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Carbonylation–decarbonylation reactions of the carbomethoxymethylcobalt complexes $CH_3O_2CCHRCo(CO)_3L$ ($R = H, CH_2CO_2CH_3; L = CO, PPh_3$) and their acyl derivatives

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Abstract

The primary and secondary alkyl- and acylcobalt carbonyl complexes $CH_3O_2CCHRCo(CO)_3L$ and $CH_3O_2CCHRC(O)Co(CO)_3L$ ($R = H$ or $CH_2CO_2CH_3$; $L = CO, PPh_3$) (**1–8**) have been prepared and studied by a variety of IR and ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ and $^{17}O\{^1H\}$ NMR spectroscopic methods. Unlike their primary analogues, all the secondary complexes readily undergo a reversible carbonylation–decarbonylation reaction. The new alkyl complex *trans*-$CH_3O_2CCH_2Co(CO)_3PPh_3$ (**3**) was characterized in solution, and exhibited remarkably different properties from the well-known homologue *trans*-$CH_3CH_2O_2CCH_2Co(CO)_3PPh_3$, i.e. it readily decomposes to $[Co(CO)_3PPh_3]_2$, suggesting homolytic dissociation of the carbon–cobalt bond, and its IR spectrum exhibits an organic $\nu(CO)$ absorbance at an unusually low frequency, pointing to an oxygen–cobalt interaction. The corresponding acyl complex *trans*-$CH_3O_2CCH_2C(O)Co(CO)_3PPh_3$ (**4**) was isolated as a stable solid, but smoothly decarbonylated in solution to **3**. Multinuclear NMR spectroscopic monitoring of this reaction suggested the intermediate formation of *cis*-$CH_3O_2CCH_2Co(CO)_3PPh_3$, providing the first direct evidence for alkyl migration in cobalt carbonyl complexes.

Keywords: Alkyl; Acyl; Carbonylation; Decarbonylation; Cobalt; Carbonyl

1. Introduction

Non-fluorinated alkyl- and acylcobalt carbonyl complexes and their CO insertion and deinsertion reactions (Eq. (1)) have attracted considerable interest in the last 15 years [1] due to their relevance to many practically important homogeneous catalytic processes [2].

$$RCo(CO)_3L + CO \underset{L = CO,\ \text{phosphines}}{\rightleftharpoons} RC(O)Co(CO)_3L \qquad (1)$$

As a result, a great number of both types of compound has been made and the general factors influencing the equilibrium in Eq. (1) have been established. Most recently, a kinetic study of the equilibrium between methyl- and acetylcobalt tetracarbonyl was reported [3].

In spite of the spectacular development of this field, however, some aspects of the preparation and characterization of alkyl- and acylcobalt carbonyls are relatively unexplored. For example, very little is known about the complexes where R is a secondary alkyl group. Furthermore, until recently infrared spectroscopy was used as the primary tool for structural characterization, but high-field multinuclear NMR spectroscopy (particularly ^{13}C and ^{31}P) can provide additional and more precise information about the structure and electronic properties of the compounds in Eq. (1). There is also limited information available about the characteristics of homologues of alkyl- and acylcobalt complexes. Recent systematic studies of alkyl- and acylmanganese pentacarbonyls, for instance, have shown that the length of the alkyl chain has a dramatic influence on their stability and the rate of CO insertion–deinsertion [4]. Finally, from a mechanistic point of view, it is widely accepted that both CO insertion and deinsertion proceed via a 1,2-alkyl-migration, which was proved by studies on complexes of metals other than cobalt [1c,5]. Thus, in the particular case of $RCo(CO)_3PR_3$ and $RC(O)$-$Co(CO)_3PR_3$, where the alkyl or acyl group and the phosphine ligand occupy mutually *trans* positions, the

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primary products of both processes should have a *cis* geometry, which has never been verified probably due to a fast rearrangement to the corresponding *trans* isomers [1k].

Recently, we have reported the preparation and characterization of the first stable *sec*-alkylcobalt tetracarbonyl $CH_3O_2CCH_2CH(CO_2CH_3)Co(CO)_4$ [1l,m], and reversible carbonylation–decarbonylation of the PPh_3-substituted derivatives $CH_3O_2CCH_2CH(CO_2CH_3)Co(CO)_3PPh_3$ and $CH_3O_2CCH_2CH(CO_2CH_3)C(O)Co(CO)_3PPh_3$ [1m]. These results prompted us to attempt carbonylation of $CH_3O_2CCH_2CH(CO_2CH_3)Co(CO)_4$ in order to complete this series of compounds, as well as to study the primary analogues $CH_3O_2CCH_2Co(CO)_3L$ and $CH_3O_2CCH_2C(O)Co(CO)_3L$ ($L = CO$, PPh_3) for comparative purposes. The latter compounds are homologues of the previously studied (ethoxycarbonyl)methyl and -acetyl derivatives [1a,k]. Here we report the preparation and IR and ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ and $^{17}O\{^1H\}$ NMR investigations of the complexes listed below (Eq. (2)).

$$CH_3O_2CCHRCo(CO)_3L + CO \rightleftharpoons CH_3O_2CCHRC(O)Co(CO)_3L \qquad (2)$$

	R	L	
1	H	CO	**2**
3	H	PPh_3	**4**
5	$CH_2CO_2CH_3$	CO	**6**
7	$CH_2CO_2CH_3$	PPh_3	**8**

2. Results and discussion

2.1. Preparation and properties of complexes 1–8

The parent primary complex $CH_3O_2CCH_2Co(CO)_4$ (**1**) was isolated as a volatile oil at room temperature in good yield from the heterogeneous reaction of solid $NaCo(CO)_4$ and methyl malonyl chloride in pentane (Eq. (3)). The reaction took place similarly in THF, but the product did not tolerate complete removal of the solvent.

$$CH_3O_2CCH_2C(O)Cl + NaCo(CO)_4 \rightarrow CH_3O_2CCH_2Co(CO)_4 + CO + NaCl \qquad (3)$$

Compound **1** has also been prepared recently from methyl bromoacetate and $NaCo(CO)_4$ [6], and the reported spectroscopic data agree well with those obtained previously, supporting its formulation as **1**. **1** has been demonstrated to be a key intermediate in the $NaCo(CO)_4$-catalyzed carbonylation of methyl chloroacetate to dimethyl malonate by methyl formate [6a], and could also be utilized as a catalyst for the carbonylation of aryl halides [6b]. In our hands, however, the reaction of $NaCo(CO)_4$ with methyl chloroacetate is not a viable preparative route to **1** (no reaction occurred under ambient conditions), probably due to the weak nucleophilicity of $[Co(CO)_4]^-$ [7].

