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The reaction between Pt- and Pd-*cis* di-chloro complexes and 4,4′-diethynylbiphenyl: synthesis and characterisation of a 'zigzag' metal/poly-yne polymer

G. Iucci*, G. Infante, G. Polzonetti

Department of Physics, E. Amaldi University 'Roma Tre' and Unità INFM, Via della Vasca Navale 84, 00146 Roma, Italy

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Abstract

The synthesis of poly-yne polymers containing transition metals inserted in the main chain has been attempted by reacting a dialkyne molecule, 4,4′-diethynylbiphenyl (or DEBP), with [$PtCl_2$(dppe)] and [$PdCl_2$(dppe)], the platinum- and palladium-*cis* square-planar di-chlorine complexes containing diphenylphosphine ethane (dppe) as bidentate ligand. The aim of this work was to obtain organometallic polymers ([Pt(dppe)DEBP]$_n$ and [Pd(dppe)DEBP]$_n$, respectively) having an all-*cis* 'zigzag' structure, by formation of a σ-acetylide bond between the transition metal complexes and the dialkyne molecule. When [$PtCl_2$(dppe)] was reacted with DEBP, the formation of a chlorine-terminated [Pt(dppe)DEBP]$_n$ oligomer was evidenced; in the reaction involving the Pd(II) complex, on the other hand, [$PdCl_2$(dppe)] seems to catalyse the polymerisation of DEBP via opening of the triple bond, producing a poly-DEBP polymer containing Pd(II) atoms inserted in the main chain.

Keywords: Organometallic polymers; X-ray photoelectron spectroscopy; Zigzag structure

1. Introduction

Organometallic π-conjugated polymers containing σ-bonded transition metals in the main chain form a new class of molecular materials that has been the object of large interest in connection with the possible applications in the field of molecular electronics [1–3]. The delocalisation of the π-system involves the metal d-orbitals [4], producing peculiar physical properties, such as photoluminescence [5] and third-order non-linear optical (NLO) properties [6], which make these materials promising candidates for the preparation of electronic devices.

Various types of organometallic polymers containing transition metals σ-bonded to carbon atoms in the main chain have been prepared, as reviewed by Hagihara et al. [7] and more recently by Nguyen et al. [8]. Σ-bonds between acetylide groups and transition metals are stabilised, with respect to other M–C σ-bonds, by the favourable interaction between the metal d-orbitals and the π-orbitals of the ethynyl carbons, which strengthens the bond [7]; ligands such as tertiary phosphines produce a further stabilisation of the bond. Metal–poly-yne polymers can be easily produced by a dehydroalogenation reaction between the corresponding dichloro complexes and terminal dialkynes, according to the reaction scheme:

$$MeCl_2(PR_3)_2 + HC{\equiv}C\text{–}S\text{–}C{\equiv}CH \rightarrow [\text{–}Me(PR_3)_2\text{–}C{\equiv}C\text{–}S\text{–}C{\equiv}C\text{–}]_n$$

where PR_3 = tertiary phosphine, S = organic spacer, Me = Pd, Pt. The reaction, catalysed by cuprous halogenydes, takes place in a basic environment (diethylamine is used as solvent) and has been successfully employed in the preparation of Pt– and Pd–poly-yne polymers containing various phosphine ligands and organic spacers. For instance, some of us reported the preparation of Pt(II) and Pd(II) polymeric complexes containing DEBP as the organic spacer [9]; when triphenylphosphine complexes were used as precursors, insoluble [$(PPh_3)_2$MeDEBP–]$_n$ polymers were obtained; the use of tributylphosphine complexes, on the other hand, leads to soluble polymers [$(PBu_3)_2$Me-DEBP]$_n$ (Me = Pd, Pt) that can be cast in the form of thin films. In all the reported systems the central metal is present in square-planar *trans* configuration, generating a rigid rod-like structure of the polymer chain. Near-edge X-ray absorption fine structure (NEXAFS) investigations on thin

* Corresponding author. Tel.: +39-06-551-73-401; fax: +39-06-551-73-390.

E-mail address: iucci@uniroma3.it (G. Iucci).

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films of $[(PBu_3)_2MeDEBP]_n$ evidenced the ordered structure of the polymer backbone and the unexpected alignment of the polymer chains even in thick films [10]. More recently, the preparation of soluble Pd– and Pt–poly-yne polymers containing thiophene spacers has been reported [11].

It is worth noticing that in the reported experimental conditions, for all the investigated systems, when a *cis* dichloro complex is used as precursor a *cis–trans* isomeristaion occurs and the central metal atom is always found in *trans* configuration in the product polymer, which has therefore a linear rod-like structure. In the present paper, we report an investigation on the reactions between DEBP and two square planar chelate complexes $[PtCl_2(dppe)]$ and $[PdCl_2(dppe)]$ containing *bis*(diphenylphosphino)ethane $Ph_2PCH_2CH_2PPh_2$ (dppe) as the ligand. It was our aim to obtain metal-intercalated poly-yne polymers containing the metal blocked in the *cis* configuration by the bidentate ligand and having therefore the 'zigzag' structure shown in Fig. 1. These polymers might be considered for the tailoring of third order NLO and photoluminescence properties. However, this goal was only partially achieved, because unexpected results were obtained; apparently, a 'locked' *cis* configuration of the precursor complex $[MeCl_2(dppe)]$ leads to more complex reaction pathways, particularly for Me = Pd. The chemical structures of the metal–poly-yne polymers were elucidated with the help of X-ray photoelectron spectroscopy (XPS) measurements.

2. Experimental

2.1. Instrumentation

Infrared spectra were recorded on nujol mulls using KBr (4000–400 cm^{-1}) optical cells on a Bruker Vector 22 FTIR interferometer.

