The Formation of 1-Aryl-Substituted Naphthalenes by an Unusual Cyclization of Arylethynes Catalyzed by Ruthenium and Rhodium Porphyrins

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The dimerization of arylethynes to give 1-aryl-substituted naphthalenes through catalysis by rhodium and ruthenium porphyrins has been investigated. When performed at temperatures above 130 °C, this reaction affords a mixture of triarylbenzenes and 1-aryl-substituted naphthalenes. The yields of naphthalene derivatives range from low to high, depending on the temperature and the phenyl substituents. The concentrations of the initial compounds affect the selectivity of the reaction: the dimerization/trimerization ratios in 1,2-dichlorobenzene increase as concentration decreases. The reaction mechanism is determined by the peculiar structure of the catalyst ligand and involves the formation of a vinylidene intermediate of the metalloporphyrins.

Introduction

The formation of carbon–carbon bonds has long been a central theme of research activity in organic and organometallic chemistry, with several new catalytic methods having been discovered and applied for the industrial production of chemicals.[1] New reactions and methods are introduced every year, and this paper reports a new application of metalloporphyrins as catalysts in alkyne chemistry.

Synthetic metalloporphyrins have exhibited catalytic properties in a number of organic reactions such as, for example, the oxidation of organic substrates,[2] the cyclopropanation of olefins,[3] the carbonyl ylide/1,3-dipolar cycloaddition reactions of α-diazoketones,[4] the insertion of carbene into the S–H bond,[5] the amination of the double bond,[6] and the olefination of aldehydes.[7]

Recently we demonstrated a new application of metalloporphyrin catalysis in the cyclotrimerization of arylethynes by rhodium porphyrins,[8] a reaction similar to, but distinct from, the classical Reppe reaction.[9] Such a reaction, starting from monosubstituted ethynes, usually gives a 1,2,4-trisubstituted benzene as the main product, together with different amounts of the 1,3,5- and 1,2,3-trisubstituted isomers.[10]

With rhodium porphyrins as catalysts, we obtained 1,3,5- and 1,2,4-triaryl-substituted benzenes from arylethynes, with relative ratios depending on the porphyrin, but independent of the temperature and solvent.[8] At the beginning of this investigation we were focusing our attention on the trimerization products. However, there was a discrepancy between the yields of the triphenylbenzenes and the phenylethyne conversion, ranging from 5% to 40%, depending on the catalyst. We therefore decided to obtain deeper insight into the process and thus found another reaction catalyzed by rhodium porphyrins: the quite unusual cyclodimerization of the arylethynes to give 1-aryl-substituted naphthalenes (Figure 1).

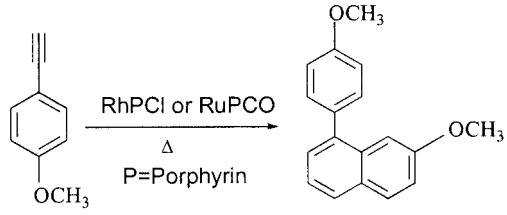

Figure 1. Reaction scheme for the cyclodimerization of 1-ethynyl-4-methoxybenzene.

The same reaction pattern was also obtained when a ruthenium porphyrin was used as the catalyst. The occurrence of both cyclodimerization and cyclotrimerization products under the same reaction conditions prompted us to examine the factors possibly affecting the selectivity.

Reactions involving the formation of vinylidene intermediates from terminal alkynes to give aromatic compounds have been reported in the literature,[11] but to the best of our knowledge this is the first simple intermolecular cycloaromatization reaction involving a dienyl system and a monosubstituted alkyne, although there have been two reports on similar reactions with disubstituted alkynes.[12] Wilkinson-like rhodium complexes are involved as catalysts in the first example, in the presence of HCl and azobenzene as co-catalysts, giving moderate yields of naphthalene derivatives. The second report involves a similar reaction cata-

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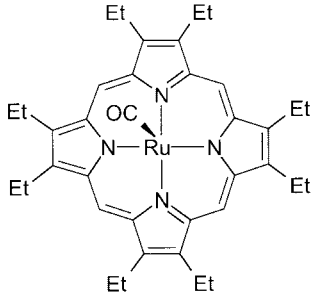
lyzed by a $RhCl_3$-Aliquat® 336 ion pair, affording lower yields of 1-aryl-substituted naphthalenes. The mechanism of this last reaction involves the presence of a metallacyclopentadiene intermediate.

