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**Registry No.** (TMTSF)<sub>2</sub>BF<sub>4</sub>, 73731-79-0; neutron, 12586-31-1.

**Supplementary Material Available:** Tables S1–S3—positional

and anisotropic thermal parameters of all atoms (20, 125, and 298 K); Table S4—some least-squares planes (20, 125, and 298 K) (6 pages); Tables S5 and S6—observed and calculated structure factors for the 20 K neutron data collected after slow cooling and fast cooling, respectively, of the (TMTSF)<sub>2</sub>BF<sub>4</sub> crystal (20 pages). Ordering information is given on any current masthead page.

## Synthesis, Characterization, and Reactivity of the ( $\eta^2$ -Acetone)pentaammineosmium(II) Complex

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**Abstract:** When [Os(NH<sub>3</sub>)<sub>5</sub>(CF<sub>3</sub>SO<sub>3</sub>)]<sup>2+</sup> is reduced in acetone a novel ( $\eta^2$ -acetone)pentaammine complex is formed which shows markedly different reactivity from the ruthenium analogue. The crystal structure has been determined and C–O, Os–O, and Os–C bond lengths are found to be 1.32, 2.06, and 2.13 Å, respectively. The  $\nu$ (C–O) has been assigned by isotopic labeling to be 1330 cm<sup>−1</sup>.

A major interest in the chemistry of ruthenium(II) and osmium(II) pentaammines has been in their high affinity for  $\pi$ -acid ligands.<sup>1</sup> Although this effect is more dramatic in osmium,<sup>2</sup> the development of this chemistry has been hampered by the instability of osmium(II) pentaammine complexes in aqueous media.<sup>3</sup>

In our search for a convenient precursor to ( $\pi$ -acid)pentaammineosmium(II) complexes, we have investigated the reduction of [Os(NH<sub>3</sub>)<sub>5</sub>(CF<sub>3</sub>SO<sub>3</sub>)](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> in acetone. Instead of the labile ruthenium analogue we had expected,<sup>4</sup> we isolated a product that resists reaction with water, is stable at elevated temperatures, and is very slow to undergo substitution by stronger  $\pi$ -acids such as CO and isonicotinamide. This product has been characterized as [Os(NH<sub>3</sub>)<sub>5</sub>((CH<sub>3</sub>)<sub>2</sub>CO)]<sup>2+</sup> (I). The complex has the unusual structural feature that the acetone is bound to the metal through both carbon and oxygen.  $\eta^2$ -bound aldehydes and ketones have been observed in relatively few organometallic compounds,<sup>5,6</sup> and in most cases the aldehyde or ketone contains electron-withdrawing groups.

Here we describe the characterization and structure determination of this novel complex and include a brief discussion of its reactivity.

### Experimental Section

**Reagents.** [Os<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub>(TFMS)](TFMS)<sub>2</sub> (TFMS = CF<sub>3</sub>SO<sub>3</sub><sup>−</sup>) was synthesized as described by Lay et al.<sup>7</sup> The acetone was purified by

**Table I.** Crystal and Diffractometer Data for [OsA<sub>5</sub>(CH<sub>3</sub>)<sub>2</sub>CO]Cl<sub>2</sub>

empirical formula	Os <sub>1</sub> Cl <sub>2</sub> O <sub>1</sub> N <sub>5</sub> C <sub>3</sub>
color of crystal	orange
space group	<i>Pbca</i>
cell dimensions, Å	
<i>a</i>	9.501 (5)
<i>b</i>	10.039 (6)
<i>c</i>	25.19 (3)
<i>Z</i>	8
<i>V</i> , Å <sup>3</sup>	2404 (3)
calcd density, g/cm <sup>3</sup>	2.23
mol wt	404.3
limits of data collection, deg	
2 $\theta$ min	2
2 $\theta$ max	55
unique reflns	3158
refln with <i>F</i> <sub>o</sub> > 3 $\sigma$	1753
<i>R</i>	0.055
<i>R</i> <sub>w</sub>	0.064
absorption correction	yes
$\mu$ , cm <sup>−1</sup>	110.488

vacuum distillation over B<sub>2</sub>O<sub>3</sub>,<sup>8</sup> Et<sub>2</sub>O by distillation over Na<sup>0</sup> and benzophenone, and MeOH by distillation over Mg(MeO)<sub>2</sub> prepared in situ by Mn<sup>0</sup> and I<sub>2</sub> under agron.<sup>9</sup> Bis(triphenylphosphoranylidene)ammonium chloride (PPNCl) (Aldrich Chemical Co.) and H<sub>2</sub><sup>18</sup>O (Stohler/KOR) were used without further purification. All solvents were thoroughly deoxygenated by purging with argon. All reactions were carried out under argon atmosphere in a Vacuum Atmospheres Corp. glovebox.

Infrared spectra were recorded on an IBM 98 FTIR spectrometer. <sup>13</sup>C and <sup>1</sup>H NMR spectra were recorded on a Varian XL-400 spectrometer.<sup>10</sup> Electrochemical experiments were performed on a PAR Model 173 potentiostat which was driven by a PAR Model 175 universal programmer. Cyclic voltammograms were taken with a gold working electrode (3 mm<sup>2</sup>), a platinum counter electrode, and a silver wire reference which was calibrated with the ferrocene/ferrocenium couple kept in situ. The peak-to-peak separation for this couple was ca. 60 mV for all cyclic voltammograms reported. Cyclic voltammograms taken at fast scan rates (1–500 V/s) were recorded on a Tektronix single-beam storage oscilloscope.

