Chair of Inorganic and Metal-Organic Chemistry
Department of Chemistry
Technical University of Munich

Homogeneous Catalysis 2: Examples

Mirza Cokoja

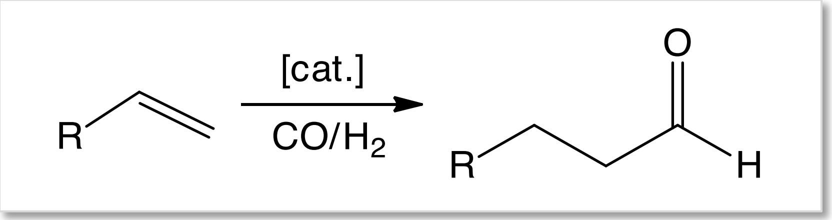
South German Catalysis Institute Grad School Course

Obertauern, March 04th, 2020

1. The oxo synthesis

Hydroformylation of olefins

First industrial catalytic process in homogeneous phase

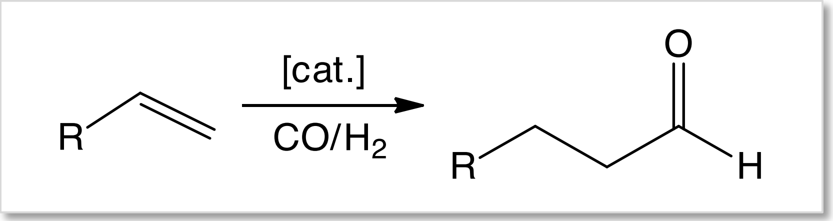


Developed by Otto Roelen (Ruhrchemie, Oberhausen) in 1938

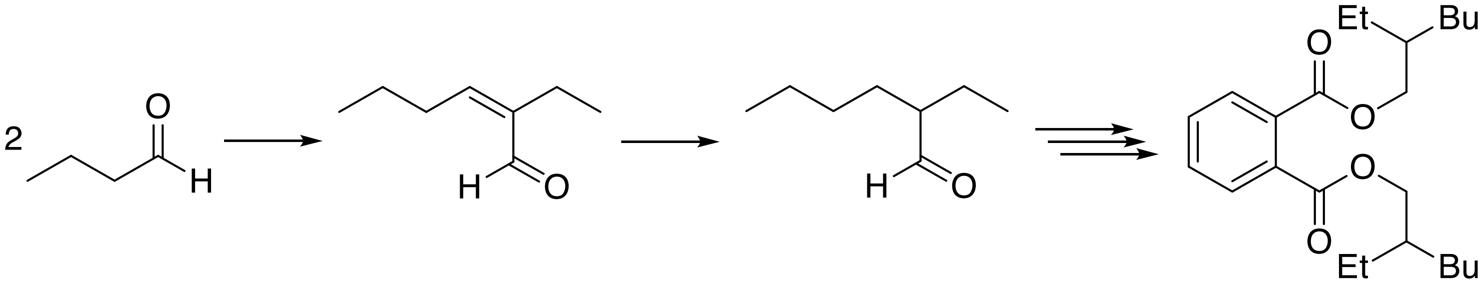
Annual production of 10 million tons → largest catalytic process in hom. phase

Hydroformylation of olefins

Applications



Hydroformylation of propene to *n*-butanal → precursor for plastics softeners

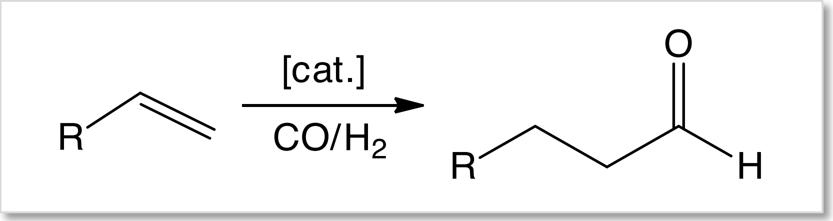


Dioctyl phtalate

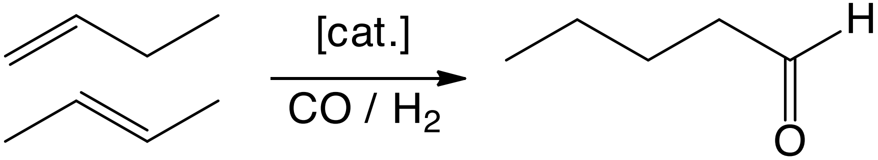
Plastics softener

Hydroformylation of olefins

Applications



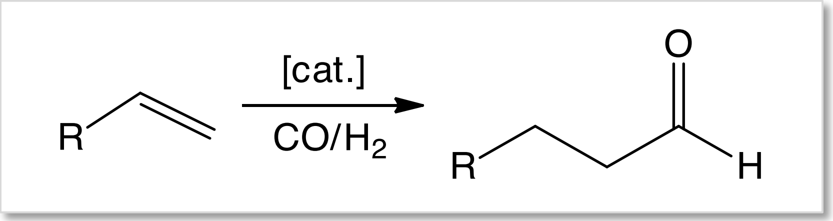
Hydroformylation of higher olefins (C_4–C_{12}) → precursors for fatty alcohols



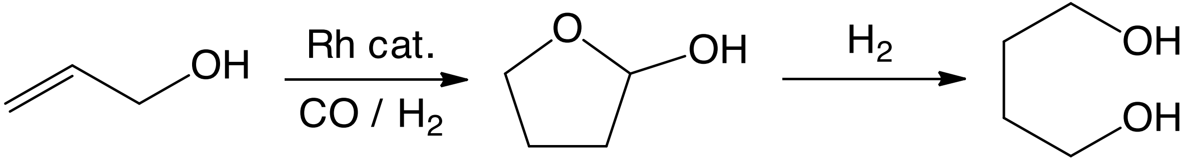
Subsequent aldol condensation and hydrogenation to C_{10} alcohols

Hydroformylation of olefins

Applications



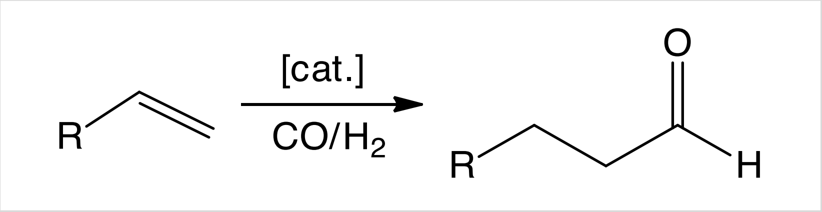
Hydroformylation of allyl alcohol → precursors for polymers



