

Polymerization of phenylacetylene catalyzed by organoiridium compounds

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Abstract

The compounds $[\text{Ir}(\text{cod})\text{X}]_2$ (cod = 1,5-cyclooctadiene; X = Cl, OMe) catalyze the polymerization of phenylacetylene, with negligible formation of oligomeric products. At variance, the monoolefin analogue $[\text{Ir}(\text{cot})_2\text{Cl}]_2$ (cot = cyclooctene) only promotes alkyne cyclotrimerization. The polymerization reaction proceeds in various solvents such as tetrahydrofuran (THF), chloroform and benzene, but it is most favored when using NEt_3 as reaction medium.

The role of the diene in the catalytic reaction is investigated, also in relation to a deactivation process of the catalyst with time. Spectroscopic studies of the catalytic reaction indicate the formation of monomeric iridium-solvent adducts, which are likely to be the initiators of the polymerization reaction. A possible reaction mechanism is proposed, according to the data reported in the literature and the results of the present investigation.

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1. Introduction

In the last years, one of the main fields of research in homogeneous catalysis has been represented by the development of catalytic systems for the polymerization of unsaturated substrates, with especial interest towards formation of π -conjugated polymers. The attention towards such compounds is due to their unique physico-chemical properties, which make them promising materials for several applications. Among such polymeric materials, polyacetylenes have drawn considerable interest because of their physico-chemical characteristics and novel properties such as conductivity, oxygen permeability, humidity

sensor, ferromagnetism and non-linear optical properties.

Polymerization of unsubstituted acetylene can be promoted by several catalytic systems, but the applicability of such reaction is limited by the characteristics of polyacetylene, which is a rather unstable, poorly soluble and hardly processable material.

Polymerization of monosubstituted acetylenes with head-to-tail regiochemistry can in principle produce four isomeric polyenes (Fig. 1), depending on the configuration of the C=C bond, as well as on the conformation (cisoidal or transoidal) of the single carbon-carbon bond of the main chain. These monomers are polymerized in the presence of catalysts belonging to two main classes: (i) compounds of group 6 metals, and (ii) rhodium organometallic derivatives. The first class includes chiefly molybdenum and tungsten complexes [1–4] which promote

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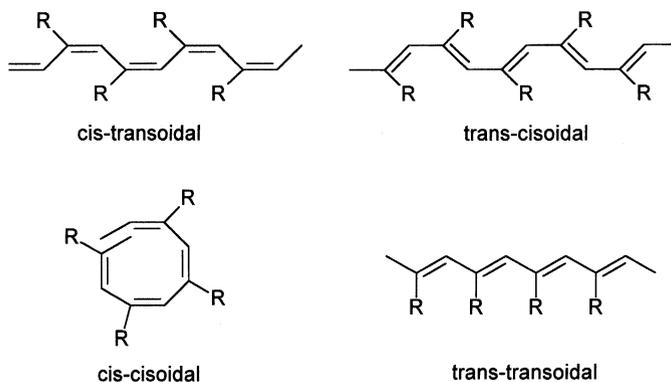


Fig. 1. Stereoisomers of polyphenylacetylenes.

polymerization via a metathesis mechanism; some of these systems are capable of polymerizing disubstituted alkynes as well. Rhodium-based catalysts [5–11] promote stereoselective polymerization of monosubstituted acetylenes to give the polyene with *cis*-transoidal geometry, in some cases in a living fashion; such polymerization reactions have been demonstrated to proceed via an insertion mechanism [7]. Some nickel and palladium catalysts active in alkyne polymerization [12–14] can be included in the same class as rhodium derivatives, as the related reactions appear to proceed via the same mechanism.

In spite of excellent catalytic properties displayed in other catalytic reactions, iridium-based catalysts have been so far neglected in the field of alkyne polymerization. Only few papers about C–C bond formation reactions of alkynes catalyzed by iridium derivatives are present in the literature, and they only report on formation of oligomeric products [15–17], with the exception of two papers where polymerization products are also mentioned [18,19].

Following our recent studies on rhodium catalysts for alkyne polymerization [20], we were interested in investigating the properties in such field of iridium compounds, starting from the simple dimeric species $[\text{IrL}_2\text{X}]_2$ ($\text{L}_2 = \text{cod}, (\text{cot})_2$; $\text{X} = \text{Cl}, \text{OMe}$). Here we report that the compounds $[\text{Ir}(\text{cod})\text{Cl}]_2$ and $[\text{Ir}(\text{cod})(\text{OMe})]_2$ are effective in promoting phenylacetylene polymerization, and although such catalytic systems are susceptible to further improvements, we demonstrate that iridium can produce some interesting catalysis also in this field of research.

