

Founded in 1912 as "Kaiser Wilhelm Institute for Coal Research"
 Most important influencers: Emil Fischer, first German chemistry Nobel Prize winner (1902) and Hugo Stinnes (big industrialist)
 The primary goal was the direct conversion of coal to electricity
 4 days after the opening, WWI started

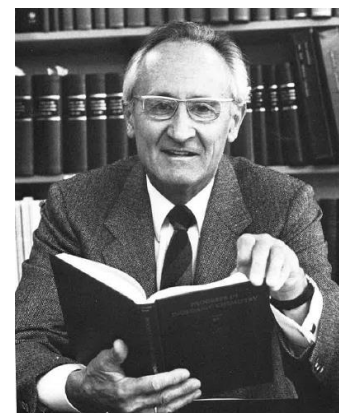
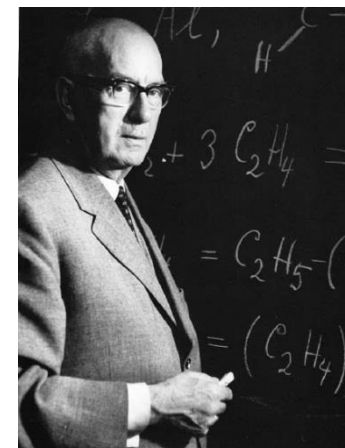
The presentation will be divided into 3 eras represented by 3 directors:

1. Director (1913-1943): **Franz Fischer** (not related to Emil Fischer),
 437 publications, 71 patents
 research was plagued by two world wars and many publications fell into the Ziegler era because they were delayed by the second world war (e.g. Koch synthesis)
 1925: patent for the Fischer-Tropsch Process (catalytic production of liquid hydrocarbons from coal); production volume in the 1940s about 600,000 tons/year
 Despite the wars he published 12 Volumes of "Summarized essays about the knowledge of coal" which can be understood as his lifework

2. Director (1943-1969): **Karl Ziegler**, shifted the institute's work to organometallic chemistry
 1949: changed the name to Max Planck Institut für Kohlenforschung
 1952: patent for "Koch Reaction"
 1953: patent for atmospheric pressure polymerization of ethylene at rt; **today: 150 mio. tons / year**
 1954: patent for the direct synthesis of $\text{Al}(\text{Et})_3$
 1954: patent for the synthesis of primary alcohols
 1956: patent for cyclodimerization & -trimerization of butadiene to COD & CDT (Wilke)
 1963: Nobel Prize for Ziegler together with Natta (Milan) *For their discoveries in the field of the chemistry and technology of high polymers*

3. Director (1969-1993): **Günther Wilke**
 1970: patent for the decaffeination of green coffee beans called "Destraktion" (Zosel)
 1973: patent for the enabling process for the electrochemical industrial Ferrocene production (Wilke)
 1979: patent for the synthesis of magnesiumhydrides used as energy storage (Bogdanovic)

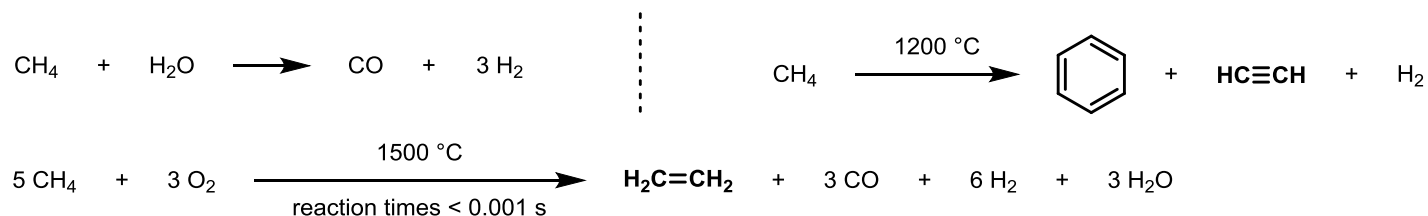
The contributions after 1993 will be covered in a later second topic presentation.



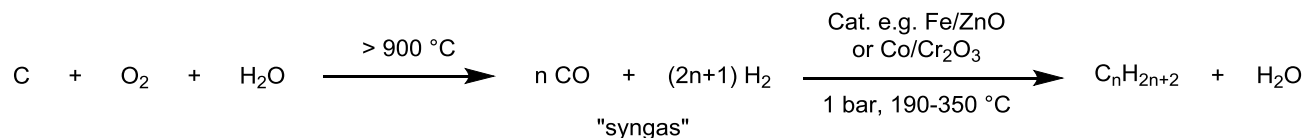
Franz Fischer (1877-1947), Director 1913-1943

Curiously became the first director because Hugo Stinnes was on the founding-board and had rich influence as a big industrialist and co-founder of RWE (big German energy provider). He heard about the possibility to convert coal directly into electricity (contemporary means was to burn coal in a steam engine to generate electricity). This provided an incentive for the electrochemist Fischer to become director of the institute for coal research.

Fischer started with work on methane because it was a very abundant sideproduct in the coal industry:



The desire for liquid fuel began to rise and many processes with various catalysts and various products were developed. The general process became famous as Fischer-Tropsch synthesis for liquification of coal.



