# Late transition metal-based catalysts for olefin cyclopropanation or olefin metathesis. Importance of catalyst unsaturation*

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Ruthenium- and rhodium-based catalysts can be designed and finely tuned to some extent so as to mediate either carbene transfer to olefins (*e.g.*, olefin cyclopropanation) or olefin metathesis. The different outcome of the reactions can be quite simply predicted based on either the ability or the absence of ability of the metal center to coordinate both the carbene and the olefin. Several available coordination sites at the metal center are favorable for metathesis to the prejudice of olefin cyclopropanation.

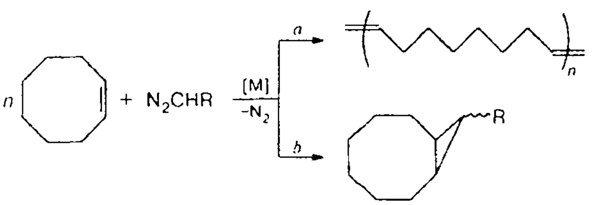
**Key words:** ruthenium- and rhodium(II)-based catalysts, olefin cyclopropanation, olefin metathesis, ring opening polymerization metathesis (ROMP).

## Introduction

In the last decade, reactions involving transition metals have been vigorously developed and employed in synthetic organic chemistry and in polymer chemistry. Among the important catalytic strategies used to construct C—C bonds, transition metal-mediated transfer of carbene fragments to substrates containing one or more unsaturated segment (most often, carbon—carbon double bonds) can be distinguished. Whereas with some catalysts this reaction results in cycloaddition products (*i.e.*, olefin cyclopropanation occurs), other carbene complexes of transition metals are more likely to induce olefin metathesis. In some cases, cycloaddition and olefin metathesis occur as competing processes. Metathesis of olefins and metathesis resulting in ring closure are unsurpassed methods for the construction of carbon—carbon double bonds. Thus, the reactions of metal—carbene bonds with olefins can yield different products, depending on the nature of the metal, its oxidation state, and the ancillary ligands present.[1—3] The purpose of this review, which is certainly not exhaustive, is to summarize the data on various reactions that appeared due to the recent adoption of new carbene complexes based on late transition metals and to propose tentatively a simple and straightforward explanation for the experimental observations. The search for catalysts based on late transition metals has been justified by the fact that catalysts based on early transition metals (Mo, W, *etc.*) are sensitive to oxygen and water and poorly compatible with polar functional groups and, additionally, they are difficult to synthesize.

General review of the chemistry of carbenes involving Group 8, 9, and 10 transition metals demonstrates that complexes of second-row elements, *viz.*, palladium and rhodium, prove to be the most efficient cyclopropanation catalysts. However, complexes of these two metals are not used to catalyze metathesis of olefins.[2—8] Meanwhile, ruthenium-based complexes can catalyze both reactions, *i.e.*, olefin metathesis and/or olefin cyclopropanation,[9—15] as sketched in Scheme 1 for cyclooctene.

**Scheme 1**



*a.* Olefin metathesis. *b.* Carbene transfer.

The present-day level of understanding of these reactions remains limited and no common view on the reactions involving transition metal carbene complexes exists to date. Many questions remain unanswered; in particular, the role played by metallacyclobutanes in the cyclopropanation of olefins is far from being clear. In addition, the factors that influence the reactivity of such

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metallacycles are poorly understood. Whereas the intermediacy of metallacyclobutanes derived from early transition metals in olefin metathesis is now well ascertained, the role of these hypothetical intermediates in the reactions catalyzed by late transition metals (including cyclopropanation) is more speculative because in a number of cases no experimental support is available.

The general trends are that electrophilic carbene complexes of transition metals (generally referred to as "metal carbene" complexes) usually react with olefins to give cyclopropanes; this cycloaddition reaction is classified as a "carbene transfer reaction." However, nucleophilic metal carbene complexes (the so-called "alkylidene" complexes) react with electrophiles such as carbonyl groups in aldehydes or ketones according to the Wittig reaction pathway to give olefins. Complexes of this second type (but not all of them) also catalyze olefin metathesis.

