TABLE I

INFRARED DATA[a]

ν(C–O), cm.$^{-1}$		ν(M–O) (M = P or As), cm.$^{-1}$	
cis-$Mo((C_6H_5)_3PO)_2(CO)_4$			
2006 w, 1878 vs, 1845 s, 1797 vs		1156 m 1148 s	1152
cis-$Mo((C_6H_5)_3AsO)_2(CO)_4$			
2003 w, 1883 vs, 1850 s, 1792 vs		880 m 868 s	874
cis-$Mo((C_6H_5)_3PO)_3(CO)_3$			
1898 m, 1757 s 1733 s	1745	1206 sh 1192 s 1185 sh 1171 s	1188
cis-$W((C_6H_5)_3PO)_3(CO)_3$			
1883 m, 1745 s 1721 s	1733	1183 s 1161 m	1172

[a] ν(P–O) for $(C_6H_5)_3PO$ is 1190 cm.$^{-1}$, ν(As–O) for $(C_6H_5)_3AsO$ is 880 cm.$^{-1}$. The spectra were recorded as Nujol mulls.

parison with values for other complexes of the same compositions.[6–8] This indicates that the phosphine and arsine oxides have relatively low π accepting capacities. Two ν(P–O) and ν(As–O) absorptions are found for the complexes $Mo((C_6H_5)_3PO)_2(CO)_4$ and $Mo((C_6H_5)_3AsO)_2(CO)_4$, as expected for a *cis* configuration. In the case of the phosphine oxide complexes of molybdenum the average ν(P–O) frequency increases from 1152 cm.$^{-1}$ in $Mo((C_6H_5)_3PO)_2(CO)_4$ to 1188 cm.$^{-1}$ in $Mo((C_6H_5)_3PO)_3(CO)_3$. This latter value is high by comparison with other transition metal phosphine oxide complexes[9] and is probably associated with weak σ bonding from the P–O group to the zerovalent molybdenum.

Experimental

Cycloheptatrienemolybdenum tricarbonyl and tricarbonyltris(methyl cyanide)molybdenum were prepared by methods previously reported in the literature.[10,11] Triphenylarsine oxide was prepared by oxidation of Eastman triphenylarsine with hydrogen peroxide. Triphenylphosphine oxide, molybdenum hexacarbonyl, and tungsten hexacarbonyl were obtained from L. Light and Co. Ltd.

Tricarbonyltris(triphenylphosphine oxide)molybdenum.—A hot saturated solution of 0.58 g. of $(C_6H_5)_3PO$ in benzene was added to a cold saturated solution of 0.19 g. of cycloheptatrienemolybdenum tricarbonyl in benzene and refluxed under nitrogen for 4 hr. A yellow product separated on the sides of the flask. The impure product was recrystallized by heating with benzene (15 ml.) to 110° for 6 hr. in an evacuated sealed tube.

Anal. Calcd. for $Mo((C_6H_5)_3PO)_3(CO)_3$: C, 67.50; H, 4.44; Mo, 9.46. Found: C, 67.02; H, 4.71; Mo, 9.96.

This complex was also isolated from the direct reaction of $(C_6H_5)_3PO$ with $Mo(CO)_6$ (3:1) in a benzene–petroleum ether mixture. The complex is stable in air for several days.

Tetracarbonylbis(triphenylphosphine oxide)molybdenum.—A hot saturated solution of 3.2 g. of $(C_6H_5)_3PO$ in diethylene glycol dimethyl ether (diglyme) was added to a hot saturated solution of 1 g. of $Mo(CO)_6$ in benzene. The solution was refluxed under nitrogen for 1.5 hr. A yellow-brown product separated from the solution. This product was recrystallized from benzene (15 ml.) in a sealed tube heated to 120°.

Anal. Calcd. for $Mo((C_6H_5)_3PO)_2(CO)_4$: C, 62.90; H, 3.93; Mo, 12.59. Found: C, 62.82; H, 4.08; Mo, 12.49.

This compound was also isolated from the reaction of tricarbonyltris(methyl cyanide)molybdenum with $(C_6H_5)_3PO$ in benzene under nitrogen and the reaction of $(C_6H_5)_3PO$ with an excess of $Mo(CO)_6$ in a benzene–petroleum ether mixture. The complex is stable in air for several days.

