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Steric and Electronic Effects in the Dissociation of Cobalt Carbonyl Derivatives.   I.   Acylcobalt Carbonyls

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The first-order reaction of acylcobalt tetracarbonyls with triphenylphosphine has been used as a means for measuring the steric and electronic effects of the acyl group upon the rate of dissociation of the complex into a lower carbonyl and carbon monoxide.   As the size of the acyl group was increased, the rate of reaction with triphenylphosphine increased, indicating steric acceleration of the dissociation.   Electron-withdrawing acyl groups decreased the rate of dissociation.   Crotonoyl- and benzoylcobalt tetracarbonyls were 61 and 34 times faster, respectively, than the acetyl compound.   Substituents on the benzoyl group had relatively little effect. Electrons can apparently be supplied directly to the metal by the unsaturated group.   4-Pentenoylcobalt tricarbonyl, in which the double bond is coördinated with the cobalt, reacts at a rate about 4 times faster than acetylcobalt tetracarbonyl but the rate drifted downward.   Possible explanations are discussed.

Introduction

Relatively little is known about the factors affecting the dissociation of metal complexes into coördinately unsaturated species and a ligand molecule.   The major difficulty has been to find systems where substituents can be varied and which can be conveniently studied kinetically.

Meriwether and Fiene[1] have investigated the kinetics of the first order exchange of phosphines with various nickel–carbonyl–phosphine complexes.   They observed that the rate of dissociation of a phosphine group from nickel dicarbonyl diphosphine complexes depended upon both the resonance and inductive effects of the phosphine ligands.   Generally, the rates of dissociation decreased as the base strength of the phosphine increased, but there were exceptions suggesting that other unknown factors were important.

Basolo and Wojcicki[2] have measured the first order rates of exchange of radioactive carbon monoxide with various metal carbonyl complexes, and the relative reactivities of different types of complexes were compared.   More recently the kinetics of the reaction of various ligands with the manganese pentacarbonyl halides were investigated by Angelici and Basolo.[3] Again the rate was first order with respect to the carbonyl compound and independent of the ligand used. Manganese pentacarbonyl chloride was more reactive than the bromide and the bromide was more reactive than the iodide.
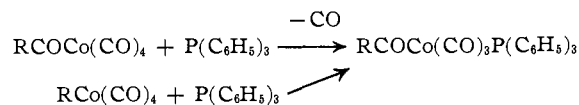
There is little more quantitative information available in the literature on the factors affecting dissociation rates of transition metal complexes.   In the present paper are reported the results of an investigation of rates of dissociation of a series of complexes in which it has been possible to vary one ligand systematically and to study steric and electronic effects relatively independently.

Previously, the reduction of acylcobalt tetracarbonyls to aldehydes by either hydrogen or cobalt hydrocar-

bonyl was found to be inhibited by carbon monoxide.[4] We concluded the reaction involved a first order dissociation into carbon monoxide and a coördinately unsaturated species, an acylcobalt tricarbonyl, for which the reducing agent and carbon monoxide competed.

$$\text{RCOCo(CO)}_4 \underset{+CO}{\overset{-CO}{\rightleftharpoons}} \text{RCOCo(CO)}_3 \overset{[H]}{\longrightarrow} \text{RCHO}$$
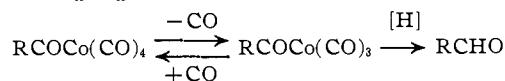
Triphenylphosphine reacts with acyl- or alkylcobalt tetracarbonyls, forming acylcobalt tricarbonyl triphenylphosphine complexes.[5]   It appeared likely that

$$\text{RCOCo(CO)}_4 + \text{P(C}_6\text{H}_5)_3 \overset{-CO}{\longrightarrow} \text{RCOCo(CO)}_3\text{P(C}_6\text{H}_5)_3$$

$$\text{RCo(CO)}_4 + \text{P(C}_6\text{H}_5)_3 \nearrow$$

these reactions also involved acylcobalt tricarbonyls as the reacting species.   Kinetic studies have confirmed this idea.   By varying the acyl groups in these complexes and measuring the rates of reaction with triphenylphosphine, it has been possible to assess the steric and electronic effects in the dissociation of acylcobalt tetracarbonyls into carbon monoxide and acylcobalt tricarbonyls.   Presumably, by analogy with the acylmanganese carbonyls,[6] it is one of the coördinated carbonyls and not the acyl carbonyl which is dissociating.

