

for Lorentz and polarization effects and reduced to structure factor amplitudes, using a p value of 0.03.²⁶ Only those 4045 unique reflections having $F_o^2 > 3\sigma(F_o^2)$ were used in subsequent calculations.

Solution and Refinement of the Structure. Atomic scattering factors were taken from Cromer and Waber's tabulation²⁷ for all atoms except hydrogen, for which the values of Steward et al. were used.²⁸ Anomalous dispersion terms²⁹ for Co and P atoms were included in F_c .

The direct method approach,³⁰ based on 650 normalized structure factors, yielded the correct positions of the Co and P atoms. All other atoms were located through the usual combination of structure factors calculations and difference Fourier syntheses. After location of the molecular $(\pi\text{-C}_7\text{H}_8)\text{Co}_4(\text{CO})_6\text{-(HC(Ph)}_2)_3$ complex, a Fourier difference map revealed the presence of a free benzene molecule in the lattice. This additional molecule was included in the model. The six phenyl rings of the

tripod ligand and the benzene molecule were entered as rigid groups, including hydrogen atoms in idealized positions (D_{6h} symmetry; C-C = 1.39 and C-H = 0.95 Å). Anisotropic thermal parameters were used for 27 atoms.

Full-matrix least-squares refinement of such a model led to $R_wF = 0.09$ and $R_{wF} = 0.11$ for the 4045 reflections. These relatively high values have to be related to the significant decomposition of the crystal in the X-ray beam.

Complete listing of positional and thermal parameters are given in Table II, and selected interatomic distances and bond angles are given in Tables IV and V.

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Registry No. 1, 28926-65-0; **2,** 82198-75-2; $\text{Ru}_3(\text{CO})_{12}$, 15243-33-1; $\text{Ru}_3(\text{CO})_9$ (tripod), 82264-79-7; $\text{Co}_4(\text{CO})_{12}$, 17786-31-1; $\text{Hf}_6\text{Co}_3(\text{CO})_{12}$, 21750-96-9; $\text{Ir}_4(\text{CO})_{12}$, 18827-81-1; $\text{Rh}_4(\text{CO})_{12}$, 19584-30-6; $\text{Co}_2\text{Rh}_2(\text{C-O})_{12}$, 50696-78-1; $\text{Co}_4(\text{CO})_9$ (tripod), 75801-99-9; $\text{Rh}_4(\text{CO})_9$ (tripod), 75790-10-2; $\text{Ir}_4(\text{CO})_9$ (tripod), 82246-60-4; $\text{Rh}_4(\text{CO})_9[\text{HC(AsPh}_2)_3]$, 82246-61-5; $\text{H}_2\text{Ru}_4(\text{CO})_9$ (tripod), 82246-62-6; $\text{Co}_2\text{Rh}_2(\text{CO})_9$ (tripod), 75790-08-8; $\text{Hf}_6\text{Co}_3(\text{CO})_9$ (tripod), 75790-06-6; $(\pi\text{-C}_7\text{H}_8)\text{Co}_4(\text{CO})_6$ (tripod), 82264-80-0; $\text{Co}_4(\text{CO})_6(\text{PMe}_3)$ (tripod), 82264-81-1; Co, 7440-48-4; Ru, 7440-18-8; Ir, 7439-88-5; Fe, 7439-89-6; Rh, 7440-16-6.

Supplementary Material Available: Complete listing of observed and calculated structure factors and Table III, derived parameters for the rigid-group atoms of $\text{Co}_4(\text{CO})_6[\text{HC(Ph)}_2)_3](\pi\text{-C}_7\text{H}_8)$ (21 pages). Ordering information is given on any current masthead page.

Reaction of $\text{HCo}(\text{CO})_4$ and CO with Styrene. Mechanism of (α -Phenylpropionyl)- and (β -Phenylpropionyl)cobalt Tetracarbonyl Formation

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Cobalt tetracarbonyl hydride and styrene react in the presence of carbon monoxide to form ethylbenzene and (α -phenylpropionyl)cobalt tetracarbonyl; both reactions are first order in $\text{HCo}(\text{CO})_4$ and $\text{PhCH}=\text{CH}_2$ and independent of CO and $\text{Co}_2(\text{CO})_8$ concentration. The kinetic data suggest a common radical pair intermediate for both reactions. (α -Phenylpropionyl)cobalt tetracarbonyl is not the final product of the reaction: it slowly decomposes into ethylbenzene, CO, and $\text{Co}_2(\text{CO})_8$ and partly isomerizes into (β -phenylpropionyl)cobalt tetracarbonyl. Accordingly, among these acyl complexes the branched-chain isomer is the kinetically controlled product and the straight-chain isomer the thermodynamically controlled product.

Introduction

The reaction between $\text{HCo}(\text{CO})_4$ and olefin is regarded as a component of the hydroformylation catalytic cycle in the presence of cobalt carbonyls, and because of the industrial significance of hydroformylation, it has been repeatedly studied.¹ The main products of this stoichiometric reaction are aldehydes (at low olefin/ $\text{HCo}(\text{CO})_4$ ratios) or acylcobalt tetracarbonyls, $\text{RCOC}(\text{CO})_4$ (at high olefin/ $\text{HCo}(\text{CO})_4$ ratios in the presence of CO). Saturated

hydrocarbons are formed as byproducts.