Rare examples of the intramolecular cyclization of conjugated dienylalkynes via ruthenium vinylidene intermediates and the rhodium cycloaromatization of acyclic 3-ene-1,5-diynes have also been reported in the literature.[13]

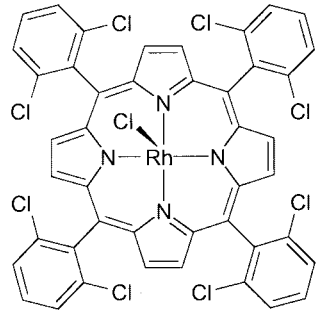
Our further investigations into the cyclodimerization of arylethynes are reported here.

Results and Discussion

The porphyrin catalysts used for this investigation (Figure 2) were Ru(OEP)CO (**1**) and Rh(TDCPP)Cl (**2**), where OEP is the dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin and TDCPP is the dianion of 5,10,15,20-tetrakis(2′,6′-dichlorophenyl)porphyrin.



catalyst **1**



catalyst **2**

Figure 2. Structures of the catalysts **1** and **2**.

We used different macrocycles for our experiments because after a check of other metalloporphyrins, we found that the compounds used in this work gave the best results.

The reactions were generally performed without solvent at 180 °C and with a substrate/porphyrin molar ratio of 5700:1, and the final products were separated by column chromatography on silica gel columns. All the catalysts were recovered by column chromatography in more than 95% yield and could be recycled at least three times without any loss of catalytic activity.

The dimerization reaction of arylethynes to give naphthalene derivatives is an unusual process, whereas the coupling of two terminal alkynes to give (*E*) and (*Z*) 1,4-but-3-en-ynes is a well known reaction.[16]

Table 1 reports the yields for the dimerization reactions of some arylethynes with catalysis by **1** and **2**, together with the total yields of the cyclotrimerization products for all the substrates. The data in Table 1 show that the selectivity is affected by the nature of the substituents on the phenyl ring of the alkynes. There is no clear trend, although it is apparent that electron-donating groups such as *para*-methoxy or -methyl direct the reaction toward 1-aryl-substituted naphthalenes as the main products, while the presence of an electron-withdrawing substituent such as chlorine results in a mixture of 1,2,4- and 1,3,5-triaryl-substituted benzenes in higher yield and good selectivity,[8] particularly so with the less electron-rich rhodium porphyrin. However, the slightly electron-attracting *meta*-methoxy group behaved more similarly to methyl than to chlorine.

The structures of the catalysts also affected the reaction pathway, with the rhodium porphyrin **2** more active in promoting the conversion of the arylethynes into 1-aryl-substituted naphthalenes with substrates possessing *para*- or *meta*-OCH_3 and *para*-CH_3 moieties, while catalyst **1** gave higher yields of dimerization products with *para*-Cl or *para*-H. As a matter of fact, with Ru(OEP)CO very similar results were obtained with almost all the substrates, in terms of yields, conversion and selectivity.

A number of questions arise when the reaction mechanism is considered, such as the role of the porphyrin ligand, if any, or whether cyclodimerization and cyclotrimerization follow different routes (competitive reactions) or proceed along the same pathway (consecutive reactions).

In our opinion, the reaction output must be related to the particular catalyst used. In fact, the metalloporphyrin complexes do not have *cis* coordination sites available on the same face of the macrocycle,[17] thus ruling out the mechanism proposed for cyclooligomerization catalyzed by other systems: the coordination of two molecules of alkyne and the formation of metallacyclopentadiene.[12b,17,18]

We think that, after a preliminary π-coordination of a molecule of alkyne to the metal, the formation of a metal vinylidene complex may occur through a [1,2]-hydrogen shift, possibly helped by acid-base reaction with one of the nitrogen atoms of the porphyrin ligand.[19] The η^2-1-alkyne→η^1–vinilydene rearrangement is a well known process,[20] but we can rule out the intermediate formation of a metal hydride because of the lack of the suitable coordination site. The reaction pathway with phenylethyne and Ru(OEP)CO is depicted in Scheme 1.

