

$(1/[C_2H_4]_{initial} - 1/[C_2H_4]_t)$ was plotted against t . Because the reaction is reversible, the points fit a curved line. A tangent drawn to the curve for the first 5 min. of reaction (approximately the first 10% of reaction) has a slope corresponding to a rate of 0.0028 l. mole⁻¹ sec.⁻¹. In conjunction with an average value of 2.38×10^{-4} sec.⁻¹ for the rate constant for ethylene displacement at -25° , this gives a value for K of $(2.38 \times 10^{-4})/(2.8 \times 10^{-3}) = 0.085$, which agrees closely with values between 0.080 and 0.087 from the composition of equilibrated mixtures (Table I).

Synthesis and Isolation of $Cs_2[C_2H_5RhCl_3(H_2O)]_2$. A flask containing 20 ml. of 1 *M* HCl in methanol was chilled in liquid nitrogen, and 1 g. of $[(C_2H_4)_2RhCl]_2$ was added. The flask was attached to a high vacuum apparatus and held at -18 to -24° as ethylene was distilled from the reaction into a trap chilled by liquid nitrogen. After 3 hr., reaction was complete as indicated by (a) complete dissolution of $[(C_2H_4)_2RhCl]_2$ and (b) constant pressure over the reaction mixture. Then a solution of 1 g. of CsCl in 75 ml. of 0.4 *M* HCl in methanol was added. A rose-colored salt separated and this was filtered and washed with methanol and ether before it was exposed to the air. It weighed 1.6 g.

Anal. Calcd. for $Cs_2C_2H_7ORhCl_3$: Cs, 34.14; C, 6.17; H, 1.82; Rh, 26.43; Cl, 27.33. Found: Cs, 35.3; C, 6.01; H, 0.74; Rh, 24.72; Cl, 28.06.

The infrared spectrum (KBr wafer) had absorptions at 3.37, 3.44, 3.53 (saturated C-H stretch), and 2.91 μ (O-H stretch).

$Cs_2[C_2H_5RhCl_3(H_2O)]_2$ (0.1 g., 0.13 mmole) was warmed with 10 ml. of aqueous 8 *M* HCl to 90° for 10 min. The evolved gas (5 ml., 0.2 mmole) was identified as ethane from its mass spectrum.

Effect of Medium on the Reaction of HCl with π - $C_5H_5Rh(C_2H_4)_2$. (a) *Ethanol.* Glass tubes (30 \times 300 mm.) were charged under nitrogen with 15 ml. of 0.001 *M* π - $C_5H_5Rh(C_2H_4)_2$ in oxygen-free ethanol and chilled in liquid nitrogen. To each tube was added 1.5 ml. of 1 *M* HCl in ethanol, and the tubes were evacuated, charged with 15 ml. of ethylene, and sealed. One tube was warmed to 25° for 10 min. to permit reaction and provide a color standard. Other tubes were held at -20 , -28 , and -35° . After 13 hr. the tubes at -20° nearly matched the blank by visual comparison, while tubes at -28° were much lighter and those at -35° had scarcely changed.

(b) *Chloroform.* Similar tubes were charged with 15 ml. of 0.001 *M* π - $C_5H_5Rh(C_2H_4)_2$ in deoxygenated, alcohol-free chloroform, chilled in liquid nitrogen, and evacuated. To each was added 10 ml. of HCl gas and 50 ml. of C_2H_4 and the tubes were sealed. As they were warmed, the characteristic color of protonated rhodium complex appeared immediately as the chloroform melted.

The Addition of Acylcobalt Carbonyls to α,β -Unsaturated Carbonyl Compounds. 1-Acyloxy- π -allylcobalt Tricarbonyl Derivatives

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Acylcobalt tetracarbonyls and alkylcobalt tetracarbonyls react with α,β -unsaturated aldehydes or ketones to form 1-acyloxy- π -allylcobalt tricarbonyls. These complexes are conveniently isolated in the form of their crystalline monotriphenylphosphine derivatives, 1-acyloxy- π -allylcobalt dicarbonyl triphenylphosphines.

