Evidence for the Existence of $[Co(CO)_4(ROH)]^+[Co(CO)_4]^-$ Complexes. Ligand-Exchange Reactions

BY EDMOND R. TUCCI AND BERNARD H. GWYNN

Reactions between dicobalt octacarbonyl and alcohols have been investigated by ion-exchange and solvent-extraction methods. The results of this study indicate the formation of an intermediate species, $[Co(CO)_4\text{-}ROH]^+[Co(CO)_4]^-$, in the homomolecular disproportionation of dicobalt octacarbonyl at low temperatures. This ionic complex was found to be stable at temperatures $\lesssim 0°$, but readily decomposed at room temperature, or higher. Radiochemical experiments, using carbon-14 tagged ethanol, were performed to verify the presence of this ionic complex. In the presence of a cation-exchange resin at $0°$, the degree of adsorption of the cationic species $[Co(CO)_4ROH]^+$ was found to differ with the nature of the alcohol. The abnormal reactions of secondary and tertiary alcohols with dicobalt octacarbonyl suggest a bimolecular nucleophilic attack by the alcohol since steric effects appear to play a major role in this reaction. Ligand-exchange reactions were found to occur at low temperatures between the $[Co(CO)_4ROH]^+$ cation and alcohols or water. Thus, methanol was found to displace 1-octanol from the complex, at $0°$. At higher temperatures ($\gtrsim 25°$) methanol functioned as a catalyst in facilitating decomposition of the dicobalt octacarbonyl. In certain cases, water was found to be capable of displacing primary alcohols from the $[Co(CO)_4ROH]^+$ cation. The limitation placed upon the exchange reaction was that the alcohol complex be fairly water-soluble for the exchange reaction to occur. Thus, it was possible to interchange low molecular weight, straight chain, primary alcohol complexes, such as methanol, ethanol, 1-propanol, and 1-butanol, quite readily with water. Primary alcohols with a carbon number greater than four were found to form complexes which were either very slightly water-soluble or completely insoluble.

Introduction

Early investigations[1,2] of the reaction between dicobalt octacarbonyl and a Lewis base, such as methanol, pyridine, and o-phenanthroline, suggested a simple displacement of one or more carbon monoxide molecules from the metal carbonyl to form a $Co_2(CO)_x\cdot$Lewis base adduct. However, it was later observed that the reaction between dicobalt octacarbonyl and a Lewis base, B, was more correctly represented by a homomolecular disproportionation[3,4] of the metal carbonyl into cobalt(II) ions and cobalt tetracarbonyl anions. In studying the reaction between the strong Lewis base, piperidine, and dicobalt octacarbonyl, Wender, Sternberg, and Orchin[3] proposed the formation of the salt, $[Co(CO)_4(piperidine)]^+[Co(CO)_4]^-$, as an intermediate product in the disproportionation reaction. Although these workers effectively showed that weak Lewis bases, such as alcohols, also facilitated a homomolecular disproportionation of dicobalt octacarbonyl, we feel they did not present convincing evidence that weak Lewis bases also form an intermediate reaction species similar to that proposed for the strong Lewis base, piperidine.

In studying the reactions between dicobalt octacarbonyl and alcohols by ion-exchange and solvent-extraction techniques, we obtained experimental evidence that the ionic species, $[Co(CO)_4(ROH)]^+[Co(CO)_4]^-$, does indeed exist for certain alcohols. Furthermore, this species was found to undergo some interesting ligand-displacement reactions. The results of these investigations are discussed in this paper.

Experimental

Materials.—Dicobalt octacarbonyl was synthesized according to known methods,[5] and the orange crystals of $Co_2(CO)_8$ were isolated as such only when a stock solution was to be prepared. Otherwise, the bulk of the $Co_2(CO)_8$ was maintained in petroleum ether under a carbon monoxide atmosphere and stored in a refrigerator.

All alcohols and solvents were of high-purity analytical grade and were further purified only when it was found necessary. Carbon-14 tagged ethanol, $CH_3C^{14}H_2OH$, was obtained in microcurie-sample size from Volk Radiochemical Co.

The cation-exchange resins (Amberlyst-15 or Dowex-50) were percolated with 6 M HCl acid at room temperature, thoroughly washed with distilled water to remove any excess acid, and oven-dried at $110°$ for several hours. When the sodium form was desired, conversion was carried out by passage of a dilute NaCl solution over the resin, washing, and drying at $110°$. The anion-exchange resins were treated with the appropriate anion solution (Cl^- or OH^-), washed, and dried at $110°$.

