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Reactions of ^{13}CO with Ethoxycarbonylcarbene-Bridged Dicobalt Carbonyl Complexes: [μ_2-{Ethoxycarbonyl(methylene)}-μ_2-(carbonyl)-bis(tricarbonylcobalt)(*Co*–*Co*)] and [Di-μ_2-{ethoxycarbonyl(methylene)}-bis(tricarbonylcobalt)(*Co*–*Co*)]

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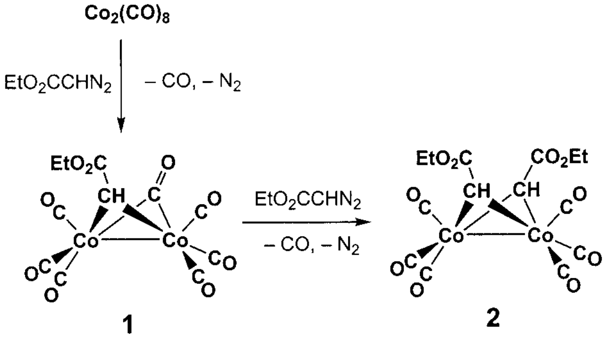
In a CH_2Cl_2 solution, under an atmospheric pressure of ^{13}CO, the bridging and terminal CO ligands of the cobalt complex [μ_2-{ethoxycarbonyl(methylene)}-μ_2-(carbonyl)bis(tricarbonylcobalt)(*Co*–*Co*)] (**1**) exchange with external ^{13}CO at the same rate. The overall rate of CO exchange is k_{obs} (10 °C) = 9.4×10^{-3} s^{-1} and k_{obs} (25 °C) = $(20.1\pm1.2)\times10^{-3}$ s^{-1}. In the presence of excess ethanol diethyl malonate (DEM), $EtO_2{}^{13}CCH_2CO_2Et$ is formed from **1** at a much smaller rate [k_{DEM} (10 °C) = 0.40×10^{-5} s^{-1} and k_{DEM} (25 °C) = $(1.2\pm0.1)\times10^{-5}$ s^{-1}]. On the other hand, the complex [di-μ_2-{ethoxycarbonyl(methylene)}bis(tricarbonylcobalt)(*Co*–*Co*)] (**2**) does not exchange its CO ligands for ^{13}CO at all at 10 or 25 °C. In the presence of excess ethanol, diethyl malonate with natural isotopic distribution, and ^{13}CO, ligands containing complex **1** are formed simultaneously and at the same rate, which is k_{obs} (10 °C) = $(15.2\pm1.1)\times10^{-5}$ s^{-1} and k_{obs} (25 °C) = $(33.5\pm1.8)\times10^{-5}$ s^{-1}. Variable temperature ^{13}C NMR spectra of **1** and **2** reveal fluxional behavior for both complexes.

Introduction

In the course of the past decades several dicobalt carbonyl complexes having no more than one or two carbene ligands have been prepared and the crystal structures of some representative examples determined.[1] In most of these complexes the substituted methylene- and vinylidene-type carbenes are in a bridging position between the two cobalt atoms,[2–18] while in a few recent examples *N*-heterocyclic carbene(s) are in terminal positions.[19,20]

Diverse methods of preparation have been applied to obtain dicobalt carbonyl carbene complexes. In the case of **1** and **2** (see Scheme 1) the two μ_2-CO ligands in $Co_2(CO)_8$ were replaced effectively one by one by ethoxycarbonylcarbene[18] using the carbene transfer reaction[21] between ethyl diazoacetate and $Co_2(CO)_8$.

The complexes [μ_2-{ethoxycarbonyl(methylene)}-μ_2-(carbonyl)bis(tricarbonylcobalt)(*Co*–*Co*)] (**1**) and [di-μ_2-{ethoxycarbonyl(methylene)}bis(tricarbonylcobalt)(*Co*–*Co*)] (**2**) were found to be intermediates in the octacarbonyldicobalt-catalyzed carbonylation of ethyl diazoacetate to ethyl malonic acid derivatives.[18] The key step in these carbonylation reactions is the facile coupling of carbon monoxide with the bridging carbene ligand to form the highly reactive ethoxycarbonyl ketene,[22] which rapidly converts in the presence of a suitable scavenger to the corresponding malonic acid monoethyl ester derivative. For example, using ethanol as the scavenger results in the formation of diethyl malonate [Equations (1) and (2)].



