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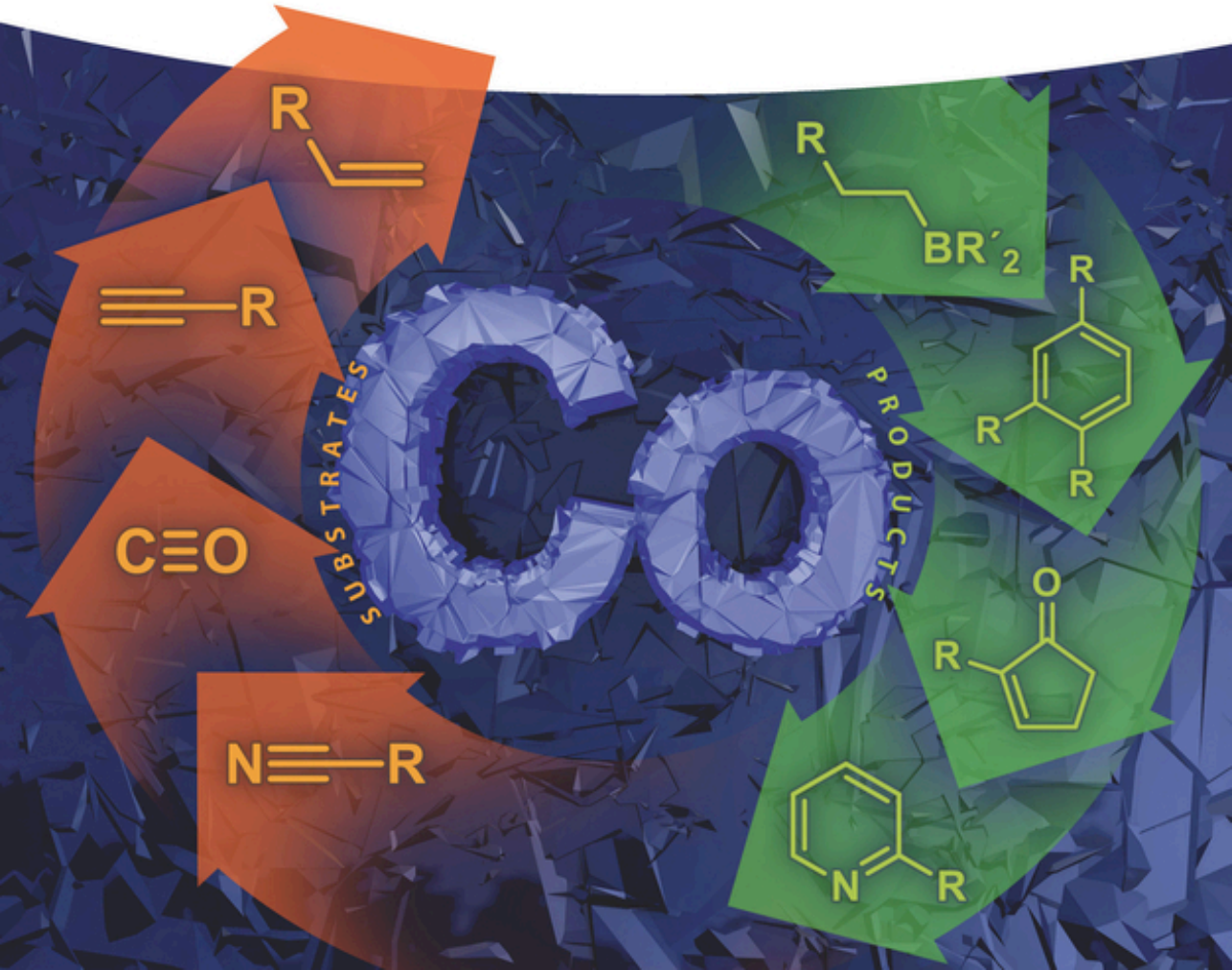

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Preface

Catalysis promoted by transition metal complexes has revolutionized the art and practice of chemical synthesis. Approximately 85% of all chemical products are made using at least one catalytic transformation, and one estimate suggests that catalytic processes account for approximately 20% of the GDP of the United States (https://catl.sites.acs.org/). Why is this so? Catalytic reactions accelerate product formation, enable or enhance selectivity, and ultimately minimize waste and energy consumption and hence carbon dioxide footprint. While the catalyst landscape has principally been dominated by precious and terrestrially rare second- and third-row transition metals, there is increased emphasis on catalysts based on more Earth-abundant elements. Among these is cobalt.

