Pergamon

Tetrahedron Letters 43 (2002) 983–987

TETRAHEDRON LETTERS

Olefin cyclopropanation catalysed by half-sandwich ruthenium complexes

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Received 23 October 2001; accepted 29 November 2001

Abstract—Ruthenium complexes of the type $[RuX(Cp')(PPh_3)_2]$ (X = Cl and H; Cp′ = Cp, Cp*, indenyl, and carboranyl) efficiently catalyse olefin cyclopropanation with diazoesters, and the *cis*/*trans* stereoselectivity of the resulting cyclopropanes strongly depends on the Cp′ ligand. With $[RuCl(Cp^*)(PAr_3)_2]$ complexes, cyclopropanation competes with the formal carbene insertion into C–H vinyl bonds of styrene, whereas ring-opening metathesis polymerisation takes place with norbornene, lending support to the formation of ruthenium–carbene and ruthenacyclobutanes as intermediates in these reactions.

In recent decades there has been an exponential increase in the use of transition metals in organic synthesis. Among the different types of transition-metal-based reagents described, carbene complexes are among the most versatile.[1] The applications of carbene complexes include both their use as catalysts for a number of important synthetic transformations[2] and their utilisation as stoichiometric reagents.[3] In the period between the discovery in the late 1950s that copper catalysed the addition of diazo compounds to olefins to yield cyclopropanes and the introduction of chiral catalysts for asymmetric cyclopropanation,[4] a wide variety of useful transition-metal-based catalysts has been discovered. Nowadays, rhodium carboxylates, discovered by Noels and Hubert in the early 1970s,[5] play a prominent role in carbene chemistry, and display some of the highest efficiency and versatility.

Ruthenium has been introduced recently as a much cheaper alternative to rhodium,[6] and quite interesting results have been reported in the literature.[7] Until now, however, limitations associated with most ruthenium complexes include failure to cyclopropanate inactivated olefins, and quite low turnover numbers. In addition, the factors governing catalyst activity and the mechanism by which ruthenium catalysts perform olefin cyclopropanation are not known.[8] Investigations were undertaken to address both of these topics in the following way: by varying the ligand sphere around the ruthenium catalyst, we wished to determine how the electronic and steric properties of the ligands affect catalyst activity. Ruthenium complexes of the type $[RuX(Cp')(PPh_3)_2]$ (X = Cl, H; Cp′ = Cp, Cp*, indenyl, and carboranyl) (**1**–**4**, Scheme 1) were chosen as potential catalysts for two reasons: (1) upon Cp′ ligand substitution, it is expected to modify the electronic contributions in these systems. The higher electron donating ability of Cp* compared to Cp is well-established,[9] and the capacity of carboranyl ligands ($[C_2B_9H_{11}]^{2-}$) to stabilise uncommon and high oxidation states of the metals as well.[10] (2) On the other hand, Cp′ substitution also results in changing the steric properties of the ligands, which are expressed by the cone angle. In this way, Cp* is obviously bulkier than Cp and, most probably, than the carboranyl ligand $[C_2B_9H_{11}]^{2-}$,[11a,b] although the relative size of the latter compared to Cp and Cp* is still a question under debate.[11c,d] The indenyl ligand poses a more complex problem since it is known to undergo a facile metal ring slippage from η^5- to η^3-coordination, leading to the creation of a vacant coordination site on the metal to host an entering ligand or substrate.[12]

Keywords: cyclopropanation; diazo compounds; metathesis; olefins; ruthenium and compounds.

