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Homobimetallic Ruthenium–N-Heterocyclic Carbene Complexes: Synthesis, Characterization, and Catalytic Applications

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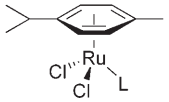
Abstract: Two new homobimetallic ruthenium-arene complexes [(*p*-cymene)Ru(μ-Cl)$_3$RuCl(η^2-C$_2$H$_4$)(L)], where L = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (**3a**) or 1,3-bis(2,4,6-trimethylphenyl)-4,5-dichloroimidazolin-2-ylidene (**3b**), were isolated in high yields upon heating a toluene solution of [RuCl$_2$(*p*-cymene)]$_2$ with 1 equivalent of carbene ligand under an ethylene atmosphere. They were characterized by NMR and TGA. Their catalytic activity was investigated in the atom transfer radical polymerization of vinyl monomers. In the polymerization of methyl methacrylate, complex **3a** displayed faster reaction rates than **3b** and the related phosphine-based complex **2a** (L = tricyclohexylphosphine), although control was more effective with the latter catalyst. When *n*-butyl acrylate or styrene served as monomer, a major shift of reactivity was observed between complex **2a** that promoted controlled radical polymerization, and complexes **3a** or **3b** that favored metathetical coupling. Further homocoupling experiments with various styrene derivatives confirmed the outstanding aptitude of complex **3a** (and to a lesser extent of **3b**) to catalyze olefin metathesis reactions. Contrary to monometallic ruthenium-arene complexes of the [RuCl$_2$(*p*-cymene)(L)] type, the new homobimetallic species did not require the addition of a diazo compound or visible light illumination to initiate the ring-opening metathesis of norbornene or cyclooctene. When α,ω-dienes were exposed to **3a** or **3b**, a mixture of cycloisomerization and ring-closing metathesis products was obtained in a non-selective way. Addition of a terminal alkyne co-catalyst enhanced the metathetical activity while completely repressing the cycloisomerization process. Thus, quantitative conversions of diethyl 2,2-diallylmalonate and *N,N*-diallyltosylamide were achieved within 2 h at room temperature using 2 mol% of catalyst precursor **3a** and 6 mol% of phenylacetylene.

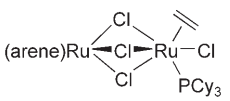
Keywords: arene ligands; homogeneous catalysis; metathesis; polymerization; radical reactions; ruthenium

Introduction

Ruthenium-arene complexes[1] are versatile and efficient catalyst precursors for various important organic transformations.[2] This is due in part to the lability of the η^6-arene ligand that can be easily removed upon thermal[3] or photochemical[4] activation to release highly active, coordinatively unsaturated species. During the 1990s, we demonstrated that [RuCl$_2$(*p*-cymene)(PR$_3$)] complexes bearing basic and bulky phosphine ligands, such as tricyclohexylphosphine (PCy$_3$, see structure **1a**), were highly effective precatalysts for ring-opening metathesis polymerization (ROMP)[5] and atom transfer radical polymerization (ATRP).[6] The past decade also witnessed the experimental reality of stable nucleophilic N-heterocyclic carbenes (NHCs), which were first isolated and characterized by Arduengo and co-workers in 1991.[7] These divalent carbon species are neutral, two-electron ligands with only little π-back-bonding tendency.[8] They behave as phosphine mimics, yet they are



1a (L = PCy$_3$)
1b (L = IMes)
1c (L = IMesCl$_2$)



2a (arene = 4-isopropyltoluene)
2b (arene = 1,3,5-triisopropylbenzene)

better σ-donors and they form stronger bonds to metal centers than most phosphines. Their electronic and steric properties are liable to ample modification simply by varying the substituents on the heterocyclic ring. Therefore, NHCs have become ubiquitous ligands in organometallic chemistry and catalysis.[9] They have also acquired a place on their own as reagents and catalysts in organic synthesis, since they behave as powerful nucleophilic agents.[10] In order to further expand the scope of ruthenium-arene catalyst precursors, we have adopted this class of ancillary ligands instead of phosphines to generate [$RuCl_2$(*p*-cymene)(NHC)] species, either preformed or *in situ*.[11] Thus, complex **1b** bearing the 1,3-dimesitylimidazolin-2-ylidene ligand (nicknamed IMes) displayed a remarkable activity for initiating ROMP of cyclooctene under visible light illumination,[12] whereas complex **1c** sporting a modified NHC ligand (4,5-dichloro-1,3-dimesitylimidazolin-2-ylidene, $IMesCl_2$) was an attractive challenger for promoting atom transfer radical addition (ATRA)[13] and polymerization[14] processes.

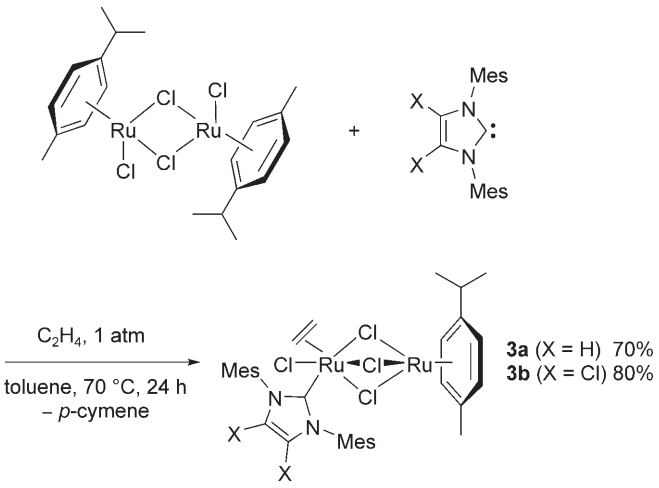
In 2005, Severin and co-workers investigated the reaction of [$RuCl_2$(*p*-cymene)]$_2$ with 1 equivalent of PCy_3 under an ethylene atmosphere. Under these conditions, the ruthenium dimer afforded a new type of molecular scaffold, in which a RuCl(η^2-C_2H_4)(PCy_3) fragment was connected *via* three μ-chloro bridges to a ruthenium-(*p*-cymene) moiety. Complex **2a** displayed an outstanding catalytic activity in ATRA reactions.[15] By varying the nature of the arene ligand, the same group also synthesized the related homobimetallic complex **2b** and successfully employed it as catalyst precursor for the ATRP of methacrylate monomers at 35 °C.[16]

In view of the enhancements brought by the replacement of phosphines by NHCs in monometallic ruthenium-arene catalyst precursors of type **1**, we decided to investigate the effect of similar modifications on the catalytic activity of complexes of type **2**. In this contribution, we disclose the synthesis, characterization, and catalytic applications of two new homobimetallic ruthenium-arene complexes **3a** and **3b** bearing, respectively, the IMes and $IMesCl_2$ ligands.

Results and Discussion

Synthesis and Characterization of Complexes 3a and 3b

The preparation of complexes **3a** and **3b** was rather straightforward and could be achieved in a single step by heating the commercially available [$RuCl_2$(*p*-cymene)]$_2$ dimer with 1 equivalent of IMes[7b,c] or $IMesCl_2$[17] in toluene under an ethylene atmosphere (Scheme 1). Both products were isolated as microcrystalline orange powders in high yields (70% for **3a**, 80% for **3b**) by simple filtration and washing. They could be conveniently handled in air for short periods of time, although prolonged exposure to oxygen and moisture led to progressive color changes indicative of degradation. Under normal atmosphere, complex **3a** began to darken after a few hours, while complex **3b** resisted a few days before showing signs of decomposition. Thus, for long-term storage, they were kept in Schlenk flasks under an inert atmosphere at −18 °C. Thermogravimetric analyses also pointed to an enhanced stability of complex **3b** compared to **3a**, since the decomposition onset occurred at 214 °C for **3b** and 120 °C for **3a**. For the sake of comparison, TGA of **2a** was also carried out. Despite its remarkable stability in open air at room temperature, this complex began loosing weight at 82 °C.



