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# Olefin Cyclopropanation Catalysed by Novel Ruthenium-Arene Complexes Containing Phosphines with Pendent Arenes

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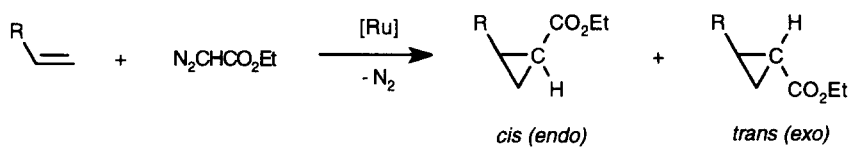
**Abstract**

Ruthenium-arene complexes containing phosphines with pendent aryl groups $[RuCl_2(\eta^6\text{-}p\text{-cymene})(PCy_2(CH_2)_3Ar)]$, Ar = $C_6H_5$ and 3,5-$(CH_3)_2$-$C_6H_3$ (**1** and **3**), and the resulting chelating complexes $[RuCl_2(PCy_2(CH_2)_3\text{-}\eta^6\text{-}Ar)]$ (**2** and **4**) mediate the cyclopropanation of olefins with ethyl diazoacetate. Comparison of the reactivity patterns of these complexes indicates that *p*-cymene disengagement is likely the key step in the reactions catalysed by non-chelating complexes **1** and **3**. 

*Keywords: Cyclopropanation; Olefins; Diazo compounds; Ruthenium and compounds.*

Particular attention has been paid recently to the use of $[RuCl_2(\eta^6\text{-arene})]_2$ complexes [1] as catalysts or catalyst precursors for a wide variety of reactions including asymmetric catalytic transfer hydrogenation of ketones [2] and imines [2a, 3] using 2-propanol or formic acid as a hydrogen source, Diels-Alder reaction [4], 6π-electrocyclisation of dienylalkynes [5], olefin metathesis [6], olefin cyclopropanation [7, 8], and atom-transfer radical polymerisation of vinyl monomers [9]. In most cases, the results obtained with $[RuCl_2(\eta^6\text{-arene})]_2$-based catalyst systems are satisfactory, indeed, excellent in terms of efficiency and selectivity. In addition, their catalytic performance has been shown to be strongly affected by the nature of the arene ligand. The mechanism of these reactions, however, has not yet been completely elucidated, and the role of the $\eta^6$-arene moiety coming from the catalyst precursor remains totally or partially unanswered. For instance, for the hydrogen transfer reaction to ketones, the arene species is assumed to be a spectator ligand throughout the catalytic process [2], whereas for olefin metathesis [6] and atom-transfer radical polymerisation [9], the catalytic activity apparently results from arene ligand disengagement. The situation is less clear for olefin cyclopropanation [7]




*cis (endo)* *trans (exo)*

and, in this context, we have been interested in comparing the catalytic activity of ruthenium-arene complexes containing phosphines with pendent aryl groups $[RuCl_2(\eta^6\text{-}p\text{-cymene})(PCy_2(CH_2)_3Ar)]$, **1** and **3**, with that of the resulting chelating complexes $[RuCl_2(PCy_2(CH_2)_3\text{-}\eta^6\text{-}Ar)]$, **2** and **4**, for the afore-mentioned reaction.

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The phosphine ligands and complexes **1-4** were easily prepared using well-established procedures [10], and fully characterized by spectroscopic methods and single-crystal X-ray analysis [11]. Screening cyclopropanation experiments performed under typical reaction conditions [7], using styrene (an activated olefin) and cyclooctene (a non-activated olefin) as model substrates, and ethyl diazoacetate as carbene precursor indicated that various parameters including the catalyst's structure, the substrate and the temperature affect the rate and the yield of the reaction, and the extent of the stereoselectivity (*cis/trans* or *endo/exo* ratio) as well (Tables 1 and 2).

We first observed the dramatic influence of the temperature on the decomposition rate of the diazo compound (Figure 1) and, hence, on the cyclopropanation yield (Table 1). With the non-chelating complexes, **1** and **3**, the reaction occurred rapidly from 40-50 °C with a slight, but significant increase in *cis* selectivity. With the corresponding chelating complexes, **2** and **4**, the decomposition rate of ethyl diazoacetate occurred sluggishly (Figure 2) and the stereoselectivity remained constant in the temperature range 20-60 °C (Table 1). However, despite the striking difference in reactivity between non-chelating and chelating complexes, the cyclopropanation yields of styrene derivatives (Table 2) were quite comparable at 60 °C. In both cases, the weight balance was attained taking into account carbene dimers (diethyl maleate and diethyl fumarate). Further, with the non-chelating complexes, **1** and **3**, homologation products **5** [12], some ethylene and substituted *trans*-stilbenes **6** resulting from the metathesis of 4-substituted styrenes, and various by-products such as arylcyclopropanes, ethyl acrylate,

