

# Dinuclear Ruthenium(I) Triazenide Complexes as Catalysts for Carbenoid Cyclopropanation Reactions

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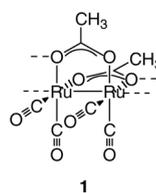
The ability of ruthenium(I) triazenide complexes  $[\text{Ru}(\text{CO})_3(\text{ArNNNAr})]_2$  ( $\text{Ar} = \text{C}_6\text{H}_4\text{-4-X}$ ,  $\text{X} = \text{CH}_3, \text{Cl}, \text{Br}$ ) to catalyze the cyclopropanation of alkenes with methyl diazoacetate is investigated. With terminal alkenes (styrene, ethyl vinyl ether, 1-hexene), the cyclopropanecarboxylic esters are formed in good to high yield and with an *E* : *Z* diastereoisomer ratio of about 1.0 in most cases. 2-Methyl-2-butene is cyclopropanated in low yield but with a *syn*-selectivity up to 90:10.

**Key words:** Catalysis, Cyclopropanation, Diazo Compounds, Ruthenium Complexes, Triazenide Ligands

## Introduction

The inter- and intramolecular cyclopropanation of alkenes by carbenoid reaction with aliphatic diazo compounds is effectively catalyzed by several late transition metal complexes of which those based on copper, rhodium, and (to a lesser extent) palladium are the most important ones [1]. In the past decade, a variety of ruthenium complexes have been found to catalyze carbenoid cyclopropanation reactions [2, 3]. Ruthenium catalysts currently emerge as interesting alternatives to the established rhodium catalysts not only because of the significantly lower price of ruthenium but also because the rich coordination chemistry of ruthenium – compared to the rhodium catalysts which are almost exclusively dinuclear rhodium carboxylates, amidates and phosphates – could offer a wider range of possibilities to control the chemo-, regio- and stereoselectivity of catalytic cyclopropanation reactions and of other carbene transfer reactions as well.

We have recently identified a dinuclear ruthenium(I) carboxylate complex,  $[\text{Ru}_2(\text{CO})_4(\mu\text{-OAc})_2]_n$  (**1**), as a suitable catalyst for the cyclopropanation of a wide range of nucleophilic alkenes with diazoacetic esters [4, 5], (trialkylsilyl)diazoacetic esters [6], (trimethylsilyl)diazomethane [7], and aryldiazomethanes [7]. A characteristic structural feature of **1** is its sawhorse configuration, with  $\text{Ru-Ru-C(O)}$  angles larger and  $\text{Ru-Ru-O}$  angles smaller than  $90^\circ$ , which is probably responsible for the unusual *syn*-selectivity in the

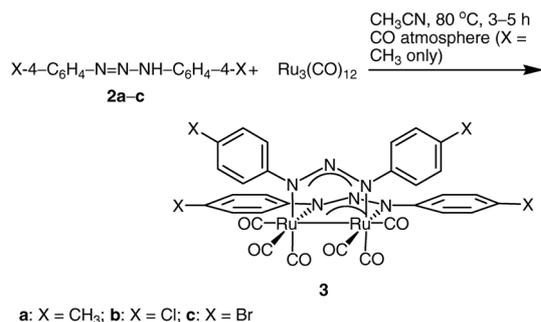
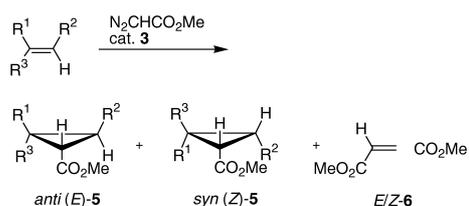


cyclopropanation of trisubstituted alkenes. Based on these results, we turned our attention to analogues of **1** in which the acetato bridges are replaced by 1,3-diaryltriazenido ligands and evaluated their performance as catalysts for alkene cyclopropanation with methyl diazoacetate.

