

Stereoselective *living* polymerization of phenylacetylene promoted by rhodium catalysts with bidentate phosphines

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Received 3 January 2001; accepted 23 April 2001

Abstract

Polymerization of phenylacetylene to give highly stereoregular *cis-transoid* polyphenylacetylene is accomplished by use of $[\text{Rh}(\text{nbd})(\text{OMe})]_2$ (nbd = norbornadiene) and $\text{Ph}_2\text{P}(\text{CH}_2)_x\text{PPh}_2$ ($x = 2$, dppe; $x = 3$, dppp; $x = 4$, dppb). The catalytic system employing the ligand dppb promotes formation of polymer products with low polydispersities. The polymerization is of *living* nature, as proved by the dependence of polymer molecular weight on conversion and on initial monomer concentration, with molecular weight distributions always maintained within a narrow range. NMR studies of the catalytic system provide information on the rhodium chemistry involved, as well as useful means of comparison to other rhodium–phosphine catalytic systems. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Rhodium; Diphosphine; Polymerization; Phenylacetylene

1. Introduction

The polymerization of substituted acetylenes has attracted increasing attention in the last decade, the resulting π -conjugated polymers being characterized by a variety of interesting physico-chemical properties such as oxygen permeability, nonlinear optical properties, conductivity, ferromagnetism and so on [1,2].

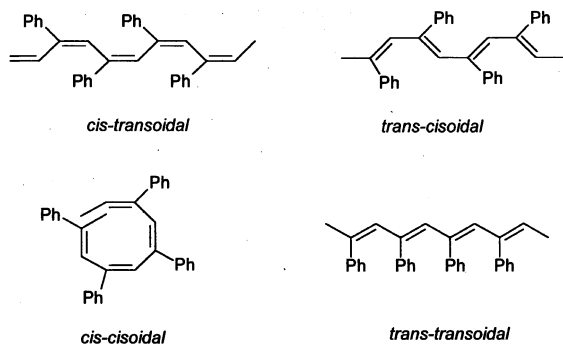


Fig. 1. Stereoisomers of polyphenylacetylene.

Catalytic systems based either on Group 5 or 6 metals or on rhodium compounds have been reported to promote such reaction. Mono- and disubstituted acetylenes are polymerized with Group 5 and 6 metal compounds [3–5], but the reaction is not stereoselective and a mixture of *cis* and *trans* polymers is obtained generally (see Fig. 1). Organorhodium compounds [6–14] are efficient catalysts for the polymerization of monosubstituted acetylenes, with formation of highly stereoregular polymers, in some cases in a *living* manner.

In particular, rhodium complexes with monodentate phosphines have been reported to promote the *living* polymerization of phenylacetylene and substituted derivatives [10a,c,14] with selective formation of *cis-transoid* polyphenylacetylene.

We were attracted by the association of rhodium to bidentate phosphines which offers advantages from the point of view of control of both stoichiometry and stereochemistry of the resulting compounds. To our knowledge, rhodium compounds with bidentate phosphines have never been reported to be active catalysts for the polymerization of alkynes.

We report here on the *living* polymerization of phenylacetylene promoted by rhodium–diphosphines

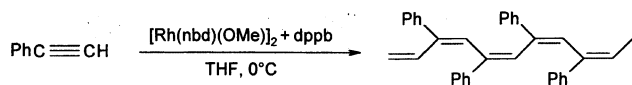
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Table 1
Polymerization of phenylacetylene catalyzed by $[\text{Rh}(\text{nbd})(\text{OMe})]_2$ + diphosphine + base

	L	Conversion %	<i>t</i> (min)	M_n	<i>D</i>
1	dppe	78	60	100 000	1.75
2	dppp	70	60	440 000	1.57
3	dppb	75	45	780 000	1.33
4	PSP	–	–	–	–
5	PNP	–	–	–	–

