

Synthesis of Highly Active Ruthenium Indenylidene Complexes for Atom-Transfer Radical Polymerization and Ring-Opening-Metathesis Polymerization**

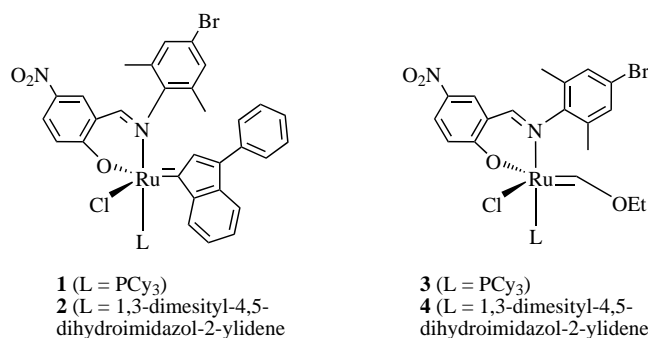
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During the last few years ruthenium-based alkylidene complexes bearing N-heterocyclic carbene ligands (NHC) have provided a rush of highly active catalysts for olefin metathesis.^[1] Soon thereafter it was recognized that these complexes have more to offer than first thought since they can be successfully introduced in controlled radical reactions, such as atom-transfer radical addition (ATRA)^[2] and atom-transfer radical polymerization (ATRP).^[3] This trump card opens up vistas for elegant processes that can ultimately streamline multistep sequences and enable diverse post-metathesis functionalizations.

ATRP has developed into one of the most robust synthetic tools available among controlled radical polymerization reactions and it has opened new synthetic routes to a variety of polymeric materials.^[4–6] These reactions combine the robustness (functional-group tolerance, an almost no sensitivity to moisture) and the possibility for scale up of a radical polymerization with the absence of the termination and transfer reactions of a living process. The basis of ATRP is the reversible transfer of a (pseudo)halogen atom from a monomeric or polymeric alkyl halide to a transition-metal complex in a lower oxidation state, thus forming an organic radical and a metal complex in a higher oxidation state. Since this equilibrium is shifted to the side of the dormant species, the number of radicals remains very low. Furthermore the exchange between oxidized catalyst and organic radical is very fast which results in an uniform growth of the polymer chains. A strategy that has proven to be very successful in olefin metathesis is the combination of a strongly binding NHC ligand and a rather labile group, such as a phosphane,^[1c,d] pyridine,^[7] or readily dissociating metal fragments.^[8] Another approach that has been pursued, is the use of so-called “dangling ligands”.^[9] Especially the last variant gives access to robust and stable catalysts at room temperature but highly active systems at slightly elevated temperatures. Sometimes it is necessary to mix monomer and catalyst at room temperature, put them in an appropriate mould, and heat the mixture to start the reaction. In this context we have successfully implemented Schiff base ligands of the salicylal-

diminato type as dangling ligands in both olefin metathesis^[10] and enol-ester synthesis with alkylidene, indenylidene, and vinylidene fragments.^[11] The two donor atoms of this ligand have opposing natures, the phenolate oxygen atom is a hard donor and is known to stabilize the higher oxidation states of ruthenium,^[12] whereas the imine nitrogen atom is in comparison soft and is a stabilizer of the lower oxidation states.^[13] This ligand fulfils the strict requirements necessary to establish the atom-transfer equilibrium in ATRA and ATRP.^[14] Following on from these investigations, we recognized that combining an N-heterocyclic carbene ligand with a bidentate salicylalimine ligand in the same compound should lead to superior performance because: 1) the strong electron-donating ability of the imidazol-2-ylidene-type ligand can facilitate the decoordination of one side of the bidentate ligand plus it can stabilize the generated intermediate;^[15] 2) the bulky mesitylene groups protect the carbene species and prevent bimolecular decomposition;^[16] 3) with a phosphane-free catalyst P–C decomposition reactions are avoided.^[17]

We synthesized four mixed-ligand ruthenium-(3-phenyl-1-indenylidene) Schiff base complexes **1–4**, and found that the reactivities of these species bear comparison with the most



active ruthenium-based systems reported to date. These easily accessible and air-stable catalysts combine high activity with a very long catalyst life-time.