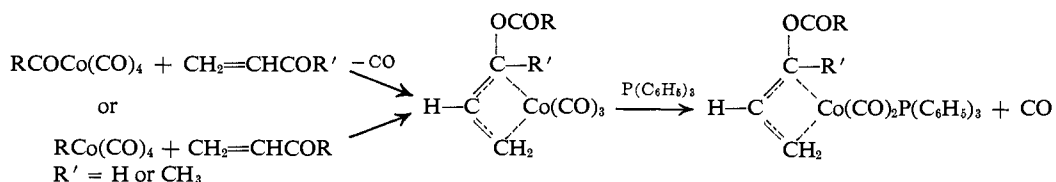
Introduction

Additions of Grignard reagents, lithium alkyls, and other nontransition metal alkyls to α,β -unsaturated carbonyl compounds are well known. Similar reactions of transition metal alkyls, however, are not. Numerous examples of the reduction of α,β -unsaturated carbonyl compounds by transition metal hydrides have been reported. These reductions probably involve addition reactions of the metal hydrides, but the mechanisms are not well understood because intermediate products cannot be isolated. Some light is shed upon these reductions and related reactions by the discovery that acylcobalt carbonyls will add to α,β -

unsaturated carbonyl compounds to give new isolable organocobalt complexes. The preparation and identification of these new complexes is the subject of this paper.

Results

Acylcobalt tetracarbonyls react in a few hours at room temperature with α,β -unsaturated aldehydes and ketones, evolving a mole of gas and producing new complexes with carbonyl absorption bands at about 1765, 2005, and 2070 cm^{-1} . Alkylcobalt tetracarbonyls react similarly, but more rapidly and without gas evolution, to produce the same products. These products react with excess triphenylphosphine at 25° to evolve a mole of carbon monoxide per mole of complex and form easily isolable, yellow to orange crystalline derivatives of the new complexes. The infrared spectra, properties, analyses, and, in one case, the n.m.r. spectrum indicate that the isolated products are 1-acyloxy- π -allylcobalt dicarbonyl triphenylphosphine de-



derivatives and that the initial products are the corresponding 1-acyloxy- π -allylcobalt tricarbonyls.

The reaction seems to be general among α,β -unsaturated aldehydes and ketones, judging by infrared spectra of the reaction mixtures, although crystalline derivatives, so far, have been obtained only from acrolein and methyl vinyl ketone. Any alkyl- or acylcobalt tetracarbonyl also seems to take part in the reaction. The four complexes which have been obtained pure are listed in Table I.

The acyloxy group appears to be directed away from the metal, at least in one example, judging by the n.m.r. spectrum of 1-acetoxy- π -allylcobalt dicarbonyl triphenylphosphine. No evidence for the presence of more than one isomeric product in any of the reaction mixtures was obtained.

The first-order rate of reaction of 1-acetoxy- π -allylcobalt tricarbonyl with triphenylphosphine at 25° under 1 atm. of carbon monoxide, in ether solution, was $4.31 \pm 0.10 \times 10^{-4} \text{ sec.}^{-1}$. Thus, the 1-acetoxy group slows down the rate of dissociation of π -allylcobalt tricarbonyl by a factor of more than 26.¹

