Metal-Terpyridine Complexes in Catalytic Application – A Spotlight on the Last Decade

Andreas Winter[a, b] and Ulrich S. Schubert*[a, b]

Dedicated to Professor Dr. Markus Antonietti on the occasion of his 60th birthday
2,2’-6,2’-Terpyridine (tpy) and its derivatives represent highly versatile ligands for the complexation of transition metal ions. Today, such complexes are employed in a highly diverse fashion – including inter alia materials science, opto-electronics, pharmacy or catalysis. Concerning the latter one, a vast development has led to new or improved applications in both “conventional” organic chemistry (i.e., catalysis of functional-group interconversions, C=H-activation or cross-coupling reactions) as well as energy-related applications (e.g., CO₂ reduction, artificial photosynthesis, dye degradation). In this respect, not only homogeneous catalysts (i.e., molecular complexes) but also heterogeneous and recyclable ones have moved to the focus of interest. These heterogeneous structures include 1D metallopolymer, metal-organic frameworks (MOFs), organic-inorganic hybrids and bio-inspired catalysts. We gave a first overview on this topic already in 2011; in here, the methods and implementations established within the last decade as well as relevant contributions from earlier works are presented and discussed.

1. Introduction

Organometallic complexes are of utmost importance in catalysis – in industrial processes as well as small-scale syntheses. The molecular structures of these complexes are highly diverse with respect to the type of the employed metal centers and (in) organic ligands. In most cases, however, the metal center is surrounded by chelating ligands which offer a certain degree of stability to the sometimes highly reactive complexes and, if a proper ligand design is used, even allow the reactions to proceed in a regio- and/or stereo-controlled fashion.[1–3] Traditionally, phosphorus-, nitrogen- and (though to a minor content) sulfur-containing chelates have been utilized for this purpose[4–6]; more recently, also N-heterocyclic carbenes (NHCs) have attracted considerable interest against the same background.[7–9] From the family of nitrogen-based ligands, the polypyridyl-type ones [e.g., 2,2’-bipyridine (bpy), 9,10-phenanthroline (phen), and 2,2’-6,2’-terpyridine (tpy)], have been widely used in the field of homogeneous catalysis and even chiral derivatives have become available, thus even enabling asymmetric variants of the catalyzed reactions.[10] The tridentate tpy motif represents a prominent example which has been combined with almost all transition and rare-earth metal ions[11] and the resultant complexes have been utilized in a range of cutting-edge applications: Materials science,[12] opto-electronics,[13–16] photovoltaics,[17] medicine,[18] etc..

Besides these, tpy complexes have been discussed in the context of organometallic catalysis and, perhaps, even more important biomimetic oxidation and reduction reactions.[19–30] A short retrospect on the early contributions in these areas is given in the following. This literature was reviewed by us in this Journal already in 2011,[31] in brief, research in the field of electrocatalytic oxidation of organic substrates was pioneered by Meyer and co-workers already in the 1980s; these authors utilized inter alia Ru(II) complexes of tpy and/or bpy.[32] Che et al. demonstrated that also the chemical oxidation of olefins by tert-butylperoxide, as the oxidant, can be achieved with such complexes.[33] Further early examples for the catalytic activity of Ru(II)-tpy mono-complexes include the photinduced cleavage of nucleic acids (i.e., photodynamic therapy, PDT),[34–36] the electrocatalytic CO₂ reduction[37] and the chemical oxidation of water in the presence of Ce(IV).[38] Noteworthy, the electrocatalytic CO₂ reduction was also realized with other transition metal complexes, i.e., Co(II), Rh(III) and Re(I).[39–41] Moreover, various tpy complexes of first-row transition metal ions [e.g., Mn(II), Fe(II) and Ni(II)] were exploited in the context of oxidation reactions. In particular, Mn(II)-tpy mono-complexes were used as water-oxidation catalysts (WOCs), thus mimicking the natural photosystem-II (PS-II) of green plants.[17,45] This approach could even be translated into a household application, in which such systems functioned as bleaching agents in dishwashing detergents.[31–32] The photocatalytic reduction of water, the so-called hydrogen-evolution reaction (HER), is known to be catalyzed by the luminescent square-planar Pt(II)-tpy mono-complexes.[45] Besides the former examples which can be summarized under main topic of “renewable energy conversion”, also some applications of terpyridine complexes, as catalysts, in organic or polymerization reactions have been mentioned. For example, Fe(II)-tpy mono-complexes, in which the tpy moieties were functionalized with imino residues in 6- and/or 6’-position, enabled the ethylene oligomerization.[46] A structurally remarkable Ni(II)-tpy mono-complex was identified as the catalytically active species in cross-coupling of alkyl electrophiles;[47] whereas, the analogous Ni(II) complex catalyzed the (co)polymerization of styrene- and norbornene-type monomers (however, control over the polymerization was not offered by this system).[48] Furthermore, a range of other tpy complexes was studied with respect to their ability to catalyze (organic) reactions: Azidination of olefins,[49] methyl isocyanoacetates as nucleophiles in aldol-type reactions,[50] alkylation of carbonyl derivatives,[51] electrocatalytic NO reduction,[52–54] nitrene transfer reactions,[55] (asymmetric) aminolysis of epoxides,[56] ATP dephosphorylation,[57] electroreduction of O₂ etc.

In our previous review we rose the question how research on terpyridines and, in particular, of their transition metal complexes would evolve.[46] Now, about a decade later, we come up with a first resumé. In the following Sections, the most
recent contributions to the various fields of catalysis will be detailed – ranging from organic-group transformations (e.g., selective alcohol oxidation), CH-activation and cross-coupling reactions to photo- and electrochemical energy interconversion (e.g., water splitting, CO₂ reduction). In particular, the conversion of (solar) light into chemical energy represents one of the key topics in today’s chemistry and this field has experienced a tremendous development.[46–48]

2. Terpyridine complexes, as catalysts for organic reactions

The available synthetic toolbox enables the preparation of tailor-made terpyridine derivatives with maximum flexibility regarding the nature and position of the substituents. These protocols have been outlined elsewhere and are not subject of this article.[11] However, the reader is reminded that the broad range of synthesized structures includes examples which were derived from the chiral terpene pool (Figure 1). These chiral terpyridines are of utmost importance concerning any application of terpyridine complexes in asymmetric catalysis. Terpyridine complexes are, in general, obtained by mixing an appropriate metal salt with a terpyridine derivative in a 1:1 or 1:2 ratio, thus forming the respective mono- or bis-complexes.[11] In most cases, such complexes are formed readily and an in-situ generation under the reactions conditions is basically possible. On the other hand, more sophisticated complexes are formed separately and added to the reaction mixtures, as catalysts. This applies, in particular, to the complexes that are only formed under relatively harsh conditions [e.g., complexes of Ru(II) ions].

Figure 1. Schematic representation of chiral terpyridines (1) and terpyridine tri-N-oxides (2).

2.1. Copper-catalyzed reactions

Copper plays an important role in the field of organometallic chemistry and catalysis that started to emerge in the late 1980s.[49] The most prominent examples in which copper is applied in organic chemistry are the conjugate cuprate addition, the various cross-coupling reactions and the Cu(I)-catalyzed azide-to-alkyne cycloaddition (CuCAAC) reaction. Copper’s rich chemistry involves various interconvertible oxidation states (from +I to +III) and, thus, the support of single- and two-electron mechanisms is basically enabled (i.e., radical
or polar pathways). It is well accepted the various Cu intermediates in such catalytic cycles can be stabilized by chelating ligands (e.g., polypropyridyl or N,N,N'-bidentate ligands). As indicated above, terpyridine-type ligands have *inter alia* been explored in this context.

### 2.1.1. Cyclopropanation of olefins

The cyclopropanation of olefins, *i.e.*, the [2 + 1]-cycloaddition reaction between an alkene and a carbenoid species, represents an important reaction for which a broad range of catalytic systems has been applied.\(^{[50-51]}\) For example, various types of copper, ruthenium and rhodium complexes have been tested in this context. When combined with chiral ligands, such as the \(C_2\)-symmetric \(N/N'-bidentate\) or \(N,N',N''\)-tridentate polypropyridyl derivatives, asymmetric variants of this reaction become available. With respect to terpyridines, the Chelucci and Kwong groups contributed to this field.\(^{[52]}\) These groups focused on Cu(I) complexes of chiral terpyridine ligands 1a-h in which the active Cu(I) species was prepared from a Cu(II) salt either by *in-situ* reduction with hydrazine or, more conveniently, by using an excess of ethyl diazoacetate (EDA). In the same context, the planar-chiral \(C_2\)-symmetric paracyclophane-equipped ligands 1j were utilized by Kanomata *et al.* (Scheme 1a); these ligands offered a significant increase in the enantioselectivity of the cyclopropanation of olefins when compared to the asymmetric ligand 1i.\(^{[53]}\) Overall, high yields as well as moderate diastereomeric and enantioselectivities were observed in the cyclopropanation of a range of di- and tri-substituted olefins (Scheme 1b). The enantioselectivity of the reaction was rationalized by steric repulsion of the ester moiety and one of the cyclophane bridges in the transition state (Scheme 1c). Moreover, a remote steric effect was identified: Bulky substituents on the outer pyridine rings (R in 1j) reduced the flexibility of the ligand and, thereby, contributed to the orientation of the groups in the transition state. This effect was most pronounced in the case of diphenylsiloxy groups.

Noteworthy, the basically same catalytic system, *i.e.*, Cu(I) and chiral tpy ligands 1, was also tested in the aliphatic oxidation of cyclic olefins. This reaction, known as the Kharasch–Sosnovsky reaction,\(^{[54]}\) yields allylic alcohols (or their esters) in good enantioselectivities when chiral pyridine-based ligands are used.\(^{[55]}\) However, the presence of tridentate chelating ligands in the coordination sphere of Cu(I) is incompatible with the reaction mechanism and, thus, no conversion was observed by Solinas *et al.* in the aliphatic oxidation.\(^{[56]}\)

### 2.1.2. Reactions of sp-hybridized carbon centers

Cu(I) is well-known for its ability to react with terminal alkynes to give Cu(I)-acetylide species, which represent important intermediates in reactions where carbon-carbon bonds are formed, *e.g.*, the Glaser and the Sonogashira (cross-)coupling reaction. One further example to be mentioned in this context is the trifluoromethylation of terminal alkynes which generates a \(C(sp^2)\)-CF\(_3\) bond in an intermolecular difunctionalization of the triple bond.\(^{[57]}\) For example, Szabo and co-workers utilized Togni’s reagent for the electrophilic trifluoromethylation of alkynes and alkynes under Cu(I) catalysis.\(^{[58]}\) Against this background, Liang *et al.* investigated the Cu(II)-catalyzed cyanotrifluoromethylation of terminal alkynes; under these reaction conditions a radical pathway was proposed [Togni’s (3) and Umemoto’s reagent (4) served as source of the involved CF\(_3^*\) radicals]. The resulting Cu-organometallic intermediates were trapped with TMS-CN to give \(\beta\)-trifluoromethylated acrylonitriles in high yields (Scheme 2). From all the tested chelating polypropyridyl ligands, parent tpy offered the best results.\(^{[59]}\) The stereoselectivity of the reaction was typically high (E/Z ratios of >20:1) and a range of functional groups on the phenyl ring was tolerated; whereas, aliphatic alkynes did not yield \(\beta\)-trifluoromethylated acrylonitriles (instead,

---

**Scheme 1.** (a) Schematic representation of the planar-chiral tpy ligands 1i and 1j.\(^{[53]}\) (b) Schematic representation of the Cu(I)-catalyzed cyclopropanation of olefins.\(^{[53]}\) (c) Schematic representation of the proposed transition states responsible for the enantioselectivity of the reaction.\(^{[53]}\)

**Scheme 2.** Schematic representation of the Cu(II)-catalyzed cyanotrifluoromethylation of terminal alkynes.\(^{[59]}\)
hydrotrifluoromethylation of the triple bond occurred). However, the method could not be generalized towards other trapping agents – tpy even fully retarded the reaction with TMS-N₃ (in absence of tpy and at elevated temperature, the corresponding 2H-azirines were obtained in high yields).

Isocyanides represent one further class of organic compounds possessing an sp-hybridized C-center. Like the aforementioned terminal alkynes, also this functional group could be cyanotrifluoromethylated in the presence of [Cu(tpy)]⁺, formed in-situ from [Cu(CH₂CN)₃](PF₆)₂ and tpy. This catalytic system enabled the reaction of aromatic isocyanides with 3 and TMS-CN to proceed in a highly selective fashion – the corresponding difunctionalized imines were obtained in moderate to high yields (Scheme 3).

Very recently, Lalic et al. reported on a remarkable C(sp)–C(sp³) bond formation facilitated by a Cu(I)-tpy catalyst. First, the catalyst reacted with a terminal alkyne to a Cu(I)-acetylide which was shielded by the tpy ligands and, thus, prevented homocoupling or polymerization (other bi- or tridentate ligands were by far less efficient in this respect). Cu(I)-acetylides are weak nucleophiles and their direct alkylation can only be realized with strong C-nucleophiles. This limitation can be overcome, to some extent, by light promotion. Accordingly, photo-excitation of the organometallic intermediate and subsequent electron transfer to an alkyl halide opened the path for the final radical cross-coupling (RCC, Scheme 4). The reaction showed a remarkable compatibility with functional groups present in the reactants (e.g., epoxides, amides, esters, etc.) and a wide scope with respect to the substrates: Aromatic and aliphatic alkynes were coupled in good to high yields with alkyl iodides, even sterically hindered tertiary ones (e.g., 1-iodoadamantane). Related to this, Chen et al. investigated the photo-induced, Cu(I)-catalyzed RCC reaction of three-components, i.e., cycloketone oxime esters, amines and terminal alkynes (Scheme 5). The method was found to be highly robust with respect to functional group tolerance; however, in contrast to the previous example, bpy-type ligands were much more efficient than their tpy-based counterparts.

### 2.1.3. Aerobic oxidation of alcohols

The selective and mild oxidation of alcohols to their corresponding carbonyl species, i.e., aldehydes and ketones, represents an active field of research. Accordingly, a plethora of methods has already been reported for this purpose. For example, the combination of CuCl and TEMPO was introduced by Semmelhack and co-workers and utilizes molecular oxygen as the oxidant. Many examples for such aerobic oxidations involving Cu-based catalysts have been reported since then. It has been demonstrated that the efficiency of the catalytic system can be increased by adding chelating ligands. In this context, also terpyridines were brought into the play.

![Scheme 3](image3.png)

**Scheme 3.** Schematic representation of the Cu(I)-catalyzed cyanotrifluoromethylation of aromatic isocyanides. Figure reproduced with kind permission; © 2018 American Chemical Society.

![Scheme 4](image4.png)

**Scheme 4.** Schematic representation of the photo-induced Cu(I)-catalyzed alkylation of terminal alkynes. Figure reproduced with kind permission; © 2018 Wiley-VCH.

![Scheme 5](image5.png)

**Scheme 5.** Schematic representation of a photo-induced Cu(I)-catalyzed three-component RCC reaction.
their initial study, Pombeiro et al. tested the catalytic activity of various Cu(II) complexes of 4'-phenyl-2,2':6',2''-terpyridine in the aerobic oxidation of benzyl alcohol in the presence of TEMPO.\[70\] From these, the complex with nitrate counterions gave best results with respect to yield (94%) and turn-over-number (TON of 320). In related study, the Cu(II) complexes of parent tpy as well as of its 4'-chloro and 4'-cyano derivatives were used as catalysts in the TEMPO-promoted aerobic oxidation of benzyl alcohols.\[71\] These complexes revealed a high efficiency in water at 70 °C when 4-(N,N-dimethylamino)pyridine (DMAP) was added, as base. Moreover, mixed-valence Cu(II)-Cu(II) complexes were formed by the reaction of CuCl, with tpy (or 4-Cl-tpy) and TEMPO. These dinuclear species exhibited an even higher catalytic activity in the aerobic oxidation of benzyl alcohols (Scheme 6, Table 1).

The same authors also utilized the di- and trinuclear Cu(II) complexes of 2,6-bis(pyrazin-2-yl)-4-phenylpyridine (bppp) for the aerobic oxidation of benzyl alcohol. The dinuclear complex was most active in acetonitrile; whereas, the trinuclear species of the composition Cu3(bppp)Cl6 performed to its best in aqueous medium.\[72\]

Li et al. synthesized a variety of terpyridine derivatives with 4,2'-6',4'-' or 3,2'-6',3'-' substitution patterns.\[73\] These ligands yielded 1D coordination polymers when combined with Cu(II) ions. Representatively, the solid-state structure of the assembly derived from NMe2-equipped ligand is depicted in Scheme 7. All coordination polymers were used as heterogeneous catalysts in the aerobic, TEMPO-mediated oxidation of benzyl alcohols. In particular, the coordination polymer of ligand 5b showed a remarkably high activity – the alcohols were oxidized almost quantitatively in water in the presence of an additional base.

### 2.1.4. Miscellaneous oxidation reactions

Beyond the aforementioned examples where Cu(II)-tpy catalysts were used in the (aerobic) oxidation of alcohols, a variety of other oxidation reactions involving such catalysts has also been reported.

Photocatalysis has attracted considerable interest in recent years, thereby targeting not only the prominent energy-related applications (i.e., water splitting and synthesis of solar fuels) but also organic synthesis.\[74\] This basically applies also to the photocatalytic oxidation of organic substrates under aerobic conditions, i.e., utilizing O2 as the oxidant. Schneider et al. employed the Cu(II)-containing fungal enzyme laccase as oxidizing agent. This particular enzyme, which is stable for days under ambient conditions, is known to oxidize a broad range of substrates (e.g., phenols, aromatic amines, metal ions) in slightly acidic media.\[75\] In the presence of Ru(bpy)32+, as photosensitizer (PS), the photocatalytic epoxidation of olefins was realized.\[76\] Inspired by this work, Chao and Zhao synthesized a dyad comprising a Ru(II)-based PS unit covalently coupled to a Cu(II)-tpy complex.\[77\] This PS-catalyst dyad was tested in the aerobic oxidation of sulfides to sulfoxides; thereby O2 served as terminal oxidant and source for O-atoms (thus, requiring no sacrificial regents, Figure 2). Aromatic and aliphatic sulfides were oxidized in high yields and remarkably high TONs of up to 32,000 were calculated for these reactions. The cooperativity between the two metal centers was verified by photophysical measurements, EPR spectroscopy and mass spectrometry.

The Cu(II) complexes of various terpyridines, equipped in 4'-position with heteroaromatic rings, were utilized in the anaerobic oxidation of alkanes and secondary alcohols using H2O2 and tert-butyl hydroperoxide (TBHP), as the respective oxidants.\[78–79\] The oxidation of alkanes yields hydroperoxides as

| Table 1. Results of the TEMPO-mediated copper-catalyzed aerobic oxidation of various alcohols. |
|---|---|---|
| **Entry** | **Alcohol** | **Catalyst** | **Yield** |
| 1 | Benzyl alcohol | Cu(tpy)Cl | 50 |
| 2 | Benzyl alcohol | Cu(4-Cl-tpy)Cl | 53 |
| 3 | Benzyl alcohol | Cu(tpy)Cl | >99 |
| 4 | 4-Chlorobenzyl alcohol | Cu(tpy)Cl | >99 |
| 5 | 4-Iodobenzyl alcohol | Cu(tpy)Cl | 96 |
| 6 | 4-Nitrobenzyl alcohol | Cu(tpy)Cl | >99 |
| 7 | 2-Methylbenzyl alcohol | Cu(tpy)Cl | 98 |
| 8 | 1-Phenyl ethanol | Cu(tpy)Cl | 3 |
| 9 | 1-Octanol | Cu(tpy)Cl | 0 |

[a] Reactions were performed at 70 °C in the presence of 15 mol-% of DMAP.

---

**Figure 6.** Schematic representation of the copper-catalyzed aerobic oxidation of benzyl alcohols. The solid-state structure of the dinuclear mixed-valence complex Cu2(tpy)Cl2 is also shown.\[71\] Figure reproduced with kind permission; © 2015 Wiley-VCH.

**Figure 7.** Schematic representation of the 3,2':6',3''-terpyridines 5 which yielded 1D coordination polymers when combined with Cu(II) ions.\[74\] Figure reproduced with kind permission; © 2015 Elsevier B.V.

---

*ChemCatChem* 2020, 12, 2890–2941 www.chemcatchem.org 2895 © 2020 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA
the primary products, which were – after reduction with PPh₃ – quantified by gas-chromatographic analysis. The regioselectivity of the alkane oxidation (using linear and branched substrates) was rationalized by radical pathway involving hydroxyl radicals. However, the investigated Cu(II)-tpy mono-complexes were less efficient in catalyzing these reactions compared to complexes derived from other tridentate ligands.

2.1.5. Diels-Alder reactions

Enzymes, as the catalysts in natural systems, have been applied in organic synthesis not to only accelerate the reaction rates but to simultaneously offer very high regio- and stereoselectivities. Cofactors are known to play an important role in such processes. DNA has also been reported to function as natural framework for the assembly of biomimetic metalloenzymes to be used in enantioselective catalysis. Among others, Cu(II)-polypyridyl complexes have been introduced as cofactors offering a high compatibility with DNA's superstructure. In this context, Li et al. combined human telemetric G-quadruplex (HAT-Gq) DNA with Cu(II)-tpy complexes as cofactors. From the various complexes tested, 6 exhibited the highest DNA-targeting behavior. The formation of the (HAT-Gq)-6 complex (Scheme 8) was confirmed by circular-dichroism (CD) spectroscopy, UV/vis melting and isothermal titration (ITC) investigations. The metalloenzyme was employed as enantioselective catalyst in Diels-Alder (DA) reactions in which enantimetric excess (ee) values of >99% were found (Scheme 8); by the same time, the reaction rates were increased by a factor of about 70 compared to 6 alone. The binding of the cofactor to the DNA strand as well as the interaction of the substrate, i.e., the dienophile, with the metalloenzyme was studied by site-specific fluorescence quenching titration experiments (for this purpose, the HT-Gq strand was functionalized with a cyanine-type dye). These studies allowed the authors to conclude, that the asymmetric DA reactions selectively occurred at the 3'-G-quartet of the assembly.

An increase in the DA reaction rate was also reported by Himiyama et al. who immobilized a Cu(II)-tpy complex, similar to 6, in the cavity of nitrobindin (Nb). Conjugates between this particular protein and metal complexes have been reported to be efficient biomimetic catalysts for various organic reactions. The protein scaffold featured a hydrophobic cavity in close proximity to the Cu(II) complex, thus offering an appropriate environment for substrate binding and the subsequent DA reaction to proceed. A high endo-selectivity was observed, but the enantioselectivity of the process was not addressed by the authors.

2.1.6. [3 + 2]-cycloaddition reactions

The CuCAAC reaction, commonly referred to the “click” reaction, represents one of the prominent reactions in today’s synthetic chemistry and its application in the fields of polymer science, medicine or opto-electronics is extensively documented in the literature. Catalysis by Cu(I) ions enables the [3 + 2]-cycloaddition to proceed in a highly regioselective fashion yielding 1,4-disubstituted 1,2,3-triazoles. A plethora of catalytic systems and reaction conditions have been reported in this context. Sharghi et al. utilized the heterogeneous catalyst 7 which was prepared by binding a Cu(II)-tpy complex to activated multi-walled carbon nanotubes (AMWCNTs). The authors tested the efficiency and fidelity of 7 not only in the classical two-component CuCAAC, i.e., the reaction between a terminal alkyne and an organic azide, but also in a one-pot, two-step variant. In the latter, the alkynes were reacted with epoxides or benzyl/alkyl halides in the presence of NaN₃ (Scheme 9). The heterogeneous catalyst could be recovered and recycled for at least five times without considerable loss of activity. The stability was attributed to the kinetic stability of the Cu(II)-tpy mono-complex in combination with the anchoring to the CNT, thus reducing the bleaching of Cu(II) ions significantly.

