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Kinetics and Mechanism of Ethyl Formate Formation from (Ethoxycarbonyl)cobalt Tetracarbonyl and H_2 or $HCo(CO)_4$

Ferenc Ungváry and László Markó*

Department of Organic Chemistry, University of Chemical Engineering, H-8201 Veszprém, Hungary

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(Ethoxycarbonyl)cobalt tetracarbonyl is hydrogenated at room temperature by H_2 or $HCo(CO)_4$ to ethyl formate and $Co_2(CO)_8$. The rate of ethyl formate formation, $EtOCOCo(CO)_4 + {}^1/_2\,H_2 \xrightarrow{k'_4} EtOCHO + {}^1/_2Co_2(CO)_8$ and $EtOCOCo(CO)_4 + HCo(CO)_4 \xrightarrow{k'_5} EtOCHO + Co_2(CO)_8$, is first order in $EtOCOCo(CO)_4$, first order in the hydrogenating agent (H_2 or $HCo(CO)_4$), and negative first order in CO. The comparison of the rate constants at 25 °C, $k'_4 = 1.15 \times 10^{-5}\ s^{-1}$ (±5%) and $k'_5 = 14.5 \times 10^{-5}\ s^{-1}$ (±10%), shows that $HCo(CO)_4$ reacts about 12 times faster than H_2 and explains why $HCo(CO)_4$ could not be detected among the products obtained with H_2. The bimolecular reaction between coordinatively unsaturated $EtOCOCo(CO)_3$ and the reducing agent is suggested as the rate-determining step.

Introduction

Alkyl formates are byproducts in the cobalt carbonyl catalyzed hydroformylation[1] and in the homogeneous Fischer–Tropsch synthesis.[2] They were suggested to be formed from aldehydes via alkoxycobalt carbonyls by carbonylation to (alkoxycarbonyl)cobalt carbonyls and their subsequent hydrogenolysis (eq 1–3).[3,4]

$$RCHO + HCo(CO)_4 \rightarrow RCH_2OCo(CO)_4 \quad (1)$$

$$RCH_2OCo(CO)_4 + CO \rightarrow RCH_2OCOCo(CO)_4 \quad (2)$$

$$RCH_2OCOCo(CO)_4 + H_2 \rightarrow RCH_2OCHO + HCo(CO)_4 \quad (3)$$

To our knowledge none of these steps has been proved individually and alkoxycobalt carbonyls have not been prepared yet at all. They are probably very reactive toward CO since an attempt to prepare an alkoxycobalt tetracarbonyl from $NaCo(CO)_4$ and an alkyl hypochlorite led to the formation of an (alkoxycarbonyl)cobalt carbonyl even at low temperatures and in the absence of CO.[5]

(Ethoxycarbonyl)cobalt tetracarbonyl was prepared in low yield in a very slow reaction from ethyl chloroformate with $NaCo(CO)_4$, and its impure crystalline triphenylphosphine derivative could be isolated.[5] Monosubstituted (ethoxycarbonyl)cobalt carbonyls could be prepared with higher yields from $NaCo(CO)_3PR_3$ (R = Ph or OPh) and ethyl chloroformate, and on the basis of their infrared spectra a trigonal-bipyramidal structure with the three carbonyls in the equatorial plane was suggested.[6] Recently the preparation of (methoxycarbonyl)cobalt tetracarbonyl from methyl (chloroformyl)formate and $NaCo(CO)_4$ in dimethyl ether was achieved through the spontaneous decarbonylation of the intermediate (methoxyoxalyl)cobalt tetracarbonyl (eq 4).[7]

$$MeOC({=}O)C({=}O)Cl + NaCo(CO)_4 \rightarrow [MeOC({=}O)C({=}O)Co(CO)_4] \xrightarrow{-CO} MeOC({=}O)Co(CO)_4 \quad (4)$$

The reaction of methyl (chloroformyl)formate with $NaCo(CO)_3PPh_3$ yields $MeOC({=}O)C({=}O)Co(CO)_3PPh_3$, which was claimed to be the first stable α,β-dicarbonyl cobalt complex.[7] Other representatives of probably less stable α,β-dicarbonyl cobalt complexes were reported earlier: Wilkinson and co-workers mentioned in a footnote[8] and later in another publication[2] the synthesis of $MeOCH_2CH_2OC({=}O)C({=}O)Co(CO)_4$ without giving experimental details.