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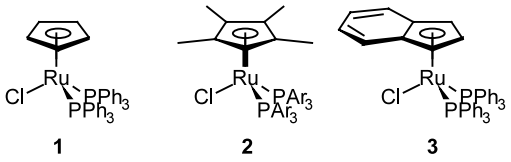
0040-4039/02/$ - see front matter
PII: S0040-4039(01)02292-4



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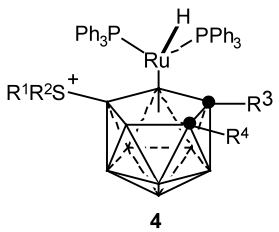
(a) Ar = C_6H_5
(b) Ar = *p*-C_6H_4-OCH_3
(c) Ar = *p*-C_6H_4-CF_3



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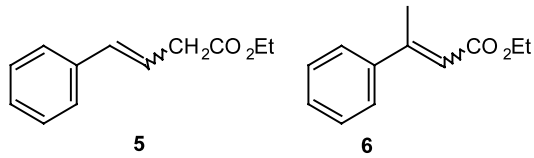
(a) $R^1 = R^2 = CH_3$, $R^3 = R^4 = H$
(b) R^1-$R^2 = (CH_2)_4$, $R^3 = R^4 = H$
(c) $R^1 = R^2 = CH_3$, $R^3 = CH_3$, $R^4 = H$

Scheme 1.

In this paper, we report that ruthenium complexes of the type $[RuX(Cp')(PAr_3)_2]$ (X = Cl, H; Cp′ = Cp,[13] Cp*,[14] indenyl, and carboranyl[15]) efficiently catalyse the cyclopropanation of styrenics with diazoesters.

To determine the relative activities and stereoselectivities of ruthenium catalysts **1**–**4**, the cyclopropanation of styrene with ethyl diazoacetate was measured under a standard set of conditions (Scheme 2, R = Ph). The results are summarised in Table 1. The half-sandwich ruthenium complex, $[RuCl(Cp)(PPh_3)_2]$ (**1**), proved to be an effective catalyst for cyclopropanation of styrene. Cyclopropane products were obtained in high yield and with predominantly *cis* stereoselectivity. To examine the influence of the Cp′ ligand toward catalyst activity, the half-sandwich ruthenium compounds **2**–**4** were then employed. Compared to **1**, complexes **2**–**4** led to the reversed stereoselectivity, with the *trans* isomer as the main product. On the other hand, ruthenacarboranes **4** gave rise to cyclopropanation yields similar to that of **1**. Noteworthy, with the related complexes, $[RuCl(Cp^*)(PPh_3)_2]$ (**2a**) and $[RuCl(Ind)(PPh_3)_2]$ (**3**), the reaction of ethyl diazoacetate with styrene proceeded smoothly. Catalysts **2a** and **3** showed a lower catalytic activity (around 60% cyclopropanation yield); however, carbene insertion into the vinylic C–H bonds was also observed to some extent. Upon monitoring by gas chromatography the reaction of styrene and ethyl diazoacetate catalysed by $[RuCl(Cp^*)(PPh_3)_2]$, it was determined that in addition to forming the cyclopropanes, the C–H insertion products **5** and **6** (Scheme 3) appear initially as well.



5 6

Scheme 3.

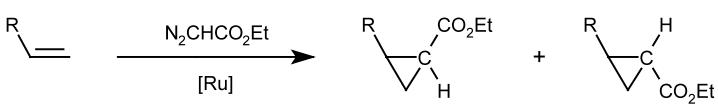
In addition, it was observed that the product distribution does not change over the course of the reaction, indicating that the products **5** and **6** are not formed by ruthenium-assisted opening of the cyclopropanes. For styrene, the combined cyclopropanation and C–H insertion products were isolated in 97% yield, and the product distribution was determined to be 57:22:18, respectively. Noteworthy, formation of C–H insertion products is distinctive of the [Ru–Cp*] fragment, and is independent of the phosphine used: [RuCl(Cp*)] complexes with isosteric *para*-substituted triarylphosphines differing only by their electronic contributions (PPh_3 (**2a**), P(*p*-C_6H_4-$OCH_3)_3$ (**2b**), and P(*p*-C_6H_4-$CF_3)_3$ (**2c**)) gave the same reactivity pattern.

