

Catalytic Heterofunctionalization

From Hydroamination to Hydrozirconation

Edited by

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Preface

Finding molecules which are able to catalyze the reaction between others is an important contribution of molecular chemists to increase the efficiency of chemical reactions whereby our daily life based on consumption of chemicals is shifted closer to an ecologically and economically tolerable equilibrium with our environment. Processes, where large amounts of energy are consumed - mostly in order to overcome the activation barrier of a reaction - will disturb significantly and irreversibly our living conditions. Considering the fact that only a small part of the world population lives under acceptable conditions, it would be cynical to call for a reduction of industrial production and development. On the contrary, the production of fine chemicals for any pharmaceutical and agricultural use must increase immensely.

Meanwhile, synthetic organic chemistry has reached a level where probably for any molecule composed of the elements carbon, hydrogen, nitrogen, and oxygen (to name only the most relevant elements of functionalized organic molecules) a suitable synthesis can be found via a retro-synthetic approach using the fund of known reaction principles [1]. However, depending on the complexity of the target molecule (which will increase with our understanding of the interaction of molecular entities with its surroundings) these syntheses correspond actually to reaction schemes including a multitude of single reaction steps. The thermodynamic parameters for any of these steps are given. Also the costs of a reaction calculated per atom (i.e. carbon, hydrogen, nitrogen, oxygen, etc.) are almost fixed by the prices of the basic chemicals on the world-market. Making a reaction sequence shorter and inevitable reaction steps faster can reach the aim of increasing the productivity while keeping energy consumption on a tolerable level. For example, the - especially stereospecific - synthesis of alcohols or amines requires often a lengthy multi-step synthesis by which suitable functionalized intermediates are formed. Clearly, the direct stereospecific addition of water or an amine to a prochiral C=C function would be the ultimate response to this problem. However, this addition is connected with a very high activation barrier and without a catalyst (which in its most elegant form may also intervene to control the stereochemistry of the addition process) this reaction is ineffective and useless.

This book is divided in eight chapters and each of them is devoted to the state-of-the-art of the homogeneously catalysed addition of E-H or E-E' heteroelement bonds* to unsaturated substrates with C=C, C≡C and C=X functions (X = O, S). Em-

* By this term we understand bonds between heteroelements in the sense of classical organic chemistry, i.e. bonds which do not include the element carbon.

phases is not only given to highlight achievements, which have been made in each domain, but also to clearly show the limitations. Reactions including the addition of dihydrogen (hydrogenations) or C-H bonds (C-H activation) are not considered and the reader is referred to recent monographs covering these topics [2,3]. The ordering of the chapters follows simply the ordering by which the heteroelement is positioned in the periodic table. The addition of reagents containing main group elements is treated first and the one of transition metal containing reagents last. Hence the first chapter discusses the catalyzed addition of boron reagents and the last one gives an overview about hydrozirconation reactions.

A catalyzed hydroboration reaction has first been described in 1985. In the beginning, the advantage of this reaction was seen in the use of cheap boron reagents which are easy to handle but little reactive in the non-catalyzed reaction. The considerable progress, concerning the development of the boron reagents and the catalysts employed in these types of reactions, is traced by N. Miyaura in the first chapter. Nowadays a wide variety of catalyst types based on complexes of Ti, Zr, Sm, Ru, Rh, Ir, Ni, Pd, and different boranes are employed which allow to control the stereoselectivity and specificity of the borane addition to a manifold of substrates containing C=C, C≡C, and C=X multiple bonds. More recently the addition of B-B, B-Si, B-Ge, and B-Sn bonds to unsaturated substrates attracted attention. These reactions are generally catalyzed by Pd(0), Pt(0) or Rh(I) complexes. They allow the elegant syntheses of highly functionalized products in few steps. Furthermore, the catalyzed cross-coupling reaction of diboranes, R_2B-BR_2 , with organic halides opened a straightforward route to aryl and allyl boranes which themselves are valuable intermediates.