The hydrogenolysis of the carbon–cobalt bond in acylcobalt carbonyls is an essential step of the hydroformylation catalytic cycle. In the last two decades dozens of publications appeared[9] discussing whether H_2 or $HCo(CO)_4$ is the actual reducing agent, but no data are available up till now which could unambiguously answer this question. Although examples for the reduction of acylcobalt carbonyls by H_2[9a,b,10] or by $HCo(CO)_4$[9a,12] are well-known, only in one case[10] has a kinetic study been made. Therefore the mechanisms suggested for these reactions are based mainly on speculations. Obviously the difficulties of working with the rather unstable acylcobalt tetracarbonyls[13] are mainly responsible for this.

(Ethoxycarbonyl)cobalt tetracarbonyl is more stable than the simple acylcobalt tetracarbonyls, and it can be prepared in pure form. With use of this possibility, we now report on the kinetics of the reaction of (ethoxycarbonyl)cobalt tetracarbonyl with H_2 and with $HCo(CO)_4$.

Results

Preparation and Properties of (Ethoxyoxalyl)cobalt Tetracarbonyl (1) and (Ethoxycarbonyl)cobalt Tetracarbonyl (2). Complexes 1 and 2 were prepared

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(1) 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.

(2) Blackborow, J. R.; Daroda, R. J.; Wilkinson, G. *Coord. Chem. Rev.* **1982**, *43*, 17.

(3) Sternberg, H. W.; Wender, I. *Spec. Publ.—Chem. Soc.* **1959**, *No. 13*, 35.

(4) Markó, L. *Proc. Chem. Soc.* **1962**, 67.

(5) Heck, R. F. *J. Organomet. Chem.* **1964**, *2*, 195. Similar to Heck's observation: *n*-BuOCl was reacted with $NaCo(CO)_4$ at −40 °C under CO or in the absence of CO and (*n*-butoxycarbonyl)cobalt carbonyl was formed.[7]

(6) Hieber, W.; Duchatsch, H. *Chem. Ber.* **1965**, *98*, 1744.

(7) Milstein, D.; Huckaby, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 6150.

(8) Daroda, R. J.; Blackborow, J. R.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1980**, 1098.

(9) E.g.: (a) Heck, R. F.; Breslow, D. S. *Actes Congr. Int. Catal. 2nd, 1960*, **1961**, 671–685. (b) Piacenti, E.; Bianchi, M.; Benedetti, E., *Chim. Ind.* (*Milan*), **1967**, *49*, 245. (c) Alemdaroglu, N. H.; Penninger, J. L. M.; Oltay, E. *Monatsh. Chem.* **1976**, *107*, 1153.

(10) The kinetics of hydrogenolysis of $CH_3COCo(CO)_2\,[P(OMe)_3]_2$ at elevated pressures shows first-order dependence on the complex and zero-order dependence on H_2. On the basis of experiments with ^{14}C-labeled CO, it was shown that $[CH_3COCo(CO)_2P(OMe)_3]$ is formed in the rate-determining step, which reacts with H_2 in a fast reaction to yield CH_3CHO and $[HCo(CO)_2P(OMe)_3]$.[11]

(11) Thomas, J. A. "The Chemical Society Autumn Meeting", University of York: York, England, 1971; Abstr. No. B24.

(12) (a) Roos, I.; Orchin, M. *J. Org. Chem.* **1966**, *31*, 3015. (b) See ref 24, p 107 and 125. The rate constant of $HCo(CO)_4$ consumption in the reduction of hexenoylcobalt tetracarbonyl with $HCo(CO)_4$ in hexane under CO at room temperature was reported to be 0.3 min^{-1}. With the assumption that $r = k[C_5H_{11}COCo(CO)_4][HCo(CO)_4][CO]^{-1}$, $k = 18 \times 10^{-5}$ s^{-1} can be calculated for the aldehyde formation.

(13) Heck, R. F. *Adv. Organomet. Chem.* **1966**, *4*, 243.

(14) "Handbook of Chemistry", Lange, N. A., Ed.; Handbook Publishing Inc.: Sandusky, OH, 1956; p 1424.

