ligand molecule. Under these conditions[1]

$$k_i = k_1/2 \qquad (18)$$

and

$$k_{NMR}(\text{ligand exchange}) = \frac{k_1(k_2 + k_3C_f/2)}{k_{-1} + k_2 + k_3C_f} \qquad (19)$$

A first-order or a second-order kinetic law for ligand exchange may be obtained as limiting forms of eq 19, depending on the complex investigated.[1] A second-order kinetic law $k_{NMR} = k_eC_f$ is observed in the present case, requiring $k_2 << k_3C_f << k_{-1}$ and $k_e = k_1k_3/2k_{-1}$. Under these assumptions, k_1(25 °C) = 3.2×10^4 and 3.4×10^3 s^{-1} for complexes **1** and **2** and $R = k_i/k_e = k_{-1}/k_3 = 4.29 \times 10^3$ for complex **1** at 25 °C. The value of R shows that the internal reattachment of one ligand molecule to the TBP intermediate is 4.29×10^3 times more probable than the addition of a ligand molecule from the bulk solvent. The nearly equal values of the activation enthalpies $\Delta H^{\ddagger}_i$ and $\Delta H^{\ddagger}_e$ for complex **1** suggest a common energy barrier due to the bond-rupture step. In contrast, the activation entropies $\Delta S^{\ddagger}_i$ and $\Delta S^{\ddagger}_e$ are widely different. The positive value $\Delta S^{\ddagger}_i = 6$ eu is in line with an expected release of the steric strain in the pentacoordinate intermediate. The negative value $\Delta S^{\ddagger}_e = -12$ eu shows, according to eq 19, that the entropy loss in the bimolecular step (III) should outweigh by ca. −18 eu the entropy loss in the internal return process. A point that remains unexplained is the negative value $\Delta S^{\ddagger}_i = -7.3$ eu obtained for complex **2**. A negative value $\Delta S^{\ddagger}_i = -29.5$ eu is also obtained for the racemization of the tris(1,10-phenanthroline)cobalt(II) complex from the kinetic data reported in the literature[39] ($k_i = 6.9$ s^{-1} and $\Delta H^{\ddagger}_i = 7.5$ kcal·mol^{-1} at 25 °C), while the corresponding $\Delta S^{\ddagger}_e$ value is positive: $\Delta S^{\ddagger}_e = 5.6$ eu, k_e(25 °C) = 0.16 s^{-1}, and $\Delta H^{\ddagger}_e = 20.2$ kcal·mol^{-1}. Further studies are therefore necessary to elucidate the problem of the signs and magnitudes of entropy variations in these processes.

Conclusions

There is a paucity of kinetic data on the racemization of optically active coordination compounds, since they often racemize very rapidly, so that a prior resolution into the pure enantiomers is not possible. This drawback can be circumvented by DNMR methods, which detect the exchange of diastereotopic nuclei between the Δ and Λ enantiomers at equilibrium. Although already described for some specific examples, the NMR methods seem to have never been applied to the archetypal case of paramagnetic trigonal tris chelates of transition-metal ions with three identical symmetric bidentate ligands. The above experiments show that a wealth of information can be obtained by using for this purpose bidentate phosphoramide ligands, due to the magnetic nonequivalence of the two nitrogen atoms in the neighborhood of each phosphorus nucleus and to appropriate isotropic shifts. This is an additional feature of these powerful chelating reagents[1] that makes them very attractive as probes for the study of optical inversion processes in metal ion complexes.

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Registry No. **1**, 26167-79-3; **2**, 21665-90-7; octamethylpyrophosphoramide, 152-16-9; nonamethylimidodiphosphoramide, 34834-03-2.

Contribution from the Department of Chemistry,
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Diosmium(IV) Complexes Containing Oxide and Carboxylate Bridges and a Weak Os–Os Interaction: Structure of (μ-Oxo)bis(μ-acetato)bis[dichloro(triphenylphosphine)osmium(IV)] as Its Diethyl Ether Solvate

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The reactions of *trans*-$OsO_2X_2(PR'_3)_2$ (X = Cl or Br; PR'_3 = PPh_3 or PEt_2Ph) with refluxing carboxylic acids have produced a new class of diosmium(IV) complexes of the type $Os_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2X_4(PR'_3)_2$ (R = CH_3 or C_2H_5). The cyclic voltammograms of these complexes show a one-electron reduction with $E_{1/2}$ values in the range +0.09 to +0.23 V vs. SCE and an irreversible one-electron reduction between −0.79 and −1.01 V. Chemical reduction of $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2$ using sodium metal has led to isolation of the Ph_4As^+ salt of the monoanion. Other characterizations of the diosmium(IV) complexes have included ^{1}H NMR, IR, electronic absorption, and magnetic moment measurements and X-ray photoelectron spectroscopy. The X-ray crystal structure of the diethyl ether solvate of $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2$ has been determined. This molecule is the only known example of a diosmium complex containing a single bent bridging oxide ligand. Besides the bridging oxide ligand, two distorted acetate ligands bridge the long Os–Os distance of 3.440 (2) Å. The distorted-octahedral coordination polyhedron about each Os atom is completed by two Cl atoms and a Ph_3P ligand. The diethyl ether molecule is disordered in the unit cell. The crystals belong to space group $P2_1/c$ with a = 13.066 (3) Å, b = 18.124 (3) Å, c = 19.619 (4) Å, β = 107.10 (2)°, V = 4441 Å^3, and Z = 4. The structure was solved by the heavy-atom method and refined by full-matrix least-squares procedures with anisotropic temperature factors to R = 0.044 for 4668 observed reflections.

Introduction

Although there are many osmium complexes containing [Os(μ-N)Os] and [Os(μ-O)$_2$Os] bridges,[1] compounds with a single Os–O–Os unit are rare. Notable exceptions are the oxyhalo anions of osmium(IV) of the type $[Os_2(\mu\text{-}O)X_{10}]^{4-}$, but only in the case of $Cs_4Os_2(\mu\text{-}O)Cl_{10}$ has this been documented by a crystal structure determination.[2] In the course of investigating the reactions of *trans*-$OsX_4(PPh_3)_2$ and

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(1) See, e.g.: Gmelin, "Handbuch der Anorganischen Chemie"; Springer-Verlag: New York, 1980; Osmium Supplement, Vol. 1.