However, this view is too simplified. There are many exceptions to this general rule and there seems to be a continuum in the variation of reactivity between both types of complexes. Variations of the metal oxidation state and/or ligands attached to it alter the reactivity of the carbene center. The nature of the substrate and the solvent used (coordinating or not) can also influence the outcome of the reaction. Thus, the border between "metal alkylidene" and "metal carbene" complexes is not clearly defined. This view is supported by the theoretical model proposed by Cundary and Gordon. In this model, a clear-cut difference between the types of bonding in "metal alkylidene" and "metal carbene" complexes is no longer needed, because the properties of the metal carbene derivatives follow from the relative statistical weights of neutral, nucleophilic, and electrophilic resonance forms.[16,17]

This model substantiates the occurrence of metal carbene and metal alkylidene competing reactions and assumes that this behavior should be most typical of second- and third-row Group 8—10 transition metals. According to these calculations, the intrinsic nature of an M=C bond can be varied within certain limits by modifying the ancillary ligands and the substituents at the carbene (alkylidene) carbon atom.[16,17] Furthermore, high polarization of the M—carbene bond in the $M^+=C^-$ fashion should correlate with a greater activity in metathesis and the heaviest metals in these fragments should ensure higher nucleophilicity of the α-carbon.

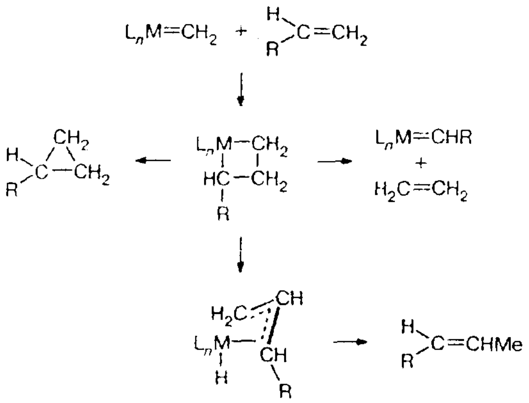
Study of amphiphilic "metal carbene" complexes seems the most informative. These complexes are not very common and examples of carbene complexes that react with both acids and bases are restricted to date to ruthenium and rhenium complexes.[18,19]

## The intermediate formation of metallacyclobutanes in cyclopropanation reactions

The chemistry of metallacyclobutane compounds has attracted considerable attention in the past two decades. Besides having been used successfully in organic synthesis, metallacyclobutanes play an important role in a number of catalytic transformations; in particular, they have been proposed as intermediates in olefin metathesis[20] and cycloaddition of alkenes.[21]

Numerous metallacyclobutane derivatives of late transition metals are known. Some of them (*e.g.*, platinacyclobutanes) are thermally stable. Decomposition of metallacyclobutanes can afford olefins, carbene olefin complexes, allyl complexes, and also cyclopropanes (see Scheme 2). These reactions are often poorly selective (for details, see the review[22]).

**Scheme 2**



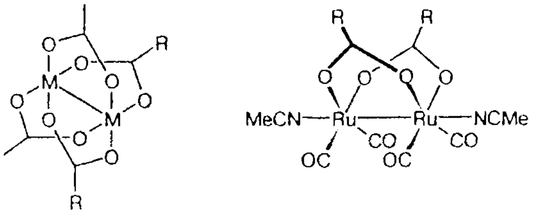
Metallacyclobutanes involved in catalyzed cyclopropanation reactions are much less documented, possibly because they undergo fast reductive elimination. Actually, the participation of metallacyclobutanes as intermediates in the formation of cyclopropane from olefins and diazo compounds remains a matter of debate. The intermediate formation of metallacyclobutanes in carbene transfer reactions is not often supported either by direct observation or by comprehensive studies of the reaction mechanisms. The formation of an intermediate metallacycle does not appear to be a general rule in olefin cyclopropanation. The formation of a metallacyclobutane requires coordination to the central metal atoms of both the olefin and the carbene. Evidence for direct reaction of the metal carbenes with alkenes without prior coordination of an olefin has been obtained. For example, olefin coordination does not take place in cyclopropanation catalyzed by dirhodium tetracarboxylate. Partial release of free carbenes from metal carbene complexes can occur, at least during the insertion of rhodium carbenoids into C—H bonds.[23] An equilibrium between free and complexed carbene has also been suggested in some cycloaddition reactions, depending on the nature of the carboxylate residues of the dirhodium(II) catalyst.[24] This certainly does not exclude the possibility that metallacyclobutanes play a crucial role in some catalyst systems, especially in reactions catalyzed by copper and palladium compounds.

Thus it can be assumed that there is no single general model for olefin cyclopropanation.[25] However, the intermediacy of metallacyclobutanes has been reliably established for some catalyzed reactions. Yet another question arises: why do some metallacyclobutanes yield cyclopropanes while others catalyze olefin metathesis? Are these two reactions in competition?

