Binding, Activation, and Transformation of Carbon Dioxide Mediated by Anionic Metal Complexes

by

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Submitted to the Department of Chemistry in partial fulfillment for the requirements for the degree of

DOCTOR OF PHILOSOPHY

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

June 2011

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Submitted to the Department of Chemistry on May 5, 2011, in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Inorganic Chemistry

Abstract

The vanadium nitride complex [Na][NV(N[Me_3]Ph) 3 ] reacts with CO to produce the vanadium tris-anilide complex V(N[Me_3]Ph) 3 and NaCO. This is the first example of complete denitrogenation of a terminal nitride complex with generation of a lower coordinate metal complex. This reactivity contrasts sharply with the reactivity of the niobium analogue, where the nitride anion complex [Na][NNb(N[Me_3]Ph) 3 ] is synthesized from the reductive decarbonylation of the niobium(IV) isocyanate complex (OCN)Nb(N[Me_3]Ph) 3 . Electrochemical studies of the niobium(IV) and vanadium(IV) isocyanate (OCN)V(N[Me_3]Ph) 3 complexes are presented.

The reactivity of the vanadium carbamate complex [(THF)_2 Na][O_2 CNV(N[Me_3]Ph) 3 ] with electrophilic reagents is presented. The carbamate complex reacts readily with silylation and alkylation reagents to form the carbamate ester complexes of the type ROC(O)NV(N[Me_3]Ph) 3 . The vanadium carbamate complex reacts with SO_2 via a decarboxylation pathway to produce the sulforyl imido complex [Na][O_2 SNV(N[Me_3]Ph) 3 ], the solid-state structure of which is presented. The reactivity of the vanadium carbamate complex with typical dehydrating reagents, e.g. organic acid anhydrides, is shown to proceed cleanly when cobaltocene, acting as an in situ reductant, is present to form the vanadium(IV) isocyanate complex (OCN)V(N[Me_3]Ph) 3 . The synthesis and structure of the bimetallic complex (TPP)MnOC(O)NV(N[Me_3]Ph) 3 (TPP = tetraphenylporphyrin) is presented. Although thermally stable, the complex undergoes a photochemical transformation that forms the vanadium isocyanate complex and putative OMn(TPP), which reacts with triphenylphosphine in the reaction mixture to produce triphenylphosphine oxide.

The synthesis the niobium carbamate complex [Na][O_2 CNNb(N[Me_3]Ph) 3 ] from the reaction of [Na][NNb(N[Me_3]Ph) 3 ] with CO_2 is presented. Its solid-state structure in the form of the ion-pair [(12-crown-4)_2 Na][O_2 CNNb(N[Me_3]Ph) 3 ] has been determined. Reaction of the niobium carbamate complex with organic acid anhydrides results in the production of five-coordinate carboxylate, acetate complexes (ROC(O)O)(OCN)Nb(N[Me_3]Ph) 3 . The reduction of these complexes by two electrons results in the regeneration of the niobium nitride complex (60-80% yield) with concomitant release of CO (30-60% yield). This three-step process represents a highly controlled conversion of CO_2 to CO via a ligand-based strategy.

The reactivity of CO_2 with anionic complexes featuring terminal multiply bonded ligands is extended to the oxo anion complex [(Et_2 O)_2 Li][OTi(N[Me_3]Ph) 3 ] resulting in the formation of the carbonate complex [(Li)][O_2 COTi(N[Me_3]Ph) 3 ]. The binding of CO_2 to the oxo complex is reversible when 12-crown-4 is bound to the lithium countercation or if the complex is dissolved in THF. The thermodynamic parameters for the CO_2 binding equilibrium have been measured. Exchanging the lithium countercation for sodium or potassium results in a significant weakening of the CO_2 binding ability of the oxo complex.
Thesis Supervisor: Christopher C. Cummins
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For all of my many mentors
Acknowledgments

This thesis would not exist without the help of many people.

Brandi has been the sunshine of my life. Her calming words and embraces gave me the power to keep moving forward when the skies were dark. The love and devotion she has shown me cannot be adequately acknowledged here.

My Parents have been a patient and supportive pair throughout the last five years. They have been a constant source of inspiration, and although a great physical distance has separated us, I knew that they would always be there to pick me up if I fell.

Kit invited me to join his lab to me at a time when there was already a large contingent of graduate students under his supervision. I will always be glad he did. Kit has pushed me to my limits as a result of his demanding style and insatiable curiosity. It has made me a more rigorous professional and I am eternally grateful for this.

I thank the members of the Cummins Group, past and present, who worked with me. Cutting straight to it, I was cantankerous on my good days and completely intolerable on my bad days. The other members of the Cummins group are saints for how understanding and supportive they have been.

Glen is a great friend who possesses an unheralded brilliance. His commentary on life and chemistry throughout my time at MIT brought welcomed levity to the everyday drudgery. He is the fantastic sounding board for ideas and thoughts, which is great resource to have when one is working on a thesis. I feel like the best is yet to come for our friendship.

mANiS, a.k.a. Christopher R. Clough, has a heart that is too big for one man. His loyalty and generosity are unmatched. At many times in the last few months, his presence calmed me in moments of frustration.

Fox introduced me to the Cummins group, and showed me the ropes. He played a pivotal role in helping me hit the ground running, and for this I thank him.

Curley, and his vast knowledge of the literature, was a great resource for when I had a crazy idea or was having trouble with an experiment.

Piro was a calm voice of reason. His level-headedness and thoughtfulness saved me many headaches.

Manuel gave the lab a unique, thoughtful, and fresh perspective. He was a pleasure to work with and a great person to have a coffee with.

The postdocs – Heather, Ivo, Montag, Rankin, Anthony, and Nazario – brought in new ideas from across the discipline. They were always a great source of knowledge and helpful experience.

Tofan, Alexandra, and Hieu, as younger group members, never let me forget that I still have so much to learn and that I should not take anything for granted. I wish them the best of luck with the rest of their graduate journeys.
Allison has been indispensable. She is one of the most effective people I have ever worked with. The group should always be grateful for her contributions. She is a true rock star.

The other professors of the inorganic chemistry division—Prof. Schrock, Prof. Nocera, Prof. Lippard, Prof. Sadighi, Prof. Peters, and Prof. Dincă—are a special group who never let a question go unanswered. They set a high bar for the students, which is why I came to MIT. It has been a pleasure to interact with every one of them.

Prof. Carl Hoff and Prof. Elena Rybak-Akimova have been wonderful collaborators throughout my time at MIT. They are passionate scientists who have made my understanding of chemistry even richer.

Peter Müller, the crystallography wizard, deserves so much credit. He wanted to not just teach you how to perform crystallographic experiments, but he wanted you to understand crystallography. He is a great resource and a wonderfully interesting person.

The DCIF Staff—Jeff, Anne, Deb, and Bob—kept the spectroscopic engine humming. They do a great job down there in the subbasement of building 18.

My cohort of classmates, who joined the department at the same time as me, has been a valuable resource for both inspiration and support.

Brian became one of my best friends; our discussions and debates ranging from philosophy to politics to science (and not in that order) were always a welcome diversion from lab.

Marshak is the most creative chemist I have ever met. He always reminded me to think outside the box, way outside the box.

Lee-Ping is brilliant. Sharing chemistry with him was like opening a treasure chest of understanding.

Yogi was always a great person to go to when I needed a critical perspective. His ability to cut through speculation and assumptions was greatly appreciated.

The MIT GSSPC was a wonderful, horizon broadening experience. Everyone on the team was stellar. It was a pleasure to work with every one of you.

The MIT Energy Club for giving me the confidence and tools to strike out beyond the lab.
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40  (Me_2NCN)V(N[Bu]Ar)_3
41  [(PhCN)V(N[Bu]Ar)_3][BAR_{CF_3}^4]
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43  (Et_2C_2)Nb(N[R]Ar_L)_2Cl_2
44  (Ph_2C_2)Nb(N[R]Ar_L)(ODipp)Cl
45  (Et_2C_2)Nb(N[R]Ar_L)(ODipp)Cl
46  (Et_2C_2)Nb(N[R]Ar_L)(ODipp)N_3
47  [NNb(N[R]Ar_L)(ODipp)]_2
48  Cl_2Nb(N[R]Ar_L)_2
Preface

The goal: convert CO\textsubscript{2} to CO. The method: a ligand-based approach with an anionic nitride complex serving as the mediating platform. This was the starting point of the dissertation described herein.

The key pieces of inspiration for the proposed CO\textsubscript{2} to CO cycle were two reports from the Cummins group. First, the reaction of CO\textsubscript{2} with the vanadium nitride anion complex [Na][NV(N\textsuperscript{5}BuAr\textsubscript{3})\textsubscript{3}] to form the N-bound carbamate complex [(THF)\textsubscript{2}Na][O\textsubscript{2}CNV(N\textsuperscript{5}BuAr\textsubscript{3})\textsubscript{2}]. Second, the formation of the niobium nitride anion complex [Na][NNb(N\textsuperscript{5}BuAr\textsubscript{3})\textsubscript{3}] from the reductive decarbonylation of the isocyanate complex (OCN)Nb(N\textsuperscript{5}BuAr\textsubscript{3}).

Thus, a three step cycle was proposed. In the first step, a nitride anion complex binds and activates CO\textsubscript{2} to form an N-bound carbamate complex (A). Subsequently, the carbamate complex is deoxygenated to form an isocyanate complex (B). Finally, the isocyanate undergoes a decarbonylation reaction upon one-electron reduction to regenerate the starting nitride anion complex (C).

As will be shown herein, the cycle has been closed. Of course, in the pursuit, new light has been shone on several areas of inorganic chemistry beyond the original scope of the original proposal.

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Chapter 1. Denitrogenation of a Vanadium Nitride by CO

1.1. Introduction

1.1.1. Metal-ligand Multiple Bond Cleavage with CO

The reaction of CO with a metal-ligand multiple bond that results in the formal two-electron reduction of the metal center is not uncommon and is typically observed in high-valent metal complexes. The multiply bonded ligands are typically nitridos, imidos, or oxos. One of the earliest reports of the reduction of a high-valent metal complex came from Herrmann and co-workers. It was observed that when rhenium oxo complexes of the type \( \text{Cp}^*\text{Re}(\kappa^2-\text{O}_2\text{CCR}_2) \) or \( \text{Cp}^*\text{Re}(\kappa^2-\text{O}(\text{NR}^\prime)\text{CO}) \) were treated with 1 atm of CO, the carbonyl complexes \( \text{Cp}^*\text{Re(CO)}_2(\kappa^2-\text{O}_2\text{CCR}_2) \) and \( \text{Cp}^*\text{Re(CO)}_2(\kappa^2-\text{O}(\text{NR}^\prime)\text{CO}) \) would form with concomitant formation of \( \text{CO}_2 \). Recently a number of groups have shown similar reactivity where terminal imido complexes (L\(\lambda\)M=N-R) are found to react with CO to release the corresponding isocyanate (OCN-R) and form the metal carbonyl complex. In some cases, the reaction of terminal imido complexes with CO would result in formation of an isocyanate ligand bound to the metal (L\(\lambda\)M=N-CN) and release of the R group. Similarly, reactivity has also been observed with hydrazido complexes (L\(\lambda\)M=N-NR\(_2\)) to give isocyanato, amido complexes (L\(\lambda\)M(NCN)(NR\(_2\))), but the metal center does not undergo a two-electron reduction in these cases. Very recently, Mindiola and co-workers discovered a terminal vanadium(V) nitride complex (nacnac)V=N(Ntol\(_2\)) that reacts with CO to produce the vanadium(III) isocyanate complex (nacnac)V(NCO)(Ntol\(_2\)). In most of the aforementioned cases, the complexes can be considered to be electrophilic as a result of the high valency of the metal center, and therefore, the reactions are often believed to proceed via a nucleophilic attack by CO on the \( \pi^* \) orbital of the metal-ligand multiple bond, in a manner analogous to the reaction of electrophilic nitrides with phosphines as originally reported by Griffith et al.

1.1.2. Previously Observed Reactivity of [Na][NV(N['Bu]Ar)₃]

The three-coordinate vanadium complex \( V(N['Bu]Ar)₃ \) (1) is readily synthesized via salt-metathesis from \( VCl₃(THF)₃ \) and three equivalents of \( (Et₂OLiN['Bu]Ar \) in \( Et₂O \). While in the Cummins group, Fickes showed that complex 1 reacts with two-electron oxidants such as organic azides and \( N \)-oxides to give the vanadium(V) complexes. Expanding upon this reactivity motif, it was later shown that the terminal nitride complex \([Na][NV(N['Bu]Ar)₃] \) (2) could be synthesized by treating 1 with excess \( NaN₃ \) in THF with concomitant extrusion of \( N₂ \). The negative charge on the complex endowed significant nucleophilicity to the terminal nitride moiety. This property allowed for the synthesis of a variety of imido complexes via salt-metathesis reactions including an iminophosphine-imido variant. In addition to salt-elimination reactions, Brask et al. observed that complex 2 reacted readily with the neutral electrophiles \( CS₂ \) and \( CO₂ \) to give the \( N \)-bound dithiocarbamato complex \([ (THF)₂Na][S₂CNV(N['Bu]Ar)₃] \) (3) and the \( N \)-bound carbamato complex \([ (THF)₂Na][O₂CNV(N['Bu]Ar)₃] \) (4, Scheme 1.1). It was observed that complex 3 underwent an intramolecular rearrangement at elevated temperatures to generate the vanadium sulfide complex \( SV(N['Bu]Ar)₃ \) and \( NaNCS \) (Scheme 1.1). In contrast, complex 4 did not undergo the analogous rearrangement to give \( OV(N['Bu]Ar)₃ \) (5) and \( NaNCO \). In conjunction with DFT calculations, it was hypothesized that the observed difference in reactivity is the result of both a greater thermodynamic driving force for thiocyanate extrusion and a larger kinetic barrier for complex 4 to form the requisite four-membered metallacyclic intermediate.

![Scheme 1.1. Reactivity of [Na][NV(N['Bu]Ar)₃] (2) with CE₂ molecules.](image)

1.2. Synthesis and Characterization of a Vanadium Isocyanate Complex
1.2.1. One-electron Oxidation of V(N[′Bu]Ar)₃ to Produce XV(N[′Bu]Ar)₃ Species

An unanswered question relevant to the goal of performing the proposed ligand-based reduction of CO₂ to CO was whether the yet to be synthesized complex (OCN)V(N[′Bu]Ar)₃ (6) was capable of undergoing the requisite reductive decarbonylation of the isocyanate ligand as was observed in the case of the niobium congener.¹⁴ To address this question, a method for synthesizing complex 6 from 1 was pursued. In this pursuit, it was discovered that 1 reacts readily with outer-sphere, one-electron oxidants to give vanadium(IV) complexes of the type XV(N[′Bu]Ar)₃ (Scheme 1.2). For example, treatment of 1 with AgOTf in THF results in a color change from dark teal to black in a matter of minutes. Following a simple workup of the reaction mixture to remove precipitated Ag⁺, Tfov(N[′Bu]Ar)₃ (7) is crystallized from n-pentane in 66% yield as black crystals. Complex 7 displays the expected physical properties for a vanadium(IV) complex: an intense, eight-line pattern in the EPR spectrum arising from the unpaired electron coupling to the vanadium nucleus, a magnetic moment of 2.0 μₜ in solution, and a paramagnetically broadened ¹H NMR spectrum.

\[ \text{Scheme 1.2. Synthesis of complexes XV(N[′Bu]Ar)₃.} \]

Using this approach, the isocyanate complex 6 is synthesized from the reaction of 1 with AgNCO in THF. Similar to the synthesis of 7, the color of the reaction mixture changes from green to black as the reaction proceeds, and following a standard workup to remove Ag⁺, complex 6 is crystallized from n-pentane in 67% yield. Complex 6 has several distinct spectroscopic and physical features: a strong band in the IR attributed to νNCO at 2207 cm⁻¹ (Figure 1.1), an eight line pattern in the EPR spectrum (20 °C, benzene solution) that results from hyperfine coupling to the \( I = 7/2 \) vanadium nucleus (\( g = 1.97, a = 6.44 \times 10^{-3} \text{ cm}^{-1} \), Figure 1.2), an effective magnetic moment of 2.0 μₜ (20 °C, benzene solution), and two broad electronic transitions centered at 490 (\( ε = 3200 \)) and 600 nm (\( ε = 2600 \)) that span the visible region of the electromagnetic spectrum.
Figure 1.1. IR spectrum of (OCN)\textsubscript{V}([^{t}Bu]Ar)_3 (6).
Thin film, KBr plates.

