Chapter 1

Introduction
1.1 General introduction

Most chemical processes in industry rely on catalytic transformations. Especially in the area of fine chemicals, many of those are based on homogeneous catalysis, which often rely on two-electron redox changes at the metal center (oxidative addition and reductive elimination). These two oxidation states should be similar in energy for turnover. However, there are few metals which possess two easily accessible oxidation states n and n+2, most of them belonging to the platinum group metals (Ru, Rh, Pd, Os, Ir, Pt and Au, metals in purple in Figure 1.1). Even though they are often used, the platinum group metals are not sustainable because they are scarce, expensive and often toxic.\(^1\)\(^2\) In Figure 1.1 are shown in red the major industrial metals, from which Al, Mg, Ti, Fe and Mn are the most abundant in Earth’s upper continental crust (green region in Figure 1.1). However, most of the most abundant (therefore cheaper) transition metals undergo only one-electron transformation, limiting their applicability in reactions that require two-electron transfer.

\[
\text{Figure 1.1 Abundance expressed in atom fraction of the chemical elements in Earth’s upper continental crust as a function of atomic number. Figure by courtesy of the U.S. Geological Survey (https://pubs.usgs.gov/fs/2002/fs087-02).}
\]

One example of the value of noble transition metals is the used of Pd in C-C bond formation by Heck, Negishi, and Suzuki (Nobel Prize for Chemistry in 2010).\(^3\)

However, efforts have been made in the past decades for developing ligands that act as electron reservoirs (redox-active ligands) to emulate noble-metal properties with first-row transition metals.
1.2 Redox-active ligands

Changes in oxidation states of a metal complex usually involve changes in oxidation state of the metal center. In contrast, when the ligand is responsible for the electron transfer and the oxidation state of the ligand-metal is clearly defined, the ligand acts as a ‘redox-active ligand’. However, in some cases this is not clearly defined due to an extensive mixing which leads to ambiguity in terms of assigning oxidation states of ligand-metal, in these cases the ligand is so-called ‘redox non-innocent’.

In this section and throughout this thesis we will focus on these ligands. The main feature for a ligand to be redox-active/non-innocent is to possess orbitals that lie close, in both energetic and spatial proximity, to the ‘d’ orbitals of the coordinated metal, often leading to extensive mixing of the metal and ligand frontier orbitals.

Electron loss could occur at the ligand rather than the metal when redox-active ligands are used (z to z+2) (Scheme 1.1) where the metal center is not involved in the process and therefore the oxidation state remains unchanged (n). This potentially avoids going through unstable metal oxidation states during chemical redox transformations, and enables new reaction pathways.

Traditional oxidative addition

\[
L_x^zM^n + A-B \rightarrow L_x^{z+2}M^{n+2} - B
\]

Oxidative addition involving a redox-active ligand

\[
L_x^zM^n + A-B \rightarrow L_x^{z+2}M^n - B
\]

Scheme 1.1 Metal complex oxidation: mediated by metal center (top) and mediated by redox-active ligands (bottom).

Oxidative addition is a fundamental transformation in organometallic chemistry that is often a key bond activation step responsible for introducing substrates into the metal coordination sphere during catalytic turnover.

To avoid the generation of unstable oxidation states of the metal center, many efforts have been made towards the synthesis and study of new metal complexes involving redox-active ligands, due to their interesting electronic structures, role in metalloenzymes, the
ability to promote unusual group transfer reactivity,24–27 and their importance in base metal catalysis.8,28–32 Nature also makes use of redox-active ligands as storage of redox equivalents for chemical transformations and catalysis.25 One example is cytochrome P450, the active site contains a heme cofactor (Fe$^{2+}$ and porphyrin as ligand).33 These species are found in all domains of life.34 In 2010, a highly reactive intermediate (P450 compound I, P450-I, Scheme 1.2) was isolated, which is an important intermediate in the catalytic cycle for biological functions through the controlled activation of C-H bonds.15 P450-I was found to contain an iron(IV)-oxo (ferryl) metal center and a singly oxidized porphyrin radical ligand (delocalized over the porphyrin and thiolate ligand), which is able to oxidize hydrocarbons to alcohols via a 2-electron process, one of which is provided by reduction of the metal center (Fe(IV) to Fe(III)) and the other by the ligand (singly oxidized porphyrin radical to porphyrin ligand).

Scheme 1.2 Active site of Cytochrome P450 (left) and P450 compound I (right).