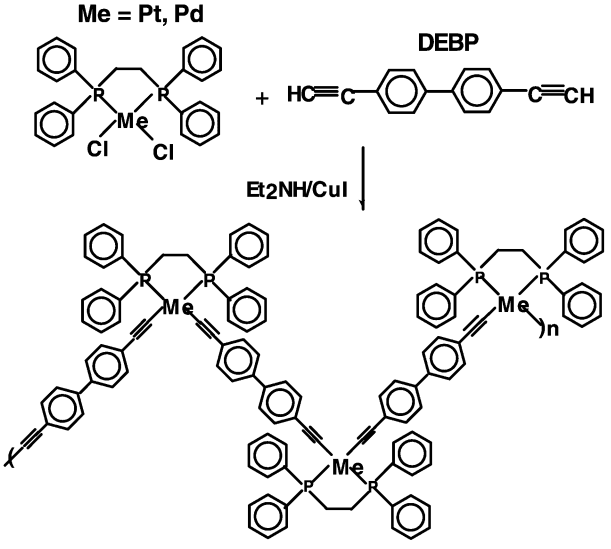

Fig. 1. Reaction scheme.

UV spectra were recorded from $CHCl_3$ solutions on a Perkin–Elmer Lambda 5 spectrophotometer.

Cleanliness of the samples was checked by thin layer chromatography analysis on silica gel using $CHCl_3$ or tetrahydrofurane as solvent.

Elemental analyses were carried out at the Chemistry Department of the University 'La Sapienza', Rome.

X-ray photoelectron spectroscopy (XPS) measurements were carried out on a custom designed XPS spectrometer. The experimental apparatus consists of an analysis chamber and a preparation chamber separated by a gate valve and is equipped with a 150 mm mean radius hemispherical analyser and with a 16-channel detector. Typical vacuum in the chamber during the measurements was in the range 10^{-9}–10^{-10} torr. AlKα (1486.6 eV) non-monochromatised radiation was used as excitation source. Insoluble samples were deposited as thin powder films onto polished stainless steel substrates; soluble samples were analysed as thin films prepared by spinning from $CHCl_3$ solutions onto polished stainless steel substrates. All the spectra were energy referenced to the C1s signal of aromatic carbons positioned at a 284.7 eV binding energy (BE) value. Quantitative evaluation of the atomic ratios was performed by analysis of the peaks intensity, using Scofield atomic cross-section values [12]. Further adjustment was made by experimentally determined sensitivity factors.

2.2. Materials

All the solvents were reagent grade (Carlo Erba) and were used without further purification. 4,4′-diethynylbiphenyl was prepared by reaction between 4,4′-dibromobiphenyl (Fluka) and trimetylsilylacetylene (Acros), according to literature procedures [13]. $[PtCl_2(dppe)]$ and $[PdCl_2(dppe)]$ were synthesised from K_2PtCl_4 (Acros) and K_2PdCl_4 (Acros), respectively, and diphenylphospino ethane or dppe (Acros), according to the procedure reported by Westland [14].

2.3. Reactions

Reactions were carried out under Argon atmosphere and in two different $[MeCl_2(dppe)]$/DEBP molar ratios (Me = Pt, Pd): 1/1 molar ratio with the aim of obtaining the polymers shown in Fig. 1, and 1/2.5 molar ratio in order to obtain metal diacetylides of the type $[Me(dppe)(DEBP)_2]$. The chemical structure of the obtained materials was not the expected one in all the cases here discussed. The reaction conditions are collected in Table 1.

(a) Reaction between $[PtCl_2(dppe)]$ and DEBP

$[PtCl_2(dppe)]$ and DEBP, in the weight ratios shown in Table 1 for 1/1 or 1/2.5 reactions, were dissolved in 20 ml of toluene/diethylamine = 3/1 v/v solution with a catalytic amount (~5 mg) of CuI; the reaction mixture was refluxed for 6 h, during which the formation of a yellow precipitate was observed. The solid was filtered, washed with ethanol and dried under vacuum; reaction yields are shown in

Table 1
Reaction conditions and results

Precursor complex	Complex/DEBP molar ratio	Complex mg (mmoles)	DEBP mg (mmoles)	Solvent	Reaction time (h)	Yield solid product (mg)	Soluble fraction (%)	Elemental analyses						
								Experimental			Calculated [a]		Calculated [b]	
								Fraction	C (%)	H (%)	C (%)	H (%)	C (%)	H (%)
$[Pt(dppe)Cl_2]$	1:1	320 (0.5)	105 (0.52)	Toluene/Et_2NH = 3/1	6	370	10	Insoluble	58.6	4.0	63.5	4.0	60.7	4.0
								Soluble	65.8	4.0			69.9	3.9
	1:2.5	320 (0.5)	250 (1.25)	Toluene/Et_2NH = 3/1	6	420	20	Insoluble	58.9	4.1			60.7	4.0
								Soluble	67.4	4.0	69.9	3.9	69.9	3.9
$[Pd(dppe)Cl_2]$	1:1	233 (0.4)	92 (0.45)	Et_2NH	3	220	–		71.8	4.2	71.5	4.2		
	1:2.5	332 (0.6)	300 (1.5)	Et_2NH	3	400	–		76.4	4.76	76.7	4.6		

[a] Values calculated for $[-Me(dppe)-DEBP-]_n$ in the 1:1 ratio, for $[Me(dppe)(DEBP)_2]$ in the 1:2 ratio.
[b] Values calculated on the basis of the chemical structures shown in Fig. 5 for the soluble and insoluble fractions.

Table 1. After treatment of the crude product with hot $CHCl_3$, an insoluble fraction (insoluble in most organic solvents, i.e. CH_2Cl_2, THF, C_6H_6; 85% of the reaction product) was obtained; by treating the residual $CHCl_3$ solution with *n*-hexane, separation of a light yellow solid product, consisting mainly of $[Pt(dppe)(DEBP)_2]$ was observed.

