Methoxycarbonylation versus Hydroacylation of Ethene; Dramatic Influence of the Ligand in Cationic Palladium Catalysis

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Dedicated to Roger Sheldon on the occasion of his 60th birthday.

Abstract: The palladium-catalysed carbonylation of ethene in methanol shows acute sensitivity towards the diphosphine ligand used. Systems based on 1,3-bis(di-*t*-butylphosphino)propane afford catalysts for fast, selective methoxycarbonylation to methyl propionate; the corresponding catalyst based on 1,2-bis(di-*t*-butylphosphino)ethane hydroacylates ethene to diethyl ketone at high rates. The use of less sterically demanding ligands, hydrogen and auxiliary acid are explored and mechanistic implications discussed.

Keywords: alkenes; carbonylation; esters; ketones; palladium; P ligand

The perfectly alternating copolymerisation of ethene and carbon monoxide has attracted much interest[1] since efficient cationic palladium catalysts were discovered two decades ago.[2] There are, in principle, a range of products available from the co-activation of CO and C_2H_4 in methanol, from high molecular weight CO/C_2H_4 copolymer, through oligomeric keto-esters/di-esters/diketones, to mono-carbonylated products (Figure 1) diethyl ketone (DEK) and methyl propionate (MEP).

MEP has received recent attention as a potential intermediate in the manufacture of methyl methacrylate,[3] and cationic Pd(II) complexes based on sterically demanding diphosphines have been shown to catalyse the methoxycarbonylation of ethene to MEP very efficiently,[4] the best reported systems being based on 1,3-bis(di-*t*-butylphospino)propane (dtbpp)[4e] and 1,2-bis(di-*t*-butylphospinomethyl)benzene (dtbpx).[4b,d,5] Efficient transition metal-catalysed synthesis of DEK, a useful solvent of relatively low volatility, generally requires the use of hydrogen gas.[6] Cole-Hamilton and coworkers recently reported a hydrogen- and water-free rhodium system showing selectivities for DEK up to 85%, though catalyst activity was poor.[7] We report here a cationic palladium system based on 1,2-bis(di-*t*-butylphosphino)ethane (dtbpe) which catalyses, to our knowledge, the fastest and most selective production of DEK from ethene and CO with methanol as a hydrogen source reported to date.

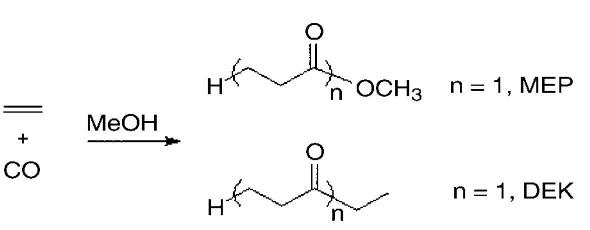

Figure 1. Products from the reaction of CO and ethene in methanol.

Table 1 shows the data from a series of ethene carbonylation experiments. The results obtained with C_3-bridged dtbpp are consistent with those reported[4b, e] when considering the higher reaction temperature used in this case; ethene is efficiently methoxycarbonylated to MEP. The carbonylation selectivity switches to 75% DEK formation on reducing the steric bulk of phosphorus substituents from *t*-Bu to *s*-Bu with dsbpp (entry 3); Tooze et al. observed a similar (though less pronounced) effect for the same reaction, between dtbpx and the catalyst based on its less sterically demanding *i*-Pr diphosphine analogue.[4b]

The most remarkable ligand effect is illustrated in entry 2; the catalyst based on the C_2-bridged diphosphine dtbpe hydroacylates ethene to DEK with 90% selectivity, and in marked contrast to the dtbpp system, only 1.5% of the product is MEP. Gas phase analysis of this reaction showed no ethane was formed; the source of hydrogen was methanol, which was dehydrogenated to formaldehyde (seen in the GLC as its dimethyl acetal in stoichiometric quantity based on DEK production). This constitutes the most active and selective hydrogen- and water-free system for catalytic DEK synthesis from ethene and CO. In fact, using hydrogen to inject the catalyst (entry 5, *cf.* entry 2) in the same reaction increases the DEK selectivity to 98%, and the activity by approximately an order of magnitude.

