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Highly efficient Kharasch addition catalysed by $RuCl(Cp^*)(PPh_3)_2$

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Abstract

Air-stable and readily available $RuCl(Cp^*)(PPh_3)_2$ is so far the best ruthenium-based catalyst precursor for promoting the addition of CCl_4 and $CHCl_3$ across olefins at a temperature as low as 40°C. © 2000 Elsevier Science Ltd. All rights reserved.

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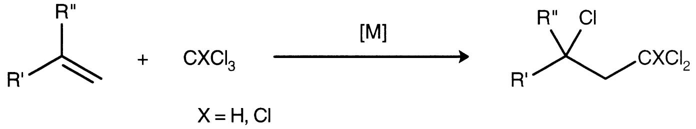
The Kharasch reaction and related processes have become increasingly important in synthetic organic chemistry because the resulting adducts may have an array of multifunctional groups which can be subjected to numerous transformations.[1] Furthermore, the extension of the Kharasch addition to the controlled radical polymerisation of vinyl monomers (ATRP, atom transfer radical polymerisation)[2] has recently revitalised the research in this area as well. This carbon–carbon and carbon–halogen bond-formation is now typically catalysed by transition metal complexes (Scheme 1).



Scheme 1.

The major drawbacks of the Kharasch addition are shown by its limited scope of (poly)-halogenated substrates and by the rather harsh reaction conditions (high reaction temperatures and long reaction times) that are generally required. To overcome its shortcomings, much effort

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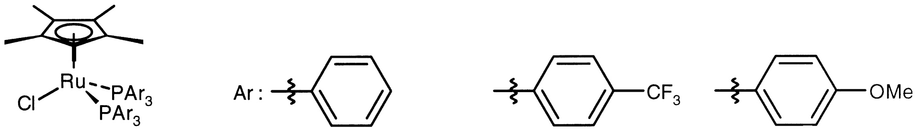
has been made on using new transition metal complexes or adding Lewis acid cocatalysts to activate the carbon–halogen bond in ATRP. Among various transition metals, ruthenium has been successfully utilised to promote the Kharasch reaction, and $RuCl_2(PPh_3)_3$ is so far the classical ruthenium complex.[3] During our study on the Kharasch process, we found that ATRP could proceed smoothly in the presence of $RuCl_2(arene)(PR_3)$ complexes with no need for a Lewis acid.[4,5] Concurrently, we also found that both the Kharasch addition and ATRP could be controlled by using $RuCl_2(=CHPh)(PR_3)_2$,[4,6] the Grubbs' ruthenium benzylidene complex which is now exceedingly popular in olefin metathesis.[7] These and other results[8] clearly indicate that some of the shortcomings of the Kharasch addition can be—partly—mitigated through ligand modification at the metal centre.[2a,b,9] In this paper, we report our preliminary results on the outstanding efficiency of $RuCl(Cp^*)(PPh_3)_2$, an air-stable and easily available complex,[10] for the Kharasch addition to olefins (Scheme 2).



1 2 3

Scheme 2.

In the first set of experiments, the Kharasch addition was realised under standard conditions,[6b] by reacting carbon tetrachloride with four representative olefins at 60–85°C, in the presence of a catalytic amount of $RuCl(Cp^*)(PPh_3)_2$ (Table 1). Only a few hours were found necessary for the complete consumption of methyl methacrylate, *n*-butyl acrylate and styrene, and for the synthesis of the resulting monoadduct with yields ranging from 85 to 100%. 1-Decene, a non-activated substrate, was found to be much less reactive, since only 46% conversion and 27% addition were reached after 24 h at 60°C. These encouraging results prompted us to perform the same experiments under milder conditions. At a temperature as low as 40°C (Table 1) and even at room temperature, the results remained quite good. Total turnover numbers of 1600–1700, and initial turnover frequencies of around 400 h^{-1} were observed, so that we can ascertain that

Table 1
Kharasch addition of carbon tetrachloride to representative olefins catalysed by $[RuCl(Cp^*)(PAr_3)_2]$ complexes **1**–**3**[a]

			Substrate conversion (%) / Kharasch addition (%)[b]		
Substrate		Catalyst :	**1**	**2**	**3**
Methyl methacrylate	40 °C	6 h	79 / 79	58 / 53	49 / 42
	85 °C	2 h	97 / 97	71 / 68	60 / 54
n-Butyl acrylate	85 °C	4 h	85 / 85	36 / 25	22 / 13
Styrene	40 °C	6 h	86 / 69	80 / 52	49 / 30
	60 °C	5 h	97 / 95	89 / 61	60 / 38
1-Decene	60 °C	24 h	46 / 27	10 / 1	2 / 1

[a] 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 (0.03 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).

