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Extension of the Preparation of New Osmium Species to the *cis*-Tetraammine Moiety

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A useful precursor *cis*-$[Os(NH_3)_4(CF_3SO_3)_2](CF_3SO_3)$ (**1**) has been synthesized by oxidation of the dinitrogen complex *cis*-$[Os(NH_3)_4(N_2)_2]Cl_2$ in CF_3SO_3H. While the reduction of **1** in aqueous solution leads to the η^2-dihydrogen complexes[1] in high yield, in acetone, and at room temperature, however, when reduced by Mg or Zn/Hg, **1** reacts rapidly with a variety of unsaturated ligands. In the presence of norbornadiene and 1,5-cyclooctadiene, the corresponding η^4-diene tetraammine complexes were obtained in recovered yields of 30% and 80%, respectively. Traces of acid left in **1** lead to much reduced yields of these and of other species we have prepared, owing to the formation of the diacetone alcohol complex as a side product in which the ligand bonds to Os(II) center in η^1-(HO–) and η^2-(O=C–) fashion. In the absence of a competing ligand, this chelate complex is the major product of the reaction. In the presence of the arenes, benzene, phenol and naphthalene, reduction of **1** was found to lead to the η^6-arene triammine complexes, the reaction yields as determined by ^{1}H NMR being 64%, 68%, and 95%.

A major interest in the chemistry of ruthenium(II) and osmium(II) ammines has been in their great affinity for π acid ligands.[2a] Because this tendency for osmium is even greater than for ruthenium,[2b,c] motivation for developing this particular aspect of the chemistry of osmium(II) has not been lacking. This development has, however, been delayed because of preparative difficulties. For the case of the pentaammines, these difficulties have in many cases been overcome. The reduction of the precursor $[Os(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$,[3] under anaerobic conditions in non-aqueous solvents, has led to efficient processes for the production of a variety of new species, among them complexes with ketones,[4] aldehydes,[5] arenes,[6] olefins,[7,8] alkynes,[9] and heterocyclics.[10] An even richer chemistry is expected for the tetraammines, for the obvious reason that variety in the auxiliary ligands is now introduced but also because, at least in the cis case, new kinds of reactivity involving interactions of adjacent groups can be expected.

We report herein details on the synthesis of the precursor *cis*-$[Os(NH_3)_4(CF_3SO_3)_2]CF_3SO_3$ and its use in the preparation of a number of new tetraammine species, including organometallic derivatives. The tetraammine complex has proven, for certain ligands, to be a valuable precursor also to triamine complexes.

Glossary

COD, 1,5-cyclooctadiene; DAA, diacetone alcohol; DMA, *N,N*-dimethyl acetamide; DME, 1,2-dimethoxyethane; NBD, norbornadiene; bpy, 2,2′-bipyridine. Numbers are used interchangeably for the cation of interest and the salt of the cation. Where there is a possibility of confusion, the modifiers "species" and "compound," respectively, are used.

Experimental Section

Reagents. All other reagents were used as supplied. All solvents were thoroughly deoxygenated by purging with argon.

Magnesium (turnings) was activated by being stirred with iodine in DME under argon for several hours, and then washed successively with DMA and ether.

Instrumentation and Techniques. All reactions except the synthesis of *cis*-$[Os(NH_3)_4(CF_3SO_3)_2](CF_3SO_3)$ were carried out under argon atmosphere in a Vacuum Atmospheres Corp. glovebox. Infrared spectra were recorded on an IBM 98 FTIR spectrometer as KBr pellets. ^{1}H NMR spectra were recorded on a Varian XL-400 or a Varian Gemini-200 spectrometer. The measurements were made on solutions of the salt, usually the triflate, in acetone-d_6 as solvent. Shifts are reported in ppm from TMS. Where reaction yields in the product solution were determined by ^{1}H NMR spectroscopy, tetramethylsilane was used as an internal standard. Cyclic voltammograms were recorded on a Princeton Applied Research Model 173 potentiostat and Model 175 universal programmer. The sample was dissolved in acetonitrile containing 1 M tetrabutylammonium hexafluophosphate as electrolyte. The measurements were made in a cell outfitted with a Pt^0 working electrode, a Pt^0 auxiliary electrode, and a reference consisting of a Au^0 button electrode immersed in a DME solution containing 0.5 M $NaCF_3SO_3$, separated from the main cell bulk by a Vycor frit. The reference was calibrated with $Fe(Cp)_2^+/Fe(Cp)_2^0$ couple ($E^\circ = 0.55$ V vs NHE) kept in situ. All potentials are reported vs the normal hydrogen electrode. The voltage range was −1.50 to +1.50 V vs NHE, and the scan rate was typically 100 mV s^{-1}.

