

Metathesis catalysts: Historical perspective, recent developments and practical applications

Okram Mukherjee Singh*

Department of Chemistry, Manipur University, Canchipur 795 003

Received 29 May 2006; accepted 02 August 2006

Metathesis, a recently developed synthetic chemical methodology, has widespread applications in industries in large-scale production of organic compounds, pharmaceutical products and polymeric materials.

Keywords: Catalysis, Drugs, Mechanism, Olefin-metathesis, Polymer

Introduction

Nobel Prize in Chemistry for 2005 has been awarded¹ to Frenchman Yves Chauvin and Americans Richard Schrock and Robert Grubbs for their contributions to metathesis. Chauvin² proposed a new mechanism of metathesis, whereas Schrock³ and Grubbs⁴ developed new catalysts for metathesis. Metathesis is a kind of organic synthesis where carbon compounds from very simple and small molecular weight to very large, complex polymers; macromolecules and even natural products are synthesized. In metathesis, double bonds are broken and made between carbon atoms in ways that cause atom groups to change places. This happens with the assistance of special catalyst molecules.

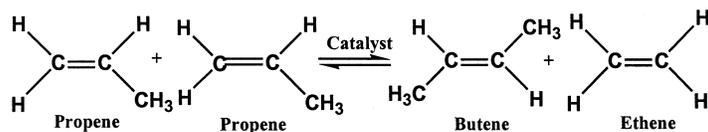
Metathesis of olefins is the reaction in which the molecules of these hydrocarbons are formally fragmented at their double bonds and new olefin molecules result by recombination of fragments originating from different molecules (Scheme 1). Metathesis reactions (Schemes 2-6) are generally reversible and, with the right catalyst system, equilibrium can be attained in seconds, even with substrate/catalyst ratios of 10^4 .

History of Catalytic Metathesis Non-catalytic metathesis of olefins has been known since 1931, when Schneider & Frolich⁵ obtained ethene and 2-butene by pyrolyzing propene at 852°C. Under first catalyzed metathesis reactions^{6,7}, propene heated with molybdenum {in the form of the metal, oxide or

[Mo(CO)₆] on alumina}, led to ethylene and 2-butenes. In 1967, 2-butene and 3-hexene were synthesized from 2-pentene by employing a catalytic system formed from tungsten hexachloride, ethanol and ethyl-aluminium dichloride and used the term olefin metathesis for the first time⁸. Calderon⁹ applied the metathesis to ring-opening polymerization of cyclo-olefins to polyalkenamers. Bradshaw *et al*¹⁰ suggested a reaction mechanism through a four-centered cyclobutanic intermediate. First order kinetic studies on propene metathesis in the heterogeneous phase were reported by Begley & Wilson¹¹ and on 2-pentene metathesis in the homogeneous phase by Hughes¹². Although the results obtained by Begley & Wilson¹¹ indicate a first order kinetics for the reaction of propene, contradicting the mechanism through a cyclobutanic intermediate, further investigations carried out in homogeneous catalysis¹³⁻¹⁴ seemed to indicate a second order kinetics. The real kinetics of the process was remaining uncertain until the discovery of Chauvin mechanism², which was awarded Nobel Prize in Chemistry for 2005.

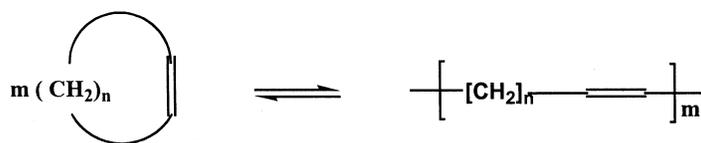
In 1970, Chauvin & Herisson¹⁵ suggested a chain mechanism for metathesis and ring opening polymerization in the homogeneous phase, through carbonic intermediates. In 1973, Chauvin published¹⁶ that $WCl_6 + MeLi$ mixture catalyzes the formation of propene by reaction of 2-butene, which was proposed to proceed *via* methylation of tungsten, followed by α -elimination in the tungsten-carbon bond of $W-CH_3$ to form $W=CH_2$ (H), then metathesis. Carbonic chain mechanism suggested by Chauvin was supported later by the new experimental results¹⁷⁻³⁰.

