New, Highly Efficient Catalyst Precursors for Kharasch Additions – [RuCl(Cp*)(PPh_3)$_2$] and [RuCl(Ind)(PPh_3)$_2$]

François Simal,*[a][‡] Lise Wlodarczak,[a] Albert Demonceau,*[a] and Alfred F. Noels[a]

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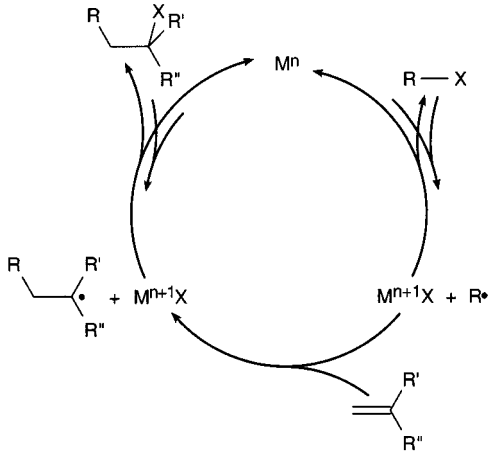
[RuCl(Cp*)(PPh_3)$_2$] and [RuCl(Ind)(PPh_3)$_2$] are excellent catalyst precursors for promoting the Kharasch addition of CCl_4 and $CHCl_3$ across olefins under mild reaction conditions (at temperatures as low as 40 °C with CCl_4). The effect of the substituents on the cyclopentadienyl ring has been investigated. In terms of efficiency and activity, [RuCl(Cp*)(PPh_3)$_2$] and [RuCl(Ind)(PPh_3)$_2$] surpass the best ruthenium systems reported so far. A two-step mechanism, in which the extrusion of a phosphane ligand occurs prior to the activation of the halogenated compound by the unsaturated ruthenium center, is suggested.

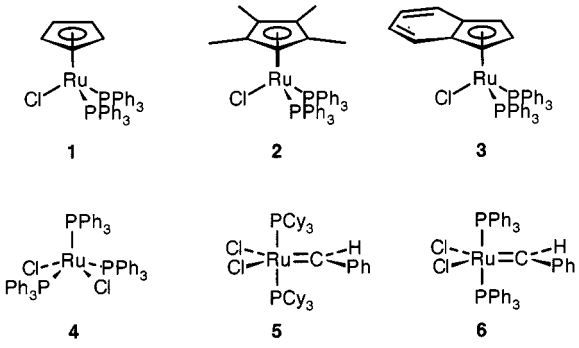
Introduction

The transition-metal-catalyzed Kharasch reaction has attracted much attention since the early seventies.[1] The reaction consists of the addition of a polyhalogenated alkane across an olefin, by a radical mechanism (Scheme 1).



Scheme 1

Diminished telomerization and oligomerization together with (good) regioselectivities have been achieved by the use of suitable transition metals in reactions formerly carried out using radical precursors such as AIBN or peroxides. Most catalytic systems so far described for Kharasch chemistry are based on Cu, Fe, Ni, Pd, Rh, and Ru. Of these, ruthenium plays a prominent role, and [$RuCl_2(PPh_3)_3$][2] is one of the most efficient and versatile catalysts to date. [$RuCl_2(PPh_3)_3$] suffers, however, from two severe limitations: a relatively high amount of catalyst is needed, and rather harsh reaction conditions (temperature = 100–120 °C) are often used.[2] In search of more active ruthenium-based systems, we and others have recently reported on the use of Grubbs' ruthenium-benzylidene complexes (**5** and **6**)[3] as efficient catalysts for Kharasch reactions.[4,5] For instance, the ruthenium compound **5**, with two tricyclohexylphosphane ligands, allows the Kharasch addition of chloroform across various olefins to be performed under reaction conditions much milder than those previously described for [$RuCl_2(PPh_3)_3$]. Because of the outstanding activity of Grubbs' catalysts in olefin metathesis, however, Kharasch reactions are limited to nonmetathesizable olefins.



