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The oligomerisation of phenylacetylenes with rhodium(I) and P ligands as the catalytic system

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Abstract

The dependence of the oligomerisation of phenylacetylene to cyclotrimers and dimers upon a Rh(I) complex with different P ligands as the catalytic system has been studied. The influence of substituents in the phenyl ring of the substrate has been examined as well. A selective cyclotrimerisation of phenylacetylenes is achieved with $[1,5\text{-}C_6H_{10}RhCl]_2$ as the catalyst. A decrease of the selectivity appears with very bulky *o*-substituents or a substitution in the 2,6-position of phenylacetylene. [P]-control maps indicate a mono-association of the ligand accompanied by a reduced activity of the system. The second association of a P ligand results in an inhibition of the cyclotrimerisation in favour of a very effective dimerisation of the phenylacetylenes. The ratio of the two dimers varies with electronic and steric changes of the substrate and with the cone angle of the P ligand. Different experimental data indicate that the oxidative addition of a terminal alkyne and a Rh hydride addition to a π-bonded phenylacetylene are rate determining steps.

Introduction

The oligomerisation of 1-alkynes opens up a possibility to synthesise different products, depending on the catalytically effective metal, the ligands, the substrate, a co-substrate and other variables, each with its properties and concentration effects [1]. Heimbach *et al.* have outlined suitable concepts for the study of such complex systems [2].

Internal acetylenes have been catalytically cyclotrimerised by complexes of cobalt [3], rhodium [4, 5] and iridium [6]. In the case of 1-alkynes, linear oligomers form an additional group of products. Rhodium(I) complexes catalyse the synthesis of co-cyclotrimers from hepta-1,6-diynes and monoynes [5], the synthesis of cyclotrimers from 3,3-dimethylbutyne-1 and from pentyne-1 [7, 8], the synthesis of dimers from octyne-1 [9] as well as from other 1-alkynes [8] and the synthesis of dimers, linear and cyclic trimers from propyne [10].

Using the Wilkinson complex, $[Ph_3P]_3RhCl$, 3-hydroxy-l-alkynes have been dimerised selectively to 1,4-disubstituted *trans*-vinylacetylenes [11]. This class of substrate has been studied further [12].

Phenylacetylene represents another reactive terminal alkyne. Its dimerisation to *trans*-1,4-diphenylbut-1-ene-3-yne using the Wilkinson complex as catalyst has been characterised [11, 13]; later on it was established that 2,4-diphenylbut-1-ene-3-yne is formed as a by-product [9, 12a]. Using $(C_5Me_5)_2TiCl_2/RMgX$ as catalyst the 2,4-substituted dimer represents the main product (see ref. 39). Cyclotrimers of phenylacetylene have been prepared using $(Ph_3P)_2NiCl_2 + NaBH_4$ [14], $NbCl_5$ or $TaCl_5$ [15], $C_5H_5NbCl_4 + Mg$ [16] or a rhodium(III) complex [17] as catalyst. The reaction to linear oligomers and polymers is catalysed by $[(CH_3CN)_4Pd](BF_4)_2$ [18], NbF_5 or TaF_5 [15] and $MoCl_5 + Ph_4Sn$ or $(nC_4H_9O)_4Ti + (C_2H_5)_3Al$ [19]; the dimerisation of phenylacetylene also gives rise to some higher oligomers [9, 11].

With a more detailed study using substituted phenylacetylenes as monomers we aim at a characterisation of the determinants for product control. Using rhodium(I) as the catalytically active metal the influence of P ligands on the activity and the selectivity of the oligomerisation has also been traced.

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Results

Rhodium(I) complex

Experiments with different rhodium(I) complexes served to select a suitable catalyst for the oligomerisation of the phenylacetylene. Desirable complexes should bear exchangeable neutral ligands and no P ligands; the results for two typical examples, the dimeric 1,5-hexadiene-μ-chloro-rhodium(I) and the dicarbonylrhodium(I)-acetylacetonate, are summarised in Table 1. Both complexes catalyse the cyclotrimerisation of phenylacetylene to 1,3,5- and 1,2,4-triphenylbenzene with a high selectivity but a low turnover. With the addition of three equivalents of triphenylphosphine per rhodium the hexadiene–rhodium complex increases its activity and the products switch from the cyclotrimers to the dimers 1,4- and 2,4-diphenylbut-1-ene-3-yne.

Using acac$Rh(CO)_2 + 3Ph_3P$ the changeover from the trimers to the dimers also results, but the activity stays low. Rhodium(I) complexes with other alkenes offered no advantages compared to $[1,5\text{-}C_6H_{10}RhCl]_2$.

Cyclotrimerisation

Phenylacetylene and 17 differently substituted phenylacetylenes were oligomerised with $[1,5\text{-}C_6H_{10}RhCl]_2$ as catalyst (ratio 200:1) at 80 °C for 4 h using toluene as the solvent. In Table 2 some data concerning the monomers and characterising the selectivity of the catalysis by three different ratios of products are given. All three product ratios from Table 2 change only for the three most bulky *o*-substituted phenylacetylenes: the share of the cyclotrimers decreases, the ratio of the two trimers shifts, the portion of the two dimers alters and a third dimer is formed.

For ten substituted phenylacetylenes with steric parameters $v \leqslant 0.36$ the ratio of the two dimers stays at 1.2 to 1.5. For 2,4-dimethylphenylacetylene this proportion is inverted to 0.67 in favour of the 1,4-disubstituted vinylacetylene. 2-Methyl- and 2-chlorophenylacetylene should react alike; unfortunately we had no reliable GLC signals for their dimers.

