THE SYNTHESIS, CHARACTERIZATION, AND REACTIVITY OF LOW-COORDINATE, METAL AMIDES

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LIST OF ABBREVIATIONS

DAB – diaza-1,3-butadiene

DIP – 2,6-diisopropylphenyl

DIP-DAB – N,N'-bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene

(DIP)$_2$NacNac – N,N'-bis(2,6-diisopropylphenyl)-1,3-diketimine

FT-IR – Fourier transform infrared spectroscopy

M - Molar mass of the analyte ($\frac{kg}{mol}$)

m - Mass of analyte divided by the volume of solvent ($\frac{kg}{m^3}$)

NacNac – 1,3-diketimine

NMR – Nuclear magnetic resonance

py – Pyridine

T - Temperature in Kelvin

THF – Tetrahydrofuran

$\Delta\nu$ - Difference between NMR peak of solvent and solvent with analyte (Hz)

$\nu$ - Frequency of the NMR (Hz)
\( \mu_{\text{eff}} \) – Effective magnetic moment

\( \rho_0 \) - Density of the pure solvent \( \frac{kg}{m^3} \)

\( \rho_s \) - Density of analyte dissolved in solvent \( \frac{kg}{m^3} \)

\( X_0 \) - Mass susceptibility of the solvent \( \frac{m^3}{kg} \)
ACKNOWLEDGEMENTS

I would like to give my thanks to Dr. Scott Bunge for lending me his knowledge. I would also like to thank the members of the defense committee for their time and the members of the Bunge research team for their advice and help. Finally I would like to thank my friends, family and Kristen for their patience and support over the years.
CHAPTER I

INTRODUCTION

The synthesis of low-coordinate transition metal amides is an area of considerable interest due to applications in ring opening polymerization catalysis\textsuperscript{1,2}, precursors for nanoparticle synthesis\textsuperscript{3,4}, and small molecule activation.\textsuperscript{5,6} Amido ligands are a prime choice for these applications because they offer a vast range of tunability in the sterics, electronics and denticity.\textsuperscript{7} One example of an amido ligand that has been used to successfully isolate low-coordinate metal complexes is the β-diketiminate (NacNac, Figure 1).\textsuperscript{8,9}

**Figure 1.** β-diketiminate: and M(NacNac) (I) and (NacNac)\textsuperscript{−} (II).

The NacNac ligand (II) is bidentate and possess a single negative charge which is delocalized through its 3-membered carbon backbone, producing a six-membered
heterocycle when complexing with a metal center (I). These properties allow the NacNac ligand to stabilize transition metal complexes which may then be used in diverse applications such as the copolymerization of ethylene and alkenes\textsuperscript{10,11} and the activation of dinitrogen\textsuperscript{6,12}.

Notably the NacNac ligand possesses a reactive β-carbon which may undergo undesired side-reactions\textsuperscript{13,14} For example, Hadzovic and coworkers have reported that three equivalents of [\textipa{(NacNac)PdCl(H2NAr)}] transforms into the trimetallic complex when allowed to stir in CH\textsubscript{2}Cl\textsubscript{2} for several days (Scheme 1)\textsuperscript{15}.

\textbf{Scheme 1.} β-C of β-diketiminate undergoing side reaction.

\[ \text{N–Ar} = \text{N} \]

A number of strategies have been reported to overcome this disadvantage. One approach is to protect the β-C with a substituent as shown in Figure 2\textsuperscript{14,16–30}.\]
**Figure 2.** Methyl substituted β-diketiminate

Another approach is to use a functionally similar amido ligand that lacks a reactive backbone site. One such ligand is diazabutadiene (DAB) (Figure 3). The DAB ligand, similar to the NacNac ligand, is a bidentate N-donor. The DAB ligand can be utilized to generate the neutral (III)\(^{31-49}\) monoanionic (IV)\(^{31,50-56}\) or dianionic (V)\(^{7,51,57-65}\) form by performing a single or double insertion reaction as described in Figure 3, resulting in a variation in anionic charge.\(^{66}\) The R groups of the backbone can also be varied with a wide variety of substituents.\(^{67}\)

**Figure 3.** The neutral (III), monoanionic (IV) and dianionic (V) forms of DAB.
Additionally the DAB ligand forms a five-membered heterocycle with a metal center generating a correspondingly smaller N-M-N bond angle about the metal center (Figure 4). Notably, variances in the angle about the metal center can give rise to unique magnetic and electrical properties due to more effective overlap in the $d_{z^2}$ and $d_{yz}$ orbitals.\textsuperscript{68}

**Figure 4.** [M$(^t$Bu$_2$(DIP-DAB))].

![Figure 4](image.png)

In general, low coordinate metal complexes (CN = 1, 2 or 3) can be difficult to synthesize due to inherent instability of an electron deficient metal center coupled with the existence of a redox-active metal. The metals are reactive with O$_2$ and water and therefore must be handled under inert anhydrous environments.

