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Iridium-catalyzed formation of *trans*-polyphenylacetylene by alkyne polymerization

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Abstract

The iridium(I) compounds $HIr(cod)(PR_3)_2$ (cod: 1,5-cyclooctadiene; PR_3: Ph_3, $P(p\text{-}MeOC_6H_4)_3$, $P(o\text{-}MeOC_6H_4)Ph_2$, $PCyPh_2$, PCy_2Ph) were employed as catalyst precursors for the polymerization of phenylacetylene. The polyene was formed as the major product with all the catalysts except the PCy_2Ph derivative, which promoted preferential formation of oligomers. In all cases the polymerization reactions were highly stereoselective, yielding 100% *trans*-polyphenylacetylene. From the catalytic mixtures the iridium(III) derivatives *fac*-$HIr(C{\equiv}CPh)_2(PR_3)_3$ (PR_3: PPh_3, $P(p\text{-}MeOC_6H_4)_3$) were isolated. The results of spectroscopic studies are also reported, which provide information on the evolution of the iridium precursors during the catalytic reaction.

Keywords: Iridium; Phosphines; Homogeneous catalysis; Alkynes; Polymerization

1. Introduction

Transition-metal catalyzed polymerization of terminal alkynes (see Scheme 1) has recently attracted considerable attention, due to the unique physico-chemical properties of the polymeric materials thus obtained. Photoconductivity, photoluminescence, oxygen permeability, humidity sensor, ferromagnetism and non-linear optical properties [1–4] are some of the properties of these polyenes, which make them potentially important materials for possible industrial applications. Accordingly, a variety of catalytic systems have been devised for the polymerization of monosubstituted acetylenes. Molybdenum and tungsten-based catalysts promote the formation of polyenes with high molecular weight, in some cases in a living manner [5–9]. More recently, nickel and palladium-based catalysts have been reported to be active in alkynes polymerization [10,11]. On the other hand, organorhodium derivatives form another class of catalytic systems which have been studied by several groups [12–20], obtaining excellent results both in terms of catalytic activity and of properties of the polyene produced—high stereoregularity, high molecular weight—and some of the reactions proceed in a living fashion.

We have recently been interested in investigating the catalytic properties of iridium organometallic derivatives in alkynes polymerization. Few reports are found in the literature on iridium catalysts which promote carbon–carbon bond formation of alkynes, and only oligomeric products are formed in the corresponding reactions [21–24]. The water soluble compounds

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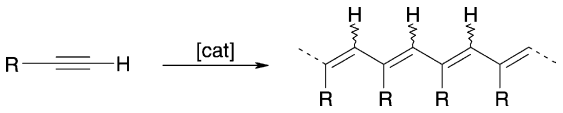


Scheme 1.

$IrCl(CO)(TPPTS)_2$ (TPPTS = $P(m\text{-}C_6H_4SO_3Na)_3$) promote the formation of a low molecular weight ($M_n = 2 \times 10^3$) polyphenylacetylene (PPA) in low yield [25], whereas in the reaction catalyzed by $IrH(CO)_2(PPh_3)_2$ the yield and M_n of the PPA formed were not reported [26].

In our previous studies we employed as catalyst precursors the dimeric compounds $[Ir(cod)X]_2$ (cod: 1,5-cyclooctadiene; X: Cl, OMe), the rhodium analogues of which are known to promote alkynes polymerization [27]. The organoiridium derivatives have been found to catalyze phenylacetylene polymerization at room temperature or lower, forming PPA with either *cis* or *trans* stereochemistry, according to the reaction temperature [28].

Here we report on the catalytic properties of the compounds $HIr(cod)(PR_3)_2$ (PR_3: PPh_3, $P(p\text{-}MeOC_6H_4)_3$, $P(o\text{-}MeOC_6H_4)Ph_2$, $PCyPh_2$, PCy_2Ph) in the polymerization of phenylacetylene. The evolution of the catalyst precursor in the presence of the monomer was followed by NMR spectroscopy, thus providing useful information on the course of the catalytic reaction.

2. Results and discussion

2.1. Catalytic reactions promoted by $HIr(cod)(PPh_3)_2$

The first experiments were aimed at testing the catalytic properties of $HIr(cod)(PPh_3)_2$ towards C–C bond formation, using phenylacetylene (PA) as monomer. By treating a boiling MeOH solution of the iridium derivative with the alkyne ([PA]/[Ir] = 100), formation of brown-red PPA was easily detected after few minutes, due to the dark red color of the reaction mixture, accompanied by precipitation of the higher molecular weight fraction of the polyene. Analysis of the reaction mixture by gas-chromatography revealed that the monomer consumption was slowing down with time and that after 5 h the reaction had stopped (see Table 1 entry 5).

The polyene was isolated by filtration, and NMR analysis of such material as well as of the final solution revealed that *trans*-PPA was the only product formed. Similar results were obtained in other solvents, such as THF, $CHCl_3$ and toluene, with the difference that, together with the polyene, formation of small amounts of the dimerization products (*E*)- and (*Z*)-butynenes was observed (see table). When the catalytic reaction was performed at lower temperature (40 °C, entries 1–3) the overall conversion lowered to 22–25%, and *trans*-PPA was the only product formed. At variance, an increase of the reaction temperature to 80 °C resulted in a higher overall yield, but formation of the

Table 1
Polymerization of phenylacetylene catalyzed by $HIr(cod)(PPh_3)_2$

Entry	*T* (°C)	Solvent	Conversion (%)	*trans*-PPA[a]	(*E*)-enyne[a]	(*Z*)-enyne[a]
1	40	THF	25	100	–	–
2	40	MeOH	22	100	–	–
3	40	$CHCl_3$	23	100	–	–
4	60	THF	47	91	9	–
5	60	MeOH	39	100	–	–
6	60	EtOH	37	93	4	3
7	60	$CHCl_3$	43	95	5	–
8	60	Toluene	44	75	20	5
9	80	Toluene	79	55	40	5
10	80	*i*-PrOH	51	70	24	6
11	110	Toluene	100	39	56	5

Experimental conditions: $[Ir] = 3.4 \times 10^{-3}$ mol l^{-1}; [sub] = 0.34 mol l^{-1}; [sub]/[Ir] = 100; Reaction time: 5 h.
[a] Product distribution (%).

dimeric products was enhanced more than polymerization; in refluxing toluene one of the oligomers, namely the (*E*)-enyne, became the main reaction product.

