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Title: Synthesis, Characterization and Reactivity of Aluminum-☒-Diimine Complexes

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Synthesis, Characterization and Reactivity of Aluminum-α-Diimine Complexes

Patrick Wise

Candidate for the degree

Bachelor of Sciences

Submitted in partial fulfilment of the requirements for

College Honors

Departmental Distinction in Chemistry Department

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Synthesis, Characterization and Reactivity of Aluminum-α-Diimine Complexes

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Introduction

Two electron redox transformations such as oxidative addition and reductive elimination (figure 1) are important steps in conventional catalytic cycles. As such, development of catalysts around precious metals, such as palladium (Pd(0)/Pd(II)), platinum (Pt(0)/Pt(II), and Iridium (Ir(I)/Ir(III)), has been well documented as the metals have easily accessed redox couples. Unfortunately because these metals are rare they are also very expensive; $30,000+ per kilogram for platinum, $18,000+ per kilogram for palladium and $16,000+ per kilogram of iridium.[1] The development of new aluminum complexes for use in catalysis is attractive because the metal is highly abundant and inexpensive. Aluminum makes up over 8% of the earth's crust and as a result costs only about $1.55 per kilogram[1]. Aluminum complexes have been effectively used for Lewis acid catalysis,[2] but have not commonly been employed for two electron redox transformations due to aluminum having a single stable oxidation state.

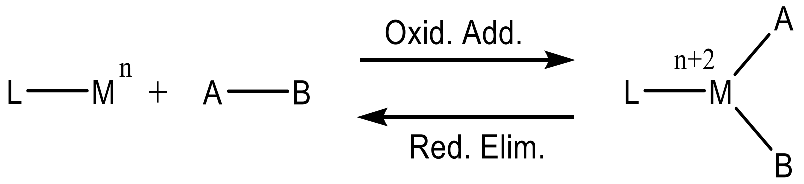


Figure 1. Redox transformation: Oxidative addition and reductive elimination

The Roesky group has prepared an Al(I)-carbene compound.[3] These Al(I)-carbene complexes were able to successfully undergo oxidative addition (figure 1), with Al(I) going to Al(III). However these complexes were limited as it was difficult for the Al(III) to undergo reductive elimination back to Al(I), thereby limiting the applicability of the complex as a catalyst. This project successfully showed that aluminum is capable of redox processes but to be applicable the complexes must be able to readily undergo *reversible* oxidation and reduction.[3]

An alternative to relying on metal-based oxidation state changes is to use redox-active ligands. With these ligands, the metal does not change oxidation state but the ligands themselves donate and accept electrons. Such an approach with aluminum would provide aluminum compounds capable of existing across several redox states without relying of redox chemistry of the metal. Several groups have taken this approach with a variety of metals that are not normally capable of performing redox processes and have successfully created capable redox-active catalysts. The Heyduk group has demonstrated the use of redox-active ligands to create complexes capable of multi-electron transfer processes. The metals that were investigated, Ti(IV), Zr(IV), Hf(IV), and Ta(V), are not normally able to perform two electron redox transformations. However the coordination of redox-active ligands allowed them to undergo both oxidative addition and reductive elimination, successfully demonstrating the ability of a redox-active ligand to support a redox-inactive metal.[4-8] In addition the Chirik group demonstrated the extension of redox ligand activity across an entire iron complex. The Chirik group was even able to demonstrate the applicability of these complexes into two electron transfer chemical processes, including hydrogenation, hydrosilation, and hydroboration of small molecules.[9-11] The development of redox-active aluminum complexes has also been carried out. The Berben group investigated complexes with aluminum coordinated to iminopyridine ligands. Electrochemical data collected for these complexes showed their capability for multi-electron processes and then were used as catalysts for the reduction of CO_2.[12-16]

Previous students that worked in the Graves group were also able to create aluminum complexes with the capability for multi-electron processes using α-diimine ligands. The α-diimine ligand was chosen because its redox chemistry has been well established, with neutral, singly reduced and doubly reduced forms offering three different oxidation species for two electron transfers to occur (Figure 2).[17]

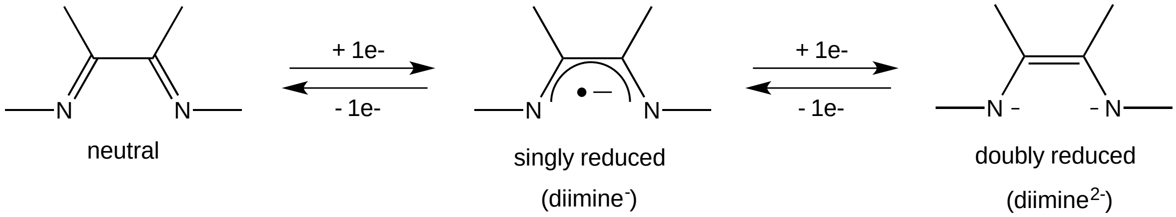


Figure 2: Oxidation states of the α-diimine ligand

The former students were able to prepare aluminum complexes of all three ligand oxidation states that through electrochemical data, demonstrated the ability to be redox active. The electrochemical data for the compounds was collected using cyclic voltammetry. When observing the CV spectrums given below, electrons are added as you move to the right (more negative potential) and with hills signifying the exact point when an electron is added. Electrons are then removed as you move to the left (more positive potential) and the valleys signify electron removals. If a compound is redox active it will have the same number of hills as valleys and they will occur at about the same voltage. Two clean hills and two clean valleys are observed in the spectra of all three aluminum compounds so the CV's prove that they are redox active.

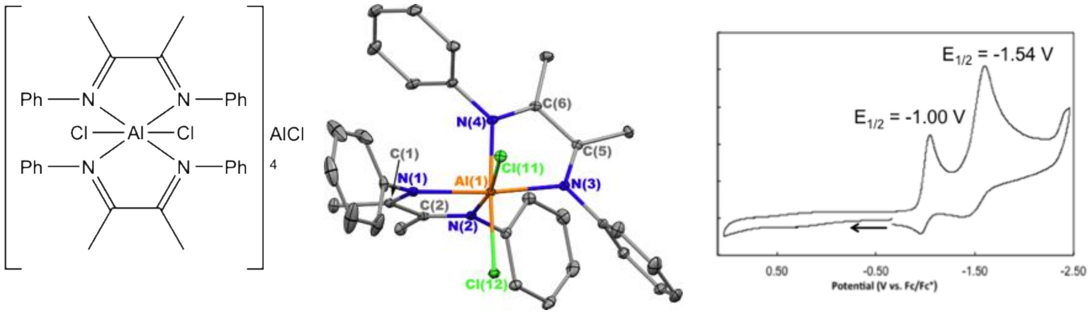


Figure 3. The chemical structure, crystal structure and CV spectrum of the neutral compound. The CV spectrum demonstrates that the neutral compound is redox active.[18]