Figure 1.2. EPR Spectrum of (OCN)\textsubscript{V}([^{t}Bu]Ar)_3 (6).
Benzene solution, 20 °C.
1.2.2. Solid-State Structure of (OCN)V(N\textsuperscript{[Bu]Ar})\textsubscript{3}

The solid-state structure of complex 6 was determined using single-crystal X-ray diffraction studies with crystals grown from concentrated \textit{n}-pentane solutions of 6 at \(-35 \, ^\circ\text{C}\) (Figure 1.3). In the solid state, 6 adopts a $C_1$ symmetric structure with the vanadium center in a pseudo-tetrahedral coordination environment. One of the anilide ligands twists \(\sim 90^\circ\) about the $V$-$N$ bond relative to the other anilides, which is attributed to a Jahn-Teller distortion to remove the degeneracy of the $d_{\pi}$ and $d_{\sigma}$ orbitals (if the z-axis is projected along the $V$-$N$ bond).\textsuperscript{15} The refinement of the crystallographic model supports the assignment of the cyanate ligand as being $N$-bound. The refinement statistics for the $N$-bound model ($wR_2 = 0.100$) are significantly better than those of the $O$-bound case ($wR_2 = 0.125$). The $V$–$N$ interatomic distance of the isocyanate ligand (1.955(1) Å) is longer than the $V$–$N$ interatomic distance of the anilide ligands (1.886(1) Å avg.). The isocyanate ligand adopts a non-linear coordination mode with a $V$–$N$–$C$ angle of 150.6(1)°, on par with other isocyanate complexes.\textsuperscript{16}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{structure.png}
\caption{Solid-state structure of (OCN)V(N\textsuperscript{[Bu]Ar})\textsubscript{3} (6). Thermal ellipsoids are drawn at 50\% probability, and hydrogen atoms have been omitted for clarity.}
\end{figure}
1.2.3. Reduction of (OCN)V(N[\text{Bu}]Ar)\textsubscript{3}

Having successfully synthesized and characterized 6, the redox chemistry of the complex was investigated. When the isocyanate complex 6 is treated with 0.5\% Na/Hg amalgam in THF, the reaction mixture changes from black to dark teal over the course of 1 h at 22 °C. As assayed by \textsuperscript{1}H NMR spectroscopy, the reaction mixture is free of the nitride complex 2. If the decarbonylation reaction had taken place, complex 2 would be the anticipated product. Instead, reduction of 6 results in dissociation of the cyanate anion with generation of the vanadium(III) complex 1 and NaNCO (Scheme 1.3). When Na/Hg amalgam is replaced with other reducing agents, such as KC\textsubscript{8} or (THF)\textsubscript{3}Mg(C\textsubscript{14}H\textsubscript{10}), similar results are observed. In the case of KC\textsubscript{8}, the yield of the KNCO product was measured (73\%) using gravimetric analysis. Given the synthetic viability of 1 and the pseudo-halide nature of NCO\textsuperscript{-}, this result was not entirely unexpected. However, it does indicate that the vanadium system is incapable of performing the requisite reductive decarbonylation of cyanate for the envisioned CO\textsubscript{2} to CO cycle.

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\includegraphics[width=\textwidth]{Scheme13.png}};
\end{tikzpicture}
\end{center}

\textbf{Scheme 1.3.} Reduction of (OCN)V(N[\text{Bu}]Ar)\textsubscript{3} (6) with Na/Hg amalgam in THF.

1.2.4. Electrochemical Studies of (OCN)V(N[\text{Bu}]Ar)\textsubscript{3} and (OCN)Nb(N[\text{Bu}]Ar)\textsubscript{3}

The electrochemical properties of complexes 6 and (OCN)Nb(N[\text{Bu}]Ar)\textsubscript{3} (8) were probed using cyclic voltammetric methods to understand if differences in reduction potentials between the complexes were partially responsible for the observed differences in reactivity. The cyclic voltammogram (CV) of 6 contains two electrochemical events (Figure 1.4). One event is assigned to the V\textsuperscript{5+}/V\textsuperscript{4+} couple with an \(E_{1/2} = -0.11\) V vs. Fc/Fc\textsuperscript{-} (Fc = (C\textsubscript{5}H\textsubscript{5})\textsubscript{2}Fe). This event displays quasireversible behavior with the \(i_{c}/i_{a}\) ratio dependent on the scan rate of the CV. The fate of the presumably generated [6]\textsuperscript{+} complex was not investigated in the course of these studies. Attempts to oxidize complex 6 with outer-sphere oxidants (e.g. AgOTf, FcBAR\textsubscript{F}_{4}, etc) yielded an intractable mixture of products. The other event in the CV is assigned to the V\textsuperscript{4+}/V\textsuperscript{3+} couple. This event appears reversible at scan rates between 10 and 300 mV/s with \(E_{1/2} = -1.56\) V vs. Fc/Fc\textsuperscript{+}. The reversibility of this event is attributed to the rate of cyanate ion dissociation being slower than the rate of diffusion of the complex away from the electrode surface. This seems very likely since
there are no alkali metal cations present to precipitate with the cyanate ion (["Bu₄N][NCO] is soluble in THF).

![CV of complex \((\text{OCN})\text{V}[\text{Bu}]\text{Ar}_3\) (6). THF, 0.2 M \([\text{"Bu}_4]\text{[BArF}_4]\), 100 mV/s scan rate.]

In comparison, the CV of the niobium analogue 8 contains two electrochemical events as well, but at very different potentials (Figure 1.5). The first event has an \(E_{1/2} = -1.1 \text{ V vs. } \text{Fc/Fc}^+\) and is assigned the \(\text{Nb}^{5+}/\text{Nb}^{4+}\) redox couple. As was observed with 6, this anodic event is quasireversible. The second event is centered at \(-2.9 \text{ V vs. } \text{Fc/Fc}^+\) and is completely irreversible. Assigned to the formal \(\text{Nb}^{4+}/\text{Nb}^{3+}\) couple, this irreversible event is consistent with the one-electron reduction resulting in the rapid decarbonylation of the isocyanate linkage to generate \([\text{NNb(N}[\text{Bu}]\text{Ar}_3]\).
1.3. Denitrogenation of the Vanadium Nitride Anion with CO

1.3.1. Reaction of CO with NaNV(N[Bu]Ar)₃ in THF

The clear preference for cyanate dissociation from the isocyanate complex 1 gave rise to the question of whether CO could effect the denitrogenation of the nitride complex 2 with formal two-electron reduction of the vanadium metal center. As mentioned earlier, the two-electron reduction of high-valent metal complexes with CO is a well-documented phenomenon, but to the best of the author's knowledge, full denitrogenation had never been observed. When a solution of 2 in THF is treated with 1 atm of CO at 23 °C, no immediate change is observed. However, over the course of 24 h, the color of the solution changes from bright yellow to deep teal-green. Removal of the volatile components from the reaction mixture under reduced pressure leaves behind dark green-brown solids. Extracting the solids into a minimal volume of n-hexane, filtering the extract through a sintered glass frit, and storing the solution at -35 °C gave dark crystals of 1 in 71% yield (Scheme 1.4).
The product was identified as the vanadium(III) complex 1 using NMR and IR spectroscopy. Interestingly, there was no evidence of CO binding to the low-coordinate vanadium center in the isolated material. Thus, the vanadium center is coordinatively unsaturated and available to participate in further chemistry, leaving the door open for potential catalytic applications. It should be noted that recent work has revealed that CO does bind, albeit very weakly, to 1 in solution (vide infra). Monitoring the reaction by $^1$H and $^{51}$V NMR spectroscopy using flame-sealed NMR tubes filled with 1 atm of CO revealed that the reaction goes to completion in the course of 24 h, and no intermediates are observed. Surprisingly, complex 2 does not react with 'BuNC under very similar conditions (3 d, THF, 23 °C). Two explanations for this observation are either that the formation of 1 and NaNCN'Bu is more favorable thermodynamically than formation of 1 and NaNCN'Bu, or the reaction of 'BuNC with 2 is much slower.

To determine if the sodium cation interaction with the nitrido ligand is playing a role in the denitrogenation reaction, [(12-crown-4)$_2$Na][NV(N'[Bu]Ar)$_3$] (9) was synthesized, and the solid-state structure was determined (Figure 1.6). As expected, the molecules of 12-crown-4 fully sequester the sodium cation and the nitrido ligand interacts only with the vanadium metal center. The vanadium-nitrogen distance in 9 is very short (1.597(3) Å), as would be expected for a vanadium-nitrogen triple bond. When the reaction with CO is performed using the 12-crown-4 sequestered species, the formation of 1 occurs at qualitatively comparable rates, as assayed by $^1$H NMR spectroscopy, providing evidence that the sodium cation interaction is not critical for the reaction to occur.
Given the well-documented nucleophilicity of anionic terminal nitrides, the proposed mechanism for the reaction involves nucleophilic attack by the nitrido ligand on the $\pi^*$ orbitals of CO. Although it cannot be definitively ruled out, a first step involving the binding of CO to the vanadium center is considered unlikely due to the steric demands of the anilide ligands and formal $d^0$ electron count of the vanadium center.

1.3.2. Quantification of OCN$^-$ Production Through Gravimetric Analysis

To confirm and quantify the formation of NaNCO in the reaction, gravimetric analysis of the NCO$^-$ ion through formation of AgNCO was pursued. In the course of the reaction, NaNCO precipitates from the THF solution, but to insure that no NaNCO remains dissolved in solution, the reaction mixture was taken to dryness and subsequently extracted using $n$-hexane. Filtering the extraction mixture through a sintered glass frit allows for the isolation of an off-white powder, presumably crude NaNCO. This powder was readily soluble in water, and when the aqueous
solution was treated with excess AgNO₃, a white powder precipitated immediately. Isolation of this powder on a tared, sintered glass frit followed by thorough drying using vacuum desiccation allowed for its quantification (77% yield). This yield is in good agreement with the 71% yield measured for the isolation of 1. The chemical identity of this material as AgNCO was confirmed using IR spectroscopy.

1.3.3. ¹³C Labeling Study of Reaction between CO and NaNV(N[ıt Bu]Ar)₃

A final confirmation for the formation of NaNCO from the reaction of CO with 2 came from performing a ¹³C labeling study. The treatment of 2 with ¹²CO was carried out in a similar manner as the treatment with natural abundance CO, but the CO was delivered via a break-seal flask. Analysis of the isolated, crude NaNCO from the reaction via ¹³C NMR spectroscopy in H₂O confirmed the identity of the ¹³C containing product as being cyanate ion (Figure 1.7). The signal from the cyanate ion (129 ppm) is the only observable signal in the spectrum and agrees well with the reported chemical shift of cyanate.¹⁷

![Figure 1.7. ¹³C NMR spectrum of NaN¹³CO produced in the reaction of ¹³CO and NaNV(N[ıt Bu]Ar)₃ (2). H₂O, 100 MHz, 20 °C. MeOH was added as internal reference (49 ppm).](image-url)
1.3.4. Reversible Binding of CO to V(N[′Bu]Ar)₃

Recently, in collaboration with Prof. Carl Hoff of the University of Miami, we began studying the binding of neutral donors to three-coordinate vanadium complex 1, with initial work focused on the binding of nitriles (See Appendix A). In conjunction with measuring the thermodynamic parameters of nitrile binding to the vanadium(III) complex 1 in solution via in situ IR spectroscopy, Prof. Hoff treated 1 with CO in toluene at ambient conditions. From his measurements, a carbonyl complex forms in solution with a distinct band in the IR spectrum at 2032 and 1990 cm⁻¹. The CO binding is hypothesized to be dynamic in this system, with a very rapid on-off process. In the reaction of the nitride complex 2 with CO in THF, it is proposed that the carbonyl complex is not observed either as a result of competition for the open coordination site with the solvent THF, or as a result of evacuating the reaction vessel and shifting the equilibrium to favor formation of 1.

1.4. Conclusions

The discovery of the denitrogenation of a terminal nitride complex to give a reduced, carbonyl free vanadium complex is intriguing. Previous examples of CO reduction of terminal ligands resulted in either the formation of bound isocyanate ligands or coordination of carbonyl ligands. Thus, the metal center in these cases remained coordinatively saturated. In contrast, the generation of 1 leaves the door open for 1 to participate in further chemistry, a characteristic that may be useful for catalytic transformations. This type of regeneration step is common in heterogeneous, metal-based oxidation systems where CO serves as the terminal reducing agent.¹⁸ In addition, this transformation may shed light onto the process of isocyanate formation observed in reaction of CO with NH₃ over transition-metal surfaces.¹⁹,²⁰

An attractive target for future work would be to develop a system where the denitrogenated nitride is derived from the scission of N₂. The tris-anilide complex 1 displays no reactivity with N₂, so alternative platforms would need to be explored if such an advance were to be realized. The molybdenum tris-anilide complex Mo(N[′Bu]Ar)₃ is capable of splitting N₂ to form the nitride complex NMo(N[′Bu]Ar)₃. The author has observed that the molybdenum(IV) isocyanate complex (OCN)Mo(N[′Bu]Ar)₃ can be synthesized from the reaction of AgNCO with Mo(N[′Bu]Ar)₃, and the formed isocyanate complex does not spontaneously eject CO to form the nitride. Thus, it is possible for the isocyanate complex to be the thermodynamic minimum in the reaction. However, the question of whether this stability is manifested as a result of the thermodynamic properties of the products and reactants or the kinetics barriers to decarbonylation were not addressed in my studies. Recently, Dr. Anthony Cozzolino, a postdoctoral scientist in the Cummins group, has begun to explore this idea in more detail, and his work has provided
several important insights into the chemistry of isocyanate ligands on early-transition-metal fragments.

1.5. Experimental Section

1.5.1. General Considerations.

All manipulations were carried out either in a Vacuum Atmospheres model MO-40M glove box under an atmosphere of N₂ or using standard Schlenk techniques. All solvents except for THF were degassed and dried using the method of Grubbs.²¹ THF was dried initially using an MBraun SPS and dried further by stirring with Na metal for 24 h followed by filtration through Celite and alumina to remove NaOH. After purification, all solvents were stored under an atmosphere of N₂ over 4 Å molecular sieves. Deuterated benzene (Cambridge Isotope Labs) was dried by stirring over CaH₂ for 24 h and was subsequently vacuum-transferred onto 4 Å molecular sieves. KC₈ was prepared by melting potassium over graphite at 200 °C under an atmosphere of argon.²² Complex 2 was prepared according to literature procedures.¹¹ Tetra(n-buty)ammonium tetrakis(pentafluorophenyl)borate was synthesized using modified literature methods.²³ All other reagents were used as supplied by the vendor without further purification. Celite 435 (EMD Chemicals), alumina (Aldrich) and 4 Å molecular sieves (Aldrich) were dried prior to use by heating at 200 °C for 48 h under dynamic vacuum. All glassware was oven dried at 220 °C prior to use. NMR spectra were obtained on either a Bruker 400-AVANCE spectrometer equipped with a Magnex Scientific superconducting magnet or a Varian Mercury 300 spectrometer equipped with an Oxford Instruments Ltd. superconducting magnet. EPR Spectra were collected on a Bruker EMX spectrometer with an ER 4199HS cavity and a Gunn diode microwave source producing X-band (8-10 GHz) radiation. UV/Vis spectra were collected on a HP8453 spectrophotometer using 1 cm quartz cells manufactured by Starna. ¹H NMR spectra were internally referenced to residual C₆D₅H (7.16 ppm).²⁴ ¹³C NMR spectra were referenced internally to the natural abundance signal from solvent. IR spectra were collected on a Perkin-Elmer 2000 FT-IR spectrophotometer. Elemental analysis was performed by Midwest Microlab, Indianapolis, IN.

1.5.2. Synthesis of TfOV(N[Bu]Ar)₃ (7)

A solution of 1 (0.893 g, 1.56 mmol) in THF (15 mL) was frozen. A solution of AgOTf (0.402 g, 1.56 mmol) in THF (10 mL) was prepared and frozen. The two mixtures were allowed to thaw and were subsequently combined. The reaction mixture was allowed to warm to 23 °C while stirring. After four hours of stirring at ambient conditions, the color of the reaction mixture had changed from green to black. The reaction mixture was filtered through a bed of Celite on a
sintered glass frit. The filtrate solution was dried under reduced pressure. The dark colored residue was taken up in a minimum volume of n-pentane (~20 mL), and the solution was stored at −35 °C for 24 h to affect the crystallization of the product. The black crystalline material was collected on a sintered glass frit via vacuum filtration and washed once with 5 mL of cold n-pentane. The crystals were dried under reduced pressure. Yield: 0.74 g (66%). \(^1\)H NMR (benzene-\(d_6\), 20 °C, 300 MHz): \(\delta\) 5.55 (br), 1.83 (br). \(\mu_{\text{eff}}\) (Evans’s Method, \(25\) benzene-\(d_6\)): 2.0 \(\mu_B\). Elem. anal. Calcd for C\(_{37}\)H\(_{54}\)F\(_3\)N\(_3\)O\(_3\)SV: C, 60.97; H, 7.47; N, 5.77. Found: C, 60.58; H, 7.36; N, 5.83.

1.5.3. Synthesis of (OCN)\(_V\)(N[\(^\text{Bu}\]Ar))\(_3\) (6)

A solution of 1 (0.579 g, 1.0 mmol) in THF (10 mL) was frozen. A slurry of AgNCO (0.150 g, 1.0 mmol) in THF (3 mL) was frozen. The two mixtures were allowed to partially thaw and were subsequently combined. The reaction mixture was stirred and allowed to warm to an ambient temperature of 23 °C. The color of the mixture changed from green to black as the reaction progressed. After stirring for one hour, the reaction mixture was filtered through a plug of Celite on a sintered glass frit. The filtrate was dried under reduced pressure to give a black residue. The residue was dissolved in a minimum volume of n-pentane and stored at −35 °C. After standing for 18 hours, black crystals had formed and were collected via vacuum filtration on a sintered glass frit. The crystals were dried under reduced pressure to give a black residue. The residue was dissolved in a minimum volume of n-pentane and stored at −35 °C. After standing for 18 hours, black crystals had formed and were collected via vacuum filtration on a sintered glass frit. The crystals were dried under reduced pressure. Yield: 0.416 g (67%). \(^1\)H NMR (benzene-\(d_6\), 20 °C, 300 MHz): \(\delta\) 2.20 (br). IR (KBr, thin film): 2974, 2917, 2863, 2207, 1599, 1585 cm\(^{-1}\). \(\mu_{\text{eff}}\) (Evans’s Method, \(25\) benzene-\(d_6\)): 2.0 \(\mu_B\). UV/Vis (22 °C, THF) \(\lambda_{\text{max}},\) nm (\(\epsilon\)): 360 (8500), 490 (3200), 600 (2600). Elem. anal. Calcd for C\(_{37}\)H\(_{54}\)N\(_4\)OV: C, 71.47; H, 8.75; N, 9.01. Found: C, 71.24; H, 8.64; N, 9.08.

