Dendritic Ruthenium Porphyrins: A New Class of Highly Selective Catalysts for Alkene Epoxidation and Cyclopropanation

Jun-Long Zhang, Hai-Bing Zhou, Jie-Sheng Huang, and Chi-Ming Che*[a]

Abstract: Attachment of Fréchet-type poly(benzyl ether) dendrons [G-*n*] to carbonylruthenium(II) *meso*-tetraphenylporphyrin (**5**) using covalent etheric bonds forms a series of dendritic ruthenium(II) porphyrins **5**-$[G\text{-}n]_m$ ($m=4$, $n=1$, 2; $m=8$, $n=0-2$). The attachment was realized by treating the carbonylruthenium(II) complex of 5,10,15,20-tetrakis(4′-hydroxyphenyl)porphyrin or 5,10,15,20-tetrakis(3′,5′-dihydroxyphenyl)porphyrin with $[G\text{-}n]OSO_2Me$ in refluxing dry acetone in the presence of potassium carbonate and [18]crown-6. Complexes **5**-$[G\text{-}n]_m$ were characterized by UV/Vis, IR, and NMR spectroscopy and mass spectrometry. All of the dendritic ruthenium porphyrins are highly selective catalysts for epoxidation of alkenes with 2,6-dichloropyridine *N*-oxide (Cl_2pyNO). The chemo- or diastereoselectivity increases with the generation number of the dendron and the number of dendrons attached to **5**, and complex **5**-$[G\text{-}2]_8$ exhibits remarkable selectivity or turnover number in catalyzing the Cl_2pyNO epoxidation of a variety of alkene substrates including styrene, *trans*-/*cis*-stilbene, 2,2-dimethylchromene, cyclooctene, and unsaturated steroids such as cholesteryl esters and estratetraene derivative. The cyclopropanation of styrene and its *para*-substituted derivatives with ethyl diazoacetate catalyzed by **5**-$[G\text{-}2]_8$ is highly *trans* selective.

Keywords: cyclopropanation · dendrimers · epoxidation · homogenous catalysis · porphyrinoids · ruthenium

Introduction

The construction of dendritic architecture on metal complexes provides a rapidly growing family of macromolecules, namely metallodendrimers,[1a] which exhibit a wide variety of unusual structural and functional properties.[1] For example, attachment of dendritic wedges to a homogeneous metal catalyst can endow the catalyst molecule with a soluble, well-defined nanoscale structure, allowing facile separation of the catalyst from the products by membrane or nanofiltration techniques with no loss of the advantages of homogenous catalysts.[2] This is different from immobilization of metal catalysts onto insoluble supports such as molecular sieves or organic polymers. On the other hand, the dendritic wedges on a metal catalyst can induce a regioselectivity or shape-selectivity by creating a proper environment around the metal center,[3] and can stabilize the catalytic center by providing an efficient site isolation in a manner similar to the peptide architecture of enzymes in biological systems.[1b] These attractive features, along with our continuing interest in developing new ruthenium porphyrin catalysts for hydrocarbon functionalizations, prompted us to attach dendritic wedges to ruthenium porphyrins.

Ruthenium porphyrins have been shown to be efficient catalysts for a variety of organic reactions, such as epoxidation[4]/aziridination[5]/cyclopropanation[6] of alkenes, and hydroxylation[7]/amidation[5b,c, 8] of alkanes. To make the catalysts readily separable from the products and reusable, we previously grafted carbonylruthenium(II) porphyrins [Ru(Por)(CO)] (Por = dianions of *meso*-tetrakis(4-chlorophenyl)-porphyrin: **1**; *meso*-tetrakis(2,6-dichlorophenyl)porphyrin: **2**; 5,10,15-tris(4′-R-phenyl)-20-(4″-hydroxyphenyl)porphyrin: **3** (R = Cl) or **4** (R = Me)) onto a surface-modified mesoporous molecular sieve (MCM-41)[9] or the Merrifield's peptide resin (MPR)[10] and prepared catalysts **1**-MCM-41, **2**-MCM-41, **3**-MPR, and **4**-MPR. The catalytic behavior of these catalysts toward alkene epoxidations with 2,6-dichloropyridine *N*-oxide (Cl_2pyNO) or *tert*-butyl hydroperoxide has been examined, which reveals a high shape-selectivity for **2**-MCM-41 and a high diastereoselectivity and versatility for **3**-MPR. However, grafting **1**–**4** onto MCM-41 or MPR invariably renders the catalysts insoluble in the catalytic systems, making it hard to elucidate the mechanism of the catalytic processes. Further, the local environments around the catalytic centers in these catalysts can not be clearly defined, and their activity or selectivity is not readily tunable by rational modification of the structures of such solid supports.

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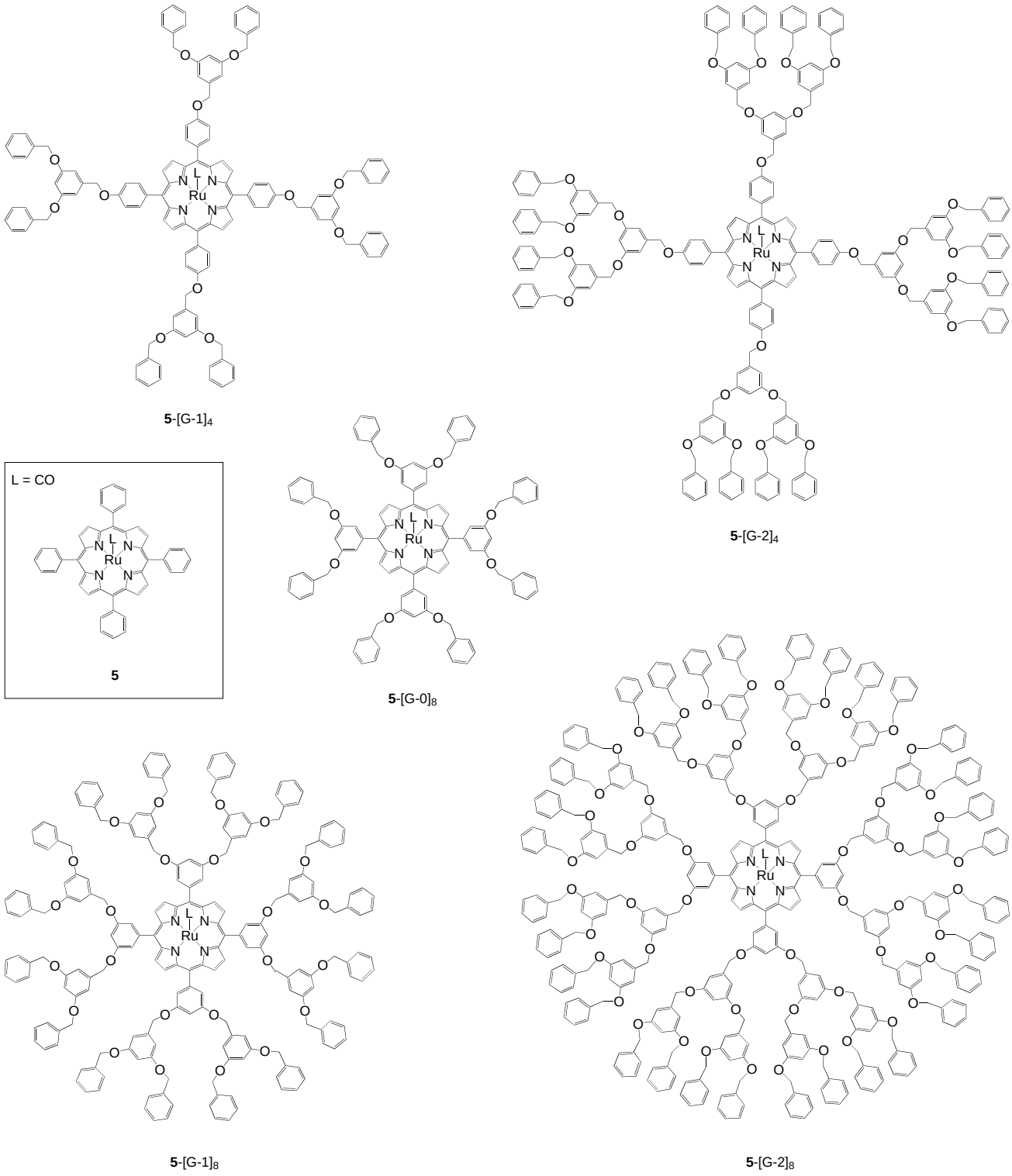
  0947-6539/02/0807-1554 $ 20.00+.50/0