The sudden rebirth of the transition-metal-catalyzed Kharasch addition (also known as "ATRA", atom-transfer radical addition) is unquestionably the result of the development of atom-transfer radical polymerization (ATRP), discovered independently in the mid-nineties by Sawamoto and Matyjaszewski.[6] ATRA and ATRP seem directly related, since ATRP may be viewed as an extension of the ATRA reaction at high ratios of olefin (monomer) to polyhaloalkane (initiator). Most of the catalysts (but not all of them) so far used for ATRP are based on those previously developed for the Kharasch reaction. This is exemplified by [$RuCl_2(PPh_3)_3$], which was reported in 1973 by Matsumoto[2] for use in the Kharasch addition, and then in 1995 by

[a] Laboratory of Macromolecular Chemistry and Organic Catalysis, University of Liège,
Sart-Tilman (B.6a), 4000 Liège, Belgium
Fax: (internat.) +32-4/366-3497
E-mail: A.Demonceau@ulg.ac.be
[‡] Present address: UCB Chemicals, Research and Technology, Anderlechtstraat 33, 1620 Drogenbos, Belgium

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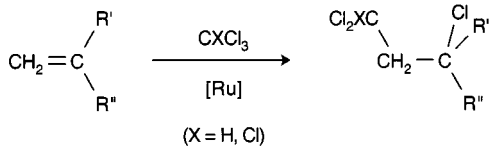
Sawamoto[7] in his seminal paper on ATRP. Very recently, though, the first two ruthenium(II) complexes not previously reported as Kharasch catalysts, $[RuCl(Cp)(PPh_3)_2]$ (**1**, Cp = cyclopentadienyl) and $[RuCl(Ind)(PPh_3)_2]$ (**3**, Ind = indenyl), have been shown to promote ATRP of vinyl monomers.[8] Although there is a relationship between ATRP and ATRA, not all catalyst precursors that are efficient in ATRP display the same activity/control in ATRA, and vice versa. For example, $[RuCl_2(p\text{-cymene})(PR_3)]$ complexes are outstanding ATRP precatalysts,[9] but very poor ATRA catalysts under Kharasch conditions.[5] We have now embarked on a program aimed at answering several pivotal questions bearing on the parameters that determine the relative efficacies for one or other process. Because of the high efficiency of $[RuCl(Cp)(PPh_3)_2]$ (**1**) and $[RuCl(Ind)(PPh_3)_2]$ (**3**) in ATRP, we thought that it would be of interest to test them, as well as the related Cp* derivative (**2**, Cp* = pentamethylcyclopentadienyl),[10] in the Kharasch reaction. We now report on the exceptional activity of these readily available and air-stable complexes in the Kharasch addition of carbon tetrachloride and chloroform to various olefins under very mild conditions (Scheme 2).



Scheme 2

As the stereoelectronic features of the ligands are of utmost importance for the control of these processes,[5,6,9] a special emphasis is laid on the effect of the substituents on the η^5-ligand. The reactivity of complexes **1**−**3** is also compared with that of other known Kharasch addition catalysts (**4**−**6**).

Results and Discussion

Effect of Olefin Structure

In a first set of experiments, we checked the catalytic activity of the ruthenium complexes **1**, **2**, and **3** with four representative olefins under standardized conditions (smooth addition of carbon tetrachloride to the olefin at 60−85 °C).[5,11] It appeared that the outcome of the reaction depended very strongly on the olefin used (Table 1).

Monoadduct production with methyl methacrylate was approximately quantitative within 2 h with all three catalysts. With styrene as substrate, longer reaction times were necessary in order to obtain high yields, and not all catalysts were equivalent. Whereas with complexes **2** and **3** around 95 and 80% of product were obtained within 5 h, 24 h was required to achieve completion with complex **1**. *n*-Butyl acrylate and 1-decene were also subjected to these conditions (Table 1 and Figure 1).

n-Butyl acrylate, an easily polymerizable substrate,[2] underwent a clean monoaddition of CCl_4 in the presence of complex **2**, yielding as much as 85% of product after only 4 h at 85 °C. Although the degree of conversion of the substrate was somewhat higher when $[RuCl(Ind)(PPh_3)_2]$ (**3**) and $[RuCl_2(PPh_3)_3]$ (**4**) were used, only 62 and 40%, respectively, of the monoadduct were formed, with olefin telomerization becoming important. The ruthenium−cyclopentadienyl complex **1** displayed the lowest activity (14% yield). In all cases, 1-decene was less prone to react with CCl_4, with only modest yields of Kharasch adduct being obtained. Complex **3** gave results comparable to those obtained when using **4** (up to 45 and 58%, respectively). No metathesis products were detected, and formation of oligomers/telomers took place.