In the second chapter, homogeneously catalyzed hydroalumination reactions of alkenes and alkynes are surveyed. Although alanes are more reactive than boranes and many hydroaluminations proceed indeed without a catalyst (especially those of alkynes), metallocene chlorides, such as Cp_2TiCl_2 or Cp_2ZrCl_2 , nickel or cobalt salts, or palladium(II) complexes not only accelerate the reaction but also influence the stereochemistry of the addition reaction. Apart from (enantioselective) hydroaluminations of carbon-carbon multiple bonds and allyl ether cleavages, the reader will learn about highly selective reductive ring opening reactions, which were invented in the group of M. Lautens who is, with M. Dahlmann, the author of this chapter. This reaction is another good example for the short and elegant synthesis of complex molecules by a novel approach using a catalytic heterofunctionalization as the key step.

The transition metal-catalyzed hydrosilylation belongs to the „old-timers“ of catalytic heterofunctionalizations and numerous applications have been established. Therefore, J. Tang and T. Hayashi concentrate in the third chapter on the progress made in enantioselective hydrosilylations. Frequently, precursor complexes with platinum and rhodium as active centres and a chiral phosphine as ligand are employed in these reactions. However, recently also palladium complexes carrying a monodendate axial-chiral phosphine were introduced as highly efficient catalysts for enantioselective hydrosilylations. Furthermore, new lanthanide and group 3 metallocene complexes were found to be active complementing the established list

of d^0 metal hydrosilylation catalysts, i.e. titanocenes and zirconocenes. Notable progress has also been made in the asymmetric syntheses of functionalized carbocycles by hydrosilylation of suitable dienes. Catalyzed by chiral palladium(II) oxazoline or rhodium(I) bisphosphine complexes, C-C, C-Si and C-H bonds are stereoselectively formed within one catalytic cycle making the efficiency of catalytic heterofunctionalizations evident.

The fourth chapter gives a comprehensive review about catalyzed hydroaminations of carbon carbon multiple bond systems from the beginning of this century to the state-of-the-art today. As was mentioned above, the direct - and whenever possible stereoselective - addition of amines to unsaturated hydrocarbons is one of the shortest routes to produce (chiral) amines. Provided that a catalyst of sufficient activity and stability can be found, this heterofunctionalization reaction could compete with classical substitution chemistry and is of high industrial interest. As the authors J. J. Brunet and D. Neibecker show in their contribution, almost any transition metal salt has been subjected to this reaction and numerous reaction conditions were tested. However, although considerable progress has been made and enantioselectivities of 95% could be reached, all catalytic systems known to date suffer from low activity ($\text{TOF} < 500 \text{ h}^{-1}$) or/and low stability. The most effective systems are represented by some iridium phosphine or cyclopentadienyl samarium complexes.

The discussion of the activation of bonds containing a group 15 element is continued in chapter five. D.K. Wicht and D.S. Glueck discuss the addition of phosphines, $\text{R}_2\text{P-H}$, phosphites, $(\text{RO})_2\text{P(=O)H}$, and phosphine oxides $\text{R}_2\text{P(=O)H}$ to unsaturated substrates. Although the addition of P-H bonds can be sometimes achieved directly, the transition metal-catalyzed reaction is usually faster and may proceed with a different stereochemistry. As in hydrosilylations, palladium and platinum complexes are frequently employed as catalyst precursors for P-H additions to unsaturated hydrocarbons, but (chiral) lanthanide complexes were used with great success for the (enantioselective) addition to heteropolar double bond systems, such as aldehydes and imines whereby pharmaceutically valuable α -hydroxy or α -amino phosphonates were obtained efficiently.

