TABLE VIII

INTERMOLECULAR CONTACTS TO 3.3 A FOR $HRe_2Mn(CO)_{14}$

$C_1\cdots O_{14}$	$(x + {}^1/_2, -y + {}^1/_2, z - {}^1/_2)$	3.15
$C_2\cdots O_7$	$(x + {}^1/_2, -y + {}^1/_2, z + {}^1/_2)$	3.19
$C_2\cdots O_{12}$	$(-x - {}^1/_2, +y - {}^1/_2, -z + {}^1/_2)$	3.27
$C_4\cdots O_{10}$	$(x - {}^1/_2, -y + {}^1/_2, z - {}^1/_2)$	3.22
$C_4\cdots O_{14}$	$(x + {}^1/_2, -y + {}^1/_2, z - {}^1/_2)$	3.30
$C_5\cdots O_1$	$(-x, -y, -z)$	3.21
$C_7\cdots O_2$	$(x - {}^1/_2, -y + {}^1/_2, z - {}^1/_2)$	3.13
$C_8\cdots O_2$	$(x - {}^1/_2, -y + {}^1/_2, z - {}^1/_2)$	3.23
$O_1\cdots O_{10}$	$(-x + {}^1/_2, +y - {}^1/_2, -z + {}^1/_2)$	3.10
$O_1\cdots O_6$	$(-x + {}^1/_2, +y - {}^1/_2, -z + {}^1/_2)$	3.19
$O_1\cdots O_{14}$	$(x + {}^1/_2, -y + {}^1/_2, z - {}^1/_2)$	3.20
$O_1\cdots C_5$	$(-x, -y, -z)$	3.21
$O_1\cdots O_5$	$(-x, -y, -z)$	3.23
$O_1\cdots O_4$	$(-x, -y, -z)$	3.24
$O_1\cdots O_{11}$	$(-x + {}^1/_2, +y - {}^1/_2, -z + {}^1/_2)$	3.26
$O_2\cdots O_{12}$	$(-x - {}^1/_2, +y - {}^1/_2, -z + {}^1/_2)$	2.96
$O_2\cdots O_7$	$(x + {}^1/_2, -y + {}^1/_2, z + {}^1/_2)$	3.00
$O_2\cdots C_7$	$(x + {}^1/_2, -y + {}^1/_2, z + {}^1/_2)$	3.13
$O_2\cdots O_8$	$(x + {}^1/_2, -y + {}^1/_2, z + {}^1/_2)$	3.20
$O_2\cdots C_8$	$(x + {}^1/_2, -y + {}^1/_2, z + {}^1/_2)$	3.23
$O_3\cdots O_{11}$	$(-x + {}^1/_2, +y - {}^1/_2, -z + {}^1/_2)$	3.13
$O_3\cdots O_8$	$(x + 1, y, z)$	3.27
$O_3\cdots O_7$	$(x + {}^1/_2, -y + {}^1/_2, z + {}^1/_2)$	3.28
$O_4\cdots O_{10}$	$(x - {}^1/_2, -y + {}^1/_2, z - {}^1/_2)$	3.14
$O_4\cdots O_{14}$	$(x + {}^1/_2, -y + {}^1/_2, z - {}^1/_2)$	3.19
$O_4\cdots O_1$	$(-x, -y, -z)$	3.24
$O_5\cdots O_1$	$(-x, -y, -z)$	3.23
$O_5\cdots O_{10}$	$(x - {}^1/_2, -y + {}^1/_2, z - {}^1/_2)$	3.25
$O_5\cdots O_{14}$	$(x - {}^1/_2, -y + {}^1/_2, z - {}^1/_2)$	3.25
$O_5\cdots O_{14}$	$(-x - {}^1/_2, +y - {}^1/_2, -z + {}^1/_2)$	3.28
$O_6\cdots O_1$	$(-x + {}^1/_2, y + {}^1/_2, -z + {}^1/_2)$	3.19
$O_6\cdots O_{12}$	$(x + 1, y, z)$	3.25
$O_7\cdots O_2$	$(x - {}^1/_2, -y + {}^1/_2, z - {}^1/_2)$	3.00
$O_7\cdots O_{11}$	$(-x, -y + 1, -z)$	3.07
$O_7\cdots C_2$	$(x - {}^1/_2, -y + {}^1/_2, z - {}^1/_2)$	3.19
$O_7\cdots O_3$	$(x - {}^1/_2, -y + {}^1/_2, z - {}^1/_2)$	3.28
$O_8\cdots O_2$	$(x - {}^1/_2, -y + {}^1/_2, z - {}^1/_2)$	3.20
$O_8\cdots O_3$	$(x - 1, y, z)$	3.27
$O_{10}\cdots O_1$	$(-x + {}^1/_2, y + {}^1/_2, -z + {}^1/_2)$	3.10
$O_{10}\cdots O_4$	$(x + {}^1/_2, -y + {}^1/_2, z + {}^1/_2)$	3.14
$O_{10}\cdots C_5$	$(x + {}^1/_2, -y + {}^1/_2, z + {}^1/_2)$	3.22
$O_{10}\cdots O_5$	$(x + {}^1/_2, -y + {}^1/_2, z + {}^1/_2)$	3.25
$O_{11}\cdots O_7$	$(-x, -y + 1, -z)$	3.07
$O_{11}\cdots O_3$	$(-x + {}^1/_2, +y + {}^1/_2, -z + {}^1/_2)$	3.13
$O_{11}\cdots O_{14}$	$(-x, -y + 1, -z + 1)$	3.17
$O_{11}\cdots O_1$	$(-x + {}^1/_2, y + {}^1/_2, -z + {}^1/_2)$	3.26
$O_{12}\cdots O_2$	$(-x - {}^1/_2, y + {}^1/_2, -z + {}^1/_2)$	2.96
$O_{12}\cdots O_6$	$(x - 1, y, z)$	3.25
$O_{12}\cdots C_2$	$(-x - {}^1/_2, y + {}^1/_2, -z + {}^1/_2)$	3.27
$O_{14}\cdots C_1$	$(x - {}^1/_2, -y + {}^1/_2, z + {}^1/_2)$	3.15
$O_{14}\cdots O_{11}$	$(-x, -y + 1, -z + 1)$	3.17
$O_{14}\cdots O_4$	$(x - {}^1/_2, -y + {}^1/_2, z + {}^1/_2)$	3.19
$O_{14}\cdots O_1$	$(x - {}^1/_2, -y + {}^1/_2, z + {}^1/_2)$	3.20
$O_{14}\cdots O_5$	$(x + {}^1/_2, -y + {}^1/_2, z + {}^1/_2)$	3.25
$O_{14}\cdots O_5$	$(-x - {}^1/_2, y + {}^1/_2, -z + {}^1/_2)$	3.28
$O_{14}\cdots C_4$	$(x - {}^1/_2, -y + {}^1/_2, z + {}^1/_2)$	3.30

