

Polymer producing palladium complexes of unidentate phosphines in the methoxycarbonylation of ethene

Graeme Smith, Nicolas R. Vautravers and David J. Cole-Hamilton*

Received 16th July 2008, Accepted 28th October 2008

First published as an Advance Article on the web 10th December 2008

DOI: 10.1039/b812132j

A wide range of unidentate phosphines have been studied as ligands for the palladium-catalysed methoxycarbonylation of ethene in the presence of methanesulfonic acid using methanol as the solvent. At high phosphine to Pd ratios, methyl propanoate is formed at a low rate. However, at P–Pd ratios of 4 : 1, some unidentate phosphines promote the formation of polyketone with moderate rates. Analysis of all the phosphines shows that good electron donating power, combined with small size, favours polyketone formation.

Introduction

Carbon monoxide and ethene represent two of the most readily available feedstocks in all of chemistry. They can react together in the presence of methanol and a suitable catalyst to give either methyl propanoate (MeP),^{1–3} a key intermediate in the production of methyl methacrylate, the monomer used for making Perspex, or a perfectly alternating copolymer (PK), which has excellent structural properties and is biodegradable.^{1,4,5} In some cases, short chain oligomers can also be produced.² The best catalysts for these reactions are cationic palladium complexes containing tertiary phosphines. Unidentate phosphines (*e.g.* PPh₃) generally give methyl propanoate, whilst bidentate phosphines (*e.g.* Ph₂P(CH₂)₃PPh₂) generally form copolymers. This observation has been rationalised^{1,6} as arising due to the sites at which the catalytic reactions occur being stabilised in the mutually *cis* position when a bidentate ligand is present, so that migration of the growing chain onto ethene can readily occur. Unidentate ligands prefer to adopt the thermodynamically more stable *trans* configuration, in which migration cannot occur and so rapid termination by reaction with methanol to give methyl propanoate occurs. (Fig. 1)

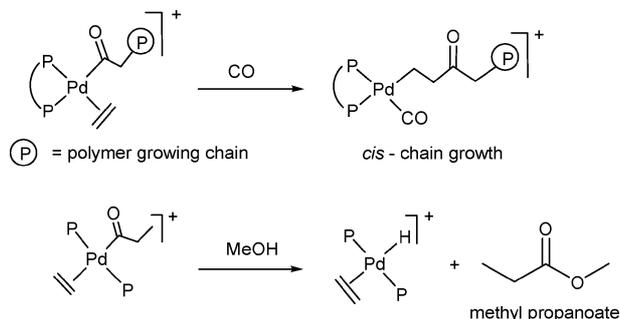


Fig. 1 Rationale of the selectivity of CO–ethene reactions (P–P = Ph₂P(CH₂)₃PPh₂, P = PPh₃).^{1,2}

In recent years however, a few bidentate ligands, mostly with bulky electron donating substituents, such as 'Bu₂P(CH₂)₃P'Bu₂'⁷ and 1,2-(^tBu₂PCH₂)₂C₆H₄,^{8,9} have been shown to be extremely effective for the selective formation of methyl propanoate. Indeed, one is so effective that it is being commercialised. These ligands call into question the argument based on mutually *cis* or *trans* active sites as being responsible for the chemoselectivity of the reaction, although it is possible that these ligands give methyl propanoate because they become unidentate at some point in the cycle.² The precise mechanistic reason for this unusual selectivity is the subject of continuing debate,^{2,10–12} but an alternative explanation has been proposed¹⁰ on the basis of careful studies of the rate of methanolysis of model palladium acetyl cations. Complexes containing *trans* bidentate diphosphines either do not react with methanol under CO or react very slowly, whilst *cis* complexes react rapidly with larger ligands being generally more reactive. These observations have led to the proposal that the population of the *cis* isomer, at least in part, determines the reactivity. The relative rate of acyl migration onto coordinated ethene and methanolysis determines the chemoselectivity between methyl propanoate and polyketone.

