Reaction of $KB_4H_9P(CH_3)_3$ with HCl. A 0.40-mmol sample of $KB_4H_9P(CH_3)_3$ was dissolved in 3.7 mL of tetrahydrofuran in a 14 mm o.d. Pyrex tube containing a magnetic spinbar. The solution was frozen with liquid nitrogen, 0.39 mmol of HCl was condensed above the frozen solution, the tube was immersed in a −80 °C bath, and the spinbar was activated. Hydrogen gas evolved rapidly as the solution melted. By the time the solution melted completely, the gas evolution had stopped. The amount of the hydrogen gas was 0.122 mmol. No further evolution of hydrogen gas could be seen even when the solution was kept at −45 °C for 3 h. The ^{11}B NMR spectrum of the resulting solution at −80 °C (and also at room temperature) contained the signals of $B_4H_8{\cdot}P(CH_3)_3$, $(CH_3)_3P{\cdot}BH_3$, and $THF{\cdot}B_3H_7$ in an intensity ratio 1:2.4:1.8. A molar ratio 1:2.2:2.2 for the three products is expected if reactions 3 and 4 occurred simultaneously and if reaction 3 was responsible for all the hydrogen gas evolved. No other signals could be detected in the spectrum.

Reaction of B_4H_{10} with $P(CH_3)_3$ in Tetrahydrofuran. A 0.448-mmol sample of $P(CH_3)_3$ was dissolved in 2 mL of tetrahydrofuran in a 10 mm o.d. Pyrex tube equipped with a stopcock. The solution was frozen, and 0.461 mmol of B_4H_{10} was condensed in the tube. The tube was immersed in a −90 °C bath, shaken to mix the reactants, and then placed in the cold (−90 °C) probe of the NMR instrument for spectrum recording. At −90 °C the signals of B_4H_{10} and $B_4H_9^-$ were strong and the weak signals of $B_3H_8^-$ and $(CH_3)_3P{\cdot}BH_3$ were seen also. As the probe temperature was raised to −70 °C, the intensity of the $B_4H_9^-$ signal diminished rapidly and the B_4H_{10} signal intensity gradually decreased. At the same time, the signals of $(CH_3)_3P{\cdot}BH_3$, $THF{\cdot}B_3H_7$, and $B_3H_8^-$ became intense. In 30 min the signals of B_4H_{10} and $B_4H_9^-$ disappeared, and the signals of $(CH_3)_3P{\cdot}BH_3$, $THF{\cdot}B_3H_7$, and $B_3H_8^-$ were in an intensity ratio 1:1:0.3.

A tetrahydrofuran solution containing $(CH_3)_3P{\cdot}BH_3$ and $THF{\cdot}B_3H_7$ in a 1:1 molar ratio was prepared and kept at room temperature. The ^{11}B NMR spectrum remained unchanged for several days. One month later, the signals of $(CH_3)_3P{\cdot}B_3H_7$ could be seen clearly, but the signals of the original two adducts were quite strong. Two months later, the intensity of $(CH_3)_3P{\cdot}B_3H_7$ was about the same as that of $THF{\cdot}B_3H_7$.

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Registry No. $KB_4H_9P(CH_3)_3$, 85185-84-8; KB_4H_9, 57406-39-0; B_2H_6, 19287-45-7; $B_4H_8{\cdot}P(CH_3)_3$, 71749-92-3; B_4H_{10}, 18283-93-7; HCl, 7647-01-0; $P(CH_3)_3$, 594-09-2.

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Preparation, Characterization, and Reactivity of Osmium(VI) Complexes of the Type *trans*-$OsO_2X_2(PR_3)_2$ (X = Cl or Br)

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At room temperature the reactions between osmium tetraoxide, concentrated hydrohalic acids (HCl or HBr), and tertiary phosphines in ethanol produce the diamagnetic, light-sensitive Os(VI) compounds $OsO_2X_2(PR_3)_2$ ($PR_3 = PPh_3$, $PMePh_2$, $PEtPh_2$, and PEt_2Ph) as intermediates on the way to *trans*-$OsX_4(PR_3)_2$ and *mer*-$OsX_3(PR_3)_3$. The compound previously formulated as $OsOBr_3(PPh_3)_2$ has been shown to be a mixture of $OsO_2Br_2(PPh_3)_2$ and *trans*-$OsBr_4(PPh_3)_2$. The reactions of $OsO_2X_2(PPh_3)_2$ (X = Cl and Br) with HL (HL = 2-hydroxypyridine, 2-hydroxy-6-methylpyridine, and picolinic acid) in refluxing ethanol give mononuclear $OsX_2(L)(PPh_3)_2$. When $OsO_2X_2(PPh_3)_2$ (X = Cl and Br) is reacted with a mixture of 1,3-diphenyltriazine and *n*-butyllithium in tetrahydrofuran, the related Os(III) species $OsX_2(PhN_3Ph)(PPh_3)_2$ are produced. In contrast to this, $OsO_2Cl_2(PEt_2Ph)_2$ reacts with 2-hydroxy-6-methylpyridine in ethanol to yield $OsCl_3(CO)(PEt_2Ph)_2$. The monocarbonyl derivatives of Os(II) $OsX(mhp)(CO)(PPh_3)_2$ are prepared by reacting *trans*-$OsX_4(PPh_3)_2$ with 2-hydroxy-6-methylpyridine (Hmhp). X-ray photoelectron spectroscopy (XPS) and ESR spectroscopy have been used to characterize many of these complexes. A comparison has been made between the redox chemistry of these Os(VI), Os(IV), and Os(III) complexes by using the cyclic voltammetry technique.

