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Development and Application of Highly Efficient Ruthenium-Based Catalysts for the Ring Opening Metathesis Polymerization

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Abstract: Various bisallylic ruthenium(IV) complexes were synthesized and tested as catalysts for the ring opening metathesis polymerization (ROMP) of norbornene. In presence of cocatalysts such as silanes or certain diazoalkanes a significant increase of the catalytic activity could be observed. With these highly efficient systems the ROMP of diolefinic norbornene derivatives (dicyclopentadiene, 5-ethylidene-2-norbornene, norbornadiene) and monomers containing functional groups was achieved (e.g. alcohols, acids, esters, amides, imides, ketones, aldehydes, ...).

INTRODUCTION

The ring opening metathesis polymerization (ROMP) discovered in 1957 (Ref. 1) is an area of great interest for industry and university. As a reaction not observed in nature metathesis can be used for the formation of synthetic polymers. In contrast to other polymerization reactions in ROMP all monomer double bonds remain in the polymer. Owing to their tolerance towards functional groups ruthenium-based catalysts can be advantageous compared to titanium, molybdenum, tungsten and rhenium complexes (Ref. 2). This exceptional position of ruthenium allows the polymerization of functionalized cyclic olefins under mild reaction conditions. Moreover, there is continuing demand for inexpensive easy-to-handle catalysts for the ring opening metathesis polymerization. We have recently reported a series of easily obtainable and exceptionally active ROMP catalysts of tetravalent ruthenium (Ref. 3).

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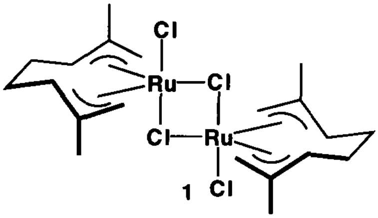
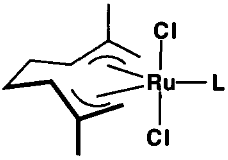
RESULTS AND DISCUSSION

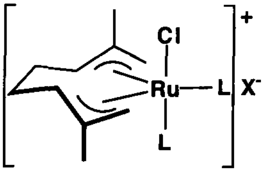
Allylruthenium(IV) Complexes for ROMP of Norbornene

The allylruthenium(IV) precursor complex **1** is obtained from isoprene and commercially available ruthenium(III) chloride (Ref. 4). Addition of ligands L results in the break of the dimeric structure leading to group I compounds. Using silver salts of non-coordinating anions cationic complexes (group II, group III) are accessible.

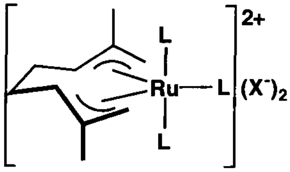




group I



group II



group III

L = NCMe, NCEt, NCPh, $P(OMe)_3$, $P(OEt)_3$, $P(O\text{-}i\text{-}Pr)_3$, PPh_3, 4-t-Bu-py, 3-Me-py, 4-Me-py

L^1 = NCMe, NCEt, NCPh

X^- = BF_4^-, $CF_3SO_3^-$, PF_6^-, SbF_6^-

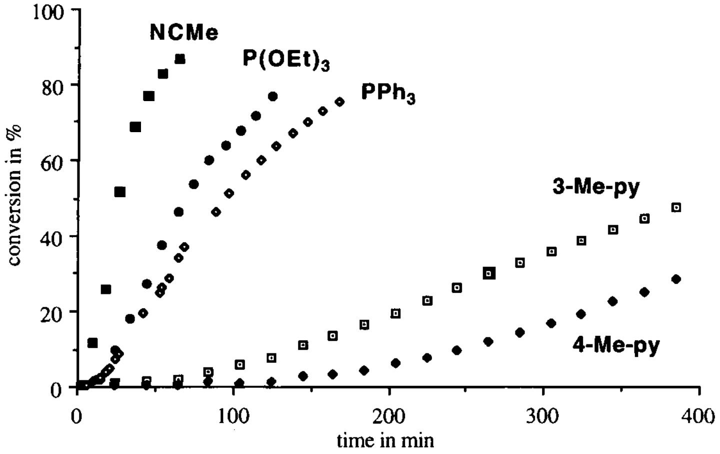


Fig. 1. Time conversion curves for the ROMP of norbornene with group I catalysts under variation of ligands L (at 50°C in C_6D_6).