Preparations. Except where otherwise indicated, it is understood that the solid was obtained by adding ether to the product solution, was collected by filtration, and was washed with ether and finally dried in vacuum.

***cis*-$[Os(NH_3)_4(CF_3SO_3)_2](CF_3SO_3)$ (1). Method A.** *cis*-$[Os(NH_3)_4(N_2)_2]Cl_2$[11] (400 mg) was dissolved in 10 g of CF_3SO_3H and 3 mL of Br_2 was added. The solution was heated from 20 to 120 °C in 10 min, then at 120 °C for 10 min, under a stream of N_2, whereupon it was cooled in an ice bath and anhydrous ether (~100 mL) was added dropwise. The recovered solid was dried by vacuum, and the yield is 90%. Anal. Calcd for $Os(NH_3)_4(CF_3SO_3)_3$: C, 5.11; H, 1.71; N, 7.94. Found: C, 4.88; H, 1.86; N, 7.42. $E_{1/2} = 0.29$ V; $E_{p,c} = -0.54$ V.

Method B. A 500-mg sample of $[Os(NH_3)_4(N_2)_2]Cl_2$ was dissolved in 10 g of CF_3SO_3H contained in a tube. The tube was put in an oil bath

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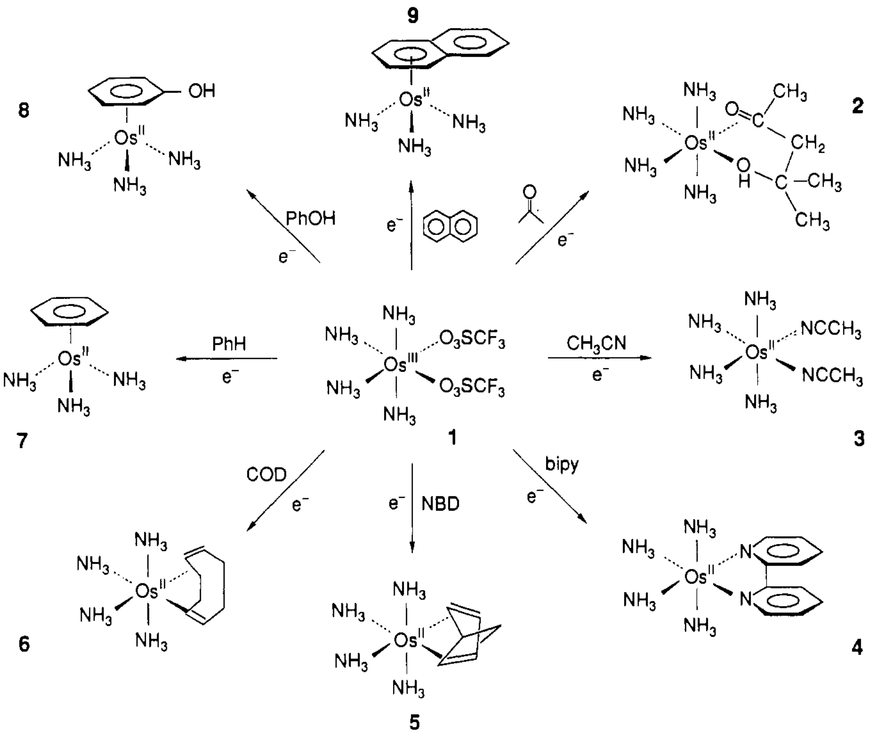
Scheme 1



and kept for 15 min at 130 °C. The color of the solution changed from yellow to green and sometimes then to purple, the result of a highly-colored binuclear osmium species present in small amount. The final yield of the solid (in this case purple) was 70%. Anal. Found: C, 5.34; H, 1.87; N, 7.45.