Therefore, in order to obtain a higher conversion of the polymeric product, a higher reaction temperature was not appropriate. We therefore examined the effect of the substituents of the phosphine ligands on the catalytic reaction.

2.2. Synthesis of the compounds HIr(cod)(L)$_2$

The catalyst precursor HIr(cod)(PPh_3)$_2$ was synthesized according to the procedure of Oro and coworkers [29]: a suspension of the iridium dimer [Ir(cod)(OMe)]$_2$ in methanol was reacted at room temperature with two equivalents of the phosphine, yielding after 3 h the desired product as a white solid.

The same procedure was successfully employed for the preparation of HIr(cod)(PR_3)$_2$, where PR_3: P(*p*-$MeOC_6H_4$)$_3$, P(*o*-$MeOC_6H_4$)Ph_2, $PCyPh_2$, PCy_2Ph (reaction 1). Selected spectroscopic data for the corresponding compounds are reported in Table 2.

$$\tfrac{1}{2}[\mathrm{Ir(cod)(OMe)}]_2 + 2\mathrm{PR_3} \rightarrow \mathrm{HIr(cod)(PR_3)_2} + \mathrm{CH_2O} \quad (1)$$

Attempts to prepare HIr(cod)(PR_3)$_2$ compounds with other phosphine ligands were unsuccessful. The synthesis of HIr(cod)(PEt_2Ph)$_2$ according to NMR data of the crude product gave the desired compound (^{31}P NMR δ + 0.87 (s), ^{1}H NMR δ − 14.07 (t, J_{PH} = 22.0 Hz)), which however we failed to isolate as a crystalline material; purification by chromatographic methods of the reaction mixture caused partial oxydation of the air-sensitive product.

We also tried to prepare the hydrido bis-phosphino compound with the ligand P(*o*-$MeOC_6H_4$)$_3$: in this case only small amounts of a monosubstituted compound were formed, the ^{31}P NMR spectrum ($CDCl_3$) of which consists in a singlet at δ + 10.50; in the ^{1}H NMR spectrum signals corresponding to coordinated cyclooctadiene at δ 4.69, 2.50 and 2.2–1.6 can be recognized, together with a singlet at 3.48 attributable to the *o*-methoxo group of the phosphine; no signals at high field to TMS are detectable. Although the presence of coordinated OMe group is not apparent from NMR, the infrared spectrum shows a strong signal at 1019 cm^{-1} which can be attributed to Ir-OMe stretching; in fact, as the product is contaminated by free P(*o*-$MeOC_6H_4$)$_3$, the resonance of the methoxo group could be hidden by that of the *o*-MeO group of the phosphine (3.75 ppm). Therefore, the compound obtained can be formulated as Ir(OMe)(cod)(P(*o*-$MeOC_6H_4$)$_3$).

We also planned to prepare the hydrido-bisphosphino compound with the ligand PCy_3, however, with such phosphine the reaction course was different. A methanol suspension of [Ir(cod)(OMe)]$_2$ and two equivalents of PCy_3 after 3 h under stirring produced a pale yellow solid, which was isolated. The ^{31}P NMR spectrum of the compound consists of a singlet at δ + 33.87, a chemical shift which suggests formation of an Ir(III) species; high field ^{1}H NMR resonances (doublet of triplets at δ − 12.16, J_{HP} = 14.7 Hz and J_{HH} = 4.4 Hz; triplet of triplets at −12.82, J_{HP} = 19.1 Hz, J_{HH} = 4.4 Hz) together with IR data (2060, 2035, 1925 and 1783 cm^{-1}) indicate formation of a hydrido-carbonyl compound. The ^{1}H NMR and IR data correspond to those reported by Oro and co-workers [30] for the compound

Table 2
Selected NMR data for HIr(cod)(PR_3)$_2$.

PR_3	^{31}P		^{1}H	
	P free	P coordinated	H-Ir	cod
PPh_3	−5.50	+7.31 (s)	−13.80(t, J_{HP} = 22.0)	3.78; 3.46; 1.80; 1.52
P(*p*-$MeOC_6H_4$)$_3$	−10.30	+2.33 (s)	−13.82(t, J_{HP} = 21.5)	3.73; 3.37; 1.78; 1.51
P(*o*-$MeOC_6H_4$)Ph_2[a]	−16.90	+3.89 (s)	−13.31(t, J_{HP} = 22.5)	4.49; 4.04; 2.19; 2.01; 1.81
$PCyPh_2$	−3.81	+10.42 (s)	−14.00(t, J_{HP} = 22.0)	3.44; 3.11; 2.2–0.5
PCy_2Ph[a]	+2.97	−0.43 (s)	−14.53(t, J_{HP} = 23.5)	4.61; 3.81; 2.6–0.9

Experimental conditions: $CDCl_3$ solutions, 25 °C. Chemical shifts expressed in ppm; coupling constants expressed in Hz.
[a] C_6D_6 solution.

mer-$H_3Ir(CO)(PCy_3)_2$; these authors obtained the carbonyl species together with *trans*-$H_5Ir(PCy_3)_2$; however, in our case the latter compound was not formed. We were intrigued to find the hydrido-carbonyl compound as the only reaction product, and repeated the synthesis in a non-alcoholic solvent, in order to avoid carbonylation: the reaction between $[Ir(cod)(OMe)]_2$ and PCy_3 was therefore repeated in $CDCl_3$ in order to follow its course by NMR. After 10 min at RT only one product was present in solution as revealed by ^{31}P NMR, which showed a singlet at $\delta + 15.32$ (PCy_3 free, +11.01). The ^1H NMR data correspond to those reported [29] for $Ir(OMe)(cod)(PCy_3)$: at δ 4.36 and 2.79 the signals of the vinyl protons of cod, at δ 2.2–1.1 the aliphatic resonances of coordinated cod as well as those for PCy_3, and at δ 3.46 a singlet attributed to the methoxo group.

