

# Cp\*Ru(II) and Cp\*Ru(IV)-catalyzed reactions of CHX with vinyl C–H bonds: competition between double bond homologation and olefin cyclopropanation by alkyl diazoacetate

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## Abstract

When diazoesters are used as carbene precursors, new Ru(II) and Ru(IV) complexes bearing various substituents tethered ligands mediate the formal carbene insertion into C–H vinyl bonds of (substituted) styrenes to yield mostly *E*- and *Z*-styrylactic esters (e.g. 4-phenylbut-3-enoates with styrene). This rarely observed reaction competes with the cyclopropanation of the double bond. The influence of steric and electronic factors on the two competitive reactions is reported. The observation that the most efficient C–H insertion catalysts also promote the ROMP of norbornene lend support to the formation of ruthenacyclobutanes as reaction intermediates. © 1998 Elsevier Science S.A. All rights reserved.

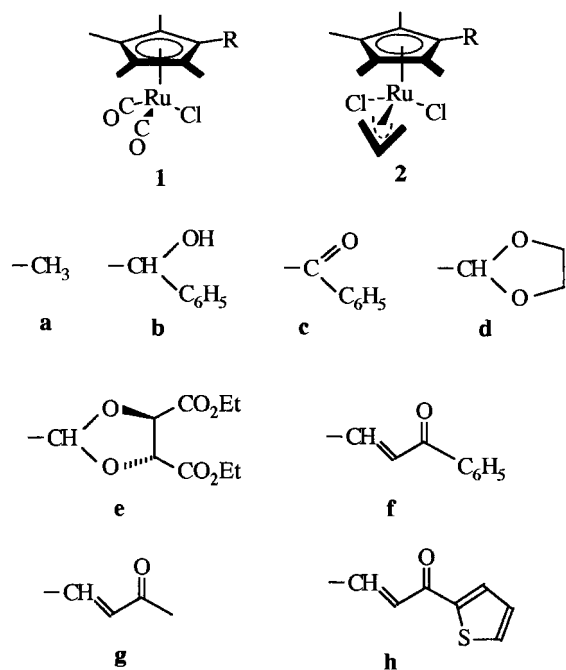
**Keywords:** Ruthenium; Ruthenium-carbene; Olefin chelate; Diazoesters; Styrene; Insertion

## 1. Introduction

The understanding of how metal complexes mediate the formation of carbon–carbon bonds is a major theme in organometallic chemistry. Much studied examples are the addition of metal–carbenes to olefins and their insertion into carbon–hydrogen bonds. The reaction products, depend on the metal, its oxidation state and its ancillary ligands [1–3]. Ruthenium-based carbene complexes have recently emerged as a new class of versatile catalysts for olefin metathesis [4–11] and olefin cyclopropanation [5,12–15,15–20]. Although intramolecular carbenoid insertion reactions into sp<sup>3</sup> C–H bonds has proved to be a powerful method for the construction of carbocycles, especially with dirhodium(II) catalysts and  $\alpha$ -diazoesters or  $\alpha$ -diazoketones as

carbene precursors [21–24], there is a dearth of information on the insertion into sp<sup>2</sup> =C–H bonds. This may be because a vinyl C–H bond is stronger than sp<sup>3</sup> C–H bonds (for average bond dissociation energies, see [25]) and that would favour either a (competitive) cycloaddition onto the C=C double bond or an insertion into an allylic C–H bond. In most of the examples reported in the literature, vinyl C–H insertions are intramolecular resulting from rearrangement of an intermediate cyclopropane [24,26–29]: we term these ‘apparent vinyl C–H insertions’. So far as we are aware, the most clear-cut examples of insertion into vinyl C–H bonds of olefins ligated to a metal were described by Werner and coworkers who recently observed the substitution of ethene C–Hs using various diazo compounds [30–32]. Rhodia- and iridia-cyclobutanes were proposed as intermediates in these reactions but no unambiguous evidence for the involvement of the metallacycles has yet been presented.

