

Rhodium N-confused porphyrin-catalyzed alkene cyclopropanation

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Rhodium N-confused porphyrins constitute unprecedented, highly efficient tools for the cyclopropanation of styrene, affording the expected cyclopropanes in excellent yields with *trans* : *cis* ratios reaching 98 : 2.

In the general context of sustainable development, the need for efficient catalysts able to accelerate reactions and maximize selectivity becomes more crucial every day. Among the possible candidates, porphyrins and porphyrin analogues are particularly promising (Chart 1).¹ Indeed, their macrocyclic structure generally confers high stability on catalysts and their chemical functionalization allows spectacular structural variations to be achieved. Accordingly, remarkable results have been obtained. For instance, the enantioselective epoxidation of styrene was carried out in quantitative yield with 97% ee and turnover numbers (TONs) exceeding 16 000 using a functionalized binaphthyl porphyrin.² However, the limited synthetic availability of these elaborate structures often hampers the wide scale use of such catalysts. For this reason, in the recent years, special emphasis has been placed on the development of alternative systems that are capable of performing catalytic reactions with great efficiency by changing the platform from normal porphyrins to similar macrocycles. While some expected results were obtained with corrole,³ porphycene⁴ and N-fused porphyrin⁵ systems, they are not so accessible or

efficient, and hence the development of a more simple system is highly anticipated.

N-confused porphyrins (NCPs)⁶ are isomers of porphyrin that display novel abilities in coordination and supramolecular chemistries.⁷ Despite their rich coordination chemistry, to date, no catalytic reactions involving metallated NCPs have been reported in the literature. Herein, we examine alkene cyclopropanations catalyzed by rhodium NCPs and find that they display superior efficiency to other porphyrinoid catalysts in both yield and regioselectivity.

The preparation of catalysts could be achieved in only 3 steps from commercially available reagents (Scheme 1). Thus, tetraaryl NCPs were prepared from pyrrole and the corresponding aryl aldehyde.^{8,9} Next, the Rh(I) complexes were synthesized according to literature procedures.¹⁰ Finally, treatment of the Rh(I) complexes with pyridine or iodine gave the catalyst precursors.¹¹ To elucidate the electronic and steric effects on the cyclopropanation reaction, the rhodium complexes of N-confused tetra(phenyl)porphyrin (NCTPP), N-confused tetrakis(mesityl)porphyrin (NCTMP)¹² and N-confused tetrakis(pentafluorophenyl)porphyrin (NCTPFPP) were synthesized as catalysts.

The catalytic experiments were carried out at room temperature using a solution of 5 μmol catalyst (0.05 mol%) in 5 mL dichloroethane, 50 mmol styrene and 10 mmol ethyl diazoacetate (EDA) as the carbene source (Scheme 2). The results of the

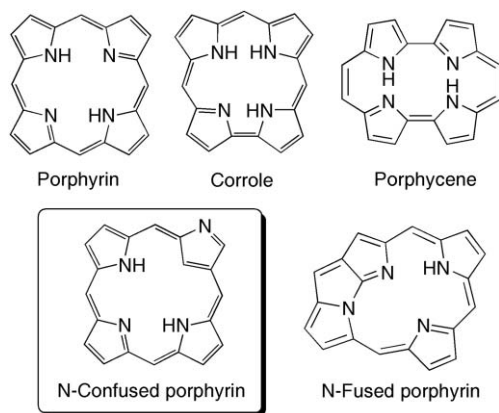
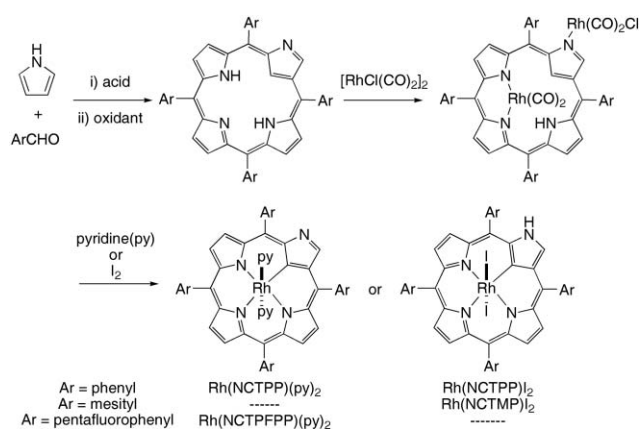


Chart 1 Structures of platform macrocycles.



Scheme 1 Preparation of the rhodium NCPs.



Scheme 2 Rhodium-catalyzed cyclopropanation of styrene.