It is interesting to ponder why precious metals have found wider use than more Earth-abundant alternatives. The answer is simple – they work! The predictable redox chemistry, resistance to deleterious autoxidation reactions, and availability of reliable synthetic precursors have enabled a broad spectrum of chemists to explore precious metals in catalytic reactions directed toward organic synthesis. Impressive advances as palladium-catalyzed cross-couplings, platinum-catalyzed hydrosilylations, ruthenium-promoted olefin metathesis, and rhodium- and ruthenium-catalyzed asymmetric hydrogenations have all been conducted on industrial scale and in many cases on advanced intermediates and densely functionalized molecules. Discovering cobalt catalysts that meet or surpass these criteria is certainly a tall order. Challenges range from realization of synthetic precursors to understanding fundamental reaction chemistry to optimized ligands for 3d transition metals [1].

This volume edited by *Hapke* and *Hilt* explores the evolving role of cobalt, a relatively Earth-abundant first-row transition metal, in catalytic reactions directed toward organic synthesis. Over the course of 11 distinct chapters each authored by leaders in the field, a contemporary view of the role of cobalt over a diverse range of catalytic transformations is presented. Importantly, each chapter blends advances in both the fundamental and the applied. Chapter 1, authored by the editors begins with an important historical overview of the element and its role in catalysis. Readers are reminded that while catalysis with cobalt and other Earth-abundant transition metals are at the forefront of modern sustainability research, application of cobalt in catalysis directed toward organic synthesis dates back nearly a century. *Roelen's* use of $Co_2(CO)_8$ in alkene hydroformylation [2] was a seminal example highlighting the impact of organometallic

cobalt catalysts on selective organic transformations and later demonstrated the utility of mechanistic understanding on improving overall catalyst performance. Interestingly, *Richard Heck* was instrumental in elucidating the mechanism of this reaction [3] and was one of the first organometallic transformations so thoroughly studied.

The following chapters are research monographs focused on a specific topic and groupings of chapters highlighting related areas of catalysis. Chapter 2 is authored by *Junge* and *Beller* and describes the explosive growth of cobalt catalysis in various classes of hydrogenation reactions. Particular emphasis is placed on complexes with multidentate ligands, as these contain many first-row metals likely because deleterious ligand dissociation pathways are suppressed. This chapter, like many others in the book, ends with a convenient infographic highlighting the various types of catalysts covered and the types of reactions each promotes. *Kim* and *Dong* in Chapter 3 cover related transformations on the hydrofunctionalization of C=C bonds. Again beginning with *Roelen's* alkene hydroformylation chemistry, the chapter tracks the evolution of cobalt-catalyzed hydroacylation, hydrocyanation, hydrocarboxylation, and related reactions. It is remarkable to notice the impact cobalt catalysts have had on expanding the scope and range of organic methods, particularly in the synthesis of small rings and in enantioselective reactions.

The selective functionalization of carbon–hydrogen bonds is one of the most active areas in modern catalysis research. The potential impact of these methods is apparent – the selective conversion of ubiquitous C—H bonds to functional groups would transform the way synthetic chemists view and approach the reactivity of organic molecules. Not surprisingly, organometallic and coordination complexes of cobalt have been widely studied for these transformations. In a comprehensive monograph on a rather large body of research, *Yoshikai* in Chapter 4 highlights the long-standing impact of cobalt catalysis on C–H functionalization research. As with other chapters, the concluding infographic on the different transformations and catalyst types helps guide readers.

Metal-catalyzed cross-coupling, recognized with prestigious honors such as the 2010 Nobel Prize in Chemistry (for C—C bond formation; https://www.nobelprize.org/prizes/chemistry/2010/summary/) and the 2019 Wolf Prize (for C—N bond formation; https://www.wolffund.org.il/index.php?dir=site&page=winners&name=&prize=3016&year=2019&field=3002), is one of the most widely used metal-catalyzed reactions, particularly in the pharmaceutical industry. Attempts to promote these reactions with first-row metals date to the 1940s and the work of *Kharasch* [4]; these have since evolved into a vibrant field of research. Chapter 5, authored by *Dorval* and *Gosmini*, accounts both the latest developments and the historical contexts of cobalt-catalyzed cross-coupling. While impressive advances have been made, considerable improvements need to be realized for these reactions to reach the broad utility reported with palladium and nickel.

