thank Mr. Jonathan M. Burton for assistance in preparing cyclen.

Supplementary Material Available: Tables of full crystallographic data, atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, bond distances, bond angles, torsion angles, and hydrogen atom coordinates for 9 (7 pages); tables of observed and calculated structure factors for 9 (16 pages). Ordering information is given on any current masthead page.

Multiple Bonds between Main-Group Elements and Transition Metals. 85.[1] Tetramethyloxoosmium(VI): Synthesis, Gas-Phase Molecular Structure, Photoelectron Spectroscopy, and Electrochemistry

Kristin Rypdal,[†] Wolfgang A. Herrmann,*,[‡] Stefan J. Eder,[‡,§] Rolf W. Albach,[‡,§]
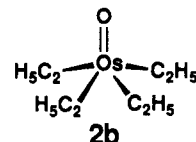Petra Watzlowik,[‡] Hans Bock,[∥] and Bahman Solouki[∥]

*Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo 3, Norway,
Anorganisch-chemisches Institut, Technische Universität München, Lichtenbergstrasse 4,
D-8046 Garching b. München, Germany, and Institut Für Anorganische Chemie
der Universität Frankfurt, Niederurseler Hang, D-6000 Frankfurt am Main 50, Germany*

Tetramethyloxoosmium(VI) (2a), the first example of methylosmium oxides $(CH_3)_xOs_yO_z$, has been synthesized from osmium tetraoxide (1a) and dimethylzinc (19% yield) or methyltris(isopropoxy)titanium (50% yield). A more directed synthesis (60% yield) is methylation of the glycolate osmium(VI) complex $O=Os(OCH_2CH_2O)_2$ (1b), which precursor compound is in turn accessible from 1a in quantitative yield. The thermally labile *ethyl* derivative tetraethyloxoosmium(VI) (2b), the first well-characterized example of its class $(C_2H_5)_xOs_yO_z$, is also reported. The title compound 2a is an orange, air-stable, volatile, crystalline compound that melts at 74 °C without decomposition. The gas-phase average molecular structure of 2a, as determined by electron diffraction techniques, is consistent with a theoretical model having C_4 symmetry, with the most important parameters being r_a(Os–C) = 209.6 (3) pm, r_a (Os=O) = 168.1 (4) pm, and $\angle$(OOsC) = 112.2 (5)°. According to PE spectroscopic data, the d ionization of 2a occurs at 8.55 eV. The title compound 2a undergoes irreversible oxidation at +2.2 V, reversible reduction at –1.58 V (cyclic voltammetry).

Introduction

Simple organorhenium oxides such as methyltrioxorhenium(VII), CH_3ReO_3, have proven effective catalysts in olefin oxidation, olefin metathesis, and olefination of aldehydes.[2,3] In spite of this rather well-established high-oxidation-state rhenium chemistry, little is known about similar and analogous compounds of any other transition metal.[2,4] Osmium tetraoxide, OsO_4, like dirhenium heptaoxide, Re_2O_7, is soluble in organic solvents. As a consequence of this similarity, one should expect alkyl and aryl derivatives of the type $R_xOs_yO_z$ to be accessible as well. Wilkinson et al.[5] have reported the preparation of the oxoosmium(VI) complexes $[(CH_3)_3SiCH_2]_4OsO$ (12% yield), $[2,4,6-(CH_3)_3C_6H_2]_2OsO_2$ (29%), and $[2,6-(CH_3)_2C_6H_3]_2OsO_2$ (44%). Recently, the synthesis of $[(CH_3)_3SiCH_2]_4OsO$ was improved by Shapley et al. (54% yield), who used $[P(C_6H_5)_4]_2[OsO_2Cl_4]$ (two-step preparation OsO_4 (ex), 87% yield) as the starting material.[6] However, no single example of a *methyl*osmium oxide has become known in the literature. In the present paper we describe the first successful, directed synthesis of a most simple organoosmium oxide, $(CH_3)_4OsO$ (2a). The ethyl derivative $(C_2H_5)_4OsO$ (2b) has been prepared for the sake of comparison with regard to thermal stability. The gas-

[†] University of Oslo.
[‡] Technische Universität München.
[§] Ph.D. Fellow of the Verband der Chemischen Industrie, Frankfurt am Main, Germany, 1990–1992.
[∥] Universität Frankfurt am Main.

$$\underset{\textbf{2b}}{\overset{\displaystyle \overset{O}{\parallel}}{H_5C_2 \diagdown \underset{H_5C_2 \diagup}{Os} \diagdown\!\!\!\diagup C_2H_5}}$$

phase molecular structure of the novel parent compound tetramethyloxoosmium(VI) (2a), determined by electron