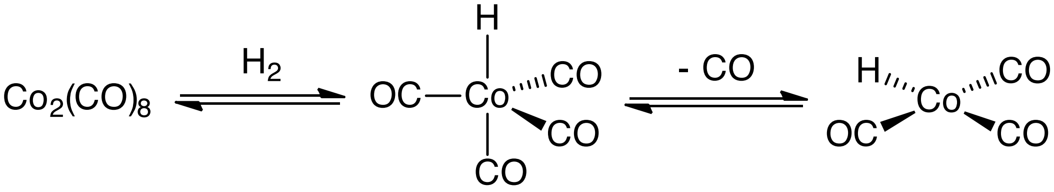
1,4-Butanediol

Hydroformylation of olefins

1st generation catalyst



Original catalyst: Cobalt carbonyl complex



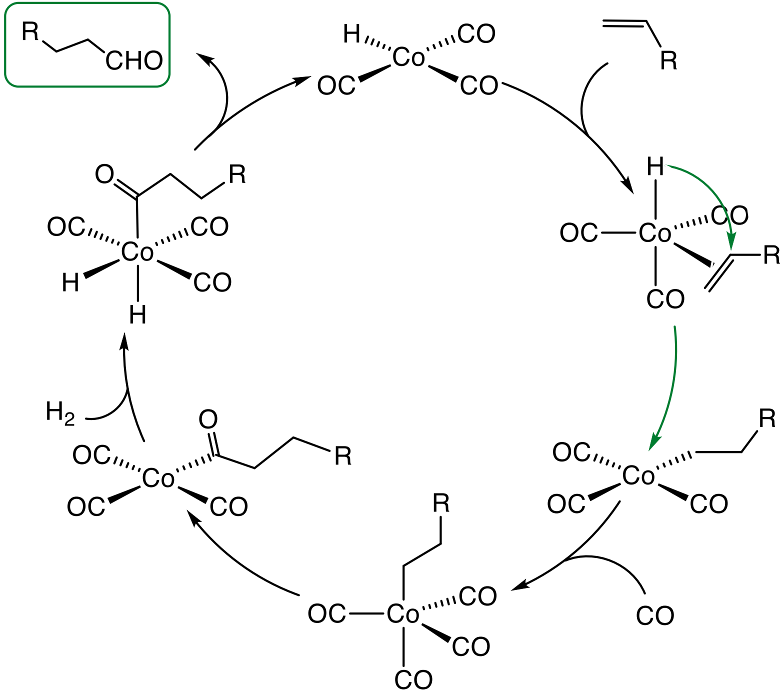
Precatalyst

18 VE

16 VE

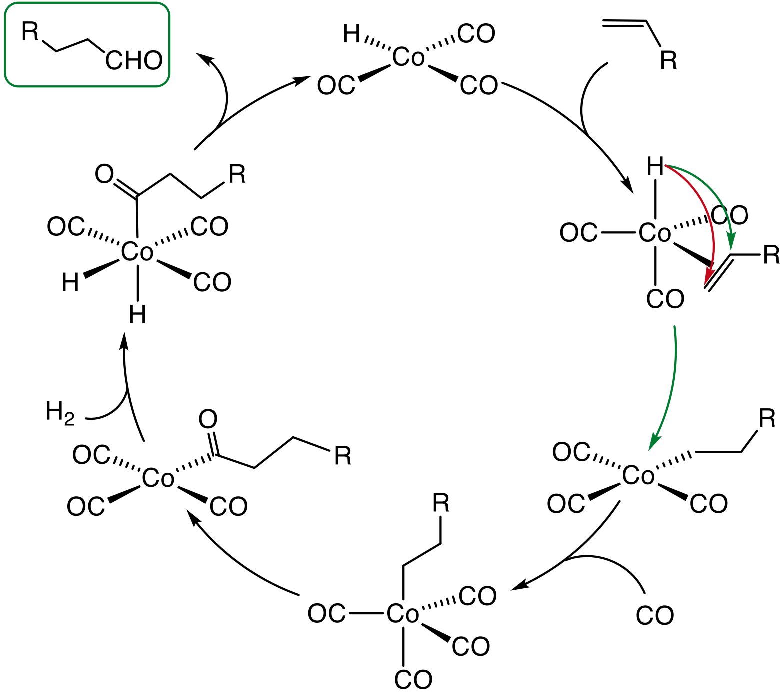
Hydroformylation of olefins

Mechanism



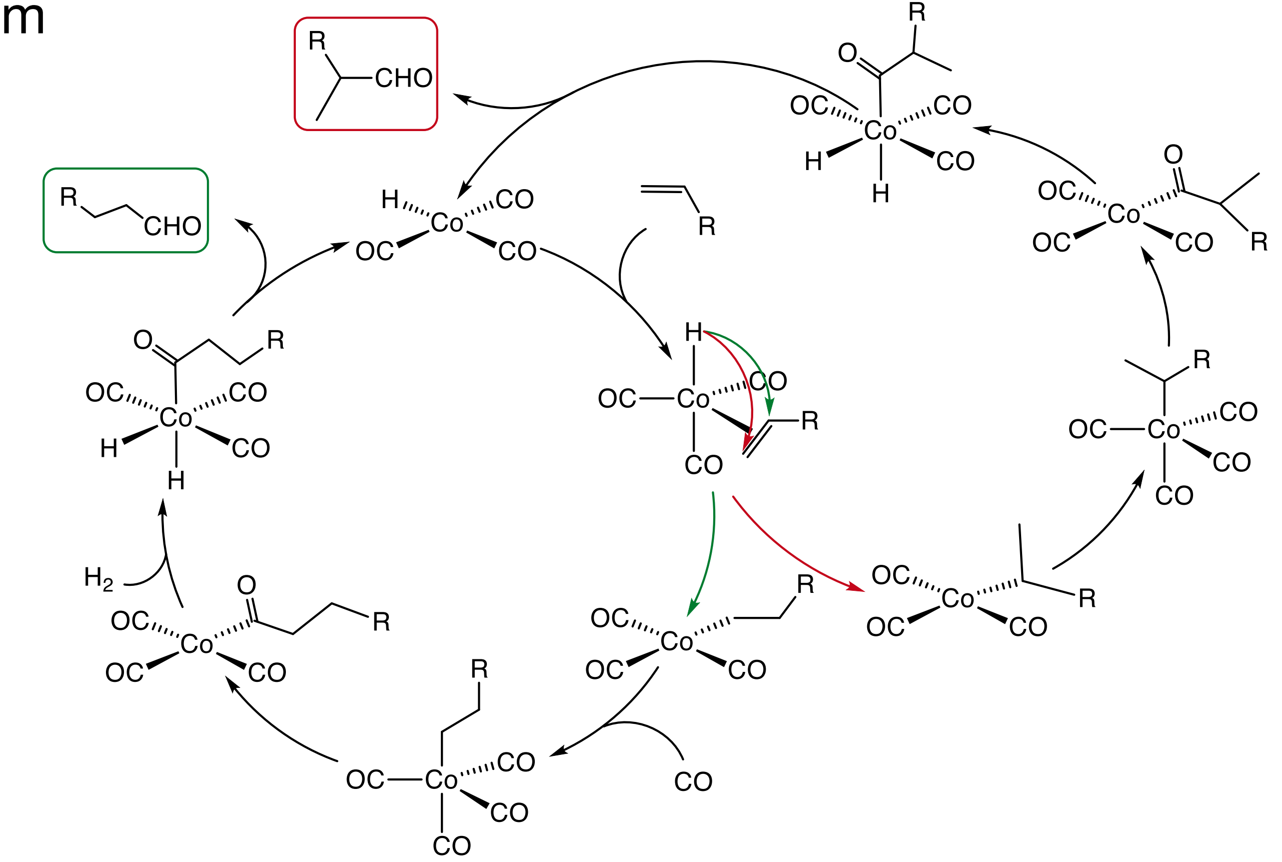
Hydroformylation of olefins

Mechanism



Hydroformylation of olefins

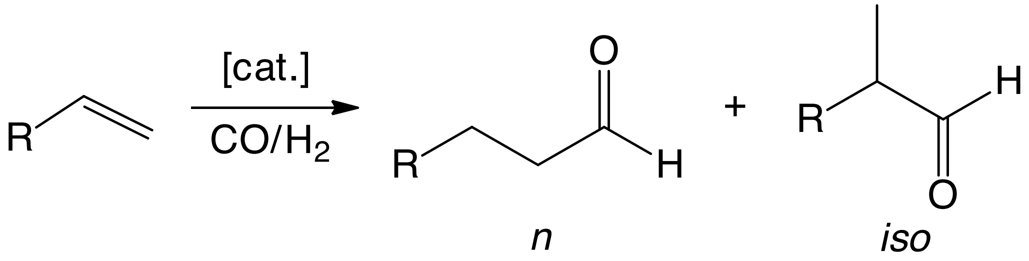
Mechanism



Hydroformylation of olefins

Activity & selectivity

Selectivity is determined by the ratio *n/iso* (*n* is desired in most cases)



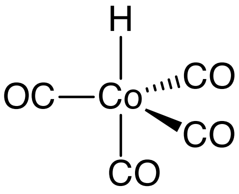
For 1st generation Co catalysts:
> 150 °C, > 200 bar

Hydroformylation of olefins

Activity & selectivity

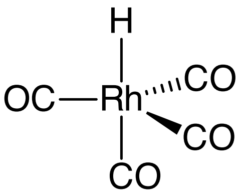
Problem of product mixtures → Development of 2nd and 3rd generation of catalysts

Carbonyl-containing catalysts



1st

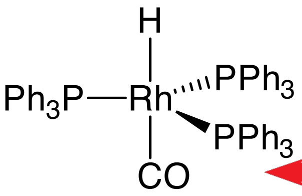
vs.



2nd

Reactivity:
Rh >> Co

Phosphine-containing catalysts

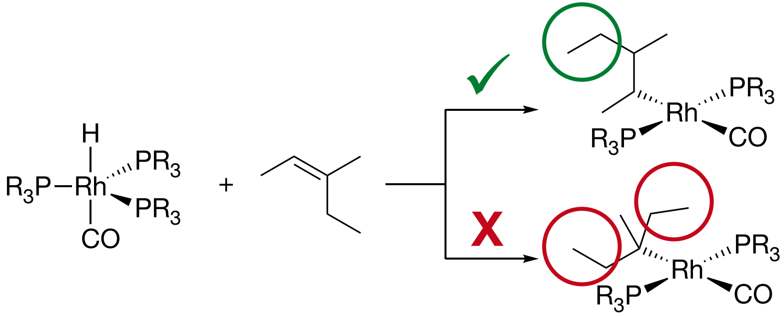


3rd

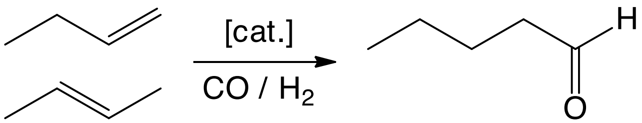
Hydroformylation of olefins

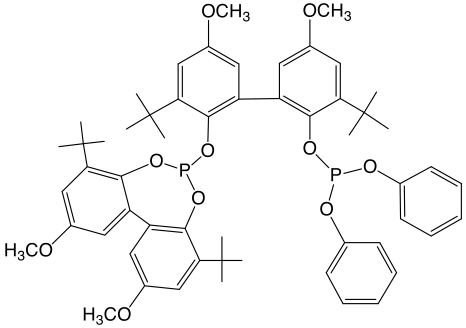
Activity & selectivity

Tailor-made phosphine ligands allow control over product selectivity



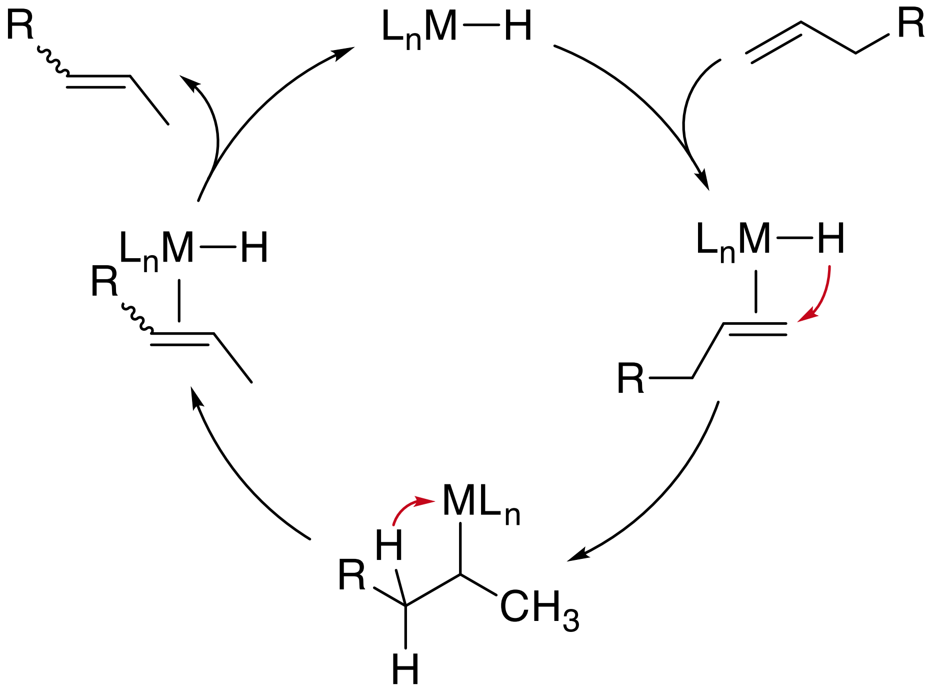
Union Carbide:
Ligand for the hydroformylation of C_4-mixtures to n-pentanal in 94 % yield





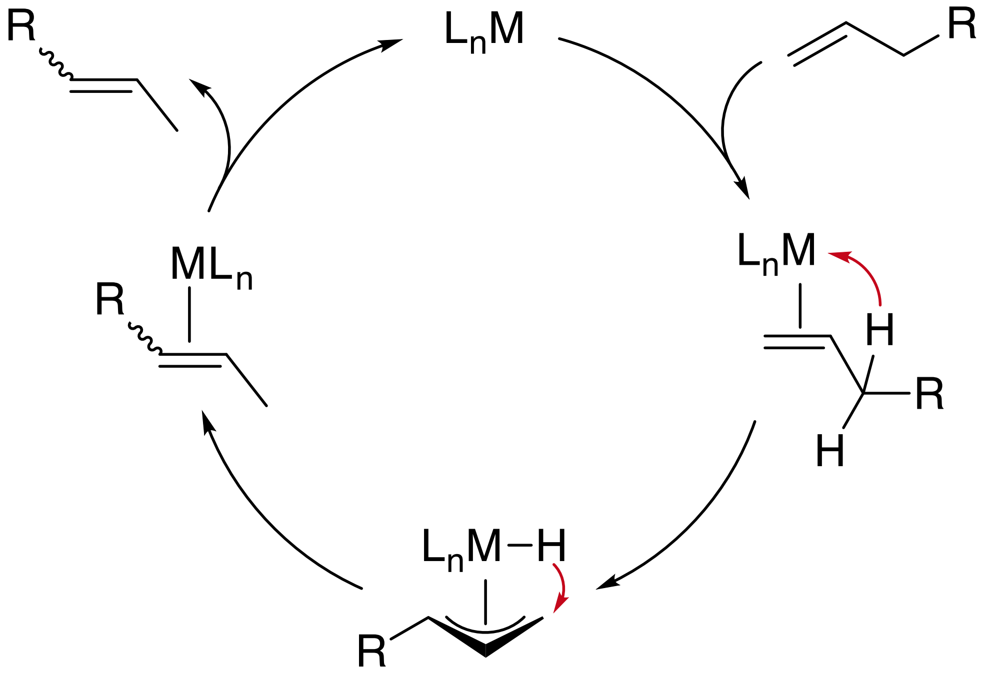
Hydroformylation of olefins

Olefin isomerization – alkyl mechanism



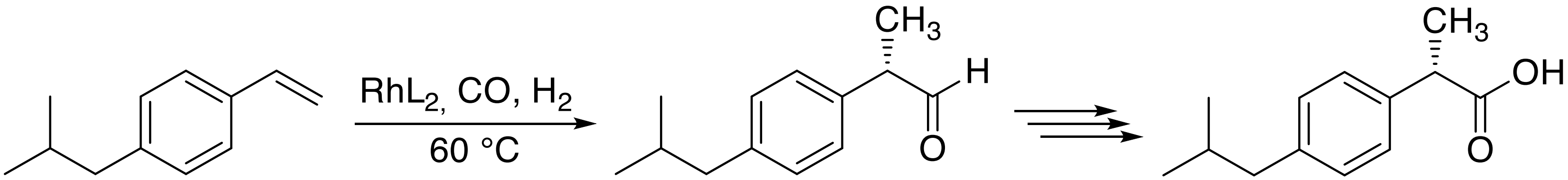
Hydroformylation of olefins

Olefin isomerization – allyl mechanism



Hydroformylation of olefins

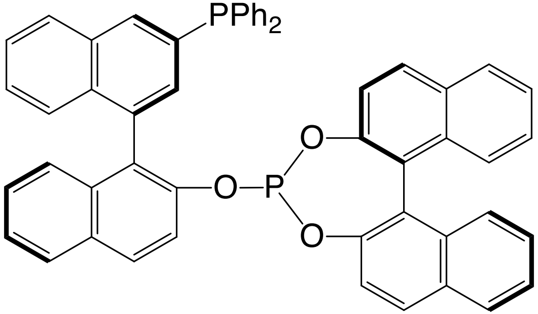
Enantioselective hydroformylation



Yield: 88 %
ee: 92 %

Ibuprofen

L =



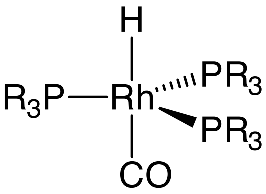
(*R*,*S*)-BINAPHOS

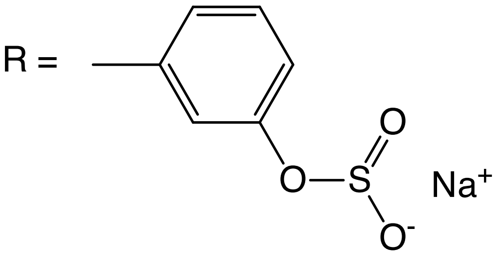
K. Nozaki et al., *J. Am. Chem. Soc.* **1993**, *115*, 7033.