Scheme 1.

$$\mathbf{2} + 2CO + EtOH \xrightarrow[1\ bar]{25\ °C} \mathbf{1} + EtO_2CCH_2CO_2Et \quad (1)$$

$$\mathbf{1} + 2CO + EtOH \xrightarrow[1\ bar]{25\ °C} Co_2(CO)_8 + EtO_2CCH_2CO_2Et \quad (2)$$

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Applying ^{13}CO in the gas phase, as in Equations (1) and (2), a clear decision could be made as to whether ^{13}CO from the gas phase or the CO from the complexes is incorporated into the diethyl malonate product.

Results and Discussion

The infrared spectrum of a solution of **1** in dichloromethane under an atmosphere of ^{13}CO changes rapidly with time. Next to the original terminal carbonyl absorptions at 2112, 2075, 2048 cm^{-1}, and next to the bridging carbonyl absorption at 1853 cm^{-1}, several new initially rapidly growing bands in the terminal ν(C≡O) range and one in the bridging ν(C=O) range appeared immediately after exposing the solution to ^{13}CO. The well separated bridging ν(^{12}C=O) and ν(^{13}C=O) bands at 1853 and 1810 cm^{-1}, respectively, were suitable for quantitative analysis and to calculate the rate of ^{13}CO exchange. The strongly overlapping various terminal ν(C≡O) bands prevented the calculation of the concentrations of the different ^{13}CO containing species. However, the relative intensity values of the different totally symmetric bands of the complexes containing one, two, three, four, and five ^{13}CO ligands at 2112, 2107, 2101, 2096, and 2090 cm^{-1}, respectively, could be established. From the beginning of the reaction a parallelity of the growing amounts of complexes having ^{13}C in the bridging CO and the shift of the relative intensity values of the total symmetric bands is observed (see Table 1). Therefore the extent of ^{13}CO incorporation as calculated from the intensity of the ν(^{13}C=O) band reflects the overall level of ^{13}CO incorporation in complex **1**. Because there is no perceptible difference in the ^{13}CO exchange rate of the bridging and the terminal CO ligands it can be concluded that the intramolecular exchange of the different CO groups in complex **1** is much faster than the rate of ^{13}CO incorporation. This is in agreement with the fluxional behavior deduced from the results of the variable temperature ^{13}C NMR experiments of **1** in CD_2Cl_2 solutions. At ambient temperature we observed only one coordinated carbonyl resonance at δ = 201.85 ppm, which splits at 185 K into resonances at 195.65, 196.95, 198.16 ppm (three different terminal CO ligands), and 227.26 ppm (bridging CO) showing virtually 2:2:2:1 integral ratios.

From the data in Table 1 the overall rate of ^{13}CO exchange of complex **1** was calculated as k_{obs} (10 °C) = 9.4×10^{-3} s^{-1}. This rate is about 50% higher than that for $Co_2(CO)_8$ extrapolated at 10 °C from literature values[23] or as measured by us in order to check our technique applied in the present work. The CO-exchange reaction of $Co_2(CO)_8$ with external CO and the fluxional behavior of $Co_2(CO)_8$ have been intensively investigated in the past On the basis of X-ray structure determination it is known that $Co_2(CO)_8$ in the solid state exists exclusively in the form of a bridged isomer with two μ_2-CO and six terminal CO ligands.[24] In solution this bridged isomer is in fast equilibrium with two nonbridged isomers.[25] The fast inter-conversion of the bridged and nonbridged structures makes it understandable that in the slower exchange reaction with external CO all eight CO ligands exchange at the same rate.[23] Because the rate of CO exchange was found not to depend on the CO concentrations it was concluded that the CO exchange happens by a dissociative mechanism with the involvement of a $Co_2(CO)_7$ intermediate.[23] A similar mechanism might be operating in the case of complex **1**, which involves the rate-determining formation of a coordinative unsaturated $Co_2(CO)_6(CHCO_2Et)$ intermediate that takes up CO in a fast reaction. A very fast intramolecular exchange of the bridging and terminal CO ligands distributes labeled car-

Table 1. The amount of ^{13}CO found in the μ_2-position of $Co_2(CO)_6(\mu_2\text{-}CO)(\mu_2\text{-}CHCO_2Et)$ (**1**) (0.0224 mmol) in a CH_2Cl_2 solution (7.0 cm^3), and the observed relative intensity values of the total symmetric ν(C≡O) bands in the reaction with CH_2Cl_2-saturated ^{13}CO (99% ^{13}C) (0.30 mmol) at 10 °C and 740 Torr total pressure at various reaction times.

