Synthesis and Oxidative Addition Reactions of a Phosphine Carbonyl Complex of Osmium(0)[1]

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Abstract: The first phosphine complex of osmium(0), $Os(CO)_3[P(C_6H_5)_3]_2$, has been prepared from a new class of osmium(II) complexes, $OsX_2(CO)_2[P(C_6H_5)_3]_2$, by zinc reduction in the presence of carbon monoxide. The osmium-(II) complexes were prepared from $OsCl_3 \cdot xH_2O$ and $(NH_4)_2OsBr_6$ using triphenylphosphine and carbon monoxide pressures of only 60 psi. The osmium(0) complex exhibits basic properties as illustrated by its reaction with hydrogen halides. This reaction proceeds through a cationic hydride intermediate to yield $OsX_2(CO)_2[P(C_6H_5)_3]_2$, identical with the original osmium(II) complexes. This basic character is further illustrated by oxidation of the osmium(0) compound with iodine and bromine to yield similar cationic complexes, $\{Os(CO)_3X[P(C_6H_5)_3]_2\}^+X^-$. In solution these compounds behave as 1:1 electrolytes and slowly undergo displacement of CO to form the original nonionic complexes $OsX_2(CO)_2[P(C_6H_5)_3]_2$. Stereochemical assignments have been made for these complexes.

New patterns of analogous reactions continue to emerge from the rapid development of inorganic chemistry. In some instances inorganic reactions can be systematized by a functional group approach similar to that long used with qualitative success in organic chemistry. One such class of inorganic transformations involves oxidative addition reactions whereby metal complexes having a d^8 configuration are converted into octahedral complexes having a d^6 configuration. Although the general nature of this type of reaction has been recognized only recently,[3,4] numerous examples can be found in the literature.[5]

Oxidative addition reactions of d^8 complexes can be divided into two categories according to whether planar, four-coordinate, "unsaturated" complexes or trigonal-bipyramidal, five-coordinate "saturated" complexes are involved (eq 1 and 2).

$$\text{(1)}$$

$$\text{(2)}$$
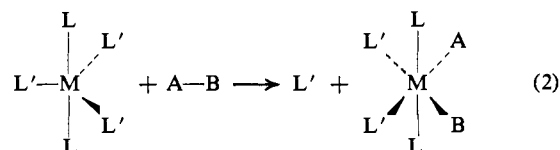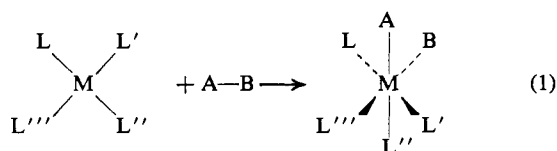
L = ligand group

Addition reactions of unsaturated d^8 complexes (eq 1) are often reversible and are probably one-step processes. Both polar and nonpolar bonds participate in these reactions. Examples include[5] hydrogen, halogens, hydrogen halides, nonmetal hydrides, reactive alkyl halides, acyl halides, sulfonyl halides,[6] mercuric

halides,[4] tin halides,[7] and acetylenes.[8,9] The stereochemistry of addition is usually stereospecific and trans.[7,9] Several homogeneous catalytic processes involve reversible oxidative additions as an essential step in the mechanism. Of particular note are hydrogenation,[10-12] hydrosilation,[13] and hydroformylation[10,14] of olefins, and trimerization of acetylenes.[9,15] The parallel between these addition reactions and chemiadsorption to the latent valences on transition metal surfaces is significant.

Addition reactions of saturated, trigonal-bipyramidal d^8 complexes (eq 2) are often accompanied by the loss of a neutral ligand. Polar bonds (electrophiles) such as halogens, hydrogen halides, methyl iodide, perfluoroalkyl iodides, and mercuric halides react with various saturated d^8 complexes.[5] The final products (eq 2) are those resulting from over-all *cis* addition; however, evidence presented herein demonstrates that a stepwise mechanism is involved.

A survey of the known oxidative addition reactions of d^8 complexes indicates that the tendency to form stable adducts of d^6 configuration increases as one goes from first- to third-row transition elements and from right to left within group VIII.[4,5] An approximate order of reactivity can be assigned: Os(0) > Ru(0) ∼ Ir(I) > Fe(0) ∼ Rh(I) > Pt(II) > Co(I) ∼ Pd(II) >> Ni(II). Direct comparisons between complexes of two isoelectronic metals containing different ligands are tenuous inasmuch as the ligands influence the reactivity.[4] For this reason, better comparisons can be made within a single triad than between different

(1) This work was supported by the National Science Foundation, the Advanced Research Projects Agency, Contract SD-100, and by the Alfred P. Sloan Foundation.

(2) Alfred P. Sloan Foundation Fellow.