The scope of 7 to function as heterogeneous catalyst in [3 + 2]-cycloadditions was also extended to the synthesis of other heterocycles, i.e., substituted 1H-tetrazoles. Benzonitriles with electron-rich or electron-poor substituents gave the corresponding 5-substituted tetrazoles in very high yields (Scheme 10). Changing the reactants to anilines and triethyl
orthoformate enabled the synthesis of 1-substituted tetrazoles in water; in this case, very high yields were also observed (Scheme 10b).

2.1.7. Miscellaneous reactions

To the end of this section some further examples have to be mentioned where Cu(I)-tpy or Cu(II)-tpy complexes were utilized as catalysts in organic syntheses.

Paul et al. assembled a metal-organic framework (MOF) from the heteroditopic ligand 8 and Cu(NO$_3$)$_2$. The structure of the assembly was analyzed by X-ray diffraction (XRD) measurements. According to these, linear supramolecular polymer chains were formed which were connected into a network via uninodal branching points (Scheme 11). The material was shown to be an efficient catalyst for the hydrocarboxylation of cyclic alkanes. The SO$_4^-$ radical anion is believed to be the reactive species and metal complexes have been found to accelerate its formation. The using aqueous ILS as reaction medium even allowed the recovery of the catalyst and its reuse in up to five reaction cycles without loss of activity. This strategy is of relevance from an environmental point of view, since the "greenness" of the MOF-type material is increased due to the avoidance of organic solvents and the potential catalyst recovery.

The Cu(I)-catalyzed synthesis of chalcogenoacetylenes from terminal alkynes and diorganyl dichalcogenides was reported by Movassagh et al. The reaction was found to be of wide scope regarding functional groups on either of the reactants; various disulfides, diselenides and ditellurides could be used in this very fast and mild synthesis under ambient conditions. Both, K$_3$PO$_4$ as base and a tpy ligand were identified as crucial to allow the reaction to result in high yields within a few minutes.

Finally, Zhou et al. assembled organic-inorganic hybrids in which Cu(II)-tpy moieties were coordinated polyoxometalate (POM) clusters – namely a Keggin, a bi-capped Keggin and a Wells-Dawson motive. These materials were fabricated into bulk-modified carbon-paste electrodes and analyzed regarding their electrocatalytic activity. In particular, the {PW$_{12}$}$_4$-Keggin-type hybrid featured a high dual electrocatalytic performance regarding the reduction of NO$_3^-$ and the oxidation of ascorbic acid.

2.2. Nickel-catalyzed reactions

Nickel as the lighter homologue to palladium features are comparable applicability in catalyzing cross-coupling reactions. Thereby, Ni does not only represent a cheap alternative to Pd –...
some specific Ni-catalyzed reactions play a prominent role in modern organic synthesis. In this respect, the cross-coupling reaction between aryl halides and organozinc compounds has to be highlighted. The 2010 Nobel prize in chemistry was inter alia awarded to Ei-ichi Negishi for his contributions in this field.\(^{[9]}\) As for copper, its neighbor in the periodic table, also for nickel a number of oxidation states is accessible and might be employed in catalytic cycles. Most commonly and in high similarity to Pd, the Ni-based catalytic cycles rely on the 0/+ II oxidation states; in addition to this, also the + I and + III states are available and, thus, other mechanistic pathways, i.e., those involving radicals, become possible.\(^{[90]}\) In many Ni-catalyzed reactions, the oxidative addition of low-valence Ni(0) or Ni(I) to aryl-heteroatom bonds represents one of the elementary steps.\(^{[99]}\) Thereby, the electron-density at the metal is reduced and stabilization by appropriate ligands, such as phosphines or polypyridyl systems, is required. In this context, terpyridines have been identified as versatile chelating ligands.\(^{[90–92]}\) Ciszelewski et al. analyzed the redox properties of various four-coordinate Ni(I)-tpy complexes, representative for the proposed intermediates in Ni-catalyzed reactions, by cyclic voltammetry (CV), EPR spectroscopy and density functional theory (DFT) calculations.\(^{[102]}\) The authors identified a profound impact of nature of the ligand (i.e., \(\text{CH}_3\) vs. \(\text{Br}^-\)) on the redox potential and the location of the unpaired electron in the ground state – despite the almost identical complex geometry, Ni(tpy)CH\(_3\) represented a ligand centered radical; whereas, the electron was located on the metal center in Ni(tpy)Br. These results are of importance to understand the role of the Ni centers in the various types of reactions catalyzed by Ni-complexes.

### 2.2.1. Reaction involving activated C–N bonds

According to the general concept of carbonyl activity, the transformation of an amide into an ester represents a thermodynamic up-hill process and is, therefore, fundamentally disabled. The Garg group demonstrated how this limitation can be overcome by making use of Ni(0)-catalysis.\(^{[103–105]}\) Ni(0) centers can be stabilized by coordinating a polypyridyl ligand. The thusly increased electron density enables the insertion of the Ni(0) center into the intrinsically robust C–N bond. From all tested polypyridyl ligands, only tpy offered a high efficiency in this respect (mono- or bidentate ligands were, by far, less suited). A broad range of aliphatic amides was reacted with primary or secondary alcohols (Scheme 12); however, Boc-activation of the amides was found to be essential (Boc: tert-butoxycarbonyl). Substrates possessing epimerizable stereo-centers or featuring considerable steric hindrance were all esterified in high yields of \(> 70\%\). On the other hand, aromatic amides or phenols did not show this reactivity, at least not under the given reaction conditions. The authors applied DFT calculations to elucidate the reaction mechanism: The results were in agreement with a catalytic cycle in which the oxidative addition represented the rate-determining step, followed by ligand exchange and reductive elimination.\(^{[104]}\) The oxidative addition was favored by \(14.2 \text{ kJ mol}^{-1}\) only for aliphatic N-Boc-activated amides; thus, rationalizing the experimental finding that aromatic or non-activated amides did not react.

Various attempts have been made to utilize the oxidative addition of Ni(0) to C–N bonds in the cross-coupling with other substrates. Garg and co-workers tested the applicability of their catalytic system for the cross-coupling of \(N\)-Boc-activated amides with boron derivatives in a Suzuki-Miyaura-type reaction. However, using tpy as stabilizing ligand was not successful (\(N\)-heterocyclic carbenes (NHCs) were found to be the ligands of choice in this case).

The oxidative addition of Ni(0) to C–N bonds was also utilized by Han and co-workers reported on the reductive cross-coupling of the activated species with aryl iodides which afforded phenones in good to high yields (up to \(96\%\), Scheme 13).\(^{[105]}\) In contrast to Garg’s protocol (see the previous example), the catalytically active species was generated \(\text{in situ}\) from NiI, Zn dust and tpy. On the basis of the experimental finding and the results published elsewhere, the authors proposed a catalytic cycle which is depicted in Scheme 13.

![Scheme 13. Schematic representation of the Ni(0)-catalyzed cross-coupling between activated amides and aryl iodides. The proposed reaction mechanism is also depicted.\(^{[105]}\) Figure reproduced with kind permission; © 2017 American Chemical Society.](image-url)
Some features of the cross-coupling reaction have to be highlighted: Firstly, the reaction represents the coupling between two electrophilic centers which is typically difficult to be accomplished (thus, highly reactive and/or sensitive nucleophiles are avoided). Secondly, transmetallation between the involved organozinc and organonickel species was excluded on the basis of control experiments. Finally, the Ni(0)-catalyst featured a high selectivity towards the activated C–N bond; whereas no insertion into the aryl C–I bond was observed (as in the case of a Pd(0)-catalyst).

2.2.2. Cross-coupling reactions

In 2004, Vicic and co-workers published the first report on a Ni-catalyzed Nigishi cross-coupling reaction presumably involving (tpy)Ni–X intermediates.[33] This assumption was later verified by detailed experimental[106–107] and computational[108] studies on the reaction mechanism. The scope of the reaction was later extended from simple alkyl halides to propargylic ones (primary and secondary derivatives).[109] The same intermediates are believed to be involved in the stereoselective formation of C-alkyl and C-aryl glucosides[110–111] as well as in the reductive coupling of glycosyl bromides with electron-poor alkenes (Scheme 14).[112] The C-aryl glucoside synthesis represented the key step in the formation of various pharmaceutically relevant salmochelin derivatives.[113]

Direct evidence for the essential role of four-coordinate Ni (I)-tpy species in such reactions was given by Budnikova and co-workers at the example of the Ni(I)-catalyzed addition of perfluoroalkyl radicals to alkenes (Scheme 15).[114–116] Thereby, the catalytically active species was generated in situ by electrochemical one-electron reduction of [(tpy)NiBr2]. The details of the reaction mechanism have been studied intensively and are summarized elsewhere.[101] In brief, the re-oxidation by a perfluoroalkyl halide gave perfluoroalkyl radicals which, in turn, added to α-methyl styrene. The resultant tertiary radicals could either be trapped by treatment with tributyltin hydride or left to dimerize.

Budnikova et al. applied their electrocatalytic cross-coupling approach also to perfluoroalkylation of aromatic compounds. The initial one-step protocol allowed to couple bromo- or iodobenzenes with perfluoroalkyl iodides; however, a sacrificial anode material was required (Scheme 16a).[117] In subsequent studies, a more sophisticated reaction system was established in which a copper anode was used.[118] The Cu(II) ions deliberated from the anode were identified to contribute to the overall reaction mechanism. Various polypyridyl ligands and metal ions were screened to identify the optimum complex for the electrocatalytic cross-coupling. From these, [Ni(tpy)Br2] was found to offer the highest yields. This finding was inter alia attributed to the low reduction potential of E = −1.30 V (e.g., compared to −1.12 V for [Ni(bpy)Br2]). The proposed mechanism for the one-step electrocatalytic coupling is depicted in Scheme 16b. The wide scope of the method is revealed by the fact that arenes and heteroarenes could efficiently be used as coupling partners (only highly electron-rich arenes and thiophenes failed to react).

The Ni(0)-catalyzed reductive homo-coupling of alkyl (pseudo)halides and allylic acetates, i.e., the coupling between two sp3-hybridized carbon centers, under mild conditions was reported by Weix and co-workers (Scheme 17).[119] The catalytically active species was formed in situ by reduction of the Ni(II) center with Mn powder; however, high yields were only obtained in the case of tpy as chelating ligand (here, the 4,4',4"-tritiert-butyl derivative was used). The less reactive derivatives...
(i.e., $X \neq Br$ or I) required further activation with NaI in a Finkelstein-type fashion.

Biscoe et al. adopted this approach and established a Ni(0)-catalyzed Negishi cross-coupling reaction between alkylzinc reagents and aryl iodides.\[120\] The coupling products were obtained in moderate to good yields and, even more important, regiospecifically (Scheme 18). In Pd(0)-catalyzed Negishi cross-coupling reactions, a “chain-walking” isomerization, due to β-hydride elimination, represents a crucial limitation. This side-reaction was fully suppressed by using Ni(II)/tpy as catalytic system (for the system Ni(II)/bpy a much lower selectivity of 70.1 was found).

Giri and co-workers reported a highly regioselective dicarbon-functionalization of non-activated alkenes via a tandem cyclization/cross-coupling method.\[121\] The method exhibited both a remarkable functional group tolerance (i.e., ketones, esters, nitriles and even halides were compatible with this reaction) and a relatively high diastereoselectivity (de ≤ 81\%).

The Negishi-type cross-coupling between geminal difluorobromides and non-activated alkylzinc derivatives was reported by Zhang and co-workers (Scheme 20).\[122\] As expected, the Ni-catalyst preferably inserted into C–Br bond, leaving the C–F bonds unaffected, and yielded the coupling products in good to high yields (up to 90\%). Thereby, a good functional group tolerance was observed: Ether, ester, acetal or heterocyclic moieties were compatible with the reaction protocol. According to in-depth mechanistic studies, a catalytic cycle involving the $\pi+1$ and $\pi+3$ oxidation states was in function, rather than a polar one involving Ni(0) and Ni(II) species.

Shrestha and Weix combined Gagné’s Ni(0)-catalyzed reduction of alkyne to alkyl halide and alkylzinc derivatives (Scheme 14) with the in-situ formation of silyl-enol ethers.\[124\] For this purpose, alkyl halides (i.e., secondary, tertiary or sterically hindered primary ones) and electrophilic olefins were reacted with a Ni(0)/tpy catalyst in the presence of a trialkylchlorosilane (Scheme 21). As in the previous example, the catalytically active species was formed in situ from a Ni(II) precursor, tri-^t^Bu-tpy and Mn powder. The reaction, which could be mechanistically related to Giri’s tandem reaction, the catalytic system was inactive in this case.\[122\]

The Negishi-type cross-coupling between geminal difluoropropargyl bromides and non-activated alkylzinc derivatives was reported by Zhang and co-workers (Scheme 20).\[122\] As expected, the Ni-catalyst preferably inserted into C–Br bond, leaving the C–F bonds unaffected, and yielded the coupling products in good to high yields (up to 90\%). Thereby, a good functional group tolerance was observed: Ether, ester, acetal or heterocyclic moieties were compatible with the reaction protocol. According to in-depth mechanistic studies, a catalytic cycle involving the $\pi+1$ and $\pi+3$ oxidation states was in function, rather than a polar one involving Ni(0) and Ni(II) species.

Shrestha and Weix combined Gagné’s Ni(0)-catalyzed reductive coupling between alkyl halides and α,β-unsaturated carbonyls (Scheme 14) with the in-situ formation of silyl-enol ethers.\[124\] For this purpose, alkyl halides (i.e., secondary, tertiary or sterically hindered primary ones) and electrophilic olefins were reacted with a Ni(0)/tpy catalyst in the presence of a trialkylchlorosilane (Scheme 21). As in the previous example, the catalytically active species was formed in situ from a Ni(II) precursor, tri-^t^Bu-tpy and Mn powder. The reaction, which could
be performed even on the gram-scale, yielded the products in good to high yields (45 to 82%). Mechanistic studies allowed the authors to exclude that organomanganese species were involved in the catalytic cycle. Structurally simple primary alkyl halides could not be used under these reaction conditions due to their fast dimerization. This limitation could be overcome by using a bulkier tpy ligand (i.e., 6,6’-dibromo-tpy). Due to a shielding effect, the dimerization could be suppressed and the reductive coupling was enabled – the silyl-enol ethers were, after trapping of the intermediate enolate with R₃SiCl, isolated in up to 82% yield (23 examples for this reaction were given).[124]

In 2004, acid fluorides were introduced as electrophiles in metal-catalyzed cross-coupling reactions.[126] Since then, this substrate class has successfully been utilized in a range of such reactions. In this context, Pan et al. showed the first example for a Ni(0)-catalyzed electrophile-electrophile cross-coupling reaction using acid fluorides and vinyl triflates as reactants (Scheme 22a).[127] As in the previous case, the catalytically active species was generated in situ from a Ni(II) precursor and tri-Bu-tpy was identified as the most versatile ligand (tpy and 4’-Bu-tpy as well as bidentate polypyridyl ligands gave lower yields).

The applicability of this method in organic synthesis was shown by the late-stage modification of structurally complex molecules, such as pharmaceuticals or natural products (some selected examples are highlighted in Scheme 22b).

The metal-mediated activation of C–H bonds in (hetero)aromatic compounds represents a versatile strategy for their direct, one-step alkylation or arylation. A broad range of catalytic systems has already been applied in this context.[128] However, when using alkyl halides as coupling partners one has to be aware that alkylmetal species prone to β-hydrogen elimination and, thus, this side-reaction needs to be suppressed. Hirano and Miura demonstrated that this can be realized by using a strong, non-nucleophilic base, such as LiOBU₄.[129] These authors investigated the metal-catalyzed alkylation of 1,3-azoles with non-activated alkyl bromides. Thereby, substantial differences in the reactivity of the substrates were observed: The alkylation of 1,3-oxazoles was catalyzed by a Pd(0) species; whereas, the functionalization of 1,3-thiazoles occurred only in the presence of a Ni(III)-tpy complex.

The chemical fixation of carbon dioxide, as a low-cost and highly abundant carbon source, currently represents a highly active field of research: CO₂ reduction, chemical “storage” as carbonates/carbamates and reductive carboxylation. All these applications require efficient catalysts which are able to sidestep the intrinsic kinetic and thermodynamic stability of CO₂. The achievements made in this field have been summarized by Maeda et al. elsewhere.[130] A remarkable example for a catalytic reductive carboxylation[131] in which the regioselectivity is controlled by the structure of the ligand was reported by Martin and co-workers. Allyl acetates are known to form π-allyl complexes with transition metal ions which, in turn, can react with nucleophiles at either of the reactive positions. Also, the utilization of electrophiles in the same context is known – the Ni(0)-catalyzed reductive carboxylation represents one example in this respect.[132] Both terminal and internal alkyl acetates were selectively carboxylated in the terminal position when using 2,9-dimethyl-9,10-phenanthroline (dmphen) as the ligand (up to 99:1 selectivity, Scheme 23). On the contrary, 6-substituted tpy ligands enabled a switch of the selectivity and the sterically more hindered position was carboxylated. The highest selectivity and yields were found for the 6-(pyridine-2-yl)-tpy ligand (qtpy, Scheme 23). The authors concluded that different mechanistic pathways were responsible for the observed ligand-controlled selectivity: On the basis of control experiments, η¹-allyl intermediates were suggested to be involved in the latter case and that the additional pyridyl arm acted as a hemilabile ligand, which moderated the catalytic activity and protected the intermediates from decomposition. The scope of the method was extended later also towards allylic alcohols – in these protocols for the site-selective reductive carboxylation the CO₂ fulfilled two different roles: (i) Facilitating the C–OH cleavage by in-situ formation of carbonic acid moieties and (ii) carbon source.[133] The observed selectivity was as high as in the reductive carboxylation of allylic alcohols.

Vannucci and co-workers investigated the photoredox-assisted reductive C(sp²)-C(sp³) cross-coupling reaction in which a cationic Ir(III) complex and a Ni(II)-tpy complex were utilized.
as PS and catalyst, respectively.[134] The photo-induced reaction was operated at low PS and catalyst loading (each 1 mol-%) without any salt/base additives and required only triethanolamine (TEOA) as sacrificial donor. In the proposed reaction mechanism, the Ni(II) precursor is reduced by the photochemically activated PS to the catalytically active Ni(0) species (Scheme 24). It was shown that the catalytic system could be applied to both the C(sp$^3$)-C(sp$^3$) homocoupling of alkyl halides as well as the C(sp$^3$)-C(sp$^3$) cross-coupling reaction; whereas, the C(sp$^3$)-C(sp$^3$) homocoupling of aryl halides was not supported (yield of > 2 %). In-depth mechanistic studies suggested an initial two-electron oxidative addition of the aryl halide to the Ni(0) center, followed by a one-electron radical reaction. Finally, the proposed Ni(III) species reductively eliminates the coupling product and the Ni(0) catalyst is regenerated by reaction with the reduced PS (Scheme 24). The photo-catalytic cross-coupling methodology featured a high functional group tolerance and could efficiently be performed on the gram-scale. The same catalytic system could also be employed in the C(sp$^3$)-N cross-coupling reaction.[135] The photocatalytic reaction between primary or secondary aromatic amines and aryl iodides afforded the corresponding secondary or tertiary aromatic amines in high yields of up to 91 %. Noteworthy, the Ir(III) photosensitizer could be replaced by a Ru(II) one without loss of efficiency.

2.3. Cobalt-catalyzed reactions

The first cobalt-catalyzed reaction, i.e., the homocoupling of Grignard reagents, was already reported by Kharasch and Fields in the 1940s.[136] Since then, a wide range of cobalt-catalyzed reactions, in particular with respect to the formation of C–C bonds, has been reported. Cahiez and Moyeux pointed out that the main advantages of using Co-based catalysts, instead of Ni- or Pd-containing ones, in this context is their ability to form C(sp$^3$)-C(sp$^3$) bonds and their compatibility with alkyl halides (β-hydrogen elimination from alkylcobalt species does not readily occur).[137] Besides the various types of homo- and cross-coupling reactions, also other prominent examples have to be named: Pauson-Khand reaction,[138] hydroformylation,[139] cyclopropanation of alkenes,[140] cycloadditions[140] and radical polymerizations.[141] In addition to these, Co complexes are widely used in the context of the hydrogen-evolution reaction, i.e., the photo- or electrocatalytic splitting of water.[142] As in the case of the aforementioned Cu- and Ni-containing catalysts, the metal center is typically stabilized by chelating ligands, e.g., polypyridyl ligands.

2.3.1. Hydroboration reaction

Basically, organoboronates are highly versatile compounds which are relatively stable and easy to handle on the one hand, but also highly reactive in C–C and C–heteroatom bond formation reactions. The metal-catalyzed hydroboration of olefins represents the most common approach in which typically Rh- or Ir-based catalysts are employed.[143] More recently, the interest has shifted towards cheaper and more earth-abundant transition metals, such as Co or Fe.

Obligacion and Chirik reported on a highly active 2,6- bis(imino)pyridyl Co complex which enabled the hydroboration of alkenes (i.e., terminal, geminal, disubstituted internal, tri- and tetra-substituted ones) using pinacolborane (HBPin).[144] For sterically hindered olefins, such as 1-methylocyclohexene, α-pinene or 2,3-dimethyl-2-butene a high anti-Markovnikov regioselectivity was found; whereas, in the case of internal
derivatives, the boron substituent was introduced selectively at the terminal positions of an alkyl chain. Thus, the isomerization-hydroboration protocol, presumably following a radical reaction pathway, enables a straightforward functionalization of remote CH₂-groups. Later, the same group showed that the Co(I)-tpy complex 9 even offered a higher reactivity than the initial catalyst (however, with increasing steric demand of the substituents, the efficiency decreased- tetra-substituted alkenes were even not converted, Scheme 25).\(^{[145]}\) Nonetheless, 9 was particularly versatile for the hydroboration of substrates containing diene or aryl moieties; whereas, the simultaneously studied Co(I) complexes with alkyl diamine ligands were more efficient in reducing sterically hindered alkenes. In a related study, Chirik and co-workers also screened various Co(I) complexes, including 9, for the isomerization-hydroboration of terminal alkenes, i.e., targeting the incorporation of the boron group in the benzylic position.\(^{[146]}\) Though a slight preference for this type of functionalization was observed for 9 (Scheme 26), the (PPh₃)₃CoH(N₂) catalyst offered a much higher activity and, even more important, selectivity with respect to functionalization in benzylic positions.