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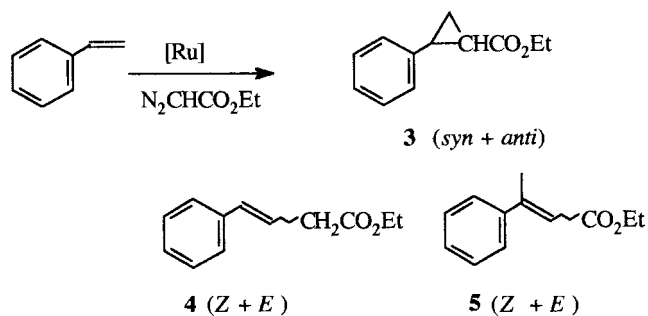
Scheme 1.

We now report on a new class of ruthenium(II) and ruthenium(IV) complexes bearing various substituents tethered ligands which mediate this rarely observed formal carbene insertion into an olefin C–H vinyl bond ('the homologation reaction'), a reaction which, as expected, competes with the cyclopropanation of the double bond.

## 2. Results and discussion

The structures of the various 18 electron-Ru(II) and Ru(IV) complexes tested as catalysts are shown in Scheme 1 [33–36].

When ethyl diazoacetate (the carbene precursor) is added slowly to an excess of styrene containing the catalyst, the unexpected compounds **4** to **5** are formed, sometimes in considerable amount, in addition to the expected cyclopropanes **3** (mixture of *syn* and *anti*-isomers), see Schemes 2 and 1.



Scheme 2.

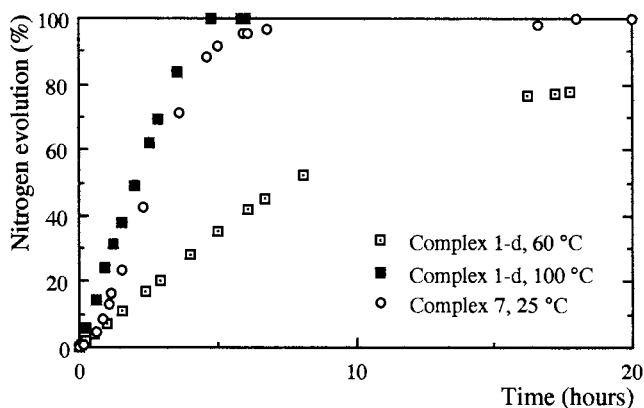


Fig. 1. Effect of the catalyst on ethyl diazoacetate decomposition.

These molecules **4** and **5** formally result from an insertion of the carbene into the different  $sp^2$  C–H bonds of the olefin. The 4-phenylbut-3-enoates **4** are obtained in a much larger amount than the 3-methylcinnamates **5** (even with the best homologation catalysts, the yield of **5** always remains below 3%) indicating a favoured carbene 'insertion' into the terminal C–H bonds and the possible importance of steric factors on the course of the reaction. Diethyl maleate and diethyl fumarate, together with some polymers and oligomers make up the rest of the reaction products. Blank experiments confirmed that the cyclopropanes were stable to the reaction conditions and were not isomerized to the homologated products, with either the Ru(II)- or the Ru(IV)-complexes.

Table 1 summarizes the results obtained with complexes **1a–h** and **2a–h**, respectively at 60 and 100°C.

The main trends showed by these results indicate that:

1. The main products are the cyclopropanes, both from the Ru(II) and the Ru(IV) complexes, at both 60 and 100°C; the Ru(II) complexes generally give more cyclopropanes than do the corresponding Ru(IV) complexes.
2. Substantial amounts of homologated products **4**, are also formed, in particular with Ru(IV) catalysts **2b–f** at 60°C. However the parent complexes, **1a** and **2a**, form more **4** at 100°C.
3. The *syn/anti* ratios of cyclopropanes are highest when the Ru(II) complexes **1a–h** are used at 60°C; for the Ru(IV) catalysts they are somewhat higher at 100°C than at 60°C and (for example, the **2b–f** series at 60°C) compare well with most of the ruthenium-based cyclopropanation catalysts described to date in the literature [5,12–15,15–20].