Methyl methacrylate (MMA) was chosen as a representative monomer and the polymerization was initiated by ethyl-2-bromo-2-methylpropionate at 85 °C. From the results summarized in Table 1, it appears that the neutral indenylidene complex **1** is moderately active for the conversion of MMA, but the polymer is produced in a well-controlled manner and possesses a very narrow molecular-weight distribution (MWD) ($M_w/M_n = 1.19$).

The molecular weight agrees with the calculated one as indicated by the high initiator efficiency ($f = 0.92$). To increase the activity of the ruthenium-indenylidene systems, a potentially more active 14-electron complex was generated in situ by treating the neutral complex with AgBF₄. In this way the chloride was abstracted at room temperature before the monomer and initiator were added.

The active species generated in this way is a cationic ruthenium complex where BF₄[–] acts as a counterion. With this cationic species, we studied the possibility to perform

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Table 1: Ruthenium-catalyzed controlled atom-transfer radical polymerization of MMA.^[a]

Conditions	Catalyst	Conversion [%]	$M_n^{[b]}$ [$\times 10^3$]	M_w/M_n	$f^{[c]}$
neutral ^[d]	1	54	23.5	1.19	0.92
cationic ^[e]	1	73	37.6	1.30	0.78
toluene/water ^[f]	1	82	46.9	1.25	0.74
neutral ^[d]	2	95	39.0	1.21	0.98
cationic ^[e]	2	97	40.0	1.31	1.00
toluene/water ^[f]	2	100	41.9	1.30	0.96
neutral ^[d]	3	74	28.9	1.22	1.0
cationic ^[e]	3	90	45.3	1.43	0.80
toluene/water ^[f]	3	99	64.3	1.57	0.62
neutral ^[d]	4	99	41.4	1.30	0.97
cationic ^[e]	4	100	45.2	1.28	0.89
toluene/water ^[f]	4	100	49.1	1.40	0.82

[a] $[MMA]_0/[initiator]_0/[Ru]_0 = 800:2:1$ (see Experimental Section).
[b] Determined with size exclusion chromatography (SEC) with PMMA calibration. [c] Initiation efficiency $f = M_{n,calcd}/M_{n,exp.}$ with $M_{n,calcd} = ([MMA]_0/[initiator]_0) \times M_{w,MMA} \times \text{conversion}$. [d] Neutral complex at 85 °C, 16 h, solvent: toluene (1 mL). [e] Cationic complex at 85 °C, 16 h, solvent: toluene (1 mL). [f] Cationic complex at 85 °C, 16 h, solvent: toluene (1 mL), water (1.5 mL).

ATRP under “suspension” conditions (for instance, with pure toluene as solvent (monomer/toluene = 40/60 v/v %) or in a mixture toluene/water (monomer/toluene/water = 25/37.5/37.5 v/v %)). Unlike conventional suspension or dispersion polymerizations, no dispersants or surfactants were added to the reaction mixture. A pronounced increase in monomer conversion is observed with the cationic species (73 %), yet this is also accompanied with a slight broadening of the MWD ($M_w/M_n = 1.30$) and a decrease in initiator efficiency is observed ($f = 0.78$). This tendency is even more conspicuous in the case of the suspension polymerization (82 %, $M_w/M_n = 1.25$, $f = 0.74$). From the kinetic experiments the apparent propagation constants in the three above mentioned situations can be calculated: $k_{app,1} = 1.28 \times 10^{-5} \text{ s}^{-1}$ (neutral **1**), $k_{app,2} = 2.16 \times 10^{-5} \text{ s}^{-1}$ (cationic **1**), $k_{app,3} = 3.2 \times 10^{-5} \text{ s}^{-1}$ (toluene/water). Under all these experimental conditions all the criteria of a living polymerization are fulfilled as indicated by a linear time dependence of $\ln([M]_0/[M])$ and a linear increase of the molecular weight versus the MMA conversion (e.g. catalyst **1** in Figure 1 and Figure 2).

