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Radical reactions catalysed by homobimetallic ruthenium(II) complexes bearing Schiff base ligands: atom transfer radical addition and controlled polymerisation

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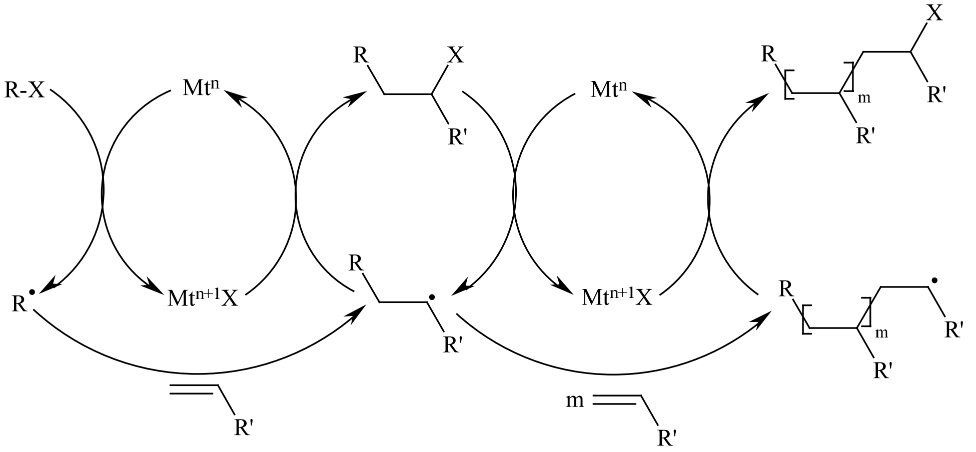
Abstract—The homobimetallic ruthenium Schiff base complexes **Ia**–**f** mediated the atom transfer radical addition (ATRA) of carbon tetrachloride across olefins in excellent yields which markedly depended on the catalyst and the substrate used. The best catalytic system **Ic** is able to compete with the highest performing ruthenium catalysts reported so far for ATRA reactions. In addition these systems are also capable of performing atom transfer radical polymerisation (ATRP) reactions with styrene in high yields and with good control over molecular weight and molecular weight distribution. © 2002 Elsevier Science Ltd. All rights reserved.

In the 60 years since the discovery of M. S. Kharasch that peroxides could promote the anti-Markovnikov addition of CCl_4 to olefins,[1] there has been extensive research on this groundbreaking reaction.[2] The discovery in the mid-1950s that this carbon–carbon and carbon–halogen forming reaction could be catalysed by transition metal complexes, lead to a repression of oligomerisation and telomerisation side processes and the awareness of both industrial and academic synthetic organic chemists in the possibilities of this reaction.[2] In the 40 years thereafter, organometallic catalytic complexes based on Cu, Fe, Ni, Pd, Rh and Ru were developed in order to improve selectivities, to extend the range of possible substrates and to perform the ATRA reaction under milder conditions.[3]

In the mid-1990s, the research in atom transfer radical addition (ATRA) got a powerful injection because of the independent discovery of Sawamoto[4] and Matyjaszewski[5] that ATRA could be extended to atom



Scheme 1. Mechanism of atom transfer radical addition and extension to atom transfer radical polymerisation.

Keywords: atom transfer radical addition; atom transfer radical polymerisation; homogeneous catalysis; ruthenium and compounds; olefins.

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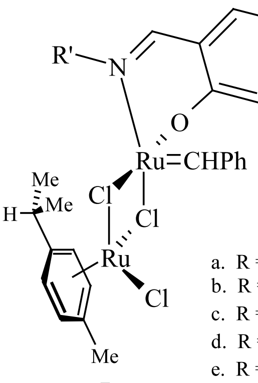
transfer radical polymerisation (ATRP). Indeed, as can be seen in Scheme 1, the mechanism of ATRP rests on the iteration of the ATRA reaction. Recently, we succeeded in synthesising and characterising a new class of homobimetallic complexes **Ia**–**f** (Fig. 1).[6] We now report on the excellent activity of these readily available and robust complexes **Ia**–**f** for ATRA of carbon tetrachloride across various olefins. Moreover, we also checked the catalytic performance of these systems in ATRP reactions.