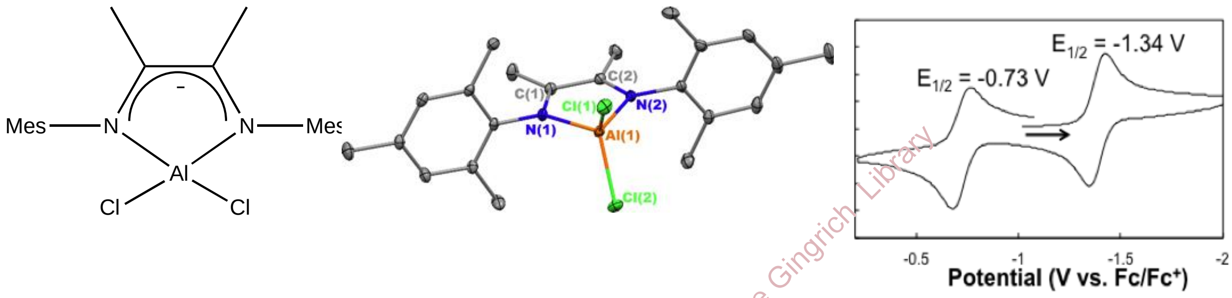


Figure 4. The chemical structure, the crystal structure and CV spectrum of the singly reduced aluminum compound. The CV spectrum demonstrates that the singly reduced compound is redox active.[18]

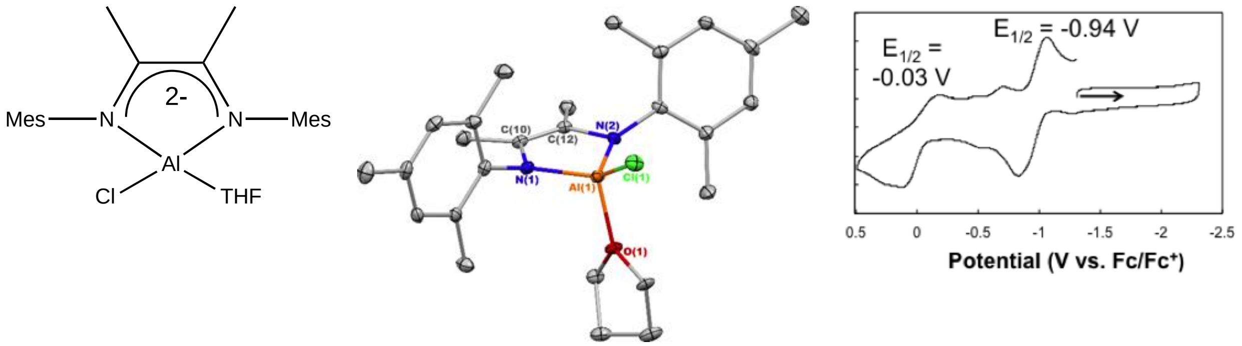


Figure 5. The chemical structure, the crystal structure and CV spectrum of the doubly reduced aluminum compound. The CV spectrum demonstrates that the doubly reduced compound is redox active.[18]

Building off the success of these former students, I worked to expand upon the reactivity of the *N*,*N*'-bis[2,4,6-trimethylphenyl]-2,3-dimethyl-1,4-diazabutadiene (L_{Mes} ligand), to create a halide series of the $(L_{Mes}^{-})AlX_2$ compounds and to investigate the oxidation chemistry of the $(L_{Mes}^{2-})AlCl(THF)$ compound.

Experimental

Direct Synthesis

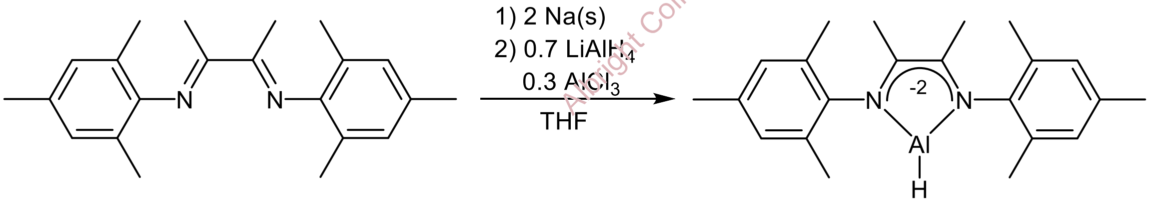
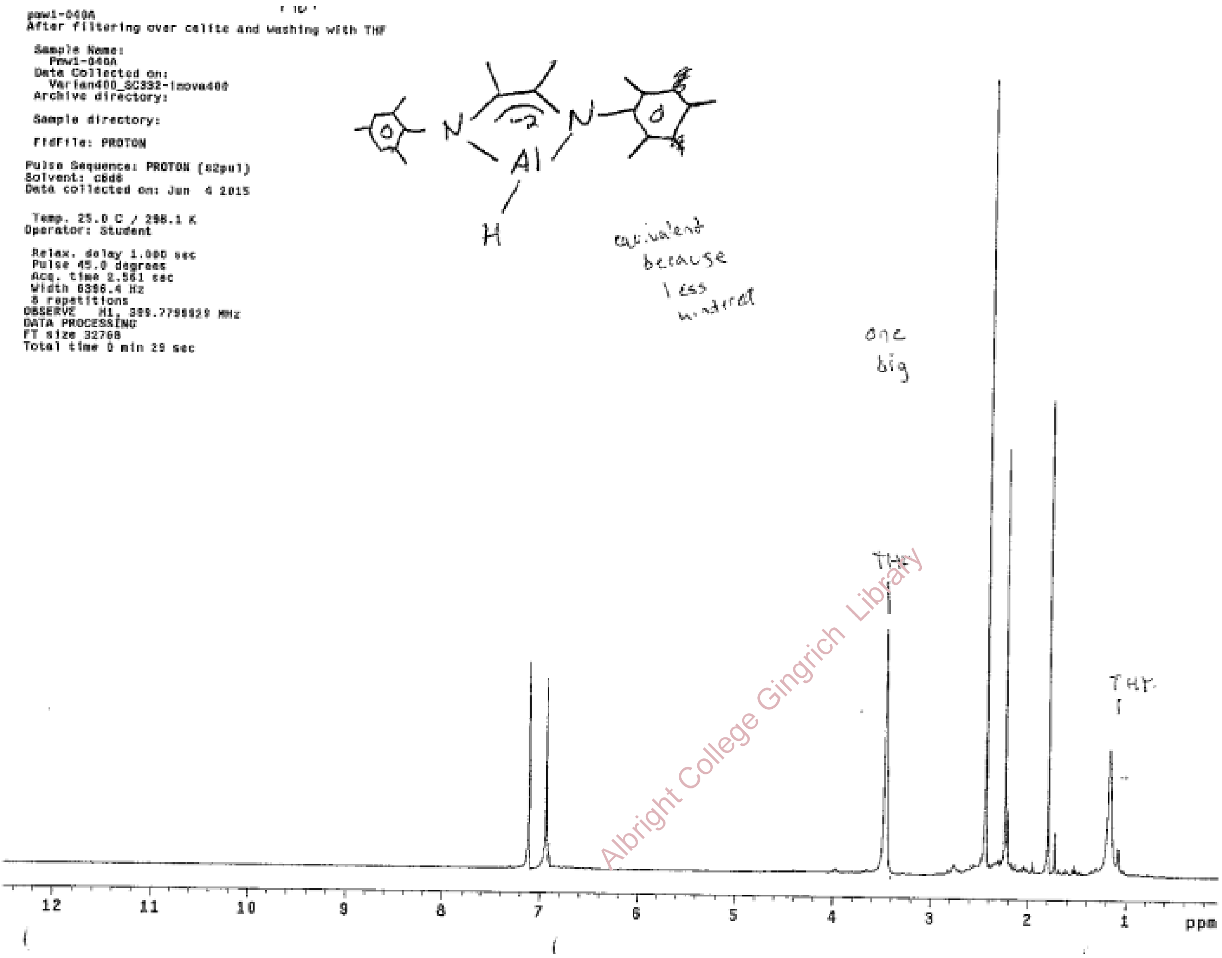


