10.66 (w), 11.15 μ (w) and in carbon disulfide at 13.38 (s), 14.12 (s) and 14.40 μ (s).

1-Carbomethoxy-π-allylcobalt Dicarbonyl Triphenylphosphine. —In a flask filled with nitrogen at 0° were placed 30 ml. of 0.07 M sodium cobalt carbonyl in ether and 2.2 ml. of 1.0 M methyl 4-bromo-2-butenoate[7] in ether. Gas slowly was evolved. After 2 hours at 0°, the solution was left at room temperature overnight. Then 3.0 ml. of 1.0 M triphenylphosphine in ether was added. After the gas evolution stopped (98 ml. or 1.2 mmoles were evolved) the solvent was evaporated under vacuum and the product was recrystallized under nitrogen several times from tetrahydrofuran and pentane. Orange-red crystals which decomposed at 135–137° were obtained.

Anal. Calcd. for $C_{25}H_{22}O_4PCo$: C, 63.02; H, 4.66. Found: C, 63.15; H, 4.92.

The infrared spectrum in carbon tetrachloride had bands at 3.24 (w), 3.39 (w), 4.81 (w), 4.98 (s), 5.10 (vs), 5.82 (m), 6.75 (w), 6.98 (m), 7.63 (m), 7.96 (w), 8.20 (w), 8.92 (m), 9.12 (w), 9.33 (w), 9.51 (w), 5.70 (w), 10.00 μ (w) and in carbon disulfide at 13.40 (m), 14.20 (m) and 14.40 μ (s).

2-Phenyl-π-allylcobalt Dicarbonyl Triphenylphosphine.— In a carbon monoxide-filled reaction flask connected to a gas buret and cooled to 0° were placed 30 ml. of 0.07 M sodium cobalt carbonyl in ether and 2.5 ml. of 1.0 M 2-phenylallyl bromide[8] in ether. The solution turned orange and slowly absorbed gas for about an hour (11 ml. absorbed) and then began evolving gas. The gas evolution stopped after reacting overnight at 25°. The reaction mixture was again cooled to 0° and 3.0 ml. of 1.0 M triphenylphosphine in ether was added. In about an hour and a half 42 ml. of gas was evolved and the reaction stopped. The solution was evaporated to dryness under vacuum and the product was recrystallized several times from ether–pentane at −80°.

(8) L. F. Hatch and T. L. Patton, *J. Am. Chem. Soc.*, **76**, 2705 (1954).

Yellow-brown crystals which decomposed at 112–114° were obtained.

Anal. Calcd. for $C_{29}H_{24}O_2PCo$: C, 70.45; H, 4.89. Found: C, 70.00; H, 5.32.

The infrared spectrum in carbon tetrachloride had bands at 3.25 (w), 4.82 (w), 5.01 (vs), 5.15 (vs), 6.27 (w), 6.77 (w), 6.82 (w), 6.98 (m), 7.67 (w), 8.43 (w), 9.12 (m), 9.70 (w), 9.98 μ (w) and in carbon disulfide at 13.03 (m), 13.40 (m), 14.20 (s) and 14.40 μ (vs).

Kinetic Measurements.—The method employed has been described previously.[3a] Again infrared spectra were taken of the reaction mixtures to confirm the structure of the products being formed. Since the π-allylcobalt carbonyl derivatives were not isolated, concentrations were determined from the amount of gas evolved when excess triphenylphosphine was added. In every experiment where triphenylphosphine was present in excess, the infrared spectra indicated complete reaction.

Reaction of π-Allylcobalt Tricarbonyl with Phosphorus Trichloride.—To 60 ml. of 0.07 M π-allylcobalt tricarbonyl in ether solution at 0° under a CO atmosphere was added 1.1 ml. of pure phosphorus trichloride. In 2 hours, 47.0 ml. (1.58 mmoles) of gas was evolved and the evolution stopped. The infrared spectrum showed an equilibrium mixture of starting material and the mono-(phosphorus trichloride) derivative was produced.

Reaction of π-Allylcobalt Tricarbonyl with Trimethyl Phosphite.—To 68 ml. of 0.055 M π-allylcobalt tricarbonyl in ether solution at 0° under a CO atmosphere was added 1.0 ml. of 1.0 M trimethyl phosphite in ether solution. In 30 min. 17 ml. (0.58 mmole) of gas was evolved. The infrared spectrum showed a mixture of the mono-(trimethyl phosphite) complex and π-allylcobalt tricarbonyl was present.

