SYNTHETIC APPROACH TO RUTHENIUM VINYLIDENE COMPLEXES AND THEIR APPLICATIONS IN METATHESIS CATALYSIS

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Convenient routes for synthesis of ruthenium vinylidene complexes have been described, the majority of which use alkynes along with a ruthenium source as the main starting materials. Their successful application as efficient precatalysts in synthesis of heterocyclic and carbocyclic compounds by ring-closing metathesis of α,ω-dienes and in the synthesis of polymers by ring-opening metathesis polymerization of cyclooctene, norbornene, 5-substituted norbornene and dicyclopentadiene are fully illustrated. Relevant aspects concerning the activity and stereoselectivity in metathesis reactions of this type of Ru complexes are highlighted.

INTRODUCTION

Over the past decade, the chemistry of transition metal vinylidene complexes has become a topic of a real challenge in the area of coordination and organometallic chemistry.[1-6] By coordination to the transition metals, vinylidene ligands (:C=CHR), high-energy tautomers of alkynes (HC≡CR), highly reactive and short-lived in free state, can be effectively stabilized and endowed with new chemical properties that are useful for targeted chemical transformations. They behave as electron-withdrawing groups and are better stabilized by coordination at the electron-rich metal cores. As result of this coordination, the α-vinylidene carbon is highly electrophilic and prone to nucleophilic addition, the M=C bond has a pronounced metal carbene charater promoting [2+2] cycloaddition of C=C and C≡C bonds with formation of metallacyclobutane and metallacyclobu-tene intermediates, respectively, and the β-vinylidene carbon is significantly nucleophilic leading to electrophilic additions.

It has been fully documented that transition metal vinylidene complexes play an important role in many catalytic processes.[7-10] Most relevant catalytic reactions are alkene and enyne metathesis, alkyne dimerization and ring-opening metathesis polymerization, cycloaromatization of conjugated enediynes, additions of oxygen, nitrogen and carbon nucleophiles to alkynes, etc.[11-14]

The coordination and organometallic chemistry of ruthenium vinylidene complexes have been comprehensively reviewed by Bruneau and Dixneuf,[15,16] by Katayama and Ozawa[17] and other research groups.[18] In such excellent reviews the reader can find important information about the synthesis, structure and reactivity of this class of transition metal complexes as well as regarding their wide application in catalysis and synthetic chemistry.

With the advent of more experimental data on ruthenium vinylidene complexes, the present paper will try to cover most relevant aspects concerning their synthesis and applications in metathesis and related chemistry.

SYNTHETIC APPROACH TO Ru VINYLIDENE COMPLEXES

There are several distinct routes that have been applied successfully for synthesis of Ru vinylidene complexes, the majority of which use alkynes

along with a Ru source as the main starting materials. It has been pointed out that conversion of alkynes into vinylidenes may proceeds either by η^2-coordination of the triple bond followed by 1,2-hydrogen migration or by oxidative addition of alkynes to transition metal to give an alkynyl metal intermediate which subsequently rearranges through 1,3-hydrogen migration or protonation[15] (Scheme 1).

Scheme 1
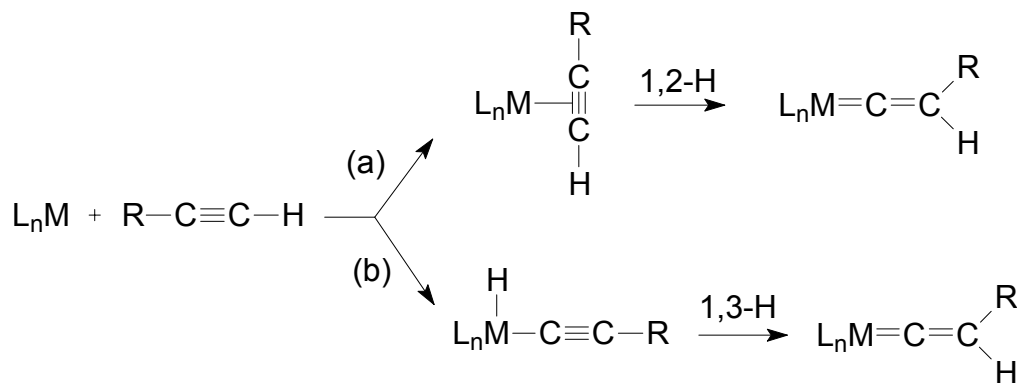
Direct isomerization η^2-alkyne-η^1-vinylidene complexes by a bimolecular mechanism has also been considered.[15] Alternately, vinylidene complexes can be produced from ruthenium hydride complexes by insertion of the triple bond to form a vinyl ruthenium intermediate which undergoes further α-hydrogen migration[17] or from ruthenium carbene by metathesis with 1,2-propadiene.[19] Internal alkynes having labile substituents readily give rise to vinylidene complexes; triallylsilyl, triphenylstannane, alkylthiol and iodide groups can migrate and generate vinylidene metal complexes.

