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Preliminary Communication

New aspects of the synthesis of dimethyl carbonate via carbonylation of methyl alcohol promoted by methoxycarbonyl complexes of palladium(II)

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Abstract

$[PdCl_2(PPh_3)_2]$ suspended in MeOH reacts with carbon monoxide (40–80 atm, 50°C), in the presence of a base such as NEt_3 to give the methoxycarbonyl complex *trans*-$[PdCl(COOMe)(PPh_3)_2]$. When the carbonylation reaction is carried out at 90–100°C reduction to Pd^0 carbonyl-phosphine complexes occurs, with formation of dimethyl carbonate, selectively and in an almost quantitative yield. The above complexes are less reactive than the acetato-analogues, which give dimethyl oxalate as the main organic carbonylation product even at 50°C.

It has been reported that palladium(II) acetate complexes are able to promote the non-catalytic carbonylation of methanol to dimethyl oxalate (DMO) and dimethyl carbonate (DMC). This reaction, which occurs with high selectivity towards the formation of DMO, is significantly influenced by ligands such as phosphines and added bases such as a trialkylamine and by the pressure of carbon monoxide [1–3]. Thus, palladium(II) acetate is easily reduced to palladium metal even at room temperature when it is allowed to react with CO (40 atm) in MeOH with formation of DMO in high yield (87%) and of DMC in trace amounts [2]. When the reaction is carried out in the presence of a phosphine such as PPh_3 (experiments were carried out with a ratio $P/Pd = 2/1$, which is equivalent to starting directly from $[Pd(OAc)_2(PPh_3)_2]$ (**1**), or with a ratio $P/Pd = 3/1$, *i.e.* with an excess of phosphine) the formation of DMO and of DMC occurs at a slightly higher temperature (50°C) and the starting palladium (II) complex is reduced to carbonyl phosphine palladium(0) complexes. Reduction to Pd^0 does not occur at room temperature, and then the palladium is recovered as $[Pd(OAc)(COOMe)(PPh_3)_2$ (**2**) [1]. The selectivity towards DMC increases when the carbonylation is carried out in the presence of a strong base such as triethylamine and diisopropylethylamine, particularly under relatively low carbon monoxide pressure (up to 61–67%, under 6 atm of carbon monoxide). The yield of DMC + DMO increases with the CO pressure, being practically quantitative at 80°C under 40 atm of carbon monoxide after 2 h, with the other reagents in the ratios Pd/P/base = 1/2/5, in the presence of an excess of MeOH. Under these conditions the main product is DMO (87% selectivity).

It has been proposed that DMC forms from the above mono methoxycarbonyl complex (**2**) upon nucleophilic attack of MeO^- that forms from MeOH and the base, whereas DMO forms from the dimethoxycarbonyl complex $[Pd(COOMe)_2(PPh_3)_2]$ (**3**) [1–3].

It has also been reported that $PdCl_2$ promotes the non-catalytic carbonylation of ethyl alcohol to diethylcarbonate in the presence of a base such as sodium carbonate [4], at 20–40°C, under 1 atm of carbon monoxide. We have found that the chloride analogues of complexes **1–3** are more stable and behave significantly different from the corresponding acetato complexes. In fact, $[PdCl_2(PPh_3)_2]$ (**1′**) is not reduced to a Pd^0 complex when carbonylated under 20–80 atm of carbon monoxide at 50°C. Under these conditions and in the presence of NEt_3, there is formation of the methoxycarbonyl complex $[PdCl(COOMe)(PPh_3)_2]$ [**2′**) in almost quantitative yield. Further, complex **1′** is not reduced to a palladium(0) complex even when heated at 90–100°C under 20–80 atm of carbon monoxide in MeOH in the absence of the base. Rather it yields complex **2′**. Also, under the above conditions complex **2′** is rather stable and does not yield DMC or DMO in detectable amounts. The stability of this complex is not surprising since it has already been reported that it is stable also under olefin hydrocarboalkoxylation experiments under similar conditions [5]. Finally, under the above conditions, and when the carbonylation is carried out in the presence of NEt_3, complex **2′** is reduced to Pd^0 complexes with formation of DMC only.