*E-mail: ok_mukherjee@yahoo.co.in



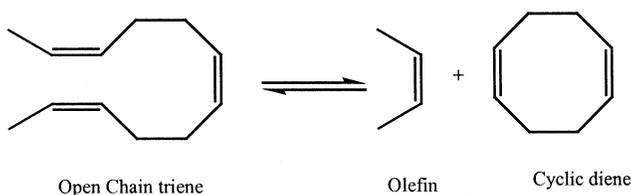
Olefin Metathesis

Scheme 1



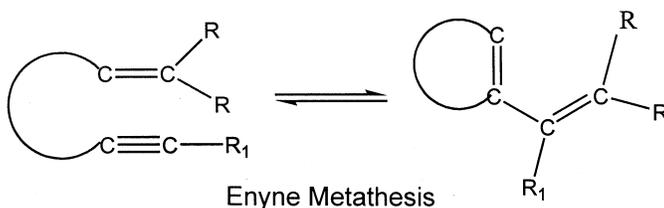
Ring opening Metathesis

Scheme 2



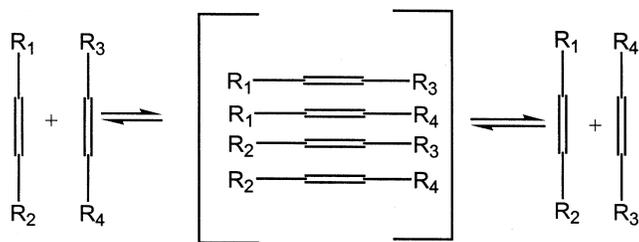
Ring-closing Metathesis

Scheme 3



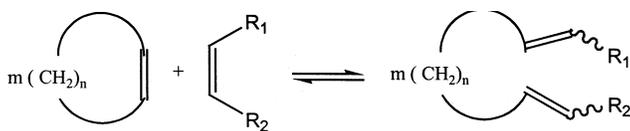
Enyne Metathesis

Scheme 4



Cross Metathesis

Scheme 5



Ring-opening Cross Metathesis

Scheme 6

Developing Catalyst Molecules

Catalyst systems for the olefin metathesis generally contain a transition metal compound, but often require the presence of a second compound (co catalyst), and sometimes a third (promoter). System most commonly used is based on the chlorides, oxides, or other easily accessible compounds of Mo, Ru, W, Re, Os, Ir, Ti, V, Cr, Co, Nb, Rh, or Ta compounds. Typical co catalysts are EtAlCl_2 , R_3AlCl_2 , R_3Al and R_4Sn ($\text{R}=\text{Ph}$, Me, Et, Bu), while promoters often contain oxygen as O_2 , EtOH or PhOH. It has now been realized that metathesis could assume great importance for organic synthesis if reliable and effective catalysts could be found. Molybdenum and tungsten soon appeared to be the most suitable metals. Some catalysts were produced with those metals, but there was still uncertainty as to what groups would bind to the metal to give stable yet active alkylidene complexes.

A breakthrough came in 1990 when Schrock *et al*³¹⁻³³ reported construction of a group very active, well-defined Mo catalyst (Scheme 7). With this discovery, chemists began to realize that olefin metathesis could be used for general purposes in organic synthesis. Metathesis gained increasing attention among researchers active in synthetic chemistry. Yet another breakthrough in the development of metathesis catalysts came in 1992 when Grubbs *et al*³⁴⁻³⁶ discovered a catalyst with the metal ruthenium. It was stable in air and demonstrated higher selectivity but lower reactivity than Mo catalysts. New catalyst also had the ability to initiate metathesis in the presence of alcohols, water and carboxyl acids (Scheme 8).

Grubbs' catalysts have become the first well-defined catalysts for general metathesis applications in ordinary laboratories. Catalyst 2 in Scheme 8 is generally named Grubbs' catalyst and has become a standard with which all new catalysts are compared. The general applicability of Grubbs' catalyst has given rise to future prospects of the possibilities of organic synthesis. Grubbs bases his catalyst design on detailed mechanical studies.

Practical Applications of Metathesis

Pharmaceutical Industries

Metathesis is an important tool for new pharmaceuticals used in treating major diseases such as bacterial infections, hepatitis C, cancer, Alzheimer's disease, Down's syndrome, osteoporosis, arthritis, inflammation, fibrosis, HIV/AIDS, migraine, etc³⁷.

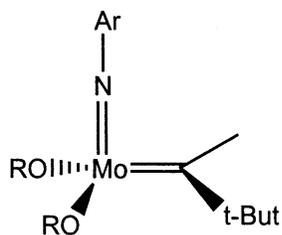
With catalytic metathesis, shorter synthetic routes to the products give higher yields. Metathesis is significant to green chemistry because: 1) Reactions are more efficient (fewer steps, fewer resources, less waste); 2) Reactions are easier to use (stable under ambient conditions); and 3) Environmentally benign (non-hazardous solvents, less hazardous waste). For example, Grubbs used a green approach, from RuCl_3 in water to the sophisticated chiral version of the second-generation ruthenium benzylidene catalyst, to provide the organic and polymer communities with most environment friendly metathesis catalysts, because of their stability to air and even to some extent to aqueous media and their high compatibility with most organic functionalities. A few examples of the synthetic applications of metathesis in pharmaceuticals are as follows:

Metathesis was used in the synthesis of a 7-membered azepin compound called balanol, which is used as anticancer agents and in controlling inflammation, cardiovascular disorders, central nervous system dysfunction, and even HIV infection. Fuerstner³⁸ & Thiel³⁹ claimed that by using ring-closing metathesis, total synthesis of this compound was shortened by 4-5 steps from the earlier methods (Scheme 9).