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diffraction techniques, the electrochemistry, and the photoelectron spectrum are also reported.
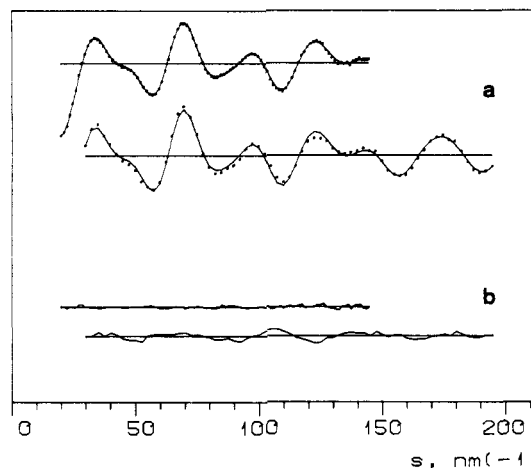
Experimental Section

All operations were carried out under nitrogen by employing standard Schlenk techniques. Diethyl ether was distilled from sodium/benzophenone and n-pentane from CaH_2 under nitrogen. Dimethylzinc was prepared from methylmagnesium iodide with $ZnCl_2$·(dioxane).[7] Methyltris(isopropoxy)titanium(IV) was prepared according to established literature syntheses.[8] For chromatography silylated silica (0.063–0.200 mm, Merck No. 7719) was used after oxygen elimination in vacuo (4 days, 200 °C). IR spectra were obtained on a Nicolet 5DX FT-IR spectrometer and NMR spectra on a JEOL-JNM-GX-270 or -GX-400 spectrometer. Chemical shifts are reported in ppm downfield from TMS for ^1H and ^{13}C NMR spectra. ^{17}O NMR data are referenced to external water with $\delta(H_2O) = 0.0$ ppm. A mass spectrometer Varian MAT 90 was used for the electron-impact mass spectra. Elemental analyses were performed by M. Barth and U. Graf in the Microanalytical Laboratory of our institute.

I. Synthesis. *Important note! Special care has to be taken when working with osmium tetraoxide, which compound is known as an extremely poisonous material of high volatility. All experiments have thus to be carried out in an effective hood.*

(1) Tetramethyloxoosmium(VI) (2a). Method A. To a stirred solution of osmium tetraoxide (1a) (2.5 g, 9.8 mmol) in diethyl ether (50 mL) was added dimethyl zinc (35 mL of a 1.0 M solution in diethyl ether, 35 mmol) at –78 °C. The stirred mixture was then warmed slowly to room temperature. After 2 h, the volatile materials were removed under reduced pressure, and the dark residue was extracted with n-pentane (2 × 100 mL). Concentration of the filtered extracts in vacuo and cooling overnight (–78 °C) afforded red-orange needles. Yield: 0.50 g (19%). Alternatively, methyltris(isopropoxy)titanium (950 mg, 3.96 mmol) was used as the methylating agent. It was added as an ether solution to a stirred solution of 250 mg (0.98 mmol) osmium tetraoxide in diethyl ether (10 mL) at –78 °C. After warming to room temperature, the solvent was removed in vacuo. The product was column-chromatographed on silylated silica with n-pentane at 0 °C and then further purified by means of sublimation in a high vacuum at ca. 50 °C. Yields up to 130 mg (50%) are thus obtained.

Method B. The starting compound 1b is prepared from osmium tetraoxide (1a) and 1,2-ethanediol in nearly quantitative yields according to a published procedure by Griffith et al.[15a] To a solution of the glycolate osmium(VI) complex 1b (660 mg, 2.0 mmol in 15 mL of diethyl ether) was added dropwise dimethyl zinc (12 mL of a 1.0 M solution in diethyl ether, 12 mmol) with cooling in an ice bath. After stirring for several hours and slowly warming to room temperature, the solvent was removed under reduced pressure. The residue was subjected column chromatography on silylated silica with n-pentane at 0 °C. Yield: 320 mg (60%). Mp: 74 °C with slow sublimation occurring at lower temperatures.

