

# Controlled Radical Polymerization of Vinyl Monomers Catalyzed by Ruthenium *N*-Heterocyclic Carbene Complexes

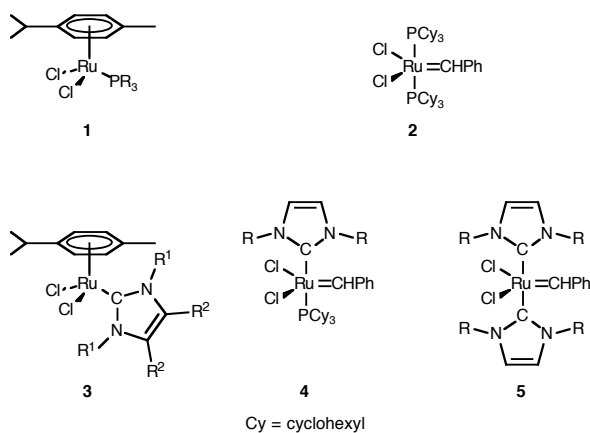
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The relative catalytic activities of a series of ruthenium-based complexes of the general formula  $[\text{RuCl}_2(p\text{-cymene})(\text{NHC})]$ ,  $[\text{RuCl}_2(=\text{CHPh})(\text{PR}_3)(\text{NHC})]$ , and  $[\text{RuCl}_2(=\text{CHPh})(\text{NHC})_2]$  (NHC is a *N*-heterocyclic carbene ligand) were determined by investigating the atom transfer radical polymerization (ATRP) of methyl methacrylate and styrene. The catalytic activity of a variety of related  $[\text{RuCl}(\text{O}^{\wedge}\text{N})(=\text{CHR})(\text{NHC})]$  complexes and of their cationic counterparts,  $[\text{Ru}(\text{O}^{\wedge}\text{N})(=\text{CHR})(\text{NHC})]^+ \text{BF}_4^-$  (R = Ph or OEt,  $\text{O}^{\wedge}\text{N}$  is a Schiff base ligand), is also reported. The results clearly demonstrate that, with both methyl methacrylate and styrene, subtle modifications of the substituents of the NHC ligand lead to dramatic changes in the ability of the resulting ruthenium complexes to favor the occurrence of a well-behaved ATRP.

The ability to control molecular architecture constitutes a major challenge for synthetic polymer chemists. Controlled radical polymerization has in recent years revitalized the rather mature field of radical olefin polymerization in an unprecedented way, and has provided access to well-defined polymers and copolymers. Stable free radicals, such as nitroxides, have been introduced for control of radical polymerization. In 1995, Sawamoto (1) and Matyjaszewski (2) have replaced the stable nitroxide free radical with transition metal species to obtain, respectively, a variety of ruthenium- and copper-mediated controlled radical polymerization systems, a methodology which goes by the name of atom transfer radical polymerization (ATRP).

Back in 1999, we found that the 18-electron complexes  $[\text{RuCl}_2(p\text{-cymene})(\text{PR}_3)]$  (*p*-cymene = 4-isopropyltoluene) (1) were highly efficient catalytic systems for promotion of the controlled radical polymerization of vinyl monomers, such as methyl methacrylate (Table 1) and styrene (Table 2) (3).



**Scheme 1.** Ruthenium-*p*-cymene and ruthenium-benzylidene complexes bearing either phosphine or NHC ligands

**Table 1.** Polymerization of Methyl Methacrylate Initiated by Ethyl 2-Bromo-2-methylpropionate and Catalyzed by Ruthenium Complexes 1 and 2

Complex	Polymer yield (%)	$M_n$	$M_w/M_n$	$f$
<b>1a</b> (PR <sub>3</sub> = PPh <sub>3</sub> )	20	25 000	1.6	0.3
<b>1b</b> (PR <sub>3</sub> = PPh <sub>2</sub> Cy)	58	41 000	1.25	0.55
<b>1c</b> (PR <sub>3</sub> = PPhCy <sub>2</sub> )	90	60 500	1.10	0.6
<b>1d</b> (PR <sub>3</sub> = PCy <sub>3</sub> )	100	41 500	1.12	0.95
<b>1e</b> (PR <sub>3</sub> = <i>i</i> Pr <sub>3</sub> )	80	40 500	1.10	0.8
<b>2</b>	95	66 000	1.28	0.6

It appeared that only basic and bulky phosphines, such as dicyclohexylphenylphosphine (**1c**), tricyclohexylphosphine (**1d**), and triisopropylphosphine (**1e**) presented both high catalytic activity and high control of the polymerization process (high initiation efficiency,  $f$ , and low molecular weight distribution,  $M_w/M_n = 1.1$ ). Under these experimental conditions, all the criteria of living polymerization were fulfilled. Indeed, the plots of  $\ln([M]_0/[M])$  vs. time and of  $M_n$  vs. monomer conversion were linear. Furthermore, the control of the polymerizations was confirmed by the addition of a second equivalent of monomer feed to the completely polymerized system. This second polymerization reaction was also quantitative, and only a slight increase in polydispersity was observed.

Surprisingly, the best catalyst systems for ATRP have been shown to be also the most active ones for the ring-opening metathesis polymerization (ROMP) of strained and low-strain cycloolefins (**4**). In both reactions, the same stereoelectronic requirements for the phosphine ligand of the ruthenium complex have been demonstrated. This observation prompted us to test  $[\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2]$ , **2**, the Grubbs ruthenium-carbene complex commonly used for olefin metathesis (**5**), as a catalyst for the radical polymerization of methyl methacrylate (Table 1) and styrene (Table 2).