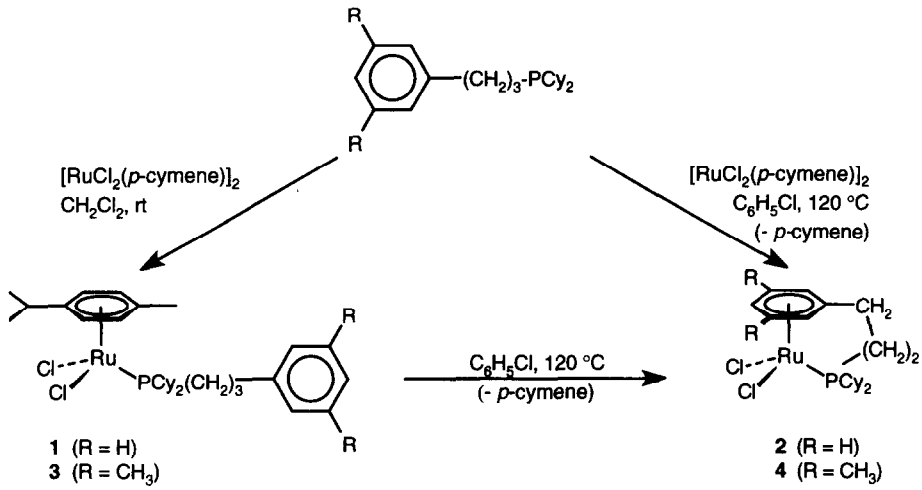



Table 1

Addition of ethyl diazoacetate to styrene and cyclooctene catalysed by complexes **1-4**[a]

| | Cyclopropanation yield, %[b] (*cis/trans* or *endo/exo* ratio) | | | |
|---|---|---|---|---|
| | Styrene | | | Cyclooctene |
| Complex | Temperature : rt | 40 °C | 60 °C | 60 °C |
| **1** | 23 (0.63) | 51 (0.69) | 71 (0.75) | 47 (0.70) |
| **2** | 19 (0.59) | 45 (0.58) | 68 (0.61) | 19 (0.68) |
| **3** | 25 (0.61) | 50 (0.76) | 71 (0.83) | 51 (0.55) |
| **4** | 12 (0.59) | 43 (0.61) | 66 (0.60) | 8 (0.54) |

[a] Reaction conditions : catalyst, 0.0075 mmol; olefin, 20 mmol; ethyl diazoacetate, 1 mmol diluted by the substrate up to 1 mL; addition time, 4 h.

[b] Based on added ethyl diazoacetate, and determined by GLC analysis using di-*n*-butyl fumarate as internal standard.

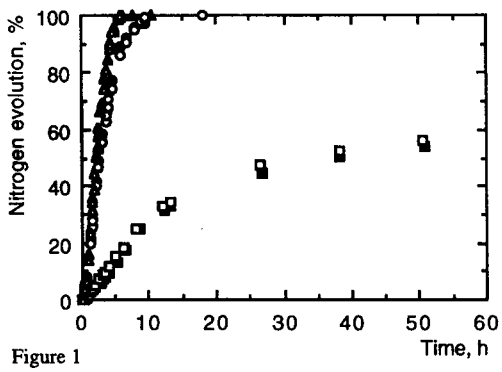



Figure 1

Influence of the temperature on the decomposition rate of ethyl diazoacetate in styrene in the presence of complexes **1** (■, ●, ▲) and **3** (□, ○, △); rt (■, □), 40 °C (●, ○), and 60 °C (▲, △).

Reaction conditions same as in Table 1.

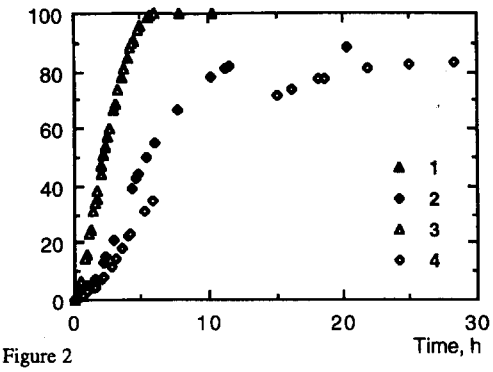
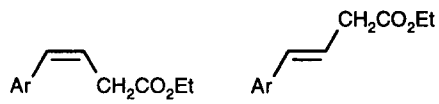



Figure 2

Influence of the catalyst on the decomposition rate of ethyl diazoacetate in styrene, at 60 °C.