The measurements required for the calculation of the equilibrium constant were performed with use of modified rotated disk technique in

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- (10) All NMR spectra are presented in ppm shift from tetramethylsilane.

**Table II.** Bond Distances in Angstroms<sup>a</sup>

atom 1	atom 2	distance
Os1	O1	2.057 (7)
Os1	C1	2.126 (11)
Os1	N1	2.125 (10)
Os1	N2	2.141 (10)
Os1	N3	2.145 (10)
Os1	N4	2.147 (10)
Os1	N5	2.118 (10)
O1	C1	1.322 (13)
C1	C2	1.553 (15)
C1	C3	1.51 (2)

<sup>a</sup>Numbers in parentheses are estimated standard deviations in the least significant digits.

**Table III.** Bond Angles for Selected Atoms

atom 1	atom 2	atom 3	angle, deg
Os1	O1	C1	74.5 (6)
Os1	C1	O1	68.7 (6)
N1	Os1	C1	162.0 (4)
N1	Os1	O1	161.2 (4)

which the electrode was stationary and the solution was rapidly stirred. A 1800- $\mu$ F capacitor was used as a low pass filter, and the scan rate was 5 mV/s.

**Crystal Structure Determination (Table I).** The data set was acquired with use of the  $\theta$ - $2\theta$  scan technique on a Syntex P(2)1 diffractometer with graphite monochromated Mo K $\alpha$  radiation (Table I). The osmium position was located by Patterson techniques and the remaining atoms by difference Fourier synthesis. No attempt was made to locate or refine hydrogen atoms. Final full-matrix least-squares refinement with use of anisotropic temperature factors was calculated on the basis of 1741 unique reflections with conditions  $F_o > 3\sigma$  and  $\sin \theta/\lambda > 0.05$ . The observed and calculated structure factors and temperature factors are available in supplementary material.

**Preparation of [Os(NH<sub>3</sub>)<sub>5</sub>((CH<sub>3</sub>)<sub>2</sub>CO)](TFMS)<sub>2</sub> (I).** [Os(NH<sub>3</sub>)<sub>5</sub>(TFMS)](TFMS)<sub>2</sub> (1.20 g) was dissolved in 20 mL of acetone, and several pieces of scraped magnesium (3.0 g) were added. The mixture was stirred for 2.5 h during which time the clear solution developed a deep orange color. The solution was then filtered and treated with diethyl ether (Et<sub>2</sub>O) (100 mL). The resulting solid was collected by filtration, washed with ether, and then dried under vacuum for 4 h. Crystals of [Os(NH<sub>3</sub>)<sub>5</sub>((CH<sub>3</sub>)<sub>2</sub>CO)](TFMS)<sub>2</sub>· $\frac{1}{2}$ ((CH<sub>3</sub>)<sub>2</sub>CO) were grown from acetone by vapor diffusion of cyclohexane. Crystals of [Os(NH<sub>3</sub>)<sub>5</sub>((CH<sub>3</sub>)<sub>2</sub>CO)]Cl<sub>2</sub> were prepared by dissolving stoichiometric amounts of I and PPNCI in MeOH followed by vapor diffusion of acetone.

Anal. Calcd for C<sub>5</sub>H<sub>21</sub>F<sub>6</sub>N<sub>5</sub>O<sub>7</sub>OsS<sub>2</sub>· $\frac{1}{2}$ ((CH<sub>3</sub>)<sub>2</sub>CO): C, 11.82; H, 3.66; N, 10.60. Found: C, 11.75; H, 3.48; N, 10.57. <sup>1</sup>H NMR<sup>10</sup> (acetone-*d*<sub>6</sub>)  $\delta$  5.53 (br, 3), 4.04 (br, 11.8), 1.63 (s, 6.0); <sup>13</sup>C NMR (D<sub>2</sub>O)  $\delta$  24.4 (s), 83.5 (s), 123.0 (q, TFMS); UV/vis (acetonitrile) 457, 327 nm; IR (KBr pellet) 1080 (s), 2850 (w), and 2950 (w) cm<sup>-1</sup> (see ref 18).

**Preparation of Isotopically Labeled Derivatives.** <sup>18</sup>O-labeled I was prepared as above with <sup>18</sup>O-labeled acetone. Deuteration of the amines was accomplished by dissolving I in a solution of degassed deuterium oxide containing a trace of triethylamine. After 2 h, Et<sub>2</sub>O was added and the resulting solid was collected and washed as above.

**Preparation of <sup>18</sup>O-Labeled Acetone.** A solution of 2 mL of H<sub>2</sub><sup>18</sup>O and 1 mL of acetone with a trace of trifluoromethanesulfonic acid (HTFMS) was allowed to stand for 1 h. CsCl was then added until a phase separation was induced. The acetone layer was pipetted off and dried over more CsCl. An NMR spectrum of the product showed approximately 1 mol % of H<sub>2</sub>O impurity. Analysis by infrared absorption showed the product to contain approximately 80% <sup>18</sup>O-labeled acetone, (CO stretch 1676 cm<sup>-1</sup>).<sup>11</sup>

