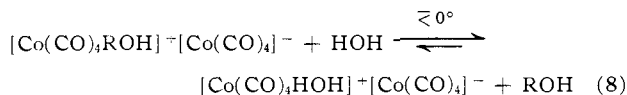


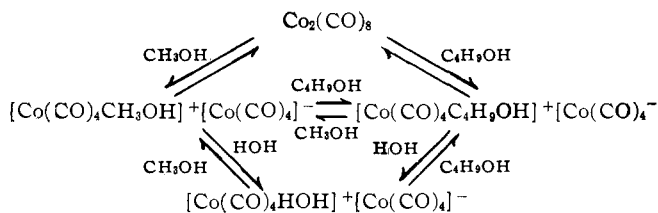
as a catalyst in facilitating decomposition of dicobalt octacarbonyl.

The following generalized equation may be written for the displacement of primary alcohols from the dicobalt octacarbonyl-alcohol complex with water.



The limitation placed upon the exchange reaction given in eq. 8 is that the alcohol complex be reasonably water-soluble for the displacement of the alcohol to occur. Thus, it is possible to interchange low molecular weight straight-chain primary alcohol complexes, such as methanol, ethanol, 1-propanol, and 1-butanol, quite readily with water. The exchange reaction with water becomes slightly more difficult as the carbon number increases in the series. However, when we reach 1-pentanol, the solubility of the dicobalt octacarbonyl complex in water is quite low, and by the time the carbon number in the alcohol complex reaches six, it is insoluble in water.

It was previously concluded that the inability to simply water extract dicobalt octacarbonyl from the 1-octanol complex was due to the high water insolubility of this complex. To check the validity of this conclusion, reactions between dicobalt octacarbonyl and excess 1-butanol were studied. Since 1-butanol is far more soluble in water than 1-octanol, one might predict a simple water extraction of the 1-butanol complex to be feasible. Indeed, this appears to be the case. The results of extracting this complex with water, or a water-methanol solution, are shown in Fig. 1. As noted from the graph, a simple water extraction was found to be quite effective since 83% of the cobalt ion was extracted into the aqueous phase. The addition of very small amounts of methanol (*ca.* 0.5 vol. %) does appear to improve the water-extraction process slightly by about 10%. Both the 1-butanol and the aquo complex of dicobalt octacarbonyl appear to be fairly water-soluble. The major ligand-exchange reactions, which are probably occurring in this system at low temperatures, may be represented as



It may also be noted from Fig. 1 that large quantities of methanol are detrimental to the water extraction of dicobalt octacarbonyl from the 1-butanol complex.

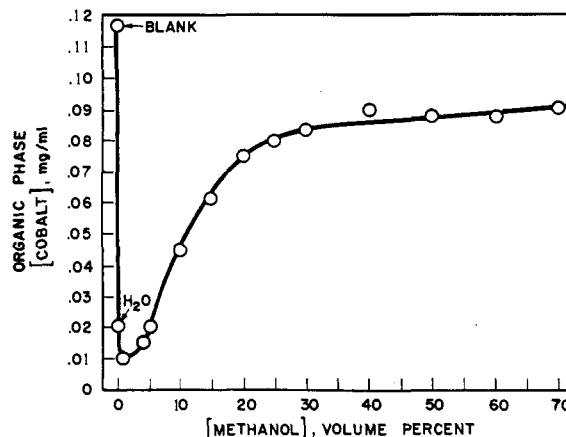


Fig. 1.—Extraction of $[\text{Co}(\text{CO})_4(\text{C}_4\text{H}_9\text{OH})]^+$, $[\text{Co}(\text{CO})_4(\text{CH}_3\text{OH})]^-$, and $[\text{Co}(\text{CO})_4]^-$ by methanol-water mixtures.

This occurrence is not surprising since the system is approaching that of a homogeneous solution rather than remaining a two-liquid-phase system. It has been observed in this work that the extraction of dicobalt octacarbonyl-alcohol complexes with a water-methanol (< 0.5 vol. %) solution is more applicable and effective when high molecular weight, primary alcohols, such as 1-heptanol, 1-octanol, or 1-decanol, are complexed to dicobalt octacarbonyl.

Acknowledgment.—The authors wish to thank Mr. H. J. Elder for preparing the dicobalt octacarbonyl, Drs. W. E. Mott and H. A. Braier for their helpful suggestions and assistance with the radiochemical experiments, and Miss E. L. Derusha for performing the cobalt carbonyl analysis.

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A Polynuclear Tetracarbonyl Hydride of Rhenium. Preparation and Properties^{1a,b}

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The preparation and properties of a new polynuclear carbonyl hydride of rhenium are reported. The compound is isolated from the treatment of $\text{Re}_2(\text{CO})_{10}$ with excess NaBH_4 in tetrahydrofuran with subsequent acidification in the presence of cyclohexane. The compound is colorless, crystalline, and diamagnetic; molecular weight and analyses fit the formula $[\text{HRe}(\text{CO})_4]_3$. Infrared spectra of this compound and its deuterated derivative, in the region 3000–290 cm^{-1} , are presented and discussed. The compound is believed to be analogous to a derivative of technetium, reported earlier from these laboratories, with which it is isomorphous in the crystalline state.

