Hydridocarbonyl Complexes of Osmium by Reaction with Alcohols[1]

BY L. VASKA

The reactions of osmium(IV) halides with triphenylphosphine or triphenylarsine in alcohols lead to hydrido-carbonyl complexes of bivalent osmium, $[OsHX(CO)L_3]$ (X = Cl, Br; L = Ph₃P, Ph₃As), the subjects of this first detailed report on the interaction of transition metal compounds with alcohols and related solvents. Formulation of these unexpected complexes is suggested by the results of infrared spectral, magnetic, molecular weight, and conductivity measurements, and complete elemental analysis. Tracer studies with deuterated and radiocarbon alcohols demonstrate the presence of the (analytically undetectable) hydride and carbonyl ligands and indicate that they originate from the solvent. The air-stable crystalline compounds are best synthesized by reaction with glycols at elevated temperatures (>120°), but one derivative, $[OsHBr(CO)(Ph_3P)_3]$, has been obtained also at 25°, demonstrating a strong tendency of osmium to dehydrogenate and decarbonylate alcohols and related species.

Introduction

When this research was initiated some six years ago, one of the objectives was to apply certain methods and conditions of synthesis which appeared to have been overlooked or neglected in preparative coordination chemistry: it was intended to study the effects of high-boiling solvents such as glycols and glycol ethers, and solvent mixtures of two or more components with different solvent characteristics. The immediate aim was to stabilize lower oxidation states of osmium by applying potentially reducing conditions of high-boiling alcohols and using as ligands tertiary phosphines which were reported to be responsible for arresting metal atoms even in their zerovalent state.[2] Osmium offered itself as a challenging element for these studies in view of the multiplicity of its possible oxidation states and because it had received relatively little attention (e.g., no osmium complexes with phosphines were known at that time (1957)).

This endeavor has proceeded through a number of perplexing phases. The first intriguing result was the discovery of monohalogeno complexes of osmium which were formulated as containing the univalent metal, $[OsXL_3]$ (X = Cl, Br; L = Ph₃P, Ph₃As).[3a] This interpretation was based chiefly on analytical data (see Table II). In the absence of direct evidence to the contrary, decomposition of solvent alcohol *and* coordination of its (analytically undetectable) fragments were not considered, following a hitherto accepted assumption.

Extension of these investigations to include other transition metals[4-7] and related work by Chatt and Shaw[8] suggested, however, that the presumably osmium(I) complexes might also contain hydride and carbonyl groups, $[OsHX(CO)L_3]$. Subsequent tracer studies indeed confirmed the presence of these ligands.[3b] These observations gave the impetus for further development and exploitation of the new synthetic methods. To date, the study of the reactions of transition metal halides with group V-A ligands (triphenyl-

phosphine has been used most extensively) in alcohols and related solvents has shown that five principal types of interactions may occur with the reaction medium, as deduced from the composition of the resulting metal complexes. The following *types* of compounds have been obtained (examples in parenthesis): (1) **solvates** ($[RuCl_3(Ph_3P)_2(CH_3OH)]$),[7] (2) **alkoxides** ($[ReOBr_2(Ph_3P)_2(OCH_2CH_2OCH_3)]$),[9] (3) **hydrides** ($[IrHCl_2(Ph_3P)_3]$),[4,6] (4) **carbonyls** ($[IrCl(CO)(Ph_3P)_2]$),[5] and (5) **hydridocarbonyls**, the subjects of the present article. As the first detailed paper[10] on these studies, this communication serves also as an introduction, and it thus requires an elaboration of the preparative procedures and of the evidence for the presence and origin of the hydride and carbonyl ligands (in $[OsHX(CO)L_3]$).

Results and Discussion

Methods of Synthesis.—The bivalent osmium compounds are synthesized from hexahaloosmate(IV), $(NH_4)_2OsX_6$ (X = Cl, Br), triphenylphosphine or triphenylarsine, and an alcohol as reacting solvent. The ranges of reaction conditions leading to these complexes are summarized in Table I, to which the following discussion refers.

Over eighty individual preparations have been carried out. Most of these were conducted in vessels open to the atmosphere. The hydridocarbonyl complexes in solution are sensitive to oxygen, but the negligible solubility of oxygen at the temperatures employed virtually isolates the compounds while they are thus dissolved. This situation also prevents oxidation of Ph₃P or Ph₃As. A liberal excess of these ligands (>5 moles per Os) favors both purity and yield of the products.

Because of their low solubility (at ordinary temperatures) and their reactivity in solution, the compounds cannot be conveniently recrystallized. It is thus essential that they result in pure crystalline form (unreactive state) *in situ*. The preparation of $[OsHCl(CO)(Ph_3P)_3]$ presents no special problems: the compound crystallizes as its concentration increases at the temperature of the reaction, or, a rapid precipitation can be effected by quenching, and there is no significant discrimination between the various reacting solvents. The bromo derivative, $[OsHBr(CO)(Ph_3P)_3]$, on the other hand, affords *pure* specimens only by reaction with 2-methoxyethanol, and a peculiar "induction

(1) Interactions of Transition Metal Compounds with Alcohols and Related Solvents. I.

(2) (a) L. Malatesta and C. Cariello, *J. Inorg. Nucl. Chem.*, **8**, 561 (1958), and references quoted; (b) J. Chatt and H. R. Watson, *J. Chem. Soc.*, 2545 (1962) [this article describes and cites later developments on the subject [.

(3) For preliminary communications, see (a) L. Vaska, *Z. Naturforsch.*, **15b**, 56 (1960); (b) L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, **83**, 1262 (1961).

(4) L. Vaska, *ibid.*, **83**, 756 (1961).

(5) L. Vaska and J. W. DiLuzio, *ibid.*, **83**, 2784 (1961).

(6) L. Vaska and J. W. DiLuzio, *ibid.*, **84**, 4989 (1962).

(7) L. Vaska, *Chem. Ind.* (London), 1402 (1961).

(8) J. Chatt and B. L. Shaw, *ibid.*, 931 (1960).

(9) Results to be published from this laboratory.

(10) Ref. 3-7 represent short reports relating to this work.

