TABLE 8.—*Infrared-active carbonyl stretching frequencies (cm.⁻¹) of metal carbonyls; nearest combination band with frequency interval (Δ) from the lowest terminal carbonyl frequency*

|	HCo(CO)₄ gas	Co₂(CO)₈ gas	Fe(CO)₅ gas	Ni(CO)₄ gas	Co(CO)₄ pyridine solution	Co₄(CO)₁₂ heptane solution
Terminal carbonyl frequencies	{ 2,066 [2]*2,049*	2,079 [2]*2,053* 2,037	[1]2,033 [1]2,012	[3]2,060	[2]*1,883*	[2]*2,058* 2,030
Bridge carbonyl frequency		1,876				1,873
Nearest combination band	2,010	2,000	1,976	2,022		1,996
Δ value	39	37	36	38		34

[1] Bands at 2,028 and 1,993 cm.⁻¹ were reported and assigned as fundamentals by Sheline and Pitzer (*121*).
[2] The most intense band is italicized.

[3] Crawford and Cross (*34*) reported the fundamental at 2,050 cm.⁻¹. In the liquid phase our value for the fundamental is 2,047 cm.⁻¹; a value of 2,045 cm.⁻¹ was reported by Margoshes (*81*).

assigned as the two infrared-active fundamentals. The reported 1,993 cm.⁻¹ band is probably a combination band which we find at 1,976 cm.⁻¹ (see table 8). Table 8 presents a summation of infrared-active carbonyl stretching frequencies for several metal carbonyls. To illustrate the empirical similarity in carbonyl spectra, table 8 also includes the combination bands nearest the terminal carbonyl frequency. The frequency interval from the lowest terminal frequency (Δ value) is nearly constant.

Applying the Pauling principle to the cobalt carbonyl anion (XXIII) and considering that
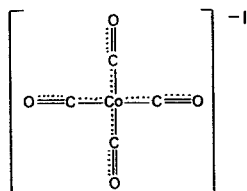
XXIII

the sum of single and double bonds must be such as to dissipate a charge of −1 from the cobalt atom, we arrive at

$$-1+0.4x-0.8(4-x)=0. \qquad (6)$$

Of the four cobalt-carbon bonds, 3.5 are double and 0.5 are single, which leads to bond orders of 1.87 and 2.13 for the Co—C and C—O, respectively. The predicted (*16*) lower bond order of the carbonyl bond in cobalt anion (2.13) as compared with the bond order in nickel carbonyl (2.33) is in good agreement with the observed lower frequency of the carbonyl band in cobalt carbonyl anion (1,883 cm.⁻¹) as compared with that of nickel carbonyl (2,060 cm.⁻¹). The band at 555 cm.⁻¹ is probably a Co—C—O bending vibration, analogous to that in Ni(CO)₄ at 545 cm.⁻¹ (*121*).

Dicobalt Octacarbonyl

PREPARATION

Metallic cobalt and cobalt salts of naphthenic acids react very slowly with pure carbon monoxide at 140° to 160° C. In the presence of hydrogen, however, the cobalt salts of these acids react rapidly. A convenient method of preparation is the following:

$$2CoCO_3+2H_2+8CO \rightarrow Co_2(CO)_8+2H_2O+2CO_2. \qquad (7)$$
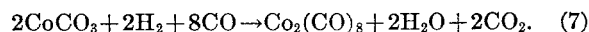
In a 500-ml. stainless steel autoclave [6] are placed 150 ml. of petroleum ether,[7] boiling range 32° to 63° C., and 15 g. of cobalt carbonate.[8] The autoclave is flushed three times with carbon monoxide and then filled with an approximately equal mixture of carbon monoxide and hydrogen to a pressure of 3,500 p.s.i. The autoclave is heated with agitation to 150° to 160° C. and maintained in this temperature range for about 3 hours. The maximum pressure (4,300 p.s.i.) is reached at 120° C., and at the end of the reaction, the pressure is about 3,900 p.s.i. at 155° C. The autoclave is cooled to room temperature, whereupon the pressure drops to about 2,600 p.s.i. The gases are then vented,[9] and the autoclave is opened in a well-ventilated hood.

The clear, dark solution of dicobalt octacarbonyl is pipetted from the autoclave with a syringe and filtered through filter paper into an Erlenmeyer flask. If difficulty with filtration of the last few millimeters is encountered, this small amount of liquid should be discarded. The Erlenmeyer flask containing the filtrate is placed in the freezing compartment of a refrigerator overnight, whereupon large, well-formed crystals of carbonyl are deposited.[10] The solvent is decanted, and the crystals are dried by passing a stream of carbon monoxide through the flask for a

[6] A commercial rocking autoclave was used. Consistently high yields were obtained after the autoclave had been used in these experiments several times. When an autoclave is used for this synthesis for the first time, it is advisable to add a few crystals of dicobalt octacarbonyl to initiate the reaction.
[7] Eimer and Amend petroleum ether, "Tested Purity," or pure n-pentane may be employed.
[8] Cobalt carbonate, C.P., which contains approximately 46 percent cobalt, is satisfactory.
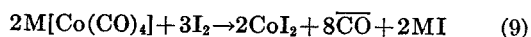[9] Care should be taken to avoid inhalation of the escaping gas, which contains large amounts of the extremely toxic cobalt hydrocarbonyl, HCo(CO)₄.
[10] Rapid cooling to very low temperature precipitates the carbonyl as a fine orange powder. In this state it decomposes in the presence of air to cobalt dodecacarbonyl, [Co(CO)₃]₄, which is pyrophoric. It is best to allow the dicobalt octacarbonyl to remain in the refrigerator under petroleum ether until the crystalline material is required.

few minutes. In one instance, the dry, orange crystals of dicobalt octacarbonyl weighed 15.3 g. (78 percent of theory); they melt at 51° to 52° C. with decomposition. If the crystalline material is not to be used immediately, it should be stored in a sealed tube under carbon monoxide.

ANALYSIS

Dicobalt octacarbonyl and cobalt carbonyl anion solutions react with iodine in pyridine or aqueous potassium iodide solution according to equations (8) and (9),

$$[Co(CO)_4]_2 + 2I_2 \rightarrow 2CoI_2 + 8\overline{CO} \qquad (8)$$

$$2M[Co(CO)_4] + 3I_2 \rightarrow 2CoI_2 + 8\overline{CO} + 2MI \qquad (9)$$

where M is either a metal or hydrogen. This reaction proceeds quantitatively and forms the basis of a gasometric determination of dicobalt octacarbonyl and cobalt carbonyl anion (133).

Cobalt carbonyl anion forms an orange, voluminous precipitate with nickel o-phenanthroline cation:

$$2[Co(CO)_4]^- + [Ni(o\text{-}Phthr)_3]^{++} \rightarrow$$
$$[Ni(o\text{-}Phthr)_3][Co(CO)_4]_2 \qquad (10)$$
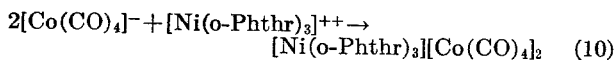
This precipitate is stable, insoluble in water and hydrocarbon solvents such as benzene, and readily soluble in polar solvents such as acetone of pyridine. Nickel o-phenanthroline cation, however, does not react with dicobalt octacarbonyl, permitting an analysis of a mixture of dicobalt octacarbonyl and cobalt carbonyl anion.

One aliquot of the solution containing dicobalt octacarbonyl and cobalt carbonyl anion is shaken with an aqueous solution of nickel o-phenanthroline chloride; the precipitate is dissolved in pyridine and decomposed with I_2, according to equation (9). In a second aliquot the total carbonyl present is obtained by decomposition with I_2 according to equations (8) and (9). The difference between the total carbonyl and total cobalt carbonyl anion is equivalent to the amount of dicobalt octacarbonyl present.

The method just described is rapid, and, as it is based on a gasometric procedure, it is well suited for the analysis of mixtures such as those from the hydroformylation reaction, which may contain cobalt salts and metallic cobalt.

