well-developed $[MoO_2]^{2+}$ unit, the $[Mo(NNR)_2]^{2+}$ moiety may also undergo considerable chemistry of its own, such as protonation, alkylation, and N–N bond cleavage.

Acknowledgment. This work was supported in part by a grant from the National Science Foundation (CHE8514634) to J.Z. We thank Peter Bishop of the University of Essex for assistance with the electrochemical studies.

Supplementary Material Available: Tables reporting bond lengths, bond angles, anisotropic temperature factors, and calculated hydrogen atom positions and thermal factors for **2**, **3a**, and **4** (33 pages); tables giving observed and calculated structure factors for **2**, **3a**, and **4** (155 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong,
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Synthesis and Reactivities of *trans*-Dioxoosmium(VI) Schiff-Base Complexes. X-ray Crystal Structure of Dioxo[*N*,*N'*-(1,1,2,2-tetramethylethylene)bis(3-*tert*-butylsalicylidenaminato)]osmium(VI)

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Received June 1, 1987

The syntheses and redox properties of *trans*-dioxoosmium(VI) Schiff-base Complexes are described. The crystal structure of *trans*-$[Os^{VI}O_2(3\text{-}t\text{-}Bu\text{-}saltmen)]$ has been determined: $C_{28}H_{38}N_2O_4Os$, space group $P2_1/c$, $a = 11.918$ (6) Å, $b = 10.416$ (1) Å, $c = 23.53$ (1) Å, $\beta = 102.91$ (3)°, $Z = 4$, $R = 0.062$ for 3651 observed Mo Kα data. The measured osmyl Os–O bond distances are 1.722 (8) and 1.760 (7) Å; other than this, the molecule conforms well to idealized C_2 symmetry. Both electrochemical oxidation and reduction of *trans*-dioxoosmium(VI) Schiff-base complexes are irreversible in acetonitrile.

Introduction

There is a growing interest in the oxidation chemistry of ruthenium and osmium complexes containing multianionic chelating ligands.[2,3] Recent studies by Groves and co-workers[3] showed that the dioxoruthenium(VI) prophyrin complex $[RuO_2(TMP)]$ (TMP = tetramethylsitylporphyrinato dianion) is an excellent catalyst for aerobic expoxidation of alkenes. We have been intrigued by this work and suspect that similar reaction chemistry of ruthenium complexes may also be observed by using inexpensive Schiff-base ligands, such as salen [*N*,*N'*-ethylenebis(salicyclidenaminato)]. In an attempt to develop the chemistry of high-valent ruthenium–salen–oxo complexes, we believe that knowledge of the physical and redox properties of the analogous osmium complexes, which are less reactive but more stable that the ruthenium system, is important. The synthesis of $[Os^{VI}O_2(salen)]$ and X-ray structure of $[Os^{IV}(salen)(SPh)_2]$ have previously been reported.[4] However, the $[Os^{IV}O_2(salen)]$ complex is virtually insoluble in common organic solvents, rendering the study of its solution chemistry difficult. In this contribution, we describe the preparation and spectroscopic and redox properties of five *trans*-dioxoosmium(VI) complexes containing different kinds of Schiff-base ligands. The osmyl Os–O bond distances in *trans*-$[Os^{VI}O_2(3\text{-}t\text{-}Bu\text{-}saltmen)]$ [3-*t*-Bu-saltmen = *N*,*N'*-(1,1,2,2-tetramethylethylene)bis(3-*tert*-butylsalicylidenaminato)] (Figure 1), as determined by X-ray crystallography, are 1.760 (7) and 1.722 (8) Å.

Experimental Section

The Schiff-base ligands (Figure 1) were prepared by the literature methods.[5] All other reagents used were of analytical grade.

