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# Optically active ruthenium porphyrins: chiral recognition and asymmetric catalysis

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**Contents**



**Abstract**

The current applications of ruthenium porphyrins in stoichiometric and catalytic asymmetric reactions are reported. Chiral recognition of racemic phosphines, isocyanides and amino esters has been studied by $^{1}$H-NMR. Experimental investigations of the oxidation mechanism of racemic phosphines and amino esters are described. The stereochemistry of catalytic asymmetric oxidation and cyclopropanation of olefins with optically active ruthenium porphyrins are also discussed. 

*Keywords:* Ruthenium; Optically active porphyrins; Chiral recognition; Asymmetric catalysis

## 1. Introduction

Development of efficient asymmetric catalysis requires the preparation of readily accessible chiral metal complexes [1]. The importance of metal porphyrin chemistry in this area has been well recognized due to hemoprotein modeling [2–6]. Thus Fe and Mn porphyrin complexes have been mainly used for catalytic oxidation reactions [7–9]. On the other hand, Zinc and Rhodium [10] and to a lesser extent Cobalt porphyrin [11,12] complexes have been used for chiral recognition. The excellent work of Ogoshi's group on the chiral recognition of amino acids using various optically active porphyrins [10,13,14] should be particularly recognized.

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In contrast, relatively few reports have been devoted to the use of Ruthenium porphyrins in asymmetric catalysis and chiral recognition.

There has been a great deal of recent interest in Ruthenium porphyrin chemistry as viewed both in the stoichiometric and catalytic contexts. These developments seem to be parallel to the use of organometallic ruthenium catalysts containing chelating bis(tertiary phosphine) ligands for asymmetric hydrogenation [15–19]. Actually, ruthenium porphyrins mediate a number of interesting stoichiometric and catalytic reactions, including carbene complexation, alkane hydroxylation and alkene epoxidation. The interest in ruthenium chemistry was inspired by the periodic relationship of ruthenium to iron and the possibility to prepare relatively stable oxoruthenium derivatives [20,21]. Much of this activity, however, has focused on oxidation reactions which mimic the cytochrome P-450 family of monooxygenases, and a number of porphyrin catalytic systems have been reported [22–26]. Much less work has been done on other reactions, though some of them appear to hold promise as synthetic methods. For a long time, it was believed that the corresponding ruthenium carbonyl derivatives are insufficiently labile and the chemistry was restricted to studies of ligand exchange at the sixth coordination site [27]. In this report, we review the use of chiral ruthenium porphyrin as new devices for chiral recognition and new catalysts for asymmetric syntheses.

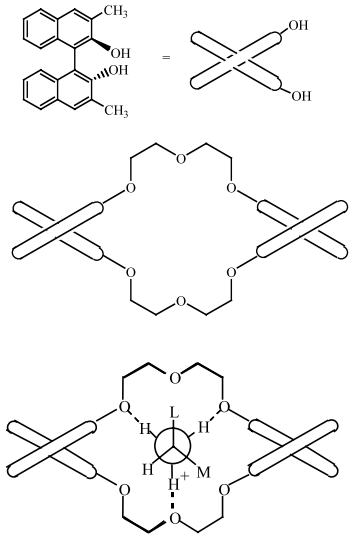


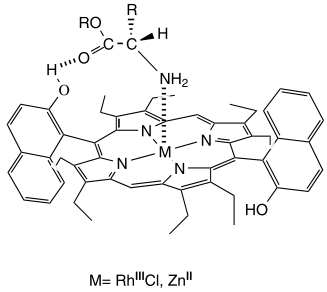

Fig. 1. Representation of a stable diastereomeric complex between a dinapthyl macrocyclic polyether (host) and an enantiomeric primary amine (guest) in which L is a large, M a medium and S a small group (adapted from [28]).

## 2. Chiral recognition

Since the pioneering work of Cram [28] and Lehn [29] on chiral recognition of racemic amines by binaphthyl hosts (Fig. 1), several approaches to the design and preparation of new chiral hosts have been reported. Recently, Ogoshi et al. utilized the porphyrin's rigid framework and a metal coordination site as a host, which can be seen as models for substrate-heme protein interactions [10]. The properties of two metal ions, Rh and Zn, were compared in detail and good enantioselectivity was obtained for valine ester with a chiral zinc porphyrin ($D/L = 7.5$) [14]. Chiral recognition of racemic amino alcohol with optically active ruthenium or cobalt porphyrins has been also reported [12,30]. Thus it is well known for a chiral molecule to distinguish between the enantiomers of a second species, that a minimum of three silmutaneous interactions must take place between the two species [14,31–33]. With metalloporphyrins, the three interactions will be: metal–nitronitrogen bonding, hydrogen bond between the carbonyl group of the ligand and OH (or NH) group of the host and a steric interaction between the lateral chain of the amino ester and the chiral cavity (Fig. 2) [14]. Our efforts in this area have been largely directed toward the systematic investigation of the reactivity of chiral ruthenium porphyrins.

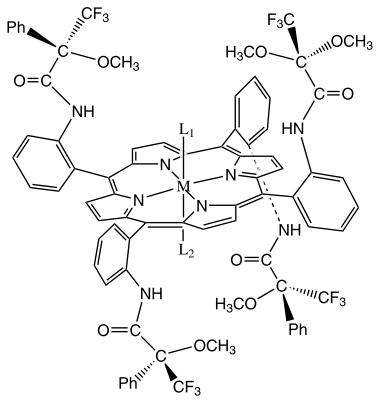
### 2.1. Racemic phosphines

We were the first to describe the preparation of ruthenium picket-fence porphyrins bearing optically active α-methoxy-α-trifluoromethyl phenyl acetic residues on both sides of the porphyrin plane [34]. The chiral pickets were prepared by coupling of the four atropisomers of *meso*-tetra(*o*-aminophenyl)porphyrin [35] with Mosher's reagent (Fig. 3) [36]. However, the symmetry properties of these porphyrins are affected both by the chiral substituents in the *ortho* positions of the four aryl units and by atropisomerism. The four atropisomers that contain four identical optically active units in their *ortho* positions are represented in Fig. 4.




M= $Rh^{III}Cl$, $Zn^{II}$

Fig. 2. Schematic representation of binding of amino acid esters to multifunctional zinc (or rhodium) porphyrin receptors (adapted from [10]).



**1**: M = 2H
**2**: M = Ru; $L_1$ = CO; $L_2$ = THF
**3**: M = Ru; $L_1 = L_2 = (CH_3)_2CH(CO_2CH_3)CHNH_2$

Fig. 3. Chiral picket-fence porphyrin bearing optically active α-methoxy-α(trifluoromethyl) phenylacetyl residues on both sides of the porphyrin plane α,β,α,βML$_1$L$_2$T(MTPA)PP (adapted from [37]).

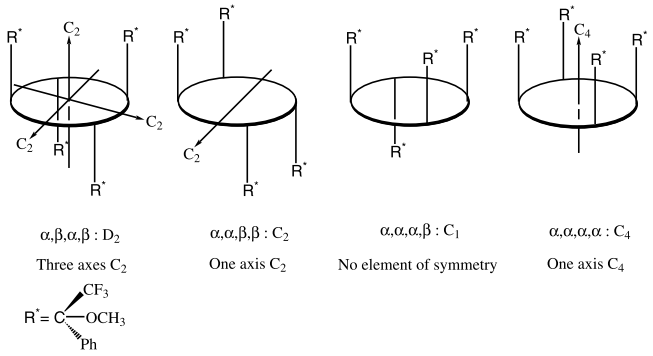



Fig. 4. Symmetries of chiral picket-fence porphyrins bearing α-methoxy-α(trifluoromethyl) phenylacetyl residues (*R**) (adapted from [34]).

Obviously, all the atropisomers are dissymmetric and hence optically active. Of these compounds, only the isomer α,α,α,β is asymmetric since this molecule does not possess a Cn rotation axis. The other atropisomers contain one or several Cn axes. In particular, the α,β,α,β isomer contains three mutually perpendicular $C_2$ axes to give the molecule $D_2$ symmetry whereas the α,α,β,β isomer contains an in plane $C_2$ axis. In both cases, the two faces are stereochemically equivalent. The two cavities on each face are different for the two other compounds. Finally, the α,α,α,α isomer contains a $C_4$ axis which is perpendicular to the porphyrin plane. These considerations are very important when the topic of nuclear magnetic resonance is discussed, for, under favorable conditions, non-equivalent atoms give rise to separate peaks in the spectrum.

In order to overcome the severe problems which attend the resolution and assignment of $^1$H-NMR signals from complex materials such as chiral porphyrins, the presence of a NMR probe in the system is needed. Of particular interest is the judicious introduction of fluorine into the chiral pickets. Thus, fluorine signals will be easier to detect than proton resonances and, because the fluorines are different for the four atropisomers, identification of each isomer will be facilited.

For the purpose of chiral recognition, it was decided that the α,β,α,β isomer offered the greater simplicity because the chiral pickets of this atropoisomer can provide a ruthenium porphyrin with two topologically identical faces. Confirmation that this was indeed the case came from the observation of the $^1$H-, $^{31}$P- and $^{19}$F-NMR spectra of the bis-trimethylphosphine ruthenium complex, prepared from addition of $PMe_3$ to the Ru(CO) complex Ru(CO)T(MTPA)PP **2** (T(MTPA)PP = 5,10,15,20-tetrakis[*o*-(2-methoxy-2-phenyl-3,3,3,trifluoropropanoylaminophenyl]porphyrin) [37]. The $PMe_3$ complex displayed only a singlet ($\delta = -68.9$ ppm) for the $CF_3$ groups of the four identical pickets, and a single $^{31}$P resonance ($\delta = -7.8$ ppm) for the phosphine.

