR spectra in KBr pellets were recorded on an IBM IR/32 FTIR spectrometer. Electrochemical studies utilized an IBM 225 electrochemical analyzer employing differential-pulse polarography (DPP) and cyclic voltammetry. A 5 mV/s sweep rate and 50-mV pulse step were used for DPP. A glassy-carbon working electrode, sodium chloride saturated calomel (SSCE) electrode as the reference, and a Pt wire as the auxiliary electrode were employed.

^1H and ^{13}C Spectra. ^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 spectra employed a radio frequency of 300.13 MHz; ^{13}C spectra employed a radio frequency of 75.46 MHz. All spectra were recorded in D_2O as solvent with TMPS reference (0.00 ppm) for ^1H spectra and *p*-dioxane (66.5 ppm) as reference for ^{13}C spectra. ^{13}C spectra were proton decoupled by using 14-Hz broad-band decoupling power.

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Table II. ^1H NMR Data for Osmium Complexes[a]

	δ								
complex	H_a	H_b	H_c	$H_{a'}$	$H_{b'}$	$H_{c'}$	H_d	$J_{a'c'}$, Hz	$J_{b'c'}$, Hz
$[Os(ND_3)_5(isobutylene)]^{2+}$				3.00 s			1.24 s		
$[Os(ND_3)_5(propene)]^{2+}$				2.90 d	2.93 d	3.35 m	1.32 d	4.50	5.79
$[Os(ND_3)_5(1,3\text{-butadiene})]^{2+}$	5.09 d	5.16 d	5.46 m	3.23 d	3.40 d	3.81 m		7.83	9.33
$[Os(ND_3)_5(1,5\text{-hexadiene})]^{2+}$	*b*	*b*	6.03 m	2.91 d	2.94 d	3.32 m	2.34 q	7.86	8.04

[a] All data collected with D_2O as solvent at 25.0 °C. For structural assignments, see Chart I. [b] Obscured by the HOD resonance.

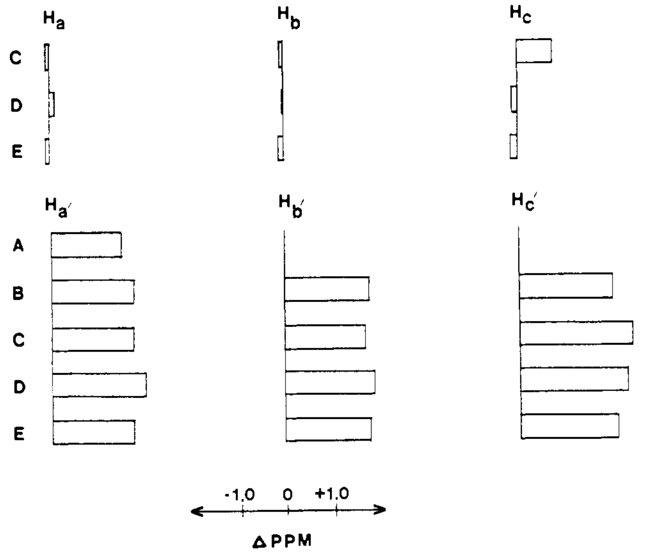


Figure 1. ^1H NMR spectral changes of olefin resonances upon coordination to $(ND_3)_5Ru^{2+}$ ($\Delta\delta$ vs free ligand in D_2O): (A) isobutylene; (B) propene; (C) 1,3-butadiene; (D) 1,4-pentadiene; (E) 1,5-hexadiene. $\Delta\delta$ = (δ(free ligand) − δ(coordinated ligand)).

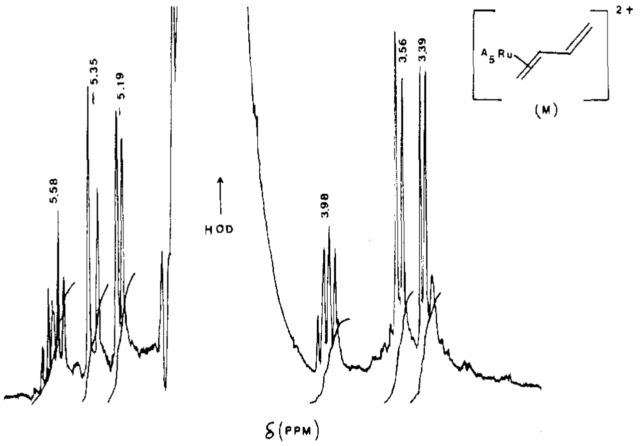


Figure 2. ^1H NMR spectrum of $(ND_3)_5Ru(1,3\text{-butadiene})^{2+}$ in D_2O at 25 °C. The weak intensity feature below δ 3.39 is an undetermined impurity.