(2) Tebbe, K. F.; Von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1973**, *396*, 66.

0020-1669/83/1322-1301$01.50/0

trans-$OsO_2X_2(PPh_3)_2$ (X = Cl or Br) with carboxylic acids and the anions of 2-hydroxypyridine, 2-hydroxy-6-methylpyridine, and 1,3-diphenyltriazene, ligands that are often effective in inducing coupling of metal centers to give complexes containing metal–metal bonds (often of multiple order),[3] we discovered a new class of diosmium(IV) complexes that are constrained to contain a bent Os–O–Os bridging unit. Our preliminary report of these results[4] followed soon after the structural characterization of the triply bonded diosmium(III) complex $Os_2(hp)_4Cl_2$ (hp = anion of 2-hydroxypyridine) by Cotton and Thompson[5] and shortly before the description by Wilkinson and co-workers[6] of a brown acetate of osmium(III) of stoichiometry $[OsCl(O_2CCH_3)_2]_n$. Whether this latter complex is a genuine acetato-bridged multiply bonded diosmium species has yet to be ascertained.

The synthesis and characterization of this series of complexes with the general formula $Os_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2X_4(PR'_3)_2$ (R = CH_3 or C_2H_5; X = Cl or Br; PR'_3 = PPh_3 or PEt_2Ph) are described fully in the present report. In addition, we provide details of the structure of the diethyl ether solvate of $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2$ as determined by X-ray crystallography.

Experimental Section

Starting Materials. Complexes of the type *trans*-$OsO_2X_2(PR'_3)_2$ (X = Cl or Br; PR'_3 = PPh_3 or PEt_2Ph) were prepared by the procedure of Salmon and Walton.[7] Osmium tetraoxide, triphenylphosphine, and other reagents and solvents were obtained from commercial sources and were used as received. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was obtained by reacting tetra-*n*-butylammonium iodide with KPF_6 in hot water. The product was recrystallized from aqueous ethanol and dried in vacuo.

Reaction Procedures. All reactions were carried out under a N_2 atmosphere, and all solvents were deoxygenated prior to use by purging with N_2 gas.

Preparation of Complexes of the Type $Os_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2X_4(PR'_3)_2$. (i) $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2$. A mixture of 0.3 g (0.37 mmol) of *trans*-$OsO_2Cl_2(PPh_3)_2$ and 25 mL of an acetic acid–acetic anhydride mixture (10:1 ratio by volume) was refluxed for 4 h in the absence of light (*trans*-$OsO_2Cl_2(PPh_3)_2$ is decomposed by light). The resulting dark brown solution was evaporated to a small volume, and diethyl ether was added to facilitate crystal growth. A brown precipitate was collected and recrystallized by dissolution in dichloromethane, with subsequent filtration to remove any unreacted *trans*-$OsO_2Cl_2(PPh_3)_2$. The solution was then evaporated to a small volume, and diethyl ether was added to initiate crystallization. The brown crystalline product was filtered off, washed with diethyl ether, and dried in vacuo; yield 0.36 g (83%). Anal. Calcd for $C_{40}H_{36}Cl_4O_5Os_2P_2$: C, 40.68; H, 3.07; Cl, 12.01; P, 5.25. Found: C, 41.35; H, 3.23; Cl, 11.38; P, 4.78. The molecular weight as determined by osmometry on a dichloromethane solution of the complex was consistent with the above formulation: calcd, 1181; found, 1180 ± 50. Spectroscopic data: ^1H NMR ($CDCl_3$) δ 7.30 (C_6H_5), 2.35 (singlet, CH_3); λ_{max} (CH_2Cl_2) 452 nm (log ϵ = 4.32). Measurement of the gram-susceptibility of this complex (-0.181×10^{-6} egsu by the Gouy method and -0.228×10^{-6} egsu by the Faraday method) confirmed its diamagnetic nature.

(ii) $Os_2(\mu\text{-}O)(\mu\text{-}O_2CC_2H_5)_2Cl_4(PPh_3)_2$. A procedure that was identical with that described in (i) except for the substitution of propionic acid–propionic anhydride for a mixture of acetic acid–acetic anhydride afforded brown crystals; yield 56%. Anal. Calcd for $C_{42}H_{40}Cl_4O_5Os_2P_2$: C, 41.73; H, 3.34; Cl, 11.73. Found: C, 42.21; H, 3.58; Cl, 11.46. Spectroscopic data: ^1H NMR ($CDCl_3$) δ 7.26 (C_6H_5), 2.55 (quartet, CH_2CH_3), 0.96 (triplet CH_2CH_3); λ_{max} (CH_2Cl_2) 452 nm (log ϵ = 4.25).

(iii) $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PEt_2Ph)_2$. This procedure followed that described in (i) except that 0.30 g (0.48 mmol) of *trans*-$OsO_2Cl_2(PEt_2Ph)_2$ was substituted for *trans*-$OsO_2Cl_2(PPh_3)_2$. The brown product was recrystallized from a dichloromethane–diethyl ether mixture; yield 0.15 g (32%). Anal. Calcd for $C_{24}H_{36}Cl_4O_5Os_2P_2$: C, 29.16; H, 3.67. Found: C, 30.10; H, 3.88. Spectroscopic data: ^1H NMR ($CDCl_3$) δ 7.50 (C_6H_5), 2.20 (singlet, O_2CCH_3), 1.90 (multiplet, PCH_2CH_3), 1.20 (multiplet, PCH_2CH_3); λ_{max} (CH_2Cl_2) 440 nm (log ϵ = 4.17).

(iv) $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Br_4(PPh_3)_2$. This complex was prepared from $OsO_2Br_2(PPh_3)_2$ (0.30 g, 0.33 mmol) as red-brown crystals by using a procedure analogous to (i); yield 0.27 g (60%). Anal. Calcd for $C_{40}H_{36}Br_4O_5Os_2P_2$: C, 35.36; H, 2.67; Br, 23.53. Found: C, 35.53; H, 2.82; Br, 23.58. Spectroscopic data: ^1H NMR ($CDCl_3$) δ 7.33 (C_6H_5), 2.43 (singlet, CH_3); λ_{max} (CH_2Cl_2) 482 nm (log ϵ = 4.29).