The same group also utilized the Co(II) high-spin complex 10 as pre-catalyst in the direct C–H borylation of (hetero)aryl compounds.\(^{[147]}\) LiOMe was required as additive in order to remove the pinacolborane byproduct which was believed to deactivate the catalyst. The reaction featured a good substrate scope and the products were formed in moderate to high yields (Scheme 27; note, that the dichloro analog of 10 and 9 were both by far less efficient under the same reaction conditions). Presumably due to the increased C–H acidity in the electron-poor arenes (R = F), a significantly higher reactivity compared to electron-rich ones (R = OMe or NMe₂) was found, i.e., longer reaction times were required to reach similar yields. For mono-substituted arenes, the regioselectivity of the borylation was moderate – the electron-rich compounds were borylated in meta- and para-positions in a ratio of ca. 70:30; whereas, the electron-poor derivatives featured an ortho-to-meta ratio of ca. 80:20. In comparison to the established catalysts bearing PNP-type pincer ligands a generally lower activity of 10 was observed; however, this constraint is leveled out by the ease 10 can be prepared and handled.

Besides the aforementioned molecular, homogeneous Co-based catalysts, heterogeneous ones were also employed in the context of borylation reactions. Lin et al. applied a solvothermal protocol to assemble a metal-organic layer (MOL) comprising tris-carboxylated tpy moieties linked via [Hf₆] subunits (Figure 3).\(^{[148]}\) The material was characterized by XRD analysis and microscopy imaging. The powder XRD spectrum confirmed the ordered 2D structure; high-resolution transmission electron microscopy (TEM) revealed a clear lattice with the dark spots which were assigned to the [Hf₆] clusters (Figure 3a/b). The
MOL-tpy assembly could be loaded with either Co(II) or Fe(II) ions without changing the overall structure. These two metallated assemblies were employed as heterogeneous catalysts (for the Fe(II)-containing materials, see Section 2.4.4). The Co(II)-loaded MOL-tpy catalyzed, after activation with Na[BHET$_3$], the benzylic C–H borylation of methylelenes. X-ray absorption, X-ray photoelectron, UV/vis/NIR absorption and EPR spectroscopy, supported by DFT calculations, were applied to identify the catalytically active species. According to these studies, the high catalytic activity (compared to homogeneous Co(II)-tpy complexes) was attributed to the presence of [Co(tpy)(THF)$_2$] species in which (tpy$^{2+}$)$^{2-}$ diradical dianions were coordinated to the Co(II) centers. Moreover, this unique 2D system was also found to be superior to analogous 3D frameworks containing Co(II)-tpy sites – due to the intrinsically high diffusion barriers, the borylation of arenes did not occur (for a recent review on C–H activation catalyzed/supported by metal-organic frameworks, see ref.146).

A straightforward self-assembly process was applied by Zhang et al. to arrange Co(II)-containing coordination polymers from CoCl$_2$ and tpy derivatives, such as 4’-(pyridine-2-yl)-tpy (ptpy).150 Thomas and co-workers have shown that Co- and Fe-based catalysts can be activated by NaOEtBu.151 In line with this report, KOTBu was identified as the most efficient activator in the hydroboration of ketones, aldehydes and imines catalyzed by poly[Co(ptpy)Cl]$_n$.156 A wide range of aliphatic and aromatic aldehydes and ketones was hydroborylated in high yields (up to 98%) even at room temperature (Scheme 28). Control experiments demonstrated a significantly higher reactivity of aldehydes, thus the selective hydroborylation of an aldehyde in the presence of a ketone was enabled. The hydroborylation of aromatic imines, however, proceeded only at elevated temperatures (refluxing in THF). The Zhang group utilized the same catalytic system also for the Markovnikov-selective hydroboration of vinylarenes.152 In most cases, a high selectivity to the unusual Markovnikov product was observed (e.g., for styrene, a 98:2 selectivity for the Markovnikov addition was found). Remarkably, the reactions proceeded in a very short time (ca. 5 min) and very low catalyst loadings were required (0.025 mol-%); turnover frequencies (TOFs) of up to 47,520 h$^{-1}$ were obtained. Very recently, similar TOF values were also reported for the hydroboration of terminal and internal alkynes.153 Alkenyboronate esters were efficiently formed within 5 to 30 min using at a pre-catalyst loading of 0.025 mol-%). Moreover, alkenes and alkyne could be discriminated by the catalytic system – a high chemoselectivity for the hydroboration of alkynes was found. Mechanistic studies suggested that in-situ generated Co–H species could be involved in the catalytic cycle.

### 2.3.2. Miscellaneous reactions

In order to develop catalysts for the oxidation of alcohols, Murugavel and co-workers prepared a series of dinuclear complexes in which the M(II)-tpy units were bridged by organophosphates (M = Mn, Co, Ni).114 From these, the Mn(II)-containing system was found to catalyze the oxidation of primary and secondary alcohols with TBHP as oxidant (see Section 2.5.1); the Co(II) and Ni(II) counterparts were less efficient in terms of substrate conversion and selectivity. The self-assembly of Co(OAc)$_2$ and ptpy in the presence of an organophosphor species yielded, in the solid state, either a mono-nuclear complex (with tert-butylphosphonate) or a coordination polymer (with 2,6-diisopropylphenyl phosphate).155 The former catalyzed the oxidation of alcohols to the corresponding carbonyl derivatives with very selectivity, i.e., overoxidation of primary alcohols to carboxylic acids was hardly observed (acetoniitrite, as solvent, offered the highest conversion and selectivity). However, the TONs of the catalytic process were only low to moderate.

Cyanooic acid is a commodity chemical that is widely used in the production of adhesives, pharmaceuticals, agrochemicals, dyes, UV absorbers, etc. From the range of synthetic protocols, the electrocarboxylation of chloroacetonitrile, as an environmentally friendly method, has received considerable attention – the main reason for this the ability to use the almost unlimited available greenhouse gas CO$_2$ as reactant.156 In general, the electrocatalytic reduction of chloroacetonitrile is performed in CO$_2$-saturated aprotic solvents in the presence of a transition metal complex. Against this background, Reynes and co-workers employed the homoleptic Co(II)-tpy complex as catalyst.157 CV measurements were conducted to elucidate the electrochemical behavior of this complex (Scheme 29). In absence of CO$_2$, the initial one-electron reduction generated a Co(I)-tpy mono-complex which, in turn reacted with chloroaenitrite to afford a Co(II)-tpy-alkyl species. The one-electron reduction thereof yielded an intermediate which decomposed into an alkyl anion and regenerated a Co(II)-tpy mono-complex. In the presence of CO$_2$, insertion of CO$_2$ into the Co(III)-alkyl bond occurred. After the second reduction step, cyanooacetate was released and the catalyst was reactivated. The authors
2.4. Iron-catalyzed reactions

The application of iron salts and complexes as catalysts in organic synthesis represents a highly active field of research. Iron, as the most abundant transition metal in the earth’s crust, is cheap, in particular compared to the heavy and precious metals that are often used in catalysis.

Moreover, many iron compounds are of low toxicity and therefore, interesting for applications in, e.g., pharmaceutical or food industry. Though other transition metals, such as palladium, are still more commonly used as catalysts in organic reactions, a broad range of examples is known where iron salts/complexes have been established.\cite{159-160} Admittedly, iron—terpyridine complexes only represent a relatively small portion in this context. The reactions in which such complexes have been used include, for example, the epoxidation\cite{161-162} or aziridination of alkenes,\cite{163} transfer hydrogenation,\cite{164} ring-opening of epoxides\cite{165} and diene polymerization.\cite{166}

\subsection{2.4.1. Cyclopropanation and epoxidation of alkenes}

The cyclopropanation and epoxidation of alkenes represent [2 + 1]-cycloaddition reactions for which a variety of Fe(II)- and Fe(III)-containing catalysts have been reported. The cyclopropanation of styrene with ethyl diazoacetate was explored by Kwong and co-workers.\cite{158} Besides the aforementioned chiral Co(II)-tpy mono-complexes also their Fe(II)- and Fe(III)-containing counterparts were studied in this respect. These catalysts yielded, after activation with an Ag(I) salt, chiral ethyl 2-phenylcyclopropane-carboxylate in good yields (39 to 78%). However, the diastereoselectivities were low compared to the results reported for the analogous Co(II) complexes (Section 2.3.2).

With respect to alkene epoxidation, the homoleptic Fe(II) complex with two 4,4',4''-trichloro-tpy ligands was identified as powerful catalyst in combination with potassium peroxy-mono-phosphate (oxone), as oxidant.\cite{163} This catalytic system enabled the synthesis of epoxides from a wide range of alkenes in very good yields and with high diastereoselectivities (Scheme 30). Furthermore, a tpy ligand bearing a PEG substituent was employed in the fashion [PEG: poly(ethylene glycol), $M_n = 7,500$ g mol$^{-1}$]. The resultant complex was as efficient in catalyzing the epoxidation of alkenes, but offered the advantage of recyclability: The ligand could be recovered, reloaded with Fe(II) ions and used as catalyst in five successive epoxidation reaction without significant loss of activity. A Fe(IV)-oxo species was identified from the reaction mixture by electron-spray ionization (ESI) mass spectroscopy — this intermediate suggested to be responsible for the observed diastereoselectivity of the epoxidation reaction. The kinetics and the mechanism of the oxidation of Fe(II)-tpy bis-complexes by oxone were analyzed by Beller et al.;\cite{167} these authors confirmed the formation of such Fe(IV) species in the rate-determine step of the autocatalytic formation of Fe(III) ions and oxidized tpy ligands.

Che and co-workers prepared a hybrid material in which a Fe(III)-tpy complex was immobilized onto SBA-15 — a mesopo-
rous molecular sieves with large surface area, big pore size and high porosity (Scheme 31). The hybrid material was characterized by XRD analysis as well as FT-IR, solid diffuse-reflectance and UV/vis absorption spectroscopy. According to atom absorption spectrophotometry (AAS), an average loading with Fe(II) ions of 1.9 weight-% was reached. This heterogeneous catalyst was successfully employed in various oxidative C=C cross-coupling reactions (Section 2.4.4) and oxidation reactions involving arenes or (cyclic) amines (Section 2.4.3). With respect to the epoxidation of alkenes, the heterogeneous catalyst gave high yields which were comparable to those reported for analogous homogeneous Fe(II) catalysts under the same reaction conditions (Scheme 31). After reloading with Fe(II) ions, the recovered SBA-15-tpy could efficiently be reemployed in further reactions (not necessarily of the same kind).

2.4.2. Addition and insertion reactions involving nitrenes

Aziridines are important building blocks in organic synthesis and can be found as substructure in various bioactive molecules. The metal-catalyzed addition of a nitrogen group to alkenes represents a versatile method to prepare such three-membered heterocycles.

Che and co-workers showed that not only the epoxidation, but also the aziridination of alkenes can be catalyzed by Fe(II)-tpy bis-complexes. The same catalysts as in Scheme 30 were used in the intermolecular aziridination with N-tosyliminophenyl-λ3-iodinane as well as in the intramolecular aziridination of sulfamides (one example for each application is depicted in Scheme 32). In general, the robust method offered high yields and substrate conversions (up to 95 % and 86%, respectively). Similar to the epoxidation of alkenes, ESI mass spectrometry gave evidence for a Fe(IV) = NTs species to be involved in the aziridination reactions.

A different type of reaction, the insertion of nitrenes into the C=H bond of aldehydes, was also reported by the Che group. From the wide range of tested polypyridyl and phosphine ligands, tpy was found to be the most efficient candidate to be combined with the FeCl₃ catalyst. The carboxamides, aliphatic as well as aromatic ones, were prepared from the corresponding aldehydes in moderate to high yields again using N-tosyliminophenyl-λ3-iodinane as nitrene source. The same Fe(IV) = NTs intermediate, as presumably operable in the aziridination of alkenes (vide supra), was also identified in the present case by ESI mass spectrometry. Thus, closely related mechanistic pathways can be accepted for these two different types of Fe(II)-catalyzed nitrene-transfer reactions.

2.4.3. Oxidation and oxidative cross-coupling reactions

Che and co-workers utilized the Fe(II) complexes with penta-, hexa- and heptadentate polypyridyl ligands for the oxidation of alkenes, arenes and alkanes as well as the demethylation of tertiary amines (Polonovski reaction), the ring-opening of N-acyl cyclic amines and the Streecker-type cross-coupling reactions between tertiary amines and NaCN. With the exception of alkene oxidation, all these reactions were also catalyzed by the SBA-15-immobilized Fe(II)-tpy complex. This catalyst has already been introduced in the context of the alkene epoxidation (Section 2.4.1, Scheme 31). Basically, the Polonovski reaction, i.e., the demethylation of tertiary N-methylamine derivatives, is demanding due to the intrinsic chemical robustness of N-methyl groups (in particular, in the presence of other functionalities); this limitation can be overcome by using a metal-mediated variant in which various types of Ru- or Fe-based catalysts have already been employed. The applicability of SBA-15-immobilized Fe(II)-tpy in combination with oxone in the Solonovski reaction was demonstrated at the example of the room-temperature demethylation of N,N-dimethylamine which afforded N-methylamine in 48 % yield (similarly, piperidine was obtained from N-methylpiperidine in 78 % yield). The same catalysts/oxidant system was further utilized for the oxidative ring-opening of N-acyl cyclic amines. The corresponding ω-(N-acylamino) acids were obtained in good yields; however, a higher reaction temperature of 80 °C was required in this application (Scheme 33a). The metal-catalyzed oxidative cross-coupling between tertiary amines and nucleophiles represents a versatile approach to prepare functionalized amino derivatives. The oxidative cyanation of tertiary amines with a peroxy, as oxidant, and sodium cyanide represents one prominent example in this respect (this reaction can be considered as a metal-catalyzed alternative to the classical
Strecker-type syntheses. One representative example for the cyanation of a tertiary amine, catalyzed by SBA-15-immobilized Fe(II)-tpy, is depicted in Scheme 33b.

Moreover, the cross-dehydrogenative coupling (CDC) represents a versatile approach to establish C–C bonds between sp^3-, sp^2-, or sp-hybridized ones on the other.\(^{(174)}\) Che et al. relied on the aforementioned immobilized Fe(II)-tpy complex to oxidatively couple tertiary amines with carbon-nucleophiles (i.e., indoles, pyrroles and terminal alkynes; Scheme 34).\(^{(168)}\) Good to high yields were obtained using tert-butylperoxide as the oxidant; much lower yields were observed when Fe(II)-Cl, tpy was employed as homogeneous catalyst (Cl, tpy: 4,4',4''-tpy). The immobilized catalyst could be recycled and showed no considerable loss of activity. In five consecutive runs without apparent loss of catalytic activity.

2.4.4. Miscellaneous reactions

The 2D MOL-tpy material (Figure 3) was also loaded with Fe(II) ions to yield a heterogeneous catalyst for the intramolecular C(sp^3)-H amination.\(^{(148)}\) Treatment of Fe(II)-loaded MOL-tpy with Na(HBEt)_3 yielded the catalytically active species. In-depth spectroscopic studies, supported by DFT calculations, suggested a similar electronic scenario as for the analogous Co(II)-based material: The Fe(II) centers were coordinated to (tpy^**)^2^− diradical dianion sites. The stabilization of this reactive species by the MOL framework was concluded from the poor catalytic activity of Fe(tpy)Br, under the same reaction conditions – N-Boc-protected α-phenyl pyrrolidine was obtained in only 3% yield; whereas, the heterogeneous catalyst offered 89% yield. The scope of the Fe(II)-catalyzed intramolecular C(sp^3)-H amination is summarized in Scheme 35. The pyrrolidine derivatives were formed in moderate to high yields; the regioselectivity of the ring-closure can be attributed to steric constraints which exclude the azetidine formation. The CH_2-homologous amines, however, yielded mixtures of piperidine and pyrrolidine derivatives with the former as main product.

The hydrosilylation of alkenes represents the most common method to establish Si–C bonds. This reaction requires a transition-metal catalyst and the long-known Speier’s or Karstedt’s catalysts are usually used for this purpose. In order to replace these Pt-based catalysts by ones containing earth-abundant metals, iron-carbonyl or iron-polypyridyl complexes have been considered. In particular, 2,6-bis(imino)pyridine Fe(0) dinitrogen complexes were found to be efficient catalysts for the hydrosilylation of alkenes; however, these catalysts are difficult to be prepared and, even more important, highly susceptible to hydrolysis. In 2012, the Nakazawa and the Chirik group independently reported on Fe-tpy complexes as alternative, yet more stable hydrosilylation (pre-)catalysts.\(^{(175–176)}\) Nakazawa and co-workers utilized Fe(II) complexes with unsymmetrical tpy ligands (i.e., bulky substituents in 6- and 5′/6′-positions).\(^{(175)}\) These ligands did not form octahedral Fe(II)-tpy bis-complexes which are inert and do not support the hydrosilylation. The catalytically active species were generated from the dibromide pre-catalyst by treatment with Na(HBEt)_3. Under optimized reaction conditions, excellent regioselectivity (i.e., addition of the silane in a selective anti-Markovnikov fashion) and high TON values of up to 1533 were observed in the monohydrosilylation of terminal alkenes with phenyl silane, diphenylsilane and methylphenylsilane. It was shown further that a two-
fold hydrosilylation could be achieved simply by increasing the catalyst loading (from 0.05 to 0.3 mol-%) – the reaction of 1-octene with phenylsilane then yielded Ph(n-octyl)SiH as the exclusive product.

Chirik’s bisalkylated complex Fe(tpy)(CH$_2$SiMe$_3$)$_2$ was synthesized either by alkylation of the Fe(tpy)Cl$_2$ precursor with LiCH$_2$SiMe$_3$ or substituting the monodentate pyridine (py) ligands of (py)$_2$Fe(CH$_2$SiMe$_3$)$_2$ by the stronger tpy chelate.

This complex efficiently catalyzed the hydrosilylation of alklenes; on the contrary, similar dialkyl Fe(II) complexes bearing, e.g., 2,6-bis(imino)pyridine ligands, were inactive in this respect. For example, 1-octene was hydrosilylated with Et$_3$SiH or (Me$_2$SiO)$_3$MeSiH almost quantitatively. Moreover, the functional group tolerance of the method was demonstrated at the example of 4-vinylcyclohexene oxide, which was hydrosilylated in very high yield without disturbance of the epoxy moiety (Scheme 36). The authors identified the electronic structure of the dialkyl complexes by XRD and magnetochemical measurements, Mössbauer spectroscopy as well as DFT calculations: The high-spin Fe(III) center showed an antiferromagnetic coupling to the tpy$^-$ radical anion ligand.

2.5. Manganese-catalyzed reactions

Along with the metals of the iron group, also manganese has recently attracted considerable interest with respect to catalysis in organic synthesis.$^{[177]}$ Manganese as an earth-abundant transition metal features a remarkable number of accessible oxidation states ranging from $-II$ to $+VII$. The high oxidation-state species (i.e., MnO$_4^-$ and MnO$_5^-$) are strong oxidants; whereas Mn behaves similar top main-group metals in the low oxidation states (e.g., formation of Grignard-like R–Mn–X organometallic compounds). Manganese complexes as catalysts in various organic reactions: alkene epoxidation, radical-mediated oxidative cyclization, hydrosilylation, C–C cross-coupling and C–H activation reactions. In many cases, these complexes contain tridentate ligands, such as 2,6-bis(imino)pyridines or terpyridines.$^{[172]}$ Early examples for catalytic applications of Mn (II)-tpy complexes include the epoxidation of terminal alkenes$^{[176]}$ and the oxidation of C(sp$^3$)-H bonds.$^{[180]}$

2.5.1. Oxygenation reactions

In the latter, the selectivity of the substrate oxidation was increased by hydrogen-bonding interactions between the catalyst and the substrate. In brief, Crabtree and Brudvig utilized an oxo-bridged dinuclear Mn(II) complex with pending carboxylic-acid moieties which functioned as recognition site for the binding of COOH-substituted substrates. Due to this supramolecular pre-organization, the substrate was selectively oxidized at the position in proximity to the active catalyst site (Figure 4).$^{[180–182]}$ The scope of this method was extended later from C(sp3)-H oxidation also towards alkene epoxidation.$^{[183]}$

Inspired by these studies, Lewis and co-workers designed an artificial metalloenzyme incorporating a Mn(II)-tpy cofactor. In contrast to the previous work, where non-covalent catalyst–substrate interaction controlled the selectivity of the C–H oxidation, the substrate binding to the protein was proposed as the origin of selectivity in the present case. The general structure of such an artificial metalloenzyme including its fundamental functions is depicted in Figure 5a.$^{[184]}$ The cysteine (Cys) mutants of the proteins tHisF and apo-nitrobindin (Nb) were selected to bind the Mn(II) complex 11 by thiol-addition to the maleimide moiety (Figure 5b)$^{[185]}$ The conjugation was verified by CD and UV/vis absorption spectroscopy as well as mass spectrometry. Metalloenzyme NB-Cys-11 was utilized as catalyst for the C–H oxygenation with oxone or peracetic acid,
Figure 5. (a) Illustration of an artificial metalloenzyme including its fundamental functions.\textsuperscript{[184]} (b) Schematic representation of the Mn(II)-tpy complex 11 which was bound, as cofactor, to protein substrates.\textsuperscript{[185]}

Figure 6. Schematic representation and solid-state structure of the dinuclear Mn(III) complex 12.\textsuperscript{[186]} Figure reproduced with kind permission; © 2018 Wiley-VCH.

as oxidant. The optimized reaction protocol enabled the benzylc oxygenation, alkene epoxidation and the oxidation of ethereal $\alpha$-C–H bonds in moderate to high yields (Scheme 37). The ability of Mn(II)-tpy complexes to catalyze these reactions was initially reported by Kamijo et al.; the catalyst was assembled \textit{in situ} from MnCl$_2$ and tri-$t$Bu-tpy and used for the various oxygenation reactions with oxone, as oxidant, in aqueous acetonitrile (the universal protocol was successfully applied to broad range of substrates).\textsuperscript{[186]} In a similar fashion, the Mn(II) mono-complexes with 4$^{ary}$-substituted tpy ligands were employed as catalysts in the epoxidation of alkenes with \textit{BuOOH}.\textsuperscript{[187]}

As pointed above (Section 2.3.2), the dinuclear organo-phosphosphate-bridged Mn(II)-tpy complex 12 (Figure 6) was used as catalyst for the oxidation of alcohols with \textit{BuOOH}, as oxidant.\textsuperscript{[188]} A range of alcohols was screened to identify the scope of the optimized oxidation protocol (Table 2). In detail, higher yields were obtained for the primary alcohols; whereas, the secondary ones offered a maximum selectivity of 100%. Making use of the subtle distinction in the reactivity of 1$^o$ and 2$^o$ alcohols, glycerol could be oxidized selectively to give glyceraldehyde. Finally, aliphatic alcohols were less reactive than those containing aryl groups (in particular, benzylc derivatives). The authors also compared the efficiency of 12 in the alcohol oxidation to that of other Mn(II)-based catalysts known from literature: 12 was found to be superior in catalyzing this reaction with one exception – the Mn(II) complex with a 2,4,6-tris(pyridine-2yl)triazine (tptz) ligand\textsuperscript{[188]} was more efficient, i.e., 12 reached a relative efficiency of ca. 85% compared to this one.