Having established that complexes **1** and **4** show the best catalytic performance for the cyclopropanation of styrene, we then investigated the reaction of ethyl diazoacetate with different styrene derivatives, 1-octene and cyclooctene as well. The reactions were carried out at 40°C, a temperature which, while being fairly moderate, allows for olefin cyclopropanation to be accomplished efficiently (Fig. 1). 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 ethyl diazoacetate with styrenics afforded the corresponding cyclopropanes in good yields, with predominantly *cis* stereoselectivity

Table 1. Ruthenium-catalysed cyclopropanation of styrene by ethyl diazoacetate[a]

	Cyclopropanation	
Complex	Yield (%)[b]	*cis*/*trans* ratio
1	85	1.85
2a	57	0.17
2b	59	0.25
2c	61	0.30
3	68	0.48
4a	85	0.48
4b	86	0.52
4c	88	0.52

[a] *Reaction conditions*: complex, 0.005 mmol; styrene, 2 mL; ethyl diazoacetate, 1 mmol diluted in 1 mL of styrene; addition time, 4 h; 40°C.
[b] Based on ethyl diazoacetate.



Scheme 2.

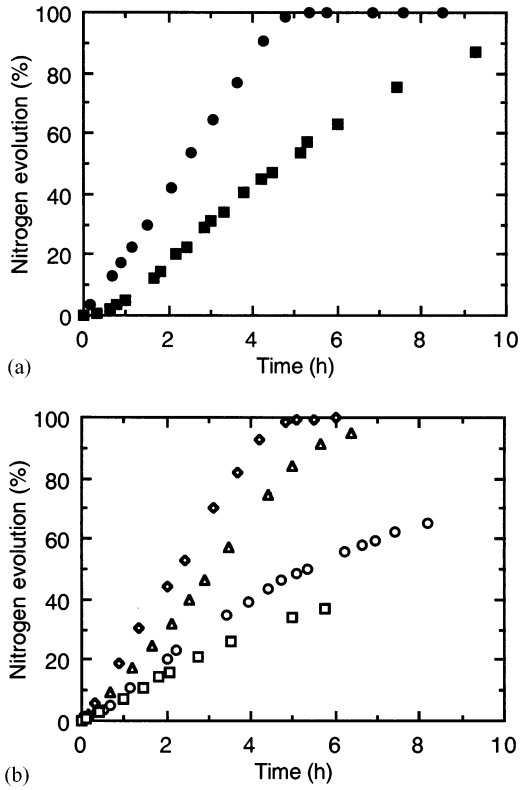
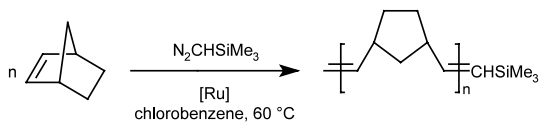


Figure 1. Influence of the temperature on the decomposition rate of ethyl diazoacetate in styrene in the presence of complexes **1** (rt (■), and 40°C (●)), and **4a** (rt (□), 40°C (○), 60°C (△) and 80°C (◇). Reaction conditions same as in Table 1.

with catalyst **1**, and *trans* stereoselectivity with complex **4a**. By contrast, non activated olefins (1-octene and cyclooctene) were much less reactive, giving mainly dimethyl maleate and only minor cyclopropanation products. Apparently, electron-rich olefins show a higher reactivity toward the intermediate carbene species, and thus carbene dimerisation can be suppressed.

