Ruthenium porphyrin bound to a Merrifield resin as heterogeneous catalyst for the cyclooligomerization of arylethynes†

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Ruthenium *meso*-tetraphenylporphyrin was bound to a solid support, the Merrifield resin, and used in the cyclooligomerization of arylethynes, obtaining high yields and selectivities in the final products with a complete recycling of the catalyst.

The carbon–carbon triple bond has been recently recognized to be one of the most important organic functions used as a building block in synthetic and material chemistry.[1–3] More recently, the alkyne scaffolds have been used as starting compounds for the synthesis of nanotubes.[4] In previous papers we showed that many arylethynes can undergo the cyclooligomerization reaction catalyzed by rhodium or ruthenium porphyrins and vanadium phthalocyanines.[5]

Synthetic metalloporphyrins are well known for their catalytic properties in many important organic reactions, such as, for example, the oxidation of organic substrates,[6] the cyclopropanation of olefins,[7] the carbonyl ylide/1,3-dipolar cycloaddition reactions of α-diazoketones,[8] the insertion of carbene into the S–H bond,[9] the amination of hydrocarbons[10] and the olefination of aldehydes.[11] All the above cited reactions were performed in homogeneous organic solutions and in many cases the recycling of the catalyst, even if possible, must undergo a tedious chromatographic recovery.

The cyclooligomerization porphyrin catalysts can be reused several times but need to be separated from the starting and final compounds by a silica gel column but this process is affected by the waste of time and money.[5] Otherwise several examples of solids supporting metalloporphyrins for catalysis were reported in the literature[12] but recently few results were presented to the scientific community. In this paper we present the synthesis of an heterogeneous porphyrin catalyst obtained by the coupling of the macrocycle with the Merrifield resin and its use in the cyclooligomerization reaction of some arylethynes with slightly complete retention of the activity.

The heterogeneous catalyst was synthesized by using the well known Merrifield technique[13] applied for the first synthesis of peptides in the solid phase. The starting porphyrin free base, **1**, was synthesized as reported in the literature[14] and ruthenium insertion was obtained by a standard method.[15] After saponification with KOH, the ruthenium porphyrin **3** was bound to the solid resin using the Williamson method for the synthesis of ethers.[16] The synthetic steps are reported in Fig. 1.

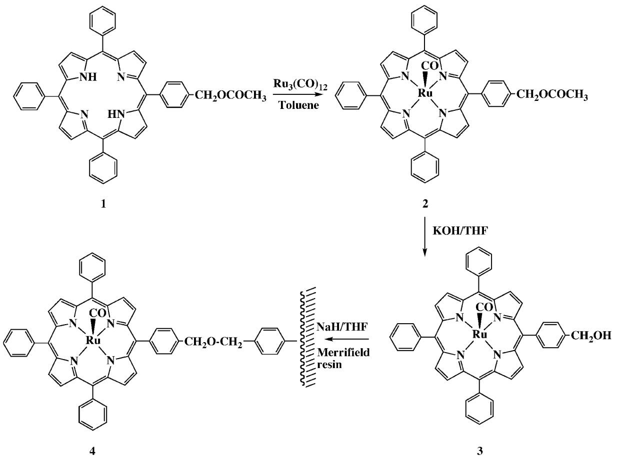

Fig. 1 Synthesis of the catalyst **4**.

From the data of the elemental analysis obtained for the catalyst **4**, we estimate the content of the ruthenium porphyrin to be around 1 mmolar per gram of solid, a value very close to those obtained for other porphyrin functionalized solids.[12] The binding of the catalyst **4** to the solid through the ethereal function allowed to separate the functionalized resin from the bulk of the reaction by vacuum filtration and reuse it for several times.

Furthermore, the robustness of the system at the high reaction temperature (160 °C) can be verified by UV/Vis methods. In fact after 48 hours of reaction no trace of free metalloporphyrin was detected in the reaction media at such temperature. In Table 1 we report the data obtained using several arylethynes as substrates in the cyclooligomerization reaction catalyzed by **4**.‡

In Fig. 2 the reaction scheme is reported.

The catalytic activity of porphyrin bound to the resin is compared with that obtained from our previous papers (in parentheses).[5a,b,d]

An inspection of the table shows that the efficiency of the new catalytic system does not seem to be affected by the presence of the matrix. In fact the conversion of the substrates is always high and comparable with that previously reported.[5a,b,d,e]

The sterically hindered substrate 2,6-dimethoxy-ethynylbenzene only gives poor results in terms of conversion (Table 1, entry 7) and this fact in our opinion can be due to the difficulty for the starting alkyne to approach the catalyst bound to a solid support. The yield of the dimerization

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Table 1 Cyclooligomerization of substituted arylethynes, *p*,*m*-X–C_6H_4–C≡CH and 1-ethynyl or 2-ethynylnaphthalene, using **4** as catalyst.[a] In parentheses the data from previous papers using metalloporphyrins are reported