[P]-control

Phenylacetylene has been oligomerised by [1,5-

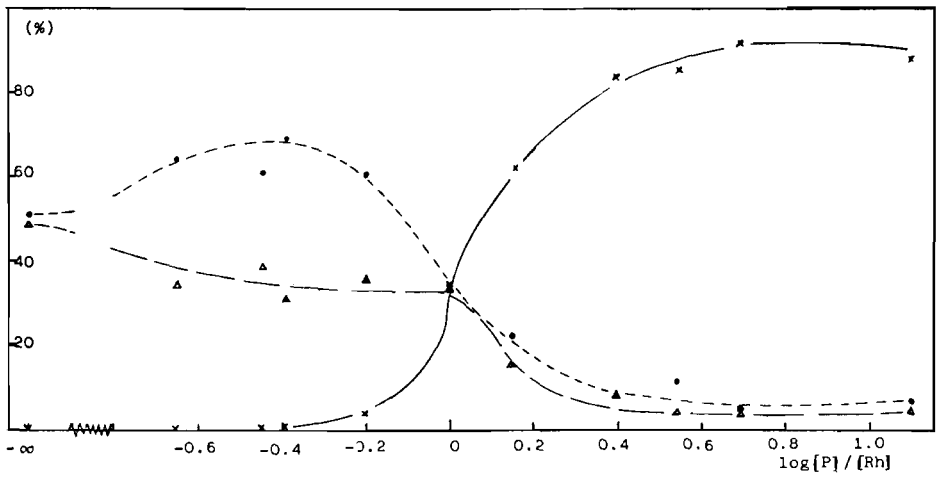
TABLE 1. The oligomerisation of phenylacetylene; 0.5 mol.% rhodium referred to the substrate (1 M/l) in toluene at 80 °C under argon

Catalyst	Turnover (%)	Dimers/trimers	2,4-Dimer/1,4-dimer	1,2,4-Trimer/1,3,5-trimer
$[1,5\text{-}C_6H_{10}RhCl]_2$	47	0.5/99.5		92/8
$[1,5\text{-}C_6H_{10}RhCl]_2 + 6P(C_6H_5)_3$	91.5	91/9	36/64	38/62
acac $Rh(CO)_2$	40	0/100		91/9
acac $Rh(CO)_2 + 6P(C_6H_5)_3$	38	85/15	32/68	58/42

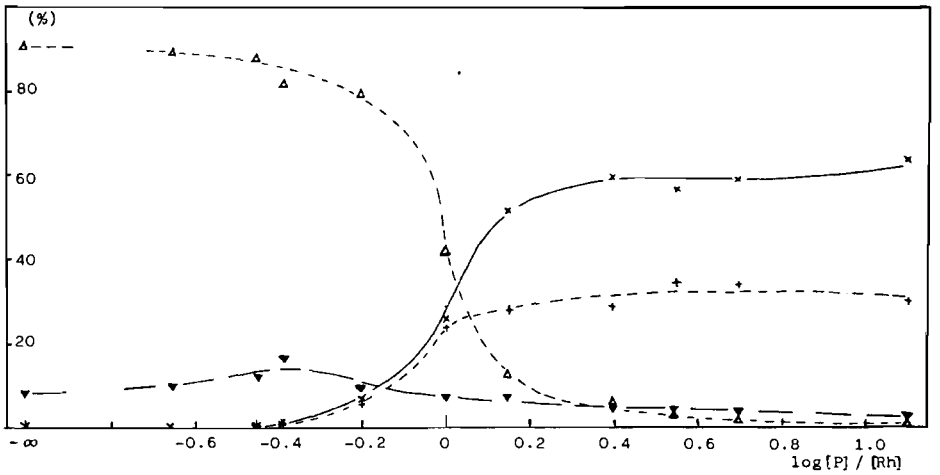
TABLE 2. The cyclotrimerisation of substituted phenylacetylenes ($R\text{–}C_6H_4\text{–}C{\equiv}CH$) using $[1,5\text{-}C_6H_{10}RhCl]_2$: the ^1H chemical shift of the acetylenic protons, a steric parameter, the turnover of the monomer and 3 ratios of products (σ constants [20], see Table 3)

R	^1H (ppm)	*v* [21]	Turnover (%)	Trimers/dimers	1,2,4-Trimer/1,3,5-trimer	2,4-Dimer/1,4-dimer
$p(C_2H_5)_2N$	2.93	0	27	92.5/7.5	94/6	55/45
pCH_3O	2.97	0	58	99.7/0.3	95/5	60/40
pCH_3	2.98	0	57	99.5/0.5	93/7	55/45
H	3.03	0	49	99.5/0.5	94/6	55/45
*p*F	3.02	0	63	99/1	93/7	55/45
*p*Cl	3.08	0	61	99.5/0.5	92/8	55/45
*p*Br	3.09	0	50	98.5/1.5	96/4	60/40
β-naphth[a]	3.10	0	67	89/11	89/11	60/40
*o*F	3.26	0.27	81	100/0	95/5	
oCH_3O	3.27	0.36	23	97/3	92/8	60/40
$2,4(CH_3O)_2$	3.20	0.36	30	90/10	92.5/7.5	60/40
α-naphth[a]	3.42		41	94.5/5.5	90/10	55/45
oCH_3	3.23	0.52	46	100/0	93/7	
$2,4(CH_3)_2$	3.16	0.52	45	94/6	92/8	40/60
*o*Cl	3.32	0.55	60	100/0	96/4	
$2,4,6(CH_3O)_3$	3.40	0.72	28	75/25	72/28	30/(15 + 55)
$2,4,6(CH_3)_3$	3.40	1.04	31	60/40	67/33	35/(20 + 45)
$o(CH_3)_3Si$	3.14	1.40	23	76/24	74/26	30/(20 + 50)

[a]naphth = Naphthylacetylene.



(a)



(b)

Fig. 1. [P]-control maps for the oligomerisation of phenyl-acetylene with $[1,5\text{-}C_6H_{10}RhCl]_2$ as catalyst and $(C_6H_5)_3P$ as ligand: (a) the monomer (- - ● - - - ● - - -), the dimers (- - - × - - - × - -), the trimers (- - △ - - △ - -); (b) the two dimers (1,4-dimer- - × - - × - - and 2,4-dimer - + - - + - -), two cyclotrimers (1,3,5-trimer - ▽ - - ▽ - - and 1,2,4-trimer - - △ - - △ - -).

