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Catalytic Carbonylation Reactions

PATRICIA HEZEKIAH

Catalysis for Clean Energy and Environmental Sustainability CRC Press This book is part of a two-volume work that offers a unique blend of information on realistic evaluations of catalyst-based synthesis processes using green chemistry principles and the environmental sustainability applications of such processes for biomass conversion, refining, and petrochemical production. The volumes provide a comprehensive resource of state-of-the-art technologies and green chemistry methodologies from researchers, academics, and chemical and manufacturing industrial scientists. The work will be of interest to professors, researchers, and practitioners in clean energy catalysis, green chemistry, chemical engineering and manufacturing, and environmental sustainability. This volume focuses on catalyst synthesis and green chemistry applications for petrochemical and refining processes. While most books on the subject focus on catalyst use for conventional crude, fuel-oriented refineries, this book emphasizes recent transitions to petrochemical refineries with the goal of evaluating how green chemistry applications can produce clean energy through petrochemical industrial means. The majority of the chapters are contributed by industrial researchers and technicians and address various petrochemical processes, including hydrotreating, hydrocracking, flue gas treatment and isomerization catalysts.

Fundamentals of Organometallic Catalysis Springer In this book leading experts have surveyed major areas of application of NHC metal complexes in catalysis. The authors have placed a special focus on nickel- and palladium-catalyzed reactions, on applications in metathesis reactions, on oxidation reactions and on the use of chiral NHC-based catalysts. This compilation is rounded out by an introductory chapter and a chapter dealing with synthetic routes to NHC metal complexes.

Polypropylene and other Polyolefins Springer Science & Business Media Catalysis, the basic principle for overcoming the kinetic inhibition of chemical reactions, is fundamental in chemistry. In particular, organometallic catalysis plays an overwhelming role in both research and industry. It opens the way to entirely novel synthetic methods and finds widespread applications ranging from mass-production of everyday polymers to stereocontrolled synthesis of bioactive chemicals used as pharmaceuticals and agrochemicals. The targeted development of improved and novel catalysts demands understanding of the relationships between their structures and catalytic properties. Accordingly, this textbook offers the reader a fundamental understanding of the course of organometallic-catalyzed reactions, starting at the molecular level. The initial chapters explain the principles of catalysis and the elementary steps in

organometallic catalysis. The book then explores important organometallic-catalyzed reactions, with a focus on mechanism. Current developments are emphasized throughout. Asymmetric synthesis is covered in depth. Finally, the book examines the catalytic behavior of particular metalloenzymes. A look at nitrogen fixation offers a comparative examination of the three major areas of catalysis - homogeneous, heterogeneous, and enzymatic. In addition to problems, the textbook offers solutions, making the book an invaluable learning tool. It is a must-have for advanced students in chemistry and biochemistry, as well as for inorganic and organic chemists, for those working with organometallics, and for those specializing in catalysis.

Directed Metallation

MDPI

The proposed book focusses on metal mediated/catalyzed “controlled/living radical polymerization” (CRP/LRP) methods. It surveys a wide variety of catalyzed polymerization reactions, making it essentially a “one stop” review in the field. A significant contribution to polymer science is “metathesis polymerization” discovered by Grubbs and others. The book will cover various metathesis polymerization methods and implications in polymer industry.

World Scientific

This dissertation, "Group 4 Complexes Bearing Tridentate Aryloxide-based Ancillary Ligands: Synthesis, Characterization and Application as Olefin Polymerization Catalysts" by Ka-ho, Tam, □□□, was obtained from The University of Hong Kong (Pokfulam, Hong Kong) and is being sold pursuant to Creative Commons: Attribution 3.0 Hong Kong License. The content of this dissertation has not been altered in any way. We have altered the formatting in order to facilitate the ease of printing and reading of the dissertation. All rights not granted by the above license are retained by the author. Abstract: Abstract of thesis entitled GROUP 4 COMPLEXES BEARING TRIDENTATE ARYLOXIDE- BASED ANCILLARY LIGANDS: SYNTHESIS, CHARACTERIZATION AND APPLICATION AS OLEFIN POLYMERIZATION CATALYSTS Submitted by Tam Ka Ho for the degree of Doctor of Philosophy at The University of Hong Kong in 2006 The preparation, characterization, crystal structures and olefin polymerization behavior of a class of Group 4 complexes, and in particular the Zr(IV) derivatives 1 1 [Zr(L)Cl (D)] [H L = 2,6-di(3-tert-butyl-5-methylphen-2-ol)pyridine; D = ethers, 2 2 ketones and Cl(HPR)], have been undertaken. These [O, N, O] catalysts exhibit excellent activities with MAO for ethylene polymerization. Studies to assess the impact of the donor group during catalysis suggest that the same active species is generated and the donor does not play an active role. Superior activities were observed with the Bu Al/Ph CB(C F) cocatalyst in ethylene polymerization and - 3 3 6 5 4 -1 -1 propylene copolymerization (36,590 and 15,700 g mmol h respectively). Insight into the behavior of the catalytic system with MAO has been derived from gel permeation chromatography and NMR analyses of the polymers prepared under 1 13 different reaction conditions. H and C NMR end-group analyses reveal