Introduction

In 1978 we published[1] the results of a study aimed at clarifying the nature of the unusual Os(V) complex $OsOCl_3(PPh_3)_2$.[2] This molecule was noteworthy, among other reasons, in that its preparation from the reaction of osmium tetroxide with triphenylphosphine and hydrochloric acid[2] did not produce a complex of the type $OsCl_4(PR_3)_2$ or $OsCl_3(PR_3)_3$ as other tertiary phosphines do.[3] In a thorough characterization of the material purported to be $OsOCl_3(PPh_3)_2$, we discovered that it was a mixture of $OsO_2Cl_2(PPh_3)_2$ and *trans*-$OsCl_4(PPh_3)_2$.[1]

In the belief that the Os(VI) complex $OsO_2Cl_2(PPh_3)_2$ was the prototype of a range of osmyl complexes of this type, we have explored further the reactions of osmium tetraoxide with tertiary phosphines and proven that this is indeed the case. The preparation and characterization of these compounds are described herein. Additionally, we have investigated the reactions of these complexes (particularly the triphenylphosphine derivatives) with those bridging ligands, e.g. 2-hydroxypyridine, 2-hydroxy-6-methylpyridine, and 1,3-diphenyltriazine, that are often very effective in inducing coupling of metal centers to give complexes containing metal–metal bonds.[4] These latter reactions are part of a detailed study we are conducting into the use of $OsO_2X_2(PR_3)_2$ (X = Cl or Br) as synthetic starting materials.[5]

Experimental Section

Starting Materials. Osmium tetraoxide, tertiary phosphines, 2-hydroxypyridine, 2-hydroxy-6-methylpyridine, picolinic acid, 1,3-

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diphenyltriazene, 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.

A. Preparation of Complexes of the Type $OsO_2X_2(PR_3)_2$. (i) $OsO_2Cl_2(PPh_3)_2$. This material was prepared according to the procedure of Salmon and Walton[1] from the reaction of osmium tetraoxide with triphenylphosphine and concentrated hydrochloric acid in ethanol.

(ii) $OsO_2Cl_2(PMePh_2)_2$. A sample of osmium tetraoxide (0.33 g, 1.3 mmol) was dissolved in a mixture comprising 17 mL of absolute ethanol and 1.7 mL (20 mmol) of concentrated hydrochloric acid. To this was added 1.5 mL (8.1 mmol) of methyldiphenylphosphine, and the mixture was stirred for 6 h in the absence of light. When the reaction mixture was filtered, an orange-brown solid was isolated. This was washed with ethanol, dried, and then recrystallized from dichloromethane following the addition of diethyl ether. The final brown light-sensitive product was filtered off, washed with diethyl ether, and dried in vacuo; yield 0.036 g (4%). Anal. Calcd for $C_{26}H_{26}Cl_2O_2OsP_2$: C, 45.03; H, 3.78. Found: C, 45.26; H, 4.32.

(iii) $OsO_2Cl_2(PEtPh_2)_2$. This procedure was similar to that described in section A(ii). A brown crystalline light-sensitive product was obtained after recrystallization; yield 13%. Anal. Calcd for $C_{28}H_{30}Cl_2O_2OsP_2$: C, 46.61; H, 4.19. Found: C, 46.37; H, 4.56.

(iv) $OsO_2Cl_2(PEt_2Ph)_2$. A procedure similar to that in section A(ii) was adopted. After the recrystallization procedure, the brown light-sensitive crystals were collected; yield 45%. Anal. Calcd for $C_{20}H_{30}Cl_2O_2OsP_2$: C, 38.40; H, 4.83. Found: C, 38.41; H, 4.89.

(v) $OsO_2Br_2(PPh_3)_2$. This material was obtained by a procedure analogous to that used in the preparation of $OsO_2Cl_2(PPh_3)_2$.[1] The tan light-sensitive complex was purified by washing with dichloromethane, which removes any *trans*-$OsBr_4(PPh_3)_2$ contaminant; yield 76%. Anal. Calcd for $C_{36}H_{30}Br_2O_2OsP_2$: C, 47.69; H, 3.34; Br, 17.63. Found: C, 47.71; H, 3.46; Br, 17.26. Measurement of this compound's ^1H NMR and electronic absorption spectral properties was precluded by its insolubility in suitable polar and nonpolar solvents (acetonitrile, dichloromethane, ethanol, diethyl ether, chloroform, and benzene).

B. Preparation of Complexes of the Type *trans*-$OsX_4(PR_3)_2$. (i) *trans*-$OsCl_4(PPh_3)_2$. This compound was prepared according to the procedure described by Salmon and Walton.[1] Electronic absorption spectral data, λ_{max} in CH_2Cl_2 (nm): 695 (log ϵ = 3.0), 465 (sh) (log ϵ = 3.4), 390 (log ϵ = 3.65).

(ii) *trans*-$OsCl_4(PR_3)_2$, Where PR_3 = PEt_3, P-*n*-Pr_3, and P-*n*-Bu_3. These complexes were isolated during attempts to synthesize the Os(VI) species $OsO_2Cl_2(PR_3)_2$ according to the recipe described in procedure A(ii). A typical procedure is as follows. A sample of osmium tetraoxide (0.67 g, 2.6 mmol) was dissolved in a solution comprising 11 mL of absolute ethanol and 1.33 mL (16 mmol) of concentrated hydrochloric acid to which was then added 2.0 mL of the appropriate trialkylphosphine. The resulting solution was chilled in a dry ice/acetone bath (−78 °C) for 1 h and then filtered to afford the dark brown *trans*-$OsCl_4(PR_3)_2$ complex, which was washed with cold ethanol and dried in vacuo; yield ca. 20%. Details of the IR and ^1H NMR spectral properties and magnetic moments of complexes of this type are available elsewhere in the literature.[3,6] Dichloromethane solutions of these complexes possessed very similar electronic absorption spectra; e.g., λ_{max} (nm) for *trans*-$OsCl_4(PEt_3)_2$: 720 (log ϵ = 3.2), 465 (log ϵ = 2.8), 380 (log ϵ = 3.8).