A method for the analysis of cobalt carbonyl anion $[Co(CO)_4]^-$, based on the gravimetric determination of the cobalt salt $[Co(o\text{-}Phthr)_3]$ $[Co(CO)_4]_2$, was reported by Hieber and Fraenkel (60).

REACTIONS WITH BASES

The reactions of a variety of organic compounds with dicobalt octacarbonyl, previously assumed to proceed by the displacement of one or more moles of carbon monoxide by the organic molecule, are explicable on a common basis:

$$3[Co(CO)_4]_2 + xB \rightarrow$$
$$2[Co(B)_x]^{++}[Co(CO)_4]^-_2 + 8CO. \qquad (11)$$
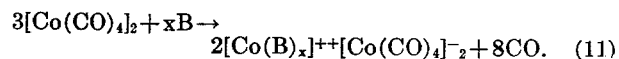
This reaction may be considered as a homomolecular disproportionation in which the uncharged dicobalt octacarbonyl disproportionates into cobalt (II) cation and cobalt carbonyl anion. B is a compound having an available unshared pair of electrons; that is, a base in the Lewis sense. As the coordination number of cobalt (II) ion is normally six, x may be six or three, depending upon the number of functional groups in B. Thus, x is six for ammonia and pyridine and three for o-phenanthroline. The function of B will be discussed in connection with the reaction mechanism.

The quantitative conversion of dicobalt octacarbonyl to cobalt cation and cobalt carbonyl anion according to equation (11) requires (1) the liberation of $2\frac{2}{3}$ moles of carbonmonoxide per mole of dicobalt octacarbonyl, (2) the formation of $1\frac{1}{3}$ moles of cobalt carbonyl anion per mole of dicobalt octacarbonyl, and (3) the conversion of one-third of the amount of cobalt present in dicobalt octacarbonyl to cobalt (II)

TABLE 9.—*Products from reactions of* $[Co(CO)_4]_2$ *with bases*

Reagent	Products, mole ratios		
	$\dfrac{CO}{[Co(CO)_4]_2}$	$\dfrac{[Co(CO)_4]}{[Co(CO)_4]_2}$	$\dfrac{Co(II)}{total\ Co}$
Methanol_____	2. 66	_____	0. 334
Ethanol_____	2. 87	1. 40	_____
Pyridine_____	2. 80	1. 41	_____
o-Phenanthroline__	2. 86	1. 34	_____

ion. The data in table 9, obtained with methanol, ethanol, pyridine, and o-phenanthroline, are consistent with the stoichiometry required by equation (11).

All reactions involving the evolution and measurement of gas were carried out in an apparatus which consisted of a gas burette and a 125-ml. Erlenmeyer flask fitted with a ground-glass joint and a sidearm for the addition of the reagent (103). A benzene solution, containing approximately the required amount of dicobalt octacarbonyl, was placed in the weighed Erlenmeyer flask; the benzene was evaporated at room temperature in a current of carbon monoxide or synthesis gas; the flask was stoppered, weighed, and attached to the gas burette; and the system was purged with carbon monoxide. The reagent was then added through the sidearm; the solution was stirred by means of a magnetic stirrer, the gas evolved was measured, and gas samples were withdrawn for analysis. The

amount of cobalt carbonyl anion formed was determined by addition of aqueous nickel o-phenanthroline chloride, [Ni(o-Phthr)₃] [Cl]₂, to the reaction mixture, filtration of the precipitate, [Ni(o-Phthr)₃] [Co(CO)₄]₂, and determination of the amount of carbon monoxide in the precipitate by a gasometric procedure (133). The reaction with methanol and analysis of products are described in detail.

To 0.8805 g. (2.58 millimoles) of dicobalt octacarbonyl was added 20 ml. of absolute methanol, and the solution was stirred. The reaction was completed at room temperature in 3 hours, during which time 154 ml. of carbon monoxide (6.88 millimoles) was evolved (2.66 moles of gas per mole of dicobalt octacarbonyl). About 72 percent of the gas was evolved during the first 15 minutes of the reaction.
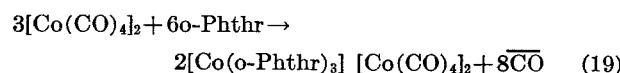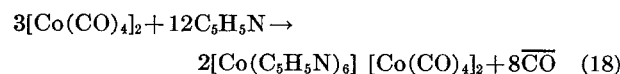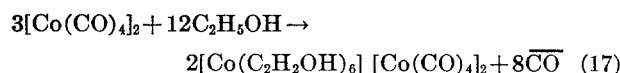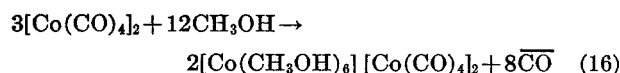
In a second experiment, the amount of cobaltous ion was determined as follows: Dicobalt octacarbonyl (0.3852 g.) was treated with 10 ml. of methanol as previously described. After completion of the reaction, 60 ml. of oxygen-free water and 25 ml. of nickel o-phenanthroline chloride solution were added to remove the cobalt carbonyl anion, and the precipitate was filtered and washed with water. The combined filtrate and wash water was evaporated to dryness, ignited, and dissolved in acid. After the removal of nickel with dimethylglyoxime, the solution was electrolyzed. The 0.0444 g. of cobalt obtained represents 33.4 percent of the cobalt in dicobalt octacarbonyl. This result is in excellent agreement with equation (11).

These results suggested a revision of the view (10, 64, 125) that the reaction between dicobalt octacarbonyl and compounds like methanol, ethanol, pyridine, and o-phenanthroline involves the displacement of one or more carbon monoxide groups of the carbonyl by the base according to equations (12), (13), (14), and (15).

$$[Co(CO)_4]_2 + CH_3OH \rightarrow Co_2(CO)_5 \cdot CH_3OH + 3\overline{CO} \qquad (12)$$

$$[Co(CO)_4]_2 + 1.5C_2H_5OH \rightarrow$$
$$Co_2(CO)_5 \cdot 1.5C_2H_5OH + 3\overline{CO} \qquad (13)$$

$$[Co(CO)_4]_2 + 4C_5H_5N \rightarrow Co_2(CO)_5 \cdot (C_5H_5N)_4 + 3\overline{CO} \qquad (14)$$

$$[Co(CO)_4]_2 + 2o\text{-Phthr} \rightarrow$$
$$Co_2(CO)_6(o\text{-phthr})_2 + 2\overline{CO} \qquad (15)$$
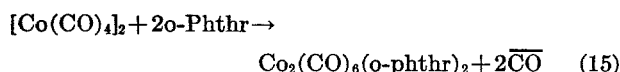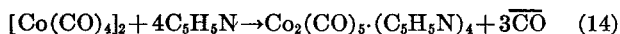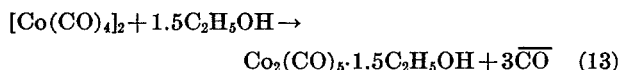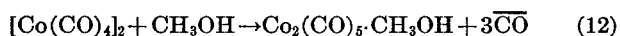
These reactions are correctly represented by equations (16), (17), (18), and (19).

$$3[Co(CO)_4]_2 + 12CH_3OH \rightarrow$$
$$2[Co(CH_3OH)_6] [Co(CO)_4]_2 + 8\overline{CO} \qquad (16)$$

$$3[Co(CO)_4]_2 + 12C_2H_5OH \rightarrow$$
$$2[Co(C_2H_2OH)_6] [Co(CO)_4]_2 + 8\overline{CO} \qquad (17)$$

$$3[Co(CO)_4]_2 + 12C_5H_5N \rightarrow$$
$$2[Co(C_5H_5N)_6] [Co(CO)_4]_2 + 8\overline{CO} \qquad (18)$$

$$3[Co(CO)_4]_2 + 6o\text{-Phthr} \rightarrow$$
$$2[Co(o\text{-Phthr})_3] [Co(CO)_4]_2 + 8\overline{CO} \qquad (19)$$

The stoichiometry of the paired equations (14) and (18) and (15) and (19) is approximately the same, and the analytical data
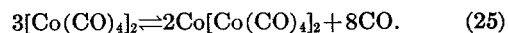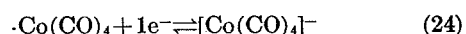
previously secured (61) to support equations (14) and (15) are also consistent with the new formulations (18) and (19). The stoichiometry of the paired equations (12) and (16) and (13) and (17) is considerably different as regards the quantity of alcohol consumed. We made no attempt to isolate the cobalt salts, but previous isolations and analyses on which equations (12) and (13) were based (64) are probably unreliable, owing to the loss of coordinatively bound alcohol during removal of solvent.

