The oligomerisation of 3-hydroxy-1-alkynes with palladium(II) diketonates and phosphorus ligands as the catalytic system

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Abstract

3-Methylhex-1-yne-3-ol has been oligomerised by use of Pd(II) acetylacetonate with 31 different phosphorus ligands as catalyst, yielding a dimer (2,4-disubstituted but-1-en-3-yne) and a linear trimer (1,4,6-trisubstituted hexa-1,3-dien-5-yne) as the two main products. By input–output relations a variation of the diketonate and the P ligand, as well as an alteration of the phosphorus/palladium ratio, has been connected with product ratios as dependent variables. Phosphines produced three association steps up to a cone angle of 170°; the third step representing a stop complex. For the first association the activity of the catalytic system and the portion of the 2,4-dimer increased with the donor character of the P ligands. Moreover the part of the 2,4-dimer was strongly favoured by an increasing cone angle of the ligand as well as by the volume of the substituents at the alkynol. The second association developed the more active systems with a modest steric effect of the ligands on product ratios. The trimerisation was favoured by π-acceptor ligands and by more electronegative substituents at the diketonate anion. The results served to support the hypothesis, that two mechanisms and ionic intermediates should be insolved.

Introduction

The oligomerisation of 1-alkynes by use of palladium complexes as catalysts has been realised with few examples. 3-Methylbut-1-yne-3-ol has been trimerised to the 1,4,6-trisubstituted hexa-1,3-dien-5-yne with a Pd(II)imine complex and triphenylphosphine [1], as well as with $[(C_6H_5)_2P(C_6H_4SO_3Na)]_2PdCl_2$ [2] as catalyst.

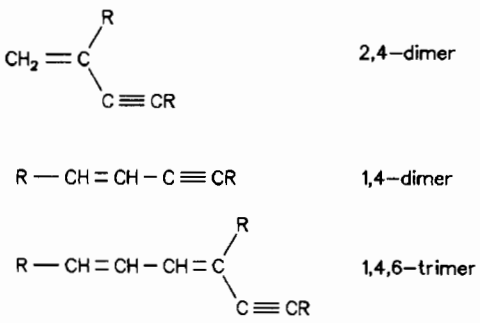
Terminal alkynes have been dimerised selectively to 2,4-disubstituted but-1-en-3-ynes by Pd(II) acetate and tri(2,6-dimethoxyphenyl)phosphine [3]; for the dimerisation of cyclopropylacetylene with Pd(II) acetate triphenylphosphine has been used as the ligand [4]. On the other hand the dimerisation of tri(phenyl, alkyl)silylacetylenes by $[(C_6H_5)_3P]_4Pd$ produced 1,4-disubstituted but-1(E)-en-3-ynes [5].

These results indicate that the oligomerisation of terminal alkynes by Pd complexes may be determined by a steric effect of the ligands at the palladium and of the alkyne's α-substituents. We present a more detailed study of effects which determine the selectivity of the oligomerisation of 1-alkyne-3-ols by Pd(II) diketonates and P ligands using the principles of input–output relations [6, 7].

Results and discussion

Association phenomena of P ligands

3-Methylhex-1-yne-3-ol has been oligomerised in *o*-xylene as the solvent at 80 °C using $Pd(acac)_2$ (ratio 1/300 to the alkyne) and 31 different P ligands. With all other reaction variables being held constant, the concentration of the ligands was varied from $lg[PR_3]_0/[Pd(acac)_2]_0 = -1$ to $+1$. Two main products were formed, the 2,4-disubstituted but-1-en-3-yne (2,4-dimer) and the 1,4,6-trisubstituted hexa-1,3-dien-5-yne (1,4,6-trimer). As a by-product the 1,4-disubstituted but-1(E)-en-3-yne (1,4-dimer) was detected (Scheme 1). Other linear trimers in minor amounts have not yet been characterised.



Scheme 1.