Discussion

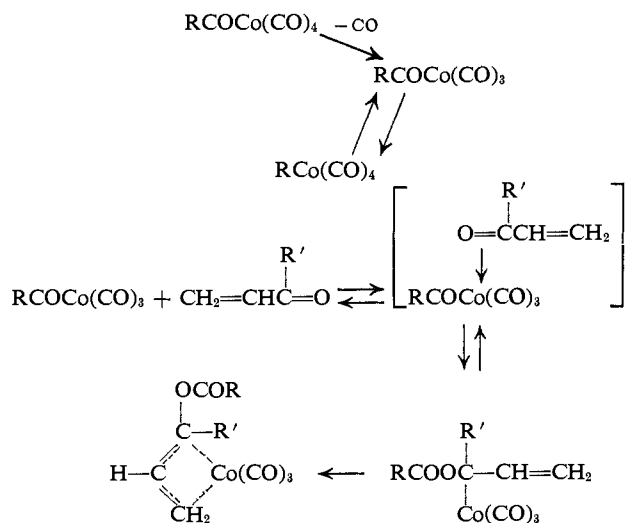
The addition of acylcobalt carbonyls to α,β -unsaturated carbonyl compounds seems to be another example of an insertion reaction.² It is particularly closely related to the reaction of acylcobalt carbonyls with conjugated dienes which was reported recently.³ The unsaturated carbonyl compound probably reacts with an acylcobalt tricarbonyl, perhaps by way of a π -complex between the carbonyl group and the cobalt compound. The insertion step must place the acyl group on oxygen and the cobalt carbonyl group on carbon. A rapid cyclization then would give the π -allyl complex. The evidence that addition did not

occur in the reverse direction giving a 1-acylmethyl- π -oxapropenylcobalt tricarbonyl is based upon infrared absorptions. The side-chain carbonyl group of 1-acetylmethyl- π -allylcobalt dicarbonyl triphenylphosphine absorbs at 1720 cm.^{-1} ³ while the acetyl carbonyl in the compound prepared from methylcobalt tetracarbonyl and acrolein and treated with triphenylphosphine absorbs at 1745 cm.^{-1} . (Although the first spectrum was taken in carbon tetrachloride solution and the second in chloroform, solvent effects are small and the spectra would be very similar in both solvents.) The difference is larger than would be expected if the two carbonyl groups were similar. Furthermore, the complexes from the α,β -unsaturated carbonyl compounds do not react with bases to give β -acylaldehydes or ketones as they would be expected to do if they had the acylmethyl- π -oxapropenyl structure, on the basis of the work with the 1-acylmethyl- π -allylcobalt tricarbonyls.⁴ Thus, it would also seem more likely that the reduction of α,β -unsaturated aldehydes and ketones by cobalt hydrocarbonyl involves 1-hydroxy- π -allylcobalt tricarbonyls as intermediates rather than the π -oxapropenylcobalt tricarbonyls proposed by Goetz and Orchin.⁵

The recently reported reaction of acetylenes with acylcobalt carbonyls appears to involve the internal addition of acylcobalt groups to α,β -unsaturated carbonyl groups to give γ -lactone derivatives π -complexed with cobalt.⁶ This cyclization is then probably just a special case of the more generalized reaction described here.

Experimental Section

1-Acetoxy- π -allylcobalt Dicarbonyl Triphenylphosphine. Into a nitrogen-filled bottle, capped with a self-sealing, rubber-lined metal cap with two small holes in it for injecting solutions by means of syringes with needles attached, was injected 30 ml. of 0.07 *M* NaCo(CO)_4 in ether, 1.0 ml. of acrolein, and 0.5 ml. of methyl iodide. The solution was let stand at room temperature overnight, and then 3.0 ml. of 1.0 *M* triphenylphosphine in ether was added. After 2 more hr., the insoluble sodium iodide was removed by centrifuging and the clear yellow-orange solution was transferred to another nitrogen-filled bottle. Evaporation of about half of the solvent at reduced pressure followed by cooling in Dry Ice caused the product to crystallize from the solution. The solid was separated and recrystallized four times by dissolving it in a minimum of methylene chloride, adding an equal volume of pentane, and cooling to 0°. There was obtained 0.30 g. of yellow-orange prisms with the properties reported in Table I.



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

(2) R. F. Heck, Mechanism of Inorganic Reactions Symposium, University of Kansas, June 1964.

(3) R. F. Heck, *J. Am. Chem. Soc.*, **85**, 3381 (1963).

(4) R. F. Heck, *ibid.*, **85**, 3383 (1963).