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Table I. Initial Decarbonylation Rates (r_1) of 1 at 15 °C in Diethyl Ether Solution under CO at Various Initial Concentrations and CO Pressures

[1], M	p_{CO},[a] mmHg	$10^6 r_1$, M·s^{-1}
0.0588	81	13.2
0.0147	397	1.5
0.0275[b]	405	3.9
0.0275[b]	405	4.3[c]
0.0275[b]	405	4.0[d]
0.0294	397	4.5
0.0588	397	12.5
0.0588	1213	12.2
0.0588	1896	13.5
0.0275[b]	406	6.7[e]
0.0621[f]	452	>2100[g]

[a] $p_{CO} = p_{total} - p_{solvent}$; for $p_{solvent}$ see ref 14. [b] The ether solution contains 5.0 vol % of *n*-octane.
[c] $[Co_2(CO)_8] = 0.012$ M. [d] $[2] = 0.0283$ M.
[e] $[HCo(CO)_4] = 0.0295$ M; 2 mol of CO evolved in 6 h.
[f] In situ reaction product of $NaCo(CO)_4$ and oxalyl chloride at 10 °C. [g] 2 mol of CO evolved within 30 s at 10 °C.

from ethyl (chloroformyl)formate and $NaCo(CO)_4$ in a way similar to the published method (eq 5 and 6).[7] The

$$\mathrm{EtOC({=}O)C({=}O)Cl + NaCo(CO)_4 \xrightarrow[0\ ^\circ C]{ether} \underset{1}{EtOC({=}O)C({=}O)Co(CO)_4}} \tag{5}$$

$$\mathrm{EtOC({=}O)C({=}O)Co(CO)_4 \xrightarrow[\text{room temp or 0 °C under vacuum}]{r_1} \underset{2}{EtOC({=}O)Co(CO)_4} + CO} \tag{6}$$

primary product of the reaction in ether is (ethoxyoxalyl)cobalt tetracarbonyl (**1**), which can be stored in ether solution at 0 °C for several hours without decomposition. The decarbonylation to **2**, however, takes place readily at room temperature or during the vacuum evaporation of the solvent at 0 °C. To obtain a pure product, a slight excess (~2%) of ethyl (chloroformyl)formate in the solution is necessary and in this way **2** may be obtained in about 90% yield. If the solution of **1** in ether contains unreacted $NaCo(CO)_4$, diethyl oxalate and $Co_4(CO)_{12}$ are formed as byproducts during the solvent removal procedure.

The rate of decarbonylation is independent of CO partial pressure (Table I). Reaction 6 can not be reversed with 83 bar of CO in 6 h at room temperature.

2 is much more stable than **1**. The rate of decomposition of a 0.0588 M solution in *n*-octane is less than 2×10^{-7} M·s^{-1} and 5.0×10^{-7} M·s^{-1} at 25 and 35 °C, respectively, measured by the slow CO evolution observed. Products of this reaction were not identified.

Oxalyl chloride reacts with $NaCo(CO)_4$ in ether in a way similar to ethyl (chloroformyl)formate leading to NaCl, but in this case no intermediate complexes could be identified. The reaction product decomposed at 10 °C very rapidly into $Co_2(CO)_8$ and 2 mol of CO just after the two reactants were mixed.

The Reaction of 2 with Ph₃P. Adding Ph_3P to solutions of **1** or **2**, $EtOCOCo(CO)_3PPh_3$ (**4**) is formed in a quantitative reaction.[15]

Table II. Initial Rates of CO Substitution (r_3) in 2 by Ph_3P under CO at Various Conditions in *n*-Octane Solution

temp, °C	10^2[2], M	10^2[CO],[a] M	10^2[Ph_3P], M	$10^6 r_3$, M·s^{-1}
25	1.50	1.124	0.60	7.49
25	1.50	1.124	0.75	8.85
25	1.50	1.123	1.10	11.1
25	1.50	1.123	2.00	15.1
25	2.83	1.159	2.90	31.9
25	1.50	1.123	9.85	22.2
20	2.83	1.132	2.90	15.4
15	2.83	0.443	2.90	9.0
15	2.83	1.090	2.90	7.54
15	2.83	1.090	8.70	9.34
15	11.3	1.088	5.80	36.6
15	3.00	1.064	0.55	3.63
15	3.00	1.064	0.75	4.65
15	3.00	1.064	9.70	10.3
15	8.54	1.064	12.2	15.8
15	1.70	3.457	8.70	4.46
15	5.66	3.42	2.90	8.9

[a] Calculated from p_{CO} and the solubility of CO in *n*-heptane.[18]

In the reaction of **2** with Ph_3P 1 mol of CO is released and the rate of CO evolution is first order in **2** and is dependent of both Ph_3P and CO concentration in a complex way (Table II). This behavior is in accordance with a reversible dissociation of CO from **2** (reaction 7)[16] followed by a reaction between Ph_3P and the intermediate $EtOCOCo(CO)_3$ (reaction 8).

$$\mathrm{2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{3}{EtOCOCo(CO)_3} + CO} \tag{7}$$

$$\mathrm{3 + Ph_3P \xrightarrow{k_3} 4} \tag{8}$$

Reacting **1** with PPh_3, the formation of **4** is accompanied by the evolution of 2 mol of CO and the initial rate of CO evolution is practically the same as the initial rate of decarbonylation of **1** to **2**. Probably, **1** is first decarbonylated to **2**, and only this latter complex is reacting with Ph_3P. This reaction was therefore not investigated in further detail.

