

Electrochemistry as a correlation tool with the catalytic activities in $[\text{RuCl}_2(p\text{-cymene})(\text{PAr}_3)]$ -catalysed Kharasch additions

Aurore Richel, Albert Demonceau* and Alfred F. Noels

Laboratory of Macromolecular Chemistry and Organic Catalysis, University of Liège, Sart-Tilman (B.6a), B-4000 Liège, Belgium

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Abstract— $[\text{RuCl}_2(p\text{-cymene})]$ complexes containing triarylphosphine ligands with various substituents at the *para* position were used to catalyse the atom transfer radical addition of carbon tetrachloride to various olefins, and their catalytic activities were nicely correlated with their electrochemical parameters.

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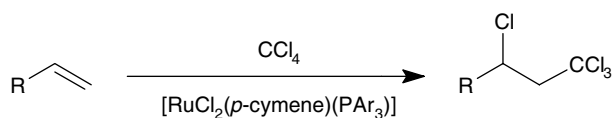
Over the past few years, the transition-metal-catalysed Kharasch addition (also known as ‘ATRA’, atom transfer radical addition) has experienced a sudden rebirth, which is unquestionably the result of the development of atom transfer radical polymerisation (ATRP), discovered independently in the mid-nineties by Sawamoto and Matyjaszewski.¹ Many varieties of metal-based catalysts, such as copper,² nickel³ and ruthenium⁴ complexes, have been proposed for Kharasch reactions. Ruthenium, in particular, has played a prominent role in Kharasch chemistry with $\text{RuCl}_2(\text{PPh}_3)_3$ ⁵ displaying some of the highest efficiency and versatility for halocarbon activation and addition to olefins.

We have been interested in the development of new catalyst systems for Kharasch addition, and a variety of novel ruthenium-based catalysts have been reported, including ruthenacarboranes,⁶ $\text{RuCl}_2(=\text{CHPh})(\text{PR}_3)_2$ ⁷ (Grubbs’ complexes) and $\text{RuCl}(\text{Cp}^\#)(\text{PAr}_3)_2$ ($\text{Cp}^\# = \text{Cp}^*$ and indenyl).⁸ Despite their high efficiency (total turnover numbers (TON) up to 9000 and initial turnover frequencies (TOF) of around 1900 h^{-1} were observed with the former complexes^{6b,c}) and their versatility, these catalyst systems suffer from their difficult, tedious and time-consuming multi-step synthesis. Given the importance of radical reactions in both fine organic synthesis and macromolecular chemistry, the need for cheap and easily synthesised catalysts (or catalyst

precursors) is crucial. $[\text{RuCl}_2(\text{arene})(\text{PR}_3)]$ complexes afford these advantages: $[\text{RuCl}_2(\text{arene})(\text{PR}_3)]$ complexes are readily available on reaction of 2 equiv of a phosphine with the $[\text{RuCl}_2(\text{arene})]_2$ dimer and are air-stable.⁹ In addition, their stereoelectronic features can be fine-tuned by using suitable phosphine ligands.

We have recently found that $[\text{RuCl}_2(p\text{-cymene})(\text{PR}_3)]$ complexes (*p*-cymene = 4-isopropyltoluene) possessing a basic and bulky phosphine (typically tricyclohexylphosphine and triisopropylphosphine) were outstanding catalyst precursors for promoting ATRP of vinyl monomers.¹⁰ Their use in Kharasch chemistry was however unsuccessful.^{7b} Conversely, $[\text{RuCl}_2(p\text{-cymene})(\text{PR}_3)]$ complexes with less basic and/or less bulky phosphines (typically triphenylphosphine) were inefficient in ATRP.¹⁰ We now report on the efficiency of catalytic systems based on $[\text{RuCl}_2(p\text{-cymene})(\text{PAr}_3)]$ for the Kharasch addition of carbon tetrachloride to olefins, especially to unactivated α -olefins (Scheme 1).