(5) R. W. Goetz and M. Orchin, *ibid.*, **85**, 2782 (1963).

(6) R. F. Heck, *ibid.*, **86**, 2819 (1964).

(7) W. Hieber, O. Vohler, and G. Braun, *Z. Naturforsch.*, **13b**, 192 (1958).

Table I. 1-Acyloxy- π -allylcobalt Dicarboxyl Triphenylphosphines

Compound	Prepared from		M.p., °C.	ν_{CO} , cm. ⁻¹ (CHCl ₃)	Formula	Analyses, %					
	Co(CO) ₂ + RX	Carboxyl compd.				Calcd.	Found	P			
$\begin{array}{c} \text{HOCOC}_6\text{H}_5 \\ \\ \text{H}-\text{C} \\ \\ \text{Co}(\text{CO})_2\text{P}(\text{C}_6\text{H}_5)_3 \\ \\ \text{CH}_2 \\ \\ \text{CH}=\text{CHO} \end{array}$	CH ₃ I	CH ₂ =CHCHO	155-158 dec.	1745 (m) 1945 (vs) 2000 (vs)	C ₂₈ H ₂₈ O ₄ PCo	63.03	4.66	6.50	63.01	4.93	6.35
$\begin{array}{c} \text{HOCOC}_6\text{H}_5 \\ \\ \text{H}-\text{C} \\ \\ \text{Co}(\text{CO})_2\text{P}(\text{C}_6\text{H}_5)_3 \\ \\ \text{CH}_2 \\ \\ \text{CH}=\text{CHO} \end{array}$	C ₆ H ₅ COCl	CH ₂ =CHCHO	133-135 dec.	1725 (s) 1945 (vs) 2000 (vs)	C ₃₀ H ₂₈ O ₄ PCo	66.92	4.49	...	66.79	4.78	...
$\begin{array}{c} \text{CH}_3\text{COCOC}_6\text{H}_5 \\ \\ \text{H}-\text{C} \\ \\ \text{Co}(\text{CO})_2\text{P}(\text{C}_6\text{H}_5)_3 \\ \\ \text{CH}_2 \\ \\ \text{CH}=\text{CHO} \end{array}$	CH ₃ I	CH ₂ =CHCOCH ₃	132-139 dec.	1740 (m) 1945 (s) 2000 (s)	C ₂₈ H ₂₈ O ₄ PCo	63.68	4.93	6.32	63.96	5.51	6.80
$\begin{array}{c} \text{CH}_3\text{COCOC}_6\text{H}_5 \\ \\ \text{H}-\text{C} \\ \\ \text{Co}(\text{CO})_2\text{P}(\text{C}_6\text{H}_5)_3 \\ \\ \text{CH}_2 \\ \\ \text{CH}=\text{CHO} \end{array}$	CH ₃ CH ₂ I	CH ₂ =CHCOCH ₃	105-107 dec.	1745 (m) 1930 (vs) 1985 (s)	C ₂₇ H ₂₈ O ₄ PCo	64.29	5.20	...	64.39	5.45	...

The n.m.r. spectrum of this complex in deuteriochloroform solution at 60 Mc. had bands (c.p.s.) at -102 (doublet, $J = 11.2$ c.p.s., assigned to the proton on carbon atom 3 of the π -allyl system), -119 (singlet, assigned to the methyl protons) (total area of these three peaks was 5), -280 (multiplet with area 1.1, assigned to the proton on carbon atom 2), -346 (doublet of area 0.9, $J = 7.5$ c.p.s., assigned to the other proton on carbon atom 3), and 444 (narrow multiplet, assigned to the triphenylphosphine protons) with respect to tetramethylsilane as an internal standard. The doublet at -102 c.p.s. corresponds to 1.5 protons; therefore, the low-field line of this doublet could also contain the high-field line of another one-proton doublet, the other half of which lies under the methyl resonance. This arrangement would produce a similar coupling constant as assigned to carbon atom 3.

