Kinetics of the Reactions of (Ethoxycarbonyl)methylcobalt Tetracarbonyl with ^{13}CO, Ph₃P, HCo(CO)₄, and H₂. A Comparison of the Reactivities of RCo(CO)₄ (R = CH₂COOEt, COOEt, and H) Complexes

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Abstract: The kinetics of the reactions of (ethoxycarbonyl)methylcobalt tetracarbonyl (**1**) with ^{13}CO, Ph₃P, HCo(CO)₄, and H₂ are consistent with initial reversible dissociation of EtOOCCH₂Co(CO)₄ (**1**) to EtOOCCH₂Co(CO)₃ and CO. The alkylcobalt tricarbonyl then reacts competitively with the other reaction partner. The relative reactivities of **2** toward Ph₃P, CO, HCo(CO)₄, and H₂ are 1.82, 1.0, 0.078, and 0.0006 at 25 °C in *n*-heptane. The rate of ^{13}CO substitution has also been measured for HCo(CO)₄, Co₂(CO)₈, and (ethoxycarbonyl)cobalt tetracarbonyl (**2**). The half-life for HCo(CO)₄ at −30 °C is 45 s, $t_{1/2}$ for EtOOCCH₂Co(CO)₄ at 15 °C is 18.8 min, and $t_{1/2}$ for EtOOCCo(CO)₄ (**2**) at 15 °C is 24.2 min. The complex **2** shows a slow ^{13}CO incorporation into the acyl carbonyl group, $t_{1/2} \approx 50$ h at 28 °C, presumably through an ethoxycobalt tetracarbonyl intermediate. The rate of ^{13}CO exchange with Co₂(CO)₈ is not influenced by the presence of HCo(CO)₄ at 0 °C in *n*-octane, indicating that exchange of cobalt centers between HCo(CO)₄ and Co₂(CO)₈ is slow compared to carbonyl exchange.

Recent work has shown that bimolecular reductive elimination between a transition-metal alkyl or acyl and a transition-metal hydride can proceed through several different mechanisms.[1] These reactions are central to a number of catalytic cycles, particularly hydrogenation and hydroformylation. Although cobalt-catalyzed hydroformylation has been widely studied, there are few reports of the kinetics of isolated steps in this reaction.[2] In a preceding publication, two of us reported a kinetic study of the reactions of an acylcobalt tetracarbonyl, namely ethoxycarbonylcobalt tetracarbonyl, with Ph₃P, HCo(CO)₄, and H₂.[3]

No similar studies have been reported for alkylcobalt tetracarbonyls because they are difficult to obtain in pure form, owing to limited stability in most cases.[4] Galamb and Pályi reported recently[5] the isolation of a series of cobalt alkyls ROOCCH₂Co(CO)₄ from the reaction of NaCo(CO)₄ and ROOCCH₂X. Using this possibility, we now report details of our investigations on a cobalt alkyl analogous to those reported earlier for the cobalt acyl.

In this study, as in the proposed mechanism for hydroformylation, coordinatively unsaturated species play a prominent role. While there is evidence for the existence of HCo(CO)₃,[6] there is no information regarding the rate of formation of this compound or analogous alkyl and acylcobalt tricarbonyls. We also report measurements of the rates of ^{13}CO exchange for each of these species. These data provide support for our proposed mechanism and furnish fundamental information relevant to the hydroformylation reaction.

Results

Reaction of EtOOCCH₂Co(CO)₄ (1) with ^{13}CO. The ^{13}CO exchange reaction (eq 1) could be followed by measuring the

$$EtOOCCH_2Co(CO)_4 + {}^{13}CO \rightarrow$$
$$EtOOCCH_2Co(CO)_3({}^{13}CO) + CO \quad (1)$$

Table I. Half-Life Times of CO Exchange with ^{13}CO ($t_{1/2}$) for RCo(CO)₄ Complexes in *n*-Heptane Solution and the Calculated First-Order Rate Constants ($k'_1 = (\ln 2)/t_{1/2}$)

R	temp, °C	$t_{1/2}$, min	$10^5 \times k'_1$, s⁻¹
(OC)₄Co	0	27.4	42[a]
	0	27.4	42[a,b]
	0	38.5	30[c]
	0		41[d]
H	−30	0.75	1540
EtOOCCH₂	25	4.3	268
	15	18.8	61.4
	5	70	16.5
EtOOC	~28	~3000	0.4[e]
	15	24.2	47.3

[a] Refers to the overall rate of ^{13}CO incorporation. Determined as described in ref 10b. [b] In the presence of 5 mol % HCo(CO)₄. [c] For the reaction of Co₂(^{13}CO)₈ (86% isotope purity prepared in situ by previously equilibrating Co₂(CO)₈ with excess ^{13}CO with ^{12}CO in the presence of 330 mol % HCo(CO)₄. [d] Reference 10b. [e] Refers to the ^{13}CO exchange of the acyl carbonyl group.

decrease of absorbance of the A₁ band of **1** at 2111.5 cm⁻¹ under 1 atm pressure of carbon monoxide enriched to 86% in ^{13}CO. Reported half-lives and rate constants for all ^{13}CO reactions have been corrected for work under 100% isotopic enrichment using standard procedures.[7]

(1) (a) Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139. (b) Nappa, M. J.; Santi, R.; Diefenbach, S. P.; Halpern, J. *J. Am. Chem. Soc.* **1982**, *104*, 619. (c) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 332. (d) Jones, W. D.; Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4415. (e) Barborak, J. C.; Cann, K. *Organometallics* **1982**, *1*, 1726.

(2) (a) Pino, P.; Piacenti, F.; Bianchi, M. "Organic Syntheses via Metal Carbonyls"; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. 2, pp 43–135. (b) Pruett, R. L. *Adv. Organomet. Chem.* **1979**, *17*, 1. (c) Orchin, M. *Acc. Chem. Res.* **1981**, *14*, 159.

(3) Ungváry, F.; Markó, L. *Organometallics* **1983**, *2*, 1608.

