Inorganica Chimica Acta 362 (2009) 1333–1342

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Reactions of triphenylphosphane-substituted ethoxycarbonylcarbene-bridged dicobalt carbonyl complexes with carbon monoxide or ^{13}CO: An experimental and theoretical study

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A R T I C L E I N F O

Article history:
Received 21 April 2008
Received in revised form 23 June 2008
Accepted 23 June 2008
Available online 1 July 2008

Keywords:
Isotopic labeling
Carbene, carbonyl and phosphane ligands
Cobalt
CC coupling
Density functional calculations

A B S T R A C T

In CH_2Cl_2 solution and under a carbon monoxide atmosphere the cobalt complexes [μ_2-{ethoxycarbonyl(methylene)}-μ_2-(carbonyl)-bis(triphenylphosphanedicarbonyl-cobalt) (*Co–Co*)] (**4**) and [μ_2-{ethoxycarbonyl(methylene)}-μ_2-(carbonyl)-(tricarbonyl-cobalt)-(triphenylphosphanedicarbonyl-cobalt) (*Co–Co*)] (**3**) are in equilibrium. The equilibrium constant $K = [\mathbf{3}][PPh_3]/[\mathbf{4}][CO]$ at 10 °C is 1.03 ± 0.11. The bridging and terminal CO ligands in complex **3** or **4** exchange with external ^{13}CO simultaneously. In accord with that variable-temperature ^{13}C NMR spectra reveal fluxional behavior for both complexes. The overall rate constant of ^{13}CO-exchange for **3** at 10 °C is $17 \times 10^{-3}\ s^{-1}$ and for **4** at 10 °C is $26 \times 10^{3}\ s^{-1}$. In the case of complex **4** the concentration of PPh_3 has practically no influence on the rate of the ^{13}CO-exchange reaction and on the rate of the reaction with CO. The coupling of the μ_2-ethoxycarbonylcarbene ligand and one of the coordinated carbon monoxide is at least one order of magnitude slower than the ^{13}CO-exchange reactions, and is faster in complex **4** than in complex **3**. The partial pressure of carbon monoxide has practically no effect on the coupling reaction.

1. Introduction

Dinuclear cobalt carbonyls were found to catalyze the substitution of the diazo group of diazoalkanes with carbon monoxide [1–3] to form selectively the corresponding ketenes [4]. Ethoxycarbonylcarbene-bridged dicobalt carbonyl complexes $Co_2(CO)_7(CHCO_2Et)$ (**1**) and $Co_2(CO)_6(CHCO_2Et)_2$ (**2**) were found to be intermediates in the catalytic carbonylation of ethyl diazoacetate [1]. The observed catalytic activities decrease in the order **2** > **1.** By the addition of triphenylphosphane to these complexes the triphenylphosphane-substituted complexes $Co_2(CO)_6(CHCO_2Et)(PPh_3)$ (**3**) and $Co_2(CO)_5(CHCO_2Et)(PPh_3)_2$ (**4**) were formed [3] according to the reactions depicted in Scheme 1.

In the presence of ethanol all of the complexes in Scheme 1 were found to be suitable catalyst precursors for the carbonylation of ethyl diazoacetate to diethyl malonate [1,3]. The catalysis is assumed to involve a coordinative unsaturated species capable of the coordination of a diazoalkane. This species may be formed in two different ways according to Scheme 2: either from a coordinative saturated precursor by ligand dissociation or from an intermediate carbene complex by an intramolecular carbene–carbon monoxide coupling. It is still unclear how the reaction conditions influence the individual steps of this mechanism, and which step in the cycle is rate-determining. More information about these reactions are necessary.

In order to come closer to an understanding of the mechanism of the individual steps of the catalytic diazoalkane carbonylation, we report now kinetic and spectroscopic results about these reactions. That is, the reaction of CO or ^{13}CO with the catalyst precursor **3** and **4**, the equilibrium between **3** and **4** under carbon monoxide, and the coupling of the μ_2-ethoxycarbonylcarbene and carbon monoxide ligands in these complexes.

2. Results and discussion

Addition of triphenylphosphane to solutions of **1** in methylene chloride under an atmosphere of carbon monoxide results in gas evolution and the quantitative formation of the monotriphenylphosphane derivative **3** according to Eq. (1)

$$\underset{\mathbf{1}}{Co_2(CO)_7(CHCO_2Et)} + PPh_3 \xrightarrow[CH_2Cl_2]{10\ ^\circ C} \times \underset{\mathbf{3}}{Co_2(CO)_6(CHCO_2Et)(PPh_3)} + CO \qquad (1)$$

Solutions obtained by the reaction of equimolar **1** and triphenylphosphane show in the infrared spectra only the presence of the characteristic absorptions of complex **3** at 2080, 2033, 2013, 1829, 1688, and 1666 cm^{-1} [3]. The initial rate of gas evolution is first order in **1**, but show a complex dependence on the concentrations of

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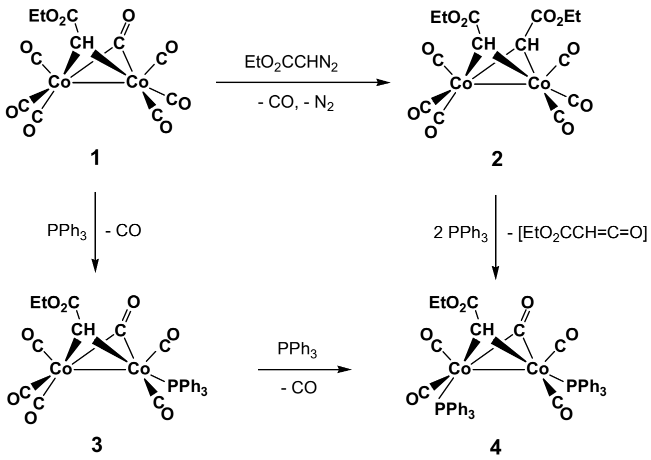
doi:10.1016/j.ica.2008.06.028



