STABILIZATION OF HIGH OXIDATION STATES IN TRANSITION METAL COMPLEXES

by

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ABSTRACT

Redox active ligands, i.e. ligands that can be reduced or oxidized, are of considerable interest due to the fact that they potentially have the ability to stabilize unusual metal species. Previous work done by Wieghardt[1-3] as well as by our lab[4] has shown that two prime examples of these types of ligands are dithiolene and α-diimine complexes. This work has shown that in some instances these ligands themselves are oxidized, while other times the metal oxidation state is altered. With this in mind, we set out to explore the use of 1,1'-diaminoferrocene (dafc), a redox active complex, as a ligand with divalent metal cations. The reasoning is that the ligand's metal center, with its increased electron density (as compared to main block elements such as carbon, nitrogen, oxygen, and their respective groups), may be able to aid in oxidation-reduction reactions and achieve otherwise rare metal oxidation states. Our work focused primarily on cobalt, which contains a large number of electrons in its d orbitals (nine in the zero-valent state). Our attempts also spilled over into metal with fewer available d electrons, such as titanium, vanadium, chromium and manganese. Synthetic routes have been explored for these compounds, yet all failed to produce the desired ligand-metal complex. Theories for the failure of current synthetic routes, as well as possible alternatives, are presented. While these compounds were not able to be synthesized in the duration of this project, the proposed compounds present an interesting study and their potential in ligand based oxidation-reduction chemistry can not be effectively ruled out.

Chapter 1

INTRODUCTION

The first row transition metals, more commonly known as the 3d metals, are prized for several reasons. First of all, they are naturally abundant and comparatively inexpensive. Additionally, they exhibit multiple oxidation states and possess the advantage of more tunable electronics when compared to main block elements. While the first half of the series (Sc-Mn) can be placed into their highest oxidation state (+7 in the case of Mn), the other half possess considerably fewer available oxidation states. With their greater effective nuclear charge, it is considerably more difficult to oxidize these metals to the +3 or +4 oxidation state. While examples of these high oxidation states exist and have been characterized, they are few and far between. Instead of reaching these oxidation states by traditional means, is it possible to oxidize these metals by using redox active ligands to encourage oxidation? The purpose of this thesis is to see if the redox active ligand, 1,1'-diaminoferrocene (dafc) is able to encourage and stabilize an unusual oxidation state of the normally divalent cobalt. Based on reasoning concerning the steric bulk of the ligand, as well as several reactions performed with different stoichiometric concentrations of ligand to metal, we believe the ligand binds to cobalt in a 2:1 ligand to metal ratio. However, all attempts at isolating and confirming that a ligand-metal complex was formed failed. Additionally, a series of ligand-metal complexes were attempted, but crystallographic data showed only the metal ion with coordinated solvent molecules.

There is precedent for using non-innocent ligands to promote a change of oxidation state of a metal. These ligands sometimes cause the metal to be oxidized, and sometimes they themselves are oxidized. This field has been explored by Wieghardt with bis(benzene-1,2-dithiolato) metal complexes[1], as well as with α-diimine ligands[2] and pyridine bisimine ligands[3]. The Wieghardt group explored reactivity primarily with nickel and other late transition metals, but examples of redox non-innocent ligands have been synthesized by our lab using similar diimine ligands. These diimine ligands have been shown by Kreisel to stabilize the formal oxidation state of chromium in these examples (figure 1)[4].
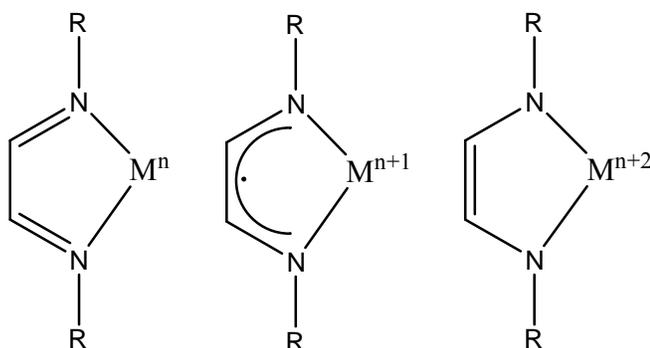

Figure 1: Taken from Kreisel[4], where M=Cr. Kreisel was able to prepare structures where the formal oxidation state of CR (by DFT calculations) ranged from –I to +II

