Angewandte Essays

Homogenous Catalysis

DOI: 10.1002/anie.201305308

# Oligomerization of Ethylene to α-Olefins: Discovery and Development of the Shell Higher Olefin Process (SHOP)

*Wilhelm Keim**

multiphase catalysis · olefins · oligomerizations · polymer chemistry · SHOP

*Dedicated to Professor Karl Ziegler and Professor Günther Wilke*

Ethylene oligomerization for the manufacture of α-olefins is one of the most significant processes of homogenous transition-metal catalysis. Over one million tonnes of α-olefins are currently manufactured every year using the Shell Higher Olefin Process (SHOP). SHOP was discovered in 1968 in the laboratories of Shell Development Company in Emeryville, California, and even after 45 years it has not lost its significance. Indeed, just recently Shell announced that a further production plant with a capacity of 200000 tonnes will be constructed in Qatar.

When the author started at Shell Development in Emeryville in 1965 the following economic environment existed:

1. Shell Chemicals had just commissioned a hydroformylation plant to manufacture fatty alcohols (Neodol) in Geismar, Louisiana. Due to ecological requirements a change away from “hard” detergents with branched chains to “soft” detergents with linear fatty alcohols was emerging. The lack of biological degradation of the branched surfactants had resulted in the accumulation of foam on rivers and seas. Furthermore, the detergents based on Neodol showed good washing performance in hard water and could be used at low washing temperatures. They also worked well in formulations with low phosphate content, which reduced the eutrophication of surface waters. The fatty alcohols produced by Shell were then in high demand, and the market developed high growth rates.
2. The olefins used in Geismar for hydroformylation were produced by the halogenation of alkanes with chlorine and elimination of HCl. This process had considerable disadvantages, as the monoolefins produced in this way shorten the lifetime of the cobalt phosphane catalyst.
3. Shell planned the construction of a large-scale gas oil cracker. A market was still needed for a major portion of the generated ethylene.

Against this background, α-olefins and linear monoolefins with an internal double bond were in demand at Shell Chemicals for hydroformylation. The research division of Shell Development Company was instructed to work on the oligomerization of ethylene to linear α-olefins and linear monoolefins. At that time α-olefins were primarily produced by cleavage of wax and the Ziegler polymerization of ethylene. The wax splitting and the Ziegler process are very expensive and give lower quality products for the manufacture of detergents.

As a chemist who had completed his dissertation under the supervision of K. Ziegler and G. Wilke, I was very familiar with the transition-metal-catalyzed C–C coupling of olefins. Numerous homogenous transition-metal catalysts with monodentate phosphane ligands had been described by which the direction of the C–C linkage could be influenced. The use of ligands containing polydentate phosphane was hardly described; hence it seemed appropriate to investigate bidentate phosphane ligands. The concept described in Figure 1 shows the basis of the underlying considerations.

The bidentate chelate ligand XY should exhibit the following properties: it should force square-planar coordination at nickel and as a donor ligand it should enable the stereochemical distinction between the *trans* (electronic factor) and *cis* positions (steric factor); the ligand should be hemilabile. Nickel was chosen as the metal as I had much experience with organonickel compounds for the C–C link-

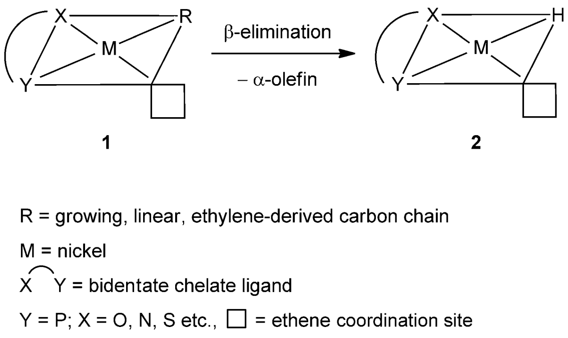

**Figure 1.** Model conception of ethylene oligomerization.

---

[*] Prof. Dr. W. Keim
Institut für Technische und Makromolekulare Chemie
RWTH Aachen University
Worringerweg 1, Aachen (Germany)
E-mail: wrkeim@t-online.de