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Steric and Electronic Effects in the Dissociation of Cobalt Carbonyl Derivatives. III. Hydrogen, Nitrosyl and Binuclear Derivatives

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The rates of reaction of various cobalt carbonyl derivatives with triphenylphosphine were used as a basis for comparing the reactivity of the complexes. The mononuclear complexes investigated were cobalt hydrocarbonyl, acetylcobalt tetracarbonyl, π-allylcobalt tricarbonyl, and nitrosylcobalt tricarbonyl. All formed only monophosphine derivatives by replacement of a carbonyl group. Cobalt hydrocarbonyl is too reactive to measure accurately. It is at least 10^4 times more reactive than acetylcobalt tetracarbonyl. Acetylcobalt tetracarbonyl, π-allylcobalt tricarbonyl, and probably cobalt hydrocarbonyl react with triphenylphosphine by a first order dissociation mechanism, while nitrosylcobalt tricarbonyl reacts by a second order mechanism. The binuclear compounds studied were dicobalt octacarbonyl, the butenolactone–cobalt carbonyl complex ($Co_2(CO)_7C_4H_2O_2$), 3-hexyne dicobalt hexacarbonyl, and acetylene dicobalt hexacarbonyl. Dicobalt octacarbonyl very rapidly forms the known bis-(triphenylphosphine)-tricarbonylcobalt (I) tetracarbonylcobaltate (−I) at a rate which is proportional to a 1:1 complex between the octacarbonyl and triphenylphosphine. The other binuclear complexes react by first-order mechanisms, forming mono- or bis-phosphine derivatives by replacement of carbonyl groups. Nickel carbonyl reacts with triphenylphosphine by a first order mechanism, forming the monophosphine tricarbonyl complex.

Introduction

Practically all known cobalt carbonyl derivatives react with triphenylphosphine to produce carbon monoxide and phosphine derivatives of the metal carbonyl. The kinetics of these reactions indicate relative reactivity and mechanisms of reaction of the cobalt carbonyl derivatives.

Basolo and Wojcicki have investigated the kinetics of the exchange reaction of radioactive carbon monoxide with various cobalt carbonyl derivatives. Cobalt octacarbonyl and the binuclear lactone complex from cobalt octacarbonyl and 1-pentyne react by a first-order mechanism[1] while cyclopentadienylcobalt dicarbonyl reacts by a second order mechanism.[2] The diphenylacetylene dicobalt hexacarbonyl complex reacts at 25°, at a rate too slow to measure.[1] Acylcobalt tetracarbonyls and π-allylcobalt tricarbonyls react with triphenylphosphine in a first order reaction in-

dependent of the phosphine concentration.[3,4] In this paper are presented kinetic data on the reaction of triphenylphosphine with several different types of mono- and binuclear cobalt carbonyl derivatives. The information obtained indicates further the effects different ligands may have upon rate and mechanism of reaction.

Results

The compounds studied and the kinetic data obtained are given in Table I. All the compounds were prepared by methods already reported in the literature. In all examples the rates were followed by measuring the rate of gas evolution.

Mononuclear Compounds.—By far the most reactive carbonyl investigated was cobalt hydrocarbonyl. The hydrocarbonyl reacts with triphenylphosphine, evolving one mole of CO and forming cobalt hydrotricarbonyl triphenylphosphine. This compound was

(1) F. Basolo and A. Wojcicki, *J. Am. Chem. Soc.*, **83**, 520 (1961).

(2) A. Wojcicki and F. Basolo, *J. Inorg. Nuclear Chem.*, **17**, 77 (1961).

(3) R. F. Heck, *J. Am. Chem. Soc.*, **85**, 651 (1963).

(4) R. F. Heck, *ibid.*, **85**, 655 (1963).

