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Topics in Organometallic Chemistry

Aims and Scope

The series *Topics in Organometallic Chemistry* presents critical overviews of research results in organometallic chemistry. As our understanding of organometallic structure, properties and mechanisms increases, new ways are opened for the design of organometallic compounds and reactions tailored to the needs of such diverse areas as organic synthesis, medical research, biology and materials science. Thus the scope of coverage includes a broad range of topics of pure and applied organometallic chemistry, where new breakthroughs are being achieved that are of significance to a larger scientific audience.

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Eike Bauer
Editor

Iron Catalysis II

With contributions by

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ISSN 1436-6002 ISSN 1616-8534 (electronic)
Topics in Organometallic Chemistry
ISBN 978-3-319-19395-3 ISBN 978-3-319-19396-0 (eBook)
DOI 10.1007/978-3-319-19396-0

Library of Congress Control Number: 2015945936

Springer Cham Heidelberg New York Dordrecht London

Printed on acid-free paper

Springer International Publishing AG Switzerland is part of Springer Science+Business Media (www.springer.com)

Preface

Catalysis is a fundamental chemical principle with huge significance in both industry and academia. Catalysts save energy and resources, increase selectivities and yields, and make compounds accessible that are otherwise difficult or impossible to synthesize. The economic impact of catalysis is tremendous and difficult to quantify. The *Pacific Northwest National Laboratory* states that the economic impact of catalysis has been valued to be over 10 trillion dollars per year worldwide. The American Chemical Society estimates that *85% of all chemical products being produced use at least one catalytic step*.

The field of homogeneous catalysis has been dominated in the last 30 years by either early or precious transition metals such as titanium, osmium, rhodium, palladium, or ruthenium. This is well demonstrated by the Nobel prizes awarded for homogeneous catalysis in 2001, 2005, and 2010, which are all related to these metals and which underline the significance of the field. However, there are serious issues associated with these metals. Due to their low natural abundance, they are high and volatile in price, and they are present in metal rich ores in only small concentrations. Furthermore, these metals are also of interest in the automotive industry and in the consumer electronic sector, creating extra competition for their sources. Finally, the toxicity poses a serious problem, e.g., in the pharmaceutical industry, where only trace amounts of toxic metals can be present in the final product to meet quality standards set by authorities.

In turn, homogeneous iron catalysis was for many years a "Sleeping Beauty" and was not as extensively investigated compared to the other metals mentioned above. Heterogeneous iron catalysis, though, has been applied for at least a century for example as in the Haber–Bosch or Fischer–Tropsch processes. However, applications in the synthesis of fine chemicals were scarce to nonexistent. This changed around the turn of the century, when the chemical community started realizing that iron has a number of advantages compared to the other metals typically applied in homogeneous catalysis. Iron is relatively cheap, nontoxic, and tolerant to a number of functional groups, making it an interesting alternative to other transition metals typically applied in catalysis, especially for applications in pharmaceutical

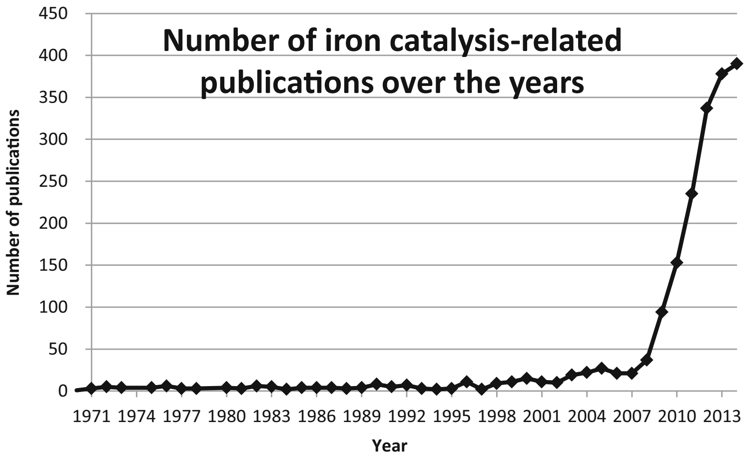

Fig. 1 Publication activity in iron catalysis over the years

industry. Its eco friendliness and catalytic activity are in line with two major principles of Green Chemistry, which calls for both catalytic processes and for chemicals that *pose little or no toxicity to human health and the environment*.

These aspects promoted increasing research activity in the field starting about 15 years ago. More and more research groups turned to iron as a basis for catalytic applications, as demonstrated by an increasing number of research articles published in the area. About 5 years ago, the field began a self-reflection. Matthias Beller raised the question of *Sustainable Metal Catalysis with Iron: From Rust to a Rising Star?* in an *Angewandte Chemie* article in 2008. In 2009, Carsten Bolm proclaimed a new *Iron Age* in a *Nature Chemistry* article. Alois Fürstner described iron as a *base metal for a noble task*. The journal *Organometallics* devoted a special issue in 2014 to the *Catalytic and Organometallic Chemistry of Earth-Abundant Metals*. The magazine *Science* published in the last 5 years 6 articles related to iron catalysis. Three of them were also highlighted in the *New York Times* in December 2013. In this article, Robert Morris, a player in the field, was quoted as saying *It shows that with the right organic molecules attached to it, we can make iron do things that weren't thought possible before*.

A look at the number of publications in the field corroborates the proclamation of a new *Iron Age*. I performed a Scopus® search in January 2015 for journal articles containing the phrase "iron catalysis". The result is depicted in Fig. 1, where the number of publications is plotted against the year of their appearance. Before around 2000, only a single digit number of publications under the search phrase were published each year. An exponential increase of publications can be observed starting around 2009.

This book provides an overview of the increasing research activities in the field of homogeneous iron catalysis. It is organized under the aspect of synthetic applications of iron catalysis, mainly in the area of the production of fine chemicals or polymers. The advances in coupling, oxidation, reduction, and polymerization reactions in the last 5 years are covered, and enantioselective as well as stoichiometric reactions of iron complexes (which play an important role in the development of catalytic processes) are also highlighted.

The book outlines new avenues for the production of a variety of organic compounds under iron catalysis. Challenges still remain. Iron complexes exhibit a number of features that are not prevalent for other transition metals. Iron is stable in a variety of oxidation states, with +2 and +3 being probably the most prevalent ones for precatalysts. Iron can undergo redox chemistry, which can be promoted by the ligands supporting a catalytically active iron complex. Many oxidation states of iron can produce paramagnetic iron complexes, which makes their investigation by NMR challenging.

Turning to iron is a smart move from both economic and environmental points of view. Still, it appears that homogeneous iron catalysis is not as common in the industrial production of fine chemicals compared to other transition metals. Some iron-catalyzed processes still require high reaction temperatures, which might be problematic for sensitive substrates as often encountered in pharmaceutical industry. However, it can be expected that the vigorous research activities in the field will provide solutions for these challenges. This book is meant to inspire chemists in the field of catalysis or chemical production to consider iron as a valuable alternative in the production of chemicals at all stages of the supply chain. Our knowledge of iron catalysis will grow as additional researchers begin investigating its potential from different perspectives. This will be important, because to say it with the words of Morris Bullock in relation to the aforementioned *Science* articles: *there is no exclusive single 'recipe' for success in developing catalysts based on cheap metals*.

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