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Review

Directing iridium-catalyzed C–C bond formation by selection of the ancillary ligands: Polymerization and cyclotrimerization of alkynes

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Dedicated to Professor Paul Pregosin for his contribution to chemistry.

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ABSTRACT

The ability of organoiridium derivatives of catalyzing oligomerization and polymerization of terminal alkynes is markedly influenced by the nature of non-participative ligands coordinated to the metal. The dimeric species $[Ir(cod)Cl]_2$ and $[Ir(cod)(OMe)]_2$ (cod = 1,5-cyclooctadiene) as well as the phosphine complexes $HIr(cod)(PR_3)_2$ ($PR_3 = PPh_3$, $P(p\text{-}MeOC_6H_4)_3$, $P(o\text{-}MeOC_6H_4)Ph_2$, $PCyPh_2$) catalyze the polymerization reaction, whereas the diphosphine derivatives HIr(cod)(P–P) ($P–P = Ph_2P(CH_2)_nPPh_2$ (n = 1–4), $o\text{-}C_6H_4(PPh_2)_2$) promote the regioselective formation of 1,2,4-trisubstituted benzenes. On the other hand, the iridium complexes with nitrogen chelating ligands Ir(cod)(N–N)X and Ir(hd)(N–N)X (hd = 1,5-hexadiene; N–N = 1,10-phenanthroline and substituted derivatives; X = halogen) catalyze alkynes polymerization. In most cases one catalytic reaction predominates over the other possible routes, so that polymerization often takes place in the absence of oligomerization side reactions, and conversely cyclotrimerization is rarely accompanied by formation of either polyene or dimers.

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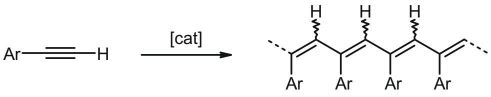
Contents

1. Introduction

The study of catalytic reactions has been gaining new impulse in recent years, as a consequence of greater awareness towards environmental issues. As stated by Anastas and Kirchhoff [1], catalysis is to be considered as a fundamental pillar of green chemistry: catalyzed reactions produce reduced amounts of waste in comparison to non-catalyzed processes, thus optimizing atom economy and *E* factors [2]. Among the most atom-economic reactions are polymerization and oligomerization, which generally form no side-products and therefore in most favourable cases afford *E* factor values close to zero.

On the other hand, the development of new polymeric materials for well defined applications is considered one of the major targets of current chemical research. Polyacetylenes produced by alkynes polymerization have attracted attention as promising materials due to their physico-chemical properties such as photoconductivity, photoluminescence, oxygen permeability, ferromagnetism and non-linear optical properties [3–6]. Polymerization of terminal alkynes (see Scheme 1) generally occurs with head-to-tail regiochemistry and it can produce different polyenes according to their C=C bond configuration (*cis* or *trans*) as well as the C–C bond conformation (*cisoidal* or *transoidal*) (Fig. 1). Another interesting reaction of alkynes is cyclotrimerization (see Scheme 2), which represents a potentially useful method for the synthesis of substituted organic compounds: unfortunately, the low selectivity usually observed for this reaction is presently limiting its applicability in organic synthesis [7].



Scheme 1.

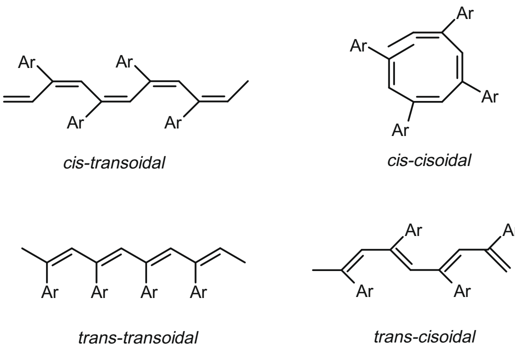
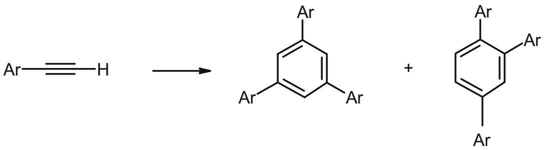


Fig. 1. Stereoisomers of polyacetylenes.



Scheme 2.