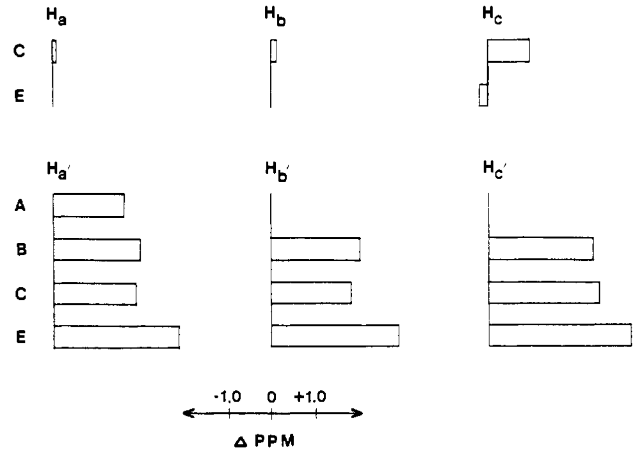


Figure 3. ^1H NMR spectral changes of olefin resonances upon coordination to $(ND_3)_5Os^{2+}$ ($\Delta\delta$ vs free ligand in D_2O): (A) isobutylene; (B) propene; (C) 1,3-butadiene; (D) 1,5-hexadiene.

Results and Discussion

^1H NMR Spectra of Monomeric Olefin Complexes. $[Ru(NH_3)_5(olefin)]^{2+}$ complexes of the following olefins were prepared and categorized by NMR spectroscopy: isobutylene, propene, 1,3-butadiene, 1,4-pentadiene, and 1,5-hexadiene. ^1H nuclear magnetic resonances are presented in Table I. The $Ru(NH_3)_5(1,5\text{-hexadiene})^{2+}$ species exhibits a complex pattern in the region of δ 1.0–2.5. Two sets of three resonances are observed with one contributing 63% and the second set about 37% of the integrated area for the 1.0–2.5 ppm region. The spectra might be explained by one complex that has the C_4–C_6 carbons extended into the solvent and a second species with this longer tail folded more closely near the $(NH_3)_5Ru^{II}$ center.

The effect on the olefinic protons of coordination to the Ru^{II} center relative to the free ligand ($\Delta\delta$) is shown in Figure 1. The respective proton assignments were confirmed by the proton–proton decoupling procedure. It can be seen from Figure 1 that all protons directly attached to the coordinating π-system ($H_{a'}$, $H_{b'}$, $H_{c'}$) are shifted from 1.5 to 2.5 ppm upfield. $H_{c'}$, the inner hydrogen of the π-system, is most dramatically affected upon coordination. This is not surprising based on the added effect of a hydrocarbon substituent also present on the same carbon. $H_{a'}$ and $H_{b'}$ do not have this hydrocarbon substituent. It is known that the substituents on the olefin carbons bend back, away from the metal center, on coordination of an olefin to a π-donating metal.[16] This change toward sp^3 hybridization from sp^2 in the unperturbed olefin will be more important when R is other than H for stereochemical reasons. Therefore, upon coordination the percent of s character is less in the carbon with the hydrocarbon substituent. This contributes to a component of upfield shift sensed by the proton on the same carbon. Coordination also has the added effect of decreasing the vicinal coupling between $H_{a'}$ or $H_{b'}$ and $H_{c'}$ in all of the olefin complexes. In some cases, this vicinal coupling completely disappears (L = 1,4-pentadiene). Although the observation or magnitude of spin–spin coupling between hydrogen atoms is not necessarily an indication of the true communication between nuclei, two reasons for this decrease in $J_{a'c'}$ or $J_{b'c'}$ are possible. First, π-donation to the π^* orbital of the olefin will lead to a carbon–carbon bond formally less than a true double bond (e.g., the change in hybridization described above). This would lead to less magnetic interaction between the vicinal protons and thus a smaller *J*. Second, the decrease in *J* may be due to interference from the Ru^{II} center, which possesses its own nuclear spin.