The products were wild mixtures of all chainlength, which could be controlled to a certain extent. A table by Fischer shows the composition differences depending on the reaction conditions:

Temp.	Pressure	cat.	product description	gas prod.	liquid prod.	solid prod.
190 °C (Co)	1 bar	Ni/Co/Fe	paraffines & olefines	little	much	little (classical Fischer-Tropsch)
> 200 °C	100 bar	?	aromatic carbohydrides	much	much	none
190 °C	5-20 bar	Co	paraffines & few olefines	little	much	much
240 °C	5-20 bar	Fe	paraffines & many olefines	little	much	little

For a summary by Fischer see:
Oel und Kohle, 1943, 517

9 Fischer Tropsch plants were built by the Nazis with a yearly production of 600,000 tons.

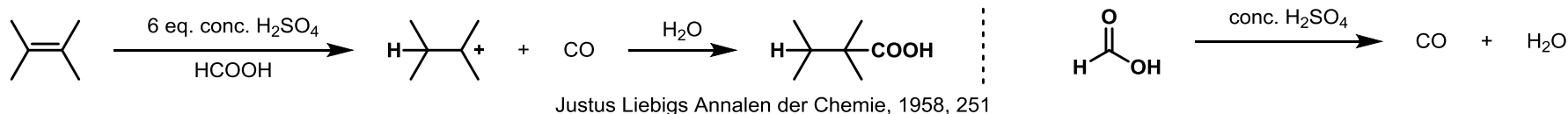
Unsatisfactory results were obtained because the sulfur containing synthesis gas from brown coal deactivated the catalysts on industrial scale. Therefore the Bergius Process (Hydrogenation of coal, Nobel Prize 1931), which delivered higher quality, was mostly used to provide liquid fuel for the war.

The Fischer Tropsch process was, however, continually used to a small degree since its discovery. Today there are 2 production plants in South Africa (covering 28% of RSA-need). Several plants are using natural gas (methane, cheaper!) and a reforming process to make syngas: "GTL" (gas to liquid) plants in Malaysia, RSA, Qatar, more plants in planning

Ben List about the Fischer-Tropsch Process: Organic chemistry can always continue, even after the oil is consumed. There will always be a way to make hydrocarbons.

Important Co-Workers of Fischer:

1. **Herbert Koch**, inventor of the Koch Synthesis for tertiary carboxylic acids from olefins and CO



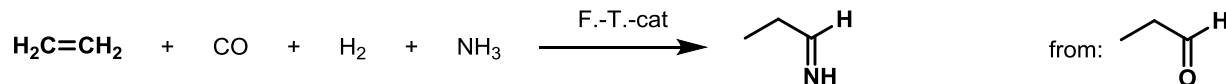
Alcohols and sometimes alkyl chlorides and alkyl esters can also function as starting materials.

The reaction is used on an industrial scale for the production of pivalic acid.

2. **Otto Roelen**, head of the pilot plant at the institute, changed to Ruhrchemie AG in 1934 where he developed the hydroformylation of olefins known as the Roelen-Reaction, hydroformylation or Oxosynthesis.

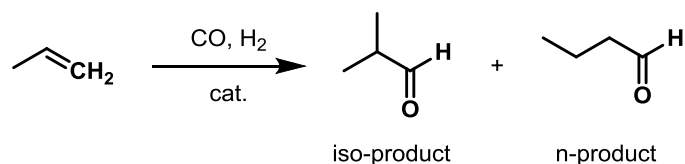
He was not really interested in publications, but more in patents. He owned more patents than publications (around 100)

Roelen did further developments of the Fischer-Tropsch synthesis and also tried to incorporate NH_3 into the product. During a disturbance of the reactor, he noticed a white solid:



His suggestion that the NH_3 only functioned as a reactant after the actual reaction was found to be right. He never made a lot of money from this patent, because German patents in other countries were declared invalid after WW2. Therefore only the small German companies paid him for this patent.

This protocol is nowadays used as a huge industrial process. The employed catalysts are usually metalcarbonylhydrides of Rh or Co. The iso- / n-product distribution can be controlled by the choice of ligands.

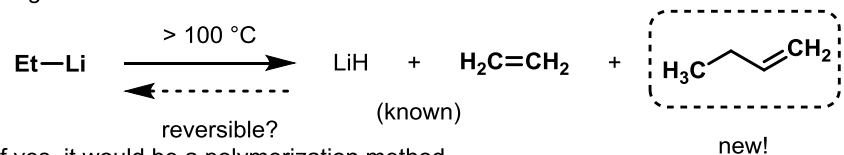


Karl Ziegler (1898-1973), Director 1943-1969, ~200 publications, Nobel Prize 1963

It is known, that he was against Hitler, but was still offered this important position, because he was too good to expulse him from Germany. They hoped the position as a director would limit his influence on students, but would still yield productive results.

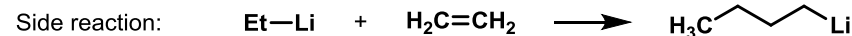
Ziegler restricted the acceptance of the position as a director to the same condition as Fischer (freedom of his resarch). He was concernd about the name of the institue that included the purpose and direction of the resarch.

