THESIS OF THE PhD DISSERTATION

INVESTIGATION OF SOME ONE- AND TWO-ELECTRON REACTIONS OF OCTACARBONYL DICOBALT ON NEW MODELS

RÓBERT TUBA

Supervisor
DR. FERENC UNGVÁRY
Professor of Chemistry

University of Veszprém
Department of Organic Chemistry

2002

I. PRELIMINARIES, AIMS OF THE WORK

Octacarbonyl dicobalt is a precursor in many important catalytic and stoichiometric reactions used in organic synthesis. The activation of the various substrates and reagents in those reactions usually happens in more or less established one- and two-electron reactions of tetracarbonylcobalt radical and heptacarbonyl dikobalt, which complexes are formed in low equilibrium concentrations by dissociation of the cobalt-cobalt bond and by dissociation of a carbon monoxide ligand, respectively:

$$2\ \bullet Co(CO)_4 \rightleftharpoons Co_2(CO)_8 \rightleftharpoons Co_2(CO)_7 + CO$$

In order to learn more about the chemistry of these complexes we made experiments to scavenge the tetracarbonylcobalt radical from solutions of octacarbonyl dicobalt using different stable organic free radicals. In addition of the characterization of the new products and the stoichiometry of the reactions we studied the kinetics as well in order to elucidate a possible mechanism. On the other hand we tried to activate the known carbene precursor ethyl diazoacetate in solutions of octacarbonyl dicobalt to generate new cobalt carbene complexes and find new synthetic applications.

II. EXPERIMENTAL METHODS

Handling of the complexes was carried out under an atmosphere of dry and deoxygenated argon or carbon monoxide utilizing standard Schlenk techniques[1]. Solvents were dried and distilled under an atmosphere of argon or carbon monoxide according to standard procedures.

The products and the stoichiometry of the reactions were determined by using standard gasometric and various analytical methods (C,H,N,Co analysis, IR, multinuclear NMR, GC, GC-MS, single-crystal X-ray diffraction).

The products were isolated by established preparative methods. In the case of the new dinuclear cobalt carbene complexes, a low temperature column chromatographic method for the separation of air- and heat-sensitive compounds was developed.

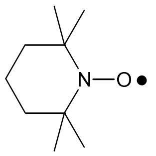
The kinetics of the reactions accompanied by gas evolution or gas absorption were studied by using a gasometric apparatus.

---

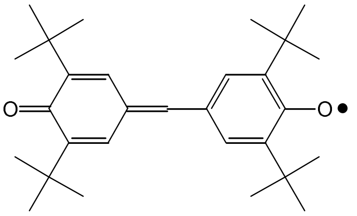
[1] D. F. Shriver, *The manipulation of Air-sensitive Compounds*, R. E. Krieger Publ. Co.: Malabar, Florida. (1982).

III. NEW SCIENTIFIC RESULTS

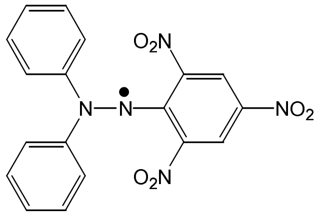
1. It was found that octacarbonyl dicobalt reacts smoothly at ambient conditions with 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), Galvinoxyl (G·) and 2,2-diphenyl-picryl-hydrazyl free radicals. These reactions lead to carbon monoxide evolution and to different type of cobalt compounds depending on the applied free radical. It was established that the reactions took place in different manner based on their kinetic behaviour.



2,2,6,6-tetramethyl-1-piperidinyloxy (Tempo)



galvinoxyl (G•)



2,2-diphenyl-picryl-hydrazyl (P•)