or less in the plane of the equatorial carbonyl groups of the $Re(CO)_5$ group, and should not significantly affect the $Re_1\cdots Re_2$–Mn angle.

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CONTRIBUTION FROM THE CYANAMID EUROPEAN RESEARCH INSTITUTE,
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The Pentacarbonyls of Ruthenium and Osmium. II. Dihydridotetracarbonylosmium and Its Substitution Reactions

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Dihydridotetracarbonylosmium, $OsH_2(CO)_4$, has been obtained in high yields by the reaction of osmium tetroxide with carbon monoxide and hydrogen at elevated temperature and pressure and also by allowing pentacarbonylosmium to react with molecular hydrogen. The nuclear magnetic resonance and infrared spectra are in agreement with a *cis*-octahedral structure of symmetry C_{2v} for the dihydridotetracarbonyl. Upon deuteration, a small shift of the carbonyl stretching vibrations is observed, which is explained by removal of the resonance interaction existing in $OsH_2(CO)_4$ between the metal–hydrogen and the carbonyl stretching vibrational states. Substitution reactions of $OsH_2(CO)_4$ are also reported. With triphenylphosphine one carbon monoxide group is substituted with formation of $OsH_2(CO)_3P(C_6H_5)_3$. Infrared and nmr data of the latter compound and the corresponding deuterated species suggest an all-*cis* configuration. Finally the room-temperature reactions of $OsH_2(CO)_4$ with carbon tetrachloride and carbon tetrabromide led to the formation of the *cis*-dihalogeno compounds $OsX_2(CO)_4$ (X = Cl, Br).

In the first paper of this series[1] we reported the infrared spectra of $Ru(CO)_5$ and $Os(CO)_5$ and suggested a trigonal-bipyramidal configuration in solution for both of them. During the synthesis of $Os(CO)_5$ a more volatile fraction than the pentacarbonyl was observed. In the present paper we wish to report that this substance has now been identified as dihydridotetracarbonylosmium, $OsH_2(CO)_4$. This compound was suspected by Hieber and Stallmann[2] to be present

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[1] F. Calderazzo and F. L'Eplattenier, *Inorg. Chem.*, **6**, 1220 (1967).

[2] W. Hieber and H. Stallmann, *Z. Elektrochem.*, **49**, 288 (1943).

in their preparation of $Os(CO)_5$. We also report a convenient method of preparation of $OsH_2(CO)_4$ and some of its substitution reactions.

Experimental Section

Although the compounds reported in this paper are rather stable toward air oxidation, their preparation and isolation were carried out systematically under an atmosphere of prepurified nitrogen.

Osmium tetroxide was purchased from H. Drijfhout and Zoon's Edelmetaalbedrijven, Amsterdam. Carbon monoxide was purified by treatment with a solution of iodine in 2,2'-diethoxydiethyl ether. Tetrahydroforan was treated with iron(II) sulfate and distilled over sodium and lithium tetrahydridoaluminate. Triphenylphosphine was sublimed before use.