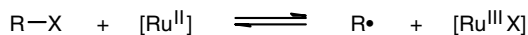
Since the Kharasch addition rests on the metal-mediated activation of a carbon–halogen bond and the concomitant one-electron oxidation of the metal centre (Scheme 2), we anticipated that simple modification to the triphenylphosphine ligand in $[\text{RuCl}_2(p\text{-cymene})(\text{PAr}_3)]$ by



Scheme 1. Kharasch addition of carbon tetrachloride across olefin.

Keywords: Catalysis; Electrochemistry; Olefins; Radicals and radical reactions; Ruthenium and compounds.

* Corresponding author. Tel.: +32 4 366 3495; fax: +32 4 366 3497; e-mail: A.Demonceau@ulg.ac.be

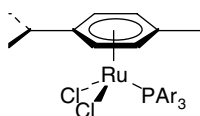


Scheme 2. Activation of an alkyl halide by ruthenium.

incorporating electron-donating or electron-withdrawing substituents at the *para* position of the aryl groups, could be used to tune the catalytic activity of the ruthenium complexes. Thus, five isosteric $[\text{RuCl}_2(p\text{-cymene})(\text{P}(p\text{-C}_6\text{H}_4\text{X})_3)]$ complexes were synthesised, in which X = OMe, Me, F, Cl and CF₃ (Scheme 3). The experimental data for the Kharasch addition of CCl₄ to representative olefins catalysed by $[\text{RuCl}_2(p\text{-cymene})(\text{PAR}_3)]$ complexes are summarised in Table 1.

When styrene was reacted with CCl₄ under anaerobic conditions, the Kharasch adduct (1,1,1,3-tetrachloro-3-phenylpropane) was obtained and, depending upon the catalyst used and the reaction time, with styrene being recovered. Small amounts of oligomers, not yet detected by gas chromatography, most probably account for the balance of the reaction. With 1-decene as the substrate, the expected 1,1,1,3-tetrachloroundecane was the only product along with the starting material (Table 1 and Fig. 1). On the other hand, reaction of CCl₄ with methyl methacrylate yielded the expected monoadduct (A, Scheme 4), together with the diadduct (B) and higher oligomers.

On the basis of the results shown in Table 1, we concluded that 1-decene, which is a difficult substrate for



Scheme 3. $[\text{RuCl}_2(p\text{-cymene})(\text{PAR}_3)]$ complexes under investigation.

Table 1. Addition of carbon tetrachloride to styrene and 1-decene catalysed by $[\text{RuCl}_2(p\text{-cymene})(\text{PAR}_3)]$ complexes^a

| $[\text{RuCl}_2(p\text{-cymene})(\text{PAR}_3)]$ | Substrate conversion (%) ^b /Kharasch addition (%) ^b | | | |
|--|---|-------------------|-------------------|--------------|
| | Styrene 60 °C | 1-Decene 60 °C | 1-Decene 85 °C | MMA 85 °C |
| Ar | | | | |
| <i>p</i> -C ₆ H ₄ OCH ₃ | 66/61 | 43/42 | 89/89 | 99/40 |
| <i>p</i> -C ₆ H ₄ CH ₃ | 64/59 | 34/33 | 79/78 | 96/47 |
| C ₆ H ₅ | 62/58 | 28/28 | 67/66 | 87/43 |
| <i>p</i> -C ₆ H ₄ F | 31/27 | 21/21 | 59/58 | 50/21 |
| <i>p</i> -C ₆ H ₄ Cl | 25/20 | 20/19 | 45/44 | 39/19 |
| <i>p</i> -C ₆ H ₄ CF ₃ | 45/43 | 12/11 | 64/63 | 51/13 |

^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), CCl₄ (13 mmol), dodecane (0.25 mL) in toluene (3 mL). Reaction time, 30 h.

