the reaction was carried out as in (1) with the H_2O added stoi-

$$18\text{-crown-6} + H_2O + HCl(g) \rightarrow [H_3O^+\cdot 18\text{-crown-6}][Cl\text{-}H\text{-}Cl] \quad (1)$$

chiometrically and the atmosphere excluded. The yield was quantitative based on the macrocycle. The reaction is done in the presence of an aromatic solvent, and liquid clathrates of composition $[H_3O^+\cdot 18\text{-crown-6}][Cl\text{-}H\text{-}Cl]\cdot 4.8C_6H_6$ and $[H_3O^+\cdot 18\text{-crown-6}][Cl\text{-}H\text{-}Cl]\cdot 3.6C_6H_5Me$ have been prepared.[18]

The structure of the $[H_3O^+\cdot 18\text{-crown-6}]^+$ cation is shown in Figure 1. The hydrogen atoms could not be located with certainty, presumably because of disorder.[19] The O(oxonium)···O(crown) separations range from 2.70 to 2.85 Å, and they all are well within the range for hydrogen bonding.[20] The six crown oxygen atoms are planar to 0.20 Å, and the oxonium oxygen atom lies 0.29 Å from this plane. However, it is noteworthy that the oxonium oxygen atom lies only 0.09 Å from the plane of the three nearest crown oxygen atoms. A distance of 0.61 Å from the plane of the hydrogen bonded oxygen atoms was found for the pyramidal oxonium oxygen atom in $[H_3O^+\cdot 18\text{-crown-6(COOH)}_4]Cl$,[3] while a distance of 0.1 Å from the plane of the six oxygen atoms of the ring was observed in $[H_3O^+\cdot 18\text{-crown-6}]_2[Mo_6O_{19}]$.[12] The title compound lends a measure of support for planar H_3O^+, but determination of the proton positions from low-temperature data will provide conclusive proof of the geometry about the oxonium oxygen atom.

The anion $[Cl\text{-}H\text{-}Cl]^-$ was first observed in 1909,[21] and its structure has been determined in several salts.[22-25] The Cl···Cl separation in the title compound, 3.11 Å, is at the low end of the range which stretches up to 3.315 Å.[25] The hydrogen atom was clearly located 1.60 and 1.57 Å from the two chlorine atoms, and the angle at the hydrogen atom is 157°. Although the $[Cl\text{-}H\text{-}Cl]^-$ anion has been studied rather extensively,[26] to our knowledge this is the first instance of it in an aromatic solution. Studies of the chemical reactivity of both $[H_3O^+\cdot 18\text{-crown-6}]^+$ and $[Cl\text{-}H\text{-}Cl]^-$ in aromatic solutions are in progress.

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Supplementary Material Available: Tables of bond distances and angles, final fractional coordinates, and thermal parameters (3 pages); listing of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

(17) In a typical experiment 1.32 g of 18-crown-6 (0.005 mol) was moistened with 0.09 mL of distilled water (0.005 mol) and ca. 30 mL of toluene was layered over the mixture which was contained in a Schlenk tube. Anhydrous HCl(g) was bubbled through the solvent. The evolution of heat was noted immediately, and in 5 min the formation of two liquid layers was apparent. The passage of HCl(g) was continued until the lower liquid layer reached constant volume (ca. 30 min). Large, colorless crystals of the title compound were obtained from the lower layer by allowing the reaction mixture to cool to room temperature. The crystals are hygroscopic and decompose quickly upon exposure to the atmosphere. Those for the X-ray diffraction study were examined under toluene and transferred while wet with toluene to thin-walled glass capillaries. The space group is the monoclinic $P2_1/c$ with $a = 10.455$ (7) Å, $b = 20.701$ (9) Å, $c = 8.552$ (7) Å, $\beta = 96.21$ (3)°, and $D_c = 1.28$ g cm^{-3} for $Z = 4$. Least-squares refinement based on 1100 observed reflections led to a final R value of 0.065. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of the crown ether were placed in calculated positions and were not refined. The hydrogen atom of the anion was located on a difference Fourier map and was not refined. The details of data collection and refinement are given in Holton et al.: Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45.