This product was slowly transformed with time into another monophosphine derivative, which was the only species in solution after 24 h. By addition of pentane it was possible to isolate this product, which is probably the square planar compound $IrCl(cod)(PCy_3)$. Such hypothesis is made on the basis of the following data: ^{31}P NMR shows a singlet at $\delta + 14.48$; ^1H NMR spectrum has resonances attributable to coordinated cod and PCy_3 (δ 4.78 and 3.15, vinyl protons of cod; δ 2.2–1.1, aliphatic protons of cod and Cy), integrating for a PCy_3:cod ratio of 1; no hydridic signals are present, as well as resonances which can be assigned to coordinated OMe group; finally, the given formulation is in agreement with elemental analysis data. The compound $IrCl(cod)(PCy_3)$ is probably formed by substitution of the methoxo group of $Ir(OMe)(cod)(PCy_3)$ with a chloride deriving from the solvent. It cannot be excluded that the reaction proceeds via β-hydrogen elimination of the methoxo group to give the hydride, with subsequent fast substitution by a chloride: the latter reaction is known to occur when iridium hydrides are dissolved in chlorinated solvents [31].

By replacing $CDCl_3$ with either benzene or THF, from the reaction between $[Ir(cod)(OMe)]_2$ and PCy_3 only $Ir(OMe)(cod)(PCy_3)$ was obtained: in all the solvents employed it was never possible to detect in solution the formation of the desired compound $HIr(cod)(PCy_3)_2$, which is probably formed in methanol, but is not observed due to the fast reaction with the solvent to give *mer*-$H_3Ir(CO)(PCy_3)_2$.

2.3. Catalytic reactions promoted by $HIr(cod)(PR_3)_2$

The influence of the substituents of the phosphine ligands on the catalytic properties of $HIr(cod)(PR_3)_2$ in promoting the polymerization of phenylacetylene was examined using the compounds prepared with the ligands $P(p\text{-}MeOC_6H_4)_3$, $P(o\text{-}MeOC_6H_4)Ph_2$, $PCyPh_2$, PCy_2Ph. The results of the corresponding catalytic reactions are summarized in Table 3. When the ligand employed was an aromatic phosphine, no marked effect of the substituents on the aromatic rings was observed on the catalytic activity and product distribution, as well as on the molecular weight of the polyene obtained. For this series of precursors, the overall conversion was never higher than 50%, and formation of the main product *trans*-PPA was accompanied by small amounts of enynes. An improvement in the catalytic activity was obtained by employing the adduct with the ligand $PCyPh_2$, with the conversion raising to up to 68% and formation of the *trans*-polyene as the main product. At variance, with the catalyst precursor $HIr(cod)(PCy_2Ph)_2$ dimerization appeared to be the main reaction, and *trans*-PPA was only a minor product in the final mixture. In some of the catalytic reactions small amounts of the cyclotrimerization products, i.e. 1,3,5 and 1,2,4-triphenylbenzene, were also detected.

With regard to the polyene formed, in all cases stereoselective formation of *trans*-PPA was observed; with the exception of the reactions catalyzed by $HIr(cod)(PCy_2Ph)_2$, GPC molecular weight determination gave M_n values between 3000 and 5500, with rather low polydispersion values ($M_w/M_n = 1.4$–1.6).

In all the catalytic reactions a deactivation process was apparent, which was influenced to a large extent neither by the solvent, nor by the phosphine coordinated to iridium. Also when $HIr(cod)(PCyPh_2)_2$ was employed as catalyst precursor, the reaction, although initially faster than with other precursors, slowed down markedly after few hours, i.e. in THF at 60 °C the conversion, which after 5 h was 68%, did not exceed 75% after 24 h. With the same precursor, by changing the [monomer]/[Ir] ratio from the usual value of 100 to 50, a higher conversion was obtained (77% in 5 h), however the polyene obtained had a lower molecular weight ($M_n < 3000$).

Table 3
Polymerization of phenylacetylene catalyzed by $HIr(cod)(PR_3)_2$

Entry	PR_3	Solvents	Conversion (%)	Dimers[a]	PPA[a]	M_n	M_w/M_n
1	PPh_3	THF	47	9	91	3040	1.41
2	PPh_3	MeOH	39	–	100	3860	1.51
3	PPh_3	$CHCl_3$	43	5	95	4840	1.42
4	$P(p\text{-}MeOC_6H_4)_3$	THF	44	8	90	3220	1.60
5	$P(p\text{-}MeOC_6H_4)_3$	MeOH	38	5	95	5330	1.49
6	$P(p\text{-}MeOC_6H_4)_3$	$CHCl_3$	39	10	90	4330	1.64
7	$P(o\text{-}MeOC_6H_4)Ph_2$	THF	39	15	75	3390	1.53
8	$P(o\text{-}MeOC_6H_4)Ph_2$	MeOH	45	5	95	3440	1.58
9	$P(o\text{-}MeOC_6H_4)Ph_2$	$CHCl_3$	35	–	80	3690	1.59
10	$PCyPh_2$	THF	68	10	90	4120	1.47
11	$PCyPh_2$	MeOH	66	10	90	4480	1.49
12	$PCyPh_2$	$CHCl_3$	55	10	90	3660	1.65
13	PCy_2Ph	THF	48	70	30	2750	1.75
14	PCy_2Ph	MeOH	18	80	20	–	–
15	PCy_2Ph	$CHCl_3$	21	80	20	–	–

Experimental conditions: $[Ir] = 3.4 \times 10^{-3}$ mol l^{-1}; [sub] = 0.34 mol l^{-1}; [sub]/[Ir] = 100; $T = 60\,^{\circ}C$. Reaction time: 5 h.
[a] Product distribution (%). Other products: 1,3,5 and 1,2,4-triphenylbenzene.

The effect of an addition of 1,5-cyclooctadiene to the reaction mixture was also tested: when the reaction with $HIr(cod)(PPh_3)_2$ was performed in THF at 60 °C with excess cod ([cod]/[Ir] = 5) the conversion after 5 h was 51%, to be compared with 47% in the absence of added diene, i.e. an almost negligible effect of added diene to the catalytic reaction.