Experimental conditions: $[\text{Rh}] = 3.6 \times 10^{-3}$ M; $[\text{L}] = 3.6 \times 10^{-3}$ M; $[\text{L}]/[\text{Rh}] = 1$; $[\text{base}] = 3.6 \times 10^{-2}$ M; $[\text{base}]/[\text{Rh}] = 10$; $[\text{Sub}] = 0.18$ M; $[\text{Sub}]/[\text{Rh}] = 50$; solvent, THF; $T = 0^\circ\text{C}$; base, pyridine. dppe, $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$; dppp, $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$; dppb, $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$; PNP, $(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{CH}_3$; PSP, $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{PPh}_2$; $D = M_w/M_n$



Scheme 1.

catalytic systems with formation of highly stereoregular *cis-transoidal* polyene. We also produce the results of spectroscopic studies providing information on the rhodium complexes formed during the catalytic reaction.

2. Results

The catalytic systems initially tested for the polymerization of phenylacetylene were prepared starting from the organorhodium precursor $[\text{Rh}(\text{nbd})(\text{OMe})]_2$ and an equivalent amount of a bidentate phosphine of the type $\text{Ph}_2\text{P}(\text{CH}_2)_x\text{PPh}_2$ ($x = 2$, dppe; $x = 3$, dppp; $x = 4$, dppb). The catalytic reactions were performed in THF, as the rhodium compounds are soluble in this solvent, and also the products of the catalytic reactions were expected to be soluble in it. A tenfold excess of a basic cocatalyst was added: pyridine or piperidine was usually preferred over the most commonly used DMAP (= 4-(dimethylamino)pyridine) [10] because of the better results obtained with such bases in a previous investigation performed in our laboratory [15]. Also the choice of the temperature was made according to the data previously obtained, as we had observed with different rhodium catalysts an improvement in the molecular weight distribution on lowering the temperature.

Polymerization of phenylacetylene is observed with all ligands in the series $\text{Ph}_2\text{P}(\text{CH}_2)_x\text{PPh}_2$ ($x = 2$ –4). By quenching the reaction mixtures with acetic acid rhodium-free polymers are obtained, which are precipitated with excess methanol. In all cases *cis-transoidal* polyphenylacetylene is the only product formed, no

oligomerization product being detected in the reaction mixtures. Selected data of the catalytic reactions with rhodium–diphosphine–basic cocatalyst systems are reported in Table 1: it can be noted that an increase in the length of the chain between the two phosphorous atoms results in a narrower molecular weight distribution of the polymer formed (polydispersity ($D = M_w/M_n$) changes from 1.75 when $x = 2$ to 1.33 when $x = 4$), whereas for the molecular weights an opposite trend is observed ($M_n = 100\,000$ for $x = 2$ and $780\,000$ for $x = 4$).

The diphosphines $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{X}(\text{CH}_2)_2\text{PPh}_2$ ($X = \text{N}(\text{C}_3\text{H}_7)$, PNP; $X = \text{S}$, PSP) were also tested with rhodium as catalyst precursors; however, the systems so obtained turned out to be completely inactive.

When the rhodium–dppb system plus basic cocatalyst was tested in CH_2Cl_2 or CHCl_3 no polymerization was observed, both at 0°C or room temperature, or at reflux temperature. The latter results appeared somewhat surprising, as both solvents can be effectively used in the polymerization of phenylacetylene when rhodium–monodentate phosphines are employed as catalytic systems [10,15].

The catalytic system employing dppb was tested in THF without the addition of basic cocatalyst (see Scheme 1): such a change results in enhanced rate of polymerization, with concomitant decrease of both molecular weight and polydispersion index of the resulting polyphenylacetylene ($M_n = 414\,000$ and $D = 1.15$). Apparently, such a catalytic system behaves differently from most of the known rhodium-based polymerization catalysts, which only give poor results when the reaction is performed in the absence of added base. The reaction without cocatalyst has been carried out in other solvents also (see Table 2). With CHCl_3 and CH_2Cl_2 no catalytic activity was observed whereas toluene proved to be a suitable choice both from the point of view of reaction rate and of the narrow weight distribution of the polymer formed. In diethyl ether the polymer formed is insoluble and the rhodium precursor and the diphosphine are only sparingly soluble; apparently, the heterogeneity of the reaction negatively affects the results. Better results are obtained in a 2:1 mixture of diethyl ether–benzene (see Table 2) which solubilizes the catalyst but not the polymer.

