

# The highly selective formation of biaryls by the cyclization of arylethynes catalyzed by vanadyl phthalocyanine†

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The dimerization of arylethynes catalyzed by vanadium phthalocyanine to give substituted biaryls has been investigated. The reaction yield is always high and for many examples is only slightly affected by the aryl substituents. This fact is also related to the results obtained with metalloporphyrins, which give lower selectivities due to the presence of variable amounts of triphenylbenzenes.

## Introduction

The importance of the chemistry of the  $C\equiv C$  triple bond has been well recognized since this function was shown to be one of the main building blocks of organic and material chemistry.<sup>1</sup> The formation of benzene rings from alkynes, named the Reppe cyclotrimerization,<sup>2</sup> has been intensively studied in the last fifty years because of the difficulty in obtaining functionalized aromatic compounds.<sup>3</sup> Recently, alkyne scaffolds have been used as starting compounds for the synthesis of nanotubes.<sup>4</sup> In previous investigations, we found that a large number of arylethynes can undergo cyclo-oligomerization reactions in the presence of a catalytic amount of rhodium or ruthenium porphyrins, giving trisubstituted benzenes and/or biaryl derivatives, depending on the nature of the catalyst, the reaction conditions and the solvent used.<sup>5</sup>

Synthetic metalloporphyrins are well known for their catalytic properties in many important organic reactions, such as, for example, the oxidation of organic substrates,<sup>6</sup> the cyclopropanation of olefins,<sup>7</sup> the carbonyl ylide/1,3-dipolar cycloaddition reactions of  $\alpha$ -diazoketones,<sup>8</sup> the insertion of carbene into the S–H bond,<sup>9</sup> the amination of hydrocarbons<sup>10</sup> and the olefination of aldehydes.<sup>11</sup> With rhodium or ruthenium porphyrins as catalysts, we previously obtained 1,3,5- and 1,2,4-triaryl-substituted benzenes from phenyl-substituted ethynylbenzenes,<sup>5a</sup> but there was a discrepancy between the yield of triphenylbenzenes and the conversion of starting material, ranging from 1–5% to more than 70%, depending on the catalyst and substrate. We found that another reaction, catalyzed by the metalloporphyrins, was operative under the same conditions, the cyclodimerization of arylethynes to give 1-aryl-substituted naphthalenes.<sup>5b</sup>

All the compounds obtained from the reactions were easily separated by the usual methods, *i.e.* low or medium pressure chromatography, affording pure products, even on a gram scale. The factors affecting the selectivity of the reaction were examined in detail from the point of view of the nature of the substrates and catalysts. However, from the obtained data,<sup>5b</sup> it was clear that both parameters affected the ratio between cyclodimers and cyclotrimers. In fact, examining the above cited results, the yield of cyclodimers spanned from 1% for 4-chloro-ethynylbenzene to 78% for 4-methoxy-ethynylbenzene. The choice of a catalyst with different electronic properties could offer the possibility of obtaining different selectivities. Phthalocyanines were taken into consideration because of their higher electron-withdrawing properties compared to porphyrins. Although phthalocyanines are well known as pigments and dyes from the beginning of the last century, and are extensively used as colorants for printing inks, textiles and paint,<sup>12</sup> they have not been well studied in catalysis because of their low solubility and activity. Some investigations concerning oxidation reactions catalyzed by metallophthalocyanines have been reported in the literature,<sup>13</sup> but the number of published papers seems low compared to the huge number of studies about the catalytic processes involving metalloporphyrins. During our recent studies on the catalytic properties of metalloporphyrins,<sup>5</sup> we found that even in the presence of an electron-poor metalloporphyrin like Rh(TDCPP)Cl, where TDCPP is the dianion of 5,10,15,20-tetrakis-(2',6'-dichlorophenyl)-porphyrin, we always obtained a mixture of products. Such products were easily separated on a column, but it should be possible to find a better catalyst giving higher selectivities. Vanadyl phthalocyanine has been our choice because of its electronic properties,<sup>14</sup> and in this paper we report our most recent results obtained using this catalyst under the same reaction conditions.

## Results and discussion

The commercially available metallophthalocyanine catalyst used for this investigation was VOPc, **1**, where Pc is the dianion of the phthalocyanine. The structure of the catalyst is reported in Fig. 1. The reactions were generally performed,

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† Electronic supplementary information (ESI) available: <sup>1</sup>H and <sup>13</sup>C NMR two-dimensional experiments for the identification of the new fluorinated compounds. Analytical data for all new compounds and <sup>1</sup>H NMR spectra for deuterated 1-phenyl-naphthalene. See DOI: 10.1039/b9nj00227h

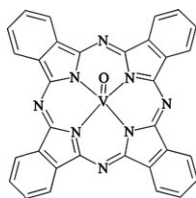


Fig. 1 The structure of catalyst 1.

unless otherwise specified, without solvent at 160–180 °C with a molar ratio substrate : catalyst = 5700 : 1, and the final compounds were quantified by GC using an internal standard.<sup>‡</sup>

As an example, a reaction scheme involving 4-chloro-ethynylbenzene as starting material is reported in Fig. 2.

