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The First Solvent-Free Cyclotrimerization Reaction of Arylethynes Catalyzed by Rhodium Porphyrins

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Different rhodium(III) porphyrin chlorides have been used as catalysts for the cyclotrimerization of several arylethynes, giving in many cases high yields in substituted benzenes and selectivities based on the steric hindrance of the macrocycles and on the substitution of the substrates.

Synthetic metalloporphyrins are efficient catalysts for the epoxidation of alkenes and hydroxylation of aromatic and aliphatic compounds.[1] Metalloporphyrins are also able to catalyze the cyclopropanation of olefins from diazo compounds[2] and the Diels−Alder reaction,[3] and recently there has been a report on the olefination of aldehydes with ethyl diazoacetate catalyzed by an iron(II) porphyrin.[4] During our studies on the catalytic properties of this interesting class of macrocycles,[5] we discovered a new application of their peculiar prerogatives, *i.e.*, the formation of benzene derivatives from acetylenic compounds.

Although the activation of the triple bond, namely, the Reppe reaction, to give aromatic compounds is a well-known process[6] and several catalysts have been used to promote it, this is the first time that metalloporphyrins were found to be able to perform such a cyclotrimerization.

Such a reaction, starting from monosubstituted ethynes, gave the 1,2,4-trisubstituted benzenes together with different amounts of the 1,3,5- and 1,2,3-trisubstituted isomers.[7]

The mechanism of the formation of the 1,2,4-trisubstituted isomer involves the presence of metallacycle compounds formed from the consecutive addition of two molecules of acetylene to the metal residue.[6] A simple trend in the formation of the products was tentatively proposed on the basis of the different metals and the steric interaction between the catalysts and the intermediates. Cobalt, rhodium, nickel, aluminum, and other metal complexes were used as catalysts for such reactions, which can give also cycloctatetraene (COT) derivatives.

In this Communication we want to report on the remarkable properties, in catalyzing the formation of benzene derivatives from substituted acetylenes, of a number of rhodium porphyrins: Rh(TPP)Cl, **1**, Rh(TDCPP)Cl, **2**, Rh(Cl$_{16}$TDMPP)Cl, **3**, Rh(TDMPP)Cl, **4**, and Rh(OEP)Cl, **5**, where TPP is the dianion of 5,10,15,20-tetrakis-phenylporphyrin, TDCPP is the dianion of 5,10,15,20-tetrakis-(2′, 6′-dichlorophenyl)porphyrin, Cl$_{16}$TDMPP is the dianion of 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis-(2′,6′-dimethoxy-3′,5′-dichlorophenyl)porphyrin, TDMPP is the dianion of 5,10,15,20-tetrakis-(2′,6′-dimethoxyphenyl)porphyrin, and OEP is the dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin. The porphyrin catalysts were all synthesized by literature methods, and their structures are reported in Figure 1.[8]

The reactions were performed without solvent at 180 °C with the molar ratio substrate/porphyrin = 5700:1, and the final products have been separated by flash chromatography, by preparative HPLC on silica gel columns, or by fractional crystallization. All the catalysts were recovered by column chromatography in more than 95% of yield and recycled at

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[1] (a) Meunier, B *Chem. Rev.* **1992**, *92*, 1411−1456. (b) Mansuy, D. *Coord. Chem. Rev.* **1993**, *125*, 129−142.

[2] (a) Maxwell, J.; Kodadek, T. *Organometallics* **1991**, *10*, 4−6. (b) O'Malley, S.; Kodadek, T. *Tetrahedron Lett.* **1991**, *32*, 2445−2448. (c) Hamaker, C. G. Mirafzall, A.; Woo, L. K. *Organometallics* **2001**, *20*, 5171−5176. (d) Hamaker, C. G.; Djukic, J.-P.; Smith, D. A.; Woo, L. K. *Organometallics* **2001**, *20*, 5189−5199.

[3] Bartley, D. W.; Kodadek, T. *Tetrahedron Lett.* **1990**, *31*, 6303−6306.

[4] Mirafzal, G. A.; Cheng, G.; Woo, L. K. *J. Am. Chem. Soc.* **2002**, *124*, 176−177.

[5] (a) Baciocchi, E.; Boschi, T.; Cassioli, L.; Galli, C.; Jaquinod, L.; Lapi, A.; Paolesse, R.; Smith, K. M.; Tagliatesta, P. *Eur. J. Org. Chem.* **1999**, 3281−3286. (b) Tagliatesta, P.; Bernini, R.; Boschi, T.; Mincione, E.; Crestini, C.; Monti, D.; Saladino, R. *J. Org. Chem.* **1999**, *64*, 5361−5365.