Hydrogenation of 2. **2** is smoothly hydrogenated to ethyl formate and $Co_2(CO)_8$ by both H_2 and $HCo(CO)_4$.

With H_2 as the reducing agent the stoichiometry of the reaction is represented by eq 9.

$$\mathrm{EtOC({=}O)Co(CO)_4 + {}^1\!/_2 H_2 \xrightarrow{r_4} EtOC({=}O)H + {}^1\!/_2 Co_2(CO)_8} \tag{9}$$

The rate of H_2 uptake agrees well with the decrease in **2** and the increase in EtOCHO and $Co_2(CO)_8$ concentrations. The three concentrations could be followed by measuring the infrared absorbancies of the reaction mixture at 1692, 1737, and 1857 cm^{-1}, respectively. No $HCo(CO)_4$ could be detected as an intermediate by IR.

In the reaction of **2** with $HCo(CO)_4$ the main products were EtOCHO and $Co_2(CO)_8$ (eq 10) but additionally small

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(15) The IR spectrum of **4** in KBr agrees completely with the published data.[6] **4**: IR (heptane) ν(CO) 2061 (w), 1996 (vs), 1983 (vs), 1671 (m) cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.05 (3 H, t, J_{HH} = 7 Hz), 4.17 (2 H, q, J_{HH} = 7 Hz), 6.93 (9 H, m), 7.38 (6 H, m); ^{13}C NMR (C_6D_6) δ 15.0 (CH_3, s), 62.1 (CH_2, s), 129 (C_3, d, $^3J_{PC_1C_2C_3}$ = 10 Hz), 131 (C_4, d, $^4J_{PC_1C_2C_3C_4}$ = 2 Hz), 133.3 (C_2, d, $^2J_{PC_1C_2}$ = 11.1 Hz), 133.8 (C_1, d, $^1J_{PC_1}$ = 44.5 Hz), 186.1 (EtOCO, d, $^2J_{PCoC}$ = 41 Hz), 199.1 ((CO)$_4$Co, d, $^2J_{PCoC}$ = 21.3 Hz); ^{31}P NMR (C_6D_6) +51.3 ppm (downfield relative to 85% H_3PO_4).

(16) Constant first-order rates, independent of phosphine concentration, have been found for the substitution of CO by Ph_3P for a great number of acylcobalt tetracarbonyls in diethyl ether solution. The rate constants of these reactions were regarded as a measure of the rate of CO dissociation from acylcobalt tetracarbonyls.[17]

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

(18) (a) Gjaldbaek, J. C. *Acta Chem. Scand.* **1952**, *6*, 623. (b) Ungváry, F. *J. Organomet. Chem.* **1972**, *36*, 363.

(19) Cook, M. W.; Hanson, D. N.; Alder, B. J. *J. Chem. Phys.* **1957**, *26*, 748.

Table III. Initial Rates of Ethyl Formate Formation with H_2 (r_4) in *n*-Octane Solution and the Observed Rate Constants ($k'_4 = r_4[CO]/[2][H_2]$) at Various Initial Concentrations and Temperatures

temp, °C	10^2-[2], M	10^3-$[H_2]$,[a] M	10^3-[CO], M	10^6r_4, M·s^{-1}	$10^5k'_4$, s^{-1}
20	5.88	4.29[b]	*d*	24.1	
20	5.88	4.30[c]	*d*	24.3	
20	5.88	2.63	4.20	0.21	0.56
25	2.94	2.72	4.32	0.21	1.13
25	5.88	2.68	4.25	0.43	1.16
25	5.88	2.69	4.27	0.40[e]	1.10
25	11.76	2.72	4.32	0.82	1.11
25	23.52	2.72	4.32	1.67	1.13
25	5.88	3.43	2.31	0.98	1.12
25	5.88	1.904	0.663	1.97	1.17
25	5.88	3.83	1.35	2.06	1.21
25	5.88	7.89	2.79	1.92	1.15
25	5.88	12.22	4.32	1.96	1.18
30	5.88	2.76	4.36	0.92	2.47
35	5.88	2.76	4.47	2.10	5.78