Results

Kinetic measurements were carried out by measuring the rate of gas evolution when triphenylphosphine was added to a solution of the acylcobalt tetracarbonyl. Constant first order rates, independent of phosphine concentration, were observed for acetylcobalt tetracarbonyl when there was a four-fold excess of either reagent or when reagent concentrations were equal. The same rate was observed in the dark and the same rate was observed with the sterically very different

(1) L. S. Meriwether and M. L. Fiene, J. Am. Chem. Soc., 81, 4200 (1959).

(2) F. Basolo and A. A. Wojcicki, ibid., 83, 520, 525 (1961).

(3) R. J. Angelici and F. Basolo, ibid., 84, 2495 (1962).

(4) R. F. Heck and D. S. Breslow, ibid., 83, 4023 (1961).

(5) R. F. Heck and D. S. Breslow, ibid., 82, 4438 (1960); 84, 2499 (1962).

(6) T. H. Coffield, J. Kozikowski and R. D. Closson, International Conference on Coordination Chemistry, London, April, 1959, Abstract 26.

Table I

Rate Constants for the Reaction of Various Acylcobalt Carbonyls with Triphenylphosphine in Diethyl Ether Solution at 0°
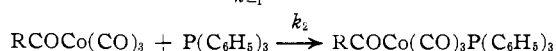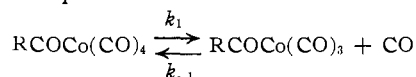
Compound	Concn., M	$P(C_6H_5)_3$ concn., M	Rate constant, sec.$^{-1}$	Relative rate
$CH_3COCo(CO)_4$	0.045	0.063	$1.01 \pm 0.02 \times 10^{-3}$	1.0
$CH_3COCo(CO)_4$	.041	.063	$9.73 \pm .08 \times 10^{-4a}$	
$CH_3COCo(CO)_4$	.043	.250	$1.00 \pm .01 \times 10^{-3}$	
$CH_3COCo(CO)_4$	.059	.021	$1.06 \pm .07 \times 10^{-3}$	
$CH_3COCo(CO)_4$	.028	.063	$2.55 \pm .18 \times 10^{-2b}$	
$CH_3COCo(CO)_4$	.061	.130^c	$1.10 \pm .10 \times 10^{-3}$	
$CH_3(CH_2)_4COCo(CO)_4$	.047	.063	$1.07 \pm .06 \times 10^{-3}$	1.1
$(CH_3)_2CHCOCo(CO)_4$	.035	.063	$2.11 \pm .05 \times 10^{-3}$	2.1
$(CH_3)_3CCOCo(CO)_4$	.033	.063	$8.6 \pm .1 \times 10^{-2}$	86
$(CH_3)_2CHCH_2COCo(CO)_4$	.044	.063	$1.21 \pm .18 \times 10^{-3}$	1.2
$(CH_3CH_2)_2CHCOCo(CO)_4$	.039	.063	$1.87 \pm .06 \times 10^{-3}$	1.9
$Cl(CH_2)_3COCo(CO)_4$	.036	.063	$7.65 \pm .17 \times 10^{-4}$	0.8
$CH_3OCH_2COCo(CO)_4$	.052	.063	$2.80 \pm .11 \times 10^{-4}$	.3
$CF_3COCo(CO)_4$	.045	.063	$9.41 \pm .02 \times 10^{-5}$	.1
$CH_3CH{=}CHCOCo(CO)_4{}^d$	.028^e	.063	$6.18 \pm .15 \times 10^{-2}$	62
$CH_3CH{=}CHCOCo(CO)_4{}^d$	.026^e	.250	$7.07 \pm .45 \times 10^{-2}$	
$C_6H_5COCo(CO)_4$	.043	.063	$3.44 \pm .25 \times 10^{-2}$	34
$p\text{-}CH_3OC_6H_4COCo(CO)_4$	.037	.063	$4.96 \pm .31 \times 10^{-2}$	50
$m\text{-}CH_3OC_6H_4COCo(CO)_4$	.035	.063	$1.81 \pm .12 \times 10^{-2}$	18
$p\text{-}NO_2C_6H_4COCo(CO)_4$	.026	.063	$1.65 \pm .07 \times 10^{-2}$	17
$p\text{-}CH_3OCOC_6H_4Co(CO)_4$	.045	.063	$1.95 \pm .10 \times 10^{-2}$	20
$o\text{-}CH_3C_6H_4COCo(CO)_4$	.036	.063	$2.82 \pm .15 \times 10^{-2}$	28
$2,4,6\text{-}(CH_3)_3C_6H_2COCo(CO)_4$	.041	.063	$1.98 \pm .03 \times 10^{-4}$	0.02
$C_6H_5CH_2COCo(CO)_4$	.043	.063	$1.32 \pm .04 \times 10^{-3}$	1.3

