

Table VI. Atom Coordinates ($\times 10^4$) of $[(9\text{-aneN}_3)_2\text{Mo}_2\text{Cl}_2(\mu\text{-OH})_2]\text{I}_2$

| atom | x | y | z |
|------|------------|-----------|-----------|
| Mol | 977 (1) | 375 (1) | 479 (1) |
| I | 5533 (1) | 8342 (1) | 4794 (1) |
| O1 | 626 (8) | 922 (7) | 4653 (7) |
| Cl1 | -916 (4) | 1278 (3) | 5996 (3) |
| N1 | 1427 (11) | 201 (8) | 7042 (9) |
| N2 | 2852 (11) | 9967 (9) | 6045 (10) |
| N3 | 1784 (11) | 8388 (9) | 6490 (9) |
| C1 | 2352 (16) | 918 (11) | 7245 (13) |
| C2 | 3328 (14) | 518 (13) | 7048 (14) |
| C3 | 3443 (15) | 9039 (14) | 6190 (14) |
| C4 | -3066 (16) | 1633 (13) | 3192 (13) |
| C5 | 1514 (15) | 8463 (11) | 7404 (13) |
| C6 | 1810 (15) | 9447 (12) | 7861 (12) |

(0.5 M) at 20 °C under argon. Anal. $[(9\text{-aneN}_3)_2\text{Mo}_2(\text{OH})_2(\text{H}_2\text{O})_2]\text{Br}_{3.5}\text{I}_{0.5}$ C, H, N, Br, I, Mo.

$[(9\text{-aneN}_3)_2\text{Mo}_2(\mu\text{-OH})_2\text{Cl}_2]\text{I}_2$ (6). (4)I₂ (0.5 g) was dissolved in 30 mL of hydrochloric acid (0.5 M) at 20 °C under an argon atmosphere. Upon addition of sodium iodide (5 g), green crystals precipitated, which were filtered off, washed with ethanol and ether, and dried under argon. Anal. C, H, N, I, Mo.

$[(9\text{-aneN}_3)_2\text{Mo}_2\text{O}_4]\text{X}_2$ (8), X = Cl⁻, Br⁻, I⁻, or ClO₄⁻. A. To a suspension of (NH₄)₂MoCl₅(OH₂) (3.3 g) in 30 mL of dimethyl sulfoxide (Me₂SO) was added a solution of 1,4,7-triazacyclononane (1.3 g) in 10 mL of ethanol under an argon atmosphere. The solution was kept at 50 °C with stirring for 3 h during which time a yellow precipitate formed. The microcrystals of (8)Cl₂ were filtered off, washed with ethanol and ether, and air-dried. The crude product was recrystallized from a minimum amount of water and sodium chloride.

A bromide, iodide, or perchlorate salt of 8 was obtained from aqueous solutions of the above chloride by adding sodium bromide, sodium iodide, and sodium perchlorate, respectively. Anal. C, H, N, Hal, Mo.

B. Identical products were obtained by dissolving (4)I₂ (1.0 g) in 20 mL of perchloric acid (0.7 M) at 40 °C. Within 1 h a clear yellow solution was generated from which the above salts were obtained upon addition of the respective sodium halide salt.

X-ray Crystallography. Details of the measurements of cell dimension and of intensity using suitable crystals for X-ray data col-

lections of 6 and 3a, respectively, are summarized in Table IV. The data were corrected for Lorentz and polarization effects. Empirical corrections for absorption effects were carried out in all cases.²¹ The structures were solved via three-dimensional Patterson syntheses, which yielded the positions of the molybdenum, iodine, and chlorine atoms, respectively. Subsequent Fourier syntheses revealed the locations of all remaining non-hydrogen atoms. Idealized positions of H atoms bound to carbon atoms were calculated (on the basis of $d(\text{C-H}) = 0.96 \text{ \AA}$ and regular tetrahedral geometry about the C atoms) and were refined as rigid moieties with fixed isotropic thermal parameters ($U = 0.067 \text{ \AA}^2$ for 3a, and $U = 0.054 \text{ \AA}^2$ for 6) and anisotropic thermal parameters for the C atoms (supplementary material). Refinements were carried out with use of anisotropic thermal parameters for all other atoms. The function minimized during least-squares refinement was $\sum w_i(|F_o| - |F_c|)^2$ ($w_i = 1/\sigma^2(F)$). The positions of H atoms bound to nitrogens of the amine ligands were not located for 6 and 3a; the H atoms of the hydroxo bridges were also not located and were not included in final refinement cycles. In structure 6 a statistical disorder of the iodide positions was found. The least-squares analysis of the occupancy factor revealed an 85% occupancy of the uncoordinated iodide positions by iodide and 15% by chloride.

Final positional parameters for 3a and 6 are given in Tables V and VI, respectively. Calculated positions of hydrogen atoms and anisotropic thermal parameters and listings of observed and calculated structure factors are available as supplementary material.

