

# Synthesis and spectroscopic characterisation of *all* the intermediates in the Pd-catalysed methoxycarbonylation of ethene

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The pathway of the palladium catalysed methoxycarbonylation of ethene to methyl propanoate has been shown to occur *via* a hydride rather than a methoxycarbonyl cycle and *all* the intermediates in this cycle have been unambiguously identified by multinuclear NMR spectroscopy and <sup>13</sup>C-labelling.

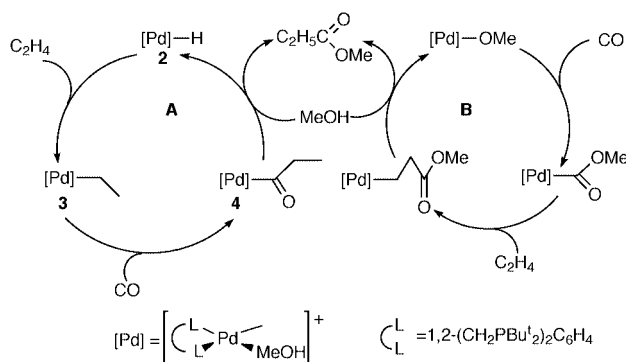
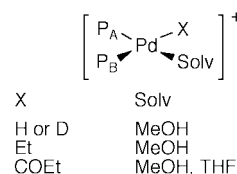
The alkoxy carbonylation of alkenes is of increasing scientific and technological importance. This reaction can give rise to a broad spectrum of products; for ethene, this can range from high melting thermoplastic polymers—the so called ‘polyketones’ to low boiling liquids such as methyl propanoate. The former materials have attracted more attention in the literature as they have been developed into commercial products.<sup>1</sup> Our work focuses on methyl propanoate, a key intermediate in the manufacture of methyl methacrylate, an important monomer produced annually on a multi-million tonne scale world wide.<sup>2</sup>

A new catalyst for the production of methyl propanoate (MeP) *via* the palladium catalysed methoxycarbonylation of ethene has recently been reported.<sup>3</sup> The catalyst, generated *in situ* *via* the reaction of [Pd(L–L)(dba)] [L–L = 1,2-(CH<sub>2</sub>PBu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>; dba = *trans,trans*-(PhCH=CH)<sub>2</sub>CO] with *e.g.* methanesulfonic acid, gives MeP with a selectivity of 99.98% at a production rate of 50 000 mol product (mol Pd)<sup>–1</sup> h<sup>–1</sup> under very mild conditions (353 K and 10 atm pressure of CO–C<sub>2</sub>H<sub>4</sub>). Two alternative mechanistic pathways have been proposed for this type of reaction, *i.e.* a hydride or a methoxy cycle (**A** and **B** respectively in Scheme 1).<sup>1</sup> Here, we report an investigation which provides unambiguous spectroscopic evidence for *all* the intermediates in the *hydride* catalytic cycle (**A** in Scheme 1).

The complex [Pd(L–L)(dba)] reacts in MeOH with HBF<sub>4</sub> or CF<sub>3</sub>SO<sub>3</sub>H in the presence of oxygen or benzoquinone (BQ) to give selectively a new compound, which can be formulated as either the neutral complex [Pd(L–L)HX] {X = [BF<sub>4</sub>]<sup>–</sup> **1a**, X = [CF<sub>3</sub>SO<sub>3</sub>]<sup>–</sup> **1b**} or the solvento-cation [Pd(L–L)H(MeOH)]X {X = [BF<sub>4</sub>]<sup>–</sup> **2a**, X = [CF<sub>3</sub>SO<sub>3</sub>]<sup>–</sup> **2b**}. We prefer the cationic formulation **2** since variable temperature <sup>31</sup>P and <sup>1</sup>H NMR