Tricarbonyltris(triphenylphosphine oxide)tungsten.—A hot saturated solution of 2.38 g. of $(C_6H_5)_3PO$ in diglyme was added to a hot saturated solution of 1 g. of $W(CO)_6$ in benzene and the solution refluxed under nitrogen for 5 hr. A small amount of an orange compound separated on the sides of the reaction flask. Insufficient material was obtained for analyses, but an X-ray powder photograph of the compound showed that it was isomorphous with tricarbonyltris(triphenylphosphine oxide)molybdenum. The complex is less stable in air than the corresponding molybdenum compound.

Tetracarbonylbis(triphenylarsine oxide)molybdenum.—A mixture of 0.96 g. of $(C_6H_5)_3AsO$ and 0.3 g. of tricarbonyltris(methyl cyanide)molybdenum was refluxed in benzene (40 ml.) under nitrogen for about 10 min. A small amount of an orange solid separated. The X-ray powder photograph of this solid showed that it was isomorphous with the corresponding $(C_6H_5)_3PO$ complex, tetracarbonylbis(triphenylphosphine oxide)molybdenum. The compound is less stable in air than the phosphine oxide complex.

Microanalyses for carbon and hydrogen were carried out by Dr. A. D. Campbell at the Microanalytical Laboratory, University of Otago. Molybdenum was determined by fusing 0.1 g. of compound with 0.2 g. of NaOH, 0.5 g. of Na_2CO_3, and 0.25 g. of Na_2O_2 in a nickel crucible, extracting the residue with water, and precipitating the molybdenum as the oxime with 8-hydroxyquinoline.

Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer Model 221 spectrometer, except that in the case of $Mo((C_6H_5)_3AsO)_2(CO)_4$ the ν(C–O) values were determined on a Perkin-Elmer Infracord.

The X-ray powder photographs were recorded with a Philips Debye–Scherrer powder camera (diameter 11.483 cm.) and the cell dimensions and space group for $Mo((C_6H_5)_3PO)_2(CO)_4$ were determined from oscillation, Weissenberg, and precession photographs. The density was determined by flotation.

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Raman Studies of Hydrido- and Deuteriorhenium Tetracarbonyl Trimer[1]

BY J. M. SMITH,[2] W. FELLMANN,[2] AND L. H. JONES[3]

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In a previous study the trimer of rhenium tetracarbonyl was found to be diamagnetic, suggesting the

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presence of hydrogen in the compound.[4] This was supported by chemical analysis, which indicated about one hydrogen per rhenium, and the compound was formulated[4] as $[Re(CO)_4H]_3$. Subsequently a proton resonance was observed on a broad-line spectrometer.[5] In the original work[4] the infrared spectra were compared for the hydride and deuteride; cyclohexane solutions were used for the CO stretching region and KBr disks were used for the rest of the spectrum. Surprisingly, the spectra of the hydride and deuteride showed only minor differences, and no evidence of a hydrogen stretching frequency was found.

In the present work, Raman spectra were measured for the hydride and deuteride. In the solid state rather striking shifts were observed in the CO stretching region. Also there is some evidence for a metal–hydrogen stretching band at the rather low frequency of 1100 cm.$^{-1}$. In an attempt to support the interpretation of the Raman spectra more detailed infrared studies of the solid in KBr disks were made. The hope was to observe a metal–hydrogen stretching frequency and to explain the shifts in the CO stretching frequencies.

Experimental

Preparation.—The trimeric tetracarbonyl hydride and deuteride of rhenium were prepared by the method of Huggins, *et al.*[4] Completeness of deuteration in the deuteride was checked on one small sample by using $NaBD_4$ in the reduction step as well as D_3PO_4 in the acidification step. The infrared spectrum of this sample in a KBr disk is identical with that found for deuterated samples obtained using $NaBH_4$ and D_3PO_4.

Recording of Raman Spectra.—Raman spectra were obtained on a Cary Model 81 Raman spectrometer, using the standard 5-ml. sample tubes for solution spectra and a conical vessel based on a design supplied by Busey and Keller[6] for spectra of the solids. Saturated solutions of the hydride and deuteride in cyclohexane gave very weak spectra, due to the low solubility of the compounds (about 1.5×10^{-3} *M*). However, we were able to observe the strong Raman shifts and these are listed in Table I.

TABLE I

RAMAN SPECTRA (CM.$^{-1}$) OF CYCLOHEXANE SOLUTIONS[a]

$[Re(CO)_4H]_3$	$[Re(CO)_4D]_3$
2125	2125
2023	2023
1983	1982

[a] Concentration is about 1.5×10^{-3} *M*. Raman peaks are all weak due to low concentration.

Spectra of the solid samples were quite intense. The CO stretching region is shown in Figure 1. Tabulated values are given in Table II.

