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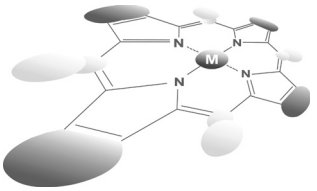

Non-peripherally alkyl substituted ruthenium phthalocyanines as catalysts in the epoxidation of alkenes

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ABSTRACT: Non-peripherally alkyl substituted ruthenium phthalocyanines were demonstrated to be highly active epoxidation catalysts. It is compatible with pyridine *N*-oxides, and especially 2,6-dichloropyridine *N*-oxide. The catalytic activity towards a variety of alkenes was comparable to that published for other catalytic systems, but superior in the cases of 1,2-dihydronaphthalene and *trans*-stilbene. Linear substituents on the non-peripheral sites of the phthalocyanine were able to reduce aggregation and increase the solubility of the catalyst without compromising its activity by steric congestion as all substituted catalysts were more reactive than the unsubstituted phthalocyanine, whereas the bulky isopentyl and cyclohexyl substituted catalysts were less active than those with linear substituents. Although the epoxidation mechanism and the exact active intermediate is still ambigious, it likely involves the coordination of the *N*-oxide to ruthenium and subsequent transfer of the oxygen to the metal to form a high-valent oxo-ruthenium species. It is proposed that the alkene approaches this metal oxo moiety from the top and that oxygen transfer to the alkene is concerted with concomitant stereoretention.

KEYWORDS: epoxidation, ruthenium, phthalocyanine, non-peripheral, pyridine *N*-oxide.

INTRODUCTION

Given the importance of epoxides in many naturally occurring molecules as well as industrial starting materials, the development of more efficient catalytic systems for epoxidation is important for both industry and academia [1–4]. Transition metals catalysts are of particular importance in this respect as the versatile transition metals not only may exist in several oxidation states, but also have a number of possible coordination numbers, thus enhancing the possibility of successfully designing a catalyst suitable to the purpose. As compatibility between the type of catalyst and the oxidant is important, an assortment of metal complexes of porphyrins, phenanthrolines, salens, phthalocyanines (Pcs) *etc*. have been developed and studied as epoxidation catalysts with various oxidants. Catalyst decomposition is a serious concern for most of these systems, though, and product yields (based on substrate) are usually low and reaction times extensive [2–5].

Since the demonstration by Groves and Quinn [6] that ruthenium porphyrins could catalyze the direct transfer of oxygen to an alkene in the absence of a co-reductant, a variety of catalytic oxidative systems based on ruthenium porphyrin complexes has emerged. Amongst them, the ruthenium porphyrin/2,6-dichloropyridine *N*-oxide oxidation system developed by Hirobe *et al.* is quite efficient with high turnover numbers (TON, stability) and selectivity being reported [7–10].

Despite the structural similarity between porphyrin and phthalocyanine, research into the use of ruthenium phthalocyanines as oxidative catalysts is surprisingly limited, with the current understanding based almost exclusively on the works of Capobianchi [11], Balkus [12], Murahashi [13] and their co-workers. Capobianchi *et al*.

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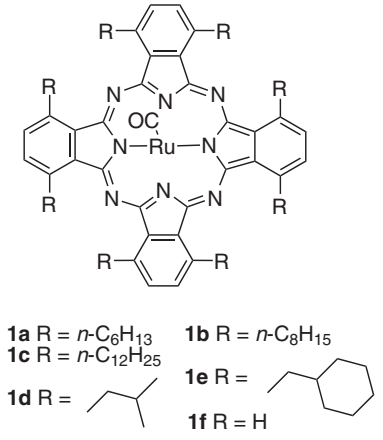
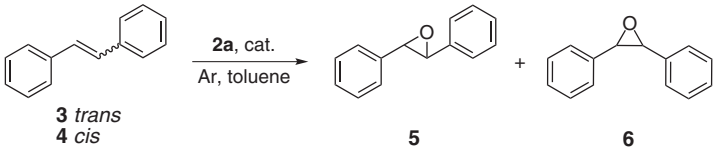


Scheme 1. Non-peripherally alkyl substituted carbonyl ruthenium phthalocyanines



Scheme 2. Epoxidation of *trans*- (**3**) and *cis*-stilbene (**4**)

[11] reported that unsubstituted ruthenium phthalocyanine, which exists as a dimer, catalyzes the aerobic oxidation of 1-octene to 2-octanone. Balkus *et al.* [12] reported the oxidation of alkanes by zeolite-encapsulated perfluorinated ruthenium phthalocyanine ($RuF_{16}Pc$) with *tert*-butyl hydroperoxide as oxidant, while Murahashi *et al.* [13] reported high TON in the aerobic alkane oxidation with perhalogenated ruthenium porphyrins (RuTPFPP)CO [TPFPP = 5,10,15,20-tetrakis(pentafluorophenyl) porphyrinato].

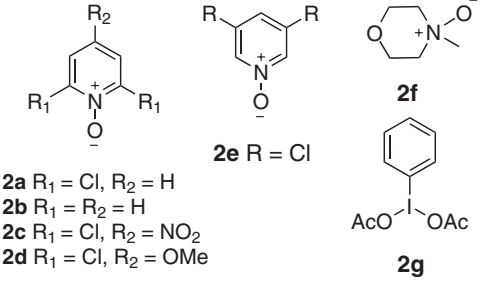
Although some research has been carried out on Fe, Mn, and Co phthalocyanines as epoxidation catalysts [14, 15], most of the studies on phthalocyanines had the objective of comparing the activity and stability of these complexes with that of the porphyrin equivalents. Development of the oxidation chemistry of phthalocyanines has also been hampered by the poor solubility of these compounds in common organic solvents due to aggregation, but since examples with alkyl substituents at the non-peripheral sites (1, 4, 8, 11, 15, 18, 22, 25) have shown much improved solubility [16, 17], these compounds were considered to have potential as catalysts in the epoxidation of alkenes.

In a recent work, we demonstrated for the first time that alkyl substituted and specifically non-peripherally alkyl substituted carbonyl[1,4,8,11,15,18,22,25-octa(alkyl) phthalocyaninato] ruthenium(II) Pc complexes **1a–1e** (Scheme 1) are efficient catalysts in the epoxidation of *trans*- **3** and *cis*-stilbene **4** with 2,6-dichloropyridine *N*-oxide (2,6-DCPNO) **2a** as terminal oxidant (Scheme 2) [18]. In this paper, we would like to report in detail on the compatibility of these catalysts with various oxidants and alkenes.