1-Benzoyloxy- π -allylcobalt Dicarboxyl Triphenylphosphine. Into a nitrogen-filled bottle as described above was injected 30 ml. of 0.07 M NaCo(CO)₂⁷ in ether, 1.0 ml. of acrolein, and 2.5 ml. of 1.0 M benzoyl chloride in ether. The solution was let stand at room temperature overnight and then warmed to 50-60° for 30 min. Then 3.0 ml. of 1.0 M triphenylphosphine in ether was added. After about 2 hr. at room temperature, the solution was centrifuged and concentrated under reduced pressure. The orange oil remaining was dissolved in 5 ml. of methylene chloride, and 7 or 8 ml. of pentane was added. The insoluble material formed initially was removed by centrifuging and the solution was cooled in ice-water. The yellow-orange crystals which separated were isolated and recrystallized twice by dissolving in 2 ml. of methylene chloride, adding 10 ml. of pentane, and cooling to 0°. There was isolated 0.30 g. of product with the properties listed in the table.

1-Acetoxy-1-methyl- π -allylcobalt Dicarboxyl Triphenylphosphine. In a gasometric apparatus⁸ at 25.0°, filled with ether-saturated carbon monoxide, was placed 30 ml. of 0.07 M NaCo(CO)₂⁷ in ether and 1.0 ml. of methyl vinyl ketone. There was no gas volume change in 15 min. The addition of 0.5 ml. of methyl iodide caused the absorption of 35 ml. of gas in 5 min., no doubt because acetylcobalt tetracarbonyl was formed.⁹ A slow evolution then set in. After about 1 hr. and 20 min. and the evolution of 30 ml. of gas, the reaction stopped. The infrared spectrum of the reaction mixture now had carbonyl absorption bands at 1765, 2005, and 2070 cm.⁻¹, indicating that 1-acetoxy-1-methyl- π -allylcobalt tricarbonyl had been formed. The addition of 3.0 ml. of 1.0 M triphenylphosphine in ether resulted in the evolution of about 30 ml. of gas in 1 hr. and the formation of the monotriphenylphosphine derivative. The solution was centrifuged and evaporated and the product was taken up in 3 or 4 ml. of methylene chloride. The addition of 5 ml. of pentane and cooling in Dry Ice gave yellow crystals of the product. Two more recrystallizations in the same manner gave 0.5 g. of product with the properties listed in Table I.

1-Methyl-1-propionyloxy- π -allylcobalt Dicarboxyl Triphenylphosphine. A solution of 30 ml. of 0.07 M NaCo(CO)₂⁷ in ether, 1.0 ml. of methyl vinyl ketone,

(8) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 4023 (1961);

(9) R. F. Heck and D. S. Breslow, *ibid.*, **84**, 2499 (1962).

and 0.5 ml. of ethyl iodide was allowed to react under a nitrogen atmosphere for 3 days at room temperature. Then 3.0 ml. of 1.0 *M* triphenylphosphine in ether was added. After reacting for 1.5 hr., the solution was centrifuged and the solvent evaporated at room temperature under reduced pressure. The residue was recrystallized twice by dissolving it in a minimum of methylene chloride, adding pentane, and cooling in Dry Ice and then twice more by dissolving it in warm ether, adding pentane, and cooling to 0°. There was obtained 0.20 g. of yellow-orange needles with the properties listed in Table I.

Rate of Reaction of 1-Acetoxy- π -allylcobalt Tricarbonyl with Triphenylphosphine. A solution of 30 ml. of 0.07 *M* NaCo(CO)₄⁷ in ether, 0.5 ml. of acrolein, and 0.5 ml. of methyl iodide in a capped, nitrogen-filled bottle was heated in warm water (~50°) for 1 hr., and then the solvent was evaporated at 0° under

reduced pressure. The residue was dissolved in 20 ml. of ether and centrifuged; the solution was put in a gasometric apparatus⁸ at 25.0° which had been filled with ether-saturated carbon monoxide. The addition of 6.0 ml. of 1.0 *M* triphenylphosphine in ether caused gas evolution to begin. A series of 14 readings was taken, measuring the volume of gas evolved and the time. The average first-order rate constant for the reaction was 4.31×10^{-4} sec.⁻¹ and the average error was $\pm 0.10 \times 10^{-4}$ sec.⁻¹. The volume of gas evolved, 89.5 ml., corresponded to a concentration of 0.041 *M* of the cobalt compound. The infrared spectrum of the solution before adding the triphenylphosphine showed that only the expected complex was present, and the spectrum after the reaction with triphenylphosphine showed that the compound had reacted completely.

