

**A POLYETHYLENE-BOUND RUTHENIUM(II) CATALYST
FOR INTER- AND INTRAMOLECULAR KHARASCH REACTIONS**

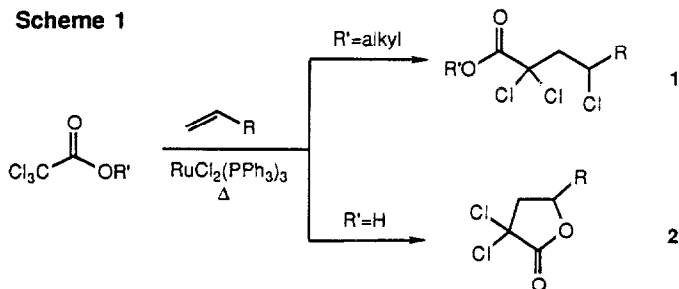
James C. Phelps and David E. Bergbreiter*
Department of Chemistry, Texas A&M University
College Station, Texas 77843

Gary M. Lee, Rosanna Villani and Steven M. Weinreb*
Department of Chemistry, The Pennsylvania State
University, University Park, Pennsylvania 16802

Summary: The preparation of a soluble, recoverable polyethylene-bound ruthenium(II) catalyst which is effective for both inter- and intramolecular additions of halocarbons to olefins (Kharasch reaction) is outlined.

We have previously described the preparation and use of a variety of transition metal catalysts attached to soluble, linear ethylene oligomers.¹ The reactivity of such catalysts is the same as their electronically equivalent low molecular weight analogs. However, the polyethylene-like character of the oligomeric ethylene ligands makes them completely insoluble at room temperature. Thus, it is possible to use them as genuine homogeneous catalysts above 90°C but to still quantitatively separate them from the reaction products and subsequently recycle the catalysts after simple filtration or centrifugation.

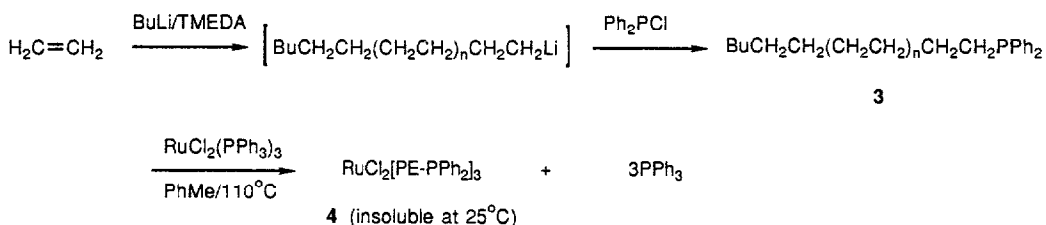
It has been found that $\text{RuCl}_2(\text{PPh}_3)_3$ is an exceptionally effective homogeneous catalyst for the Kharasch addition of a variety of halogenated substrates to olefins.² These additions are believed to proceed via metal-coordinated radicals.³ In particular, chloroacetates have proven to be useful halogenated components in these additions (Scheme 1). Depending upon whether the ester or acid is used, chloroesters 1 or α -chlorobutyrolactones 2 are produced.² In addition,



intramolecular versions of these reactions have been reported.^{2d,e,4}

In this paper we describe the preparation of a polymeric Ru(II) catalyst and its application to inter- and intramolecular Kharasch additions of chlorocarbons to alkenes. The polymeric phosphine ligand **3** was prepared from ethylene as previously described (Scheme 2).^{1a,c} Mixing polymer **3** with $\text{RuCl}_2(\text{PPh}_3)_3$ at 110°C in toluene, followed by cooling, gave a precipitate of the pink polyethylene-bound Ru(II) catalyst **4**. The clear solution remaining contained only

Scheme 2



triphenylphosphine as determined by ^{31}P NMR.

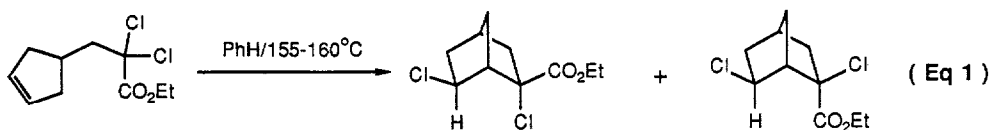
The polyethylene-bound catalyst is an effective substitute for $\text{RuCl}_2(\text{PPh}_3)_3$ in Kharasch reactions. For example, additions of tri- and dichloroacetic acid to alkenes to give chlorobutyrolactones (of **2**) proceed in yields and under conditions comparable to the non-polymeric ruthenium catalyst (Table).^{2f} Moreover, the polyethylene-bound catalyst is recyclable, provided oxygen is excluded at elevated temperatures so as to avoid conversion to the phosphine oxide (see experimental procedure below).

Table. Addition of Halogenated Carboxylic Acids to Terminal Alkenes Catalyzed by the Polymeric Ru(II) Complex **4**.