Rhodium-catalyzed alkynes polymerization has been extensively studied in the last 15 years, leading to the development of several catalytic systems, some of which behave in a *living* fashion [8–14]. During our investigations on rhodium–diphosphine catalysts for phenylacetylene polymerization [15] we realized that no iridium-based catalysis had been reported in this reaction, with the exception of two papers in which small amounts of polyacetylene formation were mentioned [16,17]; in fact, some iridium derivatives were reported to catalyze acetylenes oligomerization, generally with low selectivity [18–20].

Thus we started a research project focussed on the determination of the catalytic properties of organoiridium compounds in oligo and polymerization of alkynes. Initially the simple dimeric compounds $[Ir(cod)Cl]_2$ and $[Ir(cod)(OMe)]_2$ were tested [21], followed by studies on complexes with monodentate [22] and bidentate phosphines [23,24]; finally, derivatives with nitrogen chelating ligands were investigated [25].

Here we report a brief account of the results obtained in our studies on iridium-catalyzed polymerization and cyclotrimerization of substituted acetylenes: as will be evidenced in the following sections, iridium proves to be a suitable metal for such transformations, the nature of non-participative ligands playing a major role in favouring one specific reaction.

2. Iridium-diene catalysts

As a first approach to alkynes polymerization we tested the catalytic properties of the simple dimeric organometallic compounds $[Ir(cod)Cl]_2$ and $[Ir(cod)(OMe)]_2$; the analogous rhodium derivatives are effective catalysts for this reaction [15,26]. Polymerization of phenylacetylene catalyzed by $[Ir(cod)Cl]_2$ in tetrahydrofuran solution at 60 °C produced polyphenylacetylene together with small amounts of the cyclotrimerizatrion products 1,3,5 and 1,2,4-triphenylbenzene. The catalytic reaction suffered for a deactivation process which limited the overall conversion to 45%; similar results were obtained with the methoxo dimer $[Ir(cod)(OMe)]_2$ in THF (see Table 1, entries 2 and 4) as well as in other solvents such as chloroform, benzene and methanol at the same temperature. Substitution of the cod precursor with a monoene iridium dimer such as $[Ir(coe)_2Cl]_2$ (coe = cyclooctene) resulted in no polymerization catalysis, with formation of only cyclotrimerization products (Table 1, entry 1). The polyene produced with the cod-dimers had mainly *trans* configuration, with M_n values of about 3000. Interestingly, when the catalytic reactions were performed at 25 °C

Table 1
Polymerization of phenylacetylene catalyzed by organoiridium derivatives.

Entry	Catalyst	Solvent	*T* (°C)	Conv. (%)	*cis*-PPA[a] (%)	*trans*-PPA[a] (%)	Oligomers[a] (%)
1	$[Ir(coe)_2Cl]_2$	THF	60	10	0	0	100
2	$[Ir(cod)Cl]_2$	THF	60	45	27	71	2
3	$[Ir(cod)Cl]_2$	THF	25	20	95	5	–
4	$[Ir(cod)(OMe)]_2$	THF	60	51	21	75	4
5	$[Ir(cod)(OMe)]_2$	THF	25	36	93	2	5
6	$[Ir(cod)Cl]_2$	NEt_3	60	57	25	75	–
7	$[Ir(cod)Cl]_2$	NEt_3	25	44	68	32	–
8	$[Ir(cod)Cl]_2$	NEt_3	0	46	74	26	–
9	$[Ir(cod)(OMe)]_2$	NEt_3	60	61	24	76	–
10	$[Ir(cod)(OMe)]_2$	NEt_3	25	45	64	46	–
11	$[Ir(cod)(OMe)]_2$	NEt_3	0	48	75	25	–

Experimental conditions: $[Ir] = 8.0 \times 10^{-3}$ mol L^{-1}; [sub]/[Ir] = 50; reaction time: 5 h.
[a] Product distribution (%); PPA, polyphenylacetylene. Oligomers: 1,3,5-triphenylbenzene and 1,2,4-triphenylbenzene.

a significant change in polyene stereoselectivity was observed (see Table 1, entries 3 and 5), with prevalent formation of the *cis* product and slightly higher molecular weights (~4000). Also at 25 °C the catalytic reactions slowed down and finally stopped at conversions not exceeding 40%: the presence of free cod detected by GC analysis of the final reaction mixtures suggested that diene loss from iridium might be responsible for catalyst deactivation. This hypothesis was supported by ^1H NMR spectra of $[Ir(cod)Cl]_2$ solutions in $CDCl_3$ which were heated at 60 °C in the presence of added phenylacetylene, where the signals of free cod were clearly visible. Support to this deactivation pathway was obtained by performing a catalytic reaction with $[Ir(cod)Cl]_2$ in the presence of added cod: after 5 h in THF at r.t., with five equivalents of added diene a conversion of 53% was obtained, to be compared to 20% in the absence of excess cod.