TABLE I

PREPARATION OF HYDRIDOCARBONYL COMPLEXES BY REACTION WITH ALCOHOLS

X	mmoles	L	Moles/Os	Reacting solvent[a] (ml.)	Temp., °C.	Time, hr.	Compound[b]	Yield, %	Comments[c]
Cl	0.46–11.4	P	4–16	M. cel. (150–1000)	124	0.5–9	[OsHCl(CO)P₃]	54–95	Good method
Cl	1.1	P	12	E. cel. (200) + H₂O (50)	134	2	[OsHCl(CO)P₃]	47	
Cl	0.7	P	12	B. cel. (80)	165	1	[OsHCl(CO)P₃]	74	
Cl	0.05–1.2	P	4–16	Glyc. (1–50) + EtOH (0–60)	100–190	0.1–1	[OsHCl(CO)P₃]	5–95	
Cl	12	P	12	DEGME (500) + H₂O (200)	190	4.5	[OsHCl(CO)P₃]	92	Best method
Cl	1.1	P	10	Diglyc. (40)	240	47	[OsHCl(CO)P₃]		Detected in mixture
Br	0.43	P	5	Glyc. (30) + EtOH (50)	25	15 days	[OsHBr(CO)P₃]	5	
Br	0.43	P	11	MeOH (50)	25	16 days	[OsHBr(CO)P₃]		Detected in mixture
Br	0.43	P	8	MeOH (60)	64	42	[OsHBr(CO)P₃]		Detected in mixture
Br	0.33–1.46	P	7–12	M. cel. (80–250)	{ 25 ‹ 124	3–15 days 1–3	[OsHBr(CO)P₃]	26–98	Best method
Br	0.045–0.97	P	8–12	Glyc. (2–50) + EtOH (0–20)	100–190	0.3–18	[OsHBr(CO)P₃]	30–66	Mostly impure
Cl	0.64	As	7	M. cel. (400)	124	4	[OsHCl(CO)As₃]		Detected in mixture
Cl	0.59–1.13	As	7	Glyc. (60–150) + EtOH (50–250)	90–140	1	[OsHCl(CO)As₃]	17–82	Best method
Cl	3.4	As	12	DEGME (300) + H₂O (100)	110–190	1.5	[OsHCl(CO)As₃]	30	Impure
Br	0.38–0.7	As	10	M. cel. (600)	124	2–4	[OsHBr(CO)As₃]		Detected in mixture
Br	0.35–1.5	As	4–10	Glyc. (30–150) + EtOH (50–250)	110–140	1–2	[OsHBr(CO)As₃]	20–70	Best method

[a] MeOH = methanol; EtOH = ethanol; Glyc. = ethylene glycol; M. cel. = 2-methoxyethanol (Methyl Cellosolve); E. cel. = 2-ethoxyethanol (Ethyl Cellosolve); B. cel. = 2-butoxyethanol (Butyl Cellosolve); Diglyc. = diethylene glycol; DEGME = 2-(β-methoxyethoxy)ethanol (diethylene glycol monomethyl ether). [b] P = Ph₃P, As = Ph₃As. [c] All products were characterized by infrared spectra (Fig. 1, Tables IV and V) which was the principal method of detecting and evaluating the amount of the hydridocarbonyl complexes in mixtures. In most cases, X-ray powder patterns and melting points were also used in estimating the nature of the products.

period" at 25° has been found to be necessary prior to heating.

The preparation of triphenylarsine derivatives appears to require that the temperature *and* the environment of the reactants be varied as the over-all reaction proceeds. The conventional method of heating the reaction mixture under reflux does not allow for such variations which, however, may be accomplished simply by using a reaction medium of two or more components with different boiling temperatures and solvent properties. Various mixtures of ethanol (b.p. 78°) and ethylene glycol (b.p. 196°) have proved useful in solving many synthetic problems encountered in this series of investigations. For example, attempted preparation of [OsHBr(CO)(Ph₃As)₃] by reflux methods gave intractable mixtures, but the compound forms in reasonable purity and yield when (NH₄)₂OsBr₆ and Ph₃As are heated in a 3:2 mixture of the previously mentioned solvents. The boiling temperature is raised gradually to 140° (by allowing ethanol to evaporate) at which point the high concentration of ethylene glycol—and of the Os complex—causes the latter to precipitate. (A further increase in temperature redissolves the product and initiates its decomposition.)

A number of experiments with the reactants given in Table I have been carried out also at room temperature.[7,9] One of the present compounds, [OsHBr(CO)(Ph₃P)₃], was observed to form at these mild conditions. The corresponding chloro analog has not been prepared at this temperature. These observations relate to the solubility characteristics of the reactants and intermediates, representing an important factor in setting the path for the interactions with alcohols. (NH₄)₂OsCl₆ is virtually inert near 25° in alcoholic solvents because of its very low solubility. Partial dissolution may be effected by using water as a solvent component, but this apparently suppresses the solubility of an intermediate complex (see Reaction Course) so that no reaction with alcohols is detected within reasonable times.

Elemental Composition and Some Properties. Chemical Analysis.—Complete elemental analyses of the complexes are given in Table II. The data represent average values of determinations of elements in two to four different preparations of each compound. The samples were considered to be pure according to their melting points, visual appearance, and infrared spectra (Tables III, IV, and V).

TABLE II

ELEMENTAL ANALYSIS[a]

	Os	X[b]	L[c]	C	H	O
Found (av. 4 samples)	18.4	3.4	9.05	63.9	4.6	1.6
Calcd. for [OsClP₃]	18.8	3.5	9.2	64.05	4.5	
Calcd. for [OsHCl(CO)P₃]	18.3	3.4	8.9	63.4	4.45	1.5
Found (av. 3 samples)	17.9	7.3	8.5	61.0	4.4	1.65
Calcd. for [OsBrP₃]	18.0	7.6	8.8	61.4	4.3	
Calcd. for [OsHBr(CO)P₃]	17.5	7.4	8.6	60.8	4.3	1.5
Found (av. 2 samples)	16.5	3.25	19.0	57.15	4.0	1.9
Calcd. for [OsClAs₃]	16.6	3.1	19.6	56.7	4.0	
Calcd. for [OsHCl(CO)As₃]	16.2	3.05	19.15	56.3	3.95	1.4
Found (av. 2 samples)	15.9	6.7	18.6	54.3	3.8	1.9
Calcd. for [OsBrAs₃]	16.0	6.7	18.9	54.6	3.8	
Calcd. for [OsHBr(CO)As₃]	15.6	6.6	18.45	54.2	3.8	1.3

[a] P = (C₆H₅)₃P; As = (C₆H₅)₃As. [b] Cl or Br. [c] P or As.

When the compounds were first discovered, an examination of the analytical data for Os, halogen, P or As, C, and H did not suggest the presence of an additional element. When the original formulation was reconsidered on the basis of infrared spectral evidence, oxygen analyses were obtained and other elements were redetermined in order to ascertain the evidence from chemical analysis. In Table II the total results are compared with the quantities computed for the two elemental compositions. It is seen that there is good agreement with the calculated values for the hydridocarbonyl complexes (particularly for the phosphine derivatives), but that only the oxygen analyses discriminate between the two sets of formulas.