age of olefins in my dissertation “π-Allyl Complexes of Nickel, Palladium, and Platinum”. Ethylene should coordinate on complex **1** as shown in Figure 1 and in a subsequent step insert into the nickel–carbon bond M−R (growth). A subsequent β-elimination should release α-olefins with formation of the nickel hydride complex **2**. The latter then coordinates ethylene, which is again inserted, so that **1** is generated again. Thus a catalytic cycle occurs in which repeated ethylene coordination and insertion form the basis of chain extension.

Many nickel complexes with bidentate chelate ligands with heteroatoms P, N, O, S, and As were synthesized and reacted with ethylene in a homogenous reaction with little success.

At the same time in our group, T. Shryne pursued the rhodium-catalyzed hydrogenation of sulfolene to sulfolane. He synthesized the ligand $Ph_2PCH_2COOH$, which had been produced for the first time by K. Issleib. This also seemed to me to be of interest for my work on ethylene oligomerization. Was it the correct proposed model concept (Figure 1)? Was it a stroke of luck (“serendipity in research”)? On April 14, 1968 the reaction of $Ph_2PCH_2COOH$ with $[Ni(cod)_2]$ (cod = 1,5-cyclooctadiene) resulted in a red solution, which oligomerized ethylene to linear α-olefins with a Schulz–Flory distribution (geometrical series, Figure 2). Figure 3 shows the first GC analysis of the synthesized olefins.

Owing to economical considerations, our process had environmental and cost advantages over the wax-splitting and Ziegler methods. The marketing of all $C_4$–$C_{20}^+$ α-olefins was not feasible at this point, however. There was still only a modest market for $C_4$–$C_8$ α-olefins for the copolymerization of ethylene, and the market for 1-decene as a lubricant (SHC oils) was still in its infancy. Even with an optimal mathematical distribution, the $C_{12}$–$C_{18}$ fraction for the detergent market made up only 40–50% of the total (Figure 2). Hence the question arose, “What can we do with the $< C_{12}$ and $> C_{18}$ olefins?”.

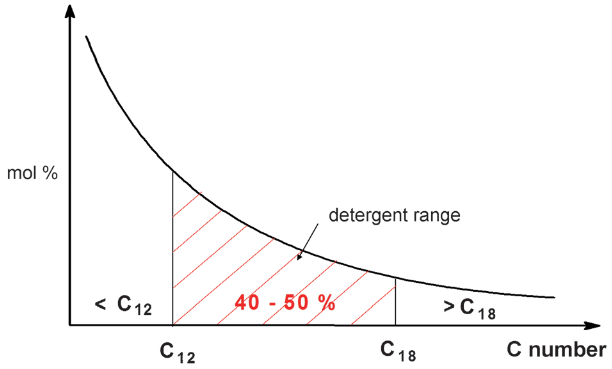

***Figure 2.*** Schulz–Flory distribution of the α-olefins.

*Wilhelm Keim studied chemistry at the Universities of Münster and Saarbrücken (diploma) and obtained his doctorate 1963 at the Max-Planck-Institut für Kohlenforschung in Mülheim. He completed a one-year postdoctorate at the Columbia University in New York (1964–1965) and worked from 1965 to 1973 as a chemist, group leader, head of department and manager for Shell Development, USA. From 1973 to 2000 he held the Lehrstuhl für Technische Chemie und Petrolchemie at RWTH Aachen. He has received numerous prestigious honors.*

In our research group we had many brain-storming sessions on how to solve the problem of product distribution. Special recognition here goes to F. Mango, who was addressing the olefin metathesis. If, for example, the olefins of the $< C_{12}$ fraction and the $> C_{18}^+$ fraction are isomerized and then converted in a metathesis reaction, then internal, linear monoolefins in the desired $C_{12}$–$C_{18}$ range are formed. A representative example is shown in Figure 4 for 1-octene and 1-eicosene.