Scheme 1. Synthesis of homobimetallic ruthenium-NHC complexes **3a** and **3b**.

Complexes **3a** and **3b** readily dissolved in dichloromethane at room temperature or in toluene upon heating. Since the alkene ligand was rather labile in solution, all NMR spectra were recorded in CD_2Cl_2 saturated with ethylene. Both complexes displayed similar ^{1}H NMR features. Integration of the various signals confirmed the presence of the NHC, ethylene, and arene ligands in 1:1:1 proportions. The η^2-C_2H_4 fragment gave rise to two multiplets centered at about 3.3 and 3.7 ppm, respectively. Only two aromatic protons from the *p*-cymene ligand were visible. They resonated as two distinct multiplets forming an AB system between 5.0 and 5.1 ppm. The two other *p*-cymene ring protons were masked by the more intense absorptions of CH_2Cl_2 and free C_2H_4 at *ca.* 5.2 and 5.3 ppm, respectively. Yet, the non-equivalence of the four aromatic protons on the arene ligand was confirmed by ^{13}C{^{1}H} NMR spectroscopy that showed four distinct lines for the carbon atoms bearing these protons. Further evidence for the asymmetric nature

Table 1. Metathesis and atom transfer radical polymerization of methyl methacrylate (MMA), *n*-butyl acrylate (*n*BA), and styrene catalyzed by complexes **2a**, **3a**, and **3b** at 85 °C or 110 °C.

Monomer	Catalyst	Metathesis Yield [%]	ATRP Yield [%]	M_n [kg mol^{-1}][a]	M_w/M_n[a]	f[b]	k_{app} [10^{-5} s^{-1}]
MMA[c]	**2a**	0	78	36.5	1.05	0.85	2.11
	3a	<1	81	40	1.25	0.8	2.81
	3b	<1	47	19	1.10	1.0	0.93
*n*BA[d]	**2a**	1	16	5	1.25	1.25	0.23
	3a	16	27	24	1.85	0.45	-[f]
	3b	41	2	-	-	-	-
Styrene[e]	**2a**	0	62	24	1.35	1.0	1.63
	3a	100	0	-	-	-	-
	3b	100	0	-	-	-	-

[a] Determined by size-exclusion chromatography in THF with PMMA or polystyrene calibration.
[b] Initiation efficiency $f = M_{n,theor.}/M_{n,exp.}$ with $M_{n,theor.} = ([monomer]/[initiator])_0 \times M_w \times$ conversion.
[c] Initiator: ethyl 2-bromo-2-methylpropionate, $[MMA]_0:[initiator]_0:[complex]_0 = 800:2:1$, 16 h at 85 °C.
[d] Initiator: ethyl 2-bromopropionate, $[nBA]_0:[initiator]_0:[complex]_0 = 600:2:1$, 16 h at 85 °C.
[e] Initiator: (1-bromoethyl)benzene, $[styrene]_0:[initiator]_0:[complex]_0 = 750:2:1$, 16 h at 110 °C.
[f] Uncontrolled polymerization.

of type **3** complexes came from the observation of five different signals for the methyl groups on the arene and NHC ligands.

The most striking difference between the NMR spectra of complexes **3a** and **3b** concerned the resonance of the imidazole C4 and C5 carbons. The replacement of hydrogen atoms by chloro substituents on these positions led to a significant decrease of their chemical shift (from 125.6 ppm in **3a** to 117.9 ppm in **3b**). The carbene center was also affected by the modification of electron density on the heterocyclic ring, although to a lesser extent (167.8 ppm for C2 in **3a**, 172.3 ppm in **3b**). These variations are in line with NMR data previously reported for ruthenium-benzylidene metathesis catalysts [$RuCl_2$(=CHPh)-(PCy_3)(NHC)] when $IMesCl_2$ was substituted for IMes.[18]

Crystals of **3a** were grown by slowly cooling a saturated toluene solution of the complex under an ethylene atmosphere. X-ray diffraction analysis at 120 K showed that each unit cell was made of two non-equivalent molecules of **3a**, one of them being disordered, and one molecule of solvent. It confirmed unambiguously the validity of the structure depicted in Scheme 1 for **3a**. Unfortunately, all our attempts to refine the structure remained unsuccessful as it was not possible to come up with an *R* parameter lower than 0.16 even when data sets were collected at low temperature on freshly synthesized crystals.

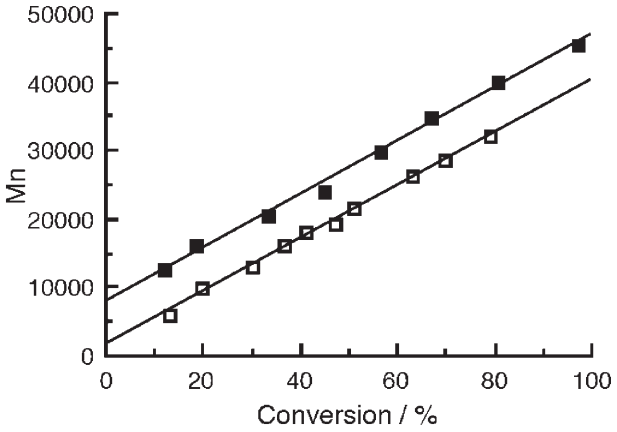


Figure 1. . Dependence of PMMA molecular weight M_n on monomer conversion with catalysts **3a** (■) and **3b** (□). See Table 1 for reaction conditions.

Catalytic Investigations

We have investigated the catalytic activity of homobimetallic ruthenium complexes in the ATRP of vinyl monomers (Table 1). First, methyl methacrylate (MMA) was polymerized using ethyl 2-bromo-2-methylpropionate as initiator under standard experimental conditions.[6] The reactions were carried out in toluene under the exclusion of oxygen for 16 h at 85 °C with an initial monomer/initiator/catalyst molar ratio of 800:2:1. With both complexes **3a** and **3b**, the molecular weights increased linearly with conversion (Figure 1). The semilogarithmic plot of $\ln([M]_0/[M]_t)$ versus time also followed a linear relationship (Figure 2). These results strongly suggest that radical polymerization took place in a controlled fashion with both catalysts.[19] The nature of the ancillary ligand significantly influenced the rate of reaction. IMes afforded a much more active catalyst than its dichloro derivative $IMesCl_2$. Indeed, the pseudo-first order rate constant (k_{app}) computed for complex **3a** was three times larger than for complex **3b**. In terms of kinetics, complex **3a** also outperformed the tricyclohexylphosphine-based bimetallic species **2a** (see Table 1

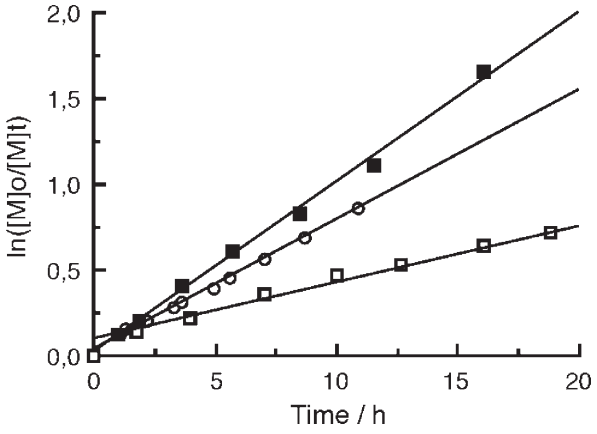


Figure 2. Time dependence of $\ln([M]_0/[M]_t)$ for the ATRP of MMA at 85 °C with catalysts **2a** (○), **3a** (■), and **3b** (□). See Table 1 for reaction conditions.

