Efficient Dimethyl Malonate Synthesis by Methoxycarbonylation of Dichloromethane catalysed by Electrogenerated [Co(CO)$_3$PBu$_3$]$^-$ Species

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Electrochemistry is used for the synthesis of [Co(CO)$_3$PBu$_3$]$^-$ complex in a methanol–methyl formate medium, which catalyses the alkoxycarbonylation of dichloromethane to dimethyl malonate in up to 75% yield.

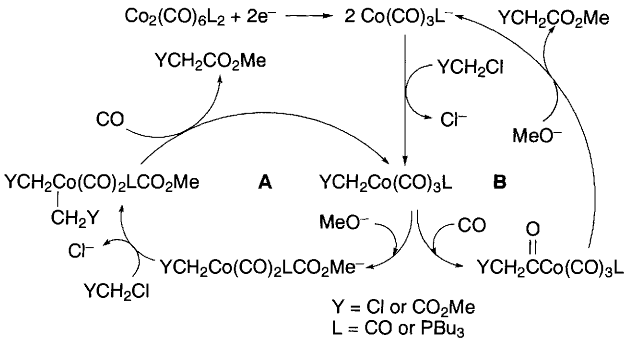
Pd, Rh and Co metal complexes have been used in homogeneous[1] and heterogeneous[2] catalysis to perform the alkoxycarbonylation of dihalomethanes into dialkylmalonates. Whatever the catalyst chosen, however, low yields have been so far obtained, especially for dichloromethane.

We have focused on the alkoxycarbonylation of CH_2Cl_2 with cobalt-based catalysts with which we believe some improvements could be obtained. Indeed, the alkoxycarbonylation of alkylchloroacetates is well known[3] and can be carried out easily with the tetracarbonylcobaltate anion as catalyst, but this compound is not very efficient for CH_2Cl_2.[4] The use of $Co_2(CO)_6L_2$ compounds or $Co_2(CO)_8$/L couples, where L is a phosphine or a phosphite, has been described in a patent to improve the reactivity with CH_2Cl_2, but the yield still remains low.[5]

$$CH_2Cl_2 + 2Base + 2CO + 2MeOH \longrightarrow CH_2(CO_2Me)_2 + 2Base{,}HCl \quad (1)$$

$$CH_2Cl_2 + Co(CO)_3L^- \longrightarrow ClCH_2Co(CO)_3L + Cl^- \quad (2)$$

$$MeOH + CO \underset{}{\overset{MeONa}{\rightleftharpoons}} HCO_2Me \quad (3)$$



Scheme 1 Catalytic cycle for the formation of dimethyl malonate from chloroacetate and dichloromethane

On the basis of literature data,[6] we assumed that the mechanism of the alkoxycarbonylation of dichloromethane [eqn. (1)] is similar to that of an alkylchloroacetate (Scheme 1, pathway A, Y = CO_2Me, L = CO) and thus, we decided to work with substituted carbonylcobaltates [Co(CO)$_3$L]$^-$ instead of the stable dimeric parent compounds $Co_2(CO)_6L_2$.

The first organometallic intermediate involved in the cobalt-catalysed reaction could then arise from the attack of CH_2Cl_2 by a cobaltate species [eqn. (2)]. The nature of the ligand L is therefore important as it allows one to increase the nucleophilicity of the cobaltate anion,[7] and we began our study with tributylphosphine, a good σ-donor ligand.

