



# Easily accessible and robust olefin-metathesis catalysts based on ruthenium vinylidene complexes

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## Abstract

Nine mixed ligand ruthenium(II) vinylidene complexes with the general formula:  $[\text{RuCl}_2\{\text{C}=\text{CHR}'\}(\text{PCy}_3)(\text{L})]$  and  $[\text{RuCl}\{\text{C}=\text{CHR}'\}(\text{PCy}_3)(\text{sal-R})]$  ( $\text{L} = N$ -heterocyclic carbene,  $\text{sal-R} =$  salicylaldiminate anion,  $\text{R}' = \text{Ph}, \text{SiMe}_3, \text{'But}$ ) has been synthesized and characterized. These complexes are easily accessible from  $[\text{RuCl}_2(p\text{-cymene})]_2$ , terminal alkynes, imidazolium salts or salicylaldimine salts and they have been found to serve as good catalyst precursors for ring-opening metathesis polymerization (ROMP) of norbornene, substituted norbornenes, polycyclic alkenes and cyclooctene and ring-closing metathesis (RCM) of  $\alpha,\omega$ -dienes. Furthermore, these precursors possess extremely high stability toward air, heat and moisture in comparison with other metathesis-active alkylidene ruthenium systems. No significant catalyst decomposition was found for several days at elevated temperatures.

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## 1. Introduction

The advancement of modern organic synthesis necessitates the wide use of catalytic reactions, which make it possible to simplify the synthesis of different target molecules, avoiding the use of toxic reagents and considerably lowering the number of steps and thus minimizing the operation costs.

One of the biggest challenges for modern organic chemists is the employment of the most efficient catalytic method for a specific part in a synthesis strategy. Olefin metathesis has long been labeled as just an industrial and less attractive method for convert-

ing unsubstituted alkenes [1]. Today after the development of numerous very tolerant single-site catalysts mainly based on molybdenum and ruthenium, it belongs to the standard arsenal for the C–C bond formation and this in both organic synthesis and polymer chemistry [2,3]. With the development of well-defined unsaturated ruthenium carbene complexes of the type,  $\text{Cl}_2(\text{PCy}_3)_2\text{Ru}(\text{C}=\text{CHPh})$  (**1**), which combine high activity under mild conditions with an excellent compatibility with polar functional groups, olefin metathesis came in a rapid which putted new lights on the mechanism and application profile of ring-opening metathesis polymerization (ROMP), acyclic diene metathesis (ADMET), ring-closing metathesis (RCM) and cross metathesis (CM) (Scheme 1) [4].

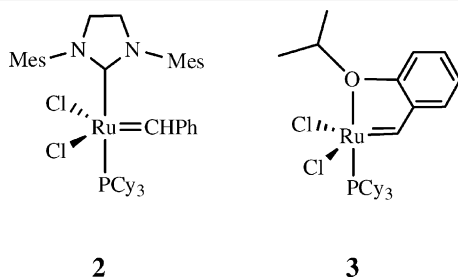
ROMP is a convenient way to synthesize polymers because it maintains backbone unsaturation and

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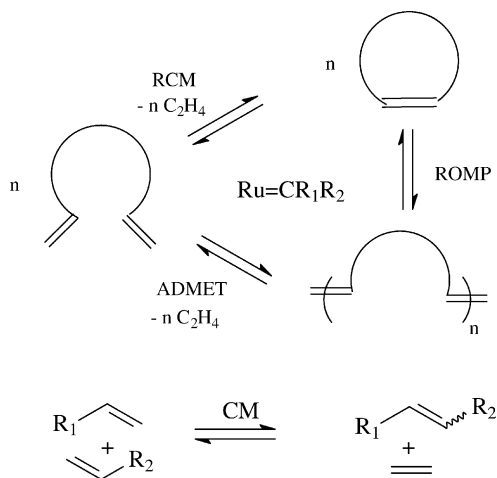
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allows the direct incorporation of functionality via the monomer. Furthermore, the polyalkenamers are capable to function as soft blocks in a more rigid matrix with low glass transition temperature ( $T_g$ ) and lead to new polymeric materials [5]. In addition to this, RCM has clearly reached the point where it is a reliable and mature technique for the formation of a diverse range of ring structures which provides a key step into the synthesis of a large array of natural- and pharmaceutical-products such as the alkaloids manzamine A and roseophilin [6].

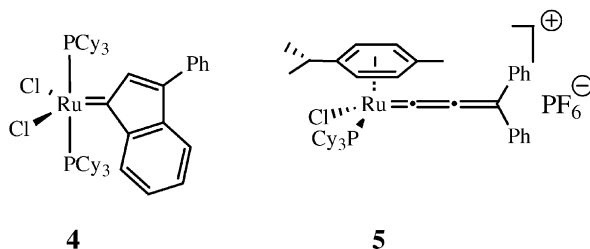


Since 1998, the superior characteristics of *N*-heterocyclic carbenes compared to phosphine ligands, are permeated in the world of olefin metathesis and today these second generation catalysts (**2**) represents the most active precedents in this area that can compete for the first time with the Mo-based systems [7]. A last type of this well-defined Ru alkylidenes is the highly active and very stable O-chelating analogue developed by the group of Hoveyda and co-workers (**3**) [8].



Scheme 1. Different olefin-metathesis reactions.

Despite the tremendous success of the Grubbs carbenes and derivatives thereof, lot of efforts were done to circumvent the quite cumbersome preparative routes to alkylidene complexes via diazo intermediates. In this context, ruthenium indenylidene and allenylidene (**4, 5**) complexes were introduced as perfect alternative because they are readily available from the reaction of common Ru-precursors such as  $\text{RuCl}_2(\text{PPh}_3)_3$  and  $[\text{RuCl}_2(p\text{-cymene})]_2$  with diphenyl propargyl derivatives [9–11].



