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Main Group Adducts of Carbon Dioxide and Related Chemistry (LDRD 149938)

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Main Group Adducts of Carbon Dioxide and Related Ligand Chemistry (LDRD 149938)

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Abstract

This late-start LDRD was broadly focused on the synthetic attempts to prepare novel ligands as complexing agents for main group metals for the sequestration of CO₂. In prior work we have shown that certain main group (p block elements) metals such as tin and zinc, when ligated to phosphinoamido- ligands, can bind CO₂ in a novel fashion. Rather than simple insertion into the metal-nitrogen bonds to form carbamates, we have seen the highly unusual complexation of CO₂ in a mode that is more similar to a chemical “adduct” rather than complexation schemes that have been observed previously. The overarching goal in this work is to prepare more of these complexes that can a) sequester (or bind) CO₂ easily in this adduct form, and b) be stable to chemical or electrochemical reduction designed to convert the CO₂ to useful fuels or fuel precursors. The currently-used phosphinoamido- ligands appear at this point to be less-stable than desired under electrochemical reduction conditions. This instability is believed due to the more delicate, reactive nature of the ligand framework system. In order to successfully capture and convert CO₂ to useful organics, this instability must be addressed and solved. Work described in the late-start LDRD was designed to screen a variety of ligand/metal complexes that a priori are believed to be more stable to polar solvents and possible mild hydrolytic conditions than are the phosphinoamido- ligands. Results from ligand syntheses and metal complexation studies are reported.

Acknowledgements

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Table of Contents

1 INTRODUCTION.....	10
2 RESULTS AND DISCUSSION.....	11
3 CONCLUSION.....	21
4 REFERENCES.....	22
5 DISTRIBUTION	23

LIST OF FIGURES

Figure 2.1.1 Diagram illustrating the electron density locations and bond polarities found in CO ₂ . The electrophilic/nucleophilic sites determine reactivity trends for CO ₂	12#
Figure 2.5.1 Possible amphoteric ligand structures based on a N-OH framework.	17#
Figure 2.5.2 Reaction of 8-hydroxyquinoline with SnCl ₂ to give Sn(quinolin-8-olato) ₂	18#
Figure 2.5.3 Crystal structure of Sn(quinolin-8-olato) ₂	18#
Figure 2.6.1 Possible ligand structures based on M-C bound frameworks.....	19#
Figure 2.6.2 Route to bis(pyridyl) metal species.	20#
Figure 2.6.3 Route to bis(pyridyl) metal species.	21#

Abbreviations

CO ₂	Carbon dioxide
DOE	Department of Energy
HMPA	Hexamethylphosphoramide
IR	Infrared spectroscopy
LDRD	Laboratory Directed Research and Development
NMR	Nuclear magnetic resonance
SNL	Sandia National Laboratories
TMEDA	Tetramethylethylenediamine

Main Group Adducts of Carbon Dioxide and Related Ligand Chemistry (LDRD 149938)

The goal of this 6-month, late-start LDRD project was to investigate the design, synthesis and characterization, and metal complexation of a number of new ligands that might prove useful for the possible sequestration and conversion of CO₂. Recently, we have shown that CO₂ at atmospheric pressure under simple bubbling can form “adducts” with certain main group metal – ligand compounds. While almost all ongoing research directed towards the fixation of CO₂ involves transition metals, we have chosen to examine main group metals. Main group metals are also called *p*-block elements, indicating that the valence electrons used in binding ligands are in *p* orbitals, not the *d* orbitals used in transition metals. While transition metals range in cost from relatively inexpensive (Fe, Co, Ni, etc.) to extremely expensive and rare (Rh, Ir, Pd, Pt, etc.), the main group metals such as tin and zinc we are interested in exploiting are quite inexpensive and plentiful. In general, when main group metals are complexed with amido-type (nitrogen-bound) ligands, CO₂ is known to insert into the M-N bond to form organic carbamates. While this reaction is of interest to produce carbamates, CO₂ plays only a role of inserting species – the types of organic product derived from CO₂ are quite limited in scope. As well, simple insertion of CO₂ into activated M-N bonds, or other M-element bonds, cannot be a catalytic process of CO₂ conversion. Our goal in this research is to examine these new “adducts” of CO₂ with main group complexes in order to convert CO₂ via chemical or electrochemical means to organic fuels or fuel precursors, preferably catalytically. In our initial samples of complexed CO₂ with main group complexes, ones in which the concept of CO₂ adduct formation was first demonstrated, the phosphinoamido- ligands appear to be less stable than required to allow reduction of CO₂. The entire issue of ligand and adduct stability is a delicate one. For example, one wants the CO₂ adduct of the metal complex to be stable, yet it cannot be so stable that it is unreactive towards reductants. So, there is a delicate balance between stability and instability that drives every complex that is formed, and every possible catalytic reaction that is done. If complexes are too stable, they can become thermodynamic “dead ends” in a catalytic conversion cycle, while if the complexes are too unstable, they do not exist long enough to perform useful reductive chemistry upon them. As well, the structural integrity of the ligand framework must also stand up under the reaction conditions used. Ligands that fall apart easily are of little use other than as sources to possibly demonstrate fundamental concepts for the complex. Conversion under electrochemical conditions requires that the metal complex, including the ligand framework, must be stable under electrochemical conditions. Unfortunately, our initial complexes that demonstrated our adduct concept are not stable enough to undergo electrochemical reduction. The work presented in this SAND report documents our initial thoughts and efforts towards the syntheses of new and novel ligands with improved stability. Also included are the synthetic strategies employed to manufacture these metal complexes using these ligands, as well as initial CO₂ complexation studies. Essentially all of our ligands and metal complexes are well-characterized, often by single crystal X-ray diffraction in addition to the typical analytical techniques used such as NMR and IR spectroscopies.