(3) J. P. Collman and W. R. Roper, *J. Am. Chem. Soc.*, **87**, 4008 (1965).

(4) R. S. Nyholm and K. Vrieze, *J. Chem. Soc.*, 5337 (1965).

(5) A summary of examples of this type of reaction are to be found in ref 3.

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(9) J. P. Collman, J. W. Kang, W. R. Roper, and C. T. Sears, Jr., Second International Symposium on Organometallic Chemistry, Madison, Wis., Aug 1965, Abstracts, p 18.

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(12) J. C. Bailar, Jr., and H. Itatani, *Inorg. Chem.*, **4**, 1618 (1965), and references therein.

(13) A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **87**, 16 (1965).

(14) J. A. Osborn, G. Wilkinson, and J. F. Young, *Chem. Commun.*, 17 (1965).

(15) A. T. Blomquist and P. M. Maitlis, *J. Am. Chem. Soc.*, **84**, 2329 (1962).

triads. Nyholm[4] has presented thermodynamic arguments to support the type of trend outlined above.

Meaningful comparisons of the tendencies of four- and five-coordinate d^8 complexes to form octahedral d^6 adducts cannot be made since the two types of compounds probably react by different mechanisms (see Discussion). However, the thermodynamic trends should remain the same as outlined above. Nyholm[16] has pointed out that the tendency for d^8 systems to become five-coordinate increases within group VIII passing from third- to first-row elements and from right to left. For example, very few five-coordinate complexes of platinum(II) are known,[17] but most iron(0) compounds are five-coordinate.

Following is an account of the preparation and reactions of monomeric phosphine carbonyl complexes of osmium(0) which stems from our general investigation of oxidative addition reactions of d^8 complexes.

At the initial stages of our general investigation of oxidative additions to d^8 systems, the only known compound of osmium(0) was the monomeric pentacarbonyl $Os(CO)_5$,[18] a colorless liquid which very readily trimerizes to $Os_3(CO)_{12}$.[19] Recent X-ray investigations[19] reveal that this trimer consists of a triangle of metal-metal bonded atoms in approximately octahedral stereochemistry about the metal. The ready trimerization of the $Os(CO)_4$ group can be considered a measure of the tendency of osmium(0) to attain an octahedral configuration by increasing its valence.[4] A preliminary account of the preparation and oxidative addition reactions of monomeric ruthenium(0) phosphine carbonyl compounds has been published.[3] Chatt[20] has recently reported a ruthenium(0) complex in equilibrium with a ruthenium(II) tautomer through the insertion of the ruthenium atom into a carbon–hydrogen bond of a ligand methyl group. This novel reaction is perhaps the best illustration of the enormous tendency of unsaturated ruthenium(0) to undergo oxidative addition.

Logical starting materials for the preparation of osmium(0) compounds would be complexes of osmium(II). Various complexes of osmium(II) containing strong π-bonding ligands which would be necessary to stabilize the zero oxidation state were known. The early work of Manchot and Hieber characterized the neutral carbonyl halides, $Os(CO)_4X_2$ (X = Cl, Br, I)[21] and the halogen-bridged species, $[Os(CO)_3X_2]_2$ (X = Cl, Br, I) as well as the complex cations, $[Os(CO)_6]Cl_2$.[18] Phosphines and arsines give complexes of the types $[Os(MR_3)_4X_2]$[22] (M = As, P) and $[Os_2Cl_3(PR_3)_6]Cl$.[23] Chatt has prepared complexes with bidentate phosphines $OsX_2(P–P)_2$[23] (P–P = $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$, n = 1, 2) which he used for the preparation of osmium hydrides, alkyls, and aryls, while Venanzi has prepared osmium complexes with tetradentate phosphines and arsines.[24]

The only reported phosphine and arsine substituted

carbonyl complexes of osmium are the hydrides $OsHCl(CO)[M(C_6H_5)_3]_3$ (M = Ar, P) described by Vaska.[25] The crystal structure of the bromide complex has been determined[26] and it is notable for revealing that the phosphine ligand *trans* to the hydride is 0.2 A further from osmium than the other two phosphines. This is probably a reflection of the strong *trans* effect of the hydride ligand.

Results and Discussion

The present study was aimed at the preparation of a phosphine-substituted carbonyl complex of osmium(0) such as $Os(CO)_3[P(C_6H_5)_3]_2$. It was originally anticipated that the required starting material, $OsX_2(CO)_2[P(C_6H_5)_3]_2$, could be obtained by the method which had previously proved useful for the ruthenium(II) analogs, viz., carbonylation of a solution of $OsCl_3 \cdot xH_2O$ in methanol followed by addition of triphenylphosphine.[3] Unfortunately $OsCl_3 \cdot xH_2O$ is much less soluble in alcohols than $RuCl_3 \cdot xH_2O$ and carbonylation (under CO at 60 psi) (eq 3) proved to be very slow and incomplete.