Figure 6. Scheme 1

Procedure PMW1-040: 78 mg of $AlCl_3$ (0.585mmol) and 8.88mg of $LiAlH_4$ (0.234mmol) were stirred in THF within a vial overnight. At the same time 250mg of the L_{Mes} ligand

(0.780mol) and 35mg of sodium (1.56 mmol) were mixed in THF within a 150mL Erlenmeyer flask overnight as well. The next day, the $AlCl_2H$ solution that has formed is added to the now burgundy sodium/ligand solution and stirred overnight. The next day the solution is filtered over a celite filled filter frit and washed with THF. The solution is then pumped down, triturated with pentane three times. The product was then taken up into THF and transferred into a vial. The solvent was pumped off and 0.2472g of solid product remained. Yield: 92%



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pmw1-040A
After filtering over celite and washing with THF

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 Archive directory:

 Sample directory:

 FidFile: PROTON

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Data collected on: Jun  4 2015

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Operator: Student

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 8 repetitions
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DATA PROCESSING
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Total time 0 min 29 sec
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Figure 7. ^1H NMR of $(L_{Mes}{}^{2-})AlH$ complex

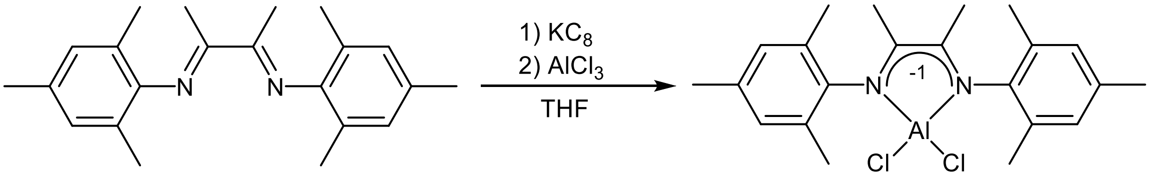


Figure 8. Scheme 2

Procedure PMW1-053: 250mg of L_{Mes} ligand (0.780mol) and 10.54 mg of KC_8 (105.4mg) were stirred in THF within a 150mL Erlenmeyer flask for 4 hours. After 4 hours 104.0mg of $AlCl_3$ (0.780mmol) were added to the flask and stirred overight. The next day the solution was filtered through a celite filled filter frit and pumped down.

