of additional side reactions should serve as a solid starting point for detailed numerical simulations of this system to be undertaken in our laboratories.

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Registry No. $S_2O_8^{2-}$, 15092-81-6; $S_2O_3^{2-}$, 14383-50-7; Cu, 7440-50-8; O_2, 7782-44-7.

Carbon-Hydrogen Bond Activation in Novel η^2-Bound Cationic Heterocycle Complexes of Pentaammineosmium(II)

Rossella Cordone, W. Dean Harman, and Henry Taube*

Contribution from the Chemistry Department, Stanford University, Stanford, California 94305.
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Abstract: Reduction of $(NH_3)_5Os(TFMS)_3$ (TFMS = trifluoromethanesulfonate) by $Co(Cp)_2$ in the presence of cationic pyridines L (L = *N*-methylpyridinium, lutidinium, pyridinium, and *N*-methyl-4-picolinium) leads to the formation of isolable pentaammineosmium(II) π complexes featuring fluxional 3,4-η^2 ligands for the former three and 2,3-η^2 for the latter. Analogously to the previously reported η^2-lutidine analogue, activation at the C4-H bond was observed for the 3,4-η^2-bound cationic ligands, yielding σ carbon-bound pyridinium ylides. In accord with observations made on other complexes containing metal-ylide carbon bonds, the resulting pentaammineosmium(II) *N*-methylpyridinium complex is unstable with respect to loss of the trans ammine.

Numerous reports on the subject of arene carbon-hydrogen bond activation by transition-metal centers exist.[1] The enhanced reactivity generally observed for arenes as compared to alkanes has been attributed to the ability of the former to form η^2-bound intermediates,[2] a pathway not available for saturated hydrocarbons. However, evidence for the existence of such complexes until recently was only indirect, as their instability rendered their identification difficult.

A recently reported example of an isolable η^2-bound precursor for aromatic C-H activation came with the discovery of the complex $[(NH_3)_5Os(\eta^2\text{-}2,6\text{-lutidine})]^{2+}$ in our laboratories.[3] This η^2 species is stable for hours in a variety of solvents; however, it undergoes intramolecular rearrangement with time to yield a carbon-bound lutidinium ylide, where the osmium moiety resides at C4 of the aromatic ring.

The observations on this complex motivated us to extend the chemistry of pentaammineosmium(II) to include cationic nitrogen heterocycles, which relative to the neutral heterocycle are better π acceptors but extremely weak nucleophiles. We report here the preparation and characterization of a series of stable complexes containing η^2-bound pyridinium ligands, the majority of which, in analogy to the previously reported lutidine complex, also proved to be precursors to activation of the aromatic C4-H bond.

Experimental Section

Abbreviations: DMA = *N*,*N*-dimethylacetamide; DME = 1,2-dimethoxyethane; TFMS = trifluoromethanesulfonate; NMepy = *N*-methylpyridinium; Hlu = 2,6-lutidinium (2,6-dimethylpyridinium); Hpy = pyridinium; NMepic = *N*-methyl-4-picolinium (1,4-dimethylpyridinium).

Instrumentation and Techniques. All nonaqueous reactions were carried out in a Vacuum Atmospheres Corp. glovebox under an argon atmosphere. All solvents were fully deoxygenated by purging with argon for 45 min. ^1H NMR spectra were recorded on a Varian XL-400 spectrometer. Cyclic voltammograms were recorded on a Princeton Applied Research Model 173 potentiostat and Model 175 universal programmer. A platinum button was used as a working electrode. A platinum wire was the auxiliary electrode, and a gold button immersed in 0.5 M NaTFMS in DME acted as the reference electrode; this electrode was separated from the bulk solution by a Vycor tip. The $Fe(Cp)_2^+/Fe(Cp)_2^0$ couple was used as a reference in situ. Voltammograms were recorded on a Hewlett-Packard 7045A X-Y recorder. The voltage range was -1.20 to +1.20 V vs NHE, and the scan rate was typically 200 mV/s. Electrochemical analysis of bulk solutions was performed by the use of a modified rotating disk technique described by Harman.[4]

Purifications and Preparations. Solvents. 1,2-Dimethoxyethane and diethyl ether were refluxed for 5 h over NaK alloy and distilled under argon. Methylene chloride was refluxed for 8 h over P_2O_5 and distilled under argon. Acetone was stirred over B_2O_3 for 3 days at room temperature and vacuum distilled.[5] *N*,*N*-Dimethylacetamide was predried over BaO for 48 h, distilled from triphenylsilyl chloride, and redistilled from CaH_2 under vacuum. Ethyl acetate was stirred over CaH_2 for 8 h and distilled under argon. All solvents were thoroughly deoxygenated by purging with argon for 45 min.

Reagents. Magnesium turnings were activated by treating with iodine in DME under argon, stirring for several hours, and washing with DMA, DME, and ether. Pyridine, 4-picoline, and 2,6-lutidine were stirred over CaH_2 for 8 h and distilled under vacuum. In order to remove unhindered pyridine contaminants, predried 2,6-lutidine was treated following the method outlined by Shepherd et al.[6] Cobaltocene (Alfa), HTFMS, and CH_3TFMS (Aldrich) were used without further purification. $(NH_3)_5Os(TFMS)_3$ was prepared according to previously reported methods.[7]

Ligands. The following preparations were performed in a glovebox. *N*-Methylpyridinium, *N*-methylpicolinium, lutidinium, and pyridinium triflates were prepared by treating 1 mL of the corresponding bases dissolved in 4 mL of ethyl acetate with 1.5 mL of cold CH_3TFMS or HTFMS (caution!), respectively. Solids were obtained upon cooling these solutions to -40 °C for 30 min.

