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Isomerism about a Dioxo Bridge. Spectroscopic and Chemical Studies on Oxoosmium(VI) Esters

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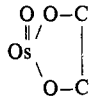
The product of the reaction of OsO_4 with tetramethylethylene (2,3-dimethyl-2-butene) was found to exist as a solvent-dependent mixture of two dimers. The osmium atoms are in a pseudo-square-pyramidal arrangement with two ester bonds, two dioxo bridge bonds, and one terminal oxygen bond. The dimers differ in that these terminal oxygens are mutually anti in one isomer and mutually syn in the second isomer. The polar syn isomer is relatively more stable in solvents with high dielectric constants. The rate of the isomerization reaction (in organic solvents) is slow on the ^1H NMR time scale, even at 90 °C, but the reaction has a half-life of ca 5 s at room temperature. Nitrogen donor ligands react with the mixture of dimers to produce octahedral monomeric complexes containing trans oxo groups. For monodentate ligands, such as pyridine, these ligands exchange rapidly on the ^1H NMR time scale. However, the bidentate ligand tetramethylethylenediamine exchanges slowly on the ^1H NMR time scale. The dimers also react with diols (ethylene glycol, pinacol, catechol) to produce square-pyramidal diester complexes with an oxo group at the apex. These diesters exhibit dramatically different reactivities toward nitrogen nucleophiles and toward diols. The carbon-13 spectra of these compounds have been investigated as an aid in structural elucidation. The shifts of the ^{13}C of pyridine on coordination are γ-C (4 ppm downfield) > β-C (1.4 ppm downfield) > α-C (0.6 ppm upfield). Of the ester carbon resonances, only the resonances of the carbons directly attached to oxygen are very sensitive to structural changes in the complexes.

Introduction

The solution chemistry of oxoosmium(VI) esters which contain the function



has been studied relatively little. These esters are usually formed during the reaction of osmium tetraoxide with carbon–carbon double bonds.[1-7] As such, they are important intermediates in the selective conversion of olefins into *cis*-diols and have been widely employed in the examination of biological molecules with electron microscopy. For example, OsO_4 reacts most readily with thymine moieties of DNA, thus providing a method of selectively introducing a heavy-metal stain suitable for electron microscopic sequencing of nucleic acids.[8] Most studies which have utilized the reaction of OsO_4 at CC double bonds have not focused on the properties of the esters; extensive kinetic investigations have been reported detailing the rates of formation of such adducts with nucleic acid constituents.[9] Since Griffith and his co-workers[2-5] were able to find a few compounds which formed crystalline materials, we initiated our study of oxoosmium(VI) esters by examining the solution chemistry of these crystalline compounds.

In this report, we will also detail changes which Os(VI) can induce in the carbon-13 spectra of pyridine. Such carbon-13 shifts may serve (1) to identify bonding sites in labile systems such as heavy-metal binding to nucleic acid derivatives and (2) to elucidate the electronic nature of the bonding in complexes of unsaturated heterocyclic ligands.[10]

Experimental Section

Instruments and Procedures. Ir spectra were recorded using a Perkin-Elmer 457-A grating instrument in KBr pellets, except as noted. ^1H NMR spectra were performed on 0.1 M solutions (when solubility allowed) and are in units of δ (ppm) referenced against internal tetramethylsilane (TMS). The 60-MHz spectra were recorded on a Varian A-60 instrument. All 100-MHz spectra were recorded with a Varian HA-100 spectrometer except the low-temperature spectra which were recorded using a Jeol MH-100 spectrometer. Probe temperatures were determined by standard techniques using methanol and ethylene glycol samples provided by the manufacturer. The MH-100 spectra were recorded using the methyl group of toluene as a lock signal at 7.5 Hz/cm. HA-100 spectra were obtained in the HR mode while sweeping the frequency. The lock signal was either the solvent or TMS (10%).

