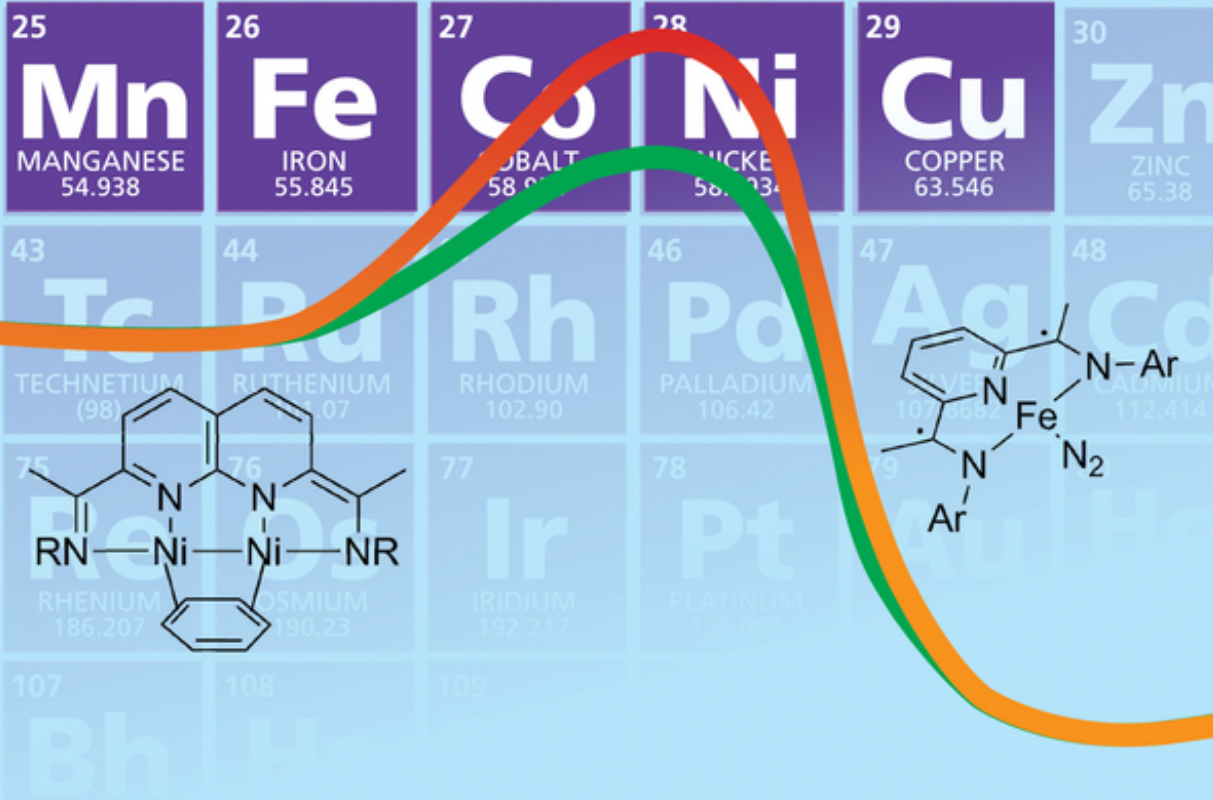Wiley-VCH

Edited by Robertus J.M. Klein Gebbink and Marc-Etienne Moret

Non-Noble Metal Catalysis

Molecular Approaches and Reactions

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Preface

Since its early development in the 1960s, the field of homogeneous catalysis has led to a plethora of industrially applied organometallic catalysts and, not the least, to an in-depth fundamental understanding of the reactivity of transition metal complexes. The threefold awarding of the Nobel Prize to the field of homogeneous catalysis in the very beginning of the twenty-first century highlights the impact the homogeneous catalysis field has made on chemistry and synthesis in general [1–3]. Remarkably, the reactions for which these awards have been given predominantly make use of noble, platinum group metals. This illustrates the historical importance and dominance of the use of noble metals in the field of homogeneous catalysis at large, from gram-scale, exploratory organic synthesis in pharmaceutical labs to large-scale industrial processes.