Osmium Compounds. $[(NH_3)_5Os(\eta^2\text{-NMepy})](TFMS)_3$ (**1**) was obtained by dissolving 75 mg of $(NH_3)_5Os(TFMS)_3$ and 0.5 of NMepyTFMS in ~5 mL of neat DME. A solution containing 19.6 mg of cobaltocene (1 equiv) dissolved in 1 mL of DME was added dropwise, with constant stirring. A black solid is present once the addition of cobaltocene is complete. This solid was stirred for 1 h in ~8 mL of DME and dried with ether. Anal. Calcd for $[(NH_3)_5Os(C_6H_8N)]$-

(1) E. G.: (a) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650. (b) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 305.
(2) Parshall, G. W. *Homogeneous Catalysis*; Wiley-Interscience: New York, 1980; Chapter 7.
(3) Cordone, R.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 8101.
(4) Harman, W. D. Ph.D. Dissertation, Stanford University, 1987.
(5) Burfield, D. R.; Smithers, R. H. *J. Org. Chem.* **1978**, *43*, 3966.
(6) Shepherd, R. E.; Taube, H. *Inorg. Chem.* **1973**, *12*, 1392.
(7) Lay, P.; Magnuson, R.; Sen, J.; Taube, H. *J. Am. Chem. Soc.* **1982**, *104*, 7658.

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$(CF_3SO_3)_3$: C, 13.24; H, 2.84; N, 10.29. Found: C, 12.93; H, 2.89; N, 9.79. ^{1}H NMR in acetone-d_6 (20 °C) (ppm): 8.4 and 6.7 (very broad resonances); 6.54 (t, 1 H); 5.35 (s, 3 H, b); 4.22 (s, 3 H); 4.15 (s, 12 H, b).

$[(NH_3)_5Os(\eta^2$-Hlu$)]$(TFMS)$_3$ (**2**) was prepared by dissolving 75 mg of $(NH_3)_5Os(TFMS)_3$ and 0.5 g of lutidinium triflate in ~3 mL of DME. A solution containing 19.6 mg of cobaltocene (1 equiv) dissolved in 1 mL of DME was added dropwise, with constant stirring. After 5 min, ~10 mL of CH_2Cl_2 was added to this dark brown solution, and the mixture was cooled to −40 °C for 30 min. The fine precipitate obtained in this manner was filtered, rinsed with DME and ether, and used without further purification. Anal. Calcd for $[(NH_3)_5Os(C_7H_{10}N)](CF_3SO_3)_3$: C, 14.46; H, 3.03; N, 10.12. Found: C, 15.33; H, 3.20; N, 9.64. ^{1}H NMR in acetone-d_6 (20 °C) (ppm): 7.50 (very broad); 6.15 (t, 1 H); 5.33 (s, 3 H, b); 4.10 (s, 12 H, b); 2.80 (broad, ~6 H).

$[(NH_3)_5Os(\eta^2$-Hpy$)]$(TFMS)$_3$ (**3**) was obtained by dissolving 50 mg of $(NH_3)_5Os(TFMS)_3$ and ~370 mg of pyridinium triflate in 4 mL of DME. A solution containing 1 equiv of cobaltocene (13.1 mg) in 1 mL of DME was added dropwise with stirring. Immediately after the addition was complete, 8 mL of CH_2Cl_2 was added to this dark brown solution, and the mixture was cooled to −40 °C for 20 min. The fine solid obtained was filtered, copiously washed with DME and ether, and used without further purification. ^{1}H NMR in acetone-d_6 (20 °C) (ppm): 7.07 (t, 1 H); 5.34 (s, 3 H, b); 4.13 (s, 12 H, b).

$[(NH_3)_5Os(\eta^2$-NMepic$)]$(TFMS)$_3$ (**4**) was made by dissolving 75 mg of $(NH_3)_5Os(TFMS)_3$ and 0.3 g of *N*-methyl-4-picolinium triflate in 8 mL of DME. A solution containing 19.6 mg of cobaltocene in 1 mL of DME was added dropwise, with stirring, causing the immediate formation of a dark brown precipitate. This product was filtered, stirred in DME for 30 min, and washed with ether. ^{1}H NMR in acetone-d_6 (ppm): 8.41 (d, 1 H); 7.15 (d, 1 H); 6.92 (d, 1 H); 5.75 (d, 1 H); 5.36 (s, 3 H, b); 3.98 (s, 12 H, b); 4.26 (s, 3 H); 2.73 (s, 3 H).

Results

Structural Assignments. The ^{1}H NMR spectra of compounds **1**–**4** in acetone-d_6 show splittings for the protons on the cis and trans ammines that exceed 1.2 ppm. Similar ammine proton shifts have thus far been observed for all η^2-ketone[8a] and -arene[8b] pentaammineosmium(II) compounds, but for none containing monodentate ligands, which display splittings of <0.7 ppm.

