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Kharasch addition and controlled atom transfer radical polymerisation (ATRP) of vinyl monomers catalysed by Grubbs' ruthenium–carbene complexes

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Abstract

The Grubbs' ruthenium–carbene complexes, $RuCl_2(=CHPh)(PR_3)_2$, mediate the Kharasch addition of CCl_4 across olefins, and the controlled atom transfer radical polymerisation of vinyl monomers with high yields and selectivities which markedly depend on the phosphine ligands of the complex (R=phenyl, cyclopentyl, and cyclohexyl). © 1999 Elsevier Science Ltd. All rights reserved.

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Since the pioneering work of Sawamoto[1] and Matyjaszewski,[2] atom transfer radical polymerisation (ATRP) has emerged as a powerful way to conduct controlled/'living' radical polymerisation.[3] This technique rests on the iteration of the Kharasch addition reaction (Scheme 1), in which a transition-metal catalyst acts as a carrier of the halogen atom in a reversible redox process. Initially, the transition-metal species, $M_T{}^n$, abstracts halogen atom X from the organic halide, R-X, to form the oxidised species, $M_T{}^{n+1}X$, and the carbon-centred radical $R^{\cdot}$. In the subsequent step, the radical, $R^{\cdot}$, reacts with alkene (for instance methyl methacrylate, MMA (Scheme 1)) with the formation of the intermediate radical species, R-MMA$^{\cdot}$. The reaction between $M_T{}^{n+1}X$ and R-MMA$^{\cdot}$ results in the target product, R-MMA-X, and regenerates the reduced transition-metal species, $M_T{}^n$, which further reacts with R-X and promotes a new redox cycle.

The high efficiency of the transition-metal catalysed halogen transfer reaction in producing the target product, R-MMA-X, in excellent yields, leads to a low concentration of free radicals, resulting in much less significant termination reactions between radicals. If polymeric halides, R-$(MMA)_i$-X, are reactive enough toward $M_T{}^n$ and the monomer is in excess, a number of atom transfer radical additions, i.e., a radical polymerisation, may occur in a controlled fashion.

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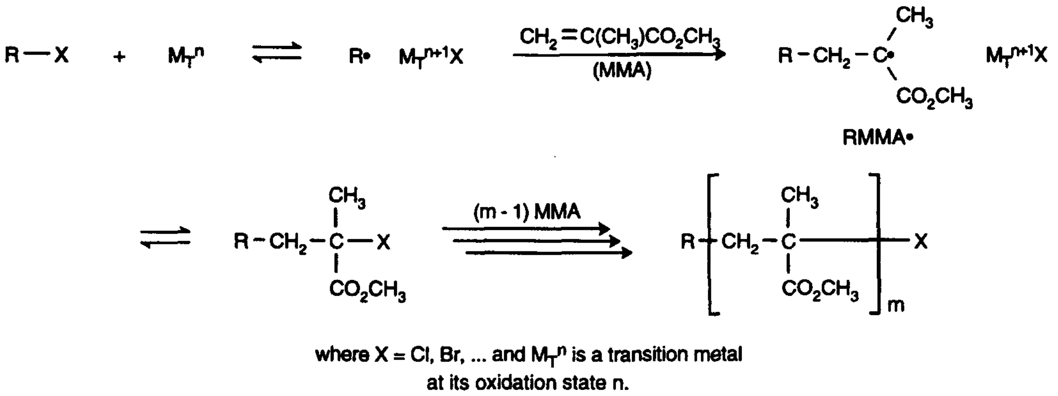
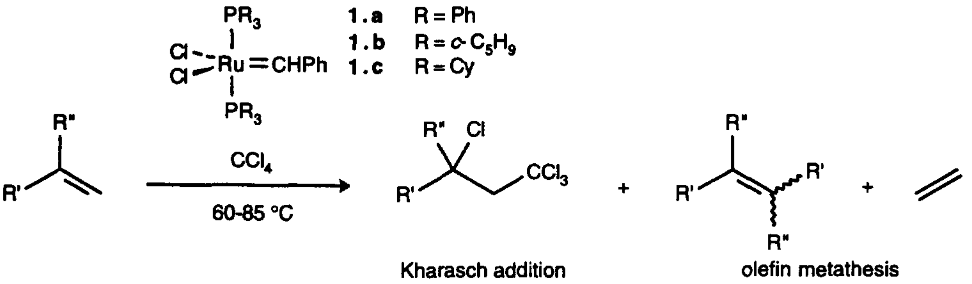


Scheme 1.

