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Cobalt catalysed carbonylation of reactive chlorides into esters by methyl formate without carbon monoxide and methanol added

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Abstract

Reactive chlorides ZCH_2Cl ($Z = C_6H_5$, $CH_3OC(O)$, CN) are readily carbonylated into esters with methyl formate as the sole source of carbon monoxide and methanol, the tetracarbonyl cobaltate anion as the catalyst and sodium carbonate as the base. The reaction occurs after in situ prior mild decomposition of methyl formate with a catalytic amount of sodium methoxide.

Keywords: Carbonylation; Chlorides; Cobalt; Esters; Formate; Methanol

1. Introduction

Transition metal catalysed carbonylation of organic halides into esters is a reaction of great interest in organic synthesis [1] (Eq. 1).

$$RX \xrightarrow[\text{[M], base}]{\text{CO, R'OH}} RCO_2R' \qquad (1)$$

However, the handling of carbon monoxide may limit its practical importance. Attention is now increasingly being drawn to methyl formate [2], which may be considered as a safe equivalent of the methanol–carbon monoxide mixture (Eq. 2).

$$HCO_2CH_3 \equiv CH_3OH + CO \qquad (2)$$

Indeed, several works have already appeared, in which use was made of methyl formate in the carbonylation of organic halides. However, most of these reports mention the need for a carbon monoxide pressure, which limits the interest of the process, and makes doubtful the real role of methyl formate as a source of carbon monoxide. Furthermore, since commercial methyl formate contains appreciable traces of methanol, the methanol needed for reaction (1) may not come from methyl formate itself [3].

To our knowledge, there is only a very limited number of successful carbonylations of organic halides with methyl formate without any carbon monoxide and (or) methanol added (Eq. 3) [4].

$$RX + HCO_2CH_3 \xrightarrow[\text{base}]{\text{[M]}} RCO_2CH_3 \qquad (3)$$

For RX being C_6H_5I, β-bromostyrene or $Cr(CO)_3C_6H_5Cl$ and [M] = Pd, the base used is sodium methoxide [4a]. Thus a rapid 'in situ' decarbonylation of methyl formate is induced by the methoxide anion, which does not (or weakly) react on these halides under these conditions, so

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that their carbonylation into esters is observed. The carbonylation of alkyl iodides with methyl formate was more recently observed with the 'exotic' use of $Mo(CO)_6$ and Bu_4NF, but the mechanism of this reaction is still obscure [5].

Carbonylation of activated chlorides ZCH_2Cl into esters with methanol and CO and a base added is a well known reaction, mainly with Co (as the $Co(CO)_4^-$ anion) and Pd (as Pd(II) complexes) as the metal catalysts [1]. Since these halides are very sensitive to the nucleophilic attack by bases, contact between them may be minimized (or suppressed) by the use of phase transfer systems [6], or poorly soluble bases such as sodium carbonate [7] or calcium hydroxide [8], or a careful addition of the halides into the catalytic system [9]

So far, there is no example of such a catalytic reaction using methyl formate with no carbon monoxide and methanol added (Eq. 4).

$$ZCH_2Cl + HCO_2CH_3 \xrightarrow[\text{base}]{[M]} ZCH_2CO_2CH_3 \qquad (4)$$

$Z = C_6H_5, CH_3OC(O), CN$

This is probably due to the above mentioned reactivity of these halides toward bases.

We describe here a system, using the tetracarbonyl cobaltate anion as the catalyst, which realizes the reaction (Eq. 4) with no addition of methanol or carbon monoxide, by a proper choice of the bases and the experimental conditions [1]. It is a successful answer to the following question: how can methyl formate be in situ decarbonylated under mild conditions *and* reactive halides be carbonylated into esters without nucleophilic attack of the bases on them?