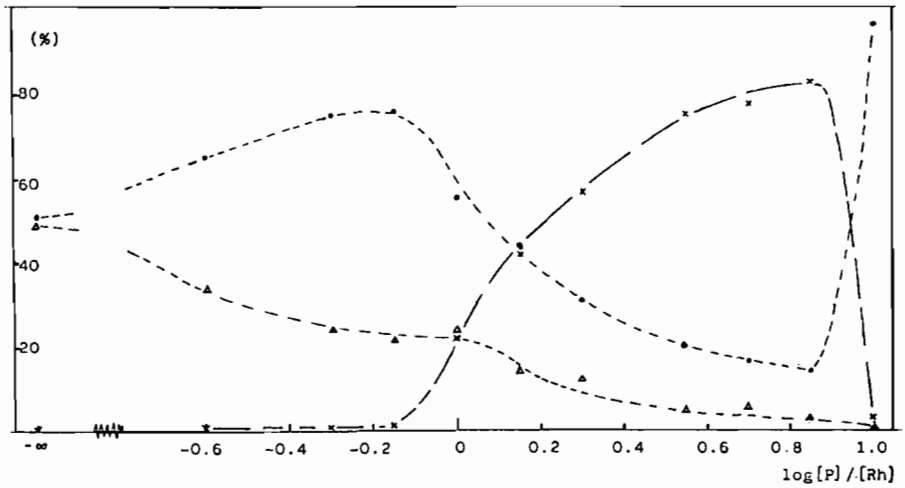
$C_6H_{10}RhCl]_2$ and Ph_3P, making use of a concentration control of the ligand [22]. The [P]-control maps (Fig. 1(a) and (b)) indicate alterations within two areas. Under-stoichiometric ratios ($lg[P]_0/[Rh]_0 < 0$) result in a decrease of the turnover of the monomer but the ratio of the two cyclotrimers varies only to a very small extent. With $P/Rh > 1$ the activity of the catalyst increases and the product distribution changes from cyclic trimers to predominantly dimers. In the [P]-control maps no further alterations arise with a further enhancement of the concentration of this phosphine.

Using 1,2-bis(diphenylphosphino)ethane the [P]-control map (Fig. 2(a)) closely resembles that of Ph_3P (Fig. 1(a)). Only at $lg[P]_0/[Rh]_0 > 1$ does the activity of the system decrease abruptly, and a stop complex is formed.

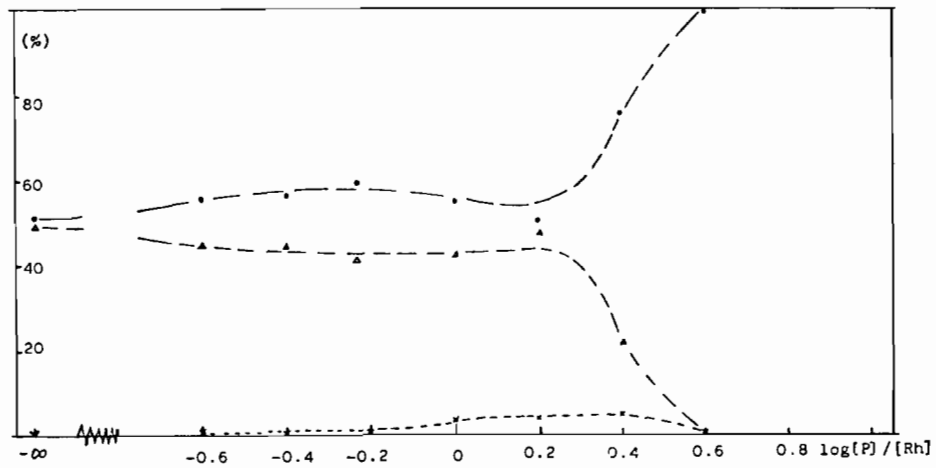
On the other hand, with an increasing concentration of *cis*-1,2-bis(diphenylphosphino)-ethene, the activity of the rhodium(I) complex drops steadily and expires at $lg[P]_0/[Rh]_0$ *c.* 0.5; 1,2-bis-(diphenylphosphino)phenylene presents a similar result (Fig. 2(b)). With these two bis-phosphines the product distribution begins to change at $lg[P]_0/[Rh]_0 > 0$; the portion of the dimers increases slightly (Fig. 2(b)) when the activity starts to decrease.

Dimerisation

For phenylacetylene and 17 substituted phenylacetylenes two characteristic sets of data and



(a)



(b)

Fig. 2. [P]-control maps for the oligomerisation of phenyl-acetylene with $[1,5\text{-}C_6H_{10}RhCl]_2$ as catalyst and bisphosphines as ligand: (a) 1,2-bis(diphenylphosphino)ethane, (b) 1,2-bis-(diphenylphosphino)phenylene; the monomer - -● - - ● , the dimers - × - - × - , the cyclotrimers - △ - - △ -.

indicative results from their dimerisation with $[1,5\text{-}C_6H_{10}RhCl]_2$ and Ph_3P as catalyst are summarised in Table 3. The yields and the ratios of the two dimers have been taken from the [P]-control maps at a $lg[P]_0/[Rh]_0$ value, where the changeover to the dimers has been accomplished.

A minimum of turnover is recorded at $lg[P]_0/[Rh]_0$ values from -0.4 to -0.2. The two bulkiest acetylenes represent an exception; for them the turnover stays low at all ligand concentrations and with the changeover from the cyclotrimers to the dimers at $P/Rh > 1$ the activity of the catalyst does not increase.

The $lg[P]_0/[Rh]_0$ values, which represent the changeover from the trimers to the dimers, vary very little; there is a shift from -0.1 to $+0.1$ from *p*-substituted to *o*-substituted phenylacetylenes.

Kinetic experiments have been performed at 80 °C with Rh/P/alkyne = 1:6:200 using *o*-xylene with 20% ethanol as solvent. About 10–15 values of the monomer concentration within a reaction time of 1 h satisfied a correlation of second order for all acetylenes up to a turnover of 60% and more.