The infrared spectra were measured on a Perkin-Elmer instrument, Model 521, equipped with grating. The spectra were recorded on expanded abscissa scale and calibrated with CO. The limit of accuracy based on instrument specifications and reproducibility of data is believed to be ± 1 cm^{-1}. The infrared spectra in the gas phase were measured in a 10-cm gas cell.

The high-pressure reactions were carried out in a 250-ml stainless steel autoclave heated in a thermostated oil bath.

Microanalyses were by Dr. A. Bernhardt, Mülheim, Germany.

Melting points (uncorrected) were measured in capillaries sealed under nitrogen.

1. **Dihydridotetracarbonylosmium.**—(a) Osmium tetroxide (0.5 g) was introduced in the autoclave together with heptane (30 ml). Carbon monoxide and hydrogen in a 3:1 ratio were then compressed to a total pressure of 180 atm. The autoclave was heated to 160° for about 6 hr. After cooling to room temperature, the gases were vented and the volatile $OsH_2(CO)_4$, together with the solvent, was then condensed *in vacuo* under exclusion of light into a flask maintained at Dry Ice temperature. The infrared spectrum of the colorless solution indicated the presence of traces of pentacarbonylosmium. The yield was substantially quantitative as indicated by the absence of any solid residue in the autoclave.

(b) For nuclear magnetic resonance spectra a similar preparation of $OsH_2(CO)_4$ was carried out in more concentrated solutions (10 ml of heptane or tetrahydrofuran). In heptane a sharp peak was obtained at τ 18.73 whereas in tetrahydrofuran the peak was at τ 18.84.

(c) The reaction of osmium tetroxide with CO and H_2 was also carried out without solvent in order to measure the infrared spectrum of the hydride in the gas phase and in benzene-d_6. The reaction conditions were the same as in (a). After the reaction, the autoclave was cooled to $-80°$, the pressure was released, and the gas was pumped off up to about 20 mm for a few seconds. The autoclave was then disconnected from the vacuum line and allowed to warm to room temperature. Finally the autoclave was connected to a preevacuated gas cell and the hydride vapors were allowed to diffuse into the gas cell. The infrared spectrum was then immediately measured (see Table I). The rest of the compound was distilled and condensed as a colorless solid in a trap cooled at $-80°$. At room temperature the dihydridotetracarbonyl is a colorless liquid which appears to be rather stable even against air.

(d) In another experiment osmium tetroxide (0.5 g) was carbonylated in 30 ml of heptane with carbon monoxide (180 atm) during 10 hr at 170°. No hydrogen was used in this first stage of the reaction. After distillation of the pentacarbonyl, which contained small amounts of the dihydride,[1] the heptane solution was treated with hydrogen (80 atm) for 6 hr at 100°. After recovery of the volatile reaction products in the usual manner, the infrared spectrum was that of pure dihydridotetracarbonylosmium (Figure 1A). No absorptions due to pentacarbonylosmium were observed.

The trimer $Os_3(CO)_{12}$ was also converted into the hydride, although in lower yields, by treatment with hydrogen at 80 atm for 6 hr at 100°.

2. **Dideuteridotetracarbonylosmium.**—$OsD_2(CO)_4$ was prepared in practically quantitative yields by procedures identical with those described in sections 1(a) and 1(c), using deuterium instead of hydrogen. The infrared spectrum of the dideuteride is shown in Table I and Figure 1b.

3. **$OsH_2(CO)_3P(C_6H_5)_3$.**—To a heptane solution (20 ml) of dihydridotetracarbonylosmium, prepared from 0.5 g (2.0 mmoles) of osmium tetroxide, 0.52 g (2.0 mmoles) of triphenylphosphine was added at room temperature. The reaction flask was protected against daylight. The solution was heated for 4 hr at about 80°. On cooling, colorless crystals separated out. The latter were decanted from the solution and recrystallized from heptane. In the solid state the compound is stable to oxygen, moisture, and daylight for a few days. It is soluble in heptane, benzene, and tetrahydrofuran. *Anal.* Calcd for $C_{21}H_{17}O_3OsP$: C, 46.84; H, 3.18; P, 5.75. Found: C, 47.01; H, 3.35; P, 5.88; mp 148–149°. The infrared and nmr data of this compound are reported in Tables I and II and in Figure 2.

4. **$OsD_2(CO)_3P(C_6H_5)_3$.**—The dideuteridophosphine derivative was obtained by a procedure similar to that described for $OsH_2(CO)_3P(C_6H_5)_3$, starting from dideuteridotetracarbonylosmium. Infrared data are in Table I and Figure 2. *Anal.* Calcd for $C_{21}H_{15}D_2O_3OsP$: C, 46.66; H + D, 3.54; P, 5.73; mol wt, 540.5. Found: C, 47.13; H + D, 3.57; P, 5.07; mol wt, 561; mp 148–149°.