In order to obtain diastereomeric ruthenium porphyrins, the red purple, six coordinate, low-spin complex Ru[P(CH$_3$)(C$_3$H$_7$)(C$_6$H$_5$)]$_2$T(MTPA)PP T(MTPA)PP = 5,10,15,20-tetrakis[*o*-(2-methoxy-2-phenyl-3,3,3,trifluoropropanoylaminophenyl]porphyrin) was first preparated from the ruthenium carbonyl precursor by treatment with eight equivalents of the racemic phosphine. As expected, signals due to magnetically equivalent fluorine atoms in the bis $PMe_3$ complex are split in the complex bearing the chiral phosphine. The signals must represent the *R*,*R*-diastereoisomer, the *R*,*S*-diastereoisomer (two signals) and the *S*,*S*-diastereoisomer. Although the integration of the NMR signals indicates only a weak preference for a particular configuration (*R*) (preference per binding site: $R/S = 1.5$), the absolute configuration of the chiral phosphine in the diastereoisomers was assigned after determination of the configuration of the free phosphine recovered at the end of the reaction (*S*) [38]. Once this NMR non-equivalence pattern was recognized, it was also possible to separate each diastereoisomer by thin layer chromatography.

In contrast, complexation of racemic benzyl methyl phenyl phosphine with the chiral ruthenium porphyrin leads to the compound Ru[P(CH$_3$)(C$_6$H$_5$CH$_2$)-(C$_6$H$_5$)]$_2$T(MTPA)PP with good chiral recognition. In this case, it was obtained as a 50/45/5 mixture of the three diastereoisomers (SS/RS/RR, respectively)(preference per binding site: $S/R = 2.6$) (Fig. 5). Moreover, an immediate precipitation with an excess of hexane, after phosphine addition, provided a SS diastereoisomer with high purity (> 95%) (preference per binding site: $S/R = 39$) as assessed by 300 MHz $^1$H- and $^{19}$F-NMR spectroscopy (Fig. 5) [37]. The excess of P(CH$_3$)(C$_6$H$_5$CH$_2$)(C$_6$H$_5$) was recovered with the *R* configuration [39]. The source of the high stereoselec-

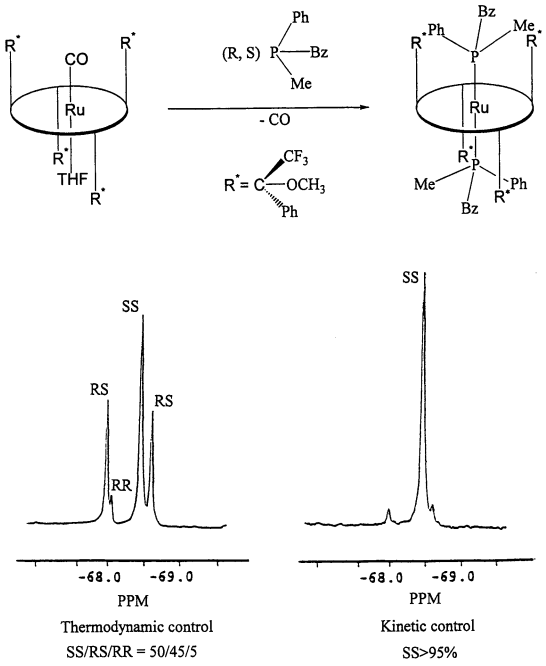



Fig. 5. $^{19}$F-NMR spectrum of Ru[P(CH$_3$)(C$_6$H$_5$CH$_2$)(C$_6$H$_5$)]$_2$T(MTPA)PP complex after 3 h reaction (thermodynamic control) and after immediate precipitation (kinetic control). Two differents $^{19}$F-NMR resonances for the chiral pickets are observed in Ru(P$_R$)(P$_S$) complex because the two porphyrin faces are different.

tivity observed in the latter reaction is attributed to steric effects. It is mainly the preferred mode of the initial binding of the chiral phosphine to the ruthenium porphyrin that determines the chiral recognition. Longer reaction times favor formation of the other isomers. For instance, addition of six equivalents of racemic P(CH$_3$)(C$_6$H$_5$CH$_2$)(C$_6$H$_5$) to the pure SS diasteroisomer in CH$_2$Cl$_2$ at 25 °C gave the above mixture (50/45/5) of the three diastereoisomers after 3 h.

## 2.2. Racemic alcohols

A different approach to *C*2-symmetric ruthenium porphyrins is to attach chiral centers directly in *meso* position, as reported by Marchon and coworkers (Fig. 6) [30]. These authors used (1R)-cis-caronaldehydic acid methyl ester and pyrrole as the starting reagents to construct directly a chiral porphyrin [40]. Starting from a racemic mixture, selective binding of the (R)-enantiomer of 2-butanol (or 2-octanol) to the chiral ruthenium complex was observed at −50 °C by $^1$H-NMR spectroscopy. The enantiomeric preference (R/S) was 2.2 for 2-octanol. The stereoselectivity was related to possible Van der Waals interaction, using the X-ray structure of the ruthenium carbonyl complex as a model. It should be noted that the complexation is under thermodynamic control since there is an equilibrium between free and complexed 2-octanol in solution.

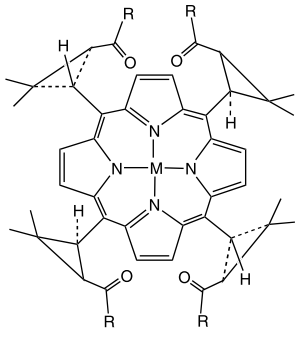



Fig. 6. Chiroporphyrin showing the $D_2$-symmetric α,β,α,β atropoisomer (adapted from [30]).

## 2.3. Racemic amino esters

Chiral recognition of amine complexation by metalloporphyrins is of current interest and is a challenging subject in biomimetic chemistry since this topic is relevant to the metabolism of amino acids [41,42]. Thus Gaudemer et al. were able to detect the magnetic non-equivalence of protons belonging to optically active amino esters as axial ligands of cobalt deuteroporphyrin due to the planar chirality of the natural porphyrin [43]. Good results have also been obtained with chiral zinc porphyrins [10,13,14,33,34] under thermodynamic control whereas absence of chiral recognition was reported with cobalt porphyrins [11].

For the purpose of chiral recognition of racemic amino esters with ruthenium porphyrins, it was also decided that the α,β,α,β isomer of the ruthenium complex **2** (Fig. 3) offered the greater simplicity because the chiral pickets of this atropisomer provide a ruthenium porphyrin with two topogically identical faces. Observation of the $^1$H and $^{19}$F spectra of the bis(acetonitrile) adduct: α,β,α,βRu(CH$_3$CN)$_2$ T(MTPA)PP T(MTPA = 5,10,15,20-tetrakis[*o*-(2-methoxy-2-phenyl-3,3,3,trifluoropropanoylaminophenyl]porphyrin) (Fig. 7), which is the precursor complex, confirms this

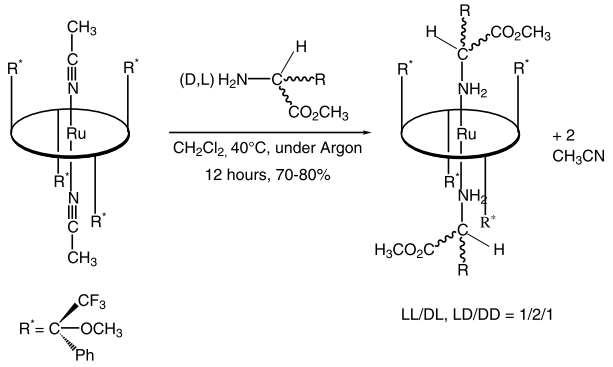



Fig. 7. Reaction of α,β,α,βRu(CH$_3$CN)$_2$T(MTPA)PP (MTPA = 5,10,15,20-tetrakis[*o*-(2-methoxy-2-phenyl-3,3,3,trifluoropropanoylaminophenyl]porphyrin) with racemic amino esters (R = CH$_3$, CH(CH$_3$)$_2$, CH$_2$Ph).

hypothesis [44,45]. The bis (acetonitrile) complex displayed only a singlet ($\delta = -68.9$ ppm) for the $CF_3$ groups of the four identical pickets. In order to obtain diastereomeric ruthenium porphyrins, the red purple, six coordinate, low-spin complex α,β,α,βRu[Val]$_2$T(MTPA)PP was first preparated from the bis (acetonitrile) precursor by treatment with ten equivalents of racemic valine methyl ester in $CH_2Cl_2$ at room temperature (r.t.) (76% yield) (Fig. 7). As expected, signals due to magnetically equivalent fluorine atoms in the bis (acetonitrile) complex are split in the complex bearing the chiral amino ester. The signals must represent the L,L-diastereoisomer, the L,D-diastereoisomer (two signals) and the D,D-diastereoisomer. Integration of the four resonances gave a ratio of 1:2:1 for the LL, DL and DD isomers, respectively (Fig. 7). Thus, these ratios indicate that the three diastereoisomers are formed in statistical proportions. Moreover, the exchange reaction between acetonitrile and amino ester was followed at an intermediate stage by $^{19}$F-NMR, and the spectra of the mixed-ligated acetonitrile-aminoester ruthenium complexes did not show any chiral recognition. By a procedure similar to that described for valine methyl ester, complexation of the racemic leucine methyl ester gave the bis(leucine) complex with no chiral recognition.

Thus, bis(amino ester) complexation on ruthenium porphyrins failed to differentiate one enantiomer from the other. This was unexpected because using the same ruthenium porphyrin excellent chiral recognition was observed with phosphine under kinetic control [37]. In contrast, complexation of amino ester *trans* to carbon monoxide illustrates how axial ligand dissociation can, on the basis of chiral carbonyl ruthenium porphyrins as hosts, lead to a large increase in the chiral recognition (Table 1) [46]. The investigation examined in detail the reactions of amino esters with chiral carbonyl ruthenium porphyrins (Fig. 8). The kinetics of axial ligand dissociation for the two enantiomers of valine were also determined by $^1$H-NMR spectroscopy using saturation transfer experiments [47]. The $^1$H-NMR study shows that the origin of the enantioselectivity in favor for the (R) valine (ca. 3:1) resides in the difference of the

Table 1
Chiral recognition amino esters with Complex **2**

| Amino acid methyl ester | e.e. (%) |
|---|---|
| Alanine | 18 |
| Valine | 45 |
| *tert*-Leucine | 52 |
| Tyosine | 8 |

Chiral recognition was observed for complexation of the ligand and the e.e. was determined by integrating the signals obtained in $^{19}$F-NMR spectrum of the mixed-ligated amino esters **2L** and **2D** complexes, e.e. = (**2L**−**2D**/**2L**+**2D**).