The logarithms of the rate constants for seven *p*-substituted phenylacetylenes correlate linearly with electronic parameters of the monomers as the Hammett constants of their substituents [20] or the ^{13}C chemical shift of the acetylenic carbons in the β-position to the phenyl group (Table 3, our values correspond well with literature data [23]). The correlation of the logarithms of the rate constants with the ^{13}C chemical shift of the carbons in the α-position to the phenyl group or with

TABLE 3. The dimerisation of substituted phenylacetylenes ($R-C_6H_4-C{\equiv}CH$) with $[1,5\text{-}C_6H_{10}RhCl]_2$ and $6(C_6H_5)_3P$: σ-constants of the substituents, the ^{13}C chemical shift of the acetylenic carbon β to the phenyl ring, the turnover of the monomer, the experimental rate constants and the ratio of the dimers (steric parameters v [21] see Table 2)

R	σ [20]	13C(β) (ppm)	Turnover (%)	In k_{exp}	k_{rel}	1,4-Dimer/2,4-dimer
pCl	0.23	78.18	98	−1.60	17	44/56
pBr	0.27	78.41	99	−1.74	14.9	51/49
β-naphth[a]	0.04	77.70	98	−1.86	13.2	51/49
$p$$CH_3O$	−0.27	75.87	100	−2.01	11.3	59/41
pF	0.06	76.84	99	−2.06	10.8	55/45
H	0	77.04	94	−2.13	10	65/35
$p$$CH_3$	−0.17	76.49	96	−2.29	8.6	66/34
$p(C_2H_5)_2N$	−0.83	74.35	73	−3.24	3.3	71/29
oF	0.93	82.42	100	−1.31	23	37/63
oCl	1.28	82.46	82	−3.44	2.7	72/28
$o$$CH_3O$	0.12	81.20	79	−3.82	1.9	73/27
2,4$(CH_3O)_2$	(−0.15)	79.63	80	−3.69	2.1	65/35
α-naphth[a]	0.50	82.11	74	−3.91	1.7	75/25
$o$$CH_3$	0.29	80.98	56	−4.13	1.4	92/8
2,4$(CH_3)_2$	(0.12)	80.12	52	−4.27	1.2	91/9
2,4,6$(CH_3O)_3$	(−0.03)	83.26	48	−4.34	1.1	80 + 10/10
2,4,6$(CH_3)_3$	(0.41)	84.53	45	−4.60	0.8	75 + 12/13
$o(CH_3)_3Si$	–	80.16	20	−5.52	0.4	80 + 9/11

[a]naphth = Naphthylacetylene.

the chemical shift of the acetylenic protons is less satisfactory, mainly because the range of these data is noticeably narrower.

Discussion

The active complex

From the [P]-control maps for phenylacetylene as the substrate and triphenylphosphine (Fig. 1) as well as other triarylphosphines as ligands it is evident that a mono-association at the rhodium represents a catalyst of low activity; it converts the phenylacetylene mainly to two cyclotrimers as does the rhodium(I) complex without a P ligand.

The active complex, which dimerises the phenylacetylenes effectively, holds two monodentate P ligands in the *trans* position, because bis-phosphines, which as strong chelate ligands are fixed to the *cis* position, cause total loss of activity, for example *cis*-1,2-bis(diphenylphosphino)ethene and 1,2-bis(diphenylphosphino)phenylene (Fig. 2(b)). The dimerisation of octyne-1 using $[(C_8H_{14})_2RhCl]_2$ is analogously influenced, monodentate ligands resulting in higher yields than bis-phosphines [8].

The 1,2-bis(diphenylphosphino)ethane acts as a monodentate ligand over a broad span of its ligand/rhodium ratio, as is indicated by the wide equivalence of its [P]-control map (Fig. 2(a)) with that of Ph_3P (Fig. 1(a)); obviously at an under-stoichiometric ratio only one P atom of this bis-phosphine is linked to a rhodium and with the ligand in slight excess two bis-phosphines act as monodentate ligands in a *trans* position. This result is clearly due to the presence of a high excess of the substrate. As the ratio bis-phosphine/substrate and bis-phosphine/rhodium rises in the [P]-control map, the 1,2-bis(diphenylphosphino)ethane starts to act as a chelate ligand and a stop complex is formed. Monodentate ligands like Ph_3P and other trisaryl- as well as trisalkylphosphines at similar high ligand/rhodium ratios do not form stop complexes. A chelate bonding of *cis*-1,2-bis(diphenylphosphino)ethene and 1,2-bis(diphenylphosphino)phenylene in comparison to the more flexible 1,2-bis(diphenylphosphino)ethane will be favoured even at a high excess of the alkyne, leading to a *cis*-bonded, inactive monoassociate of these two bis-phosphines.

A slight rise of the portion of the dimers at $\lg[P]_0/[Rh]_0 > 0$ (Fig. 2(b)) might indicate the presence of a low concentration of a complex with two ligands monodentate and in a *trans* position even for these strong chelate ligands.

Cyclotrimerisation

The cyclotrimerisation of acetylenes through metallacyclopentadienes as intermediates is widely accepted [3, 6, 7, 17, 24]. The controlling effects, which terminal alkynes exert as substrate on the ratio of the two cyclotrimers (1,3,5- and 1,2,4-trisubstituted benzenes), have been studied with a few examples and using only two different acetylenes. The findings indicate a steric control in favour of the 1,3,5-derivative. The ratio

1,3,5-/1,2,4-trisubstituted benzene has been stated for the following pairs of monomers (R–C≡C–H): R = C_6H_5 7:1 and R = n-C_4H_9 1.2:1 [16]; R = isoC_4H_9 2.3:1 and R = nC_4H_9 1:1 [25]; R = $COOtC_4H_9$ 1:6 and R = $COOCH_3$ 1:12 [26]; H = CH_3 and R = $COOC_2H_5$ 1:3 or H = CH_3 and R = $COOCH_3$ 1:99 [27]. The ligand control for the cyclotrimerisation of 3-methyl-but-1-yne-3-ol with nickel(0) as catalyst resulted in a similar effect, as the share of the symmetrically substituted benzene increased with the cone angle of the phosphines [28].

For some examples the product ratio of the two cyclotrimers is highly in favour of the 1,2,4-derivative. Using nickel(0) as catalyst the ratio is 99:1 for 2-butynoic acid methylester [27], 12:1 for propynoic acid methylester [26] and 11.5:1 for phenyl-propynoic acid methylester [27]; for 3,3-dimethylbutyne using indenylrhodium(I) it is 10:1 [29]. For these examples the regioselectivity will be controlled by the polarity of the asymmetrically substituted acetylenic bond [24c, 30].

