1
Introduction

1.1 Redox-Active Ligands: General Introduction

In the domain of coordination and organometallic chemistry, the role of "redox" processes has remained crucial to researchers for many decades [Albela et al., 1999; Bustin et al., 1953]. The redox characteristics of a complex are determined by the combined contributions of both the metal and the chelated ligands that make up its coordination sphere. The coordinated redox-active ligand frequently plays a significant role in reactions by serving as an electron reservoir, storing or releasing electrons to prevent unusual oxidation states at the metal center, which is in contrast to complexes with traditional ligands (Chart 1.1) [Broere et al., 2015a]. Oxidizing or reducing regular "redox-inactive" spectator ligands through one-electron processes demands greater energy compared to the typical redox events confined on the metal core within the complex. Consequently, alterations in the electronic configuration primarily transpire at the metal rather than at the ligands coordinated with the metal. Redox-active ligands feature energy-accessible levels suitable for oxidation or reduction [Chirik et al., 2010]. Consequently, either exclusive ligand-centered redox processes occur, leaving the metal unaffected in its oxidation state, or both the metal and ligand undergo variation in their oxidation state in a synergetic manner which introduces uncertainty regarding the electronic states of both the ligand and metal. Ligands that exhibit the potential for an oxidation state ambiguity were classified as non-innocent according to Jørgensen's initial definition of the word in 1966 [Jørgensen, 1966]. Chirik emphasizes that contemporary experimental and computational techniques frequently enable the determination of the suitable oxidation state of the metal in such instances [Chirik, 2011]. Many reports [J & Karl, 2010] consider non-innocent and redox-active ligand categories to be synonymous, while distinctions have been established in certain cases [Chirik, 2011].

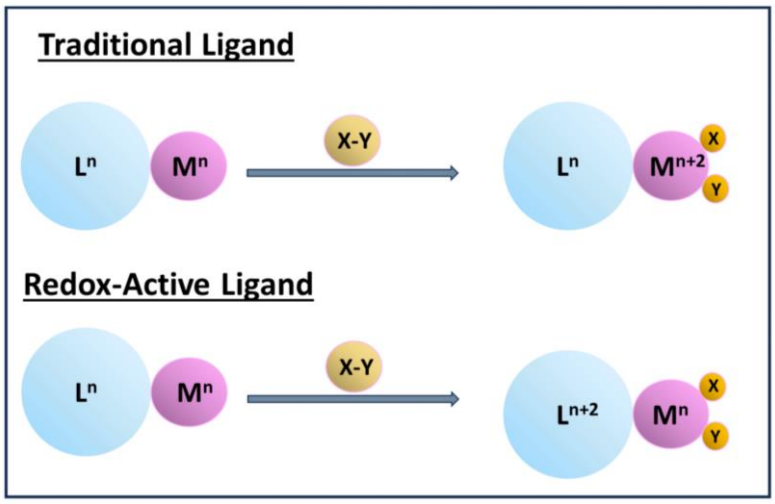


Chart 1.1: "Traditional" unreactive ligand involving changes in metal oxidation (Top). Redox-active ligand serving as an electron reservoir, maintaining the same oxidation state for the metal (Bottom).

Researchers have understood the fundamentals of redox-active ligands for many years, yet it was not long ago that these ligands were predominantly viewed as spectroscopic oddities. These ligands have capabilities that extend far beyond merely identifying intricate electronic structure configurations (Chart 1.2). These ligands have the ability to enhance the reactivity of metals by

(i) serving as an electron reservoir
(ii) producing reactive radicals centered around the ligand, which participate in the formation and cleavage of bonds
(iii) altering the Lewis acidity of the metal,
(iv) facilitating single electron transfer from redox-active ligand-to-substrate [Broere et al., 2015b]

Over the past few decades, a range of redox-active ligand classes has been synthesized and thoroughly examined, resulting in notable applications in several fields, such as catalysis and material science.

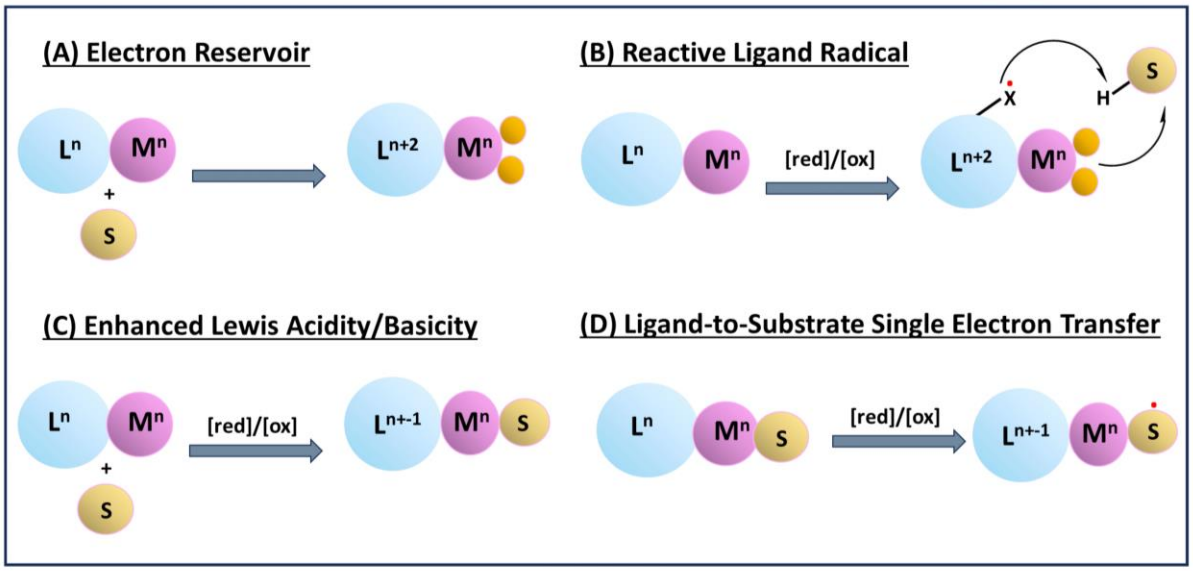


Chart 1.2: Redox-active ligands and their ability to improve metal center reactivity in several ways [Broere et al., 2015b].

Redox-active ligands offer significant potential to impart intriguing reactivity to early transition metal complexes, granted that their redox characteristics could be tailored to enable the process of electron transport within the ligand framework. Various examples of redox-active ligands promoting the metal reactivity in different ways are shown in Chart 1.3. Redox-active ligands can function as a reservoir for electrons, facilitating reactions previously considered impossible. Heyduk group reported an early instance of this chemical process, where they observed a reaction involving molecular chlorine and a zirconium(IV) complex in the formation of the Zr(IV) dichloride derivative as a result of oxidative addition [Blackmore et al., 2005]. While the primary use of redox-active ligands thus far has been serving as a reservoir for one- or two-electron reactivity at a metal, these dynamic ligands also possess various other distinctive characteristics that are pertinent to stoichiometric and catalytic applications. An exemplary instance that is currently receiving considerable focus is the capacity to produce or stabilize radicals that are substrate-centered within the coordinating sphere of a metal by single electron transfer from ligand to substrate. Soper group proposed that placing a redox-active ligand on a metal that is coordinatively saturated would prompt redox processes within the ligand itself, and this ligand would function as a coordinated substrate rather than solely providing electrons for a metal center that is coordinatively unsaturated [Lippert et al., 2011]. Altering the oxidation state of a coordinated non-innocent ligand may substantially affect Lewis basicity or acidity of the metal. As a consequence, the coordination characteristics of a hemilabile donor or substrate can undergo

notable changes, thereby facilitating redox-switchable catalysis. Rauchfuss and his team showcased how coordinated alkenes within a square planar Pt(II) complex can be activated through redox switching facilitated by a redox-active amidophenolate ligand [Boyer et al., 2009]. The utilization of 'reactive ligands' for bioinspired activation of substrates and cooperative catalysis by metal-ligand bifunctional systems has garnered significant interest in the past decade. Numerous ligand moieties have been devised to enable a broad range of bond activation processes. Heyduk and co-workers investigated the utilization of an aminophenol ONO ligand as a combined proton and electron source using Zr(IV) to reduce molecular oxygen [F. Lu et al., 2012]. The utilization of redox-active ligands, once viewed primarily as a spectroscopic novelty in coordination chemistry, has emerged as a burgeoning area of research aimed at enhancing existing reactivity or prompting novel reactions in rare earth, main group, and transition metal complexes.