The conventional literature does not have extensive information on unidentate phosphines leading to polymer, because the majority give selective methyl propanoate formation. It has been shown that the selectivity can be tuned to polyketone formation by limiting termination by controlling the reaction conditions, for example by varying the solvent, increasing pressures or changing the anion, as was reported in early research.¹³ An intriguing instance of activity to polyketone being promoted by unidentate phosphines under different reaction conditions was reported by Drent.¹⁴ He observed that under low phosphine–palladium ratios, some activity to polyketone was afforded by triphenylphosphine (35 g PK (g Pd h)^{–1}). This change in selectivity compared with the more usual methyl propanoate formation was explained by the suppression of the isomerism between the *cis/trans* species (this isomerisation is known to be catalysed by excess PPh₃) shown in Fig. 1, thus causing some *cis* intermediate to be present, and hence to polyketone. The only other system in the open literature reporting polyketone formation when using unidentate phosphines is by Keim *et al.*¹⁵ using heteroatom containing phosphines, which are

EaStCHEM, School of Chemistry, University of St. Andrews, St. Andrews, Fife, UK KY16 9ST. E-mail: djc@st-and.ac.uk; Fax: +44 1334 463 808; Tel: +44 1334 463 805

themselves capable of coordination to palladium so giving the required *cis* geometry.

The most significant and relevant consideration of unidentate phosphines, out with the conventional literature, is work patented by Nozaki (Shell),¹⁶ where catalysts of general formula $\text{PR}_1\text{R}_2\text{R}_3$ are proposed to be active for the production of polyketone, where R_1 is an alkyl group and R_2, R_3 are aryl groups.

We now report our investigation on unidentate phosphines in the methoxycarbonylation of ethene, trying to rationalise our results in terms of steric and electronic effects of the phosphines.

Experimental

All manipulations and reactions were carried out using standard Schlenk techniques, using oven-dried glassware. All experiments were performed under a nitrogen atmosphere, dried through a $\text{Cr}(\text{II})/\text{silica}$ packed glass column. Air-sensitive liquids were stored and handled under nitrogen. Air-sensitive solids were stored in the glove box and handled under nitrogen.

^1H , ^{13}C and ^{31}P NMR spectra were recorded using automated Bruker AM 300/400 spectrometers. Broad band decoupling was used for ^{31}P spectra and ^{13}C spectra, for which distortionless enhancement by polarisation transfer (DEPT) was also used. Gas chromatography was performed using a Hewlett-Packard 6890 series gas chromatograph, equipped with an Agilent 6890 series injector. Both quantitative analysis by a flame ionisation detector (GC-FID) and qualitative analysis by a Hewlett-Packard 5973 series mass selective detector (GC-MS) were performed. A Hewlett-Packard Chemstation allowed the computerised integration of peak areas.

CO and ethene were purchased from BOC gases. Methanol was distilled over magnesium ethoxide under argon. Toluene was purified using an Innovative Technologies, UK system. All reagents were purchased from Aldrich and used as received unless otherwise stated. $[(\text{COD})\text{PdMeCl}]$,¹⁷ $[\text{Pd}(\text{PPhMe}_2)_2\text{MeCl}]$,²⁷ $[\text{Pd}(\text{PMe})_2\text{MeCl}]$ ²⁷ and $[\text{Pd}(\text{PPh}_3)_2\text{MeCl}]$ ²⁸ were prepared according to the literature. Methanesulfonic acid was degassed before use.

Cone angles for phosphines were taken from the literature or calculated using a literature method.¹⁸ Electronic parameters were based on the IR spectrum of $[\text{Ni}(\text{CO})_3\text{PR}_3]$ from the literature or calculated.¹⁸

Trans- $[\text{Pd}(\text{PPh}_2\text{Me})_2\text{MeCl}]$

A solution of $[(\text{COD})\text{PdMeCl}]$ (5 mg, 0.019 mmol, $\text{COD} = 1,5$ cyclooctadiene) with 2 equiv. of PPh_2Me (6.9 μL , 0.037 mmol) in d_8 -toluene was syringed into an NMR tube and was shaken for 10 min. ^1H NMR (400.13 MHz, C_7D_8 , Me_4Si , 193 K) δ/ppm : 0.35 (3H, t, J_{PH} 6, $\text{Pd}-\text{CH}_3$), 1.15 (6H, quin, J_{PH} 8, $\text{P}-\text{CH}_3$), 6.99–7.03 (8H, br s, $\text{Ar}-\text{H}$), 7.15–7.20 (4H, br s, $\text{Ar}-\text{H}$) and 7.50–7.59 (8H, br m, $\text{Ar}-\text{H}$). ^{13}C NMR (100.6 MHz, C_7D_8 , Me_4Si , 193 K) δ/ppm : 1.2 ($\text{Pd}-\text{CH}_3$), 12.5 ($\text{P}-\text{CH}_3$), 128.0, 129.5 and 131.9. ^{31}P NMR (121.5 MHz, C_7D_8 , Me_4Si , 193 K) δ/ppm : 26.6. m/z (ESI) 521.0770 ($\text{M} - (\text{Cl}^{35})$. $\text{C}_{27}\text{H}_{29}\text{PdP}_2$ requires 521.0779).