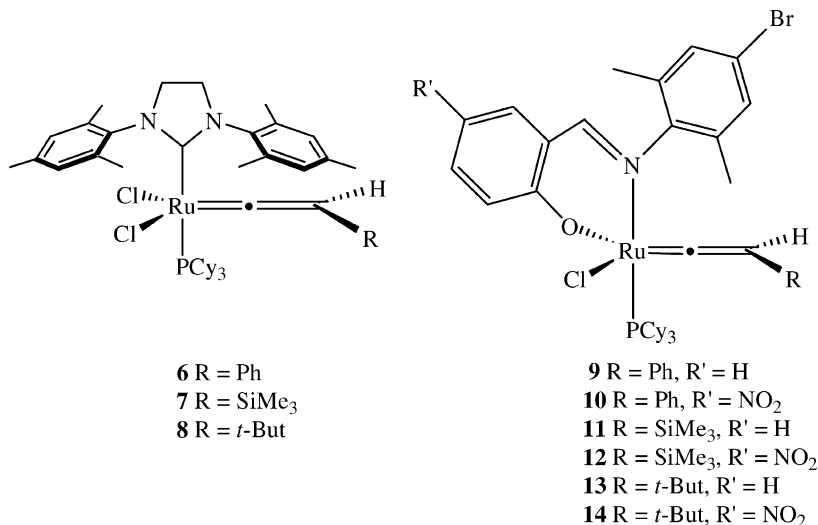
Recent publications described that Ru–vinylidene complexes of the general formula  $\text{Cl}_2(\text{PR}_3)_2\text{Ru}(\text{C}=\text{CHR}')$  ( $\text{R} = \text{Ph}, ^i\text{Pr}, \text{Cy}$ ;  $\text{R}' = \text{Ph}, \text{ferrocenyl}, ^t\text{But}$ ) provided another group of easily accessible catalytic precursors for ROMP of norbornene and its derivatives [12,13]. Although their efficiency were much lower than that of the Grubbs' alkylidene, the polymerization rate was fast enough for practical use and the resulting polymers had high molecular weights with polydispersities equivalent to the alkylidene systems.

In light of these observations our group became more and more interested in synthesizing easily accessible all-round Ru-catalysts which are ubiquitous in all facets of organic synthesis such as olefin metathesis, atom transfer radical addition, atom transfer radical polymerization and enol-ester synthesis [14]. In a first part of this study, we wanted to know if changing a phosphine entity in Ru–vinylidene complexes by a *N*-heterocyclic carbene had an analogous impact on the ROMP activity as with the Grubbs' alkylidene systems. In this way complexes **6–8** were synthesized for this purpose. A further ligand modification in these vinylidene complexes consisted off the incorporation of Schiff-base type ligands and their influence on the catalytic activity toward ROMP and RCM (**9–14**). As test substrates for ROMP, a whole range of substituted

norbornenes and cyclic olefins such as cyclooctene and dicyclopentadiene (DCPD) were chosen. Furthermore, the catalyst precursors were screened on RCM of appropriate  $\alpha,\omega$ -dienes.

lays in the fact that they can be easily prepared and electronically or sterically fine-tuned.

Recently, our group found that complex **1** bearing a bidentate salicylaldehyde ligand was active for several



## 2. Results and discussion

Ruthenium vinylidene complexes can be easily prepared from commercially available terminal alkynes and ruthenium sources. In the current investigation, the method reported by Ozawa was chosen which involves the treatment of the ruthenium dimer [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> [15], with two equivalents cyclohexylphosphine and an excess of alkyne in toluene at 70 °C during 24 h. Reaction of these vinylidene complexes with the carbene ligand 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene, in THF proceeds rapidly and delivers a clean mono-substitution. The ruthenium Schiff-base complexes **9–14** were prepared according to these previous described procedures [16].

Organometallic complexes containing Schiff-base ligands have been investigated with a variety of metals and have been used in a divergent spectrum of reactions going from oxidation of alcohols [17a–c], epoxidation and cyclopropanation of alkenes [17d,e], over addition polymerization of ethene, propene and norbornene [17f,g] through Kharasch addition and enol–ester synthesis [14c,f]. Their main advantage



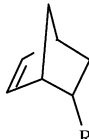
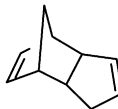
metathesis reactions especially ring-closing metathesis [18a]. The Schiff-base derivative showed unexpectedly improved thermal stability and high activity even in protic solvents [18b].

### 2.1. ROMP of cyclic olefins

In a first set of experiments, complexes **6–8** were tested on their ROMP activity toward different cyclic olefins and the results are summarized in Table 1. The monomers are mixtures of *exo* and *endo* conformers (*exo/endo* > 4). The reactions were performed at 60 °C and the monomer to catalyst ratio was 5000 for cyclooctene and 2000 for the norbornene derivatives.

From these results, it is noticed that both low-strained and high-strained cyclic monomers are converted with excellent yields with the three systems although significant differences in their behavior were observed. Under these experimental conditions, the polymerization of cyclooctene is monitored in Fig. 1. It appears that catalyst **7** is the most active system toward ROMP because quantitative conversions are reached with cyclooctene, while the conversion for **6** and **8** are, respectively, 54 and 90%. Quantitative conversions with catalyst **7** are also obtained for

Table 1  
ROMP of cyclic olefins using ruthenium vinylidene complexes **6–8**<sup>a</sup>

Substrate	Time (h)	Complex <b>6</b>			Complex <b>7</b>			Complex <b>8</b>		
		Yield (%)	$M_n$ ( $\times 10^4$ ) <sup>b</sup>	$M_w/M_n$ <sup>b</sup>	Yield (%)	$M_n$ ( $\times 10^4$ ) <sup>b</sup>	$M_w/M_n$ <sup>b</sup>	Yield (%)	$M_n$ ( $\times 10^4$ ) <sup>b</sup>	$M_w/M_n$ <sup>b</sup>
	0.5 <sup>c</sup>	54	379	1.66	99	434	1.60	90	474	1.54
	24 <sup>d,e</sup>	24	214	1.79	47	367	1.59	38	423	1.62
										
R = H	0.08 <sup>e</sup>	100	103	2.1	100	93	1.9	100	98	2.3
R = ethyl	0.5	100	178	1.78	100	122	1.88	100	130	1.80
R = butyl	0.5	100	111	1.80	100	154	1.68	100	163	1.72
R = hexyl	0.5	87	100	1.78	100	178	1.89	100	187	1.90
R = decyl	0.5	80	269	1.89	100	334	1.75	100	230	1.78
R = ethylidene	0.5	90	187	1.75	100	190	1.77	100	209	1.90
R = phenyl	2	71	150	1.69	94	202	1.54	87	214	1.67
R = cyclohexenyl	2	72	189	1.66	88	131	1.78	80	156	1.60
R = hydroxymethyl	2	15	90	1.99	45	69	2.0	38	77	1.87
R = chloromethyl	2	68	108	1.71	98	145	1.66	87	127	1.69
R = triethoxysilyl	2	70	145	1.89	100	190	1.79	89	200	1.83
	2	74	–	–	100	–	–	97	–	–

<sup>a</sup> General conditions: monomer/catalyst = 2000, solvent: toluene, 60 °C.

<sup>b</sup> Determined using Gel Permeation Chromatography with PS calibration.