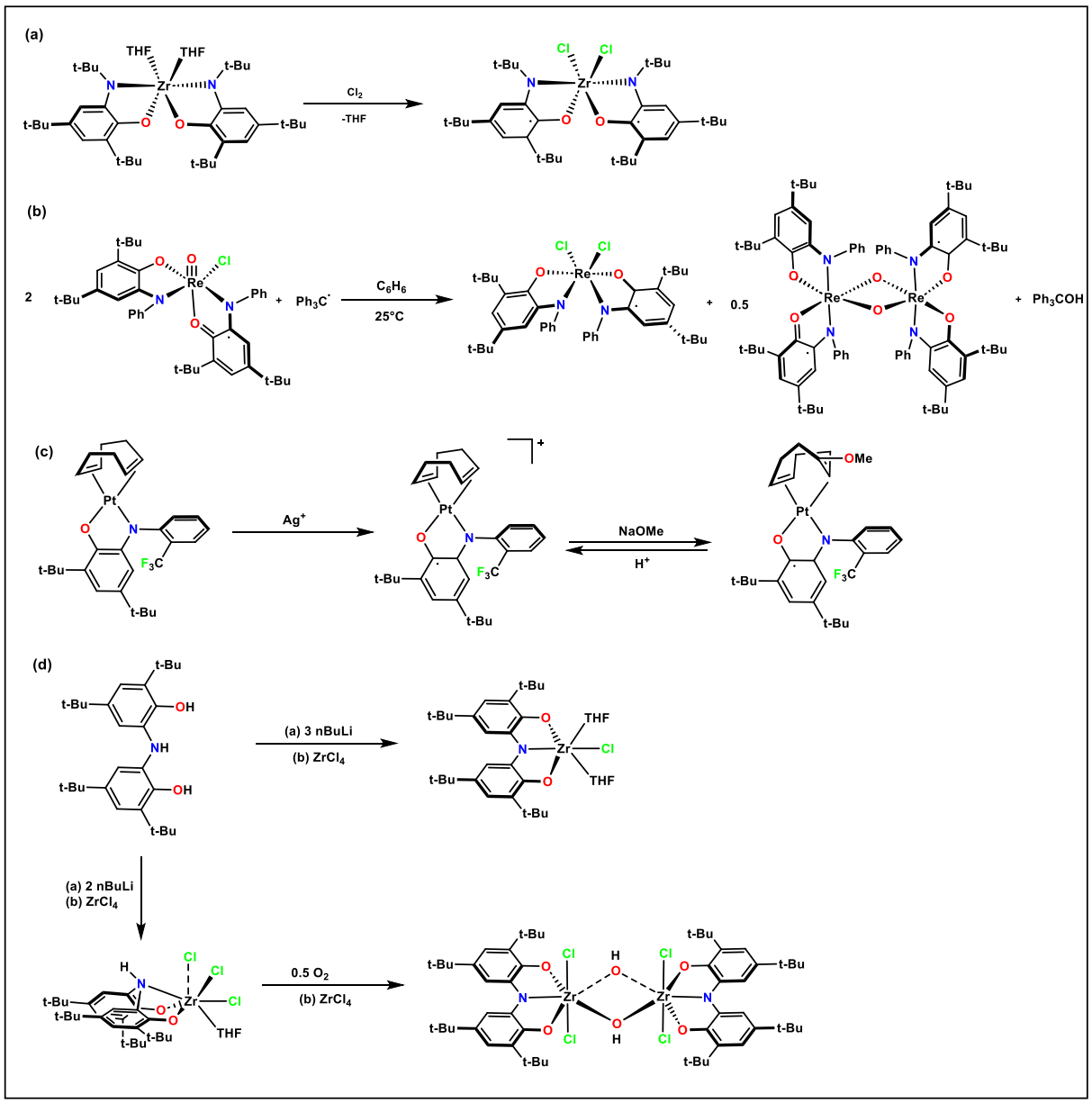


Chart 1.3: Examples of Redox-active ligands promoting the metal reactivity by (a) serving as an electron reservoir [Blackmore et al., 2005], (b) Ligand to the substrate single electron transfer [Lippert et al., 2011], (c) Altering the Lewis acidity/basicity [Boyer et al., 2009], (d) Ligand-centered cooperative reactivity [F. Lu et al., 2012].

1.2 Redox-Active Ligands in Nature

In nature, redox-active motifs, whether within the second coordination sphere of a metal cofactor or bound as ligands, are relied upon to catalyze complex processes. Nature unquestionably leads the way in employing redox-active ligands for catalysis and chemical transformations [Kaim & Schwederski, 2010]. In nature, multi-electron processes predominantly involve metals characterized by single-electron redox events, such as Cu, Fe, and Mn [Praneeth et al., 2012]. However, noble metals, such as Pd or Rh, are the primary catalysts used in homogeneous catalysis due to their propensity for undergoing two-electron reactions. Redox-active molecules are used by nature to store electrons and facilitate their transfer to metal centers, giving base metals the characteristics of noble metals. The cytochrome P450's active site, which has been found in every realm of life [Lamb et al., 2009] and functions as a catalyst for a monooxygenase reaction, is one of the well-known examples from nature. The heme cofactor that constitutes the active site of cytochrome P450 is composed of a porphyrin ligand and a Fe^{+2} center [Poulost et al., 1987]. Green and co-workers [Rittle & Green, 2010], in 2010 successfully isolated a very reactive intermediate identified as P450-I of the catalytic cycle (Chart 1.4). The P450-I, featuring a porphyrin radical ligand that is singly oxidized, has the ability to transform hydrocarbons into alcohols. The singly oxidized porphyrin radical ligand and iron(IV) center supply the redox equivalents for the P450-I-promoted conversion of hydrocarbons to alcohols, resulting in the production of a porphyrin ligand and an iron(III) center.

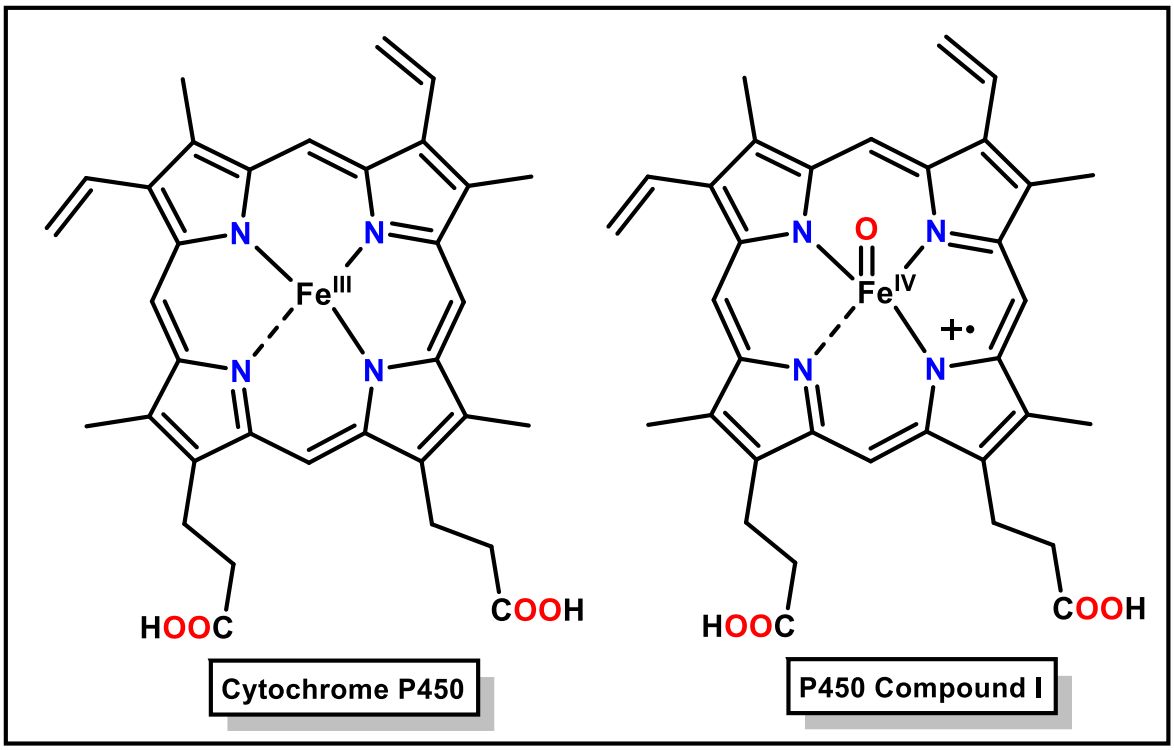
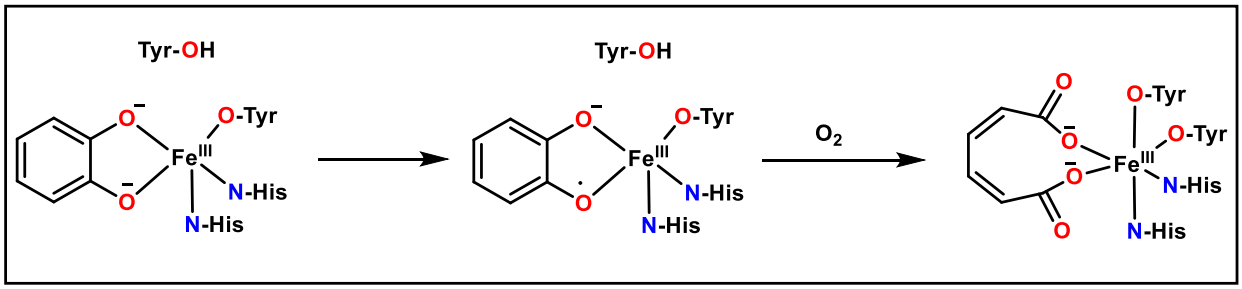


Chart 1.4: (Left) Heme cofactor constituting active site of Cytochrome P450 system and (right) highly reactive intermediate defined as P450 compound I (Rittle & Green, 2010).