***trans*-$[Os^{VI}O_2(5\text{-}i\text{-}Pr\text{-}salen)]$ (1).** $K_2[OsO_2(OH)_4]$ (0.50 g) and 5-*i*-Pr-salenH_2 (0.45 g) were stirred in methanol (150 mL) for 30 min. An orange-red solid gradually precipitated upon standing. This was filtered off, washed with a methanol/diethyl ether mixture (1:10), and dried under vacuum at room temperature (yield ~65%). Pure samples of **1** were obtained by slow diffusion of diethyl ether into a dichloromethane solution of the crude product. IR (Nujol mull): $\nu_{as}(Os{=}O)$ 845 cm^{-1}.

Table I. Microanalytical Data for the Osmium Complexes

complex	found (calcd)		
	% C	% H	% N
1	46.50 (46.14)	4.80 (4.54)	5.10 (4.89)
2	48.73 (48.98)	5.30 (5.10)	4.45 (4.67)
3	51.11 (51.12)	5.98 (5.79)	4.07 (4.27)
4	52.68 (52.63)	6.05 (6.14)	4.11 (4.09)
5	48.39 (48.59)	5.66 (6.14)	3.73 (3.44)

Table II. UV–Vis Spectral Data for the Osmium Complexes in CH_2Cl_2

complex	λ_{max}, nm (log ϵ)
1	410 (3.88), 367 (4.08), 290 (4.48), 267 (4.50), 243 (4.92), 228 (4.84)
2	405 (3.81), 367 (3.99), 293 (4.55), 267 (4.56), 245 (4.94), 238 (4.91)
3	420 (3.72), 368 (3.99), 310 (4.41), 265 (4.50), 245 (4.86), 233 (4.84)
4	408 (3.89), 369 (4.02), 305 (4.43), 267 (4.51), 243 (4.98), 231 (4.84)
5	415 (3.92), 368 (4.17), 302 (4.55), 268 (4.56), 243 (4.99), 230 (4.85)

The following complexes were similarly prepared as described for **1**: *trans*-$[Os^{VI}O_2(5\text{-}t\text{-}Bu\text{-}salen)]$ (**2**), *trans*-$[Os^{VI}O_2(3\text{-}t\text{-}Bu\text{-}saltmen)]$ (**3**), *trans*-$[Os^{VI}O_2(5\text{-}(3\text{-}Me)\text{-}Bu\text{-}saltmen)]$ (**4**), and *trans*-$[Os^{VI}O_2(5\text{-}t\text{-}Bu\text{-}saltmen)]$ (**5**).

Physical Measurements. ^1H NMR spectra were obtained on a Jeol FX-90Q Fourier transform spectrometer. Cyclic voltammetric measurements were performed by using a PAR universal programmer (Model 175), potentiostat (Model 173), and digital coulometer (Model 179). Formal potential measurements were made against a $Ag/AgNO_3$ (0.1 M in CH_3CN) electrode with ferrocene as the internal standard and pyrolytic graphite as the working electrode. Acetonitrile for electrochemical studies was distilled over CaH_2. The supporting electrolyte was $[Bu_4N]PF_6$. Microanalytical data for the newly prepared complexes are tabulated in Table I. The UV–vis spectral data and ^1H NMR and electrochemical data of complexes **1**–**5** are tabulated in Tables II–IV, respectively.

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(1) (a) University of Hong Kong. (b) The Chinese University of Hong Kong.

(2) See for example: (a) Che, C. M.; Cheng, W. K.; Leung, W. H.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1987**, 418. (b) Anson, F. C.; Collins, T. J.; Gipson, S. L.; Keech, J. T.; Krafft, T. E.; Peake, G. T. *J. Am. Chem. Soc.* **1986**, *108*, 6593. (c) Anson, F. C.; Christie, J. A.; Collins, T. J.; Coots, R. J.; Furutani, T. T.; Gipson, S. L.; Keech, J. T.; Krafft, T. E.; Santarsiero, B. D.; Spies, G. H. *J. Am. Chem. Soc.* **1984**, *106*, 4460. (d) Che, C. M.; Cheng, W. K.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1986**, 200. (e) Che, C. M.; Chung, W. C. *J. Chem. Soc., Chem. Commun.* **1986**, 386. (f) Leung, T.; James, B. R.; Dolphin, D. *Inorg. Chim. Acta* **1983**, *79*, 180.