TABLE I

RATES OF REACTION OF VARIOUS COBALT CARBONYL DERIVATIVES WITH TRIPHENYLPHOSPHINE

Compound	Solvent	Temp., °C.	Concn., M	$P(C_6H_5)_3$ concn., M	Rate constant, sec.$^{-1}$	ΔE^*, kcal.	ΔS_{25}^*, cal./mole deg.
HCo(CO)$_4$	17% pentane in ether	−72.0	0.028	0.042	~0.01^a		
CH$_3$COCo(CO)$_4$	THF	0.0	.114	.130	5.90 ± 0.16 × 10^{-4}		
CH$_3$COCo(CO)$_4$	Ether^b	.0	.045	.063	1.01 ± .02 × 10^{-3}	20.8	3.4
CH$_3$COCo(CO)$_4$	Toluene	.0	.062	.118	6.46 ± .11 × 10^{-4}		
CH$_3$COCo(CO)$_4$	Toluene	25.0	.071	.149	1.89 ± .10 × 10^{-2}	21.7	4.7
CH$_3$COCo(CO)$_4$	Methylene chloride	0.0	.060	.143	5.28 ± .30 × 10^{-4}		
π-C$_3$H$_5$Co(CO)$_3$^{c}	Ether	0.0	.053	.063	3.28 ± .14 × 10^{-4}	22.8	7.2
ONCo(CO)$_3$	Ether	25.0	.026	.063	1.59 ± .09 × 10^{-3} l./m./s.		
ONCo(CO)$_3$	Ether	25.0	.103	.038	1.63 ± .12 × 10^{-3} l./m./s.		
ONCo(CO)$_3$	Ether	25.1	.102	.210^d	8.40 ± .39 × 10^{-4} l./m./s.		
ONCo(CO)$_3$	THF	25.1	.148	.231	1.30 ± .06 × 10^{-3} l./m./s.	11.7	−34.0
ONCo(CO)$_3$	THF	49.9	.077	.285	8.70 ± .73 × 10^{-3} l./m./s.		
ONCo(CO)$_3$	THF	50.0	.183	.048	1.18 ± .09 × 10^{-2} l./m./s.		
Co$_2$(CO)$_8$	Methylene chloride	−72.0	.0087	.0305	5.64 ± .37 × 10^{-4}		
CO$_2$(CO)$_8$	Methylene chloride	−72.0	.0087	.0087	4.90 ± .27 × 10^{-4e}		
CO$_2$(CO)$_8$	Methylene chloride	−72.0	.0087	.150	5.36 ± .22 × 10^{-4}		
Co$_2$(CO)$_8$	Ether	0.0	.0526	.105	≳ 0.2		
Co$_2$(CO)$_7$C$_4$H$_2$O$_2$	Methylene chloride	.0	.068	.130	7.79 ± 0.38 × 10^{-4}		
Co$_2$(CO)$_7$C$_4$H$_2$O$_2$	Methylene chloride	.0	.146	.048	4.8 − 3.2 × 10^{-4f}		
Co$_2$(CO)$_7$C$_4$H$_2$O$_2$	Methylene chloride	25.0	.0604	.130	2.20 ± 0.14 × 10^{-2}	21.5	4.5
Co$_2$(CO)$_6$C$_2$H$_5$C$_2$C$_2$H$_5$	Toluene	59.8	.110	.083	8.51 ± .32 × 10^{-3}		
Co$_2$(CO)$_6$C$_2$H$_2$	Toluene	59.6	.042	.180	1.09 ± .04 × 10^{-3}		
Co$_2$(CO)$_6$C$_2$H$_2$	Toluene	59.8	.017	.0046	1.35 ± .16 × 10^{-3}		
Co$_2$(CO)$_6$C$_2$H$_2$	Toluene	25.0	.020	.073	5.87 ± .40 × 10^{-5}	17.0	−23.0

^{a} Maximum value (not proved to be first order). ^{b} Data taken from R. F. Heck, J. Am. Chem. Soc., 85, 651 (1963). ^{c} Data taken from R. F. Heck, ibid., 85, 655 (1963). ^{d} Concentration of bicyclic phosphite ester of trimethylolpropane. ^{e} Calculated on the basis that $d[CO]/dt = k[Co_2(CO)_8 \cdot P(C_6H_5)_3]$. ^{f} Downward drifting first order rate.

prepared previously by Hieber by treating sodium cobalt tricarbonyl triphenylphosphine with phosphoric acid.[5] The rate of the hydrocarbonyl–triphenylphosphine reaction, however, was so fast that even at −72° it was not possible to determine the order of the reaction or calculate an accurate rate constant. Assuming the reaction is first order, as our previous work on the mechanism of the hydroformation reaction indicated,[6] it is possible to estimate a maximum value for the rate constant of about 1×10^{-2} sec.$^{-1}$ at −72°. Cobalt hydrocarbonyl, then, is about 10,000 times more reactive than acetylcobalt tetracarbonyl. It is certainly not obvious why cobalt hydrocarbonyl should dissociate so readily but it is consistent with the observations of Basolo, Chatt, et al., that hydrogen exerts a very significant trans effect in the reaction of square planar complexes of the nickel group with pyridine.[7] The hydrogen group behaves as a very powerful electron-donating group when it is directly attached to a metal.

The kinetics of the reaction of acetylcobalt tetracarbonyl and of π-allylcobalt tricarbonyl with triphenylphosphine have been described in the previous papers in this series.[3,4] The rates were independent of the phosphine concentration at least down to about 0.06 M carbonyl derivative under the conditions used. The mechanism of the reactions was consistent with a reversible, first-order dissociation being the rate determining step.

Solvent effects on the acetylcobalt tetracarbonyl-triphenylphosphine reaction are small. Ether, tetrahydrofuran, toluene, and methylene chloride solvents gave rates which differed by less than a factor of two. Rates were fastest in ether solution.

(5) W. Hieber and E. Lindner, Z. Naturforsch., 16b, 137 (1961).

(6) R. F. Heck and D. S. Breslow, "Actes du Deuxieme Congres International de Catalyse," Vol. 1, Paris, 1960, Editions Technip, p. 671; Chem. Ind. (London), 467 (1960); J. Am. Chem. Soc., 83, 4023 (1961).

(7) F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson and B. L. Shaw, J. Chem. Soc., 2207 (1961).

π-Allylcobalt tricarbonyl dissociates one-third as rapidly as acetylcobalt tetracarbonyl does in ether solution.

Nitrosylcobalt tricarbonyl is a relatively stable cobalt carbonyl derivative. It reacts relatively slowly with triphenylphosphine evolving a mole of CO, forming nitrosylcobalt dicarbonyl triphenylphosphine. Contrary to the finding of Malatesta,[8] the reaction was easily stopped at the monophosphine derivative even with excess phosphine. The monotriphenylphosphine derivative was isolated as a dark red crystalline solid, m.p. 134.0–135.5° dec. The rate of the reaction of nitrosylcobalt tricarbonyl with triphenylphosphine appears to be second order in both ether and tetrahydrofuran solvents. In tetrahydrofuran the activation energy is 11.7 kcal. and the entropy of activation is −34 cal./mole/deg. Using the bicyclic phosphite ester of trimethylolpropane[9] as the ligand the rate is only about half as fast as with triphenylphosphine.