and Figure 2). When molecular weight distributions were examined, however, complex **2a** took precedence over its NHC-containing congeners. Although the number-average molecular weight (M_n) reached with this catalyst at 85 °C exceeded the value calculated from the initial monomer-to-initiator ratio (initiation efficiency $f=0.85$), polydispersity remained as narrow as $M_w/M_n=1.05$, whereas complexes **3a** and **3b** led to PDIs of 1.25 and 1.10, respectively, under the same experimental conditions. Moreover, the formation of small amounts of low molecular weight polymers that did not disappear over the course of the reaction was observed with the latter catalysts (see Supporting Information). Although minor (less than 1 % of the total polymer mass), this phenomenon was not detected with catalyst **2a**. It is attributed to the coupling or dismutation of oligomeric chains during the early stages of the polymerization process ("persistent radical effect").[20]

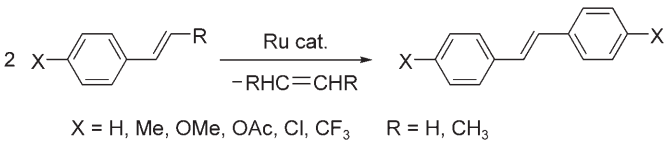
When the polymerization of MMA was carried out at 35 °C instead of 85 °C with complex **3a**, the semilogarithmic plot of $\ln([M]_0/[M]_t)$ versus time remained linear, but high molecular weight polymers were formed from the very beginning of the reaction and M_n as well as M_w/M_n remained almost constant ($\approx$76 kg mol^{-1} and 1.60, respectively) throughout the entire run. This behavior sharply contrasts with the results previously reported for complex **2b** at 35 °C that met all the criteria of controlled polymerization.[16] With the NHC-based complex **3a**, the decrease of temperature most likely induced a switch of mechanism, from controlled ATRP to a redox-initiated free-radical process,[14] although further investigations are needed to fully clarify this point.

Next, we probed the reactivity of *n*-butyl acrylate (*n*BA) at 85 °C (Table 1). The experimental procedure used with MMA was kept unchanged and the introduction of 1 mL of neat substrate in the reaction medium led to an initial monomer/initiator/catalyst molar ratio of 600:2:1. Acrylates are much more challenging monomers for ATRP than methacrylates and only a few ruthenium catalytic systems allow a good control of their radical polymerization.[21] Complex **2a** deserves a honorable mention for this task, despite the fact that only modest yields were achieved after 16 h. Complex **3a** was more active but required an induction period and did not afford any control. With complexes **3a** and **3b**, the most salient feature was the formation of significant amounts of di(*n*-butyl) fumarate and maleate in a 98:2 ratio. These products result from the homocoupling of the unsaturated ester *via* olefin metathesis. A similar reaction had also occurred with MMA. In this case, however, it remained essentially negligible compared to ATRP and only traces of (*E*)- and (*Z*)-dimethyl 2,3-dimethylbut-2-enedioate were detected by gas chromatography (GC).

In a third series of experiments, we investigated the ATRP of styrene at 110 °C with an initial monomer/initiator/catalyst molar ratio of 750:2:1 (Table 1). Complex **2a** proved once again its efficiency as a radical initiator, as it led to a well-behaved polymerization process with a satisfactory control over the molecular weight distribution and no stilbene formation. It should be pointed out, however, that a small peak due to low molecular weight polystyrene remained visible in the GPC traces during the whole duration of the reaction (see Supporting Information). A similar phenomenon already occurred in the polymerization of MMA with complexes **3a** and **3b**, although to a lesser extent. It was assigned to a persistent radical effect (*vide supra*). Most interestingly, replacement of tricyclohexylphosphine by a NHC ligand led to a complete change of selectivity. Thus, when styrene was reacted with complexes **3a** and **3b** under the same experimental conditions that were employed for **2a**, ATRP was totally suppressed and replaced by olefin metathesis. Despite the presence of (1-bromoethyl)benzene as initiator, no polystyrene was isolated and a quantitative yield of stilbene [almost exclusively the (*E*)-isomer] was obtained within 30 min.

To further evaluate the metathetical activity of homobimetallic ruthenium-(*p*-cymene) complexes, we have performed the homocoupling of styrene derivatives bearing various electron-withdrawing or -donating substituents on their aromatic rings (Table 2). The reactions were carried out in toluene at 85 °C using 0.2 mol % of catalyst. Conversions were monitored by GC at regular time intervals using an internal standard. To speed up the screening, yields were not systematically determined. However, whenever stilbene products were separated from the reaction mixtures and purified by column chromatography, isolated yields closely matched the conversions recorded,

Table 2. Metathesis of styrene derivatives catalyzed by complexes **2a**, **3a**, and **3b** at 85 °C.[a]



Entry	Substrate	Catalyst	Conversion [%][b]
1	Styrene	**2a**	0
2	Styrene	**3a**	93
3	Styrene	**3b**	70
4	4-Acetoxystyrene	**3a**	100
5	4-Chlorostyrene	**3a**	100
6	4-Methylstyrene	**3a**	89
7	4-Methoxystyrene	**3a**	91
8	4-Trifluoromethylstyrene	**3a**	70
9	*trans*-Anethole	**3a**	90

[a] *Experimental conditions:* Ru cat. (0.004 mmol), substrate (2 mL of 1 M solution in toluene, 2 mmol), 2 h at 85 °C.
[b] Determined by GC using dodecane as internal standard.

thereby confirming the validity of the analytical method employed.

With styrene itself, results obtained with complexes **2a**, **3a**, and **3b** corroborated the trends already observed under ATRP conditions (*cf.* Table 1). Thus, complex **2a** was completely devoid of metathetical activity (Table 2, entry 1), while complex **3a** was highly efficient at transforming styrene into (*E*)-stilbene and ethylene. A 93% conversion was achieved after 2 h (entry 2) and full consumption of the substrate occurred within 5 h at 85 °C. Complex **3b** displayed a lesser activity and afforded only a 70% conversion after 2 h (entry 3). The intervention of a photochemical activation step was ruled out by carrying out reactions in the dark. Results paralleled those obtained under normal lighting conditions. Upon irradiation of the reaction mixtures with a strong visible light source, rapid darkening of the catalyst solutions ensued and conversions dropped significantly.