Three later chapters of the volume are devoted to the interaction and catalytic chemistry of π-systems with cobalt. Chapter 6 is principally focused on ionic and radical chemistry of π-bonded ligands, while Chapter 7 describes various cobalt-catalyzed cycloaddition reactions. Chapter 8 by *Lindsay* and

Kerr describes the rich cobalt chemistry associated with the *Pauson–Khand* reaction. In Chapter 9, editor *Hapke* and *Gläsel* describes cobalt-catalyzed [2+2+2] cycloaddition chemistry, a field with deep historical routes but one that continues to have modern advances and opportunities. In Chapter 10, *Pellisier* focuses on asymmetric catalysis with cobalt, another rich and growing field. The final chapter nicely rounds out the book and focuses on the bioorganometallic chemistry, including vitamin B12 and related cobalt compounds.

In summary, the volume covers the breadth of modern catalysis research involving cobalt. One pervasive theme throughout is the interplay of fundamental structure, reactivity, and organometallic chemistry with advances and applications in catalysis and organic methods. Although catalysis with cobalt has been studied for decades and impressive advances have been made, there are tremendous opportunities for the future. Cobalt and other Earth-abundant metals have yet to enjoy the same widespread adoption as their precious metal counterparts. Many challenges associated with catalyst handling, reaction scope, functional group tolerance, and air-sensitivity remain. It is apparent, however, that the journey is worth the effort as cobalt, time and again, has exhibited unique reaction chemistry distinct from the precious metals and inspires continued exploration both in the fundamental and applied. This book is a valuable resource for students and researchers alike and will likely serve to inspire new directions in cobalt catalysis research.

August 2019

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Preface

Cobalt is a late member of the first-row transition metals and has only in recent years become an important catalyst metal in homogeneous catalysis and synthesis. This is quite surprising regarding the role of cobalt in the earliest developments of homogeneous catalysts on an industrial scale in the 1930s, with the hydroformylation chemistry developed at Oxo Chemie by Otto Roelen. It is even more surprising that, to date, no single monograph has been devoted solely to the catalysis and organic synthesis mediated by cobalt complexes and compounds, while all surrounding metals and group congeners like iron, nickel, ruthenium, rhodium, and iridium have been recognised this way.

The aim of the presented volume is to fill this gap and collect renowned authors and practitioners in the field of cobalt chemistry to outline the basics, increasing importance and contemporary developments in this field. The 11 chapters are headlining the various most valuable and applied classes of transformations involving cobalt complexes, including details on mechanistic aspects, elemental reaction steps, and organometallic chemistry. The application of cobalt catalysis ranges from basic transformations to evaluate the scope and limitations of the reactions up to the utilisation, e.g. in the synthesis of natural products and other complex organic molecules. In selected chapters also practical preparation procedures of some cobalt complexes have been included to illustrate the feasibility and experimental handling of cobalt catalysts in some detail.

As editors, we would like to give some additional comments. The extraordinarily large field of heterogeneous cobalt catalysis in academia and industry is not covered in this volume. However, this field has been reviewed in the literature thoroughly for an even longer time than is the case for homogeneous catalysis. The actual developments of energy conversion and storage including cobalt-containing materials is currently a very hot topic, with new results being constantly compiled and reviewed extensively in reports and commentaries. We have therefore decided to leave this topic out of the volume. As a more formal note, we would like to announce that only the names of the principal investigators are mentioned in the chapter texts, well aware that the actual work has been conducted by the co-workers and other authors of the cited papers.

We hope that the content of the book will provide valuable information to the readers and inspire researchers from academia and industry alike to include cobalt catalysts in their future research to solve synthetic challenges and take opportunity of the unique and fascinating properties of cobalt.

