*Journal of Organometallic Chemistry*, 174 (1979) 221—226

# ALCOHOL CARBONYLATION WITH PALLADIUM(II) COMPLEXES, EFFECTS OF LIGANDS, CARBON MONOXIDE, PRESSURE AND ADDED BASES

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(Received February 20th, 1979)

## Summary

The carbonylation of methanol with carbon monoxide to dimethyl oxalate and dimethyl carbonate in the presence of palladium(II) acetate has been shown to be influenced by the ligands, the CO pressure and added base. With phosphines, the ligand influence appears to be related mainly to their electronic properties. Alkylphosphines inhibit carbonylation almost completely. Low CO pressures and the presence of tertiary amines enhance the formation of dimethyl carbonate. A scheme accounting for these findings is presented.

## Introduction

Alcohol carbonylation in the presence of palladium compounds has been only briefly described in the journal literature although it has been the object of intensive investigations, as witnessed by the appearance of several patents. $PdCl_2$ has been reported [1] to promote the reaction of EtOH with CO in the presence of $Na_2CO_3$ to give diethyl carbonate according to eq. 1

$$2\ EtOH + CO + PdCl_2 + 2\ Na_2CO_3 \rightarrow (EtO)_2CO + Pd + 2\ NaCl + 2\ NaHCO_3 \quad (1)$$

Fenton [2] has described the formation of diethyl oxalate together with $(EtO)_2CO$ under more drastic conditions of oxidative carbonylation: thus $PdCl_2$, with a cocatalyst such as $CuCl_2$ or $FeCl_3$ and a dehydrating agent, catalyzes the reaction of EtOH, CO and $O_2$ according to eq. 2:

$$2\ EtOH + 2\ CO + \tfrac{1}{2}O_2 \xrightarrow{Pd,\ Cu} (COOEt)_2 + H_2O \quad (2)$$

More recently we reported [3] the synthesis of dimethyl oxalate from $CH_3OH$

and CO under mild conditions in the presence of $Pd(OAc)_2(PPh_3)_2$ according to eq. 3:

$$Pd(OAc)_2(PPh_3)_2 + 3\,CO + 2\,CH_3OH \xrightarrow[50^\circ C]{PPh_3} Pd(CO)(PPh_3)_3 + (COOCH_3)_2 + 2\,AcOH \quad (3)$$

The intermediary role of alkoxycarbonyl palladium complexes was demonstrated. We now describe the results of a more thorough investigation of the reaction, centred on the study of the effect of ligands, bases and CO pressure on the formation of oxalate esters and on the selectivity between oxalate and carbonate.

## Results

$Pd(OAc)_2$ is quite reactive in the methanol/carbon monoxide system, being reduced to palladium metal even at room temperature when suspended in $CH_3OH$ under 40 atm CO, giving dimethyl oxalate (DMO, 87%, 2 h) and only a trace of dimethyl carbonate (DMC). Adding a phosphine ligand, such as $PPh_3$, prevents formation of palladium black: instead, phosphine or carbonyl [4] palladium(O) complexes are formed, depending on the CO pressure, the temperature and the [P]/[Pd] ratio. The presence of the ligand lowers the reactivity of the palladium complex: for example with $[PPh_3]/[Pd] = 2$ a temperature of about 50°C is needed to observe reduction at 40 atm CO pressure. If the reaction is carried out at room temperature, an alkoxy carbonyl complex, i.e. $Pd(COOCH_3)(OAc)(PPh_3)_2$, which is believed to be an intermediate in the carbonylation, is isolated instead [3].

Results obtained under standard conditions (2 h, 80°C, 40 atm CO, [P]/[Pd] = 2) in the presence of various phosphine ligands are reported in Table 1. Addition of a trialkyl phosphine ($P\text{-}n\text{-}Bu_3$) or an arylalkyl phosphine such as $P(CH_3)_2Ph$ almost completely inhibits the formation of DMO as well as of DMC, although reduction of palladium(II) to palladium(O) takes place. The effect of the triaryl phosphines may be understood in terms of electronic rather than steric effects. Tris(*p*-anisyl) and tris(o-anisyl) phosphine, bearing an highly electron donor substitutent on the phenyl rings, behave similarly, giving smaller

TABLE 1

EFFECT OF VARYING THE LIGANDS ON DMO AND DMC YIELDS [a]

| Ligand | DMO [b] | DMC [b] |
|---|---|---|
| — | 99 | 3 |
| $PBu_3$ | — | — |
| $PMe_2Ph$ | 3 | — |
| $P(o\text{-}C_6H_4OCH_3)_3$ | 26 | 1 |
| $P(p\text{-}C_6H_4OCH_3)_3$ | 50 | 6 |
| $P(o\text{-}C_6H_4CH_3)_3$ | 106 | — |
| $PPh_3$ | 98 | 3 |
| $AsPh_3$ | 104 | — |
| $SbPh_3$ | 42 | 1 |

[a] $Pd(OAc)_2$ 1 mmol, ligand 2 mmol, $CH_3OH$ 10 $cm^3$, CO 40 atm, 80°C, 2 h. [b] % yields based on $Pd(OAc)_2$.