Procedure.—In the ion-exchange experiments, the resin column consisted of a 300-mm. long water-cooled condenser with the ion-exchange resin contained in the inner tube. Dry Ice was added to acetone, contained in a dewar flask, until the temperature was between 0 and $-10°$. This liquid was then pumped through the condenser jacket to cool the resin column. Additional Dry Ice was added to the flask to maintain this required temperature. A ground-glass (24/40) adapter, containing a syringe cap, was fitted to the top of the condenser for introducing the heptane solutions of $Co_2(CO)_8$, or heptane–alcohol–$Co_2(CO)_8$ solutions, with a hypodermic syringe. An outlet tube, on the top of the resin column, was connected to a gas buret to measure the evolution of carbon monoxide or hydrogen. The bottom of the column was fitted with a ground-glass (24/40) collecting tube immersed in a freezing mixture maintained at about $-10°$. The entire system was flushed and maintained in a carbon monoxide atmosphere. Approximately 30 ml. of a 0.05 M heptane solution of $Co_2(CO)_8$, or this solution containing the alcohol, was passed through the column and collected in the bottom receiver. An aliquot portion (10.00 ml.) of the initial stock solution, which served as a blank, and the effluent solutions were analyzed for cobalt carbonyls by a photometric method. All runs were performed in duplicate and found to yield similar results, within experimental error.

Equilibration experiments consisted of weighing 2.00 g. of oven-dried Amberlyst-15 (H) resin into a 25-ml. glass-stoppered volumetric flask, flushing with carbon monoxide, introducing a 10.00-ml. aliquot portion of the 0.05 M $Co_2(CO)_8$ (heptane) solution, and cooling to $0°$. The desired alcohol was introduced into this solution in twofold excess to react completely with the $Co_2(CO)_8$. The solutions were shaken for 10–15 min. at $0°$. A 5.00-ml. aliquot portion was removed and analyzed for cobalt carbonyls to determine the amount of alcohol complex adsorbed by the cation-exchange resin.

In the radiochemical experiments, an accurately weighed quantity (0.050 to 2.20 g.) of pretreated (H or Na form), oven-dried cation-exchange resin (Dowex-50 or Amberlyst-15) was introduced into the 25-ml. glass-stoppered volumetric flasks. The flasks were cooled (0 to $-10°$); an aliquot portion of the standard 0.05 M $Co_2(CO)_8$ (heptane) solution was added to the flasks; an accurately known quantity of $CH_3C^{14}H_2OH$, based on predetermined

(1) W. Hieber, F. Muhlbauer, and E. A. Ehmann, *Ber.*, **65**, 1090 (1932).

(2) A. A. Blanchard, *Chem. Rev.*, **21**, 3 (1937).

(3) I. Wender, H. W. Sternberg, and M. Orchin, *J. Am. Chem. Soc.*, **74**, 1216 (1952).

(4) W. Hieber, J. Sedlmeier, and W. Abeck, *Chem. Ber.*, **86**, 700 (1953).

(5) I. Wender, H. W. Sternberg, and M. Orchin, "Catalysis," Vol. V, Reinhold Publishing Corp., New York, N. Y., 1957, p. 73.

molar ratios of $Co_2(CO)_8$ to ethanol, was then introduced into the flasks. Whenever possible, this molar ratio was adjusted such that the removal of 1 ml. of tagged ethanol yielded 5000–6000 c.p.m. The solutions were equilibrated with the resin by agitating for 20 min. at 0 to $-10°$. The following blanks were prepared: $Co_2(CO)_8$ (heptane) and $CH_3C^{14}H_2OH$, in the absence of resin; $CH_3C^{14}H_2OH$ and resin, in the absence of $Co_2(CO)_8$; $Co(NO_3)_2$ and $CH_3C^{14}H_2OH$ in the absence and presence of cation-exchange resins; $CH_3C^{14}H_2OH$ by itself. After shaking, a 0.10- to 1.00-ml. sample was removed for counting in a Packard Tri-Carb liquid scintillation spectrometer maintained at $-5°$. The sample was introduced into a scintillation solution of PPO (2,5-diphenyloxazole) and POPOP (p-bis[5-phenyloxazolyl]benzene) dissolved in toluene. The initial series of experiments indicated large "color quenching" effects, due to the $Co_2(CO)_8$. Therefore, smaller molar concentrations of the $Co_2(CO)_8$ were used, in addition to higher $CH_3C^{14}H_2OH$ concentrations. The statistical counting error for these solutions was $\pm 1.0\%$, except for the solutions containing $Co(NO_3)_2$, which were found to have a standard deviation in counting of $\pm 1.5\%$. Solvent extraction experiments were performed in a manner similar to the ion-exchange equilibration experiments except that the resin was omitted.

