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Cyclopropanation Reactions Mediated by Group 9 Metal Porphyrin Complexes

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Dedicated to Professor Sergio Cenini on the occasion of his retirement

Keywords: Cyclopropanation / Diazo compounds / Porphyrins / Cobalt / Rhodium / Iridium

The one-pot reaction of diazo compounds with olefins represents a useful strategy to synthesise cyclopropanes, which are important both as starting materials for the synthesis of organic compounds and because of their intrinsic pharmaceutical properties. Herein we describe the catalytic activity of group 9 metal porphyrin complexes to cyclopropanate olefins that present different electronic behaviour. All the most important porphyrin-based methodologies have been reviewed, stressing the stereocontrol of the reactions achieved in each case. Moreover, mechanism investigations have provided data that can help greatly to elaborate more efficient catalytic systems in the future.

Introduction

Three-membered carbon rings, namely cyclopropanes, are an important class of molecules, both for their employment as building blocks in organic chemistry and for their presence in compounds presenting pharmaceutical properties.[1,2] The scientific interest in developing new strategies for the synthesis of cyclopropanes has steadily increased since Nozaki and Noyori reported the first copper-mediated enantioselective cyclopropanation.[3] Cyclopropanes can be obtained by a thermal or photochemical activation of a diazo compound, $RR'CN_2$, that transfers the carbene moiety [RR′C] to an unsaturated double bond. However, extreme

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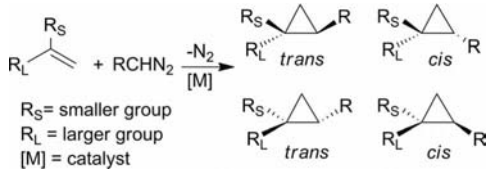
Daniela Intrieri was born in Italy in 1984. She received her master's degree in Chemistry in 2010 working in Sergio Cenini's group at the Department of Inorganic, Metallorganic and Analytical Chemistry "L. Malatesta" of the University of Milano (Italy) on the study of the mechanism of allylic aminations of olefins catalysed by ruthenium porphyrin complexes. She is PhD student at Milano University in Emma Gallo's group, and her research is mainly devoted to the synthesis of metal porphyrin complexes and their catalytic applications in C–C and C–N bond-formation reactions.

Alessandro Caselli received his PhD under the supervision of Carlo Floriani at the University of Lausanne (Switzerland) in 2000. He spent two years as post-doc in the Department of Organic and Industrial Chemistry at the University of Milano (Italy) under the supervision of Fulvia Orsini. In 2003 he joined Sergio Cenini's research group of as an assistant professor. His research interest is focussed on: (1) the employment of homogeneous catalysis of transition metal complexes with macrocyclic N-donor ligands; (2) the synthesis of new asymmetric ligands; (3) the mechanistic aspects of the catalytic reactions and (4) the study of simple techniques for the heterogenisation of chiral catalysts.

Emma Gallo received her PhD under the supervision of Carlo Floriani at the University of Lausanne (Switzerland) in 1995. She spent one year in Floriani's Group as "maitre assistant" before moving to Italy. After post-doctoral training with Sergio Cenini at the University of Milano (Italy), she first became assistant professor and then associate professor. Her research is mainly devoted to the synthesis of fine chemicals by C–C or C–N bond formation, with metal porphyrin complexes as catalysts, as well as the study of catalytic reaction mechanisms. More recently, she has focussed on the use of unconventional catalysts, such as transition metal polyoxometalates, to perform sustainable organic transformations.

experimental conditions are required and very often it is not possible to control the selectivity of the reaction because of the formation of free carbenes. To improve the selectivity of intermolecular carbene transfer reactions and to use milder reaction conditions, the presence of a transition metal catalyst is required.[4] The general reaction reported in Scheme 1 yields a mixture of two diastereoisomers (*cis* and *trans*), each of them exist as a pair of enantiomers.



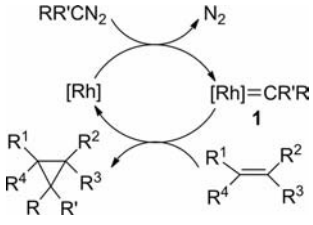
Scheme 1. Cyclopropanation of olefins by diazo compounds.[5]

As a result of the requirement of the chemical industry for efficient syntheses of fine chemicals, one of the major challenges for chemists is the development of extremely selective reactions. In the field of cyclopropanation, it is essential to optimise the diastereoselectivity and/or the enantioselectivity of the reaction. Whilst enantioselective reactions have been successfully achieved by employing several catalytic systems, only a few catalysts capable of achieving high diastereoselectivities with a wide range of substrates are known.[6]

Among catalytic systems employed in cyclopropanations, those based on porphyrins surely play a prominent role.[7–14] This microreview is focussed on the catalytic activity of porphyrin complexes of group 9 metals. Recent advances in understanding the mechanism of cyclopropanation mediated by M(porphyrin) complexes (M = Co, Rh) will be highlighted.

Rhodium-Catalysed Reactions

The catalytic competence of dirhodium(II) tetraacetate, $Rh_2(OAc)_4$, to promote the cyclopropanation of olefins by decomposition of diazo derivatives was reported several years ago.[15–19] Since then, several dirhodium compounds have been synthesised by replacement of acetates with other ligands, and very good results in both enantio- and diastereoselectivity have been achieved.[20–25] In the 1980s,[26,27] the formation of a metal carbene intermediate for rhodium-catalysed cyclopropanations was first proposed, and more recent theoretical papers have supported this hypothesis.[28,29] According to the general catalytic cycle (Scheme 2),[24] the first step of the cyclopropanation is the



Scheme 2. General mechanism for olefin cyclopropanation catalysed by rhodium complexes.

formation of an electrophilic metal carbene intermediate (**1**) that transfers the carbene unit to the incoming olefin to yield the cyclopropane. Up to now, much evidence regarding the formation of complex **1** has been provided, but, to the best of our knowledge, the formation of a carbene complex from a dirhodium compound was never established by spectroscopic or analytical methods.