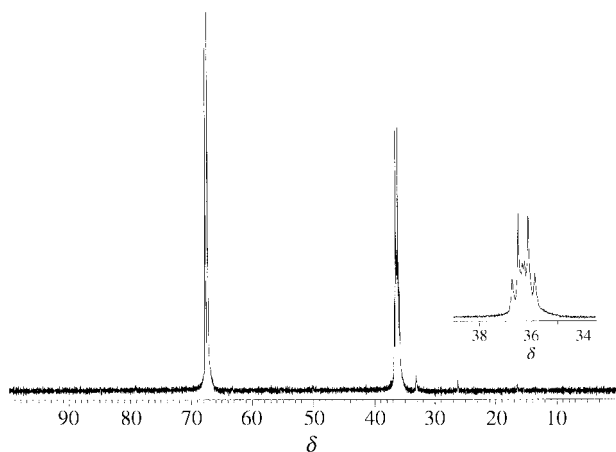
spectra of the products resulting from the reaction with HBF<sub>4</sub> do not show any coupling to fluorine. Furthermore, the <sup>31</sup>P{<sup>1</sup>H}, <sup>31</sup>P and <sup>1</sup>H NMR spectra of **2b** at room temperature in MeOH are very similar to those of **2a** and are entirely consistent with the proposed structure in which the anion is present only as a non-coordinating counter ion. Thus, the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **2b** consists of two resonances due to the inequivalent *cis*-P-atoms [ $\delta$  25.8 and 77.5; <sup>2</sup>J(P<sub>A</sub>–P<sub>B</sub>) 17 Hz] and the resonance at  $\delta$  25.8 is assigned to P<sub>B</sub> since it shows additional coupling to the *trans*-hydride [<sup>2</sup>J(P<sub>B</sub>–H) 179 Hz]. In order to avoid H/D exchange, the <sup>1</sup>H NMR spectrum was recorded in MeOH using the <sup>1</sup>H/<sup>31</sup>P correlations measured *via* zero and double quantum coherences.<sup>4</sup> The hydride resonance consists of a doublet of doublets at  $\delta$  –10 [<sup>2</sup>J(P–H) 179 and 14 Hz], due to the *trans*- and *cis*-couplings respectively).

On carrying out the above reaction in CD<sub>3</sub>OD, the new deuterides [Pd(L–L)D(CD<sub>3</sub>OD)]X {X = [BF<sub>4</sub>]<sup>–</sup> **2c**, X = [CF<sub>3</sub>SO<sub>3</sub>]<sup>–</sup> **2d**} can be isolated and their <sup>31</sup>P{<sup>1</sup>H} NMR spectra are exactly in accord with their formulation; the resonance at  $\delta$  25.8 due to P<sub>B</sub> is clearly a sextet [<sup>2</sup>J(P<sub>A</sub>–P<sub>B</sub>) 17 Hz and <sup>2</sup>J(P<sub>B</sub>–D) 27 Hz].



**Scheme 1** Alternative reactive functional groups in the methoxycarbonylation of ethene (**A**, hydride cycle; **B**, methoxycarbonyl cycle).

The hydride complex **2** reacts *immediately* with ethene at room temperature. Thus, addition of 1 equivalent of ethene to **2** results in the complete formation of the cationic complex [Pd(L–L)Et(MeOH)]X {X = [BF<sub>4</sub>]<sup>–</sup> **3a**, X = [CF<sub>3</sub>SO<sub>3</sub>]<sup>–</sup> **3b**} and there is no further reaction on addition of more ethene. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **3a** and **3b** in MeOH at 193 K consist of two doublets [ $\delta$  36.1 and 68.0; <sup>2</sup>J(P<sub>A</sub>–P<sub>B</sub>), 31 Hz] and <sup>2</sup>J(P<sub>B</sub>–H) has completely disappeared. In order to confirm the formulation of **2b** was repeated with <sup>13</sup>CH<sub>2</sub>=CH<sub>2</sub>. In this case, there is a doublet at  $\delta$  68 [<sup>2</sup>J(P<sub>A</sub>–P<sub>B</sub>), 31 Hz] in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (at 193 K) and a more complicated multiplet at  $\delta$  36.1 (Fig. 1). As a result of using <sup>13</sup>CH<sub>2</sub>=CH<sub>2</sub>, a 1 : 1 mixture of two isotopomers of **3b** is formed, *i.e.* [Pd(L–L)(CH<sub>2</sub><sup>13</sup>CH<sub>3</sub>)(MeOH)]<sup>+</sup> **3c** and [Pd(L–L)(<sup>13</sup>CH<sub>2</sub>CH<sub>3</sub>)(MeOH)]<sup>+</sup> **3d**. For **3c**, the phosphorus *trans* to the ethyl group (P<sub>B</sub>) couples only with the *cis*-phosphorus P<sub>A</sub> [<sup>2</sup>J(P<sub>A</sub>–P<sub>B</sub>) 31 Hz] whereas in **3d**, P<sub>B</sub> couples with both P<sub>A</sub> and the *trans* carbon atom [<sup>2</sup>J(P<sub>B</sub>–C) 38 Hz], resulting in a doublet of doublets (Fig. 1). The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of the 1 : 1 mixture of the two isotopomers **3c** and **3d** at 193 K consists of a singlet at  $\delta$  8 (CH<sub>3</sub>) and a doublet of doublets at  $\delta$  31 due to the CH<sub>2</sub> group [<sup>2</sup>J(P<sub>A</sub>–C) 5 Hz, <sup>2</sup>J(P<sub>B</sub>–C) 38 Hz]; the proton coupled <sup>13</sup>C NMR spectrum at 193 K shows the expected couplings due to the CH<sub>3</sub> and CH<sub>2</sub> groups [<sup>1</sup>J(C–H) 124 and 158 Hz, respectively].