2.4. Isolation and characterization of iridium-alkynyl complexes

The polyphenylacetylene produced in the catalytic reactions was routinely isolated in order to determine its stereochemistry and molecular weight. As the polyene is insoluble in methanol, when the reactions were performed in such solvent, the solid was recovered by filtration. At variance, PPA was generally soluble in other solvents employed ($CHCl_3$, THF, C_6H_6), therefore addition of an excess of methanol at the end of the reaction caused precipitation of the polyene, which was then recovered by filtration. In a typical reaction performed with $HIr(cod)(PPh_3)_2$ as catalyst precursor, the red-brown solid obtained was analyzed by ^1H and ^{13}C NMR as well as GPC. In the ^1H NMR spectrum, aside the very broad resonance at δ 7.2 of *trans*-PPA, the typical signals of the *cis* stereoisomer [32] were never detected. Interestingly, in $CDCl_3$ at high field to TMS a multiplet was observed, indicating that an iridium–phosphine compound was also present in the isolated solid. Such resonance is a doublet of triplets at $\delta - 12.12$, with $J_{PH} = 139.6$ Hz typical of a hydride *trans* to P, and $J_{PH} = 17.6$ Hz attributable to coupling of a hydride *cis* to two phosphorus atoms. The ^{31}P NMR spectrum revealed the presence of a doublet at $\delta - 6.08$ and a triplet at $\delta - 23.72$ of relative intensity 2:1 ($J_{PP} = 13.9$ Hz), which indicate the presence of three phosphines coordinated in a *fac*-configuration. The aromatic resonances in the ^{13}C NMR spectrum were almost completely obscured by those of *trans*-PPA (130–126 ppm) present as a major compound in the solid mixture, whereas two signals were clearly detectable at higher field, i.e. a singlet at δ 110.5 and a doublet of doublets at δ 95.9 ($J_{CPtrans} = 24.8$ Hz, $J_{CPcis} = 13.8$ and 0 Hz) attributable to the Cβ and Cα of Ir-C≡C–Ph, respectively. The presence of the iridium-alkynyl mojety was confirmed by the infrared spectrum, where aside the Ir-H stretching at 2095 cm^{-1} two narrow bands appear at 2142 and 2119 cm^{-1}, respectively. Therefore, the compound isolated together with the polyene was identified as the iridium(III) derivative *fac*-$HIr(C{\equiv}CPh)_2(PPh_3)_3$. Such iridium(III) coordinatively saturated compound is stable in $CDCl_3$ solution under an inert atmosphere for over 1 week, and does not behave as catalyst precursor, as confirmed by its inactivity towards phenylacetylene in experimental conditions similar

to those employed in routine polymerization reactions. Therefore, the iridium fraction which forms the trisphosphino derivative does not participate to the catalytic reaction.

Formation of the analogous compound HIr(C≡CPh)$_2$(P(*p*-MeOC$_6$H$_4$)$_3$ was observed in the catalytic reactions employing the precursor with the corresponding phosphine: this compound had ^{31}P NMR signals in $CDCl_3$ consisting in a doublet at $\delta - 10.93$ and a triplet at -27.54 ($J_{PP} = 14.8$ Hz), whereas in the ^{1}H NMR spectrum the hydridic signal appeared as a doublet of triplets at $\delta - 12.29$, with $J_{HPtrans} = 140.9$ and $J_{HPcis} = 17.6$ Hz.

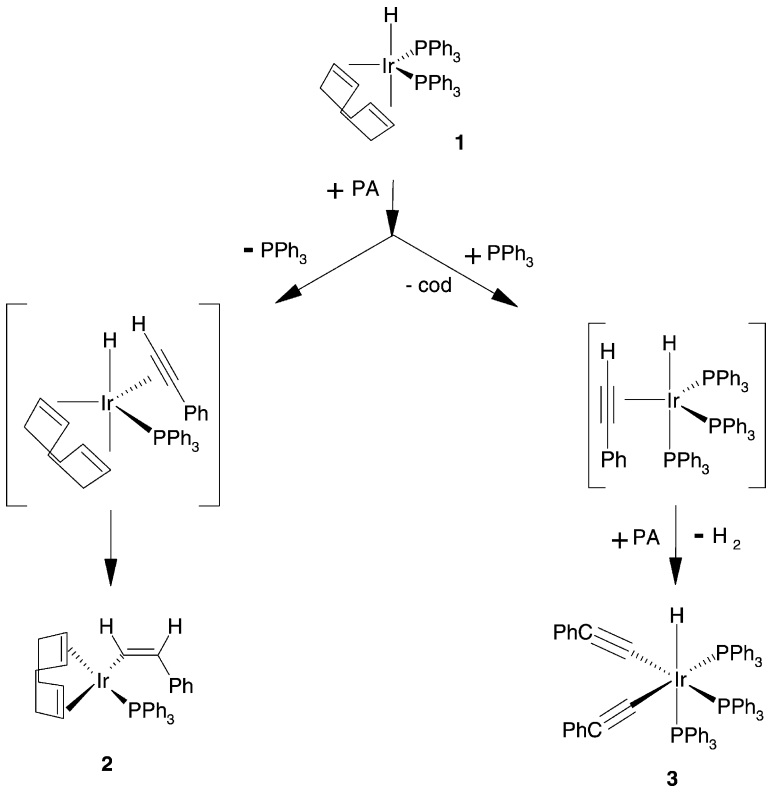
At variance, a similar species was not present in the isolated solid when the catalyst precursor was HIr(cod)(PCyPh$_2$)$_2$: in this case neither ^{31}P signals nor high field resonances in the ^{1}H NMR spectrum were detected. However, we believe that the bis-alkynyl compound is formed also in this case, but its lower concentration (suggested by higher catalytic activity) and/or higher solubility are the possible reasons why it is not detected in the methanol insoluble fraction.

Finally, the product isolated at the end of the reactions promoted by HIr(cod)(PCy$_2$Ph)$_2$ contained an iridium–phosphine species which showed only one resonance in the ^{31}P NMR spectrum ($\delta - 5.40$ (s)): this compound had no coordinated hydride according to ^{1}H NMR and IR spectra, however in the latter a band at 2156 cm^{-1} suggests the presence of an Ir–C≡C–Ph moiety. The different catalytic behaviour of HIr(cod)(PCy$_2$Ph)$_2$ in comparison to the other precursors might very well be related to a different chemistry of the iridium species in solution, probably due to the increased bulk of the phosphine ligand.