An alternative was to attempt carbonylation of the ammonium hexahaloosmates, $(NH_4)_3OsCl_6$ and $(NH_4)_2OsBr_6$. Accordingly, these were prepared from OsO_4 by the method of Dwyer and Hogarth.[27] The hexachloroosmate did not carbonylate readily (undoubtedly because of its very low alcohol solubility), but in 2-methoxyethanol at 80° under 60 psi of CO the hexabromoosmate was rapidly carbonylated (the solution turned from a dark red to a pale yellow), and addition of triphenylphosphine resulted in an almost quantitative crystallization of $OsBr_2(CO)_2[P(C_6H_5)_3]_2$ in a pure state (eq 4). This is the best synthetic route discovered so far since it readily lends itself to the preparation of analogous complexes with other phosphines and arsines, e.g., $C_6H_5P(C_2H_5)_2$, $(C_6H_5)_2PCH_3$, and $(C_6H_5)_3As$, etc.

The complex hydride $OsHCl(CO)[P(C_6H_5)_3]_2$, prepared by Vaska[25] from $(NH_4)_2OsCl_6$ and excess triphenylphosphine in a high-boiling alcohol, on treatment with HCl gave $OsCl_2(CO)[P(C_6H_5)_3]_3$. The latter complex upon treatment with CO under mild pressure readily gave $OsCl_2(CO)_2[P(C_6H_5)_3]_2$ (eq 5). However, a more convenient synthesis of this chloro complex involves the carbonylation of osmium trichloride in 2-methoxyethanol *in the presence of triphenylphosphine* (eq 6). Whereas this preparation works very satisfactorily with triphenylphosphine, it may not be so successful with other ligands.

The infrared spectra of these osmium(II) compounds were nearly identical with those of their ruthenium analogs (the two strong carbonyl absorptions were shifted to slightly lower wavenumber in the osmium compounds) and are undoubtedly of the same stereochemistry.[28] The two phosphines are *trans* and the

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(17) R. D. Carmer, R. V. Lindsey, Jr., C. T. Prewitt, and U. G. Stolberg, *J. Am. Chem. Soc.*, **87**, 658 (1965).
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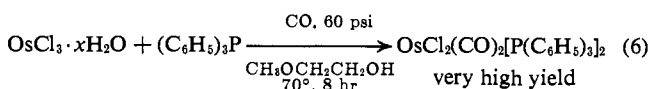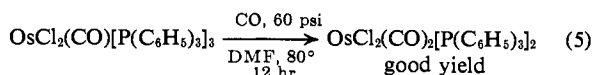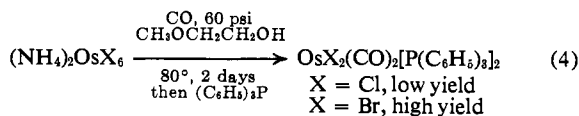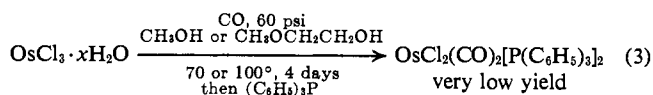(20) J. Chatt and G. M. Davidson, *J. Chem. Soc.*, 843 (1965).
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(27) F. P. Dwyer and J. W. Hogarth, *Inorg. Syn.*, **5**, 204, 206 (1957).
(28) The stereochemistry of the ruthenium(II) complexes, $RuX_2(CO_2)_2[P(C_6H_5)_3]_2$, reported in ref 3 and based on Chatt's[23] earlier assignment is incorrect. We have found[9] using the ligand dimethylphenylphosphine in conjunction with the phenomenon of virtual coupling[30] that the phosphines are mutually *trans*. The infrared spectrum in the carbonyl region fixes the carbonyls as mutually *cis*. This completely defines the stereochemistry as depicted in A. A full account of the ruthenium complexes is in preparation.
(29) J. Chatt, B. L. Shaw, and A. E. Field, *J. Chem. Soc.*, 3466 (1964).
(30) J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 279 (1963).

two carbonyls and the two halogens each mutually cis[9] (see structure A).