Recent kinetic studies² suggested that with aliphatic α -olefins an alkylcobalt tricarbonyl is the common intermediate of hydrocarbon and acylcobalt tetracarbonyl formation and that the carbonylation/hydrogenation ratio is determined by the relative reactivities of this species toward CO and $\text{HCo}(\text{CO})_4$. Furthermore it was found that CO inhibits and $\text{Co}_2(\text{CO})_8$ catalyzes these reactions. Presumably the role of $\text{Co}_2(\text{CO})_8$ is to generate radical species and thereby to facilitate the substitution of a CO ligand by an olefin in $\text{HCo}(\text{CO})_4$.

(1) P. Pino, F. Piacenti, and M. Bianchi "Organic Synthesis via Metal Carbonyls", Vol. 2, I. Wender and P. Pino, Eds., Wiley, New York, 1977, pp 43-135.

(2) F. Ungváry and L. Markó, *J. Organomet. Chem.*, 219, 397 (1981).

Table I. Initial CO Absorption Rates (r_{CO}) and Initial Stoichiometric Hydrogenation Rates (r_{H}) at 15 °C in *n*-Octane Solution and the Observed Rate Constants ($k_{\text{CO}} = r_{\text{CO}}/[\text{HCo}(\text{CO})_4][\text{styrene}]$ and $k_{\text{H}} = r_{\text{H}}/[\text{HCo}(\text{CO})_4][\text{styrene}]$) at Various Initial Concentrations

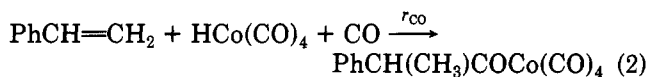
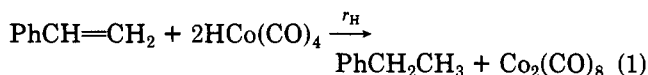
$[\text{HCo}(\text{CO})_4]$, M	$[\text{styrene}]$, M	$[\text{Co}_2(\text{CO})_8]$, M	$10^2[\text{CO}]$, M	$10^6 r_{\text{CO}}$, $\text{M}\cdot\text{s}^{-1}$	$10^6 r_{\text{H}}$, $\text{M}\cdot\text{s}^{-1}$	$10^3 k_{\text{CO}}$, $\text{M}^{-1}\cdot\text{s}^{-1}$	$10^3 k_{\text{H}}$, $\text{M}^{-1}\cdot\text{s}^{-1}$
0.0097	0.139	0.048	1.085	4.1		3.1	
0.0121	0.139	0.048	1.072	5.0	3.2	3.0	1.9
0.0153	0.139	0.048	1.086	6.5		3.1	
0.0207	0.069	0.00	1.080	4.1	2.2	2.9	1.5
0.0208	0.137	0.00	0.392	7.0	4.5	2.5	1.6
0.0207	0.139	0.048	0.528	7.9	5.2	2.8	1.8
0.0207	0.139	0.00	0.532	8.0	4.7	2.8	1.6
0.0207	0.139	0.00	1.080	8.5	4.5	3.0	1.6
0.0208	0.140	0.00	1.066	8.4	4.5	2.9 ^a	1.6 ^a
0.0207	0.297	0.00	1.078	17.8	10.3	2.9	1.7
0.0207	0.594	0.00	1.073	30	19	2.5	1.6
0.0209 ^b	0.139	0.00	1.063	17.3	10	6.0	3.4
0.0207	0.139	0.012	1.077	8.7	4.8	3.0	1.7
0.0207	0.139	0.048	1.086	8.6	4.5	3.0	1.6
0.0208	0.137	0.00	2.56	8.0	4.2	2.8	1.5
0.0207	0.139	0.00	2.45	8.9	4.7	3.1	1.6
0.0209 ^b	0.139	0.048	1.063	17.0	10.3	5.9	3.5
0.0207	0.139	0.164	1.074	8.5	4.7	3.0	1.6
0.0290	0.139	0.048	1.081	12.9		3.2	
0.0500	0.139	0.048	1.074	20.3	11.8	2.9	1.7
0.0831	0.139	0.048	1.086	33.9		2.9	
0.0967	0.139	0.048	1.073	41	24	3.0	1.8

^a In darkness. ^b $\text{DCo}(\text{CO})_4$.

We now wish to report on the reaction between $\text{HCo}(\text{CO})_4$ and styrene which shows completely different kinetic behavior.

Results

When styrene and $\text{HCo}(\text{CO})_4$ react in heptane solution, the rates of ethylbenzene (reaction 1) and of (α -phenylpropionyl)cobalt tetracarbonyl formation (reaction 2) are both first order in $\text{HCo}(\text{CO})_4$ and styrene and independent of CO and $\text{Co}_2(\text{CO})_8$ concentration (Table I).^{3,4}



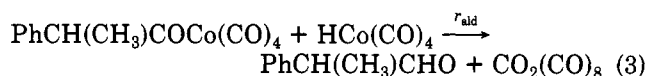
$$r_{\text{H}} = \frac{d[\text{ethylbenzene}]}{dt} = k_{\text{H}}[\text{HCo}(\text{CO})_4][\text{styrene}]$$

$$r_{\text{CO}} = -\frac{d(\text{CO})}{dt} = k_{\text{CO}}[\text{HCo}(\text{CO})_4][\text{styrene}]$$

The reaction rates are not influenced by the diffuse light in the laboratory. Both reactions have a strong inverse kinetic isotope effect, $r_{\text{H}}/r_{\text{D}} = 0.45$ and $r_{\text{CO}(\text{H})}/r_{\text{CO}(\text{D})} = 0.49$ at 15 °C (Table I).

