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## Alkene conversions with early transition metal catalysts

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# Chapter 1

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## Introduction

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### 1.1. Catalytic Alkene Conversions.

Alkenes and in particular 1-alkenes are very convenient feedstocks for chemical industry. Light alkenes (ethene, propene) are used in bulk chemical processes, such as polymerization, oligomerization, Wacker oxidation, and epoxidation to make plastics, acetaldehyde and glycols.<sup>1</sup> The higher alkenes are important intermediates for the production of biodegradable detergents, the synthesis of lubricants and plasticizer alcohols.<sup>1a,b</sup> In addition, alkenes can serve as precursors for the preparation of a broad range of pharmaceuticals.

Due to increasing environmental consciousness, there is a strong and increasing demand for short and highly efficient routes for the synthesis of organic compounds with polar functions. An attractive way to attach such special substituents in oligomers and polymers of alkenes is catalytic hydroboration of their alkene end groups. The resulting boron-alkyls can easily be transformed into alcohols, amines, aldehydes or halides, making these compounds interesting intermediates for the preparation of fine chemicals. Another possibility to produce "polar" oligomers is selective oligomerization and co-oligomerization of functionalized alkenes using early transition metal catalysts.

### 1.2. Alkene Polymerization.

Over the last four decades, catalytic polymerization of 1-alkenes has developed from Ziegler's small scale laboratory experiments to a giant industrial application (world production: 53.6 million tons in 1995).<sup>1</sup> To date, a wide range of polymers with a broad variation of chemical and mechanical properties is produced in bulk amounts from very simple alkenes, such as ethene, propene and other 1-alkenes. These polyalkenes are used on large scale for packaging, car bumpers and dashboards, fibers and films.

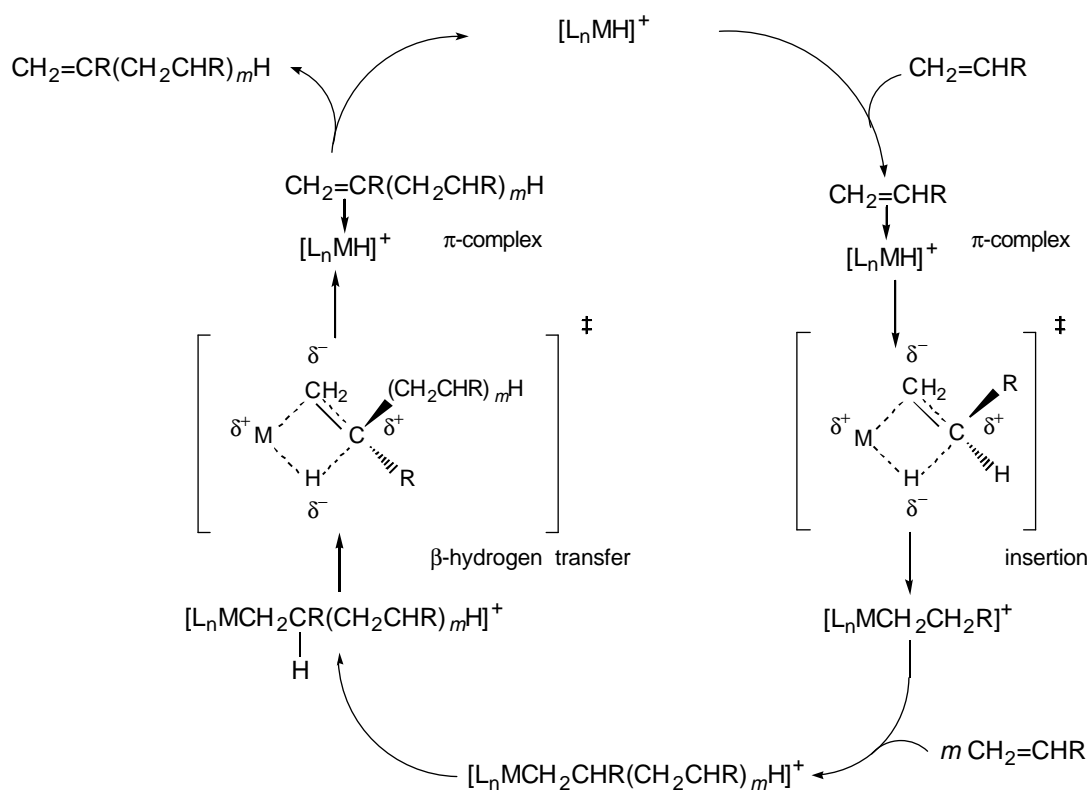
It is clear that economic aspects are the main motive to continue extensive research programs in alkene polymerization, but also environmental considerations are increasingly

important, e.g. the wish to avoid or to replace chlorine containing polymers, such as PVC. The field is also from a purely scientific point of view enormously challenging and fascinating. The central objective is to master the polymerization process in every desired detail by developing specific catalysts. Such compounds can only be designed, when the molecular aspects of the catalytic process are all well understood: What happens exactly at the metal center? Which factors do determine selectivity, polymer chain growth, chain transfer? What causes catalyst deactivation?