Natural-abundance carbon-13 spectra were obtained on a Varian CFT-20 instrument with an 8K data table. Sweep width was 4000 Hz downfield from TMS. An average of 7000 transients were collected for each spectrum. All spectra were obtained at ambient temperature with proton noise decoupling and $DCCl_3$ as a lock signal.

Table I. Crystallographic Data for $[OsO_4C_2(CH_3)_4]_2$

	This study[a]	Lit.[b]
a, Å	8.179 (2)	8.145
b, Å	14.088 (7)	14.008
c, Å	7.856 (4)	7.811
β, deg	93.07 (3)	93.24
V, Å^3	903.9 (7)	889.8
Space group	$P2_1/n$	$P2_1/n$
Z	2	2
d_{calcd}, g cm^{-3}	2.49	2.53
d_{measd}, g cm^{-3}	2.49 (1)	Not reported

[a] The reported data are based on a least-squares fit to the 2θ, ω, and χ values for 15 reflections measured on a Syntex $P1$ automated diffractometer [24 °C, Mo Kα radiation]. The crystal used had dimensions 0.08 × 0.10 × 0.60 mm. The density was measured by neutral buoyancy methods in a mixture of bromoform and carbon tetrachloride. [b] Reference 4.

$[OsO_4C_2(CH_3)_4]_2$. This compound was prepared by following Criegee's procedure.[1] Anal. Calcd for $C_{12}H_{24}O_8Os_2$: C, 21.3; H, 3.6; Os, 56.2. Found: C, 21.5; H, 3.6; Os,[11] 56.4. The compound was also characterized by x-ray (Table I) and ir data (1120 (s), 989 (s), 860 (s), 660 (s), 590 (m) cm^{-1}; lit.[3] 1122 (s), 982 (s), 860 (s), 655 (s), 588 (m) cm^{-1}).

To follow the formation of $(OsO_4C_2(CH_3)_4)_2$ by ^1H NMR, a 0.2 M stock solution of osmium tetraoxide in CH_2Cl_2 was made (0.5 g in 10 ml). Additions of $C_2(CH_3)_4$ (0.012 ml was added to a 0.5-ml aliquot of stock solution) were made after initially tuning on CH_2Cl_2; the spectra were recorded immediately following the addition of the olefin.

$OsO[O_2C_2(CH_3)_4]_2$. This was prepared by adding pinacol to a basic solution of $K_2OsO_4 \cdot 2H_2O$[12] according to Criegee.[1] Anal. Calcd for $C_{12}H_{24}O_5Os$: C, 32.9; H, 5.5; Os, 43.4. Found: C, 33.5; H, 5.7; Os, 42.9. Ir: 1122 (m), 978 (s), 860 (s), 630 (m) cm^{-1}; lit.[3] 1121 (m), 978 (s), 859 (s), 631 (m) cm^{-1}. ^1H NMR: δ 1.39, 1.27; lit.[3] δ 1.40, 1.27. Further confirmation of the identity of this compound was obtained by single-crystal x-ray diffraction methods. Crystals from benzene were photographed by Weissenberg methods. The complex crystallizes in a body-centered tetragonal cell with a = 10.27 (1) Å, c = 7.29 (1) Å, V = 768.9 Å^3, Z = 2, d_{measd} = 1.89 (1) g cm^{-3} (aqueous $ZnCl_2$), and d_{calcd} = 1.89 g cm^{-3}. These values are in good

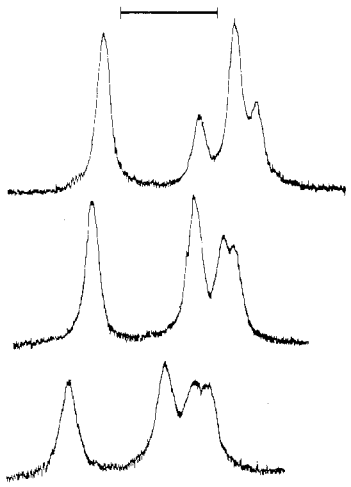


Figure 1. ^{1}H NMR spectra of the methyl groups in $[OsO_4C_2(CH_3)_4]_2$ in benzene (top), methylene chloride (middle), and 75% nitromethane-d_3–25% methylene chloride (bottom). Bar is 10 Hz; 100-MHz instrument.

agreement with the partial data previously reported[5] (tetragonal; a = 10.224 Å, c = 7.265 Å).

