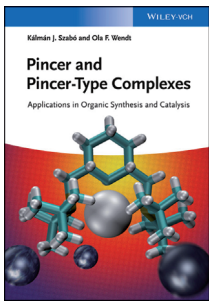
Pincer and Pincer-Type Complexes Applications in Organic Synthesis and Catalysis

Transition metal complexes are indispensable tools for every chemist engaged in synthesis. Ideally, any metal-mediated catalytic process should be fast, clean, efficient, and selective. These criteria are especially important when one considers that many of the transition metals employed in catalysis are rare and/or expensive. One of the ways of modifying and controlling the properties of transition metal complexes is the use of appropriate ligand systems such as pincer ligands. A tridentate pincer ligand is typically based on a planar scaffold consisting of a central neutral or anionic aromatic backbone, which is tethered through spacers to two, usually bulky, two-electron donor groups. In recent years, pincers with aliphatic backbones have also received considerable attention. In these families of ligands, steric, electronic, and also stereochemical parameters can be manipulated by modifications of the substituents at the donor sites and/or the spacers, allowing the possibility of a rational and modular design to generate highly active catalysts for a range of chemical transformations with high selectivity. Accordingly, pincer complexes are important tools with numerous applications in various areas of chemistry, including catalysis, due to their combination of stability, activity, and variability.

This book contains 11 chapters on a wide range of topics involving transition-metal pincer and pincer-type complexes, such as mechanistic and synthetic studies, ligand design, new applications in homogenous catalysis, and theoretical considerations. The articles are written by authors who are well-known scientists and experts in their respective fields. There is a good balance between articles on fundamental research topics and others where the main emphasis is on applications. The contents of the book are briefly summarized here.

Gunanathan and Milstein review the potential of Ru pincer complexes for the catalytic synthesis of esters, amides, and peptides. They nicely demonstrate that the pincer platform offers the opportunity to fine-tune the steric and electronic properties of the metal complexes and open up new possibilities for metal–ligand cooperation. Campora and Melero focus on the role of redox processes in reactions catalyzed by Ni and Pd complexes bearing several anionic pincer ligands. They emphasize the usefulness of catalytic reactions involving redox changes in the metal–pincer framework, which includes Kharasch and Heck reactions as well as other C–C and C–X bond-forming processes. Moore and Szymcak describe the application of pincer complexes as scaffolds for appended functionalities such as Lewis acids and bases. The contribution of Szabó provides an overview of recent examples of pincer complexes as catalysts in C–C, C–O, and C–B bond-forming reactions, including asymmetric ones. Adhikary and Guan describe Ni-catalyzed cross-coupling reactions, with special emphasis on mechanistic aspects. Turculet reports on the synthetic, bond activating, and catalytic applications of PSiP transition metal pincer complexes, and compares these with related PCP derivatives. These new pincers have emerged as a versatile new class of tridentate ligands that can accommodate a variety of transition metal centers. Chirik gives an excellent overview of the chemistry of reduced Mn, Fe, and Co complexes bearing redox-active bis(imino)pyridine pincer ligands, where fundamental questions such as "Is the ligand or the metal oxidized or reduced?" are discussed. Jonasson and Wendt discuss synthetic aspects and applications of pincer complexes with saturated frameworks. In particular, advances in the fields of NH_3 activation, hydrogenation and dehydrogenation of polar double bonds, and CO_2 activation are presented. The contribution of Takaya and Iwasawa is devoted to synthetic transformations of unsaturated hydrocarbons catalyzed by Pd complexes bearing phenylene-bridged PSiP pincer ligands and their analogs. These results may open up new possibilities for the rational design of catalytic synthetic reactions involving PSiP pincer complexes. Frech describes experimental and theoretical aspects of Pd-pincer-catalyzed cross-coupling processes, which still belong to the most important types of catalytic carbon–carbon bond-forming reactions. He discusses questions about the mechanism of the catalytic cycles, in particular whether a Pd^0/Pd^{II} or a (more controversial) Pd^{II}/Pd^{IV} mechanism is operative. Finally, Wilson, Parkes, Kemp, and Goldberg focus on reactions of square-planar d^8-pincer complexes with molecular oxygen. Both experimental and theoretical results of O_2 insertion into Pd–H bonds are described. This overview is very useful for the development of challenging organic oxidation reactions using O_2.

In most cases the chemistry discussed in these contributions is not confined to the authors' own work, but also includes many new key references to cutting-edge discoveries by other scientists, so that the reader can dig more deeply into this hot topic. A slight criticism, in view of recent trends, is that the pincer chemistry of non-precious metals, in particular that of iron, is somewhat underrepresented compared with the emphasis on precious metals. In sum, the editors have succeeded well in presenting a very comprehensive treatment of the subject in as clear a form as possible. The book aims to support chemists working in the field of organic



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synthesis who want to apply pincer and pincer-type complexes in catalytic organic transformations and/or are interested in mechanistic investigations such as C–H bond activation processes. The book is well produced and easy to read, and the chapters provide an excellent overview of the different aspects of modern transition-metal pincer chemistry and will certainly be a source of inspiration for further studies in this area. Thus, it should find a place in all chemistry libraries.

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