(b) Reaction between $[PdCl_2(dppe)]$ and DEBP

$[PdCl_2(dppe)]$ and DEBP, in the weight ratios shown in Table 1 for the 1/1 or 1/2.5 reactions, were dissolved in 20 ml of diethylamine with a catalytic amount (~5 mg) of CuI; the reaction mixture was refluxed for 3 h, during which a yellow precipitate was formed. The solid was filtered, washed with ethanol and dried under vacuum. Treating the reaction product with hot $CHCl_3$ resulted in the separation of an insoluble product and of a $CHCl_3$ solution containing mainly unreacted $[PdCl_2(dppe)]$. The insoluble product (reaction yield shown in Table 1) was isolated and analysed.

3. Results and discussion

The reactions of DEBP with the Pt- and Pd-complexes yielded products having a completely different structure; therefore they will be examined separately.

3.1. Reaction between $[PtCl_2(dppe)]$ and DEBP

$[PtCl_2(dppe)]$ seems to be less reactive towards DEBP than the corresponding triphenylphosphine and tributylphosphine complexes. In fact, the reaction required the use of a solvent having a higher reflux temperature than diethylamine and took place only very slowly when only diethylamine was used as solvent. Therefore, we used a 3/1 toluene/diethylamine mixture; toluene was used in order to increase the reaction temperature and diethylamine was necessary since it acts as a base in the dehydrochlorination reaction. As described in Section 2, reactions between $[PtCl_2(dppe)]$ and DEBP were carried out respectively in 1/1 or 1/2.5 molar ratios with the aim of obtaining a polymeric product $[Pt(dppe)DEBP]_n$ and a platinum diacetylide $[Pt(dppe)(DEBP)_2]$, respectively. In both cases, however, the reaction products consisted in a fraction insoluble in all the tested organic solvents ($CHCl_3$, CH_2Cl_2, THF, benzene, toluene) and of a fraction soluble in $CHCl_3$ and in several other solvents. The spectra of the insoluble fractions obtained using different $[PtCl_2(dppe)]$/DEBP molar ratios are very similar to each other, and the same is true for the soluble fractions. The main difference evidenced was an increase in the soluble fraction percentage upon increasing the $[PtCl_2(dppe)]$/DEBP molar ratio, though the insoluble fraction remains the predominant product even when a 1/2.5 molar ratio is used. The obtained soluble fraction is mainly the diacetylide product $[Pt(dppe)(DEBP)_2]$, while the insoluble fraction is an oligomer of $[Pt(dppe)DEBP]_n$, as we will describe in the following paragraphs.

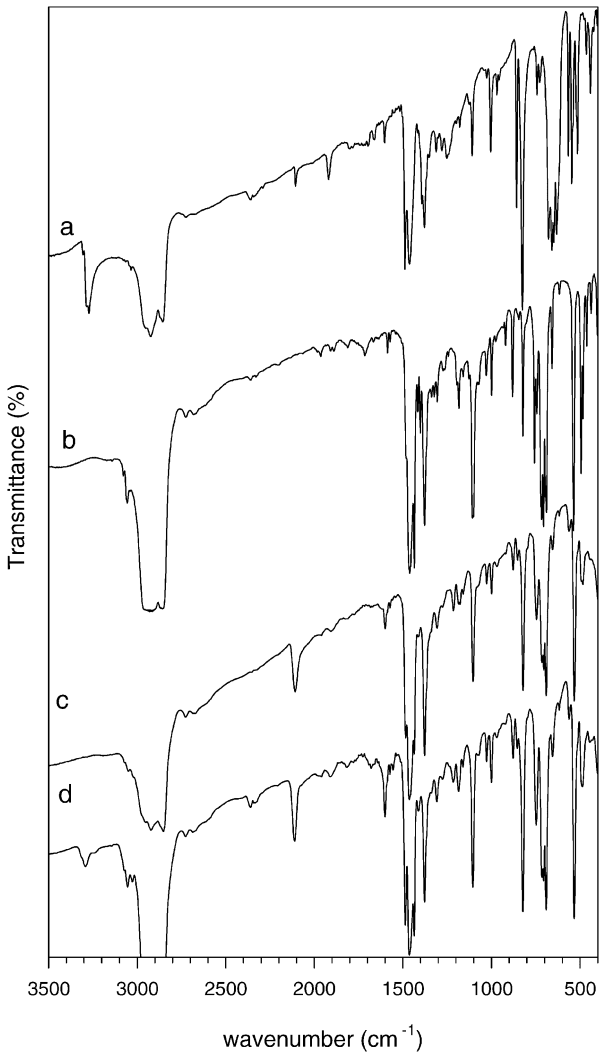

Fig. 2. Infrared spectra (nujol mulls) of DEBP (a), [Pt(dppe)Cl_2] (b), and of the insoluble [Pt(dppe)DEBP]$_n$ (c) and soluble [Pt(dppe)$DEBP_2$] (d) fractions of the reaction product.

Fig. 2 shows the infrared spectra (nujol mulls) of the two reagents DEBP (Fig. 2(a)) and [$PtCl_2$(dppe)] (Fig. 2(b)), of the insoluble fraction ([Pt(dppe)DEBP]$_n$ (Fig. 2(c))) and of the soluble fraction ([Pt(dppe)$(DEBP)_2$, (Fig. 2(d))). In the infrared spectrum of DEBP (Fig. 2(a)), many bands are connected with the presence of the triple bond, namely the C–H stretching mode of the terminal alkyne at 3272 cm^{-1}, the C≡C stretching at 2106 cm^{-1}, and the C–H bending of the alkyne group, forming a series of bands in the range 680–630 cm^{-1}. Other bands result from vibrations of the benzene ring; the most important feature is the intense peak at 825 cm^{-1} connected with the C–H out of plane bending of the phenyl rings in the typical position of 1–4 disubstituted benzenes.

The [$PtCl_2$(dppe)] spectrum (Fig. 2(b)) is dominated by the vibrations of the benzene rings of the phosphine group; the C–H out of plane bending of the aromatic rings show a double pattern of bands with a group of peaks at 757–744 cm^{-1} and another group in the range 716–689 cm^{-1}, the peak positions being typical of monosubstituted benzenes.