<sup>c</sup> Monomer/catalyst = 5000.

<sup>d</sup> Monomer/catalyst = 4000.

<sup>e</sup> Room temperature.

norbornene, ethyl-, butyl-, hexyl-, decyl-, ethylidene-, triethoxysilyl-norbornene.

Unfortunately, the molecular weights are much higher than theoretical predicted as indicated by the corresponding initiator efficiencies ( $f = M_{n,theor}/M_{n,exp}$ ,  $M_{n,theor} = [M]_0/[In]_0 \times M_{w,mon} \times \text{conversion} (\%)$ ): 13, 20, 20, 19, 20, 14 and 13%. The slow initiation compared to propagation is typical for vinylidene complexes as confirmed by the observations of Ozawa who found initiator efficiencies of 2% for the polymerization of norbornene with the bisphosphine complexes.

Cyclopentene, a typical low-strained olefin, was polymerized at room temperature and the yield after 24 h reaches 47% with a monomer to catalyst ratio of 4000. The polymerization of DCPD resulted in a cross-linked network infeasible to analyze via GPC due to the insolubility of the polymer.

The tremendous impact of the electron-donating and sterical demanding 4,5-dihydroimidazol-2-ylidene entity on the catalytic activity is best illustrated by comparing the turnover frequencies (TOF) for the ROMP of norbornene. The TOF with the Ru–vinylidene,  $Cl_2(PCy_3)_2Ru(=C=CH^t\text{But})$ , amount to  $10 \text{ min}^{-1}$

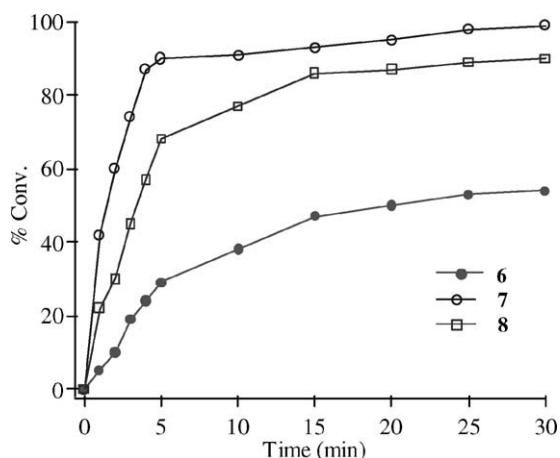


Fig. 1. ROMP of cyclooctene catalyzed with complexes **6–8**. Conditions: 60 °C, monomer/catalyst = 5000, [Ru]<sub>0</sub> = 0.1 mM, solvent: toluene.

[12] while with the corresponding mixed ligand system (**8**) the TOF reaches easily 400 min<sup>-1</sup>. Furthermore, cyclooctene was polymerized using Cl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>Ru(=C=C=CH<sup>t</sup>But) in 82% yield after 12 h and a monomer to catalyst ratio of 100, no data were available for the polymerization of cyclopentene. In general, <sup>1</sup>H-NMR spectroscopy indicated a predominately (75–90%) *trans*-olefin microstructure in the polynorbornene and polycyclooctene samples which is in agreement with other Ru-catalyzed ROMP reactions [3]. Comparing these results to the analogous alkylidene second generation catalysts, the activity of the vinylidene are much lower (TOF of 15 000 min<sup>-1</sup> and higher for the ROMP of CO using second generation Grubbs' catalysts) however these polycyclooctenes are well soluble in chloroform and the molecular weight distribution is surprisingly narrow ( $M_w/M_n = 1.54–1.66$ ) [7f]. This interesting feature favors our systems in terms of practical applicability compared to the second generation catalyst.

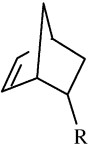
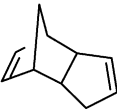

Tables 2 and 3 summarizes the ROMP activity of the Schiff-base complexes **9–14**. In these experiments we chose for a lower catalyst loading (monomer/catalyst = 800 for norbornene and 250 for cyclooctene) because lower activities were expected and the polymerization proceeded at a higher temperature (80 °C). In order to test the catalytic potential of these new Schiff-base vinylidene type precursors, the same cyclic monomers were exposed to the

Ru-complexes **9–14** and the results are depicted in Tables 2 and 3.

The ROMP of norbornene is completed after 30 min with catalysts **11–14** and almost a maximum conversion is reached with catalyst **9**, **10**. The catalytic activity of the systems **11–14** can be compared with other highly active ruthenium catalysts for ROMP of norbornene, e.g. RuCl<sub>2</sub>(=CHPh)(PCy<sub>3</sub>)<sub>2</sub> [3e] (99%, 5 min, RT, 100 eq.), RuCl<sub>2</sub>(*p*-cymene)(PCy<sub>3</sub>)/trimethylsilyl diazomethane [19] (100%, 2 h, 60 °C, 700 eq.), RuCl<sub>2</sub>(=C=CH<sup>t</sup>But)(PCy<sub>3</sub>)<sub>2</sub> [13] (98%, 10 min, 100 eq.), RuCl<sub>2</sub>(imidazol-2-ylidene)<sub>2</sub> [7b,e] (92%, 1 min, RT, 100 eq.) and is much higher than the following ruthenium catalysts: [(h<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)RuH(h<sup>2</sup>-O,P-Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)]BF<sub>4</sub> [20] (100%, RT, 16 h, 81%), TpRuCl(=C=CHPh)(PPh<sub>3</sub>) [21] (99%, 72 h, 80 °C, 100 eq.), Cp<sup>\*</sup>RuCl(=C=CHPh)(PPh<sub>3</sub>) [21] (Cp<sup>\*</sup> = pentamethylcyclopentadienyl) (19%, 24 h, 80 °C, 100 eq.). The <sup>1</sup>H-NMR spectrum of polynorbornene obtained with all the catalysts exhibited two doublets at δ 5.33 and 5.18 ppm which correspond to the vinylic proton of the main chain in *trans*- and *cis*-geometries. Relative peak integration of these signals indicated a *trans* content in the range of 80–85% in the polymer which was also confirmed by the peaks at δ 133.9 (*cis*) and 133.0 (*trans*) in the <sup>13</sup>C-NMR spectrum. As judging from the GPC analysis in Tables 2 and 3, the polymers synthesized with the Schiff-base vinylidene precursor have again much higher molecular weight than the theoretical predicted. Based on the molecular weight of the polynorbornenes obtained with **9–14** and the initial monomer/catalyst ratio we can calculate an initiator efficiency of circa 10% which is higher than the 2% from the vinylidene precursors containing two phosphine ligands but still unsatisfying [12]. Despite the higher molecular weights than theoretical predicted, the molecular weight distribution of the polynorbornene remained quite narrow with values that did not exceed 1.70.