$$OsCl_3 \cdot xH_2O \xrightarrow[\substack{70 \text{ or } 100°, 4 \text{ days} \\ \text{then } (C_6H_5)_3P}]{\substack{CO, 60 \text{ psi} \\ CH_3OH \text{ or } CH_3OCH_2CH_2OH}} OsCl_2(CO)_2[P(C_6H_5)_3]_2 \quad (3)$$
very low yield

$$(NH_4)_2OsX_6 \xrightarrow[\substack{80°, 2 \text{ days} \\ \text{then } (C_6H_5)_3P}]{\substack{CO, 60 \text{ psi} \\ CH_3OCH_2CH_2OH}} OsX_2(CO)_2[P(C_6H_5)_3]_2 \quad (4)$$
X = Cl, low yield
X = Br, high yield

$$OsCl_2(CO)[P(C_6H_5)_3]_3 \xrightarrow[\substack{DMF, 80° \\ 12 \text{ hr}}]{CO, 60 \text{ psi}} OsCl_2(CO)_2[P(C_6H_5)_3]_2 \quad (5)$$
good yield

$$OsCl_3 \cdot xH_2O + (C_6H_5)_3P \xrightarrow[\substack{CH_3OCH_2CH_2OH \\ 70°, 8 \text{ hr}}]{CO, 60 \text{ psi}} OsCl_2(CO)_2[P(C_6H_5)_3]_2 \quad (6)$$
very high yield

Considerable difficulty was at first experienced in reducing these osmium(II) complexes to the required osmium(0) complex, Os(CO)$_3$[P(C$_6$H$_5$)$_3$]$_2$ (B). The mild conditions (zinc in dimethylformamide at 80°) sufficient to effect reduction of ruthenium(II) to ruthenium(0) were not successful in the case of osmium. Longer reaction times using these conditions proved equally ineffective. However, when the temperature of the dimethylformamide was increased to 140°, the reduction proceeded in very high yield (eq 7).

$$\text{A} \xrightarrow[\substack{140°, CO \\ 60 \text{ psi} \\ 12 \text{ hr}}]{Zn, DMF} \text{B} \quad (7)$$

A: γ_{CO} 2040, 1975 cm^{-1} B: γ_{CO} 1890 cm^{-1}
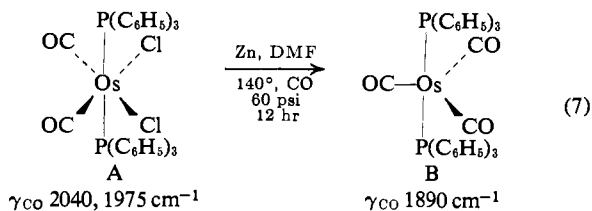
Product B was a colorless crystalline solid, soluble in tetrahydrofuran, dichloromethane, chloroform, and benzene, but insoluble in ethanol and methanol. Its infrared spectrum revealed a single very strong absorption at 1890 cm^{-1} lending to the conclusion that its stereochemistry is that of a trigonal bipyramid with the phosphine ligands trans and the carbonyl groups occupying the equatorial plane. A molecular weight measurement (osmometrically in benzene) confirmed that the compound was monomeric.

A tetrahydrofuran solution of the complex reacted readily with aqueous hydrogen acids, HX, to yield the osmium(II) complexes, OsX$_2$(CO)$_2$[P(C$_6$H$_5$)$_3$]$_2$.

$$Os(CO)_3[P(C_6H_5)_3]_2 + 2HX \longrightarrow$$
$$OsX_2(CO)_2[P(C_6H_5)_3]_2 + H_2 + CO \quad (8)$$
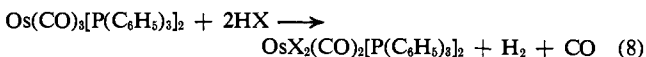
Protonation of other d^8 complexes in strong acids is well known. For example, Wilkinson[31,32] has shown that Fe(CO)$_5$, Fe(CO)$_4$P(C$_6$H$_5$)$_3$, Fe(CO)$_3$[P(C$_6$H$_5$)$_3$]$_2$, Fe(CO)$_4$AsP(C$_6$H$_5$)$_3$, and Fe(CO)$_3$As[P(C$_6$H$_5$)$_3$]$_2$ are protonated in 98% sulfuric acid as evidenced by the proton magnetic resonance signals observed at high fields. This same protonation has been invoked to explain carbonyl exchange rates of iron carbonyl complexes in the presence of strong acids.[33] Stable hydrides

cannot be isolated from these solutions. However, Malatesta[34] has shown that the five-coordinate iridium(I) hydride, Ir(CO)H[P(C$_6$H$_5$)$_3$]$_3$, reacts with perchloric acid to yield the stable compound {Ir(CO)H$_2$-[P(C$_6$H$_5$)$_3$]$_3$}ClO$_4$.[35]

Since the stereochemistry of both the osmium(0) and the resulting osmium(II) complexes are known,[28] a very reasonable mechanism for the reaction with strong acids may be put forward, involving protonation as a first step (eq 9).

$$\text{B} \xrightarrow{H^+} \text{C} \quad (9)$$
$$\text{C} \xrightarrow{X^- (-CO)} \text{D}$$
$$\text{D} \xrightarrow[-H_2]{HX} \text{OsX}_2(\text{CO})_2[\text{P(C}_6\text{H}_5)_3]_2$$