2. Experimental

2.1. General

All the reactions and manipulations were routinely performed under an argon atmosphere by 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. Naphthalene was purified by recrystallization from ethanol. All the other chemicals were reagent grade and were used as received by commercial suppliers.

The compound $[\text{Ir}(\text{cot})_2\text{Cl}]_2$ [21] was prepared according to the procedure reported in the literature. The compounds $[\text{Ir}(\text{cod})\text{Cl}]_2$ [21] and $[\text{Ir}(\text{cod})(\text{OMe})]_2$ [22] were prepared according to modified methods (vide infra).

2.2. Instrumental

^1H and ^{13}C NMR spectra were recorded on a JEOL EX400 spectrometer operating at 399.77 and 100.54 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 ($\delta = 77.0$ for CDCl_3 , $\delta = 128.0$ for C_6D_6).

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

2.3. Preparation of $[\text{Ir}(\text{cod})\text{Cl}]_2$

A 2.0 g of IrCl_3 hydrate were added into a Schlenk tube containing 30 ml of propan-2-ol and water in a 3/1 ratio. After the addition of excess 1,5-cyclooctadiene (4 ml) the resulting mixture was stirred in the air for 5 min, then argon was flowed to provide an inert atmosphere. The solution was refluxed with vigorous stirring for 3 h, during which time formation of a yellow-red solid could be observed. After cooling to room temperature, the mixture was concentrated to a volume of about 10 ml. The red crystals so obtained were filtered, sparingly washed with cold methanol and dried under vacuum. Yield was 58%.

2.4. Preparation of $[\text{Ir}(\text{cod})(\text{OMe})]_2$

An excess of anhydrous Na_2CO_3 (200 mg) in 5 ml of methanol was reacted with 200 mg of $[\text{Ir}(\text{cod})\text{Cl}]_2$ under an argon atmosphere. The mixture was heated for about 45 min in a thermostated bath at 60 °C without boiling to avoid partial decomposition. When the yellow solution started turning brown, heating was stopped. After cooling to room temperature, the yellow solid obtained was filtered under an argon atmosphere, washed several times with water and a little methanol. Finally, the solid was dried under vacuum and stored under inert atmosphere. Yield was 97%.

2.5. Catalytic reactions in Schlenk tube

A typical procedure is described as follows. A solution of $[\text{Ir}(\text{cod})\text{Cl}]_2$ (13.4 mg, 0.040 mmol of monomer) in 5.0 ml of THF (or other solvent of choice) was either heated or cooled to the desired reaction temperature under inert atmosphere. Then, addition of the GLC standard naphthalene (100 mg) was followed by the addition of phenylacetylene (204 mg, 2.0 mmol, $[\text{sub}]/[\text{Ir}] = 50$). 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 yellow-brown solids were filtered, washed repeatedly with methanol and dried in vacuo.

2.6. Catalytic reactions in NMR tube

A typical procedure is described as follows. In a small Schlenk tube, a solution of $[\text{Ir}(\text{cod})\text{Cl}]_2$ (6.7 mg, 0.02 mmol Ir) in 0.6 ml of CDCl_3 was prepared under an inert atmosphere. Addition of the desired amount of phenylacetylene (deoxygenated solution in CDCl_3) caused the solution to turn immediately dark red. The resulting solution was transferred by syringe into an NMR tube, which was kept into an appropriate Schlenk tube under an argon atmosphere. The reaction was followed by ^1H NMR for 3 h, and finally a COSY and a ^{13}C spectra were recorded. The final mixture was treated with excess methanol to isolate the polymer; the resulting yellow-brown solid was filtered, washed with methanol and dried in vacuo.

2.7. Determination of polyene stereochemistry

The stereochemistry of the polyphenylacetylene (PPA) obtained was determined by ^1H and ^{13}C NMR. For *cis-transoidal*-PPA. ^1H NMR (CDCl_3) δ : 6.95–6.93 (m, 3H, *m*- and *p*- $\text{H}(\text{C}_6\text{H}_5)$), 6.64–6.62 (m, 2H, *o*- $\text{H}(\text{C}_6\text{H}_5)$), 5.84 (s, 1H, $\text{C}=\text{CH}$); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ : 142.9 and 139.3 (quaternary carbons), 131.8 ($\text{C}=\underline{\text{C}}\text{H}$), 127.8 and 127.5 (*o*- and *m*-Ar), 126.7 (*p*-Ar).