[a] Calculated from p_{H_2} and the solubility of H_2 in *n*-octane.[19] [b] Reaction started under H_2. [c] Reaction started under D_2. [d] CO concentration in these experiments is not known but is obviously very small. [e] In the presence of $[Co_2(CO)_2] = 0.120$ M.

amounts (~10%) of EtOH could be detected by GLC (eq 11). Accordingly the rate of consumption of 2 agreed well with the rate of $Co_2(CO)_8$ formation but the rate of EtOCHO formation was found to be smaller.

$$EtOC({=}O)Co(CO)_4 + HCo(CO)_4 \xrightarrow{r_5} EtOC({=}O)H + Co_2(CO)_8 \quad (10)$$

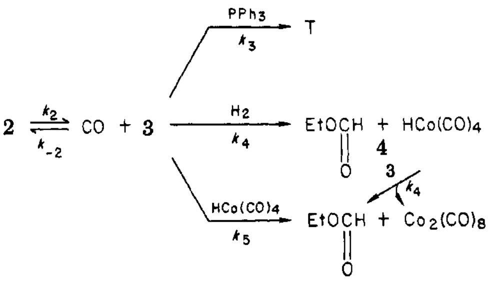
$$EtOC({=}O)Co(CO)_4 + HCo(CO)_4 \rightarrow EtOH + CO + Co_2(CO)_8 \quad (11)$$

The kinetic data compiled in Tables III and IV show a first-order dependence in 2, H_2, and $HCo(CO)_4$ concentrations and a negative first-order dependence in CO for both reactions 9 and 10.

Within the limits of experimental error, no kinetic isotope effect was observed when the reaction was conducted by using D_2 or $DCo(CO)_4$, and $Co_2(CO)_8$ had no influence on the rates of these reactions.

1 reacts with H_2 at 20 °C yielding exclusively ethyl formate, $Co_2(CO)_8$, and CO even at 83 bar of H_2 pressures. With $HCo(CO)_4$ as reducing agent, however, ethyl alcohol, $Co_2(CO)_8$, CO, and traces of 2 are the reaction products. Ethyl formate or other organic carbonyl compounds could not be detected.

Scheme I



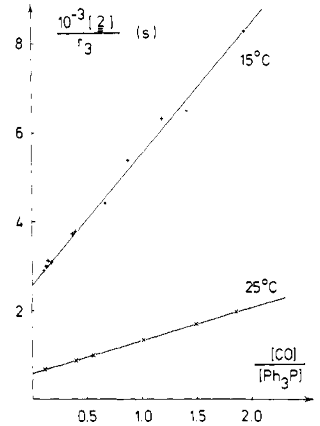


Figure 1. Reaction of 2 with Ph_3P: influence of CO and Ph_3P concentration on reaction rate.

Discussion

(Ethoxycarbonyl)cobalt tetracarbonyl (2) reacts with PPh_3, $HCo(CO)_4$, and H_2 according Scheme I. This general picture is supported by the rate equations of the three reactions. In the case of PPh_3 the experimental results could be accommodated by assuming steady-state concentration for the coordinatively unsaturated 3 which leads to the rate equation

$$-\frac{d[2]}{dt} = \frac{d[4]}{dt} = r_3 = \frac{k_2k_3[2][PPh_3]}{k_{-2}[CO] + k_3[PPh_3]}$$

Plotting $[2]/r_3$ against $[CO]/Ph_3P]$ (Figure 1), k_2 and the ratio of k_{-2} to k_3 can be calculated. With the data from Table II, we obtain $k_2 = 38.8 \times 10^{-5}$ s^{-1} and $k_{-2}/k_{-3} = 1.14$ at 15 °C and $k_2 = 173 \times 10^{-5}$ s^{-1} and $k_{-2}/k_3 = 1.29$ at 25 °C.