Although non-noble metals such as iron have been investigated from the early days of catalysis on, their noble counterparts have quickly and durably come to occupy the center of the stage. However, many recent endeavors in the field shift the focus back to non-noble metals, sometimes referred to as "base metals," in the development of new homogeneous catalysts. This move is largely driven by economic and environmental considerations. Not only are market prices of noble metals generally high, which is largely due to their relatively low abundancy in the earth crust, but these prices are often rather volatile as well. In addition, many of the noble metals are associated with toxicity issues for humans and the environment. As a consequence, the use of noble metal catalysts in, e.g., later stages of active pharmaceutical ingredient synthesis requires stringent purification procedures with the associated energetic and financial costs.

Motivated by many of these considerations, the scientific community has become interested in the study and development of homogeneous catalysts that are based on non-noble metals. The practical use of metals such as manganese, iron, and cobalt promises to alleviate, at least partly, some of these issues. A recent analysis by the EU on the criticality of raw materials furthermore shows that the late first-row transition metals are all above the economic importance threshold, whereas all except cobalt are below the supply risk threshold [4]. This is in contrast with many other raw materials, including the platinum group metals, where geopolitical issues come in to play as well.

One should not forget, though, that the current blossoming of the field of non-noble metal catalysis is for a large part simply born out of scientific curiosity. The availability of multiple oxidation states, often spaced by one-electron differences, and the strong tendency to adopt high-spin electron configurations lead to markedly different chemistry for non-noble metals with respect to noble metals, e.g. in terms of kinetic lability and lifetimes of intermediates. The investigation of non-noble metals in homogeneous catalysis is therefore expected to unravel fundamentally new reactivity patterns, leading to new catalysts, and, not unimportantly, to new applications. In contrast to the early days of catalysis, the current availability of advanced spectroscopic and analytical tools, including density functional theory and other computational methods, now allows for a detailed characterization and understanding of non-noble metal complexes, catalysts, and reactive intermediates. This situation is clearly different from the times when Kochi was exploring iron-mediated C—C coupling chemistry in the 1940s (see Chapter 11 by Neidig et al.).

Although the terms "non-noble metals" and "base metals" are broadly defined, we opted to focus this book on the late, first-row transition metals Mn, Fe, Co, Ni, and Cu, given the volume of recent interest in and the development of the catalytic chemistry of these metals. Only in selected cases will examples using other metals be discussed, and if so mainly to put recent developments in perspective. In this sense, the book adds on and complements earlier books on related topics, such as the book edited by Bullock on "catalysis without precious metals" [5].

The first four chapters of the book deal with conceptual aspects of non-noble metal catalysis in order to provide the reader with some further background. These chapters include discussions on non-innocent ligands (de Bruin, Chapter 1), computational methods (Ye, Neese, Chapter 2), multinuclear complexes (Mankad, Chapter 3), and industrial applications (Alsters, Le Fort, Chapter 4). Subsequent chapters discuss typical reaction classes, such as additions to C=C , C=N, and C=O double bonds (Chapters 5–10), the formation of C—C and C—hetero atom bonds through cross-coupling (Chapters 11–13), (formal) oxidation reactions (Chapters 14–16), and small-molecule activation (Chapters 16–20). These reaction classes are chosen to be representative of the broad range of reactions for which non-noble metal catalysts are being investigated. These chapters are presented from the point of view of synthetic method development or of catalyst development and may focus on the use of a single metal for a particular reaction or on a particular reaction itself. Accordingly, a particular reaction or catalyst may appear in more than one chapter.

We hope this book provides the more experienced reader with a contemporary overview of the current standing in the field of homogeneous non-noble metal catalysis and appeals to the less experienced reader in raising further interest in the field.

A big "thank you" not only goes out to all the contributors to this book, who have kept up with us as editors, but also the support staff at Wiley for their help and patience. We would also like to thank our collaborators within the European training network NoNoMeCat on homogeneous "non-noble metal catalysis" for the joint and stimulating efforts in further developing the field and training the

next general generation of researchers in the field [6]. Not surprisingly, many of these collaborators are contributors to this book.