In order to get a better insight into the effect of steric factors on the competitive homologation/cyclopropanation reactions, the catalysts, **2c** and **2f**, were tested with three different diazoacetates, Me-, Et- and *t*-Bu-dia-

Table 1  
Addition of ethyl diazoacetate to styrene catalyzed by ruthenium complexes **1** and **2** (a–h)<sup>a</sup>

Complex	Temperature							
	60°C				100°C			
	Cyclopropanation		Homologation ( <b>4</b> )		Cyclopropanation		Homologation ( <b>4</b> )	
	Yield, % <sup>b</sup>	<i>syn/anti</i>	Yield, % <sup>b</sup>	<i>Z/E</i>	Yield, % <sup>b</sup>	<i>syn/anti</i>	Yield, % <sup>b</sup>	<i>Z/E</i>
<b>1a</b>	70	0.39	7.5	1.0	72	0.22	19	1.0
<b>2a</b>	69	0.39	16	1.0	57	0.20	38	1.0
<b>1b</b>	62	0.51	1	2.4				
<b>2b</b>	57	0.21	30	1.7	72	0.34	18	1.3
<b>1c</b>	75	0.53	t	—	96	0.41	1.5	2.1
<b>2c</b>	60	0.19	32	1.75	84	0.41	10	1.65
<b>1d</b>	73	0.57	t	—	94	0.31	2	1.75
<b>2d</b>	57	0.18	33	1.35	71	0.22	23	1.4
<b>2e</b>	63	0.14	29	1.65	66	0.18	25	1.55
<b>2f</b>	56	0.15	37	1.15	73	0.31	17	1.13
<b>1g</b>	57	0.51	<1	—	90	0.27	2	1.45
<b>1h</b>	71	0.45	2	1.6	84	0.27	7	1.16

<sup>a</sup> Reaction conditions: complex, 0.005 mmol; styrene, 20 mmol; under air; ethyl diazoacetate, 1 mmol diluted by styrene up to 1 ml; addition time, 4 h.

<sup>b</sup> Determined by GLC analysis.

zoacetates (abbreviated hereafter as MeDA, EtDA and *t*-BuDA, respectively) at 60°C. The results of the experiments are summarized in Table 2.

The different diazoesters do have a small influence on the homologation reaction but little effect on the cyclopropanation. Using the less sterically demanding MeDA favours the 'insertion' reaction whereas the inverse trend is observed with the more bulky *t*-BuDA, although the homologation reaction is then not completely suppressed. The Ru(IV) complex **2a** without the functionality, again, does not fit in with the general trends.

Perhaps more surprising is the observation (Table 3) that the electronic factors do not seem to affect the outcome of the two reactions. Thus neither electron-donating nor electron-withdrawing groups seem to have any marked effect on the yields and stereoselectivities: both 4-methyl styrene and 4-chloro styrene give similar product distributions when reacted with EtDA in the presence of a variety of (Ru(II) or Ru(IV) catalysts. The preference for a homologation pathway with the Ru(IV) catalysts is again observed.

These data do not show any strong influence of the nature of the substituent/tether on the reactions studied: for example, neither the size nor its orientation seems to play any major role. In order to investigate further the influence of the tether, a new series of complexes, including the cationic analogue of **1a** (Scheme 3) and complexes **7** and **8**, where the substituent at CH<sub>2</sub> is (at least initially) unambiguously tethered to the metal centre, were then tested.

The results of the experiments, summarized in Table 4, show that **6** is poor for homologation but an excellent cyclopropanation catalyst (in fact the best of the series), while **7** and its cationic analogue **8** do not show any particular activity or selectivity when compared to the other catalysts. However, the cationic complex **8** proved to be a quite efficient cyclopropanation catalyst at 100°C.

The other Ru(IV) complexes **9** and **10**, are similar to the other Ru(IV) derivatives and mediate the formation of homologated products. Their cyclopropanation activity peaks at around 60–80°C and decreases significantly at higher temperature. Further analysis however indicates that there is an optimal temperature for the homologation and for the cyclopropanation reactions for all the complexes studied so far. This temperature lies around 100°C for most of the complexes in Table 1 but is lower for some other complexes such as **2a**, **7**, **9** and **10**. A partial explanation for this observation rests on the different rates of diazoester decomposition as a function of temperature with the different catalysts. As an example, the rate of decomposition of EtDA catalyzed by complexes **1d** and **2d** at 60 and 100°C is given in the figure. The decomposition catalyzed by complexes **7** (and also **9** and **10**) is comparatively faster, even at 25 or 60°C.