The linear relation between time and $\ln([M]_0/[M])$ indicates that the number of active species remains constant during polymerization (Figure 1), while a lack of transfer reactions is supported by the linearity of M_n versus conversion (Figure 2). The presence of radical intermediates was demonstrated by the total inhibition of the polymerization after addition of 5 equivalents of galvinoxyl. Furthermore, ^{13}C NMR spectroscopy showed that the poly(methyl methacrylate) (PMMA) obtained in this way is very similar to the PMMA that was radically prepared using AIBN (AIBN = 2,2'-azobis[(2-methylpropanenitrile)] as the initiator in toluene at 85 °C (tacticity: $rr:rm:mm = 58:37:5.2$, $\rho = 0.98$).^[18] When the phosphane moiety is replaced in **1** by a more σ -donating imidazol-2-ylidene ligand (**2**) the catalytic activity

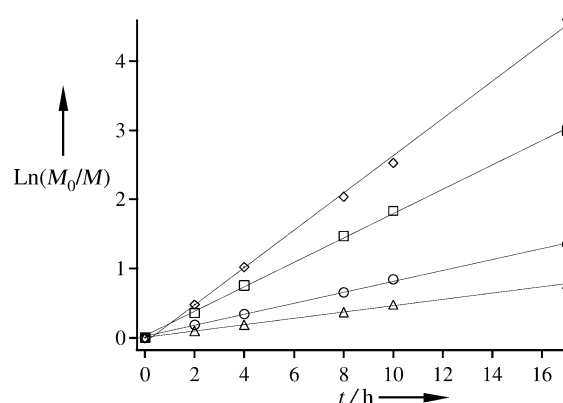


Figure 1. Time dependence of $\ln([M]_0/[M])$ at 85 °C where $[M]_0$ and $[M]$ are the MMA concentrations at times 0 and t . Catalyst **1** (Δ): $y = 0.0459x + 0.0038$; $r = 0.999$; catalyst **2** (\square): $y = 0.1769x + 0.0262$; $r = 0.999$; catalyst **3** (\circ): $y = 0.0798x + 0.0215$; $r = 0.998$; catalyst **4** (\diamond): $y = 0.2696x - 0.064$; $r = 0.998$.

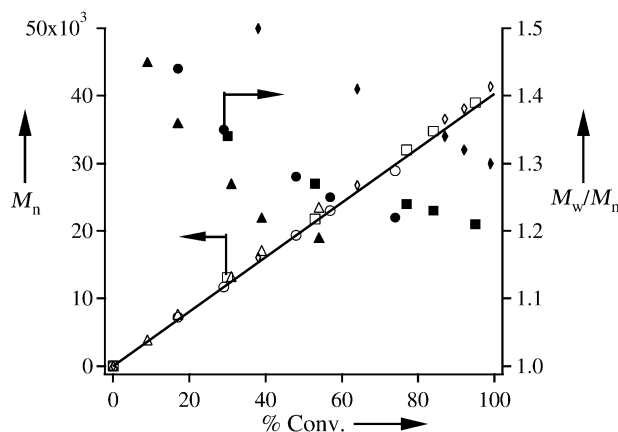


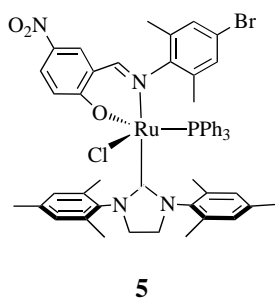
Figure 2. Plot of the molecular weight M_n and M_w/M_n versus the MMA conversion. Catalyst **1** (Δ , \blacktriangle): $y = 434.64x + 29.62$; $r = 0.999$; catalyst **2** (\square , \blacksquare): $y = 392.15x + 306.89$; $r = 0.999$; catalyst **3** (\circ , \bullet): $y = 409.68x + 291.23$; $r = 0.999$; catalyst **4** (\diamond , \blacklozenge): $y = 0.2696x - 0.064$; $r = 0.998$; — = calculated M_n .