Utrecht, July 2018   *Robertus J. M. Klein Gebbink*
                                                        Marc-Etienne Moret

References

1 The Nobel Prize in Chemistry 2001 was awarded to William S. Knowles and Ryoji Noyori "for their work on chirally catalyzed hydrogenation reactions" and to K. Barry Sharpless "for his work on chirally catalyzed oxidation reactions." See: www.nobelprize.org/nobel_prizes/chemistry/laureates/2001/.

2 The Nobel Prize in Chemistry 2005 was awarded to Yves Chauvin, Robert H. Grubbs, and Richard R. Schrock "for the development of the metathesis method in organic synthesis." See: www.nobelprize.org/nobel_prizes/chemistry/laureates/2005/.

3 The Nobel Prize in Chemistry 2010 was awarded jointly to Richard F. Heck, Ei-ichi Negishi, and Akira Suzuki "for palladium-catalyzed cross couplings in organic synthesis." See: www.nobelprize.org/nobel_prizes/chemistry/laureates/2010/.

4 European Commission. Study on the review of the list of Critical Raw Materials. https://publications.europa.eu/en/publication-detail/-/publication/08fdab5f-9766-11e7-b92d-01aa75ed71a1/language-en (accessed 19 July 2018).

5 Bullock, R.M. (ed.) (2010). *Catalysis without Precious Metals*. Wiley.

6 For information on the NoNoMeCat network see: www.nonomecat.eu (accessed 17 July 2018).

1

Application of Stimuli-Responsive and "Non-innocent" Ligands in Base Metal Catalysis

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1.1   Introduction

The development of efficient and selective catalysts is an important goal of modern research in chemistry – the science of matter and its transformations. Our society needs new catalysts to become more sustainable, and a desire for selectivity and efficiency in the preparation of medicines and materials has boosted our interest in developing new methods based on homogeneous catalysis, particularly on the development of new ligands that can be fine-tuned to specific needs. The properties of a metal complex as a whole are the result of the interaction between the metal center and its surrounding ligands. In traditional approaches, the steric and electronic properties of the spectator ligand are used to control the performance of the catalyst, but most of the reactivity takes place at the metal. Recent new approaches deviate from this concept and make use of ligands that play a more prominent role in the elementary bond activation steps in a catalytic cycle [1, 2]. The central idea is that the metal and the ligand can act in a synergistic manner to facilitate a chemical process. In this light, complexes based on the so-called "non-innocent" ligands offer interesting prospects and have attracted quite some attention.

The term "non-innocent" is broadly used, and diverse authors give different interpretations to the term. It was originally introduced by Jørgensen [3] to indicate that assigning metal oxidation states can be ambiguous when complexes contain redox-active ligands. As such, ligands that get reduced or oxidized in a redox process of a transition metal complex are often referred to as "redox non-innocent." [4, 5] With modern spectroscopic techniques, combined with computational studies, assigning metal and ligand oxidations states has become less ambiguous, and hence, many authors started to use the term "redox-active ligands" instead. Gradually, many authors also started to use the term "non-innocent" for ligands that are more than just an ancillary ligand, frequently involving ligands that have reactive moieties that can act in cooperative (catalytic) chemical transformations, act as temporary electron reservoirs, or respond to external triggers to modify the properties or reactivity of a complex.

A common objective of many of these investigations is to achieve better control over the catalytic reactivity of first-row transition metal complexes, with the ultimate goal to replace the scarce, expensive noble metals currently used in a variety of catalytic processes by cheap and abundant first-row transition metals. Instead of providing a comprehensive overview of redox non-innocent [6, 7] and cooperative ligands [1, 8, 9], this chapter is intended to provide a conceptual introduction into the topic of achieving control over the catalytic reactivity of non-noble metals using non-innocent ligands on the basis of recent examples.