Initial addition of the proton yields an intermediate hydride, C. The formal oxidation to an octahedral, d^6, osmium(II) complex is carried out in this step. Although the hydride ligand has been demonstrated to have a marked trans effect, it is almost certainly not as large as that of a carbonyl group and hence the anion X$^-$ will enter cis to the hydride in intermediate C, displacing one of the labilized carbonyl groups (marked by an asterisk). Further reaction with the acid results in the cleavage of the hydride bond in D with retention of configuration to form the observed product, OsX$_2$-(CO)$_2$[P(C$_6$H$_5$)$_3$]$_2$.

Further support for this scheme may be found in the action of other electrophiles such as bromine (eq 10) and mercury(II) halides on the osmium(0) complex, B.

Solutions of the osmium(0) complex, B, readily decolorize 1 equiv of bromine or iodine. Experiments using a gas buret revealed that carbon monoxide was not evolved in these reactions. The crystalline solids isolated from these solutions analyzed as 1:1 adducts of Os(CO)$_3$[P(C$_6$H$_5$)$_3$]$_2$ and halogen and are formulated as ionic derivatives of osmium(II), E (eq 10), with 2 equiv of iodine a triiodide salt is formed. All of these complexes are quite soluble in polar solvents, as would be expected for ionic compounds, and conductivity measurements made on dilute nitrobenzene solutions confirm that they are 1:1 electrolytes (Table I).

If solutions of these ionic complexes, E, are heated at 60° for several hours, a slow displacement of carbon monoxide occurs to yield the nonionic complexes, OsX$_2$(CO)$_2$[P(C$_6$H$_5$)$_3$]$_2$, identical with those prepared using hydrogen halides. Since these compounds are known to have trans phosphine ligands as does B, it is

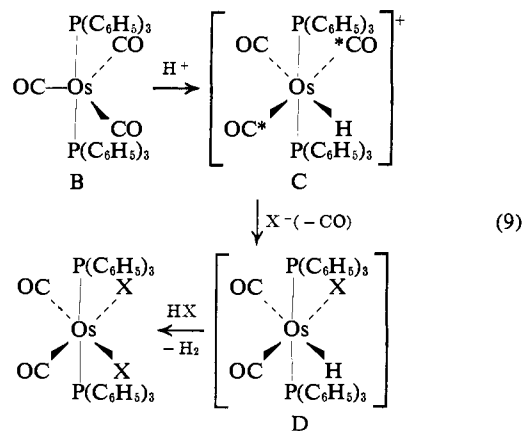(31) A. Davison and G. Wilkinson, Proc. Chem. Soc., 356 (1960).
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(34) L. Malatesta, M. Angoletta, and G. Caylio, VIIIth International Conference on Coordination Chemistry, Vienna, 1964, Abstracts, p 210.
(35) As further evidence of intermediate hydride formation, a stable hydride [Os(CO)$_3$H[P(C$_6$H$_5$)$_3$]$_2$]$^+$[PF$_6$]$^-$ has been isolated using hexafluorophosphoric acid. This and other related compounds will be reported at a later date.

Table I. Molar Conductivities in Nitrobenzene

Compound	$c \times 10^3$ mole l.$^{-1}$	Λ, ohm^{-1} cm^2 mole^{-1} (25°)
{OsBr(CO)$_3$[P(C$_6$H$_5$)$_3$]$_2$}Br	1.12	23.0
{OsI(CO)$_3$[P(C$_6$H$_5$)$_3$]$_2$}I	1.08	22.6
{OsI(CO)$_3$[P(C$_6$H$_5$)$_3$]$_2$}I$_3$	1.21	25.3

reasonable to assume that the ionic compounds, E, have this arrangement also.

$$X^- = Br^-, I^-, I_3^-$$
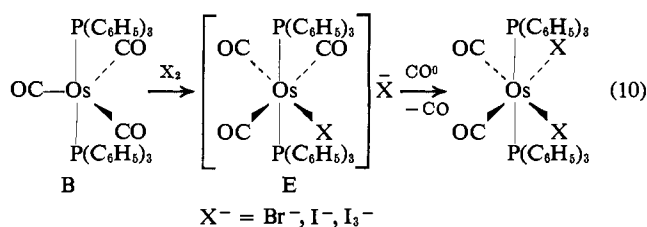
Again the anion X$^-$ enters *cis* to the other X because of the *trans*-directing effect of the CO group. The infrared spectra of the ionic complexes E (Table II) show three carbonyl absorptions. It is notable that these bands are shifted to higher wavenumber consistent with the presence of a positive charge on the central osmium atom.

