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Steric and Electronic Effects in the Dissociation of Cobalt Carbonyl Derivatives. II. π -Allylcobalt Carbonyls

BY R. F. HECK

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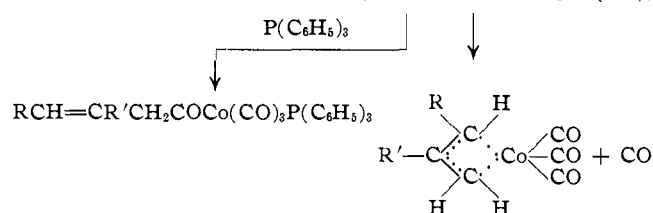
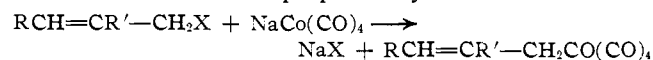
π -Allylcobalt tricarbonyl reacts with triphenylphosphine to give CO and π -allylcobalt dicarbonyl triphenylphosphine. The rate of the reaction is independent of the phosphine concentration above about 0.06 *M*. A first-order dissociation mechanism is indicated where a competition exists between CO and the phosphine for the intermediate π -allylcobalt dicarbonyl. Substituents produce relatively small but very unusual effects. The 2-methyl-, 2-bromo-, 2-chloro-, and 2-phenyl derivatives are more reactive than π -allylcobalt tricarbonyl itself by factors of 8.6, 12.3, 19.7, and 3.4, respectively, while the 1-methyl- and 1-chloro-compounds are less reactive by factors of 0.6 and 0.3, respectively. The 1-carbomethoxy derivative is 2.4 times more reactive than π -allylcobalt tricarbonyl. Possible explanations for these unusual results are presented.

Introduction

In the first paper in this series, factors influencing the dissociation of acylcobalt tetracarbonyls into carbon monoxide and an acylcobalt tricarbonyl were investigated. Steric effects appeared to be relatively unimportant until large sphenial acyl groups were introduced while electron-withdrawing acyl groups had small rate retarding effects. In the present paper are presented some results of a study of the factors influencing the dissociation of π -allylcobalt tricarbonyls into CO and π -allylcobalt dicarbonyls.

There are few quantitative or even qualitative data in the literature on the effects of substituents in π -aromatic-metal complexes upon the reactivity of the metal. Our previous discovery that π -allylcobalt tricarbonyls react readily with triphenylphosphine to give π -allylcobalt dicarbonyl triphenylphosphine derivatives and CO¹ was an obvious reaction to study to gain information on the effect of substituents in the π -allyl group on the reactivity of the cobalt atom.

π -Allylcobalt tricarbonyls are conveniently prepared by the reaction of allylic halides with sodium cobalt tetracarbonyl.^{1,2} σ -Allylcobalt tetracarbonyls are formed initially and these gradually lose CO and form the π -allyl complexes. The unstable σ -allyl compounds have not been isolated as such, but they may be observed by their infrared spectra and isolated as the triphenylphosphine adducts, vinylacetylcobalt tricarbonyl monotriphenylphosphines. The adducts of allyl- and crotylcobalt tetracarbonyl have been described previously.¹ The 3-carbomethoxyallylcobalt tetracarbonyl adduct has now been prepared by the same method.



The π -allyl complexes used in this investigation are listed in Table I. The π -allyl-,^{1,2} 1-methyl- π -allyl,^{1,2} and the 1- and 2-chloro- π -allyl-cobalt tricarbonyls² have been prepared previously. The new 2-methyl-, 2-bromo-, 2-phenyl-, and the 1-carbomethoxy- π -allylcobalt tricarbonyls were prepared from sodium cobalt carbonyl and methallyl chloride, 1,2-dibromo-2-propene, 2-phenylallyl bromide, and methyl 3-bromocrotonate, respectively. 1-Carbomethoxy- π -allylcobalt tricarbonyl and 2-phenyl- π -allylcobalt tricarbonyl

have been isolated as their monophosphine derivatives, 1-carbomethoxy- π -allylcobalt dicarbonyl triphenylphosphine and 2-phenyl- π -allylcobalt dicarbonyl triphenylphosphine.

