



Octacarbonyl dicobalt-catalyzed selective transformation of ethyl diazoacetate into organic products containing the ethoxycarbonyl carbene building block

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Abstract

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 an alcohol (methanol, ethanol, *tert*-butanol), phenol or diethylamine into the corresponding malonic acid derivatives in high yields. Ethoxycarbonyl-carbene-bridged dicobalt 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)] proved to be intermediates in the catalytic reactions.

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1. Introduction

Transition metal compounds are effective catalysts of carbene transfer reactions using diazoalkane precursors [1,2] leading to carbenes and metal carbene complexes [3–5], which are useful reagents in various reactions, such as olefin cyclopropanation, olefin metathesis, carbon–carbon double-bond formation, insertion and rearrangement reactions [6–8]. The role of the transition metal compounds in influencing the selectivity of these reactions is still not clear. We found a selective octacarbonyl dicobalt-catalyzed carbene carbon monoxide coupling reaction using

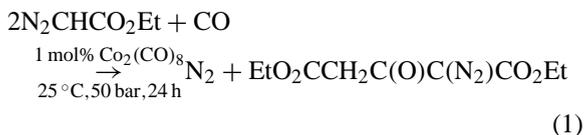
ethyl diazoacetate as the carbene precursor, which can be applied for high yield catalytic syntheses of 2-diazo-3-oxoglutarate or malonic acid derivatives.

2. Results

Ethyl diazoacetate dissolved in saturated hydrocarbons under atmospheric pressure of carbon monoxide loses dinitrogen at room temperature in the presence of 1 mol% $\text{Co}_2(\text{CO})_8$. Starting with a 1.3 molar solution of ethyl diazoacetate, a ca. 50% conversion was obtained in 2 days according to the infrared spectrum of the reaction mixture following the drop in intensity of the characteristic band of ethyl diazoacetate at 2112 cm^{-1} . At the same time, four new very strong absorptions appeared in the carbonyl stretching region

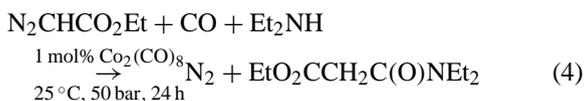
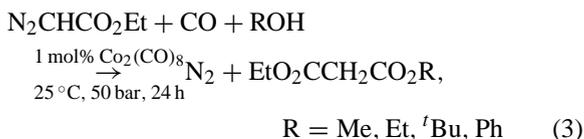
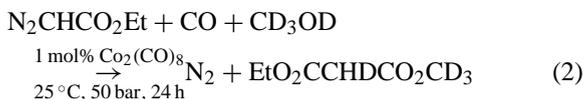
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at 2137, 1749, 1724 and 1672 cm^{-1} . Repeating the experiment but under 50 bar carbon monoxide pressure, a complete conversion of ethyl diazoacetate was found in 1 day in accord with Eq. (1).



At the end of the reaction, the IR spectrum of the reaction solution showed in addition to the four very strong bands the presence of the characteristic bands of $\text{Co}_2(\text{CO})_8$ at 2069, 2044, 2024, 1866, and 1857 cm^{-1} . GLC analysis of the gas phase showed that 52% of the total nitrogen of the starting ethyl diazoacetate was found to be in the form of dinitrogen. The work up [10] of the solution gave the known compound diethyl 2-diazo-3-oxoglutarate [9] in 91% isolated yield as a pale yellow oil, which was unequivocally identified by elemental analysis and by ^1H and ^{13}C NMR spectra.

Completely different results were obtained in the above experiments, if they were performed in the presence of an equimolar amount of additional reagents such as methanol, ethanol, *tert*-butanol, phenol or diethyl amine. Using these reagents, the selective formation of the corresponding malonate derivatives were achieved in accord with Eqs. (2)–(4). The ethyl malonate derivatives were isolated from the reaction mixtures by flash chromatography on silica gel in up to 95% yields. The identity of these products was checked by ^1H , ^2H , and ^{13}C NMR spectroscopy and GC–MS spectroscopy.