In the spectrum of the insoluble fractions of the reaction product [Pt(dppe)DEBP]$_n$ (Fig. 2(c)) we observe the disappearance of the alkyne C–H stretching (3272 cm^{-1}) and bending (~660 cm^{-1}) bands, while the C≡C stretching at 2110 cm^{-1} increases in intensity, indicating the formation of the metal–acetylide σ-bond, with substitution of the terminal hydrogen by the more electropositive platinum atom. The bands of the dppe moiety, and mainly the C–H out of plane bending of the aromatic rings, are not modified in the spectrum of [Pt(dppe)DEBP]$_n$, suggesting that the structure of the dppe is also unmodified in the reaction. The band at 825 cm^{-1}, present also in the spectrum of [$PtCl_2$(dppe)] appears more intense after the insertion of the DEBP moiety in the reaction product. On the basis of the IR data we can therefore assign the structure shown in Fig. 1 to the insoluble fraction of [Pt(dppe)DEBP]$_n$.

However, the elemental analysis of the reaction product shown in Table 1 is not in good agreement with the calculated value for the [Pt(dppe)DEBP]$_n$ polymer but shows a lower carbon content. In order to account for the elemental analysis, the formation of a chlorine-terminated oligomer can be hypothesised, and XPS measurements give evidence of this statement (see next paragraph).

The IR spectra of the soluble (Fig. 2(d)) and insoluble fractions (Fig. 2(c)) appear very similar to each other, the only difference being the weak band at 3280 cm^{-1}, present in the soluble fraction spectrum and typical of terminal alkynes ≡C–H stretching. The intensity of this band appears reduced with respect to the same band in the spectrum of the DEBP molecule; a similar effect was found in the spectrum of the [$Pt(PPh_3)_2(DEBP)_2$] *bis*-acetylide [9]. The elemental analyses of the soluble fraction, shown in Table 1 is in good agreement with the calculated values for the *bis*-acetylide.

The UV spectra ($CHCl_3$ solution) of DEBP, [$PtCl_2$(dppe)] and of the soluble fractions, i.e. [Pt(dppe)$DEBP_2$] are shown in Fig. 3; the spectrum of the reaction product reveals a new band at 340 nm, probably resulting from more extended conjugation between the π-orbitals of DEBP and the metal d-orbitals. For the [$Pt(PPh_3)_2(DEBP)_2$] diacetylide, the maximum absorption wavelength in the UV spectrum was found at 369 nm [15]; a lower delocalisation is therefore observed for the *cis* complex with respect to the *trans* one.

3.2. XPS spectra of the Pt-materials

In order to obtain more information on their chemical structure, the insoluble and soluble fractions of the [Pt(dppe)DEBP]$_n$ material were investigated by XPS spectroscopy; XPS spectra of the starting complex [$PtCl_2$(dppe)] were also recorded for comparison; the results are presented in Table 2.

The BEs measured for [$PtCl_2$(dppe)] are in agreement

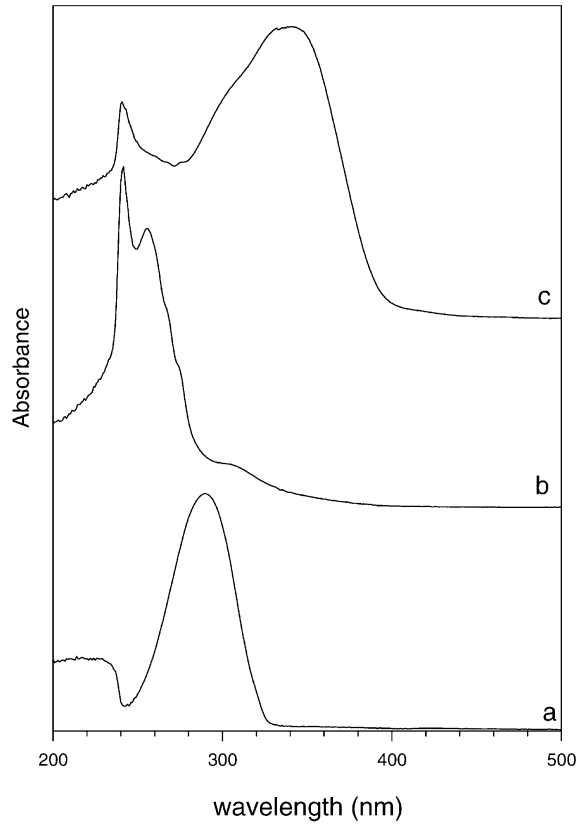

Fig. 3. UV spectra ($CHCl_3$) of of DEBP (a), [Pt(dppe)Cl_2] (b) and of the soluble fraction [Pt(dppe)$DEBP_2$] (c).

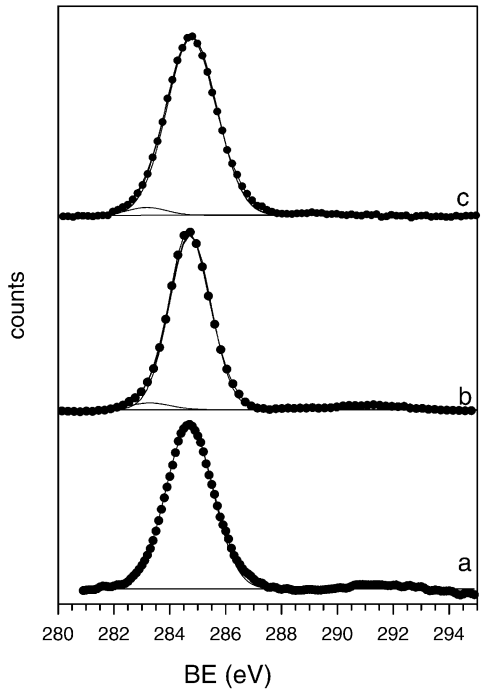

Fig. 4. C1s XPS spectra of [Pt(dppe)Cl_2] (a) and of the insoluble (b, [Pt(dppe)DEBP]$_n$), and soluble (c, [Pd(dppe)$DEBP_2$]) fractions of the reaction product.

with the values reported in the literature [16]; the BE found for the Pt4f$_{7/2}$ signal (72.6 eV) is typical of Pt(II) complexes, the measured BE for Cl2p (197.7 eV) confirms the *cis* structure of the complex [16] (a higher BE value would be expected for a *trans* dichloro complex) and the P2p signal is found at 131.4 eV, a typical BE for aromatic phosphines [17]. The measured atomic ratios are also in agreement with the calculated values. The C1s spectrum of [$PtCl_2$(dppe)], shown in Fig. 4(a) displays a shake-up satellite, connected with $\pi \rightarrow \pi^*$ transitions of the aromatic rings, at about 7 eV form the main photoemission peak.