(18) The stoichiometry of the liquid clathrates was established by ^1H NMR integration. In addition to the toluene, two resonances result: 3.07 ppm (18-crown-6), and 10.36 ppm ($[H_3O^+]$), referenced to the toluene methyl at 2.30 ppm. A resonance due to the proton of the $[Cl\text{-}H\text{-}Cl]^-$ ion was not observed.

(19) Data were collected on two different crystals, and $(\sin\theta)/\lambda$ cut-offs were employed, but the hydrogen atoms of the oxonium group could not be unequivocally located.

(20) Hamilton, W. C.; Ibers, J. A. *Hydrogen Bonding in Solids*; Benjamin: New York, 1968; p 16.

(21) Kaufler, F.; Kunz, E. *Chem. Ber.* **1909**, *42*, 385, 2482.

(22) Schroeder, L. W.; Ibers, J. A. *Inorg. Chem.* **1968**, *7*, 594 ($CsCl\cdot{}^1/_3(H_3O\cdot Cl\text{-}H\text{-}Cl)$).

(23) Williams, J. M.; Peterson, S. W. *Am. Cryst. Assoc. Prog. Abstr.*, Ottawa, Canada, 1970 ($[NMe_4][Cl\text{-}H\text{-}Cl]$).

(24) Mootz, D.; Poll, Wolfgang; Wunderlich, H.; Wussow, H.-G. *Chem. Ber.* **1981**, *114*, 3499 ([phosphonium][Cl-H-Cl]).

(25) Atwood, J. L.; Bott, S. G.; Coleman, A. W.; Zhang, H.; Means, C. M., unpublished results ($[K\cdot 18\text{-crown-6}][Cl\text{-}H\text{-}Cl]$, $[Mg\cdot 18\text{-crown-6}][Cl\text{-}H\text{-}Cl]_2$).

(26) Emsley, J. *Chem. Soc. Rev.* **1980**, *9*, 91.

Pentaammineosmium(II)-η^2-2,6-Lutidine: An Intermediate for C–H Activation

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Though a few transition-metal complexes featuring η^2-bound arene ligands are known,[1] no reports on η^2-nitrogen heterocycles are available to date. The role of η^2-bound ligands as intermediates for arene C–H activation has been established,[2] but such intermediates have heretofore not been isolated. Our interest in the reactivity of pentaammineosmium(II) with aromatic molecules has led to the discovery of a stable η^2-bound 2,6-lutidine complex. We have found that this complex is a precursor for the activation of the para carbon–hydrogen bond.

When $[(NH_3)_5Os(TMB)]^{2+}$ [3] reacts with 2,6-lutidine (lu), a new species characterized as $[(NH_3)_5Os(\eta^2\text{-lu})]^{2+}$ (**1**) can be isolated as a triflate salt.[4] The ^1H NMR spectrum[5] of **1** at −60 ° C reveals inequivalent ring proton resonances at 6.68 (d, 1 H), 5.28 (m, 1 H), and 5.22 (d, 1 H) ppm. The latter two frequencies are shifted ~2 ppm upfield from free ligand values, characteristic of protons that are adjacent to the metal coordination site.[6] Spin saturation exchange was observed between the doublets, indicating a fluxional process where the metal migrates between the [3,4] and [4,5] positions. Upon warming to room temperature, the doublets and methyl resonances broaden significantly but do not coalesce, indicating a specific rate $k < 1.3 \times 10^3$ s^{-1} for tautomerization, corresponding to $\Delta G^\ddagger > 13$ kcal mol^{-1}.[7]

Protonation of the lutidine nitrogen leads to the formation of $[(NH_3)_5Os(\eta^2\text{-luH})]^{3+}$ (**2**).[8] By arguments analogous to those outlined above, it was established that **2** also exists as the [3,4] isomer. For

$$[(NH_3)_5Os(\eta^2\text{-luH})]^{3+} \rightleftarrows [(NH_3)_5Os(\eta^2\text{-lu})]^{2+} + H^+ \quad (1)$$

a pK_a of 7.4 was obtained at room temperature.

A cyclic voltammogram of **1** displays a chemically irreversible oxidation wave at +0.45 V.[9] Upon return scan a new, also

(1) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 1883–1885, and references therein.

(2) (a) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650–1663. (b) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 305–306.