Physical Properties.—Table III summarizes some physical properties of the complexes. The oxidative and thermal stabilities of the crystalline compounds are remarkable. Pure samples of the phosphine complexes have remained unchanged in air (25°) for several years (estimates based on visual and infrared spectral evidence). Impure preparations (slightly colored samples), however, darken slowly within months or years; so do

<div align="center">

TABLE III

PHYSICAL PROPERTIES

</div>

Compound[a]	Color	M.p., °C. dec.[b] In air	M.p., °C. dec.[b] In vacuo[c]	Molecular weight Calcd.	Molecular weight Found	Molecular weight Solvent	Molar conductance[d] Ohm⁻¹	Molar conductance[d] Solvent	Magnetic suscepti-bility (10⁶), 25° χ_g	Magnetic suscepti-bility (10⁶), 25° χ_A[e]
[OsHCl(CO)P₃]	Colorless	179	277	1042	990	CHCl₃	0.3	PhNO₂	−0.54	−30
[OsHBr(CO)P₃]	Colorless	172	276	1086	1230	CHCl₃	0.3	PhNO₂	−0.53	−35
							0.2	Me₂CO		
[OsHCl(CO)As₃]	Colorless	200	247	1173	960	CHCl₃	0.1	PhNO₂	−0.47	14
							0.4	Me₂CO		
[OsHBr(CO)As₃]	Tan	195	243	1218	523	C₆H₆	0.8	PhNO₂	−0.44	39
							6	Me₂CO		

[a] P = Ph₃P; As = Ph₃As. [b] Melting points are uncorrected. [c] 10^{-2}–10^{-4} mm. [d] At 25°. Concentration range 1–4 × 10^{-4} M. [e] Gram-atomic susceptibility of osmium (in c.g.s.), i.e., corrected for the diamagnetism of the ligands using diamagnetic constants listed in P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience, New York, N. Y., 1956, pp. 78, 92, 93.

the arsine derivatives. Decomposition on melting in air probably includes a reaction with oxygen. Thermal decomposition *in vacuo* is accompanied by dissociation (and sublimation) of Ph₃P or Ph₃As.

The compounds are insoluble in water, alcohols, and aliphatic hydrocarbons, and only slightly soluble in some other common organic solvents (e.g., CHCl₃, C₆H₆, and acetone)[11] in which they slowly react (in air) to yield green solutions and ultimately (after days or weeks) gray-black precipitates. These products contain two triphenylphosphines per osmium.[9] These characteristics of the hydridocarbonyl complexes have limited those studies of their dissolved physical properties which require appreciable solubility for observation.

Thus, we have been unable to detect (in CHCl₃ or C₆H₆) a high-field proton resonance (in the range τ 20–45) which is often diagnostic for the presence of a metal–hydrogen bond.[12] Molecular weight data are rather approximate; they do, however, suggest that in solution the compounds (initially) exist as monomers except [OsHBr(CO)(Ph₃As)₃] which appears to dissociate readily. Conductivity measurements, on the other hand, require very low concentrations, and these experiments indicate that the complexes are nonelectrolytes. The minute values of molar conductances remain essentially constant over periods of hours or days, showing that decomposition in solution (see above) does not involve ionization. These observations suggest that the osmium–hydrogen linkage is covalent and remains so under the influence of polarizing solvents.

The crystals of the complexes are diamagnetic.[13] The susceptibilities are independent of the magnetic field and temperature (76–500°K.).[14] No reliable results were obtained from measurements in solution, but in one instance, [OsHBr(CO)(Ph₃As)₃] in CHCl₃ (10^{-2} M), it was established that the dissolved species was diamagnetic. The diamagnetism suggests the presence of bivalent osmium with a spin-paired d⁶ nonbonding configuration. A preliminary study of the crystal structure of [OsHBr(CO)(Ph₃P)₃] has revealed an approximately octahedral environment for the

(11) The solubility of the compounds appears to increase somewhat in the order the compounds are listed in Table III, i.e., on descending the group.

(12) For recent reviews on transition metal hydride complexes, see (a) J. Chatt, Proc. Chem. Soc., 318 (1962); (b) G. Wilkinson, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Company, New York, N. Y., 1961, p. 50; (c) M. L. H. Green, Angew. Chem., 72, 719 (1960).

(13) The small positive values for χ_A of the arsine derivatives have no significance since they result from subtracting large diamagnetic corrections from relatively small molar susceptibility.

(14) Details of the magnetic properties will be reported later.

central atom.[15] These properties imply a hydridic nature for the covalently bonded hydrogen, and this has been substantiated by chemical reactions of the hydridocarbonyl complexes.[9] According to the X-ray diffraction patterns of their crystals, the four compounds (Table III) are isostructural.[16]

Infrared Spectra and Isotopic Studies.—While the properties described in the preceding sections are compatible with the formulation of the compounds as six-coordinated osmium, [OsHX(CO)L₃], these measurements do not directly indicate that the complexes include the hydride and carbonyl groups. Direct evidence for the presence of these ligands has been obtained through the combined use of isotopic atoms and infrared spectral studies. These are detailed below. The infrared spectrum of [OsHCl(CO)(Ph₃P)₃] is shown in Fig. 1; for clarity, the bands derived from triphenyl-
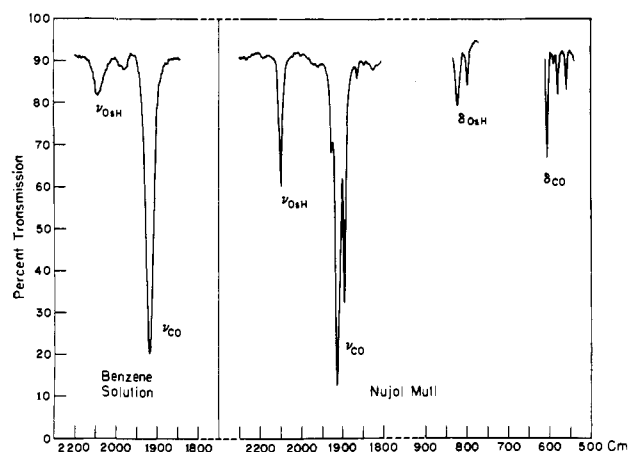

Fig. 1.—Osmium–hydrogen and carbonyl absorptions in the infrared spectrum of [OsHCl(CO)(Ph₃P)₃].

phosphine ligands are omitted.[17] The osmium–hydrogen and the carbonyl vibrational frequencies are recorded in Tables IV and V, respectively.

Osmium–Hydrogen Bond. Its Presence and Vibrational Spectrum.—In order to gain information about the origin of the bands other than those of the co-

(15) P. L. Orioli and L. Vaska, Proc. Chem. Soc., 333 (1962).

(16) The X-ray diffraction data will be published elsewhere.

(17) For practical purposes, the infrared spectrum of free triphenylphosphine (300–5000 cm.⁻¹) is identical with the spectrum of this ligand coordinated to a transition metal, except in the 500 cm.⁻¹ region where P–C (phenyl) absorptions occur [E. Steger and K. Stopperka, Ber., 94, 3023 (1961)]. In the spectrum of the coordinated Ph₃P these bands are split and shifted, and this renders a detection or assignment of new bands difficult in this region. In the higher regions of the spectrum (C–H, C–C, and ring vibrations) certain changes (intensities, splittings, and shifts) are also observed upon coordination, but these are more subtle and not readily revealed by an ordinary instrument (see Experimental). The same is true for triphenylarsine.