The same mononuclear Mn(II)-tpy-tptz complex was also employed as catalyst for the oxidation of sulfides to sulfoxides under ambient conditions using urea hydrogen peroxide, as oxidant.\textsuperscript{[189]} In the following also Mn(II)-tpy complexes were utilized for the same purpose.\textsuperscript{[190–191]} For example, Najafpour et al. used the dinuclear Mn(II) complex 13 as catalyst in the oxygen evolution reaction (OER, see Section 3.3) as well as in the sulfide oxidation.\textsuperscript{[191]} Hydrogen peroxide was utilized, as oxidant, at ambient conditions (however, imidazole was required as additive). The authors tested a wide range of substrates, including aryalkyl, diaryl, dibenzyl, benzylphenyl and dialkyl sulfides (Scheme 38) – in all cases high substrate conversion and moderate to high yields were obtained. The selectivity of the oxidation reaction was remarkably high – sulfoxides, as the potential overoxidation products, were not observed.

### 2.5.2. Miscellaneous reactions

In contrast to the broad range of oxidation reactions, as previously detailed, Mn(II) complexes have scarcely been

| Table 2. Results of the oxidation of alcohol using 12, as catalyst, and \textit{BuOOH} as oxidant.\textsuperscript{[a]}
|---|---|---|---|
| Entry | Alcohol | Yield\textsuperscript{[b]}/Selectivity [%] | TON |
| 1 | Benzyl alcohol | 73/86 | 170 |
| 2 | 2-Phenylethanol | 11/100 | 22 |
| 3 | 1-Phenylethanol | 49/100 | 98 |
| 4 | Diphenylmethanol | 42/100 | 84 |
| 5 | (Pyridin-3-yl)methanol | 58/100 | 116 |
| 6 | 1-Pentanol | 22/100 | 44 |
| 7 | Glycerol | 44$^\text{R}/100$ | 88 |
| 8 | Cyclohexanol | 38/100 | 76 |

\textsuperscript{[a]} Reaction conditions: 12 (0.5 mol-%), substrate (10 mmol), \textit{BuOOH} (1 eq.), acetonitrile (10 mL), 80 °C, 4 h. \textsuperscript{[b]} Isolated yield of the carbonyl compound.

\textsuperscript{[c]} The yield refers to glyceraldehyde as the product.
employed in the context of catalytic reductions (e.g., hydroboration of double bonds).\textsuperscript{[177–178,192]} Zhang et al. screened a variety of Mn(II)-tpy complexes with respect to their ability to catalyze the hydroboration of alkenes and carbonyl compounds (i.e., aldehydes and ketones).\textsuperscript{[193]} From these, the dialkylated Mn(tpy)(CH\textsubscript{2}SiMe\textsubscript{3})\textsubscript{2} complex was the most efficient one. Terminal alkenes were hydroborated in good to high yields (Scheme 39). Thereby, a moderate functional-group tolerance was observed – reducible functionalities were not compatible with the reaction conditions and afforded complex product mixtures (e.g., –NO\textsubscript{2}, –CN and –C≡C–groups). The regioselectivity of the hydroboration was dependent on the chemical structure of the substrate: Vinyl-substituted arynes afforded the Markovnikov-type addition products almost exclusively; whereas, aliphatic alkenes were hydroborated preferentially in an anti-Markovnikov-type fashion. A similar functional-group tolerance was also observed in the hydroboration of aldehydes and ketones where yields > 62\% were obtained (Scheme 39). In particular, the reduction of aldehydes proceeded smoothly and even allowed the selective reduction of the C–O bond in the presence of a C=C bond (i.e., cinnamaldehyde gave cinnamyl alcohol in 79\% yield without isomerization of the trans-configured double bond). Strained carbocycles were not opened under the reaction conditions, thus intermediate radical species could be excluded.

A broad range of synthetic protocols is available for the synthesis of imines, going far beyond the classical acid-catalyzed condensation of aldehydes/ketones and primary amines. In this context, also the dehydrogenative coupling between alcohols and primary amines has emerged as a promising strategy.\textsuperscript{[194]} This speciously low-cost and eco-friendly method typically involves expensive noble-metal catalysts. In order to replace these by catalysts based on earth-abundant metals, Kaur and co-workers opted for Mn(II)-polypyridyl complexes.\textsuperscript{[195]} These authors screened a variety of polypyridyl ligands and identified parent tpy as the most promising candidate to be combined with MnCl\textsubscript{2}. The imines formation, catalyzed by in-situ generated Mn(tpy)Cl\textsubscript{2}, was performed in refluxing toluene in air. A library of aldimines with functional groups on either of the components was prepared from benzylic alcohols and aromatic amines in moderate to high yields (27 examples in total).

### 2.6. Ruthenium-catalyzed reactions

Ruthenium complexes, commonly used in opto-electronic, photovoltaic, catalytic and even medicinal applications, offer some remarkable properties. Thereby, the high costs of this less abundant heavy metal are compensated by the unique properties. For example, starting from the 4d\textsuperscript{5} s\textsuperscript{1} electron configuration of Ru(0), the entire range of oxidation states from −II (as in Ru(CO)\textsubscript{5}) up to +VIII (as in RuO\textsubscript{2}) is accessible – the widest range of oxidation states for an element within the periodic table.\textsuperscript{[196]} Each oxidation state is related to special coordination geometries. Within the last decades, the range of applications in which Ru-based reagents or catalysts can be used has developed tremendously. Staring from the long-known oxidation, hydrogenation and hydrogen-transfer reactions, particular progress has been made in the field of photo- or electrocatalytic water-splitting (see Section 3.3)\textsuperscript{[197,198]} and in catalyzing the C=C bond formation (e.g., olefin metathesis or cyclo-addition reactions).\textsuperscript{[199]}

Ru(II)-tpy complexes are of significant importance as building blocks in metallo-supramolecular assemblies\textsuperscript{[200]} and as dyes in dye-sensitized solar cells (DSSCs).\textsuperscript{[201]} Moreover, a variety of organic reactions has been catalyzed by such complexes.\textsuperscript{[202]}

#### 2.6.1. Transfer-hydrogenation reactions

The first example for a Ru(II)-tpy complex to be used in transfer-hydrogenation reaction was reported by Kelso and Phengs in 2000.\textsuperscript{[203]} This catalyst, featuring two κN-coordinated pyridine-2-one ligands, efficiently catalyzed the reduction of ketones by isopropanol (yields up to 95\%, TON values > 1000). The transfer hydrogenation occurred chemoselectively – C=O bonds were reduced selectively, even in the presence of C=C bonds.
Moore and Szymczak utilized a Ru(II) complex possessing a proton-directing 6,6′-dihydroxy-2,2′,6′,2′-terpyridine ligand. The pre-catalyst exhibited hydrogen-bonding interactions of OH-groups with the chloride ligand bound to the Ru(II) center; thus, a directed interaction with substrates, coordinated to the metal center, was concluded (Scheme 40). 13 exhibited a high efficiency in catalyzing the transfer hydrogenation of ketones in isopropanol; however, KOBu was required, as additive, in order to control the chemoselectivity of the reaction and suppress the concurrent hydrogenation of olefinic double bonds (if present). Detrimentally, 13/KOµBu remained sensitive to the substrates’ structure and showed a low conversion in the case of bulky derivatives. In comparison to Kelsons catalyst, significantly lower TOFs were observed (16 h\(^{-1}\) vs. 408 h\(^{-1}\)). The Kundu group utilized a related ligand, i.e., 2-(6-hydroxy-pyridin-yl)-1,10-phenanthroline, which strongly accelerated the transfer-hydrogenation (TOFs up to 2400 h\(^{-1}\)). On the basis of control experiments, it was proposed that an outer-sphere transfer of H\(^+\)/H\(^-\) equivalents from the metal and the ligand, respectively, was involved in the catalytic cycle.\(^{[20]}\) In-depth kinetic studies were conducted and showed that the OH-groups were essential due to their ability to bind the substrate under basic conditions via ion-pairing interactions. This second-sphere interaction was identified as a prerequisite for the selective reduction of carbonyl groups in the presence of C=C bonds (Ru(II) complexes missing the directing OH-groups offered a poor chemoselectivity).

Later, the ligand structure was modified by replacing the OH-groups by mesitylamino ones. These substituents not only stabilized the resultant Ru(II) catalyst, but even offered an increased activity due to a higher electron density on the ligand. Primary alcohols were oxidized to the corresponding carboxylic acids in good to high yields and with TON values of up to 445.\(^{[206]}\)

More recently, Patra et al. reported on the transfer hydrogenation of ketones using cationic and neutral Ru(II) complexes equipped with \(4^*\)-aryl-tpy ligands (14 and 15, Figure 7).\(^{[207]}\) Due to their lower reduction potentials, the neutral ones were more efficient in reducing ketones. Complex 15a was used in the base-mediated transfer hydrogenation of ketones with isopropanol (substrate-to-catalyst ratio of 200:1). A wide range of ketones was screened: Electron-rich and electron-poor aceto-phenones, benzophenone, cyclic aliphatic ketones, 2-acetyl-heteroarenes, etc. (18 examples in total). Remarkably, the proposed catalytically active species (16a, Figure 7) could be isolated, characterized and even employed as catalyst in the base-free transfer hydrogenation of ketones. The formation of 16a was explained by the initial formation of a Ru(II)-isopropanoxide species, followed by the release of acetone via a β-H elimination pathway.

Basically, the (transfer-)hydrogenation of esters is, due to their stability, more demanding than the reduction of aldehydes and ketones. Elsevier and co-workers established reaction conditions to perform the hydrogenation of esters under Ru catalysis.\(^{[208]}\) In this context, the combination of Ru(I) or Ru(III) ions with tpy ligands was found to be unfeasible. In line with this report, complex 15a was employed in the chemoselective reduction of ketoesters in which the less reactive ester moieties were not affected under the reaction conditions.\(^{[207]}\)

Beller and co-workers extended the scope of the transfer hydrogenation catalyzed by Ru(II)-tpy complexes also to the reduction of aromatic nitro and diazo derivatives under atmospheric pressure (Scheme 41).\(^{[209]}\) The catalytically active species, Ru(tpy)H\(_2\) was prepared in situ from the [RuCl\(_2\)(p-cymene)], precursor by hydride transfer from isopropanol. The high functional-group tolerance was demonstrated at the broad range of aromatic nitro compounds which was reduced to the corresponding aniline derivatives in good to very high yields (63 to 97%); no disturbance of the reaction by, e.g., halide, amide, ester or C=C groups was observed. Furthermore, the N=N bonds of aromatic diazo derivatives were efficiently cleaved reductively by the same catalytic system.

### 2.6.2. Oxidation of alkenes, alcohols and sulfides

The heteroleptic Ru(II) complex Ru(tpy)(pydic) represents a powerful catalyst for the epoxidation of alkenes as well as for the oxidation of alcohols to aldehydes or ketones (pydic: pyridine-2,6-dicarboxylate).\(^{[210]}\) Beller et al. used H\(_2\)O\(_2\) as oxidant, to covert styrenic olefins into the corresponding epoxides (moderate to high yields were obtained); in general, a high...
substrate conversion and chemoselectivity was observed in these studies.

The mixed-ligand, mono-cationic \([\text{Ru(tpy)(bpy)Cl}]^+\) complex was also employed in the context of alkene oxidation.\[213\] This particular complex represents a popular precursor for the preparation of the corresponding aquo species \([\text{Ru(tpy)(bpy)(OH}_2]^2+.\) Making use of the Ru(II)/Ru(IV) redox couple, this complex has widely been exploited in the context of electrocatalytic oxidation reactions. For this purpose, the complex is immobilized onto electrode materials, typically via a COOH-substituent on the bpy ligand. The various studies dealing with this electrocatalytic system, starting from Meyer's pioneering work in the 1980s,\[21\] and the proposed catalytic cycle have already been summarized by us earlier.\[20\] The same also holds true for the materials where such complexes have been attached to polymer backbones.\[214\] Beyond this, \([\text{Ru(tpy)(bpy)Cl}]^+\) has been attached to peptide residues via amide linkages; these conjugates interacted with DNA strands and were able to photocatalytically cleave the phosphorodiesteric bonds (this application is of relevance for the photo-dynamic therapy (PDT) of cancer, see ref. [23]). In line with these studies, Papafotiou et al. immobilized \([\text{Ru(tpy)(bpy)Cl}]^+\) onto silica nanoparticles (a loading of 0.22 mmol Ru per g silica was concluded from thermogravimetric and elemental analyses).\[215\] The non-selective oxidation of alkenes by \(^t\)-BuOOH was tested under the conditions of heterogeneous and homogeneous catalysis using either the immobilized or the small-molecule complex, respectively (Figure 8). In comparison, SiO\(_2\)-bound \([\text{Ru(tpy)(bpy)Cl}]^+\) exhibited an increased catalytic activity; whereas, the selectivity of the catalysts was comparable.

In recent years, magnetic nanoparticles (MNPs) have emerged as a versatile support material for the immobilization of catalysts.\[216\] Besides their non-toxicity and high surface area are two properties mainly prompted this development: Superparamagnetism and the large number of hydroxy groups present on the surface. The OH-moieties can be used as anchor for the covalent binding of appropriate catalyst molecules; the magnetism allows a straightforward separation of the heterogeneous catalyst from the reaction mixture simply by magnetic decantation. This strategy was followed by Llobet, Pericàs and co-workers who attached \([\text{Ru(tpy)(NN)Br}]^+\) complexes to Fe\(_3\)O\(_4\) NMPs via a phosphonate group present on the tpy ligand (NN: bidentate ligand, such as bpy, 2,2’-bipyrimidine (bpym) or 2-phenylazopyridine (azpy)).\[217\] The catalyst-loaded MNPs were characterized by UV/vis absorption and IR spectroscopy, CV measurements as well as TEM imaging (Figure 9). When dispersed in water, the catalytically active aquo species were

![Scheme 41. Top: Schematic representation of the transfer hydrogenation of aromatic nitro and diazo compounds. Bottom: Schematic representation of the proposed catalytic cycle for transfer hydrogenation of aromatic nitro compounds.](image-url)
formed in situ. The materials were tested as heterogeneous catalysts in the olefin epoxidation olefins, using Phl(OAc)₂ as the oxidant, and offered a very high stereospecificity in the conversion of cis-configured substrates, such as cis-β-methylstyrene or cis-stilbene. The catalyst could be recycled by magnetic decantation and reused in up to five consecutive cycles without significant loss of activity with respect to conversion, yield and stereoselectivity.

In a different approach, a porous MOF was functionalized with tpy units by using the CuCAAC reaction. The thusly introduced binding sites were then loaded with RuCl₃ without affecting the overall 3D architecture of the MOF (as confirmed by powder XRD analysis). The material was employed as heterogeneous, recyclable catalyst for the oxidation of benzylic alcohols in water with H₂O₂ as the oxidant.

Beyond the aforementioned solely catalytic reactions involving Ru(II)-tpy complexes, also a range of dinuclear ensembles has been employed to photocatalytically oxidize external substrates. These dyads basically comprise a photosensitizer complex which is covalently linked to the catalyst complex. Upon photo-excitation, an electron is transferred from the light-harvesting unit to the catalytically active site where the substrate, e.g., an alcohol becomes oxidized (Figure 10a). In this intramolecular process, the linkage between the two functional centers is of utmost importance, since it controls the electronic interaction between them. In one of the earliest contributions in this respect, Rocha and co-workers synthesized the dinuclear complex 17 (Figure 10b) and investigated its ability to catalyze the light-driven oxidation of alcohols under ambient conditions in water. A range of benzylic and even aliphatic secondary alcohols could be oxidized to the corresponding aldehydes and ketones; the reasonable TONs of 100 and high selectivity of >100 for the oxidation of primary benzylic alcohols) indicated the high potential of using such dyads as photocatalysts in for the oxidation of organic substrates. In the following a variety of related dyads was reported and employed in this context in one example, Llobet et al. utilized the dinuclear species 18 (Figure 10b) as photocatalyst for the oxidation of water, benzylic alcohol and thioethers. The organic substrates could be oxidized; however, the bimolecular system of [Ru(bpy)₃]²⁺ and [Ru(tpy)₂(bpy)(H₂O)]³⁺ was by far more efficient in this respect. This finding was attributed to the nature of the bridging ligand which acted as an electron trap, thus hampering the electron transfer to the catalyst site. Therefore, a cautious molecular design is urgently required in order to assemble highly active photocatalyst dyads.

Fu and co-workers focused on homometallic trinuclear assemblies, in which two Ru(II) photosensitizer units were attached to a [Ru(tpy)(bpy)(Cl⁻)]³⁻ oxidation catalyst. The light-driven oxidation of benzylic alcohols occurred in the presence of Co(III), as the oxidant. The prosed Ru(IV)-oxo intermediate, the actually relevant species for the alcohol oxidation, was identified by UV/vis absorption spectroscopy and mass spectrometry (225). The same authors also assembled a dendritic trinuclear complex; however, this assembly required [Ru(bpy)₃]²⁺ as additional photosensitizer to enable the light-driven oxidation of alcohols. This photocatalytic system offered a very high selectivity with respect to the product formation (i.e., aldehydes and ketones) and good TON values of up to 300.

Meyer et al. followed a different strategy to employ Ru(II) complexes in the light-driven dehydrogenation of benzyl alcohol. These authors anchored [Ru(bpy)₃]²⁺ photosensitizers and [Ru(mebimpy)(bpy)(OH₂)]²⁺ oxidation catalyst to photocathode materials via their pendant phosphonate moieties (mebimpy: 2,6-bis(1-methylbenzimidazol-2-yl)pyridine). Thereby, mesoporous TiO₂ nanoparticle films or core/shell nanoparticles, comprising Sn-doped InO₂ cores covered with thin TiO₂ layers, served as photocathode materials. In such a dye-sensitized photoelectrochemical cell (DSC), the oxidation of benzyl alcohol occurred at the catalytically active Ru(IV) = O sites on the photocathode; whereas, hydrogen evolution was simultaneously observed at Pt electrode (Figure 11). The electrons required for the HER where injected at the photocathode and transferred to the Pt electrode. The structurally optimized core/shell nanoparticles were found to be a superior photocathode material compared to the mesoporous TiO₂ – the overall dehydrogenation was enhanced by a factor of ca. 10.
Noteworthy, the same molecular components, when anchored onto powdered hematite (α-Fe₂O₃) were also active in oxidizing sulfides, such as thioanisole. In a different set-up, the [Ru(tpy) (bpy)(OH)₂]²⁺ oxidation catalysts were adsorbed onto a TiO₂ photoanode via a phosphate moiety present in their terthiophene tails. These chromophores were introduced to facilitate both light absorbance and electron injection into the semiconductor phase (Figure 12). These type of DSPEC allowed the oxidation of phenol and benzyl alcohol at photo-currents of 230 and 25 μA/cm², respectively. The examples highlight the applicability of DSPECs in the field of solar-energy conversion and storage – important fields of research which were reviewed extensively by Meyer et al. in 2015.

As for the photocatalytic oxidation of alcohols, dinuclear Ru (II)-based photosensitizer–catalyst dyads have also been applied for the related oxidation of thiophetors to sulfoxides. In the initial studies, Hamelin (II)-based photosensitizer–catalyst dyads have also been applied using the dinuclear photocatalyst onto a TiO₂ semiconductor phase (Figure 12). These type of DSPEC allowed the oxidation of phenol and benzyl alcohol at photo-currents of 230 and 25 μA/cm², respectively. The examples highlight the applicability of DSPECs in the field of solar-energy conversion and storage – important fields of research which were reviewed extensively by Meyer et al. in 2015.

2.7. Rhodium-catalyzed reactions

Rhodium complexes play an important role in modern organic chemistry due to their ability to catalyze a remarkable range of reactions. Amongst others, the (asymmetric) hydrogenation, epoxidation or hydroformylation of olefins as well as the C–H activation, C–C bond formation and the various cycloaddition reactions have to be mentioned in this context. One of the earliest reports on the catalytic activity of rhodium-polyprpyridyl complexes dates back to 1985 when Creutz et al. used [Rh(bpy)₂]³⁻ as catalyst in the water-gas shift reaction. By the same time, Meyer et al. recognized the potential of Rh(III)-polyprpyridyl complexes as electrocatalysts in the CO₂ reduction. In this context, also Rh(III)-tpy complexes have been discussed. Beyond these applications, one example to organic synthesis is worth mentioning: Rh(III) complexes with chiral tpy ligands (1, Figure 1) were successfully employed in the asymmetric cyclopropanation of olefins.

In 1996, Pruchnik et al. reported on the μ-OAc bridged dinuclear Rh(III)-tpy complex in which a Rh-Rh bond between the metal centers of a σ electron configuration could be identified (Scheme 43a). This ([Rh(tpy)C]₂) μ-OAc)⁻ complex was revivified 20 years later by Wang et al. and employed as water-soluble catalyst for the oxidation of primary or secondary alcohols to carboxylic acids or ketones, respectively (Scheme 43b). This reaction involved an acceptor-free alcohol dehydrogenation, followed by an aerobic oxidation with air (in the case of aldehyde intermediates only). Remarkably, the catalyst was highly efficient even at a very low catalyst loading (substrate-to catalyst ratio of 5000), compatible with gram-scale syntheses and could be recycled at least 19 times – simply by extraction – without losing its activity. Furthermore, the same catalyst, either pre-formed or assembled in situ from [Cp*RhCl]₃, tpy and NaOAc, enabled the synthesis of esters via the dehydrogenative cross-coupling of aldehydes with alcohols or dehydrogenative cross-coupling of primary alcohols (Scheme 43c). The ester synthesis exhibited a very good functional group tolerance and chemoselectivity. The selectivity of the cross-coupling of primary alcohols was attributed to the significantly higher tendency of benzyl alcohol to undergo dehydrogenation compared to aliphatic ones. NMR spectroscopic studies suggested that both metal centers of the
dinuclear complex were involved in the catalytic cycle and the base was identified to act as a “proton shuttle”.

Complex 20 also showed a high catalytic activity with respect to the chemoselective alkylation and olefination of alkylnitriles with alcohols.\[241]\, Remarkably, the outcome of the reaction could simply be controlled via the reaction atmosphere: The alkylation product was formed under inert conditions (Ar atmosphere; whereas, the presence of O\(_2\) strongly favored the formation of the olefination product (Scheme 44). The alkylation showed a broad substrate scope, since aliphatic and benzylic derivatives, nitriles as well alcohols, could be used. One the basis of control experiments, a hydrogen-borrowing pathway was suggested, in which the conjugate reduction of an alkenyl nitrile intermediate by a [Rh-H\(_2\)] species under inert conditions afforded the alkylation product in good to high yields. Under an atmosphere of molecular oxygen, however, the [Rh-H\(_2\)] species was intercepted and the alkenyl nitrile was obtained as the final product.

The efficient valorization of lignin represents a major challenge in biomass pretreatment which is often associated with the usage of hazardous and waste-generating oxidants and reductants.\[242–243]\ These issues can be avoided by using redox-neutral catalysts for the depolymerization of lignin, i.e., cleavage of the β-O-4 linkages into ketone and phenol fragments. Against this background, Wong et al. used 20 as catalyst for the fragmentation of various lignin model substrates in water (Scheme 45a).\[244]\ The protocol could also be applied to efficiently depolymerize lignin-type polymers, alkaline lignin and even raw lignocellulose into small-molecule ketone and phenol fragments under in water under mild conditions and in absence of any additional H\(_2\) source. Mechanistic studies were conducted and identified the benzylic OH-groups as the hydrogen source which is eventually required to cleave the ethereal bonds. Overall, the observed fragmentation was rationalized by a dehydrogenation-hydrogenolysis pathway, which is summarized in Scheme 45b.

