

# Half-Sandwich Ruthenium(II) Catalysts for C–C Coupling Reactions between Alkenes and Diazo Compounds

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The complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  (**1**) and other readily available ruthenium(II) derivatives of general formula  $[(\eta^5\text{-ligand})\text{Ru}(\text{PR}_3)_2\text{X}]$  efficiently catalyze the cyclopropanation of styrene and other electron-rich alkenes in the presence of ethyl diazoacetate with a high cis stereoselectivity. When diphenyldiazomethane is employed as carbene source, the reaction with styrene, catalyzed by **1**, affords mainly 1,1,3-triphenylpropene, as result of a formal  $\text{:CPh}_2\text{--:CHCH}_2\text{Ph}$  coupling. Furthermore, appreciable amounts of the metathesis and cyclopropanation products 1,1-diphenylethene and 1,2-diphenylcyclopropanes in a 1:1 molar ratio are observed. The carbene complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(=\text{CPh}_2)(\text{PPh}_3)\text{Cl}]$  (**13**), which was detected during the catalytic process, can be readily obtained in 85% isolated yield from **1** and diphenyldiazomethane in a one-pot reaction. With styrene, complex **13** undergoes a stoichiometric carbene transfer reaction, yielding the same organic products observed in the catalytic process with **1**.

## Introduction

Although catalytic carbene transfer reactions, starting from diazo compounds, have been known for many decades, a growing number of transition metal complexes address the question of selectivity.<sup>1</sup> In this regard, the asymmetric cyclopropanation of alkenes with  $\alpha$ -diazo carbonyl compounds using chiral transition metal catalysts was intensively investigated in the past decade, because of the importance of naturally occurring cyclopropyl derivatives.<sup>2</sup> A remarkable improvement of enantioselectivity in alkene cyclopropanation was achieved with chiral copper, rhodium,<sup>3</sup> and, more recently, ruthenium complexes.<sup>4</sup> Despite the relatively sophisticated level of knowledge concerning the enantioselective reaction tuning, few efforts have been directed to inverting the common stereoselective reac-

tion pathway. As a rule, reactions of electron-rich terminal alkenes with  $\alpha$ -diazo carbonyl compounds, catalyzed by transition metal complexes, afford mixtures containing the trans isomers as the predominant products. When ethyl diazoacetate (EDA) is used, a catalytic cyclopropane carboxylate formation favoring the cis isomer was reported for only a few systems: "chiral wall" porphyrin rhodium(III) complexes,<sup>5</sup> pyrazolyborate and polypyrazole copper(I) derivatives,<sup>6</sup> the cationic complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{thf})][\text{BF}_4]$ , and most recently chiral Ru-salen compounds.<sup>7</sup> However, most of these complexes suffer from strong limitations due to the difficult and low-yielding catalyst synthesis<sup>5a</sup> or the low catalyst efficiency.<sup>7a,d</sup> By way of contrast, high cis stereocontrolled cyclopropanation of styrene was reported using  $[\text{W}(=\text{CHPh})(\text{CO})_5]$ <sup>8</sup> and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(=\text{CHPh})(\text{CO})_2]^+{}^9$  as a carbene source in stoichiometric reactions.

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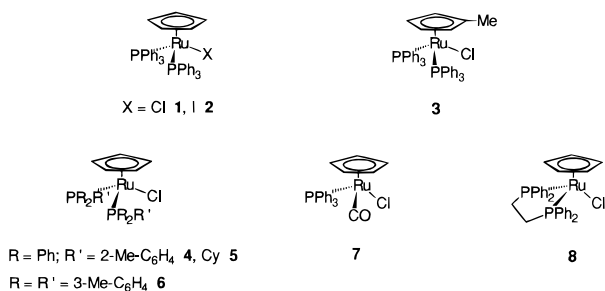
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Chart 1



