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Synthesis of Schiff Base-Ruthenium Complexes and Their Applications in Catalytic Processes

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Abstract: The synthesis of various Schiff base mononuclear and binuclear ruthenium complexes, whose additional ligands around the metal core have been selected from an array of motifs, is described. These types of ruthenium complexes, conveniently prepared from commonly available ruthenium sources, are rather stable, display good tolerance towards diverse organic functionalities and also to air and moisture. Remarkably, they exhibit a high activity and chemoselectivity in a variety of catalytic processes such as ring-closing metathesis (RCM), Kharasch addition, alkyne dimerization, enol ester synthesis, ring-opening metathesis polymerization (ROMP) and atom-transfer radical polymerization (ATRP). This review covers both homogeneous and heterogeneous hybrid Schiff base-ruthenium complexes.

1 Introduction
2 Synthesis of Schiff Base-Ruthenium Complexes
3 Synthetic Applications of Schiff Base-Ruthenium Complexes
3.1 Ring-Closing Metathesis (RCM)
3.2 Kharasch Addition
3.3 Enol-Ester Synthesis
3.4 ROMP Reactions
3.5 ATRP Reactions
3.6 Relevant Mechanistic Aspects
4 Conclusions

Keywords: catalytic activity; ligand design; N,O ligands; ruthenium; Schiff bases

1 Introduction

During the last decade the chemistry of the ruthenium complexes has experienced an unparalleled development due to disclosure of their ever increasing potential as efficient promoters in versatile catalytic processes.[1–5] Quite recently, several families of ruthenium complexes have been designed, prepared and successfully employed in a diversity of chemical reactions such as hydrogenation, hydration, oxidation, cyclopropanation, olefin metathesis, enyne synthesis and cycloisomerization, enol-ester synthesis, Kharasch addition, atom-transfer radical polymerization (ATRP) and metathesis polymerization.[6–20] The majority of these novel ruthenium complexes display an appropriate balance between the electronic and steric environment around the metal core. To ensure such an environment, currently used inorganic or organic ligands, e.g., chloride, phosphane, N-heterocyclic carbenes and Schiff bases, have been associated with arene, alkylidene, vinylidene, allenylidene or larger cumulenylidene entities.[21–38] As a result, these ruthenium complexes possess attractive catalytic properties, and particularly an enhanced activity and selectivity, in the targeted chemical transformations.[39–43] Moreover, some of the ligands bound to ruthenium impart good stability and tolerance towards various organic functionalities, air and moisture, widening thus the area of their applications.[44–46]

Of the above ligands, Schiff bases proved to be very attractive for creating new active and selective sites in ruthenium catalytic species.[47,48] As special O,N-bidentate ligands, Schiff bases allow the fine tuning of the steric and electronic environment at the ruthenium atom through an appropriate selection of bulky and/or electron-withdrawing or -donating substituents. The two donor atoms (N and O) of the chelated Schiff base exhibit opposite features: the phenolate oxygen atom is a hard donor and will stabilize a higher oxidation state of ruthenium whereas the imine nitrogen is a softer one and, accordingly, will rather stabilize the lower oxidation state

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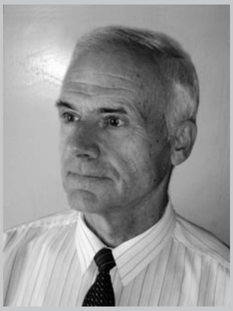

Prof. *Valerian Dragutan* is a Senior Scientist at the Institute of Organic Chemistry of the Romanian Academy. His research interests focus on structure and reactivity in organic and polymer chemistry, homogeneous catalysis by transition metals and Lewis acids, olefin metathesis and metathesis polymerization, bioactive organometallic compounds. He is coauthor of several books and book chapters in the fields of organic catalysis and polymer synthesis.

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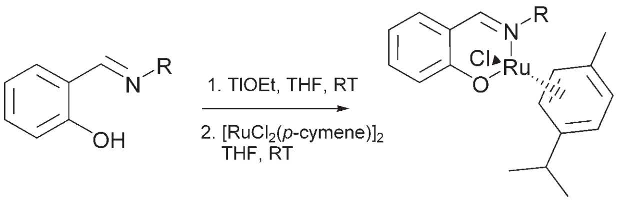
of ruthenium. In addition, Schiff bases are easily accessible through one-step procedures *via* almost quantitative condensation of common amines with aldehydes. Using this class of “dangling-ligands”, the Schiff bases, and especially those deriving from salicylaldimines, we have recently prepared and characterized a wide series of arene, alkylidene, indenylidene, vinylidene and diene ruthenium complexes. This highly reliable approach enabled us to obtain quite robust, stable and selective ruthenium catalysts that have ideally promoted numerous organic processes such as atom-transfer radical addition (ATRA or Kharasch addition), ring-closing metathesis (RCM), enol-ester synthesis, alkyne dimerization, ring-opening metathesis polymerization (ROMP), and atom-transfer radical polymerization (ATRP). The present paper focuses on the synthetic methodologies applied in manufacturing of homogeneous and immobilized Ru complexes, bearing at least one Schiff base as the key ligand, as well as on their application profile in numerous catalytic processes of wide utility in organic and polymer chemistry.

2 Synthesis of Schiff Base-Ruthenium Complexes

The Schiff base-ruthenium arene complexes **1–3** were the first to be conveniently prepared by what has emerged as a major preparative method, the two-step procedure starting from the commercially available Ru dimer [RuCl$_2$(*p*-cymene)]$_2$ and aliphatic or aromatic salicylaldimines (Scheme 1).[47,49]

An important feature of these complexes is that the labile *p*-cymene group is present along with the Schiff base, as evidenced in all spectra of the three complexes. Structures were unambiguously determined by means of infrared, Raman, ^{1}H and ^{13}C NMR spectroscopy and corroborated with data from elemental analyses. As expected, the singlets assigned to OH groups from the free Schiff-base ligands (12.96–12.85 ppm) are not found in the ^{1}H NMR spectra of complexes **1**–**3**. Striking differences in ^{1}H NMR (CDCl$_3$) and IR spectra were recorded between complexes **1** and **3**, on one hand, and **2** on the other. Thus, while in **1** and **3** the olefinic proton, N=CH, appears, as a singlet, at $\delta = 9.95$ ppm and $\delta = 9.85$ ppm, respectively, in **2** the corresponding signal is located at $\delta = 8.25$ ppm. The same is true for the IR (KBr) spectra where a newly arising vibration due to complexation (non-existent in the ligands) is at $\nu = 1920\ \mathrm{cm}^{-1}$ for both **1** and **3** but at $1933\ \mathrm{cm}^{-1}$ for **2**. Structural characteristics evidenced by the spectra are reflected in the different catalytic activity of **1** and **3**, as compared with **2**, as will be further highlighted (Section 3).

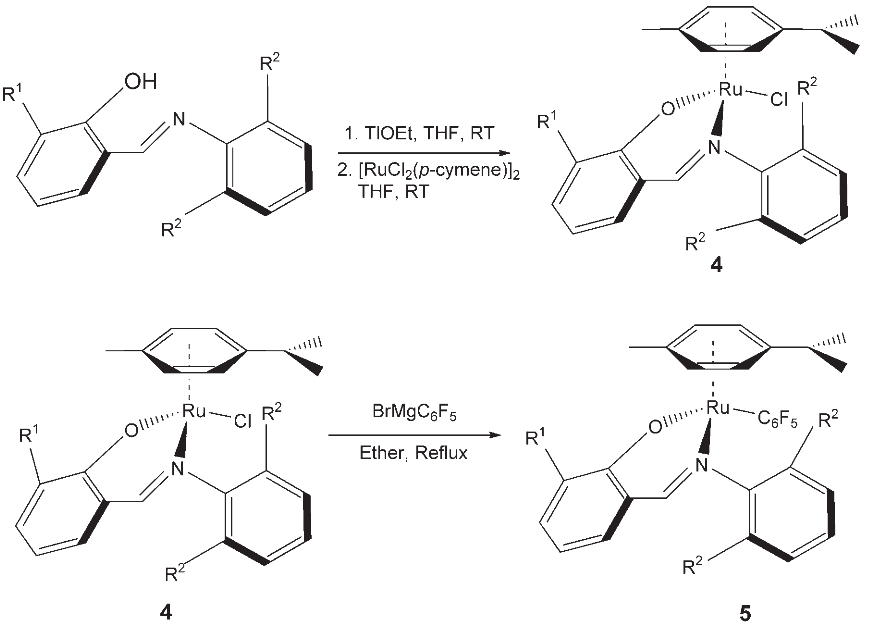


1: R = Me
2: R = *t*-Bu
3: R = 2,6-Me-4-BrC$_6$H$_2$

Scheme 1. Synthesis of Schiff base-ruthenium arene complexes **1–3**.

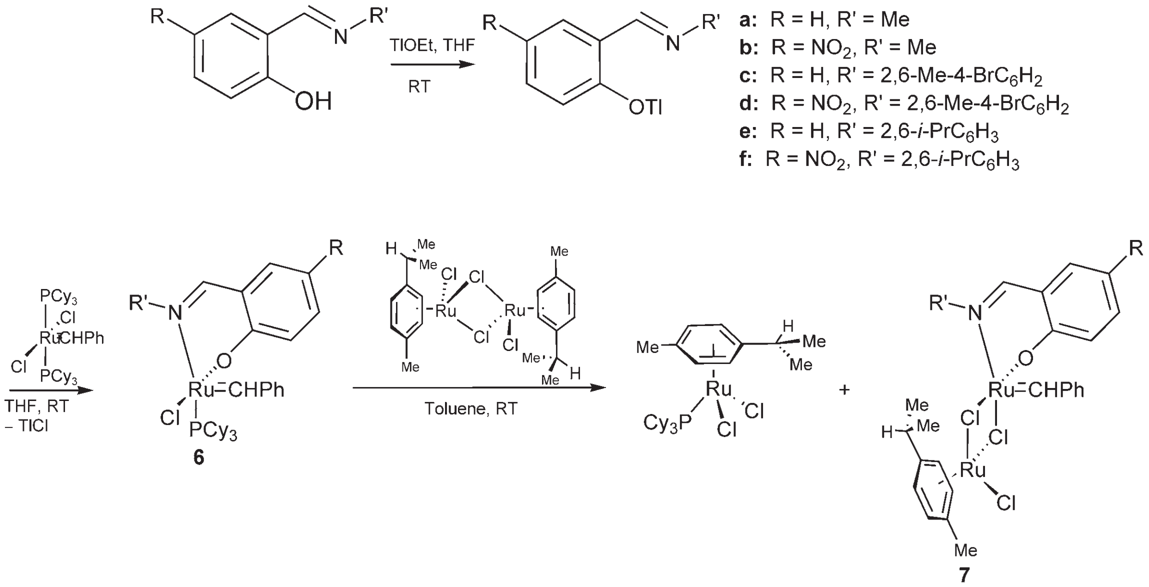
After having optimized the reaction conditions for this procedure, two new arene ruthenium complexes, **4** and **5**, have been prepared by the same pathway (Scheme 2).[29,50]

The pentafluorophenyl ligand in the complex **5** was introduced by a Grignard reaction with the appropriate reagent (C$_6$F$_5$MgBr), effected on **4**. As in the case of **1**–**3**, the IR spectra (KBr) of **4** and **5** evidenced the same vibration at $\nu = 1920\ \mathrm{cm}^{-1}$, due to complexation. The significant role of the electronic and steric structure induced by both the Schiff-base ligand and the additional ligand in the catalyst precursors **4** and **5** has been clearly evidenced in studies on ROMP and ATRP reactions, as will be further outlined.



