The cyclooligomerization of arylethynes in ionic liquids catalysed by ruthenium porphyrins: a case of real catalyst recycling†

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An efficient cyclooligomerization of arylethynes, catalysed by ruthenium(II) porphyrins in environmentally friendly ionic liquids, with an effective recycling of the catalyst and easy isolation of the products is described.

To obtain sustainable synthetic procedures is one of the most important goals that the chemists of the 21st century should consider when an old process needs to be improved. Most reaction methods have been recently modified, either by introducing environmentally friendly solvents like water or alcohols or by using catalysts with higher selectivities and yields, with the potential to be recycled several times.

The chance to have, in the same process, a suitable solvent and a catalyst that can be reused several times without any loss of activity, should be considered highly desirable. Ionic liquids (IL) have, in fact, recently been presented as a new and promising family of non-conventional solvents to be used in settling sustainable procedures for known reactions.[1–4] Their unique physical properties encourage the use of such solvents in homogeneous or biphasic catalysis, so that many reactions have been studied in such systems and there is an increasing activity in this field of research, testified by abundant recent literature on the topic.[5,6]

In a previous paper, we showed that it is possible to use rhodium porphyrins as catalysts for the cyclotrimerization of arylethynes[7] and here we report the results obtained for the same reaction catalysed by ruthenium porphyrins in ionic liquids.

Other authors reported on the cyclotrimerization of alkynes in supercritical CO_2 catalysed by palladium complexes[8] but, to our knowledge, there are no reports on the use of metalloporphyrin catalysts in pure ionic liquids as reaction media, although there has been a short communication on an oxidation in a two phase system.[9] The cyclotrimerization of terminal alkynes usually affords a mixture of trisubstituted benzenes, **2** and **3**, as the main products[10–15] but sometimes the reaction also gives the 1-arylnaphthalene derivatives **1** by a dimerization process, as shown in Fig. 1.[16,17]

The catalyst is the 5,10,15,20-tetraphenylporphyrinato ruthenium(II) carbonyl, Ru(TPP)CO (**4**) whose structure is shown in Chart 1.

The reactions were carried out in 1-butyl-3-methylimidazolium hexafluorophosphate, {[Bmim][PF_6]} (**5**), or in 1-octyl-3-methylimidazolium hexafluorophosphate, {[Omim][PF_6]} (**6**).

These last compounds were synthesized by adaptation of literature procedures[18–20] or purchased from commercial sources. The commercially available substrates used for this work were ethynylbenzene, (**7**), and 1-ethynyl-4-methoxybenzene, (**8**), (see Chart 2) which underwent the cyclooligomerization reaction in ionic liquids in the presence of the catalyst, under a nitrogen atmosphere at 150 °C, for 72 hours.‡ All the reaction products were previously isolated and characterized.[7,21] After cooling, the reaction products were extracted with diethyl ether, leaving the catalyst in the ionic liquids ready for further reaction.

The GC analysis of the products, showed that the porphyrin catalyst was able to give the 1,3,5 and 1,2,4-triarylbenzenes and the 1-arylsubstituted naphthalenes with selectivities depending on the substrates. In Table 1, the results of the cyclooligomerization reactions in ionic liquids and, for comparison, in 1,2-dichlorobenzene are reported.

In the case of substrate **7**, 1-phenylnaphthalene was isolated as the main product in both the ionic liquids and in DCB, while

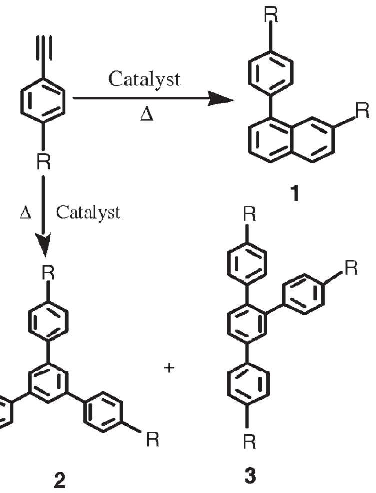

Fig. 1 The cyclooligomerization of arylethynes.

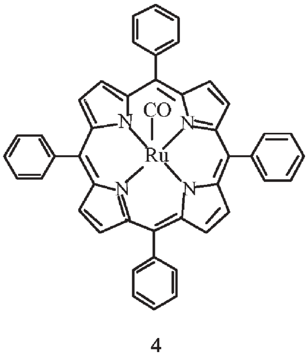

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Chart 1 The structure of the catalyst.