For *trans*-PPA. ^1H NMR (CDCl_3) δ : 7.2 (very broad); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ : 128 (very broad). The *cis* content was calculated according to the generally accepted equation [23]: % *cis* = $(A \times 10^4)/(A_{\text{tot}} \times 16.66)$, where *A* is the area of the vinylic proton at 5.84 ppm, and A_{tot} is the total area of all the signals of the polyene.

2.8. Determination of polyene molecular weight

Determination of molecular weights via GPC was always performed with 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).

2.9. Determination of stereochemistry of the cyclotrimers

Oligomers formed in the catalytic reactions are soluble in the solvent/methanol final reaction mixture. After filtration of the polymer, the solution was recovered and concentrated to dryness under vacuum. The residue obtained was dissolved in CDCl_3 and analyzed by ^1H and ^{13}C NMR. In some cases, part of the low molecular weight polyene was also detected in this fraction.

The relative amounts of the cyclomerization products 1,3,5-triphenylbenzene and 1,2,4-triphenylbenzene were preferably determined by ^{13}C NMR, where the resonances of the quaternary carbons of the two isomers are well resolved. For 1,3,5-triphenylbenzene: ^1H NMR (CDCl_3) δ : 7.77, 7.68, 7.46, 7.37; $^{13}\text{C}\{^1\text{H}\}$ 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; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ : 141.4, 141.0, 140.9, 140.5, 140.3, 139.5 (quaternary carbons), 129–125 (CH).

3. Results

The compound $[\text{Ir}(\text{cod})\text{Cl}]_2$ was initially tested as catalyst precursor for the polymerization of phenylacetylene in THF solution at 60°C . The reaction

course was rather fast at the beginning, however after 15–30 min the monomer consumption slowed down, and after 3–5 h further formation of reaction products was not observed, with an overall conversion lower than 50% (see Table 1, entry 3). The PPA so formed had mainly *trans* geometry, as revealed by the NMR analysis of the crude product, and small amounts of the cyclotrimerization products 1,3,5-triphenylbenzene and 1,2,4-triphenylbenzene were also obtained; on the contrary, formation of dimeric compounds was not detected.

When the catalytic reaction with $[\text{Ir}(\text{cod})\text{Cl}]_2$ was performed using a different solvent (methanol, chloroform or benzene, Table 1, entries 4–6) a similar behaviour was observed, with apparent deactivation of the catalytically active species with time, and with formation of *trans*-PPA as main product. The polymeric material thus formed had low M_n values (2000–3000) and polydispersion index (M_w/M_n) exceeding 2.0.

Phenylacetylene polymerization was also observed when the methoxo compound $[\text{Ir}(\text{cod})(\text{OMe})_2]$ was employed in the place of the chloro-dimer as catalyst precursor, at 60°C : in such catalytic reaction, the polyene with *trans* geometry was the main product (Table 1, entries 7–10). The two precursors undergo a similar decrease of catalytic activity with time, and the polymer molecular weight and the absence of dimeric by-products are also alike.

The catalytic polymerization in the presence of the compounds $[\text{Ir}(\text{cod})\text{Cl}]_2$ and $[\text{Ir}(\text{cod})(\text{OMe})_2]$ was also tested in aqueous solvent, as in such medium analogue rhodium compounds have been reported

Table 1
Oligo and polymerization of phenylacetylene catalyzed by $[\text{IrL}_2\text{X}]_2$

Entry	Precursor	Solvent	Conversion (%)	<i>cis</i> -PPA ^a	<i>trans</i> -PPA ^a	Oligomers ^a
1	$[\text{Ir}(\text{cot})_2\text{Cl}]_2$	THF	10	–	–	100
2	$[\text{Ir}(\text{cot})_2\text{Cl}]_2$	CHCl_3	13	–	–	100
3	$[\text{Ir}(\text{cod})\text{Cl}]_2$	THF	45	27	71	2
4	$[\text{Ir}(\text{cod})\text{Cl}]_2$	CHCl_3	50	11	79	10
5	$[\text{Ir}(\text{cod})\text{Cl}]_2$	C_6H_6	48	6	90	4
6	$[\text{Ir}(\text{cod})\text{Cl}]_2$	MeOH	33	15	76	9
7	$[\text{Ir}(\text{cod})(\text{OMe})_2]$	THF	51	21	75	4
8	$[\text{Ir}(\text{cod})(\text{OMe})_2]$	CHCl_3	53	16	79	5
9	$[\text{Ir}(\text{cod})(\text{OMe})_2]$	C_6H_6	49	10	86	4
10	$[\text{Ir}(\text{cod})(\text{OMe})_2]$	MeOH	37	16	74	10

Experimental conditions: $[\text{Ir}] = 8.0 \times 10^{-3} \text{ mol l}^{-1}$; $[\text{sub}] = 0.40 \text{ mol l}^{-1}$; $[\text{sub}]/[\text{Ir}] = 50$; $T = 60^\circ\text{C}$; reaction time, 5 h.