Further investigations on the iridium dimeric catalysts were based on the assumption that the catalytically active species was formed *via* splitting of the chloro (or methoxo) bridge by a solvent molecule: thus, use of a more coordinating solvent such as NEt_3 was expected to produce higher concentrations of the polymerization initiator. Actually, reactions performed in triethylamine at 60 °C gave conversions up to 61% of polyphenylacetylene with prevalent *trans* geometry, without formation of oligomeric products (see Table 1, entries 6 and 9). Moreover, when the catalytic reactions were repeated at lower temperatures (25 and 0 °C) the conversions observed were still higher than 40% (Table 1, entries 7,8 and 10,11). As previously observed in other solvents, by decreasing the reaction temperature both the polyene stereochemistry and molecular weights were markedly affected, the former changing from mainly *trans* to mainly *cis*, the latter showing an increase of M_n value (~3500 and ~7000 at 60 and 0 °C, respectively), whereas the polydispersion index M_w/M_n was maintained within the range 1.4–1.7.

The main indications emerging from these data can be summarized as follows: (i) the organoiridium derivatives under investigation behave as catalysts for the polymerization of acetylenes, (ii) the coordinated diene has a crucial effect on the catalytic properties, and (iii) the actual catalyst is a monomeric species. The last point was confirmed by NMR studies in $CDCl_3$ solution of the reaction between $[Ir(cod)Cl]_2$ and NEt_3, resulting in the formation of monomeric species of the type $Ir(cod)(NEt_3)Cl$.

3. Iridium-phosphine catalysts

Further studies on iridium catalyzed alkynes polymerization were devoted to phosphine-modified iridium-cyclooctadiene derivatives. Thus, the series of compounds $HIr(cod)(PR_3)_2$ ($PR_3 = PPh_3$, $P(p\text{-}MeOC_6H_4)_3$, $P(o\text{-}MeOC_6H_4)Ph_2$, $PCyPh_2$) were synthesized by reacting $[Ir(cod)(OMe)]_2$ with 2 equiv. of the phosphine, according to the following reaction:

$$1/2[Ir(cod)(OMe)]_2 + PR_3 \rightarrow Ir(OMe)(cod)(PR_3)_2 \rightarrow HIr(cod)(PR_3)_2 + CH_2O$$

The methoxy mononuclear intermediate undergoes β-elimination and upon loss of formaldehyde yields the desired hydrido compound. Interestingly, reactions with the very bulky phosphines PCy_3 and $P(o\text{-}MeOC_6H_4)_3$ only gave $Ir(OMe)(cod)(PCy_3)$ and $Ir(OMe)(cod)(P(o\text{-}MeOC_6H_4)_3)$, respectively, without undergoing subsequent β-elimination. These methoxy compounds showed poor catalytic properties towards alkynes oligo and polymerization and were not further investigated.

In contrast, the hydrido complexes $HIr(cod)(PR_3)_2$ proved to be effective catalyst precursors in phenylacetylene polymerization. Catalytic reactions performed at 60 °C in various solvents (methanol, tetrahydrofuran, chloroform, toluene) produced polyphenylacetylene as the main product, together with variable amounts of the dimerization products (E)-1,4-diphenylbut-1-yn-3-ene and (Z)-1,4-diphenylbut-1-yn-3-ene (see Table 2, entries 1–9); traces of cyclotrimers were also detected in some cases. The reaction was highly selective with regard to the polyene stereochemistry, as only *trans*-polyphenylacetylene was formed. Molecular weights (M_n) of the polyene determined by GPC were within the range 3000–5400, with polydispersion index (M_w/M_n) varying from 1.4 to 1.6. In all these reactions the overall conversion never exceeded 70%, even when longer reaction times were employed.