Significant research goals and milestones accomplished over the course of this late-start LDRD include:

- **Synthesis and characterization of Sn and Zn-based CO₂ adducts.** The inspirational chemical targets of this LDRD work were prepared and well-characterized. Although some of the work to prepare these compounds was performed earlier, further information on these new compounds is presented.
- **Initial attempts at electrochemical reduction of a Sn-based CO₂ adduct.** The initial attempts at electrochemical reduction of a Sn-CO₂ adduct were performed. The conclusions from these preliminary experiments indicate that the ligand backbone must be stabilized in order to obtain reproducible and clean results.
- **New ligand frameworks were designed.** Based on the preliminary electrochemical experiments it was determined that new ligand frameworks were required. Design and synthesis of several new framework structures were initiated and performed during this time.
- **New metal complexes were prepared and characterized during this period.** New ligands were complexed to various main group metals to form new complexes. These metal-complexes were also characterized by traditional methods, including single crystal X-ray crystallography.

1 Introduction

Carbon dioxide (CO₂) is a relatively “useless” molecule other than as a carbon source, and so the conversion of CO₂ into useful chemicals and fuels is a topic of worldwide interest as the need to mitigate global warming becomes more urgent.¹⁻⁵ In a current project, Sandia has a major research thrust in reducing CO₂ levels by using high-temperature, solar methods.^{6,7} Reduction of CO₂ at lower temperatures, ideally ambient temperature, would be a major scientific breakthrough and assembling a catalytic process for this transformation would be a technological game-changer for CO₂ fixation. Therefore, emphasis on a single, high-temperature approach from Sandia is not adequate to ensure success in this arena of CO₂ activation. Additionally, Sandia has LDRD programs examining the capture and chemical sequestration of CO₂ via a number of routes, primarily using heterogeneous or polymeric supports. In the work reported here our goal is to combine aspects of these two Sandia interests by developing a novel approach to capturing and reducing CO₂. The overall concept is based on a generalized type of metal-CO₂ “adduct” that we have discovered and characterized very recently at Sandia/UNM. It is known that direct electrochemical reduction of CO₂ is disfavored largely due to the energy required to “bend” the linear CO₂ molecule after addition of electrons. Our proposed approach is geared towards overcoming the primary barrier of efficiently reducing CO₂ electrochemically – that of the energy requirement to “bend” CO₂ after addition of these electrons – by forming coordination adducts of CO₂ that “pre-bend” CO₂ using electroactive metal catalysts. Moreover, the metals used in our suggested experiments are inexpensive and readily-available, and the CO₂-adduct formation reaction takes place at room temperature.

This report describes the efforts from the end of March 2010 to the end of September 2010 that were funded by a late-start Laboratory Directed Research and Development (LDRD 149938) project to investigate new ligands that might be useful for preparing metal-CO₂ adducts. As well, metal complexes of these new ligands were prepared and characterized. Initial electrochemical reduction studies of metal-CO₂ adducts were also performed.

2 Results and Discussion

2.1 Fundamental Description of CO₂

Carbon dioxide (CO₂), the fully oxidized form of carbon, is an energetically “spent” molecule, although this does not imply that it is non-reactive. Far from it, as CO₂ is known to undergo a wide range of reactions with various other reagents.¹ However, generally speaking the other reagent used must be activated in some way. CO₂ is an amphoteric molecule, capable of acting as a Lewis acid by attack at the electrophilic central carbon atom, or acting as a Lewis base by donation from the lone pairs of electrons located on the terminal O atoms. The diagram shown in Figure 2.1.1 illustrates this bond polarity difference, and clearly shows the modes of expected reactivities at the carbon or oxygen sites.

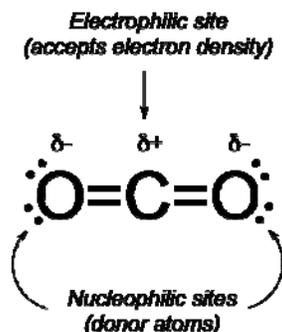


Figure 2.1.1 Diagram illustrating the electron density locations and bond polarities found in CO₂. The electrophilic/nucleophilic sites determine reactivity trends for CO₂.

A classic, long-known example demonstrating the electrophilic nature of CO₂ is the quenching of Grignard reagents (organomagnesium species) with dry ice (solid CO₂) to produce organic acids after workup.⁸ The nucleophilic organic anions attack the central carbon atom to form carboxylates, which can be converted to organic acids upon protonation. As an example of further reactivity germane to this report, CO₂ is known to insert into various polarized metal-element bonds such as metal-alkoxides or metal-amides to form important organic precursors such as metal carbonates (M-CO₂-OR) or carbamates (M-CO₂-NR₂).⁹ The insertion mode of reactivity for CO₂ to form highly thermodynamically stable products is commonly observed, and is unfortunately an undesired alternative reaction pathway in the research described in this report.

2.2 Main Group Metal-CO₂ Adducts

Recently, we have discovered a new bonding mode for CO₂ towards main group metals that is to our knowledge unprecedented in the literature. Main group metals are those metals located on the right-hand side of the periodic table that utilize *s* and *p* orbitals as

the outer bonding valence shell. These metals – examples including tin, zinc, bismuth, lead, silicon, and so forth – differ significantly in reactivity from the transition metals, which use *d* orbitals for binding to ligands. In two species based on Sn and Zn and using modified amido ligands, we have shown the extraordinary binding of CO₂ as a Lewis acid-base adduct to the metal complexes. These two species, briefly discussed in the next paragraph, form the origin for the work performed in this late-start LDRD.