0020-1693/93/$6.00

The results of the experiments for each ligand will be presented through the form of ligand concentration control maps ([L]-control maps), for which lg[L]/[Pd] values are correlated with selected product ratios [6]. For some ligands the [L]-control maps indicated distinctly three ligand association steps. A typical example is represented by $(C_6H_5)_2P(o\text{-tolyl})$ (Fig. 1(a)). For this ligand it is proposed that at $lg[L]_0/[Pd]_0 = -0.6$ to 0.0 complexes with one phosphine/palladium determine the product ratio. These intermediates produce a lower turnover than complexes with two ligands, which direct the catalytic reaction at $lg[L]_0/[Pd]_0 = 0.3$ to 0.8. A further ligand association at $lg[L]_0/[Pd]_0 > 0.8$ reduces the activity of the system by the formation of a stop complex. It is well known that $Pd(acac)_2$ forms a Pd(0) complex in the presence of an excess of $(C_6H_5)_3P$ [8], and it has been observed by Trost *et al.* that a Pd(0) complex is less reactive for the dimerisation of alkynes than Pd(II) [3].

Steric properties (cone angles θ [9]) and electronic properties (χ values [10, 11]) of the P ligands will influence their association. This became manifest when a set of ligands with an increasing cone angle but similar χ values was used. Different to $(C_6H_5)_2P(o\text{-tolyl})$ ($\theta = 161°$; $\chi = 12.8\ cm^{-1}$; Fig. 1(a)), $C_6H_5P(o\text{-tolyl})_2$ with $\theta = 178°$ ($\chi = 11.9\ cm^{-1}$) and the even bulkier $P(o\text{-tolyl})_3$ ($\theta = 194°$; $\chi = 10.9\ cm^{-1}$) produced no stop complexes (Fig. 2(a) and (b)). In addition, with these ligands the change from the 2,4-dimer to the 1,4,6-trimer as the main product is shifted to a higher ligand concentration: the ratio 2,4-dimer/1,4,6-trimer = 1.0 appears with triphenylphosphine and with $(C_6H_5)_2P(o\text{-tolyl})$ at $lg[L]_0/[Pd]_0$ *c.* −0.4, with $C_6H_5P(o\text{-tolyl})_2$ at +0.08 and with $P(o\text{-tolyl})_3$ at +0.80.

An electronic influence on the catalytic reaction became evident when tricyclohexylphosphine ($\theta = 170°$; $\chi = 1.4\ cm^{-1}$) or tri-*o*-methoxyphenylphosphine ($\theta = 188°$; $X = 1.7\ cm^{-1}$) were used. With these two stronger donors the activity of the catalytic system rises, as is indicated by a high turnover of the monomer at $lg[L]_0/[Pd]_0 < 0.0$ (Fig. 2(c) and 2(d) compared to (a) and (b)).

In the presence of phosphites, $Pd(acac)_2$ generated a lower activity for the oligomerisation of the 3-methylhex-1-yne-3-ol than with phosphines. Trialkylphosphites with χ values from 18 to 23 cm^{-1} and with cone angles < 135° gave [L]-control maps like triethylphosphite (Fig. 1(b)). With an additional increase of the π-acceptor strength ($\chi = 27$–$30\ cm^{-1}$) as for triarylphosphites the activity of the system decreased further and triarylphosphites with $\theta > 135°$ like tri(*o*-tolyl)phosphite ($\theta = 141°$) or tri(*o*-phenylphenyl)phosphite ($\theta = 152°$) developed no activity at all. From a study of nickel(0) complexes with alkynes it has been stated that the strength of the acetylene coordination decreases with an increase of the acceptor character of the P ligand [12]. Further experiments proved that these bulkier triarylphosphites do not inhibit or alter the oligomerisation of 3-methylhex-1-yne-3-ol by $Pd(acac)_2$ and triphenylphosphine. Therefore they will not be