It is noteworthy that the nature of the ancillary ligands also affects the chemoselectivity in metal-catalyzed carbene transfer reactions. Thus, diphenyldiazomethane reacts with ethene in the presence of catalysts of general formula [RhL<sub>2</sub>Cl]<sub>2</sub> (L = phosphine, stibine), and an insertion of :CPh<sub>2</sub> into an olefinic C–H bond or a remarkable :CPh<sub>2</sub>–ethene coupling yielding Ph<sub>2</sub>C=CHCH<sub>3</sub> was observed, according to the type of the neutral ligand L employed.<sup>10</sup>

Among the large number of transition metal complexes that have been used in carbenoid-mediated reactions,<sup>1</sup> ruthenium derivatives have recently emerged as a new class of versatile catalysts because of their high selectivity and their relatively low sensitivity for substrate-bearing functional groups.<sup>4a,11</sup> Recently we have found that [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Ru(PPh<sub>3</sub>)<sub>2</sub>Cl] (**1**) can decompose EDA and α-diazo ketones affording diethyl maleate (DEM) and cis-enediones of 95–99% purity, the highest values for a stereoselective carbene dimerization process reported to date.<sup>12</sup> These results prompted us to investigate **1**, and the related readily available complexes of general formula [(η<sup>5</sup>-ligand)Ru(PR<sub>3</sub>)<sub>2</sub>X] (R = aryl; X = halogen), for selective carbene transfer reactions from diazo compounds to terminal alkenes.

We now report the results of a study of reactions between styrene and EDA or diphenyldiazomethane in the presence of the complexes shown in Chart 1. With EDA cyclopropanation was observed with a high cis stereoselectivity, whereas with diphenyldiazomethane

Table 1. Cyclopropanation of Styrene with EDA Catalyzed by Half-Sandwich Ruthenium(II) Complexes<sup>a</sup>

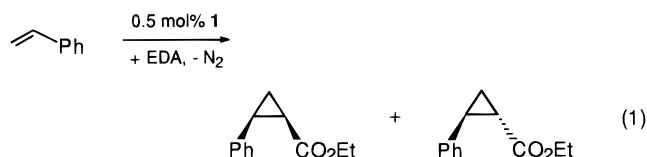
catalyst	T (°C)	t (h)	cis isomer (%)	trans isomer (%)	dimers <sup>b</sup> (%)
<b>1</b>	45	4	65	31	4
<b>2</b>	60	3	40	33	27
<b>3</b>	50	2	55	35	10
<b>4<sup>c</sup></b>	25	4	46	33	21
<b>5</b>	50	4	52	32	16
<b>6</b>	40	4	48	40	12
<b>7</b>	80	3	36	60	4
<b>8</b>	80	3	38	58	4
RuCl <sub>3</sub> ·xH <sub>2</sub> O <sup>d</sup>	50	4	10	30	17

<sup>a</sup> 0.5% catalyst. Reactions were performed in neat styrene with total conversion of EDA into the cis and trans isomers and dimers. Yields were determined by GC measurements. <sup>b</sup>DEM as main product and DEF. <sup>c</sup> Under a nitrogen atmosphere. <sup>d</sup> 57% EDA conversion.

the reaction unexpectedly leads to the trisubstituted olefin 1,1,3-triphenylpropene as the main product.

## Results and Discussion

**Cyclopropanation of Styrene Derivatives with EDA Using Half-Sandwich Ruthenium(II) Catalysts.** The half-sandwich ruthenium complexes of general formula [(η<sup>5</sup>-ligand)Ru(PR<sub>3</sub>)<sub>2</sub>X] have been proven to be effective catalysts for EDA dimerization. Thus, aiming at the catalytic cyclopropanation of styrene derivatives with EDA, we performed the reaction in pure alkene without any further solvent to prevent diethyl maleate formation. Furthermore, a premixed EDA/alkene solution was added to the catalyst (dissolved in alkene) over the course of several hours, to keep the EDA concentration low. Because cyclopropanation of styrene derivatives with EDA may also take place in the absence of catalyst and even at room temperature, the EDA/alkene mixture has to be freshly prepared prior to use. It should be noted that the thermal decomposition of EDA in the presence of styrene affords the corresponding trans and cis cyclopropyl derivatives in about 2:1 ratio. With these precautions, cyclopropane products are easily obtained in high yields and with predominantly cis stereoselectivity. In the case of precatalyst **1**, optimum conditions for the cyclopropanation of styrene were set at 45 °C and 4 h, giving rise to 95% yield of ethyl phenylcyclopropane carboxylate with a stereoselectivity of 67% cis vs 33% trans (eq 1). To examine the influence of the ligand