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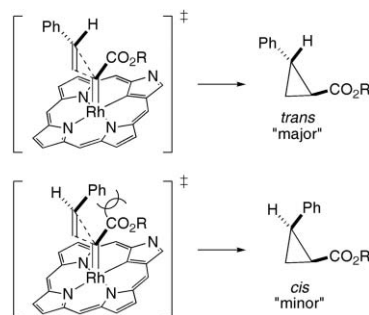
Table 1 Yield and selectivity data for catalytic cyclopropanation reactions of styrene^a

Entry	Catalyst	Yield (%)	Reaction time/h	Temperature	<i>trans</i> : <i>cis</i> ratio
1 ^b	Rh(NCTPP)I ₂	92	3	RT	91 : 9
2 ^{b,c}	Rh(NCTPP)I ₂	91	3	RT	98 : 2
3 ^b	Rh(NCTPP)(py) ₂	60	24	RT	86 : 14
4 ^b	Rh(NCTMP)I ₂	93	3	RT	83 : 17
5 ^b	Rh(NCTPFPP)(py) ₂	89	3	RT	88 : 12
6 ^b	Rh(TPP)I	71	4	RT	52 : 48
7 ¹⁵	Rh(TPP)I	71	n.r.	60 °C	47 : 53
8 ¹⁴	Fe(TPP)Cl	n.r.	10	40 °C	85 : 15
9 ³	Fe(TPFPP)Cl	43	3	RT	85 : 15
10 ³	Rh(TPFPC)(PPh ₃)	87	1	RT	67 : 33

^a TPP = tetraphenylporphyrin; TPFPP = tetrakis(pentafluorophenyl)porphyrin; TPFPC = Tetrakis(pentafluorophenyl)corrole; n.r. = not reported. ^b The yields and *trans* : *cis* ratios were determined by GC (n-pentadecane was used as internal standard). ^c *t*-Butyl diazoacetate was used in place of EDA.

catalytic experiments are summarized in Table 1, together with those of the similar tetrapyrrolic catalysts. It shows that the rhodium NCPs were actually more active and selective than their tetrapyrrolic parents. Indeed, the chemical yields measured with NCPs generally exceeded those obtained with porphyrins or corroles. The only exception concerns Rh(NCTPP)(py)₂ (Table 1, entry 3), which appeared very stable and relatively inert in the presence of EDA (24 h, 60% yield). The decoordination of the poorly-labile pyridine ligand is necessary to advance the reaction, but may not constitute the limiting step of the process because Rh(NCTPFPP)(py)₂, which maintains a similar pyridine coordination, catalyzed the reaction efficiently and afforded the expected cyclopropanes in 89% yield in 3 h (Table 1, entry 5). Apparently, the electron-withdrawing groups at the *meso*-positions influence the electron density of the π -cloud of the porphyrin ring, and consequently the central metal. Thus, this result may infer that carbene reactivity is much influenced by the degree of electron deficiency at the Rh metal center. More interestingly, the *trans* : *cis* ratio is always very favorable in the case of rhodium NCPs. The best result was obtained with Rh(NCTPP)I₂, which afforded cyclopropanes in 92% yield (TON = 1840) with a *trans* : *cis* ratio reaching 91 : 9 (Table 1, entry 1). In addition, the *trans* : *cis* ratio was even higher when the bulky *tert*-butyl diazoacetate was used instead of EDA. In the latter case, it reached 98 : 2, with the chemical yield remaining constant at 91% (Table 1, entry 2). Considering the effect of the diazo esters' steric bulk on the selectivities reported in previous studies,¹³ the *trans*-selectivity achieved here is remarkable. On the contrary, the presence of the too-distant bulky *meso*-mesityl substituent did not significantly influence the selectivity of the reaction (Table 1, entry 4). It is worth noting that slight modification of the *trans*-selectivity was observed with bulky *meso*-substituents in the case of the iron porphyrins,¹⁴ and even preferential production of the *cis*-isomer was observed in the case of the rhodium porphyrin.¹⁵ The regioselectivity trend of NCPs is apparently different to that of normal porphyrins, implying the unique role of *confusion* in the catalytic reactions.

While no direct evidence explaining the *trans* preference in the rhodium NCP-catalyzed reactions has been obtained as yet, we postulate that the *trans*-selectivity is caused by a late transition state. Since the *trans* : *cis* ratios were little affected by the *meso*-substituents and the structures of the rhodium NCPs should resemble those of normal rhodium porphyrins, the regioselectivity would originate from the intrinsic electronic nature of the NCP

**Scheme 3** Proposed transition state for the rhodium NCP-catalyzed cyclopropanation of styrene.

skeleton. Assuming that the initial step of catalysis by NCP is similar to the general pathway proposed for normal porphyrins,¹⁶ it would involve preliminary reduction of the rhodium NCP by EDA to form the corresponding rhodium carbene complex. In this complex, the high back-donating effect of the rhodium NCP would stabilize the electrophilic carbene moiety and allow the olefin to get close to the carbene in the transition state, which could result in the preferential production of the *trans*-isomer due to steric availability (Scheme 3).

In conclusion, this first report concerning the use of NCPs in catalytic reactions demonstrates their powerful potential. The catalytic cyclopropanation experiments disclosed here reveal that, in many cases, NCPs can outperform porphyrins and corroles. Accordingly, the high yields and selectivities obtained in this study are particularly significant. We believe that these promising preliminary results will open up new routes to further applications of NCPs in catalytic reactions.

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