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Registry No. 1, 87938-79-2; 2, 85923-29-1; 3a·I₃·H₂O, 87938-80-5; 3b·I₃, 87938-81-6; 4·I₂, 85939-37-3; 5·I₄, 87938-82-7; 5·Br_{3.5}I_{0.5}, 87984-19-8; 6·I₂, 87938-83-8; 7·I₂, 85923-30-4; 8 (X = Cl⁻), 87938-84-9; 8 (X = Br⁻), 87984-15-4; 8 (X = I⁻), 87984-16-5; 8 (X = ClO₄⁻), 87984-18-7; (NH₄)₂MoCl₅(OH₂), 13820-59-2.

Supplementary Material Available: Listings of elemental analyses of new compounds, anisotropic thermal parameters, calculated hydrogen atom parameters, and structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

(21) Computations were carried out on a NOVA (general data) computer using the SHELXTL program package (Revision 3.0, July 1981) by G. M. Sheldrick, University of Göttingen.

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A Linear μ -Oxo-Diosmium(IV) Molecule in Which Two Bis(diphenylphosphino)methane Ligands Bridge an Entire M-O-M Unit: $\text{Os}_2(\mu\text{-O})(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2\text{Cl}_6$

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The title compound, $\text{Os}_2(\mu\text{-O})(\mu\text{-dppm})_2\text{Cl}_6 \cdot 2\text{CHCl}_3$ (dppm = $(\text{PPh}_2)_2\text{CH}_2$), was prepared by reacting OsCl_3 with dppm. The crystal and molecular structure of this compound has been determined from three-dimensional X-ray study. The compound crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions $a = 11.138$ (3) Å , $b = 24.461$ (5) Å , $c = 12.769$ (3) Å , $\beta = 105.82$ (3)°, and $V = 3347$ (3) Å^3 with $Z = 4$. The structure was refined to $R = 0.044$ ($R_w = 0.052$). The complex molecule, which lies on a crystallographic inversion center, has a linear Os-O-Os central unit with an Os-O bond distance 1.792 (1) Å . The complex is diamagnetic. The equivalence of all phosphorus atoms is evidenced from both the ³¹P NMR spectrum (chemical shift 30.9 ppm) and the X-ray structure. The dihedral angles O-Os-P-C of two phosphine bridges are 22.2 and 27.2°. A dichloromethane solution of the complex displays one one-electron oxidative response at +1.62 V ($\Delta E_p = 200$ mV) and two one-electron reductive processes at +0.09 V ($\Delta E_p = 180$ mV) and -1.13 V. The coulometrically reduced (at -0.15 V) solution of the dimer exhibits a rhombic EPR spectrum with $g_1 = 2.022$ and $g_2 = 1.578$. The electronic spectrum of the dichloromethane solution shows absorption bands at 355 ($\epsilon = 26000$), 425 (18500), 490 (9600), and 705 nm (760). The spectroelectrochemical behavior of this complex can be interpreted by using a qualitative molecular orbital scheme, framed on the assumption that a strong Os-Os interaction exists through the linear oxide bridge.

Introduction

Both ruthenium and osmium are known to combine with potentially bridging ligands to form dinuclear complexes in which there are multiple metal-to-metal bonds.¹ However,

the known range of this chemistry is still not great and an effort is being made in this laboratory to extend it. As part of this

(1) Cotton, F. A.; Walton, R. A. "Multiple Bonds between Metal Atoms"; Wiley: New York, 1982; pp 192-198.

Table I. Crystallographic Data

| | |
|---|--|
| formula | Os ₂ Cl ₁₂ P ₄ OC ₅₂ H ₄₆ (1) |
| fw | 1616.7 |
| space group | <i>P</i> 2 ₁ / <i>c</i> |
| <i>a</i> , Å | 11.138 (3) |
| <i>b</i> , Å | 24.461 (5) |
| <i>c</i> , Å | 12.769 (3) |
| β, deg | 105.82 (3) |
| <i>V</i> , Å ³ | 3347.1 (2.7) |
| <i>Z</i> | 4 |
| <i>d</i> _{calcd} , g/cm ³ | 3.21 |
| cryst size, mm | 0.5 × 0.2 × 0.05 |
| μ(Mo Kα), cm ⁻¹ | 88.17 |
| data collection instrument | Syntex P1 |
| radiation | Mo Kα (monochromated) |
| scan method | ω-2θ |
| data collection range, deg | 4-50 (2θ) |
| total no. of data measd | 4033 |
| no. of unique data, <i>F</i> _o ² ≥ 3σ(<i>F</i> _o ²) | 3027 |
| no. of parameters refined | 358 |
| <i>R</i> ^a | 0.044 |
| <i>R</i> _w ^b | 0.052 |
| quality-of-fit indicator ^c | 0.099 |
| largest shift/esd, final cycle | 0.15 |
| abs cor | semiempirical (ψ-scan) |
| abs range | 72.5-100 |

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2]^{1/2} / \sum w|F_o|$. ^c Quality of fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{observns}} - N_{\text{parameters}})]^{1/2}$.

effort, we have examined reactions of lower-valent osmium compounds with the potentially bridging (but also potentially chelating) ligand bis(diphenylphosphino)methane, dppm. The unexpected result of one of our investigations is reported here. We have obtained a compound in which two dppm ligands are bridging not simply a pair of metal atoms but an entire linear M-O-M unit, thus forming a six-membered ring with an unprecedented stereochemistry. The complete molecular formula is Os₂(μ-O)Cl₆(dppm)₂. The compound crystallizes with CHCl₃ molecules occupying interstices between the osmium molecules, and a fully refined X-ray crystallographic structure determination has been carried out.