From a comparison of the yields of diethyl malonate at a given reaction time in experiments with different

Table 1

The effect of concentrations of $\text{Co}_2(\text{CO})_8$, ethanol, and CO on the formation of diethyl malonate (DEM) in the $\text{Co}_2(\text{CO})_8$ -catalyzed reaction of ethyl diazoacetate (EDA), ethanol and carbon monoxide at 25 °C in *n*-octane solution using 3 h reaction time

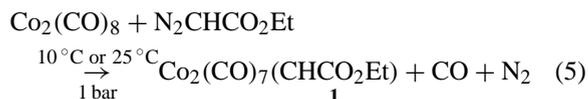
$[\text{Co}_2(\text{CO})_8]$ (mol/dm ³)	[EDA] (mol/dm ³)	[EtOH] (mol/dm ³)	P_{CO} (bar)	DEM ^a (mol/dm ³)
0.14	1.45	0.00	1.0	0.00
0.14	1.45	0.49	1.0	0.43
0.14	1.45	0.97	1.0	0.57
0.14	1.45	1.94	1.0	0.54
0.14	1.45	2.92	1.0	0.55
0.14	1.45	4.97	1.0	0.54
0.095	1.45	2.92	1.0	0.40
0.045	1.45	2.92	1.0	0.18
0.017	1.45	2.92	1.0	0.07
0.14	1.45	2.92	3.0	0.81
0.14	1.45	2.92	3.7	1.06
0.14	1.45	2.92	6.5	1.37
0.14	1.45	2.92	11.5	1.34
0.14	1.45	2.92	16.0	1.11
0.14	1.45	2.92	23.0	0.85

^a The concentration of diethyl malonate [DEM] was determined by quantitative IR analysis using the molar absorbance of diethyl malonate $\epsilon_{\text{M}} = 843 \text{ cm}^2 \text{ mol}^{-1}$ at 1747 cm^{-1} , and double checked by quantitative GLC analysis using *n*-nonane as the internal standard.

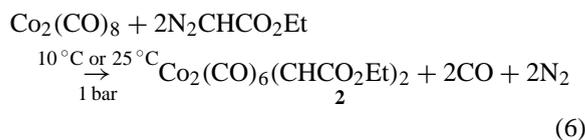
concentrations of the reactants (Table 1), it could be deduced that the rate of diethyl malonate formation is proportional with the concentration of the $\text{Co}_2(\text{CO})_8$ precatalyst, does not depend on the concentration of ethanol above a 2:1 molar ratio, and is in a complex manner dependent on the applied carbon monoxide pressure in the experiment. Although the reaction proceeds nearly to completion using 0.49 mol/dm³ ethanol and 0.14 mol/dm³ $\text{Co}_2(\text{CO})_8$ concentrations and excess ethyl diazoacetate (Entry 2), for preparative purposes, however, an equimolar ethyl diazoacetate:alcohol ratio, higher than atmospheric pressure of CO, and 1 mol% $\text{Co}_2(\text{CO})_8$ catalyst provide the best practical conditions for the isolation of the reaction product (see the examples in the Section 4).

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 Eq. (5) in evolution of 2 mol of a 1:1 mixture of carbon monoxide and dinitrogen (checked by a gas burette and gas-chromatography). At the end of the gas evolution, an orange colored cobalt complex with

the composition of $\text{Co}_2(\text{CO})_7(\text{CHCO}_2\text{Et})$ (**1**) was isolated by column chromatography at 1°C under an argon atmosphere in 82% yield as an oil. The infrared spectrum of this compound in hexane solution showed characteristic bands in the carbonyl stretching range at 2112w, 2074s, 2056m, 2047s, 2042s, 1873m, 1866m, 1854m, 1704w, and 1693w cm^{-1} .

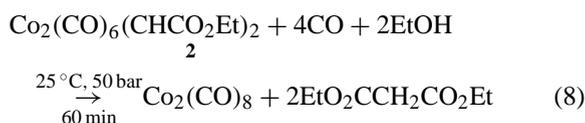
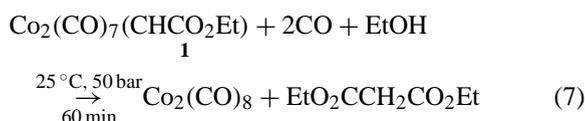


Using a 2:1 molar ratio of ethyl diazoacetate and $\text{Co}_2(\text{CO})_8$ in the above preparation the evolution of 4 mol of a 1:1 mixture of carbon monoxide and dinitrogen and the formation of an orange–yellow colored complex was observed according to Eq. (6). From the reaction mixture, a yellow oil with a composition of $\text{Co}_2(\text{CO})_6(\text{CHCO}_2\text{Et})_2$ (**2**) was isolated in 73% yield by column chromatography at 0°C under an argon atmosphere. The infrared spectrum of this compound in hexane solution showed characteristic bands in the carbonyl stretching range at 2112m, 2082s, 2063m, 2049s, and 1702w cm^{-1} .



Under 50 bar carbon monoxide pressure in the presence of ethanol both complexes **1** and **2** converted

quantitatively to $\text{Co}_2(\text{CO})_8$ and diethyl malonate according to Eqs (7) and (8). The composition of the reaction mixture was checked by quantitative infrared spectroscopy using the known molar absorbance of $\text{Co}_2(\text{CO})_8$ $\varepsilon_M = 1735 \text{ cm}^2 \text{ mmol}^{-1}$ at 1857 cm^{-1} [11] and that of diethyl malonate $\varepsilon_M = 843 \text{ cm}^2 \text{ mmol}^{-1}$ measured at 1747 cm^{-1} . The amount of diethyl malonate was double checked by quantitative gas chromatographic analysis.