## Binuclear rhodium(II) and ruthenium(II) carboxylates

When considering typical cyclopropanation catalysts, it is noteworthy that all the efficient rhodium-based systems known to date, except for some rhodium(III) porphyrins, which are stable complexes, possess a rigid dirhodium(II) framework with the "lantern" structure (as in dirhodium(II) tetracarboxylates and related dirhodium(II) carboxamidates).[1,3,26] The "lantern" fragment confers structural stability to the binuclear rhodium(II) complexes (Scheme 3, structure **A**).

Scheme 3



**A** **B**

The attached ligands are kinetically stable and occupy one coordination site at each metal atom. Calculations and the chemical behavior indicate moderate back donation to the carbene ligand, resulting in fairly labile electrophilic carbenoid species.[18,19,24] Evidently, cyclopropanation is controlled by a frontier orbital, namely, the LUMO of the complex, corresponding to the carbene p orbital. The general picture of the reaction mechanism includes interaction of the resulting rhodium carbene complex with the noncoordinated olefin in a bimolecular reaction. This model accounts for the fact that metathesis reactions are not initiated by binuclear rhodium(II) complexes; indeed, there is no room for olefin coordination and this prevents the formation of metallacyclobutane. The mechanism of cyclopropanation catalyzed by binuclear rhodium(II) complexes is similar in many aspects to the mechanism proposed for rhodium porphyrin-catalyzed cyclopropanation of alkenes by ethyl diazoacetate.[27] In the latter case, the porphyrin ligand acts as a "wall" that actually prevents *cis*-coordination of an olefin in relation to the carbene ligand. It must be stressed, however, that only very few direct experimental data related to the mechanism of the reactions of diazo compounds mediated by rhodium complexes or to metal-carbene intermediates can be found. Note that the putative intermediate carbene complex has never been observed in a catalytic system.

However, the addition of one or several equivalents of trimethylsilyl chloride to dirhodium(II) tetraacetate results in the formation of a new catalytic system, capable of performing (to a certain extent) the ring-opening metathesis polymerization (ROMP) of norbornene. Trimethylsilyl chloride is known to remove bridging acetate ligands[28] and eventually to make room for olefin coordination. If the reaction is carried out in neat olefins with the appropriate stoichiometry and in the absence of strongly coordinating ligands, olefins are expected to be bound to the metal center instead of one (or two) chelating acetato ligand. Thus, a typical and a very selective catalyst for cyclopropanation of olefins can be so designed as to induce as well metathesis of olefins.

The corresponding diruthenium tetracarboxylate ($s^2p^4d^2d^{*2}p^{*2}$, paramagnetic at room temperature) is much more labile than its dirhodium analogs.[29] Complexes of this type promote both carbene transfer reactions and olefin cross-metathesis (when they react with a mixture of styrene and norbornene).[30] However, it still remains unknown whether these different reactions are initiated by a common species (the activity in metathesis is attributed to the kinetic lability of the carboxylate bridges, which allows coordination of both the olefin and the carbene ligand). No metathesis was observed in the absence of diazo compound.

Although the activation of binuclear ruthenium(II) complexes by diazo compounds gives relatively poor ROMP catalysts, it was concluded that their activity in metathesis could probably be increased by utilizing metal complexes with more labile ligands. This has led to a study of some diruthenium(I) dicarboxylates of the general formula $[Ru_2(RCO_2)_2(CO)_4(MeCN)_2]$ (Scheme 3, compound **B**), in which the metal is axially bound to labile acetonitrile ligands; it was assumed that this would favor the simultaneous coordination of the carbene ligand and the olefin after displacement of one or several CO ligands.

However, complexes of this type also proved to be kinetically too stable. No release of CO ligands occurred at moderate temperatures. Accordingly, these complexes did not promote olefin metathesis below 100 °C but they were good cyclopropanation catalysts.* Nevertheless, some ROMP processes were initiated at 100 °C (the degree of conversion was about 5% for cyclooctene and more than 70% for more strained norbornene). Thus, although cyclopropanation is the preferred reaction pathway, the considered ruthenium complexes are also able to initiate olefin metathesis. This contrasts with what is commonly observed for binuclear rhodium carboxylates, whose ligands are kinetically inert under the reaction conditions.

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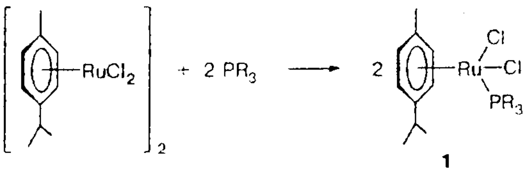
* A. F. Noels, A. Demonceau, unpublished results, 1996.