Up to 1980, exclusively heterogeneous catalysts have been applied for the preparation of polyethene under low pressure. In general, the heterogeneous systems have different catalytic sites active at the same time. All of them have their own polymerization characteristics, which results in polymer mixtures with broad molecular weight distributions. A major breakthrough was made by Kaminsky and Sinn who discovered that zirconocene dichloride ( $\eta^5\text{-C}_5\text{H}_5\text{)}_2\text{ZrCl}_2$  can be activated for catalytic polymerization of 1-alkenes by methyl aluminoxanes (MAO).<sup>2</sup> It was found that the catalytic activity of the metal as well as the average molecular weight of the polymers increased dramatically. The catalysts are soluble in the reaction medium and form, at least at the beginning of the polymerization process, a homogeneous system. Homogeneous catalysts have the advantage that catalyst fine tuning is easily done. The disadvantages are that the process control and product morphology are poorly manageable. These problems can be overcome by immobilization of the homogeneous catalyst. The observations by Sinn and Kaminsky led to an enormous activity in the area of homogeneous catalytic alkene polymerization.<sup>1c,d</sup> Several industrial and academic research groups have concentrated on the study of well-defined ionic group 4 metal complexes  $[\text{Cp}'_2\text{MR}]^+ [\text{L}]^-$  ( $\text{Cp}' = \eta^5\text{-C}_5\text{H}_{5-n}\text{Me}_n$ ;  $\text{R} = \text{H, alkyl, } n = 0-5$ ;  $\text{L} = \text{complex counter anion}$ ).<sup>3</sup> These systems polymerize ethene and propene under mild conditions with high selectivity and activity. The intense research on the polymerization of 1-alkenes with metallocene catalysts in both academic and industrial laboratories has provided broad and deep insight into the principles of C-C, C-H and C-X bond formation and cleavage reactions.

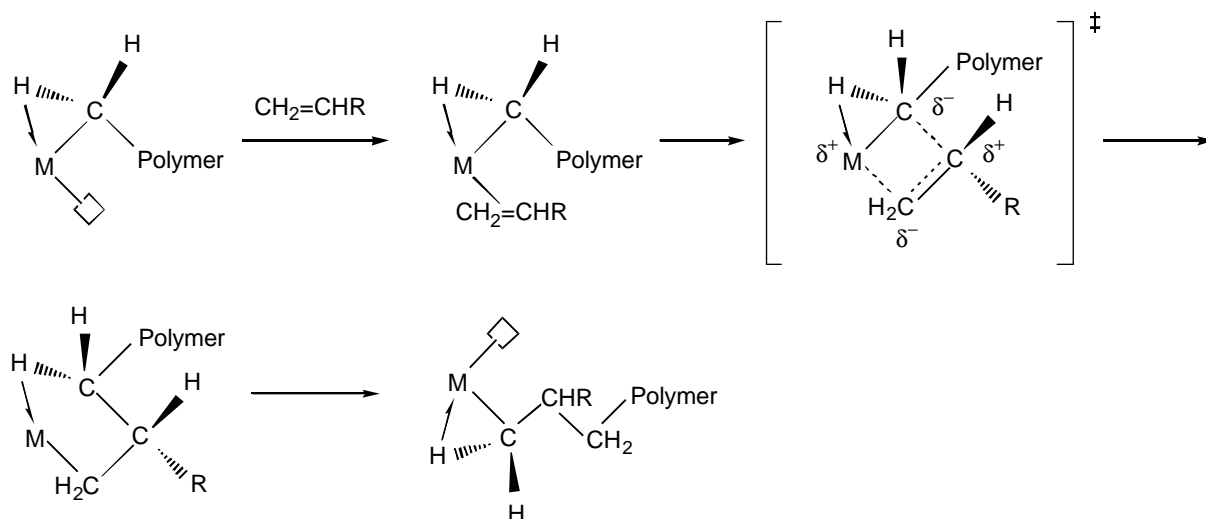
Despite the extensive and sophisticated investigations done to work out the mechanistic details of the polymerization process many questions remain open due to the complex nature of the catalysts. Nowadays, for group 4 compounds, it is generally accepted that a cationic  $d^0$ , 14 (or lower) electron system is the active species.<sup>3</sup> This view is strongly supported by the high polymerization activity of isoelectronic ( $d^0$ , 14 (or lower) electrons) neutral group 3 and lanthanide complexes.<sup>4</sup> At the moment, the most widely accepted mechanism for 1-alkene polymerization on an early transition metal catalyst is basically the same as originally proposed in the early sixties by Cossee and Arlman (Scheme 1).<sup>5</sup> The polymerization process starts by coordination of an alkene at the vacant site of a cationic group 4-alkyl complex ( $\pi$ -complex formation) followed by insertion of the alkene into the metal-alkyl bond. Subsequent alkene coordination and insertion leads to chain growth. The polymerization is a thermodynamically

down-hill process due to the transformation of  $sp^2$  C=C to  $sp^3$  C-C bonds.<sup>6</sup> Chain growth can be terminated in various ways. The most well-known is hydrogen transfer from the  $\beta$ -position of the growing alkyl chain to the active metal center, which leads to a polymer with an alkene end group and a (normally catalytically active) metal-hydride complex. This process, the microscopic reverse of alkene insertion into a metal-hydride bond, is called  $\beta$ -hydrogen elimination.<sup>7</sup>