Scheme 43. (a) Solid-state structure of the dinuclear Rh(II) complex [Rh(tpy)Cl\(_2\)(μ-OAc)]\(^{+}\) (the counterion was omitted for clarity).\[238] Figure reproduced with kind permission; © 1996 American Chemical Society. (b and c) Schematic representation of the dehydrogenation of alcohols and the dehydrogenative cross-coupling of aldehydes and alcohols, respectively.\[239–240]\n
Scheme 44. Schematic representation of the alkylation and olefination of nitriles by primary alcohols, catalyzed by 20.\[241]\ Figure reproduced with kind permission; © 2017 Wiley-VCH.

Scheme 45. (a) Schematic representation of the fragmentation of lignin model substrates into ketone and phenol derivatives, catalyzed by the redox-neutral complex 20.\[244\] (b) Schematic representation of the proposed fragmentation mechanism.\[244\] Figure reproduced with kind permission; © 2019 Wiley-VCH.
2.8. Palladium-catalyzed reactions

Palladium catalysts are widely used in the context of the various carbon–carbon or carbon-nitrogen bond formation reactions. These reactions started to emerge in the 1970s and their outstanding role in today's organic synthesis was honored when the 2010 Nobel prize in chemistry was awarded to R.F. Heck, A. Suzuki and E.-i. Negishi.\textsuperscript{246} Besides the numerous applications of these reactions which basically rely on the Pd (0)/Pd(II) redox couple, also the high-oxidation-state Pd catalysis has attracted considerable interest.\textsuperscript{246} Most commonly, phosphine-based ligands are used to stabilize the catalytically active Pd centers, but also polypyridyl-type ligands have been used in this context. Some early examples in this respect, such as the allylic substitution (the so-called Tsuji-Trost reaction), have to be mentioned in this context.\textsuperscript{247}

2.8.1. Cross-coupling reactions

In 2010, the Suzuka group introduced an amphiphilic polystyrene-poly(ethylene glycol) resin to which a tpy derivative was bound via electrostatic interactions (PS-b-PEG-tpy, Figure 13).\textsuperscript{248} When loaded with Pd(II) ions a heterogeneous catalyst was obtained which was applied in the Suzuki-Miyaura cross-coupling between aryl halides and arylboronic acids in water (17 examples, yields of 69 to 99%). The catalyst could be recovered simply by filtration and reused in up to five consecutive runs without loss of activity.\textsuperscript{249} The chemically more robust covalent variant of PS-b-PEG-tpy was, after loading with Pd(II) ions, used by the same authors for the Mizoroki-Heck- and Suzuki-Miyaura-type cross-coupling reactions.\textsuperscript{250} Both acrylic and styrenic substrates were reacted with aryl halides to afford the coupling products in excellent substrate conversions.\textsuperscript{251}–\textsuperscript{252} With respect to the latter, aryl iodides were coupled with ethynyl benzenes in high yields (> 70%); whereas, aryl bromides were found to be unreactive (yield < 2%).

The same concept, i.e., immobilization of Pd(II)-tpy complexes onto solid supports was also followed by Chen et al.; these authors used xylan-type hemicellulose as support which was functionalized with tpy units (0.92 mmol tpy per g biopolymer, according to elemental analyses, Figure 14).\textsuperscript{253} Under the optimized reaction conditions, using K$_3$CO$_3$ in methanol, the Suzuki-Miyaura cross-coupling reaction proceeded in good to high yields (78 to 98%, in the case of (het) aryl iodides and bromides) and even aryl chlorides were converted (though giving significantly lower yields only). The heterogeneous catalyst was recovered and reused in at least six successive cross-coupling reactions without losing its activity. The morphologies of the freshly prepared catalyst and the one isolated after six runs were compared by TEM imaging and only marginal changes of the micromorphology became apparent: The initial nanoparticles had an average diameter of 10 nm; whereas, a slight increase to 10 to 20 nm was observed for the recovered material (Figure 14).

In a related study, a SiO$_2$-supported Pd(II)-tpy complex was used in the Mizoroki-Heck- and Suzuki-Miyaura-type cross-coupling reactions.\textsuperscript{254} Both acrylic and styrenic substrates were reacted with aryl halides to afford the coupling products in moderate to high yields (19 examples, 48 to 92% yield). The Suzuki-Miyaura coupling between aryl iodides and arylboronic acids yielded the corresponding biphenyls in high yields (> 85%); these reactions featured short reaction times and excellent substrate conversions.

Triphenylenes represent functional organic materials which are of interest with respect to potential applications as discotic liquid crystals and in organic light-emitting devices.\textsuperscript{255} Such...
materials can be synthesized via various combinations of C–C bond formation reactions, such as the Pd(0)-catalyzed coupling of 2-iodobiphenyls and iodobenzenes – a method which involves a dual C–H bond activation and double C–C bond formation.\(^\text{[256]}\) In this context, Zhang et al. employed the complexes 21 (Scheme 46), as pre-catalysts, in the triphenylene synthesis.\(^\text{[256]}\) The robust protocol, not requiring inert reaction conditions, afforded the corresponding triphenylenes in moderate yields (Scheme 46).

**Scheme 46.** Schematic representation of the triphenylene synthesis catalyzed by the Pd(III) complexes 21. The solid-state structure of 21a is also depicted.\(^\text{[256]}\) Figure reproduced with kind permission; © 2019 Elsevier B.V.

2.8.2. Miscellaneous reactions involving Pd(0)/Pd(II) species

The polymer-supported Pd(III) complexes (Figure 13), which were found to be efficient heterogeneous catalysts for a range of C–C bond formation reactions (see the previous Section), were also employed by Suzuka and co-workers to catalyze a variety of other functional-group transformations.

In particular, the allylic alkylation – known as the Tsuji–Trost reaction – has to be named in this context. The asymmetric variant of this reaction represents a powerful tool in organic synthesis, \(e.g.,\) with respect to the total synthesis of natural products.\(^\text{[257–258]}\) Chelucci et al. already combined chiral tpy ligands (1, Figure 1) with the \([\text{Pd}(\eta^3-\text{C}_5\text{H}_5)\text{Cl}]_2\) pre-catalyst in order to alkylate allyl esters in an enantioselective fashion (though with moderate success only).\(^\text{[247]}\) Suzuka’s heterogeneous catalyst enabled the allylic alkylation of allyl esters with arylboronic acids, as nucleophiles, under aerobic conditions in water (Scheme 47).\(^\text{[239]}\) The stereochemistry of the reaction was studied by NMR spectroscopy. It was demonstrated at the example of a disubstituted cycloalkene derivative that the reaction occurred selectively under stereoinversion, typical for the allylic alkylation with hard C-nucleophiles. The same authors also reported on the allylic azidation of allyl esters with azide, as nucleophile under the same reaction conditions (Scheme 47).\(^\text{[239]}\)

The dehalogenation of aryl halides represents a major issue in environment protection – though officially banned since 2001, environmental pollution from the past causes such harmful and persistent compounds still to be widely present in nature.\(^\text{[261]}\) Amongst others, Pd-based catalysts have tested to face this challenge, \(i.e.,\) to reductively dehalogenate aryl halides ideally in water (the first example, Pd(PPh\(_3\))\(_4\)) was already reported in 1974\(^\text{[262]}\). Against this background, Suzuka et al. utilized their polymer-supported catalyst for the reductive dehalogenation with potassium formate, as hydrogen source, in water.\(^\text{[263–265]}\) Under these reaction conditions, the reduction of aryl chlorides in pure water proceeded in very high yields (14 examples, \(> 90\%\) after 3 h); whereas, the debromination and deiodination unexpectedly proceeded much slower and less efficient (74 and 0.5 % yield, respectively, after 24 h).\(^\text{[264]}\) Remarkably, the reductive dechlorination was significantly retarded when seawater was used, as solvent.\(^\text{[265]}\) Both findings, the order of reactivity (\(i.e.,\) Ar–Cl > Ar–Br > Ar–I) as well as the “solvent” effect were attributed to a deactivation of the catalyst by certain anions.\(^\text{[263]}\) Control experiments were performed and Br\(^-\) and I\(^-\) both naturally present in seawater, deactivated the catalyst. Thus, the poor yield of the deiodination could be attributed to a self-inhibition of the reaction by the deliberate iodide anions.

The aminocarbonylation of aryl iodides represents one further application in which the polymer-supported Pd(III)-tpy system has been used. Starting from Heck’s pioneering work, a broad range of protocols for this reaction has been reported.\(^\text{[266]}\) In order to circumvent the limitations associated with most of these methods, Suzuka et al. offered a phosphine-free and recyclable heterogeneous catalyst that allowed the aminocarbonylation to proceed even in water (methoxylamine...
hydrochloride was used as source for ammonia, Scheme 48.\textsuperscript{[247]} The initial protocol was later modified by using azide as nucleophile. In the absence of any further additive, yields of up to 90% were observed. Mechanistic studies suggested a dual role of the catalyst – participation in the azidocarboxylation and the subsequent Staudinger-type reaction.\textsuperscript{[248]}

A simple, yet efficient single-site Pd(II) catalyst, i.e., Pd(tpy)Cl₂, was used by Vannucci and co-workers for the hydrodeoxygenation of benzyl alcohol, benzaldehyde and benzophenone to yield toluene and diphenylmethane, respectively.\textsuperscript{[249]} The reactions proceeded chemoselectively even at room temperature – hydrogenation of the aromatic rings was not observed. The authors proposed a two-step mechanism in which first a [Pd(tpy)H⁺] species is formed which then undergoes the selective hydrodeoxygenation of the substrate. Noteworthy, the analogous Ni(II)-tpy complex was by far less reactive, offering only 5% conversion at a much higher temperature. Very recently, the same authors immobilized Pd(tpy)Cl₂ via a 4-carboxylate moiety onto amorphous SiO₂, thus generating a heterogeneous and recyclable catalyst for the hydrodeoxygenation of oxygenated aromatics.\textsuperscript{[250]} Kinetic studies revealed a significantly higher activity of this catalyst compared to the aforementioned homogeneous variant. Moreover, the strong binding of the catalytic sites to the support prevented the formation of Pd nanoparticles which could act as concurrent catalysts and decrease the chemoselectivity, e.g., by hydrogenation of the aromatic rings.

Finally, the Pd(II)-catalyzed selective oxidation of olefins under aerobic conditions represents an important method in modern organic synthesis.\textsuperscript{[271]} However, the efficient regeneration of the catalytically active Pd(II) species and the suppression of the precipitation of Pd black are the limiting factors often involved in these reactions. Jiang et al. reported on the Pd(II)-catalyzed diacetoxylation of aryl alkenes with O₂ as the exclusive source of oxygen.\textsuperscript{[272]} The catalyst was assembled \textit{in situ} from tpy and Pd(OAc)₂. Bis-pinalcolborane, PinB-BPin, was identified as versatile mediator for this reaction: The transmetallation of the initially formed organo-palladium species yielded a C–BPin bond which, in turn, was cleaved oxidatively into the diacetate product (Scheme 49); thereby, the Pd(II) catalyst was re-generated; whereas the occurrence of colloidal Pd was not observed. The method featured a remarkable functional group tolerance and high substrate conversions and product yields were obtained (49 examples, > 91% yield). The authors also tested other bi- and tridentate ligands; these, however, formed much less efficient catalysts with Pd(OAc)₂.

2.8.3. Reactions involving high-oxidation-state Pd catalysis

Catalysis involving the Pd(II)/Pd(IV) redox couple represents a rather young field of research which goes beyond the scope of conventional Pd(0)/Pd(II) catalytic cycles.\textsuperscript{[246]} Though already discussed in literature since the late 1970s, the active participation of Pd(IV) species in catalytic cycles was disclosed years later. In general, Pd(IV)-catalyzed reactions require strong oxidants which suppress alternative Pd(II)-based pathways by re-oxidation of the metal centers. This high-oxidation-state Pd catalysis has found applications in C–C and, in particular, C–heteroatom bond formation reactions. Concerning the latter, the ability to establish Cₓ₋ₓ–F bonds in a selective manner under mild conditions is of significant importance.\textsuperscript{[273–274]}

Ritter and co-workers reported on the catalytic fluorination of aryloboric acid derivatives using Selectfluor, both as fluoride source and oxidant (aryl trifluoroborates, aryloboric acids or pinacol esters as well as electron-rich MIDA boronates could be used as substrates).\textsuperscript{[275]} The proposed radical reaction pathway, involving a Pd(III) species, suppressed the homocoupling and protodeborylation as common side reactions in Pd(0)/Pd(II) catalytic cycles. Remarkably, kinetic studies indicated that the product formation indeed occurred via a SET pathway and excluded the participation of organo-palladium intermediates (Scheme 50). The unusual Pd(III)-tpy bis-complex, stabilized by the tridentate ligands, could even be isolated and characterized by X-ray single-crystal analysis. The reaction featured a high functional-group tolerance, gave the fluorinated products in good to very high yields (15 examples, 70 to 99% yield) and could efficiently be performed also on a multiple-gram scale.

More recently, the Ritter et al. also introduced a direct C–H fluorination protocol in which the heteroleptic Pd(II) catalyst 22 was used.\textsuperscript{[276]} A broad range of substrates, including some pharmaceutically important compounds, was fluorinated in moderate to high yields under remarkably mild conditions (Scheme 51). It was demonstrated that fluorinated derivatives, which are hardly accessible \textit{via} other synthetic routes, can efficiently be prepared by this \textit{de novo} method. Besides Selectfluor, also NFSI could be employed, as fluoride source and oxidant (NFSI: \textit{N}-fluorobenzenesulfonylimide). The authors pointed out, that the tpy ligand prevented the formation of Pd-aryl intermediates; in contrast to the conventional pathway involved in Pd(0)/Pd(II) catalysis, a Pd(IV)-F species was formed by oxidative addition of a F⁻ equivalent to the metal center \textit{via}
a SET process (Scheme 51). This octahedral Pd(IV) complex, in turn, interacted with the arene substrate and enabled its fluorination according to an electrophilic aromatic substitution reaction.

2.9. Miscellaneous metal-tpy catalysts

From the last-row transition metals, mainly the tpy complexes of Ir(III) and Pt(II) have attracted considerable interest with respect to catalytic applications. However, these are mainly devoted to the photocatalytic solar-fuel generation and will, thus, be discussed in Section 3.1.\[277–278\]

Concerning the other transition metals, some scattered reports can be found, where metal-tpy catalysts have been used. Recently, Delferro et al. pointed out that vanadium species play an important role, as catalysts, in a wide range of reactions. However, most of these are related to oxidation processes; whereas, catalytic reductions are rare.\[279\] Against this background, open-shell V(III) complexes equipped with redox-noninnocent ligands, i.e., \(\pi\)-radical monoanionic tpy species (\(R\)-tpy\(^{•}\), \(R = CH_2SiMe_3\) or Ph) were employed to catalyze the chemoselective hydroboration and hydrosilylation of various substrates.\[280\] Upon treatment with VCl\(_3\) and LiCH\(_2SiMe_3\), parent tpy yielded a mixture of 23 and 23H; whereas 4-Ph-tpy explosively formed 24 (Figure 15). The 23/23H mixture was employed, as catalyst, in the hydroboration of ketones and aldehydes which smoothly proceeded at room temperature to give the corresponding alcohols in 75 to 99% yield (Scheme 52); whereas, the analogous hydrosilylation was only applicable to ketones under the same reaction conditions (aldehydes gave <5% yield). Moreover, the hydroboration of esters, imines and carboxamides – in moderate to high yields – was also demonstrated.

Niobium, as vanadium’s heavier homologue, has also been combined with tpy – though in a completely different context. Nb\(_2\)O\(_5\) is known to be a water-compatible, Lewis-acidic catalyst that was used in various organic reactions, such as the formation of cyclic imides from dicarboxylic acids.\[281\] The metal...
oxide is typically prepared by calcination of niobic acid which, in turn, can be prepared by hydrolyzing NbCl₅ or Nb(OCH₃)₅. In addition, Nb(V) oxalate can be used as water-soluble precursor material. In order to assemble a reusable heterogeneous catalyst, Guo et al. hydrolyzed Nb(V) oxalate in the presence of SiO₂-supported tpy, thus forming a SiO₂-tpy@NiO₂ hybrid material (Figure 16). This material was employed as catalyst in the synthesis of N-substituted phthalimides from phthalic acids/anhydrides and primary amines. Good to very high yields were observed using either of the substrates. Moreover, the SiO₂-tpy@NiO₂ could be recovered and reused in at least eight consecutive runs without losing its activity; incorporating of the hybrid material into a continuous flow cell suggested a potential applicability in large-scale or even industrial applications.

Scattered reports on stable tpy complexes of main-group metals can be found in the literature; however, these assemblies have hardly been discussed in the context of catalyzing organic reactions. As an exception, Zhang et al. reported on an Al(III)-containing zwitterionic Meisenheimer-type complex just recently. In line with their synthesis on the V(III)-containing complexes 23 and 24 (Figure 15), these authors prepared a series of Al(III)-tpy complexes in which the central pyridine ring was deaeromatized by alkylation. In particular, complex 25 – prepared via similar protocol as for 23 – has to be highlighted (Figure 17). This complex was used as pre-catalyst in the hydroboration of C=O and C=C bonds. Both types of substrates were hydroborated in very high yields (10 carbonyl and 8 alkynyl derivatives were used). Remarkably high TON values of up to 1000 were found for both reactions, thus making 25 a highly potent pre-catalyst for these transformations and out-performing all other Al(III)-containing hydroboration (pre-)catalysts reported so far.

3. Terpyridine complexes, as catalysts in energy conversion applications

In the context of converting electrical or solar energy into chemical energy, two applications are currently in the focus of intense research: CO₂ reduction, i.e., the conversion of CO₂ into higher-energy compounds, as well as reduction and oxidation of water, i.e., the production of H₂ and O₂, respectively. In order to reach these goals a broad range of photo-, electro- and photoelectrochemical approaches, often utilizing transition metal complexes, as catalysts, has already been reported.

In the following examples, in which tpy ligands have been introduced in the coordination sphere of these complexes, will be detailed. Before doing so, it has to be emphasized that the catalytic systems discussed in the following are mainly in the focus of fundamental research and the reported TON values or catalytic efficiencies are by far too low to allow an industrial application. This issue is documented, for example, in the electrocatalytic CO₂ reduction for which a broad range of bulk metal electrodes has been studied. From these, Cu offers a high Faradaic efficiency for the formation of hydrocarbons;
whereas, the noble metals (e.g., Ag or Au) facilitate the CO₂ production. The same basically also holds true for the other energy-conversion applications: Metal chalcogenides, carbides, nitrides or phosphides as electrocatalysts in the HER[290] as well as semiconductors in the photocatalytic HER.[291]

3.1. Reduction of carbon dioxide

The current discussion how mankind can confront the fast-evolving climate change has brought the need to lower the worldwide CO₂ into the focus of interest. As one of the greenhouse gases, CO₂ significantly contributes to the global warming and methods to recycle CO₂, i.e., to re-introduce it into the “carbon cycle” are urgently required.

The electrochemical CO₂ reduction can be performed via a number of pathways, basically differing in the number of electron equivalents (ranging from two- to eight-electron reductions), and reaction conditions. Accordingly, a broad range of products can be obtained by adjusting the electrochemical reduction conditions: Carbon monoxide, formic and oxalic acid, formaldehyde, methanol, methane, ethylene, ethanol, etc.[289] All these low-carbon compounds are of relevance for further use in industrial applications; their market prices as a function of their energetic costs are highlighted in Figure 18.[294] The proton-coupled CO₂ reduction to various of these substrates occurs at negative potentials (E⁰) in the range of −0.25 to −1.00 V vs. the NHE (NHE: normalized hydrogen electrode).[295,296] However, the direct conversion of CO₂ into the CO₂⁺ radical anion, a one-electron reduction, is energetically much more demanding (E⁰ = −1.90 V vs. NHE). This is mainly attributed to the enormous reorganization energy required to force the linear CO₂ molecule into the bent geometry of the radical anion.[296] In order to lower the reduction potential and, thus, make the CO₂ reduction more favorable, catalysts have to be applied.[297] In this context, Ru(II)-polypyrrolid complexes have – amongst other heavy-metal complexes – been employed.

In 1994, Tanaka et al. demonstrated that the heteroleptic complex [Ru(tpy)(bpy)(CO)₂]⁺ can be used to catalyze the electrochemical CO₂ reduction.[298] However, as typical for most of the complexes reported in literature, the catalyst operated at a relative negative potential and offered only a slow conversion. In similar fashion, the Ru(II) complexes 26 (Figure 19) were studied with respect to their ability to electrocatalytically reduce CO₂ to CO (the aqua complexes, 26 with L = OH₂, were previously found to be versatile single-site catalysts for the water oxidation, see Section 3.3[299]). The fundamental catalytic cycle, as proposed by Meyer et al. is depicted in Figure 20.[300] Basically, a solvato complex is generated first from whatever precursor which, in turn, enters the catalytic cycle via two successive one-electron reduction steps involving the tpy and

![Figure 18](image-url)  
**Figure 18.** Representation of the market price of some selected CO₂ reduction products as a function of the energy content. The lines denote the minimum energy and CO₂ costs. For a better overview, capital costs have been neglected.[298] Figure reproduced with kind permission; © 2019 American Chemical Society.

![Figure 19](image-url)  
**Figure 19.** Schematic representation of complexes used, as catalysts, in the context of electrocatalytic CO₂ reduction.[294,296,301–305]

![Figure 20](image-url)  
**Figure 20.** Schematic representation of the electrocatalytic CO₂ reduction using a [Ru(tpy)(N(N)S)]⁺ complex, as catalyst (N(N)S denotes a bidentate ligand, such as bpy; S represents a coordinated solvent molecule).[300] Figure redrawn with kind permission; © 2011 The Royal Chemical Society.
the bidentate NN ligand. A remarkable influence of the nature of the ligands on the catalytic performance was found. The complex 26b, featuring a N-heterocyclic carbene (NHC) ligand, was reported to be the more efficient catalyst – catalytic rate constants ($k_{\text{cat}}$) of 5.5 and 19.1 s$^{-1}$ were determined in CO$_2$-saturated solutions. The increased catalytic activity of 26b was explained by an increased lability of the solvato ligand in the doubly-reduced species. Worth mentioning at this point, the hydride complex [Ru(tpy)(bpy)H]$^{+}$, which was electrogenerated in situ from 26a catalyzed the reduction of acetone to 2-propanol – a coulombic efficiency of ca. 28% was determined by gas-chromatographic (GC) analysis ($H_{2}$, as the major byproduct, was obtained with a coulombic efficiency of ca. 65%). In line with Meyer’s fundamental studies, a range of other complexes with structural variation on the tpy and/or the bpy ligand has been employed for the electrocatalytic CO$_2$ reduction. In particular, the bidentate ligand is susceptible for manipulation of its electronic nature via electron-donating or -withdrawing substituents, which directly influence the electron density at the Ru(II) center. This, in turn, controls the lability of the monodentate ligand L, which can be correlated to the CO$_2$ binding and, eventually, to the electrocatalytic activity. Ott et al. pointed out that depending on this scenario different mechanistic pathways – all enabling the CO$_2$ reduction – might be followed. For example, Masaoka et al. utilized complex 27 bearing a N ligand (Figure 19); this complex enabled the CO$_2$ reduction at much lower overpotentials as 26a. Mechanistic studies suggested that the strong P-donor ligand in trans-position to the solvato ligand facilitated its leaving and the fixation of CO$_2$. Related to this a simple CH$_3$-substituent on the bpy ligand in 28 tremendously increased the electrocatalytic activity (Figure 20). As a result of steric hindrance, the dissociation of the solvato ligand became favored. In this case, the CO$_2$ binding already occurred at the singly-reduced state and, thus, allowed to enter a catalytic cycle which is not accessible for the parent complex 26a. This catalytic cycle was characterized by a sequence of an initial electron transfer, a chemical reaction and a second electron-transfer step (ECT-type mechanism). As a result, an almost quantitative coulombic efficiency and a remarkably low overpotential of 0.47 V for the CO$_2$ reduction was found (for comparison, the overpotential of 26a was 0.87 V under the same conditions). Noteworthy, the presence of strongly electron-donating substituents does not necessarily lead to an enhanced electrocatalytic activity. The poor catalytic activity and fast deactivation was attributed an irreversible binding of CO$_2$ to the metal center; subsequent one-electron reduction afforded an inert Ru(II)-carbonyl species.