R^1 = *t*-Bu, R^2 = *i*-Pr

Scheme 2. Synthesis of Schiff base-ruthenium arene complexes **4** and **5**.



Scheme 3. Synthesis of mononuclear and dinuclear benzylidene Ru(II) complexes, **6a**–**f** and **7a**–**f**.

On applying an extended approach a wide range of mononuclear and dinuclear ruthenium benzylidene complexes, **6a**–**f** and **7a**–**f**, have also been prepared in high yields (Table 1). Syntheses started from the thallium salts corresponding to the different salicylaldimines and the bis(phosphane)Ru(II) complex RuCl$_2$(PCy$_3$)$_2$-(CHPh), followed in the case of the dinuclear counterparts by reaction of complexes **6** with the Ru-dimer [RuCl$_2$(p-cymene)]$_2$ (Scheme 3).[29,51]

Our method takes advantage of facile substitution of the labile phosphane ligand from the mononuclear complexes yielding the bridgehead dinuclear complexes **7a**–**f** in a quite convenient way. Yields and selected spectroscopic data are given in Tables 1 and 2.

Furthermore, complexes **6a**–**f** afforded cationic ruthenium benzylidene complexes **8a**–**f** by *in situ* treatment with one equivalent of the appropriate silver or trimethylsilyl salt (Scheme 4).[1d,51]

It is worth noting that in **8** both the counterion and the solvent (toluene or water-toluene) exert a remarkable effect on the activity of these catalysts. As will be shown later on, these cationic ruthenium benzylidene complexes are the first Ru-alkylidene catalysts reported so far to perform the controlled radical suspension polymerization of methyl methacrylate, methyl acrylate and styrene in water leading to high yields of polymer.

Of special interest for our studies on metathesis and controlled radical reactions proved to be the series of Schiff-base ruthenium complexes containing N-heterocyclic carbenes (NHC) as ancillary ligands. Thus, starting from the phosphane catalysts **6a**–**f** and 1,3-dimesityl-4,5-dihydroimidazolium salts, a range of ruthenium complexes **9a**–**f**, containing as ligands both NHC and Schiff bases, have been synthesized and fully characterized (^{1}H NMR, Table 2)[52,53] (Scheme 5).

Table 1. Yields (%; isolated products) for synthesis of some representative Schiff base-ruthenium catalyst precursors.[a,b,c]

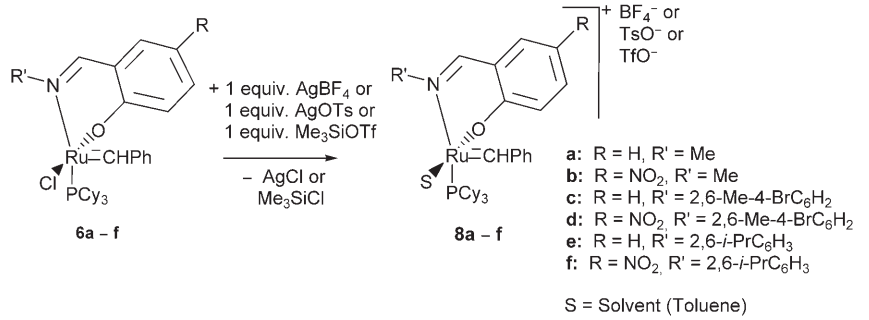
1 Catalyst precursor	**6a**	**6b**	**6c**	**6d**	**6e**	**6f**
Yield [%][a]	88	79	75	72	75[c]	82[c]
2 Catalyst precursor	**7a**	**7b**	**7c**	**7d**	**7e**	**7f**
Yield [%][a]	63	67	61	68	73	68
3 Catalyst precursor	**9a**	**9b**	**9c**	**9d**	**9e**	**9f**
Yield [%][b]	85	78	71	73	70	73

[a] Data from ref.[29]
[b] Data from ref.[53]
[c] Data from ref.[49]

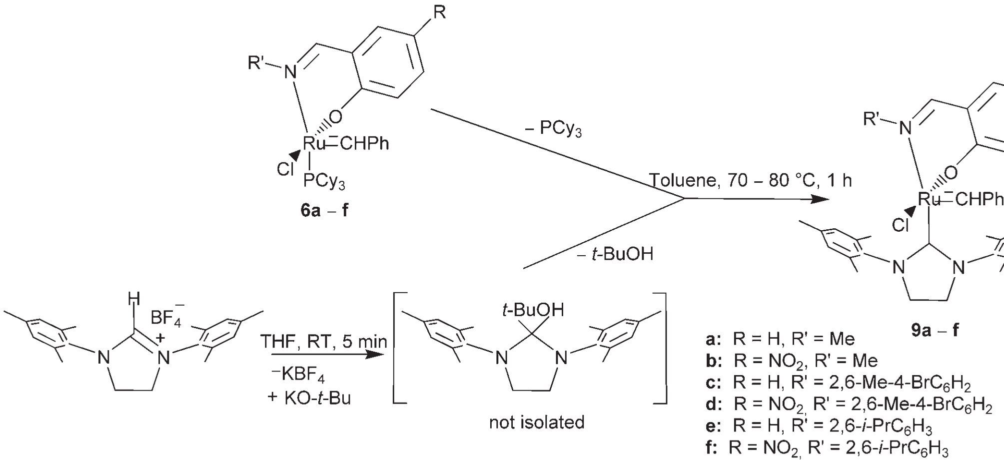
Table 2. Selected chemical shifts [^{1}H NMR, CDCl$_3$, δ (ppm)], for some representative Schiff base-ruthenium catalyst precursors.[a, b]

Entry	Proton	Catalyst precursor					
		6a	**6b**	**6c**	**6d**	**6e**[c, d]	**6f**[c, d]
1	Ru=CH(d,1H)[a]	19.95	19.99	19.45	19.49	19.68	19.77
	N=CH(d,1H)[a]	8.98	9.05	8.19	8.24	8.06	8.27
		7a	**7b**	**7c**	**7d**	**7e**	**7f**
2	Ru=CH(d,1H)[a]	19.97	20.02	19.48	19.50	19.71	19.81
	N=CH(d,1H)[a]	9.03	9.08	8.21	8.36	8.12	8.32
		9a	**9b**	**9c**	**9d**	**9e**	**9f**
3	Ru=CH(s,1H)[b]	19.91	19.96	19.42	19.51	19.61	19.66
	N=CH(d,1H)[b]	8.94	9.02	8.16	8.19	8.01	8.09

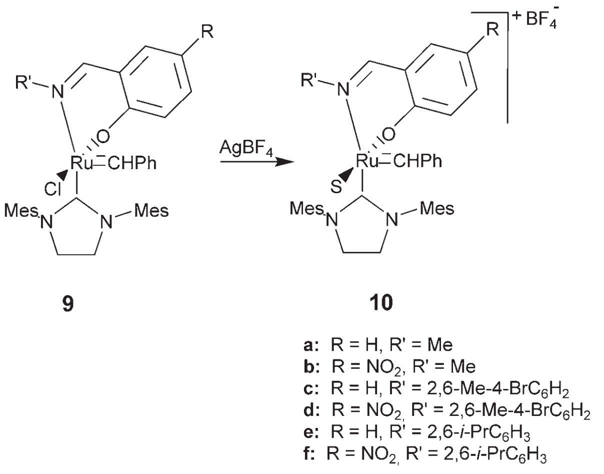
[a] Data from ref.[29]
[b] Data from ref.[53]
[c] Data from ref.[44]
[d] CD$_2$Cl$_2$



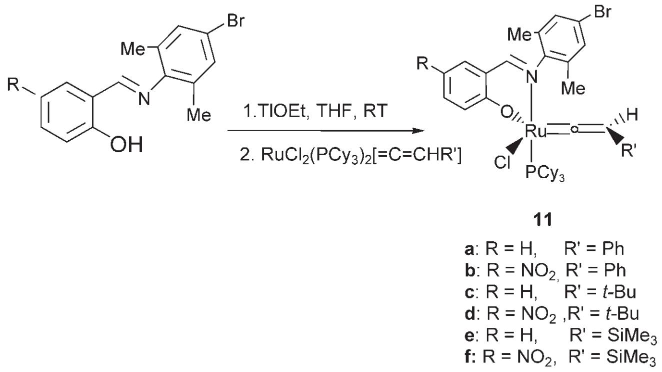
Scheme 4. Synthesis of cationic ruthenium benzylidene precatalysts **8a–f**.



Scheme 5. Synthesis of NHC- and Schiff base-containing ruthenium complexes **9a–f**.



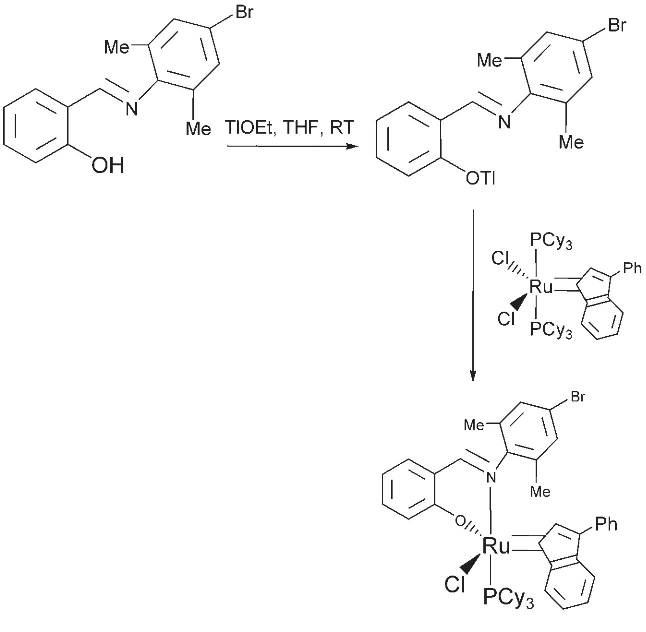
Scheme 6. Synthesis of cationic NHC ruthenium benzylidene precatalysts **10a–f**.



Scheme 7. Synthesis of Schiff base-ruthenium vinylidene complexes **11a–f**.

The *t*-BuO-protected NHC intermediate has not been isolated but instead was reacted *in situ* with the phosphane ruthenium complex to give NHC-containing ruthenium complexes in high yields (70–85%) (Table 1). Further, based on this set of neutral ruthenium complexes and $AgBF_4$, the corresponding cationic ruthenium benzylidene complexes, **10a–f**, have been obtained and their catalytic properties in ATRP of vinyl monomers investigated (Scheme 6).[53]

A new range of ruthenium vinylidene complexes **11a–f**, incorporating differently substituted Schiff bases as chelated ligands, have been made readily accessible when starting from the parent ruthenium vinylidene complex $RuCl_2(PCy_3)_2(=C=CHR')$ and an aromatic salicylaldimine (Scheme 7).[54–57]



12

Scheme 8. Synthesis of Schiff base-ruthenium indenylidene complex **12**.