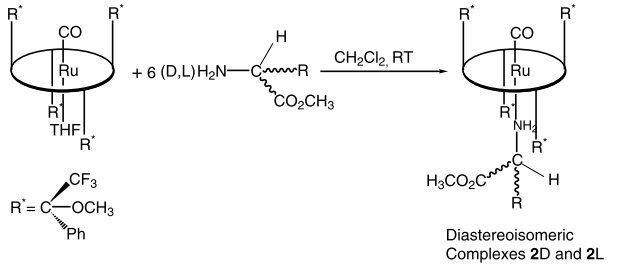



Fig. 8. Reaction of α,β,α,βRu(CO)T(MTPA)PP (MTPA = 5,10,15,20-tetrakis[*o*-(2-methoxy-2-phenyl-3,3,3,trifluoropropanoylaminophenyl]porphyrin) with racemic amino esters (R = $CH_3$, $CH(CH_3)_2$, $CH_2Ph$).

kinetics of axial ligand dissociation between the two enantiomers.

Saturation transfer NMR experiments can be used to measure first-order rate constants in reversible reactions [47]. Consider the simple chemical reaction:

$$A \rightleftarrows B$$

where A and B have unique identifiable magnetizations. If the species B is saturated, and the magnetization of A $M_A(t)$ is measured, one can write:

$$\frac{dM_A(t)}{dt} = \frac{M_0 - M_A(t)}{T_1(A)} - kM_A(t) \quad (1)$$

with $M_0 = M_A(0)$ and $T_1(A)$ is the spin lattice relaxation time of A. The constant $k$ represents the rate constant from A to B; in our case $k$ is the dissociation constant.

The amount of magnetization in A ($M_A$) after prolonged saturation of B is described by a steady state situation with ($dM_A(t)/dt = 0$), which leads to:

$$k = \frac{(\Delta M_A/M_0)}{(1 - \Delta M_A/M_0)T_1(A)} \quad (2)$$

with $\Delta M_A = M_0 - M_A$. In this method, the spin-lattice relaxation time of the non-saturated resonance is assumed to be known. Since this latter value is not directly accessible at 323 K, we used the method previously described by Mann [48]. Determination of the relaxation time ($\tau_{obs}(A)$) of the methyl group of the ligated amino ester by an inversion recovery experiment while saturating the corresponding signal of the free ligand allows the calculation of $k$ through the relation:

$$k = \frac{(\Delta M_A/M_0)}{\tau_{obs}(A)} \quad (3)$$

Table 2
Relaxation time $\tau_{obs}$ and dissociation rate constants $k$ of complexes **2L** and **2D**

| Complex | $\tau_{obs}$(s) | $k$($s^{-1}$) |
|---|---|---|
| **2L** | 0.446 | 0.15 |
| **2D** | 0.408 | 0.36 |

The $\tau_{obs}$(A) values and exchange rates derived from this method are given in Table 2.

These data are close to the constant found for the dissociation of *tert*-butylpyridine in a porphyrin ruthenium carbonyl complex (0.09 $s^{-1}$) [49]. More important, they also reveal that the dissociation rate constant for the (D) enantiomer of valine methyl ester is higher ($k_D/k_L = 2.4$) than the dissociation rate constant for the (L) enantiomer. This lead to the prediction of a chiral recognition for the (L) enantiomer with an enantiomeric excess of 41%, which is in accordance with the analysis of the $^{19}$F- and $^{1}$H-NMR spectra of the mixture of the two diastereoisomers recorded at 323 K, giving an enantiomeric excess of 45% (L/D = 2.6). Accordingly, the origin of the chiral recognition mainly resides in the kinetics of axial ligand dissociation. This result also explains the lack of selectivity in the formation of the complex α,β,α,βRu[Val]$_2$T(MTPA)PP [44], in which no ligand exchange occurs (Fig. 9). They also agree with the work of Marchon et al. on the chiral recognition of amine and amino alcohol with cobalt porphyrins [11,12].

In view of these results, we can also take advantage on the fact that assignments are known for both diastereoisomers and thus magnetization transfer spectroscopy can also be used in the presence of racemic ligand. The amount of magnetization transfer is similar for the two diastereoisomers **2L** and **2D**. Since we are now dealing with the racemic ligand, the amount of transfer for each isomer is proportional to the dissociation rate constant and to the concentration of this isomer [47]. In these reactions, the relative changes of the free ligand concentrations are neglected by assuming [D] = [L]. This simplification is valid in our system since the exchange reaction proceeds with a large excess of ligands. Consequently the ratio of saturation transfer to the two diastereoisomeric complexes (**2L** and **2D**) must reflect the ratio of their association rate constants. Thus, this experiment provides the quantitative control, and indirect evidence to show that ligand association rates are similar for the two valine enantiomers. Taken together these results indicate that the chiral recognition of amino ester by chiral ruthenium porphyrins is not

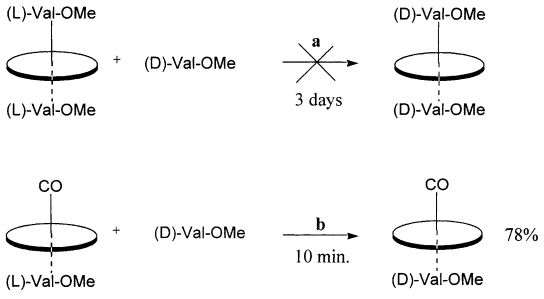



Fig. 9. (a) Reaction of α,β,α,βRu(L-Val-OMe)$_2$T(MTPA)PP with (D)-Val-OMe. (b) Reaction of α,β,α,βRu(CO)(L-Val-OMe)T(MTPA)PP with (D)-Val-OMe.

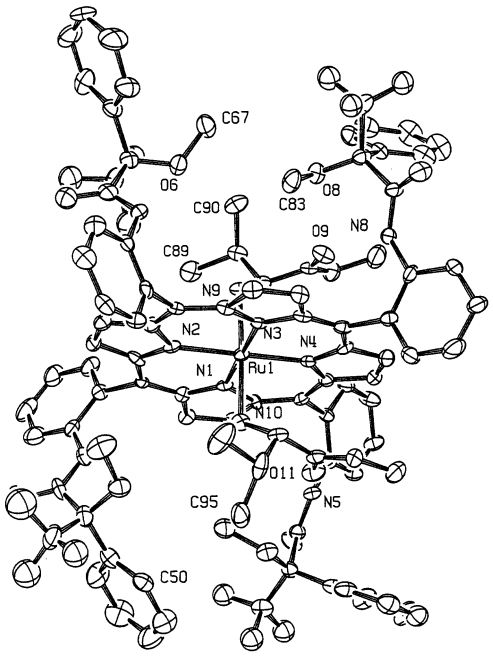



Fig. 10. A side view of the molecular structure of the α,α,β,βRuT(MTPA)PP(L-Val-OMe)$_2$ isomer illustrating possible hydrogen bonding between the carbonyl ester group and the NH amide group of the chiral picket (adapted from [44]).

governed by ligand association to the metal but by ligand dissociation. We believe this NMR method should have large applicability to other ligand exchange reactions although the magnetization transfer technique cannot be considered a general method, since ligand exchange must occur within a narrow range of rate constants (typically 0.1–20 $s^{-1}$).

The difference between the dissociation rate constants of the two enantiomers of valine methyl ester may be attributed to differences in the hydrogen bonding between the NH group of the chiral pickets and the carbonyl of the ester of the amino ester. Such interaction was indeed previously proposed by us in a chiral porphyrin ruthenium bis((L)-valine methyl ester) complex on the basis of its crystal structure (Fig. 10) [44]. Beside the coordination of the amino group, a hydrogen bond between the NH (of the chiral picket) and the ester carbonyl group, and the steric interaction of the amino ester alkyl chain with the porphyrin ring can be proposed from the X-ray characterization of this ruthenium complex (Fig. 10) [44]. As in Ogoshi's system, with Zn complexes [14], the main attractive interactions between the host and the guest molecules is coordination of the amino group to the metal. However, in ruthenium porphyrins, the metal–ligand bond is stronger than in Zn compounds and no ligand exchange is observed for the bis(amino ester) Ru complexes. This first interaction leads to conformational restrictions of the guest, as was previously reported for Co [50] and Zn [14] porphyrins, and shown in the solid state, by the X-ray structure.

Addition of the second interaction such as hydrogen bonding, would result in further conformational restriction which may occur on the Ru–$NH_2$ bond rotation. This second interaction seems to be essential for chiral recognition.

### 2.4. Racemic isocyanides

Chiral recognition of racemic isocyanides can be of major interest since optically active isocyanides are naturally occurring substances which have been found in fungi, bacteria, marine organisms and blue–green algae [51–53]. Although the possible role of metal–isocyanide interactions in the biosynthesis of naturally occurring isocyanides has never been reported to our knowledge, our interest in chiral recognition has prompted us to examine isocyanide complexation to optically active ruthenium porphyrins [54,55].