2.5. Spectroscopic studies

A series of spectroscopic studies was performed on the evolution of the catalyst precursors in the presence of phenylacetylene, in order to shed light on the formation of iridium derivatives during the catalytic reaction, as well as on their role in the polymerization catalysis. In the first experiment, a $CDCl_3$ solution of HIr(cod)(PPh$_3$)$_2$ (**1**) was treated with two equivalents of phenylacetylene, by addition of the suitable amount of a solution of the alkyne in $CDCl_3$. After the addition the pale yellow solution turned bright yellow and then orange, and after 30 min it had become red. The reaction, which was monitored with time by ^{1}H and ^{31}P NMR, appeared to be slow at 25 °C: after 30 min the major component of the mixture, according to ^{31}P NMR, was still the starting compound (**1**), and only small amounts of two new compounds were detected, appearing as a broad signal at $\delta - 11$ (**2**) and the set of signals corresponding to HIr(C≡CPh)$_2$(PPh$_3$)$_3$ (**3**). In the ^{1}H NMR spectrum the hydridic signals of **1** and **3** were present at high field to TMS, whereas in the low field region broad signals appeared between 3.9 and 3.3 ppm, which partially overlapped with the resonances of cod vinyl protons of **1**; moreover, small signals of free cyclooctadiene were visible. By following the reaction with time an increase in the signals of **2** and **3** was noticed in the ^{31}P NMR spectrum, with parallel increase of intensity of the broad signals in the vinyl region of the ^{1}H NMR spectrum. After 3 h from the monomer addition, a series of spectra recorded at lower temperatures revealed that the phosphorus broad signal became a narrow singlet ($\delta - 11.47$) at -20 °C; accordingly, in the ^{1}H NMR spectrum the broad signals in the vinyl region resolved into two signals similar to those of coordinated cod of **1**: such resonances at -20 °C have chemical shifts of 3.64 and 3.28 ppm. Moreover, even at low temperature no signals are present at high field of TMS, besides those of **1** and **3**, indicating the absence of a hydride coordinated to iridium for species **2**. Unfortunately, the stability of **2** in solution did not allow to collect a ^{13}C NMR spectrum, as decomposition occurred during the 12 h necessary to obtain a reasonable signal/noise ratio. Compound **2** cannot be unequivocally identified on the basis of the available spectral data, however we can reasonably propose that compound **2** is the Ir(I) tetracoordinated species Ir(cod)(CH=CHPh)(PPh$_3$), formed via insertion of the alkyne into the iridium-hydride bond. The dependence of the NMR spectra on temperature is probably due to exchange of the coordinated phosphine with traces of the free ligand, which is certainly present in solution. The proton signals of the CH=CHPh [24,33] are most likely covered by the resonances of the aromatic protons of the three iridium compounds which are present in the reaction mixture.

In a second experiment, a higher excess of the monomer was employed ([PA]/[Ir] = 10) with the aim to increase formation of **2** and **3**, and to observe the formation of the polyene. ^{31}P NMR analysis of the mixture revealed that formation of **2** and **3** at the



Scheme 2.

expenses of **1** was nearly complete after 1 h; on the other hand, the ^{1}H NMR spectrum showed, together with the signals of the three iridium compounds, the broad resonance of *trans*-PPA.

From the results of the spectroscopic investigations above reported, the evolution of the catalytic precursor **1** in the presence of the monomer is likely to follow the course described in Scheme 2. Part of the iridium centers undergoes dissociation of one phosphine with formation of a square planar intermediate, which then coordinates phenylacetylene in a π-fashion. Insertion of the alkyne into the iridium-hydride bond produces the vinyl compound **2**, which is likely to be the initiator of the catalytic reaction. Another fraction of the initial compound **1** picks up the phosphine released in the former sequence as well as one molecule of the monomer, with concomitant loss of cyclooctadiene: the resulting π-alkyne intermediate eliminates H_2, presumably *via* alkyne oxydative addition. Finally, oxidative addition of a second molecule of monomer produces the iridium(III) derivative **3**. The latter compound is stable in deoxygenated solution for several days, and it is catalytically inactive as demonstrated in an experiment performed by employing isolated **3** as catalyst precursor.

2.6. Remarks on the reaction mechanism

Organorhodium compounds have been known for the last 20 years to promote monosubstituted alkynes polymerization with high catalytic activity, in all cases with selective formation of the corresponding *cis*-polyene. Investigations on the behavior of rhodium-phosphine catalytic systems have demonstrated that the presence of coordinated diolefin as well as its nature are crucial factors for the polymerization reaction: as a matter of fact, substitution of the diene with two monoolefins leads to complete

loss of polymerization catalysis. Such findings appear to be also related to the catalytic properties of the organoiridium precursors $HIr(cod)(PR_3)_2$, where the presence of coordinated diene appears to be essential for the catalytic reaction. With regard to iridium-based catalysts, the dimeric compounds $[Ir(cod)X]_2$ (X: Cl, OMe) [28] show a similar behavior, with substitution of cyclooctadiene with cyclooctene resulting in a complete suppression of the polymerization reaction.

When this manuscript was nearly completed we became aware of a recent paper by Masuda and coworkers [34], which also reports on iridium-catalyzed polymerization of phenylacetylene. This group investigated on multi-component catalysts of the type $[Ir(cod)Cl]_2$/norbornadiene/PPh_3/$Ph_2C{=}C(Ph)Li$, and found that the coordinated diene has a fundamental role in the polymerization catalysis.

On the other hand, an important difference between rhodium/phosphine and iridium/phosphine catalysts is the stereochemistry of the polymerization reaction: whereas rhodium promotes the selective formation of *cis*-polyphenylacetylene, with the iridium-phosphine compounds the *trans*-polyene is obtained.