Results and Discussion

I. Interactions of Cobalt Carbonyl Complexes with Ion-Exchange Resins. A. Formation of $[Co(CO)_4$-$ROH]^+[Co(CO)_4]^-$.

—If the Lewis base (B) initiated homomolecular disproportionation of a neutral molecule of dicobalt octacarbonyl yields the intermediate species

$$Co_2(CO)_8 + B \rightleftharpoons [Co(CO)_4B]^+[Co(CO)_4]^- \quad (1)$$
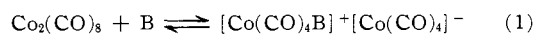
then ion-exchange techniques should be useful in analyzing product formation. As a prerequisite in studying these ion-exchange equilibria, it is desirable that the ionic reaction products given in eq. 1 possess a fair degree of stability and do not undergo further decomposition to other types of charged species. Furthermore, the free dicobalt octacarbonyl should not interact chemically or physically with the ion-exchange resin. Preliminary experiments involving the reactions of dicobalt octacarbonyl and alcohols indicated that the stability of the ionic species formed was very temperature dependent. At room temperature, or higher, decomposition of the alcohol complex readily occurred, while at temperatures below $0°$, preferably $-10°$, the ionic species appeared stable enough for ion-exchange studies. To determine the effect of cation- and anion-exchange resins on dicobalt octacarbonyl, an aliquot portion of a 0.05 M solution (n-heptane) of the metal carbonyl was passed through a cooled column of the pretreated cation or anion resin. The amount of dicobalt octacarbonyl adsorbed, which was probably due to partial decomposition in the transferring operation, was $<4\%$. Analysis of the effluent indicated that the free dicobalt octacarbonyl passed through the column chemically unchanged. However, when a similar solution of dicobalt octacarbonyl was passed through a cooled cation-exchange resin (sulfonic acid type) and eluted with methanol or 1-octanol, essentially 100% of the metal carbonyl was adsorbed by the resin. These results are presented in Table I. Since the evolution of carbon monoxide was extremely small, relative to the amount of dicobalt octacarbonyl introduced, the initial reaction of the alcohol with the metal carbonyl appeared to proceed by the formation of an intermediate ionic complex according to the reaction

$$Co_2(CO)_8 + ROH \rightleftharpoons [Co(CO)_4ROH]^+[Co(CO)_4]^- \quad (2)$$
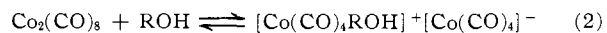
The cationic species formed in eq. 2 was then adsorbed by the cation-exchange resin, RSO_3H, to yield cobalt

TABLE I

Low Temperature Adsorption of Cobalt Carbonyl Species in the Presence of Ion-Exchange Resins

Solutions	Effluent, $[Co]_{total}$, mg./ml.
$Co_2(CO)_8$ in n-heptane (blank)	0.381
$Co_2(CO)_8$ + Amberlyst-15 (H)	0.366
$Co_2(CO)_8$ + CH_3OH + Amberlyst-15 (H)	0.001
$Co_2(CO)_8$ + CH_3OH + Dowex-50 (H), 50–100 mesh	0.001
$Co_2(CO)_8$ + $CH_3(CH_2)_7OH$ + Amberlyst-15 (H)	0.003
$Co_2(CO)_8$ + $CH_3(CH_2)_7OH$ + Dowex-1 (Cl)	0.241

hydrocarbonyl according to the reaction

$$[Co(CO)_4ROH]^+[Co(CO)_4]^- + RSO_3H \rightleftharpoons$$
$$RSO_3^-[Co(CO)_4ROH]^+ + HCo(CO)_4 \quad (3)$$
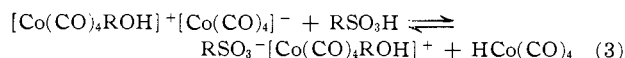
Since complete retention of the dicobalt octacarbonyl by the cation-exchange resin was observed, it appears that the cobalt tetracarbonyl anion must be undergoing an additional reaction. As shown in eq. 3, protonation of the anionic species results in the formation of cobalt hydrocarbonyl which, in turn, could be converted to dicobalt octacarbonyl by the following irreversible decomposition.