To be effective, chirality centers of metalloporphyrins need to be close to the coordination center. To built such a cavity, chiral entities should be either linked directly on the *meso* position of the ring [30] or linked to the *ortho* phenyl positions of the porphyrin ring. For the purpose of molecular recognition, it was decided that the latter possibility offered the greater synthetic simplicity. Thus we used 5,10,15,20 tetrakis(2,6-dihydroxyphenyl)porphyrin as a precursor. This is readily available from commercial 2,6-dimethoxybenzaldehyde, and was successfully used by Tsuchida [56] to synthesize porphyrins bearing eight non chiral groups, and by Gross to prepare a homochiral macrocycle [57]. The synthesis of the new porphyrin was achieved following the procedure recently reported by Collman [9]. The coupling of the porphyrin with commercially available D-α-β-isopropylideneglycerol-γ-tosylate in dimethylformamide in the presence of potassium carbonate leads to a new chiral porphyrin 5,10,15,20-tetrakis(*o*,*o*'-(R)-2,2-dimethyl-1,3-dioxolanne-4-oxymethylphenyl porphyrin T(DDO)PP in 26% yield (Fig. 11) [54,55]. As expected for a $D_4$ symmetry, all the pickets are equivalent by $^1$H-NMR spectroscopy, and thus only one singlet is observed for the pyrrole protons.

Addition of $Ru_3CO_{12}$ in *o*-dichlorobenzene at 170 °C yields the new compound **4** Ru(CO)T(DDO)PP in good yield (69%) without destruction of the porphyrin ring. In this case, the $^1$H-NMR spectrum displays two doublets instead of a singlet for the pyrrole protons due to a lower symmetry. Coordination of the carbon monoxide was confirmed by IR spectroscopy with a strong absorption at 1924 $cm^{-1}$ which is typical of porphyrin ruthenium carbonyl complexes [58].

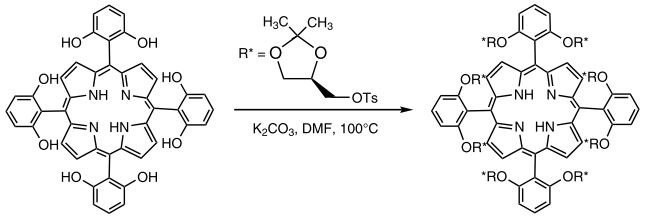



Fig. 11. Synthesis of the [5,10,15,20-tetrakis[*o*,*o*'((*S*)-2,2-dimethyl-1,3-dioxolane-4-oxymethyl)phenyl]porphyrin], T(DDO)PP (adapted from [54]).

$$\mathrm{Ru(CO)\underset{4}{T(DDO)PP} + 2CNCH(Me)(Ph) \rightarrow \underset{5}{Ru[CNCH(Me)(Ph)]_2T(DDO)PP} + CO} \quad (1')$$

Complexation of racemic 1-phenyl-ethyl-isocyanide [59] to the chiral ruthenium porphyrin **4** (Eq. (1')) leads to the compound **5** Ru[CNCH(Me)(Ph)]$_2$T(DDO)PP with chiral recognition. In a typical experiment, reaction of **4** with the isocyanide (8 equiv.) gave **5** as a 32: 51:17 mixture of the three diastereoisomers (RR/RS/SS, respectively). Integration of the NMR signals indicates the preference for a particular configuration (*R*) (preference per binding site: $R/S = 1.35$). A pure diastereoisomer **5**(RR) has been synthesized by a separate experiment, involving complexation of pure (*R*)-1-phenyl-ethyl-isocyanide to **4**, to assign the major diastereoisomer. The selectivity observed (15%) is under kinetic control, the isocyanide-ruthenium bond being quite strong (for example, no exchange was detected after addition of 8 equiv. of racemic isocyanide to **5**(R,R) in dichloromethane). The weak enantioselectivity by this chiral ruthenium porphyrin is at first surprising, given the high enantioselectivity observed ($>95\%$) for the chiral recognition in the complexation of racemic benzylmethylphenylphosphine to the ruthenium picket-fence porphyrins bearing chiral residues on both sides of the porphyrin plane [37]. Both chiral porphyrin complexes have the potential of discriminating chiral axial ligands. The source of the high stereoselectivity observed in the latter reaction is mainly attributed to steric effects. It is the preferred mode of the binding of the chiral phosphine to the ruthenium porphyrin that determines the chiral recognition. Thus the present result confirms our previous work showing that enantioselective complexation can be obtained under kinetic control. In the latter case, the observed stereoselectivity was, however, much higher because the chiral center was bound to the metal atom. The long distance Ru–isocyanide chiral center and the absence of any intramolecular hydrogen bond between the chiral picket and the chiral ligand may also explain this weak selectivity. It should be noted that negligible enantioselection was recently observed with amine adducts to chiral cobalt porphyrins [11].

The crystal structure of the ruthenium(II)bis[(*R*)-1-phenyl-ethyl-isocyanide] T((DDO)PP complex confirms the previous suggestion [55]. To our knowledge, this is the first structure of a (porphyrin)ruthenium bis(isocyanide) complex, as well as an original structure of a

metalloporphyrin bearing eight chiral pickets. The high values of the thermal parameters of the chiral groups attached to the phenyl suggest a large motion of these groups. A relatively large cavity results since the chiral groups extend far above the porphyrin mean plane. Contrary to our expectation, only weak steric effect are present and this may also explain the weak chiral recognition. Furthermore, 2D EXSY (exchange spectroscopy) NMR spectra showed the high mobility of the chiral pickets. A similar exchange was observed with the meta-phenyl protons which also indicate that aryl ring rotation was occurring on the NMR time scale at 293 K. This is quite unexpected because of the large size of the chiral substituents attached to the *ortho*-phenyl position, but such rotation has already been described with hydroxyl or alkyl groups [60,61].

Direct comparison of the selectivity observed between our previous work on chiral phosphine complexation (up to 95% of chiral recognition) [37] and chiral isocyanide complexation will need further studies. However, it should be emphasized that we previously proposed that the source of the high selectivity obtained with phosphines was due to steric interactions [37]. The same behavior could be expected with isocyanides, the weak chiral recognition being due to the long distance ($Ru–C{=}N–C^{*} = 1.99 + 1.17 + 1.46$ Å) between the asymmetric center of the ligand and the metal [the Ru–P bond distance in the (octaethylporphinato)ruthenium(II) bis(triphenylphosphine) complex is 2.43 Å]. This limits strong interactions between the macrocycle and the substrate, the top of the pickets being very flexible, as suggested by both the X-ray structure and the $^{1}$H-NMR spectra.

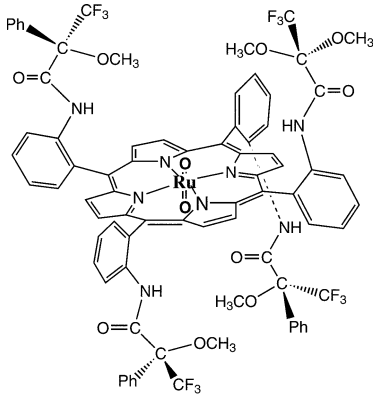
## 3. Stoichiometric oxidation

The study of the mechanism of oxygen atom transfer from an oxometalloporphyrin complex to a substrate is a challenging problem which is of current interest in the understanding of heme-containing oxygenase selectivity. Various metalloporphyrins have been investigated as models in the catalytic insertion of oxygen into organic substrates [4,8]. Especially, chiral metalloporphyrins have been used for asymmetric monooxygenations with good success [2,62,63]. In order to obtain additional information on the stereochemistry of oxygen atom transfer from metal to substrate, it is important to design a chiral metalloporphyrin system so that the nature of the reactive species can be clarified unambiguously. To achieve asymmetric syntheses, the chiral groups should also be inert to oxidation and to racemization. Another advantage of using ruthenium porphyrins as chiral oxygen atom transfer systems is that these metalloporphyrins could be models for the heme-containing monooxygenases due to the periodic relationship of ruthenium to iron.

High valent oxoruthenium complexes of porphyrins have received recent attention because of their possible relevance in the biological activation of oxygen by heme proteins [64]. By using a sterically encumbered porphyrin (tetramesitylporphyrin), Groves and Quinn isolated the first monomeric dioxoruthenium (VI) [20], whereas, more recently, dioxo ruthenium(VI) complexes with nonsterically encumbered porphyrins were prepared in good yields in coordinating solvents (methanol and ethanol) [65]. To design a metalloporphyrin, which satisfies the requirement above, we utilized an inert porphyrin framework, using Moshers reagent as chiral groups [66], and a ruthenium coordination site. Thus, in connection with our studies on molecular recognition by chiral ruthenium porphyrins, we prepared and characterized the first optically active *trans*-dioxoruthenium (VI) porphyrin complexe (Fig. 12) [67]. Later two other complexes were also prepared [68,69]. The stoichiometric reactions with these complexes will be described below.

### 3.1. Racemic phosphines [70]

The macrocycle of the first monomeric dioxoruthenium(VI) porphyrin was the tetramesitylporphyrin and the success was attributed to the steric hindrance imposed by the *ortho* methyl substituents [20]. In connection with our studies on chiral recognition with metalloporphyrins it seemed interesting to investigate the preparation of rutheniumdioxo porphyrins bearing optically active pickets. The steric hindrance imposed by these pickets may also prevent the dimerization. This method has been used successfully to stabilize dioxygen




α,β,α,β**Ru(O)$_2$ T(MTPA)PP 6**

Fig. 12. Ruthenium dioxo chiral picket-fence porphyrin bearing optically active α-methoxy-α(trifluoromethyl) phenylacetyl residues, α,β,α,βRu(O)$_2$T(MTPA)PP (adapted from [67]).

adducts of ruthenium(II) porphyrins [71]. Oxidation of α,β,α,βRu(CO)(THF)T(MTPA)PP **2** was carried out by introducing mCPBA in $CH_2Cl_2$ as previously reported by Groves [20]. Thus a new species α,β,α,βRu(O)$_2$T(MTPA)PP **6** (Fig. 12) with absorption at 422 and 516 nm was immediately formed. It was obtained in high yield and is stable in the solid state for hours at r.t. Very similar results were also obtained when the α,α,β,βRu(CO)(THF)T(MTPA)PP isomer was oxidized under the same conditions, yielding α,α,β,βRu(O)$_2$T(MTPA)PP. The success of the reaction with these two isomers is probably due to the presence of two chiral pickets on both sides of the porphyrin plane. The absence of hydrogen atom on to the pickets may also prevent any racemization.