The cyclotrimerisation of different *p*-substituted phenylacetylenes with $[1,5\text{-}C_6H_{10}RhCl]_2$ as catalyst (without a P ligand) results in a homogeneous product distribution (Table 2), therefore an effective electronic influence can be excluded within this group of monomers.

For the *o*-substituted phenylacetylenes a distinct change of the product ratio appears only for the three sterically most demanding derivatives (Table 2). The high share of the cyclic trimers is reduced from 97($\pm$3)% (mean value for 12 phenylacetylenes with $v \leqslant 0.55$) to 70($\pm$10)% (mean value for three phenylacetylenes with $v \geqslant 0.72$); parallel to this change the ratio of the two cyclotrimers shifts in favour of the 1,3,5-trisubstituted benzene: 1,2,4-/1,3,5-trimer = 13:1 for acetylenes with $v \leqslant 0.55$ and 2.5:1 for the three acetylenes with $v \geqslant 0.72$ (Table 2). These variations should originate from a preference of the 2,4- against the 2,5-disubstituted rhodacyclopentadiene as an intermediate [24c, 31]; the oxidative coupling to the 2,5-disubstituted metallacyclopentadiene will decrease in the presence of a steric demand [30, 31]. The 3,4-disubstituted rhodacyclopentadiene is not likely to participate [24c, 31, 32].

Mono-associate of the ligand

The [P]-control maps of 13 trialkyl- and triarylphosphines with phenylacetylene as the substrate indicate a minimum of the turnover at $R_3P/Rh < 1$, which is interpreted as the result of the first association of the ligand. For the oligomerisation of phenylacetylene the experimental second order rate constant as the dependent variable of a [P]-control map with the ligand Ph_3P marks an equivalent minimum.

The first association of P ligands initiates only minor alterations of the product distribution. When a second ligand is not associated, these alterations are indicated reliably: for four bulky ligands the share of the dimers at $lg[P]_0/[Rh]_0 = 0$ is 5–6% compared to about 1% without the ligand.

The $lg[P]_0/[Rh]_0$ values for the changeover from the trimers to the dimers represent the transition from a first to a second ligand association (Table 4). A correlation of these values with the two parameters of the ligands (ν_{CO} shift χ [33] and cone angle θ [34]) through a multilinear regression [28] results in a best fit for a third order of the variables χ and θ. In the resulting plane triphenylphosphine is situated in a shallow minimum and therefore represents a moderately pronounced optimum for the reactivity of the catalyst.

The $lg[P]_0/[Rh]_0$ values for the changeover of trimers/dimers with the phosphines $(C_6H_5)_nP(CH_3)_{4-n}$ ($n = 1-4$) do increase (Table 4), but there is no strict linear correlation, neither with the number of the methyl substituents nor with the cone angles or χ values of the four ligands, but an alternancy with $\pm$ deviations from a linear free energy relation [35].

The change from $(C_6H_5)_2P(cyC_6H_{11})$ to $(C_6H_5)P(cyC_6H_{11})_2$ introduces a steric effect, which causes a shift of the value for the changeover of trimers/dimers (Table 4). Even more marked changes originate from the introduction of *o*-substituents in the phenyl group, which represent less potent donor ligands. Using $(C_6H_5)P(oCH_3C_6H_4)_2$ as ligand, up to 10 equiv. per rhodium cause no changeover for the products, therefore this ligand only forms a mono-associate.

For $(oCH_3C_6H_4)_3P$ there is no complex formed in the presence of phenylacetylene up to high P/Rh ratios, because its [P]-control map indicates no alterations and the [P]-control map of triphenylphosphine over its whole range is not altered by the presence of 10 equiv. of tri-*o*-tolylphosphine or other very bulky triarylphosphines.

When a rhodium(I) complex binds a phosphine with $\theta > 170°$, such as $[(cyC_6H_{11})_3P]_2RhCOCl$ or $[(oCH_3C_6H_4)_3P]_2RhCOCl$, the P ligand is substituted by the alkyne and the product distribution corresponds to a rhodium(I) complex without a P ligand.

The position of the changeover trimers/dimers in the [P]-control map also indicates that P ligands, which contain a heteroelement at the phosphorus represent a separate group of ligands (Table 4). According to Giering and co-workers there is no continuous transition from σ-donor to σ-donor/π-acceptor ligands [36, 37] and Heimbach *et al.* proved different controlling effects for

TABLE 4. Influence of the P ligands on the oligomerisation of phenylacetylene with $[1,5\text{-}C_6H_{10}RhCl]_2$: the electronic and steric parameter of the ligands, the turning point for the changeover from cyclotrimers to dimers and the ratio of the dimers.

Ligand	χ [33] (cm^{-1})	θ [34] (°)	$U_{trim/dim}$ (lg[P]/[Rh])	1,4-Dimer/2,4-dimer[a]
$(C_6H_5)_3P$	12.2	145	−0.02	2.0
$(C_6H_5)_2PCH_3$	12.1	136	0.14	1.6
$C_6H_5P(CH_3)_2$	10.6	122	0.17	1.5
$(CH_3)_3P$	8.5	118	0.25	1.25
$(C_6H_5)_2PCH_2CH_3$	11.3	140	0.08	2.2
$C_6H_5P(CH_2CH_3)_2$	9.3	136	0.12	1.8
$(C_6H_5)_2PcyC_6H_{11}$	9.0	153	0.10	3.2
$C_6H_5P(cyC_6H_{11})_2$	5.0	161	0.30	*c.* 3.6
$(C_6H_5)_2P\text{–}CH{=}CH_2$	13.6	134	0.25	1.6
$C_6H_5P(CH{=}CH_2)_2$	14.0	122	0.45	*c.* 1.4
$(pCH_3OC_6H_4)_3P$	10.5	145	0.05	2.0
$(C_6H_5)_2PoCH_3C_6H_4$	12.8	161	0.35	3.5
$(C_6H_5)_2PoCH_3OC_6H_4$	10.3	150	0.1	2.1
$(pClC_6H_4)_3P$	16.7	145	−0.05	2.1
$(C_6H_5)_2POC_6H_5$	18.9	139	0.90	1.95
$(iC_3H_7O)_3P$	19.1	130	0.65	1.9
$C_6H_5P(OCH_3)_2$	19.5	115	0.85	1.3

[a]Ratio of the dimers when the changeover from trimers to dimers has finished.