1.5.4. Reduction of (OCN)\(_V\)(N[\(^\text{Bu}\]Ar))\(_3\) with Na/Hg

A solution of 6 (0.575 g, 0.92 mmol) in THF (15 mL) was prepared. The sodium-mercury amalgam (0.5%) was prepared in a scintillation vial and 5 mL of THF was added. The solution of 6 was added to the stirring amalgam at 23 °C using a Pasteur pipette. The originally black solution of 6 gradually changed to a deep green color over the course of 30 min. After stirring for one hour, the solution was decanted away for the amalgam and filtered through a plug of Celite on a sintered glass frit. The volatile components of the reaction mixture were removed under reduced pressure. The brown residue was then extracted with n-pentane (4 × 10 mL) and filtered through a second plug of Celite on a sintered glass frit. The brown-green filtrate solution was then concentrated to a volume of ~7 mL and was stored at −35 °C. After standing for 48 h, brown microcrystals had formed. The mother liquor was decanted from the crystals of 1 and the solids were dried under reduced pressure. Yield: 0.396 g (74%). \(^1\)H NMR (C\(_6\)H\(_6\), 20 °C, 400 MHz): \(\delta\) 39.3 (br), 14.3 (br), 3.6 (br), 3.0 ppm (br). Spectroscopic data have been reported previously.\(^{10}\)
Characterization of the sodium cyanate was not completed due to complications associated with separating the salt by-product from the Na/Hg.

1.5.5. Reduction of (OCN)V(N[1Bu]Ar)₃ with KC₈

A solution of 6 (0.320 g, 0.55 mmol) in THF (10 mL) was prepared and frozen in the cold well of the glove box. A suspension of KC₈ (0.075 g, 0.55 mmol) in THF (5 mL) was prepared and similarly frozen. The two mixtures were allowed to partially thaw and were subsequently combined. The reaction mixture was stirred and allowed to warm to 23 °C. The color changed from black to a deep turquoise after 1 minute of stirring. The reaction mixture was allowed to stir at 23 °C for 30 minutes. After stirring, the volatile components of the reaction mixture were removed under reduced pressure. The green residue was extracted with n-hexane and subsequently filtered through a plug of Celite on a sintered glass frit. The solvent was removed from the filtrate under reduced pressure, and the resulting green solids were dissolved in a minimum volume of n-pentane. The solution was stored at −35 °C. After standing for 24 h, dark green crystals had formed and were isolated by decanting away the mother liquor and subsequently drying them under reduced pressure. Yield: 0.217 g (68 %). ¹H NMR (C₆H₆, 20 °C, 400 MHz): δ 39.3 (br), 14.3 (br), 3.6 (br), 3.0 ppm (br). The solids that were not soluble in n-hexane were removed from the box and extracted into water. A solution of AgNO₃ in water was added to give an off-white precipitate. The precipitate was collected on a sintered glass frit washed with ethanol, then acetone, then petroleum ether, and dried in a vacuum desiccator for 12 h. Yield: 0.060 g (73%). IR (KBr, Nujol mull): ν_C=O 2219 cm⁻¹.

1.5.6. Reaction of CO with NaNV(N[1Bu]Ar)₃

A solution of 2 (3.8 g, 6.2 mmol) in THF (150 mL) was placed in a 500 mL round-bottom Schlenk flask. The flask was partially evacuated and the headspace was backfilled with an atmosphere of CO. The pressure of CO was maintained at an ambient pressure of 1 atm by maintaining a flow of one bubble every two seconds through a mineral oil bubbler that was connected to the Schlenk line. The reaction mixture was stirred at 23 °C for 24 h using a magnetic stir bar. During the course of the reaction the color of solution changed from bright yellow to a deep forest green. After 24 hours, the volatile components of the reaction mixture were removed under reduced pressure. The green-brown residue was extracted with n-hexane (200 mL) and filtered through a sintered glass frit. The gray solids collected on the frit were washed twice with n-hexane (15 mL) and then dried under reduced pressure. The filtrate was taken to dryness under reduced pressure. The green-brown residue from the filtrate was dissolved in a minimum of n-pentane and stored at −35 °C to give green crystals of 1. Yield: 2.59 g (71%) in two crops. The sodium cyanate collected in the initial filtration was dissolved in water and filtered through a plug
of Celite to give a colorless solution. An aqueous solution of silver nitrate was added to the filtrate to form a white precipitate. The precipitate was collected on a tared, sintered glass frit, washed twice with ethanol (10 mL), twice with diethyl ether (10 mL), and subsequently dried. Yield: 0.713 g (77%).

1.5.7. Synthesis of [(12-crown-4)₂Na][NV[N('Bu)Ar]₃] (9).

A solution of 2 (0.301 g, 0.49 mmol) in diethyl ether (10 mL) was prepared. A solution of 12-crown-4 (0.171 g, 0.98 mmol) in diethyl ether (2 mL) was prepared. The solution of 12-crown-4 was added to the solution of 2 with stirring at 22 °C. A fine yellow precipitate formed from the reaction mixture after stirring for 30 min. The reaction mixture was taken to dryness under reduced pressure. The yellow solids were suspended in n-pentane and collected on a sintered glass frit. Crystals of the complex suitable for X-ray diffraction studies were grown by dissolving the yellow solids in toluene, filtering the solution through a glass fiber filter, and storing the filtrate solution at -35 °C for 7 d. ¹H NMR (THF-d₈, 20 °C, 400 MHz): δ 6.34 (s, 3H, p-Ar), 5.66 (s, 6H, o-Ar), 3.70 (s, 16H, 12-crown-4), 1.99 (s, 18H, Ar(CH₃)₂), 1.51 ppm (s, 27H, 'Bu).

1.5.8. X-ray Crystallographic Structure Determination

Low-temperature data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo/Kα radiation (λ = 0.71073 Å), performing ω- and φ-scans. All structures were solved either by direct or Patterson methods using SHELXS and refined against F² on all data by full-matrix least squares with SHELXL-97.²⁶ A semi-empirical absorption correction (SADABS) was applied to the diffraction data for all structures.²⁷ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups).

Complex 6 crystallizes in the space group P2₁/c, and the structure was solved using direct methods. Refinement proceeded by assigning atom positions according to the electron-density difference map. No restraints were used in the refinement. Thermal ellipsoids plot was generated using PLATON.²⁸

Complex 9 crystallizes in the space group P2₁2₁2, and the structure was solved using direct methods. Refinement proceeded by assigning atom positions according to the electron-density difference map. A positional disorder in the crown ether moieties was refined by modeling the occupancy of the two positions freely while constraining the total occupancy to unity. Anisotropic displacement parameters were restrained assuming rigid bond behavior. Anisotropic displacement parameters for the smaller component of the crown ether disorder were restrained to be isotropic.
Similarity restraints were applied to 1,2- and 1,3-distances in the crown ether moieties. A thermal ellipsoid plot was generated using PLATON. ²⁸
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1.5.9. **Electrochemical Measurements**

Electrochemical measurements were made using a BAS CV-50W potentiostat with a platinum disk working electrode, platinum wire counter electrode, and a silver wire pseudoreference electrode. Potentials were internally referenced to the ferrocene/ferricenium redox couple at 0 mV. Measurements were made under an atmosphere of dinitrogen using THF solutions of 0.2 M [N("Bu)4][B(C6F5)4]. The cyclic voltammogram of 6 was collected at various sweep rates between 10 to 300 mV/s. The cyclic voltammogram of 8 was collected at a sweep rate of 300 mV/s.

1.6. **References**

(16) A search of the Cambridge Structural Database revealed an average M–N–C angle of 149.8° for isocyanate complexes.
Chapter 2. Reactivity of a Vanadium Carbamate Complex

2.1. Introduction

2.1.1. Activation of CO$_2$ with Nitrogenous Nucleophiles

The reaction of CO$_2$ with primary and secondary amines to produce the corresponding carbamates, is a very well-documented mode of reactivity. Such species are stable under basic conditions but readily decompose to CO$_2$ and the ammonium salt when solutions are acidified.$^1$ In the absence of an external base, the uptake of CO$_2$ often results in the consumption of two equivalents of the starting amine: one serves to bind the CO$_2$ and produce the carbamate anion and the other amine serves as the requisite Bronstead base and forms an ammonium cation.$^2$

The synthesis of the carbamate complex 4 from the reaction of CO$_2$ with the nitride complex 2 was initially reported by Brask et al. in 2002.$^3$ In the initial study, the structural assignment of the N-bound carbamate moiety was made using a combination of spectroscopic data and computational studies. A definitive structural assignment using X-ray crystallography proved to be elusive even though the material could be isolated in analytically pure form. Prior to the work presented herein, Dr. Nicholas Piro was able to collect a preliminary structure of 4 that revealed the material to be a sodium-bridged dimer in the solid state. However, the small, poorly diffracting nature of the crystals, coupled with a high level of disorder in the structure, prevented a refinement suitable for publication. Hence, an early goal of the project was to definitively characterize the structure of complex 4 and thus confirm the concept that CO$_2$ activation was occurring via nucleophilic attack by the nitrido ligand.

2.1.2. Solid-state Structure of [(15-crown-5)Na][O$_2$CNV(N['Bu]Ar)$_3$]

Given the problematic nature of the crystallographic data collected from the dimeric structure of 4, it was thought that forming a monomeric species through the use of a chelating ligand for the sodium countercation might allow for better crystal growth. Introducing 15-crown-5, the sodium selective crown ether,$^4$ to stirring solutions of 4 in THF resulted in displacement of the coordinated THF molecules and formation of [(15-crown-5)Na][O$_2$CNV(N['Bu]Ar)$_3$] (10).
Complex 10 could be crystallized by allowing n-pentane to diffuse slowly into saturated solutions of 10 in methylene chloride at \(-35^\circ C\). The crystals obtained in this manner were suitable for single-crystal X-ray diffraction measurements. The solid-state structure of 10 reveals the carbamate moiety to be $\kappa'N$-bound to the vanadium metal center and $\kappa^2O$-bound to the sodium cation (Figure 2.1).

![Solid-state structure of [(15-crown-5)Na][O$_2$CNV(N[\text{Bu}][\text{Ar}])$_3$] (10).](image)

The carbon-oxygen distances in the carbamate moiety (C41–O1 1.241(4) Å, C41–O2 1.249(4) Å) are elongated considerably from that of free CO$_2$ (1.17 Å), and the carbon atom is now closer to a trigonal planar geometry (O2–C41–O1 127.5(3)°). The vanadium-nitrogen distance remains short (V1–N4 1.634(3) Å). The nitrogen-carbon distance (N4–C41 1.443(5) Å) is consistent with a nitrogen-carbon single bond. These structural assignments agree with earlier DFT calculations on the simplified system [O$_2$CNV(NMe$_2$)$_3$] where a strong vanadium-nitrogen π-bonding interaction and a weak nitrogen-carbon π-bonding interaction were observed. Taken together, the most apt description of the bonding in the carbamate moiety is the vanadium triply bonded to the nitrogen, the nitrogen then singly bonded to the carbon, and the carbon bound to
the oxygens with a $\sigma$-bond to each and a single $\pi$-bond delocalized over the three positions. The nitrogen would have a formal positive charge and the vanadium a formal negative charge in this case.

2.2. Reaction with Electrophiles

2.2.1. Silylation and Alkylation Reactions

One assumed aspect of the working hypothesis in the development of the proposed CO$_2$ to CO reduction scheme was the nucleophilicity of the oxygen atoms in the carbamate functionality. The structural parameters observed in the solid-state structure of 10 appear to support this idea by being consistent with the assignment of a delocalized $\pi$-bond and therefore a negative charge on the oxygen positions. To test this hypothesis, the reactivity of complex 4 with silyl and alkyl halides and pseudo-halides was studied.

Treatment of complex 4 with Me$_3$SiCl in thawing diethyl ether produced a gradual color change from orange to deep red along with formation of a colorless precipitate over the course of 30 minutes. After removal of sodium chloride, complex Me$_3$SiOC(O)NV[N('Bu)Ar]$_3$ (11) was isolated in 79% yield as large, red crystals by cooling saturated $n$-pentane solutions to $-35$ °C (Scheme 2.1). Complex 11 displays the anticipated set of resonances in the $^1$H NMR spectrum consistent with a single anilide environment. The $^{51}$V NMR spectrum contains a sharp resonance at $-163$ ppm. The IR spectrum of 11 contains an intense peak at 1651 cm$^{-1}$, consistent with the $\nu_{CO}$ of a carbonyl group. Definitive assignment of the silyl carbamate ester functionality was obtained through solid-state structure determination using X-ray diffraction methods. The carbamate ester group remains $N$-bound to the vanadium center and is capped by the trimethylsilyl group (Figure 2.2). As expected, silylation causes pronounced changes in the C-O distances when compared with 10; the C1–O1 distance (1.334(5) Å) is lengthened and the complementary C1–O2 distance is shortened (1.211(5) Å). This terminal carbamate ester imido ligand is unique to this system but is closely related to acylimido complexes that have been synthesized previously.$^6$
Scheme 2.1. Synthesis of Me₂SiOC(O)NV(N['Bu]Ar)₃ (11) and MeOC(O)NV(N['Bu]Ar)₃ (12).

Similar to the reaction of 4 with Me₃SiCl, treatment with MeOTf (OTf = OS(O)₂CF₃) also proceeds cleanly. Treatment of 4 with MeOTf in diethyl ether produced a color change from bright orange to dark red. Analysis of the crude reaction mixture by ¹H NMR spectroscopy
revealed the formation of a single anilide containing species. Following a standard workup to remove the NaOTf byproduct, the alkylated product MeOC(O)NV(N['Bu]Ar)₃ (12) was isolated as dark red crystals in 45% yield (Scheme 2.1). Complex 12 is exceedingly lipophilic, a property that hinders its isolation and purification in higher yields.

The thermal stability of 11 was studied to compare it with the stability of the parent carbamate complex 4. Heating a solution of 11 in benzene at 80 °C for 12 h resulted in no observable changes. Specifically, no oxo complex 5 formed. This lack of reactivity contrasts sharply with reactivity observed for the niobium analogues that will be discussed in Chapter 3.

2.2.2. Additional Salt Elimination Reactions

In addition to silyl and alkyl electrophiles, the carbamate complex 4 undergoes salt-elimination reactions with stannyl and phosphoryl electrophiles. In some cases, the reaction results in straightforward functionalization of the carbamate moiety. For example, treatment of 4 with one equivalent of SnCl₂ resulted in a color change from bright orange to deep red. Analysis of the reaction mixture by 'H NMR spectroscopy confirmed the clean formation of a single diamagnetic anilide containing species that also contains one equivalent of THF. The ⁵¹V NMR spectrum also contains a single resonance at -150 ppm. The proposed formula for the product is [(THF)SnCl][O₂CNV(N['Bu]Ar)₃]. Similarly, treatment of 4 with ½ equivalent of 'BuPCl₂ resulted in a color change from bright orange to dark red. Analysis of the reaction mixture by 'H, ⁵¹V, and ³¹P NMR spectroscopies confirmed the clean formation of a single product. Again, salt-elimination is believed to be the operative mechanism and the hypothesized formulation of the product is 'BuP[O₂CNV(N['Bu]Ar)₃]₂. Given the similarities between these reactions and the previously discussed salt-elimination reactions between 4 and silyl and alkyl electrophiles, full characterization of these compounds was not pursued.

Before leaving the subject, the reaction of 4 with PCl₃ should be discussed. When complex 4 is treated with one equivalent of PCl₃ in thawing THF, the color of the reaction mixture changed from bright orange to dark red. Analysis of the crude reaction mixture by 'H and ³¹P NMR spectroscopies revealed the formation of multiple diamagnetic products, but the 'H NMR spectrum also revealed the presence of a paramagnetic product. The EPR spectrum of the crude product mixture contained an intense eight-line pattern that confirms the formation of a vanadium(IV) species. After carrying out a brief workup to remove insoluble products, dark microcrystals of this paramagnetic material were isolated. The IR spectrum of the material was collected and confirmed the presence of an intense band at 2207 cm⁻¹. Based on these data, it is proposed that the identity of the material is the isocyanate complex 6. If accurate, the isolated yield for the reaction would be 19%. The operative mechanism for production of 6 is not known, but may involve in situ or auto-reduction of the transient complex Cl₂POC(O)NV(N['Bu]Ar)₃, a hypothesis that is consistent with observed reactivity between 4, dehydrating reagents, and
cobaltocene (vide infra). Although not pursued in the course of this work, this reaction may warrant further investigation.

2.2.3. Sulfur Dioxide Displacement of CO₂

During the course of the investigations, the question of whether salt-elimination was the only route for functionalization of the carbamate complex 4 was posed. In particular, it was enticing to envision a reaction where functionalization of the carbamate position would result in the autocleavage of a carbamate C–O bond either through oxygen atom or O⁻¹ abstraction. With this in mind, SO₂ was viewed as a promising reagent to study for such reactivity. If SO₂ were capable of formal O⁻¹ abstraction, the intermediate species produced, NaSO₃, could dimerize resulting in formation of the closed shell species sodium dithionate Na₂S₂O₆ as the byproduct with 6.