Another demonstration of nature's utilization of redox-active ligands occurs in the intradiol oxidative cleavage of catechols facilitated by catechol dioxygenase (Scheme 1.1) [Borowski et al., 2004a, 2004b; Borowski & Siegbahn, 2006]. Inspired by biomimicry, chemists have recently devised strategies that harness redox-active moieties near metal to catalyze intricate changes. This method allows researchers to confer noble-metal properties to 3d transitional metals, such as Cu or Fe, which are less toxic and more cost-effective in multi-electron catalytic processes. Over the last decade, there has been a notable increase in comprehension and the identification of potential applications for this concept in the realms of catalysis, electronics, and supramolecular chemistry.



Scheme 1.1: Catechol dioxygenase facilitated intradiol cleavage of catechols [Borowski et al., 2004a, 2004b; Borowski & Siegbahn, 2006].

1.3 Redox-Active Ligands in Laboratories

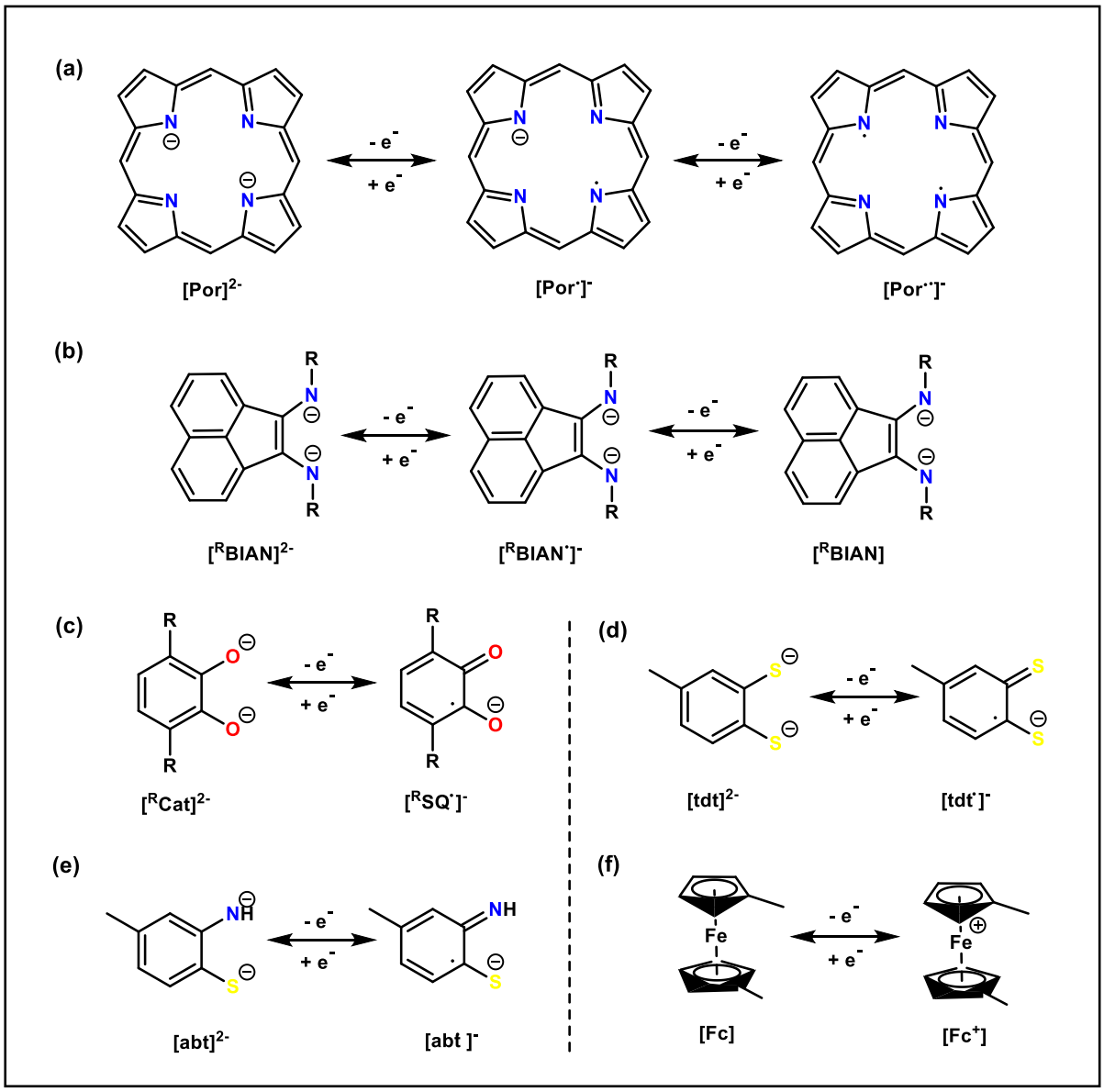


Chart 1.5: Redox-active ligands possessing redox couples that can function as electron reservoirs.: (a) porphyrinato (Por), (b) 1,2-bis(imino)acenaphthene (BIAN), (c) catecholate (Cat)/o-semiquinone (SQ), (d) 3,4-toluenedithiolate (tdt), (e) 2-amidobenzenethiolate (abt), (f) ferrocenyl (Fc) [Briand, 2023].

Drawing inspiration from nature, advancements in utilizing redox-active ligands with plentiful base metals have surged to deal with the financial, health, and environmental challenges linked to precious metals. Redox-active ligands with classic examples include anionic ligands such as o-amidophenolates (AP), catecholates (Cat), dithiolenes (mnt), 1,2-benzenedithiolates (tdt), 2-amidothiophenolates (abt), reduced α-diimides (DAB, BIAN), and ferrocenyl ligands (Fc), which undergo reversible one-electron oxidation as well as porphyrins (Por) which are known for facilitating two-electron processes (Chart 1.5) [Briand, 2023]. Consequently, complexing with these ligands facilitates the possible reversible oxidation of organometallic complexes featuring metal centers with limited or no accessible valence electrons. These ligands are employed in the preparation of transition metal complexes with beneficial catalytic applications, achieved by overpowering preferred one-electron redox reactions and promoting two-electron reactions [Broere et al., 2015a; van der Vlugt, 2019]. These ligands have been utilized in the creation of complexes exhibiting a diverse range of fascinating conductive, optical, and magnetic properties and contributing to the development of novel optoelectronic devices [Garreau-de Bonneval et al., 2010].

1.4 β-diketimine ligands

β-Diketimines also known as nacnac, 1,5-diazapentadienyl, represent a significant category of monoanionic bidentate ligands, featuring a ligand framework consisting of two nitrogens in the structure R^1-N=C(R^2)-C(R^3)=C(R^4)-NH-R^5 (Chart 1.6). The utilization of β-diketiminate ligands as a versatile auxiliary ligand is widespread [Asay et al., 2011; Bourget-Merle et al., 2002; Tsai, 2012]. The significant advantage of β-diketiminate ligands lies in their extensive tunability of steric parameters or electronic properties, which is highly beneficial in chemical research. β-diketiminate ligands are redox active in nature, which has been proven in recent times, in addition to their rich chemistry. Khusniyarov, Wieghardt, and co-workers were the first to report the oxidation of β-diketiminate ligands based on their Ni^{II} complex (Scheme 1.2(a)) [Khusniyarov et al., 2011]. EPR experiments and DFT calculations provided support for the oxidation of β-diketiminate ligands through a ligand-based mechanism.