Table II. Infrared Spectra of Osmium Complexes[a,b]

Compound	γ_{CO}, cm^{-1}		
Os(CO)$_3$[P(C$_6$H$_5$)$_3$]$_2$	1890		
OsCl$_2$(CO)$_2$[P(C$_6$H$_5$)$_3$]$_2$	2040	1975	
OsBr$_2$(CO)$_2$[P(C$_6$H$_5$)$_3$]$_2$	2035	1970	
OsI$_2$(CO)$_2$[P(C$_6$H$_5$)$_3$]$_2$	2035	1970	
{OsBr(CO)$_3$[P(C$_6$H$_5$)$_3$]$_2$}Br	2140	2065	2040
{OsI(CO)$_3$[P(C$_6$H$_5$)$_3$]$_2$}I	2135	2060	2040
{OsI(CO)$_3$[P(C$_6$H$_5$)$_3$]$_2$}I$_3$	2135	2060	2040

[a] Measured as KBr pellets. [b] All carbonyl absorptions are very strong.

It is interesting to contrast the behavior of Os(CO)$_3$-[P(C$_6$H$_5$)$_2$]$_2$ with Fe(CO)$_3$[P(C$_6$H$_5$)$_3$]$_2$ upon reaction with halogens. Hieber[36] has reported that the iron compound undergoes oxidation with loss of a phosphine ligand rather than a carbonyl ligand. This may be a reflection of relatively weaker bonding between the phosphine and iron(II).

The carbonyl absorptions for the neutral compounds listed in Table II are at slightly lower wavenumber than their ruthenium analogs, indicating that the carbon monoxide is more strongly bound in osmium than ruthenium. This is also implied by the failure to isolate intermediate ionic compounds E during the oxidation of ruthenium(0) complexes by halogens.[3]

Although OsX$_2$(CO)$_2$[P(C$_6$H$_5$)$_3$]$_2$ (X = Cl, Br) complexes have similar X-ray powder photographs, none of the osmium complexes exhibits patterns similar to their ruthenium analogs.

We consider the oxidation reactions of the osmium(0) complex discussed above to be specific examples of a general class of reactions in which a metal complex of low oxidation state acts as a base. Further examples

(36) W. Hieber and J. Muschi, *Chem. Ber.*, **98**, 3921 (1965).

of this behavior are provided by platinum(0)[37] and tungsten(0)[38] complexes. It is reasonable to expect that several types of Lewis acids such as diazonium cations, acid chlorides, tin tetrachloride, and antimony pentachloride may react with certain of these compounds. It should be noted that these formal oxidations occur without discrete electron transfer.

The striking ability of four-coordinate d^8 complexes such as Vaska's iridium(I) complex to react with nonpolar bonds will probably not be found with these five-coordinate ruthenium(0) and osmium(0) complexes unless conditions are such as to facilitate the loss of one ligand. This can be brought about by irradiation or labilizing one of the groups by utilizing the *trans* effect and/or steric effects.

Experimental Section

General. Osmium trichloride (hydrated 62% Os) was obtained from Engelhard Industries, Newark, N. J. Osmium tetroxide was Mallinckrodt analytical reagent. Ammonium hexachloroosmate and hexabromoosmate were prepared by the method of Dwyer and Hogarth,[27] the only modification being to add the fractured ampoule of osmium tetroxide *to* acid solutions rather than the reverse.

Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Conductivity measurements were made with an Industrial Instruments conductivity bridge, Type RC16B2, in conjunction with a dip type cell. X-Ray photographs were taken with a Philips 11.48-cm diameter camera using Cu Kα radiation. Exposure times were approximately 5 hr using Ilford X-ray film Type G.

All reactions under carbon monoxide were carried out in a Fischer–Porter glass pressure vessel of 750-ml capacity.

Infrared spectra were measured on a Perkin-Elmer grating instrument, Model 237B. All samples were in the form of KBr pellets.

Preparation of OsCl$_2$(CO)$_2$[P(C$_6$H$_5$)$_3$]$_2$. (a) **From OsCl$_3$·xH$_2$O.** OsCl$_3$·xH$_2$O (1 g) and of triphenylphosphine (2 g) were suspended in 40 ml of 2-methoxyethanol in a Fischer–Porter pressure vessel. Carbon monoxide was admitted, and after flushing several times the bottle was pressured to 60 psi. The solution was heated by partially immersing the bottle in a silicone oil bath at 80° and the contents were stirred magnetically. The vessel was repressured whenever necessary to maintain the initial pressure. After approximately 8 hr the initially dark colored mixture had become a thick suspension of colorless crystals. After cooling and venting, the product was filtered off and washed with cold ethanol. Recrystallization from chloroform–ethanol mixtures afforded minute colorless needles (2.5 g or 90% yield). The compound was soluble in most organic solvents and had two characteristic, strong, infrared bands at 2040 and 1975 cm^{-1}.