The polyphenylacetylene obtained with the Rh–dppb catalytic system is highly stereoregular with 97–100% of *cis-transoidal* configuration, as evaluated by the established method [7a] of integration of the ^1H -NMR spectra.

The *living* nature of the polymerization has been proved by the following experiments.

The dependence of M_n and D values on conversion has been monitored by analyzing samples withdrawn at time intervals from the reaction mixture. The results reported in Table 3 show that the molecular weight of

Table 2
Polymerization of phenylacetylene catalyzed by $[\text{Rh}(\text{nbd})(\text{OMe})]_2 + \text{dppb}$

	Solvent	Conversion %	<i>t</i> (min)	<i>M_n</i>	<i>D</i>
1	CH_2Cl_2	–	–		
2	CHCl_3	–	–		
3 ^a	THF	78	30	414 000	1.15
4	Et_2O	91	45	160 000	2.47
5	$\text{Et}_2\text{O}-\text{C}_6\text{H}_6$ (2:1)	91	30	600 000	1.58
6	$\text{C}_6\text{H}_5\text{Me}$	100	15	940 000	1.18

Experimental conditions: $[\text{Rh}] = 3.6 \times 10^{-3}$ M; $[\text{dppb}] = 3.6 \times 10^{-3}$ M; $[\text{dppb}]/[\text{Rh}] = 1$; $[\text{Sub}] = 0.18$ M; $[\text{Sub}]/[\text{Rh}] = 50$; $T = 25^\circ\text{C}$.

^a $T = 0^\circ\text{C}$.

the polymer increases as the conversion progresses whereas the molecular weight distribution remains narrow during the course of the reaction ($D = 1.09$ – 1.15).

Another proof of the *living* nature of the polymerization is provided by the dependence of the molecular weight on the initial $[\text{Sub}]/[\text{Rh}]$ ratio: the M_n value of the polymer increases linearly with increasing initial concentration of the substrate (see Table 4).

A further test for the *living* polymerization has been made by adding a second substrate feed to the reaction mixture after all the phenylacetylene initially present had been polymerized: the polyphenylacetylene formed after the first polymerization ($M_n = 500\,000$ at 100% conversion) in the presence of more monomer produced a proportionally higher molecular weight polymer ($M_n = 720\,000$ at 50% conversion) with the same reaction rate as the initial reaction.

Information on the nature of the rhodium compounds involved in the chemistry with dppb has been obtained by monitoring the catalytic solutions by ^{31}P -NMR spectroscopy. At 0°C in THF $[\text{Rh}(\text{nbd})(\text{OMe})]_2$ reacts quantitatively with dppb to form a mixture of three products: **1**, $\delta = +28.2$ ppm (d, $J_{\text{PRh}} = 132$ Hz); **2**, $\delta = +33.8$ ppm (dd, $J_{\text{PRh}} = 129$ Hz, $J_{\text{PP}} = 20.0$ Hz) and $\delta = +28.0$ ppm (dd, $J_{\text{PRh}} = 217$ Hz, $J_{\text{PP}} = 20.0$ Hz); **3**, $\delta = +49.4$ ppm (d, $J_{\text{PRh}} = 182$ Hz). Initially **1** and **2** are formed in the amount of 25 and 75%, respectively, whereas only traces of compound **3** are present; with time, **2** is converted slowly to **3**.

