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Radical reactions catalysed by ruthenium(II) complexes with anionic carborane phosphine ligands: Kharasch addition to olefins and controlled polymerisation

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Abstract

Ruthenium-carborane complexes **1**–**3** mediated the Kharasch addition of carbon tetrachloride across olefins with high yields which markedly depended on the catalyst and the substrate used. In addition, the atom transfer radical polymerisation of methyl methacrylate could be carried out in a highly controlled way. © 2000 Elsevier Science Ltd All rights reserved.

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The beginnings of the Kharasch reaction date back to 1945 when was first reported the direct addition of carbon tetrachloride to olefinic double bonds catalysed by peroxides as radical initiators. A major breakthrough occurred by the mid-1950s with the discovery that a number of transition metal complexes were able to catalyse the reaction.[1] After two decades of moderate interest, the Kharasch addition has known an incredible renaissance with Sawamoto's[2] and Matyjaszewski's[3] independent findings that the Kharasch reaction could be successfully extended to olefin polymerisation. In the presence of an excess of olefin (monomer) relative to the halogenated compound (initiator), highly controlled polymers in terms of molecular weights (M_n) and molecular weight distributions (M_w/M_n) could be synthesised provided favourable equilibria between the active species (–P•) and the dormant species (–P–X) were established (Scheme 1).[4] This is the so-called 'atom transfer radical polymerisation' (ATRP) which was coined from 'atom transfer radical addition' (ATRA)—the Kharasch addition.

Ruthenium has played a prominent role in Kharasch chemistry with $RuCl_2(PPh_3)_3$ displaying some of the highest efficiency and versatility for halocarbon activation and addition to olefins.[5]

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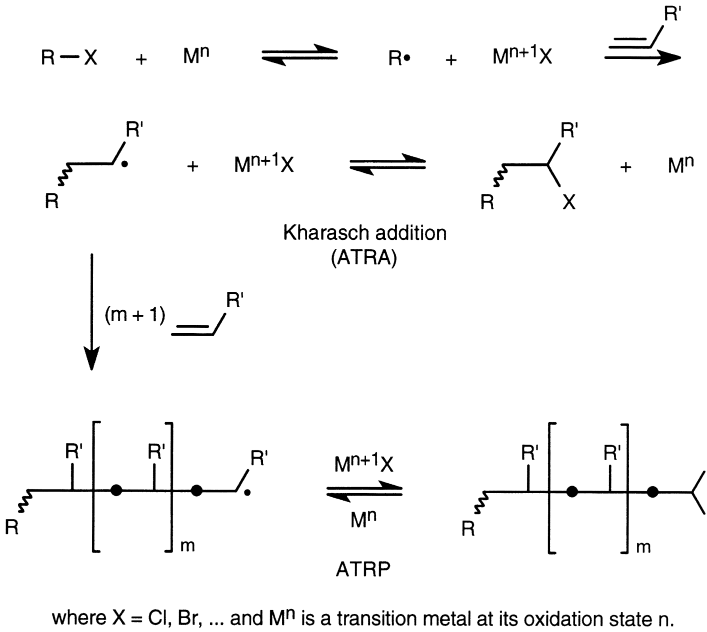


Scheme 1.

Formation of unsaturated 14-electron ruthenium species (through phosphine dissociation) is assumed to take place prior to halocarbon activation.[6] In a search for potential ruthenium catalysts in Kharasch chemistry, we recently introduced $[RuCl_2(arene)(PR_3)]$[7] and $[RuCl_2(=CHPh)(PR_3)_2]$[8] complexes for which the lability of the arene[9] and phosphine[10] ligands has been clearly demonstrated in olefin metathesis. Since ligand release depends on several factors including the ancillary ligands and the temperature, we anticipated that stable, well-defined 14-electron complexes should give a direct access to the catalytic species. Coordinatively unsaturated ruthenium complexes have often been obtained with bulky tertiary phosphines (PR_3) as ligands that provide steric protection to the empty coordination sites at the metal.[11] The steric crowding forces the R group of the ligand in close proximity to the metal centre to induce an agostic interaction between a C–H bond in the R group and the metal atom, thus preventing dimerisation or solvent coordination. Similar features have been met with ruthenium–carborane complexes in which B–H→Ru agostic bonds are favoured.[12]

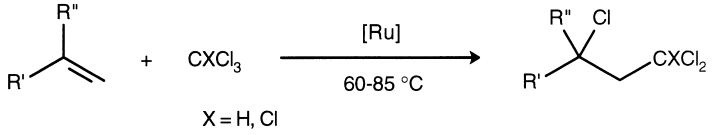
With this in mind, we investigated the catalytic activity of three 14-electron ruthenium(II) complexes (**1**, **2**, and **3**) with one or two *nido*-diphosphinocarborane anions (**L** = $7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10})^-$) for the Kharasch addition of carbon tetrachloride to four representative olefins, using standardised reaction conditions (Table 1, Scheme 2). The outcome of the reaction dramatically depended both on the substrate and the complex used. Thus, almost, 100% conversion of (meth)acrylates was observed with all three complexes, and the bis(diphosphinocarborane) compound **1** proved to be more efficient than the mono(diphosphinocarborane) derivatives **2** and **3**. Performing the reactions with styrene and 1-decene led to a striking differentiation between the former and the latter complexes. Compound **1** catalysed the reactions with a conversion lower than 10%, whereas **2** and **3** showed conversions higher than 50%, and Kharasch addition yields ranging from 40 to 80%. Examination of data gathered in Table 1 also shows that the ruthenium–hydride complex **2** is more efficient than its chloride analogue **3**. In terms of activity, catalyst