## Results and Discussion

### Synthesis and structural characterization of complexes **3a – c**

The synthesis of the dinuclear ruthenium(I) triazenide complexes **3a, b** from 1,3-diaryltriazenes **2a, b** and  $\text{Ru}_3(\text{CO})_{12}$  has been described [8]. We prepared triazenes **2a – c** according to a published procedure for the preparation of 1-methyl-3-*p*-tolyltriazenes [9] by diazotization of the corresponding *p*-substituted anilines followed by coupling with the same anilines in a basic medium (see Experimental Section). Chromatographic purification of the triazenes was not successful, because they were not stable towards silica gel and could not be recovered from neutral alumina. It turned out,

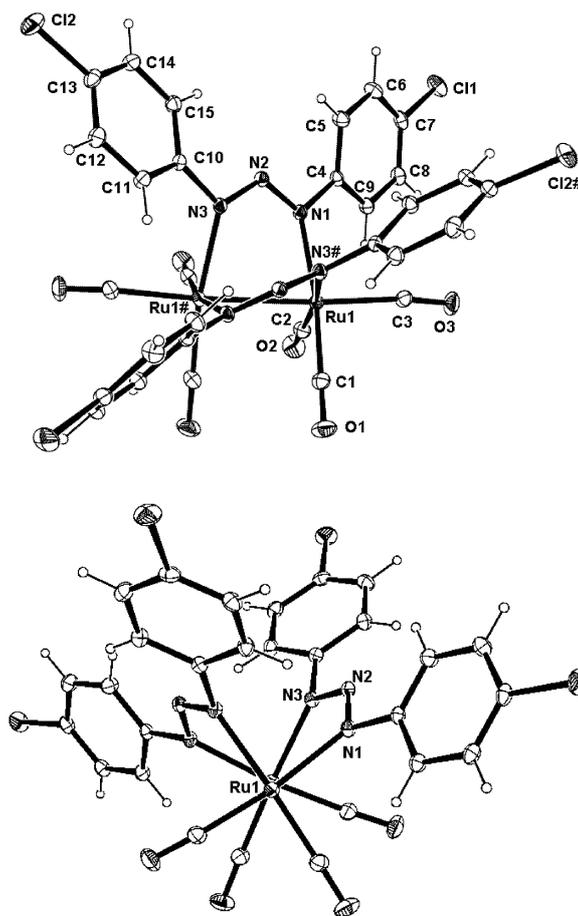
Scheme 1. Synthesis of complexes **3a-c**.

Scheme 2. Cyclopropanation of alkenes with methyl diazoacetate.

however, that the crude products, obtained after extraction with cyclohexane from the reaction mixtures, could be used without complications in the preparation of complexes **3**.

It has been reported that (1,3-di-*p*-tolyl)triazenide complex **3a** is formed in 47% yield from triazene **2a** and  $\text{Ru}_3(\text{CO})_{12}$  in refluxing benzene and under a CO atmosphere [8]. We found that with acetonitrile as solvent and a ca. four- to sixfold higher concentration of the reactants, the product was obtained after only 3 hours in 63% yield (Scheme 1). Under similar conditions, but in the absence of a CO atmosphere, complexes **3b,c** were obtained in 72 and 55% yield, respectively. In contrast to these conditions, it was reported that the synthesis of **3b** in benzene as solvent did require the presence of a CO atmosphere, because in the absence of excess carbon monoxide, the axial CO ligands in **3b** were replaced by 1,3-bis(4-chlorophenyl)triazene molecules [8]. Complex **3a** has also been prepared before from  $[\text{Ru}_2(\text{CO})_4(\mu\text{-OAc})_2]_n$  by ligand exchange with triazene **2a** in acetonitrile in 43.5% yield [8]. Again, we were able to improve the yield to 75% (see Experimental Section).

The solid-state structure of complex **3b** was determined by single-crystal X-ray diffraction analysis. A molecule plot is shown in Fig. 1, relevant bond distances and angles are given in Table 1. In the crystal, the molecules have exact  $C_2$  symmetry. The co-

Fig. 1. Structure of complex **3b** in the crystal (ORTEP plot, ellipsoids of thermal vibration shown at the 30% probability level). Top: View perpendicular to the Ru–Ru axis; bottom: view along the Ru–Ru axis (axial CO ligands not shown).