The selectivity for ethene hydroacylation to DEK increases with diphosphine dsbpe < dsbpp < dtbpe, whilst MEP formation was less than 2% in all cases [i.e.,

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Table 1. Effect of diphosphine, hydrogen and acid on Pd-catalysed ethene carbonylation.[a]

Entry	Ligand[b]	T [°C]	Activity[c] [mol (mol Pd^{-1} h^{-1})]	Ethene selectivity $H[CH_2CH_2(O)]_xOCH_3$	to products [mol %][d] $H[CH_2CH_2(O)]_yCH_2CH_3$	x = n/y = n
1	dtbpp	120	25000	x = 1 (97.4)	y = 1 (2.6)	37.5
2	dtbpe	120	4500	x = 1 (1.5)	y = 1 (89.9)	0.02
				x = 2 (7.3)	y = 2 (1.3)	5.6
3	dsbpp	120	4000	x = 1 (1.5)	y = 1 (74.6)	0.02
				x = 2 (10.6)	y = 2 (4.6)	4.1
				x = 3 (0.6)	y = 3 (0.1)	6
				ca. 10% higher	oligomers/copolymer	0.4
4	dsbpe	120	1000	x = 1 (< 0.1)	y = 1 (31.0)	< 0.01
				x = 2 (33.4)	y = 2 (4.7)	7.1
				x = 3 (9.1)	y = 3 (1.8)	5
				ca. 20% higher	oligomers/copolymer	1
5	dtbpe[e]	120	90000	x = 1 (1.2)	y = 1 (98.0)	0.01
				x = 2 (0.4)	y = 2 (0.4)	1
6	dtbpe[f]	120	1500	x = 1 (0.1)	y = 1 (33.2)	0.01
				x = 2 (5.4)	y = 2 (0.9)	5.8
				ca. 60% higher	oligomers/copolymer	nd

[a] 20 bar C_2H_4 and 20 bar CO (at room temperature) in MeOH (50 mL); catalyst (see below) injected as methanolic solution (5 mL) with 10 bar CO overpressure at reaction temperature.

[b] Catalyst: 0.1 mmol $Pd(OAc)_2$ + 0.12 mmol ligand + 0.25 mmol CH_3SO_3H; dtbpp = 1,3-bis(di-*t*-butylphosphino)propane, dtbpe = 1,2-bis(di-*t*-butylphosphino)ethane, dtbpp = 1,3-bis(di-*s*-butylphosphino)propane, dsbpe = 1,2-bis(di-*s*-butylphosphino)ethane.

[c] Based on rate of gas consumption.

[d] Ethene selectivity = C_2H_4 to product/C_2H_4 to Σ products.

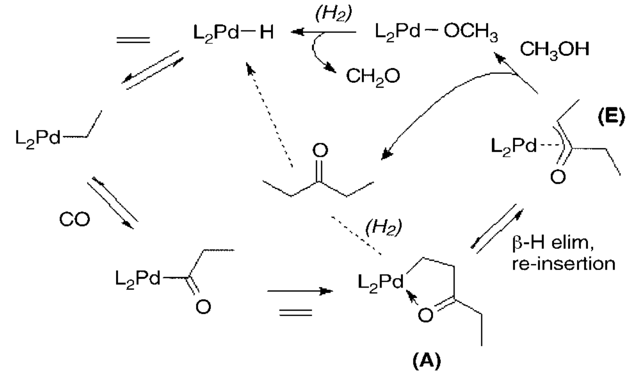
[e] Catalyst [0.01 mmol $Pd(OAc)_2$ + 0.025 mmol ligand + 0.5 mmol CH_3SO_3H] injected at reaction temperature with 20 bar H_2 overpressure.

[f] 1 mmol CH_3SO_3H in catalyst.

(x = 1/y = 1) ~ 0.01]. However the chemoselectivity for termination after insertion of a further -$CH_2CH_2C(O)$-unit was completely reversed, favouring the keto-*ester* (methyl 4-oxohexanoate) over the di*ketone* (octane-3,6-dione) product [(x = 2/y =2) ~ 6]. Another interesting feature of the catalysis with the dtbpe ligand system is that using high acid concentration (entry 6) results in an unprecedented change in product distribution. Catalyst activity decreases, while selectivity to DEK is dramatically reduced, and a significant amount of CO/C_2H_4 copolymer is produced. The same excess of acid has no effect on the analogous dtbpp system.