The carbon monoxide uptake of complexes **1** and **2** could be followed at atmospheric pressure as well by using a gasometric apparatus. Complex **2** showed a much higher reactivity toward carbon monoxide than complex **1**, and the carbon monoxide uptake in both cases was faster in the presence of ethanol. Monitoring the infrared spectra of the reaction mixture in the reaction of complex **2** with CO and ethanol at 25°C , resulted first in the simultaneous fast formation of complex **1** and diethyl malonate (Eq. (9)) and then in the slower conversion of complex **1** into $\text{Co}_2(\text{CO})_8$ and diethyl malonate (Eq. (10)) (see Table 2).

Table 2

The change in concentrations in the reaction of $\text{Co}_2(\text{CO})_6(\text{CHCO}_2\text{Et})_2$ (**2**) with carbon monoxide and ethanol at 25°C and atmospheric pressure in *n*-octane and the formation of diethyl malonate (DEM)

Reaction time (h)	[2] ^a ($\times 10^2 \text{ mol/dm}^3$)	[1] ^b ($\times 10^2 \text{ mol/dm}^3$)	[$\text{Co}_2(\text{CO})_8$] ^c ($\times 10^2 \text{ mol/dm}^3$)	[DEM] ^d ($\times 10^2 \text{ mol/dm}^3$)
0	1.23	0.00	0.00	0.00
0.5	0.63	0.60	0.00	0.60
1.0	0.27	0.93	0.00	1.10
1.5	0.00	1.13	0.10	1.30
3.0	0.00	1.03	0.20	1.40
20	0.00	0.60	0.63	1.80

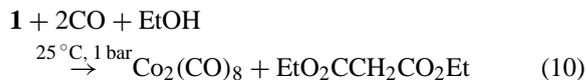
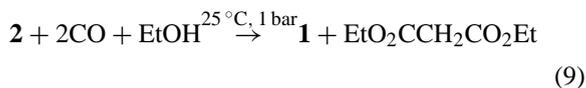
[EtOH]₀ = 0.57 mol/dm^3 .

^a The concentration of **2** was determined by quantitative IR analysis using the molar absorbance $\varepsilon_M = 8246 \text{ cm}^2/\text{mmol}$ at 2082 cm^{-1} .

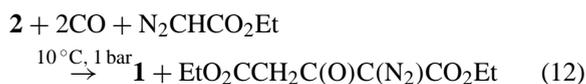
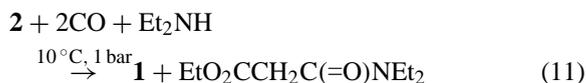
^b The concentration of **1** was determined by quantitative IR analysis using the molar absorbance $\varepsilon_M = 5484 \text{ cm}^2/\text{mmol}$ at 2074 cm^{-1} .

^c The concentration of $\text{Co}_2(\text{CO})_8$ was determined by quantitative IR analysis using the molar absorbance $\varepsilon_M = 1735 \text{ cm}^2/\text{mmol}$ at 1857 cm^{-1} [11].

^d The concentration of diethyl malonate [DEM] was determined by quantitative IR analysis using the molar absorbance of diethyl malonate $\varepsilon_M = 843 \text{ cm}^2/\text{mmol}$ at 1747 cm^{-1} , and double checked by quantitative GLC analysis using *n*-nonane as the internal standard.



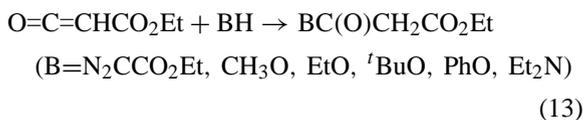
Solutions of complex **2** react with equimolar amounts of diethyl amine or ethyl diazoacetate under carbon monoxide according to Eqs. (11) and (12), respectively.



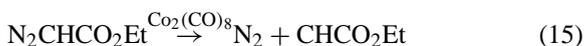
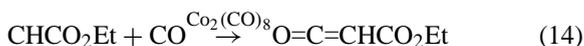
Following the carbon monoxide uptake in a gasometric apparatus at 10 °C using 0.020 mol/dm³ solutions of complex **2** and equimolar amounts of ethyl diazoacetate, ethanol or diethyl amine in *n*-octane, the initial rate of carbon monoxide uptake was found to be 0.1×10^{-5} , 0.5×10^{-5} , and 2.8×10^{-5} mol/dm³ s, respectively.