Catalytic runs

Catalytic reactions were carried out in identical 250 mL Hasteloy™ autoclaves. The reactor was purged with CO prior

to the catalytic solution containing palladium acetate (45 mg, 0.02 mmol), methanesulfonic acid (30 μL , 0.4 mmol) and the phosphine in dry methanol (10 cm^3) being cannulated in under nitrogen. The autoclave was then pressurised to 60 bar using ethene and carbon monoxide (1 : 1) and heated to 85 °C during 10 min. The pressure was allowed to fall during the reaction period (batch mode). After 2.5 h, the reaction was quenched by rapid cooling of the autoclave and the unreacted gases vented. The reaction slurry was then filtered and the liquid kept for GC analysis. In the case of polymer production, the solid was washed with fresh methanol, dried and weighed. The catalyst activity for polymer formation was determined both by the weight of the polymer produced ($\text{g PK} (\text{g Pd h})^{-1}$) and by average turnover frequency over 2.5 h ($\text{mol ethene introduced} (\text{mol Pd h})^{-1}$); the mass of the polymer was divided by 56 ($\text{CO} + \text{ethene}$) to give an approximation of the turnover number. This approximation is reasonable for longer chain polymers. This number is included in an attempt to obtain a comparison with the rates of formation of methyl propanoate. The activity for methyl propanoate and co-oligomer formation was determined by gas chromatography.

Results and discussion

Triaryl-, dialkylphenyl-, alkyldiphenyl- and trialkyl-phosphines have been examined in this study. The same catalytic conditions, pressure, temperature, reaction time, catalyst concentration as well as the same acid promoter (MeSO_3H) were applied, for ease of comparison with previous studies. The palladium to phosphine ratio was varied from 1 : 4 to 1 : 30, along with the nature of the phosphine in order to focus on the steric and electronic effects of the ligands. The results are collected in Table 1.

This related family of phosphines contains triphenylphosphine, which has historically been widely studied, particularly by early researchers such as Sen, who showed that methyl propanoate was produced along with small amounts of short chain oligomer.^{13,19} Thus, this gives a reference point from which we can rationalise the observed product selectivity of related triarylphosphine containing catalysts. When triphenylphosphine ($\text{Pd}-\text{P} = 1 : 4$) is used, both methyl propanoate and polyketone are formed, but at very low rates (runs 1–3). This observation is entirely consistent with Drent's observations²⁰ that at low phosphine to palladium ratios, some activity to polyketone can be observed, because *cis*–*trans* isomerisation in the acyl intermediate is slower.

For triphenylphosphine (runs 1–3), tris-(4-fluorophenyl)phosphine (runs 4–6) and tris-(4-methoxyphenyl)phosphine (runs 9–11) a general increase in the rate of formation of methyl propanoate can be observed from the 1 : 4 to 1 : 30 ratio for each phosphine. This observation may be also related to the increase in the rate of *cis*–*trans* isomerisation. Tris-(2-methoxyphenyl)phosphine (runs 12 and 13) totally inhibits the reaction, presumably because the high degree of steric bulk directly around the phosphorus atom provided by the *ortho* substituents prevents any monomer molecule from coordinating to palladium in the catalytic complex or leads to complexes containing only one phosphine ligand. No activity is observed using the very bulky and electron poor $\text{P}(\text{C}_6\text{F}_5)_3$ (runs 7 and 8).

In addition to this steric effect, we can also observe an electronic effect when the methyl propanoate rate is compared between the first four phosphines in Table 1 (runs 1–11). A general increase

Table 1 Rates of formation of methyl propanoate (MeP) and/or polyketone (PK) from the palladium catalysed methoxycarbonylation of ethene in the presence of various unidentate tertiary phosphines^a