Introduction of slightly deactivating acetoxy or chloro substituents on the *para*-position of the aromatic ring speeded up the reaction that became complete after 2 h with complex **3a** (entries 4 and 5). Conversely, the presence of 4-methyl or 4-methoxy groups slightly reduced the reaction rate. This effect was best evidenced after 1 h and started to level off after 2 h (entries 6 and 7). Eventually, almost quantitative yields of (*E*)-4,4′-dimethylstilbene or (*E*)-4,4′-dimethoxystilbene were obtained after 5 h. With the strongly deactivated 4-trifluoromethylstyrene, the reaction rate further dropped. A decent 70% conversion was reached after 2 h (entry 8) but did not significantly increase within the next 3 h allowed to the reaction. *trans*-Anethole [1-methoxy-4-(1-propenyl)benzene] reacted at about the same rate as styrene and was therefore more reactive than 4-methoxystyrene (entry 9). It is also an inexpensive natural product, whereas 4-methoxystyrene is not widely available. Thus, *trans*-anethole is a prime starting material to access the important class of polyhydroxystilbenes *via* olefin metathesis.[22,23] The chemical synthesis of naturally occurring stilbenoid compounds, including resveratrol (3,4′,5-trihydroxystilbene), has attracted a lot of attention recently, because of the remarkable physiological properties and potential therapeutic values of these phytoalexins.[24] Hence, we were pleased to note that the presence of a terminal methyl group on the C=C double bond of *trans*-anethole did not hinder the metathesis process. On the other hand, attempts to homocouple α-methylstyrene with complex **3a** were completely unsuccessful. This failure might be attributed to the greater steric congestion imposed to a metal-alkylidene or a metallacyclobutane intermediate by a 1,1-disubstituted double bond compared to its 1,2-disubstituted isomer or a terminal olefin. Another styrene derivative that resisted metathesis under our experimental conditions was 2-methoxystyrene. In this case, the lack of reactivity was most likely due to the formation of a stabilized ruthenium-benzylidene species possessing a chelated methoxy ligand.[23,25]

To expand the scope of homobimetallic ruthenium catalysis in olefin metathesis, we have examined the ROMP of two representative cycloalkenes in the presence of complexes **2a**, **3a**, and **3b** (Table 3). Polymerizations of cyclooctene were carried out in chlorobenzene at 60 °C for 2 h using a monomer-to-catalyst ratio of 250. In order to impede gelification and formation of insoluble cross-linked polymers, norbornene was reacted in more dilute solutions with 0.1 mol% of catalyst. Due to its high strain, ring-opening metathesis of this bicyclic monomer is particularly easy and occurs almost under any circumstances, provided that enough time is allowed to the reaction.[26] It was therefore not surprising to observe the full conversion of norbornene into polynorbornene with catalyst **2a**, along with **3a** and **3b**. Yet, recourse to the phosphine-based complex afforded a much broader molecular weight distribution and a lower proportion of *cis* double bonds in the polymer backbone, thereby underlining the influence of the ancillary ligand on the polymerization outcome.

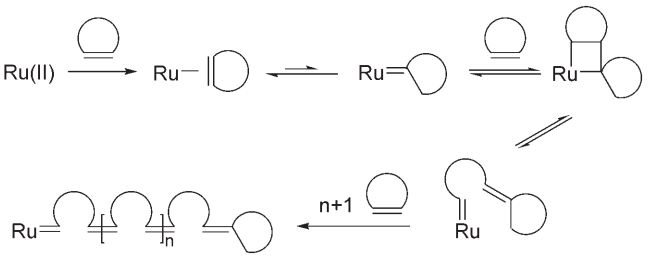
Compared to norbornene, cyclooctene is significantly more difficult to ring-open.[27] Hence, formation of polyoctenamer occurs only at a reasonable rate with highly active catalytic systems. With this monomer, a clear-cut distinction could be established between complex **2a** that did not afford any reaction after 2 h at 60 °C and the NHC-containing ruthenium-arene species **3a** and **3b**, which led to complete con-

Table 3. Ring-opening metathesis polymerization of norbornene and cyclooctene catalyzed by complexes **2a**, **3a**, and **3b** at 60 °C.

Monomer	Catalyst	Conversion [%][a]	Yield [%]	M_n [kg mol^{-1}][b]	M_w/M_n[b]	σ_{cis}[c]
Norbornene[d]	**2a**	>99	88	115	5.1	0.18
	3a	>99	91	480	1.5	0.43
	3b	>99	87	150	1.8	0.39
Cyclooctene[e]	**2a**	0	0	-	-	-
	3a	>99	93	250	1.8	0.26
	3b	>99	95	230	1.6	0.34

[a] Determined by GC using internal standards.
[b] Determined by size-exclusion chromatography in THF with polystyrene calibration.
[c] Fraction of *cis* double bonds in the polymer, determined by ^{13}C NMR spectroscopy.
[d] *Experimental conditions:* Ru cat. (0.015 mmol), PhCl (12 mL), norbornene (15 mmol), 2 h at 60 °C.
[e] *Experimental conditions:* Ru cat. (0.03 mmol), PhCl (5 mL), cyclooctene (7.5 mmol), 2 h at 60 °C.

versions under the same experimental conditions (Table 3). Although the polymerizations were not controlled, almost quantitative yields of high molecular weight polymers were obtained without the need to add a diazo compound, nor to photochemically activate the catalyst precursor, as previously required with monometallic ruthenium-arene complexes bearing phosphine[5] or NHC[12] ligands, respectively. The intimate details of the mechanism remain, however, elusive. Only a small amount of active species are generated from the bulk of catalyst precursor and all our attempts to acquire spectroscopic evidence for the transformation of ruthenium-arene complexes into the actual ruthenium-alkylidene centers required to initiate olefin metathesis have remained unsuccessful so far. While thermal or photochemical arene decoordination was postulated to be the first step with monometallic complexes of type **1**, results obtained here suggest that homobimetallic ruthenium complexes **3a** and **3b** could be activated *via* an alternative pathway involving exchange of the labile ethylene ligand for a cycloolefin monomer. Formation of a reactive carbene moiety could then occur through direct (albeit unfavorable) equilibration, as proposed by Mühlebach and co-workers,[28] although a more complex sequence involving the intermediacy of ruthenium-hydride species cannot be ruled out.[29] Subsequent steps of metallacyclization and cycloreversion follow the mechanism commonly accepted for ROMP[30] and lead to chain growth (Scheme 2).

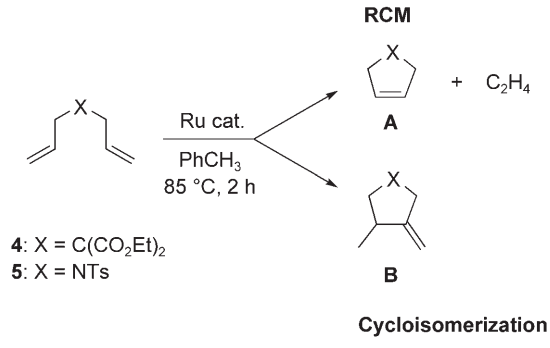


Scheme 2. Possible mechanism for the ROMP of cycloolefins.

In a final series of experiments, we probed the catalytic activity of complexes **2a**, **3a**, and **3b** in the ring-closing metathesis (RCM) of two benchmark substrates, *viz.* diethyl 2,2-diallylmalonate (**4**) and *N*,*N*-diallyltosylamide (**5**). Preliminary tests were carried out in toluene at 85 °C using 2 mol % of ruthenium catalyst. Under these conditions, no reaction occurred with the phosphine-based bimetallic species **2a**. Indeed, GC or NMR analyses performed to monitor the transformation of substrates **4** and **5**, respectively, did not show any sign of conversion (Table 4, entries 1 and 4). With the NHC-containing catalyst precursor **3a**, full consumption of the starting materials occurred within 2 h. The expected RCM cycloadduct **A** was, however, accompanied by a higher molecular weight product **B** formed in almost equimolar proportion (entries 2 and 5). Structural analysis of this product by NMR and GC-MS revealed the presence of adjacent methyl and *exo*-methylene groups on a five-membered ring. Thus, ruthenium complex **3a** acted as catalyst precursor for both RCM and cycloisomerization of the acyclic α,ω-dienes. A similar twofold reaction was also observed with complex **3b** (entries 3 and 6). Yet, conversions were slightly lower and cycloisomerization took precedence over RCM, in line with the reduced metathetical activity of **3b** compared to **3a**. Reports from the groups of Kurosawa[31] and Dixneuf[32] had already established that selected monometallic ruthenium-arene complexes displayed such a dual activity. A mechanism involving oxidative coupling of the diene to a ruthenium(II) center followed by β-elimination to generate a hydrido-ruthenium(IV) intermediate and reductive elimination was proposed to account for the cycloisomerization process (Scheme 3).[32b]