5. **Dichlorotetracarbonylosmium.**—Dihydridotetracarbonylosmium prepared according to procedure 1(c) was treated with carbon tetrachloride at room temperature. Within a few seconds the dichloro compound precipitated out as colorless crystals. These were decanted, washed with heptane, and sublimed at 60° (10^{-3} mm). From 250 mg of osmium tetroxide, 230 mg of sublimed product was obtained (63% yield). The infrared data are in Table I. *Anal.* Calcd for $C_4Cl_2O_4Os$: C, 12.87; H, 0.00; Cl, 19.00. Found: C, 13.03; H, 0.00; Cl, 18.68; mp 305° dec. The reaction of the dihydridotetracarbonylosmium is very fast even at temperatures below 0°.

6. **Dibromotetracarbonylosmium.**—The reaction of dihydridotetracarbonylosmium with carbon tetrabromide was carried out on a heptane solution of the dihydrido derivative at room temperature. After filtration the colorless crystals of the dibromo derivative were washed with heptane and sublimed at 65° (10^{-3} mm). The reaction was very fast and practically quantitative as judged from the absence of unreacted hydride in the filtrate. *Anal.* Calcd for $C_4Br_2O_4Os$: C, 10.40; H, 0.00; Br, 34.59. Found: C, 10.61; H, 0.00; Br, 34.28; mp 317° dec.

A product having an infrared spectrum identical with that of $OsBr_2(CO)_4$ (see Table I) was obtained in excellent yields by treatment of a heptane solution of $Os(CO)_5$[1] with bromine, followed by sublimation under the conditions specified above. *Anal.* Found: C, 10.33; H, 0.00.

Results and Discussion

When discussing the reaction of OsO_4 with CO in the previous paper,[1] we indicated the presence of another compound in the final reaction mixture. We can now conclude that this by-product was dihydridotetracarbonylosmium, $OsH_2(CO)_4$, since the extra band previously observed[1] at 2046 cm^{-1} in heptane (shifted to 2062 cm^{-1} in the gas phase) is, within experimental error, the strongest absorption band of the dihydride (see Table I and Figure 1A). The latter compound has now been obtained in excellent yields either by direct carbonylation of osmium tetroxide in the presence of hydrogen at superatmospheric pressure or by hydrogenation of preformed pentacarbonylosmium. The formation of the dihydride in the course of the carbonylation[1] of OsO_4 probably arose from small amounts of hydrogen present in the carbon monoxide

Table I

Infrared C–O and M–H Stretching Vibrations of Some Hydrido-, Deuterido-, and Halogenocarbonyls of Osmium

Compound	ν_{CO}, cm^{-1}	ν_{M-H}, cm^{-1}	ν_{M-D}, cm^{-1}	Solvent
$OsH_2(CO)_4$	2141 w, 2067 m, 2055 s, 2048 vs, 2016 w^{a}	1942 w	. . .	Heptane
	2139 w, 2067 m, 2055 s,^{b} 2047 vs	1938 w	. . .	C_6D_6
	2148 w, 2082 m, 2075 s,^{b} 2062 vs, 2034 w,^{a} 2029 w^{a}	1945 w	. . .	Gas
$OsD_2(CO)_4$	2140 w, 2057 m, 2049 vs, 2031 s, 2015 w,^{a} 1997 w^{a}	. . .	*c*	Heptane
	2139 w, 2057 m, 2045 vs, 2029 s	. . .	1423 w (1.362)	C_6D_6
	2146 w, 2066 m, 2062 vs, 2042 s	. . .	1427 w (1.363)	Gas
$OsH_2(CO)_3P(C_6H_5)_3$	2079 vs, 2027 s,^{b} 2018 vs	1959 w, 1922 w	. . .	Heptane
	2079 vs, 2024 s,^{b} 2061 vs	1958 w, 1920 w	. . .	C_6D_6
	2075 vs, 2029 s, 2005 vs	1955 s, 1923 s	. . .	Halocarbon
$OsD_2(CO)_3P(C_6H_5)_3$	2076 vs, 2004 vs, 1989 s, 1954 w^{a}	. . .	*d*	Heptane
	2073 vs, 1999 vs, 1983 s	. . .	*d*	C_6D_6
	2070 s, 1994 s, 1978 vs, 1948 w^{a}	. . .	1434 s^{b} (1.363) 1417 s (1.357)	Halocarbon
$OsCl_2(CO)_4$	2187 w, 2119 vs, 2092 s, 2051 s	. . .	. . .	CCl_4
$OsBr_2(CO)_4$	2179 w, 2113 vs, 2091 s, 2051 s	. . .	. . .	CCl_4

^{a} Bands attributed to ^{13}CO stretching vibrations. ^{b} Shoulders. ^{c} Bands not detectable because of solvent absorption. ^{d} Bands not detectable because of interaction with solvent and triphenylphosphine absorption.