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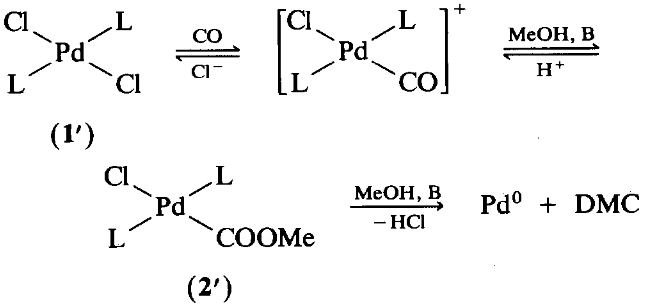
The Pd^0 complexes are $[Pd(CO)(PPh_3)_3]$ or a mixture of this and $[Pd_3(CO)_3(PPh_3)_{3\text{ or }4}]$ when the carbonylation is carried out in the presence or absence of additional PPh_3 as can be shown by IR spectroscopy [6]. The reaction occurs with practically 100% selectivity and in quantitative yield of DMC even under high pressure of carbon monoxide, *i.e*, under the conditions that favour the formation of DMO when the acetato-analogue is carbonylated. The same results are obtained when complex **1′** is carbonylated in the presence of NEt_3. Thus starting from chlorides **1′** or **2′** the selectivity is practically reversed with respect to the carbonylation of corresponding acetate complexes.

The different behaviours of $[Pd(OAc)(COOMe)(PPh_3)_2]$ (**2**) and $[PdCl(COOMe)(PPh_3)_2]$ (**2′**) indicates that OAc^- is a better leaving group than Cl^-, so that $[Pd(COOMe)_2(PPh_3)_2]$, and hence DMO, does not form easily from **2′**.

DMC is presumably formed as depicted in the following scheme, similar to that suggested for the formation of DMC from the acetato-analogue [2]:



The fact that complex (**2′**) decomposes to a Pd^0 complex only in the presence of NEt_3 suggests that the formation of DMC occurs *via* nucleophilic attack of MeO^- on the carbon atom of the carbonyl moiety of the methoxycarbonyl ligand.

Alternatively, even though it has been reported that chloroformate oxidatively adds to $[Pd(PPh_3)_4]$ at room temperature to yield complex **2′** [7], the formation of DMC may also occur through CO-assisted reductive elimination from this complex of methyl chloroformate, which is known to react promptly with MeOH to yield DMC. The yield is better in the presence of the base NEt_3 [8], which shifts the reductive elimination towards completeness.

$$\mathbf{2'} \longrightarrow Pd^0 + ClCOOMe$$

$$ClCOOMe + MeOH \xrightarrow{NEt_3} DMC + NEt_3\cdot HCl$$

It has been also reported that complexes **1′** and **2′** suspended in MeOH, in the presence of NaOMe react with carbon monoxide (2–3 atm, at 0°C, 4–5 h) to give the dimethoxycarbonyl complex **3**. Attempts in our laboratory to synthesize complex **3** in the absence of NaOMe were unsuccessful, even under 40–80 atm of carbon monoxide and at 80–95°C. This is probably the reason for the failure to obtain DMO by carbonylation of complexes **1′** and **2′**, different from what has been found when complexes **1** and **2** are carbonylated.

As already mentioned, complex **2′** is rather stable in the absence of NEt_3. This complex can also be isolated when complex **1′** is carbonylated under 40–80 atm of carbon monoxide at 80–90°C in 3 h, even in the presence of HCl (Pd/HCl = 1/1), although this complex reacts with concentrated hydrochloric acid at room temperature yielding its precursor together with MeOH [9], thus reversing the reaction of formation.

$$[PdCl(COOMe)(PPh_3)_2] + HCl \longrightarrow PdCl_2(PPh_3)_2 + MeOH + CO$$

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