$[RuCl(Cp')(PAr_3)_2]$ are 18-electron complexes, and it is generally agreed that the catalytic activity of this class of ruthenium complexes depends on the relative facility of dissociation of one phosphine.[13,16] It is therefore reasonable to assume that the initial stage of the catalytic cyclopropanation of olefins implies the generation of the carbene intermediate $[RuCl(=CHCO_2Et)(Cp')(PAr_3)]$, by reaction of the diazo compound with the 16-electron complex $[RuCl(Cp')(PAr_3)]$ formed by displacement of one phosphine ligand.[13] With this in mind, the formation of the cyclopropanes could then occur though the transfer of the carbene fragment onto a non coordinated olefin. This hypothesis, however, does not account for the formation of product **6**. According to the literature,[8,13,17] the formation of **6** (and **5** as well) would result rather from the rearrangement (likely via an η^3-allylhydrido intermediate) of a metallacyclobutane, a key intermediate in olefin metathesis which is in equilibrium with a metal–carbene–olefin complex. If we postulate the intermediacy of ruthenacyclobutanes in the formation of compounds **5** and **6**, metallacyclobutanes should be detectable by their propensity to initiate the formation of polymers from a suitable cyclic olefin. In order to test this hypothesis, we tested complexes **1**–**4** in the ring-opening metathesis polymerisation (ROMP) of norbornene (Scheme 4). Moderate amounts of polynorbornenes (up to 63% yields) were formed, essentially with catalysts **2** and **3** when activated by reaction with trimethylsilyldiazomethane, which is usually superior to diazoesters for initiating metathesis.[18] Most gratifyingly, we also noted that the most efficient catalysts for olefin homologation were also the most active ones for ROMP (Table 3), therefore supporting the assumption of the intermediacy of a ruthenacyclobutane in the homologation reaction. A speculative catalytic cycle is presented on Scheme 5.



Scheme 4.

Table 2. Ruthenium-catalysed cyclopropanation of various olefins by ethyl diazoacetate[a]

Olefin	Complex **1** Cyclopropanation		Complex **4a** Cyclopropanation	
	Yield (%)[b]	*cis*/*trans* ratio	Yield (%)[b]	*cis*/*trans* ratio
Styrene	85	1.85	85	0.48
4-Methylstyrene	87	1.17	86	0.49
4-*tert*-Butylstyrene	82	1.01	81	0.59
4-Methoxystyrene	89	1.27	84	0.68
4-Chlorostyrene	87	1.45	79	0.62
α-Methylstyrene	82	1.63	84	1.13
1-Octene	5	0.39	39	0.60
Cyclooctene	16	1.33[c]	15	0.60[c]

[a] Same as in Table 1.
[b] Same as in Table 1.
[c] *endo*/*exo* ratio.

Table 3. Ring-opening metathesis polymerisation of norbornene catalysed by complexes **1**–**4**[a]

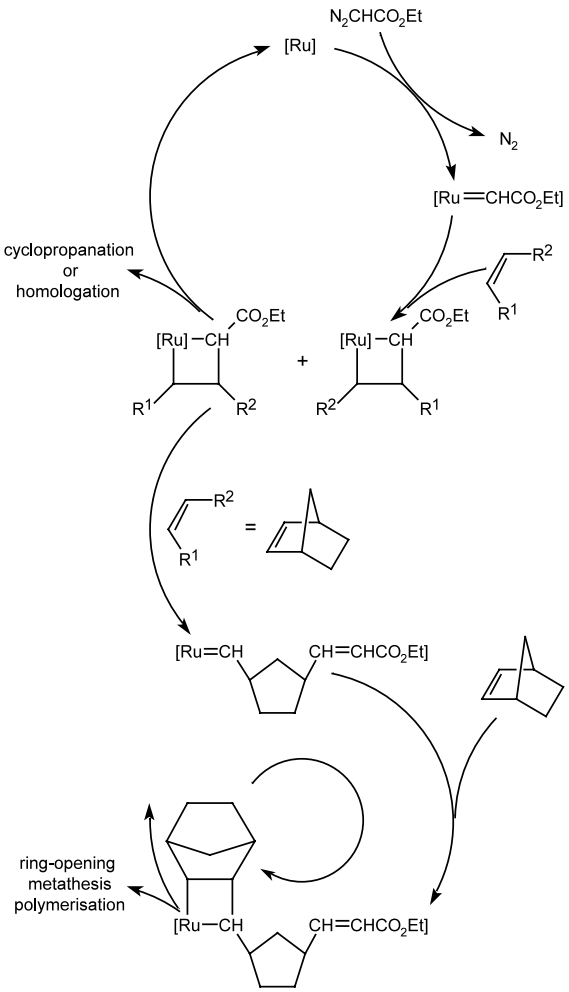
Complex	Polymer yield (%)	M_n[b]	M_w/M_n[b]	σ_c[c]
1	1	–	–	0.38
2a	26	–	–	0.54
2b	19	–	–	0.44
2c	63	–	–	0.36
3	55	35 500	7.7	0.54
4a	7	33 500	10.6	0.66
4b	1	39 000	11.5	–
4c	2	39 500	10.7	0.36