For 1,3-butadiene, the H_c resonance is shielded by 0.78 ppm while for the other complexes, the H_c resonance is deshielded by ~−0.12 ppm versus that of the free ligand ($\Delta\delta$). The ^1H NMR spectrum of the $(NH_3)_5Ru((1,3\text{-butadiene})^{2+}$ complex is shown in Figure 2. Apparently the conjugation between the coordinated and uncoordinated π-system enables H_c to also experience some benefit from the π-base effect of the Ru^{II} center. The ^1H resonances in these complexes also points out how the π-base ability of Ru^{II} can affect atoms at least two or three bonds away from the coordinated π-system. At this distance it is very unlikely that this shielding effect (even in the alkane-like part of the olefin) is due to the temperature-independent paramagnetism (TIP) of the Ru^{II} center. Communication of the back-bonding to the adjacent olefin is explained by the orientation of the $2\pi_u{}^*$ orbital shown below.

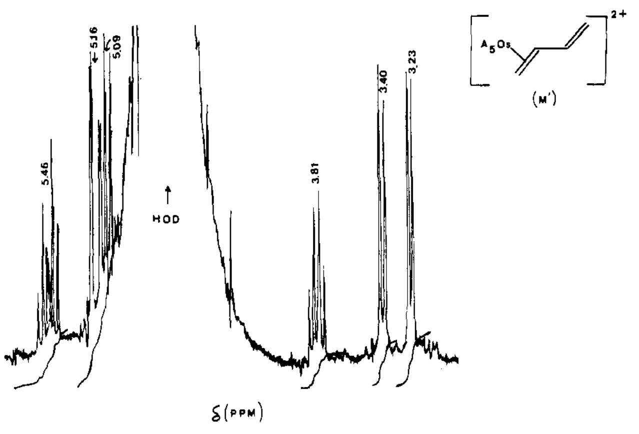
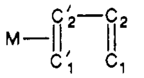


Figure 4. ^1H NMR spectrum of $(ND_3)_5Os(1,3\text{-butadiene})^{2+}$ in D_2O at 25 °C.

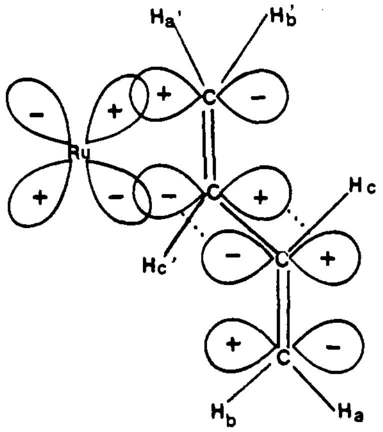
Table III. ^{13}C NMR Data



complex	$\delta^{a,c}$			
	C_1	C_2	C'_1	C'_2
1,3-butadiene^b	117.5	137.2	117.5	137.2
$[Ru(ND_3)_5(1,3\text{-butadiene})]^{2+}$	113.7	141.8	61.25	74.2
$[Os(NH_3)_5(1,3\text{-butadiene})]^{2+}$	110.1	144.7	41.5	54.2

^{a}Resonances measured in D_2O at 25.0 °C with *p*-dioxane as internal reference (66.5 ppm). ^{b}Reference 4. ^{c}Proton decoupled.

Table II shows ^1H nuclear magnetic resonance data for some $[Os(ND_3)_5(olefin)]^{2+}$ complexes (olefin = isobutylene, propylene, 1,3-butadiene, 1,5-hexadiene). Figure 3 shows the $\Delta\delta$ upon coordination for these Os^{II} complexes. The Os^{II} data parallels the trends seen in the Ru^{II} analogues but there are also new observations.



The H_a and H_b resonances for coordinated 1,3-butadiene (Figure 4) are shifted upfield, unlike for the Ru^{II} analogue. In the case of the nearby $H_{a'}$, $H_{b'}$, and $H_{c'}$, resonances for either isobutylene or 1,3-butadiene, all are upfield relative to those of free ligand but are shifted further upfield on the average by about 15%. This extra shielding by Os^{II} is primarily due to its better π-basicity compared to Ru^{II}. The TIP for Os^{II} is smaller than the TIP for Ru^{II}, and if the TIP upfield shift were dominant, Os^{II} complexes would appear downfield of Ru^{II}.