Another anticancer drug epothilone⁴⁰ and its derivatives were also prepared by using the ring closing metathesis (Scheme 10). Nicolaou *et al*⁴¹ reviewed the efficiency of ring closing metathesis in the total synthesis of macrocyclic lactones and several natural products.

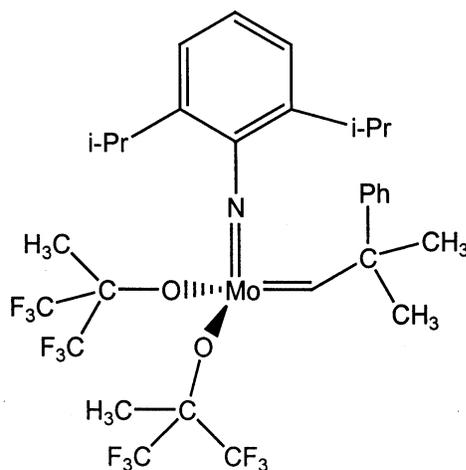
Similar type of ring closing metathesis was applied to produce Civetone⁴² (cyclo-9-heptadecenone) used in the perfume industry from ethyl oleate. Another class of natural compounds, easily obtainable through metathesis are insect pheromones, which are useful as environment friendly pest-control agents. Pederson *et al*⁴³ reported a typical metathesis reaction to yield the pheromone, 11-tetradecenyl acetate from a long chain olefinic ester and 3-hexene catalyzed by Grubbs catalyst B (Scheme 11).

Materia Medica, an international drug company has produced three pheromones: i) (*E*)-5-decenyl acetate, a pheromone of peach twig borer (*Anarsia lineatella*); ii) a mixture of (*E*)- and (*Z*)-11-tetradecenyl acetate, of omnivorous leafroller (*Platynota stultana*); and (iii) different mixture of (*E*)- and (*Z*)-11-tetradecenyl acetate, of *Sparganothis* fruit worm, a pest of cranberries and blueberries.



General Formula of Schrock,s Catalyst

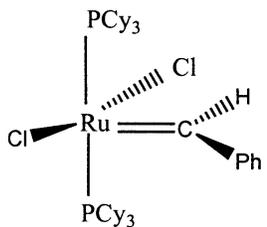
[t-But = tert-butyl, Ar = Aryl]



Schrock,s Molybdenum Catalyst

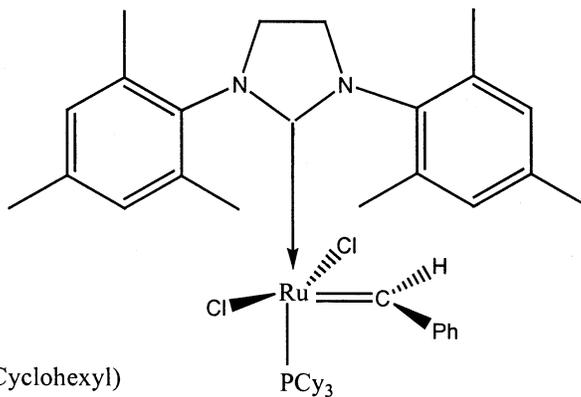
[i-Pr = iso-propyl, Ph = Phenyl]

Scheme 7



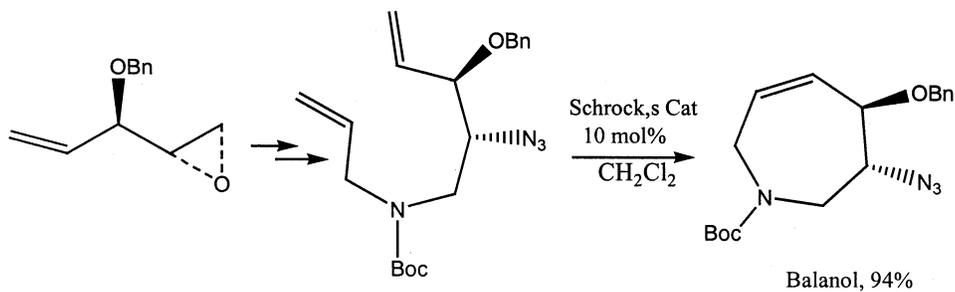
Grubbs,s Cat.A

(Ph = Phenyl, Cy = Cyclohexyl)



