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Electronic and steric effects on the stereoselectivity of cyclopropanation reactions catalysed by rhodium *meso*-tetraphenylporphyrins

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Abstract

The rhodium *meso*-tetraphenylporphyrins catalysed cyclopropanation reactions of styrene, cyclohexene and norbornene by ethyldiazoacetate (EDA), have been investigated. The electronic effects of the bromine groups in the β-positions of the porphyrins can be correlated to the *syn*/*anti* ratio obtained for the reaction products in the case of styrene, showing a good linear correlation between the sum of the Hammett's σ_p and the logarithm of the obtained selectivity. A decrease in the stereochemical ratio on increasing the number of halogen atoms was observed. This is not the case for cyclohexene and norbornene which show a different behavior and do not give good linear correlation. Furthermore, when the rhodium porphyrins have bulky methoxy substituents in the *ortho*-positions of the phenyl rings, comparing with the simple rhodium *meso*-tetraphenylporphyrin, the isomeric ratios decrease dramatically for styrene whilst for the other substrates remain almost in the same range. On the contrary, using a rhodium porphyrin bearing chlorine groups in the *ortho*-positions of the phenyl rings, the ratios increase, reaching higher values. These observations suggest the presence of different factors involved in determining the isomeric ratios. The electron-withdrawing effects of the substituents in the β-positions seem to influence the stereoselectivity giving the less hindered isomer while the chlorine bulky substituents in the *ortho*-phenyl positions can compensate this trend.

Keywords: Metalloporphyrins; Cyclopropanation; Catalysts; Rhodium; Olefins

1. Introduction

Transition metal complexes are active catalysts for the cyclopropanation of olefins by diazocompounds [1,2]. This reaction is widely employed in organic synthesis and several copper, rhodium and osmium complexes have been reported to be efficient in the formation of cyclopropanes [3–5].

Among the catalysts studied, much interest has been devoted to the metalloporphyrins because of their exquisite prerogative in reverting the *syn*/*anti* ratio of the reaction products obtained with normal catalysts [6–9]. Iron, rhodium and osmium porphyrins have been successfully used in the cyclopropanation reactions of simple olefins by ethyldiazoacetate (EDA). Reaction yields, turnovers number and stereoselectivities obtained with the use of such catalysts have been strictly correlated to the nature of the metal and the macrocycle [6–9].

The reaction mechanism of the metalloporphyrins catalysed cyclopropanation reactions is not completely elucidated because of the liability of the bond between the central metal and the acetate residue. The

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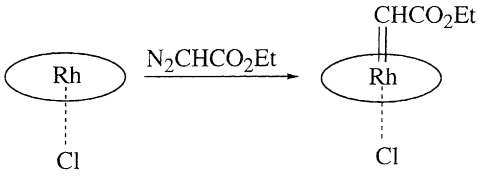
intermediate of the reaction, showed in Eq. (1), has been tentatively proposed, in the case of rhodium, by Callot and co-workers [6,7] and later studied by Maxwell and Kodadek, who used NMR spectroscopy for detecting the possible carbene species [10].



(1)

However, the key intermediate carbene species has never been isolated and fully characterised.

Recently, we have studied the synthesis and electrochemistry of several β-halogen substituted metalloporphyrins and explored their stability and reactivity during the electrochemical oxidation and reduction [11–15]. Furthermore, we have also used some manganese and iron derivatives of such porphyrins as catalysts in the oxidation reactions of organic substrates [16–18]. The possibility to vary the electronic properties and steric hindrance of the *meso*-tetraphenylporphyrins, introducing different groups on the β-positions and/or on the phenyl rings, prompted us to investigate which parameters govern the stereochemical results obtained in the cyclopropanation reactions using their rhodium derivatives as catalysts and in this paper we report the results obtained for standard olefins.

The catalysts were RhTPPCl (**1**), RhTDMPPCl (**2**), Rh(Cl_{16})TDMPPCl (**3**), Rh(Br_2)TPPCl (**4**), Rh(Br_3)TPPCl (**5**), Rh(Br_4)TPPCl (**6**), Rh(Br_8)TPPCl (**7**) and RhTDCPPCl (**8**), where TPP is the dianion of 5,10,15,20-tetraphenylporphyrin, TDMPP the dianion of 5,10,15,20-tetra(2′,6′-dimethoxyphenyl)porphyrin, (Cl_{16})TDMPP the dianion of 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetra(2′,6′-dimethoxy-3′,5′-dichlorophenyl)porphyrin, (Br_2)TPP the dianion of 2,3-dibromo-5,10,15,20-tetraphenylporphyrin, (Br_3)TPP the dianion of 2,3,12-tribromo-5,10,15,20-tetraphenylporphyrin, (Br_4)TPP the dianion of 2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrin, (Br_8)TPP the dianion of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin and TDCPP the dianion of 5,10,15,20-tetra(2′,6′-dichlorophenyl)porphyrin.