1.1. The complex formed from octacarbonyl dicobalt and TEMPO is $(TEMPO)Co(CO)_2$. The initial rate of carbon monoxide evolution is first order in TEMPO, 0.5 order in octacarbonyl dicobalt, and negative 0.5 order in carbon monoxide. The most probable mechanism in accord with the observed kinetics is the following:

$$Co_2(CO)_8 \xrightleftharpoons[\text{fast}]{K_1} Co_2(CO)_7 + CO$$

$$Co_2(CO)_7 \xrightleftharpoons[\text{fast}]{K_2} \bullet Co(CO)_3 + \bullet Co(CO)_4$$

$$\text{TEMPO} + \bullet Co(CO)_3 \xrightarrow[\text{slow}]{k_1} (\text{TEMPO})Co(CO)_3$$

$$\text{TEMPO} + \bullet Co(CO)_4 \xrightarrow[\text{slow}]{k_2} (\text{TEMPO})Co(CO)_3 + CO$$

$$(\text{TEMPO})Co(CO)_3 \xrightarrow[\text{fast}]{k_3} (\text{TEMPO})Co(CO)_2 + CO$$

$k_I(15\ ^{\circ}C)$ **$=6{,}99 \pm 0{,}36\ 10^{-6}\ s^{-1}$**

1.2. In the reaction of octacarbonyl dicobalt and Galvinoxyl a new complex, $Co(II)G_2$ (where G is the anion formed from Galvinoxyl by a one-electron uptake) is formed. The initial rate of carbon monoxide evolution is first order in both dicobalt octacarbonyl and Galvinoxyl and is independent of the carbon monoxide concentration. The mechanism below is in accord with the observed kinetics:

$$\mathrm{Co_2(CO)_8} \underset{\text{fast}}{\overset{K_1}{\rightleftharpoons}} \mathrm{Co_2(CO)_7} + \mathrm{CO}$$

$$\mathrm{Co_2(CO)_7} + \cdot\mathrm{G} \underset{\text{fast}}{\overset{K_2}{\rightleftharpoons}} \mathrm{Co_2(CO)_7G}\cdot$$

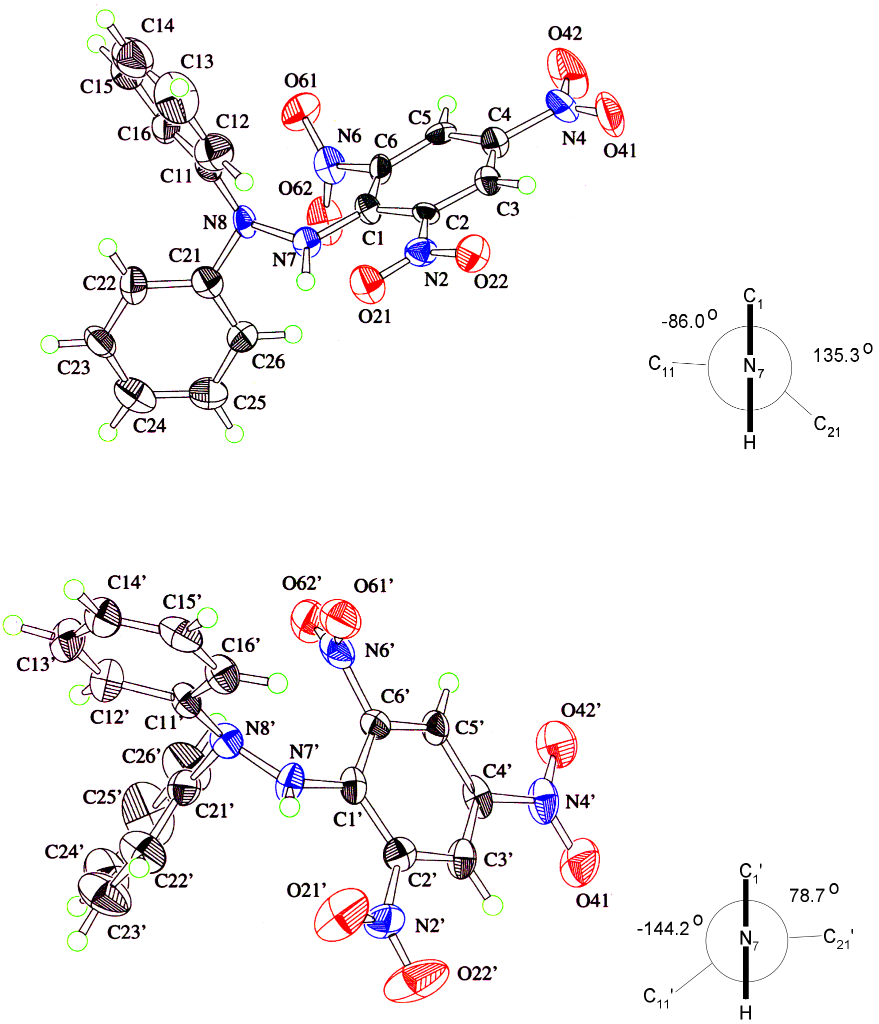
$$\mathrm{Co_2(CO)_7G}\cdot + \mathrm{CO} \xrightarrow[\text{slow}]{k_1} \mathrm{GCo(CO)_4} + \cdot\mathrm{Co(CO)_4}$$