(iii) *trans*-$OsBr_4(PPh_3)_2$. This complex was prepared from $OsO_2Br_2(PPh_3)_2$ and concentrated hydrobromic acid by a procedure analogous to that used for the preparation of *trans*-$OsCl_4(PPh_3)_2$. A purple solid was obtained after the recrystallization procedure; yield 55%. Alternatively, *trans*-$OsBr_4(PPh_3)_2$ can be isolated in small quantities from the dichloromethane washings during the purification of $OsO_2Br_2(PPh_3)_2$ (see section A(v)). Anal. Calcd for $C_{36}H_{30}Br_4OsP_2$: C, 41.80; H, 2.92; Br, 30.90. Found: C, 41.60; H, 3.15; Br, 30.78.

C. Preparation of Complexes of the Type *mer*-$OsCl_3(PR_3)_3$, Where PR_3 = $PMePh_2$, $PEtPh_2$, PEt_2Ph, PEt_3, P-*n*-Pr_3, and P-*n*-Bu_3. The filtrates from the reactions that afforded the complexes $OsO_2Cl_2(PR_3)_2$ or $OsCl_4(PR_3)_2$ (sections A(ii)–A(iv) and B(ii)) were reduced in volume to ca. 2–4 mL and were then refrigerated for 24 h. The orange-red crystalline samples of *mer*-$OsCl_3(PR_3)_3$ were filtered off, washed with cold ethanol, and dried in vacuo; yield ca. 20%. Anal. Calcd for $C_{39}H_{39}Cl_3OsP_3$ (*mer*-$OsCl_3(PMePh_2)_3$): C, 52.21; H, 4.38. Found: C, 52.28; H, 4.51. Details of the IR, ^1H NMR, and ESR spectral properties and magnetic moments of complexes of this type are available elsewhere in the literature.[3,6] Dichloromethane solutions of these complexes possessed very similar electronic absorption spectra; e.g. λ_{max} (nm) for *mer*-$OsCl_3(PMePh_2)_3$: 520 (log ϵ = 2.9), 435 (log ϵ = 3.2), 355 (sh) (log ϵ = 3.2).

D. Preparation of Complexes of the Type $OsX_2(L)(PPh_3)_2$. (i) $OsCl_2(hp)(PPh_3)_2$. A mixture of 0.30 g (0.37 mmol) of $OsO_2Cl_2(PPh_3)_2$, 0.10 g (1.1 mmol) of 2-hydroxypyridine (Hhp), and 20 mL of ethanol was heated under reflux for 20 h in the absence of light. The mixture was cooled to room temperature and filtered. The orange solid was collected and washed with diethyl ether. It was recrystallized by dissolution in dichloromethane, with subsequent filtration to remove any unreacted solid $OsO_2Cl_2(PPh_3)_2$, and evaporation to a small volume followed by the addition of diethyl ether to initiate crystallization. The orange crystals were filtered off, washed with diethyl ether, and dried in vacuo; yield 0.14 g (42%). Anal. Calcd for $C_{41}H_{34}Cl_2NOOsP_2$: C, 55.97; H, 3.90; Cl, 8.06. Found: C, 55.42; H, 4.04; Cl, 8.52. Electronic absorption spectral data, λ_{max} in CH_2Cl_2 (nm): 450 (log ϵ = 2.6).

(ii) $OsCl_2(mhp)(PPh_3)_2$. A procedure that was similar to that described in section D(i) was followed. This afforded red-orange crystals; yield 35%. Anal. Calcd for $C_{42}H_{36}Cl_2NOOsP_2$: C, 56.44; H, 4.06; Cl, 7.93; N, 1.57. Found: C, 56.55; H, 4.23; Cl, 7.72; N, 1.53. Electronic absorption spectral data, λ_{max} in CH_2Cl_2 (nm): 455 (log ϵ = 2.6).

(iii) $OsCl_2(pic)(PPh_3)_2$. This procedure followed that described in section D(i). The reaction gave a yellow product, yield 36%. Anal. Calcd for $C_{42}H_{34}Cl_2NO_2OsP_2$: Cl, 7.81. Found: Cl, 7.85. Electronic absorption spectral data, λ_{max} in CH_2Cl_2 (nm): 470 (sh) (log ϵ = 2.8), 350 (sh) (log ϵ = 3.6).

(iv) $OsCl_2(PhN_3Ph)(PPh_3)_2$. A quantity of 1,3-diphenyltriazene (PhN_3HPh) (0.15 g, 0.74 mmol) was dissolved in 20 mL of tetrahydrofuran and the solution cooled to −20 °C. A 2.1 M solution of *n*-butyllithium (0.35 mL, 0.74 mmol) was added, causing deprotonation of PhN_3HPh and a change in the color of the reaction mixture from yellow to red. To this was added 0.30 g (0.37 mmol) of $OsO_2Cl_2(PPh_3)_2$. (Note: *trans*-$OsCl_4(PPh_3)_2$ can be used in place of $OsO_2Cl_2(PPh_3)_2$ to give the same final product.) The solution was heated under reflux for 2 h in the absence of light to yield a green product. The reaction mixture was filtered to obtain a green solid, which was washed with diethyl ether. This solid was recrystallized from dichloromethane/diethyl ether. The green crystals were filtered off, washed with diethyl ether, and dried in vacuo; yield 0.10 g (28%). Anal. Calcd for $C_{48}H_{40}Cl_2N_3OsP_2$: C, 58.72; H, 4.11; Cl, 7.22. Found: C, 58.35; H, 4.32; Cl, 7.40. Electronic absorption spectral data, λ_{max} in CH_2Cl_2 (nm): 670 (log ϵ = 2.9), 440 (log ϵ = 3.8).

