From atom transfer radical addition to atom transfer radical polymerisation of vinyl monomers mediated by ruthenium indenylidene complexes

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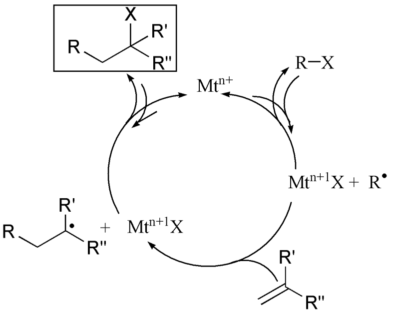
Ruthenium indenylidene complexes provide a new class of versatile catalysts for promoting the Atom Transfer Radical Addition (ATRA) of carbon tetrachloride and chloroform toward a whole array of olefins such as acrylates, methacrylates, styrene and 1-octene. The reaction was successfully extended to an Atom Transfer Radical Polymerisation (ATRP) process by changing the monomer/halide ratio. The polymerisation reaction can be accelerated by adding *n*-Bu_2NH to the reaction mixture. However this leads to an uncontrolled polymerisation. Further improvements to the catalytic activity can be made by transforming the Ru complexes in the cationic 14-electron species or exchanging the indenylidene fragment with an ethoxycarbene. A very high activity is reached when these complexes are exposed to methyl methacrylate in aqueous media while maintaining excellent control over the formed polymers.

Introduction

Transition metal-catalyzed atom transfer radical additions (ATRA), of halogenated alkanes to double bonds, sometimes referred to as Kharasch addition reactions, have received considerable attention in organic synthesis because they offer preparative routes to many natural products.[1,2] Furthermore, many techniques are available to transform a C–X bond into a more convenient C–C bond.[3] Particularly, after the discovery that the ATRA reaction (Scheme 1) could be extended to a controlled atom transfer radical polymerisation (ATRP) by subtle modifications, new impetus was given to the research in this area.[4–7]

In the beginning inorganic salts such as $FeCl_2$ and CuCl were used to perform the addition.[8–10] However, as the organometallic chemistry progressed, more complicated coordination spheres became available which lead to highly active systems that can convert more difficult substrates with remarkable selectivity. During the search for more active systems, ruthenium played a prominent role with $RuCl_2(PPh_3)_3$ in the early years[10] and $RuCl(Cp^*)(PPh_3)_2$ (Cp^* = pentamethylpentamethylcyclopentadienyl)[11] and $RuCl(Ind)(PPh_3)_2$ (Ind = Indenyl)[12,13] in the late 90's. Another important feature of Ru complexes is their versatility in different organic transformations.[14] Sometimes, it is sufficient to work in different reaction conditions or expose the catalysts to varying substrates, to steer the reaction into another direction. This property has also been used for ATRA catalysts. Several groups found that when the Grubbs' ruthenium benzylidene, $Cl_2(PR_3)_2Ru{=}CHPh$, which is known as a very active olefin metathesis catalyst,[15] operates under ATRA conditions clean addition of chlorinated alkanes to several olefins occurs.[16,17] Furthermore, Demonceau and co-workers found that this complex is also capable of performing ATRP of styrene and methyl methacrylates.[18]



Scheme 1

In light of these observations our group became more and more interested in the development of all-round Ru catalysts that can do both olefin metathesis and radical reactions such as ATRA and ATRP.[19–22]

In the late 90's a lot of research was undertaken to find equipotent Grubbs' analogues that perform olefin metathesis reactions to circumvent the rather cumbersome synthesis of the benzylidene complex.[23–27] A very convenient method is the treatment of commercially available $RuCl_2(PPh_3)_3$ with diphenylpropargyl alcohol to deliver phenylindenyl complex **1**.[28] A further modification can be performed by an appropriate exchange of the PPh_3 entities by PCy_3 and 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene using protocols described in the literature.[29] Particularly, the enormous potential of N-heterocyclic carbenes in mimicking phosphines as spectator ligands has been intensively investigated in transition metal mediated catalysis.[30] The last members of the family of Ru–indenylidene complexes are Ru systems bearing a bidentate salicylaldimine ligand (**5**–**6**) which have already successfully been introduced in enol-ester synthesis.[31]

We now report on the excellent activity of these series of Ru–(3-phenylindenylid-1-ene) complexes for ATRA of polyhalogenated alkanes toward different olefins and in a second part the systems are evaluated for the ATRP of methyl methacrylate (MMA) and styrene (Styr) (Fig. 1).