Although both diimine complexes and dafc are bidentate ligands by means of a nitrogen, the similarities end there, as diimine complexes are often reduced and dafc has only been reported as oxidized (dafc$^+$ has been reported by Shafir[5]). Alternatively, if the ligand were to be reduced to dafc$^-$, the iron would violate the 18 electron rule by containing 19 electrons). Ferrocene (Fc) and dafc are both known to

be redox active, with the dafc/dafc$^+$ redox couple calculated as $E_{1/2}$= -0.602 V relative to Fc$^{0/+}$ set at 0 mV[8]. Dafc has been isolated as a solid in the neutral state, as well as in the oxidized state using AgOTf, [Fc][PF$_6$] or TCNE and stabilized as a salt with OTf$^-$, PF$_6^-$ and TCNE^{-}[8]. By this reasoning, dafc should be able participate in ligand based redox reactions. With this in mind, we set out to explore the reactivity of dafc with regards to cobalt, a d-electron rich metal. Reactivity of this ligand was also explored with early first row transition metals in an attempt to create a set of iso-structural complexes.

The use of this ligand was first tested with cobalt, as the oxidation of cobalt could prove very interesting. Cobalt is commonly found in the literature anywhere from the -1 to the +3 state, with scattered examples of the +4 and +5 oxidation states. In these few examples, not considering extended solids with oxides and fluorides, Will[6] used a corrole ring, Guilard[7] used a porphyrin/corrole complex, and Byrne and Theopold[8] used norbornyl groups to stabilize Co(IV), and were even able to produce Co(V) via reaction with AgBF$_4$ (see figures 2-4). The use of dafc is much more similar to the example of Co(IV) from Byrne and Theopold, as the ligands are much smaller and do not include extended conjugation of a corrole or porphryin ring. Discussed further are our attempts to use dafc as a chelating, bidentate ligand that can assist in the promotion of an oxidation state or cobalt and subsequently other first row transition metals.
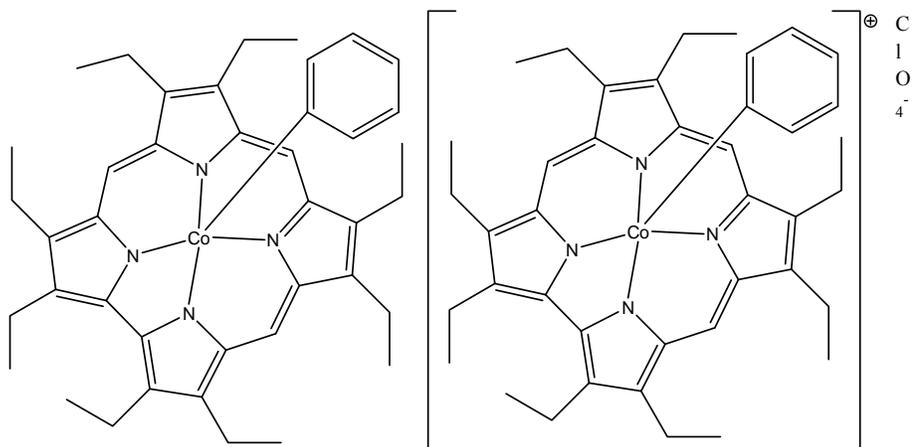
Figure 2: Cobalt(IV) (left) and Cobalt (V) (right) as synthesized by Will et al.[6]
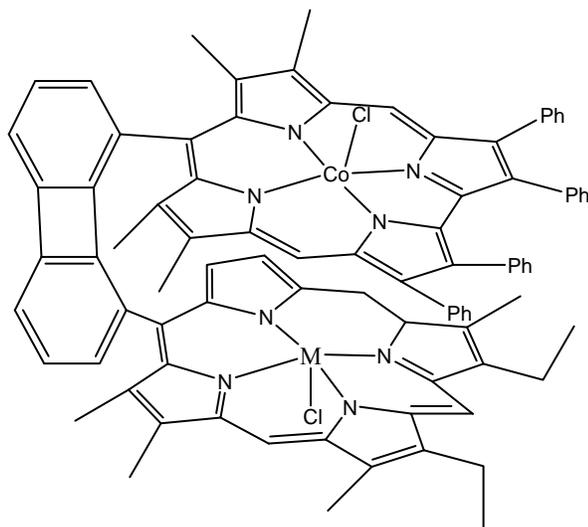
Figure 3: Cobalt (IV) as characterized by Guilard et al.[7]. Shown above is an example
of the type of compounds reported in the paper. The other compounds
simply differ with respect to the bridging group between the corrole and
porphyrin rings and the metal, M.
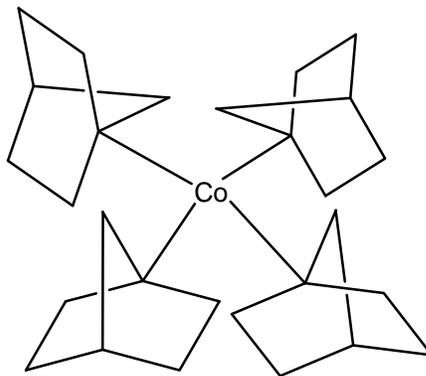
Figure 4: Cobalt (IV) as characterized by Byrne and Theopold[8]. Reaction with AgBF$_4$
yielded a Co(V) complex.