The primary products of the reaction are (α -phenylpropionyl)cobalt tetracarbonyl, ethylbenzene, and $\text{Co}_2(\text{C}-$

$\text{O})_8$. In a secondary process some α -phenylpropion-aldehyde is also formed by the reaction of $\text{HCo}(\text{CO})_4$ with (α -phenylpropionyl)cobalt tetracarbonyl (reaction 3). This reaction is of importance especially at low styrene/ $\text{HCo}(\text{CO})_4$ ratios (Table II).



The infrared spectrum of the reaction mixture just after CO absorption has stopped shows $\nu(\text{CO})$ bands characteristic of $\text{Co}_2(\text{CO})_8$ ⁸ and an acylcobalt tetracarbonyl.⁹ The frequencies of the latter can be determined as 2105 (w), 2046 (vs), 2025 (vs), 2005 (vs), and 1699 (w) cm^{-1} in heptane¹⁰ after $\text{Co}_2(\text{CO})_8$ was frozen out at -78 °C. When Ph_3P is added to the solution, the $\nu(\text{CO})$ bands of the acyl shift to 2050 (w), 1985 (vs), 1961 (vs), and 1679 (m) cm^{-1} ; the monosubstituted derivative $\text{PhCH}(\text{CH}_3)\text{COC}(\text{CO})_3$ (PPh_3) can be crystallized. The ¹H NMR spectrum of this complex [$\delta(\text{C}_6\text{D}_6)$ 1.42 (3 H, d), 4.68 (1 H, q), 6.9 (9 H, m), 7.1 (5 H, m), 7.4 (6 H, m)] supports the α -phenylpropionyl structure.

The aldehyde in the reaction mixture shows a characteristic $\nu(\text{CO})$ band at 1738 cm^{-1} in the infrared spectrum. It can be isolated as the 2,4-dinitrophenylhydrazone derivative. The ¹H NMR spectrum of this hydrazone [$\delta(\text{C}_6\text{D}_6)$ 1.22 (3 H, d), 3.30 (1 H, m), 6.33 (1 H, d)] shows that the aldehyde also has the branched structure in accordance with reaction 3.

If $\text{DCo}(\text{CO})_4$ is used instead of $\text{HCo}(\text{CO})_4$, the acyl band of $\text{PhCH}(\text{CH}_2\text{D})\text{COC}(\text{CO})_4$ appears at 1703 cm^{-1} and the aldehyde band of $\text{PhCH}(\text{CH}_2\text{D})\text{CDO}$ at 1720 cm^{-1} . The ¹H NMR spectra of the isolated derivatives confirm the branched structure and show that only one deuterium

(3) Similar kinetic characteristics were already found earlier for the stoichiometric hydrogenation of 1,1-diphenylethylene⁵ and derivatives,⁶ 9-methylidene-fluorene and related compounds,⁷ and styrene and derivatives⁶ with $\text{HCo}(\text{CO})_4$. The rate of acylcobaltcarbonyl formation (CO absorption) has not been determined, however.

(4) A slight decrease in rate of CO absorption can be observed at $\text{Co}_2(\text{CO})_8$ concentrations near to saturation (Table III). The reason for this effect is unclear.

(5) J. A. Roth and M. Orchin, *J. Organomet. Chem.*, **182**, 299 (1979).

(6) J. A. Roth and P. Wiseman, *J. Organomet. Chem.*, **217**, 231 (1981).

(7) T. E. Nalesnik and M. Orchin, *J. Organomet. Chem.*, **199**, 265 (1980).

(8) G. Bor and L. Markó, *Spectrochim. Acta*, **16**, 1105 (1960).

(9) L. Markó, G. Bor, G. Almásy, and P. Szabó, *Brennst.-Chem.*, **44**, 184 (1963).

(10) A very weak band at 2094 cm^{-1} is probably due to a small amount of $\text{PhCH}(\text{CH}_3)\text{Co}(\text{CO})_4$. This conclusion is based on the 2097- cm^{-1} band of the analogous *p*- $\text{MeC}_6\text{H}_4\text{CH}_2\text{Co}(\text{CO})_4$.¹¹

(11) V. Galamb and G. Pályi, *J. Chem. Soc., Chem. Commun.*, 487 (1982).