We have previously been interested in the insertion reactions of CO₂ into various main-group metal amides to form metal-containing carbamates.¹⁰⁻¹² In these studies, the insertion of CO₂ was desired in order to form unstable species that could upon warming eliminate isocyanates and/or carbodiimides as organic reaction products. This reaction scheme, based on work by Sita,¹³ to form these species is shown in Figure 2.2.1 below.

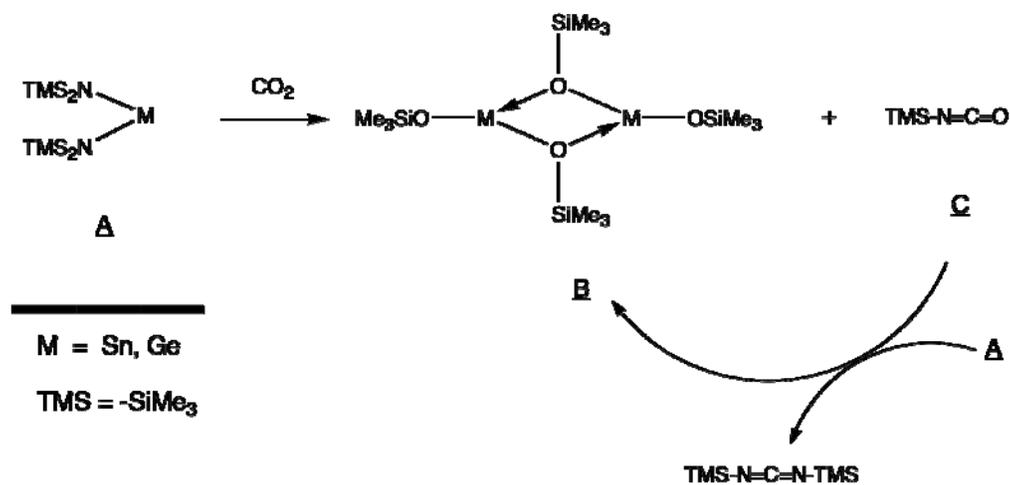


Figure 2.2.1 Reaction scheme demonstrating the insertion of CO₂ into main group metal amides to form isocyanates and/or carbodiimides.

A key element of the above scheme is the direct insertion of CO₂ into the M-N bond to form a metal carbamate, which then eliminates an R-N=C=O species (isocyanate) while concomitantly forming a strong M-OSiMe₃ bond to help drive the reaction forward. A secondary reaction in which the isocyanate inserts in place of CO₂ leads to the carbodiimide. Our academic group at the University of New Mexico has published widely on this topic. However, in the screening of various modified-amido ligands we unexpectedly discovered the formation of a new bonding mode for CO₂ – that of a main group metal-CO₂ adduct, rather than the expected inserted/eliminated product.

We utilized the [(R₂P)(Me₃Si)NH] phosphino-modified amido ligand, and the dinuclear(ligand)zinc complex was prepared using an alkane elimination reaction with ZnEt₂ that did not go to completion. However, addition of CO₂ led to the final product as shown. A classic metathesis route was used to prepare a related divalent Sn complex

that used a similar phosphino-modified amido ligand, and in this case the bis(ligand) Sn species could be formed. Rather than inserting into the metal-nitrogen bond as was expected, we instead observed that CO₂ formed a side-on bound “adduct” with the metal-containing complex after simple bubbling of CO₂ through either metal complex solution at room temperature. The example of this reaction type using zinc is shown in equation form in Figure 2.2.2, and we have confidently identified the product by single crystal X-ray diffraction, as shown below in Figure 2.2.3. We also showed a very similar structure for Sn as well, although it is not shown. What makes this reaction extremely interesting is that the expected CO₂ insertion into both Zn-N bonds to form carbamates is not observed, but rather a bent CO₂ adduct is formed, using two Lewis base/acid pairs for

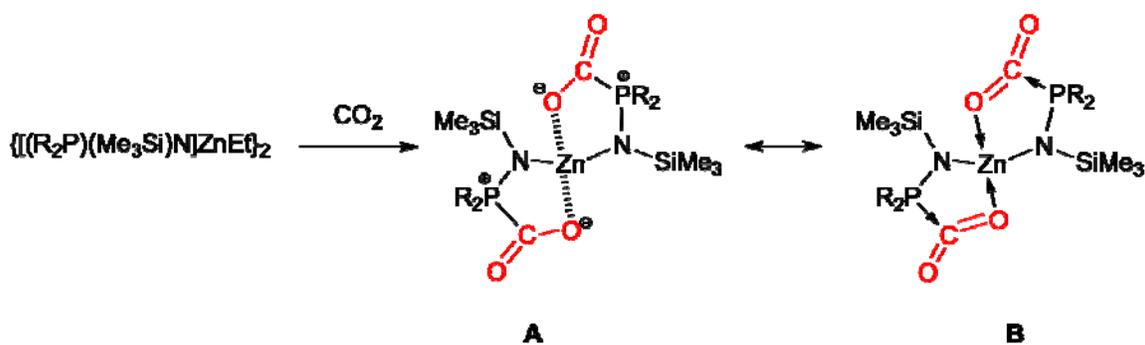


Figure 2.2.2 Synthetic scheme used to prepare Zn-CO₂ adduct.