sphere toward the product selectivity and to elucidate aspects of the reaction mechanism, the half-sandwich ruthenium compounds **2–8** were employed (Chart 1). The results of the catalytic cyclopropanation of styrene are shown in Table 1. Compared to **1**, no improvement of selectivity for the cis cyclopropyl isomer was observed by using the iodide derivative **2** or the methylcyclopentadienyl compound **3**. The use of ruthenium complexes **4** and **6**, bearing bulkier phosphines such as PPh<sub>2</sub>(2-

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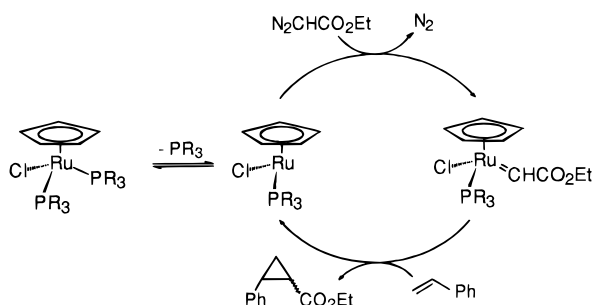
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Scheme 1



$\text{CH}_3\text{C}_6\text{H}_4$ ) and  $\text{P}(3\text{-CH}_3\text{C}_6\text{H}_4)_3$ , respectively, allows cyclopropanation of styrene at temperatures below 45 °C, but without increase of the cis/trans cyclopropyl ratio. Employment of ruthenium complexes with one carbonyl ligand **7** or with a chelate phosphine **8** yields at 80 °C a mixture of cis and trans isomers similar to that observed in the reaction performed without catalyst, suggesting that these complexes are not catalytically active. Furthermore, commercial ruthenium trichloride  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  has been found to catalyze the cyclopropanation of styrene with the trans isomer as the main product. These data show that ruthenium cyclopentadienyl complexes of general formula  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PR}_3)_2\text{X}]$  can induce carbene transfer reactions to styrene with predominant cis stereoselectivity. The cis/trans ratio values obtained in these reactions are probably the minimum ones because the uncatalyzed cyclopropanation occurred under the present reaction conditions. The catalytic activity of this class of ruthenium complexes depends on the relative facility of dissociation of one phosphine. It is conceivable that this reaction proceeds via the ruthenium carbene intermediate  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{=CHCO}_2\text{Et})(\text{PR}_3)_2\text{Cl}]$ , as proposed in our recent investigation for the dimerization of EDA (Scheme 1).<sup>13</sup> Apparently, the methyl-substituted aryl phosphines are more weakly bound to ruthenium compared with  $\text{PPh}_3$  and, therefore, more prone to dissociation in the initial step. This may explain why compounds **4** and **6** catalyze the cyclopropanation reaction even at lower temperatures than **1**. Conversely, the monocarbonyl derivative **7** and the complex **8** containing a chelating phosphine ligand show only poor catalytic performance due to the hampered ligand dissociation. In the second step of the catalytic cycle the 16-electron complex promptly reacts with EDA, through nitrogen extrusion, affording a cyclopentadienyl ruthenium carbene. The subsequent nucleophilic attack, performed by styrene, affords the cyclopropane carboxylate derivative, whereas the concomitant reaction of the carbene with EDA gives DEM. Although no spectroscopic evidence for the formation of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{=CHCO}_2\text{Et})(\text{PR}_3)_2\text{Cl}]$  was obtained in the reaction mixture, the high cis stereocontrol in carbene transfer to styrene suggests that the ruthenium carbene is a key intermediate in the cyclopropanation reaction. Steric effects, induced by the cyclopentadienyl and phosphine ligands, apparently limit the conformations of the forming cyclopropane and therefore favor the formation of the less sterically demanding isomer.<sup>12,13</sup> Having established that **1** shows the best catalytic performance for the cis cyclopropanation of styrene, we have investigated