(4) Galamb, V.; Pályi, G. *Coord. Chem. Rev.* **1984**, *59*, 203.

(5) Galamb, V.; Pályi, G.; Cser, F.; Furmanova, M. G.; Struchkov, Y. T. *J. Organomet. Chem.* **1981**, *209*, 183.

(6) (a) Wermer, P.; Ault, B. S.; Orchin, M. *J. Organomet. Chem.* **1978**, *162*, 189. (b) Sweany, R. L. *Inorg. Chem.* **1980**, *19*, 3512.

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Reactivities of RCo(CO)₄ Complexes

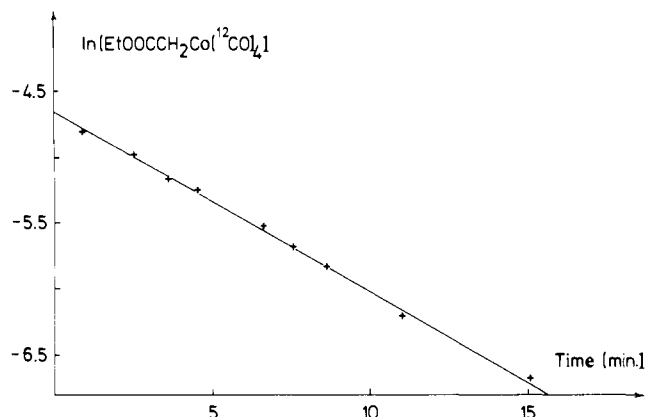*J. Am. Chem. Soc., Vol. 107, No. 3, 1985* 667

Figure 1. Plot of ln [EtOOCCH$_2$Co(^{12}CO)$_4$] through the first 3 half-lives.

The exchange showed first-order kinetics through at least three half-lives as shown in Figure 1. Half-lives and observed rate constants are summarized in Table I. The rate data at different temperatures can be used to calculate $\Delta H^{\ddagger} = 22.4 \pm 1.2$ kcal mol and $\Delta S^{\ddagger} = 4.7 \pm 4.0$ eu. During the course of the reaction, the formation of more highly substituted complexes EtOOCCH$_2$Co(^{13}CO)$_n$(^{12}CO)$_{4-n}$ could also be observed since the A$_1$ bands of all these species were well resolved.[8]
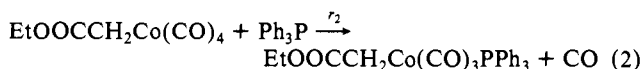
Reaction of EtOOCCo(CO)₄ (2) with ^{13}CO. The substitution of the acyl **2** with ^{13}CO was studied at 15 °C. The value of the observed first-order rate constant, 4.7×10^{-4} s^{-1}, is in good agreement with the previously published value of 3.9×10^{-4} s^{-1} for k_1 calculated on the basis of phosphine substitution at this temperature.[3] In addition, a very slow incorporation of ^{13}CO into the alkoxy acyl group was observed with samples left at room temperature for long periods of time. The estimated half-life at 28 °C for this reaction is 3000 min.

Reaction of HCo(CO)₄ with ^{13}CO. The substitution of ^{13}CO into the cobalt hydride was too fast to follow at temperatures of 25, 15, and 0 °C. Even at −30 °C, the rate of reaction is so fast that we give it as a lower limit. The half-life of 45 s was reproducible in four different experiments, and first-order plots were linear through at least four half-lives. Nevertheless, the rate of reaction could have been determined by equilibration between dissolved CO and the gas phase, despite a very high rate of stirring.

Since the rate of ^{13}CO substitution in HMn(CO)$_5$ has been shown to be increased in the presence of radical initiators,[9] precautions were taken to eliminate this possibility. Solvents were carefully purified and the reaction vessel was shielded from light. The hydride solutions were pale yellow, indicating the presence of some Co$_2$(CO)$_8$ but it was less than 0.1 mol % based on the hydride concentration as determined by the infrared spectrum.

Reaction of Co₂(CO)₈ with ^{13}CO in the Presence of HCo(CO)₄. The rate of ^{13}CO substitution of Co$_2$(CO)$_8$ at 0 °C has been studied previously.[10] We repeated this work to check our measurements, and as shown in Table I, our value is in good agreement with the previously published values. The presence of HCo(CO)$_4$ which undergoes rapid CO exchange at this temperature had no effect on the rate of exchange of ^{13}CO in Co$_2$(CO)$_8$ which was relatively slow. This was true when the hydride was present in catalytic (5 mol %) or in excess (330 mol %) amounts.

Reaction of 1 with Ph₃P. Reaction of **1** with Ph$_3$P proceeded as shown in eq 2, with no sign of formation of any acyl product

$$EtOOCCH_2Co(CO)_4 + Ph_3P \xrightarrow{r_2}$$
$$EtOOCCH_2Co(CO)_3PPh_3 + CO \quad (2)$$

at 15 and 25 °C. The monosubstituted triphenylphosphine de-

(7) Basolo, F. *Inorg. Chim. Acta* **1981**, *50*, 65.
(8) Detailed analysis of the spectra will be published.
(9) Byers, B. H.; Brown, T. L. *J. Organomet. Chem.* **1977**, *127*, 181.
(10) (a) Basolo, F.; Wojcicki, A. *J. Am. Chem. Soc.* **1961**, *83*, 520. (b) Absi-Halabi, M.; Atwood, J. D.; Forbus, N. P.; Brown, T. L. *J. Am. Chem. Soc.* **1980**, *102*, 6248.