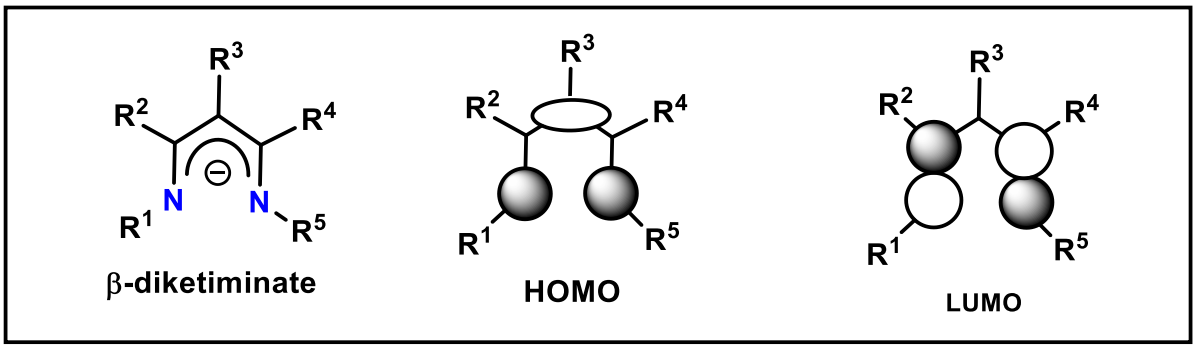
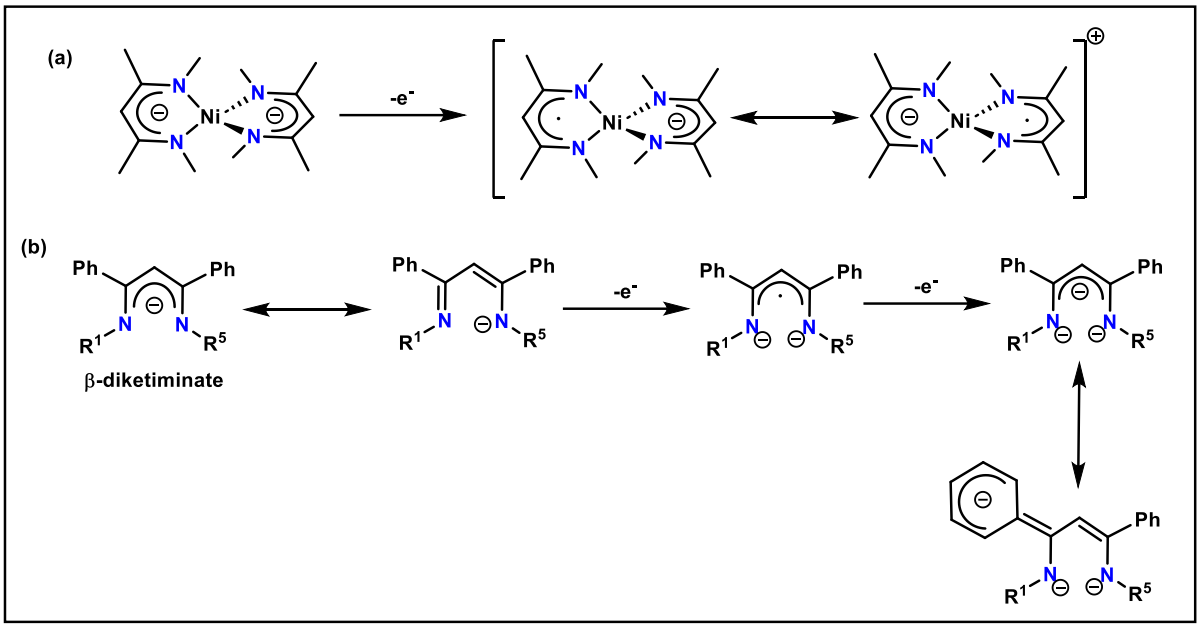


Chart 1.6: β-diketiminate ligand: General molecular structure (left), Highest occupied molecular orbital (middle), and Lowest unoccupied molecular orbital (right)

Itoh and co-workers published the very first investigation of the singly oxidized bis(β-diketiminate)Ni^{II} [Takaichi et al., 2014]. In comparison to the parent complex $[L]_2Ni^{II}$, the bond lengths of the ligand scaffold of the $([L]_2Ni^{II})^+$ exhibit minimal variation. This can be because of the nonbonding nature of the HOMO of ligands [Khusniyarov et al., 2011; Takaichi et al., 2014]. In 2002, Lappert and coworkers initially examined and structurally defined the ligand-based reduction of β-diketiminate ligands using systems of Yb and Sm complexes [Bourget-Merle et al., 2002]. The reduced bis(β-diketiminate)Sm complex exhibits distinct elongations in the C-N bond distances of one of the β-diketiminate ligands, suggesting the presence of a dianionic ligand backbone. The same group reported a ligand-based 2-electron reduction in the following year, resulting in the formation of a trianionic ligand backbone (Scheme 1.2(b)) [Avent et al., 2004;

Eisenstein et al., 2003]. This reduction was carried out using Yb and Li complexes. The observed elongations in the lengths of C-N bonds in reduced bis(β -diketiminate) based metal complexes can be attributed to the presence of orbitals that exhibit antibonding properties between carbon and nitrogen. In general, the synthesis of reduced products of β-diketiminate metal complexes requires the use of strong reducing agents, such as Yb-naphthalene complex or Li metal.



Scheme 1.2: (a) Oxidation of bis(β-diketiminate)Ni complex [Khusniyarov et al., 2011]. (b) Successive two-electron reduction of a β-diketiminate ligand [Avent et al., 2004; Eisenstein et al., 2003].

1.5 The Formazan/Ate Scaffold: An Encouraging Prospect as a Redox-Active Ligand

Formazans (Ar^1-NH-N=CR^3-N=N-Ar^5), a group of intensely colored and nitrogen-rich ligands that bear a strong resemblance to the structural composition of β-diketimines, have been recognized since the late 1800s and subjected to closer examination since the early 1940s [Gilroy & Otten, 2020a; S. Kumar, 2017; Shawali & Samy, 2015a; Sigeikin et al., 2006]. Initially synthesized by von Pechmann and Bamberger [Nineham, 1955a], these highly colored compounds act as precursors to verdazyls, a group of stable radicals [Hicks, 2007; Koivisto & Hicks, 2005] (Chart 1.7), and have been widely employed as dyes, mainly in the field of cell biology where these are primarily utilized for the precise assessment of cell viability [Ghasemi et al., 2021]. The backbone of formazans, Ar^1-NH-N=CR^3-N=N-Ar^5, serves as a foundation for structural isomerization. Bulky aryl or alkyl R^3 substituents have the propensity to promote the 'closed' isomer, whereas smaller R^3 substituents (such as CN) permit the adoption of the 'linear' (trans–anti, s-trans) and 'open' (trans–syn, s-trans) geometries (Chart 1.7). A significant correlation exists between the adopted isomer and the color of formazan ligands, wherein the 'closed' isomer displays a distinct red hue, whilst 'linear' and 'open' forms manifest yellow and orange colors, respectively.

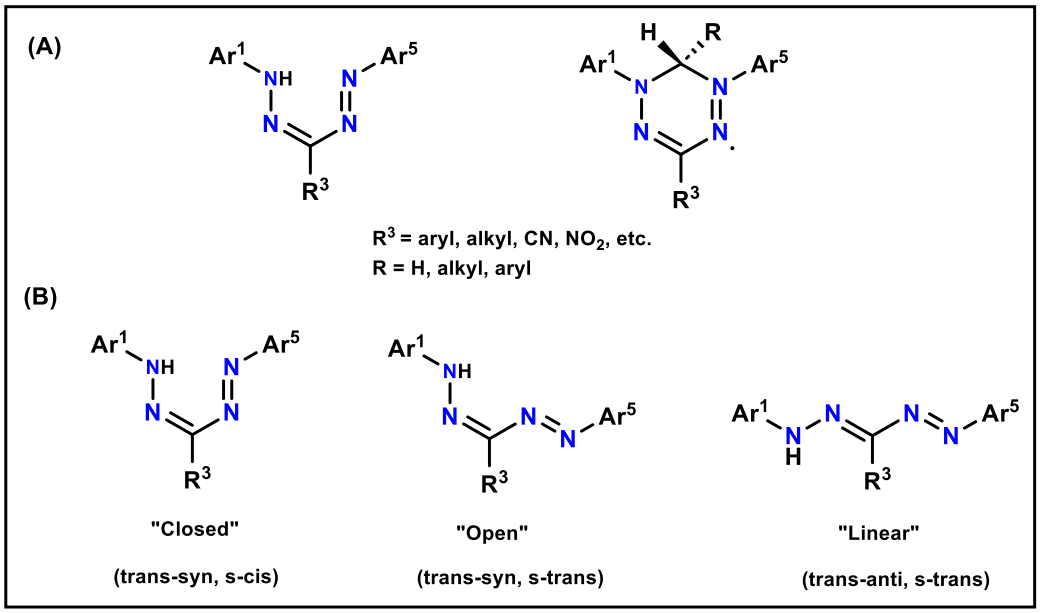


Chart 1.7: Formazan ligands: (A) General structure (left), and verdazyl radical (right) (B) Structural isomers [Gilroy & Otten, 2020a].