(v) $Os_2(\mu\text{-}O)(\mu\text{-}O_2CC_2H_5)_2Br_4(PPh_3)_2$. This complex was prepared from $OsO_2Br_2(PPh_3)_2$ and a mixture of propionic acid–propionic anhydride in a manner analogous to (ii) and (iv); yield 68%. Anal. Calcd for $C_{42}H_{40}Br_4O_5Os_2P_2$: C, 36.38; H, 2.91; Br, 23.05. Found: C, 36.47; H, 3.14; Br, 23.05. The molecular weight as determined by osmometry on a dichloromethane solution of the complex was consistent with the above formulation: calcd, 1387; found, 1405 ± 60. Spectroscopic data: ^1H NMR ($CDCl_3$) δ 7.32 (C_6H_5), 2.65 (quartet, CH_2CH_3), 1.04 (triplet, CH_2CH_3); λ_{max} (CH_2Cl_2) 486 nm (log ϵ = 4.42).

(vi) $Ph_4As[Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2]$. A piece of sodium metal (ca. 0.10 g, 4.3 mmol) was added to a mixture of 0.30 g (0.25 mmol) of $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2$ in 30 mL of freshly distilled tetrahydrofuran. This mixture was heated under reflux until the color of the mixture changed from brown to purple; this takes between 3 and 5 h. The reaction mixture was then cooled to room temperature and was carefully decanted to separate the purple-brown solution and lighter particles from the larger pieces of unreacted sodium metal. The solvent was removed by evaporation under a steady flow of N_2 gas. The resulting purple-black solid was stirred with 2 × 30 mL of dichloromethane, and the resulting brown extracts (containing mostly unreacted starting material) were discarded. The insoluble purple-black solid was then finally washed with diethyl ether and vacuum dried.[8] This material was dissolved in acetonitrile (30 mL) and mixed with 0.15 g (0.34 mmol) of $Ph_4AsCl{\cdot}H_2O$. The solution was reduced in volume by evaporation, and diethyl ether was used to precipitate the product, which was filtered off. Salt impurities were removed by stirring the product in deionized water and centrifuging. The resulting solid plug was washed with absolute ethanol, centrifuged, then washed with diethyl ether, and again centrifuged. The finely divided purple powder so obtained was finally recrystallized from dichloromethane–diethyl ether, and the purple crystals were washed with diethyl ether and dried in vacuo; yield 0.32 g (81%). Anal. Calcd for $C_{64}H_{56}Cl_4AsO_5Os_2P_2$: C, 49.14; H, 3.61; Cl, 9.07. Found: C, 48.94; H, 3.90; Cl, 9.00. Spectroscopic data: ^1H NMR ($CDCl_3$) δ 7.82 (C_6H_5 of Ph_4As^+), 7.29 and 7.06 (C_6H_5 of PPh_3), 2.98 (broad singlet, CH_3); λ_{max} (CH_2Cl_2) 487 nm (log ϵ = 4.05).

Preparation of Single Crystals of $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2{\cdot}(C_2H_5)_2O$. A sample of $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2$ was dissolved in dichloromethane. An equal volume of diethyl ether was added, and the resulting solution was allowed to stand at 20 °C for a period of 1 week. The resulting crystals were collected, washed carefully with diethyl ether, and vacuum dried.

X-ray Structure Determination. A well-formed, regularly shaped crystal was mounted on the end of a thin glass fiber with epoxy cement. The crystal was mounted on an Enraf-Nonius CAD-4 automated diffractometer where automatic location and centering of 15 reflections ($26° \le 2\theta \le 32°$) provided the unit cell parameters presented in Table I. A preliminary study showed systematic absences in $h0l$ for $l = 2n$ and $0k0$ for $k = 2n$, indicating the space group $P2_1/c$.

The crystal used in this study was chosen on the basis of peak profile analyses of several strong reflections and because of its size (0.47 ×

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(3) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.

(4) Armstrong, J. E.; Robinson, W. R.; Walton, R. A. *J. Chem. Soc., Chem. Commun.* **1981**, 1120.

(5) Cotton, F. A.; Thompson, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 6437; *Inorg. Chim. Acta* **1980**, *44*, L247.

(6) Moore, D. S.; Alves, A. S.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1981**, 1164.

(7) (a) Salmon, D. J.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 2379. (b) This paper gives information on the synthesis of *trans*-$OsO_2Cl_2(PPh_3)_2$; other complexes of this type were prepared by an analogous procedure, full details of which will shortly be published.

(8) This purple material is believed to be the sodium salt $Na[Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2]$. Anal. Calcd for $C_{40}H_{36}Cl_4NaO_5Os_2P_2$: C, 39.91; H, 3.01. Found: C, 38.90; H, 3.18. Its electrochemical and spectroscopic properties, which are discussed in the text, support this formulation.

Table I

Crystallographic Data for $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2\cdot(C_2H_5)_2O$

formula	$Os_2C_{44}H_{46}O_6P_2Cl_4$	M_r	1257.0
cryst size, mm	0.47 × 0.13 × 0.13	space group	$P2_1/c$
a, Å	13.066 (3)	β, deg	107.10 (2)
b, Å	18.124 (3)	Z	4
c, Å	19.619 (4)	d_{calcd}, g/cm³	1.880
V, Å³	4441	μ(Mo Kα), cm^{-1}	58.1

Enraf-Nonius CAD-4 Data Collection Procedures

radiation: graphite-monochromated Mo Kα (λ_α = 0.710 73 Å)
collection range: $\pm h, +k, +l$; $6 \leqslant 2\theta \leqslant 50°$
aperture width, deg: $4 + 0.2 \tan\theta$
max counting time, s: 30
no. of unique data: 7774
no. of data with $I > 5\sigma(I)$: 4668
no. of parameters varied: 443
cryst dec: negligible
$R = 0.044$
largest peak, e/Å³: 2 (1 Å from osmium atom)
temp: 23 °C

0.13 × 0.13 mm). Intensities were collected to $2\theta = 50°$ by using the ω-scan method. Standard data collection procedures have been summarized elsewhere.[9] A total of 7774 intensities were measured; Lorentz and polarization corrections, but not absorption corrections, were applied. The value of A^* varied from 1.85 to 2.40. Of the 7774 unique intensities measured, 4668 had $I > 5\sigma(I)$ and were, therefore, considered observed.