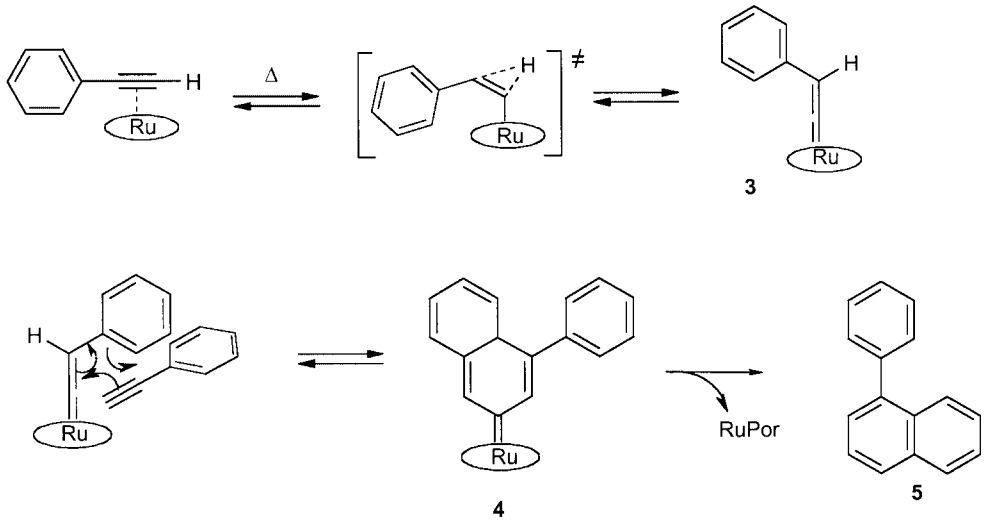
The unstable vinylidene complex **3**, activated by the metal coordination, undergoes the attack of a second molecule of alkyne in a (formal) Diels–Alder reaction, giving the intermediate **4** in a similar way to that reported for the synthesis of 2-arylated quinolines.[20b] Finally, complex **4** gives the dimerization product **5** after decomplexation and rearomatization.

It was not possible to isolate the intermediates **3** or **4** to support the above interpretation, but other authors have reported that similar cyclizations proceed through vinyli-

Table 1. Cyclooligomerization of substituted arylethynes, *p,m*-X-C_6H_4-C≡CH.[a]

Entry	Substrate X	Conversion (%)	Yield of cyclodimers (%)[b]	Yield of cyclotrimers (%)[b]
		With Ru(OEP)CO as catalyst		
1	H	91	23	68
2	*p*-Cl	88	12	75
3	*p*-OCH_3	60	28	30
4	*m*-OCH_3	61	31[c]	30
5	*p*-CH_3	71	31	39
		With Rh(TDCPP)Cl as catalyst		
6	H	42	17	25
7	*p*-Cl	99	1	98
8	*p*-OCH_3	63	49	14
9	*m*-OCH_3	99	78[c]	21
10	*p*-CH_3	99	69	30

[a] Reactions carried out at 180 °C with a substrate/porphyrin molar ratio of 5700:1. [b] Yields determined by GC analysis. [c] Two isomers (1:1 ratio).