(v) $OsBr_2(hp)(PPh_3)_2$. A procedure similar to that in section D(i) was followed to give the product as orange crystals, yield 54%. Anal. Calcd for $C_{41}H_{34}Br_2NOOsP_2$: C, 50.84; H, 3.54; Br, 16.50. Found: C, 51.07; H, 3.74; Br, 16.43. Electronic absorption spectral data, λ_{max} in CH_2Cl_2 (nm): 480 (log ϵ = 2.8), 390 (log ϵ = 3.35).

(vi) $OsBr_2(mhp)(PPh_3)_2$. This complex was obtained as a red powder by using a procedure analogous to that in section D(i); yield 36%. Anal. Calcd for $C_{42}H_{36}Br_2NOOsP_2$: C, 51.33; H, 3.69; Br, 16.26; N, 1.42. Found: C, 51.26; H, 3.78; Br, 15.92; N, 1.43. Electronic absorption spectral data, λ_{max} in CH_2Cl_2 (nm): 455 (log ϵ = 2.9), 410 (log ϵ = 3.4).

(vii) $OsBr_2(pic)(PPh_3)_2$. This orange solid was obtained by using a procedure similar to that in section D(i); yield 30%. Anal. Calcd for $C_{42}H_{34}Br_2NO_2OsP_2$: Br, 16.03. Found: Br, 15.70. Electronic absorption spectra data, λ_{max} in CH_2Cl_2(nm): 505 (log ϵ = 2.8), 355 (log ϵ = 3.4).

(viii) $OsBr_2(PhN_3Ph)(PPh_3)_2$. Green crystals of this complex were obtained by using a procedure similar to that in section D(iv); yield 29%. Anal. Calcd for $C_{48}H_{40}Br_2N_3OsP_2$: C, 53.84; H, 3.77; Br, 14.92. Found: C, 53.63; H, 3.98; Br, 14.98. Electronic absorption spectral data, λ_{max} in CH_2Cl_2 (nm): 720 (log ϵ = 2.9), 525 (sh) (log ϵ = 3.1), 435 (log ϵ = 3.8).

E. Preparation of $OsCl_3(CO)(PEt_2Ph)_2\cdot Et_2O$. A mixture of 0.55 g (0.88 mmol) of $OsO_2Cl_2(PEt_2Ph)_2$, 0.16 g (1.47 mmol) of 2-

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Table I. EPR and XPS Spectral Data and Voltammetric Half-Wave Potentials for Some Os(VI), Os(IV), Os(III), and Os(II) Compounds

	EPR[a]			XPS[c]			voltammetric half-wave potential[e]		
complex	g_1	g_2	g_3[b]	Os $4f_{7/2}$[d]	Cl $2p_{3/2}$	Br $3d_{5/2,3/2}$	$E_{1/2}(ox)$[f]	$E_{1/2}(red)$[f]	$E_{p,c}$
$OsO_2Br_2(PPh_3)_2$				54.4 (1.7)		69.2			
$OsO_2Cl_2(PMePh_2)_2$									−1.03
$OsO_2Cl_2(PEtPh_2)_2$									−1.09
$OsO_2Cl_2(PEt_2Ph)_2$				54.3 (2.2)	199.0				−1.18
trans-$OsCl_4(PEt_3)_2$								+0.22 (95)	
trans-$OsCl_4(P\text{-}n\text{-}Pr_3)_2$								+0.16 (85)	
trans-$OsCl_4(P\text{-}n\text{-}Bu_3)_2$								+0.15 (80)	
trans-$OsBr_4(PPh_3)_2$				51.8 (1.7)		68.4		+0.36 (85)	−1.01
mer-$OsCl_3(PMePh_2)_3$							+0.97 (85)		−0.40
mer-$OsCl_3(PEtPh_2)_3$							+0.93 (90)		−0.38
mer-$OsCl_3(PEt_2Ph)_3$							+0.88 (95)		−0.54
mer-$OsCl_3(PEt_3)_3$							+0.77 (60)		−0.60
mer-$OsCl_3(P\text{-}n\text{-}Pr_3)_3$							+0.78 (100)		−0.71
mer-$OsCl_3(P\text{-}n\text{-}Bu_3)_3$							+0.76 (80)		−0.70
$OsCl_2(hp)(PPh_3)_2$	2.65	2.17	1.09	51.6 (1.6)	198.5		+0.80 (70)	−0.80 (85)	
$OsCl_2(mhp)(PPh_3)_2$	2.77	2.10	1.01	51.5 (1.7)	198.5		+0.81 (85)	−0.81 (95)	
$OsCl_2(pic)(PPh_3)_2$	2.71	2.13	1.01	52.1 (1.7)	198.6		+1.02 (145)	−0.57 (145)	
$OsCl_2(PhN_3Ph)(PPh_3)_2$	2.88	1.84	0.88				+0.76 (75)	−0.62 (95)	
$OsBr_2(hp)(PPh_3)_2$	2.62	2.23	1.14	51.9 (1.7)		69.2	+0.82 (85)	−0.73 (95)	
$OsBr_2(mhp)(PPh_3)_2$	2.73	2.12	1.00	51.7 (1.9)		68.9	+0.79 (95)	−0.72 (110)	
$OsBr_2(pic)(PPh_3)_2$	2.75	2.13	0.97	52.0 (1.9)		69.2	+1.01 (155)	−0.49 (105)	
$OsBr_2(PhN_3Ph)(PPh_3)_2$	2.84	1.88	0.86				+0.79 (85)	−0.52 (85)	
$OsCl_3(CO)(PPh_3)_2 \cdot Et_2O$							+0.71 (90)	−0.87 (85)	
$OsCl(mhp)(CO)(PPh_3)_2$				51.7 (1.6)	198.0				
$OsBr(mhp)(CO)(PPh_3)_2$				51.4 (1.8)		68.5			