This latter group of ruthenium complexes displayed high activity for enol-ester synthesis *via* nucleophilic addition of carboxylic acids to terminal alkynes (yield = 64–96%, depending on the nature of the acid and alkyne),[57] as well as in metathesis-type reactions (yield = 77–100% in ROMP of 5-substituted norbornenes).[54] Following a similar route, ruthenium indenylidene complexes, e.g., **12**, have been synthesized in good yield (79% for **12**) from the corresponding bis(phosphane)ruthenium indenylidene complex and salicylaldimine containing aromatic substituents (Scheme 8).[6,57,58]

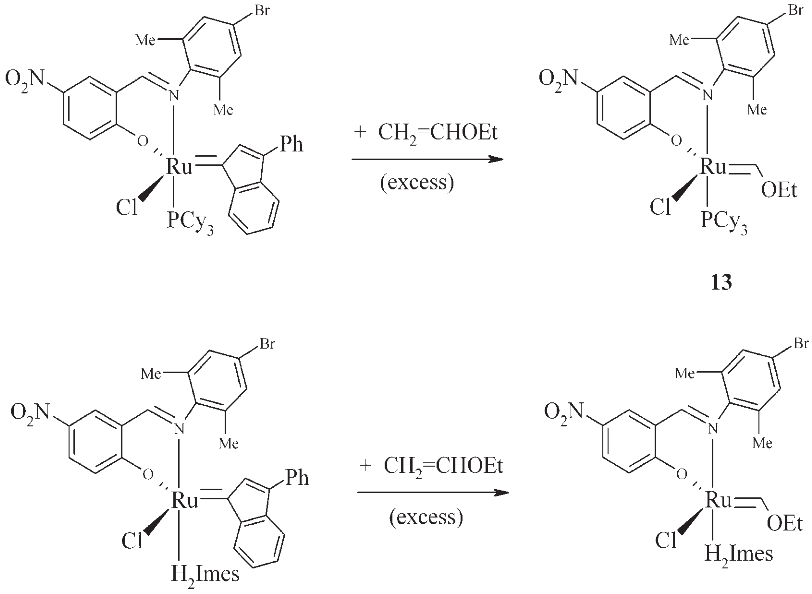
The indenylidene complex **12** is rather stable and consequently could be fully characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and elemental analysis. Like its parent bis(phosphane)ruthenium complex, the Schiff base-containing **12** exhibited a high level of activity in enol-ester synthesis (for phenylacetylene, yields are 80–98% depending on the carboxylic acid).

The new Schiff base-Ru alkylidene complexes **13** and **14**, of the Fischer-type, generated *in situ* by a metathesis route from the corresponding indenylidene counterparts and vinyl ether derivatives, intriguingly showed excellent activity in the ATRP reaction of methyl methacrylate (MMA)(conversion of 74% and 99% with **13** and **14**, respectively)[6] (Scheme 9).

This unexpected result provided an interesting insight into the electronic structure of this kind of ruthenium alkylidene complex and intermediates generated therefrom during the course of the above polymerization process employing **13** or **14**.

An alternative approach based on our synthetic methodology for Schiff base-ruthenium complexes afforded *de novo* dinuclear complexes **15** and **16** with coordinating cyclodiene ligands such as norbornadiene (NBD) and cyclooctadiene (COD)[1d] (Scheme 10).

Syntheses have been readily carried out by reaction of the usual salicylaldimine Tl salt with the corresponding Ru diene precursors, $[RuCl_2(NBD)]_n$ or $[RuCl_2(COD)]_m$, in dichloromethane at room temperature



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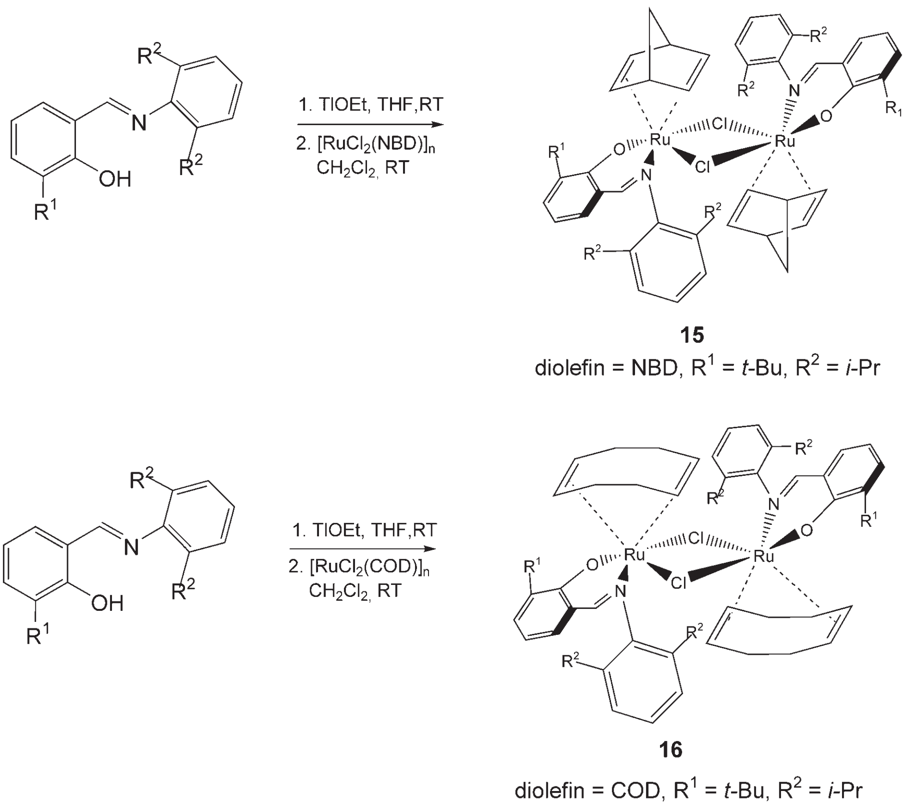
14

Scheme 9. Synthesis of the Fischer-type ruthenium alkylidene complexes **13** and **14**.



Scheme 10. Synthesis of dinuclear ruthenium cyclodiene complexes **15** and **16**.

(yield: 63%). As a result of restrained geometry of the coordinated cyclodienes in **15** and **16**, four distinct signals appear in their ^{13}C NMR spectra at $\delta = 145.88$, 140.15, 139.84, 135.14 ppm and $\delta = 84.9$, 84.5, 79.6, 78.1 ppm, respectively.[1d]

In our endeavor to design new structures of robust and effective ruthenium catalysts we also attempted to devise a system in which the homogeneous catalyst can be attached to a solid carrier by means of a non-labile tether imposing little or no steric influence at the reactive ruthenium center. Chemical tethering of organometallic compounds is recognized as one of the best strategies for anchoring a homogeneous catalyst to a solid support and it fortunately succeeded in our case too. Our studies have been mainly directed towards the synthesis and development of supported Schiff base-ruthenium catalysts for advantageous applications in RCM, ROMP, Kharasch addition, ATRP and vinylation reactions. With the aim of enhancing the present status of the commercial potential of these chemical processes through providing recyclable and efficient solid catalysts, we prepared two multifunctional Schiff base-ruthenium carbene complexes deposited on MCM-41, **17** and **18**. The method we followed was to tether the organometallic compounds onto mesoporous silica surfaces by treating the inorganic support with the tris(alkoxy)-silyl functionalized ruthenium complex. The synthetic pathways for the two supported ruthenium complexes are given in Scheme 11.[59–64]

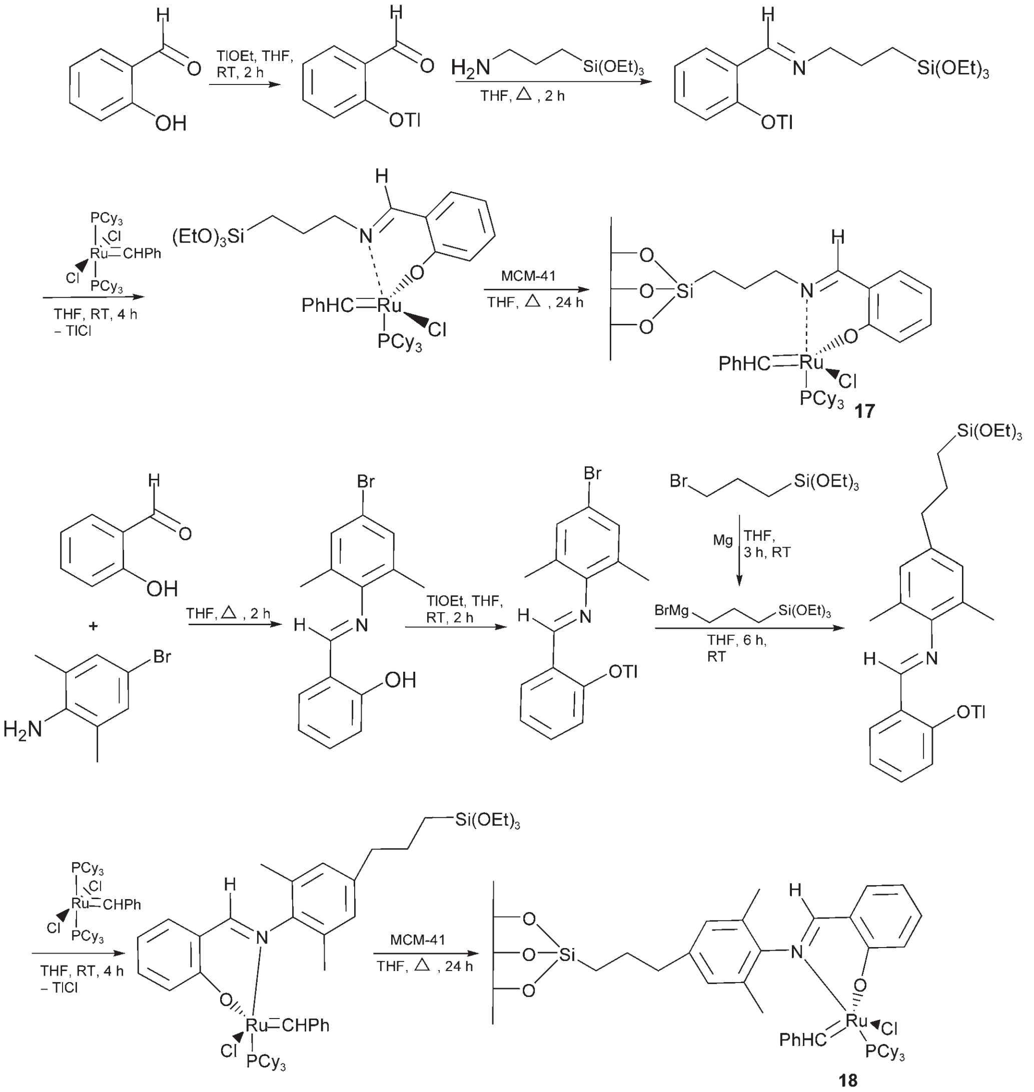
Examination by Raman spectroscopy, X-ray diffraction, X-ray fluorescence, solid state NMR spectroscopy and N_2 adsorption analysis demonstrated that in both cases the anchoring of the homogeneous catalyst onto MCM-41 occurred *via* a spacer involving several covalent bonds.

