



Cyclopropanation Reactions Catalysed by Ruthenium Complexes with New Anionic Phosphine Ligands

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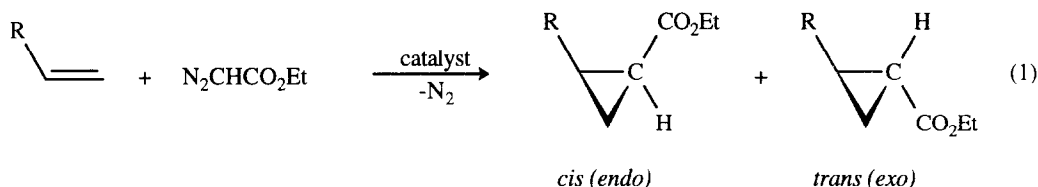
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Abstract: Novel ruthenium complexes with anionic phosphine ligands were found to be efficient in the catalytic cyclopropanation reaction of olefins with ethyl diazoacetate.

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The development of new methods for the efficient and selective preparation of cyclopropanes is of great interest in organic chemistry due to the frequent existence of these structures in biologically active compounds^{1,2} and their role as valuable synthetic intermediates.^{3,4} The direct transfer of carbene from diazo compounds to alkenes, which is the most straightforward route to cyclopropanes, is catalysed by transition metals and the use of several metal complexes has been described.⁵ Dirhodium(II) carboxylates and, later, also

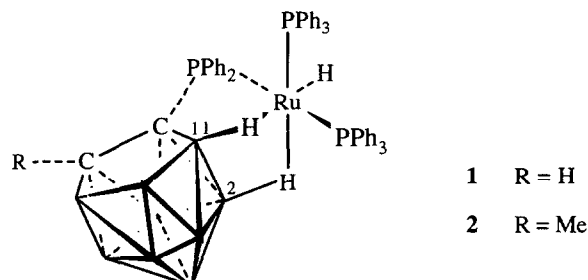


dirhodium(II) carboxamidates, as well as copper complexes modified by nitrogen-containing ligands (*e.g.*, bis-oxazoline ligands) have emerged in the last ten years as the most effective catalysts in this area.⁶ Ruthenium complexes have recently been introduced as cyclopropanation catalysts^{7,8} but none of them has been demonstrated to be really superior to rhodium-based catalysts: most of the catalysts often lack stereoselectivity. This justifies the search for alternative catalytic systems.

The synthesis of novel ruthenium complexes $[\text{RuX}(7\text{-PPh}_2\text{-}8\text{-R-C}_2\text{B}_9\text{H}_{10})\text{LL}']$, where $X = \text{H}$ or Cl , $\text{R} = \text{H}$, Me , or Ph , $\text{L} = \text{PPh}_3$, and $\text{L}' = \text{PPh}_3$, CO , tetrahydrothiophene, or ethanol, has recently been reported.⁹ In these complexes, the *exo*-monophosphino-7,8-dicarba-*nido*-undecaborate moiety, $[7\text{-PPh}_2\text{-}8\text{-R-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]^-$, behaves as a tricoordinating ligand toward $\text{Ru}(\text{II})$, and the coordination takes place by means of the *exo*-cluster PPh_2 group and boron atoms $\text{B}(2)$ and $\text{B}(11)$ through $\text{B-H}\cdots\text{Ru}$ agostic bonds. The three remaining $\text{Ru}(\text{II})$ positions may be occupied by two equivalent or distinct neutral ancillary ligands and one coordinating anion (hydride or chloride). In related rhodacarborane complexes, the PPh_3 ligands have been

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shown to readily exchange at ambient temperature.¹⁰ For these reasons, catalytic activity should be expected for these complexes. In this preliminary communication we report on the use of complexes **1** and **2** as catalysts for the cyclopropanation of olefins with ethyl diazoacetate (eq. 1).



A set of olefins has been cyclopropanated. The results are summarized in Table 1. It appeared that complexes **1** and **2** actually are excellent cyclopropanation catalysts for activated olefins such as styrene and styrene derivatives. Cyclopropane yields were however lower with cyclic olefins and with terminal linear monoolefins than with activated double bonds. These two complexes were compared for the cyclopropanation of styrene, and shown to exhibit the same activity (> 95% yield) and stereoselectivity irrespective of the carboranyl substituents. However, competitive cyclopropanation reactions between olefins (Table 2) showed that the nature of R at the 8-cluster position had a significant effect on the relative reactivity : catalyst **2** with the methyl-substituted carboranyl moiety was more discriminating than its unsubstituted analogue (**1**).

In most cases, the stereoselectivities (*cis/trans* or *endo/exo* ratio) compared with those reported for typical rhodium- and ruthenium-based catalytic systems : the *trans* (*exo*) isomer was favored. With α -methylstyrene and cyclooctene, however, the *cis/trans* and *endo/exo* ratios were close to 1. The effects of variation of the size of the diazoacetate ester substituent on the level and sense of stereoselection have been studied in the cyclopropanation of styrene using various diazoacetates in the presence of complex **2**. Increasing the steric bulk of the diazoacetate from methyl to ethyl and *t*-butyl led to a higher *trans* content [*cis/trans* ratio = 0.72

Table 1. Cyclopropanation of Representative Olefins with Ethyl Diazoacetate^a

Olefin	Catalyst :	Cyclopropanation yield, % ^b (<i>cis/trans</i> or <i>endo/exo</i> ratio)	
		1	2
Styrene, 60°C		74 (0.65) ^c	78 (0.62) ^d
Styrene, 100°C		97 (0.63)	96 (0.64)
4-Methylstyrene		96 (0.52)	96 (0.54)
4- <i>tert</i> -Butylstyrene		93 (0.50)	91 (0.48)
4-Methoxystyrene		90 (0.61)	89 (0.56)
4-Chlorostyrene		94 (0.50)	93 (0.48)
α -Methylstyrene		98 (0.95)	97 (1.02)
Cyclooctene		51 (0.86)	65 (1.08)
1-Octene		61 (0.71)	58 (0.62)
1-Dodecene		59 (0.73)	61 (0.73)

