Preparation of triphenylphosphane substituted ethoxycarbonylcarbene-bridged dicobalt carbonyl complexes and their application as catalyst precursors in the carbonylation of ethyl diazoacetate to diethyl malonate

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Abstract

The triphenylphosphane substituted derivatives $Co_2(CO)_6(CHCO_2Et)(PPh_3)$, [$\mu_2$-{ethoxycarbonyl(methylene)}-μ_2-(carbonyl)-(tricarbonyl-cobalt)-(triphenylphosphane-dicarbonyl-cobalt) (Co—Co)] (**3**) and $Co_2(CO)_5(CHCO_2Et)(PPh_3)_2$, [$\mu_2$-{ethoxycarbonyl-(methylene)}-μ_2-(carbonyl)-bis(triphenylphosphane-dicarbonyl-cobalt) (Co–Co)] (**4**) were prepared from the known $Co_2(CO)_7(CHCO_2Et)$ (**1**) and $Co_2(CO)_6(CHCO_2Et)_2$ (**2**) complexes with triphenylphosphane. The new complexes **3** and **4** as well as $Co_2(CO)_7(PPh_3)$, $Co_2(CO)_6(PPh_3)_2$, and $Co_2(CO)_6$ (dppm) (dppm = $Ph_2PCH_2PPh_2$) were found to be suitable catalyst precursors in the selective carbonylation of ethyl diazoacetate to diethyl malonate in the presence of ethanol.
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Keywords: Carbene carbon monoxide coupling; Triphenylphosphane substituted ethoxycarbonylcarbene-bridged dicobalt carbonyl complexes; Diethyl malonate

1. Introduction

Octacarbonyl dicobalt proved to be an excellent catalyst for the carbonylation of ethyl diazoacetate in the presence of an alcohol (methanol, ethanol, *tert*-butanol), phenol, or diethylamine to the corresponding malonic acid derivatives. Ethoxycarbonylcarbene-bridged dicobalt complexes $Co_2(CO)_7(CHCO_2Et)$ (**1**) and $Co_2(CO)_6(CHCO_2Et)_2$ (**2**) were found to be intermediates in those catalytic reactions [1].

We now report the reactions of these complexes with triphenylphosphane and the activity of the new PPh_3-substituted derivatives in the carbonylation of ethyl diazoacetate to diethyl malonate.

2. Results and discussion

In accord with Eq. (1) the addition of triphenylphosphane to solutions of $Co_2(CO)_7(CHCO_2Et)$ (**1**) obtained by the reaction of equimolar $Co_2(CO)_8$ and ethyl diazoacetate in *n*-pentane at room temperature gave, along with gas evolution, a cherry-red colored solution of $Co_2(CO)_6(CHCO_2Et)(PPh_3)$ (**3**). Purple crystals of **3** were isolated in 38% yield after crystallization from *n*-pentane at −40 °C, which were suitable for a single crystal X-ray structure determination.

$$Co_2(CO)_7(CHCO_2Et) + PPh_3$$
$$\mathbf{1}$$
$$\rightarrow Co_2(CO)_6(CHCO_2Et)(PPh_3) + CO \qquad (1)$$
$$\mathbf{3}$$
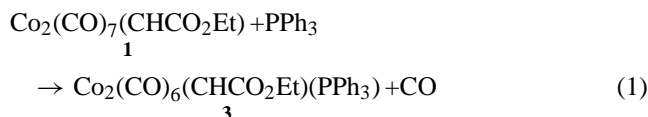
Preliminary results of the crystal structure determination of **3** [2] revealed that the ethoxycarbonylcarbene ligand is in bridging position between the two cobalt

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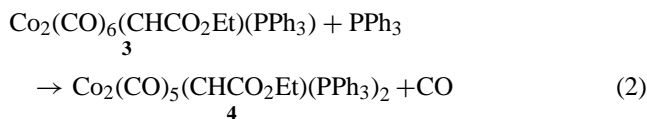
Table 1
Intensities of the ν(CO) bands of the ethoxycarbonylcarbene-bridged complexes **1**, **3**, and **4**

1 (CH_2Cl_2)		3 (CH_2Cl_2)		3 (KBr)	4 (CH_2Cl_2)		4 (KBr)
ν(CO) (cm^{-1})	ε_M (cm^2/mmol)	ν(CO) (cm^{-1})	ε_M (cm^2/mmol)	ν(CO) (cm^{-1})	ν(CO) (cm^{-1})	ε_M (cm^2/mmol)	ν(CO) (cm^{-1})
2112	937	2080	1517	2075 (s)	2040	1181	2034 (m)
2075	6537	2033	2941	2027 (s)	2005	2710	2003 (s)
				2017 (s)			
2048	4637	2013	2462	2005 (s)	1983	2050	1980 (s)
				1990 (s)	1970	1869	1964 (s)
1853	953	1829	597	1825 (s)	1786	506	1790 (s)
1691	236	1688	174		1678	205	1674 (m)
				1668 (m)			
1672	200	1666	151				