ordination geometry is similar to the triazenido complex  $[\text{Ru}(\text{ArN}=\text{N}=\text{N}(\text{Ar}))(\text{CO})_2(\text{NH}_2\text{Ar})]_2$  (Ar = *p*-tolyl) (**A**) [8], where the axial position at each Ru atom is occupied by a 4-methylaniline rather than a CO ligand, and to the pentazenido complex  $[\text{Ru}(\text{ArN}=\text{N}=\text{N}=\text{N}=\text{N}(\text{Ar}))(\text{CO})_3]_2$  (Ar = *p*-tolyl) (**B**) [10]. In contrast to related carboxylato complexes of type **1** [11], the  $\text{Ru}_2\text{N}_3$  rings adopt a twisted rather than a planar conformation which correlates with a staggered arrangement of the metal–ligand bonds at Ru1 and Ru1# as seen in the lower part of Fig. 1. As in complex **B**, the bond lengths Ru1–C3 and C3–O3 indicate that the axial carbonyl ligands are less tightly bound than the equatorial ones. The octahedral geometry at the metal centers deviates a bit from ideal values; in particular, due to the small size of the triazenide bridges, the Ru–

Bond lengths (Å)	Bond angles (°)		Torsion angles (°)		
Ru(1)-Ru(1) <sup>#1</sup>	2.6701(6)	C(1)-Ru(1)-C(2)	91.40(11)	Ru(1) <sup>#1</sup> -Ru(1)-N(1)-N(2)	35.39(15)
Ru(1)-C(1)	1.886(2)	C(1)-Ru(1)-N(1)	169.30(8)	Ru(1)-N(1)-N(2)-N(3)	-19.9(2)
Ru(1)-C(2)	1.889(3)	C(2)-Ru(1)-N(1)	95.50(9)	N(1)-N(2)-N(3)-Ru(1) <sup>#1</sup>	-17.7(2)
Ru(1)-C(3)	2.003(2)	C(1)-Ru(1)-N(3) <sup>#1</sup>	86.14(9)	Ru(1)-N(1)-C(4)-C(5)	-149.8(2)
Ru(1)-N(1)	2.148(2)	C(2)-Ru(1)-N(3) <sup>#1</sup>	171.33(8)	Ru(1) <sup>#1</sup> -N(3)-C(10)-C(15)	-140.9(2)
Ru(1)-N(3) <sup>#1</sup>	2.149(2)	N(1)-Ru(1)-N(3) <sup>#1</sup>	85.83(7)	N(1)-Ru(1)-Ru(1) <sup>#1</sup> -N(3)	-26.3(1)
N(1)-N(2)	1.306(2)	C(1)-Ru(1)-Ru(1) <sup>#1</sup>	90.48(7)	C(1)-Ru(1)-Ru(1) <sup>#1</sup> -C(2) <sup>#1</sup>	-35.7(1)
N(1)-C(4)	1.438(2)	C(2)-Ru(1)-Ru(1) <sup>#1</sup>	91.06(7)		
N(2)-N(3)	1.298(2)	C(3)-Ru(1)-Ru(1) <sup>#1</sup>	174.82(7)		
N(3)-C(10)	1.438(3)	N(1)-Ru(1)-Ru(1) <sup>#1</sup>	81.23(5)		
N(3)-Ru(1) <sup>#1</sup>	2.149(2)	N(3) <sup>#1</sup> -Ru(1)-Ru(1) <sup>#1</sup>	80.67(4)		
O(1)-C(1)	1.140(3)	N(2)-N(1)-Ru(1)	122.21(12)		
O(2)-C(2)	1.141(3)	C(4)-N(1)-Ru(1)	125.58(13)		
O(3)-C(3)	1.120(3)	N(3)-N(2)-N(1)	116.67(17)		

Table 1. Selected bond lengths, bond angles, and torsion angles for complex **3b**<sup>a</sup>.

<sup>a</sup> Symmetry transformation used to generate equivalent atoms: #1  $-x + 1/2, y, -z + 1$ .

Ru–N bond angles (80.6, 81.3°) are distinctly smaller than the Ru–Ru–C<sub>eq</sub>(O) angles (90.5, 91.1°).