The action of tert-butyl alcohol on dicobalt octacarbonyl differs from that of methanol and ethanol. Only 2.2 (instead of 2.67) moles of carbon monoxide is evolved per mole of dicobalt octacarbonyl; small brownish-black, glistening crystals separate. These are similar in appearance and solubility in benzene (64) to the tetramer, tetracobalt dodecacarbonyl, [Co(CO)₃]⁴; the solution contains no cobalt carbonyl anion. The reaction probably proceeds according to equation (20):

$$2[Co(CO)_4]_2 \rightarrow [Co(CO)_3]_4 + 4CO \qquad (20)$$
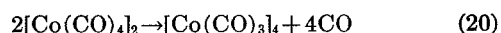
The difference in the mode of action of tert-butyl alcohol may be due to steric factors.

Equation (21) may be considered to occur stepwise, where B is a generalized base:

$$3B + 3[Co(CO)_4]_2 \rightleftharpoons 3 \begin{bmatrix} [BCo(CO)_4]^+[Co(CO)_4]^- \\ \text{XXIV} \end{bmatrix} \quad (21)$$

$$2[BCo(CO)_4]^+ \rightarrow 2B + 2Co^{++} + 8CO + 2e^- \qquad (22)$$
XXV

$$[BCo(CO)_4]^+ + 1e^- \rightarrow B + \cdot Co(CO)_4 \qquad (23)$$

$$\cdot Co(CO)_4 + 1e^- \rightleftharpoons [Co(CO)_4]^- \qquad (24)$$

$$3[Co(CO)_4]_2 \rightleftharpoons 2Co[Co(CO)_4]_2 + 8CO. \qquad (25)$$
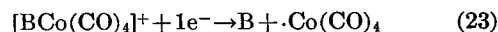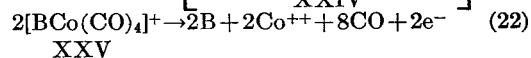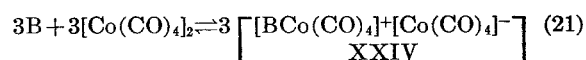
If the monomer, .Co(CO)₄, dimerized to dicobalt octacarbonyl (equation (26)), it would react further in the stepwise sequence shown in equations (21-24).

$$2 \cdot Co(CO)_4 \rightleftharpoons [Co(CO)_4]_2 \qquad (26)$$

With weak bases, such as pyridine or methanol, XXV decomposes rapidly at room temperature. Experimental support for the existence of the salt, XXIV, was obtained from a study of the reaction with piperidine.

Following the addition of this strong base in the cold to the dark solution of dicobalt octacarbonyl in xylene or toluene, the dark color changes to a light red, indicating the disappearance of the dimer. No gas is evolved, and a light greenish-yellow oil separates. The reaction is probably as follows:

The oil is readily soluble in water and contains 1 mole of cobalt carbonyl anion per mole of starting dicobalt octacarbonyl. A solution of 10 ml. of toluene containing 0.7419 g. (2.17 millimoles) of dicobalt octacarbonyl was placed in an Erlenmeyer flask; the flask was attached to the gas burette; the system was purged with nitrogen; and the gas volume was recorded. The flask was immersed in dry ice, and 2 g. of piperidine dissolved in 13 ml. of toluene was slowly added to the flask. The dry-ice bath was removed; the contents of the flask were stirred by a magnetic stirrer; and the gas volume was recorded after the solution had reached room temperature. No gas was evolved. The dark solution turned light red, and a greenish-yellow oil separated. The addition of 20 ml. of water solubilized the oil, and the color changed to light yellow. After 5 minutes of stirring, 50 ml. of nickel o-phenanthroline chloride solution was added, and the solution was stirred for 5 minutes. After acidification with 10 ml. of 6 N hydrochloric acid, the solution was filtered. Analysis for cobalt carbonyl anion gave 0.341 g. (1.99 millimoles). This is 92 percent of the anion predicted by equation (21). Drop by drop addition of dilute hydrochloric acid to XXVI results in the restoration of the color of dicobalt octacarbonyl by the reversal of reaction (27) and the removal of the piperidine as the hydrochloride.

The reaction of XXIV with excess concentrated hydrochloric acid is of interest. Some reversal of reaction (27) probably occurs as in the case of dilute acid, but the high concentration of acid leads to the formation of cobalt hydrocarbonyl. This acid is not stable and decomposes into hydrogen and dicobalt octacarbonyl (66):

$$2HCo(CO)_4 \rightarrow H_2 + [Co(CO)_4]_2. \quad (28)$$

The reaction of XXIV with concentrated hydrochloric acid may be written:

$$\begin{bmatrix} [BCo(CO)_4]^+ [Co(CO)_4]^- \\ XXIV \end{bmatrix} + 2HCl \rightarrow$$
$$2[BCo(CO)_4]^+ Cl^- + 2HCo(CO)_4. \quad (29)$$

In this example, cobalt carbonyl anion is removed, and the cation—or the neutral molecule, $Co(CO)_4Cl$—decomposes according to the scheme previously outlined in equations (21–24). The experimental data are consistent with the overall equation

$$4[[BCo(CO)_4]^+ [Co(CO)_4]^-] + 8HCl \rightarrow$$
$$2H_2 + 8CO + 3[Co(CO)_4]_2 + 2CoCl_2 + 4BHCl. \quad (30)$$

To a solution of 10 ml. of xylene containing 1.500 g. (4.38 millimoles) of dicobalt octacarbonyl, cooled in a dry-ice bath as previously described, was added 4 g. of piperidine dissolved in 19 ml. of xylene. The dry-ice bath was removed, and, after the solution had reached room temperature, a solution of 12 ml. of concentrated hydrochloric acid and 11 ml. of water was rapidly added with stirring. The resulting aqueous layer was pink, whereas the xylene solution was dark brown, indicating the presence of cobalt chloride and dicobalt octacarbonyl; the formation of these compounds is postulated in equation (30). The gas evolved (194 ml.) consisted of 20 ml. (0.89 millimole) of hydrogen and 164 ml. (7.32 millimoles) of carbon monoxide. This is 20.9 percent of the carbon monoxide in the dicobalt octacarbonyl; equation (30) requires the

evolution of 25 percent. If cobalt hydrocarbonyl had been decomposed completely (equation (28)), the hydrogen (equation (30)) would have been 0.5 mole per mole of dicobalt octacarbonyl, or 2.19 millimoles. That less hydrogen was obtained in this experiment than predicted by equation (30) is consistent with the fact that cobalt hydrocarbonyl is fairly stable in aqueous solutions (13).

Formation of Cobalt Carbonyl Anion by Electron Transfer

Equation (24) implies that the addition of an electron to cobalt carbonyl (or the dimer) leads to the formation of the cobalt carbonyl anion. If this is correct, it should be possible to form cobalt carbonyl anion from dicobalt octacarbonyl by an external source of electrons. Such a reaction was achieved by shaking a benzene solution of dicobalt octacarbonyl with sodium amalgam. No gas was evolved, and analysis of the reaction mixture showed that a quantitative conversion of dicobalt octacarbonyl to cobalt carbonyl anion had taken place:

$$2Na + [Co(CO)_4]_2 \rightarrow 2Na[Co(CO)_4]. \quad (31)$$

To 0.4931 g. (1.44 millimoles) of dicobalt octacarbonyl in 12 ml. of benzene was added 130 g. of sodium amalgam containing approximately 1 percent sodium; the mixture was stirred. The benzene solution was decolorized after 1 hour, indicating complete conversion of dicobalt octacarbonyl. Stirring was continued for 1 more hour. No gas was evolved during the reaction. Sixty milliliters of water was added, and the mixture was stirred for 2 hours to decompose excess sodium and to dissolve the sodium salt of cobalt hydrocarbonyl, $NaCo(CO)_4$. Analysis of the aqueous solution showed 0.465 g. (2.72 millimoles) of cobalt carbonyl anion (1.89 millimoles cobalt carbonyl anion per mole of dicobalt octacarbonyl).