Since most of the Ru–vinylidene precursor remained unreacted in the reaction mixture after polymerization, a recovery test was performed with the ROMP of norbornene catalyzed by system **13**. After quenching the polymer mixture in methanol, the polymer was filtered off and washed several times. The solvent was removed from this filtrate under vacuum and fresh monomer stock solution was added.

Table 2  
ROMP of cyclic olefins using ruthenium Schiff-base complexes **9–11**<sup>a</sup>

Substrate	Time (h)	Complex <b>9</b>			Complex <b>10</b>			Complex <b>11</b>		
		Yield (%)	$M_n$ ( $\times 10^4$ ) <sup>b</sup>	$M_w/M_n$ <sup>b</sup>	Yield (%)	$M_n$ ( $\times 10^4$ ) <sup>b</sup>	$M_w/M_n$ <sup>b</sup>	Yield (%)	$M_n$ ( $\times 10^4$ ) <sup>b</sup>	$M_w/M_n$ <sup>b</sup>
										
R = H	0.5	94	67.6	1.53	98	62.6	1.60	100	63.4	1.70
R = ethyl	4	89	51.4	2.36	100	49.7	2.12	100	64.1	1.99
R = butyl	4	100	93.0	2.10	100	78.1	2.15	100	96.6	1.97
R = hexyl	4	82	54.0	1.85	84	48.3	1.87	100	71.1	1.90
R = decyl	4	83	114.0	1.94	100	116.8	1.97	100	122.8	2.2
R = ethylidene	10	100	83.6	1.90	100	79.6	1.98	100	82.8	2.3
R = phenyl	4	74	46.8	1.93	80	43.9	2.08	95	60.7	1.89
R = cyclohexenyl	4	73	7.4	1.89	77	83.4	2.03	87	85.1	1.88
R = hydroxymethyl	4	10	16.4	1.87	16	13.7	2.3	59	25.7	2.21
R = chloromethyl	4	78	39.7	2.0	89	36.8	2.31	100	39.9	2.24
R = triethoxysilyl	4	71	105.6	1.71	79	100.6	2.08	100	128.8	2.15
	10	90	–	–	96	–	–	100	–	–
	15 <sup>c</sup>	10	34.7	1.70	15	30.5	1.84	93	37.9	1.54

<sup>a</sup> General conditions: monomer/catalyst = 800, solvent: toluene, 80 °C.

<sup>b</sup> Determined using Gel Permeation Chromatography with PS calibration.

<sup>c</sup> Monomer/catalyst = 250.

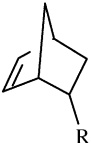
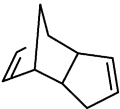

A polymer yield of 91% was obtained under the same reaction conditions as the previous run and an average molecular weight of  $55.3 \times 10^4$  Da. These results are comparable with those conducted by the first polymerizations and indicate that a main part of the vinylidene entities remains unreacted and can be subsequently activated.

When the aliphatic-substituted norbornenes are examined quantitative conversions are obtained for ethyl, butyl, hexyl, decyl and ethylidene norbornene after 4 h with systems **11** and **12**. The vinylidene systems **13** and **14** reached quantitative yields for ethyl, butyl, decyl and ethylidenenorbornene and catalysts **9**, **10** gave only quantitative yields for butyl and ethylidene norbornene.

The monomer cyclohexenylnorbornene is not totally converted with these systems and a maximum

conversion of 97% was reached with system **12**. The molecular weights of the formed polymers are again much higher than theoretical predicted (typical  $f$ -values between 10 and 35%) and the polydispersities are also higher than for norbornene (PDI = 1.40–1.70 versus 1.80–2.40). Hydroxymethylnorbornene is smoothly converted with **11**, **12** and **14** (59, 65 and 55%) but only moderate to low conversions are observed with system **9**, **10** and **13** (10, 16 and 34%) during a reaction time of 4 h. Remarkable are also the low molecular weights obtained for these polymers; however the PDI is quite broad. The monomers chloromethyl— and triethoxysilylnorbornene which are interesting building blocks for the preparation of block- and graft-copolymers, are converted in good and excellent yields for **11–14** (>91%) and moderate yields for system **9** and **10**

Table 3  
ROMP of cyclic olefins using ruthenium Schiff-base complexes **12**–**14**<sup>a</sup>

Substrate	Time (h)	Complex <b>12</b>			Complex <b>13</b>			Complex <b>14</b>		
		Yield (%)	$M_n$ ( $\times 10^4$ ) <sup>b</sup>	$M_w/M_n$ <sup>b</sup>	Yield (%)	$M_n$ ( $\times 10^4$ ) <sup>b</sup>	$M_w/M_n$ <sup>b</sup>	Yield (%)	$M_n$ ( $\times 10^4$ ) <sup>b</sup>	$M_w/M_n$ <sup>b</sup>
										
R = H	4	100	65.6	1.68	100	58.2	1.39	100	60.0	1.48
R = ethyl	4	100	60.0	2.43	100	54.3	2.0	100	55.1	1.91
R = butyl	4	100	107.0	2.20	100	108.1	2.3	100	94.8	2.07
R = hexyl	4	100	74.3	1.89	95	52.2	1.85	98	55.7	1.76
R = decyl	4	100	130.4	1.96	100	101.0	1.95	100	120.0	1.80
R = ethylidene	10	100	94.1	1.91	100	91.5	1.93	100	84.9	1.78
R = phenyl	4	98	63.5	1.99	89	48.3	1.88	92	51.5	1.80
R = cyclohexenyl	4	97	96.8	1.97	79	80.5	1.87	82	86.9	1.83
R = hydroxymethyl	4	65	30.8	1.86	34	20.5	2.23	55	22.1	2.4
R = chloromethyl	4	100	50.1	2.0	100	328.9	2.12	100	38.4	2.10
R = triethoxysilyl	4	100	131.1	2.12	91	134.9	2.18	99	130.0	2.33
	10	100	–	–	95	–	–	97	–	–
	15	100	28.9	1.76	80	30.5	1.70	88	27.9	1.83

Monomer/catalyst = 250.

<sup>a</sup> General conditions: monomer/catalyst = 800, solvent: toluene, 80 °C.

<sup>b</sup> Determined using Gel Permeation Chromatography with PS calibration.