The first 18-electron, cationic Cp-Ru-vinylidene complex, [CpRu(=C=CHPh)(PPh$_3$)$_2$][PF$_6$] (**1**), was prepared by Bruce *et al.*[20] by the reaction of CpRuCl(PPh$_3$)$_2$ with PhC≡CH, in the presence of NH$_4$PF$_6$ (88% yield) (Scheme 2).
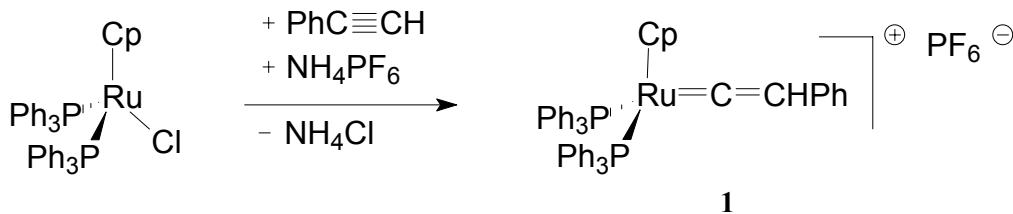
Scheme 2

Thereafter, several coordinatively saturated, cationic Ru vinylidene complexes have been prepared from terminal alkynes and Ru complexes, most of them containing Cp and various ancillary ligands.

Coordinatively unsaturated, 16-electron Ru vinylidene complexes, RuX$_2$(=C=CHR)L$_2$, (X = Cl,Br, R = *t*Bu, L = PPh$_3$) (**2**), first reported by Wakatsuki *et al.*,[21] have been obtained from RuX$_2$(PPh$_3$)$_3$ and *t*BuC≡CH (Scheme 3).
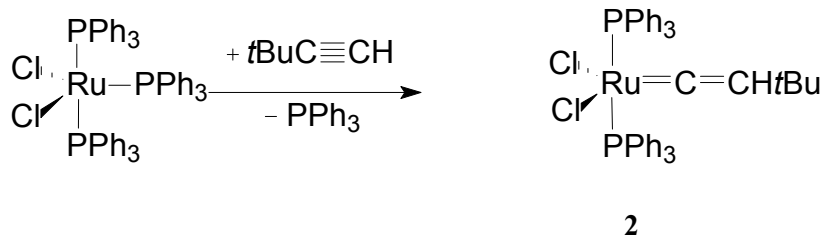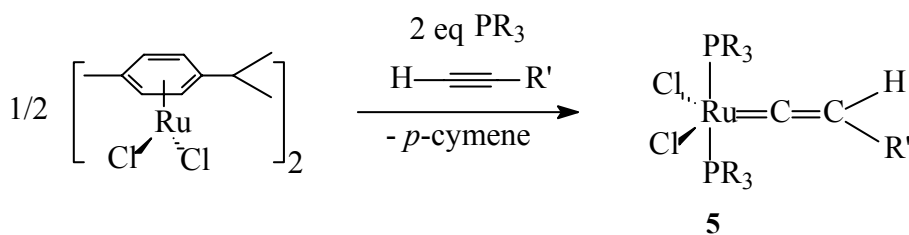