^{13}C NMR Spectra of Mononuclear Olefin Complexes. ^{13}C nuclear magnetic resonances for $[Os(ND_3)_5(1,3\text{-butadiene})]^{2+}$ and $[Ru(ND_3)_5(1,3\text{-butadiene})]^{2+}$ were recorded to further investigate the π-basicity differences between Ru^{II} and Os^{II}. ^{13}C resonances are much more sensitive to electronic effects than are ^1H resonances. Coordination of the Ru or Os nuclei should more strongly influence the ^{13}C spectrum than the ^1H spectrum for the same reason. Table III presents the ^{13}C resonances for these two complexes. The same trend is seen here as with the ^1H spectra in that Os^{II} shields the carbons in the coordinated π-system more than the Ru^{II} does. This is also a reflection on the better π-basicity of Os^{II}. One curious note is the slight deshielding of C_2 observed in both the Os^{II} and Ru^{II} complexes. This suggests a loss of electron density at this position. This is opposite of the effect on the hydrogens ($H_{a'}$, $H_{b'}$, $H_{c'}$) at these positions (Figures 1 and 3). H_a and H_b appear slightly deshielded, and H_c appears much more shielded. Perhaps this reflects the slight change in hybridization at this position upon coordination.[14]

Table IV. Formal Redox Potentials of Olefin Complexes of $Ru(ND_3)_5L^{3+/2+}$ and $Os(NH_3)_5L^{3+/2+\,a}$

L	$E_{1/2}$(Ru), V vs NHE	$E_{1/2}$(Os), V vs NHE
N_2	+0.72^e	+0.517 (+0.580)^c
NH_3	0.05^b	−0.780^c
H_2O		−0.730^c
propylene	+0.83	+0.35
isobutylene	+0.85^d	+0.30
1,3-butadiene	+0.94	+0.44
ethylene	+0.93^d	+0.40^f
1,4-pentadiene	+0.93	
1,5-hexadiene	+0.85	+0.37

^{a}In 0.10 M NaCl, $[M(NH_3)_5L^{3+/2+}] \sim 10^{-3}$ M. ^{b}Reference 15. ^{c}Reference 19. ^{d}Reference 2. ^{e}Bard, A. J.; Lund, H. *Encyclopedia of Electrochemistry of the Elements*; Marcel Dekker: New York, 1976; Vol. VI. ^{f}Reference 8.

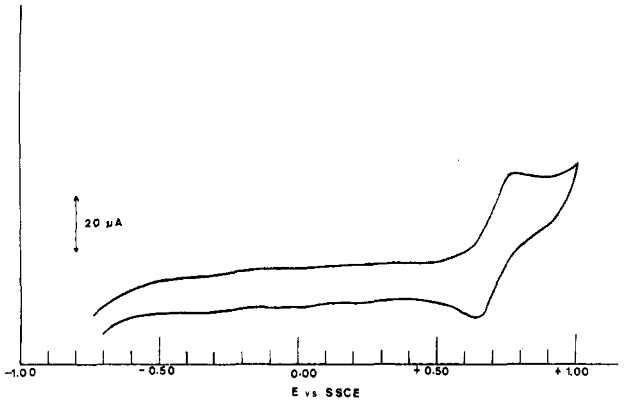


Figure 5. Cyclic voltammogram of $(NH_3)_5Ru(1,3\text{-butadiene})^{2+/3+}$ vs SSCE. Conditions: [complex] = 2.22×10^{-3} M, T = 25 °C, μ = 0.10 M (NaCl), 50 mV/s sweep at glassy-carbon working electrode, solution acidified slightly with HCl to prevent side reactions of Ru^{III}–ammine complexes.

