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Activity of a new class of ruthenium based ring-closing metathesis and ring-opening metathesis polymerization catalysts coordinated with a 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene and a Schiff base ligand

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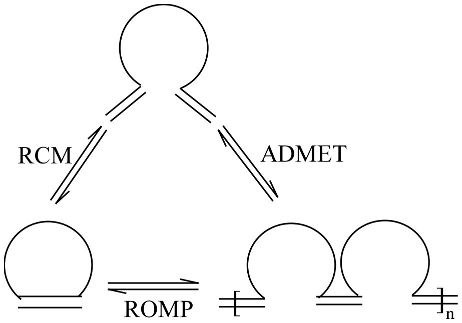
Abstract—A new class of ruthenium based catalysts coordinated with a 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene and a Schiff base ligand have been tested in ring-closing metathesis and ring-opening metathesis polymerization reactions. The results obtained point out that the synergy of Schiff base ligands with a strong Lewis basic *N*-heterocyclic carbene ligand lead to mixed ligand catalytic systems that combine very high activity with excellent stability. Furthermore, the catalytic activity of these catalysts is very dependent on the steric and electronic environment of the Schiff base. © 2002 Elsevier Science Ltd. All rights reserved.

During recent years ring-closing metathesis (RCM) and ring-opening metathesis polymerization (ROMP) have become important tools in both fine chemical and macromolecular synthetic chemistry.[1]

Olefin metathesis is a catalytic reaction in which alkenes are converted into new products via the rupture and reformation of C–C double bonds. Depending on the starting material (cyclic or acyclic alkenes) and the reaction condition parameters, RCM, acyclic diene metathesis (ADMET) or ROMP proceed (Scheme 1).[2] Mainly because of the development of Grubbs' ruthenium catalysts **1** and **2**[3] and Schrock's molybdenum complex **3** (Fig. 1),[4] olefin metathesis has bridged the gulf from an academic curiosum to a mild, efficient, reliable and industrially applicable carbon–carbon forming technique.

Since the groundbreaking discovery that the well-defined unicomponent organometallic species of type **1** could promote olefin metathesis reactions, much effort has been directed towards modification of the ligand sphere around the metal center in order to improve the performing characteristics of these catalytic systems. Concerning the activity, the best results were obtained when one of the phosphine ligands was substituted by a so-called *N*-heterocyclic carbene (NHC) ligand like 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene (e.g. catalyst **2**).[3c–3k] With respect to the thermal stability enhancement, the most spectacular success was obtained when one chloride and one phosphine ligand of type **1** systems were replaced by a chelating Schiff base ligand (e.g. catalysts **4**).[5] Recently, we tested catalytic complexes of type **4** in RCM and ROMP reactions and suggested that for these type of catalytic complexes the olefin metathesis mechanism involves the decoordination and coordination of 'one-arm' of the bidentate Schiff base ligand instead of the usual PCy_3 dissociation as for the systems **1** and **2**.[6] As NHC-ligands are very



Scheme 1. Schematic representation of the olefin metathesis reaction.

Keywords: ring-closing metathesis; ring-opening metathesis polymerization; *N*-heterocyclic carbene ligand; homogeneous catalysis; ruthenium and compounds; olefins.

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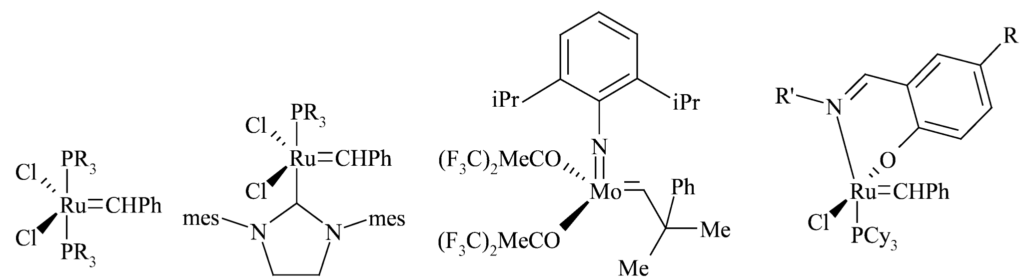