With the exception of $[(NH_3)_5Os(\eta^2$-NMepic$)]^{3+}$, the η^2-six-membered heterocycle complexes show fluxional behavior on an NMR time scale at 20 °C, as has previously been reported for the η^2-2,6-lutidine[3] and η^2-arene species.[8b] Low-temperature homonuclear decoupling was thus necessary in order to interpret the spectra of these complexes. Spin saturation exchange was observed in the decoupling experiments for all cases at the lower temperatures.

Structure of $[(NH_3)_5Os(\eta^2$-NMepy$)]^{3+}$. A ^{1}H NMR spectrum of **1** in acetone-d_6 at room temperature shows peaks at 6.55 (t, 1 H), 5.30 (3 H, b), 4.20 (3 H), and 4.10 (12 H) ppm; in addition, two very broad resonances are present at ~8.3 and 6.7 ppm. At −60 °C, these latter resonances resolve into five inequivalent ring protons of equal intensity at 9.27 (d, H_a), 7.84 (t, H_b), 7.42 (d, H_c), 6.32 (b, H_d), and 5.64 (t, H_e) ppm. Homonuclear decoupling reveals the partial vicinal ordering H_c–H_b, H_a–H_e, and H_b–H_d–H_e. Spin saturation exchange occurs between pairs $H_a \leftrightarrow H_c$ and $H_b \leftrightarrow H_e$, indicating that H_d is the 4-proton. Due to the large upfield chemical shift of the 4-proton compared to the free ligand value ($\Delta\delta$ = −2.44 ppm), it is reasonable to assume that H_d is adjacent to the metal coordination site (H_α); a similar displacement ($\Delta\delta$ = −2.68 ppm) is observed for H_e, a 3-proton. This leads to the conclusion that the dominant isomer for compound **1** over this temperature range is one where *N*-methylpyridinium is bound to the metal at the 3,4-η^2 position, in equilibrium with its chemically equivalent 4,5-η^2 tautomer. The ^{1}H NMR spectrum for this complex (at 20 and −60 °C) is shown in Figure 1.

The structures of compounds **2**, **3**, and **4** were assigned in a similar manner; the former two compounds feature ligands bound 3,4-η^2 in fluxional equilibrium with their 4,5-η^2 isomers, whereas in the preferred structure for **4** the metal tautomerizes between the 2,3-η^2 and 5,6-η^2 sites. Table I summarizes the difference chemical shifts $\Delta\delta$ between free and complexed nitrogen heterocycle ligands bound to pentaammineosmium(II). Values for $[(NH_3)_5Os(\eta^2$-lu$)]^{2+}$ are included for comparison.

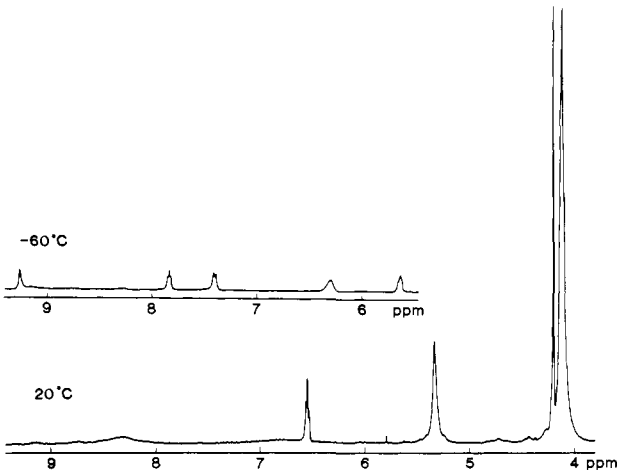


Figure 1. ^{1}H NMR spectra of $[(NH_3)_5Os(\eta^2$-NMepy$)]^{3+}$ in acetone-d_6.

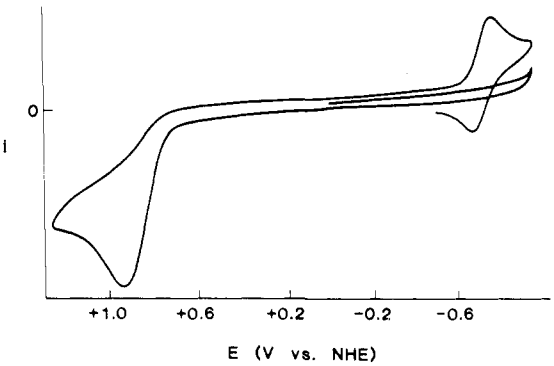


Figure 2. Cyclic voltammogram of $[(NH_3)_5Os(\eta^2$-NMepy$)]^{3+}$ in NaTFMS/DME; ν = 200 mV/s.