In order to study the stereochemistry of oxygen atom transfer, benzylmethylphenyl phosphine was chosen as substrate since a quasi-complete chiral recognition was observed with this substrate during the complexation onto optically active complex **2** [37]. The percent of phosphine versus ruthenium complex concentration was varied from 4 to 10 in a series of different experiments. At the end of each experiment, the enantiomeric excess (e.e.) of the phosphine oxide was determined following the method previously reported by Kagan and coworkers [72]. These results are summarized in Table 3. The reaction with four equiv. of phosphine is described in Eq. (2′) and Fig. 13.

$$\mathrm{Ru(O)_2T(MTPA)PP}\ \mathbf{6} + 4\mathrm{PR_3} = \mathrm{Ru(PR_3)_2} + 2\mathrm{OPR_3} \quad (2')$$

Four important conclusions can be drawn from the data presented in Table 3:

i) Using an excess of phosphine, 2 equiv. of phosphine oxide were obtained, corresponding to oxygen atom transfer from Ru to the phosphorus atom.
ii) In each experiment, the phosphine oxide is optically active with the (−) *S* configuration [39]. The e.e. is maximal when 4 equiv. of phosphine are added to the solution.
iii) When **6** was treated with 4 equiv. of racemic phosphine, a 37.5:53.5:9 mixture of the three diastereoisomers (SS:RS::RR, respectively) was obtained. The preference per binding site was $S{:}R = 2.3$. In this reaction, the e.e. of the phosphine oxide is 41% ($S{:}R = 2.4$). The configurational correlation of oxidation of this phosphine is now well established and oxidation with retention of (+)-(*R*)-benzylmethylphenylphosphine gave (−)-(*S*)-benzylmethylphenylphosphine oxide [39,73]. Accordingly, these data are consistent with oxidation with complete retention of configuration, within experimental error. Oxidation of chiral phosphines with retention of configuration has been previously reported but with quite different systems [74,75].

Table 3
Data for the oxidation of racemic benzylmethylphenylphosphine with α,β,α,βRu(O)$_2$T(MTPA)PP **6**

| *n*[P(Me)(Ph)-(CH$_2$Ph)] | 0 = P(Me)(Ph)-(CH$_2$Ph)(−)S, e.e.(%) | Complexed P(Me)(Ph)(CH$_2$Ph)-(−)S, e.e. (%) |
|---|---|---|
| 4 | 41 | 40 |
| 6 | 25 | 34.5 |
| 10 | 12 | 47.3 |

*n*[P(Me)(Ph)(CH$_2$Ph)] + **6** → Ru[P(Me)(Ph)(CH$_2$Ph)]$_2$T(MTPA)PP + 2[0 = P(Me)(Ph)(CH$_2$Ph)] + (*n* − 4)[P(Me)(Ph)(CH$_2$Ph)].

Complexation of racemic benzylmethylphenylphosphine to the α,β,α,β isomer leads to the formation of one of three possible product diastereoisomers with a high degree of selectivity (complexation of the (*S*) phosphine) (vide supra). This result was obtained under kinetic control whereas thermodynamic control yielded less favorable recognition. Surprisingly, the oxidation reaction gave the inverted selectivity since it is now the (*R*) enantiomer, which was preferably oxidized.

In order to explain the inverted selectivity and the decrease of the selectivity with increasing amount of the phosphine (Table 3), we proposed the mechanism summarized in Fig. 13. This mechanism is discussed with the first assumption of oxene transfer without chiral recognition. The reactivity of $Ru^{VI}(O)_2$ is such that it can attack either R or S isomer of the phosphine to form $Ru^{IV}(O)$ (step a). Thus the initial product of the reaction contains racemic phosphine oxide. Unlike the first step, we propose a complete stereoselectivity in the complexation of chiral benzylmethylphenylphosphine to the $Ru^{IV}(O)$ intermediate. This will lead to one of the two possible diastereoisomers: $Ru^{IV}(O)(P_S)$ (step b). It is worth noting that such stereoselectivity was previously observed during the complexation of the phosphine on to Ru [37]. The behavior of the $Ru^{IV}(O)$ complex, reported in step c, parallels that of its $Ru^{IV}(O)$ congeners [21,76], which also are capable of oxygen-atom transfer to oxidize triphenylphosphine to triphenylphosphine oxide. However, the product formed in the second oxidation, i.e. phosphine oxide, is now optically active since the substrate, i.e. the phosphine, is also optically active. We also suppose in step c a transfer without chiral recognition. Finally complexation of the two equivalents of the remaining phosphine will occur in step d. In this particular case, a simple calculation will give (*S*) phosphine oxide with 25% e.e. The experimental result gives (*S*) phosphine oxide with 41% e.e. This is evidence for an oxygen-atom transfer with chiral recognition under kinetic resolution. This

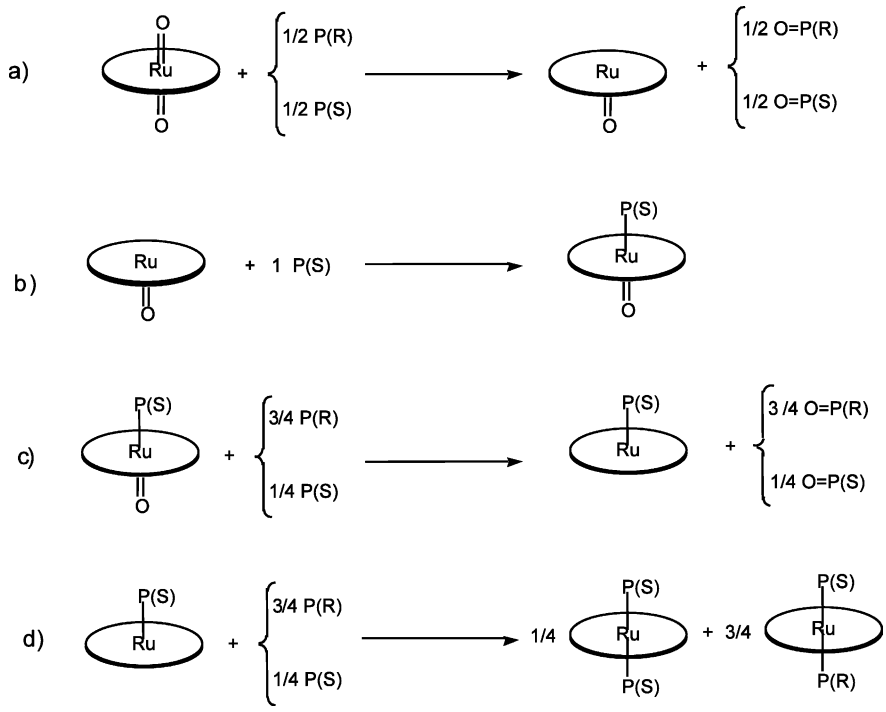



Fig. 13. Mechanism of the oxygen atom transfer from ruthenium dioxo chiral picket-fence porphyrin to benzylmethylphenylphosphine (adapted from [70]).

interpretation is also in agreement with a decrease in selectivity when a large excess of phosphine is used (10 equiv.). In this case, the contribution of chiral recognition in step b [the (*S*) phosphine complexation to the $Ru^{IV}(O)$ intermediate] is very weak (e.e.: 6.25%). The experimental result gives (*S*) phosphine oxide with 12% e.e. A weak chiral recognition during the oxygen-atom transfer is also clearly operating here, even with addition of a large excess of the racemic phosphine. The good correlation between the preference of the binding site to the ruthenium and the e.e. of the phosphine oxide also implies an oxygen atom transfer, which proceeds with retention of phosphorus configuration.

### 3.2. Amino esters

Considerable interest has been directed to the metabolism of naturally occurring amines and xenobiotics [77] because of the biological importance of these reactions [78,42]. During the oxidative deamination of amino acids, imino acids are often postulated as intermediates but rarely isolated because of their instability in solution [79]. Thus stable complexes can provide models for key intermediates and reaction steps. However multidentate imino acid ligands, in which chelation to a metal ion through oxygen atom is essential, have received the greatest attention [80–82]. Complexes of simple monodentate imines in low-oxidation states are still rare and the scope of their preparation is rather limited [83–87]. The present investigation examines in detail the reactions of amino esters with chiral high valent ruthenium porphyrins.

The source of the stereoselectivity observed in the phosphine oxidation reaction was attributed mainly to the preferred mode of the initial binding of the chiral phosphine to a possible oxoruthenium(IV) porphyrin intermediate. Thus, with phosphorus derivatives, the oxygen transfer seems weakly selective but the stereoselectivity of the complexation (phosphine *S*) is almost complete under kinetic control. In contrast, the results reported herein with amino esters, show that complexation does not give any chiral recognition under kinetic control but only under thermodynamic control and that oxidation of racemic valine ester by dioxoruthenium porphyrins can be quite selective [44,45,88].

Oxidation of racemic amino esters with chiral porphyrin dioxo ruthenium α,β,α,βRu(O)$_2$T(MTPA)PP (**6**) (Fig. 14) results in the formation of mixed ligated

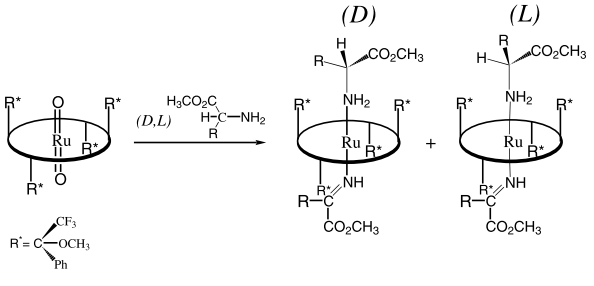



Fig. 14. Oxidation of racemic amino esters with chiral porphyrin dioxo ruthenium α,β,α,βRu(O)$_2$T(MTPA)PP (adapted from [88]).