Assuming the catalytic intermediate to be a carbene complex, the diastereocontrol of carbene transfer to an olefin is modulated by the nature of the diazo compound and the ligands on rhodium. $Rh_2(OAc)_4$ is known to give good diastereoselectivities only when diazo compounds bearing bulky substituents are used, whereas the cyclopropanation of olefins by the simple and commercially available ethyl diazoacetate (EDA) occurs with moderate stereocontrol (*cis*/*trans* = 38:62).[6]

The influence of ligands on the activity of rhodium complexes to improve the *cis*/*trans*-cyclopropane ratio was initially reported by Callot et al. in a paper in which the catalytic activity of the rhodium porphyrin complex Rh(TPP)I (TPP = dianion of tetraphenyl porphyrin) was established (Figure 1).[30]

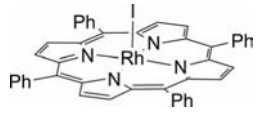


Figure 1. Molecular structure of Rh(TPP)I.

The large steric effect of the porphyrin ligand on the catalytic activity of the metal centre can be exploited for a diastereoface discrimination yielding up to 87% of *cis*-cyclopropane with EDA as carbene source, *cis*-olefins and porphyrin catalysts with different bulkiness on the peripheral substituents.[31]

The authors proposed that the olefin can approach a putative carbene perpendicularly (Figure 2a) or in parallel (Figure 2b). For internal olefins, a perpendicular approach would be more favoured than the parallel for steric reasons. Conversely, a terminal olefin can react with the intermediate carbene in a parallel approach.

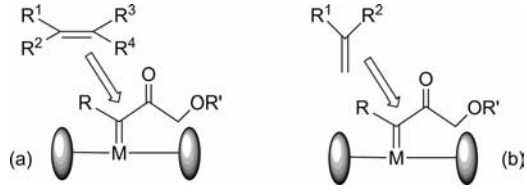
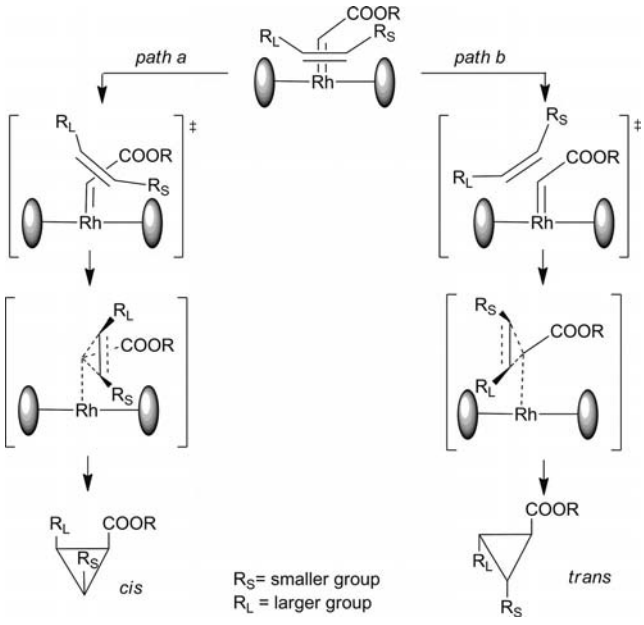


Figure 2. Perpendicular (a) and parallel (b) approach of an olefin to a putative carbene intermediate.

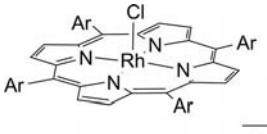
An explanation of the observed diastereoselectivity was proposed by Kodadek et al., who suggested that the cyclopropanation occurs with the concerted mechanism shown in Scheme 3.[32] According to Kodadek's proposal, the perpendicular approach of a *cis*-substituted olefin to the active carbene site pushes the larger group R_L as far away as possible from the ester group of the diazo fragment. In this scenario, there could be two possible pathways depending

on the steric hindrance of the porphyrin ligand and the ester group of the carbene. When bulky *meso*-aryl substituents are present on the porphyrin skeleton, *path a* will be preferred to minimise R_L–porphyrin interactions. The resulting clockwise rotation of the olefin, on the axis orthogonal to the rhodium–carbon bond, causes the formation of the *cis* diastereoisomer. On the other hand, a very high steric hindrance of the ester group provokes a counterclockwise rotation (Scheme 3, *path b*) with the consequent formation of the *trans*-cyclopropane. This mechanistic hypothesis can explain the high *cis*/*trans* diastereoselectivity observed by Callot with porphyrin catalysts bearing bulky *meso*-aryl groups.



Scheme 3. Mechanistic hypothesis for the cyclopropanation of unsymmetrical olefins catalysed by rhodium porphyrin complexes. (The porphyrin is represented as a line and the *meso*-aryl groups as ovals).

The influence of the steric hindrance of the porphyrin ligand in controlling the diastereoisomeric ratio of cyclopropanations was also investigated by Tagliatesta et al.[33] The electronic and steric properties of porphyrins were modulated by introducing different groups to the *ortho*-positions of the *meso*-aryl rings and β-positions of pyrroles. Some results on the cyclopropanation of three olefins by EDA are shown in Figure 3.



2: Ar = 2,6(OCH$_3$)$_2$C$_6$H$_3$
3: Ar = 2,6(Cl)$_2$C$_6$H$_3$

	styrene		cyclohexene		norbornene	
	cis/*trans*	yield %	*cis*/*trans*	yield %	*cis*/*trans*	yield %
2	0.4	88.8	0.9	59.1	1.5	55.6
3	1.7	43.7	1.5	80.1	3.5	50.2

Figure 3. Cyclopropanation of styrene, cyclohexene and norbornene catalysed by rhodium catalysts **2** and **3**.

