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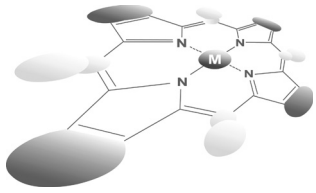

Catalytic epoxidation of stilbenes with non-peripherally alkyl substituted carbonyl ruthenium phthalocyanine complexes

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ABSTRACT: A number of novel carbonyl(1,4,8,11,15,18,22,25-octaalkylphthalocyaninato)-ruthenium(II) complexes were prepared by metal insertion with $Ru_3(CO)_{12}$. The new compounds have been characterized by ^1H NMR, ^{13}C NMR, IR, UV-vis and mass spectroscopy. This study demonstrated that this type of complexes and specifically carbonyl(1,4,8,11,15,18,22,25-octahexylphthalocyaninato)ruthenium(II) and carbonyl[1,4,8,11,15,18,22,25-octa(2-cyclohexylethyl)phthalocyaninato]-ruthenium(II), exhibit high catalytic activity and stability in the epoxidation of stilbenes with 2,6-dichloropyridine *N*-oxide as oxidant.

KEYWORDS: non-peripherally alkyl substituted phthalocyanine, carbonyl, ruthenium, epoxidation, stilbene, 2,6-dichloropyridine *N*-oxide.

INTRODUCTION

There are many domains in which phthalocyanine (Pc) chemistry have found wide application including; chemical sensing [1], the dye industry [2], catalysis [3, 4], nonlinear optics [5], medicine (mainly photodynamic therapy) [4, 6, 7], dye sensitized solar cells [4, 8] and optical limiting materials [9]. To a large extent, the applicability of phthalocyanine molecules has corresponded with the type of central metal ion and/or the substituents on the Pc. Thus, to expand the applicability of phthalocyanines, a variety of metals ions (> 70 elements) and substituents have been introduced into the Pc structure.

While some Fe, Mn, and Co containing phthalocyanines have been studied as epoxidation catalysts [10], the poor solubility of these complexes in common organic solvents due to aggregation, (which is pronounced at high concentration) has limited success in this area of research. Attachment of alkyl substituents to the non-peripheral positions of Pc complexes, however, resulted in those molecules adapting a "saddle shaped" structure with the consequence of reduced aggregation and enhanced solubility in organic solvents [11–13]. The improved solubility and associated reduced deactivation through aggregation served as impetus towards an investigation into the application of ruthenium carbonyl phthalocyanine complexes as catalysts in the epoxidation of alkenes.

In recent years, numerous ruthenium-based catalytic systems for epoxidation have been developed, a notable example being the 'Hirobe system' which employs mainly the carbonyl ruthenium porphyrins or the dioxo ruthenium porphyrins with pyridine *N*-oxides as oxidants [14–18]. Because of their structural similarity to porphyrins, and the fact that Pcs are more resistant to oxidative degradation, ruthenium phthalocyanines are attractive as catalysts in epoxidation reactions. To the best of our knowledge, the application of ruthenium phthalocyanines in catalytic epoxidation has not been reported before, though its applicability as catalyst for the oxidation of alkenes and alkanes have received some attention [4, 19, 20].

In view of utilizing the carbonyl ruthenium phthalocyanines in epoxidation reactions, we undertook the preparation of some alkyl substituted ruthenium phthalocyanines thereby extending the work of Cammidge *et al.* [21, 22].

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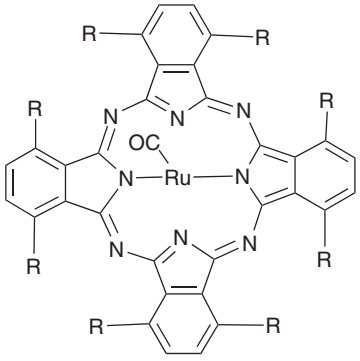