Historically, our group has been interested in the synthesis of well-defined, low-coordination d-block metal complexes.\textsuperscript{69–73} To this end we have utilized the [Li$_2$(^t$Bu$_2$DIP-DAB)] complex, the synthesis of which is depicted in Scheme 2.\textsuperscript{73}
Scheme 2. Synthesis of [Li₂(tBu₂DIP-DAB)].

This reaction results in a single set of lithiated enantiomers. Subsequently, it was then shown that an additional metal amides could be produced by reacting [Li₂(tBu₂DIP-DAB)] and ZnCl₂ as shown in Scheme 3.⁷³

Scheme 3. Synthesis of [Li(THF)₄][{(tBu)₂DIP-DAB}Zn(μ-H)Zn{(tBu)₂DIP-DAB}].

It was later found that by utilizing the THF adduct, produced by dissolving [Li₂(tBu₂DIP-DAB)] in THF, purifying by centrifuging off any by-products and recrystallizing (as
shown in Scheme 5), stable, well-defined zinc “ate” complexes could be isolated such as the product depicted in Scheme 5.\textsuperscript{72}

**Scheme 4.** Synthesis of \([\text{Li}_2(\text{Bu}_2\text{DIP-}\text{DAB})(\text{THF})_2]\).

\[
\begin{align*}
\text{Ar-N} & \quad \text{N-Ar} \\
& \quad \mathcal{N} \quad \mathcal{N} \quad \mathcal{N} \quad \mathcal{N} \quad \mathcal{N} \quad \mathcal{N} \\
& \quad \text{Ar} \quad \text{Ar}
\end{align*}
\]

\[
2\text{BuLi, 25 °C} \quad \text{Hexanes, THF}
\]

**Scheme 5.** Synthesis of \(\text{rac-}[(\text{tBu})_2\text{DIP-}\text{DAB}]\text{Zn(μ-Cl)Li(THF)}_3\).

\[
\begin{align*}
\text{Ar-N} & \quad \text{N-Ar} \\
& \quad \mathcal{N} \quad \mathcal{N} \quad \mathcal{N} \quad \mathcal{N} \quad \mathcal{N} \quad \mathcal{N} \\
& \quad \text{Ar} \quad \text{Ar}
\end{align*}
\]

\[
\text{ZnCl}_2 \quad \text{THF, Toluene, Hexane} \quad \text{-LiCl}
\]
For comparison purposes and to add to the library of structurally characterized low-coordinate compounds it was of interest to investigate the synthesis of the redox-active metals chromium and manganese. Through this investigation it was found that the oxidation state of the metal can be altered by the presence of a reductive byproduct of the insertion of tert-butyl lithium into the ligand.

This investigation will be described in two chapters. Chapter II will discuss the synthesis of three manganese (II) bromide and chromium (III) chloride complexes. These amides were produced by reacting one equivalent of DIP-DAB with one equivalent of the corresponding metal halide. The resulting metal amides; 1, 2, and 3 retained the tert-butyl substituents on the DIP-DAB backbone. It was found that by utilizing the crude \([\text{Li}_2(\text{tBu}_2\text{DIP-DAB})(\text{THF})_2]\), the chromium could be reduced from +3 to +2. In the case of the reduced complex a single halide bridged to lithium which was coordinated to three THF molecules was formed as opposed to with the non-reduced metal, in which two halide bridges were coordinated to the lithium. The synthetic pathways are shown in Schemes 6 and 7.

**Scheme 6.** Synthesis of \(\text{rac-}[\,\text{tBu}_2\text{DIP-DAB}\,\text{M}(\mu-\text{X})_2\text{Li(THF)}_3]\). (M= Cr; X= Cl).
Scheme 7. Synthesis of rac-\{\text{‘Bu}_2\text{DIP-DAB}\}M(\mu-X)\text{Li(THF)}_3\}. (M= \text{Cr, Mn}; X= \text{Cl, Br}).

Chapter III will discuss the methodology used to characterize compounds 1, 2 and 3. The results of this methodology and possible future directions of this investigation will also be discussed.
CHAPTER II

SYNTHESIS OF LOW COORDINATE METAL COMPLEXES

Introduction.

The first three coordinate manganese (II) bis(trimethylsilyl)amide was structurally characterized in 1978 by Bradley and coworkers. Later, Power and coworkers determined the structures of the isostructural chromium (III) and manganese (III) bis(trimethylsilyl)amide complexes, $M[N(SiMe_3)_2]_3$ (M=Cr, Mn), in 1989. The ball and stick structures of the Mn complex is shown in Figure 5 and representative examples of structurally characterized low-coordinate complexes are listed in Table 1. Low coordinate metal amides such as this have since been reacted with alcohols to produce alkoxides for use as precursors in metal organic chemical vapor deposition (MOCVD), living ring opening polymerization (ROP) of (di)lactones, and the breaking of nitrogen-oxygen and carbon-oxygen multiple bonds.
Figure 5. Ball and stick plot of Mn[N(SiMe₃)₂]₃ (Purple: Mn, Yellow: Si, Blue: N, Gray: C.)⁷⁵