R, R : (substituted) aliphatic or aromatic groups

Figure 1. Depiction of some well-defined unicomponent olefin metathesis catalysts.

strong and bulky Lewis bases, we came to the idea that the combination of a Schiff base and an NHC-ligand in one catalyst structure could lead to improved catalyst performance. Indeed, the presence of the bulky carbene ligand *trans* to the decoordinating part of the Schiff base should stabilize the reactive catalytic intermediate and/or prevent the decomposition of the carbene. Moreover, thermal stability should also be satisfying because these phosphine-free complexes do not suffer from the well-known P–C degradation at higher temperatures.

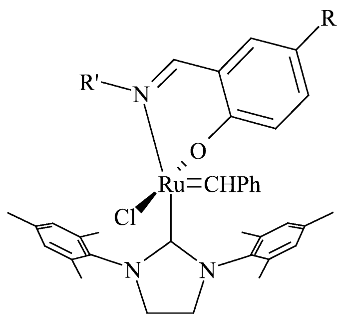
Recently, we succeeded in synthesizing and characterizing the new class of ruthenium-based catalysts **5.a**–**f** (Fig. 2).[7]

We now report on the excellent activity of these readily available and robust complexes for ROMP and RCM with some representative monomers. Moreover, we also checked the thermal stability of these systems in RCM reactions with diethyldiallylmalonate. Catalytic systems **5.a**–**f** were fully characterized by ^{1}H, ^{13}C NMR, Raman, IR and elemental analysis.[7]

In a first set of experiments, the catalytic activity of the Schiff base substituted ruthenium benzylidenes **5.a**–**f** is checked for ROMP with some representative monomers. The yields (%) and characteristics of the formed polymers are depicted in Table 1.

It is obvious from Table 1 that all catalytic systems **5.a** to **5.f** succeed in performing ROMP reactions with the monomers tested, although significant differences in their behavior were noticed. The pronounced observed conversion sequence **5.a**>**5.b**>**5.c**>**5.d**>**5.e**>**5.f** clearly shows that the bulkiness of the Schiff base and the electron-withdrawing properties of the Schiff base substituents exert a profound influence on the ROMP activity. The results gathered in Table 1 reveal that the introduction of more bulkiness in the Schiff base is detrimental for catalyst performance in ROMP reactions. For instance, cyclohexenylnorbornene is converted in 100, 83 and 77% yield for **5.a**, **5.c** and **5.e**, respectively. The influence of the electronic environment of the Schiff base is best illustrated by comparing the catalytic performance of system **5.a** with **5.b**, **5.c** with **5.d** and **5.e** with **5.f**. The data in Table 1 point out that the complex bearing the electron-withdrawing nitro substituent (**5.b**, **5.d** and **5.f**) reaches systematically lower conversions. Furthermore, it is clear that the bulkiness of the Schiff base has a greater impact on catalytic performance in ROMP reactions than the electronic influence exerted by the Schiff base substituents. When the ROMP activity of the best catalyst **5.a** is compared with that of **4.b**[6] (the most performing system for this class of catalysts in ROMP reactions, R and R′ for **4.b** are the same as for **5.b**) it is obvious that type **5** catalysts are more performing. For example, hydroxymethyl- and cyanonorbornene are converted in 43 and 38% yield with **4.b** (reaction conditions: 70°C, 4 h, catalyst/substrate = 1/800),[6] whereas **5.a** converts these substrates in 76 and 68% yield, respectively. The characteristics of the polymers obtained with the highest performing initiator **5.a** are also depicted in Table 1. As can be expected by the living nature of the ROMP reaction, the polydispersity index (PDI) of the formed polymers is quite narrow. It also deserves mention that the measured number average molecular weights (M_n) are close to the theoretical values (assuming the absence of backbiting or other chain-breaking/-terminating reactions) leading to initiation efficiencies close to unity. In accordance with the general observation for ruthenium catalysts in ROMP reactions a *trans* configuration of the polynorbornene derivatives and polycyclooctene is predominate.