Herein, we report on the attachment of readily accessible Fréchet-type poly(benzyl ether) dendrons [G-*n*] (*n* is the generation number of the dendrons)[11] to carbonylruthenium(II) porphyrin [Ru(tpp)(CO)] (**5**, tpp = *meso*-tetraphenylporphyrinato dianion) with covalent etheric bonds to form new ruthenium(II) porphyrin complexes **5**-[G-*n*]$_m$ (Scheme 1, *m* is the total number of dendrons attached to the tpp macrocycle), which represent the first examples of a dendritic ruthenium porphyrin. All the dendritic ruthenium(II) porphyrins are soluble in common organic solvents such as dichloromethane and acetone. The dendritic architecture around **5** in **5**-[G-*n*]$_m$ can be fine tuned by variables *n*, *m*, and by the location of the dendrons on the *meso*-phenyl groups of the porphyrin core. Examination of the catalytic behavior of **5**-[G-*n*]$_m$ toward alkene epoxidation with Cl_2pyNO discloses that these dendritic ruthenium complexes are highly selective



Scheme 1. Schematic structures of the dendritic ruthenium porphyrins **5**-[G-*n*]$_m$ ($m = 4$, $n = 1, 2$; $m = 8$, $n = 0-2$) prepared in this work.

  0947-6539/02/0807-1555 $ 20.00+.50/0

catalysts for such a catalytic process, and that **5**-[G-2]$_8$ is a remarkable catalyst for epoxidation of natural products such as steroids. Prior to this work, no dendritic metalloporphyrin-catalyzed epoxidation of steroids has been reported. Interestingly, **5**-[G-2]$_8$ is also effective and highly diastereoselective in catalyzing the cyclopropanation of styrenes with ethyl diazoacetate (EDA), contributing the first alkene cyclopropanation catalyzed by a dendritic metalloporphyrin.

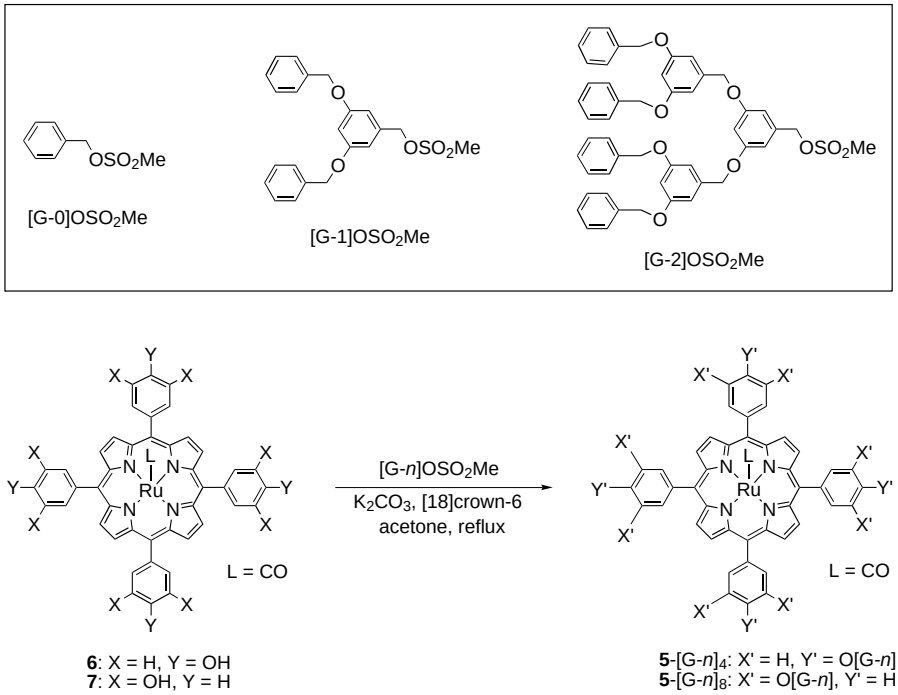
Results and Discussion

Synthesis and characterization of dendritic ruthenium(II) porphyrins 5-[G-*n*]$_m$: Dendritic metalloporphyrins can be prepared either by direct insertion of metal ions into a dendritic porphyrin free base or by attaching dendritic wedges to a simple metalloporphyrin;[1b] the latter method was employed in this work. To attach the poly(benzyl ether) dendrons [G-*n*] to **5** and prepare **5**-[G-*n*]$_m$ ($m = 4$, 8), it is necessary to functionalize the *meso*-phenyl groups of **5** to phenol groups to form the carbonylruthenium(II) porphyrins **6** and **7** shown in Scheme 2. This was readily achieved by treating [$Ru_3(CO)_{12}$] with 5,10,15,20-tetrakis(4′-hydroxyphenyl)porphyrin or 5,10,15,20-tetrakis(3′,5′-dihydroxyphenyl)-porphyrin free base, respectively, in refluxing 2,4,6-trichlorobenzene under nitrogen, which afforded **6** or **7** as red purple crystals in ≈70% yields.

We then treated **6** or **7** with excess dendritic mesylates [G-*n*]OSO_2Me ($n = 0-2$) in refluxing dry acetone in the presence of potassium carbonate and [18]crown-6 under a nitrogen atmosphere to form **5**-[G-*n*]$_m$ ($m = 4$ and 8 for **6** and **7**, respectively), as shown in reaction (1) of Scheme 2. The phenolic etherification reaction proceeded markedly faster for **6** than for **7**. The desired dendritic ruthenium porphyrins **5**-[G-*n*]$_m$ ($m = 4$, $n = 1,2$; $m = 8$, $n = 0-2$) were isolated in 15–80% yields after purification by chromatography, with higher yields obtained for the complexes of smaller *m* or *n* values. The decrease in the yield of **5**-[G-*n*]$_m$ with increasing *n* or *m* values is not surprising, since formation of **5**-[G-*n*]$_4$ and **5**-[G-*n*]$_8$ from **6** and **7**, respectively, requires alkylation of all the hydroxyl groups (O-alkylation) in **6** or **7**. This should become more difficult as more dendrons are attached or as the dendritic wedge grows, both of which would dramatically increase the steric hindrance encountered in the reaction. Note that previous attachments of Fréchet-type poly(benzyl ether) dendrons to a simple zinc porphyrin or a porphyrin free base all employ [G-*n*]Br rather than [G-*n*]OSO_2Me as the O-alkylating reagent.[12] We found that, however, the use of [G-*n*]Br instead of [G-*n*]OSO_2Me for reaction (1) rendered it hard to separate the desired dendritic ruthenium porphyrins **5**-[G-*n*]$_4$ and **5**-[G-*n*]$_8$ from unreacted [G-*n*]Br by chromatography.