$$\begin{array}{c} \text{CH}{=}\text{CH}_2 \\ \downarrow \\ \text{CH}_2\diagup\quad\diagdown\text{Co(CO)}_3 \\ | \\ \text{CH}_2\diagdown\quad\diagup \\ \text{C}{=}\text{O} \end{array}$$

(structure above)	Concn., M	$P(C_6H_5)_3$	Rate constant	Relative rate
	.038	.063	$5.8\ -\ 3.2 \times 10^{-3f}$	~ 4
	.038	250	$8.5\ -\ 5.6 \times 10^{-3f}$	

^{a} Measured in the dark. ^{b} Measured at 25.0°. $\Delta E^* = 20.8$ kcal. $\Delta S^* = 3.4$ cal. mole/deg. ^{c} Concentration of trimethyl phosphite. ^{d} Equilibrium mixture of 56% crotonoylcobalt tetracarbonyl and 44% 3-methyl-π-acrylylcobalt tricarbonyl. ^{e} Concentration of crotonoylcobalt tetracarbonyl in equilibrium mixture. ^{f} First-order rate constants decreased with time.

trimethyl phosphite. Since the first order rates remained constant throughout at least two half-lives of the reaction, carbon monoxide does not compete with the phosphine for the intermediate acylcobalt tricarbonyl under these conditions. A list of the acylcobalt carbonyls studied and the rate constants observed is given in Table I. All compounds were prepared from acid chlorides or from alkyl halides plus carbon monoxide, and sodium cobalt carbonyl, as described previously.[5] All the compounds gave good first-order kinetics except 4-pentenoylcobalt tricarbonyl, which had a downward drifting first order rate. After each rate constant is listed the average error observed. Rates relative to that of acetylcobalt tetracarbonyl also are given.

Discussion and Conclusions

The data clearly indicate a first-order dissociation mechanism. The acylcobalt tetracarbonyl dissociates in the rate-determining step into acylcobalt tricarbonyl and carbon monoxide. This step is followed by a rapid reaction of the acylcobalt tricarbonyl with triphenylphosphine to form the acylcobalt tricarbonyl triphenylphosphine complex.

$$\text{RCOCo(CO)}_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{RCOCo(CO)}_3 + \text{CO}$$

$$\text{RCOCo(CO)}_3 + \text{P(C}_6\text{H}_5)_3 \overset{k_2}{\longrightarrow} \text{RCOCo(CO)}_3\text{P(C}_6\text{H}_5)_3$$

Assuming the steady state approximation, the rate of the reaction is

$$-\frac{d[\text{RCOCo(CO)}_4]}{dt} = k_1[\text{RCOCo(CO)}_4]\frac{k_2[\text{P(C}_6\text{H}_5)_3]}{k_{-1}[\text{CO}] + k_2[\text{P(C}_6\text{H}_5)_3]}$$

Under our conditions $k_2[\text{P(C}_6\text{H}_5)_3]$ is apparently much larger than $k_{-1}[\text{CO}]$ and the rate becomes proportional to the concentration of the acylcobalt tetracarbonyl only. Thus, the rate constants are a measure of the rate of dissociation of the acyl tetracarbonyls.