Table II. Initial Rates of CO Substitution r_2 in **1** by Ph$_3$P under CO at Various Conditions in *n*-Heptane Solution

temp, °C	10^3[1], M	10^2[CO],^{a} M	10^2[Ph₃P], M	$10^6 r_2$, M s^{-1}
15	17.0	1.044	0.35	5.76
15	17.0	1.044	0.50	7.08
15	17.0	1.044	0.70	8.10
15	17.0	1.044	1.50	9.98
15	17.0	1.044	5.00	11.61
25	8.1	1.079	0.38	8.00
25	8.1	0.497	0.48	13.5
25	8.1	1.079	0.46	8.82
25	8.1	1.079	0.57	9.66
25	8.1	1.079	0.71	11.21
25	8.1	1.079	1.05	12.88
25	8.1	1.079	1.90	15.27
25	4.4	1.077	0.57	5.48
25	8.1	1.079	8.33	16.10
25	8.1	2.230	8.57	8.4
25	8.1	1.079	9.29	19.0

^{a}Calculated from p_{CO} and the solubility of CO in *n*-heptane.[12]

Table III. Initial Rates of Ethyl Acetate Production r_3 for Reaction 3 at 25 °C, 1 bar CO in *n*-Heptane. [CO]^a = 0.01079 M

10^2[1], M	10^2[HCo(CO)₄], M	$10^7 r_3$, M s^{-1}
1.2	0.4	9.5
1.2	0.9	20
1.2	1.2	30
1.2	2.0	41
1.2	2.4	47
1.2	3.6	64
1.2	6.0	105
1.2	8.0	135
1.2	10.0	155
1.2	12.0	173
1.2	14.0	189
0.4	1.2	6.5
0.7	1.2	13
1.2	1.2	28
1.2	1.2	30^b
1.2	1.2	30^c
2.1	1.2	52
4.0	1.2	120
7.0	1.2	170
9.0	1.2	215
11.0	1.2	270
14.0	1.2	366

^{a}Calculated from p_{CO} and the solubility of CO in *n*-heptane.[12] ^{b}In the presence of 0.120 M Co$_2$(CO)$_8$. ^{c}Using DCo(CO)$_4$ instead of HCo(CO)$_4$.

rivative could be isolated in about 80% yield and its infrared spectrum agreed with authentic material.[5] The rate of CO evolution was first order in **1** and depended on both Ph$_3$P and CO concentration in a complex way (Table II).

Reaction of 1 with HCo(CO)₄. **1** was smoothly reduced to ethyl acetate by HCo(CO)$_4$ as shown in eq 3. No carbonylated product

$$EtOOCCH_2Co(CO)_4 + HCo(CO)_4 \xrightarrow{r_3}$$
$$EtOOCCH_3 + Co_2(CO)_8 \quad (3)$$
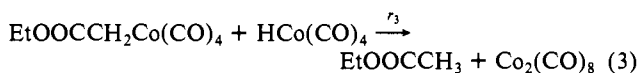
was detected either by IR or by GC analysis of the reaction mixture. The rate of the reaction could be followed spectroscopically by the decrease of the concentration of **1** or by the increase of EtOAc or Co$_2$(CO)$_8$ concentration measuring the infrared absorbances of the reaction mixtures at 1720, 1750, and 1857 cm^{-1}, respectively. Due to the air-sensitive nature of the organocobalt compounds studied, kinetic data were analyzed by the method of initial rates, rather than measurements over greater periods of time (more prone to contamination of atmospheric oxygen) under pseudo-first-order conditions. As shown by the data in Table III and Figure 2, the reaction was first order in **1** and approximately first order in HCo(CO)$_4$ at low concentrations. When the concentration of the other reactant was kept fixed, the

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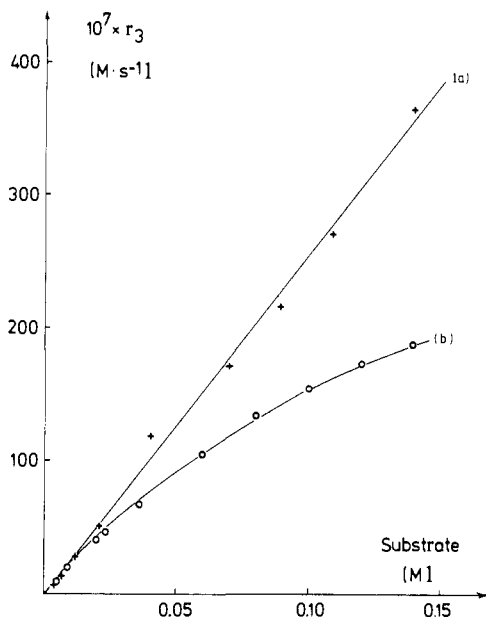
Figure 2. Influence of $EtOOCCH_2Co(CO)_4$ and $HCo(CO)_4$ concentration on rate of ethyl acetate production r_3 at 25 °C under 1 atm of carbon monoxide. (+), rate vs. $[RCo(CO)_4]$; $[HCo(CO)_4]$ = constant = 0.012 M; (O), rate vs. $[HCo(CO)_4]$; $[RCo(CO)_4]$ = constant = 0.012 M.

Table IV. Initial Rates of Ethyl Acetate Production r_3 for Reaction 3 at 25 °C in n-Heptane Solution at Various CO Pressures. $[HCo(CO)_4]$ = 0.021 M, [1] = 0.012 M

| p_{CO}, bar	$10^2[CO]$,[a] M	$10^7 r_3$, M s^{-1}
3.1	3.57	11.1
2.5	2.86	14.3
2.1	2.43	18.1
0.92	1.079	41.0
0.65	0.677	71.5

[a] Calculated from p_{CO} and the solubility of CO in n-heptane.[12]

initial rate remained first order when the concentration of the alkyl was increased, but the apparent reaction order decreased when the hydride concentration was increased.

The data in Table IV and Figure 3 show that the reaction is inhibited by CO pressure. At the relatively low concentrations studied, the order of the CO dependence was about −1.

The rate of the reaction was not influenced by the presence of even a 10-fold excess of added $Co_2(CO)_8$. The shapes of the reaction curves when followed to completion did not display the "S" shape found for autocatalytic reactions of $HCo(CO)_4$.[11] The cobalt alkyl (1) showed no signs of decomposition when stored for 10 days in the presence of a 10-fold excess of $Co_2(CO)_8$ at 25 °C. Within experimental error, there was no kinetic isotope effect when $DCo(CO)_4$ was used in place of $HCo(CO)_4$.