TABLE I
RATE CONSTANTS FOR THE REACTION OF VARIOUS π -ALLYLCOBALT TRICARBONYL DERIVATIVES WITH TRIPHENYLPHOSPHINE IN ETHER SOLUTION AT 0°

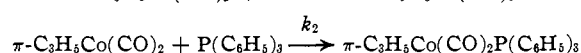
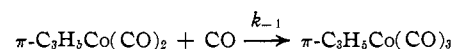
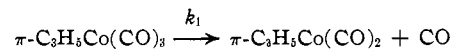
Compound	P- (C ₆ H ₅) ₃		Rate constant, sec. ⁻¹	Relative rate
	Concn., <i>M</i>	concn., <i>M</i>		
π -C ₃ H ₅ Co(CO) ₃	0.053	0.063	3.28 ± 0.14 × 10 ⁻⁴	1.0
π -C ₆ H ₅ Co(CO) ₃	.050	.250	3.37 ± .19 × 10 ⁻⁴	
π -C ₂ H ₅ Co(CO) ₃	.032	.063	1.14 ± .06 × 10 ^{-2a}	
π -C ₃ H ₇ Co(CO) ₃	.058	.063	3.24 ± .15 × 10 ⁻⁴	
π -C ₃ H ₅ Co(CO) ₃	.048	.250	3.52 ± .07 × 10 ⁻⁴	
π -C ₃ H ₅ Co(CO) ₃	.116	.037	2.62 - 1.17 × 10 ^{-4b}	
2-CH ₃ - π -C ₃ H ₅ Co(CO) ₃	.037	.063	2.81 ± 0.15 × 10 ⁻³	8.6
2-Br- π -C ₃ H ₅ Co(CO) ₃	.036	.063	4.05 ± .16 × 10 ⁻³	12.3
	.032	.250	4.15 ± .16 × 10 ⁻³	
2-Cl- π -C ₃ H ₅ Co(CO) ₃	.018	.031	6.47 ± .13 × 10 ⁻³	19.7
2-C ₆ H ₅ - π -C ₃ H ₅ Co(CO) ₃	.065	.092	1.12 ± .04 × 10 ⁻³	3.4
1-CH ₃ - π -C ₃ H ₅ Co(CO) ₃	.039	.063	1.79 ± .13 × 10 ⁻⁴	0.6
1-CH ₃ - π -C ₃ H ₅ Co(CO) ₃	.045	.250	1.84 ± .12 × 10 ⁻⁴	
1-Cl- π -C ₃ H ₅ Co(CO) ₃	.010	.063	9.36 ± .56 × 10 ⁻⁵	0.3
1-CH ₃ OCO- π -C ₃ H ₅ Co(CO) ₃	.039	.063	7.85 ± .42 × 10 ⁻⁴	2.4

^a Rate at 25.0°. $\Delta E^* = 22.75$ kcal. $\Delta S_{35}^* = 7.2$ cal./mole/deg. ^b First-order rate constants decreased with time.

Kinetic Measurements.—All the compounds listed in Table I react with triphenylphosphine to give only monophosphine derivatives and CO even in the presence of a large excess of triphenylphosphine. With excess triphenylphosphine (above 0.06 *M*), the rates of CO evolution are first order with respect to the cobalt complex and zero order in phosphine. With less than about 0.06 *M* phosphine present, π -allylcobalt tricarbonyl begins to show a decreasing first order rate. The downward drift becomes more serious as the concentration of the phosphine is decreased further. When the concentration of the π -allyl complex was 0.116 *M* and the phosphine 0.037 *M*, the first-order rate constants decreased from 2.62 to 1.17 × 10⁻⁴ sec.⁻¹ during about two half-lives. The rate increased appreciably with time when calculated on the basis

$$d[\text{CO}]/dt = k[\pi\text{-C}_3\text{H}_5\text{Co}(\text{CO})_3 \cdot \text{P}(\text{C}_6\text{H}_5)_3]$$

These data are in line with a dissociation mechanism for the reaction where there is a competition between CO and phosphine for the intermediate lower carbonyl initially formed.



Assuming a steady state concentration of the dicarbonyl intermediate, the rate of formation of product is

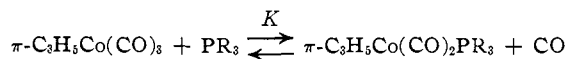
(1) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **82**, 750 (1960); **83**, 1097 (1961).