Noble metals are frequently used in several catalytic synthetic methodologies and many industrial processes [10]. Their catalytic reactivity is most frequently based on their well-established "two-electron reactivity," involving typical elementary steps such as reductive elimination and oxidative addition. These elementary steps easily occur for late (mostly second and third rows) transition metals having two stable oxidation states differing by two electrons. However, most noble metals are scarce and are therefore expensive (and sometimes toxic [11]). Therefore, it is necessary to reinvestigate the use of cheaper, abundant, and benign metals to arrive at cost-effective alternatives. This is not an easy task, as base metals (Fe, Co, Cu, Ni, etc.) often favor one-electron redox processes, and typical elementary steps commonly observed in noble metal catalysis are only scarcely observed for base metals. As such, the unique properties of non-innocent ligands are advantageous to gain better control over the reactivity of base metals. In some cases, this leads to reactivity comparable to that of noble metal complexes (but more cost-effective and benign), whereas in other cases, the combination of a base metal with a "non-innocent" ligand can actually give access to unique new types of reactivity.

This chapter has four parts. In Section 1.2, the concept of responsive ligands is discussed, giving examples of a series of ligands that can be tuned using external stimuli such as light, pH, or ligand-based redox reactions. These can trigger a change in the properties of the ligand, thereby modifying the reactivity of the metal. Section 1.3 deals with redox-active ligands that behave as electron reservoirs. In the examples provided, this feature enables oxidative addition and reductive elimination steps for first-row transition metal complexes that, without the aid of redox-active ligands, are less inclined to undergo these catalytically relevant elementary steps. Section 1.4 focuses on recent examples of cooperative catalysis, in which non-noble metal reactivity is combined with ligand-based reactivity in key substrate activation steps. The last part (Section 1.5) deals with examples in which the coordinated substrate itself acts as a redox-active moiety in key elementary steps of a catalytic reaction. More specifically, these coordinated substrates get oxidized or reduced by the metal by a single electron, thus creating "substrate radicals," which play an important role in catalytic radical-type transformations.

1.2 Stimuli-Responsive Ligands

Common ancillary (innocent) ligands in homogeneous catalysis typically control the activity and selectivity of the catalyst by affecting the steric and electronic

properties around the reactive metal center. As such, changing the reactivity of the active metal center usually requires the synthesis of new ligands, which is often associated with elaborate synthetic procedures [6]. However, the electronic and steric properties of ligands can sometimes be influenced in an easier manner by using external stimuli, involving, for example, ligand protonation/deprotonation, ligand oxidation/reduction, or (reversible) light-induced ligand transformations (Scheme 1.1) [12].

1. Redox responsive ligands

R = redox active component

2. pH responsive ligands

X = acidic/basic site
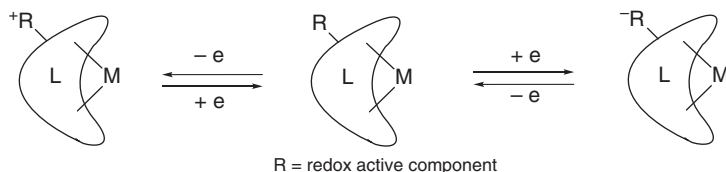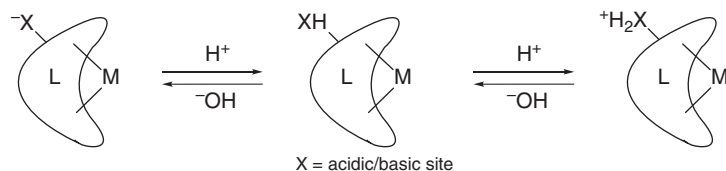
3. Light responsive ligands
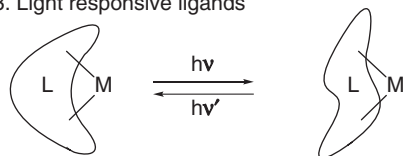
Scheme 1.1 Switching catalytic properties of a catalyst using external stimuli.