Table II. The Reaction of Styrene with $\text{HCo}(\text{CO})_4$ under CO in *n*-Octane Solution at Various Initial Concentrations and Temperatures^a

temp, °C	$[\text{HCo}(\text{CO})_4]_0$, M	$[\text{styrene}]_0$, M	$[\text{Co}_2(\text{CO})_8]_0$, M	$10^6 k_{\text{CO}}$, $\text{M}^{-1}\text{s}^{-1}$	$10^3 k_{\text{CO}}$, $\text{M}^{-1}\text{s}^{-1}$	reaction time, ^b min	mol of $\text{HCo}(\text{CO})_4$ (eq 2)	mol of EtPh^d / $\text{HCo}(\text{CO})_4$ (eq 1)	mol of aldehyde ^e / mol of $\text{HCo}(\text{CO})_4$ (eq 3)
10	0.0292	0.100	0.00	5.6	1.9	240	0.49	0.32	
						5 days	0.30	0.60	
10	0.0588	0.100	0.00	10.8	1.8	180	0.42		
10	0.0285	1.740	0.00	85	1.7	20	0.49		
10	0.532	0.317	0.00	313	1.8	180	0.40		0.38
10	0.528	0.333	0.00	311 ^g	1.8	60	0.42		0.35
10	0.556 ^f	0.354	0.00	737 ^h	3.7	60	0.44		0.33
10	0.530	0.375	0.00	380 ⁱ	1.9	60	0.37		0.35
10	0.556 ^f	0.354	0.00	700 ^j	3.6	60	0.38		0.38
15	0.188	0.225	0.00	140	3.1	60	0.39		0.22
15	0.278 ^f	0.208	0.00	341	5.9	50	0.40		0.33
15	0.0294	0.200	0.00	18.0	3.0	50	0.46	0.31	
15	0.0294	0.200	0.20 ^k	17.0	2.9	50	0.51	0.35	
15	0.0290 ^f	0.200	0.00	34.0	5.9	40	0.47	0.40	
15	0.0290 ^f	0.200	0.20	31.0	5.3	40	0.50	0.40	
25	0.0294	0.400	0.00	82	7.0	10	0.43		
25	0.0294	0.400	0.24 ^k	63	5.4	10	0.50		
25	0.0290 ^f	0.400	0.00	132	11.4	8	0.44		
25	0.0290 ^f	0.400	0.24	105	9.0	8	0.50		
35	0.0292	0.200	0.00	90	16	6	0.32		
45	0.0292	0.877	0.00	l	l	3	0.14		
45	0.0292	0.877	0.185	l	l	3	0.25		

^a The initial CO absorption rates (r_{CO}), the observed rate constants ($k_{\text{CO}} = r_{\text{CO}}/[\text{HCo}(\text{CO})_4][\text{styrene}]$), the observed maximum CO uptake, amounts of ethylbenzene and aldehyde formed. $P_{\text{total}} = 984 \pm 10$ mbar. ^b Time needed to reach maximum CO uptake. ^c Maximum CO uptake. ^d Based on gas chromatographic analysis. ^e Aldehydes were converted into solid 2,4-dinitrophenylhydrazones and measured by weight. ^f $\text{DCo}(\text{CO})_4$. ^g $P_{\text{total}} = 2820$ mbar. ^h $P_{\text{total}} = 2700$ mbar. ⁱ $P_{\text{total}} = 299$ mbar. ^j $P_{\text{total}} = 291$ mbar. ^k Saturated solution. ^l Too fast to measure.

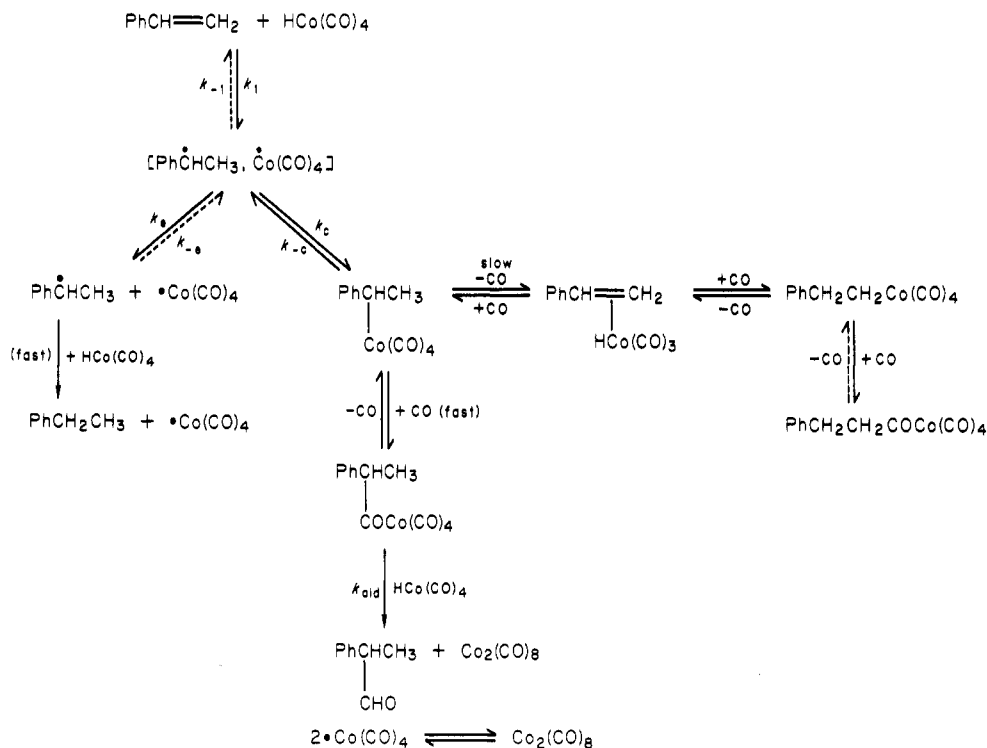
Table III. The Temperature Dependence of k_{CO} and k_{H}

temp, °C	$10^3 k_{\text{CO}}^a$, $\text{M}^{-1}\text{s}^{-1}$	$10^3 k_{\text{H}}^b$, $\text{M}^{-1}\text{s}^{-1}$	$k_{\text{CO}}/k_{\text{H}}$
8.0	1.38	0.705	1.96
15.0	2.92	1.63	1.79
20.0	4.60	3.04	1.51
25.0	7.07	5.16	1.37