[6] (a) Reppe, W.; Kutepow, N.; Magin, A. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 727−733. (b) Yur'eva L. P. *Russ. Chem. Rev.* **1974**, *43*, 48−68. (c) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1−8. (d) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539−556. (e) Maitlis, P. M. *J. Organomet. Chem.* **1980**, *200*, 161−176. (f) Shore, N. E. *Chem. Rev.* **1988**, *88*, 1081−1119. (g) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49−92.

[7] (a) Reikhsfel, V. O.; Makovetskii, K. L. *Russ. Chem. Rev.* **1966**, *35*, 510−523. (b) Maitlis, P. M. *Acc. Chem. Res.* **1976**, *9*, 93−99.

[8] (a) Traylor, P. S.; Dolphin, D.; Traylor, T. G. *J. Chem. Soc., Chem. Commun.* **1984**, 279−280. (b) Autret, M.; Ou, Z.; Antonini, A.; Boschi, T.; Tagliatesta, P.; Kadish, K. M. *J. Chem. Soc., Dalton Trans.* **1980**, 2793−2797. (c) Tagliatesta, P.; Pastorini, A. *J. Mol. Catal. A: Chem.* **2002**, *185*, 125−131

10.1021/ic0351390 CCC: $25.00

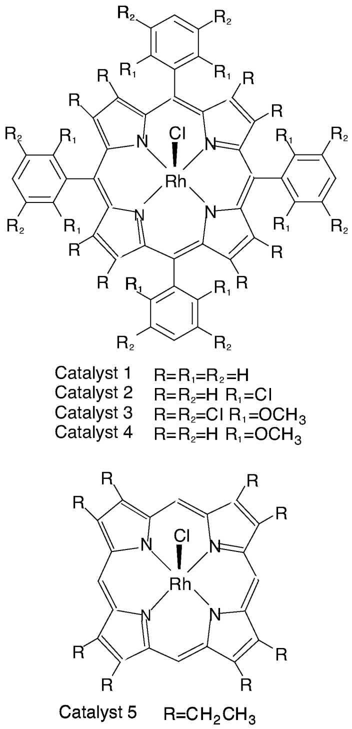


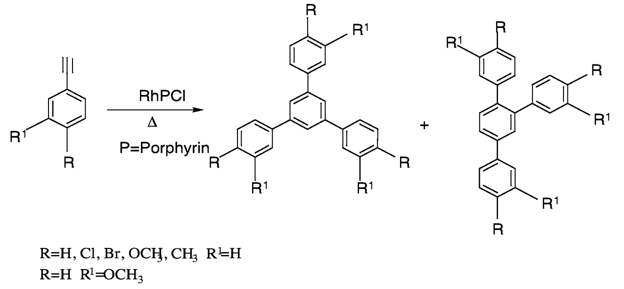
Figure 1. Molecular structures of the catalysts.

Table 1. Cyclotrimerization of Phenylethyne with Different Rhodium Porphyrins as Catalysts

catalyst	yield (%)[a,b] (conversion)	1,2,4 (%)[b]	1,3,5 (%)[b]	1,2,3 (%)[b]
1	55.0 (98)	31.8	19.8	3.4
2	24.5 (42)	8.7	14.0	1.8
3	66.7 (77)	61.2	5.5	*c*
4	90.8 (96)	61.6	27.0	2.2
5	30.0 (67)	11.0	16.6	2.4

[a] Reactions carried out at 180 °C with a molar ratio substrate/porphyrin = 5700:1. [b] Yields determined by GC analysis. [c] Trace.

Scheme 1



least three times without any loss of catalytic activity, and this fact is higly desired for obtaining large turnover numbers.

The structures of the substrates and the final products are reported in Scheme 1. The final conversion, the yield of the products, and their isomeric distribution have been determined by GC or HPLC analysis and, in the case of phenylethyne, are reported in Table 1. Lower conversions and yields have been obtained by performing the reactions at low temperature (60−140 °C) or in boiling chloroform. However, the product ratio does not change within the experimental error.

Table 2. Cyclotrimerization of Substituted Arylethynes, X−C_6H_4−C≡CH, Using Rh(TDCPP)Cl, **2**, Rh(Cl_{16}TDMPP)Cl, **3** and Rh(TDMPP)Cl, **4**, as Catalysts

catalyst	substrate	yield (%)[a,b] (conversion)	1,2,4 (%)[b,c]	1,3,5 (%)[b,c]
2	*p*-Cl	98 (99)	93.3	4.7
4	*p*-Cl	71 (72)	64.6	6.4
2	*p*-Br	92 (95)	71.0	21.0
4	*p*-Br	68 (70)	57.0	11.0
2	*p*-OCH_3	14 (63)	8.7	5.3
4	*p*-OCH_3	11 (47)	6.3	4.7
2	*m*-OCH_3	21 (99)	17.0	4.0
3	*m*-OCH_3	64 (92)	55.0	9.0
4	*m*-OCH_3	45 (85)	43.0	2.0
2	*p*-CH_3	30 (99)	19.0	11.0
3	*p*-CH_3	90 (98)	76.5	13.5
4	*p*-CH_3	68 (98)	60.3	7.7

[a] Reactions carried out at 180 °C with a molar ratio substrate/porphyrin = 5700:1. [b] Yields determined by GC analysis. [c] The 1,2,3-substitued isomers were not detected.