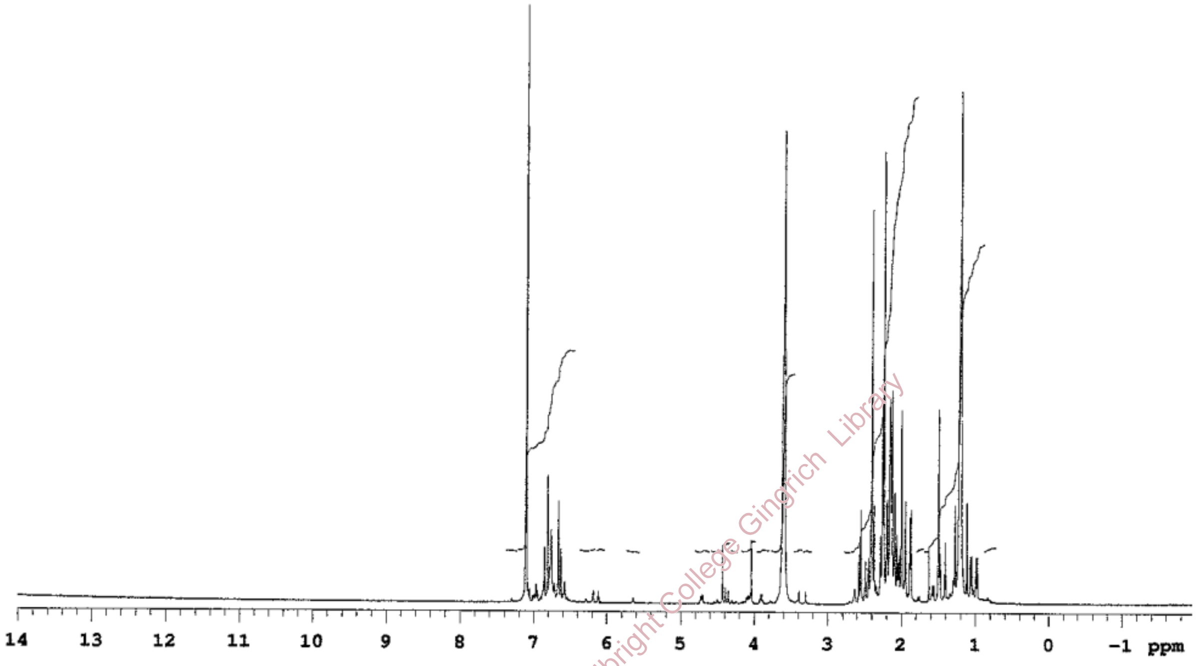


Figure 9. ^1H NMR of (L_{Mes}^-)$AlCl_2$ complex

Halide Series

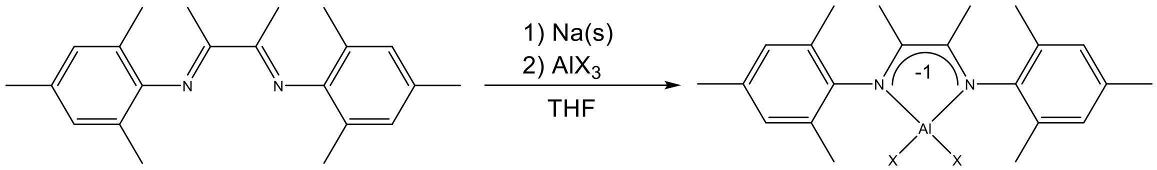


Figure 10. Scheme 3

Procedure PMW1-056: 250mg of the L_{Mes} ligand (0.780mol) and 18.5 mg of sodium (0.780mmol) were stirred in THF for 4 hours. 208mg of $AlBr_3$ (0.780mmol) were added and stirred overnight. The following day, the solution was filtered through a celite filled filter frit and pumped down. A hot gravity hexane filtration was then conducted and the solution was then pumped down again. Yield 53.16%

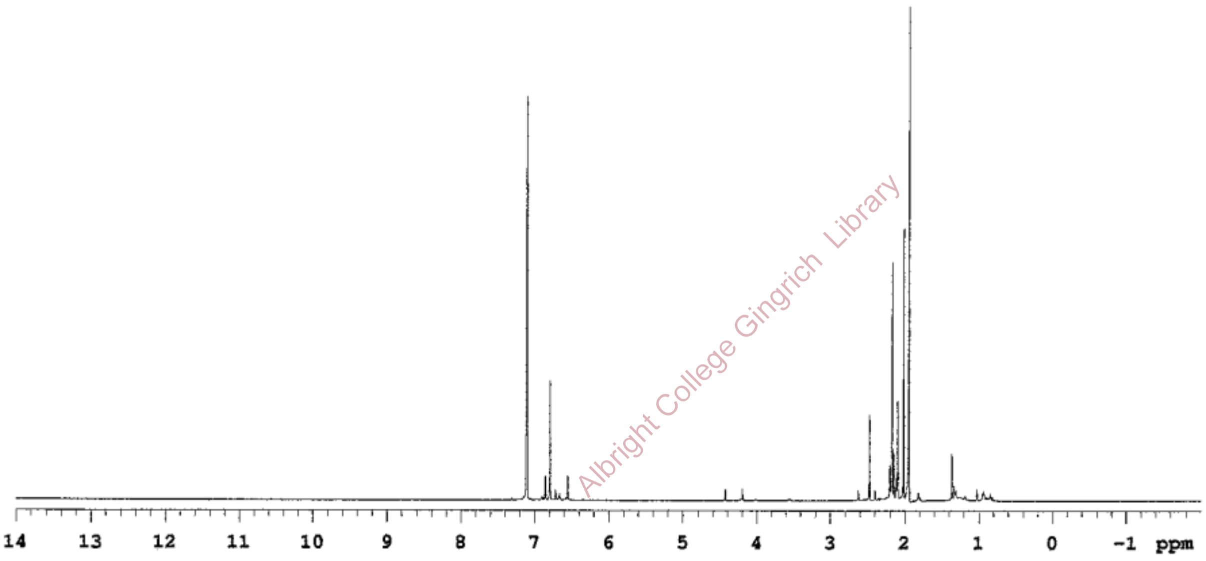


Figure 11. ^1H NMR of $(L_{Mes}^-)AlBr_2$ complex

Procedure PMW1-058: 250mg of the L_{Mes} ligand (0.780mol) and 18.5 mg of sodium (0.780mmol) were stirred in THF for 4 hours. 318.00mg of AlI3 (0.780mmol) were added and stirred overnight. The following day, the solution was filtered through a celite filled filter frit and pumped down. A hot gravity hexane filtration was then conducted and the solution was then pumped down again.