Attempts were made to synthesize $[Ru(CN)_5(olefin)]^{3-}$ complexes to test the effect that π-donation contributes, as opposed to TIP, to the shielding of the proton resonances of the coordinated olefin. $[Ru(CN)_5OD_2]^{3-}$ was prepared in D_2O by bromine oxidation of $Ru(CN)_6^{4-}$ ($[Ru(CN)_6^{4-}]$ was kept below 1×10^{-4} M). The aquo complex was then allowed to react with olefin.[15] No evidence for any coordinated olefin could be found. Apparently, the CN^- ligands reduce the π-basicity of Ru^{II} too much to interact sufficiently with the π-system of the olefin. The $(CN)_5Ru^{3-}$ moiety is known to be 40% as good as a π-donor toward N-heterocycles as the $(NH_3)_5Ru^{2+}$ center, as is evident in comparing the $M \leftarrow \sigma$-donor complexes (NH_3, H_2O) with the $M \rightarrow \pi$-acceptor complexes.[15,10c]

Electrochemical Procedures. Differential-pulse polarography and cyclic voltammetry were employed on these complexes to study the effect of coordination of olefin on the $E_{1/2}$ of Os^{II} and Ru^{II}. These data are summarized in Table IV. A representative cyclic voltammogram is shown in Figure 5. From Table IV it can be seen that coordination of any olefin to either Os^{II} or Ru^{II} greatly stabilizes the +2 oxidation state as compared to the +3 form. Os^{II} is more stabilized than Ru^{II} by about 0.4 V. This is in keeping with the stronger π-basicity of osmium. The overall shift for Os(II) upon coordination of olefin is about 1.1 V relative to the aqua complex.

Some interesting observations can be made in comparing the various olefins and their effect on the $Ru^{3+/2+}$ redox potential.

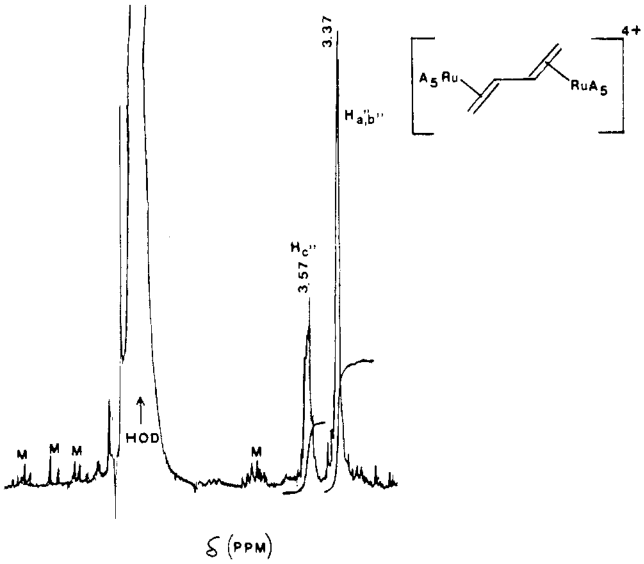


Figure 6. ^1H NMR spectrum of the binuclear $[(ND_3)_5Ru(1,3\text{-butadiene})Ru(ND_3)_5{}^{4+}]$ complex. M indicates mononuclear impurity.

Ethylene, 1,3-butadiene, and 1,4-pentadiene all have $E_{1/2}$ at ~ +0.93 V. Propylene, isobutylene, and 1,5-hexadiene have $E_{1/2}$ ~ +0.85 V. The extra stabilization in the former complexes (+0.08 V) can be due to various factors. Ethylene has no hydrocarbon substituents to decrease its π-acceptor ability (see below). Butadiene has two conjugated π-systems to accept electron density from Ru^{II}. NMR data indicate that the electron density from the Ru^{II} center is partially delocalized into the other π-system (vide supra). 1,4-Pentadiene, although not conjugated, may be at the balance point where the remote π-system is still accessible by the Ru^{II} center and the entire organic chain has not yet become a liability. Introduction of an R substitutent lowers the energy gap between the HOMO and LUMO olefin orbitals, but it raises the energy of both.[17] Therefore, π-accepting from the metal to the LUMO is decreased and the unit is easier to oxidize when R is a nonconjugated substitutent. The data in Table I indicate that the remote π-system of pentadiene is more shielded on H_a and less deshielded on H_b and H_c than that of 1,5-hexadiene. For 1,5-hexadiene, the remote π-system cannot act as an auxiliary π-acceptor, and so this unit behaves strictly as a donating group to the coordinated π-system, diminishing its π-acid ability. In propylene or isobutylene the methyl group can only serve as a donating group. This explains the nearly equivalent electrochemical behavior of R-substituted olefins.