Hydroformylation of olefins

Ruhrchemie/Rhône-Poulenc process (1984) – 4th generation catalysts

Water soluble catalysts: two-phase reaction, better product separation





Also: heterogenization of phosphine ligands to solid surfaces

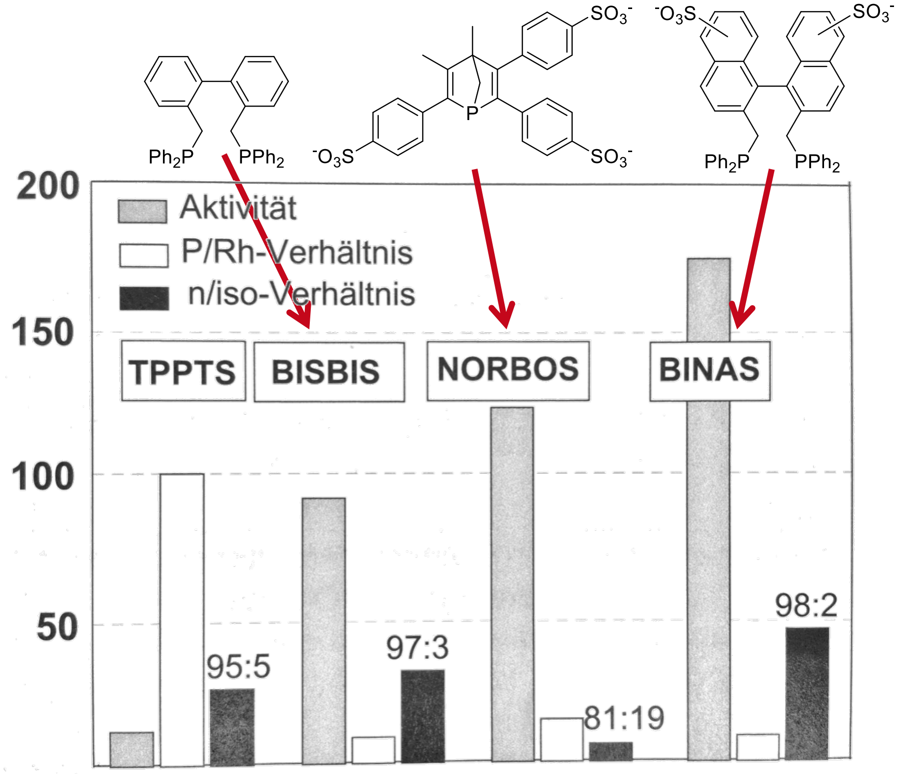
Separation → catalyst is in the solid phase, product is liquid or gaseous

However: (i) high excess of phosphine necessary

(ii) aryl prosphines decompose over time

Hydroformylation of olefins

Ruhrchemie/Rhône-Poulenc process (1984) – 4th generation catalysts



Summary

Carbonylations

⇨ Catalyst development and catalyst generations
→ Co and Rh carbonyls and –phosphines, then H_2O-soluble cat.‘s

⇨ Rh catalysts are much more active than Co catalysts
→ Dependence on substrates

⇨ Multiphase catalysis by ligand design
→ Water-soluble phosphines, phosphites

2. The polymerization of olefins

"The best things in life come in Cellophane"

"You SEE what you buy-no guesswork."

"Foods come fresh-stay fresh longer-less waste."

"...and things in Cellophane are clean and sanitary."

DU PONT Cellophane

DU PONT

BETTER THINGS FOR BETTER LIVING . . . THROUGH CHEMISTRY

Look at "Cavalcade of America" on Television

Süddeutsche Zeitung

SZ.de Zeitung Magazin

24. Oktober 2018, 14:33 Uhr Umweltschutz

EU-Parlament stimmt für Verbot von Wegwerfprodukten aus Plastik

In Europa verbraucht jeder einzelne durchschnittlich 71 Strohhalme pro Jahr (Foto: Patrick Pleul/dpa)

Von 2021 an sollen keine Plastik-Produkte wie Einweggeschirr und Wattestäbchen mehr in der EU verkauft werden dürfen. Einige deutsche Supermärkte kommen dem zuvor.

Pilotstudie mit Menschen

Mikroplastik im Darm nachgewiesen

Stand: 23.10.2018 01:09 Uhr

Plastik in Gewässern und Böden wird zunehmend zum Problem. Forscher haben winzige Plastikpartikel nun auch in menschlichen Stuhlproben gefunden - und zwar bei Probanden unterschiedlichen Alters weltweit.

Bei einer Pilotstudie haben Forscher aus Österreich nach eigenen Angaben erstmals Mikroplastik in Stuhlproben von Menschen nachgewiesen. Die Kunststoffpartikel wurden in den Proben von allen acht Studienteilnehmern gefunden, wie die Medizinische Universität Wien und das österreichische Umweltbundesamt mitteilten.

VIDEO

Erstmals gelingt Nachweis von Mikroplastik in menschlichem Organismus, tagesthemen 22:15 Uhr, 23.10.2018, Sebastian Deliga, SWR | video

AUDIO

Uni Wien Studie zu Mikroplastik im menschlichen Stuhl, Clemens Verenkotte, ARD-Hörfunkstudio Wien, 23.10.18 14:44 Uhr | audio


KAISER-WILHELM-INSTITUT·FÜR·KOHLE

BUNDESREPUBLIK DEUTSCHLAND

AUSGEGEBEN AM
14. APRIL 1960

DEUTSCHES PATENTAMT

PATENTSCHRIFT

№ 973 626

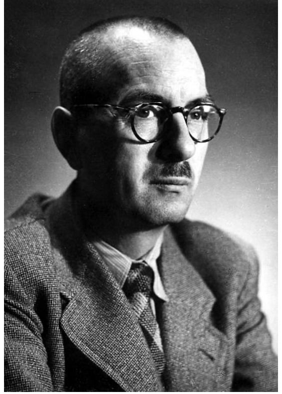
KLASSE 39c GRUPPE 25$_{01}$
INTERNAT. KLASSE C 08f ———
Z 3799 IV b / 39c

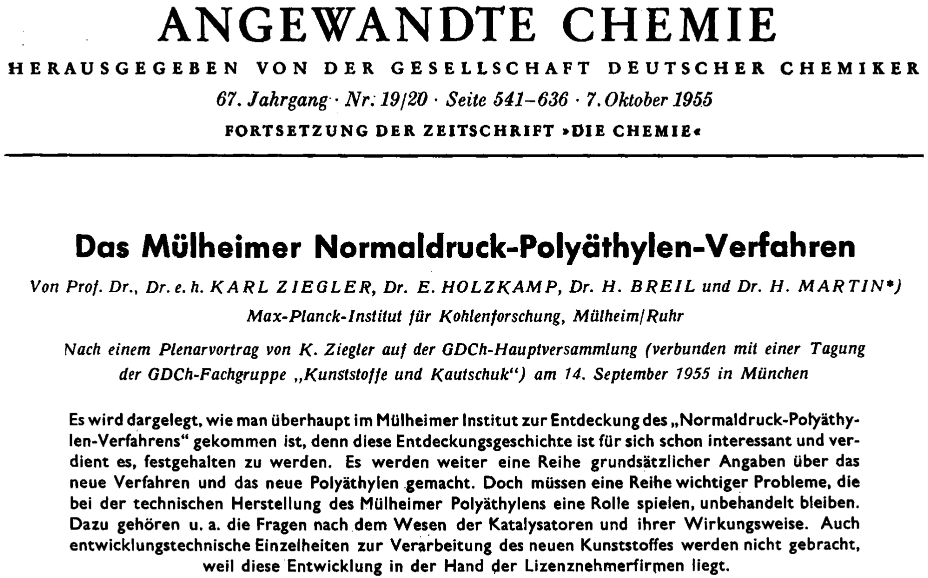
Dr. Dr. e. h. Karl Ziegler, Mülheim/Ruhr,
Dr. Heinz Breil, Oberhausen (Rhld.), Dr. Erhard Holzkamp, Düsseldorf,
und Dr. Heinz Martin, Mülheim/Ruhr
sind als Erfinder genannt worden

Dr. Dr. e. h. Karl Ziegler, Mülheim/Ruhr

Verfahren zur Herstellung von hochmolekularen Polyäthylenen

Patentiert im Gebiet der Bundesrepublik Deutschland vom 10. November 1953 an
Patentanmeldung bekanntgemacht am 4. Oktober 1956
Patenterteilung bekanntgemacht am 24. März 1960





ANGEWANDTE CHEMIE
HERAUSGEGEBEN VON DER GESELLSCHAFT DEUTSCHER CHEMIKER
67. Jahrgang · Nr. 19/20 · Seite 541–636 · 7. Oktober 1955
FORTSETZUNG DER ZEITSCHRIFT »DIE CHEMIE«

Das Mülheimer Normaldruck-Polyäthylen-Verfahren

Von Prof. Dr., Dr. e. h. KARL ZIEGLER, Dr. E. HOLZKAMP, Dr. H. BREIL und Dr. H. MARTIN)*
Max-Planck-Institut für Kohlenforschung, Mülheim/Ruhr

Nach einem Plenarvortrag von K. Ziegler auf der GDCh-Hauptversammlung (verbunden mit einer Tagung der GDCh-Fachgruppe „Kunststoffe und Kautschuk“) am 14. September 1955 in München

Es wird dargelegt, wie man überhaupt im Mülheimer Institut zur Entdeckung des „Normaldruck-Polyäthylen-Verfahrens“ gekommen ist, denn diese Entdeckungsgeschichte ist für sich schon interessant und verdient es, festgehalten zu werden. Es werden weiter eine Reihe grundsätzlicher Angaben über das neue Verfahren und das neue Polyäthylen gemacht. Doch müssen eine Reihe wichtiger Probleme, die bei der technischen Herstellung des Mülheimer Polyäthylens eine Rolle spielen, unbehandelt bleiben. Dazu gehören u. a. die Fragen nach dem Wesen der Katalysatoren und ihrer Wirkungsweise. Auch entwicklungstechnische Einzelheiten zur Verarbeitung des neuen Kunststoffes werden nicht gebracht, weil diese Entwicklung in der Hand der Lizenznehmerfirmen liegt.

Olefin polymerization

Main application of metal catalysts in industry

75 m tons polymers from olefins p.a.; 60 % with ‚Ziegler-Natta' catalysts
(→ ‚only' 10 m tons hydroformylation products p.a.)

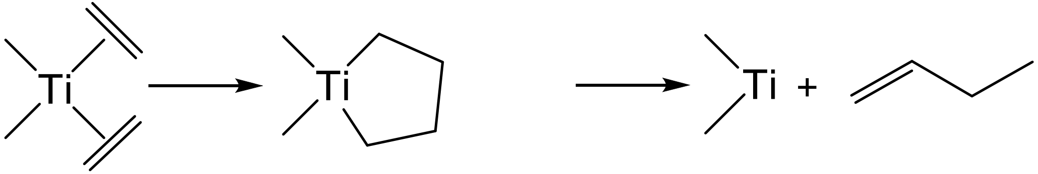
Different catalyst systems:

- Group (IV) catalysts: Ti, Zr (metallocenes) + MAO
- Late transition metals
- Metathesis catalysts for ROMP

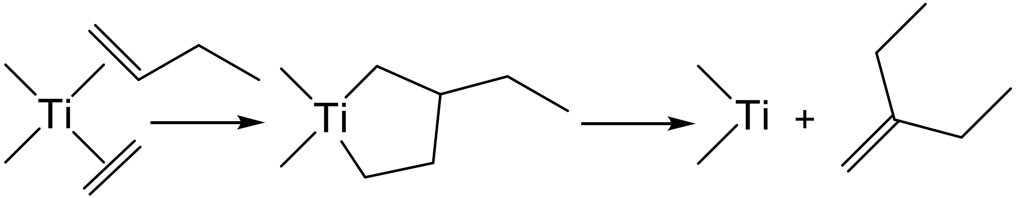
The AlphaButol process

Dimerization of ethene to 1-butene. Catalyst: Ti-complex.

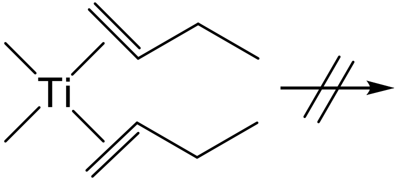
Main reaction:



Consecutive reaction:



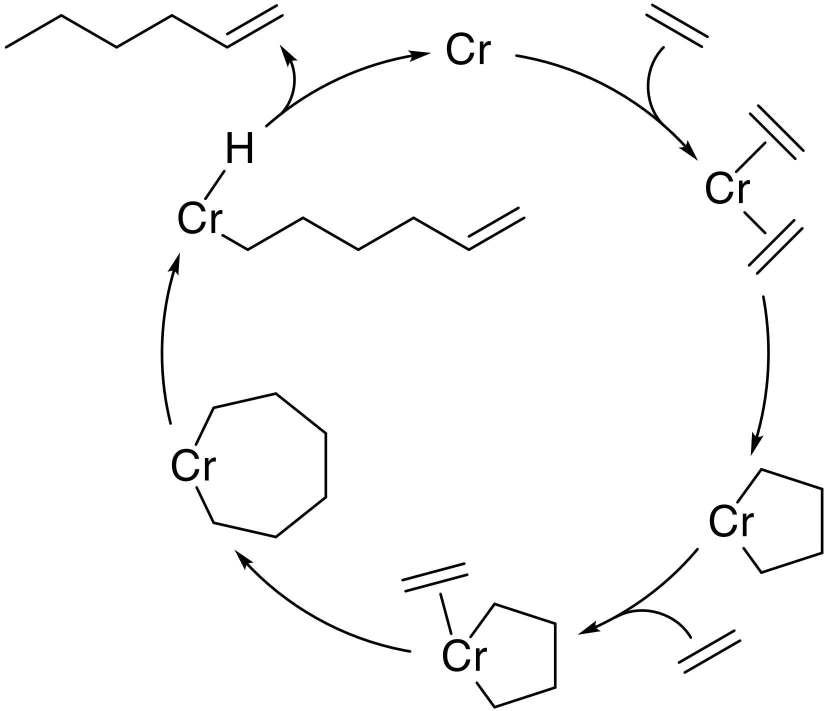
Not observed:

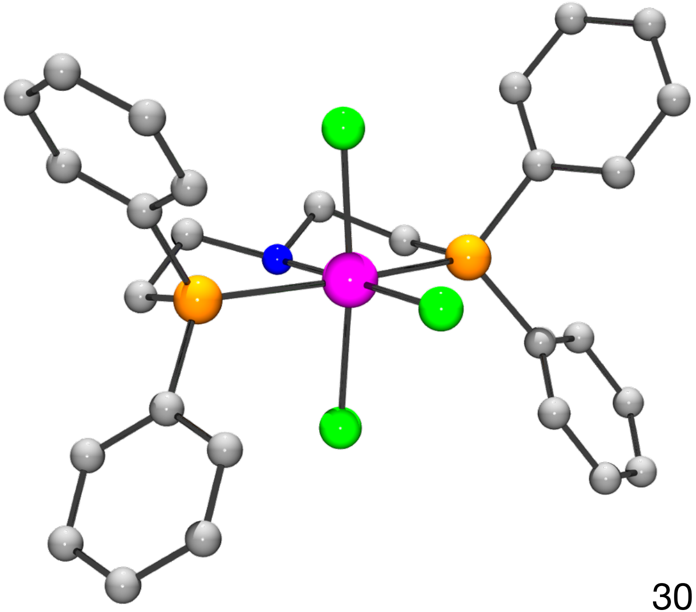


Dalton Trans. **2012**, *41*, 6625.