Ziegler tried to distill EtLi:

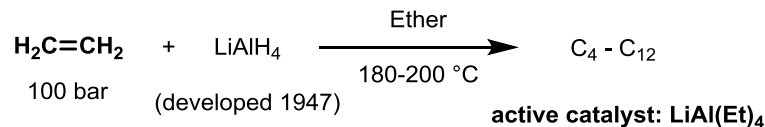


if yes, it would be a polymerization method

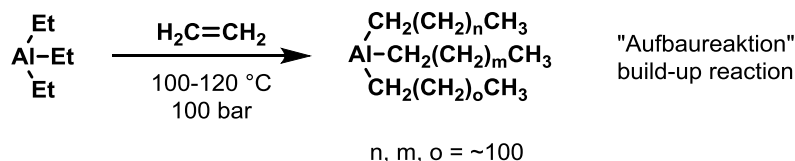
This reaction might also be the first known carbometallation



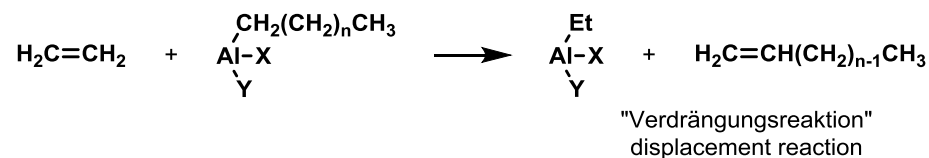
Many, many reactions later, in a desperate fashion (1949):



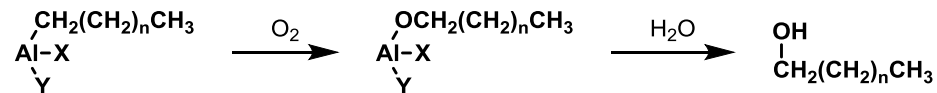
After deep investigations, they found the cheap and abundant Al was the important species and not the rare and expensive Li



Why did n, m, o never exceed beyond ~100?



Even tough the reaction was never "good enough" to yield polymers, by carefully choosing the reaction conditions, the chainlength of the alpha olefins could be controlled. This was benefical for a different industrial application:



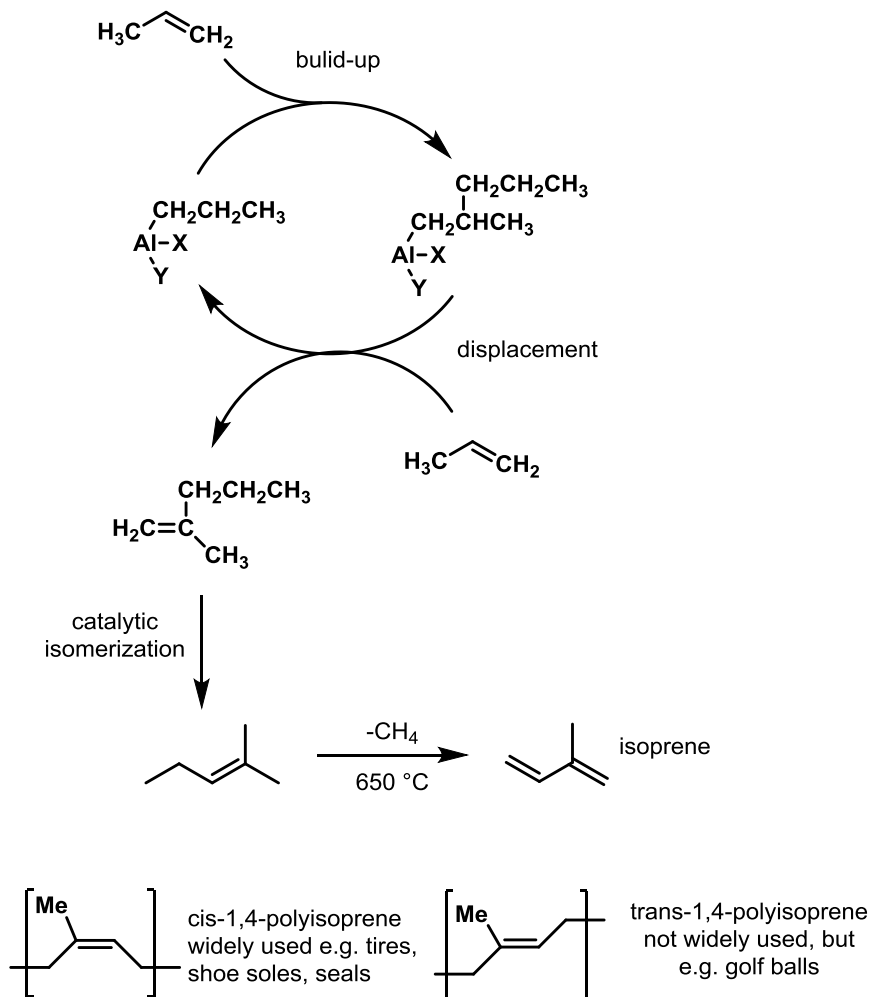
Primary C₁₂ - C₁₆ alcohols are used as biodegradable detergents and find worldwide application. The Al(OH)₃ sideproduct has several other applications. Thanks to Ziegler, pictures like these belong to the past:



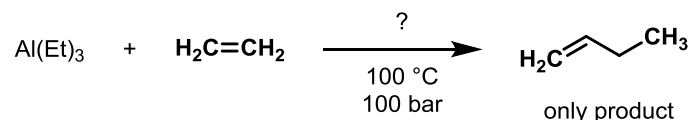
Non biodegradable detergents in the river Ruhr built foam on the surface.