^a Product distribution (%); PPA: polyphenylacetylene. Oligomers: 1,3,5-triphenylbenzene and 1,2,4-triphenylbenzene.

to be effective alkyne polymerization catalysts [10]. In our case, when the reaction was performed either in MeOH/H₂O 1/1 or in THF/H₂O 1/2 only small amounts of *cis*-PPA were formed, whereas the main reaction products were the two cyclotrimers 1,3,5-triphenylbenzene and 1,2,4-triphenylbenzene.

The catalytic behaviour of the iridium dimer [Ir(cot)₂Cl]₂, where two monoolefins have replaced the diene, was then investigated. This compound proved to be unable to promote polymerization of phenylacetylene, as only small amounts of cyclotrimerization products were formed both in chloroform and in THF (see Table 1, entries 1 and 2).

It was apparent that one of the major limitations of the polymerization catalysts [Ir(cod)Cl]₂ and [Ir(cod)(OMe)]₂ was catalyst deactivation: the catalytic reactions were therefore performed at a lower temperature, to see whether such change would slow down the catalyst deactivation more than the polymer formation. When the catalytic reactions were performed at 25 °C (Table 2), with both of the precursors the overall conversion decreased and was now lower than 40%; the monomer consumption stopped after about 4–5 h. However, two points of interest arise from such experiments: first, the stereoselectivity of the reaction has changed, for the *cis*-polyene is now the main product; second, the polymer molecular weight has increased (M_n up to 5500) with lower polydispersion ($M_w/M_n = 1.48/1.72$) in comparison to the data reported in Table 1.

The dependence of the polyene geometry on the reaction temperature needed further investigation, as thermal isomerization of *cis*-phenylacetylene to the thermodynamically favored *trans* isomer has been reported [24]. By heating a solution of *cis*-PPA in CDCl₃

at 60 °C for 5 h, NMR analysis of the resulting mixture revealed that only 15% conversion into the *trans* isomer has occurred; a more pronounced effect was observed on the polymer molecular weight, which after heating drops from the initial value $M_n = 4300$ to less than 2000. A similar behaviour was observed when heating a C₆D₆ solution of *cis*-PPA, which resulted in a comparable amount of isomerization to the *trans* polymer, albeit with lower decrease in molecular weight (final value $M_n = 3100$).

With the aim of gaining further information on the catalyst deactivation process, a series of catalytic reactions were performed in deuterated solvent in NMR tube. Thus, formation of PPA promoted by [Ir(cod)Cl]₂ in CDCl₃ solution was followed with time by ¹H NMR, revealing that although most of the catalyst precursor remained unaffected after monomer addition, after few minutes, the signals of the polyene were detected in solution. Interestingly, after 30 min, the signals of free 1,5-cyclooctadiene at δ 5.58 and 2.36 appeared, and their intensity increased at longer reaction times. When a similar experiment was performed by using [Ir(cod)(OMe)]₂ as catalyst precursor, a more complicated spectrum was obtained, however also in this case the signals corresponding to the free diene were clearly detected, and their intensity increased with reaction time. These results suggest that loss of cod might be related to the catalyst deactivation.

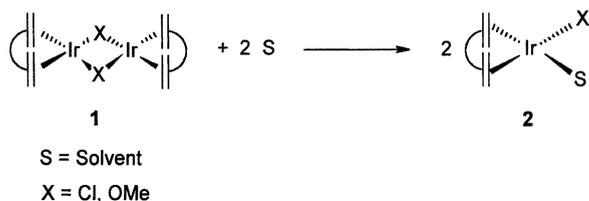
Therefore, to evaluate the importance of cod dissociation from iridium in the catalytic system, a reaction with [Ir(cod)Cl]₂ was performed in the presence of added diene. After 5 h in CDCl₃ solution at room temperature with the chloro-dimer and excess cod (added cod/Ir = 5) the monomer consumption was 58%, to be