ε_M: molar absorbance; (s): strong; (m): medium.

atoms. The phosphorus atom is *trans* to the carbene carbon atom. The phosphorus–cobalt–carbene carbon angle is 174.9(5)°. The Co–Co bond length (2.485(4) Å) is a little longer than that found (2.447(1) Å) in a phosphane-substituted carbene-bridged dicobalt carbonyl complex, $Co_2(CO)_5(PPhMe_2)(PhCNPh)_2$ [3]. On the other hand, *N*-heterocyclic carbene dicobalt carbonyl complexes exhibit much longer Co—Co bond lengths in the range of 2.6819(5)–2.6973(19) Å [4,5]. The Co-carbene carbon bond lengths in **3** (1.97(2) and 2.01(2) Å) are similar to those of other dicobalt carbonyl complexes with a bridging carbene ligand [3,6].

The infrared spectra of complex **3** in CH_2Cl_2 solution and in the solid state, as well show beside terminal ν(C≡O) bands at 2080, 2033, 2013, and 2075, 2027, 2017, 2005, 1990, a strong bridging carbonyl band at 1829 and 1825 cm^{-1}, respectively. For the intensities of these bands (see Table 1). Addition of triphenylphosphane to solutions of **3** caused the evolution of carbon monoxide and the formation of a new substituted derivative **4** according to reaction (2). The solubility of complex **4** in saturated hydrocarbons is very poor. Performing reaction (2) in *n*-pentane, complex **4** precipitates quantitatively from the solution. During attempted crystallization from CH_2Cl_2 solutions decomposition was observed.

$$Co_2(CO)_6(CHCO_2Et)(PPh_3) + PPh_3$$
$$\underset{\mathbf{3}}{}$$
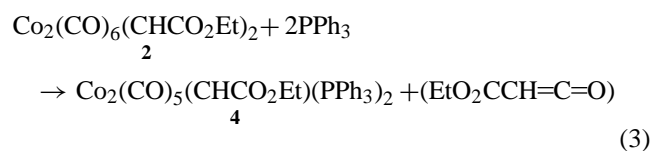$$\rightarrow \underset{\mathbf{4}}{Co_2(CO)_5(CHCO_2Et)(PPh_3)_2} + CO \qquad (2)$$

Substitution of a carbonyl ligand in **1** or **3** by triphenylphosphane results in the expected shift of the different carbonyl bands to lower wave numbers (see Table 1).

Both of the triphenylphosphane-containing complexes **3** and **4** have one of the carbonyl ligands in a bridging position, as can be deduced from the single ν(C=O) band in that region of the infrared spectra. The bridge ν(C=O) in known phosphane-substituted carbene complexes such as in $Co_2(CO)_5(C_4O_2H^nPr)[P(OPh)_3]$ or $Co_2(CO)_5(C_4O_2H^nPr)\text{-}(P(^nBu_3)$ (where $C_4O_2H^nPr = 3$-*n*-propyl-2-butene-4-olide-4-ylidene) [7] and $(Ph_3P)(CO)_2Co(CFCF_3)(CO)Co(CO)_2(PPh_3)$ or $(^nBu_3P)(CO)_2Co(CFCF_3)(CO)Co(CO)_2(P^nBu_3)$

[8] and $Co_2(CO)_6(C_4O_2HPh)(P^nBu_3)_2$ (where $C_4O_2HPh = 3$-phenyl-2-butene-4-olide-4-ylidene) or $Co_2(CO)_6(C_4O_2H^nPr)(PPh_2^iPentyl)_2$ [9] was found at a similar wave number, respectively. The ethoxycarbonylcarbene ligand in **3** and **4** is also in a bridging position, according to the solid state structure of **3**, and according to the characteristic appearance [10] of $\delta C\underline{H}$ in the ^{1}H NMR and $\delta\underline{C}H$ in the ^{13}C NMR solution spectra of **3** and **4**. The ^{31}P NMR spectrum of complex **4** in solution at ambient temperature or in the solid state [11] show the presence of only one kind of phosphorus. Therefore, it is reasonable to assume that to each of the cobalt atoms one triphenylphosphane is coordinated symmetrically in *trans* position to the carbene bridge.