Introduction

A polynuclear tetracarbonyl of Tc was recently reported² which was obtained as a by-product in the syn-

(1) (a) This work has been supported by Grant No. GP 1696 from the National Science Foundation; (b) Paper No. 28, Symposium on Metal Carbonyls and Related Complexes, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964.

thesis of $\text{HTc}(\text{CO})_5$.³ We have now discovered what we believe to be an analogous derivative of Re which we have been able to isolate from the same reaction sequence. Our first preparation of the polynuclear

(2) H. D. Kaesz and D. K. Huggins, *Can. J. Chem.*, **41**, 1250 (1963).

(3) J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, **1**, 933 (1962).

tetracarbonyl of Re followed essentially the same procedure as described for the compound of Tc,² with one exception: since it was more difficult to bring about CO cleavage from $\text{Re}_2(\text{CO})_{10}$ than from $\text{Tc}_2(\text{CO})_{10}$, it was necessary to warm the reaction mixture (tetrahydrofuran solution in contact with Na-Hg) to reflux in the initial step. The yields, however, were low. Since there had been reports of the action of NaBH_4 on $\text{Mn}_2(\text{CO})_{10}$,⁴ or $\text{Fe}(\text{CO})_5$,⁵ to form lower carbonyl hydrides or carbonyls, we were prompted to try this reagent instead of Na-Hg in the initial step. After acidification, we obtained the same product but in greatly increased yields. We will therefore describe the synthesis of the polynuclear tetracarbonyl of Re by the NaBH_4 method.

In order to establish whether our derivative contained hydrogen and at the same time identify any bands which might be associated with vibrations involving that atom, a deuterated derivative was sought. An attempted exchange of protons by treatment of the rhenium derivative with the mixed solvent system D_2O -tetrahydrofuran (3% D_2O by volume) led to a recovered product which had an identical infrared spectrum with the starting material. A more vigorous chemical transformation, however, was found to be successful. The similarity of the product obtained through the deuteration cycle with the original product was ascertained through a comparison of X-ray powder diffraction spectra.

Experimental

All operations during the synthesis of the carbonyl derivative of Re were carried out under an inert atmosphere; while the final product turned out to be air stable, certain of the intermediates were decidedly not.

Preparation of a Polynuclear Tetracarbonyl of Re.—In a typical preparation, $\text{Re}_2(\text{CO})_{10}$ (2.0 g., 3.07 mmoles) and NaBH_4 (1.6 g., 42.2 mmoles) were dissolved in 50 ml. of tetrahydrofuran (dried over CaH_2 and redistilled under N_2) and stirred with reflux for 4 hr. The solution turned yellow at first, then orange, and finally red, with gas evolution. After cooling to room temperature, the NaBH_4 was allowed to settle and the solution was decanted from the solids. The solvent was evaporated under reduced pressure, and the resulting solids were pumped under high vacuum for 2 hr. (30–35°) to remove final traces of solvent. Cyclohexane (80 ml., redistilled from CaH_2 under N_2) and sirupy H_3PO_4 (10 ml., stripped of dissolved O_2 by prolonged bubbling of N_2 and treatment with a few drops of Na-Hg) were then added over the solids. The heterogeneous system was refluxed for 2 hr. (Optimum yields of the desired product are obtained only upon prolonged heating as in the liquid-liquid extraction step, mentioned below.) Infrared spectra in the carbonyl stretching region of the cyclohexane solution before reflux showed the presence of a number of unidentified bands which could belong to some precursor to the desired product. We believe we have isolated such an intermediate in the form of yellow crystals which are under study. The heterogeneous system was then subjected to liquid-liquid extraction with hot cyclohexane until the supernatant liquid over the phosphoric acid solution no longer showed the presence of product. Upon cooling, colorless crystals were obtained from the mother liquor which were separated and recrystallized from cyclohexane once or twice to give essentially pure product; yield 850 mg., or 46% based on $\text{Re}_2(\text{CO})_{10}$.

Anal. Calcd. for the empirical formula $[\text{HRe}(\text{CO})_4]_n$: Re, 62.23; C, 16.05; H, 0.34. Found: Re, 61.12; C, 16.04; H, 0.30.⁶ Confirmatory evidence for the presence of H was obtained from the infrared spectra of deuterated material (see below).

(4) W. Hieber, W. Beck, and G. Zeitler, *Angew. Chem.*, **73**, 364 (1961).

(5) D. T. Haworth and J. R. Huff, *J. Inorg. Nucl. Chem.*, **17**, 184 (1961).

(6) Special precautions were taken to increase accuracy in analysis for H. Solvent was pumped away for a prolonged period under vacuum; contact with filter paper and other possible contaminants containing hydrogen was avoided, and blank runs were performed before and after the analyses to determine background, if any. Analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and by Miss Heather King of this department.