The Union Carbide process

Trimerization of ethene to 1-hexene. Catalyst: Cr complexes.





Chem. Commun. **2003**, 334; *JACS* **2003**, *125*, 5272.

Olefin polymerization – historic development

Before 1955

- ICI-Process (ICI = Imperial Chemical Industries); high temperatures, radical (with O_2; 3000 bar, 300°C)
- Phillips process (heterogeneous, Cr@SiO_2, 10 bar)

1953

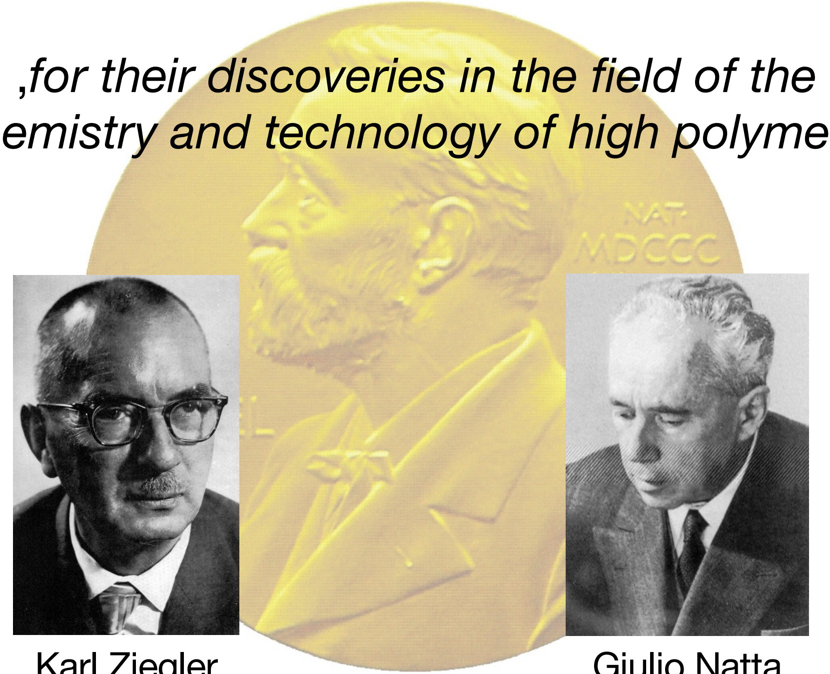
Karl Ziegler and Giulio Natta

→ low temperature/pressure process for the production of PE and PP (Niederdruckverfahren)

Ziegler-Natta olefin polymerization

Nobel Prize in Chemistry 1963

‚for their discoveries in the field of the chemistry and technology of high polymers‘



Karl Ziegler
(MPI Mülheim)

Giulio Natta
(Milan)

Olefin polymerization – most relevant products

Polyethylene

- Low density (LDPE, 0.91-0.94 g/cm^3 (foils, bags)
- High density (HDPE, 0.94-0.97 g/cm^3) (bottles, tubes …)
- Linear LDPE (foils, plastic bags, etc…)
- **H**igh **m**olecular **w**eight (HMWPE, < 1000 kg/mol)
- Ultra high MWPE (6000 kg/mol, fibres, implants …)

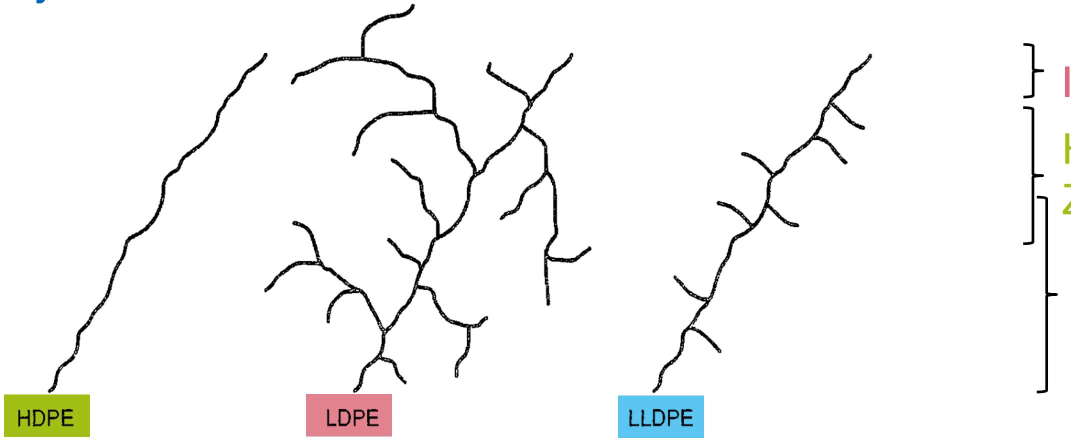
ICI, radical polym.

Heterogeneous
Ziegler-Natta cat.

Molecular catalysts

Olefin polymerization – most relevant products

Polyethylene



ICI, radical polym.

Heterogeneous Ziegler-Natta cat.

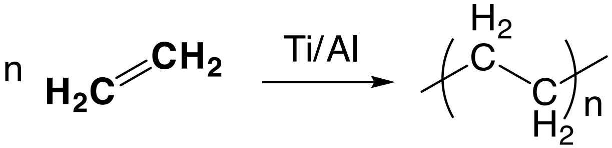
Molecular catalysts

Polypropylene

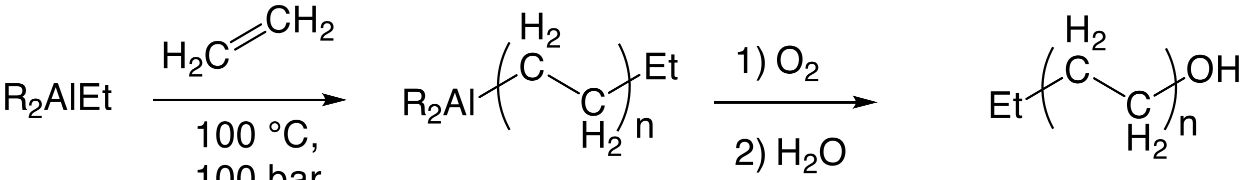
- Broader application than PE → harder material
- Plastic parts in car interior, packaging

Karl Ziegler – The nickel effect

High-density polyethene (HDPE) strictly linear; ρ = 0.94-0.97 g/cm^3



In fact, Ziegler searched for a route to synthesize aliphatic fatty alcohols



n < 200

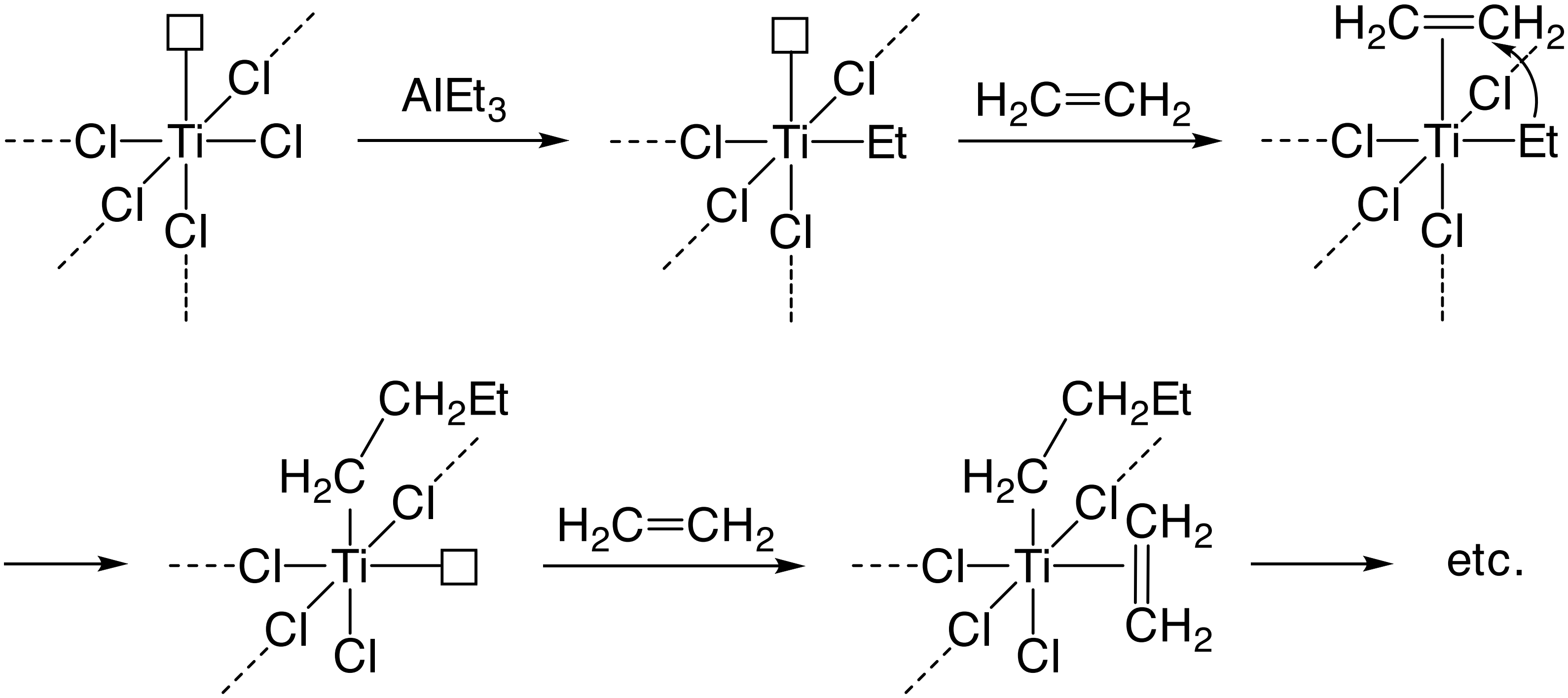
Fatty alcohols (n = 12-16)

Discovery by serendipity – an unprecedented reaction took place

→ A coworker washed the autoclave (made from Ni-alloys) with HCl…

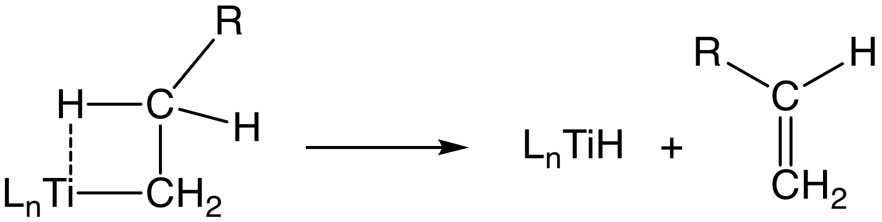
J. J. Eisch, *Organometallics* **2012**, *31*, 4817.