The reactions with H_2 and $HCo(CO)_4$ obey more simple rate laws because both k_4 and k_5 are much smaller than k_3 (and k_{-2}), and therefore instead of using the steady-state approach one can describe the kinetics of these reactions by assuming that 3 is formed by a fast preequilibrium:

$$-\frac{d[2]}{dt} = \frac{d[EtOCOH]}{dt} = r_4 = k'_4[2][H_2][CO]^{-1} = k_4\frac{k_2}{k_{-2}}[2][H_2][CO]^{-1}$$

Table IV. Initial Rates of Ethyl Formate Formation with $HCo(CO)_4$ (r_5) in *n*-Octane Solution and the Observed Rate Constants ($k'_5 = r_5[CO]/[2][HCo(CO)_4]$) at Various Initial Concentrations

temp, °C	10^2[2], M	$10^2[HCo(CO)_4]$, M	10^2[CO], M	10^6r_5, M·s^{-1}	$10^5k'_5$, s^{-1}
20	3.10	3.10	1.12	6.5	7.6
25	3.10	3.10	0.575	23	13.8
25	3.10	3.10	1.13	12.5	14.7
25	3.10	3.10	1.14	12.5[a]	14.8
25	3.10	3.10	1.15	12.0	14.4
25	3.10	3.10	3.64	4.2	15.9
25	5.88	5.88	1.12	42	13.6
25	3.10	6.20	1.13	23.4	13.9
25	6.20	3.10	1.13	25.0	14.7

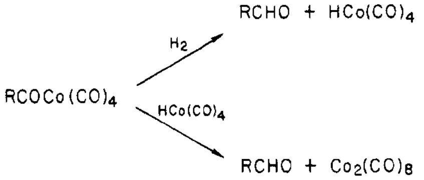
[a] In the presence of $[Co_2(CO)_8] = 0.120$ M.

$$-\frac{d[2]}{dt} = \frac{d[Co_2(CO)_8]}{dt} = r_5 =$$
$$k'_5[2][HCo(CO)_4][CO]^{-1} = k_5\frac{k_2}{k_{-2}}[2][HCo(CO)_4][CO]^{-1}$$

From the experimental results obtained at 25 °C the following rate constants could be calculated: $k_2 = 173 \times 10^{-5}\ s^{-1}$; $k_3/k_{-2} = 0.77$; $k'_4 = 1.15 \times 10^{-5}\ s^{-1}$; $k_4/k_{-2} = 0.0067$; $k'_5 = 14.5 \times 10^{-5}\ s^{-1}$; $k_5/k_{-2} = 0.084$.

Although our measurements do not provide absolute values for the rate constants of the reactions between the intermediate **3** and the four reaction partners CO, PPh_3, H_2, and $HCo(CO)_4$, the relative reactivities of these can be simply calculated from the data listed above. The following order of reactivities is obtained: CO:PPh_3:$HCo(CO)_4$:H_2 = 1:0.77:0.084:0.0067.

The most interesting conclusion that can be drawn from these results regards the relative reactivity of $HCo(CO)_4$ and H_2 against the coordinatively unsaturated EtOCO-$Co(CO)_3$ (**3**). As it might have been anticipated, the hydride proved to be the more reactive but surprisingly the difference is not that large (12:1). This is an interesting result because it suggests that in the long lasting discussion[9] about the role of H_2 and $HCo(CO)_4$ in the hydrogenolysis of acylcobalt carbonyls (an important step of the hydroformylation catalytic cycle)



both views may be correct. Accordingly we may assume that H_2 and $HCo(CO)_4$ are simultaneously responsible for the formation of aldehydes from acylcobalt carbonyls, but obviously their relative importance will depend on the structure of the acyl complex.

The higher reactivity of $HCo(CO)_4$ also explains why this complex could not be observed during the reaction between **3** and H_2: obviously it reacted as soon as it formed with **3** to yield $Co_2(CO)_8$ and ethyl formate, as shown is Scheme I.

At the present level of information little can be said about the reactivity of (ethoxyoxalyl)cobalt tetracarbonyl. Its decarbonylation to **2** is a fast and irreversible reaction that makes the investigation of other reactions rather difficult. Its reaction with $HCo(CO)_4$, which does *not* yield ethyl formate, is unexpected and merits further investigation.

Experimental Section

General Techniques. Infrared spectra were recorded on a Carl Zeiss Jena IR 75 Spectrophotometer. The spectra were calibrated in the ν(C=O) region by recording the gas spectrum of CO and using the known published wavenumbers.[20] NMR spectra were recorded either with a Tesla BS 487/C 80-MHz or with a Varian CFT 20 spectrophotometer using Me_4Si as the internal standard. UV and visible spectra were recorded on a Carl Zeiss Jena Specord UV-vis spectrophotometer. Analysis of the volatile compounds was performed on an analytical Hewlett-Packard Model 5830A gas chromatograph using 30-m glass capillary column 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 technique described by Thomas.[21]

Materials. All solvents were dried on sodium wire and were freshly distilled and stored under an Ar of CO atmosphere. Ether was distilled from sodium benzophenone ketyl immediately before use.