1a R = *n*-C_6H_{13} **1b** R = *n*-C_8H_{17}

1c R = *n*-$C_{12}H_{25}$ **1d** R =

1e R = **1f** R = *n*-$C_{10}H_{21}$

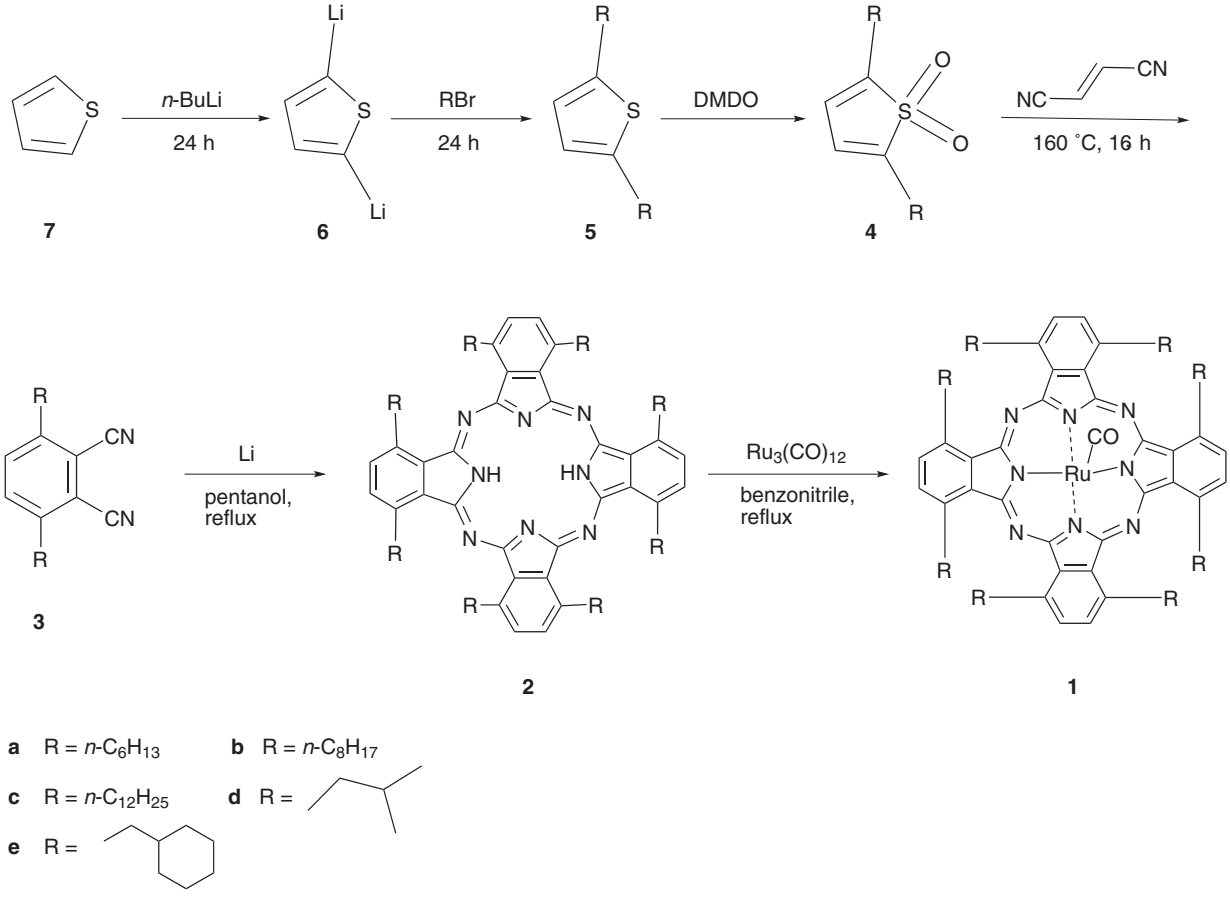
1g R = H

Scheme 1. Carbonyl ruthenium phthalocyanines **1a**–**1g**

Herein, we report on the synthesis and characterization of a series of non-peripherally alkyl-substituted carbonyl ruthenium phthalocyanines **1a**–**1e** of which all but **1b** are novel (Scheme 1). Since selectivity and activity of the catalyst in the ruthenium based porphyrin/*N*-oxide system varied with the bulkiness of the substituents on the ligand especially when applied to stilbene substrates [23–25], we also synthesized the more bulky isopentyl (**1d**) and cyclohexylethyl (**1e**) carbonyl ruthenium Pcs. Our findings on the application of non-peripherally substituted carbonyl ruthenium phthalocyanines and specifically carbonyl(1,4,8,11,15,18,22,25-octahexyl-phthalocyaninato)ruthenium(II) (**1a**) and carbonyl-[1,4,8,11,15,18,22,25-octa(2-cyclohexylethyl)phthalo-cyaninato]ruthenium(II) (**1e**) on the catalytic epoxidation of stilbenes with 2,6-dichloropyridine *N*-oxide as oxygen donor, are thus disclosed.

RESULTS AND DISCUSSION

Phthalocyanines with alkyl substituents on the non-peripheral positions (1,4,8,11,15,18,22,25-octa-substituted) are usually prepared by cyclotetramerization of the appropriate 3,6-disubstituted phthalonitriles. The challenge in the synthesis of this type of compound lies at the level of obtaining the 3,6-disubstituted phthalonitrile precursor. Starting with thiophene **7**, the 3,6-phthalonitriles **3a**–**3e** and the corresponding metal free phthalocyanine complexes **2a**–**2e** were synthesized as described in Scheme 2 [13].



a R = *n*-C_6H_{13} **b** R = *n*-C_8H_{17}

c R = *n*-$C_{12}H_{25}$ **d** R =

e R =

Scheme 2. Synthetic pathway for carbonyl ruthenium phthalocyanines **1a**–**1e**

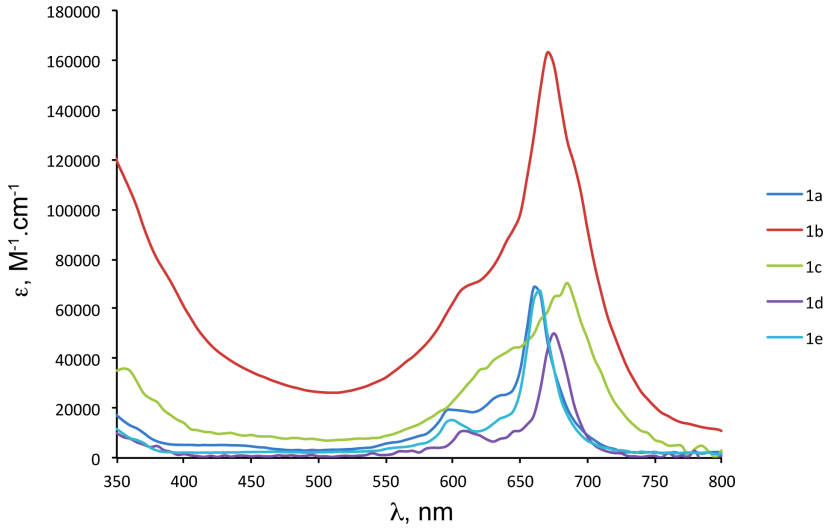


Fig. 1. UV-vis spectra of **1a**–**1e** in petroleum ether

Utilization of the methodology developed by Cammidge *et al*. [21, 22], previously employed in the synthesis of **1b** and RuPc-C10 (**1f**), *i.e.* refluxing the metal free Pc together with $Ru_3(CO)_{12}$ in benzonitrile, led to the formation of the desired ruthenium carbonyl phthalocyanines **1a**–**1e** (Scheme 1). Precipitating the products out of the benzonitrile solution by adding methanol proved to be a rather tedious process, even when large amounts of the methanol was added. So the pure products were obtained in 65–86% yields by flash column chromatography followed by recrystallization from a methanol-petroleum ether mixture (1:1). UV-vis spectroscopy, MALDI-TOF mass spectrometry, ^{1}H NMR, ^{13}C NMR, IR spectroscopy and HRMS were used to characterize each of the four new carbonyl phthalocyanine ruthenium complexes **1a**–**1e**.

Since the Q-band in the UV-visible spectra of metal substituted phthalocyanines represent one of the characteristic properties of these compounds [11–13], the prepared RuPcs **1a**–**1e** were analyzed with this technique first. The UV-vis spectra of compounds **1a**–**1e** in THF (Fig. 1) exhibited a single Q-band [**1a** = 660 nm (4.84), **1b** = 670 nm (5.21), **1c** = 685 nm (4.85), **1d** = 675 nm (4.70), **1e** = 680 nm (4.40)] of high intensity together with a blue shift (from *ca*. ~725 nm to 660–685 nm) indicative of a metal complex having been formed [21, 22].

The presence of the shoulder at the slightly lower energy side of the Q-band is probably explicable in terms of some level of aggregation in the solution while the spectra were being recorded. The fact that the intensity of the shoulder increased at higher concentrations gave additional credence to this suggestion.