Experiments to obtain mono- or bis-triphenylphosphane derivative(s) of complex **2** failed. Adding PPh_3 to solutions of **2** at room temperature or at $0\,°C$ resulted always in the formation of complex **4**. Experiments using one mol PPh_3 for one mol of **2** led to the formation of half mol of **4**, and a half mol of **2** remained unchanged. By using a gas burette in performing the reaction of **2** with PPh_3 at $10\,°C$, no gas evolution could be observed. The infrared spectra of complex **4** in CH_2Cl_2 solution and in the solid state as well show four terminal ν(C≡O) bands at 2040, 2005, 1983, 1970, and 2034, 2003, 1980, 1964, and a strong bridging carbonyl band at 1786 and 1790 cm^{-1}, respectively. For the intensities of these bands see Table 1. The starting complex **2** does not contain bridging carbonyl groups. The two bridging positions in **2** are occupied by two ethoxycarbonylcarbene ligands [1]. Apparently, the addition of PPh_3 to complex **2** expels one of the ethoxycarbonylcarbene and one of the CO ligands. This reaction is not accompanied by gas evolution, and a coupling of carbon monoxide to ethoxycarbonylketene can be expected. The infrared and NMR spectra of the reaction mixture, however, do not reveal the presence of either free [12] or coordinated ethoxycarbonylketene [13].

$$Co_2(CO)_6(CHCO_2Et)_2 + 2PPh_3$$
$$\underset{\mathbf{2}}{}$$
$$\rightarrow \underset{\mathbf{4}}{Co_2(CO)_5(CHCO_2Et)(PPh_3)_2} + (EtO_2CCH{=}C{=}O)$$
$$\qquad (3)$$

Performing reaction (3) in the presence of ethanol, the putative ethoxycarbonylketene could be trapped quantitatively in form of diethyl malonate (checked by quantitative IR spectroscopy and gas-chromatography), without affecting the formation of complex **4** (reaction (4)).

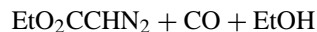$$2 + 2PPh_3 + EtOH \rightarrow 4 + EtO_2CCH_2CO_2Et \qquad (4)$$

Under CO pressure the ethoxycarbonylcarbene ligand in complex **3** could be displaced by carbon monoxide and the quantitative formation of the known $Co_2(CO)_7(PPh_3)$ complex could be inferred from the exclusive appearance of the characteristic $\nu(C\equiv O)$ bands at 2079 (4.4), 2026 (4.8), 2010 (sh), 1996 (10), and 1964 (3.0) cm^{-1} [14] in the infrared spectrum of the reaction product in *n*-hexane solution. In the presence of ethanol the formation of diethyl malonate in 66% yield could be deduced from the infrared spectrum of the reaction product using the known molar absorbance of diethyl malonate at 1747 cm^{-1} in *n*-hexane [1]

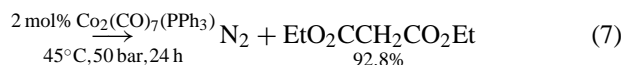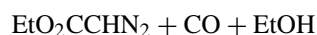$$3 + 2CO + EtOH$$
$$\xrightarrow[24\,h]{25°C,50\,bar} Co_2(CO)_7(PPh_3) + EtO_2CCH_2CO_2Et \qquad (5)$$
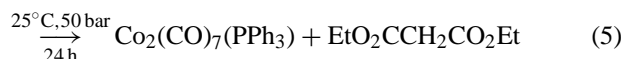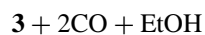
Attempts to regenerate complex **3** in *n*-heptane solution by the reaction of $Co_2(CO)_7(PPh_3)$ with ethyl diazoacetate under argon at $10\,°C$ failed. The formation of **3** could not be detected in the infrared spectrum of the reaction mixture. However, using the initial concentrations of $[Co_2(CO)_7(PPh_3)]_0 = 0.02\,mmol/cm^3$ and $[EtO_2CCHN_2]_0 = 0.02\,mmol/cm^3$, a complete decomposition of ethyl diazoacetate into N_2 and 1,2,3-triethoxycarbonylcyclopropane was observed in 5 h with an initial rate of gas evolution of $1.8 \times 10^{-6}\,mmol/(cm^3\,s)$.

Complex **3** proved to be a good catalyst precursor in the selective catalytic carbonylation of ethyl diazoacetate to diethyl malonate (Eq. (6)).

$$EtO_2CCHN_2 + CO + EtOH$$
$$\xrightarrow[45°C,50\,bar,24\,h]{2\,mol\%\,3} N_2 + \underset{100\%}{EtO_2CCH_2CO_2Et} \qquad (6)$$

Because complex **3** under 50 bar CO pressure, even at room temperature, is converted into $Co_2(CO)_7(PPh_3)$ (Eq. (5)), and the presence of this complex could be recognized in the infrared spectra of the reaction product using **3** as a catalyst, the catalytic activity of $Co_2(CO)_7(PPh_3)$ has been checked independently. According to Eq. (7) a complete conversion of ethyl diazoacetate and a 92.8% yield of diethyl malonate was found and 97% of the starting $Co_2(CO)_7(PPh_3)$ was recovered at the end of the reaction.