The data indicate that the structure of the acyl group has a marked effect upon the rate of the dissociation. Increasing the size of the acyl group increases the rate of dissociation. In the series acetyl, n-hexanoyl, isobutyryl, pivalyl, the relative rates are $1.0 : 1.1 : 2.1 : 86$. Since the addition of two methyl groups to acetylcobalt tetracarbonyl to form the isobutyryl complex had only about one-fortieth the effect of adding three to form the pivalyl complex, the effect cannot be electronic. Isovalerylcobalt carbonyl was about as reactive as n-hexanoylcobalt carbonyl and 2-ethylbutyrylcobalt carbonyl had about the same rate as the isobutyryl complex. Thus, steric strain may be a significant factor in the reactivity of pentacoördinated cobalt complexes.

The effect of electron-withdrawing substituents on the acyl group is shown in the series acetyl-, 4-chlorobutyryl-, methoxyacetyl- and trifluoroacetylcobalt tetracarbonyls. The relative rates of these compounds are $1 : 0.8 : 0.3 : 0.1$. Electron-withdrawing groups probably make dissociation more difficult because they remove electrons from the metal and make the loss of two more electrons with the departing ligand more unfavorable.

The reaction of crotonoylcobalt tetracarbonyl with triphenylphosphine is a particularly interesting example. The reaction of *trans*-crotonoyl chloride with sodium cobalt carbonyl at 0° under one atmosphere of carbon monoxide led to the evolution of 0.44 mole of carbon monoxide per mole of cobalt present. The infrared

spectrum of the reaction mixture shows two acyl carbonyl groups, one at 5.4 μ (a π-acrylcobalt band) and the other at 5.9 μ (an α,β-unsaturated acylcobalt band). These data, of course, indicate the product exists as an equilibrium mixture of a cyclic tricarbonyl form (44%) and an open-chain tetracarbonyl form (56%). Addition of excess triphenylphosphine to the

$$CH_3CH{=}CHCOCl + NaCo(CO)_4 \xrightarrow{0°}$$
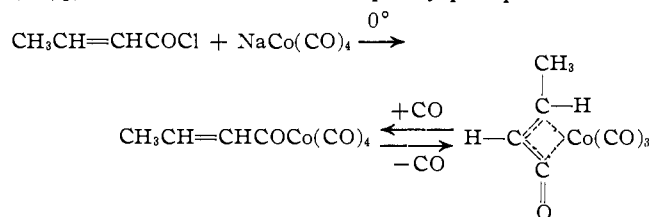
reaction mixture resulted in the evolution of 0.56 mole of carbon monoxide with the formation of a single product, crotonoylcobalt tricarbonyl triphenylphosphine. This complex was isolated as a yellow-brown crystalline solid with the expected analysis and infrared spectrum.