P ligands with P–C bonds compared to P ligands with P–heteroelement bonds [35]. Phosphites with χ values $> 21\ cm^{-1}$ inhibit the oligomerisation of phenylacetylene at P/Rh > 1. It is expected that these ligands inhibit the oxidative coupling or oxidative addition at the rhodium [38].

Second ligand association

By the association of a second tri(alkyl, aryl)phosphine to the rhodium complex the share of the cyclotrimers drops to 5%, if the cone angle of the ligand stays below 160°. It is our view that with the *trans* position of two phosphines the attack of a third phenylacetylene at the metallacyclopentadiene will be inhibited.

A steric control of the dimerisation caused by the presence of two $(C_6H_5)_3P$ in the active complex is indicated for all the phenylacetylenes by a lower share of the 2,4-dimer compared to the catalysis without the P ligand (Tables 2 and 3). It is therefore expected that the ratio 1,4-/2,4-dimer increases with the volume of the P ligands. For phosphines with cone angles between 140° and 150° (χ values 11–17 cm^{-1}) this ratio is 2.0 (Table 4); the share of the 1,4-dimer rises to 3:1 for cone angles > 150° and for the smallest ligands it decreases to about 1:1 (Table 4). The head to tail dimerisation to the 2,4-dimer is inhibited by a steric demand of the substrate as well as the ligand.

Dimerisation

The experimental rate constants for the dimerisation of six phenylacetylenes vary with the electronic properties of their *p*-substituents (Table 3). The rates increase with the acceptor strength of the substituents, that is with the acidity of the acetylenic proton, which correlates with its ^1H NMR chemical shift [39]. For the more acidic alkynes the oxidative addition should be favoured, therefore this step could determine the rate of the catalytic reaction. On the other hand the formation of a C–C bond would be accelerated by +I substituents [40].

The ratio of the two dimers is influenced by the *p*-substituents of the phenylacetylenes as well. It rises from *p*-diethylaminophenylacetylene with 29% of the 2,4-disubstituted vinylacetylene to *p*-chlorophenylacetylene with 56% 2,4-dimer (Table 3) parallel with the increasing rate of dimerisation. This shift of the dimer ratio is probably a result of changes in the C(β) charge density of the acetylenic bond (Table 3, [23]).

According to the ^1H NMR chemical shift of their acetylenic proton *o*-substituted phenylacetylenes are all more acidic than the *p*-derivatives (Table 2); this could promote their oxidative addition. But only in the case of the small fluoro-substituent does the *o*-derivative dimerise faster than the *p*-substituted compound.

Though the acetylenic proton of *o*-chlorophenylacetylene is even a little more deshielded than that of *o*-fluorophenylacetylene and clearly more deshielded than that of *p*-chlorophenylacetylene (Table 2), the rate of its dimerisation is lower (Table 3), implying a steric effect of the chloro-substituent as well as of the other *o*-substituents, whose phenylacetylenes dimerise rather slowly. A qualitative correlation is met for the relative rate constants and the steric parameter of the *o*-substituents (Tables 2 and 3).

The fastest reacting acetylene, the *o*-fluorophenylacetylene, yields the highest share of the 2,4-dimer (63%). This relation of the polarity of the acetylenic bond and the reactivity of the alkyne with the share of the 2,4-dimer is evident throughout the whole series of phenylacetylenes: the more acidic *o*-chlorophenylacetylene dimerises twice as fast as the *o*-methyl derivative (both with a similar steric parameter), and yields a higher portion of the 2,4-dimer (Table 3). From this result it is concluded that acceptor substituents influence and accelerate the reaction step, which fixes the ratio of the dimers, as well as the oxidative addition.

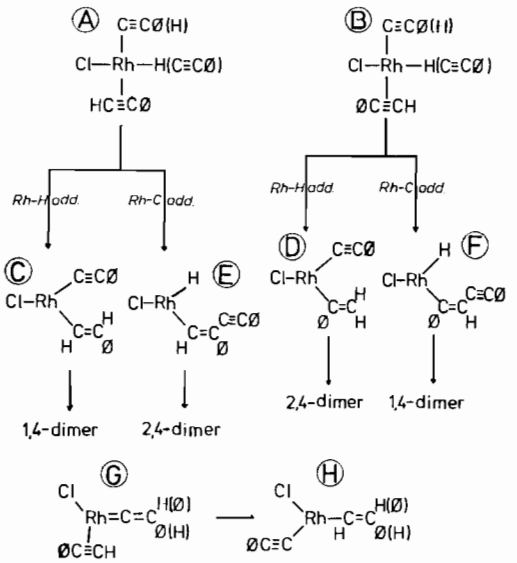
For the three bulkiest *o*-substituted phenylacetylenes the rate of dimerisation is reduced further and a third dimer is produced. For mesitylacetylene this third dimer has been isolated by HPLC and characterised by its ^{1}H NMR spectrum as the *cis*-1,4-di(mesityl)-but-1-en-3-yne (olefinic protons at 6.24(d) and 5.97(d) ppm with $J_{1,2} = 13.3$ Hz).

The rate law of the dimerisation (as well as that of the cyclotrimerisation) is second order with regard to the monomer and first order with regard to the rhodium. The arguments in favour of the oxidative addition as rate determining step are further supported by the high values of the negative entropies of activation (Table 5), as is to be expected for an oxidative addition [41] and which would be contradictory to an insertion or elimination step determining the rate of the reaction. As expected the entropies of activation decrease for bulkier monomers (Table 5).

A control of the dimerisation by the oxidative addition step of the terminal alkynes should lead to a H/D effect, as is observed for phenylacetylene, *p*-methoxy- and *o*-methylphenylacetylene (Table 6).