Entry	Substrate X	Conversion (%)	Yield of cyclodimers[b] (%)	Yield of cyclotrimers[b] (%)
1	H	80(91)	20(23)[d]	60(68)[d]
2	*p*-Cl	90(99)	48(1)[e]	31(98)[e]
3	*p*-OCH_3	61(60)	26(28)[e]	33(30)[e]
4	*m*-OCH_3	67(99)	44(78)[c,e]	20(21)[e]
5	*p*-CH_3	86(99)	58(69)[e]	25(30)[e]
7	2,6-Di (OCH_3)	12(70)	—	12(70)[g]
8	1-Ethynyl naphthalene	87(95)	38(73)[f]	44(19)
9	2-Ethynyl naphthalene	64(95)	57(36)[f]	7(4)

[a] Reactions carried out at 160–180 °C. [b] Yields determined by GC analysis. [c] Two isomers (1 : 1 ratio). [d] From ref. 5*b* with RuOEPCO as catalyst. [e] From ref. 5*d* with Rh(TDCPP)Cl as catalyst. [f] From ref. 5*d* with RuOEPCO as catalyst. [g] From ref. 5*d* with RuOEPCO as catalyst.

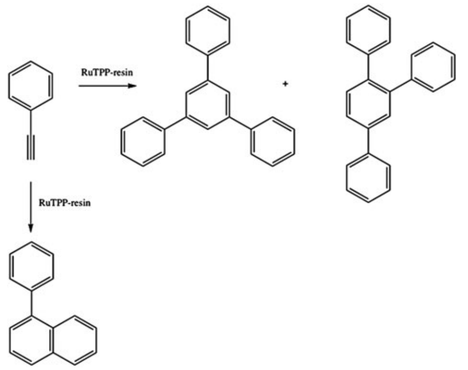

Fig. 2 The reaction scheme.

products of the substituted ethynylbenzenes slightly decreases while the trimers are produced in higher percentage.

The resistance of the resin bound metalloporphyrin to the reaction conditions was tested using phenylacetylene as substrate in three consecutive experiments of recycling of the same batch of catalyst (Table 2). The total yield of the reaction was 80% for the first experiment, 84% for the second and 77% for the third one while the trimers yield increases and that of the dimers decreases. Such an effect can be due to the differences in the conformations of the polymer induced during the first batch by the high reaction temperature. After this treatment, the resin can reach a more stable conformation which seems to influence the results of the other batches in terms of a different steric hindrance around the porphyrin catalyst.

Table 2 Cyclooligomerization of phenylacetylene using **4** as catalyst in three consecutive experiments[a]

Run	Conversion (%)	Yield of cyclodimers[b] (%)	Yield of cyclotrimers[b] (%)
1	80	20	60
2	84	52	32
3	77	49	28

[a] Reactions carried out at 160–180 °C with 10 mg of catalyst **4** in 1 mL of neat phenylacetylene (9.77 mmol). [b] Yields determined by GC analysis.

Table 3 Cyclooligomerization of phenylacetylene using **2**, **3** and **4**[a]

Catalyst	Conversion (%)	Yield of cyclodimers [b](%)	Yield of cyclotrimers [b](%)
2	74	36	38
3	91	51	40
4	80	20	60

[a] Reactions carried out at 160–180 °C with 10 mg of catalyst **4** in 1 mL of neat phenylacetylene (9.77 mmol). [b] Yields determined by GC analysis.

The difference in the activity between catalyst **4** and the porphyrin intermediates **2** and **3** was also investigated using phenylacetylene as the substrate. Such experiments could clarify which role the organic support played in directing the selectivities of the reaction. The data from the reactions with **2** and **3** as catalyst are reported in Table 3 and compared with those obtained using catalyst **4**.

The ratio between the cyclodimers and trimers seems to be affected by the solid matrix in terms of an increase of the trimers yield. This effect in our opinion should be due to the different steric hindrance which the porphyrin intermediates enclosed in the resin experience along the two reaction pathways.

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-vinilydene rearrangement. Such an intermediate could then undergo the concerted attack of a second molecule of alkyne in a (formal) Diels–Alder reaction (see Fig. 3) to give the final dimeric product while triphenylbenzenes probably derive from an open intermediate.

In conclusion we found that a ruthenium porphyrin bound to a solid matrix, the Merrifield resin, by a covalent bond can catalyze the oligomerization of the arylalkynes with good yield and selectivities. Such a system can be recovered and reused more times without any loss of catalytic activity.

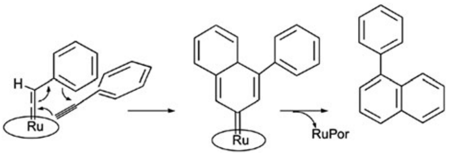

Fig. 3 Proposed mechanism for the cyclodimerization.

Notes and references

‡ *Typical procedure* for the reaction catalyzed by **4**: 10 mg of catalyst **4** were placed in 1 mL of phenylacetylene (9.77 mmol). The resulting mixture was warmed at 160–180 °C for 48 hours under nitrogen. At the end of the reaction, dodecane or tetradecane was added as an internal standard and the mixture analyzed by GC. *Separation of the catalyst*: after cooling at 40 °C, the reaction was diluted with chloroform and centrifuged for 5 minutes, after that the organic solution was separated from the catalyst using a pipette. The catalyst was washed several times with chloroform until the initial and final products were not present in the organic solution (GC analysis). The recovered catalyst was dried under vacuum at 60 °C for 2 hours and reused.

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