The fact that crotonoylcobalt carbonyl exists as a mixture of two complexes should not affect the rate of reaction of the tetracarbonyl portion with triphenylphosphine. The interconversion of the two forms very likely proceeds through the open-chain acylcobalt tricarbonyl form, which, we know from our other results, would likely react with the phosphine much more rapidly than with carbon monoxide.
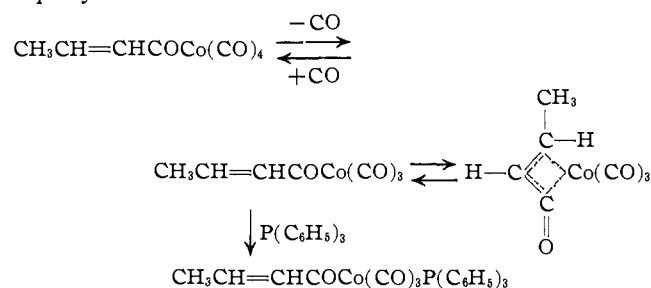
The constancy of the rate on increasing the triphenylphosphine concentration by a factor of four confirms that this compound also is undergoing a first order dissociation. A priori, the α,β-double bond would have been expected to decrease the rate of dissociation since it is usually an electron-withdrawing group. Instead the rate was increased over the acetyl complex by a factor of 62. It is conceivable that the unusual bonding between the acyl group and the cobalt atom permits the double bond to supply electrons to the cobalt atom through the carbonyl group and assist dissociation. Another explanation, however, seems more reasonable. Spectroscopic evidence suggests that acylcobalt tricarbonyls, the intermediates in the triphenylphosphine reaction, are in rapid equilibrium with alkylcobalt tetracarbonyls.[4] Therefore, a transition state in this transformation must exist where the R group is partially bonded to both the CO and to the metal.
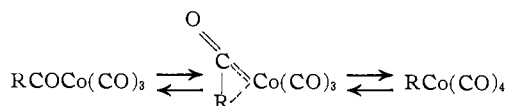
It is quite possible that a similar transition state with another CO partially bonded to the cobalt is formed when the acylcobalt tetracarbonyls dissociate. If so,
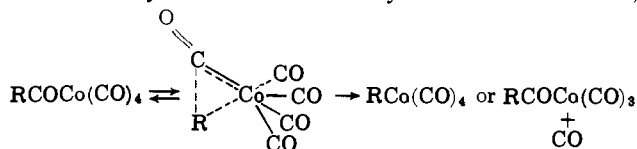
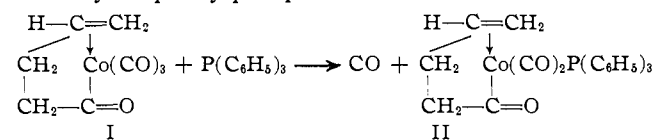the effect of the R group could be felt directly by the metal in the rate determining step.

The contribution to the transition state of the direct interaction of the R group with the metal will, of course, depend upon the steric and electronic properties of the R group. The direct interaction of the R group should be smallest when the R group is large, because of the steric problems. With small groups, the effect could be sizable. This could explain the increase in rate of the crotonoyl complex over the acetyl complex since the partially bonded propenyl group could now supply electrons directly by a resonance effect to the cobalt atom. This description also best explains data obtained on the aroylcobalt carbonyls. Presumably trimethylacetylcobalt tetracarbonyl is more reactive than acetylcobalt tetracarbonyl because the steric acceleration caused by the trimethylacetyl group is much larger than the neighboring group acceleration caused by the methyl group.

Benzoylcobalt tetracarbonyl dissociates at a rate about 34 times faster than acetylcobalt tetracarbonyl. Substituents in the aromatic ring have a relatively minor effect upon the rate. A p-methoxyl group only increased the rate by 50% while a m-methoxyl, p-nitro or p-carbomethoxyl group decreased the rate by about a half. These results could be explained on the basis of a transition state in the reaction which has the acyl group partially bonded between a CO and the metal as described above.

The o-methylbenzoylcobalt tetracarbonyl reacted a little slower and the mesitoylcobalt tetracarbonyl much more slowly than the benzoyl complex. On the basis of both steric and electronic effects, these derivatives should have reacted considerably faster than the benzoyl compound. Probably the *ortho* methyl groups make it sterically more difficult for the benzene ring to partially bond to the cobalt atom. In the mesitoyl complex the rate-retarding effect of the aromatic group is now considerably more important than the participation effect. The mesitoyl complex does not show a steric acceleration probably because the group is flat and it can avoid the coördinated carbonyl groups. The triphenylphosphine complex of the mesitoyl complex is quite stable.

It is interesting that phenylacetylcobalt tetracarbonyl dissociates only slightly faster than acetylcobalt tetracarbonyl. The insertion of the methylene group between the aromatic ring and the acyl carbonyl group has almost completely eliminated the effect of the aromatic group. There still seems to be a small effect, however, since inductively a phenyl group is similar to a methoxyl group. The rate of the phenylacetyl complex is, therefore, about three times faster than it should have been if it had the same rate of reaction as methoxyacetylcobalt tetracarbonyl. Partial bonding of the benzyl group to the metal in the transition state could also explain this rate enhancement.

