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Highly selective formation of linear esters from terminal and internal alkenes catalysed by palladium complexes of bis-(di-*tert*-butylphosphinomethyl)benzene

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The methoxycarbonylation of terminal or internal alkenes catalysed by palladium complexes of bis-(di-*tert*-butylphosphinomethyl)benzene under mild conditions leads to linear esters in 99% selectivity *via* a hydride mechanism.

The highly selective formation of terminal oxygenates from alkenes is a major goal of many homogeneous catalytic reactions. Aldehydes and alcohols from hydroformylation have been extensively studied for use as plasticizers, soaps and detergents,[1,2] but the highly selective methoxycarbonylation of alkenes to carboxylic acid esters for use in detergents as ethoxylates or *via* hydrogenation to alcohols is also an important target. Special advantages accrue if these terminal products can be synthesised from internal alkenes. A recent report shows that such reactions from internal alkenes are possible using palladium complexes of bis-adamantyl derived diphosphines, but the linear selectivity is only 80%.[3] Bis-(di-*tert*-butylphosphino)propane gave palladium complexes which were of very low activity for this reaction.[3] Bis-(di-*tert*-butylphosphinomethyl)benzene (DTBPMB) has proven to be a highly successful ligand for the palladium catalysed methoxycarbonylation of ethene to methyl propanoate[4] and, despite suggestions to the contrary,[5] there has been a brief report in a patent that this can provide linear selectivities up to 97% in the methoxycarbonylation of 1-octene under relatively high pressures (30 bar, 100 °C) and in the presence of polar aprotic solvents. The same system gave methyl pentanoate from 2-butene in 97% selectivity at 65 bar and 100 °C.[6]

We now report that this system is active under very mild conditions for the methoxycarbonylation of a variety of terminal and internal alkenes and that the linear selectivity can exceed 99.9% (see Table 1).

Bubbling carbon monoxide (1 atmosphere) through a methanol solution containing 1-octene, $[Pd_2(DBA)_3]$ (DBA = dibenzylidene acetone), DTBPMB and methane sulfonic acid gives high conversion of the 1-octene to methyl nonanoate with selectivity of 99% in <3 h. The only other detectable product is methyl 2-methyloctanoate (1%). Similar high conversions and selectivities are obtained when using 1-hexene or 1-dodecene as substrates.† Examination of partially converted solutions showed that almost all the unreacted alkene had isomerised to a mixture of all possible internal alkenes. We therefore attempted the methoxycarbonylation of 2-, 3-, and 4-octenes. Very high selectivities although with lower conversions were obtained. Under more forcing conditions, high conversions were obtained in <16 h (<3 h for 2-octene) and the linear selectivities were 99%, confirming that the catalyst system is highly active for alkene isomerisation, but that the terminal alkyl compound is trapped as the ester much more readily than any branched alkyl complexes.

In order to probe the versatility of this reaction further, we investigated a series of methyl branched pentenes. In each case, no matter what the original position of the double bond, the products always demonstrated very high selectivity to terminal esters. Interestingly, for 2-methyl-1-pentene, the product depended upon the availability of CO. Thus, when CO was bubbled through the solution, the major product (96%) was methyl-3-methylhexanoate (little double bond isomerisation had occurred) whilst if CO was passed over the stirred solution, the major product was methyl 5-methylhexanoate (the double bond had isomerised past the branching point and the least hindered terminal metal alkyl was trapped preferentially).

We have carried out preliminary mechanistic studies on the methoxycarbonylation of 1-octene, which show that two pathways from 1-octene to methyl nonanoate occur. Initially the linear product is formed by the direct methoxycarbonylation of 1-octene, but alkene isomerisation occurs in competition with this reaction. Subsequently, the linear product is formed by the tandem isomerisation of the internal alkenes, with the terminal alkyl intermediate being trapped by migration to CO. A gas uptake plot is shown in Fig. 1 for a methoxycarbonylation reaction of 1-octene carried out at 10 bar and 40 °C. It is very clear that two first order regimes are present. The first ($k = 3.9 \times 10^{-4}$ s^{-1}) corresponds to the direct methoxycarbonylation of 1-octene, whilst the second ($k = 1.7 \times 10^{-4}$ s^{-1}) corresponds to the tandem isomerisation–methoxycarbonylation of the isomerised alkenes. It is noteworthy that the pseudo first order rate constant for the second step is 44% that of the first, despite the fact that only about 5% of the octene is present as 1-octene in the later part of the reaction (once isomerisation equilibrium has been established). Confirmation that the biphasic kinetics can be attributed to these two different reactions comes from analysis of the products obtained from reactions carried out in CH_3OD. The signal from the parent ions of methyl nonanoate isotopomers obtained from a reaction carried out in CH_3OD at 30 bar and 80 °C is shown in Fig. 2. All isomers with

Table 1 The methoxycarbonylation of alkenes catalysed by palladium DTBPMB[a]

Substrate	Conversion (%)	Linear selectivity (%)
1-Octene	97.8	99.0
1-Octene[b]	82	98.6
1-Hexene[b]	100	98.3
1-Dodecene[b]	71	98.7
2-Octene	29.2	99.0
2-Octene[c]	95.6	97.1
3-Octene[d]	99.6	94
4-Octene[d]	100	93.9
2-Methyl-1-pentene[e]	100	96
2-Methyl-1-pentene[f]	100	20
3-Methyl-1-pentene	100	>99.9
4-Methyl-1-pentene	100	99.4
4-Methyl-2-pentene	100	99.0