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

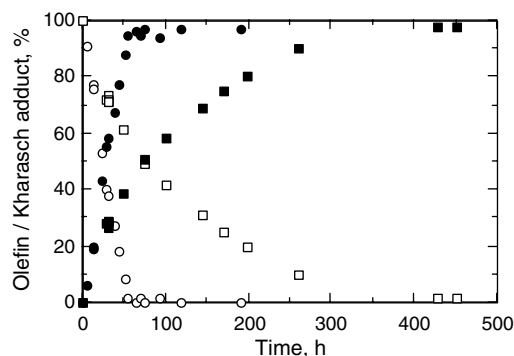
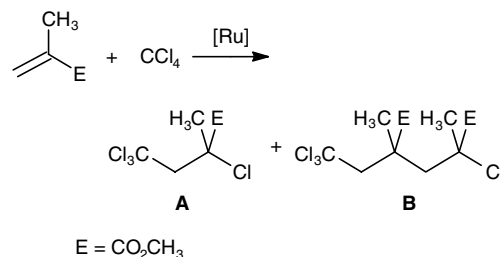


Figure 1. Influence of the substrate on the Kharasch addition of carbon tetrachloride catalysed by $[\text{RuCl}_2(p\text{-cymene})(\text{PPh}_3)]$ at 60 °C. Styrene (○) and 1-decene (□) and their Kharasch adducts (●, ■). Reaction conditions are the same as in Table 1.



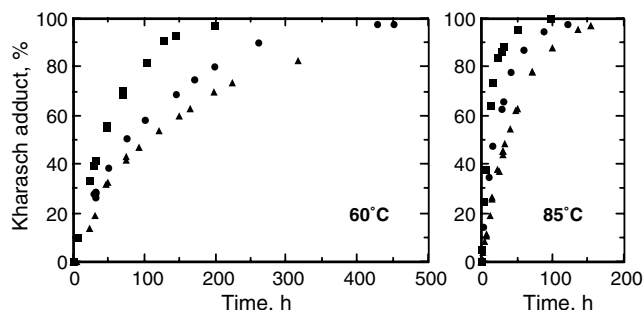
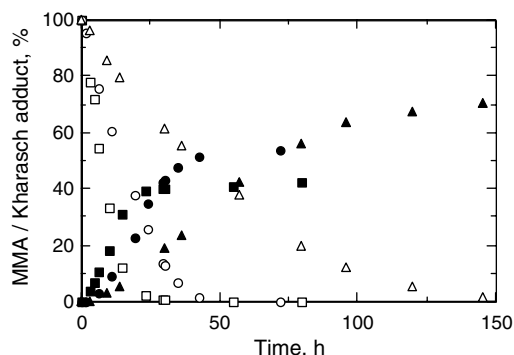
Scheme 4. Addition of CCl₄ to methyl methacrylate.

Kharasch additions,¹¹ is all things considered a substrate better than expected, at least with this class of ruthenium complexes (see also Fig. 1). This prompted us to evaluate the substrate scope of this protocol with other unactivated olefins (Table 2). When reacted with CCl₄, 1-octene and 1-dodecene were also efficiently transformed into the corresponding Kharasch adducts in excellent yields. Of note, however, is the significantly lower reactivity of 1-hexene, compared to higher α -olefins.