RESULTS AND DISCUSSION

Effect of oxidant

Since pyridine *N*-oxides, and particularly 2,6-DCPNO **2a**, are commonly employed as oxidants in ruthenium porphyrin catalyzed epoxidations, *trans*-stilbene **3** was exposed to a series of pyridine *N*-oxides **2a**–**2e**, and also other common oxidants **2f**–**2i**, in the presence of the phthalocyanine catalysts **1a** and **1d** (toluene, 80 °C, 0.23 mol.% of catalyst, catalyst/substrate/oxidant molar ratio = 1:500:750 for 24 h). Similar to results encountered for porphyrin-catalyzed epoxidations, 2,6-dichloropyridine *N*-oxide **2a** proved to be superior to all other oxidants in reactions catalyzed by Ru(II) Pc catalysts **1a** and **1d**, giving conversions of 100% and 51%, respectively (Table 1, entries 1 and 10). Whereas unsubstituted pyridine *N*-oxide **2b** was inactive under the conditions used, electron-withdrawing chloro groups in the positions *ortho* to the nitrogen rendered *N*-oxide **2a** highly active (Table 1, entry 2 *vs*. 1; entry 11 *vs*. 10). When, in an attempt to fine-tune the coordination and oxidation potential of the pyridine *N*-oxide and the non-coordinating characteristics of the resulting amine [19], the electron density of the oxidant was decreased by the addition of another electron-withdrawing group (nitro group) in the *para* position **2c**, the activity of the oxidant decreased (Table 1, entry 3 *vs*. 1; entry 12 *vs*. 10). A *para* electron donating OMe group **2d** increased the activity of the oxidant compared to **2c**, though it still performed poorer than **2a** (Table 1, entries 4, 3 and 1; entries 13, 12 and 10). The oxidant with chloro groups (known to be *ortho* and *para* deactivating) in the *meta* (**2e**) rather than the *ortho* positions also performed poorer than **2a** (Table 1, entry 5 *vs*. 1; entry 14 *vs*. 10), though the fact that the catalyst wasn't deactivated indicates that steric hindrance at the *ortho* positions is not a prerequisite for non-coordination of the formed amine to the metal as was reported for ruthenium porphyrin catalysts [9].



Scheme 3. Oxidants

Table 1. Epoxidation of *trans*-stilbene **3** catalyzed by **1a** and **1d** (0.23 mol.%) with different oxidants[a]

Entry	Cat	Oxidant	Conversion, %	Epoxide **4** (% yield)
1	**1a**	**2a**	100	95
2	**1a**	**2b**	—	—
3	**1a**	**2c**	36	32
4	**1a**	**2d**	45	37
5	**1a**	**2e**	52	42
6	**1a**	**2f**	—	—
7	**1a**	**2g**	—	—
8	**1a**	**2h**	—	—
9	**1a**	**2i**	—	—
10	**1d**	**2a**	51	30
11	**1d**	**2b**	—	—
12	**1d**	**2c**	18	14
13	**1d**	**2d**	32	27
14	**1d**	**2e**	35	32
15	**1d**	**2f**	—	—
16	**1d**	**2g**	—	—
17	**1d**	**2h**	—	—
18	**1d**	**2i**	—	—

[a]Reaction conditions: toluene, Ar, 80 °C, catalyst/substrate/oxidant molar ratio = 1:500:750 for 24 h.

N-methylmorpholine *N*-oxide **2f**, (diacetoxyiodo) benzene **2g**, *t*-butyl hydrogen peroxide **2h** and hydrogen peroxide **2i** failed to give any conversion of the substrate.

In the absence of the ruthenium Pc catalyst, only trace amounts of the epoxide (≤0.59%), could be detected after two days of reaction.

Effect of solvent and temperature

Although preliminary studies (45 °C, 0.1 mol.% of catalyst, catalyst/substrate/oxidant molar ratio 1:1000:1500, 48 h) indicated little difference in the yields obtained for the **1d**-catalyzed epoxidation of *trans*-stilbene **3** by 2,6-DCPNO **2a** in toluene or dichloromethane [18], 1,2-dihydronaphthalene **7** is commonly used as substrate in the evaluation of epoxidation catalysts [20, 21]. It was therefore decided to use this compound as substrate in the optimization of reaction conditions for this reaction. When 1,2-dihydronaphthalene **7** was subjected to 2,6-DCPNO **2a** epoxidation catalyzed by **1a** in different solvents, no reaction was, however, observed in the coordinating solvents THF or CH_3CN, whereas both conversion and epoxide yield increased with decreasing polarity of the other solvents, *i.e*. ethyl acetate (17%, 12%), dichloromethane (17%, 13%) and toluene (22%, 16%) (Table 2, entries 1–5). As was previously encountered for *trans*-stilbene **3**, an increase in temperature from 45 to 80 °C resulted in a drastic increase in 1,2-dihydronaphthalene **7** conversion (100% *vs*. 22%, Table 2, entries 5 and 7) and epoxide yield (82% *vs*. 16%) in reactions catalyzed by **1a**. A further increase in temperature from 80 to 110 °C confirmed previous results [18] indicating enhanced reaction rates (reaction time of 3 h *vs*. 6 h and TOF of 1120 *vs*. 618), but lower yield (74% *vs*. 82%) and selectivity (76% *vs*. 82%) (Table 2, entries 7 and 9). Also, as was the case for *trans*-stilbene **3**, the sterically more demanding catalyst **1d** gave slightly lower yields and selectivity compared to **1a** (77% *vs*. 82% for both selectivity and yield, Table 2, entries 7 and 11).

Epoxidation of 1,2-dihydronaphthalene 7

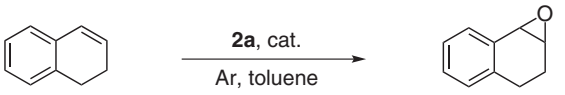
Since Berkessel and Frauenkron [21] and Che *et al*. [20] reported TONs of 880 (48 h) and 890 (3 h) in the epoxidation of 1,2-dihydronaphthalene **7** with homogeneous chiral ruthenium porphyrins and 870 (24 h) for soluble polymer-supported ruthenium porphyrin catalysts respectively, this substrate **7**, was selected for further evaluation of the catalytic capabilities of the prepared RuPc catalysts. Thus 1,2-dihydronaphthalene **7** was reacted with 2,6-dichloropyridine-*N*-oxide **2a** in the presence of 0.1 mol.% of the RuPcs (**1a–1f**) at 80 °C since the reaction with **1a** and **1d** showed 80 °C to be the optimum temperature. Complete substrate conversion to the epoxide **8** was observed within 4 h and high epoxide yields (77–83%) and selectivities (77–83%) were obtained with all the substituted ruthenium Pcs **1a–1e** (Table 2). Turnover numbers of up to 830 (in 6 h) were also comparable to those reported by Che *et al.* [20]. At 0.02 mol.% cat., turnovers (TON; product/catalyst molar ratio) of 2300–2800 were achieved in 12 h (Table 2, entries 17–21; 0.02 mol.% cat.) at a turnover frequency (TOF) of 260–457 h^{-1}.