^a Reaction conditions : catalyst, 0.0075 mmol; olefin, 20 mmol; ethyl diazoacetate, 1 mmol diluted by the olefin up to 1 mL; addition time, 4 h; temperature, 100°C. ^b Determined by GLC analysis. ^c Polymers were formed during the cyclopropanation of styrene and of its 4-X-derivatives. *e.g.*, with styrene at 60°C (reaction time, 12 h) : polymer yield = 15%, $M_n = 71,000$ and $M_w/M_n = 1.75$. ^d Polymer yield = 17%.

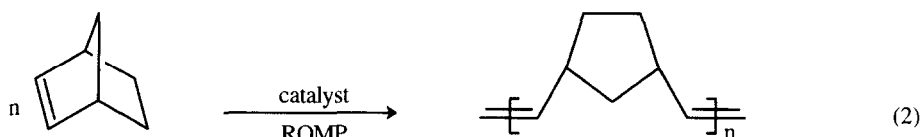
Table 2. Relative Reactivity of Representative Olefins with Ethyl Diazoacetate^a

Olefin	Catalyst :	1	2
4-Methylstyrene		1.04 (0.61 ; 0.48) ^b	1.9 (0.56 ; 0.49) ^b
Styrene		1.00 -	1.00 -
4-Chlorostyrene		0.85 (0.54 ; 0.43) ^b	0.60 (0.56 ; 0.46) ^b
Cyclooctene		0.12 (0.59 ; 0.61) ^b	0.09 (0.60 ; 0.88) ^b
1-Octene		0.12 (0.62 ; 0.60) ^b	0.08 (0.62 ; 0.55) ^b

^a Reaction conditions same as in Table 1. ^b Into brackets, the *cis/trans* ratio for styrene, and the *cis/trans* or *endolexo* ratio for the co-olefin.

(N₂CHCO₂Me), 0.64 (N₂CHCO₂Et), and 0.42 (N₂CHCO₂*t*-Bu)]. This could be improved further by using 2,6-di-*t*-butyl-4-methylphenyl diazoacetate (*cis:trans* = 1:99, based on ¹H NMR spectroscopy).

It is generally agreed that olefin cyclopropanation occurs via electrophilic metal-carbene intermediates. This was confirmed by competitive cyclopropanation reactions between olefins (Table 2 : electron-rich olefins reacted faster) as well as by insertion of carbethoxycarbene into the O-H bond of alcohols^{11,12} (isopropanol, 1- and 2-butanol : 80-85% yield at 80°C). With norbornene which is a highly strained cycloolefin, no cyclopropanation took place. Ethyl diazoacetate and trimethylsilyldiazomethane initiated, instead, the ring-opening metathesis polymerisation (ROMP) of the substrate (Eq. 2, Table 3). With a low-strain cyclic olefin such as cyclooctene (Table 1), only minute amounts of polymers were obtained. According to the mechanism of olefin metathesis, this outcome reveals the presence of two *cis* vacancies on the metal centre for coordinating *both* the carbene *and* the olefin, implying therefore the disengagement of two ligands from the coordination sphere of the ruthenium complex.¹³ In these complexes, the B-H→Ru agostic bonds are believed to be quite stable. On the other hand, in [RuCl(7-PPh₂-8-CH₃-7,8-C₂B₉H₁₀)(PPh₃)₂] - the chloride analogue of hydrido complex 2-, the phosphine ligands have been shown to be labile and, depending on the incoming ligand, either PPh₃ *trans* to

**Table 3.** Ring-Opening Metathesis Polymerisation of Norbornene Initiated by Ethyl Diazoacetate and by Trimethylsilyldiazomethane^a

Polymer	Catalyst :		2	
	N ₂ CHCO ₂ Et	N ₂ CHSiMe ₃	N ₂ CHCO ₂ Et	N ₂ CHSiMe ₃
Yield, %	30	42	20	31
<i>Cis/trans</i> ratio ^b	0.75	1.35	0.90	1.65
r _c .r _t ^c	1.15	2.55	1.55	2.4
M _n ^d	38 000	31 000	31 000	28 000
M _w /M _n	2.95	8.7	2.95	7.3

^a Reaction conditions : 0.0075 mmol of catalyst and 0.5 g of norbornene were dissolved under nitrogen in 30 mL of purified chlorobenzene. The resulting solution was heated to 60°C over 20 minutes. 0.1 mmol of diazo compound diluted in 1 mL of chlorobenzene was then added to the reaction mixture via a syringe over 0.5 h. The reaction mixture was kept at 60°C for 5 h, then cooled to room temperature, and precipitated in 700 mL of technical methanol. ^b Determined by ¹H and ¹³C NMR. ^c Blockiness parameter, determined by ¹³C NMR. ^d By GPC, using polystyrene standards.

the *exo*-cluster PPh₂, or PPh₃ *trans* to a BH participating in a B-H→Ru bond are substituted.⁹ Which of the triphenylphosphine ligands is more labile upon addition of a diazo compound, and what should be the influence of the carbene moiety on the relative lability of the remaining ligands are questions to which answers are far from being straightforward. A confirmation of this is provided by both the GPC trace and the polydispersity index (M_w/M_n) of the polynorbornenes (Table 3), which indicate that -at least- two active catalytic species are operative during the ring-opening metathesis polymerisation. Work is in progress to extend the scope of these new catalytic systems and to get insights into the mechanism of these reactions.

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