Spectroscopic data: IR (CS_2) ν(Os=O) 1013 cm^{-1} (vs), ν(C—H) 2965 cm^{-1} (m), 2884 cm^{-1} (w); ^1H NMR (270 MHz, toluene-d_8,

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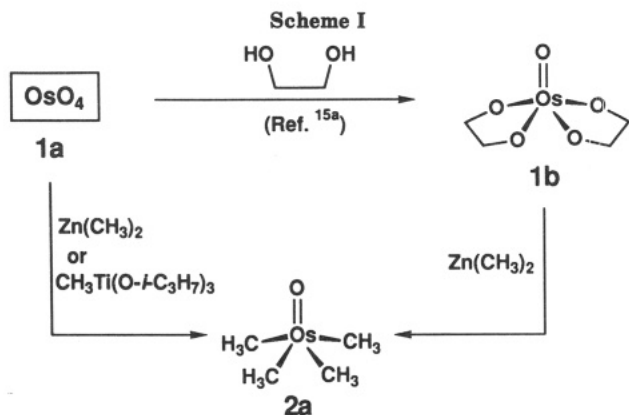
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Figure 1. (a) Theoretical (full line) and experimental (dotted line) intensity curves for $(CH_3)_4OsO$ (2a). Each data set is shown. (b) Difference curve between experimental and theoretical intensity.

20 °C) $\delta(CH_3)$ 2.74 ppm (s); $\{^1H\}^{13}C$ NMR (67.9 MHz, toluene-d_8, 20 °C) $\delta(CH_3)$ 23.91 ppm; ^{17}O NMR (54.2 MHz, toluene, 20 °C) $\delta(O)$ 512 ppm; EI MS (70 eV, m/e referenced to ^{192}Os) 268 (relative intensity 16%, [M]$^+$), 253 (4%, [M – CH_3]$^+$), 250 (10%, [M – H_2O]$^+$), 237 (60%, [M – OCH_3]$^+$, 235 (100%, [M – H_2O – CH_3]$^+$), 192 (4%, Os); UV/vis (cyclohexane) λ_{max} (ϵ, 10^3 L mol^{-1} cm^{-1}) 254 nm (1.02), 346 nm (0.26).

Elemental Anal. Calcd for $C_4H_{12}OOs$ (266.34): C, 18.04; H, 4.54; O, 6.01. Found: C, 18.12; H, 4.55; O, 6.37.

(2) Tetraethyloxoosmium(VI) (2b). To a stirred solution of 1.0 g (3.96 mmol) of osmium tetraoxide (1a) in hexane (10 mL) was added a solution of diethyl zinc [16 mL of a 1.0 M solution in hexanes (Aldrich), 16 mmol] at –78 °C. The reaction mixture was stirred for 1 h at the low temperature. Silylated silica was then added at –78 °C. The volatile materials were subsequently removed under reduced pressure, and the dark residue was subjected to column chromatography on silylated silica, with n-pentane being the eluent. *The temperature was not allowed to rise above –10 °C throughout all manipulations!* The orange solution was concentrated in vacuo. Cooling overnight at –78 °C afforded red-orange needles, which were dried at –70 °C in an oil-pump vacuum. Yield: 150 mg (12%).

Spectroscopic data: ^1H NMR (400 MHz, CDCl$_3$, 20 °C) $\delta(CH_2)$ 4.03 ppm (8 H, q, $^3J(H,H)$ = 7.3 Hz), $\delta(CH_3)$ 1.51 ppm (12 H, t, $^3J(H,H)$ = 7.3 Hz); $\{^1H\}^{13}C$ NMR (100.5 MHz, CDCl$_3$, 20 °C) $\delta(CH_2)$ 40.30 ppm, $\delta(CH_3)$ 20.29 ppm; CI MS (m/e, ^{192}Os) 324 (relative intensity 41%, [M]$^+$), 308 (9%, [M – CH_4]$^+$, 295 (28%, [M – C_2H_5]$^+$), 293 (40%, [M – OCH_3]$^+$), 265 (100%, [M – C_2H_4 – OCH_3]$^+$. Elemental analyses could not be obtained due to the pronounced thermolability of this compound.

II. Gas-Phase Electron Diffraction. The GED data were recorded on a Balzers Eldiograph KD-G2.[9] The nozzle and reservoir temperature were approximately 25 °C. The electronic wavelength was calibrated against the C–C distance (r_a = 139.75 pm) in gaseous benzene. Two sets of data were recorded, one with a nozzle-to-plate distance of 50 cm and one with a distance of 25 cm, four plates in each data set. The plates were subjected to photometry, and the data were processed by standard procedures.[10] The s limits used in the final refinements were s = 20.0–145.0 nm^{-1}, with Δs = 1.25 nm^{-1} (50 cm), and s = 30.0–195.0 nm^{-1}, with Δs = 2.50 nm^{-1} (25 cm). The backgrounds were computer-drawn, and finally the intensity curves were averaged within each set of data. Complex atomic scattering factors $f'(s)$ were taken from ref 11; tabulated values were used for osmium.[12] The molecular intensity curves for the best model are shown in Figure 1.