The corresponding acyl complex $CH_3O_2CCH_2C(O)Co(CO)_4$ (**2**), an intermediate of reaction (3), could not be isolated even at low temperatures due to a rapid CO loss resulting in the formation of **1**. Compound **2** could only be detected in situ in small amounts by ^1H NMR spectroscopy when reaction (3) was carried out in $CDCl_3$ at −20°C, but its extreme instability prevented further characterization. The rapid decarbonylation of **2** is consistent with the postulate that the acyl–alkyl equilibrium is far on the alkyl side if the alkyl moiety contains an electron-withdrawing group [1c]. Small quantities of $HCo(CO)_4$ were also detected in this reaction mixture since the CH-acidic methyl malonyl chloride protonated some of the tetracarbonylcobaltate anion [8].

The PPh_3-substituted counterpart of **1**, $CH_3O_2CCH_2Co(CO)_3PPh_3$ (**3**), was obtained in two independent ways: (i) the reaction of methyl chloroacetate with $NaCo(CO)_3PPh_3$ due to its increased nucleophilic power compared with $NaCo(CO)_4$ [10], and (ii) the thermal decarbonylation of $CH_3O_2CCH_2C(O)Co(CO)_3PPh_3$ (**4**). However, **3** could not be isolated in either case since it readily decomposed to $[Co(CO)_3PPh_3]_2$ during the reaction and work up procedures. Nevertheless, it was characterized in solution by spectroscopic means and the data are consistent with the formulation.

The spontaneous decomposition of **3** to $[Co(CO)_3PPh_3]_2$ is similar to the behaviour of $CH_3CH{=}CHCH(CH_3)C(O)Co(CO)_3PPh_3$ [1l] and $EtOCH(CH_3)Co(CO)_3PPh_3$ [1n], and suggests homolytic carbon–cobalt bond dissociation resulting in the formation of a geminate radical pair. However, compound **3** is unique in that the absence of β-hydrogens eliminates the possibility of an alternative decomposition mechanism, the β-hydride elimination reaction. The instability of **3** is also interesting because the next homologue $EtO_2CCH_2Co(CO)_3PPh_3$, and several other compounds differing only in the substituents of the ester group, were found to be much more stable under identical conditions [1a].

In contrast, complex **4**, the PPh_3-substituted counterpart of **2**, could easily be obtained as a yellow microcrystalline solid by adding PPh_3 to a solution of **1** at low temperature (Eq. (4)).

$$CH_3O_2CCH_2Co(CO)_4 + PPh_3 \rightarrow CH_3O_2CCH_2C(O)Co(CO)_3PPh_3 \qquad (4)$$

Note that the next homologue, $EtO_2CCH_2C(O)Co(CO)_3PPh_3$, was previously reported to appear as an oily substance even below room temperature [1k]. Although **4** was stable in the solid state for prolonged times, it smoothly transformed in solution into **3** by losing one molecule of CO.

The secondary alkylcobalt complexes $CH_3O_2CCH_2$-$CH(CO_2CH_3)Co(CO)_4$ (**5**) and $CH_3O_2CCH_2CH(CO_2CH_3)Co(CO)_3PPh_3$ (**7**) were not available through halide/anion reactions since both $NaCo(CO)_4$ and $NaCo(CO)_3PPh_3$ gave only mixtures of dimethyl fumarate, dimethyl succinate and the corresponding cobalt carbonyl dimers when treated with dimethyl chlorosuccinate [11]. However, $HCo(CO)_4$ and dimethyl fumarate did afford **5** as a yellow crystalline material (Eq. (5)) [1l,m].

$$\textit{trans}\text{-}CH_3O_2CCH{=}CHCO_2CH_3 + HCo(CO)_4 \rightleftharpoons CH_3O_2CCH_2CH(CO_2CH_3)Co(CO)_4 \quad (5)$$

The reaction outlined in Eq. (5) is reversible, and thus **5** was found to decompose at room temperature via β-hydride elimination to $HCo(CO)_4$ [12]. At low temperatures, however, no decomposition but CO insertion took place (Eq. (6)) and the new acyl complex **6** could be identified by NMR spectroscopy.

$$CH_3O_2CCH_2CH(CO_2CH_3)Co(CO)_4 + CO \rightleftharpoons CH_3O_2CCH_2CH(CO_2CH_3)C(O)Co(CO)_4 \quad (6)$$

On the basis of ^1H NMR spectra, 10% of **5** transformed into **6** at −20°C and under 1 atm CO, while 30% of the starting alkyl complex was present in the form of **6** at −30°C and under 3.5 atm CO pressure.

Compound **5** also reacted with synthesis gas at room temperature and under pressure and resulted in the sole formation of dimethyl formylsuccinate, which was identified by NMR spectroscopy as a 47:53 equilibrium mixture with its enol tautomer $CH_3O_2CCH_2C(CO_2CH_3){=}CHOH$. This experiment confirmed that the equilibrium in Eq. (6) can be shifted completely to either side under appropriate conditions, and both **5** and **6** are true intermediates of the cobalt-catalyzed hydroformylation of dimethyl fumarate [13].