Among other transition-metal complexes, $RuCl_2(PPh_3)_3$ (activated by aluminium compounds)[1] and CuCl (complexed by 2,2′-bipyridine ligands)[2] enable controlled radical polymerisations of methacrylates, acrylates, and styrenes. Recently, we discovered that the Grubbs' ruthenium–carbene complex, $RuCl_2(=CHPh)(PCy_3)_2$ (Cy or c-C_6H_{11}=cyclohexyl), was a very efficient catalyst for ATRP of vinyl monomers.[4] Along these lines, we then became interested in the ability of the Grubbs' complex to catalyse the Kharasch addition of CCl_4 across various olefins. The recent paper by Snapper et al.[5] prompted us to publish our results in this field.



The Kharasch addition reactions were performed using slightly modified van Koten's experimental conditions.[6] A typical experiment was carried out by heating a reddish brown solution of the Grubbs' complex (0.03 mmol), olefin (9 mmol), carbon tetrachloride (13 mmol) and toluene (4 mL) in a glass tube under nitrogen, at 60°C. The results are summarised in Table 1. With methyl methacrylate as a model substrate, at a catalyst loading of 0.3 mol%, Kharasch addition of CCl_4 occurred in very low yields (<20%), whatever the complex used. At a somewhat higher temperature (85°C), the Kharasch addition reached 73% with $RuCl_2(=CHPh)(PPh_3)_2$ (**1.a**), the best catalyst among the Grubbs' complexes. As expected, no metathesis occurred with methyl methacrylate. With styrene and 1-octene, however, Kharasch addition was less efficient (up to 57 and 26%, respectively), than with methyl methacrylate, and some olefin metathesis occurred in minute amounts (<4%).

With all of the substrates we tested so far, the highest Kharasch activity was obtained with $RuCl_2(=CHPh)(PPh_3)_2$ (**1.a**). Tricyclohexylphosphine, a basic and bulky ligand, led to a significantly less active catalytic system (**1.c**). Furthermore, quantitative yields were obtained with styrene and methyl methacrylate, and up to 61% yield was reached with 1-octene when 2.5 mol% of catalyst **1.a** was used instead of 0.3 mol%.

In light of these observations, Kharasch addition was attempted in the presence of $RuCl_2(p\text{-cymene})(PCy_3)$, a catalyst we have found to be highly efficient for promoting the controlled atom transfer

Table 1

Influence of the phosphine ligand (PR_3) on Kharasch addition and olefin metathesis catalysed by $RuCl_2(=CHPh)(PR_3)_2$ complexes[a]

Catalyst		reaction time (h) / substrate conversion (%) / Kharasch addition (%) / olefin metathesis (%)		
Styrene		**(R' = C_6H_5, R" = H)**		
1.a	60 °C	5 / 44 / 16 / 0		24 / 86 / 57 / 0
1.b	60 °C	5 / 67 / 29 / 0		24 / 87 / 45 / 0.5
1.c	60 °C	5 / 56 / 15 / 0		24 / 69 / 24 / 1
1-Octene		**(R' = *n*-C_6H_{13}, R" = H)**		
1.a	60 °C	2 / 20 / 5 / 0.5	18 / 48 / 26 / 0.5	24 / 51 / 26 / 0.5
1.b	60 °C	2 / 45 / 8 / 1	6 / 71 / 12 / 2	24 / 75 / 16 / 2
1.c	60 °C	4 / 30 / 3 / 3	6 / 44 / 4 / 4	24 / 80 / 7 / 4
Methyl methacrylate		**(R' = CO_2CH_3, R" = CH_3)**		
1.a	60 °C			24 / 78 / 18 / 0
1.b	60 °C			24 / 62 / 18 / 0
1.c	60 °C			24 / 60 / 4 / 0
1.a	85 °C	4 / 96 / 69 / 0		24 / 99 / 73 / 0
1.b	85 °C	4 / 32 / 4 / 0		24 / 84 / 32 / 0
1.c	85 °C	4 / 28 / 2 / 0		24 / 60 / 11 / 0

[a] Reaction conditions. Prior to use, the reagents, the solvent (toluene) and the internal standard (dodecane) were dried using well established procedures [7], distilled and kept under nitrogen at -20 °C. 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 at 60 or 85 °C for 24 h. The reaction was monitored by withdrawing samples at regular time intervals from the reaction mixture and analysing them by GLC.

[b] Conversion and yields, based on GLC using dodecane as internal standard.

radical polymerisation of vinyl monomers.[4] Quite surprisingly, under the reaction conditions of Table 1, no Kharasch addition products (i.e., <2%) were observed after 24 h.