Table 4
Results for the oxidation of racemic amino esters with α,β,α,βRu(O)$_2$T(MTPA)PP (**6**)

| Amino esters | *L* (%)[a] | *D* (%) | e.e. |
|---|---|---|---|
| Alanine | 55 | 45 | 10 |
| Valine | 83 | 17 | 66 |
| Leucine | 63 | 37 | 26 |
| Phenylalanine | 50 | 50 | 0 |

[a] Imino–amino ruthenium complex (Fig. 14).

(amino ester)(imino ester) complexes α,β,α,βRu[(R)($CO_2$Me)CH–$NH_2$][(R)($CO_2$Me) C=NH] T(MTPA)PP (Table 4) [88]. For the purpose of chiral recognition, oxidation of various amino acid methyl esters (10 equiv.) were tested yielding two isomers [44]. In this case, the $^{19}$F spectrum of a mixture of the two isomers exhibited four magnetically inequivalent fluorine groups. By its $C_2$ symmetry, the $^{19}$F spectrum of each isomer has two types of fluorine groups. To obtain the stereochemical identity of each isomer, the same reaction was carried out with pure D or L-amino acid ester enantiomers. The data are listed in Table 4. First, it clearly appears that the stereoselectivity favors the formation of the L-isomer. Second, the highest value of the e.e. is obtained with valine methyl ester (66%). Third, the reaction is quite sensitive to the nature of the amino acid ester: no asymmetric induction which favored the formation of one of the isomers was observed with the phenylalanine reaction. It should be also emphasized that the two isomers obtained in the ratio 83/17 with valine methyl ester can be separated by chromatography. Moreover, exchange of pure D-valine methyl ester isomer complex with pure L-valine methyl ester in dichloromethane (15 equiv.) leads slowly to the formation of the other isomer in a nearly quantitative yield. Thus the Ru–ketimine bond is stronger than the Ru-amino ester bond [89].

We have previously discussed the mechanism of the formation of imino ester complexes [45]. It was suggested that the dehydrogenation of the ligand amino ester in the corresponding imino ester may occurs via an intramolecular redox reaction from a ruthenium(IV) bis(amino ester) intermediate. Several groups have proposed a similar mechanism for the dehydrogenation of chelated amino ruthenium complexes [80,90–92]. Our electrochemical study is also consistent with the possible role of bis-amino ester Ru(IV) complex in the mechanism of these dehydrogenation reactions (Fig. 15). Thus it should be noted that the formation of imino ester/aminoester Ru(II) porphyrin complexes can be achieved either by electrochemical oxidation of amino ester complexes or by chemical oxidation of aminoesters with high valent dioxo ruthenium complex. Since (i) the complexity of such reactions has been very recently demonstrated with ruthenium hexamine complexes [93]

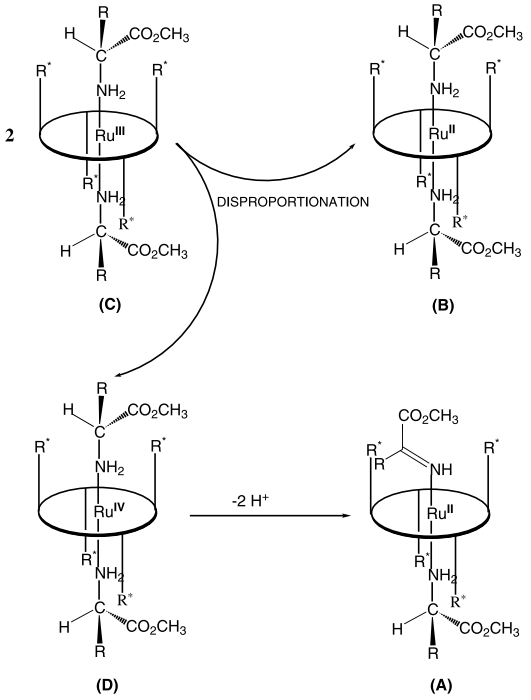



Fig. 15. Mechanism of formation of chiral porphyrin ruthenium (imino ester)(amino ester) complexes (adapted from [88]).

and (ii) metal chelation probably has a dramatic effect on the reactivity of amino esters toward oxidation, the present available results do not allow us to clarify the stereochemical aspect of the oxidation and further details of the reaction mechanism remain to be elucidated. Nevertheless, the diastereoselectivity observed in the formation of the imino complex may principally occur in this dehydrogenation since the amino ester complexation appears not to be stereoselective (vide supra).

### 3.3. Alkenes

The main difficulty in enantioselective epoxidation of unfunctionalized olefins is to introduce nonbonding interactions between the substrate and the oxidizing species to get high enantiomeric excess. Major improvements were provided by use of chiral Mn salen complexes [94–96]. Since isolation of highly reactive and chiral oxoruthenium porphyrin complexes was found possible [67,69], stoichiometric enantioselective alkene oxidations were studied to provide some new information on the catalytic system [97–99]. This subject has been recently reviewed by Groves et al. [100]. A chiral *trans*-dioxo(D4-porphyrinato)ruthenium(VI) complex has been characterized by X-ray crystal analysis (Fig. 16) [69]. The kinetics of the epoxidation of para-substitued styrenes have also been studied. The results suggest the formation of a radical intermediate for the alkene epoxidation. Enantioselectivities of the stoichio-

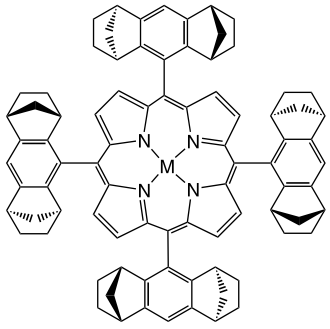



Fig. 16. Dioxoruthenium(VI) complex containing a $D_4$-porphyrinato ligand 5,10,15,20-tetrakis-[(1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracen-9-yl] porphyrin (adapted from [69]).

metric and catalytic alkene epoxidation showed good correlation (vide infra) and thus the mechanism of these reactions could involve an oxoruthenium(IV) complex as a commun intermediate [69]. Such a system was previously described by Groves and Quinn with achiral ruthenium porphyrins [22]. Enantioselective hydroxylations of benzylic C–H bonds by *D*4-symmetrical chiral oxoruthenium porphyrins were also reported by Che's group. A benzylic radical intermediate was proposed in the mechanism of this reaction [98].

## 4. Asymmetric catalysis

Recently, there is a renewal of interest in reactions catalyzed by porphyrin ruthenium(II) complexes, simultaneously with the development of new chiral ruthenium porphyrins [37,57,97,101]. These reactions focus mainly on asymmetric epoxidation of olefins [68,102], although in some cases a gradual inactivation of the catalytic system is observed due to the possible formation of inactive carbonyl complexes when *trans*-dioxo(tetramesitylporphyrinato) ruthenium(VI) is used as the catalyst [103]. In contrast, asymmetric cyclopropanation of alkenes [104–107] and diazo compound insertion into S–H and N–H bonds are still scarce [108,109]. As part of our continuing effort to promote ruthenium porphyrin chemistry, we review now the use of a homochiral porphyrin complex as catalyst for asymmetric cyclopropanation of styrene derivatives, as well as for diazo derivative insertion into S–H bonds. Asymmetric catalytic oxidations will be first described.

### 4.1. Oxidation

The first example of epoxidation catalysis by a homochiral ruthenium porphyrin was reported in 1996 by Gross et al. [68]. A remarkable effect of the solvent on the enantioselective styrene epoxidation was detected. Utilization of benzene (e.e. = 44%) instead of dichloromethane (e.e. = 4%) gave a major improvement of the enantioselectivity. Other variables such as the nature of the oxidant and the metal (Fe, Ru and Mn) were also reported by the same group [110]. Of the three metal complexes of the same chiral porphyrin (Fig. 17), much better results were obtained with iron and ruthenium than with manganese. It should be emphasized that stoichiometric and catalytic reactions can yield different e.e. with the same chiral porphyrin when the oxidant is 2,6-dichloropyridine-*N*-oxide. A possible double role of the oxidant: axial ligand and oxygen transfer, may explain these differences (Fig. 18) [6]. In contrast, with oxygen or iodosylbenzene as oxidants, stoichiometric and catalytic reactions yielded to similar enantiomeric excess [6,68,97].

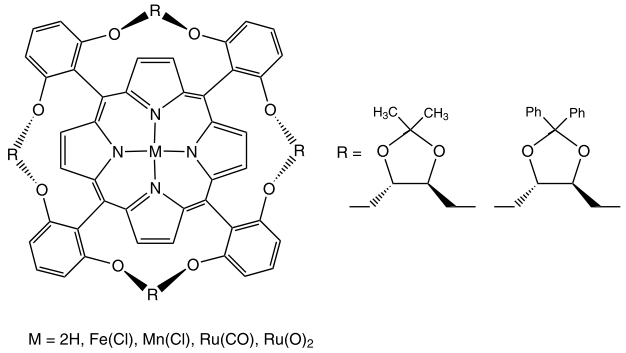



Fig. 17. Metal complexes (Fe, Ru and Mn) of a homochiral porphyrin (adapted from [110]).