Rationalisation of electronic effects in transition-metal-mediated catalytic reactions is critically important for the design of new ligands.¹² In the present case, the substituents at the *para* position of the aromatic rings of the phosphine ligands affect the catalytic activity to a great extent (Table 1, Figs. 2 and 3). The best results were obtained with $[\text{RuCl}_2(p\text{-cymene})(\text{P}(p\text{-C}_6\text{H}_4\text{OCH}_3)_3)]$, which contains the most electron-donating tris(*p*-methoxyphenyl)phosphine ligand of the series. On the contrary, $[\text{RuCl}_2(p\text{-cymene})(\text{P}(p\text{-C}_6\text{H}_4\text{Cl})_3)]$, which contains the weaker electron-donating tris(*p*-chlorophenyl)phosphine ligand was much less efficient, revealing a nice qualitative correlation between electronic features of the phosphine ligand and catalytic activity of the resulting ruthenium complex. For instance, with decene at 85 °C and 30 h runtime, yields were as follows: OMe (89%), Me (78%), H (66%), F (58%) and Cl (44%). The same trend was found with methyl methacrylate. $[\text{RuCl}_2(p\text{-cymene})(\text{P}(p\text{-C}_6\text{H}_4\text{CF}_3)_3)]$, however, bearing the least electron-donating phosphine ligand of the

Table 2. Addition of carbon tetrachloride to representative α -olefins catalysed by $[\text{RuCl}_2(p\text{-cymene})(\text{PAr}_3)]$ complexes^a

| $[\text{RuCl}_2(p\text{-cymene})(\text{PAr}_3)]$ | Substrate conversion (%) ^b /Kharasch addition (%) ^b | | | |
|--|---|-------------------------|--------------------------|-------------------------|
| | 1-Hexene | 1-Octene | 1-Decene | 1-Dodecene |
| Ar | | | | |
| <i>p</i> -C ₆ H ₄ OCH ₃ | 48/39 (82) ^c | 97/92 (95) ^c | 89/89 (100) ^c | 63/61 (96) ^c |
| <i>p</i> -C ₆ H ₄ CH ₃ | 44/31 (71) ^c | 86/77 (89) ^c | 79/78 (100) ^c | 56/55 (99) ^c |
| C ₆ H ₅ | 40/23 (59) ^c | 82/75 (87) ^c | 67/66 (99) ^c | 55/52 (95) ^c |

^a Reaction conditions are the same as in Table 1 (temperature, 85 °C; 30 h).^b Same as in footnote b (Table 1).^c Kharasch addition at complete conversion of the olefin.**Figure 2.** Influence of the catalyst system, $[\text{RuCl}_2(p\text{-cymene})(\text{PAr}_3)]$, on the Kharasch addition of carbon tetrachloride to 1-decene at 60 and 85 °C. Catalysts: $[\text{RuCl}_2(p\text{-cymene})(\text{P}(p\text{-C}_6\text{H}_4\text{OCH}_3)_3)]$ (■), $[\text{RuCl}_2(p\text{-cymene})(\text{PPh}_3)]$ (●) and $[\text{RuCl}_2(p\text{-cymene})(\text{P}(p\text{-C}_6\text{H}_4\text{Cl})_3)]$ (▲). Reaction conditions are the same as in Table 1.**Figure 3.** Influence of the catalyst system, $[\text{RuCl}_2(p\text{-cymene})(\text{PAr}_3)]$, on the Kharasch addition of carbon tetrachloride to methyl methacrylate at 85 °C. Catalysts: $[\text{RuCl}_2(p\text{-cymene})(\text{P}(p\text{-C}_6\text{H}_4\text{OCH}_3)_3)]$ (□), $[\text{RuCl}_2(p\text{-cymene})(\text{PPh}_3)]$ (○, ●) and $[\text{RuCl}_2(p\text{-cymene})(\text{P}(p\text{-C}_6\text{H}_4\text{Cl})_3)]$ (△, ▲); methyl methacrylate (□, ○, △) and its Kharasch monoadduct (A, Scheme 4) (■, ●, ▲). Reaction conditions are the same as in Table 1.

series, displayed an unpredictable reactivity profile, which depended on the substrate and the temperature. In most cases, the activity of $[\text{RuCl}_2(p\text{-cymene})(\text{P}(p\text{-C}_6\text{H}_4\text{CF}_3)_3)]$ lay between that of $[\text{RuCl}_2(p\text{-cymene})(\text{P}(p\text{-C}_6\text{H}_5)_3)]$ and $[\text{RuCl}_2(p\text{-cymene})(\text{P}(p\text{-C}_6\text{H}_4\text{F})_3)]$, except with decene at 60 °C where $[\text{RuCl}_2(p\text{-cymene})(\text{P}(p\text{-C}_6\text{H}_4\text{CF}_3)_3)]$ was the least active catalyst, presumably due to its low solubility in the reaction mixture.