In a second set of experiments, the performance of catalytic systems **5.a**–**f** were tested in RCM reactions. Table 2 summarizes the RCM results obtained with some representative substrates.

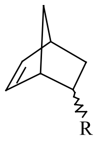


a. R = H, R' = Me
b. R = NO_2, R' = Me
c. R = H, R' = 2,6-Me-4-BrC_6H_2
d. R = NO_2, R' = 2,6-Me-$_4$-BrC_6H_2
e. R = H, R' = 2,6-iPrC_6H_3
f. R = NO_2, R' = 2,6-iPrC_6H_3

5.a-f

Figure 2.

Table 1. Yield (%) for ring-opening metathesis polymerization of some representative monomers using catalysts **5.a**–**f** and characteristics of the polymers formed with **5.a**

Substrate	Yield (%)[a]						Characteristics of the polymers formed with **5.a**			
	5.a	**5.b**	**5.c**	**5.d**	**5.e**	**5.f**	M_n ($\times 10^3$)[b]	PDI[b]	σ_c[c]	f_i[d]
Cyclooctene	100	100	93	88	84	79	109	1.53	0.45	0.94
Norbornene derivatives 										
R = H	100	100	100	100	100	100	202	1.31	0.23	0.93
R = ethyl	100	100	100	100	100	100	272	1.35	0.24	0.90
R = butyl	100	100	96	92	87	82	342	1.38	0.21	0.88
R = hexyl	100	100	93	84	88	74	420	1.30	0.22	0.85
R = decyl	100	100	90	83	83	82	579	1.34	0.25	0.81
R = ethylidene	100	100	87	77	78	73	270	1.40	0.20	0.89
R = phenyl	100	100	82	76	62	57	410	1.43	0.26	0.83
R = cyclohexenyl	100	98	83	79	77	69	430	1.39	0.27	0.81
R = ethylnorbornane	100	100	98	93	85	78	448	1.33	0.22	0.84
R = cyano	68	58	46	43	29	22	232	1.29	0.24	0.70
R = hydroxymethyl	76	69	53	51	42	37	290	1.35	0.23	0.65
R = chloromethyl	100	100	100	100	93	84	328	1.38	0.21	0.87
R = triethoxysilyl	100	100	94	90	81	82	564	1.42	0.25	0.91

[a] In a typical ROMP experiment 0.005 mmol of the catalyst solution in toluene (0.1016 M) was transferred into a 15 ml vessel followed by the addition the appropriate amount of monomer solution (800 equiv. for cyclooctene and 2000 equiv. for the norbornene derivatives) in toluene. The reaction mixture was then kept stirring at 70°C for 4 h. To stop the polymerization reaction, 2–3 ml of an ethylvinylether/BHT solution was added and the solution was stirred for 0.5 h to make sure that the deactivation of the active species was completed. The solution was poured into methanol (50 ml containing 0.1% BHT) and the polymers were precipitated and dried in vacuum overnight.

[b] M_n and the polydispersities (PDI) are determined by size-exclusion chromatography (SEC) with polystyrene calibration.

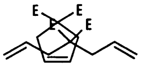
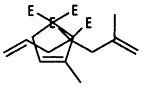
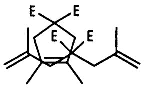
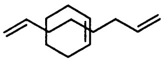
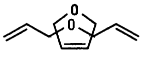
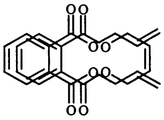
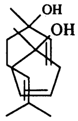
[c] Fraction of polymers with *cis* configuration.