Table I. Difference Chemical Shifts $\Delta\delta$ for η^2-Bound Six-Membered Heterocycles[a]

ligand	η^2 isomer	$\Delta\delta(H_\alpha)$	$\Delta\delta(H_\beta)$	$\Delta\delta(H_\gamma)$	$\Delta\delta(CH_3)$
Hpy[b]	3,4	−2.58 (4)	−0.10 (2)		
		−2.74 (3)	−0.58 (3)	−1.69 (2)	
NMepy	3,4	−2.44 (4)	+0.09 (2)		
		−2.68 (3)	−0.48 (3)	−1.76 (2)	−0.52 (1)
Hlu	3,4	−2.40 (4)	−0.42 (3)		+0.17 (2)
		−2.28 (3)			−0.28 (2)
lu[c]	3,4	−2.22 (4)	−0.32 (3)		+0.08 (2)
		−1.79 (3)			−0.17 (2)
Nmepic[d]	2,3	−2.26 (3)		−1.12 (3)	+0.05 (4)
		−1.92 (2)		−0.58 (2)	−0.30 (1)

[a] Values of $\Delta\delta$ with respect to free ligand resonances; in ppm in acetone-d_6; t = −60 °C unless otherwise stated. The subscripts α, β, and γ refer to the position of the proton relative to the metal coordination site; numbers in parentheses refer to relative ring positions. [b] t = −80 °C. [c] Reference 3. [d] t = 20 °C.

Cyclic Voltammetry. The cyclic voltammogram of compound **1** is shown in Figure 2. In 0.5 M NaTFMS/DME at 200 mV s^{-1}, an oxidation wave appears at +0.92 V.[9] Upon return scan there is no corresponding reduction, but a new wave is present at −0.75 V, ascribed to the reduction of the solvent complex $[(NH_3)_5Os(DME)]^{3+}$. The reaction sequence can thus be represented as follows:

$$[(NH_3)_5Os(\eta^2\text{-NMepy})]^{3+} - e^- \rightarrow [(NH_3)_5Os(\eta^2\text{-NMepy})]^{4+} \rightarrow [(NH_3)_5Os(DME)]^{3+} + NMepy^+ \quad (1)$$

That the η^2-bound ligand is lost from the osmium coordination

(8) (a) Harman, W. D.; Fairlie, D.; Taube, H. *J. Am. Chem. Soc.* **1986**, *108*, 8223. (b) Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.*, in press.

(9) All reported potentials vs NHE.

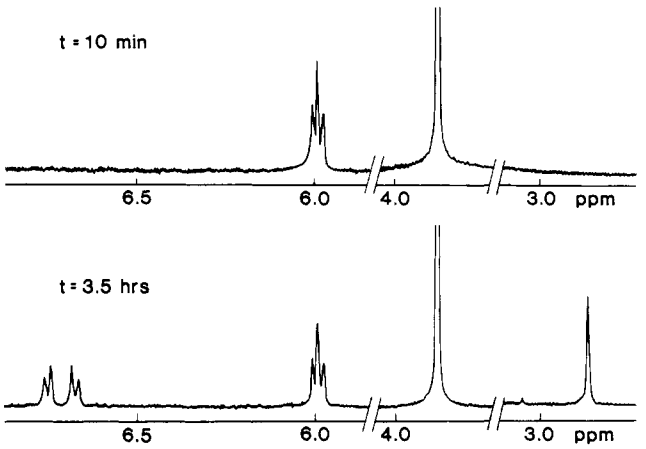


Figure 3. ^{1}H NMR spectra of $[(NH_3)_5Os(\eta^2\text{-NMepy})]^{3+}$ in D_2O over time.

sphere upon oxidation of the complex is corroborated by the appearance of an irreversible wave at −1.1 V in the cathodic return scan, corresponding to the reduction of free *N*-methylpyridinium.[10]

The cyclic voltammograms of **2**, **3**, and **4** are similar to that of **1**, displaying an irreversible oxidation wave at approximately +0.90 V upon anodic scan under the same conditions. The one-electron oxidation of the η^2-bound lutidinium complex **2** generates $[(NH_3)_5Os(DME)]^{3+}$ quantitatively, in contrast with the observed pattern for its deprotonated analogue $[(NH_3)_5Os(\eta^2\text{-lu})]^{2+}$, for which an intramolecular $\pi \rightarrow$ N isomerization is the exclusive reaction pathway upon oxidation of the metal center.[3]

Reactivity. Though the pentaammineosium(II) η^2-heterocycle complexes can be readily isolated and are stable to substitution by water and other solvents, all except **4** were observed to undergo $\pi \rightarrow \sigma$ rearrangements with time.

Solutions of **1** in DME, acetone, or H_2O turn from very dark brown to green over a period of hours. As is observed also for the complex $[(NH_3)_5Os(\eta^2\text{-lu})]^{2+}$,[3] the change in color occurs concomitantly with the appearance of a reversible couple in the cyclic voltammogram at −0.45 V (in DME) and the disappearance of the initial product wave, suggesting a $\pi \rightarrow$ C rearrangement for the η^2-*N*-methylpyridinium complex. A ^{1}H NMR spectrum of **1** in D_2O at room temperature displays a sharp singlet at 3.85 ppm (3 H) corresponding to the *N*-methyl group and a triplet at 5.97 ppm (1 H), which by comparison to the spectrum in acetone-d_6 can be ascribed to the 4-proton of the fluxional π-bound ligand.[11] After 3.5 h, doublets at 6.75 and 6.68 ppm, along with a singlet at 2.87 ppm, have appeared in a ratio of 2:2:3 (Figure 3), supporting the formation of a carbon-bound *N*-methylpyridinium species; the data suggest metal coordination to an *N*-methylpyridinium ylide at the 4-position of the ring (**5**, Scheme I). A comparison of the intensities of the peaks for the η^2-bound complex with those for the new species suggests a half-life of approximately 8 h for the $\pi \rightarrow$ C rearrangement.

