Contribution from the Department of Chemistry, Purdue University,
West Lafayette, Indiana 47907

Reactions of Osmium Tetraoxide with Triphenylphosphine. Reformulation of Oxotrichlorobis(triphenylphosphine)osmium(V)

D. J. SALMON and R. A. WALTON*

Received March 7, 1978

The osmium(V) complex $OsOCl_3(PPh_3)_2$, which was purported to be formed upon reacting osmium tetraoxide with triphenylphosphine and hydrochloric acid in refluxing ethanol, is shown to be a mixture of $OsO_2Cl_2(PPh_3)_2$ and *trans*-$OsCl_4(PPh_3)_2$. This conclusion is supported by infrared and X-ray photoelectron spectroscopic (XPS) measurements and the isolation of analytically pure samples of the osmium(VI) and osmium(IV) complexes. The dicarbonyl complex $Os(CO)_2Cl_2(PPh_3)_2$ has also been isolated from the OsO_4–PPh_3–HCl reaction mixture in ethanol when long reflux periods (6–8 h) are used. The reaction of $OsO_2Cl_2(PPh_3)_2$ with refluxing pyridine produces the osmium(II) complex $OsCl_2(py)_3(PPh_3)$, while *trans*-$OsCl_4(PPh_3)_2$ is reduced to the osmium(III) complexes $OsCl_3(py)_2(PPh_3)$ and $OsCl_3(PPh_3)_2(CH_3CN)$ by pyridine and acetonitrile, respectively. These mixed-ligand complexes exhibit a rich redox chemistry as demonstrated by cyclic voltammetry.

Introduction

The reaction of osmium tetraoxide with triphenylphosphine and hydrochloric acid in ethanol is apparently anomalous in that the osmium(V) derivative $OsOCl_3(PPh_3)_2$ is produced[1] rather than a complex of the type $OsCl_4(PR_3)_2$ or $OsCl_3(PR_3)_3$, species which are formed using other tertiary phosphines.[2] Although this synthetic route is analogous to that used to prepare the well-known rhenium(V) complex $ReOCl_3(PPh_3)_2$,[3] nonetheless, the formation of this osmium(V) complex is very surprising in view of the relatively rare occurrence of this oxidation state.[4,5] Following the isolation of $OsOCl_3(PPh_3)_2$, interest has centered on its use as a starting material for the synthesis of tertiary phosphine containing nitrido and organoimido complexes of osmium[1,6] and its use as a component of olefin disproportionation catalysts.[7]

In view of the importance of $ReOCl_3(PPh_3)_2$ as a starting material for the synthesis of the metal–metal bonded rhenium(III) acetate,[8,9] we became interested in studying the analogous reaction between $OsOCl_3(PPh_3)_2$ and acetic anhydride in an effort to synthesize a metal–metal bonded osmium acetate. This led us to reinvestigate the properties of $OsOCl_3(PPh_3)_2$, as a result of which we discovered that this material is not a pure complex but rather a mixture of variable composition. These results are now presented and the chemical composition and chemistry of so-called $OsOCl_3(PPh_3)_2$ are discussed in detail.

Results and Discussion

The reaction of osmium tetraoxide with triphenylphosphine and hydrochloric acid in refluxing ethanol for 20 min affords an insoluble orange-brown product which, as described by Chatt et al.,[1] has carbon, hydrogen, and chlorine analyses which are consistent with its formulation as the oxoosmium(V) complex $OsOCl_3(PPh_3)_2$. Furthermore, the products which were isolated in our investigation exhibit the infrared absorption band at ~840 cm^{-1} which Chatt et al.[1] attributed to the $\nu(Os{=}O)$ mode of this complex. However, it appeared to us that this was an unusually low frequency for a vibration of the type $\nu(M{=}O)$,[10] instead being typical of either $\nu(O{=}Os{=}O)$ of the linear osmyl moiety (OsO_2^{2+})[11] or $\nu(Os{-}O{-}Os)$ of a μ-oxo anion such as $Os_2OX_{10}^{4-}$, where X = Cl or Br.[11]

