# Methoxycarbonylation of vinyl acetate catalysed by palladium complexes of bis(ditertiarybutylphosphinomethyl)benzene and related ligands

**Adam J. Rucklidge,[a] George E. Morris[b] and David J. Cole-Hamilton*[a]**

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**High selectivities to methyl acetoxypropanoate esters (b : l up to 3.6 : 1) are obtained from the methoxycarbonylation of vinyl acetate catalysed by palladium complexes of bis(ditertiarybutylphosphinomethyl)benzene in the presence of acid, provided that the acid concentration does not exceed that of the free phosphine.**

Political and consumer pressures are encouraging manufacturing industries in their attempts to achieve processes and products that are both safe and environmentally friendly. It is also desirable to manufacture goods, which, when their lifetime of usage has expired, can be easily destroyed to non-toxic components. Items such as carrier bags and fast-food boxes are "use once and dispose of" items which either have to be incinerated or end up on a rubbish tip taking years to decay. The search for suitable biodegradable plastics is intensifying.

One approach involves the use of lactate esters. Ethyl lactate is a "green solvent" as it has low volatility and is biodegradable. It is non-toxic and as a result has been approved by the FDA for use in food. Lactate esters can be polymerised to form polylactic acid and if the monomers are predominantly the S enantiomer the resulting polymer is biodegradable and has properties similar to those of polyethylene and polystyrene. Currently the main synthetic route to lactate esters is the fermentation of glucose obtained from starch.[1] However, another viable route is the alkoxycarbonylation of vinyl acetate to form alkyl esters, which, upon removal of the acetoxy group give the desired hydroxypropanoic acid (lactate) esters (Fig. 1). Although vinyl acetate is derived from ethene, it is cheap and very readily available.

Only two reports of the alkoxycarbonylation of vinyl acetate have appeared. Drent[2] methoxycarbonylated vinyl acetate using palladium acetate and 1,3-bis(ditertiarybutylphosphino)propane as the catalyst system. In MeOH/diglyme at 75 °C and 40 bar CO, the methyl ester was formed with a b : l ratio of 2 : 1 at rate of 200 moles (g Pd h)$^{-1}$. Kudo[3] *et al.* showed that $PdCl_2/PPh_3$ with a catalytic amount of 2,6-lutidine can methoxycarbonylate vinyl acetate at 120 °C and 200 bar. A considerable quantity of methyl acetate was formed due to the methanolysis of vinyl acetate.

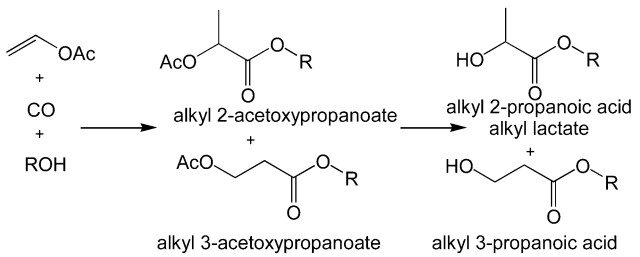


**Fig. 1** The alkoxycarbonylation of vinyl acetate as a step in the production of alkyl lactates.

*djc@st-and.ac.uk

Methoxycarbonylation of other alkenes such as ethene is well known and an attractive system involves $[(DTBPMB)PdH]^+$ (DTBPMB = 1,2-$(PBu^t_2CH_2)_2C_6H_4$) (**1**) which gives extremely high rates and good selectivity.[4] The same system is also active for the methoxycarbonylation of long chain alkenes,[5] giving very high linear selectivities and for styrene giving high branched selectivity.[6]

In this communication we report that the same system is active for vinyl acetate methoxycarbonylation under mild conditions and demonstrate how the competing methanolysis of vinyl acetate can be avoided.