A notable characteristic of formazan chemistry is the ease with which these compounds may be synthesized, enabling the preparation of libraries of these compounds and the ability to modify properties due to structural variations. Different ways for the preparation of formazans are depicted in Chart 1.8. While there are multiple synthetic pathways for the preparation of formazans, the predominant approaches include the reaction of aryldiazonium salts with compounds containing activated carbon groups. An illustration of this is the synthesis of triarylformazans, which involves the reaction of aryl diazonium salt with hydrazones in equimolar concentration [Katritzky Sergei A; Cheng Dai; Durst H Dupont, 1995; Nineham, 1955a]. The nature of this approach allows for the synthesis of 3-alkyl formazans as well as asymmetric formazans with varying Ar^1 and Ar^5 substituents [Nineham, 1955a]. As an alternative, symmetric formazans (Ar^1 = Ar^5) are produced by combining two equivalents of aryldiazonium salts with compounds that have activated methylene groups. Consequently, the activated methylene group of derivatives of phenylpyruvic acid reacts with two equivalents of aryldiazonium salts to prepare triarylformazans [A. Ibrahim et al., 1994]. Analogous reactions result in the generation of 3-nitroformazans and 3-cyanoformazans [Gilroy, Otieno, Ferguson, McDonald, et al., 2008]. While these procedures provide a moderate to fair yield of formazan products (usually between 40% and 80%), the stability of the required diazonium salts can pose challenges, particularly when introducing sterically bulky substituents.

Formazanate ligands present distinctive and potentially valuable characteristics in comparison to similar groups of ligands. A key attribute is their capacity to partake in both reductive and oxidative redox processes because of the existence of low-lying empty (electron-accepting) and high-lying filled (electron-donating) π-symmetry orbitals (depicted in Chart 1.9). The wide accessibility of formazans with various substitution patterns enables deliberate adjustment of the energies of these frontier orbitals. With further impact from the π-conjugated aromatic N-Ar^1/Ar^5 groups, the orbitals centered on the NNCNN backbone contributes the majority of both the HOMO and LUMO. As a result, groups at the para- and ortho-position of the N-aryl rings should have an impact on the energies of both of these orbitals, mostly through resonance effects. The LUMO exhibits a nodal plane that passes through the C-R^3 and is completely π-anti-bonding between the 4 nitrogens in the formazanate backbone. Therefore, structural modification at this position only affects the LUMO's energy inductively. Furthermore, the existence of the low-lying π*-orbital facilitates electronic transitions within the visible

spectrum, and modifications to the ligand structure readily tune both the emission and absorption properties of formazanate complexes.

The availability of four nitrogen in the scaffold provides coordinative flexibility, enabling the creation of chelates with four-, five-, and six-membered rings (Chart 1.9). The formazan ligand backbone, specifically those with four- and six-membered chelate rings, typically have bond lengths that fall between those of double and single bonds for the corresponding atoms, which suggests a significant level of electronic delocalization within the conjugated system. In the case of 5-membered rings, the bond distances within the formazanate scaffold often suggest a bonding arrangement that is more localized. However, this tendency appears to rely on factors such as the substitution pattern of the ligand and the identity of the central inorganic element.

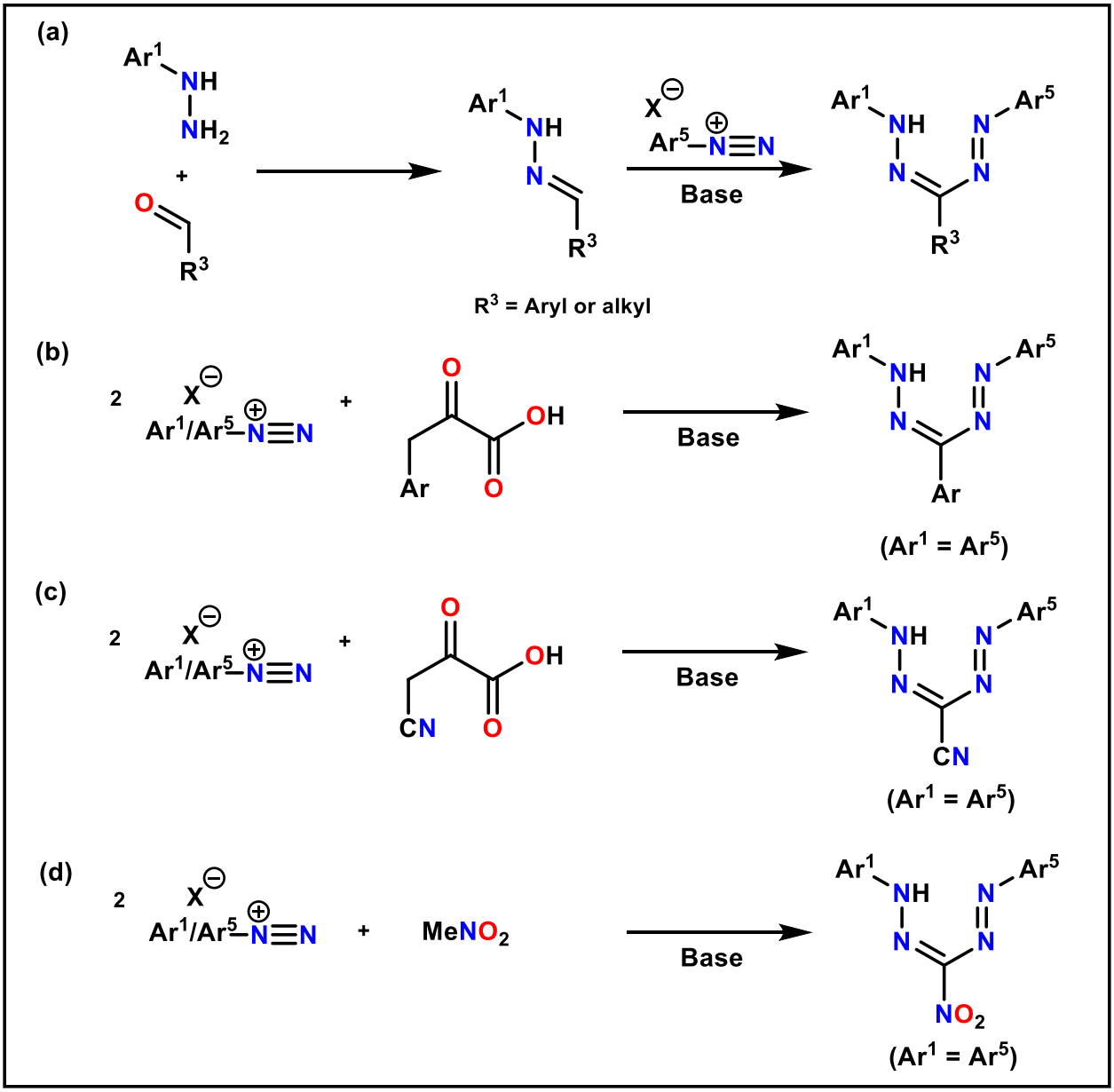


Chart 1.8: Different ways for the preparation of formazans (Gilroy & Otten, 2020).