**Scheme 1.** Catalytic 1-alkene polymerization as proposed by Cossee and Arlman.<sup>4</sup>

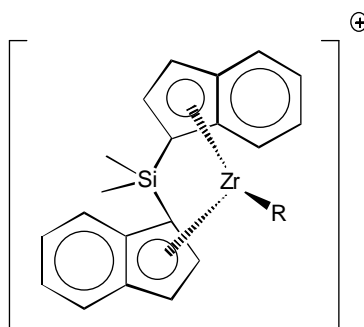
In 1983, Brookhart, Green and Rooney proposed an alternative chain growth mechanism in which electronic stabilization of the ground state and the transition state by interaction of the metal with one of the  $\alpha$ -hydrogen atoms from the polymer chain, a so-called  $\alpha$ -agostic interaction, facilitates the propagation step (Scheme 2).<sup>8</sup> Alkene insertion into a metal-hydride bond as well as chain transfer by  $\beta$ -hydrogen elimination seem to occur as proposed by Cossee and Arlman.<sup>5</sup> Supporting evidence for both chain propagation mechanisms has been found, indicating the complex nature of this key reaction.<sup>8d</sup>



**Scheme 2.** Chain propagation mechanism as proposed by Brookhart, Green and Rooney.<sup>8</sup>

Essential for successful polymerization seems to be that the catalyst is coordinatively and electronically unsaturated (14 or lower electron systems) and contains a polar M-C bond that favors a partially charged transition state.<sup>7a</sup> The highly electrophilic metal center requires stabilization by electron donating ligands. They have to meet the following criteria: inert, inexchangeable and tuneable. They also should provide sufficient steric bulk to prevent association of the metal complex *e.g.* to give bridged systems, which usually leads to poorly soluble, catalytically inactive species. Hitherto, bis(cyclopentadienyl) ligands and its derivatives (bis(indenyl), *ansa*-bis(cyclopentadienyl) and *ansa*-bis(indenyl) systems) have found to be by far the most successful stabilizing groups for cationic group 4, and neutral group 3 and lanthanide complexes. Improvement of these metallocene catalysts has mainly been achieved by varying the substituents (*e.g.* alkyl, aryl, trialkylsilyl) at the cyclopentadienyl or indenyl ring. This has led to the development of "single-site" catalysts, capable of polymerizing a wide variety of 1-alkenes in a highly stereoselective fashion, with an activity approaching "enzymatic rates".<sup>9</sup> Recent research in this area is strongly supported by theoretical studies, providing considerable information about the fundamental steps in alkene polymerization.<sup>10</sup>

Recently, one cyclopentadienyl ligand of an *ansa*-bis(cyclopentadienyl) system has been replaced by a functional group X (X = NR, O) to form monomeric "constrained geometry" catalysts.<sup>11</sup> The short bridge of this bidentate ligand probably creates more space around the metal center and therefore, in principle, easy access for incoming 1-alkenes. The steric and electronic effects can be tuned by variation of the coordinating group X and by the substituents on the cyclopentadienyl ligand. These compounds proved to be selective and active catalysts for the polymerization of a wide range of 1-alkenes.<sup>12</sup> Dow has commercialized 1-alkene (co)polymerization processes catalyzed by "constrained geometry" group 4 compounds, emphasizing the good perspectives for these systems.<sup>11a,b</sup>



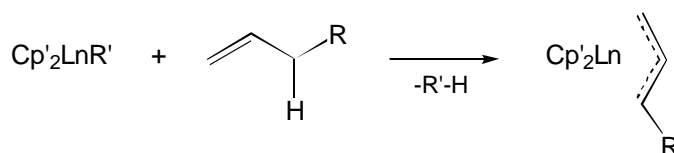
**Figure 1.** Cationic ansa-bis(indenyl) zirconium systems.

A drawback of group 4 catalysts is that they require activation by co-catalysts, of which methylaluminoxane (MAO) is at the moment the most active. MAO is prepared by partial hydrolysis of  $\text{Me}_3\text{Al}$ . A serious problem with MAO is that the synthesis is complicated and irreproducible, leading to dramatic differences in catalytic performance.<sup>1c,d</sup> The exact composition varies and the structure is still unknown, but MAO probably consists of oligomers which all contain Me-Al and O-Al bonds. Although the precise function of MAO still has to be determined, it seems that experts agree that MAO (1) alkylates  $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$  to give  $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrMe}_2$  and (2) abstracts the methyl anion to generate a  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrMe}]^+$  cation, which is the active species. MAO binds the methyl anion and these form a complex counter anion.<sup>13</sup> Another trivial, but extremely important, function of MAO is that it is a very efficient water and oxygen scavenger of the alkene feed. However, the most remarkable fact is that MAO has to be added in large excess. Under such conditions, it has been suggested, probably large counter anions are formed, which results in a long distance between the anion and the catalytically active cation.<sup>1c</sup> The more "naked" the cationic catalyst, the more active it will be toward alkene insertion, but also to chain transfer processes, such as  $\beta$ -hydrogen- or  $\beta$ -methyl elimination.<sup>7,14</sup>

