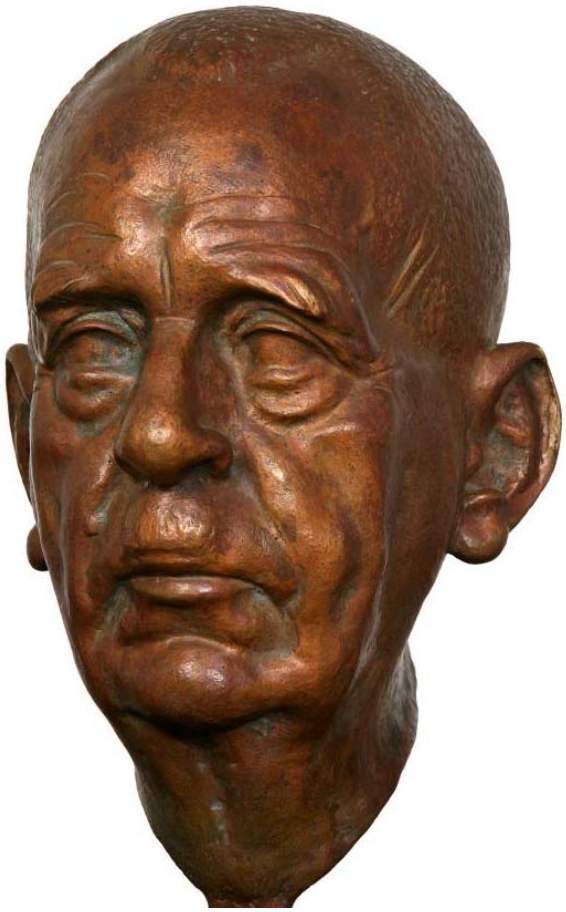
HISTORICAL LANDMARKS OF CHEMISTRY

Karl Ziegler

Mülheim an der Ruhr, 8th May 2008



Karl Ziegler, bronze bust by Professor Herbert Kühn, Mülheim an der Ruhr, 1964. Displayed in the Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr (Photo: T. Hobirk, 2008).

Kaiser-Wilhelm-/Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr. Upper: Original laboratory building from 1914, Kaiser-Wilhelm-Platz. Lower: Main laboratory building from 1967, Lembkestraße/Margaretenplatz (Photo: G. Fink, M. W. Haenel, ca. 1988).

GDCh

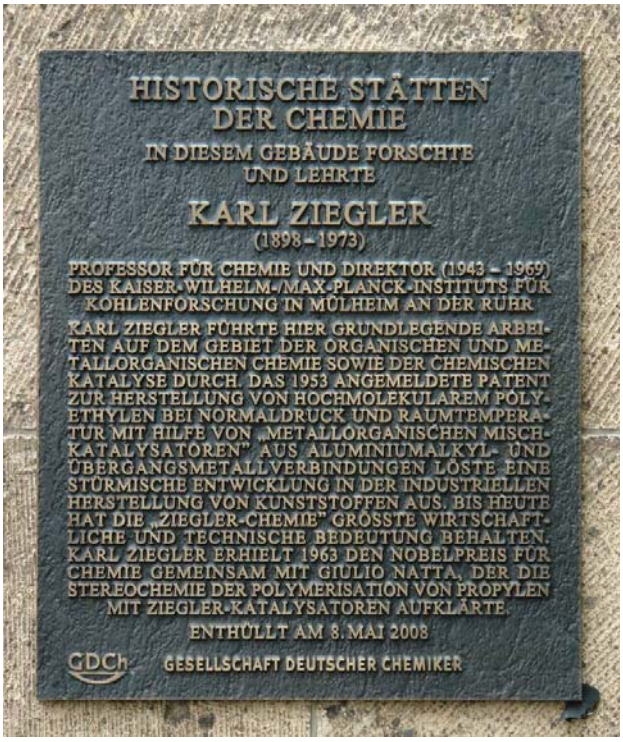
GESELLSCHAFT DEUTSCHER CHEMIKER

MAX-PLANCK-INSTITUT FÜR KOHLENFORSCHUNG · MÜLHEIM-RUHR

The programme **Historical Landmarks of Chemistry** (*Historische Stätten der Chemie*) was instigated by the *Gesellschaft Deutscher Chemiker* (*GDCh*, Society of German Chemists) in order to draw the attention of the general public to research which has been of particular significance to the development of chemistry in Germany. The objective is ultimately to further an interest in the cultural inheritance of chemistry while emphasizing its historical basis. The locations where important scientists made their most significant discoveries are recalled in an inaugural act with the unveiling of a plaque and with the publication of a booklet describing their work and its present day relevance.

On the 8th May 2008 the *GDCh* and the *Max-Planck-Institut für Kohlenforschung* (Max Planck Institute for Coal Research) in Mülheim an der Ruhr honoured the achievements of **Karl Ziegler** whose pioneering research in the field of organic chemistry led to a revolution in organometallic catalysis and organometallic chemistry. In 1953 he submitted a patent application describing the preparation of high molecular weight polyethylene at normal pressure and room temperature with the help of so-called *metallorganische Mischkatalysatoren* (organometallic mixed-catalysts) formed by treating transition metal compounds with alkyl-aluminium species and this led to an unprecedented growth in the industrial production of polyolefins. Polyolefins, such as polypropylene and polyethylene, are inexpensive, ecologically acceptable synthetic polymers which find use in a whole range of products and which make up over half of the 200-million tons of synthetic polymers produced annually. The discovery also accelerated the development of homogeneous catalysis using soluble organometallic complexes which has become one of the most innovative fields in modern chemistry and is of considerable importance in the production of organic compounds by the pharmaceutical and chemical industries. Karl Ziegler and the chemistry associated with his name found world-wide acclaim and in 1963 he was awarded the Nobel Prize for Chemistry along with the Italian Giulio Natta who had determined the stereochemistry of the polypropylene formed using Ziegler-catalysts.

A complete list of the honours which Ziegler received is shown below and includes honorary doctorates from the Technical University of Hannover (1951), the University of Gießen (1958), the University of Heidelberg (1958) and the Technical University of Darmstadt (1968). Ziegler was elected Honorary Senator of the *Max-Planck-Gesellschaft* (Max Planck Society) in 1968 and in 1964 he was awarded the *Große Verdienstkreuz* with star and shoulder band of the Federal Republic of Germany and in 1969 he was elected to the Order *Pour le Mérite* in the arts and sciences as the direct successor to Otto Hahn. In 1946 he was cofounder of the *GDCh* and until 1951 acted as its first President. In 1963 the town of Mülheim an der Ruhr awarded him the freedom of the city and in 1974 the local high school was renamed after him. Karl Ziegler was Director of the Institut für Kohlenforschung of the *Kaiser-Wilhelm-* and (after 1949) of the *Max-Planck-Gesellschaft* from 1943 to 1969. The income from his patents ensured the financial independence of the Institute for over 40 years and enabled an unprecedented expansion. The creation of the Ziegler-Fund in 1968 and the Ziegler-Foundation in 1970 ensured the continued financial support of the Institute and these still make a substantial contribution to the annual budget. Together with his wife Maria, he thanked the town of Mülheim an der Ruhr with the gift of their valuable collection of 20th century art while the generosity of their daughter Dr. Marianne Witte enables the *GDCh* to award a *Karl-Ziegler-Preis* and a *Karl-Ziegler-Förderpreis*.



Bronze plaque next to the entrance to the original laboratory building of the Kaiser-Wilhelm-/Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, Mülheim an der Ruhr (Photo: M. Teske, 2008).
Translation: Karl Ziegler (1898–1973) worked in this building as Professor of Chemistry and Director of the Kaiser-Wilhelm-/Max-Planck-Institut für Kohlenforschung in Mülheim an der Ruhr from 1943 until 1969.
Karl Ziegler carried out fundamental investigations in the areas of organic and organometallic chemistry as well as in chemical catalysis. The patent submitted in 1953 for the preparation of high molecular weight polyethylene at normal pressure and room temperature with the help of "organometallic mixed-catalysts" from aluminium alkyl and transition metal compounds led to a rapid development of the industrial production of synthetic polymers. Ziegler-chemistry is still of considerable economic and technical importance. In 1963, Karl Ziegler received the Nobel Prize for Chemistry together with Giulio Natta who had established the stereochemistry of the product of the polymerization of propylene using Ziegler-catalysts. Unveiled on the 8th May 2008.

Biographical Data

26 11 1898	Karl Ziegler is born in Helsa near Kassel as the second son of the pastor Carl August Ziegler and his wife Luise, neé Rall. He spent his early years in Helsa and, after 1910, in Marburg.
Sommer 1915	*Abitur* from the Realgymnasium of Marburg.
1916 – 1920	Chemistry student at the University of Marburg.
3 8 1920	Doctoral degree from the University of Marburg with a thesis entitled *"Untersu-*

	chungen über Semibenzole und verwandte Verbindungen" (Investigations on Semibenzenes and Related Compounds). Supervisor: Karl von Auwers.
11 3 1922	Marriage to Maria Kurtz from Marburg. The couple were to have two children – Marianne and Erhard.
1923	*Habilitation* at the University of Marburg with a thesis entitled "*Zur Kenntnis des dreiwertigen Kohlenstoffs: Über Tetra-Aryl-Allyl-Radikale und ihre Derivate"* ("Three Valent Carbon: Tetra-Aryl-Allyl-Radicals and Their Derivatives").
1925/1926	Temporary lectureship with Julius von Braun at the University of Frankfurt am Main.
1926	*Privatdozent* (lecturer) with Karl Freudenberg at the University of Heidelberg.
18 1 1928	Promotion to *außerordentlicher* (associate) Professor at the University of Heidelberg.
1936	Visiting Professor at the University of Chicago, USA.
1936 – 1945	Full Professor and Director of the Chemical Institute of the University of Halle an der Saale.
1 10 1943	Director of the Kaiser-Wilhelm-Institut für Kohlenforschung in Mülheim an der Ruhr as successor to Franz Fischer.
20 9 1946	Cofounder of the *Gesellschaft Deutscher Chemiker* (*GDCh*, Society of German Chemists) in the British zone of the divided Germany and Chairman until 1949.
15 8 1949	Honorary Professor at the Rheinisch-Westfälischen Technischen Hochschule Aachen.
1949 – 1951	President of the *GDCh* after the amalgamation of the regional branches in Frankfurt am Main on the 20 9 1949.
1952	Visiting Professor at the Universities of Madison and Urbana, USA.
1954 – 1957	Chairman of the *Deutsche Gesellschaft für Mineralölwissenschaft und Kohlechemie* (*DGMK*, German Society for Mineral Oil Science and Coal Chemistry).
1955 – 1957	Chairman of the Chemical-Physical-Technical-Section and Senator of the Max Planck Society.
9 7 1969	Retirement and appointment of Günther Wilke as his successor.
1970 – 1971	President of the *Rheinisch-Westfälische Akademie der Wissenschaften* (Academy of Science) in Düsseldorf.
11 8 1973	Karl Ziegler dies in his 74th year in Mülheim an der Ruhr and is buried in the main cemetery.

Honours

Honorary Doctorates

1951	Technical University of Hannover
1958	University of Gießen.
1958	University of Heidelberg.
1968	Technical University of Darmstadt.

Awards

1935	Liebig Memorial Medal of the *Verein Deutscher Chemiker*.
1953	Carl Duisburg Plaque of the *Gesellschaft Deutscher Chemiker*.
1955	Lavoisier Medal of the *Société Chimique de France*.
1958	Carl Engler Medal of the *Deutsche Gesellschaft für Mineralölwissenschaft und Kohlechemie e.V (DGMK).*
1961	Siemens-Ring of the Werner-von-Siemens Foundation.
1962	Jobs-Statue of the *Mülheimer Bürgergesellschaft "Mausefalle"* together with the artist Otto Pankok.
1963	Nobel Prize for Chemistry together with Giulio Natta.
1964	Swinburne Medal of The Plastics Institute, London.
1964	*Großes Bundesverdienstkreuz mit Stern und Schulterband* of the Federal Republic of Germany.
1967	International Synthetic Rubber Medal of „Rubber and Plastics Age".
1969	Order *Pour le Mérite für Wissenschaften und Künste* (formerly *Friedensklasse*) as successor to Otto Hahn.
1971	Carl Dietrich Harries Plaque of the *Deutsche Kautschukgesellschaft*.
1971	Wilhelm Exner Medal of the *Österreichische Gewerbeverein.*

Honorary Memberships

1958	Chemical Society of Japan.
1959	Society of Chemical Industry, London.
1959	Honorary Chief of the Ponca Indians (a tribe of the Sioux's).
1963	Honorary Citizen of the town of Mülheim an der Ruhr.
1966	New York Academy of Sciences.
1966	Société de Chimie Industrielle, Paris.
1968	Gesellschaft Deutscher Chemiker.
1968	Honorary Senator of the Max Planck Society.
1969	Board of the Max-Planck-Institut für Kohlenforschung.
1971	Foreign Member of the Royal Society, London.
1972	Foreign Honorary Fellow of the Royal Society of Edinburgh.

Membership in Academies

Bayerische Akademie der Wissenschaften in Munich.
Akademie der Wissenschaften in Göttingen.
Deutsche Akademie der Naturforscher Leopoldina in Halle an der Saale.
Rheinisch-Westfälische Akademie der Wissenschaften in Düsseldorf (Founder President 1970/1971).

On the 10th December 1963 (just two weeks after his 65th birthday) Karl Ziegler received the Nobel Prize for Chemistry out of the hands of King Gustav VI Adolf of Sweden along with Giulio Natta, Professor for Industrial Chemistry in Milan. In the laudatio Professor Arne Fredga of the Nobel-Prize-Committee of the Royal Swedish Academy of Sciences summarized the achievements of both laureates as follows (A. Fredga, 1972):

"Our epoch has witnessed the gradual replacement of traditional materials by synthetic ones. We have all seen that plastics can often substitute glass, porcelain, wood, metals, bones, and horn, the substitutes being frequently lighter, less fragile, and easier to shape and work. It has in fact been said that we live in the Age of Plastics."

"Plastics consist of very large molecules or macromolecules often forming long chains of thousands of atoms. They are made by joining together normal-size molecules constituting the basic units. These molecules must be reactive, but some outside help is also necessary to make them combine. This outside assistance often used to be supplied by free radicals, added to trigger off the reaction of polymerization. The term "free radical" may conjure up political connotations, and indeed free radicals have much in common with revolutionaries: they are full of energy, difficult to control, and have an unpredictable outcome. Thus, free-radical reactions give polymer chains with branches and other anomalies."

The Nobel Laureates for Chemistry 1963: Karl Ziegler (left, Photo: T. Binz) and Giulio Natta (right).

"However, Professor Ziegler has found entirely new methods of polymerization. Studying organometallic compounds, he discovered that organoaluminium compounds, which are easy to prepare, are particularly suitable for work on the industrial scale. Peculiar electrical forces operate around an aluminium–carbon bond in a hydrocarbon chain: reactive molecules are drawn in and sandwiched between the carbon atom and the aluminium atom, thus increasing the length of the chain. All this happens much more quietly than in free-radical reactions. When the chain is long enough, we detach the aluminium and thus stop the further growth of the molecule. The combination of aluminium compounds with other metallic compounds gives Ziegler catalysts. These can be used to control polymerizations and to obtain molecular chains of the required length. However, many systematic experiments – and indeed some accidental findings – were necessary to reach this stage. Ziegler catalysts, now widely used, have simplified and rationalized polymerization processes, and have given us new and better synthetic materials."

King Gustav VI Adolf of Sweden congratulating Professor Karl Ziegler on the award of the 1963 Nobel Prize for Chemistry (Photo: Kyrgogath, Stockholm).

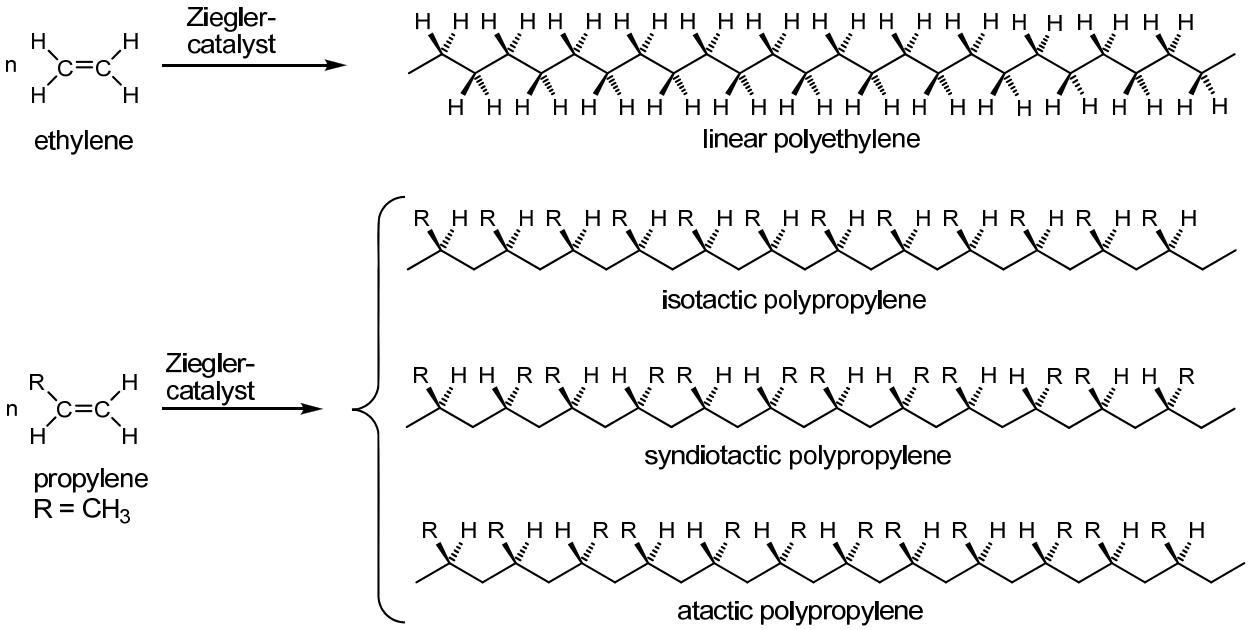
"The individual molecules strung together to form polymers are often so built that the resulting chain exhibits small side groups or side-chains at certain points, generally one at every other carbon atom. But the picture is more complicated, since these side groups can be oriented either to the left or to the right. When their orientations are randomly distributed, the chain has a spatially irregular configuration. However, Professor Natta has found that certain types of Ziegler catalysts lead to stereoregular macromolecules, *i.e.* macromolecules with a spatially uniform structure. In such chains, all the side groups point to the right or to the left, these chains being called isotactic. How is this achieved when the microstructure of the catalyst is probably highly irregular? The secret is that the molecular environment of the metal atom, at which new units are stuck on to the chain as mentioned before, is so shaped that it permits only a definite orientation of the side groups."

"Isotactic polymers show very interesting characteristics. Thus, while ordinary hydrocarbon chains are zigzag-shaped, isotactic chains form helices with the side groups pointing outwards. Such polymers give rise to novel synthetic products such as fabrics which are light and strong at the same time, and ropes which float on the water, to mention only two examples."

Karl Ziegler dancing with his granddaughter Cordula Witte during the banquet following the award of the Nobel Prize (Photo: L. Euling, Stockholm).

"Nature synthesizes many stereoregular polymers, for example cellulose and rubber. This ability has so far been thought to be a monopoly of Nature oper-

Polyethylene and Polypropylene



In the presence of Ziegler-catalysts, the molecules of the gas ethylene (CH_2=CH_2) link up to give long, straight chains of linear polyethylene ($[-CH_2-CH_2]_n-$). Each carbon atom of the polyethylene chain (shown schematically above as a two dimensional zigzag) is attached to two hydrogen atoms whereby, as a result of the tetrahedral bonding of the aliphatic carbon atoms, one hydrogen atom lies above and one below the plane. Propylene (CH_3–CH=CH_2) differs from ethylene in that one hydrogen atom has been substituted by a methyl group (CH_3–) and as a result every second carbon atom in the polypropylene chain is attached to a methyl group which can, moreover, lie either above or below the plane of the chain (this is shown above for every second carbon atom). A consequence is that stereoisomers are formed which differ in the arrangement of the methyl groups and Giulio Natta identified three structural types:
a) isotactic polypropylene in which the methyl groups adopt a regular arrangement either above or below the plane, b) syndiotactic polypropylene in which the methyl groups alternate and c) atactic polypropylene in which the methyl groups adopt a random arrangement (see above). By varying the Ziegler-catalysts, it proved possible to synthesize either isotactic or syndiotactic polypropylene in a stereospecific manner. In contrast to the atactic isomer, these are mainly crystalline in nature and isotactic polypropylene in particular has found a multitude of uses on account of its stiffness and stability.

ating with biocatalysts known as enzymes. But now Professor Natta has broken this monopoly."