Treatment of 4 with one equivalent of SO₂ (administered as a saturated, 11 M solution in THF) in THF resulted in gradual color change from bright orange to dark red/orange. Analysis of the crude reaction mixture by ¹H and ⁵¹V NMR spectroscopies indicated formation of a single new diamagnetic, anilide containing species. The IR spectrum of the crude reaction mixture contained no discernible νC=O bands. Working up the reaction mixture by washing the crude product with n-pentane allowed for the isolation of a free-flowing, orange powder. The ¹³C NMR spectrum of the product does not contain a signal that could be attributed to the carbon originating from the carbamate moiety. In efforts to determine the identity of the product, a number of subsequent reactivity studies were performed. The product reacts readily with Me₃SiOTf to give a new diamagnetic product, implying the complex is still negatively charged and capable of reacting as a nucleophile. When the unknown species was stirred over Na/Hg amalgam in THF, the only observable product, as assayed by ¹H NMR spectroscopy, was the nitride complex 2.

Given little evidence for the presence of a CO₂ moiety remaining in the complex after reaction with SO₂, the control treatment of the nitride complex 2 with SO₂ was performed. Treatment of 2 in THF with SO₂ (administered as a solution in THF) resulted in a color change of yellow to red-orange. Drying the reaction mixture under reduced pressure gave a bright orange powder whose NMR spectral signatures (¹H and ⁵¹V) were identical to those of the previously unknown product. Thus, the formulation of the product most consistent with the data is [(THF)₃Na][O₂SNV(N[’Bu]Ar)₃] (13). The reaction between SO₂ and the carbamate complex 4 to give complex the sulfurous imido complex 13 is summarized in Scheme 2.2.
To remove the ambiguity of the number of THF molecules coordinated to the sodium countercation, 15-crown-5 was added to the reaction mixture to partially sequester the sodium thus forming \([(15\text{-crown}-5)Na][O_2CNV(N[Bu]Ar)_3]\) (14). The crown ether complex displays remarkable crystallinity, allowing for the growth of single-crystals suitable for solid-state structure determination through the use of X-ray diffraction techniques (Figure 2.3). In the solid state, 14 is monomeric with the \([(15\text{-crown}-5)Na]^+\) bound to the oxygen positions of the sulfurous imido ligand. The vanadium-nitrogen distance is short (1.655(2) Å), characteristic of a vanadium-nitrogen triple bond, but is slightly longer than the vanadium-nitrogen distance observed in 10. The greater acidity of SO$_2$, compared to CO$_2$, likely results in a weaker vanadium-nitrogen interaction. The sulfur position is pyramidalized, as would be expected for an AX$_3$E$_1$ system according to VSEPR theory. To the best of the author’s knowledge,\textsuperscript{12} this is the only complex of its type, the most closely related complexes being sulfonyl imidos of the type RS(O)$_2$N=ML$_x$.\textsuperscript{13} An example of SO$_2$ interacting with a nitrogenous anion is the structurally characterized salt \([\text{NMe}_4][O_2SN_3]\).\textsuperscript{14} In the anion [O$_2$SN$_3$]$^-$, the sulfur-nitrogen distance was found to be 2.005(2) Å, which is much longer than the sulfur-nitrogen distance found in complex 14 (1.715(2) Å). The sulfur oxygen distances in [O$_2$SN$_3$]$^-$ (1.455(2) Å avg.) are slightly shorter than the sulfur-oxygen distances found in 14 (1.492(2) Å avg.).
Two possible mechanisms can be considered. The first involves charge transfer between the two reagents. The carbamate complex 4 transfers an electron to the SO₂. The resulting carbamate radical undergoes a rapid decarboxylation, generating the nitrido radical that recombines quickly with the transient SO₂⁻ radical to give complex 13. The alternative proposal involves initial acid-base reaction between SO₂ and the carbamate complex 4 to give the intermediate complex [Na][O₂SOC(O)NV(N'Bu)Ar₃] (Scheme 2.3). An intramolecular rearrangement then results in the dissociation of CO₂ and formation of 13. This rearrangement may involve the nucleophilic attack of the sulfur on the imido nitrogen, or conversely, attack by the nitrogen onto the sulfur position. Regardless, no mechanistic studies were undertaken to disambiguate between the electron transfer and acid-base mechanism in the course of these studies.
2.3. Synthesis of Isocyanate Complex via in situ Acylation

2.3.1. Reaction with Dehydrating Reagents

Having observed that salt-elimination reactions can yield clean functionalization of complex 4 when silyl and alkyl electrophiles were employed, the prospect of installing a leaving group via a similar strategy was attractive. The ultimate goal of functionalizing the carbamate group in 4 was to cleave the C-O bond. One method for achieving this would be to install a functional group prone to dissociation upon one-electron reduction. In such a scheme, the vanadium containing byproduct would be complex 6 (Scheme 2.) with the vanadium metal center serving as a reservoir for the odd electron.

Dehydrating reagents such as organic anhydrides or acid chlorides were thought to be ideal candidates for the aforementioned reaction. Installation of an acyl group on the carbamate functionality should produce a carbamic anhydride species susceptible to reductive cleavage.
However, initial treatments of 4 with organic acid anhydrides or acid chlorides did not yield the targeted molecule. In a typical treatment, a thawing solution of the anhydride or acid chloride in either THF or diethyl ether was added to a similarly thawing solution of 4. The reaction was allowed to warm to the ambient temperature without assistance. In most cases, the initially bright orange solution changed to dark brown-red as the reaction proceeded. Analysis of the crude reaction mixture by \(^1\text{H}\) and \(^{51}\text{V}\) NMR spectroscopies revealed the formation of several diamagnetic products. All attempts to isolate a single product cleanly from such reaction mixtures were unsuccessful. Reagents studied include pivalic anhydride, pivalic chloride, benzoyl chloride, benzoyl triflate, and trifluoroacetic anhydride. Sulfonyl containing dehydrating agents such as tosyl chloride and triflic anhydride were also investigated. All met with similar results.

From these results it was concluded that the proposed carbamic anhydride complexes, if formed, were not isolable. A brief survey of the organic chemistry literature reveals that carbamic anhydrides (R\(_2\)NC(O)OC(O)R\(^-'\)) are only stable at room temperature when the R and R\(^-'\) groups are certain hydrocarbyl fragments. Thus, it is not entirely unexpected that the desired complexes were unstable.

### 2.3.2. Acylation Reactions in the Presence of a Reducing Agent

Although the carbamic anhydride complexes were not isolated, isolation was not required for the purposes of the project. If the reaction between the dehydrating reagents and carbamate complex 4 were proceeding through the anticipated salt-elimination pathway, it might be possible to intercept the transient carbamic anhydride intermediate with a reducing agent before it could undergo the deleterious thermal reaction. Thus, treatment of 4 with a dehydrating reagent in the presence of an \textit{in situ} reductant was investigated. On the basis of electrochemical studies of 6 (Figure 1.4), cobaltocene was selected as a suitable reducing agent as it is not potent enough to reduce complex 6. Cobaltocene also shows no reactivity with organic acid anhydrides, as confirmed in independent control experiments.

Treatment of a thawing solution of 4 and cobaltocene in THF with a solution of pivalic anhydride resulted in a color change from red to black over the course of 1 h. Analysis of the reaction mixture by IR spectroscopy revealed the presence of an intense signal at 2207 cm\(^{-1}\), strongly characteristic of an isocyanate moiety. The EPR spectrum (benzene solution, 20 °C) displayed a distinct eight-line pattern characteristic of a vanadium(IV) species. The \(^1\text{H}\) and \(^{51}\text{V}\) NMR spectra revealed the presence of a small amount of a diamagnetic side-product but the paramagnetic species is clearly observable. Following a standard work-up to remove the salt byproducts, the vanadium-containing isocyanate complex 6 was isolated in 75% yield as a black crystalline material (Scheme 2.5). This reaction represented the first well-defined example of deoxygenation of the N-bound carbamate ligand, a critical step in the proposed CO\(_2\) to CO
reduction cycle. This observed reactivity extends to other acylating reagents, including organic acid chlorides.

Scheme 2.5. Reaction of \([(\text{THF})_{2}\text{Na}]_{2}\text{C}_{2}\text{N}V(\text{N}^{\text{Bu}}\text{Ar})_{3}\] (4) with pivalic anhydride and cobaltocene.

2.3.3. Low Temperature IR and NMR studies of Acetylation Reactions

To better understand the mechanism of the formation of 6 from 4, identifying the presumed carbamic anhydride intermediate was attempted. It was hypothesized that this species forms in the course of the reaction, but it was not clear whether this was reduced directly by the cobaltocene or if the cobaltocene intercepts a subsequent species that forms as a result of decomposition. Thus, the reaction was monitored at low temperatures using IR and NMR spectroscopies with the goal of observing the carbamic anhydride intermediate directly.

Studying the reaction at low temperature using IR spectroscopy was done in collaboration with Prof. Carl Hoff and Dr. Manuel Temprado at the University of Miami. Samples of 4 were provided by the author, and experiments were performed by Hoff and Temprado in Miami. In a typical experiment, a solution of the carbamate complex 4 in THF was prepared and cooled to \(-78^\circ\text{C}\). A solution of acetyl chloride was then added to the reaction vessel, resulting in a color change from orange to red. The reaction mixture was then introduced to the low-temperature IR cell that had been pre-cooled to \(-78^\circ\text{C}\). The IR spectrum of the reaction mixture reveals the presence of a new species with two distinct bands at 1688 and 1780 cm\(^{-1}\). Such two band patterns are characteristic of anhydride moieties.\(^{17}\) This is the first evidence that the carbamic anhydride species forms in solution. If the temperature of the reaction mixture is maintained at \(-78^\circ\text{C}\), this intermediate species persists in solution. If the reaction mixture is warmed to slightly higher temperatures, subsequent reactivity can be observed. Specifically, if the reaction mixture is allowed to warm to \(-56^\circ\text{C}\), the intermediate carbamic anhydride species converts to a species containing an isocyanate moiety over the course of one hour (Figure 2.4). In the previous preparative scale treatments, the formation of such an isocyanate species was never observed. The key difference between the earlier studies and the studies by Hoff and Temprado was the constant control of the temperature. Furthermore, if the reaction mixture was allowed to warm to room
temperature after complete consumption of the intermediate complex, the isocyanate species shows no sign of degradation, implying the formation of a stable, isolable product.

Figure 2.4. IR spectra of the product of the reaction of [(THF)$_2$Na][O$_2$CNV(N[Bu]Ar)$_3$] with acetyl chloride at \(-56 ^\circ\text{C}\) over the course of 50 min.

The results from Hoff and Temprado prompted the study of the reaction using \textit{in situ} NMR spectroscopy. Thus, the treatment was repeated in a flame-sealed NMR tube using deuterated THF as the solvent. Acetic anhydride was selected as the acylating reagent in these experiments. The \textit{in situ} analysis confirms the formation of an intermediate complex, assigned as the carbamic anhydride species. The $^{13}$C NMR spectrum contains a broad resonance at 146 ppm. This species forms slowly in the NMR tube at \(-70 ^\circ\text{C}\), perhaps due to the lack of agitation in the tube. If allowed to warm to a temperature above \(-40 ^\circ\text{C}\), the intermediate complex slowly converts to a paramagnetic species and some diamagnetic species as well.

As a result of the \textit{in situ} IR and NMR studies, the experiment was carried out on a preparative scale. Treatment of 4 with acetic anhydride in THF at \(-78 ^\circ\text{C}\) resulted in a color change from bright orange to dark red. After adjusting the cryogenic bath to a temperature of \(-55 ^\circ\text{C}\), the reaction mixture slowly changed to a dark brown color after 1.5 h. Analysis of the reaction mixture via $^1$H NMR, IR, and EPR spectroscopy were all consistent with formation of the isocyanate complex 6. Final confirmation for the formation of 6 came from collecting a preliminary solid-state structure via X-ray diffraction techniques.

Confirming the formation of 6 was a surprise. Balancing the chemical equation implies that the other product of the reaction mixture would be the acetyl radical. This species is known to

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decompose very rapidly in the gas phase to produce CO$_2$ and the methyl radical; the methyl radical would likely abstract a hydrogen atom from the THF solvent, but this could not be observed in the NMR experiments. Given that 6 is not the sole product from the reaction, it is very possible that non-radical pathways are operative. The driving force for the reaction is likely a combination of forming the stable cyanate linkage and reducing the high-valent vanadium(V) metal center. Regardless of the exact nature of the driving force for the reaction, the results confirm the initial hypothesis — installation of a good leaving group at the carbamate moiety makes the C–O bond more susceptible to cleavage.

Having shown that the isocyanate complex 6 can form spontaneously, the role of cobaltocene in the reaction was again questioned. To address this, the in situ methods outlined above were repeated. When Hoff and Temprado repeated the treatment of the carbamate complex 4 with acetyl chloride, but included cobaltocene in the reaction mixture, the carbamic anhydride intermediate was not observed, and the isocyanate complex 6 formed immediately. It can be concluded from this experiment that the cobaltocene serves not to trap the acetyl radical produced in the course of the thermal reaction, but to directly reduce the carbamic anhydride intermediate.

A summary of the reaction conditions, and net transformations are shown in Scheme 2.6.

**Scheme 2.6.** Proposed pathway for the reaction of [(THF)$_2$Na][O$_2$CNV(N[‘Bu]Ar)$_3$] (4) with acetic anhydride. **A)** Initial acetylation proceeds via salt-metathesis. **B)** Intermediate carbamic anhydride undergoes a thermal reaction to form (OCN)V(N[‘Bu]Ar)$_3$ (6) through an undetermined mechanism. **C)** The intermediate carbamic anhydride reacts directly with cobaltocene to form (OCN)V(N[‘Bu]Ar)$_3$ (6).

### 2.3.4. Reaction with Carbon-free Dehydrating Reagents

Expanding the scope of reagents that could deoxygenate complex 4 was pursued. Assisted by undergraduate researcher Alex Rubino, the reaction of 4 with OPCl$_3$ and OSCl$_2$ were investigated. Treatment of the carbamate complex 4 with OPCl$_3$ or OSCl$_2$ in thawing THF results in a color change from orange to dark red. If allowed to warm to ambient temperature unassisted, the reaction produces several products as assayed by $^1$H and $^{51}$V NMR spectroscopies, similar to what was observed in when organic acid anhydrides or chlorides were used. If cobaltocene is
included to serve as an *in situ* reductant, the reaction proceeds to give complex 6 in modest yields (Scheme 2.7). The proposed co-products in these reactions are the cobaltocenium salts [Cp₂Co][O₂PCl₂] and [Cp₂Co][O₂SCl], which likely decomposes to SO₂ and [Cp₂Co]Cl, respectively. The anion [O₂PCl₂]⁻ has been observed previously in work by Dehnicke and co-workers. This reactivity is very similar to the reaction of secondary organic carbamates with OPCI₃ in the presence of mild bases to give the organic isocyanates. In the case of the reaction of 4 with OPCI₃ or OSCI₂, the deprotonation step of the reaction is replaced by the reduction with cobaltocene.

![Scheme 2.7. Reactivity of [(THF)₂Na][O₂CNV(N[Bu]Ar)₃] (4) with OPCI₃ and OSCI₂ in the presence of cobaltocene.](image)

In many ways, these reactions can be thought of as *O¹⁻* abstraction from the carbamate complex 4. The ion *O¹⁻* is isoelectronic with a halogen atom, but its abstraction chemistry is much less developed. Although it appears that cobaltocene reacts directly with the carbamic anhydride intermediate complex, the reactivity implies that a suitable radical reagent should be able to abstract an *O¹⁻* ion from the carbamate complex 4.

### 2.4. Photochemical Deoxygenation of Carbamate Complex

#### 2.4.1. Synthesis and Structure of (TPP)MnOC(O)NV(N[Bu]Ar)₃

Having shown the feasibility of deoxygenating the carbamate complex 4 using an oxygen acceptor and a reducing agent, it was of interest to investigate if this transformation could be achieved using a single reagent. Driving the reaction photochemically was also of interest. Thus, methods for appending a photosensitive, metallic fragment to 4 for the purposes of deoxygenation were pursued. An additional goal of this transformation was to generate a metal-oxo species that would be capable of transferring the oxo moiety to external substrates in a subsequent reaction. For this reason, metalloporphyrin species were targeted as ideal substrates given their well-documented photochemical abstraction of oxygen from anionic axial ligands. For example, the manganese porphyrin complex O₂NOMn(TPP) (TPP = meso-tetraphenylporphyrinate)
undergoes homolytic N–O bond cleavage to produce NO$_2$ and OMn(TPP) when irradiated with 355 nm light.$^{26}$ For these reasons, meso- substituted manganese porphyrin complexes were selected for these investigations.

Treatment of 4 with ClMn(TPP) (TPP = meso-tetraphenylporphyrinate) in a mixture of toluene and THF results in the precipitation of an off-white solid over the course of 18 h. Following removal of the NaCl byproduct via filtration, the desired complex (TPP)MnOC(O)NV(N['Bu]Ar)$_3$ (15) was crystallized from a saturated toluene solution layered with $n$-pentane at $-35$ °C over the course of seven days (Scheme 2.8).