Like the carbonylruthenium(II) complexes of other *meso*-tetraarylporphyrin macrocycles reported in the literature,[13] complexes **6** and **7** show Soret bands at ≈412 nm and β bands at ≈530 nm in their UV/Vis spectra and exhibit intense ν(CO) bands at ≈1935 cm^{-1} in their IR spectra. Similar spectral features were observed for **5**-[G-*n*]$_4$ and **5**-[G-*n*]$_8$, consistent with the presence of a carbonylruthenium(II) porphyrin core in these dendritic metal complexes. The mass spectra of **6**, **7**, **5**-[G-*n*]$_4$, and **5**-[G-*n*]$_8$ all display the cluster peaks attributable to the fragments $[M - CO]^+$, and for **6**, **7**, and the dendritic complexes with smaller *n* values **5**-[G-1]$_4$ and **5**-[G-0]$_8$, the cluster peaks assignable to the respective parent ions $[M]^+$ are also located. The lack of peaks corresponding to **5**-[G-*n*]$_x$ with $x < 4$ in the mass spectra of **5**-[G-*n*]$_4$ or corresponding to **5**-[G-*n*]$_y$ with $y < 8$ in those of **5**-[G-*n*]$_8$ provides some evidence for the absence of partially *O*-alkylated species in **5**-[G-*n*]$_4$ and **5**-[G-*n*]$_8$.

^{1}H NMR spectroscopy provides invaluable information about the identity and purity of **6**, **7**, **5**-[G-*n*]$_4$, and **5**-[G-*n*]$_8$, the types of protons in which are depicted in Scheme 3. These complexes have a pseudo-C_{4v} symmetry. Their *meso*-phenyl groups are nearly perpendicular to the porphyrin plane.[14] Therefore, for each of these complexes, the pyrrole protons of the porphyrin ring (H_β, not shown in Scheme 3) are basically identical; the ortho protons of the *meso*-phenyl groups can be divided into two different sets (H_o and H_o'). Moreover, there are two different sets of the meta protons (H_m and H_m') in **6** or **5**-[G-*n*]$_4$ and two different sets of [G-*n*] groups ([G-*n*] and [G-*n*]′) in **5**-[G-*n*]$_8$. These structural features are in good agreement



Scheme 2. Synthesis of dendritic ruthenium porphyrins **5**-[G-*n*]$_4$ ($n = 1$, 2) and **5**-[G-*n*]$_8$ ($n = 0$, 1, 2).

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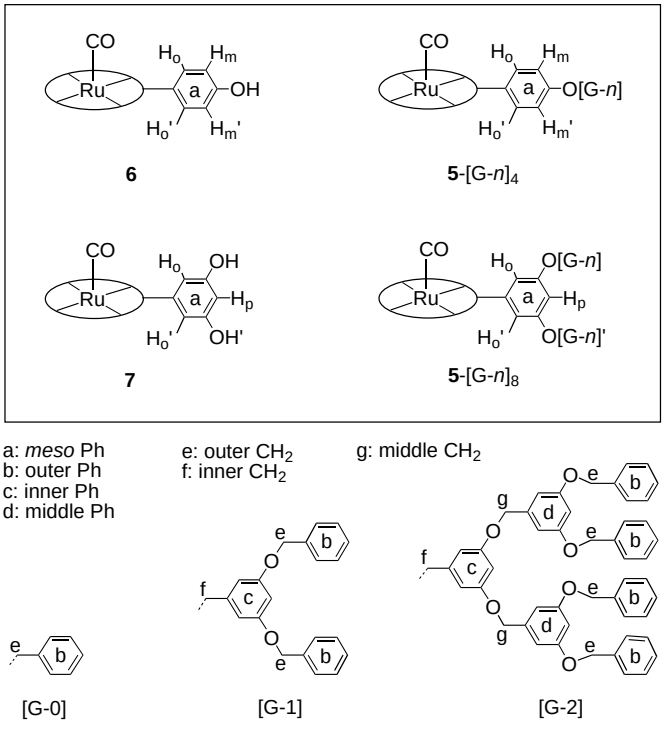


Scheme 3. The labeling of various types of protons in dendritic ruthenium(II) porphyrins **5**-[G-n]$_m$.

with the ^{1}H NMR spectra observed for **6**, **7**, **5**-[G-n]$_4$, and **5**-[G-n]$_8$, as is evident from the spectral data compiled in the Experimental Section.[15]

Epoxidation of alkenes catalyzed by dendritic ruthenium(II) porphyrins 5-[G-*n*]$_m$: Alkene epoxidation is of particular importance in the functionalization of C=C bonds, providing a unique access to epoxides, which are versatile starting materials or key intermediates in organic syntheses. The epoxidation of alkenes catalyzed by metal complexes has been subjected to tremendous investigations; however, few of these metal catalysts reported so far contain a dendritic architecture.[3, 16, 17]

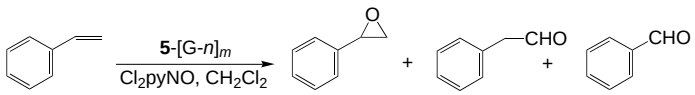
Meanwhile, alkene epoxidation is one of the most important reactions catalyzed homogeneously by cytochrome P-450 enzymes in biological systems.[18] The active center in these enzymes is an iron porphyrin embedded in the interior of a peptide shell. Since dendritic metalloporphyrins feature a metalloporphyrin core embedded in the interior of dendritic shells, and may reach a size or shape roughly comparable to those of cytochrome P-450 enzymes yet remain soluble in common solvents, they (particularly those containing the metal centers of iron and its congener ruthenium) are probably better synthetic analogues for cytochrome P-450 enzymes than simple metalloporphyrins or the metalloporphyrins immobilized onto solid supports.

Dendritic metalloporphyrins first appeared in the literature in 1993[19] and have been investigated in considerable detail regarding their photophysical, electrochemical, and dioxygen-binding properties.[1] Although numerous investigations on metalloporphyrin-catalyzed alkene epoxidations have been reported,[20] and a good number of heterogenized metalloporphyrin epoxidation catalysts have been developed,[10] the epoxidation of alkenes catalyzed by a dendritic metalloporphyrin is rarely studied. In a pioneering work by Moore, Suslick, and their co-workers,[3] attachment of poly(phenyl ester) dendrons with generation numbers of 1 and 2 to a simple manganese porphyrin catalyst, [Mn^{III}(tpp)Cl], with covalent esteric bonds, results in a significantly higher regioselectivity or shape-selectivity in catalyzing epoxidation of nonaromatic alkenes with iodosylbenzene (PhIO). Subsequent work by Kimura, Shirai, and co-workers also demonstrated that an iron porphyrin containing rigid 1,3,5-phenylene-based dendrons with generation number of 2 catalyzes the PhIO epoxidation of nonaromatic alkenes with a remarkably higher shape selectivity than [Fe^{III}(tpp)Cl)].[17]

Despite the foregoing remarkable enhancement in regioselectivity or shape selectivity, a number of questions concerning dendritic metalloporphyrin-catalyzed alkene epoxidations remain to be answered: 1) can dendritic wedges enhance the chemoselectivity (that is, the yield ratio of epoxide product versus other oxidation products) of the metalloporphyrin catalysts, 2) for a certain type of dendron, how does the number or location of the dendrons on the porphyrin macrocycle affect the catalytic behavior of the catalysts, and 3) are dendritic metalloporphyrins versatile catalysts for alkene epoxidation? These questions naturally arise because of the following aspects in the reported epoxidation reactions catalyzed by dendritic manganese or iron porphyrins.[3, 17] First, those epoxidation reactions were all performed by employing a large excess of alkene substrates with the oxygen donor as the limiting reagent, a condition that renders it hard to examine the mass balance in the catalytic processes, which is essential for assessing the chemoselectivity of the catalysts. Second, for a certain type of dendron, only the effect of the generation number of the dendron on the catalytic properties is investigated. Third, all the substrates studied, except *trans*-β-methylstyrene, are simple aliphatic or alicyclic alkenes such as 1-octene/hexene, cyclooctene/cyclohexene, and 1,4-octadiene. The performance of dendritic metalloporphyrins in catalyzing epoxidation of other alkenes such as steroids (which are well-known endogenous substrates of cytochrome P-450 enzymes[18]) remains unclear.