"Towards the end of his life, Alfred Nobel was thinking of the manufacture of artificial rubber. Since then, many rubber-like materials have been produced, but only the use of Ziegler-catalysts enables us to synthesize a substance that is identical with natural rubber."

Professor Fredga's laudatio summarizes concisely the contribution made by the two prize winners. In 1963 in Stockholm Karl Ziegler had reached the summit of an over forty year career devoted to academic research and in his Nobel-Lecture entitled "*Folgen und Werdegang einer Erfindung*" (The Consequences and Development of a Discovery) he described the "long and winding" path which started with his earliest independent research on the structure and reaction of free radicals which he had submitted as his *Habilitation*-thesis in 1923 to the University of Marburg and which led finally to the discovery of the low-pressure polymerization of ethylene in October 1953 in Mülheim an der Ruhr. This research developed in general from an interplay between experiment and observation followed by deductions which led to the design of new experiments whereby the results in one area frequently suggested new approaches in other unexplored areas of organic chemistry. The initial work on free radicals led to the investigation of the organometallic compounds of the alkali metals and of organoaluminium compounds and finally to the "organometallic mixed-catalysts" which were to become so important for the industrial production of polyolefins. Ziegler often compared this consequent

Torchlight parade in honour of Karl Ziegler on the evening of the 5th November 1963 in Mülheim an der Ruhr just after it had been announced that he had been awarded the Nobel Prize. Front row (from left): Günther O. Schenck, Maria and Karl Ziegler, Günther Wilke and Heinz Martin (Press photo: J. Küpper, Mülheim an der Ruhr).

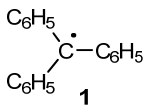
development – which had been interrupted by only few deviations – as that of a wanderer: "Actually the whole secret was that we – and I use the plural because it is clear that a whole host of talented coworkers was involved – wandered along with open eyes and an alert intelligence into an undeveloped but undoubtedly interesting area of organic chemistry". In his Nobel-Lecture he said: "My path could be compared to a journey through an unknown land which continuously presented interesting views enabling us to see part of the route which lay ahead although one had no idea where the journey would end. For decades, I had not the slightest idea that technical success would lie in my path."

CHILDHOOD AND THE MARBURG YEARS

Karl Ziegler was born on the 26th November 1898 in the vicarage of the small town of Helsa near Kassel as the second son of the pastor Carl August Ziegler and his wife Luise, neé Rall. He initially attended the Kassel-Bettenhausen primary school before moving on to the high school in Kassel. In 1910, the family moved to Marburg where he graduated from the local high school in 1915. His chemistry studies in the University of Marburg were interrupted by the year which he spent as a soldier on the Western Front during the Great War. In spite of this interruption, he obtained his doctoral degree in August 1920 "with distinction" just before his 22nd birthday with a thesis entitled "*Untersuchungen über Semibenzole und verwandte Verbindungen*" (Investigations on Semibenzenes and Related Compounds). The research was supervised by Karl von Auwers and led to three publications.

Immediately after completing his thesis, and encouraged by his supervisor, Ziegler began looking for an independent research topic. At this time free radicals of the type triphenylmethyl $(C_6H_5)_3C\cdot$ (**1**) were attracting considerable attention. **1** had been first observed in solution by Moses Gomberg in 1900 while attempting to prepare hexaphenylethane and the reason for the stability of this class of compound was the subject of much speculation. In order to investigate the role of aromatic and unsaturated aliphatic substituents in stabilizing the radical, the preparation of trivinylmethyl was considered and in 1923 Ziegler succeeded in preparing 1,1,3,3-tetraphenylallyl (**2**) as the first free radical containing an unsaturated aliphatic substituent.

Karl Ziegler in 1918, aged 19.



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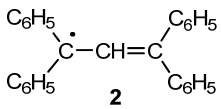

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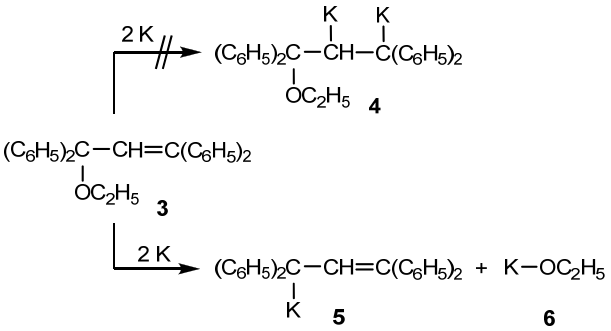
The results of these investigations formed the basis of his *Habilitation*-thesis and were published in 1923 in the *Annalen der Chemie* as the first contribution to the series "*Zur Kenntnis des dreiwertigen Kohlenstoffs*" (Concerning Three Valent Carbon). The chemistry of radicals occupied Ziegler for a further 27 years and in 1950 he published the 24th contribution to the series.

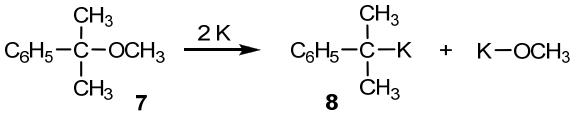
Karl Ziegler (standing, third from left) with his academic mentors Wilhelm Strecker (seated, left) and Karl von Auwers (seated, right) as well as O. Jordan, F. Krollpfeifer and H. G. Allardt (standing, left to right) in the courtyard of the Marburg Institute for Chemistry (1922).

Since the radical **2** dimerized much less readily than the triphenylmethyl radical **1**, Ziegler proposed investigating the effect of hydrogenation in order to see what role the olefinic double bond played. The radical **2,** however, resisted hydrogenation so that initially attention was concentrated on the precursor tetraphenylallylethyl ether (**3**) whereby an indirect hydrogenation procedure was envisaged involving the initial addition of an alkalimetal to the double bond followed by hydrolysis with water. Wilhelm Schlenk had shown a few years earlier that alkalimetal atoms could be added to compounds such as stilbene in which the double bond is substituted with aromatic groups. However, the product of the reaction of **3** with potassium was not the expected dipotassium compound **4**, instead the ether was cleaved to give tetraphenylallyl-potassium (**5**) and potassium ethanolate (**6**).



This novel and simple method for preparing organo-alkalimetal compounds offered an attractive entry into a new research area and by 1950 Ziegler had published 18 articles in the series "*Untersuchungen über alkaliorganische Verbindungen*" (The Investigation of Organo-Alkalimetal Compounds).

Subsequent attempts to discover the structural features which were needed to facilitate the cleavage of the ether of tertiary alcohols with an alkalimetal showed that at least one aromatic substituent must be attached to the tertiary carbon atom. The simplest ether in this class is 2-phenylisopropylmethyl ether (**7**) and the reaction of this compound with potassium gave access to 2-phenylisopropyl-potassium (**8**) as the most easily available, highly reactive organo-potassium compound known at the time.

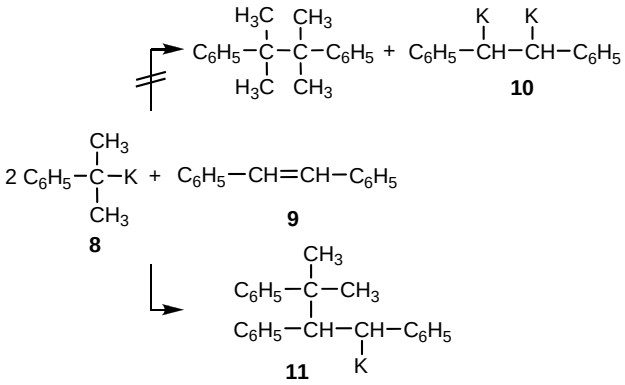


The Professors and Lecturers of the Chemistry and Physical-Chemistry Institute of the University of Heidelberg on the occasion of the retirement of the Institute's secretary Frau Weingärtner in 1930. From left to right: Herr Dürr, Emil Braun, Rudolf Lemberg, Karl Freudenberg, Herr Knopf, Frau Weingärtner, Walter Hieber, Ernst Müller, Werner Kuhn, Robert Stollé, Frl. Ella Sczendzina (the Institute's secretary, nicknamed "Chinchilla"), Wilhelm Dirscherl, Karl Ziegler and Otto Th. Schmidt.

ASSOCIATE PROFESSOR IN HEIDELBERG

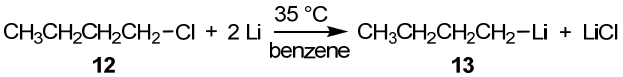
In 1925 Karl Ziegler accepted a temporary lectureship in Julius von Braun's Institute in Frankfurt am Main. From here in 1926 he moved to Heidelberg where Karl Freudenberg had just accepted the chair of organic chemistry as successor to Theodor Curtius. Following Freudenberg's recommendation, Ziegler was promoted to the position of *außerordentlicher* (associate) Professor in the University of Heidelberg on the 18th January 1928.

The investigations of the organo-alkalimetal compounds were continued in Heidelberg and once again the research received a new and important impulse from a reaction which took a completely different course from that expected. Ziegler treated 2-phenylisopropyl-potassium (**8**), which he had first prepared in Marburg, with stilbene (**9**) in the hope that the dipotassium compound **10** would be formed in analogy to the direct addition of metallic potassium to stilbene which had been reported earlier by Wilhelm Schlenk. Unexpectedly, however, the metal-carbon compound added to the C=C-double bond of the stilbene to give the potassium species **11**. In other words, the C=C-double bond had been inserted into the potassium–carbon bond of **8**.



This was the second novel reaction of an organo-alkalimetal compound which Ziegler had discovered within a short period and which, moreover, contrasted to the behaviour of the Grignard reagents which had been receiving most attention and which had been shown to add to C=O-double bonds but not to C=C-double bonds.

Further investigations showed that the reaction was limited to those olefins activated by suitable substituents such as the phenyl group in styrene (C_6H_5–CH=CH_2) or in stilbene (**9**) or the second double bond in butadiene (CH_2=CH–CH=CH_2). Olefins having alkyl substituents such as cyclohexene were unreactive whereby it should be noted that the simplest olefin ethylene (H_2C=CH_2) was at the time not available in Heidelberg. Alkyl-lithium compounds were also investigated. These were prepared using the method introduced by Wilhelm Schlenk: the thermolysis of alkyl-mercury compounds with lithium in a suitable organic solvent. The addition of the lithium species to olefins proved to be much slower than that of the potassium compound **8** and was therefore more suitable for kinetic studies. As part of these studies, the reaction of alkyl-lithium compounds with alkyl halides was investigated and this led to the discovery of a general method for the preparation of alkyl-lithium compounds directly from lithium metal and an organic halide. For example, under conditions which suppressed the C–C-coupling of two butyl groups (the Wurtz-Fittig Reaction) it proved possible to prepare butyl-lithium (**13**) from butyl chloride (**12**) and lithium metal.



This procedure has become one of the standard methods for preparing organo-lithium compounds and enabled the methodology of the Grignard chemistry with magnesium to be applied to lithium thereby opening up a highly productive research area as well as giving access to one of the most useful reagents in organic synthesis.

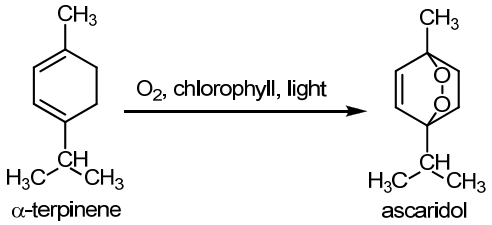
It is not improbable that the proximity of Heidelberg and Ludwigshafen (where at the BASF work was in progress with synthetic rubber) led to Ziegler's interest in the polymerization of butadiene. He was aware of the process for the polymerization of butadiene in the presence of sodium (BuNa) and he was convinced that a key step in this process was reflected in his discovery of the addition of

the potassium compound **8** to stilbene (**9**). An investigation of the polymerization of butadiene in the presence of alkyl-sodium species and butyl-lithium and the determination of the structure of the intermediates formed initially, provided evidence for a "step-wise organometallic synthesis" whereby the organo-alkalimetal compound adds to a butadiene molecule to give a new organo-alkalimetal species which in turn reacts with further butadiene. This type of repetitive reaction sequence is known as "anionic polymerization". In the case of butadiene and sodium it could ultimately be demonstrated that the reaction is initiated by the addition of two sodium atoms to a butadiene molecule.

In the early 30's, Ziegler turned his attention to a new area and between 1933 and 1954 he published 14 articles in a series entitled "*Über vielgliedrige Ringsysteme*" (Many-Membered Ring Systems) and which represented one of the few deviations in his journey through organic chemistry. His interest was apparently stimulated by Leopold Ruzicka's investigations of the musk components muscone and zibetone which contain 15- and 17-membered rings. Ziegler developed an efficient method to synthesize large, cyclic ketones containing up to 32 carbon atoms using organometallic reagents. The key step was a cyclization reaction (ring closure) in which a long-chain dinitrile is treated with an organo-lithium- or organo-sodium amide whereby the reaction is carried out under high dilution in order to suppress the formation of linear polymers. This procedure has found its way into the textbooks as the "Ruggli-Ziegler Dilution Principle". The method was applied successfully to the synthesis of the racemate of the natural product muscone. Ziegler's interest in cyclic compounds never waned and in 1955 he contributed an extensive chapter on *"Methoden zur Herstellung und Umwandlung großer Ringsysteme"* (Methods for the Preparation and Conversion of Large Ring Systems) to the encyclopaedic series "*Houben-Weyl – Methoden der Organischen Chemie*" for which Ziegler, along with Eugen Müller, Otto Bayer and Hans Meerwein, acted for many years as co-editors.

PROFESSOR AND DIRECTOR OF THE CHEMISTRY INSTITUTE OF THE UNIVERSITY OF HALLE AN DER SAALE

The originality of Karl Ziegler's contributions to a variety of areas of organic chemistry impressed his colleagues and in 1935 the *Verein deutscher Chemiker* (Association of the German Chemists) awarded him at the age of 37 the *Liebig-Denkmünze* (the Liebig Memorial Medal) for "his research on three valent carbon radicals and for his imaginatively designed and consequently accomplished syntheses of many-membered ring systems". As a result the *Reichserziehungsministerium* (Ministry for Education) could no longer ignore him, even though he and his wife made no secret of their distrust of the National Socialists, and in 1936 he was appointed Professor and Director of the Chemical Institute of the University of Halle an der Saale. As head of the institute, Ziegler had much better research facilities even though these were soon to be limited by the outbreak of the Second World War. In addition to extending his investigations of the carbon radicals, he began to explore new areas and with the introduction of N-bromosuccinimide he introduced an important reagent for the selective bromination of the allylic position of olefins which has found its way into the textbooks as the "Wohl-Ziegler-Bromination" and which is still a standard reagent in organic synthesis. Together with Günther O. Schenck, he extended his contributions to natural product chemistry and together they successfully synthesized cantharidine (the toxin produced by the Spanish-fly) as well as the phytogenic pesticide ascaridol produced by the American wormseed (*chenopodium anthelminticum*). The preparation of ascaridol from α-terpinene is a classical example of photo-oxidation by sensitization with chlorophyll whereby the chlorophyll in this case had been extracted from the leaves of spinach or stinging nettles.



These examples illustrate the width of Ziegler's chemical interests. However, from greater significance for the future was the continuation in Halle of the investigations on the polymerization of butadiene. In Heidelberg he had already shown that the organo-alkalimetal-induced polymerization of butadiene does not lead to uniform linear polymer chains. A mechanism involving organometallic intermediates can only lead to straight chain polymers if the stepwise addition of butadiene molecules proceeds in a regular 1,4-manner to the first and last carbon atoms of the butadiene molecule. However, an irregular 1,4- and

Karl Ziegler (right) and Günther O. Schenck in a laboratory of the Chemical Institute of the University of Halle an der Saale (ca. 1940).

1,2-addition was observed to give a product which seemed to be initially of little interest. In Halle, a systematic attempt was made to control the direction of addition by varying the reaction parameters and it was soon discovered that the only parameter of any importance was the reaction temperature: at low temperatures mainly 1,2-addition occurred while higher temperatures favoured 1,4-addition. Ziegler reported these observations in two review articles and in one original publication between the war years 1938 and 1943. These were presumably studied with interest in the nearby town of Schkopau where since 1937 synthetic rubber was being produced on a large scale by treating butadiene with sodium (*Buna*) as well as in Marl where the newly founded Chemische Werke Hüls in 1938 had constructed a plant for Buna-production whereby the review article entitled "*Ueber Butadien-polymerisation und die Herstellung des künstlichen Kautschuks*" (The Polymerization of Butadiene and the Production of Synthetic Rubber) which was published on the 16th February 1938 in the *Chemiker-Zeitung* must have been of particular interest. This review was preceeded by an editorial comment having the title "*Die Chemie im Dienste der nationalen Roh- und Werkstoffversorgung*" (Chemistry in the Service of the National Production of Basic Resources).

In the spring of 1943, Ziegler was contacted by the President of the Kaiser-Wilhelm-Gesellschaft, Generaldirector Dr. Albert Vögler, and offered the position as head of the Kaiser-Wilhelm-Institut für Kohlenforschung in Mülheim an der Ruhr as the successor to Franz Fischer.

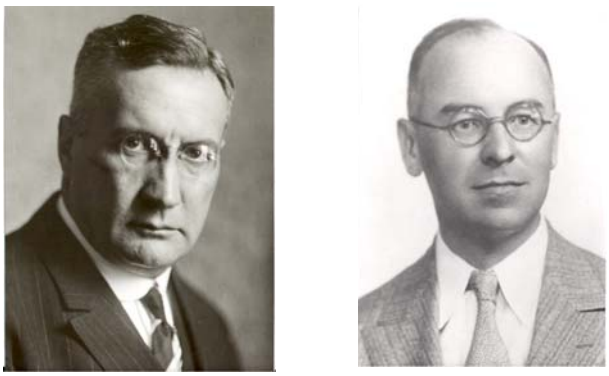
THE KAISER-WILHELM-INSTITUT FÜR KOHLENFORSCHUNG 1912-1943

The *Kaiser-Wilhelm-Institut für Kohlenforschung* in Mülheim an der Ruhr had been founded in 1912 by the *Kaiser-Wilhelm-Gesellschaft*, representatives of the local industry and the town of Mülheim an der Ruhr. The *Kaiser-Wilhelm-Gesellschaft* itself had been called into life only one year earlier in Berlin and had immediately founded two Institutes there – the *Institut für Chemie* and the *Institut für Physikalische Chemie und Elektrochemie*. The suggestion that a third Institute should be created to carry out research into the utilization of coal came from Emil Fischer, the Nobel Prize winner of 1902 and the leading organic chemist in Berlin at the time, and he suggested that for practical reasons it should be placed close to the coal and steel industry on the Rhine and Ruhr. Franz Fischer (1877–1947), Professor for Electrochemistry in the *Technische Hochschule* Berlin-Charlottenburg, was appointed as the Director in 1913 and in the summer of 1914 (after a construction time of only 9 months!) the laboratories were in operation.