$$2HCo(CO)_4 \longrightarrow H_2 + Co_2(CO)_8 \quad (4)$$
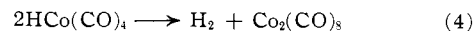
The dicobalt octacarbonyl further reacts with the alcohol according to eq. 2, and the complexation cycle is repeated until the cobalt tetracarbonyl anion has been completely converted to the cationic species and adsorbed by the cation-exchange resin. The reaction given in eq. 4 also accounts for the observed evolution of hydrogen resulting from decomposition of the cobalt hydrocarbonyl formed in eq. 3.

Referring again to Table I, it is interesting to note that passage of a dicobalt octacarbonyl–octanol solution through an anion-exchange resin resulted in the adsorption of an anionic species. The adsorbed anion was undoubtedly the cobalt tetracarbonyl anion. The amount of this anion, which was adsorbed by the resin, was found to be lower than what one might expect from the stoichiometry of eq. 2. Actually, only 74% of the amount required by eq. 2 was adsorbed by the anion-exchange resin. The difference between the observed and theoretical adsorption probably indicates that partial oxidation of the cobalt tetracarbonyl anion to dicobalt octacarbonyl is occurring and that the cationic complex is, in turn, being reduced to dicobalt octacarbonyl, perhaps through the intermediate cobalt tetracarbonyl dimer.

A number of different alcohols were equilibrated with dicobalt octacarbonyl in the presence of Amberlyst-15 (H) at $0°$. Although the degree of adsorption of the cationic alcohol complex differed between the primary alcohols in the carbon range C_1 to C_{12}, all of these alcohol complexes were more readily adsorbed than secondary or tertiary alcohols. The abnormal reactions of the secondary and tertiary alcohols suggest a bimolecular nucleophilic reaction in which the requirement for the activation process involves the separation of unlike charges. Since the activated complex in an S_N2 type reaction usually becomes more crowded than in a unimolecular nucleophilic reaction, one would expect the introduction of bulky alkyl groups to exhibit more steric retardation in the bimolecular reaction. In our

case, retardation of the bimolecular reaction appears to be due to the bulkiness of the alcohol.

B. Radiochemical Studies with Carbon-14 Tagged Ethanol.—Adsorption of the dicobalt octacarbonyl–alcohol complex by a cation-exchange resin, without the evolution of carbon monoxide, is a good indication that the intermediate species, shown in eq. 2, is being formed. However, to lend further support to the formation of this ionic complex, experiments were performed using carbon-14 tagged ethanol in the presence of a cation-exchange resin. The object in performing these experiments was to show that the cationic species, $[Co(CO)_4(ROH)]^+$, was adsorbed by the cation-exchange resin rather than Co(II) alcoholate ions.

The "salting-in" effect of $CH_3C^{14}H_2OH$ by the cation-exchange resin, which could result in a decrease in carbon-14 activity in solution, was found experimentally to be quite insignificant since it was $<3\%$. When the sodium form of the cation-exchange resin (RSO_3Na) was used instead of RSO_3H, there was observed no decrease in the carbon-14 activity in solution. Adsorption of cobalt(II) alcoholate ions by a cation-exchange resin was found to occur to the extent of 6% or less. However, when dicobalt octacarbonyl was treated with $CH_3C^{14}H_2OH$ at $0°$ in the presence of the cation-exchange resin, there was observed $>90\%$ decrease in the carbon-14 activity of the solution. Obviously, the radioactive ethanol was reacting with the metal carbonyl to form the alcohol complex shown in eq. 2, which was then adsorbed by the resin. Allowing the cold solution to reach room temperature caused an increase in carbon-14 activity in solution since the alcohol complex was decomposing and releasing the alcohol from the resin. However, the original carbon-14 activity was not restored since the radioactive cobalt(II) alcoholate ions, which were formed by decomposition of the dicobalt octacarbonyl–alcohol complex, were now being adsorbed by the cation-exchange resin. Since adsorption of this species was found to occur at low levels, most of the carbon-14 activity remained in solution. These radiochemical experiments appear to substantiate the formation of an intermediate cationic cobalt carbonyl–alcohol complex.
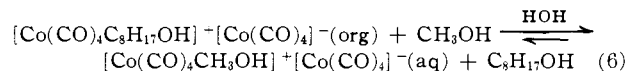
II. Ligand-Exchange Reactions between Alcohols and $[Co(CO)_4ROH]^+$.—In our cation-exchange resin studies, it was noted that the degree of adsorption of the cationic species, $[Co(CO)_4ROH]^+$, differed with the nature of the alcohol. It was also observed in this ion-exchange work that the extent of adsorption of the primary alcohol complex was a function of the alcohol chain length. The experimentally observed difference in adsorption of the primary alcohol complexes could be partly attributed to steric effects, changes in the donor character of the alcohol, or other contributing effects. Whatever factors are responsible for this phenomenon, the difference in adsorption might be expected to lead to the displacement of one alcohol from the $[Co(CO)_4ROH]^+$ cation by another alcohol. Therefore, with the intention of further elucidating these ligand-exchange equilibria, reactions between dicobalt octacarbonyl and alcohols were studied at low temperatures, by solvent extraction techniques, in the absence of ion-exchange resins.