Scheme 3

Following this report, a variety of Ru vinylidene complexes have been prepared using terminal alkynes and different Ru sources. Thus, Werner *et al.*[22-25] synthesized $RuCl_2(=C=CHPh)(PiPr_3)_2$ (**3**) from $RuH_2Cl_2(PiPr_3)_2$ and $PhC\equiv CH$ while Caulton *et al.*[26] prepared $RuHCl(=C=CHPh)(PBu_2Me)_2$ (**4**) by insertion of $PhC\equiv CH$ into $RuHCl_2(H_2)(PBu_2Me)_2$ and subsequent 1,2-hydrogen migration in the intermediate styrylruthenium complex.

Two convenient synthetic routes to Ru vinylidene complexes have been developed by Katayama and Osawa.[27,28] The first route involves the reaction of the Ru complex $Ru(methallyl)_2(COD)$ with $PiPr_3$, HCl, and $RC\equiv CH$ and proceeding through $[RuCl_2(PiPr_3)_2]_n$ as the intermediate. The second one, a more general and efficient approach, consists of heating a toluene solution of the Ru dimer $[RuCl_2(p\text{-cymene})]_2$, PR_3, and $R'C\equiv CH$ at 80°C. A set of neutral 16-electron ruthenium vinylidene complexes **5** (R = *i*Pr, Cy, R' = Ph, *t*Bu, Fc, $p\text{-MeOC}_6H_4$, $p\text{-MeO}_2CC_6H_4$) have been thus prepared in high yield from commercially available terminal alkynes and the arene ruthenium dimer[27] (Scheme 4).

Scheme 4

In case of 1,2-disubstituted alkynes having a labile ligand such as $PhC\equiv CSiMe_3$, the β-silylvinylidene Ru complex results from 1,2-silyl migration in the coordinated η²-alkyne intermediate. With less bulky phosphines, *e.g.* PMe_2Ph, the coordinatively saturated tris(phosphane) Ru-complex is formed. Unfortunately, these complexes showed only a moderate metathesis activity such as RCM of unsubstituted α,ω-dienes and ring-opening metathesis polymerization of strained norbornenes.

New cationic and neutral 18-electron ruthenium vinylidene complexes have been prepared by Grubbs and coworkers[29] *e.g.*, **6-8** by the above methodology. These complexes have been screened for metathesis activity, but their applicability remained limited to a small range of olefin substrates (Scheme 5).
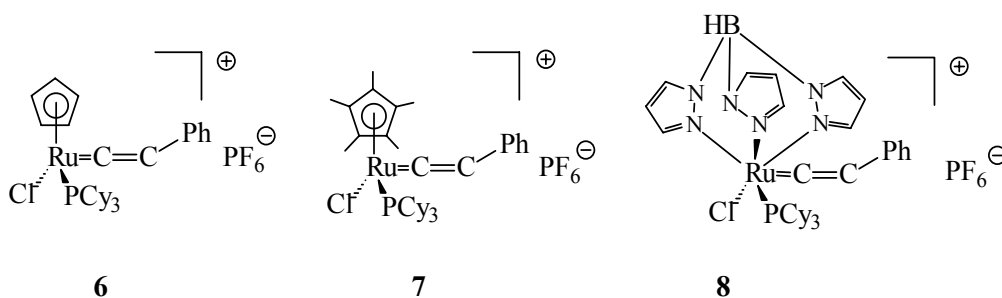
Scheme 5

Tridentate ligands of the pincer-type (PNP or NNN) have also been successfully employed as ancilary groups in synthesizing the Ru-vinylidene complexes **9-14**. It should be noted that some of these complexes showed good activity in ring-opening metathesis polymerization of highly strained cycloolefins[30-32] (Scheme 6).