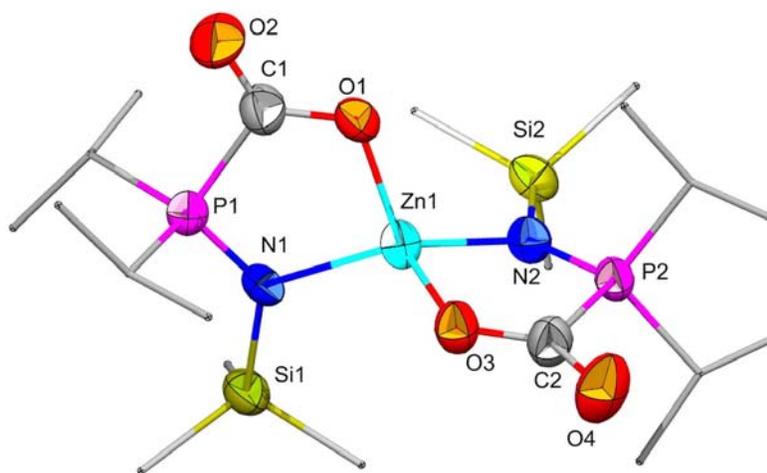


Figure 2.2.3 Thermal ellipsoid plot of Zn-CO₂ adduct.

complexation. This bonding mode can be seen more clearly in resonance structure B above with use of the four arrows to denote Lewis acid/base pairs, although we note that zwitterionic resonance form A can also describe the molecule. As mentioned, we have also observed this same reactivity mode using Sn^{2+} and related ligands to produce an acid/base adduct. We are interested in further expanding the number and types of complexes shown by varying the metals and ligand structures by examining inexpensive and readily-available metals such as tin, zinc, and others in Groups 12-15, and to design more robust ligands. Almost all research efforts involving CO_2 activation utilize transition metals, and so one of the unique aspects of this approach is the focus will be put on these main group elements. It is apparent from the crystal structures that the CO_2 adducts are significantly bent with O-C-O angles of $\sim 130^\circ$. We hypothesize that these adduct complexes of CO_2 will electrochemically accept electrons kinetically more easily than will linear CO_2 since the complexes are already bent upon complexation to the metal. This should allow more facile entry of the electrons into the CO_2 fragment to form radical anions.

2.3 Initial Electrochemical Investigation of Main Group Metal- CO_2 Adduct

The Sn- CO_2 adduct described above is relatively stable, although sitting at room temperature over a 2-3 day period will lead to elimination of organic isocyanates and other unidentified products. Thus, there is a delicate balance in the stability of this adduct. The Zn-adduct is similar in behavior, although it is more stable. This gentle instability is encouraging, as it is not desired to have the complex adducts be too stable. In our model, the adduct must exist long enough to do the reductive chemistry but not be so stable that the energy required to reduce the CO_2 is too great. Samples of the Zn- CO_2 adduct were sent to Professor William Geiger of the University of Vermont for electrochemical studies. In a brief series of initial electrochemical experiments into the Zn- CO_2 adduct it was discovered that the ligand framework did not appear to be chemically robust enough to survive the supporting electrolyte solution ($[\text{Bu}_4\text{N}][\text{PF}_6]$ in tetrahydrofuran) and electrochemical experiments.

The targeted reduction occurs just before the solvent limit and creates problems to the electrode surface. However, the compound is definitely reducible. The reduction can only be seen by using a gold electrode, with either Pt or glassy carbon showing no wave at all. After one scan, the gold electrode is at least partially passivated, so that nothing is seen on a second scan. If the electrode is taken outside the box and polished, the wave reappears in a new scan of the solution. This is typical of a system in which the reduction product coats the electrode and will pose a problem if we want to do bulk electrolysis. The potential of the reduction (irreversible) is -3.25 v vs. FcH. A typical reduction scan of the Zn- CO_2 adduct is shown in Figure 2.3.1. Initially, it appears that the ligand is degrading during reaction.

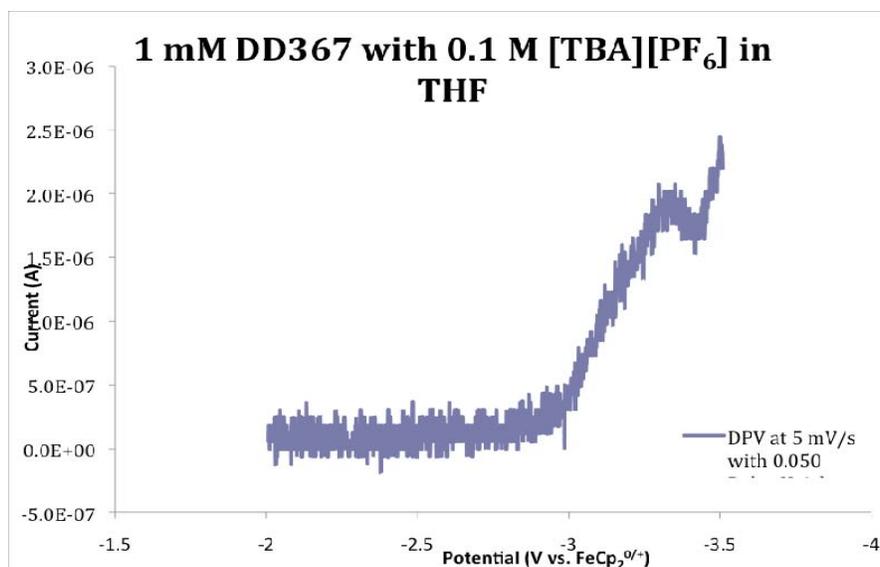


Figure 2.3.1 Electrochemical reduction scan of Zn-CO₂ adduct in [TBA][PF₆]/THF solution.