These results in Kharasch chemistry were rationalised on the basis of the electron-donating ability of the phosphine ligands, as indicated by the pK_a value of the phosphonium ion,¹³ and by measuring the changes in the redox potential^{14,15} for the different $[\text{RuCl}_2(p\text{-cymene})(\text{PAr}_3)]$ complexes.¹⁶

The cyclic voltammograms of $[\text{RuCl}_2(p\text{-cymene})(\text{PAr}_3)]$ complexes in dichloromethane (0.1 M $n\text{Bu}_4\text{NPF}_6$) displayed a reversible oxidation couple at ca. 0.6–0.8 V versus ferrocene. The electrochemical data are summarised in Table 3 and representative cyclic voltammograms of $[\text{RuCl}_2(p\text{-cymene})(\text{PAr}_3)]$ complexes (Ar = *p*-C₆H₄OCH₃, C₆H₅ and *p*-C₆H₄Cl) are shown in Figure 4. Examination of the data indicates that the redox potentials vary significantly with the nature of the phosphine ligand. Compared to $[\text{RuCl}_2(p\text{-cymene})(\text{PPh}_3)]$ ($E^0 = 0.680$ V), slightly less positive potential values of 0.595 V in $[\text{RuCl}_2(p\text{-cymene})(\text{P}(p\text{-C}_6\text{H}_4\text{OCH}_3)_3)]$ and 0.624 V in $[\text{RuCl}_2(p\text{-cymene})(\text{P}(p\text{-C}_6\text{H}_4\text{CH}_3)_3)]$ were observed, in line with the presence of the more electron-rich $\text{P}(p\text{-C}_6\text{H}_4\text{OCH}_3)_3$ and $\text{P}(p\text{-C}_6\text{H}_4\text{CH}_3)_3$ ligands that would make the Ru(II) centre more easily oxidised than that in $[\text{RuCl}_2(p\text{-cymene})(\text{PPh}_3)]$. Using similar arguments, the more positive potentials of $[\text{RuCl}_2(p\text{-cymene})(\text{P}(p\text{-C}_6\text{H}_4\text{F})_3)]$ (0.700 V), $[\text{RuCl}_2(p\text{-cymene})(\text{P}(p\text{-C}_6\text{H}_4\text{Cl})_3)]$ (0.740 V) and $[\text{RuCl}_2(p\text{-cymene})(\text{P}(p\text{-C}_6\text{H}_4\text{CF}_3)_3)]$ (0.820 V) than $[\text{RuCl}_2(p\text{-cymene})(\text{PPh}_3)]$ (0.680 V) were attributed to the electron-withdrawing effects of the *para* substituents on the aryl groups. Not surprisingly, the

Table 3. pK_a^a of the triarylphosphines, PAr_3 and cyclic voltammetry data^b of the $[\text{RuCl}_2(p\text{-cymene})(\text{PAr}_3)]$ complexes under investigation

| $[\text{RuCl}_2(p\text{-cymene})(\text{PAr}_3)]$ | pK_a | E^0 (V) ^c | ΔE (V) ^d |
|--|--------|------------------------|-----------------------------|
| Ar | | | |
| <i>p</i> -C ₆ H ₄ OCH ₃ | 5.13 | 0.595 | 0.068 |
| <i>p</i> -C ₆ H ₄ CH ₃ | 4.46 | 0.624 | 0.070 |
| C ₆ H ₅ | 3.28 | 0.680 | 0.075 |
| <i>p</i> -C ₆ H ₄ F | 1.63 | 0.700 | 0.075 |
| <i>p</i> -C ₆ H ₄ Cl | 0.87 | 0.740 | 0.078 |
| <i>p</i> -C ₆ H ₄ CF ₃ | −1.39 | 0.820 | 0.078 |