The last compound in Table I, 4-pentenoylcobalt tricarbonyl, I, was shown previously to react with triphenylphosphine to produce 4-pentenoylcobalt dicarbonyl triphenylphosphine, II.[7] The rate of the re-

action has been measured but the calculated first order rate constants drifted downward as the reaction proceeded. The constants decreased by about 45% during the first four half-lives of the reaction. Increasing the

(7) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 1097 (1961).

triphenylphosphine concentration by a factor of four had only a small effect upon the rate (40% increase) and the constants still drifted downward. Thus, the reaction is, at least predominantly, first order. Previous work has shown that the 4-pentenoylcobalt tricarbonyl goes over to π-crotylcobalt tricarbonyl on standing.[7] It is possible that a small amount of the latter compound was present or formed during the reaction and is responsible for the drift. As much as 10 or 15% of the crotyl compound probably would not affect the infrared spectrum of the solution appreciably and would not be seen. (The rate of reaction of π-crotylcobalt tricarbonyl with triphenylphosphine under these conditions is 1.8×10^{-4} sec.$^{-1}$.[8]) It is also conceivable that the 4-pentenoyl complex is giving product by two different routes. Two coordinately unsaturated intermediates could be involved, the 4-pentenoylcobalt dicarbonyl (III) and the open-chain form of 4-pentenoylcobalt tricarbonyl (IV). The former intermediate would react with triphenylphosphine in a first order reaction giving the product directly. The other intermediate, however, would give 4-pentenoylcobalt tricarbonyl triphenylphosphine which could then lose carbon monoxide at a different rate from the dissociation above. It is also possible that this last reaction is not independent of the triphenylphosphine concentration. Perhaps the most important result is
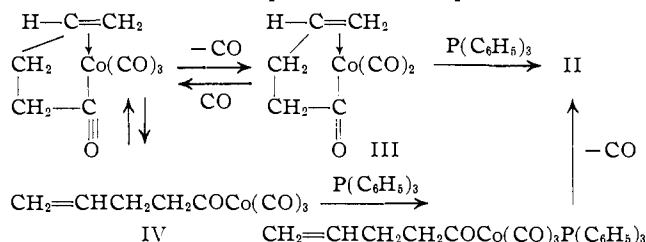
that substituting an olefinic group for a carbonyl group in the acylcobalt tetracarbonyl system increases the rate of dissociation by a factor of about four or five.

Recent work by Calderazzo and Cotton[9] has made it possible to compare quantitatively the rate of dissociation of acetylmanganese pentacarbonyl with acetylcobalt tetracarbonyl. At 25° the cobalt compound dissociates about 2250 times more rapidly than the corresponding manganese compound, the difference between the solvents, ether and the diethyl ether of diethylene glycol, being neglected.

Experimental

Acylcobalt Tetracarbonyls.—These compounds were all prepared at 0° in ether solution from acid chlorides and sodium cobalt carbonyl except for the methoxyacetyl and trifluoroacetyl derivatives. Methoxyacetylcobalt tetracarbonyl was prepared from methyl chloromethyl ether, sodium cobalt carbonyl and carbon monoxide in ether solution at 0°. Trifluoroacetylcobalt tetracarbonyl came from the reaction of trifluoroacetic anhydride and sodium cobalt carbonyl. It was very important to use anhydride or acid chlorides which were free of traces of acid and to use absolutely dry solvents, otherwise drifting rates often were observed. The detailed methods of preparation have been described previously.[4] No attempt was made to isolate the un-

(8) R. F. Heck, *J. Am. Chem. Soc.*, **85**, 655 (1963).

(9) F. Calderazzo and F. A. Cotton, *Inorg. Chem.*, **1**, 30 (1962).

stable acylcobalt tetracarbonyls from the ether solutions. All the compounds had the expected infrared carbonyl absorption spectra.