Linz and Oldenburg
September 2019

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1

Introduction to Cobalt Chemistry and Catalysis

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1.1 Introduction

Cobalt (Co) is the first and lightest element among the group 9 transition metals, further members being rhodium (Rh), iridium (Ir), and meitnerium (Mt). In contrast to their significance in organic synthesis and catalysis, cobalt is by far the most abundant element of the group in the geosphere, compared with rhodium and iridium as its heavier congeners (Co:Rh:Ir = c. 10^4 : 5 : 1) [1]. While rhodium and iridium complexes have been at the forefront of organotransition metal chemistry with relation to organic syntheses, steadily enabling novel and often unprecedented transformations of simple starting materials to complex products or opening the gate to novel fields of catalysis as has happened with C–H functionalisation reactions, cobalt stood back for a long time. Expression for the different significance of the three transition metals is also found in the literature, as monographs for either rhodium and iridium as catalyst metals for organic

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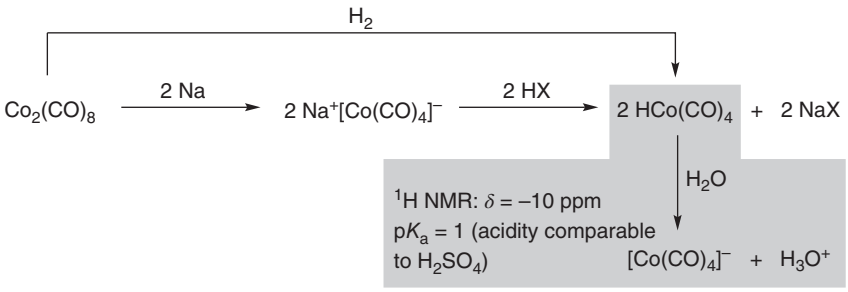
synthesis have already been published [2, 3]. However, some direct comparisons of the application of group 9 metals for organic synthesis and catalysis can be found in the literature [4]. Next to its membership in the first row of the transition metals, relative abundance, and biorelevance, it is also considered a sustainable metal, among other elements in this nowadays particularly important field [5].

Cobalt (the name is derived from the German word "Kobold" meaning goblin, due to the behaviour and confusion with silver–copper ores in medieval mining) has been isolated for the first time in 1735 by the Swedish chemist *Georg Brand*, who also recognised its elemental character. It is an essential trace element for humans and animals, and its main purpose is the constitution of vitamin B_{12} (cobalamin), which has an important role for the regeneration of erythrocytes. Cobalamines are organometallic compounds with cobalt–carbon bonds, possessing cobalt in the oxidation states +1 to +3, and provide the only known cobalt-containing natural products.

Beside the importance for the human physiology, cobalt has evolved from an unwanted and downright abhorred element during silver and copper mining to a metal of strategic industrial importance and in recent years also a rising young star in homogeneous catalysis. How does this chemical version of "rags to riches" come into play? One modern reason is the importance of cobalt as metal used in high-performance alloys (e.g. stellite), permanent magnets, rechargeable batteries, cell phones, and many more technical applications [6]. Requirements of our modern society with respect to the production of chemicals and materials also heavily rely on the late, rare, and rather expensive platinum group metals (PGM). The implementation of sustainability and efficiency thus leading the way to explore the earth-abundant metals for both homogeneous and heterogeneous catalytic purposes [7, 8].