In the presence of the catalysts with linear substituents **1a**–**1c**, the reactivity of 1,2-dihydronaphthalene **7** was similar to that of *trans*-stilbene **3** with regard to conversion, yield and selectivity (*vide infra*), though the TONs and TOFs were considerably higher for 1,2-dihydronaphthalene **7** (Table 2, entries 7, 13 and 14 and Table 3, entries 1–3). In the case of the bulkier catalysts **1d** and **1e**, 1,2-dihydronaphthalene **7** was considerably more reactive than *trans*-stilbene **3** (Table 2, entries 11 and 15, Table 3, entries 4 and 5) and *cis*-stilbene (Table 2, entries 11 and 15, Table 3, entries 20 and 21).

Epoxidation of *trans*- (3) and *cis*- (4) stilbene

As was previously reported, the epoxidation of *trans*-stilbene **3** with 2,6-DCPNO **2a** proceeded optimally at a catalyst concentration of 0.45 mol.% [18]. At this concentration, conversions above 95% and excellent selectivities (>75%) could be obtained for all the evaluated

Table 2. Catalytic epoxidation of 1,2-dihydronaphthalene **7** by 2,6-DCPNO **2a** with Ru(II)-Pc-complexes (0.1 mol.%)[a]



7 **8**

Entry	Cat	Cat., mol.%	Solvent	T, °C	t, h	Conversion, %	Epoxide yield, %	Selectivity, %	TON	TOF, h^{-1}
1	**1a**	0.1	CH_3CN	45	48	—	—			
2	**1a**	0.1	EtOAc	45	48	17	12			
3	**1a**	0.1	THF	45	48	—	—			
4	**1a**	0.1	CH_2Cl_2	45	48	17	13			
5	**1a**	0.1	Toluene	45	48	22	16			
6	**1a**	0.1	Toluene	60	48	84	68	81		46
7	**1a**	0.1	Toluene	80	6	100	82	82	820	618
8	**1a**	0.1	Toluene	90	6	100	80	80		600
9	**1a**	0.1	Toluene	100	3	>98	74	76		1120
10	**1d**	0.1	Toluene	60	48	84	57	68		138
11	**1d**	0.1	Toluene	80	6	100	77	77	770	
12	**1d**	0.1	Toluene	90	6	100	77	77	770	
13	**1b**	0.1	Toluene	80	6	100	80	80	800	
14	**1c**	0.1	Toluene	80	6	100	80	80	800	
15	**1e**	0.1	Toluene	80	6	100	83	83	830	
16	**1f**	0.45	Toluene	80	6	42	35	83	77	
17	**1a**	0.02	Toluene	80	12	53			2700	286
18	**1b**	0.02	Toluene	80	12	49			2500	295
19	**1c**	0.02	Toluene	80	12	57			2800	300
20	**1d**	0.02	Toluene	80	12	51			2500	457
21	**1e**	0.02	Toluene	80	12	46			2300	260

[a]Catalyst/substrate/oxidant molar ratio = 1:1000:1500 for 0.1 mol.% cat., 1:5000:7500 for 0.02 mol.% cat. and 1:220:330 for 0.45 mol.% cat. Product was identified by GC-MS.

catalysts, the only exception being the unsubstituted RuPc complex **1f** with which little epoxidation was observed.

To emphasize differences in activity between the different catalysts, conversion, yields, selectivity and turnover numbers were determined at 0.1 mol.% catalyst loading (catalyst/alkene/2,6-DCPNO = 1:1000:1500). The selectivity and conversions for the alkyl substituted RuPc **1a–1e** were still acceptable (77–87% and 68–100%, respectively) (Table 3, entries 1–5), while turnover numbers of up to 840 were obtained (Table 3, entry 3) after 48 h of reaction.

In order to determine if some of the catalyst might have been deactivated by aggregation or otherwise and to determine if differences in catalyst activity could be accentuated, the catalyst concentration was reduced to 0.02 mol.% (catalyst:alkene:2,6-DCPNO = 1:5000:7500) and the reaction repeated with all the prepared catalysts **1a–1e**. As indicated in Table 3 (entries 6–10), all of the catalysts, except **1e**, proved to be quite active with turnover frequencies (TOF) of up to *ca*. 170 h^{-1}. Although yields and conversions dropped quite dramatically when compared to the reactions at 0.45 mole % and 0.1 mol.% (Table 3 and Enow, Marais and Bezuidenhoudt [18]), the increase in turnover numbers indicated that the catalysts were still active up to the end of the reactions in the previous runs at the higher concentrations.

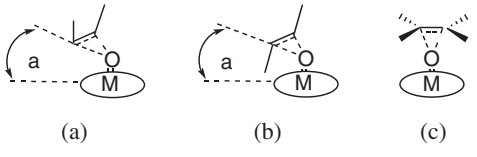
Since the best TONs reported in literature for the homogeneous epoxidation of *trans*-stilbene **3** was 243 (after 48 h) [22] and 270 (after 16 h) [20], it can be concluded that **1c** (Table 3, entry 8) with a turnover number of 1200 (after 48 h) is superior to all existing catalysts in the homogeneous epoxidation of *trans*-stilbene **3.**

This facile epoxidation of *trans*-stilbene **3** was unexpected as Hirobe [7–9], Gross [22, 23], Berkesel [21],

and Zhang [20] reported poor or no ruthenium porphyrin catalyzed epoxidation of this substrate, even with highly electron deficient ruthenium porphyrin complexes. The best conversion and turnover with homogeneous chiral ruthenium porphyrins was reported to be *ca.* 21% and 270 (after 16 h) [22, 20], respectively, while heterogeneous polymer-supported ruthenium porphyrin catalysts gave 88% conversion and 870 TON (after 24 h) [24]. The poor reactivity of *trans*-stilbene **3** with these porphyrin epoxidation systems was attributed to steric hindrance during the "side-on" approach, *i.e*. when the substrate approaches the metal oxo moiety (Ru=O) from the side and at an angle relative to the plane of the porphyrin (Fig. 1) [25]. According to this model, steric hindrance between one of the phenyl groups of *trans*-stilbene **3** and the plane of the porphyrin can be invisaged due to the angle of approach. Substituents on the porphyrin periphery, and especially bulky substituents, decreased the reactivity even further.