III. Photoelectron Spectrum. Analogous to the spectrum of $(\eta^5\text{-}C_5Me_5)ReO_3$,[13] the spectrum of 2a has been recorded by using the high-performance spectrometer Leybold Heraeus UPG 200 and calibrated by both the $^2P_{3/2}$ ionizations of Ar and Xe at 15.76 and 12.13 eV, respectively. The tentative assignment by a Koopmans analogous correlation, $IE_n^v \approx -\epsilon_j^{EHMO}$, is based on

Scheme I

Figure 2. Molecular structure of tetramethyloxoosmium(VI) (2a).[33]

EHMO calculations starting from the known gas-phase structure and using the following parameters for Os within a double-ζ basis set (Slater exponents): $\alpha(6s)$ = 8.17 eV (2.452), $\alpha(6p)$ = −4.81 eV (2.429), and $\alpha(5d)$ = −11.84 (5.571 and 2.416 with C_1 = 0.6372 and C_2 = 0.5598).[14]

IV. Electrochemistry. All cyclic voltammograms were recorded with an EG&G-PAR 173 potentiostat controlled by an HP-Vectra personal computer. A glassy-carbon working electrode of 7 mm² and a Pt counter electrode of 100 mm² were used. Acetonitrile was purified by refluxing over CaH_2 for 6 days, distillation, and passing over a 10-cm column of Al_2O_3. The solvent was N_2-saturated. The concentration of $(CH_3)_4OsO$ was 28 mmol L⁻¹.

Results and Discussion

I. Synthesis. As the most simple organoosmium oxide known to date, the title complex **2a**, *tetramethyloxoosmium(VI)*, is accessible from either osmium tetraoxide (**1a**) or the bis(glycolato-*O,O*) complex **1b** of hexavalent osmium. The first-named route, employing dimethylzinc to methylate **1a**, suffers from low yields (19%), which would preclude extensive studies of this chemistry. While the methyltitanium(IV) reagent as indicated in Scheme I gives much better yields (ca. 50%), the workup of product is much more tedious in this case, with oily side products giving rise to several extractive purification steps of unpredictable success.

Upon consideration of the *reduction* step that occurs in *any* alkylation or arylation reaction of osmium tetraoxide (Os^{VIII} → Os^{VI} or Os^{IV}),[5a–f] we designed a more straightforward synthesis. It starts with the Os^{VI}-precursor compound **1b**. This bis(glycolato-*O,O*) complex is most easily available in big quantities from the Os^{VIII} oxide **1a** and 1,2-ethanediol, according to a published procedure by Griffith et al.[15a] It reacts smoothly with dimethylzinc according to Scheme I with formation of **2a**. With yields around 60%, the workup procedure is very simple, so an effective, easy method is at hand. This glycolate method has been successfully used in several other cases concerning organic oxides of osmium(VI) and rhenium(VII).[1]

The title compound **2a** is a red-orange, crystalline, air-stable compound that sublimes in an oil-pump vacuum at room temperature as orange needles. No gaseous products can be detected when the compound is brought in contact with water (GC–MS). However, decomposition occurs when the pH is raised by addition of sodium hydroxide with predominant formation of methane. Attempts of thermal decomposition at 200 °C gave only insufficient results, with little amounts of hydrocarbons formed during the decomposition, the gas being composed of methane (65%), ethane (27%), and ethylene (8%).

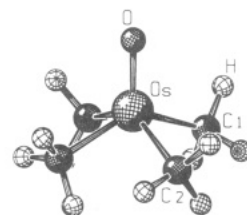For the sake of comparison (β-H abstraction?) we also prepared the first ethylosmium compound of high oxida-

tion states. *Tetraethyloxoosmium(VI)* (**2b**) like the methyl congener **2a** can be column-chromatographed on silylated silica (0.063–0.200 mm) at −10 °C. However, temperatures of −10 °C and lower are to be maintained throughout the entire preparation, workup, and storage. If one does so, **2b** is isolated as orange crystals that melt with decomposition above ca. −60 °C. The compound is more stable in solution. (¹H NMR spectra may be recorded at room temperature within a period of no more than 30 min.) Upon warming neat **2b** from −60 °C to room temperature, *extensive decomposition* occurs. While the solid residue is intractable in any solvent, the gases were identified by GC–MS as *n*-butane (48%), ethane (33%), and ethylene (17%). This indicates that not only β-hydrogens are involved in thermal decomposition; radical-type alkyl–osmium bond cleavage seems also to participate in decomposition. The methyl complex **2a** is completely stable under such conditions (see above).