This strategy has been further extended to other tridentate vinylidene structures[33,34] and to bi- and tri-metallic Ru vinylidene complexes which have been obtained in high yields but their metathesis activity has not been examined in detail.[35]

A substantial improvement to the above developed class of Ru complexes has been achieved by Louie and Grubbs[36] through the synthesis of a novel generation vinylidene complexes coordinated with an N-heterocyclic carbene (NHC) ligand (*e.g.*, imidazolylidene). This

new array of ruthenium complexes, e.g., **15** (IMes = bis(2,4,6-trimethylphenyl)-1,3-imidazol-2-ylidene, R = Cy, R' = *t*-Bu) and **16** (*i*PrIM = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene, R = Cy, R' = Ph)

has been conveniently prepared from the bisphosphane ruthenium complex **5** (R = Cy) by reaction with free imidazoline carbene or their salts (Scheme 7).
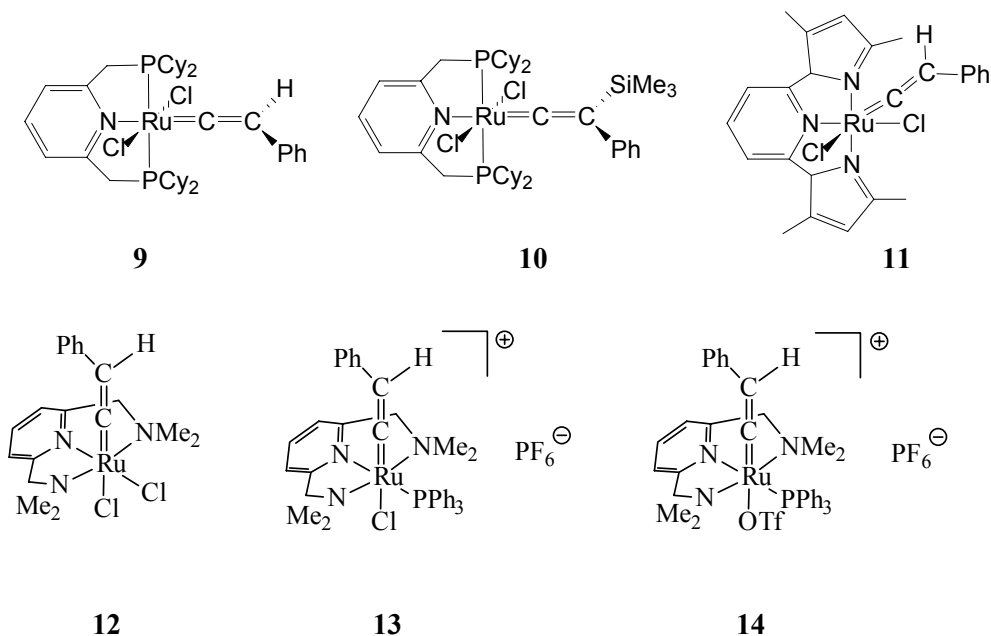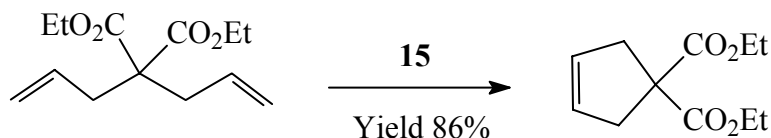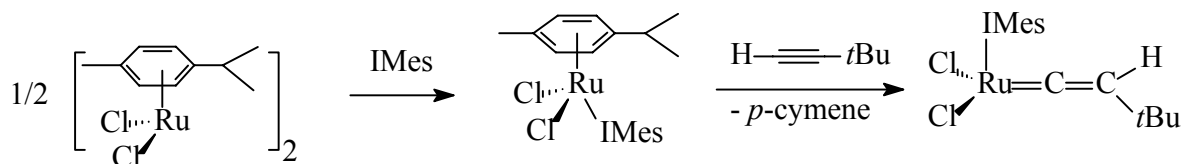