The Cossee-Arlman mechanism



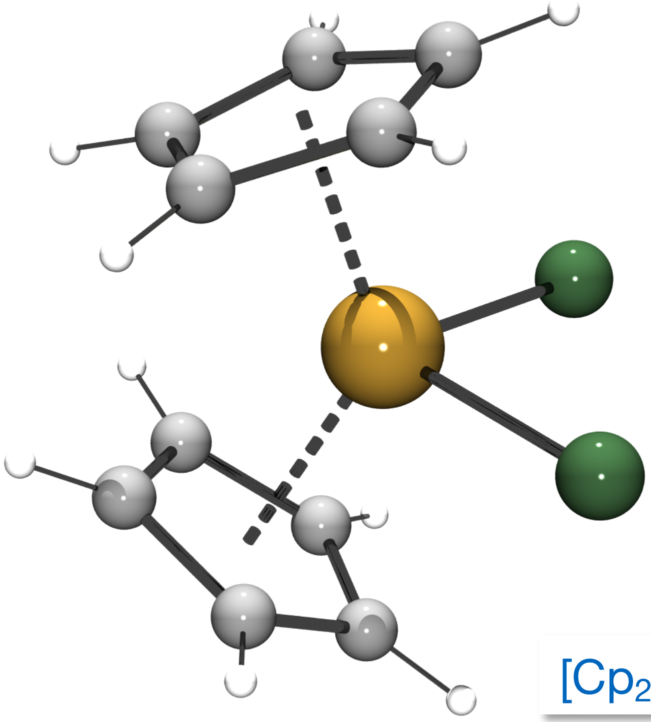
The Cossee-Arlman mechanism

Chain termination



Metallocene catalysts

Efficient homogeneous high performance catalysts



$[Cp_2TiCl_2]$

Metallocene catalysts

Development

1957: G. Natta used Cp_2TiCl_2 / Et_2AlCl as catalyst for ethylene polymerization

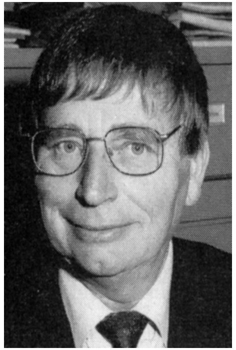
→ Low activity, no use in industry

However, traces of water drastically enhanced the catalytic activity

1980: W. Kaminsky uses another methylation agent – methylalumoxane (MAO)

→ Real breakthrough! Activity: 500 kg PE per mmol Zr per hour

Drawback: atactic PP with high degree of branching



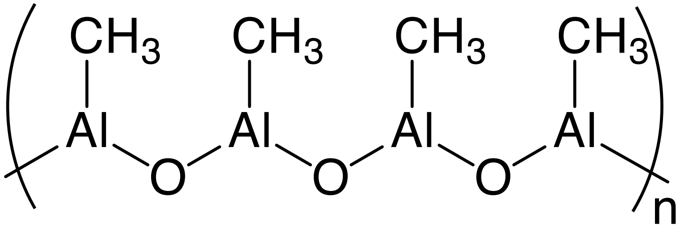
Werner Kaminsky

Metallocene catalysts

Co-catalyst: Methylalumoxane (MAO)

Irregular structure – oligomers (cyclic, acyclic)

Synthesis by partial hydrolysis of AlR_3

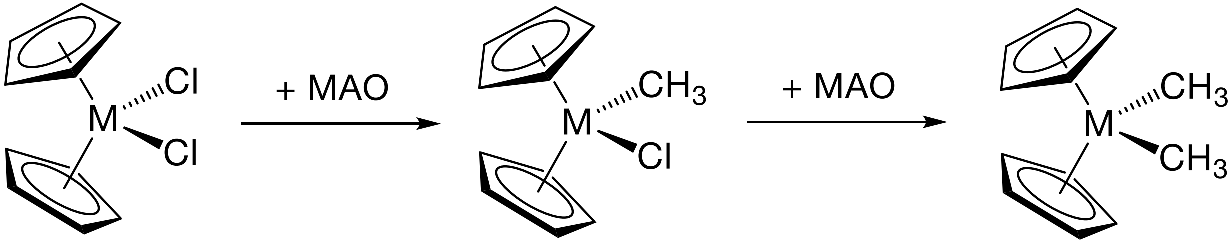


Molecular mass between 1000 and 1500 g/mol
Excess of MAO is required

Metallocene catalysts

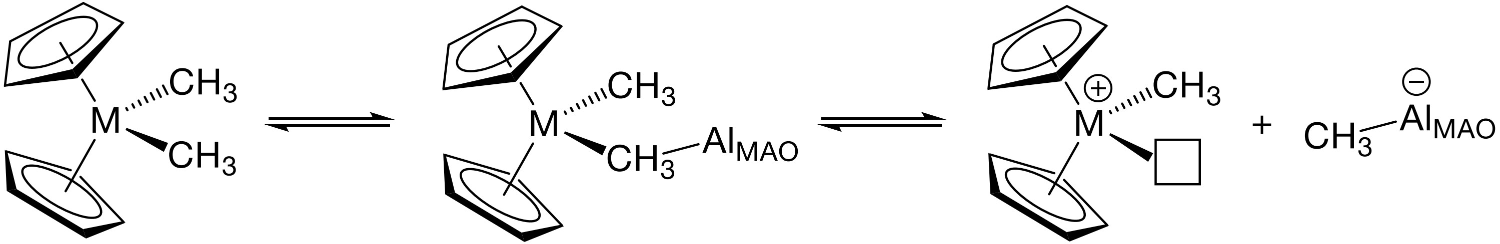
Function of MAO

1) Alkylation of the metallocene



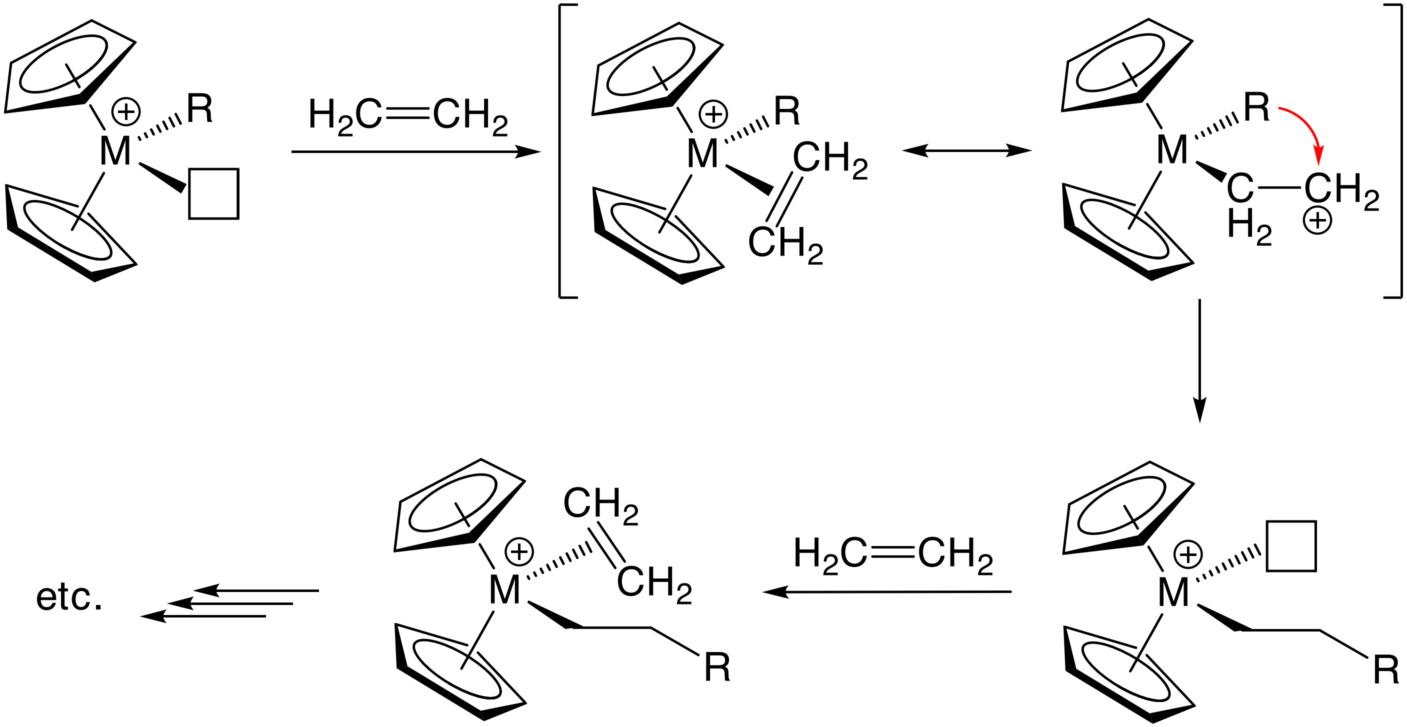
M = Ti, Zr, Hf

2) Formation of the active species



Metallocene catalysts

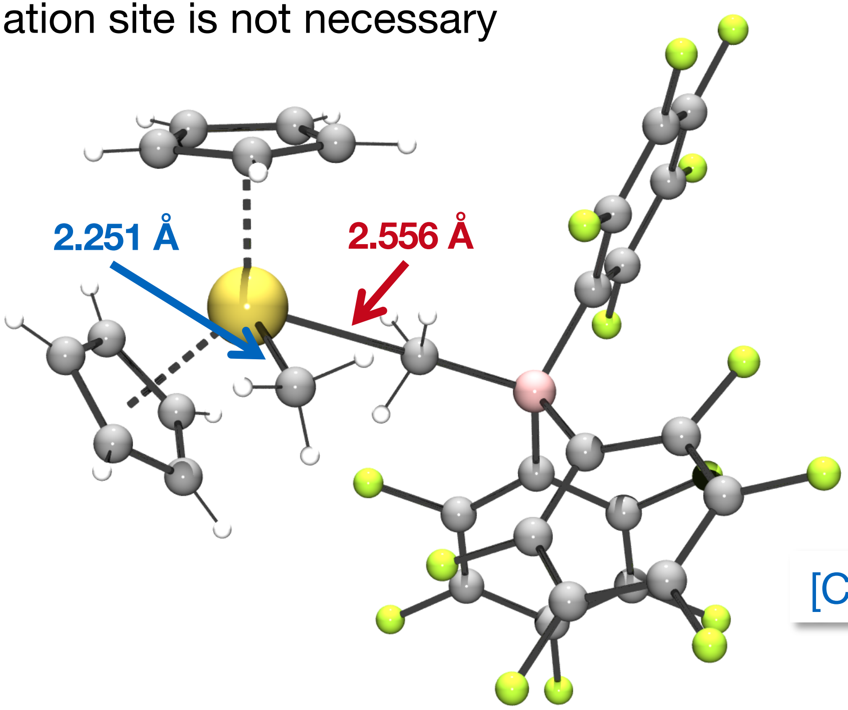
Mechanism analogous to the Ziegler-Natta catalyst



Metallocene catalysts

Are cationic group 4 metallocenes isolable?

Creation of a free coordination site is not necessary



$[Cp_2MeZr]^+[MeBAr^F_3]^-$

E. Y.-X. Chen, T. J. Marks, *Chem. Rev.* **2000**, *100*, 1391.

Metallocene catalysts

Are cationic group 4 metallocenes isolable?

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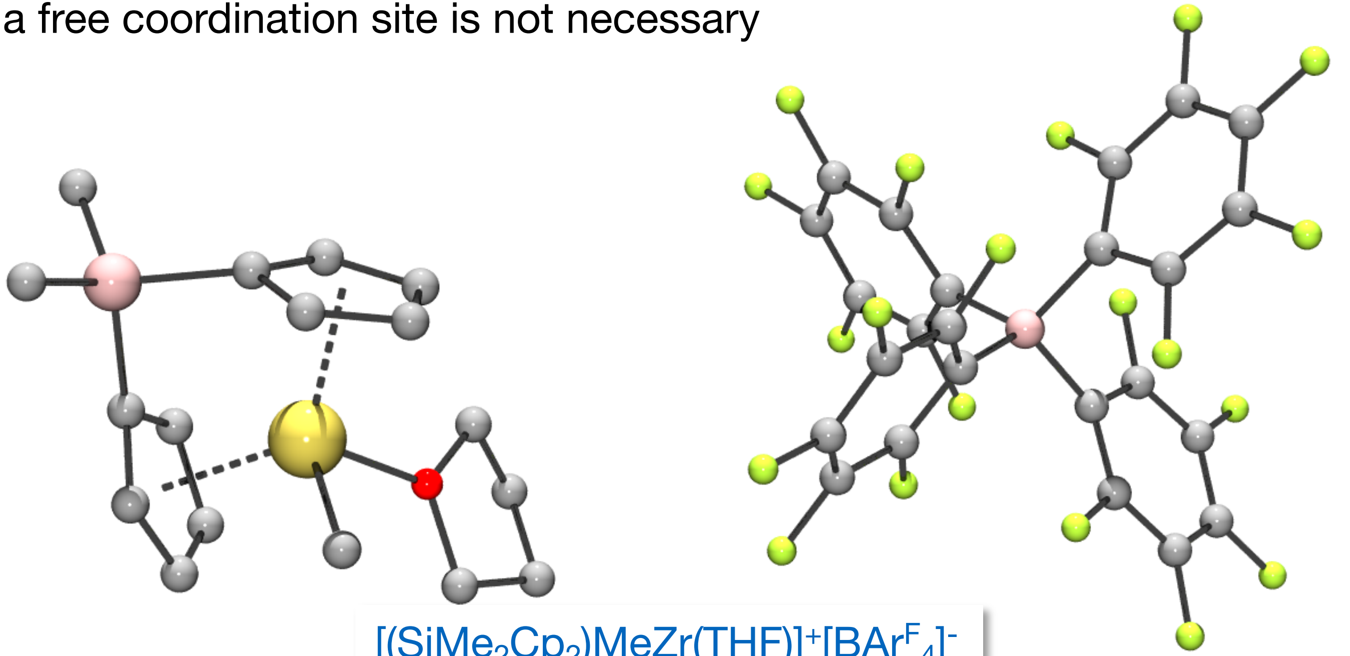


$[(SiMe_2Cp_2)MeZr(THF)]^+[BAr^F{}_4]^-$

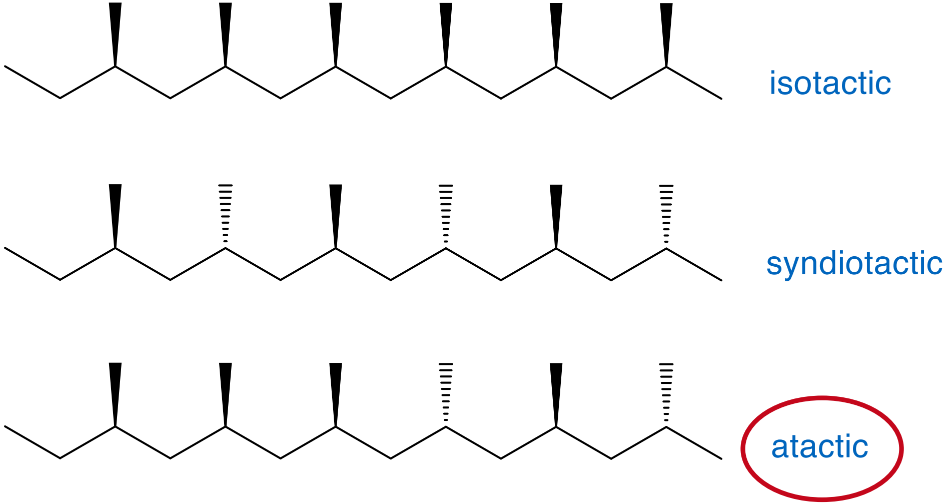
E. Y.-X. Chen, T. J. Marks, *Chem. Rev.* **2000**, *100*, 1391.