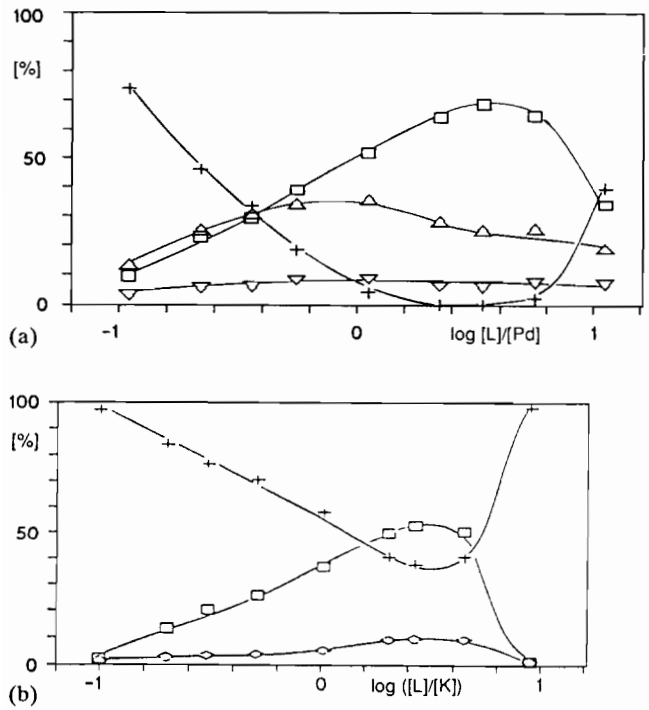


Fig. 1. [L]-control maps of the oligomerisation of 3-methylhex-1-yne-3-ol in *o*-xylene as solvent at 80 °C by the use of the catalytic system $Pd(acac)_2$ and (a) diphenyl-*o*-tolylphosphine, (b) triethylphosphite. +, monomer; □, trimer; △, 2,4 dimer; ▽, 1,4-dimer; ◇, both dimers.

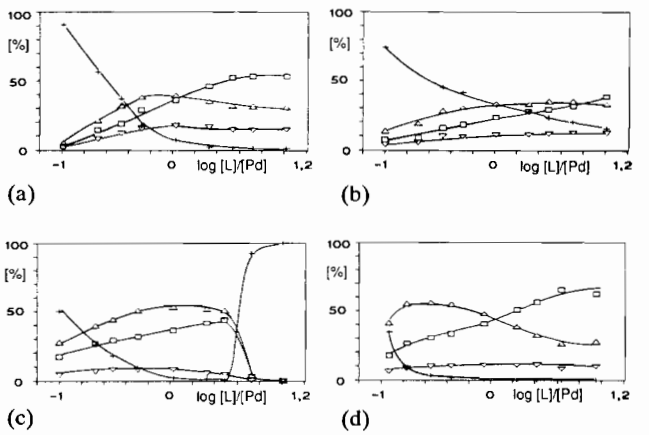


Fig. 2. [L]-control maps for the oligomerisation of 3-methylhex-1-yne-3-ol at 80 °C using $Pd(acac)_2$ as catalyst with the ligands (a) phenyldi-*o*-tolylphosphine, (b) tri-*o*-tolylphosphine, (c) tricyclohexylphosphine and (d) tri-*o*-methoxyphenylphosphine. +, monomer; □, trimer, △, 2,4-dimer; ▽, 1,4-dimer.

associated in the presence of this phosphine and the alkynol.

For the catalytic oligomerisation of terminal alkynes to linear products the oxidative addition of the alkyne is a critical step, and for it to occur the donor strength of the ligands bonded to the palladium will be essential [13, 14]. It is therefore reasonable that the activity of the $Pd(acac)_2$–PR_3 complexes increases with the σ-donor character of the P ligand and decreases with its π-acceptor strength.

The influence of the diketonate

With different substituents at the Pd(II) diketonate the activity of the system as well as the product ratio altered (Figs. 2(d) and 3(c)). Therefore at least one diketonate is retained in the active intermediates.

For further experiments Pd(II) complexes with two different diketonate anions were synthesised according to literature procedures [15, 16]. The catalytic properties of these complexes were studied and compared with the symmetric Pd(II) diketonates by the use of [L]-control maps.