The time conversion curves of group I catalysts for the ROMP of norbornene elucidate the significant influence of ligands L on the activity. Nitrile containing complexes exhibit the highest, pyridine containing complexes the lowest activities. This observation is consistent with the concept of the dissociation of L being important for the formation of the active species.

Due to their ionic character and the resulting solubility in polar solvents group II and III complexes allow polymerizations in emulsion and under precipitation (Ref. 5).

Silanes as Activating Agents for Allylic Ruthenium Complexes

One possible mechanism for the formation of the catalytically active carbene species was suggested by Ivin (Ref. 6). This consideration involves an allylic metal hydride intermediate.

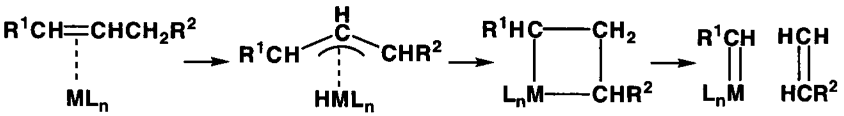


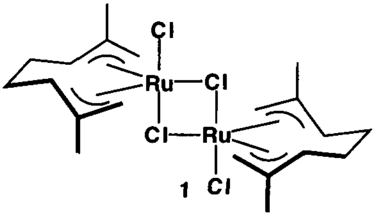
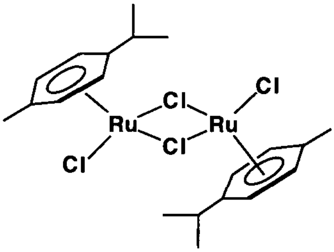
Fig. 2. Possible mechanism for the formation of a carbene species from a metal complex and an olefin (Ref. 6).

This intermediate differs only in the hydride ligand from the ruthenium complexes mentioned. Therefore, the use of hydration agents as cocatalysts for allylic transition metal complexes seemed to be promising. Silanes are known to readily react with ruthenium compounds under oxidative addition leading to a ruthenium hydrogen bond.

Mechanistical studies have shown that complex 1 undergoes an oxidative addition with triethoxysilane. In absence of cyclic olefins this is followed by a hydrosilylation of the bisallylic system. In presence of norbornene one can observe clearly higher activities for the ring opening metathesis polymerization. For non-allylic ruthenium complexes a significantly lower activity occurs. Similar observations could be made with dichloromethylsilane.

These results support the previous mechanistical considerations. Further investigations in this new concept for the activation of allylic ruthenium complexes are in progress.

Table 1: Influence of silanes on the ROMP of norbornene.

Catalyst	Silane	Time	Yield in %
 1	-	21 h	13
	$HSi(OEt)_3$	2 min	40
	-	60 min	2
	$HSi(OEt)_3$	60 min	3

Diazoalkanes as Alkylidene-Generating Agents

Although already described as alkylidene generating cocatalysts (Ref. 7) diazoalkanes have not yet been used in combination with group I, II and III complexes. The influence of various diazo compounds on the catalytic activity was studied. For all complexes mentioned the presence of ethyl diazoacetate or trimethylsilyldiazomethane leads to a significant increase of activity (Ref. 3). In contrast to this result diethyl diazomalonate provides no activation effect. A further proof for the different reactivities of diazo compounds is the dependency of the catalytic activity on the diazoalkane catalyst ratio. Trimethylsilyldiazomethane develops its full activation power only at molar ratios > 1:1 ([diazoalkane]/[catalyst]), whereas the use of ethyl diazoacetate leads to an activation maximum at molar ratios < 1:1 ([diazoalkane] / [catalyst]) (Fig. 3).

