Rhodium Catalyzed Hydroformylation

RHODIUM CATALYZED HYDROFORMYLATION

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KLUWER ACADEMIC PUBLISHERS
DORDRECHT / BOSTON / LONDON

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

ISBN 0-7923-6551-8

Published by Kluwer Academic Publishers,
P.O. Box 17, 3300 AA Dordrecht, The Netherlands.

Sold and distributed in North, Central and South America
by Kluwer Academic Publishers,
101 Philip Drive, Norwell, MA 02061, U.S.A.

In all other countries, sold and distributed
by Kluwer Academic Publishers,
P.O. Box 322, 3300 AH Dordrecht, The Netherlands.

Printed on acid-free paper

Printed in the Netherlands.

RHODIUM CATALYZED HYDROFORMYLATION

Catalysis by Metal Complexes

Volume 22

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

Preface

This book covers the developments in rhodium catalyzed hydroformylation of the last decade, one of the most important reactions in industry catalyzed by homogeneous catalysts. The work includes many of the advances that have been made by academic and industrial researchers. The field has undergone drastic changes, both in its industrial applications and in our understanding. Clearly, the new advances pose new problems and set new targets for future research.

In spite of the importance of the field, the last reviews covering a broad area in hydroformylation are outdated (Falbe 1980, Pruett 1977) and it was felt timely to bring together the recent developments. Only in the area of aqueous biphasic hydroformylation there are several exhausting reviews available. This is the first monograph on hydroformylation of this type and for other processes there not many examples.

The aim of the book is to review the mainstream of the activities in the field and not to present a complete coverage of the literature, not even the recent literature. Several thousands of papers and patents deal with rhodium-catalyzed hydroformylation and a complete review would be impossible. We have chosen for a more didactic approach, in which we have tried to avoid one-liners about publications. In the book one will find typical examples about kinetics, applications in organic chemistry, industrial processes, mechanistic understanding, etc. In the mainstream activities we have tried to include industrial developments. We may have missed new catalyst systems that are as yet small but may turn out to be of major importance later, but that can hardly be avoided. New and important developments involving other metals, such as cobalt, platinum, and palladium will also be absent.

While writing we had a broad audience in mind: chemists and engineers in industry and academia with an interest in homogeneous catalysis, whose backgrounds may be as varied as those of the present authors: inorganic, organic, organometallic, catalytic, chemical engineering. It is hoped that specialists in one area will read with interest the chapters on the neighbouring expertise. The book is also meant for PhD-students and advanced students interested in this area.

The combination of topics we have chosen is rather unique, connecting studies on ligand effects, catalyst characterization, industrial requirements regarding stability and separation, catalyst decomposition, and applications

in fine and bulk chemistry. The reader will notice the importance of one discipline for the other. In many cases these relationships have already been established, but for other cases the book might assist future developments. The key roles that ligands may play in selectivity may be an eye-opener for organic chemists and it will further enhance the large number of new applications and reactions that are being discovered. The comments in several chapters on catalyst preparation and feed purification may be useful for scientists who are not specialized in homogeneous catalysis using transition metal complexes.

Hydroformylation is also a model reaction system in homogeneous catalysis as it contains so many aspects such as ligand effects (electronic, steric, bite angle), *in situ* studies, complicated kinetics, and effects of conditions and impurities. All this, combined with its practical value, makes it an ideal topic in education.

The editors are very grateful to the authors for the good work they did and the prompt responses. The writing took only a few months, as did the production by the publisher. Writing the book has been rewarding, because we learnt many things. Most of all perhaps, we obtained a clearer view on what we still don't fully understand.

Amsterdam, Tarragona
Piet van Leeuwen, Carmen Claver

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Introduction to hydroformylation

Phosphorus ligands in homogeneous catalysis

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1.1 History of phosphorus ligand effects

In this chapter we will briefly review "phosphorus ligand effects" in homogeneous catalysis and hydroformylation more in particular. First we will have a look at a few historical landmarks in homogeneous catalysis concerned with the use of phosphorus ligands, then focus on the history of rhodium catalyzed hydroformylation, and subsequently summarize a few basic concepts. Since phosphorus ligands are the only ligands used in hydroformylation in addition to carbon monoxide, we will not discuss ligands containing other donor atoms. In later chapters we will see that in hydroformylation, as it is today, bidentate phosphorus ligands are of great importance. In the introduction we show that in the early history the positive effect of bidentates on selectivities and rates of catalytic reactions was not fully recognized [1].