As a less common strategy, also the structure of the tptz ligand was modified. For example, the tpy ligand was replaced by a ptz one [ptpz: 2,4,6-tris(pyridine-2-yl)-1,3,5-triazine]. Electrochemical studies, supported by DFT calculations, revealed that the initial two one-electron reductions of the catalytic cycle both occurred on the ptz ligand, thus generating a formal ptz$^-$ moiety (instead of the tpy$^*$ and bpy$^*$ radical anions, as in Figure 20).

In order to replace the cost-intensive, less abundant heavy-metal centers in the aforementioned complexes by earth-abundant, first-row transition metal ions, Fontecave et al. focused on the homoleptic [M(tpy)$_2$]$_2$ complexes (M = Mn, Fe, Co, Ni, Cu and Zn). Within the series, only the Ni(II) and Co (II)-containing complexes were found to be active in the electrocatalytic CO$_2$ reduction. The [Ni(tpy)$_2$]$^{2+}$ complex exhibited a high selectivity for reducing CO$_2$ to CO, while the HER was suppressed. This finding was attributed to the high-valent nature of the complex which prevent the formation of Ni-hydride species – a prerequisite for $H_2$ formation. The low-valent [Co(tpy)$_2$]$^{2+}$ complex instead yielded a mixture of CO and $H_2$. The ratio of these could be controlled by adjusting the applied overpotential: At low potentials, CO formation was favored; whereas, the CO$_2$/H$_2$ ratio decreased with increasing the potential (at a potential of $-2.1$ V, a ratio of 1 was reached). The same authors also demonstrated that the CO-to-$H_2$ ratio could be adjusted by chemical modification of the tpy ligand. The bulk electrolysis of a CO$_2$-saturated aq. DMF solution gave the highest Faradic yield for $H_2$ (23%) when a MeO-group was placed on the tpy ligand. In the absence of strongly electron-donating substituents, the $H_2$ formation was retarded (Faradic yield < 5%) and the CO formation became favored.

In a different approach, Machan and Kubiak prepared Mn(I)-tpy mono-complexes, as designated catalysts for the electrocatalytic CO$_2$ reduction. Similar complexes, based on manganese’s heavy homolog Re, were already studied in the early 1990s. The complex [Re(ph-tpy)(CO)$_2$Cl], for example, was electrogenerated. The Mn(I)-tpy complexes 30, differing in their coordination mode, both yield a dimeric Mn(0) species upon one-electron reduction; from this intermediate the catalytically active [Mn(tpy)(CO)$_2$]$_2$ complex is obtained in a second reduction step (Figure 21). The rather poor catalytic performance of this catalyst with respect to the formation of CO from CO$_2$, when compared to the much more active Mn(I)-bpy species, was attributed to an improper ligand architecture (presumably, tridentate ligands require binding sites with increased donor strength as well as bulky substituents to prevent dimerization).

Besides the aforementioned homogeneous catalysts addressing the formation of higher-energy organic products from CO$_2$ by electrochemical reduction, also heterogeneous variants have been discussed against the same background. In this approach, homogeneous catalysts are immobilized onto appropriate solid supports; if the support is conductive, the immobilization yields a chemically modified electrode for usage
in electrochemical catalysis. In particular, glassy-carbon electrodes and nanocrystalline TiO$_2$ have been utilized in this context. In pioneering work in this field, Abruña et al. coated the former with thin metallopolymers films. These films were generated by electropolymerization of a vinyl-functionalized Co(II)-tpy bis-complex.\cite{312} In this initial study, the formation of formic acid occurred in CO$_2$-saturated DMF at a potential of $-0.90$ V (thus, at a much less negative value as in the case of unmodified carbon electrodes). It was further demonstrated that too high surface coverages permitted the permeation of CO$_2$ and, therefore, lowered the overall catalytic activity [a surface coverage ($I$) of ca. $10^{-8}$ mol/cm$^2$ was used in that study]. The same authors also reported on the CO$_2$ reduction in water using carbon electrodes covered with thin films derived from various vinyl-functionalized [M(tpy)$_2$]$^{2+}$ complexes ($M$ = Cr, Ni, Co, Fe, Ru, Os).\cite{313} The electrodes loaded with complexes of the first-row transition metal ion exhibited the highest catalytic activity: The electropolymerized films of [Cr(tpy)$_2$]$^{2+}$ revealed a current efficiency of ca. 87\%; whereas, TON values of $>15,000$ were reached for the electropolymerized films of [Cr(tpy)$_2$]$^{3+}$.

Besides the modification of electrodes by electropolymerization, appropriate metal-complex monomers, also the anchoring of functionalized metal complexes or ligands to electrode materials has been investigated. For example, Tanaka et al. demonstrated the deposition of a multi-layer films on glassy-carbon (GC) electrodes by electrochemical reduction of diazonium-functionalized Ru(II) complexes (Figure 22).\cite{314} The thusly modified electrodes were employed in the electrocatalytic CO$_2$ reduction to afford CO or formic acid. In a related study, Fontecave et al. functionalized a GC electrode with vacant tpy sites which were subsequently loaded with Co(II) ions.\cite{315} This electrode was employed in the electrocatalytic proton and CO$_2$ reduction. In contrast to the former, where a high stability and good catalytic activity in organic solvents and water was found, the CO production from CO$_2$ was only moderate (presumably due to the instability of the catalyst under the experimental conditions).

Not only GC electrodes have been chemically modified in order to obtain electrocatalytically active materials. McQueen and Goldsmith functionalized single-walled carbon nanotubes (SWCNTs) with [Co(tpy)$_2$]$^{2+}$ complexes via pending pyrene substituents which interacted with the SWCNTs in a supramolecular fashion, i.e., establishing robust π-π-stacking interactions.\cite{316}

Nanocrystalline TiO$_2$ represents an important semiconducting material which has been employed, both as substrate and electron relay, to facilitate photo-induced electron-transfer (PET) processes between photosensitizers and the catalysts. It has been shown that long-lived charge-separated states (CSSs) can be populated using nanostructured dye-sensitized TiO$_2$ photodevices; these CSSs represent one prerequisite to enable the multi-electron CO$_2$ reduction.\cite{317} Against this background, Meyer et al. anchored Ott’s Ru(II) catalyzed (28, see Figure 19) onto nanocrystalline TiO$_2$, via a phosphonate moiety (additionally, a protective NIO overlayer was deposited on top of the complex layer).\cite{318} This heterogeneous assembly, as depicted in Figure 23, was applied in the electrocatalytic CO$_2$ reduction. Formation of CO occurred at a potential of $-1.65$ V vs. Fe$^+/Fe$ during a period of 4 h, a maximum TON value of 237 was reached. According to XPS analyses of the as-prepared and used catalyst, the molecular structure was not affected by the long-term electrocatalytic run. Moreover, the heterogeneous catalyst was, by far, more efficient as its homogeneous counterpart: A Faradaic efficiency of 62.5\% and a very low TON value of 3 was observed in these experiments. The poor performance was attributed to the diffusion limitation of the homogeneous catalyst, i.e., the insufficient interaction with the electrode within a certain timeframe. Thus, the immobilization of catalysts onto electrode materials is highly beneficial to reach good electrocatalytic performances.

Similar to the previous work, Chauvin et al. immobilized the Mn(II) complex 30b (Figure 21), as catalyst, and [Ru(bpy)$_3$]$^{2+}$, as photosensitizer, via their lateral phosphonate moieties onto TiO$_2$.\cite{319} The co-assembled system was found to be efficient and selective for the photoelectrochemical reduction of CO$_2$ to formic acid (a quantum yield ($\phi$) of 0.17\% upon irradiation with visible light was reached). Photoelectrochemical studies suggested that the electron transfer from the photo-excited Ru(II) center to the Mn(II) site went through the conduction band of the semiconductor. The monomeric one-electron reduced Mn(0) complex was identified as the catalytically active species. The

**Figure 22.** Schematic representation of the electrochemical functionalization of glassy-carbon electrodes and their utilization in the electrocatalytic CO$_2$ reduction.\cite{314}

**Figure 23.** Schematic representation of nanocrystalline TiO$_2$ with grafted Ru (II) complexes.\cite{314}
reader is reminded, that under homogeneous conditions dimeric Mn(0)-Mn(0) species were involved, as pre-catalyst for the formation of CO. This significantly less efficient pathway was excluded under heterogeneous catalysis, thus enabling a fully selective photoelectrochemical reduction of CO$_2$ to formic acid with a TON of 27.

In order to fully avoid precious and expensive metals, Reisner and co-workers assembled phosphate-functionalized [Co(tpy)]$_2^{2+}$ complexes onto a light-harvesting p-type Si electrode, interfaced with a layer of mesoporous TiO$_2$.[320] This photocathode reduced CO$_2$ to CO with a TON value ca. 330 and showed a good long-term stability (i.e., the activity was retained for at least 24 h under operation). Spectroelectrochemical experiments disclosed a mechanistic pathway for the heterogeneous catalyst different from the one being valid under homogeneous conditions. The heterogeneous setup enabled the light-driven catalysis to proceed at a lower potential and with increased activity – not only in aq. organic solvents but also in water.

In order to further improve the photoelectrocatalytic activity of the electrodes, the same authors prepared the copolymers 31 (Figure 24a) by free-radical polymerization and subsequently loaded them with Co(III).[321] The resultant partially cross-linked metallopolymers were immobilized onto a mesoporous inverse opal TiO$_2$ (IO-TiO$_2$) via their phosphate moieties. In this environment, the Co(III) catalyst sites were surrounded by the hydrophobic residues which enabled the selective CO$_2$ reduction in the presence of water (Figure 24b/c). This outer-sphere effect has been identified earlier to be beneficial for the selective reduction of CO$_2$ to CO, while suppressing the proton reduction.[322] A variety of electrode materials were combined with the IO-TiO$_2$/metallopolymer hybrid material and tested with respect to the production of CO and H$_2$ from CO$_2$-purged aq. acetonitrile.[321] From the systems under investigation, the photocathode with the composition Si/IO-TiO$_2$/metallopolymer yielded the highest selectivity with respect to the obtained CO-to-H$_2$, i.e., a product selectivity for CO of ca. 80% over 6 h. For comparison, the homogeneous “monomeric” [Co(tpy)]$_2^{2+}$ catalyst only offered a 2:1 ratio under the same experimental conditions.

Besides the aforementioned (light-driven) electrocatalytic reduction of CO$_2$, also the photocatalytic variant has attracted considerable interest. From the wide range of homogeneous[323–324] and heterogeneous[325] photocatalytic systems reported in the literature, the heteroleptic Ir(III) complexes of the general formula [Ir(tpy)(ppy)L]$^{2+}$ (L = Cl or CN) have to be mentioned at this point. Ishitani et al. studied the complexes 32 (Figure 25) with respect to their ability to photochemically reduce CO$_2$ in the presence of triethanolamine, as sacrificial donor.[326] From the complexes under investigation, 32b was found to be most efficient candidate for the photoreduction of CO$_2$ to CO (TON = 50, φ = 0.21). In comparison to the well-known Re(I) catalysts some advantages were listed by the authors: CO production upon irradiation with visible light in absence of an additional photosensitizer as well as increased photocatalytic activity and high selectivity in product formation – even in the presence of water. Mechanistic studies were performed and suggested the formation of an [Ir(tpy)(ppy)L]$^{2+}$ intermediate, as the virtual photocatalytically active species; moreover, the formation of dinuclear complexes was discussed as one potential deactivation pathway (Figure 25). The catalytic cycle, with a focus on the reaction of the [Ir(tpy)(ppy)L]$^{2+}$ intermediate with CO$_2$, was investigated in more detail by using spectroscopic and computational methods.[327] The two possible geometrical isomers, i.e., the C-trans and the C-cis hydride isomer, yielded the same penta-coordinate two-electron reduced [Ir(tpy)(ppy)L]$^0$ complex within the photocatalytic cycle to which CO$_2$ was subsequently bound in a C-trans-fashion. In the ground state, however, only C-trans-[Ir(tpy)(ppy)L]$^+$ reacted with CO$_2$ to give a formato adduct. This discrimination in reactivity was rationalized by the significantly different hydricity values, as derived from computational studies. Bemhard et al. paid special attention to the photophysical properties of 32a (and the analogous complex with CN$^-$ as monodentate ligand).[324] These complexes were applied as photocatalysts for the HER (see Section 3.2) and revealed a remarkable photo-
stability, in particular in strongly coordinating solvents – a prerequisite for using such complexes, as photocatalysts, for the CO₂ or proton reduction.

Sato et al. also employed the dicationic complex [Ir(tpy)(bpy)Cl]²⁺ (33, Figure 26), as photocatalyst for the CO₂ reduction. As for its cyclometalated analogs 32, the formation of the one-electron reduced hydride species [Ir(tpy)(bpy)H]⁻, involved in the selective CO production, was corroborated by in-situ spectroscopic measurements. However, at a longer irradiation time this complex was ligand-reduced further to yield the hydride complex 34 (Figure 26), which could even be isolated and structurally characterized. This species, in turn, no longer supported the CO production, but enabled the selective formation of formic acid instead. When the photocatalytic CO₂ reduction (at 436 nm) was performed in the presence of pre-formed 34, a quantum yield (ϕ) of 2.1 % for the formation of HCOOH was obtained.

Finally, Rieger et al. compared the photocatalytic performance of mononuclear [Ir(tpy)(bpy)Cl]⁻ complexes to that of analogous di- and trinuclear assemblies. For this purpose, the series of complexes 35–37 was prepared (Figure 27). The photocatalytic reduction of CO₂ yielded, in the case of 35, CO with a maximum quantum efficiency of 18%. In contrast to 36a, the dinuclear complexes 36b and 36c gave similar efficiencies. The poor ϕ value of 36a was attributed to an intramolecular quenching process, facilitated by the short spacer unit. Nonetheless, all dinuclear complexes 36 showed an improved photo-stability, as revealed by their TON values of >80 (a TON of 33 was obtained for 35). Concerning the photocatalytic activity, the TOF values were calculated and showed highest value for 35 (TOF = 35 h⁻¹), followed by 37 and 36a (TOF of 21 h⁻¹ and 12 h⁻¹, respectively).

3.2. Hydrogen-evolution reaction

Similar to the CO₂ reduction, as detailed in the previous Section, also the formation of molecular hydrogen, as potential sustainable fuel source, has attracted enormous attention. In the context of keeping up the energy supply in a time of global warming and decline of fossil resources, the artificial photosynthesis, i.e., the light-driven splitting of water into H₂ and O₂, becomes increasingly important. A broad range of homogeneous and heterogeneous catalysts have already been employed in order to reach this goal with high activity and long-term stability.

The cationic Ir(II) complexes, in particular of the general formula [Ir(ppy)₂(bpy)]⁺, have been found to be superior to, e.g., Ru(II)-based systems with respect to the quantum yield of the HER. Many structural variants of these photocatalysts have been prepared and studied with respect to photocatalyze the HER. Bernhard et al. utilized Ishitani’s Ir(III) complex 32a as chemical lead to prepare a library of related complexes (38 and 39, Figure 28). The modulation of the substitution enabled a tuning of the photophysical and electrochemical properties; typically, bright room-temperature luminescence with lifetimes (τ) close to 3 μs and quantum yields (ϕₚₜ) up to ca. 29% were found (Figure 28). When used as photosensitizer the series of complexes 32, 38, and 39 showed an improved photo-stability, as revealed by their TON values of >80 (a TON of 33 was obtained for 35). Concerning the photocatalytic activity, the TOF values were calculated and showed highest value for 35 (TOF = 35 h⁻¹), followed by 37 and 36a (TOF of 21 h⁻¹ and 12 h⁻¹, respectively).

3.2. Hydrogen-evolution reaction

Similar to the CO₂ reduction, as detailed in the previous Section, also the formation of molecular hydrogen, as potential sustainable fuel source, has attracted enormous attention. In the context of keeping up the energy supply in a time of global warming and decline of fossil resources, the artificial photosynthesis, i.e., the light-driven splitting of water into H₂ and O₂, becomes increasingly important. A broad range of homogeneous and heterogeneous catalysts have already been employed in order to reach this goal with high activity and long-term stability.

The cationic Ir(II) complexes, in particular of the general formula [Ir(ppy)₂(bpy)]⁺, have been found to be superior to, e.g., Ru(II)-based systems with respect to the quantum yield of the HER. Many structural variants of these photocatalysts have been prepared and studied with respect to photocatalyze the HER. Bernhard et al. utilized Ishitani’s Ir(III) complex 32a as chemical lead to prepare a library of related complexes (38 and 39, Figure 28). The modulation of the substitution enabled a tuning of the photophysical and electrochemical properties; typically, bright room-temperature luminescence with lifetimes (τ) close to 3 μs and quantum yields (ϕₚₜ) up to ca. 29% were found (Figure 28). When used as photosensitizer
in the photocatalytic HER with K₂PtCl₄ as pre-catalyst, and triethylamine (TEA), as sacrificial donor. The observed TONs in aq. acetonitrile, reaching a maximum of 1,500 for 39b, were significantly higher as for the complexes of the [Ir(ppy)₂(bpy)]⁺ family (these complexes prone to fast photo-degradation in strongly coordinating solvents). Complex 38f, having a “push-pull” ligand design, exhibited remarkably fast initial reaction rates (TON of 1,300 after 5 h). Though being more robust in a coordinating environment, complexes 32a, 38 and 39 still exhibited a deactivation pathway, which is the displacement of the monodentate anionic ligand (i.e., Cl⁻ or CN⁻).

In a subsequent study, the same research group synthesized the highly fluorinated Ir(III) complexes 40 and 41 as designated photosensitizers for the HER (Figure 29).[336] Thereby, a new synthetic route yielding the chloro-complexes 40 was introduced: C–F activation instead of the “traditional” C–H activation afforded the complexes in reasonable yields. When applied as photosensitizer in the light-driven HER, complex 41b featured by far the best performance in terms of TON – a value of ca. 1,300 was reached after 15 h. Concerning the chloro-complexes 40, it was shown, that increasing the degree of fluorination had a detrimental effect on the photosensitizing performance. This finding was attributed to the nature of the excited state, which was more metal-centered for the highly electron-poor (i.e., highly fluorinated) ligands. It was further reported that 40 and 41 acted as photocatalysts for decarboxylative fluorination of carboxylic acids with Selectfluor, as fluorine source (Figure 29). This special reactivity was attributed the photo-formation of an Ir(IV) species via an oxidative quenching pathway. This intermediate, in turn, was suggested to decarboxylate the substrate, leaving a radical behind which was trapped by reaction with the fluorine source.

A different structural approach was followed by Hanan, Elias and co-workers: These authors designed the monocationic Ir(III) complex 42 comprising two tridentate ligands – a bis-cyclo-metalating CNC and a tpy one.[337] In this ensemble, the lowest unoccupied molecular orbital (LUMO) is located on the tpy ligand and the UV/vis absorption is strongly red-shifted (compared to [Ir(ppy)₂(bpy)]⁺ and [Ir(NNC)₃]⁺ complexes[338], thus a visible light can be harvested much more efficiently. The terminal pyridyl moiety enabled the coordination of 42 to a cobaloxime complex (Figure 30a). Such complexes are known for their ability to function as powerful hydrogen-evolution catalysts in the presence of appropriate photosensitizers.[339] The resultant 42-cobaloxime dyad, offering a directional arrangement of the components was, by far, more efficient in producing H₂ than a bimolecular combination of the [Ir(ppy)₂(bpy)]⁺ photosensitizer and the cobaloxime catalyst (Figure 30b).

In 2009, Sakai et al. demonstrated that the structurally simple [Pt(tpy)Cl]⁺ complex represents a powerful system...
functioning as a dual mode: Photosensitization and catalysis of the light-driven HER in aqueous environment with EDTAH\textsuperscript{2-} as sacrificial donor.\textsuperscript{[344]} Control experiments ruled out that colloidal Pt was involved in \( \text{H}_2 \) production and that the \( \text{H}_2 \)-evolving catalyst was of sufficient thermal stability, even in the presence of \( \text{H}_2 \).\textsuperscript{[341]} Yamashita et al. applied X-ray absorption spectroscopy to gain further insight into the photocatalytic HER driven by [Pt(tpy)Cl]\textsuperscript{2-}.\textsuperscript{[342]} In line with Sakai’s study, these measurements corroborated mononuclear Pt(II) complexes to be the catalytically active species and Pt(0) intermediates could not be identified. Thus, the direct photocatalytic [Pt(tpy)Cl]\textsuperscript{2-} systems is simpler and more efficient when compared, to earlier examples where e. g., luminescent Pt(II)-tpy acetylene complexes and 1,4-dihydropyridines were used, as photosensitizer and hydrogen source, respectively.\textsuperscript{[344]} By placing a redox-mediating N-methylpyridinium moiety onto the tpy ligand, the photocatalytic activity of the resultant Pt(III) complex 43 was increased significantly when compared to the parent [Pt(tpy)Cl]\textsuperscript{2-} complex (Figure 31a).\textsuperscript{[344]}

Complex 43 exhibited an increased photo-stability, i.e., retaining its activity up to 12 h. The authors ascribed this stabilization to a lower deactivation rate involving substitution of the Cl\textsuperscript{-} ligand by an CH\textsubscript{3}COO\textsuperscript{-} one (this process leads to full deactivation of [Pt(tpy)Cl]\textsuperscript{2-} within 30 min). The activity of 43 in the HER could be increased further by adding a Pt(II) co-catalyst.\textsuperscript{[345]} In particular, the well-known chemotherapeutic agent cis-Pt(NH\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} strongly enhanced the photocatalytic performance when combined with 43 (Figure 31b). The authors compared this behavior to the electron-transport chain in natural photosynthesis, the so-called “Z-scheme”.

Moreover, Sakai et al. prepared the tris-carboxylated complex Na\textsubscript{3}[Pt(tctpy)Cl] which existed as fully deprotonated species at a pH value of > 4.4 (tctpy: 4,4',4''-carboxy-tpy).\textsuperscript{[346]} Photoexcited [Pt(tctpy)Cl]\textsuperscript{3+} formed an adduct with the EDTAH\textsubscript{2-} anion, in which reductive quenching occurred. This process paved the way to the eventual \( \text{H}_2 \) formation from water (Scheme 53). Noteworthy, a ligand-based proton-coupled electron-transfer (PCET) process, known to lower the activation barrier of catalytic processes, was assumed to be involved in the overall photocatalytic HER.