Reaction time [s]	^{13}CO found in the μ_2-position[a] [mmol]	Relative intensity values of the observed total symmetric ν(C≡O) bands at:						
		2112	2107	2101	2096	2090	(2087)[b]	2080 [cm^{-1}]
97	0.0035	10.0	7.4	2.2	0.5			
150	0.0051	6.1	10.0	7.7	2.7	0.4		
195	0.0066	5.1	10.0	9.1	4.6	1.0		
240	0.0076	3.1	8.7	10.0	6.0	1.6		
296	0.0087	2.0	7.3	10.0	7.6	2.7		
341	0.0095	1.2	6.0	10.0	8.9	3.9		
389	0.0099	0.8	5.0	10.0	9.5	5.1		
428	0.0105	0.6	4.4	9.5	10.0	6.0		
465	0.0110	0.5	3.8	8.8	10.0	6.4		
508	0.0116		2.1	8.0	10.0	6.8		
548	0.0120		2.1	7.8	10.0	7.5		
596	0.0123		2.0	7.5	10.0	7.6		
635	0.0128		2.0	7.3	10.0	8.0		
686	0.0130			7.1	10.0	8.2		
731	0.0132			6.6	10.0	8.5		
2028	0.0146			4.5	9.4	10.0		1.7

[a] Calculated from the intensity value of the observed ν(^{13}C=O) band at 1810 cm^{-1} using ε_M = 916 cm^2/mmol. [b] Shoulder. Its relative intensity value could not be established.

bon monoxide statistically in the bridging and terminal positions.

In the presence of ethanol, the reaction of carbon monoxide with complex **1** results in the formation of $Co_2(CO)_8$ and diethyl malonate [Equation (2)]. The data in Table 2 show that complex **1** reacts three orders of magnitude slower to form diethyl malonate and $Co_2(CO)_8$ than in the ^{13}CO-exchange reaction. Under an atmosphere of ^{13}CO, owing to the preceding fast ^{13}CO-exchange and the subsequent slow diethyl malonate formation, we could not decide whether complex-bound ^{13}CO or external ^{13}CO is incorporated in the $EtO_2{}^{13}CCH_2CO_2Et$ product. Performing the reaction of **1** with ethanol under an atmosphere of argon leads to reaction products of $Co_4(CO)_{12}$ and diethyl malonate [Equation (3)], as seen from the growing intensities of bands in the infrared spectra of the reaction solution with elapsing reaction time at 2065 and 2055 cm^{-1} [most intensive $\nu(C{\equiv}O)$ bands of $Co_4(CO)_{12}$ in CH_2Cl_2] and at 1749 and 1732 cm^{-1} [$\nu(C{=}O)$ bands of $EtO_2CCH_2CO_2Et$]. This result strongly suggests that the source of CO is one of the coordinated carbonyls in complex **1**.

$$\mathbf{1} + EtOH \xrightarrow[\text{Argon}]{25\ °C} \mathbf{1/2\ Co_4(CO)_{12}} + EtO_2CCH_2CO_2Et \qquad (3)$$

The reaction of complex **2** with ethanol under an atmosphere of argon gave **1** and diethyl malonate [Equation (4)]. The amount of complex **1** formed in the reaction [Equation (4)] was found to be only about 70% of that expected according to the stoichiometry. A reason for this might be that the missing amount served, by decomposition, as a CO source for complex **1**.

$$\mathbf{2} + EtOH \xrightarrow[\text{Argon}]{10\ °C} \mathbf{1} + EtO_2CCH_2CO_2Et \qquad (4)$$

In the absence of ethanol complex **2** and CO convert to complex **1** and the ethoxycarbonyl ketene dimer [one characteristic $\nu(C{=}O)$ band is at 1733 cm^{-1}] according to Equation (5).