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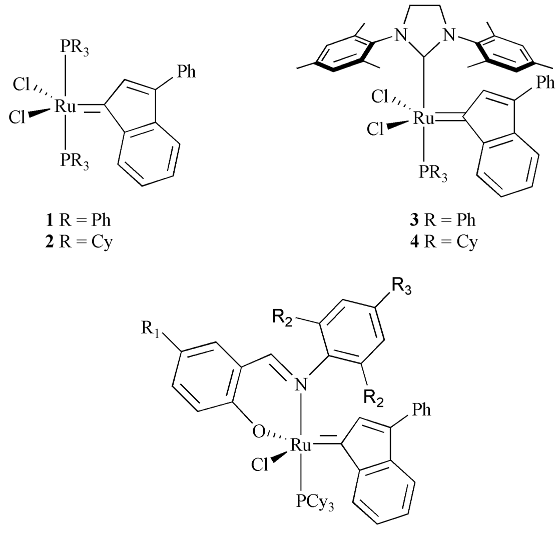


1 R = Ph
2 R = Cy
3 R = Ph
4 R = Cy

5 $R_1 = H, R_2 = i\text{-Pr}, R_3 = H$
6 $R_1 = NO_2, R_2 = Me, R_3 = Br$

Fig. 1 Tested catalytic systems.

Results and discussion

In a first set of experiments, we investigated the catalytic activity of ruthenium complexes **1**–**6** concerning the Kharasch addition of CCl_4 toward 7 representative olefins. After 17 h the samples were analysed with gas chromatography and the yields were calculated from the observation of a clear product peak and no significant amount of oligomers was detected.

From the results in Table 1, one can notice that the highest Kharasch activity is reached with the bis(triphenylphosphine) system (**1**), for all substrates. After 17 h and with a catalyst loading of 0.3 mol% high yields are obtained for the methacrylates (94 and 88%), acrylates (78 and 83%) and styrene (87%). Even the more difficult substrates acrylonitrile and 1-octene can be smoothly converted with total yields of 42 and 56% respectively. The Ru complex bearing two tricyclohexylphosphines, which are known as basic and bulky ligands, led to a significantly less active system. Even the mixed ligand complexes, **3** and **4**, are not able to reach the activity of system **1**. As an example, we take the conversion of MMA and 1-octene: with catalysts **2**, **3** and **4** the MMA conversions are 73, 79, 70% respectively, and with 1-octene conversions of 18, 30 and 12% are reached. An analogous substitution in the ligand environment of the Grubbs' benzylidene, $Cl_2Ru(=CHPh)(PR_3)_2$, led to the same trend in ATRA activity. However in that case, the conversions were lower as a MMA conversion of 73% and a 1-octene conversion of 26% were obtained with the best performing system (R = Ph) after 24 h under identical reaction conditions.[16] The ruthenium Schiff-base complexes (**5** and **6**) manifest themselves as excellent catalysts for promoting the Kharasch addition, as MMA conversions of 58 and 70% and 1-octene conversions of 11 and 40% were reached. The system with the less bulky *ortho*-methyl groups and the electron withdrawing groups (NO_2 and Br) showed a higher activity than the more bulky *ortho* isopropyl groups. The fact that the salicylaldimine ligands can be easily electronically and sterically fine-tuned toward the Kharasch addition reaction was also investigated with other ruthenium systems developed in our group.[19–22,32]

The nature of the chlorinated reagent is also crucial for promoting the Kharasch addition reaction. The results in Table 1 demonstrate that carbon tetrachloride could be added to various olefins in a regioselective way. Under these reaction conditions, no polymerisation products were detected. In contrast, when chloroform was used as the halide source (Table 2) the MMA and styrene conversion reached only 33% and 40% with the best performing system (**1**) and a significant fraction (20%, $M_n = 1200$, $M_w/M_n = 1.40$ and 15%, $M_n = 1342$, $M_w/M_n = 1.50$) of polymers precipitated from the reaction mixture when an excess of *n*-octane or methanol was added. With the systems **2** and **5** the yields for the ATRA of chloroform are negligible ($< 5\%$).

When the olefin/halide ratio was increased, the Kharasch addition reaction could be successfully extended to controlled radical polymerisation of methyl methacrylate and styrene with all the catalysts. However, we chose a new halide source, namely ethyl 2-methyl-2-bromopropionate, for the polymerisation of MMA and (1-bromoethyl)benzene for the polymerisation of styrene. A careful choice of the initiator is necessary in such a way that there is a structural analogy between the initiator and the dormant polymer chain which provides a fast exchange between dormant and active species resulting in well-controlled polymerisation.[7] Besides, CCl_4 has more than 1 halogen which can give complications during the polymerisation such as multiple initiation which is reflected in lower molecular weights than theoretically calculated. The yields and the polymer properties obtained with the different systems are summarized in Table 3.