Scheme 6
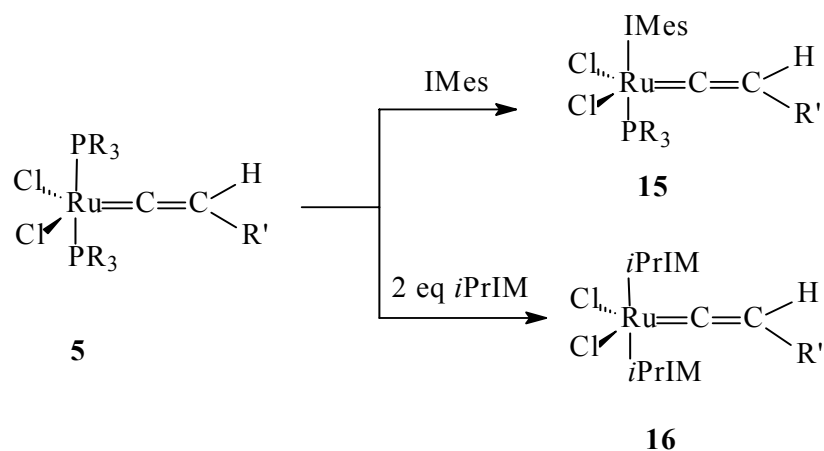
Scheme **7**

SYNTHESIS OF CYCLIC AND POLYMER COMPOUNDS USING Ru VINYLIDENE COMPLEXES

The ruthenium compound **15,** possessing a mixed ligand system, displayed a substantial metathesis activity in ring-closing metathesis of diethyl diallylmalonate to the corresponding substituted cycloolefin (86% yield), although the reaction rate was slower than that with the related imidazolylidene ruthenium carbene complex (Scheme 8).

Based on detailed mechanistic investigations of metathesis reaction with this type of ruthenium complexes, the above authors concluded that increased ligand dissociation (i.e. of phosphane) is necessary to accelerate initiation and thereby enhance the catalytic activity in metathesis. From these mechanistic data it was suggested that a coordinatively unsaturated phosphane-free ruthenium vinylidene complex **17** might be formed directly *in situ* from the commercial ruthenium dimer, N-heterocyclic carbene (IMes) as such or its salts and a terminal alkyne (Scheme 9).
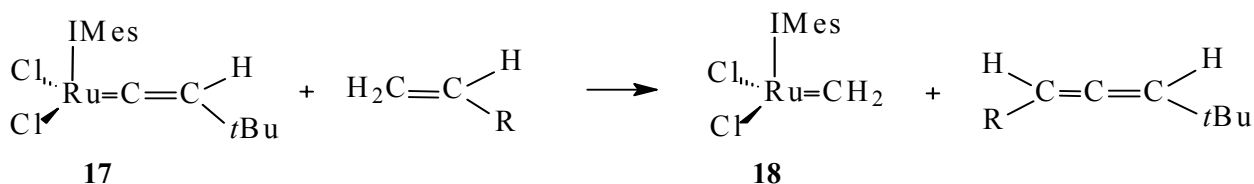
Scheme 8

Scheme 9

The pathway for generation of the real catalyst **18** from the catalyst precursor **17** by conversion with the olefin substrate was postulated as shown in Scheme 10.

Scheme 10

Examination of the catalytic activity of the complex **17** revealed that this complex is more active than the ruthenium complex **15,** evidencing a higher unsaturation in the coordination sphere of the metal. This particular behaviour of **17** has been observed in ring-closing metathesis of diethyl diallylmalonate, metathesis dimerization of allyl benzene and ring-opening metathesis polymerization of 1,5-cyclooctadiene (Scheme 11).
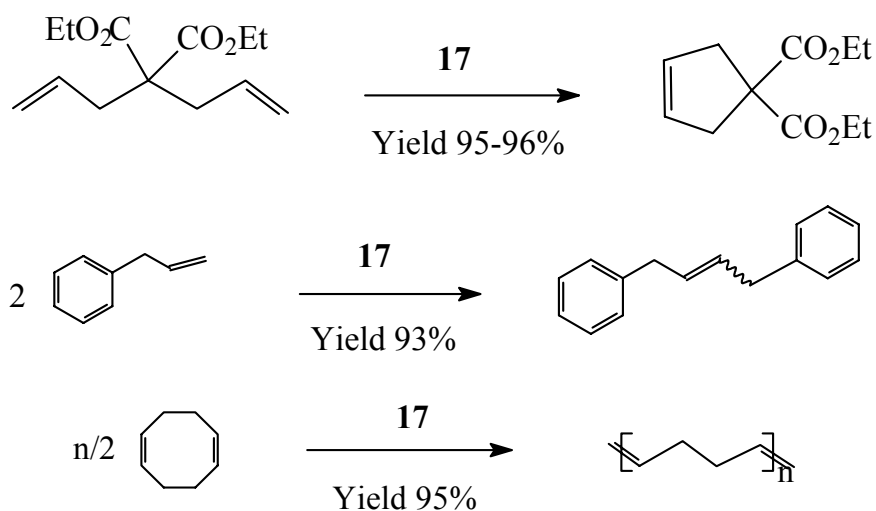
Scheme 11