In order to check the homogeneity of this product we recorded its X-ray photoelectron spectrum (XPS) and, to our surprise, observed a complex Os 4f binding energy spectrum which displayed two sets of Os $4f_{5/2,7/2}$ doublets (Figure 1A). Since the spin–orbit splitting for the Os 4f peaks is known to be ~2.7 eV,[12] this permitted us to locate the positions of the less well-defined Os $4f_{5/2}$ components (Figure 1A). The Cl 2p spectrum of this material revealed a well-resolved Cl $2p_{1/2,3/2}$ doublet at 200.4 and 198.9 eV. Increasing the reflux time in the preparation of $OsOCl_3(PPh_3)_2$ from 20 to 30 min caused a marked decrease in the relative intensity of the higher energy Os $4f_{5/2,7/2}$ doublet (see Figure 1B). This change in composition was also reflected in the IR spectra of the products, since the intensity of the 840-cm^{-1} band (assigned by Chatt et al.[1] to $\nu(Os{=}O)$) decreased dramatically with increase in the reflux time. Clearly, the product previously formulated as $OsOCl_3(PPh_3)_2$ is a mixture, containing two main components I and II, the relative amounts of which depend upon the preparative conditions.

By varying the reaction conditions, we have been able to isolate products whose properties are representative of I and II. When the reaction between OsO_4 and triphenylphosphine–hydrochloric acid mixtures in ethanol is carried out without reflux, the resulting light brown powder has Os $4f_{5/2,7/2}$ binding energies (see Figure 1C) and an IR spectrum (very intense sharp band at 840 cm^{-1}) which are in accord with its identification as component I. Furthermore, since these Os $4f_{5/2,7/2}$ binding energies are typical of such Os(VI) complexes as $Os_2O_6(py)_4$ and $K_2OsO_2(OH)_4$ (see Table I), which have Os $4f_{7/2}$ energies of 54.1 and 54.3 eV, respectively,[12,13] and the osmium–oxygen stretching frequency at 840 cm^{-1} is characteristic of the osmyl moiety (OsO_2^{2+}),[11] it is apparent that I is a derivative of osmium(VI). The IR spectrum of this product in the 4000–400-cm^{-1} region is typical of coordinated triphenylphosphine and, furthermore, shows the absence of significant amounts of phosphine oxide and hydroxide contaminants. The Cl 2p binding energy spectrum shows the presence of chlorine, the $2p_{1/2,3/2}$ doublet being present at 200.4 and 198.7 eV. Microanalytical data support the formulation of this complex as the new osmium(VI) derivative $OsO_2Cl_2(PPh_3)_2$. Its insolubility in polar and nonpolar solvents (acetonitrile, dichloromethane, ethanol, diethyl ether, chloroform, and benzene) precluded the measurement of its spectral properties in solution.

Reaction of a refluxing ethanol suspension of $OsO_2Cl_2(PPh_3)_2$ with a triphenylphosphine–hydrochloric acid mixture for 30–45 min produced an orange-brown solid which could be purified by recrystallization from dichloromethane as dark brown plates. Its IR spectrum showed that the $\nu(O{=}Os{=}O)$ mode at ~840 cm^{-1} was now absent. The Os 4f binding energies of this material (Figure 1D) confirmed that it was component II of the mixture which analyzed for $OsOCl_3(PPh_3)_2$. These Os 4f binding energies were typical of osmium(IV) complexes of the type *trans*-$OsCl_4(PR_3)_2$ (see Table I). This observation, coupled with the low-frequency infrared spectrum of II which revealed a single $\nu(Os{-}Cl)$ band at 330 cm^{-1}, characteristic of *trans*-$OsCl_4(PR_3)_2$ complexes,[15] indicated that II is a derivative of osmium(IV). Microanalytical