resonances for saturated methyl chain-end groups only, and undetectable levels of unsaturated vinyl chain ends. This indicates that for the polymerization chain-transfer mechanism, the conventional β-H transfer reactions are insignificant and the unusual chain transfer to Al pathway is vastly dominant. Group 4 complexes supported by unsymmetric tridentate [O, N, O] ligands bearing different substituents on the two aryloxide rings have been prepared, in order to develop new catalytic systems capable of stereospecific α-olefin polymerization. Their activities for ethylene polymerization with MAO are significantly lower than the symmetric [O, N, O] analogues. A number of group 4 bis(benzyl) complexes supported by tridentate pyridine-2-phenolate-6-aryl [O, N, C] ligands, with alkyl and halogen substituents at the R position ortho to the metal, have been prepared. This enabled direct comparison with the CF -substituted [O, N, C] analogues, which were recently reported to exhibit novel C-H---F-C contacts in solution with potential applications for attractive ligand---polymer interactions. The molecular structure of the Zr derivative bearing an ortho-Cl group was determined, revealing the benzyl moieties in an unusual 'anti, anti' configuration. Saliently, this polyethylene catalyst in conjunction with Bu Al/Ph CB(C F) displayed the best activity thus far observed for [O, N, C] 3 3 6 5 4 -1 -1 catalysts (8630 g mmol h). A series of group 4 bis(benzyl) complexes supported by newly designed [O, C, N] ligands bearing R substituents ortho to the metal has been prepared, such that the σ- aryl moiety resides trans to the alkyl/polymer chain, and catalyst decomposition pathways such as olefin insertion into the M-C(sp) bond are impeded. The crystal structure of the CF -substituted hafnium(IV) complex features weak intramolecular 31 C-H---F-C (CF ---methylene) interactions. The H NMR spectra of [M(O, C, N- CF)(CH Ph)] analogues revealed coupling (assigned to J [via M---F] for Hf and

Metal Carbenes in Organic Synthesis Elsevier

In this book, leading experts from academia and industry offer a comprehensive presentation and discussion of the major reaction types of carbon monoxide. The authors highlight important carbonylation reactions such as hydroformylation, alkoxy-carbonylations, co/olefin-copolymerization, Pauson-Khand reactions and others. They illustrate applications in organic synthesis and give industrial examples. This volume is designed to provide graduate students and researchers with essential information on the use of carbon monoxide in organic synthesis.

Isospecific Polymerization of Olefins Springer Science & Business Media

Stereoregular Polymers and Stereospecific Polymerizations: The Contributions of Guilio Natta and his School to Polymer Chemistry, Volume 1 covers the developments in understanding the reactions, nomenclature, and physico-chemical properties of polymers. This volume is composed of 82 chapters, and starts with surveys of the synthesis and crystal structure of polymers. Significant chapters are devoted to the characterization of crystalline polymers, with

emphasis on the determination of their viscosity and molecular weight. Other chapters deal with stereospecific polymers of olefins, mechanism of stereospecific catalysis, reaction kinetics. This volume also considers the polymerization of synthetic elastomers and the copolymerization of olefins, as well as their reaction kinetics. The remaining chapters describe the X-ray characterization of isotactic polymers. This book is directed toward polymer chemists.