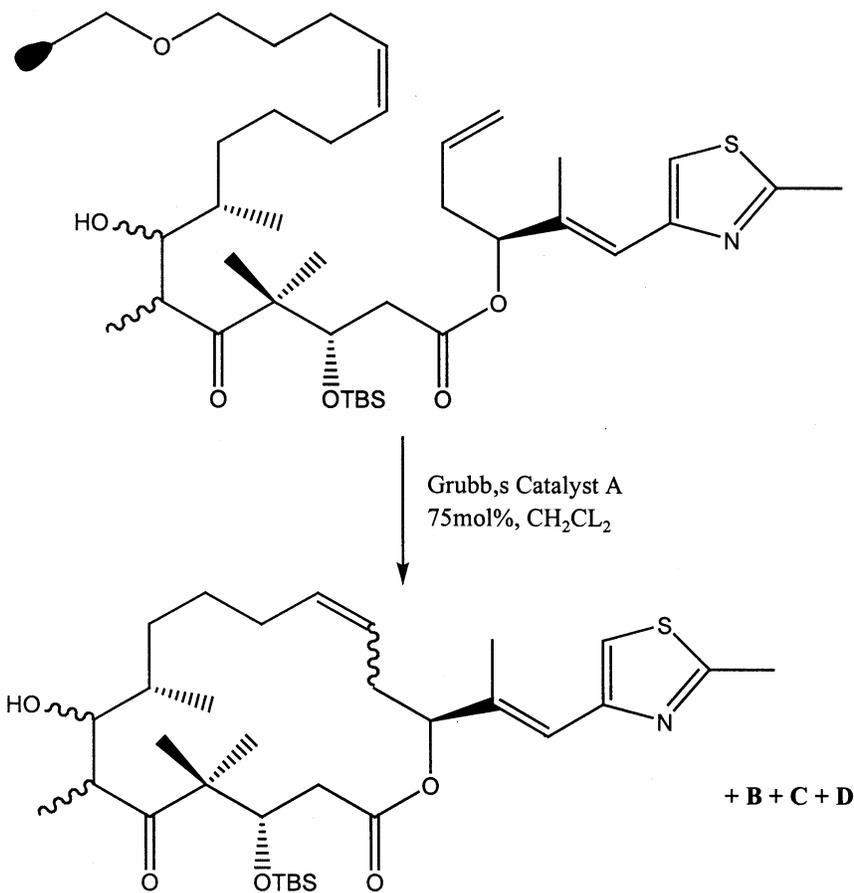
Grubbs,s Cat.B

Scheme 8



Synthesis of a drug (Balanol) using Ring-Closing Metathesis catalysed by Schrock,s Molybdenum Catalys

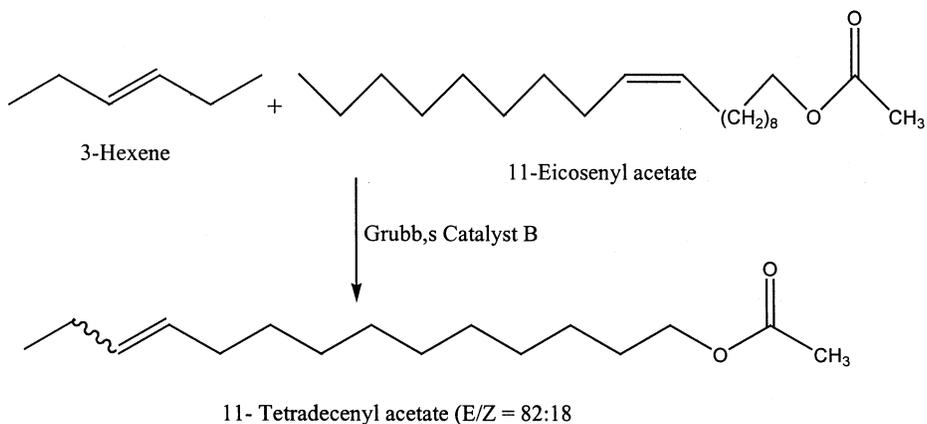
Scheme 9



Product A, Epothilone

Cyclization of an open chain compound using Grubbs, Cat. A, involving ring-closure metathesis to a drug Epithilone A and other derivatives B, C and D