**Table 2. Polymerization of Styrene Initiated by (1-Bromoethyl)benzene and Catalyzed by Ruthenium Complexes 1 and 2**

Complex	Polymer yield (%)	$M_n$	$M_w/M_n$	$f$
<b>1a</b> (PR <sub>3</sub> = PPh <sub>3</sub> )	39	26 000	1.8	0.6
<b>1b</b> (PR <sub>3</sub> = PPh <sub>2</sub> Cy)	45	20 000	1.7	0.85
<b>1c</b> (PR <sub>3</sub> = PPhCy <sub>2</sub> )	48	19 500	1.45	0.95
<b>1d</b> (PR <sub>3</sub> = PCy <sub>3</sub> )	64	28 500	1.3	0.85
<b>1e</b> (PR <sub>3</sub> = <i>Pi</i> Pr <sub>3</sub> )	40	15 500	1.2	1.0
<b>2</b>	61	29 000	1.38	0.8

The same protocol was followed for all the polymerization tests. Polymerization of methyl methacrylate: Ruthenium complex (0.0117 mmol) was placed in a glass tube containing a bar magnet and capped by a three-way stopcock. The reactor was purged of air (three vacuum–nitrogen cycles) before methyl methacrylate (1 mL, 9.35 mmol) and the initiator (ethyl 2-bromo-2-methylpropionate 0.1 M in toluene, 0.232 mL) were added ([MMA]<sub>0</sub>:[initiator]<sub>0</sub>:[Ru]<sub>0</sub> = 800:2:1). The mixture was heated in a thermostated oil bath for 16 h at 85 °C and, after cooling, dissolved in THF and the product precipitated in heptane. The polymer was filtered off and dried overnight under vacuum. The same procedure was used for the polymerization of styrene ([styrene]<sub>0</sub>:[initiator]<sub>0</sub>: [Ru]<sub>0</sub> = 750:2:1), except that the initiator was (1-bromoethyl)benzene, the temperature of the oil bath was 110 °C, and the solvent used for precipitation of the polymer was technical methanol.

$M_n$  and  $M_w/M_n$  were determined by size-exclusion chromatography with PMMA and polystyrene calibrations.

Initiation efficiency,  $f = M_{n, \text{theor.}}/M_{n, \text{exp.}}$  with  $M_{n, \text{theor.}} = ([\text{monomer}]_0/[\text{initiator}]_0) \times M_w(\text{monomer}) \times \text{conversion}$ .

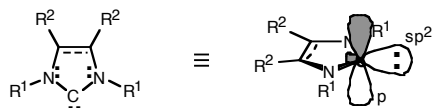
Gratifyingly, the Grubbs complex was found to be also active in ATRP, and even more active than [RuCl<sub>2</sub>(*p*-cymene)(PCy<sub>3</sub>)], **1d**, but to the detriment of polymer control (3).

Since ATRP is based on a dynamic equilibration between active propagating radicals and dormant species, it is anticipated that catalytic engineering at the metal center should shift this equilibrium to the most suitable position, so as to maintain a low concentration of propagating radicals while keeping a useful rate of polymerization for polymers to be obtained on a sensible time-scale. To further improve the catalyst efficiency in the ATRP process, we have launched an investigation on the role of the ligands associated to ruthenium.

In recent years, *N*-heterocyclic carbenes (NHCs) (**6**) have frequently been used as phosphine-substitutes for late transition metal catalysts and in many cases, an improved catalytic performance of the NHC-complexes was observed, such as in olefin metathesis (**7**) or in various palladium-catalyzed C–C coupling reactions, in particular the Heck, Suzuki, and Kumada reactions. The present contribution is aiming at illustrating how replacement of the phosphine(s) in complexes **1** and **2** by *N*-heterocyclic carbene ligands (→ **3–5**, Scheme 1) influences ATRP of vinyl monomers.

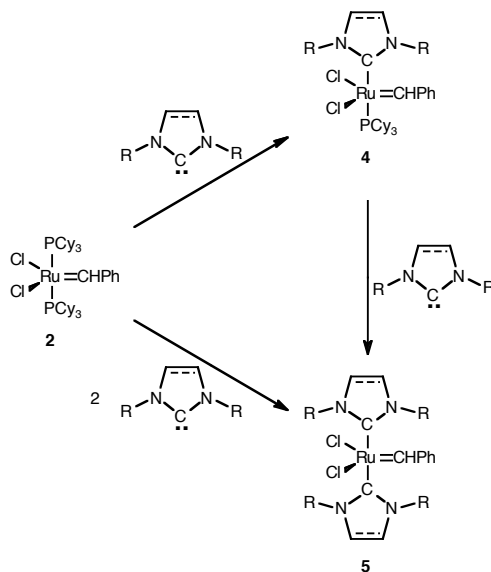
## *N*-Heterocyclic Carbenes vs. Phosphines

The electronic structure of the carbene center of a *N*-heterocyclic carbene can be seen as a strongly bent singlet carbene in which the carbene carbon is approximately  $sp^2$  hybridized (Scheme 2) (8).



**Scheme 2.** Structure of a *N*-heterocyclic carbene

The two substituents and a lone pair of electrons occupy the three  $sp^2$ -hybrid orbitals and a formally vacant p-orbital remains at carbon. The lone pair of electrons on carbon behaves chemically similar to the lone pair of electrons on phosphorous in phosphines. Guided by this simple analogy, organometallic chemists have successfully replaced the ubiquitous phosphine ligand with a NHC in a large number of organometallic complexes. However, the real strength and versatility of the new NHC ligands rest not in their similarity with phosphines, but rather in how they differ from the more conventional phosphines and in the new structural and electronic features they can introduce. In this latter respect, NHCs have their own special features to offer over phosphines. The coordinating lone pair of electrons in a NHC is harder and more basic than a phosphine lone pair. Thus, the reaction of traditional Grubbs complexes **2** and **4** with NHCs leads ultimately to the related bis(NHC) complex **5**, demonstrating experimentally the strong  $\sigma$ -donor properties of NHCs over phosphines (Scheme 3).