With triphenylphosphine as ligand and the Pd(II) diketonates $Pd(acac)_2$ (Fig. 3(a)), $Pd(F_3acac)_2$ (Fig. 3(b)) and $Pd(acac)(F_3acac)$ (Fig. 4(a)) it was demonstrated that only one of the two diketonates stays in the active complex, because the [L]-control maps given in Fig. 3(b) and Fig. 4(a) represent identical systems, but the map with $Pd(acac)_2$ and the same ligand (Fig. 3(a)) differs distinctly. Experiments with tri-*o*-methoxyphenylphosphine as the ligand and the complexes $Pd(F_3acac)_2$ (Fig. 3(c)), $Pd(F_3acac)(acac)$ (Fig. 4(b)) and $Pd(acac)_2$ (Fig. 2(d)) confirmed that it is the diketonate with the more electronegative substituent, which in the presence of the hydroxy-alkyne is retained in the intermediates. This result is different to the finding of stoichiometric substitution experiments, where the diketonate with the more electronegative substituent was more readily eliminated [17].

The first ligand association

From the [L]-control maps showing major alterations at $\lg[L]/[Pd] \leqslant 0.0$ it follows that the active complexes will be present only at a low concentration. Therefore it is not surprising that ^1H NMR experiments gave no information about a Pd hydride (similar to observations stated in the literature [18]) or a π-bonded acetylene.

For the dimerisation of terminal alkynes catalysed by Pd complexes Trost *et al.* gave two different mechanistic interpretations as a working hypothesis. A first

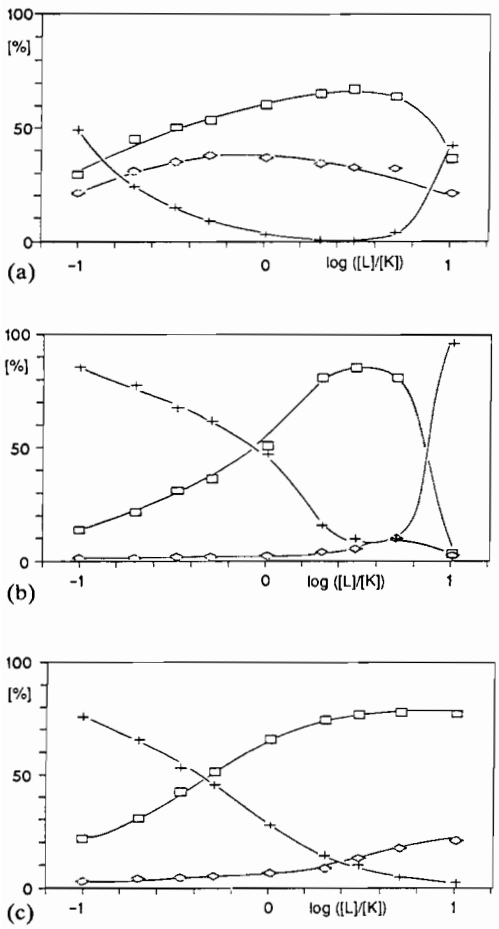


Fig. 3. [L]-control maps for the oligomerisation of 3-methylhex-1-yne-3-ol in *o*-xylene at 80 °C using as catalytic systems: (a) $Pd(acac)_2$ and triphenylphosphine, (b) $Pd(F_3acac)_2$ and triphenylphosphine, (c) $Pd(F_3acac)_2$ and tri-*o*-methoxyphenylphosphine. +, monomer, □, trimer; ◇, dimers.