Binuclear Complexes.—Cobalt octacarbonyl reacts with two moles of triphenylphosphine at 0° or below in nonpolar solvents to evolve one mole of CO and form the salt, bis-(triphenylphosphine)-tricarbonyl-cobalt (I) tetracarbonylcobaltate (−I).[10] The reaction

$$Co_2(CO)_8 + 2P(C_6H_5)_3 \longrightarrow$$
$$Co(CO)_3[P(C_6H_5)_3]_2^+ Co(CO)_4^- + CO$$
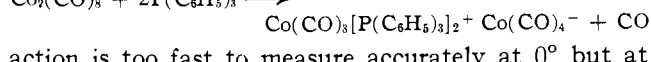
action is too fast to measure accurately at 0° but at −72° the rate could be measured. With more than two moles of phosphine per cobalt present, the rate is independent of the phosphine concentration and first order in the cobalt octacarbonyl concentration. However, with less than 2 equivalents of triphenylphosphine, the rate becomes proportional to the concentration of triphenylphosphine indicating that it is the first order decomposition of a 1:1 complex of cobalt octacarbonyl

(8) L. Malatesta and A. Aranev, ibid., 3803 (1957).

(9) W. S. Wadsworth, Jr., and W. D. Emmons, J. Am. Chem. Soc., 84, 610 (1962).

(10) A. Sacco and M. Freni, Ann. Chim. (Rome), 48, 218 (1958).
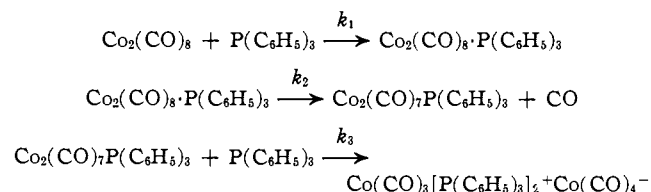
with triphenylphosphine that is actually being measured.

$$d[CO]/dt = k[Co_2(CO)_8 \cdot P(C_6H_5)_3]$$

Two other reactions of cobalt octacarbonyl which have been studied kinetically are described in the literature. Cobalt octacarbonyl exchanges with radioactive CO in a first order reaction independent of the CO concentration. A slow formation of a reactive form of $Co_2(CO)_8$ is proposed, which is followed by a rapid addition and elimination of CO.[1] Acetylenes react with cobalt octacarbonyl giving two moles of CO and an acetylene dicobalt hexacarbonyl complex.[11] The

$$Co_2(CO)_8 + RC\equiv CR' \longrightarrow 2CO + Co_2(CO)_6RC\equiv CR'$$
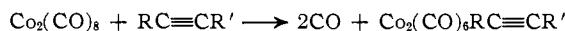
kinetics of the reaction indicated that a reactive form of cobalt octacarbonyl is formed initially which is in equilibrium with the stable form. This reactive form then probably reacts with an acetylene molecule, forming CO and an acetylene dicobalt heptacarbonyl complex. The latter complex then loses a second molecule of CO.

Clearly the triphenylphosphine reaction with cobalt octacarbonyl cannot involve the rapid formation of a reactive form of $Co_2(CO)_8$ before the formation of the 1:1 complex because the phosphine reaction is much faster than the CO exchange reaction or the acetylene reaction. A rapid second order reaction between the stable form of $Co_2(CO)_8$ and triphenylphosphine must be the initial reaction. The complex formed then evolves CO in a slower reaction. Finally another molecule of triphenylphosphine must be added rapidly to form the ionic product.

$$Co_2(CO)_8 + P(C_6H_5)_3 \xrightarrow{k_1} Co_2(CO)_8 \cdot P(C_6H_5)_3$$

$$Co_2(CO)_8 \cdot P(C_6H_5)_3 \xrightarrow{k_2} Co_2(CO)_7 P(C_6H_5)_3 + CO$$

$$Co_2(CO)_7 P(C_6H_5)_3 + P(C_6H_5)_3 \xrightarrow{k_3}$$
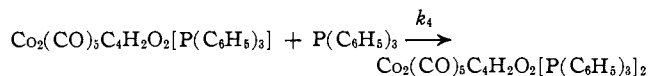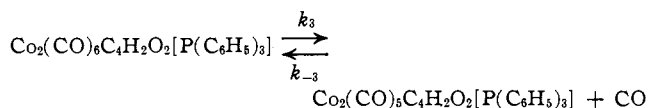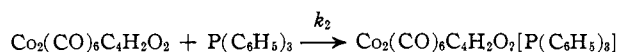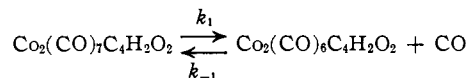$$Co(CO)_3[P(C_6H_5)_3]_2{}^+Co(CO)_4{}^-$$