Experimental Section

Osmium(III) chloride and CH₂(PPh₂)₂ (dppm) were purchased from Aldrich Chemical Co. and Strem Chemical Co., respectively.

Preparation of Hexachloro(μ-oxo)bis[μ-bis(diphenylphosphino)methane]diosmium(IV)-Bis(chloroform), Os₂(μ-O)(μ-CH₂(PPh₂)₂)₂Cl₆·2CHCl₃ (1). A mixture of 25 mL of methanol, 0.15 g (~0.5 mmol) of osmium(III) chloride, and 0.19 g (~0.5 mmol) of bis(diphenylphosphino)methane (dppm) was stirred for 10 h under a dinitrogen atmosphere. The color of the reaction mixture changed from brown to red-brown. The precipitated complex was filtered and redissolved in chloroform. Dark brown crystals were obtained in 40-60% yield by slow diffusion of hexane into the chloroform solution. The compound is moderately soluble in chloroform, dichloromethane, tetrahydrofuran, and acetonitrile. Comparable yields were obtained whether the reaction was carried out in air or under an atmosphere of nitrogen.

Measurements. Electronic spectra were recorded with a Cary 17D spectrophotometer. ³¹P NMR data were collected in CDCl₃ with a Varian XL200 PFT spectrometer, using external H₃PO₄ as standard. EPR data were obtained at X band from a Varian E-6S EPR spectrometer using DPPH as standard. Cyclic voltammetric and coulometric measurements were carried out with a Beckman Electroscan 30 analytical system. Dichloromethane and 0.1 M tetrabutylammonium perchlorate (TBAP) were used as solvent and supporting electrolyte, respectively. Solutions were degassed with dinitrogen. In the three-electrode system, a planar Beckman Model 39273 platinum-inlay working electrode, a platinum-wire auxiliary electrode, and a saturated calomel reference electrode (SCE) were used. Electrochemical measurements were made at 298 K and are uncorrected for junction potentials.

X-ray Crystallographic Procedures. The structure of 1 was obtained by using the same general procedures as described elsewhere.^{2,3} A

Table II. Positional Parameters and Their Estimated Standard Deviations in Os₂O(dppm)₂Cl₆·2CHCl₃^a

| atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> , Å ² |
|-------|-------------|-------------|-------------|---------------------------|
| Os(1) | 0.16481 (4) | 0.01200 (2) | 0.04453 (4) | 2.057 (8) |
| Cl(1) | 0.1249 (3) | 0.3920 (1) | 0.5421 (3) | 2.93 (7) |
| Cl(2) | 0.2174 (3) | 0.5815 (1) | 0.5448 (3) | 3.07 (7) |
| Cl(3) | 0.3749 (3) | 0.4682 (1) | 0.6048 (3) | 3.45 (8) |
| Cl(4) | 0.0064 (6) | 0.7676 (3) | 0.1100 (5) | 10.9 (2) |
| Cl(5) | 0.948 (1) | 0.2496 (3) | 0.0930 (6) | 14.5 (3) |
| Cl(6) | 0.2516 (6) | 0.7289 (3) | 0.5907 (8) | 13.1 (3) |
| Cl(7) | 0.4515 (6) | 0.3205 (3) | 0.7568 (5) | 9.5 (2) |
| Cl(8) | 0.3651 (9) | 0.2647 (3) | 0.5556 (6) | 13.3 (3) |
| Cl(9) | 0.4200 (6) | 0.6695 (5) | 0.4021 (6) | 15.1 (3) |
| P(1) | 0.1541 (3) | 0.5084 (1) | 0.7298 (2) | 2.32 (6) |
| P(2) | 0.1502 (3) | 0.4743 (1) | 0.3519 (3) | 2.37 (7) |
| O(1) | 0.000 | 0.500 | 0.500 | 2.1 (3) |
| C(1) | -0.011 (1) | 0.4502 (5) | 0.2851 (9) | 2.3 (3) |
| C(2) | 0.098 (2) | 0.7140 (7) | 0.525 (2) | 6.4 (5) |
| C(3) | 0.436 (2) | 0.3225 (8) | 0.616 (1) | 6.4 (5) |
| C(11) | 0.177 (1) | 0.5309 (5) | 0.269 (1) | 2.9 (3) |
| C(12) | 0.248 (1) | 0.5242 (6) | 0.195 (1) | 4.6 (4) |
| C(13) | 0.259 (2) | 0.5694 (7) | 0.128 (1) | 5.8 (5) |
| C(14) | 0.204 (2) | 0.6198 (6) | 0.139 (1) | 5.7 (5) |
| C(15) | 0.135 (1) | 0.6252 (6) | 0.215 (1) | 4.7 (4) |
| C(16) | 0.123 (1) | 0.5814 (6) | 0.281 (1) | 3.4 (3) |
| C(21) | 0.246 (1) | 0.4182 (5) | 0.325 (1) | 2.7 (3) |
| C(22) | 0.373 (1) | 0.4284 (6) | 0.351 (1) | 3.3 (3) |
| C(23) | 0.452 (1) | 0.3864 (7) | 0.334 (1) | 4.6 (4) |
| C(24) | 0.403 (1) | 0.3349 (6) | 0.293 (1) | 4.3 (4) |
| C(25) | 0.276 (1) | 0.3258 (6) | 0.273 (1) | 4.4 (4) |
| C(26) | 0.195 (1) | 0.3681 (5) | 0.287 (1) | 3.2 (3) |
| C(31) | 0.277 (1) | 0.5548 (6) | 0.8075 (9) | 2.8 (3) |
| C(32) | 0.256 (1) | 0.6105 (6) | 0.820 (1) | 3.8 (3) |
| C(33) | 0.351 (1) | 0.6440 (6) | 0.880 (1) | 4.2 (4) |
| C(34) | 0.464 (2) | 0.6197 (7) | 0.930 (1) | 5.0 (4) |
| C(35) | 0.490 (1) | 0.5653 (6) | 0.917 (1) | 4.3 (4) |
| C(36) | 0.391 (1) | 0.5310 (6) | 0.855 (1) | 3.5 (3) |
| C(41) | 0.157 (1) | 0.4541 (5) | 0.828 (1) | 2.5 (3) |
| C(42) | 0.119 (1) | 0.4646 (6) | 0.923 (1) | 3.7 (3) |
| C(43) | 0.126 (1) | 0.4231 (6) | -0.002 (1) | 4.1 (4) |
| C(44) | 0.170 (1) | 0.3719 (6) | 0.982 (1) | 4.5 (4) |
| C(45) | 0.207 (1) | 0.3619 (6) | 0.889 (1) | 4.4 (4) |
| C(46) | 0.205 (1) | 0.4036 (5) | 0.811 (1) | 3.4 (3) |

^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{1}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos \gamma)B_{12} + ac(\cos \beta)B_{13} + bc(\cos \alpha)B_{23}]$.

Table III. Some Bond Distances and Angles in Os₂O(dppm)₂Cl₆·2CHCl₃

| Bond Distances (Å) | | | |
|--------------------|-----------|------------------|------------|
| Os(1)-Cl(1) | 2.387 (3) | Os(1)-P(2) | 2.443 (4) |
| -Cl(2) | 2.360 (3) | -O(1) | 1.792 (1) |
| -Cl(3) | 2.307 (3) | P(1)-C(1) | 1.859 (12) |
| -P(1) | 2.452 (3) | P(2)-C(1) | 1.857 (12) |
| Bond Angles (deg) | | | |
| Cl(1)-Os(1)-Cl(2) | 176.1 (1) | Cl(3)-Os(1)-P(1) | 91.9 (1) |
| -Cl(3) | 88.0 (1) | -P(2) | 95.2 (1) |
| -P(1) | 98.9 (1) | -O(1) | 177.1 (1) |
| -P(2) | 83.8 (1) | P(1)-Os(1)-P(2) | 172.6 (1) |
| -O(1) | 89.20 (8) | -O(1) | 87.57 (8) |
| Cl(2)-Os(1)-Cl(3) | 88.5 (1) | P(2)-Os(1)-O(1) | 85.51 (8) |
| -P(1) | 83.1 (1) | Os(1)-P(1)-C(1) | 106.2 (4) |
| -P(2) | 94.7 (1) | Os(1)-P(2)-C(1) | 107.3 (4) |
| -O(1) | 94.26 (9) | P(1)-C(1)-P(2) | 124.6 (7) |

detailed description is available as supplementary material. The crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table I. Complete tables

- (2) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.
Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227. North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr.* **1968**, *A24*, 351.
(3) Calculations were done on the PDP-11/60 computer at B. A. Frenz and Associates, Inc., College Station, TX, with software from the Enraf-Nonius SDP-PLUS package.

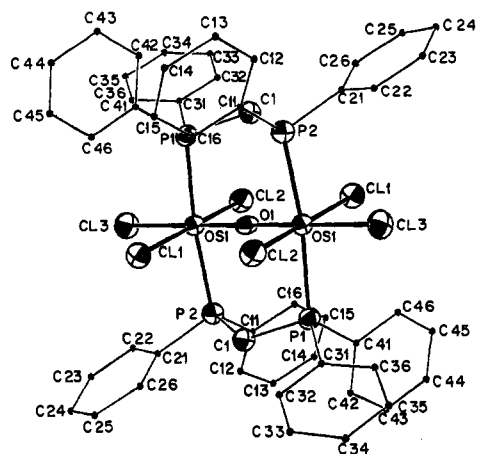


Figure 1. ORTEP drawing of the Os₂O(dppm)₂Cl₆ molecule. Atoms are represented by thermal vibration ellipsoids at the 40% level, and the atomic labeling scheme in this centrosymmetric molecule is defined.