Kovalev *et al.* have been able to characterise intermediates from the dimerisation of pentyne-1 using $[(CH_3)_3P]_3RhCl$ as catalyst [42]. It appears that the ratio of the two dimers is determined by the orientation of the two π-bonded alkynes and is fixed by the addition of a rhodium hydride to a π-bonded acetylene. Applied to our catalytic system with two phosphines in a *trans* position, this should lead to complexes like **A** and **B** (Scheme 1), which determine the ratio of the two dimers by their concentrations and their reaction rates.

The addition of a rhodium hydride to a π-bonded alkyne produces **C** and **D**, whereas the addition of an alkynyl-rhodium to a π-bonded acetylene gives **E** and **F**.



Scheme 1.

TABLE 5. Activation parameters for the dimerisation of substituted phenylacetylenes ($R-C_6H_4-C{\equiv}CH$) from 80 to 110 °C with $[1,5\text{-}C_6H_{10}RhCl]_2$ and $6(C_6H_5)_3P$ as catalyst in *o*-xylene with 20% ethanol. (The breadth of error for the data of the *p*-substituted derivatives amounts to ± 10%, of the *o*-substituted compounds to ± 15%.)

R	E_A (kJ/mol)	$\Delta S^{\ddagger}$ (J/mol K)	$\Delta G^{\ddagger}$ (kJ/mol)
H	56.5	−112	93.5
$p(C_2H_5)_2N$	47	−148	96.5
pCH_3O	57	−111	93
*p*Br	60	−100	92
*o*F	69.5	− 69	91
*o*Cl	48	−147	97
oCH_3	43.5	−166	99
$2,4,6(CH_3)_3$	35	−194	100

TABLE 6. H/D effects for the dimerisation of phenylacetylene, *p*-methoxy- and *o*-methyl-phenylacetylene

Substituent R	Temperature (°C)	k_H/k_D	Temperature (°C)	k_H/k_D
H	55	3.4	100	2.1
	80	2.5	110	1.9
p-CH_3O	55	3.2	100	2.3
	80	2.6	110	2.2
o-CH_3	55	3.2	95	2.3
	80	2.7		

A pronounced steric influence from *o*-substituted phenylacetylenes (Table 3) as well as from α-hydroxyacetylenes [12b] favours the 1,4-dimer, which fits a reaction through **C** better than through **F**, which is according to models sterically more crowded than **C**, **D** or **E**.

With very bulky phenylacetylenes the dimerisation is slowed down heavily; in this situation another reaction pass contributes a third dimer. The *cis*-1,4-disubstituted vinylacetylenes should be synthesised from a vinylidene complex (**G**) as the crucial intermediate [43]. According to the results of Werner and co-workers [44], the acetylenic proton in a π-bonded phenylacetylene is deshielded; this favouring a hydrogen shift to a vinylidene complex [45]. From **G** vinyl complexes **H** are accessible, being intermediates for the synthesis of *trans*- and *cis*-1,4-disubstituted vinylacetylenes.

Codimerisation

With the deuteration of the acetylenic proton the rate of the dimerisation of the phenylacetylenes decreases. A codimerisation of *p*-$CH_3OC_6H_4{\equiv}CH$ and *p*-$CH_3C_6H_4C{\equiv}CD$ verifies that the ^{1}H-acetylene is preferred at the oxidative addition (ratio 66:34) and that the formation of the π-complexes is independent of the H/D substitution (ratio 48:52).

Each codimerisation of phenylacetylene with 5 different, substituted phenylacetylenes yields 4 dimers and 4 codimers, which all can be assigned by GLC. In addition, the main products have been separated by HPLC and their structures confirmed by ^{1}H NMR spectra (Tables 7–10 and 'Experimental').

The product distribution for these codimerisations illustrates that the reaction sequence of the alkyne, which is oxidatively added, is inhibited for *o*-substituted phenylacetylenes (Table 11), which parallels their reduced reaction rate.

An influence of the polarity of the triple bond is manifest from the dimerisations and codimerisations of *p*-substituted phenylacetylenes but also from the codimerisation of phenylacetylene with internal alkynes. The symmetrically substituted diphenylacetylene and acetylenic dicarboxylic acid diester do not react, whereas but-2-ynoic acid ester as well as 3-phenyl-propynoic acid ester, each together with phenylacetylene, yield the expected codimers. This effect implies that the polarity of the triple bond should not only influence the oxidative addition of the alkyne but also the addition of the Rh hydride to the π-bonded acetylene.

TABLE 7. ^{1}H NMR data of the 1,4-disubstituted vinylacetylenes (1,4-dimers) from the dimerisation of substituted phenylacetylenes ($R{-}C_6H_4{-}C{\equiv}CH$).

R	Olefinic protons	Substituents
H	7.08(d), 6.42(d), 16.2 Hz	
pCH_3	6.97(d), 6.28(d), 15.0 Hz	2.35(s)
oCH_3	7.24(d), 6.36(d), 16.2 Hz	2.41(s), 2.50(s)
2,4$(CH_3)_2$	7.00(d), 6.26(d), 15.6 Hz	2.30(s), 2.35(s), 2.40(s)
2,4,6$(CH_3)_3$	7.10(d), 6.06(d), 17.1 Hz	2.33(s), 2.40(s), 2.50(s)
pCH_3O	6.85(d), 6.15(d), 15.6 Hz	3.74(s)
oCH_3O	6.98(d), 6.52(d), 15.2 Hz	3.82(s), 3.88(s)
2,4$(CH_3O)_2$	masked by aromatic protons	3.82(s), 3.87(s), 3.90(s)
2,4,6$(CH_3O)_3$	7.19(d), 6.09(d), 16.2 Hz	3.76(s), 3.82(s), 3.90(s)
*p*F	7.03(d), 6.20(d), 16.2 Hz	
*p*Cl	6.94(d), 6.29(d), 16.2 Hz	
*p*Br	6.94(d), 6.33(d), 16.8 Hz	
*o*F	6.97(d), 6.48(d), 16.2 Hz	
*o*Cl	7.17(d), 6.44(d), 16.2 Hz	
p$(C_2H_5)_2N$	6.84(d), 6.10(d), 16.2 Hz	3.28(q), 1.07(t)
o$(CH_3)_3Si$	7.31(d), 6.37(d), 16.2 Hz	0.38(s), 0.42(s)
α-naphth.	7.20(d), 6.67(d), 16.2 Hz	
β-naphth.	7.20(d), 6.60(d), 16.2 Hz	