The synthesis of well-defined low-coordinate chromium and manganese complexes is a challenge in synthetic inorganic chemistry due to their propensity to undergo decomposition in the presence of air and water.
Table 1. Metal-ligand bond lengths of select three and four-coordinate chromium and manganese amido and alkoxide complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>M-L Length (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mn{N(Si(CH₃)₃)₂}{μ- N(Si(CH₃)₃)₂}]₂</td>
<td>1.99 (L=N)</td>
<td>75</td>
</tr>
<tr>
<td>Mn[N(SiMe₃)₂]₃</td>
<td>1.89 (L=N)</td>
<td>75</td>
</tr>
<tr>
<td>Cr[N(SiMe₃)₂]₃</td>
<td>1.90 (L=N)</td>
<td>75</td>
</tr>
<tr>
<td>[(DIP)₂(NacNac)MnN(SiMe₃)₂]</td>
<td>2.05 (L=N)</td>
<td>82</td>
</tr>
<tr>
<td>[{(tBu)₃CO}Cr{ μ- OC(tBu)₃}( μ- Cl)Li(THF)₂]</td>
<td>1.88 (L=O)</td>
<td>83</td>
</tr>
<tr>
<td>[Cr(NPh₂)₂(py)₂]</td>
<td>2.15 (L=N)</td>
<td>84</td>
</tr>
</tbody>
</table>

The aim of this investigation was to generate well-defined, low-coordinate manganese and chromium amido complexes via the reaction of [MnBr₂(THF)₂] and [CrCl₃(THF)₃] with [Li₂(tBu₂DIP-DAB)(THF)₂].

Experimental.

All compounds were handled with rigorous exclusion of air and water using standard glove box techniques. All anhydrous solvents were stored under argon and used as received in sure-seal bottles. [MnBr₂(THF)₂], [CrCl₃(THF)₃] and [Li₂(tBu₂DIP-DAB)(THF)₂] were prepared as previously reported.⁶⁶ FT-IR data were obtained on a Bruker Tensor 27 Instrument using KBr pellets under an atmosphere of flowing nitrogen. Magnetic susceptibility measurements for 3 were measured at 295 K and determined in
solution by the Evans method. All NMR samples were prepared from dried crystalline materials that were handled and stored under an argon atmosphere and dissolved in toluene-$d_8$. All solution spectra were obtained on a Bruker DRX400 spectrometer at 400.1 MHz for $^1$H experiments.

**Synthesis of rac-[(tBu$_2$DIP-DAB)(Cl)Cr(μ-Cl)Li(THF)$_3$] (1).** Compound 1 was synthesized by adding [Li$_2$(tBu$_2$DIP-DAB)(THF)$_2$] to one equivalent of [CrCl$_3$(THF)$_3$] in 20 ml THF and 10 mL diethyl ether. The solution was allowed to stir for 24 hours. The ether and THF were then evaporated under vacuum at room temperature until a dry dark-purple solid remained. A (5:3:2) 10 mL mixture of hexanes, toluene and THF was then added and a solid was centrifuged off. The solution was decanted into a vial, evaporated to a minimum amount of solvent and placed in a $-37$ °C freezer to crystallize. The reaction yielded dark purple crystals which were then isolated for subsequent analysis. [Li$_2$(tBu$_2$DIP-DAB)(THF)$_2$] (0.62 mmol, 0.40 g), and [CrCl$_3$(THF)$_3$] (0.62 mmol, 0.23 g) were used. Yield 40% (0.25 mmol, 0.23 g). FT-IR (KBr, cm$^{-1}$): 3288 (s), 2981 (w), 2962 (w), 2907 (w), 1624 (m), 1459 (m), 1039 (w), 1011 (s), 859 (s), 688 (w).

**Synthesis of rac-[(THF)$(t$Bu$_2$DIP-DAB)Cr(μ-Cl)Li(THF)$_3$].** Compound 2 was synthesized by adding [Li$_2$(tBu$_2$DIP-DAB)] to one equivalent of CrCl$_3$(THF)$_3$ in 20 ml THF and 10 mL diethyl ether. The solution was allowed to stir for 24 hours. The ether and THF was then evaporated under vacuum at room temperature until a dry dark-purple solid remained a (5:3:2) 10 mL mixture of hexanes, toluene and THF were then added and a dark purple solid was centrifuged off. The solution was decanted into a vial,
evaporated to a minimum amount of solvent and placed in a -37 °C freezer to crystallize. The reaction yielded green crystals which were then isolated for later analysis. [Li₂(¹Bu₂DIP-DAB)(THF)₂] (0.62 mmol, 0.40 g), and [CrCl₃(THF)₃] (0.62 mmol, 0.23 g) were used. Yield 31% (0.19 mmol, 0.16 g). FT-IR (KBr, cm): 3399 (m), 3344 (m), 3064 (m), 2963 (s), 2869 (s), 1656 (m), 1460 (s), 1365 (s), 1258 (m), 1042 (m), 1010 (m), 849 (m).