In a first set of experiments, we checked the ability of ruthenium complexes **Ia**–**f** to catalyse ATRA of CCl_4 to six representative olefins under standardised reaction conditions (Table 1).

The results gathered in Table 1 reveal that the outcome of the reaction depended very much on the olefin and catalytic system used. It is clear that the Schiff base ligand should introduce enough steric bulkiness in the catalytic structure in order to have some reasonable catalytic activity. Indeed, the catalytic performance of systems **Ia**–**b** is much lower compared to compounds **Ic**–**f** that contain a more bulky Schiff base, and this is irrespective of the olefin used. However, the steric influence of the Schiff base is rather subtle as is demonstrated by the fact that too bulky ligands lead to a decrease in catalytic activity. Indeed, the methyl substituted aromatic Schiff base **Ic** reaches systematically higher yields than the isopropyl containing Schiff base **Ie**. Examination of data from Table 1 further shows that the electronic properties of these ligands also exert a big influence on the catalytic activity of these catalysts. This is best illustrated by comparing the yields of **Ia** with **Ib**, **Ic** with **Id** and **Ie** with **If**. In each series, the compound containing the electron withdrawing nitro group has the lowest catalytic activity. The catalytic system **Ic** clearly has the best combination of steric crowding and electronic balance, as this complex exhibits the best catalytic performance of our systems and this for all olefins. For example, when the reaction mixture is heated for 8 h at 65°C, **Ic** converts the best olefins methyl methacrylate (MMA), *n*-butylacrylate (BA) and isobutyl methacrylate (IBMA) into the monoadduct in 86, 93 and 95 yield, respectively. Also methyl acrylate (MA) and styrene (Styr.) are converted smoothly under these reaction conditions, reaching 61 and 78% yield, respectively. When the reaction is performed for 8 h at 85°C instead of 8 h at 65°C, MMA, IBMA, BA and Styr. are converted in nearly quantitative yields. When working under these reaction conditions, MA and acrylonitrile (AN) are also converted smoothly as the ATRA products are obtained in 73 and 66% yield, respectively. To the best of our knowledge, no ruthenium complex reported so far succeeds in performing ATRA of CCl_4 to AN in such good yields. Moreover, system **Ic** (i) easily surpasses the catalytic performance of the most commonly used ruthenium carbene systems today for ATRA of CCl_4 to MMA, BA and Styr. and (ii) competes with the best ruthenium system reported so far for ATRA of CCl_4 to these olefins. In what follows we will support these statements by facts. Fig. 2 depicts some ruthenium systems for which ATRA of CCl_4 to MMA, BA and Styr. was reported in literature. In 1999 Sawamoto et al. reported on the ATRP activity of systems **1** and **3**.[7] Soon thereafter Simal et al. tested these systems for their ATRA activity.[8] In 2000 Simal et al. reported on the ATRA activity of the analogous Cp* containing complexes **2a**–**c**.[9] To the best of our knowledge, **2a** is the best ruthenium system reported so far to mediate ATRA. Matsumoto reported in 1973 on the ATRA activity of system **4**.[10] Before the report on the exceptional activity of **2a**, system **4** was considered as the most efficient and versatile ruthenium catalyst for ATRA reactions. In



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a. R = H, R' = Me
b. R = NO_2, R' = Me
c. R = H, R' = 2,6-Me-4-BrC_6H_2
d. R = NO_2, R' = 2,6-Me-4-BrC_6H_2
e. R = H, R' = 2,6-iPrC_6H_3
f. R = NO_2, R' = 2,6-iPrC_6H_3

Figure 1.

Table 1. ATRA of carbon tetrachloride to representative olefins catalysed by ruthenium complexes **Ia**–**f**[a]

	Ia[b]	**Ib**[b]	**Ic**[b]	**Id**[b]	**Ie**[b]	**If**[b]	**Ic**[c]
Methyl methacrylate	26	11	86	62	79	54	94
Isobutyl methacrylate	19	<5	95	75	86	59	98
Methyl acrylate	17	7	61	47	54	31	73
n-Butyl acrylate	12	<5	93	69	84	55	96
Styrene	22	8	78	56	72	43	91
Acrylonitrile	7	<5	49	22	41	17	66

[a] Yields (%) based on GLC using dodecane as internal standard.

