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Organoiridium compounds with bidentate phosphines as highly regioselective catalysts for alkynes cyclotrimerization

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Abstract

The iridium derivatives HIr(cod)(L-L) (cod = 1,5-cyclooctadiene; L-L = $Ph_2PCH_2PPh_2$ (dppm); $Ph_2P(CH_2)_2PPh_2$ (dppe); $Ph_2P(CH_2)_3PPh_2$ (dppp); $Ph_2P(CH_2)_4PPh_2$ (dppb); *o*-$C_6H_4(PPh_2)_2$; $Cy_2P(CH_2)_2PCy_2$ (dcpe); *o*-$Me_2NC_6H_4PPh_2$ (P-NMe_2)) and Ir(OMe)(cod)(dppe-F) (dppe-F = $(C_6F_5)_2P(CH_2)_2P(C_6F_5)_2$) are active catalysts for the cyclotrimerization of phenylacetylene and substituted derivatives. The nature of the phosphine ligand has a pronounced effect on catalytic activity and selectivity of the reactions: in some cases (L-L = dcpe, dppe-F) mixtures of oligomerization and polymerization products are obtained, in others only cyclomerization is observed, with regioselectivities as high as 100% of the 1,2,4-trisubstituted benzenes in the reactions catalyzed by HIr(cod)(dppm). The observed regioselectivity is discussed in terms of preferential formation of one of the possible metallacyclic intermediates of the catalytic reaction.

Keywords: Iridium; Bidentate phosphines; Alkynes; Cyclotrimerization; Regioselectivity

1. Introduction

Although the ability of iridium derivatives to promote C–C bond formation of alkynes has been known for the last 40 years, the oligomerization of acetylenes has mainly been studied with other metals such as rhodium, ruthenium and palladium. Recently, however, some papers have appeared in the literature that suggest a renewed interest towards iridium-based catalysts which promote this reaction.

Formation of linear oligomers (dimers and trimers) has been reported in the presence of organoiridium derivatives, but the reactions often suffer from a low selectivity, as mixtures of products are usually obtained [1–4]. One important exception is the catalyst Ir(biph)$(PMe_3)_3Cl$ (biph = biphenyl-2,2′-diyl), which promotes the selective formation of the Z-enynes [5].

On the other hand, preparation of benzene derivatives via alkynes cyclotrimerization (Fig. 1) has attracted much attention in the last years, however the low regioselectivity generally observed has severely limited the applicability of the reaction for synthetic purposes. Nearly all transition metals have been reported to promote the cyclotrimerization of acetylenes, although examples of iridium-catalyzed reactions [6–10] are not very common.

During our recent studies on alkynes polymerization homogeneously catalyzed by rhodium and iridium derivatives, we found that the organoiridium compounds HIr(cod)$(PR_3)_2$ (cod = 1,5-cyclooctadiene; $PR_3 = PPh_3$, P(*p*-$MeOC_6H_4)_3$, P(*o*-$MeOC_6H_4)Ph_2$, $PCyPh_2$) promote the highly stereoselective polymerization of phenylacetylene to the *trans*-polyene (Fig. 2) [11].

We were then interested in investigating the effect of substitution of the two monodentate phosphines with one bidentate phosphine: as a matter of fact, we had previously experienced that a similar substitution in a series of rhodium derivatives had a beneficial effect on alkynes polymerization catalysis [12], especially with regard to the stability of the catalytically active species.

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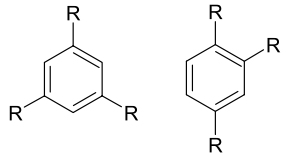


Fig. 1. Cyclotrimerization products from terminal alkynes.

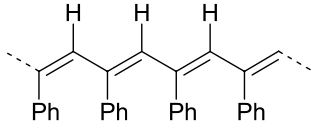


Fig. 2. *Trans*-polyphenylacetylene.

However, as we have reported in a preliminary account [13], the compounds $HIr(cod)(Ph_2P(CH_2)_nPPh_2)$ ($n = 1$–4) do not behave as polymerization catalysts, at variance they promote the cyclotrimerization of phenylacetylenes. Interestingly, in some of the catalytic reactions 1,2,4-triphenylbenzene is formed with high to excellent regioselectivity. In this contribution we now present the results of an extended study on the alkynes cyclotrimerization reaction catalyzed by iridium-bidentate phosphine derivatives: the effect on the catalytic reaction of the nature of phosphine ligand on one hand, and of substrate substituents on the other will be discussed.

2. Experimental

2.1. 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. Naphthalene was purified by recrystallization from ethanol. All the other chemicals were reagent grade and were used as received by commercial suppliers.