$$\mathbf{2} + 2CO \xrightarrow[\text{1 bar}]{10\ °C} \mathbf{1} + 1/2(EtO_2CCH{=}C{=}O)_2 \qquad (5)$$

Performing the reaction in Equation (1) under an atmosphere of ^{13}CO results in the formation of the ^{13}C-labeled complex **1** and diethyl malonate with a natural abundance of ^{13}C; these compounds were simultaneously observed in the infrared spectrum of the reaction solution. Thus, the several new $\nu(^{13}C{\equiv}O)$ absorptions in the 2107–1959 cm^{-1} range and the one new $\nu(^{13}C{=}O)$ absorption at 1810 cm^{-1} could be assigned to complex **1**, and the new $\nu(C{=}O)$ absorptions at 1749 and 1732 cm^{-1} are characteristic of $EtO_2CCH_2CO_2Et$. The observed rate of formation of complex **1** and that of diethyl malonate in Equation (1) was found to be practically the same (see Table 3). The GC-MS analysis of the reaction product confirmed the presence of diethyl malonate showing an identical mass spectrum to that of an authentic sample and the published mass spec-

Table 2. Initial rate of the overall ^{13}CO incorporation (r_{in}) and the observed rate constant ($k_{obs} = r_{in}/[\mathbf{1}]$) in the reaction of complex **1** with ^{13}CO at 740 Torr total pressure in CH_2Cl_2 solution, and the initial rate of diethyl malonate formation (r_{DEM}) and the observed rate constant ($k_{DEM} = r_{DEM}/[\mathbf{1}]$) in the presence of ethanol.

Temperature [°C]	[**1**] [mol/dm^3]	[EtOH] [mol/dm^3]	$r_{in} \times 10^5$ [mol/dm^3 s]	$k_{obs} \times 10^3$ [1/s]	$r_{DEM} \times 10^7$ [mol/dm^3 s]	$k_{DEM} \times 10^5$ [1/s]
10	0.0032	0.000	3.0	9.4	–	–
10	0.0166	0.070	–	–	0.66[a]	0.40[a]
25	0.0030	0.000	5.9	19.7	–	–
25	0.0030[b]	0.070	–	–	0.39	1.30
25	0.0061	0.070	11.7	19.2	0.71	1.16
25	0.0142	0.070	30.3	21.3	1.67	1.18
25	0.0142	0.070			4.40[c]	3.10[c]

[a] Reaction was started under an atmosphere of CO instead of ^{13}CO. [b] Using $Co_2(^{13}CO)_7(CHCO_2Et)$ with 63% ^{13}C enrichment of the coordinated carbonyl ligands. [c] Reaction was started under argon.

Table 3. The initial rate of diethyl malonate formation (r_{DEM}), the observed rate constant ($k_{DEM} = r_{DEM}/[\mathbf{2}]$), the initial rate of complex **1** formation ($r_{\mathbf{2}\to\mathbf{1}}$), and the observed rate constant ($k_{\mathbf{2}\to\mathbf{1}} = r_{\mathbf{2}\to\mathbf{1}}/[\mathbf{2}]$) in the reaction of complex **2** with ^{13}CO at 745 Torr total pressure in CH_2Cl_2 solution.

Temperature [°C]	[**2**] [mol/dm^3]	[EtOH] [mol/dm^3]	$r_{DEM} \times 10^7$ [mol/dm^3 s]	$k_{DEM} \times 10^5$ [1/s]	$r_{\mathbf{2}\to\mathbf{1}} \times 10^7$ [mol/dm^3 s]	$k_{\mathbf{2}\to\mathbf{1}} \times 10^5$ [1/s]
10	0.0166	0.070	27.0	16.3	26.4	15.9
10	0.0063	0.070	9.5	15.1	8.9	14.2
10	0.0166	0.070	9.13[a]	5.5[a]	3.3[a]	2.0[a]
10	0.0063	0.000			3.2	5.1
25	0.0063	0.070	21.7[b]	34.4[b]	20.5[b]	32.6[b]

[a] Reaction was started under argon. [b] Reaction was started under CO.

trum.[26] As the reaction progressed the $\nu(C\equiv O)$ range in the infrared spectrum became very complex with the appearance of various ^{13}CO-containing **1** products in the reaction solution. However, the $\nu(C\equiv O)$ bands of the starting complex **2** at 2112 and 2080 cm^{-1} are well recognized until the conversion according to Equation (1) is complete. This means that in contrast to complex **1** no ^{13}CO incorporation takes place in complex **2** during the contact with external ^{13}CO. Hence, the source of CO involved in the formation of diethyl malonate is one of the coordinated carbon monoxide ligands of complex **2**.