$OsO[O_2C_2H_4][O_2C_2(CH_3)_4]$. Ethylene glycol (0.20 ml, 3.73×10^{-3} mol) was added to a solution of $[OsO_4C_2(CH_3)_4]_2$ (0.25 g, 0.37×10^{-3} mol). The solution was placed in a hood and the residue after complete evaporation of the solvent was recrystallized from a minimum volume of benzene. Anal. Calcd for $C_8H_{16}O_5Os$: Os, 49.7. Found: Os, 49.2. Ir: 1122 (m), 978 (s), 860 (s), 625 (m) cm^{-1}. ^{1}H NMR (CH_2Cl_2): δ 4.75, $-CH_2CH_2-$; δ 1.47, 1.37, $-CH_3$.

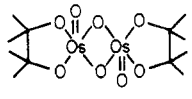
$OsO[O_2C_6H_4][O_2C_2(CH_3)_4]$. Attempts to isolate this product were not successful owing to the instability of this material. All studies were performed with the product generated in solution. In a typical ^{1}H NMR experiment, $[OsO_4C_2(CH_3)_4]_2$ (30 mg, 4.4×10^{-5} mol) and catechol (9.7 mg, 8.8×10^{-5} mol) were dissolved in CH_2Cl_2 (0.5 ml). Such solutions were stable over several days and had characteristic ir bands at 1130 (s), 978 (vs), and 870 (s) cm^{-1}. ^{1}H NMR (CH_2Cl_2): δ 1.5, 1.42, $-CH_3$; aromatic multiplets at δ 6.95 and 7.33.

$(C_5H_5N)_2OsO_2(O_2C_2H_4)$. This was prepared according to Griffith.[3] Anal. Calcd for $C_{12}H_{14}N_2O_4Os$: C, 32.7; H, 3.2; N, 6.3; Os, 43.2. Found: C, 33.2; H, 3.1; N, 6.7; Os, 43.1. Ir: 1040 (s), 870 (s), 830 (vs), 595 (s) cm^{-1}; lit.[3] 1041 (s), 867 (s), 833 (vs), 593 (s) cm^{-1}. ^{1}H NMR (CH_2Cl_2): δ 4.13, $-CH_2CH_2-$, multiplets at δ 8.91 (α), 7.93 (β), 7.83 (γ).

$(C_5H_5N)_2OsO_2[O_2C_2(CH_3)_4]$. This compound was reported previously but was prepared by a different method. In this study, pyridine (0.12 ml, 1.5×10^{-3} mol) was added to a solution of $[OsO_4C_2(CH_3)_4]_2$ (0.25 g, 0.37×10^{-3} mol) in CH_2Cl_2 (10 ml). After the solution was taken to dryness, the product was recrystallized from a minimum amount of CH_2Cl_2. Anal. Calcd for $C_{16}H_{22}N_2O_4Os$: C, 38.8; H, 4.5; N, 5.6; Os, 38.3. Found: C, 39.0; H, 4.7; N, 5.9; Os, 38.1. Ir: 1135 (s), 865 (m), 825 (s), 608 (m) cm^{-1}; lit.[3] 1126 (s), 862 (m), 829 (s), 609 (m) cm^{-1}. ^{1}H NMR pmr (CH_2Cl_2): singlet at δ 1.37, $-CH_3$; multiplets at δ 8.72 (α), 7.39 (β), 7.72 (γ).