Berkessel and Frauenkron [102] also decribed highly efficient catalytic system for the asymmetric epoxidation of unfunctionalized olefins with a different chiral porphyrin, previously reported by Halterman and Jan (Fig. 16) [101]. When 2,6-dichloropyridine was used as terminal oxidant, the epoxide of 1,2-dihydronaphtalene

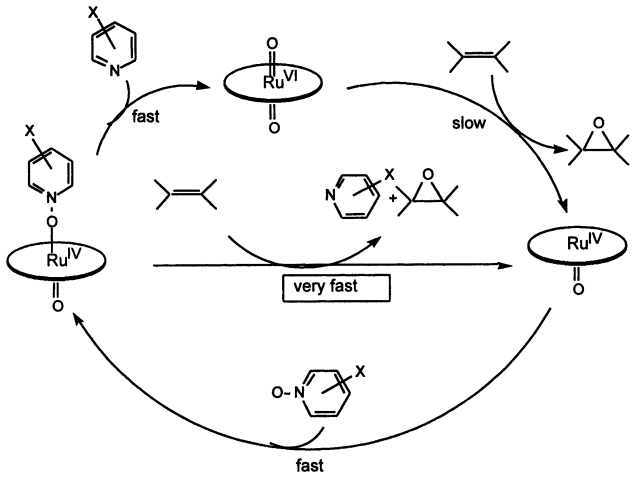



Fig. 18. Catalytic cycle for the asymmetric epoxidation of unfunctionalized olefins with chiral porphyrin ruthenium dioxo complexes using 2,6-dichloropyridine-*N*-oxide as oxidant (adapted from [6]).

was obtained with enantioselectivities up to 77% and with good yield (90%) [102].

The first example of aerobic enantioselective epoxidation of alkenes that does not use a coreductant was reported by Che et al. [69]. Aerobic enantioselective epoxidation of prochiral alkenes with enantioselectivity up to 73% were obtained at an oxygen pressure of 8 atm. Enantioselective oxidation of styrene with iodosyl benzene catalyzed by a chiral ruthenium porphyrin was also described by the same group. In contrast to previous work [110], no solvent dependance on enantioselectivity when changing the solvent from dichloromethane to benzene [97] was observed. The same *D*4-symmetric chiral dioxoruthenium(VI) porphyrin was also able to effect catalytic enantioselective hydroxylation of benzylic C–H bonds to give optically active aryl alcohols with enantiomeric excess up to 76%. A large primary kinetic effect was found for the catalytic reaction($kH/kD = 11.2$, 298 K). Surprisingly, a low kinetic effect was observed for the resolution of racemic 1-phenylethanol [97].

### 4.2. Cyclopropanation

Enantioselective carbene transfer to olefins is an important area of asymmetric synthesis [111–114]. Recent growth in the area of transition metal porphyrin chemistry has, in part, been driven by the increased interest associated with metal-catalyzed cyclopropanation. Examples involving rhodium [115–120], osmium [121], and iron [122] porphyrins as catalysts have been previously reported. Rhodium catalysts produce synthetically useful excesses of *cis* cyclopropyl esters using ethyl diazoacetate as the carbene source whereas under the same conditions, osmium and iron catalysts mainly provide the *trans* product. Catalytic production of olefins from ethyl diazoacetate has been recently reported with osmium [123] and ruthenium [124] porphyrins. Despite the periodic relationship of ruthenium to iron and osmium and the syntheses of different carbene complexes of ruthenium porphyrins, elegantly developed by Collman et al. [125–127] it is only very recently that cyclopropanation and ethyl diazoacetate insertion into heteroatom bond reactions were observed using ruthenium porphyrins as catalysts (Fig. 19a) [104]. It must be underscored, however, that the coupling products, diethyl maleate and fumarate, were obtained from the catalytic coupling of ethyl diazoacetate in the presence of Ru(CO)(TMP) (Fig. 19b) [124].

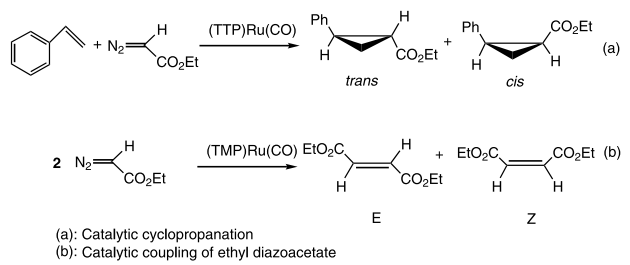



Fig. 19. Reaction of styrene with ethyl diazoacetate using ruthenium porphyrins as catalysts.

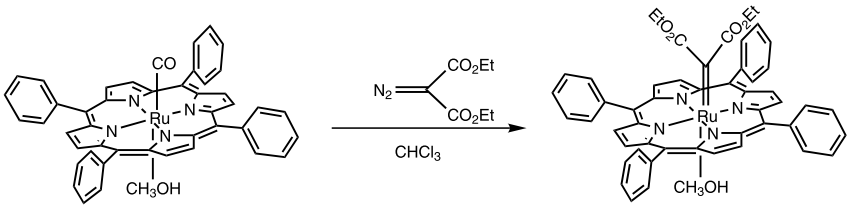
The reaction of styrene with ethyl diazoacetate in the presence of the dioxoruthenium(VI) picket-fence complex bearing optically active α-methoxy-α(trifluoroluoromethyl)phenylacetyl residues on both sides of the porphyrin plane (α,β,α,β isomer) gave a mixture (*trans*/*cis*: 9/1) of optically active cyclopropane derivatives, e.g. *trans*- and *cis*-2-phenylcyclopropanecarboxylic esters with 14 and 34% e.e., respectively [104]. Enantiomeric excesses for cyclopropyl esters were determined using the chiral shift reagent *tris*[3-(heptafluoropropyl)hydroxymethylene)-(+)-camphorato] europium(III). For the trans product, measurement of the optical rotation allowed identification of the absolute configuration as (+)-(1*S*, 2*S*) [128]. The catalytic cyclopropanations of alkenes with ethyl diazoacetate (EDA) were run in neat olefin, at r.t. under argon atmosphere, with a substrate:EDA:catalyst ratio of 500:100:1.

A second chiral complex containing four chiral threitol units (P*)Ru(CO) (Fig. 17) [68] also efficiently catalyzed the cyclopropanation of styrene [107,129], with a diastereoisomeric excess of 60% in favor of the *trans* isomer, and an e.e. of 46% for the *trans* isomer. To get some information on the stereochemistry of the reaction, we used a wide range of *para*-substituted styrene derivatives, the results being reported in Table 5. We found that the reaction time was longer (12 h) than the reaction with non chiral and less bulky porphyrin ruthenium complexes (5 h) [104], because of the congestion of the cavity created by the chiral units. In all cases, the chemical yields are good (from 85 to 95%), and e.e. of the *trans* cyclopropyl ester are very similar (from 46 to 52%). Measurement of the optical

Table 5
Asymmetric cyclopropanation of styrene derivatives with ethyl diazoacetate by the chiral complex (P*)Ru(CO) (Fig. 17)

| Substrate | Yield(%)[a] | *trans:cis*[b] | e.e. *trans* (%)[c,d] |
|---|---|---|---|
| Styrene | 85 | 4.0:1 | 46 |
| 4-Methoxystyrene | > 95 | 6.1:1 | 47 |
| 4-Methylstyrene | 92 | 9.9:1 | 46 |
| 4-Chlorostyrene | 93 | 8.6:1 | 52 |
| 4-Bromostyrene | 93 | 7.1:1 | 45 |
| 4-Fluorostyrene | 92 | 11.0:1 | 50 |

Reaction condition: catalyst, 0.0044 mmol; olefin, 2.200 mmol; ethyl diazoacetate, 0.440 mmol; addition time, 8 h; r.t.
[a] Based on ethyl diazoacetate.
[b] Determined by GC and NMR.
[c] Determined using the chiral shift reagent *tris*[3-(heptafluoropropyl)hydroxymethylene)-(+)-camphorato]europium(III).
[d] Measurement of the optical rotation allowed identification of the absolute configuration as (−)(1*R*,2*R*).




7

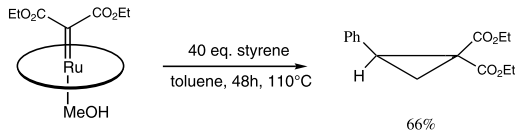
Fig. 20. Synthesis of (5, 10, 15, 20-tetraphenylporphyrin) ruthenium (diethoxycarbonyl) carbene complex (adapted from [129]).

rotation allowed identification of the absolute configuration as (−)-(1*R*,2*R*) [128]. In contrast, e.e. of the *cis* isomer is very low (10%).

Efforts have also been made to ascertain the active species in these ruthenium-catalyzed cyclopropanation reactions. Thus the synthesis, crystal structure and reactivity of air stable (5,10,15,20-tetraphenylporphyrin) ruthenium (diethoxycarbonyl)carbene complex **7** was reported (Fig. 20) [129]. To our knowledge, this is the first porphyrin ruthenium(II) carbene complex which has been characterized by single-crystal X-ray diffraction analysis.

As indicated by the structure, the carbene complex exists as six-coordinate compound, with a methanol molecule as axial ligand. As expected for such a complex, the porphyrin ligand is nearly planar. However, the ruthenium atom is slightly out of the mean porphyrin plane, 0.12 Å toward the carbene ligand. A similar situation has previously been observed with a porphyrin osmium(II) carbene complex [130] and with a porphyrin rhodium(III) carbene complex [131]. The Ru–N distances of 2.045(5)–2.048(6) Å all fall within the range previously reported for diamagnetic (TPP)Ru(CO)[EtOH] [132]. The geometry of the coordination sphere is close to an ideal octahedral geometry.

The Ru–C distance of 1.829(9) Å is slightly shorter than ruthenium-carbon double bonds reported for other molecular structures of ruthenium carbene complexes. For example, the ruthenium–carbon distances in (pybox)$Ru(Cl)_2$[:$C(CO_2Me)_2$] [113] and $Ru(Cl)_2(PPh_3)_2$-[:CH–CH=$CPh_2$] [133] are 1.880(7) and 1.887(7) Å, respectively. For comparison, the M=C distances of the rare porphyrin metal carbene complexes which have been characterized by single-crystal X-ray diffraction analysis are 1.83(3) Å in (TPP)Fe[:$C(Cl)_2$][$H_2O$] [134], 1.865(5) Å in (TTP)Os[:$C(C_6H_4$-*p*-$CH_3)_2$][THF] [130], 1.79(2) Å in (TTP)Os[:C(H)($SiMe_3$)][THF] [130], and 2.030(11) Å in (TPP)Rh($PhCH_2NC$) [:$C(NHCH_2Ph)_2$]-$PF_6$ [131].