The PPh_3-substituted derivatives of **5** and **6**, i.e. **7** and **8** respectively, were prepared according to Eq. (4) and by subsequent decarbonylation of the acyl complex [1m]. Both **7** and **8** were thermally stable in the solid state and could be stored at room temperature for several months without significant degradation. Although **7**, unlike the primary analogue **3**, was reasonably thermally stable in solution and under argon, the acyl complex **8** (like **4**) was prone to CO loss under such conditions. When 100 atm of CO pressure was applied, this reaction was reversible [1m] (Eq. (7)).

$$CH_3O_2CH_2CH(CO_2CH_3)C(O)Co(CO)_3PPh_3 \rightleftharpoons CH_3O_2CCH_2CH(CO_2CH_3)Co(CO)_3PPh_3 + CO \quad (7)$$

2.2. *Spectroscopic characterization of complexes 1–8*

All complexes except **2** and **6** were characterized by IR spectroscopy (Table 1). These data generally support a local C_{3v} symmetry typical for both the alkyl- and acylcobalt complexes, tetracarbonyls and phosphine-substituted derivatives, having a trigonal bipyramidal structure [1c,k]. In the substituted compounds **3**, **4** and **7**, **8**, the PPh_3 ligand and the alkyl or acyl group always occupy the bis-axial (mutually *trans*) positions. The frequencies and relative intensities of absorbances characteristic of the CO ligands also correspond to the values anticipated for cobalt(I) complexes containing a carbalkoxymethyl group (Table 1).

Table 1
IR spectroscopic data of carbalkoxymethyl- and acetylcobalt carbonyl complexes in the ν(CO) region

R	ν(C≡O) (cm^{-1})	ν(C=O) (cm^{-1})	"acyl" ν(C=O) (cm^{-1})	Solvent	Lit.
$RCo(CO)_4$					
$CH_3O_2CCH_2$– (**1**) [a]	2110 m, 2045 s, 2035 vs, 2026 vs	1721 w		pentane	this work
$CH_3CH_2O_2CCH_2$–	2111 m, 2046 s, 2036 vs, 2027 vs	1720 m		hexane	[1a] [b]
$CH_3O_2CCH_2CH(CO_2CH_3)$– (**5**)	2111 m-s, 2046 s, 2036 vs, 2026 vs	1744 m-w, 1720 w		hexane	[1m]
$CH_3CH_2O_2CCH(CH_3)$–	2107 m, 2041 s, 2031 vs, 2021 vs	1716 w		hexane	[1f]
$RCo(CO)_3PPh_3$					
$CH_3O_2CCH_2$– (**3**)	2056 vw, 1988 vs, 1977 vs	1657 m		THF	this work
$CH_3CH_2O_2CCH_2$–	2049 vw, 1985 s, 1974 s	1709 m		hexane	[1a] [b]
$CH_3O_2CCH_2CH(CO_2CH_3)$– (**7**)	2043 vw, 1980 vs, 1967 vs	1729 s, 1696 m		KBr	[1m]
$CH_3CH_2O_2CCH(CH_3)$–	2042 w, 1974 vs, 1964 vs	1698 w		benzene	[14]
$RC(O)Co(CO)_3PPh_3$					
$CH_3O_2CCH_2$– (**4**)	2051 w, 1991 s, 1960 vs	1743 m	1654 m	KBr	this work
$CH_3O_2CCH_2CH(CO_2CH_3)$– (**8**)	2050 w, 1984 s, 1966 vs	1736 s	1665 m	KBr	[1m]
$CH_3CH_2O_2CCH_2$–	2053 w, 1987 s, 1969 s	1747 m	1680 m	hexane	[1k]
$CH_3CH_2O_2CCH(CH_3)$–	2052 w, 1988 vs, 1966 vs	1748 w	1672 w, br	heptane	[14]

[a] Literature data: 2115 m, 2045 s, sh, 2030 vs, 1737 m [6a]. [b] IR spectra of other (alkoxycarbonyl)methylcobalt carbonyl complexes containing the ester substituents Et, Bz, ^{t}Bu, (S)-(−)-2-MeBu and (1R,3R,4S)-(−)-Ment exhibit ν(C=O) absorbances in the range 1712–1722 cm^{-1} for tetracarbonyls and 1699–1712 cm^{-1} for PPh_3-substituted derivatives.

Table 2
Selected ^{1}H NMR spectroscopic data of primary carbalkoxymethyl-and acetylcobalt complexes

Compound	δ(CH_2) (ppm) [a]	Lit.
$CH_3O_2CCH_2Co(CO)_4$ (1)	2.16	this work
$CH_3O_2CCH_2Co(CO)_3PPh_3$ (3)	2.18 d (J_{PH} = 3 Hz)	this work
$CH_3CH_2O_2CCH_2Co(CO)_3PMePh_2$	2.08–2.14 m [b]	[1d]
$CH_3O_2CCH_2C(O)Co(CO)_4$ (2)	3.98 [c]	this work
$CH_3O_2CCH_2C(O)Co(CO)_3PPh_3$ (4)	4.09	this work
$CH_3CH_2O_2CCH_2C(O)Co(CO)_3PMePh_2$	4.04	[1d]

[a] Recorded in $CDCl_3$ relative to TMS. [b] Overlap with δ(PMe) and both resonances expected to couple to phosphorus. [c] The corresponding resonance of $CH_3O_2CCH_2C(O)Cl$ was observed at δ 3.85.

Changes of the organic ν(CO) absorbances brought about by phosphine substitution merit further comment. Most interesting is the absorbance of **3** at 1657 cm^{-1} attributable to the carbomethoxy group, which exhibits a very significant (approximately 50 cm^{-1}) shift to lower frequency in comparison with the available data for similar alkyl complexes (Table 1). In fact, it is in the range of "acyl" ν(CO) absorbances of PPh_3-substituted acylcobalt carbonyls where such a decrease in the C=O bond order of the metal-bound acyl group is due to the effect of electron back-donation from cobalt to phosphorus. For example, in compound **4** the ν(CO) absorbance assigned to the same carbomethoxy group appears at 1743 cm^{-1}, and that of the acyl group at 1654 cm^{-1} (or slightly higher taking into account solvent effects), both being typical values for this type of complex (Table 1). However, such an electronic influence is unlikely in **3** where the acyl group is at three bonds distance from the phosphine ligand, and indeed was not observed in any of the previously known $RO_2CCH_2Co(CO)_3L$ complexes [1a,k], including the next homologue where R = Et. So far there has been only one example where a similar deviation occurred; the ν(CO) absorbance of the ester carbonyl group of $EtO_2CCH_2Co(CO)_2(PBu_3)_2$ appeared at 1609 cm^{-1}, which was explained by the possibility of an outer-sphere type chelating interaction between the carbonyl oxygen and the cobalt centre [1k]. We believe that the same type of interaction may also be responsible for the anomalous IR spectroscopic behaviour of **3**.