Preparation of a Deuterated Derivative.—A quantity of trimer (500 mg.) was treated with sodium amalgam in tetrahydrofuran under inert conditions which resulted in a slightly pale yellow solution whose infrared absorptions no longer resembled the pattern of the original product. Then solvent was removed, cyclohexane brought in, and the mixture acidified with sirupy D_2PO_4 (99% pure, as prepared from D_2O and P_2O_5 ,^{7a} and checked by n.m.r. for residual protons^{7b}). After a brief period of reflux to bring the formation of trimer to completion, a product was extracted from the heterogeneous mixture and recrystallized. It is possible to achieve recovery of 34% of the deuterated product; most of the losses, we feel, are incurred through handling of the small amounts reported here. The product was analogous to starting material; it had the molecular weight of a trimer and an X-ray powder pattern closely resembling starting material (see below). Also, infrared absorptions (discussed below) showed certain significant differences which could be attributed only to the presence of hydrogen in the original product which was replaced by deuterium by the chemical treatment mentioned above. The deuterated product did not exchange with protons in air or even in the mixed solvent water-tetrahydrofuran.

Molecular Weight Measurements.—On account of the very low solubility of our new derivative in the normal solvents, we found it necessary to calibrate our instrument for the concentration range in which our unknown was found to lie. We used a Mechrolab vapor pressure osmometer, with cyclohexane solutions, and benzil as a standard. Curiously enough, our derivatives of rhenium were even less soluble in benzene than in cyclohexane. Our data are presented in Table I.

TABLE I
MOLECULAR WEIGHT DATA

Compound	Concn., ^a mg./g.	ΔR (av.) ^b ohms	Molality $\times 10^3$	Mol. wt.	
				Obsd.	Calcd.
Benzil	5.400	10.47	25.7		210.23
Benzil ^c	1.080	2.30	5.14		210.23
Benzil ^c	0.540	1.25	2.57		210.23
Benzil ^c	0.1080	0.25	0.514		210.23
Rhenium tetracarbonyl hydride trimer	1.285	0.64	1.40	917 ± 50	897.8
Deuteride trimer	1.247	0.62	1.33	938 ± 50	901.8
$\text{Re}_2(\text{CO})_{10}$ ^d	1.300	0.87	1.9	685 ± 40	652.5

^a Cyclohexane solutions; for greatest accuracy, solutions were made up by weight using an analytical balance. Owing to the evaporation of solvent over longer periods of time on storage in ordinary volumetric flasks, solutions were utilized immediately after they were made. ^b The average represents five or more readings, taken only when the instrument was observed to be stable, that is, when the deviation within the readings was no more than ±1% for concentrated solutions, or up to ±5% on the most dilute samples. ^c Obtained by dilution of first listed sample. ^d Measured at these high dilutions expressly for the purpose of comparing with unknown, at the operating limits of the instrument.

Magnetic Susceptibility.—An early determination of the susceptibility of the trimer was carried out with a 90-mg. sample by Mr. Peter Wooliams on a Gouy microbalance at the Chemical Laboratories of University College, London, through the kindness of Professor R. S. Nyholm. The measurements showed that the compound was essentially diamagnetic, though under several different packings slight pulls were nevertheless observed. Owing to the stability in air of our derivatives, we had purified the sample without precautions to exclude oxygen. These results therefore led us to attempt a further purification under an inert atmosphere, leaving us finally with a highly purified sample, but of greatly reduced weight. It was necessary to make use of an instrument on which samples of about 15–20 mg. could be meas-

(7) (a) N. N. Greenwood and A. Thompson, *Inorg. Syn.*, **6**, 81 (1960).

(b) The analysis was performed by adding precisely known amounts (by weight) of H_3PO_4 (85%, Baker and Adamson analyzed reagent grade) to the sample and plotting the total signal amplitude against added protons on the Varian A-60 nuclear magnetic resonance spectrometer. Extrapolation to zero signal gives the amount of protons originally present, similar to the analysis of D_2O ; cf. "This is NMR at Work," advertisement series of Varian Associates No. 57, which appeared on the back cover of *J. Am. Chem. Soc.*, and occasionally other journals, or available directly from the manufacturer in "Technical Information Bulletin," Vol. 2, No. 4, 1959.

TABLE II

Temp., °K.	Wt.		Differ- ence, mg.	Av. differ- ence, mg.	RMS devia- tion, mg.	Diamag- netic ^b corr.	Corr. av. wt. dif- ference, mg.	Sample wt., mg.	$\chi_H \frac{dH}{dx}$	$\left(\frac{H}{dx} \frac{dH}{dx}\right)^{-1}$ $\times 10^{10}$	χ_g
	in field, mg.	out of field, mg.									
299	0.8290	0.8784	-0.0494	-0.0488	± 0.0004	+0.0491 (± 0.0002)	+0.0003 (± 0.0006)	12.754	2.3×10^{-5}	2.512	$+0.006 \times 10^{-6}$ ($\pm 0.012 \times 10^{-6}$)
	0.8294	0.8778	-0.0484								
	0.8293	0.8783	-0.0490								
	0.8297	0.8785	-0.0488								
	0.8291	0.8777	-0.0486								
78.5	0.8385	0.8878	-0.0493	-0.0487	± 0.0006	+0.0491 (± 0.0002)	+0.0004 (± 0.0008)	12.754	3.1×10^{-5}	2.512	$+0.008 \times 10^{-6}$ ($\pm 0.016 \times 10^{-6}$)
	0.8443	0.8927	-0.0484								
	0.8482	0.8975	-0.0493								
	0.8529	0.9010	-0.0481								
	0.8616	0.9100	-0.0484								

^a Obtained through the courtesy of Professor T. S. Piper, Department of Chemistry, University of Illinois, Urbana, Ill.; measurements carried out at the University of Illinois by Mr. David Lloyd, whose help we gratefully acknowledge. ^b Correction for sample bucket. ^c From measurements on standard, $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$.