A similar procedure has been applied to synthesize and characterize another heterogeneous ruthenium catalyst, **19**, that exhibited excellent stability, reusability and low leaching properties (Scheme 12).[59,64]

3 Synthetic Applications of Schiff Base-Ruthenium Complexes

Extensive exploration of the activity and chemoselectivity of the Schiff base-ruthenium complexes introduced by our group showed that they effectively initiate ring-closing metathesis (RCM) of linear dienes or heterodienes affording various cyclic compounds, promote addition of halogenated alkanes to olefins (Kharasch addition) yielding polyhalogenated alkanes and induce reactions of carboxylic acids with alkynes to form enol-esters by Markovnikov or *anti*-Markovnikov (*E* and *Z*) pathways (Scheme 13).[47,50,53,55,56,58,64–67]

Further investigations of these ruthenium complexes revealed that they are also active in ring-opening metathesis polymerization (ROMP) of cycloolefins and atom-transfer radical polymerization (ATRP) of vinyl



Scheme 11. Synthesis of immobilized ruthenium catalysts **17** and **18**.

monomers (e.g., methyl methacrylate and styrene), under usual reaction conditions (Scheme 14).[29,49,51–53]

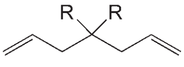
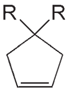
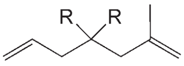
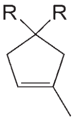
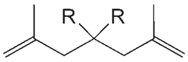
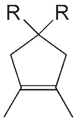
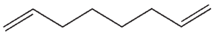
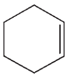
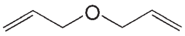
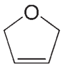
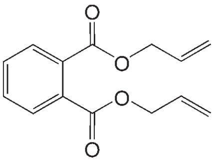
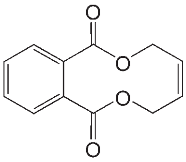
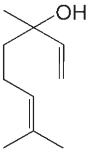
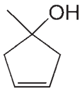
Allegedly, in ATRP with arene Ru complexes the role of the Schiff base ligand is to release the arene moiety creating the crucial coordinatively unsaturated Ru species capable of controlling the dynamic equilibrium between the propagating radicals and the dormant species.

3.1 Ring-Closing Metathesis (RCM)

The activity of ruthenium complexes **1**–**3** and **9a**–**f** in ring-closing metathesis reactions of a range of dienes is illustrated in Table 3.[47,67] Activity of these complexes is sufficiently high (at 70 °C) to allow the preparation of tri- and tetrasubstituted alkenes from the corresponding dienes in moderate to good yields. As can be seen from the selected data, diethyl diallylmalonate, 1,7-octadiene and diallyl ether were converted quantitatively to ring-closed products by all catalyst precursors employed. High conversions have been obtained with **3**, **9a** and **9b** for the majority of dienic substrates. By using more severe reaction conditions (higher temperatures and longer reaction times), the conversion increased dramatically even for the more sluggish substrates. Furthermore, with these precatalysts diallyl phthalate and linalool were converted smoothly. For these two substrates conversions in the range of 81–94% and 70–76% have been reached, respectively, using the best catalytic systems from this set (**3** and **9a** or **9b**) (Table 3).

Similar results were recorded in ring-closing metathesis reactions of the above dienes using monometallic and bimetallic catalytic systems **6a**–**f** and **7a**–**f** (Table 3) [29]. In all cases, diethyl diallylmalonate, 1,7-octadiene and diallyl ether were quantitatively converted to ring-closing products. Tri- and tetrasubstituted alkenes were also obtained from the corresponding dienes in variable yields, the bimetallic precatalysts being defi-

Table 3. Yields [%] in ring-closing metathesis of representative diolefinic substrates using ruthenium complexes **1**–**3** and **9a**–**f** as catalyst precursors.[a, b]

Substrate[c]	Product[c]	**1**	**2**	**3**	**9a**	**9b**	**9c**	**9d**	**9e**	**9f**
		100	100	100	100	100	100	100	100	100
		46	53	71	72	73	47	42	31	23
		8	15	23	41	33	19	11	<5	<5
		100	100	100	100	100	100	100	100	100
		100	100	100	100	100	100	100	100	
		62	78	94	87	81	68	66	54	53
		33	65	76	73	70	60	51	42	37

[a] Data from refs.[47,67]

[b] Yields determined by ^1H NMR analysis and confirmed by GC.

[c] R = COOEt.

Reaction conditions: 70 °C and 1 h (entries 1,4 and 5) or 85 °C and 17 h (entries 2, 3, 6 and 7) for **1**–**3** in toluene; 55 °C and 4 h for **9a**–**f** in C_6D_6.

nitely more active than the monometallic ones. Moreover, high yields were reached in ring-closing metathesis of diallyl phthalate and linalool (96% and 87%, respectively) with the best precatalyst of this set **7e** (Table 4).

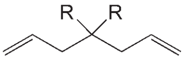
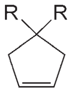
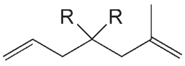
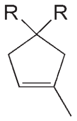
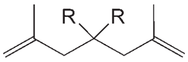
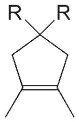
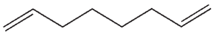
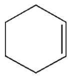
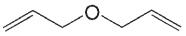
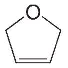
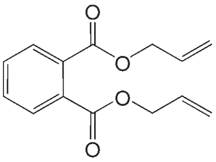
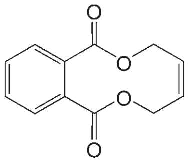
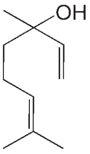
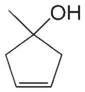
A sharp difference between the monometallic **6a**–**f** and bimetallic **7a**–**f** catalytic systems should be pointed out, i.e., whereas the bimetallic catalytic systems gave very good conversions at a temperature of 55 °C, the monometallic systems could be exploited at their full potential only above 70 °C.

3.2 Kharasch Addition

Kharasch addition reaction [named also atom-transfer radical addition (ATRA)] of carbon tetrachloride to a number of olefinic substrates was performed by us using several Schiff base-ruthenium precatalysts.[47,50,66] Results obtained with a first group of ruthenium complexes indicated that the outcome of the reaction very much depends on both the olefin and the catalytic system employed (Table 5).

Data in Table 5 indicate that methyl methacrylate and styrene underwent clean addition of carbon tetrachloride, at 65 °C in the presence of the catalytic systems **3**, **7c** and **7e**, the former substrate yielding 73, 86 and 79% chlorinated product, respectively, while the latter gave 88, 78 and 84%, respectively. At 85 °C, styrene was nearly quantitatively converted into the addition product. On performing the reaction with methyl acrylate, butyl acrylate and acrylonitrile, a striking differentiation between the catalytic systems was observed. Complexes **7c** and **7e** catalyzed the addition with moderate (49 and 41%, respectively, for acrylonitrile) to high yields (93 and 84%, respectively, for butyl acrylate) whereas the other complexes afforded addition products with yields as low as 10–20%. Detailed examination of data given in Table 5 shows that styrene and, in

Table 4. Yields [%] in ring-closing metathesis of representative diolefinic substrates using ruthenium complexes **6a**–**f** or **7a**–**f** as catalyst precursors.[a, b]

Substrate[c]	Product[c]	**6a/7a**	**6b/7b**	**6c/7c**	**6d/7d**	**6e/7e**	**6f/7f**
		100/100	100/100	100/100	100/100	100/100	100/100
		<5/13	<5/<5	<5/58	9/44	18/83	21/72
		<5/6	<5/<5	<5/41	6/29	11/62	17/49
		100/100	100/100	100/100	100/100	100/100	100/100
		100/100	100/100	100/100	100/100	100/100	100/100
		40/40	44/31	47/71	59/67	68/96	76/89
		12/32	13/25	18/69	25/66	41/87	56/74

[a] Data from ref.[29]

[b] Yields determined by ^{1}H NMR analysis and confirmed by GC.

[c] R = COOEt.

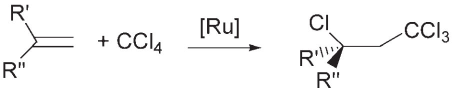
Reaction condition: 55 °C and 4 h for **6a**–**f** in C_6D_5Cl and 70 °C and 4 h for **7a**–**f** in C_6D_5Cl.

several cases, methyl methacrylate are more smoothly converted into chlorinated products than acrylates.

Similar results were recorded in Kharasch additions of carbon tetrachloride to the above olefinic substrates by using NHC-containing Schiff base-ruthenium precatalysts **9a**–**f**[53] (Table 6).

Two aspects should be discussed here in connection with the Schiff base ligand. Firstly, the steric influence that it plays on activity in the Karasch reaction is more significant in the case of the NHC-containing catalytic systems **9a**–**f** than in that of the related systems included in Table 5. Thus, catalytic performance of **9a** and **b** is much lower, as compared to **9c**–**f** which contain larger Schiff base ligands. However, too bulky ligands led to a decrease of the catalytic activity; for instance, the isopropyl-containing Schiff base ligand in **9e** systematically induced inferior yields than the methyl-substituted Schiff base ligand in **9c**. Secondly, electronic properties of Schiff base ligands exert a strong influence on the cat-

Table 5. Yields [%] in Kharasch additions of carbon tetrachloride to olefinic substrates using ruthenium complexes **1**–**3**, **6a**, **c**, **e** and **7a**, **c**, **e** as catalyst precursors.[a, b]

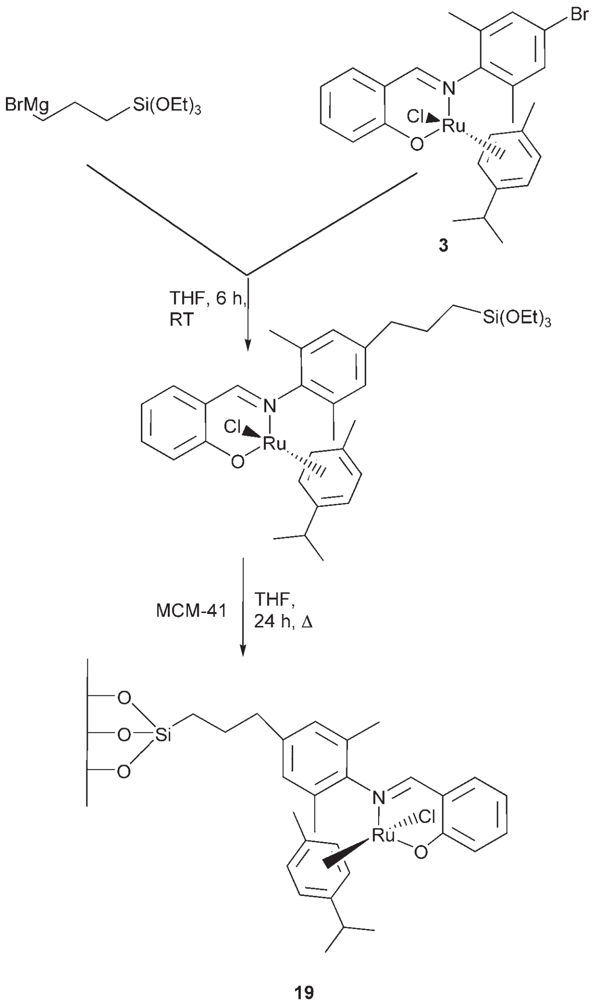


Catalyst precursor[c]									
Substrate	**1**	**2**	**3**	**6a**	**6c**	**6e**	**7a**	**7c**	**7e**
Methyl methacrylate	62	66	73	7	18	11	26	86	79
Isobutyl methacrylate	24	26	34	5	12	6	19	95	86
Methyl acrylate	18	22	26	6	15	7	17	61	54
Butyl acrylate	9	12	12	<5	11	8	12	93	84
Styrene	72	72	88	58	82	68	22	78	72
Acrylonitrile	<5	<5	<5	<5	8	<5	7	49	41
Diethyl allylmalonate	38	42	56	66	78	71	–	–	–

[a] Data from refs.[47,50,66]

[b] Yields based on GLC using dodecane as internal standard.