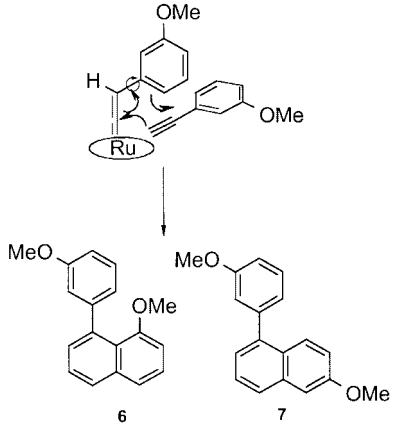
Scheme 1. Tentative reaction pathway for the cyclodimerization of phenylacetylene.

dene derivatives.[11,20] Furthermore, Ogoshi et al. have proposed the hypothesis of the presence of a vinylidene intermediate in the reaction between phenylacetylene and a rhodium porphyrin to give a metal-coordinated acetyl residue.[21]

Experiments to verify the mechanistic hypothesis of Scheme 1 were designed.

a) In the dimerization of 1-ethynyl-3-methoxybenzene, with both catalysts, two isomers, **6** and **7** (Scheme 2), were isolated in a 1:1 molar ratio (Table 1, entries 4 and 9), consistently with a statistical attack of the second molecule of arylethyne at the phenyl 2- or 6-positions in the vinylidene intermediate, as a consequence of the rotation around the C_β–Ph bond.

b) No reaction occurred when disubstituted alkynes (1-phenylprop-1-yne or diphenylethyne) were treated with catalysts **1** or **2** at 180 °C. However, a mixture of phenylacetylene and diphenylacetylene in a 1:1 molar ratio reacted in the presence of Ru(OEP)CO, thus attesting to the necessity of the hydrogen atom on the *sp* carbon. In fact, only the presence of the terminal alkyne proton allows the formation

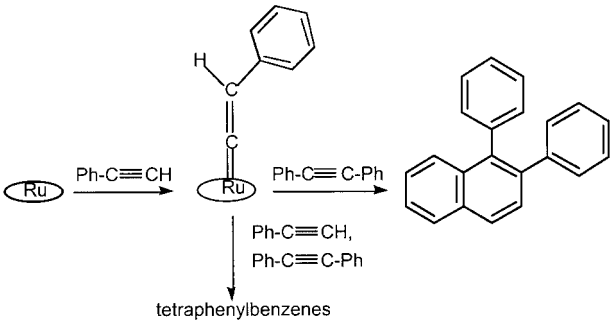


Scheme 2. Reaction mechanism for the cyclodimerization of 1-ethynyl-3-methoxybenzene.

of the vinylidene derivative through the hydrogen migration.

The vinylidene derivatives are also involved, in our opinion, in the formation of the cyclotrimerization products,

and this is supported by the same reaction between phenylacetylene and diphenylethyne in 1:1 molar ratio in the presence of Ru(OEP)CO. At 180 °C we observed (by GC-MS analysis) traces of tetraphenylbenzenes originating from the attack of diphenylethyne on the porphyrin vinylidene derivative among the cyclotrimerization products, together with the diphenylnaphthalene (Scheme 3).[22]



Scheme 3. Reaction of phenylacetylene with diphenylacetylene in the presence of ruthenium catalysts **1**.

Thus, we can deduce that the metal vinylidene derivative is a common intermediate giving rise both to cyclodimers and to cyclotrimers.

(c) Dependence on the temperature. Other conditions being equal, heating of phenylethyne in the presence of Ru(OEP)CO at 140 °C essentially gave only the naphthalene derivatives, in low yields, while at 180 °C the triphenylbenzenes were prevalent and the yields higher (see Table 2, entries 1 and 2). The result can be explained in terms of kinetic control, driving the reaction to the dimerization products at lower temperature. The formation of the adduct may be reversed (retro-Diels–Alder) at higher temperatures, resulting in the more stable triphenylbenzenes (thermodynamic control).