(2) W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties and B. W. Howk, *ibid.*, **83**, 1601 (1961).

$$\frac{d(\pi\text{-C}_3\text{H}_5\text{Co}(\text{CO})_2\text{P}(\text{C}_6\text{H}_5)_3)}{dt} = \frac{d[\text{CO}]}{dt} = \frac{k_1[\pi\text{-C}_3\text{H}_5\text{Co}(\text{CO})_3] \frac{k_2[\text{P}(\text{C}_6\text{H}_5)_3]}{k_{-1}[\text{CO}] + k_2[\text{P}(\text{C}_6\text{H}_5)_3]}}{k_{-1}[\text{CO}] + k_2[\text{P}(\text{C}_6\text{H}_5)_3]}$$

When the concentration of the triphenylphosphine exceeds about 0.06 *M* at 0°, the reaction becomes approximately first order because $k_{-1}[\text{CO}]$ is much less than $k_2[\text{P}(\text{C}_6\text{H}_5)_3]$. With lower triphenylphosphine concentrations all the terms are significant. It is not possible to determine the absolute values of k_2 and k_{-1} from the data obtained, but the ratio of k_{-1} to k_2 may be calculated, since we do know k_1 . Using the example above in which the triphenylphosphine concentration was 0.037 *M* and the π -allylcobalt tricarbonyl 0.116 *M* at 0° in ether solution, the average value of k_{-1}/k_2 was 1.8 ± 0.2 (average of 12 values). Thus, carbon monoxide is actually 1.8 times more effective at reacting with the intermediate dicarbonyl than triphenylphosphine, but the CO reaction is only significant when the concentration of the phosphine is reduced to less than about 10 times the concentration of the CO (0.0077 *M* at 0° under 1 atmosphere of CO).

Attempts were made to measure k_{-1}/k_2 values for other ligands but a new complication appeared. Both phosphorus trichloride and trimethyl phosphite react with π -allylcobalt tricarbonyl to evolve CO, but less than one mole of gas is given off. Apparently, the addition of the phosphine to π -allylcobalt dicarbonyl is also reversible and an equilibrium mixture is obtained when these poorer ligands are used. No attempt has been made to evaluate the rate constants in these reactions. The equilibrium constants for the reaction



have been estimated, however. At 0° in ether solution with one atmosphere of CO present, *K* is apparently fairly large when PR_3 is triphenylphosphine. It is about 0.025 when PR_3 is phosphorus trichloride and about 0.22 when PR_3 is trimethyl phosphite. Triphenylstibine does not react with π -allylcobalt tricarbonyl to a measurable extent under the same conditions or even at 25°. Thus, π -allylcobalt tricarbonyl undergoes carbonyl replacement reactions, at least with triphenylphosphine and trimethyl phosphite, less readily than acetylcobalt tetracarbonyl does.

Substituent Effects.—Three different positions exist for substitution in π -allylcobalt tricarbonyl: on the center carbon of the π -allyl system, the 2-position; on the end carbon closest to the metal, the 1-*endo* position; and on the end carbon away from the metal, the 1-*exo* position.

Consider first the 2-substituted derivatives. The 2-methyl complex dissociates 8.6 times more rapidly than π -allylcobalt tricarbonyl does. By itself this result is not surprising. On the basis of the previous work with the acylcobalt tetracarbonyl, electron-supplying groups should make dissociation easier.^{3a} It is not so easy to explain why the electron-withdrawing groups, 2-bromo-, 2-chloro-, and 2-phenyl-, also increased the rate of dissociation, however, to 12.3, 19.7, and 3.4 times that of π -allylcobalt tricarbonyl, respectively. Since bromine is larger than chlorine, steric factors cannot be responsible either. It is quite possible that tautomeric effects in π -allyl-metal systems are more important than in benzene systems.^{3b}

The situation is just as unusual with the 1-substituted derivatives. It is not certain that the three 1-substi-

tuted complexes investigated are the same isomer. Presumably, since the 1-methyl compound has been shown to be largely the *exo* product,^{2,4} the others are mainly the *exo* isomers also. If they are mixtures, the two components must react at similar rates since constant first order rates were observed. The *exo*-1-methyl isomer dissociated at a rate 0.6 that of π -allylcobalt tricarbonyl, the 1-chloro complex, 0.3 as fast, and the 1-carbomethoxy derivative, 2.4 times faster. The 1-methyl and 1-chloro groups are slightly rate retarding, showing that electronic changes on the 1-carbon of the π -allyl system have less effect and the effects are opposite those of the 2-substituents. The relatively higher rate of the 1-carbomethoxy derivative may be the result of one of the carboxyl oxygens assisting the dissociation by a neighboring group effect. As expected, the product of the phosphine reaction was 1-carbomethoxy- π -allylcobalt dicarbonyl triphenylphosphine, m.p. 135–137° dec. Previous work did indeed indicate that a carbomethoxy group can coordinate with cobalt.⁵ Obviously there are not enough data available to be certain that these explanations are correct. Perhaps the most important conclusion which can be drawn is that substituent effects, at least in this π -allylcobalt tricarbonyl system, are relatively small and there is not much hope of radically changing the reactivity of these complexes by adding substituents.