Chapter 2

RESULTS AND DISCUSSION

The synthesis of 1,1'-diaminoferrocene had been previously reported by Shafir[5] in 2000, and can be reached via a four step process (figure 5, the dilithio complex had previously been synthesized and reported). We followed this
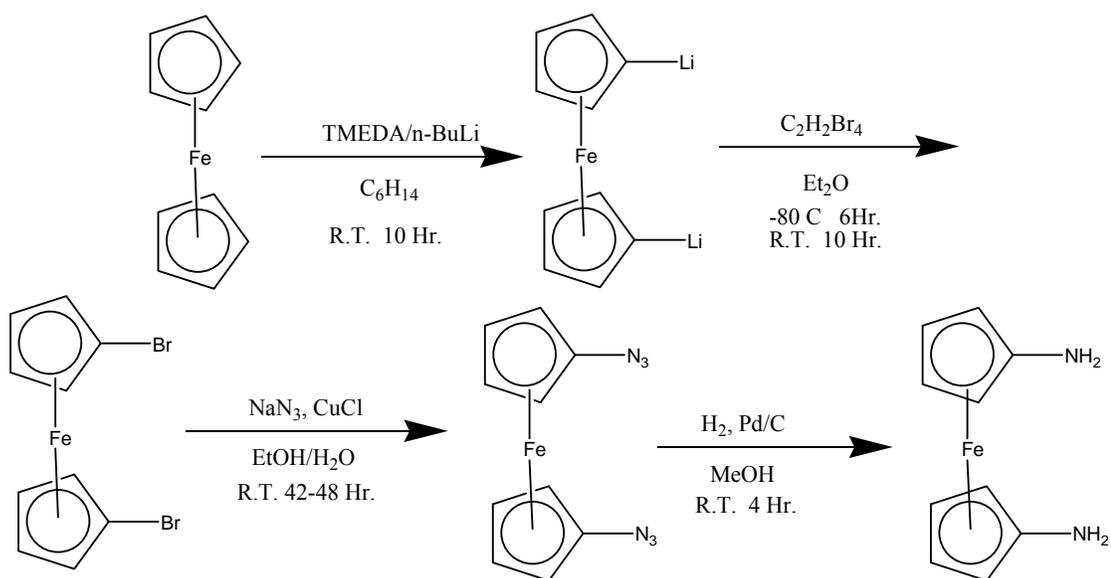
Figure 5: Reported synthetic scheme of dafc[5]

procedure, with only minor deviations, as follows. The workup of the diazido product was done under reduced light (half of the lab lights were turned off and the hood lights off as well), and the intermediate was stored wrapped in foil. Additionally, in the hydrogenation step, we used more catalyst (0.20 grams for us, while 0.10 grams was

reported[5]) and the system was placed in a pressure vessel and pressurized to two atmospheres of hydrogen gas for no less than 24 hours. While these slight changes should not have reduced the yield (if anything they should have increased or maximized it), ligand yields were extremely low. In ten attempts starting with twenty grams of ferrocene each time, only once were we able to synthesize roughly two grams of dafc.

Following successful synthesis and confirmation by ^{1}H NMR, reactions were begun with dafc and $CoCl_2$. Our initial reasoning was that we should be able to add two moles of ligand for every one mole of metal, creating a four coordinate system. Additionally, we hoped to add the ligand as a mono anion of the ligand type LX (where L=neutral ligand and X=anion ligand), thus displacing the chloride ions from $CoCl_2$ and creating a neutral species (figure 6). To do this, we would first need to deprotonate the ligand with base, according to the following reactions:

$$Dafc + n\text{-}BuLi \longrightarrow BuH + Fc(NH_2)(NHLi)$$

$$2\ Fc(NH_2)(NHLi) + CoCl_2 \longrightarrow Co(Fc(NH_2)(NH))_2 + 2LiCl$$
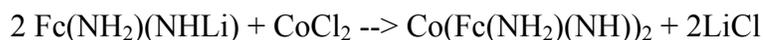
However, when the deprotonated ligand solution was added to $CoCl_2$, the reaction
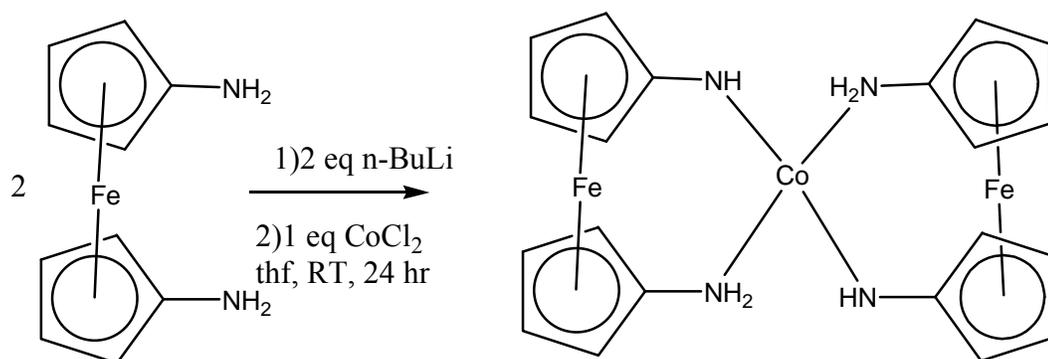

Figure 6: Attempting addition of the Ligand as an LX type ligand

immediately turned black, and after several (usually between two and five) filtrations the solution turned green. In terms of solvent, we began by using diethyl ether and later switched to tetrahydrofuran (THF). The ligand readily dissolved in both of these polar solvents, whereas it appeared to be insoluble when added to pentane or toluene. Reactions appeared to be independent of whether THF or diethyl ether was used, and THF was chosen as it was more readily available from the still. As for the base, triethyl amine was used at first. When the suspected deprotonated ligand solution (orange) was added to the $CoCl_2$ solution in THF, a color change to aqua-blue green was observed. However, we were never able to properly crystallize the product, and feared that the base may have been too weak. We net switched to n-BuLi, a much stronger base. Previous research performed by Blank used n-BuLi[9] to deprotonate the ligand in order to add additional functionality to dafc. This procedure was performed via a one pot synthesis, and we hoped that those results would be duplicated in our hands.

After several reactions performed on the milligram scale (reactant total weight of 60-80mg) that yielded insufficient powder for analysis after filtration, a reaction was attempted on the quarter gram scale. This reaction yielded some green solid, though only enough to run a ^{1}H NMR and a Mass spectrum. When the powder was placed onto weighing paper however, there was not enough to cause the scale to recognize the solid.

The ^{1}H NMR was unique from the reactants, but was not particularly helpful in verifying the structure or providing evidence of synthesis, as the peak ratios were not typical for hydrogens in a Cp ring. The mass spectrum of our green powder however gave us some data to work with. The spectrum (figure 7) produced major

peaks at 343.9, 341.9, 322.0, 320.0, 266.0, 264.0, 186.0, 184.0, 134.9 128.1 and 121.0. The compound, if synthesized properly, should have weighed 426.9 (2dafc + Co -2H atoms), but no peaks were observed in that range.
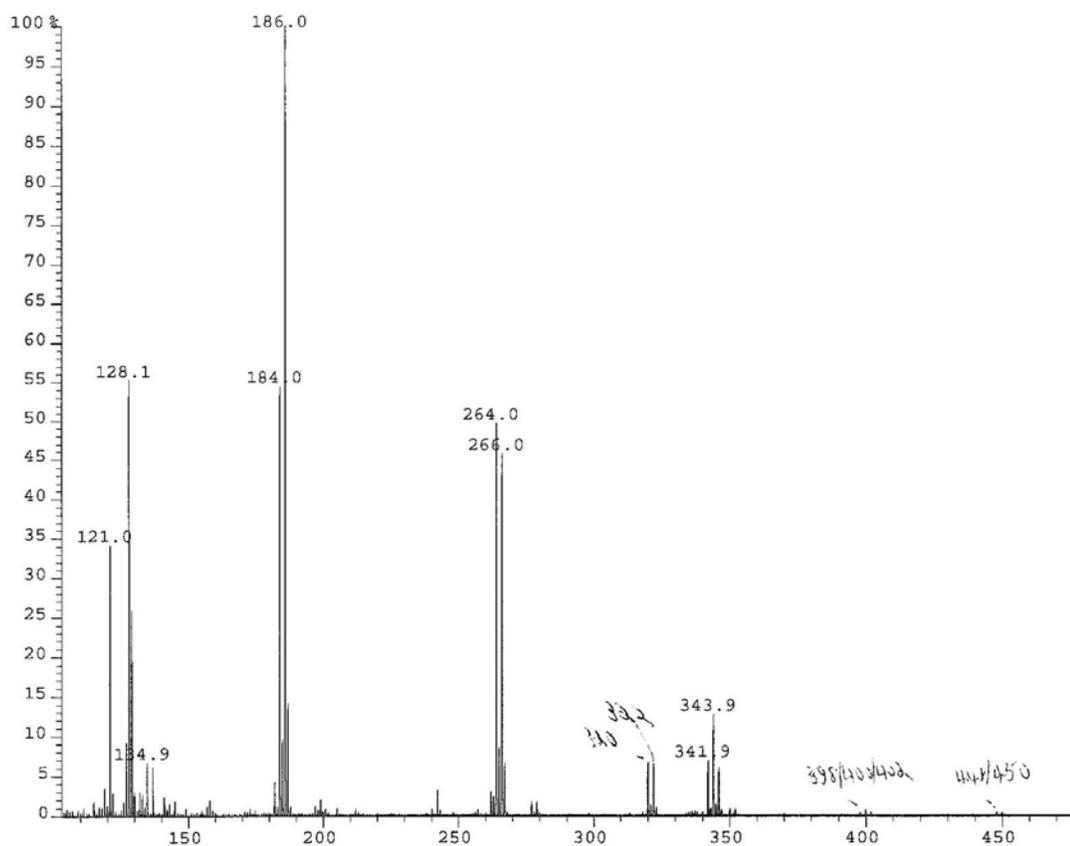