Within the assumption that a metal oxo species is involved in the ruthenium phthalocyanine catalytic cycle, the facile epoxidation of *trans*-stilbene **3** by the alkylsubstituted ruthenium phthalocyanines in the current investigation suggest either a difference in steric hindrance around the metal oxo (Ru=O) moiety or an approach to the reactive centre other than the "side-on" one. Non-peripherally alkyl substituted Pcs tend to be non-planar and to adopt saddle shaped structures [26]. The metal free isopentyl phthalocyanine, for example, is inclined at an angle of 32° from the core of the complex [26]. Such a distortion from planarity, if present in the ruthenium phthalocyanine complexes prepared in this study, will expose the reactive metal oxo (Ru=O) part of the complex and therefore facilitate its interaction with the substrate. With regards to approach, a mechanism involving a "top-on" approach of the olefin to the Ru=O (Fig. 1c), as suggested by Liu *et al.* [27], will sufficiently account for the high activity despite the bulkiness of the ligand substituents.

The use of *cis*-stilbene **4** in the epoxidation reactions to obtain information on the mechanistic pathway is quite prevalent [20, 25, 28, 29]. Extension of the study to include Pcs **1a**–**1f** (0.45 mol.% cat., 90 °C) confirmed epoxidation with stereoretention (Table 3, entries 11–16). This almost stereospecific formation of *cis*-stilbene oxide **6** suggests that oxygen transfer from the ruthenium Pc to the alkene occurs *via* a concerted oxene insertion rather than a one-electron oxidation which would allow rotation around the C–C bond [22, 30].* The stability and activity of complexes **1a**–**1e** in the epoxidation of *cis*-stilbene **4** was further evaluated through the determination of turnover number (TON) and frequency (TOF) at 0.1 mol.% catalyst loading and 90 °C for 48 h (Table 3, entries 17–21). High TONs of up to 570 (after 48 h) at TOFs of 25 to 45 h^{-1} (after 1 h) were obtained.



(a) (b) (c)

Fig. 1. The "side-on" approach of *cis*- (a) and *trans*-alkenes (b) to the metal oxo moiety; and (c) the "top-on" approach

For both *trans*- **3** and *cis*-stilbene **4**, superior epoxide yields were obtained with the alkyl substituted RuPcs **1a–1e** in comparison to the unsubstituted catalyst **1f** (Bezuidenhoudt and co-workers [18] and Table 3, entries 11–16). The activities and selectivities obtained with the alkyl substituted catalysts **1a–1d** were the same within experimental error and these catalysts were furthermore more active than their counterpart with the bulkier cyclohexyl **1e** substituent (Bezuidenhoudt and co-workers [18] and Table 3, entries 11–16). This observation is in agreement with Groves' report that oxygen transfer is sensitive to the steric bulk in the vicinity of the active metal centre [25] and is corroborated by the near planar *trans*-stilbene **3** (phenyl-vinyl torsions of 2.2 and 5.4°) [31] being more reactive than the non-planar *cis*-isomer **4** (with phenyl pyrimidalization towards the olefinic carbons and the phenyl rings twisted to alleviate van der Waals repulsion by each other; phenyl-vinyl torsions of 43°) [32, 33]. During a "top-on" approach, the twisted phenyl groups in the *cis*-isomer **4** would thus experience more steric interaction with the non-peripheral substituents of the catalyst four bondlengths away from the Ru=O moiety than the phenyl groups of the *trans*-isomer (**3**).

Competitive epoxidation of *cis*- 4 and *trans*-stilbene 3

Since it is claimed in literature that the homogeneous [7, 9] and heterogeneous [34] ruthenium porphyrin-*N*-oxide systems show preference towards the epoxidation of *cis*-stilbene **4** over the *trans*-isomer **3**, this aspect of the current RuPc catalysts was subsequently evaluated, especially given that our results with RuPcs **1a**–**1e** indicated *trans*-stilbene **3** to be more reactive than *cis*-stilbene **4** (*vide supra*). A 1:1 mixture of *cis*- **4** and *trans*-stilbene **3** was thus subjected to the epoxidation conditions (catalyst concentration of 0.23 mol.%, 24 h reaction period).

Both the *trans*-epoxide **5**: *cis*-epoxide **6** ratio obtained after 24 h (Table 4) and the kinetic profiles (Fig. 2) indicated the *trans*-epoxide **5** to be forming 1.14–1.35 times faster than the *cis*-epoxide **6** (53–57% *trans*-epoxide **5** after 24 h). The *cis*-*trans* ratio furthermore remained essentially constant during the reaction catalyzed by **1a**

*The small amounts of *trans*-epoxide 5 (*ca*. 4–5%) observed in all of the reactions might be the result of a competing radical mechanism [27] and/or of a *trans*-stilbene **3** impurity in the commercial samples of *cis*-stilbene **4** (sold with >96% purity).

Table 3. Epoxidation of *trans*-stilbene **3** and *cis*-stilbene **4** by 2,6-DCPNO **2a** with Ru(II)-Pc-complexes[a]

Entry	Substrate	Catalyst	Cat. mol.%	Conversion, %	*trans*-epoxide (**5**) yield, %	*cis*-epoxide (**6**) yield, %	Benzaldehyde (**9**) yield, %	Selectivity to major epoxide, %	TON[b] (TOF[c], h^{-1})
1	**3**	**1a**	0.1	100	82			82	820
2	**3**	**1b**	0.1	100	78			78	780
3	**3**	**1c**	0.1	100	84			84	840
4	**3**	**1d**	0.1	73	56			77	560
5	**3**	**1e**	0.1	68	59			87	590
6	**3**	**1a**	0.02	22	22			100	1085 (151)
7	**3**	**1b**	0.02	23	23			100	1150 (169)
8	**3**	**1c**	0.02	24	24			100	1200 (147)
9	**3**	**1d**	0.02	18	17			94	850 (139)
10	**3**	**1e**	0.02	20	20			100	1002 (93)
11	**4**	**1a**	0.45	100	4	84	2	84	
12	**4**	**1b**	0.45	100	4	86	1	86	
13	**4**	**1c**	0.45	100	5	85	1	85	
14	**4**	**1d**	0.45	94	4	83	2	88	
15	**4**	**1e**	0.45	76	4	60	1	79	
16	**4**	**1f**	0.45	20	1	11	1	55	
17	**4**	**1a**	0.1	64	3	40	9	63	520 (41)
18	**4**	**1b**	0.1	66	3	44	10	67	560 (40)
19	**4**	**1c**	0.1	72	2	46	9	64	570 (45)
20	**4**	**1d**	0.1	55	3	34		62	490 (32)
21	**4**	**1e**	0.1	46	3	26		57	340 (25)

See Enow, Marais and Bezuidenhoudt [18] for 0.45 mol.% cat. in *trans*-stilbene **3** epoxidation. [a]Reaction conditions: Toluene (2 mL); 90 °C; 24 h for 0.45 mol.% cat. and 48 h for 0.1 and 0.02 mol.% cat.; catalyzt/substrate/oxidant molar ratio = 1:1000:1500 for 0.1 mol.% cat., 1:5000:7500 for 0.02 mol.% cat. and 1:220:330 for 0.45 mol.% cat. [b]Determined after 48 h. [c]Determined after 1 h.