It is worth noting that the solvent (hexane or tetrahydrofuran) played an important role for the generation *in situ* of the ruthenium catalyst from these starting materials.

An array of ruthenium vinylidene complexes **19**-**24**, containing Schiff-bases as chelating ligands, were prepared in our team[37-41] from the parent ruthenium vinylidene complexes

$RuCl_2(PCy_3)_2(=C=CHR')$ (R' = Ph, SiMe$_3$ or tBu) and various aromatic salicylaldimines (Scheme 12, R = H or NO$_2$ and R' = Ph, SiMe$_3$ or tBu). This class of ruthenium complexes, easily accessible from the dimer $[RuCl_2(p\text{-cymene})]_2$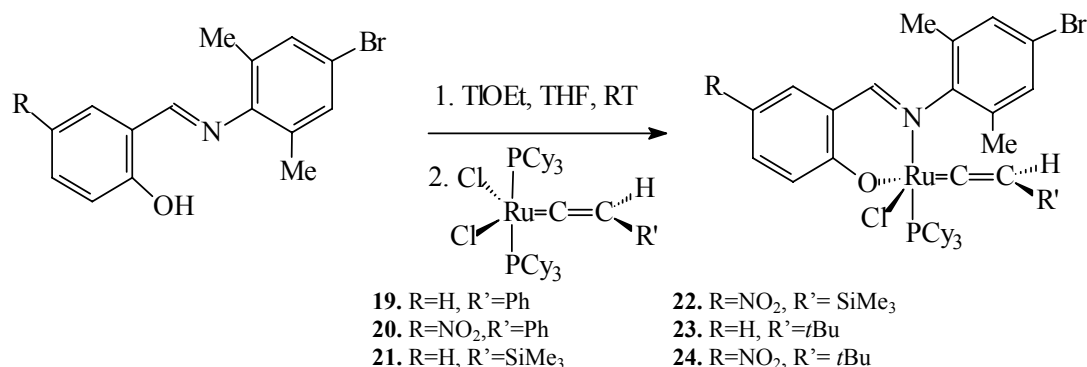, terminal akynes and salicylaldimine salts, showed good activity in olefin metathesis. They possess extremely high stability toward air, heat and moisture in comparison with parent Ru alkylidene systems and have been found to serve as excellent pre-catalysts in RCM of α,ω-dienes and ring-opening metathesis polymerization of norbornene and 5-substituted norbornene, cyclooctene and dicyclopentadiene. This result has been assigned to the "one-arm" de-coordination ability of the bidentate Schiff-base ligand in creating unsaturation in the coordination sphere of the metal. As Table 1 illustrates, synthesis of carbocyclic and heterocyclic compounds by ring-closing metathesis of ethyl diallylmalonate, 1,7-octadiene and diallyl ether, under the reaction conditions (5 mol% catalyst, 80°C, 24h reaction time), occurred quantitatively with **21-24**.

