Rare-earth catalysts in C-C-linkage of olefins I ytterbium catalyzed linear oligomerization of ethylene

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Ytterbium catalysts such as $YbCl_3$/n-BuLi and $(Cp_2YbCl)_2$/RLi (R = Me, t-Bu, n-Bu, $-CH_2SiMe_3$) have been applied for the C-C-linkage of ethylene. Highly linear oligomers (n-alkanes) and polymers (high molecular weight polyethylene) were obtained. A reaction mechanism based on ytterbium-hydrides is proposed.

Keywords: Catalysis; rare-earths; lanthanides; ytterbium; oligomerization; polymerization; ethylene

1. Introduction

The transition metral catalyzed oligomerization/polymerization of ethylene is both of academic and industrial interest. Various homogeneous cataysts, especially those based on titanium, zirconium and nickel have been used in the oligomerization/polymerization of monoolefins [1]. However, the application of rare-earth catalysts is quite limited, although they have been successfully used in the polymerization of dienes [2], alkynes [3] and epoxides [4].

The catalysts $CeCl_3$/n-BuLi and $CeCl_3$/RMgX were reported to oligomerize ethylene to higher, straight-chain olefins [5]. The catalysts $M(acac)_3/Al_2Et_3Cl_3/PPh_3$ (M = rare-earth metals) have been described for the dimerization of propene [6,7]. Watson [8] elucidated that the isolated complexes $Cp_2^*MCH_3 \cdot L$ ($Cp^* = C_5(CH_3)_5$-; M = Yb, Lu; L = Et_2O, THF and $AlEt_3$) catalyzed the oligomerization of propene [8], but the oligomers were not fully characterized.

In this paper we present our work on the linear oligomerization of ethylene using ytterbium catalysts.

2. Experimental

All operations regarding the syntheses of the complexes and the catalysis studies were performed in an atmosphere of purified argon. The solvents used were all refluxed and distilled over either finely divided $LiAlH_4$ or sodium before use.

Anhydrous ytterbium chloride ($YbCl_3$ 99.9%) was commercially available from the Alfa Co. The alkyllithium reagents were used as purchased from Aldrich without further treatment. The molar concentration of the alkyllithium reagents and the corresponding solvents are as follows: MeLi 1.6 M in diethylether, n-BuLi 1.6 M in hexane, t-BuLi 1.4 M in pentane, Me_3SiCH_2Li 1.0 M in pentane. The dicyclopentadienylytterbium chloride $(Cp_2YbCl)_2$ was synthesized according to the literature [9].

The general procedure for the preparation of the catalysts and for the ethylene oligomerization was as follows: into a solution of $(Cp_2YbCl)_2$ in toluene, which was cooled to −78 °C, the amount of alkyllithium calculated was added dropwise under stirring. The solution was allowed to warm up slowly to −20 °C and then transfered to a 75 ml steel autoclave equipped with a magnetic stirrer. When using $YbCl_3$ instead of $(Cp_2YbCl)_2$ the alkyllitium reagent was added at room temperature, and a suspension was obtained instead of a clear solution. Ethylene and/or, as indicated in the table 1 hydrogen was introduced into the autoclave (see table 1 for pressure). The reaction was carried out in an oil bath at temperatures given in the table 1. The oligomerization products were analyzed by gas chromatography (Sichromat 1 50 m OVIQ) and characterized by GC-MS or by spectroscopic comparison with known samples.

$YbCl_3$/n-BuLi

$YbCl_3$: 0.22 mmole, n-BuLi/Yb = 8/1 (molar ratio), $t = 15$ hrs, 15 ml toluene.

$(Cp_2YbCl)_2$/LiR

For reaction conditions see table 1.

INFLUENCE OF DONOR LIGANDS

$(Cp_2YbCl)_2$ (0.22 mmole), ethylene (300–500 mmole) Yb-complex/ligand = 1:1 (molar ratio), $T = 80\,^\circ C$, $t = 3$ hrs, 15 m toluene.

3. Results and discussion

The reaction of $YbCl_3$ with n-BuLi in toluene yielded a suspension, which was reacted with ethylene or ethylene/hydrogen mixtures. At low turn over

Table 1
Reaction of the in-situ prepared complex Cp_2YbR with ethylene

Cp_2YbCl (mmole)	RLi (mmole)	C_2H_4 (mmole)	H_2 (bar)	t (hrs)	Oligom. (%)	Polym. (%)	TON
0.130	CH_3	300	10	15	0	0	0
0.247	n-C_4H_9	480	0	18	0	0	0
0.323	n-C_4H_9	290	12	3	43.7	56.3	298
0.244	t-C_4H_9	270	0	17	0	0	0
0.244	t-C_4H_9	370	5	17	0	0	0
0.273	CH_2SiMe_3	428	0	5	0	100	344

$Cp_2YbCl/RLi = 1/1$ (molar ratio); $T = 80\,^\circ C$; solvent: 15 ml toluene.

numbers of 10–50 alkenes (α-olefins) and alkanes were obtained. Most remarkable is the linearity of the product formed amounting up to 100%. With hydrogen, the oligomers consisted of n-alkanes in the range of butane to decane.