In contrast, when the reaction between $[\text{Rh}(\text{nbd})(\text{OMe})]_2$ and dppb is performed in CDCl_3 only one product is formed, namely complex **1**, which can now be identified spectroscopically as the pentacoordinated rhodium(I) compound $\text{Rh}(\text{OMe})(\text{nbd})(\text{dppb})$ shown in Scheme 2. Its ^{31}P -NMR spectrum consists of a doublet at $+27.0$ ppm ($J_{\text{PRh}} = 136$ Hz), whereas in the ^1H -NMR spectrum, besides the signals of aromatic protons, we observe a singlet at δ 3.47 ppm assigned to the methoxy group, signals at 3.54, 3.07 and 1.10 ppm assigned to coordinated norbornadiene, and two broad multiplets at 2.81 and 1.45 ppm assigned to dppb. In the ^{13}C spectrum a singlet at δ 61.0 ppm (OMe) is accompanied by the signals assigned to the diene at

52.5, 50.7 and 47.5 ppm, and by a multiplet at 23.7 ppm attributed to the methylene chain of dppb. All the assignments have been made according to 2D NMR spectra.

From the analysis of the ^1H -NMR spectra of **1** in CDCl_3 and of the mixture of **1**–**3** in deuterated THF we conclude that compound **2** is not a hydridic species, as no high-field signals are observed. Therefore, the most reasonable formulation for **2** is that reported in Scheme 2: such a compound is proposed to be isomeric to **1**, having the methoxy group coordinated in an equatorial position, and the two nonequivalent phosphorous atoms giving rise to the two doublets in the ^{31}P -NMR spectrum.

Finally, the cationic square-planar structure is assigned tentatively to complex **3** also shown in Scheme 2.

The spectroscopic investigations then proceeded with the analysis of the reaction of the rhodium compounds with phenylacetylene.

Table 3
Polymerization of phenylacetylene catalyzed by $[\text{Rh}(\text{nbd})(\text{OMe})]_2 + \text{dppb}$

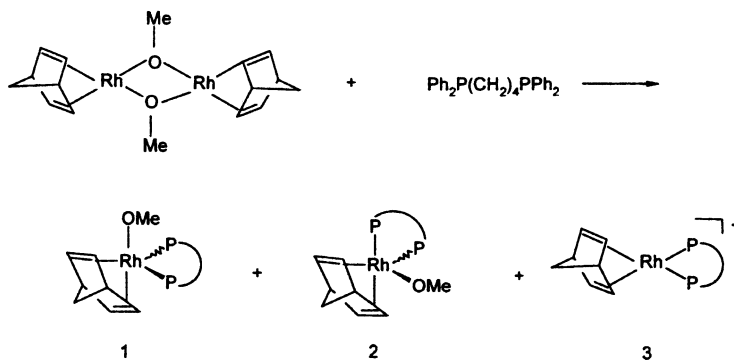
	Conversion %	<i>t</i> (min)	<i>M_n</i>	<i>D</i>
1	40	5	260 000	1.09
2	67	15	380 000	1.10
3	78	30	414 000	1.15

M_n and *D* values as a function of polymer yield. Experimental conditions: $[\text{Rh}] = 3.6 \times 10^{-3}$ M; $[\text{dppb}] = 3.6 \times 10^{-3}$ M; $[\text{dppb}]/[\text{Rh}] = 1$; $[\text{Sub}] = 0.18$ M; $[\text{Sub}]/[\text{Rh}] = 50$; $T = 0^\circ\text{C}$; solvent, THF.