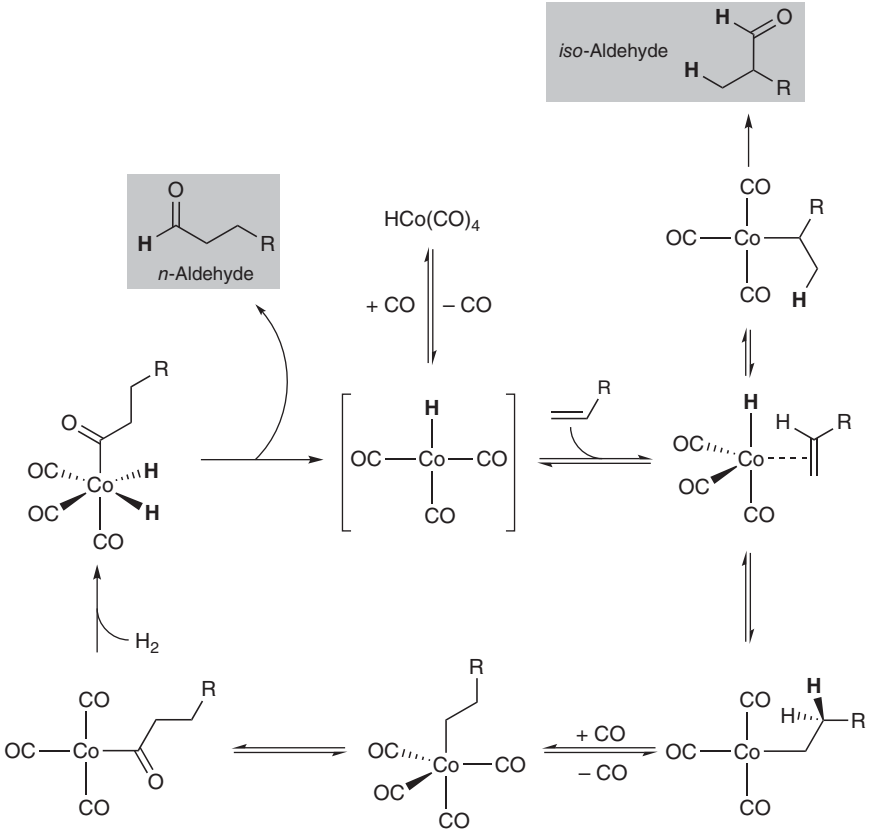
From a chemical and catalytical point of view, cobalt already inherits the role of a major player in the awakening of homogeneous organometallic catalysis in the first half of the twentieth century [9]. *Otto Roelen* at Ruhrchemie (now Oxea) in Oberhausen discovered the "oxo synthesis" in 1938, today named hydroformylation reaction, and introduced $HCo(CO)_4$ as catalyst for this reaction. Still today beside rhodium as metal with higher reactivity cobalt complexes are used as catalysts. Basis for this reaction was work from *Walter Hieber* on the synthesis of carbonyl metallates via the so-called "*Hieber* base reaction", affording $H_2Fe(CO)_4$ by the reaction of $Fe(CO)_5$ with NaOH. Because for cobalt no mononuclear binary carbonyl compound is known, therefore the related compound $HCo(CO)_4$ was generated from the prominent carbonyl complex $Co_2(CO)_8$ by reductive splitting with sodium metal and protonation or even directly by oxidative splitting by molecular hydrogen itself (Scheme 1.1). The resulting cobalt carbonyl hydride is a proton donor, able to protonate water with an acidity comparable to sulfuric acid.

The mechanism of the hydroformylation process using $HCo(CO)_4$ and related compounds $HCo(CO)_3L$ (L = phosphine) has been studied in great detail, first proposed by *Breslow* and *Heck* [10]. Scheme 1.2 displays the now generally accepted mechanistic pathway for the cobalt-catalysed process [11]. Starting from the hydridic $HCo(CO)_4$, reversible dissociation of a CO ligand followed by reversible olefin coordination led to migratory insertion, which would pave the way to either the *n*-aldehyde or *iso*-aldehyde, depending on the course of the



Scheme 1.1 Synthesis of cobalt carbonyl hydride (the reaction with H_2 can be reversible).

insertion. Following the reaction cycle, alkyl migration led to formation of an acylcobalt species, which after oxidative addition of hydrogen was reductively eliminated as the *n*-aldehyde. This catalytic cycle combines all the significant elementary steps of homogeneous catalysis with metal complexes and provides a taste on the complexity for studying such reaction mechanisms in detail. Interest



Scheme 1.2 Mechanism of the classical cobalt-catalysed hydroformylation reaction of terminal olefins.

and detailed studies in these first molecularly defined catalysts for the purpose of synthesising structurally advanced organic molecules has since filled the knowledge of organometallic chemistry.

1.2 Organometallic Cobalt Chemistry, Reactions, and Connections to Catalysis

Cobalt is a d^9-metal and the by far mostly frequently occurring oxidation states in its compounds are −1, 0, +1, +2, and +3. The latter oxidation states also play the major role in stoichiometric/catalytic reactions, while complexes with the oxidation states −1 and 0 are found in some prominent complexes and starting materials. The preference of formal +1/+3 oxidation states in many catalytic transformations is in close relation to the catalytic behaviour of the heavier congeners, rhodium and iridium. In general, the largest number of contemporary catalytic processes include a catalyst generation step, in which, e.g. Co(II) salts are introduced, together with an appropriate ligand and a reducing agent or other additives to lower the oxidation state to +1, from which the species enters the catalytic cycle. On the other hand, a large number of organometallic compounds based on the unsubstituted cyclopentadienyl (Cp), related substituted cyclopentadienyl (Cp′), or pentamethylcyclopentadienyl (Cp*) ligands are reported and well known, beside numerous isolated complexes with P- and N-donor atom-containing ligands. However, the coordination and organometallic chemistry of cobalt is a wide and multifaceted field and has been involved in ground-breaking research in either area [12].