Reaction of 1 with H₂. The hydrogenation of 1 with H_2 proceeded as shown in eq 4.

$$2EtOOCCH_2Co(CO)_4 + H_2 \xrightarrow{r_4} 2EtOOCCH_3 + Co_2(CO)_8 \tag{4}$$
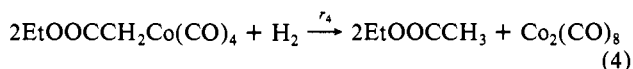
$$r_4 = \frac{k_1 k_4 [RCo(CO)_4][H_2]}{k_{-1}[CO]} \tag{4a}$$

The concentrations of 1, ethyl acetate, and $Co_2(CO)_8$ were all monitored by IR spectroscopy during the reaction, and the stoichiometry agreed with that shown in eq 4. The reaction was first order in 1, first order in H_2, and minus first order in CO. Added $Co_2(CO)_8$ had no influence on the rate of ethyl acetate formation. Kinetic data for this reaction are shown in Table V. The bulk of this work was done at 35 °C, since reaction 4 was too slow to follow at 25 °C.

(11) Ungváry, F. *Acta Chim. (Budapest)* **1982**, *111*, 117.
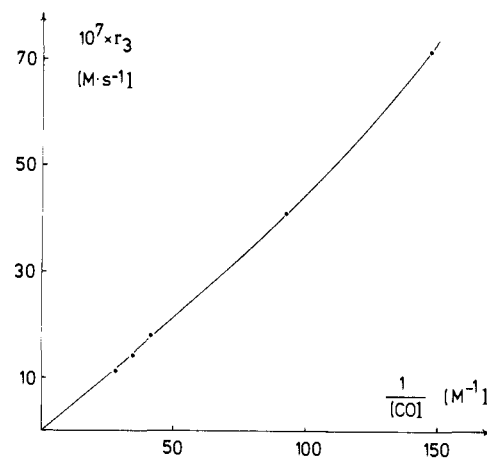
Figure 3. Influence of carbon monoxide concentration on rate of ethyl acetate production r_3 at 25 °C in n-heptane solution. [EtOOCCH₂Co-$(CO)_4$] = 0.012 M; [$HCo(CO)_4$] = 0.021 M.

Table V. Initial Rates of Ethyl Acetate Formation with H_2 (r_4) in n-Heptane Solution and the Observed Rate Constants (k'_4 = $r_4[CO]/[1][H_2]$) at Various Initial Concentrations

temp °C	$10^2[1]$, M	$10^3[H_2]$,[a] M	$10^3[CO]$,[b] M	$10^7 r_4$, M	$10^5 k'_4$, M s^{-1}
25	6.0	3.69	1.29	2.6	0.15
35	1.9	3.68	1.31	3.6	0.67
35	6.0	3.68	1.31	10.3	0.61
35	6.0	9.94	3.56	9.6	0.57
35	11.4	3.68	1.31	22	0.69
35	6.0	3.30	2.30	6.2	0.72
35	6.0	2.59	4.16	2.6	0.70
35	6.0	2.13	5.35	1.5	0.63
35	6.0	2.13	5.35	1.4[c]	0.59

[a] Calculated from pH_2 and the solubility of H_2 in n-heptane.[13] [b] Calculated from p_{CO} and the solubility of CO in n-heptane.[12] [c] In the presence of $[Co_2(CO)_8]$ = 0.114 M.

Discussion

The goal of this research was an understanding of the reductive elimination of alkanes from alkylcobalt tetracarbonyls. This is the final step in alkene hydrogenation, a competing reaction in cobalt-catalyzed hydroformylation. Recent work, primarily with catalytically inactive metals, has shown the danger of extrapolating mechanistic conclusions from one metal to another. Even for the same metal, manganese, four different pathways have been deduced for reductive elimination depending on the nature of the alkyl group and experimental conditions.[1b]

Kinetic study of the important alkylcobalt tetracarbonyls is difficult owing to their instability. Carbonyl insertion to yield an acylcobalt tetracarbonyl and β-elimination to regenerate a cobalt hydride are the characteristic pathways for decomposition. The compound we have studied, $EtOOCCH_2Co(CO)_4$, undergoes neither of these reactions under moderate conditions. The factors which allowed this study to be performed (the stability of the cobalt alkyl) restrict generalization of our results. The conditions under which the study was conducted, alkane solvents and relatively low temperatures, must be kept in mind as well as the somewhat special nature of the alkyl group. Within these limitations, a fairly consistent picture emerges in which facile, reversible loss of coordinated carbon monoxide is the dominant reaction pathway. As in any kinetic study, this mechanistic conclusion is not definitive.[23]

(12) (a) Gjaldbaek, J. C. *Acta Chem. Scand.* **1952**, *6*, 623. (b) Ungváry, F. *J. Organomet. Chem.* **1972**, *36*, 363.
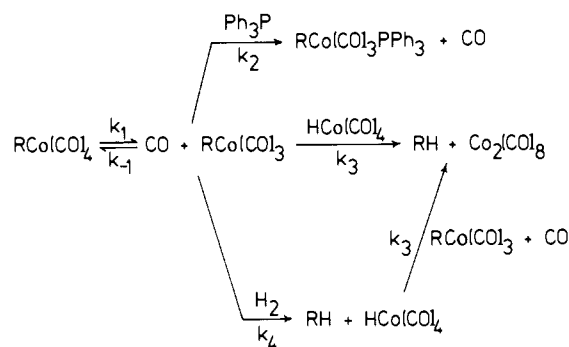(13) Cook, M. W.; Hanson, D. N.; Alder, B. J. *J. Chem. Phys.* **1957**, *26*, 748.
(14) Ikariya, T.; Yamamoto, A. *J. Organomet. Chem.* **1976**, *116*, 231.
(15) (a) Heck, R. F. *J. Organomet. Chem.* **1964**, *2*, 195. (b) Milstein, D.; Huckaby, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 6150.
(16) Coville, N. J.; Stolzenberg, A. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1983**, *105*, 2499.

