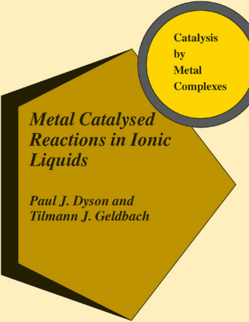

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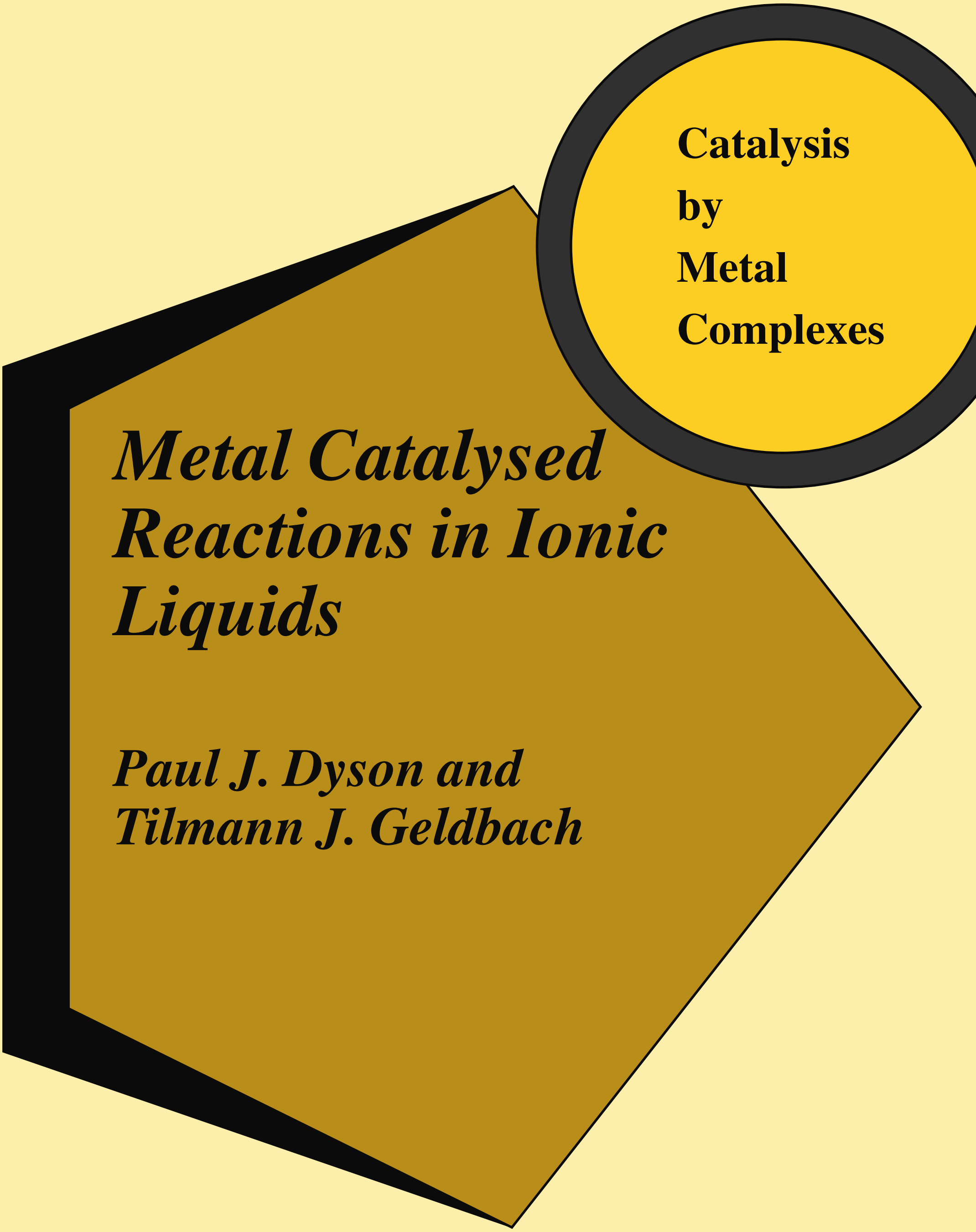

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Catalysis by Metal Complexes

Volume 29

The titles published in this series are listed at the end of this volume.