2. Results and discussion

2.1. Decomposition of methyl formate with bases

Methyl formate is generally made by reaction of methanol on carbon monoxide with the methoxide anion as catalyst [2] (Eq. 5).

$$CO + CH_3OH \overset{CH_3O^-Na^+}{\rightleftharpoons} HCO_2CH_3 \qquad (5)$$

Meanwhile, this reaction has not been used as much in the reverse sense. We have observed that, at room temperature, there is no (or very slow) reaction between methyl formate and a catalytic amount of sodium methoxide (2.5% vs. formate). By raising the temperature to 60°C rapid decomposition occurs, giving about 60% of methanol and carbon monoxide after ten minutes. Since current commercial methyl formate may contain up to 4% of remaining methanol, we may speculate if it can be decomposed with the carbonate anion as the base, since the methoxide anion may be generated according to the equilibrium (Eq. 6):

$$CH_3OH + CO_3^{2-} \rightleftharpoons CH_3O^- + HCO_3^- \qquad (6)$$

However, no decarbonylation was observed when commercial methyl formate containing 4% CH_3OH was reacted with potassium carbonate at 60°C for 1 h.

2.2. Carbonylation of reactive halides ZCH_2Cl

In a first series of experiments, the reagents were introduced altogether into the autoclave ('batch' conditions, gathered in runs 1, 2, 3 of Table 1) and the reaction run at 60°C under stirring for one night. Low conversions with modest selectivities in esters were observed, along with appreciable hydrogenolysis, especially for $ClCH_2CN$.

In a second series (runs 4–12), methyl formate (15 ml), sodium methoxide (3.4 mmol), sodium tetracarbonyl cobaltate (1.5 mmol) and sodium carbonate (30 mmol) were first introduced into the autoclave. Then the temperature was raised to 60°C; the pressure increased to 10–15 atm within 10 min. Then a solution of the halide (25 mmol) in methyl formate (14 ml) was gradually introduced within 30 min into the autoclave by the means of a high pressure pump. After one night at 60°C under stirring, an almost quantitative carbonylation of the halides into esters was obtained (runs 5, 6, 7, 9, 12, Table 1).

[1] In a recent patent the preparation of ethyl cyanoacetate from ethyl formate, triethylamine, dicobalt octacarbonyl and chloroacetonitrile (in a reported 52.4% yield) has been claimed [10].

Table 1
Cobalt catalysed carbonylation of reactive halides with methyl formate

Run	Z	T (°C)	t (h) [b]	P_{obs} [c] (atm)	Conv. (%)	Selectivity (%)			Yield (%) [d] of
						$ZCH_2CO_2CH_3$	ZCH_2OCH_3	ZCH_3	$ZCH_2CO_2CH_3$
1 [a]	C_6H_5	60	15	3	13	82	traces	18	11
2 [a]	$CH_3OC(O)$	60	15	3	22	65	–	35	14
3 [a]	CN	60	15	3	13	40	–	60	5
4	C_6H_5	60	1	16	40	100	–	–	40
5	C_6H_5	60	15	13	97	100	–	–	97
6	p-$CH_3C_6H_5$	60	15	14	100	100	–	–	100
7	p-$CH_3OC_6H_5$	60	15	13	100	100	–	–	100
8	$CH_3OC(O)$	60	1	10	25	100	–	–	25
9	$CH_3OC(O)$	60	15	13	94	99	1	–	93
10	$CH_3OC(O)$	70	1	25	68	94	6	–	64
11	$CH_3OC(O)$	110	1	50	73	13	87	–	9
12	CN	60	15	12	91	100	–	–	91

[a] 'Batch' experiments.
[b] After the end of injection of ZCH_2Cl.
[c] At the indicated T, at the end of the indicated t.
[d] GC yield.

This procedure was optimal. A shorter reaction time lowered the yields (runs 4, 8, 10). Increasing temperature lowered selectivity (runs 10, 11). Lower amounts of $NaCo(CO)_4$ or $NaOCH_3$ gave lower yields.