66%

Fig. 21. Stoichiometric reaction of the tetraphenylporphyrin ruthenium (diethoxycarbonyl) carbene complex with styrene.

The postulate of metallo-carbenes as possible active intermediates in cyclopropanation reactions [135] together with our recent results in catalysis [104,108] prompted us to investigate the reactivity of **7** towards ethyl diazoacetate (EDA) and styrene.

Firstly, we examined the possibility of the stoichiometric carbene transfer reaction from **7** to styrene although the complex is quite stable (Fig. 21). This transfer was successful upon addition of a 40-fold excess of olefin to **7** in refluxing toluene, yielding the corresponding cyclopropane [136] in 66% yield. Analysis of the ruthenium complex mixture at the end of the reaction showed the presence (TPP)Ru(CO) (IR: $\nu = 1954\ cm^{-1}$, 15%) together with unidentified products. Such decarbonylation of acid derivatives by metalloporphyrin complexes is not unusual and has already been observed [137,138].

Then we investigated the potential of **7** in the catalyzed formation of olefins and cyclopropanation of styrene by EDA. When a dichloromethane solution of **7** is treated with excess ethyl diazoacetate, rapid evolution of gas is observed and high yield (> 95%) of diethyl maleate and fumarate are obtained in the ratio 13.8/1 (Fig. 22)(a). During this catalytic reaction, **7** is partially transformed (ca. 10%) into a new complex **8**. Its $^1$H-NMR spectrum displays a singlet at 13.03 ppm, which allowed us to characterize this product as (TPP)Ru[:$C(CO_2Et)$(H)] by comparison with an authentic sample prepared from (TPP)Ru(CO)[EtOH] and $N_2$=$CH(CO_2Et)$. However, in contrast to the catalytic formation of olefins with porphyrin osmium carbene

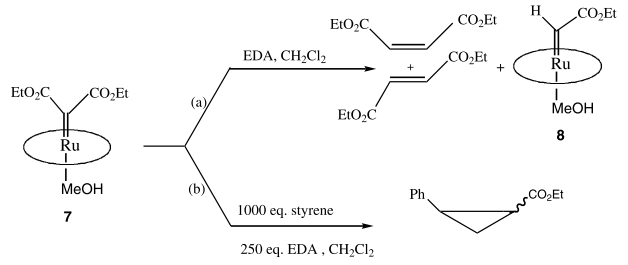



Fig. 22. Catalytic reaction of the tetraphenylporphyrin ruthenium (diethoxycarbonyl) carbene complex: (a) with ethyl diazoacetate; (b) with styrene.

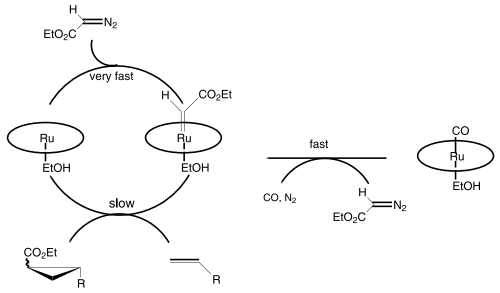



Fig. 23. Catalytic cycle for the cyclopropanation of alkenes with porphyrin ruthenium complexes (adapted from [109]).

complexes [123], where a bis-carbene derivative was proposed to be the intermediate, no evidence of such species could be obtained with **7** as catalyst. The catalytic reaction of styrene and EDA was also carried out to give the corresponding ethyl 2-phenyl cyclopropane carboxylate in 85% yield (Fig. 22)(b), with *trans*/*cis* selectivity (14.0/1) similar to that observed when (TPP)Ru(CO)[EtOH] was used as the catalyst [104]. The final products are essentially the original carbene complex and traces of **7**. Consequently, all these catalytic reactions seem to involve a commun intermediate which may be the bare 14-electron ruthenium porphyrin complex [(TPP)Ru] or a 16-electron ruthenium porphrin [(TPP)RuL], L being a solvent molecule (Fig. 23). However, much work is needed to address the mechanistic issues of these ruthenium-catalyzed processes since it is known that vacuum pyrolysis of Ru(porphyrin)$(pyr)_2$ yields the metal–metal bonded species $[Ru(TPP)]_2$ with tetraphenylporphyrin [27,125] whereas the same method yields the bare [(TMP)Ru] with tetramesitylporphyrin [139].

Berkessel et al. [106] and Che et al. [140,141], also reported independently that the ruthenium complex of the same chiral porphyrin, previously reported by Halterman, can be used to catalyze the cyclopropanation of styrene. This reaction is particularly interesting since the e.e. are quite high (90%). Surprisingly, changing the solvent from 1,2-dichloroethane to benzene resulted in an inversion of the absolute configuration of the major enantiomer for the *cis*-cyclopropane and no change for the *trans* cyclopropane [106].

More recently, Gross et al. described asymmetric cyclopropanation of styrene by an enantiopure carbenoid under catalysis by ruthenium porphyrins [107]. A comparison with the classical approach, chiral porphyrin and non chiral carbenoid provides significant insight into the mechanistic aspects of these reactions. Using different metal porphyrin complexes (Ru, Fe, Os and Rh), the authors clearly demonstrate that the absolute configurations of the major diastereomer are related not to the metal but rather to a porphyrin effect.

### 4.3. Carbene insertion

The insertion of diazo compounds into heteroatom-H bonds remains of considerable importance in organic synthesis [142]. After the pioneering work of Yates on the copper-catalyzed decomposition of diazoketones in the presence of thiophenol and aniline [143], little subsequent work was done in this area until the Paulissen group discovered the high catalytic activity of rhodium(II) acetate [144]. While the intramolecular version of the insertion has found the widest use in synthesis, intermolecular reactions are still interesting, particularly as a possible way to optically active derivatives. Only a few studies have been done in this area and with low enantioselectivities.

The complex Ru(II)(TMP)CO [145], in catalytic amounts, reacts with ethyl diazoacetate in the presence of thiols to give α-thio ethyl esters [108]. Both aromatic and aliphatic thiols can be used as substrates. The insertion process is chemoselective since dithiothreitol reacts to give the S–H insertion product without any trace of the ether compound.

Extension of the insertion process to α-methyl-α-diazo esters is also possible; treatment of 2-diazo-propionic acid ethyl ester [146] with thiophenol, in presence of the ruthenium porphyrin catalyst at r.t., afforded the corresponding α-thio ethyl ester in moderate yield (71%). This insertion reaction can be developed to investigate further the possibility of diastereoselectivity in the S–H insertion of ruthenium carbenoids (Fig. 24), using chiral ruthenium porphyrin complexes, prepared as described previously by Gross et al. (Fig. 17) [68]. The results are summarized in Table 6.

As previously, the crowded porphyrin slows down the reaction with bulky substrates. For example, only a 16% yield is obtained with 2-methyl-2-propanethiol. In contrast, yields are very good with thiophenols, but e.e.s are still low and in the range of those reported by Brünner et al. [147] with rhodium and copper catalysts.

Metalloporphyrin-catalyzed amidation of saturated C–H bonds are still rare [148–152]. However, the enantioselective amidation of a saturated C–H bond by [*N*-(*p*-toluenesulfonyl)-imino]phenyliodinane (PhINTS), using chiral ruthenium porphyrin as catalysts, has been recently reported by Che and coworkers [153]. Enantiomeric excesses in the range 30–58% were obtained in this elegant work using the ruthenium complex of the chiral porphyrin previously reported by

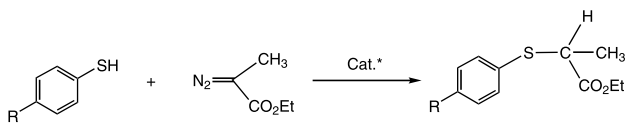



Fig. 24. Asymmetric insertion of 2-diazopropionic ethyl ester S–H bond with a homochiral porphyrin ruthenium complex used as catalyst (adapted from [105]).

Table 6
Asymmetric insertion of 2-Diazopropionicacid ethyl ester into S–H bonds by the chiral complex (P*)Ru(CO) (Fig. 24)

| R | Yield (%)[a] | e.e. (%)[b] |
|---|---|---|
| H | > 95 | 6[c] |
| Cl | 86 | 8 |
| $OCH_3$ | 76 | < 5 |

Reaction conditions: catalyst, 0.0030 mmol; thiol, 0.900 mmol; ethyl diazoacetate, 0.300 mmol; toluene, 250 ml; addition time, 5 h; r.t.
[a] Based on diazo compound.
[b] Determined using the chiral shift reagent *tris*[3-(heptafluoropropyl)hydroxymethylene)-(+)-camphorato]europium(III).
[c] Measurement of the optical rotation allowed identification of the absolute configuration as (+)-(R).

Halterman's method [101]. The authors also succeeded to prepare the first complex of a chiral imidometalloporphyrin, which has also been used in stoichiometric reactions. The e.e.s obtained for the stoichiometric and the catalytic reactions were rather similar, suggesting that the chiral imido ruthenium complex may function as the active species in these reactions [153].

Using the same reagent (PhINTS), catalytic asymmetric aziridination by a chiral ruthenium complex has also been reported quite recently [154]. Styrene aziridination by [*N*-(*p*-toluenesulfonyl)-imino]phenyliodinane (PhINTS) was particularly inefficient with a chemical yield of 4% and 20% e.e. However, it should be emphasized that, until now, there are very few asymmetric aziridination with metalloporphyrins [155].

## 5. Conclusion

The work described in this review confirms the observation that chiral ruthenium porphyrins are particularly well adapted as asymmetric devices both for chiral recognition and asymmetric syntheses. Our efforts in these area will continue as we seek to design highly convergent strategies for the synthesis of structure controlled novel asymmetric catalysts, using ruthenium porphyrins as building block.

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