Acetylene reacts with cobalt carbonyl and CO at 75° and 210 atmospheres to produce a peculiar binuclear butenolactone–cobalt carbonyl derivative, $C_4H_2O_2Co_2(CO)_7$.[12] This compound reacts with triphenylphosphine, evolving about 2 moles of CO per mole of complex. A dark red complex can be isolated from the reaction mixture which gave the correct analysis for the bisphosphine derivative. The infrared spectrum still shows coördinated carbon monoxide bands as well as a bridging carbonyl and a lactone carbonyl. It appears that one CO on each cobalt has been replaced. All the infrared carbonyl bands of this bisphosphine complex are about 0.1–0.2 μ higher in wave length than in the heptacarbonyl it was prepared from. The electronic effects of the phosphine groups are apparently transmitted to the lactone carbonyl group even though there are two, formally single bonds, together, through which the effects must pass.

The rate of the reaction of triphenylphosphine with the lactone complex in methylene chloride solution is first order if the triphenylphosphine concentration is about 0.1 M or higher. At lower concentrations the competition between the phosphine and CO apparently becomes significant and a decreasing first order rate was observed. Thus, the second mole of CO must either be evolved at about the same rate or evolved much more rapidly than the first. The following mechanism is consistent with the data.

(11) M. R. Tirpak, J. H. Wotiz and C. A. Hollingsworth. *J. Am. Chem. Soc.*, **80**, 4265 (1958).

(12) H. W. Sternberg, *et al.*, *ibid.*, **81**, 2339 (1959).

$$Co_2(CO)_7C_4H_2O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co_2(CO)_6C_4H_2O_2 + CO$$

$$Co_2(CO)_6C_4H_2O_2 + P(C_6H_5)_3 \xrightarrow{k_2} Co_2(CO)_6C_4H_2O_2[P(C_6H_5)_3]$$

$$Co_2(CO)_6C_4H_2O_2[P(C_6H_5)_3] \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}}$$
$$Co_2(CO)_5C_4H_2O_2[P(C_6H_5)_3] + CO$$

$$Co_2(CO)_5C_4H_2O_2[P(C_6H_5)_3] + P(C_6H_5)_3 \xrightarrow{k_4}$$
$$Co_2(CO)_5C_4H_2O_2[P(C_6H_5)_3]_2$$

Under the conditions used, k_1 is the rate-determining step. The activation energy for this reaction is 21.5 kcal. and the entropy of activation is 4.5 cal./mole/ deg. These values are quite close to those obtained from the acetylcobalt tetracarbonyl and the π-allylcobalt tricarbonyl reactions with triphenylphosphine as would be expected if the mechanism were similar. Attempts to measure the rate of the triphenylphosphine–cobalt lactone complex reaction in ether led to increasing first-order rates presumably because the intermediate monophosphine derivative crystallized out during the reaction and the rate of the second step became comparable with that of the first step.

The lactone group has a considerable stabilizing effect upon the cobalt carbonyl system since the lactone is much less reactive than cobalt octacarbonyl is toward triphenylphosphine.

The rate of reaction of the lactone complex with triphenylphosphine compares closely with the rate of exchange of radioactive carbon monoxide with the corresponding propyl derivative of the lactone complex studied by Basolo and Wojcicki.[1] The propyl chain on the lactone group would not be expected to have much effect upon the rate of dissociation of the complex. Basolo and Wojcicki found the first order rate of exchange of the propyl derivative in toluene at 0° was 9.2×10^{-4} sec.$^{-1}$, while, in this work in methylene chloride at 0°, the rate of reaction of the parent complex with triphenylphosphine was 7.8×10^{-4} sec.$^{-1}$. With this type of complex, the CO exchange reaction and the triphenylphosphine do appear to take place by similar mechanisms, probably involving the same rate determining dissociation reaction. Basolo and Wojcicki have suggested that the rate determining step in their exchange reaction may be the formation of an activated form of the lactone complex where either the cobalt–cobalt bond or one of the bridging carbonyl bonds is broken. The activated form then could rapidly add on another molecule of CO and eliminate a different molecule of CO.[1] The fact that the energy and entropy of activation of this reaction are very similar to those found for the acetylcobalt tetracarbonyl and π-allylcobalt tricarbonyl dissociations suggests that the lactone complex may be reacting by dissociation, rather than by forming an activated complex. Equilibration of the coördinated and bridged carbonyl groups would most probably take place after the dissociation had occurred. The bridging carbonyl group then could be accommodated easily on the cobalt which lost the carbonyl group; thus the electron deficiency would be distributed between both cobalt atoms.

The complexes of acetylenes with cobalt octacarbonyl, which already have been mentioned above, are unusually stable organocobalt complexes.[13] They react with triphenylphosphine, evolving a mole of CO and apparently giving only monophosphine derivatives, at least below 60° with the two examples investigated.

(13) H. W. Sternberg, *et al.*, *ibid.*, **78**, 120 (1956).