$\Delta H_{25}^{\ddagger}(\text{CO}) = 15.6 \pm 0.3$ kcal·mol⁻¹
 $\Delta S_{25}^{\ddagger}(\text{CO}) = -16 \pm 1$ cal·mol⁻¹·K⁻¹
 $\Delta H_{25}^{\ddagger}(\text{H}) = 19.1 \pm 1$ kcal·mol⁻¹
 $\Delta S_{25}^{\ddagger}(\text{H}) = -5 \pm 3$ cal·mol⁻¹·K⁻¹

^a $\pm 5\%$. ^b $\pm 10\%$.

Scheme I



atom is incorporated into the acyl complex but two deuterium atoms are incorporated into the aldehyde: $\text{PhCH}(\text{CH}_2\text{D})\text{COC}(\text{CO})_3(\text{PPh}_3)$ [$\delta(\text{C}_6\text{D}_6)$ 1.42 (2 H, d), 4.68 (1 H, t)]; $\text{PhCH}(\text{CH}_2\text{D})\text{CDNNHC}_6\text{H}_3(\text{NO}_2)_2$ [$\delta(\text{C}_6\text{D}_6)$ 1.22 (2 H, d), 3.30 (1 H, t)].

If the reaction mixture is left standing at room temperature, a slow evolution of CO sets in, and in a few days 30–60% of the CO absorbed is liberated. The rate of this process is low; initial rates are as follows: $r_{-\text{CO}} = (0.72 \times 10^{-2})r_{\text{CO}}$ at 10 °C, $r_{-\text{CO}} = (0.78 \times 10^{-2})r_{\text{CO}}$ at 15 °C, and $r_{-\text{CO}} = (0.93 \times 10^{-2})r_{\text{CO}}$ at 25 °C.

This decarbonylation is accompanied by a gradual increase of the amount of ethylbenzene and a change in the $\nu(\text{CO})$ bands in the infrared spectrum. The acyl $\nu(\text{CO})$ band at 1699 cm^{-1} of (α -phenylpropionyl)cobalt tetracarbonyl gradually decreases, and simultaneously the acyl $\nu(\text{CO})$ band of (β -phenylpropionyl)cobalt tetracarbonyl appears at 1715 cm^{-1} .¹² In accordance with this observation the acylcobalt tricarbonyl triphenylphosphine derivatives obtained from the reaction mixture after several hours are mixtures of the branched- and straight-chain isomers. After 24 h at 20 °C (α -phenylpropionyl)cobalt tetracarbonyl practically vanishes, and the triphenylphosphine derivative of (β -phenylpropionyl)cobalt carbonyl can be isolated.

In the case of $\text{PhCH}(\text{CH}_2\text{D})\text{COC}(\text{CO})_4$ the same isomerization takes place and the acyl band of the β -phenyl isomer appears at about 1718 cm^{-1} . The ^1H NMR spectrum of the triphenylphosphine derivative [$\delta(\text{C}_6\text{D}_6)$ 2.87 (m), 3.53 (m)] shows the presence of both possible deuterated β -phenylpropionyl isomers, $\text{PhCH}_2\text{CHDCOC}(\text{CO})_3(\text{PPh}_3)$ and $\text{PhCHDCH}_2\text{COC}(\text{CO})_3(\text{PPh}_3)$, in about equal amounts.

Discussion

We propose the mechanism shown on Scheme I for the observed reactions.

Assuming steady-state concentration for the intermediate radical pair and not including k_c since it is negligible as compared to k_e ($r_{-\text{CO}} \ll r_{\text{CO}}$), the following equations are obtained for the initial rates:

$$r_{\text{H}} = k_e[\text{Ph}\dot{\text{C}}\text{HCH}_3, \dot{\text{C}}\text{Co}(\text{CO})_4] = \frac{k_e k_1}{k_{-1} + k_e + k_c} [\text{PhCH}=\text{CH}_2][\text{HCo}(\text{CO})_4]$$

$$k_{\text{H}} = \frac{k_e k_1}{k_{-1} + k_e + k_c}$$

$$r_{\text{CO}} = k_c[\text{Ph}\dot{\text{C}}\text{HCH}_3, \dot{\text{C}}\text{Co}(\text{CO})_4] = \frac{k_c k_1}{k_{-1} + k_e + k_c} [\text{PhCH}=\text{CH}_2][\text{HCo}(\text{CO})_4]$$

$$k_{\text{CO}} = \frac{k_c k_1}{k_{-1} + k_e + k_c}$$

$$\frac{r_{\text{CO}}}{r_{\text{H}}} = \frac{k_{\text{CO}}}{k_{\text{H}}} = \frac{k_c}{k_e}$$

The relative rates of carbonylation and hydrogenation are determined by the ratio of the rate constants for the coupling reaction k_c and the escape reaction k_e of the radical pair. The relative values of these constants are not influenced by any of the reactants since both processes may be regarded as monomolecular. The ratio of the two reaction rates is therefore constant, e.g., 1.79 at 15 °C. When the temperature is increased, the relative rate of hydrogenation increases (Table III).