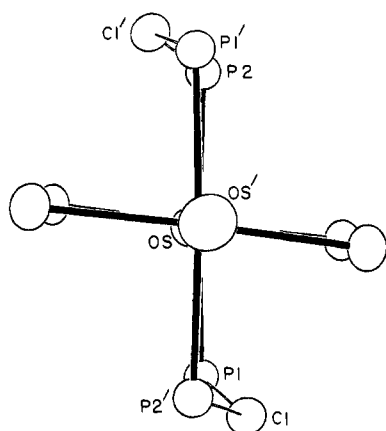


Figure 2. ORTEP drawing of the central portion of the molecule.

of anisotropic thermal parameters and structure factor data are available as supplementary material.

Results

Structure. The atomic coordinates and equivalent isotropic thermal vibration parameters are listed in Table II. Important bond distances and angles are presented in Table III, and Figure 1 shows the structure of the osmium molecule and defines the numbering system used in the tables. The crystals are composed of molecules of Os₂(μ-O)(μ-dppm)₂Cl₆, located on inversion centers. In addition there are two reasonably well-defined chloroform molecules of crystallization per molecule of the dimer without interactions other than packing contacts. The molecule as a whole has symmetry approximating C_{2h}, where the plane would pass through C(1), C(1)', and O(1) and be perpendicular to the Os—O—Os axis. If only the Os—O—Os unit and its 10 ligand atoms are considered, D_{2h} symmetry is approached. However, as shown in Figure 2, which is a view of the central region of the molecule down the Os—O—Os line, there are significant deviations from this higher symmetry, apart from the presence of C(1) and C(1)'. Thus, the set of Cl—Os—Cl angles involving Cl(1), Cl(1)', Cl(2), and Cl(2)', instead of all being equal, form two sets. Two are acute, 83.8 (1) and 83.1 (1)°, while the other two are obtuse, 98.9 (1) and 94.7 (1)°. This appears to be a result of internal crowding in which the dppm phenyl groups exert unequal pressures on Cl(1) and Cl(2).

Electrochemistry. The redox chemistry was studied by cyclic voltammetry and constant-potential coulometry, with platinum electrodes in dichloromethane containing 0.1 M TBAP as a supporting electrolyte. Potentials were measured vs. a saturated calomel electrode (SCE) at 298 K. The molecule dis-

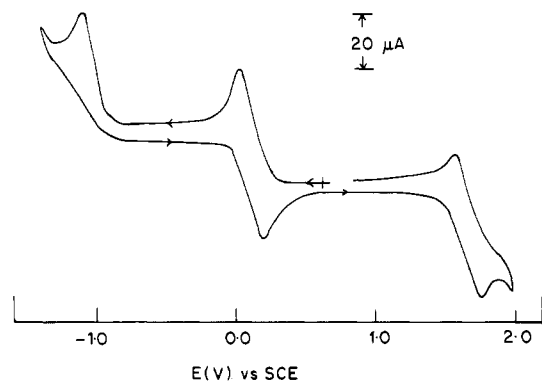


Figure 3. Cyclic voltammogram of Os₂O(dppm)₂Cl₆ in dichloromethane (0.1 M TBAP) at a platinum electrode (scan rate 40 mV s⁻¹, concentration 1 × 10⁻³ M).

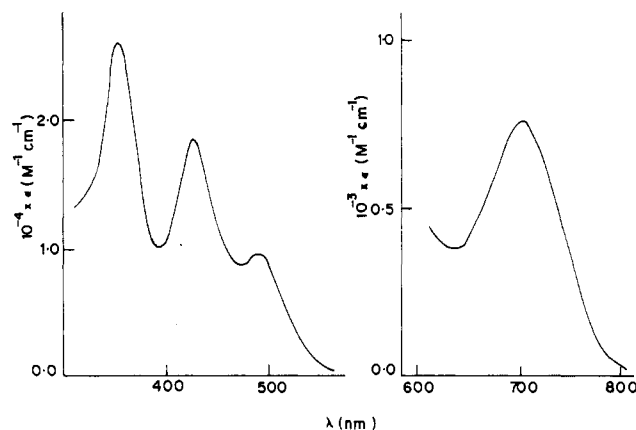
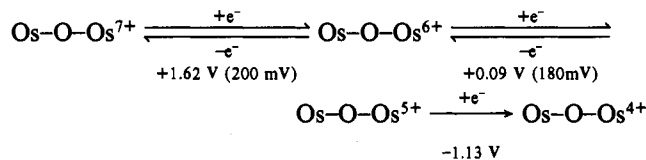