An analogous $\pi \rightarrow$ C isomerization was observed for complex **2**. The carbon-bound product in this case is identical with that obtained from its deprotonated homologue $[(NH_3)_5Os(\eta^2\text{-lu})]^{2+}$,[3] as confirmed by ^{1}H NMR and cyclic voltammetry; however, the rearrangement

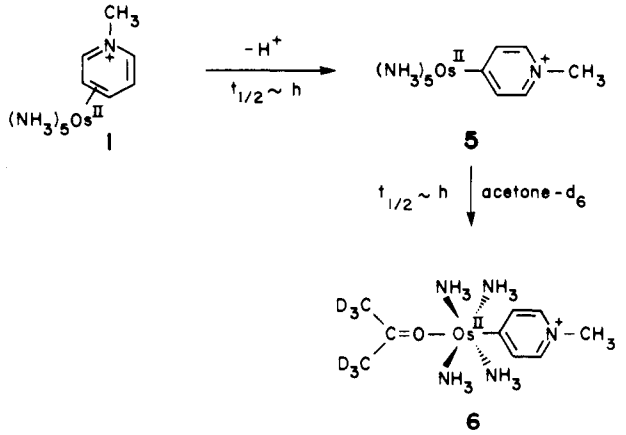
$$[(NH_3)_5Os(\eta^2\text{-Hlu})]^{3+} \rightarrow [(NH_3)_5Os(C\text{-lu})]^{2+} + H^+ \quad (2)$$
2

is slower than the corresponding isomerization for the lutidine complex.

The fate of the η^2-pyridinium complex is somewhat different from that of its congeners, due to the availability of another coordination position at the pyridine nitrogen. Solutions of **3** in DME decay with time to yield $[(NH_3)_5Os(N\text{-pyridine})]^{2+}$ as the major product, as evidenced by cyclic voltammetry and ^{1}H NMR

(10) Raghavan, R.; Iwamoto, R. T. *J. Electroanal. Chem.* **1978**, *92*, 101.
(11) Due to rapid exchange of ammonia protons by deuterium, no ammine peaks are observed in the spectra of these complexes in D_2O.

Scheme I



spectroscopy.[12] The $\eta^2 \rightarrow$ N rearrangement is catalyzed by base and retarded by acid, which suggests that a preequilibrium involving the deprotonation of the pyridine nitrogen occurs prior to the rearrangement:

$$[(NH_3)_5Os(\eta^2\text{-Hpy})]^{3+} \rightleftharpoons [(NH_3)_5Os(\eta^2\text{-py})]^{2+} + H^+ \quad (3)$$
3

$$[(NH_3)_5Os(\eta^2\text{-py})]^{2+} \rightarrow [(NH_3)_5Os(N\text{-py})]^{2+} \quad (4)$$

While the reactivity of the η^2-pyridinium complex is dominated by the formation of $[(NH_3)_5Os(N\text{-py})]^{2+}$, a pathway involving a $\pi \rightarrow$ C isomerization appears to contribute to the decomposition of $[(NH_3)_5Os(\eta^2\text{-Hpy})]^{3+}$ in acidic solutions. The ^{1}H NMR spectrum of **3** in 0.2 M D^+/D_2O after a period of hours displays peaks of equal intensity at 6.72 (d) and 6.63 (t) ppm, which agree quite well with the corresponding ring proton frequencies for the C-bound *N*-methylpyridinium complex (**5**, Scheme I). While this spectrum is complicated by the presence of other unidentified species, on the basis of these data it seems reasonable to propose that one of the products of the decomposition of $[(NH_3)_5Os(\eta^2\text{-Hpy})]^{3+}$ is a 4-substituted carbon-bound pyridinium complex analogous to **5**.

Complex **4** in acetone solution does not rearrange to a σ-bound species or release its π-bound ligand at 30 °C over a period of 1 week. Cyclic voltammograms and ^{1}H NMR spectra of acetone solutions of this material remain virtually unchanged during this period.

Because displacement of the η^2-ligand in acetone would result in the irreversible formation of the inert $[(NH_3)_5Os(\eta^2\text{-acetone})]^{2+}$ complex,[8a] we conclude that the above-mentioned rearrangements are intramolecular.

It is not known whether the $\pi \rightarrow \sigma$ isomerizations discussed above are of reversible nature, as addition of excess acid to the σ-bound products causes their rapid one-electron oxidations to the respective Os(III) C- or N-bound species. Addition of base to compound **1** does not seem to alter the rate of the $\eta^2 \rightarrow$ C4 rearrangement.[13]

As was observed for the lutidinium ylide complex,[3] the carbon-bound *N*-methylpyridinium species **5** is unstable with respect to loss of the trans ammine. If solutions of **5** in acetone-d_6 are allowed to stand for several hours, original ligand resonances at 7.20 (2 H, d), 7.00 (2 H, d), and 3.09 (3 H, s) ppm are replaced by peaks at 7.34, 7.06, and 3.23 ppm, respectively, concomitant with the disappearance of the trans-ammine resonance at 4.25 ppm. Parallel changes are observed in the cyclic voltammogram, where a new wave at −0.35 V supplants that characteristic of the pentaammine $Os^{3+/2+}$ couple with time. This pattern is taken as an indication of substitution by the solvent to yield the *trans*-(acetone)tetraammine carbon-bound complex **6** (Scheme I).