For reliable, reproducible catalysis, systems are preferred, which are synthetically easy to access and fully defined. Hence, much attention has been paid not only to the development of well-defined cationic group 4 complexes,<sup>3</sup> but to counter anions as well.<sup>15</sup> Perfluorinated tri- and tetra phenyl borates appear to be weakly bonded counter anions that lead to highly reactive "naked" cationic metal centers.<sup>15</sup> By adjusting the phenyl substituents at boron, the stability, activity and selectivity of the catalyst can be improved dramatically. For example, trialkylsilyl substitution at the *para*-position of the perfluorinated phenyl ring has led to thermally more stable, better soluble and more active catalysts for the polymerization of ethene.<sup>16</sup>

A cocatalyst is not necessary to initiate activity for alkene polymerization for isoelectronic neutral group 3 or lanthanide catalysts. These compounds appear to be highly active for the polymerization of ethene,<sup>4</sup> but also for the cleavage of C-H bonds in, for

example, methane and benzene.<sup>17</sup> This C-H activation also dominates during the polymerization of 1-alkenes, resulting in  $\gamma$ -hydrogen transfer to the active metal center to yield stable lanthanide( $\eta^3$ -allyl) species, which hamper further alkene insertion or make it totally impossible (Scheme 3). This phenomenon is well-known as catalyst deactivation by allylic C-H activation.<sup>4c</sup> Recently, Bercaw *et al.* synthesized well-defined silicon-bridged bis(cyclopentadienyl)yttrium hydrides, which can act as single-component Ziegler-Natta 1-alkene polymerization catalysts.<sup>18</sup> For higher 1-alkenes, high molecular weight polymers are produced, probably indicating that allylic C-H activation does not take place. In this case, it is also possible that an yttrium( $\eta^3$ -allyl) compound is formed, but can easily be transformed into an yttrium( $\eta^1$ -allyl) complex, which affords alkene insertion. These observations may open the way for the development of polymerization catalysts, which do not require activation by a co-catalyst.



**Scheme 3.** Catalyst deactivation by allylic C-H activation.<sup>4c</sup>

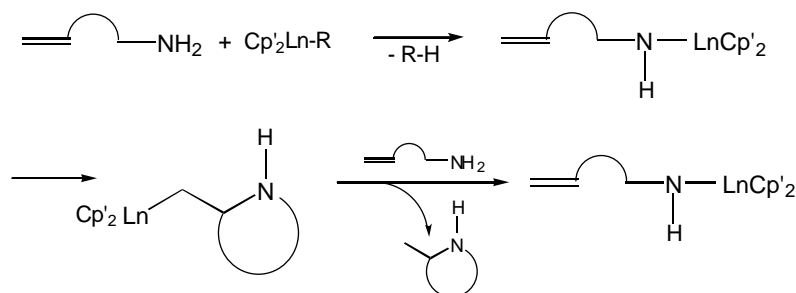
Whilst writing this thesis, Brookhart *et al.* found that cationic palladium (II) and nickel (II) complexes are highly active catalysts for the polymerization of ethene and 1-alkenes.<sup>19</sup> These well-defined systems have also a much higher tolerance for polar functions than the early transition metal based catalysts. This has been clearly shown by the fact that copolymerization of ethene and propene with functionalized vinyl monomers, such as acrylates could be achieved; an enormous breakthrough in the field of alkene polymerization.<sup>20</sup> No indications for catalyst deactivation by C-X- or C-H activation were observed. Without any doubt, these catalyst systems will find a strong position in industry, *e.g.* DuPont has filed a patent application on the technology discovered by Brookhart with about 500 claims.<sup>21</sup>

### 1.3. Shortcomings of Modern and Classical Ziegler-Natta Systems.

In general, the polyalkenes obtained with classical or modern Ziegler-Natta catalysts are build from regular 1-alkenes. This gives apolar polymers which are sometimes difficult to be used for particular applications (*e.g.* dyeing or mixing with polar polymers). A commercially very attractive extension of the range of applications of polyalkenes could be realized when it would be possible to build-in polar functions at wish. (Co)polymers containing polar substituents are very promising for use in industry because of improved adhesive properties, affinity for dyes

and compatibility with other polar polymers (e.g. polyacrylates), compared to regular polyalkenes. This area of partly functionalized polyalkenes is commercially so attractive that it seems very probable that industrial research has already focused on the oligomerization and polymerization of functionalized 1-alkenes. However, so far reports and patents on these polymers have scarcely been published. This may indicate the high complexity of the subject.

Functionalization e.g. by building in polar functions through co-polymerization of 1-alkenes with polar substituent containing alkenes is virtually impossible with Ziegler-Natta catalysts and their modern analogues. The catalysts normally do not tolerate alkenes with polar functions (C-X bonds). The presence of polar C-X bonds (X = heteroatom) in the alkene usually leads to highly exothermic formation of M-X bonds<sup>22</sup> and results in deactivation of the catalyst.<sup>23</sup> The only exception so far has been published by Marks *et al.* who reported the organolanthanide-catalyzed hydroamination/cyclization of 1-amino-4-alkenes and 1-amino-5-alkenes.<sup>24</sup> It has been demonstrated that the cyclic amines are formed via insertion of the alkene into Ln-NR<sub>2</sub> bond (Scheme 4). This illustrates that M-X bond formation does not necessarily mean a thermodynamic sink and suggests that by carefully tuning the catalyst tolerance for polar functionalities can be improved.