$$\mathrm{GCo(CO)_4} \xrightarrow[\text{fast}]{k_2} \mathrm{CoG} + 4\ \mathrm{CO}$$

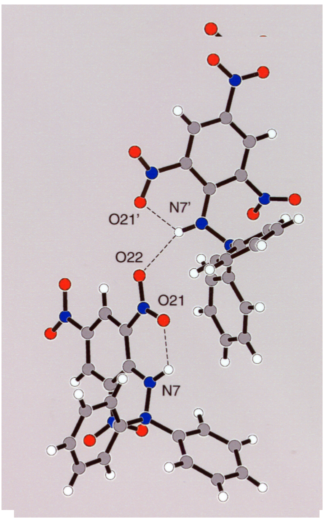
$$\mathrm{CoG} + \cdot\mathrm{G} \xrightarrow[\text{fast}]{k_3} \mathrm{CoG_2}$$

k_I(15 °C) **=1,03±0,07 $M^{-1}s^{-1}$**

1.3. In the reaction of octacarbonyl dicobalt and 2,2-diphenyl-picryl-hydrazyl free radical along with carbon monoxide evolution cobalt(II) hydroxide is formed. From the reaction mixture a new crystal modification of 2,2-diphenyl-picryl-hydrazine was isolated and identified by single crystal röntgen diffraction analysis:



X-Ray strucures of the 2,2-diphenyl-picryl-hydrazyne conformers



Hydrogen bonding between the 2,2-diphenyl-picryl-hydrazyne conformers

The initial rate of carbon monoxide evolution is first order in 2,2-diphenyl-picryl-hydrazyl free radical, 0.5 order in octacarbonyl dicobalt, and is independent of the carbon monoxide concentration. A mechanism with a rate-determining reaction between tetracarbonyl cobalt and the 2,2-diphenyl-picryl-hydrazyl free radical is in accord with the observed kinetics:

$$Co_2(CO)_8 \underset{\text{fast}}{\overset{K_1}{\rightleftharpoons}} 2\ {\cdot}Co(CO)_4$$

$$\cdot\,Co(CO)_4 + P\cdot \xrightarrow[\text{slow}]{k_1} PCo(CO)_4$$

$$PCo(CO)_4 \xrightarrow[\text{fast}]{k_2} CoP + 4\ CO$$

$$CoP + \cdot P \xrightarrow[\text{fast}]{k_3} CoP_2$$

$$CoP_2 + 2\,H_2O \xrightarrow[\text{fast}]{k_4} Co(OH)_2 + 2\,PH$$

k_I(15 °C) **=0,11±0,0075 $M^{-1/2}s^{-1}$**

2. The reaction of octacarbonyl dicobalt with ethyl diazoacetate at room temperature and atmospheric pressure of carbon monoxide results in new one- and two-carbene-bridged cobalt complexes along with the release of carbon monoxide and nitrogen. The new complexes were separated and isolated by column chromatography.

2.1. By mixing an equimolar amount of ethyl diazoacetate with solutions of octacarbonyl dicobalt in *n*-octane at room temperature under atmospheric pressure of carbon monoxide results according to the equation in evolution of 2 mole of a 1:1 mixture of carbon monoxide and dinitrogen (checked by a gas burette and gas-chromatography), and the formation of an orange-red solution, from which an orange colored cobalt complex with the composition of $Co_2(CO)_7(CHCO_2Et)$ (**1**) was isolated by column chromatography at 0 °C under an argon atmosphere in 82% yield as an oil.