**Synthesis of rac-[(THF)(¹Bu₂DIP-DAB)Mn(µ-Br)Li(THF)₃]** (3). Compound 3 was synthesized by adding [Li₂(¹Bu₂DIP-DAB)(THF)₂] to one equivalent of [MnBr₂(THF)₂] in 20 ml THF and 10 mL diethyl ether. The solution was allowed to stir for 20 minutes at 60 °C, a dark brown precipitate was then removed via centrifuge. The ether and THF were then evaporated under vacuum at room temperature until a dry, brown solid remained. Hexanes, toluene and THF were then added and a dark brown and gray solid was centrifuged off. The solution was decanted into a vial, evaporated to a minimum amount of solvent and placed in a -37 °C freezer to crystallize. The reaction yielded light yellow crystals which were then isolated for later analysis. [Li₂(¹Bu₂DIP-DAB)(THF)₂] (0.41 mmol, 0.25 g), and [MnBr₂(THF)₂] (0.41 mmol, 0.15 g) were used. Yield 46% (0.19 mmol, 0.16 g). FT-IR (KBr, cm⁻¹): 3032 (w), 2865 (s), 1586 (w), 1460 (m), 1411 (s), 1364 (m), 1300 (w), 1234 (s), 1196 (m), 1657 (w), 1196 (w), 1146 (w), 1107 (w), 1045 (s), 996 (w), 896 (m), 843 (w), 757 (w), 653 (w), 590 (w). μeff 5.77.

**X-Ray Crystal Structure Information.** X-ray crystallography was performed by mounting each crystal onto a thin glass fiber from a pool of Fluorolube™ and
immediately placing it under a liquid N$_2$ cooled N$_2$ stream, on a Bruker AXS diffractometer. The radiation used was graphite monochromatized Mo K$_\alpha$ radiation ($\lambda = 0.7107$ Å). The lattice parameters were optimized from a least-squares calculation on carefully centered reflections. Lattice determination, data collection, structure refinement, scaling, and data reduction were carried out using APEX2 version 1.0-27 software package.

Each structure was solved using direct methods. This procedure yielded the heavy atoms, along with a number of the C and N atoms. Subsequent Fourier synthesis yielded the remaining atom positions. The hydrogen atoms were fixed in positions of ideal geometry and refined within the XSHELL software. These idealized hydrogen atoms had their isotropic temperature factors fixed at 1.2 or 1.5 times the equivalent isotropic U of the C atoms to which they were bonded. The final refinement of each compound included anisotropic thermal parameters on all non-hydrogen atoms. Additional information concerning the data collection and final structural solutions of compounds 1 - 3 can be found at the end of the present chapter. Any variations from standard structural solution associated with the representative compounds, are discussed below.

**Results and Discussion**

**Synthesis.**

The synthesis of 1 is shown in Scheme 8. The synthesis of 2 is shown in Scheme 9. The synthesis of 3 is shown in Scheme 10.
**Scheme 8.** Synthesis of compounds 1.

\[ \text{Scheme 8. Synthesis of compounds 1.} \]

**Scheme 9.** Synthesis of compound 2.

\[ \text{Scheme 9. Synthesis of compound 2.} \]
Scheme 10. Synthesis of compound 3.

\[
\text{[Li_2(Bu_2DIP-DAB)(THF)_2]} \text{ was synthesized by reacting two equivalents of tert-butyl lithium with one equivalent of DIP-DAB in hexane. The crude product was then filtered and washed with hexane and recrystallized from tetrahydrofuran. For the synthesis of compounds 1 and 3, [Li_2(Bu_2DIP-DAB)(THF)_2] was purified by centrifuging the crude mixture, decanting the solution, and recrystallizing by slow evaporation in an argon atmosphere. In 2, crude [Li_2(Bu_2DIP-DAB)(THF)_2] was used and chromium (III) was converted to chromium (II) \textit{in situ}. Each complex was then prepared by dissolving [CrCl_3(THF)_3] or [MnBr_2(THF)_2] and [Li_2(Bu_2DIP-DAB)(THF)_2] in tetrahydrofuran and diethyl ether respectively. The lithium amide solution was then added dropwise to the metal halide solution. The solution was allowed to stir and a precipitate was removed via centrifugation. The diethyl ether and THF were then removed \textit{en vacuo} and the solids were then dissolved in toluene, hexane and THF. The compounds had limited solubility in toluene and hexane but would not crystallize from}
\]
THF. Therefore a 5:3:2 mixture of the three was used. This solvent mixture made Evan’s method difficult because of the unavailability of deuterated forms of the necessary solvents. The solubility issues also made removal of the lithium halide byproduct difficult, precluding elemental analysis. The remaining solid was removed via centrifuge and the solution decanted into a vial. The solution was taken to a minimal concentration and allowed to crystallize in a -37°C freezer.