In principle, two types of reaction mechanism are possible for the type of ethene carbonylation described here, a Pd-methoxy or Pd-hydride cycle.[1d] Tooze and coworkers have shown that the dtbpx system for ethene methoxycarbonylation to MEP operates *via* the hydride cycle,[5] and it is reasonable to assume this is also the case for the dtbpp system. With regard to the dtbpe catalyst for methanolic ethene hydroacylation to DEK, the hydride cycle *must* be operating, by the very nature of the product (Scheme 1).[6]

Unlike its methoxycarbonylating counterparts[4] the dtbpe catalyst inserts ethene into the first Pd-acyl to generate the Pd-alkyl oxo-chelate (**A**).[8] Perhaps more surprising is the reluctance of this oxo-chelate to chain propagate *via* CO insertion, instead undergoing rapid methanol protonolysis *via* the enolate (**E**)[9] to generate DEK and Pd-methoxide; subsequent β-H elimination and loss of formaldehyde regenerates the Pd-hydride. The same mechanism has previously been proposed for Pd-catalysed ethene hydroacylation in methanol to DEK.[10] We suggest the effect of hydrogen on this reaction is to bring about fast, direct hydrogenolysis of oxo-chelate (**A**), but until a detailed mechanistic study has been undertaken, H_2-assisted regeneration of the Pd-hydride from the Pd-methoxide cannot be ruled out.[11] Regarding the effect of extra acid dramatically altering the course of the reaction (entry 6), we can only



Scheme 1. Postulated hydride mechanism for DEK formation (L_2 = dtbpe).

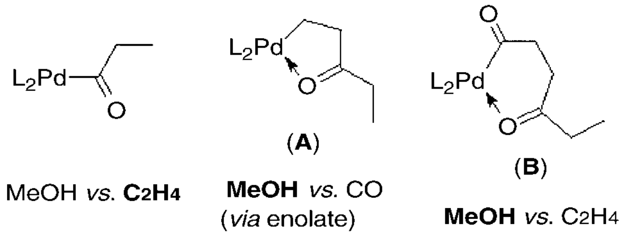


Figure 2. Competition between substrate molecules for reaction intermediates (dtbpe catalyst).

speculate as to why this increases the amount of chain propagation (CO insertion into **A**) over chain transfer (MeOH protonolysis); perhaps the higher acid concentration destabilizes oxo-chelate (**A**) *via* proton interaction with the β-carbonyl.

The selectivity for the dtbpe reaction (Table 1, entry 2) can be explained by considering competition for substrate molecules at each elementary step (Figure 2). Following ethene insertion into Pd-H and CO insertion into the subsequently formed Pd-alkyl (Scheme 1), competition for the first Pd-acyl determines the course of the carbonylation; with this dtbpe catalyst, in contrast to its dtbpp and dtbpx analogues, a second ethene insertion (98.5%) wins over alcoholysis by methanol (1.5%). This must be a direct consequence of the smaller bite angle[12] of the C_2-bridged diphosphine; it could be that the resulting extra space at the 'vacant' site on palladium promotes ethene binding and insertion into the Pd-acyl over its methanolysis. This steric argument is backed up by the observations that the dsbpp and dsbpe systems also show similar values for competition at the first Pd-acyl; the dsbpp catalyst has the same bite angle as the methoxycarbonylating dtbpp system, but the smaller *s*-butyl phosphorus substituents allow further ethene insertion to compete with methanolysis.

As discussed above Pd-alkyl oxo-chelate (**A**) reacts preferentially with MeOH *via* rearrangement to the enolate (89.9%, affording DEK) instead of inserting a second molecule of CO (8.6%). A second Pd-acyl (**B**) is thus formed which unlike the first Pd-acyl is now much more susceptible to termination by MeOH *cf.* ethene insertion. We ascribe this to the 6-membered oxo-chelate nature of this second Pd-acyl (**B**)[13] promoting methanolysis relative to further ethene insertion, possibly by the chelating carbonyl taking up H^+ from methanol, thus increasing the methoxide concentration around palladium,[14] and/or by hindering ethene coordination. It is again noteworthy that this reversal in substrate reactivity towards the first and second Pd-acyl is also observed in the dsbpp and dspbe systems.