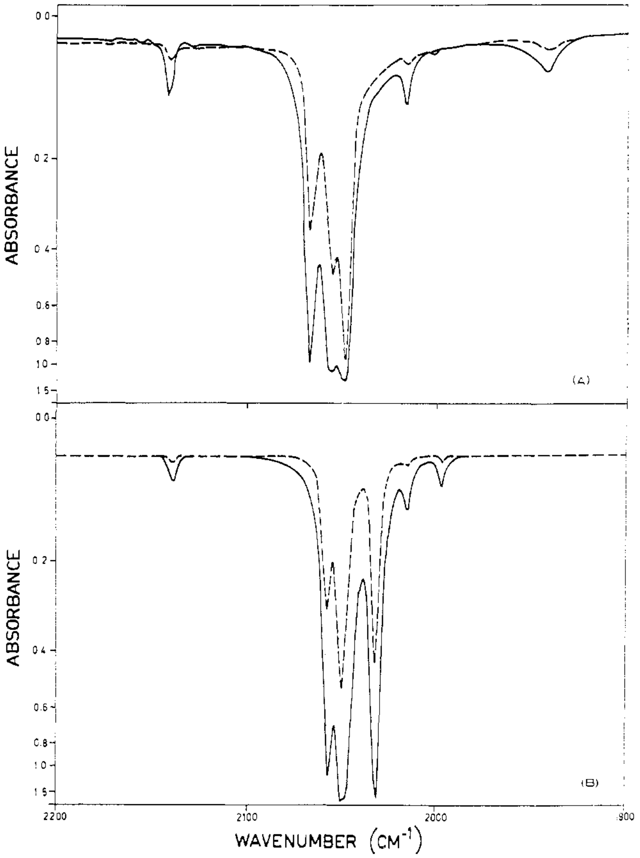

Figure 1.—Infrared spectra of $OsH_2(CO)_4$ (A) and $OsD_2(CO)$ (B) in heptane solution in the carbonyl and metal–hydrogen stretching region; 0.1-mm cell. The dashed curves represent more dilute solutions.

used for reaction. As noted above, in the early synthesis of $Os(CO)_5$ from OsO_4 and CO, Hieber and Stallmann[2] had detected a more volatile fraction which was suspected to contain a carbonyl hydride of osmium. The compound was, however, not characterized at that time and a recent review[3] has stated that the evidence for $OsH_2(CO)_4$ is questionable. This compound has now been completely characterized by nmr and infrared spectra and through the isolation of the substitution products obtained from it.

The nmr spectrum of $OsH_2(CO)_4$ shows a single peak at τ 18.73 in heptane, a position which is characteristic of hydrido complexes of transition metals.[3] Changing solvent from heptane to tetrahydrofuran did not affect considerably the position of the resonance (τ 18.84), thus suggesting the absence of important solvent–solute interactions.

The infrared spectrum is consistent with the formulation of the hydride as *cis*-$OsH_2(CO)_4$. A carbonyl derivative of this type having C_{2v} symmetry should give rise to four C–O stretching vibrations ($2\ A_1 + B_1 + B_2$) and to two metal–hydrogen stretching vibrations ($A_1 + B_1$). As shown in Figure 1A and Table I, four main bands are observed in the carbonyl stretching region. Besides that, taking as reference the spectra in heptane solution, the comparison with the spectrum of the deuterido derivative makes it possible to assign the 1942-cm^{-1} band to a metal–hydrogen stretching and the 2016-cm^{-1} band to a ^{13}C–O stretching. In benzene-d_6 and in the gas-phase spectra of $OsD_2(CO)_4$ the metal–deuterium stretching region around 1400 cm^{-1} becomes observable and a new band appears, the isotopic frequency ratio being 1.36. The presence of only one metal–hydrogen stretching is hardly surprising. First of all, the 1942-cm^{-1} band of $OsH_2(CO)_4$ and that around 1400 cm^{-1} of the dideuterido derivative are rather broad and could contain both vibrations. The alternative explanation of a coincidence between one of the metal–hydrogen vibrations and one of the C–O stretching vibrations is not consistent with the observation of only one metal–deuterium stretching. Examples of metal hydrides in which no conclusive evidence for infrared metal–hydrogen stretching vibrations was found are known in the literature, in particular with 5d transition elements.[4,5] Also OsH_2-

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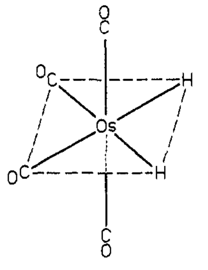
(3) A. P. Ginsberg, "Transition Metal Chemistry," Vol. 1, R. L. Carlin, Ed., M. Dekker, Inc., New York, N. Y., 1965, pp 111–237.