2a and **2b** are the most simple organoosmium oxides known. Other examples include $[(CH_3)_3SiCH_2]_4OsO$,[5a,6] *cis*-$[(CH_3)_3SiCH_2]_2(CH_3)_2OsO$,[1] $(CH_3)_2OsO_2(py)_2$,[1] $[(CH_3)_2OsO_2(py)]_3$,[1] $[(CH_3)_3SiCH_2]OsO_2(py)_2$,[1] and $\overline{(CH_3)_2OOsOC(CH_3)_2C(CH_3)_2O}$.[1] However, there is no alkylosmium complex known in an oxidation state higher than +VI, nor has a homoleptic alkyl OsR₆ yet been seen.

II. Electron Diffraction Study. The GED data are consistent with a square-pyramidal model of symmetry C_{4v} (not considering the hydrogen atoms, otherwise C_4). If we assume that the methyl groups are twisted in an equal manner, this model has six independent parameters, namely three bond distances [r_a(Os—C), r_a(Os=O), and r_a(C—H)], two bond angles [$\angle$(COsC) and $\angle$(OsCH)], and *one* torsion angle [ϕ(OOsCH)]. The latter is defined as zero when all methyl groups are staggered with respect to the osmium–oxo bond. A model of the molecule is shown in Figure 2. These parameters along with six root-mean-square amplitudes were refined by a least-squares fit of a theoretical intensity curve to the two experimental curves. Nonrefined amplitudes were fixed at values determined by trial and error and experience from similar compounds. Too few vibrational frequences are known for a force field analysis. The most important geometrical parameter values and root-mean-square amplitudes are listed in Table I. All least-squares standard errors are multiplied by a factor of 2.5 to compensate for the assumptions made when the model is defined and for systematic errors in the experiment. Of the correlation coefficients for the parameters of main interest, r_a(Os=O), r_a(Os—C), and $\angle$(OOsC), only the $\angle$(OOsC) correlation with $\angle$(COsC) is of serious concern (72%). The radial distribution curve is shown in Figure 3. The most important peaks are indicated by bars having length proportional to nZ_iZ_j/R_{ij} (where the Z's are the atomic numbers, R_{ij} is the distance between the two atoms, and n is the multiplicity). The R factor ($R = [\sum(I_{obs} - I_{exp})^2/\sum I_{obs}^2]^{1/2}$) for the best model was 5.9%. The second (25 cm) data set contains little information about the structure; the listed parameters

	r_a	l
Bond Distances (pm)		
Os—C	209.6 (3)	6.1 (6)
Os=O	168.1 (4)	2.9 (1.5)
C—H	111.0 (4)	7.4 (7)
Nonbonded Distances (pm)		
Os···H	267 (2)	15 (2)
O···C	314 (1)	13 (2)
C(1)···C(2)	274 (1)	8 (2)
C(1)···C(3)	388 (1)	[11.0][b]
Bond Angles (deg)		
OOsC	112.2 (5)	
OsCH	108.7 (1.1)	
C(1)OsC(2)	81.8 (4)	
Torsional Angles (deg)		
OOsCH	24 (8)	

[a] Least-squares standard errors are multiplied by a factor of 2.5 to compensate for errors introduced when defining the model and for systematic errors in the experiment. [b] Values in square brackets are not refined.
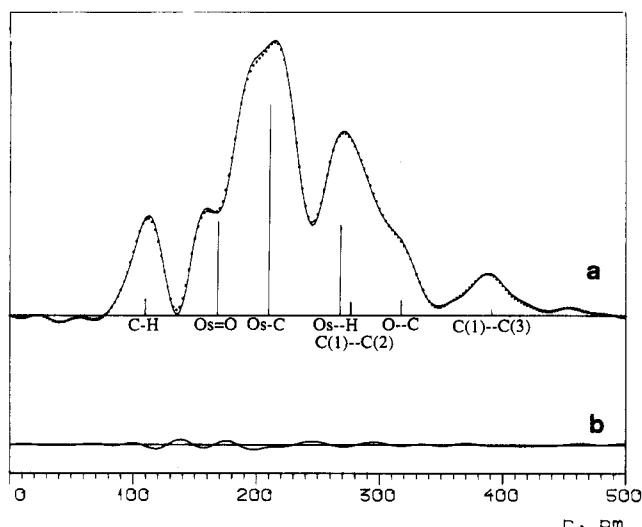
Figure 3. (a) Theoretical (full line) and experimental (dotted line) radial distribution curves for $(CH_3)_4OsO$ (2a). The most important peaks are indicated by bars. (b) Difference curve between experimental and theoretical radial distribution curves. The artificial damping is 40 pm^2.

Figure 4. He I photoelectron spectrum of $(CH_3)_4OsO$ (2a) with tentative EHMO assignment.

are mainly determined from the 50-cm data set, having an R factor of 4.0%.