Figure 4. Electronic spectrum of Os₂O(dppm)₂Cl₆ in dichloromethane.

plays two quasi-reversible voltammograms at +0.09 V (peak to peak separation, ΔE_p, of 180 mV) and +1.62 V (ΔE_p = 200 mV) and an irreversible response at -1.13 V (Figure 3). These were shown to be one-electron processes by constant-potential coulometry and peak current measurements. While the voltammogram at +1.62 V is due to oxidation, the other two responses are due to successive reductions. The redox processes along with the formal potentials E_{1/2} and ΔE_p values (in parentheses) are summarized in the following scheme. For the irreversible step the cathodic peak potential, E_{pc}, is given:



The solutions generated after coulometric oxidation or reduction are unstable. The EPR spectrum (at liquid-nitrogen temperature, 77 K) of the coulometrically reduced solution at -0.15 V displays a rhombic pattern with g₁ = 2.022 and g₂ = 1.578. We could not observe g₃ within the scan limit. At room temperature (298 K) a broad average EPR spectrum was observed at g_{av} = 2.397.

Electronic Spectra. A dichloromethane solution exhibits several absorption bands in the visible and near-UV region (Figure 4). There are three intense bands at 355 (ε = 26000), 425 (18500), and 490 nm (9600) and a weaker one at 705 nm (ε = 760).

The coulometrically reduced (at -0.15 V) solution, which is yellow, is unstable and is easily reoxidized to the neutral molecule as evidenced by the electronic spectrum. However, a band was observed at 450 nm with moderate intensity. An ethanolic solution of NaBH₄ was found to be effective in bringing about reduction, giving a yellow solution that dis-

played a band at 450 nm and two shoulders at 380 and 300 nm. When the solution was allowed to stand, however, it became colorless. We think that the reduced species reacts slowly with further NaBH_4 to give an uncharacterized product.⁴

Discussion

Perhaps the most remarkable feature of the compound reported here is the presence of the bridging dppm ligands spanning the linear Os—O—Os unit in which the Os...Os distance is 3.584 (1) Å. We thus have two six-membered rings fused on two collinear bonds. As is evident from Figure 2, the entire central set of four phosphorus atoms and the Os—O—Os group are virtually coplanar, but the carbon atoms, C(1) and C(1)', are bent out of that mean plane. The torsional angles O(1)—Os(1)—P(1)—C(1) and C(1)—Os(1)—P(2)—C(1)' are 22.2 and 27.2°, respectively. For the dppm ligand to form part of such an unusual ring, some angular distortions are naturally required. The angles at the phosphorus atoms are not unusual, viz., 106.2 (4) and 107.3 (4)°. The O—Os—P angles are acute, viz., 85.51 (5) and 87.57 (8)°, but not remarkably so. The place where nearly all of the accommodation to the unusual ring conformation is made is in the P—C—P angle, which has the remarkable high value of 124.6 (7)°. It seems remarkable that the observed structure is adopted in view of the strains engendered, rather than either (a) a different ligand arrangement in which the dppm ligands would be chelating or (b) a cis relationship of the bridging ligands together with a bent Os—O—Os group, as found recently in the $\text{Os}_2(\mu\text{-O})(\mu\text{-CH}_3\text{CO}_2)_2\text{Cl}_4(\text{PPh}_3)_2$ molecule.⁵ Of course, the dppm ligand does have a significantly larger bite than the carboxyl group, so that the arrangement we have found here, under some strain, would doubtless be entirely impossible in the carboxylato-bridged species.

Another remarkable feature of this compound is its origin—in fairly good yield—under reaction conditions that need not be intentionally oxidizing from osmium(III) chloride. The preparation was first carried out under a blanket of nitrogen, but it was subsequently found that a comparable yield is obtained under laboratory air. We do not know whether atmospheric O_2 is responsible for oxidizing the Os^{III} to Os^{IV} and for supplying the $\mu\text{-O}$ atom. If it is, then we must suppose that when the reaction was run under nitrogen there had been oxygen present adventitiously. In any event, however, the important point is that the preparation can be carried out without the use of a protective atmosphere. We cannot rule out the possibility that impurities in the osmium(III) chloride may play a role. Since the goal of our work was *not* to obtain this product, interesting though it is in its own way, we do not plan to investigate its origin or properties further.