In principle, thermal isomerization might be considered to be responsible for such difference, as the catalytic reactions with iridium catalysts require a higher temperature (60 °C) than those with rhodium (20 °C or lower). Thermal *cis-trans* polyene isomerization is known to occur at high reaction temperature, however the temperatures reported in the literature [1,35] for such process are higher than those of our catalytic reactions. We have tested the effect of a thermal treatment of *cis*-polyene solutions in the same experimental conditions used for the catalytic reactions, and the result was that only a small amount (10–15%) of isomerization occurred. Such findings indicate that the polyene obtained in our catalytic reactions at 60 °C has 100% of *trans* geometry, as any amount of *cis* isomer formed would not completely disappear by isomerization, and therefore it should be detectable in the final products.

Noteworthy, most of the catalytic systems which promote alkynes polymerization either form the *cis*-polyene (rhodium-based catalysts) or give rise to polymers with variable *cis-trans* distribution along the main chain (molibdenum-based catalysts); only some examples of tungsten compounds are reported to promote stereoselective polymerization to the *trans*-polyene [5,36]. The interest towards *trans*-acetylenes lies on the physico-chemical properties of such polymers, particularly the non-linear optical properties, which have been experimentally demonstrated to be enhanced with increasing *trans*-conjugation length in these polyenes [3].

In spite of the difference in the geometry of the polyene obtained, it would be reasonable to believe that the polymerization reaction catalyzed by $HIr(cod)(PR_3)_2$ proceeds via the insertion mechanism proposed for rhodium-based catalysts [14]: the stereochemistry observed might be the result of a *cis*-insertion followed by an iridium-catalyzed isomerization, or possibly of a *trans*-insertion as proposed by Zhang and Yang for palladium-based catalysts [37].

On the other hand, one cannot rule out the possibility that the catalytic reaction proceeds *via* a different mechanism. Even if metathesis, which is operative for molibdenum-promoted polymerization, would in principle seem unlikely for the iridium catalysts, however several iridium–carbenes are known, which are possible initiators of reactions which follow a metathesis path; moreover, in the literature are reported [38–40] some examples of iridacyclobutenes, similar to reaction intermediates involved in the metathesis mechanism.

3. Conclusions

The compounds $HIr(cod)(PR_3)_2$ (PR_3: PPh_3, P(*p*-$MeOC_6H_4)_3$, P(*o*-$MeOC_6H_4)Ph_2$, $PCyPh_2$) were successfully employed as catalyst precursors for the polymerization of phenylacetylene. The catalytic reactions are highly selective, as only *trans*-polyphenylacetylene is formed together with small amounts of oligomerization products. The catalytic activity suffers from a deactivation process, which stops the reaction after a few hours. The evolution of the catalyst precursor in the course of the catalytic reaction has been investigated by spectroscopic studies, the results of which, together with the isolation of catalytically inactive Ir(III) alkynyl derivatives, allowed us to gain useful information both on the nature of catalytically active species and on the deactivation process.

4. Experimental section

4.1. General

All the reactions and manipulations were routinely performed under an argon atmosphere using standard Schlenk tube techniques.

Tetrahydrofuran (THF) was distilled over sodium benzophenone ketyl just before use; benzene and dichloromethane were distilled over CaH_2, methanol was distilled over CaO, and they were stored under an inert atmosphere. Naphtalene was purified by recrystallization from ethanol. All the other chemicals were reagent grade and were used as received by commercial suppliers.

The compounds $[Ir(cod)(OMe)]_2$ [28] and $HIr(cod)(PPh_3)_2$ [29] were prepared according to the procedures reported in the literature.

4.2. Instrumental

^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 chemical shifts are reported relative either to tetramethylsilane ($CDCl_3$ solutions) or to solvent peak (C_6D_6 solutions); ^{13}C chemical shifts are reported relative to solvent peak (δ 77.0 for $CDCl_3$, 128.0 for C_6D_6); ^{31}P chemical shifts are reported relative to external 85% H_3PO_4, with downfield shift positive. Infrared spectra were recorded in Nujol mull on a Perkin-Elmer System 2000 FT-IR spectrometer.

Chemical yields of the catalytic reactions were determined by GLC on a Carlo Erba 6000 VEGA Series 2 equipped with a SE30 column, using naphtalene as internal standard.

Molecular weight distributions of the polymers were determined by GPC in $CHCl_3$ at 25 °C on a Milton Roy CM4000 instrument using a UV spectrometer detector operating at 270 nm, equipped with CHROMPACK Microgel-5 columns.

4.3. Preparation of $HIr(cod)(P(p\text{-}MeOC_6H_4)_3)_2$

A suspension of 80 mg (0.12 mmol) of $[Ir(cod)(OMe)]_2$ in 24 ml of methanol was treated with 170 mg (0.48 mmol) of $P(p\text{-}MeOC_6H_4)_3$. The resulting mixture was stirred at room temperature for 5 h, yielding a white solid which was filtered, washed with methanol and dried under vacuum. Yield 68%.

IR (Nujol): 2109 cm^{-1} (Ir-H). ^{31}P $\{^1H\}$NMR ($CDCl_3$, 25 °C): $\delta + 2.33$ s.

^1H NMR ($CDCl_3$, 25 °C): δ 7.19 (m, 12H, *m*-Ar); 6.64 (d, 12H, *o*-Ar); 3.75 (s, 18H, OMe); 3.73 (bs, 2H, C=CH); 3.37 (bs, 2H, C=CH); 1.78 (m, 4H, CH_2); 1.51 (m, 4H, CH_2); −13.82 (t, 1H, Ir-H, $J_{HP} = 21.5$ Hz).

4.4. Preparation of $HIr(cod)(P(o\text{-}MeOC_6H_4)Ph_2)_2$

A suspension of 80 mg (0.12 mmol) of $[Ir(cod)(OMe)]_2$ in 26 ml of methanol was treated with 140 mg (0.48 mmol) of $P(o\text{-}MeOC_6H_4)Ph_2$. The resulting mixture was stirred at room temperature for 6 h, yielding a white solid which was filtered, washed with methanol and dried under vacuum. Yield 48%.

IR (Nujol): 2134 cm^{-1} (Ir-H). ^{31}P $\{^1H\}$NMR (C_6D_6, 25 °C): $\delta + 3.89$ s.

