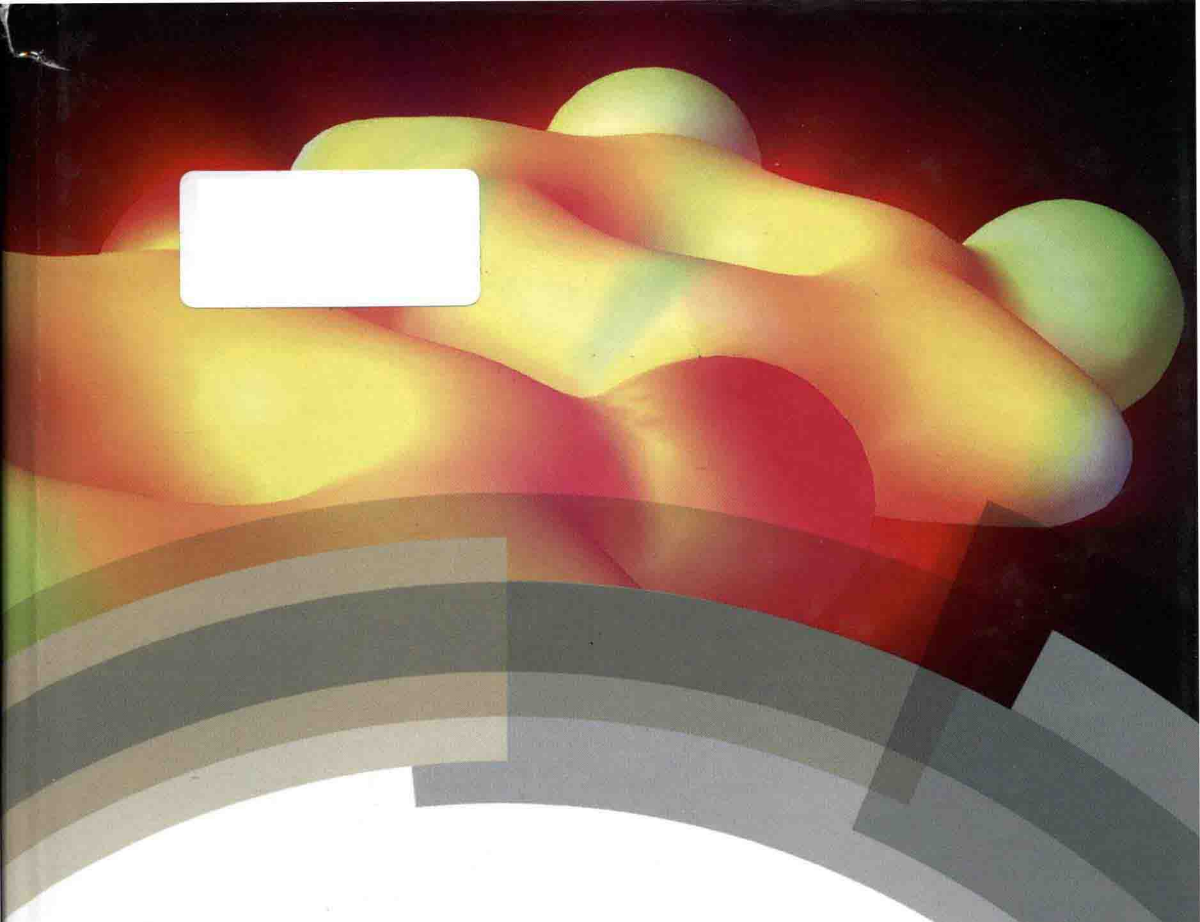

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Economic Synthesis of Heterocycles

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Xiao-Feng Wu and Matthias Beller

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OF **CHEMISTRY**

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Preface

Around 90% of naturally occurring molecules have heterocycles as their core structure, and heterocyclics have broad applications in pharmaceuticals, agrochemicals, dyes, and many others. With this background, syntheses of heterocyclic compounds have become one of the largest branches in modern organic chemistry. After decades developing experience, numerous synthetic methodologies have been successfully introduced. Nowadays, with the advent of sustainable development, the application of cheap metal salts as catalysts in heterocyclic synthesis has become important and attractive. Among the family of cheap metals, zinc, iron, copper, cobalt, manganese, and nickel are representative examples, as they are inexpensive, have low toxicity, are biocompatible, and are environmentally benign.

This book outlines the main contributions in this are. The contents are organized according to the catalyst applied and then subdivided by the size of the ring formed. The text starts with a short introduction, followed by chapters on the use of salts of the above metals in the synthesis of heterocyclic compounds.