Since a metal catalysed atom transfer is involved in both reactions, the relationship between ATRP and ATRA is beyond dispute. However, not all catalysts that are efficient in ATRA display the same activity in ATRP. Indeed in the literature some examples are known, for instance the catalyst $Cl_2Ru(p\text{-cymene})(PCy_3)$, which is a well-established ATRP system, showed totally no activity in ATRA reactions with the same initiator.[12,16]

Table 1 ATRA of carbon tetrachloride to olefins catalysed by ruthenium complexes **1**–**6**[a]

	Yield (%)[b]					
Substrate	**1**	**2**	**3**	**4**	**5**	**6**
Methyl methacrylate	94	73	79	70	58	70
Isobutyl methacrylate	88	76	78	74	60	73
Methyl acrylate	78	59	76	55	47	38
n-Butyl acrylate	83	60	63	56	40	44
Styrene	87	72	75	69	67	83
Acrylonitrile	42	12	15	9	23	30
1-Octene	56	18	30	12	11	40

[a] General conditions: prior to use, the reagents, solvent and internal standard were dried using well established procedures. The catalyst (0.03 mmol) was dissolved in toluene (1 ml) and subsequently added through a septum to the solution of alkene (9 mmol), CCl_4 (13 mmol), dodecane (0.25 ml) in toluene (3 ml). The reaction mixture was heated to 80 °C for 17 h. [b] Yields of Kharasch adducts are determined with GC using dodecane as internal standard.

Table 2 ATRA of chloroform to olefins catalysed by ruthenium complexes **1**–**6**[a]

	Yield (%)[b]					
Substrate	**1**	**2**	**3**	**4**	**5**	**6**
Methyl methacrylate	33	< 5	19	7	< 5	20
Styrene	40	< 5	30	10	< 5	13

[a] General conditions: prior to use, the reagents, solvent and internal standard were dried using well established procedures. The catalyst (0.03 mmol) was dissolved in toluene (1 ml) and subsequently added through a septum to the solution of alkene (9 mmol), $CHCl_3$ (13 mmol), dodecane (0.25 ml) in toluene (3 ml). The reaction mixture was heated to 80 °C for 17 h. [b] Yields of Kharasch adducts are determined with GC using dodecane as internal standard.

Table 3 ATRP of MMA and styrene catalysed by ruthenium complexes **1**–**6**[a]

Substrate		1	2	3	4	5	6
MMA	Yield (%)	40	54	67	73	41	54
	M_n ($\times 10^3$)[b]	17.0	23.6	30.6	29.4	15.9	23.5
	M_w/M_n[b]	1.23	1.25	1.24	1.21	1.23	1.19
	f[c]	0.95	0.92	0.88	1.0	1.0	0.92
Styr	Yield (%)	37	44	71	75	30	56
	M_n ($\times 10^3$)[b]	17.0	20.5	30.6	29.9	13.8	23.8
	M_w/M_n[b]	1.30	1.32	1.30	1.33	1.3	1.12
	f[c]	0.91	0.90	0.93	1.0	0.91	0.98

[a] General conditions: the catalyst (0.0117 mmol) was dissolved in toluene (1 ml) and subsequently added through a septum to the solution of monomer (9.35 mmol) and initiator (0.0234 mmol). The reaction mixture was heated to 85 °C for MMA and 110 °C for styrene during 17 h. [b] Determined using size exclusion chromatography with PMMA and PS standards. [c] Initiation efficiency: $f = M_{n,\,theor}/M_{n,\,exp}$ with $M_{n,\,theor}$ = ([Monomer]$_0$/[Initiator]$_0$) $\times$ M_w(monomer) $\times$ conversion.

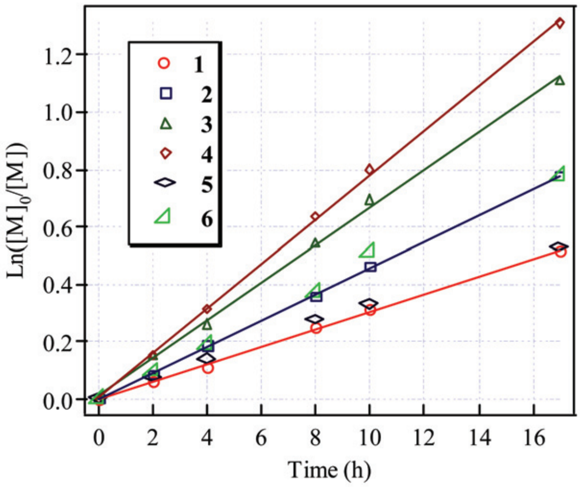


Fig. 2 Time dependence of ln([M]$_0$/[M]) at 85 °C where [M]$_0$ and [M] are the MMA concentrations at times 0 and t. catalysts: **1** $y = 0.0305x - 0.0016$, $r^2 = 0.9976$; **2** $y = 0.0459x - 0.0025$, $r^2 = 0.9996$; **3** $y = 0.0655x - 0.0121$, $r^2 = 0.9983$; **4** $y = 0.0776x + 0.00046$, $r^2 = 0.994$; **5** $y = 0.031x + 0.0118$, $r^2 = 0.9971$; **6** $y = 0.0462x + 0.0056$, $r^2 = 0.998$.