### Cyclopropanation reactions

The potential of complexes **3a–c** to catalyze the carbene transfer from methyl diazoacetate to various alkenes (Scheme 2) was tested. In order to minimize the formation of the formal carbene dimers dimethyl maleate and dimethyl fumarate (**Z-6**, **E-6**), the diazo ester was gradually added during 10 hours to the alkene phase containing the catalyst. Table 2 shows the results obtained at 20 °C with styrene at three different catalyst concentrations, in styrene/dichloromethane solutions and in neat styrene. It turned out that even with a catalyst loading of 0.1 mol-%, high yields of cyclopropanes **5** were obtained, but the reaction time of about 3–4 weeks was unreasonably long. With 3 mol-% of catalyst, the reaction was completed almost immediately after the addition of diazo ester. The yields were usually better in neat rather than diluted styrene, and catalyst **3b** in general gave the best results. Therefore, **3b** was also applied to compare the effectiveness of cyclopropanation of a standard set of alkenes (Table 3). It was found that terminal alkenes (styrene, ethyl vinyl ether, 1-hexene) are cyclopropanated in good to high yield, while alkenes with 1,2-di- and 1,2,3-trisubstituted double bonds (cyclohexene, 2-methyl-2-butene) give only low yields of the corresponding cyclopropanes. In contrast, the structurally similar ruthenium(I) acetate complex **1** catalyzes not only cyclopropanation of terminal alkenes in good to high yields but also that of several internal double bonds (*e.g.* 68% yield from cyclohexene and 61% from 2-methyl-2-butene), while its effectiveness decreases significantly only in the case of a tetra-substituted double bond (2,3-dimethyl-2-butene, 47%

Table 2. Cyclopropanation of styrene with methyl diazoacetate catalyzed by **3a–c** at 20 °C.

Catalyst	Catalyst loading (mol-%)	Yield <sup>a</sup> (%) of	
		<i>E-5</i> + <i>Z-5</i>	Relative ratio <sup>a</sup> <i>E-5</i> : <i>Z-5</i>
<b>3a</b>	0.1	57	59:41
	1.0	61 (79)	50:50 (49:51)
	3.0	60 <sup>b</sup> (70)	49:51 (46:54)
<b>3b</b>	0.1	98	63:37
	1.0	87 (98)	51:49 (53:47)
	3.0	90 <sup>c</sup> (87)	46:54 (48:52)
<b>3c</b>	0.1	88	69:31
	1.0	71 (96)	52:48 (48:52)
	3.0	74 <sup>d</sup> (80)	51:49 (48:52)

<sup>a</sup> Yields and diastereomer ratios were determined by GC. The values for the reaction in styrene-CH<sub>2</sub>Cl<sub>2</sub> (1 mmol of diazoester, 10 mmol of styrene, 1–1.7 ml of CH<sub>2</sub>Cl<sub>2</sub>) are given first; the values in parentheses refer to the reaction in neat styrene (1 mmol of diazoester, 26 mmol of styrene); <sup>b</sup> at 40 °C: 64% yield (48:52); <sup>c</sup> at 40 °C: 95% yield (49:51); <sup>d</sup> at 40 °C: 94% yield (46:54).

yield) [4]. These results indicate that cyclopropanation reactions catalyzed by triazenido-ruthenium(I) complexes **3**, by comparison with acetate complex **1**, are even more dominated by the steric demand than by the nucleophilicity of the olefin. The electrophilic character of ruthenium-catalyzed cyclopropanation reactions has been established [2, 12, 13], and the observation that the yields of styrene cyclopropanation in general decrease in the order **3b** > **3c** > **3a** indicates an influence of remote electron-withdrawing substituents on the electrophilic character of the catalytically active species as well. However, ruthenium-based cyclopropanation catalysts are typically much less electrophilic than, *e.g.*, the established dinuclear rhodium acetate and amidate complexes.

According to the generally accepted mechanistic picture [1, 2], metal-carbene intermediates are involved in the carbene transfer reaction. With the coordinatively saturated complexes **3a–c**, it is required that

Table 3. Cyclopropanation of different alkenes with methyl diazoacetate catalyzed by **3b** (3 mol-%).