The phosphine *o*-$Me_2NC_6H_4PPh_2$ [14] and the compounds $[Ir(cod)(OMe)]_2$ [15] and HIr(cod)(dppm) [16] were prepared according to the procedures reported in the literature. All the iridium derivatives were stored under inert atmosphere, to avoid decomposition.

2.2. 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 to tetramethylsilane; ^{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 GC on a HP 6890 instrument, using naphthalene as internal standard. Molecular weight distributions of the polymers were determined by SEC 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 HIr(cod)(L-L) (L-L = dppe, dppp, dppb, o-$C_6H_4(PPh_2)_2$, o-$Me_2NC_6H_4PPh_2$)

A suspension of 100 mg (0.15 mmol) of $[Ir(cod)(OMe)]_2$ in 15 ml of methanol was treated with 0.30 mmol of the ligand L-L. The resulting mixture was stirred at room temperature for 3–5 h, yielding a solid product which was filtered, washed with methanol and dried under vacuum. Yields 72–78%.

2.4. Spectroscopic data for HIr(cod)(dppe)

^{31}P $\{^1H\}$NMR (C_6D_6, 25 °C): δ + 43.8 d and +29.7 d ($J_{PP} = 2.0$ Hz). ^1H NMR (C_6D_6, 25 °C): δ 8.2–7.0 (m, 20H, Ar); 5.15 (bm, 1H, allyl); 5.07 (bm, 1H, allyl); 4.01 (m, 1H, allyl); 2.5 (bm, 2H, dppe); 2.0 (bm, 2H, dppe); 2.2–1.8 (multiplets, 9H, Ir–CH and CH_2); −11.55 (dd, 1H, Ir–H, $J_{HP} = 20.6$ and 14.7 Hz).

^{13}C $\{^1H\}$NMR (C_6D_6, 25 °C): δ 138–128 (Ar); 91.3 (s, allyl); 63.2 (d, allyl, $J_{CP} = 37.2$ Hz); 56.5 (s, CH_2); 55.3 (d, CH_2, $J_{CP} = 13.9$ Hz); 35.7 (m, dppe); 33.0 (dd, Ir–C, $J_{PC} = 72.6$ and 4.6 Hz); 29.6 (m, dppe); 29.4 (s, CH_2); 27.0 (d, CH_2, $J_{PC} = 29.3$ and 13.9 Hz).

2.5. Spectroscopic data for HIr(cod)(dppp)

^{31}P $\{^1H\}$NMR (C_6D_6, 25 °C): δ – 13.1 s. ^1H NMR (C_6D_6, 25 °C): δ 7.8–7.0 (m, 20H, Ar); 3.77 (bs, 4H, C=CH); 2.5 (bm, 4H, dppp); 2.0 (bm, 2H, dppp); 2.2–1.9 (multiplets, 8H, CH_2); −13.35 (t, 1H, Ir–H, $J_{HP} = 21.5$ Hz).

2.6. Spectroscopic data for HIr(cod)(dppb)

^{31}P $\{^1H\}$NMR ($CDCl_3$, 25 °C): δ +0.8 s. ^1H NMR (C_6D_6, 25 °C): δ 7.8–7.0 (m, 20H, Ar); 3.84 (bs, 4H, C=CH); 2.1–1.8 (multiplets, 8H, CH_2); 2.7, 2.4, 1.6, 1.1 (multiplets, 2H each, dppb); −13.51 (t, 1H, Ir–H, $J_{HP} = 21.6$ Hz).

^{13}C $\{^1H\}$NMR (C_6D_6, 25 °C): δ 143–127 (Ar); 39.1 (t, C=CH, $J_{CP} = 13.9$ Hz); 24.2 (CH_2).

2.7. Spectroscopic data for HIr(cod)(o-$C_6H_4(PPh_2)_2$

^{31}P {^1H}NMR (C_6D_6, 25 °C): δ +39.3 d and +28.4 d (J_{PP} = 2.0 Hz). ^1H NMR (C_6D_6, 25 °C): δ 8.0–6.7 (m, 24H, Ar); 4.79 (bm, 1H, allyl); 4.73 (bm, 1H, allyl); 4.63 (m, 1H, allyl); 2.5–1.8 (multiplets, 9H, Ir–CH and CH_2); −11.14 (dd, 1H, Ir–H, J_{HP} = 19.5 and 15.6 Hz). ^{13}C {^1H}NMR (C_6D_6, 25 °C): δ 135–127 (Ar); 89.8 (s, allyl); 75.2 (s, allyl); 64.7 (d, allyl, J_{CP} = 37.1 Hz); 56.8 (s, CH_2); 55.4 (d, CH_2, J_{CP} = 12.4 Hz); 34.5 (dd, Ir–C); 29.1 (s, CH_2); 26.9 (s, CH_2).

