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Synthesis and Evaluation of Ruthenium Catalysts Containing Diamine-Based Ligands in Olefin Cyclopropanation

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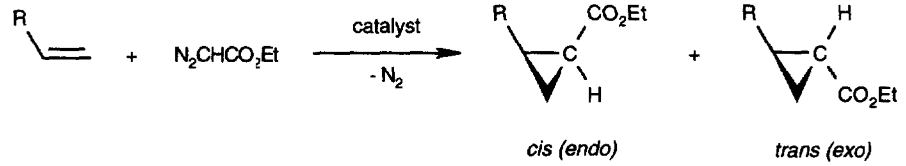
Abstract

Ruthenium complexes with *N*-(*p*-toluenesulfonyl)-diamine ligands were found to be efficient in the catalytic cyclopropanation reaction of olefins with alkyl diazoacetate.

Keywords: Cyclopropanation; Alkenes; Diazo compounds; Ruthenium and compounds.

Olefin cyclopropanation is a very useful tool for synthetic organic chemists, because cyclopropanes are present in many biologically active compounds [1], and because they often serve as intermediates in organic synthesis [2]. This has led to the development of many methods for cyclopropanation reactions, including the Simmons-Smith reaction [3] and the now quite popular transition metal-catalysed reactions of diazo compounds with olefins [4].



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To date, the need for cheap, readily available, and highly stereoselective cyclopropanation catalysts remains however largely unmet. In this regard, ruthenium has recently been introduced as a substitute for copper-based complexes and dirhodium(II) tetracarboxylates [5, 6]. Although the ruthenium-based complexes do not yet display the same level of activity than the classical rhodium carboxylates, they induce selectivities (including enantioselectivities [7]) that are comparable or even better than that of the rhodium catalysts.

Recent developments have highlighted the use of nitrogen ligands in homogeneous catalysis [8]. For instance, the recent work of Noyori *et al.* in hydrogen transfer reactions is particularly noteworthy [9]. In -asymmetric- cyclopropanation this resulted in the emergence

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of copper complexes containing Schiff base, bis(dihydrooxazole), semicorrin, 5-azasemicorrin and tris(pyrazolyl) ligands, cobalt complexes bearing α-camphorquinonedioximato ligands, and rhodium carboxamidates [8]. Recently, rhodium- [10], iron- [11], osmium- [12] and ruthenium-porphyrin complexes [13], bis(oxazoline) and bis(oxazolinyl)pyridine ruthenium complexes have also been effectively used in cyclopropanation reactions [7].

The present article describes the use of a homologous series of fully characterised Ru^{II} complexes **1-6** as catalysts for promoting the cyclopropanation of olefins by ethyl diazoacetate (eq. 1). The principle of synthesizing RuCl(*p*-cymene)(TsN-NR$_2$) (*p*-cymene = 4-isopropyltoluene) consists in the addition of the monotosylated diamine on [RuCl$_2$(*p*-cymene)]$_2$ dimer in the presence of triethylamine, according to the literature [9a].

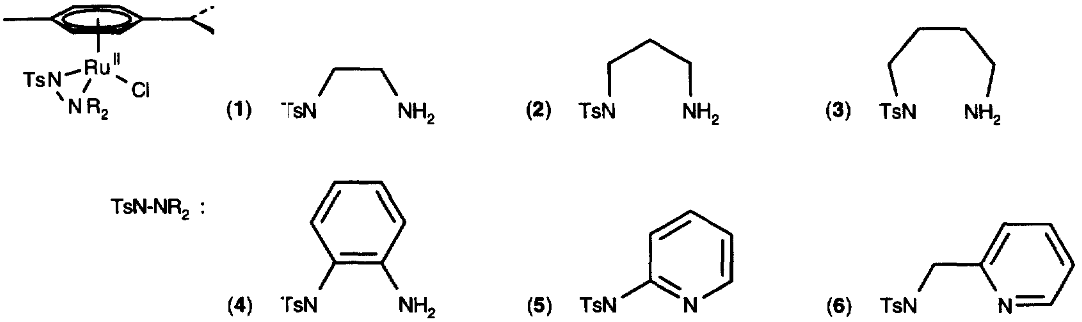

Table 1

Cyclopropanation of styrene and cyclooctene with ethyl diazoacetate catalysed by RuCl(*p*-cymene)(TsN-NR$_2$) complexes[a]

	Cyclopropanation yield, %[b] (*cis*/*trans* or *endo*/*exo* ratio)			
	Styrene		Cyclooctene	
Complex	60 °C	100 °C	60 °C	100 °C
RuCl(*p*-cymene)(TsN-NR$_2$-**1**)	78 (0.56)	89 (0.59)	34 (0.73)	66 (0.68)
RuCl(*p*-cymene)(TsN-NR$_2$-**2**)	94 (0.58)	81 (0.66)	10 (0.65)	89 (0.88)
RuCl(*p*-cymene)(TsN-NR$_2$-**3**)	80 (0.60)	90 (0.60)	12 (0.54)	58 (0.54)
RuCl(*p*-cymene)(TsN-NR$_2$-**4**)	75 (0.62)	87 (0.65)	52 (0.97)	83 (0.65)
RuCl(*p*-cymene)(TsN-NR$_2$-**5**)	65 (0.60)	85 (0.54)	20 (0.69)	88 (0.70)
RuCl(*p*-cymene)(TsN-NR$_2$-**6**)	77 (0.54)	86 (0.53)	45 (0.37)	82 (0.79)

[a] Reaction conditions : catalyst, 0.005 mmol; olefin, 20 mmol; ethyl diazoacetate, 1 mmol diluted by the olefin up to 1 mL; addition time, 4 h.