Only very few structures of simple organoosmium compounds are known. The osmium–methyl bond length of 209.6 (3) pm is markedly longer than the average osmium–phenyl distance of 199.4 (1.2) pm observed in Os-$(C_6H_5)_4$,[5e] the tolyl and cyclohexyl derivatives Os[2-$(CH_3)C_6H_4]_4$ and $Os(C_6H_{11})_4$,[5b,e] the oxo aryl compounds [2,4,6-$(CH_3)_3C_6H_2]_2OsO_2$[5d] and [2,6-$(CH_3)_2C_6H_3]_2OsO_2$,[5f] with values ranging from 197.7 (11) to 206.0 (6) pm. In the aryl compounds the Os–C bond is probably shortened by a π-bonding contribution, so reliable comparative data are really missing. In $Os_2(\eta^3$-$C_3H_5)_2[CH_2C(CH_3)_3]_6$ the Os(III)–C(alkyl) bonds are 214 (2) and 219 (2) pm.[5c] Compared to the title compound, however, this particular complex is sterically strained. The Os–C distance of 2a should be the standard value for a relatively unstrained Os–C single bond. The recently published X-ray crystal structure of [$(CH_3)_3SiCH_2]_4OsO$ exhibits Os–C bond lengths (ranging from 205.7 (9) to 209.9 (9) pm) similar to

those of $(CH_3)_4OsO$ (2a).[6] In CH_3ReO_3, recently investigated by GED, the Re(VII)–C bond is shorter (206.0 (8) pm).[16] From the position in the periodic table we would expect an Os–C bond to be slightly shorter. CH_3ReO_3 is sterically even less strained (CN 4) than 2a (CN 5); in addition we compare Re(VII) with Os(VI). In the more crowded hexamethyltungsten, $W(CH_3)_6$, the W(VI)–C bond is even longer: 214.6 (3) pm (GED).[17] The difference in length between the W–C and the Os–C bonds is as expected from the close neighborhood of these elements in the periodic table. The OOsC bond angle is wide, 112.2 (5)°. In Cl_4OsO (GED) the corresponding OOsCl angle is 108.3 (4)°.[18] This angle reflects the strong repulsion of the methyl groups from the osmium–oxygen double bond compared to methyl–methyl repulsions.

The square pyramid is the most common coordination geometry for other organometals of electronic d^2 configuration. For example, the related Re^V complexes (η^5-$C_5Me_4Et)ReBr_3(CH_3)$[19] and (η^5-$C_5Me_5)Re(CH_3)_4$[20] have the same structure. While these compounds behave as Lewis acids, forming adducts with triphenylphosphane, e.g. (η^5-$C_5Me_5)ReCl_4[P(C_6H_5)_3]$,[21] no base addition reactions

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could be achieved with the title compound **2a**. For example, neither tertiary phsophanes nor amines react with **2a**. No ^{17}O NMR shift is observed upon addition of any of these potential ligands to solutions of **2a**, in marked contrast with the behavior of CH_3ReO_3.[2,28]

III. Photoelectron Spectroscopy.[22] The molecule $(CH_3)_4OsO$ contains 42 valence electrons, which, according to a useful rule of thumb $[\sum(1s_H + np_E + md_M)/2 = IE_n^v$ (He I)],[23] should give rise to $n = 15$ ionizations within the He I measurement region. The photoelectron spectrum[23] (Figure 4) exhibits three isolated bands at low energy and a tremendous ionization hill between 11 and 16 eV, resulting from at least 12 overlapping ionizations, as estimated from the approximate intensity ratio of 1:1:1:12. Due to the unpredictable and widely differing electronic relaxations of individual radical-cation states of medium-sized organometallic compounds,[24] only a tentative though plausible assignment can be suggested. It is based on a double-ζ EHMO calculation for the gas-phase electron diffraction structure of C_4 symmetry. Accordingly (cf. Figure 4), the ground state of the $(CH_3)_4OsO$ radical cation $\tilde{X}(^2B)$ at 8.55 eV should arise from d electron ionization at the (formally) hexavalent metal center. The next two bands at 9.55 and 9.97 eV, respectively, are Koopmans correlated to the two π ionizations from the $Os(d_{zx}, d_{zy})/O(p_x, p_y)$ multiple bond, with the calculated degeneracy (Figure 4, 5e) being removed presumably due to spin/orbit coupling. For the assignment of the PE spectrum of osmocene,[25] a spin/orbit coupling constant $\zeta = 0.38$ eV has been used, which would satisfactorily explain the observed split, $IE_3^v - IE_2^v = 0.42$ eV, in the PE spectrum of tetramethyloxoosmium (Figure 4). Further support is provided by a relativistic EHMO calculation,[26] which yields for the highest occupied orbitals the eigenvalues −11.2, −12.2, −12.4, and −13.2 eV. Although the calculated split of only 0.2 eV is too small, nevertheless, the degeneracy of the e-type orbital is removed. The succeeding two peaks, recognizable in the low-energy flank of the ionization represent M^{•+} states with predominant contributions from $Os(d_{x^2-y^2}, d_{z^2})/C(p)$ bonds (Figure 4, 4b and 6a). The remaining and strongly overlapping bands between 12 and 16 eV are assigned by an approximate Koopmans correlation, $IE_n^v \approx -\epsilon_j^{EHMO}$, to less characteristic ionizations of the title compound. They generate radical-cation states, in which the positive charge is delocalized over the σ-framework with varying contributions from σ(OsC), σ(CH), and σ(OsO) bonds.