2. Experimental

2.1. General

Dry chloroform ($CHCl_3$) was distilled over P_2O_5 under nitrogen before the use. All other reagents and solvents were of the highest analytical grade and used without further purification. Chromatographic purifications were performed on silica gel (35–70 mesh, Merck) columns. Thin-layer chromatography was carried out using Merck Kiesegel 60 F254 plates.

^{1}H NMR spectra were recorded as $CDCl_3$ solutions on a Bruker AM 400 instrument using tetramethylsilane (TMS) as an internal standard. Electronic absorption spectra of the compounds were recorded on a Varian Cary 50 scan UV–VIS spectrophotometer. FAB mass spectra were measured on a VG-Quattro spectrometer using *m*-nitrobenzylic alcohol as a matrix.

GC analyses were performed on a Carlo Erba HRGC 5160 instrument equipped with a 30 m Supelco SPB-35 GC column and FID detector.

Elemental analyses (C, H and N) were carried out by the Analytical Laboratory of the University of Padova (Italy) and are all in excellent agreement with the expected values.

2.2. Synthesis of the porphyrins

The free base porphyrins were synthesised by literature methods [12,14,19–21].

2.3. Rh(III) derivatives

The insertion of rhodium in the free bases has been carried out according to literature procedures [22]. In a typical preparation, the free base (100 mg) was dissolved in benzene and $[Rh(CO)_2Cl]_2$ (100 mg) was added. The reaction mixture was stirred at 60 °C for 3 days, while protecting by a $CaCl_2$ valve and in the presence of air oxygen. After the evaporation of the solvent under vacuum, the residue was dissolved in chloroform and purified by column chromatography on silica gel, eluting with chloroform. The fraction containing the desired product was evaporated to small volume and methanol was added to precipitate the pure compound. The yields of the metal insertions were always in the range 60–70%. The UV–VIS, mass and ^{1}H

Table 1
UV–VIS characterisation of the new rhodium porphyrin compounds in $CHCl_3$

Compound	λ (nm) (× 10^{-4} ε dm^{-3} mol^{-1} cm^{-1})
RhTDMPPCl	420 (2.25); 532 (0.37); 607 (0.16)
Rh(Cl_{16})TDMPPCl	449 (6.40); 561 (0.87); 596 (0.28)
Rh(Br_2)TPPCl	426 (22.5); 538 (2.12); 571 (0.38)
Rh(Br_3)TPPCl	426 (23.1); 538 (2.30); 568 (0.56)
Rh(Br_4)TPPCl	433 (20.6); 546 (1.96); 581 (0.92)
Rh(Br_8)TPPCl	456 (20.0); 567 (1.97); 605 (0.46)
RhTDCPPCl	420 (6.07); 534 (10.96); 567 (0.25)

NMR data for the new compounds have been reported in Tables 1 and 2, respectively.

2.4. General procedure for the cyclopropanation reactions

The reactions and work-up were performed as reported in the literature [23]. The GC analysis of the products were performed under the following conditions: initial (5 min) and final temperatures of 70 and 200 °C, respectively, heating rate 10 °C min^{-1}. The chemical yields were not optimised. The obtained data were reproducible within ±2% for several experiments.

Table 2
NMR and mass spectra characterisation of the new porphyrin compounds

RhTDMPPCl (**2**)
δH: 8.69 (s, 8H, pyrr.); 7.65–7.76 (m, 8H, *m*-phenyl); 6.96–7.05 (m, 4H, *p*-phenyl); 3.51 (s, 24H, $–OCH_3$)
FAB-mass: 955 $(M - H–Cl)^+$

Rh(Cl_{16})TDMPPCl (**3**)
δH: 7.93 (s, 4H, *p*-phenyl); 3.00 (s, 24H, $–OCH_3$)
FAB-mass: 1508 $(M + H–Cl)^+$

Rh(Br_2)TPPCl (**4**)
δH: 8.68–9.06 (m, 6H, pyrr.); 8.01–8.19 (m, 8H, *o*-phenyl); 7.71–7.79 (m, 12H, *m,p*-phenyl)
FAB-mass: 871 $(M - 2H–Cl)^+$