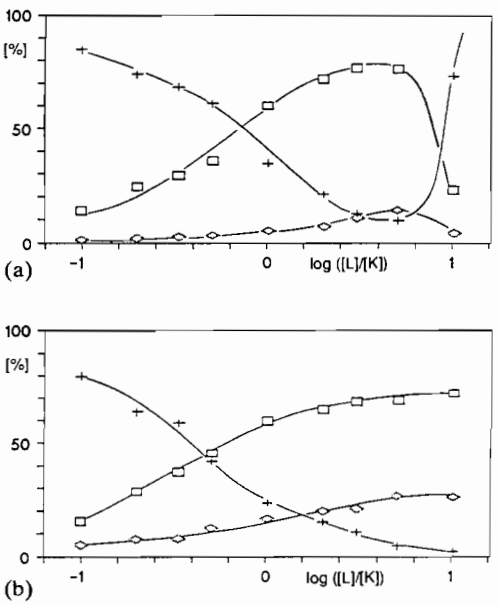
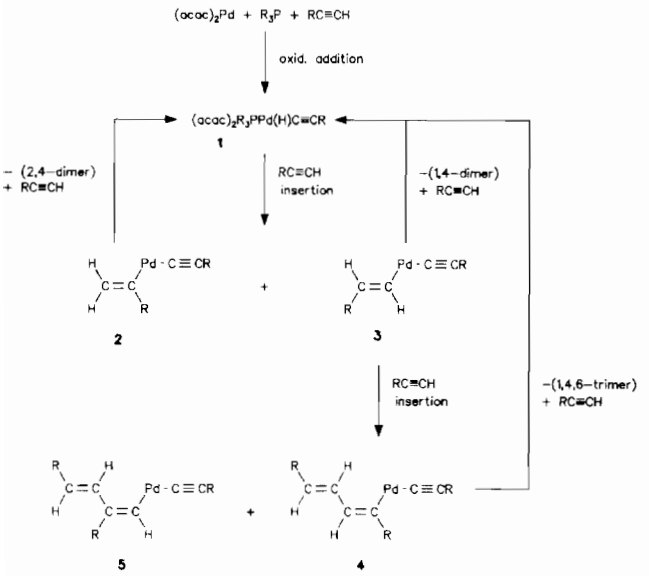


Fig. 4. [L]-control maps for the oligomerisation of 3-methylhex-1-yne-3-ol using as catalyst (a) $Pd(F_3acac)(acac)$ and triphenylphosphine; (b) $Pd(F_3acac)(acac)$ and tri-*o*-methoxyphenylphosphine. +, monomer; □, trimer; ◇, dimers.

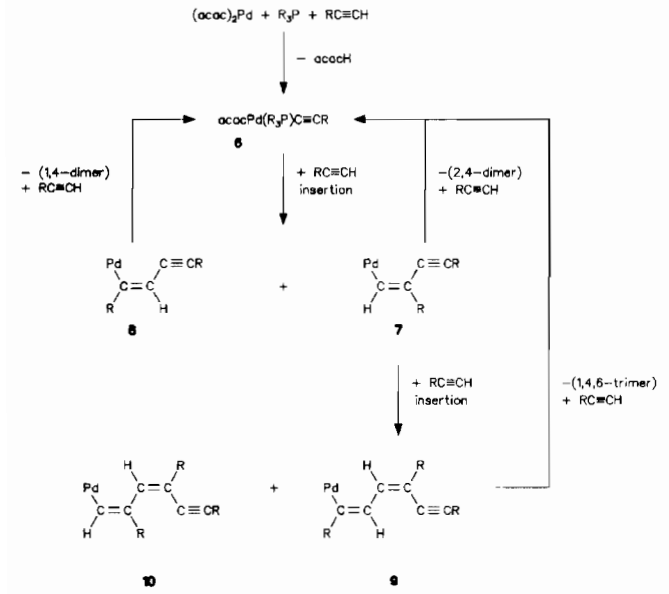
one involves ≡C–H bond activation followed by the addition of the Pd hydride to a coordinated triple bond [3]. The second proposal includes the addition of a Pd acetylide to a coordinated alkyne [19].

For the three main products of the dimerisation and trimerisation of methylhexynol these two alternatives link either the 1,4-dimer and the 1,4,6-trimer (Scheme 2) or the 2,4-dimer and the 1,4,6-trimer (Scheme 3) to the same intermediate.

We focussed our attention on steric effects with the idea that an α-substituted vinyl group as in **2**, **4**, **8** and **9** might inhibit further insertion steps and that a head to tail (even more a tail to tail) C–C bond formation



Scheme 2.