**Structural Descriptions**

Chromium and manganese-nitrogen (amide) bonds in three and four coordinate metal complexes are typically 1.9-2.1 Å as shown in Table 1.

*rac*-[**THF**]{(tBu)$_2$**DIP-DAB**(Cl)Cr(μ-Cl)Li(THF)$_3$} (1). Compound 1 crystallizes in the orthorhombic space group Pca2$_1$ (Z=4) and its structure is represented by the thermal ellipsoid plot shown in Figure 6. The chromium center adopts a distorted tetrahedral (τ$_4$ = 0.70)$^{86}$ geometry with an N-Cr-N angle of 83.9°, a Cl-Cr-Cl angle of 98.6° and N-Cr-Cl angles of 131°. The Cr-Cl bond lengths are 2.3 Å each and the N-Cr bonds were found to be 1.88 Å which is shorter than other Cr-N bonds shown in Table 1. The structural differences between 1 and 2 are due to the difference in oxidation state and coordination number of the metal centers.

*rac*-[**THF**]{(tBu)$_2$**DIP-DAB**}Cr(μ-Cl)Li(THF)$_3$} (2). Complex 2 crystallizes in the monoclinic space group P2$_1$/n, (Z=4) the structure of which is represented by the thermal ellipsoid plot shown in Figure 7. The chromium center adopts a four coordinate geometry (τ$_4$ = 0.49) that is distorted to a degree that it is neither square planar nor tetrahedral with
an N-Cr-N angle of 85.6°, an N-Cr-Cl angle of 106°, N-Cr-O angles of 141.80° and 97.09° and an O-Cr-Cl angle of 91.4°. The N-Cr-Cl angles of compound 1 is wider than complex 2 while the bond length of Cr-Cl in 1 is about 2.4 Å which is slightly larger than the analogous bond length in 1. Complex 2 is coordinated to the neutral THF ligand instead of a second chloride as in complex 1. The Cr-N bonds in 2 are 1.97 and 1.99 Å, which are the average bond length for a low-coordinate chromium-nitrogen bond. Complex 2 is significantly more distorted than complex 1, with a geometry between tetrahedral and square planar geometries.

rac-[(THF)(tBu)2DIP-DAB]Mn(μ-Br)Li(THF)3] (3). Complex 3 cocrystallized in the triclinic space group P\textbar (Z=2) as two crystallographically unique complexes, 3a and 3b, with Mn atoms in distorted tetrahedral geometries (~τ₄ = 0.70). The structures of 3a and 3b are represented by the thermal ellipsoid plots shown in Figures 8 and 9. The N-Mn-N angle of 87.7° and metal-halogen bond length of 2.5 Å are slightly larger than either compound 1 or 2. On the other hand, the N-Mn-Br angle of 113.59° is significantly different from the N-Cr-Cl angles of either 1 or 2. The overall geometry of the metal center is very similar to that of complex 1. In 3b there is disorder in the THF group containing O(7). The Mn-N bonds are 2.0 Å which is expected for a low-coordinate manganese amide (See Table 1).

Magnetic and Spectroscopic Studies

A magnetic technique used in this investigation is the Evans method. The Evans method is a magnetic technique in which the proton NMR of a paramagnetic material is
recorded simultaneously with a sample of the pure solvent. This allows the difference in shifts to be measured. This difference can then be related to the $\mu_{\text{eff}}$ of the complex with equation 1.

$$\mu_{\text{eff}} = \sqrt{797.8 \times T \times M \left[ \left( \frac{6}{m} \right) \left( \frac{\Delta \nu}{\nu} \right) + X_0 + X_0 \left( \frac{\rho_0 - \rho_s}{m} \right) \right]}$$  \hspace{1cm} (1)

Where T is the temperature in Kelvin, $m$ is the mass of analyte divided by the volume of solvent ($\frac{kg}{m^3}$), $\Delta \nu$ is the difference between a peak of pure solvent and a peak of solvent with dissolved paramagnetic analyte (Hz), $\nu$ is the frequency of the NMR (Hz), $\rho_0$ is the density of the pure solvent ($\frac{kg}{m^3}$), $\rho_s$ is the density of analyte dissolved in solvent ($\frac{kg}{m^3}$), $X_0$ is the mass susceptibility of the solvent ($\frac{m^3}{kg}$) and $M$ is the molar mass of the analyte ($\frac{kg}{mol}$). Equation 2 relates the $\mu_{\text{eff}}$ to the number of unpaired electrons in the analyte.

$$\mu_{\text{eff}} = \sqrt{n(n + 2)}$$  \hspace{1cm} (2)