Entry	Alkene			Yield <sup>a</sup> (%) of <i>E-5</i> + <i>Z-5</i> (or <i>anti</i> + <i>syn</i> )	Relative ratio <i>E-5</i> : <i>Z-5</i> (or <i>anti</i> : <i>syn</i> )
	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>		
1	Ph	H	H	90 / 95 / 87	46:54 / 49:51 / 48:52
2	EtO	H	H	83 / – / –	63:37 / – / –
3	<i>n</i> Bu	H	H	61 / – / –	52:48 / – / –
4	–(CH <sub>2</sub> ) <sub>4</sub> –		H	29 / 13 <sup>b</sup> / 7 <sup>c</sup>	52:48 / 60:40 / 56:44
5	Me	Me	Me	18 / 16 / 22	13:87 / 10:90 / 11:89

<sup>a</sup> Yields and diastereomer ratios were determined by method A (entries 1, 4, 5) or method B (entries 2, 3), see experimental section. Values are given for the following conditions: alkene–CH<sub>2</sub>Cl<sub>2</sub>, 20 °C / alkene–CH<sub>2</sub>Cl<sub>2</sub>, 40 °C / neat alkene, 20 °C. The scale was the same as in Table 2, except for entries 2 and 3 (10 mmol of diazoester, 100 mmol of alkene); <sup>b</sup> 46% yield (50:50) with catalyst **3c**; <sup>c</sup> 27% yield (49:51) with catalyst **3a**.

an axial carbonyl ligand is replaced by the ethoxy-carbonylcarbene moiety. It is interesting to note that this ligand exchange appears to occur readily at 20 °C. A reaction temperature of 40 °C provides slightly increased yields with the terminal alkenes, but has obviously no beneficial effect on cyclopropanation of the internal alkenes (Tables 2 and 3).

The cyclopropanation of terminal alkenes and of cyclohexene using 1 or 3 mol-% of catalysts **3a–c** provides in most cases, and irrespective of the particular catalyst, almost equal amounts of *Z*- and *E*- (or *syn*- and *anti*-) cyclopropanes **5**. With 2-methyl-2-butene, however, a high *syn*-selectivity is found (Tables 2 and 3). Thus, catalysts **3a–c** induce a higher amount of the thermodynamically less favored *Z*-(*syn*-) isomer as compared to the related ruthenium acetate catalyst **1**, and virtually the same *syn* preference as **1** in the case of trisubstituted alkenes. The increased amount of the *Z*-cyclopropane in the case of terminal alkenes is worth being noted, but clearly it is still far away from the high *cis*-selectivity achieved with Mezzetti's Ru<sup>II</sup>(P,P,N,N) complexes [3, 13] and Katsuki's Ru<sup>II</sup>(NO<sup>+</sup>)(salen) catalysts [3e]. Remarkably, the ratio of *E-5* in the case of styrene is significantly higher when only 0.1 mol-% of catalyst is applied (Table 2). Such a dependence of the diastereoselectivity on the catalyst concentration is unusual, and we have no straightforward explanation at hand.

In conclusion, the dinuclear ruthenium(I) triazenide complexes [Ru(CO)<sub>3</sub>(ArNNAr)]<sub>2</sub> effectively catalyze the cyclopropanation of nucleophilic terminal alkenes with methyl diazoacetate but provide only low yields when internal alkenes are used. When compared with the structurally related ruthenium(I) acetate com-

plex [Ru<sub>2</sub>(CO)<sub>4</sub>(μ-OAc)<sub>2</sub>]<sub>n</sub>, they are inferior in terms of yield for internal alkenes, but they give rise to higher amounts of the thermodynamically less favored *cis*- or *syn*-cyclopropane with both terminal alkenes and cyclohexene.

## Experimental Section

### General information

NMR spectra: Bruker DRX 400 (<sup>1</sup>H: 400.13 MHz; <sup>13</sup>C: 100.62 MHz); as the internal standard, TMS was used for the <sup>1</sup>H spectra and the solvent signal (δ(CDCl<sub>3</sub>) = 77.0 ppm) for the <sup>13</sup>C spectra. – IR spectra: Bruker Vector 22. – GC: Varian CP-3800 with a flame ionization detector. – Mass spectrometry, MALDI-TOF: Bruker Daltonic Reflex III. – Elemental analyses: Elementar Vario EL.