Scheme 3.

producing **5** or **10** would be retarded. This hypothesis is supported by the fact that from **5** or **10** further insertion steps should lead easily to a linear tetramer or even higher oligomers, but these have not been detected.

The product portions for ligands with similar χ values but different cone angles have been collected in Table 1. At a ligand to palladium ratio of $\lg[L]_0/[Pd]_0 \leqslant -0.3$, which represents the first ligand association, an increasing cone angle of the ligands produced a sharp increase of the portion of the 2,4-dimer at a cone angle of $>150°$ and of the 1,4-dimer at a cone angle of $>170°$. In each case it is the trimer fraction, which is reduced. This separated connection of both dimers with the trimer should be an indication that both mechanisms contribute to the catalytic reaction. The acetylenic substituent in **7** could be the reason that the change 2,4-dimer/trimer appeared at a lower cone angle.

A variation of the electronic parameter χ exhibited a small influence on the catalysis (Table 2); but the continuity of the data is cut when phosphines were replaced by phosphites (class II by class III ligands [20]). The better donors reduced the amount of the trimer fraction. Therefore a good donor with a big cone angle should be the necessary choice for the synthesis of the 2,4-dimer; Trost *et al.* used Pd(II) acetate and 2,6-disubstituted triphenylphosphines for the selective synthesis of this dimer from different 1-alkynes [3].

The formation of the 1,4,6-trimer is favoured by a weaker donor with a cone angle $\leqslant 145°$ such as triphenylphosphine, as has been realised by literature procedures [1, 2]. An even higher portion of the trimer by the use of stronger acceptor ligands like phosphites (Table 2) was accompanied by a lower turnover. The selectivity of the trimerisation could be improved further by the use of a more electronegative substituent at the diketonate, for example with $Pd(F_3acac)_2$ (Table 2).

Effects originating from steric bulk at the alkynol (Table 3) indicated that more voluminous substituents at the substrate shift the ratio 2,4-dimer/trimer in favour of this dimer. This result fits the mechanism presented in Scheme 3, where a steric influence of the α-substituent at the vinyl group should favour intermediate **7** to **9** (and **8**). The ratio 1,4-dimer/trimer is affected as well (Table 3) but not to the same extent. A steric influence of the α-substituent at the vinyl group should favour similarly intermediate **3** to **4** (and **2**). We take this as another hint that both reaction passes will be involved.

The second ligand association

The [L]-control maps using the ligands diphenylvinylphosphine and *cis*-1,2-bis(diphenylphosphino)ethene (Fig. 5(a) and (b)) differ with respect to the turnover of the monomer, which stays $<40\%$ with the chelating

TABLE 1. The influence of the cone angle θ [8] of P ligands on product portions from the oligomerisation of 3-methylhex-1-yne-3-ol with $Pd(acac)_2$ in *o*-xylene at 80 °C. Data for the first ligand association at $lg[L]_0/[Pd]_0 = -0.5$ to -0.3; data for the second ligand association at $lg[L]_0/[Pd]_0 = 0.3$ to 0.7 in parentheses

Ligand	$^{FT}\chi$ (cm^{-1})	θ (°)	2,4-Dimer (%)	1,4-Dimer (%)	1,4,6-Trimer (%)
$CH_3P(C_6H_5)_2$	12.1	136	30 (29)	10 (9.5)	60 (61.5)
$CH_2{=}CHP(C_6H_5)_2$	13.6	140	33 (31)	10 (10)	57 (59)
$P(C_6H_5)_3$	13.3	145	31.5 (27)	9.5 (7)	59 (66)
$P(p\text{-}CH_3OC_6H_4)_3$	10.5	145	35 (25)	10 (7)	55 (68)
$cy\text{-}C_6H_{11}P(C_6H_5)_2$	9.0	153	49 (39)	10 (6.5)	41 (54.5)
$o\text{-}CH_3C_6H_4P(C_6H_5)_2$	12.8	161	46 (26)	10 (6.5)	44 (67.5)
$(o\text{-}CH_3C_6H_4)_2PC_6H_5$[a]	11.9	178	49 (31)	19 (15)	32 (54)
$P(o\text{-}CH_3C_6H_4)_3$[a]	10.9	194	53 (39)	18 (15)	29 (46)

[a]Second association only partly developed.