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

The compound $NaCo(CO)_4$ was prepared from $Co_2(CO)_8$ and 1.5% Na/Hg in ether[22] and used as an ether solution. Its concentration was determined by cobalt analysis after treatment of 2.0-mL samples with 8 mL of 6% H_2O_2 and 8 mL of 6% HNO_3.

Stock solutions of $HCo(CO)_4$ were prepared in *n*-octane from $Co_2(CO)_8$, DMF, and concentrated HCl.[23]

$DCo(CO)_4$ was prepared from $HCo(CO)_4$ solutions by hydrogen and deuterium exchange with a 50-fold molar excess of D_2O.[24] Isotopic purity was >95% as calculated from mass spectrometric measurements of its decomposition products. The concentration of $HCo(CO)_4$ and $DCo(CO)_4$ solutions were determined by 0.1 N alkaline titration at 0 °C under Ar.

Ethyl (chloroformyl)formate was prepared from ethyl oxalate and $SOCl_2$.[25]

Preparation of (Ethoxyoxalyl)cobalt Tetracarbonyl (1) in Ether Solution. To 576 mL of a 0.0653 M colorless solution of $NaCo(CO)_4$ (37.6 mmol) in diethyl ether was added 4.30 mL (38.4 mmol) of ethyl (chloroformyl)formate with stirring at 0 °C. Immediately a light yellow solution and a white precipitate (NaCl) were formed. Filtration at -40 °C gave 530 mL light yellow solution of **1** (0.0650 M based on Co) that could be stored on dry ice for several days or at 0 °C for several hours without decomposition. The IR spectrum of a diluted sample (1:9 with *n*-heptane) at 0 °C in a thermostated cell showed the following absorbances: ν(CO) 2118 (m), 2055 (s), 2043 (vs), 2030 (vs), 1743 (m), and 1703 (w) cm^{-1}. IR spectra at ambient temperature showed a rapid decline of the absorptions at 1743 and 1703 cm^{-1} and the growing of a new band at 1692 cm^{-1} without a change in the intensity of the other carbonyl bands.

Preparation of (Ethoxycarbonyl)cobalt Tetracarbonyl (2). From 500 mL of a 0.065 M solution of **1** was removed diethyl ether in vacuo at 0 °C, and 50 mL of dry CO-saturated pentane was added to the remaining yellow oil. After filtration and removal of pentane in vacuo at 0 °C, 7.36 g of **2** (30.1 mmol, 92.6% yield) results as a yellow oil, which does not crystallize even at -79 °C. It could be stored on dry ice without decomposition for more than a year: IR (heptane) ν(CO) 2118 (m), 2111 (vw), 2055 (s), 2043 (vs), 2030 (vs), 1692 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 0.93 (3 H, t, J_{HH} = 7 Hz), 3.94 (2 H, q, J_{HH} = 7 Hz); ^{13}C NMR (C_6D_6) δ 14.7 (CH_3, s), 64.4 (CH_2, s), 177.9 (COEt, s), 196.6 ($(CO)_4Co$, br); UV-vis (octane) 226, 254 nm. Essential for the success of the above preparation of **2** is to avoid an eventual excess of $NaCo(CO)_4$ in the preparation of **1**, otherwise a rapid decomposition occurs during ether removal. Among the decomposition products were identified diethyl oxalate and $Co_4(CO)_{12}$ by IR spectra.

Reaction of $NaCo(CO)_4$ with Oxalyl Chloride. A 9.8-mL sample of a 0.0653 M solution of $NaCo(CO)_4$ (0.64 mmol) in ether was placed into a gasometric apparatus and was thermostated at +10 °C. Adding 28 μL of oxalyl chloride (0.32 mmol) with stirring, 25.0 mL of gas (10 °C, 740 mmHg, saturated with ether, corresponds to 0.638 mmol of CO) was rapidly evolved. The infrared spectrum of the reaction mixture, taken 30 s after adding oxalyl chloride, did show only absorptions characteristic for $Co_2(CO)_8$.

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 millimeters of Hg by using on open mercury manometer measuring the pressure difference between the atmosphere and the reaction vessel.

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Decarbonylation of 1. The reaction was started by injecting 9.0 mL of a 0.065 M solution of 1 in ether into vigorously stirred (magnetic stirring bar) known amounts of CO-saturated ether under CO. The change of gas volume as a function of time was plotted, and the initial rates were determined below 5% conversion. The total volume of gas evolved during the reaction corresponded to 0.98 ± 0.02 mol of CO/mol of 1.