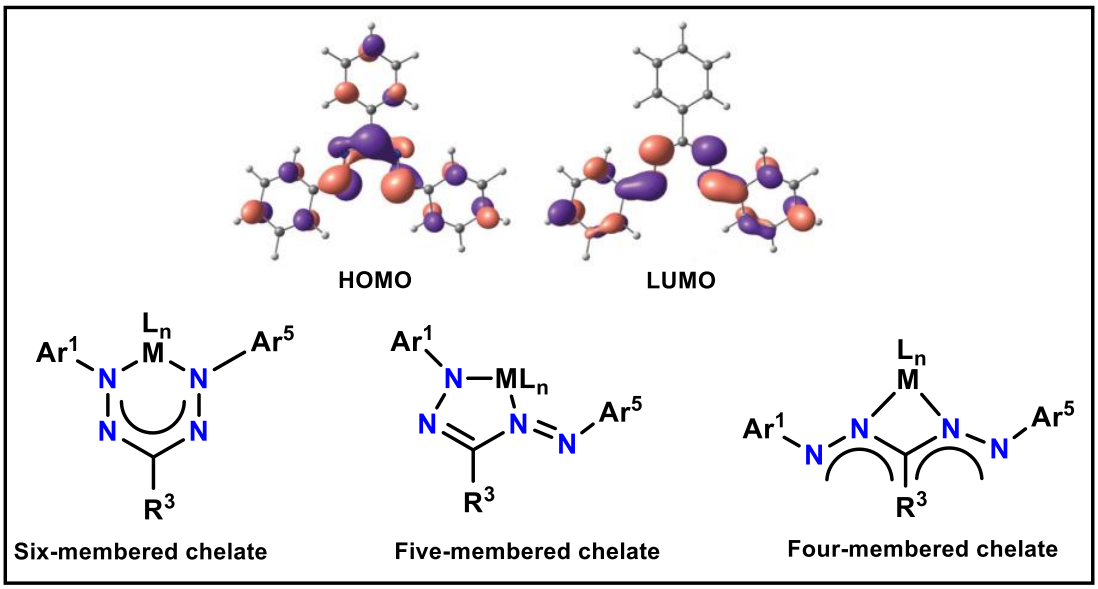
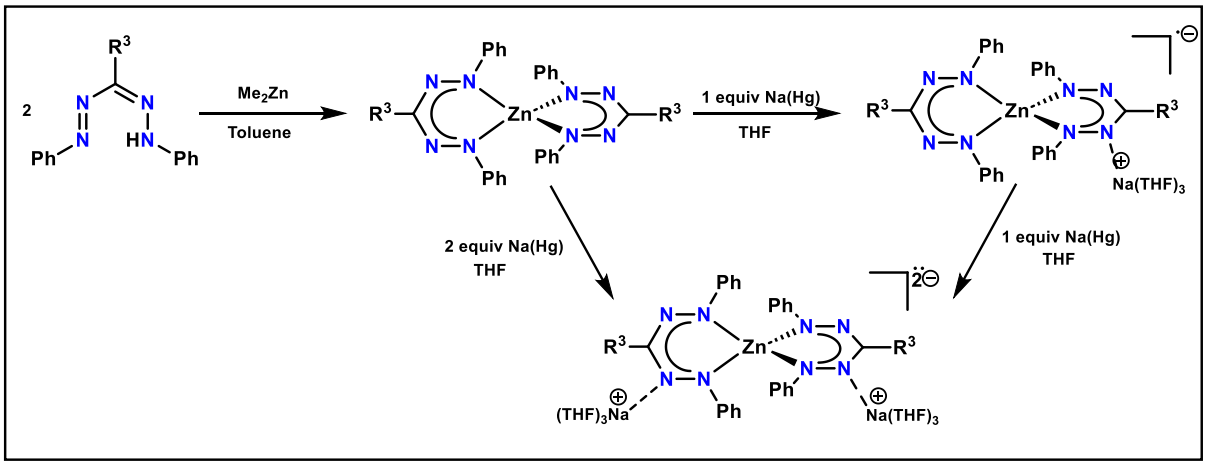


Chart 1.9: Top: Frontier (Kohn–Sham) orbitals of the triphenylformazanate anion in the well-known 'closed' form, determined by DFT (B3LYP/6-31G(d)). Bottom: Commonly observed binding modes by formazanate ligands [Gilroy & Otten, 2020a].

1.5.1 Formazanate Ligands as Electron Reservoirs

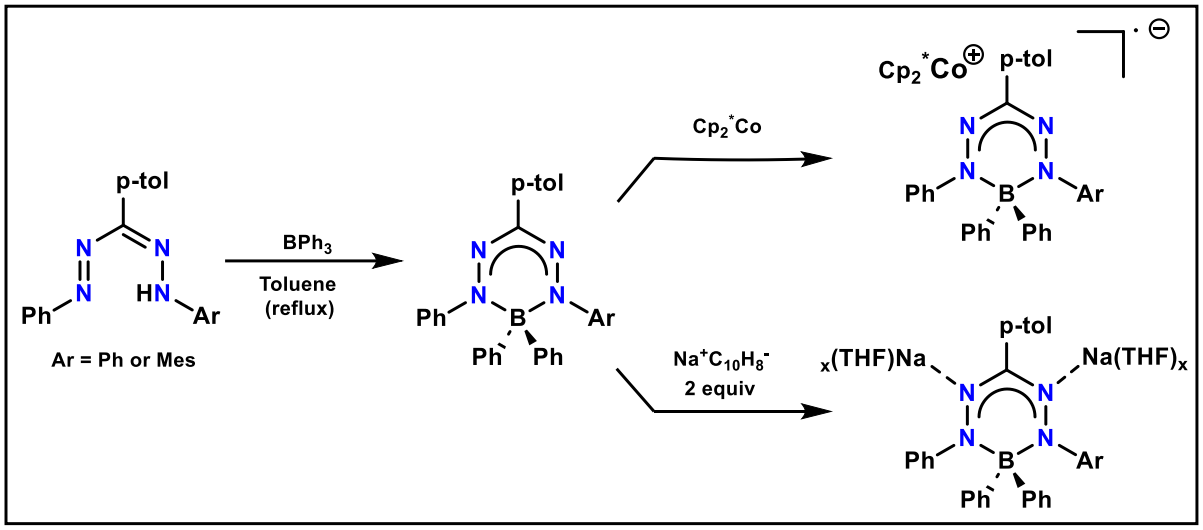
Formazanate-based metal compounds have distinct redox characteristics, which are commonly characterized by reversible redox processes focused on the ligand. In 2007, Hicks and colleagues documented the conversion of formazanate boron diacetate compounds into radical anions, marking the initial study showcasing formazanates as redox-active ligands and laying the foundation for subsequent investigations [Gilroy et al., 2007a]. Zinc complexes containing formazanate ligands exhibit highly efficient and reversible redox reactions, enabling comprehensive characterization of bis(formazanate)Zn complexes in charge-neutral, anionic, or dianionic redox states (Scheme 1.3). Ligand-centered processes resulting in one- and two-electron reductions were identified, generating anionic and dianionic radicals. In these processes, each ligand gains 1 e^- [Chang et al., 2014].



Scheme 1.3: Formazanate-based Zn(II) complexes depicting ligand-based reduction, R^3 = p-tol, tBu [Chang et al., 2014].

Furthermore, the efficacy of the formazanate moiety in functioning as an electron sink was demonstrated by the use of monoformazanate boron complexes (Scheme 1.4) [Mondol et al., 2017]. These complexes have the capacity to accommodate the addition of up to two electrons,

which results in the creation of a dianionic formazanate complex and this study demonstrated that the reversibility of the second reduction event may be influenced by steric limitations. Gilroy and coworkers also observed comparable results in boron difluoride complexes based on formazanate ligands, where the ligand acts as a 2 e^- reservoir, albeit the stability of the doubly reduced species is lower in this case [Barbon et al., 2014a]. Formazanate complexes with Aluminum [Mondol & Otten, 2019], Iron [Broere et al., 2018a], Iridium [Kabir et al., 2019], and Platinum [Kabir et al., 2018] have also been recognized for their ability to store electrons. The redox potentials of complexes, including the transition and main group metals, are greatly affected by the characteristics of groups bound to the nitrogen atoms. There is a shift in reduction potentials towards the anode due to electron-withdrawing groups, which helps to facilitate reduction processes.



Scheme 1.4: Reduction of mono(formazanate) boron complex [Mondol et al., 2017].

1.5.2 Diverse Biological Significance of Formazans

Formazans have been investigated to hold significant medical potential owing to their diverse range of activities, including anti-inflammatory, anti-HIV, antiviral, analgesic, antifungal, anticancer, antimicrobial, and more [Shawali & Samy, 2015b]. A number of formazan molecules have been studied for their potential antimicrobial properties, with the most noteworthy being compounds shown in Chart 1.10 [Bayazeed et al., 2022]. Formazans have also exhibited promising activities in anti-parkinsonian, anti-fertility, and anticonvulsant domains. Several researchers have documented the efficacy of this particular group of chemicals against the Gomphrena mosaic virus (GMV), mosaic virus (TMV), and Ranikhet disease virus [Misra & Dhar, 1980]. Formazan derivatives have been extensively employed in the assessment of cell viability and the screening of anti-HIV agents, as well as the evaluation of their cytotoxicity. Some formazan derivatives have been reported to possess antiviral properties, with the antiviral effect attributed to the presence of an intact C–N=N group and C=N-NH group [Mariappan et al., 2010a]. Formazan compounds have also been reported to be utilized for the detection and quantification of target molecules, such as antigens, antibodies, or polynucleotides. Recently, a crown formazan derivative has been identified as a replicase inhibitor specifically targeting the bovine viral diarrhea virus [Fryšová et al., 2006]. The reproduction of laboratory-adapted and primary HIV-1 isolates, as well as cell-to-cell fusion, was efficiently suppressed by synthetic formazan, exhibiting minimal cytotoxicity [Barltrop et al., 1991]. There are reports on formazan metal complexes that indicate they may be a promising drug candidate that inhibits the growth of microbial strains, efficiently scavenges free radical species, and has the capacity to cause cytotoxic effects on carcinoma cells.