Table 4. Competitive *cis*/*trans*-stilbene **4**/**3** epoxidation by 2,6-DCPNO **2a** with Ru(II)-Pc-complexes at 0.23 mol.% catalyst concentration[a]

Entry	Cat.	*Trans*-epoxide (**5**) yield, %	*Cis*-epoxide (**6**) yield, %	Ratio (**5**:**6**)
1	**1a**	91	70	1.3:1
2	**1b**	89	74	1.2:1
3	**1c**	98	73	1.34:1
4	**1d**	84	74	1.14:1
5	**1e**	37	31	1.19:1
6	**1f**	16	12	1.35:1

[a]Reaction conditions: Toluene (2 mL), 90 °C, 0.23 mol.% catalyst, 1:1 mixture of *cis*- (**4**) and *trans*-stilbene (**3**) for 24 h.

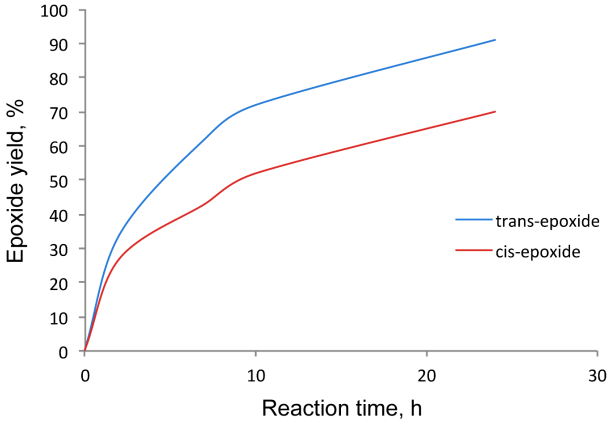


Fig. 2. Time course plot for the competitive epoxidation of *cis*-stilbene (**4**) and *trans*-stilbene (**3**) catalyzed by RuPc **1a** (0.23 mol.% cat., toluene, 90 °C)

(*ca.* 1.3:1, Fig. 2). The higher reactivity of the *trans*-alkene represents the opposite of what was found for the porphyrin system (*vide supra*) and resembles the *m*-chloroperoxybenzoic acid epoxidation of *cis*-**4** and *trans*-stilbene **3** in methylene chloride [21].

Epoxidation of styrenes

Treatment of planar styrene **10** (phenyl-vinyl dihedral angle of 0°) [35] with **2a** (1.5 eq.) and **1a**–**1e** (0.45 mol.%) in toluene at 90 °C for 24 h, gave the styrene oxide **12** in moderate selectivity (39–57%) with 17–44% substrate conversions (Table 5, entries 1–5), while the unsubstituted Pc **1f** again led to only 7% conversion (entry 6).

While no clear trend or influence on selectivity could be identified originating from the alkyl substituents attached to the Pcs, it was noticed that reaction time played a crucial role in the product distribution. For the RuPc **1b** reaction, for example, a product distribution of 47:33:20 (42, 29 and 18% in terms of yield) were obtained for epoxide **12**, benzaldehyde **9** and the rearrangement product, phenylacetaldehyde **15**, at 44% conversion after 24 h. When the reaction with **1b** was left to run for 36 h, benzaldehyde **9** became the main product with a product distribution of 31:48:21 (25, 38 and 17% in terms of yield) for **12**, benzaldehyde **9** and phenylacetaldehyde **15** at 77% substrate conversion. Trace amounts of benzaldehyde **9** was similarly only observed after *ca.* 15 h reaction time in the *cis*-stilbene **4** reaction, whereas *cis*-stilbene oxide **6** decomposed into benzaldehyde **9** when subjected to the epoxidation reaction conditions for 15 h. This confirms that decomposition of the epoxide, rather than competitive oxidative alkene cleavage, occurs to form the benzaldehyde **9** [27, 36–38]. Similar variations in the product ratios have been observed in ruthenium porphyrin catalyzed epoxidation of styrene with **2a**, PhIO or TBHP (*t*-butylhydroperoxide) as oxidants [39].

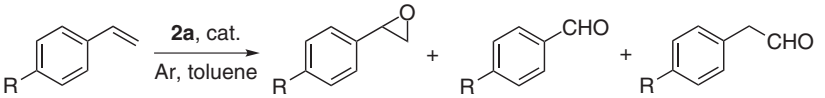
(Ep)oxidation of the more electron rich 4-methoxy-styrene **11** (Table 5, entries 7–11) catalyzed by 0.45 mol.% of the RuPc complexes **1a–1e** in toluene resulted in increased substrate conversions (51–92% within 24 h), though selectivities towards the desired epoxide product **13** were still moderate (32–64%). While the epoxide **13** remained the major product and the electron donating properties of the 4-methoxy group had a beneficial effect on the production of the desired epoxide (17–44 *vs.* 51–92%), it also enhanced decomposition of the epoxide to the benzaldehyde **14** and rearrangement towards the phenylacetaldehyde **16**.

(Ep)oxidation of *trans*-β- (**17**), *cis*-β- (**18**) and α-methylstyrene **19** catalyzed by complexes **1a–1d** (0.1 mol.% cat., for 48 h at 90 °C) gave the desired epoxides in acceptable yields. Moderate to high conversions (74–90%), good selectivities (66–91%), and moderate turnovers (640–750, 48 h) were obtained for all substituted RuPcs, except for **1e** (Table 6). As for all the other substrates, the unsubstituted Pc **1f** gave low conversions (<20%) for all the substituted styrenes tested (Table 6).

The alkyl substituted ruthenium Pcs tested during the current investigation are considerably more reactive than both the Jorgenson system (Fe(II)Pc/PhIO) [16], which gave only 63% conversion with a turnover number of <50 in the epoxidation of *trans*-β-methylstyrene **17**, and the homogeneous ruthenium porphyrin/*N*-oxide system used by Che [20] with a substrate conversion of only 24% at the same catalyst loading, whereas it is comparable to the heterogeneous ruthenium porphyrin/*N*-oxide system reported on by Zhang and Che [24], which gave TON of up to 890 (24 h).