Franz Fischer and his coworkers instigated a program involving both basic research into the origin and constitution of coal as well as its conversion into solid, liquid and gaseous products. Among others, his name is associated with the extraction of coal with benzene under pressure at 270°C to remove the bitumen fraction, with the production of tar by carbonization of coal in the Fischer-retort and with the so-called "lignin-theory" which suggested lignin to be the main precursor of humus coals on account

The Kaiser-Wilhelm-Institut für Kohlenforschung in 1914 (Postcard collection of U.-B. Richter).

of its resistance to biochemical degradation. It is also remarkable, in view of the modern interest in fuel cells and the conversion of gaseous fuels into electric current, that almost a century ago Fischer reported attempts to generate electricity by the "electrical combustion" of solid coal. However, without doubt, the most famous of Fischer's discoveries was the Fischer-Tropsch-Synthesis which he developed in 1925 together with the Group Leader Hans Tropsch and in which the gases carbon monoxide and hydrogen are converted into liquid hydrocarbons in the presence of a solid catalyst (a so-called heterogeneous catalyst) containing cobalt, iron, nickel or ruthenium. The carbon monoxide/hydrogen mixture (known as Synthesis Gas) was prepared by treating coal or coke with steam and oxygen at temperatures above 900°C. The product of the reaction was a mixture of liquid alkanes (C_5–C_{23}), waxes and a solid paraffin fraction (>C_{23}) containing some olefins and alcohols but no aromatic compounds. The main side products were water and small amounts of C_1–C_4 gases as well as water soluble, low-molecular weight alcohols, aldehydes, ketones and carboxylic acids. This two step process was the second of two important methods for converting the solid coal into liquid fuels. Earlier in 1913, Friedrich Bergius had demonstrated that coal could be directly hydrogenated by treating it with hydrogen at high pressure and 450°-500°C in the presence of a catalyst and a solvent to give a so-called "coal-oil".



Franz Fischer (left, ca. 1925) and Hans Tropsch.

In order to exploit his patents, Fischer in 1925 registered the *Studien- und Verwertungsgesellschaft mbH* in the Institute's name and in 1926 he used part of the income to build a pilot plant (*Fabrikbau*) next to the main laboratory building in order to demonstrate the industrial feasibility of the Fischer-Tropsch-Synthesis and this was

followed in 1929 by the construction of a lecture hall to seat 280. The Fischer-Tropsch-Synthesis went into commercial operation in the mid 30's: initially in the neighbouring town of Oberhausen with the *Ruhrchemie* as the main licensee and by the early 40's the process was operating in nine German plants and producing some 600 000 tons per year of liquid hydrocarbons. The *Ruhrchemie* also licensed four plants in Japan as well as in France and Manchuria. However, with the end of the Second World War and with the general availability of crude oil, the production of synthetic fuels became in general unprofitable. Political reasons were behind the decision by the Republic of South Africa to construct a plant in the 50's and at present the two large units operated by Sasol Synfuels in Sasolburg produce annually 6.6 million tons of gasoline and diesel from 45 million tons of coal and cover some 28% of the South African market. Synthesis Gas can, however, be prepared more cheaply from natural gas than from coal either by treating it with steam and oxygen (reforming) or by partial oxidation with pure oxygen and in 1993 Shell in Malaysia and PetroSa in South Africa started to operate Fischer-Tropsch plants based on natural gas. The GTL-Process (**G**as-**T**o-**L**iquid) in Malaysia has an annual production of 0.6 million tons of liquid fuels (equalling the total production of all nine German plants 65 years ago!) while that of the PetroSa plant is around 1.96 million tons per year. In 2007, Sasol and Qatar Petroleum started operating a plant on the Persian Gulf which has an annual capacity of 1.4 million tons while in the same area Shell together with Qatar Petroleum are constructing a third and even larger GTL-plant with a planned annual output of 5.6 million tons. Further plants are planned or under construction including one near Escravos in the Niger delta. Eighty years after its discovery, the Fischer-Tropsch-Synthesis is indeed experiencing an unprecedented boom.

The main lecture hall on the North side of the Institute in 1929 (Postcard collection of U.-B.Richter).

The *Kaiser-Wilhelm-Institut für Kohlenforschung* was initially financed by the coal and steel consortium on the Rhine and Ruhr with (after 1935) a contribution from the income derived from licensing the Fischer-Tropsch-Synthesis. In 1939 Franz Fischer changed the status of the Institute into that of an independent foundation (which it enjoys to this day) thereby giving it greater flexibility in its negotiations with the local industry as well as with the central administration of the *Kaiser-Wilhelm-Gesellschaft*. The objectives of the foundation were defined as the support of the scientific investigation of coal for the "common weal".

Max Planck (middle, in his role as President of the Kaiser-Wilhelm-Gesellschaft) with Franz Fischer (right) and his coworker Otto Roelen inspecting the products of the Fischer-Tropsch-Synthesis during a visit to the Institute on the 5th June 1934.

In the spring of 1942, Fischer – 65 years old and in poor health – submitted his resignation and suggested two of his group leaders – Herbert Koch (1904–1967) and Helmut Pichler (1904–1974) – as potential successors. However, neither Hermann Kellermann who had been Chairman of the Board of Governors of the Institute since 1935 and who was also Director of the mining company *Gutehoffnungshütte Oberhausen AG* and Chairman of the *Rheinisch-Westfälische* Coal Syndicate nor Dr. Albert Vögler in his role as President of the *Kaiser-Wilhelm-Gesellschaft* and Chairman of the *Vereinigte Stahlwerke AG* were of the opinion that either of them were suitable candidates. Vögler emphasised in a discussion with Kellermann in October 1942 that "it is not absolutely necessary that we choose somebody from coal chemistry and it would perhaps be better to look for a highly talented chemist with ideals who has no experience in coal chemistry and who would attack things without prejudice and perhaps introduce some new ideas". The search for a successor rested mainly in Vögler's hands and, among others, he contacted Otto Hahn, Richard Kuhn and Heinrich Wieland for suggestions. The potential candidates included the physical chemist Klaus Clusius as well as three organic chemists: Rudolf Criegee, Georg Wittig and Karl Ziegler. The Ministry for Education blocked Clusius's candidature presumably because he was needed in his chair in Munich where he was involved in isotope-separation as part of the Uranium-Project. Criegee was serving as a soldier on the Eastern Front and the attention focused finally on Karl Ziegler and, after the Ministry had given its approval, Albert Vögler contacted Ziegler in February 1943 and offered him the Directorship of the *Institut für Kohlenforschung* in Mülheim an der Ruhr.

Karl Ziegler's initial reaction was to turn the offer down since he was sceptical about carrying out objective-orientated research which was apparent in both the Institute's name as well as in its status. However, during the negotiations both the President of the *Kaiser-Wilhelm-Gesellschaft* as well as the Chairman of the Board of Governors made it clear that they were willing to accept the main condition under which Ziegler was prepared to move to Mülheim: "I must have complete freedom to work in the whole area of the chemistry of carbon compounds (orga-

nic chemistry) without making any allowances for whether my work has anything directly to do with coal". This was accepted and the Board of Governors of the *Institut für Kohlenforschung* appointed Karl Ziegler as its new Director on the 16th April 1943. At the same time, however, efforts were being made to persuade him to remain in Halle and these received the support of such authorities as Emil Abderhalden (President of the *Deutsche Akademie der Naturforscher Leopoldina* in Halle) and Adolf Windaus (the Nobel Laureate from Göttingen). The Ministry for Education, however, ignored these efforts and relieved Ziegler from his responsibilities in Halle for one year so that he could take up the temporary position as Director and Professor in Mülheim on the 1st October 1943. After further negotiations, he was appointed as the Director of both Institutes for one year. The increase in the intensity of air raids on West German towns led him to extend this double function until the end of the war in order to "have at least one functioning work place should total destruction occur"! The main research was carried out in Halle where Ziegler's family remained and he travelled backwards and forwards between the two centres. In June 1945 and shortly after the end of the Second World War, he and his family along with his co-workers were evacuated during the withdrawal of the American troops into their occupied zone in the West and then transported to Mülheim an der Ruhr.

The historian Manfred Rasch has investigated in detail the circumstances surrounding Ziegler's appointment in 1942/1943 and based on the available material he has suggested that the NS-Ministry for Education was keen to keep Ziegler in Germany, in spite of his political unreliability, and hoped that his appointment to an institution outside of the universities would limit his influence on students.

After his retirement in 1943, Franz Fischer returned to Munich where in the summer of 1944 his house was destroyed in an air raid and this was to repeat itself in his second apartment. He remained in contact with the Institute as an *auswärtiges Wissenschaftliches Mitglied* (external scientific member) and as a member of the Board of Governors. He died on the 1st December 1947 in Munich in his 70th year and is buried in the main cemetery in Mülheim an der Ruhr where in 1959 one of the streets near the Institute was named after him.

DIRECTOR OF THE INSTITUT FÜR KOHLENFORSCHUNG IN MÜLHEIM AN DER RUHR 1943 – 1969

During the night of the 22nd and 23rd June 1943 two thirds of the centre of Mülheim an der Ruhr was destroyed in an air raid. By a miracle, the *Kaiser-Wilhelm-Institut für Kohlenforschung* remained intact. However, by the end of the war, the Institute's financial bolster had melted away – the patents for the Fischer-Tropsch-Synthesis had expired while the industries based on these patents had either been completely destroyed or their operation had been forbidden. In February 1948 the *Max-Planck-Gesellschaft* was founded in Göttingen as the successor to the *Kaiser-Wilhelm-Gesellschaft* and this together with the coal mining syndicate put the Institute's finances on a new footing and in 1949 the Institute was officially renamed the *Max-Planck-Institut für Kohlenforschung*.

Initially the investigations into the Fischer-Tropsch-Synthesis were continued under the supervision of Fischer's Group Leaders, Herbert Koch and Helmut Pichler. In 1946 Pichler moved to Hydrocarbon Research in the USA and in 1948 he was appointed as *auswärtiges Wissentschaftliches Mitglied (*external scientific member) of the Institute and in 1956 he accepted the position as Professor for Chemical Technology and Director of the Engler-Bunte-Institute of the *Technische Hochschule* in Karlsruhe. Koch was promoted to *Wissenschafliches Mitglied* of the *Kaiser-Wilhelm-Gesellschaft* in 1947 and the research in his department on the synthesis of hydrocarbons finally came to an end in 1950. However, he continued to work with carbon monoxide and in 1952 he reported a new synthesis of carboxylic acids by reacting carbon monoxide with water and olefins which became known as the Koch-Haaf-Carboxylic-Acid-Synthesis and which found industrial application.

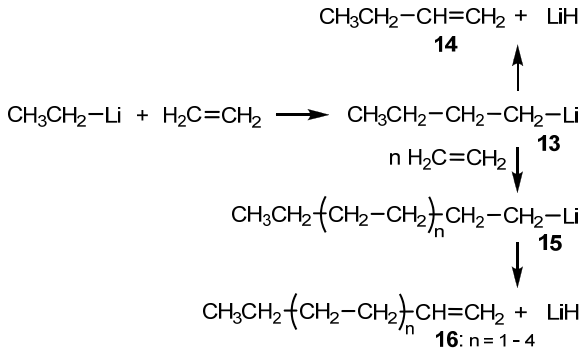
Maria and Karl Ziegler in front of the main entrance to the Institute on the Kaiser-Wilhelm-Platz in Mülheim an der Ruhr (presumably March 1948).

In 1954, during his participation at the sixty-fifth birthday celebrations for the General Secretary of the *Kaiser-Wilhelm-/Max-Planck-Gesellschaft*, Dr. Ernst Telschow, Ziegler admitted that when he took up office in 1943 he would have had trouble answering questions about the objectives of his future research. Initially he had only a handful of co-workers, most of whom were involved in the Fischer-Tropsch-Synthesis, so he decided to return to the problem of the distillation of alkyl-lithium compounds which he had been working on in Heidelberg in 1936 just before he moved to Halle. Ethyl-lithium had been described by Wilhelm Schlenk in 1917 as a crystalline, colourless solid which was soluble in hydrocarbons and which partially sublimed during attempts to determine its melting point in the usual capillary tubes. The reaction between alkyl chlorides and lithium metal which Ziegler had discovered in Heidelberg enabled alkyl-lithium compounds to be readily prepared on a large scale and he decided to investigate their properties more closely. Attempts had been made in Heidelberg to determine whether, in contrast to the analogous compounds of sodium and potassium which are ionic salts, they could be distilled but these had been inconclusive. In Mülheim he was able to show that the lower molecular weight alkyl-lithium compounds can indeed be distilled unchanged if heated in an

ultra-high vacuum and with a short distillation path. However, of greater importance than this observation was the fact that above 100 °C the alkyl-lithium species eliminates an olefin and generates lithium hydride. For example, ethyl-lithium reacts with elimination of ethylene:

$$H_3C{-}CH_2{-}Li \rightleftharpoons LiH + H_2C{=}CH_2 \qquad (1)$$

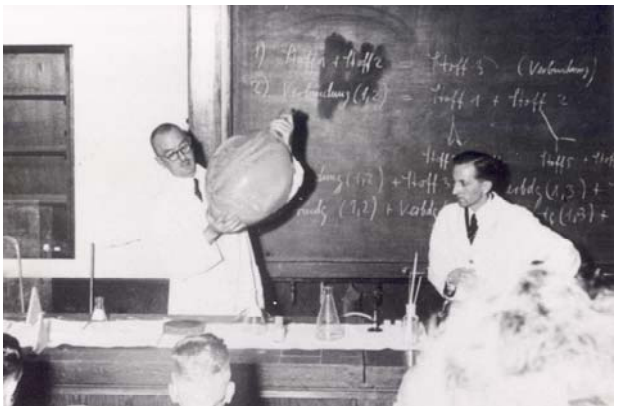
This observation was, however, not completely unexpected since a few years previously American authors had reported a similar reaction for ethyl-sodium while Ziegler himself in Heidelberg had observed the formation of lithium-hydride from the further reaction of specific organolithium compounds. What was unusual, however, was that during the decomposition of ethyl-lithium 1-butene (**14**) was formed in addition to ethylene. In other words an insertion reaction had taken place in which an ethylene molecule inserts into the carbon–lithium bond of ethyl-lithium to give butyl-lithium (**13**) which then reacts further with elimination of 1-butene:



Further experiments showed that if the alkyl-lithium compound is heated with ethylene under pressure then a stepwise, multiple insertion of ethylene molecules occurs to give higher alkyl-lithium species (**15**) which in turn undergo thermolysis to give lithium hydride and an α-olefin (**16**). Based on these observations, Ziegler concluded that if the degradation of ethyl-lithium according to equation 1 is reversible and ethylene can be inserted into lithium hydride (broken arrow), then under suitable conditions lithium hydride should catalyse the conversion of ethylene into higher α-olefins:

$$n\,H_2C{=}CH_2 \xrightarrow[?]{\text{cat.: LiH}} H{-}(CH_2{-}CH_2)_{n-1}{-}CH{=}CH_2$$

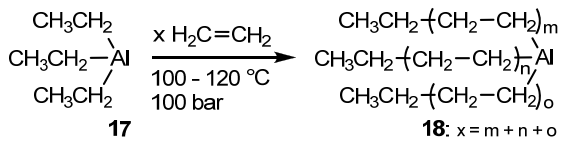
However, all attempts to carry out the reverse reaction, i.e. the addition of lithium-hydride to ethylene (equation 1), were unsuccessful – presumably because of the insolubility of the hydride in common solvents. However, in 1949 just as the investigations appeared to have reached a dead end, Ziegler's attention was drawn to a publication by Irving Schlesinger in the United States who had reported in 1947 that during the war he had been able to prepare lithium aluminium hydride ($LiAlH_4$) and that this was a soluble salt. In one last experiment, Ziegler's co-worker Hans-Georg Gellert heated an ethereal solution of $LiAlH_4$ with ethylene at 180–200 °C and 100 bar and observed a rapid decrease in the pressure with the formation of a mixture of almost pure α-olefins (C_4–C_{12}). In other words, the oligomerization of ethylene, which had up until then eluded them, was catalysed by lithium aluminium hydride. Soon after it became apparent that the



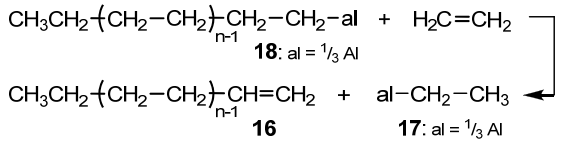
Karl Ziegler and Hans-Georg Gellert performing an experiment in the main lecture hall of the Institute (ca. 1948).

actual catalyst was not $LiAlH_4$ but was the lithium tetraethyl-aluminium ($LiAl[CH_2CH_3]_4$) which is formed at 120 °C by the reaction of lithium aluminium hydride with ethylene. Moreover, the initial assumption (based on the reaction of alkyl-lithium species with ethylene) that the reaction takes place at the lithium atom and that the aluminium fragment was responsible for the solubility was made unlikely after it had been shown that aluminium trihydride (AlH_3) when treated with ethylene gives triethyl-aluminium (**17**) and that this reacts further with ethylene in an even more efficient manner. This stepwise insertion of ethylene into the aluminium–carbon-bond has gone down in the text books as the *Aufbau*-Reaction and its discovery is a classical example of the scientific methodology whereby conclusions following experiment and observation lead to the design of new experiments. Furthermore, what had only been partially achieved with the relatively exotic and expensive lithium species could now be carried out more efficiently with a readily available and relatively cheap organoaluminium compound thereby enabling the development of a potential industrial process for preparing α-olefins.

The *Aufbau*-Reaction between triethyl-aluminium (**17**) and ethylene at 100 °C and under pressure led to the formation of higher trialkyl-aluminium species (**18**) and in the extreme case up to 100 ethylene molecules can be inserted into the aluminium–carbon-bond:



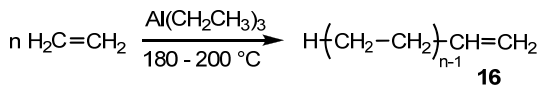
Commercially available polyethylene, however, is the product of the coupling of over 1000 ethylene molecules and this cannot be reached with the *Aufbau*-Reaction since the ethylene itself induces chain termination with the liberation of an α-olefin (**16**) and the formation of a new aluminium-ethyl fragment:



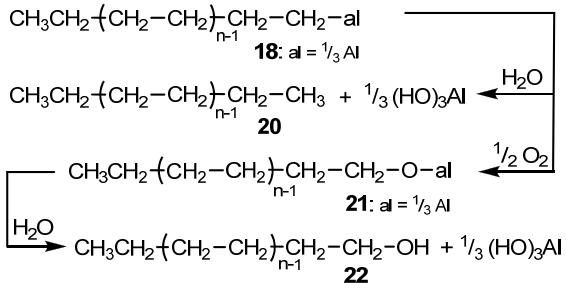
Mechanistically this chain-transfer step could occur either in one step involving a cyclic transition state similar to

that proposed for the Meerwein-reduction of aldehydes and ketones with triethyl-aluminium (**17**) or alternatively in a two step process with elimination of a dialkyl-aluminium hydride (R_2Al-H) followed by the addition of an ethylene molecule.

The rate of the displacement reaction increases upon raising the temperature and at 180–200 °C the trialkyl-aluminium acts as a catalyst for the conversion of ethylene into an α-olefin (**16**) whereby the composition of the product depends upon the relation between the growth and elimination steps and can be controlled by varying the parameters pressure, temperature and time. The production of α-olefins with longer chains is, however, preferably carried out in a two step process in which the growth reaction and the elimination reaction are carried out separately.