Run	Phosphine	P-Pd ratio	Turnover frequency (TOF)/h ⁻¹			Cone angle
			MeP	PK	PK rate/g (g Pd h) ⁻¹	
1	PPh ₃	4	4.5	—	<1	145
2		10	10.5	0	0	
3		30	19.8	0	0	
4	P(4-C ₆ H ₄ F) ₃	4	5	0	0	*
5		10	23.2	0	0	
6		30	67.8	0	0	
7	P(C ₆ F ₅) ₃	4	0	0	0	184
8		30	0	0	0	
9	P(4-C ₆ H ₄ OMe) ₃	4	4.1	0	0	*
10		10	5.4	0	0	
11		30	8.8	20.1	5	
12	P(2-C ₆ H ₄ OMe) ₃	4	0	0	0	*
13		30	<1	0	0	
14	PPh ₂ Me	4	0.6	289	72	136
15		30	2.0	0	0	
16	PPh ₂ Et	4	1.0	5.2	1.3	140
17		30	10.4	0	0	
18	PPh ₂ Pr	4	1.8	35	8.7	141
19		30	20.4	0	0	
20	PPh ₂ ⁱ Pr	4	2.8	14.1	3.5	150
21		30	62.4	0	0	
22	PPh ₂ ^t Bu	4	2.3	0	0	157
23		30	140	0	0	
24	PPhMe ₂	4	0.5	409	101.8	122
25		30	0.8	0	0	
26	PPhEt ₂	4	0.3	413	102.8	136
27		30	0.7	0	0	
28	PMe ₃	4	0.8	220	54.8	118
29		30	0.6	0	0	
30 ^b		30	0.5	39	9.8	
31	PEt ₃	4	0.3	165	41.1	132
32		30	0.7	0	0	
33 ^b		30	0.6	111	27.6	
34	P ⁱ Bu ₃	4	0.7	0	0	182
35		30	0	0	0	
36	P ⁱ Bu ₃	4	0.1	0	0	143
37		30	0.4	0	0	
38	P ⁿ Bu ₃	4	0.3	365	90.9	132
39		30	0.8	0	0	
40	P(oct) ₃	4	0.6	323	80.4	132
41		30	0.6	0	0	

^a Reaction conditions: catalyst (0.02 mmol), MeSO₃H (0.4 mmol), MeOH (10 cm³), $p_{\text{CO}} = 30$ bar, $p_{\text{Ethene}} = 30$ bar, temp = 85 °C, $t = 2.5$ h. TOF's are averaged over 2.6 h. ^b MeSO₃H (0.8 mmol), * = not determined.

in the rate of methyl propanoate formation moving from the electron donating 4-methoxy groups, through triphenylphosphine, to the electron withdrawing 4-fluoro groups is apparent at all ratios studied. However, this rate increase is most pronounced when the P-Pd ratio is high (runs 3, 6 and 11). This result is unsurprising, as it can be related to previous work on the effect of electronic substituents on product rate when using bidentate phosphines.²¹ Electron donating bidentate phosphines increase the rate of polyketone formation through intermediate stabilisation, whilst electron withdrawing substituents are expected to increase the rate of termination by nucleophilic attack by methanol, thus affording the high rates of methyl propanoate observed. Methanolysis is believed to be rate determining in these reactions.^{10,22} These electronic arguments do not, however, rationalise the behaviour of bidentate ligands like 1,2-C₆H₄(CH₂PⁱBu₂)₂.

The only unexpected result from the triarylphosphines is that some activity (TOF = 20 h⁻¹) to polyketone is observed when

using tris-(4-methoxyphenyl)phosphine under high phosphine-palladium ratios (run 11). Even though this seems a moderate rate, the productivity in g PK (g Pd h)⁻¹ shows that the weight of polymer produced is small. This result is still surprising and may suggest that this phosphine in some way favours the *cis* isomer of the palladium complex.[†]

Unusually for unidentate phosphines, all of the alkyldiphenylphosphines, except the very bulky Ph₂P^tBu (run 22), give polyketone at low P-Pd ratios (runs 14, 16, 18 and 20). Productivities of 1.3, 8.7 and 3.5 g PK (g Pd. h)⁻¹ for the ethyl, *n*-propyl and *i*-propyl are observed, corresponding to moderate TOFs. The rate of polyketone formation decreases when using Ph₂PR along the series Me > Pr > ⁱPr > Et > ^tBu (runs 14, 18, 20, 16 and 22). Either steric or electronic effects (or both) could be responsible

[†] A referee has suggested that this result may arise from contamination with P(4-C₆H₄OMe)₂Bu.

for this effect. Similarly, it is not possible to deconvolute steric and electronic effects upon the rate of formation of methyl propanoate when using alkyldiphenylphosphines, which increases along the series Me > Et > Pr > ^tPr > ^tBu, especially at high P–Pd ratios, where polyketone is not formed (runs 15, 17, 19, 21 and 23).