2.8. Spectroscopic data for HIr(cod)(o-$Me_2NC_6H_4PPh_2$)

^{31}P {^1H}NMR (C_6D_6, 25 °C): δ +25.8 s. ^1H NMR (C_6D_6, 25 °C): δ 8.2–6.7 (m, 14H, Ar); 5.12 (bm, 1H, allyl); 4.86 (bm, 1H, allyl); 3.79 (m, 1H, allyl); 2.51 (s, 6H, NMe); 2.2–1.4 (multiplets, 9H, Ir–CH and CH_2); −9.64 (d, 1H, Ir–H, J_{HP} = 21.5 Hz). ^{13}C {^1H}NMR (C_6D_6, 25 °C): δ 141–118 (Ar); 96.3 (s, allyl); 73.6 (s, allyl); 63.2 (d, allyl, J_{CP} = 39.2 Hz); 54.8 (s, CH_2); 54.2 (s, NMe); 51.3 (d, CH_2); 29.8 (s, CH_2); 26.0 (m, IrCH); 17.5 (d, CH_2, J_{CP} = 7.7 Hz).

2.9. Preparation of HIr(cod)(dcpe)

A solution of 80 mg (0.12 mmol) of $[Ir(cod)(OMe)]_2$ in 2 ml of THF was treated with 101 mg (0.24 mmol) of dcpe. The resulting solution was stirred at room temperature for 2 h, after which time it was concentrated to approx. 1 ml. Addition of pentane caused precipitation of a yellow solid which was filtered, washed with pentane and dried under vacuum. Yield: 48%.

^{31}P {^1H}NMR (C_6D_6, 25 °C): δ +47.9 d and +36.3 d (J_{PP} = 3.0 Hz). ^1H NMR (C_6D_6, 25 °C): δ 5.14 (bm, 2H, allyl); 4.60 (m, 1H, allyl); 2.1–1.8 (multiplets, 9H, Ir–CH and CH_2); −12.44 (t, 1H, Ir–H, J_{HP} = 18.6 Hz).

^{13}C {^1H}NMR (C_6D_6, 25 °C): δ 85.8 (s, allyl); 69.9 (s, allyl); 60.0 (d, allyl, J_{CP} = 36.9 Hz); 57.3 (d, CH_2, J_{CP} = 13.1 Hz); 56.1 (s, CH_2); 39.0 (d, Ir–C, J_{PC} = 22.3 Hz); 30–25 (CH_2 and Cy).

2.10. Preparation of Ir(OMe)(cod)(dppe-F)

A suspension of 89 mg (0.14 mmol) of [Ir(cod)(OMe)]$_2$ in 30 ml of methanol was treated with 207 mg (0.27 mmol) of dppe-F. The resulting mixture was stirred at room temperature for 24 h, yielding a yellow solid which was filtered, washed with methanol and dried under vacuum. Yield 61%. IR (Nujol): 1090 and 1037 cm^{-1} (Ir–OMe).

^{31}P {^1H}NMR ($CDCl_3$, 25 °C): δ +0.8 s (major isomer) and +122.7 s (minor isomer). ^1H NMR ($CDCl_3$, 25 °C): major isomer δ 3.77 (bm, 4H, C=CH); 3.48 (s, OMe); 2.5–2.0 (multiplets, 12H, CH_2 of cod and dppe-F); minor isomer δ 3.51 (s, OMe); 2.91 (bm, 4H, C=CH); 2.5–2.0 (multiplets, 12H, CH_2 of cod and dppe-F). ^{13}C NMR not obtained due to low solubility.

2.11. Cyclotrimerization reactions

A typical procedure for the catalytic reactions is described in the following. A solution of HIr(cod)(L-L) (0.017 mmol) and of the GC standard naphthalene (100 mg) in 5.0 ml of solvent (usually THF) was thermostatted at the appropriate 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 for GC analysis. The final reaction mixture, after evaporation of the solvent, was analyzed by ^1H and ^{13}C NMR.