In Table 1, the results obtained from the cyclooligomerization of arylethyne in the presence of catalyst 1 are reported and compared with the data obtained using Rh(TDCPP)Cl or Ru(OEP)CO and reported from our previously published papers.<sup>5</sup>

From our results with catalyst 1, some new considerations can be extrapolated. First of all, the vanadyl phthalocyanine gives higher selectivities for the cyclodimerization *vs.* the cyclotrimerization reaction, giving different results compared to those obtained with metalloporphyrins. Looking, for example, at the result for 4-chloro-ethynylbenzene (entry 2), the yield of dimer increases from 1 to 50%, useful enough for preparative synthesis. The results are in agreement for all of the other substrates. In fact, the cyclodimerization seems to be the preferred pathway for reactions catalyzed by 1. Incidentally, in the case of the 4-fluoro-ethynylbenzene (entry 6), a valuable difluorinated phenylnaphthalene was isolated. Because of the oxidation state of the vanadium atom during the catalytic cycle, we were not able to isolate any stable vinylidene intermediate, and we can only suppose the presence, after oxygen cleavage, of a V(IV)-carbene intermediate. To obtain more information on the mechanism of the reaction, which, in the case of porphyrins, we previously proposed to involve the formation of a vinylidene intermediate,<sup>5b</sup> we decided to conduct the reaction using 2,6-dimethoxy-ethynylbenzene.<sup>15</sup> Such a substrate, bearing two substituents on both *ortho* positions of the phenyl ring, could not undergo the dimerization reaction because of the impossibility of facilitating the final rearomatization due to the presence of the methoxy group at the naphthalene ring junction, as reported in Scheme 1.

<sup>‡</sup> Typical procedure for the reaction catalyzed by vanadyl phthalocyanine 1: 1.0 mg of catalyst (1.7 μmol) was dissolved in 1 mL of phenylacetylene (9.77 mmol). The resulting solution was warmed at 160–180 °C for 48 h under nitrogen. At the end of the reaction, dodecane or tetradecane was added as an internal standard and the mixture analyzed by GC.

Typical procedure for the reaction catalyzed by vanadyl phthalocyanine 1 in 1,2-dichlorobenzene: 1.0 mg of catalyst (1.7 μmol) was dissolved in 3 mL of 1,2-dichlorobenzene and 1.38 g of 1-ethynyl-naphthalene (9.1 mmol) was added. The resulting solution was warmed at 160 °C for 48 h under nitrogen. At the end of the reaction, dodecane or tetradecane was added as an internal standard and the mixture analyzed by GC.

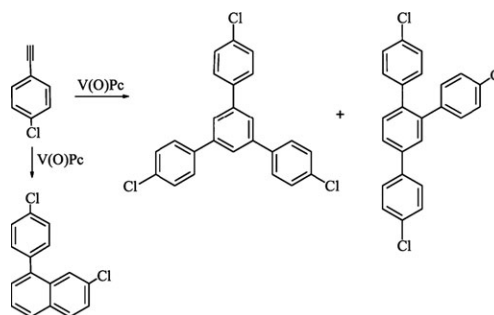


Fig. 2 The cyclooligomerization reaction catalyzed by 1.

Vinylidene intermediate **A** can react with a second molecule of arylethyne to give adduct **B**, but this complex cannot give final naphthalene derivative **C**, and can be only subjected to a retro-Diels–Alder reaction, affording again, after decomplexation, the initial compound. In fact, from the reaction catalyzed by 1 or Ru(OEP)CO, we were only able to isolate the 1,3,5- and 1,2,4-triarylbenzenes, without any trace of dimer **C**, as reported in Scheme 2. For comparison, the final triarylbenzene derivatives were also obtained by a Suzuki coupling from the 1,2,4- and 1,3,5-tribromo-benzenes, respectively, and 2,6-dimethoxyphenylboronic acid.<sup>16</sup>

This fact, in our opinion, supports the presence of a labile vinylidene complex during the catalytic cycle for the other studied substrates. The presence of a cationic mechanism can be excluded on the basis of a crossover experiment we performed using 4-chloro- and 4-methoxy-ethynylbenzene in an equimolar mixture. The expected dimers were obtained in almost the same equimolar quantity, but also with the presence of the scrambled examples.<sup>§</sup> Such a result is in agreement with the lack of any polar intermediate. To further investigate the reaction mechanism, we decided to use commercially available 2-deuterium-labelled ethynylbenzene. Considering the reaction mechanism proposed in previous papers,<sup>5</sup> the [1,2]-deuterium shift should give the labile vinylidene complex which, reacting with a second molecule of arylethyne, should afford the 1-phenyl-2,4-dideutero-naphthalene through the intermediate **E**, as reported in Scheme 3.