TABLE 8. ^{1}H NMR data for 2,4-disubstituted vinylacetylenes (2,4-dimers) from the dimerisation of substituted phenylacetylenes ($R{-}C_6H_4{-}C{\equiv}CH$)

R	Olefinic protons	Substituents
H	6.02(d), 5.75(d), 1.8 Hz	
2,4,6$(CH_3)_3$	5.84(d), 5.28(d), 2.4 Hz	2.33(s), 2.40(s), 2.50(s)
*o*Cl	6.03(d), 5.80(d), 1.8(d)	
β-napth.	6.54(d), 6.28(d), 1.8 Hz	

TABLE 9. ^{1}H NMR data for 1,3,5-trisubstituted cyclotrimeres of substituted phenylacetylenes (R–C_6H_4–C≡CH)

R	Aromatic protons of 1,3,5-subst.ring	Aromatic protons of substituents	Protons of R
H	7.74(s)	7.25(m)	
$p$$CH_3$	7.70(s)	7.25(m)	2.34(s)
$o$$CH_3$	7.64(s)	7.25(m)	2.40(s)
2,4$(CH_3)_2$	7.68(s)	7.29(m)	2.40(s), 2.33(s)
$p$$CH_3O$	7.60(s)	7.05(m)	3.80(s)
$o$$CH_3O$	7.58(s)	7.03(m)	3.85(s)
2,4$(CH_3O)_2$	7.56(s)	6.96(m)	3.80(s), 3.84(s)
pCl	7.66(s)	7.50(m)	
pBr	7.65(s)	7.52(m)	
oF	7.74(s)	7.33(m)	
oCl	7.58(s)	7.38(m)	

TABLE 10. ^{1}H NMR data for 1,2,4-trisubstituted cyclotrimers of substituted phenylacetylenes (R–C_6H_4–C≡CH)

R	Resonances of the substituents R	
	Position 1,4	Position 2
$p$$CH_3$	2.25(s)	2.34(s)
$o$$CH_3$	2.23(s)	2.47(s)
$p$$CH_3O$	3.64(s)	3.70(s)
$o$$CH_3O$	3.75(s)	3.42(s)
oSi$(CH_3)_3$	0.29(s)	0.42(s)

TABLE 11. Share of the dimers for different codimerisations with phenylacetylene (A) and a substituted phenylacetylene (B)

Dimer	Substituted phenylacetylene (B) (%)			
	$p$$CH_3O$	pBr	$o$$CH_3O$	oCl
2,4-AA	9.5	6.5	9.5	8.0
1,4-AA	14.5	19.0	20.0	16.0
2,4-AB[a]	12.0	7.0	0.5	2.0
1,4-AB[a]	15.5	20.0	3.0	0.5
2,4-BA[a]	8.5	7.0	12.5	10.0
1,4-BA[a]	16.0	16.0	29.0	48.0
2,4-BB	11.5	7.0	18.0	3.5
1,4-BB	12.5	17.5	7.5	12.0
π-complex of B	48.5	47.5	67.0	73.5
Oxidative addition of B	51.5	52.5	29.0	18.0

[a] The monomer noted last holds the triple bond.

Experimental

Compounds

Rhodium(III) chloride hydrate was from Degussa (Hanau), the P ligands from Strem Chemicals and phenylacetylene from Fluka. The starting compounds for the preparation of the substituted phenylacetylenes were from Merck-Schuchardt and Aldrich.

The substituted phenylacetylenes were prepared from the corresponding acetophenones and PCl_5 with a subsequent dehydrochlorination [46–48]. Higher yields (50–70%), a lower content of by-products and a shorter reaction time were obtained by the conversion of the corresponding benzaldehydes with triphenylphosphinylalkylenes [49, 50]. o-Trimethylsilylphenylacetylene was prepared according to the literature method [51]. [1,5-C_6H_{10}RhCl]$_2$ [52] and $(CH_3COCHCOCH_3)Rh(CO)_2$ [53] were synthesised using an established procedure.

Equipment

The ^{1}H NMR spectra were recorded in $CDCl_3$ with TMS as internal standard using a Bruker WH 90 and the ^{13}C NMR spectra using a Bruker AM 200.

The turnover of the monomers was determined by GLC using a Carlo Erba Fractovap 2200 with FID and a 2 m column (SE 52). For the analysis of the products a Carlo Erba Vega 2000 with FID and a 25 m capillary column (i.d. 0.25 mm; SE 52) was used. The chromatograms were recorded with a Chromato-Integrator D 2000 (Merck-Hitachi).

For the HPLC separations equipment from Abimed and columns from Bischoff (25 cm; i.d. 4.6 or 8.0 mm; nucleosil C 18) were used.

Reactions

Kinetic runs of dimerisations were conducted with a 1 M solution of the phenylacetylene in o-xylene containing 20% ethanol and 0.5 mol.% rhodium at 80 °C or another temperature between 50 and 110 °C. Mesitylene served as internal standard, argon as the inert atmosphere. The ratio $(C_6H_5)_3P$ to rhodium was chosen as 6:1. The reactions were started by the addition of the rhodium complex.

For the experiments of the [P]-control maps a 1 M solution of the alkyne in toluene was used. The ratio of the monomer to rhodium was fixed at 200:1, the reaction time at 4 h and the reaction temperature at 80 °C.

Oligomers

^{1}H NMR data for the dimers and the cyclotrimers are collected in Tables 7–10.

The 1,4-codimer oCH$_3$OC$_6$H$_4$–CH=CH–C≡C–C$_6$H$_5$ shows resonances at 7.23 (m, 9H), 7.00 (d, 16.2 Hz, 1H), 6.47 (d, 16.2 Hz, 1H), 3.91 (s, 3H) ppm; for the codimer oClC$_6$H$_4$–CH=CH–C≡C–C$_6$H$_5$ the resonances appear at 7.39 (m, 9H), 7.12 (d, 16.2 Hz, 1H) and 6.40 (d, 16.2 Hz, 1H) ppm.

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