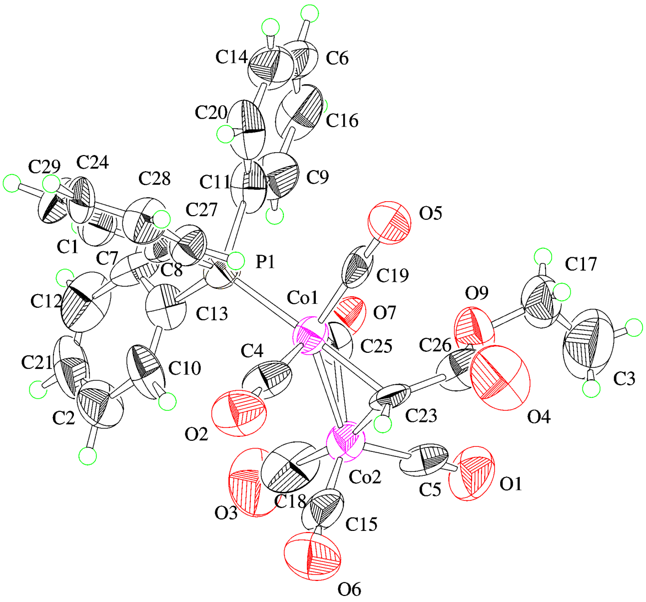
$$Co_2(CO)_8 + N_2CHCO_2Et \longrightarrow Co_2(CO)_7(CHCO_2Et) + CO + N_2$$

1

2.1.1 The reaction of complex **1** and triphenyl phosphine in a 1:1 molar ratio results in crystalline $Co_2(CO)_6(CHCO_2Et)(PPh_3)$ (**3**). Single crystal röntgen diffraction analyses has shown that the carbene ligand in complex **3** is in bridging position.The triphenyl phosphine is in opposite direction from the carbene carbon; the P_1, Co_1 and C_{23} atoms are practically along a straight line.

$$Co_2(CO)_7(CHCO_2Et) + PPh_3 \longrightarrow Co_2(CO)_6(CHCO_2Et)(PPh_3) + CO$$

1 **3**



X-Ray strucure of the complex **3**

2.1.2. One mole of carbon monoxide has been replaced in complex **3** by adding triphenyl phosphine to solutions of complex **3**. A solid copmlex $Co_2(CO)_5(CHCO_2Et)(PPh_3)_2$ (**4**) was isolated from the reaction mixture. Based on the spectroscopic properties of this complex, a carbene and a carbon monoxide ligand are in bridging position, and to each cobalt belongs a triphenyl phosphine in terminal position.

$$Co_2(CO)_6(CHCO_2Et)(PPh_3) + PPh_3 \longrightarrow Co_2(CO)_5(CHCO_2Et)(PPh_3)_2 + CO$$

3 **4**

2.2. Using a 2:1 molar ratio of ethyl diazoacetate and $Co_2(CO)_8$ in the reaction the evolution of 4 mole of a 1:1 mixture of carbon monoxide and dinitrogen and the formation of an orange-yellow colored complex was observed according to the equation. From the reaction mixture a yellow oil with a composition of $Co_2(CO)_6(CHCO_2Et)_2$ (**2**) was isolated in 73% yield by column chromatography at 0 °C under an argon atmosphere.

$$Co_2(CO)_8 + 2\ N_2CHCO_2Et \longrightarrow Co_2(CO)_6(CHCO_2Et)_2 + 2\ CO + 2\ N_2$$

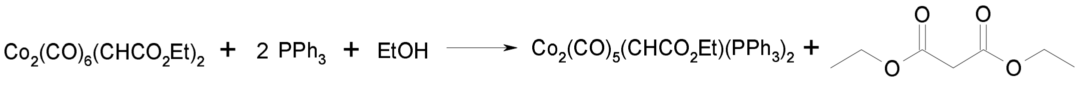
2

Spectroscopic evidences suggest that both carbene ligands in complex **2** are in bridging position, and the complex show dynamic properties according to the reversible reaction below:

$$Co_2(CO)_6(CHCO_2Et)_2 \rightleftharpoons Co_2(CO)_5(O{=}C{=}CHCO_2Et)(CHCO_2Et)$$