The structure was solved by Patterson and Fourier methods and refined[10] by full-matrix least squares. A three-dimensional Patterson synthesis provided the two osmium atom positions. Following three cycles of isotropic least-squares refinement, the remaining non-hydrogen atoms were located from difference Fourier syntheses. The ether molecule was seen to be disordered into two positions, both of which exhibited a common terminal carbon atom (C(54)). Convergence of refinement (with equal weights) of an anisotropic model with rigid phenyl rings for the dinuclear osmium molecule and isotropic temperature factors and constrained bond distances for the disordered ether molecule (C–C = 1.54 ± 0.01 Å, C–O = 1.43 ± 0.01 Å) produced an R value of 0.044. The disorder of the ether molecule between the two sites was not statistically different from 1:1.

The largest shift:error ratio in the final cycle was 0.05 in the dinuclear osmium molecule and 0.7 in a disordered ether molecule. Although a difference peak with a magnitude of about 2 e/Å³ was seen at about 1 Å from the osmium atoms, no significant electron density was observed at chemically reasonable distances from the other atoms.

Final positional parameters are given in Table II. Values of F_o vs. F_c for the 4668 observed data are available as supplementary material.

Physical Measurements. Infrared spectra of Nujol mulls were recorded in the region 4000–200 cm^{-1} with a Beckman IR-12 spectrophotometer. A Perkin-Elmer R32 90-MHz spectrometer was used to obtain the ^{1}H NMR spectra. Samples were dissolved in deuterated solvents, and resonances were usually referenced internally to tetramethylsilane (Me_4Si). X-ray photoelectron spectra (XPS) were recorded with a Hewlett-Packard 5950A spectrometer. Binding energies were internally referenced to a C 1s binding energy of 285.0 eV for the carbon atoms of the coordinated tertiary phosphine ligands. Magnetic susceptibility measurements were determined at 22 °C by the Gouy method. Electronic absorption spectra were recorded on dichloromethane solutions with a Varian series 634 spectrophotometer in conjunction with a Varian Model 9176 recorder. Electrochemical measurements were made on dichloromethane and acetonitrile solutions containing 0.2 M tetra-n-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values (taken as $(E_{p,a} + E_{p,c})/2$) were referenced to the saturated potassium chloride calomel electrode (SCE) at 22 ± 2 °C and were uncorrected for junction potentials. Cyclic voltammetry experiments were performed by using a BioAnalytical Systems Inc. Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035 X-Y recorder. Potential control for coulometric experiments was maintained with a potentiostat purchased from BioAnalytical Systems Inc. Values of n, where n is the total number of equivalents of electrons transferred in exhaustive electrolysis at constant potentials, were calculated after measuring the total area under current vs. time curves for the complete reaction. The reactions were judged to be complete when the current had fallen below 1% of the initial value. All voltammetric measurements were made at a platinum-bead electrode in solutions deaerated with a stream of dry nitrogen.

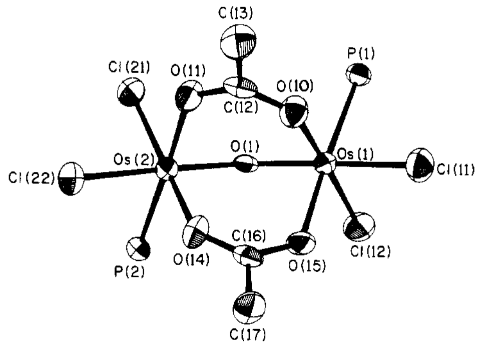

Figure 1. ORTEP representation of the $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2$ molecule with the phenyl rings of the PPh_3 ligands omitted. A representation of the full structure with the appropriate numbering scheme is available as supplementary material.

Elemental microanalyses were performed by Dr. C. S. Yeh of the Purdue University microanalytical laboratory, by Chemalytics, Inc., Tempe, AZ, and by Galbraith Laboratories, Inc., Knoxville, TN. The molecular weight measurements were determined by osmometry using dichloromethane as the solvent at 37 °C.

Results and Discussion

Synthesis and Spectroscopic Characterizations. The reactions between osmium(VI) complexes of the type *trans*-$OsO_2X_2(PR'_3)_2$ and refluxing carboxylic acid–anhydride mixtures provide a high-yield route to a new class of diosmium(IV) complexes of stoichiometry $Os_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2X_4(PR'_3)_2$ for X = Cl or Br, R = CH_3 or C_2H_5, and PR'_3 = PPh_3 or PEt_2Ph. These brown crystalline complexes are air stable and show little tendency to undergo simple ligand-exchange reactions with either carboxylic acids or tertiary phosphines.[11] This group of complexes is diamagnetic as judged by magnetic susceptibility measurements on $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2$ and the sharp resonances in the ^{1}H NMR spectra of all the complexes (details are given in the Experimental Section). Dichloromethane solutions of the complexes exhibit an intense absorption band in their electronic absorption spectra (440-450 nm for X = Cl and 480–490 nm for X = Br), which is charge transfer in origin (log $\epsilon \sim 4.3$). The infrared spectra of Nujol mulls show bands characteristic of carboxylate (e.g., ν_{as}(COO) in the region 1540–1525 (s) cm^{-1}) and osmium–halogen bonds (ν(Os–X) at 350–340 (s) cm^{-1} for X = Cl and 240–225 cm^{-1} for X = Br) but no absorption that could be assigned to ν(Os–O–Os).[12]

An additional property of note, concerns the X-ray photoelectron spectra (XPS or ESCA) of these complexes. The pertinent core electron binding energies of four of these complexes are listed in Table III. The measured Os 4f binding

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(9) Jaecker, J. A.; Robinson, W. R.; Walton, R. A. *J. Chem. Soc., Dalton Trans.* **1975**, 698.

(10) All crystallographic computing was performed at the Purdue University Computing Center with use of the program "SHELX-76 Program for Crystal Structure Determination" by George Sheldrick, University Chemical Laboratory, Cambridge, England, 1977.

(11) The reaction between $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2$ and tri-n-propylphosphine in hot toluene led to reduction of the neutral complex to its purple monoanion $[Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2]^-$ (as demonstrated by cyclic voltammetry). Workup of this solution afforded a purple solid whose IR spectrum was consistent with the formulation $[n\text{-}Pr_3PH][Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2]$.