Another example is galactose oxidase35, which makes use of an organic ligand that can be oxidized. In this oxidized form, the copper oxidation state remains unaltered while the ligand is the one bearing an unpaired electron (one-electron oxidized tyrosyl radical that is stabilized by a nearby tryptophan), generating an active form of the enzyme towards selective oxidation (Scheme 1.3).

Scheme 1.3 Activation of galactose oxidase by oxidation of the redox-active ligand.
Scientists have been focussing in the past decades to mimic nature and expand the number of redox-active ligands. Although some examples of redox active ligands have been elucidated in the last decades, such as catechol, o-aminophenol, o-phenylenediamine and o-dithiol, represented in Figure 1.2 as a) cat, b) o-O,N, c) o-N,N and d) o-S,S, respectively, still the diversity of redox-active ligands is very limited. Therefore, there is a need to develop new redox-active ligand scaffolds that are easily accessible, tunable in their steric and electronic properties, and can provide high chemical stability in various oxidation states.

**Figure 1.2** Skeleton of catecholate derivatives (top) and their three possible oxidation states (bottom).

### 1.3 β-diketimine ligands

#### 1.3.1 β-diketiminate as supporting ligand

β-diketimines (nacnac, 1,5-diazapentadienyl) are an important class of monoanionic bidentate ligands which contain two nitrogens in the ligand framework R1-N=C(R2)-C(R3)=C(R4)-NH-R5. The generated anionic charge, upon deprotonation of the ligand, is delocalized throughout the conjugated π-system over the –N–C–C–N– moiety (Figure 1.3, section 1.3.2). Structural, electronic and magnetic properties, and reactivity of the metal centers can be controlled mainly by the substituents introduced either in the nitrogen atoms (R1 and R5) or in the carbon ones (R2–R4). In most cases, the steric control on the coordination sphere is mainly due to the nitrogen substituents (R1 and R5). On the other hand, the carbon substituents (R2–R4) are also important in tuning the electron donor ability of the supporting ligands.
This ligand has been highly explored with a wide variety of metals in different oxidation states.\textsuperscript{46-48} Due to the wide variety of complexes that have been studied, there are many reactions involving \(\beta\)-diketimimates as supporting ligands for application in catalysis\textsuperscript{49}. However, little attention has been focused on the redox activity (redox non-innocence) of the supporting ligand itself.

1.3.2 \(\beta\)-diketiminate as redox-active ligand

Diketiminate can be reduced or oxidized acting as non-innocent supporting ligand.\textsuperscript{50} The first ligand-based reduction was mentioned and characterized by Lappert et. al in 2002 involving Sm and Yb as metal centers.\textsuperscript{48} Crystallographic analysis suggests a dianionic ligand framework based on elongation of the N-C bond lengths with the interaction of one Li\textsuperscript+ per ligand \([\text{SmL}_2]^-\) (L\textsuperscript{' } in Scheme 1.4). A year later, a ligand-based 2-electron reduction was reported within the same group with Yb and Li as metal centers.\textsuperscript{51,52} In this radical dianion (L\textsuperscript{''} in Scheme 1.4) as well as in the radical anions L\textsuperscript{'}, the elongation of the N-C bond lengths is due to population of orbitals that have antibonding character between C and N (Scheme 1.4).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.3.png}
\caption{Ligand framework upon deprotonation (\(\beta\)-diketiminate, \textit{nacnac}): general structure (left), LUMO (center), HOMO (right).}
\end{figure}

\begin{scheme}[h]
\centering
\includegraphics[width=\textwidth]{scheme1.4.png}
\caption{Consecutive two-electron reduction of a \(\beta\)-diketiminate ligand.}
\end{scheme}

The first diketiminate ligand-based oxidation was reported for a bis(\(\beta\)-diketiminate)Ni(II) complex in 2011 by Khusniyarov, Wieghardt et. al.,\textsuperscript{53} almost a decade later than the first example of reduction of a \(\beta\)-diketiminate complex was reported. Four years later the first crystallographic study of a singly oxidized \(\beta\)-diketiminate complex, also involving a bis(\(\beta\)-diketiminate)Ni(II).\textsuperscript{54} However, there were no substantial changes in the metrical parameters of the ligand framework comparing with its neutral form. This could be explained based on the non-bonding character of the HOMO of the \(\beta\)-diketiminate ligand (Figure 1.3).
Although in some complexes β-diketiminate could act as redox-active ligand, there are not many examples where the corresponding reduced complexes have been synthesized and characterized. This is due to their low reduction potential, some examples that could be synthesized show reduction potentials of -1.75, -2.21, -2.31 V when the metal centers Yb²⁺, Li⁺, Ca²⁺ are present, (respectively, potentials vs. SCE).⁵⁵ Thus, strong reducing agents as Li metal or Yb-naphtalene complex are required.