The magnetic moment of compound 3 was measured in toluene-d$_8$ by the Evan’s method.$^{85}$ Data collection parameters for this experiment are listed in Table 2. This measurement produced a $\mu_{\text{eff}}$ that is consistent with a high spin d$^5$ complex with five unpaired electrons. Complex 3 possess a heteroligated psudo-tetrahedral splitting pattern.
Table 2. Data Collection Parameters for Evans' Method of 3 in toluene-D$_8$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$ (Hz)</td>
<td>400.13 × 10$^6$</td>
</tr>
<tr>
<td>$\Delta \nu$ (Hz)</td>
<td>262.22</td>
</tr>
<tr>
<td>$m \left( \frac{kg}{m^3} \right)$</td>
<td>20.71</td>
</tr>
<tr>
<td>$M \left( \frac{kg}{mol} \right)$</td>
<td>0.863</td>
</tr>
<tr>
<td>$\rho_0 \left( \frac{kg}{m^3} \right)$</td>
<td>943.00</td>
</tr>
<tr>
<td>$\rho_s \left( \frac{kg}{m^3} \right)$</td>
<td>963.71</td>
</tr>
<tr>
<td>$X_0 \left( \frac{m^3}{kg} \right)$</td>
<td>9 × 10$^{-9}$</td>
</tr>
<tr>
<td>T (K)</td>
<td>295</td>
</tr>
<tr>
<td>$\mu_{eff}$</td>
<td>5.77</td>
</tr>
</tbody>
</table>
The IR spectra compounds 1, 2 and 3 each demonstrate peaks associated with the alkyl and aryl functional groups. The IR spectra for 1 — 3 closely resemble each other and the spectra of the previously synthesized \([\text{Li}_2(\text{Bu}_2\text{DIP-DAB})(\text{THF})_2]\).\(^{73}\) The FT-IR spectra of each metal amide complex exhibited an absence of a strong peak from 1620 to 1650 cm\(^{-1}\) corresponding to a lack of imine bonds that are seen in the spectra of the DIP-DAB starting material.

**Conclusions**

Three low-coordinate transition metal compounds were synthesized and structurally characterized. The metathesis of \([\text{Li}_2(\text{Bu}_2\text{DIP-DAB})(\text{THF})_2]\) with \([\text{CrCl}_3(\text{THF})_3]\) and \([\text{MnBr}_2(\text{THF})_2]\) resulted in compounds 1 and 3. Compound 2 was synthesized via the reaction of crude \([\text{Li}_2(\text{Bu}_2\text{DIP-DAB})]\) with \([\text{CrCl}_3(\text{THF})_3]\). The reduction of the chromium in compound 2 demonstrated not only the synthesis of a well-defined, low-coordinate redox active metal amide but also that it is possible to vary their oxidation state of the resultant complex based on the starting reagents. The reaction of \([\text{Li}_2(\text{Bu}_2\text{DIP-DAB})(\text{THF})_2]\) with \([\text{MnBr}_2(\text{THF})_2]\) also resulted in the production of two crystallographically unique monomers.
Table 3. X-Ray Data Collection Parameters for 1 – 3.

<table>
<thead>
<tr>
<th>Compound</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>chemical formula</td>
<td>C$<em>{46}$H$</em>{66}$Cl$_2$CrLiN$_2$O$_3$</td>
<td>C$<em>{50}$H$</em>{66}$Cl CrLiN$_2$O$_4$</td>
<td>C$<em>{100}$H$</em>{172}$Br$_2$Li$_2$Mn$_2$N$_4$O$_8$</td>
</tr>
<tr>
<td>formula weight</td>
<td>824.85</td>
<td>873.60</td>
<td>1842.00</td>
</tr>
<tr>
<td>temp (K)</td>
<td>188 (2)</td>
<td>188 (2)</td>
<td>183 (2)</td>
</tr>
<tr>
<td>space group</td>
<td>Orthorhombic Pca$_2_1$</td>
<td>Monoclinic P2$_1$/n</td>
<td>Triclinic P-1</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>18.2007(6)</td>
<td>13.5781(12)</td>
<td>12.9450(12)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>15.9133(6)</td>
<td>16.9521(15)</td>
<td>20.3606(18)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>16.9527(6)</td>
<td>22.676(2)</td>
<td>21.5361(19)</td>
</tr>
<tr>
<td>$\alpha$ (deg)</td>
<td>103.362(2)</td>
<td>89.691(2)</td>
<td>66.1780(10)</td>
</tr>
<tr>
<td>$\beta$ (deg)</td>
<td>89.925(2)</td>
<td>89.925(2)</td>
<td>89.925(2)</td>
</tr>
<tr>
<td>$\gamma$ (deg)</td>
<td>4910.1(3)</td>
<td>5078.1(8)</td>
<td>5192.6(8)</td>
</tr>
<tr>
<td>$\nu$ (Å$^3$)</td>
<td>4910.1(3)</td>
<td>5078.1(8)</td>
<td>5192.6(8)</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>$\bar{D}_{calcd}$ (Mg/m$^3$)</td>
<td>1.116</td>
<td>1.143</td>
<td>1.178</td>
</tr>
<tr>
<td>$\mu$(Mo, K$\alpha$) (mm$^{-1}$)</td>
<td>3.86 (4.35)</td>
<td>5.97 (12.16)</td>
<td>11.13 (15.54)</td>
</tr>
<tr>
<td>R$_1^a$ (%) (all data)</td>
<td>11.29 (12.25)</td>
<td>16.43 (22.02)</td>
<td>29.92 (31.34)</td>
</tr>
<tr>
<td>wR$_2^b$ (%) (all data)</td>
<td>11.29 (12.25)</td>
<td>16.43 (22.02)</td>
<td>29.92 (31.34)</td>
</tr>
</tbody>
</table>