## Results and Discussion

**Crystal Structure.** The principal feature of I is that the acetone ligand is bound to osmium in a  $\eta^2$ -mode with the M-C and M-O bond lengths being almost the same (2.13 and 2.06 Å, respectively) (Table II). The carbonyl lies in a common plane with three of the amines forming pentagonal bipyramidal coordination (Table III). The C-O bond length has been increased from its uncoordinated value of 1.22 to 1.32 (1) Å. This increase is consistent with an increase of electron density in the ligand  $\pi^*$  orbital due

**Table IV.** Positional Parameters for the Structural Determination of I<sup>a</sup>

atom	x	y	z	B, Å <sup>2</sup>
Os1	0.02701 (5)	0.22065 (5)	0.11922 (2)	1.820 (8)
Cl1	0.2842 (4)	0.5318 (4)	0.4767 (2)	3.35 (8)
Cl2	0.3432 (5)	0.5688 (5)	0.3018 (2)	4.5 (1)
O1	0.299 (1)	0.602 (1)	0.1309 (4)	2.9 (2)
N1	0.315 (1)	0.281 (1)	0.3929 (6)	3.8 (3)
N2	0.562 (1)	0.526 (1)	0.1266 (6)	3.6 (3)
N3	0.560 (1)	0.430 (1)	0.3932 (5)	2.7 (3)
N4	0.485 (2)	0.245 (2)	0.2976 (5)	3.6 (3)
N5	0.450 (1)	0.686 (1)	0.0368 (5)	3.2 (3)
C1	0.251 (2)	0.726 (1)	0.1306 (5)	2.2 (2)
C2	0.698 (2)	0.786 (2)	0.3162 (6)	3.6 (3)
C3	0.340 (2)	0.263 (2)	0.0837 (6)	3.0 (3)

<sup>a</sup>Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as the following:  $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$ .

**Table V.** Structural Features of  $\eta^2$  Aldehydes and Ketones

complex	C-O, Å	$\Delta$ C-O, Å	$\beta$ , deg	M-C, Å	M-O, Å	$\Delta$ M-C, M-O <sup>a</sup> , Å
L <sub>2</sub> Ni((CF <sub>3</sub> ) <sub>2</sub> CO) <sup>b</sup>	1.32	0.09	48	1.89	1.87	-0.02
L <sub>2</sub> Ni(Ph <sub>2</sub> CO) <sup>c</sup>	1.33	0.10	63	1.97	1.85	0.12
[(NH <sub>3</sub> ) <sub>5</sub> Os(CH <sub>3</sub> ) <sub>2</sub> CO] <sup>2+</sup>	1.32	0.10	55	2.13	2.06	0.07
(CO) <sub>2</sub> L <sub>2</sub> OsCH <sub>3</sub> O <sup>d</sup>	1.58	0.37		2.19	2.04	0.15
L <sub>3</sub> Mo(PhCHO) <sup>e</sup>	1.33	0.10		2.26	2.07	0.19
(Cp) <sub>2</sub> Mo(CH <sub>2</sub> O) <sup>f</sup>	1.36	0.15		2.25	2.05	0.20

<sup>a</sup>Bond length (M-C) - bond length (M-O). <sup>b</sup>L = PPh<sub>3</sub>; from ref 5a. <sup>c</sup>L = PEt<sub>3</sub>; from ref 5c. <sup>d</sup>L = PPh<sub>3</sub>; ref 5e. <sup>e</sup>Cp(Mo( $\eta^2$ -PhCHO)( $\eta^2$ -C[2-Py][Ph]NHMe)(CO)); ref 51. <sup>f</sup>Reference 5g.

**Table VI.** NMR of [Os(NH<sub>3</sub>)<sub>5</sub>((CH<sub>3</sub>)<sub>2</sub>CO)](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> in Various Deuterated Solvents

solvent	DN	trans	cis	methyl
(CD <sub>3</sub> ) <sub>2</sub> NCOH	24.0	5.62 (3)	4.10 (11.6)	1.55 (5.6)
CD <sub>3</sub> OH	20.0	5.19	3.74	1.49
D <sub>2</sub> O	18	a	3.80 (12)	1.55 (5.5)
(CD <sub>3</sub> ) <sub>2</sub> CO	17.0	5.53 (3)	4.04 (11.8)	1.63 (6.1)
CD <sub>3</sub> CN	14.1	4.85 (3)	3.39 (11.6)	1.47 (6.3)
(CD <sub>3</sub> )C/CD <sub>3</sub> CN <sup>b</sup>		5.00 (3)	3.55 (11.8)	1.57 (5.6)

<sup>13</sup>C NMR in D<sub>2</sub>O<sup>c</sup> 24.39, 83.51 ppm

<sup>a</sup>Trans peak lies beneath HOD impurity. <sup>b</sup>Solution is 30% acetone to 70% acetonitrile (v/v). <sup>c</sup>Proton-decoupled spectrum; 300-MHz spectrophotometer; *p*-dioxane reference.

to back-bonding from the high-energy 5d orbitals of the osmium. Acetone does not exhibit a noticeable trans influence, as the M-N bond length of the ammine trans to acetone does not differ significantly from that of the cis amines. The organic ligand itself deviates greatly from planarity as is the case with most unsaturated ligands which are  $\pi$ -bound.<sup>5b</sup> To describe the amount of distortion of the unsaturated ligand, the angle  $\beta$  has been defined as the angle between the C-O bond and the normal to the substituent plane of the carbonyl group.<sup>12</sup>  $\beta$  for the present structure is 55° whereas for unbound acetone  $\beta$  would be 90°.