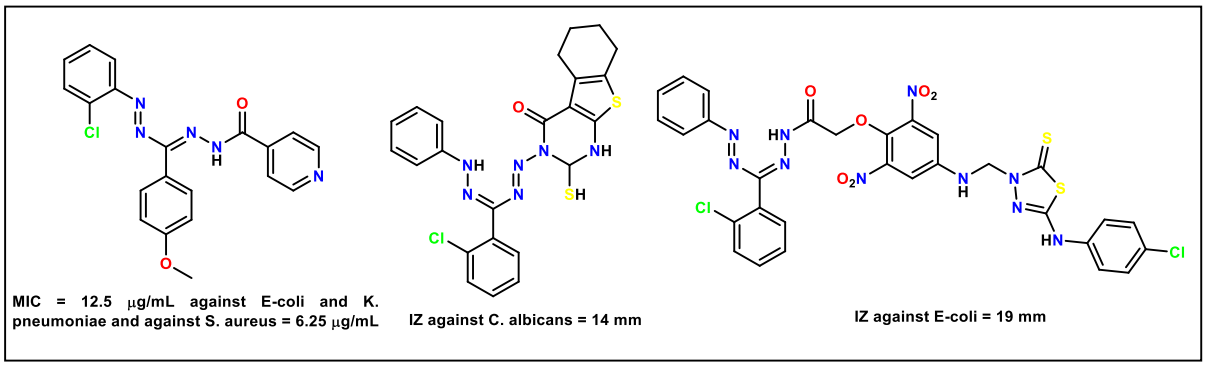
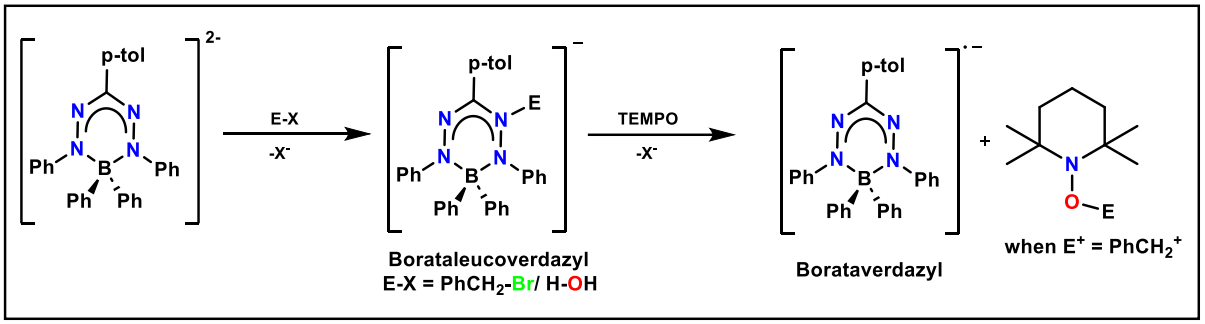


Chart 1.10: Examples of formazan derivatives reported as anti-microbial agents (Lakshmi et al., 2009; Raval et al., 2009; Sah et al., 2014).

1.5.3 Formazanate Redox Non-innocence for Catalytic Processes

The capability of formazan ligands to store and transfer redox equivalents has paved the way for innovative approaches in catalysis, where critical steps are predominantly governed by ligand-mediated redox processes. Promising reactivity has been demonstrated by reduced formazanate species in catalysis and bond activation. As an illustration, the stored electrons in the boron compound (Scheme 1.5) are utilized to catalyze nucleophilic attacks on compounds of the E-X type (with E^+ being Bn^+ or H^+), resulting in the production of the respective leucoverdazyl-type compounds. Adding one equivalent of TEMPO leads to the formation of the stable borataverdazyl radical anion, highlighting the weak N-E interaction within these entities [Mondol & Otten, 2018].



Scheme 1.5: Two-electron reduced boron compound depicting electrophilic addition [Mondol & Otten, 2018].

The term "switchable catalysis" refers to the regulation of reactivity through external stimuli. Embedded within the catalyst's structure are functional groups that can undergo reversible reactions triggered by light, coordination with metal ions, shifts in pH, or changes in redox state. These functionalities enable the promotion of various chemical reactions during catalysis. In this context, redox-active moieties can function as triggers, their efficacy contingent upon their respective redox states. Otten and co-workers have documented the redox-switching mechanism exhibited by a dinuclear formazanate zinc catalyst during the ring-opening polymerization (ROP) of lactide (Chart 1.11). Employing a redox-active ligand bound to an inactive metal ion (Zn^{2+}) facilitates the control of catalytic activity via reversible oxidation/reduction reactions taking place within a purely organic component. The findings from the kinetic and spectroscopic data provide evidence supporting the significant involvement of the ligand in both the redox activation process and the initiation of the polymerization reaction, ultimately leading to the synthesis of cyclic polylactide (PLA) [De Vries & Otten, 2022a]. Thus, the utilization of formazanate ligands is highly attractive for the development of redox-switchable systems unbound by the necessity of a metal ion serving as the locus for oxidation/reduction due to their convenient accessibility, adaptability, and cost-effectiveness. This approach could have broader applicability in achieving spatiotemporal control in various catalytic reactions.

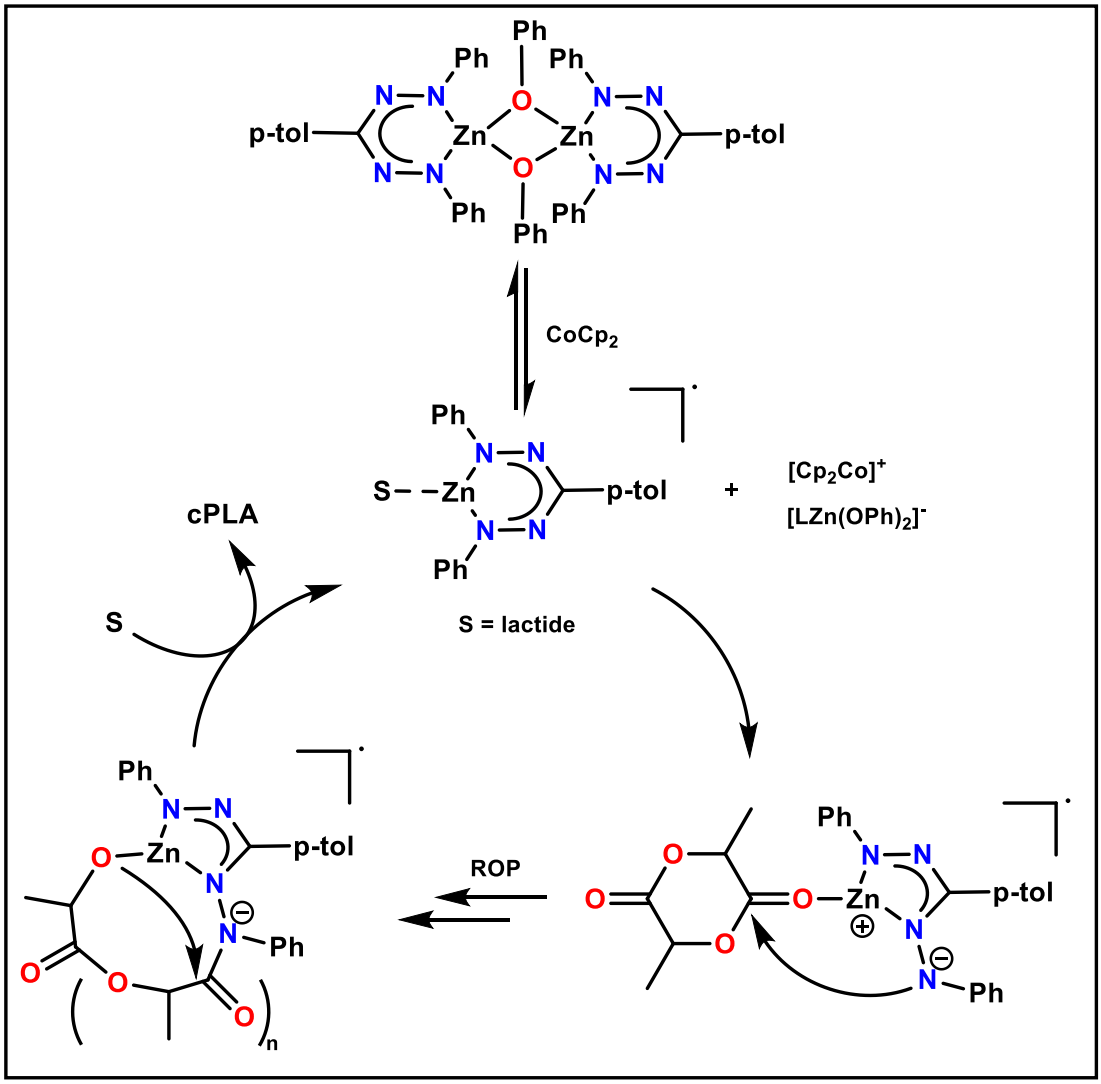


Chart 1.11: Proposed mechanism for switching ROP by a formazanate Zn(II) complex [De Vries & Otten, 2022a].