2.12. Determination of product distribution and stereochemistry

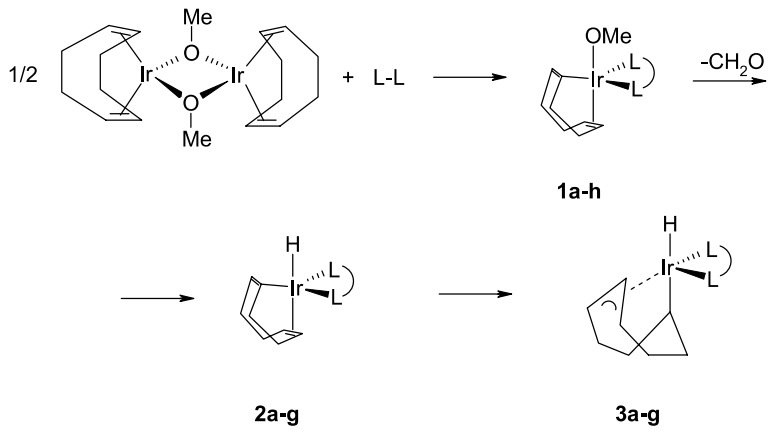
Yields of 1,3,5-triaryllbenzene and 1,2,4-triarylbenzene were determined by GC analysis, and confirmed by ^1H and ^{13}C NMR [13]. Yields of (E)-1,4-diphenyl-1-butyn-3-ene and (Z)-1,4-diphenyl-1-butyn-3-ene were determined by ^1H NMR ($CDCl_3$) by integration of the signals of the corresponding vinyl protons [11].

The stereochemistry of the polyphenylacetylene obtained was determined by ^1H and ^{13}C NMR [11]. Determination of polyene molecular weights via SEC 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 polystyrene standards.

3. Results and discussion

3.1. Preparation and properties of iridium-diphosphines compounds

The compounds HIr(cod)($Ph_2P(CH_2)_nPPh_2$) (n = 1, bis(diphenylphosphino)methane (dppm); 2, 1,2-bis(diphenylphosphino)ethane (dppe); 3, 1,3-bis(diphenylphosphino)propane (dppp); 4, 1,4-bis(diphenylphosphino)-butane (dppb)) were synthesized according to the procedure reported by Oro et al. [16] for the derivative with dppm. A suspension of [Ir(cod)(OMe)]$_2$ in methanol was treated with one equivalent of the phosphine at room temperature: initial formation of the mononuclear methoxo species **1a–d**, a red compound partially soluble in the reaction medium, was followed by hydrogen β-elimination which was expected to give the off-white or pale yellow hydride derivative **2a–d** (see Scheme 1). In fact the structure of the product with dppm, reported by Oro, reveals that with this ligand **3a** has actually been obtained, where



Scheme 1.

the diene is coordinated to iridium in an unusual η^1, η^3-binding mode.

We now find that also in the analogue reaction with dppe the carbocyclic ligand of the product **3b** is coordinated in the same fashion, as indicated by the ^{1}H NMR spectrum in C_6D_6, where the hydride signal is a doublet of doublets at δ −11.55 (J_{HP} = 20.6 and 14.7 Hz) and the allylic protons resonate as multiplets at δ 5.15, 5.07 and 4.01 ppm, whereas the ^{31}P NMR spectrum shows two inequivalent phosphorous nuclei at δ +43.8 and +29.7 (doublets, J_{PP} = 2.0 Hz). The ^{13}C NMR data (see Section 2) are in agreement with the proposed structure.

A more intriguing situation is present for the reaction of [Ir(cod)(OMe)]$_2$ and dppp, as a mixture of two products is obtained: compound **2c** with "normally" coordinated η^2,η^2-cod, and compound **3c** with an η^1,η^3-binding mode of carbocyclic ligand, with an intensity ratio of about 8:1. The ^{31}P NMR spectrum in C_6D_6 consists in a singlet at δ −13.1 (**2c**) and two doublets at δ −6.5 and −14.9 (J_{PP} = 23.7 Hz, **3c**). The ^{1}H NMR resonances of the vinyl protons of cod in **2c** at δ 3.77 are accompanied by multiplets at δ 5.29, 4.35 and 3.35, assignable to iridium-allyl protons of **3c**; in the hydride region a major triplet at δ −13.35 (J_{HP} = 21.5 Hz, **2c**) and a smaller one at δ −11.28 (J_{HP} = 17.7 Hz, **3c**) are detected. Interestingly, a variable temperature NMR study showed that by increasing the temperature of a C_6D_6 solution containing **2c** and **3c** the former compound was partially converted into the latter: whereas at r.t. the ratio between **2c** and **3c** was 8:1, at 35 °C it lowered to 2:1, and at 55 °C it was 1:3, i.e. the prevalent compound was now **3c**; a further increase of the temperature (up to 75 °C) caused no change in the product ratio. The conversion of **2c** into **3c** was irreversible, as the final intensity ratio of 1:3 was maintained when the sample temperature was eventually lowered to 20 °C. Notably, this interconversion takes place also at room temperature, as observed by recording the ^{1}H NMR spectrum after an overnight accumulation for the ^{13}C spectrum: in the final mixture the signals of both **2c** and **3c** were detectable in a 1:2 ratio.