3. Discussion

The formation of the organic products can be rationalized by assuming the reaction of an ethoxycarbonylketene intermediate with ethyl diazoacetate, alcohols, phenol or diethylamine, respectively (Eq. (13)).

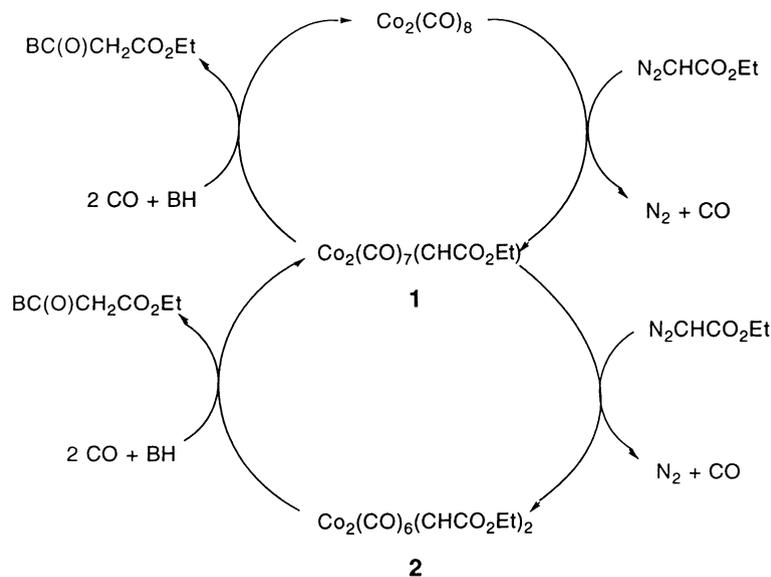


The possible source of the ethoxycarbonylketene might be the cobalt-mediated coupling reaction of carbon monoxide with ethoxycarbonylcarbene (Eq. (14)) which latter can be formed by the cobalt-mediated dinitrogen-loss of ethyl diazoacetate (Eq. (15)).



Carbene transfer from nitrogen to various transition metal complexes are well known [6,7]. With octacarbonyl dicobalt, however, only the reaction with bis(trifluoromethyl)diazomethane has been established so far, leading at room temperature in 28 days to the complex [μ_2 -{bis(trifluoromethyl)methylene}- μ_2 -(carbonyl)-bis(tricarbonyl-cobalt)(Co–Co)], which was isolated in 54% yield [12]. We found that Co₂(CO)₈ react with ethyl diazoacetate at ambient conditions in a much faster reaction to give mono- and diethoxycarbonylcarbene-bridged dicobalt carbonyl complexes **1** and **2** depending on the applied molar ratio and reaction conditions. Structurally similar dicobalt carbonyl complexes with bridging carbene ligands are known [13–19] which were prepared by other methods. Diazoalkanes, however, were successfully applied in the preparation of dinuclear cobalt carbene complexes containing η^5 -cyclopentadienyl ligands [20–25], and in the case of Co₂(CO)₆(DPPM) (DPPM = bis(diphenylphosphino)methane) as the starting complex [26].

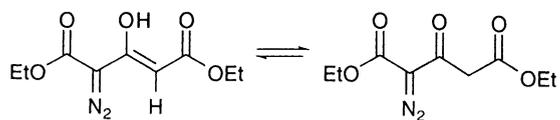
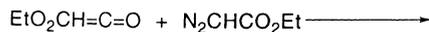
Examples and indirect evidences for the metal-mediated coupling of a carbene with carbon monoxide to form the corresponding ketene are numerous. However, only one of them reports a catalytic reaction in which the formation of a ketene intermediate can be assumed. Miyashita et al. [27] found that the reaction of Co₂(CO)₈ and the carbene precursor CH₂Br₂ in the presence of Zn results in a cobalt ketene complex Co₂(CH₂=C=O)(CO)₇ which catalyzes the methoxycarbonylation or aminocarbonylation of a mixture of CH₂Br₂ and Zn under carbon monoxide pressure yielding methyl acetate (385%) or *N,N*-diethylacetamide (184%) using methanol or diethylamine as the additional reagents in the reaction, respectively. In our experiments, Co₂(CO)₈ showed a so far unprecedented carbene transfer reactivity with ethyl diazoacetate as the carbene precursor. A few examples are known for the coupling of a free carbene with carbon monoxide even in the absence of a metal [28,29]. The infrared and NMR spectra of the reaction mixture in our case did not reveal the presence of either free [30] or coordinated ethoxycarbonylketene [31]. However, it is reasonable to assume that in the coordination sphere of cobalt the coupling of ethoxycarbonylcarbene with carbon monoxide does occur in an equilibrium reaction. This equilibrium is probably far on the left side keeping