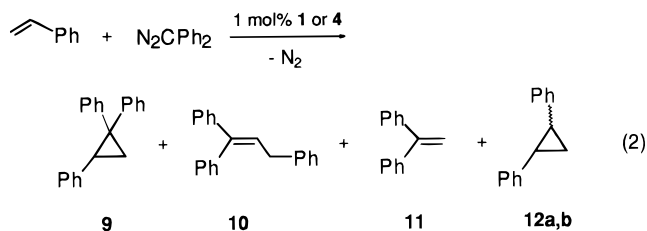
Table 2. Cyclopropanation of Functionalized Alkenes with EDA Catalyzed by **1**<sup>a</sup>

<i>T</i> (°C)	alkene	cis isomer (%)	trans isomer (%)	dimers <sup>b</sup> (%)
45	<i>p</i> -methyl styrene	45	24	31
45	$\alpha$ -methyl styrene	56	32	12
45	<i>n</i> -butyl vinyl ether	45	30	25

<sup>a</sup> 0.5% catalyst, 4 h. Reactions were performed in neat alkene with total conversion of EDA into the cis and trans isomers and dimers. Yields were determined by GC measurements. <sup>b</sup>DEM as main product and DEF.

the reaction of EDA with different terminal electron-rich olefins, and the results of the cycloaddition reactions are displayed in Table 2. In line with the previous data obtained with styrene as starting material, the reactions of EDA with *p*-methyl styrene,  $\alpha$ -methyl styrene, and butyl vinyl ether afford the corresponding cyclopropanes in good yields and with predominately cis stereoselectivity. By contrast, alkyl-substituted alkenes (e.g., 2,5-dimethyl-1,5-hexadiene) give mainly DEM and only minor cyclopropanation products. Apparently, the terminal electron-rich olefins show a higher reactivity toward the carbene intermediate, and thus dimerization of the diazo compounds can be suppressed. In summary the easily available complex **1** is an efficient catalyst for cyclopropanation of styrene and other terminal olefins with EDA, the cis selectivity being similar to that reported for the most selective systems. Work is needed to address the mechanistic issues of this ruthenium-catalyzed stereoselective process.

**Formation of 1,1,3-Triphenylpropene from Styrene and Diphenyldiazomethane Catalyzed by **1** and **4**.** Regarding the chemistry of diphenyldiazomethane, it is well-known that treatment of styrene with  $\text{N}_2\text{CPh}_2$  gives 1,1,2-triphenylcyclopropane **9** under thermal or photochemical elimination of dinitrogen.<sup>14</sup> Unexpectedly, when a catalytic amount of complex **1** (1 mol % referred to  $\text{N}_2\text{CPh}_2$ ) is added to a benzene-*d*<sub>6</sub> solution of styrene and diphenyldiazomethane (1.2:1 molar ratio), 1,1,3-triphenylpropene **10** (58%) together with a 1:1 mixture of 1,1-diphenylethene **11** (17%) and 1,2-diphenylcyclopropanes<sup>15</sup> **12a,b** (16%) form, as established by <sup>1</sup>H, <sup>1</sup>H-2D COSY, <sup>13</sup>C NMR DEPT, and GC measurements (eq 2). Only 9% of the expected cyclo-



propyl derivative **9** is present in the final solution. If the catalyst **4** is used instead of **1**, the propene derivative **10** is obtained at lower temperature and in higher

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**Table 3. Reaction of Diphenyldiazomethane with Styrene Catalyzed by **1** and **4**<sup>a</sup>**

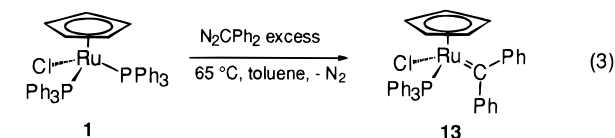
catalyst	<i>T</i> (°C)	<i>t</i> (h)	<b>9</b> (%)	<b>10</b> (%)	<b>11</b> (%)	<b>12a,b</b> (%)
<b>1</b>	65	2.5	9	58	17	16
<b>4</b>	40	2.0	<2	67	15	16
<b>c</b>	80	3.0	55			