TABLE IV

OSMIUM-HYDROGEN AND OSMIUM-DEUTERIUM VIBRATIONAL FREQUENCIES (CM.$^{-1}$)^a

Compound^c	ν_{OsH}	ν_{OsD}	ν_{OsH}/ν_{OsD}^d	δ_{OsH}	δ_{OsD}	$\delta_{OsH}/\delta_{OsD}^d$	C$_6$H$_6$	CH$_2$Cl$_2$
			Spectra of crystals^b				ν_{OsH} in solution	
[OsHCl(CO)P$_3$]	2097	1506	1.393	825, 801	645, 612	1.28, 1.31	2083	2073
[OsHBr(CO)P$_3$]	2100	1508	1.393	827, 796	642, 609	1.29, 1.31	2096	2088
[OsHCl(CO)As$_3$]	2085	..	...	823, 807	...	...	2069	2064
[OsHBr(CO)As$_3$]	2087	..	...	822, 801	...	...	2080	2074

^{a} Relative intensities and the shapes of the spectral bands are evident from Fig. 1. For accuracy of the measurements and the instruments used, see Experimental (see also ref. 28). ^{b} In Nujol (300–5000 cm.$^{-1}$) and halocarbon (1300–5000 cm.$^{-1}$) mulls. ^{c} P = Ph$_3$P; As = Ph$_3$As. ^{d} Calcd., 1.414 (or $\sqrt{2}$).

TABLE V

CARBONYL VIBRATIONAL FREQUENCIES (CM.$^{-1}$)^a IN
[OsHX(CO)L$_3$]

Compound^b	Crystals^{c,d}	ν_{CO} In C$_6$H$_6$	In CHCl$_3$	δ_{CO} Crystals^d	In CH$_2$Cl$_2$	Other bands Crystals^d
[OsHCl(CO)P$_3$]	1912, 1894, 1927	1916	1911	607	606	582, 560
[OsHBr(CO)P$_3$]	1913, 1896, 1930	1922	1915	601	599	580, 558
[OsHCl(CO)As$_3$]	1905, 1888, 1929	1912	1906	605	606	578, 558
[OsHBr(CO)As$_3$]	1906, 1891, 1923	1914	1910	598	600	570, 532

^{a} Relative intensities and the shapes of the spectral bands are evident from Fig. 1. For accuracy of measurements and the instruments used, see Experimental section (see also ref. 28). ^{b} P = Ph$_3$P; As = Ph$_3$As. ^{c} The three bands are listed in the order of decreasing intensities (see Fig. 1), i.e., the principal absorption for each compound is given in the first column. ^{d} Measured in Nujol mulls.

ordinated triphenylphosphine or triphenylarsine[17] in the infrared spectrum (Fig. 1), the compounds were subjected to deuteration by refluxing a suspension of the complex in CH$_3$OD or C$_2$H$_5$OD for several days. Alternatively, the compounds were prepared as indicated in Table I except that D$_2$O was added to the initial reaction mixture containing 2-methoxyethanol or ethylene glycol as the reacting solvent.[18] The products thus obtained (from both types of experiments) gave X-ray diffraction patterns identical with those of authentic samples of [OsHX(CO)L$_3$]. The infrared spectra of the deuterated species showed decreased intensities (ca. 50% of the original values) for the strong and sharp absorption near 2100 cm.$^{-1}$ and the two weaker bands in the 800 cm.$^{-1}$ region. Concurrently, the spectra exhibited three new and lower lying absorptions (near 1510, 640, and 610 cm.$^{-1}$), each of them related to a (different) higher frequency band of decreased intensity by a factor approximating the theoretical value for hydrogen–deuterium isotopic shift, $\sqrt{2}$.

The results thus indicate that the 2100 cm.$^{-1}$ absorption and the doublet near 800 cm.$^{-1}$ are associated with hydrogen motions, and they are assigned to osmium–hydrogen stretching (ν_{OsH}) and bending (δ_{OsH}) vibrations, respectively, by analogy with other hydrido complexes of transition metals. The ν_{MH} of the tertiary phosphine-stabilized metal hydrides has been observed in the range from 1600 to 2250 cm.$^{-1}$, and the δ_{MH} in the 800 cm.$^{-1}$ region.[12a,19]

In the present series of studies,[4–6,9,20,21] with triphenylphosphine as ligand, the ν_{MH} has been found to occur always higher than 1950 cm.$^{-1}$, i.e., in the region

(18) Both types of experiments were carried out in the absence of air and H$_2$O.
(19) D. M. Adams, "Spectroscopy" [Report of the Conference Organized by the Hydrocarbon Research Group of the Institute of Petroleum and held in London, March, 1962[, The Institute of Petroleum, London, 1962, p. 265. [This study deals with solvent effects on the infrared spectra of hydrido complexes in conjunction with their stereochemistry.[
(20) L. Vaska and J. W. DiLuzio, J. Am. Chem. Soc., 84, 679 (1962).
(21) S. S. Bath and L. Vaska, ibid., 85, 3500 (1963).

well separated from vibrations associated with most organic and inorganic compounds. When CO is present concurrently (as in the subjects of this paper), its absorption has been observed at a lower energy than ν_{MH} (Fig. 1 and ref. 5, 20, 21).[22] The shape and the relative intensity of the ν_{OsH} band in the spectrum of the crystals, shown in Fig. 1, are typical of most of the metal hydride complexes discovered in this laboratory. These characteristics, altogether, render the high-frequency spectral band quite diagnostic of metal–hydrogen bonds in the types of compounds under discussion.[25]

Infrared spectral absorptions derived from metal–hydrogen bending motions have been reported only in a few previous cases, and it has been stated that these are "sometimes observed"[12a] because strong bands due to other ligands may obscure the 800 cm.$^{-1}$ spectral region.[23] In our studies we have found the δ_{MH}, ranging from 730 to 870 cm.$^{-1}$, most useful[26] in detecting and identifying metal hydride complexes. These absorptions accompany the M–H stretching band in the spectra of all the hydrides we have prepared. Thus, a simultaneous occurrence of the lower frequency absorptions and the stronger band near 2000 cm.$^{-1}$ virtually assures the presence of a metal–hydrogen bond. In one peculiar instance, we have found that one isomer of [IrHCl$_2$(Ph$_3$P)$_3$][27] shows only a weak (in most solid samples an undetectable) Ir–H stretching band, while the bending absorptions are relatively strong and characteristic. We have observed usually two M–H bending motions ("in-plane" and "out-of-plane") in octahedral monohydrides.