[b] Determined by GLC analysis.

Comparison studies of the efficiency of complexes **1-6** as catalysts for cyclopropanation of styrene and cyclooctene by ethyl diazoacetate are summarised in Table 1. Phenylenediamine-based complex **4** was the most effective catalyst for cyclopropanation resulting in chemical yields of 52 and 75% with cyclooctene and styrene, respectively, when the reaction was carried out at 60 °C. 2-(Aminomethyl)pyridine-based complex **6** however resulted in the highest level of stereocontrol (*endo*/*exo* ratio = 0.37 with cyclooctene; *cis*/*trans* ratio = 0.54 with styrene, at 60 °C). Furthermore, the cyclopropane stereoselectivity was highly dependent on the nature of the ester group of the diazo compound :

cis/trans ratios = 0.68 (N_2CHCO_2Me, 85% yield), 0.62 (N_2CHCO_2Et, 75%) and 0.40 (N_2CHCO_2t-Bu, 74%) for cyclopropanation of styrene catalysed by complex **4** at 60 °C.

The temperature also played a crucial role on both the yield and the stereochemical outcome of the reaction as clearly shown for the cyclopropanation of cyclooctene (Table 1). The ruthenium-catalysed reactions of alkyl diazoacetates with alkenes also proceeded with pronounced chemoselectivity with regard to the electronic properties of the olefin substituents : activated alkenes (styrenes) were more reactive than non-activated ones (1-octene and cyclooctene) (Tables 1 and 2). Under the same reaction conditions norbornene was not cyclopropanated but polymerised via ring-opening metathesis [14]. The preference of electron-rich C-C double bonds could be rationalized in terms of the electrophilic character of the postulated [$Ru{=}CHCO_2Alk$] complex. Attempts to trap or provide evidence for a carbene complex intermediate during the reaction of methyl diazoacetate with complex **6** have not been successful.

To date, the effect of the diamine ligand is unclear with regard to the donating ability of the nitrogens, the size and the bite angle of the chelating ligand. Figure 1 shows that some complexes quite sluggishly decomposed the diazo compound. Insertion of carbenes into N-H bonds [15] and ruthenium-catalysed alkylation of pyridines by olefins [16] are processes which could account for partial deactivation of the complexes through ligand modification.

Table 2

Cyclopropanation of representative olefins with ethyl diazoacetate catalysed by RuCl(*p*-cymene)(TsN-NR_2-4)[a]

Olefin	Cyclopropanation yield, %[b] (*cis/trans* ratio)	Olefin	Cyclopropanation yield, %[b] (*cis/trans* or *endo/exo* ratio)
Styrene	91 (0.62)	α-Methylstyrene	92 (0.95)
4-Methylstyrene	93 (0.53)	β-Methylstyrene	89 (0.45)
4-*t*-Butylstyrene	88 (0.50)	Cyclooctene	70 (0.92)
4-Methoxystyrene	87 (0.43)	Norbornene	0 [c,d]
4-Chlorostyrene	85 (0.40)	1-Octene	62 (0.47)

[a,b] Reaction conditions same as in Table 1, except the temperature (80 °C).

[c] With ethyl diazoacetate as the initiator, polymer yield = 29%; σ_c (fraction of *cis* double bonds) = 0.22; $r_c = 0.39$; $r_t = 2.9$; $r_c.r_t = 1.15$ (r_c, r_t, and $r_c.r_t$ are the blockiness parameters); $M_n = 30\ 000$; $M_w/M_n = 19$. With trimethylsilyldiazomethane as the initiator, polymer yield = 84%; $\sigma_c = 0.65$; $r_c = 2.4$; $r_t = 1.03$; $r_c.r_t = 2.5$; $M_n = 8\ 200$; $M_w/M_n = 4.4$.

[d] For experimental details, see ref. 14.

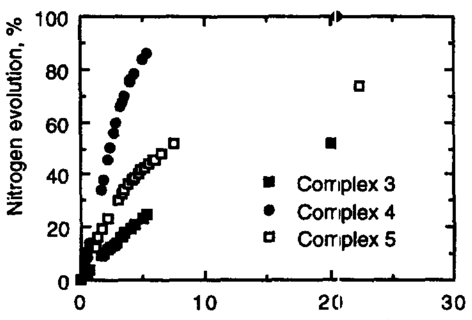

Figure 1

Influence of the complex on the decomposition rate of ethyl diazoacetate in cyclooctene, at 60 °C.

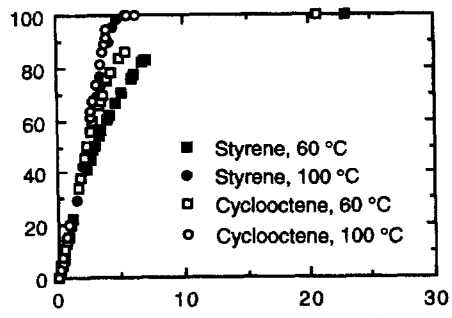

Figure 2

Influence of the temperature on the decomposition rate of ethyl diazoacetate in the presence of complex 4.

Further studies on the mechanism and the stereochemical course of the reactions are in progress.

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