^1H NMR (C_6D_6, 25 °C): δ 7.8–6.4 (m, 28H, Ar); 4.49 (bs, 2H, C=CH); 4.04 (bs, 2H, C=CH); 2.95 (s, 6H, OMe); 2.19 (bm, 2H, CH); 2.01 (bm, 2H, CH_2); 1.81 (bm, 4H, CH_2); −13.31 (t, 1H, Ir-H, $J_{HP} = 22.5$ Hz).

4.5. Preparation of $HIr(cod)(PCyPh_2)_2$

A suspension of 100 mg (0.15 mmol) of $[Ir(cod)(OMe)]_2$ in 32 ml of methanol was treated with 161 mg (0.60 mmol) of $PCyPh_2$. The resulting mixture was stirred at room temperature for 5 h, yielding a white solid which was filtered, washed with methanol and dried under vacuum. Yield 75%.

IR (Nujol): 2127 cm^{-1} (Ir-H). ^{31}P $\{^1H\}$NMR ($CDCl_3$, 25 °C): $\delta + 10.42$ s.

^1H NMR ($CDCl_3$, 25 °C): δ 7.3–6.8 (m, 20H, Ar); 3.44 (bs, 2H, C=CH); 3.11 (bs, 2H, C=CH); 2.2–0.5 (multiplets, 30H, CH_2 (cod) and Cy); −14.00 (t, 1H, Ir-H, $J_{HP} = 22.0$ Hz).

4.6. Preparation of $HIr(cod)(PCy_2Ph)_2$

A suspension of 66 mg (0.10 mmol) of $[Ir(cod)(OMe)]_2$ in 15 ml of methanol was treated with 110 mg (0.40 mmol) of PCy_2Ph. The resulting mixture was stirred at room temperature for 3 h, yielding a pale

yellow solid which was filtered, washed with methanol and dried under vacuum. Yield 48%.

IR (Nujol): 2142 cm^{-1} (Ir-H). ^{31}P $\{^1H\}$NMR (C_6D_6, 25 °C): δ − 0.43 s.

^1H NMR (C_6D_6, 25 °C): δ 7.6–7.0 (m, 10H, Ar); 4.61 (bm, 2H, C=CH); 3.81 (bm, 2H, C=CH); 2.6–0.9 (multiplets, 52H, CH_2 (cod) and Cy); −14.53 (t, 1H, Ir-H, J_{HP} = 23.5 Hz).

4.7. Preparation of mer-$H_3Ir(CO)(PCy_3)_2$

A suspension of 100 mg (0.15 mmol) of [Ir(cod)-(OMe)]$_2$ in 32 ml of methanol was treated with 168 mg (0.60 mmol) of PCy_3. The resulting mixture was stirred at room temperature for 3 h, yielding a pale yellow solid which was filtered, washed with methanol and dried under vacuum. Yield 79%.

IR (Nujol): 2060, 2035, 1925 cm^{-1} (Ir-H); 1783 cm^{-1} (CO).

^{31}P $\{^1H\}$NMR ($CDCl_3$, 25 °C): δ + 33.87 s. ^1H NMR ($CDCl_3$, 25 °C): δ 2.4–1.1 (multiplets, 66H, Cy); −12.16 (dt, 2H, Ir-H, J_{HP} = 14.7 Hz, J_{HH} = 4.4 Hz); −12.82 (tt, 1H, Ir-H, J_{HP} = 19.1 Hz, J_{HH} = 4.4 Hz).

4.8. Catalytic reactions in Schlenk tube

A typical procedure is described as follows: a solution of $HIr(cod)(PR_3)_2$ (0.017 mmol) and of the GLC standard naphtalene (100 mg) in 5.0 ml of THF (or other solvent of choice) was heated to the desired reaction temperature under inert atmosphere. Then 173 mg of phenylacetylene (1.7 mmol, [sub]/[Ir] = 100) were added. Samples were withdrawn from the reaction mixture at time intervals, and disappearance of the monomer was followed with time by GLC. The final reaction mixture was treated with an excess of methanol to precipitate the polymeric products; the resulting red-brown solid was filtered, washed repeatedly with methanol and dried in vacuo.

4.9. Determination of product distribution and stereochemistry

The stereochemistry of the polyphenylacetylene obtained was determined by ^1H and ^{13}C NMR. For *cis-transoid* polyphenylacetylene: ^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=*C*H), 127.8 and 127.5 (*o*- and *m*-Ar), 126.7 (*p*-Ar). For *trans*-polyphenylacetylene: ^1H NMR ($CDCl_3$) δ 7.2 (very broad); ^{13}C $\{^1H\}$ NMR ($CDCl_3$) δ 128 (very broad).

The yields of (*E*)-1,4-diphenyl-1-butyn-3-ene and (*Z*)-1,4-diphenyl-1-butyn-3-ene were determined by ^1H NMR ($CDCl_3$) by integration of the signals of the corresponding vinyl protons. For the (*E*) isomer: δ 7.09 (d) and 6.43 (d) (J_{HH} = 16.3 Hz); for the (*Z*) isomer: δ 6.75 (d) and 5.97 (d) (J_{HH} = 11.9 Hz).

Formation of 1,3,5-triphenylbenzene and 1,2,4-triphenylbenzene was detected by ^1H NMR, whereas the relative amount of the two isomers was determined by integration of the ^{13}C NMR signals of the quaternary carbon atoms. For 1,3,5-triphenylbenzene: ^1H NMR ($CDCl_3$) δ 7.74, 7.46, 7.37; ^{13}C NMR ($CDCl_3$) δ 142.3 and 141.1 (quaternary carbons), 129–125 (CH). For 1,2,4-triphenylbenzene: ^1H NMR ($CDCl_3$) δ 7.84, 7.77, 7.46, 7.37; ^{13}C NMR ($CDCl_3$) δ 141.4, 141.0, 140.9, 140.5, 140.3, 139.5 (quaternary carbons), 129–125 (CH).

4.10. Determination of polyene molecular weight

Determination of molecular weights via GPC was performed on freshly prepared chloroform solutions of the polymer. The number average molecular weight (M_n) and polydispersion index (M_w/M_n) of the polymers were calculated on calibrations using the following polystyrene standards: M_p = 21,000 (Polymer Laboratories), M_p = 9200 (Polysciences), M_p = 4000 (Aldrich), M_p = 980 (Polymer Laboratories).