Table IV summarizes the infrared spectral data related to Os–H and Os–D vibrations.[28] The ν_{OsH} were measured also in CHCl$_3$ solution; the results were essentially the same as found in dichloromethane which are shown. In other regions of the Os–H,D spectrum, measurements in solution were unsuccessful because of lower intensities of bands coupled with solvent inter-

(22) This observation is, of course, accidental with the types of compounds cited, for the absolute position of ν_{MH} depends on the nature of other ligands present, on the stereochemistry of the complex, and particularly on the type of the ligand trans to hydrogen (ref. 19; for large trans effects, see ref. 23 and 24).
(23) J. Chatt and R. G. Hayter, J. Chem. Soc., 2605 (1961).
(24) L. Malatesta and R. Ugo, ibid., 2080 (1963).
(25) In solution, the Os–H stretching absorption has a decreased intensity due to the low solubility and probably as a result of reaction with dissolved oxygen, i.e., the shape and weakness of the band are not characteristic of a M–H spectrum in solution.[9] The band is shown in Fig. 1 in order to demonstrate that the ν_{OsH} is essentially the same in crystals and in solution of the complex. The weak band between ν_{OsH} and ν_{CO} is due to solvent.
(26) Below 760 cm.$^{-1}$ a band of Ph$_3$P or Ph$_3$As may interfere, but at least one δ_{MH} has always been found to occur above that frequency.
(27) Isomer II, Table I of ref. 6.
(28) The ν_{OsH} and ν_{CO} (both of the crystals) of the first two compounds in Tables IV and V differ somewhat from the values reported in the preliminary communication, ref. 3b. The latter were obtained on a less accurate and lower resolution instrument (see Experimental section).

ference. [OsHCl(CO)(Ph₃As)₃] was deuterated in the same fashion as the Ph₃P derivatives, but the product failed to show a spectral band attributable to ν_{OsD} (possibly because it was obscured by an absorption of Ph₃As).

Comparison of osmium–hydrogen vibrational frequencies shows that there are small but definite differences among the four derivatives and between the two solutions of each compound (cf. ref. 19). These are related to the total environment of the Os–H bond in the isostructural molecules. A discussion of spectra–structure correlations in these and other hydride complexes[4–6,9,20,21] will be presented after publication of structural details and other pertinent data.

As a footnote to this section, an unexpected observation on the results of the deuteration studies, described above, ought to be added. When high-boiling alcohols and D₂O were used at temperatures of 120–190°, the infrared spectra of the deuterated complexes showed a series of new bands in addition to those derived from the Os–D vibrations. These bands were found to result from a partial deuteration of the phenyl groups of the coordinated triphenylphosphine, as verified by separate experiments in which free Ph₃P was treated under the same conditions. One of the Ph₃P–D bands occurs in the same region as ν_{OsD} and is usually stronger than the latter in a partially deuterated osmium complex. On the other hand, at lower temperatures of deuteration, by using CH₃OD (64°) or C₂H₅OD (78°), there was no readily detectable exchange with phenyl hydrogens, although the osmium hydride was converted to the deuteride as above. Details of the ligand deuteration will be reported later, but the observation is mentioned here as a caution and possible aid for interpreting infrared spectra in related cases.

The Presence, Origin, and Vibrational Spectrum of Coordinated Carbon Monoxide.—The very strong absorption (with accompanying bands in the spectrum of the solid) near 1900 cm.⁻¹ (Fig. 1) remained unaffected in the spectra of the partially deuterated complexes. Although the position, intensity, and shape of these bands appeared, at first sight, to suggest the presence of a carbonyl complex, such an interpretation seemed incompatible with the fact that the reactants were void of carbon monoxide or carbonyl compounds. On the other hand, direct oxygen analysis (Table II) indicated that the compounds contain one oxygen per Os. According to the infrared spectra, this oxygen was not associated with a normal hydroxo[29] or oxo group, a solvent molecule, or triphenylphosphine oxide, possible forms of oxygen that have been observed to be present in some compounds obtained from similar systems.[7,9]

In order to determine whether the solvent was the source of CO, the triphenylphosphine complexes were synthesized by using radiocarbon ethylene glycol as reaction medium (190°). The activity of the compounds thus prepared was counted and compared with that of the starting ¹⁴C-ethylene glycol. For the chloro compound the activity corresponded to 1.05 ¹⁴C per formula weight of [OsHCl(CO)(Ph₃P)₃]; for the bromide, the result was 0.85 ¹⁴C/[OsHBr(CO)(Ph₃P)₃]. The agreement with the calculated value is good, considering the small amounts of materials involved (see Experimental section) and the fact that the purity of the bromo complex suffers when prepared by this method (see Table I and Methods of Synthesis).

The results prove that interaction with the solvent includes cleavage of the C–C bond in ethylene glycol with resultant incorporation of one carbon atom in the metal complex. This, in conjunction with oxygen analyses and infrared spectra, provides unequivocal evidence for the presence of one coordinated carbon monoxide and for its origin.

For a monocarbonyl complex a single CO stretching band is expected, and this is found in the spectra of the complexes in solution. The multiple absorptions in the spectra of the solid samples[28] arise probably from the presence of more than one different molecular site in the crystal. The satellite bands do not, as shown above, reflect a polycarbonyl species. Neither do they derive from the presence of more than one molecular isomer in the solid. The single Os–H stretching band and the crystal structure data of [OsHBr(CO)(Ph₃P)₃][15] contradict such a possibility. The proximity of the principal ν_{CO} of the solid and the ν_{CO} of the solution suggests that the same molecular structure prevails in both phases. The same is inferred from the corresponding positions of ν_{OsH}.

The ν_{CO} were measured also in CH₂Cl₂; the values obtained were the same as in chloroform solution, shown in Table V. The small but measurable differences between the CO band positions of the four compounds, and also the solvent effects (cf. ref. 19), will be discussed in a subsequent communication.

In the lower region of the spectrum there is one prominent absorption near 600 cm.⁻¹, and at least two weaker bands below that frequency (Fig. 1, Table V), all three of which appear to be associated with the vibrations of the coordinated carbonyl group. Other monocarbonyl complexes prepared in this laboratory[5,7,9,20,21,30] exhibit bands in the same portion of their spectra.[9] The neutral ligands do not absorb in this region (550–650 cm.⁻¹ for Ph₃P; 500–650 cm.⁻¹ for Ph₃As); and the three bands are absent in the spectra of related complexes lacking carbonyl, e.g., [OsBr₂(Ph₃P)₃] and [OsBr₃(Ph₃As)₃].[7] Below this region, new bands cannot be ascertained unambiguously because of interfering absorption due to the neutral ligands.[17,31] However, in the spectrum of [OsHCl(CO)(Ph₃As)₃] a relatively strong band is found at 350 cm.⁻¹ which is well separated from the arsine absorptions. This band is assigned to an Os–Cl stretching frequency by analogy with the recently reported spectra of transition metal halides[32] and their complexes.[33]

(29) In cases of very strong hydrogen bonding between certain ligands in some complexes, OH stretching frequencies have been observed as low as 1725 cm.⁻¹, appearing as weak and broad bands. (See F. A. Cotton, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, pp. 390, 391.) The author thanks a referee for pointing out that the ν_{OH} lowered in energy by very strong hydrogen bonding appear as *intense* and *broad* bands rather than weak ones as cited in the above mentioned review article. (See G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco, Calif., 1960, pp. 70, 94, 101–111; N. Sheppard, "Hydrogen Bonding," D. Hadži, Ed., Pergamon Press, New York, N. Y., 1959, p. 87.) Because of the latter band characteristic, the 1900 cm.⁻¹ absorptions (Fig. 1) were not considered as being derived from ν_{OH}.