The Japanese and French teams were able to tune their catalytic systems to promote exclusively the transformation of α,ω-dienes into metathesis prod-

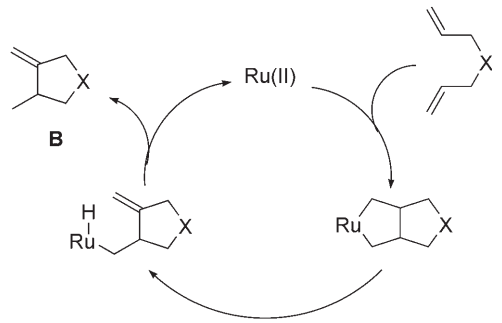
Table 4. Ring-closing metathesis and cycloisomerization of α,ω-dienes catalyzed by complexes **2a**, **3a** and **3b** at 85 °C.



Entry	Substrate	Catalyst	Conversion [%]	**A**:**B**
1	**4**[a]	**2a**	0	-
2	**4**[a]	**3a**	99	53:47
3	**4**[a]	**3b**	98	40:60
4	**5**[b]	**2a**	0	-
5	**5**[b]	**3a**	98	49:51
6	**5**[b]	**3b**	96	41:59

[a] *Experimental conditions:* Ru cat. (0.004 mmol), substrate (2 mL of 0.1 M solution in toluene, 0.2 mmol), 2 h at 85 °C. Conversions and product distributions were determined by GC using *n*-dodecane as internal standard.

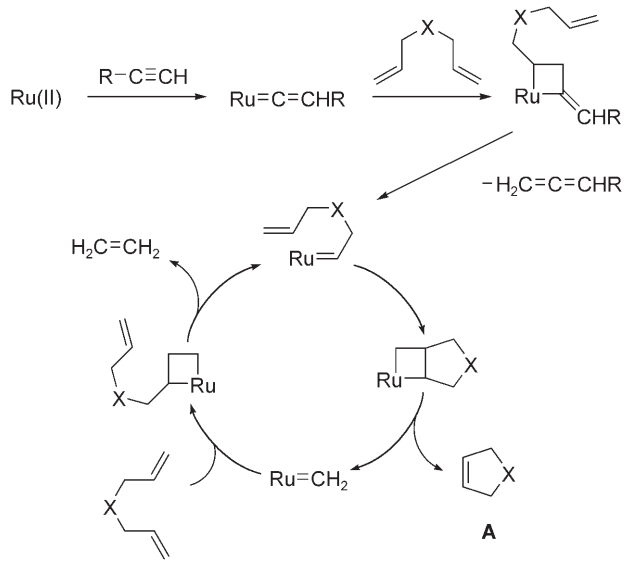
[b] *Experimental conditions:* Ru cat. (0.002 mmol), substrate (1 mL of 0.1 M solution in toluene-d_8, 0.1 mmol), 2 h at 85 °C. Conversions and product distributions were determined by ^{1}H NMR spectroscopy.



Scheme 3. Catalytic cycle for the cycloisomerization of α,ω-dienes.

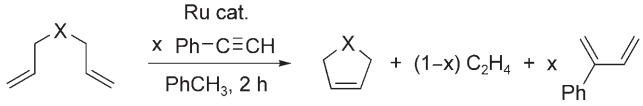
ucts, while completely inhibiting the cycloisomerization process, by adding a small amount of terminal alkyne to the reaction media.[31,32] The alkyne co-catalyst probably reacts with coordinatively unsaturated ruthenium centers to form vinylidene species. Although less active than their alkylidene counterparts, complexes featuring an Ru=C=CHR moiety are well-known initiators for various types of olefin metathesis, including ROMP and RCM (Scheme 4).[33]

We have applied this strategy to alter the course of the reaction between α,ω-dienes and our homobimetallic ruthenium-arene complexes. Thus, substrates **4** and **5** were reacted with catalyst precursors **2a**, **3a**, and **3b** (2 mol%) in the presence of phenylacetylene (6 mol%). The results are listed in Table 5. To our great satisfaction, the alkyne co-catalyst was highly effective at suppressing the cycloisomerization process altogether. At the same time, it significantly increased the rate of metathesis. Hence, with catalyst **3a** addi-



Scheme 4. Catalytic cyclic for the RCM of α,ω-dienes in the presence of a terminal alkyne.

Table 5. Ring-closing metathesis of α,ω-dienes catalyzed by complexes **2a**, **3a** and **3b** at 25 or 85 °C in the presence of phenylacetylene.



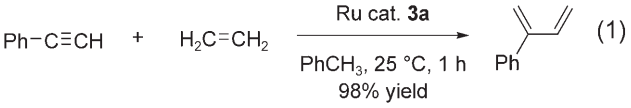
4: X = C(CO$_2$Et)$_2$
5: X = NTs

Entry	Substrate	Catalyst	Temperature [°C]	Conversion [%]
1	**4**[a]	**2a**	85	81
2	**4**[a]	**3a**	25	98
3	**4**[a]	**3b**	25	87
4	**5**[b]	**2a**	85	62
5	**5**[b]	**3a**	25	99
6	**5**[b]	**3b**	25	71

[a] *Experimental conditions:* Ru cat. (0.004 mmol), phenylacetylene (0.012 mmol), substrate (2 mL of 0.1 M solution in toluene, 0.2 mmol), 2 h. Conversions and product distributions were determined by GC using *n*-dodecane as internal standard.

[b] *Experimental conditions:* Ru cat. (0.002 mmol), phenylacetylene (0.006 mmol), substrate (1 mL of 0.1 M solution in toluene-d_8, 0.1 mmol), 2 h. Conversions and product distributions were determined by ^{1}H NMR spectroscopy.

tion of phenylacetylene allowed us to lower the reaction temperature from 85 °C to 25 °C while maintaining a quantitative conversion within 2 h (entries 2 and 5). Replacement of the IMes ligand with its 4,5-dichloro derivative in complex **3b** once again reduced the catalytic efficiency toward metathesis, although more than satisfactory conversions were achieved already at 25 °C in the presence of the alkyne co-catalyst (entries 3 and 6). Complex **2a** that was completely inactive on its own (*cf.* Table 4) also benefited from the adjuvant and became moderately active at promoting RCM. Heating was, however, still required to achieve satisfactory conversions (entries 1 and 4). In all cases, small amounts of 2-phenylbutadiene were detected in the reaction media (up to 6 mol% compared to the main cycloadducts). Formation of this byproduct formally results from an enyne metathesis between phenylacetylene and ethylene. A control experiment was performed by stirring a 0.1 M phenylacetylene solution in toluene under 0.5 bar of ethylene for 1 h at 25 °C in the presence of complex **3a** (2 mol%). After solvent evaporation and fractional distillation under reduced pressure, 2-phenylbutadiene was isolated in 98% yield [Eq. (1)].