Further experiments were performed at higher temperatures using toluene or 2-propanol as solvents: typical results are reported in Table 2, entries 10–12. By raising the temperature to 80 and 100 °C an increased (up to 100%) substrate consumption was obtained, however the higher conversion was mainly due to alkyne dimerization, which became the major catalytic reaction at 100 °C.

On the whole, the data reported in Table 2 suggest that starting from the compounds $HIr(cod)(PR_3)_2$ two different catalytically active species were formed, one of which promoted polymerization, the other one dimerization of the alkyne. Formation of the latter was apparently favoured by higher reaction temperatures, therefore in order to favour the polymerization reaction moderate temperatures must be selected. Actually, at 60 °C the dimerization reaction became the minor process, on the other hand deactivation of the polymerization catalyst was apparently limiting the polyene yields; further tests performed at temperatures lower than 60 °C gave low conversions. At first, the catalyst deactivation was thought to occur via loss of cod from the coordination sphere of iridium, however such hypothesis was soon discarded on the basis of the following results: (i) no significant amount of free cod was detected in the final reaction mixtures; (ii) addition of excess cod to the catalytic reactions resulted in a minor – although positive-effect on the conversion.

A clue to the deactivation pathway – as well as to the nature of the catalytically active species – was provided by a closer analysis

Table 2
Polymerization of phenylacetylene catalyzed by $HIr(cod)(PR_3)_2$.

Entry	PR_3	Solv.	*T* (°C)	Conv. (%)	Dimers[a] (%)	PPA[a] (%)
1	$PCyPh_2$	THF	60	68	10	90
2	$PCyPh_2$	MeOH	60	66	10	90
3	$P(p\text{-}MeOC_6H_4)_3$	THF	60	44	8	90
4	$P(p\text{-}MeOC_6H_4)_3$	MeOH	60	38	5	95
5	$P(o\text{-}MeOC_6H_4)Ph_2$	THF	60	39	15	75
6	$P(o\text{-}MeOC_6H_4)Ph_2$	MeOH	60	45	5	95
7	PPh_3	THF	60	47	9	91
8	PPh_3	MeOH	60	39	0	100
9	PPh_3	toluene	60	44	25	75
10	PPh_3	*i*-PrOH	80	51	30	70
11	PPh_3	toluene	80	79	45	55
12	PPh_3	toluene	100	100	61	39

Experimental conditions: $[Ir] = 3.4 \times 10^{-3}$ mol L^{-1}; [sub]/[Ir] = 100; reaction time: 5 h.

[a] Selectivity (%); PPA, *trans*-polyphenylacetylene; dimers: (E)-1,4-diphenylbut-1-yn-3-ene and (Z)-1,4-diphenylbut-1-yn-3-ene. Other products: 1,3,5 and 1,2,4-triphenylbenzene.

of the product isolated at the end of the reactions catalyzed by $HIr(cod)(PPh_3)_2$: the red-brown polyene contained a new iridium/phosphine species, which was identified as the bis-alkynyl trisphosphine compound $HIr(C{\equiv}CPh)_2(PPh_3)_3$. Such compound was itself tested as catalyst precursor, but it proved to be thoroughly inactive. Analogous bis-alkynyl species were isolated from the catalytic reactions performed with the $PCyPh_2$, $P(p\text{-}MeOC_6H_4)_3$ and $P(o\text{-}MeOC_6H_4)Ph_2$ derivatives: all of them were catalytically inactive.

Spectroscopic studies were performed to shed light on the fate of iridium hydride catalysts, in experimental conditions similar to those of the catalytic reactions, although at higher iridium concentration and lower [alkyne]/[Ir] ratio. ^1H, ^{13}C and ^{31}P NMR spectra sided by infrared measurements revealed that the evolution of HIr $(cod)(PPh_3)_2$ followed the path described in Scheme 3. Initial substitution of a coordinated phosphine by phenylacetylene leads to an intermediate hydrido-alkyne species, which undergoes insertion to form the vinyl compound $Ir(cod)(CH{=}CHPh)(PPh_3)$. The phosphine released in this step reacts with a second molecule of $HIr(cod)(PPh_3)_2$ *via* loss of cod: the subsequent reactions leading to the bis-alkynyl compound $HIr(C{\equiv}CPh)_2(PPh_3)_3$ probably include coordination of a first molecule of alkyne, CH oxidative addition followed by H_2 reductive elimination, and finally oxidative addition of a second molecule of phenylacetylene. The catalytically active species is likely to be the vinyl derivative Ir(cod) $(CH{=}CHPh)(PPh_3)$: unfortunately all attempts to isolate such compound from the reaction mixture were unsuccessful.