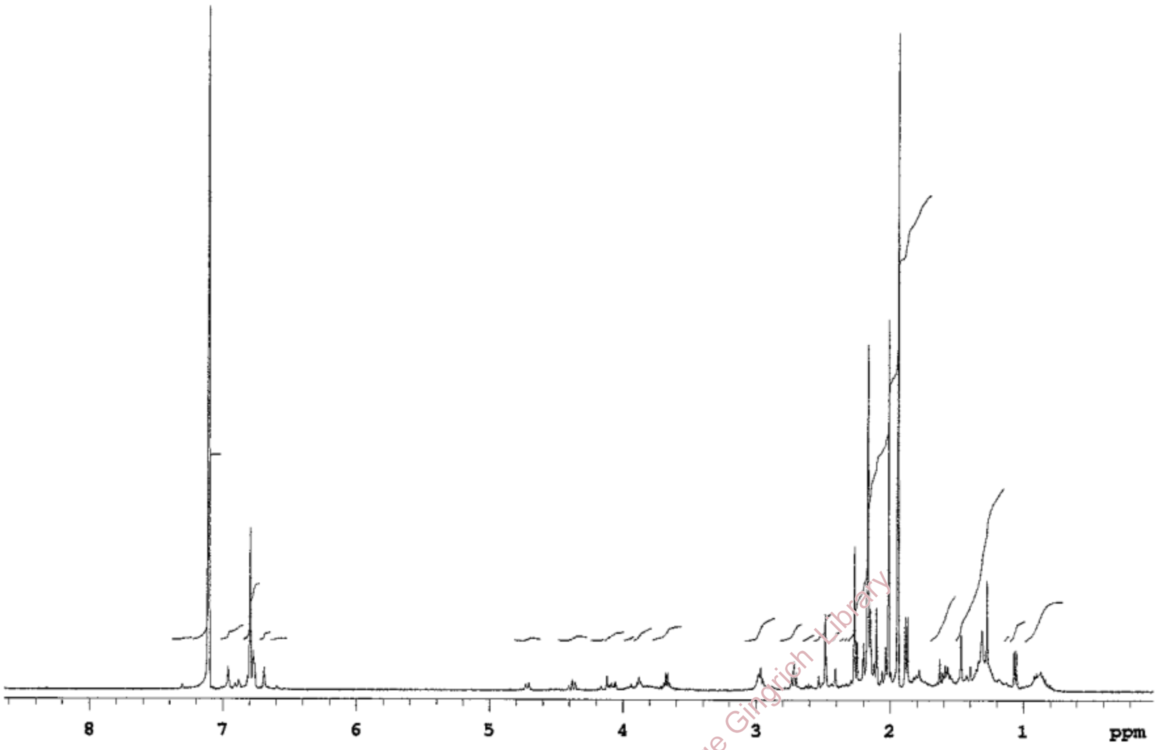


Figure 12. ^{1}H NMR of $(L_{Mes}^-)AlI_2$ complex

Oxidative Functionalization

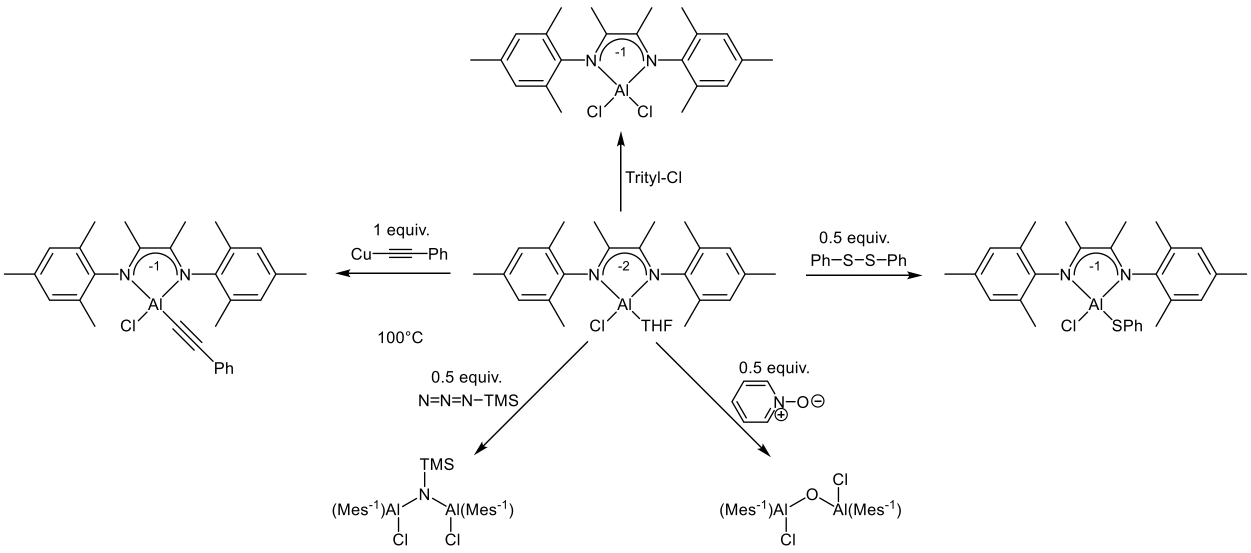
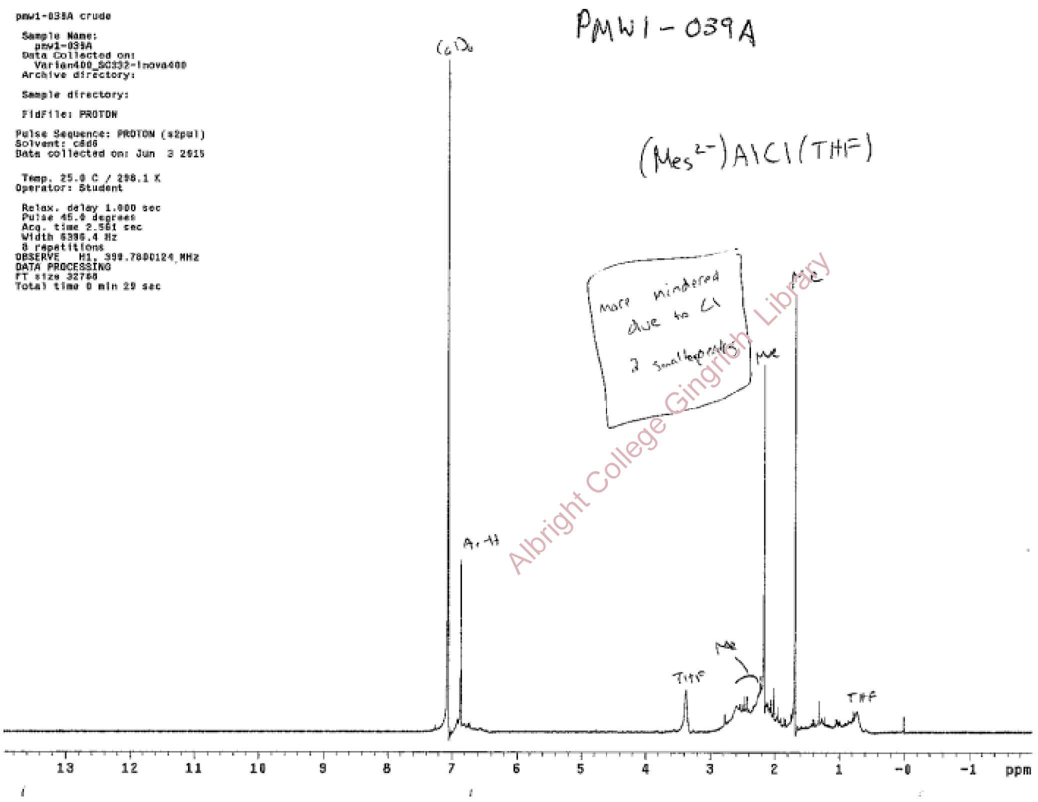


Figure 13. Oxidation schemes for (L_{Mes}^{2-})AlCl(THF) complex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pmw1-039A crude

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Solvent: c6d6
Data collected on: Jun  3 2015

 Temp. 25.0 C / 298.1 K
Operator: Student

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.561 sec
 Width 6396.4 Hz
 8 repetitions
OBSERVE   H1, 399.7800124 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec
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Figure 14. ^{1}H NMR of (L_{Mes}^{2-})AlCl(THF) starting material

(L_{Mes}^{2-})AlCl(THF) with trityl chloride

Procedure PMW1-055: 25mg of (L_{Mes}^{2-})AlCl(THF) (0.055mmol) was stirred with 15.33mg of trityl chloride (0.055mmol) within toluene in a vial overnight. The next day it was pumped down.