(12) Full details of the spectroscopic properties of these complexes, can be obtained from R.A.W. upon request.

Table II. Positional Parameters and Their Estimated Standard Deviations for $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2\cdot(C_2H_5)_2O^{a,b}$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Os(1)	0.14016 (4)	−0.00739 (3)	0.26649 (3)	C(32)	0.5374 (6)	0.0903 (5)	0.3433 (5)
Os(2)	0.24537 (5)	−0.02073 (3)	0.12550 (3)	C(33)	0.5949 (6)	0.0896 (5)	0.4156 (5)
P(1)	0.2250 (3)	0.0886 (2)	0.3452 (2)	C(34)	0.5408 (6)	0.0863 (5)	0.4671 (5)
P(2)	0.3454 (3)	−0.1320 (2)	0.1376 (2)	C(35)	0.4291 (6)	0.0838 (5)	0.4464 (5)
Cl(11)	−0.0081 (3)	0.0053 (2)	0.3066 (2)	C(36)	0.4398 (8)	−0.1414 (6)	0.0850 (6)
Cl(12)	0.2185 (4)	−0.0982 (2)	0.3497 (2)	C(37)	0.4590 (8)	−0.2104 (6)	0.0598 (6)
Cl(21)	0.3928 (3)	0.0571 (2)	0.1441 (2)	C(38)	0.5370 (8)	−0.2183 (6)	0.0247 (6)
Cl(22)	0.2200 (3)	−0.0249 (2)	0.0041 (2)	C(39)	0.5958 (8)	−0.1571 (6)	0.0147 (6)
O(1)	0.2386 (7)	−0.0166 (4)	0.2172 (4)	C(40)	0.5765 (8)	−0.0880 (6)	0.0399 (6)
O(10)	0.0559 (8)	0.0646 (5)	0.1869 (5)	C(41)	0.4985 (8)	−0.0802 (6)	0.0750 (6)
O(11)	0.1483 (8)	0.0759 (5)	0.1071 (6)	C(42)	0.2541 (8)	−0.2106 (5)	0.1139 (5)
C(12)	0.0736 (11)	0.0919 (7)	0.1325 (7)	C(43)	0.2230 (8)	−0.2491 (5)	0.1661 (5)
C(13)	−0.0050 (13)	0.1506 (9)	0.0928 (9)	C(44)	0.1526 (8)	−0.3086 (5)	0.1469 (5)
O(14)	0.1013 (7)	−0.0783 (5)	0.0984 (5)	C(45)	0.1133 (8)	−0.3295 (5)	0.0755 (5)
O(15)	0.0502 (9)	−0.0896 (5)	0.1979 (5)	C(46)	0.1444 (8)	−0.2910 (5)	0.0233 (5)
C(16)	0.0391 (12)	−0.1001 (7)	0.1316 (8)	C(47)	0.2148 (8)	−0.2316 (5)	0.0425 (5)
C(17)	−0.0567 (13)	−0.1445 (9)	0.0909 (8)	C(48)	0.4303 (8)	−0.1513 (5)	0.2276 (4)
C(18)	0.1866 (8)	0.0975 (5)	0.4272 (4)	C(49)	0.4606 (8)	−0.0952 (5)	0.2783 (4)
C(19)	0.1671 (8)	0.0356 (5)	0.4639 (4)	C(50)	0.5292 (8)	−0.1108 (5)	0.3459 (4)
C(20)	0.1457 (8)	0.0441 (5)	0.5290 (4)	C(51)	0.5676 (8)	−0.1823 (5)	0.3629 (4)
C(21)	0.1440 (8)	0.1144 (5)	0.5576 (4)	C(52)	0.5373 (8)	−0.2384 (5)	0.3122 (4)
C(22)	0.1636 (8)	0.1763 (5)	0.5210 (4)	C(53)	0.4686 (8)	−0.2228 (5)	0.2445 (4)
C(23)	0.1849 (8)	0.1678 (5)	0.4558 (4)	C(54)	0.7025 (15)	0.0085 (10)	0.2383 (9)
C(24)	0.1912 (8)	0.1790 (4)	0.3027 (6)	C(55)	0.7474 (36)	0.0359 (15)	0.1787 (20)
C(25)	0.0827 (8)	0.1972 (4)	0.2790 (6)	O(56)	0.6908 (32)	0.1008 (15)	0.1477 (15)
C(26)	0.0510 (8)	0.2663 (4)	0.2489 (6)	C(57)	0.7568 (22)	0.1643 (14)	0.1659 (18)
C(27)	0.1277 (8)	0.3172 (4)	0.2425 (6)	C(58)	0.6989 (22)	0.2312 (12)	0.1264 (14)
C(28)	0.2361 (8)	0.2990 (4)	0.2662 (6)	C(59)	0.7318 (24)	0.0642 (17)	0.1883 (15)
C(29)	0.2679 (8)	0.2299 (4)	0.2963 (6)	O(60)	0.6374 (39)	0.0889 (22)	0.1363 (21)
C(30)	0.3716 (6)	0.0846 (5)	0.3742 (5)	C(61)	0.6264 (20)	0.1671 (23)	0.1372 (44)
C(31)	0.4258 (6)	0.0878 (5)	0.3226 (5)	C(62)	0.7339 (17)	0.2038 (12)	0.1419 (11)

[a] Estimated standard deviations in the least significant digits are shown in parentheses. [b] The ether solvate molecule is disordered in the crystal lattice and can take up either of two positions with a common terminal carbon atom of C(54): (1) C(54)–C(55)–O(56)–C(57)–C(58) or (2) C(54)–C(59)–O(60)–C(61)–C(62).

Table III. Core Electron Binding Energies (eV) of Diosmium(IV) Complexes[a]

complex	Os $4f_{7/2}$[b]	Cl $2p_{3/2}$	Br 3d
$Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2$	53.0 (1.6)	198.8	
$Os_2(\mu\text{-}O)(\mu\text{-}O_2CC_2H_5)_2Cl_4(PPh_3)_2$	52.8 (2.0)	198.5	
$Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Br_4(PPh_3)_2$	52.5 (2.4)		69.1
$Os_2(\mu\text{-}O)(\mu\text{-}O_2CC_2H_5)_2Br_4(PPh_3)_2$	53.0 (2.0)		69.1

[a] Binding energies referenced to a C 1s value of 285.0 eV for the tertiary phosphine ligands. [b] Full-width at half-maximum (fwhm) values are given in parentheses.