The presence of an axial CO ligand in all of the prepared RuPc complexes (**1a–1e)** was confirmed by a strong absorption band at 1952–1965 cm^{-1} in the IR spectra of these compounds. Further evidence as to the presence of a metal inside the cavity of the phthalocyanine came from the absence of any N–H stretching vibrations at *ca*. 3300 in the IR spectra of all of the metal complexes.

The ^{1}H NMR spectra of complexes **1a–1e** displayed all the expected proton signals and were almost identical to those of the metal-free Pcs **2a–2e**, the only differences being the disappearance of the inner NH resonances (at δ = -0.29–0.32 ppm in the spectra of the metal-free compounds) and a splitting of the benzylic signals into two multiplets for **1a**; **1b**, **1d**, and **1e** [δ = 4.65–4.62 and 4.59–4.55 for **1a**; 4.65–4.60 and 4.57–4.52 for **1b**; 4.67–4.61 and 4.60–4.55 for **1d**; 4.65–4.61 and 4.60–4.56 for **1e**), indicating non-equivalence of these protons and thus two possible orientations for the alkyl substituents.

In the case of **1c**, the resonance from the benzylic protons appears as a very broad singlet (δ = 5.05–4.70) probably due to more than two orientations of the alkyl groups originating from severe restricted rotation. The pressence of the CO ligand in the complexes was further confirmed by a CO resonance at δ = 183.34, 180.25, 181.32, 174.77 and 183.32 for **1a**, **1b**, **1c**, **1d,** and **1e**, respectively in the ^{13}C NMR spectra.

Contrary to the ^{13}C NMR spectra of the metal free Pcs (**2a**–**2e**) where all the aromatic carbons were equivalent, these carbons in the ruthenium complexes **1a**–**1e** were visible as four separate signals at *ca.* δ = 129–145 ppm. The presence of ruthenium in the structures of complexes **1a**–**1e** were also confirmed by the isotope pattern found in the MALDI-TOF mass spectra (Fig. 2) where the spectra of **1a**, **1b**, and **1c** showed a signal cluster for both the [M] and [M–CO] isotopes, whereas those of **1d** and **1e** were represented by a cluster of isotope peaks at an *m/z* value corresponding to [M–CO]. Further proof of the structures of **1a**, **1b**, **1c**, and **1d** came from the high resolution mass spectra (HRMS) of these compounds where [M$^+$] (except in the case of **1c**) and [M$^+$ + CH_3OH] (except in the case of **1d**) ions were found at *m/z* = 1314.8062 and 1346.7935

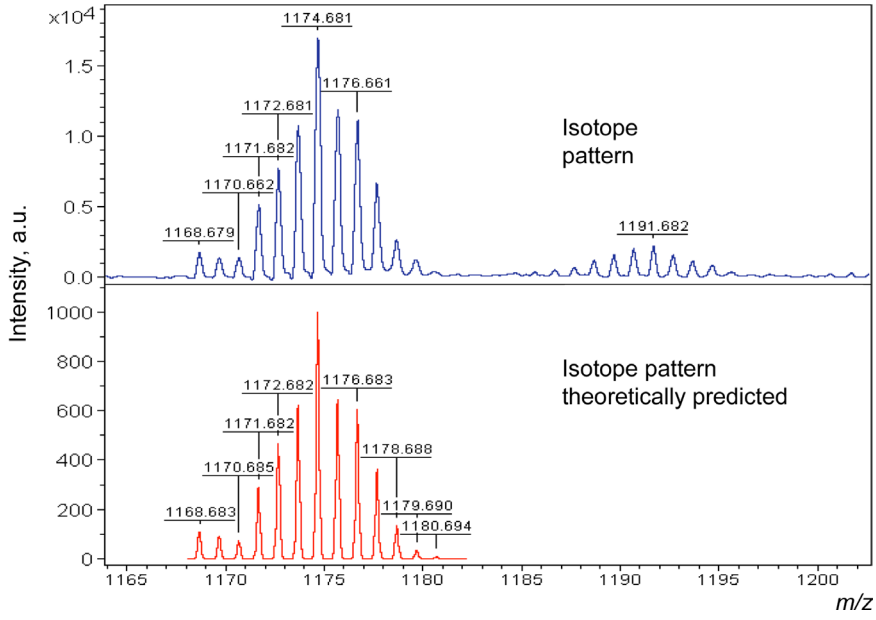
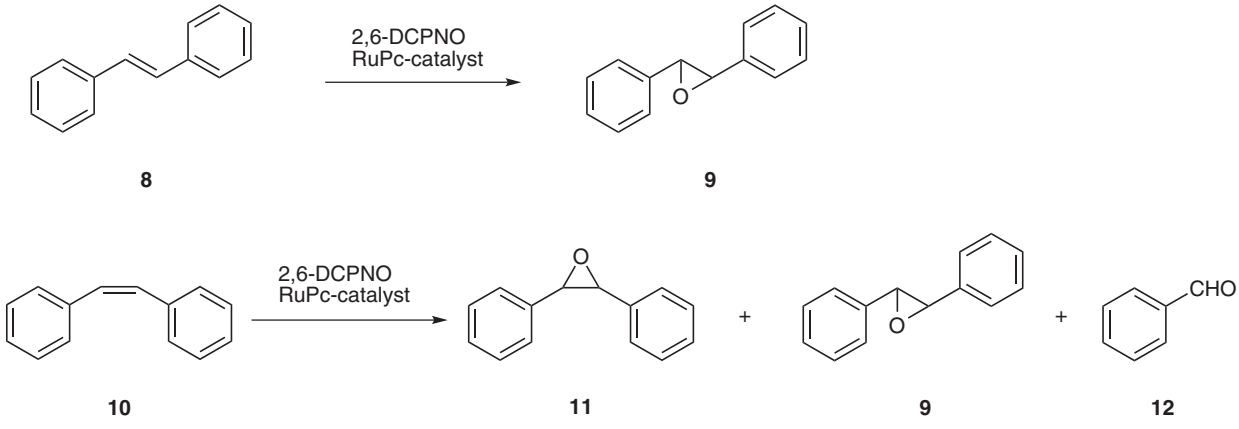


Fig. 2. MALDI-TOF mass spectrum of **1d**

for **1a**, 1539.0474 and 1572.0377 for **1b**, 2020.5658 for **1c** and 1202.6756 for **1d**.