1964
dpa picture alliance

The build-up reaction is much slower with α -olefins (e.g. propylene) and is stopped after dimerization by the displacement reaction (steric reasons). In the case of propylene this reaction is also used for an industrial process (**Goodyear-Scientific-Design-Process**):



The serendipity and tenacity that led to the nobel prize:



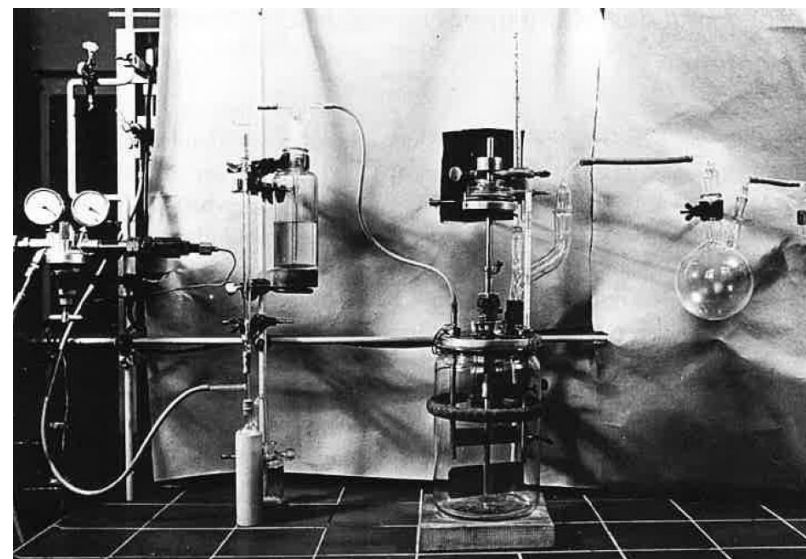
Erhard Holzkamp
(PhD student)
repeated the
known reaction
but got a different
result

After weeks of investigations a small amount of poorly soluble nickelphosphate was identified as the reason for the fast displacement reaction. The reactor was previously used for a hydrogenation reaction and some nickel remained in little cuts in the wall. The reactor was cleaned with HNO_3 and a phosphor containing detergent which left small amounts of nickelphosphates in the reactor. The aluminumalkyls reduced the nickel, which enhanced the displacement reaction. The enhancement of the displacement to only form dimers became known as the *nickel effect*.

Now, what does any other metal do?

Investigations into chromium, platinum, gold, copper...(insert most metals)...uranium and thorium revealed titanium as a very reactive catalyst for the elusive polymerization. Dr. Heinz Martin found a way to polymerize at atmospheric pressure and rt by employing TiCl_4 and $\text{Al}(\text{Et})_2\text{Cl}$ as "mixed catalyst".

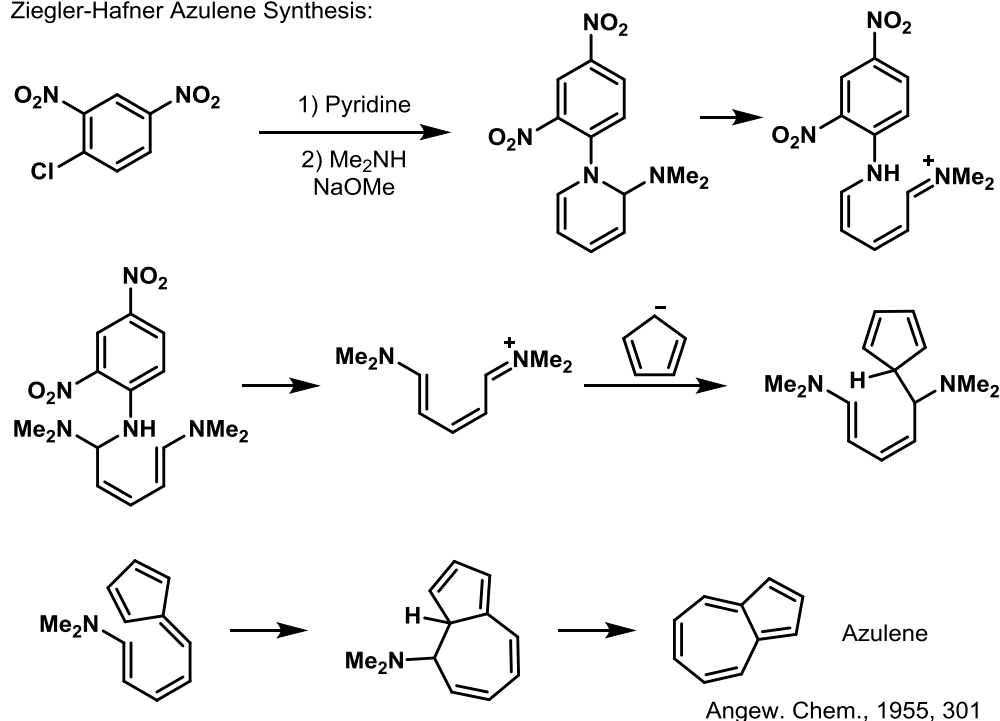
A 5 liter preserving jar from Ziegler's wife was used as a reactor:



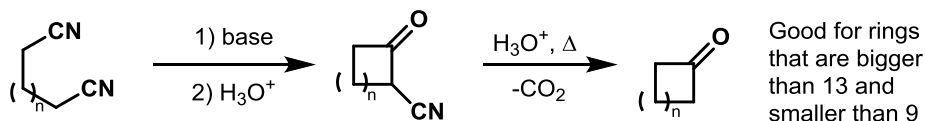
The first patent was submitted only 3 weeks after the discovery and recognized Erhard Holzkamp, Heinz Breil, Heinz Martin and Karl Ziegler as inventors.

Patent fights over more than 30 years were all won by the Max Planck Institute and therefore supplied enough money to finance the institute for 40 years. Heinz Martin was the main defender of these patents and wrote a book *Polymers, Patents, Profits* about this journey.