In order to obtain soluble catalysts, dicyclopentradienylytterbium chloride $[Cp_2YbCl]_2$ was reacted with various alkyllithium reagents listed in table 1. It can be assumed that the reaction according to eq. (1) [10–12] proceeds.

$$[Cp_2YbCl]_2 + 2\ RLi \rightarrow 2\ Cp_2YbR + 2\ LiCl \tag{1}$$

$$R = Me,\ t\text{-}Bu,\ n\text{-}Bu,\ Me_3SiCH_2\text{-}\ \text{and}\ C_6H_4CH_3\text{-}(p)$$

The catalysts prepared in situ were pressurized with ethylene or ethylene/hydrogen respectively and reacted as given in table 1.

With $[Cp_2YbCl]_2/MeLi$ no ethylene conversion could be observed. This can be explained by considering that MeLi was dissolved in diethylether, which easily can block coordination sites mandatory for ethylene reactions [8].

Also with $[Cp_2YbCl]_2$/n-BuLi no reaction was observed. However, the addition of hydrogen yielded an active system producing alkanes, which are practically hundred percent linear as is evident from fig. 1.

In weight percent the oligomeric alkanes follow a Schulz-Flory type distribution. The polymeric material is of waxy nature (softening point 92 to 106 ° C). With $[Cp_2YbCl]_2$/t-BuLi no products could be isolated. This can be understood by a reduction of $[Cp_2YbCl]_2$ to Cp_2Yb via t-BuLi [10].

Interestingly, the use of $[Cp_2YbCl]_2/Me_3SiCH_2Li$ gave only polymers (linear polyethylene) with a softening point of 130 ° C indicative for high molecular weight material.

It is noteworthy that H. Imamura using a heterogeneous ytterbium catalyst couldn't effectively produce ethylene oligomers/polymers although other rare earths like samarium were active [13].

MECHANISTIC CONSIDERATIONS

Active catalysts were obtained from the following systems: $YbCl_3$/n-BuLi; $YbCl_3$/n-BuLi/H_2; Cp_2YbCl/n-BuLi; Cp_2YbCl/n-BuLi/H_2; Cp_2YbCl/