With the series of carbonyl ruthenium phthalocyanines (**1a**–**1e**) in hand, the catalytic activity thereof towards the epoxidation of alkenes could be investigated (Scheme 3). Although some metal-containing phthalocyanines have been employed in the catalytic epoxidation of alkenes, yields and selectivities towards the epoxide were generally poor [26–29]. Attention was thus shifted to Ru-based systems and since pyridine *N*-oxides, and especially 2,6-dichloropyridine *N*-oxide (2,6-DCPNO), are commonly employed as oxidants in ruthenium porphyrin catalyzed epoxidations, 2,6-DCPNO was also selected as oxidant in the current investigations. As Hirobe *et al*. [14–16] performed Ru porphyrin epoxidations in either dichloromethane or benzene at room temperature or 30 °C, our investigation was started at 30 °C in dichloromethane with 0.1 mol% of catalyst **1d** (catalyst/substrate/oxidant molar ratio 1:1000:1500). Under these conditions, poor conversion and epoxide yield (<6%) were obtained for *trans*-stilbene **8**, even after extended reaction times (2 days). When the reaction temperature was increased to 45 °C, 26% conversion and a 13% yield of **9** could be obtained after 48 h (Table 2, entry 1). Changing the solvent to toluene, the replacement for carcinogenic benzene, led to 22% conversion and a 12% yield of **9** (Table 2, entry 2).

As almost similar yields were obtained in dichloromethane and toluene and considering that Berkessel and co-workers [17] found conversion rates, yields and turnover frequencies (TOF) to be promoted by higher reaction temperatures in a ruthenium porphyrin/*N*-oxide system, the higher boiling solvent, toluene, was selected for further investigations. An increase



Scheme 3. RuPc catalyzed epoxidation of stilbenes **8** and **10** by 2,6-DCPNO

Table 1. Catalytic epoxidation of *trans*-stilbene (**8**) by 2,6-DCPNO with Ru(II)–Pc complexes (0.1 mol%)[a]

Entry	Catalyst	T, °C	t, h	Conversion, %[c]	Product (% yield)	Selectivity, %	TOF, h^{-1}
1[b]	**1d**	45	48	26	13	50	
2	**1d**	45	48	22	12	55	
3	**1d**	90	48	73	56	77	104
4	**1d**	115	8	83	61	74	174
5	**1a**	60	48	23	21	91	30
6	**1a**	90	48	>99	82	82	120

[a] Reaction conditions: unless specified otherwise, toluene was used as solvent (2 mL); catalyst/substrate/oxidant molar ratio 1:1000:1500; [b] CH_2Cl_2; [c] Conversions were determined by GC using dodecane as internal standard.

Table 2. Epoxidation of stilbenes **8** and **10** with 2,6-DCPNO catalyzed by ruthenium phthalocyanines **1a**–**1e** and **1g**

Entry	Substrate	Catalyst	Cat., mol%	Conversion, %[b]	Yield, %	Selectivity, %
1	**8**	**1a**	0.1	68	57	84
2	**8**	**1a**	0.23	>95	92	97
3	**8**	**1a**	0.45	100	95	95
4	**8**	**1b**	0.45	100	99	99
5	**8**	**1c**	0.45	100	100	100
6	**8**	**1d**	0.45	100	75	75
7	**8**	**1e**	0.45	95	84	88
8	**8**	**1g**	0.45	27	18	67
9	**10**	**1a**	0.45	100	84[c]	84
10	**10**	**1e**	0.45	76	60[c]	79

[a]Reaction conditions: Toluene, 90 °C, 24 h; [b]Conversions were determined by GC using dodecane as internal standard; [c]Small amounts of *trans*-stilbene oxide (**9**) formed together with the *cis*-isomer (**11**).

in temperature from 45 to 90 °C facilitated a drastic increase in substrate conversion (73% *vs.* 2%) and epoxide **9** yield (56% *vs.* 12%, Table 1, entries 2 and 3). A further increase in temperature to 115 °C drastically reduced the required reaction time to only 8 h and increased both conversion (83% *vs.* 73%) and yield (61% *vs.* 56%) with a slightly lower selectivity (74% *vs.* 77%) towards the epoxide (Table 1, entries 3 and 4). The sterically more demanding catalyst **1d** was less reactive than **1a**, resulting in only 73% conversion of **8** and 56% yield of **9** at 90 °C compared to the > 99% conversion and 82% yield obtained with **1a** (Table 1, entries 3 and 6). As expected, an increase in temperature from 60 to 90 °C in the presence of RuPc **1a** also promoted conversion (>99% *vs.* 23%) and yields (82% *vs.* 21%) (Table 1, entries 5 and 6), though, as was encountered with **1d**, selectivity towards the epoxide decreased (82% *vs.* 91%) with increase in temperature. In addition, though the epoxide formed faster at higher temperatures as is also evident from the turnover frequencies (TOF) (Table 1, entries 3 and 4; entries 5 and 6), catalyst decomposition was also enhanced at increased temperatures as was evident from the rapid color change of the reaction mixture from blue to brown.

The effect of catalyst concentration on the epoxidation rate was subsequently investigated at concentrations of **1a** ranging from 0.1 to 0.45 mol% over a 24 h period at 90 °C (Table 2). Though the epoxidation rate is clearly higher at higher catalyst concentrations (68, 95, and 100% respectively for 0.1, 0.23, 0.45 mol%), the overall epoxide yields obtained with 0.23 and 0.45 mol% catalyst (Table 2, entries 2 and 3) are so close that it can be concluded that once a certain threshold catalyst concentration is attained, the epoxidation rate remains unaffected by further increases in catalyst concentration.

With the reaction conditions optimized (0.45 mol% catalyst at 90 °C), the activities of the different RuPc complexes (**1a**–**1f**) towards the epoxidation of *trans*-stilbene (**8**) with 2,6-DCPNO were thus investigated in a comparative study. With the exception of the **1g**-catalyzed epoxidation (Table 2, entry 8), excellent conversions (> 95%), high yields (> 75%) and excellent selectivities (>75%) were obtained (Table 2). These results furthermore undoubtedly prove that the attachment

of substituents to the non-peripheral positions increases the catalytic activity of the ruthenium phthalocyanines, most probably due to reduced levels of aggregation in solution due to the acquired "saddle shape" [11–13]. It was further evident that activities and selectivities obtained with the linear alkyl catalysts **1a**, **1b,** and **1c** were the same within experimental error (Table 2, entries 3–5) and that these catalysts were more active than the bulkier isopentyl-(**1d**) and cyclohexyl-substituted (**1e**) complexes (Table 2, entries 6 and 7). Optimum yields were obtained within 10 to 12 h with **1a** and **1e**, where after epoxide decomposition resulted in a drop in yield.