When using such responsive ligands, the metal oxidation state is typically unaffected, but its reactivity is nonetheless influenced by the new electronic and steric properties of the ligand. Furthermore, the solubility of the metal complex can sometimes be significantly influenced by such external stimuli. In most current literature, these ligands are nevertheless considered to be "innocent" ligands as they are not directly involved in substrate bond making/breaking processes nor lead to ambiguities in assigning the metal oxidation state. Stimuli-responsive ligands are particularly useful to influence the catalyst *during* a catalytic reaction and are therefore mainly applied to develop switchable catalytic systems.

1.2.1 Redox-Responsive Ligands

Oxidation or reduction of a complex containing one or more redox-active ligands can lead to oxidation or reduction of the ligand rather than the metal. As such, the ligand can switch between one or multiple oxidized and reduced states, by which the electronic properties of the ligand (and thereby the metal) change.

These redox processes can be triggered either chemically or electrochemically [13]. Often metallocenes such as ferrocene or cobaltocene are used because of their reversible oxidation and reduction cycles [14]. In other cases, the redox-active part of the ligand of interest is actually a metallocene moiety [15]. Upon oxidation of a ferrocenyl to a ferrocenylium group attached to the ligand, the electron density of the donor ligand decreases and thereby also that of the metal bound to this ligand, as can be observed in a shift of the CO stretch frequency to higher wavenumbers for carbonyl complexes [16]. Recently, a review appeared reporting a variety of chemical oxidants and reductants that allow the design of new catalysts with switchable ligands at a specific desired potential [17]. Examples of the use of redox-active ligands in catalysis frequently involve redox processes that partly occur at the redox-active ligand and partly at the catalytic metal center (see Section 1.3). Examples of redox-responsive ligands in catalysis wherein ligand-based redox processes affect the metal center and its catalytic properties indirectly are rare, especially for base metals. The main application of such reported examples is in the field of switchable catalysis. Furthermore, the solubility of the ligand can change significantly because of charge buildup, thus enabling separation of the catalyst from the reaction mixture after a catalytic reaction [18].

By oxidation or reduction of the ligand, the overall charge of the complex changes, which affects the catalytic activity of the central metal, and in some cases, this can be used to switch a catalyst ON and OFF. Most of the recently reported examples of such switchable catalysts involve systems based on noble metals [18–20], but a few examples of base metals are known as described below. One of the first redox-responsive base metal catalysts reported involves a titanium-based salen-type ligand substituted with two ferrocene (Fc) moieties (Figure 1.1a) [21]. The catalyst was used in the ring-opening polymerization of
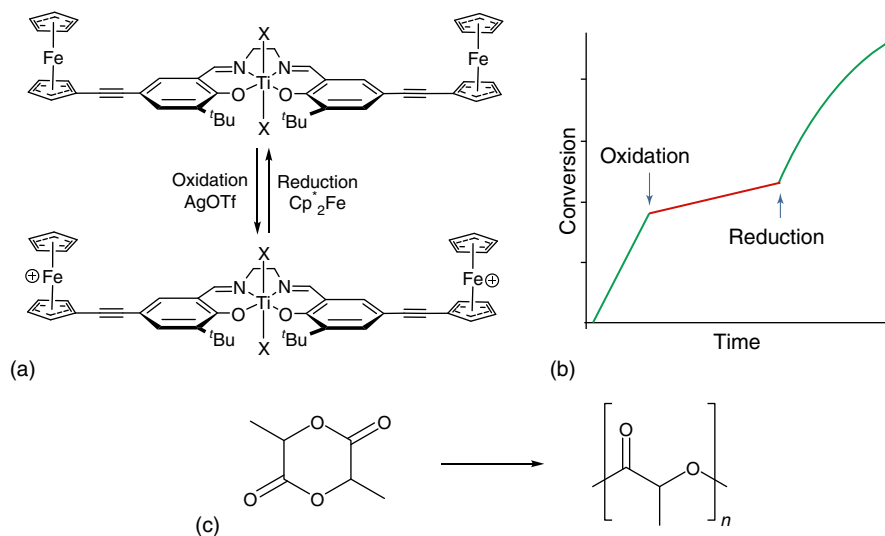
Figure 1.1 Titanium-based redox-switchable catalyst (a) and the effect of switching on the catalysis (b) on the polymerization reaction (c).

lactides, during which the neutral catalyst showed a 30-fold enhanced rate with respect to the oxidized complex. Oxidation of the ferrocenyl moieties of the catalyst does not completely shut down the catalytic activity, but by addition of small amounts of oxidant or reductant, the catalyst can nonetheless be switched between a more active (ON) and less active (OFF) state *during catalysis* (Figure 1.1b).

