Highly selective biaryl formation by the cyclooligomerization of arylethynes catalyzed by rhodium and ruthenium porphyrins†

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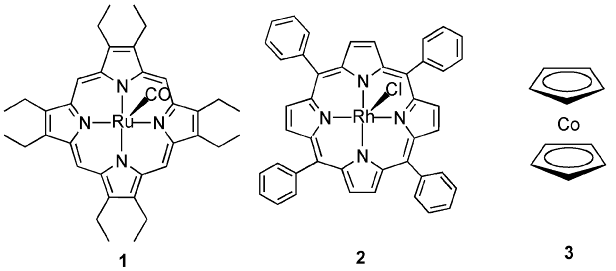
Rhodium and ruthenium porphyrins catalyze the one-pot formation of biaryl derivatives from arylethynes with high selectivity, giving interesting derivatives not easy to obtain using other different methods; the porphyrin catalysts can be recovered and reused after several experiments with no change of activity.

The rich chemistry of the carbon–carbon triple bond has been the subject of intense research in the past two decades due to the well recognized importance that this function shows as a building block in organic and materials chemistry.[1] Among all the reactions which use the alkyne reactivity to form new carbon–carbon bonds, the most fascinating one remains the formation of benzene rings, the Reppe cyclotrimerization of alkynes.[2] Such reactions have been deeply studied in the last fifty years because they give functionalized aromatic compounds which are difficult to obtain using the usual methods.[3]

Moreover, the alkyne scaffolds represent a new source of compounds useful for the synthesis of nanotubes.[4]

Recently we found that the arylethynes can undergo to the cyclooligomerization reaction in the presence of a catalytic amount of metalloporphyrins, giving trisubstituted benzenes and/or arylsubstituted naphthalenes, depending on the nature of the catalyst, the reaction conditions and the solvent used.[5]

Biaryl compounds are an important class of organic compounds and are found in several natural products. Furthermore they are extensively used as chiral ligands of catalysts for the synthesis of optically active compounds. In this paper we report on the use of the porphyrin catalysts for obtaining, with high selectivity, biaryl derivatives starting from 1- or 2-ethynylnaphthalene, **4** and **6**, and 9-ethynylphenanthrene, **5**. The starting compounds **4** and **6** were available from commercial sources while compound **5** was synthesised by the Sonogashira reaction.[6]

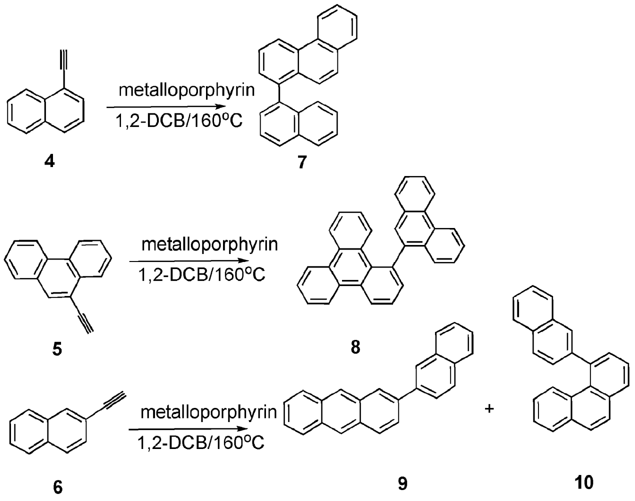


Scheme 1 The structure of catalysts **1**, **2** and **3**.

The catalysts used for this work were (2,3,7,8,12,13,17,18-octaethylporphyrinato)ruthenium(II) carbonyl, **1**, (5,10,15,20-tetraphenylporphyrinato)rhodium(III) chloride, **2** and cobaltocene, Cp_2Co, **3**. The structure of the catalysts are reported in Scheme 1. Catalysts **1** and **3** are commercially available while **2** was synthesized by literature methods.[7] The structures of the starting compounds and the biaryl products obtained from the cyclodimerization reactions, are reported in Scheme 2.