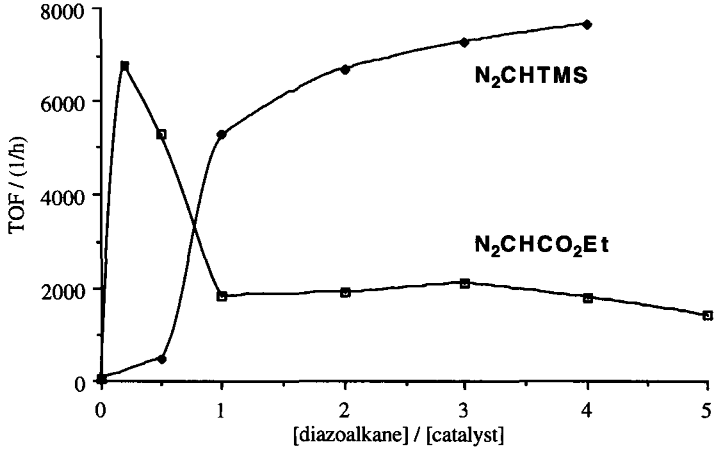


Fig. 3. Catalyst activity (TOF / h^{-1}) as a function of the molar ratio diazoalkane / catalyst.

Obviously, ethyl diazoacetate undergoes a side reaction with the propagating species. Recent studies indicate this reaction to be a chain termination reaction leading to telechelic polymers with two ethyl ester end groups. The end groups were identified by ^{1}H-NMR spectroscopy.

The most active catalyst system to date comprises group III complexes and ethyl diazoacetate in methanol. Turnover frequencies up to 10^5 h^{-1} can be achieved. Furthermore, the experimental requirements are easy to met: polymerizations can be carried out in air, without supply of thermic energy, and in undried solvents.

Control of Molecular Weight

The molecular weight is given by the monomer catalyst ratio and the solvent composition. In a mixture of methanol as a precipitation agent and dichloromethane as a solvent for polynorbornene the number average molecular weight ($\overline{M_n}$) can be varied by the ratio methanol / dichloromethane. At a constant monomer / catalyst ratio of 1 000 $\overline{M_n}$ can be adjusted within the range 300 000 g/mol up to 10^6 g/mol simply by the variation of the ratio solvent / non-solvent (Fig. 4).

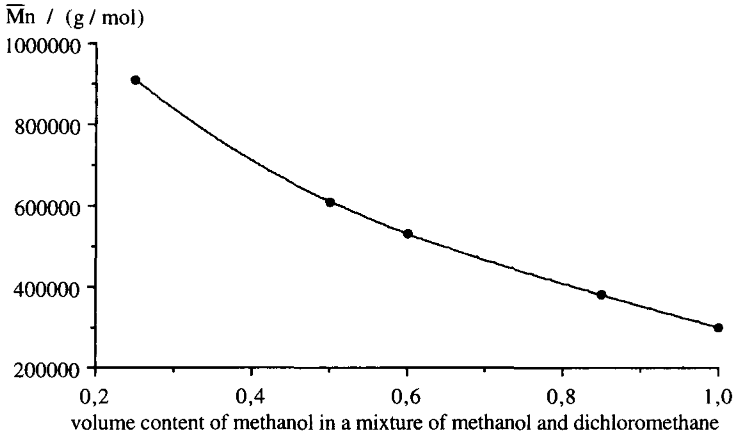


Fig. 4. Dependency of the number average molecular weight on the solvent composition.

1-Alkenes are reported to act as chain transfer agents for various ROMP-systems. In case of our dicationic complex in presence of ethyl diazoacetate, 1-octene was used to yield lower molecular weights down to 2 000 g/mol (Fig. 5). Furthermore, the molecular weight of resulting polynorbornenes can be restricted by an excess of ethyl diazoacetate. Consequently, this chain termination involves a limited yield.

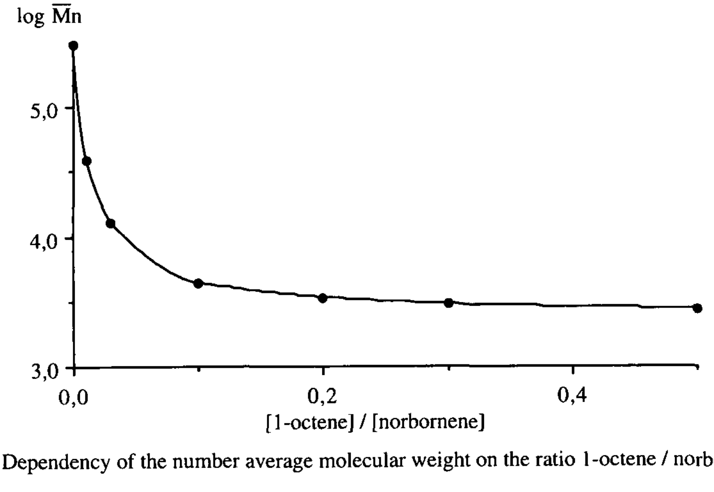


Fig. 5. Dependency of the number average molecular weight on the ratio 1-octene / norbornene.