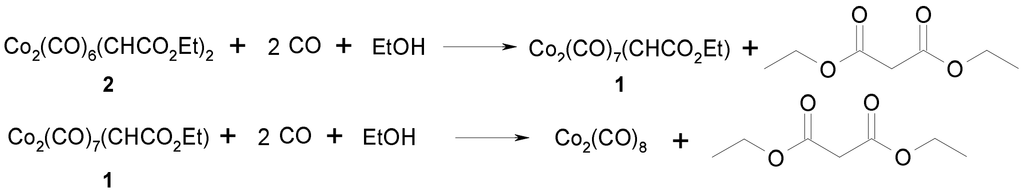
2

2.2.1. In the reaction of complex **2** with triphenyl phosphine complex **4** is formed. In the presence of ethanol, however, diethyl malonate is an additional product of the reaction. The formation of diethyl malonate can be rationalized by assuming the reaction of an ethoxycarbonylketene intermediate with ethanol.



2 **4**

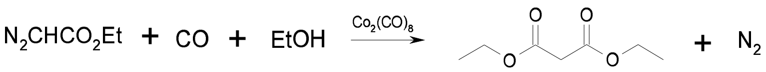
2.3. Under carbon monoxide both complex **1** and **2** are converted quantitatively to $Co_2(CO)_8$. In the presence of ethanol the $Co_2(CO)_8$ formation proceeds with the quantitative formation of diethyl malonate according to the equations below. Here again an intermediate keten-formation can be assumed by a dynamic coupling of the carbene ligand(s) with carbon monoxide, and the scavenging of the ethoxycarbonyl ketene by ethanol to form diethyl malonate.



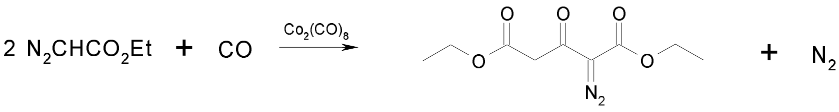
2 **1**

1

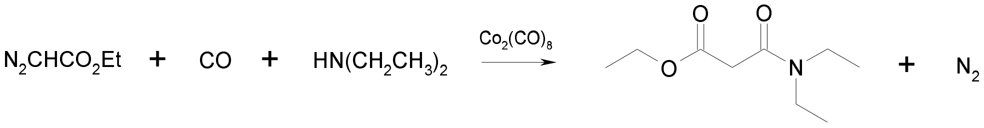
2.4. In the presence of catalytic amounts of octacarbonyl dicobalt and at least equimolar amounts of ethanol ethyl diazoacetate and carbon monoxide converts into diethyl malonate.



2.5. Ethyl diazoacetate dissolved in saturated hydrocarbons under atmospheric pressure of carbon monoxide decomposes at room temperature in the presence of 1 mol% $Co_2(CO)_8$. Repeating the experiment but under 50 bar carbon monoxide pressure a complete conversion of ethyl diazoacetate into diethyl 2-diazo-3-oxo-pentanedicarboxylate was found in 1 day in accord with the depicted equation:

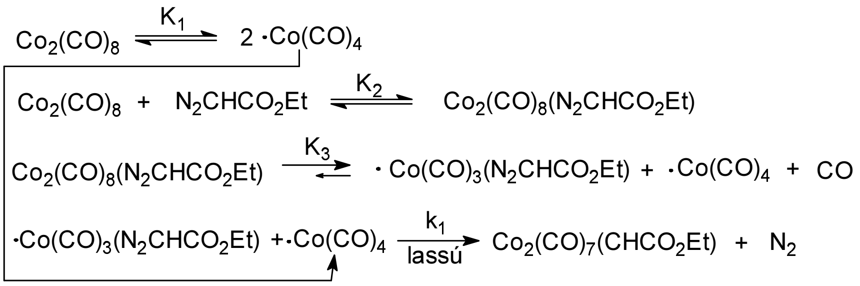


2.6. Octacarbonyl dicobalt was found to catalyze the conversion of ethyl diazoacetate and carbon monoxide in the presence of diethylamine into $EtO_2CCH_2C(O)NEt_2$. The formation of this product can be explained by the scavenging of the ethoxycarbonylketene intermediate by diethylamine.