(78 and 89% for the chloro-substituted and 71 and 79% for the triethoxy congeners). The polycyclic monomer, DCPD is quantitatively converted during a period of 10 h with all tested systems **6** and **7** however the polymers remains insoluble in any courant solvent indicating that a cross-linking may be occurred.

Finally, the polymerization of the less strained monomer cyclooctene is monitored during 15 h at 80 °C. The conversion curves for the different systems are depicted in Fig. 2. A great discrepancy is observed between systems **11**–**14** on one hand and systems **9**–**10** on the other.

From these results we can conclude that the silylvinylidene complex (**11** and **12**) is the most performing system. Looking to the substitution pattern of the Schiff-base ligand it is clear that the highest

activity is obtained with the electron withdrawing nitro group in *para*-position.

Another interesting feature inherent to this catalysts is that they combine the advantage of fine-tuning the Schiff-base ligand with the high stability against bimolecular decomposition in solution even at elevated temperatures [16]. A prove of their stability against bimolecular decomposition of the Schiff-base ruthenium vinylidene complexes, is that they can be kept for at least 1 month in toluene without losing their catalytic performance. In solid phase they are stable for at least 3 months without significant lose of activity.

The catalyst lifetime of ruthenium vinylidene precursor **14** was investigated by doing a ROMP experiment of ethylidenenorbornene at timed intervals. One solution of catalyst **14** was continuously kept in toluene at room temperature and a second solution



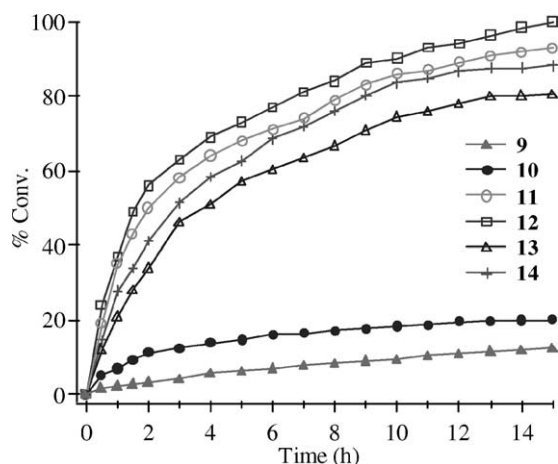


Fig. 2. ROMP of cyclooctene catalyzed with complexes **9–14**. Conditions: 80 °C, monomer/catalyst = 250,  $[Ru]_0 = 6.9$  mM, solvent: toluene.

of catalyst **14** was made, the appropriate amount was added to a monomer solution and afterwards the remaining catalyst solution was dried under vacuum. This strategy was repeated over a period of 3 months. The results of this “lifetime” study over a period of 3 months are depicted in Fig. 3. Furthermore, when a solution of catalyst **14** ( $C_6D_6$ ) is kept at 50 °C, after 3 days the vinylidene species is still present as was monitored with  $^1H$ -NMR. This indicates that this Ru-systems decomposes very slowly even at high temperatures.

In order to improve the control of the molecular weights, the polymerization of cyclooctene is per-

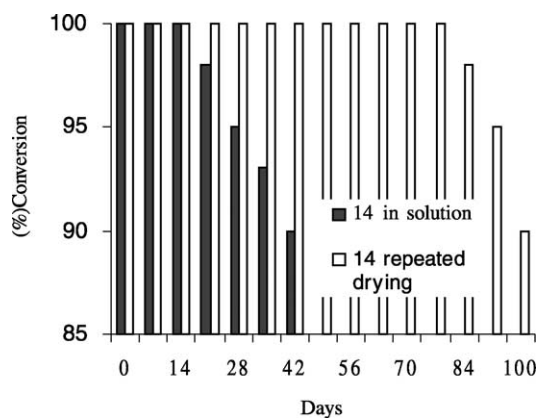


Fig. 3. ROMP of ethylidene norbornene mediated by **14** over a time period of 3 months. Conditions: 80 °C, monomer/catalyst = 800,  $[Ru]_0 = 5.4$  mM, solvent: toluene.

formed with the best systems at two temperature intervals and the results are summarized in Table 4.

From these results it is seen that polydispersity index decreases with the temperature. Furthermore, the initiator efficiencies are somewhat higher. For instance with catalysts **7** and **8**, a typical  $f$ -value of 20% was found at room temperature, whereas at higher temperatures this values was half as high. An analogous tendency was observed with the salicylaldimine systems ( $f = 30$ –40% versus 20–30%).

## 2.2. RCM of $\alpha,\omega$ -dienes

All the synthesized complexes were subjected to a RCM of different diolefins and the results of these

Table 4  
ROMP of cyclooctene using catalysts **7**, **8** and **11–14** at two temperature levels

Catalyst	25 °C			40 °C		
	Yield (%)	$M_n (\times 10^4)^a$	$M_w/M_n^a$	Yield (%)	$M_n (\times 10^4)^a$	$M_w/M_n^a$
<b>7</b> <sup>b</sup>	62	163.2	1.47	80	224.2	1.50
<b>8</b> <sup>b</sup>	58	159.8	1.45	74	297.1	1.49
<b>11</b> <sup>c</sup>	63	15.0	1.52	78	19.2	1.60
<b>12</b> <sup>c</sup>	69	15.2	1.57	81	17.4	1.68
<b>13</b> <sup>c</sup>	50	17.8	1.62	76	21.0	1.67
<b>14</b> <sup>c</sup>	58	13.3	1.66	79	19.7	1.70

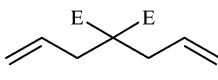

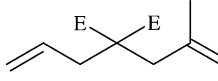
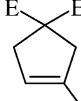
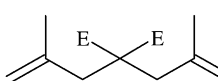
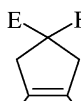
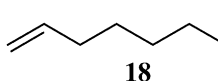
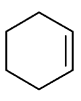
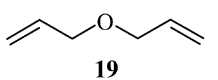

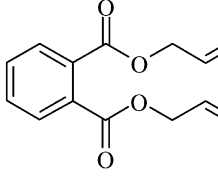
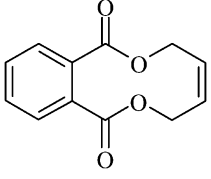
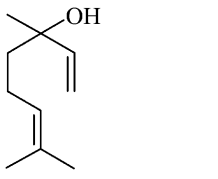
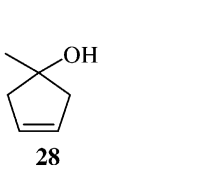
<sup>a</sup> Determined using Gel Permeation Chromatography with PS calibration.

<sup>b</sup> General conditions: monomer/catalyst = 5000, solvent: toluene, 10 h.