Triazenes **2a–c** were prepared by analogy to a literature method [9] and were used without purification. Reaction conditions: a) X = CH<sub>3</sub>: conc. HCl, KNO<sub>2</sub>, H<sub>2</sub>O, –10 °C; X = Cl, Br: conc. HCl, 12 h at r.t., then KNO<sub>2</sub>, –10 °C. b) Na<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>O, H<sub>2</sub>N–C<sub>6</sub>H<sub>4</sub>–4-X, 0 °C.

### Preparation of triazenido ruthenium(I) complexes **3a–c**

*Hexacarbonylbis(μ-1,3-di-p-tolyltriazenido)diruthenium(II) (3a)*: Method 1: A solution of 1,3-di-*p*-tolyltriazene (**2a**, 0.39 g, 1.7 mmol) and diruthenium dodecacarbonyl (0.19 g, 0.3 mmol) in acetonitrile (8 ml) was heated at reflux for 5 h under an atmosphere of carbon monoxide, then allowed to stand at 20 °C under CO atmosphere. The precipitate was collected, washed with acetonitrile and ethanol and recrystallized from dichloromethane–ethanol to give yellow microcrystals, yield 0.15 g (63%), m.p. 180–181 °C (lit. [8]: 180–184 °C). The IR and <sup>1</sup>H NMR data agree with those reported [8]. – <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.62 MHz): δ = 20.8 (CH<sub>3</sub>), 122.5, 129.0, 134.9, 154.6, 181.3 (CO), 199.8 (CO).

Method 2: The literature procedure [8] was followed at a larger (fivefold) scale: A solution of 1,3-di-*p*-tolyltriazene (2.50 g, 11.2 mmol) in acetonitrile (50 ml) was prepared and triethylamine (8 ml) and [Ru<sub>2</sub>(CO)<sub>4</sub>(μ-OAc)<sub>2</sub>]<sub>n</sub> (1.25 g, 2.95 mmol) were added. The mixture was heated at reflux for 3 h under an atmosphere of carbon monoxide. The further procedure was as described above, yielding 1.82 g (75%) of **3a**, m.p. 179–181 °C (lit. [8]: 43.5% yield, m.p. 180–184 °C).

*Hexacarbonylbis(μ-1,3-di-p-chlorophenyltriazenido)diruthenium(II) (3b)*: A solution of 1,3-di-*p*-chlorophenyltriazene (1.60 g, 6.0 mmol) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.64 g, 1.0 mmol) in acetonitrile (10 ml) was heated at reflux for 5 h. The product crystallized on standing at 20 °C for 15 h. Recrystallization from dichloromethane–ethanol gave 0.91 g (72%) of yellow microcrystals, m.p. 203–204 °C (lit. [8]: 206–209 °C). The IR and <sup>1</sup>H NMR data agree with those reported [8]. –

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.62 MHz):  $\delta = 123.6, 128.8, 131.4, 154.7, 180.8$  (CO), 198.8 (CO).

*Hexacarbonylbis( $\mu$ -1,3-di-*p*-bromophenyltriazenido)diruthenium(I/I) (3c):* A solution of 1,3-di-*p*-bromophenyltriazene (0.96 g, 2.68 mmol) and  $\text{Ru}_3(\text{CO})_{12}$  (0.22 g, 0.34 mmol) in acetonitrile (5 ml) was heated at reflux for 3 h. Crystallization started after one hour and was complete after standing at 20 °C for 15 h. The product was washed with acetonitrile and ethanol (2 × 2 ml each) and recrystallized from dichloromethane–ethanol: 0.19 g (55%) of yellow microcrystals, m.p. 212–214 °C. – IR (KBr):  $\nu = 2083, 2063, 2024, 2013, 1998$  (all s, CO), 1481 (m), 1365 (s)  $\text{cm}^{-1}$ . –  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400.13 MHz):  $\delta = 7.09–7.11$  (m, 8H), 7.31–7.43 (m, 8 H). –  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.62 MHz):  $\delta = 119.2, 123.9, 131.8, 155.2, 180.8$  (CO), 198.8 (CO). – MALDI-TOF:  $m/z = 1192$  [M + 4 CO], 1136 [M + 2 CO], 768 [M – 2 PhBr]. –  $\text{C}_{30}\text{H}_{16}\text{Br}_4\text{N}_6\text{O}_6\text{Ru}_2$  (1087.2): calcd. C 33.42, H 1.50, N 7.79; found C 33.39, H 1.49, N 7.68.