In the synthesis of the iridium hydride with the ligand dppb compound **2d** was formed, as evidenced by spectroscopic data: ^{31}P NMR showed a singlet at δ +0.8, whereas ^{1}H and ^{13}C spectra were consistent with a carbocyclic ligand coordinated as a typical diolefin (see Table 1 and Section 2). However, also in this case at higher temperature the irreversible isomerization **2d** → **3d** took place, as evidenced by a variable temperature NMR experiment: compound **3d** was detected at 35 °C albeit in traces (^{31}P NMR δ +4.7 d and −2.3 d, J_{PP} = 14.8 Hz; ^{1}H NMR δ −11.40 t (Ir–H, J_{HP} = 16.6 Hz); 5.13, 4.24, 3.2 (bm, allyl protons)); the amount of **3d** slightly increased at higher temperature up to 8% of the total mixture.

Besides the ligands of the series $Ph_2P(CH_2)_nPPh_2$, other bidentate phosphines where employed for the syntheses of the corresponding iridium-hydrides. The reaction of [Ir(cod)(OMe)]$_2$ with *o*-$C_6H_4(PPh_2)_2$ with the usual procedure gave compound **3e**, as evidenced by ^{31}P NMR data (two doublets at δ +39.3 and +28.4, J_{PP} = 2.0 Hz) as well as ^{1}H and ^{13}C spectra (see Table 1 and Section 2).

The corresponding synthesis with dcpe (= 1,2-bis (dicyclohexylphosphino)ethane) in methanol only produced decomposition products; the preparation was successfully performed in THF solution at r.t. for 2 h, after which time the mixture was concentrated, and the product was recovered by addition of pentane. Also in this case the NMR spectra (see Table 1) indicated that product **3f** with the rearranged carbocyclic ligand was obtained.

The ligand *o*-$Me_2NC_6H_4PPh_2$ (P-NMe_2), which can coordinate in a bidentate fashion through P and N atoms, was also reacted with [Ir(cod)(OMe)]$_2$: the isomerization product **3g** was produced also with this hybrid ligand (see Table 1).

Table 1
Selected NMR data for HIr(cod)(L-L)

L-L (compound)	^{31}P	^{1}H	
		H-Ir	cod
dppe (**3b**)	+43.8 d; +29.7 d ($J_{PP} = 2.0$)	−11.55 dd ($J_{HP} = 20.6$ and 14.7)	5.15 (1H); 5.07 (1H); 4.01 (1H); 2.2–1.8 (9H)
dppp (**2c**)	−13.1 s	−13.35 t ($J_{HP} = 21.5$)	3.77 (4H); 2.2–1.9 (8H)
dppb (**2d**)	+0.8 s	−13.51 t ($J_{HP} = 21.6$)	3.84 (4H); 2.1–1.8 (8H)
o-$C_6H_4(PPh_2)_2$ (**3e**)	+39.3 d; +28.4 d ($J_{PP} = 2.0$)	−11.14 dd ($J_{HP} = 19.5$ and 15.6)	4.79 (1H); 4.73 (1H); 4.63 (1H); 2.5–1.8 (9H)
dcpe (**3f**)	+47.9 d; +36.3 d ($J_{PP} = 3.0$)	−12.44 t ($J_{HP} = 18.6$)	5.14 (2H); 4.60 (1H); 2.1–1.8 (9H)
P-NMe_2 (**3g**)	+25.8 s	−9.64 d ($J_{HP} = 21.5$)	5.12 (1H); 4.86 (1H); 3.79 (1H); 2.2–1.4 (9H)

Experimental conditions: C_6D_6 solutions, 25 °C.
Chemical shifts expressed in ppm; coupling constants expressed in Hz.

The results of these syntheses suggest that with bidentate phosphines which on coordination form comparatively small chelate rings such as dppm (four-membered chelate ring) and dppe, *o*-$C_6H_4(PPh_2)_2$, dcpe, P-NMe_2 (five-membered chelate rings) the rearrangement of cod to the η^1,η^3-binding mode is favoured. By increasing the chelate ring size to six- (dppp) and seven-membered rings (dppb) such isomerization is observed at high temperature, and in the latter case only to a small extent. According to the studies reported by Oro on the dppm derivative [16], the rearrangement occurs via a succession of olefin insertions into the metal-hydride bond and β-eliminations from the iridium-alkyl. A similar situation was reported by some of us [17] with the compound HIr(cod)(PNP) (PNP = $C_3H_7N(CH_2CH_2PPh_2)_2$) where the insertion product Ir(PNP)(σ,η^2-C_8H_{13}) was stabilized by coordination to the metal of the nitrogen atom of the phosphine ligand, thus preventing the successive steps of the rearrangement. With regard to the compounds object of the present studies, we are presently investigating on the factors which determine the rearrangement of cod by photoemission spectroscopy using Synchrotron Radiation; the results of such measurements will be compared with DFT calculations on the same iridium compounds.