Table 1. Kharasch addition of carbon tetrachloride to representative olefins

Catalyst	Substrate[a]	*T* [°C]	Time [h]	Conv.[b] [%]	Yield[b] [%]
1	*n*-butyl acrylate	85	4	16	14
1	methyl methacrylate	85	2	97	97
1	styrene	60	5	58	36
1	1-decene	60	24	17	2
2	*n*-butyl acrylate	85	4	85	85
2	methyl methacrylate	85	2	97	97
2	styrene	60	5	97	95
2	1-decene	60	24	46	27
3	*n*-butyl acrylate	85	4	92	62
3	methyl methacrylate	85	2	98	98
3	styrene	60	5	100	81
3	1-decene	60	24	60	45
4	*n*-butyl acrylate	85	4	92	40
4	methyl methacrylate	85	2	97	65
4	styrene	60	5	91	70
4	1-decene	60	24	80	58

[a] Reaction conditions: olefin (9 mmol), carbon tetrachloride (13 mmol), catalyst (0.03 mmol), toluene (4 mL), dodecane (0.25 mL), under a nitrogen atmosphere. − [b] Conversion and yield are based on the olefin, and determined by GC using dodecane as internal standard.

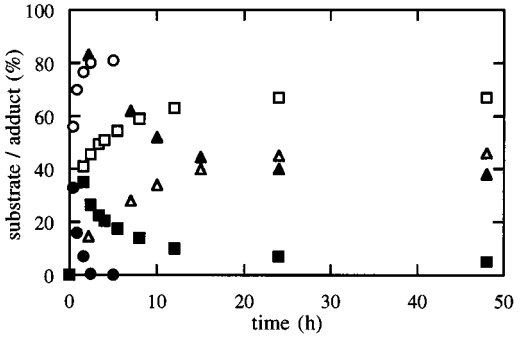


Figure 1. Substrate (■, ●, ▲) and adduct (□, ○, △) vs. time for the Kharasch addition of carbon tetrachloride to *n*-butyl acrylate (■, □), styrene (●, ○), and 1-decene (▲, △), catalyzed by $[RuCl(Ind)(PPh_3)_2]$ (**3**), at 60 °C (reaction conditions as in Table 1)

Effect of Temperature

On the basis of the encouraging catalytic achievements of ruthenium complexes **1**−**3** when using MMA and styrene at

60−85 °C, we then moved on to lower reaction temperatures: 40 °C and room temperature (Table 2 and Figure 2).

Table 2. Kharasch addition of carbon tetrachloride to methyl methacrylate and styrene under mild conditions

Catalyst	Substrate[a]	*T* [°C]	Time [h]	Conv.[b] [%]	Yield[b] [%]
1	methyl methacrylate	40	6	62	5
1	styrene	40	6	24	10
2	methyl methacrylate	rt	24	54	36
2	methyl methacrylate	40	6	79	79
2	styrene	rt	24	100	90
2	styrene	40	6	86	69
3	methyl methacrylate	rt	24	9	4
3	methyl methacrylate	40	6	83	83
3	styrene	rt	24	31	10
3	styrene	40	6	74	69
4	methyl methacrylate	40	6	17	7
4	styrene	40	6	34	16
5	methyl methacrylate	40	6	5	1
5	styrene	40	6	27	19
6	methyl methacrylate	40	6	25	4
6	styrene	40	6	14	12

[a] Same as in Table 1. − [b] Same as in Table 1.

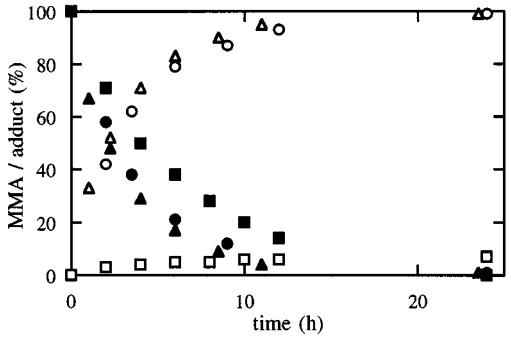


Figure 2. MMA (■, ●, ▲) and adduct (□, ○, △) vs. time for the Kharasch addition of carbon tetrachloride to methyl methacrylate, catalyzed by complexes **1** (■, □), **2** (●, ○), and **3** (▲, △), at 40 °C (reaction conditions as in Table 1)