increased dramatically ($k_{app} = 4.9 \times 10^{-5} \text{ s}^{-1}$ Figure 1). The cationic analogue is highly active (> 95 % conversion) and polymers with predetermined molecular weights and narrow polydispersities are obtained ($M_w/M_n < 1.31$). To elaborate the influence of the ruthenium carbene unit, a modification of the indenylidene entity was performed. The most straightforward route to achieve this transformation is to apply a metathesis step with vinyl ether derivatives. Such compounds can rapidly and selectively react in an irreversible way with the ruthenium carbene fragment to generate the corresponding alkoxycarbene derivative.^[19] On this basis the Fischer homologues (**3** and **4**) were generated in situ and tested for the ATRP of MMA. Our results show that catalyst **4** belongs to the most active ruthenium-carbene systems known to date with an almost quantitative conversion, giving polymer with a polydispersity index of 1.30 and an initiation efficiency of 0.97. Furthermore, the cationic congeners are very active (100 % conversion) in pure toluene and in water/toluene

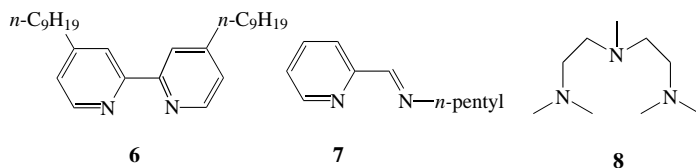
mixture and in both cases the observed molecular-weight distribution remains narrow ($M_w/M_n = 1.28$ and 1.4). The exact role of the carbene entity is not unambiguously clear and needs further investigations. We believe that the active ATRP species is derived from the carbene fragment. This is strongly indicated by the fact that the phosphane-containing system, **5**, is not active for ATRP. The

results obtained with the best performing systems (**4**) can compete with well-established copper systems for the polymerization of MMA. At present the most active copper system is CuBr/Me₆TREN (TREN = tris(2-(dimethylamino)ethyl)amine). Although it is generally very active for acrylates its activity for MMA polymerization is lower.^[20] In Table 2 we compare three copper systems that are very active for the polymerization of methacrylates.^[21–23] Ligands **6–8** are used in these systems. From Table 2 it is clear that complex **4** and more specific its cationic congener (**4**⁺) bear comparison with the copper-based systems in terms of activity. However, the copper-based systems still have a better control over the polymers formed which is indicated by the very small molecular-weight distribution combined with a high initiator efficiency.

Complexes **1** and **2** were also tested for the ring-opening-metathesis polymerization (ROMP) of some typical low-strain cyclic olefins namely cyclooctene (CyO) and cyclopentene (Cyp; Table 3).



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Table 2: Comparison of Ru catalyst **4** with the first generation Grubbs catalyst and some conventional Cu catalysts.

Catalyst	Monomer/Cat.	<i>t</i> [h]	Conversion [%]	<i>M_n</i> [× 10 ³]	<i>M_w/M_n</i>	<i>f</i>	<i>k_{app}</i> [s ^{−1}]
4	800	16	99	41.4	1.30	0.97	4.9 × 10 ^{−5}
4 ⁺	800	16	100	45.2	1.28	0.89	15.7 × 10 ^{−5}
CuCl/ 6 ^[a]	445	20	95	19.8	1.09	1.10	4.2 × 10 ^{−5}
CuBr/ 7 ^[b]	100	4	85	8.9	1.23	0.95	12.6 × 10 ^{−5}
CuBr/ 8 ^[c]	200	8.5	76	15.2	1.16	0.82	–

[a] [Cu]:[initiator]:[**6**] = 1:2:2, initiator = MePhSO₂Cl, *T* = 90 °C, 4.67 M in diphenyl ether.^[20] [b] [Cu]:[initiator]:[**7**] = 1:1:2, initiator = ethyl-2-bromo-2-methylpropionate, *T* = 90 °C, 50 v/v% in toluene.^[21] [c] [Cu]:[initiator]:[**8**] = 1:1:2, initiator = ethyl-2-bromo-2-methylpropionate, *T* = 90 °C, bulk.^[22]

