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Highly active and selective catalysts for the production of methyl propanoate *via* the methoxycarbonylation of ethene

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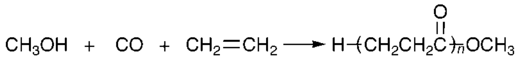
A highly active and selective catalyst for the production of methyl propanoate *via* the methoxycarbonylation of ethene is described, based on the new zero valent palladium complex $L_2Pd(dba)$ [where L_2 = 1,2-bis(di-*tert*-butylphosphinomethyl)benzene and dba = *trans,trans*-dibenzylideneacetone].

The alkoxycarbonylation of alkenes is of growing importance. Eqn. (1) shows that a range of products is accessible, from high

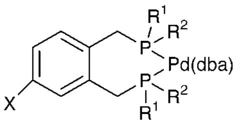


$$CH_3OH + CO + CH_2{=}CH_2 \longrightarrow H\left(CH_2CH_2\overset{O}{\overset{\|}{C}}\right)_n OCH_3 \qquad (1)$$

molecular weight 'polyketones', which have useful properties as engineering thermoplastics,[1] to methyl propanoate [n = 1 in eqn. (1)], a potential intermediate in the manufacture of methyl methacrylate.[2] Palladium catalysts for this transformation show a marked selectivity dependence on the nature of the phosphine ligand, with monodentate phosphines generally giving methyl propanoate and bidentate phosphines giving high molecular weight co-polymers.[3] Examples of bidentate phosphines contradicting this paradigm are rare.[4]

We report here results using catalysts based on the bidentate phosphine ligand 1,2-bis(di-*tert*-butylphosphinomethyl)benzene which offer exceptional activity, selectivity and stability as ligands for methyl propanoate production.[5] This ligand has been previously described by Shaw[6] and some of its chemistry explored by Spencer;[7] however, prior to our work little structural characterisation and no catalytic studies have been reported.

Addition of this ligand to $Pd_2(dba)_3$ (dba = *trans,trans*-dibenzylideneacetone) gave a complex of formula $L_2Pd(dba)$ **1** (where L_2 = the bidentate phosphine). Treatment of this complex with a sulfonic acid (*e.g.* MsOH) in MeOH generates a complex capable of converting ethene, CO and MeOH to methyl propanoate at a rate of 50 000 mol of product per mol of catalyst per hour with a selectivity of 99.98%. The reaction conditions are very mild (80 °C and 10 atm combined pressure of ethene and CO).[8] In our hands catalysts based on another bidentate phosphine reported to have high activity and selectivity for methyl propanoate,[4a] namely 1,3-bis(di-*tert*-butylphosphino)propane, will typically give values of 15 000 and 98% for turnover frequency and selectivity, respectively, in these batch reactions. Under continuous operation others have reported that catalysts based on PPh_3 have only modest stability, achieving 1800 turnovers on palladium.[9] Our catalyst has now also been operated under steady state conditions for extended periods, giving total turnover numbers on palladium in excess of 100 000.



1 $R^1 = R^2 = Bu^t$, X = H
2 $R^1 = R^2 = Bu^t$, X = NO_2
3 $R^1 = R^2 = Bu^t$, X = OMe
4 $R^1 = R^2 = Pr^i$, X = H
5 $R^1 = R^2$ = Cy, X = H
6 $R^1 = R^2$ = Ph, X = H
7 $R^1 = Bu^t$, R^2 = Cy, X = H

Whilst functionalisation of the aryl bridge with classical electron-releasing or -withdrawing groups (MeO and NO_2) has no significant effect on catalyst performance (presumably being too remote from the palladium centre) slight modifications of the substituents on phosphorus give dramatic results (Table 1). Thus activity is reduced by a factor of 60 on going from the *tert*-butyl substituted ligand **1** to the isopropyl analogue **4**. These numbers are lower than those reported above for the preferred catalyst system due to poor mass transfer in the laboratory glass autoclave compared to that obtained in the well-agitated metal autoclave used for more detailed characterisation of the preferred system. The selectivity of the reaction also changes with ligand structure: using the tetraphenyl analogue **6** the products are a mixture of polyketone oligomers and polymers.