Using this method it should be possible to bring all not directly marketable $< C_{12}$ and $> C_{18}$ olefins into the detergent sector. The internal linear $C_{12}$–$C_{18}$ monoolefins thus obtained could then be transformed by hydroformylation into terminal linear alcohols in the $C_{12}$–$C_{18}$ range by the Shell hydroformylation process, the key to the SHOP process.

The purity of the olefin starting materials is extremely important for the olefin metathesis. In particular, branched monoolefins and dienes are not suitable, which obviates wax cleavage and the catalytic Ziegler process developed by Gulf Oil.

The task for Shell Research was now to develop a process from the three individual steps of ethylene oligomerization, olefin isomerization, and olefin metathesis. Everyone who has been involved in developing a single new process knows what difficulties can arise. In this case, three processes were supposed to be developed and integrated. It was decided to work on the oligomerization in the USA and to carry out the isomerization and metathesis in the Shell laboratories in Amsterdam.

In the development of the process there were many “valleys of death”. Two are described here:

1. Phillips Petroleum dominated olefin metathesis with many patents. Difficult license negotiations put the developments at Shell in question. It was again F. Mango who found a patent from 1957 from Standard Oil of Indiana, in which olefin metathesis was first described in 1960 and thus allowed the use of metathesis by Shell.[1]
2. The oligomerization catalysts were very expensive, so that the question of ending the development work was also raised here. Again it was “serendipity in research” which helped the breakthrough. Up to this point I had used toluene as the solvent in all catalysis experiments. One day, my laboratory assistant A. Nabong swopped the solvent bottles and used acetonitrile instead of toluene. When the autoclave was opened there were two phases: a white phase consisting of pure α-olefins and a red phase containing the catalyst in acetonitrile. Another stroke of luck! The possibility of catalyst recirculation in a two-phase procedure was born. Now the optimal solvent had to be found. Around this time, the development of the sulfolane process at Shell Development in Emeryville for the extraction of aromatics and dienes was completed. The