In Table V, values of  $\beta$  are given for the other  $\eta^2$ -aldehydes and ketones which have been reported. It is not known to what extent the *cis*-ammines sterically hinder the methyl groups, but as we report below, there is no indication of a rotational barrier about the  $\sigma$  axis, even at a temperature of -90 °C.

**Carbon and Proton NMR.** The <sup>1</sup>H and <sup>13</sup>C NMR (Table VI) of I are consistent with an  $\eta^2$ -bound acetone complex in which the acetone rotates freely about the metal-ligand  $\sigma$  bond. The proton NMR in acetone-*d*<sub>6</sub> shows three peaks in a ratio of 3 (5.53 ppm):12 (4.04 ppm):6 (1.63 ppm) which are assigned to *trans*- and *cis*-ammines and the methyl singlet, respectively. Upon oxidation, these peaks decay proportionately, there is a paramagnetic shift,<sup>13</sup>

(11) IR spectrum taken of neat liquid on KBr salt plate.

(12) Stalick, J. K.; Ibers, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 5333.

Table VII.  $^{13}\text{C}$  Shifts for Various  $\Pi$ -Bound Unsaturated Ligands

complex	$\Delta\delta(\text{C}_{\text{CO}})^a$ ppm	$\delta(\text{C}_{\text{CO}})$ ppm	$\delta(\text{C}_{\text{CO}})$ (free ligand), ppm
(Cp) $_2$ Zr(PhCOPh) <sup>b</sup>	99	92.5	191
L $_2$ (CO) $_2$ Fe(HCOH) <sup>c</sup>	116	73.7	~190
[P(O- <i>o</i> -tolyl) $_3$ ] $_2$ NiCH $_2$ CH $_2$ <sup>d</sup>	75.4 <sup>f</sup>	47.4 <sup>f</sup>	123 <sup>f</sup>
Me $_2$ CpTa(CH $_3$ ) $_2$ CO <sup>e</sup>	104	111	215
[(NH $_3$ ) $_5$ Os(CH $_3$ ) $_2$ CO]	132	83	215

<sup>a</sup>The difference in chemical shifts of the carbonyl carbon for the free and bound ligands. <sup>b</sup>Reference 5h. <sup>c</sup>L = P(OCH $_3$ ) $_3$ ; ref 5j. <sup>d</sup>Reference 19. <sup>e</sup>Reference 5d. <sup>f</sup>Values refer to the olefinic carbon.

Table VIII.  $E_{1/2}$  for Various [OsA $_5$ L] $^{(2+/3+)}$  Complexes

L	$E_{1/2}$ (vs. NHE), V	ref
H $_2$ O	-0.73	28
NH $_3$	-0.78	28
CH $_3$ CN	-0.29	7
PhCN	-0.20	16
isn	-0.24	29

and quantitative release of acetone to the solvent is observed.

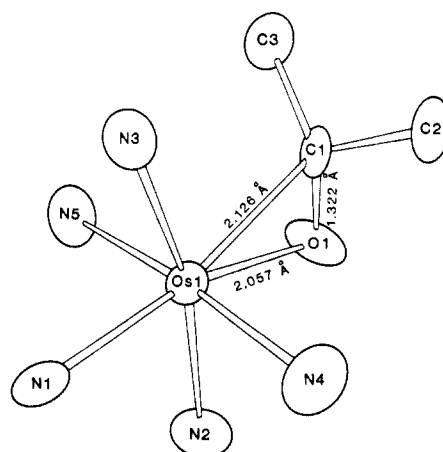
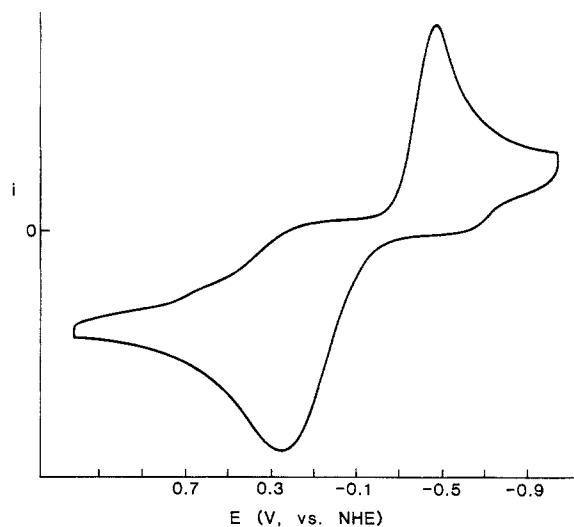
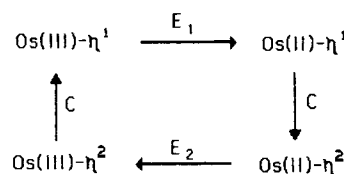
A low-temperature study of I was carried out in acetone- $d_6$ . Even at -93 °C, there is no broadening or splitting of the *cis*-ammine signal at 4.05 ppm, suggesting that there is minimal steric interaction between the ligand methyl groups and the *cis*-ammines.