While this is disappointing, it is not totally surprising as the ligand framework consists of relatively delicate and reactive Zn-N, N-Si, and N-P bonds. These highly-polarized bonds are susceptible to a variety of reactions, including reaction with any miniscule sources of protons or base. The initial results from the electrochemistry experiments indicated to us that the stability of the ligand must be improved, and the rest of this report will document our attempts at preparing new, more chemically-robust ligands that can function in the same manner as the more delicate $-\text{N}(\text{SiMe}_3)(\text{PR}_2)$ ligands.

2.4 Introduction to the Design and Preparation of New Ligands

When designing new ligands to prepare CO₂ adducts from main group metal complexes, there are several features that can be generalized and will be common to all ligand types. First, the goal of the research is to prepare more stable ligands, so the use of reactive, highly-polarized bonds should be minimized. At first glance, one would wonder why reactive bonds in the frameworks of ligands should not be avoided totally, not just minimized. However, as an overall goal in this project we are also interested in understanding why these ligands behave as they do in forming metal-CO₂ adducts in place of the expected inserted products, and as such we must also study the complexes (and related ligand structures) that we know will produce adducts. However, we have focused largely on new structures in ligands. Secondly, the new ligands must provide a site of Lewis basicity (likely a lone pair of electrons) that can attack the electrophilic carbon center in CO₂ to form a bond or interaction. This feature is considered critical for the preparation of adducts. Thirdly, the location of the Lewis base site on the ligand must be close enough to the metal center to allow the nucleophilic O ends of the CO₂ to coordinate to the Lewis acidic metal center. Design of various ligand frameworks will

allow us to determine what is the optimal ring size for a coordinated CO₂ adduct. The ligand must be capable of forming a strong interaction with the metal, and a strong metal-ligand bond must be present. As well, the ligand must be flexible enough to allow the coordinated CO₂ to bend upon coordination, which is a key feature of these adducts. The rest of this report will summarize the ideas behind and synthetic chemistry of these new ligands.

2.5 Mixed N-OH Species as New Ligands

In order to improve the stability of the ligands mixed N-OH ligands have been prepared and treated with Sn(II) reagents. Several of these ligands are shown in Figure 2.5.1. All are compounds that can be expected (after conversion to the alkoxides) to bind to the metal through a more robust and stable M-O bond. The Lewis base functionality of each new ligand is provided by an amine group that can provide the lone pair needed for binding to the electrophilic C atom of CO₂.

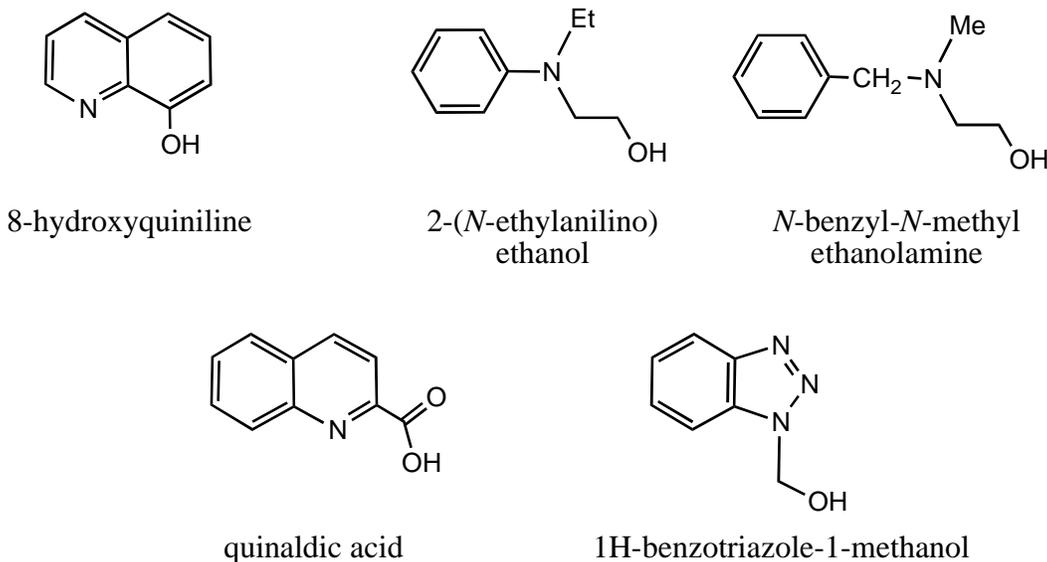


Figure 2.5.1 Possible amphoteric ligand structures based on a N-OH framework.

The first Sn(II) complex prepared with these rings systems was bis(quinolin-8-olato)tin(II) and was based on the method used by Kitamura and coworkers.¹⁴ The preparation of these types of complexes are in methanol. The complex was isolated in essentially quantitative yield (98%) and the structure verified by ¹H and ¹³C{¹H} NMR spectroscopy and X-ray crystallography. The reaction scheme is shown in Figure 2.5.2 and the single crystal X-ray structure of the Sn complex is shown in Figure 2.5.3.

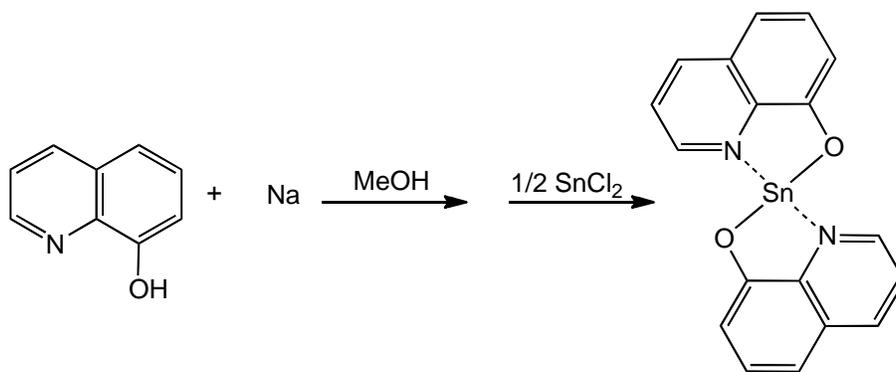


Figure 2.5.2 Reaction of 8-hydroxyquinoline with SnCl_2 to give $\text{Sn}(\text{quinolin-8-olato})_2$.