Table IV. Important Bond Lengths and Bond Angles with Their Estimated Standard Deviations for $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2\cdot(C_2H_5)_2O^{a-c}$

Bond Lengths, Å

Os(1)–Os(2)	3.440 (2)	Os(1)–Cl(12)	2.332 (4)
Os(1)–O(1)	1.830 (10)	Os(1)–P(1)	2.374 (3)
Os(2)–O(1)	1.828 (9)	Os(2)–O(11)	2.131 (10)
Os(1)–O(10)	2.083 (9)	O(10)–C(12)	1.260 (19)
Os(1)–O(15)	2.118 (9)	O(11)–C(12)	1.252 (20)
Os(1)–Cl(11)	2.306 (4)	C(12)–C(13)	1.523 (19)

Bond Angles, deg

Os(1)–O(1)–Os(2)	140.2 (4)	O(15)–Os(1)–Cl(11)	85.5 (4)
O(1)–Os(1)–O(10)	87.7 (4)	O(15)–Os(1)–Cl(12)	89.8 (3)
O(1)–Os(1)–O(15)	86.9 (4)	Cl(11)–Os(1)–P(1)	89.0 (1)
O(1)–Os(1)–P(1)	98.3 (3)	Cl(11)–Os(1)–Cl(12)	94.0 (2)
O(1)–Os(1)–Cl(11)	168.7 (2)	Cl(12)–Os(1)–P(1)	92.1 (1)
O(1)–Os(1)–Cl(12)	94.3 (3)	Os(1)–O(10)–C(12)	133.9 (10)
O(10)–Os(1)–O(15)	83.8 (4)	O(10)–C(12)–O(11)	127.2 (12)
O(10)–Os(1)–P(1)	94.1 (3)	O(10)–C(12)–C(13)	116.4 (14)
O(10)–Os(1)–Cl(11)	83.2 (3)	O(11)–C(12)–C(13)	116.5 (13)
O(10)–Os(1)–Cl(12)	173.2 (3)	Os(2)–O(11)–C(12)	128.2 (9)
O(15)–Os(1)–P(1)	174.4 (3)	Os(1)–O(15)–C(16)	128.8 (10)

[a] Estimated standard deviations in the least significant digits are shown in parentheses. [b] The ether solvate molecule is disordered in the crystal lattice and can take up either of two positions with a common terminal carbon atom of C(54): (1) C(54)–C(55)–O(56)–C(57)–C(58) or (2) C(54)–C(59)–O(60)–C(61)–C(62). (See supplementary material.) [c] Bond lengths and bond angles involving the phenyl rings have been omitted from this table since these rings were treated as rigid bodies in the refinement. Full details are available in the supplementary material.

energies are in excellent agreement with data reported by us previously for other mixed halide–phosphine complexes of osmium(IV).[7a] The Os 4f values (53.0–52.5 eV) are higher than those measured for comparable osmium(III) and osmium(II) species.

Structure Determination of $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2\cdot(C_2H_5)_2O$. Important bond lengths and bond angles for this complex are given in Table IV, and the representation of the crystal packing in the unit cell is available in the supplementary material. The diethyl ether lattice molecules are disordered in the unit cell and do not interact in any significant way with the diosmium complex. The core of the diosmium complex (i.e., omitting phenyl groups and hydrogen atoms), viewed at right angles to the metal–metal vector, is shown in Figure 1, where the atomic numbering scheme is also defined. The overall geometry of the molecular core in Figure 1 is approximately C_2.

The $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2$ molecule is best viewed as being a derivative of the well-characterized $[Os_2(\mu\text{-}O)Cl_{10}]^{4-}$ anion,[1,2] which has D_{4h} symmetry. For each osmium atom of the $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2$ molecule, one phosphine ligand and one oxygen atom from each of two intramolecular acetate bridges are substituted for three of the Cl atoms of each planar $OsCl_4$ unit of the $[Os_2(\mu\text{-}O)Cl_{10}]^{4-}$ anion. The constraints imposed by the two bridging carboxylate ligands cause the Os–O–Os unit to become bent (140.2 (4)°). This change from a linear to bent Os–O–Os geometry is accompanied by a lengthening of the associated Os–O bonds from 1.778 (15) in $[Os_2(\mu\text{-}O)Cl_{10}]^{4-}$ to 1.829 (10)

Table V. Voltammetric Half-Wave Potentials for $Os_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2X_4(PR'_3)_2$ (R = CH_3, C_2H_5; X = Cl, Br; R'_3 = Ph_3, Et_2Ph) Complexes[a]

complex	$E_{1/2}$[b]	$E_{p,c}$
$Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2$[c]	+0.18 (75)[d]	−0.93
$Os_2(\mu\text{-}O)(\mu\text{-}O_2CC_2H_5)_2Cl_4(PPh_3)_2$	+0.16 (90)	−1.01
$Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PEt_2Ph)_2$	+0.09 (90)	−0.97
$Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Br_4(PPh_3)_2$	+0.23 (80)	−0.79
$Os_2(\mu\text{-}O)(\mu\text{-}O_2CC_2H_5)_2Br_4(PPh_3)_2$	+0.21 (70)	−0.82

[a] In volts vs. SCE with a Pt-bead electrode and 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte in dichloromethane. [b] Values of $E_{p,a} - E_{p,c}$ (in mV) at a sweep rate of 200 mV/s are given in parentheses. [c] In 0.1 M tetra-*n*-butylammonium hexafluorophosphate–acetonitrile this complex exhibits a reversible reduction at $E_{1/2}$ = +0.30 V and an irreversible reduction at $E_{p,c} \simeq -0.9$ V vs. SCE.