TABLE III
X-RAY DIFFRACTION DATA

$\text{Re}_3(\text{CO})_{12}\text{H}_3$	$\text{Re}_3(\text{CO})_{12}\text{D}_3$	$\text{Os}_3(\text{CO})_{12}$
8.124 ^a (1) ^b	8.162 ^a (2) ^b	7.381 ^a (2) ^b
7.583 (2)	7.634 (4)	7.219 (9)
7.213 (10)	7.237 (10)	7.031 (9)
6.794 (2)	6.794 (3)	6.779 (3)
6.758 (2)		6.607 (5)
6.554 (2)	6.549 (3)	5.491 (10)
	5.890 (2)	5.173 (1)
5.651 (3)	5.669 (4)	4.303 (1)
4.062 (1)	4.069 (2)	4.075 (1)
	3.959 (2)	3.798 (3)
3.590 (1)	3.600 (2)	3.577 (1)
	3.587 (2)	3.431 (2)
3.484 (2)	3.484 (3)	3.357 (2)
3.473 (1)	3.420 (1)	3.292 (1)
3.377 (1)	3.376 (1)	3.220 (1)
	3.335 (2)	3.211 (2)
	3.255 (2)	3.166 (1)
3.149 (2)	3.150 (3)	3.015 (2)
3.037 (2)	3.036 (4)	2.953 (6)
3.032 (2)		2.905 (1)
3.013 (2)		2.771 (3)
2.932 (1)	2.938 (2)	2.739 (2)
2.860 (2)	2.863 (2)	2.696 (1)
	2.378 (2)	2.557 (1)
	2.249 (1)	2.532 (2)
	2.130 (2)	2.242 (1)
2.028 (2)	2.030 (2)	2.159 (1)
2.023 (2)		2.128 (1)
1.972 (1)		2.098 (1)
1.967 (1)		1.977 (1)
	1.624 (1)	1.905 (3)
		1.889 (1)
		1.873 (1)

^a *d*-Spacings. ^b Visually estimated intensity.

ured, and this was kindly made available to us by Professor Piper of the University of Illinois. The results of the determination, performed on a Faraday⁸ microbalance, are presented in Table II. The observed susceptibility given in the last column of the table is small, positive, and temperature independent in the range studied. The results for the highly purified sample essentially bore out the observations on the initial sample, so only the data for the former are presented here.

Molecular diamagnetism is characterized by a small susceptibility, is temperature independent, and may have either a negative or a positive value.⁹ By estimating diamagnetic corrections

(8) W. E. Hatfield, R. C. Fay, C. E. Pfluger, and T. S. Piper, *J. Am. Chem. Soc.*, **85**, 265 (1963).

(9) P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1956, p. 83.

from the best available information to date (which is none too good for atoms or groups of atoms in carbonyl derivatives), we would predict a susceptibility of $\chi_g = -0.254 \times 10^{-6}$.¹⁰ When subtracted from the observed susceptibility this leaves a net residual paramagnetic susceptibility $\chi_g^{\text{corr}} = +0.260 \times 10^{-6}$. The compound therefore does not possess any unpaired electrons and may be termed essentially diamagnetic. Also, a tally of electrons around the metal is consistent with the effective atomic number rule of Sidgwick.

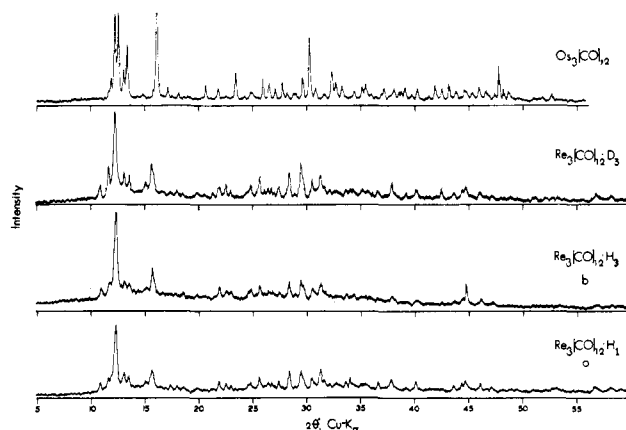


Fig. 1.—X-Ray powder patterns: $\text{Re}_3(\text{CO})_{12}\text{H}_3$ (a) product obtained from original reaction mixture; (b) product obtained from chemical cycle like that used for deuteration, but with H_3PO_4 in the final step; $\text{Re}_3(\text{CO})_{12}\text{D}_3$, product obtained from deuteration cycle, 99% D, D_3PO_4 in the final step; $\text{Os}_3(\text{CO})_{12}$, structure previously determined, see ref. 11.