In the course of investigating the reactivity of I, the  $^1\text{H}$  NMR was recorded in several deuterated solvents. In contrast to the methyl resonance, the ammines show a strong solvent dependence, shifting by as much as 0.7 ppm downfield in a good cation stabilizing solvent like DMF (DN = 24.0) compared to a poor cation stabilizer like acetonitrile (DN = 14.1).<sup>14</sup>

The  $^{13}\text{C}$  NMR of I in D $_2$ O shows the carbonyl and methyl carbons of the coordinated acetone to be shifted considerably upfield relative to free acetone.<sup>15</sup> In particular, the carbonyl resonance has shifted from 215 to 83.5 ppm, whereas  $\eta^1$ -carbonyls which are bonded to a metal through an oxygen lone pair exhibit  $^{13}\text{C}$  shifts within 20 ppm of their uncoordinated value.<sup>16</sup> The carbonyl shift for I is consistent with other  $\eta^2$  ketones in the literature,<sup>5h,e,d</sup> and suggests the loss of  $\text{sp}^2$  hybridization. Tolman has shown that in  $\eta^2$ -bound olefins, there is a direct correlation between the upfield shift of the olefinic carbon upon coordination and the degree of  $\pi$  back-bonding.<sup>17</sup> In Table VII,  $^{13}\text{C}$  shifts for several  $\eta^2$ -bound unsaturated ligands are compared.

**Infrared Spectra and Assignment of C-O Stretch.** In previous studies infrared absorptions in the range of 1000–1200  $\text{cm}^{-1}$  have been assigned to the C-O stretch for  $\eta^2$ -aldehydes and ketones.<sup>5d,8</sup> However, in no case has this assignment been verified by an isotopic exchange study.

Infrared peaks of coordinated acetone in I appear at 1083, 2850, and 2950  $\text{cm}^{-1}$ . Additional peaks at 470, 1016, 1173, and 1330  $\text{cm}^{-1}$  are revealed, after conversion to the chloride salt and deuteration of the ammines, and these are also assigned to the bound acetone.<sup>18</sup> Synthesis of I with  $^{18}\text{O}$ -labeled acetone yielded a product which showed only a negligible shift in the peak at 1080  $\text{cm}^{-1}$ , yet isotopic exchange caused a significant shift to lower

Figure 1. ORTEP drawing of [Os(NH $_3$ ) $_5$ (CH $_3$ ) $_2$ CO] $^{2+}$ .Figure 2. A cyclic voltammogram of [Os(NH $_3$ ) $_5$ (CH $_3$ ) $_2$ CO] $^{2+}$  in 0.5 N TBAH. Scan rate = 100 mV/s.Figure 3. A schematic of a cyclic ECEC mechanism for [Os(NH $_3$ ) $_5$ (CH $_3$ ) $_2$ CO] $^{2+}$ .

energy in the peaks at 1330 and 470 to 1312 and 461  $\text{cm}^{-1}$ , respectively. These peaks are thus assigned to the C-O and Os-O stretches. The isotopic shifts above are consistent with other  $^{18}\text{O}$  shifts found in the literature, being somewhat smaller than those predicted for a diatomic oscillator with the same stretching frequency.<sup>19</sup>

It is interesting to note that the value we have assigned to the C-O stretch is similar to that assigned to acetone adsorbed onto a Ru(001) surface in a side-on configuration (1280  $\text{cm}^{-1}$ ).<sup>6</sup> The electron energy loss spectrum (EELS) in that study also reveals vibrational modes at 990 and 1170  $\text{cm}^{-1}$ , which are assigned as "isopropyl-like" rocking modes.

**Electrochemistry.** A cyclic voltammogram of I in a 0.5 N tetrabutylammoniumhexafluorophosphate (TBAH) acetone solution taken at 100 mV/s reveals a broad, irreversible oxidation wave at +0.30 V (NHE). The peak position is scan rate dependent, shifting toward positive potentials as the scan rate is increased. On the return scan there is a single irreversible re-

(13) The sample contained benzene in a capillary tube as an internal standard and a drop of benzene in the deuterated solvent for comparison. Upon exposure to air, there was a downfield shift of the external benzene peak indicating formation of paramagnetic material: Evans, D. F. *Proc. Chem. Soc.* **1958**, 115.

(14) Gutmann, V. *Chimia* **1977**, 31, 1.

(15) An independent experiment shows that the  $^{13}\text{C}$  NMR spectrum of acetone has resonances at 215 and 30.2 ppm in D $_2$ O.

(16) Brown, J. M.; Chaloner, P. A. *J. Chem. Soc., Perkin Trans. 2* **1982**, 711–719.

(17) Tolman, C. A.; English, A. D.; Manzer, L. E. *Inorg. Chem.* **1975**, 14 (10), 2353.

(18) Additional absorptions in I occur at 3400–3200, 1646, 1323, and 819  $\text{cm}^{-1}$ , which are assigned to the ammines, and at 628, 767, 1030, 1169, and 1253  $\text{cm}^{-1}$ , which are assigned to ionic TFMS. These assignments are based on isotopic shift upon deuteration of the ammines and comparison with the IR spectrum of NaTFMS, respectively.

(19) Pinchas, S.; Lauicht, I. In *Infrared Spectra of Labelled Compounds*; Academic: London, 1971; p 238.