[b] Reaction conditions. Prior to use, the reagents, the solvent (toluene) and the internal standard (dodecane) were dried using well established procedures, distilled and kept under nitrogen at −20°C. The catalyst (0.006 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 catalyst loading was thus 0.066 mol%. The reaction mixture was heated at 65°C for 8 h.

[c] Same as [b] but here the reaction mixture was heated at 85°C for 8 h.

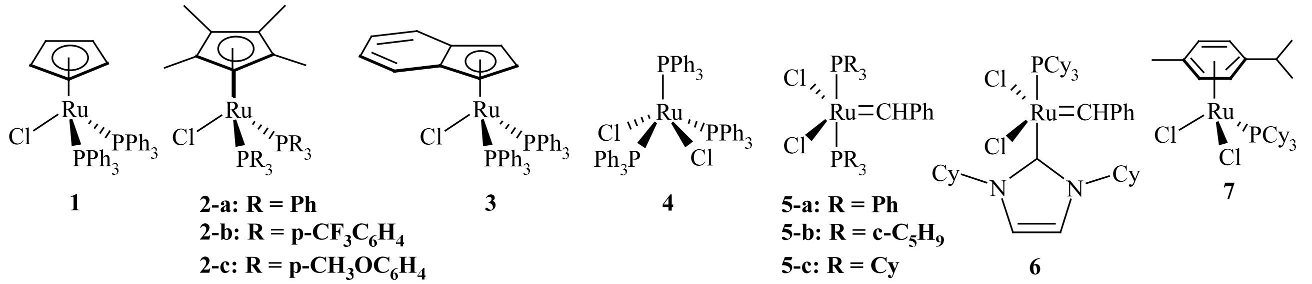

Figure 2. Depiction of some ruthenium systems for which the ATRA reaction of CCl_4 to MMA, BA and Styr. was reported in literature.

1999, the groups of Snapper et al.[11] and Simal et al.[3,12,13] showed that catalytic complexes **5** and **6**, which are known to be highly active olefin metathesis catalysts, were also highly active for promoting ATRA reactions of CCl_4 to electron poor olefins. In this class of ruthenium carbene catalysts, complex **5a** is by far the most active system reported so far. Catalytic compound **7**, developed in the laboratory of Noels et al. and being the highest performing catalytic ruthenium system reported so far for ATRP of vinyl monomers,[14] was tested in 1999 by Simal et al. in ATRA reactions.[12] Table 2 summarises the yields (%) of these ruthenium catalysts for the above-mentioned ATRA reactions. When comparing the results from Table 1 and Table 2, the first thing one observes is the superior activity of our homobimetallic ruthenium carbene complex **Ic** in comparison with the class of ruthenium carbene complexes **5a**–**c** and **6**.

For these types of ruthenium complexes, our related system **Ic** exhibits by far the best catalytic activity in ATRA reactions reported so far. Our complex is also much more performing than system **4**, which set the standards in the field of ruthenium catalysed ATRA reactions from 1973 until 1999. When comparing the catalytic performance of systems **1**, **2b**–**c** and **3** with our highest performing system **Ic**, one has to bear in mind that (i) despite the fact that these catalysts reach high yields in considerable less time than our system, at the time the yields were determined, for system **3** almost quantitative total conversions (this includes the conversion of the substrates in ATRA products, telomers and oligomers) were obtained and (ii) the difference in catalyst loading with a factor of 5. This leads to the conclusion that our system again performs better. Comparing the catalytic performance of system **2a** (the most active ruthenium system reported so far) with our complex **Ic** reveals that they have comparable turnover numbers. However, the turnover frequencies of system **2a** are considerably higher than those obtained with **Ic**. For example, the turnover numbers/turnover frequencies for MMA, BA and Styr. with catalyst **Ic** (tested at 85°C for 8 h) varies around 1400 and 175 h^{-1}, respectively, whereas for **2a** values of around 1600–1700 and 400 h^{-1}, respectively, were reported. A major drawback of system **2a**, however, is the very difficult, tedious and time-consuming synthesis of the complex requiring the use of stringent reaction conditions and rigorously dried and purified solvents and reactants.[15] In contradiction to this, the synthesis of our complex is very easy and moreover most of the reaction intermediates are air stable.[6] So despite the lower turnover frequencies, it is reasonable to state that our complex is able to compete with system **2a** because of their comparable turnover numbers and the much faster, easier, cheaper and more efficient synthesis of our complex.