To the best of our knowledge, no Kharasch reactions mediated by ruthenium complexes at such low temperatures have ever been reported. The results clearly show that, with complexes **2** and **3**, around 80% of MMA had been cleanly converted into the monoadduct after only 6 h. Under the same conditions, all the other ruthenium complexes (**1**, **4**, **5**, and **6**) produced small quantities of the expected product. The same trend was observed when styrene was employed as the substrate, although slightly lower yields were obtained. Finally, working at room temperature for longer reaction times (24 h) allowed us to discriminate between complexes **2** and **3**. From Table 2, it is clear that the Ru−Cp* complex (**2**) was much more efficient than its indenyl counterpart (**3**), the yield with styrene remaining impressive (90%) even at room temperature. Furthermore, total turnover numbers of 1600−1700, and initial turnover frequencies of around 400 h^{-1} were observed (Figure 3 and Figure 4), clearly demonstrating that complex **2** is the most active ruthenium-based catalyst for the Kharasch addition reaction to date, and at least as reactive as van Koten's diaminoarylnickel(II) "pincer" complexes, which also operate effectively at ambient temperatures under mild reaction conditions.[11]

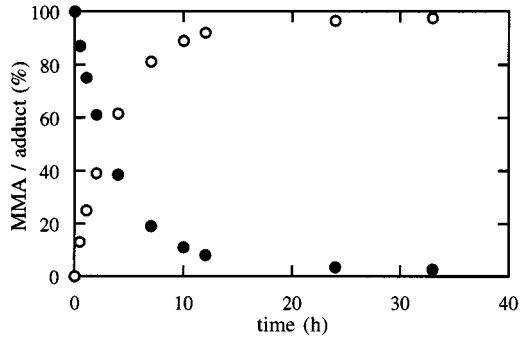


Figure 3. MMA (●) and adduct (○) vs. time for the Kharasch addition of carbon tetrachloride to methyl methacrylate, catalyzed by [RuCl(Cp*)(PPh_3)$_2$] (**2**) at 40 °C (reaction conditions: MMA (45 mmol), carbon tetrachloride (65 mmol), catalyst (0.03 mmol), toluene (20 mL), dodecane (1.25 mL), under a nitrogen atmosphere)

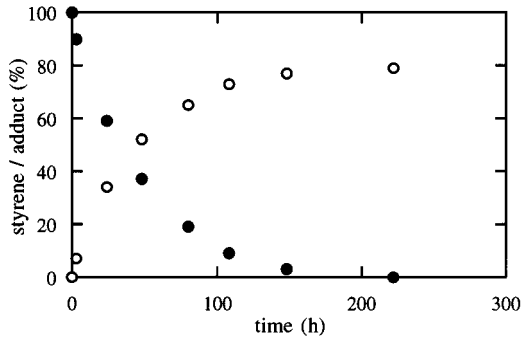


Figure 4. Styrene (●) and adduct (○) vs. time for the Kharasch addition of carbon tetrachloride to styrene, catalyzed by [RuCl(Cp*)(PPh_3)$_2$] (**2**) at room temperature (reaction conditions: styrene (63 mmol), carbon tetrachloride (91 mmol), catalyst (0.03 mmol), toluene (28 mL), dodecane (1.75 mL), under a nitrogen atmosphere)

Kharasch Addition of Chloroform

Prompted by the outstanding efficiency of complexes **2** and **3**, we then turned our attention to a more difficult reaction: the Kharasch addition of chloroform to MMA and styrene. $CHCl_3$ is known to be less prone to add across olefins, and so harsh conditions are usually required.[2,12,13] Snapper et al. recently reported on the good activity of Grubbs' ruthenium−tricyclohexylphosphane complex **5** for the Kharasch addition of $CHCl_3$ across various olefins with, inter alia, almost quantitative monoadduct formation with styrene and MMA at 65 °C.[4] The major drawback of this catalyst system, however, is the large amount of catalyst **5** needed (from 2.5 mol % for styrene to 7.5 mol % for MMA). When **5** was employed under our reaction conditions (0.33 mol %, Table 3), a marked depletion in monoadduct yields was observed, these reaching only 20% for

MMA and 45% for styrene. Complexes **1**, **2**, and **3** were also tested under the same reaction conditions, and while **1** and **3** afforded practically no adducts, **2** again displayed the highest activity and surpassed the best catalyst so far reported (Table 3).