Hieber and Schulten (65) reported that dicobalt octacarbonyl reacts with aqueous solutions of strong bases, for example, $Ba(OH)_2$ or $NaOH$, principally according to equation (32):

$$3Co(CO)_4 + 2OH^- \rightarrow 2HCo(CO)_4 + Co(CO)_3 + CO_3^{--}.$$
$$\text{(dimer)} \qquad\qquad \text{(polymer)}$$
$$(32)$$

These authors reported that even in strong alkaline solutions the reaction did not proceed uniformly according to equation (32) and that some carbon monoxide was evolved according to equation (33):

$$3Co(CO)_4 + 2H_2O \rightarrow 2HCo(CO)_4 + Co(OH)_2 + 4CO.$$
$$\text{(dimer)}$$
$$(33)$$

In the light of the new concepts, the reaction between dicobalt octacarbonyl and aqueous solutions of strong bases may consist of an electron transfer and/or a homomolecular disproportionation, the former predominating at high hydroxyl ion concentrations, equations (34–36) (80). At low hydroxyl ion concen-

trations, water acts like ammonia in equation (11).

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^-, E^\circ_B = -0.401 \quad (34)$$

$$2[Co(CO)_4]_2 + 4e^- \rightarrow 4[Co(CO)_4]^- \quad (35)$$

$$2[Co(CO)_4]_2 + 4OH^- \rightarrow 4[Co(CO)_4]^- + 2H_2O + O_2 \quad (36)$$

This hypothesis is supported by the following experiments: A benzene solution of dicobalt octacarbonyl was treated with 4 N sodium hydroxide until the benzene solution had become colorless. Analysis of the aqueous solution showed that 1.72 moles of cobalt carbonyl anion was formed per mole of dicobalt octacarbonyl. In a similar experiment in which distilled water was used instead of sodium hydroxide solution, the amount of cobalt carbonyl anion formed corresponded to 1.48 moles per mole of dicobalt octacarbonyl.

Equations (32) and (33), suggested by Hieber and Schulten (65), exclude the formation of more than 1½ moles of cobalt carbonyl anion per mole of dicobalt octacarbonyl.

The electron transfer concept may also help to explain the complicated reaction that constitutes one of the standard methods for the preparation of cobalt carbonyl anion (13)

$$12KOH + 2K_4Co(CN)_6 + 11CO \rightarrow$$

$$3K_2CO_3 + 12KCN + 6H_2O + 2KCo(CO)_4. \quad (37)$$
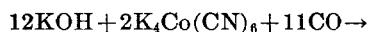
In this reaction cobalt (II) ion gains electrons in its transformation to the anion $Co(CO)_4^-$, and very likely these electrons are furnished by the alkali (equation (34)). The appearance of carbonate is consistent with this view and is explained by the oxidation of the carbon monoxide.

According to equation (11) carbon monoxide is evolved when dicobalt octacarbonyl is treated with a Lewis base such as water, methanol, ethanol, ammonia, pyridine, or o-phenanthroline. However, no carbon monoxide is evolved when excess dimethylamine is condensed onto cobalt octacarbonyl at $-80°$ C. and the mixture allowed to warm to room temperature. Analysis of the reaction product showed that 2 moles of cobalt carbonyl anion was formed per mole of cobalt (II) ion as required by equation (11) and that dimethylformamide was present with small amounts of tetramethylurea. Evidently the carbon monoxide usually given off as gas (equation (11) reacted with dimethylamine to yield dimethylformamide as the principal reaction product:

$$3[Co(CO)_4]_2 + 20(CH_3)_2NH \rightarrow$$

$$2[Co[(CH_3)_2NH]_6] [Co(CO)_4]_2 + 8HCON(CH_3)_2. \quad (38)$$
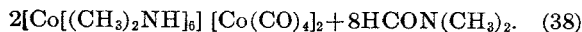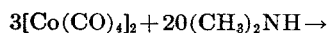
As no carbon monoxide was evolved in this reaction and as dimethylamine is a gas at room temperature, it was possible, by weighing the reaction product, to determine the amount of dimethylamine absorbed per mole of dicobalt octacarbonyl. Instead of 20 moles of dimethylamine (equation (38)), 24 moles of dimethylamine was absorbed, 8 moles per mole of dicobalt octacarbonyl. As will be shown later, this excess of dimethylamine in the product is probably due to complex formation between cobalt carbonyl anion and dimethylamine. Based on these results the reaction between dicobalt octacarbonyl and dimethylamine may now be represented by equation (39):

$$3[Co(CO)_4]_2 + 24(CH_3)_2NH \rightarrow$$

$$2[Co[(CH_3)_2NH]_6][Co(CO)_4]_2 \quad (39)$$

$$8HCON(CH_3)_2 + 4(CH_3)_2NH \text{ (complexed)}$$
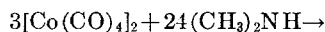
Dry dimethylamine was prepared by dropping an aqueous solution, containing about 50 percent of the hydrochloric acid salt, on excess NaOH. The gas was swept with nitrogen through two drying towers (filled with soda lime) into a flask provided with an inlet and an outlet tube. The outlet tube was closed by a mercury valve. The flask contained a weighed amount of dicobalt octacarbonyl and was immersed in a dry-ice bath. After an excess of amine had been condensed in the flask, the inlet tube was closed, the bath was removed, and the amine was allowed to evaporate until no more gas was given off at room temperature.

In a tared flask 1.57 g. of dicobalt octacarbonyl (4.59 millimoles) was treated with excess amine as described above. After removal of the dry-ice bath, the inlet tube was closed, and the outlet tube was connected to a gas burette filled with aqueous 10 percent sulfuric acid. A mass spectrometric analysis of the gas not absorbed by the acid solution showed that it consisted of nitrogen and 10 ml. normal temperature and pressure (n.t.p.) carbon monoxide. If all of the carbon monoxide contained in the dicobalt octacarbonyl had been liberated, 223 ml. (n.t.p.) would have been evolved. After no more gas was given off at room temperature, the flask was stoppered and weighed. The increase in weight was 1.75 g., which corresponds to 39 millimoles of dimethylamine. Thus, 8.5 millimoles of dimethylamine had been adsorbed per mole of dicobalt octacarbonyl. Mass spectrometric analysis of the reaction product indicated the presence of dimethylamine, dimethylformamide, and tetramethylurea, the last corresponding to about 10 percent of the dimethylformamide present. The reaction product gave the spectrum shown in figure 4. A microdistillation of a few drops of the reaction product at atmospheric pressure and a bath temperature of 150° to 200° C. gave a distillate which contained 33.5 percent dimethylformamide, 3.5 percent tetramethylurea, and appreciable percentages of dimethylamine and water as determined by mass spectrometric analysis.