Figure 7: Mass spectrum of a green solid produced via reaction of nBuLi (2eq), dafc (2eq) and CoCl$_2$ (1 eq).

After brief analysis of the mass spectrum peaks, it was thought that the Co-dafc reaction could possibly be on a one to one mole ratio based on peaks at 343.9 being the species Co(dafc)Cl$_2$ (Mw=345.9, if deprotonated twice, Mw=343.9). However,

the smaller peak two units lower could not be properly rationalized. Neglecting 322.0 and 320.0, a loss of 78 and 80 mass units is seen. These were initially rationalized to be $CpNH_2$ derivatives (Mw=80). After more consideration, $FcBr_2$, with a molar mass of 343.9 and a possible isotope at 341.9, was found to be a better fit for the data. Additionally, the loss of 78 and 80 could be bromine, again accounting to the isotope peaks two units lower at 266.0/264.0 and 186.0/184.0. Yet the powder sent off was green, while $FcBr_2$ is an orange solid, making this rationalization also suspect to error. However, before we suspected $FcBr_2$ as the culprit, several reactions were tried with $CoCl_2$ and dafc in a 1:1 mol ratio, and without base, as we feared that the base may be the source of the color change to black. These subsequent reactions immediately turned and remained green. This appeared to verify our claims that base was not required and that the ligand could be added to the metal as an L_2 type ligand, forming dative bonds with the cobalt ion. However, with regard to the mole to mole ratio, when the 1:1 reactions were concentrated down to produce crystals, blue $CoCl_2$ crystals as THF adducts crystallized first. After reactions were scaled back up to a 2:1 ligand to metal ratio, these blue crystals disappeared. Attempts to crystallize the intermediate LX ligand yielded crystals that did not contain the amino functional groups, and two lithiums for every ferrocene suggesting that either n-BuLi was displacing the amino groups with lithium ions, or that the batch of dafc was tainted. Since Blank had used both NaH and n-BuLi with success on dafc[9], we reasoned that the current batch of dafc contained a detrimental impurity or was an intermediate rather than the desired product of the Shafir synthesis. Subsequent ^{1}H NMR runs of the dafc sample lacked the reported shifts for the ligand, especially the reported peaks

corresponding to the amino group. This vial was subsequently discarded as it was not our ligand.

Before green crystals of the proposed [Co(dafc)$_2$]Cl$_2$ were able to be verified using X-ray crystallography, we attempted to extend our synthesis to other first row metals with d electrons equal to or less than five in the divalent state (termed as 'electron deficient' metal cations). If the cobalt reaction had worked as intended, we hoped to extend this synthetic scheme to these other first row transition metals, yielding compounds **1-5** according to figure 8.