To determine what were the primary causes of the methanolysis of vinyl acetate a stability test was carried out. Vinyl acetate was stirred with MeOH in toluene together with combinations of promoters such as a basic phosphine and an organic acid (Table 1). Vinyl aceate is stable with respect to DTBPMB but if methanesulfonic acid (MSA) is present, the majority of the vinyl acetate is converted to MeOAc even at room temperature, confirming that the transesterification of vinyl acetate is catalysed by acid. However, if both the acid and the phosphine are present together there is minimal degradation of the vinyl acetate. As expected the higher the reaction temperature the greater the extent of the side reaction, although the side reaction is still inhibited if both acid and base are added together (*i.e.* the phosphonium salt is present rather than the free acid). Tanaka and co-workers have shown that polymeric acids can also reduce the side reactions

**Table 1** Results from the determination of the stability of vinyl acetate in the presence of MeOH[a]

| | | 25 °C | | 80 °C | |
|---|---|---|---|---|---|
| MSA/ mmol | DTBPMB/ mmol | VAM (%) | MeOAc (%) | VAM (%) | MeOAc (%) |
| 0 | 0 | 100 | 0 | 100 | 0 |
| 1 | 0 | 50 | 50 | 0 | 100 |
| 0 | 1 | 100 | 0 | 100 | 0 |
| 1 | 1 | 100 | 0 | 100 | 0 |

[a] Reaction conditions: vinyl acetate (VAM) (2 cm$^3$), MeOH (2 cm$^3$), toluene (9 cm$^3$), reaction time 3 h. MSA = methanesulfonic acid

 

**Table 2** Methoxycarbonylation of vinyl acetate with DTBPMB complexes

| Temperature/ °C | CO pressure/ bar | Conversion (%) | Selectivity to esters (%) | b : l |
|---|---|---|---|---|
| 80 | 30 | 100 | 100 | 1.2 |
| 80 | 3 | 100 | 100 | 2.2 |
| 25 | 30 | 37 | 100 | 3.3 |
| 25 | 3 | 35 | 100 | 3.6 |

[a] $Pd_2(dba)_3$ (0.05 mmol, dba = dibenzilideneacetone), DTBPMB (0.5 mmol), methanesulfonic acid (0.5 mmol), MeOH (11 $cm^3$), vinyl acetate (21 mmol), reaction time 3 h.

whilst allowing activity from the same catalytic system.[6] An understanding of the effect of acid on vinyl acetate degradation means that it is possible to tailor the reaction conditions so that no free acid is present in the system and hence that no degradation occurs. Catalytic results show that the phosphonium salt derived form DTBPMB and MSA is sufficiently acidic to protonate the palladium centre and initiate the catalytic reaction.

The methoxycarbonylation of vinyl acetate was carried out using DTBPMB complexes with a Pd : DTBPMB : MSA ratio of 1 : 5 : 5 (see Table 2). At 80 °C and 30 bar CO, the desired esters were formed in quantitative yield with 100% selectivity in 3 h. The branched to linear ratio (b : l) was 1.2 : 1. Lowering the temperature or pressure improved the b : l ratio, but the reaction rate was reduced at lower temperature. The best selectivity to the desired branched product (b : l = 3.6 : 1) was obtained at 25 °C and 3 bar of CO. In all of these experiments the selectivity to the esters was 100% and no MeOAc was detected (Table 2).

To determine whether the DTBPMB ligand gave the best selectivity to the branched ester various alternative ligands were investigated (Fig. 2). The results, shown in Table 3, demonstrate

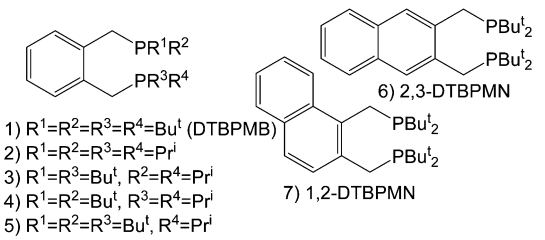


**Fig. 2** Structures of ligands used for the methoxycarbonylation of vinyl acetate.

**Table 3** Methoxycarbonylation of vinyl acetate at 25 °C and 3 bar of carbon monoxide

| Ligand | Conversion (%) | Selectivity to esters (%) | b : l |
|---|---|---|---|
| **1** | 35 | 100 | 3.6 |
| **2** | 0 | N/A | N/A |
| **3** | 7 | 100 | 0.8 |
| **4** | 47 | 28 | 1.4 |
| **5** | 13 | 85 | 2.0 |
| **6** | 15 | 100 | 3.6 |
| **7** | 18 | 100 | 3.6 |

[a] $Pd_2(dba)_3$ (0.05 mmol), ligand (0.5 mmol), methanesulfonic acid (0.5 mmol), MeOH (11 $cm^3$), vinyl acetate (21 mmol), carbon monoxide pressure (3 bar), temperature 25 °C, reaction time 3 h.