The *cis*/*trans* ratio of the reaction catalysed by **2** depends on the nature of the olefin. With styrene, the *trans* diastereoisomer becomes the major product, although the cyclopropanation of norbornene gives a reasonable yield of *cis*-cyclopropane. This experimental result can be due to the formation of a transition state in which the phenyl group of styrene is pushed far away from the ester group of the carbene intermediate already pointing towards the *ortho*-methoxy groups of the aryl moieties.[34] According to the authors, this process is more difficult for norbornene because of its low flexibility, consequently the stereoselectivity of the reaction is controlled by the steric interactions between the olefin and the porphyrin, and a higher *cis*/*trans* ratio was obtained. This effect was enhanced when methoxy groups were replaced by chlorine to give complex **3**. The *cis*-selectivity observed with every olefin, when employing **3** as catalyst, indicated that the mechanism reported by Kodadek was operative.[32]

An inversion of the reaction diastereoselectivity was observed by replacing porphyrins with *N*-confused porphyrins. Rhodium complexes shown in Figure 4 exhibited very good catalytic activity, styrene was cyclopropanated in yields up to 93% and a *trans*/*cis* ratio of 98:2.[35]

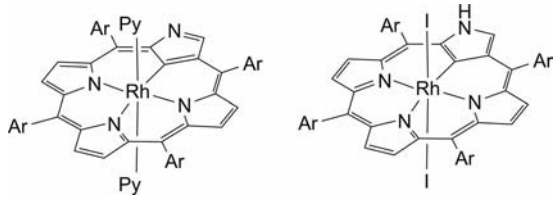
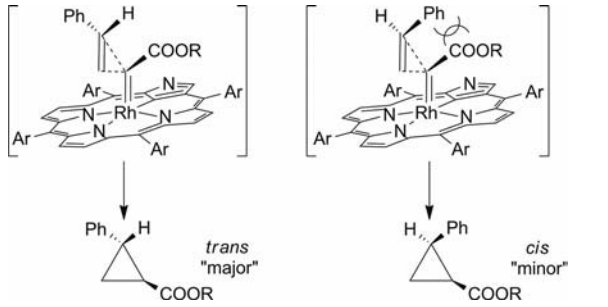


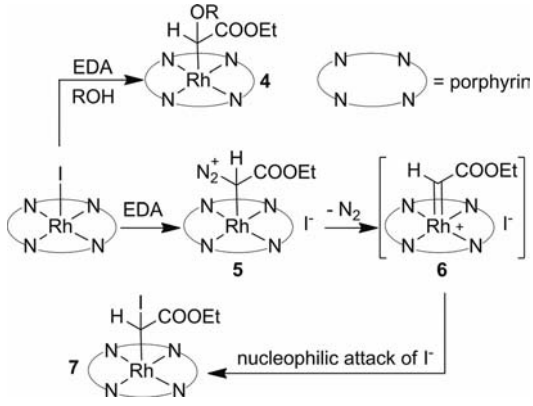
Figure 4. Cyclopropanation of styrene catalysed by rhodium *N*-confused porphyrins.

The best results were obtained by employing *tert*-butyl diazoacetate as carbene source; however, the reaction of EDA with styrene gave the corresponding cyclopropanes in yields up to 92% and a *trans*/*cis* ratio of 91:9. According to the authors, the diastereoselectivity inversion, *trans*/*cis* ratio > 1, could be due to the electronic differences between the two classes of ligands. The authors suggested that the higher back-donating effect of rhodium *N*-confused porphyrins would stabilise the carbene intermediate with the consequent formation of a late transition state. In such a scheme the terminal olefin approaches the carbene moiety in a parallel fashion, and the stabilisation of the electrophilic carbene should allow the olefin to come much closer to the active site, which results in the preferred formation of the *trans* isomer (Scheme 4). Conversely, the perpendicular approach of the internal olefin and an early transition state (Scheme 3) proposed by Kodadek should favour the formation of *cis*-cyclopropane when the reaction is run in the presence of bulky rhodium porphyrins. The mechanism of the cyclopropanations mediated by rhodium *N*-confused porphyrins was not investigated in detail; therefore, in our opinion, further studies are necessary to confirm the mechanistic hypothesis reported above.



Scheme 4. Proposed transition state for the cyclopropanation of styrene catalysed by rhodium *N*-confused porphyrins.

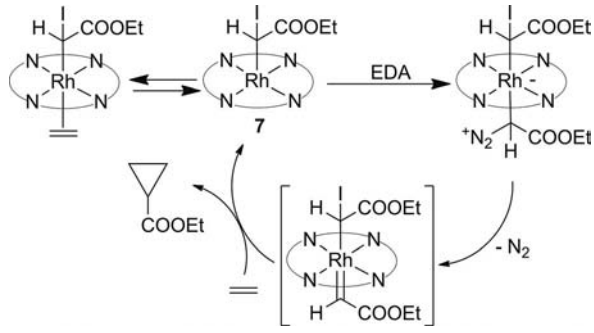
All data reported up to now indicates a strong dependence of the reaction stereoselectivity on the nature of the porphyrin skeleton. It is also clear that the design of the appropriate ligand is enabled by the comprehension of the reaction mechanism. With this idea in mind, the first study on the reactivity of rhodium(III) porphyrins towards diazo compounds was performed by Callot, who analysed the reaction of Rh(TPP)I with EDA in the presence of alcohols. It was suggested that the isolated alkylrhodium(III) porphyrin **4** (Scheme 5) should result from the addition of the alcohol to an intermediate carbene species.[36]



Scheme 5. Stoichiometric reaction of EDA with Rh(TPP)I in the absence of an olefin.

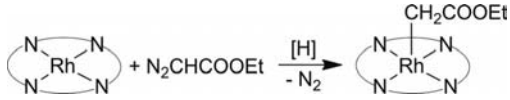
A more detailed study of the mechanism of cyclopropanation catalysed by rhodium porphyrins was then performed by Kodadek et al. in an interesting series of papers.[37–39] They demonstrated that the first step of the stoichiometric reaction between Rh(TPP)I and EDA was the coordination of the diazo compound to the metal centre to give complex **5** (Scheme 5). The following release of molecular nitrogen yielded a supposed carbene complex **6**, too reactive to be either isolated or spectroscopically identified. In the absence of an olefin, complex **6** yielded the rhodium alkyl species **7**, which was fully characterised by NMR spectroscopy.