**Fig. 1**  $^{31}\text{P}$  NMR spectrum at 193 K of the two isotopomers **3c** and **3d** formed on reaction of  $^{13}\text{CH}_2=^{12}\text{CH}_2$  with  $[\text{Pd}(\text{L-L})\text{H}(\text{MeOH})]^+$  **2**, in MeOH.

The ethyl complex **3** is also quite stable in THF at low temperature. In this solvent the species  $[\text{Pd}(\text{L-L})\text{Et}(\text{THF})]^+$  **3e** is present [in THF at 193 K,  $\delta(\text{P}_\text{A})$  67.9,  $\delta(\text{P}_\text{B})$  37.1;  $^2J(\text{P}_\text{A}-\text{P}_\text{B})$  31.5 Hz]. On adding 1 equivalent of CO to **3e** in THF,  $[\text{Pd}(\text{L-L})(\text{COEt})(\text{THF})]^+$  **4** is formed *immediately* and the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at 193 K consists of two doublets [ $\delta$  79.9 and 32.5;  $^2J(\text{P}_\text{A}-\text{P}_\text{B})$  40 Hz]. On using  $^{13}\text{CO}$ , both  $^{31}\text{P}$  resonances become doublets of doublets owing to additional couplings [ $^2J(\text{P}_\text{B}-\text{C})$  82.9 Hz,  $^2J(\text{P}_\text{A}-\text{C})$  18.2 Hz] and, in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum at 193 K, the  $^{13}\text{C}(\text{O})\text{C}_2\text{H}_5$  group is clearly identified at  $\delta$  232 as a doublet of doublets due to *cis* and *trans*  $^2J(\text{P}-\text{C})$ .

On addition of a trace of MeOH to a THF solution of **4**, even at low temperature, there is an immediate reaction to regenerate the palladium hydride complex **2** with the formation of  $\text{EtCO}_2\text{Me}$  (MeP). In methanol solution, **3** reacts immediately, even at low temperatures, with CO to give **2** and MeP, presumably *via* an acyl intermediate analogous to **4**.

The synthesis and reactivity of **2** provides important information on the mechanism involved in the methoxycarbonylation of ethene promoted by this particular class of catalyst. The nature of *all* the intermediates (**2**, **3** and **4**) involved

in the hydride catalytic cycle (**A** in Scheme 1) has been determined and the chemical connections between these intermediates demonstrated.

It has been previously claimed that both the catalytic cycles, *i.e.* **A** and **B** in Scheme 1, are involved for the catalysts used for the synthesis of polyketones.<sup>1,5</sup> Moreover, it has been suggested that the methoxy cycle is the dominant cycle in the presence of oxidants (*e.g.* BQ).<sup>1</sup> These data have always been explained on the basis of the fact that Pd-hydrides are usually oxidised to give Pd-methoxy complexes in MeOH in the presence of oxidants.<sup>1,6</sup> However, we find that **2** is very stable in the presence of oxidants; oxygen can be bubbled through a methanol solution of **2** for 20–30 min at temperatures as high as 353 K without reaction; **2** is also stable in the presence of an excess of BQ (< 7 equivalents) on the timescale of the catalysis. In all cases, the only reaction observed on addition of further BQ is the metallation of the phosphine ligands<sup>3</sup> and there is no evidence for the formation of any methoxy complex. Hence, all the above data provide strong evidence in support of the hypothesis that the methoxycarbonylation of ethene promoted by  $[\text{Pd}(\text{L-L})(\text{dba})]$  follows the hydride catalytic cycle (**A** in Scheme 1).

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## Notes and references

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