Anal. Calcd for C$_{38}$H$_{30}$Cl$_2$O$_2$OsP$_2$: C, 54.23; H, 3.59; Cl, 8.42; P, 7.36. Found: C, 54.26; H, 3.74; Cl, 8.41; P, 7.20.

If the preparation is carried out by attempting to carbonylate the osmium trichloride alone (at various temperatures and for various times), followed by addition of triphenylphosphine, only very small yields of the desired compound are obtained.

(b) **From OsCl$_2$(CO)[P(C$_6$H$_5$)$_3$]$_3$.** The required starting material was obtained from OsHCl(CO)[P(C$_6$H$_5$)$_3$] by treatment with HCl. This is most conveniently done by carrying out the preparation as described by Vaska until the solid hydride has separated, and then adding several drops of concentrated HCl and heating and stirring for 1 hr. The white crystalline product has no osmium hydride band in the infrared but has a single, strong, carbonyl absorption at 1950 cm^{-1}. This compound was not otherwise characterized but used immediately in the next step. A solution containing 1 g of OsCl$_2$(CO)[P(C$_6$H$_5$)$_3$]$_3$ dissolved in 30 ml of dimethylformamide was placed in the pressure bottle, pressured to 60 psi with carbon monoxide, stirred, and heated at 80° for 12 hr. After cooling and venting the solution was stripped to dryness under reduced pressure

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(38) M. C. Ganorkar and M. H. B. Stiddard, *Chem. Commun.*, 22 (1965).

and the resulting solid recrystallized, yielding 0.7 g of $OsCl_2(CO)_2$-$[P(C_6H_5)_3]_2$. The product was shown to be identical with that described above by its infrared spectrum and X-ray powder photograph.

Preparation of $OsBr_2(CO)_2[P(C_6H_5)_3]_2$. $(NH_4)_2OsBr_6$ (1 g) was suspended in 60 ml of 2-methoxyethanol in the pressure bottle. After stirring and heating at 80° under 60 psi of CO for a few minutes, the osmium salt dissolved to give a deep red solution. This solution slowly became lighter, and after approximately 4 hr a perfectly clear, pale yellow solution was obtained. The bottle was vented and 1 g of triphenylphosphine was added and then the solution was heated at 80° and stirred for an additional 20 min. Steady evolution of carbon monoxide was observed during this period and the solution became quite colorless. Cooling this solution in an ice bath produced 1.1 g (85% yield) of colorless, crystalline $OsBr_2(CO)_2[P(C_6H_5)_3]_2$. The compound may be recrystallized from ethanol-chloroform as colorless needles. The infrared spectrum has bands at 2035 and 1970 cm⁻¹.

Anal. Calcd for $C_{38}H_{30}Br_2O_2OsP_2$: C, 49.05; H, 3.25; Br, 17.17; P, 6.66; mol wt, 931. Found: C, 49.46; H, 3.42; Br, 17.00; P, 6.57; mol wt, 938 (determined osmometrically in benzene).

Preparation of $Os(CO)_3[P(C_6H_5)_3]_2$. A solution containing 2 g of $OsCl_2(CO)_2[P(C_6H_5)_3]_2$ ($OsBr_2(CO)_2[P(C_6H_5)_3]_2$ may be used with equal success) in 40 ml of dimethylformamide was placed in the pressure bottle together with approximately 5 g of granulated zinc (30 mesh). The solution was heated to 140° under a minimum pressure of 60 psi of CO for 12 to 16 hr. The solution at this stage was not clear but had much of the desired osmium(0) complex suspended in it. After venting, the dimethylformamide slurry was decanted from the zinc granules. The zinc was then washed with a little hot tetrahydrofuran and the washings were added to the dimethylformamide slurry. This solution was then stripped to dryness under reduced pressure. The resulting sticky solid was extracted with 400 ml of boiling tetrahydrofuran. After filtration, the clear, almost colorless tetrahydrofuran extract was reduced in volume to 50 ml, and 200 ml of ethanol was added. Crystals (1.75 g, 92% yield) of $Os(CO)_3[P(C_6H_5)_3]_2$ were rapidly deposited. The compound was soluble in hot benzene, tetrahydrofuran, chloroform, and methylene chloride; insoluble in ethanol, methanol, and hexane. Its infrared spectrum showed a single strong carbonyl absorption at 1840 cm⁻¹.

Anal. Calcd for $C_{39}H_{30}O_3OsP_2$: C, 58.64; H, 3.79; Os, 23.81; P, 7.76; mol wt, 799. Found: C, 58.78; H, 3.70; Os, 23.70; P, 7.76; mol wt, 809.