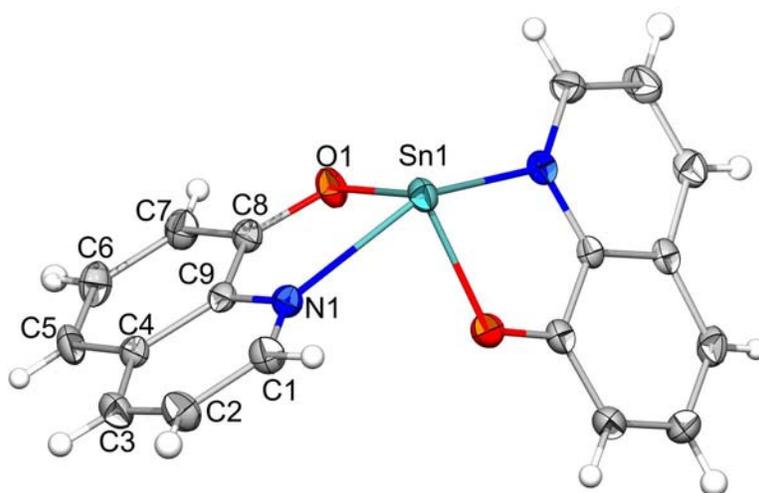


Figure 2.5.3 Crystal structure of $\text{Sn}(\text{quinolin-8-olato})_2$.

Bis(quinolin-8-olato)tin(II) was unfortunately not reactive towards CO_2 in methanol at atmospheric pressure. However, when the pressure was raised to 90 psig of CO_2 the clear yellow solution in methanol of the complex turned cloudy after about 10 minutes. The IR of the isolated crude product indicated a new complex. Efforts to purify the product are currently underway.

The bis(benzotriazole-methoxy)tin(II) complex was prepared similarly to bis(quinolin-8-olato)tin(II). Isolation of the crude product gave a light yellow solid from which clear colorless, very thin crystals were grown. Unfortunately they were too thin for X-ray crystallography determination. However, the ^1H NMR spectrum indicated that a CO_2 complex had been prepared. Efforts are still in progress at the time of this writing to grow crystals suitable for X-ray diffraction studies and reactions with CO_2 at atmosphere and at elevated pressures are also in progress.

The attempted syntheses of bis(*N*-benzoyl-*N*-methyl-ethoxy-aniline)tin(II), bis(2-(*N*-ethylanilino)ethoxy)tin(II) and bis(2-(*N*-ethylanilino)ethoxy)tin(II) gave oils and oligomers. Considerable efforts were made to isolate and identify these products. The oils seem to show more promise and may eventually lead to isolation and identification.

The final complex in this ring series was with sodium salt of quindalic acid in methanol with SnCl₂ to give the expected bis(2-(quinolino-carboxylate)tin(II). This reaction proceeded smoothly to give a crude yellow solid in good yield. Purification of this solid and identification of the complex is also underway at the time of this writing.

2.6 Carbon-Metal Bound Species as New Ligands

Another route to new ligands to be evaluated for the eventual formation of CO₂-adducts with main group metals involves formation of direct metal-carbon bonds as the point of attachment. While M-C bonds do suffer some reactivity towards protic species, they can be more stable than their M-N counterparts, particularly when using the main group metals. These new ligands that we have been working on still contain the “Lewis acid-Lewis base” pair functionalities that are required for preparing adducts. Examples of these types of structures are shown in Figure 2.6.1.

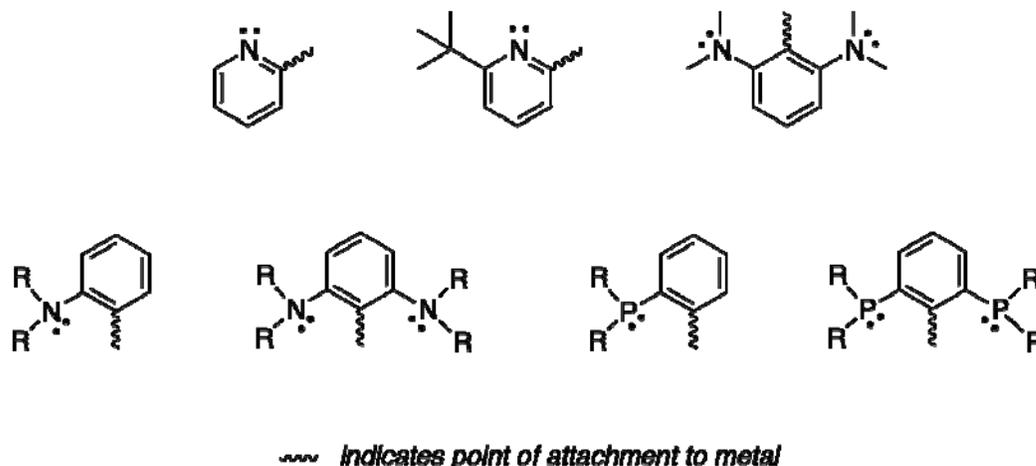


Figure 2.6.1 Possible ligand structures based on M-C bound frameworks.