Complex **2** in solution shows fluxional behavior. In $CDCl_3$ at ambient temperature only one coordinated carbonyl resonance at δ = 196.63 ppm can be seen in the ^{13}C NMR spectrum. However, in CD_2Cl_2 solution at 200 K this resonance splits into resonances at 195.91 and 197.84 ppm with an integral ratio of 1:2. GIAO NMR shielding calculations gave the same qualitative results (see Table 4).

Table 4. GIAO and experimental ^{13}C chemical shifts δ [ppm] and intensity ratios (in parenthesis) of the coordinated carbonyl ligands of $Co_2(CO)_8$, $Co_2(CO)_7(CHCO_2Et)$ (**1**), and $Co_2(CO)_6(CHCO_2Et)_2$ (**2**).

Complex	Calculated ^{13}C chemical shifts at the B3LYP/6-31G* level of theory	Experimentally found ^{13}C chemical shifts
$Co_2(CO)_8$	193.3, 201.3, 237.8 (1:2:1)	182, 234 (approximately 4:1)[a]
1	195.9, 199,7, 205.2, 234.8 (2:2:2:1)	195.65, 196.95, 198.16, 227.26 (2:2:2:1)[b]
2	200.5, 201.5 (1:2)	195.91, 197.84 (1:2)[b]

[a] See ref.[32] [b] This work.

Conclusions

The results of experiments with complex **1** and **2** in the presence and in the absence of the reagents ^{13}CO, CO, and ethanol suggest that the origin of the new organic carbonyl group, formed through the coupling of CO and a μ_2-ethoxycarbonylcarbene ligand of the complexes, is one of the complex-bound carbonyl ligands and not an external CO.

Experimental Section

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.[27] Solvents were dried and distilled under an atmosphere of argon according to standard procedures.[28] IR spectra were recorded with a Thermo Nicolet Avatar 330 FTIR spectrometer using 0.00265, 0.00765, 0.02095, or 0.05097 cm CaF_2 solution cells, calibrated by the interference method.[29] ^{13}C NMR spectra were recorded with a Bruker 400 MHz spectrometer at 100 MHz using CD_2Cl_2 as the solvent. Chemical shifts δ are reported in ppm relative to CH_2Cl_2 (δ = 53.10 ppm). The GC-MS analyses were performed with an HP 5890 instrument equipped with a mass-selective detector working at 70 eV. Octacarbonyldicobalt[30] and the μ_2-ethoxycarbonylcarbene complexes **1**[18] and **2**[18] were prepared by literature procedures. ^{13}CO was obtained from Sigma–Aldrich.

^{13}CO Exchange Experiment with $Co_2(CO)_8$: The ^{13}CO exchange reactions were performed in a magnetically stirred thermostatted glass reactor (18, 35, or 61 cm^3 total volume), equipped with a gas inlet and with a silicon disk port. The gas inlet was connected through a two-way stopcock to a vacuum pump and a ^{13}CO-filled gas burette. A stainless-steel cannula connected to a 3-port T-valve was immersed close to the bottom of the reactor through the silicon disk. A Hamilton TLL syringe (2.5 cm^3 volume) and the IR cell (through a PTFE tube) were connected to the two other ports of the valve. Samples from the reaction mixture for IR analyses were withdrawn through the stainless steel cannula, and pumped into the IR cell continuously by using the Hamilton TLL syringe, allowing the liquid sample to return from the IR cell to the reactor through a second PTFE tube. The solvent and the solution of the reactant were added to the ^{13}CO-filled reactor through the silicon disk using Hamilton TLL syringes. IR spectra were recorded at every minutes or less. The initial rates of ^{13}CO exchange were calculated from the intensity values of the $\nu(^{13}C{=}O)$ band using the first 3 to 8 points. The ε_M of the $\nu(^{13}C{=}O)$ band was calculated from the known ε_M value of the $\nu(^{12}C{=}O)$ band[18,31] by multiplying it with the mass correction value $(12/13)^{-0.5}$ = 0.96077. In a typical experiment using the reactor with a 35-cm^3 total volume, the reactor and its connected parts were first evacuated then filled with ^{13}CO, and CH_2Cl_2 (4.5 cm^3) was added. After stirring at 10 °C for 10 min the reaction was started by injection of $Co_2(CO)_8$ (0.064 mmol) in a precooled CH_2Cl_2 solution (2.5 cm^3). Infrared spectra were recorded from four scans after 38, 75, 114, 164, 207, 253, 297, 345 s, and so on, until ^{13}CO enrichment of 65% had been reached. The rate constant of the overall ^{13}CO exchange $(6.0\pm1.2)\times10^{-3}$ s^{-1} was calculated from the initial changes of the $Co_2(CO)_8$ concentration as obtained from the intensity values measured at 1847 cm^{-1} (ε_M = 938 cm^2/mmol), or that of $Co_2(^{13}CO)_x(CO)_{8-x}$ from the intensity values measured at 1807 cm^{-1} (ε_M = 902 cm^2/mmol) by dividing the observed initial rate by the initial $Co_2(CO)_8$ concentration.