Table I. Core Electron Binding Energies (eV) of Osmium Complexes[a]

complex	metal oxidn state	Os $4f_{7/2}$[b]	Cl $2p_{3/2}$	N 1s	source
OsO_4	VIII	57.1			*c*
$K_2OsO_2(OH)_4$	VI	54.3			*c*
$OsO_2Cl_2(PPh_3)_2$	VI	54.3 (1.5)	198.6		this work
K_2OsCl_6	IV	53.1			*c*
trans-$OsCl_4(PEt_3)_2$	IV	52.8	199.1		*d*
trans-$OsCl_4(PMe_2Ph)_2$	IV	53.2	199.1		*d*
trans-$OsCl_4(PPh_3)_2$	IV	53.3 (1.4)	199.0		this work
mer-$OsCl_3(PMe_2Ph)_3$	III	51.8	198.4		*d*
$OsCl_3(PPh_3)_2(CH_3CN)$	III	52.2 (1.5)	198.7	400.3	this work
$OsCl_3(py)_2(PPh_3)$	III	52.0 (1.1)	198.3	400.2	this work
trans-$OsCl_2(PMe_2Ph)_4$	II	50.7	198.3		*d*
$OsBr_2(PPh_3)_3$	II	51.3			*e*
$OsCl_2(py)_3(PPh_3)$	II	50.4 (1.1)	198.0	400.3	this work
$Os(CO)_2Cl_2(PPh_3)_2$	II	52.4 (1.3)	198.2		this work
$Os(CO)_2Br_2(PPh_3)_2$	II	52.6			*e*

[a] Binding energies referenced to a C 1s value of 285.0 eV for the tertiary phosphine ligands or, in the case of OsO_4, $K_2OsO_2(OH)_4$, and K_2OsCl_6, to a Au $4f_{7/2}$ energy of 83.8 eV. For a general discussion of different referencing procedures, see ref 14. [b] Full-width half-maximum (fwhm) values are given in parentheses for new Os $4f_{7/2}$ data only. [c] Data taken from ref 12 and corrected by +0.8 eV. [d] Data taken from G. J. Leigh and W. Bremser, *J. Chem. Soc., Dalton Trans.*, 1216 (1972). [e] Data taken from ref 21.

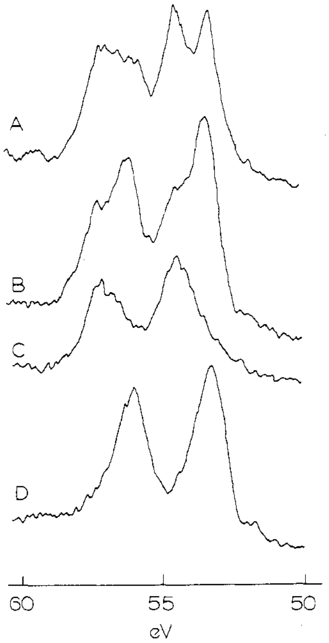

Figure 1. Os 4f binding energy spectra of products from the reaction of osmium tetraoxide with triphenylphosphine in ethanol–hydrochloric acid: A, insoluble product after a reaction time of 20 min; B, insoluble product after a reaction time of 30 min; C, $OsO_2Cl_2(PPh_3)_2$; D, *trans*-$OsCl_4(PPh_3)_2$.

data are consistent with the formulation of this complex as *trans*-$OsCl_4(PPh_3)_2$ and the flawless agreement between the X-ray powder diffraction pattern of this complex and that of the well-characterized rhenium analogue *trans*-$ReCl_4(PPh_3)_2$[16,17] is convincing support for our conclusions.

Cyclic voltammetry of a solution of *trans*-$OsCl_4(PPh_3)_2$ in 0.2 M TBAH–CH_2Cl_2 demonstrates that the complex possesses two reductions (Figure 2). The first one-electron reduction at $E_{1/2}$ = +0.39 V vs. SSCE was reversible and the second reduction $E_{p,c} \approx -1.40$ V was totally irreversible. The irreversible reduction led to formation of a product at $E_{p,a} \approx$ 1.25 V. The source of this new wave is probably PPh_3 (a sample of PPh_3 in CH_2Cl_2–0.2 M TBAH has an irreversible oxidation at $E_{p,a} \approx 1.25$ V). The electrochemical generation of $[OsCl_4(PPh_3)_2]^-$ is consistent with the ease with which tertiary phosphine complexes of osmium(III) are formed[2] whereas the rapid decomposition of $[OsCl_4(PPh_3)_2]^{2-}$ with release of PPh_3 probably reflects the need for at least three phosphine ligands to be bound to osmium(II)[2] or the presence of other π back-bonding ligands[18] in order to stabilize this oxidation state.