### 3. Mechanistic implications

At this stage of the study, the reaction mechanism remains speculative, although some rationalizations can

Table 2  
Addition of representative diazoacetates to styrene at 60°C<sup>a</sup>

Complex	Diazoacetate	Cyclopropanation		Homologation ( <b>4</b> )		Cyclopropanation/homologation ratio
		Yield, % <sup>b</sup>	<i>syn/anti</i> ratio	Yield, % <sup>b</sup>	Z/E ratio	
<b>1a</b>	N <sub>2</sub> CHCO <sub>2</sub> Me	66	0.54	6	1.43	11
	N <sub>2</sub> CHCO <sub>2</sub> Et	70	0.39	7.5	1.00	9.5
	N <sub>2</sub> CHCO <sub>2</sub> <i>t</i> -Bu	66	0.38	3	0.98	22
<b>2a</b>	N <sub>2</sub> CHCO <sub>2</sub> Me	75	0.40	13	1.04	5.8
	N <sub>2</sub> CHCO <sub>2</sub> Et	69	0.39	16	1.00	4.3
	N <sub>2</sub> CHCO <sub>2</sub> <i>t</i> -Bu	65	0.16	25	0.85	2.6
<b>2c</b>	N <sub>2</sub> CHCO <sub>2</sub> Me	57	0.20	37	1.65	1.55
	N <sub>2</sub> CHCO <sub>2</sub> Et	60	0.19	32	1.75	1.85
	N <sub>2</sub> CHCO <sub>2</sub> <i>t</i> -Bu	60	0.06	29	1.85	2.05
<b>2f</b>	N <sub>2</sub> CHCO <sub>2</sub> Me	53	0.16	40	1.18	1.32
	N <sub>2</sub> CHCO <sub>2</sub> Et	56	0.15	37	1.15	1.5
	N <sub>2</sub> CHCO <sub>2</sub> <i>t</i> -Bu	58	0.05	33	1.07	1.75

<sup>a,b</sup> Reaction conditions same as in Table 1.

be made based upon some quite simple assumptions on the known chemistry of metal–carbene complexes. All the catalysts employed here are initially 18 electron-ruthenium(II) or (IV) complexes. In order to obtain the metal–carbene—the key intermediate—the release of one or more ligand(s) is necessary to create sites at which the reaction can then proceed. This explains why heating is needed to start the reaction and why the different diazo compounds decompose at different rates with the different ruthenium complexes.

The relative rates of decomposition of the diazo compounds may be anticipated to be related to the relative ease of the vacant site, in other words, to the lability of the ligand. Thus, for example, the ruthenium(II) complexes are expected to replace one CO ligand by the diazo compound to form the key 18 electron-ruthenium–carbene intermediate. This latter complex could then react further with a non coordinated olefin to yield a cyclopropane, in a manner similar to that proposed for the dirhodium(II) catalysts [37,38]. The situation for the ruthenium(IV) complexes is more complex: one route by which they may be activated is by loss of an allyl halide to yield a heavily unsaturated Cp\*RuCl, a 14 electron species which would allow the coordination at the metal centre both of the carbene species and of the olefin. That could give a ruthenacyclobutane. The chemistry of four-membered metallacycles in general and that of ruthenacyclobutanes in particular is quite varied and presently not well understood [39]. Many reaction pathways are possible including the reductive elimination of a cyclopropane as well as decomposition to yield homologated products. However, examples of the latter reaction are relatively rare [39,40] and have not yet been reported in the chemistry of ruthenium. In the present case, formation of isomers **4** and **5** can be readily explained by assuming a  $\beta$ -hy-

drogen shift followed by migration of the hydride ligand to a terminal carbon atom of the allyl group yielding the homologated molecule and reforming the catalytically active species, as sketched in Scheme 4.

The preferential formation of **4** also suggests that metallacyclobutane formation and its reaction(s) are governed by steric and conformational factors. According to the proposed reaction pathway, preferential formation of **4** implies preferential formation of ruthenacyclobutane **11** relative to **12**. This scheme also rationalizes the relatively higher stereoselectivities in cyclopropanation observed with ruthenium(IV) complexes, the formation of metallacycles corresponding to more sterically constrained transition states. The somewhat higher relative amount of homologation products with ruthenium(II) complexes at 100°C might be due to a more important participation of the ruthenacyclobutane reaction pathway because of a (partial) disengagement of the second CO ligand at this temperature. It is also worth noting in this context that a significant increase of homologated products is only obtained with the less sterically hindered complex, the non-tethered **1a**.