Insertion Polymerization Springer Science & Business Media

The discoveries of organometallic catalysts for olefin polymerization by Karl Ziegler and that of stereoregular olefin polymers by Giulio Natta are probably the two most important achievements in the areas of catalysis and polymer chemistry in the second half of this century. They led to the development of a new branch of chemical industry, and to a large volume production of high-density and linear low-density polyethylene, isotactic polypropylene, ethylene-propylene rubbers, isotactic poly l-butene, and poly-4-methyl-l-pentene. These discoveries merited the Nobel prize, which was awarded to K. Ziegler and G. Natta in 1963. The initial works of Ziegler and Natta were followed by an "explosion" of scientific papers and patents covering all aspects of polymerization chemistry, catalyst synthesis, and polymerization kinetics as well as the structural, chemical, physical, and technological characteristics of stereo regular polyolefins, polydienes, and olefin copolymers. It is sufficient to say that in the twenty-five years after the first publications more than 15,000 papers and patents appeared on subjects related to the area. . The development brought about the establishment of several prominent groups of scientists occupied with the study of olefin polymerization. The most important of these were scientific schools in Italy, Germany, England, the United States, Japan, the Soviet Union, Czechoslovakia, and Venezuela. In addition, many major chemical and petrochemical corporations throughout the world established labora tories devoted to the development of the technology of catalyst synthesis and olefin polymerization.

Synthesis and Evaluation of New Polymers Prepared by Stereospecific Catalysis Elsevier

This book provides a comprehensive summary and critical overview of a topic in organometallic chemistry. Research in this rapidly developing transdisciplinary field is having profound influence on other areas of scientific investigation, ranging from catalytic organic synthesis to biology, medicine and material science. The book is complemented by a review of metallodendritic exoreptors for the redox recognition of oxo-anions and halides.

The Contributions of Giulio Natta and His School to Polymer Chemistry Springer Science & Business Media

Including recent advances and historically important catalysts, this book overviews methods for developing and applying polymerization catalysts – dealing with polymerization catalysts that afford commercially acceptable high yields of polymer with respect to catalyst mass or productivity. • Contains the valuable data needed to reproduce syntheses or

use the catalyst for new applications • Offers a guide to the design and synthesis of catalysts, and their applications in synthesis of polymers • Includes the information essential for choosing the appropriate reactions to maximize yield of polymer synthesized • Presents new chapters on vanadium catalysts, Ziegler catalysts, laboratory homopolymerization, and copolymerization Polymerization and Characterization Springer Since the beginning of the 1960s, the coordinative polymerization of conjugated dienes has continuously improved. Today, chemists know how to polymerize conjugated dienes stereospecifically and in a controlled fashion, both petro-sourced (nowadays also bio-sourced) and those of natural origin. The industry has greatly improved the performances of the catalytic systems—covering a wide range of elements including metals from groups 4–6 and 8–10, and rare earths—with the aim of optimizing the preparation of synthetic polymers for a large range of industrial applications. Nowadays, there is a better understanding of the polymerization mechanism involving allyl-active species, thanks in particular to the support of more efficient calculation methods. In addition, statistical copolymerization of 1,3-dienes with olefin or styrene comonomers and innovative approaches to coordinative chain transfer polymerization allow the production of copolymers with controlled topology, while a last challenge is about to be solved with the preparation of stereoregular polydienes that are also end-functionalized. This issue brings together several important aspects of this chemistry that remain at the forefront of both academic and industrial research.

State-of-the-art and Perspectives Springer Science & Business Media A metallocene catalyst system for the polymerization of .alpha.-olefins to yield stereospecific polymers including syndiotactic, and isotactic polymers. The catalyst system includes a metal and a ligand of the formula ##STR1## wherein: R.sup. 1, R.sup. 2, and R.sup. 3 are independently selected from the group consisting of hydrogen, C.sub. 1 to C.sub. 10 alkyl, 5 to 7 membered cycloalkyl, which in turn may have from 1 to 3 C.sub. 1 to C.sub. 10 alkyls as a substituent, C.sub. 6 to C.sub. 15 aryl or arylalkyl in which two adjacent radicals may together stand for cyclic groups having 4 to 15 carbon atoms which in turn may be substituted, or Si(R.sup. 8).sub. 3 where R.sup. 8 is selected from the group consisting of C.sub. 1 to C.sub. 10 alkyl, C.sub. 6 to C.sub. 15 aryl or C.sub. 3 to C.sub. 10 cycloalkyl; R.sup. 4 and R.sup. 6 are substituents both having van der Waals radii larger than the van der Waals radii of groups R.sup. 1 and R.sup. 3 ; R.sup. 5 is a substituent having a van der Waals radius less than about the van der Waals radius of a methyl group; E.sup. 1, E.sup. 2 are independently selected from the group consisting of Si(R.sup. 9).sub. 2, Si(R.sup. 9).sub. 2 -- Si(R.sup. 9).sub. 2, Ge(R.sup. 9).sub. 2, Sn(R.sup. 9).sub. 2, C(R.sup. 9).sub. 2, C(R.sup. 9).sub. 2 -- C(R.sup. 9).sub. 2, where R.sup. 9 is C.sub. 1 to C.sub. 10 alkyl, C.sub. 6 to C.sub. 15 aryl or C.sub.