To answer the questions 1) and 2), we examined the catalytic behavior of the dendritic ruthenium porphyrins **5**-[G-n]$_m$ toward epoxidation of styrene (**8**) with excess Cl_2pyNO. We chose Cl_2pyNO rather than PhIO as the oxygen donor because of the exceptional catalytic properties of certain ruthenium porphyrins for alkene epoxidation with Cl_2pyNO.[4c, 9b, 10] Table 1 shows the results obtained for the reaction of styrene with 1.1 equivalents of Cl_2pyNO in dichloromethane at room temperature in the presence of $\approx$0.03 mol% of **5**-[G-n]$_m$. Under these conditions, the reaction afforded styrene oxide (**9**) in 82–94% yields (depending on the m and n values in **5**-[G-n]$_m$) with styrene conversions close to 100%, accompanied by formation of small or trace amounts of phenylacetaldehyde (**10**) and benzaldehyde (**11**) (see reaction (2) in Table 1).[21] The ratio of the yield of **9** versus the sum of the yields of **10** and **11** (which can be considered as the chemoselectivity in reaction (2)) for each of catalysts **5**-[G-n]$_m$ is also listed in Table 1.

Table 1. Epoxidation of styrene with Cl_2pyNO catalyzed by dendritic ruthenium(II) porphyrins **5**-[G-*n*]$_m$.[a]



8 **9** **10** **11**

Entry	Catalyst	Conversion [%]	Yield [%][b]			Chemoselectivity[c]
			9	**10**	**11**	
1	**5**-[G-0]$_8$	> 99	82	18	trace	4.6
2	**5**-[G-1]$_8$	98	90	10	trace	9.0
3	**5**-[G-2]$_8$	99	94	3	3	16
4	**5**-[G-1]$_4$	> 99	84	16	trace	5.3
5	**5**-[G-2]$_4$	> 99	88	11	1	7.3

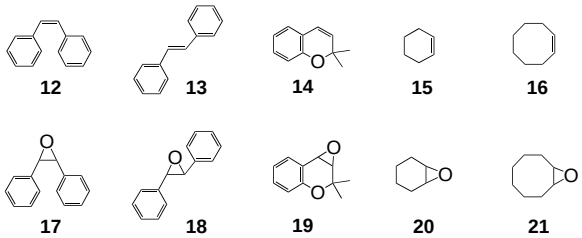
[a] All reactions were carried out at room temperature for 48 h with a catalyst:Cl_2pyNO: alkene molar ratio of 1:3300:3000. [b] Based on the amount of styrene consumed. [c] Defined as the ratio of the yield of **9** versus the sum of the yields of **10** and **11**.

It is reported that complex **5** catalyzes the epoxidation of styrene with Cl_2pyNO to form epoxide **9** in 25% yield under the conditions analogous to those for **5**-[G-*n*]$_m$.[4c] Evidently, attachment of the poly(benzyl ether) dendrons [G-*n*] to **5** to produce **5**-[G-*n*]$_m$ dramatically increased the epoxide yield in the catalytic styrene oxidation reaction.[22] Worthy of note is that the chemoselectivity of the dendritic catalysts **5**-[G-*n*]$_m$ significantly increases with the generation number of the attached dendrons. For example, in the case of catalysts **5**-[G-*n*]$_8$, increasing the generation number of the dendron from 0 to 2 led to an over threefold increase in the chemoselectivity (entries 1–3, Table 1). On the other hand, since higher chemoselectivity was obtained for **5**-[G-*n*]$_8$ than for **5**-[G-*n*]$_4$ (compare entries 2 and 4, or entries 3 and 5, Table 1), it appears that attaching more dendritic wedges [G-*n*] to the ruthenium porphyrin is beneficial to enhancement of the chemoselectivity.

The results in Table 1 indicate that catalyst **5**-[G-2]$_8$ shows higher chemoselectivity than any of the other **5**-[G-*n*]$_m$ catalysts. Therefore, unless otherwise specified, the catalyst employed for the subsequent catalytic studies described in this work was always **5**-[G-2]$_8$. Time-course experiments for reaction (2) in Table 1 catalyzed by **5**-[G-2]$_8$ revealed that the reaction proceeded smoothly without an induction period. The total turnover number of **5**-[G-2]$_8$ in this reaction was 2.9×10^3, indicating that this dendritic ruthenium porphyrin catalyst is highly robust toward the styrene oxidation reactions.[23]

To answer question 3) above, we first investigated the catalytic properties of **5**-[G-2]$_8$ for Cl_2pyNO epoxidation of other aromatic alkenes including *cis*-stilbene (**12**), *trans*-stilbene (**13**), and 2,2-dimethylchromene (**14**) and cyclic alkenes including cyclohexene (**15**) and cyclooctene (**16**). When the reactions were performed under the same conditions as those indicated in Table 1, except for a shorter reaction time for **12** and **16**, the predominant products detected were exclusively the respective epoxides **17**–**21** as depicted in Table 2 (entries 1–5). Remarkably, for substrates **12**, **14**, and **16**, their epoxides were formed in nearly quantitative yields (based on the substrates consumed) with excellent substrate conversions. An excellent substrate conversion is also achieved for cyclohexene (**15**, entry 4, Table 2), but the chemoselectivity is significantly lower in this case, like the Cl_2pyNO epoxidation of the same alkene catalyzed by the polymer-supported ruthenium porphyrin **3**-MPR.[10] The conversion of *trans*-stilbene (**13**) is moderate (entry 2, Table 2). However, the chemoselectivity in the **5**-[G-2]$_8$-catalyzed epoxidation of **13** is exceptionally high, as reflected by a 98% yield of epoxide **18** formed in the reaction. In contrast, our previous work on the Cl_2pyNO epoxidation of **13** by employing catalysts **3**-MPR[10] and **2**-MCM-41[9b] shows that the former catalyst results in formation of **18** in 90% yield whereas the latter one afforded no **18**. The catalyst turnover numbers for the epoxidation of **12**–**16** range from 1.4×10^3 to $> 2.9 \times 10^3$ (entries 1–5, Table 2, {**5**-[G-2]$_8$}:Cl_2pyNO:alkene molar ratio = 1:3300:3000). In the case of cyclooctene (**16**), the most reactive alkene substrate among **12**–**16**, we also performed the epoxidation reaction by employing a {**5**-[G-2]$_8$}:Cl_2pyNO:alkene molar ratio of 1:17000:15000. Under such a low catalyst loading, we obtained an 82% conversion of **16** and a nearly quantitative yield of epoxide **21**