[c] Reaction conditions: 65 °C and 17 h for **1**–**3** or **6a**, **c**, **f**, and 85 °C and 8 h for **7a**, **c**, **f**.



Scheme 12. Synthesis of supported arene ruthenium complex **19**.

Table 6. Kharasch additions of carbon tetrachloride to olefinic substrates using ruthenium complexes **9a–f** as catalyst precursors[a] (Yields, %).[b]

Substrate	**9a**[c]	**9b**[c]	**9c**[c]	**9d**[c]	**9e**[c]	**9f**[c]	**9d**[c]	**9d**[c]
Methyl methacrylate	22	36	74	85	54	61	96	66
Isobutyl methacrylate	19	27	69	78	78	53	93	62
Methyl acrylate	16	33	64	70	41	44	89	60
Butyl acrylate	11	29	60	67	37	43	75	42
Styrene	20	34	69	73	43	48	84	55
Acrylonitrile	<5	8	38	46	17	21	63	24
Diethyl allylmalonate	35	43	83	91	61	72	98	70

[a] Data from ref.[53]

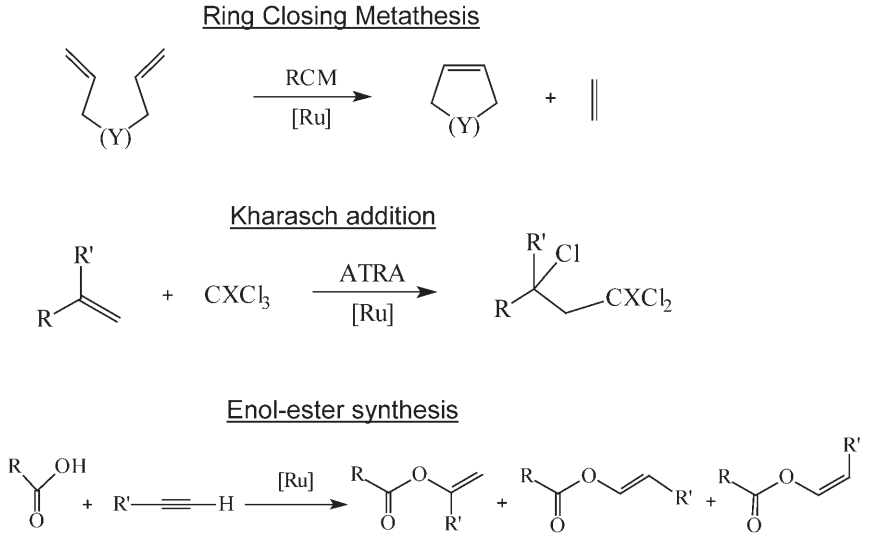
[b] Yields based on GLC with dodecane as internal standard.

[c] Reaction conditions: precatalyst (0.03 mmol) in toluene (1 mL); olefin (9 mmol), CCl_4 (13 mmol) dodecane (0.25 mL) in toluene (3 mL); temperature 65 °C; time 8 h.

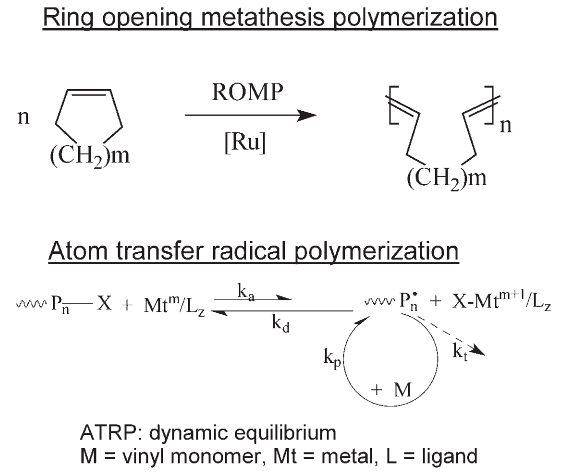
[d] As in footnote[c] but the reaction mixture was heated at 85 °C for 8 h.

[e] As in footnote[c] but the amount of added precatalyst was 0.006 mmol.

alyst activity. This trend is best illustrated by comparing yields obtained with the following precatalyst pairs: **9a** with **9b**, **9c** with **9d**, and **9e** with **9f**; it can be seen that complexes containing the electron-withdrawing nitro group displayed higher catalytic activity. Obviously, complex **9d**, exhibiting the highest catalytic performance with all olefinic substrates, enjoys an optimum interplay of the steric and electronic effects.



Scheme 13. Ring-closing metathesis (RCM), Kharasch addition and enol-ester synthesis in the presence of ruthenium precatalysts.


Ring opening metathesis polymerization

Atom transfer radical polymerization

ATRP: dynamic equilibrium
M = vinyl monomer, Mt = metal, L = ligand

Scheme 14. ROMP and ATRP reactions in the presence of ruthenium precatalysts.

3.3 Enol-Ester Synthesis

The reaction of carboxylic acids, e.g., formic and acetic acid, with acetylenes to form enol-esters is readily catalyzed by a broad array of Schiff base-ruthenium complexes pertaining to this class.[47,53,66] With octadiyne as a substrate, the reaction of both formic and acetic acids, induced by Ru complexes **1**, **2**, **3** and **9a–f**, resulted in selective formation of (*E*)-alk-1-enyl esters, corresponding to regio- and stereoselective *anti*-Markovnikov addition of the carboxylic acid to the triple bond. Besides the (*E*)-alk-1-enyl ester, small amounts of Markovnikov product, (*Z*)-alk-1-enyl ester and disubstituted enol ester were also formed (Table 7). The percentage of (*E*)-alk-1-enyl ester was more or less the same, varying in the range of 71–83% for all catalytic systems and both acids. The total yield, however, depended on the type of catalyst precursor and carboxylic acid. Complexes **3** and **9e** and **f** were the most active yielding addition products in the range of 71–73%, with formic acid, and in the range of 76–77%, with acetic acid. It is worth mentioning that the above Schiff base-ruthenium complexes are, to our best knowledge, among the most active ruthenium catalytic systems reported so far for selective synthesis of (*E*)-alk-1-enyl esters starting from alkadiynes and saturated carboxylic acids.

When phenylacetylene is used as the starting material in conjunction with carboxylic acids and in the presence of Schiff base-ruthenium complexes, alkyne dimerization (pathway b) becomes an important competitive reaction to enol-ester synthesis (pathway a)[47,53,66] (Scheme 15).

As shown in Table 8, in the presence of the very active Ru complexes **2** and **9a–f** dimerization of phenylacetylene is the major reaction pathway, leading predominantly to (*E*)-enyne with selectivities in the range of 73–81%. In some cases yields in excess of 90% could be attained.

By contrast, catalyst precursors **1** and **3** exhibited a totally different behavior; the outcome of the reaction between phenylacetylene and carboxylic acids depended essentially on the carboxylic acid employed. With formic acid, both precatalysts formed selectively the (*E*)-alk-1-enyl ester (64 and 79%, respectively) whereas with acetic acid these two complexes led selectively to (*E*)-enyne (71 and 78%, respectively). In the latter case, precatalyst **3** allowed even high yields (up to 96%) in (*E*)-enyne to be reached.

3.4 ROMP Reactions

Schiff base-ruthenium complexes of this class display a broad range of activity and selectivity in ring-opening metathesis polymerization of low- and high-strained cycloolefins. The yields [%] and polymer characteristics, such as number average molecular weight (M_n) and polydispersity index (PDI), recorded in ROMP of several representative monomers, induced by precatalysts **6a–f** and **7a–f**, are compiled in Table 9.[29]

Analysis of data from Table 9 shows that both catalytic systems **6a–f** and **7a–f** succeed rather well in performing ROMP reactions with the monomers selected, although substantial differences in their behavior have been noticed. Thus, for the monometallic catalytic system **6** sequence of conversions was **6b** > **6a** > **6d** > **6c** > **6f** > **6e**, whereas for the bimetallic initiator **7** it was reversed to **7e** > **7f** > **7c** > **7d** > **7a** > **7b**. These striking results indicated that for both the monometallic and bimetallic systems the bulkiness of the Schiff base and the electron-withdrawing properties of its substituents have a strong effect on their ROMP activity. For instance, 5-phenylnorbornene was converted in 98%, 80% and 69% yield with **6a**, **6c** and **6e**, respectively, and in 19%, 61% and 100% yield with **7a**, **7c** and **7e**, respectively. The above results impose the conclusion that introduction of more bulky groups in the Schiff base is beneficial for the systems **6** but detrimental for the systems **7**. The influence of the electronic environment in the Schiff base is highlighted by comparing the catalytic performance of the system **6a** with **6b**, **6c** with **6d**, **6e** with **6f**, as well as **7a** with **7b**, **7c** with **7d** and **7e** with **7f**. Also significantly, in the monometallic series the complex bearing the electron-withdrawing nitro substituent (**6b**, **6d** and **6f**) reached substantially higher conversions whereas for the parent bimetallic complexes **7** the opposite trend was observed.

ROMP of 5-substituted norbornenes initiated by NHC-Schiff base-ruthenium complexes **9a–f** also led to interesting results.[67] As above, for the same monomer range, bulkiness of the Schiff base and electron-withdrawing propensity of its substituents considerably affect the catalyst activity of ruthenium complexes **9a–f** (Table 10).

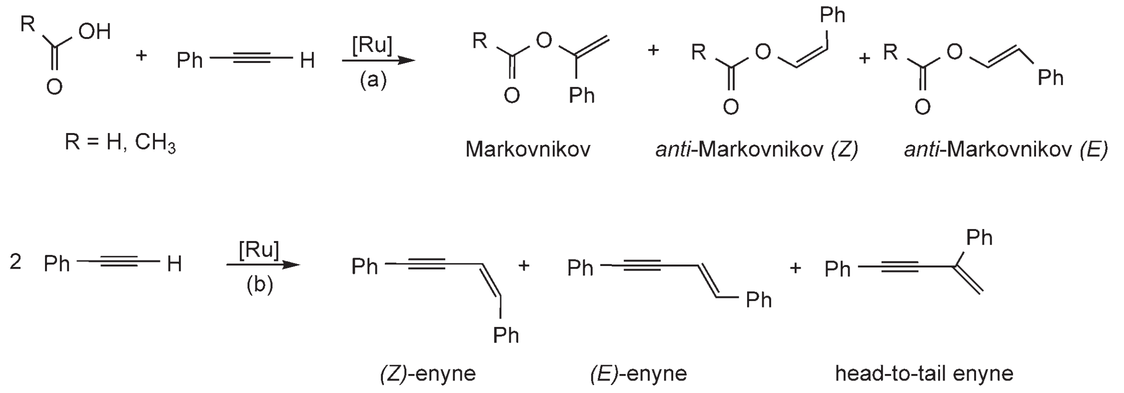
As for bimetallic complexes **7**, introduction of more bulky groups or more electron-withdrawing substituents

Table 7. Synthesis of enol-esters from 1,7-octadiyne and carboxylic acids using Schiff base-ruthenium complexes as catalyst precursors.[a, b]

Entry	Catalyst Precursor	Carboxylic Acid	Yield [%]	Markovnikov [%]	*anti*-Markovnikov, *Z*/*E* [%]	Disubstituted Enol-Ester [%]
1	**1**	Formic acid	19	12	10/72	6
		Acetic acid	49	14	6/75	5
2	**2**	Formic acid	25	12	9/71	8
		Acetic acid	64	14	9/73	4
3	**3**	Formic acid	71	11	6/76	7
		Acetic acid	76	13	5/79	3
4	**6a**	Formic acid	40	14	11/67	8
		Acetic acid	45	15	8/72	5
5	**6b**	Formic acid	31	13	12/69	6
		Acetic acid	36	11	10/70	9
6	**6c**	Formic acid	12	16	9/71	4
		Acetic acid	40	13	7/75	5
7	**6d**	Formic acid	<5	11	9/73	7
		Acetic acid	21	–	–	–
8	**9a**	Formic acid	49	9	7/81	3
		Acetic acid	56	10	6/78	6
9	**9b**	Formic acid	37	8	8/80	4
		Acetic acid	43	11	4/83	2
10	**9c**	Formic acid	67	9	4/74	3
		Acetic acid	70	13	5/76	6
11	**9d**	Formic acid	61	11	3/79	7
		Acetic acid	66	12	6/78	4
12	**9e**	Formic acid	73	8	7/79	6
		Acetic acid	77	9	5/83	3
13	**9f**	Formic acid	64	11	7/77	5
		Acetic acid	72	10	8/82	–

[a] Data from refs.[47,53,66]

[b] Reactions were carried out by using 4.4 mmol of carboxylic acid, 4.4 mmol of alkyne and 0.04 mmol of catalyst precursor, in 3 mL toluene, at 100 °C, for 4 h under an inert atmosphere.