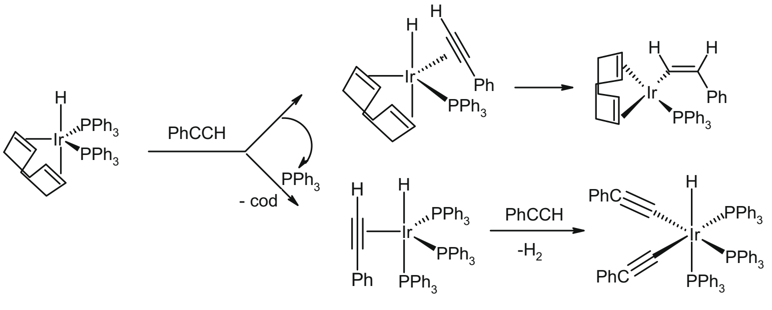
4. Iridium-bidentate phosphine catalysts

The iridium catalysts so far discussed share as a common weak point a lack of stability, which causes deactivation processes severely limiting the final conversion. A possible strategy to avoid such problem was to consider the substitution of monodentate phosphines with bidentate chelating ligands, which might offer increased stability to the catalytically active species, preventing reactions of the type shown in Scheme 3. Previous successful examples of this approach we had experienced with rhodium-diphosphine catalysts, for which the bidentate phosphines proved to have a beneficial effect on catalyst stability in comparison to the corresponding derivatives with monodentate phosphines [15].

In this paragraph we report on the catalytic properties of iridium catalysts with bidentate phosphines, whereas in the next paragraph the results of studies on iridium catalysts with nitrogen chelating ligands will be discussed.

Initial catalytic tests performed on phenylacetylene with HIr(cod)(dppe) (dppe = $Ph_2PCH_2CH_2PPh_2$) evidenced that clean and efficient C–C bond formation was taking place, yielding the cyclotrimerization products 1,2,4 and 1,3,5-triphenylbenzene: no alkyne polymerization or dimerization were observed. The same behaviour was found when using the analogous derivatives with dppm, dppp and dppb (dppm = $Ph_2PCH_2PPh_2$; dppp = $Ph_2P(CH_2)_3$-PPh_2; dppb = $Ph_2P(CH_2)_4PPh_2$): from a perusal of typical results reported in Table 3 (entries 1–4) one can observe that only cyclotrimers were formed, with a remarkable regioselectivity towards formation of 1,2,4-triphenylbenzene. The catalytic activity decreased from dppm to dppb, *i.e.* with increasing the length of the carbon chain connecting the phosphorous atoms; the regioselectivity followed the same trend. In particular, the catalyst HIr (cod)(dppm) promoted the fast and highly selective formation of the asymmetric cyclotrimer: such reaction represents an unusual example of highly regioselective cyclotrimerization, together with few other reported reactions [27–29].

With regard to the complexes HIr(cod)(P–P) (P–P = dppm, dppe, dppp, dppb), some considerations are due to the coordination mode of the diene, which presents uncommon features. As previously evidenced by Oro and coworkers [30], the formula HIr (cod)(dppm) does not fully describe the compound (which was

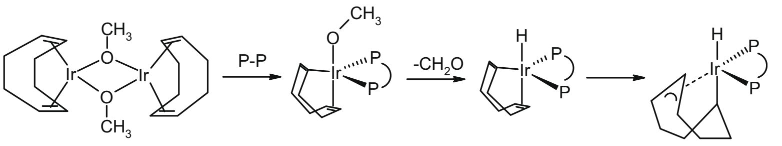


Scheme 3.

Table 3
Cyclotrimerization of phenylacetylene catalyzed by iridium/chelating phosphine complexes.