(B = N₂CCO₂Et, CH₃O, EtO, ^tBuO, PhO, Et₂N)

Scheme 1.

the ketene concentration low but still sufficient to be scavenged by a suitable nucleophile. The observation that the CO uptake of the carbene complexes **1** and **2** is faster in the presence of ethanol or other potential ketene scavenger support this assumption. Ketenes either free [30] or coordinated to a transition metal [31] are prone to nucleophilic attack on the α -carbon atom and are effectively scavenged by an *O*- or *N*-nucleophiles such as an alcohol, phenol, or diethylamine. If such nucleophile is not present in the reaction mixture, ethyl diazoacetate act obviously as an efficient *C*-nucleophile. The highly reactive ethoxycarbonylketene [32] and ethyl diazoacetate give accordingly diethyl 2-diazo-3-oxoglutarate (Eq. (16)).



(16)

A similar nucleophilic addition of ethyl diazoacetate to benzoylketene was reported to give the corresponding product, 2-diazo-3,5-dioxo-5-phenylpentanoic acid

ethyl ester [33]. The nucleophilic addition of an acyldiazomethane to aldehydes or imines requires a base to remove the inherent acidic hydrogen of the acyldiazomethane [34]. Based on the observed intermediates **1** and **2** and their reactions with nucleophiles, the formation of the organic products in the cobalt-mediated carbene transfer reactions of ethyl diazoacetate is depicted in Scheme 1.

In summary, the presented highly efficient octacarbonyl dicobalt-catalyzed selective transformation of ethyl diazoacetate into ethyl-2-diazo-3-oxoglutarate or into various unsymmetrical malonic acid derivatives might be a useful method in synthetic chemistry.

4. Experimental

4.1. General comments

Handling of the complexes was carried out under an atmosphere of dry (P₄O₁₀) and deoxygenated (BTS contact) argon or carbon monoxide utilizing standard Schlenk techniques [35]. Solvents were dried and distilled under an atmosphere of argon or carbon monoxide according to standard procedures

[36]. IR spectra were recorded on a Specord IR 75 Carl Zeiss Jena spectrometer using 0.0265, 0.0765, or 0.212 mm CaF₂ solution cells, calibrated by the interference method [37]. ¹H, ²H, and ¹³C NMR spectra were recorded on a Varian Unity 300 spectrometer at 300, 46, and 75.42 MHz, respectively. Chemical shifts were referenced to residual solvent signals and reported in ppm relative to TMS (δ 0 ppm). Mass spectra were obtained on a HP 5890II/5971 GC-MSD at 70 eV using a 25 m HP5, 0.2 μ m column. Gas chromatographic analyses were performed on a HP 5890 instrument with FID, using a SPB 1 30 m, 0.32 μ m column. TLC tests were performed on Whatman MK6F silica gel 40 Å analytical plates. The *R_f* values refer to TLC tests using Et₂O:CH₂Cl₂ = 1:9. Octacarbonyl dicobalt was prepared by a literature procedure [38], and was double recrystallized under an atmosphere of carbon monoxide first from methylene chloride and then from *n*-heptane. All other reagents and solvents were obtained from Sigma-Aldrich. Column chromatography was carried out using silica gel, 200–400 mesh, 60 Å. Microanalyses were performed using a CHNS-O EA1108-Elemental Analyser (Carlo Erba).

4.2. Preparation of EtO₂CCH₂C(O)C(N₂)CO₂Et, diethyl 2-diazo-3-oxoglutarate

Ethyl diazoacetate (6.51 g, 57 mmol) and *n*-pentane (40 ml) were placed into a stainless-steel autoclave (107 ml total capacity) containing an open glass-insert loaded with Co₂(CO)₈ (171 mg, 0.5 mmol) and was pressurized at room temperature with CO to 50 bar pressure. Shaking at room temperature was started after the pressurized autoclave was first cooled to 0 °C and then the precatalyst (Co₂(CO)₈) dissolved by turning the autoclave upside down. After 24 h the pressure was slowly released through a cold trap (−79 °C) and the gas was analyzed on a 25 m, 0.53 mm column packed with 0.54 μ m molecular sieve. The solvent from the resulting reaction mixture was removed under vacuum and the brown oily residue was subjected to flash chromatography [10] on silica gel 60 Å, 200–400 mesh using 9:1 = methylene chloride:diethylether as the eluent to give EtO₂CCH₂C(O)C(N₂)CO₂Et as a pale yellow oil after concentration in vacuum (5.93 g 26 mmol, 91% yield). *R_f* = 0.59. Analysis: Calculated for C₉H₁₂O₅N₂: C, 47.37; H, 5.30;