Recording of Infrared Spectra.—Infrared spectra were obtained on a Perkin-Elmer Model 521 infrared grating spectrometer using the KBr pellet technique and 1.0 and 0.4 mm. KBr solution cells. Pellet concentrations of about 0.1 to 0.3 mg./100 mg. of KBr were used for the carbonyl stretching region, and about 10 to 20 mg./100 mg. for the region 700 to 1200 cm.$^{-1}$. Saturated cyclohexane solutions were used for the solution spectra. We were prompted to re-examine the infrared spectra after observing what might possibly be assigned as metal–hydrogen and metal–deuterium absorptions at 1100 and 787 cm.$^{-1}$, respectively, in the Raman spectra. Also, it was desirable to obtain infrared spectra of the carbonyl stretching region for the solids for comparison with the excellent Raman spectra of these samples. The carbonyl stretching frequencies are shown in Figure 2 and tabulated in Table III.

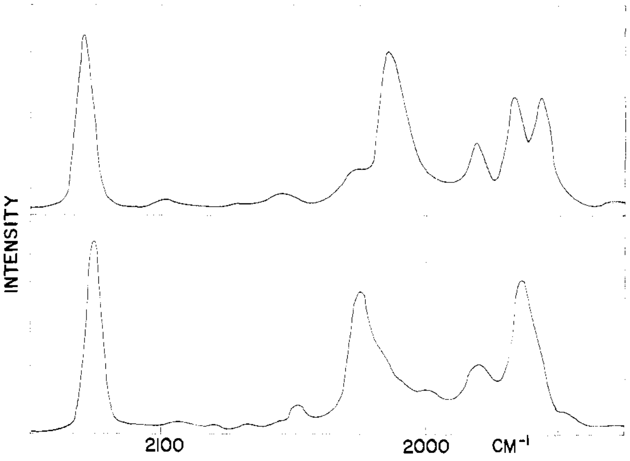

Figure 1.—Raman spectra of solid $[Re(CO)_4H]_3$ (upper curve) and solid $[Re(CO)_4D]_3$ (lower curve).

TABLE II

RAMAN SPECTRA OF SOLID $[Re(CO)_4H]_3$ AND $[Re(CO)_4D]_3$

H		D	
ν, cm.$^{-1}$	Int.[a]	ν, cm.$^{-1}$	Int.[a]
2127	31	2124	53
2095	1	2093	1.5
2058	2	2047	6
2025	4	2023	35
2012	27	2015	10 sh?
(2007 sh?)		2000	4 ?
1979	7.5	1979	12
1965	19	1962	43
1954	19	1956	5–10 sh?
1928	0.5	1946	2– 4 ?
1100	v br; vw	787	13 br
622	5	621	10
560	2.5	563	2.5
491	100	487	100
		478	63 sh
452	18 sh	452	25
420	2.5	421	5
371	7.5	372	10
170	...	169	5
147	...	145	5
		104	7
91	...	91	5
81	5	77	9

[a] The intensities are normalized to 100 for the most intense band for each molecule.

Discussion

The search for a metal–hydrogen stretching frequency was only partially successful. A very weak and very broad band was observed at 1100 cm.$^{-1}$ in the Raman spectrum of $[Re(CO)_4H]_3$. This was not present for the deuteride, for which a new Raman band appeared at 787 cm.$^{-1}$. The shift from 1100 to 787 cm.$^{-1}$ is quite reasonable for a Re–H → Re–D vibration. The hydride band is much broader than the deuteride band, perhaps because the greater amplitude of the H atom vibration leads to more interaction with the environment. It is reasonable to assign 1100

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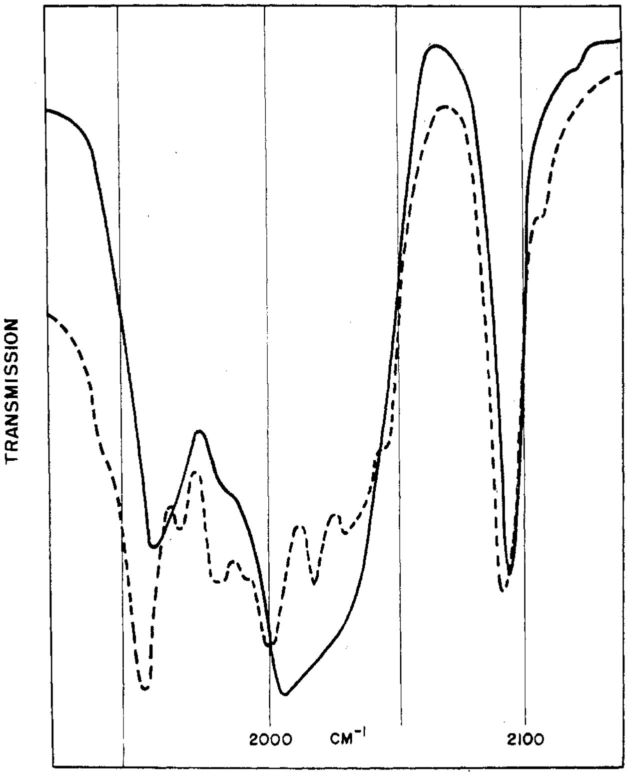