In a second set of experiments we checked the catalytic activity of our complexes **Ia**–**f** in ATRP reactions with MMA and IBMA (initiator: ethyl 2-methyl-2-bromopropionate), MA and BA (initiator: methyl 2-bromopropionate) and Styr. (initiator: (1-bromoethyl)benzene). None of our catalysts was able to convert MA, BA, MMA, IBMA or AN. Although the relationship between ATRP and ATRA is beyond dispute, not all catalysts that are efficient in ATRA display the same control/activity in ATRP, and vice versa. For example, the outstanding ATRP catalyst **7** exhibits a very poor ATRA activity. However, when styrene is used as a monomer our systems display a totally different behaviour. The yields (%) and characteristics of the formed polystyrene with **Ia**–**c** are

Table 2. Yields (%) of some ruthenium catalysts for which the ATRA reaction of CCl_4 to MMA, BA and Styr. was reported in literature[a]

	1	2a[b]/2b/2c	3	4[c]	5a/5b/5c[c]	6[c]	7[c]
MMA (2 h, 85°C)	97	97/68/54	98	60	73/32/11	4	<2
n-BuA (4 h, 85°C)	14	85/25/13	62	45	–	4	<2
Styr. (5 h, 60°C)	36	95/61/38	81	88	57/45/24	29	<2

[a] Yields (%) based on GLC using dodecane as internal standard. The catalyst loading was in all cases 0.33 mol%.

[b] Here the authors reported that with the substrates indicated, turnover numbers up to 1600–1700 and turnover frequencies of around 400 h^{-1} could be reached.

[c] Here the reaction mixture was allowed to react for 24 h at the indicated temperature.

Table 3. Yield (%) for the ATRP of styrene catalysed by **Ia–f** and properties of the formed polymers with systems **Ia–f**

	Monomer = styrene					
	Ia	**Ib**	**Ic**	**Id**	**Ie**	**If**
Yield (%)[a]	11	–	71	44	63	36
M_n[b] ($\times 10^3$)	–	–	34	25	31	27
M_w[b] ($\times 10^3$)	–	–	46	38	44	40
(M_w/M_n)[b]	–	–	1.35	1.51	1.42	1.49
f_i[c]	–	–	0.87	0.73	0.85	0.56

[a] Reaction conditions: $[\text{monomer}]_0$: $[\text{initiator}]_0$: $[\text{Ru}]_0 = 800:2:1$, initiator: (1-bromoethyl)benzene, temperature: 110°C, reaction time: 17 h.

[b] M_n, M_w and the PDIs are determined by size-exclusion chromatography (SEC) with polystyrene calibration.

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

depicted in Table 3. Again catalyst **Ic** is the best performing. Besides a good yield of 71%, the good initiation efficiency of 0.87 and the polydispersity (M_w/M_n) of 1.35 indicate that the polymerisation proceeds in a controlled fashion. For **Ic** we also followed the monomer conversion and the number average molecular weight (M_n) in function of time. The dependence of molecular weight and polydispersity on monomer conversion are illustrated in Fig. 3. The linear dependence observed for M_n is in agreement with a controlled process with a constant number of growing chains. In addition, the significant decrease of the polydispersity with polymerisation time indicates that the radicals are long-lived. Moreover, also the first order kinetic plot is linear, so that one can conclude that termination reactions are almost completely excluded (Fig. 4).