The supposed radical pair character of the common intermediate is in accordance with the branched-chain structure of the primary acylcobaltcarbonyl product which proves that the hydrogen of $\text{HCo}(\text{CO})_4$ is transferred ex-

(12) (β -Phenylpropionyl)cobalt tetracarbonyl was prepared from $\text{NaCo}(\text{CO})_4$ and $\text{PhCH}_2\text{CH}_2\text{COCl}$ by the method of Heck.¹³ The terminal $\nu(\text{CO})$ spectrum of this acylcobalt tetracarbonyl in heptane is identical with that of the α -phenyl isomer; the acyl $\nu(\text{CO})$ band, however, appears at 1715 cm^{-1} . The monosubstituted derivative $\text{PhCH}_2\text{CH}_2\text{COC}(\text{CO})_3(\text{PPh}_3)$ has $\nu(\text{CO})$ bands at 2050 (w), 1984 (vs), 1961 (vs), and 1686 (w) cm^{-1} in heptane. The ^1H NMR spectrum of this complex shows unambiguously the straight-chain structure [$\delta(\text{C}_6\text{D}_6)$ 2.87 (2 H, t), 3.53 (2 H, t), 7.0–7.4 (20 H, m)].

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

clusively to the terminal carbon atom of the double bond. The inverse kinetic isotope effect is similar to that observed by Halpern for the hydrogenation of α -methylstyrene by $\text{HMn}(\text{CO})_5$ ¹⁴ and by Orchin for the hydrogenation of 1,1-diphenylethylene by $\text{HCo}(\text{CO})_4$ ⁵ in which for both cases, similar radical pair intermediates were proved unambiguously.^{14,15} It should be mentioned here that also for the hydrogenation of 9-ethylidene-fluorene⁷ by $\text{HCo}(\text{CO})_4$ and α -methylstyrene by $\text{HM}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3$ (M = Mo, W)¹⁶ inverse kinetic isotope effects were found.

We have no strong evidence for or against the reversibility of step 1 at the moment, which was assumed by analogy.⁵ The incorporation of one D atom into (α -phenylpropionyl)cobalt tetracarbonyl if $\text{DCo}(\text{CO})_4$ is used suggests k_{-1} to be very small, the inclusion or omission of k_{-1} does not influence the kinetic evaluation of the results, however.

The kinetic experiments were performed with a large excess of styrene over $\text{HCo}(\text{CO})_4$ (Table I). The formation of aldehydes according to reaction 3 is negligible under such conditions and does not interfere with the kinetic results especially since initial rates were measured and evaluated. If $\text{HCo}(\text{CO})_4$ is used in about equimolar amounts, most of the (α -phenylpropionyl)cobalt tetracarbonyl formed is transformed into α -phenylpropionaldehyde within the reaction time needed to complete CO absorption (Table II). The rate of reaction 3 is apparently comparable with the rate of acylcobalt carbonyl formation, but we did not investigate this process in more detail.

If a large excess of styrene is used, the total measured amount of absorbed CO agrees well with the amount which can be calculated from the $k_{\text{CO}}/k_{\text{H}}$ ratio. For example at 15 °C this ratio is 1.79 from which the absorption of 0.473 mol of CO/mol of $\text{HCo}(\text{CO})_4$ can be calculated, and the experimental value is 0.46 mol (Table II). This shows that the reaction continues at the initial rate up until 100% $\text{HCo}(\text{CO})_4$ conversion. Obviously the amount of absorbed CO is lower if no large excess of styrene is present, since in this case the formation of aldehydes (reaction 3) also uses hydride. Increasing the temperature of the reaction also diminishes CO absorption since $k_{\text{CO}}/k_{\text{H}}$ decreases (Table III). On the other hand, large concentrations of $\text{Co}_2(\text{CO})_8$ increase CO absorption (Table II) probably by increasing $[\text{-Co}(\text{CO})_4]$ and thereby the probability of PhCHCH_3 and $\cdot\text{Co}(\text{CO})_4$ radical recombinations.

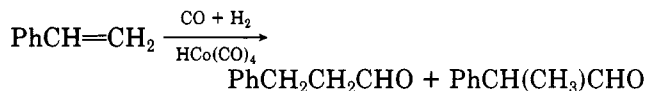
The acyl complex formed initially is the branched-chain isomer $\text{PhCH}(\text{CH}_3)\text{COC}(\text{CO})_4$ as shown by the ¹H NMR spectrum of its PPh_3 derivative. The aldehyde which is formed if higher concentrations of $\text{HCo}(\text{CO})_4$ are used is also the branched isomer $\text{PhCH}(\text{CH}_3)\text{CHO}$, again supported by the ¹H NMR spectrum of its dinitrophenylhydrazone. The amount of linear isomers in samples prepared immediately after the reaction is completed at 15 °C has to be less than 5% as can be estimated from the NMR spectra.