Decarbonylation of 1 in the presence of $HCo(CO)_4$ was performed in the gasometric apparatus described above by first adding 1.0 mL of a 0.590 M solution of $HCo(CO)_4$ in *n*-octane to 10.0 mL of CO-saturated ether and then starting the reaction by injecting 9.0 mL of a 0.0612 M solution of 1 in ether. Immediately CO evolution set in and ceased after 6 h at 1.93 mol of CO/mol of 1. The IR spectrum of the product showed the formation of 0.90 mol of $Co_2(CO)_8$/mol of 1 and 0.07 mol of 2/mol of 1 but practically no ethyl formate, and 0.80 mol of ethanol/mol of 1 was found by GLC.

Reduction of 1 with H_2. A 5-mL sample of a 0.065 M solution of 1 in ether was placed at 0 °C in a 20-mL stainless-steel rocking autoclave and pressurized to 83 bar with H_2. After 5 h of agitation at 20 °C the IR spectrum of the reaction mixture showed quantitative conversion to $Co_2(CO)_8$ and ethyl formate in a 1:2 molar ratio.

Reaction of Ph_3P with 1 or 2. These reactions were performed in the gasometric apparatus described above and started by injecting neat 2 or ether solutions of 1 into solutions containing known amounts of Ph_3P. In both cases crystalline 3 could be prepared in at least 80% yield from the reaction mixtures by evaporating the solvent and recrystallizing the residue from a 20-fold benzene-heptane (1:8) mixture.

Reduction of 2 with $HCo(CO)_4$. The reaction was started by injecting neat 2 into the vigorously stirred and thermostated solution of $HCo(CO)_4$ in *n*-octane under CO. The change of IR spectra was followed from samples taken with a cold (−10 °C) syringe and measured in a cold (0 °C) CaF_2 IR cell. (Absorbancies: 1857 ($\epsilon_M(Co_2(CO)_8)$ 1735),[26] 1737 (ϵ_M(EtOCHO) 1050), and 1692 cm^{-1} (ϵ_M(2) 1266 $cm^2\ mmol^{-1}$).) Initial rates were calculated from graphical plots below 10% conversions.

Registry No. 1, 86970-71-0; 2, 86970-72-1; EtOCOCOCl, 4755-77-5; $NaCo(CO)_4$, 14878-28-5; oxalyl chloride, 79-37-8; $HCo(CO)_4$, 16842-03-8; Ph_3P, 603-35-0.

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Synthesis, Characterization, and Solution Behavior of (η^3-Allyl)(carbene)palladium(II) Complexes

A. Scrivanti*

Centro Chimica Metallorganica C.N.R., 35100 Padova, Italy

G. Carturan

Facoltà Chimica Industriale, S. Marta, Venezia, Italy

B. Crociani

Istituto Chimica Generale, 90123 Palermo, Italy

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The complexes $[PdCl(\eta^3\text{-allyl})(CNC_6H_4X)]$ (η^3-allyl = η^3-2-MeC_3H_4, C_6H_4X = *p*-C_6H_4Cl, *p*-C_6H_4OMe, *p*-C_6H_4Me) undergo selective nucleophilic attack by HNR'_2 (R′ = Me, Et) on the isocyanide carbon atom. Under mild conditions the reaction gives allyl carbene complexes of the type $[PdCl(\eta^3\text{-allyl})\{C(NHC_6H_4X)(NR'_2)\}]$. These products have been characterized and identified by usual spectroscopic techniques. Variable-temperature NMR experiments allow the detection of solution conformers of the allyl carbene complexes and the study of interconversion equilibria among different isomers. Results are interpreted and discussed in terms of restricted rotation around the $Pd-C_{carbene}$ bond, which results in preferential conformations.

Introduction

In transition-metal allyl complexes, the nature of ancillary ligands affects and sometimes promotes the reactivity of the allylic moiety in both catalytic and stoichiometric processes.[1-4] Following our interest in the synthesis and reactivity of allylic platinum(II) and palladium(II) complexes,[5,6] we have investigated the preparation of new derivatives having allyl and carbene ligands coordinated on the same metal center. The simultaneous presence of these groups on the same complex molecule might result in cooperative bonding effects leading to new reactions involving either the allyl or the carbene moieties or both. Although carbene complexes with a variety of ancillary ligands have been extensively studied,[7,8] to the

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