Scheme 10

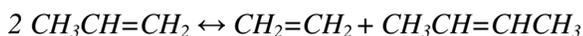


Synthesis of insect pest 11-Tetradecenyl acetate which is known as omnivorous leafroller (OLR) using olefin-metathesis

Scheme 11

Hydrocarbon Industries

First metathesis process applied on an industrial scale, developed by Phillips Petroleum Co., USA, and known as The Triolefin Process⁴⁴, produces high-purity ethene and but-2-ene from propene. This process operated for 6 years from 1996 by Shawanigan Chemicals near Montreal in Canada (capacity, 50,000 tons/year). It is based on the following metathesis reaction:



The reaction is carried out in a tubular reactor with a fixed bed of catalyst. The catalyst used was WO_3/SiO_2 , doped with sodium to prevent double-bond shift reactions at 350-425°C. The 2-butene (yield, 90%), obtained by this process, can be used as a starting material for gasoline or it can be isomerized to but-1-ene, which is in demand as a co-monomer in polyethylene production. The Triolefin Process was modified afterwards to produce higher olefins such as hexenes, heptenes and octenes. An important industrial method, which produces ethene and butadiene through propene metathesis, starts directly from a naphtha cracker.

In 1969, the Phillips Petroleum Co. started producing 3,3-dimethylbut-1-ene (neohexene) as an important intermediate in the synthesis of musk perfume. In 1985, the Lyondell Petrochemical Co., started producing 136000 tons of propene per year at a plant in Channelview, Texas, USA. In this process, part of the ethane from ethane-cracking unit was dimerized to but-2-ene using a homogeneous Ni-catalyst developed by Phillips, which reacts via the reverse Phillips triolefin process with the rest of the ethene to produce propene. The Institut Français du Pétrole (IFP) and the Chinese petroleum corporation (Taiwan) have jointly developed a commercial process, called Meta-4, in which ethene and but-2-ene react with each other in the liquid phase in the presence of an $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst.

A large-scale industrial process incorporating olefin metathesis is the Shell Higher Olefins Process (SHOP)⁴⁵ for converting ethene to detergent-range alkenes for the production of lubricants, plasticizer alcohols, detergent alcohols, synthetic fatty acids etc. In the second stage, these alkenes undergo double-bond isomerization over a solid alkali-metal based isomerization reactor to an equilibrium mixture of internal alkenes. In third stage, mixture is

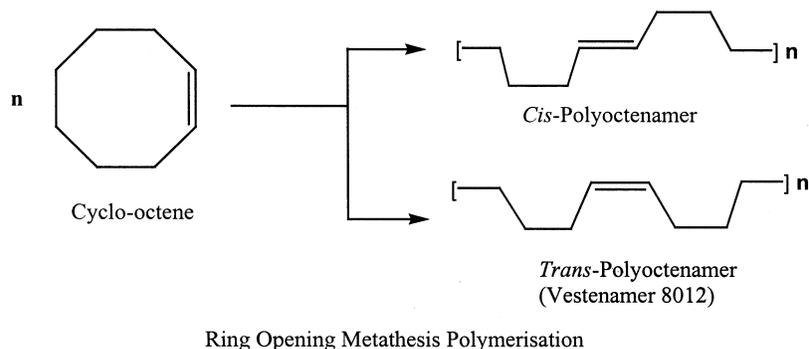
disproportionated by metathesis to detergent range internal olefins ($\text{C}_{11}\text{-C}_{14}$) in the disproportionation reactor, and the product is fractionated in distillation columns, into fractions of higher olefins.

Shell Chemicals began large-scale production of detergent alcohols and esters, which are made of long chain alkenes that are prepared from ethane using metathesis procedure⁴⁵. Shell Chemicals produced 200000 tons of detergent-range alkenes in 1979 in Geismar, Louisiana (USA), the capacity increased in 1989 to 590000 tons per year. A second plant came in 1982 in Stanlow (UK) to produce 270000 tons per year of higher alkenes. Similarly, various other industrial companies have developed metathesis process⁴⁶ for the production of 2-methylbut-2-ene (isoamylene, a precursor for isoprene, and α , ω -disubstituted olefins, starting materials of aroma chemicals, pharmaceuticals, and agricultural chemicals. A representative example of α , ω -disubstituted olefins, hexa-1,5-diene was produced in 1987 by FEAST (Further Exploitation of Advanced Shell Technology) in a plant (capacity of 3000 tons/year) at Berre 1, Etang (France).

