



# Mechanism of the cobalt-catalyzed carbonylation of ethyl diazoacetate

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Dedicated to Professor László Markó on the occasion of his 80th birthday.

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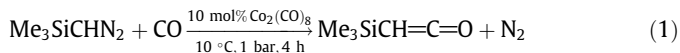
## ABSTRACT

Carbonyl cobalt complexes serve as catalysts or catalyst precursors for the facile and selective transformation of primary diazoalkanes into the corresponding ketene. The mechanism of this carbonylation reaction has been elucidated in the case of ethyl diazoacetate as model diazoalkane using octacarbonyl dicobalt as the catalyst precursor. Dinuclear cobalt complexes having ethoxycarbonylcarbene ligand(s) in bridging position(s) have been identified as active intermediary of the catalytic cycles and their relevant chemical properties have been explored. Key step of the carbonylation is the formation of the highly reactive ethoxycarbonylketene by intramolecular coupling of a carbonyl ligand with the ethoxycarbonylcarbene ligand. DFT calculations reveal that the ketene formation takes place via a rapid coupling of the carbene ligand with one terminal CO followed by coordination of an external carbon monoxide and by a facile intramolecular rearrangement and ketene elimination. The ethoxycarbonylketene can be *in situ* trapped by OH, NH, or CH acid compounds or by *N*-substituted imines. In the presence of ethanol diethyl malonate is the only product of the catalytic carbonylation of ethyl diazoacetate. On the bases of the kinetics of the composing steps of the catalytic cycles, localization of the rate-determining step(s) under various reaction conditions has been made.

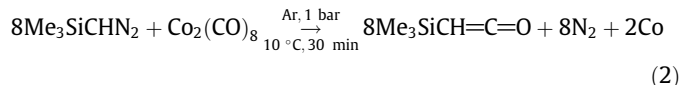
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## 1. Introduction

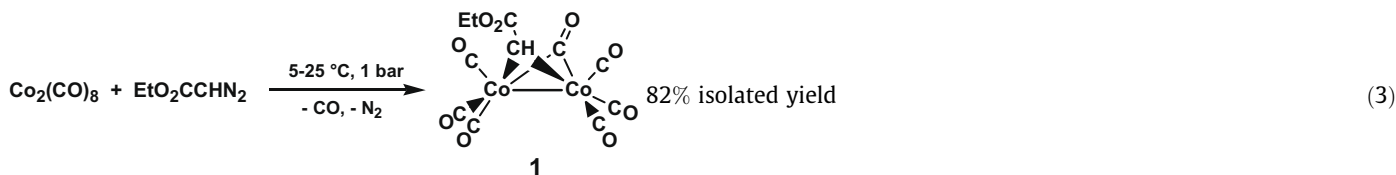
Octacarbonyl dicobalt was found to be an effective dediazotation reagent for (trimethylsilyl)diazomethane [1] or ethyl diazoacetate [2]. In the dediazotation reaction of (trimethylsilyl)diazomethane with  $\text{Co}_2(\text{CO})_8$  (trimethylsilyl)ketene is formed selectively either under catalytic (reaction 1) or under stoichiometric (reaction 2) reaction conditions. In the presence of 10 mol%  $\text{Co}_2(\text{CO})_8$  solutions of (trimethylsilyl)diazomethane in *n*-heptane are selectively carbonylated at 10 °C under an atmosphere of carbon monoxide to (trimethylsilyl)ketene in up to 80% isolated yield (reaction 1).



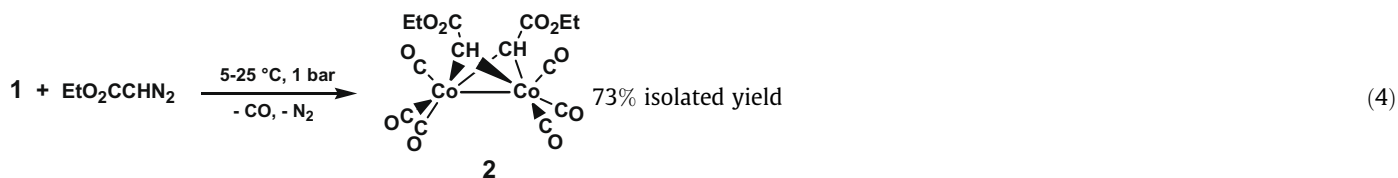
In the absence of external carbon monoxide the coordinated carbon monoxide ligands of octacarbonyl dicobalt are consumed in the (trimethylsilyl)ketene formation (reaction 2).