1.4 Formazan ligands

1.4.1 General features of formazans

Formazans closely resemble the structure of β-diketimines, but contain two extra nitrogen atoms in the backbone R₁-N=N-C(R₃)=N-NH-R₅ than their β-diketiminate analogues. Although extensive studies have been performed on metal complexes containing β-diketiminate ligands (see above) formazanates have been largely neglected.

The two extra nitrogens present in the formazanate framework provide it an increased flexibility in their coordination chemistry. This allows not only the 6 membered ring coordination to the metal center through the two terminal nitrogens as shown in all the cases for β-diketiminate, but also a five membered ring coordination through coordination of one terminal and one internal nitrogen to the metal center (Scheme 1.5).⁵⁶

Formazans have been known as dye for more than hundred years.⁵⁷–⁵⁹ The reduction of tetrazolium salts by dehydrogenases and reductases lead to the formation of colorful formazan compounds, ranging from orange, deep-red to violet. MTT (oxidized form of formazans) are used in assays to evaluate the cell metabolic activity by applying the chromogenic properties of the formazan.⁶⁰
Formazans are the precursors of verdazyls, a class of stable organic radicals first reported in 1963 by Trischmann and Kuhn. Verdazyl radicals are resonance stabilized six-membered heterocyclic radicals with the structure shown in Figure 1.4. Verdazyls and 6-oxoverdazyls (seven π electrons, left and center in Figure 1.4, respectively), benefit from significant delocalization and stabilized frontier molecular orbitals due to the presence of four nitrogen atoms in their heterocyclic backbones. They can be reversibly oxidized to cations (six π electrons) and anions (eight π electrons). Their versatile applications, ranging from molecular magnets, as ESR spin labels, polymerization inhibitor and mediators in living radical polymerizations amongst others, is due to their unusual stability to air and moisture. Verdazyl radicals remain monomeric in both, solution and solid state, without relying on bulky substituents.

Closely related Kuhn-type verdazyls and 6-oxoverdazyls (seven π electrons), which also benefit from significant delocalization and stabilized frontier molecular orbitals due to the presence of four nitrogen atoms in their heterocyclic backbones, exhibit similar redox behavior and can be reversibly oxidized to cations (six π electrons) and anions (eight π electrons).

The exceptional stability of verdazyl radicals is attributed to the delocalization of its unpaired electron across all four nitrogen atoms in the ring with the unpaired electron residing in a low energy SOMO.

In the next section 1.4.2, we will introduce how by changing the methylene, carbonyl or phosphine oxide depicted in Figure 1.4 by a metal center the resulting formazanate can still act as an electron reservoir.
1.4.2 Redox-active properties

The use of β-diketiminate as redox-active ligands are limited due to the poor accessibility of reduced forms (very negative potentials)\textsuperscript{51,52} and low stability of the oxidized forms\textsuperscript{53} (see section 1.3.2). In contrast, formazanate complexes show more accessible reduction potentials (-0.86 to -1.86 V vs. Fc\textsuperscript{0/+})\textsuperscript{56-74} than their analogous β-diketimimates (-1.75 to -2.31 V vs. SCE)\textsuperscript{55}. The combination of the accessibility and stability of the reduced formazanate complexes make the formazan an interesting ligand platform, not only as a supporting but also as a potential redox-active ligand.

The first synthesis of a reduced formazanate complex was reported in 2007 by Hicks and co-workers\textsuperscript{70} based on boratatetrazines (formazanate)\textsubscript{B(OAc)}\textsubscript{2}. Cyclic voltammetry studies on this neutral complex indicate an accessible reversible redox wave at -0.86 V vs. Fc\textsuperscript{0/+}. Although the corresponding ligand-based reduction product [(formazanate)\textsubscript{B(OAc)}\textsubscript{2}][CoCp\textsubscript{2}] could not be isolated in pure form it was characterized by EPR and UV/Vis spectra (Figure 1.5).