$[Os(NH_3)_4(DAA)](CF_3SO_3)_2$ (2). Compound **1** (50 mg) was dissolved in acetone (5 mL), and one drop of neat CF_3SO_3H and several pieces of magnesium (1 g) were added. The mixture was stirred for 20 min during which time the solution developed an orange color. The solution was filtered and treated with ether (20 mL). Yield: 70%. Anal. Calcd for $Os(NH_3)_4[(CH_3)_2C(OH)CH_2COCH_3](CF_3SO_3)_2$: C, 14.28; H, 3.60; N, 8.33. Found: C, 14.54; H, 3.41; N, 8.05. ^1H NMR: δ 5.61 (br, 3H), 4.91 (br, 3H), 4.77 (br, 3H), 3.65 (br, 3H), 2.55 (d, 1H, $J = 15.2$ Hz), 1.82 (s, 3H), 1.78 (d, 1H, $J = 15.2$ Hz), 1.30 (s, 3H), 1.20 (s, 3H). $E_{p,a} = 0.58$ V; $E_{p,c} = -0.24$ V.

***cis*-$[Os(NH_3)_4(CH_3CN)_2](CF_3SO_3)_2$ (3).** A 50-mg sample of **1** was dissolved in 10 mL of CH_3CN and 1 g of granulated Zn amalgam was added. After being kept, with stirring, for 1 h, the solution was treated with ether. Yield >90%. Anal. Calcd for $[Os(NH_3)_4(CH_3CN)_2](CF_3SO_3)_2$: C, 11.29; H, 2.84; N, 13.16. Found: C, 10.85; H, 2.61; N, 12.52. ^1H NMR: δ 3.73 (br, 6H), 3.65 (br, 6H), 2.93 (S, 6H). $E_{1/2} = 0.29$ V.

$[Os(NH_3)_4(bpy)](CF_3SO_3)_2$ (4). Compound **1** (100 mg) was dissolved in 5 mL of acetone and bpy (200 mg) added. After the solution was stirred for 1 h, it turned dark purple. Granulated Zn amalgam (1 g) was added, and the mixture was stirred for 1 h and treated with ether. Yield: 94 mg (92%). Anal. Calcd for $[Os(NH_3)_4(C_{10}H_8N_2)](CF_3SO_3)_2$: C, 20.22; H, 2.83; N, 11.94. Found: C, 20.30; H, 2.83; N, 11.44. ^1H NMR: δ 9.2 (d, 2H), 8.24 (d, 2H), 7.05 (t, 2H), 6.92 (t, 2H), 5.05 (br, 6H), 2.86 (br, 6H). $E_{1/2} = 0.16$ V.

$[Os(NH_3)_4(\eta^4\text{-NBD})](B(C_6H_5)_4)_2$ (5). Compound **1** (100 mg) was dissolved in acetone (5 mL), and NBD (0.5 g) and granulated Zn amalgam (1.0 g) were added. The mixture was stirred 3 h and then filtered and treated with ether (20 mL). To separate **5** from a small amount of side product **2** which formed in the reaction, an ion-exchange resin (Sephadex-SP, C-25) column was charged with the solid dissolved in water. The column was eluted with 0.1–0.4 M NaCl solution, and the collected solution was precipitated by $NaB(C_6H_5)_4$ solution and then filtered and washed with water and dried under vacuum. Anal. Calcd for $[Os(NH_3)_4(C_7H_8)](B(C_6H_5)_4)_2 \cdot H_2O$: C, 65.60; H, 6.21; N, 5.56. Found: C, 65.74; H, 6.02; N, 5.67. ^1H NMR: δ 5.1 (br, 6H), 4.4 (br, 2H), 4.37 (d, 4H), 3.97 (br, 6H), 1.29 (S, 2H). Isolated yield: 30%. Most of the osmium ammine may be held up in the polymer which forms in the course of the reaction and which accounts for most of the NBD used.

Table 1. ^1H NMR Data (δ, ppm) for $[Os(NH_3)_4(\eta^6\text{-arene})]^{2+}$ Complexes

	^1H NMR data		
arene	arene in **7–9**	free arenes	ammines
C_6H_6	6.18 (s, 6 H)	7.35 (s, 6H)	4.67 (br, 9H)
C_6H_5OH	6.18 (t, 2H)		
	5.76 (d, 2H)	6.80 (d, 3H)	4.50 (br, 9H)
	5.68 (t, 1H)	7.17 (t, 2H)	
$C_{10}H_8$	7.92 (q, 2H)[a]		
	7.71 (q, 2H)	7.50 (q, 4H)	4.45 (br, 9H)
	6.98 (q, 2H)		
	6.30 (q, 2H)	7.90 (q, 4H)	

[a] Hidden under a peak contributed by free naphthalene.