Cyclic voltammetry of the $(NH_3)_5Os(1,3\text{-butadiene})^{2+}$ and $(NH_3)_5Ru(1,3\text{-butadiene})^{2+}$ yield the same respective $E_{1/2}$ values given in Table IV as were determined by the differential-pulse procedure for the 3+/2+ wave. The $Ru^{3+/2+}$ and $Os^{3+/2+}$ couples for the 1,3-butadiene complexes are representative. These cyclic voltammograms exhibit quasi-reversible behavior even at scan rates as low as 5 mV/s. For example, $(NH_3)_5Ru(1,3\text{-butadiene})^{3+/2+}$ waves show the following peak-to-peak widths at the specified scan rates: 5 mV/s, 110 mV; 50 mV/s, 130 mV; 300 mV/s, 320 mV. The related behavior for $(NH_3)_5Os(1,3\text{-butadiene})^{3+/2+}$ is as follows: 50 mV/s, 100 mV separation; 100 mV/s, 100 mV; 300 mV/s, 200 mV. Thus the $Os^{3+/2+}$ couples show more reversibility than do the $Ru^{3+/2+}$ waves. The relative peak heights (i_c/i_a) decrease as the scan rate decreases, which suggests the inherent instability of the M^{III}–olefin species. However, the $(NH_3)_5Os(\text{styrene})^{3+/2+}$ couple was shown both to be reversible and to have an i_c/i_a ratio of 1.0.[18] This shows the change in i_c/i_a for the straight-chain olefins in this report at slower scans is due to the chemical aquation of the M^{III}–olefin unit and is not due to a diffusional problem at the glassy-carbon surface.

Binuclear 1,3-Butadiene Complexes. When 1 equiv of $[A_5Ru(1,3\text{-butadiene})^{2+}]$ ($A = NH_3$) is combined with 1 equiv of $A_5RuOD_2{}^{2+}$ in D_2O under Ar for a total of 11 h, a new species is detected (Figure 6). A solid providing a similar ^1H NMR spectrum is produced during the synthesis of the $[A_5Ru(1,3\text{-butadiene})^{2+}]$ monomer species as a side reaction product; addition of acetone precipitated the binuclear complex. Formation of the binuclear bridged complex is expected to be slow due to the addition of $A_5RuOH_2{}^{2+}$ to a dication as the ligating species. The reaction was monitored by ^1H NMR spectroscopy throughout the 11-h reaction period.

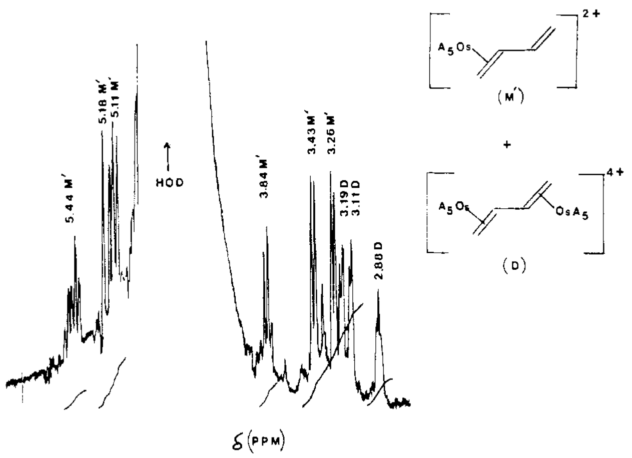


Figure 7. ^1H NMR spectrum of the mixture of binuclear $[(ND_3)_5Os(1,3\text{-butadiene})Os(ND_3)_5{}^{4+}]$ complex and its mononuclear precursor in D_2O at 25 °C.

The typical spectrum of $[A_5Ru(1,3\text{-butadiene})^{2+}]$ is slowly replaced by two broad resonances at 3.58 and 3.37 ppm after 11 h. These two resonances are the only significant ones remaining in the spectrum. The residual monomeric species is denoted as M in Figure 6. The integration is a 1:2 ratio, and the signals are assigned as shown in Figure 6.