The formation of adduct **5** between rhodium porphyrin and EDA was detected at a low temperature of –40 °C by IR and NMR spectroscopy. By warming the reaction solution, complex **5** was transformed into **7** with the evolution of molecular nitrogen. Complex **6** was never identified, but a kinetic study supported the formation of such carbene intermediates. Complex **7** showed good catalytic activity. Scheme 6 reports a plausible catalytic cycle in which **7** is involved.[39]



Scheme 6. Proposed mechanism for the cyclopropanation of olefins catalysed by iodorhodium porphyrin.

The authors suggested that the olefin, in addition to being the substrate, can inhibit the reaction by competing with EDA for coordination on the free axial position. The reversible coordination of olefins was established by UV spectroscopy and can explain why different olefins react at different rates even though kinetics indicate carbene formation as the rate-determining step of the reaction. It should be noted that up to now every attempt to isolate a carbene complex from the reaction of rhodium(III) porphyrins with diazo compounds has failed. Even the reaction of rhodium(II) complexes with EDA yielded rhodium(III) porphyrin alkyl compounds by abstraction of a hydrogen atom from the diazo compound (Scheme 7).[40]



Scheme 7. Reaction between Rh^{II}(porphyrin) complexes and EDA.

To improve the synthetic utility of cyclopropanations mediated by rhodium porphyrins, the use of diazo compounds, such as glycine ethyl ester, as precursors was also explored. By employing this methodology, several aromatic and aliphatic olefins were transformed into the corresponding cyclopropanes in good yields but unfortunately with low diastereoselectivity.[41]

Considering the high *cis*-selectivity of cyclopropanations mediated by rhodium porphyrins, some efforts have been made to fine-tune an enantioselective catalysis. Kodadek reported the synthesis of "chiral wall"[42] and "chiral fortress"[43] (compounds **8** and **9**, respectively) rhodium porphyrins that efficiently catalysed the cyclopropanation of different olefins with high turnover numbers. However, in spite of the good *cis*/*trans* diastereoselectivity observed in several cases, the enantiomeric excesses achieved were generally modest. Several years later, Che and co-authors reported *ee* values up to 68% by using the rhodium *D*4-porphyrin complex[44] **10**, but a common *trans*-diastereoselectivity was observed. The chiral complexes **8**, **9** and **10** are shown in Figure 5.

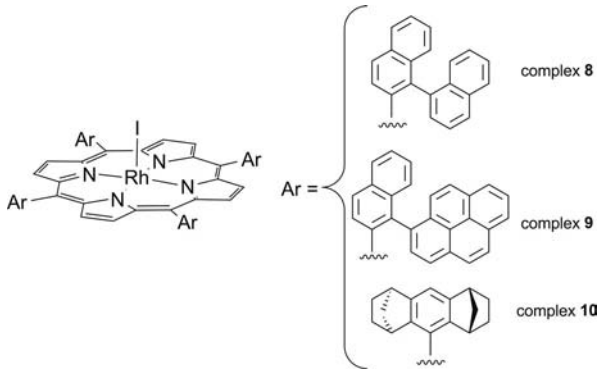


Figure 5. Molecular structures of complexes **8**, **9** and **10**.

In conclusion, all data reported up to now clearly indicate that to achieve a very high *cis*-stereochemical induction it is not sufficient to use porphyrin complexes bearing bulky groups. It is necessary to take into account other parameters such as steric properties of the diazo compounds and the olefins.

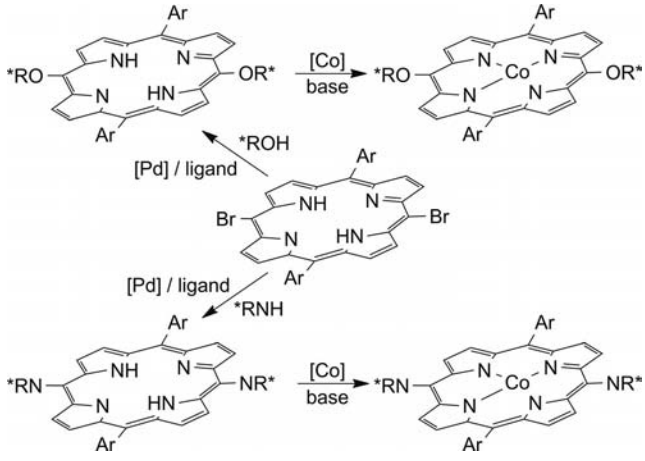
Cobalt-Catalysed Reactions

The catalytic activity of cobalt complexes in the stereoselective cyclopropanation of olefins was first established by Nakamura et al. by using cobalt(II) complexes of camphorquinonedioximes.[45–48] The reactions of several olefins with diazo compounds yielded the corresponding cyclopropanes with enantioselectivity up to 88% *ee*, but generally equal amounts of *cis* and *trans* isomers were obtained. Camphor-derivative ligands were also employed by Jommi et al.[49] to synthesise cobalt(II) complexes that are active for the cyclopropanation of simple olefins such as 1-octene. The observed diastereoselectivity was low (*cis*/*trans* = 1:1.8) but the *trans* isomer reached 97% *ee*.

Both diastereo- and enantiocontrol in intermolecular cyclopropanations of olefins were independently reached by Katsuki and Yamada by using cobalt complexes of chiral Schiff bases and ketoiminato ligands, respectively.[50] Katsuki et al. demonstrated that the diastereoselectivity of the reaction can be driven towards the formation of the *trans* or the *cis* isomer by changing the oxidation state of the metal[51–53] and adjusting the steric and electronic properties of substituents on the C3(3′) and C5(5′) positions of the Schiff base.[51,54,55] For example, the reaction of styrene with α-diazoacetate gave, in the presence of different cobalt catalysts, the corresponding *cis* and *trans* isomers with very high diastereo- and enantioselectivity. The *cis*-cyclopropane was obtained with 99% *dr* and 98% *ee*,[56] whereas the *trans* isomer was formed with 82% *dr* and 86% *ee*.[57]

Yamada et al. developed a catalytic system based on chiral ketoiminatocobalt(II) complexes to attain very good diastereo- and enantiomeric excesses.[58] The nature of the cobalt ligand promoted a *trans* selectivity; the cyclopropanation of styrene by EDA yielded 90% of the corresponding *trans*-cyclopropane with 96% *ee*.[59] The effect of the addition of a coordinating ligand, such as *N*-methylimidazole (NMI), to enhance the stereocontrol of cyclopropanation reactions was also investigated.[60] On the basis of theoretical analyses,[61,62] it was suggested that the positive effect of a coordinating ligand is due to a reduction of the activation energy to form the cobalt–carbene intermediate, which results in a more efficient catalytic process.