Both catalysts **1a** and **1b** were more active towards the catalytic epoxidation of *trans*-stilbene (**8**) than *cis*-stilbene (**10**) (Table 2, entries 3 and 9 for **1a** and entries 7 and 10 for **1e**). These results greatly contrast those obtained in the homogeneous and heterogeneous epoxidation of *trans*-stilbene (**8**) by the ruthenium porphyrin/*N*-oxide system as reported by Hirobe [31], Gross [33], Berkessel [17], and Zhang [30]. These workers reported poor or no epoxidation of this substrate even with highly electron deficient ruthenium porphyrin complexes.

The activity and stability of catalysts **1a** and **1e** during the epoxidation of both *trans*- (**8**) and *cis*-stilbene (**10**) was further evaluated through the determination of turnover number (TON) and frequency (TOF) (Table 3, entries 1 and 4). In this case, the catalyst (0.1 mol%) was reacted with 1000 equiv. of substrate and 1500 equiv. oxidant at 90 °C for 48 h. Since catalyst concentrations were lower, reaction rates also dropped with the consequence of increased decomposition of epoxide **11** and thus lower epoxide yields and selectivities. A relatively high TON of 520 after 48 h at a TOF of 41 h^{-1} were obtained for the epoxidation of *cis*-stilbene (**10**) catalyzed by ruthenium phthallocyanine **1a** (Table 3, entry 1), whereas the bulkier **1e** was less active with a TON of 340 after 48 h at a TOF of 25 h^{-1} (Table 3, entry 4).

Both catalysts **1a** and **1e** once again proved to be more reactive towards *trans*-stilbene (**8**) than *cis*-stilbene (**10**) (Table 3, entry 2 *vs.* 1 and entry 5 *vs.* 4), with turnovers of up to 820 being obtained with complex **1a** after 48 h. For a homogeneous catalytic system, these results are quite pleasing as the best conversion and turnover for *trans*-stilbene (**8**) with homogeneous chiral ruthenium porphyrins were reported to be *ca.* 21% and 270 (after 16 h) [33, 30], respectively, while heterogeneous polymer-supported ruthenium porphyrin catalysts gave 88% conversion and TON of 870 after 24 h [35].

In order to determine if some of the catalyst might have been deactivated by aggregation and to see if differences in catalyst activity could be accentuated, the catalyst concentration was reduced even further to 0.02 mol% (catalyst:alkene:2,6-DCPNO = 1:5000:5000) and the reactions repeated. Although yields and conversions dropped quite dramatically when compared to the reactions performed with 0.1 mole% catalyst (Table 3, entry 3 *vs.* 2 for **1a** and entry 6 *vs.* 5 for **1b**), the increase in turnover numbers indicated that the catalysts were still active up to the end of the reactions as in the previous runs at the higher concentrations.

EXPERIMENTAL

Techniques

All reagents and solvents were of reagent-grade quality purchased from Sigma-Aldrich and were used as supplied. Infrared spectra (thin films between NaCl plates of either pure liquids or Nujol mulls of solids) were recorded on a Hitachi model 270–50 spectrophotometer. UV-vis spectra were recorded on a Varian Cary 50 UV/vis dual beam spectrophotometer at 25 °C. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM 300 or a Bruker 600 FT-spectrometer at 296 K with tetramethylsilane (TMS) as internal standard. Mass spectrometry was performed by means of electron impact (EI) ionization through direct injection onto the mass spectrometer of a Shimadzu GC-MS Qp-2010 gas chromatograph-mass spectrometer. MALDI-TOF spectra were collected by a Bruker Microflex LRF20 in the positive mode with the minimum laser power required to observe signals. High resolution MS (ES-MS, +ve) was performed by either PMBMS, University of KwaZulu-Natal, or Cambridge University Chemical Laboratory. Melting points were recorded on a Barloworld Scientific Stuart Melting

Table 3. Catalytic epoxidation of stilbenes **8** and **10** by 2,6-DCPNO with RuPc complexes **1a** and **1e**

Entry	Alkene	Catalyst	Cat., mol%	Conversion, %	Product (% yield, % selectivity)	TON[a] (TOF[b] (h^{-1}))
1	**10**	**1a**	0.1	64	**11** (40, 63)	520 (41)
2	**8**	**1a**	0.1	100	**9** (82, 82)	820
3	**8**	**1a**	0.02	22	**9** (22, 100)	1085 (151)
4	**10**	**1e**	0.1	46	**11** (26, 57)	340 (25)
5	**8**	**1e**	0.1	68	**9** (59, 87)	590
6	**8**	**1e**	0.02	20	**9** (20, 100)	1002 (93)

[a]Determined after 48 h; [b]Determined after 1 h.

Point (SMP3) apparatus. GC analyses were performed on a Shimadzu GC-2010 fitted with a PONA column (50.0 m × 0.20 mm × 0.50) 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. Products were identified by GC-MS analyses on a Shimadzu GC-MS Qp-2010 fitted with a similar column and operated under conditions similar to that of the GC with helium as carrier gas.

Ligand synthesis

By varying the alkyl groups (-R) on the thiophene, phthalonitriles with carbon side chains of different lengths were synthesized. From these the corresponding metal free and ruthenium complexed phthalocyanines were prepared.

***General procedure A* [13].** Preparation of 2,5-dialkylthiophenes compounds (**5a**–**5e**). In a typical experiment, thiophene (**7**) (9 g, 0.107 mol) in dry THF (50 cm^3) was treated with *n*-butyllithium in hexane (2.5 M, 107 cm^3, 0.267 mol, 2.5 equiv.) at -78 °C under an argon atmosphere. The solution was allowed to warm to room temperature and stirred for 24 h, before it was cooled again to -78 °C and the alkylhalide (2.5 equiv.) added drop wise over 30 min. The mixture was then poured into iced water (500 cm^3) and extracted into diethyl ether (3 × 150 cm^3). The combined organic layers were washed with brine (100 cm^3), dried over magnesium sulfate, filtered, and concentrated under reduced pressure to give the 2,5-dialkylthiophene as a pale yellow oil, which was used without further purification.