[a] $[Pd_2(DBA)_3]$ (0.0457 g, 0.1 mmol), DTBPMB (0.197 g, 0.5 mmol), methane sulfonic acid (65 µl, 1 mmol), alkene (2 cm^3, 12.74 mmol), methanol (10 cm^3), 20 °C, bubbling CO (1 atm), 3 h. [b] As *a* but in a closed vessel under CO (4 bar). [c] As *a* but 30 bar and 80 °C, 3 h. [d] 30 bar and 80 °C, 16 h. [e] Bubbling CO through the solution, methyl 5-methylhexanoate (4%). [f] Passing CO over the solution, methyl 5-methylhexanoate (80%).

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0–15 D atoms are present, but d_1-methyl nonanoate is present in much larger quantities than expected on the basis of a simple distribution. This is further confirmed in the total ion current (inset in Fig. 2). We interpret this as arising because direct carbonylation of 1-octene leads to d_1-methyl nonanoate, whilst the tandem reaction leads to the products with multiple deuterium exchange. If the reaction is carried out under the same conditions but in methanol–toluene (1 : 4) as solvent, the same products are observed, but d_1-methyl nonanoate no longer predominates. This suggests that attack of methoxide on the acyl complex formed by alkyl migration onto CO is rate determining in the formation of methyl nonanoate. We note that the presence of d_0-methyl nonanoate in the product mixtures from these reactions confirms that the hydride mechanism shown in Fig. 3 is operating.[7]

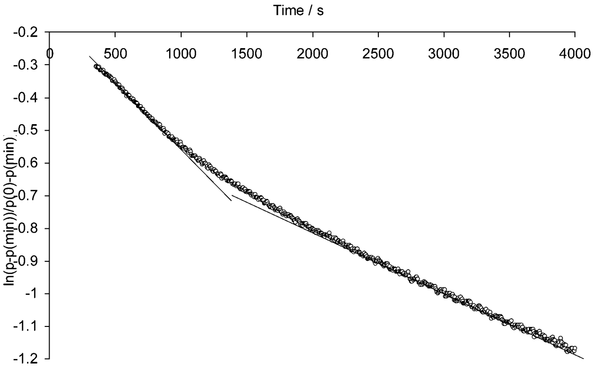

Fig. 1 Gas uptake plot for methoxycarbonylation of 1-octene at 10 bar and 40 °C. The lines are to guide the eye to the two first order regions.

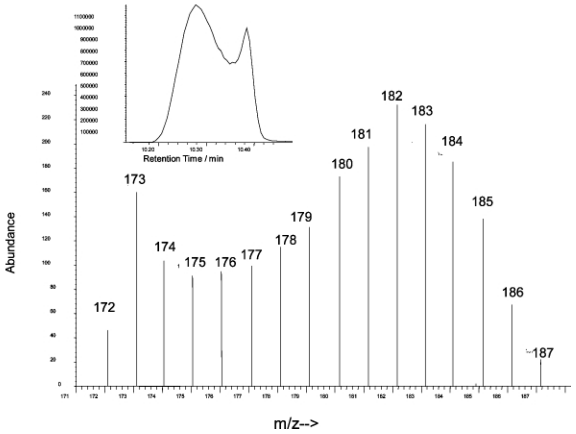

Fig. 2 Parent ions from methyl nonanoate formed using CH_3OD. Note increased peak at *m*/*z* 173 arising from d_1-methyl nonanoate. This is more obvious from the total ion count, inset. The sharp peak is from d_1-methyl nonanoate, whilst the broad envelope contains the other isomers. Note that the more highly deuteriated isomers (higher mass) elute from the GC column first.

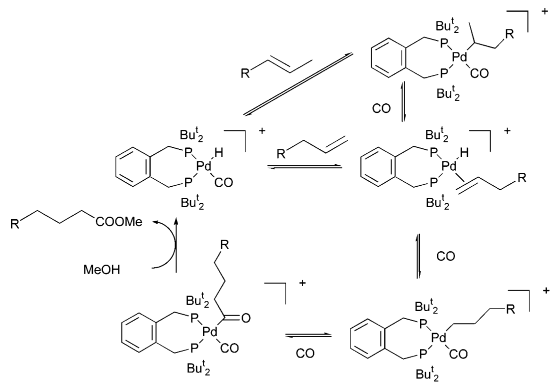

Fig. 3 Proposed mechanism for the highly selective methoxycarbonylation of alkenes. Attack of methanol is rate determining.

In conclusion, we have shown that complexes formed *in situ* from $[Pd_2DBA_3]$, DTBPMB and methane sulfonic acid provide highly active catalysts for the methoxycarbonylation of terminal alkenes or the tandem isomerisation–methoxycarbonylation of internal alkenes to linear carboxylic acid esters. The reactions occur *via* a hydride mechanism with rate determining trapping of the acyl species by methanol.

A patent covering these findings has been filed.[8]

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Notes and references

† It is possible that the high observed yield in these reactions could arise because some of the substrate is being flushed from the reactor in the CO stream, but similar yields and selectivities are obtained if the reactions are carried out in sealed bottles under 4 bar of CO.

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