This is also demonstrated with the results from Table 3. The highest activity among the bisphosphine systems is now obtained with tricyclohexyl phosphine as the ligand (**2**) and this for both polymerisations (54 and 44% *versus* 40 and 37% for **1**) while the highest ATRA activity was obtained with triphenylphosphine. It should be mentioned that a different halogen source is used (CCl_4 *versus* ethyl 2-methyl-2-bromopropionate) and totally different reaction conditions (excess CCl_4) are applied when an ATRA reaction is targeted. The availability of R–X compounds in different concentrations or changing the entity of the R–X compound, can generate species with different performances towards ATRA and ATRP.[16–18] Complex **1** showed slightly better control over the formed polymers as the experimental MMA molecular weight are closer to the theoretically predicted one ($f = 0.95$ *versus* 0.92 and 0.91 *versus* 0.90) and the molecular weight distribution is very narrow (1.23 *versus* 1.25).

The ruthenium systems bearing an imidazol-2-ylidene ligand (**3** and **4**) exhibit even a higher ATRP activity and the experimental molecular weights of the polymers fit perfectly the theoretical ones with preservation of a narrow molecular weight distribution. Unfortunately, the polymer yields obtained with the Schiff-base systems are the lowest ($< 55\%$) of all tested catalysts. However with these systems we found the lowest polydispersities of all these experiments ($M_w/M_n = 1.19$ and 1.12 respectively for PMMA and PS with catalyst **6**).

Under these experimental conditions, all the criteria of living polymerisation are fulfilled. The kinetics plots of ln([M]$_0$/[M]) *versus* time with all the catalysts are depicted in Fig. 2 for MMA and in Fig. 3 for styrene and showed a very high correlation. The linear time dependence of the molecular weight indicates that no transfer reactions occurred during the polymerisation (Figs. 4 and 5).

The following relative trend from least to most reactive system can be deduced from Fig. 2 for the polymerisation of MMA: **1** ($k_{app} = 8.47 \times 10^{-6}$ h^{-1}), **5** ($k_{app} = 8.6 \times 10^{-6}$ h^{-1}), **2** ($k_{app} = 1.27 \times 10^{-5}$ h^{-1}), **6** ($k_{app} = 1.29 \times 10^{-5}$ h^{-1}), **3** ($k_{app} = 1.82 \times 10^{-5}$ h^{-1}), **4** ($k_{app} = 2.16 \times 10^{-5}$ h^{-1}). Exactly the same tendency was observed in olefin metathesis where phosphine dissociation from the metal centre was shown to take place. The presence of radical intermediates was evidenced by the fact that the polymerisation was totally inhibited after the addition of a radical scavenger (*e.g.* galvinoxyl). To demonstrate the living character of the MMA polymerisation, a re-growth experiment was performed with the most active system (**4**). After a polymerisation time of 10 h (PMMA yield: 55%, $M_n = 23\,433$, $M_w/M_n = 1.25$) a second amount of monomer was added to the reaction mixture and only a slight increase in polydispersity was observed ($M_n = 51\,552$, $M_w/M_n = 1.43$).

In order to increase the ATRP activity of systems **1**–**4** the following catalyst modifications were undertaken: 1) addition of additives; 2) transforming the Ru complexes into cationic species by treating them with $AgBF_4$; 3) transforming the indenylidene moiety into an ethoxy carbene and 4) a combination of the transformations given in 2 and 3 (Scheme 2).

Recently it was demonstrated by the group of Sawamoto[33] that addition of amine derivatives to Ru-catalysed ATRP reactions, can dramatically improve the catalytic activity. In an analogous experiment we checked the catalytic activity of catalysts **1**–**4** for the polymerisation of MMA and styrene in the presence of 4 equivalents of dibutylamine (relative to the catalyst) and the results are presented in Table 4. These results demonstrate that the addition of dibutylamine has a remarkable impact on the polymerisation behaviour of all systems. This is clearly seen for systems **1** and **2** where PMMA is obtained in 60 and 66% yield and the PS conversions are