Recently, a heterobimetallic assembly, in which a bis-cyclometalated Au(III) complex was attached, as sensitizer, to the [Pt(tpy)]\textsuperscript{2+} fragment via an ethinyl bridge, was reported by Su et al.\textsuperscript{[347]} Though the HER occurred with a maximum TON of 91, the short excited-state lifetime reduced the photocatalytic efficiency of the dyad, in particular when compared to Hanan’s and Elias’ catalyst (Scheme 30).\textsuperscript{[317]}

Yamashita et al. immobilized the [Pt(tpy)Cl]\textsuperscript{2+} photocatalyst onto amino-functionalized mesoporous SiO\textsubscript{2}.\textsuperscript{[348]} Due to the close proximity of the complex sites within the support’s channels bright photoluminescence at 630 nm (attributed to metallophilic Pt... interactions between adjacent complexes) as well as photocatalysis of the HER was observed. At a Pt(II) loading of 2.4 wt-%, the heterogeneous catalysts revealed an increased activity when compared to the homogenous variant under the same experimental conditions.

Figure 31. Schematic representation of the Pt(II)-tpy complex 43. (a) The plot shows the light-driven \( \text{H}_2 \) evolution catalyzed by 43 (in presence and absence of EDTAH\textsubscript{2-} and [Pt(tpy)Cl]\textsuperscript{2-})\textsuperscript{[343]} (b) Relative HER activity of various two-component systems (i.e., 43 in the presence of a co-catalyst; eda: 1,2-ethylenediamine).\textsuperscript{[346]} Figure reproduced with kind permission; © 2012 The Royal Chemical Society and Wiley-VCH.

Scheme 53. Schematic representation of photocatalytic HER using the anionic complex [Pt(tpy)Cl]\textsuperscript{2-} as photocatalyst (EDTAH\textsubscript{2-} denotes the dianion of EDTAH\textsubscript{2-})\textsuperscript{[346]} Figure redrawn with kind permission; © 2015 The Royal Chemical Society.
The same authors also employed layered $K_NbO_4$, as solid support to obtain a heterogeneous photocatalyst for the HER.\textsuperscript{(349)} The photophysics of $K_NbO_4$, can be modulated by intercalating photoactive dyes, such as transition metal complexes. The intercalation of [Pt(tpy)Cl]$^{2+}$ afforded a hybrid material which exhibited a similar room-temperature emission as the aforementioned SiO$_2$-based material. Also, in this case, a strong increase in the photocatalytic activity compared to homogeneous [Pt(tpy)Cl]$^{2+}$ was found (Figure 32). The heterogeneous photocatalyst could easily be recovered and reused – without Pt(II) bleaching or loss of activity over several photocatalytic experiments.

An even more sophisticated hybrid material targeting the photocatalytic HER in water was reported by Kishimoto \textit{et al.}\textsuperscript{(350)} The authors assembled a layered structure comprising titanate and tungstate nanosheets in a strictly alternating fashion (the layers were covalently linked by thiol-ene reactions). [Ru (bpy)$_3$]$^{2+}$, as photosensitizer, was embedded between the layers and [Pt(tpy)Cl]$^{2+}$ units were attached to the edges of the $[Tb_{6}O_{24}]^{0.36}$ nanosheets. As depicted in Figure 33, photoexcitation of the PS enabled a highly directional electron transfer from the valence band of $[W_{4}O_{12}]^{2-}$ to the conduction band of $[Tb_{6}O_{24}]^{0.36}$. The kinetics of this process were studied and showed that the forward electron-transfer process was dominant over the backward one (1.16x10$^{-4}$ s$^{-1}$ vs. 1.02x10$^{-5}$ s$^{-1}$). Subsequently, the electrons were transferred further to the [Pt(tpy)Cl]$^{2+}$ catalyst sites which, in turn, produced $H_2$ from water. In this scenario, the interlayer organics served as hole scavenger, i.e., they became oxidized by the hole generated in the conduction band of the $[W_{4}O_{12}]^{2-}$ nanosheets.

In a different approach, MOFs were assembled from the carboxylated Ru(II)-tpy bis-complex 44 and metal-oxo cluster units. These robust materials were employed, as photocatalysts, for the HER or the CO$_2$ reduction (see Section 3.1).\textsuperscript{(351-353)} The MOF comprising 44, as photosensitizer and Ti-oxo clusters, as catalyst for proton reduction, was demonstrated to produce $H_2$ upon irradiation with visible light up to 620 nm (Figure 34). The efficiency of the photocatalyst could be improved by deposition of colloidal Pt onto the MOF. From the sacrificial donors tested, TEOA showed the best $H_2$ evolution performance (11 μmol over 6 h). In control experiments, the hybrid material simply derived from the adsorption of 44 onto Evonik’s AEROXIDE® TiO$_2$ P-25 was photocatalytically inactive. The authors concluded that the defined molecular environment, as offered in the high-ordered MOF ensemble is important for the electron transfer from the photo-excited Ru(II) centers to the Ti-oxo clusters.

In all previous homogeneous or heterogeneous systems addressing the photocatalytic HER, precious transition metal complexes were employed. Substantial progress has also been made in employing molecular catalysts based on earth-abundant metals for the same purpose.\textsuperscript{(353)} From the various complexes based on Fe(II), Co(II) or Ni(II) ions, one example incorporating Ni(II)-tpy bis-complexes has to be mentioned in this context. Zhang \textit{et al.} synthesized an inorganic-organic hybrid material by immobilizing the HER catalyst 45 onto NH$_2$-functionalized CdS nanosheets, as photosensitizing substrates (Figure 35).\textsuperscript{(354)} Upon irradiation with visible light, the hybrid...
A photocatalyst yielded a TON of ca. 45,000 (vs. Ni(II) sites on the substrate) and a TOF of 0.47 s\(^{-1}\) over 26 h; the quantum yield for the HER reached ca. 10%. The authors pointed out that the covalent linkage between the substrate and the complexes was beneficial for the photocatalytic performance: The amount of generated H\(_2\) was much higher as observed for a mixed system containing DETA-loaded CdS and a molecular \([\text{Ni(tpy)}]^{2+}\) complex under the otherwise identical experimental conditions (DETA: diethylenetriamine).

As discussed in Section 3.1, Fontecave et al. employed Co (II)-tpy bis-complexes for the electrocatalytic reduction of CO\(_2\) to CO\(_x\)). When grafted onto GC electrodes, this reaction was found to be in competition with the HER. Thereby, the obtained CO-to-H\(_2\) ratio could be adjusted via the applied voltage and the chemical structure of the tpy ligand. In line with these studies, these authors prepared the library of Co(II) complexes 46 (Figure 36) and tested them in the electrocatalytic HER from acetic acid in acetonitrile solutions. The ligand architecture had a profound impact on the catalytic performance of the complexes with respect to their stability and overpotential (e.g., complex 46a readily decomposed in the presence of AcOH). The NMe\(_2\)-equipped complexes (46b and 46f–h) exhibited the highest catalytic activity and stability; moreover, H\(_2\) production was enabled at low overpotentials. The authors applied DFT calculations to gain insight into the reaction mechanism and to different pathways could be identified: In the case of complexes 46a–e, the HER involved the intermediate reduction of the central pyridyl rings of the ligands, while retaining the six-coordinate geometry at the Co(II) centers. For the other complexes within the series, 46f–h, the amino-substituents acted as a proton relay for the N-protonation of an outer pyridyl ring which paved the way to form a Co(II)-hydride intermediate. The experimental data suggested that the latter pathway is more efficient with respect to the overall HER. Recently, Padhi et al. reported on a quinol-4-yl-substituted Co(II)-tpy bis-complex which showed a similar behavior as the amino-bearing complexes 46f–h. However, the hydride intermediate was not observed in the electrocatalytic studies in protic environments; instead, solvato complexes were suggested, as catalytically active species.

### 3.3. Water-oxidation reaction

The complementary reaction to the HER, the oxygen-evolution reaction (OER), has also attracted considerable interest. Consider-
ering the water electrolysis (Scheme 54a), the cathodic half-reaction, i.e., the H₂ formation, is thermodynamically more favored than the anodic O₂ formation (ΔG of +475 kJ per mol O₂). In total, the electrochemical splitting of water represents an “uphill” process, which is further hampered by kinetic barriers – the overpotentials. With respect to the four-electron oxidation of water, not only the four electron and proton equivalents have to be diverted – also an intrinsically weak O–O single bond has to be established, as intermediate. Basically, transition metal complexes can be employed to support the electron outward flow and, simultaneously, reduce the energetic cost related to the formation of the O–O single bond. As pointed out by Nocera et al., two distinct mechanistic pathways can be distinguished: The acid-base interaction and the radical coupling. In either case, a high-valent metal-oxo intermediate is required which results from the corresponding aquo complex via proton-coupled electron-transfer steps (Scheme 54b). In short, the reactivity of the metal-oxo species strongly depends on the nature of the transition metal center (i.e., its d-electron configuration) and the overall ligand field. In the first case, water attacks, as nucleophile, the electrophilic oxo-ligand. Noteworthy, the electrophilicity correlates with the oxidation state and the molecular environment offered by the surrounding ligands. The coupling of two oxo-radical species, thus yielding the intermediate O–O single bond, represents the alternative pathway.

A wide range of water-oxidation catalysts (WOCs), based on Mn, Ir, Fe, Cu, and Ru ions has been reported so far. However, Ru has, by far, attracted the greatest attention in the last decades. The presumably first indication for an OER from water involving a Ru(IV) species, in-situ generated from ReO₃, by reduction with H₂O₂ or Fe(II), and ceric ammonium nitrate (CAN), as oxidant, was published by Gortsema and Cobble in 1959. Later, Meyer et al. synthesized stable Ru(IV)-oxo complexes via PCET processes. Special tribute has to be paid to Meyer and co-workers who introduced the first structurally characterized WOC, namely the dinuclear μ-O-bridged Ru(II) complex 47 (Figure 37), which is often referred to as the “blue dimer”. Starting from this seminal work a range of dinuclear complexes, representing the 1st generation WOCs, was prepared and some notable examples (48 to 50) containing tpy ligands are depicted in Figure 37. Tanaka’s catalyst (49) for example, produced O₂ in water (at a pH value of 4) with a TON of 33,500 when using an ITO electrode for the electrolysis.

A paradigm change happened when Thummel et al. introduced mononuclear Ru(II) complexes which could catalyze the OER. “One site is enough.” Before this, it was believed that the multi-electron nature of this process could not be stemmed by a single-site complex. This opinion arose from the knowledge on the structure of the multi-centered Mn cluster, as the O₂-evolving species in the PS-II and the non-existence of catalytically active mononuclear complexes. On the basis of this finding, the groups of Thummel, Sakai and Meyer almost simultaneously published a range of mononuclear Ru(II) complexes, as the 2nd generation WOCs.

In detail, Thummel et al. screened a library of [Ru(tpy)(bpy)Cl]⁺ (51a–e) as well as various Ru(II)-polypyridyl complexes (51f–l, 52 and 53; Figure 38). From these, 51a–f and 51l exhibited a catalytic activity in OER fromaq. CH₃CN with CAN, as oxidant; however, only moderate TONs in the range of 110 to 570 were found. In the same way, O₂-evolution with TONs of 95 and 135 was reported for 52 and 53, respectively. Berlinguette et al. investigated the influence of electron-donating and -withdrawing substituents on the polypyridyl ligands on the catalytic performance in more detail. Basically, electron-poor substituents on the bpy ligand (as in 51d) lowered the catalytic activity while increasing the TON. Electron-rich substituents (as in 51c) had the opposite effect, as revealed by increased catalytic rates and decreased WOC stabilities. The formation of bpy-N₄,N₄'-dioxides was observed in the presence of an excess of CAN at low pH values. This finding was attributed to a dissociation of the bpy ligand and its subsequent oxidation under the reaction conditions. Thus, a

Scheme 54. (a) Schematic representation of the water electrolysis. (b) Schematic representation of the two different mechanistic pathways to enable the metal-catalyzed formation of the O–O single bond.
potential decomposition/deactivation pathway for the WOCs 51 could be identified. Thummel et al. also reported that the catalytic activity could be increased significantly by using a tetradentate polypyridyl ligand in the coordination sphere of the Ru(II) center: The complex [Ru(dpp)(pic)]$_2$ $^{2+}$ (dpp: 2,9-di(pyridine-2-yl)-1,10-phenanthroline) offered a TON of 416 with a $O_2$-evolution rate 0.330 mol/min and a TOF of 27.5 $s^{-1}$. This complex represents the first example of 3$^{rd}$ generation Ru(II)-based WOCs where tetra- or even pentadentate polypyridyl ligands are employed.

By the same time, Sakai et al. also studied the water oxidation using WOC 51a in the presence of CAN, as oxidant. The authors identified an induction period after which $O_2$-evolution started; whereas, the corresponding aquo complex 54 immediately produced $O_2$. Thus, the latter was suggested as the factual catalytically active species, which was generated in situ from 51 in a ligand-exchange reaction. This assumption was corroborated by NMR spectroscopic studies in which this process was monitored: Almost 55% of 51a was converted into 54 within 7 h. Thummel et al. also compared the catalytic activity of various halide complexes, such as 55 (Figure 38), to that of parent 51a and 54. Remarkably, 55b showed no induction period with the initial rate of $O_2$-evolution being similar to that found for 54. It was speculated that a seven-coordinate [Ru(tpy)(bpy)(H$_2$O)]$^{2+}$ might have formed and, thus, the Ru-I bond remained intact course of the catalytic cycle. This assumption, however, was disapproved later by Pushkar et al. on the basis of EPR and X-ray absorption spectroscopic studies. Instead, initial oxidation of 55b to the Ru(III) species was readily followed by a reductive cleavage of the Ru-I bond and the resultant intermediate coordinated water to yield 54, as the active WOC.

In line with Thummel’s and Sakai’s work on Ru(II)-polypyridyl complexes, as WOCs, Meyer et al. focused on the aquo variants of 51j and 51k and reported the first in-depth mechanistic study on the OER. The proposed catalytic cycle, as derived from electrochemical and photophysical studies, is depicted in Figure 39. The three-electron oxidized Ru(V)-oxo species was considered as essential intermediate for thermodynamic reasons – the water-oxidation involving such highly-oxidized Ru(V) species is exergonic; whereas, the involvement of Ru(IV) species is slightly endergonic (Scheme 55a). Moreover, the peroxy species [Ru(V)-OOH]$_3^{2+}$ and [Ru(V)-OO]$_2^{2+}$ were discussed as high-energy intermediates contributing to the oxidation of $H_2O$ to $H_2O_2$ (Scheme 55b); the latter was suggested as a “resting state” within the catalytic cycle. However, this mechanism was opposed by Pushkar et al. who confirmed [Ru(V)-O(OH)]$_2^{2+}$ to be the predominant steady-state species within the catalytic cycle when using 54, as WOC (ca. 95% abundancy). EPR measurements ruled out an involvement of paramagnetic Ru(V) species as rate-limiting intermediates. The EPR signature was assigned to Ru(III)-peroxy species with an overall contribution of ca. 5%. The authors concluded that the proposed [Ru(V)=O]$_2^{2+}$ species was, for thermodynamic reasons, not accessible under the experimental conditions. The revised catalytic cycle, bypassing this intermediate is shown in Figure 40.

Concerning the kinetics of the OER, some contradictory statements have been made: The $O_2$-evolution reaction using 54 and CAN (30 to 200 eq.), as WOC and oxidant, respectively, was found to follow 1$^{st}$ order kinetics with respect to 54; whereas 0$^{th}$ order kinetics were evidenced for CAN. Thus, the electron-transfer processes appeared not to be the rate-

![Figure 38. Schematic representation of the Ru(II)-polypyridyl WOCs 51–55 (pic: 4-picoline).](image-url)

![Figure 39. Schematic representation of the proposed mechanism for the catalytic water-oxidation reaction according to Meyer et al.](image-url)

**Scheme 55.** (a) Thermodynamics of the water-oxidation reaction involving Ru(V) or Ru(IV) intermediates. (b) Oxidation of the water to hydrogen peroxide, presumably involving peroxy complexes, as intermediates.
limiting steps; whereas, the formation of the O–O single bond or the final release of O\(_2\) might well be rate limiting. On the other hand, the OER was reported to obey 1st order kinetics for both 54 and CAN (10 eq.).\(^{[375]}\) According to Yagi et al., these findings can be rationalized by a Michaelis-Menten-type behavior of the OER in which the order of the kinetics is mainly governed by the concentration of the CAN oxidant.\(^{[376]}\)

The further structural development of Ru(II)-polypyridyl WOCs was mainly devoted to utilizing ligands with increased denticity, in the easiest case 2,2\(^{\prime}\)-bpy-6,6\(^{\prime}\)-dicarboxylate ligands, which offer a more robust coordination environment and, e.g., prevent isomerization processes.\(^{[377]}\) Introducing carboxylate moieties on the polypyridyl ligands, as additional anionic binding sites, enables the stabilization of higher oxidation states of the coordinated metal center and, simultaneously, lowers the associated redox potentials. This strategy was first realized in some dinuclear complex and later extended to obtain charge-neutral Ru(II) complexes with tetradentate 2,2\(^{\prime}\)-bpy-6,6\(^{\prime}\)-dicarboxylate ligands occupying the four equatorial positions of the octahedral coordination sphere.\(^{[357]}\) Such complexes bind water, as the initial step of the OER, to yield seven-coordinate intermediates.

Llobet et al. utilized the analogous tpy-based ligand to obtain the Ru(II) complex 56 in which the pentadentate ligand was coordinated in a \(k^4\)-type fashion with one pending carboxylate moiety.\(^{[380]}\) As verified by X-ray diffraction analysis, the two-electron oxidized Ru(IV) species was, due to the increased electrophilicity of the Ru ion, able to coordinate the ligand in a \(k^4\)-type fashion, thus forming a seven-coordinate Ru(IV) complex (Scheme 56). This species, in turn, was found undergo a ligand-exchange reaction in a neutral or basic aqueous environment – one carboxylate arm was de-coordinated and the resultant vacant binding site was occupied by OH\(^-\). In the next step, the catalytically active Ru(V)-oxo intermediate was generated and \(O_2\)-evolution became enabled. The OER was supported by the pending carboxylate moiety which acted as an “internal base”, thus facilitating the nucleophilic attack of water at electrophilic Ru(V)-oxo site in a PCET process. The electrocatalytic water oxidation, at an onset potential of ca. 1.2 V (vs. Ag/AgCl) under pH-neutral conditions in the neutral pH regime with 56, as WOC, yielded a remarkable TOF of 8,000 s\(^{-1}\).\(^{[382]}\)

In related studies, also the Ru(II) complexes 57 and 58 were studied (Figure 41). The missing carboxylate arm of 57, compared to 56, had a detrimental effect on the activity as WOC as revealed by electrochemical studies of 56 and 57 under the same experimental conditions (pH value of 10 to 11, phosphate buffer, scan rate of 100 mV/s in CV measurements).\(^{[383]}\) Thus, the “internal base” effect, facilitating the intramolecular transfer of protons, is highly beneficial when aiming for efficient WOCs. Llobet et al. prepared the Ru(II) complex 58 featuring an aquo ligand in an axial position.\(^{[384]}\) Mechanistic studies suggested at this pre-catalyst is converted into a seven-coordinate Ru(V)=O species in which the axial position of the oxo-ligand prevented hydrogen-bonding interactions with the carboxylate moieties of the equatorial ligand. As a result, the “internal base effect” was switched off and,
consequently, a much lower TOF was observed (compared to 56 under the same experimental conditions) and the free activation (e.g. $G^*$) for the formation of the O–O single grew by 21.8 kJ/mol relative to 56. This finding again emphasizes the crucial role of “dangling” carboxylate moieties with respect to the catalytic activity of the WOCs. Following this concept, but using a completely different ligand design, Schwalbe et al. investigated the designated WOC 59 (Figure 41). The substituents, the so-called “hangman motif”, was introduced by Nocera et al. earlier and found to improve the catalytic activity of metal complexes in the oxygen-reduction reaction (ORR) or OER. However, complex 59 did not exhibit an increased catalytic activity in the OER with CAN, as oxidant, when compared to, e.g., 51a, 54 or 55b (Figure 38). However, under cautious control of the pH value, i.e., matching the pK$_\text{a}$ value of the substituent, the electrocatalytic O$_2$-evolution in the presence of 59 was accelerated by a factor of four compared to 55b.

Similar to the approaches discussed in the context of the CO$_2$ reduction and HER, the Ru(II)-based WOCs have also been immobilized, for example, by incorporating them into a robust MOF structure. Independently from each other, the Morris and Ott groups followed basically the same strategy. Ott et al. assembled a thin MOF film onto a conductive FTO substrate, as electrode (Figure 42). The step-wise synthesis involved the formation of a UiO-67 framework, in which the Zr$_6$O$_4$(OH)$_8$ clusters were linked via biphenyl-4,4’-dicarboxylate (bpdc) moieties; subsequently, the MOF was doped with the WOC 60 in a post-synthetic exchange reaction (i.e., replacing some of the bpdc units by the equally sized WOCs). According to inductively coupled plasma (ICP) analysis, a degree-of-exchange of 6.43% was reached. When applied as electrocatalyst in the water-oxidation reaction, continuous O$_2$-evolution occurred over hours at a potential of 1.5 V (current density of 11.5 $\mu$A/cm$^2$); the Faradaic efficiency for the OER was determined as 82%. In-operando electrochemical studies revealed the high stability of the assembly under electrocatalytic conditions: The Ru$^2$/Ru$^3$ redox wave in the CV curves was stable in time over several hours. Thus, the deactivation of the WOC, e.g., by agglomeration into clusters, was efficiently suppressed by incorporating them into a rigid-robust environment.

Inspired by the O$_2$-evolving active site in the natural PS-II, which is a Mn$_4$CaO$_4$ cluster (Figure 43a), Brudvig, Crabtree et al. introduced the dinuclear $\mu$-O-bridged mixed-valence Mn(III)/Mn(IV) complex 61 as WOC (Figure 43b). This complex represents a prominent example for a molecular WOC in which precious transition metals are avoided (for a review on Mn compounds employed in the context of water oxidation, see refs. [392–393]). In the presence of 61, O$_2$-evolution from water with NaOCl, as oxidant, occurred over 6 h; thereafter the catalyst was decomposed into MnO$_2$ (presumably due to the disproportionation of the Mn(V)/Mn(IV) intermediate). Mechanistic studies suggested that the Mn(IV)/Mn(IV) species, characterized my mass spectrometry and UV/vis absorption spectroscopy, was dominant in solution. Furthermore, $^{18}$O-labelling experiments confirmed that the oxygen atoms of the generated O$_2$ originated exclusively from water molecules. The proposed catalytic cycle is summarized in Scheme 57. Hou et al. analyzed the thermal stability of 61 in solution and decomposition, accompanied by a change in the valency occurred at ca. 60 °C. The authors speculated that the thermal deactivation of the natural Mn$_4$CaO$_4$ cluster might be associated with such a process. Remarkably, a Mn-containing precipitate (presumably a Mn-oxo oligomer) was formed at elevated temperatures which was still active in the OER.

Though 61 was found to be a WOC in the presence of NaOCl or oxone, as oxidant, no O$_2$ production was observed when using CAN, as oxidant. Yagi et al. addressed this issue and reported that O$_2$-evolution efficiently occurred when the catalyst is absorbed onto a heterogeneous matrix, such as clays (Figure 44). For example, when Kaolin clay was used, as support, 13.5 mol of O$_2$ per mol WOC 61 were produced over 7 days.

