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## Formazanate as redox-active, structurally versatile ligand platform

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## Perspective

In this thesis, synthetic procedures of formazan ligand and corresponding zinc and boron complexes have been developed. The redox-active nature of formazanate ligand was established by electrochemical and chemical methods. The results presented in this thesis provide a strong basis for future research using formazanate ligands. In the following sections, the perspective of my research and potential research directions that make use of the unique properties of formazanate ligands are described.

The first challenge encountered in this work is the formazan synthesis. Even though several synthetic procedures for preparing formazan ligands have been reported, the outcome of synthetic methods for new formazan derivatives is still hard to predict. The results in *Chapter 2* show that using different starting materials the reaction conditions and purification procedures to obtain the final product can be different. For example, in order to introduce a mesityl substituent on the formazan N atom (**1c**), a solvent mixture of acetone/water is used. The reason for using acetone/water mixture is to find a balance between dissolving all necessary chemicals (NaOH, hydrazone, and diazonium salt) and the stability of diazonium salt. In addition to the unpredictable reaction conditions, another general challenge of formazan synthesis is to introduce sterically demanding substituents to the ligand backbone, which is a frequently used strategy to control reactivity and selectivity of catalysts. Unfortunately, for formazan ligands, bulky substituents, such as 2,6-di-iso-propylphenyl groups, are not easy to introduce due to the low stability of the corresponding diazonium salt. Therefore, it is necessary to develop new synthetic procedures to access formazan ligands having bulky substituents.

In *Chapter 3*, bis(formazanate)zinc complexes (compound **5**) were synthesized and fully characterized. The synthetic method to obtain the heteroleptic bis(formazanate)zinc complex (**5aj**) has a great potential to combine two different ligand system into one metal complex, in which the redox-active formazanate ligand can be used to store redox equivalents and the second ligand system can be used to control the reactivity and selectivity of the metal complex. At the end of *Chapter 3*, we discovered a potential method to synthesize a triazole from the reaction of the heteroleptic bis(formazanate)zinc complex (**5aj**) with BF<sub>3</sub>. However,

more work is needed to understand the mechanism, establish substrate scope and to develop the observation into a proper synthetic procedure for triazole synthesis starting from 3-cyanoformazan ligands.

The challenge encountered in *Chapter 6* is to isolate and characterize all the BN-heterocycles that are obtained upon 2-electron reduction of the (formazanate)boron difluoride precursor (compound **6a**). The formation of a series of BN-heterocyclic products suggests that formazanate ligands are capable of stabilizing reactive B(I) centers. Unfortunately, the initial attempts of trapping the (formazanate)B(I) species were not successful. However, it is still worth trying to isolate the (formazanate)B(I) species and compare its reactivity with known B(I) species in literature. In addition, the results of this chapter indicate that redox-active ligands is not simply being reservoirs for redox equivalents; the ligand-based reduction can lead to interesting structural rearrangements.

In *Chapter 7*, the thermally induced intramolecular hydride transfer of the (formazanate)boron dihydride complexes results in the formation of aminoborane products, which are a bioisosteric replacement of imidazoles and pyrazoles. The potential challenges of studying aminoborane products are the synthetic procedures of both (formazanate)boron dihydride complexes (compounds **10**) and aminoborane products (compounds **18**). The yield of the current synthetic procedure of (formazanate)boron dihydride complexes are very low (10-30%) and the purifications of the aminoborane products are not established.

Potential research directions of formazanate complexes:

#### *Ligand-Based Oxidation*

In this thesis, the ligand-based reduction of formazanate ligand has been established; but unlike the research of the  $\beta$ -diketiminato ligand system, which shows both ligand-based reduction and oxidation reactions, the ligand-based oxidation reactions of formazanate complexes are still not clear. The ligand-based oxidation reaction will make formazanate ligands a promising candidate for participating 2-electron process by changing its oxidation states between the 1-electron reduction product ( $L^{-2}$ ) and the 1-electron oxidation product ( $L^0$ ). The advantages of this process are that the 1-electron reduction product is easily accessible, and there is no need to reach the reactive (or unstable) 2-electron reduction product. Therefore,

there is clear motivation to study the formazanate-based oxidation reactions.

The cyclic voltammogram of both zinc and boron complexes bearing formazanate ligands do not show any evidences of oxidation reactions under measuring conditions. By synthesizing metal complexes having electron-rich metal centers and easily access d-electrons, both of which can stabilize oxidation products, the ligand-based oxidation of formazanate complexes is possible to reach. The preliminary results from Dr. Barbara Milani prove this concept. The cyclic voltammogram of a bis(formazanate)palladium complex ( $L_2Pd$ ) shows a clear evidence of a (quasi)reversible ligand-based oxidation. The next steps in this direction are to synthesize and characterize the oxidation products as well as to develop suitable catalytic reaction based on this system.

#### *Oxidative Addition of (Formazanate)Al(I) Complexes*

The low-valent group 13 complexes, especially Al(I), bearing formazanate is an attractive complex to made. Based on the results of the boron chemistry presented in *Chapter 6*, the formazanate ligands are capable of stabilizing reactive B(I) center. We can expect that the (formazanate)Al(I) complexes will be more stable than the B(I) complexes due to the inert pair effect. The higher stability of (formazanate)Al(I) complexes makes it as a potential candidate for the study of oxidative addition reactions.

#### *Base-Metal Complexes*

Replacing precious metals by base metals from catalysts is one of the ultimate goals for researches of redox-active ligands. Therefore, preparing base metal complexes bearing formazanate ligands is a research direction worthy studying. From my point of view, Fe and Co complexes are very attractive targets for the future research of the formazanate ligand. The successful researches of Fe and Co complexes bearing tridentate redox-active ligands have been reported by Paul and co-workers (please see *Chapter 1*), but the bidentate analogue of Fe and Co complexes are still limited. The desired Fe and Co complexes bearing formazanate ligands will give us not only comparisons with tridentate ligand system but also more insight about the role of redox-active ligand in catalytic reactions.