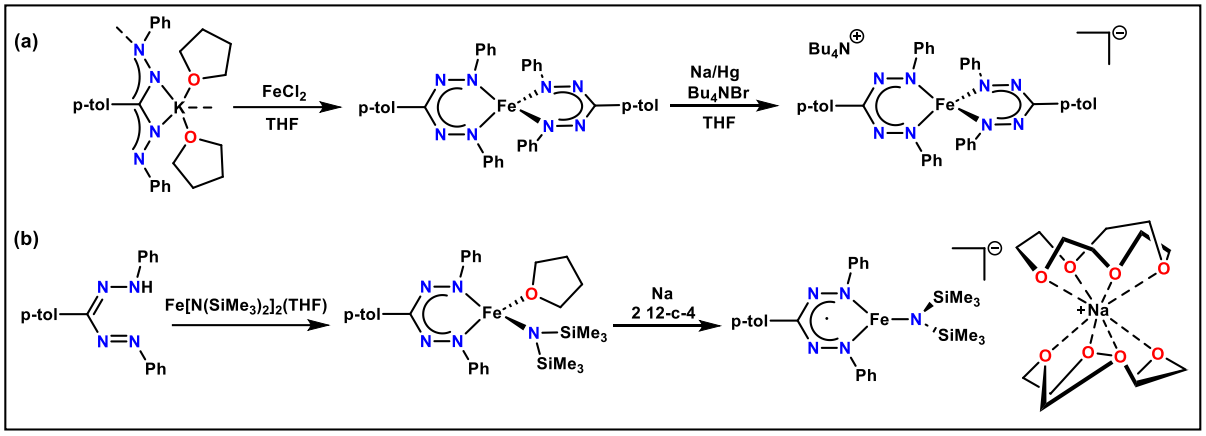
1.5.4 Formazanate Complexes: Spin-Crossover Attributes and Introduction to the Domain of Resistive Memory Devices

- **Spin-Crossover in Bis(Formazanate) Iron Complexes**

Electronic bistability in molecular compounds is a topic of significant importance in the advancement of switches, data storage devices, and sensors [Létard et al., 2006; Sato et al., 2007]. Various categories of these compounds are derived from coordination complexes of transition metals, which have the ability to transition between low- and high-spin states in response to external stimuli such as pressure, temperature, or light. Octahedral complexes that possess two states with close energy have the ability to demonstrate the phenomena known as spin-crossover (SCO). The unexpected manifestation of spin-crossover in the bis(formazanate) iron(II) complex was attributed to π-back interaction between the lower-lying formazanate π*-orbital and the iron center leading to notable stabilization of one of the high-energy orbitals (t^2). As a result, ligand-field inversion occurs, leading to a 2-over-3 splitting that bears resemblance to the splitting observed in six-coordinate octahedral complexes. Remarkably, the anionic bis(formazanate) iron(II) complex may be isolated through the chemical one-electron reduction of the bis(formazanate) iron complex. The complex under investigation was characterized as a low-spin (S = 1/2) Fe(I) complex, as evidenced by structural, spectroscopic, and computational data (Scheme 1.6(a)) [Travieso-Puente et al., 2016d]. This complex is characterized by closed-shell,

monoanionic formazanate ligands. Thus, although the formazanate ligands are redox-active, the first reduction in this scenario primarily takes place at the iron core.

Holland and co-workers later described a distinct scenario involving a mono(formazanate) iron(II) amide complex and its one-electron reduction product where various spectroscopic approaches indicate that the reduction is formazanate centered (Scheme 1.6(b)) [Broere et al., 2018b]. It is crucial to emphasize that although the formazanate ligand plays a distinct role in the reduction chemistry of the two iron complexes documented by Otten and Holland, the distinctive characteristics observed in both compounds can be attributed to the existence of a low-lying vacant π*-orbital. In one case, this orbital is involved in π-back donation, while in the other case, it enables formazanate participation in the redox event. This statement underscores the possibility of formazanate iron complexes attaining a synergistic relationship between the redox-active ligand and the redox-active metal.



Scheme 1.6: (a) One-electron reduction of the bis(formazanate) iron complex [Travieso-Puente et al., 2016d], and (b) mono(formazanate) iron(II) amide complex and its one-electron reduction product.

- **Introducing Formazanate Based Metal Complexes to the Domain of Resistive Memory Devices**

As the amount of data continues to grow exponentially, there is an urgent need to develop new high-performance memory devices. Resistive memory devices hold considerable promise for enabling high-density data storage while maintaining a compact device size [Chen et al., 2010; Zahoor et al., 2020a]. Resistive memory, often called resistive random-access memory (ReRAM or RRAM), is one of the propitious candidates for next-generation data storage in electronic devices. Altering the resistance of a solid-state material when subjected to an electric field enables data storage in a non-volatile manner, leading to resistive random-access memory (RRAM) behavior. The approach to designing resistive memory materials involves creating distinct electronic states under the influence of an electric field. This can be accomplished by adjusting the electron-donating and electron-accepting properties and the charge-transport characteristics of the formazanate-based metal complexes [Shao et al., 2019a]. Formazanate metal complexes frequently feature highly reversible and easily accessible redox couples, making them ideal candidates for electronic applications. By modifying the redox-active formazan based ligands and their bonding with metals, the optoelectronic properties can be fine-tuned, enabling the synthesis of new materials for information storage. Formazan-based molecules have been employed in designing conductors, secondary batteries, and spin memory devices. Very recently, our research group has introduced formazans to the field of resistive memory devices. Chapters 1, 2, and 3 of the thesis explore the synthesis and application of an organotin ionic complex and two Zn(II)-based complexes, each derived from formazan-based ligands, as active materials for resistive switching memory devices [Birara, Betal, et al., 2023b; Birara, Saini, et al., 2023].

1.6 Scope of Thesis

The sections discussed above explain the importance of formazanate-based metal complexes in the advancement of novel applications that use the versatile electrochemistry and unique optoelectronic characteristics offered by formazanate ligands. The objective of the research outlined in this thesis is to synthesize novel formazanate ligands with tunable properties and investigate their coordination behavior with various metal centers with the goal of revealing their potential uses in various domains. The following section provides a detailed description of the thesis work that focuses on the contribution of formazan metal complexes:

1. An ionic organotin complex, **1** based on a 2-pyridine substituted formazan ligand, is synthesized and characterized by a set of characterization techniques, including SC-XRD. Complex **1** was further employed as an active material for a write-once-read-many (WORM) memory device.
2. A distorted octahedral bis(formazanate)zinc complex ([$Zn^{II}L_2$], **2**) is synthesized and characterized by a set of characterization techniques, including SC-XRD. Complex **2** was further employed in the fabrication of a non-volatile resistive switching memory device.
3. A Benzothiazole substituted bis(formzanate) Zn(II) complex, ([$Zn^{II}L1_2$], **3**), where L1H = *1-(benzothiazol-2-yl)-5-(2-benzoyl-4-chlorophenyl)-3-phenyl formazan* is prepared and characterized by a set of characterization techniques, including SC-XRD. Complex **3** was further employed in the fabrication of a non-volatile resistive switching memory device leading to its higher switching memory performance compared to [$Zn^{II}L_2$] (**2**).
4. Two novel molecular cathodes, bis(formazanate) Fe(II) complexes, [$Fe^{II}(L2)_2$] (**4**), where L2H = *1-(benzothiazol-2-yl)-5-phenyl-3-(pyren-1-yl)formazan* and [$Fe^{II}(L1)_2$] (**5**), where L1H = *1-(benzothiazol-2-yl)-5-(2-benzoyl-4-chlorophenyl)-3-phenyl formazan* are prepared and structurally charactreized. Complexes **4** and **5** were coated on a glassy carbon electrode, and modified electrodes were further employed in a one-compartment H_2O_2 fuel cell design.
5. A distorted square pyramidal mercury complex, ([Hg^{II}(L3)Cl], **6**), based on a quinoline-substituted formazan ligand L3H, *[3-Cyano-1,5-(quinolin-8-yl)formazan],* is prepared and structurally characterized. Complex **6** was further evaluated for its anti-bacterial activity *in vitro,* followed by *in silico* studies.