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Topics in Organometallic Chemistry

Aims and Scope

The series *Topics in Organometallic Chemistry* presents critical overviews of research results in organometallic chemistry. As our understanding of organometallic structure, properties and mechanisms increases, new ways are opened for the design of organometallic compounds and reactions tailored to the needs of such diverse areas as organic synthesis, medical research, biology and materials science. Thus the scope of coverage includes a broad range of topics of pure and applied organometallic chemistry, where new breakthroughs are being achieved that are of significance to a larger scientific audience.

The individual volumes of *Topics in Organometallic Chemistry* are thematic. Review articles are generally invited by the volume editors. All chapters from Topics in Organometallic Chemistry are published OnlineFirst with an individual DOI. In references, Topics in Organometallic Chemistry is abbreviated as Top Organomet Chem and cited as a journal.

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Editors

The Privileged Pincer-Metal Platform: Coordination Chemistry & Applications

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Preface

Pincer ligands are extensively used in many diverse areas of chemistry primarily as a means to direct and modulate the properties of a metal center to which it is bonded. The title framework emerged in the late 1970s during the pioneering organometallic chemical studies by Shaw and coworkers. In the present day, the pincer platform, with its tridentate arrangement of donor sites, is used with great success in both ligand-metal mediated catalysis, (bio)inorganic chemistry, and materials science. The first series of review papers on Pincer chemistry, published in *Topics in Organometallic Chemistry* (2013: Vol. 40), discussed primarily those aspects of the chemistry and applications of the prototypical monoanionic pincer-metal compounds. In this formulation, the metal center is covalently bonded via a central (sp^2 or sp^3 hybridized) C-metal bond in addition to two complementary interactions with neutral heteroatom donors.

An important characteristic of the pincer platform is the fact that its three ligating sites are well organized by the backbone of the ligand and hence this allows for the possible formation of five- or six-membered chelate rings which have the central metal-heteroatom bond in common. Recent developments have made use of this modular nature of the pincer platform. Up to now, a multifaceted combination of donor sets has been explored and includes combinations of, e.g., neutral, anionic, Lewis basic and acidic, arene, heteroaromatic, and carbene donor sites. Moreover, in some cases, the pincer platform itself acts as a non-innocent ligand (NIL) or provides, with its pincer-metal manifold, a system that is suitable for executing metal-ligand cooperative (MLC) behavior in, e.g., catalytic processes. At present, the number of possibilities seems to have no limit; most excitingly many of these novel pincer-ligand metal combinations lead to the discovery of new catalysts for, e.g., C–X bond forming processes in organic synthesis, new polymerization technologies, the chemical conversion of CO_2, and the activation of bonds that so far were considered as primarily unreactive. The present volume comprises a series of ten chapters, some of which touch on a variety of these issues.

First of all, it is a great pleasure to start with an introductory chapter that is dedicated to the celebration of the 85th birthday of Prof. Bernard L. Shaw. Prof. Shaw was the first, together with Dr. C.J. Moulton, to report examples of 2,6-bis [(diphenylphosphine)methyl]phenyl metal-d^8 halide compounds. We now recognize these materials as the benchmark pincer complexes.

The volume then continues with a chapter "Pincer Complexes of Lithium, Sodium, Magnesium and Copper: a Discussion of Solution and Solid-state Aggregated Structure and Reactivity" discussing the synthesis and structural features of pincer-metal (Li, Na, Mg, and Cu) compounds that, in some cases, are indispensable as transmetallation reagents for the clean preparation of the corresponding pincer-transition metal derivatives. Incorporation of N-heterocyclic carbenes in the donor set of the pincer platform gives rise to the pincer chemistry presented in chapter "Late Transition Metal Complexes with Pincer Ligands that Comprise N-Heterocyclic Carbene Donor Sites" and entails attractive benefits for the development of novel, robust catalysts and for uses in materials science and the medicinal chemistry areas.

A vast number of complexes based on combinations of novel pincer ligands and rare earth metals have been described in chapter "Rare Earth Pincer Complexes: Synthesis, Reaction Chemistry and Catalysis" with a special focus on the properties of these complexes as polymerization catalysts. Chapter "New Chemistry with Anionic NNN-Pincer Ligands" provides an overview of the synthesis of anionic pincer-metal catalysts based on a combination of three N-donor sites and includes their reactivity in organic synthesis.

The synthesis of pincer-metal complexes using a pincer platform that contains thione sulfur groupings as neutral donor sites is presented in chapter "Pincer Complexes with Thione Sulfur Donors." The high-yield syntheses of POCOP pincer nickel complexes and their application as catalysts in, e.g., selective organic synthesis are described in chapter "Recent Advances on the Chemistry of POCOP Nickel Pincer Compounds." It was at an early stage of pincer-metal chemistry that a unique property of some pincer platforms was recognized. The ability to stabilize uncommon (high or low) formal oxidation states of the bound metal center was observed and later exploited in catalysis. In chapter "Pincer-Like Cyclic Systems for Unraveling Fundamental Coinage Metal Redox Processes," the synthesis of rare arylcopper(II) and copper(III) species, in which the aryl anion is part of a cyclic pincer platform, is discussed. With these arylcopper species, the intimate steps of catalytic processes involving C–X bond formation are demonstrated.

In the final two chapters, the use of pincer-metal complexes in alkane dehydrogenation (chapter "Recent Advances in Alkane Dehydrogenation Catalyzed by Pincer Complexes") and the synthesis and properties of soluble nanomaterials with multiple, immobilized pincer metal units as homogenous catalysts (chapter "Tethered Pincer Complexes as Recyclable Homogeneous Catalysts") are discussed. It is obvious that the chemistry presented in the greater part of these chapters has only been possible due to the fascinating and unique high kinetic and thermal stability of the pincer-metal manifold.

It is with great pleasure that we present these chapters that have been submitted by many important players in the field. We hope that their results and discussions will be an inspiration to our many colleagues active in organometallic chemistry, organic synthesis, nanotechnology, and materials science.

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