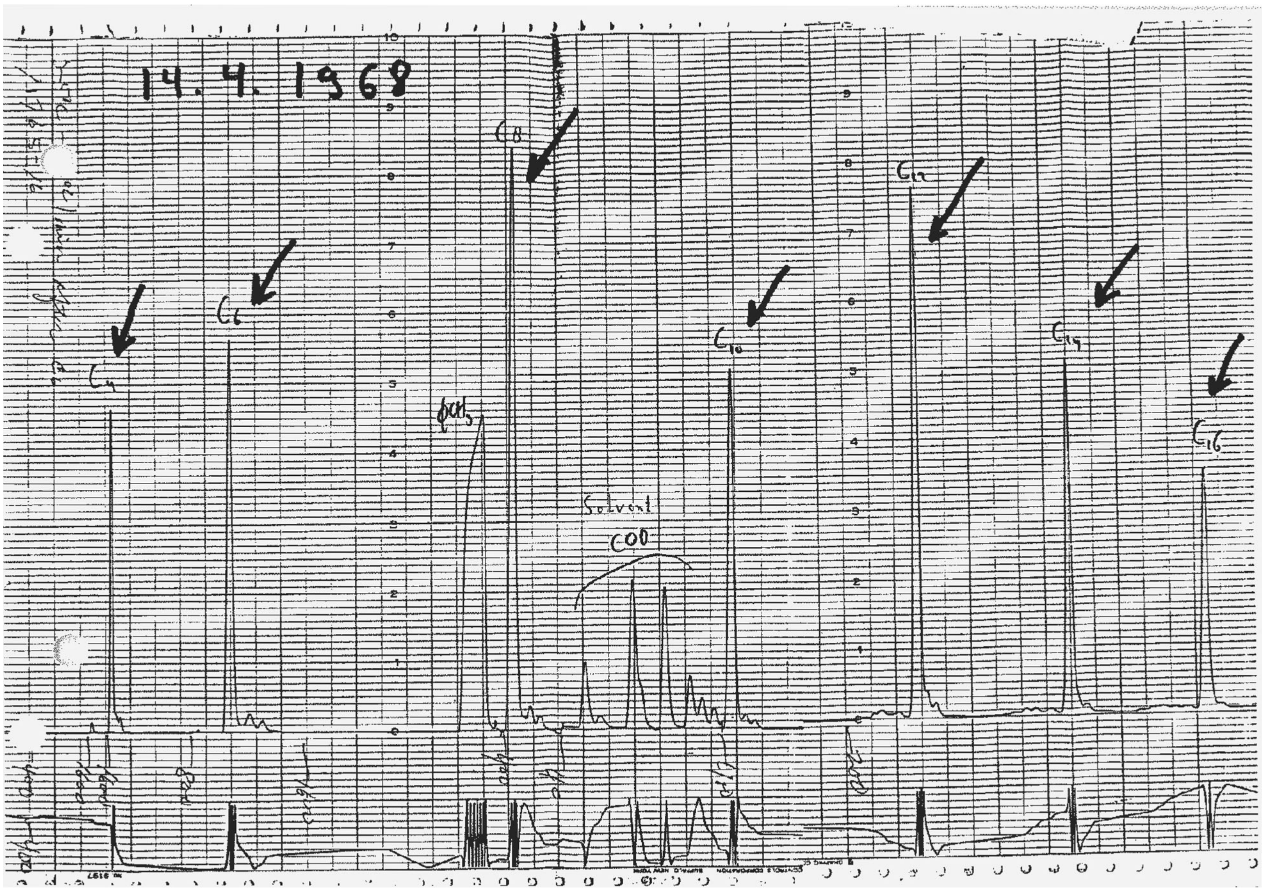

*Figure 3.* First GC analysis of the first SHOP experiment.

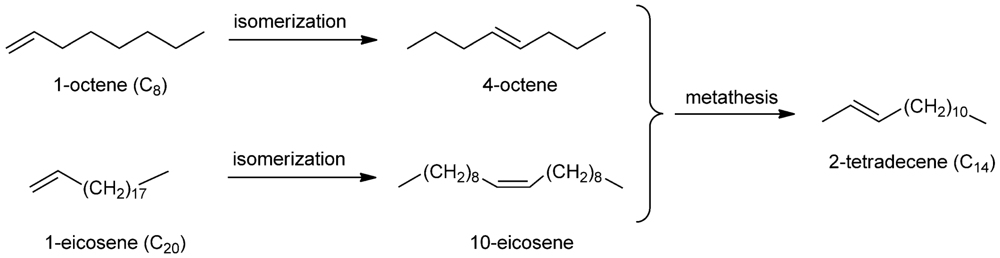

*Figure 4.* Metathesis of 1-octene and 1-eicosene.

chemical engineers involved in the development of the sulfolane process possessed considerable knowledge about solvents, which in our case should demonstrate the following properties: suitable partition coefficient, good solubility for ethylene, poor solubility for the synthesized α-olefins, catalyst stability, and good heat exchange. 1,4-Butanediol proved to be a suitable solvent.

The next step was the construction of three pilot plants: one for the oligomerization in USA and one each for the isomerization and metathesis in Amsterdam. Due to the closure of the laboratories in Emeryville, the process development for ethylene oligomerization was conducted in a bigger pilot plant in Deer Park near Houston. Finally, in 1977, the first large production plant (represented schematically in Figure 5) was put into operation in Geismar.