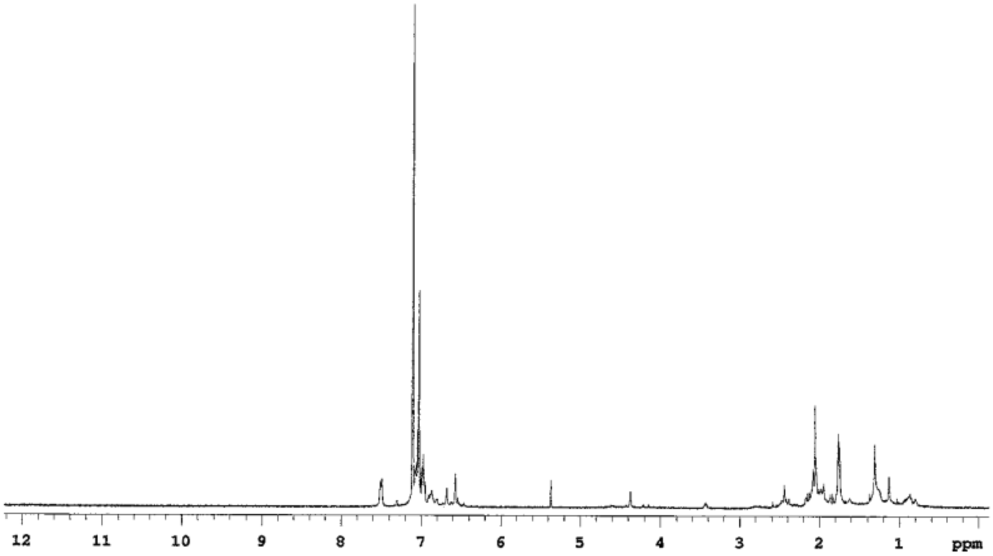

Figure 15. ^{1}H NMR of (L_{Mes}^{-})$AlCl_2$ complex

(L_{Mes}^{2-})AlCl(THF) with 1 equiv copper (I) acetylide

Procedure PMW1-067: 250mg of (L_{Mes}^{2-})AlCl(THF) (0.550mmol) was stirred with 84mg of copper (I) acetylide (0.550mmol) within toluene in a 150mL Erlenmeyer flask overnight. The next day it was pumped down.

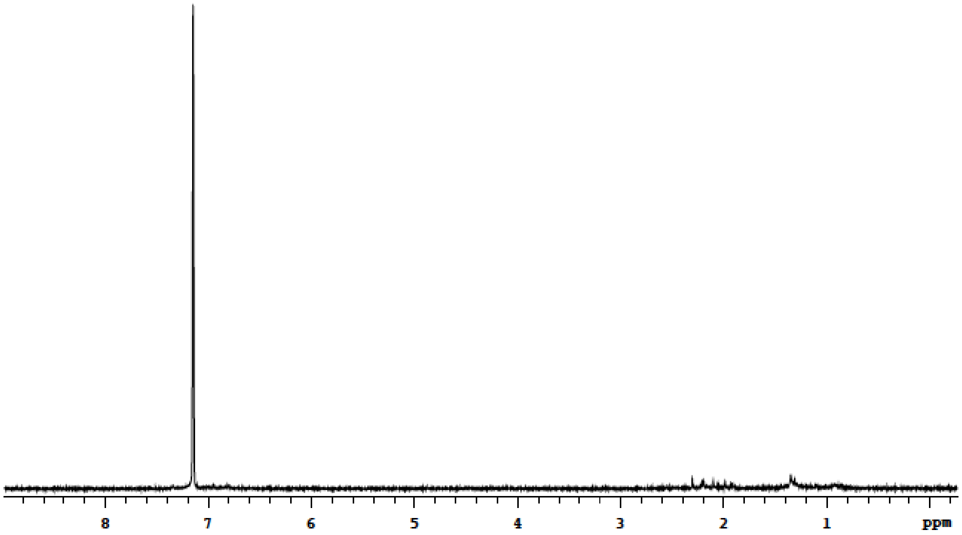

Figure 16. ^{1}H NMR of (L_{Mes}^-)Al(CCPh)Cl complex

(L_{Mes}^{2-})AlCl(THF) with .5 equiv diphenyl disulfide

Procedure PMW1-063: 50mg of (L_{Mes}^{2-})AlCl(THF) (0.110mmol) was stirred with 12.01mg of diphenyl disulfide (0.055mmol) within toluene in a vial overnight. THe next day it was pumped down.

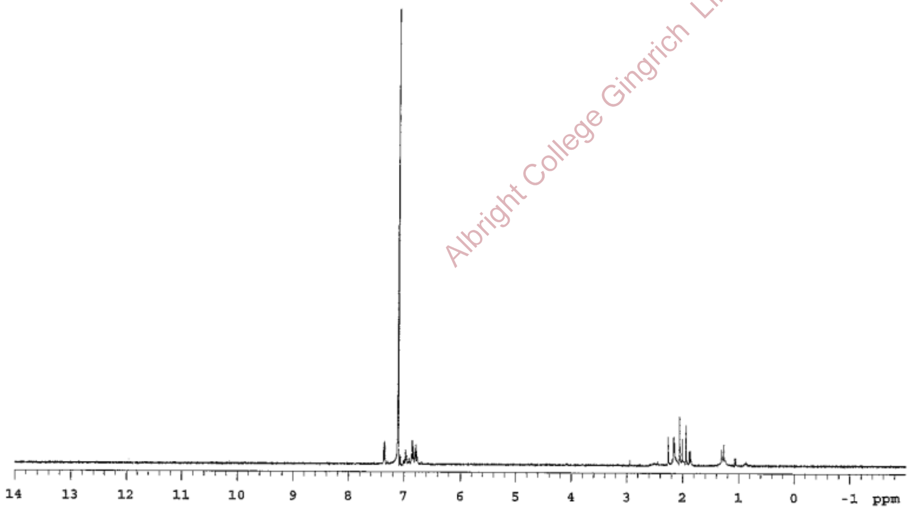

Figure 17. ^{1}H NMR of (L_{Mes}^-)Al(SPh)Cl complex

(L_{Mes}^{2-})AlCl(THF) with 0.5 equiv TMS azide

Procedure PMW1-050: 50mg of (L_{Mes}^{2-})AlCl(THF) (0.110mmol) was stirred with 0.0055mL of TMS azide (0.055mmol) within toluene in a vial overnight. The next day it was pumped down.