Reactivities of RCo(CO)₄ Complexes

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Scheme I

$$RCo(CO)_4 \xrightarrow[k_2]{Ph_3P} RCo(CO)_3PPh_3 + CO$$

$$RCo(CO)_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CO + RCo(CO)_3 \xrightarrow{HCo(CO)_4}_{k_3} RH + Co_2(CO)_8$$

$$k_3 \diagup RCo(CO)_3 + CO$$

$$\xrightarrow[k_4]{H_2} RH + HCo(CO)_4$$

Table VI. Rate Constants for the Reactions in Scheme I at 25 °C[a]

rate constant	R = EtOOCCH₂	R = EtOOC (3)
$k'_1 \times 10^5$ (s⁻¹)[a]	268, 61.4[b]	47.3[b]
$k_1 \times 10^5$ (s⁻¹)	286[c]	
	250,[d] 74[b,d]	173,[d] 39[b,d]
k_2/k_{-1}	1.82	0.77
k_3/k_{-1}	0.078	0.084
k_4/k_{-1}	0.0006	0.0067

[a] Assigned error limits for all calculated rate constants do not exceed 15%, k_1 refers to direct measurement of CO substitution calculated from rate data assuming an irreversible first-order reaction. [b] At 15 °C. [c] Derived from the reaction with HCo(CO)₄. [d] Derived from the reaction with Ph₃P.

The three most likely pathways we considered for this reaction involved (i) coordinatively unsaturated intermediates, (ii) free radicals or radical pairs, and (iii) a polar, concerted reaction. The inverse effect of CO pressure common to all the reactions we studied supports a mechanism involving coordinatively unsaturated intermediates. The lack of influence on the reaction of added Co₂(CO)₈ (a source of Co(CO)₄ radicals) argues against a radical pathway. Even though HCo(CO)₄ is a strong acid in donor solvents, a polar reaction in alkane medium is less favored and does not explain the retarding influences of CO pressure. Failure to observe a kinetic isotope effect when DCo(CO)₄ is used relatively of HCo(CO)₄ also argues against it. These observations, as well as kinetic studies discussed in more detail below, support the common mechanism shown in Scheme I.
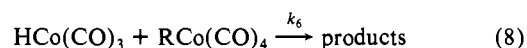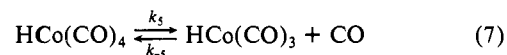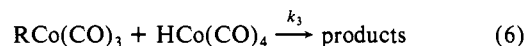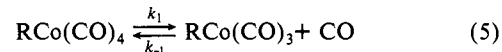
The kinetic behavior found for CO substitution by Ph₃P (reaction 2) is in accord with a reversible dissociation of CO from 1 followed by a fast reaction between Ph₃P and the proposed intermediate RCo(CO)₃. Assuming steady-state concentration for RCo(CO)₃, k_1 and the ratio of k_2 to k_{-1} can be calculated from the intercept and the slope by plotting $[1]/r_2$ against $[CO]/[Ph_3P]$. Such a plot is shown in Figure 4, and the constants derived in this way are shown in Table VI.

The observed first-order rate constants k_1 determined for the ¹³CO exchange reaction and shown in Table I should be consistent with the rate constants k_1 for CO dissociation. The excellent agreement of k_1 with the k_1 values obtained from the Ph₃P reaction

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

(18) Pino, P.; Oldani, F.; Consiglio, G. *J. Organomet. Chem.* **1983**, *250*, 491.

(19) Thomas, G. *Chem.-Ztg. Chem. Appar.* **1961**, *85*, 567.

(20) Ungváry, F.; Markó, L. *Organometallics* **1982**, *1*, 1120.

(21) Roos, L. Ph.D. Dissertation, University of Cincinnati, Cincinnati, OH, 1965; p 81.

(22) Spindler, F.; Bor, G.; Dietler, U. K.; Pino, P. *J. Organomet. Chem.* **1981**, *213*, 303.

(23) One of the referees has pointed out that the critical intermediate in these reactions might be R(OC)Co(CO)₃ rather than RCo(CO)₃. In view of work done with osmium alkyl hydrides,[1a] this cannot be ruled out. Related work with manganese alkyls, however, does not invoke this intermediate.[1c] While failure to detect aldehyde products does not preclude the formation of acyl intermediates, it does seem unlikely (particularly for cobalt, in view of the tendency to produce carbonylated products, and in view of our earlier work with a cobalt acyl³). The simplest mechanism consistent with all the data is proposed in Scheme I.

Figure 4. Reaction of EtOOCCH₂Co(CO)₄ with Ph₃P. Influence of CO and Ph₃P concentration on the rate of CO substitution r_2.

(see Table VI) further supports the proposed mechanism shown $[1]/r_2$ Scheme I.

In the reaction of 1 with HCo(CO)₄ the inhibiting effect of CO (Figure 3) again suggests formation of a coordinatively unsaturated intermediate by CO loss. In this case, however, there are two possible routes for the formation of ethyl acetate and Co₂(CO)₈ which satisfy this requirement. The first involves the alkylcobalt tricarbonyl and HCo(CO)₄ (eq 5 and 6), the other one involves HCo(CO)₃ and 1 (eq 7 and 8).

$$RCo(CO)_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RCo(CO)_3 + CO \qquad (5)$$

$$RCo(CO)_3 + HCo(CO)_4 \xrightarrow{k_3} products \qquad (6)$$

$$HCo(CO)_4 \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} HCo(CO)_3 + CO \qquad (7)$$

$$HCo(CO)_3 + RCo(CO)_4 \xrightarrow{k_6} products \qquad (8)$$

In a first attempt to distinguish between these alternatives, we studied the rates of exchange of ¹³CO, since it has been proposed that generation of the coordinatively unsaturated species is rate determining.[1a] This proved inconclusive, however, since both compounds exchanged CO faster than the overall rate of reaction 3 (HCo(CO)₄ exchanges much faster than RCo(CO)₄).