Reaction conditions same as in Table 1.




**5.a** **5.b** **5.c** **6**

ethyl cinnamates [13] were formed with 12-15 % overall yield. With cyclooctene, ring-opening metathesis polymerisation (ROMP, 8 % based on cyclooctene) occurred competitively with olefin cyclopropanation (± 50 % based on added diazo compound), whereas ROMP was the sole reaction to be observed with norbornene. In sharp contrast, the chelating complexes, **2** and **4**, gave no homologation, nor metathesis except some ROMP with norbornene (5-6 %). On the other hand, activated olefins (styrenes) have been shown to be more reactive than non-activated α- and cyclo-olefins (Table 2). Further, the latter were more reactive in the presence of the non-chelating complexes than in the presence of the chelating ones, an observation which could be explained by the low solubility of those complexes in such olefinic substrates.

Table 2

Addition of ethyl diazoacetate to representative olefins catalysed by complexes **3** and **4**[a]

| Olefin | Cyclopropanation yield, %[b] (*cis*/*trans* or *endo*/*exo* ratio) | |
|---|---|---|
| | Complex **3** | Complex **4** |
| Styrene | 71 (0.83) | 66 (0.60) |
| 4-Methylstyrene | 74 (0.58) | 70 (0.44) |
| 4-*t*-Butylstyrene | 67 (0.54) | 65 (0.42) |
| 4-Methoxystyrene | 72 (0.48) | 68 (0.45) |
| 4-Chlorostyrene | 72 (0.44) | 67 (0.42) |
| α-Methylstyrene | 82 (0.73) | 78 (0.53) |
| 1-Octene | 46 (0.79) | 9 (0.66) |
| 1-Decene | 42 (0.72) | 8 (0.55) |
| 1-Dodecene | 44 (0.72) | 12 (0.49) |
| Cyclohexene | 22 (0.36) | 5 (0.29) |
| Cyclooctene | 51 (0.55) | 8 (0.54) |
| Norbornene | 0 - | 0 - |

a,b Reaction conditions same as in Table 1 (temperature 60 °C).

All the catalysts employed here are initially 18 electron-ruthenium(II) complexes. In order to obtain the metal-carbene (the key intermediate in the catalytic process), the release of one or more ligand(s) is necessary to create sites at which the reaction can then take place. This explains why heating is needed to start the reaction and why ethyl diazoacetate decomposes at different rates with the different ruthenium complexes. The relative rates of decomposition of the diazo compound may be anticipated to be related to the relative ease of the vacant site, in other words, to the lability of the ligand. Thermogravimetric analyses (TGA) indicate a direct relationship between *p*-cymene release and catalyst activity (TGA : 183 and 185 °C for the non-chelating complexes, **1** and **3**, respectively) while, with the corresponding complexes, **2** and **4**, the chelating phosphine-arene ligand is lost at a much higher temperature : 296 and 305 °C. Furthermore, the latter complexes have been shown by $^1$H-NMR spectrocopy to be stable at 115 °C for 24 h in deuterated aromatic solvents such as toluene and chlorobenzene.

*p*-Cymene disengagement is likely the key step in the reactions catalysed by non-chelating complexes **1** and **3**, so that a 14 electron-ruthenium-carbene species would then coordinate an olefin giving rise to a ruthenacyclobutane whose decomposition would lead to (*1*) olefin cyclopropanation via reductive elimination, (*2*) olefin homologation via β-hydrogen shift, and (*3*) olefin metathesis. By contrast, chelating complexes **2** and **4**, whose stability has been demonstrated up to 115 °C in the *absence* of a diazo compound, were found to promote selectively olefin cyclopropanation. At this stage of the study, the activation process of these chelating complexes by a diazo compound remains speculative. However, the generation of a 16 electron-species is sufficient to account for the formation of a 18 electron-ruthenium-carbene intermediate which would then transfer the carbene moiety onto an olefin non-coordinated to the metal.

In conclusion, the different reactivities (Figure 2) and stereoselectivities (Table 2) exhibited by the non-chelating (**1** and **3**) and chelating complexes (**2** and **4**) could be rationalized by assuming the formation of two different ruthenium-carbene species depending on the catalyst precursor (non-chelating *versus* chelating complexes) and, hence, two different mechanistic pathways for olefin cyclopropanation (a ruthenacyclobutane pathway *versus* a bimolecular process).

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