Table 2
Polymerization of phenylacetylene catalyzed by [Ir(cod)X]₂

Entry	X	Solvent	Conversion (%)	<i>cis</i> -PPA ^a	<i>trans</i> -PPA ^a	M_n	M_w/M_n
1	Cl	CHCl ₃	26	69	31	3980	1.72
2	Cl	C ₆ H ₆	32	85	10	4010	1.65
3	Cl	THF	20	95	5	3200	1.48
4	OMe	CHCl ₃	37	88	12	5560	1.59
5	OMe	C ₆ H ₆	34	91	6	4550	1.54
6	OMe	THF	36	93	2	3650	1.70

Experimental conditions: [Ir] = 8.0×10^{-3} mol l⁻¹; [sub] = 0.40 mol l⁻¹; [sub]/[Ir] = 50; T = 25 °C; reaction time, 5 h.

^a Product distribution (%); PPA: polyphenylacetylene. Other reaction products: 1,3,5-triphenylbenzene and 1,2,4-triphenylbenzene.



Scheme 1.

compared with 26% obtained in the absence of added cod (Table 2, entry 1). This result supports the hypothesis that the catalyst deactivation occurs via diene loss from iridium.

The NMR spectra of the catalytic reactions performed in CDCl_3 above described indicate that only a small fraction of the catalyst precursor has reacted with the monomer. The reactivity of the iridium dimer with the alkyne was even lower when using C_6D_6 as reaction medium; methanol is not suitable for such investigations owing to the low solubility of the catalyst precursors in this solvent.

We then reasoned that, if the formation of the catalytically active species occurs via bridge splitting of the dimer by a solvent molecule (Scheme 1), a more coordinating solvent such as NEt_3 might improve the catalytic activity of our dimeric compounds, in comparison to previously used solvents.

The results obtained when the catalytic reactions were performed by using NEt_3 solutions of either $[\text{Ir}(\text{cod})\text{Cl}]_2$ or $[\text{Ir}(\text{cod})(\text{OMe})]_2$ are reported in Table 3. At 60°C with both precursors the monomer consumption after 5 h was around 60%, with prevalent formation of the *trans*-polyene over the *cis* isomer; no oligomeric products were detected in the reaction mixture. Also in NEt_3 solution, a catalyst degradation

process was apparent after 30 min from monomer addition. Interesting variations occurred to the reaction when the temperature was lowered to 25 and 0°C . First, the conversion decreased only to a small extent changing from 60 to 25°C (57–44 and 61–45% for the chloro- and methoxo-dimer, respectively); moreover, no significant change in monomer consumption changing from 25 to 0°C was detected (entries 2 and 3, and 5 and 6). Second, the stereoselectivity was markedly dependent on the reaction temperature, as the amount of *cis*-polyene increased by decreasing the temperature, e.g. with $[\text{Ir}(\text{cod})\text{Cl}]_2$ the isomer ratio *cis/trans* was 1/3 at 60°C and 3/1 at 0°C . Third, the polymer molecular weight was also affected by the reaction temperature, as it increased when the temperature was lowered, e.g. going from 60 to 0°C the M_n values obtained with the chloro-dimer changed from 3610 to 7180.

Therefore, the choice of NEt_3 as the reaction solvent produced a beneficial effect on the catalytic system, from the point of view of both catalytic activity and polymer molecular weight. The effect of the amine on the reactivity of the iridium dimer was investigated by monitoring the ^1H NMR spectra of a CDCl_3 solution of $[\text{Ir}(\text{cod})\text{Cl}]_2$ after addition of 3 eq. of NEt_3 . At room temperature after 10 min, aside the signals of free NEt_3 at δ 2.64 and 1.09 ($J = 7.3$ Hz), two new multiplets appeared, namely a quartet at δ 3.08 ppm and a triplet at 1.33 ppm ($J = 7.3$ Hz), which are correlated to each other as confirmed by a COSY experiment: such signals can be assigned to metal-coordinated NEt_3 . When this experiment was repeated in C_6D_6 , the same reaction only proceeded to a small extent, but also here the appearance of two new multiplets suggests the formation of a NEt_3 -iridium adduct. Addition of 1 eq. of phenylacetylene to either the CDCl_3 or the C_6D_6

Table 3
Polymerization of phenylacetylene catalyzed by $[\text{Ir}(\text{cod})\text{X}]_2$ in NEt_3 solution

Entry	X	T ($^\circ\text{C}$)	Conversion (%)	<i>cis</i> -PPA ^a	<i>trans</i> -PPA ^a	M_n	M_w/M_n
1	Cl	60	57	25	75	3610	1.41
2	Cl	25	44	68	32	4420	1.59
3	Cl	0	46	74	26	7180	1.72
4	OMe	60	61	24	76	3380	1.58
5	OMe	25	45	64	46	5590	1.68
6	OMe	0	48	75	25	6680	1.66

Experimental conditions: $[\text{Ir}] = 8.0 \times 10^{-3} \text{ mol l}^{-1}$; $[\text{sub}] = 0.40 \text{ mol l}^{-1}$; $[\text{sub}]/[\text{Ir}] = 50$; reaction time, 5 h.