In conclusion, the catalytic system **Ic** is the most active ruthenium carbene catalyst reported so far for the ATRA reaction of CCl_4 across olefins. Moreover, our homobimetallic catalytic complex **Ic** can compete with **2a**, which is the highest performing system of all types of ruthenium catalysts ever published for promoting ATRA reactions. Furthermore, **Ic** also exhibits good activity and control in ATRP reactions with styrene.

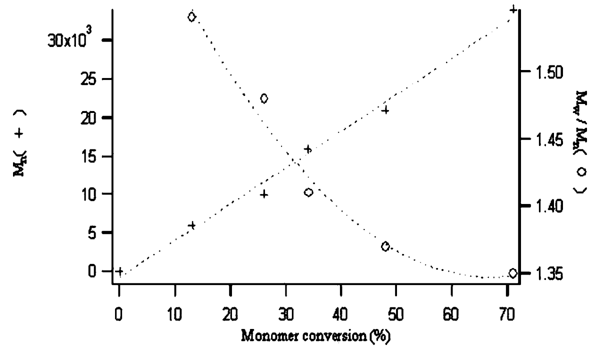

Figure 3. Dependence of the molecular weight M_n and M_w/M_n on monomer conversion for styrene and using catalytic system **Ic**.

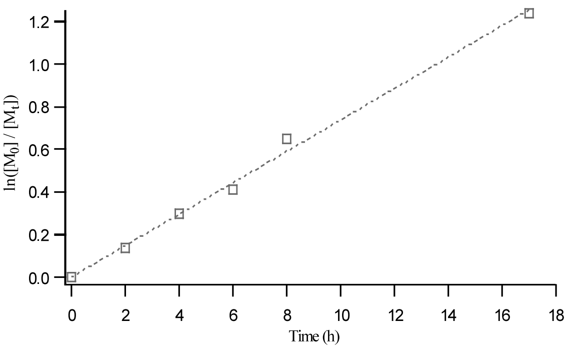

Figure 4. Time dependence of $\ln([M_0]/[M_t])$ for the ATRP of styrene and using catalytic system **Ic**. $[M_0]$ and $[M_t]$ are the monomer concentrations at times 0 and t ($y = 0.074x$; $r^2 = 0.9948$).

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References

1. Kharasch, M. S.; Jensen, E. V.; Urry, W. H. *Science* **1945**, *102*, 128.
2. (a) Minisci, F. *Acc. Chem. Res.* **1975**, *8*, 165; (b) Iqbal, J.; Bhatia, B.; Nayyar, N. K. *Chem. Rev.* **1994**, *94*, 519; (c) Gossage, R. A.; Van De Kuil, L. A.; Van Koten, G. *Acc. Chem. Res.* **1998**, *31*, 423.
3. Simal, F. Ph.D. Thesis, University of Liège, 2000.
4. Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.
5. Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.
6. De Clercq, B.; Verpoort, F. *Adv. Synth. Catal.* **2002**, accepted.
7. Takahashi, H.; Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1999**, *32*, 3820.
8. Simal, F.; Wlodarczac, L.; Demonceau, A.; Noels, A. F. *Eur. J. Org. Chem.* **2001**, 2689.
9. Simal, F.; Wlodarczac, L.; Demonceau, A.; Noels, A. F. *Tetrahedron Lett.* **2000**, *41*, 6071.
10. Matsumoto, H.; Nakano, T.; Nagai, Y. *Tetrahedron Lett.* **1973**, *14*, 5147.
11. Tallarico, J. A.; Malnick, L. M.; Snapper, M. L. *J. Org. Chem.* **1999**, *64*, 344.
12. Simal, F.; Demonceau, A.; Noels, A. F. *Tetrahedron Lett.* **1999**, *40*, 5689.
13. Simal, F.; Demonceau, A.; Noels, A. F. *Recent Res. Devel. Organic. Chem.* **1999**, *3*, 455.
14. Simal, F.; Demonceau, A.; Noels, A. F. *Angew. Chem., Int. Engl. Ed.* **1999**, *38*, 538.
15. (a) Fagan, P. J.; Mahoney, W. S.; Calabrese, J. C.; Williams, I. D. *Organometallics* **1990**, *9*, 1843; (b) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166.