In a second experiment the amount of cobalt carbonyl anion was determined with nickel o-phenanthroline chloride solution (133). Dicobalt octacarbonyl (0.833 g., 2.43 millimoles), treated with excess dimethylamine as just described, gave 0.533 g. (3.11 millimoles) of cobalt carbonyl anion; that is, 1.28 moles of anion per mole of dicobalt octacarbonyl. This
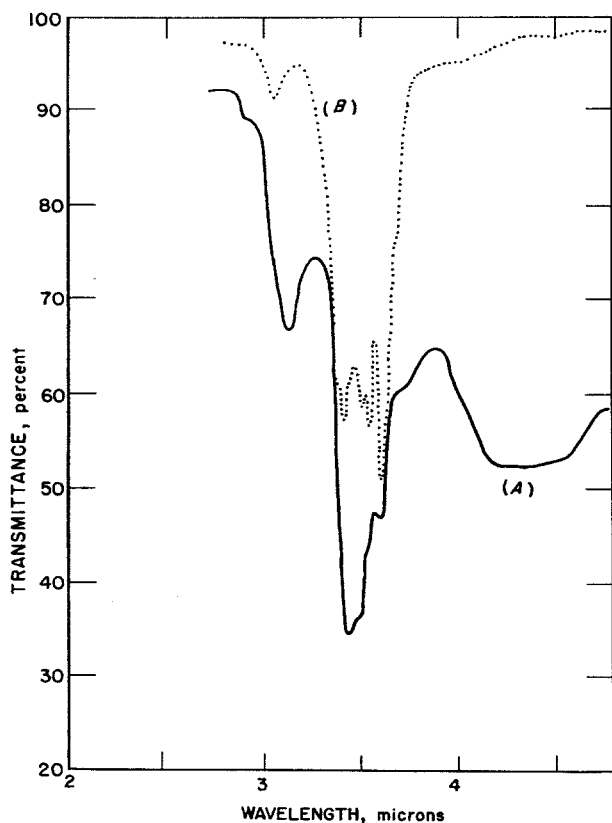
(A) —, reaction product obtained according to equation 38. (B) . . ., dimethylamine (saturated CCl₄ solution).

FIGURE 4.—Infrared Spectra Illustrating Complex Formation.

result is in good agreement with equation (39), which requires the formation of 1.33 moles of anion per mole of dicobalt octacarbonyl. In equation (39) the cation is shown coordinated only with dimethylamine; however, the cobalt cation may also be coordinated with dimethylformamide. Dimethylformamide is capable of coordinating with cobalt (II) ion; this was shown by an experiment in which dicobalt octacarbonyl was treated with this compound. The amount of carbon monoxide evolved and the amount of anion formed were consistent with equation (11), where B is dimethylformamide.

According to equation (39), stoichiometric amounts of dicobalt octacarbonyl are needed to furnish the carbon monoxide required for the conversion of dimethylamine to dimethylformamide. However, if equation (11) could be reversed by employing a high partial pressure of carbon monoxide, dicobalt octacarbonyl might function as a transfer agent for carbon monoxide, and only catalytic quantities of the carbonyl might be required. This possibility was realized when dimethylamine was carbonylated as follows:

Dimethylamine was treated with 1 mole-percent dicobalt octacarbonyl in the presence of 200 atm. of (initial pressure) carbon monoxide at 200° to 220° C. Dimethylformamide was obtained smoothly and without side products in 60-percent yield. Mass spectrometric analysis of the product showed no dimethylamine nor tetramethylurea. The yield of 60 percent represents a minimum yield because of probable losses of dimethylamine during the sealing and flushing of the bomb. In an extension of the reaction, the experiment was repeated with piperidine in place of dimethylamine; the yield of N-formylpiperidine was 78 percent of theoretical.

The experimental details of these reactions are described as follows.

An ice-cooled solution of benzene (115 ml.) saturated with dimethylamine and containing 15.5 g. (345 millimoles) of dimethylamine was poured into an ice-cooled bomb, and 10 ml. of benzene, containing 1.26 g. (3.7 millimoles) of dicobalt octacarbonyl, was added. The bomb was flushed three times with nitrogen before being pressured to 200 atm. with carbon monoxide. Sealing and flushing took 4 minutes, during which time some dimethylamine may have escaped. The yield (1,493 g., 205 millimoles) thus represents a minimum. The reaction occurred at 200° to 210° C., as judged by the pressure drop. The product was a clear yellow liquid that contained no dimethylamine nor tetramethylurea, as determined by mass spectrometric analysis. The bulk of the benzene was distilled, and the residue was fractionated from a small Claisen flask. Boiling ranges, yields, and compositions of fraction, as determined by mass spectrometric analysis, are as follows:

| Fraction	Temperature, ° C.	Yield, grams	Composition, grams	
			Dimethylformamide	Benzene
I	60–84	84.0	0.84	83.16
II	84–146	14.7	3.81	10.89
III	146–154	10.3	10.28	.02

The total dimethylformamide (14.93 g., 205 millimoles) represents a 59.4 percent yield based on dimethylamine.

A solution of 99 ml. of piperidine (1 mole) and 30 ml. of benzene containing 5.1 g. (0.015 mole) of dicobalt octacarbonyl was subjected to 2,000 atm. of carbon monoxide pressure, heated to 220° C., and kept at this temperature for 4 hours. After cooling, the autoclave was opened, and the products were removed. Benzene was evaporated from the reaction product at 40° C. and 20 mm. Hg. The residue was distilled to dryness at 20 mm. Redistillation yielded 88 g. of a constant-boiling (70° C. at 5 mm.) distillate, it was identified as N-formylpiperidine by its complex with mercuric chloride (43). The yield of constant-boiling distillate was 88 g., or 78 percent of theory.

Mechanism of the Reaction

When excess dimethylamine is condensed onto dicobalt octacarbonyl at atmospheric pressure and −80° C., and when the mixture is allowed to warm to room temperature, the original dark brown-black solution slowly changes to light greenish yellow, and, as excess amine evaporates, it changes to a final dark

red. These two color changes correspond to two steps of the reaction. The dark brown at the start of the reaction is due to dicobalt octacarbonyl. The light greenish yellow, which appears as the solution approaches the boiling point of dimethylamine (7.4° C.), is caused by the formation of XXVII,

$$[Co(CO)_4]_2 + (CH_3)_2NH \rightarrow [(CH_3)_2NHCo(CO)_4]^+ \cdot [Co(CO)_4]^- \cdot \quad (40)$$
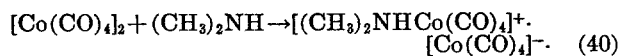
XXVII

a reaction analogous to that expressed by equation (27).

To show that a salt such as XXVII is formed in the presence of excess dimethylamine, dicobalt octacarbonyl was allowed to react with an excess of a saturated solution of dimethylamine in toluene. The product contained one-half of the dicobalt octacarbonyl as cobalt carbonyl anion, $[Co(CO)_4]^-$. The change from the initial color to the characteristic dark red of the final product is due to the formation of a salt of the type $[Co(B)_6]$ $[Co(CO)_4]_2$, where B is a base.

The reaction vessel consisted of a 300-ml. Erlenmeyer flask provided with a magnetic stirrer, a stopper fitted with a dropping funnel, and an outlet tube dipping in a mercury pool to prevent access of air. Ten milliliters of toluene, containing 0.5981 g. (0.75 millimole) of dicobalt octacarbonyl, was placed in the Erlenmeyer flask; the stopper was inserted; and nitrogen was passed through the dropping funnel to displace air. The flask was placed in a dry-ice bath, and 12 ml. of toluene, containing 1.28 g. (28 millimoles) of dimethylamine, was added. The dry-ice bath was removed, and the liquid was stirred while warming to room temperature. The solution furned light yellow, and a brownish-yellow oil separated. Twenty milliliters of water placed in the separatory funnel and forced into the flask under pressure of nitrogen readily dissolved the oil. Fifty milliliters of aqueous nickel o-phenanthroline chloride was added to precipitate the anion $[Co(CO)_4]^-$ as $[Ni(o-Phthr)_3]$ $[Co(CO)_4]_2$. The precipitate was filtered and washed with benzene and water, and the amount of carbon monoxide was determined (133). Carbon monoxide corresponded to 0.276 g. (0.807 millimole) of dicobalt octacarbonyl, or 46 percent of the amount of original dicobalt octacarbonyl.

The fact that all the carbon monoxide available from the decomposition of dicobalt octacarbonyl according to equation (11) was consumed in the formation of dimethylformamide suggests that the transfer of carbon monoxide from the carbonyl to the dimethylamine is achieved by means of an intermediate complex and that free carbon monoxide is never available as such.