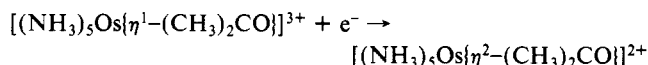
duction wave at  $-0.45$  V (NHE), which is not present when the upper scan limit is set to  $0.0$  V (Figure 2). When  $[\text{Os}(\text{NH}_3)_5\text{TFMS}](\text{TFMS})_2$  is allowed to react in a solution of dry acetone for 4 h, the cyclic voltammogram of the resulting product in acetone shows an irreversible reduction wave at  $-0.45$  V which we assign to the reduction of the ( $\eta^1$ -acetone)pentaammine-osmium(III) cation. The above data suggest an ECEC mechanism<sup>20</sup> in which there is a rapid opening of the oxymetallacycle<sup>21</sup> upon oxidation and rapid closure upon reduction, (Figure 3). Attempts to measure the chemical kinetics by scanning at high scan rates ( $500$  V/s) were unsuccessful, but a lower limit for the rate of oxymetallacycle formation for the ( $\eta^1$ -acetone)osmium(II) complex has been estimated as  $10^3$  s<sup>-1</sup>.<sup>22</sup>

**Reactivity. (i) Substitution.** NMR and electrochemical studies of I show there to be no significant substitution of water, methanol, *N,N*-dimethylformamide, acetonitrile, or isonicotinamide after 6 h. NMR spectra of a solution of I in acetonitrile-*d*<sub>3</sub> were taken daily, and the half-life for the formation of the (acetonitrile)-pentaammineosmium(II) complex in neat acetonitrile was determined to be approximately 1 week.<sup>23a</sup>

**I As a Reducing Agent.** In spite of what the above electrochemical results might suggest, I is capable of acting as a reasonably strong homogeneous reducing agent. When an acetone solution of I is added to  $0.5$  equiv of  $[\text{Os}(\text{NH}_3)_5(\text{PhCN})]^{3+}$  (PhCN = benzonitrile), the solution immediately turns deep red, indicating the rapid formation of  $[\text{Os}(\text{NH}_3)_5(\text{PhCN})]^{2+}$ , even though the potential for the  $3+/2+$  couple of the benzonitrile complex,  $-0.20$  V (NHE), is substantially more negative than the oxidation wave of I at low scan rates. This qualitative observation was confirmed by electrochemical experiments which showed the reduction of the pentaammine(benzonitrile)osmium(II) complex to be virtually complete within several seconds. In contrast, when the identical experiment is performed with the acetonitrile analogue,  $-0.25$  V (NHE), a measurable equilibrium is rapidly established in which approximately one-third of the Os(II) is in the form of the (acetonitrile)pentaammine complex. By measuring the relative concentrations of the four osmium species in solution,<sup>24</sup> a value of  $1.2$  was calculated for the equilibrium constant  $K$  where

$$K = \frac{[\text{Os}(\text{NH}_3)_5(\text{NCCH}_3)]^{2+}[\text{Os}(\text{NH}_3)_5((\text{CH}_3)_2\text{CO})]^{3+}}{[\text{Os}(\text{NH}_3)_5(\text{NCCH}_3)]^{3+}[\text{Os}(\text{NH}_3)_5((\text{CH}_3)_2\text{CO})]^{2+}}$$

This leads to a value of  $-0.30$  V (NHE) for  $E^\circ$  of the half-reaction

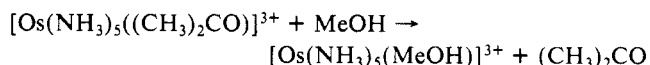
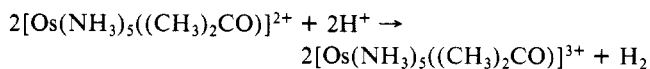


The facility with which the homogeneous electron transfer processes occur contrasts with the electrochemical behavior. This has prompted a more complete investigation of the homogeneous and heterogeneous electron transfer of I, the results of which will be reported separately.

Although I persists in protic solvents for several hours, over the course of several days in slightly acidic methanol-*d*<sub>4</sub> all NMR resonances vanish, and electrochemical experiments<sup>25</sup> indicate the formation of an electroactive species in the oxidized form of a

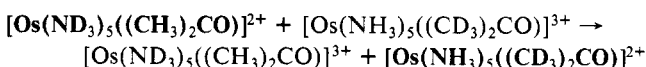
reversible couple at  $-0.75$  V NHE which we ascribe to pentaammine(methanol)osmium( $3+/2+$ ). The reaction was repeated under rigorously anaerobic conditions in protic methanol with toluene added as a integration standard. The NMR spectrum of this reaction mixture in acetone-*d*<sub>6</sub> was taken every 24 h. Over a period of 3 days the resonance of I at  $1.63$  ppm decayed and simultaneously a resonance at  $2.08$  ppm grew in, this being indicative of the formation of free acetone. After 3 days the integrated intensity for the  $2.08$ -ppm resonance was equal to the initial intensity of the resonance at  $1.63$  ppm.

The reaction course which we infer from these observations is represented by the reactions



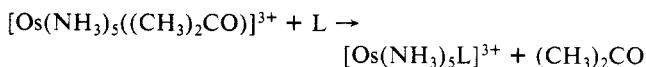
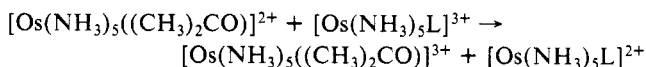
Gas evolution was not observed presumably because of the slow rate of formation. Efforts were made to detect the formation of 2-propanol or an acetal among the products without success.