$$EtO_2CCHN_2 + CO + EtOH$$
$$\xrightarrow[45°C,50\,bar,24\,h]{2\,mol\%\,Co_2(CO)_7(PPh_3)} N_2 + \underset{92.8\%}{EtO_2CCH_2CO_2Et} \qquad (7)$$
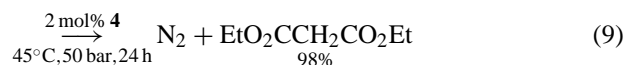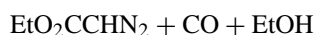
Under CO pressure the ethoxycarbonylcarbene ligand in complex **4** could be displaced by carbon monoxide and the quantitative formation of the known $[Co(CO)_3(PPh_3)_2]$
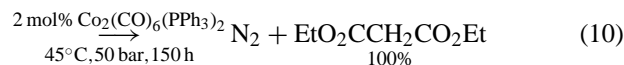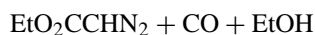
$[Co(CO)_4]$ complex could be inferred from the appearance of the characteristic $\nu(CO)$ bands at 2010 and 1889 cm^{-1} [15] in the infrared spectrum of the reaction product in CH_2Cl_2 solution. In the presence of ethanol the formation of diethyl malonate in 66% yield could be deduced from the infrared spectrum of the reaction product (Eq. (8)) using the known molar absorbance of diethyl malonate at 1747 cm^{-1} in *n*-hexane [1].

$$4 + 3CO + EtOH$$
$$\xrightarrow[24\,h]{25\,°C,50\,bar} [Co(CO)_3(PPh_3)_2][Co(CO)_4]$$
$$+ EtO_2CCH_2CO_2Et \qquad (8)$$
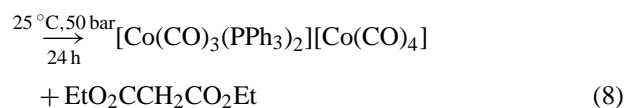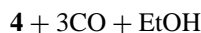
Complex **4** proved to be suitable as a catalyst precursor in the catalytic carbonylation of ethyl diazoacetate to diethyl malonate in CH_2Cl_2 solution (Eq. (9)). The infrared spectrum of the product revealed beside the very strong bands of diethyl malonate at 1749 and 1732 cm^{-1}, bands of $[Co(CO)_3(PPh_3)_2][Co(CO)_4]$ at 2110 and 1889 cm^{-1}, and traces of $Co_2(CO)_6(PPh_3)_2$ at 1957 cm^{-1}.

$$EtO_2CCHN_2 + CO + EtOH$$
$$\xrightarrow[45°C,50\,bar,24\,h]{2\,mol\%\,4} N_2 + \underset{98\%}{EtO_2CCH_2CO_2Et} \qquad (9)$$

It is well known that the complex $[Co(CO)_3(PPh_3)_2]$ $[Co(CO)_4]$ is converted, with loss of CO, above room temperature into $Co_2(CO)_6(PPh_3)_2$ [15–17]. We found that $Co_2(CO)_6(PPh_3)_2$, despite of its low solubility in organic solvents, is also suitable as a catalyst in the carbonylation of ethyl diazoacetate; however, a much longer reaction time is necessary for a complete conversion (Eq. (10)).

$$EtO_2CCHN_2 + CO + EtOH$$
$$\xrightarrow[45°C,50\,bar,150\,h]{2\,mol\%\,Co_2(CO)_6(PPh_3)_2} N_2 + \underset{100\%}{EtO_2CCH_2CO_2Et} \qquad (10)$$

Repeating the above reaction under identical conditions but using $[Co(CO)_3(PPh_3)_2][Co(CO)_4]$ as the catalyst precursor gave the same total conversion of ethyl diazoacetate to diethyl malonate. The red–brown color of the reaction product and a very weak band at 1957 cm^{-1} in the infrared spectrum of the solution indicate that the cobalt complex $Co_2(CO)_6(PPh_3)_2$ is present at the end of the reaction.

The same high selectivity but a little higher activity was found in the carbonylation of ethyl diazoacetate when $Co_2(CO)_6(dppm)$ [18,19] (dppm = $Ph_2PCH_2PPh_2$) was used as the catalyst.