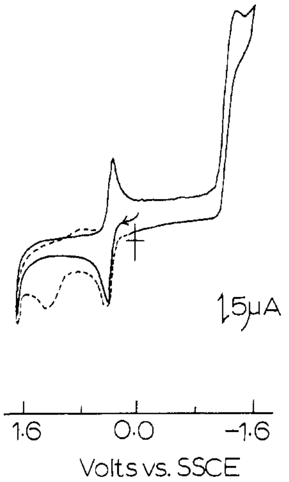

Figure 2. Cyclic voltammogram (scan rate 200 mV/s at a Pt-bead electrode) of a solution of *trans*-$OsCl_4(PPh_3)_2$ in 0.2 M TBAH–CH_2Cl_2. The partial second sweep (---) shows the presence of an irreversible wave ($E_{p,a}$ = 1.24 V) due to the formation of free PPh_3.

When the product formulated by Chatt et al.[1] as $OsOCl_3(PPh_3)_2$, and shown by us to be a mixture of $OsO_2Cl_2(PPh_3)_2$ and *trans*-$OsCl_4(PPh_3)_2$, was reacted with refluxing pyridine, a mixture of two compounds was produced. These same products, $OsCl_2(py)_3(PPh_3)$ and $OsCl_3(py)_2(PPh_3)$, were obtained in a pure state by reacting pyridine with $OsO_2Cl_2(PPh_3)_2$ and *trans*-$OsCl_4(PPh_3)_2$, respectively. This observation further demonstrates the true nature of "$OsOCl_3(PPh_3)_2$".

The osmium(IV) complex *trans*-$OsCl_4(PPh_3)_2$ was also reduced by refluxing acetonitrile to afford the red crystalline complex $OsCl_3(PPh_3)_2(CH_3CN)$. Unlike the diamagnetic osmium(II) derivative $OsCl_2(py)_3(PPh_3)$, the osmium(III) complexes $OsCl_3(py)_2(PPh_3)$ and $OsCl_3(PPh_3)_2(CH_3CN)$ were paramagnetic (μ_{eff} = 1.91 and 1.87 μ_B, respectively) and each possessed a room-temperature ESR spectrum which displayed a broad resonance (peak-to-peak separation of 900–1000 G) with a *g* value of 2.21 and 2.16, respectively. The XPS of these three new mixed-ligand complexes are in accord with their formulation as derivatives of osmium(II) and osmium(III). The appropriate Os $4f_{7/2}$ binding energy data are summarized in Table I where comparisons are made with literature data

Table II. Voltammetric Half-Wave Potentials for Osmium Complexes in Dichloromethane[a]

complex	$E_{1/2}(1)$	$E_{1/2}(2)$
$OsCl_3(py)_2(PPh_3)$	−0.64	+0.96
$OsCl_3(PPh_3)_2(CH_3CN)$	−0.52	+0.98
$OsCl_2(py)_3(PPh_3)$	−0.13	+1.39

[a] With 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. [b] Volts vs. the saturated sodium chloride calomel electrode (SSCE) with a Pt-bead working electrode.

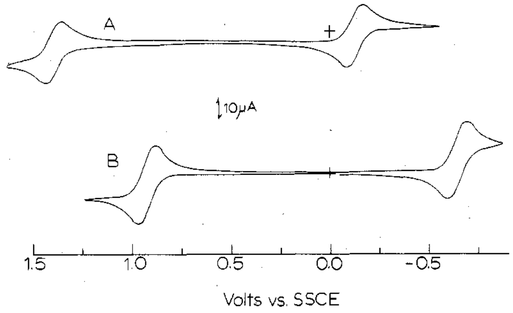

Figure 3. Cyclic voltammograms (scan rate 200 mV/s at a Pt-bead electrode) in 0.2 M TBAH–CH_2Cl_2: A, $OsCl_2(py)_3(PPh_3)$; B, $OsCl_3(py)_2(PPh_3)$.

for other pertinent complexes.