Results and Discussion

Addition of OsO_4 to nonaqueous solutions of tetramethylethylene (2,3-dimethyl-2-butene) leads to the formation of a crystalline product which has been shown crystallographically to have structure I.[4] These esters were shown to



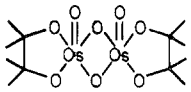
I

be sexivalent and diamagnetic. Two lines of evidence were presented[3] which suggested that the oxo-bridged structure was retained in solutions of noncoordinating solvents. These are as follows: (1) molecular weight determinations showed the material was dimeric (osmium esters of several other unsaturated molecules were also found to be dimers) and (2) ir spectra of the solids and solutions were similar and consistent with the presence of only one compound. Additionally, the ^{1}H NMR spectrum of the tetramethylethylene derivative was reported to contain two methyl signals consistent with structure I. At 60 MHz (CH_2Cl_2), the spectrum we obtained appeared to contain three resonances, but at 100 MHz the upfield resonance appeared as two unresolved signals (Figure 1). We will now present evidence which very strongly suggests that the solutions of the tetramethylethylene product contain an equilibrium mixture of I and II.

Table II. ^{1}H NMR Spectra of $[OsO_4C_2(CH_3)_4]_2$ in Several Solvents at 100 MHz

Solvent	Chem shift, δ				I:II
	Isomer I		Isomer II		
C_6H_6	1.20	1.05	1.11	1.02	3.2
CCl_4[a]	1.49	1.40	~1.36		2.6
50% CH_2Cl_2–50% C_6H_6	1.36	1.24	1.24	1.21	2.0
CH_2Cl_2	1.54	1.43	1.39	1.38	2.0
25% CH_2Cl_2–75% CD_3NO_2	1.53	1.43	1.40	1.39	1.2
CD_3NO_2	1.54	1.44	1.40	1.39	~0.7
C_6F_6[b]	1.63	1.57	1.45	<1.20[c]	
$CDCl_3$[b,d]	1.62	1.50	~1.47		

[a] Values reported in ref 3: δ 1.29 and 1.13. [b] Ratios not determined. [c] Resonance difficult to identify. [d] Recorded at 60 MHz. Upfield resonances not resolved.



II

As a first consideration, it was conceivable that, although the preparation of I is very straightforward, in our hands a different product or a mixture of different products was obtained. The product was therefore prepared in several different solvents using different batches of OsO_4 and olefin. Furthermore, the reactions of the olefin and the OsO_4 were monitored by ^{1}H NMR. In all of these experiments, the ^{1}H NMR spectra were identical within experimental error and the signals of the products did not correspond to those reported by Griffith.[3] Large crystals of the product were grown (from benzene), and the black elongated crystals were examined by x-ray diffraction methods, Table I. These data were compared with those reported for the black elongated crystals studied previously,[4] Table I. The similarity in the crystal dimensions and space group leaves little doubt that the product has structure I in the solid state. As further evidence, the ir spectral properties of the product prepared in this study and of that reported previously[3] are essentially identical. In view of such data, the similar methods of preparation and, finally, the requirement in space group $P2_1/n$ that dimers must have an inversion center, there is no doubt that the crystals we prepared are those of product I. The ^{1}H NMR spectrum of a single such crystal, recorded within 10 s of dissolution, is characteristic of all other spectra obtained for the OsO_4/tetramethylethylene product.

An equilibrium between I and II cannot be concentration dependent. If the additional ^{1}H NMR signals we observe are attributable to a monomer or to an oligomer, then one would anticipate that the ratio of ^{1}H NMR signals would vary greatly with total osmium concentration. In an experiment in which the total osmium concentration (CH_2Cl_2) was varied from 0.109 to 0.007 M, the ratios of signals at these two extreme concentrations as well as at four intermediate concentrations were identical within experimental error (ratios obtained in various solvents (Table II) will be discussed below). This dilution experiment also rules out the possibility that some