(12) Cyclic voltammetry: −0.45 V, reversible; ^{1}H NMR (ppm): 8.68 (2 H(2), d), 7.86 (1 H(4), t), 6.84 (2 H(3), m), 4.56 (3 H, trans), 3.85 (12 H, cis).
(13) Addition of base to **2** and **3** leads to their deprotonations at the pyridine nitrogen.

Discussion

Structures. Low-valent metal η^2 coordination to olefins[14] and arenes[8b] results in upfield chemical shifts of the protons adjacent to the binding site, H_α. This effect manifests itself also in the cationic η^2-bound six-membered heterocycles, for which osmium(II) coordination causes H_α shifts typically >2 ppm upfield from free-ligand values (Table I).

The H_α shifts for the 3,4-η^2 cationic heterocycle isomers show a trend, parallel to the electron-withdrawing properties of the ligand: upfield shifts of larger magnitude are observed for stronger π-acidic molecules. The trend can be extended to include the neutral ring 2,6-lutidine, which, relative to the cationic ligands, has diminished π-acidic properties associated with the loss of positive charge. An inverse relation between the H_α shifts of pentaammineosmium η^2-bound arene complexes and the arene substitution rates was observed by Harman;[8b] this shift was taken to reflect the strength of the osmium–η^2-ligand bond.

It has been argued that C=O bonds in aldehydes and ketones are more effective π acceptors than the C=C bonds in the corresponding alkenes.[15] Accordingly, the same relation might hold between the C=N and C=C groups in an aromatic *N*-heterocycle. Given that the stability of the pentaammineosmium(II) π complexes is presumed to be a consequence of metal backbonding, a complex where the osmium resides at the C=N portion of the heterocycle, i.e., an η^2-imine, might have been expected. In fact, no 1,2-η^2 isomers were observed for the heteroaromatic ring complexes of pentaammineosmium(II). A 3,4-η^2 structure unambiguously is the preferred one for these compounds, unless the steric influence of a methyl group in the 4-position, e.g., 1,4-dimethylpyridinium, dictates otherwise. That steric effects are significant for the structural choice of the metal center in pentaammineosmium η^2-arene complexes has been pointed out by Harman et al.[8b] However, the evident lack of an η^2-imine bond in the case of pyridinium ion, a ligand for which all positions are sterically equivalent, may illustrate an electronic discrimination. Alternatively, the 1,2-η^2 isomer may be inherently unstable, rapidly converting to the N-bound form; however, given the stability of the 3,4-η^2 isomer, this hypothesis would impose an anomalously high activation barrier for a 3,4-$\eta^2 \rightleftharpoons$ 1,2-η^2 exchange and hence seems unlikely. The binding site in $[(NH_3)_5Os(\eta^2\text{-Hpy})]^{3+}$ and the other complexes may well be a consequence of the diminished nucleophilicity of a $C{=}N^+$ π bond compared to a C=C moiety; although π back-donation is expected to dominate the bonding interaction between the electron-rich Os(II) moiety and the heterocycles, the binding position is affected by σ donation from the ligand as well. Electrostatic repulsion between the positive charges of the aromatic nitrogen and the metal center would also destabilize a 1,2-η^2 interaction.

Within the limits of detection, the NMR data for the η^2 species indicate that single structures prevail at −80 °C in all cases, thus suggesting that the difference in free energy for the possible isomers of the osmium(II) complexes is at least 2 kcal at this temperature. The invariance of the 4-proton chemical shifts upon warming ($\Delta\delta < 0.2$ ppm for **1** and **2**, ~0.4 ppm for **3**) further implies that the same isomer is still dominant at room temperature. For the latter case, the larger shift difference may be due to small contributions from the 2,3-η^2 and/or 1,2-η^2 form at 20 °C.

Sweet et al.[1b] have postulated two types of mechanisms to account for the fluxionality in $[(\eta\text{-}C_5H_5)Re(NO)(CO)(\eta^2\text{-arene})]^+$ complexes. One possible pathway would involve metal migration around the ring through σ-bound arenium structures, analogous to those found in aromatic electrophilic attack; alternatively, formation of hydrido–aryl intermediates by an oxidative addition of the metal to the arene C–H bonds could account for the tautomerization processes.[16] The slower exchange rate for $[(NH_3)_5Os(\eta^2\text{-NMepic})]^{3+}$ compared to its homologues could be rationalized if either of the above mechanisms is operative. If it is assumed that the 2,3-$\eta^2 \rightleftharpoons$ 5,6-η^2 exchange process for this ligand also passes through a 3,4-η^2 (and 4,5-η^2) isomer, the σ-bound intermediates for the picolinium complex would involve either coordination of the osmium(II) moiety to the sterically hindered 4-position via arenium-like intermediates or an energetically unfavorable oxidative addition across the C4–methyl bond.[17]

Mechanistically, carbon–hydrogen bond activation in metal–arene systems is commonly thought to proceed through η^2 coordination of the arene prior to formation of the carbon–metal σ bond.[2] Two frequently invoked pathways involve either oxidative addition across the C–H bond or electrophilic attack at the arene carbon. While no hydridic products were detected, an electrophilic attack by the electron-rich osmium(II) seems unlikely, given the regiospecificity of the metal-substituted products;[18] in addition, no analogous process was found to occur for any of the many pentaammineosmium(II) η^2-arene complexes synthesized to date, contrary to the pattern observed in electrophilic substitution for the free arenes as compared to pyridine rings.[19] The difference in acidity of the ring protons in these aromatic molecules may account for the enhanced reactivity observed in the heterocyclic ligands.