(4) D. K. Huggins, W. Fellmann, J. M. Smith, and H. D. Kaesz, *J. Am. Chem. Soc.*, **86**, 4841 (1964).

(5) J. M. Smith, W. Fellmann, and L. H. Jones, *Inorg. Chem.*, **4**, 1361 (1965).

$(PF_3)_4$, which has a *cis* configuration according to its nmr spectrum, has only one metal–hydrogen stretching vibration.[6]

A closer examination of the infrared data of Table I shows some interesting features. Upon deuteration, two of the terminal C–O stretching bands of $OsH_2(CO)_4$ show a small shift to lower wavenumbers. This can be explained by a resonance interaction phenomenon or, more exactly, by the removal, upon deuteration, of such a resonance between the vibrational states of $OsH_2(CO)_4$. Of the four infrared-active C–O stretching vibrations, the $A_1{}^{1a}$ and the B_1 involve axial CO groups[7] (*i.e.*, *trans* to each other), whereas the two others ($A_1{}^{1b}$ and B_2) are associated with the equatorial CO groups, *i.e.*, *trans* to the hydrogen ligands. Since the energies of the C–O and metal–hydrogen stretching vibrations are very close, resonance interaction will occur between them to an extent inversely proportional to their energy difference.[8] The restriction is, however, imposed that the interaction should occur between vibrations belonging to the same representations. As the two metal–hydrogen stretchings are of types A_1 and B_1, the resonance interaction should in principle affect three of the four C–O stretching vibrations of $OsH_2(CO)_4$. In practice, only two of these vibrations, those *trans* to the hydrogen ligands, are affected; the $A_1{}^{1a}$ band is at too high an energy to interact appreciably.



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Effects of the type described here have been reported also by Vaska[9] for some hydridocarbonyls of rhodium, iridium, and osmium.

The conversion of $Os(CO)_5$ to $OsH_2(CO)_4$ according to the stoichiometry

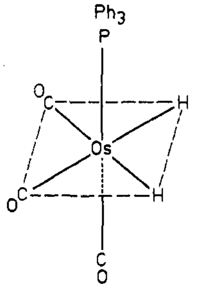
$$Os(CO)_5 + H_2 \longrightarrow OsH_2(CO)_4 + CO \qquad (1)$$

deserves some words of comment. From the best of our knowledge, this is the first example of a hydridocarbonyl obtained by the direct reaction of a *monomeric* metal carbonyl with molecular hydrogen. Formation of hydridocarbonyls by reaction of hydrogen with binuclear metal carbonyls is well known in the case of $Co_2(CO)_8$[10] and $Mn_2(CO)_{10}$,[11] giving $CoH(CO)_4$ and $MnH(CO)_5$. Cleavage of the relatively weak metal–metal bonds (the metal–metal bond dissociation energies by mass spectrometric techniques are 11.5 ± 4.6 kcal for $Co_2(CO)_8$[12] and 18.9 ± 1.4 kcal for $Mn_2(CO)_{10}$[13]) is necessary in these cases without change in the coordination number of the metal. Reaction 1, on the other hand, requires CO substitution with simultaneous increase of both the coordination number and the oxidation state. Reaction 1, in which a derivative of configuration d^6 is obtained from a d^8 compound, belongs to that class of reactions recently classified[14] as oxidative addition reactions. The present study suggests that these reactions are perhaps even more common than previously thought, especially with osmium which is considered to be the transition element with the highest tendency to give complexes of d^6 configuration.[15] Obviously, the reaction of pentacarbonylosmium with bromine to form $OsBr_2(CO)_4$ represents a further example of these oxidative addition reactions.

The thermal stability of $OsH_2(CO)_4$—the compound is prepared at 100° at elevated pressures of hydrogen—is exceptional for a hydridometal carbonyl. Considering that $FeH_2(CO)_4$ decomposes[16] at −10°, the behavior of the carbonyl hydrides of the iron subgroup seems in contradiction with the generally accepted view[3] that the thermal stability of hydridocarbonyls decreases in descending a vertical triad of elements.

Substitution Reactions of Dihydridotetracarbonylosmium

(a) Substitution of CO Groups.—The substitution of carbon monoxide groups of $OsH_2(CO)_4$ by triphenylphosphine can be achieved under relatively mild conditions with formation of $OsH_2(CO)_3P(C_6H_5)_3$. Three geometrical isomers are possible for a compound of this type, namely, **2–4**. The nmr spectrum, showing a symmetrical doublet at τ 18.00 with a coupling constant J = 24 cps (see Table II), suggests the presence of two equivalent hydrogens split by phosphorus. The value of J is that expected for phosphorus and hydrogen ligands in *cis* position.[6] Structure **4** is therefore to be excluded. Of paramount importance is the ratio between the observed integrated areas for the different types of protons present in the molecule, since this



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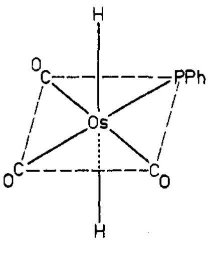