N, 12.27. Found: C, 47.32; H, 5.24; N, 12.03. IR (*n*-hexane) 2137 (ϵ_M = 635 cm²/mmol), 1747 (ϵ_M = 588 cm²/mmol), 1724 (ϵ_M = 867 cm²/mmol), 1672 (ϵ_M = 475 cm²/mmol) cm^{−1}. ¹H NMR (CDCl₃) δ 1.25 (t, 3H), 1.30 (t, 3H), 3.83 (s, 2H), 4.17 (q, 2H), 4.27 (q, 2H) ppm. ¹³C NMR (CDCl₃) δ 14.01 (CH₃CH₂), 14.20 (CH₃CH₂), 46.41 (CH₂C=O), 61.18 (C(N₂)), 61.29 (CH₃CH₂), 61.68 (CH₃CH₂), 161.10 (CH₂C(O)), 167.02 (C(N₂)CO₂Et), 185.21 (EtO₂CCH₂) ppm.

4.3. Preparation of malonic acid derivatives

The procedure described above for the preparation of EtO₂CCH₂C(O)C(N₂)CO₂Et was applied, but 60 mmol of the reagent BH (BH = MeOH, CD₃OD (99.8 at.% D), EtOH, ^tBuOH, PhOH, Et₂NH) was added in addition to the solution of ethyl diazoacetate (6.51 g, 57 mmol) in *n*-pentane (40 ml).

4.3.1. EtO₂CCH₂CO₂Me

7.74 g, 53 mmol, 93%, *R_f* = 0.61. ¹H NMR (CDCl₃) δ 1.26 (t, 3H), 3.36 (s, 2H), 3.73 (s, 3H), 4.19 (q, 2H) ppm. ¹³C NMR (CDCl₃) δ 14.00 (CH₃CH₂), 41.36 (CH₂), 52.45 (CH₃O), 61.45 (CH₃CH₂), 166.47 (CO₂CH₂CH₃), 167.03 (CO₂CH₃) ppm.

4.3.2. EtO₂CCHDCO₂CD₃

7.95 g, 53 mmol, 93%, *R_f* = 0.61. ¹H NMR (CDCl₃) δ 1.26 (t, 3H), 3.36 (s, 1H), 4.19 (q, 2H) ppm. ²H NMR (CHCl₃) δ 3.36 (s, 1D), 3.73 (s, 3D) ppm. ¹³C NMR (CDCl₃) δ 13.99 (CH₃CH₂), 41.34 (CHD), 52.00 (CD₃O), 61.53 (CH₃CH₂), 166.45 and 167.03 (CO₂) ppm.

4.3.3. EtO₂CCH₂CO₂Et

8.2 g, 51 mmol, 90%, *R_f* = 0.63. IR (*n*-hexane) ν (C=O) 1762 (ϵ_M = 699 cm²/mmol), 1747 (ϵ_M = 843 cm²/mmol) cm^{−1}. ¹H NMR (CDCl₃) δ 1.26 (t, 6H), 3.34 (s, 2H), 4.19 (q, 4H) ppm. ¹³C NMR (CDCl₃) δ 14.04 (CH₃CH₂), 41.63 (CH₂), 61.45 (CH₃CH₂), 166.58 (CO₂) ppm.

4.3.4. EtO₂CCH₂CO₂^tBu

9.2 g, 52 mmol, 92%, *R_f* = 0.67. ¹H NMR (CDCl₃) δ 1.26 (t, 3H), 1.45 (s, 9H), 3.26 (s, 2H), 4.18 (q, 2H) ppm. [[39]; ¹H NMR (CCl₄) δ 1.28 (t, 3H), 1.45 (s, 9H), 3.13 (s, 2H), 4.15 (q, 2H) ppm.] ¹³C NMR

(CDCl₃) δ 14.04 (CH₃CH₂), 27.87 (CCH₃), 42.92 (CH₂), 61.24 (CH₃CH₂), 81.94 (CCH₃) 165.79 and 166.98 (CO₂) ppm.

4.3.5. EtO₂CCH₂CO₂Ph

10.7 g, 55 mmol, 96%, $R_f = 0.69$. ¹H NMR (CDCl₃) δ 1.31 (t, 3H), 3.59 (s, 2H), 4.25 (q, 2H), 7.10–7.40 (m, 5H) ppm. ¹³C NMR (CDCl₃) δ 14.06 (CH₃CH₂), 41.65 (CH₂), 61.80 (CH₃CH₂), 121.3 (*o*-C₆H₅), 126.19 (*p*-C₆H₅), 129.48 (*m*-C₆H₅), 150.37 (*ipso*-C₆H₅), 165.13 and 166.16 (CO₂) ppm.