Cobalt is also a widely used catalyst metal for heterogeneously catalysed processes. Especially the famous *Fischer–Tropsch* process is still relying on cobalt as the principal catalyst metal, as it was already from the initial reports on this large-scale industrial process [13]. Further modern applications in heterogeneous catalysis are often related to the conversion of small molecules in steam-reforming or partial oxidation processes (ethanol, methane) towards the formation of syngas, together with other applications for the allocation of clean energy. A highly current topic is therefore, e.g. the use of cobalt in heterogeneously catalysed electrochemical water splitting [14] or the reduction of CO_2 on cobalt-containing surfaces [15]. Analysis of the chemistry and catalytic performance of cobalt on surfaces is still a topic of ongoing investigations [16].

1.2.1 Cobalt Compounds and Complexes of Oxidation States +3 to −1

Cobalt is an electron-rich transition metal, like its latter group congeners; however, it is a first-row transition metal, which inherits also significant differences. Due to its electron richness, it belongs to the so-called "base metals", including the neighbouring first-row transition metals manganese, iron, nickel, and copper. The abundance of low oxidation states (0, −1) is, however, quite unique for cobalt and also rather known for the compounds of neighboring iron than for

the heavier metals of group 9. Comparable especially to rhodium catalysis is the oxidation state +3 as usually highest occuring state during catalytic reactions.

1.2.1.1 Co(III) Compounds

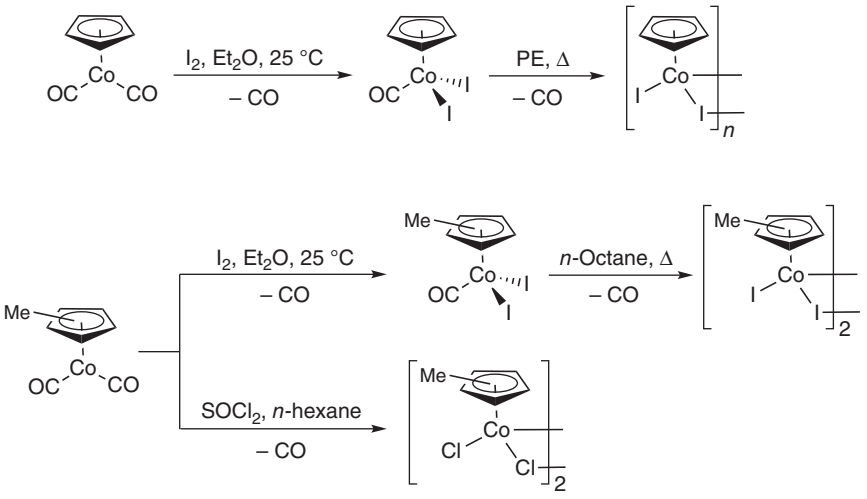
Isolated cobalt complexes in the oxidation state +3 are most often found in coordination compounds, because the d^6 configuration is highly stable with ligands possessing a strong ligand field. There is only a limited number of Co(III) compounds commercially available and from the halides, only the binary CoF_3 is known, which is an oxidant and can be used as fluorinating agent. This is in stark contrast to rhodium and iridium, where the oxidation state +3 is well known in compounds and all binary halides MX_3 (X = F, Cl, Br, I) are available for these metals. $RhCl_3$ and $IrCl_3$ and their hydrated versions are usually the starting materials for synthesising numerous precursor compounds and precatalysts for catalytic purposes, while $CoCl_3$ is an unstable compound [17].