X-Ray Powder Patterns.—In order to ascertain the similarity of original product with that which was produced through a deuteration cycle, we obtained X-ray powder patterns. These are shown in Fig. 1 and the *d*-spacings listed in Table III. A pattern for $\text{Os}_3(\text{CO})_{12}$,¹¹ a compound we believed might be structurally related to our derivatives, is also included. These were obtained through the courtesy of Professor W. Gary Ernst of the Geology Department of this University, with the aid of Mrs. Eva Vary, whose help we gratefully acknowledge. Spectra were taken on powders mounted on glass slides; a Norelco X-ray diffraction unit was utilized with $\text{Cu K}\alpha$ radiation and NaCl as a standard.

Infrared Absorptions.—We scanned the region $4000\text{--}290\text{ cm}^{-1}$ in the infrared for the two derivatives using a combination of instruments. The maxima observed are listed in Table IV. In the region $4000\text{--}400\text{ cm}^{-1}$ it was convenient to scan the samples in KBr pellets; these are shown on Fig. 2. This was accomplished on a Perkin-Elmer 421 spectrophotometer, equipped

(10) $\chi_g(\text{Re}^{-1}) \sim -0.27 \times 10^{-6}$, estimated by extrapolation of data from ref. 9, p. 78, and by Korol'kov's method, *cf.*, *Chem. Abstr.*, **57**, 9346j (1962); $\chi_g(\text{H}^{-1}) \sim -9.9 \times 10^{-6}$, W. Klemm, "Magnetochemie," Akademische Verlag, Leipzig, 1936, p. 150; and $\chi_g(\text{CO}) \sim -0.153 \times 10^{-10}$, from Pascal's constants.

(11) The structure of this compound has been reported by E. R. Corey and L. F. Dahl, *Inorg. Chem.*, **1**, 521 (1962).

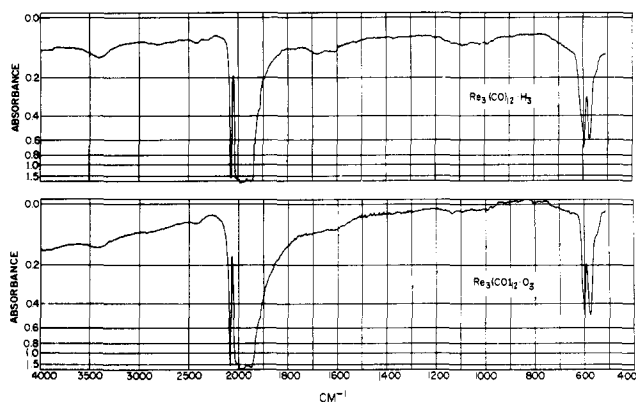


Fig. 2.—Infrared spectra, Perkin-Elmer 421 (ruled grating), KBr pellet, approximately 2.3 mg./100 mg. concentration.

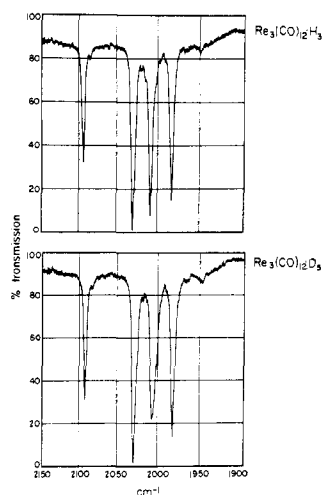


Fig. 3.—High resolution infrared spectra, Beckman IR-4, LiF prism, cyclohexane solutions, approximately 1 mg./ml. ($\sim 10^{-6}$ mole/ml.).

with a diffraction grating. The carbonyl stretching bands, which also occur in this region, are not well displayed through this sampling technique, so they were scanned in cyclohexane solution. The bands thus observed, in the region 2150–1900 cm^{-1} , are shown in Fig. 3. These were obtained on a Beckman IR-4 spectrophotometer equipped with a LiF prism, under the same instrumental conditions and calibration of spectra as described previously.³ Finally, for the low energy region, 900–290 cm^{-1} , the KBr pellets mentioned above were transported to a Beckman IR-5A spectrophotometer equipped with a CsBr prism, and the spectra thus obtained are shown in Fig. 4. The advantage of the KBr pellet (containing about 2.5% compound, by weight) is that it is essentially transparent in the entire region 4000–290 cm^{-1} (providing the disk thickness remains at 0.3 mm. or less).

Nuclear Magnetic Resonance.—Despite the low solubility of the tetracarbonyl trimer of rhenium in most solvents, an attempt was nevertheless made to seek any possible proton resonance for this derivative. We scanned the region from τ 0 to 40 to no avail. It is clear that special techniques will be needed in order to obtain positive evidence from magnetic resonance for the protons which we know must be there.

Discussion

Chemical and Spectroscopic Properties.—Both the protonated and the deuterated tetracarbonyl hydrides described above have unusual chemical and spectroscopic properties when compared with the earliest discovered hydride complexes of this metal, namely, $(\text{C}_5\text{H}_5)_2\text{ReH}$ ¹² and $\text{HRe}(\text{CO})_5$.¹³ However, from later developments including some as yet unpublished ob-

(12) G. Wilkinson and J. M. Birmingham, *J. Am. Chem. Soc.*, **77**, 3421 (1955).