A possible mechanism of the catalytic formation of diethyl malonate from ethyl diazoacetate, CO, and ethanol is a cobalt-mediated diazo decomposition and a consecutive cobalt-mediated ethoxycarbonylcarbene/carbon monoxide coupling reaction leading to ethoxycarbonylketene, which is trapped by ethanol. The cobalt species involved in this catalysis might be **3** and **4** because their reaction with CO and ethanol produces diethyl malonate (Eqs. (5) and (8)). The

catalytic cycle can be closed by regeneration of **3** and **4** from $Co_2(CO)_7(PPh_3)$ and $[Co(CO)_3(PPh_3)_2][Co(CO)_4]$ or $Co_2(CO)_6(PPh_3)_2$ by the reaction with ethyl diazoacetate. Experimental evidence for both steps of such a mechanism has been described in the literature in the case of $Co_2(CO)_6(dppm)$. First, the reaction of $Co_2(CO)_6(dppm)$ with ethyl diazoacetate gives the carbene complex $Co_2(CO)_5$ $(CHCO_2Et)(dppm)$, along with CO and N_2 [20]. Second, the reaction of $Co_2(CO)_5(CHCO_2Et)(dppm)$ with CO and CD_3OD give $EtO_2CCH=C=O$, $EtO_2CCHDCO_2CD_3$ and $Co_2(CO)_6(dppm)$ [21], through the assumed intermediate.

3. Experimental

3.1. General comments

Handling of $Co_2(CO)_8$ and other carbonyl cobalt complexes was carried out in an atmosphere of dry (P_4O_{10}) and deoxygenated (BTS contact, room temp.) argon or carbon monoxide utilizing standard Schlenk techniques [22]. Solvents were dried and distilled under an atmosphere of argon or carbon monoxide according to standard procedures [23]. IR spectra were recorded on a Thermo Nicolet Avatar 330 FTIR spectrometer using 0.00265, 0.00765, or 0.02153 cm CaF_2 solution cells, calibrated by the interference method [24]. Gas chromatographic analyses were performed on a HP 5890 instrument with FID, using a SPB 1 30 m, 0.32 μm column and *n*-nonane was used as an internal standard. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian Unity 300 spectrometer at 300, 75.4, and 121.4 MHz, respectively using $CDCl_3$ as the solvent. Chemical shifts δ are reported in ppm, for ^1H and ^{13}C relative to $CHCl_3$ (7.26 and 77.00 ppm, respectively) and for ^{31}P relative to H_3PO_4. Octacarbonyl dicobalt was prepared by a literature procedure [25], and was recrystallized twice in an atmosphere of carbon monoxide, first from CH_2Cl_2 and then from *n*-heptane. All other reagents and solvents were obtained from Sigma–Aldrich. The gas volume change in reactions at atmospheric pressure was determined using a thermostatted glass reactor having an inner volume of 55 cm^3, which was connected to a thermostatted mercury-filled gas burette. The reactions were started by injecting the reactant into the reactor as a stock solution, using a Hamilton TLL syringe, through a silicon disk port. Reactions under 50 bar CO pressure were performed in a stainless-steel autoclave with a glass liner (total capacity = 12.8 cm^3) [26]. Microanalyses were performed using a CHNSO EA1108-Elemental Analyser (Carlo Erba). Cobalt and phosphorus analyses were performed using established micro analytical methods.

3.2. Preparation of $Co_2(CO)_6(CHCO_2Et)(PPh_3)$, $[\mu_2-\{ethoxycarbonyl(methylene)\}-\mu_2-(carbonyl)-(tricarbonyl-cobalt)-(triphenylphosphane-dicarbonyl-cobalt) (Co–Co)]$ (**3**)

A solution of $Co_2(CO)_8$ (2.61 g, 7.63 mmol) and ethyl diazoacetate (0.8 cm^3, 7.62 mmol) in *n*-pentane (200 cm^3) was stirred in an atmosphere of carbon monoxide at room temperature for 1 h. Addition of triphenylphosphane (2.63 g, 10 mmol) and stirring the mixture for 10 min resulted in gas evolution and the formation of a cherry-red solution with a flaky precipitate. Filtration under argon and crystallization at −40 °C gave **3** as 0.1–0.4 mm size purple-red crystals (1.84 g, 38%). (A second crop or a longer triphenylphosphane addition procedure gave a less attractive grayish-red solid product!) **3**, IR (CH_2Cl_2) $\nu(C\equiv O)$ 2080 ($\varepsilon_M = 1316$ cm^2/mmol), 2033 ($\varepsilon_M = 2773$ cm^2/mmol), 2013 ($\varepsilon_M = 2578$ cm^2/mmol), $\nu(C=O)$ 1829 ($\varepsilon_M = 565$ cm^2/mmol), 1688 ($\varepsilon_M = 174$ cm^2/mmol), 1666 ($\varepsilon_M = 151$ cm^2/mmol) cm^{-1}. IR (KBr) $\nu(C\equiv O)$ 2075 (s), 2027 (s), 2017 (s), 2005 (s), 1990 (s), $\nu(C=O)$ 1825 (s), 1668(m) cm^{-1}. Analysis: calculated for $C_{28}H_{21}O_8Co_2P$: C, 53.02; H, 3.34, Co, 18.58; P, 4.88. Found: C, 52.86; H, 2.99; Co, 18.48; P, 4.80. ^1H NMR ($CDCl_3$) δ 1.26 (t, 3H), 4.12 (q, 2H), 5.66 (s, 1H), 7.42–7.52 (m, 15H) ppm. ^{13}C NMR ($CDCl_3$) δ 14.22 (CH_3), 60.80 (CH_2), 91.40 (CH), 130.85–133.39 (C_6H_5), 180.31 (org. CO), 200.97 (term. CO) ppm. ^{13}C NMR (solid state) δ 14.42 (CH_3), 60.14 (CH_2), 90.54 (CH), 130.30 (C_6H_5), 180.63 (org. CO), 208.99 (term. CO) ppm. ^{31}P NMR ($CDCl_3$) δ 49.74 ppm.