Metallocene catalysts

Polymerization of propylene – Stereoselectivity issues

Cp_2MCl_2 / MAO is a very efficient catalyst system for ethene polymerization

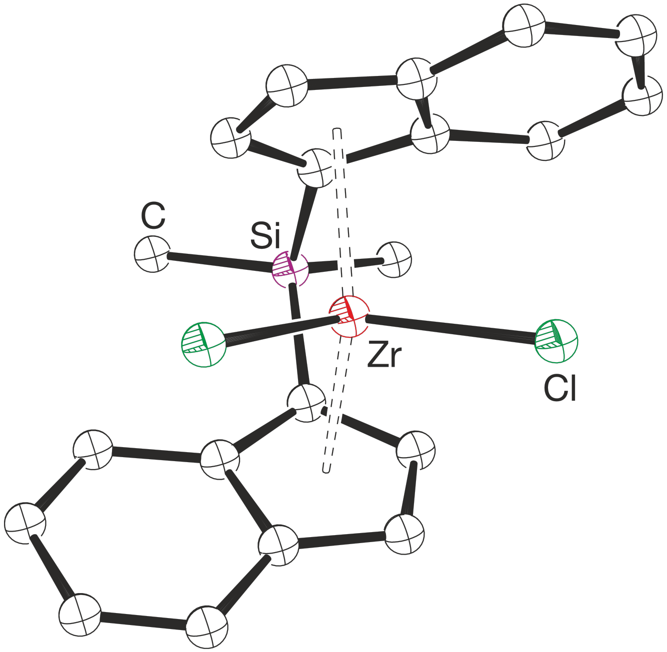
For propene a random distribution of polymer chain structures is obtained

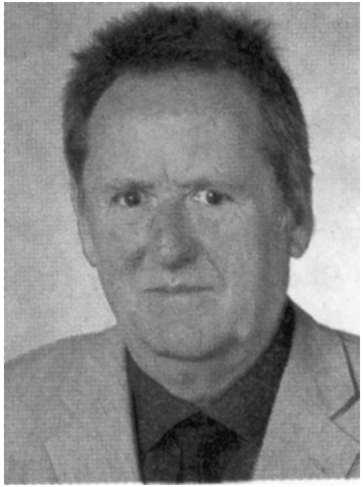


A regular ordering of the methyl groups is desired
(effect on melting point, hardness, etc…)

Stereoselective *ansa*-metallocene catalysts

This compound produces 12 kg of highly isotactic PP per g Zr in 1 h (60 °C, 1 bar)



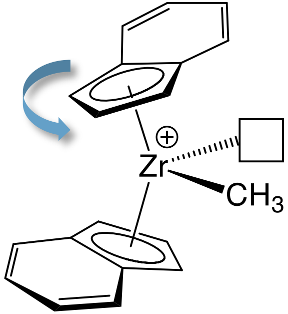


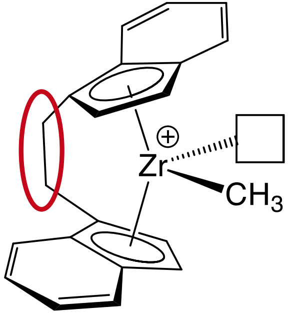
H.-H. Brinzinger

W. A. Herrmann et al., *Angew. Chem. Int. Ed.* **1989**, *28*, 1511.
H. H. Brintzinger et al., *Angew. Chem. Int. Ed.* **1995**, *33–34*, 1143.

Stereoselective *ansa*-metallocene catalysts

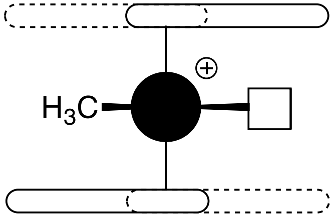
Development of chiral catalysts via ligand modification

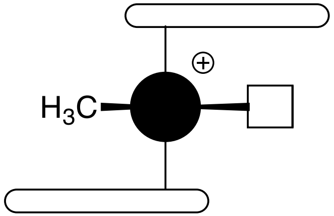




Rotation of the indenyl (Cp) ring possible; no steric control

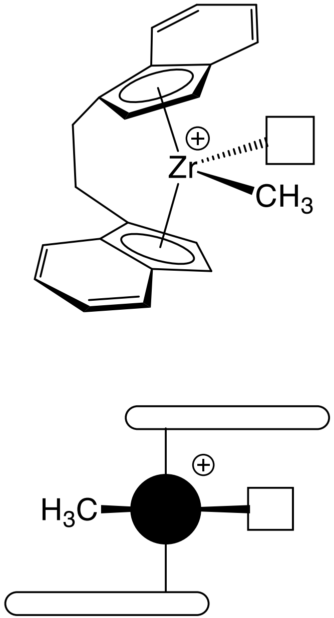
Rotation not possible;
Geometric chirality



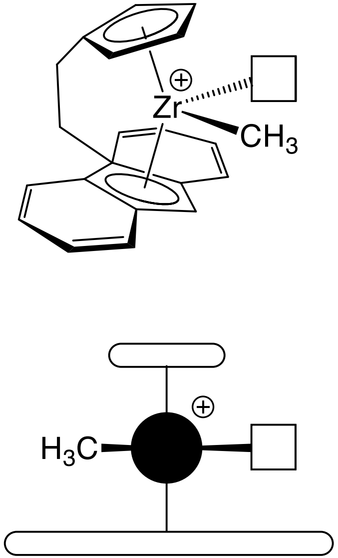


Stereoselective *ansa*-metallocene catalysts

Influence of the catalyst symmetry

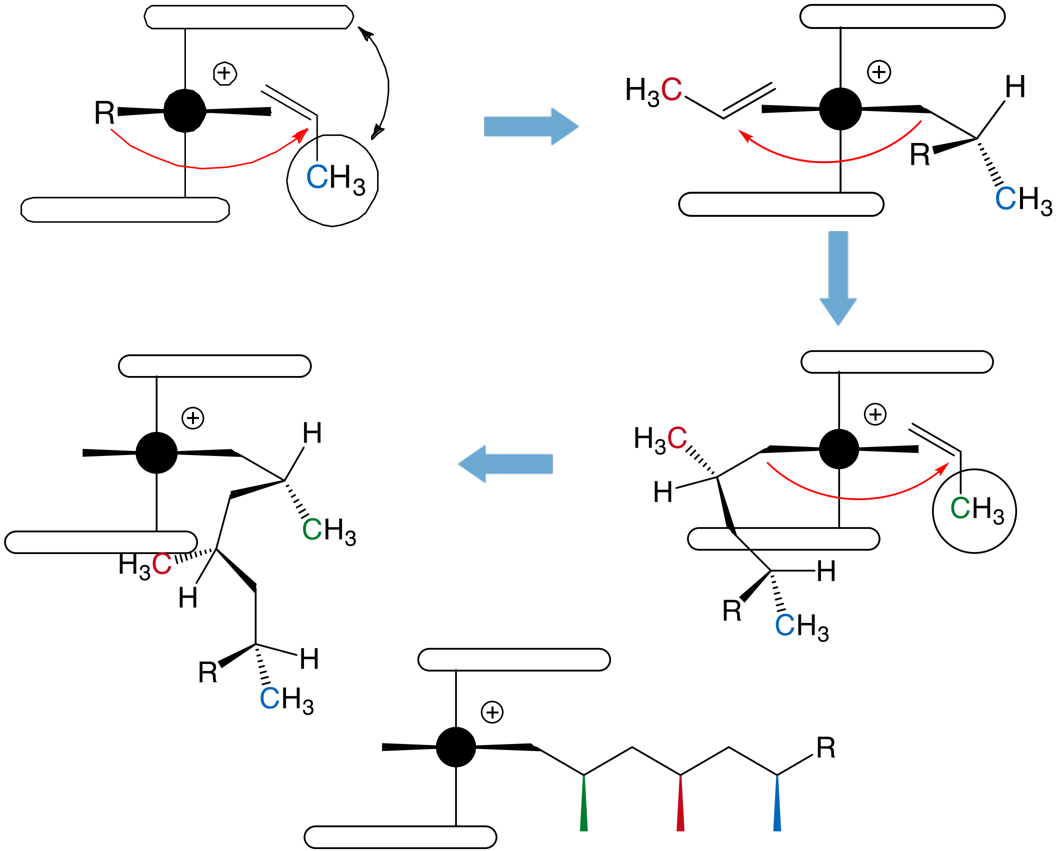


Gives isotactic PP

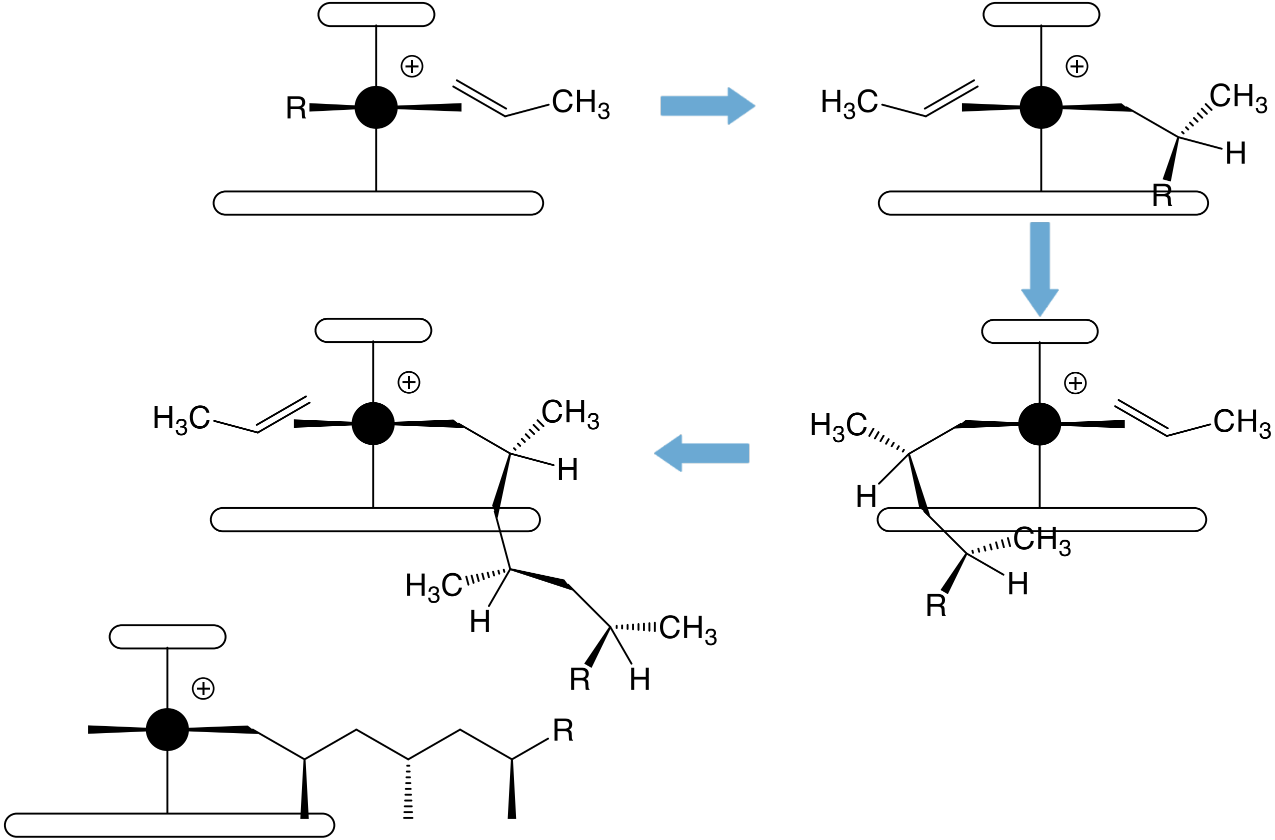


Gives syndiotactic PP

Stereoselective *ansa*-metallocene catalysts



Stereoselective *ansa*-metallocene catalysts

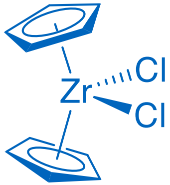


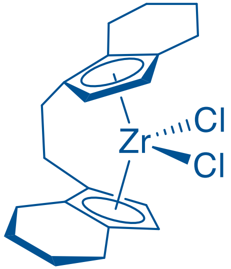
Stereoselective *ansa*-metallocene catalysts

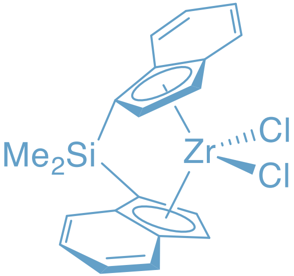
Substituents on the Cp ring allow an increase of the catalyst activity