<sup>c</sup> General conditions: monomer/catalyst = 800, solvent: toluene, 15 h.



Table 5  
 Ring-closing metathesis of  $\alpha,\omega$ -diolefins using catalysts 6–14<sup>a,b</sup>

Substrate <sup>b</sup>	Product	Time (h)	6	7	8	9	10	11	12	13	14
 <b>15</b>	 <b>22</b>	2 <sup>c</sup> 24 <sup>d</sup>	90 –	100 –	100 –	– 96	– 98	– 100	– 100	– 100	– 100
 <b>16</b>	 <b>23</b>	2 <sup>c</sup> 24 <sup>d</sup>	60 –	76 –	71 –	– 36	– 43	– 59	– 69	– 48	– 53
 <b>17</b>	 <b>24</b>	10 <sup>c</sup> 24 <sup>d</sup>	10 –	44 –	34 –	– <5	– 11	– 23	– 36	– 16	– 26
 <b>18</b>	 <b>25</b>	1 <sup>c</sup> 10 <sup>d</sup>	92 –	100 –	100 –	– 98	– 99	– 100	– 100	– 100	– 100
 <b>19</b>	 <b>26</b>	1 <sup>c</sup> 10 <sup>d</sup>	96 –	100 –	100 –	– 97	– 98	– 100	– 100	– 100	– 100
 <b>20</b>	 <b>27</b>	2 <sup>c</sup> 24 <sup>d</sup>	71 –	90 –	83 –	– 51	– 60	– 72	– 83	– 67	– 80
 <b>21</b>	 <b>28</b>	2 <sup>c</sup> 24 <sup>d</sup>	69 –	89 –	80 –	– 27	– 54	– 70	– 81	– 68	– 75

<sup>a</sup> Yield % as determined with <sup>1</sup>H-NMR and mesitylene as internal standard.

<sup>b</sup> E = COOEt.

<sup>c</sup> Reaction conditions: 60 °C, 5 mol% catalyst, C<sub>6</sub>D<sub>6</sub>.

<sup>d</sup> Reaction conditions: 80 °C, 5 mol% catalyst, C<sub>6</sub>D<sub>6</sub>.

experiments are summarized in Table 5. As can be expected the catalysts 6–8 were more active and will be discussed separately. In line with previous observations, the catalytic activity of complexes 9–14 toward RCM decreases in the order 12 > 11 > 14 > 13 > 10 > 9.

The reactions of catalysts 6–8 were performed during 1 and 2 h at 70 °C with a catalyst loading of 5 mol%. The yields were determined by following the methylene protons with <sup>1</sup>H-NMR spectroscopy.

The ring-closing metathesis of diethyldiallylmalonate, 1,7-octadiene and diallylether yielded quantitatively the ring-closing product without any detectable side products with catalysts 7 and 8. These results were quite satisfying because the cyclization of diethyldiallylmalonate with an analogous Ru–vinylidene, Cl<sub>2</sub>(P<sup>*i*</sup>Pr<sub>3</sub>)<sub>2</sub>Ru(=C=CH(<sup>*t*</sup>But)), reached 96% after 24 h at 60 °C (substrate/catalyst = 50).

The more sterical substrates 16 (trisubstituted) and 17 (tetrasubstituted) were converted with 76 and 44% conversion with system 7 and with 71 and 34% for system 8.

The diallylester (25) and the terpene (26) are converted in excellent yields with catalysts 7 (90 and 89%) and 8 (83 and 80%).

The RCM of these substrates with catalysts 9–14 demands more prolonged reaction times and higher temperatures. The ring-closing metathesis of diethyldiallylmalonate, 1,7-octadiene and diallylether delivered quantitatively the ring-closing product with systems 11–14. The yields for the inferior systems 9 and 10 were not 100% but also very high (>95%). The formation of the cyclic trisubstituted compound (28) is low for the four best systems at 80 °C with yields of, respectively, 59, 69, 48 and 53%. The tetra substituted substrate (22) is more difficult to convert even under these harsh conditions with yields in the range of 15–40%. The diallylester (25) and the terpene (26) are converted in good yields with the best systems (72, 83, 67, 80% and 70, 81, 68, 75%).

### 3. Conclusions

Our investigation clearly demonstrate that ruthenium vinylidene complexes bearing one *N*-heterocyclic carbene operate as excellent metathesis catalyst for

polymerisation of different cyclic olefins, such as cyclooctene, cyclopentene and norbornene derivatives and the preparation of interesting ring-closing products. Although the reactivity is less pronounced as the corresponding benzyldiene analogues, they can be used for practical purposes because of the following reasons: they are readily available from commercial products such as alkynes, PCy<sub>3</sub>, imidazolium salts and [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub>, the produced polymers are soluble in chloroform and the corresponding polydispersities are comparable with well-established olefin-metathesis catalysts, the complexes are long-lived and extremely tolerant toward oxygen and moisture.

In a second part, we have demonstrated that the ruthenium(II) Schiff-base vinylidene complexes can successfully be implemented in the series of precursors for ROMP of cyclic olefins and RCM of α,ω-dienes. These complexes are easily made in high yields starting again from courant products (e.g. [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub>, alkynes, salicylaldehydes, ...) and so is the cost dramatically lowered. The formed complexes are very stable in solution and even more in the solid phase. These last two arguments are decisive in choosing a robust system that can operate in various reaction conditions.

## 4. Experimental

### 4.1. General

Unless otherwise noted, all manipulations were performed under argon atmosphere by using standard Schlenck-tube techniques. Argon was first dried by passing through a P<sub>2</sub>O<sub>5</sub> (Aldrich, 97%) column. <sup>1</sup>H (299, 89 MHz) <sup>13</sup>C (75, 41 MHz) and <sup>31</sup>P-NMR (121, 40 MHz) spectra were recorded on a Varian Unity 300 spectrometer. NMR chemical shifts are reported downfield from tetramethylsilane (TMS) as the internal standard for proton en carbon NMR spectra and phosphoric acid for phosphorus spectra. Elemental analyses were carried out on a Carlo-Erba EA 1110. GC–MS analysis is performed using a Varian 4600 GC coupled with a Finnigan MAT mass spectrometer. The molecular weights and the molecular weight distribution of the polymers were determined by Gel Permeation Chromatography (CHCl<sub>3</sub>, 25 °C) using a

Waters Maxima 820 system equipped with a PL gel column (60 cm,  $\varnothing = 7.5$  mm) and the calibration was performed using polystyrene standards. IR spectra were taken with a Mattson 5000 FTIR spectrometer. Dichloromethane was dried over CaO, toluene and THF were dried over sodium/benzophenone. These solvents were distilled and stored over molecular sieves (MS4A) under an argon atmosphere.  $\text{CDCl}_3$  and  $\text{C}_6\text{D}_6$  were dried over MS4A and stored under argon.