(13) W. Hieber and G. Braun, *Z. Naturforsch.*, **14b**, 132 (1959).

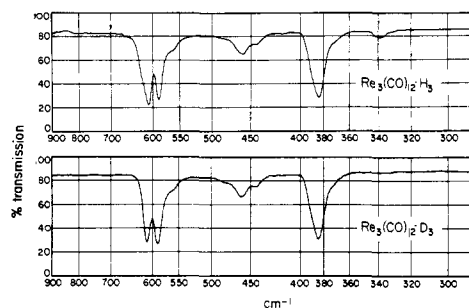


Fig. 4.—Infrared spectra, Beckman IR-5A, CsBr prism, KBr pellet, approximately 2.3 mg./100 mg. concentration.

servations, it appears that the unusual properties of the present derivatives are not entirely unique.

We found the above described tetracarbonyl hydride trimers of rhenium to be air stable apparently indefinitely. This is also true for the solutions of these derivatives in cyclohexane, and even in carbon tetrachloride. By contrast, both $(\text{C}_5\text{H}_5)_2\text{ReH}$ and $\text{HRe}(\text{CO})_5$

TABLE IV
INFRARED ABSORPTIONS FOR CARBONYLS IN THE REGION
3000–290 CM^{-1}

$\text{Re}_3(\text{CO})_{12}\text{H}_9$	$\text{Re}_3(\text{CO})_{12}\text{D}_9$
KBr pellet ^a	
3420 vw, ^b	3410 vw, ^b
2410 vw	2430 vw
2310 vw	
Cyclohexane solution ^c	
2093 m	2093 m
2083 m	2083 vw
2030 vs	2030 vs
2018 vw	2018 vw
2008 s	2005 m
1983 m	1982 m
1948 vw	1947 vw
KBr pellet ^a	
1684 vw	1675
1613 vw	1565 vw, ^b
1090	1135
990 vw, ^b	992 vw, ^b
KBr pellet ^d	
625 sh	
609 s	612 s
588 s	588 s
560 vw, ^b	560 vw, ^b
461 m	461 m
444 w	443 w
384 s	385 s
339 w	

^a Perkin-Elmer 421 spectrophotometer; see Fig. 2 for spectra: vw = very weak (absorbance < 0.1), b = broad. The bands in the carbonyl stretching region, 2150–1900 cm^{-1} , were viewed separately in solution (see below). The region 625–500 cm^{-1} overlaps with the next trace; the bands observed here are reported with the next group. ^b Possibly due to last traces of water in the pellet. ^c Beckman IR-4 spectrophotometer; see Fig. 3 for spectra; LiF prism. ^d Beckman IR-5A spectrophotometer; see Fig. 4 for spectra; CsBr prism.

are rapidly oxidized in air in the pure state and in solution; also, the former is observed to be attacked rapidly in solution in carbon tetrachloride. On the other hand, more recently it has been reported that $((\text{C}_6\text{H}_5)_3\text{P})_2\text{ReH}_3$ and $((\text{C}_6\text{H}_5)_3\text{P})_4\text{ReH}_3$ ¹⁴ are air stable, so the

(14) L. Malatesta, M. Freni, and V. Valenti, *Angew. Chem.*, **73**, 273 (1961).

similar air stability of our derivatives is somewhat less surprising.

Extensive work now exists on metal hydride complexes, and particularly on infrared spectroscopic data for metal-hydrogen or metal-deuterium stretching frequencies, such as in the work of Vaska¹⁵ or Chatt¹⁶ and their co-workers and also in the review by Green.¹⁷ Taking the information from the infrared spectra of $(C_5H_5)_2ReH$ and $(C_5H_5)_2ReD$,¹⁸ and also from the information available in the above-mentioned work on the heavier transition metal complexes in general, we might expect the Re-H or the Re-D stretching absorptions anywhere in the regions 2100-1800 or 1600-1200 cm^{-1} , respectively. Certainly no absorption in the region specified above may be seen for the protonated trimer (top trace, Fig. 2) unless it is obscured by the very intense carbonyl absorptions. If so, then deuteration should have shifted such a band away from the carbonyl region (approximately 500 to 600 cm^{-1} to lower energy), but again, in the lower trace of Fig. 2 (containing the absorptions of the deuterated trimer), no distinct bands in the region specified above may be identified. The absence of a sharp absorption in both of these cases still remains to be explained, though from other pieces of evidence presented in this paper, it may be certain that hydrogen (or deuterium as the case may be) must certainly be present in the molecule. This is not the first instance of a weak or, at times, undetectable metal-hydrogen stretching frequency in metal hydride complexes, and particularly those of the heaviest transition metals of the 5d-transition period.^{19,20} However, in the present work, we have noticed other unmistakable evidence for a change in the spectrum in going from the protonated derivative to the deuterated derivative in the bands of the lower energy regions and one band of the carbonyl stretching absorptions. In the lower energy region, the shoulder at 625 cm^{-1} in the upper trace of Fig. 4 is absent in the lower trace. Possibly, it has been shifted by about 40 cm^{-1} in the lower spectrum such that it is hidden under the absorption at 588 cm^{-1} (it is observed that this band has increased in relative intensity in the lower trace against the band near 610 cm^{-1} which appears to remain constant in both spectra). Also the band at 339 cm^{-1} in the upper trace has disappeared in the lower spectrum, possibly shifted by about 50 cm^{-1} or more to lower energy, which would shift the band beyond the present range of scan. Both these shifts are of the order of magnitude of about 50 cm^{-1} , which shifts we would expect for metal-hydrogen modes in these regions.^{15,21} We have also ascertained that these subtle changes are reproducible and reversible. However, it should be emphasized that the full chemical cycle mentioned in the Experimental section is needed to bring about these changes. The trimer is remarkable in that the hydrogen atoms do not exchange with D_2O , by contrast to the behavior of $HRe(CO)_5$, which is observed to exchange