^a Product distribution (%); PPA: polyphenylacetylene.

solution produced mixtures which gave NMR spectra crowded with new signals, complexity of which prevented further assignments; however, once again the formation of free cyclooctadiene was detected after 30 min from addition of the monomer.

4. Discussion

The rhodium compounds $[\text{Rh}(\text{diene})\text{Cl}]_2$ (diene = cod, norbornadiene) have been reported to be very active catalysts for the polymerization of phenylacetylenes, promoting the stereoselective formation of the corresponding polyenes with *cis* geometry. The effect of the coordinated diolefin has been investigated [23], and it appears to play a major role in determining the catalytic activity and the polyene molecular weight, i.e. the norbornadiene adduct shows both higher activity and polymer M_n values than the cod analogue. Such findings have been interpreted in terms of the stronger σ -donating and π -back-bonding acceptor capabilities of norbornadiene in comparison to cyclooctadiene. In contrast, the compound $[\text{Rh}(\text{cot})_2\text{Cl}]_2$ where a monoolefin has replaced the diene shows no catalytic activity in alkynes polymerization. Also the methoxy-dimers $[\text{Rh}(\text{diene})(\text{OMe})_2]$ display a similar behaviour, with the norbornadiene species possessing superior catalytic properties in comparison to the cod adduct [25].

We now find that the iridium analogue compounds $[\text{Ir}(\text{cod})\text{Cl}]_2$ and $[\text{Ir}(\text{cod})(\text{OMe})_2]$ are also catalytically active in promoting phenylacetylene polymerization. Not surprisingly, both the catalytic activity and polyene molecular weight are markedly lower than those reported for the analogue rhodium compounds, however some interesting features of the iridium catalysts deserve further discussion.

First of all, to the best of our knowledge only two previous reports are present in the literature about iridium-based alkyne polymerization catalysts. In a paper by Wilkinson and coworkers [18] phenylacetylene polymerization is reported to be catalyzed by $\text{IrH}(\text{CO})_2(\text{PPh}_3)_2$, however no details on the stereochemistry and molecular weight of the polyene formed are provided. The second paper is concerned with the water soluble species $\text{IrCl}(\text{CO})(\text{TPPTS})_2$ (TPPTS = $\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_3$) which promotes phenylacetylene polymerization in $\text{CHCl}_3/\text{H}_2\text{O}$ or $\text{MeOH}/\text{H}_2\text{O}$ at high

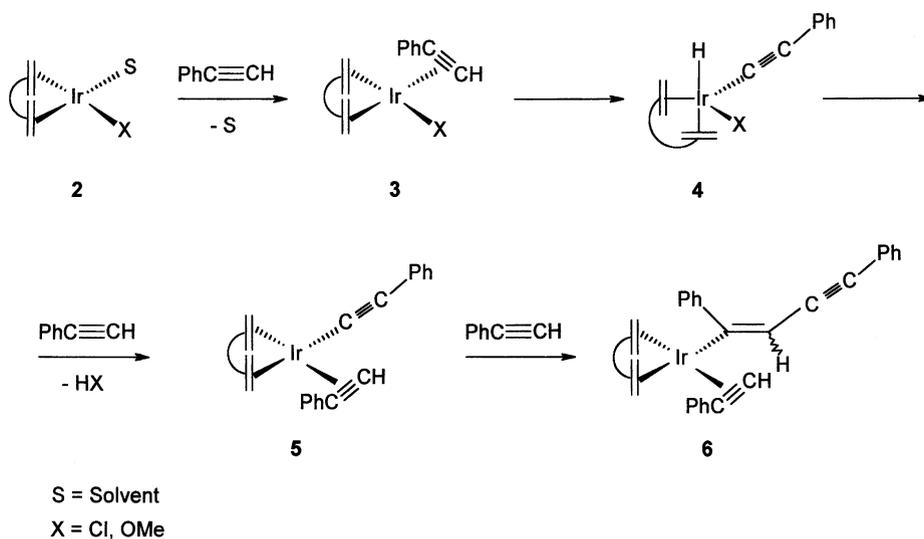
temperature, forming the *trans*-polyene with $M_n = 2400$ in moderate yield [19].