Complexing of cobalt carbonyl anion with secondary amines involving hydrogen bonds is demonstrated by the spectrum (fig. 4) of the reaction product obtained according to equation (39) and by the spectrum (fig. 5) of
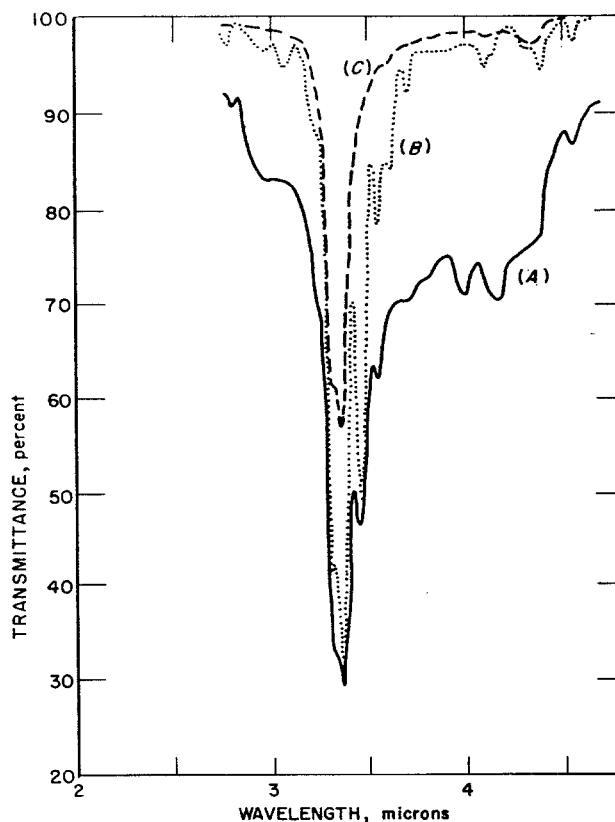

(A)—,[Co(Pyr)₆] [Co(CO)₄]2-piperidine in complex infpyridine solution. (B) . . . ., solution of piperidine in pyridine in same molar ratio as in curve (A). (C) . . . ., [Co(Pyr)₆] [Co₄CO)₂]2 in pyridine solution.

FIGURE 5.—Infrared Spectra Illustrating Complex Formation.

a pyridine solution containing 1 mole of piperidine per mole of $[Co(Pyr)_6]$ $[Co(CO_4]_2$. These spectra indicate that complex formation involves the $-NH$ group of dimethylamine (fig. 4) and piperidine (fig. 5), respectively. Excess dimethylamine in the product (equation (39)), therefore, can probably be attributed to coordination through complex formation.

The formation of tetramethylurea from dimethylamine and dicobalt octacarbonyl must arise from some type of overall dehydrogenation:

$$2(CH_3)_2NH + CO \rightarrow (CH_3)_2N - \overset{\overset{\displaystyle O}{\displaystyle \|}}{C} - N(CH_3)_2 + H_2 \quad (41)$$
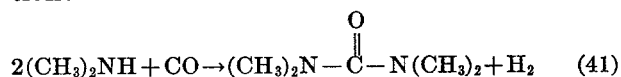
Such dehydrogenations have been shown to occur in the presence of dicobalt octacarbonyl (98, 148), probably by the formation and decomposition of cobalt hydrocarbonyl, $HCo(CO)_4$.

REACTION WITH ALKYNES

Acetylene and substituted acetylenes, $RC \equiv CR'$, readily displace the two bridge carbonyl

TABLE 10.—*Acetylenic dicobalt hexacarbonyls*

Compound	Formula	Description	Melting point, ° C.	Analysis, weight-percent					
				Calculated			Found		
				Carbon	Hydrogen	Cobalt	Carbon	Hydrogen	Cobalt
Acetylene dicobalt hexacarbonyl.	C₈H₂O₆Co₂	Dark red oil, boiling point 64–66° C. at 3.5–4 mm	13.0–13.6	30.80	0.65	--------	30.76	0.62	--------
2-Butyne dicobalt hexacarbonyl.	C₁₀H₆O₆Co₂	Dark-red oil		35.32	1.78	--------	35.38	1.84	--------
1,7-Octadiyne tetracobalt dodecacarbonyl.	C₂₀H₁₀O₁₂Co₄ [1]	Red crystals	85.0–85.4 [2]	35.43	1.49	34.77	35.62	1.64	34.78
Phenylacetylene dicobalt hexacarbonyl.	C₁₄H₆O₆Co₂	Dark-red oil		43.33	1.56	--------	42.92	1.61	--------
Diphenylacetylene dicobalt hexacarbonyl.	C₂₀H₁₀O₆Co₂ [3]	Dark-purple crystals, sublimes at 90° C. at 1 mm	109.5–110.0 [4]	51.75	2.17	25.40	51.61	2.22	25.6
Cyclodecyne dicobalt hexacarbonyl.	C₁₆H₁₆O₆Co₂	Dark-red oil		45.52	3.82	--------	45.94	4.04	--------
Isopropenylacetylene dicobalt hexacarbonyl.	C₁₁H₆O₆Co₂	Dark reddish-brown crystals	31.8–32.8	37.53	1.72	--------	37.47	1.84	--------
Propargyl alcohol dicobalt hexacarbonyl.	C₉H₄O₇Co₂	Orange-red needles	52.2–52.6 [5]	31.60	1.18	34.49	31.65	1.26	34.33
2-Butyne-1,4-diol dicobalt hexacarbonyl.	C₁₀H₆O₈Co₂	Orange-red needles	About 135 (d.) [6]	32.28	1.63	31.69	32.24	1.67	31.67
2,7-Dimethylocta-3,5-diyne-2,7-diol tetracobalt dodecacarbonyl.	C₂₂H₁₄O₁₄Co₄	Dark greenish-black crystals	D. without melting [5]	35.80	1.91	--------	36.59	2.08	--------
Propylpropiolic acid dicobalt hexacarbonyl.	C₁₂H₁₈O₈Co₂	Dark reddish-brown crystals	83–85 (d.) [5]	36.21	2.03	--------	36.26	2.09	--------
Pentylpropiolic acid dicobalt hexacarbonyl.	C₁₄H₁₂O₈Co₂	Dark-red oil		39.46	2.84	--------	40.15	3.08	--------
Phenylpropiolic acid dicobalt hexacarbonyl.	C₁₅H₆O₈Co₂	Dark purple-brown crystals.	About 120 (d.) [7]	41.69	1.40	--------	41.81	1.50	--------

[1] Molecular weight: Calculated, 678; found, 669±15 (ebullioscopic in benzene).
[2] Recrystallized from ethanol.
[3] Molecular weight: Calculated, 464; found, 463±5 (cryoscopic in cyclohexane).
[4] Recrystallized from methanol.
[5] Recrystallized from petroleum ether; boiling point, 60–68° C.
[6] Recrystallized from ethanol-water.
[7] Recrystallized from pentane.

groups in dicobalt octacarbonyl, $Co_2(CO)_8$, to yield a new type of organometallic compound, $RC_2R'Co_2(CO)_6$. The reaction, which proceeds smoothly and quantitatively at room temperature, can be represented by equation (42):

$$RC \equiv CR' + Co_2(CO)_8 \rightarrow RC_2R'Co_2(CO)_6 + 2\overline{CO} \qquad (42)$$
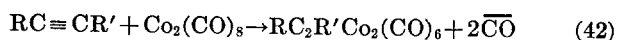
XXVIII

The reaction is general and occurs with all types of alkynes (see table 10). If the alkyne contains two triple bonds, each reacts with a mole of dicobalt octacarbonyl. There is no discernible steric effect with a conjugated diacetylene, because 1 mole of dicobalt octacarbonyl reacts with each of the two triple bonds in 2,7-dimethylocta-3,5-diyne-2,7-diol.