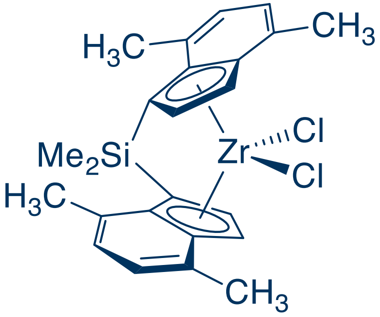
Control over the physical properties of the obtained polymers

Catalyst	Activity (kg PE/mol$_{Zr}$·h)	M_W(PE) (kg/mol)
Cp_2ZrCl_2	60 900	62
$En(IndH_4)_2ZrCl_2$	22 200	1000
$Si(Ind)_2ZrCl_2$	36 900	260
$Si(IndMe_2)_2ZrCl_2$	111 900	250





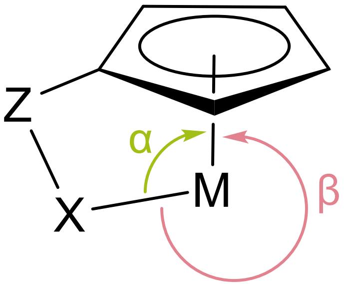


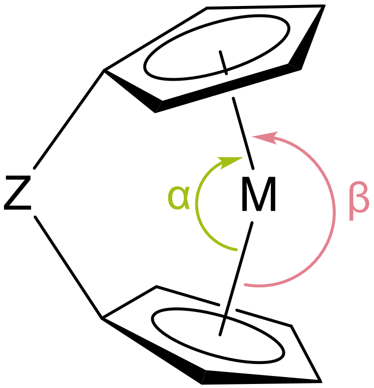


Ansa metallocenes

Constrained Geometry Catalysts (CGC)

Comparison with ‚classic‘ metallocenes





business

SINGLE-SITE CATALYSTS

New tailor-made plastics with superior properties are scoring big with film producers as polyolefin makers vie to get in the game

Alexander H. Tullo
C&EN Northeast News Bureau

In the mid 1990s, word that Exxon, Dow Chemical, and others were manufacturing the first plastics using single-site catalysts (SSCs) on a commercial scale was big news for the chemical industry. The significance of these developments was considered akin to ICI's discovery of low-density polyethylene in the 1930s and, later on, Phillips Petroleum's pioneering work in high-density polyethylene.

SSCs—catalysts with one active site—such as metallocenes, which are metal complexes with two cyclopentadienyl (Cp) or substituted Cp groups, offer the promise of tailoring polyolefins to meet virtually any end-user need. But markets for these innovative plastics evolved much more slowly than most hoped.

SSC-based polymers have faced many difficulties. It took time for polyolefin companies to convince their clients that the superior properties of the new plastics were worth the extra cost per pound. Producers also feared that expensive awards resulting from long court battles over patents would punish them for offering the innovative products. Moreover, SSC technologies posed more technical problems than expected because using the catalysts in the most popular and efficient polyolefin processes was sometimes problematic.

Now the polyolefin industry has jumped most of these hurdles. Resins produced with SSCs are winning over plastic processors, and volumes are growing significantly. The pace of litigation is slowing down, allowing more companies to develop and license technology freely. And companies have made SSC technologies more reliable, as evidenced in the number of resin makers who are announcing commercial production.

Consolidation has been the backdrop for this entire scene. Though SSCs did not drive any of the big petrochemical combinations of the past three years, these catalysts have been greatly affected by industry dealmaking.

Mergers resolved some issues in SSC technology. For example, the oil merger between Exxon and Mobil settled a $170 million metallocene patent infringement suit between them. Deals have also put SSC technology in the hands of new management. This was the case in the formation of Targor by Hoechst and BASF, and it will be a factor in the Dow/Union Carbide and Targor/Montell/Elenac mergers that are expected to be completed soon.

Mergers also raise other issues. The Dow/Union Carbide merger brings antitrust concerns over polyethylene catalyst technologies to the forefront because of the possible link of Dow's Insite catalyst platform with ExxonMobil's Exxpol metallocene technology by way of the ExxonMobil/Union Carbide joint venture, Univation, which licenses polyethylene technology.

The biggest sign that the industry is getting over its growing pains is that the size of the market for SSC-based resins is becoming significant. According to Robert J. Bauman, vice president of Chem-Systems, a Tarrytown, N.Y.-based chemical consultancy, consumption of SSC-based plastics in the U.S., which represents about half of the global market, was 830 million lb in 1999. Elastomers and plastomers represent 300 million lb of this, and the rest is mostly linear low-density polyethylene (LLDPE).

Bauman forecasts that the U.S. market will jump to about 1.1 billion lb this year. He is projecting annual growth averaging 25% through 2005, when it will taper off to 15%. Worldwide, he estimates that demand in 1999 was 1.7 billion lb, growing to nearly 6 billion lb by 2005.

The earlier slow market acceptance of SSC-based LLDPE had weighed down SSC growth as a whole, Bauman says. SSC-based LLDPE didn't catch on as fast as originally expected because it is difficult to work with. "It doesn't process as well as the materials it is replacing, so many companies have had to modify their extrusion equipment," he says. "But the value-in-use [utility] is really strong."

According to Bauman, SSC-based resins are picking up steam in markets where their properties, such as impact resistance, offer the greatest benefit to end users. "In cases where something is prone to damage and conventional LLDPE has problems, you can go to a metallocene-based polymer," he says.

For example, Bauman says, almost all of the bananas exported from Costa Rica are wrapped in SSC-based films. He explains that the

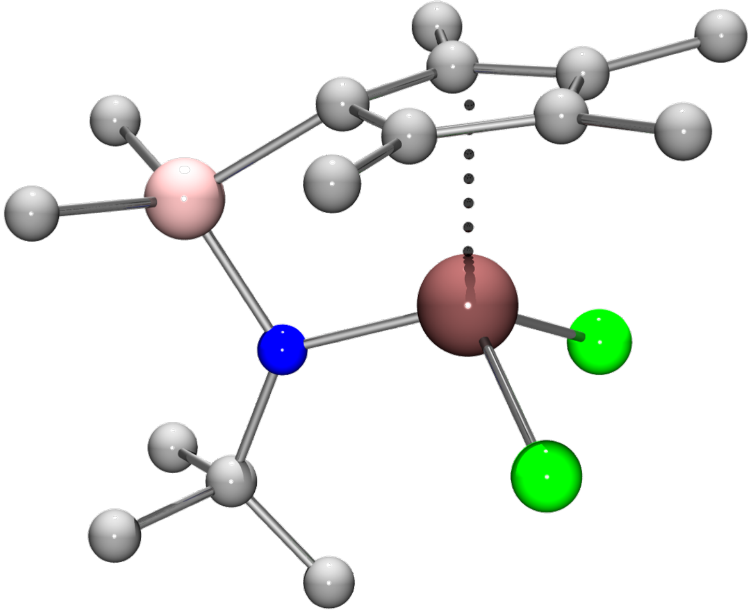
Impact resistance is a key feature of SSC-based film, this one made with Dow's Elite polyethylene.

AUGUST 7, 2000 C&EN **35**

Ansa metallocenes – new generations

Constrained Geometry Catalysts (CGC)

Control over the physical properties of the obtained polymers



Tobin J. Marks

Dow and Exxon:
ethene/1-octene co-polymers

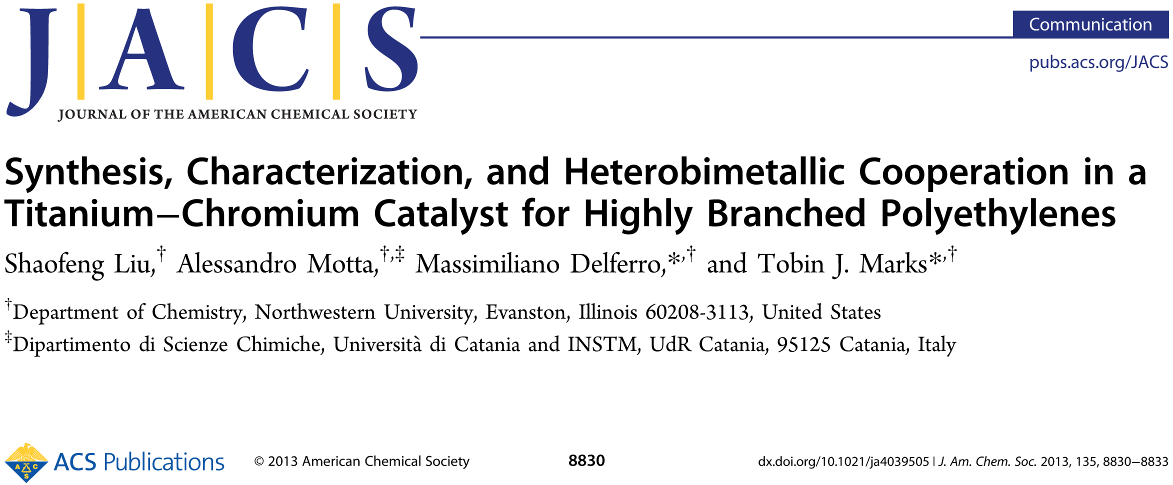
→ ‘ultra low density PE‘ (ULDPE)

Advantage: less oxophilic

Problem: β-H elimination hindered by rather weak σ-donors

CGR catalysts

Heterobimetallic catalysts for specialty polymers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Communication
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Synthesis, Characterization, and Heterobimetallic Cooperation in a Titanium–Chromium Catalyst for Highly Branched Polyethylenes

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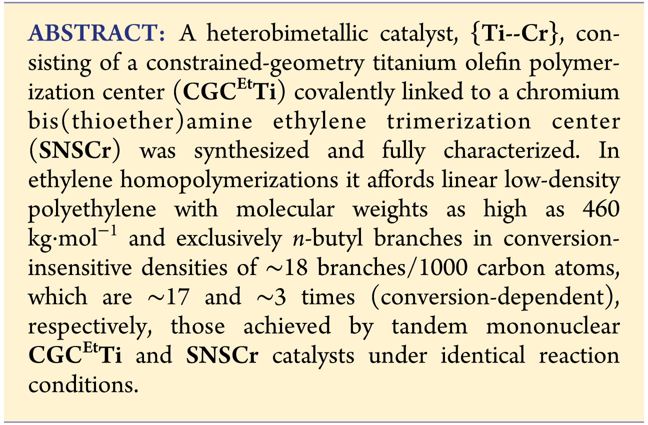
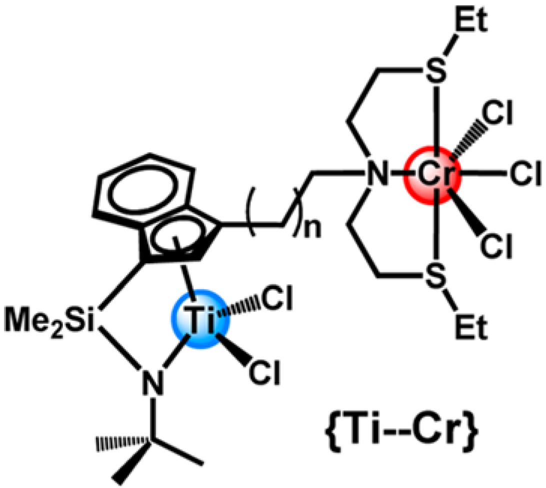
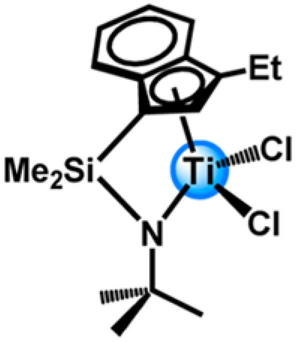

ABSTRACT: A heterobimetallic catalyst, {**Ti--Cr**}, consisting of a constrained-geometry titanium olefin polymerization center (**CGC^{Et}Ti**) covalently linked to a chromium bis(thioether)amine ethylene trimerization center (**SNSCr**) was synthesized and fully characterized. In ethylene homopolymerizations it affords linear low-density polyethylene with molecular weights as high as 460 kg·mol^{-1} and exclusively *n*-butyl branches in conversion-insensitive densities of ~18 branches/1000 carbon atoms, which are ~17 and ~3 times (conversion-dependent), respectively, those achieved by tandem mononuclear **CGC^{Et}Ti** and **SNSCr** catalysts under identical reaction conditions.