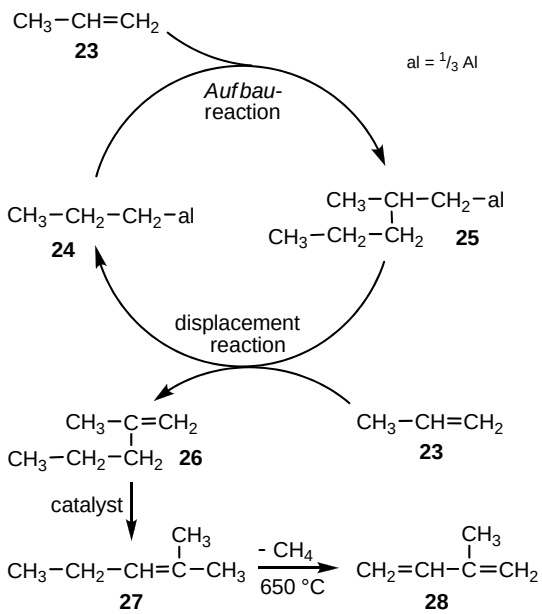
Hydrolysis of the trialkyl-aluminium species (**18**) formed in the reaction between triethyl-aluminium and ethylene led to the liberation of a long-chain alkane (**20**) containing an even number of carbon atoms and having a molecular weight corresponding to a hard or soft paraffin. The corresponding reaction with trimethyl- or tripropyl-aluminium led to a product having an odd number of carbon atoms. Although the reaction could not be used to prepare polyethylene (see above), Ziegler did succeed in integrating the *Aufbau*-Reaction into an industrial process for the production of long-chain primary alcohols (**22**) by first oxidizing the aluminium species (**18**) with air followed by hydrolysis of the resulting aluminium alcoholate (**21**):



The resulting straight-chain C_{12}- to C_{16}-alcohols (**22**) are ideal starting materials for the production of bio-degradable detergents. The process was licensed and by 1962 the Ziegler-Alcohol-Process was being used world-wide (Alfol-Process: Conoco, USA, 1962; Condea Chemie, Brunsbüttel, Germany, 1964; Ufa, Russland, 1981; Yiling, China, 1998; – Epal-Process: Ethyl Corp./Amoco, USA, 1964). In 1968 (the year of Ziegler's 70th birthday) the global annual production had reached 150 000 tons. The aluminium hydroxide formed in the reaction is also a commercially viable product and finds use in the production of aluminium oxide (alumina) for catalysts, ceramics, chromatography material and hygienic adsorption products (e.g. cat litter). An important side effect of the Ziegler-Alcohol-Process is that the mountains of foam which polluted our rivers and lakes in the 50's and 60's and which were associated with detergents having branched alkyl-chains, became a thing of the past.

Foam on the Ruhr in Duisburg in 1964 (Photo: dpa Picture-Alliance GmbH, Frankfurt am Main).

The *Aufbau*-Reaction of α-olefins with trialkyl-aluminium proceeds at a much slower rate than that involving ethylene and after only one step termination occurs since the branched-chain alkyl group generated, having additional substituents on the β-carbon atom, is less prone to further insertion. Furthermore, this branching favours the elimination step and as a result the product of the reaction of an α-olefin in the presence of catalytic amounts of a trialkyl-aluminium species at 200 °C is a dimer. For example, the product of the reaction of propylene (**23**) with tripropyl-aluminium (**24**) at 200 °C and 200 bar is almost exclusively 2-methyl-1-pentene (**26**): initially the branched-chain alkyl-aluminium species **25** is formed and this then reacts further with displacement of the dimer **26** and reformation of tripropyl-aluminium (**24**). This reaction also found industrial use and in 1963 the Goodyear-Scientific-Design-Process went into operation with an annual output of 50 000 tons of isoprene which is used in the production of synthetic rubber: the 2-methyl-1-pentene (**26**) is first isomerised to 2-methyl-2-pentene (**27**) and then converted into isoprene (**28**) by methane cleavage in a cracking plant.



However, before the organoaluminium compounds could be used on an industrial scale, an economic and

efficient synthesis had to be developed. This problem was solved in an elegant manner in 1954 when it was discovered that ethylene (or any other α-olefin) and hydrogen react directly with metallic aluminium to give the required trialkyl-aluminium species (equation 4). In the case of triethyl-aluminium (**17**), the reaction is best carried out in a two step manner with the intermediate formation of diethyl-aluminium hydride in order to suppress the *Aufbau*-Reaction (equations 2 and 3). Some 40 000 tons of trialkyl-aluminium compounds are still produced annually using this direct synthesis which is, moreover, an early example of what is now known as an "atomically economic" and "ecologically clean" process since no undesirable side products are produced.

$$2\,Al(CH_2CH_3)_3 + 1.5\,H_2 + Al \longrightarrow 3\,H\text{-}Al(CH_2CH_3)_2 \quad (2)$$

$$3\,H\text{-}Al(CH_2CH_3)_2 + 3\,CH_2{=}CH_2 \longrightarrow 3\,Al(CH_2CH_3)_3 \quad (3)$$

$$Al + 1.5\,H_2 + 3\,CH_2{=}CH_2 \longrightarrow Al(CH_2CH_3)_3 \quad (4)$$

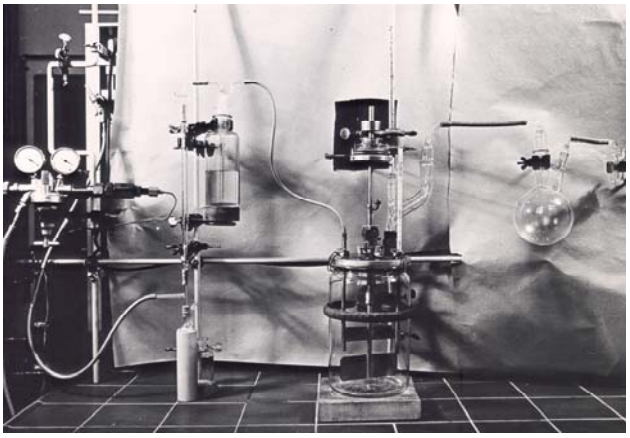
The Discovery of the Mülheim Low-Pressure-Polyethylene-Process

Over the years Ziegler and his coworkers had carried out the *Aufbau*-Reaction dozens of times – an autoclave was charged with triethyl-aluminium, ethylene at 100 bar was pressed in, the temperature was raised to 100 °C and a mixture of butyl-, hexyl-, octyl- and higher aluminium alkyls (**18**) was formed. However, in early 1953 and in the hands of the graduate student Erhard Holzkamp, the reaction unexpectedly took a different course: instead of higher alkyl-aluminium species (**18**) he obtained a quantitative yield of 1-butene (**14**) in additon to unchanged triethyl-aluminium (**17**), i.e. the triethyl-aluminium had catalysed the dimerization of ethylene. It was assumed that traces of some foreign material were present which had dramatically accelerated the displacement reaction and Ziegler ordered an intensive search for the impurity. A few weeks later, the culprit had been identified as minute traces of colloidal nickel. It turned out that the graduate student's autoclave had previously been used for an hydrogenation reaction and traces of nickel had been deposited in the hair-lines on the inside surface of the autoclave. The autoclave had then been rinsed out with nitric acid and cleaned with a phosphate-containing detergent which had led to the formation of traces of insoluble nickel phosphate which had then been reduced by the triethyl-aluminium.

The influence of the "Nickel-Effect" on the course of the further investigations was two fold. Firstly, it was recognized that the introduction of nickel was a far more effective method than increasing the temperature to accelerate the elimination reaction and this found immediate use in the research devoted to the conversion of ethylene into 1-butene and higher α-olefins and secondly, and characteristically, Ziegler instigated a systematic investigation of the effect of other transition metal compounds on the *Aufbau*-Reaction. Preliminary experiments were carried out by Erhard Holzkamp in May 1953 with chromium compounds but the results were somewhat inconclusive. However, after the summer break (in those days the Institute closed down for the month of August!) a new graduate student, Heinz Breil, was given the task of carrying out a systematic search and he discovered that in addition to nickel only cobalt and platinum accelerated the displacement reaction whereas iron and the other Group 8 metals as well as copper, silver and gold showed hardly any effect.

Then on the 26th October 1953, Heinz Breil carried out the reaction which was to revolutionize polymer chemistry: he treated triethyl-aluminium (**17**) with ethylene in the presence of zirconium acetylacetonate. The reaction was carried out under the standard conditions used for the *Aufbau*-Reaction (100 °C, 100 bar) but took a completely different course – a white mass of polyethylene was formed which could even be pressed into a translucent disc. Further experiments showed that similar results could be obtained using a combination of an alkyl-aluminium species and dialkyl-aluminium chloride with transition metal compounds of the Groups 4, 5 and 6 as well as with thorium and uranium while under some conditions a polymerization catalyst could be generated from other transition metal compounds including iron. However, the most effective catalysts turned out to be those involving titanium. In view of the importance of this discovery, it became clear that the investigations could not be completed in one thesis and the topic was divided between Heinz Breil, who carried out the experimental work, and the postdoctoral assistant Heinz Martin who concentrated on the more technical problems. It was Martin who first succeeded in polymerizing ethylene at normal pressure and room temperature using a catalyst consisting of diethyl-aluminium chloride ($[CH_3CH_2]_2AlCl$) and titanium tetrachloride ($TiCl_4$). Originally a 5-litre conserving jar from Maria Ziegler's kitchen was used as the reaction vessel (see photo below) and the ethylene was bubbled into a stirred solution of the catalyst in two liters of a suitable solvent such as petroleum ether. The temperature immediately increased and after a few minutes polyethylene flakes began to form. The temperature in the reaction mixture was kept at around 70 °C by cooling with a stream of air and within 1.5 hours 400 litres of ethylene had been polymerized and the stirrer came to a halt. A grey to brown suspension was formed, depending on the catalyst, but this changed to snow-white after air had been introduced. Practically all of the residual catalyst could be washed out with anhydrous alcohol to give 400 g of dry polyethylene.

This experiment in a conserving jar at room tempera-



The apparatus used to polymerize ethylene. The 5-litre conserving jar was contributed by Karl Ziegler's wife Maria.

ture and atmospheric pressure was a sensation and fascinated both visitors to the Institute as well as potential licensees. Up to this time, polyethylene was being produced commercially treating ethylene at 200–300 °C and 1500–3000 bar in the presence of oxygen, or some other radical precursor, using a process developed in 1933 by ICI in England. These drastic conditions are necessary to induce radical polymerization but as a result the growing polymer chain is subject to radical-transfer reactions with accompanying chain-branching and the high-pressure-polyethylene produced is a soft material with a relatively low density which makes it eminently suitable for the production of a number of products including plastic bags. The Mülheim low-pressure-polymerization, in contrast, proceeds by the step-wise insertion of ethylene molecules into the metal–carbon bond of the growing chain and as a result has a linear, straight-chain structure and is a hard, partially crystalline material with a relatively high density more suitable for molding into tubing and containers.

The "Ziegler-Polymerization" on a laboratory scale. The snow-white powder filling the conserving jar is polyethylene.

Patents and Licenses – the Polypropylene Dispute

Karl Ziegler submitted a patent to the German Patent Office on the 17th November 1953, only three weeks after Heinz Breil's original experiment. A claim was made for a method to prepare high molecular weight polyethylene by treating ethylene at 10 bar or more and at a temperature above 50 °C with an organometallic *Mischkatalysator* (mixed catalyst) consisting of a trialkyl-aluminium species and a transition metal compound of titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum or tungsten. As co-inventors he named Erhard Holzkamp, Heinz Breil and Heinz Martin. This patent was quickly followed by another four which described, among others, the application of the catalysts at room temperature and normal pressure as well as extending the catalyst to include uranium compounds, dialkyl-aluminium chlorides and the alkyl-compounds of magnesium and zinc. Ziegler limited the claims originally to ethylene because in a preliminary experiment Breil had shown that the product of the reaction involving propylene was not a solid. The first indication that propylene could in principle be polymerized was obtained in January 1954 when Martin was able to isolate a copolymer from the reaction of ethylene together with propylene. However, a systematic study had to wait until the low pressure polymerization of ethylene had been explored in detail. In July 1954, Martin finally demonstrated that both pure propylene and 1-butene could be easily polymerized by the new catalysts and a sixth patent was submitted on the 3rd August 1954 extending the scope to α-olefins such as propylene and 1-butene.

Shortly after, Ziegler discovered that two Italian patents for the preparation of polypropylene had been submitted on the 8th June and the 27th July 1954 by the Italian chemical company Montecatini with Giulio Natta, Piero Pino and Giorgio Mazzanti as the inventors. Previously, in January 1953, Montecatini had signed an agreement with Ziegler covering the technical use of the reactions of organoaluminium compounds which included an extension to further developments and which was to give the company exclusive licensing rights in Italy for certain aspects. In order to gain experience in the preparation and handling of alkyl-aluminium species, Montecatini had sent two chemists and an engineer to work in the Institute from the end of February until the middle of December 1953. These guests were of course aware of the sensational discoveries which were being made during the second half of 1953. Whether the new organometallic mixed-catalysts formed part of the contract between Montecatini and the Institute was a moot point and was interpreted differently by the two parties. Early in 1954, Ziegler sent Montecatini copies of his German patent applications and had written in an accompanying letter: "I expect and assume that the further development of this group of new catalysts will be left solely and completely in our hands".

Giulio Natta was at the time a consultant to Montecatini and had access to all the information associated with the contract with the Institute and this enabled him to quickly move into the new field. Ever since his stay with Hermann Staudinger in Freiburg in 1932, Natta had devoted his attention to linear, high-molecular weight polymers and had in particular concentrated on their structural characterization using X-ray- and electron-diffraction methods. In view of his expertise in polymer and technical chemistry, the Italian government and industrial circles had in 1938 given him the task of promoting research in Italy in the area of synthetic rubber. He himself had begun to work in the area of the polymerization of olefins and diolefins. As he remarked in his 1963 Nobel-Lecture, his experience and knowledge in the area of industrial olefin chemistry enabled him to immediately recognize the importance and originality of the dimerization of α-olefins which Ziegler had described in 1952 during an important lecture which he had given during the annual meeting of the *Gesellschaft Deutscher Chemiker* in the Achema-Industrial-Fair in Frankfurt am Main and entitled "*Aluminium-organische Synthese im Bereich olefinischer Kohlenwasserstoffe"* (Organoaluminium Syntheses in the Area of Olefinic Hydrocarbons). In this lecture, Ziegler had described how it was possible with the help of alkyl-aluminium species to prepare a single dimer from each α-olefin in contrast to the known cationic catalysis which led to the formation of a complex mixture of isomers. It was Natta who suggested that Montecatini contact Ziegler and this had led to the licensing contract of January 1953.

The inauguration of Karl Ziegler as Honorary Chief "Mu-guh-gal-a" (medicine maker) of the Ponca Indians (a Sioux tribe) on the 29th May 1959. The ceremony was carried out by the Chiefs Big Buffalo and Little Buffalo during a visit to mark the start-up of the Alfol-Pilot-Plant in the Conoco-Research-Center in Ponca City, Oklahoma, USA.

In February 1954, Natta and his co-workers began to repeat the experiments which Ziegler had described in his patent application. Impressed by the activity of the catalyst, he decided to extend the experiments to olefins other than ethylene and in particular to α-olefins and vinyl species such as styrene ($C_6H_5CH{=}CH_2$). Using the Ziegler-catalysts based on titanium tetrachloride and triethyl-aluminium or diethyl-aluminium chloride he was able to prepare polymers from propylene, 1-butene and styrene. In the case of styrene, Natta noticed that the polymer had quite different properties from that formed in the presence of light or radicals while the initial product of the polymerization of propylene, 1-butene and styrene in the presence of the alkyl-aluminium/$TiCl_4$-catalyst was not uniform but consisted of a mixture of various components some of which were amorphous, non-crystalline and soluble while others were crystalline and relatively insoluble. After separation of the amorphous fraction by solvent extraction, the crystalline fraction was isolated and, in the case of polypropylene and polystyrene, it was shown with the help of X-ray diffraction that all the tertiary substituted carbon atoms (those attached to methyl or phenyl groups) had the same configuration for which Natta introduced the term isotactic (see p. 5). The carbon chains in crystalline, isotactic polypropylene and polystyrene form a spiral having either a left or a right hand screw whereby three monomer units form one turn of the screw (a so-called 3_1-helix) with the methyl or phenyl groups all pointing outwards. The unusual properties of these polymers are a result of the regular crystal packing of the spiral chains of the macromolecule. The Italian patent of the 8th June 1954 mentioned above and submitted by Natta and Montecatini covered the preparation of polypropylene using a catalyst derived from triethyl-aluminium and titanium tetrachloride as well as the crystalline polymer whose regular structure had been determined by X-ray diffraction. In the second patent of the 27th July 1954, the claims were extended to include the preparation of related crystalline polymers from olefins having four or more carbon atoms. In both patents, Natta described the catalyst used as a "Ziegler-catalyst" thereby clearly acknowledging the origins of his investigations. Later he modified the composition of the catalyst by, for example, using crystalline titanium trichloride instead of liquid titanium tetrachloride and this enabled him to polymerize propylene in a stereospecific manner to give practically pure crystalline isotactic polypropylene and in 1962, by using a catalyst based on vanadium tetrachloride (VCl_4) and a dialkyl-aluminium chloride species (R_2AlCl), he succeeded in preparing the crystalline syndiotactic isomer in which the methyl groups are arranged in an alternating manner (see p. 5).

Karl Ziegler sent a specimen of polypropylene to Milan on the 21st July 1954 and using X-ray diffraction Natta established that it had a 45-percent crystallinity. In other words, the polypropylene prepared in Mülheim and Milan using the new Ziegler-catalysts had similar structures. The submission of the Italian patents without informing Ziegler let alone obtaining his permission, strained the relationship between the two Nobel Prize winners and also led to a complicated patent dispute between Montecatini and the Institute which was to last some three decades. In Germany, the Montecatini applications were subjected to a lengthy examination after various companies had lodged serious objections and in 1966 they were rejected on formal grounds. As a result, Ziegler's application of the 3rd August 1954, which after a partial agreement with Montecatini had been put to one side, became of fundamental importance in the granting of licenses for the production of polypropylene. The processing of the patent was resumed in 1967 but it was only finally accepted in 1973 because a number of companies (who had failed to be granted licenses) had attempted to delay the procedure. In the end the German Patent Court intervened but by this time Ziegler had died and the patent coverage had lapsed three years earlier.

The most important market for polypropylene, however, was in the United States and the main dispute between Ziegler and Montecatini was carried out between the years 1960 and 1983 before the American Patent Office and in a variety of court rooms. In order to improve their chances with a foreign application, the two contestants were forced to cooperate and both parties submitted their applications on the same day to avoid mutual interference. After a lengthy procedure, in 1969 the American Patent Office accepted the priority of the application of the 3rd August 1954 and rejected those of Montecatini and Natta of the 3rd June 1954 and 27th July 1954 on the grounds that the initial Italian patent cited Giulio Natta as the sole inventor whereas in the American application, based on both patents, three inventors had been cited (Giulio Natta, Piero Pino, Giorgio Mazzanti). This was not acceptable in American law and the second application of the 27th July 1954 was classified as an "improvement" which had no influence on Ziegler's application. Ziegler's submission that the priority claimed by Montecatini was based on an illegal act was deemed no longer relevant. As a result Montecatini broke off all contacts with Ziegler in America and for many years attempted, through the courts, to reverse the question of the priority in their favour and to hinder the granting of patent rights to Ziegler for the polymerization of propylene and other α-olefins. Both without success. In 1983 the matter was finally settled out of court and Montecatini withdrew its allegations and priority claims and paid damages to the Institute. Previously (in 1981, in a court case not involv-

ing Ziegler) Montecatini had lost its "state-of-matter" claim for polypropylene, which they had been granted in 1971, in favour of Phillips Petroleum. The priority dispute with Montecatini and Natta also played a role in the lengthy processes which Ziegler was forced to carry through in the American courts against a variety of US chemical companies from 1966 on and in 1982 Judge C. M. Wright (District Court, Wilmington, Delaware), during a dispute with the company Dart concerning the priority for the preparation of polypropylene, ruled that: "Through application of Ziegler's discovery (catalyst), Natta at Montecatini, Martin at the Max-Planck-Institute, and subsequently, many others were able to produce crystalline polypropylene on a commercial scale." Two years later this was reinforced by the highest court of appeal in Washington D. C.: "It was Ziegler and his named co-inventors who invented those catalysts and told Natta about them. It is here immaterial who was the first to use those catalysts to polymerize propylene." The American courts classified the patent covering the Ziegler-catalysts as a "Pioneer-Patent" which deserved the widest possible protection whereas Natta's contribution was judged to be dependent on the information he had obtained from Ziegler.