Unexpectedly, (α -phenylpropionyl)cobalt tetracarbonyl is not stable in heptane solution at room temperature, not even under 1 atm of CO. It is slowly transformed into its straight-chain isomer, $\text{PhCH}_2\text{CH}_2\text{COC}(\text{CO})_4$. The rate of this reaction is about 2 orders of magnitude smaller than the rate of (α -phenylpropionyl)cobalt tetracarbonyl formation. This ratio of reaction rates is in agreement with the observation that the primary acyl complex is at least 95% branched chain isomer. We propose the mechanism

shown on Scheme I for this isomerization.¹⁷

The equilibrium between the two acyl complexes is shifted far toward the straight-chain isomer. This is another example of the unusually low stability of phenylacetyl-cobalt tetracarbonyls as compared to other aliphatic cobalt carbonyl complexes. It has been demonstrated already several years ago that phenylacetyl-cobalt tetracarbonyl and its PPh_3 derivatives easily lose CO and become the benzyl complexes.¹⁹

Accordingly, in the reaction between styrene, $\text{HCo}(\text{CO})_4$, and CO, (α -phenylpropionyl)cobalt tetracarbonyl is the kinetically controlled product and the β isomer is the thermodynamically controlled one. At low temperatures and short reaction times when kinetic factors determine product composition, the branched isomer predominates; at higher temperatures and longer reaction times when the system can approach equilibrium more closely, the straight-chain isomer will be the main product. The structure of aldehydes formed in catalytic hydroformylation is obviously determined by the structure of the intermediate acyl complexes. Since it can be assumed that the ratio of aldehyde isomers should correlate to a certain extent with the ratio of acyl complex isomers in the reaction mixture, it may be expected that the amount of straight-chain aldehyde obtained by hydroformylating styrene should increase with increasing temperature. Recent work²⁰ proves that this is actually the case between 60 and 120 °C.



Finally it should be mentioned that even (β -phenylpropionyl)cobalt tetracarbonyl is not indefinitely stable in octane solution at room temperature. When the reaction products are stored for several days, CO is slowly evolved and additional amounts of ethylbenzene and $\text{Co}_2(\text{CO})_8$ are formed. A small but finite value for k_{-1} (i.e., the not strictly irreversible character of radical pair formation) resulting in the slow evolution of $\text{HCo}(\text{CO})_4$ may explain this process. Furthermore, bands appear in the IR spectrum which belong to new and up until now not identified cobalt carbonyls. The investigation of these complexes is in progress.

Experimental Section

Styrene and *n*-octane were distilled under carbon monoxide. A stock solution of $\text{HCo}(\text{CO})_4$ was prepared in *n*-octane. The frozen solution can be stored over dry ice for more than 1 month without change. $\text{DCo}(\text{CO})_4$ was prepared from $\text{HCo}(\text{CO})_4$ solutions by exchange with D_2O .²¹ Isotopic purity was >95% as calculated from mass spectrometric measurements. The concentrations of these solutions were determined by alkaline titration.

Kinetic runs were performed under CO in a gasometric apparatus by using an appropriate large buffer flask connected to the leveling vessel of the gas burette. Experiments were run between 291- and 2820-mbar total pressure. The reaction was started by injecting styrene into the vigorously stirred and thermostated solutions of $\text{HCo}(\text{CO})_4$. The initial rate of CO

(17) Isomerization of acylcobalt carbonyls has been already proposed by Takegami¹⁸ to explain some results obtained in the reaction of olefins with $\text{HCo}(\text{CO})_4$. In that work the structure of the acyl complexes was inferred from the structure of esters obtained by decomposing the acyl complexes in ethanol solution by I_2 .

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uptake was calculated from the change of gas volume by time. The amount of ethylbenzene was measured after a few percent of $\text{HCo}(\text{CO})_4$ conversion by gas chromatography (Hewlett-Packard 5830/A, SE 30 10-m glass capillary column, 40 °C, 2 mL of Ar/min) from the reaction mixtures after being quenched with pyridine. An aluminum foil covered reaction vessel was used to run the reaction in darkness.

The 2,4-dinitrophenylhydrazone was prepared by adding 10% molar excess of perchloric acid stabilized 2,4-dinitrophenylhydrazine in water to the reaction mixture followed by cooling overnight in the refrigerator and filtration of the precipitate.

The PPh_3 -substituted acylcobalt carbonyls were prepared by adding 20% molar excess of PPh_3 (based on Co) in heptane

to the product mixture after the $\text{Co}_2(\text{CO})_8$ crystals have been removed at -78 °C. Pale yellow crystals formed overnight.

The infrared spectra were made after $\text{Co}_2(\text{CO})_8$ has been removed by crystallization at -78 °C, from the pale yellow supernatant solution with compensation of the solvent, styrene, and traces of remaining $\text{Co}_2(\text{CO})_8$.