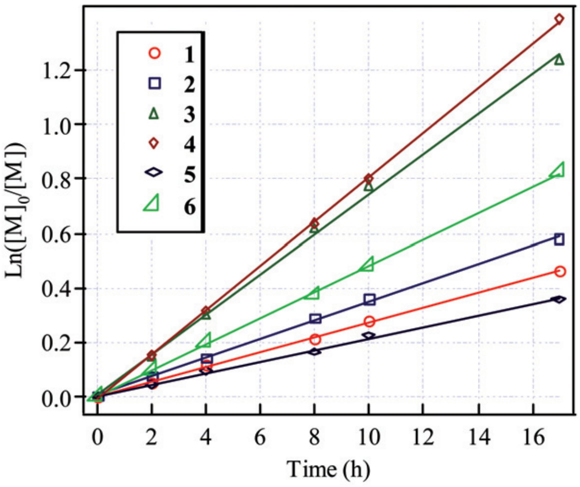


Fig. 3 Time dependence of ln([M]$_0$/[M]) at 110 °C where [M]$_0$ and [M] are the styrene concentrations at times 0 and t. catalysts: **1** $y = 0.0271x + 0.0004$, $r^2 = 0.9991$; **2** $y = 0.0343x + 0.0049$, $r^2 = 0.9989$; **3** $y = 0.0735x + 0.0112$, $r^2 = 0.9982$; **4** $y = 0.0816x - 0.0103$, $r^2 = 0.9998$; **5** $y = 0.021x + 0.0024$, $r^2 = 0.9969$; **6** $y = 0.0481x - 0.0015$, $r^2 = 0.9995$.

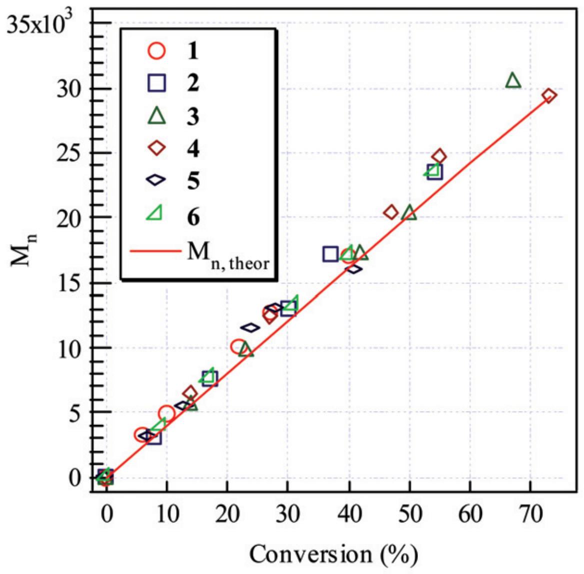


Fig. 4 Dependence of the PMMA molecular weight M_n on monomer conversion using systems **1**–**6**. catalysts: **1** $y = 426.26x + 539.74$, $r^2 = 0.9945$; **2** $y = 445.33x - 103.22$, $r^2 = 0.9978$; **3** $y = 443.27x - 465.23$, $r^2 = 0.9929$; **4** $y = 411.37x + 731.19$, $r^2 = 0.9929$; **5** $y = 408.93x + 454.14$, $r^2 = 0.9755$; **6** $y = 434.64x + 29.62$, $r^2 = 0.999$.

respectively 86 and 94%. Unfortunately, the control over the MMA polymerisation is lost as the molecular weight is much higher than theoretically calculated ($f < 0.35$) and a very broad polymer distribution is observed ($M_w/M_n > 1.6$). In contrast, the PS molecules are generated in a controlled manner. However the results are inferior to those without the addition of n-Bu$_2$NH.

In a last aspect we focused on some chemical transformations of catalysts **1**–**4** and checked their performance toward the ATRP of MMA. The first aspect that was investigated was the abstraction of a chloride in complexes **1**–**4** by treating them with AgBF$_4$ during 30 min at room temperature. In this way, catalysts **7**–**10** are generated *in situ* before the monomer and initiator are added (Scheme 2). The results for the ATRP of MMA in toluene and in a toluene/water mixture are summarized in Table 5.

From these results it is seen that the 14-electron complexes **7**–**10** act as active catalysts for promoting the ATRP of MMA. When toluene is used as solvent, the polymer yields are slightly increased in comparison with the neutral

