Cyclopropanation of alkenes with ethyl diazoacetate catalysed by ruthenium porphyrin complexes

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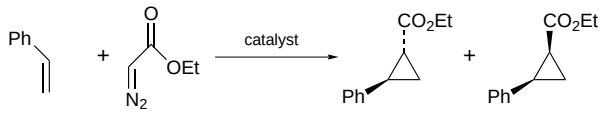
Ruthenium porphyrin complexes are active catalysts for the cyclopropanation of styrene derivatives by ethyl diazoacetate with good to very good diastereoselectivity; moderate enantiomeric excesses (34%) are observed using a chiral porphyrin as catalyst.

The development of efficient and selective methods for the synthesis of cyclopropanes is of great interest in organic synthesis, in particular because of their role in biological processes.[1] Several years ago, Callot *et al*. reported that rhodium porphyrins catalysed the cyclopropanation of alkenes by ethyl diazoacetate (EDA).[2] Recently, efficient asymmetric cyclopropanation of alkenes with diazoacetates catalysed by bis(oxazolinyl)pyridine ruthenium complexes has been reported by Nishiyama and co-workers.[3,4] Very recently, osmium[5] and iron[6] porphyrins were also found to be active catalysts for the formation of cyclopropanes in good yield. Despite the periodic relationship of ruthenium to iron and osmium, and the syntheses of ethoxycarbonyl carbene complexes of ruthenium 5,10,15,20-tetratolylporphyrin[7] and ruthenium 5,10,15,20-tetramesitylporphyrin,[8] no cyclopropanation reactions were observed using ruthenium porphyrins as catalysts; only the coupling products diethyl maleate and fumarate were found.[8] We present herein the first ruthenium porphyrin-catalysed cyclopropanation of styrene derivatives by ethyl diazoacetate.

The complexes Ru^{II}(por)(CO) (por = TPP,† TMP†)[9,10] or Ru^{VI}(por)$(O)_2$[10] (por = TMP†), in catalytic amounts, quickly react with ethyl diazoacetate in the presence of an excess of styrene to give quantitatively‡ the corresponding cyclopropyl esters, with a large excess of the *anti* isomer (Scheme 1). The diastereoselectivity (Table 1) is reminiscent of that observed with osmium and iron catalysts and differs from the *syn* selectivity observed with rhodium porphyrins.[2,11] As shown in the data, the porphyrin structure is important since the use of the unencumbered TPP instead of the crowded TMP results in an increase in the *anti* : *syn* ratio of the cyclopropyl esters from 7.9 to 13.1. The cyclopropane formation also exhibits a substrate shape preference that may be useful for selective cyclopropanation of polyalkenes. Only alk-1-enes and 1,1-disubstituted alkenes react efficiently. Thus styrene and α-methylstyrene are cyclopropanated efficiently, whereas with β-methylstyrene and cyclohexene, diethyl maleate and fumarate are formed in very high yield in a ratio of up 30 : 1 under the same conditions.[8] These coupling products are typically produced when the carbene transfer to the alkene is not observed.[8] The catalyst is also sensitive to the electronic nature of the alkene since aromatic alkenes are better substrates, as previously observed with iron or osmium porphyrins.[5,6] For example, only traces of the cyclopropane products are detected when the reaction is carried out with 4-vinylcyclohex-1-ene.



Scheme 1

Table 1 Cyclopropanation of styrene derivatives by ethyl diazoacetate using ruthenium porphyrin complexes as catalysts

Substrate	Catalyst	Ratio of *anti* : *syn* products[a]	Alkene yield[b] (%)
Styrene	Ru(TPP)(CO)	13.1	7
Sytrene	Ru(TMP)(CO)	7.9	< 5
Styrene	Ru(TMP)$(O)_2$	7.1	< 5
α-Methylstyrene	Ru(TPP)(CO)	3.1	7
α-Methylstyrene	Ru(TMP)(CO)	1.6	< 5
α-Methylstyrene	Ru(TMP)$(O)_2$	1.5	< 5
p-Chlorostyrene	Ru(TPP)(CO)	14.0	8
p-Chlorostyrene	Ru(TMP)(CO)	8.2	< 5

[a] Determined by GC. [b] Diethyl maleate and fumarate.