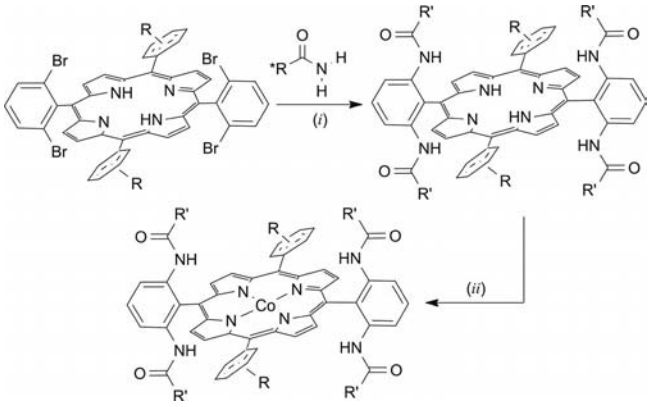
The catalytic activity of several cobalt complexes of modified Schiff bases,[63–65] terpyridines,[66] nitrogen macrocycles,[67] pincer ligands[68] and polyoxometallates[69] was also reported. However, porphyrin ligands represent, along with Schiff bases, the most frequently used class of ligands to synthesise cobalt cyclopropanation catalysts. The catalytic activity of achiral Co^{II} porphyrin complexes in the cyclopropanation of olefins, independently reported by Zhang[70] and our group[71] in 2003, revealed a general *trans* selectivity and the absence of maleate and fumarate byproducts resulting from coupling reactions of EDA.[72] An enantiomeric version of cyclopropanations catalysed by cobalt porphyrins was then reported by Zhang et al. by using vitamin B_{12}[73] and *meso*-chiral porphyrin complexes[74] as catalysts. These last porphyrins were prepared by employing synthetic procedures reported in Scheme 8.



Scheme 8. Synthesis of *meso*-chiral cobalt porphyrin complexes.

The reaction of several olefins with EDA catalysed by vitamin B_{12} afforded the *cis*-cyclopropane as the major isomer; the best recorded diastereo- and enantioselectivity were 67 and 78%, respectively. On the other hand, a *trans* selectivity was observed by running cyclopropanations in the presence of porphyrin complexes reported in Scheme 8, but unfortunately enantioselectivities were not satisfying. Since then, Zhang et al. developed the synthetic procedure[75,76] shown in Scheme 9, by using bromoporphyrins as synthons, to reach a wide pool of chiral porphyrins with D_2 symmetry (Figure 6).

An initial screening of the catalytic activity of these porphyrins showed that both R and R′ groups affect the reaction stereoselectivity, which can be strongly improved by adding a coordinating ligand.[75] The asymmetric cyclopropanation of styrene by *t*BDA (*tert*-butyldiazoacetate) run in the presence of 1% **12** and 0.5 equiv. [4-(dimethylamino)-pyridine] (DMAP) yielded cyclopropanes with a *trans*/*cis*



Scheme 9. Synthesis of chiral cobalt porphyrin complexes. (*i*) $Pd(OAc)_2$/XantPhos, Cs_2CO_3; (*ii*) $CoCl_2$, 2,6-lutidine.

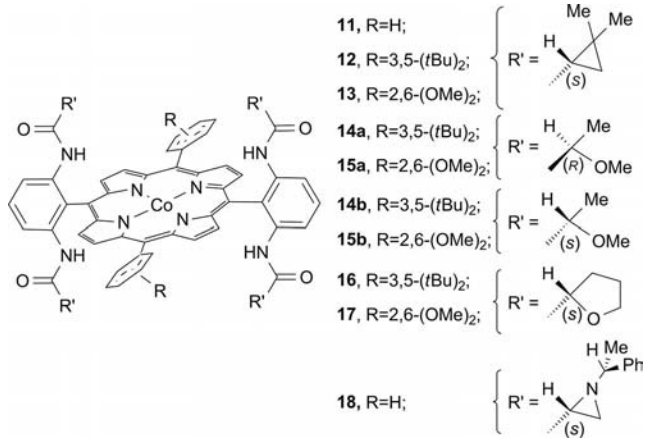
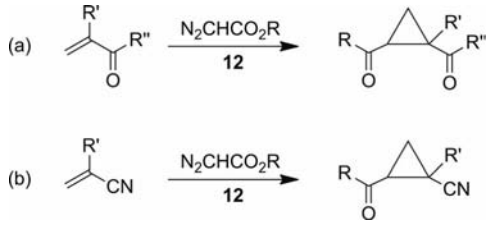


Figure 6. Chiral porphyrins used as cyclopropanation catalysts.

ratio greater than 99:1 and 98% *ee*. The positive *trans* effect of DMAP was disclosed by studying the influence of several coordinating additives on the catalytic efficiency of the reaction.[77] It should be noted that DMAP must be used in a substoichiometric amount to avoid a partial inhibition of the reaction. Probably, when an excess of DMAP is employed, both axial coordinative sites of the metal centre can be occupied, with a resulting decrease in the catalytic activity of the cobalt porphyrin. With **12** as the catalyst and the synthetic protocol reported above, a broad range of styrene derivatives, bearing both electron-withdrawing and electron-donating substituents, were cyclopropanated in high yields and excellent diastereo- and enantiomeric excesses.[78]

Complex **12** not only exhibited an exceptional catalytic activity in the cyclopropanation of electron-sufficient olefins, but it also was a competent catalyst for the cyclopropanation of electron-deficient olefins (Scheme 10).[79] Very high enantioselectivities (up to 97%) and diastereoselectivities (*trans*/*cis* ratio up to 99:1) were obtained.