Figure 2.—Infrared spectra of KBr disks of $[Re(CO)_4H]_3$ (solid line) and $[Re(CO)_4D]_3$ (dashed line).

TABLE III
INFRARED SPECTRA OF SOLID $[Re(CO)_4H]_3$ AND $[Re(CO)_4D]_3$ IN CO STRETCHING REGION

$[Re(CO)_4H]_3$		$[Re(CO)_4D]_3$	
ν, cm.$^{-1}$	Int.[a]	ν, cm.$^{-1}$	Int.[a]
2095	m	2093	m
		2045	w
2030	m, sh	2030	m
		2018	m
2005	s	2000	s
1985	w, sh	1982	m
		1970	w
1962	m	1958	s

[a] Intensities are rough estimates: s, strong; m, medium; w, weak; sh, shoulder.

cm.$^{-1}$ as a rhenium–hydrogen stretching frequency.[7] We believe this to be a vibration involving a hydrogen bridge between two rhenium atoms (Re–H–Re), as postulated previously.[4] Such an assignment is consistent with the unusually low value of the hydrogen stretching frequency and constitutes the first reported observation of a bridging hydrogen between two transition metal atoms.

In the Raman spectra of the solids, rather striking differences appear in the CO stretching region. For example, peaks at 2012 and 1954 cm.$^{-1}$ for the hydride are shifted to 2023 and 1962, cm.$^{-1}$ respectively, for the deuteride. There are other less dramatic changes also. In the infrared spectrum the shifts are somewhat less pronounced and more difficult to assign because of the number of peaks. The shifts specified above for the CO stretching region are too small, and in the wrong direction, for a hydrogen vibration. However, we can certainly conclude that the substitution of deuterium for hydrogen has led to definite changes in the CO stretching frequencies. Thus the hydrogen (or deuterium) is part of the molecular entity.

A reasonable explanation of the shifts in CO stretching frequencies can be offered. The Re–H stretching vibration at 1100 cm.$^{-1}$ may have an overtone, or combination with another Re–H frequency, in the 2000–2100 cm.$^{-1}$ region. This overtone or combination could then interact through Fermi resonance with nearby CO stretching vibrations of proper symmetry, depressing their frequencies. For the deuteride the analogous overtone, or combination, would be out of the CO stretching region and thus would not interact.

It is surprising that the Raman solution spectra of the hydride and deuteride do not show the differences brought out in the spectra of the solids. Thus from the three peaks reported in Table I it would be impossible to distinguish hydride from deuteride. In the infrared[4] the differences are very slight for solutions of the hydride and deuteride. Apparently the hydrogen stretching frequency interacts with the CO stretching frequencies only weakly in solution but quite strongly in the solid. This may be because the symmetry is lower in the solid than in solution, giving increased possibility of Fermi resonance.

NOTE ADDED IN PROOF.—The highest observed Raman frequency (2125 cm.$^{-1}$, strong) and the highest observed infrared frequency (2093, strong),[4] in aqueous solution, can be assigned as the $A_1{}^1$ and E^1 vibrations, derived from the axial A_1 mode of the hypothetical isolated $Re(CO)_4$ group.[8] A fuller analysis[9] shows that the A_1 mode is split due to interaction of carbonyl groups on different metal atoms. A similar phenomenon is found in $Mn_2(CO)_{10}$,[10] but the interaction is stronger in these molecules (which contain a direct metal–metal bond) than in $[Re(CO)_4H]_3$ (in which the metal–metal bonds are almost certainly hydrogen-bridged).

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[7] Unfortunately the infrared spectra showed only very weak and ill-defined absorptions in this region, even using saturated solution in 1-mm. cells and concentrated KBr pellets. Thus they offered no further support to such an assignment.

[8] Assignments were made assuming D_{3h} symmetry. See ref. 4, Figure 1b, and related discussion in the text.

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On the Structure of Germanium Selenide and Related Binary IV/VI Compounds

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It is known that certain binary compounds exhibit the structural characteristics of the elements in their