Table 2. Epoxidation of *cis*-stilbene (**12**), *trans*-stilbene (**13**), 2,2-dimethylchromene (**14**), cyclohexene (**15**), and cyclooctene (**16**) with Cl_2pyNO catalyzed by dendritic ruthenium(II) porphyrin **5**-[G-2]$_8$.[a]



12 **13** **14** **15** **16**

17 **18** **19** **20** **21**

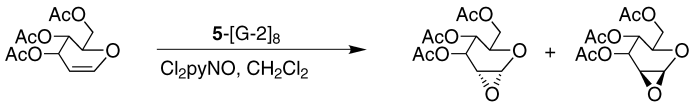
Entry	Substrate	Reaction time [h]	Conversion [%]	Product	Yield[b] [%]	Turnovers[c]
1	**12**	36	> 99	**17**	> 99	$> 2.9 \times 10^3$
2	**13**	48	49	**18**	98	1.4×10^3
3	**14**	48	90	**19**	98	2.7×10^3
4	**15**	48	92	**20**[d]	66	1.8×10^3
5	**16**	24	96	**21**	> 99	$> 2.9 \times 10^3$
6[e]	**16**	96	82	**21**	> 99	$> 1.2 \times 10^4$

[a] Unless otherwise specified, all reactions were carried out in CH_2Cl_2 at room temperature, with a {**5**-[G-2]$_8$}:Cl_2pyNO:alkene molar ratio of 1:3300:3000. [b] Based on the amount of alkenes consumed. [c] (Moles of epoxide products):(moles of catalyst). [d] Other products: cyclohex-2-en-1-one (24%) and cyclohex-2-en-1-ol (10%). [e] The reaction was performed at 40 °C, with a {**5**-[G-2]$_8$}:Cl_2pyNO:alkene molar ratio of 1:17000:15000.

0947-6539/02/0807-1558 $ 20.00+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 7

(based on the **16** consumed), which gives a very high turnover number of $>1.2\times10^4$, comparable to that of the polymer-supported catalyst **3**-MPR.[10]

Next, we examined the catalytic properties of **5**-$[G\text{-}2]_8$ for Cl_2pyNO epoxidation of 3,4,6-tri-*O*-acetyl-D-glucal (**22**), a glycal derivative. After the reaction was carried out in dichloromethane at 40 °C for 48 h ({**5**-$[G\text{-}2]_8$}:Cl_2pyNO:alkene molar ratio = 1:1100:1000), an 80% conversion of **22** was achieved. A mixture of the corresponding epoxides α-**23** and β-**23** were formed [Eq. (3)] in a total of 83% yield based on consumed **22**, with the ratio of α-**23** versus β-**23** being 9:1. This



22 α-**23** β-**23**

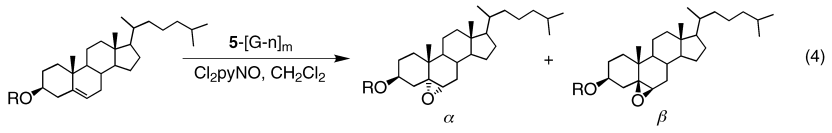
α:β ratio is significantly higher than that obtained for catalyst **2**-MCM-41 (α-**23**:β-**23** = 3:1)[9b] but lower than that for catalyst **3**-MPR (only α-**23** was formed in that case).[10]

Lastly, we investigated the catalytic properties of **5**-$[G\text{-}2]_8$ for the Cl_2pyNO epoxidation of a series of unsaturated steroids including cholesteryl esters and an estratetraene derivative. Previously, ruthenium-porphyrin-catalyzed epoxidation of unsaturated steroids had been realized only in the "$[Ru^{VI}(tmp)(O)_2]$ (tmp = *meso*-tetramesitylporphyrinato dianion) + air or dioxygen" system developed by Marchon and co-workers,[4b, 24] which features nearly complete β-stereoselectivity (β:α > 99:1) for some sterol esters with catalyst turnover numbers of < 20. In this work, we treated cholesteryl esters **24**–**26** (Table 3) with Cl_2pyNO in dichloromethane at 40 °C in the presence of 0.1 mol% of **5**-$[G\text{-}2]_8$. The reactions gave > 99% substrate conversions after 48 hours, affording a mixture of the respective α- and β-epoxides (**27**–**29**) in 75–83% yields (entries 1–3, Table 3). The β-stereoselectivities (β:α = 99:1 for all the three substrates) are comparable to, whereas the catalyst turnover numbers (up to ≈820) are much higher than, those obtained for the same cholesteryl esters in the above "$[Ru^{VI}(tmp)(O)_2]$ + air" epoxidation system. Especially striking is the high catalytic activity of **5**-$[G\text{-}2]_8$ toward epoxidation of the benzoic ester **25** and the long-chain aliphatic ester **26**, which led to nearly 100% substrate conversion within two days. In contrast, the epoxidations of **25** and an analogue of **26** by "$[Ru^{VI}(tmp)(O)_2]$ + air" need to proceed for six or seven days before the reactions reach completion.[24a]

Because cholesteryl esters **24**–**26** are much bulkier than styrene, the relationship between the catalytic properties and structures of **5**-$[G\text{-}n]_m$ for the epoxidation of **24**–**26** might be different from that found for the epoxidation of styrene described above. In this context, we examined the reactions of **24** with Cl_2pyNO in the presence of other **5**-$[G\text{-}n]_m$ catalysts described above under the conditions identical to those for **5**-$[G\text{-}2]_8$. The results are shown in entries 4–7 of Table 3, which reveals that the dependence of chemoselectivity on the structure of **5**-$[G\text{-}n]_m$ in the epoxidation of **24** (compare the yields of **27** among entries 1, 4–7 in Table 3) is basically similar to that in the epoxidation of styrene. Interestingly, the β-stereoselectivity in the epoxidation of **24** also significantly increases with the generation number of the dendron for either **5**-$[G\text{-}n]_4$ or **5**-$[G\text{-}n]_8$. Again, complex **5**-$[G\text{-}2]_8$ is the best catalyst among all the **5**-$[G\text{-}n]_m$ catalysts prepared in this work in terms of either chemoselectivity or β-stereoselectivity.

Remarkably, under the same conditions as indicated in Table 3, the epoxidation of estratetraene derivative **30** with Cl_2pyNO catalyzed by **5**-$[G\text{-}2]_8$ afforded the epoxide **31** in 95% yield with a complete β-stereoselectivity ([Eq. (5); reaction conditions: 40 °C, 48 h, {**5**-$[G\text{-}2]_8$}:Cl_2pyNO:30 = 1:1100:1000]). The β-configuration of **31** has been confirmed by X-ray crystallography.[25] No α-**31** was detected in the reaction. The catalyst turnover number is 8.6×10^2, higher than those obtained for substrates **24**–**26**. To our knowledge,

Table 3. Epoxidation of cholesteryl esters with Cl_2pyNO catalyzed by dendritic ruthenium(II) porphyrins **5**-$[G\text{-}n]_m$.[a]

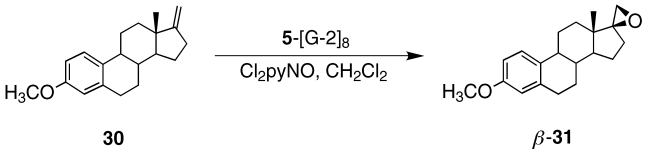


R = Ac: **24**; PhCO: **25**; $C_{15}H_{31}CO$: **26**

R = Ac: α-**27** and β-**27**; PhCO: α-**28** and β-**28**; $C_{15}H_{31}CO$: α-**29** and β-**29**