(1)

Conclusions

By heating a toluene solution of the commercially available $[RuCl_2(p\text{-cymene})]_2$ dimer and 1 equivalent of IMes or $IMesCl_2$ under an ethylene atmosphere, we were able to isolate two new homobimetallic ruthenium-arene complexes **3a** and **3b** in high yields. The catalytic activity of these new compounds bearing NHC ligands was first investigated in the ATRP of vinyl monomers. In the polymerization of MMA, complex **3a** displayed faster reaction rates than **3b** and the related phosphine-based complex **2a**, although control was more effective with the latter catalyst. When *n*-butyl acrylate or styrene served as monomer, a major shift of reactivity was observed between complex **2a** that promoted controlled radical polymerization, and complexes **3a** or **3b** that favored metathetical coupling. Further homocoupling experiments with various styrene derivatives confirmed the outstanding aptitude of complex **3a** (and to a lesser extent of **3b**) to catalyze olefin metathesis reactions. Contrary to monometallic ruthenium-arene complexes of type **1** that were previously investigated in our group, the new homobimetallic species of type **3** did not require the addition of a diazo compound or visible light illumination to initiate the ROMP of norbornene or cyclooctene. When α,ω-dienes were exposed to **3a** or **3b**, a mixture of cycloisomerization and RCM products was obtained in a non-selective way. Addition of a terminal alkyne co-catalyst provided a convenient method to enhance the metathetical activity while completely repressing the cycloisomerization process. Thus, quantitative conversions of substrates **4** and **5** were achieved within 2 h at room temperature using 2 mol% of catalyst precursor **3a** and 6 mol% of phenylacetylene.

To sum up, our results clearly demonstrate that ancillary ligands exert a critical influence on the catalytic activity of homobimetallic ruthenium-arene complexes. Whereas phosphine-containing species are active only for controlled radical reactions, the new compounds **3a** and **3b** bearing NHC ligands are highly efficient catalyst precursors for various types of olefin metathesis. Thus, they significantly broaden the application field of their predecessors **2a** and **2b**, and they provide a valuable alternative to preformed ruthenium-alkylidene catalysts for initiating metathetical transformations in polymer chemistry and fine organic synthesis.

Experimental Section

General Remarks

All syntheses were carried out under an inert atmosphere using standard Schlenk techniques. Solvents and monomers were distilled from appropriate drying agents and deoxygenated prior to use. The $[RuCl_2(p\text{-cymene})]_2$ dimer was purchased from Strem. 1,3-Bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (IMes)[7b,c] and 1,3-bis(2,4,6-trimethylphenyl)-4,5-dichloroimidazolin-2-ylidene ($IMesCl_2$)[17] were synthesized according to published procedures. ^1H and ^{13}C NMR spectra were recorded at 298 K on a Bruker DRX 400 spectrometer operating at 400.13 and 100.62 MHz, respectively. Chemical shifts are listed in parts per million downfield from TMS and are referenced from the solvent peaks or TMS. Thermogravimetric analyses were performed on a TA Q500 instrument. Gas chromatography was carried out on a Varian 3900 instrument equipped with a flame ionization detector and a WCOT fused silica column (stationary phase: CP-Sil 5CB; column length: 15 m; inside diameter: 0.25 mm; outside diameter: 0.39 mm; film thickness: 0.25 μm). Gel permeation chromatography was performed in THF at 45 °C on a SFD S5200 autosampler liquid chromatograph equipped with a SFD 2000 refractive index detector and a battery of 4 PL gel columns fitted in series (particle size: 5 μm; pore sizes: 10^5, 10^4, 10^3, and 10^2 Å; flow rate: 1 mL min^{-1}). The molecular weights (not corrected) are reported versus monodisperse polystyrene or PMMA standards used to calibrate the instrument. Elemental analyses were carried out in the Laboratory of Pharmaceutical Chemistry at the University of Liège.

Synthesis of Complexes 3a and 3b

A suspension of $[RuCl_2(p\text{-cymene})]_2$ (0.4 g, 0.65 mmol) and IMes or $IMesCl_2$ (0.65 mmol) in dry toluene (20 mL) was heated at 70 °C for 24 h under an ethylene atmosphere. After cooling to room temperature, the reaction mixture was allowed to settle down and the supernatant solution was removed with a cannula. The solid product was rinsed with small portions of *n*-pentane and dried under high vacuum.

Complex **3a** was isolated as an orange powder; yield: 0.37 g (70%). ^{1}H NMR (400 MHz, $CD_2Cl_2+C_2H_4$, 25 °C): $\delta=1.19$ [d, $^3J_{H,H}=6.4$ Hz, 6H, $CH(CH_3)_2$], 2.03 (s, 9H, *o*-CH_3 Mes+CH_3 *p*-cym), 2.06 (s, 6H, *o*-CH_3 Mes), 2.29 (s, 6H, *p*-CH_3 Mes), 2.68 [sept, $^3J_{H,H}=6.4$ Hz, 1H, $CH(CH_3)_2$], 3.23 (m, 2H, C_2H_4), 3.60 (m, 2H, C_2H_4), 4.97 (d, $^3J_{H,H}=5.6$ Hz, 1H, CH_{ar} *p*-cym), 5.05 (d, $^3J_{H,H}=5.6$ Hz, 1H, CH_{ar} *p*-cym), 5.24 (2 H CH_{ar} *p*-cym+free C_2H_4), 6.56 (s, 2H, CH Im), 6.83 (d, $J=6.0$ Hz, 4H, CH_{ar} Mes); ^{13}C NMR (100 MHz, $CD_2Cl_2+C_2H_4$, 25 °C): $\delta=17.9$ (CH_3), 18.4 (CH_3), 18.5 (CH_3), 20.5 (CH_3), 20.8 (CH_3), 22.0 (CH_3), 30.6 [$CH(CH_3)_2$], 60.0 (C_2H_4), 77.6 (CH_{ar} *p*-cym), 77.9 (CH_{ar} *p*-cym), 78.2 (CH_{ar} *p*-cym), 78.7 (CH_{ar} *p*-cym), 95.1 (C_{ar} *p*-cym), 100.4 (C_{ar} *p*-cym), 125.6 (CH Im), 127.8 (CH_{ar} Mes), 136.5 (C_{ar} Mes), 136.7 (C_{ar} Mes), 137.6 (C_{ar} Mes), 167.8 (CRu Im); analysis (%) calcd. for $C_{33}H_{42}Cl_4N_2Ru_2$ (810.65): C 48.89, H 5.22, N 3.46; found C 50.36, H 5.32, N 3.06.

Complex **3b** was isolated as an orange powder; yield: 0.46 g (80%). ^{1}H NMR (400 MHz, $CD_2Cl_2+C_2H_4$, 25 °C): $\delta=1.27$ [d, $^3J_{H,H}=6.4$ Hz, 6H, $CH(CH_3)_2$], 2.08 (s, 6H, *o*-CH_3 Mes), 2.11 (s, 3H, CH_3 *p*-cym), 2.13 (s, 6H, *o*-CH_3 Mes), 2.75 [sept, $^3J_{H,H}=6.4$ Hz, 1H, $CH(CH_3)_2$], 3.26 (m, 2H, C_2H_4), 3.66 (m, 2H, C_2H_4), 5.05 (d, $^3J_{H,H}=4.0$ Hz, 1H, CH_{ar} *p*-cym), 5.14 (d, $^3J_{H,H}=4.0$ Hz, 1H, CH_{ar} *p*-cym), 5.40 (2 H CH_{ar} *p*-cym+free C_2H_4), 6.96 (d, $J=4.8$ Hz, 4H, CH_{ar} Mes); ^{13}C NMR (100 MHz, $CD_2Cl_2+C_2H_4$, 25 °C): $\delta=17.9$ (CH_3), 18.4 (CH_3), 20.6 (CH_3), 21.4 (CH_3), 21.9 (CH_3), 30.5 [$CH(CH_3)_2$], 61.0 (C_2H_4), 77.5 (CH_{ar} *p*-cym), 77.8 (CH_{ar} *p*-cym), 78.2 (CH_{ar} *p*-cym), 78.8 (CH_{ar} *p*-cym), 95.3 (C_{ar} *p*-cym), 100.4 (C_{ar} *p*-cym), 117.9 (CCl Im), 128.0 (CH_{ar} Mes), 134.1 (C_{ar} Mes), 137.6 (C_{ar} Mes), 137.8 (C_{ar} Mes), 138.7 (C_{ar} Mes), 172.3 (CRu Im); analysis (%) calcd. for $C_{33}H_{40}Cl_6N_2Ru_2$ (879.54): C 45.06, H 4.58, N 3.18; found C 44.12, H 4.88, N 3.07.