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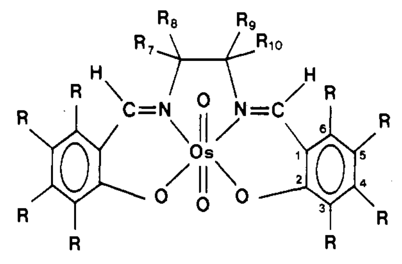
Table III. ^1H NMR Data for Complexes 1–5

com-plex	azomethine N=C-H	ethylene bridge $-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-$	tetramethyl-substituted ethylene bridge $-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-$	*tert*-butyl $-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$	5-isopropyl $-\overset{CH_3}{\underset{CH_3}{C}}-H$	5-(3-methylbutyl) $-CH_2CH_2\overset{CH_3}{\underset{H}{C}}CH_3$	R_3	R_4	R_5	R_6
1	8.38 (2 H, s)	4.28 (4 H, s)			2.88 (2 H, h) 1.23 (12 H, d)		7.37, 7.26 (2 H)	7.54, 7.52, 7.45, 7.42 (2 H)		7.18, 7.15 (2 H)
2	8.44 (2 H, s)	4.28 (4 H, s)		1.34 (5-position, 18 H, s)			7.25, 7.15 (2 H)	7.75, 7.72, 7.65, 7.62 (2 H)		7.39, 7.36 (2 H)
3	8.64 (2 H, s)		1.61 (12 H, s)	1.56 (3-position, 18 H, s)				7.38, 7.29, (2 H)	6.81, 6.73, 6.45 (2 H)	7.65, 7.64, 7.57, 7.55 (2 H)
4	8.57 (2 H, s)		1.63 (12 H, s)			1.71 (2 H, t) 1.31 (12 H, s) 0.74–0.82 (8 H)	7.23, 7.13 (2 H)	7.66, 7.64, 7.56, 7.54 (2 H)		7.34, 7.31 (2 H)
5	8.57 (2 H, s)		1.63 (12 H, s)	1.35 (5-position, 18 H, s)			7.23, 7.12 (2 H)	7.73, 7.70, 7.63, 7.60 (2 H)		7.40, 7.37 (2 H)

[a] Abbreviations: s, singlet; d, doublet; dd, doublet doublet; t, triplet; h, heptet.



Complexes		Ligand (L)	
[OsO$_2$(5-i-pr-salen)] **1**	L_1	$R_5 = -\overset{CH_3}{\underset{H}{C}}-CH_3$	$R_3=R_4=R_6=R_7=R_8=R_9=R_{10}=H$
[OsO$_2$(5-t-Bu-salen)] **2**	L_2	$R_5 = -\overset{CH_3}{\underset{CH_3}{C}}-CH_3$	$R_3=R_4=R_5=R_7=R_8=R_9=R_{10}=H$
[OsO$_2$(3-t-Bu-saltmen)] **3**	L_3	$R_3 = -\overset{CH_3}{\underset{CH_3}{C}}-CH_3$	$R_4=R_5=R_6=H$ $R_7=R_8=R_9=R_{10}=CH_3$
[OsO$_2$(5-(3-Me)-Bu-saltmen)] **4**	L_4	$R_5 = -CH_2-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-H$	$R_3=R_4=R_6=H$ $R_7=R_8=R_9=R_{10}=CH_3$
[OsO$_2$(5-t-Bu-saltmen)] **5**	L_5	$R_5 = -\overset{CH_3}{\underset{CH_3}{C}}-CH_3$	$R_3=R_4=R_6=H$ $R_7=R_8=R_9=R_{10}=CH_3$

Figure 1. Structures of complexes **1–5**.