$^a$R$_1 = \Sigma | |F_o|-|F_c|| / \Sigma |F_o| x 100$

$^b$wR$_2 = [\Sigma w (F_o^2-F_c^2)^2 / \Sigma (w|F_o|^2)]^{1/2} x 100$
Table 4. Selected inter-atomic distances (Å) and angles (°) for 1 and 2.

<table>
<thead>
<tr>
<th>Complex 1</th>
<th>Distance (Å)</th>
<th>Complex 2</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(1)-N(1)</td>
<td>1.873(2)</td>
<td>Cr(1)-N(2)</td>
<td>1.976(3)</td>
</tr>
<tr>
<td>Cr(1)-N(2)</td>
<td>1.884(2)</td>
<td>Cr(1)-N(1)</td>
<td>1.990(3)</td>
</tr>
<tr>
<td>Cr(1)-Cl(1)</td>
<td>2.2810(10)</td>
<td>Cr(1)-O(1)</td>
<td>2.191(3)</td>
</tr>
<tr>
<td>Cr(1)-Cl(2)</td>
<td>2.3293(9)</td>
<td>Cr(1)-Cl(1)</td>
<td>2.4043(13)</td>
</tr>
<tr>
<td>Cl(2)-Li(1)</td>
<td>2.364(6)</td>
<td>Li(1)-O(1)</td>
<td>2.307(9)</td>
</tr>
<tr>
<td>N(1)-Cr(1)-N(2)</td>
<td>83.85(10)</td>
<td>Cl(1)-Li(1)</td>
<td>2.307(9)</td>
</tr>
<tr>
<td>Cl(1)-Cr(1)-Cl(2)</td>
<td>98.60(4)</td>
<td>O(1)-Li(1)-O(2)</td>
<td>110.74(4)</td>
</tr>
<tr>
<td>N(1)-Cr(1)-Cl(2)</td>
<td>131.31(8)</td>
<td>O(3)-Li(1)-O(2)</td>
<td>103.7(3)</td>
</tr>
<tr>
<td>N(2)-Cr(1)-Cl(1)</td>
<td>131.71(8)</td>
<td>O(1)-Cl(1)-Cl(1)</td>
<td>119.31(17)</td>
</tr>
<tr>
<td>Cr(1)-Cl(2)-Li(1)</td>
<td>129.45(17)</td>
<td>Li(1)-Cl(1)-Cr(1)</td>
<td>119.95(17)</td>
</tr>
<tr>
<td>O(1)-Li(1)-O(3)</td>
<td>109.2(3)</td>
<td>C(25)-N(1)-Cr(1)</td>
<td>119.68(17)</td>
</tr>
<tr>
<td>N(2)-Cr(1)-N(1)</td>
<td>85.59(13)</td>
<td>O(4)-Li(1)-O(3)</td>
<td>110.31(17)</td>
</tr>
<tr>
<td>N(2)-Cr(1)-Cl(1)</td>
<td>106.04(10)</td>
<td>O(4)-Li(1)-O(2)</td>
<td>106.04(4)</td>
</tr>
<tr>
<td>O(1)-Cr(1)-Cl(1)</td>
<td>91.44(8)</td>
<td>O(3)-Li(1)-O(2)</td>
<td>113.3(4)</td>
</tr>
<tr>
<td>Li(1)-Cl(1)-Cr(1)</td>
<td>147.3(2)</td>
<td>O(1)-Cr(1)-Cl(1)</td>
<td>113.3(4)</td>
</tr>
</tbody>
</table>


Table 5. Selected inter-atomic distances (Å) and angles (°) for 3a and 3b.