Reaction of $Os(CO)_3[P(C_6H_5)_3]_2$ with Hydrogen Halides. (a) Hydrogen Chloride. To a solution of 400 mg of $Os(CO)_3[P(C_6H_5)_3]_2$ in 400 ml of warm tetrahydrofuran was added several drops of concentrated aqueous hydrochloric acid. The solution was evaporated on a water bath until the volume was reduced to about 10 ml. Addition of ethanol and cooling resulted in the crystallization of $OsCl_2(CO)_2[P(C_6H_5)_3]_2$, yield 400 mg. The material was identified by comparison of its infrared spectrum and X-ray powder photograph with those of an authentic sample of $OsCl_2(CO)_2[P(C_6H_5)_3]_2$.

(b) Hydrogen Bromide. In exactly the same manner using 48% aqueous hydrobromic acid, $OsBr_2(CO)_2[P(C_6H_5)_3]_2$ was isolated and identified.

(c) Hydrogen Iodide. Following the above procedure, but using 47–50% aqueous hydriodic acid, 400 mg (80% yield) of pale yellow crystalline $OsI_2(CO)_2[P(C_6H_5)_3]_2$ was isolated. Its infrared spectrum showed bands at 2035 and 1970 cm⁻¹. The compound was quite soluble in most organic solvents and crystallized from warm ethanol.

Anal. Calcd for $C_{38}H_{30}I_2O_2OsP_2$: C, 44.53; H, 2.95; P, 6.05. Found: C, 44.65; H, 3.18; P, 6.12.

Reaction of $Os(CO)_3[P(C_6H_5)_3]_2$ with Halogens. (a) Bromine. In a gas buret system 400 mg of $Os(CO)_3[P(C_6H_5)_3]_2$ dissolved in 30 ml of chlorobenzene was mixed with 80 mg of bromine dissolved in 20 ml of chlorobenzene. No evolution of gas was observed although the bromine color was instantly discharged. Very pale yellow crystals of $\{OsBr(CO)_3[P(C_6H_5)_3]_2\}Br$ were deposited (400 mg). The compound was characterized by conductivity measurement in nitrobenzene (Table I) and by its infrared spectrum (Table II).

Anal. Calcd for $C_{39}H_{30}Br_2O_3OsP_2$: C, 48.84; H, 3.15; Br, 16.67. Found: C, 48.78; H, 2.95; Br, 16.51.

A solution of 200 mg of $\{OsBr(CO)_3[P(C_6H_5)_3]_2\}Br$ in 25 ml of chloroform was kept at 60° for 1 hr. Upon reducing the volume to 10 ml and adding 30 ml of ethanol colorless crystals of $OsBr_2(CO)_2[P(C_6H_5)_3]_2$ were deposited. The product was identified by comparing its infrared spectrum and X-ray photographs with those of an authentic sample.

(b) Iodine. A solution of 400 mg of $Os(CO)_3[P(C_6H_5)_3]_2$ in 20 ml of methylene chloride was added to 130 mg of iodine dissolved in 20 ml of the same solvent. The iodine color was immediately discharged. Since the ionic product, $\{OsI(CO)_3[P(C_6H_5)_3]_2\}I$, is insoluble in the nonpolar solvent, benzene, this product was conveniently removed from the methylene chloride solution by addition of 50 ml of benzene and removal of methylene chloride under reduced pressure. Pale yellow crystals of $\{OsI(CO)_3[P(C_6H_5)_3]_2\}I$ (450 mg) slowly appeared. This crystallization procedure has the advantage of yielding a product free of $OsI_2(CO)_2[P(C_6H_5)_3]_2$ which may also be formed, since this compound is very soluble in both methylene chloride and benzene. The ionic product was characterized by conductivity measurement (Table I) and its infrared spectrum (Table II).

Anal. Calcd for $C_{39}H_{30}I_2O_3OsP_2$: C, 44.47; H, 2.87; I, 24.10. Found: C, 44.80; H, 2.72; I, 24.17.

By following the above procedure but using 2 equiv of iodine, a red-brown crystalline triiodide may be isolated. This has a carbonyl pattern in the infrared spectrum identical with $\{OsI(CO)_3[P(C_6H_5)_3]_2\}I$ (see Table II). The molar conductivity is listed in Table I.

Anal. Calcd for $C_{39}H_{30}I_4O_3OsP_2$: C, 35.87; H, 2.32; I, 38.87. Found: C, 35.71; H, 2.55; I, 38.45.

If either of the above two ionic complexes is dissolved in chloroform and kept at 60° for 1 hr, the only product in quantitative yield is $OsI_2(CO)_2[P(C_6H_5)_3]_2$, identified by comparison of its infrared spectrum and X-ray powder photograph with those of an authentic sample.