^a pK_a of phosphonium ion.¹³^b Sample, 2 mM; $n\text{Bu}_4\text{NPF}_6$ (0.1 M) in dry and degassed CH_2Cl_2 , under nitrogen at room temperature; scan rate, 50 mV s^{−1}; potentials are reported in volt versus ferrocene as an internal standard.¹⁷^c $E^0 = (E_{pa} + E_{pc})/2$; E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively.^d $\Delta E_p = |E_{pa} - E_{pc}|$.

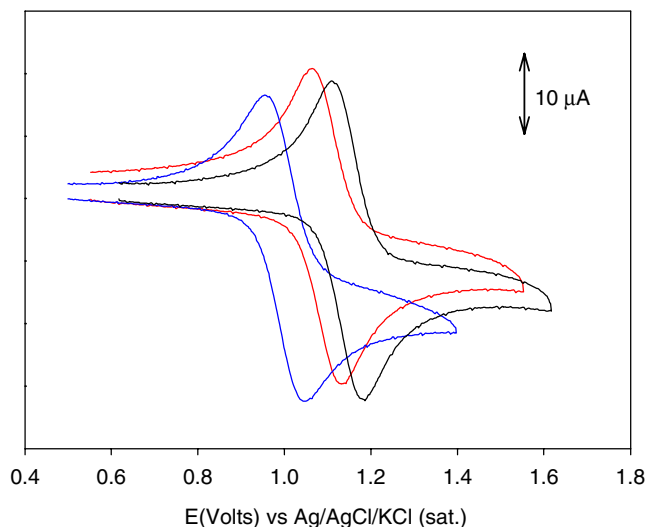


Figure 4. Cyclic voltammograms of $[\text{RuCl}_2(p\text{-cymene})(\text{PAR}_3)]$ complexes in dichloromethane. $[\text{RuCl}_2(p\text{-cymene})(\text{P}(p\text{-C}_6\text{H}_4\text{OCH}_3)_3)]$ (—), $[\text{RuCl}_2(p\text{-cymene})(\text{PPh}_3)]$ (—) and $[\text{RuCl}_2(p\text{-cymene})(\text{P}(p\text{-C}_6\text{H}_4\text{Cl})_3)]$ (—).¹⁷

relative activities of the $[\text{RuCl}_2(p\text{-cymene})(\text{PAR}_3)]$ complexes were supported by electrochemical studies.

In conclusion, $[\text{RuCl}_2(p\text{-cymene})(\text{PAR}_3)]$ are highly active catalyst precursors for the Kharasch addition of carbon tetrachloride to olefins, especially to unactivated olefins such as α -olefins. They are however somewhat less active than $\text{RuClCp}^\#(\text{PPh}_3)_2$ ($\text{Cp}^\# = \text{Cp}^*$, indenyl and carboranyl), which set so far the standard in the field, but have the simplicity and accessibility, which is ideally required for practical applications. In addition, we have shown that the catalytic activities of the $[\text{RuCl}_2(p\text{-cymene})(\text{PAR}_3)]$ complexes are effectively correlated with their electrochemical parameters.

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17. Cyclic voltammetry experiments were conducted at room temperature with a Princeton Applied Research EG & G 236 A potentiostat, using a conventional three-electrode configuration consisting of a 3 mm diameter glassy carbon working electrode, a platinum auxiliary electrode and an Ag/AgCl/saturated KCl reference electrode. Tetrabutylammonium hexafluorophosphate was used as the supporting electrolyte and all the potentials were referenced to ferrocene, $E^0(\text{Fc}/\text{Fc}^+) = 0.0 \text{ V}$, added at the end of the experiment.