METAL CATALYSED REACTIONS IN IONIC LIQUIDS

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A C.I.P. Catalogue record for this book is available from the Library of Congress.

ISBN-10 1-4020-3914-X (HB)
ISBN-13 978-1-4020-3914-0 (HB)
ISBN-10 1-4020-3915-8 (e-book)
ISBN-13 978-1-4020-3915-7 (e-book)

Published by Springer,
P.O. Box 17, 3300 AA Dordrecht, The Netherlands.

www.springeronline.com

Printed on acid-free paper

Printed in the Netherlands.

FOREWORD

Sceptics were predicting that the field of ionic liquids would slow down or even reverse – but such a situation could not be further from the truth. In fact, in the last year or so, more and more researchers and technologists in increasingly diverse areas have become interested in ionic liquids. While this is great for the subject, it presents somewhat of a nightmare to anyone foolish enough to contemplate writing a book on the subject, even a book restricted to metal catalysed reactions facilitated by ionic liquids.

At the time we started writing on this book, we were still optimistic that we could give a comprehensive overview on metal-catalysed reactions in ionic liquids. Yet, a literature search with the term “ionic liquid” gives some 3,100 references up to the end of 2004, of which more than 1,000 stem from 2004 alone. Thus, at some point we were forced to concede defeat and it is likely that some important contributions have been overlooked. This is probably particularly true for those papers, which are less easily accessible and for which no translated versions exist. We tried to include papers that appeared during the writing for as long as possible, but it could be that some of the most recent publications do not get the detailed description they should deserve.

Nevertheless, we hope to have succeeded in providing a useful overview of what has been done in the field of metal catalysed reactions in ionic liquids, covering most of the literature until early 2005. Not all reactions described on the following pages are strictly within the theme of this series – “Catalysis with Metal Complexes” – as reactions catalysed by simple metal salts are also described.

There are now several nomenclatures for ionic liquids in use and we hope that the system we settled on is sufficiently easy to comprehend.

Finally, we would like to thank those to help us spotting the most obvious errors in various chapters, notably Dr. Andre Ohlin, Dr. Zhaofu Fei, Adrian Chaplin and Prof. Paul Pregosin.

Lausanne, May 2005

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Chapter 1

INTRODUCTION

Changing the way chemists think and work

1.1 A Brief History of Biphasic Catalysis

Like the first paper dealing with ionic liquids – their history will be described later on – the origin of the concept of biphasic catalysis is not entirely clear. In the book edited by Cornils and Herrmann entitled ‘Aqueous-Phase Organometallic Catalysis’, Cornils and Kuntz credit the field to Manassen at the Weizmann Institute in Israel.[1] Due to the popularity of this book with those working in the field, many authors have subsequently cited the seminal work of Manassen, published in 1973, as representing the first paper on biphasic catalysis.[2] Yet, at the same time, Joó at the University of Debrecen in Hungary was also working on the concept of aqueous-organic biphasic catalysis.[3] In a recent publication, Cornils (one of the pioneers of the field), acknowledges the seminal contribution by Joó: “He [Joó] has always been recognised as the earliest pioneer in this field, but I was not previously aware that his first publications on the subject in 1973 (which were somewhat hidden away in Hungarian journals) appeared at the same time as those of Manassen’s group, and that therefore the two developed the ideas independently.”[4]

However, in 1972, one year before Manassen’s and Joó’s first publications, Parshall working at Dupont in Delaware reported that the hydrogenation and alkoxycarbonylation of alkenes could be catalysed by $PtCl_2$ when dissolved in tetraalkylammonium chloride/tin dichloride at temperatures of less than 100ºC.[5] It was even noted that the product could be separated by decantation or distillation. Parshall recognised the separation problem associated with homogeneous catalysis and in this paper states, ‘An approach that seems under utilised is the use of molten salts as stable, non-volatile solvents from which organic products are readily separated by distillation … or decantation’. An even earlier report by a group working for the U.S.

Industrial Chemicals Co. on biphasic catalysis can be found in a 1962 edition of the *Journal of the American Chemical Society* describing hydrogenations with $[Co(CN)_5H]^{3-}$ under aqueous-organic conditions.[6] Although we are not yet aware of any publication prior to that, it is highly likely that biphasic catalysis has a longer history than thought until recently. Yet, it was the systematic studies of Joó and Manassen that really laid the foundations to the field.