$OsCl_3(PPh_3)_2(CH_3CN)$, $OsCl_3(py)_2(PPh_3)$, and $OsCl_2(py)_3(PPh_3)$ are sufficiently soluble in dichloromethane to permit the measurement of their voltammetric half-wave potentials (Table II). These compounds exhibit two reversible[19] one-electron (by coulometry) redox waves. The cyclic voltammograms of $OsCl_2(py)_3(PPh_3)$ and $OsCl_3(py)_2(PPh_3)$ in 0.2 M TBAH–CH_2Cl_2 are presented in Figure 3. In the case of the two osmium(III) complexes, the more cathodic wave is a reduction while the anodic wave is an oxidation, i.e.

$$[OsCl_3(py)_2(PPh_3)]^+ \xleftarrow{-e^-} OsCl_3(py)_2(PPh_3) \xrightarrow{+e^-} [OsCl_3(py)_2(PPh_3)]^-$$

with similar behavior being exhibited by $OsCl_3(PPh_3)_2(CH_3CN)$. For the osmium(II) complex $OsCl_2(py)_3(PPh_3)$, both waves represent oxidations, i.e.

$$[OsCl_2(py)_3(PPh_3)]^{2+} \xleftarrow{-e^-} [OsCl_2(py)_3(PPh_3)]^+ \xleftarrow{-e^-} OsCl_2(py)_3(PPh_3)$$

This kind of extensive redox chemistry has been observed for many other third-row transition-metal complexes.[20] All electrochemical transformations performed on these complexes were found to be reversible, and the ions formed were quite stable; for example, no reaction occurred when tetraethylammonium chloride was added to $[OsCl_2(py)_3(PPh_3)]^+$.

Although $OsO_2Cl_2(PPh_3)_2$ reacts with triphenylphosphine–hydrochloric acid to give *trans*-$OsCl_4(PPh_3)_2$, this reaction is fairly complex since an additional product can be produced in the same reaction mixture from which the osmium(IV) complex is isolated. This pale brown material has intense IR-active ν(CO) absorptions at ~2040 and ~1960 cm^{-1}, indicating that an osmium–carbonyl derivative has been formed by decarbonylation of the ethanol solvent. It can be purified by treatment with refluxing pyridine, a procedure which dissolves all impurities leaving behind analytically pure white crystals of $Os(CO)_2Cl_2(PPh_3)_2$. Although this complex is insoluble in polar and nonpolar solvents (acetone, acetonitrile, benzene, ethanol, dichloromethane, chloroform, and pyridine), its Nujol mull IR spectrum, which exhibits ν(CO) absorptions at 2048 and 1968 cm^{-1} (both very strong) and ν(Os–Cl) at 313 and 291 cm^{-1}, is very similar to that of other complexes of the type $Os(CO)_2Cl_2(PR_3)_2$ which have cis arrangements of Os–Cl and Os–CO bonds.[18] This formulation is also supported by XPS measurements which show that its Os $4f_{7/2}$ binding energy (Table I) is identical with that of the bromide analogue $Os(CO)_2Br_2(PPh_3)_2$.[21] Furthermore, XPS demonstrates the absence of any N 1s binding energies, thereby ruling out the presence of pyridine in this product.