3 to C.sub. 10 cycloalkyl; and the ligand may have C.sub. S or C.sub. 1 - symmetry. Preferred metals are selected from the group consisting of group III, group IV, group V or lanthanide group elements. The catalysts are used to prepare stereoregular polymers including polypropylene from .alpha.-olefin monomers.

N-Heterocyclic Carbenes in Transition Metal Catalysis Springer Science & Business Media
Multiphase catalysis is a key technology for the competitive and sustainable production of fine chemicals in coming decades. A joint academic and industry consortium has developed tools for considering complex chemical and process-based requirements when setting up a catalytic system. This book shows how the resulting competence covers such supercritical fluid (SCF) technology in catalysis, ionic liquids (Il), ligand design for SFCs and Ils, thermomorphic solvent systems, reactor design and more.

Organometallic Oxidation Catalysis CRC Press
This book provides the broad scientific readership with a comprehensive summary and critical overview of a topic in organometallic chemistry. A wide variety of catalytic functionalization reactions of C-H bonds by the utilization of a chelation have been developed recently and are comprehensively discussed in this book by leading experts. In addition, new approaches to directed hydrometalation and directed carbometalation as a key step are also discussed.

Synthesis, Characterization and Application as Olefin Polymerization Catalysts Springer
More than 30 years after the discovery of transition metals and organometal lics as catalysts for olefin polymerization these catalysts did not have lost their fascination. Since 1953 when Karl Ziegler has discovered the catalytic polymerization of ethylene leading to plastically formable polymers which are mechanically stable up to temperatures of about 100°C, synthetic polymers and rubbers have made their way right into private houses. This discovery has been a main impetus for the fast growing production of plastics. The stereoselective poly merization of propylene and other long-chain a-olefins first detected by Giulio Natta leads to an even broadened field of applications. Another enforcing factor were the developments of Standard Oil of Indiana and Phillipps Petroleum Company who engaged in the polymerization of a-olefins supported molybdenum, cobalt and later on chromium catalysts which clearly indicates the wide variety of suitable systems. This kind of research acknowledged merit when in 1963 the Nobel prize of chemistry was awarded to Ziegler and Natta. Although to a great extent there is a technical application for these catalysts, up to now the nature of the active centres and many reaction mechanisms are not completely known.

Regulated Systems for Multiphase Catalysis CRC Press
With contributions by numerous experts

Macromolecular Design of Polymeric Materials Stereospecific Olefin Polymerization CatalystsA metallocene catalyst system for the polymerization of .alpha.-olefins to yield stereospecific polymers including syndiotactic, and isotactic polymers.