The C1s spectrum of the soluble (Fig. 4(b)) and insoluble (Fig. 4(c)) fractions and their curve-fitting deconvolution are also shown in the figure; both spectra show a shoulder at about 283.0 eV on the low BE side of the main photoemission peak, connected with the presence of carbon atoms having a higher electron density than the aromatic carbons of the phosphine groups and of the DEBP moieties. We have attributed this new signal to the negatively charged alkyne carbons σ-bonded to the platinum atoms (≡C–Pt); a similar effect was evidenced in the XPS spectra of the *trans* metal-intercalated polymer [Pd(PBu_3)$_2$DEBP]$_n$ [17]. The shake-up satellite, due to the benzene rings of dppe and DEBP can also be detected in the figure, at about 7 eV from the main signal.

XPS data concerning the core-level signals analysed for the insoluble fractions, i.e. the [Pt(dppe)DEBP]$_n$ materials, are presented in Table 2. A Cl2p signal, having the same BE measured for [$PtCl_2$(dppe)], and therefore bonded to the Pt atom is still present in the spectra of the insoluble samples obtained from either 1/1 and 1/2.5 molar ratio reactions. The measured Pt/Cl ratio is 1/0.4 for both samples revealing that [Pt(dppe)DEBP]$_n$ is actually a chlorine-terminated oligomer, consisting, on average, of 4–5 –Pt(dppe)– subunits linked by DEBP spacers. Concerning the P2p signal, we observe that the BE has not been modified with respect to the pristine complex and that the Pt/P ratio is till 1/2; the phosphine is therefore still bonded to platinum and no oxidation of the phosphorus atoms of dppe has taken place. The Pt4f$_{7/2}$ signal appears also substantially unmodified with respect to the pristine complex.

On the basis of the XPS data, we can therefore hypothesise for the insoluble fractions of [Pt(dppe)DEBP]$_n$ the chemical structure shown in Fig. 5; the chain length shown in the figure (four Pt-capped Pt(dppe)DEBP monomer units) may be considered as an average length, the real material consisting of longer and shorter molecules. The calculated atomic ratios and elemental analyses for the chemical structure shown in Fig. 5 are in good agreement with that determined experimentally, as displayed in Tables 1 and 2. The possibility of formation of cyclic oligomers (mainly tetramers) cannot be completely excluded; cyclic tetramers of similar Pt-complexes have been prepared, for instance by Stang et al. [18,19]. However, since cyclic tetramers should contain no chlorine and have exactly the

Table 2
XPS data on the reference complexes and on the reaction products (BE = binding energy; FWHM = full width at half maximum)

Compound	Signal	BE (eV)	FWHM (eV)	Stoichiometry	
				Experimental	Calculated
[Pt (dppe)Cl_2]	C1s	284.7	1.8	31	26
	$Pt4f_{7/2}$	72.6	1.9	1	1
	$P2p_{3/2,1/2}$	131.4	2.1	2	2
	$Cl2p_{3/2,1/2}$	197.7	3.0	2.1	2
[Pd(dppe)Cl_2]	C1s	284.7	2.0	28.8	26
	$Pd3d_{5/2}$	338.0	2.2	1	1
	$P2p_{3/2,1/2}$	131.3	2.4	1.8	2
	$Cl2p_{3/2,1/2}$	197.7	3.1	1.9	2
[Pt(dppe)DEBP]$_n$ 1/1	C1s	284.7	2.0	44	38.8[a]
Insoluble fraction	$Pt4f_{7/2}$	72.7	2.0	1	1[a]
	$P2p_{3/2,1/2}$	131.4	2.3	2	2[a]
	$Cl2p_{3/2,1/2}$	198.0	3.1	0.4	0.4[a]
[Pt(dppe)$DEBP_2$] 1/1	C1s	284.7	1.9	64	58[a]
Soluble fraction	$Pt4f_{7/2}$	72.6	1.6	1	1[a]
	$P2p_{3/2,1/2}$	131.4	2.1	2.3	2[a]
[Pt(dppe)DEBP]$_n$ 1/2.5	C1s	284.7	2.1	45	38.8[a]
Insoluble fraction	$Pt4f_{7/2}$	72.8	1.9	1	1[a]
	$P2p_{3/2,1/2}$	131.6	2.0	2	2[a]
	$Cl2p_{3/2,1/2}$	198.2	3.1	0.4	0.4[a]
[Pd(dppe)DEBP] 1/1	C1s	284.7	1.9	60	
	$Pd3d_{5/2}$	337.0	3.0	1	
	$P2p_{3/2,1/2}$	132.2	2.4	1.1	
	$Cl2p_{3/2,1/2}$	198.5	3.4	0.6	
[Pd(dppe)DEBP] 1/2.5	C1s	284.7	2.3	80	
	$Pd3d_{5/2}$	337.0	3.0	1	
	$P2p_{3/2,1/2}$	132.1	2.6	1.6	
	$Cl2p_{3/2,1/2}$	198.5	3.5	0.7	

[a] Values calculated on the basis of the structures shown in Fig. 5 for the soluble and insoluble fractions, respectively.

same elemental composition of the long-chain polymers, we think that the chlorine-terminated oligomers are the main reaction products.