In the first step, the oligomerization is carried out in a polar solvent in reactor 1. In step 2 the phases are separated and the catalyst is recirculated. In step 3 the directly marketable α-olefins (Neodene) are separated by distillation. The nonmarketable portion goes into the olefin isomerization in reactor 4, followed by the olefin metathesis in reactor 5. At this point, all $C_{11}$–$C_{14}$ monoolefins for Shell's hydroformylation technology and benzene alkylation for detergents could be separated by distillation. The $< C_{10}$ and $> C_{14}$ fraction undergoes isomerization and metathesis again and is converted into internal $C_{11}$–$C_{14}$ monoolefins. SHOP is described in detail in the literature.[2]

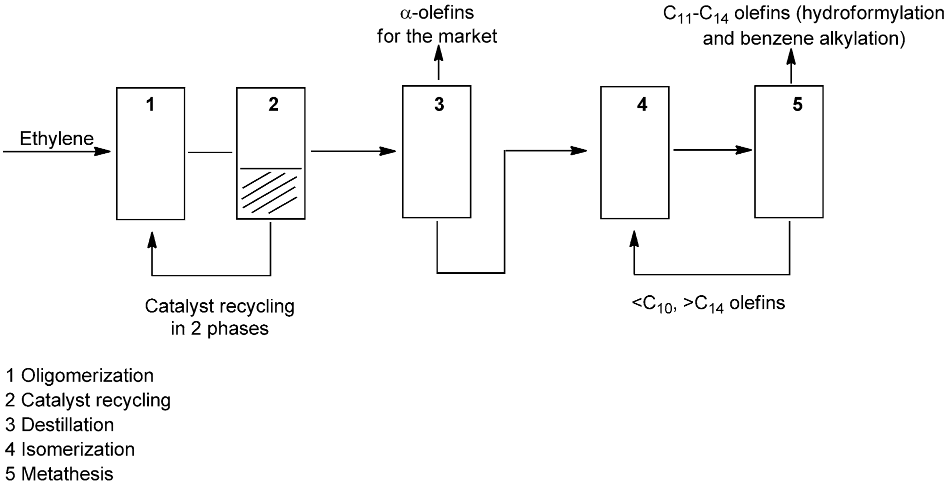

***Figure 5.*** Flow diagram of the SHOP production plant.

Shell started the first 300000 metric tonne SHOP production plant in Geismar in 1977. In Stanlow, England, a SHOP plant was commissioned followed by an extension in 1987. Together, all production plants generate more than one million tonnes of α-olefins per annum. SHOP is distinguished by its tremendous flexibility. A range of linear even-numbered α-olefins and linear internal monoolefins of any C-number, pure or as mixtures, can be produced by combining olefin isomerization, metathesis, and distillation.

Only nine years passed from the discovery to the first commissioning. A large number of employees from Shell Chemical USA and S.I.R.M. Shell in Amsterdam were involved. They worked under enormous pressure, as other companies also pursued the use of transition metals for ethylene oligomerization. For example, A. W. Langer at Exxon had developed a method based on titanium and zirconium.[3] In 2009, a zirconium catalyst was put into operation in the 150000 metric ton α-Sablin process in Saudi Arabia, which was developed by Linde and Sabic together.[4] Mitsui Petrochemical developed an homogenous catalyzed process with titanium-based catalysts.[5]

It is worth highlighting that the market has changed significantly since the 1960s. The requirement for $C_4$–$C_8$ α-olefins for polyethylene (low-density polyethylene (LDPE) and high-density polyethylene (HDPE)) has grown dramatically. Furthermore, a new market for 1-decene for lubricants (SHC oils) has arisen. Both of these have made it possible today to live with the Schulz–Flory distribution. In Shell's new SHOP plant in Qatar the part of the isomerization and metathesis will be relinquished.