The favorable effects of phosphine ligands in catalysis have been known for more than half a century. One of the first reports involves the use of triphenylphosphine in the "Reppe" chemistry, the reactions of alkynes, alcohols and carbon monoxide to make acrylic esters [2]. An early example of a phosphine-modified catalytic process is the Shell process for alkene hydroformylation using a cobalt catalyst containing an alkylphoshine [3].

Hydrocyanation as applied by Du Pont is another early example of an industrially applied catalytic reaction employing ligands [4]. The nickel catalyzed reaction uses aryl phosphite ligands for the production of adiponitrile from butadiene and hydrogen cyanide. The development of this process has played a key-role in the introduction of the now common study

P.W.N.M. van Leeuwen and C. Claver (eds.), Rhodium Catalyzed Hydroformylation, 1–13.

of "ligand effects" in the field of homogeneous catalysis using organometallic complexes [5].

Both academia and industries made important contributions to the new field in the early sixties with the appearance of the first phosphine modified and other hydrogenation catalysts. An early example of a phosphine-free ruthenium catalyst was published by Halpern [6]. In 1963 Cramer (Du Pont) reported a triphenylphosphine-modified platinum-tin catalyst for the hydrogenation of alkenes [7]. In the same year Breslow (Hercules) included a few phosphine complexes of late transition metals in a hydrogenation study employing metal salts reduced by aluminum alkyls, but interestingly the systems containing phosphine were less active [8]!

Rhodium catalyzed hydrogenation was discovered in the mid-sixties by Wilkinson and coworkers [9]. The mechanism of this reaction using $RhCl(PPh_3)_3$ as the catalyst was studied in great detail. These studies by Wilkinson and many others have been a major stimulant for workers in this area. Substitution at the aromatic ring revealed an electronic effect on the reaction rate, electron donors giving higher rates [10]. A few months later Vaska published his first work on the rhodium and iridium catalyzed hydrogenation of alkenes [11].

Rhodium-catalyzed hydroformylation using catalysts modified with alkylphosphines and arylphosphines was reported by Wilkinson's group [12]. Phosphine ligand variation hardly affected the rate and selectivity under the circumstances used (70 °C and 100 bar). Pruett (Union Carbide Corporation) found that phosphites can also be used, and the type of phosphite had a profound effect on rates and selectivities [13].

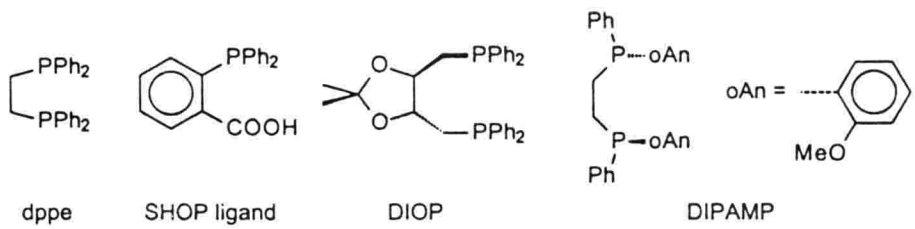


Figure 1. Structures of dppe, SHOP ligand, DIOP, and DIPAMP

Bidentate ligands have played an important role in the development of the chemistry of metal organic complexes. The synthesis of dppe was reported as early as 1959 [14]. Chatt and Hieber [15] explored the coordination chemistry of several diphosphines with an ethane bridge, but it took a while before diphosphines became routinely included in catalysis studies. In the early sixties diphosphines were mentioned in patents, but specific advantages are not apparent. In their exploration of carbonyl chemistry of cobalt related to carbonylation catalysis, Heck and Breslow

[16] reported that $HCo(CO)_4$ gave unidentifiable complexes with dppe. The use of dppe in cobalt catalyzed hydroformylation was reported by Slaugh [17], but compared to PBu_3 it had little effect on the rate and the selectivity of the cobalt carbonyl catalyst. Copolymerization of butadiene and propylene oxide using nickel bromide and dppe was published in 1965 [18].