Figure 43. (a) Schematic representation of the structure of the Mn$_4$CaO$_4$ cluster and its position within the protein environment. (b) Schematic representation and solid-state structure of the dinuclear mixed-valence Mn(III)/Mn(IV) complex 61.
Basically, the same behavior was observed by Das et al. who encaged 61 in the pores of a MOF of the MIL101-type (this particular MOF is well-known for its large pore volumes and high surface area). In the absence of a support, the O₂ formation was sub-stoichiometric; the highly acidic regime required to stabilize the CAN (pH value of ca. 1) induced a reductive disproportionation into mononuclear Mn(II) species. Below a pH value of 2.5, the Mn(IV)/Mn(IV) species was found to dimerize into a tetrameric Mn(IV) complex, which could even be characterized by XRD analysis (Figure 45). Remarkably, this tetranuclear assembly was also active as WOC when absorbed onto clay or under electrocatalytic conditions; however, under homogeneous conditions fast degradation by CAN, as oxidant, into MnO₂ and Mn(II) species occurred.

In order to further mimic photosynthesis, Crabtree, Brudvig, Batista et al. attached 61 to TiO₂ nanoparticles. The direct interaction between 61 and the near-amorphous TiO₂ afforded a hybrid material in which one of the aquo ligands was substituted by the TiO₂ (Figure 46a). This binding scenario was corroborated by EPR, UV/vis absorption and electrochemical measurements as well as computational modelling. However, the binding of 61 onto crystallized TiO₂ yielded surface-deposited tetranuclear Mn(IV) complexes instead. The same authors also assembled a TiO₂-chromophore-WOC material by first attaching tpy-chromophore units to the TiO₂ nanoparticles. The tpy sites were loaded with Mn(II) ions and oxidized with KMnO₄ to generate a dinuclear Mn(III)/Mn(IV) complex, similar to 61 (Figure 46b). Though the anticipated electron transfer from the complex site to the TiO₂ could be evidenced by EPR measurements, no photocatalytic activity of the hybrid material was observed.

A different immobilization strategy was followed by Yagi et al. who utilized the pyridyl-equipped dinuclear complex 62 which was stable in aq. medium (Figure 47a). This complex was adsorbed onto saponite or mica clays, presumably as the diprotonated species. The immobilized complex acted as WOC in the presence of CAN, as oxidant (moderate TONs of 5.6 and 14 in the case of saponite and mica, respectively); whereas,
no O₂-evolution was detected under homogeneous conditions (Figure 47b).

Finally, Najafpour et al. studied if also other types of Mn-tpy architectures can be employed as catalysts in the water-oxidation reaction. For this purpose, the dinuclear Mn(II) "back-to-back" complex 13, which has already been discussed in the context of the oxidation of organic sulfides (Section 2.51., Scheme 38, was tested as heterogeneous WOC in aq. medium, at a pH value of 4, in the presence of oxone, as oxidant. Under these conditions O₂-evolution with a TON of 37 over 35 min was observed. This study demonstrated, that the μ-O-bridge, as present in archetypal, biomimetic dinuclear complex, such as 61, is not necessarily required to enable the OER. The authors applied EPR and UV/vis absorption spectroscopy, supported by DFT calculations, to suggest a mechanism in which a Mn(III)-oxyl radical species was discussed as the key intermediate to react with oxone and, thus, produce O₂.

3.4. Oxygen-reduction reaction

The oxygen-reduction reaction (ORR) represents one of the key processes in fuel cells, in particular proton exchange membrane fuel cells (PEMFCs). In such electrochemical cells, the four-electron reduction of molecular oxygen to water occurs at the cathode. Both the anodic, i.e., the hydrogen-oxidation reaction (HOR), and the cathodic process are commonly catalyzed by noble-metal nanoparticles in combination with carbon electrodes (e.g., carbon black or graphite). The electrocatalytic HOR is a highly efficient process, characterized by a very fast reaction rate, and can be run at low anodic catalyst loadings. However, the cathodic ORR represents the more demanding partial reaction in fuel cells for which the reaction kinetics are less defined and significantly higher catalyst loadings are required. In order to overcome these limitations and to avoid the usage of cost-intensive noble metals, a variety of earth-abundant metal species has been introduced as next-generation ORR catalysts: Nitrides, carbides and phosphides. The latter are of interest also for some other cutting-edge applications (e.g., photovoltaics, energy storage, water splitting), but their preparation is hampered by required reaction conditions. Typically, an inert atmosphere, high temperatures and the pyrophoric nature of the phosphidating agent have to be considered.

Against this background, Raj et al. employed the Co(II)-tpy bis-complex 63, as single-source precursor, for the carbothermal production of mesoporous nitrogen-doped carbon-embedded cobalt phosphide (NC-CoP) nanoparticles (Scheme 58). Note-worthy, (bi)metallic nanoparticles have already been fabricated by the pyrolysis of metallopolymer precursor materials. For example, Wong et al. prepared magnetic FePt nanoparticles from a metallopolymer equipped with Pt(II)-tpy complexes and ferrocene sites. Remarkably, Raj et al. achieved the phosphidation of cobalt by the accompanying PF₆⁻-anion, thus no additional source for P was required. It was demonstrated that a proper carbon content in the precursor complex was crucial to obtain well-defined NC-CoP nanoparticles – neither [Co(bpy)₃](PF₆)₂ nor [Co(tpy)₃](PF₆)₂ yielded such nanoparticles under the conditions of a carbothermal reduction. The prepared NC-CoP materials had large surface area of ca. 120 m²/g, as determined by nitrogen adsorption-desorption measurements. The electrocatalytic ORR was investigated and revealed a high selectivity for the four-electron reduction of O₂ to water at low resistance.

![Figure 47](image-url)
overpotentials (the competing two-electron reduction to peroxide was not observed). The authors carried out control experiments with pristine NC and proposed a synergy between the NC support and the CoP nanoparticles which facilitated the O₂ adsorption and enhanced the electron-transfer kinetics of the ORR.

4. Conclusion & Outlook

2,2’:6’:2”-Terpyridine (tpy) was first reported by Morgan and Burstaw in 1932.[61] Since then, a plethora of tpy derivatives and transition metal complexes thereof have been prepared and employed in the context of various application, catalysis represents one notable example for this.[62]

We have shown that a broad range of organic reaction can be catalyzed by metal complexes featuring tpy ligands in their coordination sphere. In particular, the progress recently made in cross-coupling reactions between two basically electrophilic reagents has to be named exemplarily. However, one has to be aware that no universal catalytic system is known and, as shown at the example of the diverse Ni-catalyzed reactions, various parameters have to be considered; these include the denticity of the ligand as well as the nature of substituents which might contribute to the catalytic activity via steric and/or electronic effects. Thus, terpyridines might represent appropriate ligands to stabilize catalytically active metal centers, whereas in other cases no conversion can be observed.

With respect to the catalysis of organic reactions, the range of transition metal ions is not limited to the precious, thus cost-intensive metals. Many examples have already been published where tpy complexes of earth-abundant metals have successfully been employed to catalyze such reactions (e.g., Mn, Fe, Co, Ni, Cu). This, however, does not hold true for the energy-related applications. Concerning the CO₂ reduction as well as the reductive or oxidative water splitting, i.e., the production of H₂ and O₂, mainly tpy complexes of Ru(II), Ir(III) and Pt(II) ions have proven their reliability. As an exception from this, the biomimetic Mn(III)/Mn(IV) complexes utilized as WOCs deserve special mentioning.

As a future challenge, precious metal ions in catalysis should be fully replaced by low-cost ones in order to increase the sustainability. It is questionable if this can be realized on the basis of tpy complexes. Other tridentate ligands with increased donor strength, e.g., the N-heterocyclic carbones (NHCs) have already proven their applicability in this respect and the high catalytic activity of their transition metal complexes often levels out the higher synthetic costs when compared to analogous tpy complexes.[7-8,413–415] Nonetheless, their ease of synthesis and robustness represent the main advantages of the latter which make them useful catalysts in organic synthesis and energy interconversion. The same also applies for the various biological and pharmaceutical applications; however, a discussion of these fields goes far beyond the scope of this review.[16,33,416–417]

Acknowledgements

Financial support by the Deutsche Forschungsgemeinschaft (CRC-TRR 234 “CataLight”, projects B01 and B02, as well as priority program 2102 “LCRMC”, grant number SCHU1229-16/1) is kindly acknowledged.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: electrocatalyst · metal complexes · photocatalyst · photoelectrocatalyst · transition-metal catalyst

[1] D. Astruc, Organometallic Chemistry and Catalysis, Springer Verlag, Berlin Heidelberg, 2007.
[2] R. Noyori, Angew. Chem. Int. Ed. 2002, 41, 2008–2022; Angew. Chem. 2002, 2114, 2108–2123.
[3] F. Fache, E. Schulz, M. L. Tommasino, M. Lemaire, Chem. Rev. 2000, 100, 2169–2232.
[4] G. Rothenberg, Catalysis - Concepts and Green Applications, Wiley-VCH, Weinheim, 2008.
[5] G. Helmchen, U. Kazmaier, S. Förster, in Catalytic Asymmetric Synthesis (Ed.: I. Ojima), John Wiley & Sons Inc., Hoboken, New Jersey, 2010, pp. 497–642.
[6] G. Helmchen, A. Pfaltz, Acc. Chem. Res. 2000, 33, 336–345.
[7] W. A. Herrmann, Angew. Chem. Int. Ed. 2002, 41, 1290–1309; Angew. Chem. 2002, 114, 1342–1363.
[8] E. Peris, R. H. Crabtree, Coord. Chem. Rev. 2004, 248, 2229–2246.
[9] M. Poyatos, J. A. Mata, E. Peris, Chem. Rev. 2009, 109, 3677–3707.
[10] G. Chelucci, R. P. Thummel, Chem. Rev. 2002, 102, 3129–3170.
[11] U. S. Schubert, A. Winter, G. R. Newkome, Terpyridine-Based Materials, Wiley-VCH, Weinheim, 2011.
[12] G. R. Whittle, M. D. Hager, U. S. Schubert, I. Manners, Nature Mat. 2011, 10, 176–188.
[13] M. Higuchi, in Electrochromic Smart Materials: Fabrication and Applications (Eds.: J. W. Xu, M. H. Chua, K. W. Shah), The Royal Society of Chemistry, Cambridge, 2019, pp. 406–429.
[14] C.-L. Ho, W.-Y. Wong, Coord. Chem. Rev. 2011, 255, 2469–2502.
[15] D. Saccone, C. Magistris, N. Barbero, P. Quagliotto, C. Barolo, G. Viscardi, Materials 2016, 9, 137.
[16] A. Winter, M. Gottschaldt, G. R. Newkome, U. S. Schubert, Curr. Top. Med. Chem. 2012, 12, 158–175.
[17] J. Limburg, J. S. Vrettos, L. M. Liable-Sands, A. L. Rheingold, R. H. Crabtree, G. W. Brudvig, Science 1999, 283, 1524–1527.
[18] J. J. Conception, W. J. Jurs, M. K. Brennanman, P. G. Hoeter, A. O. T. Patrocino, N. Y. Murakarni Iha, J. L. Templeton, T. J. Meyer, Acc. Chem. Res. 2009, 42, 1954–1965.
[19] S. Rau, D. Walther, J. G. Vos, Dalton Trans. 2007, 9, 915–919.
[20] A. Winter, G. R. Newkome, U. S. Schubert, ChemCatChem 2011, 3, 1384–1406.
[21] B. A. Moyer, A. J. Thompson, T. J. Meyer, J. Am. Chem. Soc. 1980, 102, 2310–2312.
[22] C.-M. Che, C. Ho, T.-C. Lau, J. Chem. Soc. Dalton Trans. 1991, 1901–1907.
[23] C. S. Allardycye, P. J. Dyson, Platinum Met. Rev. 2001, 45, 62–69.
[24] K. E. Erkkila, D. T. Odom, J. K. Barton, Chem. Rev. 1999, 99, 2777–2796.
[25] C. M. Bolinger, B. P. Sullivan, D. Conrad, J. A. Gilbert, N. Story, T. J. Meyer, J. Chem. Soc. Chem. Commun. 1985, 796–797.
[26] B. Mondal, M. G. Walawalkar, G. K. Lahiri, J. Chem. Soc. Dalton Trans. 2000, 4209–4217.
[27] A. R. Guadalupe, D. A. Usifer, K. T. Potts, H. C. Hurrell, A. E. Mogstad, H. D. Abraha, J. Am. Chem. Soc. 1988, 110, 3462–3466.
[28] P. Paul, B. Tyagi, A. K. Bilakhiya, M. M. Bhadbhade, E. Suresh, G. Ramachandrala, Inorg. Chem. 1998, 37, 5733–5742.
[29] T. Yoshida, K. Tsutsui, S. Teratani, K. Yasufuku, M. Kaneko, J. Chem. Chem. Commun. 1993, 631–632.
[199] A. Winter, U. S. Schubert, Chem. Soc. Rev. 2016, 45, 5311–5357.
[200] M. K. Nazeeruddin, P. Pechy, T. Renouard, S. M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. A. Bignozzi, M. Grätzel, J. Am. Chem. Soc. 2001, 123, 1613–1624.
[201] H. A. Younas, W. Su, N. Ahmad, S. Chen, F. Verpoort, Adv. Synth. Catal. 2015, 357, 383–389.
[202] E. P. Kelson, P.-P. Phengsy, J. Chem. Soc. Dalton Trans. 2000, 4023–4024.
[203] C. M. Moore, N. K. Szymczak, Chem. Commun. 2013, 49, 400–402.
[204] B. Paul, K. Khalabartti, S. Kundu, Dalton Trans. 2015, 44, 11162–11171.
[205] M. Moore, B. Bark, N. K. Szymczak, ACS Catal. 2016, 6, 1981–1990.
[206] E. W. Dahl, T. Louis-Goff, N. K. Szymczak, Chem. Commun. 2017, 53, 2287–2289.
[207] A. Malty, A. Sil, S. K. Patra, Eur. J. Inorg. Chem. 2018, 4063–4073.
[208] M. C. van Engelen, H. T. Teunissen, J. G. de Vries, C. J. Elsevier, E. P. Kelson, P. P. Phengsy, W. Mägerlein, C. Dreisbach, H. Hugl, M.-K. Tse, M. Klawonn, S. Bhor, M. C. Moore, B. Bark, N. K. Szymczak, ACS Catal. 2016, 6, 1981–1990.
[209] F. Shi, M.-K. Tse, M. Beller, Chem. Asian J. 2007, 2, 411–415.
[210] F. Papafotiou, K. Karidi, A. Garoufis, M. Louloudi, F. Shi, M.-K. Tse, M. Beller, C. Catal. Today, 2009, 140–150.
[211] M. K. Nazeeruddin, P. Pechy, T. Renouard, S. M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. A. Bignozzi, M. Grätzel, J. Am. Chem. Soc. 2001, 123, 1613–1624.
[212] H. A. Younas, W. Su, N. Ahmad, S. Chen, F. Verpoort, Adv. Synth. Catal. 2015, 357, 383–389.
[213] E. P. Kelson, P.-P. Phengsy, J. Chem. Soc. Dalton Trans. 2000, 4023–4024.
[214] C. M. Moore, N. K. Szymczak, Chem. Commun. 2013, 49, 400–402.
[215] B. Paul, K. Khalabartti, S. Kundu, Dalton Trans. 2015, 44, 11162–11171.
[216] M. Moore, B. Bark, N. K. Szymczak, ACS Catal. 2016, 6, 1981–1990.
[217] E. W. Dahl, T. Louis-Goff, N. K. Szymczak, Chem. Commun. 2017, 53, 2287–2289.
[218] A. Malty, A. Sil, S. K. Patra, Eur. J. Inorg. Chem. 2018, 4063–4073.
[219] M. C. van Engelen, H. T. Teunissen, J. G. de Vries, C. J. Elsevier, E. P. Kelson, P. P. Phengsy, W. Mägerlein, C. Dreisbach, H. Hugl, M.-K. Tse, M. Klawonn, S. Bhor, M. C. Moore, B. Bark, N. K. Szymczak, ACS Catal. 2016, 6, 1981–1990.
[220] F. Shi, M.-K. Tse, M. Beller, Chem. Asian J. 2007, 2, 411–415.
[221] F. Papafotiou, K. Karidi, A. Garoufis, M. Louloudi, F. Shi, M.-K. Tse, M. Beller, C. Catal. Today, 2009, 140–150.
[222] M. K. Nazeeruddin, P. Pechy, T. Renouard, S. M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. A. Bignozzi, M. Grätzel, J. Am. Chem. Soc. 2001, 123, 1613–1624.
[223] H. A. Younas, W. Su, N. Ahmad, S. Chen, F. Verpoort, Adv. Synth. Catal. 2015, 357, 383–389.
[224] E. P. Kelson, P.-P. Phengsy, J. Chem. Soc. Dalton Trans. 2000, 4023–4024.
[225] C. M. Moore, N. K. Szymczak, Chem. Commun. 2013, 49, 400–402.
[226] B. Paul, K. Khalabartti, S. Kundu, Dalton Trans. 2015, 44, 11162–11171.
[227] M. Moore, B. Bark, N. K. Szymczak, ACS Catal. 2016, 6, 1981–1990.
[228] E. W. Dahl, T. Louis-Goff, N. K. Szymczak, Chem. Commun. 2017, 53, 2287–2289.
[229] A. Malty, A. Sil, S. K. Patra, Eur. J. Inorg. Chem. 2018, 4063–4073.
[230] M. C. van Engelen, H. T. Teunissen, J. G. de Vries, C. J. Elsevier, C. J. Catal. A 2003, 205, 185–192.
[231] R. V. Jagadeesh, G. Wienhöfer, F. A. Westerhaus, A.-E. Surkus, H. Junge, K. Junge, M. Beller, Chem. Eur. J. 2011, 17, 14375–14379.
[232] W. Mägerlein, C. Dreisbach, H. Hugl, M.-K. Tse, M. Klawonn, S. Bhor, M. Beller, Catal. Today 2007, 121, 140–150.
[233] M. K. Nazeeruddin, P. Pechy, T. Renouard, S. M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. A. Bignozzi, M. Grätzel, J. Am. Chem. Soc. 2001, 123, 1613–1624.
[234] H. A. Younas, W. Su, N. Ahmad, S. Chen, F. Verpoort, Adv. Synth. Catal. 2015, 357, 383–389.
[235] E. P. Kelson, P.-P. Phengsy, J. Chem. Soc. Dalton Trans. 2000, 4023–4024.
[236] C. M. Moore, N. K. Szymczak, Chem. Commun. 2013, 49, 400–402.
[366] E. L. Lebeau, S. A. Adeyemi, T. J. Meyer, Inorg. Chem. 1998, 37, 6476–6484.
[367] T. Wada, K. Tsuge, K. Tanaka, Inorg. Chem. 2001, 40, 329–337.
[368] T. Wada, K. Tsuge, K. Tanaka, Angew. Chem. Int. Ed. 2000, 39, 1479–1482; Angew. Chem. 2000, 112, 1539–1542.
[369] C. Sens, I. Romero, M. Rodríguez, A. Lloret, T. Parella, J. Benet-Neto, J. Catal. Am. Chem. Soc. 2004, 126, 7798–7799.
[370] R. Zong, R. P. Thummel, J. Am. Chem. Soc. 2005, 127, 12802–12803.
[371] J. J. Concepcion, J. W. Jurss, J. L. Templeton, T. J. Meyer, J. Am. Chem. Soc. 2008, 130, 16462–16463.
[372] H. Y. Zong, J. T. Muckerman, R. Thummel, Inorg. Chem. 2008, 47, 11763–11773.
[373] D. J. Wasylelenko, C. Ganesamoorthy, B. D. Koivisto, M. A. Henderson, C. P. Berlinguette, Inorg. Chem. 2010, 49, 2202–2209.
[374] D. J. Wasylelenko, C. Ganesamoorthy, M. A. Henderson, B. D. Koivisto, H. D. Osthoff, C. P. Berlinguette, J. Am. Chem. Soc. 2010, 132, 16094–16106.
[375] S. Masaoka, K. Sakai, Chem. Lett. 2009, 38, 182–183.
[376] N. Kaveevitchai, R. Zong, H.-W. Tseng, R. Chitta, R. P. Thummel, Inorg. Chem. 2012, 51, 2930–2939.
[377] L. Yan, R. Zong, Y. Pushkar, J. Catal. 2015, 330, 255–260.
[378] Y. Pushkar, D. Moonshiram, V. Purohit, L. Yan, I. Alperovich, J. Am. Chem. Soc. 2014, 136, 11938–11945.
[379] M. Yagi, S. Tajima, M. Komi, H. Yamazaki, Dalton Trans. 2011, 40, 3802–3804.
[380] L. Duan, A. Fischer, Y. Xu, L. Sun, J. Am. Chem. Soc. 2009, 131, 10397–10399.
[381] R. Matheu, M. Z. Ertem, J. Benet-Buchholz, E. Coronado, V. S. Batista, X. Sala, A. Llobet, J. Am. Chem. Soc. 2015, 137, 10786–10795.
[382] R. Matheu, S. Neudeck, F. Meyer, X. Sala, A. Llobet, ChemSusChem 2016, 9, 3361–3369.
[383] T. Fan, L. Duan, P. Huang, H. Chen, Q. Daniel, M. S. M. Ahlquist, L. Sun, ACS Catal. 2017, 7, 2956–2966.
[384] R. Matheu, M. Z. Ertem, C. Gimbert-Surinach, J. Benet-Buchholz, X. Sala, A. Llobet, ACS Catal. 2017, 7, 28–32.
[385] P. Wrzolek, S. Wahl, M. Schwab, Catal. Today 2017, 290, 28–32.
[386] P. Wrzolek, M. Schwab, Eur. J. Inorg. Chem. 2015, 2015, 4373–4378.
[387] R. McGuire Jr, D. K. Dogutan, T. S. Teets, J. Suntivich, Y. Shao-Horn, D. G. Nocera, Chem. Sci. 2010, 1, 411–414.
[388] R. K. Dogutan, R. McGuire, D. G. Nocera, J. Am. Chem. Soc. 2011, 133, 9178–9180.
[389] B. A. Johnson, A. Bhunia, S. Ott, Dalton Trans. 2017, 46, 1382–1388.
[390] S. Lin, Y. Pineda-Galvan, W. A. Maza, C. C. Epley, J. Zhu, M. C. Kessinger, Y. Pushkar, J. J. Morris, ChemSusChem 2017, 10, 514–522.
[391] L. Limburg, G. W. Brudvig, R. H. Crabtree, J. Am. Chem. Soc. 1997, 119, 2761–2762.
[392] M. M. Najafpour, S. I. Allakhverdiev, Int. J. Hydrogen Energy 2012, 37, 8753–8764.
[393] K. J. Young, B. J. Brennan, R. Tagore, G. W. Brudvig, Acc. Chem. Res. 2015, 48, 567–574.
[394] W. Chen, R. Tagore, G. Olack, J. S. Vrettos, T.-C. Weng, J. Penner-Hahn, R. H. Crabtree, G. W. Brudvig, Inorg. Chem. 2007, 46, 34–43.

Manuscript received: December 9, 2019
Revised manuscript received: January 29, 2020
Accepted manuscript online: January 30, 2020
Version of record online: March 9, 2020