$[Os(NH_3)_4(\eta^4\text{-COD})](B(C_6H_5)_4)_2$ (6). The method was same as that for **5**. Isolated yield: 83%. Anal. Calcd for $[Os(NH_3)_4(C_8H_{12})](B(C_6H_5)_4)_2$: C, 66.93; H, 6.42; N, 5.58. Found: C, 66.73; H, 6.45; N, 5.88. ^1H NMR: δ 4.75 (br, 6H), 4.12 (br, 10H), 2.1–2.4 (m, 8H).

$[Os(NH_3)_3(\eta^6\text{-benzene})](CF_3SO_3)_2$ (7). Compound **1** (200 mg) was dissolved in acetone (10 mL). Benzene (5 mL) and Zn/Hg (1 g) were added. The solution was stirred for 6 h and then filtered and treated with ether. The yield as determined by ^1H NMR in the product solution was 64%. Isolated yield: 48%. See Table 1 for ^1H NMR data.

$[Os(NH_3)(\eta^6\text{-phenol})](B(C_6H_5)_4)_2$ (8). Compound **1** (60 mg), phenol (300 mg), and Zn/Hg (1.0 g) were added to acetone (5 mL). The mixture was stirred for 3 h and then filtered. At this point, the yield of the desired species, as determined by ^1H NMR in the product solution, was 68%. Isolated yield: 50%. A solid was recovered by precipitation with ether and purification was done as for **5**. When a solution of $Na[B(C_6H_5)_4]$ was added to the fraction collected, a light yellow precipitate formed. This was collected, washed with water, and vacuum dried. Anal. Calcd for $[Os(NH_3)_3(C_6H_5OH)](B(C_6H_5)_4)_2 \cdot 2H_2O$: C, 64.22; H, 5.89; N, 4.16. Found: C, 63.90; H, 5.73; N, 4.11. For ^1H NMR data, see Table 1.

$[Os(NH_3)_3(\eta^6\text{-naphthalene})](B(C_6H_5)_4)$ (9). The method was the same as that described for **8**. Reaction yield: 95% (by ^1H NMR). Isolated yield: 64%. Anal. Calcd for $[Os(NH_3)_3(C_{10}H_8)](B(C_6H_5)_4)_2$: C, 69.12; H, 5.7; N, 4.17. Found: C, 68.93; H, 5.48; N, 4.37. For ^1H NMR data, see Table 1. $E_{1/2} = 1.05$, 0.63 V.

Results and Discussion

Characterization. The results of the preparative work are summarized in Scheme 1.

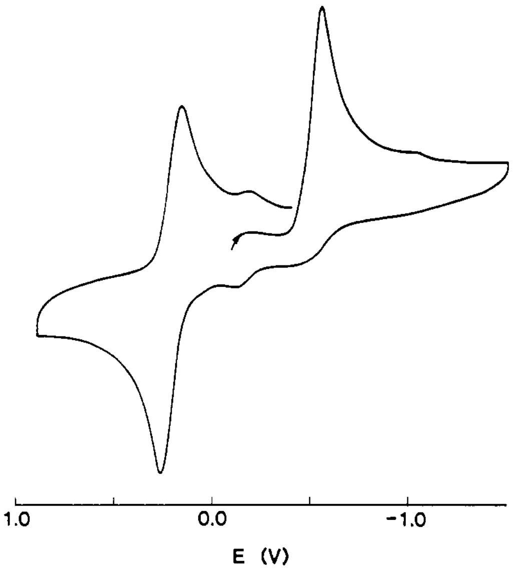


Figure 1. Cyclic voltammetric behavior for *cis*-$[Os(NH_3)_4(CF_3SO_3)_2]^+$ in acetonitrile. Scan rate: 100 mV s^{-1}. Electrolyte: 1 M tetrabutylammonium hexafluorophosphate. *E* is given vs NHE.

Although the reaction in method B is carried out in air, the release of dinitrogen may not be the result of oxidation by O_2. An experiment was conducted in which a stream of argon was passed through the solution, and reaction in this case also was observed to be complete in 15 min. It is conceivable that protons are involved in the release of N_2, by acting as oxidants. Alternatively, under the extreme reaction conditions, N_2 may be reduced, but this possibility remains to be investigated.