Perhaps most significant is the similarity between the postulated intermediates for C–H activation and fluxional processes in aromatic rings. Of the pentaammineosmium η^2-heterocycle complexes that undergo isomerizations to carbon-bound products, the absence of a 3-substituted species, even in the case of unhindered pyridines, is noteworthy. The coordination sites of the ligands for the former complexes are all 3,4-η^2, in rapid equilibrium with their 4,5-η^2 tautomers. A fluxional process that is restricted to these two positions must go through a σ-bound 4-substituted intermediate. The underlying implication is that the intermediate for tautomerization may be necessary for C–H bond activation. This reasoning could account for the exclusive regiospecificity observed for the $\eta^2 \rightarrow$ C rearrangement of the pyridine ligands on osmium(II). In accord with this hypothesis, a facile $\pi \rightarrow$ C isomerization was not observed for $[(NH_3)_5Os(4,5\text{-}\eta^2\text{-}N,N'\text{-dimethylimidazolium})]^{3+}$, a complex for which no fluxional processes were detected at room temperature.[20]

The aromatic C–H bond activation readily observed for the Os(II) η^2-nitrogen heterocycles is thus far unique to pyridine rings. Five-membered rings such as *N*,*N*′-dimethylimidazolium and pyrroles[20] η^2-bound to pentaammineosmium(II) have not been observed to change to σ carbon-bound species over a period of days.

The lack of a $\pi \rightarrow$ C rearrangement for complex **4** is not surprising. The *N*- and 4-methyl groups in the ligand sterically hinder the 2- and 3-carbon sites and would be expected to hamper the formation of a C-bound species; electronic factors may also contribute to this lack of reactivity, as C4, the binding position in the other heterocyclic ylide complexes, is not available for coordination to the metal center in *N*-methyl-4-picolinium. However, its inertia toward ligand substitution is rather striking, especially when compared to the arene analogue. The complex $[(NH_3)_5Os(2,3\text{-}\eta^2\text{-}p\text{-}C_6H_4(CH_3)_2)]^{2+}$ is among the most labile of the series of Os(II) arene complexes, the half-life for substitution in a *p*-xylene ligand being approximately 4 h in neat acetone at room temperature.[8b] Under the same conditions, no changes were detected in solutions of **4** for over a week, implying that the rate of substitution of the η^2-bound heterocycle must be at least 2 orders of magnitude slower than that for the corresponding arene.[21] As electrostatic arguments would predict a diminished σ interaction

(14) (a) Lehmann, H.; Schenck, K. J.; Chapuis, G.; Ludi, A. *J. Am. Chem. Soc.* **1979**, *101*, 6197. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 3.
(15) Ittel, S. D. *J. Organomet. Chem.* **1977**, *137*, 223.
(16) Sweet, J. R.; Graham, W. A. G. *Organometallics* **1983**, *2*, 135.
(17) Reference 14b, Chapter 5.
(18) The 4-position in free pyridinium rings is highly deactivated toward electrophilic attack; thus, nitration or sulfonation of pyridinium ion yields predominantly 3-substituted products. See: March, J. *Advanced Organic Chemistry*; McGraw-Hill: New York, 1977; Chapter 11.
(19) Pyridines are much less susceptible to electrophilic attack than the analogous arenes.[18]
(20) To be reported separately.
(21) This estimate is based on the kinetic stability of the solvent complex, $[(NH_3)_5Os(\eta^2\text{-acetone})]^{2+}$.[8a]

of the metal with the cationic ligand compared to the neutral xylene homologue, this difference in reactivity is yet another manifestation of the importance of back-bonding in the chemistry of Os(II) centers.

Conclusion

The existence of stable η^2 complexes of pentaammineosmium(II) with poor σ donors such as the above-mentioned cationic heterocycles is remarkable. The interaction of Os(II) with protic ligands such as pyridinium ion is even more striking, given the highly reducing properties of the pentaammineosmium(II) moiety, which render it unstable with respect to oxidation in the presence of protons, and must be a reflection of the high affinity of this electron-rich metal for unsaturated centers.

Reports on η^2-bound nitrogen aromatic heterocycles are scarce. The few reported cases feature coordinatively unsaturated metals with N,C-bound ligands that either are formally doubly reduced[22] or have lost an ortho proton[23] and hence differ markedly from the free ligands. The present work on pentaammineosmium(II) thus represents a unique example of metal π coordination to nitrogen heterocycles. Furthermore, it provides a useful model in the study of aromatic C-H bond activation by transition metals.