**Self-Exchange Behavior.** An NMR spectrum of recrystallized I in acetone-*d*<sub>6</sub> shows negligible exchange of the acetone ligand after 24 h. In protic solvents, we were unable to detect scrambling of the methyl protons with deuterium after 24 h. We found that by introducing a trace amount of (acetone)pentaammine-osmium(III) to a pure sample of I we were able to induce rapid exchange of acetone. When a stoichiometric amount of acetone-*d*<sub>6</sub>pentaammineosmium(III) was added to a sample of I in which the amines were fully deuterated but the acetone was fully protonated, the NMR in acetone-*d*<sub>6</sub> indicated a rapid growth in the resonances at  $4.05$  and  $5.53$  ppm and a synchronous decrease of the singlet at  $1.63$  ppm, indicating the following self-exchange redox reaction:<sup>26</sup>



(bold indicates diamagnetic and, hence, NMR active species)

When a trace of Os(III) was added to a solution of I in benzonitrile there was an immediate color change to the orange-red pentaammine(benzonitrile)osmium(II) complex. The reaction was monitored by visible absorption,<sup>23b</sup> and after several hours it was complete. A control reaction in which no Os(III) was added does not show any significant substitution over the same time period. This catalytic effect can be understood by considering a mechanism in which substitution takes place on the Os(III)  $\eta^1$  complex:



This reaction should be a general one for substitution of any ligand in which the redox step above is exoergic.

**(ii) Decarbonylation.** Although I remains virtually unchanged after being heated under vacuum at  $100^\circ\text{C}$  over a period of 24 h, when a sample is heated at  $150^\circ\text{C}$  under similar conditions for 8 h, decomposition occurs, resulting in the formation of the pentaamminecarbonylosmium(II) complex which is characterized by an infrared absorption at  $1891$  cm<sup>-1</sup>.<sup>27</sup>

These results are consistent with our findings for other pentaammineosmium(II) complexes, some of which we find to be more easily thermolyzed than I. Among these are the  $\eta^2$ -acetaldehyde and *N,N*-dimethylformamide complexes which undergo

(20) Bard, A. J.; Faulkner, L. R. *Electrochemical methods fundamentals and applications*; Wiley: New York, 1980.

(21) We make no distinction between an oxymetallacycle and a  $\pi$ -bound carbonyl complex in this paper.

(22)  $k$  has been estimated assuming reversible electron transfer kinetics for the  $\eta^1$  form, a switching potential =  $-0.8$  V, scan rate =  $500$  V/s,  $E^\circ_1 \approx -0.47$  V (NHE), and anodic peak current  $<10\%$  cathodic peak current.  $t_{1/2} \approx 4 \times 10^{-4}$  s.

(23) (a) The formation of  $[\text{Os}(\text{NH}_3)_5(\text{CH}_3\text{CN})]^{2+}$  is based on the formation of resonances at  $3.19$  and  $3.04$  ppm, which have been independently assigned to trans and cis amines, respectively. The compounds  $[\text{Os}(\text{NH}_3)_5\text{L}](\text{TFMS})_2$  ( $\text{L} = \text{CH}_3\text{CN}$  and  $\text{PhCN}$ ) have been fully characterized by M. Sekine and W. D. Harman and will be reported separately. (b) The visible spectrum for  $[\text{Os}(\text{NH}_3)_5(\text{PhCN})](\text{TFMS})_2$  has  $\lambda_{\text{max}}$  at  $509$  nm ( $3.4 \times 10^3$ ) and  $403$  nm ( $1 \times 10^4$ ).

(24) Relative concentrations were measured by a modified rotated disk apparatus described above.

(25) Cyclic voltammograms and modified rotated disk.

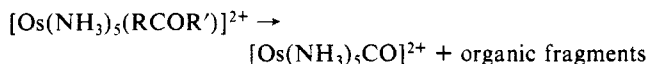
(26) Independent experiments have confirmed that the ammine protons do not exchange over the time scale of minutes.

(27) Buhr, J. D.; Taube, H. *Inorg. Chem.* **1979**, *18*, (8), 2208.

(28) Gulens, J.; Page, J. A. *J. Electroanal. Chem.* **1976**, *67*, 215.

(29) Sen, J.; Taube, H. *Acta Chem. Scand.* **1979**, *33*, 125.

thermal degradation at room temperature. This decomposition behavior appears to be rather general for pentaammineosmium(II) complexes containing organic ligands which include a carbonyl group.



Details of these reactions and structural and spectroscopic properties of other pentaammineosmium(II) complexes of  $\eta^2$ -bound unsaturated ligands will be described separately.

To our knowledge,  $[\text{Os}(\text{NH}_3)_5((\text{CH}_3)_2\text{CO})]^{2+}$  is the first example of a carbonyl-bound  $\eta^2$  in a pentaamine complex. The reactions of pentaammineosmium(II) and unsaturated organic ligands promise to expand substantially the interface between

organometallic and traditional coordination chemistry.

**Acknowledgment.** Support of this work by National Institutes of Health Grant GM13638-20 and National Science Foundation Grant CHE85-11658 are gratefully acknowledged.

**Registry No.** 1, 105164-48-5;  $\text{I}^-/1/2(\text{CH}_3)_2\text{CO}$ , 105164-49-6;  $\text{I}^-$  ( $^{18}\text{O}$  labeled), 105164-54-3;  $[\text{Os}(\text{NH}_3)_5(\text{TFMS})](\text{TFMS})_2$ , 83781-30-0;  $[\text{Os}(\text{NH}_3)_5((\text{CH}_3)_2\text{CO})]\text{Cl}_4$ , 105164-50-9;  $[\text{Os}(\text{NH}_3)_5(\text{PhCN})]^{3+}$ , 105164-51-0;  $[\text{Os}(\text{NH}_3)_5(\text{PhCN})]^{2+}$ , 105164-52-1;  $[\text{Os}(\text{NH}_3)_5\text{Co}]^{2+}$ , 70528-08-4.