Table 3: ROMP of low-strain cyclic olefins using catalysts **1–2**.^[a]

Catalyst	Monomer	Monomer/Cat.	<i>t</i>	Conversion [%]	<i>M_n</i> ^[b] [× 10 ⁴]	<i>M_w/M_n</i> ^[b]	<i>f</i> ^[c]
1	CyO	10000	17 h	53	88.5	1.79	0.66
2	CyO	10000	< 15 min	100	121	1.60	0.91
1	Cyp	5000	17 h	41	20	1.78	0.70
2	Cyp	5000	17 h	78	31.6	1.55	0.84

[a] solvent: toluene, room temperature. [b] Determined with size exclusion chromatography (SEC) with PMMA calibration. [c] Initiation efficiency $f = M_{n,calcd}/M_{n,exp.}$ with $M_{n,calcd} = ([Mon]_0/[initiator]_0) M_{w,mon} \cdot conversion$.

From these results it is clear that complex **1** but especially complex **2** are highly active catalysts for the ROMP of cyclopentene and cyclooctene. The phosphane-free system seems to be the best performing one, as a quantitative CyO conversion is obtained at room temperature in less than 15 min. With a turnover frequency of 667 min^{−1} at room temperature for the polymerization of cyclooctene, complex **2** is an alternative to the second-generation Grubbs-type catalysts (for which when monomer/cat. = 10000, conversion is complete in 30 min, no gel permeation chromatography (GPC) data are reported)^[24] what is more it gave access to well controlled high-molecular-weight polymers that are soluble in chloroform which is not the case for the system reported by Grubbs and Bielawski.^[24] The contribution of transfer reactions is suppressed as the initiator efficiencies are all lower than unity. Cyclopentene, a more challenging monomer to polymerize by ROMP, is also converted in 78 % yield after 17 h with a molecular weight that almost fits the theoretical predicted one.

Since the ruthenium-benzylidene analogues are also highly active in all kind of metathesis reactions and they are more readily accessible than other highly active systems, these types of catalyst have great potential.^[25,26]

In conclusion we have succeeded in synthesizing a new type of ruthenium indenylidene complex bearing a bidentate Schiff base and/or N-heterocyclic carbene ligands which show a pronounced activity for the controlled radical polymerization of methyl methacrylate. Further fine-tuning of the catalyst into a cationic variant or transforming the indenylidene entity into a Fischer-type carbene improves the activity and give access to well-controlled polymers with a narrow polydispersity. These systems are also highly active for the ROMP of low-strain cyclic olefins. We believe that this system has the highest dual activity in ROMP and ATRP.

Experimental Section

All reagents and solvents were dried, distilled, and stored under nitrogen by using conventional techniques. Catalyst **1** was made as described in ref. [11b].

Analytical data for **1** (see Figure 3): dark brown solid (yield 80 %), ¹H NMR (299.89 MHz, [D₆]Benzene, 25 °C, TMS): δ = 8.29 (d, 1 H, H7), 8.22 (dd, *J*(H,H) = 6.9 Hz, 1 H, H23), 7.74 (d, *J*(H,H) = 4.6 Hz, 2 H, H26), 7.57 (d, 1 H, H5), 7.05 (d, *J*(H,H) = 9.4 Hz,

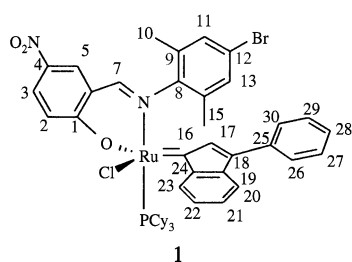


Figure 3. Numbering scheme for 1.