As concerns photoelectron spectra of analogous alkyl-metal oxides, on which an additional comparison by equivalent radical-cation states by perturbation arguments[27] could be based, the single case known to us is that of methyltrioxorhenium.[28] Its first ionization energy amounts to 11.78 eV, clearly indicating that CH_3ReO_3 due to its formal Re(+VII) center contains *no* d electrons. The radical-cation ground state of the C_{3v} molecule is tentatively assigned $\tilde{X}(^2A_1)$, i.e. to a predominant contribution of the σ(CRe) bond, and closely followed at 12.0 eV by a band of double intensity, presumably due to an $\tilde{A}(^2E)$ state arising largely from the π(ReO) bonds. At first sight, the
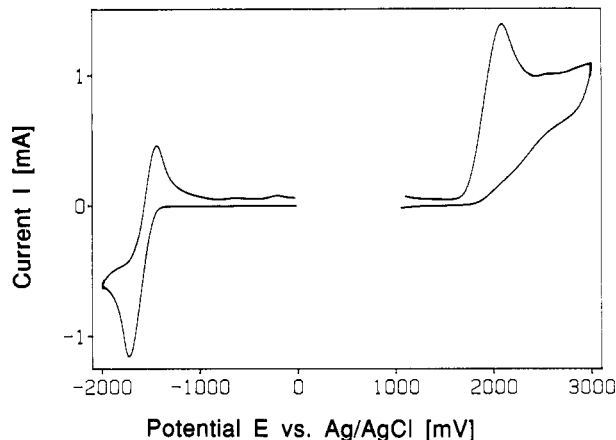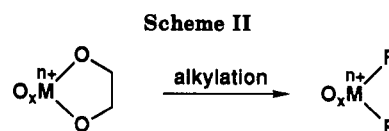

Figure 5. Cyclovoltammogram of $(CH_3)_4OsO$ (**2a**) in acetonitrile/0.1 M $[(n-C_4H_9)_4N][PF_6]$. Potentials are referenced versus Ag/AgCl/3 M KCl; the scan rate is 200 mV s⁻¹.

Scheme II

observed shift of the π-metal–oxo ionization by 2.5 eV from 9.5 eV for $(CH_3)_4OsO$ (Figure 4) on substituting three methyl groups by two oxygen centers to 12.0 eV for CH_3ReO_3 seems to be a reasonable assumption, although the two molecules differ in composition, structure, and symmetry.

IV. Electrochemistry. As another probe for the stability of the title compound, we investigated the redox properties by cyclic voltammetry. In acetonitrile, $(CH_3)_4OsO$ can be quasi-reversibly $(\Delta E \geq 186$ mV, $i_{pa}/i_{pc} \leq 0.7)$ reduced to the corresponding anion at −1.58 V vs Ag/AgCl, and above 2.2 V it is irreversibly oxidized. Considering $E_0(Ag/AgCl) = 0.208$ V vs NHE, these potentials can be compared with the electrochemical couples $Sn^{2+} + 2e^- = Sn$ (−1.583 V vs Ag/AgCl) and $O(g) + 2H^+ + 2e^- = H_2O$ (2.213 V vs Ag/AgCl) in aqueous solution.[29]