(3) TMB = 1,2,3,4-tetramethylbenzene, see: Harman, W. D.; Taube, H. *Inorg. Chem.* **1987**, *26*, 2917.

(4) Preparation of **1**: Pure 2,6-lutidine (0.5 mL) is added to 0.15 mmol of $[(NH_3)_5Os(TMB)]^{2+}$ [3] in 8 mL of DME solution. After 1 h cold CH_2Cl_2 (15 mL) is added, and the precipitate is filtered and washed with Et_2O.

(5) (a) All NMR spectra recorded in acetone-d_6. (b) Additional peaks: *cis*- and *trans*-ammines, 3.65 (12 H), 4.97 (3 H) ppm; methyl groups, 2.24 (3 H), 2.48 (3 H) ppm.

(6) Harman, W. D. Ph.D. Thesis, Stanford University, 1987. Sekine, M., unpublished results.

(7) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982; pp 79, 96.

(8) Full characterization of **2** will be reported separately.

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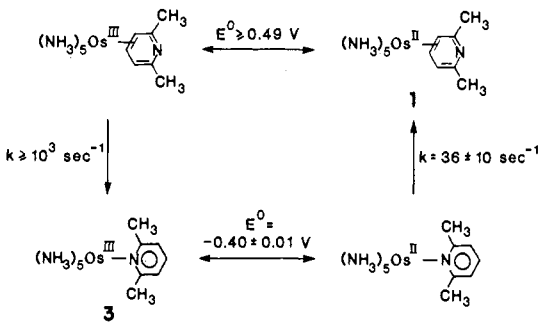
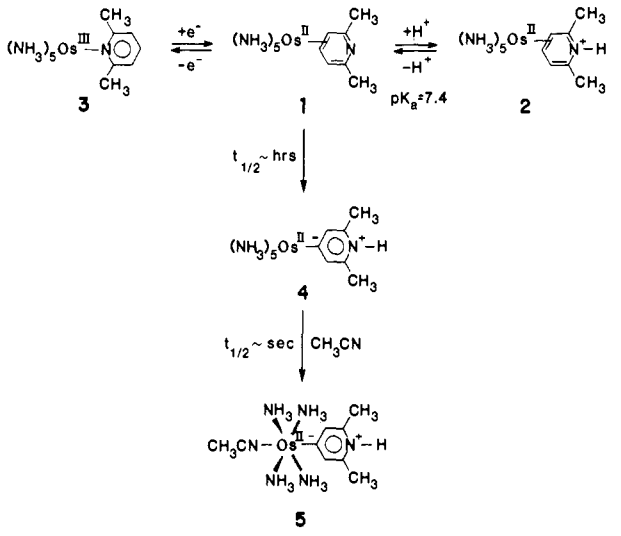
Scheme I



Scheme II



chemically irreversible wave is present at −0.45 V, attributed to the reduction of a new species, **3**. Compound **3** can be generated by chemical oxidation of **1** and persists in DME solution for several hours. Reduction of **3** regenerates **1** quantitatively, suggesting a reversible redox-induced linkage isomerization. Given that $E°$ for the 3+/2+ couples of the pyridine and 3-picoline complexes under the same conditions is approximately −0.45 V,[10] we postulate that **3** is a nitrogen-bound 2,6-lutidine complex of Os(III).

From data obtained at fast scan rates (ν = 10–100 V/s), certain of the relevant dynamic parameters could be determined[11] and are summarized in Scheme I. Attempts to synthesize **3** directly from $(NH_3)_5Os(TFMS)_3$ and 2,6-lutidine failed.

Over a period of hours, **1** rearranges intramolecularly in solution to a new product, **4**, which can be isolated as a deep green solid[12] (Scheme II). A cyclic voltammogram of **4** shows a reversible wave at −0.50 V. A ^{1}H NMR spectrum of this solid shows resonances at 9.92 (s, 1 H, b), 6.95 (s, 2 H), 4.16 (s, 3 H, b), 3.70 (s, 12 H, b), and 1.80 (s, 6 H) ppm, suggesting metal coordination at the para position of a lutidine tautomer, formally a lutidinium ylide. The ^{13}C NMR spectrum[13] of **4** shows singlets at 19.2, 136.8, 141.0 ppm, and a weak resonance at 210.2 ppm, which we attribute to the para carbon.