(30) L. Vaska, *Science*, **140**, 809 (1963).

(31) The spectra of [OsHX(CO)L₃] show three to four bands (of weak to medium intensities) between 400 and 500 cm.⁻¹; these are of uncertain origin.

(32) (a) D. M. Adams and H. A. Gebbie, *Spectrochim. Acta*, **19**, 925, (1963); (b) D. M. Adams, J. Chatt, J. M. Davidson, and J. Gerrat, *J. Chem. Soc.*, 2189 (1963); (c) R. J. H. Clark and T. M. Dunn, *ibid.*, 1198 (1963).

There is considerable confusion in the assignment of observed absorptions below 700 cm.$^{-1}$ in the infrared spectra of metal carbonyls and their substituted derivatives. It appears, however, that in cases in which both of the two fundamentals, the metal–carbonyl stretching (ν_{M-CO}) and the carbonyl bending (δ_{CO}) frequencies, are reported and specified, the latter occur at higher wave numbers than the former.[34,35] For pure carbonyls, Edgell has summarized the situation by stating that "the metal–CO stretching frequencies are found between 350 and 475 cm.$^{-1}$... The metal–C–O bending frequencies are more scattered and fall between 275 and 650 cm.$^{-1}$ depending in part upon phase of the motion."[36] For substituted carbonyls, fewer data are available, but, roughly, the ranges are 350–500 cm.$^{-1}$ for ν_{M-CO} and 450–630 cm.$^{-1}$ for δ_{CO}.[35]

Based on this information, the 600 cm.$^{-1}$ band in the spectrum of [OsHX(CO)L$_3$] is tentatively assigned to δ_{CO}. The two weaker absorptions in the 550–588 cm.$^{-1}$ region may also be associated with δ_{CO}, ν_{Os-CO}, or represent some combination bands. The 600 cm.$^{-1}$ absorptions were measured also in benzene solution; the data obtained were the same as in CH$_2$Cl$_2$ solution, given in Table V.

Reaction Course.—The reactions leading to the hydridocarbonyl complexes do not lend themselves to convenient study of their mechanism. The over-all heterogeneity of the reactions, elevated temperatures, the complexity of some reacting alcohols, and/or the use of mixed solvents render these systems unsuitable for direct observation of the reaction course. However, pertinent information is available from closely related systems, and it is reasonable to assume that similar steps are involved in the present case.

We have found that the hydride ligand in [IrHCl$_2$(Ph$_3$P)$_3$] originates from the α-carbon of the reacting ethanol, and probably from a corresponding source when other primary or secondary alcohols or related solvents (e.g., ethers) are used as reactants, i.e., from the carbon atom attached to a functional group.[6] Decomposition of the alcohol in this process yields a proton,[4] and an aldehyde[6,8,37,38] or a ketone[37,38] depending on whether primary or secondary alcohols are used, respectively. Thus, for synthesis of monohydride complexes by reaction with primary alcohols (Table I) the fate of the reactant can be written as in eq. 1.[6,39]

$$RCH_2OH \longrightarrow RCHO + H^+ + H^-(\text{metal complex}) \quad (1)$$
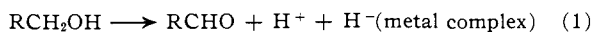
For the origin of the carbonyl ligand in [OsHX(CO)-(Ph$_3$P)$_3$] there is only one choice when the reacting sol-

vent contains a single type of CO group, i.e., simple alcohols, ethylene glycol, etc.[40] Glycol ethers present more possibilities; for example, in 2-(β-methoxyethoxy)-ethanol there are three types of oxygens and five different –CO– units. No information is presently available as to which of the several groups may be involved, although it is reasonable to think that the CO is furnished by the alcoholic group, by analogy with simple alcohols.

In the reactions of iridium halides with tertiary phosphines and alcohols we have observed that a hydride complex, [IrH$_2$Cl(Ph$_3$P)$_3$],[4] is a precursor of hydrido-carbonyl and carbonyl complexes, [IrHCl$_2$(CO)(Ph$_3$P)$_2$] and [IrCl(CO)(Ph$_3$P)$_2$].[5] This raises the possibility that the carbonyl complexes result from a reaction with the aldehyde produced by the preceding reaction (1). A separate experiment has, in fact, shown that [IrCl(CO)(Ph$_3$P)$_2$] can be prepared directly from iridium(III) chloride, Ph$_3$P, and an aldehyde (butanal).[5]
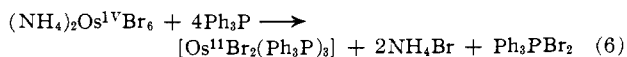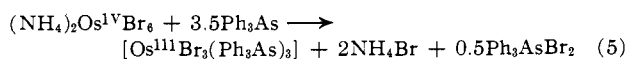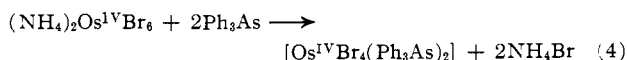
$$RCHO \longrightarrow RH + CO(\text{metal complex}) \quad (2)$$
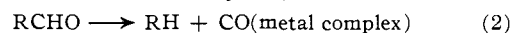
With osmium and ruthenium halides the reactions with Ph$_3$P or Ph$_3$As and alcohols have not yielded any (isolable) hydride-only complexes, i.e., without containing CO. The same systems have, however, afforded nonhydride carbonyl complexes.[7] These observations do not, of course, necessarily indicate a sequence of steps in the formation of [OsHX(CO)L$_3$].

Shaw has studied systems related to ours, and he reports in an abstract[37] that treatment of a ruthenium complex, [Ru$_2$Cl$_3$(Et$_2$PhP)$_6$]Cl, with KOH in methanol yields [RuHCl(CO)(Et$_2$PhP)$_3$] and hydrogen as byproduct. With ethanol and 1-propanol as reactants, methane and ethane are produced, respectively. This information is compatible with our findings outlined above, and the over-all reaction of the alcohol can thus be written (eq. 1 + eq. 2)

$$RCH_2OH \longrightarrow RH + H^+ + H^-CO(\text{metal complex}) \quad (3)$$
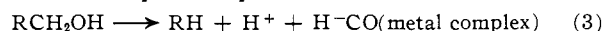
The reduction of osmium(IV) halide to osmium(II) complex may be effected by either the solvent alcohol or the neutral ligand (Ph$_3$P, Ph$_3$As) used in excess. In many related systems, where lower valent compounds are used as starting materials, no reduction of the central metal atom accompanies the reaction with alcohols to give hydrido, hydridocarbonyl, and carbonyl complexes.[4,5,7,8,37,38] There is, therefore, probably no direct relation between the reaction with alcohols and the reduction of the metal in the present case. In the absence of contrary evidence, we consider that the reducing agent for osmium is the phosphine or arsine.