A further decision of the American Patent Office in Washington proved to be unexpectedly lucrative for the Mülheim Institute. During the appraisal of one of the earliest applications in the USA, the examiner had requested that the application be divided into two since he was of the opinion that the process used to polymerize ethylene and α-olefins should be independent of the preparation of the catalyst on the grounds that one could in principle market the catalyst without it necessarily being used to polymerize ethylene. Ziegler had no choice but to submit to this request even though he was annoyed at the resulting delay in granting the patent. As a result, the patent covering the Ziegler-catalysts was granted in 1963 while the second covering the process was delayed until 1978 on account of lengthy "interference processes" which had to be carried through in order to determine the priority of the individual claims. At this time in the USA patent protection ran for 17 years to commence *after the patent had been granted* and since the process patent was granted only two years before the catalyst patent expired, the Institute enjoyed a total of 32 years of protection (1963–1995) for the polymerization of propylene. The American chemical industry protested at what they regarded as a double-patent, however, without success since the highest instance decided that the original division of the patent having been made at the request of the examiner at the end of the 50's was valid. Subsequently, American patent laws have been altered and brought into line with global practise which allows protection for the 20 years *following the submission* of the patent application so that there is unlikely to be a repeat of the "Lex-Ziegler".

The development outlined above gives some indication of Ziegler's astuteness in defending his original discoveries and in exploiting them commercially through options and licenses. Between the years 1952 and 1994, 80–90 options and licenses were granted world wide to various companies among which were the giants of the chemical and petrochemical industry whereby it proved advantageous that the necessary administrative organization already existed in the *Studien- und Verwertungsgesellschaft mbH* which had been created by Franz Fischer back in 1925 and which was renamed the *Studiengesellschaft Kohle mbH* in 1955. As a result, Ziegler was not only Director of the Institute but was also the Manager of the organization representing the Institute's interests. The licensing and administration of the income was, however, only one side of the medal, the other was the defence of the patents and between 1956 and 1999, 149 infringements and objections had to be warded off. Numerous interested parties had attempted to hinder the granting of the patents or at least to limit their scope. The patent dispute with Montecatini and Natta outlined above ran for 29 years while it took 18 years before it was ruled that the US company Dart was guilty of a patent infringement. Although Ziegler retired as Director of the Institute in 1969 he remained, until his death in 1973, the head of the *Studiengesellschaft Kohle mbH*. The new Director, Günther Wilke, was automatically a member of the Board of Executive Directors while Heinz Martin had been a member since 1970. Martin was a co-inventor of the process for polymerizing propylene and for many years parallel to his scientific investigations, he had assisted Ziegler with the technological aspects as well as with patent matters and until well into the 90's he represented the Institutes's interests in negotiations with potential licensees and in disputes over infringements. In 2002 he published a book entitled "*Polymere und Patente – Karl Ziegler, das Team, 1953-1998*" (English edition 2007: "Polymers, Patents, Profits – A Classic Case Study for Patent Infighting") in which he described in detail the complicated and fascinating story surrounding the discovery of the Ziegler-catalysts which Joseph Straus (Director at the Max-Planck-Institute for Intellectual Property, Competition and Tax Law) has described as "the most successful worldwide commercial exploitation ever of discoveries resulting from non-industrial research".

Karl Ziegler (middle) and officials of Hercules Powder during the inauguration in Parlin, New Jersey of the HITAX-plant in June 1957. The first plant for the production of High-Density-Polyethylene in the USA.

The income which accumulated enabled the Institute to operate as a financially independent organization for 40 years (until 1995) and even today the Ziegler-Fund and the Ziegler-Foundation, which he created in 1968 and 1970 and which he later transferred to the Institute, make a significant contribution to the Institute's income. The

annual production of polypropylene world-wide has now reached 40 million tons while that of polyethylene (high density and linear low density) is around 30 million tons and these are being produced using processes which have their origins in the discoveries made by Ziegler in 1953.

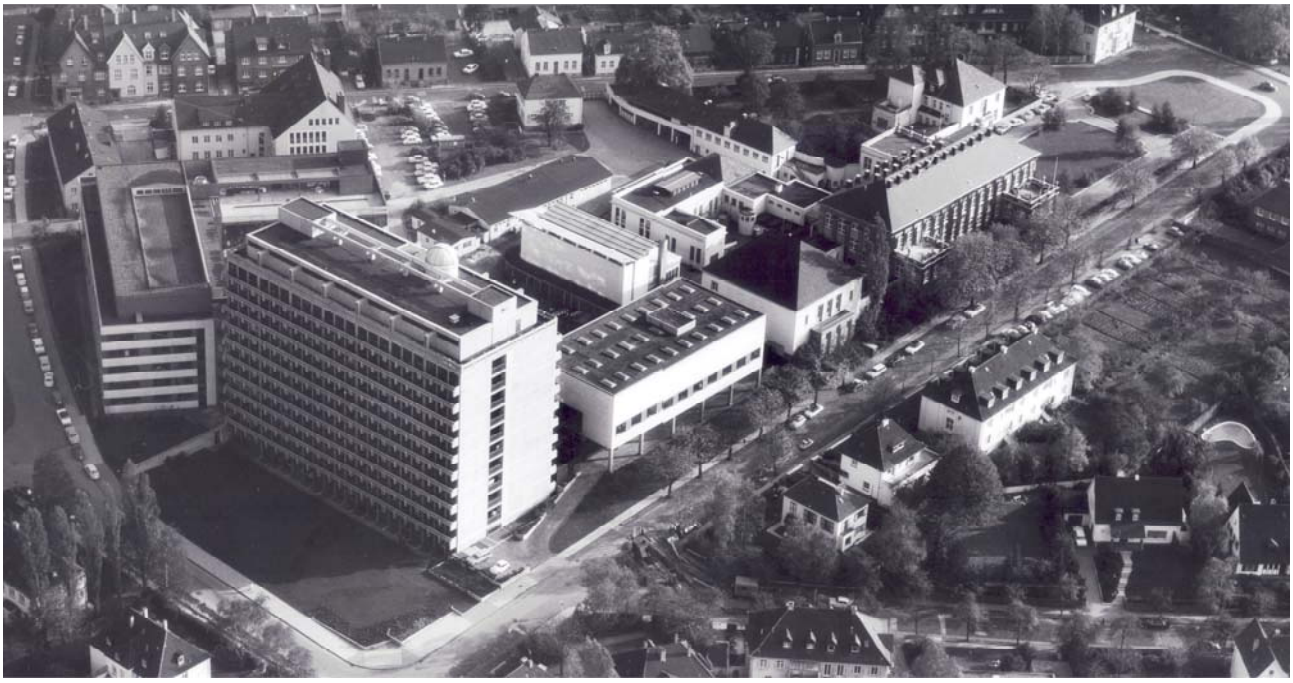
Expansion: New Buildings and New Co-workers

The Institute's income from licenses and options in 1954 amounted to almost 19 million D-Marks (while the annual budget was only 1.2 million D-Marks) enabled Ziegler to carry out much needed renovation and expansion plans. In 1954/55, the old laboratory building and the lecture hall were refurbished and, under the supervision of Karl Zosel, a new pilot plant building was constructed to extend Franz Fischer's *Fabrikbau*. It was at last possible to carry out safely high pressure experiments on a semi-technical scale and in 1957 several thousand litres of trialkyl-aluminium, which the licensing companies were still unable to provide, could be prepared for a variety of projects. In 1956 a provisional, prefabricated building (*die Baracke)* was constructed and this served for many years as the laboratories for Günther Wilke's research group. 1956 also saw the erection of the building to house the central heating system (*das Kesselhaus)*. In 1962, a three story building was completed to house the library and the administration and a start was made on the construction of the ten-floor main laboratory building (*das Hochhaus)* which was completed in 1967. In order to extend the width of the Institute's research, an independent department was established in 1958 to carry out research in radiation chemistry. The Director, Günther O. Schenck, had been one of Ziegler's graduate students during his time in Halle and had subsequently accepted a professorship at the University of Göttingen. Ziegler provided the means to establish the department while the further financing and the construction of an independent building in the 60's was in the hands of the *Max-Planck-Gesellschaft* with support from the Federal Ministry for Atomic Energy. This independent department later became the *Max-Planck-Institut für Strahlenchemie* (MPI for Radiation Chemistry) with, in 1981, three Directors – Oskar E. Polansky, Dietrich Schulte-Frohlinde and Kurt Schaffner. In the 90's the Institute passed into the hands of Karl Wieghardt and Wolfgang Lubitz and the research scope was redefined and in 2003 it was renamed the *Max-Planck-Institut für Bioanorganische Chemie* (MPI for Bioinorganic Chemistry).

When Ziegler arrived in Mülheim in 1943, the Institute had a working area of some 30 000 m^2 and by the time he retired in 1969 this had increased to 90 000 m^2. In the same period, the number of employees had grown from 13 to around 350. If the department for *Strahlenchemie* is included, the working area covered some 140 000 m^2 with 550 employees and at the time it was the largest institution administered by the *Max-Planck-Gesellschaft*.

Electrochemical Syntheses

In 1953 an observation made during the development of a new method to prepare triethyl-aluminium led Ziegler to invest considerable time and effort in the field of electrochemistry – in particular in the electrochemical syntheses of metal-alkyls and in the refining of aluminium. In the so-called "cryolite method", the mixture of diethyl-alumi-



An aerial photograph of the Max-Planck-Institut für Kohlenforschung in Mülheim an der Ruhr taken at the time of Karl Ziegler's retirement in 1969. At the time it was the largest of the Max-Planck-Institutes (view from N.W., Photo: W. Moog, Kettwig; released by the Reg. Präs. Düsseldorf, Nr.: 19/51/4785). The main laboratory building *(das Hochhaus)* is on the left facing the Margaretenplatz and is followed in the Lembkestraße by the library/administration building, the main lecture hall and the original laboratory building (*der Altbau*) facing the Kaiser-Wilhelm-Platz. The pilot plant building with its folded roof lies behind the lecture hall and next to the *Fabrikbau* from Fischer's era and behind these lies the prefabricated building (*die Baracke*) housing Günther Wilke's laboratories. The building housing the heating system *(das Kesselhaus,* with the steep roof) and the department for radiation chemistry (which later became an independent Institute) lies behind the main laboratory building. In 1977/78 a workshop was built on the parking lot next to the Kesselhaus and in 1979/80 the pilot plant was extended behind the administration building to house high-pressure facilities and the *Fabrikbau* was replaced by the Physics-Building (*Physikbau)* for the spectroscopic departments and this now also houses the Theory Department. *Die Baracke,* which was intended to be a temporary structure in 1956, was finally demolished in May 1982.

nium chloride and two equivalents of sodium fluoride was thermally converted to triethyl-aluminium along with cryolite (Na_3AlF_6) and sodium chloride. It was observed that at 100–120 °C, the sodium fluoride reacts further with the triethyl-aluminium to give sodium triethyl-aluminium fluoride (**29**) which then unexpectedly adds a second equivalent of triethyl-aluminium to give sodium hexaethyl-dialuminium fluoride (**30**, Et = CH_2CH_3):

$$\underset{}{NaF} + AlEt_3 \rightarrow \underset{\mathbf{29}}{Na^+[Et_3Al{-}F]^-} \underset{}{\overset{AlEt_3}{\rightleftharpoons}} \underset{\mathbf{30}}{Na^+[Et_3Al{\cdots}F{\cdots}AlEt_3]^-}$$

These salts (**29**) and (**30**) melt at 72 °C and 35 °C, respectively, and in the molten state conduct electric current. One of Ziegler's graduate students, Herbert Lehmkuhl, discovered that during the electrolysis of the 1:2-complex (**30**) pure aluminium is deposited on the cathode while at a copper or iron anode the ethyl radicals generated react further to ethane and ethylene. If, however, an aluminium anode is used, then this slowly dissolves to give triethyl-aluminium. In other words, an electrochemical cell results which can be used either to refine aluminium or for the cathodic coating of metal objects without consumption of the organo-aluminium electrolyte (**30**). On the other hand, using a lead anode the electrolysis consumes triethyl-aluminium to give quantitatively tetraethyl-lead which separates out as a liquid layer at the bottom of the cell. A continuous operation can be achieved by adding triethyl-aluminium and removing the tetraethyl-lead as it forms whereby it is necessary to periodically remove the aluminium and to renew the anode. The aluminium can then be reconverted into triethyl-aluminium by the direct reaction with hydrogen and ethylene as described earlier (equation 4, p. 14). The sum total of these individual steps is that it is possible to produce tetraethyl-lead from lead, hydrogen, ethylene and electric current. In a similar manner, anodes of magnesium, mercury, tin and antimony as well as sodium or potassium could be converted into the corresponding alkyl-metal species. Tetraethyl-lead was at the time being used as an anti-knock additive to gasoline (the annual production in 1957 in the USA alone was about 200 000 tons) and an electrochemical synthesis was of considerable commercial interest.

Ziegler and a number of co-workers spent 15 years trying to develop a technically viable process. The continuous removal of the aluminium deposited on the cathode proved to be an insoluble problem and the process had to be modified so that the metal was deposited in the form of a liquid which could then be removed. By using an electrolyte consisting of molten sodium tetraethyl-aluminium $Na^+[AlEt_4]^-$, it did prove possible to deposit liquid sodium at the cathode at temperatures above 100 °C but this introduced a new complication since for each sodium atom formed at the cathode, an ethyl radical was formed at the anode along with triethyl-aluminium and as a result a 4:1-mixture of triethyl-aluminium and tetraethyl-lead was formed at the lead anode which had then to be separated. Furthermore, secondary reactions occurred between the sodium and the products formed at the anode and the electrolysis could no longer be carried out in a simple two-electrode cell. This problem was solved using a mercury cathode which formed a liquid amalgam with the sodium and which could then be removed. The electrolyte, sodium tetraethyl-aluminium, could be regenerated by reacting sodium hydride (prepared from the elements) with triethyl-aluminium to give $Na^+[Et_3AlH]^-$ which was then reacted further with ethylene:

Georg Wittig, Otto Th. Schmidt, Karl Ziegler and Karl Freudenberg (left to right) on the occasion of the award to Ziegler of an honorary doctorate by the University of Heidelberg on the 18th November 1958 just before his 60th birthday.

$$Na + {}^1/_2\,H_2 \rightarrow NaH \xrightarrow{AlEt_3} Na^+[AlEt_3H]^- \xrightarrow{C_2H_4} Na^+[AlEt_4]^-$$

The process was actually even more complicated than that described above and over the years a variety of cells were constructed whereby those having rotating cathodes and anodes proved to be particularly effective. In 1969 an apparatus was set-up in the Institute's pilot plant to demonstrate that the whole procedure could indeed be operated in a continuous manner. However, a number of technical problems, including the circulation of the electrolyte, had still to be solved and in 1972 the project was finally abandoned. In the mean time, Ziegler had retired and tetraethyl-lead had fallen into ecological disrepute and alternative additives for gasoline had been developed.

However, the experience which had been gained in the electrolysis of organometallic compounds was not lost. The original graduate student, Herbert Lehmkuhl, was by now a Group Leader and until his retirement in 1991 he was involved in the development of, among others, a technical process for the electrochemical production of ferrocene (see p. 24) and processes for aluminium coating (see below).

In the early 80's, industry began to consider the possibility of using an organo-aluminium electrolyte for electrocoating with aluminium. The driving force was the search for a non-toxic alternative to zinc and cadmium for corrosion protection. The necessity to work with the organo-aluminium compounds in a closed system, which was originally regarded as a disadvantage, was now seen in a different light since one could thereby avoid pollution problems. Based on the procedure developed in Mülheim, Siemens introduced the SIGAL-process (**S**iemens-**G**alvano-**Al**uminium) and in 1983 the company Schempp & Decker in Berlin started operating the first plant. The electrolyte was 15 000 litres of a 50% solution of an ionic salt related to (**30**) dissolved in toluene. Further plants followed in Bergisch-Gladbach, Troisdorf-Spich and Herschbach, none of which are still operating. However,

in 2006 a plant was constructed in Montabauer-Heiligenroth by the *Aluminium Oberflächentechnik GmbH* which has an electrolyte capacity of 80 000 litres. The electrolyte, which was developed in the Institute by Herbert Lehmkuhl and Klaus Mehler, is a toluene solution of the 1:2-complexes of sodium or potassium fluoride with various trialkyl-aluminium species ($M^+[Al_2R_6F]^-$, M = Na or K, R = C_1–C_6-alkyl). A second plant is being operated in the USA by Alumiplate.

In the 80's and 90's a small plant was operated by the *Vereinigte-Aluminium-Werke* (VAW) in Grevenbroich to produce ultra-pure aluminium for microchips and condenser-foil using an electrolyte containing a salt related to (**30**) and modified so that the system could be operated at a ten fold higher current. In 1990, the *AUDI AG* in Ingolstadt, together with the Institute, developed an electrolyte which could be used to deposit an Al/Mg-alloy onto the steel screws used in the construction of the aluminium-magnesium gear box in automobile engines thereby helping to hinder local corrosion.

THE FURTHER DEVELOPMENT OF THE ZIEGLER-CHEMISTRY

The discovery of the Ziegler-catalysts in 1953/54 led to a revolution in macromolecular chemistry. Options and licenses were granted world-wide to the largest chemical companies and this led to a rapid development in polymerization and related areas. One of the earliest licenses in the USA was granted to Goodrich Gulf Chemical and they discovered in 1954/55 that isoprene (**28**) could be polymerized by a Ziegler-catalyst prepared from triethylaluminium and titanium tetrachloride to give either *cis*-1,4-polyisoprene (having the structure of natural rubber) or *trans*-1,4-polyisoprene (having the structure of gutta-percha) depending upon the ratio of the catalyst components while variation of the catalyst composition enabled butadiene to be converted into either *cis*- or *trans*-1,4-polybutadiene. In 1956, Günther Wilke in the Institute discovered at the same time as Giulio Natta in Milan that the treatment of butadiene with a catalyst prepared from triethylaluminium and titanium tetrabutanolate leads to the formation of 1,2-polybutadiene and one year later he discovered that butadiene is cyclotrimerized to the 12-membered ring cyclododecatriene by a catalyst prepared from titanium tetrachloride and an alkyl-aluminium species. This cyclotrimerization of an olefin by a Ziegler-catalyst was completely unexpected and later found use in the production of polyamides (see p.23).

The President of the Max-Planck-Gesellschaft, Adolf Butenandt (left), together with Karl Ziegler in the original library during a visit to the Institute on the 17th October 1961.

The economic and technical importance of the Ziegler-catalysts led to a dramatic increase in research activities in the field which continues unabated to this day. One of the original objectives was to increase the activity of the catalyst since in the earliest procedure the catalyst had to be deactivated upon completion of the polymerization and washed out of the polymer because traces of titanium chlorides and alkyl-aluminium chloride reacted with moisture liberating hydrogen chloride which tended to corrode the machinery used to process the polymer. Over the decades the activity has been increased a thousand fold and this has allowed the catalyst concentration to be so reduced that traces need no longer be removed from the product.

Catalysts of the 2nd generation were generated by preparing titanium trichloride particles with a much increased surface area and treatment of these with alkyl-aluminium species led to higher activities. This was followed by the deposition of the titanium component onto an inorganic supporting material and Montecatini in particular developed a supported catalyst involving crystalline magnesium dichloride ($MgCl_2/TiCl_4 + AlR_3$). The activity and stereospecificity could be increased even further by adding so-called donors such as benzoic acid alkyl ester, silyl ether, alkoxysilanes or 1,3-diether compounds. These catalysts of the 4th and 5th generation have become known as "high speed", "high mileage" or even "super high active" catalysts.