[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 min, and 0.1 mmol of trimethylsilyldiazomethane diluted in 1 mL of chlorobenzene was then added to the reaction mixture via a syringe. 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 GPC, using polystyrene standards.

[c] Fraction of *cis* units, determined by ^1H and ^{13}C NMR.

The formation of ruthenacyclobutanes infers that the carbene and the olefin are both coordinated to the metal centre, and hence the presence of two *cis* vacancies resulting either from the displacement of two phosphine ligands from the $[RuCl(Cp')(PAr_3)_2]$ complexes or the release of only one phosphine and metal ring-slippage of indenyl in $[RuCl(Ind)(PPh_3)_2]$. The formation of ruthenacyclobutanes also infers the generation of Ru^{IV} species. Not surprisingly, the Cp* and indenyl ligands are known to display electron-releasing properties that are much more pronounced than those of Cp.[19] Accordingly, the [RuCl(Cp′)] moiety (Cp′=Cp* and Ind) should stabilise the Ru^{IV}–cyclobutane more reliably than [RuClCp], favouring therefore a metathetical reaction pathway.



Scheme 5.

The intermediacy of ruthenacyclobutanes in the homologation reaction of olefins remains, however, questionable, and observing olefin metathesis does not infer that homologation takes place via the same ruthenacyclobutane intermediate. Alternative mechanisms could be proposed to account for olefin homologation. Nevertheless, it is well-known in organometallic chemistry that ruthenacyclobutanes are very unstable species, and only very few have been synthesised and fully characterised.[20] In olefin metathesis, a reaction in which the intermediacy of a metallacyclobutane seems to be no doubt, ruthenacyclobutanes have never been detected despite numerous efforts world-wide.[21] In addition, theoretical studies, including molecular dynamics simulations,[22] revealed the formation of a ruthenacyclobutane intermediate, but in a very high-energy state. In the present case, since the activity of the ruthenium catalysts for olefin homologation parallels pretty well that for olefin metathesis, the involvement of a common ruthenacyclobutane intermediate for both reactions is quite plausible, though speculative. However, due to the transient nature of ruthenacyclobutanes, a clear spectroscopic evidence for their intermediacy in the homologation reaction seems to be out of reach nowadays.

In conclusion, we have shown that $[RuCl(Cp)(PPh_3)_2]$ (**1**) and their carboranyl derivatives (**4**) are highly efficient catalyst precursors for promoting olefin cyclopropanation under mild conditions, with **1** exhibiting a high *cis* stereoselectivity and **4** a significant preference for the *trans* isomers. In addition to forming cyclopropanes, $[RuCl(Cp^*)(PAr_3)_2]$ (**2**) also catalyses the insertion of carbenes into vinylic C–H bonds likely via a ruthenacyclobutane intermediate. A detailed understanding of the reaction mechanism must await further study, and improvements with this family of ruthenium(II) complexes through modification of the stereoelectronic parameters of the ligands are now under investigation.

Acknowledgements

This work was financially supported by a grant-in-aid (O.T.) joined to the project MAT98-0921 from CICYT (Spain). Part of this work has also been carried out in the framework of the COST D17/006/00 and TMR-HPRN CT 2000-10 'Polycat' programmes. The Belgian team is also grateful to the 'Fonds National de la

Recherche Scientifique' (F.N.R.S.), Brussels, for the purchase of major instrumentation.

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