<sup>a</sup> 1% catalyst. Reactions were performed in C<sub>6</sub>D<sub>6</sub>, under an argon atmosphere. Yields were determined by <sup>1</sup>H NMR measurements. Tetraphenylethene was detected in trace amounts by GC measurements. <sup>b</sup> Cis and trans isomers of 1,2-diphenylcyclopropane. <sup>c</sup> Without catalyst **9** was the only product of the carbene transfer to styrene.

yield (67%), whereas **9** forms in trace amounts (Table 3). When **1** is employed, the <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra of the reaction mixture reveal the formation of the carbene complex [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Ru(=CPh<sub>2</sub>)(PPh<sub>3</sub>-Cl)], **13**,<sup>16</sup> which is the only ruthenium intermediate detected during the reaction. Moreover, tetraphenylethene, the product of :CPh<sub>2</sub> dimerization, was detected in very low concentration in the reaction mixture, thus indicating that the carbene **13** ought to undergo a faster attack by the alkene compared to the diazo compound, in contrast to the aforementioned species [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Ru(=CHCO<sub>2</sub>Et)(PR<sub>3</sub>)Cl]. It is generally accepted that many metal-catalyzed C–C bond forming reactions starting from diazo compounds imply generation of transient electrophilic metal carbenes. However, it is important to note that there is a striking paucity of catalytically active ruthenium carbene complexes that have been isolated<sup>11a,m,17</sup> or directly observed during catalysis.<sup>11e,18</sup> As regard to the mechanism involved in the formation of the trisubstituted alkene **10**, it is unlikely that this product results from a cyclopropane rearrangement of **9**. In fact, although a number of functionalized cyclopropyl derivatives have been specifically transformed to their corresponding ring-opened alkenes via transition-metal-assisted reactions,<sup>19</sup> no conversion of the cyclopropane **9** to the alkene **10** occurs using **1** as catalysts in benzene-*d*<sub>6</sub> at 70 °C, even after 4 h. Probably, the cyclopropyl product **9** forms in our mixture as a result of a thermal side reaction from styrene and diphenyldiazomethane, as suggested by the observation that using catalyst **4**, which works at lower temperature, a minor amount of **9** is obtained. Noteworthy, the related complexes [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ru(PPh<sub>3</sub>)<sub>2</sub>Cl] or [(η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)Ru(PPh<sub>3</sub>)<sub>2</sub>Cl] show a lower catalytic activity in the formation of **10**, whereas [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] and [(*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub> have been found not active under our experimental conditions.

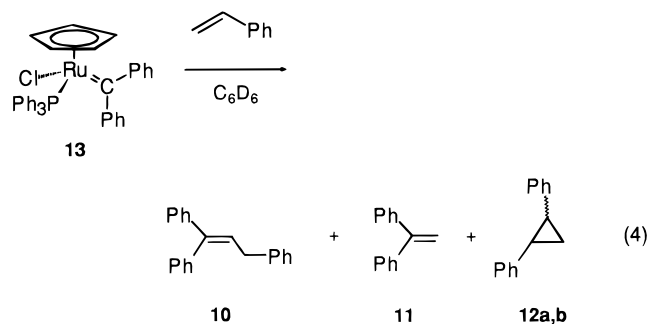
With the aim to elucidate the mechanism of formation of the trisubstituted olefin **10** from styrene and the diazo derivative and to understand the nature of the key steps occurring at the metal center, we have studied the reaction of styrene with the carbene complex **13**, which is the intermediate observed in the reaction mixture

during catalysis. The metal carbene compound **13** was previously obtained by Werner and co-workers in a multistep synthesis starting from **1** via formation of the acetato complex [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Ru(η<sup>2</sup>-O<sub>2</sub>CMe)(PPh<sub>3</sub>)].<sup>16</sup> We have now found that the green product **13** is easily available in 85% isolated yield by direct reaction of **1** with diphenyldiazomethane (eq 3). Heating of **1** at 65



°C in toluene is necessary to cause phosphine dissociation,<sup>13</sup> and an excess of N<sub>2</sub>CPh<sub>2</sub> has to be added during the reaction to obtain complete conversion of **1** into **13**, because of the slow N<sub>2</sub>CPh<sub>2</sub> decomposition.