Entry	Catalyst	Conv. (%)	1,2,4-$Ph_3C_6H_3$ (%)	1,3,5-$Ph_3C_6H_3$ (%)	PPA (%)
1	HIr(cod)(dppm)	100[a]	99	1	–
2	HIr(cod)(dppe)	98	97	1	–
3	HIr(cod)(dppp)	47	45	2	–
4	HIr(cod)(dppb)	31	28	3	–
5	HIr(cod)(*o*-$C_6H_4(PPh_2)_2$)	92	88	4	–
6	HIr(cod)(dcpe)	31	3	3	18
7	HIr(cod)(P-NMe_2)	20	6	6	8

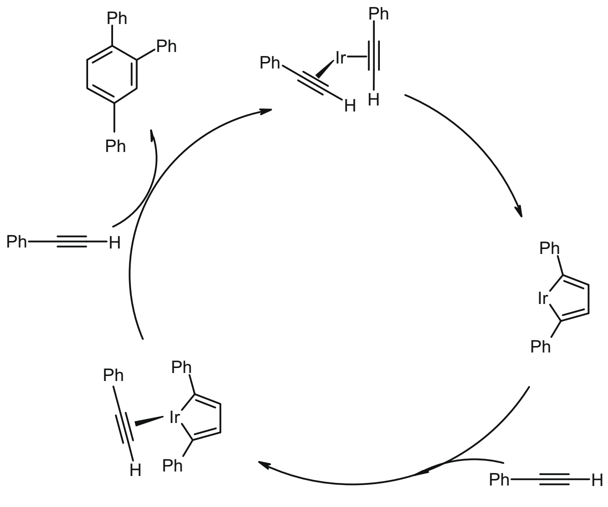
Experimental conditions: [Ir] = 3.4×10^{-3} mol L^{-1}; [sub]/[Ir] = 100; solvent: THF; $T = 60$ °C; reaction time: 6 h. PPA= *trans*-polyphenylacetylene.
[a] Reaction time 15 min.



Scheme 4.

structurally characterized), as actually in this derivative the diene is coordinated in η^1,η^3 fashion (see Scheme 4). We found that a similar diene isomerization takes place for the dppe derivative, whereas the compound with dppp is present at r.t. as a mixture of the η^2,η^2 and η^1,η^3 isomers. Variable-temperature NMR experiments evidenced that isomerization of η^2,η^2 isomer into η^1,η^3 is favoured at higher temperatures and it is an irreversible reaction. Also compound HIr(cod)(dppb), which is present at r.t. as only η^2,η^2 isomer, at higher temperatures is partially converted to the η^1,η^3 product. Further spectroscopic studies performed with other bidentate phosphines evidenced that a crucial factor in determining the extent of η^2,η^2–η^1,η^3 isomerization is the chelate Ir-diphosphine ring size: with four or five-membered chelate rings (*e.g.* with dppm and dppe) the rearrangement of cod to η^1,η^3 coordination mode appears to be favoured, whereas with larger chelate rings (*e.g.* with dppp and dppb) significative isomerization only occurs at temperatures higher than r.t.

With regard to the dependence of regioselectivity on the nature of the bidentate phosphine observed in the series HIr(cod)(P–P) (P–P = dppm, dppe, dppp, dppb), a possible explanation relates to the regioselective formation of the metallacyclopentadiene intermediate, which is likely to be the step determining the product selectivity. Formation of 1,2,4-triphenylbenzenes requires that, of the two possible diarylbenzene intermediates, only the asymmetric 2,5-disubstituted species is obtained (see Scheme 5). Such metallacycle becomes disfavoured by increasing the chain length between phosphorous atoms, which translates into increased steric hindrance of the phosphine. Selective formation of the metallacycle with the alkyne substituents in α-position to the metal has been reported by other authors and in a study on cobalt catalysts such intermediates have been isolated [31].



Scheme 5.

An extension of the studies to iridium derivatives with other bidentate phosphines evidenced different catalytic properties: apart from HIr(cod)(*o*-$C_6H_4(PPh_3)_2$) which only promotes cyclotrimerization (Table 3, entry 5), the complexes HIr(cod)(dcpe) (dcpe = $Cy_2P(CH_2)_2PCy_2$) and HIr(cod)(P-NMe_2) (P-NMe_2 = *o*-$Me_2NC_6H_4PPh_2$) resulted to be both less active and less selective, as mixtures of polyphenylacetylene and cyclotrimers were formed (see Table 3, entries 6 and 7).