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† Electronic supplementary information (ESI) available: experimental and analytical data of the new products. See http://www.rsc.org/suppdata/cc/b4/b415462b/

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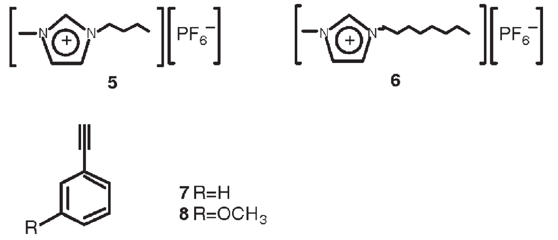

Chart 2 The structures of the ionic liquids and substrates.

Table 1 The cyclooligomerization of arylethynes **7** and **8** catalysed by **4** in ionic liquids **5** and **6** and in 1,2-dichlorobenzene (DCB)[a]

Entry	Solvent	Substrate	Yield[b] (%) **1**	Yield[b] (%) **2**	Yield[b] (%) **3**
1	5	7	32	17	30
2	6	7	60	6	9
3	5	8	21[e]	[c]	[c]
4	6	8	67[e]	[c]	[c]
5	DCB[d]	7	59	7	4
6	DCB[d]	8	78[e]	[c]	[c]

[a] Reactions carried out at 150 °C with a molar ratio Substrate/Porphyrin = 5700:1 and a volume ratio substrate/ionic liquids 1:3; [b] Yields determined by GC analysis; [c] Trace; [d] Reactions carried out at 190 °C with a molar ratio Substrate/Porphyrin = 5700:1 and a volume ratio substrate/ionic liquids 1:3; [e] Two isomers

1,3,5- and 1,2,4-triphenylbenzenes were obtained as minor products (entries 1, 2 and 5). For compound **8**, two naphthalene derivatives were isolated, 8-methoxy-1-(3-methoxyphenyl)naphthalene and 6-methoxy-1-(3-methoxyphenyl)naphthalene in 1:1 isomeric ratio, while the triarylbenzenes were detected in trace amounts (entries 3, 4 and 6). The turnover number for some experiments was over 3000 for the first run and this characteristic is highly desired when the cost of the catalysts is an important parameter. Table 1 also shows that the results obtained by using ionic liquid **6** are superior, for both the substrates, in terms of yield of naphthalene derivatives, to those obtained in **5**. The results reported are interesting considering the few reports on the one-pot synthesis of arylnaphthalene derivatives, which are an important class of biologically active natural compounds.[22–24]

The analysis of the data also shows that the results in DCB are comparable to those obtained in **6** and this fact could be due to the lower polarity of **6** which makes this solvent more similar to DCB. Reactivity and selectivity found with the title reaction are important *per se*. However, we feel that even more important is the re-use of the ionic liquid–catalyst system. In fact we tested the recyclability in consecutive experiments performed with the solution of metalloporphyrin in ionic liquid after the stripping of the reaction products.

Table 2 shows the catalytic efficiency of the catalyst **4** in IL **6** after 5 runs with ethynylbenzene as substrate. As reported in the table, it is clear that the recycling of the catalyst slightly affects the conversion and the total yield of the cyclooligomerization products.

After the first reaction, the yield is influenced by the water content of the IL but it can be almost stabilized by high vacuum pumping.

In conclusion, the properties of the ionic liquid–metalloporphyrin system makes the oligomerization of arylethynes in this system very appealing.

Table 2 Conversion of **7** with subsequent use of the same catalyst–ionic liquid system

Run	Conversion (%)[a]	Yield (%)[a]	Yield[a] (%) Napht.	Yield[a] (%) 1,3,5	Yield[a] (%) 1,2,4
1	100	75	60	6	9
2	100	70	56	6	8
3	98	68	53	7	8
4	100	70	57	6	7
5	99	66	53	6	7

[a] Based on the substrate and determined by GC analysis

The possibility of recycling the catalyst several times and the use of environment friendly solvents, compared with the other cyclotrimerization catalyst–solvent systems, can be considered of high value as also shown by other authors for the olefination of aldehydes catalysed by an iron porphyrin in the same media.[25]

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Notes and references

‡ Before any experiment, the ionic liquids were dried under high vacuum at 80 °C for at least 8 hours to avoid the presence of water. After that, dry nitrogen was used for the reaction but even using such precautions, the corresponding acetophenones were produced in variable yields.

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