Table III. Carbon-13 NMR Spectral Data for Several Osmium(VI) Compounds

Compd	Solvent	Chem shifts, δ				
				Pyridine carbons		
		Ester carbons	Methyl carbons	α	β	γ
$[OsO_4C_2(CH_3)_4]_2$	$CDCl_3$-Cr(acac)$_3$	96.54, 96.28	24.75, 24.46, 24.26			
	75% C_6H_6-25% $CDCl_3$	96.18	24.55, 24.36, 24.05			
$[(py)_2OsO_4C_2(CH_3)_4]$	$CDCl_3$	90.10	24.71	149.33	125.01	139.99
	75% C_6H_6-25% $CDCl_3$	90.37	24.82	149.31	124.51	139.54
$(py)_2OsO_4C_2H_4$	$CDCl_3$	82.19		149.55	125.33	140.57
$OsO_5(C_2(CH_3)_4)_2$	$CDCl_3$	93.83	24.90, 24.20			
$OsO_5(C_2H_4)(C_2(CH_3)_4)$	$CDCl_3$	94.42, 83.02[a]	24.98, 24.26			
$OsO_5(C_6H_4)(C_2(CH_3)_4)$	$CDCl_3$	96.98	24.95, 24.53	125.59[b]		114.75[b]

[a] Ethylene carbons. [b] Catechol resonances.

substance in our solvent was causing the extra signals and water and ethanol had no effect on the percentages of I and II in CH_2Cl_2.

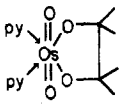
The symmetries of I, C_{2h}, and II, C_{2v}, require two methyl signals for both isomers accounting for the four signals observed. However, from symmetry considerations, it is not possible to assign either which set of signals is attributable to I or which signal in each set corresponds to the methyl groups vicinal to the terminal oxo group. The four-line spectrum containing two sets of resonances, each set having different intensities, is difficult to rationalize in terms of dimer–monomer equilibria or dimer–oligomer equilibria or δ and λ conformers of the five-membered rings. The signals do not correspond to possible decomposition products such as acetone or pinacol (the diol of tetramethylethylene).

The variation of the ^1H NMR spectrum of the product obtained from the addition of OsO_4 to tetramethylethylene with solvent both supports the existence of equilibrium 1 and

$$I \rightleftharpoons II \quad (1)$$

provides a method of assigning the sets of resonances. From Table II and Figure 1, it is clear that the signals which are upfield and represent the minor component in CH_2Cl_2 solution generally increase with increasing dielectric constant of the solvent. Isomer I has an inversion center and thus will not have a dipole moment. Isomer II, the syn isomer, will have a net dipole. Thus, isomer II should become increasingly stable as the dielectric constant of the solvent increases.[13] On this basis we tentatively assign the upfield closely spaced set of signals in CH_2Cl_2 to II.

Aromatic solvent induced shifts (ASIS) could provide a basis for the assignment because usually more polar molecules experience greater shifts than less polar molecules. However, even molecules which are not polar, but which have local dipoles, will experience ASIS.[14] Both I and II have similar ASIS for each resonance (0.34, 0.38, 0.28, 0.36 ppm upfield to downfield resonances, respectively). It seems likely that the local dipole set up by the oxo group is dominating the ASIS effects. In fact, some of the osmium compounds examined in this study exhibit rather unusual ASIS effects. The solvent hexafluorobenzene was introduced by Verkade[15] because, unlike benzene, which solvates methyl groups using the electron-rich upfield shielding π cloud, C_6F_6 solvates these groups with the electron-rich downfield shielding fluoride periphery. Thus, typically, opposite ASIS effects are observed with these two aromatic solvents. The upfield signal we have assigned to isomer II shifts upfield in both C_6H_6 and C_6F_6. Another unusual ASIS effect is observed for III[16] (py = pyridine). The methyl signals of III shift downfield in going