3.3. Preparation of $Co_2(CO)_5(CHCO_2Et)(PPh_3)_2$, $[\mu_2-\{ethoxycarbonyl(methylene)\}-\mu_2-(carbonyl)-bis(triphenylphosphane-dicarbonyl-cobalt) (Co–Co)]$ (**4**)

3.3.1. Method A

A solution of $Co_2(CO)_8$ (0.59 g, 1.72 mmol) and ethyl diazoacetate (0.63 cm^3, 6.00 mmol) in *n*-pentane (140 cm^3) was stirred in an atmosphere of argon at room temperature for 1 h. Addition of triphenylphosphane (1.38 g, 5.26 mmol) and stirring the mixture for 15 min resulted in the formation of a light yellow solution and a brick-red precipitate. Filtration under argon gave **4** as a red powder (1.48 g, 99%).

3.3.2. Method B

Addition of triphenylphosphane (2.0 g, 7.63 mmol) under argon to a stirred, filtered solution obtained from $Co_2(CO)_8$ (2.61 g, 7.63 mmol), ethyl diazoacetate (0.8 cm^3, 7.62 mmol) and triphenylphosphane (2.63 g, 10 mmol) in *n*-pentane (200 cm^3) as described above in the preparation of **3**, gave, within 10 min, a pale yellow solution and a brick-red precipitate. Filtration under argon gave **4** as a red powder (4.64 g, 70%).

4, IR (CH_2Cl_2) $\nu(C\equiv O)$ 2040 ($\varepsilon_M = 1181$ cm^2/mmol), 2005 ($\varepsilon_M = 2710$ cm^2/mmol), 1983 ($\varepsilon_M = 2050$ cm^2/mmol), 1970 ($\varepsilon_M = 1869$ cm^2/mmol), $\nu(C=O)$ 1786 ($\varepsilon_M = 506$ cm^2/ mmol), 1678 ($\varepsilon_M = 205$ cm^2/mmol), cm^{-1}. IR (KBr) $\nu(C\equiv O)$ 2034 (m), 2003 (s), 1980 (s), 1964 (s), $\nu(C=O)$ 1790 (s), 1674 (m) cm^{-1}. Analysis: calculated for $C_{45}H_{36}O_7Co_2P_2$: C, 62.23; H, 4.18, Co, 13.57; P, 7.13. Found: C, 61.85; H, 4.03, Co, 13.23; P, 6.82. ^1H NMR ($CDCl_3$) δ 1.02 (t, 3H), 3.77 (q, 2H), 4.35 (t, $J(^{31}P-^1H = 7.7$ Hz),1H), 7.31–7.51 (m, 15H) ppm. ^{13}C NMR ($CDCl_3$) δ 14.16 (CH_3), 60.13 (CH_2),

89.93 (CH), 130.85–133.39 (C_6H_5), 181.63 (org. CO). ^{31}P NMR (CDCl$_3$) δ 45.60 (broad) ppm.

3.4. Reaction of [di-μ_2-(ethoxycarbonyl(methylene)-bis(tricarbonyl-cobalt) (Co−Co)] (2) with triphenylphosphane in the presence of ethanol

To a magnetically stirred solution of 0.20 mmol of PPh$_3$ and 0.40 mmol of anhydrous ethanol in *n*-octane (3.0 cm^3) in a gasometric apparatus at 10 °C a solution of 0.10 mmol of **2** [1] in 2.0 cm^3 *n*-octane was injected. Within a minute a powdery orange–red solid began to precipitate, and the color of the solution became light yellow. In one hour reaction time no change in gas volume occurred, and the reaction mixture became almost colorless. The infrared spectrum in the 2200–1600 cm^{-1} range showed two strong ν(C=O) absorptions of diethyl malonate at 1762 and 1747 cm^{-1}. From their intensities using the molar absorbance in *n*-hexane solvent $\varepsilon_M = 699$ cm^2/mmol and $\varepsilon_M = 843$ cm^2/mmol, respectively, a diethyl malonate concentration of 0.019 mmol/cm^3 could be calculated, which corresponds to a 95% yield. Isolation of the precipitate by filtration gave 77 mg of **4** as a dark orange–red powder, which corresponds to a 89% yield.