**Scheme 4.** Organolanthanide-catalyzed hydroamination/cyclization of aminoalkenes.<sup>24</sup>

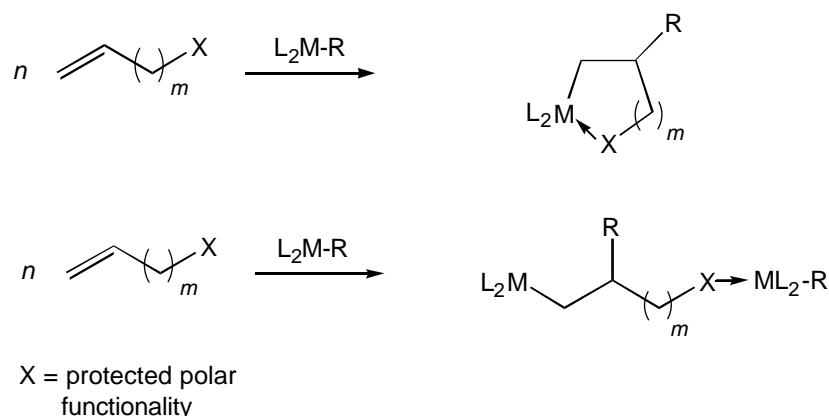
Another elegant route to functionalize polymers is catalytic hydroboration of their alkene end groups (resulting from e.g. chain transfer by  $\beta$ -hydrogen elimination). The produced boron-alkyls can easily be converted into alcohols, amines, aldehydes or halides. In addition to a possible application for the functionalization of polyalkenes, the hydroboration methodology could form an attractive route for the preparation of fine chemicals.



### 1.4. Catalytic (Co)polymerization of Functionalized Alkenes.

Early transition metal-catalyzed alkene polymerization of polar alkenes can be divided in two parts: (a) polymerization of  $\alpha,\beta$ -unsaturated ketones and esters, such as acrylates<sup>25</sup> and caprolactones,<sup>26</sup> and (b) polymerization of 1-alkenes containing a protected polar function.<sup>27</sup> The polymerization of acrylates and lactones has been well-established. In general, mixtures of polymers are obtained with a very narrow molecular weight distribution. However, (co)polymerizations with functionalized 1-alkenes (ether, thioether, amine) are still largely unsuccessful, with one exception reported by Waymouth *et al.*<sup>27</sup>

As stated above the question of how to avoid C-X activation and formation of catalytically inactive M-X bonds most probably is the main problem when attempting to develop catalysts for copolymerization of 1-alkenes and polar alkenes. A way to avoid the formation of stable M-X bonds by reaction of the catalyst with C-X bonds in the alkene substrate is to use alkenes with protected polar functionalities,<sup>28</sup> which block C-X activation by the catalytically active metal species. It has been found that (thio)ketals, (thio)ethers, silylethers and diisopropylamine groups are excellent protective groups which are not immediately attacked by early transition metal compounds.<sup>23,27,29</sup>