Scheme 10. Cyclopropanation of electron-deficient olefins catalysed by **12**.

With this methodology, acrylates (Scheme 10a, R′ = H; R′′ = OEt or O*t*Bu), methacrylates (Scheme 10a, R′ = Me; R′′ = OMe), acrylamide (Scheme 10a, R′ = H; R′′ = NH_2), its mono- (Scheme 10a, R′ = H; R′′ = NH*i*Pr) and disubstituted derivatives (Scheme 10a, R′ = H; R′′ = NMe_2), acryl ketones (Scheme 10a, R′ = H or Me; R′′ = Et or Me or *n*Pe) and acrylonitriles (Scheme 10b, R′ = H, Me) were cyclopropanated.

To expand the scope of the reaction, several diazo compounds other than EDA or *t*BDA were tested. The catalytic system showed an excellent efficiency also with use of diazosulfones,[76] α-nitrodiazoacetates,[80] succinimidyl diazoacetate[81] and α-cyanodiazoacetate[82] (Figure 7).

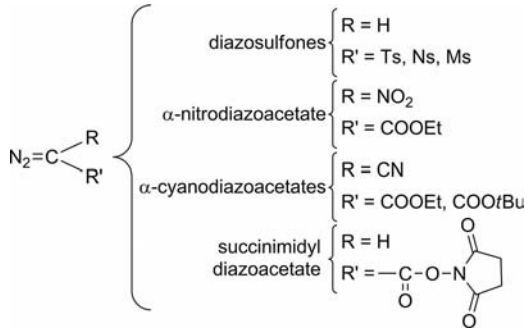


Figure 7. Diazo compounds employed in cyclopropanation reactions.

The synthesis of cyclopropanes bearing the different R and R′ groups listed in Figure 7 represents an important synthetic result for several reasons. Firstly, acceptor/acceptor-substituted diazo compounds are not generally reactive in other catalytic systems; therefore, the synthesis of the corresponding cyclopropanes indicated the high efficiency of the methodology based on cobalt porphyrins. In addition, cyclopropanes bearing such R or R′ groups can be further modified to yield biologically important cyclopropanes.

The exceptional enantioselectivity observed in cyclopropanation reactions catalysed by chiral cobalt(II) porphyrins[83] shown in Figure 6 can be due to a particular arrangement of their molecular structure in which chiral R* units are forced toward the centre of the porphyrin. However, the electronic and steric behaviour of the putative cobalt–carbene derivative should be responsible for the outstanding diastereoselectivities.

To study the steric and conformational ligand requirements to obtain stereocontrol of the reaction, several years ago we synthesised the cobalt(II) complex[84] **19** (Figure 8) of the chiroporphyrin already reported by Marchon et al.[85]

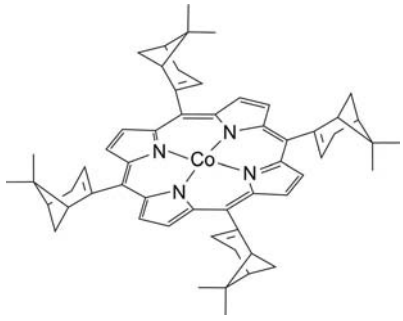


Figure 8. Structure of **19**.

The cyclopropanation of α-methylstyrene by EDA catalysed by **19** afforded the corresponding cyclopropanes with low diastereo- and enantioselectivity. The observed experimental results were justified by theoretical calculations, which disclosed the existence of **19** as a pool of interconverting atropisomers. We did obtain better catalytic results by using the more rigid complexes **20**,[86] **21**[87,88] and **22**[89] reported in Figure 9.

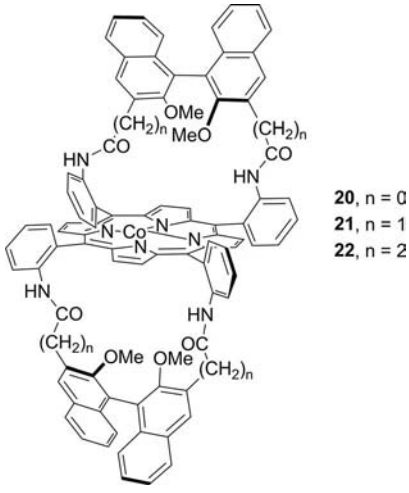
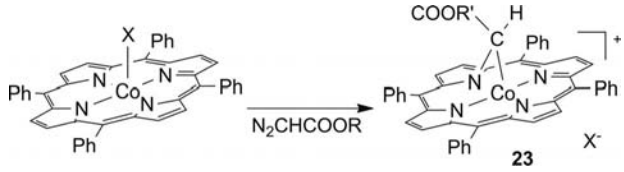


Figure 9. Structures of chiral cobalt bis(binaphthyl)porphyrins.

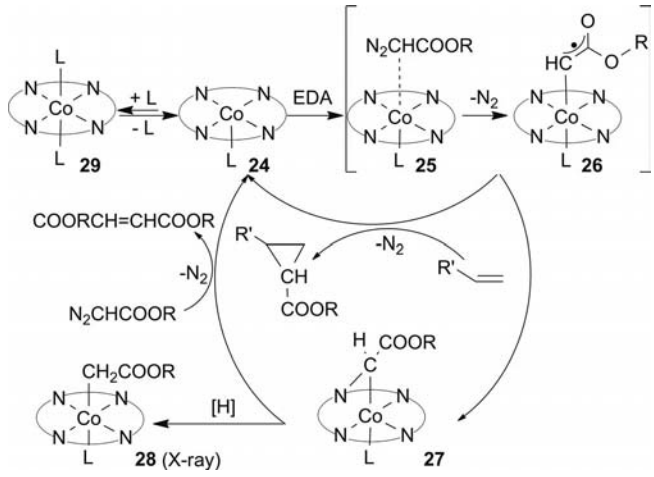
Among the cobalt(II) complexes of chiral bis(binaphthyl) porphyrins reported in Figure 9, complex **21** showed the best catalytic activity. Several olefins were tested in the reaction with EDA, and good yields as well as good enantioselectivities (up to 90% *ee*) were observed with *cis*/*trans* ratios reaching 11:89.