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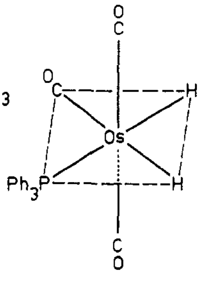

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Table II

Proton Magnetic Resonance of Osmium Hydrido Compounds

Compound	Solvent	Chemical shift,[a] τ, ppm	Multiplicity	J, cps	Integrated area	Assignment
$OsH_2(CO)_4$	Heptane	18.73	Singlet	...	...	
	THF[b]	18.84	Singlet	...	...	
$OsH_2(CO)_3P(C_6H_5)_3$	THF[b]	18.00	Doublet	24	2	Hydrogen bonded to metal
		2.15–2.63	Complex pattern	...	15	Phenyl hydrogens

[a] From tetramethylsilane (τ 10) as internal reference. [b] THF = tetrahydrofuran.

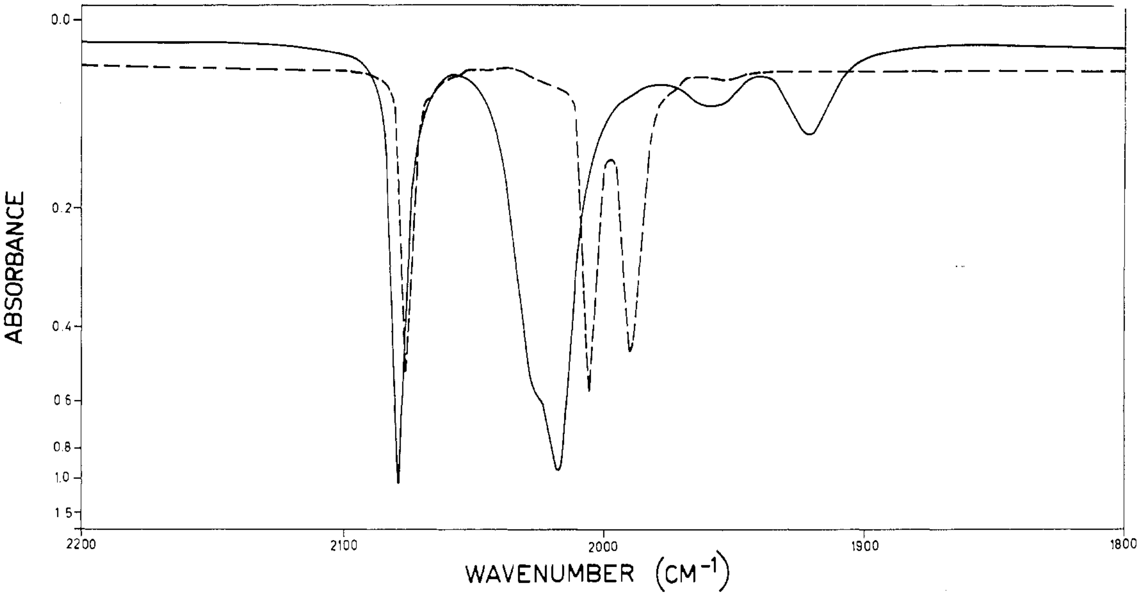
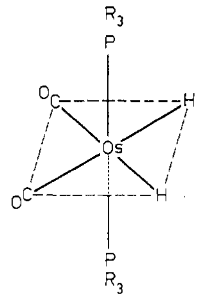


Figure 2.—Infrared spectra of triphenylphosphine-substituted osmium carbonyls in heptane solutions; 0.1-mm cell: ———, $OsH_2(CO)_3P(C_6H_5)_3$; – – – –, $OsD_2(CO)_3P(C_6H_5)_3$.

definitely establishes the presence of two hydridic hydrogens in this molecule and consequently in the parent dihydridotetracarbonyl.

The infrared spectrum of $OsH_2(CO)_3P(C_6H_5)_3$ has three main carbonyl stretching vibrations (2 A′ + A″) and two metal–hydrogen stretching vibrations (A′ + A″) (see Table I and Figure 2). This rules out structure **3**. We are therefore left with structure **2** of symmetry C_s which is in agreement with both the nmr and the infrared data. In the infrared spectrum of the dideuterido derivative $OsD_2(CO)_3P(C_6H_5)_3$ all three CO stretching vibrations are shifted to lower wavenumbers with respect to the nondeuterated compound. This is again explained by a phenomenon of resonance interaction of the type indicated above. The two metal–deuterium stretching vibrations were not easy to detect because of interference with bands of the solvent or of triphenylphosphine. In halocarbons, however, one band at 1417 cm^{-1} is observed and the second metal–deuterium stretching appears as a shoulder at 1434 cm^{-1} (Table I). The isotopic frequency ratios observed (1.363 and 1.357) are slightly lower than expected but still in the range of the isotopic shifts observed for interacting vibrational states.[9]

It is interesting to notice that by operating with a large excess of the liquid tri-*n*-butylphosphine, nmr evidence for the presence of a disubstitution product was obtained. Besides a doublet centered at τ 18.97 with J = 25 cps, a second resonance at τ 19.42 was observed, the latter being split into a triplet. These results can be explained by the formation of both a monosubstitution product of structure similar to **2** and a bisubstitution product. A possible structure which can account for the observed triplet is **5**. This suggests that the second phosphine molecule enters *trans* to the first in the monosubstituted compound.