The development of *soluble* Ziegler-catalysts opened up a whole new area. Soon after the discovery of the original *insoluble* catalysts, it had been reported that soluble catalysts for the polymerization of ethylene could be prepared by reacting organometallic compounds such as bis(cyclopentadienyl)titanium dichloride (titanocene dichloride, $(C_5H_5)_2TiCl_2$) with alkyl-aluminium species. These were not particularly active but being soluble in organic solvents, they were ideal for kinetic and mechanistic studies. Using such a soluble catalyst, Gerhard Fink (head of the Institute's macromolecular and polymer department from 1980 to 2004) was able to show with the aid of ^{13}C-nuclear magnetic resonance spectroscopy that, in contrast to the *Aufbau*-Reaction, the polymerization of ^{13}C-enriched ethylene occurs with insertion into the titanium–carbon bond and not as was originally suggested into the aluminium–carbon bond and it is now generally accepted that the transition metal atom is the active centre in Ziegler-polymerization. Around 1980 it was also discovered that soluble titanocene and zirconocene derivatives react with methyl aluminoxane (MAO, the complex product of the partial hydrolysis of trimethyl-aluminium with a structure consisting of [–O–Al(CH_3)–] units) to give a more active catalyst capable of polymerizing propylene in an unstereospecific manner. The further development in the 80's involved the preparation of compounds in which the two five-membered rings of the titanocene derivative are linked together through rigid one or two atom bridges which in turn can be substituted by bulky substituents. Unexpectedly, H.-H. Brintzinger and W. Kaminsky in Germany and J. A. Ewen in the USA discovered that soluble catalysts of this nature containing chiral bridged metallocene compounds of titanium or zirconium and activated by MAO polymerize propylene and other α-ole-

fins in an highly stereospecific manner whereby the reaction can be directed to a particular product by varying the substituents. Since all of the catalyst centres in these stereorigid metallocene derivatives are structurally uniform (so-called single-site-catalysts), the reaction can be controlled in a precise manner. Using catalysts of this nature (the 6th generation), it has proved possible to control the microstructure and properties of the product and to extend the polymerization to cyclic olefins. The relationship between the catalyst structure and the architecture of the resulting polymer is now so well understood that it has even proved possible to predict the structures of the product using modern theoretical methods. The industrial utilization of the metallocene/MAO-catalysts has been made possible by depositing the catalyst onto an inorganic support such as silica gel and the resulting heterogeneous system can then be used in established processes. The development of the Ziegler-catalysts in the last fifty years has been described in detail in a number of review articles including those by Ludwig L. Böhm, Hans-Herbert Brintzinger et al., Gerhard Fink and Rolf Mülhaupt.

Karl Ziegler wearing the order *Pour le Mérite für Wissenschaft und Künste* which he was awarded in 1969 as successor to Otto Hahn (Photo: E. Serwotke).

The discovery of the Ziegler-catalysts not only accelerated the growth of macromolecular chemistry but it also led to an explosive development in the area of organo-transition metal compounds and their use in catalysis. Although it had been shown that the salt-like compound $K^+[(CH_2{=}CH_2)PtCl_3]^-$, discovered by the Danish pharmacist William Christopher Zeise as early as 1827, contained an ethylene molecule bonded to a platinum atom, interest in the area was limited and over the next 120 years only a handful of related organo-transition metal compounds had been reported and many of these had been discovered by accident. Most text books identify the birth of modern organo-transition metal chemistry with two discoveries made in the early 50's: the synthesis of ferrocene in 1951 (independently by two groups in England and the USA) and the discovery of the Ziegler-catalysts in 1953. The unusual stability of ferrocene $(C_5H_5)_2Fe$ – an orange, distillable solid soluble in many organic solvents – attracted considerable attention and led to a systematic investigation of this and related sandwich compounds in which unsaturated organic molecules are π-bonded to a transition metal atom whereby Geoffrey Wilkinson, Ernst Otto Fischer and Günther Wilke have made particularly significant contributions. The discovery and the investigation of these novel organometallic species and their use as catalysts have opened up one of the most innovative areas of modern organic chemistry.

We have already remarked that Karl Ziegler frequently compared his scientific career with a journey into an unmapped area of organic chemistry. He rarely seems to have lost his way and, with only a few diversions, he kept to the main path. During this journey, he scaled some of the highest peaks in organometallic chemistry whereby (as an enthusiastic mountaineer) he frequently chose the *diretissima* to the summit. Among these peaks were the preparation of alkyl-lithium compounds from metallic lithium and an alkyl chloride in analogy to the Grignard reaction. This procedure was developed further by Georg Wittig who used it to prepare phenyl-lithium which he described as his *Wünschelrute* (magic wand) and which played an important role in the development of his chemistry. Wittig was one of Ziegler's life-long friends and they had remained in contact ever since their time together with Karl von Auwers in Marburg and they even occasionally undertook mountain tours together in the Alps. Other important peaks in Ziegler's journey were the direct synthesis of alkyl-aluminium compounds from aluminium, olefins and hydrogen, the dimerization of α-olefins with alkyl-aluminium species, the use of the *Aufbau*-Reaction to prepare straight chain alcohols and finally the Mülheim polymerization process which towers over his other achievements in much the same way that the Matterhorn towers over the surrounding peaks in the Swiss Alps. Ziegler did actually climb the Matterhorn (via the Hörnligrat) in 1952 in the company of his son Erhard and his successor Günther Wilke.

Karl Ziegler's achievements had a remarkable influence on the development of chemistry in the 20th century and more than anyone else he can justifiably be regarded as one of the fathers of the age of synthetic polymers.

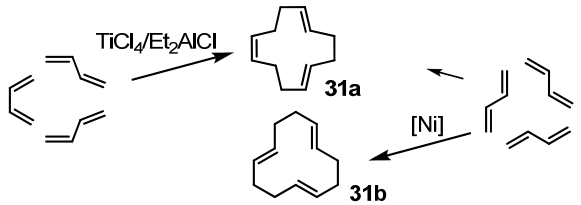
Karl Ziegler the mountaineer (presumably in the 30's).

KARL ZIEGLER'S SUCCESSORS

THE MAX-PLANCK-INSTITUT FÜR KOHLENFORSCHUNG 1969–1993: DIRECTOR GÜNTHER WILKE

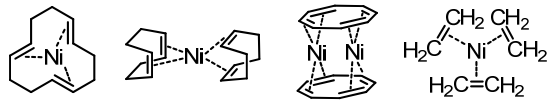
Karl Ziegler officially retired in 1969. His successor was Günther Wilke who had joined the Institute in 1951 after having completed his doctoral thesis with Karl Freudenberg in Heidelberg. In 1960 he submitted his *Habilitation*-thesis to the *Rheinisch-Westfälische Technische Hochschule* (University) in Aachen and in 1963 he was elected as *Wissenschaftliches Mitglied* (scientific member) of the *Max-Planck-Gesellschaft* shortly after several universities had offered him a chair of chemistry. The offer of a chair by the *Eidgenössische Technische Hochschule* (ETH) in Zürich led to his appointment in 1967 as Co-Director in the Institute with the prospect of becoming Ziegler's successor. From 1978–1990 he was Vice-President of the *Max-Planck-Gesellschaft*. In 1969, Roland Köster, who had joined the Institute in 1952 after having received his doctorate, was also elected as *Wissenschaftliches Mitglied* of the *Max-Planck-Gesellschaft*. Köster initially carried out investigations in the field of organo-aluminium chemistry but in the mid 50's he turned to organo-boron chemistry and by the time he retired in 1992 he had become a recognized authority in the area.

We have already mentioned that in 1956 Günther Wilke had discovered that butadiene could be selectively polymerized to 1,2-polybutadiene using a Ziegler-catalyst prepared from titanium tetrabutanolate and triethyl-aluminium. This observation contrasted to that of Heinz Martin that the same catalyst dimerized ethylene to 1-butene. It was therefore of interest to see how a typical catalyst for the polymerization of ethylene would react with butadiene and to Wilke's suprise, the reaction of butadiene in the presence of titanium tetrachloride and diethyl-aluminium chloride (Ti:Al = 1:4.5) led to a cyclotrimerization reaction of three butadiene molecules to give in over 80% yield the 12-membered ring compound *trans,trans,cis*-1,5,9-cyclododecatriene (*t,t,c*-1,5,9-CDT, **31a**):



Further experiments showed that in the presence of chromium oxychloride (CrO_2Cl_2) and triethyl-aluminium a 40:60-mixture of *t,t,c*-1,5,9-CDT (**31a**) and *all-trans*-1,5,9-CDT (**31b**) is formed while a catalyst prepared from nickel bis(acetylacetonate) and an alkyl-aluminium species converts butadiene into 80% *all-trans*-1,5,9-CDT (**31b**) along with the *t,t,c*-isomer (**31a**, 9%) and a third isomer *t,c,c*-1,5,9-CDT (11%, not shown).

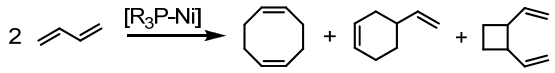
A particularly active catalyst is formed if the nickel salt is first reduced with triethyl-aluminium in the presence of butadiene whereby the nickel atoms produced are captured by the butadiene in the form of π-complexes before they can form larger nickel particles and precipitate. The orange-red solution reacts catalytically with further butadiene to give 1,5,9-CDT. This procedure subsequently became a standard method for preparing π-complexes of olefins with many transition metals. For example, the nickel complexes **32-34** could be isolated from the reduction of nickel bis(acetylacetonate) with alkyl-aluminium species in the presence of *all-trans*-1,5,9-CDT (**31b**), 1,5-cyclooctadiene (1,5-COD, **36**) or cyclooctatetraene. The simplest example in this family, the extremely labile tris-(ethylene)nickel (**35**), was however prepared by displacing the CDT-molecule from **32** by reaction with ethylene.



32 **33** **34** **35**

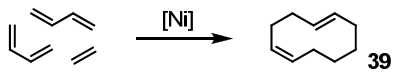
The nickel complexes **32** and **33** also catalyse the cyclotrimerization of butadiene to 1,5,9-CDT (**31**): at room temperature the excess butadiene displaces the 1,5,9-CDT-molecule from **32** as well as both 1,5-COD-molecules from **33** to give the 1,5,9-CDT-Ni-complex (**32**). Wilke introduced the term "naked-nickel" for nickel atoms in complexes of this type in which the reaction partner (here butadiene) completely displaces the original organic ligands.

Blocking a coordination site at the nickel atom in the catalyst with a phosphorus-containing donor ligand (a tertiary-phosphine or -phosphite), which is not displaced by butadiene, converts the cyclotrimerization catalyst into a cyclodimerization catalyst and a mixture of 1,5-COD (**36**), 4-vinylclohexene (**37**) and *cis*-1,2-divinylcyclobutane (**38**) is formed. Systematic investigations of this reaction subsequently showed that the product selectivity is dependent upon both the steric and electronic properties of the phosphorus-containing ligands and can be tailored to produce 1,5-COD with over 95%-selectivity.



36 **37** **38**

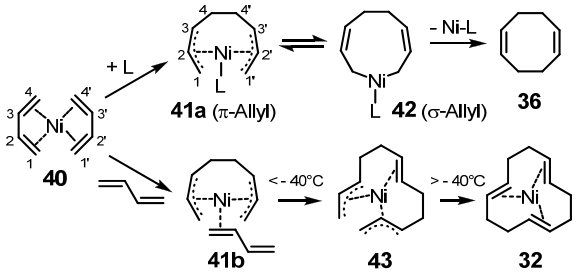
The "naked-nickel" catalyst is also able to convert two molecules of butadiene and one molecule of ethylene into the 10-membered ring *cis,trans*-1,5-cyclodecadiene (**39**) with a selectivity as high as 80%. The reactions discussed above provide a surprisingly simple and efficient access to 8-, 10- and 12-membered ring systems which had previously only been accessible through complicated, multi-step syntheses.



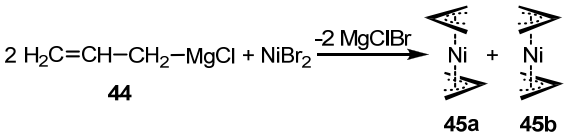
39

The novel sandwich-like compound **34** in which two cyclooctatetraene molecules are complexed to two nickel atoms proved to be the most efficient catalyst for the nickel-catalysed cyclotetramerization of acetylene to give cyclooctatetraene. This reaction had been discoverd by Walter Reppe in the laboratories of the BASF during the Second World War. The experimental observations suggest that **34** is the active species in the process and that it proceeds by the displacement of one of the two complexed cyclooctatetraene molecules by excess acetylene followed by the further reaction of four acetylene molecules with the two neighbouring nickel atoms to regenerate **34**.

Low temperature investigations of the nickel-catalysed cyclodimerization and cyclotrimerization of butadiene enabled a number of nickel-containing intermediates to be isolated and Wilke and his coworkers were able to show that in additon to π-olefin complexes of butadiene related to bis(butadiene)nickel (**40**), π-allyl-complexes are also involved. Complexes of this type, in which three neighbouring carbon atoms are coordinated to the metal atom, had previously received little attention and it could be shown that the two butadiene molecules in **40** couple to give an eight-membered chain bonded to the nickel atom through two terminal π-allyl groups (**41a**) with one coordination site occupied by a phosphorus-donor ligand. Further reaction with butadiene proceeds through the formation of the σ-allyl species **42** from which the 8-membered ring 1,5-COD (**36**) is liberated. The other cyclic dimers **37** and **38** are the products of the further reaction of related σ-allyl isomers. In the absence of a phosphorus-donor ligand, the bis(π-allyl)nickel species (**41b**) reacts with a third butadiene molecule with insertion into a nickel-allyl group and generation of an intermediate containing a nickel-bonded 12-membered chain (**43**) which reacts further with ring closure to give **32** from which 1,5,9-CDT (**31**) is displaced by further butadiene with regeneration of bis(butadiene)nickel (**40**).

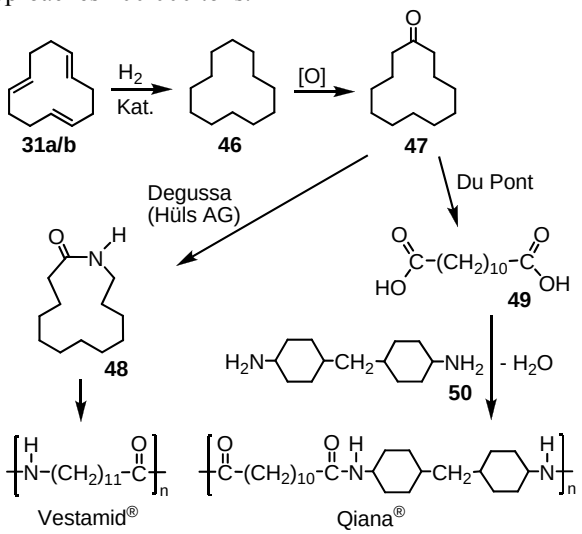


In order to confirm the involvement of π-allyl-nickel species in these catalytic reactions, the compound bis(π-allyl)nickel was prepared from allyl-magnesium chloride (**44**) and nickel dibromide: a 3:1-mixture of the *trans*- and *cis*-isomers **45a**/**45b** is formed.



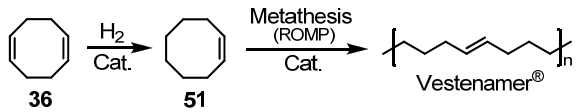
In addition to the olefin-nickel species **32** and **33**, bis(π-allyl)nickel (**45a**/**45b**) also catalyses the cyclotrimerization of butadiene to 1,5,9-CDT whereby in the first step of the catalytic cycle a butadiene-induced coupling and displacement of the two allyl groups as 1,5-hexadiene ($H_2C{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2$) occurs in a manner analogous to that proposed for the ring closure reaction of the bis(π-allyl)nickel intermediates **41a** and **43** in the cyclodimerization and cyclotrimerization of butadiene. Subsequent spectroscopic investigations enabled these intermediates to be identified and characterized. These investigations on the nickel-catalysed and ligand-controlled cyclodimerization and cyclotrimerization of butadiene provided a detailed insight into the mechanism of the catalytic processes and had a pioneer character in homogeneous catalysis and organometallic chemistry in general.

In the first publication on the synthesis of cyclododecane derivatives in the *Angewandte Chemie* in 1957, Wilke drew attention to the possibility of converting the cyclic compounds derived from butadiene into technically interesting polyamides and shortly afterwards industrial processes were in operation for producing nylon-related products, technically interesting olefins as well as polymers from the cyclodimers and cyclotrimers of butadiene. Degussa (Hüls AG) has been producing 1,5,9-CDT (**31**) since the 70's and the annual production now approximates 26 000 tons. The 1,5,9-CDT (**31**) is converted, through the intermediacy of cyclododecane (**46**), cyclododecanone (**47**) and laurine lactam (**48**) into nylon-12 (Vestamid®). Further plants for the production of CDT are operating in France (Shell), USA (du Pont) and Japan (Mitsubishi Chemicals) and the world-wide capacity approaches 100 000 tons.



Vestamid®, on account of its rigidity and stability, is the preferred polymer for a number of products including hydraulic tubing in heavy vehicles, fuel pipes, soles of sport shoes, cable isolation and special textiles. The polyamide fibre Qiana® introduced by du Pont and which has the feel of natural silk has found use in the *haut couture* and is prepared by the oxidation of cyclododecanone (**47**) to decane-1,10-dicarboxylic acid (**49**) followed by condensation with diamino-dicyclohexyl-methane (**50**).

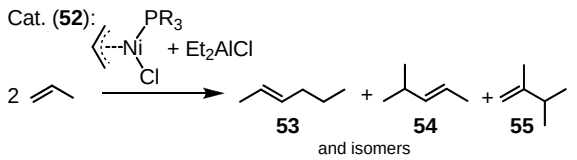
In 1980, Degussa (Hüls AG) began to produce 1,5-COD (**36**) on a large scale by the cyclodimerization of butadiene. This is then partially hydrogenated to cyclooctene (**51**) and reacted further by ring-opening-metathesis-polymerization (ROMP) to give the special rubber polyoctenamer (Vestenamer®) as the product of catalytic cleavage and recoupling of the double bond:



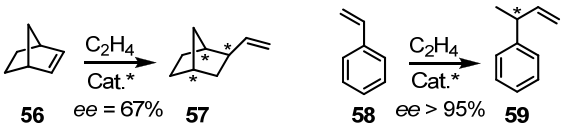
The annual production of Vestenamer® is some 12 000 tons and the polymer is used as an additive in the processing of rubber compositions. Recently it has also found use in highway construction where it serves as the bonding material between the asphalt and powdered rubber prepared from recycled tyres. In addition, Shell has developed the so-called FEAST-Process in which cyclooctene

(**51**) and cyclododecene (prepared by the partial hydrogenation of 1,5,9-CDT **31**) are subject to a metathesis reaction with ethylene to give the technically interesting olefins 1,9-decadiene and 1,13-tetradecadiene.

A further impressive example of ligand-control in a nickel-catalysed reaction is provided by the dimerization of propylene which was discovered by Günther Wilke and Borislav Bogdanović in the 60's. The treatment of an π-allyl-nickel-chloride phosphine complex with diethyl-aluminium chloride produces a highly active catalyst (**52**) which, depending upon the nature of the substituents attached to the phosphorus-atom, converts propylene selectively into either 2-hexene (**53**) and 2-methyl-3-pentene (**54**) or 2,3-dimethyl-butene (**55**). Based on these investigations, the Institut Français du Pétrole has developed a process for converting propylene, n-butene and ethylene into a mixture of branched olefins which can be used as fuel additives. This Dimersol-Process is being operated world-wide on a 2.5 million tons per year scale.



Phosphine-control of a nickel-catalysed C–C bond formation reaction also plays a central role in the catalytic enantioselective reactions which attracted Wilke's attention in the late 60's. An enantioselective synthesis is one in which a chiral centre is generated whereby one of the two enantiomers (mirror-image stereoisomers) is formed preferentially. For example, the product of the codimerization of norbornene (**56**) with ethylene in the presence of the nickel catalyst **52** modified by a phosphine containing a chiral substituent is chiral *exo*-2-vinyl-norbornane (**57**, the chiral C-atoms are marked) having an enantiomeric excess (*ee*) of 67%. These codimerization reactions of a cyclic olefin with ethylene were the first examples of a catalytic enantioselective synthesis in which a chiral compound is formed in high enantiomeric excess by C–C-bond formation. Later Wilke reported that the catalyst **52** modified by a chiral aminophosphole dimer was able to codimerize styrene (**58**) and ethylene to give chiral 3-phenyl-1-butene (**59**) having an *ee*-value of 95.2%, i.e. only 2.4% of the mirror-image enantiomer is formed. This reaction, which is now known as hydrovinylation, can be used for the enantioselective synthesis of Ibuprofen® and structurally related pharmaceuticals.