Complexes **1**–**8** were also characterized by ^{1}H, ^{13}C{^{1}H} (except **2**) and ^{31}P{^{1}H} NMR (where accessible) spectroscopy, and the results are fully consistent with the formulations. Although the quadrupole moment (in fact the medium to fast quadrupolar relaxation) of the ^{59}Co nucleus was previously invoked as a reason for difficulties in acquiring the NMR spectra of similar cobalt(I) carbonyl compounds [1k], we had no problems with the ^{13}C{^{1}H} and ^{31}P{^{1}H} observations, while the proton resonances were occasionally broad probably due to traces of paramagnetic impurities (Co^{2+}).

The ^{1}H NMR spectra in Tables 2 and 3, though they help to identify the complexes, do not provide substantial information about the electronic effects generated

Table 3
Selected ^{1}H NMR spectroscopic data of *sec*-carbalkoxymethyl- and acetylcobalt complexes [a]

ML_n	δ(CH^a) (ppm)	δ(CH^b) (ppm)	δ(CH^x) (ppm)	Lit.
$CH_3O_2CCH\ ^aH\ ^bCH^x(CO_2CH_3)$–$ML_n$				
$Co(CO)_4$ (5)	3.11 dd (J_{ax} = 12 Hz, J_{ab} = 17 Hz)	2.56 dd (J_{bx} = 3 Hz, J_{ab} = 17 Hz)	3.33 dd (J_{ax} = 12 Hz, J_{bx} = 3 Hz)	[1m]
$Co(CO)_3PPh_3$ (7)	3.2 dd (J_{ax} = 12 Hz, J_{ab} = 17 Hz)	2.7 dd (J_{bx} < 5 Hz, J_{ab} = 17 Hz)	3.3 dd (J_{ax} = 12 Hz, J_{bx} < 5 Hz)	[1m]
$C(O)Co(CO)_4$ (6)	2.70 dd (J_{ax} = 7 Hz, J_{ab} = 18 Hz)	2.91 dd (J_{bx} = 7 Hz, J_{ab} = 18 Hz)	4.56 dd (J_{ax} = 7 Hz, J_{bx} = 7 Hz)	this work
$C(O)Co(CO)_3PPh_3$ (8)	2.79 dd (J_{ax} = 8 Hz, J_{ab} = 17 Hz)	2.91 dd (J_{bx} = 6 Hz, J_{ab} = 17 Hz)	4.75 dd (J_{ax} = 8 Hz, J_{bx} = 6 Hz)	[1m]
$CH_3O_2CCH\ ^aDCH^x(CO_2CH_3)$–$ML_n$				
$Co(CO)_4$ (5-d_1)	3.09 d (J_{ax} = 12 Hz)	2.54 [b]	3.33 d (J_{ax} = 12 Hz)	[12]
$Co(CO)_3PPh_3$ (7-d_1)	3.20 dd (J_{ax} = 12 Hz), (J_{HD} = 3 Hz)	2.66 [b]	3.31 dd (J_{ax} = 12 Hz), (J_{PH} = 4 Hz)	this work
$C(O)Co(CO)_4$ (6-d_1)	2.68 d (small J_{ax})	(n.o.) [b]	4.55 d (J_{ax} = 6 Hz)	this work
$C(O)Co(CO)_3PPh_3$ (8-d_1)	2.77 d (J_{ax} = 9 Hz)	2.84 [b]	4.74 d (J_{ax} = 9 Hz)	this work

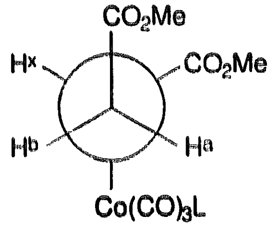
[a] Recorded in $CDCl_3$ relative to TMS. [b] ^{2}H NMR data.

Table 4
Selected ^{13}C NMR spectroscopic data of primary carbalkoxymethyl- and acetylcobalt complexes [a]

Compound	δ(CH$_2$) (ppm)	δ(CO$_2$) (ppm)	δ(C=O) (ppm)	δ(C≡O) (ppm)	Lit.
$CH_3O_2CCH_2Co(CO)_4$ (**1**)	7.0	178.7		196.1	this work
$CH_3CH_2O_2CCH_2Co(CO)_4$	6.8	163.7		195.7	[1d]
$PhCH_2O_2CCH_2Co(CO)_4$	7.6	177.2		196.1	[1k]
$CH_3O_2CCH_2Co(CO)_3PPh_3$ (**3**)	4.7 d (J_{PC} = 17 Hz)	181.6		198.6 d (J_{PC} = 26 Hz)	this work
$CH_3CH_2O_2CCH_2Co(CO)_3PMePh_2$	4.6 d (J_{PC} = 16 Hz)	181.1		198.4 d (J_{PC} = 21 Hz)	[1d]
$PhCH_2O_2CCH_2Co(CO)_3PPh_3$ [b]	5.6 d (J_{PC} = 17 Hz)	179.8		199.5 d (J_{PC} = 22 Hz)	[1k]
$PhCH_2O_2CCH_2Co(CO)_3AsPh_3$ [b]	5.9	180.6		200.3	[1k]
$CH_3O_2CCH_2C(O)Co(CO)_3PPh_3$ (**4**)	67.1 d (J_{PC} = 25 Hz)	166.7	232 d (J_{PC} = 38 Hz)	198.3 d (J_{PC} = 21 Hz)	this work
$CH_3CH_2O_2CCH_2C(O)Co(CO)_3PMePh_2$	66.7 d (J_{PC} = 23 Hz)	165.3	233.5 d (J_{PC} = 33 Hz)	196.5 d (J_{PC} = 22 Hz)	[1d]

[a] Recorded in $CDCl_3$ unless noted otherwise. [b] In C_6D_6.

by changes in the ligand sphere. For example, the α-methylene (or methine) proton resonances are indicative of the presence (low-field signal) or absence (high-field signal) of an electron-withdrawing acyl C=O group in the acyl and alkyl complexes respectively, but are not sensitive to phosphine substitution or changes of the basicity of the phosphine. Obviously, the ^1H NMR behaviour of the secondary complexes **5**–**8** is more interesting due to the presence of diastereotopic methylene protons (H^a and H^b in **A**), which give rise to an ABX spin–spin coupling system with the methine proton (H^x in **A**).