The strong dependence of the catalytic performance on the electronic and steric nature of the porphyrin ligand prompted the scientific community to clarify the reaction mechanism, in order to design new and more efficient catalysts. First, spectroscopic studies of the reaction between cobalt(III) porphyrins and diazoacetates suggested the insertion of the carbene unit into the bond between the cobalt and a porphyrin nitrogen atom to give the cobalt(III)-bridged carbene complex **23a**, whose catalytic activity was not further investigated (Scheme 11).[90–92] More recently, a *N*-bridged carbene cobalt(III) corrole was isolated and fully characterised.[93] A spectroscopic study revealed an equilibrium between a bridged carbene complex and an axial carbenoid compound, which was the only active species in the cyclopropane formation.



Scheme 11. Synthesis of the bridged carbene complex **23**.

A more complete mechanistic study of cyclopropanations catalysed by cobalt(II) porphyrins was undertaken a few years ago by our group. The reaction between EDA and α-methylstyrene was studied in the presence of Co(TPP)[71] or complex **21**[89] and on the basis of spectroscopic reactions and kinetic data, we proposed the cycle shown in Scheme 12.

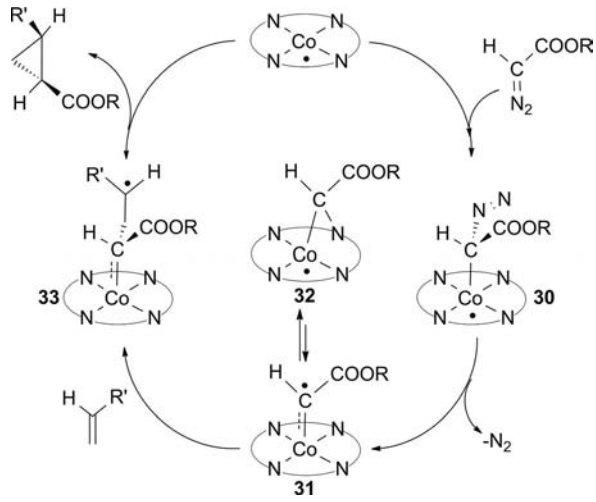


Scheme 12. Catalytic cycle for the Co(porphyrin)-catalysed cyclopropanation suggested on the basis of kinetic data and experimental studies.

The spectroscopic investigation of the reaction catalysed by Co(TPP) revealed the formation of a bridged carbene complex, **27**[94] (L = none), which, instead of being the active species, could be responsible for the formation of maleate and fumarate both formed by a reaction with an additional EDA molecule when the olefin is present in very low concentrations. Conversely, with an excess of olefin, the catalytically active species (**25** or **26**) rapidly reacted with the unsaturated substrate to yield cyclopropanes, and the formation of coupling compounds was not observed. Both of these reactions regenerate Co(TPP) (**24**, L = none). Alternatively, complex **27** can be transformed into the catalytically inactive $Co^{III}(TPP)(CH_2COOR)L$ (R = Et; L = none) (**28**) by a hydrogen atom abstraction. Complex **28** was characterised by X-ray analysis.

A similar mechanism was also suggested for the reaction catalysed by **21**. In addition, we also studied the crucial role of NMI usually used as a promoter in this class of reaction. UV/Vis spectroscopic studies of the cyclopropanation of α-methylstyrene showed an isosbestic point on both the Soret and the Q-bands for the reaction of **21** with NMI, which suggests the formation of **29** (L = NMI) without the accumulation of any long-lived intermediate. On the basis of the Soret band shift observed when EDA was added to **29**, we proposed that during the catalytic cycle one NMI ligand must be lost to allow the coordination of EDA to the metal centre and form either **25** or **26**; therefore, a high NMI concentration disfavours ligand replacement with a consequent inhibition of the catalytic reaction. Moreover, the modification of the catalyst induced by a coordinating ligand was also studied by NMR spectroscopy by exploiting the presence of methoxy groups in the skeleton of the porphyrin ligand in **21**.[95] The paramagnetism of the cobalt complexes prevented a direct NMR spectroscopic study, hence a zinc bis(binaphthyl) porphyrin was used instead. The OCH_3 groups of the binaphthyl handles (Figure 9), being very close to the metal centre, were used as "NMR probes" to observe modifications of the porphyrin core. NMR spectroscopic data indicated a conformation change of the binaphthyl handles induced by NMI, and in our opinion this particular arrangement of the porphyrin skeleton was responsible for the enhancement of enantioselectivities observed in the reaction catalysed by **21** in the presence of NMI. Finally, the radical nature of the reaction mechanism was supported by the strong inhibiting effect of TEMPO (2,2,6,6-tetramethylpiperidine *N*-oxide) when added to the cyclopropanation of α-methylstyrene catalysed by either Co(TPP) or **21**.

However, our mechanistic investigations did not unequivocally indicate a catalytic cycle, and many aspects remained unsolved until exhaustive mechanistic surveys were carried out very recently by B. De Bruin and X. P. Zhang.[96–99] The key to the elucidation of the mechanism was a deep theoretical study that took into account experimental data on the nature of the catalytic intermediate. EPR spectroscopic and ESI-MS analyses of the reaction between complex **12** (Figure 6) and EDA disclosed the presence of both "bridging" and "terminal" carbene species, which are in equilibrium in solution.[97] DFT calculations indicated that the bridging carbene is a metal-centred radical whilst the terminal carbene is a carbon-centred radical (Scheme 13, complexes **32** and **31**, respectively). The energy difference among the two species is not so large, thus the possible existence of a dynamic equilibrium is confirmed. The DFT study identified the terminal carbene as the species that reacts with the olefin, which, according to the authors, approaches the carbene in a parallel way (Scheme 13). The reaction of **31** with the olefin yields a γ-carbon radical species **33** that collapses to form the cyclopropane and the Co(porphyrin) complex. This kind of reaction was also observed in the synthesis of several cyclopropanes from allylcobaloximes. A radical species was responsible for the homolytic displacement of cobaloxime(II) from the allylcobaloxime(III) complex, and then a ring-closure reaction yielded the desired cyclopropane.[100]



Scheme 13. Catalytic cycle for the Co(porphyrin)-catalysed cyclopropanation proposed on the basis of DFT and experimental studies.