The ligands are all related by two structural features – the binding to metals by a metal-carbon bond, and the location of a lone pair of electrons on nitrogen or phosphorus near the binding site to the metal. The preparation of the ligands range in synthetic complexity from simple, one-step routes to difficult, multi-step procedures. Reactions that have been performed at the time of this writing will be discussed further. Preparation of other ligands will await further funding.

The 2-pyridyl anion can be prepared by lithiating 2-bromopyridine at low temperature. This anion can then be added to MX_2 ($\text{M} = \text{Mg}, \text{Sn}, \text{Zn}$) to form a bis(pyridyl) metal complex after workup. The reaction scheme is shown in Figure 2.6.2.

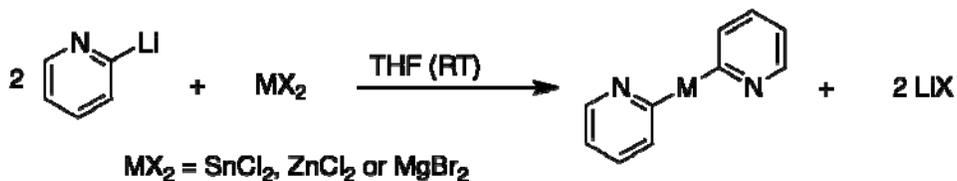


Figure 2.6.2 Route to bis(pyridyl) metal species.

While all of the species could be prepared, all were hampered by a severe lack of solubility in common organic solvents. The insolubility is most likely due to polymerization via the pyridyl nitrogen and a neighboring metal center. This has obviously prevented any NMR studies and further reaction with CO_2 has not been investigated. Attempts to improve product solubility included heating the insoluble products in the presence of TMEDA or HMPA. Introduction of TMEDA or HMPA prior to salt elimination were attempted as well. These variations were unsuccessful at fixing solubility issues. Residues from filtrates (w/ or w/o TMEDA or HMPA) were recovered; however their NMR spectra were overly busy, and the weights of the residue were miniscule. In order to prepare a more-soluble version of these pyridyl ligands, we next attached a bulky *t*-butyl group adjacent to the N atom of the pyridine.

The *t*-butyl version of the pyridyl ligand was prepared in several steps starting with 2,6-dibromopyridine. The multi-step reaction sequence for the preparation of *t*-butyl version is shown in Figure 2.6.3. The work up to obtain clean (by NMR) 6-*t*-butyl-2-bromopyridine took 2.5 days and required ~800 mL conc. $\text{NH}_4\text{OH}_{(\text{aq})}$ and ~800 mL of brine. This resulted in ~2 g of product after distillation of the pure product. This process can only be scaled up by using even more NH_4OH and brine and a larger separatory funnel (already using 1000 mL).

All reactions resulted in translucent solutions which were pumped down resulting in oily solids. LiX salts were separated by dissolving the targeted products in toluene and filtering. LiX masses were reasonably close to expected weights (70-105%). In contrast to the 2-pyridyl derivative, the addition of the *t*-butyl group did improve the solubility of the products significantly.

The washed Mg and Sn products resulted in oily solids whereas the Zn product is an orange powder. All products show *t*-butyl proton peaks with shifts differing from the position seen in 6-*t*-butyl-2-bromopyridine. Large, shallow, broad humps were often seen in the NMR spectra surrounding the *t*-butyl peak, and the pyridyl region is full of an assortment of peaks. The Zn compound has two *t*-butyl peaks of approximately equal

integration, which may suggest dimerization through a M-N interaction. The NMR of this proposed dimer also reveals a pyridyl:*t*-butyl integration of 1:2.5 (1:3 is ideal).

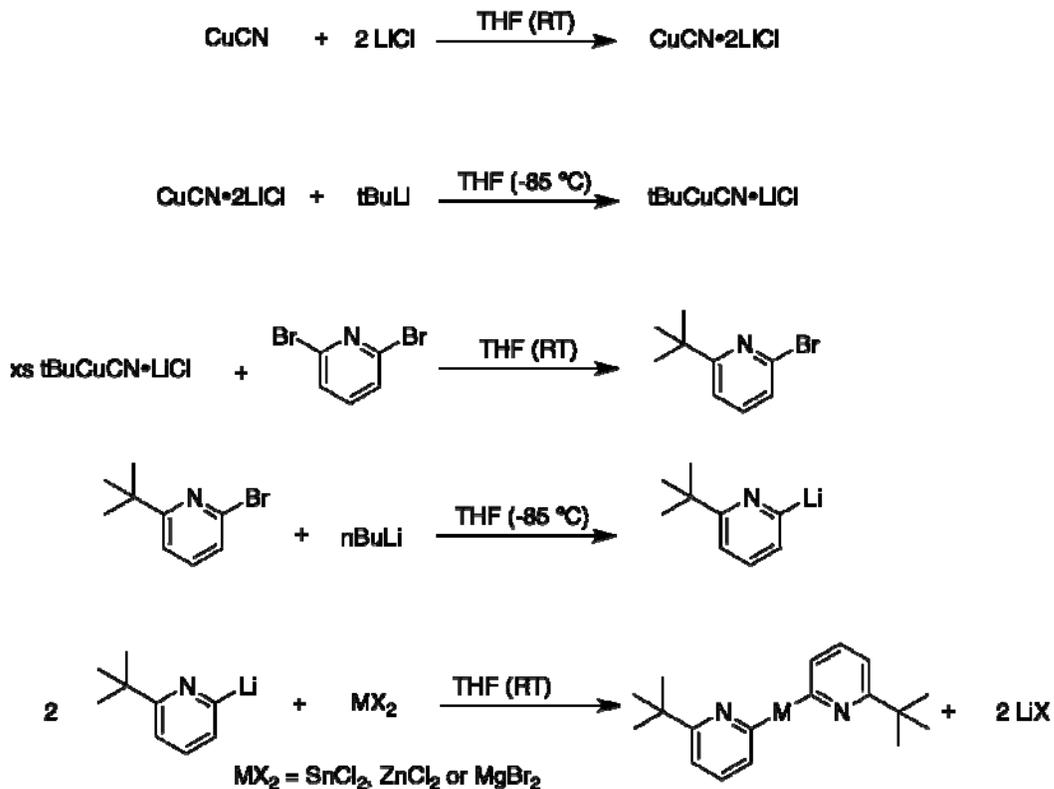


Figure 2.6.3 Route to bis(pyridyl) metal species.