Registry No. $\text{PhCH}=\text{CH}_2$, 100-42-5; $\text{HCo}(\text{CO})_4$, 16842-03-8; PhCH_2CH_3 , 100-41-4; $\text{PhCH}(\text{CH}_3)\text{COC}(\text{CO})_4$, 82182-04-5; CO , 630-08-0; $\text{Co}_2(\text{CO})_8$, 10210-68-1; $\text{PhCH}(\text{CH}_3)\text{CHO}$, 93-53-8; $\text{PhCH}(\text{CH}_3)\text{COC}(\text{CO})_3(\text{PPh}_3)$, 82182-05-6; $\text{PhCH}(\text{CH}_3)\text{CHO}$ 2,4-dinitrophenylhydrazone, 5530-36-9; $\text{PhCH}_2\text{CH}_2\text{COC}(\text{CO})_3(\text{PPh}_3)$, 82182-06-7; $\text{PhCH}_2\text{CH}_2\text{CHO}$, 104-53-0; $\text{PhCH}_2\text{CH}_2\text{CHO}$ 2,4-dinitrophenylhydrazone, 1237-68-9; $\text{PhCH}_2\text{CH}_2\text{COC}(\text{CO})_4$, 82182-07-8.

Stereochemically Nonrigid Bis(olefin)rhodium Poly(1-pyrazolyl)borato Complexes. 1. Synthesis and Conversion into New Rhodium(I) and Rhodium(III) Complexes. The Crystal and Molecular Structure of (Tetrakis(1-pyrazolyl)borato)diodocarbonylrhodium(III) Methylene Chloride Solvate

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The bis(olefin)rhodium(I) poly(1-pyrazolyl)borato complexes $\text{HB}(\text{pz})_3\text{Rh}(\text{C}_2\text{H}_4)_2$, 1, $\text{HB}(\text{pz})_3\text{Rh}(\text{cod})$, 2, and $\text{B}(\text{pz})_4\text{Rh}(\text{LL})$ ($\text{LL} = (\text{C}_2\text{H}_4)_2$, 3; $\text{LL} = \text{cod}$, 4; $\text{LL} = \text{nbd}$, 5; $\text{LL} = \text{duroquinone}$, 6) and related species have been prepared, and their physical and chemical properties have been investigated. ¹H NMR measurements in CDCl_3 at room temperature indicate rapid exchange of all pyrazolyl groups of $\text{B}(\text{pz})_4$ in 3-5. In 6, pyrazolyl group exchange is slow at room temperature but rapid at 85 °C. The olefin ligands in 1, 2, 4 and 6 are kinetically labile and are displaced by CO at atmospheric pressure to give the new rhodium(I) carbonyl complexes $[\text{RB}(\text{pz})_3]\text{Rh}_2(\text{CO})_3$ (8, $\text{R} = \text{H}$; 9, $\text{R} = \text{pz}$). A structure involving three μ -CO ligands is proposed for these complexes on the basis of IR data. 9 reacts with iodine to give the Rh(III) complex $\text{B}(\text{pz})_4\text{RhI}_2(\text{CO})$ (14) and similar complexes have been isolated from the reaction of 8 with Cl_2 and I_2 and of 9 with Br_2 and $\text{C}_3\text{F}_7\text{I}$. Lewis bases displace CO from the Rh(III) complexes, e.g., with triphenylphosphine 14 yields $\text{B}(\text{pz})_4\text{RhI}_2(\text{PPh}_3)$ (17). Crystals of $\text{B}(\text{pz})_4\text{RhI}_2(\text{CO})$ (14) are monoclinic of space group $C2/c$ with eight molecules in a unit cell of dimensions $a = 22.713$ (2) Å, $b = 12.249$ (2) Å, $c = 15.211$ (2) Å, and $\beta = 94.29$ (1)°. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations; $R = 0.066$ for 4061 reflections with $I > 3\sigma(I)$. There is disorder (2/3:1/3) of one of the iodine atoms and the CO ligand. The rhodium atom has octahedral coordination. The nondisordered Rh-I bond has a length of 2.634 (1) Å, and the $\text{B}(\text{pz})_4\text{Rh}$ moiety has normal geometry with $\text{Rh}-\text{N} = 2.039$ -2.082 (7) Å.

Introduction

Two important groups of bis(olefin)rhodium(I) complexes are typified by the four-coordinate, 16-electron, 2,4-pentanedionato derivative $(\text{acac})\text{Rh}(\text{C}_2\text{H}_4)_2$ and the five-coordinate, 18-electron, η -cyclopentadienyl species $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{H}_4)_2$, respectively. The contrasting structural²⁻⁵ and chemical⁵⁻⁸ properties of these and related

complexes have received much attention in recent years. (Hydrotris(1-pyrazolyl)borato)bis(ethylene)rhodium(I), $\text{HB}(\text{pz})_3\text{Rh}(\text{C}_2\text{H}_4)_2$ ($\text{pz} = 1$ -pyrazolyl, 1; originally described by Trofimenko⁹) is a potential bridge between the two groups of olefin complexes described above. The hydrotris(1-pyrazolyl)borato ligand may function as a bidentate ligand (resembling *acac*) or in a tridentate fashion (formally analogous to cyclopentadienide).¹⁰ Thus complex 1 may exist as a four-coordinate, 16-electron square-coplanar rhodium(I) complex, 1a, or as a trigonal-bipyramidal five-coordinate 18-electron species, 1b. In solution a dy-

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