There has been much published about the use of the P–Pd–P bite angle in such complexes to aid the development of structure–property relationships.[10] To this end we have undertaken a detailed study of the structure of **1**, **4**, **5** and **6**. All show the expected η^2 binding of one of the alkene groups of dba and the chelating binding of the phosphine giving a trigonal planar environment around the palladium. The measured bite angle is very constant across this series and is much larger (104 *vs.* 87°) than that reported in the only other published structure of a similar compound containing dppe as the ligand.[11] For **1** this

Table 1 Comparative catalytic results for complexes **1**–**7**[a]

Complex	Activity[b]	Selectivity[c] (%)	P–Pd–P bite angle[d] (°)	Parallel pocket angle[d] (°)
1	12 000	99.9	103.9	127.7
2	11 500	99.9		
3	11 800	99.9		
4	200	20	104.3	157.9
5	200	25	103.9	150.5
6	400	20	104.6	145.4
7	500	30		

[a] *Conditions*: reactions were carried out in an identical fashion to that described in ref. 7, except that a glass Bucchi autoclave was used, agitated by means of a magnetic follower and heated by an oil bath. [b] Activity = moles of ethene consumed per mole of palladium per hour. [c] Selectivity to methyl propanoate measured by GC (details as in ref. 7), remainder oligomers and polymers. [d] Determined by X-ray crystallography, see text.

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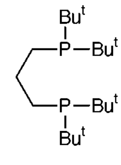
appears to be at the expense of a longer Pd–P bond (2.36 *vs.* 2.29 Å). It has been argued that the observed ligand bite angle is the result of constraints imposed by the metal and ligand; here, where we have tried to eliminate many of these, the measured parameter still appears to lack sensitivity. Analysis based on the concept of parallel pocket angle[12] does show some variation. This hints that there may indeed be an optimum steric environment, dictated by the nature of the phosphine substituents rather than the bridge length, that controls single and multiple substrate insertions prior to chain termination. These arguments will be developed in a subsequent full paper.

Recognising that the likely active species is based on divalent palladium and intrigued as to why 1,2-bis(di-*tert*-butylphosphinomethyl)benzene and 1,3-bis(di-*tet*-butylphosphino)propane **8** seem unusual amongst bidentate phosphines in producing highly active catalysts selective to methyl propanoate, we have also studied the coordination chemistry of these ligands with $Pd(OAc)_2$. A standard experimental procedure was adopted whereby the ligand was added as an acetone solution to $Pd(OAc)_2$ (also in acetone solution) in equimolar proportions. The reaction mixture was stirred overnight, during which time a precipitate formed. With ligand **1** the above procedure yielded a pale green solid **9**, the spectroscopic characterisation of which is consistent with a doubly orthometallated structure.[13] Recrystallisation (from CH_2Cl_2) of the yellow–green reaction product formed when ligand **8** is added to $Pd(OAc)_2$ gives the tetrameric compound **10**, the structure of which is shown in Fig.1.‡ Inspection of the salient bond lengths and angles shows that each palladium has achieved *trans* disposition of two phosphine ligands, with the relatively long Pd–P bond lengths appropriate to this geometry. Only small deviations are observed from square planar geometry around each palladium centre.