Table 3. Kharasch addition of chloroform to methyl methacrylate and styrene

Catalyst	Substrate[a]	*T* [°C]	Time [h]	Conv.[b] [%]	Yield[b] [%]
1	methyl methacrylate	85	24	16	0
1	styrene	60	24	2	1
2	methyl methacrylate	85	24	63	29
2	styrene	60	24	69	69
3	methyl methacrylate	85	24	50	12
3	styrene	60	24	3	2
4	methyl methacrylate	85	24	17	1
4	styrene	60[c]	24	14	1
5	methyl methacrylate	85	24	55	19
5	styrene	60	24	55	45

[a] Same as in Table 1. – [b] Same as in Table 1. – [c] At 85 °C, 13% conversion, 2% yield.

Mechanistic Insights

The Kharasch reaction probably takes place through a radical mechanism, as already demonstrated by Sawamoto for the ATRP reaction catalyzed by complexes **1**, **3**, and **4**.[7,8] In our case, this was confirmed by the addition of a radical scavenger to the reaction medium, and also by carrying out the reactions under air. In both cases, formation of the expected adducts was inhibited completely.

Our preliminary results from investigation of the nature of the catalytic active ruthenium species are as follows. They have been tentatively rationalized by invoking a two-step mechanism involving: (i) the extrusion of a PPh_3 ligand from the 18-electron complexes, followed by (ii) pseudo-oxidative one-electron addition of the carbon–halogen bond of the polyhalogenated compound, formally yielding ruthenium(III) species.

Role of the Phosphane Ligand

Ruthenium complexes based on η^5-coordinated π ligands[14] such as Cp, Cp*, and Ind have already found wide applications in catalysis.[15] It is known that the 18-electron complexes **1**–**3**, containing two triphenylphosphanes, can exchange at least one of these ligands for another ligand (carbon monoxide, isonitriles, phosphanes, ...), by way of an unsaturated 16-electron transient species, under more or less forcing conditions, depending on the nature of the η^5-ligand linked to the metal center.[16,17] The unsubstituted Cp ring allows one PPh_3 to be exchanged for one CO under rather forcing conditions (150 atm CO), whereas smooth substitution proceeds under mild conditions (2 atm. CO) with the Cp* analogue.[16] Interestingly enough, $[RuCl(Cp)(CO)_2]$ and $[RuCl(Cp^*)(CO)_2]$ were inactive for Kharasch addition under the reaction conditions shown in Table 1. The high activity of complex **2** might thus result from an increase in both the electron density and the steric congestion at the ruthenium center provided by the Cp* ligand, which would allow some stabilization of the 16-electron intermediate. In order to assess the importance of the release of the PPh_3 ligand, kinetic studies of the reactions involving complexes **2**, **3**, and **4** in the presence of an excess of PPh_3 (5 and 10 equiv. relative to ruthenium) were undertaken. In all cases, the reactions were clearly slowed down (10% maximum conversion of the substrates under the conditions in Table 1), and produced only minute amounts of the adducts. With this in mind, we then investigated the ruthenium complexes **1**–**3** by ^{31}P NMR spectroscopy, with the aim of observing free triphenylphosphane. In $[D_8]$toluene under argon, these complexes were stable for days. Addition of 10 equiv. of carbon tetrachloride (with respect to the ruthenium complex), however, resulted in the rapid disappearance of $[RuCl(Cp^*)(PPh_3)_2]$ (Figure 5).

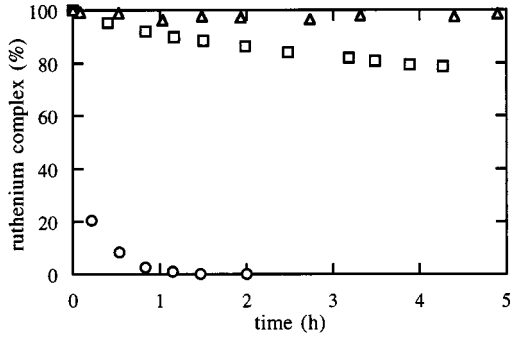


Figure 5. Decomposition of $[RuCl(Cp)(PPh_3)_2]$ (**1**; △), $[RuCl(Cp^*)(PPh_3)_2]$ (**2**; ○), and $[RuCl(Ind)(PPh_3)_2]$ (**3**; □) upon addition of CCl_4 at 20 °C; reaction conditions: complex, 0.015 mmol; toluene/$[D_8]$toluene, 2.5 mL (4:1 v/v); CCl_4, 10 equiv. (14.5 μL); under nitrogen