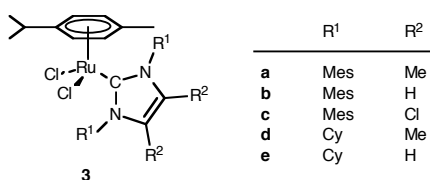
**Scheme 3.** Synthesis and reactivity of ruthenium–NHC complexes **4** and **5**

On the other hand, the formally vacant p-orbital at the carbene center has the potential to function as a weak  $\pi$ -acceptor, but has different directional character than P–X  $\sigma^*$ -bonds (or d-orbitals) on a phosphine. The planar NHCs also present a steric profile that is greatly different from that of phosphines.

Within the last decade, numerous variations of the basic NHC structure have appeared and have found application in modern catalysis as carbene–metal complexes. However, in contrast to phosphine-based transition metal catalysts, NHC-based catalysts exhibit longer lifetimes in catalytic cycles, which may be due to better retention of the NHC ligands over their phosphine analogues on the metal center. Furthermore, NHC complexes generally possess better stability against air and moisture than their phosphine analogues.

### Ruthenium–*p*-Cymene Complexes Bearing a NHC Ligand

Polymerization of methyl methacrylate initiated by ethyl 2-bromo-2-methylpropionate and ruthenium–NHC complexes **3a–f** was investigated at 85 °C under inert atmosphere.

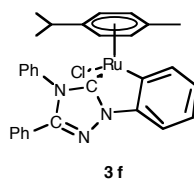


Mes = 2,4,6-trimethylphenyl (mesityl), Cy = cyclohexyl

**Scheme 4.** Ruthenium–*p*-cymene complexes bearing a NHC ligand

Complexes **3b** and **3c** with R<sup>1</sup> = mesityl and R<sup>2</sup> = H or Cl, respectively, were the most efficient catalysts for this reaction (Table 3). The semilogarithmic plots of  $\ln([M]_0/[M])$  vs. time were linear in both cases with a pseudo-first order rate constant ( $k_{app}$ ) of  $10.6 \times 10^{-6} \text{ s}^{-1}$  for **3b** and  $3.85 \times 10^{-6} \text{ s}^{-1}$  for **3c**, indicating that the radical concentration remained constant throughout the polymerization run (Figure 1b). With these two complexes, the molecular weights increased linearly with conversion, indicative of a good control over  $M_n$  (Figure 1c). Polydispersities ( $M_w/M_n$ ) were quite low (typically *ca.* 1.3) and decreased with monomer conversion (Figure 1d). By contrast, complex **3a** displayed an induction period after which the semilogarithmic plot was almost linear ( $k_{app} = 16.4 \times 10^{-6} \text{ s}^{-1}$ ) (Figure 1a). Furthermore,  $M_n$  did not increase linearly with conversion and did not agree with theoretical values (Figure 1c) (9).

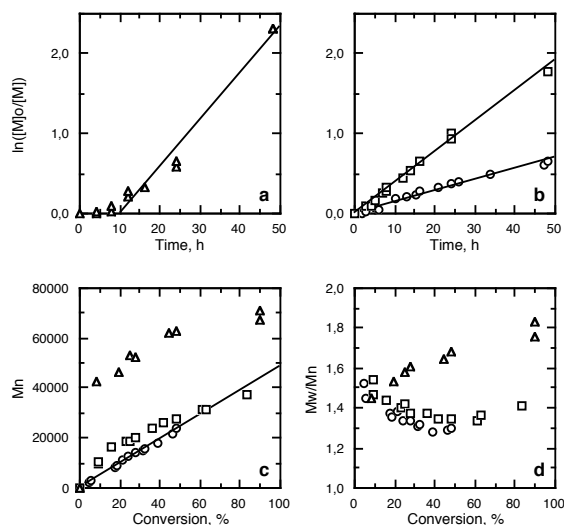
When styrene was subjected to ATRP, complex **3e** proved to be the most efficient catalyst (Table 4). The polymerization was well controlled as indicated by the linearity of the plots of  $\ln([M]_0/[M])$  vs. time (Figure 2a) and of  $M_n$  vs. conversion (Figure 2b). Accordingly,  $M_w/M_n$  decreased steadily with time and reached a low of 1.25 upon completion of the reaction (Figure 2c). All the other R<sup>1</sup>–R<sup>2</sup> combinations tested resulted in poorly or uncontrolled polymerizations. Indeed, replacement of hydrogen atoms by methyl groups on both olefinic carbons of the NHC ligand dramatically altered the course of the reaction.



**Scheme 5.** Ruthenium-*p*-cymene complex bearing an *ortho*-metallated NHC ligand (11)

**Table 3. Polymerization of Methyl Methacrylate Initiated by Ethyl 2-Bromo-2-methylpropionate and Catalyzed by Ruthenium Complexes 3**

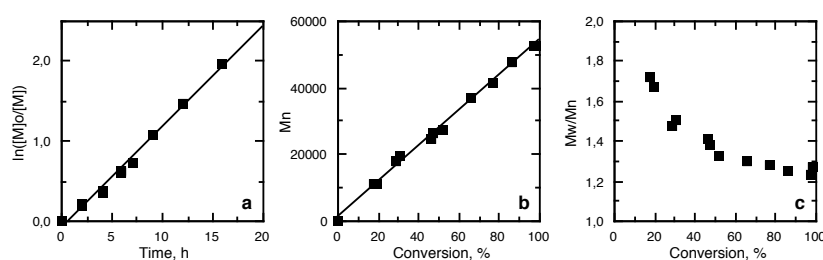
Complex	Polymer yield (%)	$M_n$	$M_w/M_n$	$f$
<b>3a</b>	28	52 000	1.6	0.2
<b>3b</b>	49	28 000	1.35	0.7
<b>3c</b>	24	12 900	1.33	0.75
<b>3d</b>	94	160 000	2.45	0.25
<b>3e</b>	51	36 000	1.75	0.55
<b>3f</b>	100	52 000	2.0	0.75