From the reaction mixture of the acetylene derivative, however, the monophosphine could not be obtained pure. Instead disproportionation seemed to take place and the dark brown product isolated, m.p. 207–208° dec., was the bisphosphine derivative. Hübel[14] has reported obtaining both the mono- and the bis-triphenylphosphine derivative from the diphenylacetylene cobalt carbonyl complex at 70°.

The rates of the reaction of the 3-hexyne- and acetylenecobalt hexacarbonyls with triphenylphosphine are first order in toluene solution. The 3-hexyne complex is about 6.3 times more reactive than the acetylene complex. A small downward drift (~25.% during 3 half-lives) was noted in the first order rate constant obtained from the 3-hexyne–complex reaction. It was obvious that some decomposition of the product was taking place during the reaction giving $Co_2(CO)_6$-$[P(C_6H_5)_3]_2$ as an insoluble brown solid. This decomposition would result in the absorption of CO and is probably the reason for the decreasing rate.

The acetylene cobalt hexacarbonyl complex is about 10^5 times less reactive toward triphenylphosphine than is cobalt octacarbonyl.

The activation energy for the acetylene cobalt hexacarbonyl triphenylphosphine reaction is 17.0 kcal. and the entropy of activation is −23.0 cal./mole/deg. The considerable change in these values compared with the previous, first-order dissociations indicates that a different type of transition state, with much lower entropy, must be involved in this reaction. One possible explanation is that as a CO departs another co-ordinated CO from the second cobalt atom moves over and becomes bridged in the transition state and a bridged intermediate could be formed. Since the
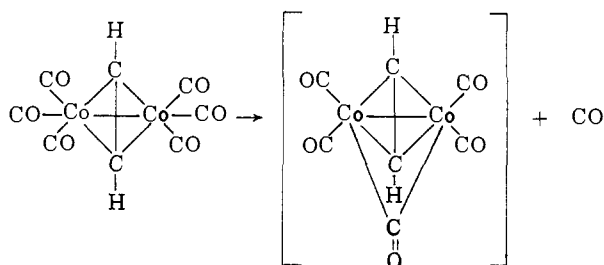
acetylene carbons are above the cobalt–cobalt bond,[15] the geometry would probably permit this type of intermediate to be formed.

Several attempts were made to measure the rate of reaction of cyclopentadienylcobalt dicarbonyl with triphenylphosphine but consistent data could not be obtained. Reaction occurred at 50–75° evolving CO, but more than one mole of CO was evolved per mole of triphenylphosphine with excess cyclopentadienylcobalt dicarbonyl. No stable phosphine derivatives could be isolated. Only green amorphous product was formed. Apparently the monophosphine complex decomposed rapidly under the reaction conditions.

Nickel Carbonyl.—In order to make a direct comparison of a mononuclear metal carbonyl–radioactive carbon monoxide exchange reaction with a metal carbonyl–phosphine reaction, nickel carbonyl was investigated. Basolo and Wojcicki have reported that nickel carbonyl exchanges with radioactive CO in a first order reaction at a rate of 7.5×10^{-4} sec.$^{-1}$ in toluene at 0°.[1] Under the same conditions triphenylphosphine reacts with nickel carbonyl, also in a first order reaction, producing nickel tricarbonyl triphenylphosphine at a rate of about 4.3×10^{-4} sec.$^{-1}$. This agreement is reasonably good, considering the different

methods employed. The triphenylphosphine reaction in ether solution is about 65% as fast as in toluene. The data are given in Table II.

TABLE II

RATE OF REACTION OF NICKEL CARBONYL WITH TRIPHENYLPHOSPHINE AT 0°

Solvent	Concn. of $Ni(CO)_4$	Concn. of $P(C_6H_5)_3$	Rate constant, sec.$^{-1}$
Ether	0.064	0.083	$2.81 \pm 0.05 \times 10^{-4}$
Toluene	.094	.110	$4.47 \pm 0.07 \times 10^{-4}$
Toluene	.100	.038	$4.16 \pm 0.12 \times 10^{-4}$

Conclusions.—The reaction of triphenylphosphine with various derivatives of cobalt carbonyl has proved to be a very general reaction. The rates of these reactions have been used as a basis for comparing the reactivity of the various derivatives. In the mononuclear complexes the reactivity decreased from cobalt hydrocarbonyl, to acetylcobalt tetracarbonyl, to π-allylcobalt tricarbonyl, to nitrosylcobalt tricarbonyl. Cobalt hydrocarbonyl is more than 10^4 times more reactive than acetylcobalt tetracarbonyl. In the binuclear series the rates of reaction decreased from dicobalt octacarbonyl, to the butenolactone–cobalt carbonyl complex, to 3-hexyne dicobalt hexacarbonyl, to acetylene dicobalt hexacarbonyl. There was a factor of about 10^5 in rate between cobalt octacarbonyl and the acetylene complex. The ligands on the cobalt carbonyl group not only affect the reactivity of the complex toward triphenylphosphine, but they also may affect the mechanism of reaction. Acetylcobalt tetracarbonyl, π-allylcobalt tricarbonyl, the lactone complex $(Co_2(CO)_7C_4H_2O_2)$, and the two acetylene cobalt hexacarbonyl complexes appear to react by first-order processes probably involving dissociation as the first and rate-determining step. Nitrosylcobalt tricarbonyl reacts by a second-order mechanism with phosphines. (It is interesting that the isoelectronic nickel carbonyl reacts with phosphines by a first-order dissociation mechanism.) Cobalt octacarbonyl appears to form rapidly a 1:1 complex with triphenylphosphine which then more slowly evolves CO. Cobalt hydrocarbonyl was too reactive toward triphenylphosphine to measure accurately. Presumably it reacts by a first-order dissociation mechanism, but this mechanism has not yet been tested. The effects produced by variation of ligands are probably largely, if not entirely, electronic rather than steric.