Å in $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2$. This presumably reflects (in part) a decrease in the $Os(d_\pi)$–$O(p_\pi)$–$Os(d_\pi)$ overlap, which is maximized in the linear arrangement. The planes of cis atoms now become unparallel and tilt inwardly toward the carboxylate ligands. However, the pseudooctahedral arrangement of coordinated atoms about each osmium atom is maintained. Looking down the osmium–osmium axis reveals that each pair of oxygen atoms on an acetate ligand are staggered because of the strain imposed by the large bite distance of the ligand. This twist causes each carboxylate ligand and the Os–O–Os unit to partake in the formation of two "chairlike" $\overline{\mathrm{OsOOsOCO}}$ rings. Within these rings each acetate ligand is twisted, making the oxygen atoms on an acetate ligand different with respect to the Os–O bond distance and the appropriate bond angles. Another contribution to this inequivalence may be the different trans effects of PPh_3 vs. Cl^- since the oxygen atoms of each acetate bridge have different trans ligands. One oxygen atom from one acetate ligand can be rotated to an equivalent oxygen atom position on the other ligand via the pseudo-C_2 axis (e.g., O(11) → O(15)).

A particularly instructive structural comparison can be made to the dimethyldithiocarbamate (dtc) complex $Os_2(\mu\text{-}N)(\mu\text{-}S_2CN(CH_3)_2)_4$.[13] The dtc complex has one bent (164.6 (18)°) bridging nitride ligand, analogous to the bent (140.2 (4)°) bridging oxide ligand of the acetate complex, and one bridging dtc ligand instead of two bridging acetates. Thus the electron count associated with N^{3-} and $(CH_3)_2NCS_2^-$ is equivalent to that of O^{2-} plus two $CH_3CO_2^-$ groups. Consequently, these two molecules can be considered formally to be "isoelectronic". This relationship is further reflected in a striking similarity in Os–Os distances: 3.485 (5) Å for the dtc complex and 3.440 (2) Å for the acetate complex.

As a consequence of the presence of both oxide and carboxylate bridges in $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2$, the Os–Os distance is quite short, being less than that in the "parent" chloride $OsCl_4$ (3.560 (1) Å), in which it can be argued[14] there is no Os–Os bonding. Whether some degree of metal–metal bonding exists in $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2$ cannot be inferred from the diamagnetism of the complex; superexchange through the oxide and/or acetate bridges may equally well account for this particular property of the molecule.

Redox Properties. The electrochemical properties of $Os_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2X_4(PR'_3)_2$ (X = Cl or Br; R = CH_3 or C_2H_5; PR'_3 = PPh_3 or PEt_2Ph) complexes were investigated by the cyclic voltammetry technique. Voltammetric half-wave potentials vs. SCE for 0.2 M tetra-*n*-butylammonium hexafluorophosphate–dichloromethane solutions are presented in Table V. In all cases these complexes exhibit a one-electron reversible reduction (n = 1.0 ± 0.1 by coulometry) with associated $E_{1/2}$ values in the range +0.09 to +0.23 V and a one-electron irreversible reduction with an $E_{p,c}$ value between −0.79 and −1.01 V vs. SCE.

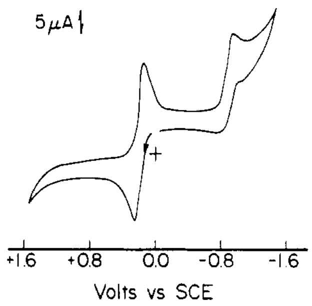

Figure 2. Cyclic voltammogram in 0.2 M tetra-*n*-butylammonium hexafluorophosphate–dichloromethane of $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2$.

In the case of the couple between +0.09 and +0.23 V, $i_{pa}/i_{pc} \simeq 1$, for sweep rates (v) between 50 and 400 mV/s, and the ratio $i_p/v^{1/2}$ was constant in accord with diffusion control. The potential separation between the anodic and cathodic peaks, ΔE_p, was greater than 60 mV, being in the range 75–90 mV for a sweep rate of 200 mV/s. These properties are (with our cell configuration)[15] consistent with an electron-transfer process that is reversible or approaches reversibility.

The cyclic voltammogram of $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2$, a representative example, can be seen in Figure 2. The complex has a reversible one-electron reduction at +0.18 V and an irreversible one-electron reduction at −0.93 V. Comparing these voltammetric data with the potentials for $Os_2(\mu\text{-}O)(\mu\text{-}O_2CC_2H_5)_2Cl_4(PPh_3)_2$, we see that for the propionate complex the values are shifted to more negative potentials (Table V). This may reflect the somewhat greater electron-donating ability of the propionate ligand compared to that of acetate and, consequently, the increased difficulty of reducing this complex. Likewise, upon comparing the electrochemical properties of $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2$ and $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PEt_2Ph)_2$, we see that the $E_{1/2}$ and $E_{p,c}$ values for the latter complex are shifted to more negative potentials due to the greater basicity of the diethylphenylphosphine ligand compared to that of triphenylphosphine. A final comparison is that between analogous chlorides and bromides; as expected, the bromide complexes are more readily reduced and this is reflected by the higher positive $E_{1/2}$ and $E_{p,c}$ values (Table V). These correlations are related to those observed by us previously in our studies[16] of the electrochemistry of carboxylato complexes of dirhenium(III).

The first one-electron reduction of these complexes occurs at potentials (Table V) that suggested salts of the monoanions could be isolated. Studies along these lines were carried out on $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2$. Bulk electrolysis of a dichloromethane solution (0.2 M in TBAH) at +0.10 V permitted the generation of the purple monoanion, solutions of which were quite stable as judged by cyclic voltammetric measurements. The neutral complex can be regenerated upon oxidizing the monoanion at +0.30 V. This reduction can be accomplished chemically by the reduction of $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2$ with sodium metal in tetrahydrofuran. This affords the sodium salt,[8] which can be converted to the more readily characterizable tetraphenylarsonium salt upon treatment with a solution of $Ph_4AsCl\cdot H_2O$. The reaction of these salts with hot acetic acid–acetic anhydride mixtures

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regenerates the neutral complex. Dichloromethane solutions of $Ph_4As[Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2]$ (containing 0.2 M TBAH as supporting electrolyte) exhibit an oxidation at $E_{1/2} = +0.20$ V vs. SCE and an irreversible reduction at $E_{p,c} \simeq -0.97$ V. Acetonitrile solutions of the sodium and tetraphenylarsonium salts (0.1 M in TBAH) have a reversible oxidation at $E_{1/2} = +0.31$ V vs. SCE; the same couple is observed in acetonitrile solutions of the neutral derivative, but it now corresponds to a reduction (see footnote *c* in Table V). Solutions of $Ph_4As[Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2]$ in dichloromethane have electronic absorption spectra that exhibit an intense absorption at 487 nm (an acetone solution of the sodium salt has this band maximum at 500 nm) and a weaker band at ~1060 nm ($\epsilon \sim 500$). The latter could be associated with an intervalence charge-transfer transition.