Finally, a different behaviour was observed in the synthesis of the derivative with 1,2-bis(dipentafluorophenylphosphino)ethane (dppe-F): reaction of this ligand with $[Ir(cod)(OMe)]_2$ produced a mixture of two isomers of the methoxo derivative **1h**. Further reaction to give the hydride species was not observed even at longer reaction times and higher temperatures: apparently, the ligand with perfluoro phenyl groups stabilized the methoxo compound with regard to the β-elimination reaction.

3.2. Catalytic reactions with iridium/diphosphine complexes

The iridium complexes HIr(cod)(L-L) (L-L = dppm, **3a**; dppe, **3b**; dppp, **2c**; dppb, **2d**; *o*-$C_6H_4(PPh_2)_2$, **3e**; dcpe, **3f**; P-NMe_2, **3g**) and the methoxo compound Ir-(OMe)(cod)(dppe-F) (**1h**), synthesized as above described, were employed as catalysts for the cyclotrimerization of phenylacetylene. In a typical catalytic reaction, the light yellow solution of the iridium derivative, thermostatted at the appropriate temperature, was treated with the alkyne, thus giving an orange–brown solution. The reaction was followed by GC analysis of samples withdrawn at time intervals, and the final products were analyzed by GC and ^{1}H and ^{13}C NMR and – when the polyene was formed – by SEC (size exclusion chromatography) to determine its molecular weight and polydispersion.

The results obtained in the catalytic reactions with phenylacetylene in THF are reported in Table 2; similar results were obtained in other solvents such as toluene and methanol, in spite of the limited solubility of the iridium derivative in the latter, whereas dichloromethane and chloroform caused partial decomposition of the catalysts.

The series of compounds with the ligands dppm, dppe, dppp and dppb (entries 1–4) promoted the cyclotrimerization of the alkyne, whereas no formation of either polyphenylacetylene (PPA) or linear dimers was detected in the corresponding reactions. Notably, formation of triphenylbenzenes occurred with high to excellent regioselectivity (90–99%) towards the asymmetric isomer 1,2,4-triphenylbenzene. Both catalytic activity and regioselectivity decreased in the order dppm > dppe > dppp > dppb, i.e. with increasing the iridium-

Table 2
Cyclotrimerization of phenylacetylene with iridium/diphosphine catalysts

Entry	Catalyst	Conversion (%)	*trans*-PPA (%)	1,2,4-$Ph_3C_6H_4$ (%)	1,3,5-$Ph_3C_6H_4$ (%)
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*-$C_6H_4(PPh_3)_2$)	92		88	4
6	HIr(cod)(dcpe)	31[b]	18	3	3
7	HIr(cod)(P-NMe_2)	20	8	6	6
8	Ir(OMe)(cod)(dppe-F)	32	22	5	5

Experimental conditions: $[Ir] = 3.4 \times 10^{-3}$ mol l^{-1}; [sub] = 0.34 mol l^{-1}; [sub]/[Ir] = 100; solvent = THF; $T = 60$ °C; reaction time: 6 h. PPA = polyphenylacetylene.
[a] Reaction time 15 min.
[b] Dimerization products also obtained.

diphosphine chelate ring size. Among the other catalysts employed, only the adduct with *o*-$C_6H_4(PPh_2)_2$ gave comparable results (Table 2 entry 5), as it only promoted formation of the cyclotrimers with good regioselectivity.

At variance, in the reactions catalyzed by the iridium derivatives with dcpe, P-NMe_2 and dppe-F (Table 2 entries 6–8) mixture of products were obtained: formation of triphenylbenzenes was not regioselective, and it was always accompanied by the polymerization product. In one case (entry 6) also enynes were formed *via* phenylacetylene dimerization. With regard to the polymerization reaction, the polyene produced had similar properties as that obtained in the reactions catalyzed by HIr(cod)$(PR_3)_2$ [11]: high stereoselectivity (virtually 100% of trans sequences), M_n between 3000 and 8000, polydispersion index of 1.3–1.7.

3.3. Cyclotrimerization of arylacetylenes

In order to study the influence of the nature of the alkyne on the catalytic reaction, as well as the generality of the cyclotrimerization, the substituted phenylacetylenes *p*-$MeOC_6H_4C{\equiv}CH$, *p*-$CF_3C_6H_4C{\equiv}CH$ and *o*-$CF_3C_6H_4C{\equiv}CH$ were also employed. For this investigation we selected, among the series above reported, two catalysts which only promote the cyclotrimerization reaction, i.e. HIr(cod)(dppm) (**3a**) and HIr(cod)(dppb) (**2d**). The results of the corresponding catalytic reactions are reported in Tables 3 and 4.