## Ruthenium(II) arene complexes

The search for metal complexes containing more labile ligands has led to the discovery of yet another class of versatile and very efficient catalyst precursors based on the air-stable and readily available $[(ArH)RuCl_2]_2$ complexes. Depending on the ligand they react with, these dimeric species give new monomeric complexes that can promote either olefin metathesis or olefin cyclopropanation. For instance, upon reaction with an equimolar amount of phosphine, they give the mononuclear complexes **1** (Scheme 4). When a bulky and basic phosphine, namely, tricyclohexylphosphine $PCy_3$, is used, the resulting complex is an outstanding precursor of an olefin metathesis catalyst.

Scheme 4



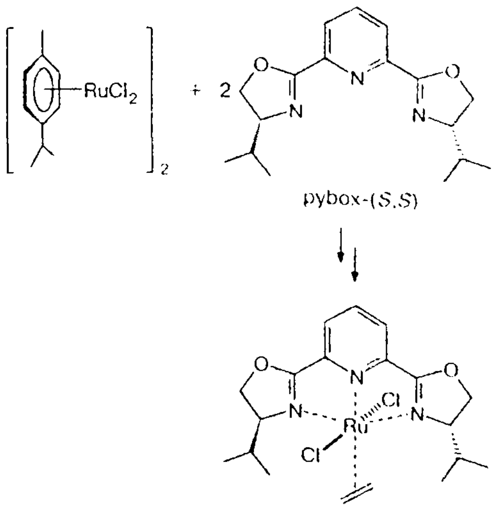
**1**

Complexes such as $(p\text{-cymene})RuCl_2PCy_3$ promote spontaneously not only the ROMP of norbornene derivatives (*i.e.*, strained cycloolefins) to give polynorbornenes with high molecular weights but they are also effective in the polymerization of cyclooctene, functionalized cyclooctenes, and other low-strain cycloolefins to polyalkenomers when activated *in situ* by the addition of a diazo compound.[31] For instance, cyclooctene undergoes immediate ROMP when a catalytic amount of (trimethylsilyl)diazomethane is added to the reaction mixture. The diazo compound reacts with the ruthenium complex to afford highly active alkylidene species, $[Ru]{=}CHSiMe_3$, which are sufficiently stable against organic functional groups and initiate the ROMP. The catalytic activity for olefin metathesis is attributed to the easy release of the arene ligand upon the addition of diazo compounds, which permits olefin coordination and the subsequent formation of ruthenacyclobutanes.[31] However, the formation of ruthenacyclobutane has not been demonstrated.

Upon reactions with chelating bi- or tridentate ligands, $[(p\text{-cymene})RuCl_2]_2$ forms 18-electron complexes **2**, which do not promote olefin metathesis (Scheme 5, the only labile ligand is ethene). This can again be rationalized by the fact that only one site at the metal atom is available for coordination. Therefore, these complexes are no longer able to participate in olefin metathesis but act only as carbene transferring agents (olefin cyclopropanation), sometimes with high enantioselectivity.[32–34]

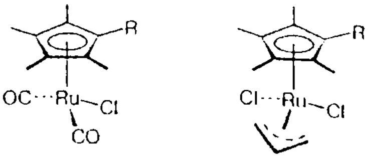
However, the chemistry of metal carbene complexes is far from being fully apprehended. Indeed, a new class of ruthenium(II) and ruthenium(IV) complexes containing various substituents in the ligands (see Scheme 6 for catalysts and Scheme 7 for reactions) was recently reported to mediate a rarely observed formal carbene insertion into an olefin C—H bond of styrene (so-called "homologization reaction").[35]