The cyclodimerization reactions were performed in 1,2-dichlorobenzene (DCB) at 160 °C for 48 h‡ and the reaction products were easily separated by preparative medium-pressure column chromatography and characterized by EI and/or GC-MS, ^{1}H and ^{13}C NMR and elemental analysis.

The reaction conditions used in this work were optimized on the basis of those found from our previous studies.[5] All the catalysts were reused at least four times in consecutive experiments, after the stripping of the reaction products.



Scheme 2 Starting compounds and cyclodimerization products.

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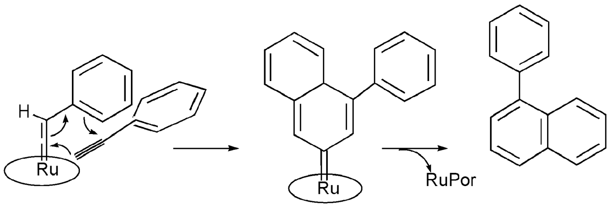
† Electronic supplementary information (ESI) available: Spectroscopic (^{1}H NMR and EI mass spectra) data for all the compounds reported in Table 1. ^{1}H NMR and ^{13}C NMR bidimensional experiments for the identification ot biaryl compounds. Experimental conditions for the synthesis of the triarylbenzenes from tribromobenzenes and boronic acid derivatives and the procedure for obtaining 9-phenanthrene boronic acid. See DOI: 10.1039/b806025h



Scheme 3 Proposed mechanism for the cyclodimerization.

In a previous paper[5b] we proposed a mechanism for the cyclodimerization of phenylacetylene to give the 1-phenylnaphthalene, catalyzed by ruthenium porphyrins, in terms of the formation of a vinylidene intermediate of the metal complex by a η^2-1-alkyne → η^1-vinylidene rearrangement.[8] Such an intermediate could then undergo the concerted attack of a second molecule of alkyne in a (formal) Diels–Alder reaction (see Scheme 3) to give the final dimeric product while triphenylbenzenes probably derive from an open intermediate.

The yield of the dimeric products is also related to the use of solvent in the reaction with the best results obtained in dichlorobenzene.

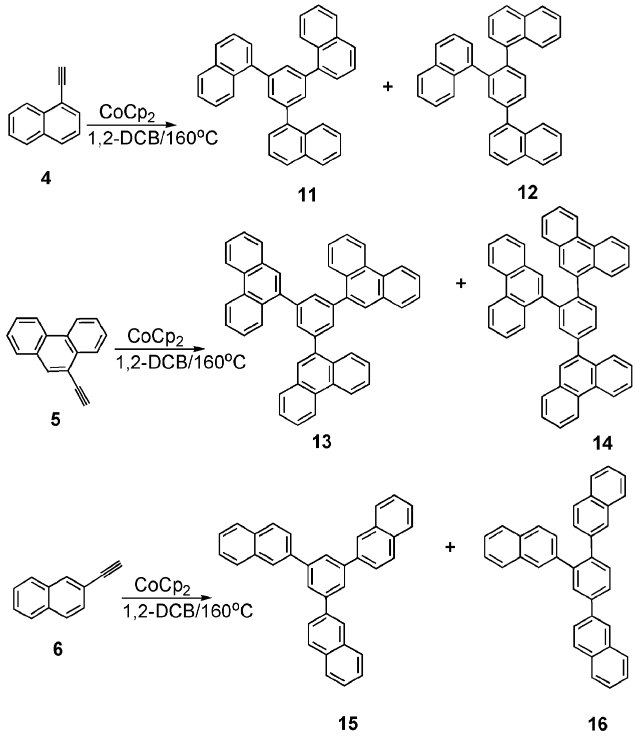
Investigating our proposed reaction mechanism, the next application of the metalloporphyrins catalysis should be directed to the possibility of obtaining other more complicated biaryl derivatives. The approach simply consisted in the use of ethynyl derivatives of naphthalene and phenanthrene. 1- and 2-ethynylnaphthalene and 9-ethynylphenanthrene could be good candidates for obtaining the dimerization reaction and in fact in the presence of catalyst **1** or **2**, substrates **4** and **5**, afford the biaryls **7** and **8**, respectively, while substrate **6**, which has two possibilities of attack at C1 and C3, gives mainly compound **10** while **9** was obtained in trace amount. This last result probably derives from the slightly different stability of the anthracene and phenanthrene polynuclear aromatics ($\Delta\Delta G_f \approx 6$ kcal mol^{-1}).[9] In Table 1 the reaction yields for all the substrates, compared with those obtained using cobaltocene catalyst are reported.