Scheme 15. Competitive enol-ester formation and phenylacetylene dimerization with Schiff base-ruthenium complexes.

in the Schiff base moiety of complexes **9a–f** diminishes the catalyst performance; in this latter case, bulkiness of the Schiff base has, however, a greater impact on catalytic activity than the electronic influence of substituents in the Schiff base.

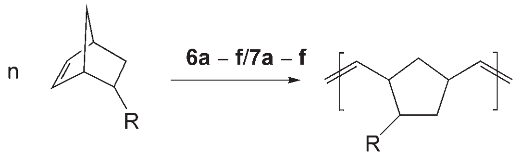
Table 8. Reaction products from phenylacetylene and carboxylic acids using Schiff base-ruthenium complexes as catalyst precursors.[a, b]

Entry	Catalyst Precursor	Carboxylic Acid	Yield [%]	Markovnikov [%]	*anti*-Markovnikov, *Z*/*E* [%]	Enyne *Z*/*E* [%]	Head-to-tail Enyne [%]
1	**1**	Formic acid	16	19	17/64	–/4	–
		Acetic acid	44	5	3/10	9/71	2
2	**2**	Formic acid	78	7	2/9	6/76	–
		Acetic acid	80	7	2/7	8/74	4
3	**3**	Formic acid	74	12	–/79	4/5	–
		Acetic acid	96	3	2/9	5/78	3
4	**6a**	Formic acid	87	9	5/34	4/48	–
		Acetic acid	98	14	8/29	5/42	2
5	**6b**	Formic acid	81	11	4/39	2/44	–
		Acetic acid	88	10	7/36	5/38	4
6	**6c**	Formic acid	76	15	6/11	4/42	2
		Acetic acid	95	18	9/27	6/37	3
7	**6d**	Formic acid	67	12	8/30	7/41	2
		Acetic acid	75	16	11/29	8/36	–
8	**9a**	Formic acid	69	6	3/12	4/73	2
		Acetic acid	74	10	–/5	6/76	3
9	**9b**	Formic acid	61	7	–/11	4/73	5
		Acetic acid	68	4	2/8	3/80	3
10	**9c**	Formic acid	79	9	3/7	5/76	–
		Acetic acid	83	7	–/9	6/78	–
11	**9d**	Formic acid	71	9	–/7	11/73	–
		Acetic acid	78	8	–/10	3/79	–
12	**9e**	Formic acid	93	5	–/11	3/81	–
		Acetic acid	99	3	–/14	5/78	–
13	**9f**	Formic acid	86	8	2/9	2/79	–
		Acetic acid	92	7	4/10	5/74	–

[a] Data from refs.[47,53,66]

[b] Reactions were carried out with 4.4 mmol of carboxylic acid, 4.4 mmol of alkyne and 0.04 mmol of catalyst precursor, in 3 mL toluene, at 100 °C, for 4 h under inert atmosphere.

Table 9. ROMP of 5-substituted norbornenes using Schiff-base ruthenium complexes **6a**–**f** and **7a**–**f** as catalyst precursors.[a]



Substituent (R)	Catalyst precursor – Yield [%]							
	6a/7a	**6b/7b**	**6c/7c**	**6d/7d**	**6e/7e**	**6f/7f**	$[M_n \times 10^3]$[b]	PDI[b]
H	100/59	100/48	100/87	100/78	100/100	100/96	84/95	1.51/1.37
Ethyl	100/41	100/33	100/79	100/66	100/100	100/91	111/138	1.63/1.35
Butyl	100/34	100/24	95/70	98/61	91/100	93/84	138/83	1.55/1.31
Hexyl	100/18	100/11	92/55	97/49	89/100	92/73	176/207	1.62/1.37
Phenyl	98/19	100/15	80/61	88/50	69/100	77/86	170/206	1.68/1.36
Ethylnorbornane	100/41	100/36	95/76	96/67	79/100	88/83	186/225	1.66/1.39
Cyano	31/9	38/< 5	11/27	17/19	< 5/66	8/43	66/123	1.52/1.27
Hydroxymethyl	38/15	43/< 5	19/39	23/28	12/74	17/51	74/153	1.57/1.33
Chloromethyl	100/51	100/36	98/85	100/67	81/100	87/97	136/158	1.71/1.40

[a] Data from ref.[29]

[b] Polymer characteristics for catalyst precursors **6b**/**7e**.

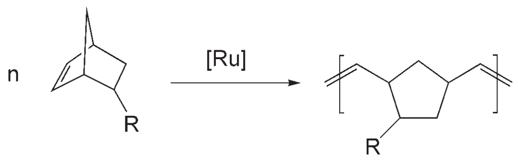
Table 10. ROMP of 5-substituted norbornenes using Schiff-base ruthenium complexes **9a–f** as catalyst precursors.[a]

Substituent (R)	Catalyst precursor – Yield [%]							
	9a	**9b**	**9c**	**9d**	**9e**	**9f**	$[M_n \times 10^3]$[b]	PDI[b]
H	100	100	100	100	100	100	202	1.31
Ethyl	100	100	100	100	100	100	272	1.35
Butyl	100	100	96	92	87	82	342	1.38
Hexyl	100	100	93	84	88	74	420	1.30
Phenyl	100	100	82	76	62	57	410	1.43
Ethylnorbornane	100	100	98	93	85	78	448	1.33
Cyano	68	58	46	43	29	22	232	1.29
Hydroxymethyl	76	69	53	51	42	37	290	1.35
Chloromethyl	100	100	100	100	93	84	328	1.38

[a] Data from ref.[67]

[b] Polymer characteristics for the catalyst precursor **9a**.

Table 11. ROMP of 5-substituted norbornenes using Schiff base-ruthenium complexes **17** and **18** as catalyst precursors.[a]



Entry	Substituent (R)	Yield [%]/M_n ($\times 10^3$)/PDI			
		Catalyst precursor/Solvent			
		17/$C_6H_5CH_3$	**18**/$C_6H_5CH_3$	**17**/CH_2Cl_2	**18**/CH_2Cl_2
1	H	78/222/1.73	65/227/2.11	86/208/1.39	76/191/1.74
2	Ethyl	100/119/1.63	100/132/2.14	100/107/1.43	100/116/1.70
3	Butyl	100/154/1.69	100/179/2.03	100/143/1.36	100/150/1.63
4	Hexyl	83/154/1.64	76/157/1.96	89/155/1.40	79/139/1.69
5	Decyl	81/214/1.70	71/218/1.99	84/183/1.38	72/163/1.65
6	Ethylidene	34/55/1.67	28/56/2.13	45/61/1.46	32/43/1.76
7	Phenyl	70/138/1.83	61/151/2.08	77/136/1.42	64/121/1.78
8	Cyclohexenyl	100/196/1.81	87/209/2.17	100/176/1.47	94/175/1.63
9	Ethylnorbornane	82/149/1.75	73/162/2.01	93/156/1.42	79/143/1.68
10	Cyano	17/77/1.98	5/Ins/Ins	68/94/1.52	53/84/1.77
11	Hydroxymethyl	21/Ins/Ins	8/Ins/Ins	74/102/1.56	66/102/1.79
12	Chloromethyl	79/106/1.59	74/132/1.93	98/116/1.29	91/117/1.53
13	Triethoxysilyl	100/270/1.67	86/299/1.98	100/230/1.37	90/222/1.62

[a] Data from ref.[60]

Characteristics of polymers obtained with the best performing precatalyst **9a** confirm excellence in catalytic properties of this class of ruthenium initiators. First, the measured number average molecular weights (M_n) were comparable with the theoretical values, leading to initiation efficiencies close to unity and demonstrating the absence of back-biting or other chain-terminating processes. Moreover, as expected from the living nature of the ROMP reactions, the polydispersity index (PDI) of polymers formed with this system is quite narrow and varying with monomer nature. Additionally, a predominantly *trans* configuration ($\sigma_c = 0.20–0.27$) of the polynorbornene derivatives was recorded with **9a** as the catalyst precursor, in agreement with the majority of the data obtained in ROMP reactions using ruthenium complexes.

Moving now to immobilized Schiff base-ruthenium complexes **17** and **18**, it is remarkable that both precatalysts produced moderate to excellent results in ROMP of low- and high-strain cycloolefins, when working under normal reaction conditions.[60] The isolated yields [%] and polymers characteristics (M_n and PDI) obtained from 5-substituted norbornenes (in toluene and dichloromethane as a solvent) are presented in Table 11.

Table 12. Polymer yields [%] in ATRP of vinyl monomers induced by Schiff base-ruthenium complexes **6a**–**f** and **9a**–**f**.[a, b]

Entry	Monomer	Catalyst Precursor					
		6a	**6b**	**6c**	**6d**	**6e**	**6f**
1	Methyl methacrylate	<5	<5	11	28	7	10
2	Isobutyl methacrylate	<5	<5	9	19	<5	7
3	Methyl acrylate	<5	<5	12	26	8	9
4	Butyl acrylate	<5	<5	9	16	<5	7
5	Styrene	10	10	74	88	56	65
		9a	**9b**	**9c**	**9d**	**9e**	**9f**
6	Methyl methacrylate	<5	6	24	27	11	15
7	Isobutyl methacrylate	<5	<5	14	20	7	10
8	Methyl acrylate	<5	<5	10	24	12	13
9	Butyl acrylate	<5	<5	12	15	<5	9
10	Styrene	8	10	67	75	43	51

[a] Data from refs.[51,52]

[b] Reaction conditions: [Ru]:[Initiator]:[Monomer] = 1:2:800; temperature was 85 °C for methacrylates and acrylate and 110 °C for styrene; reaction time 17 h.