Kinetic data obtained at high concentrations of the reagents distinguish the two possibilities. The rate equations for the two mechanisms obtained by using simple steady-state approximations are shown in eq 9 and 10 for a mechanism involving eq 5 and 6

$$r_3 = \frac{k_1 k_3 [HCo(CO)_4][RCo(CO)_4]}{k_{-1}[CO] + k_3[HCo(CO)_4]} \qquad (9)$$

$$r_3 = \frac{k_5 k_6 [HCo(CO)_4][RCo(CO)_4]}{k_{-5}[CO] + k_6[RCo(CO)_4]} \qquad (10)$$

or eq 7 and 8, respectively. As shown in the data in Table III and the graph in Figure 2, the reaction order in HCo(CO)₄ decreases at high concentrations, while RCo(CO)₄ remains first order. This supports the mechanism proposed in eq 5 and 6. The value of k_1 calculated on the basis of eq 9 is 2.86×10^{-3} s⁻¹, in excellent agreement with the values obtained from ¹³CO substitution (2.68×10^{-3}) and PPh₃ substitution (2.5×10^{-3}). Since ¹³CO exchange is much faster for HCo(CO)₄ than for RCo(CO)₄, the second steps of the proposed mechanisms (eq 6 and 8) control the course of the reaction. The presumed intermediate (R)-(H)Co₂(CO)₇ can be formed through an intermediate bridged hydride species in eq 6; formation of the same intermediate through eq 8 probably has a much higher activation energy, since attack of a coordinatively unsaturated species at a metal–alkyl bond appears to be unfavorable.[1]

The alkyl (1) can also be cleaved with H_2. This reaction is rather slow and leads to ethyl acetate and $Co_2(CO)_8$ because the hydride formed in the primary step (Scheme I, reaction 4) rapidly reacts with the alkyl present according to reaction 3. The only other reaction between H_2 and a cobalt(I) alkyl reported up till now is shown in eq 11.[14]

$$MeCo(Ph_2PCH_2CH_2PPh_2)_2 + H_2 \xrightarrow[20\ °C]{1\ bar}$$
$$CH_4 + HCo(Ph_2PCH_2CH_2PPh_2)_2 \quad (11)$$
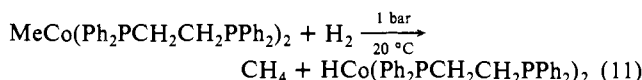
The relative rates of cleavage by $HCo(CO)_4$ and H_2 are $0.078/0.0006 = 130/1$ in the case of the alkyl (1) (Table VI). This compares to a value of about $12/1$ reported earlier for the cleavage of the acyl compound (2).[3] Such a large difference in the relative reactivities of the seemingly similar complexes 1 and 2 toward H_2 is rather unexpected since, for example, the reactivities of 1 and 2 toward $HCo(CO)_4$ are very similar and also the reactivities toward PPh_3 are not very different ($1.82/0.77 = 2.4/1$). Steric factors can hardly play a role in determining the reactivity toward H_2; the effect has to be primarily electronic in origin. Since the hydrogenolysis of cobalt alkyls and acyls is of crucial importance in the hydroformylation process, further study of the factors governing their relative reactivities toward H_2 and $HCo(CO)_4$ are in progress.
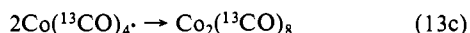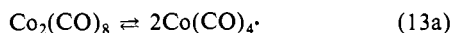
The rate of ^{13}CO exchange for the alkyl and acyl compounds 1 and 2 support the mechanism proposed in Scheme I. It was of additional interest to observe the slow incorporation of ^{13}CO into the alkoxy acyl group, presumably through the mechanism shown in eq 12. The rate of incorporation into the acyl group

$$ROOCCo(CO)_4 \underset{+CO}{\overset{-CO}{\rightleftharpoons}} ROOCCo(CO)_3 \rightleftharpoons RO-Co(CO)_4 \quad (12)$$
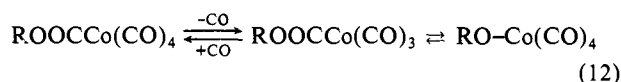
is about 3 orders of magnitude slower than into the terminal carbonyls. Attempted synthesis of alkoxy carbonyls has been shown to yield the corresponding alkoxy acyl complexes in good yield,[15] suggesting the equilibria of eq 12 are strongly shifted to the left. This may explain the slow rate of ^{13}CO incorporation into the acyl group.

In regard to the rapid exchange of ^{13}CO with $H-Co(CO)_4$, we can make no mechanistic conclusions. The rate of exchange of $H-Mn(CO)_5$, proposed to involve the formyl intermediate $H-C-O-Mn(CO)_4$,[9] is much faster than the rate of exchange of the corresponding dimer $Mn_2(CO)_{10}$.[16] Therefore, it is not surprising that the exchange with $HCo(CO)_4$ is even faster than that of $Co_2(CO)_8$. The hydride solutions used contained less than 0.1 mol % of $Co_2(CO)_8$; however, it seemed possible that this could be the catalyst for a radical pathway. It therefore was of interest to look at the reverse question—will the presence of hydride catalyze the exchange reaction of the dimer?