2.7. The initial rate of the gas evolution in the reaction of ethyl diazoacetate and octacarbonyl dicobalt is first order in octacarbonyl dicobalt, 0.5 order in ethyl diazoacetate, and negative 0.5 order in carbon monoxide. In analogy to the suggested mechanism[2] of the reaction of octacarbonyl dicobalt and tributylphosphine by T. L. Brown, a sequence of reactions below is in accord with the observed kinetics:

N. P. Forbus, R. Oteiza, S. G. Smith, T. L. Brown, *J. Organomet. Chem.* **193** (1980) C71-C74.



$$Co_2(CO)_8 \underset{}{\overset{K_1}{\rightleftharpoons}} 2\ \cdot Co(CO)_4$$

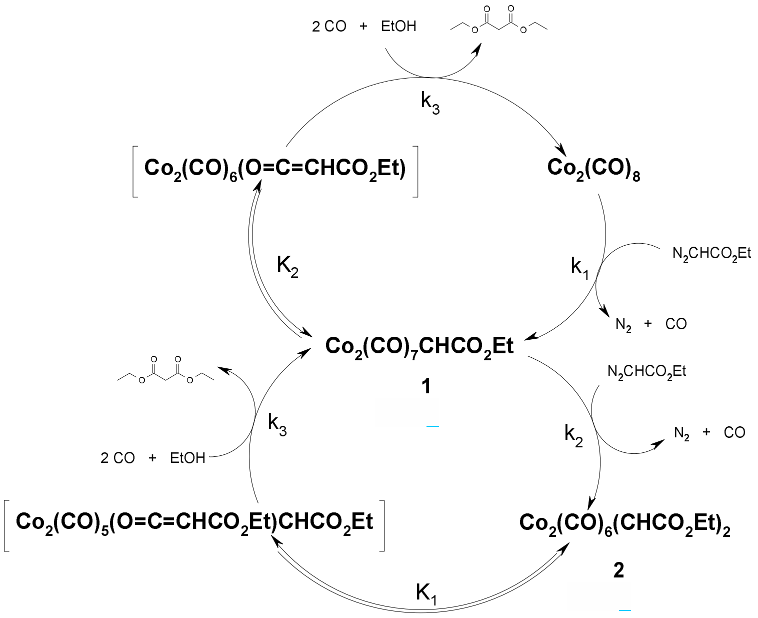
$$Co_2(CO)_8 + N_2CHCO_2Et \overset{K_2}{\rightleftharpoons} Co_2(CO)_8(N_2CHCO_2Et)$$

$$Co_2(CO)_8(N_2CHCO_2Et) \overset{K_3}{\rightleftharpoons} \cdot Co(CO)_3(N_2CHCO_2Et) + \cdot Co(CO)_4 + CO$$

$$\cdot Co(CO)_3(N_2CHCO_2Et) + \cdot Co(CO)_4 \xrightarrow[\text{lassú}]{k_1} Co_2(CO)_7(CHCO_2Et) + N_2$$

k_I(10 °C) = **(4,03 ± 0,23) 10^{-4} s^{-1}**

2.8. Based on the observed intermediates **1** and **2** and their reactions with ethanol, the catalytic formation of diethyl malonate in the cobalt-mediated decomposition of ethyl diazoacetate is depicted in this Scheme:



Proposed catalytic cycle of diethyl malonate formation

From the two possible catalytic cycle the second one seems to be the dominant at low partial pressure of carbon monoxide based on the observation that complex **2** reacts much faster with ethanol than complex **1**.

IV. SIGNIFICANCE OF SCIENTIFIC RESULTS

The established new reactions of octacarbonyl dicobalt with stable organic free radicals and with ethyl diazoacetate support the idea that in solutions of octacarbonyl dicobalt tetracarbonylcobalt radical and heptacarbonyl dicobalt are indeed the reactive intermediates.