Concluding Remarks. The present study has clearly demonstrated that the product previously formulated as $OsOCl_3(PPh_3)_2$[1] is a mixture of $OsO_2Cl_2(PPh_3)_2$ and *trans*-$OsCl_4(PPh_3)_2$. Our results also explain the failure of Chatt et al.[1] to obtain nitrido–osmium complexes by the reaction of hydrazine salts with "$OsOCl_3(PPh_3)_2$", since this material does not in fact contain the OsO^{3+} moiety which was anticipated to react in an analogous fashion to ReO^{3+}. Similarly, although phosphine imines react with $ReOCl_3(PPh_3)_2$ to afford arylimido complexes and phosphine oxides,[22] analogous reactions do not occur with "$OsOCl_3(PPh_3)_2$",[6] although complexes which were formulated as $[OsCl_2(NC_6H_4X)(PPh_3)_2]$, where X = H, Cl, or OMe, were produced when $Ph_3P{=}NCO{\cdot}C_6H_4X$ was used in place of $Ph_3P{=}NR$. In the light of the reformulation of "$OsOCl_3(PPh_3)_2$", the results of these earlier reactivity studies[1,6] need to be reassessed.

Experimental Section

Starting Materials. The complex formulated by Chatt et al.[1] as $OsOCl_3(PPh_3)_2$ was prepared from OsO_4 by the literature procedure.[1] The sample of *trans*-$ReCl_4(PPh_3)_2$, whose X-ray powder pattern was recorded, was available from an earlier study.[17] Solvents were reagent grade and were used as received. Triphenylphosphine was purchased from Strem Chemicals, Inc., and osmium tetraoxide was supplied by Fisher Scientific Co. Solvents were reagent grade and were used as received.

Physical Measurements. Infrared spectra of Nujol mulls were recorded in the region 4000–200 cm^{-1} with Beckman IR-12 and Acculab 6 spectrophotometers. Cyclic voltammetry experiments were performed with a BioAnalytical Systems, Inc., Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035B x–y recorder. Potential control for coulometric experiments was maintained with a potentiostat purchased from BioAnalytical Systems, Inc. All voltammetric measurements were made on dichloromethane solutions containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte using a platinum-bead electrode. X-ray photoelectron spectra (XPS) were recorded using a Hewlett-Packard 5950A spectrometer. Binding energies were internally standardized to a coordinated tertiary phosphine C 1s binding energy of 285.0 eV. X-Band ESR spectra of solid samples were recorded at room temperature with a Varian E-109 spectrometer. Magnetic moments were calculated using the expression $\mu = g(s(s+1))^{1/2}$. Conductivity measurements were made in dry acteonitrile using an Industrial Instruments Bridge, Model RC16B2. X-ray powder patterns were recorded using a General Electric recording diffractometer with a Cu Kα (1.5405 Å) radiation source. The sample was deposited on an adhesive tape attached to a microscope slide. Measured diffraction angles (2θ) were converted to interplanar spacings (*d*) by use of published tables.

Reactions. (i) $OsO_2Cl_2(PPh_3)_2$. Osmium tetraoxide (1.0 g) was dissolved in a mixture comprising 30 mL of ethanol and 5 mL of concentrated hydrochloric acid. To this was added 5 g of triphenylphosphine dissolved in 20 mL of ethanol. The reaction mixture was stirred for a few minutes, and then filtered, and the insoluble product was washed with water, ethanol, and diethyl ether and then dried. Purification was achieved by washing with dichloromethane which removed a soluble contaminant and left the complex $OsO_2Cl_2(PPh_3)_2$ as a light brown-gray powder. Anal. Calcd for $C_{36}H_{30}Cl_2O_2OsP_2$: C, 52.88; H, 3.70; Cl, 8.67. Found: C, 51.97; H, 3.64; Cl, 8.74; yield 2.5 g.

(ii) *trans*-$OsCl_4(PPh_3)_2$. A suspension of $OsO_2Cl_2(PPh_3)_2$ (0.5 g) in 25 mL of ethanol, to which was added 2 g of triphenylphosphine and 2 mL of concentrated hydrochloric acid, was refluxed for about 30 min. The insoluble orange-brown material was filtered off, washed with ethanol and diethyl ether, and dried. It was recrystallized from dichloromethane (or dichloromethane–diethyl ether mixtures) as dark brown plates. This recrystallization procedure permits the separation of *trans*-$OsCl_4(PPh_3)_2$ from any unreacted $OsO_2Cl_2(PPh_3)_2$. Anal. Calcd for $C_{36}H_{30}Cl_4OsP_2$: C, 50.47; H, 3.53; Cl, 16.56. Found: C, 50.59; H, 3.44; Cl, 15.48; yield 0.4 g. Although the chlorine microanalytical data for this complex were consistently ~6% low, the related carbon and hydrogen microanalyses were always in excellent agreement with the theoretical figures. The spectroscopic data and X-ray powder diffraction pattern for this complex leave no doubt as to its identity.