As a prerequisite in studying these ligand-exchange reactions, it was necessary to determine the extent of reaction between dicobalt octacarbonyl (solid) and water. It was found that the direct reaction of water with dicobalt octacarbonyl to form $[Co(CO)_4HOH]^+$ $[Co(CO)_4]^-$ appeared to be a minor side reaction, within the time required for an alcohol-exchange reaction to occur. When dicobalt octacarbonyl was treated with excess 1-octanol to form the corresponding alcohol complex and the solution was extracted with water for several hours at $<0°$, the dark organic phase containing the alcohol complex did not undergo any color change during extraction. Analysis of the aqueous phase indicated it contained only small amounts of cobalt ion. In this system, water might be expected to function as a Lewis base and exchange with the alcohol contained in the complex, according to the reaction

$$[Co(CO)_4C_8H_{17}OH]^+[Co(CO)_4]^-(org) \underset{}{\overset{HOH}{\rightleftharpoons}}$$
$$[Co(CO)_4HOH]^+[Co(CO)_4]^-(aq) + C_8H_{17}OH \quad (5)$$
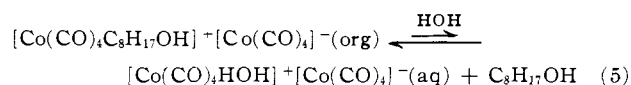
Since the aqueous phase was found to contain only small amounts of cobalt ion, it appears that the displacement of the 1-octanol ligand by water is not very favorable. The inability to water extract the alcohol complex may be attributed to the equilibrium in eq. 5 being predominantly in the direction of the formation of the water-insoluble $[Co(CO)_4C_8H_{17}OH]^+$ species rather than the water-soluble aquo complex. What we are confronted with in this system is really a solubility problem. It is interesting to note that the addition of trace amounts of methanol to water greatly facilitates extraction of the octanol complex into the aqueous phase, at $<0°$. What appears to be occurring is the ligand displacement of 1-octanol by methanol, according to the reaction

$$[Co(CO)_4C_8H_{17}OH]^-[Co(CO)_4]^-(org) + CH_3OH \underset{}{\overset{HOH}{\rightleftharpoons}}$$
$$[Co(CO)_4CH_3OH]^+[Co(CO)_4]^-(aq) + C_8H_{17}OH \quad (6)$$

The methanol complex is miscible with water, thereby facilitating water extraction. Although solubilization of the 1-octanol complex in the methanol–water solution, without the occurrence of ligand exchange, might also be expected to account for the observed increase in extraction, it is highly unlikely that such minute quantities of methanol could be so effective. Instead, what really appears to be taking place is a series of ligand-exchange reactions. The reaction does not cease upon displacement of the 1-octanol from its dicobalt octacarbonyl complex by methanol. On the contrary, since the methanol complex is in equilibrium with the aqueous phase, a second ligand-exchange reaction occurs with water, according to the reaction