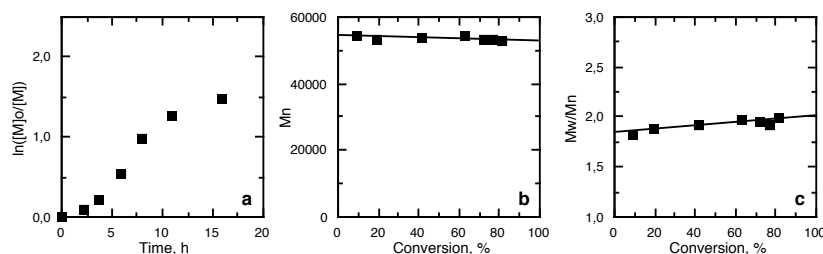
**Figures 1, a and b.** Time dependence of  $\ln([M]_0/[M])$  for the polymerization of MMA catalyzed by complexes **3a** ( $\Delta$ ), **3b** ( $\square$ ), and **3c** ( $\circ$ ). **Figures 1, c and d.** Dependence of the PMMA molecular weight  $M_n$  and molecular weight distribution  $M_w/M_n$  on monomer conversion for the polymerization of MMA catalyzed by complexes **3a** ( $\Delta$ ), **3b** ( $\square$ ), and **3c** ( $\circ$ ) (see Table 3).

**Table 4. Polymerization of Styrene Initiated by (1-Bromoethyl)benzene and Catalyzed by Ruthenium Complexes 3**

Complex	Polymer yield (%)	$M_n$	$M_w/M_n$	$f$
<b>3a</b>	66	53 000	1.75	0.5
<b>3b</b>	51	28 000	1.8	0.7
<b>3c</b>	10	10 200	1.9	0.4
<b>3d</b>	77	53 000	1.9	0.55
<b>3e</b>	86	47 000	1.25	0.7



**Figure 2.** (a) Time dependence of  $\ln([M]_0/[M])$  for the polymerization of styrene catalyzed by complex **3e**. (b) Dependence of the polystyrene molecular weight  $M_n$  and (c) molecular weight distribution  $M_w/M_n$  on monomer conversion for the polymerization of styrene catalyzed by complex **3e** (see Table 4).



**Figure 3.** (a) Time dependence of  $\ln([M]_0/[M])$  for the polymerization of styrene catalyzed by complex **3d**. (b) Dependence of the polystyrene molecular weight  $M_n$  and (c) molecular weight distribution  $M_w/M_n$  on monomer conversion for the polymerization of styrene catalyzed by complex **3d** (see Table 4).

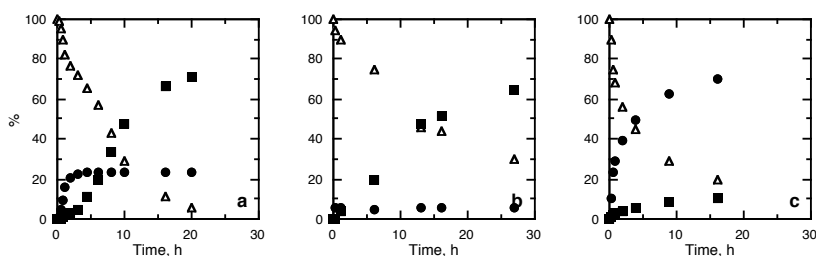
With complex **3d**, the semilogarithmic plot of  $\ln([M]_0/[M])$  vs. time was no longer linear (Figure 3a), and  $M_n$  as well as  $M_w/M_n$  remained constant ( $\approx 55\ 000$  and 1.9, respectively) throughout the run (Figure 3, b and c). A similar trend was observed for the polymerization of MMA using **3e** ( $M_n \approx 35\ 000$  and  $M_w/M_n \approx 1.75$ , cf. Table 3), indicating that both reactions were most likely taking place through a redox-initiated free radical process (9).

**Table 5. Polymerization vs. Metathesis of Styrene in the Presence of (1-Bromoethyl)benzene and Ruthenium Complexes 3**

$\text{Ph-CHBr-CH}_3$   
**3 a-e**  
 110 °C, 16 h

Polymerization:  $\text{H}_3\text{C} \left[ \text{C}(\text{Ph})_n \text{Br} \right]$   
 Metathesis:  $\text{Ph-CH=CH-Ph} + \text{C}_2\text{H}_4$

Complex	Polymer yield (%)	Metathesis (%)
<b>3a</b>	66	25
<b>3b</b>	51	5
<b>3c</b>	10	70
<b>3d</b>	77	0
<b>3e</b>	86	0



**Figure 4.** Time dependence of styrene ( $\Delta$ ), polystyrene ( $\blacksquare$ ), and stilbene ( $\bullet$ ) in the presence of catalysts **3a** (a), **3b** (b), and **3c** (c) (see Table 5).

An important result in the frame of this discussion was that styrene underwent metathesis in addition to radical polymerization when ruthenium–NHC catalyst precursors bearing  $R^1$  mesityl groups were present in the reaction medium (Table 5). Thus, *cis*- and *trans*-stilbene (the latter isomer being largely predominant) were obtained in varying proportions according to the  $R^2$  substituents (Table 5). With complexes **3a** ( $R^2 = \text{Me}$ ) and **3b** ( $R^2 = \text{H}$ ), stilbene formation accounted for 25 and 5 % of the monomer conversion, respectively, whereas ATRP gave rise to polystyrene in 66 and 51 % yields, respectively. With complex **3c** ( $R^2 = \text{Cl}$ ), olefin metathesis took the precedence over polymerization and afforded a 70 % yield of stilbene after 16 h at 110 °C. Within the same period, a mere 10 % polymer yield was obtained. Furthermore, examination of the evolution of the reaction products, polystyrene and stilbene, vs. time (Figure 4) indicated that in all cases, in the early stages of the reaction, metathesis of styrene was much faster than polymerization. However, the metathetic activity of catalyst **3b** dropped rapidly to the benefit of the polymerization, whereas with **3c**, a high metathetic activity was maintained throughout the reaction. Under the same conditions, catalyst **3a** displayed a borderline reactivity profile.