Complex 15 has several unique spectroscopic features. The Soret band in the UV/Vis spectrum is centered at 475 nm (Figure 2.5). Complex 15 is paramagnetic with an effective magnetic moment $\mu_{\text{eff}} = 5.06$ $\mu$B in solution. This value is consistent with the spin-only value for an $S = 2$ system,$^{27}$ which is expected for a high-spin manganese(III) complex. This paramagnetism manifests itself in the $^{1}$H NMR spectrum, where the resonances are broad and shifted significantly from the values typical of a diamagnetic species. The $^{51}$V NMR spectrum contains a very broad resonance at $-72$ ppm (Figure 2.6). The IR spectrum contains an absorbance at 1614 cm$^{-1}$ attributed to the $\nu_{C=O}$ of the carbamate linkage, consistent with localization of the $\pi$-bond on one of the C–O bonds and consistent with $\kappa^1$- coordination to the manganese. Complex 15 displays limited solubility in low polarity, aliphatic solvents such as $n$-pentane, $n$-hexane, and diethyl ether, but is very soluble in aromatic solvents, such as benzene, and higher polarity solvents like THF and methylene chloride. Thermally, 15 is stable in benzene solutions at 70 °C for several days.
The solid-state structure of 15 was determined using X-ray diffraction techniques on a single crystal that was grown from a concentrated solution of 15 in 1:1 toluene:hexane at \(-35 \, ^\circ\text{C}\).
In 15, the carbamate unit serves as an axial ligand for the [Mn(TPP)]$^{+}$ and is bound in a κ$^1$-fashion. As a result, the π-bond in the O–C–O linkage is localized, thus giving rise to inequivalent O–C distances (1.225(4) and 1.280(4) Å).

![Figure 2.7. Solid-state structure of (TPP)MnOC(O)NV(N[Bu]Ar)$_3$ (15).](image)

Thermal ellipsoids are drawn at 50% probability, and hydrogen atoms and interstitial solvent molecules have been omitted for clarity.

2.4.2. Photochemical Reactivity

Finding ways to cleave the carbon-oxygen bond in 15 selectively became the focus of the project. Since complex 15 was known to be thermally stable, I turned my attention to studying its photochemical properties. Irradiation of 15 in benzene (0.02 M) in the presence of PPh$_3$ in quartz vessels with low-pressure mercury-vapor lamps results in the complete consumption of 15 over the course of 60 h. The complete consumption of the starting material was determined using $^{51}$V NMR spectroscopy. According to the $^1$H NMR spectrum, the production of diamagnetic species is minimal. The EPR spectrum of the reaction mixture contains an intense eight-line pattern,
consistent with the formation of a vanadium(IV) species. The IR spectrum of the crude reaction mixture contains an intense absorbance at 2208 cm\(^{-1}\), consistent with the formation of a cyanate linkage. Analysis of the reaction mixture via UV/Vis spectroscopy reveals the formation of the manganese(II) complex, Mn(TPP). If the \(^{31}\)P NMR spectrum is collected in benzene, no phosphorus species are observed, but changing to pyridine reveals that the crude reaction mixture contains four phosphorus-containing species, two of which remain unidentified, and the other two being OPPh\(_3\) and unreacted PPh\(_3\). Based on this spectroscopic evidence, it is proposed that irradiation of 15 results in generation of the isocyanate complex 6 and the manganese(IV) complex OMn(TPP). The PPh\(_3\) present in the reaction mixture serves as a trapping reagent for OMn(TPP), deoxygenating the manganese center, to produce OPPh\(_3\) and Mn(TPP) (Scheme 2.9).

![Scheme 2.9. Proposed pathway for photolysis of (TPP)MnOC(O)NV(N[Bu]Ar)\(_3\) in benzene in the presence of PPh\(_3\).](image)

The paramagnetic nature of the vanadium-containing product 6 precluded the in situ determination of the yield via NMR spectroscopy. Instead, the yield was measured using IR spectroscopy by constructing a concentration dependent calibration curve of the \(\nu\)\(_{OCN}\) absorbance of 6 in benzene. Using this measured value, the concentration of 6 in aliquots of the crude reaction mixture could be calculated. From these data, it was determined that the reaction proceeds to produce 6 in 34% yield over the course of 60 h. Qualitatively, this value agrees with
the production of OPPh$_3$, which typically represented 35-40% of the phosphorus-containing products as determined by $^{31}$P NMR spectroscopy.

It was found that radiation with the higher energy UV radiation that was accessible using the Hg vapor lamps was important for producing 6 in the highest possible yield. Replacing the low-pressure Hg-vapor lamps with lower energy broad band lamps or introducing low-pass filters to absorb higher energy photons resulted in the formation of significant amounts of the imido complex HNV(N['Bu]Ar)$_3$ (16) as assayed by the $^1$H and $^{51}$V spectroscopies. It is hypothesized that the formation of 16 occurs through an independent photochemical process that involves the homolytic cleavage of the Mn-O bond to give the radical species [-0 2 CNV(N['Bu]Ar)$_3$]. This species likely loses CO$_2$ to give the imido radical [-NV(N['Bu]Ar)$_3$], which quickly abstracts a hydrogen atom from a species in solution to produce 16. This result is further supported by the fact that the yield of 16 in the reaction is significantly higher when the treatments are carried out in Pyrex glassware (320 nm cutoff) rather than quartz glassware (<200 nm cutoff). These observations have led me to conclude that there are two different electronic transitions involved in the photolysis of 15: a low energy pathway that results in homolytic cleavage of the Mn-O bond and a higher energy pathway that results in homolytic cleavage of the C-O bond.

2.5. Conclusions

After structurally characterizing the vanadium carbamate complex as the 15-crown-5 coordinated species 10, the nucleophilic reactivity of the parent carbamate complex 4 was examined. It has been shown that the CO$_2$ derived moiety can be effectively deoxygenated using a combination of dehydrating reagents with an in situ reductant. This observation marks the first evidence to support the hypothesis that the binding of CO$_2$ to the nitride complex enhances its reactivity toward eventual conversion to CO. The formation of 6 from the photolysis of 15 provides encouraging evidence that the critical deoxygenation step in the proposed cycle can incorporate photochemical transformations.

Key improvements still need to be made if the ultimate goal of CO$_2$ to CO conversion is to be realized. As was discussed in Chapter 1, the vanadium tris-anilide platform is incapable of performing the requisite reductive decarbonylation of the isocyanate ligand in 6. This lack of competency inspired me to study the reactivity of the analogous niobium nitride system, which will be discussed in Chapter 3. Additionally, a more selective electrophilic oxygen acceptor needs to be identified. Ideally, the oxygen acceptor would not react with the starting nitride complex. Furthermore, although the photolysis of 15 provides a nice precedent for a desirable photochemical oxygen transfer from CO$_2$, the poor selectivity, yield, and recyclability of the Mn(TPP) fragment provide ample areas for improvement.

2.6. Experimental Section
2.6.1. General Considerations.

All manipulations were carried out either in a Vacuum Atmospheres model MO-40M glove box under an atmosphere of N₂ or using standard Schlenk techniques. All solvents were purified using a Glass Contour solvent purification system. After purification, all solvents were stored under an atmosphere of N₂ over 4 Å molecular sieves. Deuterated benzene (Cambridge Isotope Labs) was dried by stirring over CaH₂ for 24 hr and was subsequently vacuum-transferred onto 4 Å molecular sieves. Complex 4 was prepared according to literature methods.³ (C₃H₅)₂Co was purchased from the vendor (Strem Chemicals) and sublimed prior to use. All other reagents were used as supplied by the vendor without further purification. Celite 435 (EMD Chemicals), alumina (Aldrich) and 4 Å molecular sieves were dried prior to use by heating at 200 °C for 48 hr under dynamic vacuum. All glassware was oven dried at 220 °C prior to use. NMR spectra were obtained on either a Bruker 400-AVANCE spectrometer equipped with a Magnex Scientific superconducting magnet or a Varian Inova 500 spectrometer equipped with an Oxford Instruments Ltd. superconducting magnet. Proton NMR spectra were referenced to residual C₆D₅H (7.16 ppm). ⁵¹V NMR spectra were referenced externally to OVCl₃ (0.0 ppm). ¹³C NMR spectra were referenced internally to C₆D₆ (128.39 ppm). IR spectra were collected on a Perkin-Elmer 2000 FT-IR spectrophotometer. Elemental analysis was performed by Midwest Microlab, Indianapolis, IN.


A solution of 2 (5.8 g, 9.4 mmol) in THF (150 mL) was prepared and placed in a 300 mL round-bottom Schlenk flask fitted with a rubber septum. The solution was stirred using a PTFE-coated stir bar and cooled to 0 °C. The flask was placed under an atmosphere of nitrogen gas. Carbon dioxide was sparged through the solution for 10 minutes, which procedure led to an immediate change in the color of the solution from yellow to orange. After sparging, the reaction mixture was taken to dryness under reduced pressure. The orange residue was dissolved in n-pentane (75 mL), and 15-crown-5 (2.07 g, 9.4 mmol) was added. After stirring for approx. one minute, a bright yellow precipitate formed. The yellow powder was collected via filtration on a sintered glass frit and dried under reduced pressure. Yield: 7.25 g (88%). Crystals suitable for X-ray diffraction studies were grown from a vapor diffusion of n-pentane into a solution of 10 in methylene chloride. ¹H NMR (benzene-d₆, 20 °C, 400 MHz): δ 6.75 (s, 3H, p-H), 3.57 (br, 10H, 15-crown-5 CH₂), 3.06 (br, 10H, 15-crown-5 CH₂), 2.23 (s, 18H, ArCH₃), 1.83 (s, 27H, t-Bu). ⁵¹V NMR (benzene, 20 °C, 105.2 MHz): δ -303.76 (Δv₁/₂ = 356 Hz). ¹³C NMR (benzene, 20 °C, 100.56 MHz): δ 155.4 (s, ipso-Ar), 136.1 (s, Ar), 129.0 (s, Ar), 126.1 (s, Ar), 69.5 (s, 15-crown-5), 62.9 (s, N-CMe₃), 32.9 (s, ArMe), 21.5 (s, N-CMe₃). IR (Nujol mull, KBr): 1593 cm⁻¹.

A solution of 4 (0.805 g, 1.0 mmol) in diethyl ether (30 mL) was cooled to −196 °C. A solution of Me₃SiCl (0.112 g, 1.04 mmol) in Et₂O (5 mL) was cooled to −196 °C. The solutions were allowed to partially thaw and were subsequently combined. The mixture was stirred and the color of the solution changed from orange to red upon warming to 23 °C. After stirring for one hour at 23 °C, the reaction mixture was filtered through a plug of Celite and a sintered glass frit. The filtrate was taken to dryness under reduced pressure, and the resulting red residue was dissolved in a minimum volume of n-pentane. The solution was stored at −35 °C and after standing for 24 hours, red crystals had formed. The solids were isolated via vacuum filtration on a sintered glass frit. Yield: 0.562 g (79%). Crystals suitable for X-ray diffraction studies were grown from saturated solutions of 11 in a 1:1 mixture of toluene:n-pentane at −35 °C over the course of 48 hours. ¹H NMR (benzene-d₆, 20 °C, 400 MHz): δ 6.91 (br, 3H, o-Ar), 6.70 (s, 3H, p-H), 4.87 (br, 3H, o-Ar), 2.12 (s, 18H, ArCH₃), 1.48 (s, 27H, t-Bu), 0.46 (s, 9H, SiMe₃). ⁵¹V NMR (benzene, 20 °C, 105.2 MHz): δ −163.0 (Δν₁/₂ = 331 Hz). ¹³C NMR (benzene, 20 °C, 100.56 MHz): δ 155.4 (s, ipso-Ar), 137.1 (s, Ar), 127.6 (s, Ar), 65.8 (s, N–CMe₃), 33.1 (s, ArMe), 22.0 (s, N–CMe₃), 0.5 (s, SiMe₃). IR (Nujol mull, KBr): 1651, 1599, 1585 cm⁻¹. Elem. anal. Calcd for C₄₀H₆₃N₄O₂SiV: C, 67.57; H, 8.93; N, 7.88. Found: C, 67.56; H, 8.82; N, 7.81.


A solution of 4 (0.805 g, 1.0 mmol) in diethyl ether (15 mL) was cooled to −196 °C. A solution of MeOSSO₂CF₃ (0.164 g, 1.0 mmol) in diethyl ether (3 mL) was prepared and cooled to −196 °C. The solutions were allowed to partially thaw and were subsequently combined. The mixture was stirred and allowed to warm to an ambient temperature of 23 °C. After stirring for 1 hour, the reaction was taken to dryness under reduced pressure to give a dark red residue. The residue was extracted with n-pentane (2 × 3 mL) and filtered through a plug of Celite and a sintered glass frit. The red filtrate was taken to dryness under reduced pressure. The red residue was dissolved in a minimum volume of n-pentane and stored at −35 °C. After standing for 24 hours, red crystalline solids had formed and were collected via vacuum filtration. Yield: 0.296 g (45%). ¹H NMR (benzene-d₆, 20 °C, 400 MHz): δ 6.87 (br, 3H, o-Ar), 6.69 (s, 3H, p-H), 4.92 (br, 3H, o-Ar), 3.66 (s, 3H, O–Me), 2.12 (s, 18H, ArCH₃), 1.51 (s, 27H, t-Bu). ⁵¹V NMR (benzene, 20 °C, 105.2 MHz): δ −154.0 (Δν₁/₂ = 301 Hz). ¹³C NMR (benzene, 20 °C, 100.56 MHz): δ 155.4 (s, ipso-Ar), 137.1 (s, Ar), 127.6 (s, Ar), 65.8 (s, N–CMe₃), 53.4 (s, O–Me) 33.0...
(s, ArMe), 21.9 (s, N-CMe₃). IR (thin film, KBr): 1667, 1598, 1585, 1284 cm⁻¹. Elem. anal. Calcd for C₃₈H₅₇N₄O₂V: C, 69.91; H, 8.80; N, 8.58. Found: C, 69.96; H, 8.81; N, 8.69.


A 100mL, round-bottom, Schlenk flask containing a solution of 2 (0.532 g, 0.88 mmol) in THF (20 mL) was cooled to 0 °C. A 50 mL, round-bottom Schlenk flask with THF (20 mL) was sparged with SO₂ for 30 minutes at 0 °C. An aliquot of 0.1 mL was removed via syringe from the SO₂-saturated THF solution. The aliquot was introduced to the stirring solution of 2. The solution changed from yellow-green to deep orange-red after the addition. The reaction mixture was allowed to stir at 0 °C for 10 minutes. After no further observable change, the solvent was removed under reduced pressure. A bright orange powder remained after removal of all volatile components. n-Pentane (10 mL) was added to the orange solids and the mixture was stirred. The orange slurry was filtered through a medium porosity frit, permitting the collection of a bright orange powder and a dark orange filtrate. The powder was dried under reduced pressure. Yield: 0.518 g. The orange powder was dissolved in a 1:3 mixture of pentane and THF. The solution was stirred and a pentane solution of 15-crown-5 (3mL pentane; 0.170 g, 0.77 mmol 15-crown-5) was added. The orange solution slowly became heterogeneous with a bright orange precipitate. The mixture was stirred for 10 minutes after which, the vial was stored in the freezer for 30 minutes. The mixture was filtered through a medium porosity frit. The yellow powder collected was dried under reduced pressure. Yield: 0.574 g (73%).

1H NMR (benzene-d₆, 20 °C, 400 MHz): δ 6.7 (br, 3H, o-Ar), 6.74 (s, 3H, p-H), 5.4 (br, 3H, o-Ar), 5.4 (br, 10H, 15-crown-5), 3.09 (br, 10H, 15-crown-5), 2.22 (s, 18 H, Ar(CH₃)₂), 1.84 (s, 27H, t-Bu). 51V NMR (benzene, 20 °C, 105.2 MHz): δ -214.0 (Δv1/2 = 360 Hz). Elem. anal. Calculated for C₄₆H₇₄N₄NaO₇SV: C, 61.31; H, 8.28; N, 6.22. Found: C, 61.54; H, 8.25; N, 6.27.


Method A - 4 with pivalic anhydride and cobaltocene: A solution of 4 (0.919 g, 1.14 mmol) and cobaltocene (0.216 g, 1.14 mmol) in THF (15 mL) was cooled to -78 °C. A solution of pivalic anhydride (0.234 g, 1.14 mmol) in THF (3mL) was prepared and added dropwise to the stirring solution of 4 and cobaltocene using a stainless steel cannula. The mixture was stirred and allowed to warm to 22 °C. Upon warming, the color of the solution changed from red to black with concomitant formation of a fine precipitate. The mixture was stirred for 2 hours after which time the solvent was removed under reduced pressure. The black residue was extracted with n-pentane (2 x 20mL) and filtered through a sintered glass frit. The filtrate was concentrated and stored at -35 °C to afford a black crystalline material which was collected on a sintered glass frit via vacuum filtration and dried under reduced pressure. Yield: 0.469 g (73%).


$d_6$, 20 °C, 300 MHz): 2.20 (br). IR (thin film, KBr): 2207, 1599, 1585 cm⁻¹. $\mu_{\text{eff}}$ (Evans’s Method, benzene-$d_6$): 2.0 $\mu_B$. Elem. anal. Calculated for C$_{37}$H$_{54}$N$_4$OV: C, 71.47; H, 8.75; N, 9.01. Found: C, 71.24; H, 8.64; N, 9.085.

Method B: OPCI$_3$ and cobaltocene. A solution of 4 (0.801 g, 1.0 mmol) and cobaltocene (0.188 g, 1.0 mmol) in THF (25 mL) was cooled to −78 °C. A solution of OPCI$_3$ (0.5 mL, 5.4 mmol) in THF (55.75 mL) was prepared. An aliquot of the OPCI$_3$ solution (12 mL, 1.0 mmol of OPCI$_3$) was added via syringe to the stirring solution of 4 and cobaltocene. After the addition, the color of the solution changed from red to black. The mixture was stirred for 2 hours and allowed to warm to room temperature. The solvent was removed under reduced pressure to give a black residue. The residue was extracted into n-pentane (2 × 20 mL) and filtered through a plug of Celite and a sintered glass frit. The filtrate was concentrated under reduced pressure, and the solution stored at −35 °C to afford a black crystalline material which was collected on a sintered glass frit via vacuum filtration. Yield: 0.360 g (58%).