Experimental

Cobalt Carbonyl Derivatives.—All the carbonyl derivatives were prepared by methods reported in the literature. Cobalt hydrocarbonyl was prepared by the method of Sternberg[16] and kept in pentane solution at −80°. Nitrosylcobalt tricarbonyl was prepared by the reaction of nitric oxide with sodium (or potassium) cobalt carbonyl[17] in ether solution. Cobalt octacarbonyl was prepared as described by Wender.[18] The lactone-cobalt carbonyl complex also was prepared by Sternberg's method.[12] Finally the two acetylene–cobalt carbonyl complexes were prepared from the appropriate acetylene and cobalt octacarbonyl and purified by distillation before use.[13]

Kinetic Measurements.—The rates of reaction were measured by rate of evolution of carbon monoxide as described previously.[3] The measured infinity values were used in the calculation of the rate constants. In all cases except the 3-hexyne dicobalt hexacarbonyl reaction, the products of the reaction have been isolated and identified. When excess triphenylphosphine was used, the infrared spectrum of the reaction mixture was always determined to be certain all the starting carbonyl had reacted. Temperature control was accurate to about ±0.2° at 0° and above but only to about ±0.5° at −72°.

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Cobalt Hydrotricarbonyl Triphenylphosphine.—This compound can be isolated from the kinetic experiments, but since it is relatively unstable it is more conveniently prepared as follows. To a solution of 0.080 g. of triphenylphosphine in 10 ml. of pentane under nitrogen at 0° was added 1.0 ml. of 0.29 M cobalt hydrocarbonyl in pentane. Gas was evolved immediately and on cooling to −80°, the clear solution deposited pale yellow crystals of the triphenylphosphine hydride complex. On warming to 25° or on exposure to air the hydride decomposes into the brown dicobalt hexacarbonyl bistriphenylphosphine complex and hydrogen. The hydride is the same compound reported by Hieber, judging by its infrared spectrum and reactivity.[5]

Nitrosylcobalt Dicarbonyl Triphenylphosphine.—A solution of nitrosylcobalt tricarbonyl, prepared from 30 ml. of 0.07 M sodium cobalt carbonyl in ether solution and nitric oxide at 25°, was treated with 3.0 ml. of 1.0 M triphenylphosphine in ether solution. After standing overnight at 25° the solution was evaporated and the red crystalline product obtained was recrystallized twice from methanol. The product decomposed at 134.0–135.5°.

Anal. Calcd. for $C_{20}H_{15}O_3PNCo$: C, 59.00; H, 3.73. Found: C, 59.00; H, 3.74.

The complex in carbon tetrachloride had bands in the infrared region at 3.23 (w), 4.88 (s), 5.02 (vs), 6.75 (m), 6.98 (m), 8.50 (w), 9.11 (m), 9.71 (w) and 10.01 (w) μ. In carbon disulfide there were bands at 13.42 (s), 14.19 (m) and 14.42 (s) μ.

Reaction of the Butenolactone–Cobalt Carbonyl Complex with Triphenylphosphine.—To a solution of 0.41 g. (1.04 mmoles) of $Co_2(CO)_7C_4H_2O_2$[12] in 10 ml. of ether at 0° under carbon monoxide, was added 4.0 ml. of 1.0 M triphenylphosphine in ether. After about 70 minutes gas evolution stopped. The product had partially crystallized during the reaction. The solvent was removed under vacuum and the residue was dissolved in 5 ml. of methylene chloride. Insoluble material was removed by centrifuging, and

addition of 5 ml. of pentane gave red-brown crystals of the phosphine derivative. Two more crystallizations from methylene chloride gave the pure complex. The product had no melting point but it gradually decomposed on heating.

Anal. Calcd. for $C_{45}H_{32}O_7P_2Co_2$: C, 62.51; H, 3.73. Found: C, 62.07; H, 4.03.

The infrared spectrum in chloroform had bands at 3.22 (w), 3.30 (w), 4.83 (s), 4.91 (vs), 4.98 (vs), 5.58 (m), 5.81 (s), 6.58 (m), 6.73 (m), 6.97 (m), 7.63 (w), 8.42 (w), 9.13 (m), 9.71 (w), 10.00 (w), 10.40 (w) and 11.28 (w) μ. In carbon bisulfide bands were at 13.49 (w), 13.77 (w) and 14.44 (m) μ.