![Figure 1.5 Synthesis of the first reduced formazanate complex (borataverdazyl radical anion L' [LB(OAc)\textsubscript{2}]\textsuperscript{-}].](image)

In the following years, Gilroy and co-workers made several contributions to the synthesis of various (formazanate)boron difluoride complexes\textsuperscript{71-74} and they studied the substituent dependency in the optical and electrochemical properties. In general, substitution on the 1- and 5-position of the formazanate backbone (N-R1, N-R5) has a higher effect than the 3-substitutions on those properties. This behaviour is similar to the one observed previously by Kuhn-type verdazyls and 6-oxoverdazyls due to a Singly Occupied Molecular Orbital (π-SOMO) with a nodal plane, and therefore little electron density in the 3-position (right in Figure 1.4).\textsuperscript{75,76}

Most of the boron complexes studied by Gilroy and co-workers upon increasing the π conjugation of the system increase the fluorescence quantum yields and the reduction potentials (being easier to reduce) and lead to a red-shift of the maximum absorption and...
emission. Although changes in the symmetry of the complexes did not change significantly the absorption or electrochemical properties, the quantum yields increase upon breaking their symmetry. This is in line with previous studies on BODIPYs and (N-donor)BF₂ complexes. Enhancement of the emission quantum yields can be also achieved by substitution on 3-position of the formazanate framework with substituents that increase the conjugated π system (3-cyano- and 3-nitro).

(Formazanate)boron difluoride complexes (LBF₂, six π electrons) show in all the cases two reversible one-electron reduction waves, first leading to the formation of the corresponding ligand-centered radical anions (seven π electrons) and the second to the dianions (eight π electrons). Several of LBF₂ show additional irreversible oxidation events. This stabilization is due to the 4 nitrogens present which allows the delocalization of the unpaired electron similarly to the verdazyl discussed in section 1.4.1. In general, modification of the N-aryl electron donating/with-drawing character lead to lower/higher reduction potentials, being more difficult/easier to reduce the corresponding complexes, respectively.

In 2014, the synthesis and isolation of the one- and two-electron reduction products of bis(formazanate)zinc complexes was reported by our group (Figure 1.6). The stability of these complexes is due to the “metallaverdazyl”-type structures obtained. The first electron transfer process (-1.52 V vs. Fe⁰⁺, I/I’, ZnL’L, radical anion) corresponds to the reduction of one of the formazanate ligands, and a subsequent reduction is observed at a somewhat more negative potential corresponding to reduction of the other formazanate (-1.84 V vs. Fe⁰⁺, II/II’, ZnL’L, radical dianion). The lower reduction potential for the latter is evidence for electronic communication between the two ligands. The third and fourth redox couples correspond to the 2-electron reduction of each formazanate ligand (L””, reductions III and IV).
Figure 1.6 Cyclic voltammogram of bis(formazanate)zinc (R1 = R5 = Ph, R3 = p-tol) showing the presence of four reduction waves.

Within the same year, also studies on mono(formazanate)boron difluoride complexes were performed by our group. These show two accessible and reversible redox couples, suggesting the viability of two-electron reduction in a single formazanate ligand ([LBF₂]⁺, L⁻). The single electron reduced product could be isolated by reduction with cobaltocene (-0.98 V vs. Fe⁰/+, [LBF₂]⁺, L⁻). However, the lower reduction potential of the second redox couple requires Na as reducing agent (-2.06 V vs. Fe⁰/+, Na), leading to the releasing of NaF and the formation of N-heterocyclic boron carbenoid, present in the isolated unusual BN heterocycles.

A two-electron reduced formazanate boron compound has been isolated recently. The use of phenyl, instead of fluoride, as B-substituents avoids the release of NaF, allowing the isolation of compounds containing the formazanate ligand in the two-electron reduced form (L⁻).

In 2016, Sundermeyer and co-workers reported a series of formazanate complexes involving heavier group 13 elements (LMMe₂, M = Al, Ga and In). Aluminium and gallium mononuclear complexes present a tetrahedral coordination around the metal center. In contrast, the indium analogue present an oligomeric structure in non-coordinating solvents in which they propose dimeric species with a 5-coordinated indium by N-bridging. In coordinating solvents the oligomer is cleaved, maintaining the 5-coordinated indium by the coordination of pyridine or 4-dimethylaminopyridine, according to NMR and X-ray crystallographic studies. Electrochemistry studies of these complexes reveal irreversible electron transfer in all the cases, tentatively attributed due to labile radical metal alkyls.