These signals are broad with a frequency width at half-height of ca. 15 Hz. Either an excess of $A_5RuOH_2{}^{2+}$ or precipitation of the monomer from solution is necessary to force binuclear ion formation. The $H_{a''}$ and $H_{b''}$ resonances are equivalent in the binuclear ion. The acetone-precipitated complex is contaminated by coprecipitated monomer complex.

An analogous method was used to prepare the (Os^{II}, Os^{II}) binuclear complex with 1,3-butadiene. Although a longer reaction time was allowed (16 h), the solution still has a large amount of $[A_5Os(1,3\text{-butadiene})]^{2+}$ present as shown in Figure 7. New resonances for (Os^{II}, Os^{II}) are observed and assigned as follows: $H_{a''}$, 3.12 ppm; $H_{b''}$, 3.19 ppm; $H_{c''}$, 2.88 ppm. Unlike the ruthenium case, $H_{a''}$ and $H_{b''}$ are distinguishable for (Os^{II}, Os^{II}) and $H_{c''}$ emerges as the most upfield signal. As in the monomers, the Os^{II} binuclear complex resonances are more upfield than for (Ru^{II}, Ru^{II}). The effect of two very good π-donors like Os^{II} in close proximity accounts for $H_{c''}$ being the most shielded resonance. In (Ru^{II}, Ru^{II}) the $H_{c''}$ resonance is shielded more than the $H_{a''}$ or $H_{b''}$ resonance compared to the monomer, but Ru^{II} is not a good enough π-donor to shield the $H_{c''}$ resonance as much as in the Os^{II} binuclear species.

Preparation of the (Ru^{II}, Os^{II}) hybrid binuclear ion was achieved by reacting $[A_5Os(1,3\text{-butadiene})]^{2+}$ with $[A_5RuOD_2]^{2+}$ in D_2O under an argon atmosphere with Zn/Hg present. After approximately 12-h reaction time, the typical $[A_5Os(1,3\text{-butadiene})]^{2+}$ spectrum is replaced by a series of ^1H resonances between 2.90 and 3.70 ppm as shown in Figure 8. Although these signals are not assignable to the individual resonances in the mixed-metal binuclear species, the signals are upfield of the (Ru^{II}, Ru^{II}) complex and downfield of the (Os^{II}, Os^{II}) ion.

No signals attributable to the uncoordinated part of the olefin (as in Figure 4) for the Os^{II} monomer complex are observed downfield of HOD. Therefore the spectrum shown in Figure 8 must be the mixed-metal (Ru^{II}, Os^{II}) 1,3-butadiene-bridged complex.

Br_2 Reaction with 1,3-Butadiene Complexes. Reaction of the $[A_5Ru(1,3\text{-butadiene})]^{2+}$ or $[A_5Os(1,3\text{-butadiene})]^{2+}$ complex with Br_2 was followed by ^1H NMR spectroscopy. All resonances

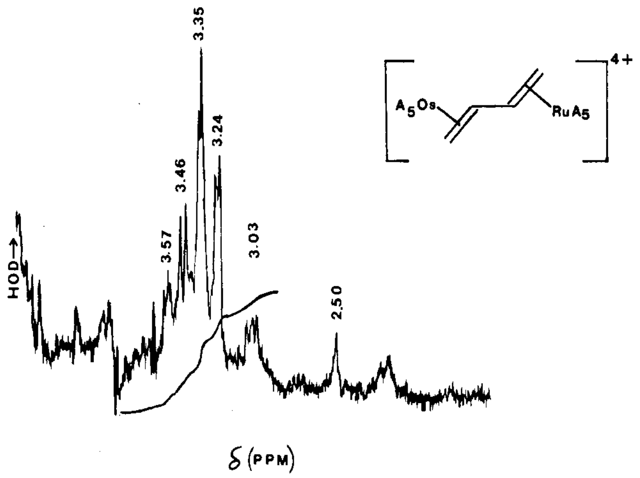


Figure 8. ^1H NMR spectrum of the heterobinuclear complex $[(ND_3)_5Os(1,3\text{-butadiene})Ru(ND_3)_5{}^{4+}]$ in D_2O at 25 °C.

attributable to H_a, H_b, H_c for the pendant olefin unit disappear, and new resonances appear in the 3.00–4.00 ppm region. Resonances from $H_{a'}$, $H_{b'}$, and $H_{c'}$ of the coordinated olefin fragment are still observed. No evidence for oxidation of the Ru^{II} or Os^{II} centers is found even with addition of excess Br_2. Therefore Br_2 undergoes electrophilic addition to the uncoordinated π-system of 1,3-butadiene only. Coordination of the other π-system to the A_5M^{II} moiety has a 2-fold effect. First, the metal is no longer rapidly oxidizable by Br_2. Second, the coordinated π-system of 1,3-butadiene is protected from bromination.