For both catalytic systems the polymer yield varied considerably with monomer nature and, in many cases, with the solvent too. On working in toluene, the lowest yields were obtained from 5-cyano- and 5-hydroxymethylnorbornene but by changing the solvent for dichloromethane polymer yields increased dramatically. In dichloromethane as a solvent, high yields were recorded also for the other 5-substituted norbornenes. When comparing activity of initiators **17** and **18** in the same solvent, complex **17** was more active than **18**, irrespective of the monomer employed. In addition, the solvent is decisive for characteristics of the polymers. The lower PDIs obtained in dichloromethane indicate that polymerization proceeds in this solvent in a more controlled fashion, this behavior being independent of the monomer nature. Thus, for catalyst precursor **17** and dichloromethane as the solvent, in some cases excellent yields combined with a polydispersity index typical for living polymerization. As a special merit of immobilized complexes **17** and **18**, and in contrast to ROMP polymers obtained with homogeneous ruthenium catalytic systems where after work-up the products are highly colored by ruthenium residues, these heterogeneous precatalysts provided practically colorless substituted polynorbornenes.

3.5 ATRP Reactions

Preparation of well-defined polymers with controlled topology and functionality has recently become one of the most promising synthetic methods for producing new materials with complex polymer architectures. Schiff base-ruthenium complexes proved to be quite efficient and productive initiators for preparing such polymers using the ATRP methodology. On performing ATRP reactions on a set of common vinyl monomers with catalyst precursors **6a**–**f** and **9a**–**f**, yields and polymer characteristics (number average molecular weights, polydispersity index and initiator efficiency) were found to depend substantially both on the precatalyst and type of the monomer[51,52] (Tables 12–14).

As clearly shown in Table 12, only complexes **6c** and **d** and **9c** and **d** could conveniently catalyze the polymerization of acrylates and methacrylates. By contrast, all precatalysts were able to convert styrene, although significant differences in their performance have been observed; with the systems exhibiting the lowest activity, **6a** and **b** and **9a**, only 10 and 8% conversions of styrene were reached, respectively, whereas the most active systems, **6d** and **9d**, efficiently converted styrene in 88 and 75% yields, respectively. Moreover, with the latter two precatalysts the obtained poly(methyl methacrylate) displayed the lowest polydispersity (1.22 and 1.18, respectively) (Tables 13 and 14).

Table 13. Characteristics of polymers prepared with the catalytic systems **6c**–**f**.[a]

Entry	Monomer	Catalyst Precursor	$M_n \times 10^3$	PDI	f_i
1	Methyl methacrylate	**6c**	6.3	1.25	0.70
2	Methyl acrylate		5.7	1.31	0.72
3	Styrene		38	1.65	0.81
4	Methyl methacrylate	**6d**	13	1.22	0.87
5	Methyl acrylate		9.5	1.28	0.94
6	Styrene		41	1.44	0.89
7	Methyl methacrylate	**6e**	4.8	1.56	0.51
8	Methyl acrylate		4.5	1.52	0.55
9	Styrene		29	1.75	0.67
10	Methyl methacrylate	**6f**	6.6	1.51	0.61
11	Methyl acrylate		5.3	1.48	0.58
12	Styrene		32	1.71	0.85

[a] Data from ref.[51]

Table 14. Characteristics of polymers prepared with the catalytic systems **9c**–**f**.[a]

Entry	Monomer	Catalyst Precursor	$M_n \times 10^3$	PDI	f_i
1	Methyl methacrylate	**9c**	14.8	1.23	0.65
2	Methyl acrylate		5	1.28	0.69
3	Styrene		37	1.33	0.75
4	Methyl methacrylate	**9d**	13.3	1.18	0.81
5	Methyl acrylate		9.4	1.21	0.88
6	Styrene		37	1.25	0.84
7	Methyl methacrylate	**9e**	8.6	1.34	0.51
8	Methyl acrylate		7.5	1.39	0.55
9	Styrene		27	1.44	0.67
10	Methyl methacrylate	**9f**	11.6	1.31	0.52
11	Methyl acrylate		7.7	1.38	0.58
12	Styrene		33	1.48	0.64

[a] Data from ref.[52]

Table 15. Polymer yields [%] in ATRP of vinyl monomers induced by cationic Schiff base-ruthenium complexes **10a**–**f** in toluene and toluene-water as the solvent.[a]

Entry	Monomer	Catalyst Precursor/Toluene					
		10a	**10b**	**10c**	**10d**	**10e**	**10f**
1	Methyl methacrylate	16	27	75	84	51	63
2	Isobutyl methacrylate	12	20	63	77	33	45
3	Methyl acrylate	<5	7	22	33	10	18
4	Butyl acrylate	<5	<5	15	28	<5	5
5	Styrene	24	37	84	92	60	73
		10a	**10b**	**10c**	**10d**	**10e**	**10f**
6	Methyl methacrylate	21	34	83	97	64	70
7	Isobutyl methacrylate	18	25	80	90	42	57
8	Methyl acrylate	9	13	35	42	9	23
9	Butyl acrylate	<5	10	21	32	7	10
10	Styrene	33	48	94	99	78	85

[a] Data from ref.[52]

ATRP of the above set of vinyl monomers occurred intriguingly in a different way in the presence of the cationic Schiff base-ruthenium complexes **10a**–**f**.[52] The polymer yields recorded for reactions performed in toluene and water-toluene mixture as the solvent are summarized in Table 15.

The following remarks should be emphasized in this connection: (i) firstly, from comparing data presented in Tables 12 and 15, it is noticeable that polymer yields vary widely as a function of the monomer and catalyst precursor; (ii) secondly, a superior activity of the cationic complexes **10a**–**f** was systematically recorded as compared with the neutral complexes **9a**–**f** or **6a**–**f**, regardless of the solvent; (iii) thirdly, polymerization yields are substantially higher in the water-toluene mixture than in toluene alone, reaching sometimes for styrene nearly quantitative conversions (polystyrene yield of 99% with **10d**).

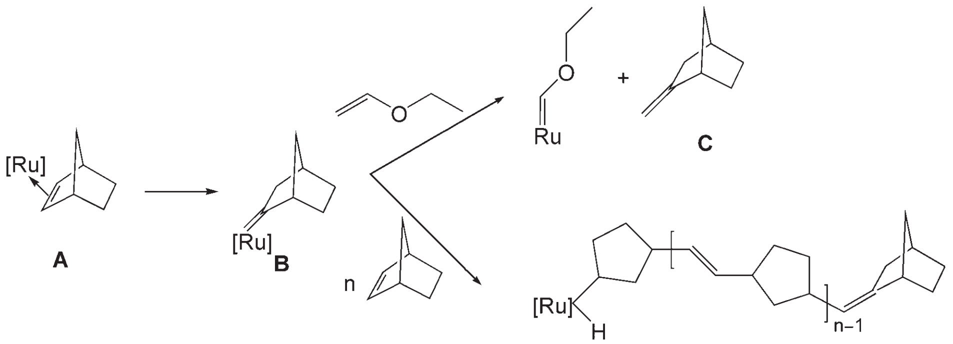
For these cationic systems variations in polymer characteristics (polydispersity index and initiator efficiency) were also observed on changing the solvent, the polymerization process being less controlled in toluene than in a water-toluene mixture.

3.6 Relevant Mechanistic Aspects

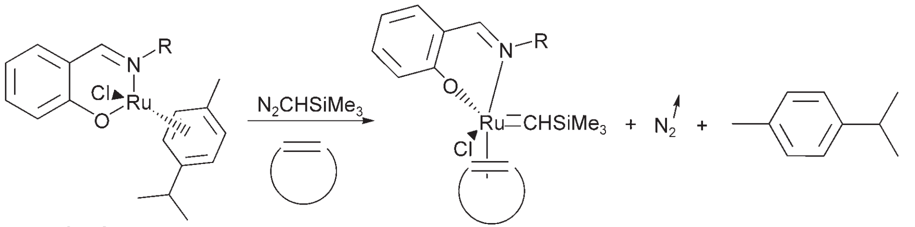
Most relevant mechanistic aspects related to reactions induced by different classes of Schiff base-ruthenium complexes will be briefly reviewed below.

Firstly, it should be pointed out that arene complexes (e.g., **1**–**3**) catalyze Kharasch addition and ATRP reactions without any cocatalyst.[47] However, when used in olefin metathesis (RCM and ROMP), such complexes usually need to be activated by trimethylsilyldiazomethane (TMSD) in order to attain a high conversion of the substrate.[29,49,67] Thus, in the presence of TMSD complexes **1**–**3** lead almost quantitatively to polynorbornene, whereas without TMSD these catalysts just polymerize norbornene slowly (monomer conversion of 6%). The result obtained in the absence of TMSD has been rationalized assuming that the 18-electron ruthenium complex (**1**, **2** or **3**) initiates polymerization of norbornene through loss of the *p*-cymene moiety, followed by coordination of a monomer unit to give **A** and subsequent rearrangement of the coordinated monomer in **A** to a ruthenium carbene complex **B** which propagates the polymerization reaction (Scheme 16).[49]

Strong evidence for this mechanism came from partial trapping of the ruthenium carbene complex **B** with methyl vinyl ether and identification of methylenenorbornane **C** as a by-product in norbornene polymerizations catalyzed by **1**–**3**.[49] This unprecedented finding was corroborated with the amount of *p*-cymene released into the medium during the reaction. In contrast, in the presence of TMSD, the initial ruthenium complex (**1**–**3**) loses *p*-cymene generating a different ruthenium car-



Scheme 16. Mechanism for norbornene polymerization with catalysts **1–3**.[49]



Scheme 17. Mechanism of cycloolefin coordination with ruthenium complexes **1–3**, in the presence of TMSD.

bene species, directly able to coordinate the cycloolefin and propagate polymerization (Scheme 17).

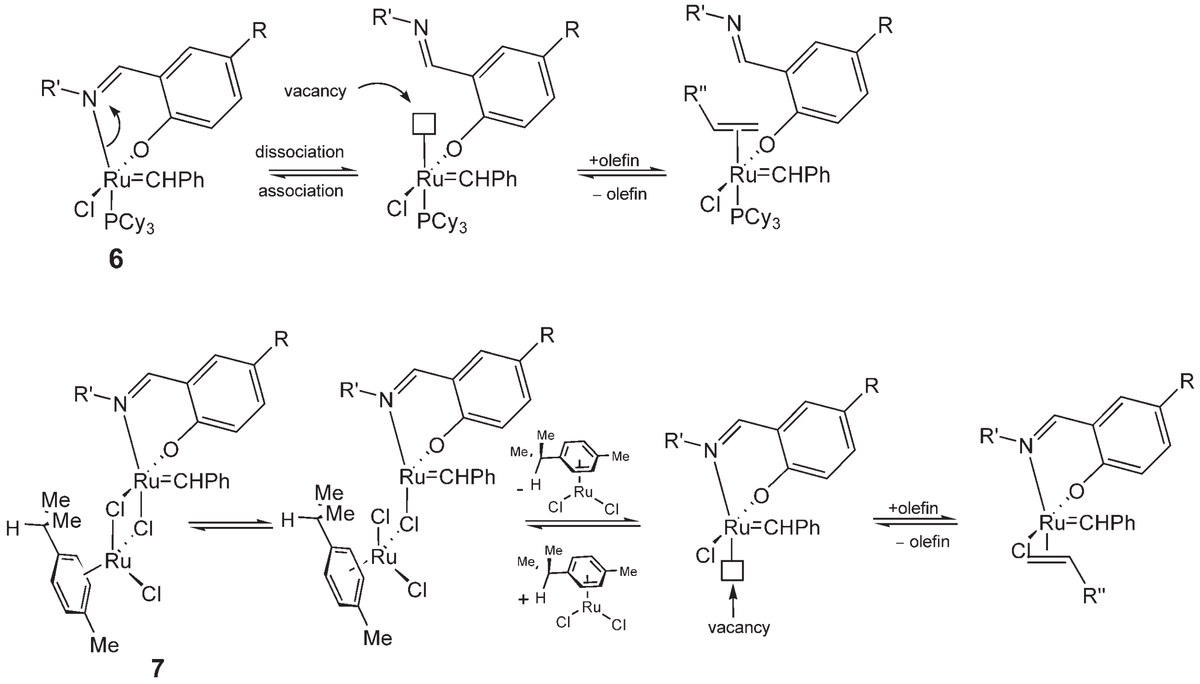
Other research groups also considered the release of the arene ligand as a critical step in generating the active species from similar ruthenium arene complexes in olefin metathesis or related radical reactions.[68–71]

As discussed in a previous section, the mononuclear and dinuclear ruthenium complexes **6** and **7** displayed high activity in the RCM of linear dienes and the ROMP of cyclooctene and norbornene derivatives. In the case of the dinuclear catalytic system **7**, this behavior suggests a synergistic effect between the Schiff-base ligand and the already existing, coordinatively labile, ligands around ruthenium. Results have been interpreted admitting two distinct dissociative mechanisms, for **6** and **7**, in the initiation step of the above processes[29,72,73] (Scheme 18).