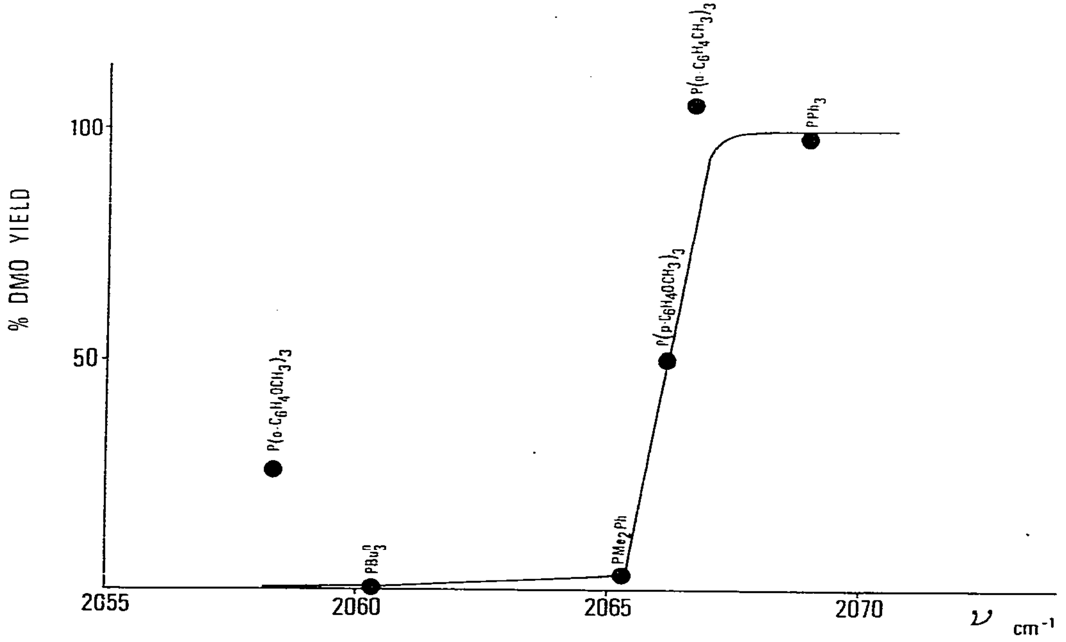


Fig. 1. Correlation between Tolman's ν electronic parameter and yield of DMO.

amounts of DMO (26 and 50%, respectively). Tris(*o*-tolyl) phosphine behaves like $PPh_3$, both giving DMO in about 100% yield.

Yields in Table 1 can be roughly ordered by use of Tolman's ν electronic parameter [5], as depicted in Fig. 1. The point for tris(*o*-anisyl) phosphine might suffer from an inaccurate estimate of the electronic properties for this ligand by the ν parameter: the large difference between the values reported for tris(*o*-anisyl) and tris(*p*-anisyl) phosphine (7.8 $cm^{-1}$) appears to be anomalous in view of the fact that tris(*o*-tolyl) and tris(*p*-tolyl) phosphine exhibit values very close to one another (2066.6 and 2066.7 $cm^{-1}$, respectively).

The behaviour observed in the presence of phosphines bearing alkyl substituents has precedents in the literature, in that failure to form alkoxycarbonyl complexes has been noted. Replacement of $PPh_3$ by $P(CH_3)_2Ph$ was reported [6] to reduce greatly the reactivity of $Pt(OCOCF_3)_2L_2$ towards CO in methanol. Thus, whereas $Pt(COOCH_3)(OCOCF_3)(PPh_3)_2$ is easily obtained by bubbling CO into a suspension of $Pt(OCOCF_3)_2(PPh_3)_2$ in methanol, the analogous alkoxycarbonyl complex with $P(CH_3)_2Ph$ cannot be obtained even under 100 atm CO pressure.