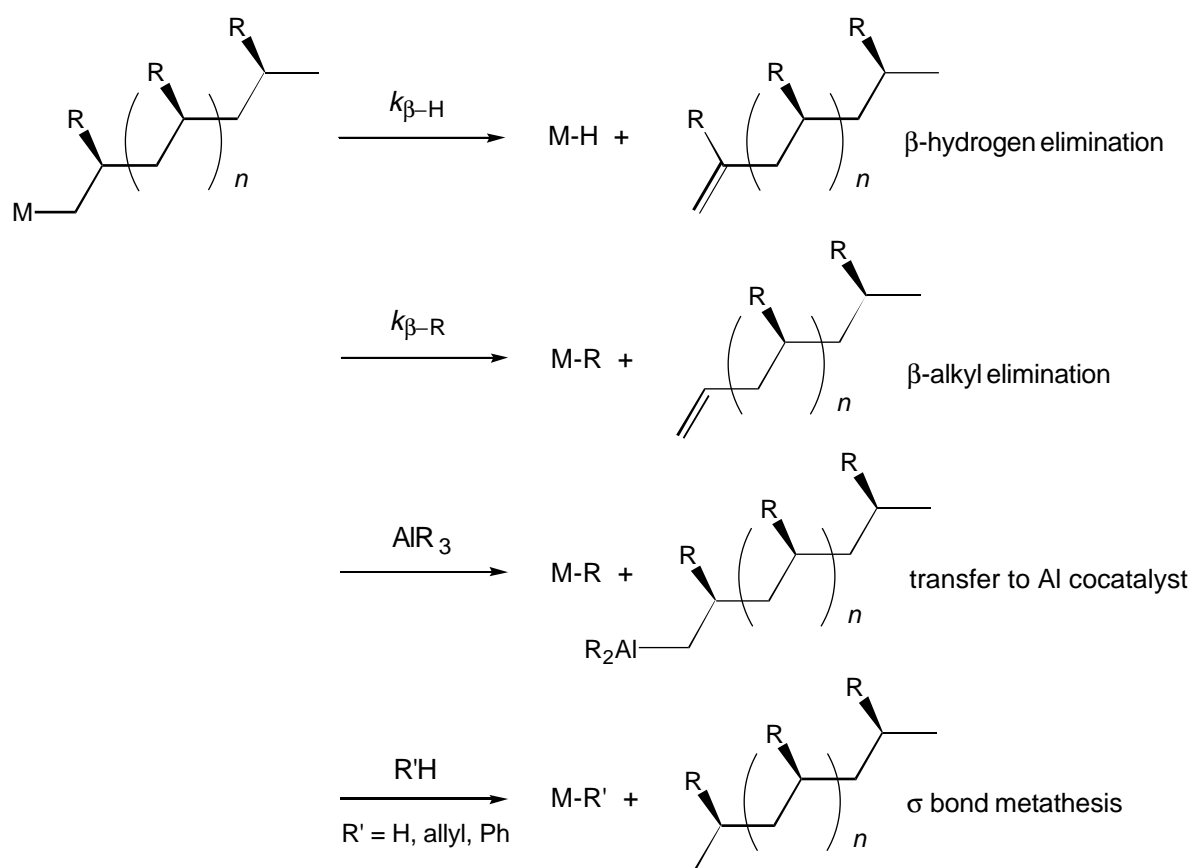


**Figure 2.** Intra- and intermolecular stabilization of the active metal by heteroatom coordination.

Another problem can be that after one insertion of a protected functionalized 1-alkene, intramolecular coordination of the heteroatom X to the metal takes place, forming a stable cyclic intermediate, which blocks further alkene insertion (Figure 2).<sup>30</sup> A possibility to avoid this loss of catalytic activity is the use of bulky protective groups, thus hindering coordination of the polar function to the metal. Moreover, in order to disfavor the formation of cyclic intermediates, one can adjust the length of the chain between the alkene and the polar function.

However, in this case, it is possible that intermolecular stabilization of active species can take place (Figure 2), which also will hamper further alkene insertion.

A literature study has been carried out to select potential catalysts for the oligomerization of functionalized alkenes. They have to meet the following criteria: (1) Well-defined, synthetically easily accessible systems. (2) Proven alkene polymerization activity. (3) Resistant to catalyst deactivation routes, such as C-X activation,<sup>22,23</sup> allylic and vinylic C-H activation.<sup>4c,31</sup> (4) Relatively high rate for chain transfer by  $\beta$ -hydrogen elimination to increase the selectivity of the reaction.<sup>7</sup> (5) Low tendency for competing side reactions, such as isomerization,<sup>32</sup> and termination reactions, e.g.  $\beta$ -alkyl elimination,<sup>14,33,34</sup> alkyl transfer from the catalyst to the co-catalyst,<sup>31a,35</sup> and  $\sigma$ -bond metathesis<sup>36</sup> (Scheme 5).

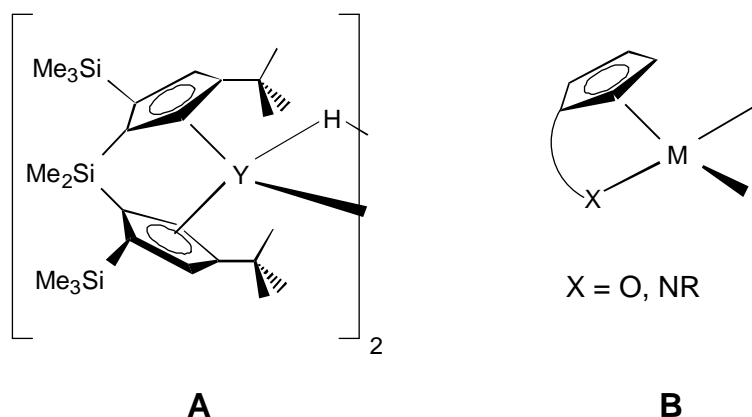


**Scheme 5.** Various chain transfer processes in 1-alkene polymerization.

Recently, Waymouth *et al.* found that several higher 1-alkenes, such as 1-hexene, and 1-alkenes, containing *tert*-butyldimethylsilyloxy and tertiary amine functions, could be oligomerized using *in situ* generated  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrMe}][\text{B}(\text{C}_6\text{F}_5)_4]$  and  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrMe}][\text{MeB}(\text{C}_6\text{F}_5)_3]$  catalysts (Scheme 6).<sup>27</sup> The presence of vinylidene end groups in the oligomers obtained is consistent with chain transfer by  $\beta$ -hydrogen elimination. Only for the



Unfortunately, the polymerization activity is quite low, but the stereospecificity is high and chain transfer seems to occur exclusively by  $\beta$ -hydrogen elimination. Consequently, this yttrium compound may be a candidate for catalytic functionalized alkene oligomerization. A drawback can be the complicated synthesis of the yttrium hydride.



**Figure 3.** Dimeric silicon-bridged-bis(cyclopentadienyl) yttrium hydride (**A**) and "constrained geometry" catalysts (**B**).