2,5-di(2-cyclohexylethyl)thiophene (5e). Using general procedure A, thiophene (**7**) (9 g, 0.107 mol) in dry THF (50 cm^3) was treated with *n*-butyllithium (2.5 M in hexane, 107 cm^3, 0.267 mol, 2.5 equiv.) followed by 2-cyclohexylethylbromide (51 g, 0.267 mol, 2.5 equiv.) to give 2,5-di(2-cyclohexylethyl)thiophene (**5e**) (22.5 g, 69%) as a pale yellow oil. ^{1}H NMR (600 MHz, C_6D_6): δ_H, ppm 6.69 (2H, s), 2.81 (4H, t, J = 7.94), 1.74–1.69 (10H, m), 1.67–1.63 (4H, m), 1.27–1.19 (8H, m) 0.95–0.88 (4H, m). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ_C, ppm 143.44, 123.30, 39.68, 37.38, 33.46–33.44, 27.78, 26.95, 26.93, 26.58. IR (neat): λ_{max}, cm^{-1} 2910, 2850 (CH), 1447, 1346, 1261, 1078, 1025, 962, 889, 843, 797, 689 (CH_3). MS (EI): *m/z* 304 ($[M]^+$, 65%), 126 (C_9H_{18}, 100%). HRMS (ES-MS, +ve): *m/z* $C_{20}H_{33}S^+$ $[M + H]^+$ requires 305.2303, found 305.2307.

***General procedure B* [13].** Preparation of 2,5-dialkylthiophene-1,1-dioxides (**4a**–**4e**). In a typical experiment, a mixture of H_2O (330 cm^3), acetone (240 cm^3) and $NaHCO_3$ (180 g, 2.14 mol) was added to a solution of 2,5-dialkylthiophene (**5**) (0.015 mol) in dichloromethane (270 cm^3) in a 3 litre 2-necked flask equipped with an efficient stirrer and a large CO_2-acetone condenser. The resulting heterogeneous mixture was cooled in an ice bath before solid oxone (300 g, 1.97 mol, 131.4 equiv.) was carefully added over 30 minutes with efficient stirring. Stirring continued for a further 16 h at room temperature before water (1,500 cm^3) was added to dissolve most inorganics. The decanted aqueous layer, and all remaining solids were extracted into dichloromethane (750 cm^3), the combined organic phases washed with water (1,500 cm^3) and dried over magnesium sulfate before solvent removal and re-crystallization of the residue from ethanol gave the 2,5-dialkylthiophene-1,1-dioxides.

2,5-di(2-cyclohexylethyl)thiophene 1,1-dioxide (4e). Using general procedure B: 2,5-di(2-cyclohexylethyl)-thiophene (**5e**) (4.57 g, 0.015 mol), DCM (270 cm^3), H_2O (330 cm^3), acetone (240 cm^3), $NaHCO_3$ (180 g, 2.14 mol), oxone (300 g, 1.97 mol, 131.4 equiv.) gave 2,5-di(2-cyclohexylethyl)thiophene 1,1-dioxide (**4e**) (3.5 g, 69.5%) as off white needles: mp 111 °C. ^{1}H NMR (600 MHz, C_6D_6): δ_H, ppm 5.58 (2H, s), 2.44 (4H, t, J = 7.95), 1.72–1.62 (10H, m), 1.24–1.11 (8H, m), 0.85–0.79 (4H, m). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ_C, ppm 144.32, 121.47, 37.20, 33.95, 33.00, 26.51, 26.19, 21.69. IR (neat): λ_{max}, cm^{-1} 2957, 2918, 2850, 1469, 1445, 1385, 1367, 1277 (–SO_2), 1139 (–SO_2), 1118, 1097, 841, 627, 610, 558. MS (EI): *m/z* 336.30 ($[M]^+$, 33.42%), 185.15 (100%). HRMS (ES-MS, +ve): *m/z* $C_{20}H_{32}O_2SNa^+$ $[M + Na^+]$ requires 359.2021, found 359.2196.

***General procedure C* [13].** Preparation of 3,6-dialkyl-phthalonitriles (**3a**–**3e**). In a typical experiment, 2,5-dialkylthiophene-1,1-dioxide (**4**) (0.015 mol) and fumaronitrile (1.14 g, 0.015 mol, 1 equiv.) in chloroform (1 cm^3) were heated in a sealed tube at 150 °C for 18 h. The contents of the tube were dissolved in chloroform and the solvent removed under reduced pressure at 90 °C until the residue stopped liberating bubbles. The dark residue was then purified by column chromatography over silica gel with toluene as eluent to give the 3,6-dialkylphthalonitrile.

3,6-di(2-cyclohexylethyl)phthalonitrile (3e). Using general procedure C: 2,5-di(2-cyclohexylethyl)thio-phene-1,1-dioxide (**4e**) (5.0 g, 0.015 mol), fumaronitrile (1.14 g, 0.015 mol, 1 equiv.), in chloroform (1 cm^3) gave 3,6-di(2-cyclohexylethyl)phthalonitrile (**3e**) (2 g, 40%) as off white needles: mp 147.5 °C. ^{1}H NMR (300 MHz, C_6D_6): δ_H, ppm 6.75 (2H, s), 2.60 (4H, t, J = 8.27), 1.75 (10H, m), 1.41–1.34 (2H, m), 1.26–1.15 (8H, m), 0.99–0.88 (4H, m). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ_C, ppm 146.56, 133.37, 115.59, 115.09, 38.51, 37.40, 33.06, 31.92, 26.49, 26.18. IR (neat): λ_{max}, cm^{-1} 2919, 2855, 2845, 2226 (C≡N), 2147, 1556, 1486, 1236, 1187, 882, 841, 660, 595, 557. MS (EI): *m/z* 348.30 ($[M]^+$, 100%). HRMS (ES-MS, +ve): *m/z* $C_{24}H_{32}N_2Na^+$ $[M + Na]^+$ requires 371.2463, found 371.2455.

***General procedure D* [13].** Preparation of 1,4,8,11,15,18,22,25-octaalkyl-phthalocyanines (**2a**–**2e**). In a typical experiment, 3,6-dialkylphthalonitrile (**3**) (0.001 mol) was dissolved in warm (80 °C) pentanol (10 cm^3). An excess of clean lithium metal (0.35 g, 0.05 mol, 30–40 equiv.) was added in small portions at 110 °C and the mixture refluxed for 16 h. The cooled (rt) deep green coloured suspension was stirred with acetone (50 cm^3), the solution filtered, and the solids washed with acetone (50 cm^3) before the combined acetone solutions were concentrated *in vacuo* to *ca.* 25 cm^3. Acetic acid (50 cm^3) was added, the heterogeneous mixture stirred for 30 min, and the precipitate collected to afford, after recrystallization from THF-methanol, the 1,4,8,11,15,18,22,25-octaalkyl-phthalocyanine.