In addition, the reactivity of the carbonyl cations $Pt(X)(CO)L_2^+$, where X is an anionic and L is a neutral ligand, towards nucleophiles such as water or alcohols, has been shown [7] to be greatly influenced by the nature of X and L. For example, for X = SCN, $NO_3$ or $C_6F_5$, no reaction with methanol is observed when L = $PEt_3$ whereas alkoxycarbonyl derivatives are readily obtained for L = $PPh_3$. The lack of reaction can be related to the *trans* influence of X as well as to the electron donating properties of the ligand L, both lowering the reactivity of carbonyl carbon in the cation towards a nucleophile such as methanol. From this point of view, the effect of phosphines on DMO and DMC formation may be related to their influence, as determined by their electronic properties, on the

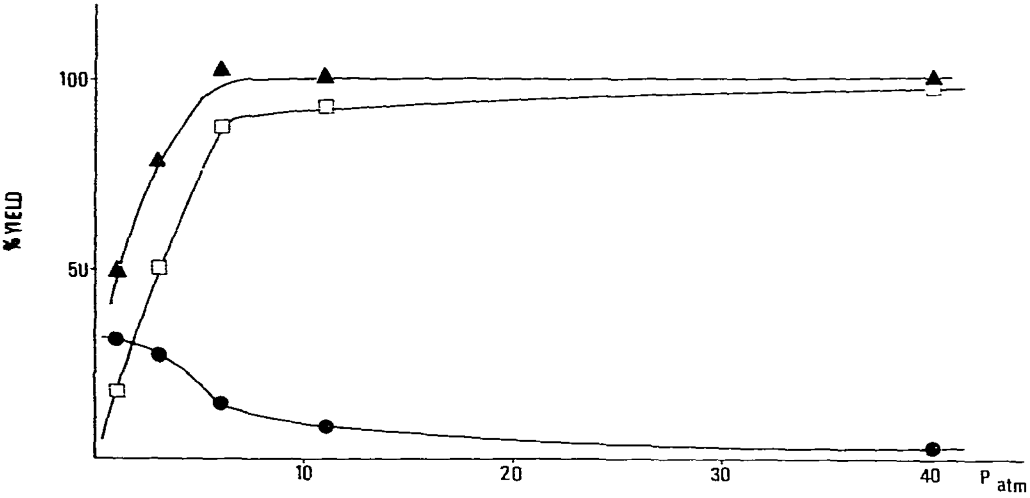


Fig. 2. Effect of CO pressure on DMO (□), DMC (●) and DMO + DMC (▲) yields.

ease of formation of alkoxy carbonyl species, thereby confirming them as intermediates in the reaction.

The effect of replacing phosphorus by As or Sb in the ligand is also illustrated in Table 1: the formation of DMO appears to be lowered only in the presence of $SbPh_3$, selectivity between DMO and DMC is quite high at 40 atm CO (Table 1). However, lower CO pressures give both lower selectivities and lower total yields of carbonylated products. Oxidation of the alcohol by palladium(II) [1,8] may become competitive at the lowest CO pressures. Effects of pressure on yields and selectivities are shown in Figs. 2 and 3, respectively, for L = $PPh_3$ (2 h, 80°C, [P]/[Pd] = 2). The effect is pronounced only at the lowest pressures, DMO being formed in moderate yield (18%) even at atmospheric CO pressure.

The effect of adding a base to the system is shown in Table 2. Formation of

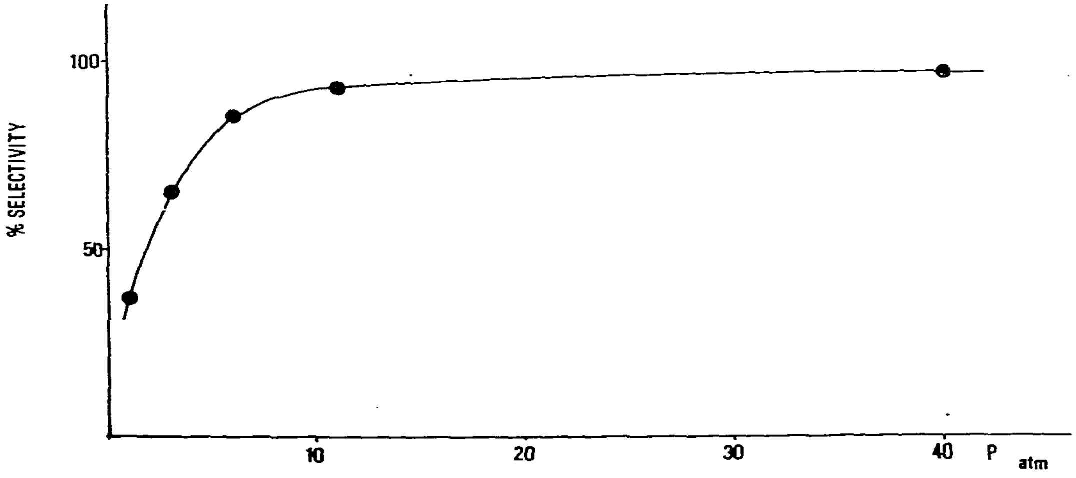


Fig. 3. Effect of CO pressure on selectivity, $S = [DMO]/\{[DMO] + [DMC]\}$.