In the presence of the dppm derivative **3a**, the catalytic reactions with the *para*-substituted phenylacetylenes at 60 °C were rather fast (Table 3 entries 1–3), therefore a lower temperature was employed to appreciate differences in reaction rates. At 40 °C a trend was

Table 3
Cyclotrimerization of arylacetylenes catalyzed by HIr(cod)(dppm)

Entry	Substrate	T (°C)	t	Conversion (%)	1,2,4-$Ar_3C_6H_4$ (%)	1,3,5-$Ar_3C_6H_4$ (%)
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	5 h	85[a]	22	38
5	$PhC{\equiv}CH$	40	1.5 h	98	95	3
6	*p*-$MeOC_6H_4C{\equiv}CH$	40	1 h	100	97	3
7	*p*-$CF_3C_6H_4C{\equiv}CH$	40	2 h	98	97	1

Experimental conditions: $[Ir] = 3.4 \times 10^{-3}$ mol l^{-1}; [sub] = 0.34 mol l^{-1}; [sub]/[Ir] = 100; solvent = THF.
[a] Other products: *trans*-PPA and dimers.

Table 4
Cyclotrimerization of arylacetylenes catalyzed by HIr(cod)(dppb)

Entry	Substrate	Conversion (%)	1,2,4-$Ar_3C_6H_4$ (%)	1,3,5-$Ar_3C_6H_4$ (%)
1	$PhC{\equiv}CH$	31	28	3
2	*p*-$MeOC_6H_4C{\equiv}CH$	39	36	3
3	*p*-$CF_3C_6H_4C{\equiv}CH$	40	39	1
4	*o*-$CF_3C_6H_4C{\equiv}CH$	26[a]	n.d.	n.d.

Experimental conditions: see Table 3. $T = 60$ °C; reaction time 6 h.
[a] Products: *trans*-PPA, dimers and cyclotrimers.

evidenced in the reaction rates, which increase on increasing the electrodonating properties of the substituent on the phenyl ring: p-$CF_3C_6H_4C{\equiv}CH <$ $PhC{\equiv}CH < p$-$MeOC_6H_4C{\equiv}CH$. With these substrates the cyclotrimerization reactions catalyzed by **3a** were highly regioselective, notably with the alkyne bearing the *para*-methoxy group the corresponding 1,2,4-triarylbenzene was obtained with 100% yield.

On the other hand, the reactions of the *p*-substituted phenylacetylenes catalyzed by the dppb derivative **2d** were as expected much slower (see Table 4 entries 1–3), however in this case there was no apparent trend of reaction rate and regioselectivity as a function of electronic properties of the substituent.

At variance, with both catalysts in the reactions of the ortho substituted phenylacetylene o-$CF_3C_6H_4C{\equiv}CH$ a mixture of products was obtained, including comparable amounts of the cyclotrimers, *trans*-polyene and enynes (see Table 3 entry 4 and Table 4 entry 4). Apparently, with this more sterically demanding alkyne different reaction pathways are operative, probably also involving catalytic species with the phosphine coordinated in a monodentate fashion.

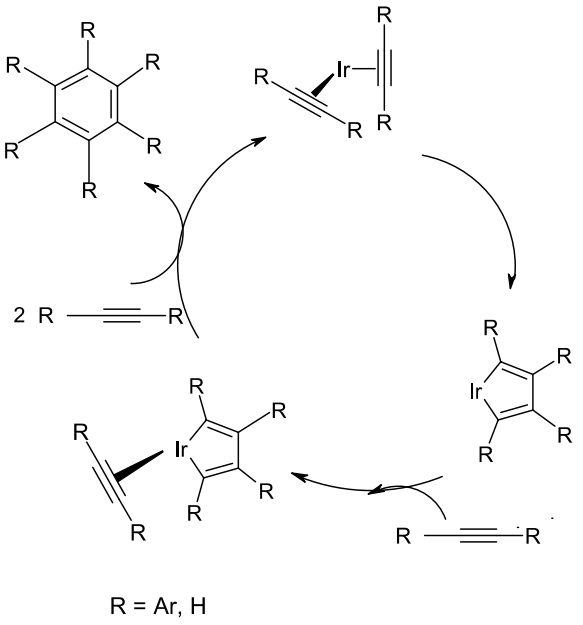
Finally, the catalysts under investigation do not promote the cyclotrimerization of disubstituted acetylenes, as evidenced by reactions performed with phenylpropyne ($PhC{\equiv}CMe$) in the presence of either **3a** or **3b**, which produced neither oligomeric nor polymeric products.