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(22) Neithamer, D. R.; Pārkānyi, L.; Mitchell, J. F.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 4421.
(23) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Shaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.

Regioselective Oxidation Catalysis in Synthetic Phospholipid Vesicles. Membrane-Spanning Steroidal Metalloporphyrins

John T. Groves* and Ronny Neumann†

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08544. *Received August 22, 1988*

Abstract: A membrane-spanning porphyrin has been synthesized by attaching four 3β-hydroxy-5-cholenic acid moieties to $\alpha,\beta,\alpha,\beta$-*meso*-tetrakis(*o*-aminophenyl)porphyrin. The resulting steroidal porphyrin, H_2ChP, and the corresponding metalloporphyrins, MChP, were shown by gel permeation chromatography, ^{31}P NMR, and differential scanning calorimetry to intercalate into vesicle bilayers. The steroidal porphyrin was found to be in a well-defined and highly ordered microenvironment within the bilayer. The anisotropic ESR spectra of Cu^{II}(ChP) in orientated bilayer assemblies on Mylar film clearly indicated that the plane of the porphyrin ring was parallel to the plane defined by the bilayer-water interface. The porphyrin ring was also found to be in the middle of the bilayer with fluctuations of ±3-4 Å around the center. This was shown by use of tethered imidazole ligands of the general formula $Im(CH_2)_nCOOH$ as molecular probes. Ligation to Co^{II}(ChP) could be monitored by ESR as a function of the length of the tethered ligand and conclusively demonstrated that only ligands where $n > 6$ were able to coordinate to the metal. Iron(III) and manganese(III) steroidal porphyrins were then used as regioselective epoxidation and hydroxylation catalysts. Diolefinic sterols were epoxidized exclusively at the side chain. Epoxidation of polyunsaturated fatty acids was preferred by a ratio of 2/1 at the more hydrophobic terminus and it was found that by increasing the rigidity of the bilayer by the addition of cholesterol the selectivity could be raised to 9/1. Finally, it was shown that cholesterol could be selectively hydroxylated at the C_{25} tertiary carbon.

Major efforts have been made in recent years to formulate regioselective and stereoselective catalytic systems. The importance of such systems is borne out by the significant impact made by processes such as shape-selective catalysis by zeolites[1] and homogeneous chiral hydrogenations[2] and catalytic asymmetric oxidations.[3] Among the many diverse catalytic systems investigated, those mimicking enzymatic biocatalysis have attracted particular attention. The development of synthetic chemical models that mimic the active site of heme proteins has afforded a detailed understanding of the oxygen binding by globins[4] and oxidations mediated by cytochrome P-450.[5] The binding or arrangement of a potentially reactive substrate in a spatially selective manner so that only a certain defined reaction pathway is possible is another important aspect of enzyme catalysis. The guest-host interactions of crown ethers,[6] cyclodextrins,[7] and molecular clefts[8] have been used extensively to mimic selective binding. Intramolecular geometric control of reactions has also been achieved by appending carefully designed reactive reagents to target substrates.[9] Finally, the intrinsic molecular order found in the microenvironments of monolayers, micelles,[10] and vesicle bilayers[11] has been used with more limited success to specially

* Author to whom correspondence should be addressed.
† Current address: Casali Institute of Applied Chemistry, The Hebrew University of Jerusalem, Israel.

(1) Whyte, T. E.; Dalla Betta, R. A. *Catal. Rev.-Sci. Eng.* **1982**, *24*, 567 and references therein.
(2) (a) Morrison, J. D.; Masler, W. F.; Neuberg, M. K. *Adv. Catal.* **1976**, *25*, 81. (b) Brown, J. M.; Cholener, P. A.; Murrer, B. A.; Parker, D. *ACS Symp. Ser.* **1980**, *119*, 169. (c) Halpern, J. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1985; Vol. 5, p 41.
(3) (a) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974. (b) Rossiter, B. E.; Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1982**, *103*, 464. (c) Rossiter, B. E. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1985; Vol. 5, p 194.
(4) Traylor, T. J.; Koga, N.; Deardurff, L. A. *J. Am. Chem. Soc.* **1985**, *107*, 6504 and references therein.
(5) Ortiz de Montellano, P. *Cytochrome P-450*; Plenum: New York, 1986.
(6) Stoddart, J. F. *New Compr. Biochem.* **1984**, *6*, 529.
(7) (a) Bender, M. L.; Komiyama, M. *Cyclodextrin Chemistry*; Springer: New York, 1978. (b) Tabushi, I.; Kuroda, Y. *Adv. Catal.* **1983**, *32*, 417. (c) Breslow, R. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic: New York, 1984; Vol. 3, p 473.
(8) (a) Rebek, J.; Askew, B.; Killoran, M.; Nemeth, D.; Lin, F.-T. *J. Am. Chem. Soc.* **1987**, *109*, 2426. (b) Rebek, J.; Askew, B.; Nemeth, D.; Parris, K. *J. Am. Chem. Soc.* **1987**, *109*, 2432.
(9) Breslow, R. *Acc. Chem. Res.* **1980**, *13*, 170.
(10) Fendler, J. H. *Membrane Mimetic Chemistry*; Wiley: New York, 1982.

0002-7863/89/1511-2900$01.50/0