In the sixth chapter the activation of O-H bonds of water, alcohols and carboxylic acids, and their addition to multiple bonds is reported. Since the formally oxidative addition of ROH gives rise to hydrido(hydroxo) complexes, $[\text{MH(OR)Ln}]$ which are postulated as intermediates in many important reactions (water gas shift reaction, Wacker-chemistry, catalytic transfer hydrogenations etc.) the authors of this chapter, K. Tani and Y. Kataoka, begin their discussion with an overview about the synthesis and isolation of such species. Many of them contain Ru, Os, Rh, Ir, Pd, or Pt and complexes with these metals appear also to be the most active catalysts. Their stoichiometric reactions, as well as the progress made in catalytic hydrations, hydroalcoxylations, and hydrocarboxylations of triple bond systems, i.e. nitriles and alkynes, is reviewed. However, as in catalytic hydroaminations the „holy grail“, the addition of O-H bonds across non-activated C=C double bonds under mild conditions has not been achieved yet.

H. Kuniyasu continues the discussion of the activation of group 16 element bonds with an overview on S(Se)-X additions to unsaturated substrates. For some time, it

was believed that sulfur compounds „poison“ systematically transition metal complexes by forming very robust metal sulfides. However, as it is shown in this seventh chapter, a wide variety of thiols, disulfides, diselenides, silyl and germyl sulfides and selenides, and thioboranes can be successfully added to carbon carbon multiple bonds, especially alkynes, with the aid of metal catalysts. Frequently, the „ubiquitous“ metal complexes used in homogeneous catalysis like the phosphine complexes of palladium, platinum, and rhodium can be used to afford a wide range of chalcogenato compounds. Also cobalt, nickel, and ruthenium complexes, and some Lewis-acids were studied as catalysts.

A chapter written by A. Igau reviewing hydrozirconations concludes this book. As was demonstrated in recent years, the addition of the Schwartz reagent, $[\text{Cp}_2\text{ZrHCl}]_n$, to unsaturated substrates containing $\text{C}=\text{C}$, $\text{C}\equiv\text{C}$, $\text{C}=\text{N}$, $\text{C}=\text{P}$, and $\text{C}=\text{O}$ entities allowed the synthesis of a wide range of highly functionalized zirconium derivatives which proved to be valuable intermediates in organic synthesis. Since the primary products of the hydrozirconation reaction contain a highly polar zirconium(δ^+) X(δ^-) bond ($\text{X} = \text{C}, \text{N}, \text{O}$, etc), they can be easily transformed further by substitution reactions with halides or insertion reactions of another equivalent of an unsaturated substrate into the Zr-X bond. Although catalytic hydrozirconations are just being discovered and most of the reactions described in this chapter are stoichiometric, the reader will find many useful applications of this type of heterofunctionalization.

For some of the reactions described in this book, rather precise and detailed ideas about the reaction mechanism exist. However, for many catalytic reactions, the mechanistic understanding is very poor and further experimental studies are certainly needed. Calculations proved to be a highly valuable tool to gain a more precise picture of the reaction pathways. However, mostly only model systems can be studied due to the complexity of the problem. Anyway, it is the firm believe of the authors that for any reaction with an activation barrier a suitable catalyst can be found. This book shall give an insight into what has been achieved in this area concerning the synthesis of heterofunctionalized organic molecules. It is the hope of all contributors that future retro-synthetic schemes will include the catalytic approaches outlined in this book.