The <sup>1</sup>H- and <sup>2</sup>H-NMR spectra of the final dimer show that we obtained the final 1-phenyl-naphthalene with 58% of the label on C-2, while C-3 and C-4 retained almost 100% of the label. This fact can be explained only if we imagine a reaction pathway with a rapid intramolecular shift of the deuterium from C-2 to C-3 for intermediate **E**, and a consequent decomplexation and rearomatization, with scrambling of H and D at position C-2 by abstraction from the initial compound.<sup>¶</sup>

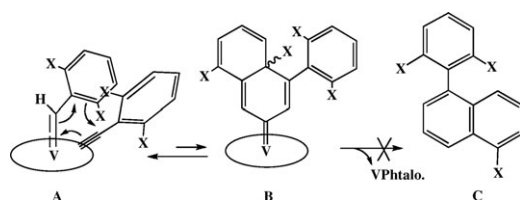
<sup>§</sup> It was not possible to separate and fully characterized the scrambled dimers, which were detected using GC and GC-MS.

<sup>¶</sup> A kinetic isotopic effect was also determined for 2-*D*-ethynylbenzene compared with the non-deuterated compound. A modest but significant effect ( $k_H/k_D = 2.0 \pm 0.08$ ) was observed, suggesting the presence of a secondary effect due to some rehybridization of the alkyne in the transition state of the reaction.

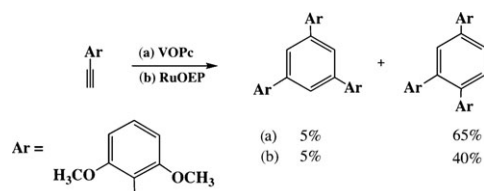
**Table 1** The cyclooligomerization of substituted aryethynes  $p,m\text{-X-C}_6\text{H}_4\text{-C}\equiv\text{CH}$  and 1-ethynyl- or 2-ethynyl-naphthalene using **1** as the catalyst.<sup>a</sup> Data from previous papers are reported in parentheses

Entry	Substrate X	Conversion (%)	Yield of cyclodimers (%) <sup>b</sup>	Yield of cyclotrimers (%) <sup>b</sup>
1	H	93	72 (23) <sup>d</sup>	21 (68) <sup>d</sup>
2	<i>p</i> -Cl	98	50 (1) <sup>e</sup>	48 (98) <sup>e</sup>
3	<i>p</i> -OCH <sub>3</sub>	99	66 (49) <sup>e</sup>	33 (14) <sup>e</sup>
4	<i>m</i> -OCH <sub>3</sub>	99	93 (78) <sup>c,e</sup>	6 (21) <sup>e</sup>
5	<i>p</i> -CH <sub>3</sub>	94	82 (69) <sup>e</sup>	12 (30) <sup>e</sup>
6	<i>p</i> -F	99	40	59
7	1-Ethynyl-naphthalene <sup>f</sup>	99	89 (86) <sup>g</sup>	— (4) <sup>g</sup>
8	2-Ethynyl-naphthalene <sup>f</sup>	98	97 (89) <sup>g</sup>	— (7) <sup>g</sup>

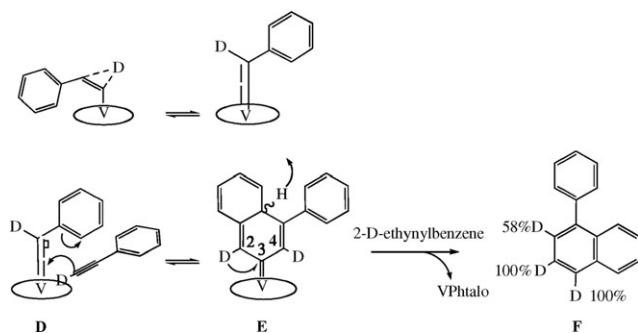
<sup>a</sup> Reactions carried out at 160–180 °C with a molar ratio of substrate : catalyst = 5700 : 1. <sup>b</sup> Yields determined by GC analysis. <sup>c</sup> Two isomers (1 : 1 ratio). <sup>d</sup> From ref. 5b with Ru(OEP)CO as the catalyst. <sup>e</sup> From ref. 5a with Rh(TDCPP)Cl as the catalyst. <sup>f</sup> In 1,2-dichlorobenzene at 160 °C. <sup>g</sup> From ref. 5d with Ru(OEP)CO as the catalyst.



**Scheme 1** The cyclooligomerization mechanism does not operate for a 2,6-disubstituted ethynylbenzene.



**Scheme 2** Reaction products and yields for the cyclooligomerization of 2,6-dimethoxy-ethynylbenzene.



**Scheme 3** The reaction mechanism and the deuterium fate of the 2-deutero-ethynylbenzene.

## Conclusions

In this paper, we have reported an improvement in the dimer yield for the cyclooligomerization of aryethynes by the use of a vanadium phthalocyanine. Furthermore, we made observations that support our hypothesis about the presence of a vinylidene intermediate during the cyclooligomerization reaction.

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