3.5. Reaction of [μ_2-{ethoxycarbonyl(methylene)}-μ_2-(carbonyl)-(tricarbonyl-cobalt)-(tri-phenylphosphane-dicarbonyl-cobalt) (Co-Co)] (3) with CO in the presence of ethanol

A solution of complex **3** (51.7 mg, 0.0815 mmol) and anhydrous ethanol (0.030 cm^3, 0.51 mmol) in 1.2 cm^3 of CH$_2$Cl$_2$ was pressurized with CO in an autoclave and was shaken at 25 °C for 24 h. The CH$_2$Cl$_2$ was removed from the brown colored product in vacuum, and the residue was dissolved in 4.0 cm^3 of *n*-hexane. The infrared spectrum in the 2200–1600 cm^{-1} range showed the characteristic ν(CO) bands of Co$_2$(CO)$_7$(PPh$_3$) and diethyl malonate. Comparison of the spectrum with that of known concentrations of authentic samples of Co$_2$(CO)$_7$(PPh$_3$) revealed the presence of 0.079 mmol of this complex in the reaction product, corresponding to a 97% yield. The concentration of diethyl malonate was calculated by using the known molar absorbance, which gave a 66% yield.

3.6. Reaction of ethyl diazoacetate with CO and ethanol in the presence of 2 mol% of 3

A solution of complex **3** (33.0 mg, 0.0520 mmol), ethyl diazoacetate (0.274 cm^3, 2.60 mmol), and anhydrous ethanol (0.22 cm^3, 3.75 mmol) in CH$_2$Cl$_2$ (5.0 cm^3) was pressurized with carbon monoxide (50 bar) at room temperature and shaken for 24 h at 45 °C. The infrared spectrum of the reaction mixture in the range of 2200–1600 cm^{-1} showed no bands of unchanged ethyl diazoacetate (ε_M(CH$_2$Cl$_2$, 2112 cm^{-1}) = 800 cm^2/mmol, and ε_M(CH$_2$Cl$_2$, 1692 cm^{-1}) = 605 cm^2/mmol) to be present, but strong ν(C=O) bands of diethyl malonate at 1749 and 1732 cm^{-1}, corresponding to a concentration of 0.4747 mmol/cm^3 (100% yield), which was calculated using the molar absorbance of diethyl malonate ε_M(CH$_2$Cl$_2$, 1749 cm^{-1}) = 579 cm^2/mmol, and ε_M(CH$_2$Cl$_2$, 1732 cm^{-1}) = 666 cm^2/mmol.

3.7. Reaction of ethyl diazoacetate with CO and ethanol in the presence of 2 mol% of Co$_2$(CO)$_7$(PPh$_3$)

A solution of Co$_2$(CO)$_7$(PPh$_3$) [14] (37.2 mg, 0.0645 mmol), ethyl diazoacetate (0.340 cm^3, 3.233 mmol), and anhydrous ethanol (0.284 cm^3, 4.84 mmol) in CH$_2$Cl$_2$ (6.1 cm^3) was pressurized with carbon monoxide (50 bar) at room temperature and shaken for 24 h at 45 °C. The infrared spectrum of the reaction mixture in the range of 2200–1600 cm^{-1} showed no bands of unchanged ethyl diazoacetate at 2112 and 1692 cm^{-1} to be present, but strong ν(CO) bands of diethyl malonate at 1749 and 1732 cm^{-1}, corresponding to a concentration of 0.445 mmol/cm^3, a 92.8% yield, which was calculated using the molar absorbance of diethyl malonate in CH$_2$Cl$_2$ (see above). The only other bands present were at 2078 (s), 2023 (s), 1988 (vs), and 1958 (m), characteristic of Co$_2$(CO)$_7$(PPh$_3$).

3.8. Reaction of complex 4 with CO in the presence of ethanol

A solution of complex **4** (43.4 mg, 0.05 mmol) and anhydrous ethanol (0.014 cm^3, 0.24 mmol) in 1.0 cm^3 of CH$_2$Cl$_2$ was pressurized with CO (50 bar) in an autoclave and was shaken at 25 °C for 24 h. The infrared spectrum of the light yellow colored product solution in the 2200–1600 cm^{-1} range showed the characteristic strong ν(CO) bands of [Co(CO)$_3$(PPh$_3$)$_2$][Co(CO)$_4$] [5] at 2010 and 1889 cm^{-1}, and those of diethyl malonate at 1749 and 1732 cm^{-1}. By using the molar absorbance of [Co(CO)$_3$(PPh$_3$)$_2$][Co(CO)$_4$] ε_M(CH$_2$Cl$_2$, 2010 cm^{-1}) = 1704 cm^2/mmol; and ε_M(CH$_2$Cl$_2$, 1989 cm^{-1}) = 2280 cm^2/mmol and those of diethyl malonate in CH$_2$Cl$_2$ (see above) for the calculation of the concentrations showed that practically all of the cobalt from the starting complex to be present in the form of [Co(CO)$_3$(PPh$_3$)$_2$][Co(CO)$_4$], and the yield of diethyl malonate is 96%.