$[RuCl(Ind)(PPh_3)_2]$, however, was much more stable upon addition of 10 equiv. of CCl_4, whereas $[RuCl(Cp)(PPh_3)_2]$ only showed some signs of decomposition after three days (Figure 5). Temperature also proved to be of utmost importance in that the higher the temperature, the faster the decomposition rate (Figure 6). Furthermore, when decomposition in the presence of excess triphenylphosphane (5 equiv.) was examined, its rate was found to have slowed significantly (Figure 7). This observation supports the assumption that the catalytic activity of the ruthenium systems depends on the dissociation of a phosphane ligand,[18] and slowing the rate of decomposition with the addition of excess phosphane should also inhibit Kharasch addition. Higher quantities of carbon tetrachloride, in contrast, accelerated the decomposition process (Figure 8), so much so that decomposition of $[RuCl(Cp^*)(PPh_3)_2]$ was almost instantaneous upon addition of 430 equiv. CCl_4 [conditions used in typical Kharasch reactions (see Table 1)] at room temperature. Most importantly, the ^{31}P NMR spectra, over the course of the decomposition reactions, showed neither free PPh_3 nor additional signals beside that of the starting ruthenium complex, even in the range $\delta = +1000$ to $\delta = -1000$. This observation could be explained by the forma-

tion of paramagnetic ruthenium species, as confirmed by EPR spectroscopy. A detailed investigation of the nature of the organometallic radical species thus produced is beyond the scope of the present paper and will be published elsewhere.

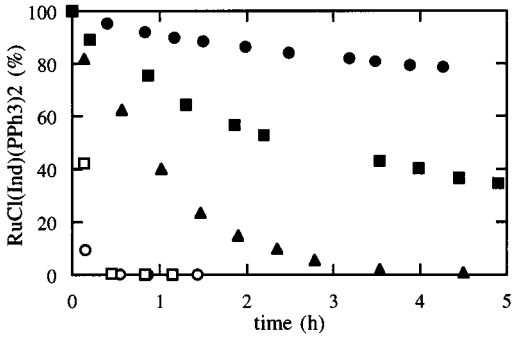


Figure 6. Temperature dependence of the decomposition of $[RuCl(Ind)(PPh_3)_2]$: (●) 20 °C, (■) 35 °C, (▲) 50 °C, (□) 65 °C, and (○) 80 °C; reaction conditions as in Figure 5

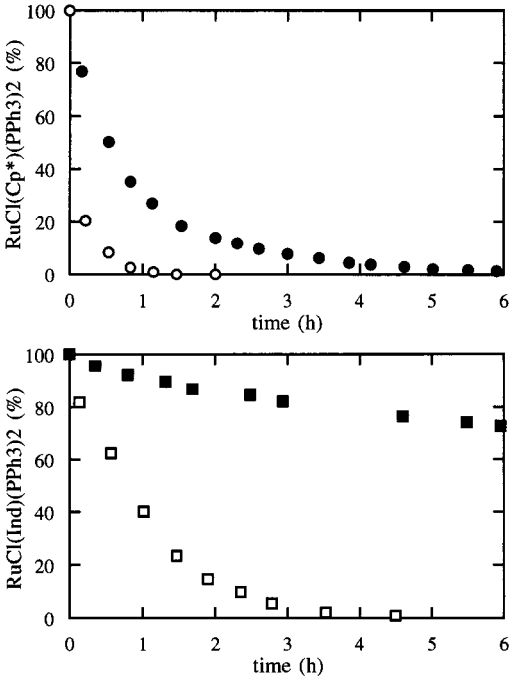


Figure 7. Triphenylphosphane dependence of decomposition of $[RuCl(Cp^*)(PPh_3)_2]$ at 20 °C (○, ●), and $[RuCl(Ind)(PPh_3)_2]$ at 50 °C (□, ■); no added PPh_3 (○, □), 5 equiv. PPh_3 (●, ■); reaction conditions as in Figure 5

The differences in reactivity between complexes **1**, **2**, and **3** could therefore be interpreted in terms of the relative ease of formation of a 16-electron species through triphenylphosphane dissociation. Similarly, mechanisms in which the generation of the catalytically active species is the result of the release of a PPh_3 ligand have already also been postulated for the Kharasch reaction mediated by $[RuCl_2(PPh_3)_3]$,[19] for the insertion of carbenes into N−H