^{13}CO Exchange Experiments with Complex 1: In a typical experiment using the reactor with an 18-cm^3 total volume, the reactor and its connected parts were first evacuated and then filled with ^{13}CO (740 Torr total pressure), and then CH_2Cl_2 (4.5 cm^3) was added. After stirring at 10 °C for 10 min the reaction was started by injection of a precooled solution of complex **1** (0.0224 mmol) in CH_2Cl_2 (2.5 cm^3). Infrared spectra were recorded from four scans after 97, 150, 195, 240, 296, 341 s, and so on (see Table 1), until a ^{13}CO enrichment of 63% had been reached in ca. 34 min. The rate constant of the overall ^{13}CO incorporation (9.4×10^{-3} s^{-1}) was calculated from the initial changes of the concentration of complex **1**, as obtained from the intensity values measured at 1853 cm^{-1} (ε_M = 953 cm^2/mmol), or that of $Co_2(^{13}CO)_x(CO)_{7-x}(CHCO_2Et)$ from the intensity values measured at 1810 cm^{-1} (ε_M = 916 cm^2/mmol), by dividing the observed initial rate by the initial concentration of complex **1**.

At higher initial concentrations of complex **1** and at 25 °C the reactor with a volume of 35 or 61 cm^3 was used in order to achieve at least 50% ^{13}CO enrichment at the end of the reaction.

Diethyl Malonate Formation from Complex 1 and Ethanol under ^{13}CO: Absolute ethanol (0.029 cm^3, 0.496 mmol) was added to a solution of complex **1** in CH_2Cl_2 (7.0 cm^3, 0.003 mol/dm^3) with 62.6% ^{13}C-enrichment, obtained in a reactor with a 61-cm^3 volume at 25 °C under a ^{13}CO atmosphere in 10 min. The initial rate of diethyl malonate formation (r_{DEM}) was calculated from the intensity values measured at 1749 cm^{-1} (ε_M = 579 cm^2/mmol, unlabeled diethyl malonate), at 1731 cm^{-1} (ε_M = 597 cm^2/mmol, 62.6% ^{13}C-labeled and 37.4% unlabeled diethyl malonate), and at 1713 cm^{-1} (ε_M = 640 cm^2/mmol, ^{13}C-labeled diethyl malonate) The observed rate constant (k_{DEM}) was obtained from the initial rate of diethyl malonate formation by dividing it with the initial concentration of complex **1**. The GC-MS analyses of the diethyl malonate product show an $M^{+\cdot}$ peak at m/z = 161, and the characteristic fragment peaks: M – 27, M – 45, and M – 72 at m/z = 134, 116, and 89, respectively.

Diethyl Malonate Formation from Complex 1 and Ethanol under Ar: Absolute ethanol (0.031 cm^3, 0.531 mmol) was added to a solution of complex **1** (0.1075 mmol) in CH_2Cl_2 (7.5 cm^3) under an atmosphere of argon at 25 °C, and the initial rate of diethyl malonate formation (r_{DEM}) and the observed rate constant (k_{DEM}) were determined as described above but using the intensity values measured at 1749 and 1732 cm^{-1}.