The nature of the chlorinated reagent is also crucial for promoting Kharasch addition. The results of Table 1 clearly demonstrate the ability of carbon tetrachloride to add regioselectively across various olefins. Under these reaction conditions, olefin polymerisation was not observed. By contrast, when chloroform was used instead of CCl_4 (Table 2), Kharasch addition to methyl methacrylate at 85°C reached only 6% in the presence of $RuCl_2(=CHPh)(PPh_3)_2$,[5] and poly(methyl methacrylate) was precipitated from heptane in 19% yield. In the presence of $RuCl_2(=CHPh)(PCy_3)_2$, addition of $CHCl_3$ to MMA reached 25% and PMMA was formed in 5% yield. These results confirm the importance of the stereoelectronic effects of the phosphine ligands on the outcome of the reaction. Furthermore, they indicate that the balance of these reactions should likely be attained by taking into account short oligomers of the substrate.

When the olefin was in excess, the Grubbs' ruthenium–carbene complexes in combination with CCl_4 as initiator, successfully extended the Kharasch addition to the controlled atom transfer polymerisation of methyl methacrylate and styrene (Table 3). These initiating systems afforded controlled polymers with fairly narrow molecular weight distribution, M_w/M_n=1.2–1.5.[1,8]

Again, the activity of the catalytic systems markedly depended both on the phosphine ligands of the ruthenium–carbene complex, and the substrate. As a further proof, 1-octene did not polymerise under the reaction conditions of Table 3.

Both Kharasch addition and olefin polymerisation apparently proceed by a radical mechanism, as indicated by the following results. For example, addition of galvinoxyl (a well-known inhibitor for

Table 2
Reaction of chloroform with methyl methacrylate catalysed by $RuCl_2(=CHPh)(PR_3)_2$ complexes[a]

Catalyst		Kharasch addition[b]	Polymer yield (%)	M_n[c]	M_w/M_n[c]
1.a	85 °C	24 / 55 / 6 / 0	19	1450	1.45
1.b	85 °C	24 / 90 / 18 / 0	22	1650	1.45
1.c	85 °C	24 / 88 / 25 / 0	5	-	-

[a] Reaction conditions same as in Table 1.
[b] Reaction time (h) / substrate conversion (%) / Kharasch addition (%) / olefin metathesis (%).
[c] Size exclusion chromatography calibrated with PMMA standards.

Table 3
Polymerisation of methyl methacrylate and of styrene catalysed by ruthenium–carbene and $RuCl_2(p\text{-cymene})(PCy_3)$ complexes[a]

Monomer	Catalyst	Polymer yield, %	M_n[b]	M_w/M_n[b]
Methyl methacrylate, 85 °C	$RuCl_2(=CHPh)(PPh_3)_2$	76	17 000	1.25
	$RuCl_2(=CHPh)(P(c\text{-}C_5H_9)_3)_2$	7	5 000	1.50
	$RuCl_2(=CHPh)(PCy_3)_2$	7	4 400	1.38
	$RuCl_2(p\text{-cymene})(PCy_3)$	0	-	-
Styrene, 110 °C	$RuCl_2(=CHPh)(PPh_3)_2$	54	13 800	1.23
	$RuCl_2(=CHPh)(P(c\text{-}C_5H_9)_3)_2$	15	6 000	1.43
	$RuCl_2(=CHPh)(PCy_3)_2$	45	12 500	1.30
	$RuCl_2(p\text{-cymene})(PCy_3)$	31	11 500	1.43

[a] Reaction conditions : catalyst, 0.0117 mmol; initiator (CCl_4), 0.0234 mmol (solution 0.1 M in toluene, 0.25 mL); monomer, 1 mL; polymerisation time, 24 h (for details, see ref. [4-b]).
[b] Size exclusion chromatography calibrated with PMMA and PS standards, respectively.

radical reactions) to methyl methacrylate (10 equiv. galvinoxyl relative to the catalyst, **1.a** or **1.b**), severely inhibited the formation of the expected Kharasch product (<2% instead of 73 and 32% yield in the absence of radical inhibitor (Table 1)). On the other hand, the polymerisations were perfectly inhibited by the addition of 1,1-diphenyl-2-picrylhydrazyl (DPPH) or galvinoxyl (5 equiv. relative to CCl_4). Furthermore, **1.a** and **1.c** were also subjected to typical reaction conditions with styrene (60°C) and methyl methacrylate (85°C) as substrates under air and, as before, no Kharasch addition products (i.e., <2%) were observed.

In conclusion, we have demonstrated that Grubbs' ruthenium–carbene complexes catalyse the Kharasch addition of carbon tetrachloride across olefins, and its subsequent extension to the controlled atom transfer radical polymerisation of methyl methacrylate and styrene. These results pave the way for new developments and new applications of these complexes in fine organic synthesis, and in macromolecular chemistry as well.

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