The infrared spectrum of **1** showed no bands attributable to coordinated water or N_2. Strong peaks appear in the frequency region 1000 to 1400 cm^{-1}, characteristic of sulfonate esters.[12] The IR spectrum differs little from that of $[Os(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$[3].

In Figure 1 is shown the cyclic voltammogram of compound **1** taken in acetonitrile. On the first scan, no oxidation wave is observed, but a broad wave appears at −0.54 V which we ascribe to the reduction of the cation of **1**. There is no corresponding oxidation wave, but on continuing the scan, reversible couples are observed at $E_{1/2} = -0.09$ and +0.29 V, which we assign to species in which, respectively, one and two triflate anions have been replaced by acetonitrile. The latter value corresponds exactly to that observed for species **3** under the same conditions.

Species **2** was first encountered in reducing compound **1** in acetone with Mg. The ^1H NMR spectrum is reproduced exactly when DAA, which results from the union of two acetone molecules,[13] is used as entering ligand,[14] and it corresponds to a structure in which this ligand is bound in chelate form to the metal ion. The broad peaks, each corresponding to 3H, at δ 5.61, 4.91, 4.77, and 3.65 are assigned to ammine protons. The large spread in values suggests that the carbonyl is bound in the η^2 mode, just as it is in the pentaammineacetone complex.[4] A clear AB system (2.55, doublet, 1H, $J = 15.2$ Hz, and 1.78, 1H, doublet, $J = 15.2$ Hz) is assigned to the CH_2 group, which in the chelate form is not free to rotate. (In free DAA, the CH_2 appears as a single peak at δ 2.63.) The remaining peaks are assignable to the CH_3 groups of DAA.

The conclusion that the keto group is bound in η^2 fashion is supported by the electrochemical data, which resemble those reported[4] for $[Os(NH_3)_5(\eta^2\text{-}(CH_3)_2CO)]^{2+}$ and by the observation that when **2** is dissolved in acetonitrile, there is no detectable substitution even after several days. The latter observation suggested that the utility of the DAA complex as a precursor for the preparation of other complexes is more limited than it is by the method which was adopted. This does not mean however that it may not prove to be valuable for certain purposes. It does have the advantage that it can be prepared and stored as a stable solid.

Early in our work, the yield of other desired species was much reduced by the side reaction to form the DAA complex. On repeated crystallization of **1** from acetone, the yields were much improved. We ascribe the improvement to removal of the residual acid from the solid, which can act as a catalyst for the conversion of acetone to DAA. There is no reason to believe that the condensation waits on the reduction of Os(III) to Os(II), and in fact this is contraindicated by the observation[4] that the rate of exchange of methyl protons with the environment is very much reduced when acetone is bound in the η^2 mode to Os(II).

The ^1H NMR spectrum of species **3** is very simple with two broad peaks at δ 3.73 and 3.65 and a sharp peak at δ 2.93 ppm, in a 1:1:1 ratio, the first two of which we assign to the two kinds of ammine protons expected for a cis configuration and the last to the methyl protons.

The ^1H NMR spectrum for species **4** is fully consistent with a cis configuration, which in this case is the only reasonable possibility when the bifunctional ligand is chelated. In species **4** the two kinds of ammine protons are widely separated, appearing at δ 5.05 and 2.86.

The two broad peaks at δ 5.1 and 3.97 in the ^1H NMR spectrum of **5** are assigned to trans and cis ammines. The three other peaks at δ 4.40 (singlet), 4.37 (doublet, $J = 2.37$ Hz), and 1.29 (singlet) in the ratio 2:4:2 are assigned to CH, CH═CH, and CH_2 groups, respectively. The upfield shifts of NBD on being ligated, by 0.64 ppm for CH_2 and 2.37 ppm for CH═CH, indicate the operation of a strong diamagnetic Fermi contact effect[15] and are consistent with the proposed structure.

The two broad peaks in the ^1H NMR spectrum of **6** (tetraphenylborate salt) are assigned to the ammines. On converting **6** to the triflate salt[16] the peak at δ 4.12 separates into two, one now at δ 4.09, the other at δ 3.92, in a ratio of 4:6, and accordingly the peak at δ 4.09 is attributed to the CH═CH function. The multiple peaks (relative intensity 8H) in the region 2.1–2.4 are assigned to the four CH_2 groups. The pattern for the ligand resembles that recorded for $Os(COD)(C_3H_5)_2$, in which the CH═CH resonances appear at δ 3.81 and 1.20 and the CH_2 resonances at δ 1.4–3.4.[17]

The ^1H NMR data for the arene complexes are summarized in Table 1. The resonances we measured for **7** are very close to those reported for $[Os(NH_3)_3(\eta^6\text{-}C_6H_6)](PF_6)_2$ as prepared by a different procedure[18] (δ 6.17 (S, 6H), 4.6 (9H) measured in acetone-d_6).