ROMP of Diolefinic Monomers

Ruthenium is reported to be comparatively inefficient in the metathesis of diolefinic compounds (Ref. 8). Two explanations for this behaviour can be given. First, monomers can act as bidental ligands. Secondly, after a ring opening step the second double bond can form a π-bond to the active ruthenium species. In both cases one coordination site is blocked and the electron density is increased at the central metal. Using the coordinately fairly unrestricted and Lewis acidic complexes of group II and III exceptionally good results for 5-ethylidene-2-norbornene, norbornadiene and *endo-* dicyclopentadiene can be attained.

Copolymerization

The catalyst sytems are also suitable for copolymerizations. Interestingly, the most active monomer norbornene is only slightly preferred in presence of less reactive norbornene derivatives. The use of *endo*-dicyclopentadiene and norbornene as comonomers leads to copolymers with monomer contents similar to the initial ratio of the comonomer concentrations. This can be observed for the monocationic (group II) and the dicationic (group III) complexes analogously (Fig. 6).

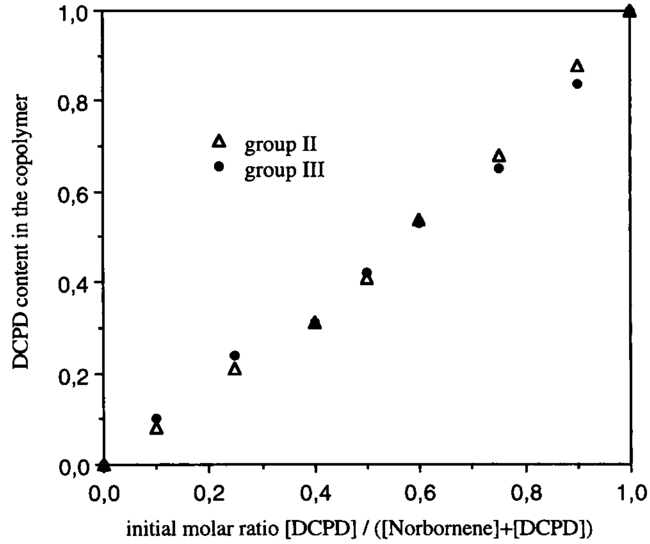


Fig. 6. Copolymerization diagramm for norbornene and dicyclopentadiene as comonomers (monomer conversion < 5%).

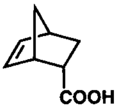
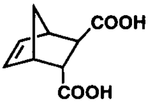
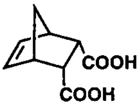
The glass transition temperature is one property which can be controlled in the range of 40^0C up to 100^0C by the dicyclopentadiene content. Only one glass transition point can be observed indicating a statistical incorporation. An additional ^{13}C-NMR analysis of the dyads proved the resulting polymers to be perfectly random copolymers.

ROMP of Functionalized Monomers

By Diels-Alder reactions of cyclopentadiene or furan and dienophiles functionalized norbornene or 7-oxanorbornene derivatives are readily available. With our systems ROMP polymers from monomers containing several functionalities (alcohols, carbon acids, esters, amides, imides, hydroxylimides, ketones, aldehydes) can successfully be polymerized.

Especially, monomers with functional groups usually acting as catalyst poison for other metathesis-active metals are of particular interest. The example of carbon acid derivatives elucidates that 'tolerance' towards functional groups depends on the individual geometry of the monomer.

Table 2. Yields of ROMP polymers with group III catalysts in presence ethyl diazoacetate.

Monomer	Time in min	Yield in %
	50	92
	60	94
	60	2

Furthermore, the catalysts were successfully applied in polymerization of chromophore or amino acid containing polymers.

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