

## Asymmetric Cyclopropanation of Alkenes and Diazocarbonyl Insertion Into S-H Bonds Catalyzed by a Chiral Porphyrin Ru(II) Complex.

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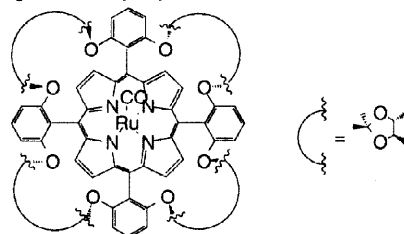
**Abstract:** A homochiral porphyrin ruthenium(II) complex catalyzes the cyclopropanation of styrene derivatives with ethyl diazoacetate with good yields and moderate enantiomeric excesses (46-52 %). The catalyst is also active for diazocarbonyl compound insertion into S-H bonds, but with low ee.

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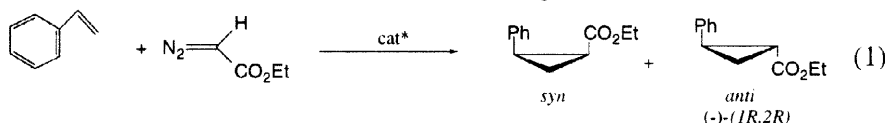
Recently, there is a renewal of interest in reactions catalyzed by porphyrin ruthenium(II) complexes, simultaneously with the development of new chiral porphyrins.<sup>1-3</sup> These reactions focus mainly on asymmetric epoxidation of olefins.<sup>4,5</sup> In contrast asymmetric cyclopropanation of alkenes<sup>6-8</sup> and diazo compound insertion into S-H and N-H bonds are still scarce.<sup>9</sup> As part of our continuing effort to promote ruthenium porphyrin chemistry, we report now the use of a homochiral porphyrin complex as catalyst for asymmetric cyclopropanation of styrene derivatives, as well as for diazo derivatives insertion into S-H bonds.

The chiral metalloporphyrin, P\**Ru* was prepared as described previously by Gross *et al.* (Scheme 1).<sup>3</sup>

**Scheme 1.** Structure of the homochiral porphyrin ruthenium complex used as catalyst.



The catalytic cyclopropanations of alkenes with ethyl diazoacetate (EDA) were run in neat olefin, at room temperature under argon atmosphere, with a substrate:EDA:catalyst ratio of 500:100:1. The complex (P\*)*Ru*(CO) efficiently catalyzed the cyclopropanation of styrene (equation 1), with a diastereoisomeric excess of 60% in favour of the *anti* isomer, and an enantiomeric excess (ee) of 46% for the *anti* isomer. Measurement of the optical rotation allowed identification of the absolute configuration as (-)-(1*R*,2*R*).<sup>10</sup>



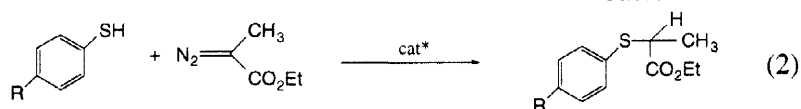
**Table 1.** Asymmetric Cyclopropanation of Styrene Derivatives with Ethyl Diazoacetate.<sup>a</sup>

substrate	yield(%) <sup>b</sup>	<i>anti</i> : <i>syn</i> <sup>c</sup>	ee <i>anti</i> (%) <sup>d</sup>
styrene	85	4.0 : 1	46
4-methoxystyrene	>95	6.1 : 1	47
4-methylstyrene	92	9.9 : 1	46
4-chlorostyrene	93	8.6 : 1	52
4-bromostyrene	93	7.1 : 1	45
4-fluorostyrene	92	11.0 : 1	50

<sup>a</sup> reaction conditions: catalyst, 0.0044 mmol; olefin, 2.200 mmol; ethyl diazoacetate, 0.440 mmol; addition time, 8h; room temperature. <sup>b</sup> based on ethyl diazoacetate. <sup>c</sup> determined by GC and NMR. <sup>d</sup> determined using the chiral shift reagent tris[3-(heptafluoropropyl) hydroxymethylene]-(+)-camphorato]europium(III).

To get some informations on the stereochemistry of the reaction, we used a wide range of *para*-substituted styrene derivatives, the results being reported in Table 1. We found that the reaction time was longer (12 h) than the reaction with a non chiral and less bulky porphyrin ruthenium complexes (5 h),<sup>6</sup> because of the congestion of the cavity created by the chiral units. In all cases, the chemical yields are good (from 88 to 95%), and enantiomeric excesses of the *anti* cyclopropyl ester are very similar (from 46 to 52%). In contrast, ee of the *syn* isomer is very low (10%).

We next investigated the S-H insertion reaction (equation 2) since only few studies have been done in this area,<sup>11</sup> and with low enantioselectivities.<sup>12</sup> Our results are summarized in Table 2.



**Table 2.** Asymmetric Insertion of 2-Diazoacetic Acid Ethyl Ester into S-H Bonds.<sup>a</sup>

R	yield(%) <sup>b</sup>	ee (%) <sup>c</sup>
H	>95	6 <sup>d</sup>
Cl	86	8
OCH <sub>3</sub>	76	< 5

<sup>a</sup> reaction conditions: catalyst, 0.0030 mmol; thiol, 0.900 mmol; ethyl diazoacetate, 0.300 mmol; toluene, 250  $\mu$ l; addition time, 5h; room temperature. <sup>b</sup> based on diazo compound. <sup>c</sup> determined using the chiral shift reagent tris[3-(heptafluoropropyl)hydroxymethylene]-(+)-camphorato]europium(III). <sup>d</sup> Measurement of the optical rotation allowed identification of the absolute configuration as (+)-(*R*)<sup>13</sup>.

As precedently, the crowded porphyrin slows down the reaction with bulky substrates. For example, only a 16% yield is obtained with 2-methyl-2-propanethiol. In contrast, yields are very good with thiophenols, but ee are still low and in the range of those reported by Br nner *et al*<sup>12</sup> with rhodium and copper catalysts.

In conclusion, this work confirms the potentiality of porphyrin ruthenium complexes as catalysts of organic reactions.

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