3.9. Reaction of ethyl diazoacetate with CO and ethanol in the presence of 2 mol% of 4

A solution of complex **4** (40.5 mg, 0.0466 mmol), ethyl diazoacetate (0.245 cm^3, 2.33 mmol), and anhydrous ethanol (0.20 cm^3, 3.41 mmol) in CH$_2$Cl$_2$ (4.0 cm^3) was pressurized with carbon monoxide (50 bar) at room temperature and shaken for 24 h at 45 °C. The infrared spectrum of the tea-colored reaction product in the range of 2200–1600 cm^{-1} using a 0.00265 cm CaF$_2$ solution cell showed no bands of unchanged ethyl diazoacetate, but strong ν(C=O) bands of diethyl malonate at 1749 and 1732 cm^{-1}, corresponding

to a concentration of 0.522 mmol/cm^3, a 98% yield. An infrared spectrum of the product using a 0.02153 cm CaF$_2$ solution cell revealed bands of [Co(CO)$_3$(PPh$_3$)$_2$][Co(CO)$_4$] at 2110 and 1888 cm^{-1}, and traces of Co$_2$(CO)$_6$(PPh$_3$)$_2$ at 1957 cm^{-1}.

3.10. Reaction of ethyl diazoacetate with CO and ethanol in the presence of 2 mol% of Co$_2$(CO)$_6$(PPh$_3$)$_2$

A mixture of Co$_2$(CO)$_6$(PPh$_3$)$_2$ [5] (25.7 mg, 0.0317 mmol), ethyl diazoacetate (0.166 cm^3, 1.58 mmol), and anhydrous ethanol (0.140 cm^3, 2.38 mmol) in CH$_2$Cl$_2$ (3.0 cm^3) was pressurized with carbon monoxide (50 bar) at room temperature and shaken for 150 h at 45 °C. The infrared spectrum of the tea-colored reaction product in the range of 2200–1600 cm^{-1} showed no bands of unchanged ethyl diazoacetate at 2112 cm^{-1} and 1692 cm^{-1}, but strong ν(C=O) bands of diethyl malonate at 1749 and 1732 cm^{-1}, corresponding to a concentration of 0.477 mmol/cm^3, a 100% yield).

Repeating the above reaction under identical conditions but using [Co(CO)$_3$(PPh$_3$)$_2$][Co(CO)$_4$] (26.8 mg, 0.032 mmol) as the catalyst precursor gave the same total conversion of ethyl diazoacetate to diethyl malonate.

3.11. Reaction of ethyl diazoacetate with CO and ethanol in the presence of 2 mol% of Co$_2$(CO)$_6$(dppm)

A mixture of Co$_2$(CO)$_6$ (dppm) [18,19] (25.9 mg, 0.0386 mmol), ethyl diazoacetate (0.205 cm^3, 1.58 mmol), and anhydrous ethanol (0.176 cm^3, 3.0 mmol) in CH$_2$Cl$_2$ (4.0 cm^3) was pressurized with carbon monoxide (50 bar) at room temperature and shaken for 96 h at 45 °C. The infrared spectrum of the light yellow–orange colored reaction product in the range of 2200–1600 cm^{-1} showed no bands of unchanged ethyl diazoacetate at 2112 cm^{-1} and 1692 cm^{-1}, but characteristic ν(CO) bands of Co$_2$(CO)$_6$(dppm) and diethyl malonate (IR Co$_2$(CO)$_6$(dppm) in CH$_2$Cl$_2$: ν(C≡O) 2045 ($\varepsilon_M = 2808$ cm^2/mmol), 2012 ($\varepsilon_M = 3406$ cm^2/mmol), 1985 ($\varepsilon_M = 3751$ cm^2/mmol), ν(C=O) 1820 ($\varepsilon_M = 823$ cm^2/mmol), 1794 ($\varepsilon_M = 1066$ cm^2/mmol) cm^{-1}). Using the molar absorbance in the quantitative analysis of the spectra [Co$_2$(CO)$_6$(dppm)] = 0.0088 mmol/cm^3, and [diethyl malonate] = 0.423 mmol/cm^3, were obtained corresponding to a 99% recovery of the starting Co$_2$(CO)$_6$(dppm) and a 95% yield of diethyl malonate at the end of the reaction.

Acknowledgements

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[2] CCDC-268330 contains the crystallographic data for complex **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk).

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