Rh(Br_3)TPPCl (**5**)
δH: 8.71–9.08 (m, 5H, pyrr.); 8.06–8.25 (m, 8H, *o*-phenyl); 7.71–7.79 (m, 12H, *m,p*-phenyl)
FAB-mass: 952 $(M - Cl)^+$

Rh(Br_4)TPPCl (**6**)
δH: 8.68 (s, 4H, pyrr.); 8.0–8.17 (dd, 8H, *o*-phenyl); 7.6–7.8 (m, 12H, *m,p*-phenyl)
FAB-mass: 1031 $(M - Cl)^+$

Rh(Br_8)TPPCl (**7**)
δH: 8.0–8.25 (dd, 8H, *o*- phenyl); 7.6–7.9 (m, 12H, *m,p*-phenyl)
FAB-mass: 1346 $(M - H–Cl)^+$

RhTDCPPCl (**8**)
δH: 8.70 (s, 8H, pyrr.); 7.7–7.85 (m, 8H, *m*-phenyl); 7.65–7.7 (m, 4H, *p*-phenyl)
FAB-mass: 1026 $(M - H–Cl)^+$

3. Results and discussion

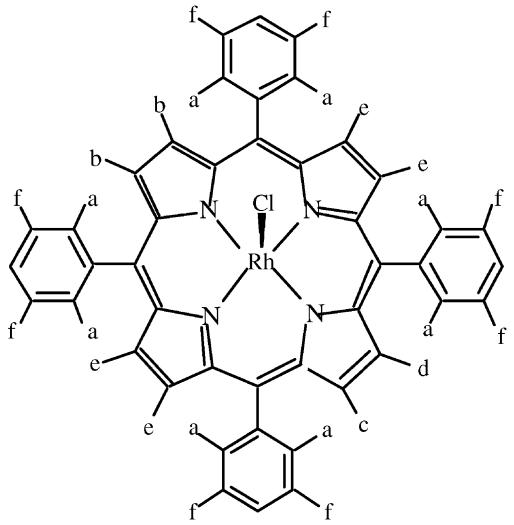
The molecular structures of the catalysts employed in this study are reported in Fig. 1.

It is well known from previous studies [11–13,15,24] that (PorBr$_x$)M, where PorBr$_x$ is the dianion of different β-halogenated TPP, M = Fe, Co, Zn or H_2 and $x \geq 3$ or 4, show saddle-shaped distortion of the macrocycles and formation of a pocket on both sides of the ring. This fact suggested the possibility to direct the cyclopropanation reaction to give the most hindered isomer in excess without building complicated porphyrinic structures [8]. For this purpose, we decided to use RhTDMPPCl (**2**) and RhTDCPPCl (**8**), which show good steric hindrance on both sides of the macrocycle due to presence of bulky groups. The starting free bases of such metal derivatives are now available in grams quantity by new synthetic methods much cheaper than those previously reported in the literature and comparable with those for obtaining the simple TPP [21].

We also used the rhodium derivative (**3**) of a perchlorinated porphyrin similar to those showing distorted and hindered structures [24]. Furthermore, we examined the possibility to quantify the influence of the β-bromine groups on the stereoselectivity of the reaction. Looking at the *syn*/*anti* ratios given in Tables 3, 4 and 5 and comparing them with the results obtained for the reactions catalysed by CuCl, it is evident that the situation is complicated and not easy to rationalise.

From the data obtained for styrene (Table 3; entries 2–6), it is clear that there is a small but evident influence of the β-bromination on the stereoselectivity of the reaction and plotting the logarithm of the *syn*/*anti* ratio against the sum of the Hammett's σ_p of the bromine groups, a good linear correlation ($r^2 = 0.98$; $\rho = -0.132$) is evident (Fig. 2).

The selectivity changes on increasing the number of the halogens and this fact, in our opinion, is due



Porphyrin	a	b	c	d	e	f
RhTPPCl	H	H	H	H	H	H
RhTDMPPCl	OCH_3	H	H	H	H	H
Rh(Cl_{16})TDMPPCl	OCH_3	Cl	Cl	Cl	Cl	Cl
Rh(Br_2)TPPCl	H	Br	H	H	H	H
Rh(Br_3)TPPCl	H	Br	Br	H	H	H
Rh(Br_4)TPPCl	H	Br	Br	Br	H	H
Rh(Br_8)TPPCl	H	Br	Br	Br	Br	H
RhTDCPPCl	Cl	H	H	H	H	H

Fig. 1. Rhodium(III) porphyrins employed in this work.