These reactions have shown some promise both in improvements in solubility as shown by NMR; however, the NMR spectra are not clean and indicate a number of products are formed. This has led to problems in recrystallization, which has hampered the ability to obtain pure products. This is a major issue currently with the *t*-butyl derivatives.

Syntheses of the 2,6-dialkylaminopyridine ligands also require multiple steps. As of the writing of this report, we have prepared the 2,6-dimethylaminopyridine ligand by two different routes. While we first used the standard literature preparation, an improved route was developed by us that transferred the methyl groups to 2,6-diaminopyridine using (MeO)₃P=O rather than excess MeI that was used previously. At the current time we have prepared the lithium salt of this ligand and reacted it with SnCl₂ in an attempt to prepare the bis(ligand)Sn complex.

3 Conclusion

This late-start LDRD was broadly focused on the synthetic attempts to prepare novel ligands as complexing agents for main group metals for the sequestration of CO₂. In prior work we have shown that certain main group (p block elements) metals such as tin and zinc, when ligated to phosphinoamido- ligands, can bind CO₂ in a novel fashion. Rather than simple insertion into the metal-nitrogen bonds to form carbamates, we have seen the highly unusual complexation of CO₂ in a mode that is more similar to a chemical “adduct” rather than complexation schemes that have been observed previously. The overarching goal in this work is to prepare more of these complexes that can a) sequester (or bind) CO₂ easily in this adduct form, and b) be stable to chemical or electrochemical reduction designed to convert the CO₂ to useful fuels or fuel precursors. The currently-used phosphinoamido- ligands appear at this point to be less-stable than desired under electrochemical reduction conditions. This instability is believed due to the more delicate, reactive nature of the ligand framework system. In order to successfully capture and convert CO₂ to useful organics, this instability must be addressed and solved. Work described in the late-start LDRD was designed to screen a variety of ligand/metal complexes that *a priori* are believed to be more stable to polar solvents and possible mild hydrolytic conditions than are the phosphinoamido- ligands.

4 References

1. Aresta, M.; Dibenedetto, A., *Dalton Trans.* **2007**, 2975-2992.
2. Sakakura, T.; Choi, J.-C.; Yasuda, H., *Chem. Rev.* **2007**, *107*, 2365-2387.
3. Arakawa, H.; Aresta, M.; Armor, J. N.; Barteau, M. A.; Beckman, E. J.; Bell, A. T.; Bercaw, J. E.; Creutz, C.; Dinjus, E.; Dixon, D. A.; Domen, K.; DuBois, D. L.; Eckert, J.; Fujita, E.; Gibson, D. H.; Goddard, W. A.; Goodman, D. W.; Keller, J.; Kubas, G. J.; Kung, H. H.; Lyons, J. E.; Manzer, L. E.; Marks, T. J.; Morokuma, K.; Nicholas, K. M.; Periana, R.; Que, L.; Rostrup-Nielson, J.; Sachtler, W. M. H.; Schmidt, L. D.; Sen, A.; Somorjai, G. A.; Stair, P. C.; Stults, B. R.; Tumas, W., *Chem. Rev.* **2001**, *101* (4), 953-996.
4. Song, C., *Catal. Today* **2006**, *115*, 2-32.
5. Jessop, P. G.; Joo, F.; Tai, C.-C., *Coord. Chem. Rev.* **2004**, *248* (21-24), 2425-2442.
6. Miller, J. E.; Allendorf, M. D.; Diver, R. B.; Evans, L. R.; Siegel, N. P.; Stuecker, J. N., *J. Mater. Sci.* **2008**, *43*, 4714-4728.
7. Diver, R. B.; Miller, J. E.; Allendorf, M. D.; Siegel, N. P.; Hogan, R. E., *J. Sol. Energy Eng.* **2008**, *130* (4), 041001.
8. http://en.wikipedia.org/wiki/Grignard_reaction.
9. Dell'Amico, D. B.; Calderazzo, F.; Labella, L.; Marchetti, F.; Pampaloni, G., *Chem. Rev.* **2003**, *103*, 3857-3897.
10. Tang, Y.; Kassel, W. S.; Zakharov, L. N.; Rheingold, A. L.; Kemp, R. A., *Inorg. Chem.* **2005**, *44*, 359-364.
11. Tang, Y.; Zakharov, L. N.; Rheingold, A. L.; Kemp, R. A., *Organometallics* **2004**, *23* (20), 4788-4791.
12. Tang, Y.; Felix, A. M.; Manner, V. W.; Zakharov, L. N.; Rheingold, A. L.; Moasser, B.; Kemp, R. A., *ACS Symp. Ser.* **2006**, *917* (Modern Aspects of Main Group Chemistry), 410-421.
13. Sita, L. R.; Babcock, J. R.; Xi, R., *J. Am. Chem. Soc.* **1996**, *118* (44), 10912-10913.
14. Kitamura, C.; Maeda, N.; Kamada, N.; Ouchi, M.; Yoneda, A., *J. Chem. Soc., Perkin Trans. 1* **2000**, 781-785.

5 Distribution

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