None of the dialkylphenyl or trialkyl phosphines studied showed any significant activity for methyl propanoate formation, even at high (P–Pd) ratios, where no activity to any product was observed (runs 25, 27, 29, 32, 35, 37, 39 and 41). These results are particularly surprising due to the significant rates achieved with their alkyldiphenylphosphine analogues. One possible reason for this lack of activity is that the highly basic phosphines may neutralise the acid and hence inhibit the formation of the catalytically active hydrido-palladium species. We note, however, that diprotonated 1,2-C₆H₄(CH₂P^tBu)₂ is sufficiently acid to protonate the related Pd complexes.²³ Support for the suggestion that excess phosphine does prevent protonation of the Pd centre is provided by the results obtained using PR₃ (R = Me or Et) with a Pd–P–H⁺ ratio of 1 : 30 : 40, where polyketone formation is again observed (runs 30 and 33).

The excellent chemoselectivity to polyketone that the dialkylphenyl and trialkylphosphines, with the exception of P^tBu₃ (run 34) and PⁱBu₃ (run 36), at low phosphine ratios (runs 24, 26, 28, 31, 33, 38 and 40) is unprecedented for unidentate phosphines apart from PPh₂Me (see above). We note also that small amounts of CO–ethene oligomers are formed when using these more basic phosphines. These are discussed in detail below.

In order to attempt to rationalise the differences in selectivity between these related alkyl phosphines in terms of the ligand structure, the productivity for polyketone formation has been plotted in a Tolman Map in Fig. 2. Steric-electronic maps were devised by Tolman and were first described in his seminal paper of 1977.¹⁸

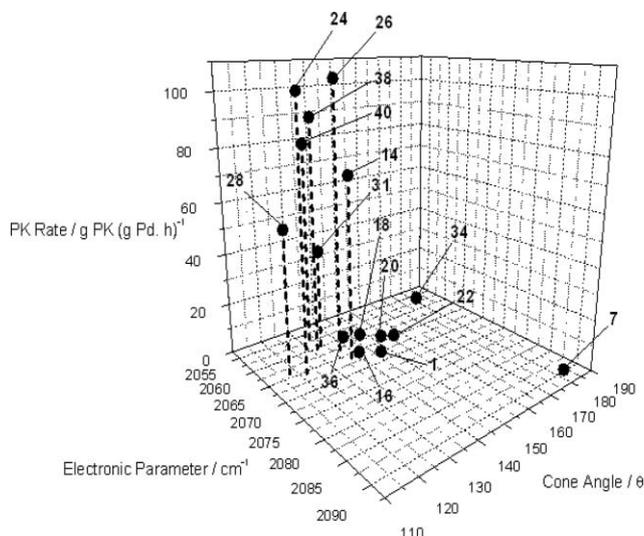


Fig. 2 Tolman map of trialkyl-, dialkylphenyl- and alkyldiphenyl-phosphines (1 : 4, Pd–P) in the palladium-catalysed methoxycarbonylation of ethene. The parameters are defined in ref. 18. **1** PPh₃, **7** P(C₆F₅)₃, **14** PPh₂Me, **16** PPh₂Et, **18** PPh₂Pr, **20** PPh₂^tPr, **22** PPh₂ⁱBu, **24** PPhMe₂, **26** PPhEt₂, **28** PMe₃, **31** PEt₃, **34** P^tBu₃, **36** PⁱBu₃, **38** PⁿBu₃, **40** P(Oct)₃.

They relate a parameter of interest, in this case the polyketone productivity rate, to the steric and electronic parameters of the ligands, which may be calculated according to empirical rules.¹⁸ By showing the relationships in three-dimensions, even if a parameter of interest is dependant on a mixture of steric and electronic properties, the qualitative deconvolution of both effects is possible. Fig. 2 shows the averaged polyketone rates for all the phosphines studied. It shows that there is a well defined area in terms of steric and electronic parameters for active and selective polymer formation when using unidentate phosphines. The parameters required seem to be a combination of good electron donating ability and small size. How subtle this reliance is can be shown by the examples of methyl- and ethyldiphenyl-phosphine (runs 14 and 16). The cone angles are 136° and 140°, respectively, for these phosphines, but one is active and the other has very low activity. Thus, an increase in steric bulk by 4° seems to cause an almost complete loss of activity to polyketone, which is a very surprising, but reproducible observation.