TABLE 2. The influence of an increasing χ value [10, 11] on the oligomerisation of 3-methylhex-1-yne-3-ol using $Pd(acac)_2$ in *o*-xylene at 80 °C; data for the first ligand association at $lg[L]_0/[Pd]_0 = -0.5$ to -0.3. The data for the second ligand association from the [L]-control at $lg[L]_0/[Pd]_0 = 0.3$ to 0.7 are added in parentheses.

Ligand	$^{FT}\chi$ (cm^{-1})	θ (°)	Turnover[a] (%)	2,4-Dimer (%)	1,4-Dimer (%)	1,4,6-Trimer (%)
$P(p\text{-}Me_2NC_6H_4)_3$	5.3	145	40 (95)	45 (41)	11 (10)	44 (49)
$P(p\text{-}CH_3OC_6H_4)_3$	10.5	145	60 (95)	35 (25)	10 (7)	55 (68)
$P(C_6H_5)_3$	13.3	145	80 (100)	31.5 (27)	9.5 (7)	59 (66)
$P(p\text{-}ClC_6H_4)_3$	16.7	145	40 (95)	31 (24)	9 (5)	60 (71)
$P(o\text{-}cy\text{-}C_6H_{11})_3$	18.0	134.5	25 (75)	19 (16)	1.5 (2.5)	79.5 (81.5)
$P(o\text{-}isoC_3H_7)_3$	18.9	130.5	30 (50)	17.5 (13)	2.5 (3)	80 (84)
$P(C_6H_5)_3$[b]	13.3	145	30 (90)	2.5 (5)	2.5 (3)	95 (92)

[a]Turnover of the monomer (GLC). [b]Using $Pd(F_3acac)_2$.

TABLE 3. Steric influence of the alkynol $R_1R_2C(OH)C{\equiv}CH$ on its oligomerisation using $Pd(acac)_2$ and tri(*p*-methoxyphenyl)phosphine. Volumes V^a of the substituents R_1 and R_2 were taken from the literature [21]. Data for the first ligand association at $lg[L]_0/[Pd]_0 = -0.5$ to -0.3; data for the second ligand association taken from the [L]-control at $lg[L]_0/[Pd]_0 = 0.3$ to 0.7 in parentheses.

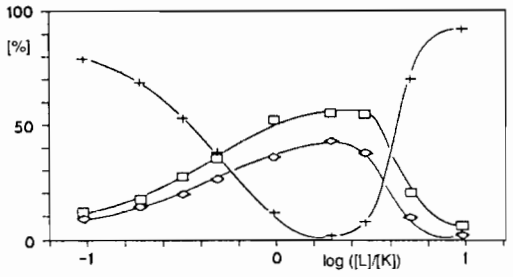
R_1	R_2	$V^a \times 10^2$	2,4-Dimer (%)	1,4-Dimer (%)	Trimer fraction (%)
CH_3	CH_3	5.7	10 (11)	4 (7.5)	86 (81.5)
C_2H_5	CH_3	7.1	30 (20)	7 (7.5)	63 (72.5)
nC_3H_7	CH_3	7.6	35 (25)	10 (7)	55 (68)
iC_3H_7	iC_3H_7	11.5	60 (64)	10 (13)	30 (23)

bisphosphine. The steric influence on the product selectivity in the presence of P ligands at the second association phenomenon (Table 1) is much less important than it is for the first ligand association. These results could be indicative of a *trans* position of two P ligands representing the more effective catalytic system compared to a *cis* position. As expected steric bulk at the alkynol affected the product ratio to a similar degree as at the first ligand association (Table 3).

