Catalytic and asymmetric cyclopropanation of styrenes catalysed by ruthenium porphyrin and porphycene complexes

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Ruthenium porphyrin and porphycene complexes catalyse stereospecific cyclopropanation of styrenes; high product turnovers with up to 90.8% ee were achieved with the [Ru(P*)(CO)(EtOH)] catalyst (H_2P* = chiral D_4 porphyrin).

Metalloporphyrins are well known to be effective catalysts for alkane hydroxylation,[1] olefin epoxidation[2] and cyclopropanation.[3–5] When compared to metallosalens, porphyrin catalysts usually have a greater catalytic stability resulting in higher product turnover numbers.[6] However, their practical applications would require high regio-, stereo- and enantio-selectivities to be achieved. To our knowledge, the best reported chiral metalloporphyrins are the manganese threitol-strapped porphyrins[7] and the iron 'twin-coronet' porphyrins[8] which gave 88 and 89% ee in the epoxidation of 1,2-dihyronaphthalene and 2-nitrostyrene by iodosobenzene, respectively. Herein is described that ruthenium porphyrin and porphycene complexes are effective catalysts for stereospecific cyclopropanation of styrenes. With the D_4 porphyrin (H_2P*) reported by Halterman and Jan,[9] it is possible to achieve high product turnovers and with up to 90.8% ee which is comparable to the best ee reported with the non-porphyrin chiral metal catalysts.[10–14]

The [Ru(P)(CO)(EtOH)] catalysts (Fig. 1) used in this work were prepared by literature methods.[15,16] Refluxing [$Ru_3(CO)_{12}$] with H_2P* in decalin for 8 h gave [Ru(P*)(CO)] in a 90% yield, which was recrystallised from a CH_2Cl_2–EtOH mixture to give [Ru(P*)(CO)(EtOH)]. Its structure determined by a X-ray crystal analysis features one of the few structures of chiral ruthenium porphyrins.[17] As shown in Fig. 2, the porphyrin ligand has a pseudo D_4 symmetry. The ruthenium atom coordinates with one CO and one EtOH in the axial direction and is in the centre of the mean plane defined by the four nitrogen atoms of the porphyrin ligand. There are two CH_2Cl_2 and one EtOH solvent molecules in the unit cell with 0.5 site occupancy. Hydrogen bonding interactions exists between the coordinated EtOH and the EtOH solvent molecules with O–O distance of 2.8 Å in the unit cell. The measured C(85)–O(1) and Ru–O(Et) distances of 1.188(2) and 2.241(2) Å, respectively are comparable to the corresponding values of 1.16(3) and 2.21(2) Å found in [Ru(TPP)(CO)(EtOH)].[18]

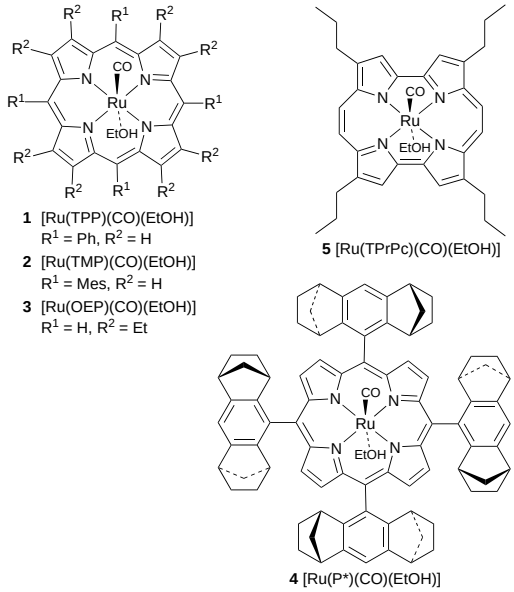

Fig. 1 Ruthenium porphyrinoid complexes used in the catalytic cyclopropanation of alkenes

The [Ru(P)(CO)(EtOH)] complexes are excellent catalysts for the cyclopropanation of some styrenes by ethyl diazoester (EDA) with very good diastereoselectivities. The results are listed in Table 1. At a catalyst : EDA : alkene ratio of 1 : 300 : 600, the product yields based on EDA are moderate to good for **1** and **2** but the reactions become less effective for the less bulky catalysts **3** and **5**. A notable point is the high *trans* product selectivity. For example, the *trans* : *cis* ratio of 9.2 obtained from the reaction between styrene and EDA catalysed by **1** is comparable to the value of 9.5 obtained from the same reaction catalysed by [Os(TPP)(CO)(py)][3] but is considerably higher than that of 1.1 by Rh(TPP)I.[4]