Oligoketone formation

Analysis of the distribution of soluble oligomers (containing 2–5 –CH₂CH₂C(O)– units) produced during copolymerisation of CO and ethene in methanol can also help to give information on the origins of the selectivity of the reaction.¹¹ As the bite angle of a bidentate phosphine increases, the pocket angle decreases and it has been argued that this favours termination¹¹ so that the Flory-Schulz constant, α (rate of propagation/(rate of propagation + rate of termination)) will be lower. For unidentate ligands, the pocket angle is expected to be smaller for the larger cone angle ligands, so they should favour termination over chain growth and hence should favour methyl propanoate production.

Under our conditions, negligible amounts of co-oligomers are obtained when using any of the triaryl phosphines, P^tBu₃ or PⁱBu₃ (only methyl propanoate is formed) or when using PMePh₂ (only polyketone is formed). The amounts are extremely small for PR₂Ph (R = Me or Et) and for PR₃ (R = Me, Et or Oct), all of which produce predominantly polyketone. Significant amounts of co-oligomers are observed only for the catalysts which produce smaller amounts of polyketone and significant amounts of methyl propanoate; those containing PRPh₂ (R = Et, Pr, ^tPr and ^tBu). In all cases, the oligomers have one keto and one ester end group, although traces of 2-pentanone are also observed in some cases. The end group analysis shows that only one mechanism (probably carried by Pd–H) operates.¹ Quantitative analysis of the soluble co-oligomers formed for PRPh₂ (R = Et, Pr, ^tPr and ^tBu) shows a Flory-Schulz distribution with α (see Table 2) being 0.49 for R = Et dropping to 0.41 (R = ^tBu) as the bulk of the ligand increases.

These results indicate that bulky ligands promote methyl propanoate formation, but that, as the bulk of the phosphine is reduced, the rate of chain growth increases relative to that of

Table 2 Flory-Schulz constants (α) for soluble oligoketones formed using different ligands (Pd–P = 1 : 4)^a

Ligand	PEtPh ₂	PPrPh ₂	P ^t PrPh ₂	P ^t BuPh ₂
α	0.49	0.47	0.46	0.41

^a Calculated as described in ref. 25 and 26.

termination. Only the smallest ligands give polyketone. These results then reinforce the conclusions made on the basis of bidentate ligands that the reaction selectivity is determined largely by the size of the pocket angle, with smaller pocket angles favouring termination.¹¹

It is noteworthy that co-oligomers and polyketone are only ever observed when the P–Pd ratio is low. Most of the ligands promote methyl propanoate formation at higher phosphine loading. One possible explanation is that monophosphine complexes, which will have even wider pocket angles may promote polyketone formation at low P–Pd ratios. This observation does not appear to be consistent with the suggestion that the reduction of electron density on Pd caused by a bulky electron donating ligand becoming unidentate leads to faster attack by methanol and hence, favours methyl propanoate formation.²

Studies of model complexes

In order to try to obtain more information about possible catalytic intermediates and their stereochemistry, [Pd(COD)MeCl] was treated with phosphines (2 mol) in order to synthesise [PdClMeP₂] (P = PPh₂, PMe₃,²⁷ PPh₃²⁸ and PPh₂Ph²⁷), a model for the ethyl intermediate in the copolymerisation. Using PPh₂Me, a singlet was observed at 26.6 ppm in the ³¹P{¹H} NMR spectrum suggesting that the phosphines must be coordinated *trans* about the metal centre. (Fig. 3)

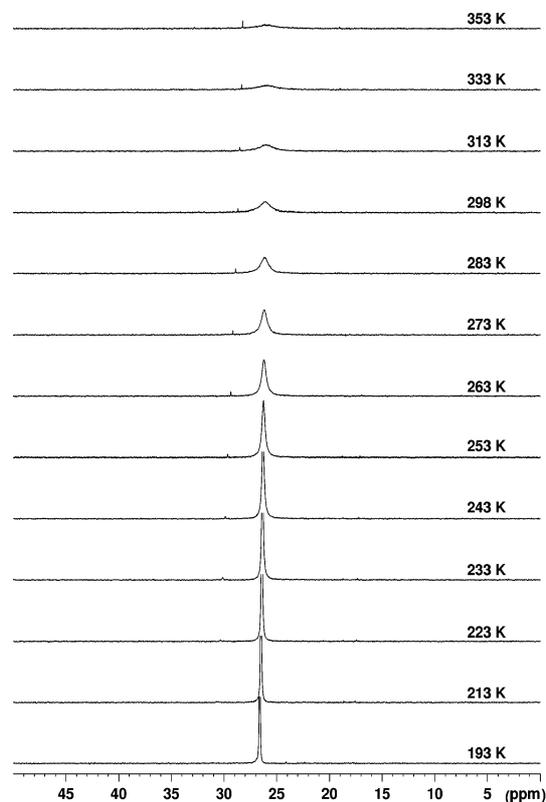


Fig. 3 Variable-temperature ³¹P{¹H} NMR spectra of a d₈-toluene solution of [(COD)PdMeCl] with 2 equiv. of PPh₂Me.