Ziegler-Hafner Azulene Synthesis:



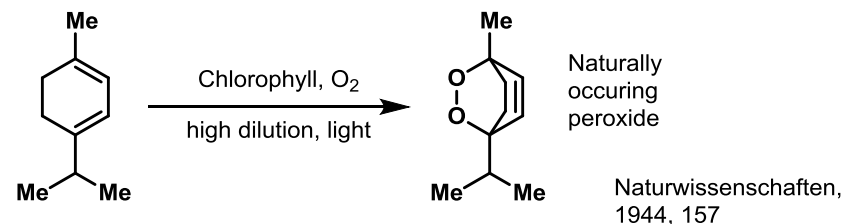
Thorpe-Ziegler Reaction (makes use of the Ziegler-Ruggli dilution principle)



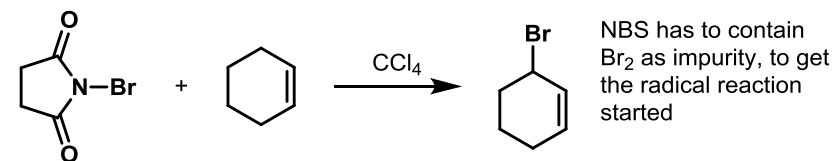
Ziegler receiving congratulations from the king of Sweden for his Nobel Prize

Important work by Ziegler that was not done in Mülheim:

Total Synthesis of Ascardiol:



Wohl-Ziegler Bromination of the allylic position:



Simplification of the BuLi synthesis:

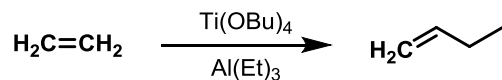
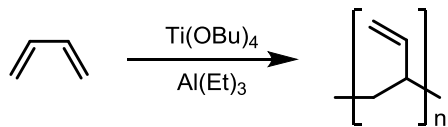


Günther Wilke, 1925-2016, Director 1969-1993, "He is the man who brought sex into chemistry" (Robert A. Welch, 1965)

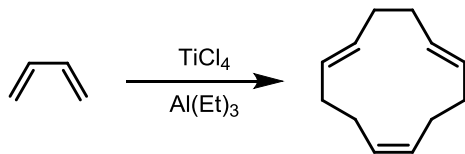
Wilke already worked several years under Ziegler and some of the reactions presented here were discovered in the Ziegler era.

He renovated the old "director's house" and made a canteen out of it. Ziegler's comment after seeing this: "Well that's how it is. I earned the money with hard work and you are throwing it out."

Wilke found the following two reactions:



Then he questioned, what a classical ethylene-polymerization-catalyst would do in the case of butadiene?



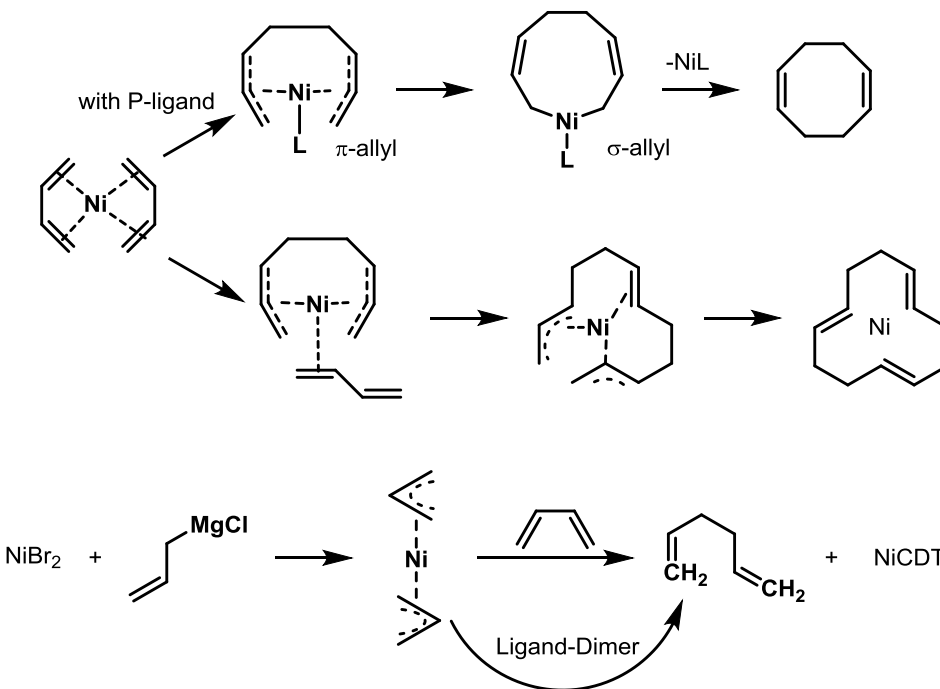
The E/Z configuration of the double bond in the trimerization product could be controlled by the employed transition metal. Nickel was suited best for the all trans product (>80%). It was also revealed that Nickel forms complexes with these olefines as ligands. These complexes became famous as "naked nickel".



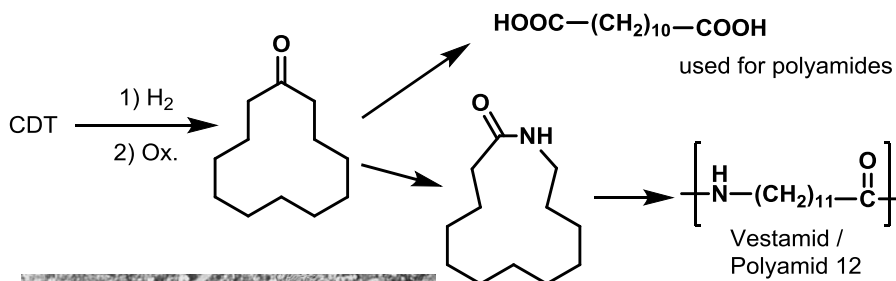
When one coordination site in the nickel was blocked by a phosphor-ligand, which could not be displaced by butadien, the trimerization would be prohibited and the dimerized product $\text{Ni}(\text{COD})_2$ was formed. NiCDT is a trimerization catalyst itself.