In 1973 I returned to Germany to work as a professor in academic research. At the Institute for Technical Chemistry at the RWTH Aachen I pursued the questions: "What is the mechanism of the oligomerization? Were the model conceptions for the mechanism (Figure 1), which led to the red oil that oligomerized ethylene correct?" In many dissertations the mechanism shown in Figure 6 could be substantiated by isolation of complexes, X-ray structure analyses, and in situ NMR spectroscopy.[6]

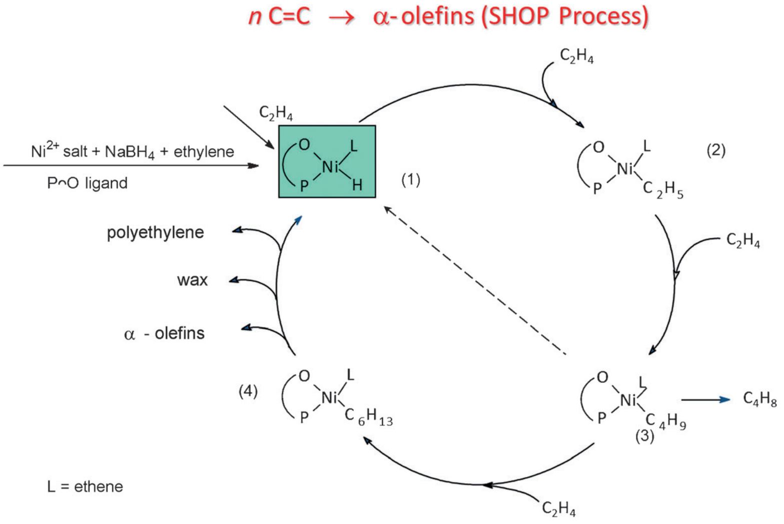

***Figure 6.*** Mechanism of ethylene oligomerization.

Catalyst **1** is generated from a nickel salt, $NaBH_4$, a P–O ligand, and ethylene. Ethylene coordination and insertion give the complexes **2** and **3**, a nickel–butyl intermediate, from which 1-butene and **1** are generated by β-elimination. The catalytic cycle for the formation of 1-butene is thus complete. A part of the intermediate **3** reacts further to a nickel–hexyl species **4**. The formation of α-olefins which follow a geometrical sequence can be explained by this mechanism. Waxes and polyethylene can also be formed in this way.

At the start of every research project, mechanistic model conceptions should be postulated. These must be based on existing knowledge and should not be too speculative. There should be little room for "trial and error" in today's catalyst research.

Future research activities in the field of ethylene oligomerization will be directed toward a narrow product distribution and the manufacture of single α-olefins. The dimerization to 1-butene and trimerization to 1-hexene are state of the art. The group of J. T. Dixon, Sasol Technology South Africa, has achieved the very selective tetramerization of of ethylene to 1-octene. Sasol is currently constructing a 100000 metric tonne plant in the USA. Here the mechanism is not the Ni–hybrid mechanism, but possibly the metallacycle mechanism. Will it be possible to produce single $C_{10}$–$C_{18}$ α-olefins selectively in the future?

At the end of the chronicle of the SHOP story one question remains: "Who is the inventor of the SHOP process?" Is it K. Issleib, who first synthesized $Ph_2PCH_2COOH$? Is it T. Shryne, who synthesized Issleib's P-O ligand at Shell? Is it F. Mango, who was fundamentally involved in the olefin metathesis? Is it A. Nabong, who happened to choose the "wrong" solvent? In an internal report at Shell it is stated that it was "luck, green thumbs, and nine years of hard work on the part of hundreds of people. That's what goes into a project like SHOP".[8] This is also my opinion. Many, very many, contributed to the success of SHOP.