$[\text{RuCl}_2(p\text{-cymene})]_2$  was prepared according to the literature [18]. Norbornene was dried over sodium, vacuum transferred and stored under argon. The substituted norbornene derivatives were obtained from INEOS N.V. in high purity (>99.9%) and used as received. The other products are obtained from Aldrich and used as received. Complexes **9**, **10** and **13**, **14** were synthesized according to literature procedures [14c]. The vinylidene complexes  $\text{Cl}_2\text{Ru}\{\text{C}=\text{C}(\text{H})\text{Ph}\}(\text{PCy}_3)_2$  and  $\text{Cl}_2\text{Ru}\{\text{C}=\text{C}(\text{H})^t\text{But}\}(\text{PCy}_3)_2$  were also prepared according well-established methods [15].

#### 4.2. Synthesis $\text{Cl}_2\text{Ru}\{\text{C}=\text{C}(\text{H})\text{SiMe}_3\}(\text{PCy}_3)_2$

To a suspension of  $[\text{RuCl}_2(\text{kern}1\text{tp-cymene})]_2$  (0.72 g, 1.17 mmol) in 45 ml toluene, the phosphine  $\text{PCy}_3$  (1.32 g, 4.7 mmol) was added and stirred at room temperature. The mixture instantly changed into a reddish brown solution.  $\text{Me}_3\text{SiC}=\text{CH}$  (3.34 ml, 23.5 mmol) was added and the solution was stirred for 1 h at room temperature. The solution instantly darkened to a dark red solution. After 1 h, the temperature was gradually risen to  $60^\circ\text{C}$  and stirred during one night. The analytical pure compound was obtained (65% yield) after washing the crude product with methanol.  $\text{Cl}_2\text{Ru}\{\text{C}=\text{C}(\text{H})\text{SiMe}_3\}(\text{PCy}_3)_2$ :  $^1\text{H-NMR}$  (299.89 MHz,  $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ )  $\delta$  3.65 (dt,  $J_{(\text{RuH})} = 1.9$  Hz,  $J_{(\text{PH})} = 2.8$  Hz,  $^1\text{H}$ ,  $=\text{CHSiMe}_3$ ), 2.68–2.59, 2.13–1.97, 1.89–1.64, 1.26–1.16 (each m, 66H,  $\text{PCy}_3$ ), 0.29 (s, 9H,  $\text{SiCH}_3$ ).  $^{13}\text{C-NMR}$  (75.41 MHz,  $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ )  $\delta$  274.30 (dt,  $J_{(\text{RuH})} = 57.2$  Hz,  $J_{(\text{PC})} = 15$  Hz,  $\text{Ru}=\text{C}=\text{C}$ ), 81.20 (dt,  $J_{(\text{RuH})} = 16$  Hz,  $J_{(\text{PC})} = 5$  Hz,  $\text{Ru}=\text{C}=\text{C}$ ), 35.46 (pseudo triplet,  $J = 8.7$  Hz,  $\text{C}^1$  of  $\text{PCy}_3$ ), 30.14 (s,  $\text{C}^{3,5}$  of  $\text{PCy}_3$ ), 27.83 (pseudo triplet,  $J = 4.2$  Hz,  $\text{C}^{2,6}$  of  $\text{PCy}_3$ ), 26.35 (s,  $\text{C}^4$  of  $\text{Pcy}$ ).  $^{31}\text{P-NMR}$   $\{^1\text{H}\}$  (121.40 MHz,  $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ , ref.  $\text{H}_3\text{PO}_4$ )  $\delta$  31.50

(s). IR (KBr):  $\nu(\text{C}=\text{C})$   $1630\text{ cm}^{-1}$ , Anal. Calcd. for  $\text{C}_{41}\text{H}_{76}\text{Cl}_2\text{P}_2\text{SiRu}$ : C, 59.26; H, 9.58. Found: C, 59.52; H, 10.10.

#### 4.3. Synthesis of complexes **6–8**

A typical procedure for the preparation of complexes **6–8** is as follows. A 400 ml flame-dried Schlenk flask equipped with a magnetic stirrer was charged with 4,5-dihydroimidazol-2-ylidene tetrafluoroborate salt (4.0 g, 10.2 mmol, STREM) and 50 ml dry THF. A solution of potassium *tert*-butoxide was slowly added (10.2 ml, 1 M in ether, Aldrich) to the rapidly stirred suspension. The tetrafluoroborate salt immediately dissolved to give a light yellow solution. The reaction was allowed to stir at room temperature for 1 h. This solution was then transferred to another Schlenk flask via cannula where already 200 ml toluene was added. After 5 min, the vinylidene complex ( $\text{Cl}_2(\text{PCy}_3)_2\text{Ru}(\text{C}=\text{CHR})$ ) (7.2 mmol) was added and the mixture was heated to  $70^\circ\text{C}$  for 1 h and subsequently cooled to room temperature. The volatiles were removed under high vacuum, and the residue was washed with anhydrous methanol ( $4 \times 10$  ml).

*Selected data for complex 6:*  $^1\text{H-NMR}$  (299.89 MHz,  $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ )  $\delta$  7.13–7.06, 7.0–6.85, 6.8–6.73 (m, 5H, Ph), 7.04 (br, 2H, Mes), 6.83 (br, 2H, Mes), 3.92 (t,  $J_{\text{PH}} = 4.3$  Hz, 1H, CHPh), 3.61 (s, 4H, imidazolium), 2.79–2.67 (m, 3H,  $\text{C}^1$   $\text{PCy}$ ), 2.10–2.01, 1.63, 1.23–1.15 (m, 30H,  $\text{PCy}$ ).  $^{31}\text{P-NMR}$   $\{^1\text{H}\}$  (121.40 MHz,  $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ , ref.  $\text{H}_3\text{PO}_4$ )  $\delta$  21.42 (s). IR (KBr):  $\nu(\text{C}=\text{C})$   $1640\text{ cm}^{-1}$ , Anal. Calcd. for  $\text{C}_{47}\text{H}_{65}\text{N}_2\text{Cl}_2\text{PRu}$ : C, 65.57; H, 7.61; N, 3.25. Found: C, 66.03; H, 8.03; N, 3.81.