[a] Measured at X-band frequencies for dichloromethane glasses at −160 °C. [b] Approximate values of broad, weak signals. [c] Binding energies referenced to a C 1s value of 285.0 eV for the tertiary phosphine ligands. [d] Full-width half-maximum (fwhm) values are given in parentheses. [e] In volts vs. SCE with a Pt-bead electrode and 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte in dichloromethane. [f] Values of $E_{p,a} - E_{p,c}$ (in mV) at a sweep rate of 200 mV/s are given in parentheses.

hydroxy-6-methylpyridine (Hmhp), and 20 mL of ethanol was refluxed for 20 h in the absence of light by using a procedure similar to that in section D(ii). The mixture was cooled to room temperature and filtered. A blue-gray solid was collected and washed with diethyl ether. The solid was recrystallized by dissolution in a small amount of dichloromethane followed by the addition of diethyl ether to initiate crystallization. The blue-gray product was filtered off, washed with diethyl ether, and dried in vacuo; yield 0.086 g (13%). Anal. Calcd for $C_{25}H_{40}Cl_3O_2OsP_2$: C, 41.07; H, 5.51; Cl, 14.55. Found: C, 40.73; H, 5.27; Cl, 14.30. IR data (Nujol mull): $\nu(C{\equiv}O)$ 1917 (s) cm^{-1}. The presence of diethyl ether in this product was confirmed by the ^1H NMR spectrum of a $CDCl_3$ solution, which showed a characteristic CH_2 quartet at δ 3.48.

F. Preparation of Complexes of the Type $OsX(mhp)(CO)(PPh_3)_2$. (i) $OsCl(mhp)(CO)(PPh_3)_2$. A mixture of 0.20 g (0.23 mmol) of *trans*-$OsCl_4(PPh_3)_2$, 0.10 g (0.92 mmol) of 2-hydroxy-6-methylpyridine (Hmhp), and 30 mL of absolute ethanol was heated under reflux for 5 h. The mixture was cooled to room temperature and then filtered. The resulting brown solid was added to 0.025 g (0.23 mmol) of Hmhp and 30 mL of ethanol, and the mixture was refluxed for another 5 h. The mixture was filtered, and the filtrate was reduced in volume to 15 mL. Diethyl ether (15 mL) was added to the filtrate, which was then refrigerated for 1 week. Pale green crystals were collected upon filtration and dried in vacuo; yield 0.024 g (12%). Anal. Calcd for $C_{43}H_{36}ClNO_2OsP_2$: C, 58.27; H, 4.09; Cl, 4.00; N, 1.58. Found: C, 58.18; H, 4.85; Cl, 4.43; N, 1.67. IR data (Nujol mull): $\nu(C{\equiv}O)$ 1926 (vs) cm^{-1}.

(ii) $OsBr(mhp)(CO)(PPh_3)_2$. A procedure identical with that in section F(i) was followed to afford the product as pale green crystals, yield 15%. Anal. Calcd for $C_{43}H_{36}BrNO_2OsP_2$: C, 55.49; H, 3.90; Br, 8.58. Found: C, 56.24; H, 4.66; Br, 8.64. IR data (CH_2Cl_2): $\nu(C{\equiv}O)$ 1918 (vs) cm^{-1}.

Physical Measurements. These were carried out as described previously.[5] Elemental microanalyses were performed by Dr. C. S. Yeh of the Purdue University microanalytical laboratory, Chemalytics, Inc., Tempe, AZ, and Galbraith Laboratories, Inc., Knoxville, TN.

Results and Discussion

Synthesis and Spectroscopic Characterizations. We have shown previously[1] that the chloride complex $OsOCl_3(PPh_3)_2$ is in reality a mixture of $OsO_2Cl_2(PPh_3)_2$ and *trans*-$OsCl_4(PPh_3)_2$, and we have described how pure samples of both complexes can be isolated from the resultant reaction mixtures. In the present work we have confirmed that this is also the case for the analogous bromide system. When the reaction between osmium tetraoxide, triphenylphosphine, and concentrated HBr is carried out at room temperature, the principal product is $OsO_2Br_2(PPh_3)_2$, which can easily be freed from any *trans*-$OsBr_4(PPh_3)_2$ by washing with dichloromethane. The latter complex is formed in good yield when the reactants are heated for ca 30 min. The tan, light-sensitive complex $OsO_2Br_2(PPh_3)_2$ shows the characteristic IR-active $\nu(O{=}Os{=}O)$ mode[1,7] at 847 cm^{-1}. The Os 4f core-electron binding energies of these two complexes as measured by X-ray photoelectron spectroscopy (XPS) are listed in Table I and are in excellent agreement with the corresponding data for $OsO_2Cl_2(PPh_3)_2$ and *trans*-$OsCl_4(PPh_3)_2$.[1]