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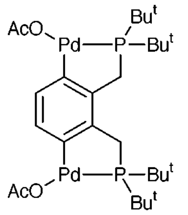

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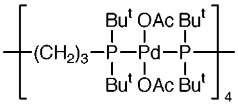

$$\left[-(CH_2)_3-\underset{Bu^t}{\overset{Bu^t}{P}}-\underset{OAc}{\overset{OAc}{Pd}}-\underset{Bu^t}{\overset{Bu^t}{P}}-\right]_4$$

10

Thus the ligands which ultimately produce catalysts with high selectivity to methyl propanoate seem loath to adopt the classical bidentate chelate structure on reaction with a source of divalent palladium; this *cis* chelate structure has been observed for 1,3-bis(diphenylphosphino)propane, the archetypal ligand for the formation of ethene–CO copolymers.[14] Whilst we are not suggesting that the compounds described here are significant catalytic intermediates, it is tempting to speculate that this reluctance to adopt *cis*-chelate structures may be related to the *cis–trans* isomerisation thought to be responsible for the production of low molecular weight materials from the analogous methoxycarbonylation reaction using PPh_3 as the ligand. This selectivity is thus thought to be driven by the thermodynamic considerations which force the phosphine ligands into a *trans* geometry, isolating the growing chain from the vacant site.[3]

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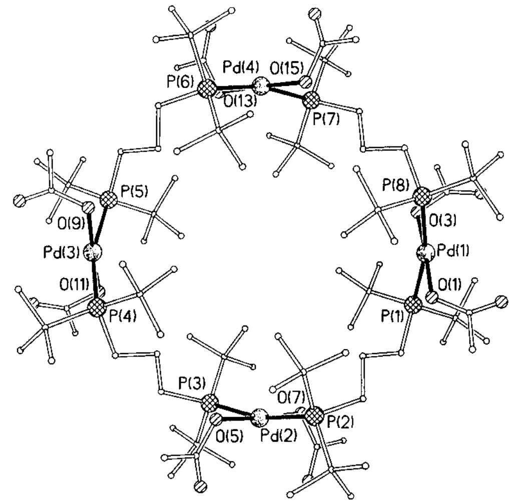

Fig. 1 Molecular structure of **10** without hydrogen atoms. Selected bond lengths (Å) and angles (°): Pd(1)–P(1) 2.382(2), Pd(1)–P(8) 2.403(2), Pd(2)–P(2) 2.397(2), Pd(2)–P(3) 2.391(2), Pd(3)–P(4) 2.394(2), Pd(3)–P(5) 2.388(2), Pd(4)–P(6) 2.397(2), Pd(4)–P(7) 2.402(2), Pd(1)–O(1) 2.024(5), Pd(1)–O(3) 2.035(5), Pd(2)–O(5) 2.039(6), Pd(2)–O(7) 2.037(5), Pd(3)–O(9) 2.044(6), Pd(3)–O(11) 2.015(6), Pd(4)–O(13) 2.039(5), Pd(4)–O(15) 2.038(5), P(1)–Pd(1)–P(8) 166.66(8), P(2)–Pd(2)–P(3) 166.58(7), P(4)–Pd(3)–P(5) 163.71(8), P(6)–Pd(4)–P(7) 166.55(8), O(1)–Pd(1)–O(3) 176.5(2), O(5)–Pd(2)–O(7) 176.5(2), O(9)–Pd(3)–O(11) 177.3(2), O(13)–Pd(4)–O(15) 177.5(2).

Notes and references

‡ *Crystal data* for **10**: $C_{92}H_{192}O_{16}P_8Pd_4\cdot 10.5CH_2Cl_2$, M = 3119.5, orthorhombic, space group $Pca2_1$, a = 38.530(2), b = 19.1969(9), c = 20.3787(10) Å, U = 15073.2(13) Å^3, D_c = 1.375 g cm^{-3}, Z = 4, Mo-Ka radiation (λ = 0.71073 Å), μ = 0.98 mm^{-1}, T = 180 K, $R1$ = 0.0723 ($F^2 > 2\sigma$), $wR2$ = 0.1680 (all data) for 33354 unique data and 1420 parameters. Solvent molecules were restrained to have similar geometry. CCDC 182/1371. See http://www.rsc.org/suppdata/cc/1999/1877/ for crystallographic data in .cif format.

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