Polymer Industries

Catalyzed metathesis was discovered in the industry following observations in the 1950s of the polymerization of ethylene by Ziegler (Nobel Prize in Chemistry 1963)^{47,48}. Polymerization of cyclopentene to polypentenamer found application immediately after the discovery of olefin metathesis⁴⁹. Trans- and cis- polypentenamer produced by the metathesis has aroused the rubber industry as the former has properties close to those of natural rubber while the latter is similar to some special rubbers⁵⁰. Chemische Werke Huls, Marl, Germany, first marketed the ring-opened polymer of cyclooctene, under the trade name Vestenamer 8012 (Scheme 12)^{51,52}.

Vestenamer 8012 possesses extremely unusual properties for an elastomer. At 20°C, it is hard and has an exceptionally high viscosity; above 60°C it becomes a fluid with a honey-like consistency. It is especially suitable for use in blends with other rubbers and blending was improved in terms of excellent co-vulcanization with other elastomers, higher hardness and elasticity of vulcanizate and very high stability against thermal, oxidative and photochemical degradation. In 1976, CdF Chimie and Elf Atochem in Carling, France started producing polymers of norbornene⁵³. Monomer was made by the Diels-Alder reaction of cyclopentadiene and ethane.



Scheme 12

Ring-opening metathesis used a RuCl_3/HCl catalyst in butanol. The polymer is marketed as a moulding powder under the trade name Norsorex and contains a small amount of non-staining antioxidant. It can be moulded and cured in the usual way up to 185°C . Vulcanized product has important special applications, particularly for engine mountings, anti-vibration mounts, shock-proof bumpers, and flexible couplings. Another extension plant using ring-opening metathesis of norbornene and related multi-ring monomers enable the Nippon Zeon Co. (1991) to produce a polymer and marketed under the trade name Zeonex⁵⁴. The amorphous, transparent and low moisture absorption properties of this polymer makes it suitable for application in optical properties such as disks, lenses, prisms etc.

Conclusions

Metathesis is at the forefront of “green chemistry” owing to shorter synthetic paths and providing more facile access to therapeutic agents under increasingly more environment friendly catalytic conditions. The pioneering works of Yves Chauvin² has brought a new shape in metathesis with a successful mechanistic approach. Chauvin mechanism was supported unambiguously by experimental works³ of Schrock, who contributed first stable metal-methylene and -alkylidene complexes. Similarly, Grubbs⁴ provides organic and polymer communities the air and water stable second generation ruthenium benzylidene catalysts with what are now the most environmentally friendly metathesis catalysts. Schrock-type and Grubbs-type metathesis catalysts are also complementary in terms of efficiency, compatibility of functional groups and stability. Together, the laureates contributions have brought a major significance in the chemicals industry, opening up new opportunities for synthesizing molecules that will

streamline the development and industrial production of pharmaceuticals, plastics and other materials.

Acknowledgements

Author thanks DST, New Delhi, Govt of India for a BOYSCAST fellowship and grateful to Prof P J Stang, Department of Chemistry, University of Utah, USA for the encouragement.

References

- 1 *The 2005 Nobel Prize in Chemistry*, <http://nobelprize.org/chemistry/laureates/2005/press.html>.
- 2 Chauvin Y, Olefin metathesis: The early days (Nobel lecture), *Angew Chem Int Ed*, **45** (2006) 3740-3747.
- 3 Schrock R R, Multiple metal-carbon bonds for catalytic metathesis reactions (Nobel lecture), *Angew Chem Int Ed*, **45** (2006) 3748-3759.
- 4 Grubbs R H, Olefin-metathesis catalysts for the preparation of molecules and materials (Nobel lecture), *Angew Chem Int Ed*, **45** (2006) 3760-3765.
- 5 Schneider V & Frolich P K, Mechanism of formation of aromatics from lower paraffins, *Ind Eng Chem*, **23** (1931) 1405-1410.
- 6 Banks R L & Bailey G C, Olefin disproportionation: A new catalytic process, *Ind Eng Chem Prod Res Dev*, **3** (1964) 170-173.
- 7 Eleuterio H S, Olefin metathesis: chance favors those minds that are best prepared, *J Mol Catal*, **65** (1991) 55-61.
- 8 Calderon N, Chen H Y & Scott K W, Olefin metathesis, a novel reaction for skeletal transformations of unsaturated hydrocarbons, *Tetrahedron Lett*, **34** (1967) 3327-3329.
- 9 Calderon N, Olefin metathesis reaction, *Acc Chem Res*, **5** (1972) 127-132.
- 10 Bradshaw C P W, Howmen E J & Turner L, Olefin dismutation: Reactions of olefins on cobalt oxide-molybdenum oxide-alumina, *J Catalysis*, **7** (1967) 269-276.
- 11 Begley J W & Wilson R T, Kinetics of propylene disproportionation, *J Catalysis*, **9** (1967) 375-395.
- 12 Hughes W B, Kinetics and mechanism of the homogeneous olefin disproportionation reaction, *J Am Chem Soc*, **92** (1970) 532-537.
- 13 Lewis M J & Wills G B, Initial rates of propylene disproportionation, *J Catalysis*, **15** (1969) 140-143.