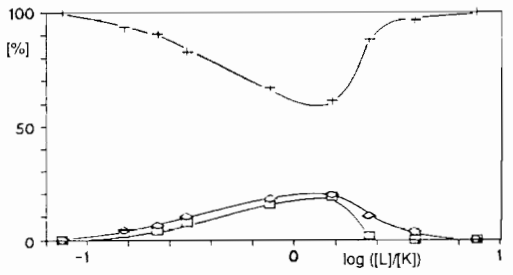
On the other hand the influence of the electronic parameter of the P ligands is quite distinct and as expected more pronounced than at the first association of the same ligands (Table 2). The trimerisation could be accelerated by a fast second insertion relative to the elimination of the dimer. This effect that the second insertion is faster than the first one has been observed by Brookhart *et al.* [22] at the oligomerisation of ethene using a cobalt complex as catalyst. On the other hand the trimerisation is retarded by steric effects from ligands and from substituents at the alkynol, which favour the dimerisation, especially at the first ligand association.

A catalytic cycle with ionic complexes describes our hypothesis for the oligomerisation at ligand/Pd ratios >1 (Scheme 4). The reversible coordination of one P ligand [23] or the switch of an acetylacetonate to a monodentate bond would keep the coordination number $\leqslant 6$.

Cationic Pd complexes with acetylacetonate as the anion are well known [17]. A marked solvent dependence of the oligomerisation supports this view. $Pd(acac)_2$, tricyclohexylphosphine and 3-methylhex-1-yne-3-ol (ratio 1:2:300) at 80 °C gave 60% of the trimer in *o*-

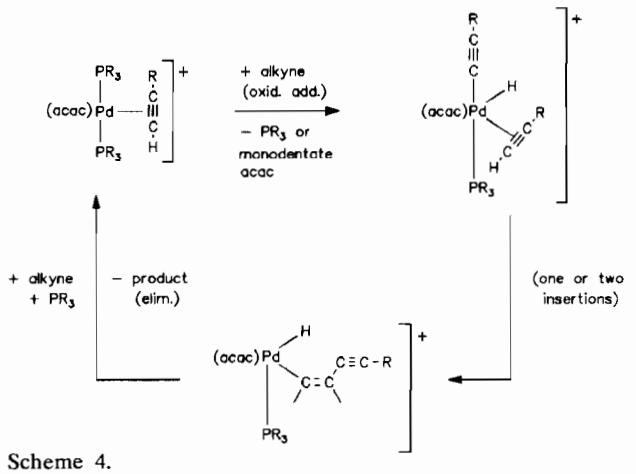


(a)



(b)

Fig. 5. [L]-control maps for the oligomerisation of 3-methylhex-1-yne-3-ol in *o*-xylene at 80 °C using as catalytic system $Pd(acac)_2$ and the ligands (a) diphenylvinylphosphine and (b) *cis*-1,2-bis(diphenylphosphino)ethene. +, monomer; □, trimer; ◇, dimers.



Scheme 4.

xylene, 77% in ethanol and 93% in ethanol with 15% water.

Experimental

Compounds

Palladium(II) acetylacetonate and the other Pd(II) diketonates were prepared according to literature methods [15, 16], recrystallised from dichloromethane and purified by column chromatography using silica gel.

The phosphorus ligands were obtained from Strem Chemicals. Palladium(II) chloride was a generous donation from Degussa (Hanau) and 3-methylhex-1-yne-3-ol was a gift from BASF (Ludwigshafen).

Equipment

The turnover of the monomer and the analysis of the products were determined by GLC using a Carlo Erba Fractovap 2200 with FID and a two meter column (5% SE 30). The chromatograms were recorded and integrated with a Servogor model RE 647.

Reactions

For the experiments necessary for the [L]-control maps a 2 M solution of the 3-methylhex-1-yne-3-ol in *o*-xylene with 5% mesitylene as internal standard was degassed and flushed with argon. A solution of $Pd(acac)_2$ (2.04 mg/ml) in *o*-xylene was prepared under an atmosphere of argon. The solvent had been dried, distilled, degassed and saturated with argon.

The oligomerisations were performed in 20 ml tubes fitted with screw caps and teflon seals. The ratio of the alkynol to palladium was held at 300:1. The P ligands were either directly weighted or added as a solution. Sets of experiments were heated to 80 °C for 5 h using a thermostat.

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