4.3.6. EtO₂CCH₂C(O)NEt₂

3.2 g, 17 mmol, 30%, $R_f = 0.16$. IR (*n*-hexane) ν (C=O) 1749 ($\epsilon_M = 336$ cm²/mmol), 1666 ($\epsilon_M = 854$ cm²/mmol) cm⁻¹. MS (70 eV, EI): m/z (%): 187 (78) [M⁺], 142 (52) [M⁺-OEt], 100 (57) [M⁺-CH₂CO₂Et], 72 (100) [M⁺-EtO₂C, Et, CH]. ¹H NMR (CDCl₃) δ 1.11 (t, 3H), 1.16 (t, 3H), 1.25 (t, 3H), 3.27 (q, 2H), 3.35 (q, 2H), 3.39 (s, 2H), 4.18 (q, 2H) ppm. ¹³C NMR (CDCl₃) δ 12.75 ((CH₃CH₂)₂N), 14.07 (CH₃CH₂O), 41.23 ((CH₃CH₂)₂N), 42.56 (CH₂), 61.33 (CH₃CH₂O), 165.11 and 167.83 (CO₂) ppm.

4.4. Preparation of Co₂(CO)₇(CHCO₂Et),

[μ_2 -{ethoxycarbonyl(methylene)}- μ_2 -(carbonyl)-bis(tricarbonyl-cobalt) (Co–Co)] (**1**)

A solution of Co₂(CO)₈ (342 mg, 1 mmol) and ethyl diazoacetate (160 mg, 1.4 mmol) in *n*-pentane (30 ml) was stirred under an atmosphere of carbon monoxide at 0 °C for 3.5 h. The solvent was removed in a vacuum and the residue was dissolved in methylene chloride (3 ml) and purified by column chromatography (450/10 mm) at 1 °C under argon using methylene chloride as the eluant. The first fraction (40 ml) gave after concentration and crystallization at -79 °C pure unreacted Co₂(CO)₈ (36 mg, 10.5%). The second fraction (90 ml) gave after concentration pure **1** as an orange oil (340 mg, 82%). The third fraction (100 ml) gave after concentration **2** as a yellow oil (2 mg, 4%). **1**, IR (*n*-hexane) ν (C≡O) 2112 ($\epsilon_M = 818$ cm²/mmol), 2074 ($\epsilon_M = 5484$ cm²/mmol), 2056 ($\epsilon_M = 3003$ cm²/mmol), 2047 ($\epsilon_M = 5329$ cm²/mmol), 2042 ($\epsilon_M = 5484$ cm²/mmol), ν (C–O) 1873 ($\epsilon_M = 876$ cm²/mmol), 1866 ($\epsilon_M = 646$ cm²/mmol), 1854 ($\epsilon_M = 1399$ cm²/mmol),

1707 ($\epsilon_M = 263$ cm²/mmol), 1693 ($\epsilon_M = 213$ cm²/mmol) cm⁻¹. Analysis: Calculated for C₁₁H₆O₉Co₂: Co, 29.465. Found: Co, 29.04. ¹H NMR (CDCl₃) δ 1.21 (t, 3H), 4.08 (q, 2H), 5.73 (s, 1H) ppm. ¹³C NMR (CDCl₃) δ 13.94 (CH₃), 61.48 (CH₂), 94.60 (CH), 178.34 (CO₂), 201.85 (CO) ppm.

4.5. Preparation of Co₂(CO)₆(CHCO₂Et)₂, [di- μ_2 -(ethoxycarbonyl-(methylene))-bis(tricarbonyl-cobalt) (Co–Co)] (**2**)

To a solution of Co₂(CO)₈ (411 mg, 1.2 mmol) in *n*-pentane (36 ml) ethyl diazoacetate (308 mg, 2.7 mmol) was added drop-wise at 5 °C under an atmosphere of CO and stirred for an additional 30 min applying a continuous purging with argon. The solvent was removed in vacuum and the residue was dissolved in methylene chloride (3 ml) and purified by column chromatography (silica gel 60 Å, 200–400 mesh, 450/10 mm) at 1 °C under argon using methylene chloride as the eluant. The first fraction (30 ml) gave after concentration **1** (46 mg, 8%). The second fraction (260 ml) gave after concentration pure **2** as a yellow oil (403 mg, 73%). **2**, IR (*n*-hexane) ν (C≡O) 2112 ($\epsilon_M = 1670$ cm²/mmol), 2082 ($\epsilon_M = 8246$ cm²/mmol), 2063 ($\epsilon_M = 3360$ cm²/mmol), 2049 ($\epsilon_M = 6400$ cm²/mmol), ν (C≡O) 1702 ($\epsilon_M = 647$ cm²/mmol) cm⁻¹. Analysis: Calculated for C₁₄H₁₂O₁₀Co₂: C, 36.706; H, 2.641; Co, 25.729. Found: C, 36.54; H, 2.81; Co, 25.49. ¹H NMR (CDCl₃) δ 1.23 (t, 3H), 4.08 (q, 2H), 4.55 (s, 1H) ppm. ¹³C NMR (CDCl₃) δ 14.30 (CH₃), 61.70 (CH₂), 113.41 (CH), 179.60 (CO₂), 196.63 (CO) ppm.