With respect to the sequence, there is evidence that the reduction to osmium(II) takes place prior to the hydridocarbonyl formation. We have isolated, in high yield (>90%), a series of neutral adducts of Os(IV), Os(III), and Os(II) from the same reaction mixtures but at different conditions[7]

$$(NH_4)_2Os^{IV}Br_6 + 2Ph_3As \longrightarrow$$
$$[Os^{IV}Br_4(Ph_3As)_2] + 2NH_4Br \quad (4)$$

$$(NH_4)_2Os^{IV}Br_6 + 3.5Ph_3As \longrightarrow$$
$$[Os^{III}Br_3(Ph_3As)_3] + 2NH_4Br + 0.5Ph_3AsBr_2 \quad (5)$$

$$(NH_4)_2Os^{IV}Br_6 + 4Ph_3P \longrightarrow$$
$$[Os^{II}Br_2(Ph_3P)_3] + 2NH_4Br + Ph_3PBr_2 \quad (6)$$

(33) G. E. Coates and C. Parkin, J. Chem. Soc., 421 (1963).

(34) For pure carbonyls see, for example (a) W. F. Edgell, W. E. Wilson, and R. Summitt, Spectrochim. Acta, 19, 863 (1963); (b) L. H. Jones, ibid., 19, 329 (1963).

(35) For substituted carbonyls, see (a) G. Bouquet and M. Bigorgne, Bull. Soc. Chim. France, 433 (1962); (b) R. Poilblanc and M. Bigorgne, ibid., 1301 (1962); and references quoted in these papers.
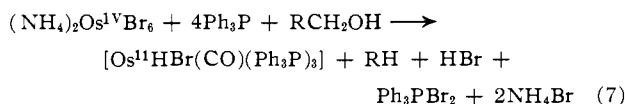
(36) W. F. Edgell, Spectrochim. Acta, 19, 391 (1963).

(37) B. L. Shaw and J. Chatt, Proceedings of 7th International Conference on Coordination Chemistry, Stockholm, 1962, p. 293.

(38) J. Chatt and B. L. Shaw, J. Chem. Soc., 5075 (1962).

(39) It should be noted in this context that the preparation of the partially deuterated osmium complexes by reaction with a mixture of D$_2$O and, e.g., ethylene glycol, described earlier in this paper, did not pinpoint the origin of the hydride (or deuteride) ligand. Isotopic studies on the synthesis of iridium hydrides gave negative evidence for hydroxylic hydrogens of the alcohol and water. Accordingly, the partially deuterated osmium compounds are considered to result from a H–D exchange between the hydride product ([OsHX(CO)(Ph$_3$P)$_3$]) and some deuterated species of the solvent (e.g., C$_2$H$_4$(OD)$_2$).

(40) The possibility that hydroxylic oxygen combines with a carbon not bonded to it (i.e., other than α-carbon) to produce CO is considered remote. In any event, such a case cannot include methanol (Table I, see also ref. 7).

To summarize the information regarding the reaction course (eq. 1–6), the over-all stoichiometry emerges as expressed in eq. 7.

$$(NH_4)_2Os^{IV}Br_6 + 4Ph_3P + RCH_2OH \longrightarrow$$
$$[Os^{II}HBr(CO)(Ph_3P)_3] + RH + HBr +$$
$$Ph_3PBr_2 + 2NH_4Br \quad (7)$$

Summary and Concluding Remarks

The experimental data and their interpretation, detailed in the preceding sections, indicate that osmium(IV) halides react with triphenylphosphine or triphenylarsine in alcohols to yield bivalent osmium adducts which, *in situ*, undergo further reaction with the solvent by abstracting hydride and carbonyl groups from the alcohol and incorporating these in the resulting complexes, [OsHX(CO)L₃]. The new compounds represent the most stable type of metal–hydrogen compounds discovered to date.[12a]

Alcohols and related solvents have been used for a long time in preparative coordination chemistry, and with the assumption that they do not participate in the final product, except possibly as solvates. Thus, in addition to obvious future possibilities in synthetic chemistry, the study reported here may also bring reinterpretation of some past work.

The primary purpose of this exposition has been to present a verification of the unsuspected reactions. Further studies on these compounds will be reported in forthcoming papers.

Experimental

Materials.—Ammonium hexachloroosmate(IV)[41] and ammonium hexabromoosmate(IV)[42] were prepared according to the methods described in the literature. The compounds were identified and their purity was established by elemental analysis, X-ray powder patterns, and magnetic susceptibility measurements at several temperatures and magnetic field strengths.

All other materials were reagent grade chemicals purchased from commercial sources.

Microanalyses (Table II) and **molecular weight** measurements (by an isopiestic method in the absence of air, Table III) were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Electrical conductances of the solutions were measured (in air) on a Model RC-16B2 bridge (Industrial Instruments, Inc.). The small conductance values found for the pure solvents were subtracted from those of solutions before calculating Λ_M given in Table III. The conductance of each solution was recorded immediately after dissolving the compound and was then followed over a period of many hours or days. No time dependence was observed.

Magnetic susceptibilities (Table III) were determined with a novel type magneto-balance which incorporates both the Faraday and Gouy methods of measurements in one unit. The apparatus utilizes a Varian 4-in. electromagnet and a recording vacuum microbalance with a load capacity of an ordinary analytical balance (200 g.). Details of this instrument will be described elsewhere. The measurements reported in this paper were made by the Faraday method on small solid samples (10–60 mg.) at three different magnetic fields.

Infrared Spectra.—The spectra of selected samples of each compound were measured on a Beckman IR-9 (prism-grating; 400–4000 cm.⁻¹), a Beckman IR-4 (CsBr optics; 300–700 cm.⁻¹), and a Perkin-Elmer Model 112 (CaF₂ optics; ν_{CO}, ν_{OsH}, and ν_{OsD} bands) spectrometer. Based on instrument specifications, reproducibility of data, and a good agreement between spectrom-

eters in overlapping spectral regions (see above), the observed absorption frequencies are considered to be accurate within 2 cm.⁻¹. The data given in Tables IV and V represent average values of several measurements. The spectrum reproduced in Fig. 1 was obtained on the Beckman IR-9.

The spectra of all preparations (Table I, footnote *c*) were measured routinely on a Beckman IR-4 from 600 to 5000 cm.⁻¹ using NaCl optics. The reproducibility of band positions in the 1900–2100 cm.⁻¹ range was within 10–15 cm.⁻¹, and 5 cm.⁻¹ in the lower applicable regions. The results thus obtained were reported in a preliminary communication.[3b] The shoulder of the ν_{CO} band near 1930 cm.⁻¹ (Fig. 1, Table V) was not observed with this instrument, and there were no readily recognizable differences between the band positions (650–3200 cm.⁻¹) of the coordinated Ph₃P or Ph₃As and those of the free ligands. On the Beckman IR-9, however, small but definite shifts and other changes of these bands became evident (see ref. 17).

Preparation of Complexes.—The various conditions which have been applied for the syntheses of the hydridocarbonyl complexes are summarized in Table I. Below, the preparation of each compound by a procedure considered to yield best results is described in greater detail.