The reaction of styrene with ethyl diazoacetate in the presence of the dioxoruthenium(vi) picket-fence complex bearing optically active α-methoxy-α-(trifluoromethyl)phenylacetyl residues on both sides of the porphyrin plane (α,β,α,β isomer)[12] (Fig. 1) gave a mixture (*anti* : *syn* = 9 : 1) of optically active cyclopropane derivatives, *e.g*. *anti* and *syn* ethyl 2-phenylcyclopropane-1-carboxylic esters with 14 and 34% enantiomeric excess, respectively.§

We presume that the active intermediate in the ruthenium porphyrin-catalysed reactions is a ruthenium carbene species formed by reaction of ruthenium(ii) with ethyl diazoacetate, by analogy to previous work in which it was demonstrated that osmium(ii) porphyrin carbenes are catalytically active.[5] Actually, when the reaction is monitored at room temperature, a Ru^{II} carbene complex is detected by ^{1}H NMR spectroscopy when Ru(TMP)(CO) is used as the catalyst. As expected,[8] the α-carbon proton appears in the proton spectrum at δ 13.23.¶ The presence of both the carbene ligand and the carbonyl group coordinated to the ruthenium has been confirmed, by IR (ν_{CO} = 1941 cm^{-1}) after isolation of the complex at the end of the reaction, when Ru(TMP)(CO) is used as catalyst. Such a

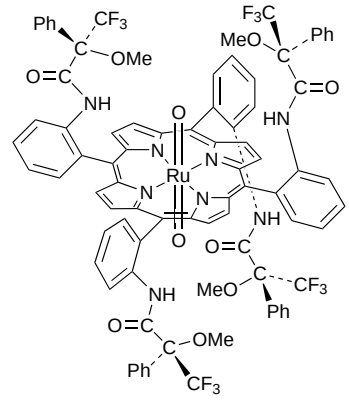


Fig. 1

carbene is also observed with ethyl diazoacetate in the presence of the optically active dioxoruthenium(vi) picket-fence complex and a large excess of the alkene, but is not detectable when the porphyrin is the TPP.

In conclusion, the ruthenium porphyrin compounds described here, which are more easily handed than their air-sensitive iron(ii) porphyrin analogues, are promising catalysts for cyclopropanation reactions.

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Footnotes

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† Abbreviations used: TPP = 5,10,15,20-tetraphenylporphyrin dianion; TMP = 5,10,15,20-tetramesitylporphyrin dianion.

‡ Based on ethyl diazoacetate conversion. In a typical experiment, ethyl diazoacetate (1.14 mmol) is slowly added over approximately 4 h to a vigorously stirred solution of the ruthenium catalyst (2.6 μmol) and alkene (1.71 mmol) at room temperature under inert atmosphere. The reaction mixture is then stirred for 1 h and the cyclopropyl ester formation is analysed by GC.

§ Enantiomeric excesses for cyclopropyl esters were determined using the chiral shift reagent tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium(iii). For the *trans* product, measurement of the optical rotation allowed identification of the absolute configuration as (+)-(1*S*,2*S*).[13]

¶ *Selected spectral data*: ^{1}H NMR ($CDCl_3$): δ 13.23 (carbene CH, s, 1 H), 8.28 (Hβ, s, 8 H), 7.25 (H_m s, 4 H), 7.20 ($H_{m'}$, s, 4 H), 2.67 (CH_2, q, 2 H, *J* 7.3 Hz), 2.63 (*p*-Me, s, 12 H), 1.94 (*o*-Me, s, 12 H), 1.80 (*o*′-Me, s, 12 H), 0.30 (CH_3, t, 3 H, *J* 7.3 Hz)

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