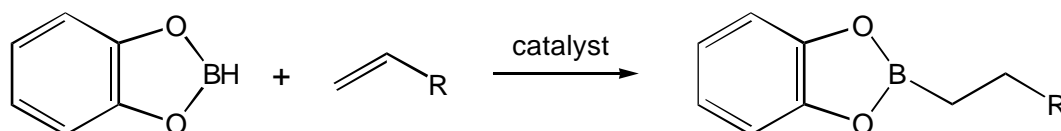
Although early transition metal-catalyzed polymerization of alkenes with polar functions is still dominated by the classical bis(cyclopentadienyl) catalysts, the "constrained geometry" catalysts have proved to possess several attractive properties (Figure 3B).<sup>11,12</sup> In these systems, one cyclopentadienyl ligand has been replaced by an alkylamido or suchlike group. The two spectator ligands have been connected to form a bidentate dianionic system. The steric bulk appears to be less than of two cyclopentadienyl-type ligands. The electronic and steric effects can be studied by varying the coordinating group X and also by changing the substituents on the cyclopentadienyl ligand. This opens attractive perspectives for tuning catalytic activity.

Bercaw *et al.* anticipated that the bidentate tetramethylcyclopentadienyl-amido scandium system would differ from the permethylscandocenes electronically, since the amido group should make the metal more electron deficient and thus more Lewis acidic.<sup>38</sup> The bidentate cyclopentadienyl-amide scandium compounds catalyze the oligomerization of propene, 1-butene, and 1-pentene with average oligomerization degrees between 40 and 70.<sup>12</sup> Compared to ionic group 4 systems the activity is relatively low, but the chain transfer, which seems to take place exclusively via  $\beta$ -hydrogen elimination, is slow. Moreover, these catalysts show excellent stability.<sup>39</sup> The scandium compounds may oligomerize functionalized alkenes, although the large space available around the metal center may facilitate heteroatom coordination to yield coordinatively more saturated species and consequently further alkene insertion is hampered.

From the literature, it can be concluded that several catalysts are suitable for oligomerization of functionalized 1-alkenes. Bis(pentamethylcyclopentadienyl) complexes seem to be systems of choice, because the metal center may be sufficiently shielded to prevent coordination of the protected polar function. Moreover, these systems are well-defined and synthetically easy to access. It was decided to concentrate on  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrMe}][\text{B}(\text{C}_6\text{F}_5)_4]$  and  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrMe}][\text{MeB}(\text{C}_6\text{F}_5)_3]$ , as these have proven to be active for the oligomerization of some functionalized 1-alkenes.<sup>27</sup>

### 1.5. Catalytic Hydroboration of Alkenes.

As discussed above, hydroboration of alkene functions of polyalkenes (or oligoalkenes) could be a possible route to introduce polar functions. In addition, hydroboration of alkenes and oligoalkenes is also interesting for fine chemical industry owing to the versatile reactivity of the boron-alkyl function. Hydroboration products can easily be transformed into a large variety of organic compounds, such as alcohols, aldehydes and amines. However, in general, the (late transition metal-catalyzed) hydroboration process is accompanied with the formation of several side products and, in most cases, decomposition of the borane reagent.



**Figure 4.** Catalytic hydroboration of 1-alkenes.

Group 3 metal catalysts are very selective, as has been observed by Harrison and Marks.<sup>40</sup> Since our laboratory has available a wide range of new early transition metal complexes, which meet the requirements for possible alkene hydroboration activity, *viz.* the compounds are coordinatively and electronically unsaturated, form metal-hydrides easily, insert alkenes into the M-H bond and contain polar bonds in order to favor a partially charged four-centered transition state, a comparative study was undertaken. As a model system, the hydroboration of 1-hexene using catecholborane as hydroboration reagent was chosen (Figure 4).

## 1.6. Scope of the Investigation.

The main purpose of this research project was to study (co)polymerization of alkenes containing protected polar functions. When catalytic C-C bond formation was not observed, the reasons for the lack of catalytic activity were studied in detail. With the knowledge obtained, attempts were undertaken to tune oligomerization activity of functionalized alkenes by adjusting the substrate, but also by varying the catalyst (*e.g.* variation in metal).

A possible spin-off of the (co)polymerization studies, (co)oligomerization, is in potential also very interesting. These products may be valuable as intermediates for the preparation of fine chemicals. Co-oligomerization of various substituted 1-alkenes has also actively been studied.

Furthermore, as an extension to the scope of the polymerization of acrylates, polymerization of 2-cycloalken-1-ones has been investigated. The resulting products may be attractive, as they can easily be converted into a broad range of new compounds by reactions, such as reductive amination and addition/elimination, with the carbonyl group.

Finally, early transition metal-catalyzed hydroboration of 1-hexene has been studied. Several group 3 and group 4 complexes have been tested. The results have been compared with those reported for lanthanide catalysts.<sup>40</sup> In this way, further insight in the hydroboration process has been obtained.

## 1.7. Contents of the Thesis.

Chapter 1 gives an overview of recent important developments in transition metal catalyzed alkene polymerization. The scientific and practical relevance of extension of this area of research to oligomerization and polymerization of protected functionalized 1-alkenes is discussed in detail. On the basis of a literature study, it is concluded that cationic bis(pentamethylcyclopentadienyl) group 4 complexes  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrMe}][\text{MeB}(\text{C}_6\text{F}_5)_3]$  and  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrMe}][\text{B}(\text{C}_6\text{F}_5)_4]$  are good candidates for reactions with 1-alkene containing protected polar functions, as the small space available around the active metal may prevent interaction with the heteroatom. Functionalization of oligomers can also be accomplished by hydroboration of the alkene end groups.