III

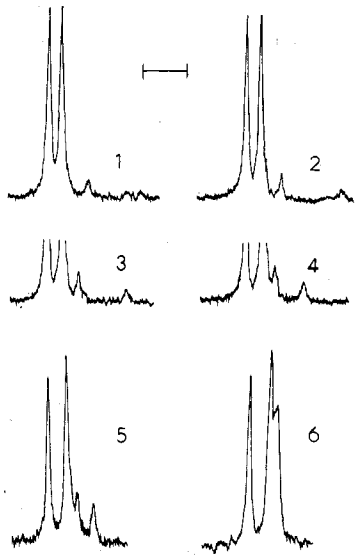


Figure 2. ^1H NMR spectra of the methyl groups in $[OsO_4C_2(CH_3)_4]_2$ in the following solutions: (1) 0.5 ml of C_6F_6; (2) solution 1 + 0.05 ml of CH_2Cl_2; (3) solution 1 + 0.1 ml of CH_2Cl_2; (4) solution 1 + 0.2 ml of CH_2Cl_2; (5) solution 1 + 0.3 ml of CH_2Cl_2; (6) solution 1 + 0.5 ml of CH_2Cl_2. Bar is 20 Hz; 60-MHz spectrometer.

from CH_2Cl_2 (δ 1.37) to C_6H_6 (δ 1.79) and upfield in going from CH_2Cl_2 to C_6F_6 (δ 1.32). The solvent, C_6F_6, is also unusual in that the signals we attribute to isomer I are the only signals readily observable in this solvent (Figure 2). However, on adding CH_2Cl_2, two signals barely detectable in the noise in pure C_6F_6 increase in size and are apparently the signals of isomer II. Such mixed-solvent experiments were performed with every solvent in Table III in order to rule out any possible miscorrelations of signals in the different solvents. The reasons for the extraordinary stability of isomer I in C_6F_6 are not clear at this time.

The carbon-13 spectra of the mixture of I and II were obtained in several solvents, Table III. Again the symmetry of the two isomers does not permit a structural assignment on this basis. Additionally, since the intensities of carbon-13 signals are not exactly related to the number of carbons in the molecules giving rise to the signals, it is not even possible definitely to establish sets of signals, as was done with the ^1H NMR spectra. However, two valuable pieces of information were obtained. First, it is a requirement of the mixture of I and II that only two ester carbon signals be observed and two were found. These carbons have no attached protons and therefore give only weak signals. We tentatively assign the upfield signal, which can be observed without the use of tris(acetylacetonato)chromium(III), to isomer I, the most abundant isomer. The similarity in chemical shifts for these two carbons and the similarity in shift values for the methyl carbons (only three signals can be observed) support the

Table IV. Carbon-13 NMR Spectral Data for Mixtures of Pyridine and $(OsO_4C_2(CH_3)_4)_2$[a]

py:Os	Mole fraction of py	Chem shifts, δ: Pyridine carbons α	β	γ	Ester carbons	Methyl carbons
	1	149.90	123.70	135.90		
4.0	0.8	149.59	124.39	137.98	90.08	24.71
2.0	0.67	149.33	125.01	140.00	90.09	24.70
1.36	0.58	150.14	125.11	140.41	*b*	24.71
1.0	0.50	150.31	125.10	140.50	*b*	24.71
0.72	0.42	~150.33[c]	125.11	140.49	*b*	~24.67[c]
0.24	0.19	151.16	125.14	140.83	~96.50[d]	24.72
0.12	0.11	151.25	125.15	140.85	~96.40[d]	24.68, 24.36
0.0	0.0				96.54, 96.28	24.75, 24.46, 24.26

[a] py:Os ratios of less than 2.0 were made by combining $(py)_2OsO_4C_2(CH_3)_4$ and $[OsO_4C_2(CH_3)_4]_2$ in appropriate ratios. Ratios of 2.0 and greater were made by adding pyridine to $[OsO_4C_2(CH_3)_4]_2$. [b] Too broad to observe. [c] Broad. [d] Very broad.

occurrence of equilibrium 1. Carbon-13 shifts are very sensitive to the chemical environment and such similar shifts are most consistent with two very similar compounds such as I and II.