Table IV. Electrochemical Data for Complexes 1–5[a]

complex	potential, V oxidn[b]	potential, V redn[b]
1	0.94	−1.12, −1.31, −1.61
2	0.95	−1.15, −1.35, −1.60
3	0.94	−1.28, −1.40, −1.77
4	0.93	−1.24, −1.40, −1.79
5	0.92	−1.26, −1.38, −1.78

[a] In acetonitrile with 0.1 M $[Bu_4N]PF_6$ as supporting electrolyte; working electrode is pyrolytic graphite. All the potential values were reported against $Cp_2Fe^{+/0}$, with a scan rate of 100 mV s^{-1}. [b] All the oxidative and reductive waves are irreversible.

X-ray Structural Study of *trans*-[Os^{VI}O$_2$(3-*t*-Bu-saltmen)] (3). Diffraction measurements were made on a Nicolet R3m four-circle diffractometer (graphite-monochromatized Mo Kα radiation, λ = 0.71069 Å), and determination of the crystal class, orientation matrix, and accurate unit cell parameters was performed according to established procedures.[6]

Intensities were recorded at 22 °C, and data collection and processing parameters are summarized in Table III. The raw intensities were processed with the learnt-profile procedure,[7] and absorption corrections were based on a pseudoellipsoidal fit to azimuthal scans of selected strong reflections over a range of 2θ values.[8]

The structure of **3** was solved by Patterson and Fourier methods. All non-hydrogen atoms in the molecule were subjected to anisotropic re-

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Table V. Data Collection and Processing Parameters

mol formula	*trans*-[Os^{VI}O$_2$(3-*t*-Bu-saltmen)], $C_{28}H_{38}N_2O_4Os$
fw	656.82
a, Å	11.918 (6)
b, Å	10.416 (1)
c, Å	23.53 (1)
β, deg	102.91 (3)
V, Å^3	2847 (2)
Z	4
d_{flotatn}, g cm^{-3}	1.52
d_{calcd}, g cm^{-3}	1.532
space group	$P2_1/c$
abs coeff, cm^{-1}	45.16
cryst size, mm	0.36 × 0.32 × 0.26
mean μr	0.70
transmission factors	0.162–0.244
scan type; speed, deg min^{-1}	ω–2θ; 2.02–8.37
scan range	1° below Kα_1 to 1° above Kα_2
bkgd	stationary cts for half the scan time at each end
colln range	$h,k,\pm l$; $2\theta_{\max} = 50°$
no. of unique data measd	4193
no. of obsd data with $\|F\| > 3\sigma(\|F\|)$, n	3651
no. of variables, p	346
$F(000)$	1311.7
$R_F = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.062
weighting scheme, w	$w = [\sigma^2(\|F_o\|) + 0.0005\|F_o\|^2]^{-1}$
$R_w = [\sum w(\|F_o\| - \|F_c\|)^2/w\|F_o\|^2]^{1/2}$	0.075
$S = [\sum w(\|F_o\| - \|F_c\|)^2/(n-p)]^{1/2}$	2.333

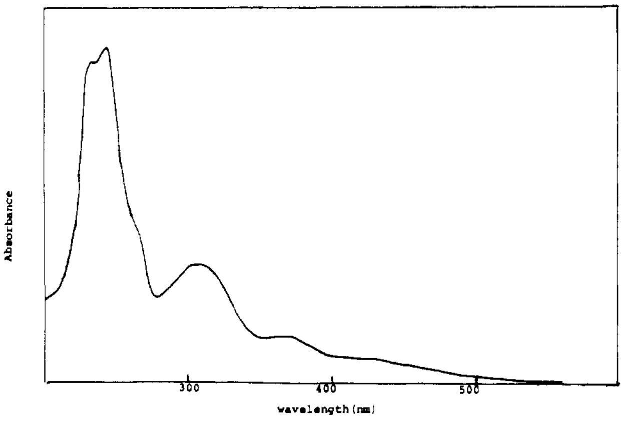

Figure 2. Optical spectrum of **3** in CH_3CN.

finement. The hydrogen atoms of the Schiff-base ligand were generated geometrically (C–H fixed at 0.96 Å) and included in structure factor calculations with assigned isotropic thermal parameters; the methyl groups were treated as rigid groups, and the remaining hydrogen atoms were allowed to ride on their respective parent carbon atoms.