Although the bridging dppm ligands are unusual, the $\text{Os}_2(\mu\text{-O})(\text{dppm})_2\text{Cl}_6$ molecule is otherwise a member of a fairly large and important class of linearly oxo-bridged dinuclear complexes with short M—O distances and strong metal—metal interactions through the π orbitals of the metal and bridging oxygen atoms.^{6–13} Structurally characterized ex-

amples of this type of compound containing osmium atoms are restricted to the decahalo complexes $[\text{Os}_2\text{OX}_{10}]^{4-}$ ($\text{X} = \text{Cl}, \text{Br}$), which have a linear Os—O—Os arrangement.¹² The recently reported⁵ structure of $\text{Os}_2(\mu\text{-O})(\mu\text{-CH}_3\text{COO})_2\text{Cl}_4(\text{PPh}_3)_2$, as already noted, shows a bent Os—O—Os bridging unit, and there is no structural information on $[\text{Os}_2\text{O}(\text{bpy})_2(\text{terpy})_2]^{4+}$ and $[\text{Os}_2\text{OCl}_8(\text{OH})_2]^{4-}$ ($\text{bpy} = 2,2'$ -bipyridine, $\text{terpy} = \text{terpyridine}$), which presumably have Os—O—Os central units.^{14,15}

The Os—O distance, 1.792 (1) Å, is obtained with high accuracy here since the oxygen atom resides on an inversion center. Thus, the Os—O distance is simply half of the Os—Os distance, which is obtained very accurately because of the precise positional parameters obtained for the heavy metal atom. For the same reason the Os—O distance in $\text{Cs}_4[\text{Os}_2\text{OCl}_{10}]$, 1.778 (2) Å, is also known very precisely.¹² The small difference between these two distances, 0.014 (2) Å, is statistically significant because of the high accuracy of each of the individual values, but it is scarcely significant chemically. In the kinked molecule, $\text{Os}_2\text{O}(\text{CH}_3\text{CO}_2)_2(\text{PPh}_3)_2\text{Cl}_4$, the two Os—O bonds are crystallographically independent and were found to have lengths of 1.830 (10) and 1.828 (9) Å, from which an average of 1.829 (7) Å can be obtained. This differs from the one we have found by 0.037 (7) Å, which is statistically significant and probably also large enough to imply that the Os—O bonds are slightly weaker in the bent molecule.

The Os—O distances in this molecule as well as in $[\text{Os}_2\text{OCl}_{10}]^{4-}$ are consistent with the M—O distances in other such species having 0–4 electrons per metal ion, in terms of the generally accepted bonding scheme of Dunitz and Orgel.¹⁶ These comparisons have recently been discussed in detail.¹³ It may be noted that in $\text{Os}_2\text{O}(\text{dppm})_2\text{Cl}_6$ the Os—Cl axial distance, 2.307 (3) Å, is shorter than the Os—Cl equatorial distances, 2.360 (3) and 2.387 (3) Å, whereas a longer distance might have been expected by comparison with $[\text{Os}_2\text{OCl}_{10}]^{4-}$, where the axial distance is 0.06 (1) Å longer than the average of the equatorial ones. However, in other such species¹³ the $\text{ax} \leq \text{eq}$ relationship has been seen, especially in $[\text{Ru}_2\text{OCl}_{10}]^{4-}$, where the axial distance is 0.045 (10) Å shorter than the average of the equatorial ones. In the present case the longer Os—P bonds and the general bending of the equatorial ligands toward the oxygen atom leaves more room for a closer approach of the axial chlorine atom. Thus, on several grounds the observed relationship between the axial and equatorial Os—Cl bond lengths is understandable.

The electrochemical behavior of **1** can be compared with that of $\text{Os}_2(\mu\text{-O})(\mu\text{-O}_2\text{CH}_3)_2\text{X}_4(\text{PPh}_3)_2$ ($\text{X} = \text{Cl}, \text{Br}$), which undergoes⁵ successive one-electron reductions, one at $E_{1/2} = +0.2$ V and another within -0.7 to -1.0 V. However, no oxidation was reported. The electrochemical behavior of a series of $[(\text{AA})_2\text{XRuORuX}(\text{AA})]^{n+}$ species ($\text{AA} = 2,2'$ -bipyridine or 1,10-phenanthroline) has also been reported,¹⁷ but because of the strong π interactions between the metal atoms and the AA ligands, as well as the presence of Ru in place of Os, comparisons between these compounds and the present one are not very pertinent. Unfortunately, it does not appear

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that electrochemical data have been reported for the $[M_2OCl_{10}]^{4-}$ species with $M = Ru$ or Os .

To conclude this report, we shall discuss the spectroscopic and electrochemical data for this compound in the light of an appropriate form of the bonding scheme for the linear, dinuclear, oxo-bridged species. The well-known scheme originally put forward by Dunitz and Orgel¹⁶ for the $[Ru_2OCl_{10}]^{4-}$ ion, which has D_{4h} symmetry, can easily be modified if we idealize the symmetry of the $Os_2OP_4Cl_6$ skeleton of our molecule to D_{2h} , using as before the $M-O-M$ direction as the z axis and calling the plane containing the phosphorus atoms the xz plane and the one containing the four equatorial chlorine atoms the yz plane. The principal consequence of changing from a D_{4h} $[M_2OCl_{10}]^{4-}$ unit to a D_{2h} $M_2OP_4Cl_6$ unit is that the degeneracies of the e_u and e_g orbitals are lifted, e_u splitting into $b_{2u} + b_{3u}$ and e_g into $b_{2g} + b_{3g}$.