H3), 7.49 (d, $J(\text{H,H}) = 5.5$ Hz, 1H, H28), 7.46 (dd, $J(\text{H,H}) = 6.3$, 2.6 Hz, 2H, H27), 7.42 (s, 1H, H17), 7.32 (td, $J(\text{H20}, \text{H21}) = J(\text{H21}, \text{H22}) = 7.0$ Hz, 1H, H21), 7.30 (td, $J(\text{H21}, \text{H22}) = J(\text{H22}, \text{H23}) = 7.5$ Hz, 1H, H22), 7.23 (dd, $J(\text{H,H}) = 7.0$ Hz, H20), 6.98 (s, 2H, H11), 6.74 (d, $J(\text{H,H}) = 9.3$ Hz, 1H, H2), 2.42 (q, $J(\text{H,H}) = 12$ Hz, 3H, PCy₃), 2.39 (s, 3H, H10), 1.92–1.56 (m, 20H, CH₂ of PCy₃), 1.42 (d, $J(\text{H,H}) = 6.7$ Hz, 3H, H15), 1.17 ppm (m, 10H, CH₂ of PCy₃); ¹³C NMR (75.41 MHz, [D₆]Benzene, 25°C, TMS): $\delta = 292.04$ (s, $J(\text{P,C}) = 7.8$ Hz, C16), 166.00 (s, C7), 165.70 (s, C1), 142.97 (s, C8), 142.50 (s, C24), 140.08 (s, C19), 138.66 (s, C18), 137.75 (d, $J(\text{C,H}) = 172$ Hz, C17), 135.00 (s, C25), 133.6 (s, C4), 132.22 (d, $J(\text{C,H}) = 162$ Hz, C23), 131.38 (s, C9), 130.8 (d, C22), 128.22 (s, C11), 127.93 (d, C21), 127.82 (d, C3), 127.78 (s, C5), 127.00 (d, C28), 126.7 (d, C26, C30), 120.2 (d, C4), 119.1 (s, C6), 118.5 (d, $J(\text{C,H}) = 155$ Hz, C20), 35.0 (CH), 33.4, 31.5, 29.3, 28.6, 24.5 (CH₂ of PCy₃), 18.08 ppm (q, $J(\text{C,H}) = 124.9$ Hz, C10, C16). ³¹P NMR (121.40 MHz, [D₆]benzene, 25°C, H₃PO₄): $\delta = 48.40$ ppm (s). Elemental analysis calcd (%) for C₄₈H₅₅BrClN₂O₃PRu: C 60.35, H 5.80, N 2.93; found: C 60.97, H 6.34, N 3.17. Complex 2 was synthesized according to literature procedures.^[21,27]

Polymerization of MMA: Ruthenium complex (0.0117 mmol) was added to a glass vial that contained toluene (1 mL) and a magnetic stirring bar. The vessel was purged with argon before the monomer (9.35 mmol) and the initiator (0.0234 mmol, 465 μ L of a 0.05 M stock solution) was added. The reaction mixture was heated for a set time in a thermostated oil bath at 85°C. After cooling the mixture it was dissolved in chloroform and the product was precipitated in *n*-octane. The cationic complexes were generated by adding ruthenium complex (0.0117 mmol) to toluene (1 mL) and subsequently adding a 0.2 M AgBF₄ stock solution (56 μ L) in toluene. After stirring for 20 min, a turbidity of AgCl was detected and the monomer and initiator were then added. In the case of the suspension polymerization at this stage distilled water (1.5 mL) was added. The ethoxy Fischer carbene complex was also obtained in situ by adding 10 equiv of vinyl ether to the catalyst solution (1 or 2) and subsequently stirring for 30 min at room temperature. The cationic variants were also generated by adding AgBF₄ to the ethoxy ruthenium–carbene solution.

A typical ROMP experiment: catalyst solution (100 μ L; 0.1 M) was added to a purged glass vessel containing a magnetic stirrer, toluene (5 mL) and monomer (13 mL CyO, 4.4 mL Cyp). The reaction was thermostated at the appropriate temperature and after 17 h the reaction mixture was transferred into a beaker containing CHCl₃ (10 mL), ethyl vinyl ether (0.1 mmol), and 2,6-di-*tert*-butyl-4-methylphenol (1 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, sticky polymer obtained in this way was collected by filtration, washed with methanol, and dried under vacuum.

Keywords: carbene ligands · homogeneous catalysis · polymerization · ruthenium · Schiff bases

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