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Preliminary communication

Selective formation of malonate by a double CO insertion reaction into a μ-alkylidene complex of palladium

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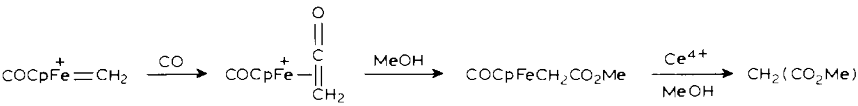
Abstract

Whereas μ-alkylidene complex $Fe_2[\mu\text{-}CH_2(CO)_8]$ reacts with CO and ROH to give mainly the ester CH_3CO_2R, the μ-alkylidene complex $Pd_2[\mu\text{-}CH_2(PPh_2\text{-}CH_2PPh_2]I_2$ gives the malonate $CH_2(CO_2R)_2$ with a selectivity of 88%.

One of the industrial problems which has not yet been solved is the direct transformation of CH_2X_2 (X = halogen) into malonates in the presence of CO and ROH. Recently, model reactions directed towards the synthesis of malonic acid esters have been developped by Cutler and coworkers [1,2]. These reactions are mainly based on the stepwise carbonylation of mononuclear complexes of iron via carbalkoxymethyl complexes of this metal (eq. 1). The purpose of the present communication is to describe the selective synthesis of malonates starting from μ-alkylidene complexes. We previously [3] described the reaction of the μ-alkylidene complex **4** with CO in the presence of alcohols to give, besides the ester, the product of monocarbonylation/solvolysis [4], small amounts of malonates, and the product of the dicarbonylation reaction. The last product was formed with a selectivity of 6% under our standard conditions. We have since shown that the ratio of malonate to ester depends strongly on the reaction conditions.



$$\overset{+}{\mathrm{COCpFe}}{=}\mathrm{CH_2} \xrightarrow{\mathrm{CO}} \overset{+}{\mathrm{COCpFe}}-\underset{\mathrm{CH_2}}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}} \xrightarrow{\mathrm{MeOH}} \mathrm{COCpFeCH_2CO_2Me} \xrightarrow[\mathrm{MeOH}]{\mathrm{Ce^{4+}}} \mathrm{CH_2(CO_2Me)_2} \qquad (1)$$

(1) (2) (3)

Thus, the amount of malonate was significantly improved by carrying out the reaction in the presence of external ligands, especially amines (Table 1). Such an improvement was also achieved by the use of less nucleophilic (or more hindered) alcohols, but with, in some cases, lower conversions (Table 1). But the most striking change in the selectivity is observed when the metal is changed. Thus, in using the

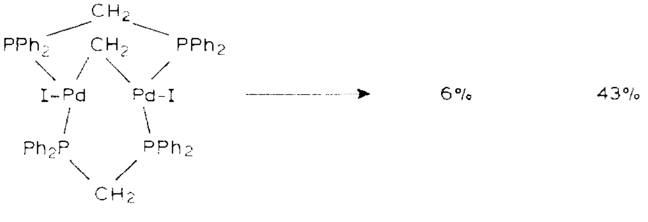
Table 1

Formation of malonates and esters prepared from μ-alkylidene complexes with CO in the presence of alcohols and external ligands

Complex [e]	Ligand	ROH	Ester [f]	Malonate [g]	Yield (%)
1		[a]	94	6	44
1	Et_3N	[a]	60	40	42
1	Bu_3N	[a]	74	26	38
1	Et_3N	[b]	30	70	13
1	Et_3N	[c]	84	16	49
1	Et_3N	[d]	76	24	68
5 [f]		[c]	12	88	49

[a] 1-Dodecanol. [b] 4-Decanol. [c] β-Ethylphenethylalcohol. [d] β-Butoxyethanol. [e] Solvent hexane. [f] Solvent toluene. [g] Selectivity.

(4)



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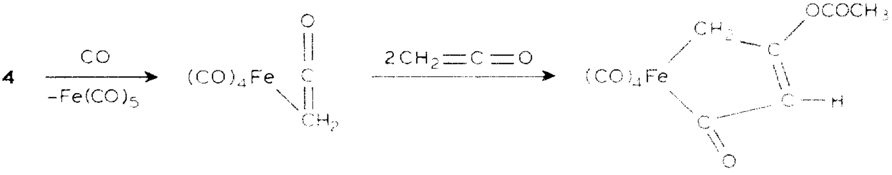
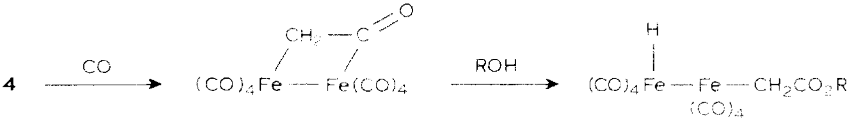
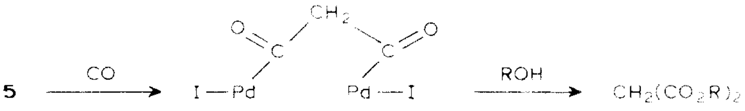


(6) (7)



(8) (9)



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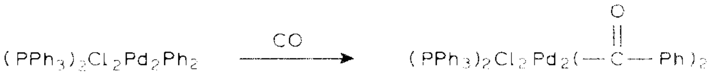

(11) (12)

$$CH_2X_2 + Pd_2(Ph_2PCH_2PPh_2)_3 \longrightarrow Pd_2X_2(\mu\text{-}CH_2)(PPh_2CH_2PPh_2)_2 \longrightarrow CH_2(CO_2R)_2$$

μ-alkylidene complex of palladium (**5**) we observed a fairly good conversion (~ 50%) into a mixture of ester and malonate, with a selectivity towards malonate of 88%.

The preferential formation of ester in the case of the iron complex, and of malonate in the case of the palladium complex can be interpreted in the light of the following observations (Scheme 1).(a) In the case of complex **4** in the absence of nucleophiles we observed the formation of a mononuclear ketene trimer complex **7** [5]. It is thus probable that in the presence of alcohols the preferential formation of ester can be ascribed to the solvolysis of free or coordinated ketene.

(b) Even if the solvolysis reaction takes place in the coordination sphere of iron via complex **9**, a carboalkoxymethyl complex of iron, the second carbonylation reaction should be difficult. Cutler did indeed show [1] that carboalkoxymethyl complexes of iron, such as **3**, are difficult to carbonylate, the reaction taking place only after the oxidation of the metal. These considerations could provide an explanation for the low yield of malonate in the carbonylation of complex **4**.

(c) In the case of palladium, we can only speculate on the mechanism of the formation of malonate. Nevertheless, it seems reasonable to assume that both the carbonylation and the solvolysis reactions take place on a dinuclear complex. It has been shown by Anderson [6] that in the case of complexes **11**, the carbonylation reaction does not lead to a mononuclear acyl complex, a reaction which is observed in the case of the dinuclear platinum complex, but to the diacyl complexes **12**. It is therefore reasonable to assume that the role of the bidentate ligand in complex **5** is to hold the two metal centres together, thus allowing the double carbonylation to occur. Since complex **5** is obtained [7,8] by a double oxidative addition of CH_2X_2 ($X = Cl$, I) to $Pd_2(Ph_2CH_2Ph_2)_3$, its transformation into malonate can thus be related to the difunctionalization of CH_2X_2 species.

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