Among the few η^6 phenol complexes reported is that with the moiety $Rh(NBD)_2$ which shows ^1H NMR frequencies at δ 6.7–6.8.[19] The frequency region for **8** is not far removed from that of the rhodium complex, but the range covered by the signals for the ring protons is much greater in our case. The 2:2:1 pattern observed for the arene protons is consistent with the η^6 structure, which is well established by the fact that a single resonance is observed for the ammine protons. The failure to observe the

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(14) Prepared in neat DAA by reducing **1** with Zn/Hg for 1 h. The solid which formed on adding ether was collected, and washed with ether, then dried in vacuum. ^1H NMR (acetone-d_6): 5.60 (br, 3H); 4.91 (br, 3H), 4.77 (br, 3H); 3.64 (br, 3H); 2.54 (d, 1H, $J = 15.0$ Hz); 1.82 (s, 3H); 1.78 (d, 1H, $J = 15$ Hz); 1.29 (s, 3H), 1.20 (s, 3H).

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(16) To an acetone solution of **6**, add tetrabutylammonium trifluoromethansulfonate and then precipitate by adding CH_2Cl_2.

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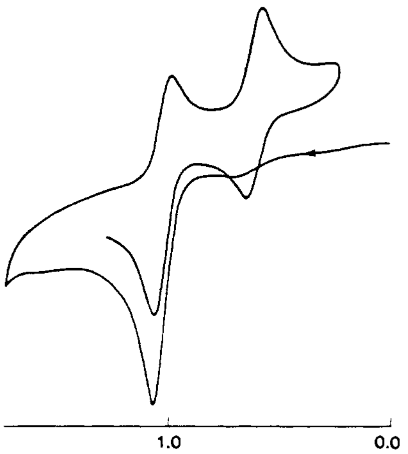

Figure 2. Cyclic voltammetric behavior for $[Os(NH_3)_3(\eta^6\text{-naphthalene})][B(C_6H_5)_4]_2$. Conditions same as Figure 1.

hydroxyl proton may be the result of exchange with residual D_2O in the solvent.

For species **9**, the ammine resonances as a singlet, and the four arene resonances in the ratio of 9:2:2:2:2 support the η^6 structure assigned to it. A similar pattern has been observed[20] for $Ru[(C_{10}H_8)_2](PF_6)_2$. Binding of Os(II) to benzene and to phenol in the η^6 mode cause the arene proton peaks to undergo marked upfield shifts. In the naphthalene complex two peaks shift upfield while two shift downfield. In taking account of the results for the monoring cases, it is reasonable to assign the protons for naphthalene which experience the upfield shifts, to the ring which bears the metal ion.

In Figure 2, the cyclovoltammetric trace obtained for **9** dissolved in CH_3CN is shown. At the particular scan rate of the experiment, 100 mV s^{-1}, an oxidation wave above 1.0 V is accompanied by a reduction wave of considerably lower amplitude ($E_{1/2}$ for the couple = 1.05 V), which is followed by a reversible couple at $E_{1/2}$ = 0.63 V. We infer that, on oxidation of species **9**, the aromatic ligand is partially lost and that the feature at $E_{1/2}$ = 0.63 V corresponds to the $[Os(NH_3)_3(CH_3CN)_3]^{3+/2+}$ couple. The fact that **9** in the oxidized state persists as long as it does may suggest that on 1e^- oxidation a conversion from η^6 mode to η^4 or η^2 mode takes place. Another possibility is that there is scope for the investigation of mixed-valence molecules of aromatic fused ring systems when $Os(NH_3)_2$ is attached in the η^6 mode. A serious difficulty which has been encountered in η^2 attachment is the tendency for both osmium(II) centers to attach to the same ring. This is not likely to be a problem in the η^6 attachment mode.