In addition, the triplet Pd–Me ($J_{\text{PH}} = 6$ Hz) signal in the ¹H NMR spectrum confirms *trans* co-ordinating phosphines, at least in the methyl complex.²⁴ There is no evidence of any *cis*-

Table 3 Coalescence temperatures (T) for exchange of free and bound phosphine in [PdMeCl(PR₃)₂] as determined from variable-temperature NMR studies of solutions containing [PdMeCl(COD)] and 2PR₃^a

Ligand	PMe ₃	PMe ₂ Ph	PMePh ₂	PPh ₃
T/K	300	250	340	>350

^a Traces of excess phosphine are present in all the solutions. The coalescence temperature is defined as the temperature at which the line width is highest.

species despite the selectivity towards polyketone formation when using this phosphine. Upon heating, the singlet broadens and shifts slightly to lower frequency, presumably because of exchange between free and bound phosphine. This has been confirmed by studying reactions in which the Pd–P ratio is 1 : 4. In this case, singlets are observed at $\delta_{\text{P}} = 26.6$ and -16.5 ppm from the bound and the free phosphine, respectively. Upon heating, both broaden together with the coalescence temperature being >353 K. At any given temperature, the resonance from the phosphines attached to Pd are slightly broader when excess phosphine is present. An Eyring plot (P–Pd = 4) based upon simulation of the line shapes over the temperature range 223–293 K gives activation parameters: $\Delta H^{\ddagger} = 19.9$ kJ mol⁻¹ and $\Delta S^{\ddagger} = -119$ J mol K⁻¹. The high negative entropy of activation confirms that the exchange is associative. Very similar behaviour is observed for PPh₃ ($\delta_{\text{P}} = -14.5$ ppm), PPh₂Ph ($\delta_{\text{P}} = -1.9$ ppm) and PPh₃ ($\delta_{\text{P}} = 30.5$ ppm). The coalescence temperatures (Table 3) are in the order PPh₃ > PPh₂Ph > PPh₃ > PPh₂Ph, suggesting that the exchange of free and bound phosphines is faster for the smaller more basic ligands, as expected for an associative process, with steric effects dominating. The position of PPh₃ is slightly anomalous, perhaps because its poor π -acceptor properties leading to a lower stability of the proposed 5-coordinate intermediate.²⁹

Finally, addition of excess COD to a solution containing [Pd(COD)MeCl] and 2PPh₂Me leads to a sharpening of the ³¹P NMR signal ($\delta_{\text{P}} = 26.0$ ppm) at room temperature, suggesting that exchange of free and bound P is accelerated by excess COD. In no case can signals from the *cis* isomer be observed.

Conclusions

It has been shown that the copolymerisation of carbon monoxide and ethene is possible using a wide range of unidentate phosphines when the P–Pd ratio is low (4 : 1). This is an unexpected result, as most of the literature teaches that methyl propanoate should be selectively produced. Our results show that active, selective catalysts for polyketone formation can be generated from palladium complexes containing simple unidentate phosphines, although the rates are not very high compared with the best previously reported using *e.g.* Ph₂P(CH₂)₃PPh₂, which can be as high as 6000 g PK (g Pd. h)⁻¹. Analysis of the results shows that unidentate phosphines must lie within a well defined area of steric and electronic properties to provide active catalysts for polyketone formation, with phosphines having low steric bulk and high electron density being most favoured. Analysis of the Flory-Schulz constants (we are grateful to a referee for suggesting this) for the formation of co-oligomers, which are only significantly observed for alkyldiphenylphosphines, shows, as suggested previously,¹¹ that steric bulk favours methyl propanoate

formation. A P–Pd ratio of 4 allows polyketone formation when using smaller ligands, but higher phosphine ratios give methyl propanoate or inhibit the reaction. This would appear to indicate that monophosphine complexes, if they form, do not favour methyl propanoate formation. The one ligand which gives polyketone formation at high loading P–Pd (even 30 : 1) is P(4-C₆H₄OMe)₃.