(15) L. Vaska, *J. Am. Chem. Soc.*, **86**, 1943 (1964), and references cited therein.

(16) J. Chatt, *Proc. Chem. Soc.*, 318 (1962), and references cited therein.

(17) M. L. H. Green, *Angew. Chem.*, **72**, 719 (1960).

(18) M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3916 (1958).

(19) L. Vaska and J. W. Di Luzio, *J. Am. Chem. Soc.*, **84**, 4989 (1962).

(20) J. A. Chopoorian, J. Lewis, and R. S. Nyholm, *Nature*, **190**, 528 (1961).

(21) F. A. Cotton, J. L. Down, and G. Wilkinson, *J. Chem. Soc.*, 833 (1959).

instantly (in cyclohexane solution or in the gas phase, when brought in contact with D_2O).

One final shift in the infrared spectra should be mentioned, and that is the one illustrated in Fig. 3 for the carbonyl stretching absorptions. It is seen that only one band, at 2008 cm^{-1} , is appreciably affected; in the deuterated sample, it appears at 2005 cm^{-1} and somewhat broader. At times, we could almost resolve a double maximum, possibly denoting that the original absorption had been weakly split into a doublet. This effect is reproducible and reversible though we have no explanation for it at present. We have learned of related phenomena in the work of Vaska,²² who observed that in some hydride complexes containing carbonyl groups, the CO stretching bands were caused to shift to varying degrees upon deuteration of the M-H bond. This interesting phenomenon is presently under further investigation at least for our own derivatives in these laboratories.

Structure.—Attempts to determine a structure by X-ray diffraction are in progress, but it has not been possible thus far to obtain suitable single crystals. Preliminary results²³ show that the trimer of rhenium is isomorphous with the previously isolated trimer of technetium,² but not with a trimer of osmium whose structure had been determined earlier.¹¹

We may obtain some indication of a possible structure with the aid of models and also guided by the infrared absorptions in the carbonyl stretching region. The relative simplicity of the pattern (Fig. 3) is highly suggestive that the carbonyls are equally distributed on all three Re atoms and are in equivalent environments. These conditions may be achieved in a closed three-membered ring rather than in an open chain. Also, we infer that there are no bridging carbonyl groups. This suggests a trimer something like $Os_3(CO)_{12}$ ²⁴ except that in the present derivative we have an additional atom (hydrogen) on each metal.

We conceive therefore that the trimer is composed of equivalent repeating units of a tetracarbonyl hydride of rhenium in which the metal would be seven-coordinate. The three-membered ring is formed by metal-metal bonds at two adjacent positions of each of three seven-coordinate polyhedra. There are two principal isomers of seven-coordinated polyhedra to consider; these may best be represented by starting with the hypothetical six-coordinate species $HRe(CO)_4$, in which the group L (either *cis* or *trans* to H) is replaced by two metal-metal bonds in the repeating unit in the polymer.

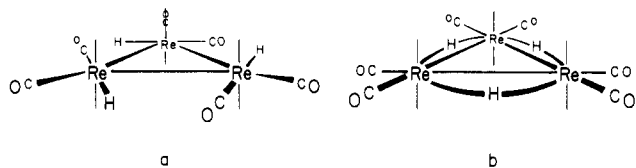
At present, we tend to favor a structure for the trimer

(22) (a) L. Vaska, private communication, and also as revealed in open discussion following the presentation of our work at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964. We have observed that one of the principal carbonyl absorptions in $HRe(CO)_5$, at 2006 cm^{-1} , is shifted to 2000 cm^{-1} in $DRe(CO)_5$.

(23) Professor L. F. Dahl, Department of Chemistry, University of Wisconsin, private communication.