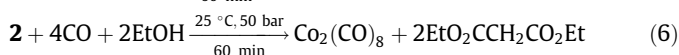
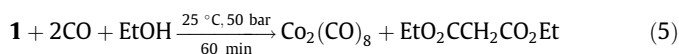
No intermediary cobalt complexes were detected by infrared spectroscopy in reactions 1 and 2. Ethyl diazoacetate behaves differently in the dediazotation reaction. At ambient conditions ethoxycarbonylcarbene-bridged dicobalt carbonyl complexes **1** and **2** were isolated from the reaction mixtures in good yields (reactions 3 and 4). Under an atmosphere of carbon monoxide the ethoxycarbonylcar-



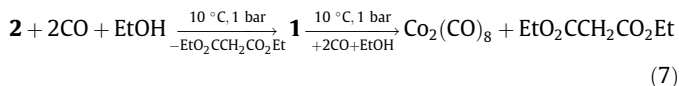
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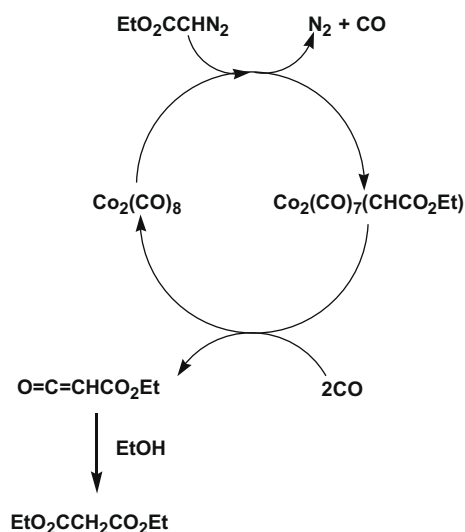
benzene ligand(s) of these complexes couple(s) with CO to give the highly reactive ethoxycarbonylketene, which can not be isolated but can be scavenged *in situ* by OH, NH, or CH acid compounds [2,3] or by *N*-substituted imines in a [2 + 2] cycloaddition reaction [4]. In the presence of ethanol both complexes **1** and **2** convert quantitatively to  $\text{Co}_2(\text{CO})_8$  and diethyl malonate (reactions 5 and 6).



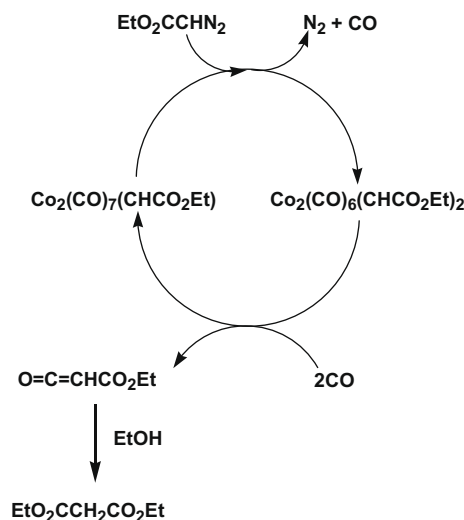
Experiments at atmospheric pressure of carbon monoxide have shown that complex **2** converts first rapidly to **1** and diethyl malonate, and in a much slower reaction complex **1** converts further to octacarbonyl dicobalt and to a second mol of diethyl malonate (Eq. (7)).



In both steps the formation of the highly reactive ethoxycarbonylketene was assumed by coupling of the ethoxycarbonylcarbene ligand with one of the coordinated carbon monoxide [2]. The combination of reactions 3–6 led to an effective one-pot procedure for the preparation of diethyl malonate by catalytic carbonylation of ethyl diazoacetate in the presence of a few mol% of octacarbonyl dicobalt [2]. Since diethyl malonate may be the product from both complex **1** and **2** two different catalytic cycles can be imagined depicted in Schemes 1 and 2.



Scheme 1.



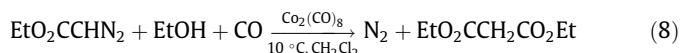
Scheme 2.

Triphenylphosphane- or  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ -substituted derivatives of complex **1** were found to show similar catalytic activity in ethyl diazoacetate carbonylation as  $\text{Co}_2(\text{CO})_8$ , or complexes **1** or **2** [5–7].

In order to obtain a more detailed mechanism of the catalytic dediazotation and carbonylation of ethyl diazoacetate we investigated the kinetics of the catalytic reaction and the kinetics of the reactions in Schemes 1 and 2 at 10 °C in methylene chloride solutions.

## 2. Results

### 2.1. Experiments using $\text{Co}_2(\text{CO})_8$ as the catalyst precursor



The effect of the concentrations of  $\text{Co}_2(\text{CO})_8$ , ethyl diazoacetate, ethanol, and carbon monoxide on the rate of diethyl malonate formation in the catalytic carbonylation of ethyl diazoacetate (Eq. (8)) was studied in experiments performed between 1 and 100 bar pressure of carbon monoxide with various initial concentrations at 10 °C in  $\text{CH}_2\text{Cl}_2$  solutions using 3 h reaction time (Table 1). The data in Table 1 show that under atmospheric pressure of carbon monoxide ( $[\text{CO}] = 0.00507\text{--}0.00515\text{ mol/dm}^3$ ) the rate of diethyl malonate formation is practically linear with the initial concentrations of  $\text{Co}_2(\text{CO})_8$  and that of ethyl diazoacetate, and independent of the ethanol concentrations (entries 1–15). The carbon monoxide concentration has a strong positive effect on the rate in the range between 0.005 and 0.03  $\text{mol/dm}^3$  (compare entries 1–15 with that of entries 16 and 17). On the other hand the carbon monoxide concentration has a little negative effect on the rate in the range between 0.44 and 1.12  $\text{mol/dm}^3$  (entries 29–33).

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