A

In order to attribute correctly the resulting dd patterns to the three different protons, ^1H and ^2H NMR spectra of the monodeuterated derivatives of **5**–**8**, i.e. **5**-d_1–**8**-d_1, were also recorded, thus reducing the complexity of the spin system. For the alkyl complexes **5** and **7**, where the rotation around the $-CH_2CH-$ axis is hindered, these results are consistent with the assignments shown in Table 3 and structure **A**, which were established previously on the basis of the characteristic coupling constants and crystal structure of **7** [1m]. In the case of **7**-d_1, we were also able to observe a D–H coupling ($J \approx 3$ Hz) between the geminate hydrogen and deuterium nuclei. For the acyl complexes **6** and **8**, however, the J_{ax} and J_{bx} values are practically uniform and the average (around 8 Hz) of those of **5** and **7**, suggesting free rotation around the $-CH_2CH-$ axis. Thus, the assignments for these complexes were made by taking into account that CO insertion should take place with retention of the configuration at carbon [5]. Consequently, the shielding of geminate protons in **6** and **8** is opposite to that in **5** and **7**.

As expected, the $^{13}C\{^1H\}$ NMR spectra (Tables 4 and 5) revealed subtle electronic changes along the molecule "backbones" generated by substituent effects both in the ligand sphere and on the alkyl chain, and made possible more extensive comparisons with the literature data than the proton spectra due to negligible solvent effects. On the basis of comparisons it is evident that all the carbon resonances and J_{PC} coupling constants of the new compounds have typical values. In general,

Table 5
Selected $^{13}C\{^1H\}$ NMR spectroscopic data of *sec*-carbalkoxymethyl- and acetylcobalt complexes [a]

ML$_n$	δ(CH) (ppm)	δ(CH$_2$) (ppm)	δ(CO$_2$) (ppm)	δ(C=O) (ppm)	δ(C≡O) (ppm)	Lit.
$CH_3O_2CCH_2CH(CO_2CH_3)$-ML_n						
$Co(CO)_4$ (**5**)	20.0	39.6	171.6, 169.9		194.1	[1m]
$Co(CO)_3PPh_3$ (**7**)	17.0 d (J_{PC} = 20 Hz)	40.2	179.8, 170.9 d (J_{PC} = 6 Hz)		197.1 d (J_{PC} = 23 Hz)	[1m]
$C(O)Co(CO)_4$ (**6**)	69.3	31.7	165.6, 169.1	222	193.4	this work
$C(O)Co(CO)_3PPh_3$ (**8**)	69.6 d (J_{PC} = 23 Hz)	31.1	166.7, 169.8	236 d (J_{PC} = 39 Hz)	196.9 d (J_{PC} = 22 Hz)	[1m]

[a] Recorded in $CDCl_3$ relative to TMS.

substitution of a CO ligand in the tetracarbonyl derivatives of both the alkyl and acyl complexes results in deshielding of all types of CO carbon, consistent with a decrease in the bond order indicated by the IR spectra. However, upon CO insertion into the alkyl complexes the ester carbonyl carbon resonance shifts upfield, which is also in accord with the IR spectra. There is no indication of the irregular frequency decrease of the organic ν(CO) absorbance of **3** in the $^{13}C\{^1H\}$ NMR spectrum. P–C couplings between the coordinated phosphine and CO ligands are very similar ($J_{PC} \sim 22$ Hz) in both the substituted alkyl and acyl complexes, indicating identical (*trans*) structures where these particular ligands occupy mutually *cis* positions, consistent again with the IR spectra.

Interestingly, the chemical shift of the C^{β} (methylene) carbon is changing in contrast to that of the C^{α} (methine) carbon in the secondary complexes **5–8** (Table 5), which seems to be inconsistent with a dominant inductive electronic effect of X anticipated for a saturated $-C^{\beta}H_2C^{\alpha}HX-$ system. Fortunately, $^{13}C\{^1H\}$ NMR data of a great number of substituted dimethyl succinates have been analyzed in order to derive substituent effects [15], and it was concluded that the shielding effects were strongly dependent upon steric and conformational differences in addition to normal electronic influences of the substituents. We described the dependence of the mutual changes of $\delta(CH_2)$ and $\delta(CH)$ on various substituents in dimethyl succinates, and found a direct correlation between these resonances for substituents which seem to have primarily an inductive contribution (Fig. 1). Other substituents, like $Co(CO)_3L$ and $C(O)Co(CO)_3L$ as well as 1-MePr, 2-MePr, ^{t}Bu and CHO, result in an inverse correlation and probably have a substantial steric and/or conformational contribution as well. In the case of cobalt complexes (**5–8**), a "heavy atom" effect [16] may also be considered.

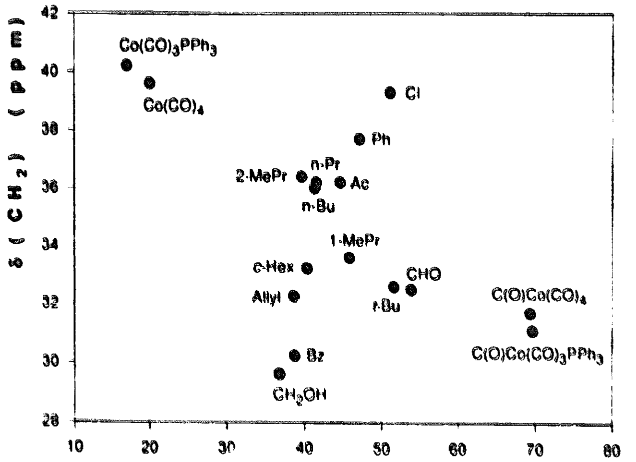


Fig. 1. Correlations between the chemical shifts of the methylene and methine carbons of various substituted dimethyl succinates.