to different factors; the electrophilic character of the metal is clearly enhanced by the electron-withdrawing effects of the β-substituents and can be related to the mechanism proposed by Kodadek and co-workers [9] for the rhodium porphyrins catalysis. In this mechanism, the olefin can approach the metallocarbene intermediate in a perpendicular orientation relative to the metal–carbon bond axis and giving after a rotation the arrangement found in the final *syn* or *anti* product. Our results are in agreement with this interpretation but we also believe that, during the catalytic process, styrene can approach the core of the macrocycle through a π–π interaction with the higher halogenated pyrrole rings stabilising the transition state which leads to the *anti* product. Accordingly with this mechanism, it might be also expected that bulky groups located on the porphyrin, like methoxy, could give higher ratios. This is not the case for catalysts **2** and **3**, the first having bulky electron-donating methoxy groups on all the *ortho*-positions of the phenyl rings [14] and the second also bearing chlorine atoms on all the β-pyrrole and *meta*-phenyl positions, show an opposite trend with a *syn*/*anti* ratio around 0.4/0.5 (Table 3; entries 7 and 8). Similar data were also reported for osmium(II) and iron(II) catalysed reactions [9,25] but only for styrene and the results obtained

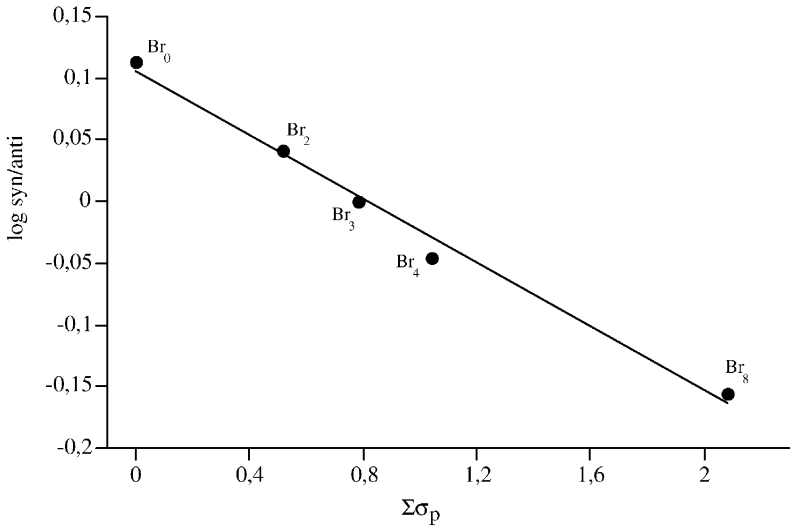
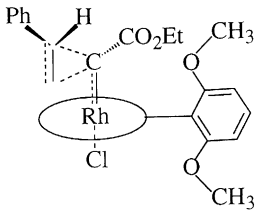


Fig. 2. Correlation diagram of the logarithm of the *syn*/*anti* ratio vs. the sum of Hammett's σ_p for the cyclopropanation of styrene catalysed by Rh(Br_x)TPPCl.

for our catalysts are in agreement with the model proposed for the iron in which the larger substituent, i.e. phenyl, in the transition state, is projected far from the ester group of the pre-formed carbene. In our case, this effect could be emphasised by the methoxy groups which insist in the same direction of the carbene ester, pushing the phenyl of styrene in the opposite side. A tentative schematic representation of the substrate approaching the catalyst–carbene intermediate is reported in Eq. (2).



(2)

Table 3
Molar ratios (*syn*/*anti*) and yields in parentheses for the cyclopropanation reaction of styrene with EDA catalysed by rhodium porphyrins

Entry[a]	Catalyst	Molar ratio
1	CuCl	0.6 (79.3)
2	RhTPPCl	1.3 (70.4)
3	Rh(Br_2)TPPCl	1.1 (95.0)
4	Rh(Br_3)TPPCl	1.0 (90.1)
5	Rh(Br_4)TPPCl	0.9 (91.2)
6	Rh(Br_8)TPPCl	0.7 (26.5)
7	Rh(Cl_{16})TDMPPCl	0.5 (27.7)[b]
8	RhTDMPPCl	0.4 (88.8)
9	RhTDCPPCl	1.7 (43.7)[b]

[a] Reactions were carried out at 60 °C with substrate/EDA/catalyst molarratio = 2500/1000/1.
[b] Room temperature.