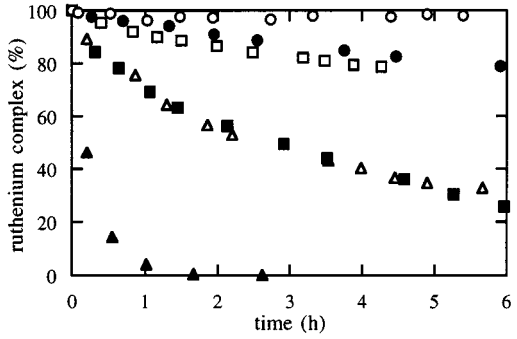


Figure 8. Decomposition of $[RuCl(Cp)(PPh_3)_2]$ and $[RuCl(Ind)(PPh_3)_2]$ upon addition of various amounts of CCl_4: $[RuCl(Cp)(PPh_3)_2]$, 20 °C: 10 equiv. CCl_4 (○) and 100 equiv. CCl_4 (●); $[RuCl(Ind)(PPh_3)_2]$, 20 °C: 10 equiv. CCl_4 (□) and 1000 equiv. CCl_4 (■); $[RuCl(Ind)(PPh_3)_2]$, 35 °C: 10 equiv. CCl_4 (△) and 1000 equiv. CCl_4 (▲); reaction conditions as in Figure 5

and S−H bonds,[20] and for carbene−carbene coupling reactions catalyzed by $[RuCl(Cp)(PPh_3)_2]$.[21]

The exact fate of the triphenylphosphane thus liberated is unclear. It is known that when triphenylphosphane, carbon tetrachloride, and benzaldehyde are allowed to stand at room temperature for 48 h or are heated at 60 °C for 2−3 h, β,β-dichlorostyrene and α,α-dichlorotoluene are formed in high yield, presumably via the intermediacy of triphenylphosphane dichloromethylene ylide $[(C_6H_5)_3P{=}CCl_2]$ and triphenylphosphane dichloride $[(C_6H_5)_3P{\cdot}Cl_2]$.[22] Formation of those intermediates is therefore a viable side reaction in Kharasch additions mediated by metal complexes bearing labile phosphanes. Addition of authentic $[(C_6H_5)_3P{\cdot}Cl_2]$ to reaction mixtures containing methyl methacrylate and styrene {1 equiv. $[(C_6H_5)_3P{\cdot}Cl_2]$ relative to **3**, reaction conditions in Table 2 (40 °C)} did not significantly affect either the conversion or the Kharasch addition yield. Because of its instability, the effect of authentic $[(C_6H_5)_3P{=}CCl_2]$ could not be checked. However, blank experiments in which carbon tetrachloride, triphenylphosphane (5 equiv. relative to CCl_4) and an excess of methyl methacrylate were refluxed for 4 h under nitrogen gave neither cyclopropanation, nor Wittig-type reaction in the case of MMA, whether with added catalyst **3** or without.

Role of the η^5-Coordinated π Ligand

The enhanced reactivity of indenyl complexes relative to their cyclopentadienyl analogues is generally explained as the result of facile metal ring slippage from η^5- to η^3-coordination of indenyl and the consequent creation of a vacant coordination site to host the entering ligand or substrate. This is the so-called "indenyl effect",[23] which has been suggested to account for the high activity of complex **3** in ATRP reactions.[8] However, some inverse indenyl effects are also known for the iron triad and, once more, substitution reactions proceeding through a dissociative pathway have been encountered.[24] On the other hand, the indenyl ligand can stabilize an electron-deficient intermediate more reliably than Cp because of its higher electron-releasing ability.[17] Similarly, Cp* is known to display electron-releas-

ing properties that are much more pronounced than those of Cp, again supporting the assumption of the formation of a 16-electron-species in the key step. It is therefore likely that the efficiency of ruthenium complexes **1**−**3** might be connected more to the strength of the Ru−P bond,[25] and hence to the releasing ability of triphenylphosphane, than to the formation of ring-slipped η^3-intermediates.