1,4,8,11,15,18,22,25-octa(2-cyclohexylethyl)phthalocyanine (2e). Using general procedure D: 3,6-di(2-cyclohexylethyl)phthalonitrile (**3e**) (0.35 g, 0.001 mol), warm pentanol (10 cm^3), and clean lithium metal (0.35 g, 0.05 mol) gave 1,4,8,11,15,18,22,25-octa(2-cyclohexylethyl)phthalocyanine (**2e**) (0.19 g, 14%) as a green solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H, ppm 7.88 (8H, s), 4.48 (16H, t, J = 7.7), 1.95–1.90 (32H, m), 1.69–1.64 (24H, m), 1.27–1.18 (32H, m), 1.04–0.98 (16H, m). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ_C, ppm 139.14, 130.57, 77.21, 77.00, 76.79, 38.28, 37.26, 33.71, 29.89, 29.69, 26.73, 26.42. UV-vis (petroleum ether): λ, nm (log ε) 734 (0.91), 695 (0.79), 674 (0.26), 639 (0.10), 364 (0.30). IR (neat): λ_{max}, cm^{-1} 3300 [N–H], 3302, 2910, 2848, 1596, 1508, 1425, 1313, 1032, 882, 816, 762, 716. MS (MALDI-TOF): *m/z* 1396.04 [M].

Synthesis of the carbonylphthalocyanine ruthenium complexes

General procedure E. Preparation of ruthenium(II) carbonyl(1,4,8,11,15,18,22,25-octaalkylphthalocyanines (**1a**–**1e**) [21]. To a flame dried flask under an argon atmosphere was added 1,4,8,11,15,18,22,25-octaalkylphthalocyanine (**2**) (0.23 mmol) and triruthenium dodecacarbonyl (0.3 g, 0.47 mmol, 2 equiv.). Benzonitrile (10 cm^3) was added and the reaction mixture was heated at reflux for 100 min. The cooled reaction mixture was poured into cold methanol (400 cm^3) causing the formation of some crystals. After cooling to 5 °C for a further 72 h, the excess solvent was decanted. The crude product was purified by flash column chromatography (eluting with methanol to remove benzonitrile and then with petroleum ether 40–60 °C). Reprecipitation (petroleum ether-methanol) gave the 1,4,8,11,15,18,22,25-octaalkylphthalocyaninatoruthenium.

Carbonyl(1,4,8,11,15,18,22,25-octahexylphthalocyaninato)ruthenium(II) (1a). Using general procedure E: 1,4,8,11,15,18,22,25-octahexylphthalocyanine [11] (**2a**) (0.28 g, 0.23 mmol), triruthenium dodecacarbonyl (0.3 g, 0.47 mmol, 2 equiv.), benzonitrile (10 cm^3), gave carbonyl(1,4,8,11,15,18,22,25-octahexylphthalocyaninato)ruthenium(II) (**1a**) (0.25 g, 80%) as a dark blue amorphous solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H, ppm 7.87 (8H, s), 4.65–4.62 (8H, m), 4.59–4.55 (8H, m), 2.30–2.22 (16H, m), 1.75–1.68 (16H, m), 1.46–1.39 (16H, m), 1.38–1.34 (16H, m), 0.89 (24H, t, J = 7.2). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ_C, ppm 183.34, 145.17, 137.95, 136.57, 129.79, 32.68, 32.31, 30.88, 29.10, 22.76, 14.15. UV-vis (petroleum ether): λ, nm (log ε) 660 (4.84). IR (neat): λ_{max}, cm^{-1} 2953, 2925, 2855, 1958 (Ru-C=O), 1600, 1573, 1468, 1433, 1329, 1261, 1167, 1108, 1017, 911, 801, 726.1936. MS (MALDI-TOF): *m/z* 1313.688 [M], 1295 [M - CO]. HRMS (ES-MS, +ve): *m/z* $C_{81}H_{112}N_8ORu$ requires 1314.7997 found 1314.8062.

Carbonyl(1,4,8,11,15,18,22,25-octaoctylphthalocyaninato)ruthenium(II) (1b) [21]**.** Using general procedure E: 1,4,8,11,15,18,22,25-octaoctylphthalocyanine [11] (**2b**) (0.33 g, 0.23 mmol), triruthenium dodecacarbonyl (0.3 g, 0.47 mmol, 2 equiv.), benzonitrile (10 cm^3) gave carbonyl(1,4,8,11,15,18,22,25-octaoctylphthalocyaninato)ruthenium(II) [16] (**1b**) (0.3 g, 86%) as a dark blue amorphous solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H, ppm 7.86 (8H, s), 4.65–4.60 (8H, m), 4.57–4.52 (8H, m), 2.27–2.22 (16H, m), 1.72–1.67 (16H, m), 1.46–1.39 (16H, m), 1.35–1.29 (16H, m), 1.27–1.23 (32H, m), 0.84 (24H, t, J = 6.9). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ_C, ppm 180.25, 145.16, 137.93, 136.57, 129.72, 32.62, 31.91, 30.89, 30.01, 29.40, 29.36, 22.62, 14.02. UV-vis (petroleum ether): λ, nm (log ε) 670 (5.21). IR (neat): λ_{max}, cm^{-1} 2954, 2922, 2852, 1963 (Ru-C=O), 1502, 1466, 1328, 1167, 1112, 913, 721. MS (MALDI-TOF): *m/z* 1539.777 [M], 1511.85 [M–CO]. HRMS (ES-MS, +ve): *m/z* $C_{97}H_{144}N_8ORu$ requires 1539.0501, found 1539.0474.

Carbonyl(1,4,8,11,15,18,22,25-octadodecylphthalocyaninato)ruthenium(II) (1c). Using general procedure E: 1,4,8,11,15,18,22,25-octadodecylphthalocyanine [13] (**2c**) (0.43 g, 0.23 mmol), triruthenium dodecacarbonyl (0.3 g, 0.47 mmol, 2 equiv.), and benzonitrile (10 cm^3) gave carbonyl(1,4,8,11,15,18,22,25-octadodecylphthalocyaninato)-ruthenium(II) (**1c**) (0.32 g, 70%) as a dark blue amorphous solid. ^{1}H NMR (600 MHz, C_6D_6 with a drop of pyridine): δ_H, ppm 7.95 (8H, d, J = 22.9 Hz), 5.05–4.70 (16H, m), 2.49–2.41 (16H, m), 1.89–1.84 (17H, m), 1.57–1.37 (128H, m), 0.95 (24H, t, J = 6.7 Hz). ^{13}C NMR (150.9 MHz, C_6D_6 + pyridine): δ_C, ppm 181.24, 145.37, 138.13, 137.40, 130.08, 32.84, 32.36, 32.02, 31.14, 30.29, 29.91, 29.84, 29.59, 29.51, 29.15, 22.81, 14.07. UV-vis (petroleum ether): λ, nm (log ε) 685 (4.85). IR (neat): λ_{max}, cm^{-1} 2921, 2852, 1967 (Ru-C=O), 1456, 1328, 1172, 1111, 1021, 803, 720. MS (MALDI-TOF): *m/z* 1988.324 [M], 1960.862 [M–CO]; $C_{129}H_{208}N_8ORu{\cdot}CH_3OH$ requires 2020.5810, found 2020.5658.