In order to test the proposed mechanism and the intermediacy of metallacycles, we have tested some of our catalyst systems in the ring-opening-metathesis-polymerization (ROMP) of bicyclo[2.2.1]hept-2-ene (norbornene). It is now accepted that metallacyclobutanes are intermediates in olefin metathesis [4] and, if we postulate their intermediacy in the homologation reaction, the metallacycle should be detectable by its propensity to initiate the formation of polymers from a suitable cyclic alkene, e.g. norbornene. Thus, a competitive reaction might lead to the formation of ROMP products with this strained olefin, the relief of the olefin ring-strain driving the reaction toward the formation of polynorbornene according to Scheme 5.

Table 3  
Addition of ethyl diazoacetate to 4-X-styrenes (X = H, Me, Cl) at 60°C<sup>a</sup>

Complex	Olefin	Cyclopropanation		Homologation (4)	
		Yield, % <sup>b</sup>	<i>syn/anti</i>	yield, % <sup>b</sup>	Z/E
<b>1a</b>	Styrene	70	0.39	7.5	1.0
	4-methylstyrene	73	0.34	8	1.2
	4-chlorostyrene	75	0.31	7	0.88
<b>2a</b>	Styrene	69	0.39	16	1.0
	4-methylstyrene	65	0.30	15	1.06
	4-chlorostyrene	76	0.22	15	0.85
<b>1d</b>	Styrene	73	0.57	t	—
	4-methylstyrene	67	0.45	2	2.2
	4-chlorostyrene	71	0.44	1	—
<b>2d</b>	Styrene	57	0.18	33	1.35
	4-methylstyrene	59	0.16	35	1.4
	4-chlorostyrene	63	0.15	32	1.16
<b>2f</b>	Styrene	56	0.15	37	1.15
	4-methylstyrene	52	0.16	36	1.2
	4-chlorostyrene	60	0.15	34	0.95

<sup>a, b</sup> Reaction conditions same as in Table 1.

Polymer formation is thus especially expected to be observed with the ruthenium(IV)-based complexes. Table 5 indicates that this is exactly what is observed (even at 60°C!). Moderate amounts of polynorbornenes (up to 54% conversion) are formed, essentially with

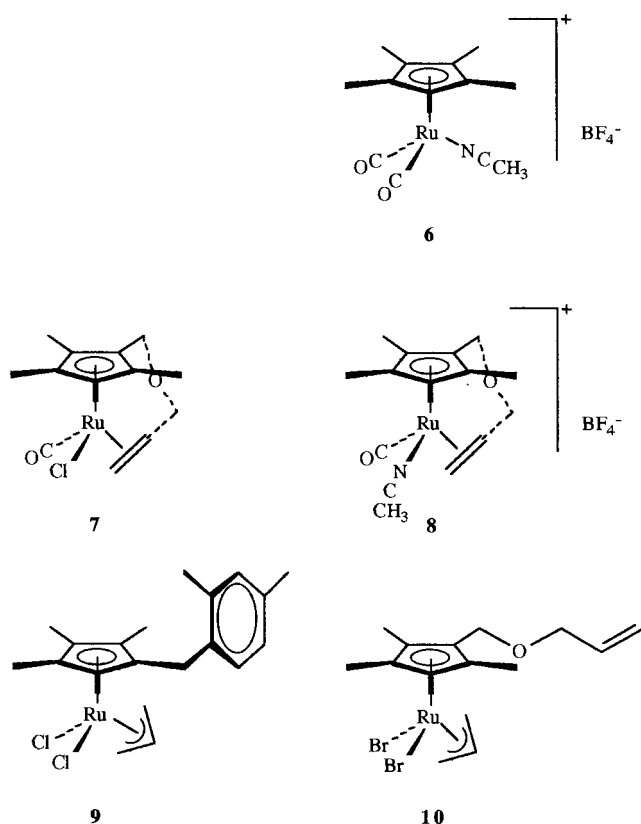
ruthenium(IV) catalysts when activated by reaction with trimethylsilyldiazomethane (TMSD, which is usually superior to diazoesters for initiating metathesis) [41]. The polymers contain mostly *cis*-double bonds, as often observed with Ru-based ROMP catalysts. The relatively modest monomer conversions can be rationalized by the fact that the two competing reactions (homologation and cyclopropanation) are of course chain termination steps in ROMP.