1: M=Co, X=Cl
2: M=Ti, X=Cl
3: M=V, X=Cl
4: M=Cr, X=Cl
5: M=Mn, X=I
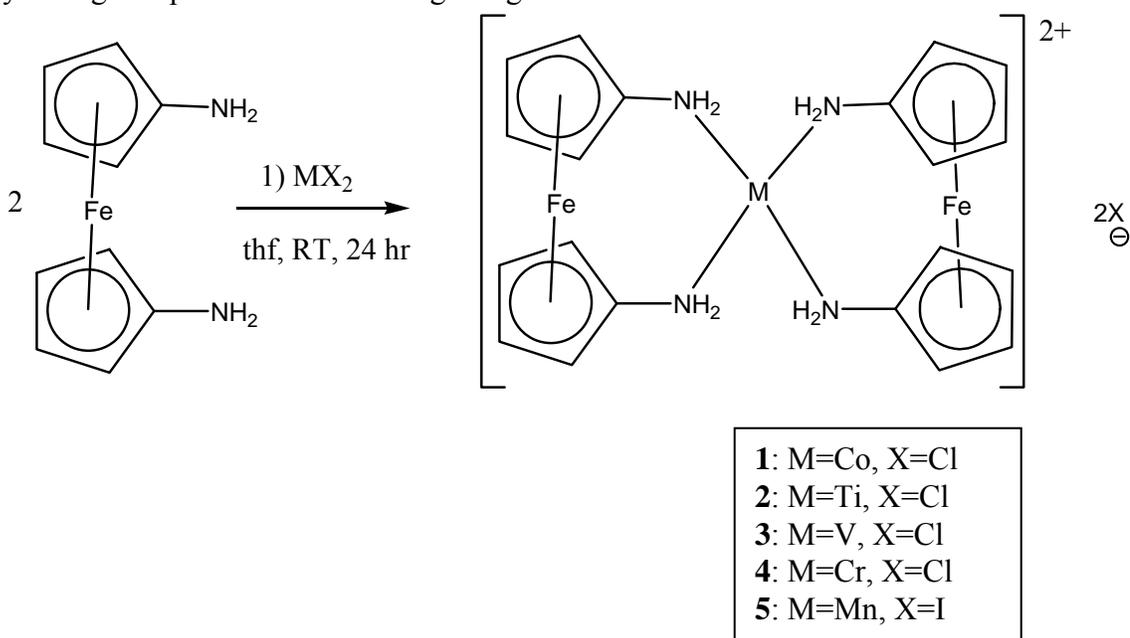
Figure 8: Proposed synthetic schemes of divalent metal halides with dafc

While the reaction of the orange ligand solution with the blue solution of CoCl$_2$ produced an almost immediately color change to green, reactions of the ligand solution with the four other metal halides produced much subtler color changes. When the products of these reactions were concentrated to produce crystals, all yielded

crystals of the metal halide THF adduct, except for the vanadium, whose crystals were instead ferrocene. This suggests that somewhere along the way, either the ligand was displaced from the metal, or that THF binds to the metal better than dafc. Additionally, because ferrocene was found in the vanadium mixture, it is possible that the dafc either decomposed or was not properly synthesized. ^{1}H NMR had confirmed that at least two grams had been isolated, and all five IR spectra contained peaks that belonged to a primary amino group. With evidence of a primary amino group, it is more likely that THF displaced dafc during crystallization, and it would be more effective to use a non-coordinating solvent instead.

When consulting the literature for possible reasons why these reactions do not readily occur or crystallize as desired, it is noticed that in reported complexes that contain dafc as a ligand, dafc itself is never the actual ligand, but rather a derivative of dafc with functional groups on the nitrogen[9,10]. For example, Blank[9] These groups were added prior to reaction with another metal species, which is indicative of the fact that they might add stability to the metal-ligand complex subsequently formed. Functionalizing the amino groups may help to sustain the nitrogen metal bond we are trying to form, making it possible for these complexes to be explored as postulated by this paper.

Chapter 3

EXPERIMENTAL

3.1   General Considerations

The ligand, 1,1'-bisdiamminoferrocene (dafc) was synthesized according to Arnold[5] with only a few minor deviations (see Results and Discussion section and figure 5). Once the diazido intermediate was characterized several times via ^{13}C NMR, isolation and characterization of the intermediate was skipped and the direct procedure for dafc from 1,1'-dibromoferrocene was utilized. Dafc was confirmed with ^{1}H NMR prior to use. All manipulations of compounds were carried out using standard Schlenk, high vacuum line, and glovebox techniques under an atmosphere of nitrogen. Solvents were purchased from Fisher Scientific, degassed, and dried by passing through activated alumina. Solvents were subsequently tested for purity with sodium benzophenone ketyl. THF-d8 and C_6D_6 was purchased from Cambridge Isotopes Laboratory and stored under vacuum over Na/K alloy. ^{1}H NMR spectra were taken on a Bruker DRX-400 spectrometer and were referenced to the residual protons of the solvent. FTIR spectra were taken on Mattson Alpha Centauri or Mattson Genesis Series spectrometers. Mass spectra were obtained by the University of Delaware Mass Spectrometry Facility.