3.4. Mechanism of cyclotrimerization

Although the cyclotrimerization of alkynes has been studied by several research groups with a variety of early and late transition metal derivatives, regioselective formation of one of the possible isomeric products has rarely been reported. Recently, Ladipo and coworkers described supported titanium-arene complexes which catalyze the cyclotrimerization of phenylacetylene to 1,2,4-triphenylbenzene with 99% yield [18]; the same reaction occurs with 96% selectivity in the presence of a cobalt carbonyl cluster [19]. Regioselective cyclotrimerization of p-$MeC_6H_4C{\equiv}CH$ has been reported with palladium complexes, with yields in the asymmetric isomer up to 95% [20].

Therefore, the regioselectivity observed in some of the reactions we are reporting here, and particularly those performed with the catalyst HIr(cod)(dppm), where yields of 1,2,4-triarylbenzenes up to 100% are obtained, is unprecedented but for the titanium-based catalysts of Ladipo [18].

As reported in previous studies [21–24], metal-mediated cyclotrimerization reactions typically proceed through formation of metallacyclopentadiene intermediates (see Scheme 2). The final step of the reaction has been proposed to occur either via a metallacycloheptatriene intermediate or in a concerted fashion, however in most cases proofs in support of the concerted mechanism have been produced.



Scheme 2.

In the iridium-catalyzed cyclotrimerization here reported, selective formation of the 1,2,4-trisubstituted benzenes is possibly determined by regioselective formation of the metallacyclopentadiene intermediate. As a matter of fact, both 2,5 and 3,4-diarylmetallacycles (see Fig. 3) can only form the asymmetric arene independently by the orientation of addition of the third alkyne, whereas from the 2,4-diarylmetallacycle either isomers of the trisubstituted arene can be produced, according to the regiochemistry of the subsequent alkyne addition.

We believe that selective formation of the intermediate 2,5-diarylmetallacycle is responsible for the regioselective cyclotrimerization to the 1,2,4-triarylbenzene catalyzed by the iridium-diphosphines complexes. As a matter of fact, the dependence of both reaction rate and regioselectivity on the chelate ring size in the series dppm–dppe–dppp–dppb (vide supra) indicates a dramatic effect of the chain length connecting the two phosphorous atoms on the catalytic reaction. In other words, an increase of the bite angle of the diphosphine has a negative effect on the cyclotrimerization reaction. These results suggest that the iridacyclopentadiene with

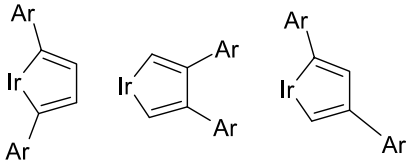


Fig. 3. Iridacyclopentadienes.

the substituents adjacent to iridium is the intermediate involved in the catalytic reaction, as the stability of this species is expected to be heavily dependent on the steric hindrance in the coordination sphere of iridium, and in the series of ligands considered it would be most stabilized by dppm which has the smallest bite angle. It is to be noted that steric factors are often invoked as determining the regioselectivity of alkynes cyclotrimerization [18,25]. Moreover, the suggestion of selective formation of the 2,5-diarylmetallacycle is in agreement with the results of Wakatzuki and coworkers, who isolated a series of cobaltacyclopentadiene intermediates: in all cases selective formation of one of the possible metallacycles was observed, i.e. the adduct where the cobalt is bound to the carbon atoms bearing the bulkier substituents [26].

The alternative possibility, i.e. formation of 1,2,4-triarylbenzenes via intermediate 2,4-diarylbenzene followed by approach of the third alkyne with controlled orientation, cannot however be ruled out on the basis of the results so far obtained.

Further investigations are underway to identify the iridium derivatives involved in the catalytic cycles; by these means we propose to establish the origin of the regioselectivity, as well as the reasons of the observed trend of catalytic activity as a function of the electronic properties of the alkyne substituents.

4. Conclusions

A series of organoiridium derivatives with bidentate phosphines of the type HIr(cod)(L-L) has been synthesized and characterized. In these compounds, according to the phosphine employed the diene can be coordinated either in a "normal" diolefin fashion, or it can be rearranged to an η^1,η^3-binding mode; such rearrangement appears to be disfavoured by an increase of the iridium-phosphine chelate ring size.

The iridium derivatives catalyze the regioselective cyclotrimerization of phenylacetylenes to the corresponding 1,2,4-triarylbenzenes with yields up to 100%. The results of the catalytic reactions have been discussed, and the observed regioselectivity has been rationalized in terms of selective formation of one of the possible metallacyclopentadienyl intermediates. Studies concerning the mechanism of the catalytic reaction are currently in progress.

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