Table 4
Molar ratios (*syn*/*anti*) and yields in parentheses for the cyclopropanation reaction of cyclohexene with EDA catalysed by rhodium porphyrins

Entry[a]	Catalyst	Molar ratio
1	CuCl	0.2 (60.4)
2	RhTPPCl	0.8 (61.5)
3	Rh(Br_2)TPPCl	0.6 (51.7)
4	Rh(Br_3)TPPCl	0.5 (69.0)
5	Rh(Br_4)TPPCl	0.6 (59.8)
6	Rh(Br_8)TPPCl	0.5 (8.2)
7	Rh(Cl_{16})TDMPPCl	0.7 (9.4)[b]
8	RhTDMPPCl	0.9 (59.1)
9	RhTDCPPCl	1.5 (80.1)[b]

[a] Reactions were carried out at 60 °C with substrate/EDA/catalyst molarratio = 2500/1000/1.
[b] Room temperature.

Table 5
Molar ratios (*syn*/*anti*) and yields in parentheses for the cyclopropanation reaction of norbornene with EDA catalysed by rhodium porphyrins

Entry[a]	Catalyst	Molar ratio
1	CuCl	0.4 (90.7)
2	RhTPPCl	1.4 (71.0)
3	$Rh(Br_2)TPPCl$	1.5 (31.8)
4	$Rh(Br_3)TPPCl$	1.5 (53.6)
5	$Rh(Br_4)TPPCl$	1.0 (66.4)
6	$Rh(Br_8)TPPCl$	0.6 (10.1)
7	$Rh(Cl_{16})TDMPPCl$	1.2 (80.6)[b]
8	RhTDMPPCl	1.5 (55.6)
9	RhTDCPPCl	3.5 (50.2)[b]

[a] Reactions were carried out at 60 °C with substrate/EDA/catalyst molarratio = 2500/1000/1.
[b] Room temperature.

The situation is different for cyclohexene or norbornene, which show different behaviours.

For cyclohexene, the most conformationally flexible substrate among those examined, we obtained almost the same *syn*/*anti* ratio for all the above cited catalysts (Table 4; entries 2–6). This is not surprisingly and such effect can be attributed to the possibility for cyclohexene to have the access to different conformations. This fact can help the approach to the metal centre, minimising the steric effects induced by the bulky substituents of the catalysts **2** and **3** or by the saddle-shaped deformations of the macrocycle **7**. On the contrary, norbornene, a more rigid substrate, shows a non-linear decrease in the stereochemical ratio, as observed for styrene, on increasing the number of the halogen atoms on the β-positions. For the catalysts **2** and **3** having bulky groups in the *ortho*-phenyl positions, the stereochemical ratios for norbornene increase again (Table 5; entries 7 and 8) and this fact might be due to a decreasing in the conformational freedom of the norbornene in the porphyrins cavity. Finally, porphyrin **8** shows the most interesting results among all reported in this paper.

When compared with the data obtained by Callot and co-workers [6,7], who used the rhodium derivatives of porphyrins bearing other bulky substituents as catalysts for the reaction of EDA with the same substrates, we were able to obtain a good improvement of the stereochemical results (Tables 3, 4 and 5; entries 9).

For styrene we obtained a ratio of 1.7/0.98, for cyclohexene 1.5/1.17 and for norbornene 3.5/2.14, at room temperature. These last results, in our opinion, are quite remarkable for several reasons, first of all because of the low cost of the starting free base. Furthermore, the result for norbornene, to the best of our knowledge, is the higher so far reported in the literature and also the other ratios obtained for styrene and cyclohexene are interesting even compared with the values obtained by O'Malley and Kodadek who used more complicated and expensive porphyrin catalysts [8].

4. Conclusions

The stereoselectivity of the rhodium tetraphenylporphyrins catalysed cyclopropanation reaction is the result of different factors which can be tentatively rationalised in terms of steric and/or electronic demands. The electron-withdrawing properties of the substituents in the β-positions decrease the *syn*/*anti* ratios for all the examined substrates. This effect is more pronounced in the case of styrene, which also show a good linear correlation between the number of halogen atoms and the stereochemical results. This change of stereoselectivity can be attributed to the geometry of the approach of the substrate to the core of the macrocycle which is more similar to that reported for the iron porphyrins catalysis. For the catalysts having methoxy groups in the 2′,6′-phenyl positions, the effect of the bulky groups goes in the same direction, while the catalyst bearing chlorine in the same positions gives better results.

Other studies on porphyrin catalysts bearing halogens in 2′,6′-positions and electron-donating groups in β-position are currently underway.

5. Synopsis

The rhodium porphyrins cyclopropanation reactions of three standard olefins have been widely studied. The isomeric ratios of reaction products has been correlated to the structures of the catalysts. The perchlorinated macrocycle RhTDCPPCl affords good stereochemical results.

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