On an industrial scale, biphasic catalysis was first employed in the Shell Higher-Olefin Process (SHOP), which involves the use of two immiscible organic solvents, one containing the catalyst and substrates, the other being the formed product, which is immiscible with the reaction phase. The process consists of the nickel-catalysed oligomerisation of ethylene to give the majority of the worlds linear α-olefins, which are used in various applications, most importantly as detergents.[7] Subsequently, it did not take long for the first aqueous-organic biphasic processes to be implemented on an industrial scale (see below).

In the past decades, a number of alternatives to common organic solvents and water for use in biphasic catalysis have emerged. These include fluorous solvents, supercritical fluids and ionic liquids. The concept of fluorous biphasic catalysis originated from the work of Horváth and Rábai who were searching for a novel approach to selectively oxidise methane to methanol, and noticed that the solubility of methanol in fluorous solvents is low while the solubility of oxygen is extremely high.[8] When they realised that the miscibility of perfluoroalkanes, perfluorodialkyl ethers and perfluorotrialkylamines is low with many common organic solvents they demonstrated the utility of the technique, and elegantly showed that at low temperature the fluorous and organic solvents formed two phases, which on warming gave a single phase.[8,9] By careful design the reaction can be carried out homogeneously with the added advantage of a biphasic separation of catalyst and products after the reaction. This technique is particularly applicable to those reactions where non-polar compounds are converted to products with a higher polarity since the solubility of compounds in the fluorous phase decreases with increasing polarity. Apart from oxidation, many different reactions have been studied in fluorous phases including hydroformylation,[10] hydrogenation,[11] Diels-Alder,[12] C-C cross coupling reactions [13] and polymerisations,[14] to name but a few.

Supercritical fluids, another class of alternative reaction medium, have been used as solvents in catalysis for many years. Ipatiev reported the isomerisation of cyclohexane to methylcyclopentane under supercritical conditions using Al_2O_3 as the catalyst[15] and shortly afterwards communicated the oligomerisation of supercritical ethylene catalysed by $AlCl_3$.[16] However, it took another 60 years before supercritical fluids were used as solvents for homogeneous catalysts, which was reported by Kramer and Leder working at Exxon. In their patent, the isomerisation of hexane to methylpentane or dimethylbutane in a supercritical hexane/CO_2 mixture employing $AlBr_3$ as the catalyst is described ($AlCl_3$ is only poorly soluble under the conditions used).[17] To date, many homogeneously and heterogeneously catalysed reactions in supercritical fluids are known, and those employing gaseous substrates, such as hydrogenation and oxidation reactions, are particularly well characterised.[18] The use of supercritical CO_2 in industrial processes such as decaffeination of coffee[19] and polymerisation of ethylene[20] has been known for many years. Recently the first continuous flow supercritical fluid plant, with a capacity of up to 1,000 tons per year, has been developed by Thomas Swan & Co with the intention of conducting small-scale custom synthesis of high value products.[21]

Ionic liquids continue to receive increasing interest as alternative solvents for catalysis and the historical developments in the field are described in Section 1.4.

1.2 The Importance of Biphasic Catalysis

In a relatively short time biphasic catalysis, and notably aqueous-organic biphasic catalysis, has had an enormous impact on the way many chemists work. The study of alternative solvents is clearly of considerable academic interest, but it is perhaps the demand for cleaner chemical processes that has led to the explosion of research activity in this area. A major challenge for chemists today, when developing new products or more economic routes to existing products, is to do so with a consideration of minimising the impact that the synthesis of the product may have on the environment. Critical issues include the amount of materials and energy used in manufacture, the dispersion of chemicals in the environment, the use of resources and the durability and recyclability of the products. There are numerous approaches by which the above criteria can be achieved. These include the development of new synthetic pathways that require fewer steps and/or are more selective, alternative reaction conditions and improved solvents or methods for higher selectivity and energy minimisation. One of the most effective methods that influences all of the above criteria is to reduce or remove volatile organic compounds, i.e. solvents. Solvents are among the most ubiquitous classes of chemicals throughout society and the chemical industry because their applications are so broad and varied. In particular, solvents are used on a huge scale in manufacturing as a reaction medium for chemical transformations.