A coordinatively unsaturated 16-electron ruthenium center thus having been generated, pseudo-oxidative addition of the carbon−halogen bond could then occur, yielding both the 17-electron ruthenium(III) species and the radical $R^{\bullet}$, which would eventually add to the olefin or, most probably, recombine with the halogen, according to the relative position of the equilibrium outlined in Scheme 1. At that stage, the redox potentials of complexes **1**−**3** would be of utmost importance. Cyclic voltammetry measurements for [RuCl(η^5-ligand)(PPh_3)$_2$] in dichloromethane indicated that indenyl or pentamethylcyclopentadienyl complexes are oxidized at lower potentials than cyclopentadienyl complexes.[17] It is therefore feasible that pentamethylcyclopentadienyl and indenyl, acting as electron reservoirs toward the metal fragment [RuCl(PPh_3)$_2$] in **2** and **3**, respectively, or [RuCl(PPh_3)] in the transient species, favor ruthenium−phosphorous bond rupture or stabilize the 16-electron intermediate. The cyclic voltammetry results are in agreement with this interpretation, since the easier oxidation of the pentamethylcyclopentadienyl and indenyl complexes suggests higher electron density at the metal, a phenomenon facilitating the pseudo-oxidative addition of the carbon−halogen bond on the metal center.

Conclusions

Air-stable and readily available [RuCl(Cp*)(PPh_3)$_2$] and [RuCl(Ind)(PPh_3)$_2$] are the best ruthenium-based catalyst precursors found so far for promotion of the addition of CCl_4 across olefins, at temperatures as low as 40 °C. A two-step mechanism, in which a phosphane ligand disengagement occurs prior to the activation of the halogenated compound by the unsaturated ruthenium center, is suggested. Although a detailed understanding of the reaction mechanism (including the factors that favor ATRA over ATRP) must await further study, further improvements with this family of ruthenium(II) initiators can be expected. Various stereoelectronic variations of the ligands are now under investigation, together with further study of the mechanism.

Experimental Section

General: All reactions were performed under an atmosphere of dry nitrogen, using standard Schlenk and vacuum-line techniques. All reagents and solvents were dried, distilled, and stored under nitrogen at −20 °C, according to standard procedures.[26] Complexes **1**/**4**, and **3**/**5** were purchased from Aldrich and Stem, respectively, and used as received. Complexes **2**[27] and **6**[3] were prepared according to published procedures. NMR spectra were recorded on a Bruker AM 400 spectrometer. − Infrared spectra were measured on a Perkin−Elmer FT−IR 1720 X spectrometer with a selected resolution of 2 cm^{-1}. − GLC analyses were performed on a Perkin−Elmer 8500 gas chromatograph equipped with a FID and an internal integrator (column, RSL-150, 0.32 mm × 30 m; injector temperature, 290 °C; detector temperature, 290 °C; temperature program, 60 °C, 10 °C·min^{-1}, 220 °C, 15 min).

General Procedure for the Kharasch Addition: The ruthenium complex (0.03 mmol) was placed in a glass tube containing a bar magnet and capped with a three-way stopcock. The reactor was purged of air (three vacuum/nitrogen cycles) and a solution containing toluene (4 mL), dodecane (0.25 mL), CCl_4 (13 mmol), and alkene (9 mmol) was added. The reaction mixture was then heated in a thermostated oil bath (see tables and figures for details). Conversion and yield are based on the olefin, and were determined by GC using dodecane as internal standard. The Kharasch adducts were characterized by comparison with literature data.

Typical Decomposition Experiment: The ruthenium complex (0.015 mmol) was weighed out in a Wilmad screw-cap 10 mm NMR tube, which was then purged of air (three vacuum/nitrogen cycles) before addition of [D_8]toluene (0.5 mL) and toluene (2 mL). The NMR tube was shaken to dissolve the complex, and the t_0 ^{31}P NMR spectrum was then recorded at 293 K. Tetrachloromethane (14.5 μL, 0.15 mmol, 10 equiv. relative to ruthenium complex) was then added, and the NMR tube was shaken. The decomposition reaction was monitored by ^{31}P NMR at various temperatures (see captions for further details) to simulate Kharasch addition. Each complex's decomposition was repeated at least twice independently (on different days) to establish reproducibility. ^{31}P NMR: [RuCl(Cp)(PPh_3)$_2$]: δ = 39.87 (s); [RuCl(Cp*)(PPh_3)$_2$]: δ = 41.05 (s); [RuCl(Ind)(PPh_3)$_2$]: δ = 47.62 (s); PPh_3, δ = −5.00 (s).

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