*Selected data for complex 7:*  $^1\text{H-NMR}$  (299.89 MHz,  $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ )  $\delta$  7.03–6.96 (br, 2H, Mes), 6.92–6.86 (br, 2H, Mes), 3.49 (s, 4H, imidazolium), 2.44–2.103, 1.99–1.84 (br, 18H, Mes), 2.12 (m, 3H,  $\text{C}^1$   $\text{PCy}_3$ ), 1.55–1.52, 1.39, 1.02–0.96 (m, 30H,  $\text{PCy}$ ) 0.046 (s, 9H,  $\text{SiCH}_3$ ),  $-0.147$  (dt,  $J_{(\text{RuH})} = 1.9$  Hz,  $J_{(\text{PH})} = 2.8$  Hz, 1H,  $=\text{CHSiMe}_3$ ).  $^{31}\text{P-NMR}$   $\{^1\text{H}\}$  (121.40 MHz,  $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ , ref.  $\text{H}_3\text{PO}_4$ )  $\delta$  28.03 (s). IR (KBr):  $\nu(\text{C}=\text{C})$   $1634\text{ cm}^{-1}$ , Anal. Calcd. for  $\text{C}_{44}\text{H}_{69}\text{N}_2\text{Cl}_2\text{PSiRu}$ : C, 61.66; H, 8.11; N, 3.27. Found: C, 62.28; H, 9.03; N, 3.86.

*Selected data for complex 8:*  $^1\text{H-NMR}$  (299.89 MHz,  $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ )  $\delta$  7.09–6.96 (br, 2H, Mes), 6.92–6.82

(br, 2H, Mes), 3.55–3.51 (m, 4H, imidazolium), 2.33 (t,  $J_{\text{PH}} = 4$  Hz, 1H, =C=CHCMe<sub>3</sub>), 2.24–2.08, 1.95–1.90 (br, 18H, Mes), 2.05 (m, 3H, C<sup>1</sup> PCy<sub>3</sub>), 1.56–1.52, 1.50, 1.44–1.35 (m, 30H, PCy), 1.1 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>31</sup>P-NMR {<sup>1</sup>H} (121.40 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, ref. H<sub>3</sub>PO<sub>4</sub>) δ 17.33 (s). IR (KBr): ν(C=C) 1638 cm<sup>-1</sup>, Anal. Calcd. for C<sub>45</sub>H<sub>69</sub>N<sub>2</sub>Cl<sub>2</sub>PRu: C, 64.27; H, 8.27; N, 3.33. Found: C, 64.89; H, 8.60; N, 3.99.

#### 4.4. Synthesis of complex **11** and **12**

To a solution of Cl<sub>2</sub>Ru{=C=CHSiMe<sub>3</sub>}(PCy<sub>3</sub>)<sub>2</sub> (2.5 g, 3 mmol) in THF (5 ml) was added a solution of the corresponding Ti-salt of the salicylalimine in 10 ml THF [18]. The reaction mixture was stirred at room temperature for 4 h. The formed TiCl was removed via filtration. The solid residue was recrystallized from pentane at -70 °C to give the Ru Schiff-base complex **11**, **12** as a dark brown solid. Selected data for complex **11** brown solid (81%): <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 7.53 (d,  $J = 5.5$  Hz, 1H), 7.24–7.055 (m, 6H), 3.57 (t,  $J = 4.2$  Hz, Ru=C=CHSiMe<sub>3</sub>), 2.48 (s, 3H), 1.72–1.27 (m, 20H), 1.27 (s, 6H), 1.19 (m, 10H), 0.305 (s, 9H, SiMe<sub>3</sub>); <sup>31</sup>P-NMR {<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 43.51 Hz (s), Anal. Calcd. for C<sub>38</sub>H<sub>56</sub>BrClN<sub>2</sub>OPRuSi: C, 55.77; H, 6.90; N, 1.71. Found: C, 56.13; H, 7.12; N, 1.83.

Selected data for complex **12** dark brown solid (80%): <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 8.24 (d,  $J = 2.5$  Hz, 1H), 8.10–7.11 (m, H), 3.61 (t,  $J = 5$  Hz, Ru=C=CHSiMe<sub>3</sub>), 2.51 (s, 3H), 1.78–1.30 (m, 20H), 1.54 (s, 6H), 0.32 (s, 9H, SiMe<sub>3</sub>); <sup>31</sup>P-NMR {<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 47.07 Hz (s), Anal. Calcd. for C<sub>38</sub>H<sub>55</sub>BrClN<sub>2</sub>O<sub>3</sub>PRuSi: C, 52.86; H, 6.42; N, 3.24. Found: C, 53.10; H, 6.62; N, 3.37.

#### 4.5. ROMP of substituted norbornenes **8–19**

Norbornene (1.2 g, 12.75 mmol) was dissolved in toluene (2.0 ml) and treated with a solution of catalyst **6–8** (64 μl, 0.1 M, 0.0064 μmol) in toluene. Then the vessels were flushed with argon and kept at a constant temperature of 60 °C in an oil bath. After 5 min the mixture was transferred in a beaker and treated with CH<sub>2</sub>Cl<sub>2</sub> (10 ml) containing 2,6-di-*tert*-butyl-4-methylphenol (0.04 mmol) and ethylvinylether (0.4 mmol). The resulting solutions

were stirred for 1 h and after filtration through a short silica gel columns, precipitated into vigorously stirred methanol. The white, tacky polymer obtained in this way was filtrated, washed with methanol and dried under vacuum. An analogous procedure was used with the other monomers (12.8 mmol), cyclopentene (25.6 mmol) and cyclooctene (32 mmol). An analogous procedure was followed for complexes **9–14** however in this case 5.12 mmol of the norbornenes and 1.6 mmol cyclooctene were used at 80 °C.

#### 4.6. Ring-closing metathesis of α,ω-dienes

In a 10 ml Schlenck-tube, 0.095 mmol substrate, 13.2 μl (0.095 mmol) mesitylene, and 50 μl of a 0.1 stock solution of catalyst were added to 1 ml of benzene-d<sub>6</sub> and heated with stirring to 70 or 80 °C (as mentioned in Table 3). The formed ethylene was removed in vacuo at 10 min intervals. After 2 h, the solution was cooled to room temperature and was poured into an NMR tube. The yields are determined with <sup>1</sup>H-NMR analysis by integration of allylic protons. The formation of cyclo-isomers, oligomers or telomers was ruled out by GC-MS analysis of the reaction mixture. The reaction products were identified by purification of the concentrated reaction mixture by flash column chromatography over a silica gel column (hexane:ethylacetate = 6:1,  $R_f = 0.3$ ).

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