From the ^1H NMR dissolution experiment, the half-life for the isomerization of I to II would have to be of the order of at least seconds. It was therefore conceivable that increasing the temperature would cause a collapse of the four resonances into one. However, in bromoform (Varian HA-100 100-MHz spectrometer), the signals did not collapse even up to 90 °C. Above this temperature, the mixture rapidly decomposes to acetone. The three upfield signals were not resolvable at temperatures greater than 50 °C. The spectrum of the mixture did not change appreciably when the temperature was lowered from +28 to −52 °C ($CDCl_3$–toluene, 25:75 v/v).

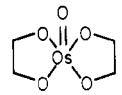
Addition of a large excess of pyridine (or other N donors such as 1-methylimidazole) to solutions of I and II results in the immediate and complete conversion of I and II into III (Table IV). Separate signals for free and coordinated pyridine were not observed, suggesting a rapid exchange reaction. However, when a bidentate N donor was added, separate signals could be observed for all species. For example, tetramethylethylenediamine gives complexed signals at δ 3.01 and 2.73 and free signals at δ 2.35 and 2.22 assigned to the methylene and methyl signals, respectively (^1H NMR). The ester methyl singlet has a shift of δ 1.28.

Although the behavior of the mixture of I and II in the presence of pyridine is consistent with equilibrium 1, the actual mechanism of exchange must be complex. It is difficult to imagine a simple pathway whereby the dimers are converted to III. Our data suggest that some intermediates are formed and that these are contributing to the changes in line shift and shape in both the ^1H NMR spectra and carbon-13 spectra at py:Os ratios less than 2. The sharpening of the methyl ^1H NMR resonance at a py:Os ratio of 1 suggests that a five-coordinate monopyridine or a bis(pyridine) dimer may be formed.

In a series of pyridine or substituted-pyridine complexes of pentacyanoferrate(II),[17] the α carbon was found to shift ca. 8 ppm downfield whereas the β- and γ-carbon resonances were shifted upfield by lesser amounts. For pyridine, these shifts were found to be as follows: α, 7.5 ppm, downfield; β, 0.9 ppm, upfield; γ, 1.6 ppm, upfield. Such results would suggest that the bonding mode of ligands could be identified by carbon-13 spectra. However, we have found[18] that, in some cobalt(III) complexes, the γ-C resonance shifts to a larger extent than the α-C resonance. The osmium compounds examined here exhibit a pattern similar to those of Co(III) and Pt(II) compounds.[19] For compound III, the α-carbon resonance exhibits an *upfield* shift of 0.57 ppm, but the β- and γ-carbon resonances were found to shift *downfield* by 1.4 and 4.1 ppm, respectively. As the (I + II):py ratio decreases, the α-C resonance shifts first *upfield* and then, at a ratio below 2, *downfield*.

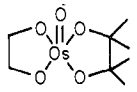
Proton resonances are less sensitive to variations in the local electron density, and smaller shifts are observed for such resonances. However, proton shifts are also less sensitive to the asymmetry in the charge distribution at the nucleus, as are shifts of heavier elements. Therefore, proton shifts may, in fact, be better indicators of bonding mode. In this regard, as the py:Os ratio in the experiment just described is lowered, the pyridine proton resonances shift in the downfield direction only.

Addition of diols to the mixture of I and II leads to the formation of diester compounds which are five-coordinated square pyramidal in geometry, by analogy to the structure of one such diester, that of ethylene glycol (IV).[5] Thus addition

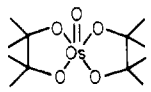


IV

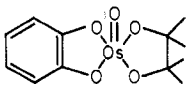
of the diols ethylene glycol, pinacol, and catechol to CH_2Cl_2 solutions of I and II leads to products which have ^1H NMR and carbon-13 spectra consistent with structures V–VII,



V



VI



VII

respectively. Compound VI has been reported previously and we were able to establish both by spectral comparison (Table III and Experimental Section) and by x-ray diffraction (Experimental Section) that the product we obtained from the addition of pinacol was identical with the product reported in the literature.[3] The reactions of these diols with I and II are immediate and complete.