#### General procedures for cyclopropanation experiments

Method A (analytical scale): The catalyst (**3a–c**; 0.1, 1.0 or 3.0 mol-%) was dissolved in a mixture of alkene (8 mmol) and dichloromethane (1 ml). By means of a syringe pump, a solution of methyl diazoacetate (1 mmol) in alkene (2 mmol) and dichloromethane (0.7 ml) was added during 10 h. The complete consumption of the diazo compound was then monitored by IR spectroscopy. A defined amount of naphthalene was added as an internal standard, and the yields and diastereomer ratios of cyclopropanes **5** were determined by gas chromatography, using a Varian CP-WAX 52 column (30 m × 0.32 mm, film thickness 0.25  $\mu\text{m}$ ) fitted with a retention gap. The response factor of each cyclopropane was determined using a sample prepared, purified and isolated according to Method B.

Method B (preparative scale): The catalyst (**3a–c**, 0.3 mmol) was dissolved in a mixture of alkene (80 mmol) and dichloromethane (10 ml). By means of a syringe pump, a solution of methyl diazoacetate (10 mmol) in alkene (20 mmol) and dichloromethane (2 ml) was added during 20 h. The diazoester had been consumed completely within 30 min after the addition was over (IR control). Silica gel (Merck Kieselgel 60, 0.063–0.200 mm, 7 g) was added, and the volatiles were evaporated at 20 °C/800–600 mbar. The residue was then transferred on top of a column charged with silica gel (40 g) and the product mixture was separated

by flash chromatography. Elution with pentane gave excess alkene in the first fraction, elution with pentane–ether (1:7) afforded the two diastereomers of cyclopropanes **5** which were collected in one fraction. Finally, elution with ether yielded dimethyl fumarate and dimethyl maleate (*E*- and *Z*-**6**, ca. 1:1 mixture). All cyclopropanes are known and were identified by comparison of their NMR data with literature data.

Selected yields (catalyst used / cyclopropanes **5** / carbene dimers **6**): a) From ethyl vinyl ether: **3a** / 58% / 20%; **3b** / 83% / 14%; **3c** / 56% / 2%. b) From 1-hexene: **3a** / 40% / 28%; **3b** / 61% / 24%; **3c** / 50% / 38%. c) From cyclohexene: **3b** / 29% / 31%.

#### Crystal structure determination of complex **3b**

Suitable crystals were obtained by slow diffusion of ethanol into a dichloromethane solution of **3b**. Data collection was performed at 220 K with an imaging-plate diffractometer (IPDS, STOE) using monochromated Mo- $K\alpha$  radiation ( $\lambda = 0.71073$  Å). The structure was solved with direct methods and refined with a full-matrix least-squares procedure using  $F^2$  values [14]. Hydrogen atoms are in calculated positions and were treated by the riding model. *Crystal data:*  $\text{C}_{30}\text{H}_{16}\text{Cl}_4\text{N}_6\text{O}_6\text{Ru}_2$ ,  $M = 900.45$ , monoclinic, space group  $I2/a$  (no. 15);  $a = 16.912(3)$ ,  $b = 8.514(1)$ ,  $c = 23.598(4)$  Å,  $\alpha = 90$ ,  $\beta = 101.01(2)$ ,  $\gamma = 90^\circ$ ;  $V = 3335.5(10)$  Å $^3$ ,  $Z = 4$ ,  $D_c = 1.793$  g  $\text{cm}^{-3}$ . *Data collection:* crystal size 0.54 × 0.46 × 0.38 mm, 12512 reflection data in the range  $\theta = 2.55–25.86^\circ$ , 3075 independent reflections ( $R_{\text{int}} = 0.0268$ ). *Structure refinement:* 3075 data, 217 parameters; the final  $R$  indices were  $R_1 = 0.0254$ ,  $wR_2 = 0.0545$ , the corresponding values for reflections with  $I > 2\sigma(I)$  were  $R_1 = 0.0214$ ,  $wR_2 = 0.0529$ ; residual electron density between 0.32 and  $-0.56$  e Å $^{-3}$ .

Crystallographic data have been deposited as CCDC-225446. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033).

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