The ring nitrogen in **4** is not deprotonated by excess proton sponge (pK_a = 12.4) in acetone, though exchange is rapid in the presence of D_2O. An increase by 7 units in the pK_a of pyrazinium ion occurs upon coordination to pentaammineosmium(II), a striking effect attributable to back-bonding.[14] A similar enhancement in the basicity of the ring nitrogen would be expected for the isoelectronic, pentaammineosmium(II) ylide complex **4**.

Compound **4** is unstable with respect to loss of trans NH_3, a feature observed for certain other carbon-bound pentaammine systems.[15] Upon dissolution in acetonitrile, **4** reacts rapidly to form a new product, **5** (Scheme II). A ^{1}H NMR spectrum of **5** confirms the trans coordination of the nitrile ligand.[16] In general, **4** readily reacts with a variety of ligands[17] to yield the corresponding trans substituted tetraammine complexes quantitatively.

Though the preparations and measurements outlined above were performed in rigorously dried nonaqueous solvents, it is noteworthy that once formed **1** resists attack by water and O_2. NMR evidence suggests that in D_2O the rearrangement of **1** to the carbon-bound species takes place over a period of hours.[18]

We have observed analogous carbon–hydrogen bond activation in certain η^2-cationic pyridines,[19] though this reaction has not been detected in any of the many other pentaammineosmium(II) η^2-arenes which have been studied.[1,6] The enhanced reactivity in the heterocyclic systems is in marked contrast to the pattern observed for electrophilic aromatic substitution in the free ligands.

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(9) (a) All redox potentials versus NHE. (b) Electrochemical conditions unless otherwise specified: 0.5 M NaTFMS in DME; ν = 200 mV/s; Pt° working electrode; $Fe(Cp)_2^+/Fe(Cp)_2$ internal reference.

(10) Unpublished results.

(11) (a) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; John Wiley and Sons: New York, 1980; pp 453, 454. (b) Measurements in Scheme I taken in acetone saturated with NaTFMS assuming reversible electron transfer in the range ν = 20–200 mV/s.

(12) Preparation of **4**: Solutions of **1**[4] are allowed to stand for 3 h. Addition of Et_2O (15 mL) causes precipitation of the product which can be purified from acetone and Et_2O.

(13) Proton decoupled; triflate resonance at 123 ppm (q).

(14) Sen, J.; Taube, H. *Acta Chem. Scand.* **1979**, *A33*, 125–135.

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(16) ^{1}H NMR spectrum of **5**: 10.71 (1 H, b), 7.17 (2 H), 3.47 (12 H, b), 2.88 (3 H), 1.98 (6 H) ppm.

(17) E.g., DMSO, pyridine, benzonitrile, isonicotinamide.

(18) Ligand resonances appear with time at 6.53 and 1.63 ppm (ratio 1:3) concomitant with the disappearance of **1**.

(19) Work on pyridinium, *N*-methylpyridinium, 2,6-lutidinium, and *N*-methyl-4-picolinium complexes will be reported separately.

Biosynthesis of Ansatrienin. Nonincorporation of Shikimic Acid into the mC_7N Unit and Stereochemistry of Its Conversion to the Cyclohexanecarboxylic Acid Moiety

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Recent studies on the biosynthesis of ansatrienin A (mycotrienin I) (**1**), a metabolite of *Streptomyces collinus*[1,2] and *S. rishiriensis*,[3-5] have shown that this antibiotic contains two structural moieties originating from the shikimate pathway of aromatic biosynthesis. The cyclohexanecarboxylic acid moiety attached via an alanine residue to the ansa ring is derived intact from the seven carbon atoms of shikimic acid, possibly via 1-cyclohexenecarboxylic acid and 1,4-cyclohexadienecarboxylic acid.[6] The mC_7N unit, representing the benzoquinone ring with the attached nitrogen and C-17, originates specifically from 3-amino-5-hydroxybenzoic acid (AHBA),[6] itself derived via the shikimate pathway.[7-20] However, the exact mode of formation

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(5) Sugita, M.; Sasaki, T.; Furihata, K.; Seto, H.; Ōtake, N.; *J. Antibiot.* **1982**, *35*, 1467.

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