<table>
<thead>
<tr>
<th>Complex 3a</th>
<th></th>
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<tbody>
<tr>
<td>Mn(1)-N(2)</td>
<td>2.018(7)</td>
<td>Li(1)-O(2)</td>
<td>1.919(17)</td>
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<tr>
<td>Mn(1)-N(1)</td>
<td>2.024(6)</td>
<td>Li(1)-O(3)</td>
<td>1.932(15)</td>
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<tr>
<td>Mn(1)-O(1)</td>
<td>2.206(6)</td>
<td>Li(1)-Br(1)</td>
<td>2.486(14)</td>
</tr>
<tr>
<td>Mn(1)-Br(1)</td>
<td>2.5461(14)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li(1)-O(4)</td>
<td></td>
<td></td>
<td>1.886(17)</td>
</tr>
</tbody>
</table>

|              |                  |                  |                  |
| N(2)-Mn(1)-N(1)          | 87.7(3)          | O(4)-Li(1)-O(2)  | 110.1(8)         |
| N(2)-Mn(1)-O(1)          | 127.5(3)         | O(4)-Li(1)-O(3)  | 113.8(7)         |
| N(1)-Mn(1)-O(1)          | 100.8(3)         | O(2)-Li(1)-O(3)  | 103.4(8)         |
| N(2)-Mn(1)-Br(1)         | 113.67(19)       | O(4)-Li(1)-Br(1) | 110.6(7)         |
| N(1)-Mn(1)-Br(1)         | 135.09(19)       | Li(1)-Br(1)-Mn(1)| 147.4(3)         |
| O(1)-Mn(1)-Br(1)         | 96.26(17)        |                  |                  |

<table>
<thead>
<tr>
<th>Complex 3b</th>
<th></th>
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<tbody>
<tr>
<td>Mn(2)-N(4)</td>
<td>2.030(6)</td>
<td>Li(2)-O(6)</td>
<td>1.92(2)</td>
</tr>
<tr>
<td>Mn(2)-N(3)</td>
<td>2.031(6)</td>
<td>Li(2)-O(8)</td>
<td>1.93(3)</td>
</tr>
<tr>
<td>Mn(2)-O(5)</td>
<td>2.229(6)</td>
<td>Li(2)-O(7)</td>
<td>1.933(19)</td>
</tr>
<tr>
<td>Mn(2)-Br(2)</td>
<td>2.5449(14)</td>
<td>Li(2)-Br(2)</td>
<td>2.48(2)</td>
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</table>

|              |                  |                  |                  |
| N(4)-Mn(2)-N(3)          | 88.1(2)          | O(6)-Li(2)-O(8)  | 108.6(11)        |
| N(4)-Mn(2)-O(5)          | 125.4(3)         | O(6)-Li(2)-O(7)  | 106.8(11)        |
| N(3)-Mn(2)-O(5)          | 100.4(2)         | O(8)-Li(2)-O(7)  | 110.9(12)        |
| N(4)-Mn(2)-Br(2)         | 113.59(17)       | O(6)-Li(2)-Br(2) | 104.7(10)        |
| N(3)-Mn(2)-Br(2)         | 134.3(2)         | Li(2)-Br(2)-Mn(2)| 142.7(5)         |
| O(5)-Mn(2)-Br(2)         | 98.18(17)        |                  |                  |
Figure 6. Thermal ellipsoid plot of 1. Ellipsoids are drawn at 30 % level. H atoms have been omitted for clarity.
Figure 7. Thermal ellipsoid plot of 2. Ellipsoids are drawn at 30% level. H atoms have been omitted for clarity.
Figure 8. Thermal ellipsoid plot of 3a. Ellipsoids are drawn at 30% level. H atoms have been omitted for clarity.
Figure 9. Thermal ellipsoid plot of 3b. Ellipsoids are drawn at 30 % level. H atoms have been omitted for clarity.
CHAPTER III

CONCLUSIONS

It was found that by reacting [MnBr$_2$(THF)$_2$] and [CrCl$_3$(THF)$_3$] with [Li$_2$(tBu$_2$DIP-DAB)(THF)$_2$], the corresponding low-coordinate metal amides could be synthesized. These complexes were characterized with IR spectroscopy, single crystal X-ray diffraction and the Evans method. X-ray diffraction was used to determine the structure of the compound and the Evans method was used to verify that the number of unpaired electrons in solution is consistent with the geometry of the metal center found in the solid-state. Elemental analysis was hindered due to the presence of solvated lithium halide as a by-product that was difficult to remove. The Evans method of the chromium complexes was also hindered by the relative insolubility of these compounds in benzene. In the future the solvent ratios will be further tuned in order to remove lithium halide. Additional deuterated solvents will also be used in an attempt to perform the Evans method on the chromium complexes.

It was found that reduction of Cr (III) to Cr (II) could be achieved by utilizing the crude form of the [Li$_2$(tBu$_2$DIP-DAB)] complex. In the future it will be of interest to investigate similar pathways with the Mn(III) complex to Mn(II) complex. It will also be of interest to examine similar reactivity in a redox active Yb complex in order to extend this work to the lanthanide series. The reported complexes may also be reacted with oxidants such as trimethylamine N-oxide and dinitrogen.
In the future it will also be of interest to isolate a single enantiomer of the [Li$_2$(tBu$_2$DIP-DAB)(THF)$_2$] complex in order to investigate stereoselective catalysis. Elemental analysis and/or mass spectral analysis of all complexes also needs to be further attempted.
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