In the ruthenium(II) series, only complexes **7** and **8** give significant amounts of polymers. This can be rationalized by assuming a relatively easy loss of the CO ligand in complex **7** and of both the olefin and the nitrile ligand in **8**. This hypothesis is also supported by the observation that **7** is also the ruthenium(II) complex which promotes the formation of higher amounts of homologated products.

The at first sight unexpectedly small effects of the size and nature of the CH<sub>2</sub> substituent on the reaction course may be due to the fact that the substituent is normally bent back away from the metal. This tendency is shown by a number of X-ray structure determinations, which the substituent are always found bent back. That the complexes with a tethered side chain show similar effects suggests that the tether may become unhooked early during the reaction.

#### 4. Conclusions

New ruthenium complexes have been shown for the first time to catalyze the insertion of carbenes into vinylic C–H bonds (homologation reaction). Metalla-



Scheme 3.

Table 4  
Addition of ethyl diazoacetate to styrene catalyzed by ruthenium complexes 6–10<sup>a</sup>

Complex	Temperature							
	60°C				100°C			
	Cyclopropanation		Homologation (4)		Cyclopropanation		Homologation (4)	
Yield, % <sup>b</sup>	<i>syn/anti</i>	Yield, % <sup>b</sup>	Z/E	Yield, % <sup>b</sup>	<i>syn/anti</i>	Yield, % <sup>b</sup>	Z/E	
6	93	0.61	2.5	1.55	93	0.63	2.5	1.85
7	78	0.24	12	1.10	77	0.34	15.5	1.10
8	52	0.63	1.5	0.77	91	0.64	2.5	1.06
9	83	0.46	8	1.03	60	0.26	33	1.08
10	42	0.51	4	1.25	68	0.29	32	1.15

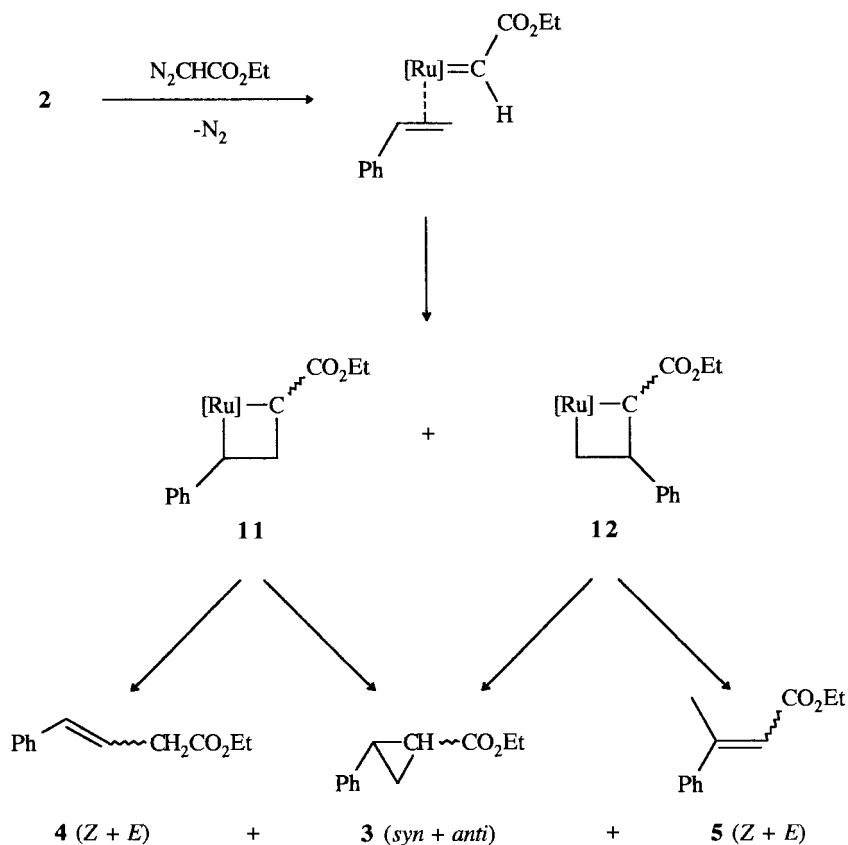
<sup>a, b</sup> Reaction conditions same as in Table 1.

cyclobutanes are the putative intermediates responsible for the homologation reaction, a reaction essentially promoted by Ru(IV) complexes. Cyclopropanation of the C=C double bond is competitive with homologation and becomes the principal reaction with most of the Ru(II) complexes, to the extent that some of them are good cyclopropanation catalysts. Further studies are now needed to assess the scope and limitations of the catalyst systems and their potential in synthetic organic chemistry.