Going through the data, it is possible to see that the yield in cyclotrimerization products is highly affected by the nature of the catalyst. In fact catalyst **4**, with electron-donating methoxy groups in the 2′, 6′ phenyl positions, gives the highest yield in the cyclotrimerization products and substrate conversion while catalyst **2**, bearing in the same positions electron-withdrawing groups (Cl), affords the lowest ones. The other catalysts, **1**, **3**, and **5**, give intermediate results.

A small amount, between 1.8 and 3%, of the 1,2,3-trisubstituted isomer is also present in the reaction products, with almost all the catalysts, and this last interesting result is unusual with other catalytic systems.

Looking at the isomeric distribution of the cyclotrimerization products, it is clear that catalyst **3**, having a more hindered macrocycle core due to the saddle-shaped conformation of the porphyrin,[9] gives the 1,2,4-trisubstituted isomer with the highest selectivity. On the contrary, catalyst **5**, an almost flat macrocycle, affords a moderate selectivity for the 1,3,5-trisubstituted isomer.

This behavior can be easily understood considering that, during the formation of the benzene ring, the more crowded catalysts can favor the formation of the less symmetric isomer. Other interesting observations derive from the inspection of Table 2, which reports the results of the cyclotrimerization of several substituted phenylethynes, catalyzed by **2**, **3**, and **4**.

The nature of the substituents appears to influence the results. Electron-withdrawing groups located on the substrates, like methoxy in *meta* or chlorine in *para* positions, seem to positively affect the yields of the reaction and drive the isomeric distribution toward a high selectivity for the 1,2,4-trisubstituted derivatives. On the contrary, the strong electron-donating methoxy group, located in the *para* position of the starting alkyne, lowers both the reaction yield and the selectivity, enhancing the amount of the 1,3,5-trisubstituted isomer.

Noticeably, the 1,2,3-trisubstitued isomer is absent in all the reactions. This fact can be easily interpreted on the basis

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(9) Ochsenbein, P.; Ayougou, K.; Mandon, D.; Fischer, J.; Weiss, R.; Austin, R. N.; Jayaraj, K.; Gold, A.; Terner, J.; Fajer, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 348−350.

of the increased steric interaction that 1,2,3-trisubstituted phenyl rings experience inside the metalloporphyrins during the reaction pathway.

It is important to remark that, in our opinion, a complicated reaction mechanism is involved in the porphyrin-catalyzed reactions but first of all we exclude the formation of the metallacycle intermediate in a [4 + 2] reaction mechanism.[10]

Such intermediates should involve the formation of two σ metal−carbon bonds on the same face of the macrocycle, and this possibility can be ruled out for rhodium, which does not have suitable orbitals for binding.

Ogoshi *et al.*[11] reported the isolation of a vinylidene complex from the reaction of phenylethyne with a rhodium porphyrin at room temperature, and this compound, in our opinion, can be considered a good candidate as the first reaction intermediate.[12] In this case the reaction might then proceed with a [2 + 2 + 2] mechanism.[13]

In conclusion, rhodium porphyrins are efficient catalysts for the cyclotrimerization of arylethynes and can be finely tuned with different substituents, thus affecting the product selectivity. In our opinion this is a remarkable property that is difficult to find in other catalyst families. Compared with the other cyclotrimerization catalysts, they can be reusable and give high turnover numbers that for some reactions are over 5000. The yields and selectivities are, in many cases, also comparable with those reported in the literature for similar compounds.[6b,7] Moreover, the reaction, although occurring also in chloroform, works better without solvent. The goal of further work will be to get a deeper insight of the mechanism, in order to account for the formation of all the products.

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Supporting Information Available: Experimental details and analytical data for all the isolated compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Kirchner, K.; Calhorda, M. J.; Schmid, R.; Veiros, L. F. *J. Am. Chem. Soc.* **2003**, *125*, 11721−11729.

(11) Ogoshi, I.; Setsune, J.; Nambo, Y.; Yoshida, Z. *J. Organomet. Chem.* **1978**, *159*, 329−339.

(12) (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197−257. (b) Puerta, M. C.; Valerga, P. *Coord. Chem. Rev.* **1999**, *193*, 977−1025.

(13) (a) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081−1119. (b) Fletcher, J. T.; Therien, M. J. *J. Am. Chem. Soc.* **2000**, *122*, 12393−12394.