Attempted ^{13}CO Exchange Experiments with Complex 2: In a typical experiment using the reactor with a 35-cm^3 total volume, the reactor and its connected parts were first evacuated and then filled with ^{13}CO (745 Torr total pressure), and finally CH_2Cl_2 (4.3 cm^3) was added. After stirring at 10 °C for 10 min the reaction was started by injection of a precooled solution of complex **2** (0.0475 mmol) in CH_2Cl_2 (3.2 cm^3). Infrared spectra were recorded from 16 scans after 2, 10, 15, 20 min, and so on, until almost all of complex **2** was converted to complex **1** (8 h), afterwhich conversion could be followed by the gradual decrease of intensity of the characteristic bands of complex **2** at 2112 cm^{-1} (ε_M = 1100 cm^2/mmol) and 2080 cm^{-1} (ε_M = 3768 cm^2/mmol) and the increase of intensity of the characteristic ν(C=O) bands of the labeled and unlabeled complex **1** at 1810 cm^{-1} (ε_M = 916 cm^2/mmol) and 1853 cm^{-1} (ε_M = 953 cm^2/mmol), respectively. At the end of the reaction 57% ^{13}CO enrichment of complex **1** was found based on the intensity values measured at 1853 and 1810 cm^{-1}. From the initial rate of the formation of complex **1** ($r_{\mathbf{2}\rightarrow\mathbf{1}} = 3.2\times10^{-7}$ mol/dm^3 s) the observed rate constant ($k_{\mathbf{2}\rightarrow\mathbf{1}} = 5.1\times10^{-5}\,s^{-1}$) was calculated by dividing the observed initial rate by the initial concentration of complex **2**.

Diethyl Malonate Formation from Complex 2 and Ethanol under ^{13}CO: In a typical experiment the reactor (35-cm^3 total volume) and its connected parts were first evacuated and then filled with ^{13}CO until a barometric pressure of 740 Torr. CH_2Cl_2 (1.0 cm^3) and absolute ethanol (0.033 cm^3, 0.565 mmol) were added. After stirring at 10 °C for 10 min the reaction was started by injection of complex **2** (0.133 mmol) into a precooled CH_2Cl_2 solution (7.0 cm^3) maintaining the pressure in the reactor at 740 Torr by means of the connected gas burette. Infrared spectra were recorded from four scans after 61, 107, 164, 221, 300, 427, 530, 645, 750, 865 s, and so on, until the infrared spectrum showed no more changes in the 2200–1600 cm^{-1} range (3.5 h). The rate constant for the formation of $EtO_2CCH_2CO_2Et$ was calculated from the initial changes of its concentration as obtained from the intensity values measured at 1749 cm^{-1} (ε_M = 579 cm^2/mmol) and at 1732 cm^{-1} (ε_M = 666 cm^2/mmol) by dividing the observed initial rate by the initial concentration of complex **2**. The GC-MS analyses of the diethyl malonate product show an $M^{+\cdot}$ peak at m/z = 160, and the characteristic fragment peaks: M – 27, M – 45, and M – 72 at m/z = 133, 115, and 88, respectively.

Diethyl Malonate Formation from Complex 2 and Ethanol under Ar: Absolute ethanol (0.033 cm^3, 0.565 mmol) was added to a solution of complex **2** (0.133 mmol) in CH_2Cl_2 (8.0 cm^3) under an atmosphere of argon at 10 °C, and the initial rate of diethyl malonate formation (r_{DEM}) and the observed rate constant (k_{DEM}) were determined as described above using the intensity values of diethyl malonate measured at 1749 and 1732 cm^{-1}.

Variable-Temperature ^{13}C NMR Spectra of Complex 1 and 2: From freshly chromatographed dichloromethane solutions of complex **1** and **2**, or from ^{13}CO enriched samples of complex **1** (see above), 0.25 mol/dm^3 solutions in CD_2Cl_2 were prepared by removing the dichloromethane solvent at –5 °C in vacuo (17 Torr) and dissolving the oily residue in CD_2Cl_2 under an atmosphere of argon. The ^{13}C NMR spectra were recorded at 273, 233, 200, and 185 K.

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