Table 1
Kharasch addition of carbon tetrachloride and chloroform to representative olefins catalysed by ruthenium complexes **1**–**3**[a]

			Substrate conversion (Kharasch addition) (%)[b]		
Substrate	alkyl halide	temperature (°C)	Ru-**1**	Ru-**2**	Ru-**3**
1-Decene	CCl_4	60	8 (7)	64 (44)	52 (42)
Styrene	CCl_4	60	8 (3)	90 (78)	56 (46)
n-Butyl acrylate	CCl_4	85	99 (40)	99 (23)	99 (17)
Methyl methacrylate	CCl_4	85	96 (69)	91 (51)	97 (40)
Styrene	$CHCl_3$	60	0 (0)	8 (0)	18 (0)

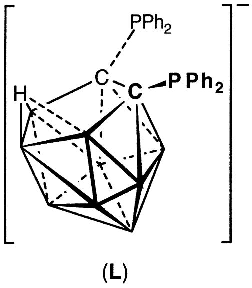
[a] Reaction conditions. Prior to use, the reagents, the solvent (toluene) and the internal standard (dodecane) were dried using well established procedures, distilled and kept under nitrogen at -20 °C. The catalyst (0.03 mmol) was dissolved in toluene (1 mL) and subsequently added through a septum to the solution of alkene (9 mmol), CCl_4 or $CHCl_3$ (13 mmol), dodecane (0.25 mL) in toluene (3 mL). The reaction mixture was heated at 60 or 85 °C for 24 h.

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



Scheme 2.

loading and reaction conditions, complexes **1**–**3** compare favourably with $RuCl_2(PPh_3)_3$ which is so far the most active ruthenium catalyst in Kharasch chemistry.[5,13] Interestingly, with the hydride complex **2**, addition of carbon tetrachloride to styrene reached 78%. Addition of chloroform to olefins is a much more difficult task in Kharasch chemistry. As already observed with $RuCl_2(PPh_3)_3$, complexes **1**–**3** were inefficient for the addition of $CHCl_3$ to styrene at 60°C. In most instances, whatever the halogenated compound used, low molecular weight polymers were obtained upon precipitation of the reaction mixture in methanol or heptane. It is therefore inferred that the difference between substrate conversion and Kharasch addition yield likely stems from the formation of short oligomers or telomers. Furthermore, it is worth noting that no metathesis occurred under these reaction conditions.



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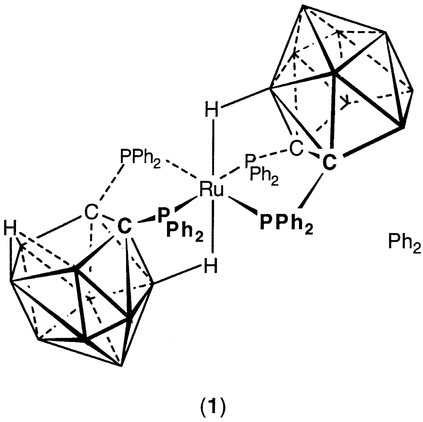
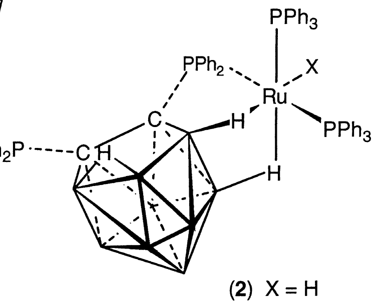


(1)



(2) X = H
(3) X = Cl

When the olefin was in excess relative to carbon tetrachloride, ruthenium complexes **1**–**3** successfully extended the Kharasch addition to the polymerisation of methyl methacrylate and styrene (Table 2). Most of the polymerisations were not controlled. However, the hydride complex **2** polymerised methyl methacrylate at 85°C in high yield and, very interestingly, in a highly controlled way since the molecular weight distribution was as narrow as 1.25. Also noteworthy is the observation that complex **2** is highly efficient without cocatalyst activation, whereas $RuCl_2(PPh_3)_3$ (the standard ruthenium complex in ATRP) requires Lewis acid addition for being active. From the preparative viewpoint, complex **2** constitutes therefore a valuable tool for ATRP of methacrylates. A series of halogenated compounds were employed successfully as initiators in order to examine the effects of the initiator-halogen on the polymerisation of MMA. Furthermore, suitable Lewis acid cocatalysts such as aluminium derivatives also exerted a pronounced influence on the polymerisation control. A detailed report thereon will be published elsewhere.[14]

Table 2
Polymerisation of methyl methacrylate and styrene catalysed by ruthenium complexes **1**–**3**[a]

Monomer	catalyst	polymer yield (%)	M_n[b]	M_w/M_n[b]
Methyl methacrylate, 85 °C	**1**	8	4 700	2.3
	2	84	28 000	1.25
	3	72	13 000	1.95
Styrene, 110 °C	**1**	52	30 000	1.75
	2	61	28 000	2.25
	3	60	23 000	1.9

[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, 16 h.

[b] Size exclusion chromatography calibrated with PMMA and PS standards, respectively.

In conclusion, unsaturated 14-electron ruthenium complexes with two B–H→Ru agostic interactions are highly efficient catalysts for promoting radical reactions, and they appear to be attractive for manifold catalytic applications.[15]

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