In the late sixties at Shell Development, Keim and coworkers discovered that certain bidentates containing an oxygen and a phosphorus donor atom formed excellent catalysts with nickel for the oligomerization of ethene [19]. Typical ligands are diphenylphosphinoacetic acid or 2-diphenylphosphinobenzoic acid (SHOP ligand, Figure 1). The ligand required a relatively laborious ligand synthesis for those days. In addition it was the first process utilizing the concept of two-phase catalysis. This discovery led to the Shell Higher Olefins Process that came on stream in 1977.

Hata [20] reported a phosphine-free iron catalyst for the codimerization of butadiene and ethene in 1964. A year later this was followed by phosphine-free rhodium catalysts [21]. The oldest publication describing *advantageous* results for diphosphines we found is by Iwamoto and Yuguchi (1966) who studied the same reaction using iron catalysts containing a range of diphosphines varying in bridge lengths [22]. In many instances the activity of catalysts containing dppe instead of PPh_3 is lower. For example, the hydrogenation of styrene using rhodium(I) chloride and dppe is 70 times slower as compared to the PPh_3 based system [23]. The strong chelating power of the diphosphine was held responsible for this. Thus, initially the use of dppe and other bidentate phosphines in catalysis found little support as they were supposed to lead mostly to more stable complexes, rather than more active or selective catalysts.

Theoretical work of Thorn and Hoffmann [24] explained why migration reactions in complexes containing for instance dppe were slow. The constrained P-M-P angle would slow down the migration reaction, since ideally the phosphine ligand coordinated in the position cis to the migrating group, would have a tendency to widen the P-M-P angle in the process to "pursue" the migrating group.

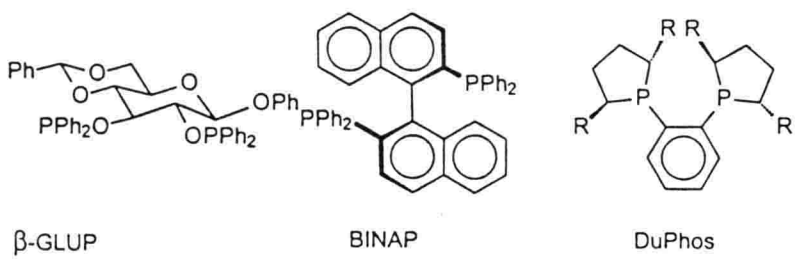
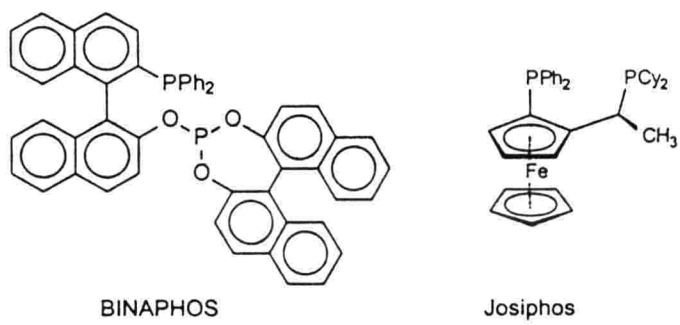


Figure 2. Structures of Phenyl-β-GLUP, BINAP, and DuPhos

A beneficial use of bidentate diphosphines was discovered in 1971 by Kagan [25] who reported the use of DIOP modified rhodium for the hydrogenation of N-acetylphenylalanine. Monophosphines for asymmetric hydrogenation of similar substrates were reported by Knowles [26]. His discovery of the P-chiral diphosphine DIPAMP, also a bidentate ligand, led to the commercial application of the asymmetric hydrogenation of the Levodopa precursor. For the same process Selke developed another ligand, a sugar based bisphosphonite Phenyl-β–GLUP [27]. The company VEB-Isis applied this ligand for many years in Germany.