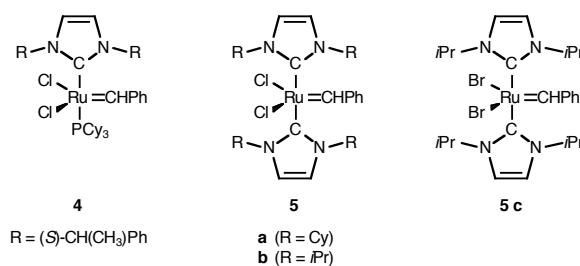
Interestingly, complexes **3d** and **3e** bearing *N*-cyclohexyl-substituted NHC ligands were devoid of any significant activity for the metathesis of styrene and initiated only the radical polymerization process, with a very good control in the case of **3e**. Therefore,



with both methyl methacrylate and styrene, subtle modifications of the R<sup>1</sup> and R<sup>2</sup> substituents led to dramatic changes in the ability of the resulting ruthenium complexes to favor the occurrence of a well-behaved ATRP.

### Ruthenium–Benzylidene Complexes Bearing NHC Ligands

In a first set of experiments, we checked the catalytic activity of ruthenium benzylidenes **2**, **4**, and **5** with methyl methacrylate (Table 6) (12). All of the complexes were found to catalyze the polymerization of MMA in high yield and in a fairly well controlled way, although significant differences in their behavior were noticed.



**Scheme 6.** Ruthenium–benzylidene complexes bearing NHC ligands

**Table 6. Polymerization of Methyl Methacrylate Initiated by Ethyl 2-Bromo-2-methylpropionate and Catalyzed by Ruthenium Complexes 2, 4 and 5**

Complex	Polymer yield (%)	$M_n$	$M_w/M_n$	$f$
<b>2</b>	95	66 000	1.28	0.6
<b>4</b>	85	58 000	1.35	0.6
<b>5a</b>	99	42 000	1.47	0.95
<b>5b</b>	90	43 000	1.6	0.85
<b>5c</b>	97	49 500	1.47	0.8

**Table 7. Polymerization of Styrene Initiated by (1-Bromoethyl)benzene and Catalyzed by Ruthenium Complexes 2, 4 and 5**

Complex	Polymer yield (%)	$M_n$	$M_w/M_n$	$f$
<b>2</b>	61	29 000	1.38	0.8
<b>4</b>	48	22 000	1.6	0.85
<b>5a</b>	89	39 000	1.53	0.9
<b>5b</b>	78	36 000	1.8	0.85

Thus, mixed ligand complex **4** exhibited the lowest activity, whereas little difference was observed between bis(NHC) complexes **5a** (R = Cy) and **5b** (R = *i*Pr); both of them afforded PMMA possessing essentially the same features ( $M_n$  and  $M_w/M_n$ ). Complex **2** bearing two PCy<sub>3</sub> ligands gave the narrowest molecular weight distribution ( $M_w/M_n = 1.28$ ), although the molecular weight was higher than the calculated value ( $f = 0.6$ ). Broader  $M_w/M_n$  values resulted from substitution of one or both PCy<sub>3</sub> by a *N*-heterocyclic carbene. With complexes **5**,  $M_n$  were fairly well controlled by the monomer to the initiator ratio ( $f \approx 0.9$ ).

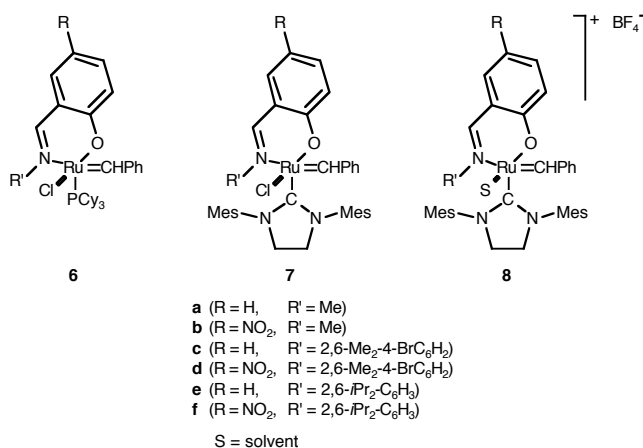
Complexes **2**, **4**, and **5** also polymerized styrene (Table 7). With complex **2**, a smooth polymerization took place. The conversion reached 61 % in 16 h, with a molecular weight distribution near 1.4.  $M_w/M_n$  were however broader for polystyrenes obtained using ruthenium–NHC complexes **4** and **5** ( $M_w/M_n = 1.55$ – $1.8$ ).

A mechanistic investigation revealed that ATRP was mediated by ruthenium species bereft of the benzylidene moiety (12). Indeed, as monitored by <sup>1</sup>H-NMR at 85 °C, under conditions mimicking polymerization of MMA, complete disappearance of the benzylidene fragment of complex **4** was observed within 20 min., whereas complexes **2** and **5b** showed 55 and 88 % decomposition, respectively, over the same period of time.

### Ruthenium–Benzylidene Complexes Bearing Schiff Base and NHC Ligands

In recent years, Schiff base ligands have been used extensively in homogeneous catalysis due to their very attractive properties. Indeed, Schiff bases are easily accessible through one-step procedures *via* almost quantitative condensation of an aldehyde with an amine. These O,N-bidentate ligands are also more resistant to oxidation than phosphines. Furthermore, the steric and electronic properties of Schiff base ligands can be easily modulated by varying the nature, the number and the position of the substituents in the compound, offering therefore ample possibilities for catalyst engineering and fine tuning. 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 the metal whereas the imine nitrogen is a softer one and, accordingly, will rather stabilize the lower oxidation state of the metal.