In the $^{31}P\{^1H\}$ NMR spectra, singlet resonances appeared at δ 60.8, 49.9, 58.2 and 48.9 for the PPh_3-substituted complexes **3**, **4**, **7** and **8** respectively. Most of these data agree well with those of other PPh_3-substituted alkyl- and acylcobalt carbonyls [1j,n], and confirm the *trans* configuration. For **3**, however, the resonance at δ 60.8 appears about 4 ppm downfield from the average value, but there is no sufficient information to make a connection between the spectroscopic data and the unusual reactivity of this compound.

Attempts were also made to record $^{17}O\{^1H\}$ NMR spectra of the title compounds, but with little success. For example, in the spectrum of **4** only one resonance was observed at δ 322, which was attributed to the coordinated CO ligands. However, the $^{17}O\{^1H\}$ NMR spectrum of methyl malonyl chloride containing similar oxygen environments to those in the organic moiety of **4** exhibited three resonances at δ 525 (s, 1O, C(=O)Cl), 370 (s, 1O, C(=O)O) and 150 (s, 1O, OCH_3). The lack of organic oxygen resonances in **4** (and other cobalt(I) complexes) may result from traces of Co^{2+} which might coordinate to the oxygens having free electron pairs (not available at the coordinated CO ligands), and thus cause significant line broadening.

2.3. *Decarbonylation of trans-$CH_3O_2CCH_2C(O)Co(CO)_3PPh_3$ (4)*

To our surprise, when decarbonylation of **4** was monitored by $^{31}P\{^1H\}$ NMR spectroscopy, a new resonance could be observed at δ 55.4 in addition to those of the starting material and **3** at δ 49.9 and 60.8 respectively. It was also evident that the new resonance indicated the presence of a relatively stable intermediate of the reaction, which appeared prior to the formation of **3** and accumulated in significant concentrations until the conversion of **4** was complete (around 6 h) (Fig. 2). Switching back and forth between the $^{31}P\{^1H\}$ and ^1H detections, a singlet methylene proton resonance at δ 2.15 could be attributed to this species. As the reaction proceeded, a strong doublet evolved at δ 2.18 ($J_{PH} = 3$ Hz) along with a methyl signal at δ 3.64, both being characteristic of **3** (the methyl resonance of the intermediate was overlapped with that of **4** at δ 3.68). In the $^{13}C\{^1H\}$ NMR spectrum of the reaction mixture only weak resonances could be observed at δ 193.6 (CO_2) and 53.4 (CH_3), in addition to those of **3**. A very weak doublet was also apparent at δ −2.1 ($J_{PC} = 12$ Hz), suggesting a metal-bound methylene carbon, but no CO_2 resonance could be distinguished. Thus, on the basis of a substantial amount of NMR data, we propose that the intermediate might be *cis*-$CH_3O_2CCH_2Co(CO)_3PPh_3$, a plausible but never detected intermediate of the 1,2-alkyl-migration process of alkyl- or acylcobalt carbonyls, resulting in CO insertion and deinsertion respectively in/from the carbon–cobalt bond. Note

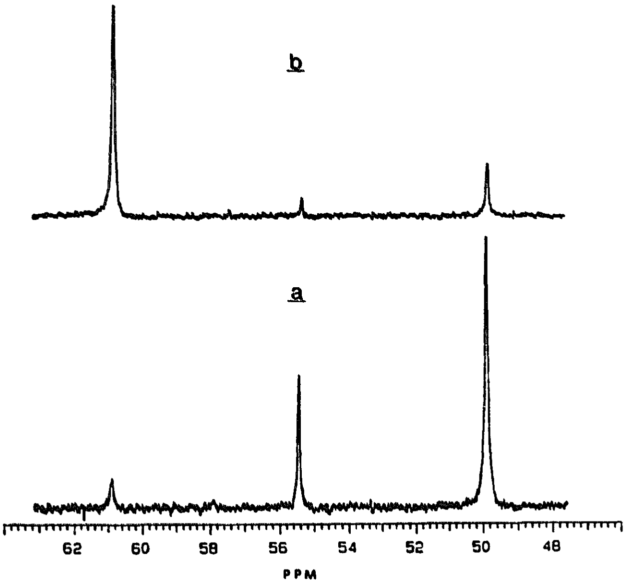


Fig. 2. $^{31}P\{^1H\}$ NMR spectroscopic monitoring of the spontaneous decarbonylation of $CH_3O_2CCH_2C(O)Co(CO)_3PPh_3$ (4): (a) recorded immediately after the dissolution of 4; (b) recorded after 6 h standing at room temperature.

that the only *cis*-$RCo(CO)_3L$ type complex reported so far is *cis*-$CF_2{=}CFCF_2Co(CO)_3PPh_3$ [17] which, however, has no relevance to the alkyl migration process; the lack of ^{31}P and ^{13}C NMR data also prevents any further comparison.

3. Experimental section

All manipulations involving the air-sensitive cobalt carbonyl complexes were carried out under CO using standard Schlenk techniques [18] with deoxygenated, dry solvents and gases. Infrared spectra were recorded on a Specord IR 75 (Carl Zeiss, Jena) spectrometer in CaF_2 cells (for solutions) and KBr pellets, and were calibrated against benzene (1959.6 cm^{-1}) and polystyrene (1601.4 cm^{-1}). ^1H (300.0 MHz), ^2H (46.0 MHz), $^{13}C\{^1H\}$ (75.4 MHz), $^{31}P\{^1H\}$ (121.4 MHz) and $^{17}O\{^1H\}$ (40.7 MHz) NMR investigations were carried out on a Varian Unity 300 spectrometer in $CDCl_3$ solutions of approximately 10 mg ml^{-1} concentration for ^1H and ^{31}P NMR measurements and 80–150 mg ml^{-1} concentrations for the other nuclei. The chemical shifts were referenced to external TMS and 85% H_3PO_4 (^{31}P). IR and selected ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data are compiled in Tables 1–5. Complexes $CH_3O_2CCH_2CH(CO_2CH_3)Co(CO)_4$ (5) [11,m], $CH_3O_2CCH_2CH(CO_2CH_3)Co(CO)_3PPh_3$ (7) [1m], $CH_3O_2CCH_2CH(CO_2CH_3)C(O)Co(CO)_3PPh_3$ (8) [1m] and $CH_3O_2CCHDCH(CO_2CH_3)Co(CO)_4$ (5-d_1) [12] were prepared according to literature methods.