Acknowledgment. The n.m.r. spectrum was measured by Dr. M. M. Anderson of these laboratories.

Electron Transfer through Organic Structural Units. II. Conjugated and Reducible Ligands as Bridging Groups in Oxidation-Reduction Reactions¹

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*Contribution from the Division of Materials Sciences,
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The specific rates of reduction of 33 pentaamminecobalt(III) complexes (containing a variety of acyclic, alicyclic, aromatic, and heterocyclic ligands) with Cr²⁺ have been measured and their dependence on [H⁺] noted. The values cover a range of over seven powers of ten. Non-carboxylated complexes, derived from imidazole, pyridine, and dimethylformamide, react much more slowly than those bound through carboxyl, emphasizing the effectiveness of the bound carboxyl group as an electron-transfer bridge. *o*-Aminocarboxylato complexes in acid solution are reduced at rates about half those for the usual ortho-substituted benzoato complexes, suggesting one-sided electrostatic shielding by the protonated nitrogen substituent; rate laws contain no inverse acid term, ruling out reduction through a chelated path involving amino nitrogen. In reduction of the *o*-iodoso compound IX and, possibly, the complex of pyridine-2,6-dicarboxylic acid *N*-oxide (X), preliminary rapid reduction of the I-O or N-O group is followed by reduction of Co(III) in the usual way. The terephthalato complex XII is reduced at the "normal" rate of 0.20 l. mole⁻¹ sec.⁻¹, ruling out appreciable contribution by remote attack in this case. Additional examples of rate enhancement in the reductions of *o*-carbonylbenzoato derivatives are noted, the large (acid-independent) values for these rate constants supporting transient chelation in the transition state and electron transfer, at least in part, through the carbonyl group. The

spectra of the Cr(III) products from reduction of a number of heterocyclic complexes (derived from pyrazole, pyridine, and pyrazine) indicate chelation, and the very high specific rates for these reductions support chelation in the activated complexes as well. With both the pyrazole (XXVI) and the pyrazine (XXIV and XXV) complexes, only one of the two ring nitrogens is protonated at the highest acidity used, the other nitrogen remaining free for chelation. Hence, there is no inverse acid dependence, as was observed for the pyridine-2-carboxylato and pyrrole-2-carboxylato complexes. The chelated paths for reduction of the pyrrole and pyrazole complexes are slower, by several powers of ten, than those for the pyridine and pyrazine complexes; this is attributed to the greater angular strain in forming fused 5,5 bicyclic systems and to nonplanarity of the bonds about tetrahedral nitrogen in the five-ring systems. The gluconato complex XXXIII is reduced at a rate comparable to other hydroxylated aliphatic derivatives, but the *S*-benzylthioglycolato complex XXXIV reacts surprisingly rapidly, suggesting rate enhancement by chelation with the alkylmercapto group in a situation where an alkoxy group is found to be inert. Further examples of remote attack, involving the *p*-formylbenzoato (II), *trans,trans*-muconato (XXXVI), and cinnoline-4-carboxylato (XXXVII) systems, are noted, and the proposal is made that this phenomenon is confined to ligands that are reducible. Reduction of pyrazine derivatives XXIV and XXV, and their parent acids, with Cr²⁺ yields intensely absorbing green species which are reduced rapidly with (NH₃)₅CoCl²⁺; the possibility that these are radical cations of the type XXXVIII is considered.

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