Quite recently, Verpoort extended our approach to Schiff base–ruthenium complexes bearing either tricyclohexylphosphine (**6**) or NHC (imidazolinyldene) ligands (**7** and **8**) (13). On performing ATRP reactions on a set of common vinyl monomers with catalyst precursors **6** and **7**, yields and polymer characteristics ( $M_n$  and  $M_w/M_n$ ) were found to depend substantially both on the precatalyst and type of the monomer. Indeed, as shown in Table 8, only complexes **6d**, **7c**, and **7d** could conveniently catalyze the polymerization of methyl methacrylate. By contrast, all precatalysts were able to convert styrene, although significant differences in their performance were observed (Table 9). With the systems exhibiting the lowest activity (**6a** and **b**, and **7a** and **b**), only 8–10 % conversion was reached, whereas the most active systems, **6d** and **7d**, efficiently converted styrene in 88 and 75 % yields, respectively. Moreover, with catalyst systems **6d** and **7d**, both PMMA (Table 8) and polystyrene (Table 9) displayed the lowest polydispersity. Furthermore, the corresponding cationic complexes **8** have also been investigated. Comparative studies on ATRP of MMA and styrene, using both toluene and water/toluene mixtures as the solvent, demonstrated that the solvent was crucial for the activity and controllability of the process. Moreover, in aqueous/organic biphasic conditions, the ruthenium cationic complexes **8** were highly active and polymers with controlled molecular weights and narrow molecular weight distributions were formed.



**Scheme 7.** Ruthenium–benzylidene complexes bearing Schiff base and NHC ligands

**Table 8. Polymerization of Methyl Methacrylate Initiated by Ethyl 2-Bromo-2-methylpropionate and Catalyzed by Ruthenium Complexes 6 and 7**

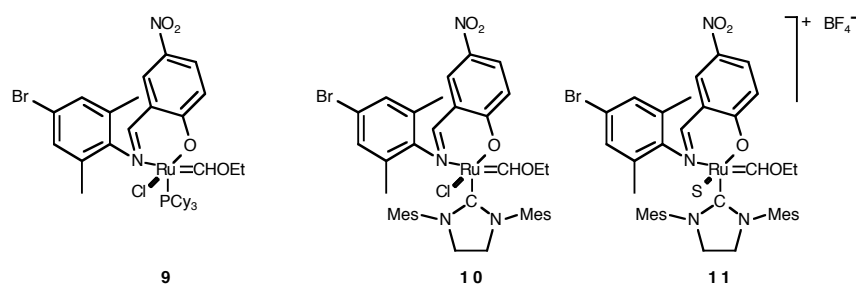
Complex	Polymer yield (%)	$M_n$	$M_w/M_n$	$f$
<b>6a</b>	<5			
<b>6b</b>	<5			
<b>6c</b>	11	6 300	1.25	0.70
<b>6d</b>	28	13 000	1.22	0.87
<b>6e</b>	7	4 800	1.56	0.51
<b>6f</b>	10	6 600	1.51	0.61
<b>7a</b>	<5			
<b>7b</b>	6			
<b>7c</b>	24	14 800	1.23	0.65
<b>7d</b>	27	13 300	1.18	0.81
<b>7e</b>	11	8 600	1.34	0.51
<b>7f</b>	15	11 600	1.31	0.52

Of note is the behavior of the Fischer-type Schiff base–ruthenium alkylidene complexes **9** and **10** (14). When tested for ATRP of MMA, catalyst **10** manifested itself as one of the most active Ru–carbene systems known to date, leading to almost quantitative conversion of the monomer. Significantly, catalyst **10** gave a polymer with a polydispersity index of 1.30 and an initiation efficiency of 0.97.

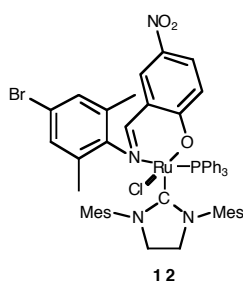
Furthermore, the cationic congener, **11**, was also very active (100 % conversion) in pure toluene and water/toluene mixtures. In both cases, the observed  $M_w/M_n$  remained relatively narrow (1.28 and 1.40, respectively). The exact mode of action of the carbene entity is not clear yet. It is presently assumed that the active ATRP species derive from

**Table 9. Polymerization of Styrene Initiated by (1-Bromoethyl)benzene and Catalyzed by Ruthenium Complexes 6 and 7**

Complex	Polymer yield (%)	$M_n$	$M_w/M_n$	$f$
<b>6a</b>	10			
<b>6b</b>	10			
<b>6c</b>	74	38 000	1.65	0.81
<b>6d</b>	88	41 000	1.44	0.89
<b>6e</b>	56	29 000	1.75	0.67
<b>6f</b>	65	32 000	1.71	0.85
<b>7a</b>	8			
<b>7b</b>	10			
<b>7c</b>	67	37 000	1.33	0.75
<b>7d</b>	75	37 000	1.25	0.84
<b>7e</b>	43	27 000	1.44	0.67
<b>7f</b>	51	33 000	1.48	0.64



**Scheme 8.** Fischer-type ruthenium–alkylidene complex bearing Schiff base and NHC ligands



**Scheme 9.** Ruthenium–triphenylphosphine complex bearing Schiff base and NHC ligands

the carbene fragment. This assumption is strongly supported by the observation that the phosphine-containing system, **12**, is inactive in ATRP (14, 15).