3.1. (Methoxycarbonyl)methylcobalt tetracarbonyl (1)

$NaCo(CO)_4$ (1.94 g, 10 mmol) was placed in a Schlenk tube under CO and 20 ml of pentane was added. The suspension was cooled to 0°C with vigorous stirring, and 1.05 ml (10 mmol) of methyl malonyl chloride (Fluka) was injected, resulting in instant gas evolution. When the gas evolution had ceased (after about 30 min), the mixture was allowed to warm to room temperature under continuous stirring. After 1 h, stirring was stopped and a brown solid settled. At this point, an IR spectrum of the clear yellow solution indicated practically pure $MeO_2CCH_2Co(CO)_4$. The solution was then decanted and the remaining solid washed with 5 × 5 ml of pentane or until a colourless solution was obtained. The combined solutions were evaporated to dryness to obtain **1** as a volatile brown oil (approximately 90% yield). Its purity was judged by spectroscopic methods. Heating or keeping at room temperature under vacuum caused complete decomposition of **1** to an unidentified, insoluble brown mass. ^1H NMR ($CDCl_3$): δ 2.16 (s, 2H, CH_2), 3.62 (s, 3H, CH_3) ppm. (Lit.: (THF-d_8) δ 2.2 (CH_2), 3.56 (CH_3) ppm [6a].) $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 7.0 (s, CH_2), 51.5 (s, CH_3), 178.7 (s, CO_2), 196.1 (s, CO) ppm. (Lit.: (THF-d_8) δ 7.6 (CH_2), 51.6 (CH_3), 178.8 (CO_2), 197.6 (CO) ppm [6a].)

3.2. (Methoxycarbonyl)acetylcobalt tetracarbonyl (2)

$NaCo(CO)_4$ (0.07 g, 0.36 mmol) and 1.0 ml of $CDCl_3$ were placed under CO atmosphere in an NMR tube and cooled to −20°C. Methyl malonyl chloride (38 μl, 0.35 mmol) was injected into this mixture which was shaken occasionally, but no perceptible gas evolution was observed. A ^1H NMR spectrum of the yellow, decanted solution containing **2** was recorded at −20°C shortly after. Fairly broad resonances attributable to a mixture of acyl (**2**) and alkyl (**1**) complexes were observed. Upon diluting or heating this sample to room temperature, gas evolution occurred. ^1H NMR ($CDCl_3$): δ 3.71 (s, 3H, CH_3), 3.98 (s, 2H, CH_2) ppm.

3.3. (Methoxycarbonyl)methylcobalt tricarbonyl triphenylphosphine (3)

Method A. To a stirred THF solution of $NaCo(CO)_3PPh_3$ (13 ml, 0.2 M), 0.32 ml (3 mmol) of methyl chloroacetate was added dropwise at room temperature under argon. After an initial period of 15 min, NaCl began to precipitate, and the reaction was complete in around 1 h. However, a considerable amount of $[Co(CO)_3PPh_3]_2$ also precipitated by this time. An IR spectrum of the resulting orange solution confirmed formation of the expected alkyl complex **3**. This solution was evaporated to dryness and the remaining red–

brown solid extracted with pentane–CH_2Cl_2, but no cobalt complex was detected in the extract by spectroscopic methods, while the solid was identified as pure $[Co(CO)_3PPh_3]_2$. Allowing the original reaction mixture to stand at room temperature for a few days also resulted in the complete precipitation of $[Co(CO)_3PPh_3]_2$.

Method B. $MeO_2CCH_2C(O)Co(CO)_3PPh_3$ (**4**) (0.91 g, 1.8 mmol) was dissolved in 10 ml of CH_2Cl_2 under argon and stirred at room temperature to complete decarbonylation. However, continuous precipitation of insoluble $[Co(CO)_3PPh_3]_2$ again took place and no cobalt complex was detected in the solution by IR spectroscopy. Performing a similar experiment in the NMR probe at 24°C with 20–60 mg of **4** dissolved in 0.7 ml of $CDCl_3$ under CO atmosphere revealed that **3** had a lifetime under such conditions long enough to record ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra. ^1H NMR ($CDCl_3$): δ 2.18 (d, $^3J_{PH} = 3$ Hz, 2H, CH_2), 3.64 (s, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 4.7 (d, $^2J_{PC} = 17$ Hz, CH_2), 50.9 (s, CH_3), 128.8 (d, $^3J_{PC} = 10.7$ Hz, *m*-Ph), 131.0 (d, $^4J_{PC} = 2.6$ Hz, *p*-Ph), 133.0 (d, $^2J_{PC} = 10.7$ Hz, *o*-Ph), 133.2 (d, $J_{PC} = 47$ Hz, *ipso*-Ph), 181.6 (s, CO_2), 198.6 (d, $^2J_{PC} = 26$ Hz, CO) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 60.8 ppm.

3.4. *(Methoxycarbonyl)acetylcobalt tricarbonyl triphenylphosphine (4)*

10 ml of a cold (−20°C) pentane solution (0.2 M) of **1** was injected into PPh_3 (0.47 g, 1.8 mmol) dissolved in a minimum amount of ether. A voluminous yellow crystalline precipitate appeared instantly, but the mixture was stirred and allowed to warm towards room temperature to ensure complete reaction. The brown solution was decanted after around 30 min, and the crystals were washed with 3 × 3 ml of pentane at −20°C and dried under reduced pressure. Complex **4** was obtained in nearly quantitative yield, and was pure on the basis of NMR spectra. It was stable in the solid state at −20°C for at least several months. ^1H NMR ($CDCl_3$): δ 3.68 (s, 3H, CH_3), 4.09 (s, 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 51.9 (s, CH_3), 67.1 (d, $^3J_{PC} = 25$ Hz, CH_2), 128.9 (d, $^3J_{PC} = 10.1$ Hz, *m*-Ph), 130.9 (d, $^4J_{PC} = 1.7$ Hz, *p*-Ph), 132.7 (d, $J_{PC} = 44$ Hz, *ipso*-Ph), 133.0 (d, $^2J_{PC} = 11.4$ Hz, *o*-Ph), 166.7 (s, CO_2), 198.3 (d, $^2J_{PC} = 21$ Hz, CO), 232 (d, $^2J_{PC} = 38$ Hz, $C(O)CH_2$) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 49.9 ppm.