19. R=H, R'=Ph
20. R=NO$_2$, R'=Ph
21. R=H, R'=SiMe$_3$
22. R=NO$_2$, R'= SiMe$_3$
23. R=H, R'=tBu
24. R=NO$_2$, R'= tBu

Scheme 12

On using various substituted and unsubstituted α,ω-dienes as substrates in ring-closing metathesis, the activity of precatalysts **19-24** ranged in the following order **22>21>24>23>20>19** indicating that the catalyst activity is significantly determined by the nature of substituent from the Schiff-base and vinylidene fragment. It is noteworthy that the most active precatalyst **22** contains both the electron withdrawing group NO$_2$ on the Schiff-base and the labile SiMe$_3$ group on the vinylidene. As it can be observed, the most active catalyst contained the labile group SiMe$_3$ at the vinylidene fragment giving high yields or quantitative conversions in the majority of reactions examined. These results are quite satisfactory taking into account that cyclization of diethyl diallylmalonate with the analogous $RuCl_2(PiPr_3)_2(=C=CHtBu)$ reached 96% after 24h at 60°C.

Ring-opening metathesis polymerization of cycloolefins is a common reaction encountered in metathesis chemistry that provides a lot of mechanistic information and a variety of products unavailable by the standard polymerization processes. Carrying out ring-opening metathesis polymerization of a variety of cycloolefins with precatalysts **19-24**, except a few cases, both low-strained (*e.g.*, cyclooctene) and highly-strained monomers (*e.g.*, norbornene and its derivatives) displayed good to excellent reactivity leading to the corresponding high molecular weight polymers in high yields (Tables 2 and 3). Again the most active precatalysts proved to be **22** and **21** following the same order of activity as in ring-closing metathesis of α,ω-dienes. An interesting feature of cycloolefin polymerization with precatalysts **19-24** is that the molecular weights of polymers are much higher than theoretical predicted from the monomer to catalyst precursor ratios. This result evidences a low initiation rate as compared to propagation in agreement with the data of Yamaguchi and Ozawa[5] who reported very low initiator efficiencies in ring-opening metathesis polymerization of norbornene with the bisphosphane complexes. As a consequence, most amount of the catalyst can be recovered (>90%) after monomer consumption and reused in a new polymerization cycle at the same level of performance (high yield and molecular weight).

As Table 3 shows, the poorest precatalyst in polymerization of 5-substituted norbornene was **19** and the less reactive monomers norbornenes having as substituents phenyl, cyclohexyl and

hydroxymethyl. The slow initiation step can be rationalized by a mechanism involving [2+2] cycloaddition between the Ru=C bond of the vinylidene ligand and norbornene with generation of a new ruthenium carbene species able to propagate faster the polymerization process (Scheme 13). This type of process has been documented by Ozawa[42] in ROMP of norbornene with $[RuCl_2(PPh_3)_2(=C=CHFc)]$ (Fc = ferrocenyl) and by Kirchner in a stoichiometric reaction using a Tp-coordinated ruthenium complex (Tp = tris(pyrazolyl)borohydride).[43]

Another important feature, inherent to this type of precatalysts, is that they combine the advantage of fine-tuning the Schiff-base with the high stability toward bimolecular decomposition in solution even at elevated temperatures; thus, they can be kept for at least one month in toluene solution without losing their catalytic activity. Moreover, in solid phase they are stable for over three months without significant loss of the catalytic performance. Along similar lines, related ruthenium vinylidene complexes containing imidazolin-2-ylidene ligands displayed good stability even for several days at high temperatures.

Table 1

Isolated yields (%) in synthesis of carbocyclic and heterocyclic compounds
from α,ω-dienes using Schiff-base Ru vinylidene precatalysts **19-24** .[a]

α,ω-Diene substrate	Product	Time, h	**19**	**20**	**21**	**22**	**23**	**24**
		24	96	98	100	100	100	100
		24	36	43	59	69	48	53
		24	5	11	23	36	16	26
		24	98	99	100	100	100	100
		10	97	98	100	100	100	100
		24	51	60	72	83	67	80
		24	27	54	70	81	68	75

a) Reaction conditions: catalyst loading 5 mol%, temperature 80°C, solvent C_6D_6.