The acetylenic dicobalt hexacarbonyls are generally deeply colored. In the ultraviolet region diphenylacetylene dicobalt hexacarbonyl has a broad band near 2800 A. with a molar extinction coefficient, ϵ, of about 21,000. Acetylenic dicobalt hexacarbonyls have weak intermolecular forces of attraction. This is indicated by their high volatility, their high solubility in organic solvents, and the ease with which they can be eluted from a column of activated alumina. For example, acetylene dicobalt hexacarbonyl, with a molecular weight of 312, distills at 64° to 66° C. at 3.5 to 4 mm. pressure.

Diphenylacetylene dicobalt hexacarbonyl, with a molecular weight of 464, sublimes at 90° C. at 1 mm. pressure and can be eluted from a column of activated alumina with a small volume of an aliphatic hydrocarbon solvent; 1,7-octadiyne tetracobalt dodecacarbonyl, with a molecular weight of 678, is soluble in pentane at room temperature.

Since the reaction of an alkyne with dicobalt octacarbonyl is accompanied by an evolution of gas, an attempt was made to determine the stoichiometry of the reaction by following it gasometrically. The reaction was studied in a flask connected to a gas burette. Two sets of experiments were carried out, one with excess alkyne, the other with excess dicobalt octacarbonyl. Both reagents were dissolved in toluene and mixed under an atmosphere of carbon monoxide or synthesis gas. The reaction mixture was then stirred by a magnetic stirrer, and the gas evolved was measured.

When the alkyne was in excess, 2 moles of carbon monoxide was evolved per mole of dicobalt octacarbonyl. When dicobalt octacarbonyl was in excess, 2 moles of carbon monoxide was evolved per mole of alkyne. Therefore, the reaction of 1 mole of the alkyne with 1 mole of dicobalt octacarbonyl results in the evolution of 2 moles of carbon monoxide as illustrated by equation (42).

Alkyne and dicobalt octacarbonyl were allowed to react at room temperature for at

least 1 hour in an inert, low-boiling solvent such as pentane, low-boiling petroleum ether, or diethyl ether, in a flask fitted with a mercury valve to permit the escape of evolved carbon monoxide. Stoichiometric amounts or an excess of the alkyne or dicobalt octacarbonyl were used, depending upon the subsequent purification procedure. The reaction mixture was then usually filtered to remove insoluble impurities, and the filtrate was dried in a stream of nitrogen. The acetylenic dicobalt hexacarbonyl residue was purified either by recrystallization, distillation, and sublimation, or by dissolving it in a suitable solvent, filtering to remove insoluble impurities, and evaporating the solvent in a stream of nitrogen. In most cases the purpose of the preparation was to obtain pure material, and no attempt was made to determine yields or to obtain maximum yields. The compounds are described in table 10.

For example, diphenylacetylene dicobalt hexacarbonyl was prepared as follows:

To a solution of 29.6 g. (8.65×10^{-2} moles) of $Co_2(CO)_8$ in 150 ml. of petroleum ether (boiling point, 35° to 55° C.) in an Erlenmeyer flask was added 14.8 g. (8.31×10^{-2} moles) of diphenylacetylene. A mercury valve on the flask permitted the escape of carbon monoxide. The mixture was allowed to stand overnight. Solvent was removed at room temperature in a stream of nitrogen, and the solid residue was recrystallized from 1 liter of methanol. Filtration gave 29.0 g. (75.2 percent yield) of dark, purple crystals of diphenylacetylene dicobalt hexacarbonyl; the melting point was 108.4° to 110.0° C. The mother liquors were concentrated and cooled. Filtration gave 2.5 g. (6.5 percent yield) of diphenylacetylene dicobalt hexacarbonyl, with a melting point of 108.4° to 109.8° C. Both solid fractions were combined, and after a second recrystallization from methanol, they yielded 23.5 g. (61 percent yield), with a melting point of 109.2° to 109.7° C.

## The Infrared Spectra of Acetylenic Dicobalt Hexacarbonyls

The infrared spectrum of dicobalt octacarbonyl contains a group of three bands at 4.83, 4.89, and 4.94μ and a single band at 5.38μ (see fig. 6). The group of three bands was assigned to the terminal carbonyl groups in $Co_2(CO)_8$, and the single band was assigned to the bridge carbonyl groups in $Co_2(CO)_8$ (23, 46).

Infrared spectra (fig. 6) were obtained for the acetylenic dicobalt hexacarbonyls described in table 10. Each spectrum contains a characteristic group of three sharp bands at approximately 4.78, 4.88, and 4.94μ. Their positions are similar to those at 4.83, 4.89, and 4.94μ, attributable to terminal carbonyl groups in $Co_2(CO)_8$. The band at 5.38μ in $Co_2(CO)_8$, attributable to bridge carbonyl groups, is absent from the spectra of acetylenic dicobalt hexacarbonyls. Hence, the 2 moles of carbon monoxide that are displaced from $Co_2(CO)_8$ on

treatment with an alkyne are both bridge carbonyl groups.

Bands characteristic of the carbon-carbon triple bond are absent from the spectra of the acetylenic dicobalt hexacarbonyls. Spectra of acetylenic dicobalt hexacarbonyls derived from terminal acetylenes contain a band at 3.23μ, characteristic of an olefinic or an aromatic C—H stretching frequency. The appearance of this band in the spectrum of acetylene dicobalt hexacarbonyl and the concurrent disappearance of the acetylenic C—H stretching band in the 3.1μ region are illustrated in figure 6.

The spectrum of isopropenylacetylene dicobalt hexacarbonyl

$$\underset{\qquad\qquad\quad |}{CH_3}$$
$$H—C_2—C=CH_2 \cdot Co_2(CO)_6$$
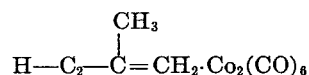
has a band at 6.16μ, attributable to a conjugated terminal ethylenic bond (see fig. 6). The position of the conjugated terminal ethylenic band in isopropenylacetylene

$$\underset{\qquad\qquad\;\; |}{CH_3}$$
$$HC \equiv C—C=CH_2,$$
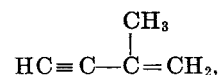
is at 6.18μ.

The spectrum of phenylpropiolic acid dicobalt hexacarbonyl, $C_6H_5—C_2—COOH \cdot Co_2(CO)_6$, has a band at 6.00$\mu$, and the spectra of both propylpropiolic and pentylpropiolic acid dicobalt hexacarbonyl, $R — C_2 — COOH \cdot Co_2(CO)_6$ (R =propyl, pentyl), have bands at 5.98μ. These absorptions are characteristic of a conjugated carboxy group—about 5.80μ for saturated carboxylic acids, 5.90μ for conjugated olefinic acids such as crotonic acid, 5.94μ for benzoic acid, 5.92μ for pentylpropiolic acid, and 5.94μ for phenylpropiolic acid. The conjugated nature of the acetylenic dicobalt hexacarbonyls is also indicated by the absorption in the visible and near ultraviolet regions.

In the spectrum of propargyl alcohol dicobalt hexacarbonyl, $H — C_2 — CH_2OH \cdot Co_2(CO)_6$, in carbon tetrachloride solution, the associated hydroxyl group absorption band becomes weaker with dilution, whereas the band due to the nonassociated group becomes stronger. This indicates that the hydrogen bonding is intermolecular.