CGR catalysts

Heterobimetallic catalysts for specialty polymers



{Ti--Cr}



$\text{CGC}^{\text{Et}}\text{Ti}$

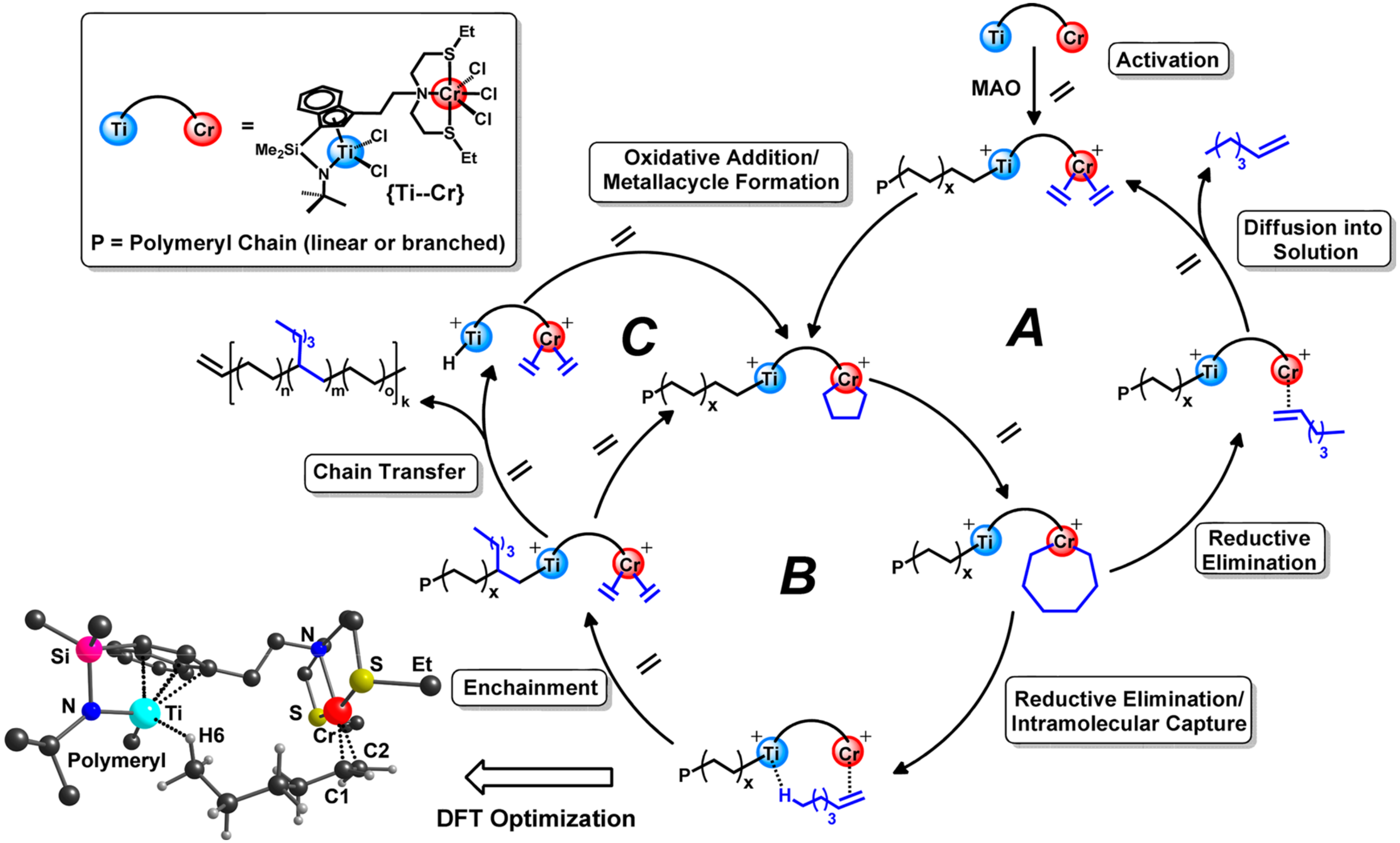
SNSCr

⇨ Highly selective production of n-butyl branched polyethylene (LLDPE)

⇨ Ethylene is the only feedstock!

T. J. Marks et al., *JACS* **2013**, *135*, 8830.

CGR catalysts

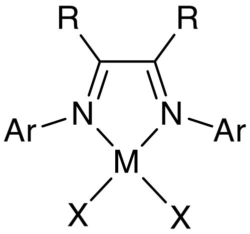


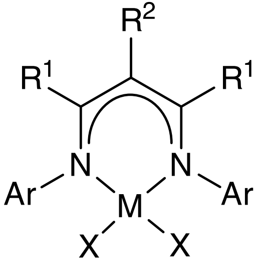
T. J. Marks et al., *JACS* **2013**, *135*, 8830.

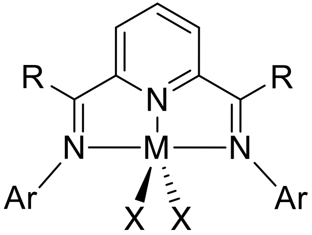
Polymerization with late transition metals

Brookhart complexes

Suitable for co-polymerization of ethene with polar co-monomers



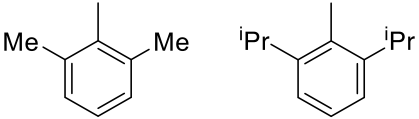




M = Fe, Co, Ni, Pd

Maurice Brookhart

Ar =

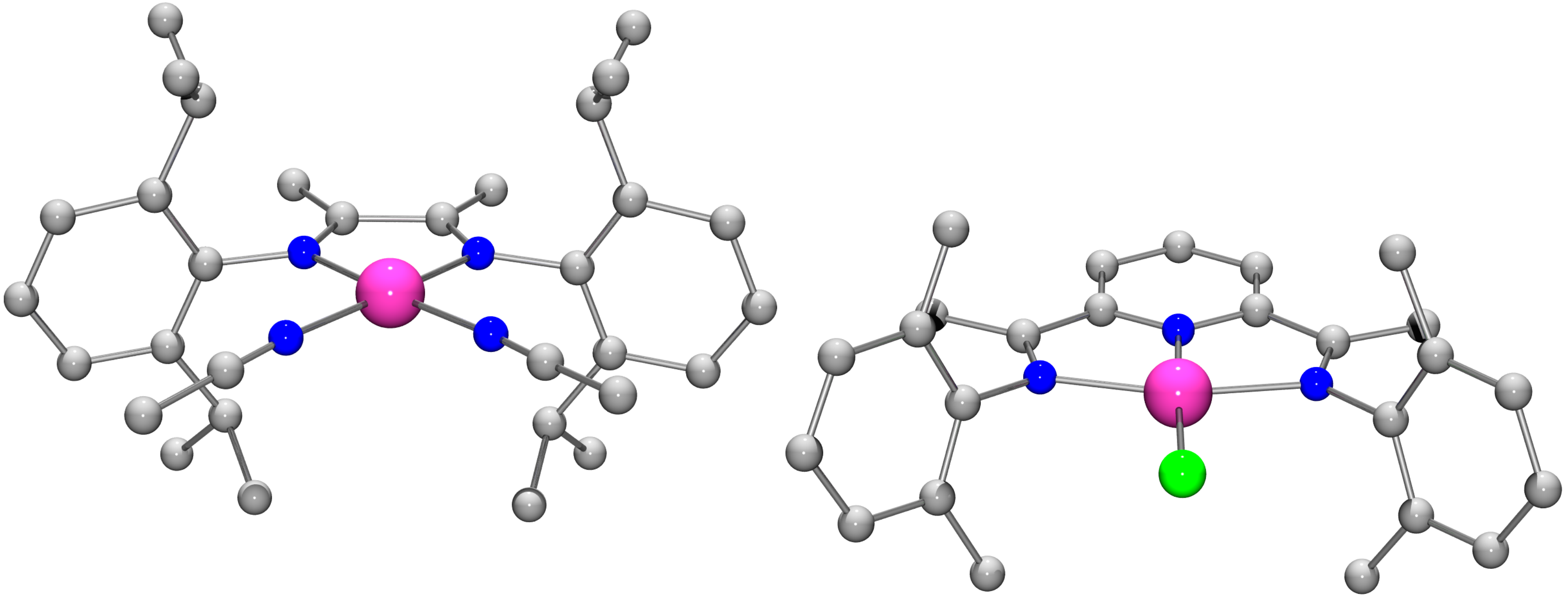


X = halides, methyl, solvent (ether, nitriles,…)

M. Brookhart et al., *Chem. Rev.* **2000**, *100*, 1169.

Polymerization with late transition metals

Single crystal X-ray structures



Polymerization with late transition metals

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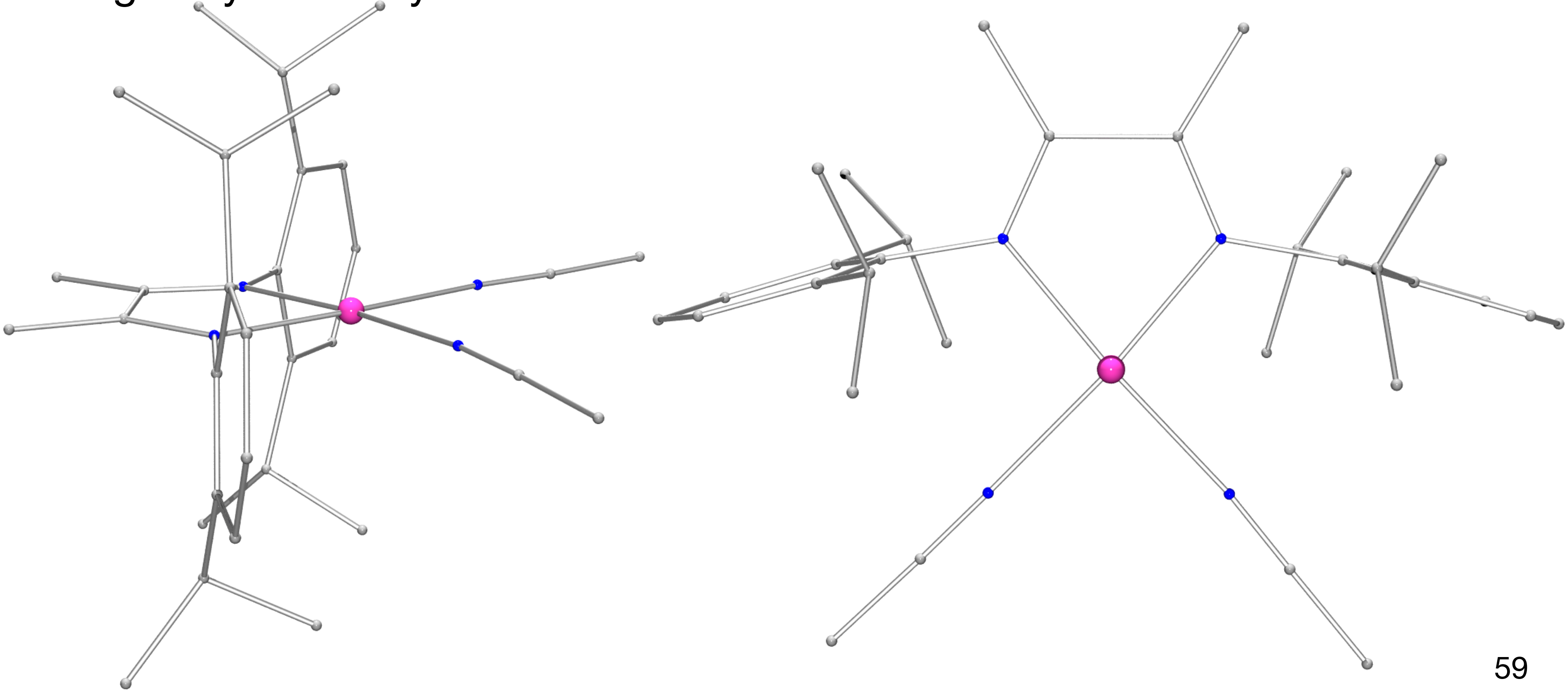
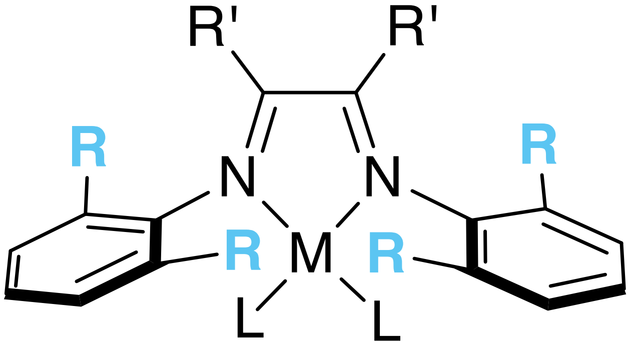
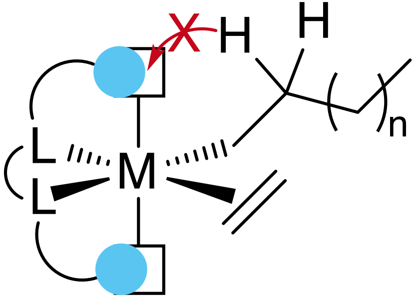


Polymerization with late transition metals

The ligand influences the axial coordination site





With an excess of substrate, β-H atoms of the polymer chain cannot come close to the coordination sphere, i.e. the axial sites of the metal.

M. Brookhart et al., *Chem. Rev.* **2000**, *100*, 1169.

Summary

The polymerization of olefins

⇨ Ziegler-Natta catalysts are immobilized Ti(IV) salts
→ Activation with triethylaluminum

⇨ Group IV metallocenes (Ti, Zr) very active in solution
→ Activation by methylalumoxane

⇨ Free coordination sites are very important
→ Weakly coordinating anions

⇨ Late transition metals are also active (Fe, Ni, Pd)
→ Higher tolerance to moisture/functional groups, but easier β-H elim.

⇨ Stereoselectivity possible by ligand design
→ Ligand geometry is important