In the presence of [Co(CO)$_3$PBu$_3$]$^-$, CH_2Cl_2 reacts with CO and MeONa in a methanol–methyl formate mixture to give dimethyl malonate, methyl methoxyacetate, dimethoxymethane and traces of methyl acetate (see Table 1). Two main competing reactions (carbonylation and substitution) were controlled by choosing particular experimental conditions. Thus, the methanol–methyl formate equilibrium catalysed by methanolate anions [eqn. (3)] which consumes carbon monoxide in the solution and delays the alkoxycarbonylation, was quickly reached by starting with a 80:20 mixture of methanol–methyl formate (equilibrium ratio under 15 bar CO and at 80 °C).[8] Furthermore, the competition between cobaltate and methanolate ions as nucleophilic species able to attack chlorinated substrates, required a fairly low base : catalytic precursor ratio in order to limit the formation of side-products such as dimethoxymethane and methyl methoxyacetate. As mentioned above, $Co_2(CO)_8$ and $Co_2(CO)_6(PBu_3)_2$ give poor yields of malonate ester and 40 h are necessary to complete the reaction (runs 1,2). The mechanism probably proceeds *via* the production of cobaltate anions in both cases, quickly for the poor nucleophile [Co(CO)$_4$]$^-$ and more slowly for the better nucleophile [Co(CO)$_3$PBu$_3$]$^-$. This assumption is supported by the fact that a preliminary chemical reduction of $Co_2(CO)_6(PBu_3)_2$ over Na(Hg) amalgam reduced the reaction time by 15 h (run 3).

Table 1 Products obtained from the methoxycarbonylation of dichloromethane

Run	Precursor	Reduction method	F:Co	Base : CH_2Cl_2	Base : precursor	t/h	$CH_2(CO_2Me)_2$ (%)[e]	$MeOCH_2CO_2Me$ (%)[e]	$CH_2(OMe)_2$ (%)[e]
1	$Co_2(CO)_8$[a]	—	—	1	54	40	6	5	79
2	$Co_2(CO)_6(PBu_3)_2$[a]	—	—	1	54	40	14	3	70
3	$Co_2(CO)_6(PBu_3)_2$[a]	Na(Hg)	—	1	54	25	17	3	60
4	$Co_2(CO)_6(PBu_3)_2$[a,b]	Na(Hg)	—	1	27	25	28	3.5	42
5	$Co_2(CO)_6(PBu_3)_2$[c]	Zn/e$^-$	1.1	0.5	81	15	30	4	26
6	$Co_2(CO)_6(PBu_3)_2$[c]	Zn/e$^-$	8.2	0.5	81	15	49	3.5	17.5
7	$Co_2(CO)_6(PBu_3)_2$[c]	Sn/e$^-$	8.2	0.5	81	15	34	4	28
8	$Co_2(CO)_6(PBu_3)_2$[c]	Al/e$^-$	6.8	0.5	81	15	44	2.5	17.5
9	$Co_2(CO)_6(PBu_3)_2$[d]	Zn/e$^-$	5.5	0.5	54	15	74.5	3	8

[a] $Co_2(CO)_6(PBu_3)_2$ (1 g; 1.45 × 10^{-3} mol), CH_2Cl_2 (5 ml; 78 × 10^{-3} mol), MeOH (15 ml; 370 × 10^{-3} mol), HCO_2Me (5.5 ml; 90.5 × 10^{-3} mol), MeONa (4.2 g, 78 × 10^{-3} mol), P_{co} = 15 bar, 80 °C. [b] $Co_2(CO)_6(PBu_3)_2$ (2 g; 2.9 × 10^{-3} mol). [c] $Co_2(CO)_6(PBu_3)_2$ (1 g; 1.45 × 10^{-3} mol), CH_2Cl_2 (15 ml; 234 × 10^{-3} mol), MeOH (36 ml; 888 × 10^{-3} mol), HCO_2Me (13.5 ml; 222 × 10^{-3} mol), MeONa (6.3 g, 117 × 10^{-3} mol), P_{co} = 15 bar, 80 °C, j = 3.75 × 10^{-3} A cm^{-2}. [d] $Co_2(CO)_6(PBu_3)_2$ (1.5 g; 2.175 × 10^{-3} mol), CH_2Cl_2 (15 ml; 234 × 10^{-3} mol), MeOH (36 ml; 888 × 10^{-3} mol), HCO_2Me (13.5 ml; 222 × 10^{-3} mol), MeONa (6.3 g; 117 × 10^{-3} mol), P_{co} = 15 bar, 80 °C, j = 3.75 × 10^{-3} A cm^{-2}. [e] Yield based on initial MeONa.