A comparison with two other recently published complexes of metal d² configuration, tetrakis(2-methylphenyl)molybdenum(IV)[30] and tetrakis(norbonyl)molybdenum(IV),[31] reveals analogous features for all three compounds: a reversible wave at negative potentials, an irreversible wave at positive potentials. However, the oxidation of the title compound $(CH_3)_4OsO$ (**2a**) occurs at substantially higher potentials (2.2 V as compared to 0.63[30] and 1.25 V,[31] respectively). The reduction waves of $(CH_3)_4OsO$ $(E_{1/2}^{red} = -1.58$ V) and $(C_6H_4-o-CH_3)_4Mo$ $(E_{1/2}^{red} = -1.89$ V) are assigned to single-electron transfers, as shown for **2a** by comparison with ferrocene, to the corresponding d³ anions. By way of contrast, the reversible wave of tetrakis(norbornyl)molybdenum(IV) (−0.15 V vs Ag/AgCl) has been interpreted as an oxidation of this complex.[31] To our surprise, $[(CH_3)_3SiCH_2]_4OsO$ and $[(CH_3)_3SiCH_2]_4RuO$ behave completely different in cyclovoltammetry. While they show one-electron oxidations at 1.19 and 1.20 V, respectively, no reversible reduction waves are observed.[6]

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Conclusion

Alkylation of glycolate-*O,O* derivatives of metal oxides is a better, more direct way to organometal oxides, especially when the metal is in the correct oxidation state (Scheme II). As we show in other cases,[1] a glycolate ligand is replaced by two alkyl groups much more selectively than an oxo group. This rule should be kept in mind with attempts to synthesize other organometal oxides, a class of compounds that is still missing for most transition metals. We have recently also been successful with this general procedure in organorhenium chemistry.[32] Further

work with these and other metals is in progress.

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Synthesis and Structure of a Highly Branched Polycarbosilane Derived from (Chloromethyl)trichlorosilane

Chris K. Whitmarsh and Leonard V. Interrante*

Chemistry Department, Rensselaer Polytechnic Institute, Troy, New York 12180

Received August 29, 1990

A highly branched hydridopolycarbosilane has been prepared by Grignard coupling of (chloromethyl)trichlorosilane, followed by reduction with lithium aluminum hydride. Trapping studies show that the initial step in the polymerization is a nearly quantitative formation of the Grignard compound Cl_3-$SiCH_2MgCl$. This Grignard compound undergoes head-to-tail (Si–C) coupling almost exclusively, and due to its trifunctional $SiCl_3$ "tail", a complicated, branched, polycarbosilane polymer results, which contains the following structural units: $SiCl_3CH_2$–, –$SiCl_2CH_2$–, >$SiClCH_2$–, and >$SiCH_2$–. The chloropolycarbosilane undergoes side reactions with ether, leading to incorporation of small amounts of ethyl and ethoxy functionality. During the reduction step the ethoxy groups are eliminated, yielding a polymer with the approximate formula $[SiH_{1.85}Et_{0.15}CH_2]_n$, which has been characterized by ^1H, ^{13}C, and ^{29}Si NMR, IR, GPC, and elemental analysis. This polymer is of interest as a precursor to near-stoichiometric silicon carbide.

Introduction

Highly branched silicon-containing polymers have been previously reported in conjunction with studies on silicon carbide precursors. Schilling et al.[1] have investigated several systems in which various mixtures of Me_3SiCl, Me_2SiCl_2, and $H_2C=CHSi(Me)Cl_2$ were treated with potassium, resulting in the formation of complicated, branched polysilanes. The branching was induced by reaction of the vinyl groups with potassium, leading to formation of $SiCH_2CHSi_2$ units in the polymer. Baney[2] has prepared polymers composed of complicated arrangements of fused polysilane rings. These polymers are prepared by treating mixtures of partially chlorinated disilanes of the general formula $Me_{6-x}Cl_xSi_2$ (*x* = 2–4) with Bu_4PCl at elevated temperatures. Kriner[3] reported the formation of polymeric byproducts during the "reverse Grignard" reaction of (chloromethyl)dichloromethylsilane employed to prepare various cyclic carbosilane compounds. These

byproducts were presumably branched polycarbosilanes but were not investigated in any detail.

We report herein the characterization of a novel polycarbosilane with a highly branched structure. Due to the complex nature of this polymer, precise naming is difficult. The polymer isolated from the initial Grignard coupling reaction and its $LiAlH_4$-reduced analogue will be referred to as chloropolycarbosilane and hydridopolycarbosilane, respectively. The theoretical "average" formulas for these polymers would be $[SiCl_2CH_2]_n$ and $[SiH_2CH_2]_n$; however, due to their highly branched nature and side reactions with the ether solvent, the actual structures are much more complicated. The hydridopolycarbosilane is potentially useful as a precursor to silicon carbide ceramics, as it has nearly at 1:1 Si:C ratio and undergoes facile thermal cross-linking reactions leading to high ceramic yields.

Experimental Section

General Procedures. All manipulations involving air-sensitive materials were carried out in oven-dried glassware by using standard inert-atmosphere techniques.[4] Solvents were distilled under nitrogen from appropriate drying agents.[5] Magnesium powder (No. 50 mesh) was reground by using a modified pepper

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