Table 2

Isolated yields (%) in ring-opening metathesis polymerization of cyclooctene and dicyclopentadiene
using Schiff-base Ru vinylidene precatalysts **19-24**.[a]

| Substrate	Time, h	**19**	**20**	**21**	**22**	**23**	**24**
Cyclooctene	15	10	15	93	100	80	88
Dicyclopentadiene	10	90	96	100	100	95	97

b) Reaction conditions: monomer:catalyst = 8000, temperature 80°C, solvent toluene.

Table 3

Isolated yields (%) in polymer synthesis by ring-opening metathesis polymerization of 5-substituted norbornene using Schiff-base Ru vinylidene precatalysts **19-24**.[a]

5-Substituted Norbornene (X)	Time, h	19	20	21	22	23	24
X = Hydrogen	0.5	94	98	100	100	100	100
Ethyl	4	89	100	100	100	100	100
Butyl	4	100	100	100	100	100	100
Hexyl	4	82	84	100	100	95	98
Decyl	4	83	100	100	100	100	100
Ethylidene	10	100	100	100	100	100	100
Phenyl	4	74	80	95	98	89	92
Cyclohexyl	4	73	77	87	97	79	82
Hydroxymethyl	4	10	16	59	65	34	55
Chloromethyl	4	78	89	100	100	100	100
Triethoxysilyl	4	71	79	100	100	91	99

c) Reaction conditions: monomer:catalyst = 8000, temperature 80°C, solvent toluene.
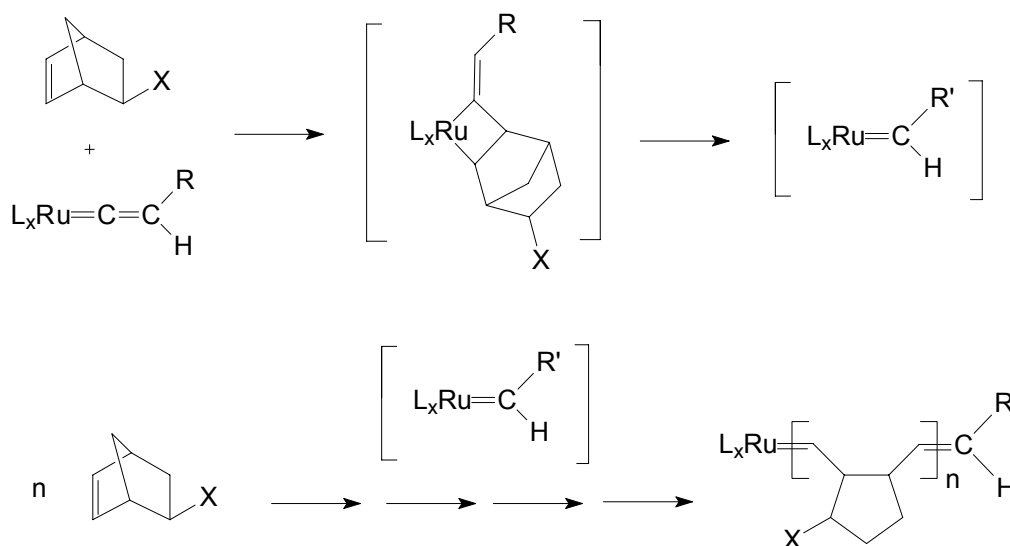
Scheme 13

CONCLUSIONS

Design and application of ruthenium vinylidene complexes in olefin metathesis reactions seems to be a convenient alternative to the classical bisphosphane ruthenium alkylidene complexes applied extensively in organic synthesis and polymer chemistry. A first advantage resides in employing commercially and easily available starting materials. Secondly, the special design of this class of coordinatively unsaturated ruthenium complexes afforded considerable metathesis activity; furthermore, this family of metathesis precatalysts exhibits good stability and robustness enabling them to be reused for several cycles without losing their initial activity. Combining vinylidene ligands with other fine-tunable ligands in the coordination sphere of ruthenium (*e.g.*, imidazolylidene, Schiff-bases, etc.) opens a new way for highly efficient ruthenium metathesis precatalysts.

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