Previous work[3] has demonstrated that when ethanol–concentrated hydrochloric acid solutions of osmium tetraoxide and trialkylphosphines or mixed phenylalkylphosphines are heated, complexes of stoichiometry $OsCl_4(PR_3)_2$ or $OsCl_3(PR_3)_3$ are formed. It seemed very likely that in all such instances the Os(VI) species $OsO_2Cl_2(PR_3)_2$ are formed as intermediates but that the reaction conditions previously employed have not been mild enough to permit their isolation. We have confirmed this in the case of the phosphines $PMePh_2$, $PEtPh_2$, and PEt_2Ph, since the complexes $OsO_2Cl_2(PR_3)_2$ can be synthesized with a procedure very similar to that used for the isolation of $OsO_2Cl_2(PPh_3)_2$. The microanalytical data and IR, ^1H NMR, and electronic absorption spectral properties of $OsO_2Cl_2(PR_3)_2$ are in accord with this formulation (e.g., $\nu(O{=}Os{=}O)$ at ca. 840 cm^{-1}).[8] XPS data for $OsO_2Cl_2(PEt_2Ph)_2$ are presented

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(7) (a) Griffith, W. P. *J. Chem. Soc. A* **1969**, 211. (b) Collin, R. J.; Jones, J.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* **1974**, 1094.

(8) The electronic absorption spectra of CH_2Cl_2 solutions of these complexes show absorption maxima in the ranges 540–515 nm (log ϵ = 2.5–3.0) and 410–395 (sh) nm (log ϵ = 2.8–3.3). Details of the ^1H NMR spectra are available elsewhere (Armstrong, J. E. Ph.D. Thesis, Purdue, 1982).

in Table I and confirm its identity as an Os(VI) derivative. These complexes resemble $OsO_2X_2(PPh_3)_2$ (X = Cl or Br) in being light sensitive, and accordingly, they should whenever possible be stored in the dark.

In the case of the reactions between osmium tetraoxide and the trialkylphosphines PEt_3, P-*n*-Pr_3, and P-*n*-Bu_3, attempts to prepare $OsO_2Cl_2(PR_3)_2$ were unsuccessful; even under mild reactions conditions the Os(IV) complexes *trans*-$OsCl_4(PR_3)_2$ were formed. It appears that these particular phosphines are much too potent as reducing agents to permit the isolation of stable $OsO_2Cl_2(PR_3)_2$ compounds.

From a workup of the filtrates from the reactions that afforded $OsO_2Cl_2(PR_3)_2$ or $OsCl_4(PR_3)_2$, it was possible in all instances, except the triphenylphosphine system, to isolate reasonable quantitites of *mer*-$OsCl_3(PR_3)_3$. Thus, depending upon the basicity of the phosphine and the reaction conditions (temperature, equivalents of phosphine used, etc.), it is possible to isolate Os(VI), Os(IV), or Os(III) species as defined in the sequence

$$\begin{array}{llll} OsO_4 \rightarrow & OsO_2Cl_2(PR_3)_2 \rightarrow & trans\text{-}OsCl_4(PR_3)_2 \rightarrow & \\ \mathrm{Os(VIII)} & \mathrm{Os(VI)} & \mathrm{Os(IV)} & \\ & & & mer\text{-}OsCl_3(PR_3)_3 \\ & & & \mathrm{Os(III)} \end{array}$$

The bidentate ligands 2-hydroxypyridine (Hhp), 2-hydroxy-6-methylpyridine (Hmhp), and picolinic acid (Hpic) react with $OsO_2X_2(PPh_3)_2$ (X = Cl and Br) in ethanol under reflux conditions to yield yellow, orange, and red Os(III) complexes of the type $OsX_2(L)(PPh_3)_2$ (L = hp, mhp, and pic). In other reactions, mixtures of 1,3-diphenyltriazene (PhN_3HPh) and *n*-butyllithium in tetrahydrofuran at −20 °C afforded $OsX_2(PhN_3Ph)(PPh_3)_2$. The measured Os 4f (and Cl 2p or Br 3d) core-electron binding energies of several of these compounds are presented in Table I. These values are consistent with core-electron binding energy values for other Os(III) compounds.[1] Each of these d^5, low-spin Os(III) complexes exhibited characteristic X-band ESR spectra in dichloromethane at −160 °C; three *g* values (~2.7, ~2.1, and ~1.0) were observed as expected[6] for molecules of such low symmetry (see Table I).

Our efforts at exploring the reactions of these bidentate ligands with the osmium(VI) complexes focused principally upon $OsO_2X_2(PPh_3)_2$ (X = Cl and Br), since these were the two derivatives that we isolated in highest yield. However, the reaction course is dependent upon the nature of the phosphine, as witnessed by the reaction between $OsO_2Cl_2(PEt_2Ph)_2$ and Hmhp in which the paramagnetic carbonyl product $OsCl_3(CO)(PEt_2Ph)_2$ ($\nu(CO) = 1916\ cm^{-1}$) is obtained; the CO ligand presumably arises through abstraction from the ethanol solvent. Although there are a large number of carbonyl complexes of Os(II), Os(I), and Os(0),[9] *neutral* carbonyl-containing derivatives of Os(III) are scarce.[10] This blue-green compound is ESR active, and a CH_2Cl_2 glass gave a broad signal at $g = 2.48$, corresponding to an effective magnetic moment of 2.15 μ_B.