3.2   Synthesis attempts at [Co(dafc)₂]Cl₂

A solution of dafc in THF was prepared by adding 0.130 grams to 10 ml of THF. The orange solution was stirred until the solid completely dissolved, and then

cooled to -30 C for 30 minutes. Once the solution was cold, 0.185 ml of n-BuLi (3.45 M) was added dropwise. The solution immediately turned darker orange. This solution was allowed to stir for a half hour, and no other noticeable color changes were observed. While the dafc/n-BuLi solution was stirring, another solution was prepared by adding 0.0406 grams of $CoCl_2$ to 10 ml of THF and stirring until the solid dissolved. Then the orange solution was added dropwise to the blue $CoCl_2$ solution. The solution briefly turned green, and then changed to black. The reaction was allowed to stir overnight. After 24 hours, the solvent was removed via vacuum, and the residue was washed with pentane until the pentane was clear. The slight orange yellow pentane solution was filtered through celite via gravity, and the solution was set aside. The rest of the residue was extracted with THF and also filtered via gravity through celite. The black slurry turned a darker green, and anywhere from one to three filtrations was required before the solution was a solid green color. However, on drying via vacuum, very little solid was produced (<5 mg). This green solid was characterized via NMR, Mass Spec, and FTIR spectroscopies. The ^{1}H NMR produced major peaks at 7.37, -3.87, -11.60 and possibly a very broad peak at -55.80. The IR spectrum showed major peaks at 3243.89, 3097.38, 2961.69, 2922.87, 2854.51, 1646.18, 1580.51, 1475.25, 1409.98, 1260.92, 1106.04, 1033.02, 1002.16, 929.82, and 816.26. Mass spectrum produced faint peaks at 450/448, 402/400/398 and major peaks at 343.9, 341.9, 322.0, 320.0, 266.0, 264.0, 186.0, 184.0, 134.9 128.1 and 121.0. Analysis of this mass spectrum can be found in the Results and Discussion section (pages 8-10).

When the reactions were performed with a 2:1 mol ratio of dafc to $CoCl_2$ and no base, the apparent yields rose and no blue solution or crystals were observed.

For the 2:1 reaction, 80mg (0.37mmol) of dafc were dissolved into THF and stirred for approximately 15 minutes. Another solution of 22mg (0.17mmol) $CoCl_2$ was prepared by dissolving the solid into THF and stirring for ten minutes. The orange ligand solution was then added dropwise to the blue $CoCl_2$ solution over the period of about one minute. The resulting solution immediately turned green, and was allowed to stir for 24 hours. The THF was then removed via vacuum, and the green residue was washed with pentane and filtered through celite. The orange pentane solution was set aside, and the green residue was then extracted with THF and filtered through celite. The THF was again removed via vacuum, and 57 mg of green powder **1** was obtained (59.7% yield). NMR and IR data obtained for green powder did not differ from the previous low yield reactions. Addition of 5 ml of THF to crystallize the product produced crystals of $CoCl_2$ with coordinated THF. Exposure of the NMR tube to air did not produce a color change after half an hour.

3.3   Synthesis attempts at [Ti(dafc)$_2$]Cl$_2$

For the titanium complex, 40mg (0.185mmol) of dafc was dissolved into THF and allowed to stir for fifteen minutes. A separate solution of 25mg (0.210mmol) of $TiCl_2$ was dissolved into THF and allowed to stir for approximately ten minutes. The orange ligand solution was added dropwise to the purple metal solution dropwise over the period of one minute. While there was no immediate color change, after stirring for 24 hours, the solution became yellow-green. The solvent was then removed under vacuum, and the solid residue washed with pentane and filtered through celite. The remaining residue was then extracted with THF and filtered through celite via gravity. The solvent was removed again under vacuum, producing

54 mg of gray-black powder **2** (26.5% yield). The NMR spectrum produced major peaks at 7.24, 4.11, 3.17, and 2.48. The FTIR spectrum showed peaks at 3183.57, 3096.50, 2973.52, 2904.65, 1471.34, 1458.65, 1106.08, 1040.73, 1012.61, 920.69, 853.17, and 818.06. Dissolving the solid into five milliliters of THF produced crystals of $TiCl_2$ with coordinated solvent and no evidence of dafc. Exposure of the NMR tube to air did not produce a color change after half an hour.