We find that the simple catalytic systems $[\text{Ir}(\text{cod})\text{Cl}]_2$ and $[\text{Ir}(\text{cod})(\text{OMe})_2]$ in the absence of added cocatalysts promote the polymerization of phenylacetylene at room temperature (or lower), with negligible formation of oligomeric by-products. As demonstrated for rhodium, also for iridium dimeric compounds the presence of coordinated diene is a crucial factor in determining the catalytic activity. As a matter of fact, NMR studies on the catalytic reactions reveal formation of free cyclooctadiene increasing with time, which parallel the decrease in catalytic activity observed after the first 30 min after monomer addition. The comparison between the catalytic reactions performed with and without an excess of cyclooctadiene confirm that catalyst deactivation occurs via loss of the diene. The importance of the coordinated diene for the catalytic activity is further confirmed by the lack of ability of $[\text{Ir}(\text{cot})_2\text{Cl}]_2$ to promote alkyne polymerization: with such compound only small amounts of cyclotrimerization products are obtained.

As reported in the Section 3, although different solvents such as chloroform, THF and methanol appear to be suitable reaction media for alkyne polymerization, an improvement in both catalytic activity and polyene molecular weight is observed when using NEt_3 as solvent. Such findings can be related to the higher coordinating ability of the amine in comparison to the other solvents tested.

Formation of the catalytically active species probably occurs via NEt_3 coordination to iridium with subsequent Cl-bridge (or methoxo-bridge) splitting, to give the square planar derivative $\text{Ir}(\text{cod})\text{X}(\text{NEt}_3)$ (see Scheme 1). NMR studies on the reaction between $[\text{Ir}(\text{cod})\text{Cl}]_2$ and NEt_3 , indicating the formation of a NEt_3 -coordinated species, support such hypothesis. A similar reaction is proposed by Tabata et al. to occur when $[\text{Rh}(\text{nbd})\text{Cl}]_2$ is treated with excess NEt_3 [6].

With regard to the mechanism of the catalytic reaction, two different reaction paths have been described for alkyne polymerization, namely: (i) alkyne insertion, and (ii) metathesis. It has been demonstrated that rhodium-based catalysis proceeds via the former mechanism, which has been proposed for nickel and palladium derivatives as well [12–14], whereas the polymerization via metathesis is operative for molybdenum and tungsten-based catalysts.



Scheme 2.

It seems reasonable to propose that also for the iridium catalysts under investigation the polymerization reaction occurs via the insertion mechanism. A possible reaction path for the $[\text{Ir}(\text{cod})\text{X}]_2$ catalyzed alkyne polymerization is reported in Scheme 2. Reaction between the catalytically active species **2** and the monomer initially gives the π -adduct **3**, with subsequent fast rearrangement to the oxidative addition product **4**. In the next step, a second molecule of the substituted acetylene coordinates to iridium, with concomitant loss of HX by reductive elimination. Species **4**, thus, formed undergoes formal alkyne insertion into the iridium–carbon bond to give the iridium–vinyl compound **6**, the vacant coordination site being readily occupied by a new molecule of the monomer. Further insertion and monomer coordination cause the lengthening of the polymer fragment coordinated to the metal.

The dependence of the polymer geometry on the reaction temperature, i.e. the increase in *trans* content on raising the temperature, remains to be explained, as the results of the tests performed on thermal treatment of *cis*-PPA suggest that isomerization alone cannot be responsible for the marked change of stereoselectivity going from 0 to 60 °C. In fact, in the nickel and palladium-catalyzed polymerization, where the polyene geometry depends on the substituents on the alkyne, a *trans* insertion has been proposed [26] to

be operative when the *trans*-polyene is selectively formed. Possibly this might be the case also for the iridium catalysts, which undergo the alkyne insertion with either *cis* or *trans* stereochemistry, thus yielding a mixture of *cis* and *trans* sequences, whose relative amounts depend on the reaction temperature.

With regard to the comparison between iridium and rhodium-based systems, sensible correlations between series of analogue compounds of the two metals will hopefully make accessible a better understanding of the metal atom effect on the catalytic reaction. Further studies in our laboratories on iridium derivatives with phosphine ligands are currently providing useful information on this matter.