Method C: SOCl$_2$ and cobaltocene. This preparation was carried out using the procedure outlined in Method B with 0.801 g of 4, 0.118 g (1.0 mmol) of SOCl$_2$, and 0.190 g (1.0 mmol) of Cp$_2$Co. Yield 0.317 g (51%).

2.6.7. Synthesis of (TPP)MnOC(O)NV(N[1Bu]Ar)$_3$ (15)

A solution of ClMn(TPP) (1.83 g, 2.6 mmol) in toluene (60 mL) was prepared in a 200 mL round bottom flask. A solution of 4 (2.09 g, 2.6 mmol) in a 10:1 mixture of toluene:THF (22 mL) was similarly prepared. At 23 °C, the solution of 4 was added to the stirring solution of ClMn(TPP) in a dropwise manner over the course of 15 minutes. The reaction mixture was allowed to stir at room temperature for 18 hours. The reaction mixture was then filtered through a bed of Celite on a sintered glass frit. The filtrate was dried under reduced pressure. The resulting dark green residue was dissolved in a minimum volume of toluene (30 mL), and the solution was layered with 30 mL of n-pentane and stored at −35 °C. After standing for 7 d, a microcrystalline solid was observed to have formed in the flask. The solids were collected on a medium porosity sintered glass frit via vacuum filtration, washed once with n-pentane (10 mL), and dried under reduced pressure. Yield: 2.529 g (75%). $^{51}$V NMR (benzene, 20 °C, 105.2 MHz): δ = −72 (Δν1/2 = 1107 Hz). $\mu_{\text{eff}}$ (Evans’s Method, benzene-$d_6$): 5.1 $\mu_B$. UV/Vis $\lambda_{\text{max}}$ (M⁻¹ cm⁻¹): 475 (96000), 529 (5700), 580 (9900), 615 nm (9400). IR (Nujol mull, KBr): 1614, 1599, 1585 cm⁻¹. Elemental analysis: Calculated for C$_{81}$H$_{82}$N$_8$O$_2$MnV: C, 74.52; H, 6.33; N, 8.58. Found: C, 74.59; H 6.42; N 8.43.
2.6.8. Irradiation of (TPP)MnOC(O)NV(N[Bu]Ar)₃ (15)

A solution of 15 (0.095 g, 0.0728 mmol) in benzene (3.02 g, 3.436 mL) was prepared (0.021 M). PPh₃ (0.019 g, 0.072 mmol) was subsequently dissolved in the solution. The reaction mixture was transferred to a PTFE sealed, quartz reaction vessel. The reaction mixture was irradiated using 254 nm low-pressure Hg vapor lamps. The reaction progress was monitored by collecting the IR spectra of aliquots of the reaction mixture. Specifically, the absorbance at 2208 cm⁻¹ was tracked as this corresponds to the λₘₐₓ for pure isocyanate complex. After 58 h, the reaction was deemed complete by a lack of production of more product as assayed via IR spectroscopy. The concentration of the isocyanate complex 6 was calculated to be 0.0071 M. This corresponds to a spectroscopic yield of 34%. The proton, ⁵¹V, and ³¹P NMR spectra were collected in pyridine-d₅. No starting material could be observed as assayed by the ⁵¹V NMR spectrum. The ³¹P NMR spectrum contained four major signals. A peak at 27 ppm was attributed to OPPh₃ (38% total integration). The ³¹P resonance for pure OPPh₃ in pyridine was measured to be 27 ppm. The broad peak at −1 ppm was attributed to PPh₃ (40% total phosphorus integration). The ³¹P resonance of pure PPh₃ in pyridine was measured to be −5.7 ppm. Adding pure PPh₃ to the reaction mixture sample resulted in an increase in the intensity of the peak at −1 ppm. Other peaks were present at 129 ppm and −11 ppm.

2.6.9. Crystallographic Details

Low-temperature data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo/Kα radiation (λ = 0.71073 Å), performing ω- and ϕ-scans. All structures were solved either by direct or Patterson methods using SHELXS and refined against $F^2$ on all data by full-matrix least squares with SHELXL-97. A semi-empirical absorption correction (SADABS) was applied to the diffraction data for all structures. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups).

Complex 10 crystallizes in the space group $P2_12_12_1$ and the structure was solved using direct methods. Refinement proceeded by assigning atom positions according to the electron-density difference map. No restraints were used in the refinement. The thermal ellipsoid plot was generated using PLATON.

Complex 11 crystallizes in the space group $P2_1/n$ and the structure was solved using Patterson methods. The anilide ligands suffer from a positional disorder of the aryl moieties. The ratio of the positions was refined freely while constraining the total occupancy to unity. 1,2- and 1,3- similarity distance restraints were applied to the disordered portions of the molecule. The
anisotropic displacement parameters for all atoms were restrained using rigid bond restraints. The thermal ellipsoid plot was generated using PLATON. Complex 14 crystallizes in the space group $P2_1/n$ and the structure was solved using direct methods. Refinement proceeded by assigning atom positions according to the electron-density difference map. There are three interstitial molecules of methylene chloride in the asymmetric unit. Two of these suffer from positional disorder. The ratio of the two positions was refined freely while constraining the total occupancy to unity. The anisotropic displacement parameters of the methylene chloride units were restrained assuming rigid bond behavior. 1,2- and 1,3-distance similarity restraints were applied as well. The thermal ellipsoid plot was generated using PLATON.

Complex 15 crystallizes in the space group $Par{1}$ and the structure was solved using direct methods. Refinement proceeded by assigning atom positions according to the electron-density difference map. The anilide ligands suffer from a positional disorder of the aryl moieties. The ratio of the positions was refined freely while constraining the total occupancy to unity. A phenyl group in the porphyrin unit suffers from positional disorder. The ratio of the two positions was refined freely while constraining the total occupancy to unity. 1,2- and 1,3-similarity distance restraints were applied to the disordered portions of the molecule. The anisotropic displacement parameters for all atoms were restrained assuming rigid bond behavior. The unit cell contains 2 molecules of toluene which have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON. The thermal ellipsoid plot was generated using PLATON.
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Table 2.2. Crystal Data for [(15-crown-5)Na][OaSNV(N['Bu]Ar)$_3$] (14) and (TPP)MnOC(O)NV(N['Bu]Ar)$_3$ (15).

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2.7. References

Chapter 3. Ligand-based Conversion of CO$_2$ to CO$^*$

3.1. Introduction

3.1.1. Reduction of CO$_2$ to CO Using Metal Complexes

The reduction of CO$_2$ to CO using metal complexes has been extensively explored. Several strategies to achieve this transformation have been developed, each with certain salient features. Although by no means exhaustive, the following examples are intended to provide the reader with a few notable motifs of reactivity. A good place to begin is with the seminal work of Floriani and coworkers on the reaction of CO$_2$ with titanocene and zirconocene derivatives to produce CO and form either bridging oxo or carbonato ligands. The driving force for the reaction is the formation of the strong metal-oxygen bonds that are characteristic of oxophilic early metals. Recent investigations by Meyer and coworkers on the reactivity of low-valent uranium complexes with CO$_2$ complement this work. By tuning the steric properties of the ligand scaffold, they have shown that the reduction of CO$_2$ by uranium(III) complexes can result in the formation of monomeric $\eta^1$-OCO complexes, or result in the cleavage of the carbon-oxygen bond to make bridging oxo complexes via a bimolecular activation mechanism. This type of reductive cleavage of CO$_2$ is not limited to early metals. Peters and coworkers have shown that a low valent iron(I) tris-phosphinoborate complex reacts with CO$_2$ to cleave the carbon-oxygen bond and form the bimetallic $\pi$-$\eta^1$-CO, $\mu$-O complex. In these previously mentioned cases, the formation of the strong metal oxo bonds provide the thermodynamic driving force in the reaction, but as a result, the catalytic potential of the systems is limited. A notable catalytic system comes from the work of Sadighi and coworkers where the reduction of CO$_2$ to CO occurs with a diborane serving as both the reducing agent and oxygen acceptor. The catalyst is a copper(I) carbene complex. Here, the formation of the two boron-oxygen bonds in the final product provides the requisite driving force for cleavage of a copper-oxygen bond that forms in an intermediate step. Thus, catalytic turnover is achieved. Although each of these examples involves a different metal and ligand.

combination, a unifying feature between them is formation of metal-oxygen bonds, a potential thermodynamic sink that can shut down subsequent reactivity.

To overcome this challenge, a simple solution would be to avoid the formation of metal-oxygen bonds altogether. It was this idea that inspired the ligand-based reduction scheme. Ideally, by mediating the bond making and breaking events at the ligand scaffold of a metal complex and by keeping the metal-center coordinately saturated, the formation of metal-oxygen bonds could be avoided, but the redox-active metal center would still be available to mediate one-electron processes. In addition, by centering the transformation at a ligand, a greater variety of deoxygenation reagents could be surveyed. Thus, such a system could provide for a multitude of pathways for the conversion of CO$_2$ to CO. The key would be to find a system that could activate CO$_2$ in an early step and eventually release CO at a later step. Presented herein are the results pertaining to a successful three-step process that achieves this transformation with an anionic niobium nitride complex serving as the mediating platform.

3.1.2. Synthesis of [Na][NNb(N['Bu]Ar)$_3$]  

Treatment of the niobium(IV) isocyanate complex 8 with excess reducing equivalents in the form of 0.5% Na/Hg amalgam has been shown to produce the niobium nitride anion complex [Na][NNb(N['Bu]Ar)$_3$] (17) via decarbonylation of the isocyanate ligand (Scheme 3.1). This transformation remains one of the few examples of decarbonylation of an isocyanate ligand to give a nitride ligand. The rarity of this transformation is even more remarkable when one considers the considerable precedent for azide ligands, which are isoelectronic to isocyanate ligands, to serve as nitride installation reagents. The reactivity of the vanadium tris-anilide system that was discussed in Chapter 1 is a perfect example of the divergent behavior of isocyanate and azide complexes. Clearly, the formation of the niobium-nitrogen triple bond in complex 17 provides the necessary driving force to overcome the stability of the cyanate linkage.

![Scheme 3.1. Synthesis of [Na][NNb(N['Bu]Ar)$_3$] (17).](image)

The formation of the nitride linkage with concomitant generation of CO is a pivotal step in the CO$_2$ to CO cycle that had been envisioned at the start of the research project. However, none
of the other steps required for the cycle, namely \( \text{CO}_2 \) activation and subsequent deoxygenation, had been investigated for the niobium system. Investigating these reactions was thus undertaken.

Described herein is the discovery of a controlled method for converting \( \text{CO}_2 \) to \( \text{CO} \) using the niobium nitride complex 17 as the mediating platform. The oxygen is transferred to dehydrating reagents (e.g. organic acid anhydrides) as the oxide ion after the two-electron reduction is performed.

### 3.2. Niobium Carbamate Complex

#### 3.2.1. Synthesis and Spectral Properties

The nitride complex 17 reacts with one equivalent of \( \text{CO}_2 \) at 0 °C to form the carbamate complex \([\text{Na}][\text{O}_2\text{CNNb(N}[^{13}\text{Bu}]\text{Ar})_3]\) (18) in 81% isolated yield (Scheme 3.2). Complex 18 is isolated solvate free and has limited solubility in hydrocarbon solvents such as \( n \)-hexane, diethyl ether, or benzene. The \(^1\text{H} \) and \(^{13}\text{C} \) NMR spectra contain the expected resonances for a species with a single anilide environment. When \(^{13}\text{CO}_2 \) was used in the reaction, the \(^{13}\text{C} \) chemical shift of the carbamate group was definitively identified at 161 ppm, in agreement with the chemical shifts observed for traditional carbamate moieties.\(^{11}\) The IR spectrum contains a diagnostic stretch for the carbamate group, \( v_{\text{CO}} = 1598 \text{ cm}^{-1} \), which shifts to 1537 cm\(^{-1} \) when \(^{12}\text{CO}_2 \) is used, typical of carbamate groups.\(^{11}\)

![Scheme 3.2. Synthesis of \([\text{Na}][\text{O}_2\text{CNNb(N}[^{13}\text{Bu}]\text{Ar})_3]\) (18).](image)

Complex 18 is stable indefinitely as a solid or in solution at 23 °C under an inert atmosphere. At higher temperatures, complex 18 gives rise to the terminal oxo complex ONb(N[^{13}\text{Bu}]Ar)_3 (19, 80 h, 70 °C, THF) with sodium cyanate as the co-product, whose formation was confirmed by \(^{13}\text{C} \) NMR spectroscopy (Scheme 3.3). An analogous intramolecular metathesis has been observed in the reaction of CS\(_2 \) with the terminal nitride anion complex of vanadium 2 to give sodium thiocyanate and the terminal sulfide complex SV(N[^{13}\text{Bu}]Ar)_3.\(^{12}\) This reactivity is also consistent
with previous observations that acylimido complexes can extrude organic nitriles with formation of terminal oxo ligands.13-17

\[ \text{Scheme 3.3. Thermal conversion of } [\text{Na}[\text{O}_2\text{CNNb(N['Bu]Ar)_3}]] (18) \text{ to ONb(N['Bu]Ar)_3} (19). \]

3.2.2. Solid-State Structure of Niobium Carbamate Complex

Crystals of the carbamate complex 18 suitable for single-crystal X-ray diffraction studies were grown by encapsulating the sodium cation with two equivalents of 12-crown-4 and cooling a saturated solution of \([\text{(12-crown-4)_2Na}[\text{O}_2\text{CNNb(N['Bu]Ar)_3}]] (20)\) in 1:1 toluene:diethyl ether to \(-35 \degree C\). The solid-state structure of the complex anion reveals a terminal N-bound carbamate functional group with the oxygen atoms extended away from the niobium metal center (Figure 3.1). The short Nb–Nimido distance of 1.764(2) Å is comparable to other structurally characterized niobium imido groups (1.779 Å avg.) and is characteristic of a niobium nitrogen triple-bond.8 The C–O distances (avg. 1.236(4) Å) show significant elongation when compared to free CO\(_2\) (1.17 Å),19 but are slightly shorter than those found for organic carbamate functional groups (1.275 Å avg.).18 Although we refer to the N–CO\(_2\) functionality as an N-bound carbamate, it may be thought of as an imido ligand bearing a CO\(_2\) substituent and is closely related to the acylimido functional group, for which a number of examples have been synthesized and structurally characterized.13,15,16,20-24 The metrical parameters for the carbamate moiety are strikingly similar with those of the structurally characterized vanadium carbamate complex 10. The carbon-oxygen distances (1.245(4) Å avg.) are statistically identical as is the carbon-nitrogen distance (1.443(5) Å). It should be noted that the vanadium complex 10 contains a carbamate-sodium interaction, whereas the niobium complex 20 does not. Recent DFT calculations on these related carbamate anion complexes in the gas phase predicted very similar metrical parameters between the vanadium and niobium analogues.25 The metrical parameters predicted in that study agree well with the experimentally observed values presented here.
3.3. Deoxygenation of Carbamate Functionality via Acylation

3.3.1. Synthesis and Spectral Properties of Five-Coordinate Niobium Complexes

Deoxygenation of complex 18 became a primary goal. As discussed in Chapter 2, it had been shown that dehydrating reagents (e.g., organic acid anhydrides) reacted with the vanadium carbamate complex 4 in the presence of cobaltocene to give the vanadium isocyanate complex 6. This strategy can be thought of as derivatization with an electrophile to incorporate a carbamate oxygen into a good leaving group, thus rendering a C–O bond susceptible to reductive cleavage. Reactivity studies between the niobium carbamate complex 18 and dehydrating reagents were thus pursued to see if such a strategy could be extended beyond the vanadium system.

Treatment of a solution of the niobium carbamate complex 18 in THF with acetic anhydride at −78 °C produced a color change from pale brown to bright orange along with a colorless precipitate. After removal of precipitated sodium acetate, the product was isolated as a bright orange powder by removing solvent in vacuo and washing the residue with n-pentane (Scheme 3.4). Using a combination of $^1$H and $^{13}$C NMR spectroscopy and IR spectroscopy ($v_{\text{NCO}} = 2208$ cm$^{-1}$, $v_{\text{OCO}} = 1698$ cm$^{-1}$, Figure 3.2) the reaction product was formulated as the acetate,
isocyanate complex \((\text{AcO})(\text{OCN})\text{Nb(N'\text{Bu}\text{Ar})}_3\) \((21)\). Definitive evidence for this formulation came in the form of a solid-state structure determination \((\text{vide infra})\).

![Scheme 3.4. Synthesis of \((\text{AcO})(\text{OCN})\text{Nb(N'\text{Bu}\text{Ar})}_3\) \((21)\).](image)

This mode of reactivity can be extended to other reagents. The reaction between the niobium carbamate complex \(18\) and trifluoroacetic anhydride or pivaloyl chloride were found to produce \((\text{F}_3\text{C(O)O})(\text{OCN})\text{Nb(N'\text{Bu}\text{Ar})}_3\) \((22)\) and \((\text{'BuC(O)O})(\text{OCN})\text{Nb(N'\text{Bu}\text{Ar})}_3\) \((23)\), respectively. It is proposed that these reactions proceed through a carbamic intermediate that undergoes a rapid intramolecular rearrangement to form the five-coordinate complexes (Scheme 3.5). However, in the case of the formation of the acetate derivative \(21\), said intermediate could not be observed by \(^1\text{H}\) or \(^{13}\text{C}\) NMR spectroscopy at \(-80\, ^\circ\text{C}\), indicating that the rate of rearrangement is on par with the rate of the initial salt-elimination reaction (Figure 3.3). The proposed mechanism also implies that the carbamate carbon becomes incorporated into the isocyanate ligand, and this was confirmed by performing a \(^{13}\text{C}\) labeling study. The \(^{13}\text{C}\) chemical shift of labeled \(21\) is observed at 132 ppm, a shift characteristic of isocyanate, not carboxylate, moieties (Figure 3.3).\(^{27}\) The IR
spectrum further confirms this conclusion with the $v_{\text{OCN}}$ shifting from 2208 cm$^{-1}$ to 2149 cm$^{-1}$ and the $v_{\text{OCC}}$ remaining unchanged (Figure 3.4).