Substituting one of the phenyl groups of stilbene with a methyl group resulted in decreased conversions and yields for the *trans*-isomer **17** (with the exception of the reaction catalyzed by RuPc **1d**) (Table 6, entries 1–5, Table 3, entries 1–5), even though the phenyl-vinyl dihedral angles are close to 0° for both isomers (0° for **17** [35] and 2.2 and 5.4° for **3** [31]). This difference in activity might therefore be ascribed to increased steric

Table 5. Epoxidation of styrene **10** and 4-methoxystyrene **11** with 2,6-DCPNO **2a** catalyzed by ruthenium phthalocyanines **1a–1f** at 0.45 mol.% catalyst concentration[a]



10 R = H
11 R = OMe

12 R = H
13 R = OMe

9 R = H
14 R = OMe

15 R = H
16 R = OMe

Entry	Substrate	Cat.	Conversion, %	Selectivity, % epoxide	Benzaldehyde	Phenylacetaldehyde
1	**10**	**1a**	39	**12** (39)	**9** (33)	**15** (15)
2	**10**	**1b**	44	**12** (42)	**9** (29)	**15** (18)
3	**10**	**1c**	28	**12** (57)	**9** (36)	**15** (15)
4	**10**	**1d**	35	**12** (51)	**9** (31)	**15** (17)
5	**10**	**1e**	17	**12** (41)	**9** (35)	—
6	**10**	**1f**	7	**12** (35)	**9** (20)	**15** (19)
7	**11**	**1a**	90	**13** (51)	**14** (29)	**16** (14)
8	**11**	**1b**	92	**13** (44)	**14** (25)	**16** (14)
9	**11**	**1c**	69	**13** (32)	**14** (25)	**16** (7)
10	**11**	**1d**	67	**13** (64)	**14** (21)	**16** (13)
11	**11**	**1e**	51	**13** (41)	**14** (35)	**16** (12)

[a]Reaction conditions: toluene, 90 °C, catalyst/substrate/oxidant molar ratio = 1:220:330 for 24 h. Products were identified by GC-MS.

interaction between the methyl group and the catalyst compared to the phenyl group being co-planar to the double bond in *trans*-stilbene **3**. In the case of the *cis*-isomer **18**, conversion and epoxide yields drastically increased when the twisted phenyl of *cis*-stilbene **4** was replaced by a methyl group (**18**) (Table 3, entries 17–21, Table 6, entries 7–11), to render a phenyl-vinyl moiety with a smaller dihedral angle (43° for **4** [32, 33] and 35° for **18** [35]). The importance of a planar phenyl-vinyl moiety is further corroborated by *cis*-β-methylstyrene **18** also being less reactive than 1,2-dihydronaphthalene **7** (Table 6, entries 7–11 *vs*. Table 2, entries 11–15°; phenyl-vinyl dihedral angles of 35° for **18** and 15° for **7** [7]).

For α-methylstyrene **19,** conversions and yields were remarkably comparable to those obtained for the epoxidation of *cis*-β-methylstyrene **18** in the presence of all of the catalysts except for RuPc **1c**, which performed considerably poorer with this substrate [79% conversion, 52% yield, 66% selectivity and 640 TON, Table 6, entry 15 *vs.* 90% conversion, 72% yield, 80% selectivity and 720 TON in 48 h for *cis*-β-methylstyrene **18**, Table 6, entry 9]. The reason for this outlier result is currently not clearly understood, but the similarities point to the similar steric interference between these substrates and the catalyst in the transition state. The phenyl-vinyl dihedral angle is 35° for both α-methylstyrene **19** and *cis*-β-methylstyrene **18** [35].

In the case of the bulkier catalysts (**1d** and **1e**), *trans*-β-methylstyrene **17** (dihedral angle of 0°) [35] showed better conversion than both *cis*-β-methylstyrene **18** and α-methylstyrene **19** (dihedral angles of 35°) [35] (Table 6, entries **4** and **5** *vs*. 10 and 11; entries 16 and 17), whereas the non-conjugated [32] more nucleophilic **18** and **19** performed slightly better with the linear catalysts (Table 6, entries 1–3 *vs.* 7–9 and 13–15).

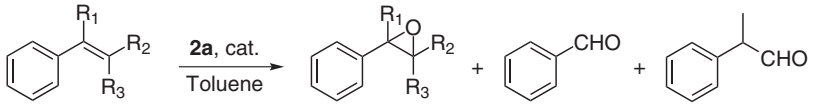
Epoxidation of cyclooctene 24

Moving away from conjugated double bonds, cyclooctene **24** was chosen as the next substrate. With 0.45 mol.% of the alkyl substituted ruthenium pthalocyanine complexes **1a–1e**, the catalytic epoxidation of cyclooctene **24** by 2,6-dichloropyridine *N*-oxide **2a** proceeded efficiently to afford cyclooctene oxide **25** as the only identifiable product (Table 7, entries 1–5) in high yields (68–86%) and selectivity (80–87%) within only 15 h.

Epoxidation of 1,5-cyclooctadiene 26 and limonene 29

After establishing that cyclooctene **24** could indeed be epoxidized in good yield and selectivity by the substituted ruthenium phthalocyanine catalysts, it was decided to study the selectivity of these catalysts towards the double bonds of dienes. 1,5-Cyclooctadiene **26**, which can be epoxidized to the mono-epoxide **27** or bis-epoxide **28** (Table 8), was thus selected as the next model compound.

Table 6. Epoxidation of *trans*-β- (**17**), *cis*-β- (**18**) and α-methylstyrene **19** with 2,6-DCPNO **2a** catalyzed by ruthenium phthalocyanines **1a–1f** at 0.1 mol.% catalyst concentration[a]



17 $R_1 = R_3 = H$, $R_2 = CH_3$ **20** $R_1 = R_3 = H$, $R_2 = CH_3$ **9** **23**
18 $R_1 = R_2 = H$, $R_3 = CH_3$ **21** $R_1 = R_2 = H$, $R_3 = CH_3$
19 $R_2 = R_3 = H$, $R_1 = CH_3$ **22** $R_2 = R_3 = H$, $R_1 = CH_3$