Among the new cobalt complexes prepared, the ethoxycarbonylcarbene-bridged docobalt carbonyl complexes [μ_2-{ethoxycarbonyl(methylene)}-μ_2-(carbonyl)-bis(tricarbonyl-cobalt)(*Co*-*Co*)] and [di-μ_2-{ethoxycarbonyl(methylene)}-bis(tricarbonyl-cobalt)(*Co*-*Co*)] show a high reactivity towards carbon monoxide. Most probably by combination of the ethoxycarbonylcarbene and the carbon monoxide ligands in the coordination sphere of cobalt, an ethoxycarbonylketene intermediate is formed, which give with ethanol or diethylamine the corresponding malonic acid derivatives. The understanding of these stoichiometric reactions paved the road to successfull catalytic applications with significant synthetic value. In the presence of 1 mol% octacarbonyl dicobalt ethyl diazoacetate can be transformed at room temperature and carbon monoxide pressure selectively into diethyl 2-diazo-3-oxo-pentanedicarboxylate or in the presence of ethanol or diethylamine into the corresponding malonic acid derivatives in up to 99% yield.

The unprecedented high reactivity of the cobalt intermediates in the deduced carbene-carbon monoxide coupling reaction may serve as a starting point for considering it as a possible C-C bond forming step in the Fischer-Tropsch reaction and in the alcohol homologation reaction.

SCIENTIFIC PUBLICATIONS AND PRESENTATIONS RELATED TO THE THESIS

PUBLICATIONS

1. R. Tuba, F. Szeifert, F. Ungváry
Kinetic Investigation of the Reaction of Octacarbonyl Dicobalt with 2,2,6,6-Tetramethylpiperidin-1-oxyl
J. Clust. Sci. **9** (1998) 289-294

2. R. Tuba, F. Ungváry
Reaction of octacarbonyldicobalt with the free radicals galvinoxyl and 2,2-diphenyl-1-picrylhydrazyl. Attempts to scavenge the tetracarbonylcobalt radical
Inorg. Chim. Acta. **334** (2002) 308-312

3. R. Tuba, F. Ungváry
Octacarbonyl dicobalt-catalyzed selective transformation of ethyl diazoacetate into organic products containing the ethoxycarbonyl carbene building block
J. Mol. Cat. (accepted for publication)

PRESENTATION

4. M. G. Newton, J. P. Rose, B.-C. Wang, Z.-J. Liub, R. Tuba, F. Ungváry
A New Crystal Modification for Diphenylpicrylhydrazine
XVIIIth IUC Congress and General Assembly, Glasgow, Scotland, Aug 4-13, 1999. Book of Abstracts p. 391. P06.06.017XIV.

FURTHER SCIENTIFIC PUBLICATIONS

5. R. Tuba, L. T. Mika, A. Bodor, Z. Pusztai, I. Tóth, I. T. Horváth
The Mechanism of the Pyridine Modified Cobalt-Catalyzed Hydromethoxycarbonylation of 1,3-Butadiene
Organometallics (accepted for publication)

6. R. Tuba
Combinatorial Catalysis - Homogeneous
Encyclopedia of Catalysis (ed. IT Horvath) Vol. 2. p. 644-699, Wiley, New York (2002)
http://www.mrw.interscience.wiley.com

7. Sz. Csihony, H. Mehdi, R. Tuba, L.T. Mika, I.T. Horváth,
Reaction Monitoring in Conventional Green solvents by ReactIR
Green Solvents For Catalysis, Bruchsal, Germany, Oct 13-16, 2002. Book of Abstract, p. 50.

8. R. Tuba, L. T. Mika, A. Bodor, Z. Pusztai, I. Tóth, I. T. Horváth
The Mechanism of the Pyridine Modified Cobalt-Catalyzed Hydromethoxycarbonylation of 1,3-Butadiene
Symposium on green chemistry in Hungary 2nd management committee meeting of cost action D29, Budapest, Hungary, Dec 13-14, (2002)

9. R. Tuba, L. T. Mika, A. Bodor, Z. Pusztai, I. Tóth, I. T. Horváth
The Mechanism of the Pyridine Modified Cobalt-Catalyzed Hydromethoxycarbonylation of 1,3-Butadiene
6th International Symphosium on Catalysis Applied to Fine Chemicals, Delft, The Netherlands, April 6-10, (2003)