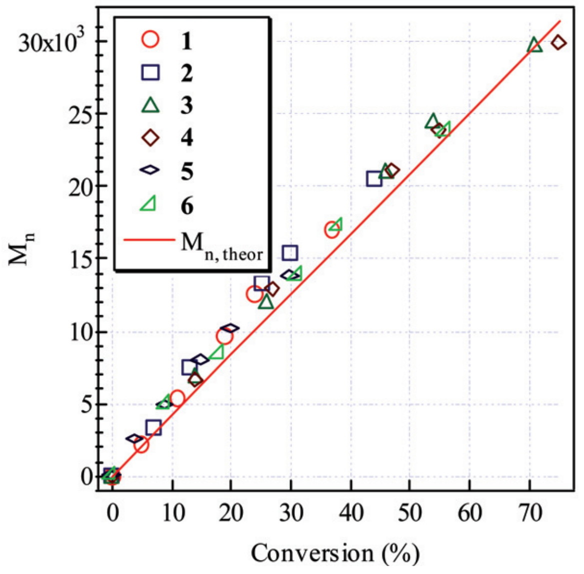
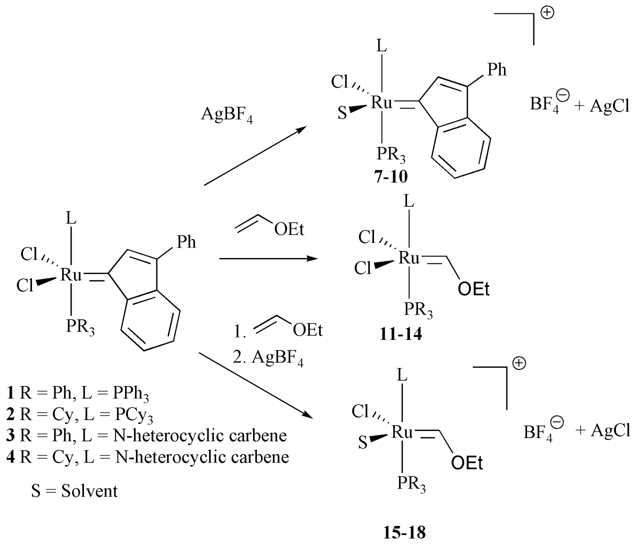


Fig. 5 Dependence of the PS molecular weight M_n on monomer conversion using systems **1**–**6**. catalysts: **1** $y = 475.66x + 179.3$, $r^2 = 0.9909$; **2** $y = 474.59x + 622.37$, $r^2 = 0.9891$; **3** $y = 426.22x + 729.31$, $r^2 = 0.995$; **4** $y = 403.57x + 1066.6$, $r^2 = 0.9912$; **5** $y = 458.26x + 599.33$, $r^2 = 0.9916$; **6** $y = 421.96x + 662.1$, $r^2 = 0.9969$.



Scheme 2

Table 4 ATRP of MMA and styrene catalysed by ruthenium complexes **1**–**4** with n-Bu$_2$NH as additive[a]

		1	2	3	4
MMA	Yield (%)	60	66	75	81
	M_n ($\times 10^3$)[b]	160.0	103.0	100.6	105.2
	M_w/M_n[b]	2.00	1.70	1.60	1.67
	f[c]	0.15	0.26	0.30	0.33
Styr	Yield (%)	86	94	96	98
	M_n ($\times 10^3$)[b]	41.0	51.1	50.2	48.8
	M_w/M_n[b]	1.31	1.43	1.42	1.39
	f[c]	0.88	0.77	0.80	0.84

[a] General conditions: [Monomer]:[Ru]:[In]:[n-Bu$_2$NH] = 800:1:2:4 The reaction mixture was heated to 85 °C for MMA and 110 °C for styrene during 17 h. [b] Determined using size exclusion chromatography with PMMA and PS standards. [c] Initiation efficiency: $f = M_{n,\ theor}/M_{n,\ exp}$ with $M_{n,\ theor} = ([\text{Monomer}]_0/[\text{Initiator}]_0) \times M_w(\text{monomer}) \times \text{conversion}$.

Table 5 ATRP of MMA catalysed by ruthenium complexes **7**–**10**[a]

Cat.	Solv.	Yield (%)	M_n ($\times 10^3$)[b]	M_w/M_n[b]	f[c]
7	Tol.	46	23.7	1.23	0.78
8		60	30.2	1.25	0.80
9		69	35.2	1.26	0.79
10		70	34.3	1.21	0.82
7	Tol./H$_2$O	70	38.6	1.44	0.73
8		91	43.5	1.47	0.84
9		70	35.2	1.46	0.80
10		80	39.3	1.45	0.82

[a] General conditions: MMA = 1 ml, Ru = 0.0117 mmol, Initiator = 465 μl (0.05 M in toluene). The reaction mixture was heated to 85 °C during 17 h. Solvent: 1 ml toluene. [b] Determined using size exclusion chromatography with PMMA and PS standards. [c] Initiation efficiency: $f = M_{n,\ theor}/M_{n,\ exp}$ with $M_{n,\ theor} = ([\text{Monomer}]_0/[\text{Initiator}]_0) \times M_w(\text{monomer}) \times \text{conversion}$.