Entry	Cat.	Substrate	Conv., %	Epoxide[b] yield, %	Aldehyde yield, %	Epoxide selectivity, %	TON
1	**1a**	**17**	84	70	**9** (3)	83	700
2	**1b**	**17**	82	68	**9** (4)	83	680
3	**1c**	**17**	85	75	**9** (6)	88	750
4	**1d**	**17**	84	67	**9** (3)	80	670
5	**1e**	**17**	62	49	**9** (3)	79	490
6	**1f**	**17**	10	4	**9** (1)	40	50
7	**1a**	**18**	88	72	**9** (4)	82	720
8	**1b**	**18**	87	70	**9** (4)	81	700
9	**1c**	**18**	90	72	**9** (3)	80	720
10	**1d**	**18**	74	67	**9** (3)	91	670
11	**1e**	**18**	53	46	**9** (3)	87	460
12	**1f**	**18**	10	7	**9** (1)	70	70
13	**1a**	**19**	88	72	**23** (3)	82	750
14	**1b**	**19**	87	70	**23** (2)	80	720
15	**1c**	**19**	79	52	**23** (2)	66	640
16	**1d**	**19**	74	64	**23** (2)	86	660
17	**1e**	**19**	53	46	**23** (2)	87	480
18	**1f**	**19**	18	12	**23** (<1)	67	120

[a]Reaction conditions: toluene, 90 °C catalyst/substrate/oxidant molar ratio = 1:1000:1500 for 48 h. Products were identified by GC-MS. [b] **13** and **14** could not be distinguished from each other as the retention times were identical (23.04 min).

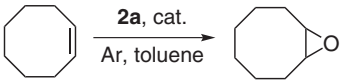
Employing 0.45 mole % catalysts, GC-MS analysis showed 1,5-cyclooctadiene **26** to be converted to the mono-epoxide **27** only. Bhattacharjee and Anderson [40] reported similar observations in the manganese-salen/O_2-aldehyde system and explained that **27**, once formed, is less prone to oxidation than **26**. Previous work by Larsen and Jorgensen [16] showed that the epoxidation of this substrate with the iron(II) Pc/iodosylbenzene system afforded a mixture of both epoxides [mono-epoxide **27** (25%), bis-epoxide **28** (5%)], whereas only the bis-epoxide **28** was selectively formed in 76% yield by a polymer supported ruthenium porphyrin/*N*-oxide system [41].

Conversion, yield and selectivity were drastically lower for this substrate compared to that of cyclooctene **24** (Table 8 *vs*. Table 7). This might be ascribed to differences in the allylic bond angles, 1,5-cyclooctadiene **26** being in a boat conformation and cyclooctene **24** in a chair conformation [40, 42].

When (+)-limonene **29** was exposed to the epoxidation conditions with 0.45 mol.% of the ruthenium phthalocyanine complexes for 24 h, the electron-rich trisubstituted double bond was favored over the terminal double bond, affording epoxide **30** as only identifiable product (Table 9).

Comparable results were obtained for all the alkyl substituted ruthenium phthalocyanine **1a–1e** catalyzed reactions with conversions above 92% (Table 9, entries 1–5). Yields (40–47%) and epoxide selectivity (40–51%) were however low, which indicates that side reactions and/or decomposition of the epoxide is prevalent. This deduction is supported by the increase in epoxide yield and selectivity when bulkier catalysts were used (Table 9, entries 4 and 5 *vs*. 1–3). The low yields and selectivities found are similar to that reported for the ruthenium-bisoxazole catalyzed epoxidation of this substrate by the molecular oxygen/isobutylaldehyde system [39]. Contrary

Table 7. Epoxidation of cyclooctene **24** with 2,6-DCPNO **2a** catalyzed by ruthenium phthalocyanines **1a–1f**[a]

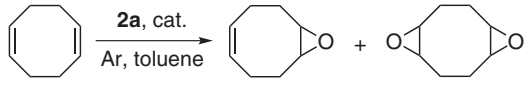


24 **25**

Entry	Cat.	Cat., mol.%	Conversion, %	Yield, %	Selectivity, %	TON after 48 h	TOF, h^{-1} [b]
1	**1a**	0.45	100	82	82		
2	**1b**	0.45	100	84	84		
3	**1c**	0.45	100	86	86		
4	**1d**	0.45	93	74	80		
5	**1e**	0.45	78	68	87		
6	**1f**	0.45	15	10	67		
7	**1a**	0.23	79	61	77	305	43
8	**1b**	0.23	93	73	73	362	41
9	**1c**	0.23	87	73	84	365	40
10	**1d**	0.23	82	62	76	310	42
11	**1e**	0.23	66	44	67	220	40

[a]Reaction conditions: toluene, 90 °C, catalyst/substrate/oxidant molar ratio = 1:220:330 for 20 h for 0.45 mol.% catalyst and 1:500:750 for 0.23 mol.% catalyst. [b]TOF after 2 h.

Table 8. Epoxidation of 1,5-cyclooctadiene **26** by 2,6-DCPNO **2a** (oxidant:substrate 1.5:1) catalyzed by ruthenium phthalocyanines **1a–1f** at 0.45 mol.% catalyst concentration[a]

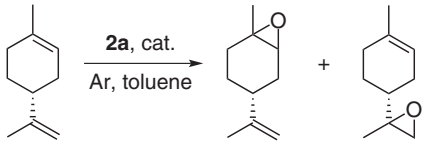


26 **27** **28**

Entry	Cat.	Conversion, %	Yield, %	Selectivity to **27**, %	TON after 24 h
1	**1a**	52	24	46	53
2	**1b**	48	31	65	68
3	**1c**	62	34	55	75
4	**1d**	50	24	48	53
5	**1e**	53	28	53	62
6	**1f**	11	4	36	11

[a]Reaction conditions: toluene, 90 °C, catalyst/substrate/oxidant molar ratio = 1:220:330 for 24 h. Product identified by GC-MS.

Table 9. Epoxidation of (+)-limonene **29** by 2,6-DCPNO **2a** catalyzed by ruthenium phthalocyanines **1a–1f** at 0.45 mol.% catalyst concentration[a]



29 **30** **31**

Entry	Cat.	Conversion, %	Yield, %	Selectivity to **30**, %	TON after 24 h
1	**1a**	100	40	40	88
2	**1b**	100	40	40	88
3	**1c**	100	42	42	92
4	**1d**	92	47	51	103
5	**1e**	96	46	48	101
6	**1f**	13	trace	—	—

[a]Reaction conditions: toluene, 90 °C, catalyst/substrate/oxidant molar ratio = 1:220:330 for 24 h.

to the current results, the epoxidation of limonene **29** with the homogeneous ruthenium porphyrin/*N*-oxide system previously reported, resulted in mixtures of **30** and **31** in varying ratios [43].