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(b) **Substitution of Hydrogens.**—Although the chemical evidence suggests relatively strong metal–hydrogen bonds in $OsH_2(CO)_4$, the two hydrogens can be replaced very readily by halogen ligands upon reaction with carbon tetrachloride and carbon tetrabromide. Such a reaction is typical of complexes having direct metal–hydrogen bonds and is known to take place in platinum hydride chemistry. For example[17] *trans*-$PtCl_2(P(C_2H_5)_3)_2$ is obtained from *trans*-$PtHCl(P(C_2H_5)_3)_2$ with carbon tetrachloride. The infrared spectra of $OsCl_2(CO)_4$ and $OsBr_2(CO)_4$ in the carbonyl stretching region (see Table I) are consistent with a *cis*-octahedral configuration of symmetry C_{2v} for the two compounds. These dihalogenotetracarbonylosmium derivatives were already synthesized some years ago by Hieber and Stallmann[18] by carbonylation of osmium halides in the presence of copper. Whereas these authors report the isolation of a yellow and a colorless $OsBr_2(CO)_4$, indicating the presence of *cis* and *trans* isomers, we did not find any evidence of isomerization in solution.

The *cis*-dibromotetracarbonylosmium compound was also obtained by direct reaction of bromine with pentacarbonylosmium. A similar reaction of pentacarbonylruthenium has been reported previously.[1]

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On the Interaction of CO Stretching Modes in Metal Carbonyls. Effect on Intensity[1a,b]

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Calculations based on a recent analysis of the force constants for CO vibrations in $M(CO)_5X$ derivatives confirm that the observed intensity ratio for the A_1 modes cannot be accounted for solely through vibrational coupling. The improved force constants have made it possible to calculate from the intensity data both an angle between oscillators, θ, and the effective dipole moment derivative for each of the chemically different CO groups. We have also calculated from the intensities of the all-^{12}CO derivatives the expected intensities of ^{13}CO-substituted molecules, from which the concentration of various specifically labeled species can be deduced. Finally it is shown that the observed infrared frequencies for *cis*-disubstituted tetracarbonyl derivatives $M(CO)_4X_2$ require a minimum ratio between the force constants k_c/k_c' which must be greater than 1.00.

I. Introduction

The relative intensities of the CO absorptions in $M(CO)_5X$ derivatives of C_{4v} symmetry were first discussed by Orgel[2] and by El-Sayed and Kaesz.[3] Several further treatments of these have appeared recently,[4–7] each of which has been handicapped by lack of the necessary vibrational data. A recently completed improved vibrational analysis of pentacarbonyl derivatives using isotopically labeled molecules[1b,8] and absorption data measured by Abel and Butler[9] enables us now to discuss with greater detail the intensities of the carbonyl stretching modes in these derivatives.

II. The Effect of Vibrational Coupling

The four carbonyl modes of $M(CO)_5X$ molecules and the secular equations for these vibrations have been given before.[8] The observed frequencies of the A_1 modes are related to the force constants through the equations

$$\lambda(1) = G(k_1 - 2k_c \tan \phi) \qquad (1)$$

$$\lambda(2) = G(k_2 + 2k_c' + k_t + 2k_c \tan \phi) \qquad (2)$$

where $\lambda = 5.888 \times 10^{-7}\nu^2$, $G = (1/m_c) + (1/m_o) = 0.145757$, and ϕ is defined as

$$\phi = \frac{1}{2} \tan^{-1} \frac{4k_c}{k_2 + 2k_c' + k_t - k_1} \qquad (3)$$

The normal coordinates are usually expressed in terms of the symmetry coordinates

$$q(1) = L_{11}q(\mathrm{a}) + L_{21}q(\mathrm{r}) \qquad (4)$$

$$q(2) = L_{12}q(\mathrm{a}) + L_{22}q(\mathrm{r}) \qquad (5)$$

The mixing coefficients can be conveniently expressed in terms of ϕ

$$L_{11} = L_{22} = \sqrt{G} \cos \phi \qquad (6)$$

$$L_{12} = -L_{21} = \sqrt{G} \sin \phi \qquad (7)$$

To the extent that vibrational coupling is exclusively responsible for the distribution of intensity between the two A_1 modes, each will be directly proportional to the amount of $A_1(a)$ character it possesses (in this model

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