As far as the electrochemistry is concerned, the details of these splittings, so long as they are not large, are unimportant. We are still dealing with a system in which the LUMO is an orbital that is π antibonding with respect to the $Os-O-Os$ unit and the HOMO is one of a set of approximately nonbonding orbitals. Reduction of the molecule places an electron in an antibonding (π^*) orbital, which accounts for the instability of the reduced species. Further reduction places still another electron in a set of π^* orbitals already singly occupied, and thus the very negative potential (-1.13 V) is not surprising, nor is the fact that this step is irreversible. Somewhat surprising is the high oxidation potential of $+1.62$ V. Thus, the HOMO may be more bonding in character than the qualitative picture of the electronic structure suggests. For $Os_2O(CH_3CO_2)_2(PR_3)_2$ species two voltammetric reductions were found at ca. $+0.2$ V (reversible) and -0.7 to -1.0 V (irreversible) with exact values depending on the identities of R and X.

While the electronic absorption spectrum (Figure 4) shows quite discrete, symmetrical bands, it is impossible to propose

firm assignments, not only because of the low molecular symmetry but also because the spectrum of the obvious reference species $[Os_2OCl_{10}]^{4-}$ is poorly characterized.^{7b,18} It appears that dissociation (or some other type of disintegration) of the dinuclear species occurs rapidly in solution, thus creating uncertainty as to what spectral features genuinely belong to the $[Os_2OCl_{10}]^{4-}$ ion. From the work of San Filippo, Fagan, and DiSalvo,^{7b} however, it does appear that there is a band at 558 nm that must be associated with the $Os-O-Os$ group and probably also another at 395 nm. For the more stable $[Ru_2OCl_{10}]^{4-}$ ion the spectrum is well-defined and there is good evidence that a band at 480 nm is due to a transition in the $Ru-O-Ru$ group. San Filippo et al. suggest that it can be assigned to the $e_g(\pi\text{-nonbonding})$ to $e_u(\pi\text{-antibonding})$ transition.

The spectrum of $Os_2O(dppm)_2Cl_6$ is rather similar to that of $[Ru_2OCl_{10}]^{4-}$ except that instead of a broad band at 375 nm ($\epsilon = 10\,000$) and another at 480 nm (5200) in the ruthenium compound there are three strong bands, as shown in Figure 4. Both compounds have a weak band in the near-IR, as does $[Os_2OCl_{10}]^{4-}$. Perhaps one or both of the strong bands characteristic of the $[M_2OCl_{10}]^{4-}$ ions have been split (by $3000\text{--}5000\text{ cm}^{-1}$) by the change from a D_{4h} Os_2OCl_{10} central group to a D_{2h} $Os_2OP_4Cl_6$ central group.

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Supplementary Material Available: Details of the crystal structure determinations, tables of structure factors and anisotropic thermal parameters, complete lists of bond distances and bond angles, and tables of least-squares planes and torsional angles (30 pages). Ordering information is given on any current masthead page.

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Kinetics and Mechanism of Iron(II), Cobalt(II), and Nickel(II) Mono Complex Formation with Acetohydroxamic Acid

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The temperature-jump method has been used to determine the rate constants for the formation of complexes of Fe(II), Co(II), and Ni(II) in aqueous solution with bidentate acetohydroxamic acid at ionic strength 0.10 M ($NaNO_3$). The formation rate constants for reaction of the uninegatively charged, deprotonated form of ligand with Ni(II) and Co(II) are consistent with the dissociative (Eigen) mechanism of octahedral substitution. They are, at 20.0 ± 0.1 °C, for Ni(II) and Co(II) complex formation, $(3.25 \pm 1.18) \times 10^4$ and $(4.69 \pm 1.17) \times 10^6\text{ M}^{-1}\text{ s}^{-1}$ and, for complex dissociation, 1.63×10^{-1} and $3.21 \times 10^{-1}\text{ s}^{-1}$, respectively. For reaction of Ni(II) and Co(II) at the same temperature with the neutral, protonated form of the ligand the formation rate constants are $(7.17 \pm 0.08) \times 10^2$ and $(3.59 \pm 0.08) \times 10^4\text{ M}^{-1}\text{ s}^{-1}$ and the dissociation rate constants are 8.03×10^6 and $6.38 \times 10^8\text{ M}^{-1}\text{ s}^{-1}$, respectively. The complex formation and dissociation rate constants for reaction of the protonated form of ligand with Fe(II) at 10 ± 1 °C are 6.69×10^4 and $2.37 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$. Complex formation with the protonated form of ligand for all three ions is slower than that predicted by the Eigen mechanism: this effect is most likely due to rate-determining proton transfer from ligand to solvent.

The role of hydroxamic acid containing molecules in metal ion complexation is receiving much attention due to its clinical and biological significance.^{1,2} The hydroxamic acid group is the moiety responsible for Fe(III) complexation in many

siderophores, including the linear and cyclic ferrioxamines, ferrichromes, and aerobactin. The hydroxamate-containing chelator ferrioxamine B is used to treat acute iron toxicity.³ The kinetics of interaction of Fe(III) with acetohydroxamic