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References

[1] R. D'Amato, T. Sone, M. Tabata, Y. Sadahiro, M.V. Russo, A. Furlani, Macromolecules 31 (1998) 8660.

[2] Yu.P. Yampolskii, A.P. Korikov, V.P. Shantarovich, K. Nagai, B.D. Freeman, T. Masuda, M. Teraguchi, G. Kwak, Macromolecules 34 (2001) 1788.
[3] J.L. Bredas, C. Adant, P. Tackx, A. Persoons, Chem. Rev. 94 (1994) 243.
[4] B.R. Weinberger, E. Ehrenfreund, A. Pron, A.J. Heeger, A.G. MacDiarmid, J. Chem. Phys. 72 (1980) 4749.
[5] J. Kunzler, V. Percec, J. Polym. Sci. Part A: Polym. Chem. 28 (1990) 1221.
[6] S. Hayano, T. Masuda, Macromolecules 31 (1998) 3170.
[7] T. Masuda, S. Hayano, E. Iwawaki, R. Nomura, J. Mol. Catal. A: Chem. 133 (1998) 213.
[8] T.A. Vijayaraj, G. Sundararajan, Organometallics 16 (1997) 4940;
G. Bhukta, R. Ramanujachary, G. Sundararajan, J. Organomet. Chem. 601 (2000) 16.
[9] M.B. Mula, A.J. Beaumont, K.O. Doyle, M.L. Gallagher, A.D. Rooney, J. Mol. Catal. A: Chem. 148 (1999) 23.
[10] R. Wang, F. Belanger-Gariepy, D. Zargarian, Organometallics 18 (1999) 5548.
[11] X. Zhan, M. Yang, J. Mol. Catal. A: Chem. 169 (2001) 27; X. Zhan, M. Yang, H. Sun, J. Mol. Catal. A: Chem. 169 (2001) 63.
[12] A. Furlani, C. Napoletano, M.V. Russo, A. Camus, N. Marsich, J. Polym. Sci. Part A 27 (1989) 75.
[13] M. Tabata, W. Yang, K. Yokota, J. Polym. Sci. Part A: Polym. Chem. 32 (1994) 1113.
[14] Y. Kishimoto, P. Eckerle, T. Miyatake, T. Ikariya, R. Noyori, J. Am. Chem. Soc. 116 (1994) 12131;
Y. Kishimoto, P. Eckerle, T. Miyatake, M. Kainosho, A. Ono, T. Ikariya, R. Noyori, J. Am. Chem. Soc. 121 (1999) 12035.
[15] Y. Misumi, T. Masuda, Macromolecules 31 (1998) 7572;
K. Kanki, Y. Misumi, T. Masuda, Macromolecules 32 (1999) 2384.
[16] Y. Goldberg, H. Alper, J. Chem. Soc., Chem. Commun. (1994) 1209.
[17] H. Katayama, K. Yamamura, Y. Miyaki, F. Ozawa, Organometallics 16 (1997) 4497.
[18] J. Yao, W.T. Wong, G. Jia, J. Organomet. Chem. 598 (2000) 228.
[19] M. Falcon, E. Farnetti, N. Marsich, J. Organomet. Chem. 629 (2001) 187.
[20] P. Mastrorilli, C.F. Nobile, A. Rizzuti, G.P. Suranna, D. Acierno, E. Amendola, J. Mol. Catal. A: Chem. 178 (2002) 35.
[21] C.S. Chin, G. Won, J. Song, Bull. Korean Chem. Soc. 15 (1994) 961.
[22] S.-I. Lee, S.-C. Shim, T.-J. Kim, J. Polym. Sci. Part A: Polym. Chem. 34 (1996) 2377.
[23] T. Ohmura, S. Yorozuya, Y. Yamamoto, N. Miyaura, Organometallics 19 (2000) 365.
[24] C.S. Chin, H. Lee, H. Park, M. Kim, Organometallics 21 (2002) 3889.
[25] K.-S. Joo, S.Y. Kim, C.S. Chin, Bull. Korean Chem. Soc. 18 (1997) 1296.
[26] C.K. Brown, D. Georgiou, G. Wilkinson, J. Chem. Soc. (A) (1971) 3120.
[27] M. Tabata, T. Sone, Y. Sadahiro, Macromol. Chem. Phys. 200 (1999) 265.
[28] M. Marigo, N. Marsich, E. Farnetti, J. Mol. Catal. A: Chem. 187 (2002) 169.
[29] M.J. Fernandez, M.A. Esteruelas, M. Covarrubias, L.A. Oro, J. Organomet. Chem. 316 (1986) 343.
[30] M.J. Fernandez, M.A. Esteruelas, M. Covarrubias, L.A. Oro, M.C. Apreda, C. Foces-Foces, F.H. Cano, Organometallics 8 (1989) 1158.
[31] E. Farnetti, G. Nardin, M. Graziani, J. Chem. Soc., Chem. Commun. (1989) 1264.
[32] A. Furlani, S. Licoccia, M.V. Russo, A. Camus, N. Marsich, J. Polym. Sci. Part A: Polym. Chem. 24 (1986) 991.
[33] H.E. Selnau, J.S. Merola, Organometallics 12 (1993) 3800.
[34] K. Kanki, Y. Misumi, T. Masuda, J. Polym. Sci. Part A: Polym. Chem. 40 (2002) 1075.
[35] F. Ishii, S. Matsunami, M. Shibata, T. Kakuchi, J. Polym. Sci. Part B: Polym. Phys. 37 (1999) 16.
[36] T. Szymanska-Buzar, J. Mol. Catal. A 123 (1997) 113.
[37] X. Zhan, M. Yang, J. Mol. Catal. A: Chem. 169 (2001) 57.
[38] J.C. Calabrese, D.C. Roe, D.L. Thorn, T.H. Tulip, Organometallics 3 (1984) 1223.
[39] J.M. O'Connor, L. Pu, S. Woolard, R.K. Chadha, J. Am. Chem. Soc. 112 (1990) 6731.
[40] Y.-C. Cheng, Y.-K. Chen, T.-M. Huang, C.-I. Yu, G.-H. Lee, Y. Wang, J.-T. Chen, Organometallics 17 (1998) 2953.