Table 4. Reagent ratios

Catalyst (mole%)	Stilbene	Dodecane	2,6-DNPNO
0.45	110 μmol, 220 equiv.	25 μl, 110 μmol, 220 equiv.	27 mg, 165 μmol, 330 equiv.
0.1	500 μmol, 1000 equiv.	114 μl, 500 μmol, 1000 equiv.	122 mg, 750 μmol, 1500 equiv.
0.02	2500 μmol, 5000 equiv.	570 μl, 2500 μmol, 5000 equiv.	615 mg, 3750 μmol, 7500 equiv.

Carbonyl(1,4,8,11,15,18,22,25-octaisopentylphthalocyaninato)ruthenium(II) (1d). Using general procedure E: 1,4,8,11,15,18,22,25-octaisopentylphthalocyanine [11] (**2d**) (0.25 g, 0.23 mmol), triruthenium dodecacarbonyl (0.3 g, 0.47 mmol, 2 equiv.), and benzonitrile (10 cm^3) gave carbonyl(1,4,8,11,15,18,22,25-octaisopentylphthalocyaninato)-ruthenium(II) (**1d**) (0.18 g, 65%) as a dark blue amorphous solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H, ppm 7.86–7.81 (8H, d, J = 13), 4.67–4.61 (8H, m), 4.60–4.55 (8H, m), 2.12–2.08 (16H, m), 1.97–1.93 (8H, m, H-3'), 1.09 (48H, d, J = 6.5). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ_C, ppm 174.77, 145.03, 138.05, 136.62, 129.62, 40.29, 30.23, 27.13, 23.12. UV-vis (petroleum ether): λ, nm (log ε) 675 (4.70). IR (neat): λ_{max}, cm^{-1} 2952, 2929, 2866, 1958 (Ru-C=O), 1601, 1502, 1449, 1329, 1180, 1104, 1025, 917, 794, 759. MS (MALDI-TOF): *m/z* 1174.681 [M–CO]. HRMS (ES-MS, +ve): *m/z* $C_{73}H_{96}N_8ORu$ requires 1202.6751, found 1202.6756.

Carbonyl[1,4,8,11,15,18,22,25-octa(2-cyclohexylethylphthalocyaninato]ruthenium(II) (1e). Using general procedure E: 1,4,8,11,15,18,22,25-octa(2-cyclohexylethyl)phthalocyanine (**2e**) (0.33 g, 0.23 mmol), triruthenium dodecacarbonyl (0.3 g, 0.47 mmol, 2 equiv.), and benzonitrile (10 cm^3) gave cabonyl-[1,4,8,11,15,18,22,25-octa(2-cyclohexylethyl)-phthalocyaninato]-ruthenium(II) (**1e**) (0.25 g, 70%) as a dark blue amorphous solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H, ppm 7.84 (8H, s), 4.65–4.61 (8H, m), 4.60–4.56 (8H, m), 2.10 (16H, dd, J = 14.4, 7.4), 2.02 (16H, s, br), 1.76 (16H, d, J = 12.3), 1.73–1.65 (16H, m), 1.34–1.21 (24H, m), 1.09 (16 H, dd, J = 24.0, 12.0). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ_C, ppm 183.32, 145.13, 138.20, 136.56, 129.58, 38.70, 36.85, 33.88, 29.59, 26.82, 26.50. UV-vis (petroleum ether): λ, nm (log ε) 680 (4.40). IR (neat): λ_{max}, cm^{-1} 2920, 2854, 2227, 1972 (Ru-C=O), 1456, 1326, 1077, 1035, 881, 796. MS (MALDI-TOF): *m/z* 1494.863 [M–CO].

Catalysis

A 15 mL Schlenk flask was charged with catalyst **1a** (0.7 mg, 0.5 μmol, 1 equiv.) or **1e** (0.8 mg, 0.5 μmol, 1 equiv.), stilbene, dodecane (internal standard) and dry toluene (2 mL) under an argon atmosphere (Table 4). 2,6-Dichloropyridine-*N*-oxide (2,6-DNPNO) was added and the solution stirred at 90 °C. Reactions were followed by gas chromatography.

CONCLUSION

Sterically hindered RuPc complexes with non-peripheral hexyl- (**1a**), octyl- (**1b**), dodecyl- (**1c**), isopentyl- (**1d**) and 2-cyclohexylethylsubstituents (**1e**), have been synthesized and characterized by NMR, IR, UV-vis, MS and elemental analysis. Compound **1b** had been previously reported in literature [10, 16], while compounds **1a**, **1c**, **1d**, and **1e** prepared by extending the procedure for **1b** to a range of ligands, are new compounds. The formation of a huge amount of by-product alongside the metal-free Pcs (**2a**–**2e**) during cyclisation of the phthalonitriles (**3a**–**3e**) in refluxing pentanol largely account for the poor yields observed in this step. Improving on the yield of this step would be critical if these compounds are to be used as catalysts and this aspect will receive attention in a follow-up study.

In this study it was also demonstrated for the first time that ruthenium phthalocyanines can be used in the epoxidation 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 mol%). Complete conversion and high turnovers (>800 in 48 h for 0.1% catalyst load), comparable to or better than those published for other catalytic systems, could be obtained for *trans*-stilbene (**8**). At low catalyst loading (0.02 mole%), TONs above 1000 in 48 h and TOFs above 90 h^{-1} could be obtained for *trans*-stilbene (**8**). The epoxidation of *trans*-stilbene (**8**) proceeded unexpectedly facile, whereas results for *cis*-stilbene (**10**) were comparable to those reported for other catalytic systems (*vide supra*).

All substituted ruthenium phthalocyanines (**1a**–**1e**) performed markedly better as epoxidation catalysts than the unsubstituted equivalent (**1g**), 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 substituents attached to the phthalocyanine lowered the catalytic activity to some extent.

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