The effect of substituents on the alkyne was also investigated, by performing a series of catalytic reactions with *p*-$MeOC_6H_4C{\equiv}CH$, *p*-$CF_3C_6H_4C{\equiv}CH$ and *o*-$CF_3C_6H_4C{\equiv}CH$. Selected results of reactions promoted by HIr(cod)(dppm) are reported in Table 4: analysis of entries 1–3 evidences similar results of the alkynes substituted in *para* position, as in all cases total conversion was attained within few minutes, with a regioselectivity close to 100%. The catalytic reaction with *o*-$CF_3C_6H_4C{\equiv}CH$ (entry 4) required longer reaction times (5 h) and produced mixtures of oligo and polymerization products. It was convenient to repeat the reactions at lower temperature (40 °C) in order to appreciate the differences as a function of the nature of substrate: the data reported in entries 5–7 of Table 4 evidence that the conversion of the catalytic reactions increased in the order *p*-$CF_3C_6H_4C{\equiv}CH < PhC{\equiv}CH <$ *p*-$MeOC_6H_4C{\equiv}CH$, in other words the reaction was favoured by the presence of electron-releasing substituents on the alkyne phenyl ring. Finally, the catalytic reaction was examined using as substrates internal alkynes such as phenylpropyne ($PhC{\equiv}CMe$): in all cases no reaction (neither oligomerization nor polymerization) was observed.

5. Iridium catalysts with nitrogen chelating ligands

Iridium derivatives with nitrogen chelating ligands such as 1,10-phenanthroline and substituted derivatives, which are known to promote transfer hydrogenation of ketones [32], were studied as

Table 4
Cyclotrimerization of arylacetylenes catalyzed by HIr(cod)(dppm).

Entry	Substrate	*T* (°C)	*t* (min)	*conv.* (%)	1,2,4-$Ph_3C_6H_3$ (%)	1,3,5-$Ph_3C_6H_3$ (%)
1	$PhC{\equiv}CH$	60	5	90	89	1
2	*p*-$MeOC_6H_4C{\equiv}CH$	60	5	100	100	–
3	*p*-$CF_3C_6H_4C{\equiv}CH$	60	5	87	86	1
4	*o*-$CF_3C_6H_4C{\equiv}CH$	60	300	85	22	38
5	$PhC{\equiv}CH$	40	90	98	95	3
6	*p*-$MeOC_6H_4C{\equiv}CH$	40	60	100	97	3
7	*p*-$CF_3C_6H_4C{\equiv}CH$	40	120	98	97	1

Experimental conditions: [Ir] = 3.4×10^{-3} mol L^{-1}; [sub]/[Ir] = 100; solvent: THF.

Table 5
Polymerization of phenylacetylene catalyzed by Ir(diene)(N–N)X in toluene.

Entry	Catalyst	[NaOH]/[Ir]	Conv. (%) (*t* = 1 h)	Conv. (%) (*t* = 5 h)
1	Ir(cod)(phen)Cl	2	22	23
2	Ir(cod)(phen)Cl	–	0	0
3	Ir(hd)(phen)Cl	2	20	25
4	Ir(hd)(phen)Cl	–	15	31
5	Ir(hd)(phen)I	–	28	59
6	Ir(hd)(Me_4phen)Cl	–	28	32
7	Ir(hd)(Me_4phen)I	–	38	58

Experimental conditions: [Ir] = 6.8×10^{-3} mol L^{-1}; [sub]/[Ir] = 50; *T* = 110 °C.

catalysts precursors for alkynes polymerization. The cod-derivatives Ir(cod)(N–N)Cl (N–N = 1,10-phenanthroline (phen), 4,7-dimethyl-1,10-phenanthroline (Me_2phen), 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4phen), 4,7-diphenyl-1,10-phenanthroline (Ph_2phen)) were initially tested as catalysts for oligo and polymerization of phenylacetylene. The first part of the studies on these catalysts was useful to clarify some features of the reactions, namely: (i) the compounds showed low to moderate catalytic activity, (ii) in all cases only polyphenylacetylene was formed, oligomers being totally absent in the reaction mixtures, and (iii) the presence of a basic cocatalyst such as NaOH had a beneficial effect on the reaction. Choice of the solvents was limited by poor solubility of the iridium derivatives, therefore at temperatures lower than 100 °C only alcohols could be employed, whereas toluene was a suitable solvent at higher temperatures. Entries 1 and 2 of Table 5 report typical results obtained in toluene at 110 °C: in this case no reaction was observed in the absence of base, whereas in other reactions performed in methanol or 2-propanol conversions around 5% were obtained without added base.