4.6. Reaction of **1** with EtOH under CO pressure

A solution of complex **1** (20 mg, 0.05 mmol) and ethanol (4.6 mg, 0.1 mmol) in *n*-hexane (5 ml) was placed into a glass liner of a stainless-steel autoclave (total capacity = 12.8 ml) and pressurized at room temperature with CO to 50 bar and was shaken for 60 min. The resulting brown solution showed the presence of Co₂(CO)₈ (0.05 mmol, 100%) and diethyl malonate (0.049 mmol, 98%) by quantitative infrared spectroscopy at 1857 ($\epsilon_M = 1735$ cm²/mmol [11]) and at 1747 ($\epsilon_M = 843$ cm²/mmol) cm⁻¹, respectively. Gas chromatographic analysis using *n*-nonane

internal standard gave 0.048 mmol, 96% diethyl malonate (response factor = 0.347).

4.7. Reaction of **2** with EtOH under CO pressure

A solution of complex **2** (23 mg, 0.05 mmol) and ethanol (18.5 mg, 0.4 mmol) in *n*-hexane (5 ml) was placed into a glass liner of a stainless-steel autoclave (total capacity = 12.8 ml) and pressurized at room temperature with CO to 50 bar and was shaken for 60 min. The resulting brown solution showed the presence of Co₂(CO)₈ (0.049 mmol, 98%) and diethyl malonate (0.095 mmol, 95%) by quantitative infrared spectroscopy. Diethyl malonate found by gas chromatographic analysis was 0.093 mmol, 93%.

4.8. Reaction of **2** with EtO₂CCHN₂ under atmospheric pressure of CO

To a solution of ethyl diazoacetate (23 mg, 0.2 mmol) in *n*-octane (5.98 ml) in a thermostated glass reactor connected to a gas burette at 10 °C under an atmosphere of CO a 4.0 ml aliquot of a 0.05 mol/dm³ stock solution of **2** in *n*-octane was injected. The initial rate of CO uptake (0.1×10^{-5} mol/dm³ s) was calculated from the first 15 readings (frequency: 30 s) of the gas burette. In 24 h, 0.28 mmol CO was absorbed and quantitative infrared spectroscopy revealed a 94% conversion of complex **2** into complex **1** with a simultaneous formation of EtO₂CCH₂C(O)C(N₂)CO₂Et (0.18 mmol).

4.9. Reaction of **2** with ethanol under atmospheric pressure of CO

To a solution of ethanol (9.2 mg, 0.2 mmol) in *n*-octane (5.98 ml) in a thermostated glass reactor connected to a gas burette at 10 °C under an atmosphere of CO a 4.0 ml aliquot of a 0.05 mol/dm³ stock solution of **2** in *n*-octane was injected. The initial rate of CO uptake (0.5×10^{-5} mol/dm³ s) was calculated from the first 20 readings (frequency: 30 s) of the gas burette. In 10 h, 0.35 mmol CO was absorbed and quantitative infrared spectroscopy revealed a 98% conversion of complex **2** into complex **1** with a simultaneous formation of EtO₂CCH₂CO₂Et (0.18 mmol).

4.10. Reaction of **2** with diethylamine under atmospheric pressure of CO

To a solution of diethylamine (14.6 mg, 0.2 mmol) in *n*-octane (5.98 ml) in a thermostated glass reactor connected to a gas burette at 10 °C under an atmosphere of CO a 4.0 ml aliquot of a 0.05 mol/dm³ stock solution of **2** in *n*-octane was injected. The initial rate of CO uptake (2.8×10^{-5} mol/dm³ s) was calculated from the first nine readings (frequency: 20 s) of the gas burette. In 3 h, 0.32 mmol CO was absorbed and quantitative infrared spectroscopy revealed a 97% conversion of complex **2** into complex **1** with a simultaneous formation of EtO₂CCH₂C(O)NEt₂ (0.17 mmol). Flash chromatography on silica gel 60 Å (200–400 mesh) with Et₂O/CH₂Cl₂ = 1:4 gave 28 mg, 74% isolated yield of EtO₂CCH₂C(O)NEt₂.

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