ATRP of Vinyl Monomers

A ruthenium complex (0.0117 mmol) was placed in a glass tube containing a magnetic stirring bar and capped with a three-way stopcock. Air was expelled by three vacuum-nitrogen cycles before methyl methacrylate (1 mL, 9.35 mmol) and ethyl 2-bromo-2-methylpropionate (0.1 M in toluene, 0.25 mL) were added. All liquids were handled with dried syringes under nitrogen. The reaction mixture was heated for 16 h in an oil bath at 85 °C under an inert atmosphere. After cooling to room temperature, it was diluted with THF (5 mL) and poured in *n*-heptane (600 mL) under vigorous stirring. The precipitated polymer was filtered with suction, dried overnight under dynamic vacuum, and characterized by GPC.

n-Butyl acrylate and styrene were polymerized according to similar procedures. Poly(*n*-butyl acrylate) was isolated by evaporating the reaction mixture. Polystyrene was precipitated from methanol. In all experiments, 1 mL of monomer was used (see Table 1 for further information on the initiator, temperature, and reaction time).

Self-Metathesis of Styrene

A ruthenium complex (0.004 mmol) was placed in a 15-mL Schlenk tube containing a magnetic stirring bar and capped with a septum. Air was expelled by three vacuum-argon cycles before 2 mL of a styrene solution (1 M in toluene, 2 mmol) was added with a dried syringe under argon. The reaction mixture was heated for 2 h in an oil bath at 85 °C under an inert atmosphere. The conversion was monitored by gas chromatography using *n*-dodecane as internal standard. After cooling to room temperature, the crude mixture was purified by column chromatography on silica gel using a 10:1 v/v mixture of petroleum ether (b.p. 40–60 °C) and ethyl acetate as eluent to afford pure (*E*)-stilbene.

Other styrene derivatives were reacted using the same experimental procedure (see Table 2 for their list).

ROMP of Cycloolefins

A ruthenium complex (0.03 mmol) was placed in a 25-mL round-bottom flask containing a magnetic stirring bar and capped with a three-way stopcock. Air was expelled by three vacuum-argon cycles before dry chlorobenzene (5 mL) and cyclooctene (1 mL, 7.5 mmol) were added. All liquids were handled with dried syringes under argon. The reaction mixture was stirred for 2 h in an oil bath at 60 °C under an inert atmosphere. The conversion was monitored by gas chromatography using the cyclooctane impurity of cyclooctene as an internal standard. After cooling, the resulting gel was diluted with $CHCl_3$ (20 mL) and slowly poured into methanol (500 mL) under vigorous stirring. The precipitated polyoctenamer was filtered with suction, dried under dynamic vacuum, and characterized by GPC and NMR spectroscopy.

Norbornene was polymerized following a similar procedure (see Table 3 for further information on the relative proportions of catalyst, monomer, and solvent).

RCM of Diethyl 2,2-Diallylmalonate

A ruthenium complex (0.004 mmol) was placed in a 15-mL Schlenk tube containing a magnetic stirring bar and capped with a septum. Air was expelled by three vacuum-argon cycles before 2 mL of a diethyl 2,2-diallylmalonate solution (0.1 M in toluene, 0.2 mmol) possibly containing 6 mol% of phenylacetylene was added with a dried syringe under argon. The reaction mixture was stirred for 2 h at 25 or 85 °C. Conversions and product distributions were monitored by GC using *n*-dodecane as internal standard.

RCM of *N,N*-Diallyltosylamide

A ruthenium complex (0.002 mmol) was placed in a NMR tube equipped with a J. Young valve. Air was expelled by three vacuum-argon cycles before 1 mL of a *N,N*-diallyltosylamide solution (0.1 M in toluene-d_8, 0.1 mmol) possibly containing 6 mol% of phenylacetylene was added with a dried syringe under argon. The reaction was monitored by ^{1}H NMR spectroscopy for 2 h at 25 or 85 °C.

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References

[1] For reviews, see: a) H. Le Bozec, D. Touchard, P. H. Dixneuf, *Adv. Organomet. Chem.* **1989**, *29*, 163–247; b) M. A. Bennett, *Coord. Chem. Rev.* **1997**, *166*, 225–254; c) F. C. Pigge, J. J. Coniglio, *Curr. Org. Chem.* **2001**, *5*, 757–784; d) J. H. Rigby, M. A. Kondratenko, *Top. Organonomet. Chem.* **2004**, *7*, 181–204.

[2] a) H. Küçükbay, B. Çetinkaya, S. Guesmi, P. H. Dixneuf, *Organometallics* **1996**, *15*, 2434–2439; b) B. Çetinkaya, I. Özdemir, P. H. Dixneuf, *J. Organomet. Chem.* **1997**, *534*, 153–158; c) A. Fürstner, T. Müller, *J. Am. Chem. Soc.* **1999**, *121*, 7814–7821; d) R. Castarlenas, P. H. Dixneuf, *Angew. Chem. Int. Ed.* **2003**, *42*, 4524–4527; e) R. Castarlenas, M. Eckert, P. H. Dixneuf, *Angew. Chem. Int. Ed.* **2005**, *44*, 2576–2579; f) M. Yiğit, B. Yiğit, I. Özdemir, E. Çetinkaya, B. Çetinkaya, *Appl. Organomet. Chem.* **2006**, *20*, 322–327.

[3] L. Quebatte, M. Haas, E. Solari, R. Scopelliti, Q. T. Nguyen, K. Severin, *Angew. Chem. Int. Ed.* **2005**, *44*, 1084–1088.

[4] a) A. Hafner, A. Mühlebach, P. A. van der Schaaf, *Angew. Chem. Int. Ed.* **1997**, *36*, 2121–2124; b) A. Fürstner, L. Ackermann, *Chem. Commun.* **1999**, 95–96; c) A. Fürstner, M. Liebl, C. W. Lehmann, M. Picquet, R. Kunz, C. Bruneau, D. Touchard, P. H. Dixneuf, *Chem. Eur. J.* **2000**, *6*, 1847–1857.

[5] a) A. W. Stumpf, E. Saive, A. Demonceau, A. F. Noels, *Chem. Commun.* **1995**, 1127–1128; b) A. Demonceau, A. W. Stumpf, E. Saive, A. F. Noels, *Macromolecules* **1997**, *30*, 3127–3136; c) D. Jan, L. Delaude, F. Simal, A. Demonceau, A. F. Noels, *J. Organomet. Chem.* **2000**, *606*, 55–64.