Entry	Catalyst	Substrate	Reaction time [h]	Conversion [%]	Yield [%][b] (α + β)	β:α ratio[c]	Turnovers[d]
1	**5**-$[G\text{-}2]_8$	**24**	48	> 99	83	99:1	$>8.2\times10^2$
2	**5**-$[G\text{-}2]_8$	**25**	48	> 99	82	99:1	$>8.1\times10^2$
3	**5**-$[G\text{-}2]_8$	**26**	48	> 99	75	99:1	$>7.4\times10^2$
4	**5**-$[G\text{-}1]_4$	**24**	24	> 99	80	76:1	$>7.9\times10^2$
5	**5**-$[G\text{-}2]_4$	**24**	24	> 99	75	84:1	$>7.4\times10^2$
6	**5**-$[G\text{-}0]_8$	**24**	24	> 99	72	90:1	$>7.1\times10^2$
7	**5**-$[G\text{-}1]_8$	**24**	48	> 99	83	93:1	$>8.2\times10^2$

[a] All reactions were carried out in CH_2Cl_2 at 40 °C, with a catalyst:Cl_2pyNO:alkene molar ratio of 1:1100:1000. [b] Yield of isolated product. [c] Determined by ^{1}H NMR spectroscopy as described in reference [24a]. [d] (Moles of epoxide products):(moles of catalyst).



30 β-**31** (5)

this is the first case where an estratetraene derivative has been efficiently epoxidized by employing a metal complex catalyst.

Cyclopropanation of alkenes with EDA catalyzed by dendritic ruthenium(II) porphyrin 5-[G-2]$_8$: Cyclopropanation of alkenes with diazo compounds N_2CRR' catalyzed by metal complexes has attracted widespread attention. It is proposed that these catalytic reactions most probably proceed via monocarbene M=CRR′[26] or biscarbene R′RC=M=CRR′[6f, 27] active intermediates, which are analogous to the proposed monooxo M=O[4i, 9b] or dioxo O=M=O[4a,d] active intermediates in metal-complex-catalyzed epoxidation of alkenes with oxygen donors such as Cl_2pyNO or PhIO. Since the carbene groups are usually sterically much more demanding than the oxo group, a question arises whether or not a metal complex embedded in the interior of bulky dendritic wedges can efficiently catalyze the cyclopropanation of alkenes with a diazo compound (notice the current absence of alkene cyclopropanations catalyzed by a typical dendritic metal complex[2a]).

The efficiency of **5**-[G-2]$_8$ in catalyzing the Cl_2pyNO epoxidation of bulky substrates **24**–**26** and **30** encouraged us to examine the catalytic behavior of this dendritic ruthenium porphyrin toward cyclopropanation of alkenes with EDA. Interestingly, treatment of styrene or its *para*-substituted derivative *p*-X–$C_6H_4CH{=}CH_2$ (X = Me, **32**; OMe, **33**; Cl, **34**; Br, **35**) with excess EDA in the presence of 0.1 mol% of **5**-[G-2]$_8$ in dichloromethane at room temperature for about 34 h afforded respective cyclopropyl esters **36**–**40** (mixtures of *trans* and *cis* isomers) in 65–98% yields with moderate-to-good substrate conversions (reaction (6) in Table 4). The reactions are highly *trans* selective, with *trans*/*cis* ratios of up to 16, which are comparable to those reported for ruthenium-pybox[28] or non-dendritic ruthenium porphyrin catalysts[6] but much higher than those attained for semicorrin- or bis(oxazoline)–copper catalysts.[29]

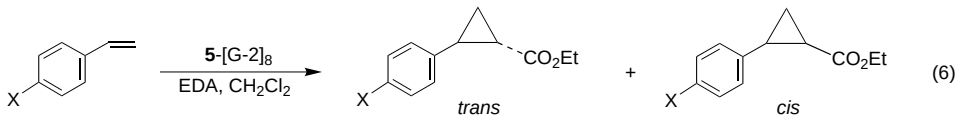
Conclusion

We have prepared several dendritic ruthenium porphyrins by attaching poly(benzyl ether) dendritic wedges [G-*n*] to carbonylruthenium(II) *meso*-tetraphenylporphyrin **5** with covalent etheric bonds. The dendritic ruthenium porphyrins **5**-[G-*n*]$_m$ obtained ($m = 4$, $n = 1, 2$; $n = 8$, $m = 0-2$) constitute a new class of highly selective metal catalysts for Cl_2pyNO epoxidation and EDA cyclopropanation of alkenes. Our work reveals that the chemo- or diastereoselectivities in the Cl_2pyNO epoxidation of aromatic alkenes (such as styrene) and unsaturated steroids (such as cholesteryl acetate) catalyzed by **5**-[G-*n*]$_m$ significantly increase with the generation number of the dendron or the number of the dendrons attached to **5**. Catalyst **5**-[G-2]$_8$ exhibits remarkably high selectivity or catalyst turnover in catalyzing Cl_2pyNO epoxidation of a variety of alkenes including styrene derivatives, 2,2-dimethylchromene, cyclooctene, cholesteryl esters, and an estratetrene derivative. The substrate conversions of up to 81% and yields of cyclopropyl esters of up to 98% with *trans*:*cis* ratios of up to 16:1 in the **5**-[G-2]$_8$-catalyzed EDA cyclopropanation of styrenes first demonstrate the efficiency of a dendritic metalloporphyrin in catalyzing alkene cyclopropanation reactions.

Experimental Section

General: $[Ru_3(CO)_{12}]$ (Strem), [18]crown-6 (Aldrich), cholesteryl esters **24**–**26** (ACROS), glycal derivative **22** (Aldrich), and EDA (Aldrich) were used as received. Styrene, *para*-substituted styrenes *p*-X–$C_6H_4CH{=}CH_2$ (X = Me, MeO, Cl, Br), *cis*- and *trans*-stilbene, cyclohexene, cyclooctene, and 2,2-dimethylchromene were purified by the standard procedures before use. Estratetraene derivative **30**,[30] Cl_2pyNO,[31] 5,10,15,20-tetrakis(4′-hydroxyphenyl)porphyrin, and 5,10,15,20-tetrakis(3′,5′-dihydroxyphenyl)porphyrin,[32] and [G-*n*]OSO_2Me[33] were prepared by the literature methods. All solvents were of the AR grade. ^1H and ^{13}C NMR spectra were

Table 4. Cyclopropanation of aromatic alkenes with EDA catalyzed by dendritic ruthenium(II) porphyrin **5**-[G-2]$_8$.[a]



(6)

X = H: **8**, Me: **32**, OMe: **33**, Cl: **34**, Br: **35**

X = H: *trans*-**36**, *cis*-**36**; Me: *trans*-**37**, *cis*-**37**; OMe: *trans*-**38**, *cis*-**38**; Cl: *trans*-**39**, *cis*-**39**; Br: *trans*-**40**, *cis*-**40**

Entry	Substrate	Product	Conversion [%]	Yield [%][b]	*trans*/*cis* ratio[c]
1	**8**	α- + β-**36**	51	77	12
2	**32**	α- + β-**37**	54	98	14
3	**33**	α- + β-**38**	81	80	16
4	**34**	α- + β-**39**	40	65	8
5	**35**	α- + β-**40**	33	71	10

[a] All reactions were performed in dichloromethane at room temperature for ≈34 h with a {**5**-[G-2]$_8$}:EDA:alkene ratio of 1:1200:1000. [b] Yield of isolated product based on the alkene consumed. [c] Determined by GC.