Wilke about the $\text{Ni}(\text{COD})_2$ synthesis: "We handled the synthesis in our pilot plant on a 10 kg scale without any interference. The synthesis belongs to the indispensable practice-tasks for new students."

Mechanism:

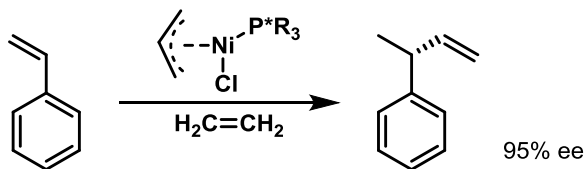


Two of the many industrial applications of CDT:

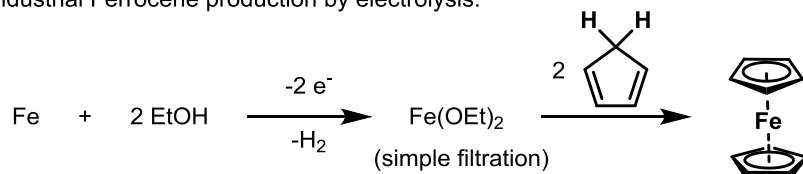


Wilke's contribution to Germany winning the WC 1974: the pins under the shoes are made out of Vestamid.
The picture shows the winning goal for the 2:1 victory over the Netherlands

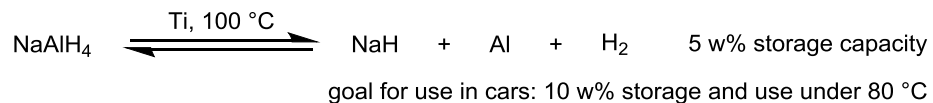
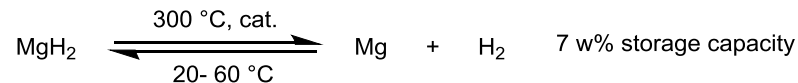
Chiral P-Ligands were able to add ethylene enantioselective:



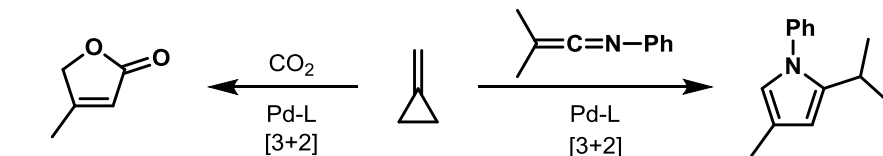
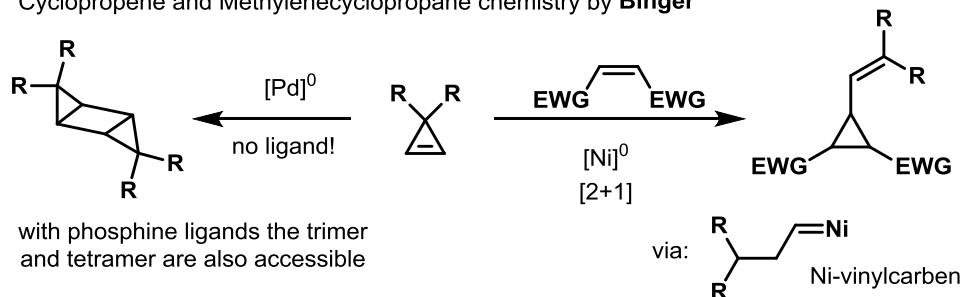
Industrial Ferrocene production by electrolysis:



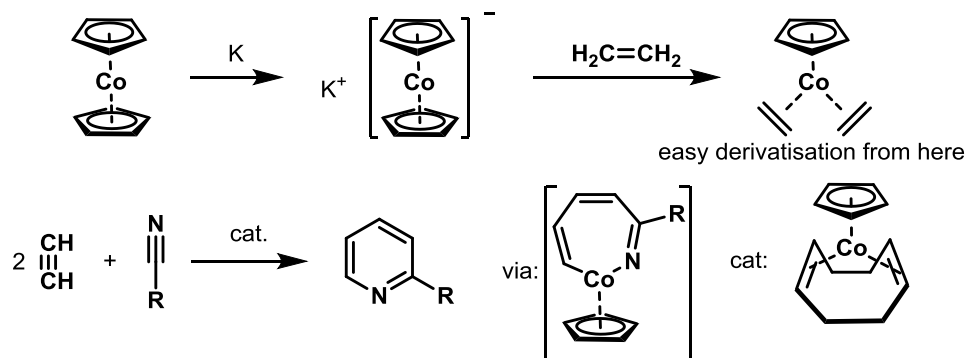
"hydrogen storage" by **Bogdanovic**



Cyclopropene and Methylene cyclopropane chemistry by **Binger**

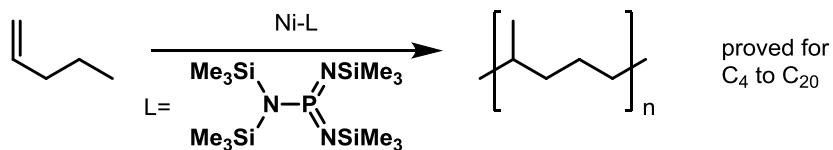


Metallocene chemistry by **Jonas**

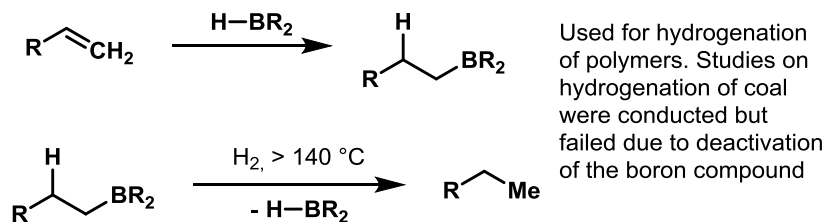


Recent Advances in
Mechanistic and Synthetic
Aspects of Polymerization, 515

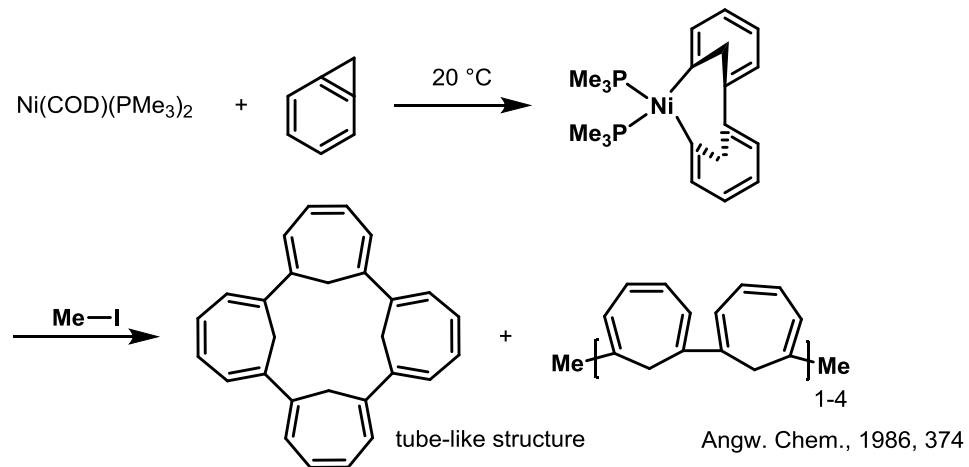
Unusual polymerization by **Fink**:



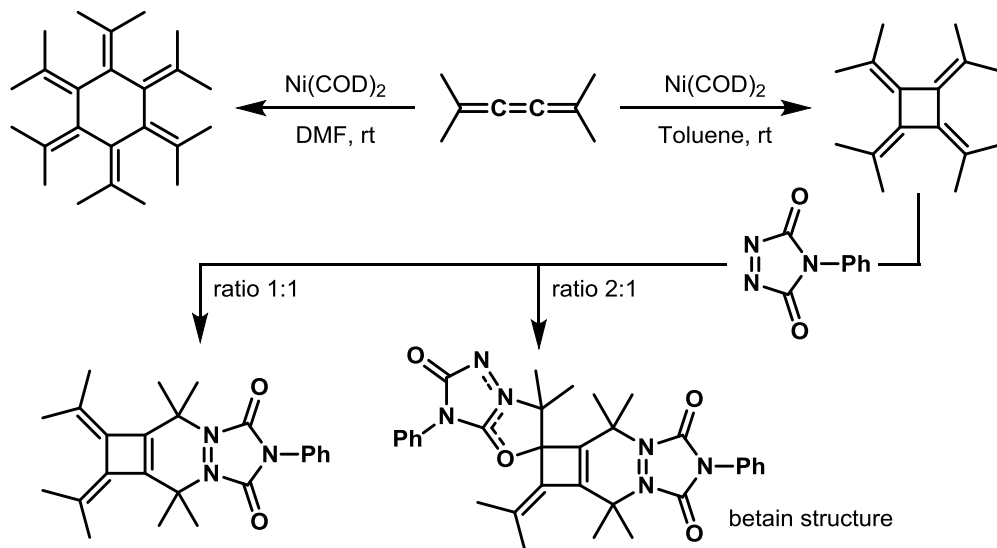
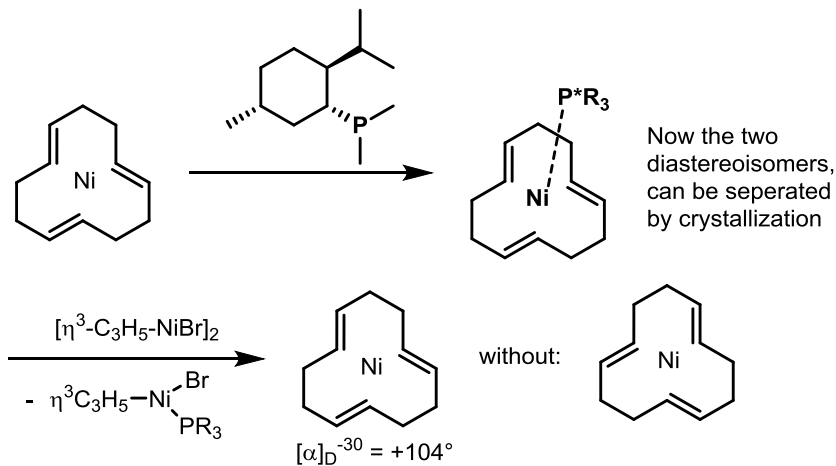
Hydrogenation without catalysts by **Köster**:

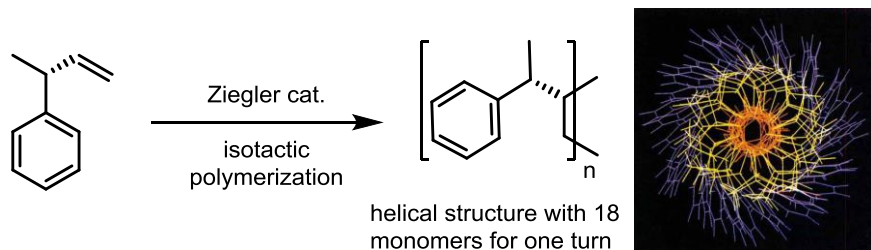


Basic research: interesting structures without any application?!