The catalyst system includes a metal and a ligand of the formula ##STR1## wherein: R.sup. 1, R.sup. 2, and R.sup. 3 are independently selected from the group consisting of hydrogen, C.sub. 1 to C.sub. 10 alkyl, 5 to 7 membered cycloalkyl, which in turn may have from 1 to 3 C.sub. 1 to C.sub. 10 alkyls as a substituent, C.sub. 6 to C.sub. 15 aryl or arylalkyl in which two adjacent radicals may together stand for cyclic groups having 4 to 15 carbon atoms which in turn may be substituted, or Si(R.sup. 8).sub. 3 where R.sup. 8 is selected from the group consisting of C.sub. 1 to C.sub. 10 alkyl, C.sub. 6 to C.sub. 15 aryl or C.sub. 3 to C.sub. 10 cycloalkyl; R.sup. 4 and R.sup. 6 are substituents both having van der Waals radii larger than the van der Waals radii of groups R.sup. 1 and R.sup. 3 ; R.sup. 5 is a substituent having a van der Waals radius less than about the van der Waals radius of a methyl group; E.sup. 1, E.sup. 2 are independently selected from the group consisting of Si(R.sup. 9).sub. 2, Si(R.sup. 9).sub. 2 -- Si(R.sup. 9).sub. 2, Ge(R.sup. 9).sub. 2, Sn(R.sup. 9).sub. 2, C(R.sup. 9).sub. 2, C(R.sup. 9).sub. 2 -- C(R.sup. 9).sub. 2, where R.sup. 9 is C.sub. 1 to C.sub. 10 alkyl, C.sub. 6 to C.sub. 15 aryl or C.sub. 3 to C.sub. 10 cycloalkyl; and the ligand may have C.sub. S or C.sub. 1 - symmetry. Preferred metals are selected from the group consisting of group III, group IV, group V or lanthanide group elements. The catalysts are used to prepare stereoregular polymers including polypropylene from .alpha.-olefin monomers.Handbook of Transition Metal Polymerization Catalysts The first NATO Advanced Study Institute on Olefin Metathesis and Polymerization Catalysts was held on September 10-22, 1989 in Akcay, Turkey. Based on the fundamental research of RRSchrock, RGrubbs and K.B.Wagener in the field of ring opening metathesis polymerization (ROMP), acyclic diene metathesis (ADMET) and alkyne polymerization, these areas gained growing interest within the last years. Therefore the second NATO-ASI held on metathesis reactions was on Ring Opening Metathesis Po lymerization of Olefins and Polymerization of Alkynes on September 3-16, 1995 in Akcay, Turkey. The course joined inorganic, organic and polymer chemists to exchange their knowledge in this field. This volume contains the main and short lectures held in Akcay. To include ADMET reactions better into the title of this volume we changed it into: Metathesis Polymerization of Olefins and Alkyne Polymerization. This volume is addressed to research scientists, but also to those who start to work in the area of olefin metathesis and alkyne polymerization. The topics of the course were: mechanism of ROMP reactions/ new catalysts for ROMP/ new products by ROMP/ new catalysts for ADMET/ new products by ADMETI degradation of polymer by metathesis reactions/ alkyne polymerization and metathesis/ industrial application of metathesis reactions. The Advanced Study Institute was generously sponsored by the Scientific Affairs Division of NATO and the editor gratefully acknowledges this sponsorship. We also thank the Members of the Local Organizing Committee for their

engagement on a successful NATO-AS!. *Surface and Interfacial Organometallic Chemistry and Catalysis* Springer "It is desired to prepare oriented polymeric materials for use as radiation and thermally stable solvent resistant materials. The use of heterogeneous catalyst systems to achieve the above purpose is under investigation. Research on the mechanism of these heterogeneous catalysts is being undertaken for application in the development of new catalytic systems"--P. 1. Ziegler-Natta Catalysts Polymerizations Walter de Gruyter GmbH & Co KG Chemical Synthesis: Gnosis to Prognosis (XTUllKtl ~uv8eoTr ana TT) rVWOT) OTT) npaYVWOT)) " . . . . other things being equal, that field has the most merit which contributes most heavily to, and illuminates most brightly, its neighbouring scientific disciplines[l] One hundred scientists, a blend of students, industrialists, and academics from twenty countries gathered to circumscribe, understand, and elaborate this topic in the magical setting of Ravello, Italy. The mandate of this workshop? To survey existing knowledge, assess current work, and discuss the future directions of chemical synthesis as it impinges on three exciting interdisciplinary themes of science in the 1990's: bioactive molecules, man-made chemical materials, and molecular recognition. This tempting but inexact menu summoned diverse students and scientists who wished to seriously reflect upon, dissect, and eject ideas and own experiences into open debate on this topic, which is at a crossroad in internal evolution and impact on the life and material sciences. The group arrived from many directions and in various forms of transportation, matters soon forgotten, when it found itself in the village which nurtured Wagner's inspiration and set to work immediately to ponder the question which has received extensive thought, prediction, and caveat from illustrious chemists over a period of time [2], two of which, to the delight of all, in presence among the Lectures. Fundamentals to Applications Elsevier This book presents recent advances in computational methods for polymers. It covers multiscale modeling of polymers, polymerization reactions, and polymerization processes as well as control, monitoring, and estimation methods applied to polymerization processes. It presents theoretical insights gained from multiscale modeling validated with exprimental measurements. The book consolidates new computational tools and methods developed by academic researchers in this area and presents them systematically. The book is useful for graduate students, researchers, and process engineers and managers.

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