It should be noted that, in the case of the benzene complexes, no hint of an η^2 or η^4 adduct was observed in the ^1H NMR traces. The time elapsed from mixing the reagents to making the measurements on a recovered solid product however is several hours. Some of the arene preparations were done in acetone-d_6 as solvent, and this makes possible product characterization in the reaction solution. Among these arenes featured in our work, naphthalene reacts most rapidly and benzene the least. In an experiment with naphthalene ^1H NMR measurements were made 30 min after onset of reaction, and again, 2.5 hr later. These traces are shown in Figure 3A,B. At the earlier time, in the arene region, the signals for the final product are seen, and as well, four additional peaks, also in the 2:2:2:2 ratio (see Figure 3A). With time these diminish in intensity and those for the η^6 product grow (see Figure 3B). The simplicity of the pattern for the intermediate is consistent with η^4 binding of $Os(NH_3)_4^{2+}$ to naphthalene and not with that recorded for the η^2 binding of $Os(NH_3)_5^{2+}$ adduct, which shows a much more complex signal.[21]

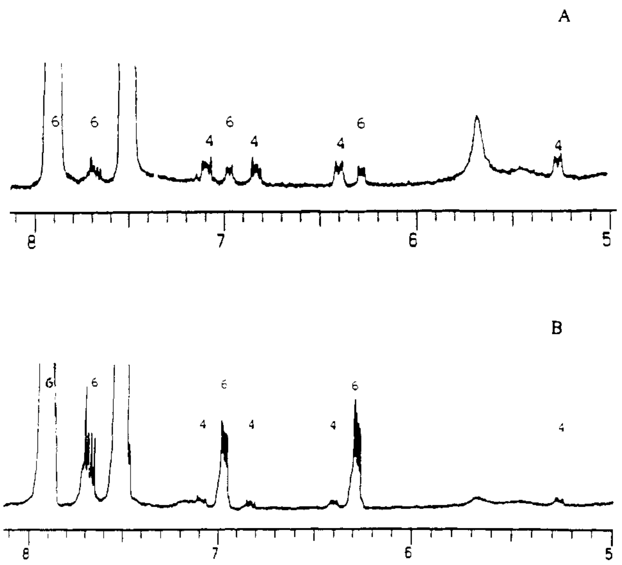

Figure 3. ^1H NMR spectra on the conversion of *cis*-$[Os(NH_3)_4(CF_3SO_3)_2]^+$ to $Os(NH_3)_3(\eta^6\text{-naphthalene})]^{2+}$ in acetone-d_6 as solvent taken (a) 30 min after onset of reaction or (b) 2.5 h later. The numbers 4 and 6 identify the bands ascribed to the η^4 intermediate and the η^6 final product, respectively.

In the case of phenol, an intermediate species prior to collapse to the η^6 form is also observed, but because of the lower symmetry, we are unable to distinguish between η^2 and η^4 binding. Although an intermediate η^4 binding stage was not observed for benzene as entering ligand, there is little doubt that it is involved in the reaction to produce the η^6 product. The experience on the relative ease of replacement from $Os(NH_3)_5^{2+}$ of benzene compared to acetone makes it altogether likely that assistance from the cis position through an η^4 intermeidate enables the formation of the final η^6 product.

General Comments

The work described shows that preparative chemistry of the organometallic complexes of tetraammineosmium(II) and related species is tractable, making possible in-depth investigation of new kinds of molecules. Moreover, the facile conversion of the tetraammine to a triammine by coordination to an arene has promise of leading to extension of the field of the triammines.

That the preparative chemistry succeeds in acetone as a solvent, in the face of the known high affinity of acetone for $[Os(NH_3)_5^{2+}$, is quite remarkable and is worthy of consideration. The diacetone alcohol adduct to Os(II), at least for some ligands, has been shown to be stable to conversion and cannot figure as an intermediate. The fact that product yields are improved when the conditions are less conducive to the formation of DAA supports the conclusion. The reduction to the 2+ state cannot be rate determining, given the relative constancy of factors such as the ratio of solid reductant to solution volume and stirring rate, because this would lead to a rather uniform rate of product formation in the different cases, which is far from the case. Thus, an intermediate must accumulate, which is either a triflate or a solvento (acetone) adduct. In all likelihood, such an adduct would contain at least one acetone molecule in the η^2-bound form. This then appears to limit the scope of this particular preparative method to ligands which lead to complexes more stable than those with acetone-bound η^2, but it is clear from this work that this is not a severe limitation on its usefulness.

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