The substrate conversion was always higher than 95% for all the experiments. From the data reported in Table 1, it is clear that the ruthenium and rhodium porphyrins, used for this work, afford biaryl compounds with moderate to high yield and good selectivity while cobaltocene, a classic catalyst used in the cyclooligomerization of ethynes[3] gives mainly a mixture of 1,3,5- and 1,2,4-triarylbenzenes with small amount of the cyclodimers. The structures of the final cyclotrimerization compounds are reported in Scheme 4.

Table 1 Cyclooligomerization of arylethynes, **4**, **5** and **6** in DCB[a] by Ru(OEP)CO, **1**[b], RhTPPCl, **2**[b] and Cp$_2$Co, **3**[c]

			Yield[d] (%)		
Entry	Catalyst	Substrate	Biaryl	1,3,5-Triaryl	1,2,4-Triaryl
1	**1**	**4**	73.4	5.7	13.8
2	**1**	**5**	33.2	Trace	1.6
3	**1**	**6**	62.2[e]	5.9	13.6
4	**2**	**4**	86.0	1.3	3.0
5	**2**	**5**	35.7	1.4	2.9
6	**2**	**6**	89.7[e]	Trace	7.2
7	**3**	**4**	1.2	27.0	66.3
8	**3**	**5**	1.2	25.2	60.1
9	**3**	**6**	1.7	21.8	75.8

[a] Volume ratio DCB : substrate = 3 : 1. [b] Reactions carried out at 160 °C with a molar ratio substrate : porphyrin = 5700 : 1. [c] Reactions carried out at 150 °C with a molar ratio substrate : cobaltocene = 5700 : 1. [d] Yields determined by GC or flash chromatography analysis. [e] Two isomers.



Scheme 4 Cyclotrimerization products.

All the triarylbenzene final products were also synthesized, for comparison, by the Suzuki coupling of the 1,3,5- or 1,2,4-tribromobenzene with the suitable boronic acid derivatives.[10]

In the case of substrate **5** the yield in biaryl compounds, for both the porphyrin catalysts, was lower than those obtained for the ethynylnaphthalenes due to the presence of polymeric material in the final mixture. Such result, in our opinion, derives from the presence of a steric hindrance effect in the reaction intermediate which does not allow a good cyclization rate compared with that for polymer formation. Moreover all the isolated dimers show interesting properties as new materials for OLED building.

In fact they all present a strong fluorescence band in the blue region as has been reported by other authors for similar compounds.[11]

The catalytic properties of the metalloporphyrins in the one-pot formation of asymmetric biaryls make this reaction a good alternative to the well known methods. The possibility to recycle the metalloporphyrins several times compared with the other cyclotrimerization catalysts can be considered as of high significance.

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‡ *Typical procedure* for the reaction catalyzed by metalloporphyrin **1**: 1.8 mg of catalyst **1** (2.4×10^{-3} mmol), were dissolved in 3 ml of 1,2-dichlorobenzene and 1 g of arylethyne was added. The resulting solution was warmed at 160 °C for 48 h, under nitrogen. The crude product was purified by flash chromatography (SiO_2, hexane–diethyl ether). The fractions containing the desired cyclodimerization products were collected, recrystallized and identified by ^1H and ^{13}C mono- and bi-dimensional NMR and EI mass spectra. The yields were between 33 and 90% depending on the substrates and the catalyst. For the reactions catalyzed by cobaltocene **2**, a similar procedure was used.

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