The book took around 10 months to complete, and every attempt was made to ensure that the literature cited is as up-to-date as possible and that out descriptions are accurate. However, it is always possible that some literature might have been missed and there may be errors, for which we apologize. We sincerely hope that overall the content of this book will be useful to all those working in the field of heterocyclic synthesis.

Xiao-Feng Wu

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This book is dedicated to my wife and children, Qing-Yuan Wei, Nuo-Yu Wu and Nuo-Lin Wu, who are gratefully thanked for their understanding and support.

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CHAPTER 1

Introduction

Around 90% of naturally occurring molecules have heterocycles as their core structure, and heterocyclics have broad applications in pharmaceuticals, agrochemicals, dyes, and many other areas. With this background, syntheses of heterocyclic compounds have become one of the largest branches of modern organic chemistry.[1] After decades developing experience, numerous synthetic methodologies have been successfully introduced. Among these procedures, methods involving transition metal catalysts constitute a large percentage.

In recent years, sustainable development has been accepted by the wider social community. With the combination of transition metal catalysts and the concept of sustainable development, the use of cheap metal salts as catalysts has attracted the interest of synthetic chemists. Although the catalytic abilities of noble metals in coupling reactions are impressive, as demonstrated by the award of the 2010 Nobel Prize in Chemistry jointly to Richard F. Heck, Ei-ichi Negishi and Akira Suzuki for palladium-catalyzed cross-couplings in organic synthesis,[2] their high cost and toxicity are clear disadvantages.

Of the available cheap metals, zinc (Zn), iron (Fe), copper (Cu), cobalt (Co), manganese (Mn) and nickel (Ni) are representative examples: they are inexpensive, have low toxicity, are biocompatible and are environmentally benign.

Zinc is the 24th most abundant element in the Earth's crust. It was first discovered as a pure metal in 1746 by the German chemist Andreas Sigismund Marggraf by heating a mixture of calamine and carbon in a closed vessel without copper, and this process had become commercially practical by 1752. As a material, the major application of zinc is in the corrosion-resistant zinc plating of steel, with other applications in batteries and alloys. Biologically, zinc is an essential mineral with great biological and public health importance, and it is an essential component of thousands of

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proteins in plants, although it is toxic in excess. Zinc deficiency may cause many diseases in adults and also lead to growth retardation, delayed sexual maturation, infection susceptibility and diarrhea in children.[3] Chemically, zinc metal has the electron configuration $[Ar]3d^{10}4s^2$ and is a strong reducing agent. Zinc tends to form bonds with a greater degree of covalency and it forms much more stable complexes with N- and S-donors. Complexes of zinc are mostly 4- or 6-coordinated, but 5-coordinated complexes are also known. The applications of zinc in organic chemistry are mainly used in the preparation of organozinc compounds for organic synthesis, such as the applications of zinc reagents in the Reformatsky reaction, Frankland–Duppa reaction, Negishi reaction, Fukuyama reaction and so on.[4] The application of zinc complexes as catalysts for organic transformations has also been explored, but they are mainly limited by their 'Lewis acid' properties.[5] They are still undeveloped in the area of coupling reactions.

Iron is the fourth most common element in the Earth's crust, with a wide range of oxidation states (-2 to $+6$). Based on this property, iron catalysts have been widely applied in redox reactions.[6] Concerning cross-coupling reactions, the catalytic abilities of iron catalysts have also been explored, especially the iron-catalyzed cross-coupling of organohalides with Grignard reagents, which have even been applied in the total synthesis of biologically active molecules.[7] Iron is also abundant biologically. Iron-containing proteins are found in all living organisms, ranging from the evolutionarily primitive Archaea to humans. The color of blood is due to hemoglobin, an iron-containing protein.

The catalytic activities of copper salts are more remarkable, even comparable to those of noble metals such as palladium catalysts in cross-coupling reactions.[8] Numerous catalytic systems have been developed for C–O, C–N, C–S and C–C bond formation. Biologically, copper is an essential trace element in plants and animals and copper proteins have diverse roles in biological electron transport and oxygen transportation.