The calculated TS energy barrier values for *cis*- and *trans*-cyclopropanations indicated that, probably for steric reasons, the *trans*-cyclopropanation is more favoured than the *cis*-cyclopropanation. The theoretical data was in agreement with the experimental results reported by Zhang in previous papers.[76–82]

It is worth noting that theoretical calculations indicated carbene complex **31** to be a "radical Fischer carbene" with a partial nucleophilic character, which explains its good catalytic activity in the cyclopropanation of electron-deficient olefins. This feature of **31** is due to the presence of a *redox-noninnocent carbene ligand*, which controls the progress of the reaction.[98] Very recently, Woodcock et al.[99] theoretically described the electronics of **31**-like carbene species (Figure 10).

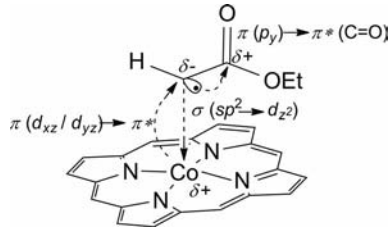
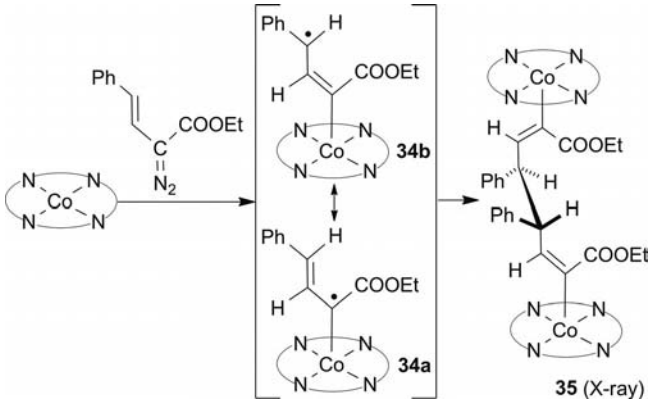


Figure 10. Formation of the cobalt–carbon bond in the radical carbene complex.

According to this study, the cobalt–carbon single bond is formed through a σ donation from the sp^2 molecular orbital of the ligand to the singly occupied d_{z^2} atomic orbital on the metal centre, associated to a back-donation from the π-symmetry orbitals of the cobalt atom into the Co–C π* molecular orbital. This process establishes an electron density δ^- on the carbene carbon atom that is stabilised by back-donation into a π* orbital of the acceptor C=O group.

As reported in Scheme 13, the radical carbene intermediate **31** should form the γ-radical species **33** by reaction with an olefin. Chemical evidence for the formation of such radical species was provided by Zhang and De Bruin who studied the reaction of Co(TPP) with ethyl styryldiazoacetate in the absence of any other olefin (Scheme 14).[96] The synthetic strategy reported in Scheme 14 has already been employed to trap iridium radical species.[101]



Scheme 14. Reaction of Co(TPP) with ethyl styryldiazoacetate to yield **35**.

The electronic nature of this diazo compound allows for the allylic radical resonance **34a** ↔ **34b**. Then γ-radical species **34b**, instead of reacting with a hydrogen donor to form a cobalt(III) alkyl compound,[71] self-dimerises to yield compound **35**, which was isolated and fully characterised by X-ray analysis. DFT calculations indicated that the formation of **35** is preferred over a hydrogen-atom abstraction because of the higher energy barrier related to this latter reaction. It is important to point out that the isolation of **35** was fundamental in defining the mechanism illustrated in Scheme 13, initially supported on the basis of EPR spectroscopic, ESI-MS and DFT studies.

All results reported up to now highlight the excellent performance of cobalt porphyrins in catalysing the cyclopropanation of a wide range of olefins by different diazo derivatives. Moreover, the information accumulated by investigations on the mechanism of the cyclopropanation reaction has laid the foundation for new and more efficient catalytic systems.

Iridium-Catalysed Reactions

Although iridium Schiff bases have been used by Katsuki et al. as catalysts in cyclopropanations of olefins by diazo compounds,[102–104] to the best of our knowledge the catalytic efficiency of iridium porphyrins remains almost unexplored. The lack of iridium(II) porphyrin complexes as cyclopropanation catalysts may be due to their easy transformation, by reaction with simple olefins such as ethene, into iridium(III) porphyrin anionic radical species. The intramolecular electron-transfer reaction, from the Ir^{II} centre to the porphyrin ligand, is responsible for the formation of a $(P)^{\cdot-}Ir^{III}(CH_2{=}CH_2)$ radical species.[105,106] The formation of such a species during cyclopropanation reactions can explain the low catalytic activity of iridium(II) porphyrins.

The SciFinder database contains only an oral communication by Woo et al.[107] on the employment of CH_3-Ir^{III}(TTP) (TTP = dianion of tetratolylporphyrin) and Ir^{III}(TTP)X(CO) (X = Cl, Br and I) as cyclopropanation catalysts. Surely the use of iridium(III) porphyrins in the field of catalytic carbene-transfer reactions will be a topic to explore in the near future.

Conclusions

The aim of this microreview is to show that rhodium and cobalt porphyrin complexes represent a class of useful catalysts for the direct insertion of a carbene unit into olefin double bonds. The synthesis of cyclopropanes were performed with excellent diastereo- and enantioselectivity in several cases. The choice of the opportune catalyst made it possible to drive the cyclopropanation towards the synthesis of only one diastereoisomer with outstanding enantiocontrol. Finally, the reported insights into the mechanism of the cyclopropanation of olefins by diazo compounds will be crucial in planning new methodologies suitable for the synthesis of organic compounds with high added value.

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