- 14 Luckner R C, McCouchie G E & Wills G B, Initial rates of propylene disproportionation over tungsten trioxide on silica catalysts, *J Catalysis*, **28** (1973) 63-68.
- 15 Chauvin Y & Hérisson J L, Catalysis of olefin transformations by tungsten complexes. II. Telomerization of cyclic olefins in the presence of acyclic olefins, *Makromol Chem*, **141** (1971) 161-176.
- 16 Chauvin Y, Commereuc D & Cruypelinck D, Catalysis of olefin transformation by tungsten complexes, 5. Tungsten carbonyl carbenes activated by titanium tetrahalides as catalysts for the ring-opening polymerization of cyclopentene, *Makromol Chem*, **177** (1976) 2637-2647.
- 17 Amass A J & Zurimendi J A, The kinetics of the metathesis polymerization of cyclopentene initiated by tungsten hexachloride-triisobutylaluminum complexes, *J Mol Catalysis*, **8** (1980) 243-252.
- 18 Ofstead E A, Lawrence J P, Senyck M L & Calderon N, Stereochemistry of olefin metathesis - steric control and molecular weight regulation in polypentenamer synthesis, *J Mol Catalysis*, **8** (1980) 227-242.
- 19 Dolgoplosk B A, Kopieva I A, Oreshkin I A & Tiniyakova E I, Inhibition of chain process of cycloolefin ring-opening and metathesis by transition to less reactive carbene complexes *Eur Polymer J*, **16** (1980) 547-548.
- 20 Katz T J, Lee S J, Nair M & Savage E B, Induction of olefin metathesis by acetylenes, *J Am Chem Soc*, **102** (1980) 7940-7944.
- 21 Katz T J & Lee S J, Initiation of acetylene polymerization by metal carbenes, *J Am Chem Soc*, **102** (1980) 422-424.
- 22 Ivin K J, Lapienis G, Stewart C D & Rooney J J, Structural sequences in ring-opened polymers and copolymers of cycloalkenes as a guide to the mechanism of olefin metathesis, *J Mol Catalysis*, **8** (1980) 203-218.
- 23 Rooney J J, Laverty D T, McKervy M A & Stewart A, Mechanism of initiation of ring-opening polymerization of norbornene catalyzed by transition metal halides, *J Chem Soc Chem Commun*, (1976) 193-194.
- 24 France M B, Grubbs R H, McGrath V & Paciello R A, Initiation of ring-opening metathesis polymerization in protic media. Extension of $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$ catalyzed polymerizations to less-strained cyclic monomers, *Macromolecules*, **26** (1993) 4742-4747.
- 25 Schrock R R & Parshall G W, -Alkyl and -aryl complexes of the Group 4-7 transition metals, *Chem Rev*, **76** (1976) 243-268.
- 26 Schrock R R, Alkylidene complexes of niobium and tantalum, *Acc Chem Res*, **12** (1979) 98-104.
- 27 Schrock R R, Catalysis by transition metals: metal-carbon double and triple bonds, *Science*, **219** (1983) 13-18.
- 28 Schrock R R, Rocklage S M, Wengrovius J H, Rupprecht G & Feldmann J, Preparation and characterization of active niobium, tantalum, and tungsten metathesis catalysts, *J Mol Catal*, **8** (1980) 73.
- 29 Wengrovius J H, Schrock R R, Churchill M R, Missert J R & Youngs W J, Tungsten-oxo alkylidene complexes as olefin metathesis catalysts and the crystal structure of $\text{W}(\text{O})(\text{CHCMe}_3)(\text{PEt}_3)\text{Cl}_2$, *J Am Chem Soc*, **102** (1980) 4515.
- 30 Wood C D, McLain S J & Schrock R R, Multiple metal carbon bonds preparation and characterization of monocyclopentadienyl mononeopentylidene complexes of niobium and tantalum including the first details of an α -H abstraction process, *J Am Chem Soc*, **101** (1979) 3210-3222.
- 31 Murdzek J S & Schrock R R, Well-characterized olefin metathesis catalysts that contain molybdenum, *Organometallics*, **6** (1987) 1373-1374.
- 32 Schrock R R, Murdzek J S, Barzan G C, Robbins J, DiMare M & O'Regan M, Synthesis of molybdenum imido alkylidene complexes and some reactions involving acyclic olefins, *J Am Chem Soc*, **112** (1990) 3875-3886.