5. Conclusions

The iridium compounds $[\text{Ir}(\text{cod})\text{Cl}]_2$ and $[\text{Ir}(\text{cod})(\text{OMe})_2]$ promote the polymerization of phenylacetylene, with negligible formation of oligomeric products. The presence of the diene in the coordination sphere of iridium plays a key role in the polymerization catalysis, as demonstrated by the lack of activity of the monoolefin analogue $[\text{Ir}(\text{cot})_2\text{Cl}]_2$, as well as by the catalyst deactivation with time, which proceeds via loss of diene from the iridium center. The stereochemistry of PPA formed in the catalytic

reactions is dependent on the temperature, with a higher *cis* content at 0 °C, and increasing amounts of the *trans*-polyene with increasing the reaction temperature. Spectroscopic evidence has been provided of formation of a monomeric iridium species, which is the likely initiator of the catalytic reaction.

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References

- [1] J. Kunzler, V. Percec, *J. Polym. Sci. Part A: Polym. Chem.* 28 (1990) 1221.
- [2] T. Masuda, S. Hayano, E. Iwawaki, R. Nomura, *J. Mol. Catal. A: Chem.* 133 (1998) 213.
- [3] T.A. Vijayaraj, G. Sundararajan, *Organometallics* 16 (1997) 4940.
- [4] T. Szymanska-Buzar, *J. Mol. Catal. A: Chem.* 123 (1997) 113.
- [5] A. Furlani, C. Napoletano, M.V. Russo, A. Camus, N. Marsich, *J. Polym. Sci. Part A: Polym. Chem.* 27 (1989) 75.
- [6] M. Tabata, W. Yang, K. Yokota, *J. Polym. Sci. Part A: Polym. Chem.* 32 (1994) 1113.
- [7] Y. Kishimoto, P. Eckerle, T. Miyatake, M. Kainosho, A. Ono, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* 121 (1999) 12035, and references cited therein.
- [8] Y. Misumi, T. Masuda, *Macromolecules* 31 (1998) 7572.
- [9] Y. Goldberg, H. Alper, *J. Chem. Soc. Chem. Commun.* (1994) 1209.
- [10] B.Z. Tang, W.H. Poon, S.M. Leung, W.H. Leung, H. Peng, *Macromolecules* 30 (1997) 2209.
- [11] H. Katayama, K. Yamamura, Y. Miyaki, F. Ozawa, *Organometallics* 16 (1997) 4497.
- [12] R. Wang, F. Belanger-Gariepy, D. Zargarian, *Organometallics* 18 (1999) 5548.
- [13] X. Zhan, M. Yang, *J. Mol. Catal. A: Chem.* 169 (2001) 27.
- [14] X. Zhan, M. Yang, H. Sun, *J. Mol. Catal. A: Chem.* 169 (2001) 63.
- [15] C.S. Chin, G. Won, J. Song, *Bull. Kor. Chem. Soc.* 15 (1994) 961.
- [16] S.-I. Lee, S.-C. Shim, T.-J. Kim, *J. Polym. Sci. Part A: Polym. Chem.* 34 (1996) 2377.
- [17] T. Ohmura, S. Yorozuya, Y. Yamamoto, N. Miyaura, *Organometallics* 19 (2000) 365.
- [18] C.K. Brown, D. Georgiou, G. Wilkinson, *J. Chem. Soc. (A)* (1971) 3120.
- [19] K.-S. Joo, S.Y. Kim, C.S. Chin, *Bull. Kor. Chem. Soc.* 18 (1997) 1296.
- [20] M. Falcon, E. Farnetti, N. Marsich, *J. Organomet. Chem.* 629 (2001) 187.
- [21] J.L. Herdè, J.C. Lambert, C.V. Senoff, *Inorg. Synth.* 15 (1974) 18.
- [22] G. Pannetier, P. Fourgeroux, R. Bonnaire, N. Platzer, *J. Less Common Met.* 24 (1971) 83.
- [23] M. Tabata, T. Sone, Y. Sadahiro, *Macromol. Chem. Phys.* 200 (1999) 265.
- [24] M. Tabata, T. Sone, Y. Sadahiro, K. Yokota, Y. Nozaki, *J. Polym. Sci. Part A: Polym. Chem.* 36 (1998) 217.
- [25] M. Falcon, N. Marsich, E. Farnetti, unpublished results.
- [26] X. Zhan, M. Yang, *J. Mol. Catal. A: Chem.* 169 (2001) 57.