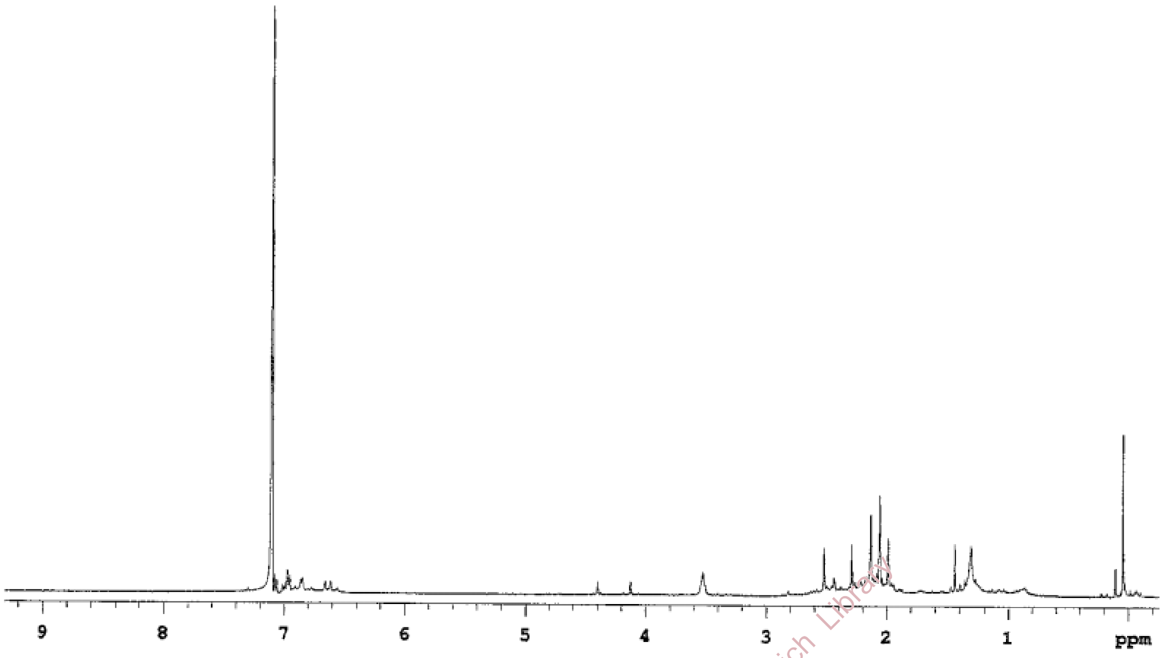

Figure 18. ^{1}H NMR of (L_{Mes}^{-})$_2$Al$_2$N(TMS)Cl$_2$ complex

(L_{Mes}^{2-})AlCl(THF) with 0.5 equiv pyridine-n-oxide

Procedure PMW1-048: 250mg of (L_{Mes}^{2-})AlCl(THF) (0.550mmol) was stirred with 26.12mg of pyridine-n-oxide (0.275mmol) within toluene in a 150mL Erlenmeyer flask.

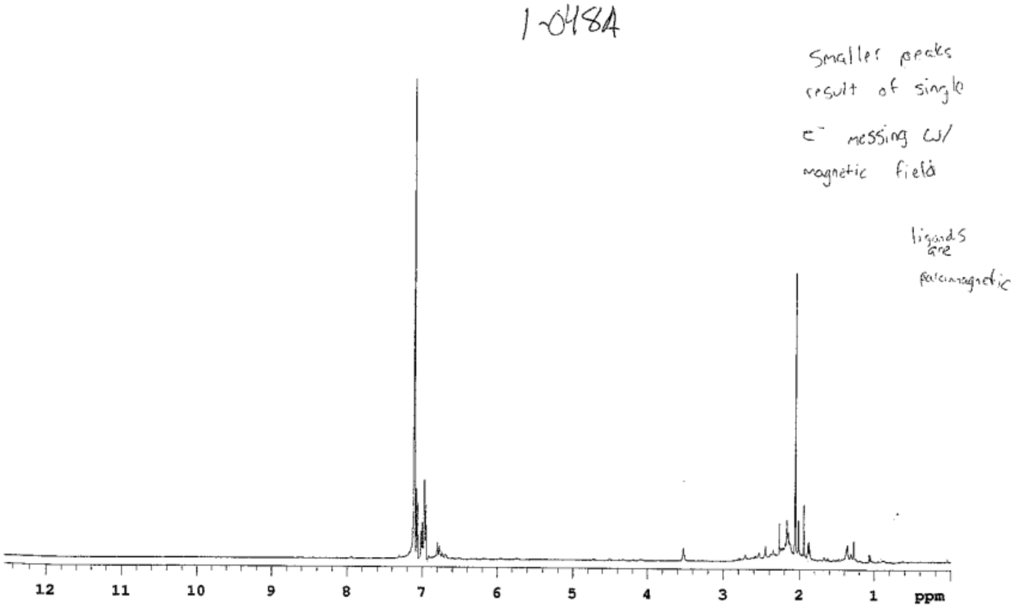

Figure 19. ^{1}H NMR of $(L_{Mes}^{-})_2Al_2OCl_2$ complex

Discussion

The first project that was carried out was to investigate the reactivity of the L_{Mes} ligand across various oxidation states with different aluminum starting materials. First, the doubly reduced ligand was prepared via reaction scheme 1. The ^{1}H NMR (figure 7) that was obtained is promising because unlike complexes like $(L_{Mes}^{2-})AlCl(THF)$ (figure 14), it demonstrates an unhindered structure. Complexes such as $(L_{Mes}^{2-})AlCl(THF)$ are hindered around the aluminum, so two tiny peaks for the two methyl groups of the diimine background exist. This can be seen at around 2.45ppm and occurs since the two separate methyl groups possess slightly different hydrogen environments due to the hindered structure. The aluminum hydride complex has less attached to the aluminum center so it is unhindered and this causes all the methyl group hydrogens of the diimine backbone to possess the same environment. This is seen as one large peak appearing at about 2.45 ppm instead of two tiny ones. Crystals of the product were sent for x-ray diffraction, but unfortunately they did not diffract properly so a crystal structure was not obtained.

We also investigated the reactivity of singly reduced L_{Mes} ligand with various AlX3 reagents (X = halide). First, an alternate pathway to creating $(L_{Mes}^{-})AlCl_2$ complex was developed and this is seen in reaction scheme 2. This reaction was successful and a crystal structure was obtained by X-ray diffraction, with the product possessing the expected structure (figure 6).