- 33 Teng X, Cefalo D, Schrock R R & Hoveyda A H, Enhancement of enantioselectivity by THF in asymmetric Mo-catalyzed olefin metathesis. Catalytic enantioselective synthesis of cyclic tertiary ethers and spirocycles, *J Am Chem Soc*, **124** (2002) 10779-10784.
- 34 Nguyen S T, Johnson L K, Grubbs R H & Ziller J W, Ring-opening metathesis polymerization (ROMP) of norbornene by a Group VIII carbene complex in protic media, *J Am Chem Soc*, **114** (1992) 3974-3975.
- 35 Sanford M S, Ulman M & Grubbs R H, New insights into the mechanism of Ruthenium catalyzed olefin metathesis reactions, *J Am Chem Soc*, **123** (2001) 749-750.
- 36 Grubbs R H, Olefin metathesis, *Tetrahedron*, **60** (2004) 7117-7140.
- 37 Grubbs R H, *Handbook of Metathesis*, vols 1-3: *Catalyst Development* (vol.1); *Applications in Organic Synthesis* (vol. 2); *Applications in Polymer Synthesis* (vol. 3) (Wiley-VCH, Weinheim) 2003.
- 38 Fürstner A, Olefin metathesis and beyond, *Angew Chem Int Ed*, **39** (2000) 3013-3043.
- 39 Fürstner A & Thiel O R, Formal total synthesis of (-)-balanol: Concise approach to the hexahydroazepine segment based on RCM, *J Org Chem*, **65** (2000) 1738-1742.
- 40 Nicolaou K C, Winsinger N, Pastor J, Ninkovic S, Sarabia F, He Y, Vourloumis D, Yang Z, Li T, Giannakakou P & Hamel E, Synthesis of ephedrine A and B in solid and solution phase, *Nature*, **387** (1997) 268-272.
- 41 Nicolaou K C, Bulger P G & Sarlah D, Metathesis reactions in total synthesis, *Angew Chem Int Ed*, **44** (2005) 4490-4527.
- 42 Tsuji J & Hashiguchi S, Application of olefin metathesis to organic synthesis. Syntheses of civetone and macrolides, *Tetrahedron Lett.*, 1980, 2955-2958.
- 43 Pederson R L, Fellows I M, Ung T A, Ishihara H & Hajela S P, Applications of olefin cross metathesis to commercial products, *Advanced Synthesis & Catalysis*, **344** (2002) 728-735.
- 44 Banks R L, Banasiak D S, Hudson P S, Norell J K, Specialty chemicals via olefin metathesis, *J Mol Catal*, **15** (1982) 21.
- 45 Freitas E R, Gum C R, Shell's higher olefins process, *Chem Eng Progr*, **75** (1979) 73.
- 46 Banks R L & Bailey R B, Synthesis of isoamylene via olefin disproportionation, *Ind Eng Chem Prod Res Dev*, **10** (1971) 46-51.
- 47 Natta G, Dall'Asta G & Porri L, Polymerization of cyclobutene and of 3-methylcyclobutene by RuCl_3 in polar protic solvents, *Makromol Chem*, **81** (1965) 253-257.
- 48 Grubbs R H & Tumas W J, Polymer synthesis and organotransition metal chemistry, *Science*, **243** (1989) 907-915.
- 49 Graulich W, Swodenk W, & Theisen D, Make new TPR [trans-1,5-polypentenamer] rubber from C5's *Hydrocarbon Processing*, **51** (1972) 71-75.
- 50 Dall'Asta G, Preparation and properties of polyalkenamers, *Rubber Chem Technol*, **47** (1974) 511-596.

- 51 Natta G, Dall'Asta G, Bassi I W & Carella G, Stereospecific ring cleavage homopolymerization of cycloolefins and structural examination of the resulting homologous series of linear crystalline trans-polyalkenamers, *Makromol Chem*, **91** (1966) 87-106.
- 52 Calderon N, Ofstead E A & Judy W A, Ring-opening polymerization of unsaturated alicyclic compounds, *J Polymer Sci A.1*, **5** (1967) 2209-2217.
- 53 Schrock R R, Krouse S A, Knoll K, & Feldmann J, Controlled ring-opening metathesis polymerization by molybdenum and tungsten alkylidene complexes, *J Mol Catal*, **46** (1988) 243-253.
- 54 Komiya Z, Pugh C, Schrock R R, Synthesis of side chain liquid crystal polymers by living ring opening metathesis polymerization, *Macromolecules* **25** (1992) 6586-6604.