However, we were struck by the absence of an improvement to the yield of malonate ester since the cobaltate moiety present at the beginning of the reaction would have had to compete with methanolate ions and give more product. In addition, for the same reaction time the decrease of the base : catalytic precursor ratio allowed a yield of 28% to be achieved instead of 17% (runs 3,4), which confirmed the crucial importance of having enough cobaltate ions in solution at the beginning of the reaction. In order to overcome the difficulty of obtaining pure $[Co(CO)_3PBu_3]^-$, which is very sensitive towards oxygen and which is probably at the origin of this discrepancy, we tried to produce cobaltate anions *in situ* by an electrochemical method that usually allows the clean production of reduced species.

The CV of our starting mixture [MeOH 24 ml, CH_2Cl_2 8 ml, MeONa 3.10^{-2} mol dm^{-3} $Co_2(CO)_6(PBu_3)_2$ 3.10^{-3} mol dm^{-3} platinum working electrode, $v = 0.1$ V s^{-1}] exhibits a shoulder on the cathodic wall with an anodic peak at -0.54 V *vs.* SCE on the reverse scan, typical of the production of cobaltates in solution.[9] Therefore, we carried out the electrochemical reduction of $Co_2(CO)_6(PBu_3)_2$ at 25 °C in our mixture before heating to prevent the formation of dimethoxymethane while synthesizing the active species. An autoclave fitted with a steel cathode and a sacrificial metallic anode was employed and cobaltates were produced under constant current. Zinc anodes were used mainly, but tin or aluminium anodes are suitable and give rise to almost identical results, although some drawbacks arise, such as the deposition of metal on the cathode in the former case (the current efficiency is consequently lower), or chemical consumption of the anode in the latter (runs 6–8). Thus, the metal of the electrode does not seem to be involved in the formation of a mixed anodic metal–cobalt active species.[10]

When the electrolysis current is disconnected just after 1.1 F of Co have passed, the amount of electricity necessary to obtain a complete electroreduction of the dimeric cobalt compound, we can observe that a 30% yield of dimethyl malonate is reached with 12 catalyst turnovers† (run 5). However, upon continuation of the electrolysis during the reaction, a further increase of about 20% was obtained. The possibility of the production of methanolate anions either electrochemically on the cathode or chemically on the anode by reduction of methanol solvent in order to increase the yield is ruled out by the fact that zinc or magnesium methanolates are totally inefficient as bases in this reaction. Thus, this catalysis becomes electro-assisted and the catalyst turnovers are then *ca.* 20 (runs 6,9) to reach a 75% yield of malonate ester with only a few side-products. An electroregeneration of the catalyst or the formation of a new compound by electroreduction of a key species of the catalytic cycle could explain this yield enhancement.

Although the exact nature of the catalytic cycle for dimethyl malonate formation is not known, two pathways seem plausible (Scheme 1, Y = Cl or CO_2Me, L = PBu_3). Path A is similar to that proposed by Foa *et al.* (see above) where the authors mention that an alkyl–acyl transformation seems very unlikely because of the unfavourable effect of the electron-withdrawing group on CO insertion. In order to support their mechanism they show the production of complexes $[NCCH_2CO(CO_2Me)(CO)_3]^-$ and $[EtOOCCH_2Co(CO_2Me)(CO)_3]^-$ by attack of a methoxide ion on, respectively, a (cyano)- or (ethoxycarbonyl)methyl-cobalt tetracarbonyl species. On the other hand, Galamb *et al.* also show that $ClCH_2Co(CO)_4$ reacts with methoxide ion to yield $[ClCH_2Co(CO_2Me)(CO)_3]^-$, but above all they prove that an alkyl–acyl transformation under a CO atmosphere is possible in the case of $ClCH_2Co(CO)_3L$ where L = CO or PPh_3. Indeed, they manage to isolate and characterize both the chloromethyl and chloroacetyl cobalt species. Consequently, path B is also conceivable.

In both pathways, methyl chloroacetate should be produced in the first run of the catalytic cycle, but it has never been detected in solution. In fact, when added to a starting mixture, this reagent is quickly consumed to give dimethyl malonate and methyl methoxyacetate, which explains its absence in our analyses.

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† Calculated as two turnovers per mol of ester per mol of cobalt.

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