(iii) $Os(CO)_2Cl_2(PPh_3)_2$. When the reaction used to prepare *trans*-$OsCl_4(PPh_3)_2$ was carried out using a longer reflux period (~6–8 h), a lighter colored material was sometimes produced. This could be readily separated from other reaction products by a flotation procedure since it was the least dense material and floated on the surface of the reaction medium. Its purification was effected by adding ethanol (20 mL) and pyridine (2 mL) to 0.5 g of this material and refluxing the resulting reaction mixture for several hours until the only insoluble portion which remained was a crop of white crystals (0.2 g). This procedure removes $OsO_2Cl_2(PPh_3)_2$ and *trans*-$OsCl_4(PPh_3)_2$ since they both react with pyridine to afford soluble complexes (see (v) and (vi)). Anal. Calcd for $C_{38}H_{30}Cl_2O_2OsP_2$: C, 54.2; H, 3.57; Cl, 8.44; N, 0.0. Found: C, 54.19; H, 3.53; Cl, 7.93; N, <0.1.

(iv) $OsCl_3(PPh_3)_2(CH_3CN)$. Acetonitrile (20 mL) and triphenylphosphine (1 g) were added to 0.5 g of *trans*-$OsCl_4(PPh_3)_2$, and the mixture was refluxed for ~8 h until an orange solution formed. The hot reaction mixture was cooled, and the resulting red crystals (0.2 g) were filtered off and washed with ethanol and diethyl ether. Anal. Calcd for $C_{38}H_{33}Cl_3NOsP_2$: C, 52.93; H, 3.86; Cl, 12.33; N, 1.62. Found: C, 52.23; H, 4.05; Cl, 12.43; N, 1.77.

(v) $OsCl_3(py)_2(PPh_3)$. The osmium(IV) complex *trans*-$OsCl_4(PPh_3)_2$ (0.5 g) was refluxed with ethanol (20 mL) and pyridine (2 mL) for a period of 3–5 h. Upon cooling the clear orange solution, the yellow-orange complex $OsCl_3(py)_2(PPh_3)$ (0.4 g) precipitated. It was filtered off, washed with diethyl ether, and dried. Anal. Calcd for $C_{28}H_{25}Cl_3N_2OsP$: C, 46.90; H, 3.51; Cl, 14.83; N, 3.91. Found: C, 47.14; H, 3.51; Cl, 15.41; N, 3.73. An acetonitrile solution of this complex (~10^{-3} M) was nonconducting.

(vi) $OsCl_2(py)_3(PPh_3)$. A similar procedure to that described in (v) but using $OsO_2Cl_2(PPh_3)_2$ (1.0 g) in place of *trans*-$OsCl_4(PPh_3)_2$ afforded red crystals (0.5 g) of the osmium(II) complex $OsCl_2(py)_3(PPh_3)$. Anal. Calcd for $C_{33}H_{30}Cl_2N_3OsP$: C, 52.10; H, 3.98; Cl, 9.32; N, 5.52. Found: C, 51.92; H, 3.81; Cl, 9.69; N, 5.61. An acetonitrile solution of this complex (~10^{-3} M) was nonconducting.

Analytical Procedures. Elemental microanalyses were performed by Dr. C. S. Yeh of the Purdue University microanalytical laboratory and Chemalytics, Inc., Tempe, Ariz.

Acknowledgment. Support from the National Science Foundation (Grant CHE74-12788A02) is gratefully acknowledged.