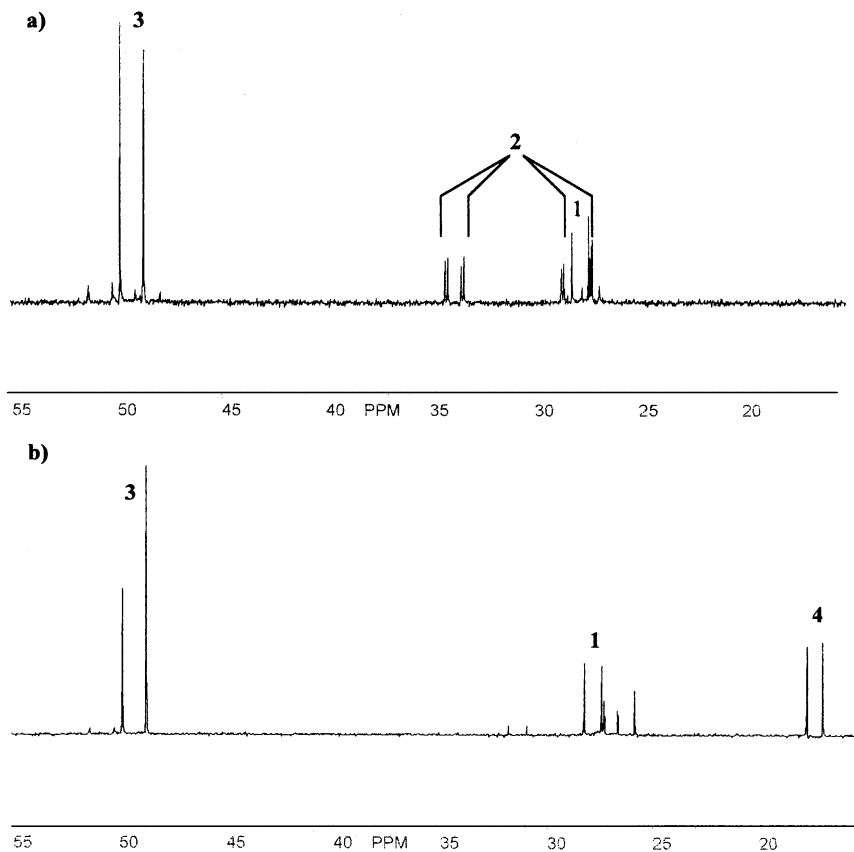
Table 4
Polymerization of phenylacetylene catalyzed by $[\text{Rh}(\text{nbd})(\text{OMe})]_2 + \text{dppb}$

	$[\text{Sub}]/[\text{Rh}]$	<i>M_n</i>
1	25	270 000
2	50	530 000
3	100	920 000
4	150	1 300 000

M_n values as a function of initial monomer concentration. Experimental conditions: $[\text{Rh}] = 3.6 \times 10^{-3}$ M; $[\text{dppb}] = 3.6 \times 10^{-3}$ M; $[\text{dppb}]/[\text{Rh}] = 1$; $T = 0^\circ\text{C}$; solvent, THF.



Scheme 2.

Fig. 2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra ($\text{Et}_2\text{O}/\text{C}_6\text{D}_6$, 0°C) of $[\text{Rh}(\text{nbd})(\text{OMe})]_2$ + dppd before (a) and after (b) addition of phenylacetylene.

By adding ten equivalents of the alkyne to the THF solution of **1** and **2** (and **3** in traces) at 0°C , and immediately recording the ^{31}P -NMR spectrum of the resulting solution, we observe that while **1** remains unreacted in the mixture, **2** has disappeared immediately, giving rise to two new compounds **4** and **5**, compound **4** characterized by a signal at $+17.5$ ppm (d , $J_{\text{PRh}} = 122$ Hz) and compound **5** showing two doublets of doublets at $\delta +14.2$ and $+40.4$ ppm ($J_{\text{PRh}} = 134$ Hz; $J_{\text{PP}} = 41$ or 34 Hz).

On the other hand, addition of phenylacetylene to the CDCl_3 solution of **1** as expected produces no reac-

tion, which is in accordance with both the inactivity of the catalytic system in CHCl_3 and the behavior of the reaction mixture in THF.

To get further information on the reaction between the rhodium species and the alkyne we then monitored the evolution of the catalytic system Rh -dppb in a 1:1 mixture of diethyl ether- C_6D_6 , which dissolves the rhodium complexes but does not dissolve polyphenylacetylene. By reaction of $[\text{Rh}(\text{nbd})(\text{OMe})]_2$ with dppb a mixture of **1** (about 15%), **2** (35%) and **3** (50%) is formed (Fig. 2a). Addition of a tenfold excess of phenylacetylene results in an exothermic reaction with forma-

tion of a red insoluble polymer. As the catalytically active rhodium fragment, in the absence of quenching, is very likely bound to the insoluble polymeric chain, the remaining solution is expected to contain only the rhodium species which did not participate in the catalytic reaction. The ^{31}P -NMR spectrum of this solution (Fig. 2b) shows **1** and **3** in unvaried amounts, indicating that both compounds have not reacted with the alkyne; moreover, compound **2** has disappeared completely, whereas compound **4** was formed in an amount comparable to **1**. One can therefore conclude that of the three compounds, only **2**, which was initially present, has reacted with phenylacetylene partly to form **4** (vide infra), and partly to catalyze the polymerization to give a rhodium–polymer adduct insoluble in diethyl ether–benzene.