Reactions of *trans*-$OsX_4(PPh_3)_2$ (X = Cl and Br) and Hmhp in ethanol under reflux conditions produced pale green crystals of $OsX(mhp)(CO)(PPh_3)_2$. These carbonyl-containing complexes each exhibit a single intense IR-active $\nu(CO)$ absorption at ca. 1920 cm^{-1}.[11]

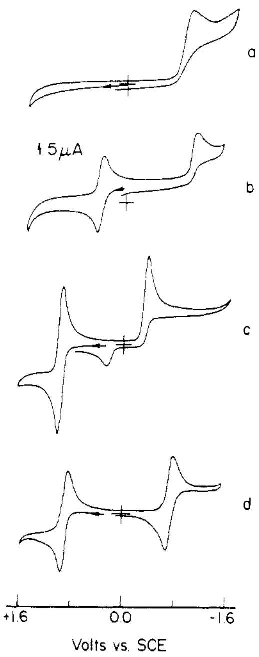

Figure 1. Cyclic voltammograms ($v = 200$ mV/s at a Pt-bead electrode) in 0.2 M TBAH/CH_2Cl_2: (a) $OsO_2Cl_2(PMePh_2)_2$; (b) *trans*-$OsBr_4(PPh_3)_2$; (c) *mer*-$OsCl_3(PMePh_2)_3$; (d) $OsCl_2(hp)(PPh_3)_2$.

Electrochemical Properties. The electrochemical properties of the above compounds were explored by using the cyclic voltammetry (CV) technique. Voltammetric half-wave potentials were measured vs. the saturated potassium chloride calomel electrode (SCE) for 0.2 M tetra-*n*-butylammonium hexafluorophosphate/dichloromethane solutions and are listed in Table I. All reversible reductions and oxidations are one-electron processes ($n = 1.0 \pm 0.1$ by coulometry) with $i_{p,a}/i_{p,c} \simeq 1$. For sweep rates (v) between 50 and 400 mV/s 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 usually greater than 60 mV, generally being in the range of 60–100 mV for a sweep rate of 200 mV/s. These properties are (with our cell configuration)[12] consistent with electron-transfer processes that are reversible or approach reversibility.

The three Os(VI) complexes $OsO_2Cl_2(PR_3)_2$, where PR_3 = $PMePh_2$, $PEtPh_2$, and PEt_2Ph, each exhibit an irreversible reduction between −1.0 and −1.2 V, the actual value of which, as expected, correlates with the basicity of the phosphines and the more basic phosphine giving the complex that is hardest to reduce. A representative cyclic voltammogram is shown in Figure 1a.

The Os(IV) complexes of the type *trans*-$OsX_4(PR_3)_2$ (X = Cl when PR_3 = PEt_3, P-*n*-Pr_3, and P-*n*-Bu_3; X = Br when PR_3 = PPh_3) gave cyclic voltammograms that showed a reversible one-electron reduction between +0.4 and +0.1 V (Table I). This high positive value implies that the anion $[trans\text{-}OsX_4(PR_3)_2]^-$ should be stable and easily accessible via the chemical reduction of *trans*-$OsX_4(PR_3)_2$. This prediction has been shown to be correct by the work of Douglas and Shaw[13] when they synthesized $Ph_4As[OsCl_4(PEt_2Ph)_2]$ from the reaction of *trans*-$OsCl_4(PEt_2Ph)_2$ with $NaBH_4$ in the presence of Ph_4As^+. Only the molecule *trans*-$OsBr_4(PPh_3)_2$ showed a second one-electron reduction (Figure 1b), a result that is in accord with our previous observations concerning the elec-

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(9) Griffith, W. P. "The Chemistry of The Rarer Platinum Metals (Os, Ru, Ir, and Rh)"; Interscience: New York, 1967.

(10) Taqui Kan, M. M.; Shareef, S.; Hamed, A. *J. Inorg. Nucl. Chem.* **1976**, *38*, 331.

(11) This $\nu(CO)$ value for $OsX(mhp)(CO)(PPh_3)_2$ seems reasonable when contrasted with data for other monocarbonyl derivatives of osmium(II); see, for example: Bottomley, F.; Lin, I. J. B.; White, P. S. *J. Chem. Soc., Dalton Trans.* **1978**, 1726.

(12) Zietlow, T. C.; Klendworth, D. D.; Nimry, T.; Salmon, D. J.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 947.

(13) Douglas, P. G.; Shaw, B. L. *J. Chem. Soc. A* **1970**, 334.

trochemistry of *trans*-$OsCl_4(PPh_3)_2$ ($E_{1/2}$(red) = +0.39 V and $E_{p,c}$ = −1.40 V).[1]

In the case of *mer*-$OsCl_3(PR_3)_3$, where PR_3 = $PMePh_2$, $PEtPh_2$, PEt_2Ph, PEt_3, P-*n*-Pr_3, and P-*n*-Bu_3, both a reversible one-electron oxidation ($E_{1/2}$ between +1.0 and +0.7 V) and an irreversible one-electron reduction ($E_{p,c}$ between −0.3 and −0.8V) are seen to characterize these systems (Table I and Figure 1c). The presence of an oxidation and a reduction within the potential range +1.4 to −0.8 V were found previously[1] to be typical behavior for derivatives of the osmium(III) halides. Note that the derivatives containing trialkylphosphines have their $E_{1/2}$ and $E_{p,c}$ values (Table I) shifted to more negative values relative to the mixed phenylalkylphosphine derivatives and $OsCl_3(PPh_3)_2(CH_3CN)$.[1] This reflects an increase of basicity in the order $PPh_3 < PRPh_2 < PR_2Ph < PR_3$ and thus the anticipated increase in the ease of oxidizing and decrease in ease of reducing the complexes containing the trialkylphosphine ligands.[14]