More recently, new titanium and zirconium catalysts were developed based on salfan (Y = NMe) and thiolfan (Y = S) ligands (Figure 1.2a) containing a ferrocene moiety closer to the metal center [22]. The reduced and oxidized catalysts showed opposing rates for the ring-opening polymerization of L-lactide and ϵ-caprolactone, respectively (Figure 1.2b). By switching between the two states during the polymerization reaction, the catalyst can be used to generate block copolymers with a high degree of regularity. In particular, this last example elegantly shows the power of switchable catalysts for application in polymerization reactions. Given the potential of such systems, we expect that many more examples of redox-switchable catalysts used for a variety of other catalytic reactions are likely to be disclosed in the next couple of years.

1.2.2 pH-Responsive Ligands

Ligands that can be easily protonated or deprotonated by applying relatively mild pH changes are commonly used to affect the solubility of catalysts. With this method, homogeneous catalysts can be easily recycled, thus saving cost and avoiding metal contamination in the products. Reversible protonation of amine groups to obtain water-soluble complexes has been applied to noble-metal-catalyzed reactions such as olefin metathesis [23] and cross-coupling reactions [24]. The selectivity of rhodium metathesis catalysts can be further altered upon protonation of the ligand [25]. By using similar
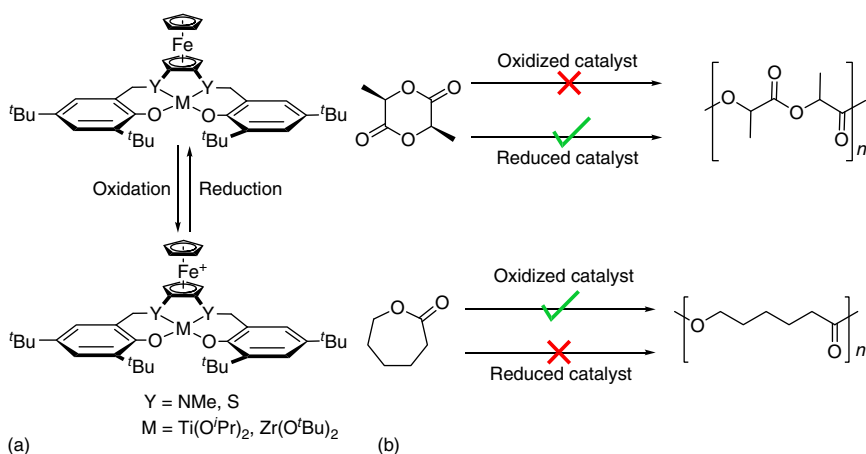
Figure 1.2 Ferrocene containing redox-switchable catalysts (a) and inverted reactivity for the resulting oxidized and reduced complexes (b). Source: Wang et al. 2014 [22]. Reproduced with permission of ACS.

ammonium-tagged NHC ligands, a copper-catalyzed click reaction in water was developed by Li and coworkers [26]. The products could simply be extracted in order to recycle the catalyst several times with a small loss of overall yield, but the catalyst was not switchable. In 2012, the same group reported a similar copper complex for the carbonylation of boronic acids, benzoxazoles, and terminal alkynes [27]. In this case, the catalyst precipitates upon protonation and could be separated by centrifugation (Figure 1.3). The catalyst can be recycled up to four times with only moderate loss in activity. Related copper-catalyzed reactions based on NHC complexes with pendant bases have also been reported [28], but the effects of deprotonation on the catalysis or recyclability of the complex were not discussed in detail for these systems.