In order to optimize the product yield, the reaction between 1,1-diphenylethylene and EDA catalysed by **1** was investigated. The product yield was found to increase with increasing ratio of alkene : EDA. The effectiveness of the catalyst in cyclopropanation is clearly demonstrated by the very high turnover number of 1855 and yield of 92.3% achieved at a catalyst : EDA : diphenylethylene ratio of 1 : 2000 : 20 000.

The ruthenium porphyrins catalysed the cyclopropanation of alk-1-enes and 1,1-disubstituted olefins very efficiently, but alkenes with other substitution patterns were poor substrates. *cis*- or *trans*-β-Methylstyrene could not be cyclopropanated. This shape selectivity is reminiscent of that observed for Os(TTP)-catalysed cyclopropanation[3] but constrasts with the much broader substrate compatibility of rhodium porphyrin-catalysed reactions.[5] In the latter case, only tetrasubstituted alkenes are sluggish substrates.

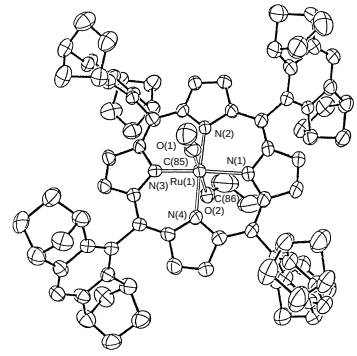

Fig. 2 Perspective view of [Ru(P*)(CO)(EtOH)]. Selected bond lengths (Å) and angles (°): Ru(1)–N(1) 2.082(2), Ru(1)–N(2) 2.068(2), Ru(1)–N(3) 2.043(2), Ru(1)–N(4) 2.057(2), Ru(1)–C(85) 1.776(2), Ru(1)–O(2), 2.241(1), O(2)–C(86) 1.437(2), C(85)–O(1) 1.188 Å; N(1)–Ru(1)–N(2) 89.6(1), N(1)–Ru(1)–N(3) 173.7(1), N(2)–Ru(1)–N(3) 90.6(1), N(1)–Ru(1)–N(4) 88.9(1), N(2)–Ru(1)–N(4) 174.4(1), N(3)–Ru(1)–N(4) 90.3(1), Ru(1)–C(85)–O(1) 178.4(2)°.

The catalytic enantioselective cyclopropanation of alkenes was investigated using the ruthenium complex of a D_4-symmetric porphyrin (Fig. 1). The results are shown in Table 2. The absolute configuration of the product from the reaction between styrene and EDA was determined by comparison with literature data.[10]

With styrene as substrate and at room temperature, a product *trans* : *cis* ratio of 18 : 1 was obtained and the ee of the *trans* product was 87% with absolute configuration of (1*S*,2*S*). A high catalyst turnover number of 1665 was achieved. At 0 °C, the *trans*–*cis* selectivity improved to 24 : 1 and ee of the *trans* product increased to 91%. Similar results with very high *trans*–*cis* selectivities and high enantioselectivities for the *trans* product have also been found with other substituted styrenes. Thus, the bulky aryl groups appended on the porphyrin ring of the catalyst **4** can produce a good steric and chiral environment around the reaction site. The reactive intermediate of the cyclopropanation has also been studied. The reaction of **4** with EDA in benzene at room temperature immediately gave a species showing λ_{max} at 407 and 534 nm observed by UV–VIS spectroscopy. This species was unstable and was observed to decay gradually. When monitored with ^{1}H NMR, singlets at δ 13.79 and 8.99 were observed. This intermediate species can be tentatively assigned as the carbene complex [Ru(P*)(CH-CO_2Et)], with the NMR peaks at δ 13.79 and 8.99 being assigned to the carbene and the pyrrolic protons, respectively. These values are similar to the respective NMR peaks at δ 13.79 and 8.55 of [Ru(TMP)($CHCO_2$Et)].[19] The present work highlights that chiral ruthenium carbene complexes of porphyrins could be generated and spectroscopically characterised.