It is interesting that the apparently similar π -cyclopentadienylcobalt dicarbonyl complex reacts by a different mechanism. Wojcicki and Basolo⁶ have shown that π -cyclopentadienylcobalt dicarbonyl exchanges with radioactive CO in a second order reaction rather than by a first order reaction as is found for the π -allylcobalt tricarbonyls.

Experimental

π -Allylcobalt Tricarbonyls.—About a 10% excess of the allylic halides were added as 1.0 *M* ether solutions to 0.07 *M* sodium cobalt carbonyl in ether at 25°. After standing 2 hours to about 20 hours, the solutions were heated at 80° in hot water for about 1–3 hours to complete the reactions, except in the case of 2-phenylallyl bromide where the reaction went to completion at 25° in 15 hours. The final heating was necessary in several examples to complete the conversion of the σ -allyl derivatives into the π -complexes and to decompose small amounts of cobalt octacarbonyl and other materials which were sometimes produced in side reactions. The infrared spectra of several of these products have been reported previously.^{1,2} The new derivatives have carbonyl bands in ether solution as follows: 2-methyl- π -allylcobalt tricarbonyl, 1990 (vs) and 2062 (s) cm^{-1} ; 2-bromo- π -allylcobalt tricarbonyl, 2009 (vs), 2056 (w) and 2073 (s) cm^{-1} ; 2-phenyl- π -allylcobalt tricarbonyl, 2005 (vs), 2040 (w) and 2080 (s); 1-carbomethoxy- π -allylcobalt tricarbonyl, 1730 (m), 2010 (vs), 2044 (w) and 2077 (s) cm^{-1} .

Kinetic measurements were carried out with these ether solutions without isolating the π -allyl complexes.

4-Carbomethoxy-3-butenylcobalt Tricarbonyl Triphenylphosphine.—In a nitrogen-filled bottle at 0° were placed 30 ml. of 0.07 *M* sodium cobalt carbonyl in ether, 3.0 ml. of 1.0 *M* triphenylphosphine in ether and 2.5 ml. of 1.0 *M* methyl 4-bromo-2-butenate⁷ in ether. The solution was thoroughly mixed and let stand at 0° for one hour. The solvent then was evaporated under vacuum at 0°. The residue was extracted several times with small portions of pure tetrahydrofuran. The extracts were centrifuged to remove insoluble material and then concentrated by evaporating them under vacuum to about 4 or 5 ml. Addition of pentane and cooling gave clusters of pale tan needles. Two more crystallizations from tetrahydrofuran–pentane gave a product which decomposed at 95–96°.

Anal. Calcd. for $\text{C}_{27}\text{H}_{22}\text{O}_6\text{PCo}$: C, 60.92; H, 4.17. Found: C, 61.50; H, 4.41.

The infrared spectrum in carbon tetrachloride had bands at 3.24 (w), 3.39 (w), 4.85 (m), 5.05 (vs), 5.68 (s), 5.98 (s), 6.74 (w), 6.98 (m), 7.68 (w), 7.87 (m), 8.06 (w), 8.31 (w), 8.68 (w), 9.11 (m), 9.31 (w), 9.59 (w), 9.70 (w), 9.99 (w), 10.18 (w),

(4) D. W. Moore, H. B. Jonassen and T. B. Joyner, *Chem. Ind.* (London), 467 (1960).

(5) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **84**, 2499 (1962).

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

(7) W. J. Bailey and J. Bello, *J. Org. Chem.*, **20**, 525 (1955).

(3) (a) R. F. Heck, *J. Am. Chem. Soc.*, **85**, 651 (1963). (b) A referee has suggested that the rate enhancing effect of the electron-withdrawing groups might be the result of a weaker metal–carbon monoxide pi-bonding caused by a greater positive charge on the metal.

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 Dicarboxyl 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-butenolate⁷ 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 Dicarboxyl 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 bromide⁸ 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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[CONTRIBUTION FROM THE RESEARCH CENTER OF THE HERCULES POWDER COMPANY, WILMINGTON, DELAWARE]

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 mechanism¹ 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 hydro-tricarbonyl 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).