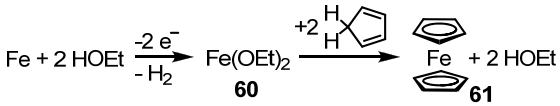


These investigations of ligand-control in homogeneous catalysis with transition metal complexes have attracted world-wide attention and, in addition to various awards, Günther Wilke has received honorary degrees from the University of Aachen, Louvain-la-Neuve and Chicago (1976), Oviedo (1982), New York at Binghamton (1990), Modena (1994) and Rostock (2003).

In 1973, an electrochemical process for the preparation of ferrous ethanolate (**60**) was developed together with

Günther Wilke in 1989 (Photo: W. Joppek).

Herbert Lehmkuhl and Wilhelm Eisenbach. The iron compound is then converted further into ferrocene (**61**) by filtering off the insoluble ferrous ethanolate from the electrolyte (a 0.15 molar solution of sodium bromide in ethanol) and by reacting it further with two equivalents of cyclopentadiene to give ferrocene and ethanol. The electrolysis can be run in a semi-continuous manner, interrupted only by the exchange of the iron anode, while the only side product is hydrogen. The design of the electrolysis cell made use of experience gained years earlier during the investigation of the electrochemical synthesis of tetraethyl-lead in Ziegler's era and consisted of a replaceable iron-anode and an adjustable, rotating cathode. The annual production of ferrocene (**61**), which is becoming of increasing importance as an additive and is, for example, added to heating oil as a combustion regulator, amounted to 300 tons.



In 1970, Kurt Zosel developed a process for the extraction of caffeine from green (unroasted) coffee beans using supercritical carbon dioxide which is now used world-wide in the production of decaffeinated coffee. Zosel had been appointed by Ziegler as the head of the pilot plant and in 1962, while working on the *Aufbau*-Reaction, he had observed that supercritical gases can be used as solvents. The initial observation was made with ethylene. At room temperature ethylene is only 10–15 °C above its critical temperature and, because the weight of the gas in the autoclave containing the triethyl-aluminium was considered to be a more reliable guide than the pressure in regulating the composition of the reaction mixture, Zosel compressed the ethylene into a weighed autoclave and then vented the excess gas before heating the reaction mixture up to 100 °C. Triethyl-aluminium catches fire on contact with the air and for safety reasons the vented gas was passed through a condenser cooled in dry ice. To Zosel's surprise considerable amounts of high boiling material condensed in the cold-trap. Later a dispute with a licensee led Zosel to systematically investigate the ability of ethylene under pressure to transport high boiling materials and ultimately to the recognition of the general principle involved which culminated in the development of a highly selective method to decaffeinate green coffee beans using supercritical carbon dioxide. This process, which was initially operated in 1980 by the Hag AG in Bremen, has

displaced earlier, less selective procedures using toxicologically questionable solvents such as methylene dichloride and ethyl acetate.

Soluble (homogeneous) catalysts can also be used in the synthesis of inorganic compounds and in 1979 Borislav Bogdanović (who had joined Wilke in the 60's as a doctoral student and later became a Group Leader) discovered that in the presence of a homogeneous catalyst, magnesium powder could be hydrogenated under mild conditions to give highly reactive magnesium dihydride (MgH_2). The catalysts were prepared by reacting a transition metal chloride ($CrCl_3$, $TiCl_4$ or $FeCl_3$) with the magnesium powder in the presence of anthracene in tetrahydrofuran as the solvent. The resulting MgH_2, which precipitates with the catalyst, is highly reactive and, moreover, if heated to 300 °C releases the hydrogen to give a reactive magnesium powder which in turn reacts with hydrogen at 20–60 °C reforming the dihydride and releasing 75 kJ mol^{-1} of thermal energy. The high hydrogen content of this transition metal-doped MgH_2/Mg-system of ca. 7% by weight makes it a potential candidate for either the reversible storage of either hydrogen or of thermal energy. The system is, however, not suitable for use in the storage tanks of hydrogen-driven vehicles since the exhaust temperature after combustion is too low to induce hydrogen release from the dihydride. However, together with the *Institut für Kernenergetik und Energiesysteme* of the University of Stuttgart and the commercial company HTC Solar in Lörrach, a prototype of a small solar power plant has been constructed along with solar-based systems for cooking and refrigeration.

In 1995, Boris Bogdanović observed that the reversible dehydrogenation of sodium aluminium tetrahydride ($NaAlH_4 = NaH + Al + {}^3/_2\ H_2$) could be accelerated by adding catalytic amounts of a titanium compound. Further investigations, both within the Institute and elsewhere, have enabled the system to be optimized and $NaAlH_4$ is now one of the most promising hydrogen-storage materials. The storage capacity of over 5% by weight at 100 °C approaches that required for the implementation in vehicles (ca. 10% by weight at below 80 °C) and since 1998, the investigations being carried out by Boris Bogdanović and Ferdi Schüth have received support from the automobile company Adam Opel AG/General Motors Company.

The research carried out between 1969 and 1993 outlined above has concentrated mainly on that supervised by Günther Wilke and which has led to technical processes. In addition, however, basic research on a broad basis has also been carried out in the fields of organometallic chemistry, homogeneous catalysis, polymer chemistry, coal chemistry, structural chemistry and analytical chemistry in a number of independent research groups and service departments. This research was supervised by a group of senior scientists many of whom had joined the Institute towards the end of the Ziegler era. These coworkers and their main research interests are listed below:
Reinhard Benn (nuclear magnetic resonance spectroscopy of organometallic compounds), Helmut Bönnemann (homogeneous catalysis, nano-particles, organocobalt- and organorhodium-chemistry), Borislav Bogdanović (homogeneous catalysis, hydrogen-storage chemicals), Paul Binger (organometallic chemistry, homogeneous catalysis with, among others, reactive methylenecyclopropane and cyclopropene derivatives), Wilhelm Eisenbach (pilot plant facilities), Gerhard Fink (polymerization catalysis), Wolfgang Haaf (technology, high pressure facilities), Matthias W. Haenel (coal- and aromatic-chemistry), Paul Heimbach (homogeneous catalysis), Dieter Henneberg (mass spectrometry), Heinz Hoberg (homogeneous catalysis with, among others, carbon monoxide, carbon dioxide and acetylene derivatives), Ernst G. Hoffmann (instrumental analysis, nuclear magnetic resonance spectroscopy), Peter W. Jolly (homogeneous catalysis and complex chemistry with nickel-, palladium and chromium-catalysts), Klaus Jonas (complex chemistry), Roland Köster (organoboron chemistry), Carl Krüger (structural chemistry and X-ray diffraction), Herbert Lehmkuhl (organometallic chemistry and electrochemistry), Heinz Martin (polymerization catalysis, Studiengesellschaft Kohle mbH), Richard Mynott (nuclear magnetic resonance spectroscopy), Klaus Pörschke (complex chemistry), Wolf J. Richter (library- and information-service), Roland Rienäcker (chemistry of aliphatic hydrocarbons and terpenes), Gerhard Schomburg (chromatography and capillary electrophoresis), Klaus Seevogel (optical molecular spectroscopy), Engelbert Ziegler (data processing and computer facilities) and Kurt Zosel (pilot plant facilities).

THE MAX-PLANCK-INSTITUT FÜR KOHLENFORSCHUNG TODAY

In 1993 Manfred T. Reetz left the University of Marburg where he had been Professor of Organic Chemistry since 1980 to become Günther Wilke's successor as Director of the Institute. His main chemical interests were centred on new catalytic processes, transition metal colloids and the directed evolution of enantioselective enzymes. Not only did he instigate a scientific reorientation of the Institute but he also undertook a fundamental restructuring of the organization with the establishment of five departments each having a *Wissenschaftliches Mitglied* of the *Max-Planck-Gesellschaft* as Co-Director. Reetz himself headed a department devoted to "Synthetic Organic Chemistry" and in 1995 Andreas Pfaltz from the University of Basel was appointed Director of the department of "Homogeneous Catalysis" and this was followed in 1998 by the appointments of Ferdi Schüth and Alois Fürstner to the departments of "Heterogeneous Catalysis" and "Organometallic Chemistry" respectively. In 1999 Walter Thiel took on the task of creating a department of "Theoretical Chemistry". Pfaltz returned to Basel in 1998 and his department remained vacant until the appointment of Benjamin List in 2005. These five Directors are together responsible for running the Institute. The role of Managing Director is rotated on a three year basis and has been carried out successively by Manfred T. Reetz (1993–2002), Ferdi Schüth (2003–2005), Walter Thiel (2006–2008) and Alois Fürstner (since 2009).

The Institute remains dedicated to carrying out basic research in catalysis with the goal of attaining the highest possible selectivity (chemo-, regio- and stereo-selectivity) for chemical processes under conditions which minimize the use of energy and resources. Catalysis is now recognized by the global chemical industry as the key techno-

logy in the development of economically and ecologically optimized processes. The combination of homogeneous and heterogeneous catalysis, organo-catalysis, bio-catalysis, organometallic- and synthetic-organic chemistry as well as theoretical chemistry within one institution is unique and ensures that the Institute maintains the "critical mass" needed to justify its excellent instrumental facilities and to encourage the synergy which is essential to successful modern research.

All the Institutes administered by the *Max-Planck-Gesellschaft* are subject to regular evaluation by international experts and the research reports for the *Max-Planck-Institut für Kohlenforschung* are accessible through the internet (www.kofo.mpg.de) and contain detailed information on current research projects.

The Directors of the Max-Planck-Institut für Kohlenforschung in 2008 standing at the bottom of the stairway of the original laboratory building opened in 1914: Benjamin List, Manfred T. Reetz, Ferdi Schüth, Alois Fürstner, Walter Thiel (left to right. Photo: M. Teske).

CATALYSIS RESEARCH: THE FIRST HUNDRED YEARS

As we have already mentioned, the original suggestion to establish an Institute devoted to the chemistry of coal on the Ruhr came from the Berlin chemist and Nobel Laureate Emil Fischer. In his address to leading representatives of the mining and steel industries as well as selected scientists and politicians which he held during the inauguration ceremony on the 29th July 1912 in the Raffelberg Spa in Mülheim an der Ruhr, he outlined the objectives of the new Institute and besides research into coal he mentioned the liquefaction of solid fuels as well as "the unlimited scope of catalysis" as a worthwhile objective. At this time (almost a century ago), catalysis was in its infancy and centred mainly on reactions in the gas phase such as the oxidation of sulphur dioxide to sulphur trioxide (Contact Process) which had revolutionized the production of sulphuric acid, the Haber-Bosch-process which the BASF had developed for the large scale production of ammonia and processes for the hydrogenation of the double bonds in vegetable- and fish liver-oils while initial studies had been carried out on the catalytic formation of methane from carbon monoxide and hydrogen. Bearing this in mind, one has to acknowledge Fischer's prophetic insight in recognizing the potential of catalysis and his vision in suggesting that it could form the basis of an Institute devoted to finding new uses for coal.

For the last one hundred years, the *Max-Planck-Institut für Kohlenforschung* in Mülheim an der Ruhr has an unbroken tradition of research into catalysis which has led to a number of discoveries and developments which have had a world-wide impact whereby, particularly in the fifties, the scientists involved were seldom specialists in the field. The initial triumph was Franz Fischer's discovery in 1925 of the Fischer-Tropsch-Synthesis which solved the fundamental problem of converting a solid fuel into a liquid fuel which is as important today as ever. A second, and perhaps even more significant success, was the discovery by Karl Ziegler in 1953 of the organometallic polymerization catalysts whereby it was not obvious in 1943 that his research interests would be of particular relevance to catalysis. Both of these discoveries make use of insoluble heterogeneous catalysts. The development of homogeneous catalysis using soluble transition metal species by Günther Wilke opened up a whole new field in which the complexation of ligands to the transition metal atom not only hinders the formation of metallic particles but also enables the course of the reaction to be controlled. The restructuring of the Institute and the reorientation of the research by Manfred T. Reetz has introduced new aspects including biocatalysis, organic catalysis as well as theoretical studies and the Institute today has a basis wider than ever before in its history. The current research concentrates on biocatalysis and the directed evolution of enantioselective enzymes (Reetz), heterogeneous catalysis with nano-structured solid catalysts and combinatorial methods (Schüth), organo-catalysis and enantioselective reactions (List), natural product syntheses using novel organometallic catalysts (Fürstner) and the theoretical modelling of catalytic processes (Thiel).

The *Max-Planck-Institut für Kohlenforschung* in Mülheim an der Ruhr is about to celebrate its one hundredth anniversary whereby, in fulfilment of Emil Fischer's prophetic vision, it can look back on a long and successful tradition of research in the field of catalysis.

PUBLICATIONS

Selected publications by Karl Ziegler

(A complete collection has been assembled by G. Wilke in the obituary published in *Liebigs Ann. Chem.* **1975,** 805-833).

K. Ziegler, Zur Kenntnis des „dreiwertigen" Kohlenstoffs, I: Über Tetra-aryl-allyl-Radikale und ihre Derivate (submitted as Thesis of Habilitation to the faculty of philosophy of the University of Marburg), *Liebigs Ann. Chem.* **1923**, *434*, 34–78.

K. Ziegler, B. Schnell, Zur Kenntnis des „dreiwertigen" Kohlenstoffs, II: Die Umwandlung von Äthern tertiärer Alkohole in organische Kaliumverbindungen und sechsfach substituierte Äthanderivate, *Liebigs Ann. Chem.* **1924**, *437*, 227–255.

K. Ziegler, K. Bähr, Über den vermutlichen Mechanismus der Polymerisationen durch Alkalimetalle (preliminary communication), *Ber. Dtsch. Chem. Ges.* **1928**, *61*, 253–263.

K. Ziegler, H. Colonius, Untersuchungen über alkali-organische Verbindungen, V: Eine bequeme Synthese einfacher Lithiumalkyle, *Liebigs Ann. Chem.* **1930,** *479*, 135–149.

K. Ziegler, H. Eberle, H. Ohlinger, Über vielgliedrige Ringsysteme, I: Die präparativ ergiebige Synthese der Polymethylenketone mit mehr als 6 Ringgliedern, *Liebigs Ann. Chem.* **1933**, *504*, 94–130.

K. Ziegler, Die Bedeutung der alkalimetallorganischen Verbindungen für die Synthese, *Angew. Chem.* **1936**, *28*, 455–460 und 499–502.

K. Ziegler, Ueber Butadienpolymerisation und die Herstellung des künstlichen Kautschuks, *Chem. Ztg.* **1938**, *62*, 125–127.

K. Ziegler, G. Schenck, E. W. Krockow, A. Siebert, A. Wenz, H. Weber, Die Synthese des Cantharidins, *Liebigs Ann. Chem.* **1942**, *551*, 1–79.

K. Ziegler, A. Späth, E. Schaaf, W. Schumann, E. Winkelmann, Die Halogenierung ungesättigter Substanzen in der Allylstellung, *Liebigs Ann. Chem.* **1942**, *551*, 80–119.

K. Ziegler, A. Späth, E. Schaaf, W. Schumann, E. Winkelmann, Die Halogenierung ungesättigter Substanzen in der Allylstellung, *Liebigs Ann. Chem.* **1942**, *551*, 80–119.

G. Schenck, K. Ziegler, Die Synthese des Ascaridols, *Naturwissenschaften* **1944**, *32*, 157.

K. Ziegler, H.-G. Gellert, Untersuchungen über alkali-organische Verbindungen, XVI: Die thermische Beständigkeit von Lithiumalkylen, *Liebigs Ann. Chem.* **1950**, *567*, 179–184.

K. Ziegler, H.-G. Gellert, Untersuchungen über alkali-organische Verbindungen, XVIII: Addition von Lithiumalkylen an Äthylen, *Liebigs Ann. Chem.* **1950**, *567*, 195–203.

K. Ziegler, Neuartige katalytische Umwandlungen von Olefinen, *Brennst.-Chem.* **1952**, *33*, 193–200.

K. Ziegler, H. Breil, E. Holzkamp, H. Martin (Studien- und Verwertungsgesellschaft), Verfahren zur Herstellung von hochmolekularen Polyäthylenen, DBP 973626 (filed 18.11.**1953**, patented 14.04.**1960**).

K. Ziegler, H.-G. Gellert (Studien- Verwertungsgesellschaft), Verfahren zur Herstellung von Aluminiumtrialkylen und Aluminiumalkylhydriden (Direktsynthese von Aluminiumalkylen), DBP 961537 (filed 02.02.**1954**, patented 28.04.**1957**).

K. Ziegler, H. Breil, H. Martin, E. Holzkamp (Studien- und Verwertungsgesellschaft), Verfahren zur Homopolymerisation von Propylen und α-Butylen, DBP 1257430 (filed 03.08.**1954**, patented 18.07.**1974**).

K. Ziegler (Studien- und Verwertungsgesellschaft), Verfahren zur Herstellung primärer Alkohole (Basisverfahren für die Herstellung biologisch abbaubarer Waschmittel), DBP 1014088 (filed 07.08.**1954**, patented 20.11.**1959**).

K. Ziegler, Gelenkte Polymerisation des Äthylens und seiner Homologen, *Brennst.-Chem.* **1954**, *35*, 321–325.

K. Ziegler, Aluminium-organische Synthese im Bereich olefinischer Kohlenwasserstoffe, *Angew. Chem.* **1952**, *64*, 323–329.

K. Ziegler, E. Holzkamp, H. Breil, H. Martin, Polymerisation von Äthylen und anderen Olefinen, *Angew. Chem.* **1955**, *67*, 426.

K. Ziegler, E. Holzkamp, H. Breil, H. Martin, Das Mülheimer Normaldruck-Polyäthylen-Verfahren, *Angew. Chem.* **1955**, *67*, 541–547.

K. Ziegler, Methoden zur Herstellung und Umwandlung großer Ringsysteme, *Methoden Org. Chem. (Houben-Weyl), 4th Ed. 1952–2001*, Vol. 4/2, **1955**, pp. 729–822.

K. Ziegler, H. Martin, Polyäthylen als Vorlesungsexperiment, *Makromol. Chem.* **1956**, *18/19*, 186–194.

K. Ziegler, H. Lehmkuhl, Die elektrolytische Abscheidung von Aluminium aus organischen Komplexverbindungen, *Z. Anorg. Allg. Chem.* **1956**, *283*, 414–424.

K. Ziegler, Metallorganische Verbindungen in der Petrochemie, *Brennst.-Chem.* **1959**, *40*, 209–240.

K. Ziegler, H.-G. Gellert, H. Lehmkuhl, W. Pfohl, K. Zosel, Metallorganische Verbindungen, XXVI: Aluminiumtrialkyle und Dialkylaluminiumhydride aus Olefinen, Wasserstoff und Aluminium, *Liebigs Ann. Chem.* **1960**, *629*, 1–13.

K. Ziegler, R. Köster, H. Lehmkuhl, K. Reinert, Metallorganische Verbindungen, XXX: Neue Komplexverbindungen der Aluminiumalkyle, *Liebigs Ann. Chem.* **1960**, *629*, 33–49.

K. Ziegler, F. Krupp, K. Zosel, Metallorganische Verbindungen, XL: Synthese von Alkoholen aus Organoaluminium-Verbindungen, *Liebigs Ann. Chem.* **1960**, *629*, 241–250.

K. Ziegler, H. Lehmkuhl, E. Hüther, W. Grimme, W. Eisenbach, H. Dislich, Die elektrochemische Synthese von Metallalkylen, *Chem.-Ing.-Tech.* **1963**, *35*, 325–331.

K. Ziegler, Die elektrochemische Synthese von Metallalkylen, *Angew. Chem.* **1963**, *75*, 218–219.

H. Lehmkuhl, R. Schäfer, K. Ziegler, Kombinierte Herstellung von Tetraethylblei und Tetramethylblei, *Chem.-Ing.-Tech.* **1964**, *36*, 612–616.