3.4 Synthesis attempts at [V(dafc)₂]Cl₂

For the vanadium complex, 40mg (0.185mmol) of dafc was dissolved into THF and allowed to stir for fifteen minutes. A separate solution of 22mg (0.181mmol) of VCl_2 was dissolved into THF and allowed to stir for approximately ten minutes. The orange ligand solution was added dropwise to the yellow-brown metal solution dropwise over the period of one minute. The solution became darker after half an hour and after stirring for 24 hours, the solution became orange-brown. The solvent was then removed under vacuum, and the solid residue washed with pentane and filtered through celite. The remaining residue was then extracted with THF and filtered through celite via gravity. The solvent was removed again under vacuum, producing 10 mg of brown powder **3** (4.9% yield). The NMR spectrum produced major peaks at 10.88, 7.96, 7.33, 7.20, 4.69, 2.97, 1.28, 0.87, and 0.33. The FTIR spectrum showed peaks at 3286.71, 3093.41, 2961.35, 2961.35, 2925.05, 2867.38, 1620.67, 1497.79, 1409.28, 1260.73, 1105.96, 1022.08, 1002.99, 929.76, 816.3, and 801.10. Dissolving the solid into five milliliters of THF produced crystals of ferrocene and lacked traces of metal and dafc. Exposure of the NMR tube to air did not produce a noticeable change in color after half an hour.

3.5   Synthesis attempts at [Cr(dafc)$_2$]Cl$_2$

For the chromium complex, 50mg (0.231mmol) of dafc was dissolved into THF and allowed to stir for fifteen minutes. A separate solution of 22mg (0.179mmol) of CrCl$_2$ was dissolved into THF and allowed to stir for approximately ten minutes. The orange ligand solution was added dropwise to the olive colored metal solution dropwise over the period of one minute. While there was no immediate color change, after stirring for 24 hours, the solution became yellow-beige color, and solid that was visible during the initial hour of the reaction had dissolved. The solvent was then removed under vacuum, and the solid residue washed with pentane and filtered through celite. The remaining residue was then extracted with THF and filtered through celite via gravity. The solvent was removed again under vacuum, producing 20 mg of gray-brown powder **4** (7.8% yield). The NMR spectrum produced major peaks at 7.11, 4.09 and -0.49. The FTIR spectrum showed peaks at 3238.61, 3194.32, 3105.48, 2978.57, 2878.08, 1482.99, 1459.78, 1106.36, 1030.77, 919.18, and 877.08. When the solid was dissolved into five milliliters of THF, the solution only produced crystals of CrCl$_2$ with coordinated THF. Exposure of the NMR tube solution to air did not produce a visible color change after one half hour.

3.6   Synthesis Attempts at [Mn(dafc)$_2$]I$_2$

For the manganese complex, 40mg (0.185mmol) of dafc was dissolved into THF and allowed to stir for fifteen minutes. A separate solution of 57mg (0.185mmol) of MnI$_2$ was dissolved into THF and allowed to stir for approximately

ten minutes. The orange ligand solution was added dropwise to the faint orange metal

solution dropwise over the period of one minute. The resulting solution became

darker immediately and after stirring for 24 hours, the solution remained orange. The

solvent was then removed under vacuum, and the solid residue washed with pentane

and filtered through celite. The remaining residue was then extracted with THF and

filtered through celite via gravity. The solvent was removed again under vacuum,

producing 67mg of dark orange powder **5** (24.4% yield). The NMR spectrum

produced major peaks at 11.64, 3.98 and -2.22. The FTIR spectrum showed peaks at

3200.80, 3093.66, 2975.05, 2891.87, 1474.35, 1105.66, 1029.43, 920.63, 866.85, and

816.31. Dissolving the solid into five milliliters of THF only produced crystals of

MnI_2 with coordinated THF. Exposure of the NMR tube solution to air produced no

visible change after half an hour.

Chapter 4

CONCLUSIONS

In conclusion, we have proposed the synthesis of several metal ligand complexes using the previously reported ligand 1,1' diaminoferrocene (dafc). However, despite IR spectral data that displayed typical primary amino peaks, proposed complexes of dafc **1-5** were not verified by x-ray crystallography, and thus their synthesis can not be confirmed. While only polar solvents such as THF and diethyl ether were used based on the solubility of the ligand, solvent mixtures of these two with less polar solvents such as pentane or toluene may yield the appropriate crystals. A drawback to using THF is its ability to coordinate to metal ions, and from the crystallography gathered, it appears to have a greater affinity for the metal ion than the ligand.

If these compounds could have been synthesized, their electrochemical potentials and redox activity would provide an interesting study. The major drawback to using dafc is its proposed synthetic route. While Arnold reports a four step synthesis with an over all yield of around 32%, the synthesis was not able to be efficiently replicated within our lab. Higher yields in ligand synthesis would lead to a better understanding of how dafc could be used in ligand based oxidation of metals, as there would be more ligand to experiment with. Additionally, in the reported complexes that contain dafc as a ligand, dafc itself is never the ligand, but rather a derivative with functional groups on the nitrogen[9,10]. These groups were added prior

to reaction with another metal species, which is indicative of the fact that they might add stability to the metal-ligand complex subsequently formed.

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