The kinetic results on the rate of ^{13}CO for $Co_2(CO)_8$ in the presence of catalytic (5 mol %), or excess (330 mol %) amounts of $HCo(CO)_4$ indicate that interaction between these two compounds, through radical (see eq 13a–c) or cluster intermediates,

$$Co_2(CO)_8 \rightleftharpoons 2Co(CO)_4\cdot \quad (13a)$$

$$\cdot Co(CO)_4 + HCo(^{13}CO)_4 \rightarrow HCo(CO)_4 + Co(^{13}CO)_4\cdot \quad (13b)$$

$$2Co(^{13}CO)_4\cdot \rightarrow Co_2(^{13}CO)_8 \quad (13c)$$

is slow compared to the rate of ^{13}CO exchange of $Co_2(CO)_8$ at $0\ °C$ in alkane solution. Since the hydride exchanges CO extremely fast at $0\ °C$, we conclude that either eq 13a or eq 13b does not occur rapidly compared to carbonyl exchange. A similar conclusion was reached regarding $Mn_2(CO)_{10}$ using isotopic labeling experiments.[16]

Finally, it is of interest to compare the reactivities of the alkyl (1, R = $EtOOCCH_2$) and acyl (2, R = EtOOC) to what is known about the interaction of $HCo(CO)_4$ in the reactions illustrated by Scheme I (assuming R = H).

Despite considerable study on the reactions of the cobalt hydride, the mechanisms of none of the reactions analogous to these depicted in Scheme I can be said to be well understood. Compared

to the reactions of the alkyl and acyl, the reactions with ^{13}CO (this work) and PPh_3[17] are very fast. On the other hand, recent work has shown that even at $100\ °C$ there is no significant H,D exchange under active hydroformylation conditions, indicating little interaction with hydrogen.[18] The reactions of the hydride with the alkyl and acyl complexes are not influenced by $Co_2(CO)_8$ and are relatively fast. The reactions of the hydride with itself (decomposition to H_2 and $Co_2(CO)_8$)) is catalyzed by the presence of $Co_2(CO)_8$ and is relatively slow. While rationalizations can be offered for this behavior, none of them is convincing. Despite considerable work over several decades by many groups, cobalt-catalyzed hydroformylation remains a challenging problem.

Experimental Section

General Techniques. Infrared spectra were recorded on a Carl Zeiss Jena IR 75 or UR 20 spectrophotometer. NMR spectra were recorded with a Tesla BS 487/c 80 MHz spectrometer. Analysis of the volatile compounds was performed on an analytical Hewlett-Packard Model 5830A gas chromatograph using 30-m glass capillary columns with 0.15 μm OV-1 or SP-2100 stationary phase. All manipulations involving air-sensitive organometallic compounds were carried out by using the anaerobic procedure described by Thomas.[19]

Materials. All solvents were dried on sodium wire and were freshly distilled and stored under an Ar or CO atmosphere.

Dicobalt octacarbonyl was doubly recrystallized first from CH_2Cl_2 and then from n-heptane under CO.

Stock solutions of $HCo(CO)_4$ were prepared in n-octane from $Co_2(CO)_8$, DMF, and concentrated HCl.[20]

$DCo(CO)_4$ was prepared from $HCo(CO)_4$ solutions by H,D exchange with 50-fold molar excess of D_2O.[21] Isotopic purity was 95% as calculated from mass spectrometric measurements of its decomposition products.

^{13}CO was obtained from Isotopes, Inc., USSR, and used as supplied without further purification. The isotopic purity was 86%.

The compound $EtOOCCH_2Co(CO)_4$ was prepared as described in the literature[5] as was $EtOOCCo(CO)_4$.[3]

The low-temperature infrared cell used was purchased from Carl Zeiss, Jena. Gas-tight syringes, valves, adapters, and Teflon tubing were purchased from Hamilton Products, Reno, NV.

Reactions with ^{13}CO. General. The thermostated reaction vessel was evacuated and the solvent added by syringe through a rubber septum protected by a stopcock. The vessel was then filled with 1 atm of 86% ^{13}CO by using a manifold and pump consisting of a three-way stopcock and a gas-tight syringe. A second gas-tight syringe, filled with ^{13}CO, was depressed during the reaction to maintain the pressure at 1 atm as samples were withdrawn for infrared analysis. The infrared cell was thermostated to the same temperature as the reactor and filled by using a device similar to that described.[9] The total volume of the reactor and associated tubing was about 70 mL, and the volume of the reactor itself was 55 mL. In a typical reaction, 10 mL of heptane was used. After filling with ^{13}CO and waiting for temperature equilibration, the sample to be studied, stored at $-50\ °C$, was injected to make a 0.01 M solution. Thus, about 0.1 mmol of sample was studied in the presence of 2–3 mmol of ^{13}CO. Since the samples were withdrawn during the reaction, and additional ^{13}CO added, isotopic dilution of the gas phase was less than 5%. The reaction mixture was magnetically stirred, and with the exception of $HCo(CO)_4$ (see below), there was no indication that the rate of reaction was comparable to equilibration between dissolved CO and that in the gas phase.

Reaction of $EtOOCCH_2Co(CO)_4$ with ^{13}CO. The alkyl was studied at 25, 15, and $5\ °C$, and the data obtained are shown in Table I. The reactions were first order through 3 half-lives, and typical experimental data are shown in the graph in Figure 1. There was no incorporation of ^{13}CO into the ester group on samples left for several days at room temperature.

Reaction of $EtOOCCo(CO)_4$ with ^{13}CO. The kinetics of ^{13}CO insertion was studied at $15\ °C$ for the acyl compound, and data obtained are shown in Table I. After the sample was equilibrated with regard to substitution of the terminal carbonyls, there was still no sign of incorporation into the acyl position. After several hours at room temperature there was a slight decrease in the acyl band at 1692 cm^{-1}, and corresponding increase in the ^{13}CO band at 1653 cm^{-1}, identical in position with the band observed in concentrated solutions of natural abundance CO. The sample was left overnight at an average temperature of $28\ °C$. A spectrum run the next day showed a further decrease in the band at 1692 cm^{-1} and a compensating increase in the band at 1653 cm^{-1}. There were no other changes in the spectrum, notably no production of $Co_2(CO)_8$ or $Co_4(CO)_{12}$.