The soluble fractions were also analysed in the form of thin polymer films; the obtained results are shown in Table 2.The measured BEs of the $Pt4f_{7/2}$ and P2p signals are the same as the pristine complex and the insoluble fractions; no Cl2p signal was detected. The measured atomic ratios, shown in Table 2, are in agreement with the chemical structure of the *bis*-acetylide, shown in Fig. 5.

3.3. Reaction between [$PdCl_2$(dppe)] and DEBP

When [$PdCl_2$(dppe)] was reacted with DEBP, in 1/1 or 1/2.5 molar ratio, only an insoluble product was obtained; the IR spectra of the synthesised materials using different molar ratios are extremely alike, and therefore only the spectrum of the product obtained from 1/1 molar ratio is shown in Fig. 6. The spectrum appears completely different from the IR spectrum of [Pt(dppe)DEBP]$_n$, shown in Fig. 2(c). The intense band at 2106 cm^{-1}, resulting from the C≡C stretching vibration is absent in the Pd-polymer, and only a few low intensity bands are detected in the range 2000–2200 cm^{-1}; the other bands connected with the triple bond (≡C–H stretching and bending) disappeared as well. The C–H out of plane bending vibration of the benzene ring of DEBP moiety, on the other hand, appears very intense, evidencing the incorporation of DEBP in the reaction product. Finally, the phosphine bands in the range 700–750 cm^{-1} appear strongly modified. Though the Pd-material clearly is not a σ-acetylide metal-intercalated polymer, in the following for simplicity we will call it [Pd(dppe)DEBP].

The spectrum shown in Fig. 6 clearly resembles the IR spectra of poly (4,4′-diethynylbiphenyl) (p-DEBP), obtained by polymerisation reactions performed with Pd-containing catalysts such as [$Pd(PPh_3)_2Cl_2$] and [$Pd(PPh_3)_2(DEBP)_2$][20]. Pd-complexes were found very active in the polymerisation of DEBP via opening of the triple bond, producing a linear polyene chain, with the $–C_6H_4–C_6H_4–C{\equiv}CH$ moiety remaining unchanged as a

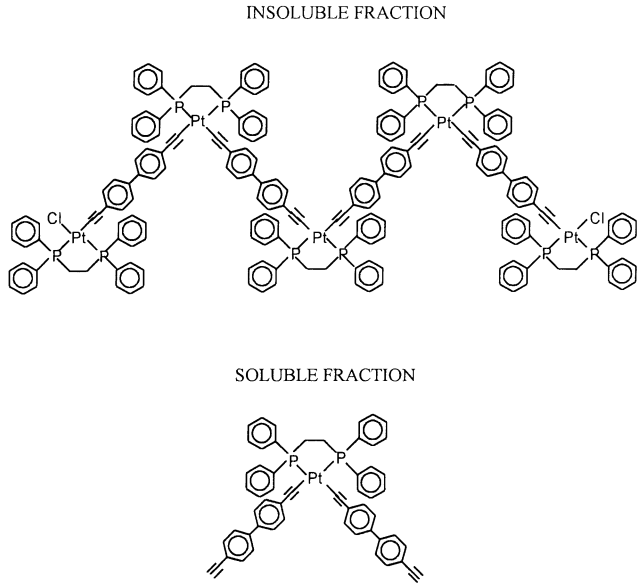

Fig. 5. Chemical structure of the insoluble and soluble fractions of the [Pt(dppe)Cl_2] + DEBP reaction product.

pending group. However, in the spectrum of the polymer obtained from the [Pd(PPh_3)$_2Cl_2$] catalyst, the signals of the triple bond stretching vibrations of the pending group are almost absent [20], suggesting the opening of both triple bonds of the DEBP monomer.

Concerning the present [Pd(dppe)DEBP] spectrum, the comparison with the spectra of p-DEBP suggests that the Pd-complex may induce not only the formation of the metal–carbon σ-bond but also the linear polymerisation of DEBP via opening of the triple bond. The absence of the C≡C and ≡C–H stretching vibrations suggests that both triple bonds can be opened in the polymerisation reaction.

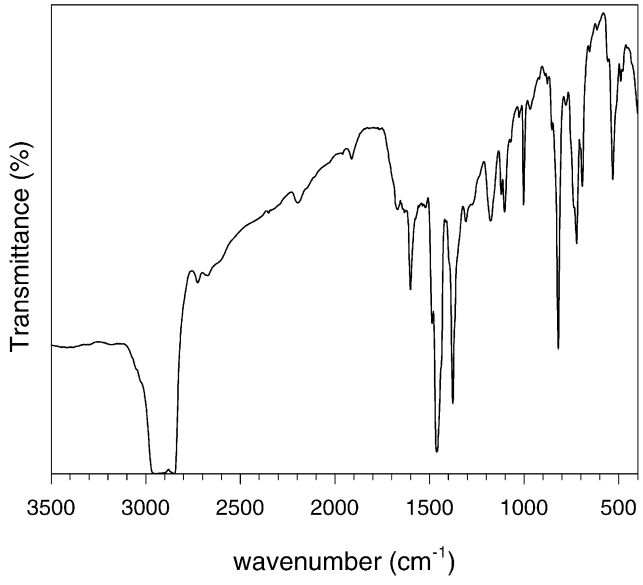

Fig. 6. Infrared spectrum (nujol mulls) of the [Pd(dppe)Cl_2] + DEBP reaction product ([Pd(dppe)DEBP]).