(24) Four principal bands are observed (footnote 7 of ref. 2) for a purified sample of $Os_3(CO)_{12}$, D_{3h} symmetry (ref. 11); four principal bands are also observed for the tetracarbonyl halide dimers of Mn, Tc, and Re (M. A. El-Sayed and H. D. Kaesz, *Inorg. Chem.*, **2**, 158 (1963)) of D_{3h} symmetry (L. F. Dahl and C.-H. Wei, *Acta Cryst.*, **16**, 611 (1963)). This pattern of carbonyl absorptions is characteristic of the *cis*- $M(CO)_4$ group either in monomeric derivatives, $L_2M(CO)_4$, of C_{2v} idealized symmetry (R. Poilblanc and M. Bigorgne, *Bull. soc. chim., France*, 1301 (1962)) or in polynuclear derivatives which contain this group as a repeating unit. In the cases so far studied, the polymer is of a higher symmetry which contains the C_{2v} point group as a subgroup. For cases where the polymer might be of a lower symmetry, we would expect more than four bands from the repeating $M(CO)_4$ units only if coupling of carbonyl groups across the metal-metal bond is significant.

proceeding from the repeating unit related to *cis*-HLRe(CO)₄ such as structure Ia (in which the axial



I

carbonyl groups have been omitted for purposes of clarity). This structure is favored for a number of reasons. For one, the carbonyl groups are less crowded; this can be seen on models constructed from atoms whose dimensions were taken similar to those in Os₃(CO)₁₂.¹¹ In addition the *cis* six-coordinated species HLRe(CO)₄ is probably the more likely precursor to the formation of trimer, since reactions of derivatives XM(CO)₅ are observed to give predominantly *cis* substitution.²⁵

We would expect, however, that a trimer such as Ia would give rise to more than four principal absorptions in the region 2150-1900 cm.⁻¹. Four carbonyl and one metal-hydrogen stretching absorptions are expected in this region, arising from each of the repeating units and therefore at least as many could be expected in the trimer as a whole. However, the position of the hydrogen atoms in structure Ia suggests a remedy which would be in keeping with the lack of a metal-hydrogen stretch-

(25) F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, **3**, 79 (1961).

ing frequency in the high energy region. A small displacement of each hydrogen toward the adjacent metal, as in Ib (in which the axial carbonyl groups have been omitted for purposes of clarity) would result in hydrogen-bridged metal-metal bonds and an increase in the coordination number of the metal to eight, neither of which possibilities are excluded by any principles in theory that we know. In this model the correct number of carbonyl bands is predicted either from the symmetry of the repeating unit, C_{2v}, or of the trimer as a whole, D_{3h}.²⁴ Also, it would explain the lack of a distinct metal-hydrogen stretching frequency in the infrared in the region where these have been observed to occur, which we failed to observe for the present derivative. Such an arrangement of bridging hydrogen atoms would probably be reflected by some unusual length for the Re-Re bond. Of course, the hydrogen atoms would be located only through a neutron diffraction study which would have to follow a single crystal X-ray study.

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Metal Ion Catalysis in Transamination. II. Pyruvate-Glycinate Equilibrium Systems with Some Divalent Metal Ions^{1,2}

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The complexes of MPG, MPG₂⁻, MP₂G₂⁻² (P⁻ = pyruvate, G⁻ = glycinate, and M = Mn(II), Ni(II), or Zn(II), and CaPG have been found to form in solution and their stabilities have been determined. The "mixed" complexes containing both P⁻ and G⁻ have substantially greater stabilities than the analogous simple complexes. With the different metal ions the PG⁻² combination is shown to behave similarly to the tridentate ligand, iminodiacetate. The intrinsic stabilities of the MP₂G₂⁻² species are greater than those of the MPG complexes, a property which seems to be characteristic of coordination to unsaturated nitrogen. Spectral data give further evidence that this is so. These results support the recent conclusions of a p.m.r. study that the complexed ligands are condensed as a Schiff base. An evaluation of the temperature dependences of the equilibria qualitatively shows that entropy contributions are important in stabilizing the Ni(II)- and Zn(II)-PG⁻² systems, but appear to be less important with Mn(II).

Transamination between oxo and amino acids is one of the enzymatic reactions that can be duplicated in model systems containing metal ions.³⁻⁸ The reactive species appear to be "mixed" complexes in which it is thought the ligands are condensed as Schiff bases. A complicating factor in the interpretation of the results

is the extensive dissociation of most Schiff bases in aqueous solutions.

The application to these systems of the Bjerrum "pH-titration" technique, which is capable of providing much information, and the use of a high-speed computer to analyze the data has recently been proposed.⁹

In a study^{1,9} of the Ni(II)-pyruvate-glycinate system, mixed complexes of unusually high stabilities were found. In order to discover more of the properties of these mixed complexes, the earlier work has been extended to include Ca(II), Mn(II), and Zn(II). The behavior at temperatures other than 25° was examined.

(1) Part I in this series: D. L. Leussing, *Talanta*, **11**, 189 (1964).

(2) Supported by a grant from the National Science Foundation.

(3) D. E. Metzler and E. E. Snell, *J. Am. Chem. Soc.*, **74**, 979 (1952).

(4) L. Davis, F. Roddy, and D. E. Metzler, *ibid.*, **83**, 127 (1961).

(5) H. N. Christensen, *ibid.*, **80**, 2305 (1958).

(6) H. Mix, *Z. physiol. chem.*, **515**, 1 (1959).

(7) L. J. Nunez and G. L. Eichhorn, *J. Am. Chem. Soc.*, **84**, 901 (1962).

(8) B. E. C. Banks, A. A. Diamantis, and C. A. Vernon, *J. Chem. Soc.*, 4235 (1961).

(9) D. L. Leussing, *J. Am. Chem. Soc.*, **85**, 231 (1963).