The Os(III) complexes $OsX_2(L)(PPh_3)_2$ (X = Cl or Br; L = hp, mhp, pic, or PhN_3Ph) and $OsCl_3(CO)(PEt_2Ph)_2$ each have a reversible one-electron oxidation with $E_{1/2}$ between +1.1 and +0.7 V and a reversible one-electron reduction with $E_{1/2}$ between −0.4 and −0.9 V (Table I and Figure 1d). The stability of the Os(IV), Os(III), and Os(II) oxidation states in these complexes is reflected by the reversibility of these processes:

$$[OsX_2(L)(PPh_3)_2]^+ \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} OsX_2(L)(PPh_3)_2 \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [OsX_2(L)(PPh_3)_2]^-$$

Concluding Remarks. In this work we have demonstrated that in the reactions of osmium tetraoxide with tertiary phosphines in ethanol/hydrohalic acid mixtures, the Os(VI) derivatives are intermediates in the formation of the more familiar species *trans*-$OsX_4(PR_3)_2$ and *mer*-$OsX_3(PR_3)_3$. Since the reaction of $OsO_2X_2(PR_3)_2$ with carboxylic acid/anhydride mixtures affords the diosmium(IV) complexes $Os_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2X_4(PR_3)_2$,[5,15] we have examined how these same osmyl complexes react with the anions of 2-hydroxypyridine, 2-hydroxy-6-methylpyridine, and 1,3-diphenyltriazine. In all instances, the magnetically dilute mononuclear Os(III) complexes $OsX_2(L)(PR_3)_2$ are formed. This difference in reaction course might be explained by the greater reducing propensity of the hydroxypyridines and the $Ph_2N_3^-$ ligand (compared to carboxylate ligands) and the reluctance to form the distorted type of bridge that is necessary to span two *weakly* interacting osmium(IV) atoms at a long distance from one another. Of additional note is the failure of these ligands to couple the Os(III) centers once reduction has occurred. This is especially noteworthy since they can be very effective at stabilizing dinuclear units containing very short metal–metal bonds.[4] Examples include the triple-bonded diosmium complex $Os_2(hp)_4Cl_2$,[16] a species prepared directly from osmium(III) chloride. It appears that the presence of phosphine ligands, as in the system we have studied, have a destabilizing influence, in ways not yet fully understood, upon the formation of osmium–osmium multiple bonds.[17]

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Registry No. $OsO_2Br_2(PPh_3)_2$, 85317-76-6; $OsO_2Cl_2(PMePh_2)_2$, 85282-44-6; $OsO_2Cl_2(PEtPh_2)_2$, 85282-45-7; $OsO_2Cl_2(PEt_2Ph)_2$, 84960-62-3; *trans*-$OsCl_4(PEt_3)_2$, 36965-63-6; *trans*-$OsCl_4(P(n\text{-}Pr)_3)_2$, 20500-75-8; *trans*-$OsCl_4(P(n\text{-}Bu)_3)_2$, 85282-46-8; *trans*-$OsBr_4(PPh_3)_2$, 85282-47-9; *mer*-$OsCl_3(PMePh_2)_3$, 85282-48-0; *mer*-$OsCl_3(PEtPh_2)_3$, 22671-03-0; *mer*-$OsCl_3(PEt_2Ph)_3$, 23677-84-1; *mer*-$OsCl_3(PEt_3)_3$, 22358-10-7; *mer*-$OsCl_3(P(n\text{-}Pr)_3)_3$, 22358-11-8; *mer*-$OsCl_3(P(n\text{-}Bu)_3)_3$, 22670-96-8; $OsCl_2(hp)(PPh_3)_2$, 85282-49-1; $OsCl_2(mhp)(PPh_3)_2$, 85282-50-4; $OsCl_2(pic)(PPh_3)_2$, 85282-51-5; $OsCl_2(PhN_3Ph)(PPh_3)_2$, 85282-52-6; $OsBr_2(hp)(PPh_3)_2$, 85282-53-7; $OsBr_2(mhp)(PPh_3)_2$, 85282-54-8; $OsBr_2(pic)(PPh_3)_2$, 85282-55-9; $OsBr_2(PhN_3Ph)(PPh_3)_2$, 85282-56-0; $OsCl_3(CO)(PPh_3)_2$, 85282-57-1; $OsCl(mhp)(CO)(PPh_3)_2$, 85282-58-2; $OsBr(mhp)(CO)(PPh_3)_2$, 85282-59-3; $OsO_2Cl_2(PPh_3)_2$, 66984-36-9; *trans*-$OsCl_4(PPh_3)_2$, 60479-38-1.

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(14) In the case of *mer*-$OsCl_3(PR_3)_3$, the irreversible reduction is followed on the second sweep of the cyclic voltammogram (Figure 1c) by the appearance of a wave between 0 and +0.26 V (the actual value of $E_{p,a}$ depends on the nature of the phosphine). This signifies the formation of a chemical product (as yet unidentified) following the reduction.

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

(16) Cotton, F. A.; Thompson, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 6437.

(17) A recent development of note in diosmium chemistry has been the preparation and structural characterization of the triply bonded diosmium(III) carboxylates $Os_2(O_2CR)_4Cl_2$; see: Moore, D. S.; Alves, A. S.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1981**, 1164. Stephenson, T. A.; Tocher, D. A.; Walkinshaw, M. D. *J. Organomet. Chem.* **1982**, *232*, C51.