Although thermally stable, **13** can transfer quantitatively its carbene ligand :CPh<sub>2</sub> to styrene in a stoichiometric reaction. So, treatment of **13** with styrene in 1:3 molar ratio in C<sub>6</sub>D<sub>6</sub> at 45 °C affords, within 1.5 h, compounds **10**, **11**, and **12a,b** (eq 4), with a distribution



fairly similar to that observed in the reaction of styrene with N<sub>2</sub>CPh<sub>2</sub> catalyzed by **1** and closer to that of the reaction catalyzed by **4** at lower temperature. It should be emphasized that under these experimental conditions no cyclopropanation of styrene was observed, thus confirming that compound **9**, which was observed in the catalytic reaction, forms as result of a thermal side reaction from styrene and diphenyldiazomethane. Although the <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **13** with styrene in excess suggest formation of [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Ru(styrene)(PPh<sub>3</sub>)Cl] (δ<sub>H</sub> = 4.09 ppm for Cp; δ<sub>P</sub> = 53.6 ppm in toluene-*d*<sub>8</sub>) in line with our previous work with diethylmaleate,<sup>13</sup> we were not able to isolate the olefinic complex.

Concerning the mechanism of the catalytic process, it is important to note that the composition and distribution of the products formed in the stoichiometric reaction between **13** and styrene is similar to that observed in the catalytic cycle. Employment of solvents different from benzene-*d*<sub>6</sub>, such as CDCl<sub>3</sub> or acetone-*d*<sub>6</sub>, or addition of NEt<sub>4</sub>Cl (CDCl<sub>3</sub>) to prevent chloride ligand dissociation from **1** or **4** during catalysis, results in no change of chemoselectivity. Therefore it is reasonable to assume that the initial stage of the catalytic process implies the generation of the carbene intermediate [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Ru(=CPh<sub>2</sub>)(PR<sub>3</sub>)Cl], **B**, by reaction of the diazo compound with the 16-electron complex [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Ru(PR<sub>3</sub>)Cl], **A**, formed by displacement of one phosphine from **1** or **4**.<sup>13</sup> Formally **10** results from a C–C coupling

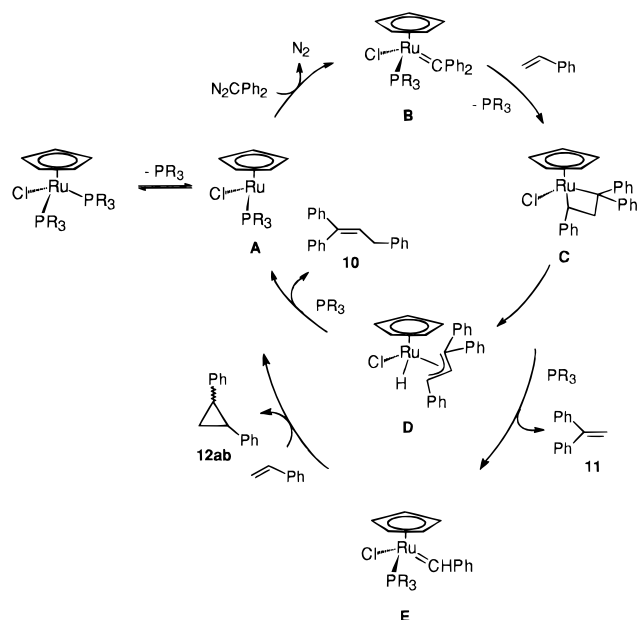
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Scheme 2