Scheme 1.

triphenylphoshane and carbon monoxide (Table 1). Assuming the steps in Scheme 3, and steady-state concentration of the intermediate $Co_2(CO)_6(CHCO_2Et)$, the rate can be described by Eq. (2) or after rearrangement by Eq. (3)

$$r = k_2[Co_2(CO)_6(CHCO_2Et)][PPh_3] = \frac{k_1k_2[Co_2(CO)_7(CHCO_2Et)][PPh_3]}{k_{-1}[CO]+k_2[PPh_3]} \tag{2}$$

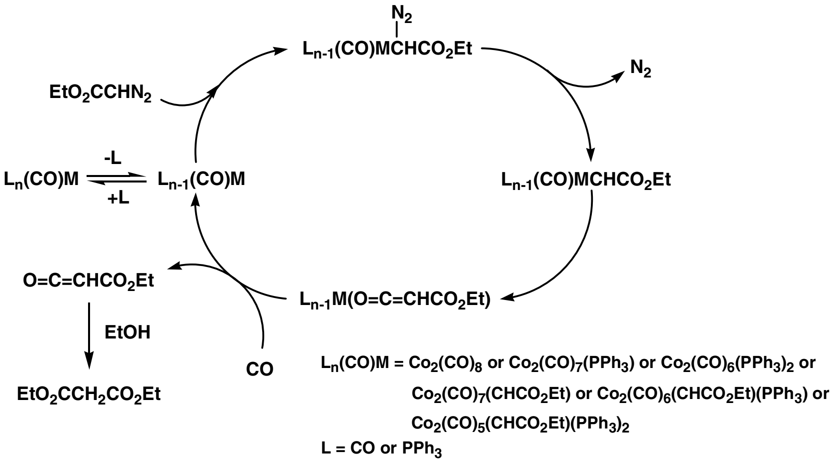
$$\frac{[Co_2(CO)_7(CHCO_2Et)]}{r} = \frac{k_{-1}}{k_1k_2}\frac{[CO]}{[PPh_3]}+\frac{1}{k_1} \tag{3}$$

A plot of $[\mathbf{1}]_0/[r_{CO}]$ against $[CO]_0/[PPh_3]_0$ using the experimental initial concentrations and the observed initial rates from Table 1 allows k_1 (10 °C) = (22 ± 2) × 10^3 s^{-1} and k_1/k_2 (10 °C) = 2724 to be calculated from the intercept and the slope, respectively (Fig. 1).

According to calculations at the B3LYP/6-31G(d) level of theory the dissociation of one of the equatorial CO ligands *cis* to the bridging ethoxycarbonylcarbene ligand in complex **1** is the most favorable to form the coordinative unsaturated $Co_2(CO)_6(CHCO_2Et)$ intermediate [8], which reacts practically irreversibly with PPh_3 to form $Co_2(CO)_6(CHCO_2Et)(PPh_3)$.

By the addition of more than equimolar amounts of triphenylphosphane to complex **1**, the infrared spectra revealed the formation of complex **4** at 2040, 2005, 1983, 1970, 1786, and 1678 cm^{-1}, beside the bands of complex **3**. The formation of **4** was incomplete even if triphenylphosphane was applied in a fivefold molar excess in methylene chloride solution and under an atmosphere of carbon monoxide. Dissolving solid complex **4** in methylene chloride under carbon monoxide give solutions which contain mixtures of **4** and **3** according to the infrared spectra. Complex **4** can be completely recovered from such solutions by removing the dissolved carbon monoxide in vacuum below 0 °C. Obviously there is an equilibrium between the complexes **4** and **3** in the presence of carbon monoxide according to Eq. (4)

$$Co_2(CO)_5(\underset{\mathbf{4}}{CHCO_2Et) + PPh_3)_2} + CO \overset{CH_2Cl_2}{\leftrightarrows} \times Co_2(CO)_6(\underset{\mathbf{3}}{CHCO_2Et)(PPh_3)} + PPh_3 \tag{4}$$



Scheme 2.

Table 1

The effect of initial concentrations of $Co_2(CO)_7(CHCO_2Et)$ (**1**), PPh_3, and CO on the initial rate of CO evolution (r_{CO}) in the reaction: $Co_2(CO)_7(CHCO_2Et) + PPh_3 \rightarrow Co_2(CO)_6(CHCO_2Et)(PPh_3) + CO$ at 10 °C in methylene chloride solution

$[\mathbf{1}]_0 \times 10^3$ (mol/dm^3)	$[PPh_3]_0 \times 10^3$ (mol/dm^3)	$[CO]$[a] $\times 10^3$ (mol/dm^3)	$r_{CO} \times 10^5$ (mol/dm^3 s)
10.0	10.0	5.19	12.6
8.6	8.6	5.10	10.9
8.6	8.0	5.06	10.2
10.0	5.0	5.19	9.1
5.0	20.0	5.19	8.4
5.0	10.0	5.19	6.4
5.0	5.0	5.19	5.1
2.5	5.0	5.19	2.3
5.0	10.0	[b]	9.7
5.0	5.0	[b]	6.1
5.0	2.5	[b]	4.8

[a] Calculated from the partial pressure of CO and the known solubility of CO in CH_2Cl_2 (see Refs. [6,7]).

[b] Reaction was started under argon.