The expected paramagnetism of the monoanion is supported by magnetic susceptibility measurements. Solid samples of the sodium and tetraphenylarsonium salts had room-temperature magnetic moments of 1.3 ± 0.1 and 1.7 ± 0.1 μ_B, respectively, when measured at 5 kG by the Gouy method. However, we were unable to obtain an ESR signal under any of the following conditions: (1) electrochemically generated dichloromethane solutions of the monoanion at ambient or low (−160 °C) temperatures; (2) the powdered sodium and tetraphenylarsonium salts at ambient temperatures or in various glasses at ambient or low (−160 °C) temperatures.[17]

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Registry No. $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2\cdot(C_2H_5)_2O$, 81282-99-7; $Os_2(\mu\text{-}O)(\mu\text{-}O_2CC_2H_5)_2Cl_4(PPh_3)_2$, 84960-56-5; $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PEt_2Ph)_2$, 84960-57-6; $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Br_4(PPh_3)_2$, 84960-58-7; $Os_2(\mu\text{-}O)(\mu\text{-}O_2CC_2H_5)_2Br_4(PPh_3)_2$, 84960-59-8; $Ph_4As[Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2]$, 84960-61-2; $OsO_2Cl_2(PPh_3)_2$, 66984-36-9; $OsO_2Cl_2(PEt_2Ph)_2$, 84960-62-3; $OsO_2Br_2(PPh_3)_2$, 81240-84-8.

Supplementary Material Available: Figures showing the crystal packing in the unit cell and the complete crystal structure with the numbering scheme and tables giving a listing of all bond lengths, bond angles, thermal parameters, and observed and calculated structure factors (36 pages). Ordering information is given on any current masthead page.

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(17) Attempts are under way to grow single crystals of $Ph_4As[Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Cl_4(PPh_3)_2]$ in order to determine the crystal structure of this salt. Until this is done, we defer further discussion of the spectroscopic and magnetic properties of this complex.

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Stereochemistry of $R_2PX_2^-$ Ligands (X_2 = S_2, OS, or O_2) in Molybdenum(II) Dimers and Polymers. A Facile Isomerization about the $Mo\overset{4}{-}Mo$ Core

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Stoichiometric reactions of $K_4Mo_2Cl_8$ with MS_2PR_2 (M = K or Na; R = C_2H_5 or C_6H_5) in aqueous methanolic media yielded green, diamagnetic tetrakis((diorganophosphino)dithioato)dimolybdenum(II) species, $Mo_2(S_2PR_2)_4$, characterized by analysis and by IR, NMR, and UV–visible spectroscopy. The diphenyl derivative was also synthesized from the reaction of $Mo_2(OAc)_4$ with excess $(C_6H_5)_2PS_2H$ in diglyme. An X-ray crystal structure analysis of $Mo_2(S_2PEt_2)_4$ revealed the presence of two bridging and two chelating (diethylphosphino)dithioato groups coordinated with virtual C_{2v} symmetry to the Mo_2 core having a Mo–Mo separation of 2.137 (1) Å. The complex crystallizes from toluene and hexane in the triclinic space group $P\bar{1}$ with $a = 11.543$ (1) Å, $b = 14.526$ (1) Å, $c = 11.293$ (1) Å, $\alpha = 92.03$ (1)°, $\beta = 107.33$ (1)°, $\gamma = 85.82$ (1)°, and $Z = 2$. Two Lewis base adducts of $Mo_2(S_2PEt_2)_4$ have also been isolated. The THF complex, $Mo_2(S_2PEt_2)_4\cdot THF$, is a tetrabridged isomer of the preceding compound with virtual D_{4h} symmetry and crystallizes from THF solution in space group $P\bar{1}$ with $a = 10.722$ (1) Å, $b = 9.741$ (2) Å, $c = 10.356$ (1) Å, $\alpha = 108.71$ (1)°, $\beta = 116.79$ (1)°, $\gamma = 79.88$ (1)°, and $Z = 1$. The structure, refined to a residual $R = 0.044$, displays a Mo–Mo bond length of 2.123 (1) Å and a single axially coordinated THF molecule with a Mo–O distance of 3.017 (12) Å. The analogous pyrazine complex, $Mo_2(S_2PEt_2)_4\cdot C_4H_4N_2$, crystallizes from toluene and is found to be isomorphous with $Mo_2(S_2PEt_2)_4\cdot THF$ by X-ray powder diffraction. The novel equilibrium between the two isomers of $Mo_2(S_2PEt_2)_4$ was investigated by ^{31}P NMR spectroscopy and appears to be the first such equilibrium reported for a Mo_2^{4+} system. In noncomplexing solvents, the C_{2v} isomer is favored by 5:2, while in THF the concentrations of the two isomers are approximately equal. Tetrakis((diethylphosphino)thioato)dimolybdenum(II), $Mo_2(SOPEt_2)_4$, and the bis(dialkylphosphinato)molybdenum(II) compounds. $[Mo(O_2PRR')_2]_x$ (R = R′ = *n*-octyl or C_6H_5; R = Me and R′ = C_6H_5) were all prepared by metathesis between $K_4Mo_2Cl_8$ and the potassium salts of $SOPEt_2^-$ or $O_2PRR'^-$, respectively. The first was isolated as a THF monoadduct and found to be tetrabridged by ^{31}P NMR spectroscopy and a partial X-ray single-crystal structure determination. The last three are polymeric, weakly paramagnetic materials in which the molybdenum(II) ions are separated and probably in distorted octahedral environments.

Introduction

As part of a program of study of low-dimensional synthetic metals we have been searching for a family of metal-bridging ligands that would promote the formation of infinite, linear, multiply bonded metal chains. Some potentially interesting systems employed dialkylphosphinato, (dialkylphosphino)thioato, or (dialkylphosphino)dithioato ligands and the quadruply bonded Mo_2^{4+} species; the former are known to act as three-atom bridges[1,2] and the latter is known for its multiply

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