Table 6 ATRP of MMA catalysed by ruthenium complexes **11**–**18**[a]

Cat.	Solv.	Yield (%)	M_n ($\times 10^3$)[b]	M_w/M_n[b]	f[c]
11	Tol.	54	25.9	1.20	0.84
12		66	33.2	1.24	0.80
13		82	41.8	1.27	0.79
14		86	42.2	1.26	0.82
15		46	24.9	1.25	0.74
16		72	36.5	1.44	0.73
17		76	40.3	1.36	0.76
18		84	33.7	1.20	1.0
15	Tol./H_2O	96	46.9	1.11	0.82
16		91	47.6	1.40	0.77
17		79	55.4	1.32	0.57
18		90	70.4	1.50	0.51

[a] General conditions: MMA = 1 ml, Ru = 0.0117 mmol, Initiator = 465 μl (0.05 M in toluene). The reaction mixture was heated to 85 °C during 17 h. Solvent: 1 ml toluene eventually with 1.5 ml H_2O. [b] Determined using size exclusion chromatography with PMMA and PS standards. [c] Initiation efficiency: $f = M_{n,\ theor}/M_{n,\ exp}$ with $M_{n,\ theor} = ([\text{Monomer}]_0/[\text{Initiator}]_0) \times M_w(\text{monomer}) \times \text{conversion}$.

complexes except for catalyst **10**. Moreover, a very good control is maintained during the polmerisation process as indicated by the fact that the transformation did not affect the polydispersities. When a toluene/water mixture is used very high conversions are reached with all catalytic systems ($>70\%$) but a slight broadening of the molecular weight distribution is observed ($M_w/M_n = 1.45$).

Another aspect that is highlighted in this study, is the role of the indenylidene unit. Therefore we transformed the indenylidene moiety into the corresponding Fischer carbene by an appropriate metathesis reaction with ethyl vinyl ether (10 eq., catalysts **11**–**14**, Scheme 2). Furthermore, the cationic variant of these systems can also be generated *in situ* by analogous treatment with $AgBF_4$. The ATRP results of MMA are shown in Table 6.

A marked increase in the polymerisation rate was observed with complexes **11**–**14** while preserving an excellent control. This is clearly demonstrated when the kinetic plots of $\ln([M]_0/[M])$ *versus* time are analysed (Fig. 6). In this way the relative order in increasing activity toward the MMA polymerisation is as follows: **11** ($k_{app} = 1.29 \times 10^{-5}$ h^{-1}), **12** ($k_{app} = 1.77 \times 10^{-5}$ h^{-1}), **13** ($k_{app} = 2.83 \times 10^{-5}$ h^{-1}), **14** ($k_{app} = 3.25 \times 10^{-5}$ h^{-1}). In these circumstances the number-average molecular weight (M_n) of PMMA increased linearly with monomer conversion (Fig. 7) which confirms the lack of transfer reactions.

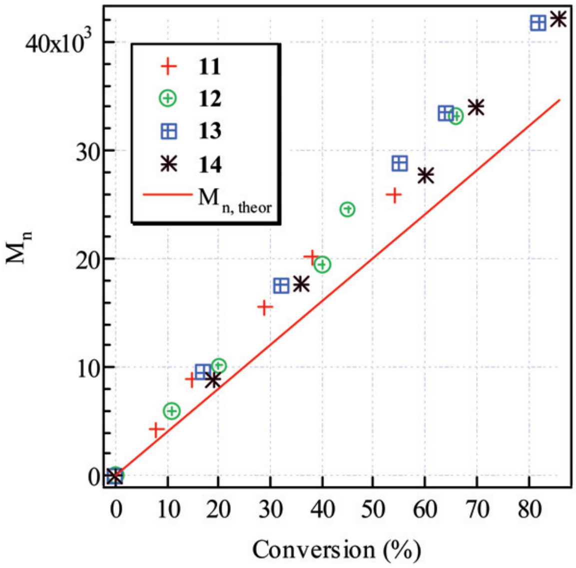


Fig. 6 Time dependence of $\ln([M]_0/[M])$ at 85 °C where $[M]_0$ and $[M]$ are the MMA concentrations at times 0 and t. catalysts: **11** $y = 0.0464x - 0.0098$, $r^2 = 0.9971$; **12** $y = 0.0636x - 0.0133$, $r^2 = 0.9981$; **13** $y = 0.1017x - 0.0103$, $r^2 = 0.9997$; **14** $y = 0.1172x - 0.0099$, $r^2 = 0.999$.

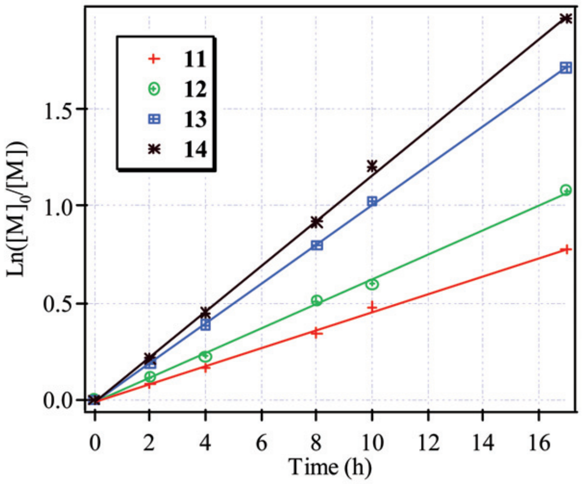


Fig. 7 Dependence of the PMMA molecular weight M_n on monomer conversion using systems **11**–**14**. catalysts: **11** $y = 486.4x + 772.96$, $r^2 = 0.9917$; **12** $y = 507.04x + 174.96$, $r^2 = 0.995$; **13** $y = 509.21x + 647.28$, $r^2 = 0.999$; **14** $y = 486.68x - 229.83$, $r^2 = 0.9984$.