Hydridochlorocarbonyltris(triphenylphosphine)osmium(II).—Ammonium hexachloroosmate(IV) (5.262 g., 12 mmoles) and triphenylphosphine (37.2 g., Ph₃P/Os = 12) were treated with 2-(β-methoxyethoxy)ethanol (500 ml.) and water (200 ml.). (The latter is not essential for the reaction to occur, but it was used to facilitate dissolution of the osmium salt, and thus to shorten the time of the experiment.) The reaction mixture, in an open beaker, was stirred and heated for 4.5 hr., during which time the temperature was gradually raised to 190° as the water was allowed to evaporate and the color of the continuously boiling solution changed from red-brown to yellow-orange. Crystals appeared *ca.* 3 hr. after start of the experiment. When heating was discontinued, the bulk of the product precipitated within minutes from the still hot (>100°) solution. Stirring was continued for another hour, the colorless crystals were then filtered, washed with methanol, and dried in vacuum desiccator. The yield was 10.754 g. or 86% based on Os used. An additional crop of slightly impure product (0.729 g. or 6%) was obtained by adding methanol (1000 ml.) to the filtrate and treating the resulting precipitate as above.

Hydridobromocarbonyltris(triphenylphosphine)osmium (II).—A reaction mixture of ammonium hexabromoosmate(IV) (0.253 g., 0.36 mmole), triphenylphosphine (1.10 g., Ph₃P/Os = 12), and 2-methoxyethanol (110 ml.), in a stoppered 125 ml. erlenmeyer flask, was allowed to stand at 25° for 5 days. A dark red-brown solution developed when the reagents were mixed, and this color persisted during the period indicated. The flask was then opened, and the contents (there were also a few dark-colored crystals present) were heated, giving a clear pale yellow solution. This solution was boiled (124°) to 25 ml. (1 hr.), heating was ceased, and methanol (100 ml.) was added to the hot solution: colorless crystals were formed immediately. The product (0.371 g. or 98%) was collected and handled as described for the chloro compound.

Hydridochlorocarbonyltris(triphenylarsine)osmium(II).—Ammonium hexachloroosmate(IV) (0.260 g., 0.59 mmole) and triphenylarsine (1.3 g., Ph₃As/Os = 7) were treated with ethylene glycol (150 ml.) and ethanol (200 ml.), and the mixture was stirred and heated in an open flask. As the temperature rose, the reactants dissolved slowly and a dark orange-brown solution resulted; 1 hr. after commencement of heating the temperature was 120°, and the volume of the orange-colored boiling solution *ca.* 200 ml. At this point a white precipitate appeared. Heating was discontinued, methanol (250 ml.) was added, and the mixture was stirred until it had cooled to 25°. The crystalline product (0.567 g. or 82%) was treated as the preceding compounds.

Hydridobromocarbonyltris(triphenylarsine)osmium(II).—This complex was prepared by the same procedure as [OsHCl(CO)(Ph₃As)₃]. The quantities of materials used were (NH₄)₂OsBr₆ (0.479 g., 0.68 mmole), Ph₃As (2.0 g., Ph₃As/Os = 10), ethylene glycol (150 ml.), and ethanol (250 ml.). The reaction mixture was heated to 140° (1 hr.; vol. of solution, *ca.* 170 ml.), treated with methanol (250 ml.), and the product was handled as previously described. The yield was 0.564 g. or 69% based on Os.

Deuteration of Hydride Complexes.—In a typical experiment, 2 ml. of CH₃OD (min. isotopic purity, 99%) were added through

(41) F. P. Dwyer and J. W. Hogarth, *J. Roy. Soc. N.S. Wales*, **84**, 194 (1951).

(42) F. P. Dwyer and N. A. Gibson, *Nature*, **165**, 1012 (1950).

a side-arm assembly to a flask containing a small sample (0.1 g.) of [OsHBr(CO)(Ph₃P)₃] under atmospheric pressure of dry nitrogen. Alternatively, the deuterated alcohol was vacuum distilled into the reaction flask which was then filled with nitrogen. The resulting suspension was refluxed (64°) for 10 days, the alcohol was removed by distillation under reduced pressure, and the solid residue was dried by pumping. [OsHCl(CO)(Ph₃P)₃] was treated similarly. Deuterated ethanol (95% C₂H₅OD in D₂O, min. isotopic purity, 98%) was also used, and in the same manner as CH₃OD.

In another type of experiment, (NH₄)₂OsCl₆ (0.151 g.) and Ph₃P (1.07 g., Ph₃P/Os = 12) were treated with 2-methoxyethanol (50 ml.) and D₂O (10 ml.) under dry nitrogen. The mixture was heated for 3 hr. to 124°, during which time the solvent was slowly evaporated (distilled under N₂) until 20 ml. remained. The crystalline complex which resulted (0.315 g., 88% based on Os) was handled as usual. The same procedure, but using ethylene glycol and D₂O as solvents gave similar results.

All these experiments yielded hydride–deuteride mixtures containing ca. 30–60% [OsDX(CO)(Ph₃P)₃] as estimated from the relative intensities of the Os–H and Os–D bands in the infrared spectra of the products.

In one experiment, deuterium gas (100 mm.) was circulated over powdered crystals of [OsHCl(CO)(Ph₃P)₃] for 2 hr. at 25° and another 2 hr. at 100°.[43] No H–D exchange was observed.

Radiocarbon Experiments.—A standard solution of ¹⁴C-ethylene glycol (0.5 mcurie) was prepared and an aliquot part (2.00 ml.) was added to a mixture of (NH₄)₂OsCl₆ (0.100 g.) and

Ph₃P (0.48 g., Ph₃P/Os = 8) in a 5 ml. flask fitted with a condenser and separated from the surroundings by a CaCl₂ trap. The contents were heated (25 min.) to boiling (190°), cooled to 25°, and the resulting crystals were separated by filtration. The solid was washed with 2500 ml. of methanol for 8 hr. to assure complete removal of ¹⁴C-ethylene glycol (and also to dissolve excess Ph₃P present in the precipitate), and it was then dried in vacuum desiccator over Mg(ClO₄)₂ for 2 days. The product (0.226 g., 95% based on Os) was identified as [OsHCl(CO)(Ph₃P)₃] by its X-ray powder pattern and melting point. The corresponding bromide, [OsHBr(CO)(Ph₃P)₃], was prepared from (NH₄)₂OsBr₆ (0.032 g.), Ph₃P (0.095 g., Ph₃P/Os = 8), and ¹⁴C-ethylene glycol (2 ml.) by the same procedure and treated and identified as above.

Small samples (10 mg.) of the compounds were dissolved in toluene scintillator solution and the activity counted. The absolute activity of the samples was compared with that of the starting ¹⁴C-ethylene glycol by adding standard ¹⁴C-toluene to the sample.[44] The results are cited in a preceding section (Infrared Spectra and Isotopic Studies).

(44) The counting experiments were carried out in the Radiation Research Laboratories of this Institute under the direction of Dr. R. H. Schuler to whom the author is indebted for valuable suggestions and for supplying radiocarbon materials.

(43) Courtesy of Dr. W. Keith Hall.