(d) Dependence on concentration. If the results of the reaction carried out without solvent and with increasing amounts of solvents (Table 2, entries 1, 4 and 5) at the same temperature are compared, the relative 1-phenylnaphthalene/triphenylbenzene ratios increased from 1:3 (neat) to 1:1.5 (3 mL 1,2-dichlorobenzene), to 1:0.4 (10 mL 1,2-dichlorobenzene). Again, with the same concentration but at lower temperatures (Table 2, entries 3 and 4), the reaction was directed more towards the cyclodimerization, at 120 °C reaching a 5:1 ratio in favor of 1-phenylnaphthalene. The dilution effects also shift the reaction output towards cyclodimerization with rhodium catalyst, giving a 15% yield of conversion and a 1-phenylnaphthalene/triphenylbenzenes ratio of 2.5:1 in 10 mL of 1,2-dichlorobenzene. Furthermore, the reaction of an alkyne different from phenylethyne, 4-chloro-1-ethynylbenzene, with catalyst **2**, which gave a 98% yield of the cyclotrimerization products in the absence of solvent,[8] afforded a 56% yield of 7-chloro-1-(4-chlorophenyl)naphthalene and a 42% yield of triphenylbenzenes when performed in 3 mL of 1,2-dichlorobenzene. These results are in line with the proposed mechanism.

Conclusions

Rhodium and ruthenium porphyrins are efficient catalysts for the cyclooligomerization of arylethynes, depending on the metal, the electronic situation of the macrocycles, and the substituents on the substrates. The reaction pathway is also affected by temperature and initial concentration of the arylethynes: at higher temperatures and lower concentrations we observed the formation of phenylnaphthalenes and triarylbenzenes in different yields, and the product selectivity can be tuned on the basis of the parameters cited above.

In our opinion these properties are interesting and make the rhodium and ruthenium porphyrins a family of catalysts capable of forming aromatic compounds. In comparison with the other catalysts, they can be reusable and give high turnover numbers that in many cases are over 4000 for the first run. Furthermore, the metalloporphyrins used in this work afford a new synthetic method for the one-pot synthesis of arylnaphthalene derivatives, which are an important class of biologically active natural compounds. Although cyclodimers are always accompanied by cyclotrimers, they can be very easily separated. This, together with the recovery and potential recycling of catalysts, the option of avoiding solvents, and the simple reaction procedure, makes the metalloporphyrin-catalyzed cyclodimerization an appealing reaction.

Experimental Section

General Procedures: Chromatographic purifications were performed on silica gel (35–70 mesh, Merck) columns. Thin-layer chromatography was carried out with Merck Kieselgel 60-F254 plates. ^{1}H NMR spectra were recorded as $CDCl_3$ solutions on a Bruker AM 400 instrument with tetramethylsilane (TMS) as an internal standard. FAB mass spectra were measured on a VG-Quattro spectrometer with *m*-nitrobenzyl alcohol (NBA) as a matrix. GC-MS spectra were obtained with a VG-Quattro spectrometer with a 30 m Supelco SPB-5 capillary column.

Table 2. Reaction of phenylethyne catalyzed by Ru(OEP)CO under different conditions.[a]

Entry	Conversion (%)[b]	Yield of cyclo-dimers (%)[b]	Yield of cyclo-trimers (%)[b]	Solvent[c]	Temperature
1	91	23	68	none[d]	180 °C
2	23	13	10	none[d]	140 °C
3	6	5	1	3 mL[e]	120 °C
4	82	31	46	3 mL[e]	180 °C
5	27	18	7	10 mL[e]	180 °C

[a] Reactions carried out with a substrate/porphyrin molar ratio of 5700:1. [b] Yields determined by GC analysis. [c] 1,2-Dichlorobenzene. [d] 18 h. [e] 36 h.

GC Separation Conditions: The product yields and the isomeric ratios for all the reactions were determined by GC analyses performed on a Carlo Erba HRGC 5160 instrument with a 30 m Supelco SPB-5 capillary column and a FID detector. Chemical yields were determined by addition of a suitable internal standard (dodecane or tetradecane) to the reaction mixture at the end of each experiment and were reproducible within ±2% for multiple experiments.