[6] a) F. Simal, A. Demonceau, A. F. Noels, *Angew. Chem. Int. Ed.* **1999**, *38*, 538–540; b) F. Simal, S. Sebille, L. Hallet, A. Demonceau, A. F. Noels, *Macromol. Symp.* **2000**, *161*, 73–85; c) F. Simal, D. Jan, L. Delaude, A. Demonceau, M.-R. Spirlet, A. F. Noels, *Can. J. Chem.* **2001**, *79*, 529–535.

[7] a) A. J. Arduengo, III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361–363; b) A. J. Arduengo, III, H. V. Rasika Dias, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1992**, *114*, 5530–5534; c) A. J. Arduengo, III, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall, M. Unverzagt, *Tetrahedron* **1999**, *55*, 14523–14534; d) A. J. Arduengo, III, *Acc. Chem. Res.* **1999**, *32*, 913–921.

[8] D. Bourrisou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–91.

[9] For recent reviews, see: a) L. Jafarpour, S. P. Nolan, *Adv. Organomet. Chem.* **2001**, *46*, 181–222; b) W. A. Herrmann, T. Weskamp, V. P. W. Böhm, *Adv. Organomet. Chem.* **2002**, *48*, 1–69; c) W. A. Herrmann, *Angew. Chem. Int. Ed.* **2002**, *41*, 1290–1309; d) I. Dragutan, V. Dragutan, L. Delaude, A. Demonceau, *Arkivoc* **2005**, *(x)*, 206–253.

[10] For reviews, see: a) V. Nair, S. Bindu, V. Sreekumar, *Angew. Chem. Int. Ed.* **2004**, *43*, 5130–5135; b) D. Enders, T. Balensiefer, *Acc. Chem. Res.* **2004**, *37*, 534–541; c) V. César, S. Bellemin-Laponnaz, L. H. Gade, *Chem. Soc. Rev.* **2004**, *33*, 619–636.

[11] L. Delaude, A. Demonceau, A. F. Noels, *Curr. Org. Chem.* **2006**, *10*, 203–215.

[12] a) L. Delaude, A. Demonceau, A. F. Noels, *Chem. Commun.* **2001**, 986–987; b) L. Delaude, M. Szypa, A. Demonceau, A. F. Noels, *Adv. Synth. Catal.* **2002**, *344*, 749–756.

[13] A. Richel, S. Delfosse, C. Cremasco, L. Delaude, A. Demonceau, A. F. Noels, *Tetrahedron Lett.* **2003**, *44*, 6011–6015.

[14] L. Delaude, S. Delfosse, A. Richel, A. Demonceau, A. F. Noels, *Chem. Commun.* **2003**, 1526–1527.

[15] L. Quebatte, E. Solari, R. Scopelliti, K. Severin, *Organometallics* **2005**, *24*, 1404–1406.

[16] M. Haas, E. Solari, Q. T. Nguyen, S. Gautier, R. Scopelliti, K. Severin, *Adv. Synth. Catal.* **2006**, *348*, 439–442.

[17] A. J. Arduengo, III, F. Davidson, H. V. R. Dias, J. R. Goerlich, D. Khasnis, W. J. Marshall, T. K. Prakasha, *J. Am. Chem. Soc.* **1997**, *119*, 12742–12749.

[18] A. Fürstner, L. Ackermann, B. Gabor, R. Goddard, C. W. Lehmann, R. Mynott, F. Stelzer, O. R. Thiel, *Chem. Eur. J.* **2001**, *7*, 3236–3253.

[19] a) K. Matyjaszewski, J. Xia, *Chem. Rev.* **2001**, *101*, 2921–2990; b) M. Kamigaito, T. Ando, M. Sawamoto, *Chem. Rev.* **2001**, *101*, 3689–3745.

[20] W. Tang, N. V. Tsarevsky, K. Matyjaszewski, *J. Am. Chem. Soc.* **2006**, *128*, 1598–1604.

[21] a) Y. Watanabe, T. Ando, M. Kamigaito, M. Sawamoto, *Macromolecules* **2001**, *34*, 4370–4374; b) O. Tutusaus, S. Delfosse, F. Simal, A. Demonceau, A. F. Noels, R. Nuñez, C. Viñas, F. Teixidor, *Inorg. Chem. Commun.* **2002**, *5*, 941–945.

[22] S. Chang, Y. Na, H. J. Shin, E. Choi, L. S. Jeong, *Tetrahedron Lett.* **2002**, *43*, 7445–7448.

[23] a) K. Ferré-Filmon, L. Delaude, A. Demonceau, A. F. Noels, *Eur. J. Org. Chem.* **2005**, 3319–3325; b) J. Velder, S. Ritter, J. Lex, H.-G. Schmalz, *Synthesis* **2006**, 273–278.

[24] K. Ferré-Filmon, L. Delaude, A. Demonceau, A. F. Noels, *Coord. Chem. Rev.* **2004**, *248*, 2323–2336.

[25] a) J. S. Kingsbury, J. P. A. Harrity, P. J. Bonitatebus, Jr., A. H. Hoveyda, *J. Am. Chem. Soc.* **1999**, *121*, 791–799; b) S. B. Garber, J. S. Kingsbury, B. L. Gray, A. H. Hoveyda, *J. Am. Chem. Soc.* **2000**, *122*, 8168–8179; c) S. Gessler, S. Randl, S. Blechert, *Tetrahedron Lett.* **2000**, *41*, 9973–9976; d) H. Wakamatsu, S. Blechert, *Angew. Chem. Int. Ed.* **2002**, *41*, 794–796; e) H. Wakamatsu, S. Blechert, *Angew. Chem. Int. Ed.* **2002**, *41*, 2403–2405; f) K. Grela, S. Harutyunyan, A. Michrowska, *Angew. Chem. Int. Ed.* **2002**, *41*, 4038–4040; g) A. Michrowska, S. Harutyunyan, V. Sashuk, G. Dolgonos, K. Grela, *J. Am. Chem. Soc.* **2004**, *126*, 9318–9325.

[26] B. Lebedev, N. Smirnova, Y. Kiparisova, K. Makovetsky, *Makromol. Chem.* **1992**, *193*, 1399–1411.

[27] B. Lebedev, N. Smirnova, *Macromol. Chem. Phys.* **1994**, *195*, 35–63.

[28] A. Mühlebach, P. Bernhard, N. Bühler, T. Karlen, A. Ludi, *J. Mol. Catal.* **1994**, *90*, 143–156.
[29] a) P. Alvarez, J. Gimeno, P. Lastra, *Organometallics* **2002**, *21*, 5678–5680; b) B. Al Samak, V. Amir-Ebrahimi, D. G. Corry, J. G. Hamilton, S. Rigby, J. J. Rooney, J. M. Thompson, *J. Mol. Catal. A: Chem.* **2000**, *160*, 13–21.
[30] a) K. J. Ivin, J. C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, San Diego, **1997**; b) *Handbook of Metathesis*, (Ed.: R. H. Grubbs), Wiley-VCH: Weinheim, **2003**.
[31] Y. Miyaki, T. Onishi, S. Ogoshi, H. Kurosawa, *J. Organomet. Chem.* **2000**, *616*, 135–139.
[32] a) B. Çetinkaya, S. Demir, I. Özdemir, L. Toupet, D. Séméril, C. Bruneau, P. H. Dixneuf, *New J. Chem.* **2001**, *25*, 519–521; b) D. Séméril, C. Bruneau, P. H. Dixneuf, *Helv. Chim. Acta* **2001**, *84*, 3335–3341.
[33] C. Bruneau, P. H. Dixneuf, *Angew. Chem. Int. Ed.* **2006**, *45*, 2176–2203.