Epoxidation of aliphatic acyclic alkenes

Aliphatic acyclic substrates are amongst the most difficult to oxidize substrates. Only trace amounts (~2%) of the epoxides corresponding to 1-octene **32** and *trans*-2-octene **33** could be detected after 24 h in the presence of 0.45 mol.% catalyst and **2a** (5 eq.). Increasing the catalyst load to up to 3 mol.% or raising the temperature to 100 °C did not increase the yield of the epoxide at all. The conversion (up to *ca*. 5%) obtained for both 1-octene

32 and *trans*-2-octene **33**, was comparable to that obtained with the chiral ruthenium porphyrin catalyzed epoxidation of 1-octene [21].

EXPERIMENTAL

All chemical reagents were obtained from Aldrich, Fluka or Merck and used without further purification. Solvents were freshly distilled using standard methods. Carbonyl ruthenium phthalocyanines **1a–1f** were synthesized as reported earlier [18, 44, 45]. The oxidant 2,6-dichloro-4-methoxypyridine-*N*-oxide **2a** was prepared according to a published procedure [21].

GC analyses were performed on a Shimadzu GC-2010 fitted with a PONA column (50.0 m × 0.20 mm × 0.50 μm) and FID detector. The N_2/Air (carrier gas) linear velocity was 1.07 mL/min and the injector and detector temperatures 200 °C and 290 °C, respectively. Injections were made in the split mode. The initial column temperature of 60 °C was kept for 5 min, whereafter it was increased to 250 °C at 5 °C/min and kept at this temperature for the rest of the analysis. Retention times were compared to those of commercially available samples. Where indicated in the discussion, products were identified by GC-MS analyses (electron impact ionization) on a Shimadzu GC-MS Qp-2010 fitted with a column and operated under conditions similar to that of the GC, but with helium as carrier gas. Conversions and yields were determined by GC using dodecane as internal standard.

Catalytic Reactions: A 15 mL Schlenk flask was charged with the catalyst (0.5 μmol, 1 eq.), the olefin, dodecane (internal standard) and dry toluene (2 mL) under an argon atmosphere. 2,6-Dichloropyridine-*N*-oxide **2a** was added and the solution stirred at 90 °C. The reactions were followed by gas chromatographic analysis.

CONCLUSION

In this study it was demonstrated for the first time that ruthenium phthalocyanines can be used in the epoxidation of a variety of alkenes and that non-peripherally alkyl substituted ruthenium phthalocyanines in particular are highly active catalysts with true catalytic activities at very low concentrations (<0.45 mole %). Complete conversion and high turnovers (>800 in 48 h for 0.1% catalyst loading) comparable to or better than those published for other catalytic systems could be obtained for 1,2-dihydronaphthalene **7** and *trans*-stilbene **3**. At low catalyst loading (0.02 mole %), TONs larger than 2000 in 12 h and TOFs above 260 h^{-1} were obtained for 1,2-dihydronaphthalene **7**. The same catalyst concentration gave TONs above 1000 in 48 h and TOFs above 90 h^{-1} for *trans*-stilbene **3**. Results for the other substrates commonly used to evaluate the activity of epoxidation catalysts, *i.e*. *cis*-stilbene **4**, *cis*- **18** and *trans*-β-methylstyrene **17**, α-methylstyrene **19**, styrene **10**, 4-methoxystyrene **11**, cyclooctene **24**, 1,5-cyclooctadiene **26**, limonene **29**, 1-octene **31** and *trans*-2-octene **32**, were comparable to those reported for other catalyst systems.

For all the substrates tested, all of the substituted ruthenium phthalocyanines **1a**–**1e** performed markedly better as epoxidation catalysts than the unsubstituted equivalent (**1f**), most probably because of reduced levels of aggregation in solution due to the acquired "saddle shape" of substituted ruthenium phthalocyanines with non-peripheral substituents. Increasing the steric bulk of the substituents attached to the phthalocyanine lowered the catalytic activity with a general order of reactivity **1a** ≈ **1b** ≈ **1c** > **1d** > **1e**. RuPc **1e** had the lowest activity towards all substrates evaluated, which might be ascribed to steric congestion. Linear substituents on the nonperipheral sites of the phthalocyanine were thus able to reduce aggregation and increase the solubility of the catalyst without compromising its activity by steric congestion.

These non-peripherally substituted ruthenium phthalocyanines proved to be highly effective towards the epoxidation of conjugated and cyclic alkenes and, in the presence of non-equivalent double bonds, showed selectivity towards the more substituted double bond above the terminal double bond. 1-Octene **32** and *trans*-2-octene **33** could not be epoxidized in the presence of these catalyzts, which correlates with the known low reactivity of these substrates.

Though the mechanism is still ambigious and the exact active intermediate not established (several high-valent oxo-ruthenium species with oxidation numbers ranging from IV to VIII are possible, for example)[36], the epoxidation mechanism simplistically presented likely involves the coordination of the *N*-oxide to ruthenium and subsequent transfer of the oxygen to the metal to form a high-valent oxo-ruthenium species [14, 46–49].

The approach of the alkene to the metal oxo moiety seems to be different from the "side-on" approach proposed for alkene epoxidation by porphyrins as *trans*-stilbene **3** and *trans*-β-methylstyrene **17** were highly reactive. A step-wise mechanism with intermediate radical formation (which allows for rotation around the C–C$^{\bullet}$ bond) was furthermore ruled out by the stereospecific epoxidation of *cis*-stilbene **4**. A "top-on" approach and concerted oxygen transfer with concomitant stereoretention is thus proposed.

The reactivity of the substrates depended on the degree of planarity around the double bond (phenyl-vinyl dihedral angle), nucleophilicity of the double bond (degree of conjugation and the presence of electron-withdrawing or -donating substituents), the steric bulk of the remainder of the molecule and the allylic angle. For phenyl-vinyl systems, reactivity decreased in the order (phenyl-vinyl dihedral angle given in brackets): 1,2-dihydronaphthalene **7** (15°) [35] > *trans*-stilbene **3** (2.2 and 5.4°) [31] >

trans-α-methylstyrene **17** (0°) [35] > *cis*-β-methylstyrene **18** (35°) [35] ≈ α-methylstyrene **19** (35°) [35] > *cis*-stilbene **4** (43°) [32, 33]. Reactivity decreased in the following order for cyclic alkenes (allylic angle in brackets): cyclooctene **24** (124.7, 126.4°, chair) [42] > (+)-limonene **29** (*ca*. 123.5° for the more substitued double bond in analogy to cyclohexene) [40] > 1,5-cyclooctadiene **26** (122.7, 122.8; 137.4, 137.6°, boat) [42, 40]. The aliphatic acyclic alkenes 1-octene **32** and *trans*-2-octene **33** gave only trace amounts of the epoxides.

Acknowledgements

Financial support from Sasol Ltd is gratefully acknowledged.

Supporting information

A list of GC retention times are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

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