Cobalt(III) complexes played an important role in the development of the theory of coordination compounds by *Alfred Werner*, concerning the complexes of $CoCl_3$ with different equivalents of ammonia, NH_3. The complexes $[Co(NH_3)_4Cl_2]Cl$ exist in the form of two stereoisomers (*cis*- and *trans*-isomers of the octahedral polyhedron), allowing to address the stereochemistry of coordination compounds. The Co(III) complexes are kinetically inert, octahedral complexes with the configuration t_{sg}^6. Due to the inertness, indirect methods of synthesis are common, meaning to use Co(II) salts as starting compounds, coordination with desired ligands, and subsequent oxidation by, e.g. oxygen, to furnish the desired Co(III) complexes.

There are more organometallic Co(III) compounds known, owing to the strong ligand field of many groups used as organometallic ligands. As an example, cobaltocene, Cp_2Co is a rather unstable, 19-electron Co(II) complex, which can act as efficient one-electron reducing agent, yielding the stable cobaltocenium Co(III) cation (Cp_2Co^+), being isoelectronic with ferrocene. While for ferrocene an extremely rich and diverse chemistry has been developed, e.g. as ligand backbone for phosphine ligands, such application of the cobaltocenium cation is lacking and started to develop only recently [18]. In addition, the synthesis of half-sandwich CpCo(III) complexes is well known and shares common features with Cp*Co complexes. This is best exemplified by the reaction of the $CpCo(CO)_2$ and $Cp^*Co(CO)_2$ with elemental halides, furnishing the corresponding Co(III) complexes, which has been reported already during the time when the Cp–metal chemistry was still in its infancy (Scheme 1.3) [19, 20]. Especially $Cp^*CoI_2(CO)$ has become a precursor for a wide range of precatalyst compounds. The chemistry and catalytic applications of CpCo(III) and Cp*Co(III) complexes as well as some structurally related Cp′Co(III) complexes has been compiled very recently [21].

1.2.1.2 Co(II) Compounds

Compared with its higher homologs, rhodium and iridium, the oxidation state +2 is one out of the two most important, while for the other two elements, it has only minor importance. All halides of this oxidation state are known and commercially available, stable compounds, being the starting material for a



Scheme 1.3 Synthesis of CpCo- and Cp*Co-halides as synthetically useful precursors and precatalysts.

large number of complexes, e.g. as the hydrate $CoCl_2 \cdot 6H_2O$. The configuration of Co(II) ions as being d^7 does not favour a particular ligand arrangement for such paramagnetic complexes. Examples of coordination geometries comprise linear (e.g. $[Co\{N(SiMe_3)_2\}_2]$), tetrahedral (e.g. $[CoCl_4]^{2-}$, $[Co(N_3)_4]^{2-}$, $[CoCl_3(NCMe)]^-$), square-based pyramidal (e.g. $[Co(CN)_5]^{3-}$), and dodecahedral (e.g. $[Co(NO_3)_4]^{2-}$) forms, among many others, depending on the ligand properties [17].

Co(II) salts used as precatalysts in catalytic reactions are usually reduced by less noble metals, such as zinc or manganese to Co(I), which upon complexation to an appropriate ligand acts as catalytically active species. The salts can be introduced separately as halide salts and free ligand or as the isolated complex. The synthesis conditions of some typical Co(II) complexes are compiled in Scheme 1.4 [22]. A useful and very recently reported alternative to complexes of the type $[Co(R)_2(Py)_2]$ is the compound $[Co(R)_2(TMEDA)_2]$ (R = CH_2SiMe_3, CH_2CMe_3, CH_2CMe_2Ph), allowed facile substitution of the "dummy" ligand for *N*-heterocyclic carbene (NHC) ligands or bidentate phosphines [23].

The reduction depends on conditions like the applied Co(II) salt, solvents, reductants involved, and even additives like *Lewis* acids, being able to remove a remaining halide from the metal centre [24]. In cross-coupling reactions utilising cobalt(II) precatalysts, the reduction to Co(I) or even Co(0) can also be achieved by an excess of the organometallic coupling reagent, often *Grignard* reagents [25].

Recently, novel Co(II) precursor compounds for catalytic applications came to the forefront and opened the door also for the synthesis of complexes being comparable to known precursor molecules with the latter homologs, e.g. $[M(COD)Cl]_2$ (M = Rh, Ir) or $[Rh(COD)_2](BF_4)$. *Chirik* introduced $(Py)_2Co(CH_2SiMe_3)_2$ as precursor for the coordination to bisphosphines and subsequent asymmetric hydrogenation reactions, providing evidence for the

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