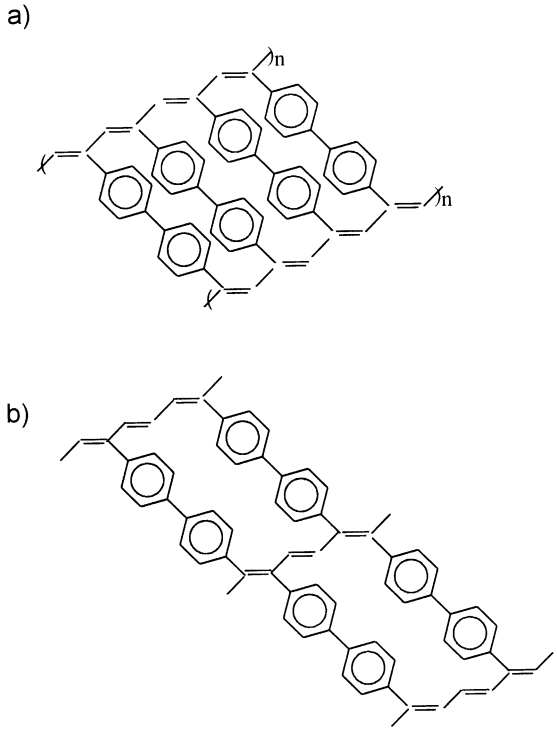

Fig. 7. Proposed chemical structure of [Pd(dppe)DEBP].

In order to account for the experimental results we can hypothesise either the growth of two parallel polyene chains separated by biphenyl moieties, as shown in Fig. 7(a), and/or the formation of a more complicated cross-linking between different polymer chains generating a more complex network (Fig. 7(b)). In our opinion, the first hypothesis appears to be more likely owing to the simple stereochemical consideration; however, the structures shown in Fig. 7 must be considered as speculative.

A large part (~60%) of the pristine complex was recovered unmodified after the reaction, showing that not all the palladium complex has been incorporated in the product polymer.

3.4. XPS spectra of the Pd-materials

The chemical structure of the [Pd(dppe)DEBP] material has also been investigated by XPS spectroscopy; the XPS data for the [Pd(dppe)DEBP]$_n$ samples obtained either from 1/1 or 1/2.5 [Pd(dppe)Cl_2]/DEBP molar ratio reactions and for the relative pristine complex [$PdCl_2$(dppe)] are presented in Table 2. The C1s, Cl2p and P2p spectra of the precursor complex [$PdCl_2$(dppe)] are similar to the ones of the corresponding Pt-complex; the $Pd3d_{5/2}$ BE is in agreement with the value expected for Pd(II) complexes [16].

In the spectra of [Pd(dppe)DEBP] major modifications are detected on the $Pd3d_{5/2}$ signal, that appears to have shifted to lower BE by approximately −1.0 eV and significantly broader (2.9 eV) than the corresponding signal of the

[$PdCl_2$(dppe)] complex. A curve-fitting deconvolution of the Pd3d spectra of the two samples obtained form 1/1 and 1/2.5 molar ratio ((Fig. 8(b)) and (Fig. 8(c)), respectively) is shown in Fig. 8 and compared with the spectrum of the pristine complex (Fig. 8(a)). Spectra b and c actually consists of two unresolved components, one having the same BE of the pristine complex signal, the other shifted to much lower BE (−1.5 eV). Modifications take place also in the P2p spectrum, whose BE is significantly higher (+0.8 eV) than the value found for [$PdCl_2$(dppe)]; moreover, for the material obtained from 1/1 molar ratio, the Pd/P ratio found is approximately 1/1, revealing that the dppe moiety bonded to Pd in the pristine complex has been partially oxidised and partially lost in the course of the reaction.

In previous investigations on the polymerisation of monosubstituted alkynes by means of Pd(II) catalysts containing the triphenylphospine (PPh_3) ligand, the incorporation of the Pd catalyst in the growing polymer chain has been evidenced [21,22]. In the polymerisation of ethynyltrimethylsilane, for instance, two different types of Pd species were found in the polymer product, one having the same BE of the pristine Pd(II) catalyst, the other at −1.6 eV from the pristine catalyst signal and attributed to Pd atoms that had lost the phosphine ligand and were coordinated to the double bonds of the polymer chain [21]. A decrease in the $Pd3d_{5/2}$ BE with respect to the pristine catalyst was evidenced also in the XPS spectra of two Pd-containing polymers obtained from propargyl derivatives [22]. In both systems the PPh_3 ligand was oxidised in the course of the polymerisation reaction, as evidenced by the BE increase of the P2p XPS signal, and partially or totally released from the Pd complexes. Pd(II) complexes, in fact, are known to catalyse the oxidation of PPh_3 to the corresponding $OPPh_3$ oxide, by insertion of oxygen in the Pt–P bond [23]. $OPPh_3$ can be subsequently released form the Pd complex, since the bond between $OPPh_3$ and palladium is weak.

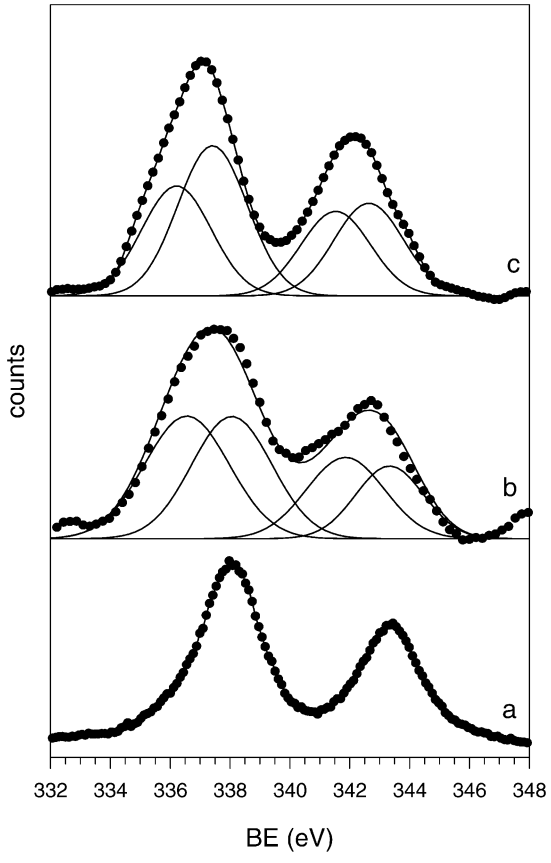

Fig. 8. $Pd3d_{3/2,5/2}$ XPS spectra of [Pd(dppe)Cl_2] (a) and of [Pd(dppe)DEBP]$_n$ obtained from 1/1 (b) and 1/2.5 (c) molar ratio reactions.