[d] f_i = initiation efficiency = $M_{n,\ theor.}/M_{n,\ exp.}$ with $M_{n,\ theor.}$ = ([monomer]$_0$/[initiator]$_0$)×MW(monomer)×conversion.

When analyzing the results gathered in Table 2, one observes the same order in catalyst performance for RCM and ROMP reactions. For instance, the tetrasubstituted malonatederivative (entry 3, Table 2) is converted with 41, 33, 19, 11, <5 and <5% with systems **5.a**, **5.b**, **5.c**, **5.d**, **5.e** and **5.f**, respectively. The conclusions about the steric bulk of the Schiff base ligands and the electronic-withdrawing properties of the Schiff base substituents that were made for the ROMP reactions can also be drawn here. Catalytic RCM of dienes diethyldiallylmalonate (entry 1), 1,7-octadiene (entry 4) and diallylether (entry 5) was performed quantitatively by all systems. As can further be seen from the data in Table 2, the reactivity of the complexes is sufficiently high to allow the preparation of tri- and tetrasubstituted cycloalkenes in good to moderate yields (entries 2 and 3). Furthermore, diallylphtalate (entry 6) and linalool (entry 7) are also converted smoothly. With the best catalytic system **5.a** and when heating the reaction mixture for 4 h at 55°C, conversions of 87 and 73%, respectively, are reached. When the RCM activity of the best catalyst **5.a** is compared with that of **4.f**[6] (the best performing system for this class of catalysts in RCM reactions, R and R′ for **4.f** are the same as for **5.f**) it is again clear that type **5** catalysts are better performing. For example, the trisubstituted and tetrasubstituted malonatederivative (entries 2 and 3, respectively) are converted in 21 and 17% with **4.f** (reaction conditions: 70°C, 4 h, 5 mol% catalyst),[6] whereas **5.a** converts these substrates in 72 and 41%, respectively. The outstanding stability of the initiators of type **4** have already been demonstrated by Grubbs et al. In order to assess the stability of catalytic systems **5.a**–**f**, they were stored for 1 week in the solid state under an air atmosphere after which we tested them in RCM reactions with diethyldiallylmalonate (reaction conditions identical to those in Table 2). The results of these experiments indicated no noteworthy loss of performance. The same conclusion could be drawn when these complexes were transferred into a solution of deuterated benzene under inert atmosphere. Again, after 1 week, no loss of activity was revealed in RCM experiments using diethyldiallymalonate as substrate (reaction conditions identical to those in Table 2). Even when a solution of **5.a** is heated to 85°C in deuterated benzene under an inert atmosphere for 17 h, no signs of decomposition appear.

In conclusion, the catalytic systems **5.a**–**f** are highly efficient catalysts for promoting ring-closing metathesis and ring-opening metathesis polymerization reactions under mild reaction conditions. We succeeded in our goal to improve catalytic performance of type **4** systems while maintaining their excellent stability characteristics.

Table 2. Yield (%) for RCM of some representative substrates using catalytic systems **5.a**–**f**[a]

				Catalyst					
	Entry	Substrate[b]	Product	**5.a**	**5.b**	**5.c**	**5.d**	**5.e**	**5.f**
	1			100	100	100	100	100	100
	2			72	73	47	42	31	23
	3			41	33	19	11	<5	<5
	4			100	100	100	100	100	100
	5			100	100	100	100	100	100
	6			87	81	68	66	54	53
	7			73	70	60	51	42	37

[a] All reactions were performed on the benchtop in air by weighing 5 mol% of the catalyst into a dry NMR tube and dissolving the solid in 1 ml C_6D_6. A solution of the appropriate substrate (0.1 mmol) in C_6D_6 (1 ml) was added. The tube was then capped, wrapped with parafilm, and shaken for 4 hours at 55 °C. Product formation (all reaction products were unambiguously identified previously[8] and diene disappearance were monitored by integrating the allylic methylene peaks. The formation of cycloisomers, oligomers or telomers was ruled out by GC-analysis of the reaction mixture. [b] E = COOEt.

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