Registry No. $OsO_2Cl_2(PPh_3)_2$, 66984-36-9; *trans*-$OsCl_4(PPh_3)_2$, 60479-38-1; $OsCl_3(PPh_3)_2(CH_3CN)$, 66984-35-8; $OsCl_3(py)_2(PPh_3)$, 66984-34-7; $OsCl_2(py)_3(PPh_3)$, 66984-33-6; $Os(CO)_2Cl_2(PPh_3)_2$, 16591-90-5; OsO_4, 20816-12-0; $OsOCl_3(PPh_3)_2$, 25398-91-8.

References and Notes

(1) J. Chatt, C. D. Falk, G. J. Leigh, and R. J. Paske, *J. Chem. Soc. A*, 2288 (1969).

(2) J. Chatt, G. J. Leigh, D. M. P. Mingos, and R. J. Paske, *J. Chem. Soc. A*, 2636 (1968).

(3) J. Chatt and G. A. Rowe, *J. Chem. Soc.*, 4019 (1962).

(4) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed, Wiley-Interscience, New York, N.Y., 1972, p 1016.

(5) W. P. Griffith, "The Chemistry of the Rarer Platinum Metals", Interscience, New York, N.Y., 1967, p 50, 74, 83.

(6) B. Bell, J. Chatt, J. R. Dilworth, and G. J. Leigh, *Inorg. Chim. Acta*, **6**, 635 (1972).

(7) W. B. Hughes, *Adv. Chem. Ser.*, **No. 132**, 192 (1974).

(8) G. Rouschias and G. Wilkinson, *J. Chem. Soc. A*, 465 (1966).

(9) H. D. Glicksman, A. D. Hamer, T. J. Smith, and R. A. Walton, *Inorg. Chem.*, **15**, 2205 (1976).

(10) Complexes of the type $MOCl_3L_2$ usually exhibit ν(M=O) above 950 cm^{-1}. See, for example, E. I. Stiefel, *Prog. Inorg. Chem.*, **22**, 63 (1976); this article gives data for molybdenum(V) complexes $MoOCl_3L_2$.

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

(12) D. L. White, S. B. Andrews, J. W. Faller, and R. J. Barrnett, *Biochim. Biophys. Acta*, **436**, 577 (1976).

(13) The data from ref 12 are reported relative to a Au $4f_{7/2}$ binding energy standard of 83.0 eV. To make these energies more compatible with our referencing procedure (i.e., a C 1s energy of 285.0 eV for the triphenylphosphine ligand), we have corrected them by +0.8 eV in order to make them relative to the more usual Au $4f_{7/2}$ standard of 83.8 eV (see ref 14).

(14) G. Johansson, J. Hedman, A. Berndtsson, M. Klasson, and R. Nilsson, *J. Electron Spectrosc. Relat. Phenom.*, **2**, 295 (1973).

(15) J. Chatt, G. J. Leigh, and D. M. P. Mingos, *J. Chem. Soc. A*, 1674 (1969).

(16) G. Rouschias and G. Wilkinson, *J. Chem. Soc. A*, 489 (1968).

(17) R. A. Walton, *Inorg. Chem.*, **10**, 2534 (1971).

(18) J. Chatt, D. P. Melville, and R. L. Richards, *J. Chem. Soc. A*, 1169 (1971).

(19) $\Delta E_p \simeq 60$ mV and $i_{p,a}/i_{p,c} \approx 1$: see R. W. Murray and C. N. Reilley, "Electroanalytical Principles", Interscience, New York, N.Y., 1963.

(20) See, for example: (a) A. H. Dix, J. W. Disveld, and J. G. M. Van Der Linden, *Inorg. Chim. Acta*, **24**, L51 (1977); (b) J. Hahn, T. Nimry, W. R. Robinson, D. J. Salmon, and R. A. Walton, *J. Chem. Soc., Dalton Trans.*, in press.

(21) P. Brant, Ph.D. Thesis, University of Arizona, 1977, p 80.

(22) J. Chatt and J. R. Dilworth, *J. Chem. Soc., Chem. Commun.*, 549 (1972).