Acknowledgements

We thank the E. C. for support through the IDECAT Network of Excellence (No. NMP3-CT-2005-011730) (N. R. V.).

Notes and references

- 1 E. Drent and P. H. M. Budzelaar, *Chem. Rev.*, 1996, **96**, 663.
- 2 R. A. M. Robertson, and D. J. Cole-Hamilton, in *Catalytic Synthesis of Alkene-Carbon Monoxide Copolymers and Co-oligomers*, ed. A. Sen, Kluwer Academic Publishers, Dordrecht, The Netherlands, 2003.
- 3 R. A. M. Robertson and D. J. Cole-Hamilton, *Coord. Chem. Rev.*, 2002, **225**, 67.
- 4 A. Sen, *Adv. Polym. Sci.*, 1986, **73–4**, 125.
- 5 A. Sen, *Acc. Chem. Res.*, 1993, **26**, 303.
- 6 E. Drent, J. A. M. Van Broekhoven and M. J. Doyle, *J. Organomet. Chem.*, 1991, **417**, 235.
- 7 E. Drent, and E. Kragtwijk, *Eur. Pat.*, 495 548, 1992.
- 8 G. R. Eastham, R. P. Tooze, X. L. Wang, and K. Whiston, *Int. Pat.*, 9 619 434, 1996.
- 9 W. Clegg, G. R. Eastham, M. R. J. Elsegood, R. P. Tooze, X. L. Wang and K. Whiston, *Chem. Commun.*, 1999, 1877.
- 10 P. W. N. M. Van Leeuwen, M. A. Zuideveld, B. H. G. Swennenhuis, Z. Freixa, P. C. J. Kamer, K. Goubitz, J. Fraanje, M. Lutz and A. S. Spek, *J. Am. Chem. Soc.*, 2003, **125**, 5523.
- 11 E. Zuidema, C. Bo and P. W. N. M. van Leeuwen, *J. Am. Chem. Soc.*, 2007, **129**, 3989.
- 12 S. M. A. Donald, S. A. Macgregor, V. Settels, D. J. Cole-Hamilton and G. R. Eastham, *Chem. Commun.*, 2007, 562.
- 13 A. Sen and T. W. Lai, *J. Am. Chem. Soc.*, 1982, **104**, 3520.
- 14 E. Drent, *US Pat.*, 4 835 250, 1989.
- 15 W. Keim, H. Mass and S. Mecking, *Z. Naturforsch., B: Chem. Sci.*, 1995, 50.
- 16 K. Nozaki, Shell, *US Pat.*, 3 694 412, 1972.
- 17 R. E. Rulke, J. M. Ernsting, A. L. Spek, C. J. Elsevier, P. W. N. M. van Leeuwen and K. Vrieze, *Inorg. Chem.*, 1993, **32**, 5769.
- 18 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.
- 19 A. Sen, J. T. Chen, W. M. Vetter and R. R. Whittle, *J. Am. Chem. Soc.*, 1987, **109**, 148.
- 20 E. Drent, *Eur. Pat.*, 1984, 0121965; *Chem. Abstr.*, 1985, 102, p. 46423.
- 21 R. I. Pugh and E. Drent in *Catalytic Synthesis of Alkene-Carbon Monoxide Copolymers and Co-oligomers*, ed. A. Sen, Kluwer Academic Publishers, Dordrecht, The Netherlands, 2003, p. 9.
- 22 G. R. Eastham, R. P. Tooze, M. Kilner, D. F. Foster and D. J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.*, 2002, 1613.
- 23 A. J. Rucklidge, G. E. Morris, A. M. Z. Slawin and D. J. Cole-Hamilton, *Helv. Chim. Acta*, 2006, **89**, 1783.
- 24 L. K. Knight, Z. Freixa, P. W. N. M. van Leeuwen and J. N. H. Reek, *Organometallics*, 2006, **25**, 954.
- 25 T.-W. Lai and A. Sen, *Organometallics*, 1984, **3**, 866.
- 26 G. Henrici-Olivé and S. Olivé, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 138.
- 27 Y. Kayaki, I. Shimizu and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 917.
- 28 B. Bacchi, M. Carcelli, C. Pelizzi, G. Pelizzi, P. Pelagetti and S. Ugolotti, *Eur. J. Inorg. Chem.*, 2002, 2179.
- 29 T. G. Appleton, H. C. Clark and L. E. Manzer, *Coord. Chem. Rev.*, 1975, **10**, 335.