The second type of proton-switchable ligands is composed of bipyridine and phenanthroline ligands equipped with moieties that can be (de)protonated. Many late transition metal catalysts based on iridium [29–31], rhodium [32], and rhenium [33] have been reported to use this class of ligands. Recent base metal examples include a switchable copper catalyst for the Ullmann reaction of aryl bromides. The catalyst can be deprotonated in basic water to obtain a highly active catalyst, which could be recycled by acidification (Figure 1.4) [34].

Figure 1.3 Proton-switchable copper catalyst.

Figure 1.4 Reversible deprotonation of a 4,7-dihydroxy-1,10-phenanthroline (including dotted lines) or 4,4'-dihidroxy-2,2'-bipyridine (excluding dotted lines)-based complex.

(1) Diarylethene

(2) Azobenzene

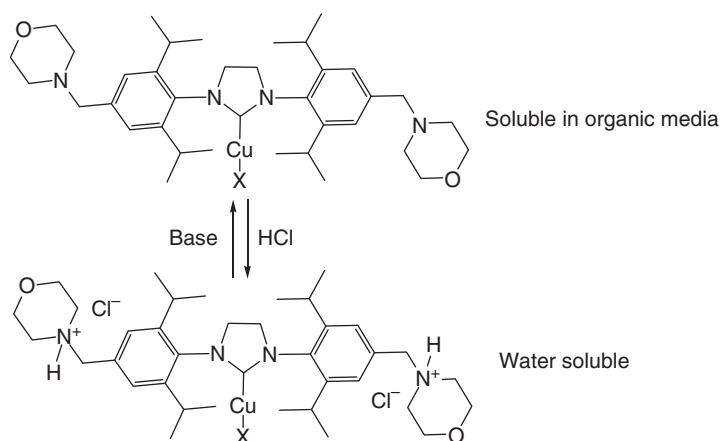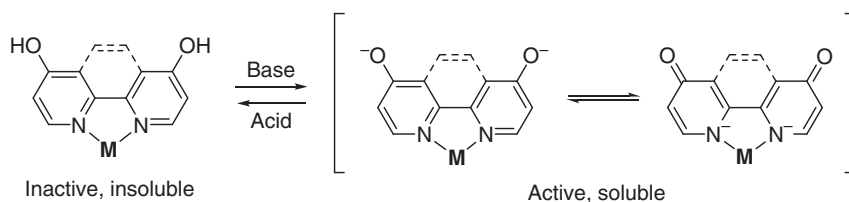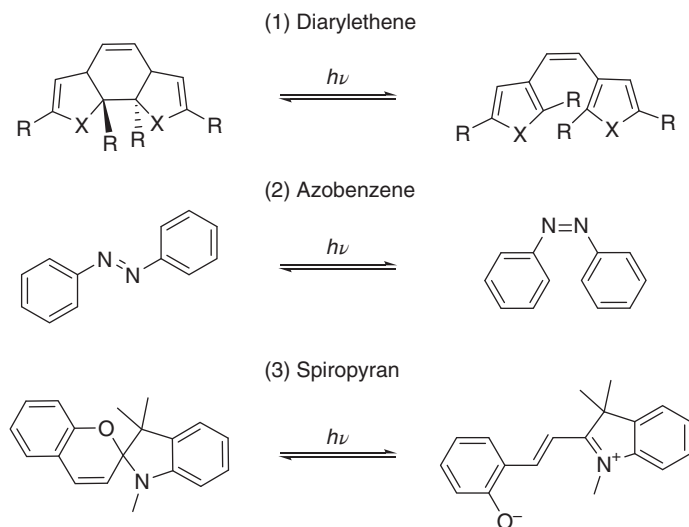(3) Spiropyran

Figure 1.5 Light-active scaffolds that undergo structural changes upon irradiation.

Another example of a proton-switchable catalyst involves a cobalt complex based on bipyridine for the hydrogenation of carbon dioxide to formate [35]. The alcohol substituents were introduced either at the 4,4′- or the 6,6′-positions. The obtained complexes show a large dependence on the concentration of base as the deprotonated complex is active and more stable under the reaction conditions. Recyclability data were not reported for these systems, but the complexes do, however, show a significantly higher activity after deprotonation of the ligand.