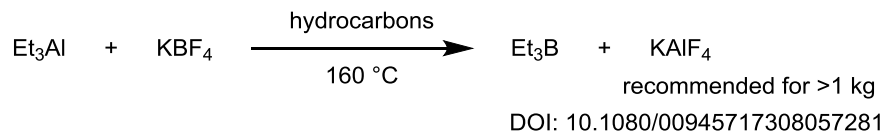
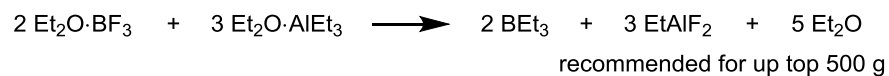
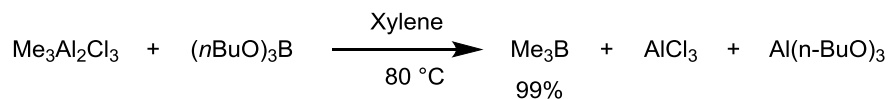


Is NiCDT chiral? Yes it is! The fourth free coordination site was used to separate the two enantiomers (by **Wilke**)

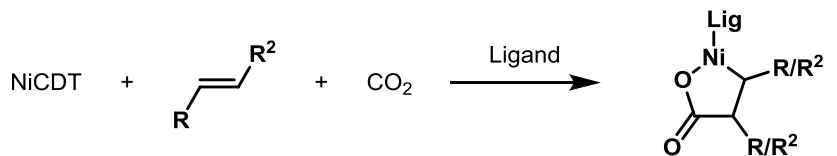




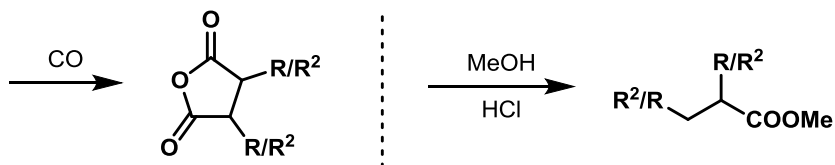
Convenient preparation of Boroalkyls by **Köster**:



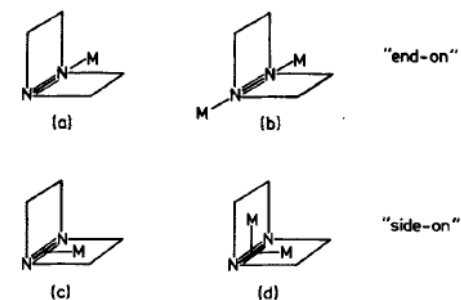
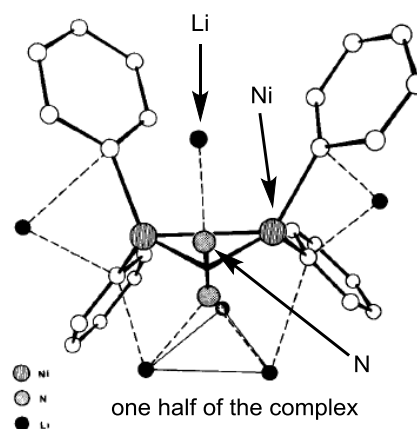
Reactions of alkenes & alkynes with CO_2 by **Hoberg**:



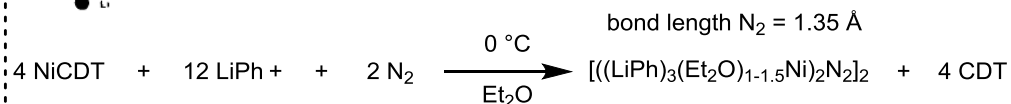
J. Organom. Chem., 1984, 203



The first "side-on" complexes of N_2 by **Jonas**:

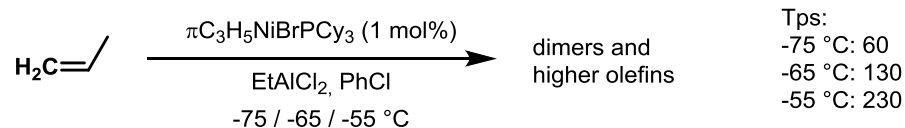


enzymes activate via "side on"



Turnover per seconds WR by **Bogdanovic**

Angew. Chemm, 1980, 622



Tps:
-75 °C: 60
-65 °C: 130
-55 °C: 230
extrapolation to 25 °C: ~60,000 tps
Meaning: 150 tons of product per hour and per 1 g of Ni capable of competing to enzymes!

Discovery of CO_2 as a solvent by **Zosel**:



Supercritical CO_2 dissolves highly selectively the caffeine in green coffee beans. Called "Destruction". Industrial process for producing caffeine free coffee. Much better than the prevailing extraction with DCM or EtOAc...