All computations were performed on a Data General Nova 3/12 minicomputer with the SHELXTL system.[9] Analytic expressions of neutral-atom scattering factors incorporating the real and imaginary components of anomalous dispersion were employed.[10] Blocked-cascade least-squares refinement[11] converged to the R indices and other parameters listed in Table V.

The final atomic coordinates for compound **3** are listed in Table VI. Bond distances and angles, hydrogen coordinates, anisotropic thermal parameters, and structure factor tables are available as supplementary material as mentioned in the last paragraph of this paper.

Results and Discussion

The synthesis of *trans*-dioxoosmium(VI) Schiff-base complexes **1–5** follows the same procedure as for *trans*-[Os^{VI}O$_2$(salen)].[4] These complexes, which are soluble in most common organic solvents such as CH_2Cl_2 and CH_3CN, are diamagnetic and show one intense IR ν_{as}(Os=O) stretch at 840–852 cm^{-1}. Table III summarizes the ^{1}H NMR data in CD_2Cl_2. The azomethine and bridging methylene protons of the Os(VI) complexes at δ = 8.3–8.6 and 4.2–4.3, respectively, are shifted downfield when compared with those in the *trans*-[Os^{IV}(salen)(OR)$_2$] (R = Me, Et) system.[4] The optical spectra of complexes **1–5** in CH_2Cl_2 show intense absorption bands in the 300–400-nm region, which are likely the charge-transfer transitions from the Schiff-base ligand to the Os(VI) ion. A typical optical spectrum of these complexes is shown in Figure 2.

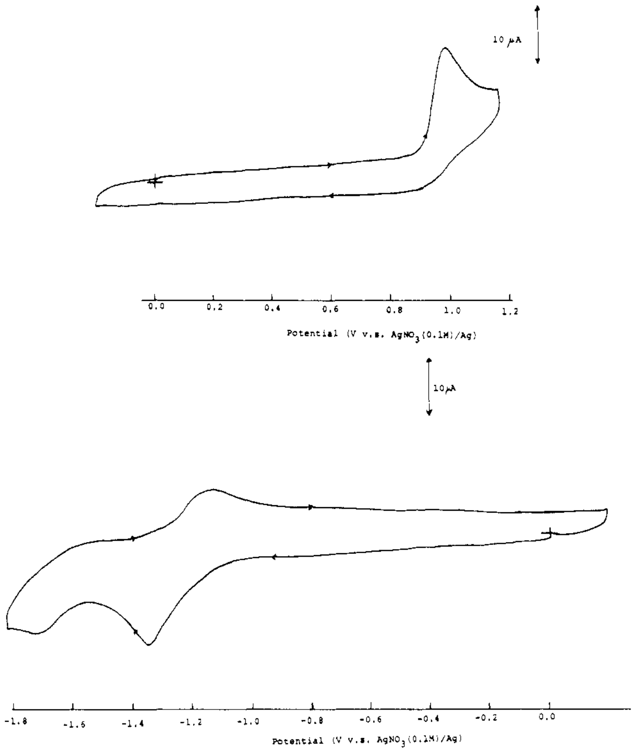

Figure 3. Cyclic voltammograms of **3** in 0.1 M [Bu$_4$N]PF$_6$–acetonitrile solution (scan rate 100 mV s^{-1}; working electrode pyrolytic graphite).