$$[Co(CO)_4CH_3OH]^+[Co(CO)_4]^- + HOH \rightleftharpoons$$
$$[Co(CO)_4HOH]^+[Co(CO)_4]^- + CH_3OH \quad (7)$$
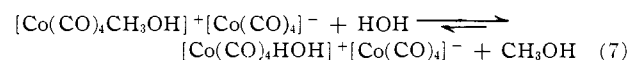
The observation that only catalytic amounts of methanol are required to extract the dicobalt octacarbonyl from the water-insoluble octanol complex and bring it into the aqueous phase is a good indication that the equilibrium in eq. 7 is predominantly in favor of forming the aquo complex. The free methanol may again enter the organic phase to repeat the reactions shown in eq. 6 and 7. The cationic complex $[Co(CO)_4CH_3OH]^+$, and very likely the corresponding aquo complex, seem to be fairly stable at $0°$, or lower. At temperatures near $25°$, or higher, both species decompose to form divalent cobalt ions, carbon monoxide, and water, or the free alcohol. Thus, at high temperatures, methanol functions
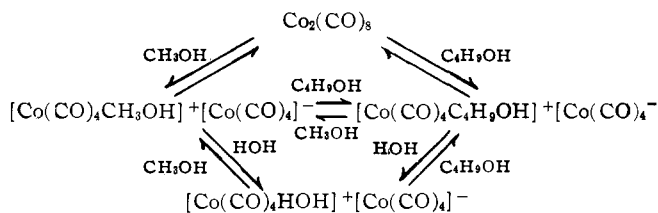
as a catalyst in facilitating decomposition of dicobalt octacarbonyl.

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

$$[Co(CO)_4ROH]^-[Co(CO)_4]^- + HOH \xrightarrow[]{\lesssim 0°}$$

$$[Co(CO)_4HOH]^+[Co(CO)_4]^- + ROH \quad (8)$$
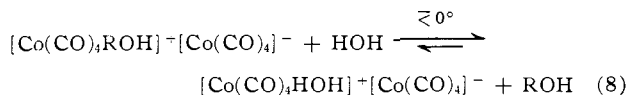
The limitation placed upon the exchange reaction given in eq. 8 is that the alcohol complex be reasonably water-soluble for the displacement of the alcohol to occur. Thus, it is possible to interchange low molecular weight straight-chain primary alcohol complexes, such as methanol, ethanol, 1-propanol, 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

$$Co_2(CO)_8$$

$$CH_3OH \nearrow \quad \nwarrow C_4H_9OH$$

$$C_4H_9OH$$

$$[Co(CO)_4CH_3OH]^+[Co(CO)_4]^- \rightleftharpoons [Co(CO)_4C_4H_9OH]^+[Co(CO)_4^-$$

$$\nwarrow HOH \quad CH_3OH \quad H_2OH \nearrow$$

$$CH_3OH \searrow \quad C_4H_9OH$$

$$[Co(CO)_4HOH]^+[Co(CO)_4]^-$$

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.
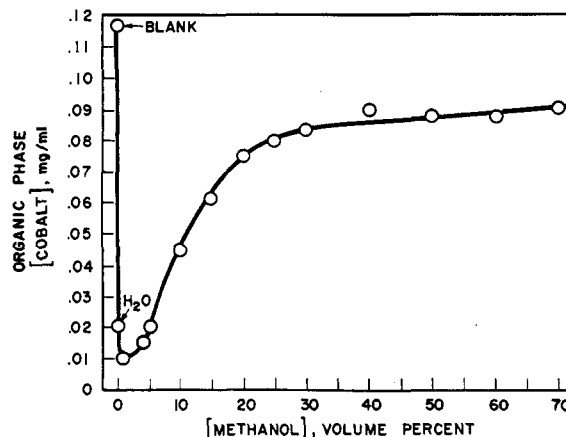

Fig. 1.—Extraction of $[Co(CO)_4(C_4H_9OH)]^+$, $[Co(CO)_4(CH_3OH)]^-$, and $[Co(CO)_4]^-$ by methanol–water mixtures.

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 ($\lesssim 0.5$ 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.

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A Polynuclear Tetracarbonyl Hydride of Rhenium.   Preparation and Properties[1a,b]

BY D. K. HUGGINS, W. FELLMANN, J. M. SMITH, AND H. D. KAESZ

The preparation and properties of a new polynuclear carbonyl hydride of rhenium are reported. The compound is isolated from the treatment of $Re_2(CO)_{10}$ 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 $[HRe(CO)_4]_3$. 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 reported[2] which was obtained as a by-product in the syn-

thesis of $HTc(CO)_5$.[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

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(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).