2.3. The role of the methoxide anion and the carbonate anion

2.3.1. Methoxide and carbonate anions as bases

The generally admitted mechanism for the decarbonylation of methyl formate is depicted in Eq. 7 [2] and prior decomposition of methyl formate in our system occurs according to this mechanism.

$$HCO_2CH_3 + CH_3O^- \rightleftharpoons CH_3OH + \{{}^-CO_2CH_3\}$$

$$\{{}^-CO_2CH_3\} \rightleftharpoons CO + CH_3O^- \qquad (7)$$

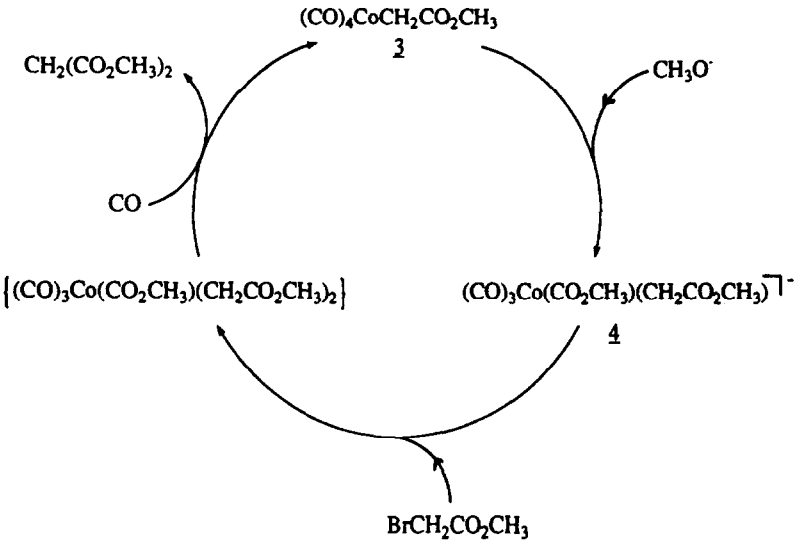
We have already seen that sodium carbonate cannot induce this decomposition under mild conditions. Meanwhile the equilibrium (Eq. 6), weakly shifted to the right, contributes to the catalytic system depicted in Scheme 1 (see below). Methanol needed for the transformation of the halide into ester did not come from a continuous decomposition of methyl formate with sodium carbonate, as established by the following experiment: the reaction (8) was run under carbon monoxide pressure (12 atm), without $NaOCH_3$ added, but with a calculated defect of methanol (x% vs. methyl chloroacetate).

$$ClCH_2CO_2CH_3 + xCH_3OH \xrightarrow[\substack{NaCo(CO)_4\ (5\%)\\ CO/60\,^\circ C\ Na_2\ CO_3}]{HCO_2CH_3\ (solvent)} x\,CH_2(CO_2CH_3)_2 \qquad (8)$$

After one night of reaction time, the GC yield into methyl malonate exactly matched the calculated amount of methanol introduced (checked for two runs, $x = 19\%$ and 48%).

2.3.2. The methoxide anion as a nucleophile

It is well known that the methoxide anion readily reacts with coordinated carbon monoxide. For instance the adduct **1** of the reaction (9a) has been firmly characterized by X-ray structural determination [11], and there is strong spectroscopic evi-



Scheme 1.

dence that a similar adduct **2** is produced in the reaction (9b) [8]:

$$(CO)_4CoCO_2CH_3 + CsOCH_3 \rightleftharpoons [(CO)_3Co(\underset{1}{CO_2CH_3})_2]Cs \quad (9a)$$

$$NCCH_2Co(CO)_4 + CH_3ONa \rightleftharpoons [NCCH_2Co(\underset{2}{CO})_3CO_2CH_3]Na \quad (9b)$$

We have completed these observations by a careful monitoring of the reaction of sodium methoxide on the complex **3** (obtained after reaction of methyl bromoacetate on the tetracarbonyl cobaltate anion, according to a procedure similar to that of Palyi et al. [12] (Eq. 10).

$$CH_3OC(O)\underset{3}{CH_2}Co(CO)_4 + CH_3ONa \rightleftharpoons [CH_3OC(O)CH_2Co(\underset{4}{CO})_3CO_2CH_3]Na \quad (10)$$

An excess of sodium methoxide was added at −50°C to a solution of complex **3** in dry THF (Eq. 10). Spectroscopic data of complex **4** (IR, ^1H and ^{13}C NMR) agree well with the proposed formula (see Experimental part), and were found consistent with data given for similar adducts in the reactions (9a) and (9b).