K. Ziegler, Folgen und Werdegang einer Erfindung (Nobel Lecture, Dec. 12, 1963, Stockholm), *Angew. Chem.* **1964**, *76*, 545–553. In English: Consequences and development of an invention, in *Nobel Lectures Including Presentation Speeches and Laureates Biography, Chemistry 1963–1970* (Ed.: Nobel Foundation), Elsevier, Amsterdam, **1972**, pp. 6–24.

K. Ziegler, Metallalkyle – Erfolge und zukünftige Möglichkeiten in der industriellen Chemie, *Brennst.-Chem.* **1964**, *45*, 194–200.

K. Ziegler, Vom Triphenylmethyl zum Polyethylen – Wenig Bekanntes aus der Vorschichte der Mülheimer Erfindung (lecture on the occasion of the 13th Meeting of the Nobel laureates in Lindau on June 23,1964), *Naturwiss. Rundsch.* **1965**, *18*, 1–7.

H. Lemkuhl, K. Ziegler, Aluminium-organische Verbindungen, *Methoden Org. Chem. (Houben-Weyl), 4th Ed. 1952–2001*, Vol. 13/4, **1970**, pp. 9–314.

Selected publications by Giulio Natta

G. Natta, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Mazzanti, G. Moraglio, Crystalline High Polymers of α-Olefins, *J. Am. Chem . Soc.* **1955**, *77*, 1708–1710.

G. Natta, Stereospezifische Katalysen und isotaktische Polymere, *Angew. Chem.* **1956**, *68*, 393–403.

G. Natta, I. Pasquon, A. Zambelli, Stereospecific Catalysts for the Head-to Tail Polymerization of Propylene to a Crystalline Syndiotactic Polymer, *J. Am. Chem . Soc.* **1962**, *84*, 1488–1490.

G. Natta, Von der stereospezifischen Polymerisation zur asymmetrischen autokatalytischen Synthese von Makromolekülen (Nobel Lecture, Dec.12,1963, Stockholm), *Angew. Chem.* **1964**, *76*, 553–566. In English: From the stereospecific polymerization to the asymmetric autocatalytic synthesis of macromolecules, in *Nobel Lectures Including Presentation Speeches and Laureates Biography, Chemistry 1963–1970* (Ed.: Nobel Foundation), Elsevier, Amsterdam, **1972**, pp. 27–60.

Selected publications on Karl Ziegler and his chemistry

L. Horner, E. H. Winkelmann, Neuere Methoden der präparativen organischen Chemie II, 14. N-Bromsuccinimid, Eigenschaften und Reaktionsweisen, Studien zum Ablauf der Substitution XV, *Angew. Chem.* **1959**, *71*, 349–365.

G. Bier, Hochmolekulare Olefin-Mischpolymerisate hergestellt durch Verwendung von Ziegler-Mischkatalysatoren, *Angew. Chem.* **1961**, *73*, 186–197.

G. Wilke, Karl Ziegler 70 Jahre, Chemie in unserer Zeit, **1968**, *1*, 194–200.

A. Fredga, Presentation Speech for the Nobel Prizes in Chemistry 1963, in *Nobel Lectures Includeing Presentation Speeches and Laureates Biography, Chemistry 1963–1970* (Ed.: Nobel Foundation), Elsevier, Amsterdam, **1972**, pp. 3–5.

G. Wilke, Nachruf auf Karl Ziegler, *Liebigs Ann. Chem.* **1975**, 805–833.

F. M. McMillan, The Chain Straighteners, Fruitful Innovation: the Discovery of Linear and Stereoregular Synthetic Polymers, The MacMillan Press Ltd., London, **1979**, 207 pages.

K. Weissermel, H. Cherdron, Raw Materials and Energy: A Challenge for Polymer Research, *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 764–771.

G. Fink, R. Mülhaupt, H.-H. Brintzinger (Eds.), Ziegler Catalysts, Springer, Berlin, **1995**, 511 pages.

H.-H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. Waymouth, Stereospecific Olefin Polymerization with chiral Metallocene Catalysts, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1143–1170.

M. Rasch, Karl Zieglers Berufung 1943 zum Direktor des Kaiser-Wilhelm-Instituts für Kohlenforschung, *Zeitschrift des Geschichtsvereins Mülheim a. d. Ruhr*, **1998**, *issue 70*, pp. 155–206; see also in *Die Kaiser-Wilhelm-/Max-Planck-Gesellschaft und ihre Institute, Studien zu ihrer Geschichte: Das Harnack-Prinzip* (Eds.: Bernhard vom Brocke, Hubert Laitko), Walter de Gruyter, Berlin, **1996**, pp. 469–504.

Städtisches Museum Mülheim an der Ruhr, G. Uelsberg (Ed.), *Sammlung Karl und Maria Ziegler*, *2nd ed*., Plitt Druck und Verlag GmbH, Oberhausen, **1998**, 230 pages.

K. Hafner, 100. Geburtstag von Karl Ziegler – Hommage an Karl Ziegler, *Nachr. Chem. Tech. Lab.* **1999**, *47***,** 24–29.

G. Uelsberg, Meisterwerke aus der Sammlung Ziegler, *Mülheimer Jahrbuch* (Eds.: Tourist Office and Public Relation Office of the City of Mülheim a. d. Ruhr), Buchdruckerei R. Thierbach, Mülheim a. d. Ruhr, **1999**, *54*, pp. 121–126.

H. Martin, Polymere und Patente – Karl Ziegler, das Team, 1953–1998, Wiley-VCH, Weinheim, **2002**, 310 pages. English Edition: Polymers, Patents, Profits – A Classic Case Study for Patent Infighting, Wiley-VCH, Weinheim, **2007**, 273 pages.

G. Wilke, Fifty Years of Ziegler Catalysts: Consequences and Development of an Invention, *Angew. Chem. Int. Ed.* **2003**, *42*, 5000–5008.

L. L. Böhm, Die Ethylene Polymerization with Ziegler Catalysts: Fifty Years after the Discovery, *Angew. Chem. Int. Ed.* **2003**, *42*, 5010–5030.

R. Mülhaupt, Catalytic Polymerization and Post Polymerization Catalysis Fifty Years After the Discovery of Ziegler's Catalysts, *Macromol. Chem. Phys.* **2003**, *204*, 289–327.

G. Wilke, 50 Jahre Ziegler-Katalysatoren – Werdegang einer Erfindung, in *Nordrhein-Westfälische Akademie der Wissenschaften, Naturwissenschaften und Medizin, Vorträge N 463, Symposium „50 Jahre Ziegler-Katalysatoren" am 28./29. Sept. 2003*, Verlag Ferdinand Schöningh, Paderborn, **2004**, pp. 5–24.

H. Martin, 50 Jahre Ziegler-Katalysatoren – Eine Erfindung und ihre Folgen, in *Nordrhein-Westfälische Akademie der Wissenschaften, Naturwissenschaften und Medizin, Vorträge N 463, Symposium „50 Jahre Ziegler-Katalysatoren" am 28./29. Sept. 2003*, Verlag Ferdinand Schöningh, Paderborn, **2004**,pp. 25–45.

G. Fink, Polymerization on Molecular Catalysts, in *Handbook of Heterogeneous Catalysis, 2nd Ed., Vol. 8* (Eds.: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp), Wiley-VCH, Weinheim, **2008**, pp. 3792–3830.

Selected publications by Franz Fischer on the Fischer-Tropsch-Synthesis and the Kaiser-Wilhelm-Institut für Kohlenforschung 1912–1943

E. Fischer, Die Aufgaben des Kaiser-Wilhelm-Instituts für Kohlenforschung, *Stahl und Eisen* **1912**, *32*, 1898–1903; see also in F. Fischer (Ed.), *Gesammelte Abhandlungen zur Kenntnis der Kohle*, Vol. 1, Verlag Gebrüder Borntraeger, Berlin, **1917**, pp. 323–336.

F. Fischer, H. Tropsch, Über die Herstellung synthetischer Ölgemische (Synthol) durch Aufbau aus Kohlenoxyd und Wasserstoff, *Brennst.-Chem.* **1923**, *4*, 276–285.

F. Fischer, H. Tropsch, Verfahren zur Gewinnung mehrgliedriger Paraffinkohlenwasserstoffe aus Kohlenoxyden und Wasserstoff auf katalytischem Wege, DRP 484337 (filed 22.07.**1925**, patented 03.10.**1929**).

F. Fischer, H. Tropsch, Die Erdölsynthese bei gewöhnlichem Druck aus den Vergasungsprodukten der Kohlen, *Brennst.-Chem.* **1926**, *7*, 97–104.

F. Fischer, Überblick über die Synthesen aus Kohlenoxyd und Wasserstoff, *Öl Kohle* **1943**, *39*, 517–522.

Franz Fischer (Ed.), *Gesammelte Abhandlungen zur Kenntnis der Kohle*, 13 Volumes, Verlag Gebrüder Borntraeger, Berlin, **1917**–**1957**.

H. Koch, Franz Fischer – Leben und Forschung, *Brennst.-Chem.* **1949**, *30*, 3–9.

O. Roelen, Die Entdeckung der Fischer-Tropsch-Synthese, *Erdöl Kohle, Erdgas, Petrochem. Brennst.-Chem.* **1978** *31*, 524–529.

M. Rasch, Geschichte des Kaiser-Wilhelm-Instituts für Kohlenforschung 1913–1943, VCH Verlagsgesellschaft, Weinheim, **1989**, 461 pages.

A. P. Steynberg, M. E. Dry (Eds.), Fischer-Tropsch Technology, *Studies in Surface Sciences and Catalysis, Vol. 152*, Elsevier, Amsterdam, **2004**.

M. W. Haenel, 80 Jahre Fischer-Tropsch-Synthese – Renaissance eines Klassikers der Kohleverflüssigung, *Erdöl Erdgas Kohle* **2006**, *122*, 78–80.

Günther Luxbacher, Kohle – Öl – Benzin: Die Fischer-Tropsch-Synthese in der interinstitutionellen Kooperation 1933–1944, in *Gemeischaftsforschung, Bevollmächtigte und der Wissenstransfer: Die Rolle der Kaiser-Wilhelm-Gesellschaft im System kriegsrelevanter Forschung des Nationalsozialismus* (Ed.: Helmut Maier), Wallstein Verlag, Göttingen, **2007**, pp. 453–502.

M. E. Dry, The Fischer-Tropsch (FT) Synthesis Process, in *Handbook of Heterogeneous Catalysis, 2nd. Ed., Vol. 6* (Eds.: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp), Wiley-VCH, Weinheim, **2008**, pp. 2965–2994.

T. J. Remans, G. Jenzer, A. Hoek, Gas-to-Liquids, in *Handbook of Heterogeneous Catalysis, 2nd. Ed., Vol. 6* (Eds.: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp), Wiley-VCH, Weinheim, **2008**, pp. 2994–3010.

Selected publications by Günther Wilke and on the Max-Planck-Institut für Kohlenforschung 1969–1993

G. Wilke (Studiengesellschaft Kohle), Verfahren zur Herstellung von Cyclododecatrienen-1,5,9 neben anderen ringförmigen Kohlenwasserstoffen, DBP 1050333 (filed 23.02.**1956**, patented 30.07.1959).

G. Wilke, E. W. Müller (Studiengesellschaft Kohle), Verfahren zur katalytischen Di- bzw. Trimerisation von 1,3-Diolefinen (Synthese von Cyclooctadien-1,5), DBP 1140569 (filed 22.12.**1959**, patented 20.10.**1966**).

G. Wilke, B. Bogdanović, P. Borner, H. Breil, P. Hardt, P. Heimbach, G. Herrmann, H.-J. Kaminsky, W. Keim, M. Kröner, H. Müller, E. W. Müller, W. Oberkirch, J. Schneider, J. Stedefeder, K. Tanaka, K. Weyer, Cyclooligomerization of Butadiene and Transition Metal π-Complexes, *Angew. Chem. Int. Ed. Engl.* **1963**, *2*, 105–115.

H. Breil, P. Heimbach, M. Kröner, H. Müller, G. Wilke, Synthese von Cyclododecatrienen-1,5,9; I. Mitt. über die katalytische Umwandlung von Olefinen, *Makromol. Chem.* **1963**, *69*, 18–40.

G. Wilke, B. Bogdanović, P. Hardt, P. Heimbach, W. Keim, M. Kröner, W. Oberkirch, K. Tanaka, E. Steinrücke, D. Walter, H. Zimmermann, Allyl-Transition Metal Systems, *Angew. Chem. Int. Ed. Engl.* **1966**, *11*, 151–164.

W. Ring, J. Gaube, Zur technischen Synthese von Cyclododecatrien-(1,5,9) – Reaktionskinetische Untersuchungen und Berechnungen zum Reaktionsablauf in einem Rohrreaktor, *Chem.-Ing.-Tech.* **1966**, *38*, 1041–1045.

B. Bogdanović, G. Wilke, Propylendimerisation – Wege und Bedeutung, *Brennst.-Chem.* **1968**, *49*, 323–329.

B. Bogdanović, P. Heimbach, M. Kröner, G. Wilke, E. G. Hoffmann, J. Brandt, Über die katalytische Umwandlung von Olefinen, II: Zum Reaktionsablauf der Cyclotrimerisiation von Butadien-1,3, *Liebigs Ann. Chem.* **1969**, *727*, 143–160.

P. Heimbach, G. Wilke, Über die katalytische Umwandlung von Olefinen, III: Synthese von *cis*,*cis*-Cyclooctadien-(1,5) und *cis*-1,2-Divinylcyclobutan, *Liebigs Ann. Chem.* **1969**, *727*, 161–182.

W. Brenner, P. Heimbach, H. Hey, E. W. Müller, G. Wilke, Über die katalytische Umwandlung von Olefinen, IV: Synthese von *cis*,*trans*-Cyclodecadien-1,5 und Decatrien-1,*trans*-4,9 – Mischoligomerisation von Butadien mit Äthylen, *Liebigs Ann. Chem.* **1969**, *727*, 183–193.

K. Zosel (Studiengesellschaft Kohle), Verfahren zur Entkoffeinierung von Kaffee, DBP 2005293 (filed 05.02.**1970**, patented 10.01.**1974**).

E. Ziegler, D. Henneberg, G. Schomburg, Computer Systems for Chemical Research, *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 348–357.

D. Henneberg, K. Casper, E. Ziegler, B. Weimann, Computer-Aided Analysis of Organic Mass Spectra, *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 357–366.

G. Schomburg, F. Weeke, B. Weimann, E. Ziegler, Data Processing in Gas Chromatography, *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 366–375.

E. G. Hoffmann, W. Stempfle, G. Schroth, B. Weimann, E. Ziegler, J. Brandt, The Use of a Computer in Nuclear Magnetic Resonce Spectroscopy, *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 375–386.

W. Eisenbach, H. Lehmkuhl, G. Wilke (Studiengesellschaft Kohle), Verfahren zur elektrochemischen Synthese von organischen Metallverbindungen (z. B. Eisen(II)ethanolat für die Herstellung von Ferrocen), DBP 2349561 (priority in Austria 5.10.**1972**, patented 13.04.**1978**).

K. Fischer, K. Jonas, P. Misbach, R. Stabba, G. Wilke, The "Nickel-Effekt", *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 943–953.

B. Bogdanović, B. Henc, A. Lösler, B. Meister, H. Pauling, G. Wilke, Asymmetric Syntheses with the Aid of Homogeneous Transition Metal Catalysts, *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 954–964.

H. Bönnemann, C. Grard, W. Kopp, W. Pump, K. Tanaka, G. Wilke, The Allylcobalt System, *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 964–975.

P. Heimbach, Cyclooligomerizations with Transition Metal Catalysts, *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 975–989.

P. W. Jolly, G. Wilke, The Organic Chemistry of Nickel, Vol. 1 and 2, Academic Press, New York, **1974** and **1975**.

K. Zosel, Separation with Supercritical Gases: Practical Applications, *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 702–709.

B. Bogdanović (Studiengesellschaft Kohle), Verfahren zur Herstellung von Magnesiumhydriden (Grundpatent zur Wasserstoff- und Energiespeicherung), EP 0003564 (priority in Germany 02.02.**1978**, patented 07.04.**1982**).

B. Bogdanović, B. Spliethoff, G. Wilke, Dimerization of Propylene with Catalysts Exhibiting Activities Like Higly-Active Enzymes, *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 622–623.

B. Henc, P. W. Jolly, R. Salz, G. Wilke, R. Benn, E. G. Hoffmann, R. Mynott, G. Schroth, K. Seevogel, J. C. Sekutowski, C. Krüger, Transition Metal Allyls, III: The $(\eta^3\text{-Allyl})_2M$ Complexes of Nickel, Palladium and Platinum – Structural Considerations, *J. Organometal. Chem.* **1980**, *191*, 425–448.

G. Wilke, Contributions to Homogeneous Catalysis 1955 – 1980, *J. Organometal. Chem.* **1980**, *200*, 349–364.

W. Eisenbach, H. Lehmkuhl, Elektrosynthese von Ferrocen, *Chem.-Ing.-Tech.* **1982**, *54*, 690–691.

R. Köster, Organobor-Verbindungen I–III, *Methoden Org. Chem. (Houben-Weyl), 4th Ed. 1952–2001*, Vol. 13/3a, **1982**, 910 pages; Vol. 13/3b, **1983**, 893 pages; Vol. 13/3c, **1984**, 932 pages.

K. Angermund, K. H. Claus, R. Goddard, C. Krüger, High-Resolution X-ray Crystallography – An Experimental Method fort he Description of Chemical Bonds, *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 237–247.

H. Bönnemann, Organocobalt Compounds in the Synthesis of Pyridines – An Example of Structure-Effectivity Relationships in Homgeneous Catalysis, *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 248–262.

B. Bogdanović, Catalytic Synthesis of Organolithium and Organomagnesium Compounds and of Lithium and Magnesium Hydrides – Applications in Organic Synthesis and Hydrogen Storage, *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 262–273.

P. W. Jolly, η^3-Allylpalladium Compounds, *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 283–295.

K. Jonas, Reactive Organometallic Compounds Obtained from Metallocenes and Related Compounds and Their Synthetic Applications, *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 295–311.

R. Rienäcker, J. Graefe, Catalytic Transformation of Sesquiterpene Hydrocarbons on Alkali Metal/Aluminum Oxide, *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 320–321.

R. Benn, A. Rufińska, High-Resolution Metal NMR Spectroscopy of Organometallic Compounds, *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 861–881.

P. Binger, H. M. Büch, Cyclopropenes and Methylenecyclopropanes as Multifunctional Reagents in Transition Metal Catalyzed Reactions, *Top. Curr. Chem.* **1987**, *135*, 77–151.

H. Hoberg, S. Groß, A. Milchereit, Nickel(0)-Catalyzed Production of a Functionalized Cyclopentanecarboxylic Acid from1,3-Butadiene and CO_2, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 571–572.

R. Mynott, G. Fink, W. Fenzl, Ethylene Insertion with Soluble Ziegler Catalysts, III: The System $Cp_2TiMeCl/AlMe_2Cl/^{13}C_2H_4$ Studied by ^{13}C NMR Spectroscopy – The Time-Development of Chain Propagation and Oligomer Distribution, *Angew. Makromol. Chem.* **1987**, *154*, 1–21.

G. Wilke, Contributions to Organo-Nickel Chemistry, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 185–206.

W. Keim, Nickel: An Element with Wide Application in Industrial Homogeneous Catalysis. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 235–244.

B. Bogdanović, A. Ritter, B. Spliethoff, Active MgH_2-Mg-Systems for Reversible Chemical Energy Storage, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 223–234.

W. Bonrath, K. R. Pörschke, S. Michaelis, On a (1,4-Diazabutadiene)bis(ethen)nickel(0) Complex and Related Compounds, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 298–300.

G. Schomburg, Problems and Achievements in the Instrumentation and Column Technology for Chromatography and Capillary Electrophoresis, *Chromatographia* **1990**, *30*, 500–508.

M. W. Haenel, Recent Progress in Coal Structure Research, *Fuel* **1992**, *71*, 1211–1223.

P. W. Jolly, G. Wilke, Hydrovinylation, in *Applied Homogeneous Catalysis with Organometallic Complexes* (Eds.: B. Cornils, W. A. Herrmann), VCH, Weinheim, **1996**, pp. 1024–1048.

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