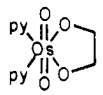
Although the compounds V–VII appear to be similar structurally, the properties of these compounds differ greatly, particularly with regard to the reactions and stability of the compounds. For example, the addition of pyridine to solutions of VI causes no change in the ^1H NMR spectrum suggesting that pyridine does not add to the five-coordinate complex. Addition of pyridine to solutions of V on the other hand causes the immediate conversion of V into III, with the release of ethylene glycol. Since no attempt was made to keep the solutions anhydrous, the additional hydrogens and the additional oxygen needed for the reaction are probably derived from adventitious moisture. Addition of pyridine to solutions of VII leads to an immediate conversion of the two methyl signals of VII into a complex set of three signals (δ 1.50, 1.45, 1.41). This intermediate, which was not identified, is unstable and decomposes to pinacol.

Addition of catechol to a solution of V immediately generates VII and ethylene glycol. If excess catechol is added, or if catechol is added to VII, then pinacol is formed. The osmium-containing product which is formed in this reaction is insoluble and, thus, it could be neither purified nor studied spectrally in solution. The ir spectra of the material suggested the presence of catechol and/or "OsO_2"[6] but the product was not investigated further. In contrast to V and VII, VI was decomposed to only a small extent by catechol (to pinacol) after 3 days.

The strong sterically hindered base tri-*n*-butylamine neither adds to V or VI nor decomposes them. However, VII is converted into VI by this base. Attempts to isolate VII were unsuccessful because the material obtained after the isolation procedure was shown to contain (^{1}H NMR) approximately 30% VI. Thus, even in the absence of base, VII is unstable with respect to the formation of VI.

Phosphorus or sulfur donor ligands, as well as ligands which contain primary or secondary amines, will decompose the esters. For example, addition of trimethyl phosphite (3:1) converts VII immediately and completely to pinacol and acetone. All of the added trimethyl phosphite is oxidized to trimethyl phosphate. Compound V reacts similarly but not completely to form trimethyl phosphate, pinacol, and acetone. Ethylene glycol signals were obscured by trimethyl phosphate. However, trimethyl phosphite (3:1) and VI formed trimethyl phosphate to only a small extent after 20 min. Appreciable but not complete reaction was observed after 18 h and pinacol and trimethyl phosphate were formed.

The greater stability of VI evidenced in all of the above reactions is most probably a consequence of steric hindrance. The eight methyl groups in VI effectively shield the osmium from the attack of reagents. It is well-known that ligands such as pyridine also stabilize osmate esters such as I and II to hydrolysis. It seems unlikely that steric factors are responsible for such stabilization since the cyanide ligand will also stabilize the osmium ester grouping. Steric hindrance can further stabilize the bis(pyridine) esters. A large *excess* of catechol decomposed III to acetone and pinacol only slowly. However, VIII was unstable to catechol even in a 1:1 ratio (ethylene



VIII

glycol was formed). Behrman and co-workers[20,21] have observed that ester exchange is hindered if the two pyridine ligands are replaced by bipyridine.

Dioxo-bridged Mo(V) complexes generally have the syn conformation.[22] Singly bridged Mo(V) complexes with the grouping OMo–O–MoO have been found to have both cis and trans arrangements of the terminal oxygens, depending on the nature of the other ligands attached to Mo. Such compounds have characteristically different ir spectra. The syn and anti *isomers* observed here cannot be differentiated by ir spectroscopy.

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Registry No. $[OsO_4C_2(CH_3)_4]_2$, 50649-09-7; $[(py)_2OsO_4C_2(CH_3)_4]_2$, 53241-81-9; $(py)_2OsO_4C_2H_4$, 39019-05-1; $OsO_5(C_2(CH_3)_4)_2$, 52782-38-4; $OsO_5(C_2H_4)(C_2(CH_3)_4)$, 59069-62-4; $OsO_5(C_6H_4)(C_2(CH_3)_4)$, 59069-61-3; pyridine, 110-86-1; osmium tetraoxide, 20816-12-0; $C_2(CH_3)_4$, 563-79-1; ^{13}C, 14762-74-4.

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