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measured on a Bruker DPX 300 or 400 spectrometer by using tetramethylsilane (TMS) as an internal standard; the chemical shifts are relative to TMS. Infrared spectra (KBr) were recorded on a Bio-Rad FTS-7 FT-IR spectrometer. UV/Vis spectra were measured on a Milton Roy Spectronic 3000 diode-array spectrophotometer. FAB mass spectra were measured on a Finnigan MAT 95 mass spectrometer, matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra on a Biflex III spectrometer (Bruker Daltonics Co., USA), and high-resolution mass spectra (HRMS) on a Jasco spectrometer. GC measurements were carried out on a HP 5890 Series II gas chromatograph equipped with a flame ionization detector and a 3396 Series II integrator. Elemental analyses were performed by the Institute of Chemistry, the Chinese Academy of Sciences.

Preparation of ruthenium(II) porphyrins 6 and 7: A mixture of $[Ru_3(CO)_{12}]$ (200 mg) and the corresponding porphyrin free base (200 mg) in 2,4,6-trichlorobenzene (50 mL) was refluxed under nitrogen for 24 h. The resulting red solution was then purified by column chromatography on silica gel, with hexane as eluent. The desired product was eluted by ethyl acetate/hexane (2:1, v/v). Removal of the solvent followed by recrystallization of the residue from dichloromethane/methanol (6:1, v/v) afforded complex **6** or **7** as red purple crystals.

6: Yield: 66%; ^{1}H NMR (300 MHz, CD_3OD): $\delta = 8.77$ (s, 8H; H_β), 8.04 (dd, 4H; H_o or H_o'), 7.94 (dd, 4H; H_o or H_o'), 7.18 (m, 8H; H_m and H_m'); UV/Vis (MeOH): λ_{max} (log ε) = 412 (5.01), 529 (4.31) nm; IR: $\tilde{\nu} = 1935$ cm^{-1} (Ru−*CO*); FAB MS: *m*/*z*: 806 $[M]^+$, 778 $[M-CO]^+$.

7: Yield: 70%; ^{1}H NMR (300 MHz, CD_3OD): $\delta = 8.76$ (s, 8H; H_β), 7.16 (m, 4H; H_o or H_o'), 7.08 (m, 4H; H_o or H_o'), 6.67 (t, 4H; H_p); UV/Vis (MeOH): λ_{max} (log ε) = 413 (5.12), 532 (4.37) nm; IR: $\tilde{\nu} = 1936$ cm^{-1} (Ru−*CO*); FAB MS: *m*/*z*: 870 $[M]^+$, 842 $[M-CO]^+$.

Preparation of dendritic ruthenium(II) porphyrins 5-[G-*n*]$_m$: [G-*n*]OSO_2Me (4.4 equiv for **5**-[G-*n*]$_4$; 8.8 equiv for **5**-[G-*n*]$_8$) was added to a solution of complex **6** or **7** in anhydrous acetone (30 mL) containing K_2CO_3 (2.5 equiv) and [18]crown-6 (0.5 equiv). The mixture was refluxed under a nitrogen atmosphere until **6** or **7** was completely consumed (this took 48–96 h, as monitored by TLC). After treatment with water (100 mL), the mixture was extracted with dichloromethane (3 × 20 mL). The organic extract was collected, dried with $MgSO_4$, and evaporated to remove the solvent. The residue was purified by column chromatography very slowly on silica gel with dichloromethane as eluent followed by recrystallization from dichloromethane-methanol, affording the respective dendritic ruthenium(II) porphyrin as a red powder.

5-[G-1]$_4$: Yield: 70%; ^{1}H NMR (400 MHz, [D$_6$]acetone): $\delta = 8.68$ (s, 8H; H_β), 8.13 (dd, 4H; H_o or H_o'), 8.01 (dd, 4H; H_o or H_o'), 7.44–7.34 (m, 48H; H_m, H_m', and outer Ph), 6.97 (d, 8H; inner Ph), 6.73 (t, 4H; inner Ph), 5.38 (s, 8H; inner CH_2), 5.21 (s, 16H; outer CH_2); ^{13}C NMR (300 MHz, $CDCl_3$): $\delta = 159.70$, 157.17, 144.37, 139.27, 136.59, 135.33, 134.93, 131.77, 128.58, 128.06, 127.61, 121.64, 113.05, 106.96, 101.94, 70.29, 70.17; UV/Vis (acetone): λ_{max} (log ε) = 413 (5.21), 532 (4.45) nm; IR: $\tilde{\nu} = 1938$ cm^{-1} (Ru−*CO*); FAB MS: *m*/*z*: 2016 $[M]^+$, 1988 $[M-CO]^+$; elemental analysis calcd (%) for $C_{129}H_{100}N_4O_{13}Ru \cdot MeOH$ (2047.31): C 76.27, H 5.12, N 2.73; found: C 76.20, H 5.42, N 2.13.

5-[G-2]$_4$: Yield: 30%; ^{1}H NMR (400 MHz, [D$_6$]acetone): $\delta = 8.63$ (s, 8H; H_β), 8.05 (dd, 4H; H_o or H_o'), 7.95 (dd, 4H; H_o or H_o'), 7.43–7.25 (m, 88H; H_m, H_m', and outer Ph), 6.91 (d, 8H; inner Ph), 6.79 (d, 16H; middle Ph), 6.68 (t, 4H; inner Ph), 6.61 (t, 8H; middle Ph), 5.28 (s, 8H; inner CH_2), 5.10 (s, 16H; middle CH_2), 5.07 (s, 32H; outer CH_2); ^{13}C NMR (300 MHz, $CDCl_3$): $\delta = 160.11$, 160.02, 158.48, 144.55, 139.54, 139.21, 136.93, 136.84, 135.56, 135.43, 135.19, 131.98, 128.75, 128.19, 127.75, 121.90, 113.18, 107.04, 106.76, 106.67, 106.60, 102.03, 101.90, 70.32, 70.26, 70.24; UV/Vis (acetone): λ_{max} (log ε) = 413 (5.39), 532 (4.58) nm; IR: $\tilde{\nu} = 1938$ cm^{-1} (Ru−*CO*); MALDI-TOF: *m*/*z*: 3685 $[M-CO]^+$; elemental analysis calcd (%) for $C_{241}H_{196}N_4O_{29}Ru \cdot 2H_2O$ (3749.25): C 77.20, H 5.38, N 1.49; found: C 77.23, H 5.43, N 1.15.

5-[G-0]$_8$: Yield: 80%; ^{1}H NMR (400 MHz, [D$_6$]acetone): $\delta = 8.72$ (s, 8H; H_β), 7.61–7.35 (m, 48H; H_o, H_o', and outer Ph), 7.18 (t, 4H; H_p), 5.38 (d, 16H; outer CH_2); ^{13}C NMR (300 MHz, $CDCl_3$): $\delta = 158.78$, 157.84, 144.17, 143.86, 136.65, 131.16, 128.49, 127.92, 127.54, 119.54, 115.05, 70.23; UV/Vis (acetone): λ_{max} (log ε) = 414 (5.28), 532 (4.49) nm; IR: $\tilde{\nu} = 1938$ cm^{-1} (Ru−*CO*); FAB MS: *m*/*z*: 1592 $[M]^+$, 1564 $[M-CO]^+$; elemental analysis calcd (%) for $C_{101}H_{76}N_4O_9Ru \cdot 2H_2O$ (1626.81): C 74.57, H 4.96, N 3.44; found: C 74.36, H 4.93, N 3.23.