Scheme 5



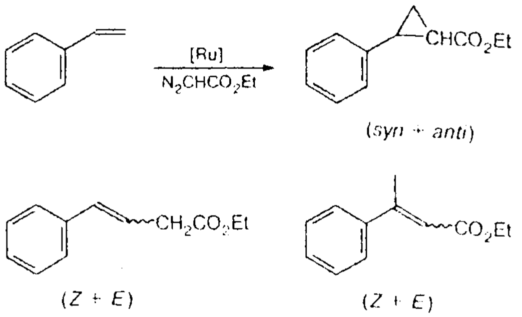
$Ru(pybox)Cl_2$, **2**

Scheme 6



**3** **4**

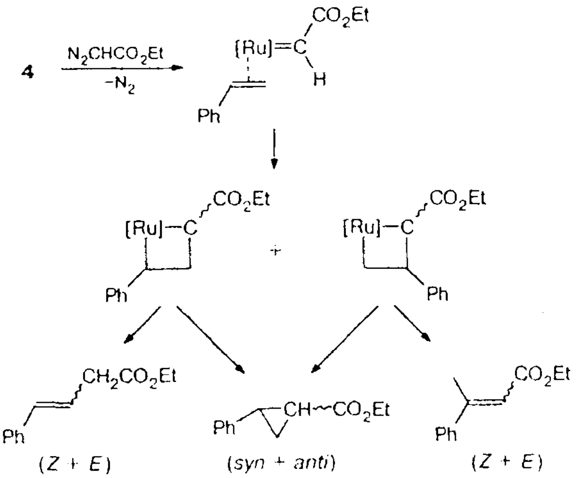
Scheme 7



This reaction was found to be catalyzed most efficiently by $Ru^{IV}$ complexes. However, cyclopropanation of the C=C double bond in styrene competes with the homologization reaction and becomes the principal reaction with most of the $Ru^{II}$ complexes tested; some of these complexes are good cyclopropanation catalysts.

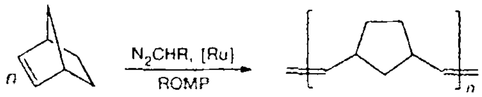
In this case, too, some explanation can be made based on the same quite simple assumptions of the known chemistry of metal carbene complexes. Metallacyclobutanes are proposed to be the intermediates responsible for the homologization reaction. All the catalysts employed are initially 18 electron-ruthenium(II) or ruthenium(IV) complexes. To form the metal carbene, *viz.*, the key intermediate, the complex should lose one or more ligands to create sites at which the reaction can then proceed. Catalytic activity is thus related to the lability of the ligands. Thus, for example, one CO ligand in the ruthenium(II) complexes is presumably replaced by a diazo compound to form the key 18-electron ruthenium carbene intermediate. The latter complex can subsequently react with a noncoordinated olefin to yield a cyclopropane in a manner similar to that proposed for the catalysts based on binuclear rhodium(II) complexes.[6,8] In the case of ruthenium(IV) complexes, the situation is more complex; in fact, one route by which they can be activated is the loss of an allyl halide to yield a highly unsaturated Cp*Ru(II)Cl, a 14-electron species, which would allow the coordination at the metal center of both the carbene and the olefin. This could give a 16-electron ruthenacyclobutane, for which many reaction pathways are possible, including the reductive elimination of cyclopropane and decomposition to give homologization products. These different reaction pathways are sketched in Scheme 8.

Scheme 8



The proposed mechanism and the intermediate formation of metallacycles in the homologization reaction are supported indirectly by the known tendency of ruthenacyclobutanes to initiate the formation of polymers from suitable cyclic alkenes, *e.g.*, norbornene. Thus, a competitive reaction might lead to the formation of ROMP products with this strained olefin and the relief of the strain inherent in cyclic olefins is the driving force of the reaction yielding polynorbornene according to Scheme 9.

Scheme 9



Thus, polymer formation is the most probable process. This is exactly what is observed with ruthenium(IV) complexes. Moderate amounts of polynorbornenes (up to 54% conversion) were formed with ruthenium(IV)-based catalysts. Further studies are, however, needed in order to fully evaluate the scope and limitations of these catalytic systems and their potential utilization in synthetic organic chemistry. In this case, too, olefin coordination is apparently a crucial factor for observing metathesis-related reactions. Although this naive approach ignores a number of important factors such as collinear or perpendicular binding of the incoming olefin to the M=C bond or puckering of the metallacycles,[36,37] which might influence the outcome of the reaction, it agrees well with the observations made so far and seems to have a good predictive efficiency, at least, for the family of ruthenium-based catalysts discussed here.

Grubbs and coworkers[38] have recently reported on analogous catalytic systems and have isolated well-defined and air-stable ruthenium(II) carbene complexes of the general formula *trans*-$(PCy_3)RuCl_2$=CHR. These 16-electron complexes are precursors of catalysts for olefin metathesis. Studies of the reaction mechanism indicate that, during metathesis, the ruthenium complex reversibly dissociates with elimination of the phosphine.[39] Thus, the "real" active species is formally a 14-electron species. These and related ruthenium(II) complexes are very efficient catalysts. They promote the ROMP of low-strain cyclic olefins and catalytic ring-closing metathesis of a variety of functionalized dienes[14,38,39]; the increasing role of complexes of this type in organic synthesis has been widely recognized. These findings also confirm the observation that highly unsaturated ruthenium complexes are the key to high catalytic activity in olefin metathesis.

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