## Phosphines vs. *N*-Heterocyclic Carbene Ligands in ATRP: Cyclic Voltammetry Investigations

### [RuCl<sub>2</sub>(*p*-cymene)(L)] complexes, L = PR<sub>3</sub> or NHC

In order to rationalize the effect of the ligand L in [RuCl<sub>2</sub>(*p*-cymene)(L)] complexes (L = PR<sub>3</sub> (**1**) or NHC (**3**)), we investigated these complexes by means of electrochemistry (16). As indicated in Table 10, all of the [RuCl<sub>2</sub>(*p*-cymene)(PR<sub>3</sub>)] complexes (**1**) were reversibly oxidized at a potential,  $E^\circ$ , ranging from +0.570 to +0.690 V referenced to the ferrocene/ferrocenium couple. Noteworthy, a qualitative correlation could be deduced between  $E^\circ$  and [RuCl<sub>2</sub>(*p*-cymene)(PR<sub>3</sub>)]'s activities for the polymerization of MMA (Table 1). Indeed, the complexes with a lower redox potential, [RuCl<sub>2</sub>(*p*-cymene)(PR<sub>3</sub>)] with PR<sub>3</sub> = PPhCy<sub>2</sub> (**1c**), PCy<sub>3</sub> (**1d**), and *Pi*Pr<sub>3</sub> (**1e**), induced a faster polymerization. For the polymerization of styrene (Table 2), a correlation was found with complexes **1a–d**, but not with [RuCl<sub>2</sub>(*p*-cymene)(*Pi*Pr<sub>3</sub>)] (**1e**).

**Table 10. Cyclic Voltammetry Data for Ruthenium Complexes 1 and 3<sup>a</sup>**

<i>Complex</i>	$E^\circ$ (V)	$\Delta E$ (V)	<i>Complex</i>	$E^\circ$ (V)	$\Delta E$ (V)
<b>1a</b> (PR <sub>3</sub> = PPh <sub>3</sub> )	0.680	0.075 <sup>b</sup>	<b>3a</b>	0.325	0.090 <sup>b</sup>
<b>1b</b> (PR <sub>3</sub> = PPh <sub>2</sub> Cy)	0.690	0.069 <sup>b</sup>	<b>3b</b>	0.450 <sup>c</sup>	_.b,d
<b>1c</b> (PR <sub>3</sub> = PPhCy <sub>2</sub> )	0.630	0.066 <sup>b</sup>	<b>3c</b>	0.555	0.110 <sup>b</sup>
<b>1d</b> (PR <sub>3</sub> = PCy <sub>3</sub> )	0.575	0.060 <sup>b</sup>	<b>3d</b>	0.470 <sup>c</sup>	_.b,d
<b>1e</b> (PR <sub>3</sub> = <i>Pi</i> Pr <sub>3</sub> )	0.600	0.060 <sup>b</sup>	<b>3e</b>	0.590	0.080 <sup>b</sup>

<sup>a</sup> Sample, 2 mM; *n*Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) in dry and degassed CH<sub>2</sub>Cl<sub>2</sub>, under nitrogen at room temperature; scan rate, 50 mV s<sup>-1</sup>; potentials are reported in volt vs. ferrocene as an internal standard.

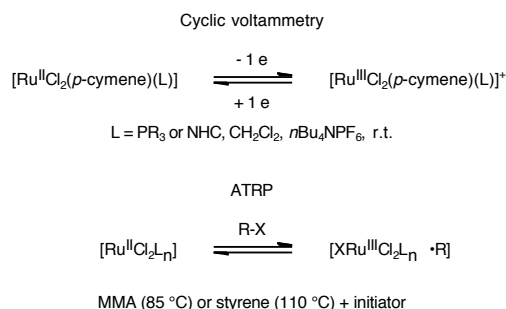
<sup>b</sup> Under our conditions (Ag/AgCl/saturated KCl reference electrode), the  $E_p^{\text{ox}}$  and  $E_p^{\text{red}}$  peak separation ( $\Delta E$ ) of the ferrocene/ferrocenium couple was 0.060 V for complexes **1**, and 0.080 V for complexes **3**, depending on the set of electrodes used, whereas the theoretical value for a reversible one-electron transfer process is 0.059 V.

<sup>c</sup> Oxidation potential,  $E_p^{\text{ox}}$ .

<sup>d</sup> Irreversible redox couple.

[RuCl<sub>2</sub>(*p*-cymene)(NHC)] complexes **3a**, **3c**, and **3e** gave rise to accessible and reversible one-electron redox couples. Complexes **3b** and **3d**, on the other hand, displayed irreversible redox couples, in apparent contradiction with the polymerization results. Indeed, complex **3b** catalyzed a well-controlled ATRP of MMA, whereas **3d** and **3e** promoted the redox-initiated free-radical polymerization of styrene and MMA. Comparison of the redox potentials,  $E^\circ$ , of complexes **3c** and **3e** posed an additional problem. Although the  $E^\circ$  values (0.555 and 0.590 V, respectively) were quite similar, complexes **3c** and **3e** displayed different abilities to control ATRP, suggesting that  $E^\circ$  is not necessarily predictive of the catalyst's efficiency for ATRP with this particular series of ruthenium–NHC complexes.

Steric and/or conformational constraints around the ruthenium atom may explain this discrepancy. We may also argue that, although they seem to be related, cyclic voltammetry and ATRP are basically different processes (Scheme 10). Cyclic voltammetry experiments are indeed performed on well-defined [Ru<sup>II</sup>Cl<sub>2</sub>(*p*-cymene)(L)] complexes, which are –formally– oxidized to the corresponding radical cations [Ru<sup>III</sup>Cl<sub>2</sub>(*p*-cymene)(L)]<sup>+</sup> (unless the oxidized species undergo further reactions) through a one-electron transfer.

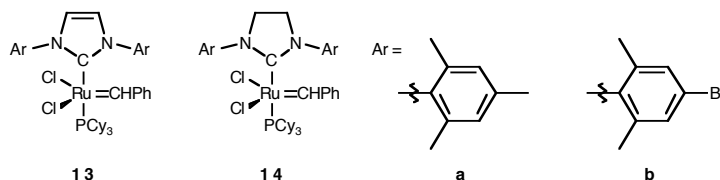


**Scheme 10.** Cyclic voltammetry vs. ATRP

In ATRP, the ruthenium(II) species is oxidized through halogen transfer from the covalent R–X bond of the initiator or the polymer chain ends. Therefore, a more plausible explanation for the discrepancies between cyclic voltammetry data and catalytic activities is that the well-defined [RuCl<sub>2</sub>(*p*-cymene)(L)] complexes used for the polymerization of MMA and styrene are precatalysts. The actual catalytic active species are indeed likely devoid of the *p*-cymene ligand, as indicated by <sup>1</sup>H-NMR spectroscopy, under conditions mimicking polymerization of MMA and styrene (16).