![Scheme 3.5. Proposed pathway for formation of (AcO)(OCN)Nb(N[\text{tBu}]Ar)$_3$ (21).](image)

Figure 3.3. In situ $^{13}$C NMR spectrum from the treatment of $[\text{Na}][\text{O}_2\text{CNb(N[\text{tBu}]Ar)}_3]$ (18) with Ac$_2$O. $-80^\circ$C, THF-$d_8$, 400 MHz. Starting material carbamate signal (162 ppm) and the final product isocyanate signal (132 ppm).
3.3.2. Solid-state Structures of Five-Coordinate Complexes

The solid-state structure of the acetate, isocyanate complex 21 was determined using single-crystal X-ray diffraction methods (Figure 3.5). Crystals of 21 were grown from concentrated solutions in 1:1 THF:n-pentane at –35 °C. In complex 21, the niobium center is in a pseudo-trigonal bipyramidal coordination environment with two anilide ligands and the acetate in the equatorial plane. The Nb–N_Co distance (2.156(2) Å) is considerably longer than the Nb–N_Carbamate distance (1.764(2) Å) found in complex 18. The Nb–N–C angle is 165.2(2)°. This type of five-coordinate motif is very rare for the tris-(tert-butylanilido) complexes. Other examples include the dimethyl cyanamide complex (η^2-N_CNMes)_2Mo(N[′Bu]Ar)_3, and the metallacycle complex (κ^2O,κ^1N-NC(Ph)NO)Mo(N[′Bu]Ar)_3.
Given the rarity of such five-coordinate complexes, the pivalate derivative 23 was crystallized and its solid-state structure was determined using single-crystal X-ray diffraction methods to provide a comparison (Figure 3.6). Crystals of 23 were grown from a saturated solution in diethyl ether at $-35 \, ^\circ\mathrm{C}$. Similar to what was observed for the acetate derivative 21, the niobium center in 23 adopts a pseudo-trigonal bipyramidal coordination environment with the pivalate and two of the anilide ligands in the equatorial positions. In comparing metrical parameters between the acetate derivative 21 and the pivalate derivative 23, there are only very small differences. The most noticeable difference between the two is the Nb–N–C angle of the isocyanate ligand ($165.2(2)^\circ$ for 21, $159.7(2)^\circ$ for 23), but this may simply be the result of packing effects in the crystal. In surveying structurally characterized isocyanate complexes, the range for metal-nitrogen-carbon angles is from $99^\circ$ to $180^\circ$. It should be noted that in the solid state, there are two distinct anilide positions, but in the $^1\mathrm{H}$ NMR spectrum for these compounds, only a single anilide environment is observed, albeit the resonances are broad. A likely explanation for this observation is that the anilide ligands are able to exchange positions via a Berry pseudorotation mechanism at a rate that is faster than the NMR timescale.

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3.4. Reduction Chemistry of Five-Coordinate Niobium Complexes

3.4.1. Electrochemical Studies of \((\text{RC(O)O})(\text{OCN})\text{Nb(N}[^\text{Bu}]\text{Ar})_3\) (8)

The fact that the reaction of organic acid anhydrides or acid chlorides resulted in the high-yielding formation of the carboxylate, isocyanate complexes was an exciting result for two main reasons. First, the reaction cleaves one of the C–O bonds that was originally part of CO₂. Second, upon cleavage of the C–O bond, a cyanate moiety is formed bound to the niobium metal center as an isocyanate ligand. Thus, regenerating the nitride anion complex remained a viable possibility.

In order to generate the isocyanate complex \((\text{OCN})\text{Nb(N}[^\text{Bu}]\text{Ar})_3\) (8), the precursor to the nitride complex 17, from the acetate, isocyanate complex 21, the one-electron reduction of 21 would need to result in selective dissociation of acetate ion over cyanate ion. To gain insight into the redox properties of the carboxylate, isocyanate complexes, electrochemical studies of the three analogous complexes were carried out. The cyclic voltammogram (CV) of the acetate...
derivative 21 contains three observable features (Figure 3.7). When scanning cathodically, the first redox event (I) is an irreversible reduction that occurs at -2.0 V vs. Fe/Fe⁺ \( (\text{Fc} = (\text{C}_5\text{H}_5)_2\text{Fe}) \), assigned as an Nb⁵⁺/⁴⁺ couple. If the cathodic scan is reversed after this event, a new irreversible anodic event (II) is observed at -0.9 V and is assigned to a Nb⁴⁺/⁵⁺ couple. If the cathodic scan is allowed to continue beyond -2.0 V, a reduction event (III) is observed at -2.8 V and is assigned to a Nb⁴⁺/³⁺ couple. The potentials of II and III agree with electrochemical events of complex 8 that were reported in Chapter 1 (Figure 1.5). This observation supports the hypothesis that the cathodic event I is a one-electron reduction of the niobium metal center that results in rapid dissociation of the acetate ligand to generate the isocyanate complex 8. In comparison, the CVs of the trifluoroacetate derivative 22 and the pivalate derivative 23 contain three similar features. For 22, event I is shifted to -1.7 V, this shift representing the most pronounced difference between the three CVs. This positive shift of the reduction potential is expected for the trifluoroacetate derivative since the electron-withdrawing properties of the trifluoromethyl group will make the trifluoroacetate ligand a poorer donor. This results in the niobium metal center being more electron deficient and therefore more oxidizing. Events II and III are nearly identical for all three complexes, again consistent with the idea that carboxylate dissociation occurs rapidly upon one-electron reduction of the complexes to generate the isocyanate complex 8 in each case. This reduction pathway is summarized in Scheme 3.6.
Figure 3.7. CVs of complexes (RC(O)O)(OCN)Nb(N[′Bu]Ar)₃. THF, 0.2 M [TBA][BAR₄]'₂, 300 mV/s.
3.4.2. One-electron Reduction with SmI₂

Following electrochemical measurements, the chemical reduction of the acetate, isocyanate complex 21 was studied. To carry out a one-electron reduction of 21, SmI₂ was chosen as a reducing agent given its documented selectivity for one-electron reductions of niobium(V) complexes.³¹ Treatment of 21 with SmI₂ in THF at 23 °C produced a deep purple reaction mixture. After stirring the mixture for 1 h, SmI₂(OAc) was removed, and the niobium isocyanate complex 8 was isolated as purple crystalline material in 55% yield by storing saturated solutions in n-pentane at −35 °C (Scheme 3.7).

3.4.3. Two-electron Reduction with Na/Hg Amalgam

Alternatively, reduction of 21 with excess of 0.5% Na/Hg amalgam in THF resulted in generation of the nitride anion complex 17 in 63% isolated yield, agreeing well with the 66% yield determined by ³¹H NMR spectroscopy (Scheme 3.8).
Scheme 3.8. Reduction of $(\text{AcO})(\text{OCN})\text{Nb}([\text{Bu}]\text{Ar})_3$ (21) with Na/Hg amalgam.

One hypothesis for the incomplete conversion of 21 to 17 is that under the reaction conditions, isocyanate dissociation competes with acetate dissociation upon reduction. Corroborating this idea is the observation that reduction of the trifluoroacetate derivative 22 with Na/Hg amalgam under similar conditions results in formation of the nitride anion complex 17 in 79% yield as determined by $^1$H NMR spectroscopy (Scheme 3.9). Presumably, this increased production of 17 is due to an enhanced proclivity of trifluoroacetate to undergo dissociation rather than the isocyanate ligand.

Scheme 3.9. Reduction of $(\text{F}_3\text{CC}(\text{O})\text{O})(\text{OCN})\text{Nb}([\text{Bu}]\text{Ar})_3$ (22) with Na/Hg amalgam.

3.4.4. Quantification of CO Production

To verify formation of CO during the reduction of the carboxylate, isocyanate derivatives, a two-pot, three-phase chemical trapping experiment was performed. Volatile materials produced in the reaction are transported in the vapor phase from the reaction vessel to a second vessel where $\text{Cp}^*\text{RuCl}([\text{PCy}_3])$ is present (Figure 3.8). Reaction with CO results in formation of $\text{Cp}^*\text{RuCl}([\text{PCy}_3])(\text{CO})$, which is indicated by a dramatic color change from blue to yellow as well as by clear $^3$P NMR signatures. These experiments confirm formation of gaseous CO with $\text{Cp}^*\text{RuCl}([\text{PCy}_3])(\text{CO})$ production assessed at 27% for the reduction of the acetate derivative 21 with Na/Hg amalgam and 56% for reduction of the trifluoroacetate derivative 22 with Na/Hg.
Partially accounting for the incomplete carboxylation of Cp*RuCl(PCy$_3$) is the observed formation of the hexacarbonyl niobate complex [Na(THF)$_6$][Nb(CO)$_6$], in small but reproducible yields (1-5%). Given the highly reducing conditions employed in this reaction as well as the aggressive nature of CO as a ligand, the formation of such a byproduct is not surprising and underscores the importance of developing carboxylation-resistant ancillary ligand combinations. Fickes also observed the formation of this product in the original synthesis of the nitride anion complex 17. 33

3.5. Summarizing the Cycle

In the case of acetic anhydride as the oxide acceptor, the net reaction accomplished with the simple three-step cycle is summarized in the balanced chemical equation below (Eq. 3.1):

$$\text{CO}_2 + \text{Ac}_2\text{O} + 2e^- \rightarrow \text{CO} + 2\text{AcO}^-$$  (Eq. 3.1)
The overall process is the two-electron reduction of \( \text{CO}_2 \) to \( \text{CO} \) with an anhydride serving as the oxide ion acceptor, and an essential component of the system is the coupling of sequential metal-based one-electron steps to bond-making and -breaking processes taking place at the nitrido ligand. This ligand-based approach allows for a great degree of control over the reaction pathway, giving a high degree of selectivity for the formation of \( \text{CO} \) from \( \text{CO}_2 \) (Scheme 3.10).

![Diagram of the CO2 to CO cycle](image)

Scheme 3.10. Overall \( \text{CO}_2 \) to \( \text{CO} \) cycle.

There are certain areas where improvements could be made. One of the most noticeable needs is to find a deoxygenation reagent that reacts with the carbamate complex 18 but does not react with the nitride complex 17. Both complexes are nucleophilic, and thus react readily with electrophiles. In an envisioned catalytic scheme, the deoxygenation reagent would be present in large quantities with the catalyst. The organic acid anhydrides or acid chlorides that serve this
role currently readily react with the nitride anion 17 to form the acylimido complexes. Alternative reagents should be surveyed.

Selectivity issues in the reduction of the carboxylate, isocyanate derivatives also need to be addressed. The formation of significant amounts of the oxo complex 19 during the reduction reaction is likely the result of dissociation of the isocyanate ligand occurring before dissociation of the carboxylate ligand can occur. The formation of the oxo complex 19 was always a concern. The hypothesis was that the sterically encumbering nature of the tert-butylanilide ligands would prevent the niobium metal center from expanding it coordination number from four to five, thus avoiding metal-oxygen bond formation. Modifying the system to avoid this, either through changes in the ancillary ligand set, changes in the deoxygenating reagent, or changes in the reaction conditions could be pursued.

With regard to the ancillary ligand set, modifications here might be needed for other reasons as well. The propensity for metal-amide bonds to react with CO$_2$ to form carbamate complexes is well known.$^{34}$ This type of reactivity has also been observed by Mendiratta et al. in work with titanium tris-anilide,$^{35}$ and by the author in work with vanadium tris-anilide (Chapter 4). Thus, moving to a more robust, carboxylation resistant ancillary ligand set would be desirable.

In addition to carbamate complex formation, the observed formation of the hexacarbonyl niobate complex [Na][Nb(CO)$_6$] during the reduction of the isocyanate complex 8 must be circumvented. Modification of the anilide ligands may be one solution to this obstacle, and changing the reduction conditions may be another. Specifically, exploring alternative reducing agents and investigating the feasibility of bulk electrolysis are two options.

Finally, there is some concern about the stability of the terminal nitride functionality. It has been shown that the carbamate complex 18 transforms to the terminal oxo complex 19 at elevated temperatures with loss of sodium cyanate (Scheme 3.3). As a result, the active mediating platform is lost. One solution to circumvent this would be to use an anionic terminal oxo complex as the mediating platform in place of an anionic nitride platform. By using an oxo complex, intramolecular rearrangement to lose a stable salt byproduct could not occur. Such investigations are presented in Chapter 4.

### 3.6. Related Chemistry of the Carbamate Complex

In exploring the reactivity of the niobium carbamate complex 18 for the purpose of converting CO$_2$ to CO, other important observations of reactivity were made. Notably, the niobium carbamate complex 18 reacts with other electrophiles in a way that is different than the vanadium carbamate complex 4.

In the synthesis of the niobium carbamate complex 18, treating the nitride complex 17 with no more than one equivalent of CO$_2$ is important. If excess CO$_2$ is introduced to a solution of 17 in THF, the major product in the reaction mixture is the oxo complex 19. Similarly, if a solution
of previously isolated niobium carbamate complex 18 in THF is treated with additional equivalents of CO₂, the oxo complex 19 also forms. These observations have led to the hypothesis that CO₂ serves as a catalyst for the conversion of the carbamate complex 18 to expel sodium cyanate and form the oxo complex 19. The mechanism for this transformation involves the reaction of complex 18 with CO₂ to form a carboxylic, carbamic anhydride intermediate. Given that CO₂ is the anhydride of carbonic acid and the known reactivity of anhydrides with 18, this seems feasible. If this intermediate were able to form a six-membered metallacyclic isomer, cyanate could be rapidly extruded from the complex resulting in formation of a putative niobium(V) carbonate complex (CO₃)Nb(N[′Bu]Ar)₃. Such a species would likely be unstable with respect to decarboxylation, thus regenerating CO₂ and forming the oxo complex 19 (Scheme 3.11). Clearly, this type of reactivity, although not entirely unexpected, is disadvantageous to the concept of performing the CO₂ to CO conversion in a catalytic manner.

![Scheme 3.11](image)

This type of reactivity is not limited to CO₂. The anhydride of sulfurous acid SO₂ reacts with the carbamate complex 18 in a similar fashion. Treatment of a solution of 18 in THF with a solution of SO₂ in THF results in the rapid formation of the oxo complex 19 (Scheme 3.12). Qualitatively, the reaction of 18 with SO₂ is much faster than the reaction with CO₂. In this case, multiple mechanisms can be envisioned. One possibility is a mechanism similar to what is
proposed for the reaction of 18 with CO₂. The other possibility might be the formation of a sulfurous imido complex, similar to what was observed for the reaction the vanadium carbamate complex 4 with SO₂ (Scheme 2.2), which then quickly extrudes sodium thiazate NaNSO.¹⁶

Some electrophiles react with the carbamate complex 18 to leave the carbamate linkage intact. For example, treatment of complex 18 in THF with Me₃SiCl results in formation of the silyl carbamate complex Me₃SiOC(O)NNb(N[‘Bu]Ar)₃ (24, Scheme 3.13). This complex displays spectroscopic signals that are very similar to those observed for the vanadium analogue 11. Unlike the vanadium analogue 11, complex 24 is not thermally stable. At elevated temperatures (70 °C), complex 24 converts to the oxo complex 19 and Me₃SiNCO over the course of several days (Scheme 3.13). This reactivity parallels the thermal stability of the parent carbamate complex 18.

To further compare the reactivity of the niobium carbamate complex 18 with that of the vanadium carbamate complex 4, the reactivity of 18 with alternative dehydrating regents was studied. Treatment of the carbamate complex 18 in thawing THF with one equivalent of OPCl₃ results in an immediate reaction as indicated by the color change from colorless to orange. Analysis of the reaction mixture by ¹H NMR spectroscopy revealed that the reaction proceeds to
form a complicated mixture of products. Encouraged by the clear evidence for a reaction, the treatment was modified to include cobaltocene. Treatment of a solution of 18 and cobaltocene in thawing THF with one equivalent of OPCl₃ resulted in a gradual color change from dark red to deep purple over the course of one hour with warming to room temperature. Following a workup to remove the salt by-products, the isocyanate complex 8 was isolated in 53% yield by crystallizing the product from n-pentane at −35 °C (Scheme 3.14). The yield is greater but a small amount of oxo 19 that formed in the reaction co-crystallized with the isocyanate complex 8 in subsequent crystallization crops. This observation is an exciting extension of the deoxygenation chemistry achieved with organic acid anhydrides and acid chlorides (vide supra).

![Scheme 3.14](image)

**Scheme 3.14.** Reaction of [K][O₂CNNb(N[³Bu]Ar)₃] (18) with OPCl₃ in the presence of Cp₂Co.

### 3.7. Conclusions

In conclusion, we have developed a synthetic cycle for CO₂ to CO conversion where the transformation is mediated by an anionic niobium nitride complex. These findings expand the field of CO₂ reduction chemistry and illustrate the promise of ligand-based approaches. Furthermore, this work, in conjunction with previously reported nitride transfer cycles, demonstrates the versatile chemistry available to terminal nitride ligands. To make a catalytic version of the chemistry summarized in Scheme 3.10, the nitride nucleophile must be able to discriminate between the CO₂ and the oxide ion acceptor electrophiles.