The word 'cobalt' is derived from the German kobalt, from kobold meaning 'goblin,' a superstitious term used for the ore of cobalt by miners. As an element, cobalt has the electron configuration as $[Ar]4s^23d^7$ and has oxidation states $2+$ and $3+$. Cobalt has many applications in a wide range of areas. In materials, cobalt is primarily used as the metal in the preparation of magnetic, wear-resistant and high-strength alloys. In biology, cobalt is the active center of coenzymes called cobalamins, the most common example of which is vitamin B_{12}. As such it is an essential trace dietary mineral for all animals. Cobalt in inorganic form is also an active nutrient for bacteria, algae and fungi. In chemistry, various cobalt compounds are used in chemical reactions as oxidation catalysts. Cobalt acetate is used for the conversion of xylene to terephthalic acid, the precursor to the bulk polymer polyethylene terephthalate. Typical catalysts are the cobalt carboxylates (known as cobalt soaps). They are also used in paints, varnishes and inks as 'drying agents' through the oxidation of drying oils. The same carboxylates are used to improve the adhesion of steel to rubber in steel-belted radial tires. Cobalt-based catalysts are also important in reactions involving carbon monoxide.[9] Steam reforming, useful in hydrogen production, uses cobalt oxide-based catalysts. Cobalt is a catalyst in the Fischer–Tropsch process, used in the hydrogenation of carbon monoxide to give liquid fuels. The hydroformylation of alkenes often relies on cobalt octacarbonyl as the catalyst, although such processes have been partially displaced by more efficient iridium- and rhodium-based catalysts, *e.g.*, in the Cativa process. The hydrodesulfurization of petroleum uses a catalyst derived from cobalt and molybdenum. This process helps to rid petroleum of sulfur impurities that interfere with the refining of liquid fuels.

Manganese is a silvery gray metal that resembles iron. It is hard and very brittle, difficult to fuse, but easy to oxidize. The most common oxidation states of manganese are +2, +3, +4, +6 and +7, although oxidation states from −3 to +7 are observed. In biology, manganese is an essential trace nutrient in all known forms of life. The classes of enzymes that have manganese cofactors are very broad. The reverse transcriptases of many retroviruses (although not lentiviruses such as HIV) contain manganese. There is about 12 mg of manganese present in the human body, which is stored mainly in the bones; in the tissues, it is mostly concentrated in the liver and kidneys. In the human brain, manganese is bound to manganese metalloproteins, most notably glutamine synthetase in astrocytes. Manganese is also important in photosynthetic oxygen evolution in chloroplasts in plants. In chemistry, manganese is mainly used as oxidant for organic substrates.[10] Recently, its catalytic properties have also been explored.

Nickel was first isolated and classified as a chemical element in 1751 by Axel Fredrik Cronstedt, and has two electron configurations, $[Ar]4s^2 3d^8$ and $[Ar]4s^1 3d^9$, with very close energies. From the application point of view, nickel plays important roles in the biology of microorganisms and plants. The plant enzyme urease (an enzyme that assists in the hydrolysis of urea) contains nickel. The [NiFe] hydrogenases contain nickel in addition to iron–sulfur clusters. Such [NiFe] hydrogenases characteristically oxidize H_2. In synthetic chemistry, nickel catalysts have been explored in carbonylation reactions, coupling reactions and many other types of catalytic transformations. More recently, nickel-catalyzed C–O bond activation has made important achievements and showed superior activity to palladium.[11] In $C(sp^3)$–X transformations, nickel gave excellent activities with boronic acids and organozinc reagents as coupling partner. Nickel catalysts have also been studied in the area of heterocycle synthesis.

With this background, it is extremely interesting and important to develop methodologies that involve Zn, Fe, Cu, Co, Mn and Ni as catalysts in the heterocycle syntheses. In the following chapters, we present detailed discussions on this topic. The chapters are subdivided according to the sizes of the rings formed. The book concludes with a personal outlook.

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CHAPTER 2

Zinc-Catalyzed Heterocycle Synthesis

Zinc is elementally essential in our daily lives, with a wide range of applications in materials, and in addition the adult body contains about 2–3 g of elemental zinc. Zinc salts have also been used in plant fertilizers. In organic synthesis, zinc salts are mainly used as Lewis acids. With the accepted importance of heterocyclic compounds and the environmentally benign properties of zinc salts, it is of interest to explore the applications of zinc catalysts in heterocycle syntheses.[1]

2.1 Five-Membered Heterocycles

2.1.1 Zinc-Catalyzed Synthesis of Carbonates

The application of zinc catalysts in the polymerization of epoxides and CO_2 has been known for many years,[2] and the alternative production of carbonates from epoxides and CO_2 by changing the reaction conditions and using zinc catalyst is also of interest. Carbonates are aprotic polar solvents (and nowadays considered as 'green' solvents) and are used as intermediates for pharmaceuticals and fine chemicals.[3] Various procedures have been developed, and the systems are becoming more well-defined or heterogenized.

Based on previous reports on zinc-catalyzed cyclization and copolymerization of CO_2 and peroxides, Kim and colleagues carried out a detailed mechanistic study.[4] A pyridinium alkoxy ion-bridged dimeric zinc complex was isolated and characterized. Subsequently, they carried out a systematic study. The reactions of CO_2 and epoxides to produce cyclic carbonates were performed in the presence of a catalyst $[L_2ZnX_2]$ ($L = $ pyridine or substituted pyridine; $X = Cl, Br, I$). The effects of pyridine and halide ligands on the

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