5-[G-1]$_8$: Yield: 30%; ^{1}H NMR (400 MHz, [D$_6$]acetone): $\delta = 8.68$ (s, 8H; H_β), 7.49–7.22 (m, 88H; H_o, H_o', and outer Ph), 7.13 (t, 4H; H_p), 6.82 (dd, 16H; inner Ph), 6.62 (m, 8H; inner Ph), 5.26 (d, 16H; inner CH_2), 5.03 (d, 32H; outer CH_2); ^{13}C NMR (300 MHz, $CDCl_3$): $\delta = 160.45$, 160.00, 159.84, 157.70, 144.11, 143.64, 139.26, 136.58, 136.52, 131.67, 128.36, 127.80, 127.34, 121.41, 114.53, 114.27, 106.75, 106.37, 105.37, 101.93, 101.61, 101.16, 69.92, 69.86; UV/Vis (acetone): λ_{max} (log ε) = 414 (5.41), 532 (4.66) nm; IR: $\tilde{\nu} = 1940$ cm^{-1} (Ru−*CO*); MALDI-TOF: *m*/*z*: 3261 $[M-CO]^+$; elemental analysis calcd (%) for $C_{213}H_{172}N_4O_{25}Ru \cdot 8H_2O$ (3450.86): C 74.52, H 5.52, N 1.63; found: C 74.52, H 5.50, N 1.17.

5-[G-2]$_8$: Yield: 15%; ^{1}H NMR (400 MHz,[D$_6$]acetone): $\delta = 8.66$ (s, 8H; H_β), 7.47–7.21 (m, 168H; H_o, H_o', and outer Ph), 7.06 (brs, 4H; H_p), 6.78–6.73 (m, 16H; inner Ph), 6.64–6.57 (m, 48H; middle Ph), 6.49 (brs, 8H; inner Ph), 5.10 (brs, 16H; inner CH_2), 5.06 (brs, 32H; middle CH_2), 4.89 (brs, 64H; outer CH_2); ^{13}C NMR (300 MHz, $CDCl_3$): $\delta = 160.04$, 159.97 (br), 157.71, 144.12, 139.20, 139.13, 136.62 (br), 131.83, 128.48, 127.91, 127.40, 120.72, 106.27, 105.57, 101.45, 101.20, 100.33, 69.97, 69.79; UV/Vis (acetone): λ_{max} (log ε) = 414 (5.29), 532 (4.61) nm; IR: $\tilde{\nu} = 1940$ cm^{-1} (Ru−*CO*); MALDI-TOF: *m*/*z*: 6662 $[M-CO]^+$; elemental analysis calcd (%) for $C_{437}H_{364}N_4O_{57}Ru \cdot 9H_2O$ (6846.77): C 76.66, H 5.62, N 0.82; found: C 76.93, H 5.60, N 0.40.

Procedure for Cl_2pyNO epoxidation of alkenes catalyzed by dendritic ruthenium(II) porphyrins 5-[G-*n*]$_m$: *1) Simple alkene substrates **8** and **12**–**16***: A mixture of alkene (0.60 mmol), Cl_2pyNO (0.66 mmol), and **5**-[G-2]$_8$ or other **5**-[G-*n*]$_m$ catalyst (0.2 μmol) in dichloromethane (5 mL) was stirred at room temperature. When the reaction was complete, as revealed by TLC measurements, the catalyst was precipitated by addition of methanol (30 mL). After filtration, the organic products in the filtrate were identified by GC or ^{1}H NMR spectroscopy and quantified by the same spectroscopic method in the presence of appropriate internal standards.

*2) Substrates **22**, **24**–**26**, and **30***: A mixture of substrate (1 mmol), Cl_2pyNO (1.1 mmol), and **5**-[G-2]$_8$ or other **5**-[G-*n*]$_m$ catalyst (1 μmol) in dichloromethane (6 mL) was stirred at 40 °C under nitrogen. When the reaction was complete, as revealed by TLC or ^{1}H NMR measurements, the catalyst was precipitated by addition of methanol (50 mL). The epoxide products except **23** were isolated after the filtrate was purified by column chromatography on silica gel with ethyl acetate/hexane (1:6, v/v) as eluent. The isolation and quantification of epoxide **23** were performed as described elsewhere.[9b, 10]

β-**29**: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.32$ (m, 1H), 3.10 (d, $J = 2$ Hz, 1H), 2.28–1.09 (m, 56H), 1.02 (s, 3H), 0.89 (m, 12H), 0.66 (s, 3H); HRMS: *m*/*z* ($[M]^+$) calcd for $C_{43}H_{76}O_3$ 640.5794, found: 640.5792.

β-**31**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.21$ (d, $J = 8.6$ Hz, 1H), 6.71 (dd, $J = 8.6$, 2.6 Hz, 1H), 6.64 (d, $J = 2.3$ Hz, 1H), 3.78 (s, 3H), 2.97 (d, $J = 4.9$ Hz, 1H), 2.86 (m, 2H), 2.65 (d, $J = 4.9$ Hz, 1H), 2.33–1.21 (m, 13H), 0.92 (s, 3H); HRMS: *m*/*z* ($[M]^+$) calcd for $C_{20}H_{26}O_2$ 298.1933, found: 298.1932.

Procedure for EDA cyclopropanation of alkenes catalyzed by dendritic ruthenium(II) porphyrin 5-[G-2]$_8$: A solution of EDA (1.2 mmol) in dichloromethane (5 mL) was added dropwise to a solution of alkene (1 mmol) and **5**-[G-2]$_8$ (1 μmol) in dichloromethane (5 mL) over 10 h at room temperature under an argon atmosphere. The mixture was then stirred for an additional 24 h. After removal of the unreacted EDA by flash chromatography on a short column of silica gel, the substrate conversion and the ratio of *trans* and *cis*-cyclopropyl esters were determined by GC using an analytic column with tribromobenzene as an internal standard. Pure cyclopropyl esters were obtained upon further column chromatography on silica gel with hexane/ethyl acetate (20:1 v/v) as eluent.

Acknowledgements

This work was supported by the Generic Drug Research Program of The University of Hong Kong, the Hong Kong Research Grants Council (HKU 7077/01P), the Hong Kong University Foundation, and Area of Excellence Scheme (AoE/P-10/01), University Grants Committee of the Hong Kong SAR, China. J.S.H. is grateful to The University of Hong Kong for a Postdoctoral Fellowship. We thank Prof. Zhong-Yuan Zhou for the X-ray structure determination of epoxide *β*-**31**.

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[23] This is rather surprising considering the presence of potentially reactive benzylic C–H bonds in the poly(benzyl ether) dendrons of **5**-[G-2]$_8$, which might render the catalyst susceptible to oxidative degradation as mentioned in reference [3a]. The high stability observed for catalyst **5**-[G-2]$_8$ might be rationalized by considering the following possibilities. First, the alkene double bond in styrene could be significantly more reactive than the foregoing benzylic C–H bonds toward the attack of the active intermediate in the oxidation process. Second, the benzylic C–H bonds on the bulky dendritic wedges might be hardly accessible by the oxidizing groups in the active species due to geometric constraint or steric hindrance.

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Received: August 21, 2001 [F3501]

  0947-6539/02/0807-1562 $ 20.00+.50/0