Attempts have been made to isolate compound **2** from the reaction of $[\text{Rh}(\text{nbd})(\text{OMe})]_2$ and dppb in THF at 0°C : the solution obtained was treated with cold methanol giving an orange solid which was filtered under an inert atmosphere. However, upon standing rapid decomposition of the precipitate occurred, with the formation of an oil, which was recovered with light petroleum. Such a product (**6**) has a ^{31}P -NMR signal in CDCl_3 consisting of one broad singlet at δ 32.1 ppm. A CD_2Cl_2 solution of this compound shows no change in signal width and multiplicity on lowering the temperature, and at -90°C it still appears as a broad singlet, no coupling to rhodium becoming apparent even at that temperature.

Compound **6** was tested as a catalyst precursor and it was found actually to promote polymerization of phenylacetylene in THF; however, the reaction was two orders of magnitude slower, and the polymer formed had higher D and M_n (1.55 and 910 000, respectively, at 50% conversion), than the polymer formed by the catalytic system prepared in situ.

Interestingly, a catalytically active rhodium complex bound to a growing polymer chain was isolated by the addition of methanol to the reaction mixture in THF: such rhodium–polyphenylacetylene species, whose ^1H -NMR spectrum shows the typical resonances of *cis-transoid* polyphenylacetylene, had $M_n = 170\,000$ and $D = 1.08$. When this adduct was dissolved in THF and treated with excess phenylacetylene a new polymerization was observed, with proportional increase of the initial polymer chain length with time, until all the monomer was consumed. This experiment provides further evidence for the *living* nature of the polymerization reaction. Unfortunately, identification of the rhodium–polyphenylacetylene complex was impossible, as its ^{31}P -NMR spectrum only consists of weak signals attributable to traces of **4** and **6**, which are present probably as impurities. In fact, due to the low number of rhodium active sites bound to the polymer chain, one can hardly expect to detect the phosphorous atoms

of dppb coordinated to the rhodium–polyphenylacetylene species.

3. Discussion

The association of $[\text{Rh}(\text{nbd})(\text{OMe})]_2$ and a bidentate phosphine produces a catalytic system which promotes the stereoselective polymerization of phenylacetylene. The system employed in the present work is most efficient in the absence of basic cocatalysts, in contrast with all previously reported rhodium–phosphine catalysts for such a reaction, with the exception of the catalytic system $[\text{Rh}(\text{nbd})\text{Cl}]_2/\text{Ar}_2\text{C}=\text{C}(\text{Ph})\text{Li}/\text{PPh}_3$ reported by Masuda et al. [14a].

The *living* nature of the catalyst is proved by monitoring the values of M_n and D with increasing conversion, by the increase of the polymer molecular weight with increasing initial monomer concentration, by the results obtained by addition of a second monomer feed to the reaction mixture after reaching 100% conversion of the initial monomer feed, and finally by isolation of a catalytically active rhodium–polyphenylacetylene adduct.

A few papers have been published on rhodium–diene–phosphine catalysts which promote alkyne polymerization [10,11,14]. Such rhodium catalysts have been reported to possess one monodentate phosphine and the diene coordinated in bidentate fashion throughout the catalytic cycle. Moreover, in the case of rhodium catalysts the polymerization reaction has always been proposed — and in one case proven [10a] — to proceed via a 2,1-insertion mechanism, which requires the presence of a free coordination site at rhodium, available for substrate coordination.