Chapter 2 describes the investigations on reactions of  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrMe}][\text{MeB}(\text{C}_6\text{F}_5)_3]$  and  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrMe}][\text{B}(\text{C}_6\text{F}_5)_4]$  with 3-alkoxy(alkylthio)-1-propenes. Three model reactions are used to test the catalytic possibilities of the substrates, *viz.* (1) reactions in a 1 : 1 ratio, (2) homo-oligomerization and (3) co-oligomerization with simple 1-alkenes, such as 1-hexene. Reactions between the ionic group 4 systems and the 3-functionalized-1-propenes in a 1 : 1 ratio only result in the formation of stable 1-oxa(thia)-2-zirconacyclopentanes. They originate from alkene insertion into the Zr-Me bond, followed by intramolecular coordination of the

heteroatom to the metal. The zirconium complexes studied showed no catalytic activity for both homo-oligomerization and co-oligomerization due to the formation of stable 1-oxa(thia)-2-zirconacyclopentanes. Attempts to create a vacant site on zirconium by complexation of the (thio)ether function by a Lewis acid failed. Polymerization activity for ethene was restored when trimethylaluminum was used as initiator, but was found to be due to formation of the cationic Zr-Me species  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrMe}]^+$ . An approach to tune the substrate for enhanced oligomerization activity by increasing the steric bulk on the polar function gave stable 1-thia-2-zirconacyclopentanes. These decompose thermally by hydrogen abstraction from a methyl substituent of the cyclopentadienyl ligand to give a cationic fulvene  $[(\eta^5\text{-C}_5\text{Me}_5)(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)\text{Zr}]^+$  compound. 1-Hexene inserts into the Zr-CH<sub>2</sub> bond and gives after hydrolysis 1-(2'-methylhexyl)-2,3,4,5-tetramethylcyclopentadiene. This shows that pentamethylcyclopentadienyl ligands are not inert, but participate actively in competing reactions.

In Chapter 3 reactions of  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrMe}][\text{MeB}(\text{C}_6\text{F}_5)_3]$  and  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrMe}][\text{B}(\text{C}_6\text{F}_5)_4]$  with 2-(alkenyl)-1,3-dithianes are reported. Dithianes are attractive protective groups for ketones and aldehydes. The distance between the alkene function and the polar substituent has been varied by changing the number of methylene groups, in the hope to disfavor the formation of stable metallacycles. Substrates with longer spacers indeed show marked differences with respect to the stability of the intermediates formed. They insert the alkene easily, but then decompose by *e.g.*  $\beta$ -hydrogen and  $\beta$ -methyl elimination. Homo-oligomerization does not occur in toluene and bromobenzene due to rapid catalyst deactivation by hydrogen abstraction from a methyl substituent of the cyclopentadienyl ligand. When performing the reactions in benzene, co-oligomers of 2-(alkenyl)-1,3-dithiane with 1-hexene have been obtained, albeit in very low yield and presumably not catalytic.

In Chapter 4, a study of the oligomerization of 2-cyclopenten-1-one and 2-cyclohexen-1-one is described. Early transition metal complexes ( $d^0$ , 14 electrons) appear to be active catalysts. For the oligomerization of 2-cycloalken-1-ones an unusual temperature effect has been found: the average degree of oligomerization ( $P_n$ ) increases with temperature. On the basis of an Eyring plot, it has been suggested that the large difference in activation entropy between the propagation and chain transfer step causes the increasing  $P_n$  with temperature.  $P_n$  also increases when using catalysts with smaller radius of the metal.

Chapter 5 describes a study of the catalytic hydroboration of 1-hexene with well-defined early transition metal compounds, which all meet the criteria for possible activity. The results are compared with those reported for other catalysts. For lanthanum catalysts the activity is high, while the rate of reaction drops with smaller metal centers (Y, Zr, Ti). Other ligand systems (bis(cyclopentadienyl), bis(benzamidinate) and mixed cyclopentadienyl-benzamidinate) have found to be less effective in stabilizing the catalysts. Bidentate ligand systems based on cyclopentadienyl ligands with pending anionic functions (aryloxo, amido)

form stable catalysts. From this study, it can be concluded that the rate of hydroboration depends on steric effects rather than on electronic variables.

### 1.8. IOP-Catalysis.

In order to stimulate cooperation between research groups in industry and at universities, the Ministry of Economic Affairs of the Dutch Government has created an Innovation Oriented Research Program (IOP). This program should open new routes to increase efficiency in the use of chemicals and energy, and lead to better protection of the environment as well. Owing to the increased economic and environmental value of the products with polar functions, the area of functionalized alkene oligomerization and derivatization of oligomers has attracted a great deal of attention of Dutch chemical industry.<sup>41</sup> These conversions practically all need efficient catalysts, which have to meet the criteria mentioned above.

The research project described in this thesis has been performed within the framework of IOP-Catalysis. The initial program concentrated on two themes: catalyst development via inorganic chemistry and catalysis as a powerful tool for the synthesis of fine chemicals. An attractive possibility to prepare intermediates for the production of fine chemicals is homo-oligomerization of functionalized alkenes and co-oligomerization of functionalized alkenes with simple alkenes, such as ethene, propene and 1-hexene, using well-defined early transition metal catalysts.

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