Despite the expanded number of formazanate complexes synthesized in the last decade (Pd⁹², Co⁹³, Ni⁹⁴,⁹⁵, Cu⁹⁶, Pt⁹⁹ among others⁹⁷) and their proven redox-activity (vide supra), the role
of the formazanate in the most of the reactions described to date is as a supporting ligand without involving their potential redox-activity (see section 1.4.3).

One of the few examples where the observed reactivity involves the redox-active nature of the formazanate was reported by Tolman and co-workers in 2009.96 Electron deficient formazanate copper(I) [LCu(CH₃CN)] was reacted with oxygen leading to the formation of bis(hydroxo)dicopper(II) at room temperature and bis(μ-oxo)dicopper at − 80 °C. Studies on this last compound and its intermediates suggest the formation of a metallaverdazyl radical complex intermediate due to the 'non-innocent' potential of the formazanate.

Although some complexes containing formazanate ligands have been reported to be active catalysts for chemical transformations including H₂O₂ decomposition⁹⁸ and ethylene oligomerization⁹²,⁹⁹,¹⁰⁰ is worth to mention that in all these cases the formazanate act as 'innocent' supporting ligand without exhibiting redox-activity. Thus, there is a need for a better understanding of the ways in which the distinctive electronic properties of formazanates (including their reduced froms) influence the properties and reactivity of their metal complexes in order to make full use of the potential of these ligands.

1.5 Overview of the thesis

In this thesis we expand the study on formazanate complexes by employing formazanate metal complexes that have not been explored till date such as alkali (Na and K), alkaline earth (Mg and Ca) and first row transition (Fe) metal complexes.

In Chapter 2, we present the synthesis and characterization of alkali metal salts of formazanate ligands (ML, M = Na, K), which open up a new synthetic pathway towards formazanate complexes via salt metathesis. The salts discussed in this chapter show the high coordination flexibility of the formazanate framework that results from the presence of 4 nitrogen atoms in the ligand backbone.

In Chapter 3, we discuss the synthesis of alkaline earth formazanate complexes employing magnesium and calcium (ML₂(THF)₆, M = Mg, Ca). This can be achieved through two different pathways: (a) direct synthesis from the formazan ligand and a metal alkyl/amide or (b) through metathesis of alkali metal salts discussed in Chapter 2 and a metal halide source. All complexes are characterized using different spectroscopic techniques and they were
compared in terms of steric and electronic effect of the ligand and the Lewis acidity of the metal center.

In Chapter 4, we investigate the decomposition reactions that occur for formazanate Mg/Ca complexes containing a $C_6F_5$-substituent. The organic products are identified as tetrazepine and arylazoidazole derivatives, which are formed as a result of nucleophilic aromatic substitution. The electrochemical properties of these products are also presented.

In Chapter 5, the photochemical switching behaviour of a new class of azoheteroarenes (arylazoindazoles and functionalized derivatives) are investigated. Photostationary states, quantum yields, fatigue resistance, kinetic and theoretical studies are discussed and compared for the different compounds.

In Chapter 6, the synthesis and characterization of a series of mono- and bis(formazanate)zinc complexes are covered ($L\text{ZnMe}$ and $\text{ZnL}_2$, respectively). In this chapter we describe preliminary studies on the activity of those and some representative magnesium and calcium complexes (from Chapter 3) towards lactide oligomerization/polymerization. To extend these studies, a series of alkoxide zinc and magnesium formazanate complexes were synthesized and characterized ($[\text{LMOR}]_n$, $M = \text{Mg, Zn}$) Redox properties of (formazanate) zinc alkoxides are also presented.

In Chapter 7, the synthesis and characterization of a bis(formazanate)iron complex is presented ($\text{FeL}_2$). The $\pi$-acceptor properties of the formazanate ligand lead to unusual properties and as a result a rare example of spin-crossover in a pseudo-tetrahedral is presented in detail. Cyclic voltammetry studies reveal reversible and accessible formation of the singly reduced complex, and isolation and characterization of this species is addressed ($[\text{FeL}_2][\text{NBu}_4]$). The properties of both complexes are investigated through several spectroscopic, magnetic and computational techniques to obtain insight in the factors that contribute to their unusual electronic structure.
1.6 References

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Introduction


Chapter 1

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