Reaction of $HCo(CO)_4$ with ^{13}CO. This reaction was studied at 25, 15, and $0\ °C$. The reaction was too fast to obtain reliable data. These

studies were useful in the sense that they ensured that equilibration of CO between the solution and the gas phase was not a limiting factor (since the rate of substitution was so much faster than that for the other compounds). In reactions at −30 °C with only moderate stirring, plots of ln *A* vs. time were linear through only 1 half-life, and the rates corresponded to $t_{1/2}$ about 4 min. With more vigorous stirring, such that the reaction vessel shook from the vibration of the stirrer, the plots were linear through 4 half-lives and a $t_{1/2}$ of 45 ± 10 s was obtained in four separate experiments. We therefore consider the half-life of 45 s to be an upper limit, and the actual value may be lower. A more detailed investigation of this reaction is in progress.

Reaction of $Co_2(CO)_8$ with ^{13}CO in the Presence of $HCo(CO)_4$. The rate of substitution of $Co_2(CO)_8$ with ^{13}CO at 0 °C in heptane was measured and as shown in Table I agrees with the previously reported values. In a second experiment, $HCo(^{13}CO)_4$ (with 86% substitution) was prepared and 5 mol % added shortly after initiation of the reaction. The rates of reaction were identical within experimental error to those in the absence of added $HCo(CO)_4$.

In a third experiment, $Co_2(^{13}CO)_8$ substituted to **Presence** extent of 86% was prepared. The rate of substitution of ^{12}CO was studied in these reactions in the presence of 330 mol % of $HCo(^{12}CO)_4$. The rate of incorporation of ^{12}CO was slightly slower in these reactions but not outside the limits of experimental error.

Reaction of 1 with $HCo(CO)_4$. All reactions were run in thermostated vessels at 25 °C and normally 1 atm of CO. The reactions run at higher pressures were measured by using a mechanical gauge, accurate within 10% as calibrated against a mercury manometer. The reactions were initiated by injecting a solution of the hydride to the vigorously stirred solution of the alkyl. The course of the reaction was followed by the infrared spectrum, following the production of $Co_2(CO)_8$ and EtOAc, and the decrease in concentration of 1 using the extinction coefficients quoted below. The concentration of the hydride solutions was determined by alkaline titration and the concentration of the alkyl solutions by cobalt analysis. Ethyl acetate was also measured at the end of the reactions using GC. The stoichiometry in every case corresponded to that shown in eq 1, and there was no sign of carbonylated products in either the IR or the GC. Initial rates were determined from the first 0–15% of reaction. Solutions of 1 stored for 10 days at room temperature under CO in the presence of a 10-fold excess of $Co_2(CO)_8$ showed no signs of decomposition, as detected by IR spectroscopy.

Reduction of 1 with H_2. One milliliter of a 0.057 M solution of 1 in *n*-heptane was placed in a 5-mL glass rocking autoclave and pressurized to 25 bar with H_2. The color of the solution gradually turned brown. After 40 min of agitation at 32 °C, the IR spectrum of the reaction mixture showed 69% conversion to $Co_2(CO)_8$ and ethyl acetate in a 1:2 molar ratio.

Kinetic runs were performed in a gasometric apparatus fitted with a mercury-filled gas burette. A 5-L buffer flask was connected to the leveling vessel of the gas burette and kept at the pressure of the reaction vessel. All parts of the apparatus were thermostated (±0.05 °C). The actual total pressure was determined in mmHg by using an open mercury manometer measuring the pressure difference between the atmosphere and the reaction vessel. The change of IR spectra was followed from samples taken with a syringe and measuring in a CaF_2 IR cell: Absorbances 1857 cm⁻¹, $\epsilon_M(Co_2(CO)_8)$ 1735 cm² mmol⁻¹;[22] 1745 ϵ_M(EtO-COCH₃) 743; 1715, $\epsilon_M(1)$ 820. Initial rates were calculated from graphical plots below 5% conversions.

Reaction of 1 with Ph_3P. These reactions were performed in the gasometric apparatus described above and started by injecting 1 in *n*-heptane into solutions containing known amounts of Ph_3P in *n*-heptane. Pale yellow crystalline $EtOOCCH_2Co(CO)_3(PPh_3)$ could be isolated with 80% yield from the reaction mixtures after 92% of the calculated amount of CO was given off in 48 h at 25 °C. Initial rates were calculated from graphical plots below 5% conversions.

Theoretical Studies of Radical Recombination Reactions. 1. Allyl and Azaallyl Radicals

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Abstract: The reaction paths for the recombination of methyl radicals with allyl, 1-azaallyl (both for attack on C and N), and 2-azaallyl radicals have been studied by using the MNDO approximation to molecular orbital theory with 3 × 3 CI and complete geometrical optimization. The methyl/allyl and methyl/2-azaallyl recombinations are predicted to have activation enthalpies of 5.5 and 5.6 kcal/mol, respectively, while the methyl/1-azaallyl recombination is predicted to have activation enthalpies of 3.9 and 11.0 kcal/mol for attack on C and N, respectively.

The recombination of two free radicals to form a stable covalent bond (or bond homolysis, the reverse reaction) is a process that is fundamental to the study of chemical reactivity. As such, it is discussed in virtually all textbooks on organic chemistry. The process is generally thought to occur without any activation energy (presumably, this is what would be expected by analogy to the recombination of two hydrogen atoms) except in cases, such as the recombination of two Ph_3C radicals, where steric hindrance may be involved. Despite the lack of direct evidence for it, and a growing body of evidence that suggests that there may be causes of activation for recombination of two radicals other than steric hindrance, this idea persists.

In fact, activation energies have long been reported for recombination of alkyl radicals (for example, ethyl[1]) and for chain termination of various radical polymerization reactions.[2] Similarly, differences in the rates of radical recombination reactions that might be expected to have the same Arrhenius preexponential factors have been reported. Thus, two methyl radicals recombine 6 times as fast as two trifluoromethyl radicals.[3]

(1) (a) Shepp, A.; Kutchke, K. O. *J. Chem. Phys.* **1957**, *26*, 1020. (b) Fessenden, R. W. *J. Phys. Chem.* **1964**, *68*, 1508.
(2) Walling, C. "Free Radicals in Solution"; Wiley: New York, 1957; p 95.