TABLE 2

EFFECTS OF BASE ON DMO AND DMC YIELDS AND ON SELECTIVITY[a]

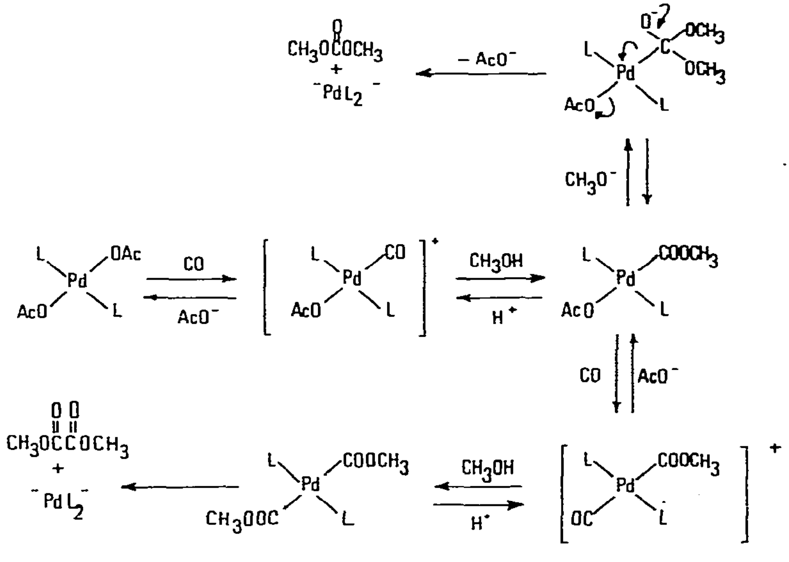
| Base | $P$[b] | DMO[c] | DMC[c] | $S$[d] |
|---|---|---|---|---|
| — | 40 | 98 | 3 | 97 |
| Trietylamine | 40 | 81 | 12 | 87 |
| — | 6 | 87 | 14 | 86 |
| Pyridine | 6 | 51 | 17 | 75 |
| Triethylamine | 6 | 32 | 51 | 39 |
| Diisopropylethylamine | 6 | 30 | 61 | 33 |

[a] $Pd(OAc)_2$ 1 mmol, $PPh_3$ 2 mmol, base 5 mmol, $CH_3OH$ 10 $cm^3$, 80°C, 2 h. [b] CO pressure, atm. [c] % yields based on $Pd(OAc)_2$. [d] Selectivity as [DMO]/{[DMC] + [DMO]}.

DMC is enhanced in the presence of strong bases such as triethylamine and diisopropylethylamine, particularly when low CO pressures are employed. However the selectivity in favour of DMO is significantly lowered, even at 40 atm CO pressure in the presence of triethylamine. The effects observed are quite similar for $Et_3N$ and the sterically hindered $(i\text{-}Pr)_2EtN$, which should be similar in basicity but rather different as ligands. Moreover, pyridine, a much weaker base, exhibits only a minor effect on selectivity even at low CO pressures. This suggests that the effect of adding the amines must be related mainly to their base strengths rather than to their ability to act as ligands towards palladium.

The results can be understood in terms of the postulated reaction route [3], characterized by replacements of $AcO^-$ by CO to give cationic carbonyl and alkoxycarbonyl intermediates. The formation of cationic carbonyls by substitution of $AcO^-$ ligands is clearly related to the pressure of CO. Nucleophilic attack of the alcohol at the carbon atom of the coordinated carbonyl ligand gives the alkoxycarbonyl species. In the case of $PtCl(COOCH_3)(PPh_3)_2$ this reaction has been reported [9] not to be base dependent, implying that an alcohol molecule

SCHEME 1



rather than an alkoxide ion acts as nucleophile. Reductive elimination on a bis-(alkoxycarbonyl) species could give the oxalate, whereas nucleophilic attack of alcohol or alkoxide, whether precoordinated to the metal or not, at the carbonyl of the alkoxycarbonyl group could account for the formation of carbonate (Scheme I). The latter route is likely to be base catalyzed, explaining the dependence of the selectivity on added bases.

## Experimental

Synthesis of $(i\text{-}Pr)_2EtN$ [10], $P(o\text{-}C_6H_4OCH_3)_3$ [11] and $P(p\text{-}C_6H_4OCH_3)_3$ [11,12] was as previously described. All other compounds used were commercial products.

The reactions were carried out in a Teflon-coated stainless steel autoclave which was charged, purged with nitrogen and CO, pressurized with CO at the required pressure and warmed in a glycerol bath with magnetic stirring. At the end of the reaction the autoclave was vented and the liquid filtered and analyzed for DMO and DMC by GLC using an 8 ft. × 1/4 in. column filled with 20% Carbowax 20M on Chromosorb WS 60—80 mesh with benzofuran or cumene as internal standards. Analyses were performed on a Hewlett-Packard 5710A gas chromatograph equipped with thermal conductivity detector and programmed temperature unit.

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