1.2.3 Light-Responsive Ligands

Light, being rather non-invasive, is perhaps the most interesting external trigger to switch a bistable catalyst. Upon irradiation with light, many molecules such as diarylethenes, azobenzenes, or spiropyrans can undergo structural rearrangement (Figure 1.5). Incorporation of these switchable moieties in a catalyst could result in easy control of its catalytic activity [36, 37], and use of different wavelengths typically allows two-way switching of these scaffolds.

An elegant example of this type of responsive catalyst was reported by the group of Branda for a copper-catalyzed cyclopropanation reaction (Figure 1.6) [38].

Upon reversible isomerization of the open ligand (Figure 1.6, right complex) to the cyclized complex (Figure 1.6, left complex), almost all stereoselectivity was lost. Although switching the ligand was more difficult after copper coordination, it was still feasible after addition of a small amount of a coordinating solvent to the reaction mixture.
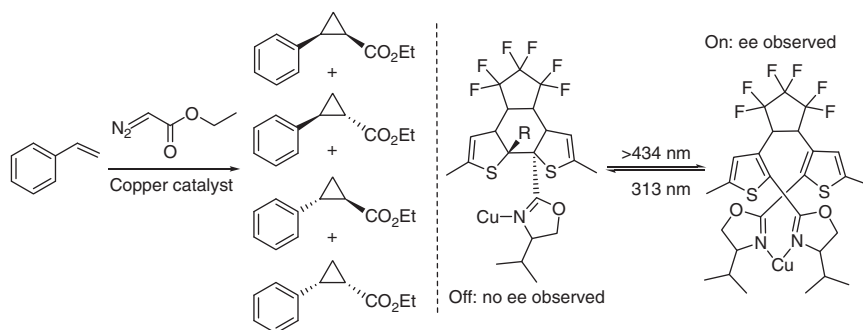
Figure 1.6 Light-induced enantioselective cyclopropanation.

1.3 Redox-Active Ligands as Electron Reservoirs

The most straightforward application of redox-active ligands is as electron reservoir, to facilitate redox processes for base metals that would otherwise be difficult or impossible. As such, redox-active ligands can participate in key redox processes of a catalytic cycle, such as oxidative addition or reductive elimination steps (Scheme 1.2). The ligand can temporarily store or release additional electrons allowing the metal complex to perform multielectron steps, avoiding formation of high-energy oxidation states of the metal if the energy levels of redox-active ligands are more accessible [39]. In this way, even purely ligand-centered redox processes become possible leaving the metal in the same oxidation state throughout an entire catalytic cycle. As such, by making use of redox-active ligands, the reactivity of first-row transition metals can be tuned toward catalytic properties more typically observed for noble metals [40].
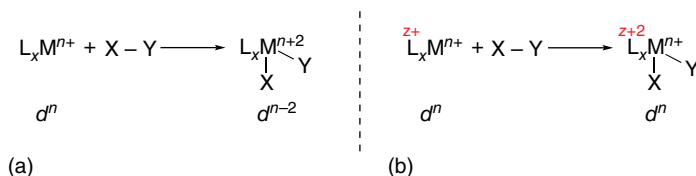
Scheme 1.2 (a) Classic oxidative addition and (b) oxidative addition in metal complexes with redox-active ligands.

1.3.1 Bis(imino)pyridine (BIP)

The bis(imino)pyridine (BIP) ligand (Scheme 1.3) has perhaps been most frequently used as an electron reservoir. This class of ligands consists of pyridine derivatives with imine functionalities at the 2,6-positions and stabilizes metals in low (formal)-oxidation states. The three nitrogen centers of the ligand bind to a metal in a tridentate manner, forming pincer complexes (Scheme 1.3, left). The obtained non-innocent ligand can have more than one oxidation state, as the ligand π^*-orbitals can accept several electrons. The ligand can easily be synthesized