Catalytic synthesis of monoketones from CO and higher olefins,[15] or ethene and CO with hydrogen or H_2O has been previously disclosed.[6] The dtbpe-based cationic palladium complex reported here catalyses the first really efficient hydroacylation of ethene to DEK with methanol as a source of hydrogen, arresting CO/ethene copolymerisation at the second Pd-alkyl. The use of H_2 gas increases selectivity to DEK by 10% to 98% and activity to a staggering 90,000 mol/mol Pd/hr. The use of the more sterically demanding diphosphine dtbpp terminates the catalysis one stage earlier at the first Pd-acyl to generate MEP by methanolysis; reducing ligand bulk (dsbpp and dsbpe) reduces DEK selectivity in favour of higher oligomers and low molecular weight copolymer. Chelating phosphine-Pd-hydride based mechanisms are proposed for this methanolic carbonylation catalysis, and selectivity is rationalised by substrate competition at intermediate Pd-species.

Experimental Section

General Remarks

Product analysis of reaction mixtures was performed by gas-liquid chromatographic (GLC) analysis on a Perkin-Elmer 8500 equipped with two capillary columns, Chrompack 50 m CP-sil-5 and 50 m FFAP. Structural analysis was performed with GLC-mass spectroscopic (GC/MS) analysis on a Finnagin-9610 gas chromatograph fitted with the CP-sil-5 column and coupled to a Finnigan-4000 triple-stage mass-spectrometer using electron impact ionisation. ^1H (chemical shifts relative to residual solvent) and $^{31}P\{^1H\}$ (chemical shifts to high frequency of H_3PO_4) NMR spectra were recorded on either a Varian 300 MHz or Inova 400 MHz spectrometer at the ambient temperature of the probe unless otherwise stated, using deuterated solvents to provide the field/frequency lock.

Materials

Palladium acetate, methanol (Pro-analysis grade) and methanesulfonic acid were obtained from Merck and were used as supplied. The diphosphines used were synthesised by standard preparation techniques, involving the reaction between the respective dialkylphosphine and 1,3 dibromopropane or 1,2 dibromoethane to give the double HBr salt of the respective diphosphine. Neutralisation with sodium hydroxide, and subsequent distillation afforded the diphosphine.[16] Purity of the applied phosphines was always higher than 95%, measured by ^1H and ^{31}P NMR; phosphine-monoxide was observed as the main impurity. The enantiomeric composition of dsbpp and dsbpe was statistical. The air-sensitive phosphines were all stored and handled in a glovebox under nitrogen. Ethene of polymer grade quality was used and was obtained from in-house sources. Commercial quality carbon monoxide (98%) was obtained from Air Products.

Procedures

All hydrocarbonylation experiments were carried out in a 250-mL magnetically stirred, electrically heated Hastelloy™ C autoclave. A typical experimental procedure was as follows:

The autoclave was charged with 50 mL methanol, pressurised with 20 bar of CO and then with 20 bar of ethene. In about 10–15 minutes the closed autoclave was heated to the desired temperature and kept at this temperature by a Thermo-Electric 100 temperature control unit. In a nitrogen glovebox, the catalyst components as specified in Table 1 were dissolved in 5 mL methanol contained in a small closable bottle. The components were allowed to react until no solid palladium acetate was visible. The methanolic catalyst solution was then injected into the autoclave at reaction temperature with either 10 bar CO or 20 bar H_2 overpressure. The pressure was continuously recorded by using a Transamerica Instruments pressure transducer, series 2000. Activity data during the experiment were calculated from the pressure decrease in time and from GLC analysis of the reaction product at the end of a reaction period of 2 hours (or until all the ethene was consumed; this was within 5 minutes for entries 6 and 7). After that time, the autoclave was allowed to cool, depressurised and opened. Selectivity data were obtained from a standard analysis of the final reaction product by GLC. Product identification was by GC/MS analysis. The rate data in the tables are "initial" rates, averaged over a period corresponding to $<30\%$ conversion.

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