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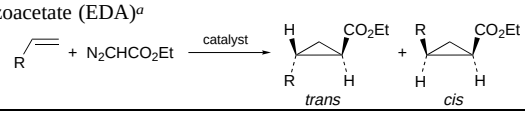
Table 1 Ruthenium catalysed cyclopropanation of alkenes with ethyl diazoacetate (EDA)[a]



Alkene	Catalyst	Product Yield (%)[b]	*trans* : *cis*[c]	Catalyst turnovers[d]
Styrene	**1**	45	9.2 : 1	135
	2	68	7.7 : 1	198
	3	25	12 : 1	62
	5	39	11 : 1	117
4-Methylstyrene	**1**	58	11.2 : 1	176
	2	66	7.5 : 1	208
	3	36	9.6 : 1	114
	5	52	9.9 : 1	162
4-Methoxystyrene	**1**	71	8.1 : 1	214
	2	81	7.3 : 1	252
	3	41	5.8 : 1	121
	5	44	7.2 : 1	133
4-Chlorostyrene	**1**	44	13.7 : 1	138
	2	53	10.5 : 1	164
	3	23	11.0 : 1	67
	5	21	12.3 : 1	63
α-Methylstyrene	**1**	50	2.8 : 1	155
	2	68	1.7 : 1	225
	3	36	2.0 : 1	106
	5	23	2.7 : 1	60

[a] Reaction conditions: catalyst : EDA : alkene = 1 : 300 : 600, CH_2Cl_2, room temp., *ca.* 8 h for addition of EDA then stirring for 8–12 h. [b] Isolated product yields based on EDA. [c] Determined by HPLC. [d] Calculated as the amount of cyclopropyl esters divided by the amount of catalyst.

Table 2 Enantioselective cyclopropanation of alkenes with EDA using **2** as catalyst[a]

Alkene	Product Yield (%)	*trans* : *cis*	*trans* % ee[c]	*cis* % ee[c]	Turnover number
Styrene	83	17.8 : 1	86.5 (1*S*,2*S*)	3.8	1665
Styrene[b]	63	23.6 : 1	90.8 (1*S*,2*S*)	4.0	1267
α-Methylstyrene	69	3 : 1	87	35	1384
1,1-Diphenylethylene	76	—	81		1532
4-Chlorostyrene	66	23.1 : 1	90.4	4.0	1328
4-Methylstyrene	78	18.0 : 1	80.8	8.6	1570
4-Methoxystyrene	61	15.3 : 1	85.4	8.0	1235

[a] Reaction conditions same as Table 1, except catalyst : EDA : alkene = 1 : 2000 : 10 000. [b] Reaction temp. = 0 °C. [c] Determined by chiral HPLC.

Footnotes

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† *Crystal data* for [Ru($C_{84}H_{76}N_4$)CO·EtOH]·CH_2Cl_2·0.5(EtOH): $C_{89}H_{87}Cl_2N_4O_{2.5}Ru$, M = 1428.6, monoclinic, space group $P2_1$, a = 9.849(1), b = 28.164(2), c = 14.399(1) Å, β = 102.83(1)°, U = 3894(2) Å^3, Z = 2, D_c = 1.214 g cm^{-3}, λ (Mo-Kα) = 0.71073 Å, F(000) = 1492, μ = 3.20 cm^{-1}, crystal dimensions 0.40 × 0.40 × 0.40 mm. Intensity data (3.0 < 2θ < 55.0°) were collected on a Rigaku RAXIS IIc imaging-plate system using Mo-Kα radiation (λ = 0.71073 Å) from a RU-200 rotating-anode X-ray generator at room temperature. The data were corrected for absorption and Lorentz polarisation effects. The structure was solved by direct methods and refined by full-matrix least-squares using Siemens SHELXTL PLUS (PC Version). The H-atoms were generated geometrically. 13493 Independent reflections were obtained. 12118 Reflections with $|F_0| > 6.0\sigma(|F_0|)$ were considered observed and used in the structural analysis. The last least-squares cycle was calculated with 933 parameters giving R = 0.071, R_w = 0.089 and goodness of fit = 2.24. The weighing scheme used was $w^{-1} = \sigma^2(F) + 0.0006F^2$. The final Fourier-difference map showed residual extrema in the range of +1.37 to −0.86 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/396.

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