For the mononuclear complex **6**, the main feature of the mechanism is the N-decoordination and subsequent coordination at "one-arm" of the Schiff-base ligand, that takes place instead of the usual PCy_3 dissociation encountered in conventional transition metal complexes.[74–78] Moreover, such a dissociative mechanism is highly probable in low-spin metal complexes where there is a maximum pairing of all available *d* electrons of the transition metal.[79,80] Additionally, in this type of chelation the strength of the [Mt]–N bond is very much affected by steric effects.[81–83] A different two-step dissociation mechanism involving a sequential heterolytic cleavage of the chloro-bridges in the dinuclear complex **7** and liberation of the coordinatively labile module {$RuCl_2$(*p*-cymene)} seems to be the key step in olefin metathesis reaction.[29]

At this point we should also mention the high activity in the ATRP of vinyl monomers shown by the cationic catalysts **8a–f**, prepared *in situ* from the corresponding neutral complexes **6a–f**.[51,52] Additionally, these cationic ruthenium benzylidene complexes were the first, to the best of our knowledge, to perform the controlled radical suspension polymerization of methyl methacrylate, methyl acrylate and styrene in water in good to excellent yields. The fact that these catalytic systems exhibit outstanding reactivity in both the ROMP and ATRP reactions enabled us to combine these two techniques to make block copolymers with valuable properties.

Elaborate studies on RCM of dienes, ROMP of cycloolefins, Kharasch addition of carbon tetrachloride to olefins and enol esters or enyne syntheses induced by catalysts of the type **9** constantly indicated high activity and excellent stability of the NHC ruthenium catalysts as compared to the parent phosphane congeners.[53,66,67] On the other hand, parallel research on the radical polymerization of hydrophobic monomers such as methyl methacrylate, methyl acrylate and styrene, using both toluene and water-toluene mixtures as the solvent, demonstrated that with the cationic systems **10a–f**, derived from **9a–f**, the solvent is decisively important for the activity and controllability of the polymerization;[51] under aqueous-organic biphase conditions these ruthenium cationic complexes are highly reactive and controlled molecular weights and narrow molecular weight distributions can be achieved.[52]

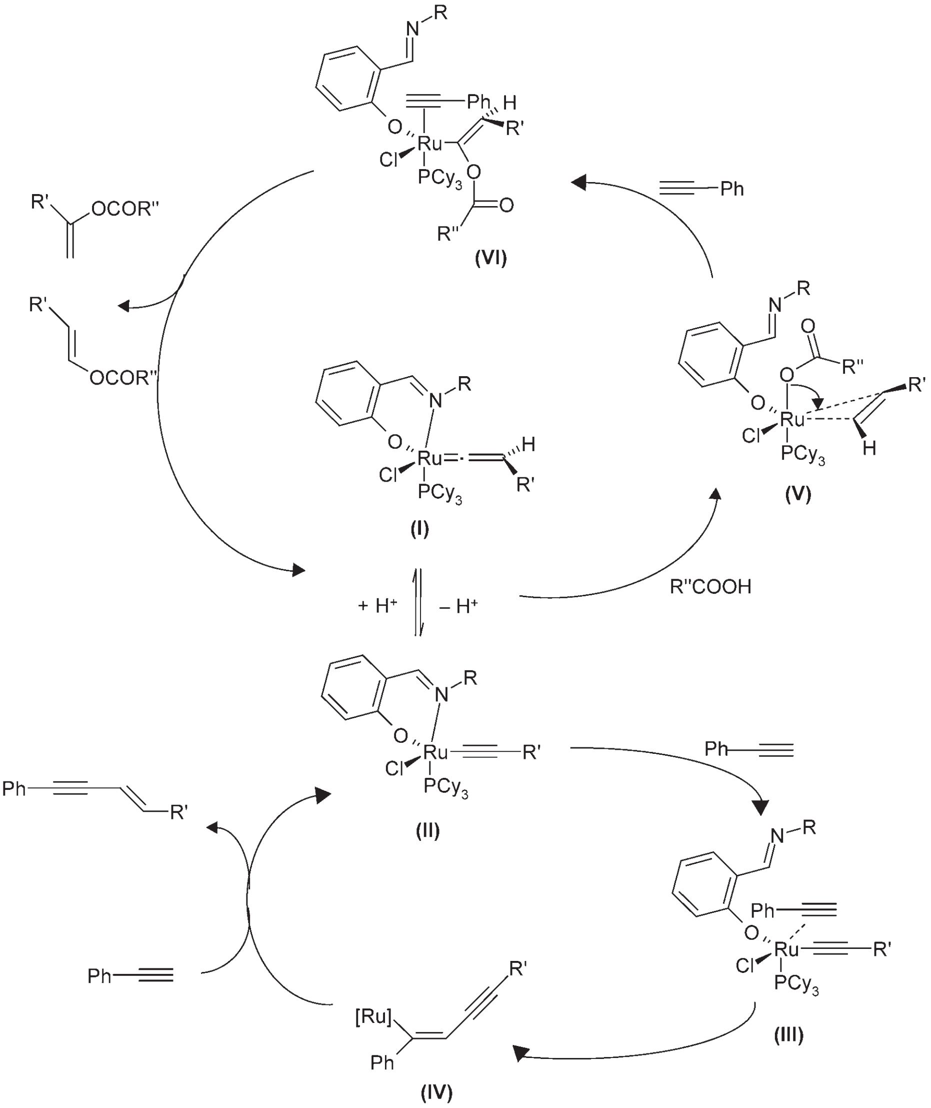


Scheme 18. Dissociative mechanisms for olefin metathesis with mononuclear and dinuclear complexes **6** and **7**.

A unique behavior in enol ester synthesis has been observed with the Schiff base-ruthenium vinylidene and indenylidene catalysts **11** and **12**, prepared from the easily accessible corresponding bis(phosphane) complexes.[84–89] Using the vinylidene catalysts **11a–f** in enol ester synthesis, which proceeds *via* nucleophilic addition of carboxylic acids to terminal alkynes, a wide range of activities have been recorded, but superior in all cases to that obtained with the parent ruthenium indenylidene catalysts **12**.[90] To explain these unexpected results a reaction mechanism similar to that suggested earlier for olefin metathesis with ruthenium catalysts **6a–f** and **7a–f**, has been advanced. This mechanism stipulates that, when an alkyne is used as the substrate, the vacant site is generated from the bidentate chelated salicylaldimine ligand also *via* "one-arm" decoordination (Scheme 19).[90]

We assumed that in this system an equilibrium between the organometallic compounds (**I**) and (**II**) is readily occurring [91]. When weak acids (e.g., acetic acid, isovaleric acid) are added, alkyne dimerization is favored (lower cycle). In contrast, stronger acids (e.g., benzoic acid, formic acid) bind preferentially at the ruthenium center and attack the C-1 or C-2 atom of the coordinating alkyne.[92–94] The attack of the acid on C-1 or C-2 sites of the alkyne should be governed by the steric factors in the Ru environment. Since the active species involved in both enol ester synthesis and alkyne dimerization are of the vinylidene type, it is not surprising that catalysts **11** showed higher activity as compared to the indenylidene complexes **12**.

An expeditious access for obtaining numerous economical advantages in catalysis is the well-established methodology based on immobilized catalysts.[95–118] Interesting results have been acquired in RCM, Kharasch addition and ROMP using the supported hybrid ruthenium catalysts **17–19**.[59–63] For example, in norbornene polymerization with catalyst **19** polydispersities were substantially narrower, as compared to the homogeneous analogue under similar reaction conditions, although lower yields have been recorded.[63] A closely related outcome was encountered in cyclooctene polymerization with the catalyst **19**. Data indicated that with this heterogeneous system a much more controlled polymerization can be achieved. To rationalize these results we assumed that in the case of the above hybrid ruthenium catalysts only one heterogeneous active species is formed, yet diffusion limitations can occur in the channels of the MCM-41. The anchoring of the homogeneous catalyst onto the solid support probably limits the intervention of back-biting reactions because the channels induce a certain steric hindrance, which impedes the polymer from folding itself into a position suitable for back-biting. Also, the fact that dismutation and coupling reactions are eliminated through immobilization of the catalytic species to the mesoporous carrier, results in narrowing the PDI of the formed polymers.[63] Even though these new hybrid systems generally showed lower activity in RCM, Kharasch addition and ROMP than the homogeneous counterparts, the comparatively easy separation of the reaction products and the efficient recovery of the catalysts hold good promise for using them in metathesis-related catalytic processes.[60,63]



Scheme 19. Mechanism for enol ester synthesis with Schiff base-Ru complexes **11** [identified as (**I**) in this scheme].

4. Conclusions

This paper reviews recent work conducted in our group concerning novel homogeneous and/or supported ruthenium catalysts that contain one or more Schiff bases as O,N-chelated ligands, associated around the ruthenium core with diverse other inorganic and organic ligands (i.e., chloride, phosphane, arene, alkylidene, N-heterocyclic carbenes, vinylidene, indenylidene and cyclodienes). Successful applications of these newly synthesized complexes in an array of organic reactions such as olefin metathesis (RCM), Kharasch addition (ATRA), alkyne dimerization and enol ester synthesis are highlighted. Significantly good results have also been obtained by using this class of Schiff base-ruthenium complexes as efficient promoters in ring-opening metathesis polymerization (ROMP) of cycloolefins and atom-transfer radical polymerization (ATRP) of vinyl monomers.

Through modelling of the steric and electronic configuration within the Schiff base moiety, the catalytic activity, stability and selectivity of the ruthenium complexes could be finely tuned to obtain quite stable and active catalysts. Complexes covered in this work are tolerant towards various organic functionalities, air and moisture. At the same time, several heterogeneous hybrid ruthenium catalysts, in which the Schiff base-ruthenium complexes are anchored on the solid support MCM-41, have been developed. Application of the latter in organic syntheses and polymer chemistry looks highly promising owing to some important advantages they provide such as easy isolation of the reaction products, catalyst reusability, and openings for operating in continuous processes.

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