The atomic ratios calculated on the basis of the XPS data are also shown in Table 2; the C/Pd ratio is higher in the polymer obtained from 1/2.5 molar ratio than in the 1/1 polymer. The carbon content in these materials is partly due to the dppe ligand (26 C atoms per dppe moiety) and partly to the DEBP organic spacer (16 C atoms per DEBP moiety). If we subtract to the C/Pd ratio the contribution due to the dppe units (0.6 and 0.8 dppe units on average, corresponding to 15.6 and 20.8 carbon atoms, for the 1/1 and 1/2.5 [Pd(dppe)DEBP] materials, respectively, as evidenced by the P/Pd ratio shown in Table 2) we can calculate the number of DEBP moieties per Pd atoms in the two polymers; a DEBP/Pd ratio of approximately 3/1 and 4/1 was found for the 1/1 and 1/2.5 [Pd(dppe)DEBP] polymers, respectively. A chlorine termination of the Pd-complex is also evidenced with approximately 0.6–0.7 Cl atoms per Pd.

A comparison between XPS and IR data for the [Pd(dppe)DEBP] material suggests that when the Pd-complex is used, the formation of the metal–alkyne σ-bonding is followed by the polymerisation of DEBP via opening of the triple bond. The absence of the ≡C–H stretching mode in the IR spectra suggests the reaction of both triple bonds of DEBP with the formation of the polymer structure shown in Fig. 7. XPS data show that the palladium catalyst remains incorporated in the reaction product and may undergo a partial loss of the phosphine ligand; different Pd-sites are therefore found in the polymer. The modifications in the Pd3d signal suggest modifications taking place in the coordination sphere of palladium that may be due to phosphine loss and/or to coordination to the double bonds of the polymer chain, as already evidenced for ethynyltrimethylsilane [21], or for propargyl derivatives [22]. Two different kinds of structures can be hypothesised for the coordinated Pd-sites. If the phosphine moiety is only oxidised, but remains bonded to Pd, we obtain Pd-sites having the structure shown in Fig. 9(a). The Pd atoms can also undergo loss of the phosphine ligand and coordinate the double bonds of another polymer chain (Fig. 9(b)), as already evidenced for similar metal-containing polymers [18]. The high BE and low BE components evidenced in the Pd3d spectra, therefore, might correspond to Pd atoms bound to the phosphine ligand (Fig. 9(a)) and to the polyene double bonds of the polymer chains (Fig. 9(b)), respectively.

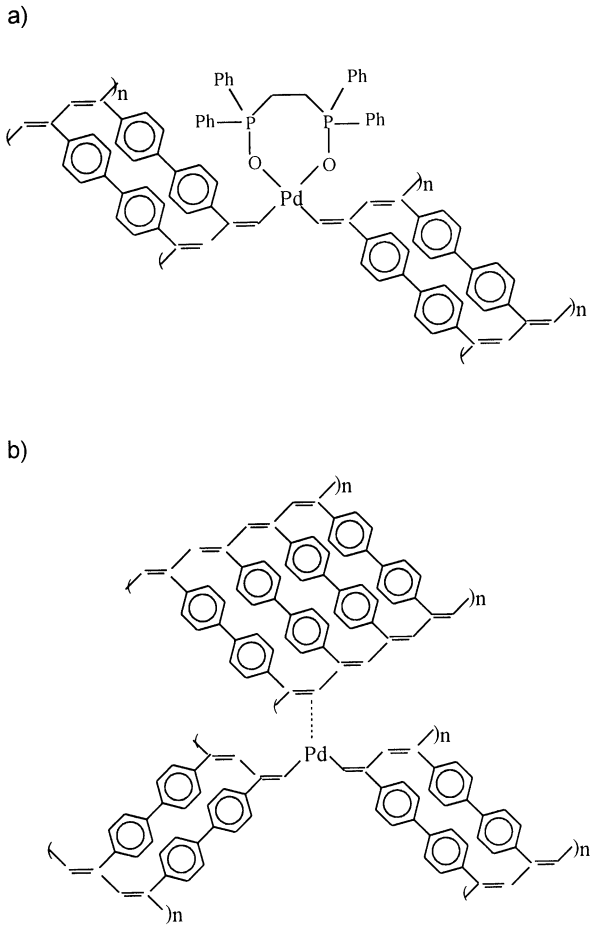

Fig. 9. Proposed chemical structure of the Pd-sites in [Pd(dppe)DEBP].

Though the structures here presented must be considered speculative, they account well for the experimental results obtained.

4. Conclusions

The synthesis of new polymeric all-*cis* square planar organometallic Pt- and Pd-complexes, having a zigzag structure and containing diphenylphospino ethane as bidentate ligand and diethynylbiphenyl as organic spacer, $[Pt(dppe)DEBP]_n$ and $[Pd(dppe)DEBP]_n$, was attempted by reacting the corresponding dichloro complexes, $[Pt(dppe)Cl_2]$ and $[Pd(dppe)Cl_2]$, with the dialkyne DEBP.

The Pt-material is actually a chlorine terminated oligomer, as evidenced by XPS spectroscopy, containing on average 4–5 Pt(dppe) units linked together by DEBP moieties through ≡C–Pt σ-bonds, producing a zigzag chain.

The reaction with $[Pd(dppe)Cl_2]$, on the other hand, is found to produce not only the formation of a C–Pd σ-bond, but also to induce the polymerisation of the DEBP molecule via opening of the triple bond. A polymer containing Pd-sites intercalated in the backbone is obtained.

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