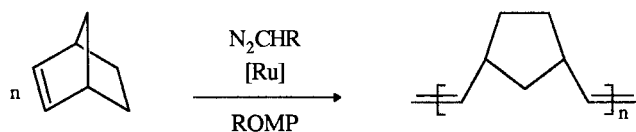
## 5. Experimental section

### 5.1. General methods

The reactions were performed under nitrogen using standard Schlenk or vacuum-line techniques. Solvents and monomers were freshly distilled from standard drying agents and kept under nitrogen. Ethyl diazoacetate and trimethylsilyldiazomethane were reagent grade and used without further purification. The ruthenium



Scheme 4.



Scheme 5.

mium complexes were prepared according to literature [33–36]. Products were identified by comparison of their retention times with authentic samples on two different GC capillary columns and by coupled GC-MS. GC analysis were performed on a 30 m  $\times$  0.32 mm WCOT FFAP-CB column and a 30 m  $\times$  0.53 CP-Sil8-CB column, with FID and nitrogen as carrier gas.

### 5.2. Cyclopropanation and homologation reactions

In a typical experiment, the catalyst (0.005 mmol) and the olefin (20 mmol) were put into a round-bottomed flask and heated to the reaction temperature (usually 60 or 100°C) under nitrogen. One ml of a solution of the diazoester in the olefin (1 mol l<sup>-1</sup>) was then added dropwise over 4 h to the vigorously stirred system via a syringe pump. When necessary, heating was continued for a few more hours, especially with the less active catalysts (see text). The reaction products were then analyzed by gas chromatography. The yields

Table 5  
Ring-opening metathesis polymerisation of norbornene initiated by ethyl diazoacetate and by trimethylsilyldiazomethane<sup>a</sup>

Complex	Diazo compound	Polymer yield, %	$\sigma_c^b$	$M_n^c$
1a	N <sub>2</sub> CHSi(CH <sub>3</sub> ) <sub>3</sub>	<0.5	—	—
2a	N <sub>2</sub> CHSi(CH <sub>3</sub> ) <sub>3</sub>	<0.5	—	—
1c	N <sub>2</sub> CHSi(CH <sub>3</sub> ) <sub>3</sub>	<0.5	—	—
2c	N <sub>2</sub> CHSi(CH <sub>3</sub> ) <sub>3</sub>	54	0.75	21 000
2c	N <sub>2</sub> CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	4	0.82	7000
1d	N <sub>2</sub> CHSi(CH <sub>3</sub> ) <sub>3</sub>	<0.5	0.74	—
2d	N <sub>2</sub> CHSi(CH <sub>3</sub> ) <sub>3</sub>	50	0.72	19 000
2d	N <sub>2</sub> CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	3	0.66	—
6	N <sub>2</sub> CHSi(CH <sub>3</sub> ) <sub>3</sub>	<0.5	—	—
7	N <sub>2</sub> CHSi(CH <sub>3</sub> ) <sub>3</sub>	47	0.45	34 000
7	N <sub>2</sub> CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	23	0.58	22 000
8	N <sub>2</sub> CHSi(CH <sub>3</sub> ) <sub>3</sub>	39	0.73	22 000
8	N <sub>2</sub> CHCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	<0.5	0.80	—
9	N <sub>2</sub> CHSi(CH <sub>3</sub> ) <sub>3</sub>	7	0.87	—
10	N <sub>2</sub> CHSi(CH <sub>3</sub> ) <sub>3</sub>	19	0.71	—

<sup>a</sup> Reaction conditions: 0.015 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 min. 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.

<sup>b</sup> Fraction of *cis* units, determined by <sup>1</sup>H- and <sup>13</sup>C-NMR.

<sup>c</sup> Determined by GPC, using polystyrene standards.

were based on the diazo compound and calculated with dibutyl fumarate or diethyl phthalate as internal standards.

### 5.3. Polymerization reactions

The reaction were carried out in chlorobenzene (catalyst 0.0075 mmol, diazo compound 0.1 mmol) and the polymers (polynorbornenes) isolated and identified along the lines reported in ref. [11] and [41].

### Acknowledgements

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