3.5. *(2,3-Bis(methoxycarbonyl)propanoyl)cobalt tetracarbonyl (6) and (2,3-Bis(methoxycarbonyl)propanoyl-3-d_1)cobalt tetracarbonyl (6-d_1)*

About 5 mg (0.02 mmol) of **5** was dissolved in 0.7 ml of $CDCl_3$ at −20°C in an NMR tube under 1 atm CO. The ^1H NMR spectrum recorded at −20°C (Table 3) clearly exhibited a 9 : 1 molar mixture of **5** and the corresponding acyl complex **6**. When the CO pressure was increased to 3.5 atm in the NMR tube and the spectrum was recorded at −30°C, a 7 : 3 molar mixture of the two compounds was present. These conditions allowed the $^{13}C\{^1H\}$ NMR spectrum of **6** to be obtained in a more concentrated sample. ^1H NMR ($CDCl_3$): δ 2.70 (dd, $J_{ax} = 7$ Hz, $J_{ab} = 18$ Hz, 1H, CH^a), 2.91 (dd, $J_{bx} = 7$ Hz, $J_{ab} = 18$ Hz, 1H, CH^b), 3.69 (s, 3H, CH_3), 3.78 (s, 3H, CH_3), 4.56 (dd, $J_{ax} = 7$ Hz, $J_{bx} = 7$ Hz, 1H, CH^x) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 31.7 (s, CH_2), 50.4 (s, CH_3), 51.1 (s, CH_3), 69.3 (s, CH), 165.6 (s, CO_2), 169.1 (s, CO_2), 193.4 (s, CO), 222 (s, $C(O)CH_2$) ppm. $CH_3O_2CCHDCH(CO_2CH_3)C(O)Co(CO)_4$ (**6**-d_1) was prepared similarly from **5**-d_1 under CO and characterized in situ by ^1H NMR spectroscopy. Unfortunately, no ^2H NMR spectrum could be obtained. ^1H NMR ($CDCl_3$): δ 2.68 (d, small J_{HH}, 1H, CHD), 3.69 (s, 3H, CH_3), 3.78 (s, 3H, CH_3), 4.55 (d, $J_{HH} = 6$ Hz, 1H, CH) ppm.

3.6. *(2,3-Bis(methoxycarbonyl)propanoyl-3-d_1)cobalt tricarbonyl triphenylphosphine (8-d_1)*

This compound was prepared similar to **8**, starting from a 28 ml pentane–CH_2Cl_2 (13 : 1 v/v) solution of **5** (1.27 g, 4 mmol) and PPh_3 (1.07 g, 4 mmol). Yield 1.37 g (2.4 mmol, 60%). ^1H NMR ($CDCl_3$): δ 2.77 (d, $J_{HH} = 9$ Hz, 1H, CHD), 3.67 (s, 3H, CH_3), 3.73 (s, 3H, CH_3), 4.74 (d, $J_{HH} = 9$ Hz, 1H, CH) ppm. ^2H NMR ($CDCl_3$): δ 2.84 ppm. The $^{13}C\{^1H\}$ NMR spectrum was identical to that of the perprotio congener [1m].

3.7. *(1,2-Bis(methoxycarbonyl)ethyl-2-d_1)cobalt tricarbonyl triphenylphosphine (7-d_1)*

This compound was prepared similar to **7**, starting from **5** [1m]. ^1H NMR ($CDCl_3$): δ 3.20 (dd, $J_{HH} = 12$ Hz, $J_{HD} = 3$ Hz, 1H, CHD), 3.31 (dd, $J_{HH} = 12$ Hz, $^3J_{PH} = 4$ Hz, 1H, CH), 3.65 (s, 3H, CH_3), 3.70 (s, 3H, CH_3) ppm. ^2H NMR ($CDCl_3$): δ 2.66 ppm.

3.8. *Reaction of 5 with synthesis gas*

0.18 g (0.56 mmol) of $CH_3O_2CCH_2CH(CO_2CH_3)Co(CO)_4$ was dissolved in 2 ml of $CDCl_3$ at −20°C and transferred into a 10 ml test-tube autoclave under CO atmosphere. The autoclave was pressurised to 55 atm by applying a gas mixture of H_2 (53 mol%) and CO (47 mol%), and was allowed to stand for three days at room temperature. The reaction mixture was analysed by IR and NMR spectroscopy, which showed complete conversion of the starting material into $Co_2(CO)_8$ as the sole cobalt-containing product and an equilibrium mixture of the aldo–enol tautomers of dimethyl formylsuccinate. Data for $CH_3O_2CCH_2CH(CHO)CO_2CH_3$ are as follows: ^1H NMR ($CDCl_3$): δ 2.93 (m, 3H, CH_2CH), 3.69 (s, 3H, CH_3), 3.77 (s, 3H, CH_3), 9.91 (s, 1H, CHO) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 32.6 (s, CH_2), 51.7 (s, CH_3), 52.8 (s, CH_3), 53.9 (s, CH), 168.4 (s, CO_2), 171.9 (s, CO_2), 195.4 (s, CHO) ppm. Data for $CH_3O_2CCH_2C(=CHOH)CO_2CH_3$ are as follows: ^1H NMR ($CDCl_3$): δ 3.07 (s, 2H, CH_2), 3.70 (s, 3H, CH_3), 3.82 (s, 3H, CH_3), 7.09 (d, $J = 13$ Hz, 1H, =CH), 11.48 (d, $J = 13$ Hz, 1H, OH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 29.6 (s, CH_2), 52.1 (s, CH_3), 51.9 (s, CH_3), 98.9 (s, =CH), 162.9 (s, CHOH), 171.4 (s, CO_2), 171.7 (s, CO_2) ppm.

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