Substitution of a monodentate with a bidentate phosphine may in principle create a situation of coordinative saturation which is not compatible to this type of catalysis. Now we find that organorhodium–diphosphine catalysts efficiently promote the polymerization of phenylacetylene. We must therefore assume that one phosphorous atom goes out of the coordination sphere of rhodium to generate the catalytically active species.

As reported in Section 2, the ligands PNP and PSP do not form catalytically active systems with rhodium. The lack of catalytic activity might be due, in this case, to irreversible coordination of the ligand in a bidentate or even tridentate fashion, the latter being not unlikely especially for PNP [16].

An initially unexpected result, the lack of activity of the Rh–dppb catalyst in CHCl_3 and CH_2Cl_2 , has been explained actually by the spectroscopic investigations: in such solvents only the rhodium compound **1** is formed, which does not react with phenylacetylene.

In contrast, in other solvents such as THF, together with unreactive **1**, the catalytically active species **2** is

formed: most of this compound, however, reacts with phenylacetylene to form inactive **4**, therefore only a small fraction of **2** actually gives rise to the catalytic cycle, thus explaining the very low initiation efficiency (< 1%) of the catalytic system.

When this work was already in progress a paper by Noyori and coworkers was published [17], reporting on catalytic tests made with a rhodium–dppb system, which proved to be totally inactive. The precursor employed by the authors was $\text{Rh}(\text{C}\equiv\text{CC}_6\text{H}_5)(\text{nbd})\text{-(dppb)}$. By comparison of the spectroscopic data reported for this compound with those obtained in our experiments we could conclude that it corresponds to our compound **4**, produced by stoichiometric reaction of complex **2** initially formed with phenylacetylene (see Scheme 3). Therefore our results are in agreement with those reported by Noyori, as we also find that **4** is catalytically inactive: in our system, together with **4** another compound is formed, and the latter is responsible for the catalytic activity observed.

In the same paper, new results which provide an explanation for the need of addition of DMAP in the rhodium– PPh_3 catalyzed polymerization are also reported: an excess of such base is required to prevent the formation of a dinuclear rhodiacyclopentadiene compound, which itself is an active — but *nonliving* — polymerization catalyst, giving rise to polyphenylacetylene with a high polydispersion index. A similar compound cannot be formed when the bidentate phosphine dppb is present in the place of PPh_3 , therefore for the catalyst prepared with rhodium and the latter ligand the basic cocatalyst is not required.

With regard to the mechanism of the catalytic reaction, there are two major reasons that have prevented obtaining useful evidence. On the one hand, the high polymerization rate together with the low initiation efficiency causes fast formation of high molecular weight polymer. This exceedingly complicates spectroscopic analysis of the chain ends of the polyene, which is essential to draw conclusions both on the initiation and on the termination steps of the reaction. On the other hand, the presence of several rhodium compounds in the reaction mixture creates difficulties in the detection of intermediates such as rhodium hydrides, which have been invoked [17] as catalytically active species in rhodium-catalyzed polymerization of alkynes.

Actually, formation of a rhodium hydride via $\beta\text{-H}$ abstraction from **2** appears likely, although in our reaction mixtures hydride signals in ^1H -NMR spectra have never been detected.

Altogether, it is reasonable to propose that the catalytic cycle proceeds via the well-known insertion mechanism [17], the high regioselectivity of the insertion step being responsible for the selective production of *cis-transoid* polyphenylacetylene.

4. Conclusions

Rhodium–diphosphine catalyzed polymerization of phenylacetylene has been accomplished with the formation of highly stereoregular *cis-transoid* polyphenylacetylene.