**[RuCl<sub>2</sub>(=CHPh)(PCy<sub>3</sub>)(L)] complexes, L = PCy<sub>3</sub> or NHC**

Several studies in the literature have been devoted to studying the donor properties of saturated and unsaturated NHC vs. phosphine ligands. As illustrated above (Scheme 3) there can be no doubt that NHC ligands are significantly more electron-donating than phosphines. This has been confirmed recently (17) on comparing the Ru(II)/Ru(III) redox potential of the Grubbs complex [RuCl<sub>2</sub>(=CHPh)(PCy<sub>3</sub>)<sub>2</sub>] (**2**) (*E*<sup>o</sup> = +0.585 V) with that of the parent Ru–NHC complexes **13a** (*E*<sup>o</sup> = +0.455 V) and **14a** (*E*<sup>o</sup> = +0.447 V).



**Scheme 11.** Representative Grubbs complexes

**Table 11. Cyclic Voltammetry Data for Representative Grubbs Complexes**

<i>Complex</i>	<i>E</i> <sup>o</sup> (V)	$\Delta E$ (V)
<b>2</b>	0.585	0.087
<b>13a</b>	0.455	0.082
<b>13b</b>	0.536	0.075
<b>14a</b>	0.447	0.077
<b>14b</b>	0.537	0.074

Thus, replacing a single tricyclohexylphosphine ligand by a NHC ligand resulted in a cathodic shift of the redox potential by *ca.* 130 mV, while the redox potentials of the unsaturated NHC–Ru complex **13a** and the saturated NHC–Ru complex **14a** were almost identical. On the other hand, the two bromine substituted complexes **13b** and **14b** were anodically shifted by *ca.* +85 mV with respect to **13a** and **14a**, indicating that variation of the group at the *para* position of the aryl substituents of the NHC ligand has a profound influence on the redox potential Ru(II)/Ru(III).

A more systematic investigation of the influence of the remote *para*-substituents revealed significant shifts of the Ru(II)/Ru(III) redox potentials, in agreement with the electron donating ability of the remote substituents. The fact that the aryl rings are electronically decoupled from the *N*-heterocycle provides strong evidence of the  $\pi$ -face coordination of the aryl groups on the ruthenium center, so that the donor properties of aryl substituted NHCs are not only characterized by lone pair donation from the carbene carbon, but also by donation of electron density of the aromatic  $\pi$ -face of the NHC aryl groups towards the metal. It is also worth noting that in olefin metathesis, no correlation could be found between the redox potential Ru(II)/Ru(III) and the catalytic activity. A similar investigation is needed in ATRP catalyzed by ruthenium–benzylidene complexes to gain information on the electronic situation at the metal center in complexes **2** and **4–11**.

## Conclusions

In exploring the reactivity of a series of ruthenium-based complexes of the general formula  $[\text{RuCl}_2(p\text{-cymene})\text{L}]$  and  $[\text{RuCl}_2(=\text{CHPh})\text{LL}']$  (L and L' are either a bulky and basic phosphine, such as PCy<sub>3</sub>, or a *N*-heterocyclic carbene ligand), it was found that ruthenium–PCy<sub>3</sub> complexes were more efficient than their ruthenium–NHC analogues. By contrast, within the family of  $[\text{RuCl}(\text{O}^{\wedge}\text{N})(=\text{CHPh})\text{L}]$  complexes (O<sup>^</sup>N is a Schiff base ligand), the polymer yields and the molecular weights were not significantly affected by the ligand, L (PCy<sub>3</sub> or NHC), although ruthenium–NHC complexes **7** were generally superior to the ruthenium–PCy<sub>3</sub> derivatives, **6**, when the polymer distributions were compared.

The ruthenium–*p*-cymene complexes **3**,  $[\text{RuCl}_2(p\text{-cymene})(\text{NHC})]$ , described in this study are of special interest since, depending on the substituents of the carbene ligand, they can be tuned to promote ATRP or olefin metathesis of carbon–carbon double bonds. Complexes **3b** and **3c** with R<sup>1</sup> = mesityl and R<sup>2</sup> = H or Cl, respectively, were most suitable for promoting the ATRP of methyl methacrylate. Their use resulted in well-behaved polymerizations and afforded polymers with narrow molecular weight distributions and high initiation efficiencies. In the case of styrene, complex **3e** (R<sup>1</sup> = Cy, R<sup>2</sup> = H) was the most efficient catalyst precursor for initiating a controlled radical polymerization. A switch in the reaction pathway could be induced, however, by replacing the cyclohexyl group with a mesityl substituent on the nitrogen atoms. Thus, complexes **3a–c** displayed a dual activity and afforded both the ATRP and the cross-metathesis products. Among the three species tested, the chloro derivative **3c** led to the highest proportion of stilbene compared to polystyrene.

At the present time, it remains difficult to put forward general guidelines to rationalize the choice of a specific ruthenium–NHC catalyst precursor for a given reaction. Depending on the monomer and the experimental conditions adopted (presence of an initiator, solvent, temperature, ...), the coordination sphere around the metal center must be specifically tailored to afford the most efficient catalytic system. Fine tuning of

the electronic, steric, and solubility parameters of the carbene ligand undoubtedly contributes to these adjustments, but any correlation between well-defined ruthenium–NHC complexes and the active coordinatively unsaturated species generated *in situ* is blurred by the elusive nature of the actual catalytic system.

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