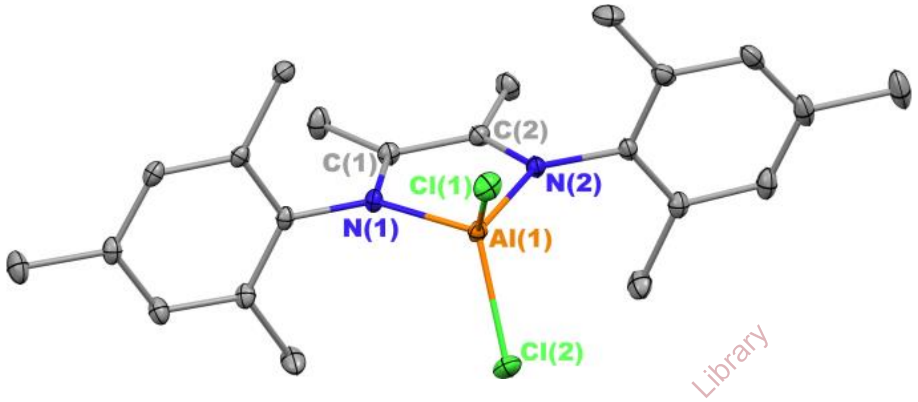

Figure 20. Crystal structure of $(L_{Mes}^{-})AlCl_2$ complex

With the successful creation of $(L_{Mes}^{-})AlCl_2$ complex, the synthesis of the full halide series for the $(L_{Mes}^{-})AlX_2$ complexes was attempted using reaction scheme 3. The $(L_{Mes}^{-})AlBr_2$ was successfully created and a crystal structure was obtained (figure 7). We suspect that the $(L_{Mes}^{-})AlI_2$ was prepared as well, but the compound was very reactive and resulted in the ring-opening of THF solvent. This ring-opened product was crystalized as a dimer (figure 8). Attempts to prepare the $(L_{Mes}^{-})AlF_2$ complex were not successful. Due to the murky color of the reaction and ^{1}H NMR obtained we speculate that reaction did not work due to the strong Al-F bond.

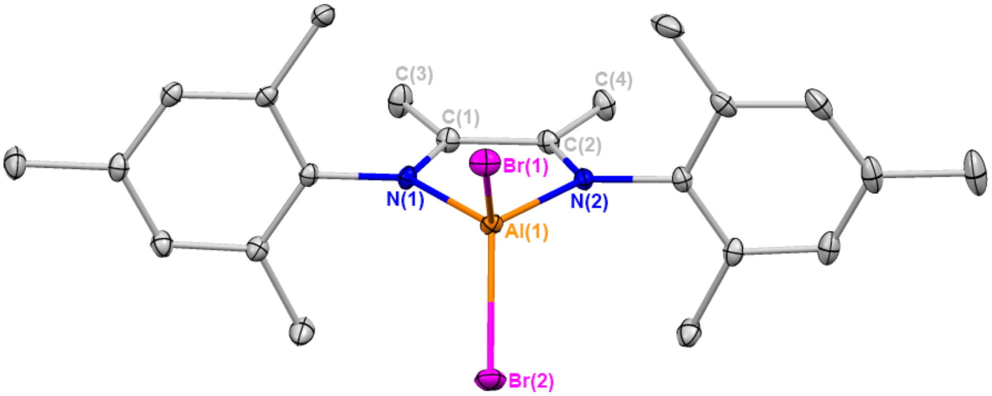

Figure 21. Crystal structure of (L_{Mes}^-)$AlBr_2$ complex

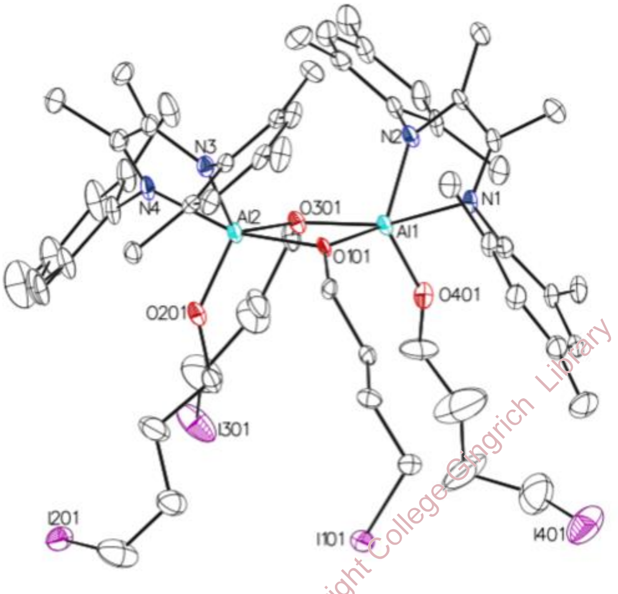

Figure 22. Crystal structure of (L_{Mes}^-)AlI_2 complex

We were also interested in investigating the reaction chemistry of the doubly reduced complex, (L_{Mes}^{2-})AlCl(THF). Specifically, the oxidation chemistry of the doubly reduced (L_{Mes}^{2-})AlCl(THF) compound was investigated by reacting it with various 1-

electron (diphenyl disulfide, triphenylmethyl chloride and copper (I) phenylacetylide) and 2-electron (trimethylsilyl azide, pyridine-*N*-oxide) oxidizing agents. None of these reactions were successfully characterized by x-ray diffraction. However, based on the consistency of the red-orange color of the final products and the ^{1}H NMR spectra of the compounds it is strongly suggested that the oxidations were success. The ^{1}H NMR's are conclusive because the signals of the complex are now reduced in size and broadened due to the paramagnetic character of the complexes. The paramagnetic character causes this ^{1}H NMR phenomenon because the electron spin of the single electron interferes with the relaxation of the spin flip state of the protons being measured. The spin state of the electron either causes the flip to happen so quickly it can't be measured (reduction in size) or each time the energy is different (signal is broadened).

Conclusion

The reactivity of the Mes ligand was successfully explored, although the crystal structure of the aluminum hydride complex has not yet been determined and the creation/ characterization of the ($L_{Mes}{}^{2-}$)AlX_2 complex was achieved for X=Cl, Br. The oxidative chemistry of the ($L_{Mes}{}^{2-}$)AlCl(THF) was also thoroughly explored and although the products are not yet characterized by x-ray diffraction, the ^{1}H NMR's are promising. The next step moving forward will be to determine the crystal structures for all the desired products, to further expand upon the reactivity and eventually demonstrate that the aluminum complexes created are redox active through electrochemistry.

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