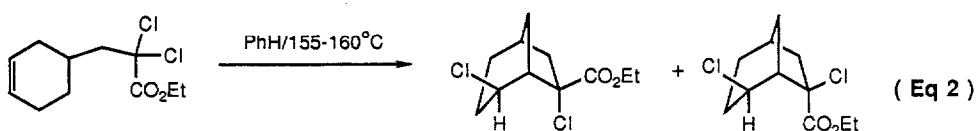
Alkene	Halogenated Carboxylic Acid	Product	% Yield ^a
1-Octene	Trichloroacetic Acid	2,2-Dichloro-4-hexylbutyrolactone	80(65) ^b
			80(49) ^c
1-Decene	Trichloroacetic Acid	2,2-Dichloro-4-octylbutyrolactone	82(64) ^d
1-Decene	Dichloroacetic Acid	2-Chloro-4-octylbutyrolactone	67(55) ^c
			60(41) ^e

^aYields were measured by gas chromatography. Isolated yields are listed in parentheses. Products were isolated by distillation and characterized by ^1H and ^{13}C NMR spectroscopy as well as by GC-MS. ^bThe yield in the reaction using $\text{RuCl}_2(\text{PPh}_3)_3$ as a catalyst is 81% (62%) as reported in ref 2f. ^cThe catalyst was recycled once. ^dThe yield in the reaction using $\text{RuCl}_2(\text{PPh}_3)_3$ as a catalyst is 85% (70%) as reported in ref 2f. ^eThe catalyst was recycled three times.

The polymeric catalyst is also as efficacious as $\text{RuCl}_2(\text{PPh}_3)_3$ in promoting intramolecular Kharasch cyclizations of various halo olefin substrates. The unsaturated α,α -dichloroesters shown in **equations 1** and **2** cyclize in yields and with stereoselectivities very similar to those found with the non-polymeric catalyst.^{4b,5}

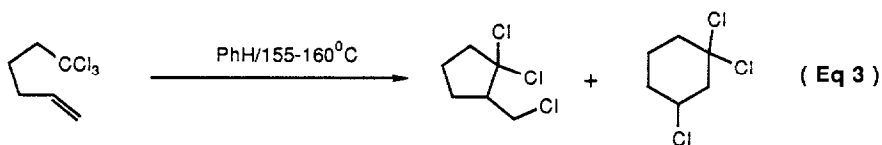


$\text{RuCl}_2(\text{PPh}_3)_3$ (1.3% mol %) 3h	37%	53%
$\text{RuCl}_2(\text{PEPPH}_2)_3$ (1.0 mol %) 86h	34%	51%

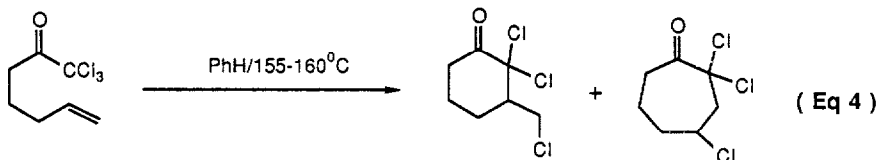


$\text{RuCl}_2(\text{PPh}_3)_3$ (1.0% mol %) 8h	39%	44%
$\text{RuCl}_2(\text{PEPPH}_2)_3$ (0.8 mol %) 88h	38%	51%

Two trichloromethyl alkene substrates have also been examined (**Eq 3** and **4**).^{4c,5} Once again, in these systems, product yields, as well as regio- and stereoselectivities, are comparable for the polymeric and the $\text{RuCl}_2(\text{PPh}_3)_3$ catalysts. As can be seen in **Eq 4**, the polymeric Ru catalyst can be recycled with no reduction in the yield of products.



$\text{RuCl}_2(\text{PPh}_3)$ (5 mol %) 41 h	79%	10%
$\text{RuCl}_2(\text{PEPPH}_2)_3$ (0.41 mol %) 59h	72%	8%



$\text{RuCl}_2(\text{PPh}_3)$ (2 mol %) 48h	44%	45%
$\text{RuCl}_2(\text{PEPPH}_2)_3$ (0.54 mol %) 72h	39%	46%
$\text{RuCl}_2(\text{PEPPH}_2)_3$ (0.90 mol %) 72h (recycled)	42%	50%

Synthesis of Polyethylene-Bound Ru(II) Complex 4. To a 200 mL Schlenk flask fitted with a condenser was added 1.5 g (0.64 mmol/g, 0.96 mmol) of PEPPh₂ 3^{1a,c} and 0.36 g (0.32 mmol) of RuCl₂(PPh₃)₃. After evacuating and purging the flask three times with nitrogen, degassed toluene was added and the suspension was heated to reflux. After 8 h the solution was cooled to room temperature. The resulting precipitate of 4 was collected in a fritted glass funnel and washed with ether, giving 1.5 g of salmon-pink product upon vacuum drying.

Typical Kharasch Reaction with Polymer 4. A mixture of 0.7 g (0.21 mmol of Ru) of RuCl₂(PE-PPh₂)₃, trichloroacetic acid (9.0 g, 55 mmol) and 1-decene (7.0 g, 50 mmol) was placed in a 150 mL Schlenk flask fitted with a reflux condenser and 30 mL of dry degassed toluene was added. After three freeze-thaw cycles in which the frozen suspension was evacuated and flushed with nitrogen, the catalyst was dissolved by heating the reaction mixture to reflux under nitrogen. After 12 h the reaction mixture was cooled, filtered through a medium porosity fritted funnel under nitrogen, followed by washing the collected solid with diethyl ether. The crude lactone product was isolated by removal of the solvent from the filtrate and either analyzed directly by GC or GC/MS or purified by distillation under reduced pressure (Table).

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- Reactions were run in a sealed tube.

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