Structure of Acetylenic Dicobalt Hexacarbonyls

The stoichiometry of the reaction of alkynes with dicobalt octacarbonyl and ultimate analyses and infrared spectra of the products, acetylenic dicobalt hexacarbonyls XXVIII, indicate that the two bridge carbonyl groups
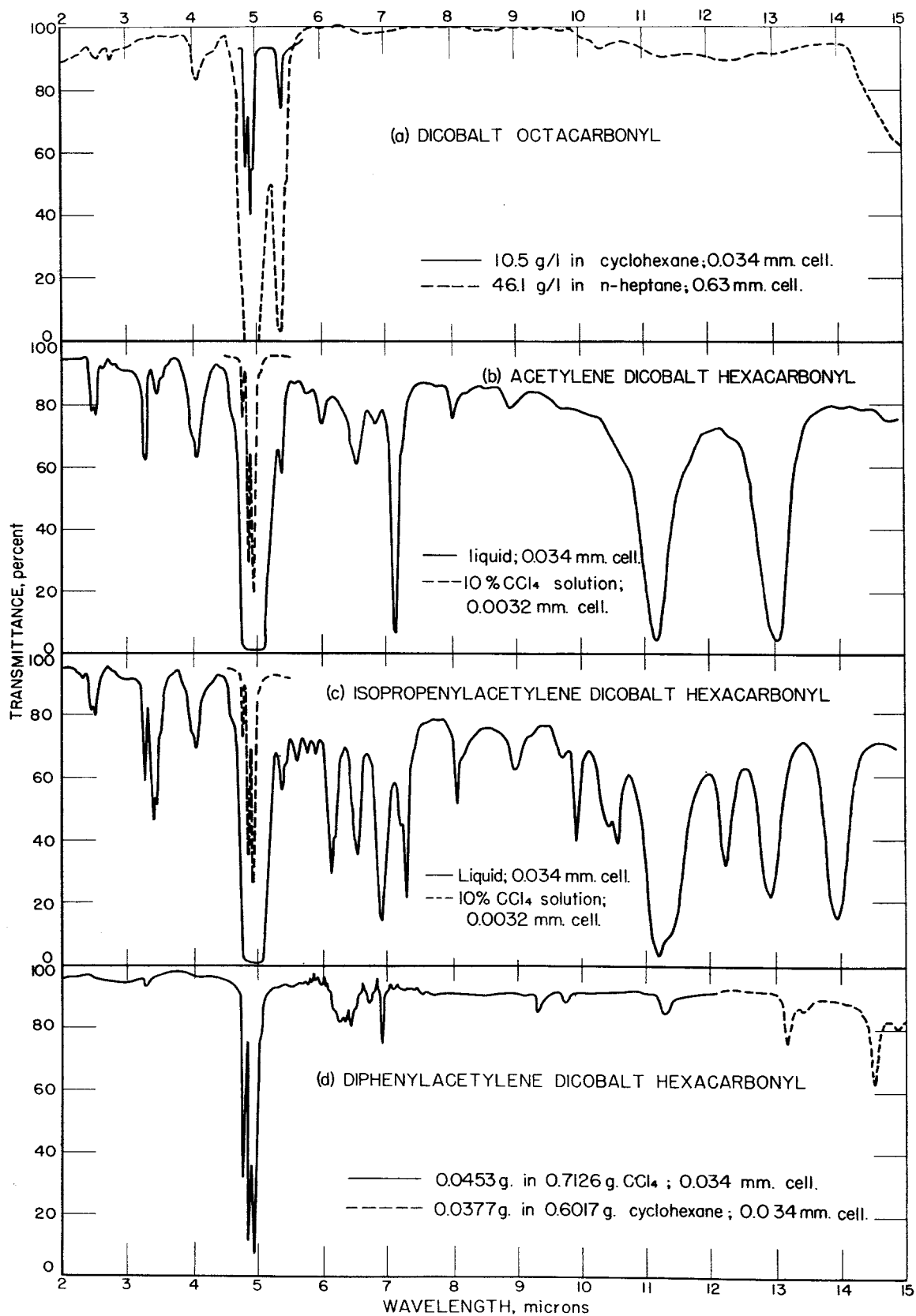
FIGURE 6.—Infrared Spectra of Dicobalt Octacarbonyl and Acetylenic Dicobalt Hexacarbonyls.

in $Co_2(CO)_8$ have been replaced by the alkyne. Although the position of the C—C bond with respect to the Co—Co bond is not known, only the following three arrangements need be considered:

The C—C axis is parallel to the Co—Co axis (structure A); the C—C axis is perpendicular to the Co—Co axis and either in the same plane (structure B) or a different plane (structure C).

XXVIII (A)   XXVIII (B)or(C)
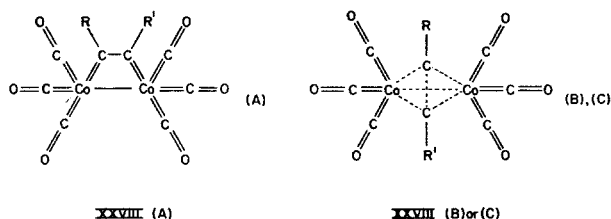
Of these structures, only B possesses a center of symmetry, provided it is derived from acetylene or a symmetrically substituted alkyne, and provided the carbonyl groups are symmetrically arranged. From analogy with dicobalt octacarbonyl (*23, 46*) it may be assumed that the carbonyl groups are arranged to give a center of symmetry. Structure B should therefore be distinguishable from A and C by its dipole moment. The dipole moment of diphenylacetylene dicobalt hexacarbonyl (XXVIII, R—R'=C_6H_5) is 2.0 to 2.1 D. Except for an extremely large anomalous atomic polarization (*29*), this result appears to eliminate B as a possible structure.

Each of the acetylenic dicobalt hexacarbonyls contains the same number (three) of infrared absorption bands in the region of the terminal carbonyl groups. This is unexpected on the basis of symmetry considerations. Structure B, in which R=R', has C_{2h} symmetry, for which group theory predicts three infrared-active terminal carbonyl stretching frequencies; structures A and C, having lower symmetry, should give rise to a greater number of infrared-active terminal carbonyl stretching frequencies. Furthermore, when R=R', each of the three proposed structures should give rise to more than three infrared-active terminal carbonyl stretching frequencies.

The predicted additional frequencies are unobservable, perhaps because of the nature of the bonding between the acetylenic portion and the dicobalt hexacarbonyl portion in XXVIII. Possibly, this bonding is similar to that in aromatic molecular complexes of the electron donor-acceptor type (*6*). Information about the infrared spectra of these complexes is very meager. Unpublished work in this laboratory indicates that they show little if any difference from the summation of the spectra of the com-

ponents when all spectra are determined in the same physical state.

Investigations of the geometry of XXVIII by means of X-ray and/or electron diffraction might supply the information necessary to choose among the postulated structures.

The structure of an acetylenic dicobalt hexacarbonyl may be somewhat analogous to intermediates in heterogeneous catalysis involving the adsorption of a molecule on dual-surface sites. Such intermediates have been proposed, for example, for the adsorption of ethylene and the adsorption of methylene radicals on a solid surface (*78*), and in a mechanism for the Fischer-Tropsch reaction (*135*).

Physical Constants of Diphenyl-acetylene Dicobalt Hexacarbonyl

Magnetic susceptibility measurements on diphenylacetylene dicobalt hexacarbonyl indicate that this compound is diamagnetic.

Dielectric constant and density measurements for solutions of diphenylacetylene dicobalt hexacarbonyl in benzene at 30° C. gave a value of 204 ± 4 for the total molar polarization of the solute (table 11).

TABLE 11.—*Physical constants for diphenylacetylene dicobalt hexacarbonyl in benzene solutions at 30° C.*

Solution	Mole fraction of solute	Density	Dielectric constant	Molar polarization, P [1]
Pure solvent	0	0.86823	2.2627	
1	0.0026122	.87236	2.2802	209
2	.0040660	.87484	2.2902	209
3	.0052331	.87751	2.2964	199
4	.0062175	.87976	2.2054	203

[1] Average P=204±4

The molecular refraction for the D-sodium line was calculated from bond refractivities for structures A and B. Denbigh's values of 1.25, 2.73, and 1.69 were used for the (C—C), (C—C) benzene, and (C—H) bond moments, respectively (*36*). Published values for the refractive indices (*79*) and densities (*72*) of iron pentacarbonyl and nickel carbonyl served to claculate their molecular refractions of 40.8 and 35.1, respectively. The results were a value of 8.2 for the total (Fe=C=O) bond moment, 8.8 for the total (Ni=C=O) bond moment, and an estimated 8.4 for the (Co=C=O) bond moment. With 5.98 for the induced polarization of carbon monoxide (*142*), the (Co—C) bond moment was estimated to be between 3 and 5, with a probable value of 3.4; the (Co—C) bond moment between 4 and 6, probable value 5; and the (Co—Co) bond moment between 2 and 11, probable value 7. The calculated