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1

Hydroboration, Diboration, Silylboration, and Stannylboration*Norio Miyaoura*

1.1

Introduction

In this work, particular attention will be given to the synthesis of organoboron compounds via the metal-catalyzed addition and coupling reactions of H-B, B-B, B-Si, and B-Sn reagents [1, 2]. The classical methods for the synthesis of organoboron compounds are based on the reaction of trialkyl borates with Grignard or lithium reagents (transmetalation) or the addition of H-B reagents to alkenes or alkynes (uncatalyzed hydroboration) [3]. Although these methods are now most common and convenient for large-scale preparations, the metal-catalyzed reactions are advantageous in terms of efficiency and selectivity of the transformations. Hydroboration of alkenes and alkynes is one of the most studied of reactions in the synthesis of organoboron compounds and their application to organic synthesis. However, catalyzed hydroboration did not attract much attention until Männig and Nöth in 1985 [4] reported that a Wilkinson complex $[\text{RhCl}(\text{PPh}_3)_3]$ catalyzes the addition of catecholborane to alkenes or alkynes. Although the transition metal complexes significantly accelerate the slow reaction of (dialkoxo)boranes, the catalyzed hydroboration is a more interesting strategy to realize the different chemo-, regio-, diastereo-, and enantioselectivities, relative to the uncatalyzed reaction, because the catalyzed reaction can change the metal-hydride species which interacts with the unsaturated C-C bond. The addition of diboron tetrahalides B_2X_4 ($\text{X}=\text{F}, \text{Cl}, \text{Br}$) to unsaturated hydrocarbons (diboration), first discovered by Schlesinger in 1954 [5, 6], is an attractive and straightforward method to introduce boryl groups into organic molecules, but the synthetic use has been severely limited because of the instability and limited availability of the reagents. Although tetra(alkoxo)diboron dramatically enhances the stability of the B-B species at the expense of reactivity for organic nucleophiles, the B-B compounds oxidatively add to low-valent transition metals with the B-B bond cleavage, thus allowing the catalyzed transfer of boron to unsaturated organic substrates. The metal-catalyzed addition of B-B, B-Si, or B-Sn reagents to alkenes or alkynes provides a new class of boron compounds including heterofunctionalized alkyl-, alkenyl-, and allylboronates. The cross-coupling reaction of metal-boryl

reagents is an alternative to the transmetalation method and perhaps a more convenient and direct protocol for the synthesis of organoboron compounds from organic halides and other electrophiles.

Much attention has recently been focused on organoboronic acids and their esters because of their practical usefulness for synthetic organic reactions including asymmetric synthesis, combinatorial synthesis, and polymer synthesis [1, 3, 7–9], molecular recognition such as host-guest compounds [10], and neutron capture therapy in treatment of malignant melanoma and brain tumor [11]. New synthetic procedures reviewed in this article will serve to find further applications of organoboron compounds.

1.2

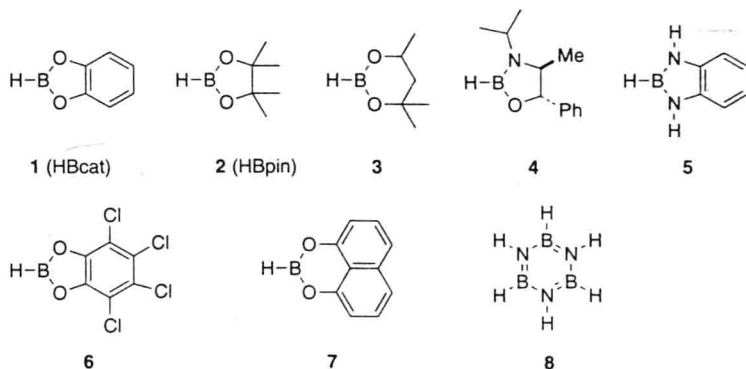
Metal-Catalyzed Hydroboration

1.2.1

Hydroboration of Alkenes and Alkynes

Most studies of catalyzed hydroboration have employed catecholborane **1** (HBcat) [12] because of its high reactivity for various transition metal catalysts (Scheme 1-1). However, pinacolborane **2** (HBpin) [13] has recently been found to be an excellent alternative because it is a more stable, easily stored and prepared hydroboration reagent. The high stability of the resulting products (pinacol esters of alkyl- or 1-alkenylboronates) to moisture and chromatography is also very convenient for organic chemists. Other borane reagents including 4,4,6-trimethyl-1,3,2-dioxaborinane (**3**) [14], oxazaborolidines (**4**) [15], benzo-1,3,2-diazaborolane (**5**) [16], and borazine (**8**) [17] may also be used, but the scope of these reagents remains to be explored.

There is no systematic study of the effect of borane reagents, and the best choice would be highly dependent on the catalysts and substrates. A series of di(alkoxy)boranes have recently been synthesized and subjected to hydroboration of cyclopentene at ambient temperature in the presence of $\text{RhCl}(\text{PPh}_3)_3$ (Scheme 1-2) [18]. The



Scheme 1-1 Borane Reagents for Catalyzed Hydroboration