From these experiments it is clear that the nature of the carbene entity plays a pivotal role in the course of the polymerisation and is not just a spectator ligand. The catalytic activity remains constant after abstracting a chloride and a slight increase in polydispersity is observed; however if the polymerisations are performed in a toluene/water mixture very high yields are observed (80–96%) with surprisingly good control. In this case the bis(triphenylphosphine) analogue exhibits the highest activity (96%) with a very narrow polydispersity ($M_w/M_n = 1.11$) and quite good initiation efficiency (0.82).

The exact role of all the intermediates in the mechanism have to be cleared up but demand further investigations.

Conclusion

We have demonstrated that easily accessible ruthenium indenylidene complexes with a multivariate ligand environment are efficient and versatile catalysts for the controlled radical addition of chloroform and carbon tetrachloride toward different olefins. In an extension these catalysts act as excellent atom transfer radical polymerisation catalysts for the polymerisation of methyl methacrylate and styrene in high yields and good control. Furthermore, the catalytic activity can be dramatically improved by transforming the complexes into cationic species by a careful treatment with $AgBF_4$. The polymerisation rate can be accelerated by exposing the catalysts to ethyl vinyl ether, whereby in a pre-metathesis step the indenylidene is transformed into an ethoxycarbene. Changing from neutral to cationic species makes it possible to perform polymerisations in aqueous media with remarkable activity and control.

Experimental

Materials

Unless otherwise noted, all manipulations were performed under argon atmosphere by using standard Schlenk-tube techniques. Argon was first dried by passing through a P_2O_5 (Aldrich 97%) column. The molecular weights and the molecular weight distribution of the polymers were determined by gel permeation chromatography ($CHCl_3$, 25 °C) using a Shimadzu Class-VP system equipped with a series of 3 PL gel columns (PSS SDV 30 cm, Ø = 8 mm, 10^3, 10^4, 10^5 Å) and the calibrations were performed using PL polystyrene and PMMA standards. All solvents were dried using standard procedures and stored over molecular sieves (MS-4 Å) under an argon atmosphere. The monomers: methyl methacrylate, isobutyl methacrylate (IBMA) (Acros, 99%), methyl acrylate (MA) (Acros, 99%), butyl acrylate (BA) (Acros, 99+%) and styrene (Aldrich 99+%), were first distilled from CaH_2 before use. ATRP of methacrylates and styrene was carried out with respectively ethyl 2-methyl-2-bromopropionate and (1-bromoethyl)benzene as initiator and were used as received. Catalysts **1**–**6** were prepared using a previously described methodology.[27,29,31]

Kharasch addition

Ruthenium complex (0.03 mmol) was dissolved in 1 ml toluene and subsequently added through a septum to the solution of alkene (9 mmol), halide (13 mmol) and dodecane (0.250 ml) in toluene (3 ml) under argon. The reaction mixture was then heated at 80 °C for 17 h. Conversion and yields are based on GLC using dodecane as internal standard.

ATRP procedure

The polymerisations were carried out under an argon atmosphere in sealed glass vials. Ruthenium complex (0.0117 mmol) was added to a glass vial containing 1 ml toluene and a magnetic stirring bar. The vessel was purged with argon before the monomer (9.35 mmol) and the initiator (0.0234 mmol, 465 μl of a 0.05 M stock solution) were added. The reaction mixture was then heated during timed intervals in a thermostated oil bath at 85 °C for the methacrylates and 110 °C for styrene. After cooling the mixture was dissolved in chloroform and the product was precipitated in *n*-octane for methyl methacrylate and in methanol for styrene. The polymer was filtered off and dried overnight at 50 °C under vacuum. The cationic indenylidene complexes were generated by adding (0.0117 mmol) ruthenium complex to 1 ml toluene and subsequently adding 56 μl of a 0.2 M $AgBF_4$ stock solution in toluene. After stirring during 30 minutes, turbidity of AgCl was detected and the monomer and initiator were added. After the polymerisation the same procedure was followed as with the neutral catalysts. In the case that a mixture of water and toluene was used, 1.5 ml of distilled water was added to the reaction mixture. The ethoxy Fischer carbene complexes (**7**–**10**) were also synthesised *in situ* by adding 10 equivalents of ethyl vinyl ether to the catalyst solution and subsequently stirring for 30 min at room temperature. The cationic variants were generated by adding $AgBF_4$ to the ethoxy carbene solution.

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