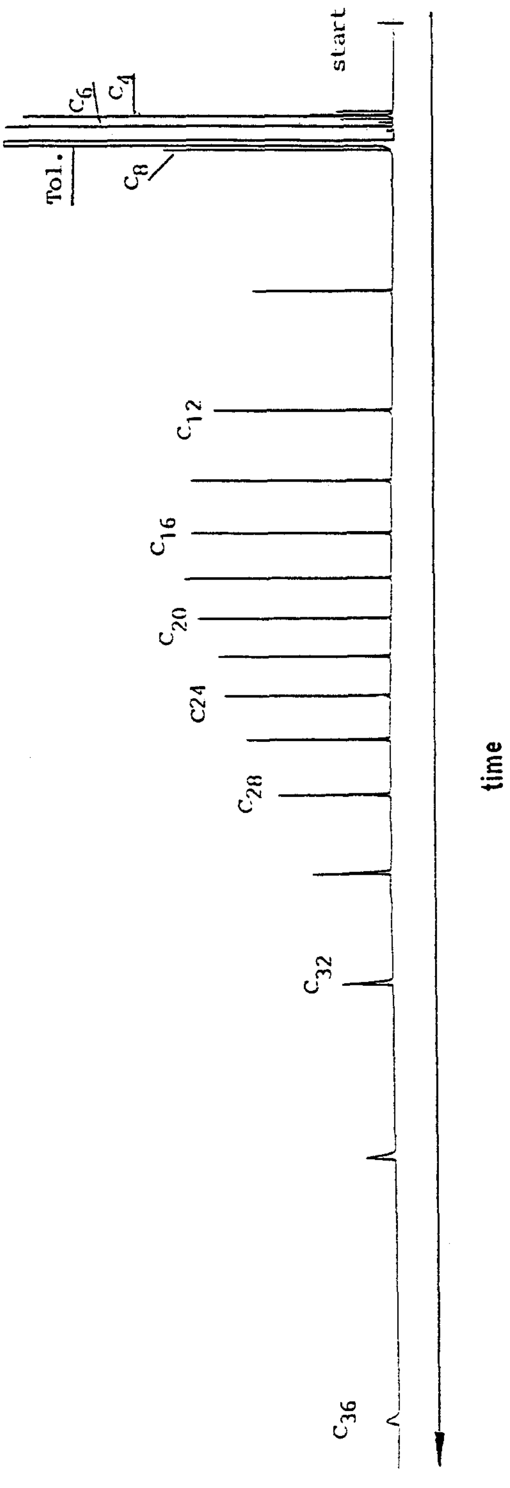
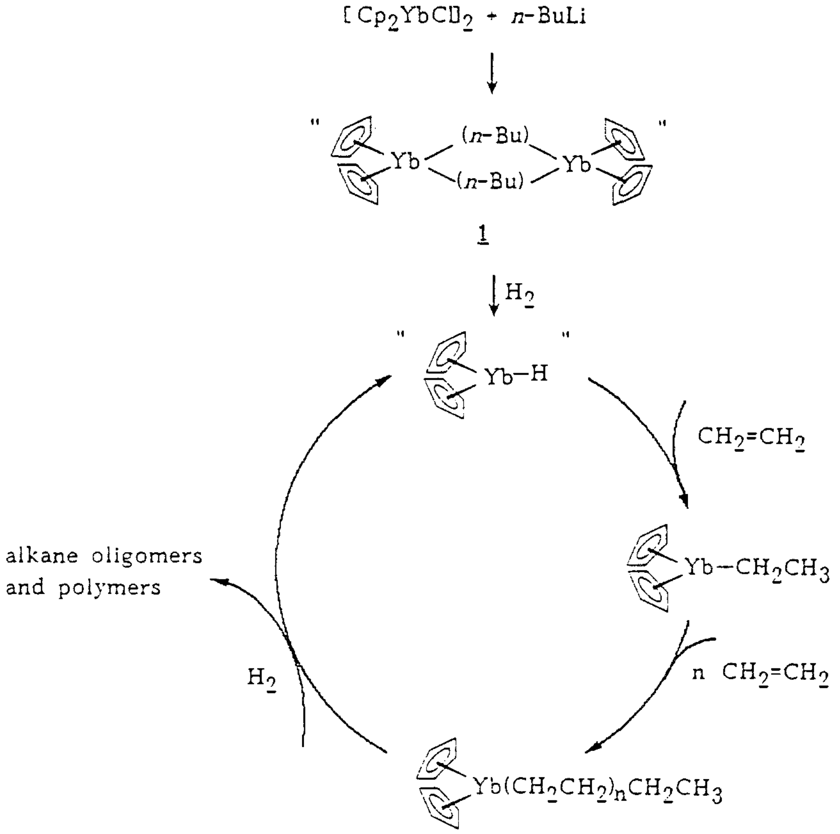


Fig. 1. Gas chromatogram of the oligomers $(Cp_2YbCl)_2$/n-BuLi.

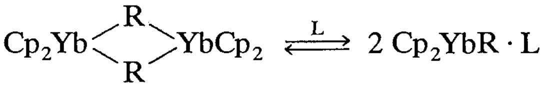


Scheme 1. Mechanism for the oligomerization and polymerization of ethylene by in-situ prepared complex $Cp_2Yb(n\text{-}Bu)$ in the presence of hydrogen.

$LiCH_2SiMe_3$. The first four yield oligomers whereas $Cp_2YbCl/LiCH_2SiMe_3$ gave only polymers. For the oligomerization/polymerization a metal-hydride mechanism is proposed as shown in scheme 1.

The role of hydrogen can be seen in converting of the dimeric intermediate $[CpYbR]_2$ into the ytterbium hydride complex, as is known from the literature [14,15]. The Yb-H complex, thus obtained, produces in a selfexplanatory way of propagation and elimination–as outlined in scheme 1–linear alkanes (oligomers and polymers). The Yb-H intermediate can also be obtained via butene elimination: $Cp_2Yb(CH_2)_3CH_3 \rightarrow$ "Cp_2YbH" + n-butene.

Instead of hydrogen electron donor ligands L can be used to convert the dimeric complexes in to monomeric ones (eq. (2)).



$$Cp_2Yb(\mu\text{-}R)_2YbCp_2 \overset{L}{\rightleftharpoons} 2\,Cp_2YbR \cdot L \qquad (2)$$

The four ligands diethylether, triethylamine, triphenylphosphine and pyridine were applied.

Indeed, with Et_3N a quite reactive system for the polymerization of ethylene was obtained (TON = 360). The polyethylene produced has a high molecular weight (softening point 131° C). No oligomers were found.

The failure of the other donors to give active catalysts can be understood: diethylether is too strong a donor thus blocking coordination sites needed for ethylene; triphenylphosphine is too weak a donor and no splitting of the dimeric ytterbium complex occurs. Pyridine causes a "metallation" similar to that reported for a permethylcyclopentadienyl ytterbium [16]. Indeed, a rapid color change from orange to violet-blue is observed.

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