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

$RuCl(Cp^*)(PPh_3)_2$ greatly surpasses the best ruthenium systems reported so far.[3,6b] Its outstanding efficiency was further confirmed when we reacted chloroform (a substrate reluctant to undergo Kharasch addition) to methyl methacrylate and styrene (Table 2). Again, $RuCl(Cp^*)(PPh_3)_2$ proved to be highly active at moderate temperatures, especially with styrene, whereas $RuCl_2(PPh_3)_3$ showed a similar reactivity only at temperatures around 120°C.[3]

Table 2
Kharasch addition of chloroform to methyl methacrylate and styrene catalysed by $[RuCl(Cp^*)(PAr_3)_2]$ complexes **1**–**3**[a]

			Substrate conversion (%) / Kharasch addition (%)[b]		
Substrate		Catalyst :	**1**	**2**	**3**
Methyl methacrylate	85 °C	24 h	63 / 29	74 / 1	82 / 2
Styrene	60 °C	24 h	69 / 69	70 / 43	73 / 45

[a] Reaction conditions same as in Table 1.

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

Since it is generally agreed that the key step in the Kharasch reaction is the pseudo-oxidative addition of the haloalkane onto the metal complex (M^n), we anticipated that the oxidative process and, hence, the efficacy of the catalyst, should be fine-tuned through ligand modification (Scheme 3).

$$R{-}X \; + \; M^n \; \rightleftharpoons \; R\bullet \; M^{n+1}X$$

Scheme 3.

First, we used $RuCl(Cp)(PPh_3)_2$ whose cyclopentadienyl ligand is less electron-donating than Cp*, and we observed that it was much less efficient that $RuCl(Cp^*)(PPh_3)_2$, except with methyl methacrylate. Second, we replaced the PPh_3 ligands in **1** by *p*-substituted triarylphosphines so as to modify the electronic properties of the phosphine while maintaining the cone angle constant at 145°. Thus, two phosphines were selected on the basis of their electron-donating ability: $P(p\text{-}CF_3C_6H_4)_3 < PPh_3 < P(p\text{-}CH_3OC_6H_4)_3$.[11] An examination of the results collected in Tables 1 and 2 reveals that the corresponding ruthenium–phosphine complexes **2** and **3** were less efficient than the parent complex **1**. In all cases, the reactivity order was $\mathbf{3} < \mathbf{2} < \mathbf{1}$, at variance with the electron-donating ability of the phosphines ($\mathbf{2} < \mathbf{1} < \mathbf{3}$). These results suggest that the stabilisation of the $Ru^{III}Cl$ intermediate species by the phosphine ligand is not predominant. Instead, the reactivity order correlates very well with the ruthenium–phosphine bond energy, as indicated by the enthalpies of formation of $RuCl(Cp^*)(PAr_3)_2$ from the reaction of $RuCl(Cp^*)(COD)$ (COD = 1,5-cyclooctadiene) with $P(p\text{-}XC_6H_4)_3$: $-\Delta H = 18.1$ (**1**, PPh_3) < 20.7 (**2**, $P(p\text{-}CF_3C_6H_4)_3$) < 21.8 (**3**, $P(p\text{-}CH_3OC_6H_4)_3$) kcal/mol.[12] These results suggest therefore that the release of a phosphine ligand from $RuCl(Cp^*)(PAr_3)_2$ is of utmost importance and most likely occurs prior to the activation of the halogenated compound by the unsaturated ruthenium centre.

In conclusion, $RuCl(Cp^*)(PPh_3)_2$ is so far the best ruthenium-based catalyst precursor for promoting the Kharasch addition of CCl_4 and $CHCl_3$ across olefins under mild reaction conditions. A better understanding of the exact nature of ligand effects should help our synthetic and catalytic research efforts. Further investigations are presently underway.

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