Naturally, ethylene oligomerization was there at the start, a technical breakthrough that was crucial to SHOP. The work on ethylene oligomerization clearly bears the signature of K. Ziegler and G. Wilke, who supervised my PhD research. Education and the transfer of research from academia to industry contribute substantially to innovation and technical progress. This can also be confirmed, for example, by the development of on the tetramerization of ethylene to 1-octene by Sasol. The Institute of Technical Chemistry at the RWTH Aachen cultivated a close cooperation with Sasol for many years. Many Sasol employees were educated in Aachen. The use of polydentate ligands was one of the research areas.[9] At Sasol, the tetramerization of ethylene to 1-octene was then discovered.

Ethylene oligomerization thus also provides a very good example of the value of scientific schools and tradition in research.

Received: June 20, 2013

Translated by Geoffrey Hills, Essen (Germany)

---

[1] H. S. Eleuterio, E. F. Peters, L. Evering, Standard Oil of Indiana, US-Pat. 2 963 447, **1960**.
[2] a) E. R. Freitas, C. R. Gum, *Chem. Eng. Prog.* **1979**, 73–76; b) E. L. T. M. Spitzer, *Seifen Oele Fette Wachse* **1981**, 6; c) W. Keim, A. Behr, M. Röper in *Comprehensive Organometallic Chemistry, Vol. 5* (Ed.: G. Wilkinson), Pergamon, Oxford, **1982**, pp. 371–462; d) W. Keim in *Proceedings of the International Symposium on Future Aspects of Olefin Polymerization*, Kodansha, Tokyo, **1986**, pp. 201–213; e) W. Keim, *Chem. Ing. Tech.* **1984**, *56*, 850–853; f) W. Keim, *Angew. Chem.* **1990**, *102*, 251–260; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 235–244; g) W. Keim, *New J. Chem.* **1994**, *18*, 93–96; h) D. Vogt in *Applied Catalysis with Organometallic Compounds* (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, **2002**, pp. 240–253; i) A. Behr, P. Neubert in *Applied Homogeneous Catalysis*, Wiley-VCH, Weinheim, **2012**, pp. 303–307; j) E. F. Lutz, *J. Chem. Educ.* **1986**, *63*, 202–203.
[3] A. W. Langer, *J. Macromol. Sci. Part A* **1970**, *4*, 775–780.
[4] A. Meiswinkel, A. Wöll, W. Müller, H. V. Bölt, F. M. Mosa, A. Al-Hazmi, *Oil Gas Eur. Mag.* **2012**, *2*, 103–106.
[5] H. Olivier-Bourbigou, A. Forestiere, L. Saussine, L. Magna, F. Favre, F. Hugues, *Oil Gas Eur. Mag.* **2010**, *2*, 97–102.
[6] a) W. Keim, F. H. Kowaldt, R. Goddard, C. Krüger, *Angew. Chem.* **1978**, *90*, 493; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 466–467; b) M. Peuckert, W. Keim, *Organometallics* **1983**, *2*, 594–597; c) W. Keim, *J. Mol. Catal.* **1989**, *52*, 19–25; d) V. Müller, W. Keim, C. Krüger, P. Betz, *Angew. Chem.* **1989**, *101*, 1066–1067; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1011–1013; e) K. Hirose, W. Keim, *J. Mol. Catal.* **1992**, *73*, 271–276; f) W. Keim, R. P. Schulz, *J. Mol. Catal.* **1994**, *92*, 21–33.
[7] http://www.yourpetrochemicalsnews.com/sasol+commences+basic+engineering+for+tetramerization+technology41743.html.
[8] "Quest" Shell Broschure published by Shell Oil Company for employees, **1974**, *3*, 8.
[9] a) D. McGuiness, P. Wasserscheid, W. Keim, C. Hu, U. Englert, J. T. Dixon, C. Grove, *J. Chem. Soc. Chem. Commun.* **1990**, 1715–1716; b) D. McGuiness, P. Wasserscheid, W. Keim, D. Morgan, J. T. Dixon, A. Bollmann, H. Maumela, F. Hess, U. Englert, *J. Am. Chem. Soc.* **2003**, *125*, 5273–5280.