Substitution of cyclooctadiene in the catalyst precursor with a more labile diolefin such as 1,5-hexadiene (hd) could in principle lead to more active species, as previously evidenced in hydrogen transfer reactions: therefore the catalytic activity of Ir(hd)(N–N)X (X = Cl, Br, I) was tested and compared to that of the corresponding cod derivatives. The results concerning the phen complexes are reported in Table 5: if on one hand the reactions with basic cocatalyst seemed to be little influenced by the nature of diene (entries 1 and 3), interestingly with the hexadiene precursor the polymerization took place also without added base (entry 4). In fact, comparison between the reactions with and without cocatalyst is slightly in favour of the latter with regard to final conversion, in spite of the lower initial polyene yield. The effect of nature of the nitrogen ligand can be evidenced by comparison of entries 4–6 and 5–7 (Table 5), which shows a higher catalytic activity of the derivatives with Me_4phen with respect to those with phen. Also the halogen appears to play a significant role in the catalytic reaction, according to comparison between chloro and iodo derivatives (Table 5, entries 4, 5 and 6, 7) which favours the latter compounds.

Throughout Table 5 the conversions reported for two different reaction times (1 h and 5 h) suggest that catalyst deactivation was important in the presence of basic cocatalyst, whereas when the cocatalyst was absent the decrease of conversion after 1 h was not as pronounced.

Further increase of conversion could be obtained by performing the catalytic reactions in mesitylene at 160 °C (see Table 6). Also in these experimental conditions, without basic cocatalyst the hexadiene complexes were superior to cod derivatives (entries 2 and 4) and the halogen effect was confirmed (Cl < Br < I, entries 4–6). The effect of substituents on the nitrogen ligand was also clearly observed at longer reaction times (see entries 7–10), indicating that more electron-releasing phenanthrolines give rise to more active catalysts [33]. Spectroscopic studies regarding the reaction between phenylacetylene and either Ir(cod)(phen)Cl or Ir(hd)(phen)Cl indicated that in the first case the diene remained coordinated to iridium, whereas in the latter hexadiene left the coordination sphere, apparently giving rise to a different catalytic species.

With regard to the stereochemistry of the polyene formed, in all cases the reactions promoted by Ir(diene)(N–N)X catalysts yielded *trans*-polyphenylacetylene; M_n values of the polyene were in the range 7000–10,000 and polydispersion index between 1.5 and 1.8.

6. Final remarks

Organoiridium catalysts promote various C–C bond formation reactions of substituted acetylenes: the reactions can be governed

Table 6
Polymerization of phenylacetylene catalyzed by Ir(diene)(N–N)X in mesitylene.

Entry	Catalyst	[NaOH]/[Ir]	Time (h)	Conv. (%)
1	Ir(cod)(phen)Cl	2	5	58
2	Ir(cod)(phen)Cl	–	5	46
3	Ir(hd)(phen)Cl	2	5	46
4	Ir(hd)(phen)Cl	–	5	73
5	Ir(hd)(phen)Br	–	5	97
6	Ir(hd)(phen)I	–	2	98
7	Ir(hd)(Ph_2phen)Cl	–	10	58
8	Ir(hd)(phen)Cl	–	10	81
9	Ir(hd)(Me_2phen)Cl	–	10	86
10	Ir(hd)(Me_4phen)Cl	–	10	94

Experimental conditions: [Ir] = 6.8×10^{-3} mol L^{-1}; [sub]/[Ir] = 50; *T* = 160 °C.

by the appropriate choice of the ancillary ligands as well as of the experimental conditions. Polymerization of phenylacetylene to the corresponding polyphenylacetylene could be obtained with 100% *trans* stereochemistry in the presence of iridium derivatives with either monodentate phosphines or substituted phenanthrolines; at variance, mainly *cis*-polyphenylacetylene was formed in reactions catalyzed by $[Ir(cod)Cl]_2$ and $[Ir(cod)(OMe)]_2$ at temperatures as low as 0 °C. In most of the polymerization reactions no oligomers were formed. On the other hand, regioselective cyclotrimerization of phenylacetylenes was attained by employing iridium derivatives with bidentate phosphines, with the favoured product 1,2,4-triarylbenzene formed in up to 100% yield.

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