Chemicals: All the reagents and solvents (Aldrich) were of the highest analytical grade and were used without further purification. The free bases H_2TDCPP and H_2OEP, where TDCPP is the dianion of 5,10,15,20-tetrakis(2′,6′-dichlorophenyl)porphyrin and OEP is the dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin, were synthesized by literature methods.[14] Ru(OEP)CO was obtained by literature methods.[15] Rh(TDCPP)Cl was synthesized as described in another paper from our laboratory.[3j] All the cyclotrimerization products reported in this paper have been described previously.[8]

Reactions

Typical Procedure for the Reaction Catalyzed by Metalloporphyrins 1 or 2: The catalyst (1.8 mg, 1.7 or 2.7 μmol) was dissolved in phenylacetylene (1.4 mL, 13.7 mmol) and the resulting solution was warmed between 120° and 180 °C for 18 hours, under nitrogen.

Typical Procedure for the Reaction Catalyzed by Metalloporphyrin 1 or 2 in 1,2-Dichlorobenzene: The catalyst (1.8 mg, 1.7 or 2.7 μmol) was dissolved in 1,2-dichlorobenzene (3 mL unless otherwise stated), and phenylacetylene (1.1 mL, 0.98 mmol) was added. The resulting solution was warmed at 130–140 °C for 36 hours or at 180 °C for 18 hours, under nitrogen.

Reaction between Phenylacetylene and Diphenylacetylene: Catalyst **2** (1.8 mg, 1.7 μmol) was dissolved in phenylacetylene (1.4 mL, 13.7 mmol). Diphenylacetylene (2,43 g, 13.7 mmol) was added and the resulting solution was warmed at 180 °C for 18 hours under nitrogen.

The crude products of all the reactions were purified by column chromatography (SiO_2, hexane/diethyl ether). The fractions containing the desired compounds were evaporated under vacuum, and the 1-arylnaphthalenes and isomeric triphenylbenzenes were separated by column flash chromatography and identified by their ^{1}H NMR and mass spectra. An authentic sample of 1-phenylnaphthalene, available from Aldrich, was used for the identification of the reaction products from phenylacetylene. All the elemental analysis gave satisfactory results.

Analytical data

7-Methoxy-1-(4-methoxyphenyl)naphthalene: M.p. 62–63 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, J = 8.8 Hz,1 H), 7.80 (t, J = 4.8 Hz, 1 H), 7.49 (d, J = 8.8 Hz, 2 H), 7.41 (d, J = 4.4 Hz, 2 H), 7.30 (d, J = 1.6 Hz, 1 H), 7.21 (dd, J = 8.8, 1.6 Hz, 1 H), 7.08 (d, J = 8.8 Hz, 2 H). EI MS: m/z(%) = 264 (100), 240 (12).

7-Methyl-1-(4-methylphenyl)naphthalene: Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, J = 8.4 Hz, 2 H), 7.72 (s, 1 H), 7.38–7.54 (m, 4 H), 7.32–7.37 (m, 3 H). EI MS: m/z (%) 232 (100), 217 (70), 202 (50).

7-Chloro-1-(4-chlorophenyl)naphthalene: M.p. 40–41 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, J = 8.4 Hz, 2 H), 7.82 (s, 1 H), 7.45–7.57 (m, 4 H), 7.56–7.40 (m, 3 H). EI MS: m/z (%) 272 (65), 237 (14), 202 (100).

8-Methoxy-1-(3-methoxyphenyl)naphthalene: Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, J = 9.2 Hz, 1 H), 7.72 (d, J = 8 Hz, 1 H), 7.45 (t, J = 7.6 Hz, 1 H), 7.36 (t, J = 7.6 Hz, 1 H), 7.26 (d, J = 6.8 Hz, 1 H), 7.23 (s, 1 H), 6.93–7.08 (m, 4 H), 3.91 (s, 3 H), 3.82 (s, 3 H). EI MS: m/z (%) 264 (100).

6-Methoxy-1-(3-methoxyphenyl)naphthalene: Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, J = 8 Hz, 2 H), 7.35–7.48 (m, 3 H), 7.21–7.26 (m, 3 H), 6.84–6.90 (m, 2 H), 6.76 (d, J = 7.6 Hz, 1 H), 3.79 (s, 3 H), 3.48 (s, 3 H). EI MS: m/z (%) 264 (100).

Acknowledgments

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