reaction between the  $\text{:CPh}_2$  fragment and the styrene isomer  $\text{:CHCH}_2\text{Ph}$ . A similar catalytic reaction was reported by Werner and co-workers, who found that the rhodium complex  $[\text{Rh}(\text{P}(\text{Pr}_3)_2)_2\text{Cl}]_2$  catalyzes the synthesis of 1,1-diphenylpropene starting from ethene and diphenyldiazomethane. According to the mechanism proposed by Werner, we tentatively assume that also in our case in the second stage of the reaction both substrates, the olefin and the carbene, coordinate to the metal, affording a metallacyclobutane **C** derivative (Scheme 2).<sup>10,20</sup> This complex can give, via an  $\eta^3$ -allylhydrido intermediate **D** and subsequent hydride migration to the terminal CH carbon of the allyl group, the alkene **10**, affording the coordinatively unsaturated species **A**. However, in the absence of a deeper investigation, the mechanism and the nature of the intermediate in the formation of the trisubstituted olefin still remain to be confirmed.

The metallacycle **C**, postulated in the principal catalytic cycle, also has the structural features of the key species for olefin metathesis reactions and can account for the formation, in a side reaction, of small amounts of **11** and **12a,b** (Scheme 2). Thus, the proposed metallacycle **C** may give a second competitive reaction, which leads via metathesis to one molecule of alkene **11** and the complex **E** containing the carbene moiety  $\text{:CHPh}$ . Subsequent transfer of the electrophilic phenylcarbene from ruthenium to styrene terminates the cycle, affording the cis and trans cyclopropane derivatives **12a,b** in almost equimolar amount with respect to **11**. In this regard we have to point out that we have also investigated the reaction between styrene and  $\text{N}_2\text{CHPh}$ <sup>21</sup> catalyzed by **1**. In this process, which leads to the formation of the expected cyclopropane derivatives **12a,b**, in a cis/trans ratio of ca. 1, the ruthenium carbene intermediate **E** is likely to form in accordance with the aforementioned results with styrene and EDA.

The catalytic cycle reported in Scheme 2 should be considered as an attempt to rationalize the formation of **10**, **11**, and **12a,b**. Further investigations are needed to give definitive evidence of the proposed reaction paths and the features of the intermediates.

## Concluding Remarks

Cyclopentadienyl ruthenium complexes of general formula  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PR}_3)_2\text{X}]$  have been found to catalyze cis cyclopropanation and an unusual C–C coupling reaction from diazo compounds and terminal alkenes. Although there is strong evidence that carbene intermediates of the type  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{=CR}'\text{R}'')(\text{PR}_3)\text{X}]$  ( $\text{R}' = \text{H}$ ,  $\text{R}'' = \text{Ph}$ ,  $\text{CO}_2\text{Et}$ ;  $\text{R}'$ ,  $\text{R}'' = \text{Ph}$ ) easily form during the catalytic reactions, their stability and reactivity is strongly affected by the  $\text{R}'$  and  $\text{R}''$  substituents. The presence of two aryl groups ( $\text{R}'$ ,  $\text{R}'' = \text{Ph}$ ) apparently stabilizes the metal carbene, in comparison with the highly reactive analogue  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{=CHCO}_2\text{Et})(\text{PPh}_3)\text{Cl}]$ , as suggested by the detection of **13** during catalysis and its isolation. The different behavior of the cyclopentadienyl ruthenium carbene intermediates in  $\text{:CR}'\text{C}''$  transfer reactions to olefins, according to the  $\text{R}'$  and  $\text{R}''$  substituents, holds promise for new catalytic conversions at this metal center. Current investigations in our laboratories focus on expanding the preparative scope of the readily accessible half-sandwich ruthenium catalysts,<sup>22</sup> as well as gaining further mechanistic insight to understand the factors that govern the chemo- and stereoselectivity.