Complex **4** is thermally labile and decomposes above −40°C. Its thermolysis mainly gave $CH_3CO_2CH_3$ (95%) along with only 5% methyl malonate (GC). But if the thermolysis was run under CO after addition of an equivalent of $BrCH_2CO_2CH_3$, a 70% yield (GC) of methyl malonate was observed. All these results are consistent with the catalytic cycle depicted in scheme 1, which is also in agreement with similar observations made by Foa et al. on adduct **2**.

3. Experimental

Methyl formate (99%) was supplied by Aldrich. Activated halides (Aldrich) were degassed before use. Na_2CO_3 (Aldrich) was dried under vacuum above 100°C. All carbonylation experiments were conducted into a 100 ml stainless steel autoclave ('Autoclave Engineers'). For carbonylations with progressive introduction of ZCH_2X, a HPLC Gilson 307 pump was used.

IR spectra were recorded on a Perkin Elmer 1430 spectrometer. ^1H and ^{13}C NMR spectra on a Bruker AC 300 (^{13}C at 75.47 MHz). GC analyses were made on a HP 5890 equipped with a 25×0.25 mm SE 30 capillary column or a Car-

bowax 25 × 0.32 mm for CH_3OH/HCO_2CH_3 ratio determinations.

Methyl phenylacetate, methyl malonate and methyl cyanoacetate were identified by comparison (GC, ^1H NMR) with authentic commercial samples. Quantitative measurements (GC) used diisopropylbenzene (for methyl phenylacetate and methyl malonate) and n-octane (for methyl cyanoacetate) as internal standards.

4. Catalytic experiments

Typical batch experiments (runs 1–3): the 100 ml autoclave was charged with 15 ml HCO_2CH_3 (243 mmol) 185 mg $NaOCH_3$ (3.4 mmol; 1.4% vs. HCO_2CH_3), 3.18 g (30 mmol) Na_2CO_3, ZCH_2Cl (25 mmol), $NaCo(CO)_4(THF)_3$ (1.25 mmol in 4 ml THF; 5% (mol) vs. ZCH_2Cl) then heated at 60°C overnight under stirring.

Typical experiments with progressive introduction of the reactive halide (runs 4–12): the same reagents and same quantities as for batch experiments were introduced into the autoclave excepted ZCH_2Cl (25 mmol in 14 ml HCO_2CH_3) gradually introduced at 0.8 mmol/min for 30 min by means of a HPLC pump. After the end of the addition, the temperature was kept at 60°C for 1 or 15 h (see Table 1).

5. Synthesis and spectroscopic data of complexes 3 and 4

$(CO)_4CoCH_2CO_2CH_3$ (**3**) was synthesized according to Palyi's method [12] except that one equivalent of $BrCH_2CO_2CH_3$ was added in place of $BrCH_2CO_2C_2H_5$. IR (cm^{-1}): 2115 (m) 2045 (s,sh) 2030 (vs) (C≡O) 1737 (m) (C=O). ^1H NMR (d_8 THF) 2.2 (2H,s), 3.56 (3H,s). ^{13}C NMR (d_8 THF) δ 7.6 (CH_2,s) 51.6 (CH_3,s) 178.8 (CO_2,s) 197.6 (CO,s).

$[(CO)_3Co(CO_2CH_3)(CH_2CO_2CH_3)]Na$ (**4**): 1.1 equiv. CH_3ONa was added to a cooled (−50°C) solution of **3** (1 equiv.) in THF. THF was stripped off under vacuum at −40°C and **4** characterized at this temperature. IR (THF) 2020 (w) 1950 (vs) 1935 (vs,sh) (C≡O) 1635 (m) 1592 (s) (C=O). ^1H NMR (d_8 THF) δ 1.35 (2H,s) 3.26 (3H,s) 3.4 (3H,s). ^{13}C NMR (d_8 THF) δ0.85 (CH_2,s) 50.3 (CH_3,s) 50.4 (CH_3,s) 186 ($CH_2CO_2CH_3$,s) 204.5 ($CoCO_2CH_3$,s) 204.6 (CO,s).

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