Electrochemistry of the brominated adducts shows the same result. $[A_5Os(1,3\text{-butadiene})]^{2+}$ has an $E_{1/2}$ of +0.44 V. The brominated adduct has an $E_{1/2}$ of +0.60 V. A more positive potential for the brominated adduct supports the conclusions reached from the NMR studies. For such a high oxidation potential, a good π-acceptor ligand must still be coordinated to the A_5Os^{II} unit and be a better acceptor than 1,3-butadiene. This is consistent with a strongly withdrawing olefin substituted as in the dibromo adduct.

A parallel experiment was performed by bubbling H_2 gas through a solution of $A_5Ru(1,3\text{-butadiene})^{2+}$ at ca. 1×10^{-2} M. After 1-h reaction time no change was observed in the ^1H NMR spectrum from that of the original complex. Therefore, hydrogenation of the unprotected olefin did not proceed as readily as the bromination reaction.

Exposure of the $[A_5Os(isobutylene)]^{2+}$ complex to Br_2 shows no change in the NMR spectrum and the $E_{1/2}$ for the complex stays constant with time. Therefore, coordination of an olefin to A_5Ru^{II} on A_5Os^{II} yields complexes where the metal is much harder to oxidize and renders the coordinated olefin site less susceptible to electrophilic attack. The uncoordinated unit of the 1,3-butadiene complexes remain susceptible to electrophilic additions.

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Registry No. $Ru(NH_3)_5OH_2{}^{2+}$, 21393-88-4; $[Ru(NH_3)_5Cl]Cl_2$, 18532-87-1; $Ru(ND_3)_5OD_2{}^{2+}$, 115590-55-1; $[Ru(ND_3)_5(isobutylene)]^{2+}$, 115590-46-0; $[Ru(ND_3)_5(propene)]^{2+}$, 115590-47-1; $[Ru(ND_3)_5(1,3\text{-butadiene})]^{2+}$, 115590-48-2; $[Ru(ND_3)_5(1,4\text{-pentadiene})]^{2+}$, 115590-49-3; $[Ru(ND_3)_5(1,5\text{-hexadiene})]^{2+}$, 115590-50-6; $[Os(NH_3)_5tfms](tmfs)_2$, 83781-30-0; $[Os(NH_3)_5OH_2]^{2+}$, 115590-60-8; $[Os(ND_3)_5OD_2]^{2+}$, 115590-61-9; $[Os(ND_3)_5(isobutylene)]^{2+}$, 115590-51-7; $[Os(ND_3)_5(propene)]^{2+}$, 115590-52-8; $[Os(ND_3)_5(1,3\text{-butadiene})]^{2+}$, 115590-53-9; $[Os(ND_3)_5(1,5\text{-hexadiene})]^{2+}$, 115590-54-0; $[Os(NH_3)_5(propene)]^{2+}$, 115590-56-2; $[Os(NH_3)_5(isobutylene)]^{2+}$, 115590-57-3; $[Os(NH_3)_5(1,3\text{-butadiene})]^{2+}$, 115590-58-4; $[Os(NH_3)_5(1,5\text{-hexadiene})]^{2+}$, 115590-59-5; $[Os(NH_3)_5(1,3\text{-butadiene})OS(NH_3)_5]^{4+}$, 115590-62-0; $[Os(ND_3)_5(1,3\text{-butadiene})Os(ND_3)_5]^{4+}$, 115590-63-1; $[Os(ND_3)_5(1,3\text{-butadiene})Ru(ND_3)_5]^{4+}$, 115590-64-2; propylene, 115-07-1; isobutylene, 115-11-7; 1,3-butadiene, 106-99-0; ethylene, 74-85-1; 1,4-pentadiene, 591-93-5; 1,5-hexadiene, 592-42-7.