## Experimental Section

**General Procedures.** Toluene and heptane were distilled over sodium. Styrene (Aldrich) was freshly distilled before use, whereas EDA (Aldrich) was used without further purification. The starting materials  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  (**1**),<sup>23</sup>  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{I}]$  (**2**),<sup>24</sup>  $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  (**3**),<sup>25</sup>  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PR}_3)_2\text{Cl}]$  ( $\text{PR}_3 = \text{PPh}_2(2\text{-MeC}_6\text{H}_4)$ , **4**;  $\text{PPh}_2\text{Cy}$ , **5**;  $\text{P}(3\text{-Me-C}_6\text{H}_4)_3$ , **6**),<sup>13</sup>  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})(\text{PPh}_3)\text{Cl}]$  (**7**),<sup>26</sup>  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_2\text{-CH}_2\text{CH}_2\text{PPh}_2)\text{Cl}]$  (**8**),<sup>27</sup> and  $\text{Ph}_2\text{CN}_2$ <sup>28</sup> were synthesized according to literature methods.  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^1\text{H}, ^1\text{H}$ -2D COSY NMR experiments were recorded on a Bruker AC200 spectrometer. GC–MS measurements were performed with Fisons TRIO 2000 and Hewlett-Packard 5970 B instruments.

**Catalytic Cyclopropanation of Alkenes with EDA.** All experimental details are given in Tables 1 and 2. In a typical procedure, 0.05 mmol of the ruthenium complex was dissolved in the corresponding alkene (100 mmol). A mixture of EDA/alkene (10 mmol/100 mmol) was added to the stirred solution containing the catalyst over the course of several hours at the appropriate temperature. Then, the reaction mixture was stirred for 30 min, and the product distribution was determined by integration of the GC signals. With catalysts **1**, **5**, and styrene as well as catalyst **1** and *n*-butyl vinyl ether the organic product distribution was also checked by  $^1\text{H}$  NMR. In

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this case the excess alkene was removed under reduced pressure and the product distribution of the residual oil was determined by  $^1\text{H}$  NMR spectroscopy. To purify the crude product, the oil was chromatographed on a column of silica gel and eluted with a 1% ethyl acetate/pentane mixture to yield a mixture of cyclopropane isomers and a mixture of the byproducts DEM and DEF, which are the only compounds detected in the reaction mixtures by NMR and GC-MS.

**Catalytic Formation of 1,1,3-Triphenylpropene (10).** Diphenyldiazomethane (55 mg, 0.283 mmol) and **1** (2 mg, 2.8  $\mu\text{mol}$ ) were added to a solution of styrene (40  $\mu\text{L}$ ,  $d = 0.91$  g/mL, 0.350 mmol) in 0.5 mL of  $\text{C}_6\text{D}_6$ . The red solution was heated at 65  $^\circ\text{C}$  for 2.5 h under argon, allowing dinitrogen evolution. The distribution of the organic products was determined by  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR and GC-MS.

Similarly, compound **4** was used as catalyst at 45  $^\circ\text{C}$ , causing the reaction to be complete after 2 h.

**Synthesis of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(=\text{CPh}_2)(\text{PPh}_3)\text{Cl}]$  (**13**).** Compound **1** (609 mg, 0.839 mmol) and  $\text{N}_2\text{CPh}_2$  (510 mg, 2.63 mmol) were dissolved in 30 mL of toluene, and the solution was stirred at 65  $^\circ\text{C}$  under argon (1 atm) for 30 h. During this period, new  $\text{N}_2\text{CPh}_2$  (130 mg, 0.669 mmol) was added after 10 h, and a second addition of  $\text{N}_2\text{CPh}_2$  (90 mg, 0.463 mmol) was made after 20 h. The solution was concentrated to about 5 mL,

heptane (25 mL) was added, and a green product separated. After crystallization from toluene/heptane the resulting complex was dried under reduced pressure and identified as **13** by comparison of the  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{31}\text{P}\{^1\text{H}\}$  NMR data with those reported in the literature.<sup>16</sup> Yield: 450 mg, 85%.

**Reaction between 13 and Styrene.** Complex **13** (20 mg, 0.032 mmol) was dissolved in 0.5 mL of  $\text{C}_6\text{D}_6$ , and styrene (9  $\mu\text{L}$ ,  $d = 0.91$  g/mL, 0.079 mmol) was added under argon. The green solution was gently heated at 45  $^\circ\text{C}$  for 1.5 h, resulting in complete conversion of **13** into the organic products **10**, 68%, **11**, 16%, and **12a,b**, 16% yield, as established by  $^1\text{H}$  NMR measurements.

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