**Table 4** Comparison of $\nu_{CO}$ of $Mo(CO)_4L$ complexes for bidentate phosphine ligands[a]

| L | $\nu_{CO}$ |
|---|---|
| dppe | 2021[7] |
| **2** | 2019 |
| **3** | 2013 |
| $Et_2PCH_2CH_2PEt_2$ | 2012[8] |
| **6** | 2007 |
| **7** | 2007 |
| **1** | 2006 |

[a] Spectra recorded in $CH_2Cl_2$ solution.

the importance of the $Bu^t$ groups. When 1 group is replaced by $Pr^i$ (compound **5**) the conversion and branched selectivity are reduced. As further substitution is carried out the conversion and selectivity continue to drop, whilst the ligand with 4 $Pr^i$ groups (**2**) does not give an active catalyst. Retaining the phenyl backbone of the ligand, but altering the electronic effect slightly by using napthalenes in place of the benzene ring does not affect the b : l ratio, but does reduce the reaction rate.

The electron donating effects of the ligands, L, were studied by synthesising $[Mo(CO)_4L]$ complexes from [(norbornadiene)-$Mo(CO)_4$] The value of the $\nu_{CO}$ was used to evaluate the ligand donor properties. The lower the wavenumber of the $\nu_{CO}$ band the greater the electron donating power of the ligand. As can be seen from Table 4, the ligands with 4 $Bu^t$ substituents on phosphorus (**1**, **6** and **7**) are the most electron donating of those we have studied. They also give the highest rates and selectivities to the branched product in the methoxycarbonylation of vinyl acetate. However, they are also the most sterically congested of the ligands, so it is difficult to disentangle steric from electronic effects in this case. The catalytic mechanism for alkene methoxycarbonylation for other substrates has clearly been shown to proceed *via* a hydride mechanism.[5,9,10] A greater electron density on the metal centre would be expected to lead to more of the palladium centres being present in a catalytically active form ($[PdH(DTBPMB)X]^+$, X = CO, MeOH or vinyl acetate) and hence a higher rate.

Using ligand **7** the effect of acid concentration on the methoxycarbonylation of vinyl acetate was studied. As can be seen in Fig. 3 the maximum TON (in 3 h) occurs when a Pd : MSA

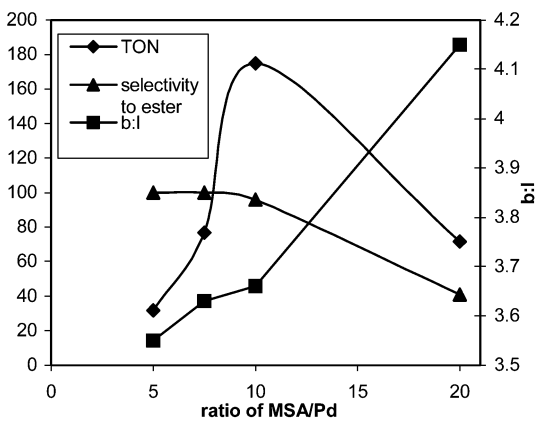


**Fig. 3** Effect of acid on the methoxycarbonylation of vinyl acetate. $Pd_2(dba)_3$ (0.5 mmol), **7** (5 mmol), MeOH (11 $cm^3$), vinyl acetae (21 mmol), CO pressure (3 bar), temperature 25 °C, reaction time 3 h.

ratio of 1 : 10 is used. However, under these conditions, a small amount of vinyl acetate degradation to methyl acetate occurs (4%), because excess acid (2 mol (mol $Pd^{-1}$)) is present. With a greater acid concentration the degradation to MeOAc markedly increases, because of the increased free acid concentration.

We conclude that vinyl acetate can be methoxycarbonylated to methyl acetoxypropanoate esters in high yield using Pd/DTBPMB/$H^+$. The selectivity to the esters is quantitative provided that the presence of free acid is avoided. Selectivities to the branched product can be as high as 78%. These results have been patented.[11]

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**Adam J. Rucklidge,[a] George E. Morris[b] and David J. Cole-Hamilton*[a]**
*[a]School of Chemistry, University of St Andrews, St Andrews, Fife, UK KY16 9ST. E-mail: djc@st-and.ac.uk; Fax: +44 (0)1334 463808; Tel: +44 (0)1334 463805*
*[b]BP Chemicals, Saltend, Hull, UK HU12 8DS*

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