Acetylene Dicobalt Tetracarbonyl Bis-triphenylphosphine.—To a solution of 0.31 g. of $Co_2(CO)_6C_2H_2$ (1.0 mmole) in 10 ml. of toluene at 60° was added 1.1 ml. of 1.0 M triphenylphosphine in toluene. After the gas evolution stopped (about one hour), the solvent was evaporated at room temperature and the product was extracted from the residue with ether. A small amount of insoluble $Co_2(CO)_6[P(C_6H_5)_3]_2$ was removed by centrifuging. The ether was evaporated to about 5 ml. and 10 ml. of pentane was added. On cooling to −80° red-brown prisms of the product slowly separated from the solution. Three further recrystallizations from ether–pentane gave a pure sample of the bisphosphine, m.p. 207–208° dec.

Anal. Calcd. for $C_{42}H_{32}O_4Co_2P_2$: C, 64.46; H, 4.12. Found: C, 64.76, 64.81; H, 4.31, 4.32.

The infrared spectrum in methylene chloride had bands at 3.25 (w), 4.94 (s), 5.09 (vs), 6.77 (w), 6.98 (m), 7.16 (w), 7.65 (w), 8.43 (w), 9.11 (m), 9.31 (w), 9.70 (w), 9.98 (w) and 11.10 (w) μ. In carbon disulfide there were additional bands at 13.40 (m), 14.16 (m) and 14.40 (s) μ.

[Contribution from the John Curtin School of Medical Research, Australian National University, Canberra City, Act, Australia]

Stereospecific Influences in Metal Complexes Containing Optically Active Ligands.   Part VI. Oxalato-l-propylenediaminecobalt(III) Complexes

By Francis P. Dwyer,[1a] Thomas E. MacDermott[1b] and Alan M. Sargeson

Sodium bis-(oxalato)-l-propylenediaminecobaltate(III) and oxalatobis-(l-propylenediamine)-cobalt(III) iodide have been prepared by direct syntheses from cobalt(II) salts, l-propylenediamine and oxalate ions using lead(IV) oxide as the oxidizing agent, and the dextro and levo isomers of the complexes separated. The Dl and Dll isomers of these two complexes predominated over the Ll and Lll isomers, respectively, at equilibrium in aqueous solution at 25°. For the former complex K = Dl/Ll = 1.63, ΔF = −270 cal./g. mole, and for the latter K = Dll/Lll = 1.40, ΔF = −200 cal./g. mole. Rotatory dispersion measurements showed that Dl and Dll forms of the complexes had the same configuration as the dextro forms of the bis-(oxalato)-ethylenediaminecobaltate(III) and oxalatobis-(ethylenediamine)-cobalt(III) ions.

With the exception of the optically active polyaminocarboxylic acids, 1,2-propanediamine- and *trans*-1,2-cyclohexanediaminetetraacetic acids, which appear to be completely stereospecific in their sexadentate and quinquedentate octahedral metal complexes because of atom crowding,[2] quantitative information is lacking on the free energy differences[3] between the optical isomers of complexes containing a single asymmetric ligand. Both isomers appear to have been detected in cobalt complexes containing one molecule of d-cyclopentanediamine, or l-propylenediamine,[4a,b] and in the cation bis-(ethylenediamine)-l-propylene platinum(IV).[5] The value found with the latter complex for the ratio Dl/Ll = 1 was probably due to the similar rates of formation of the isomers rather than to the establishment of equilibrium between them.

In complex ions containing two asymmetric ligands, such as $[\text{Co-}l\text{-pn}_2(\text{NO}_2)_2]^+$,[6] $[\text{Co-}l\text{-pn-}d\text{-pn}(\text{NO}_2)_2]^+$,[7] and

$[\text{Co-}l\text{-pn}_2\text{CO}_3]^+$,[8,9] evidence has been obtained for the existence of a few of the possible isomers, but equilibrium data on these systems are lacking.

The anion bis-(oxalato)-l-propylenediaminecobaltate-(III), which can exist only in the optically isomeric forms Dl and Ll, has been prepared in a similar manner to the bis-(oxalato)-ethylenediaminecobaltate(III) ion[10] by the oxidation of a mixture of cobalt(II) acetate, potassium oxalate and l-propylenediamine with lead(IV) oxide. The isomeric mixture was isolated as the sparingly soluble salt of the d,l-oxalatobis-(ethylenediamine)-cobalt(III) cation, transformed to the very soluble, purplish-violet sodium salts, and then resolved with the optical forms of $[\text{Coen}_2(\text{C}_2\text{O}_4)]^+$ cation. The optical isomers, designated Dl and Ll by comparison with the rotatory dispersion curves of the corresponding $[\text{Coen}(\text{C}_2\text{O}_4)_2]^-$ ions,[10] Fig. 1, were isomerized at 25° on charcoal, and the equilibrium concentrations calculated

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