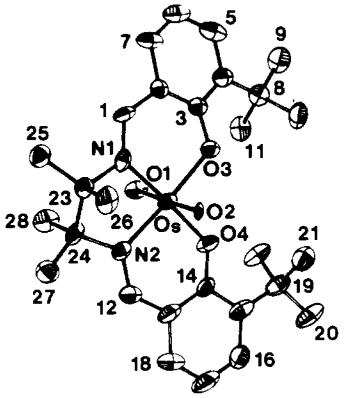

Figure 4. Perspective view of *trans*-[Os^{VI}O$_2$(3-*t*-Bu-saltmen)] (**3**) with atom labeling. The thermal ellipsoids are drawn at the 35% probability level. Selected bond distances (Å) and angles (deg): Os–O(1) = 1.760 (7), Os–O(2) = 1.722 (8), Os–O(3) = 2.052 (8), Os–O(4) = 2.037 (9), Os–N(1) = 2.025 (9), Os–N(2) = 2.017 (10); O(1)–Os–O(2) = 176.6 (4), N(1)–Os–N(2) = 81.5 (4), O(3)–Os–O(4) = 88.9 (4), N(1)–Os–O(3) = 95.1 (4), N(2)–Os–O(4) = 94.5 (4), O(osmyl)–Os–L(Schiff base) = 87.8–91.9 (3); N(1)–C(23)–C(24)–N(2) = 42 (1).

Complexes **1–5** are stable both in the solid state and in solution. These species are inert toward epoxidation of olefins even upon irradiation with UV light.[12] Table IV summarizes the electrochemical data of complexes **1–5**. The cyclic voltammogram of

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Table VI. Atomic Coordinates ($\times 10^5$ for Os; $\times 10^4$ for Other Atoms) and Thermal Parameters[a] ($Å^2 \times 10^4$ for Os; $Å^2 \times 10^3$ for Other Atoms) for *trans*-[$Os^{VI}O_2$(3-*t*-Bu-saltmen)] (**3**)

atom	*x*	*y*	*z*	U_{eq}
Os	35904 (4)	4655 (4)	25219 (2)	404 (2)
O(1)	3346 (6)	2132 (6)	2464 (3)	42 (3)
O(2)	3914 (7)	−1146 (7)	2587 (3)	48 (3)
O(3)	3395 (7)	371 (7)	1634 (3)	46 (3)
O(4)	1877 (7)	95 (9)	2413 (4)	58 (3)
N(1)	5305 (8)	815 (8)	2692 (4)	41 (3)
N(2)	3873 (8)	625 (8)	3396 (4)	44 (4)
C(1)	5865 (11)	1094 (11)	2286 (6)	55 (5)
C(2)	5330 (10)	1148 (10)	1622 (5)	42 (4)
C(3)	4167 (10)	842 (10)	1371 (5)	42 (4)
C(4)	3814 (11)	1055 (1)	772 (6)	53 (5)
C(5)	4618 (13)	1490 (14)	455 (7)	71 (6)
C(6)	5759 (13)	1767 (15)	748 (7)	73 (7)
C(7)	6116 (13)	1602 (13)	1329 (7)	63 (6)
C(8)	2527 (12)	852 (13)	436 (6)	59 (5)
C(9)	2338 (15)	1142 (16)	−205 (7)	85 (8)
C(10)	2208 (15)	−610 (13)	470 (7)	78 (7)
C(11)	1721 (13)	1661 (14)	708 (7)	71 (6)
C(12)	3082 (11)	297 (11)	3675 (6)	55 (5)
C(13)	1945 (12)	−146 (13)	3444 (7)	64 (6)
C(14)	1371 (11)	−210 (11)	2826 (7)	52 (5)
C(15)	240 (12)	−725 (12)	2656 (7)	63 (6)
C(16)	−307 (14)	−1072 (14)	3110 (7)	73 (6)
C(17)	218 (14)	−964 (16)	3693 (8)	97 (9)
C(18)	1306 (16)	−512 (17)	3860 (8)	92 (8)
C(19)	−399 (11)	−822 (14)	2013 (7)	66 (6)
C(20)	−1607 (12)	−1381 (15)	1939 (9)	92 (8)
C(21)	280 (13)	−1758 (14)	1726 (8)	78 (7)
C(22)	−464 (14)	553 (14)	1718 (8)	87 (8)
C(23)	5922 (11)	726 (10)	3340 (5)	45 (4)
C(24)	5014 (10)	1198 (10)	3689 (6)	53 (5)
C(25)	7014 (11)	1512 (12)	3457 (6)	59 (5)
C(26)	6218 (13)	−707 (10)	3453 (7)	61 (6)
C(27)	5403 (13)	791 (13)	4326 (6)	64 (6)
C(28)	4902 (13)	2703 (12)	3667 (7)	69 (7)