In the area of asymmetric hydrogenation chiral diphosphines have played a center role since and many applications have been developed. Important new ligands that have been introduced comprise Noyori's BINAP [28], DuPhos (Burk) [29], Takaya's BINAPHOS [30], and C_1-symmetric ferrocene-based ligands introduced by Togni [31]. Industrial products, of which the synthesis uses enantioselective phosphine-derived metal-catalysts are for instance menthol, metolachlor, biotin, and several alcohols, e.g. (R)-1,2-propanediol, For details about the applications the reader is referred to reviews and references therein [32, 33]. Substituents and backbones have an enormous influence on the performance of the ligands, but usually rationalizations are lacking.

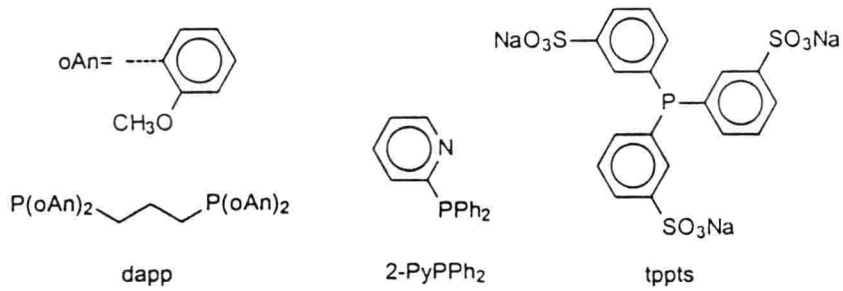


BINAPHOS Josiphos

Figure 3. Asymmetric phosphine ligands BINAPHOS and Josiphos

In carbonylation chemistry using phosphine or phosphite complexes of palladium or rhodium a number of breakthroughs achieved in the seventies and eighties should be mentioned; hydroformylation will be reviewed in section 1.2. Here we will concentrate on those that have found industrial application or may find application in the near future. In the early eighties Sen [34] and Drent [35] discovered that ethene and carbon monoxide can polymerized in an alternating fashion leading to polyketones. The catalyst is a palladium complex containing phosphines and non-coordinating anions in methanol as the solvent. Drent's bidentate phosphine containing catalysts proved by far to be the fastest ones. Especially diphosphines having a propane bridge give a fast reaction to high molecular weight products.

Shell's process-related patents often use the propane bridged 1,3-bis-(di-2-anisylphosphino)propane as the ligand (dapp) [36]. Carilon, Shell's trade name for the terpolymer of ethene, CO and propene – added for lowering the processing temperature of the product – has been in commercial production on a relatively small scale in the late nineties.



dapp 2-PyPPh$_2$ tppts

Figure 4. Ligands for bulk chemical processes

Another impressive ligand effect reported by Drent and coworkers [37] concerns the methoxycarbonylation of propyne to form methyl methacrylate. Triphenylphosphine modified palladium catalysts give low rates, but using 2-pyridyldiphenylphosphine instead gives very high rates and selectivities. The mechanism is still a matter of debate [38].

Tris-m-sulfonatophenylphosphine (tppts) plays an important role in the history of homogeneous catalysis [39], mainly due to its use in the Ruhrchemie/Rhône-Poulenc hydroformylation process [40], now operated by Celanese (see 1.2 and Chapter 7). It is also used in a number of fine chemical processes, such as selective hydrogenation with ruthenium [41], carbon-carbon bond formation with rhodium [42], and the Heck reaction [43]. Monosulfonated triphenylphosphine (tppms) is used for the preparation of nonadienol [44] (see Figure 5).

In C-C, C-O, and C-N bond formation reactions catalyzed by palladium and nickel, ligand effects have been explored in an extremely wide area [33]. The data available on ligand effects for these reactions are numerous. In asymmetric allylic alkylation the "embracing" effect of the bidentate ligand explains the efficacy of the ligand in many instances [45]; the longer the backbone, - i.e. the larger the bite angle (vide infra) - and the more effective the ligand interacts with the substrate. For the Heck reaction the ligand size seems to be a dominant factor, as bulky phosphines [46], phosphites [47], and amidites [48] were found to lead to highly effective catalysts. For amidites it was shown that the bulky ligands lead to mono-ligand complexes which are effectively more prone to substrate coordination than bis-ligand complexes. This effect was first observed by us for the same bulky phosphites in rhodium catalyzed hydroformylation [49] (Figure 5).