**Supplementary Material Available:** Listings of bond lengths, bond angles, and plane calculations (9 pages); tables of structure factors (13 pages). Ordering information is given on any current masthead page.

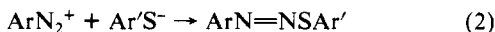
## Mechanistic and Kinetic Studies of the Thiodediazoniation Reaction

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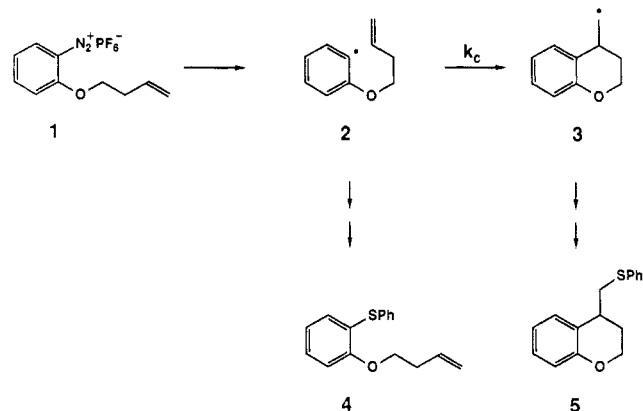
**Abstract:** Treatment of the diazonium salt, **1**, with sodium benzenethiolate in  $\text{Me}_2\text{SO}$  affords mixtures of uncyclized (**4**) and cyclized (**5**) products. Formation of the latter involves ring closure of the substituted aryl radical, **2**. The variation in the relative yields of **4** and **5** with reactant concentration shows that thiodediazoniation involves two key propagation steps: coupling of aryl radicals with thiolate anions to give radical anions, and electron transfer from the latter to the diazosulfide formed in a fast initial equilibration. The rate constant,  $k_N$ , for the reaction of **2** with  $\text{PhS}^-$  is given by  $\log k_N = (9.57 \pm 0.28) - (1.74 \pm 0.37)/2.3RT$  where  $E_{\text{act}}$  is in  $\text{kcal mol}^{-1}$ .

The reaction between arenediazonium salts and arenethiolate ions is a well-known and convenient means of preparing diaryl sulfides<sup>1,2</sup> (eq 1). However, mechanistic information on such thiodediazoniation reactions is surprisingly limited. Several workers dating back to the 19th century have suggested that the reaction proceeds via an intermediate diazosulfide (eq 2) which



undergoes decomposition, liberating nitrogen to yield the diaryl sulfide.<sup>1a,c,i,2</sup> A number of such diazosulfides have indeed been isolated and characterized.<sup>3</sup> A recent report<sup>2</sup> postulates that electron transfer from arenethiolate ions to the diazosulfide may be the key activation step in the decomposition of the latter species. On the other hand, Beckwith and Meijs,<sup>4</sup> whose preliminary studies have demonstrated the intermediacy of aryl radicals in thiode-

Scheme 1



diazoniation reactions, have suggested that such reactions may be initiated by electron transfer from thiolate ions to diazonium cations (eq 3).



In order to resolve these questions, we decided to study the reaction between benzenethiolate ions and *o*-(but-3-enyloxy)-benzenediazonium ions in  $\text{Me}_2\text{SO}$  solution. It was expected that the intermediate *o*-(but-3-enyloxy)phenyl radical, **2** (Scheme 1), the rate of cyclization of which has recently been determined,<sup>5</sup>

(1) (a) Ziegler, J. H. *Chem. Ber.* **1890**, *23*, 2469; **1895**, *28*, 1674. (b) Mayer, F. *Chem. Ber.* **1909**, *42*, 3046. (c) Hilbert, G. E.; Johnson, T. B. *J. Am. Chem. Soc.* **1929**, *51*, 1526. (d) Leandri, G.; Mangini, A.; Passerini, R. *Gazz. Chim. Ital.* **1954**, *84*, 3. (e) Szamant, H. H.; Levitt, G. *J. Am. Chem. Soc.* **1954**, *76*, 5459. (f) Truce, W. E.; Tate, D. P.; Burdge, D. N. *J. Am. Chem. Soc.* **1960**, *82*, 2872. (g) Cumper, C. W. N.; Read, J. F.; Vogel, A. I. *J. Chem. Soc.* **1965**, 5860. (h) Oae, S.; Khim, Y. H. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1716. (i) Spencer, H. *Chem. Br.* **1977**, *13*, 240.

(2) Petrillo, G.; Novi, M.; Garbarino, G.; Dell'Erba, C. *Tetrahedron Lett.* **1985**, *26*, 6365.

(3) (a) Hantzsch, A.; Freese, H. *Chem. Ber.* **1895**, *28*, 3237. (b) Price, C. C.; Tsunawaki, S. *J. Org. Chem.* **1963**, *28*, 1867. (c) Van Zwet, H.; Kooyman, E. C. *J. Chem. Soc., Chem. Commun.* **1965**, 313. (d) Newmann, W. P.; Lind, H.; Alester, G. *Chem. Ber.* **1968**, *101*, 2845.

(4) Meijs, G. F.; Beckwith, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 5890.

(5) Abeywickrema, A. N.; Beckwith, A. L. *J. Chem. Soc., Chem. Commun.* **1986**, 464.