[a] The equivalent isotropic temperature factor U_{eq} is defined as one-third of the trace of the orthogonalized **U** matrix.

3 (Figure 3) in CH_3CN reveals that both oxidation and reduction of *trans*-dioxoosmium(VI) Schiff-base complexes are irreversible. The oxidation of **3** at 1.0 V vs the $Cp_2fe^{+/0}$ couple presumably generates an Os(VII)–dioxo complex, which is unstable and may oxidize the π-unsaturated Schiff-base ligand. The cause for the irreversibility of the reduction of Os(VI) to Os(V) is not yet understood, and further electrochemical studies are in progress.

Figure 4 shows a perspective view of the [$Os^{VI}O_2$(3-*t*-Bu-saltmen)] molecule (**3**). The structure constitutes the first reported example of a *trans*-dioxoosmium(VI) Schiff-base complex. The coordination geometry of osmium is distorted octahedral, and the trans-osmyl moiety is almost linear [O(1)–Os–O(2) = 176.6 (4)°] and perpendicular to the equatorial plane defined by the atoms N(1), N(2), O(4), and O(3). The measured osmyl Os–O bond distances of 1.760 (7) and 1.722 (8) Å, which are comparable to those values found in *trans*-$[OsO_2(en)_2]^{2+}$ [1.74 (1) Å],[13] $[OsO_2(NH_2CH_2COO)_2]$ (1.731 (3) Å)[14] and *trans*-[OsO_2(*o*-oxobenzoato)$(py)_2$] [1.729 (7) and 1.738 (7) Å],[15] appear to be significantly different, but it is known that pyridine-containing Os(VI) monoesters are asymmetric around the metal atom and contain osmyl groups that are bent.[16] The average Os–O(phenoxide) and Os–N(imine) bond distances, 2.044 (8) and 2.021 (9) Å, respectively, are in good agreement with those found for [Os^{IV}(salen)$(SPh)_2$].[4] The bond distances and angles within the ligand itself (see supplementary material) are not unusual in comparison with those values found for the [CoO_2(3-*t*-Bu-saltmen)(bzimid)] molecule.[5]

The five-membered chelate ring comprising Os, N(1), C(23), C(24), and N(2) takes the gauche form, so that the two sets of vicinal methyl substituents are staggered with respect to each other. Except for the slight asymmetry in the osmyl group, complex **3** conforms well to idealized C_2 molecular symmetry, with a pseudo-2-fold axis passing through the Os atom and the midpoint of the C(23)–C(24) bond.

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Registry No. **1**, 111380-03-1; **2**, 111380-04-2; **3**, 111380-05-3; **4**, 111380-06-4; **5**, 111380-07-5; $K_2[OsO_2(OH)_4]$, 77347-87-6.

Supplementary Material Available: Tables of hydrogen coordinates, anisotropic thermal parameters, and bond distances and angles (7 pages); a table of structure factors (22 pages). Ordering information is given on any current masthead page.

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