Kinetic Measurements.—The gasometric apparatus and the general techniques used have been described already.[4] Thermostated solutions of the acylcobalt tetracarbonyls in ether solution, usually 30 ml. of a 0.07 M solution, were equilibrated with carbon monoxide at atmospheric pressure in the apparatus. The triphenylphosphine then was added also in ether solution at the temperature of the reaction, by injecting it with a hypodermic syringe through a rubber stopper on the reaction vessel. Generally, 10 ml. of 0.25 M triphenylphosphine in ether was added, but in three cases 10 ml. of 1.0 M solution was used instead. The gas evolution then was measured at atmospheric pressure by means of a mercury gas buret which was thermostated at the reaction temperature. Ordinarily about 10 separate points were taken through two or three half-lives of the reaction. In the very fast pivalylcobalt tetracarbonyl reaction, there was time for only three points. Experimental infinities, after 8 or 10 half-lives, were always used in the rate constant calculations. In several cases experimental infinity values were shown to be in good agreement with the calculated values. At the conclusion of the reactions, the infrared spectra in the carbonyl region were taken. In all cases where excess phosphine was used the tetracarbonyls had reacted completely and only the spectra of the phosphine complexes were seen.

Reaction of Crotonyl Chloride with Sodium Cobalt Carbonyl.—In the gasometric apparatus at 0° with one atmosphere of carbon monoxide present, were placed, by injection with a hypodermic syringe, 30 ml. of 0.07 M sodium cobalt carbonyl in ether and 2.5 ml. of 1.0 M *trans*-crotonoyl chloride in dry ether. The solution turned orange and gas was given off.

In two hours and 15 minutes the evolution stopped after a total of 0.93 mmole had been evolved (44% of one mole per mole of cobalt present). The infrared spectrum had coördinated carbonyl bands at 4.8 μ (m) and 4.96 μ (vs) as well as acyl carbonyl bands at 5.45 μ (m) and 5.92 μ (w). The 5.45 μ acyl carbonyl is characteristic of the highly strained π-acrylyl system[7] and the 5.92 acyl group is from the open-chain (conjugated) crotonylcobalt-acyl group.[7] Addition of 3.0 ml. of 1.0 M triphenylphosphine in ether solution led to the evolution of another 1.08 mmoles of carbon monoxide in two hours. The infrared spectrum now had coördinated carbonyl bands at 4.88 μ (w) and 5.07 μ (vs). Only one acyl carbonyl, at 6.01 μ (m), was observed. Evaporation of the reaction mixture at 0° under vacuum led to an orange, semi-solid material. The product was extracted under nitrogen from the residue with several small portions of methylene chloride. The extracts were centrifuged and evaporated under vacuum and the complex was recrystallized four times from ether–pentane at 0°. Yellow-brown prisms were obtained which turned brown at about 90° and gradually turned black on further heating. The infrared spectrum of the compound had bands at 3.23 (w), 4.84 (m), 5.01–5.08 (vs), 5.99 (m), 6.19 (m), 6.72 (w), 6.96 (m), 7.87 (w), 8.41 (w), 8.93 (w), 9.11 (m), 9.50 (w), 9.70 (w), 10.32 (w), 10.79 (w) and 11.12 μ (w) in CCl$_4$ and at 13.39 (s), 14.12 (s) and 14.40 μ (s) in CS$_2$.

Anal. Calcd. for: C$_{25}$H$_{20}$O$_4$PCo: C, 63.30; H, 4.25. Found: C, 63.35; H, 4.34.

Mesitoylcobalt Tricarbonyl Triphenylphosphine.—In a nitrogen-filled bottle at 0° were placed 30 ml. of 0.07 M sodium cobalt tetracarbonyl in ether and 2.5 ml. of 1.0 M mesitoyl chloride in ether. After about an hour at 0°, the solid was removed by centrifuging, 10 ml. of 0.25 M triphenylphosphine in ether was added, and the rate of the reaction was measured. When complete, the solvent was evaporated, and the yellow product was recrystallized several times from a mixture of methylene chloride and pentane. Yellow, diamond-shaped crystals, melting point 151° dec., were obtained.

Anal. Calcd. for: C$_{31}$H$_{26}$O$_4$PCo: C, 67.39; H, 4.75. Found: C, 67.56; H, 5.52.