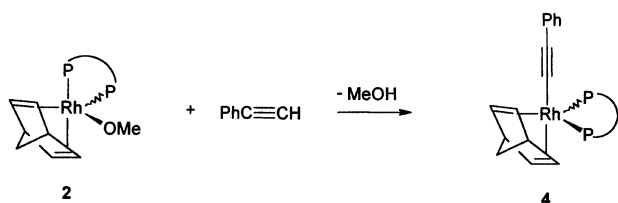
The catalytic system formed from $[\text{Rh}(\text{nbd})(\text{OMe})]_2$ and dppb produces a low polydispersity polymer in the absence of basic cocatalyst. The *living* nature of the catalyst is proved by the increase of polymer molecular weight with conversion whereas maintaining a narrow molecular weight distribution, by the increase of molecular weight with increasing monomer initial concentration, and by the increase of polymer chain length by addition of monomer after 100% conversion. Spectroscopic investigations have provided useful information on the rhodium species formed in the catalytic mixtures, although no final evidence has been attained on the nature of the catalytically active species.

5. Experimental

All the reactions and manipulations were performed routinely under an Ar atmosphere by using standard Schlenk tube techniques. Tetrahydrofuran and Et_2O were distilled over sodium benzophenone ketyl just before use; CH_2Cl_2 and $\text{C}_6\text{H}_5\text{Me}$ were distilled over CaH_2 and stored under an inert atmosphere. All the other chemicals were reagent grade and were used as received from commercial suppliers. $[\text{Rh}(\text{nbd})\text{Cl}]_2$ was prepared according to the procedure reported in the literature [18].

^1H -, ^{13}C - and ^{31}P -NMR spectra were recorded on a JEOL EX400 spectrometer operating at 399.77, 100.54 and 161.82 MHz, respectively. ^1H and ^{13}C chemical shifts are reported relative to Me_4Si , whereas ^{31}P chemical shifts are reported relative to external H_3PO_4 (85%) with downfield shifts positive.

Chemical yields of the catalytic reactions were determined by GLC on a Carlo Erba 6000 VEGA Series 2 equipped with a SE30 column. Molecular weight distributions of the polymers were determined by GPC in CHCl_3 at 25°C on a Milton Roy CM4000 instrument using an UV spectrometer detector operating at 270 nm, equipped with CHROMPACK Microgel-5



Scheme 3.

columns. The number average molecular weight (M_n) and polydispersion index ($D = M_w/M_n$) of the polymers were calculated on standard polystyrene calibrations.

5.1. Preparation of $[Rh(nbd)(OMe)]_2$

An excess of anhydrous Na_2CO_3 (250 mg) in 8 ml of MeOH is reacted with 250 mg of $[Rh(nbd)Cl]_2$ under an Ar atmosphere. The mixture is heated at reflux for 1 h. After cooling to room temperature the yellow solid obtained is filtered under an Ar atmosphere, washed repeatedly with warm water, dried under vacuum and stored under inert atmosphere. Yield 80%.

5.2. Catalytic reactions

A solution of $[Rh(nbd)(OMe)]_2$ (10.1 mg, 0.045 mmol of monomer) in 12.5 ml of THF (or other solvent of choice) is treated at 0°C with 0.045 mmol of the diphosphine, then addition of the GLC standard naphthalene is followed by addition of phenylacetylene. Samples are withdrawn from the reaction mixture at time intervals, and each sample is treated with a tenfold excess of AcOH for quenching; disappearance of the monomer is followed by GLC.

5.3. Polymer isolation

The final reaction mixture is quenched with an excess of glacial AcOH; the polymer is precipitated by addition of CH_3OH (ca. four times the volume of THF), then filtered, washed repeatedly with CH_3OH and dried in vacuo. The polyphenylacetylene obtained has a *cis-transoidal* structure as evidenced by spectroscopic data: 1H -NMR ($CDCl_3$): δ 6.95–6.93 (m, 3H, *m*- and *p*-H(C_6H_5)), 6.64–6.62 (m, 2H, *o*-H(C_6H_5)), 5.84 (s, 1H, C=CH); $^{13}C\{^1H\}$ -NMR ($CDCl_3$): δ 142.9 and 139.3 (quaternary carbons), 131.8 (C=CH), 127.8 and 127.5 (*o*- and *m*-Ar), 126.7 (*p*-Ar).

Acknowledgements

The authors thank the Italian Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST)

for financial support. Helpful suggestions by the referees are also gratefully acknowledged.

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