### 3.8. Experimental Section

#### 3.8.1. General Considerations.

All manipulations were carried out either in a Vacuum Atmospheres model MO-40M glove box under an atmosphere of N₂ or using standard Schlenk techniques. All solvents were degassed and dried using a solvent-purification system provided by Glass Contour. After purification, all
solvents were stored under an atmosphere of N₂ over 4 Å molecular sieves. Deuterated benzene (Cambridge Isotope Labs) was dried by stirring over CaH₂ for 24 h and was subsequently vacuum-transferred onto 4 Å molecular sieves. Deuterated tetrahydrofuran (Cambridge Isotopes Labs) was dried by stirring over sodium metal with a catalytic amount of benzophenone and subsequently vacuum-transferred onto 4 Å molecular sieves. Acetic anhydride was purified by refluxing over magnesium turnings for 48 h, distilling under vacuum, and then freeze-pump-thaw degassing. Complexes 17 and Cp*RuCl(PCy₃)₃ were prepared by literature methods. Tetra(n-butyl)ammonium tetrakis(pentafluorophenyl)borate ([TBA][BArF₄]) was synthesized using modified literature methods. All other reagents were used as supplied by the vendor without further purification. Celite 435 (EMD Chemicals), alumina (Aldrich) and 4 Å molecular sieves (Aldrich) were dried prior to use by heating at 200 °C for 48 h under dynamic vacuum. All glassware was oven dried at 220 °C prior to use. NMR spectra were obtained on either a Varian 500 Inova spectrometer equipped with a Oxford Instruments Ltd. superconducting magnet, a Bruker 400-AVANCE spectrometer equipped with a Magnex Scientific superconducting magnet, or a Varian Mercury 300 spectrometer equipped with an Oxford Instruments Ltd. superconducting magnet. Proton NMR spectra were referenced to residual C₆D₅H (7.16 ppm) or residual C₄H₁D₇O (3.58 ppm). ¹³C NMR spectra were referenced internally to naturally abundant ¹³C benzene (128.39 ppm), chloroform (77.23 ppm), or THF (67.57 ppm). ³¹P NMR spectra were referenced externally to H₃PO₄. ¹⁹F NMR spectra were referenced externally to CFCl₃. IR spectra were collected on a Perkin-Elmer 2000 FT-IR spectrophotometer. Elemental analysis was performed by Midwest Microlab, Indianapolis, IN.


A solution of 17 (2.75 g, 4.2 mmol) in THF (50 mL) was prepared in a 100 mL round-bottom Schlenk flask. The solution was cooled to 0 °C while under an atmosphere of nitrogen gas. A slight vacuum was established in the flask. While stirring the solution, a stoichiometric volume of CO₂ (0.102 L, 4.2 mmol) was added to the reaction vessel using a hypodermic needle and syringe. The reaction mixture was allowed to stir for 30 minutes at 0 °C. The reaction mixture was then placed under reduced pressure to remove solvent. n-Hexane was added to the dark brown residue, and the resulting suspension was stirred for 15 minutes. The solvent was removed under reduced pressure to give a pale brown powder. The trituration procedure was repeated. The brown powder was subsequently suspended in diethyl ether and mixture was filtered through a sintered glass frit. Complex 18 was collected as a white powder on the frit and dried under reduced pressure. Yield: 2.4 g (81%). ¹H NMR (THF-d₈, 20 °C, 500 MHz): δ 6.74 (s, 3 H, p-H), 5.82 (br, 6 H, o-H), 2.13 (s, 18 H, Ar-CH₃), 1.32 (s, 27 H, t-Bu). ¹³C NMR (THF-d₈, 20 °C, 125 MHz): δ 161.5 (s, O₂CN), 149.6 (s, ipso-Ar), 136.5 (s, o-Ar), 130.7 (s, m-Ar), 126.8 (s, p-Ar), 60.0 (s, NC(CH₃)₃), 32.3 (s, NC(CH₃)₃), 21.1 ppm (s, Ar-CH₃). IR (KBr, thin film): 2963, 2915,
2863, 1598 (vs), 1588 cm$^{-1}$. Elemental analysis was performed on crystals used for crystallographic characterization of the 12-crown-4 solvated species $\text{20} \cdot \text{C}_7\text{H}_8$ Calculated for $\text{C}_{60}\text{H}_{94}\text{N}_4\text{NaNbO}_{10}$: C, 62.81; H, 8.26; N, 4.88%. Found: C, 62.15; H, 8.32; N, 4.96%.


A solution of 18 (0.042 g) in THF-$d_6$ (0.75 mL) was prepared and loaded into an NMR tube fitted with a 14/20 joint. A PTFE valve adaptor was connected to the tube. The solution was freeze-pump-thaw degassed and then left under static vacuum. The tube was removed from the glove box and flame sealed. The reaction mixture was a homogeneous yellow solution. The NMR tube was then placed in an oil bath at 70 °C. After standing for 36 h at 70 °C, the $^1$H and $^{13}$C NMR spectra were collected. The reaction was approximately 50% complete. After 70 h, the reaction was $\geq$95% complete as assayed by the NMR spectra. After 80 h, complex 18 could not be observed by proton or $^{13}$C NMR spectroscopies. The only observable species in solution was ONb(N[^Bu]Ar)$_3$. The $^{13}$C labeled product could not be observed. A fine white precipitate could be observed on the bottom of the NMR tube. The NMR tube was returned to the glove box, cracked, and the supernatant solution was decanted away from the white solids. The solids were washed with THF (1 mL). The NMR tube containing the insoluble white powder was removed from the glove box, and extracted into D$_2$O. The solution was filtered through a glass fiber filter. The $^{13}$C NMR spectrum was collected. The only observable resonances could be attributed to THF, THF-$d_6$, and NaNCO (129 ppm).


A solution of 20 (1.25 g, 1.18 mmol) in diethyl ether (50 mL) was frozen in the cold well of the glove box. A solution of acetic anhydride (0.121 g, 1.18 mmol) in diethyl ether (5 mL) was frozen similarly. The solutions were allowed to partially thaw and subsequently combined. The reaction mixture was stirred and allowed to warm to 23 °C. After stirring for one hour, the brown solution had changed to a deep orange. The solvent was removed under reduced pressure to give an orange residue. The residue was triturated once with n-hexane to give a bright orange powder. The powder was dissolved in diethyl ether and filtered through a plug of Celite on a sintered glass frit. The filtrate was dried under reduced pressure and the resulting residue was washed with n-pentane to give a bright orange powder that was isolated via vacuum filtration. Yield: 0.625 g (73%). $^1$H NMR (benzene-$d_6$, 20 °C, 400 MHz): $\delta$ 6.59 (s, 3 H, $p$-H), 6.43 (br, 6 H, $o$-H), 2.29 (s, 3H, OC(O)CH$_3$), 2.07 (s, 18 H, Ar-CH$_3$), 1.30 (s, 27 H, t-Bu). $^{13}$C NMR (C$_6$D$_6$, 20 °C, 100 MHz): $\delta$ 172.4 (s, OC(O)CH$_3$), 151.6 (s, ipso-Ar), 136.8 (s, o-Ar), 126.7 (s, m-Ar), 126.7 (s, m-Ar), 126.7 (s, m-Ar), 65.7 (s, NC(CH$_3$)$_3$), 30.2 (s, NC(CH$_3$)$_3$), 24.5 (s, OC(O)CH$_3$) 21.5 (s, Ar-CH$_3$). IR (KBr, thin film): 2969, 2921, 2865, 2208, 1698, 1601, 1587 cm$^{-1}$. Elem. anal. Calcd. for C$_{39}$H$_{57}$N$_4$NbO$_3$: C, 64.81; H, 7.95; N, 7.75%. 96
Found: C, 66.34; H, 7.55; N, 7.32%. Crystals for 21 used in X-ray diffraction studies contained ½ equiv of THF per molecule of 21. The analyzed material was recrystallized from toluene solutions, and if ½ equiv of toluene is included in the composition calculation, the results are in better agreement with the experimental values. Calcd. for C_{42.5}H_{61}N_{4}NbO_{6}: C, 66.39; H, 8.00; N, 7.29.

3.8.5. Synthesis of (F_{3}CC(O)O)(OCN)Nb(N[\text{Bu}]Ar)_{3} (22)

A suspension of 18 (0.620 g, 0.88 mmol) in diethyl ether (20 mL) was prepared and loaded into a 100 mL round-bottom Schlenk flask fitted with a rubber septum. The solution was cooled to −78 °C. A solution of trifluoroacetic anhydride (0.185 g, 0.88 mmol) in diethyl ether (5 mL) was prepared and was added to the solution of 18 in a dropwise manner via a syringe. The reaction mixture changed from pale brown to bright orange after the addition. The solution was stirred at −78 °C for 1.5 h and subsequently allowed to warm to 23 °C. The solution was taken to dryness under dynamic vacuum. The residue (bright orange) was triturated with n-hexane (10 mL). The resulting orange powder was extracted with diethyl ether (15 mL) and the orange solution was filtered through a pad of Celite on a sintered glass frit to remove sodium trifluoroacetate. The filtrate was taken to dryness under reduced pressure and subsequently dissolved in a minimum volume of n-hexane: diethyl ether: toluene (-3 mL, 1:1:1). The solution was stored at −35 °C. After standing for 72 hours, a small amount of crystals had formed in the bottom of the vial. The solution was layered with n-pentane (3 mL) to encourage further crystal formation. After standing for another 72 hours, the crystals were collected via vacuum filtration on a sintered glass frit and washed with cold n-pentane (2 mL). The solids were dried under reduced pressure. Yield: 0.375 g (55%). \(^1\)H NMR (benzene-d₆, 20 °C, 400 MHz): δ 6.57 (s, 3 H, p-H), 6.45 (br, 6 H, o-H), 2.04 (s, 18 H, Ar-CH₃), 1.22 (s, 27 H, t-Bu). \(^{13}\)C NMR (CDCl₃, 20 °C, 100 MHz): δ 159.7 (q, J_{CF} = 37.4 Hz, OC(O)CF₃), 150.2 (s, ipso-Ar), 137.1 (s, o-Ar), 128.6 (s, m-Ar), 126.2 (s, p-Ar), 116.5 (q, J_{CF} = 292 Hz, OC(O)CF₃), 66.4 (s, NC(CH₃)₃), 30.0 (s, NC(CH₃)₃), 21.7 (s, Ar-CH₃). \(^{19}\)F NMR (benzene-d₆, 20 °C, 282 MHz): δ −74.7 (s). IR (KBr, thin film): 2974, 2917, 2863, 2212, 1722, 1599, 1585 cm⁻¹. Elem. anal. Calcd for C₃₉H₅₄F₃N₄NbO₃: C, 60.30; H, 7.01; N, 7.21%. Found: C, 60.40; H, 7.05; N, 7.32%.

3.8.6. Synthesis of (BuC(O)O)(OCN)Nb(N[\text{Bu}]Ar)₃ (23).

A solution of 18 (1.10 g, 1.56 mmol) in THF (40 mL) was prepared and loaded into a 100 mL round-bottom Schlenk flask fitted with a rubber septum. The solution was cooled to −78 °C. A solution of pivaloyl chloride (0.189 g, 1.56 mmol) in THF (10 mL) was prepared and was added to the cool solution of 18 in a dropwise manner via a syringe. The reaction mixture changed from
pale brown to bright orange after the addition. The solution was stirred at $-78 \, ^\circ\text{C}$ for 1.5 h and subsequently allowed to warm to 23 $^\circ\text{C}$. The reaction mixture was taken to dryness under reduced pressure. The resulting orange residue was triturated twice with $n$-hexane (15 mL) to give a bright orange powder. The powder was extracted into diethyl ether (30 mL) and filtered through a bed of Celite on a sintered glass frit. The filtrate was concentrated under reduced pressure to a volume of 10 mL, $n$-hexane (30 mL) was added, and the resulting mixture concentrated again to 10 mL. An orange powder began precipitating from solution at this point and mixture was stored at $-35 \, ^\circ\text{C}$ for 18 hours. The orange precipitate was collected via vacuum filtration and dried under reduced pressure. Yield: 0.810 g (68%).

$^1\text{H}$ NMR (benzene-$d_6$, 20 $^\circ\text{C}$, 400 MHz): $\delta$ 6.73 (br, 6 H, o-H), 6.66 (s, 3 H, p-H), 2.18 (s, 18 H, Ar-CH$_3$), 1.50 (s, 9 H, OC(O)C(CH$_3$)$_3$), 1.26 (br, 27 H, $t$-Bu). $^{13}\text{C}$ NMR (CDCl$_3$, 20 $^\circ\text{C}$, 100 MHz): $\delta$ 172.4 (s, OC(O)CH$_3$), 150.3 (s, ipso-Ar), 136.8 (s, p-Ar), 128.2 (s, m-Ar) 126.5 (o-Ar), 66.4 (s, NC(CH$_3$)$_3$), 40.7 (s, OC(O)C(CH$_3$)$_3$), 30.1 (s, NC(CH$_3$)$_3$), 27.8 (s, OC(O)(CH$_3$)$_3$) 21.5 (s, Ar-CH$_3$). IR (KBr, thin film): 2973, 2927, 2868, 2209, 1672, 1601, 1586 cm$^{-1}$. Elem. anal. Calcd for C$_{42}$H$_{63}$N$_4$NbO$_3$: C, 65.95; H, 8.03; N, 7.32%. Found: C, 65.70; H, 8.31; N, 7.33%.

3.8.7. Monitoring the Reaction between Acetic Anhydride and [Na][O$_2$CNNb(N[IBu]Ar)$_3$] (18) at Low Temperature via NMR Spectroscopy.

A solution of acetic anhydride (0.015 g, 0.15 mmol) in THF-$d_6$ was prepared, transferred to a medium walled NMR tube, and frozen in the cold well. A solution of 18 (0.098 g, 0.14 mmol) in THF-$d_6$ was prepared, a small amount of HMDSO was added, and the solution was added to the NMR tube and the still frozen portion of acetic anhydride solution. The NMR tube was cooled in the cold well to insure that the two solutions remained frozen. The tube was evacuated, quickly removed from the glove box, and placed in a liquid-nitrogen filled Dewar flask. The NMR tube was flame sealed. The NMR tube was placed into the spectrometer (cooled to $-80 \, ^\circ\text{C}$) while still frozen (Caution! Liquid nitrogen cooled NMR tubes can easily break when being placed into the spinners and, occasionally, will break spontaneously upon rapid temperature changes. Wear safety glasses when manipulating such tubes.). The spectrometer was locked and shimmed. The $^1\text{H}$ and $^{13}\text{C}$ NMR spectra were collected. The $^1\text{H}$ NMR spectrum contains broadened resonances and anilide containing species with inequivalent aryl-methyl and ortho-aryl proton resonances. The $^{13}\text{C}$ NMR spectrum revealed the presence of two species with the $^{13}\text{C}$ label. One of the species is unreacted 18. The other species is the product complex acetate, isocyanate complex 21. No other species could be definitively identified. The temperature of the sample was raised to $-70 \, ^\circ\text{C}$. Spectra were collected. The amount of 18 had decreased, but no other intermediate species could be observed. The temperature of the sample was raised in increments of 10 $^\circ\text{C}$ and
the spectra were collected. The anilide resonances eventually sharpened at higher temperatures, but the ortho-aroyl resonances remained very broad.

3.8.8. Reduction of 21 with SmI₂.

A solution of diiodoethane (0.277 g, 0.89 mmol) in THF (6 mL) was added to a stirring suspension of samarium (0.296 g, 2 mmol) in THF (2 mL) at 23 °C. The mixture was stirred for 1.5 h during which time the THF solution became deep blue in color. This solution was filtered through a plug of Celite and a glass fiber filter and was subsequently added to a stirring orange solution of 21 (0.625 g, 0.89 mmol) in THF (6 mL). Upon addition, the solution became deep purple in color. After stirring for 2 h, the reaction mixture was taken to dryness under reduced pressure. The residue was extracted with diethyl ether and filtered through a bed of Celite on a sintered glass frit. The purple filtrate was taken to dryness under reduced pressure, and the residue was redissolved in a minimum volume of n-pentane. The solution was stored at −35 °C to afford purple crystals. Yield: 0.315 g (55 %) in two crops. Identity of complex 8 confirmed by IR and EPR spectroscopy.

3.8.9. Reduction of 21 with Na/Hg.

A solution of 21 (0.455 g, 0.63 mmol) in THF (40 mL) was prepared at 23 °C. The solution was added to a stirring mixture of THF (10 mL) and sodium/mercury amalgam (0.116 g Na, 23 g Hg). The reaction mixture, originally a deep orange color, was allowed to stir for 12 hours. Over the course of the 12 hours, the color changed from orange to purple to brown. The reaction mixture was decanted off of the amalgam and filtered through a pad of Celite on a sintered glass frit. The filtrate was taken to dryness under reduced pressure and the residue was triturated once with toluene (10 mL) and n-hexane (10 mL). The resulting brown powder was suspended in n-pentane (50 mL) and filtered through a sintered glass frit. The off-white powder that was collected was dried under reduced pressure. Yield: 0.260 g (63%). In characterizing the product mixture by IR spectroscopy, a band at 1861 cm⁻¹ could be observed. The chemical species responsible for this absorbance was confirmed by isolating the molecule through selective crystallization from the crude reaction mixture. The bright yellow crystals were [Na(THF)₆][Nb(CO)₆]. This species could be isolated from similar treatments in varying yields (1-5%). Identity of this complex was confirmed using IR spectroscopy (νCO = 1860 cm⁻¹) and unit-cell determination via single-crystal X-ray diffraction techniques.

3.8.10. Spectroscopic yield of 17 from the Reduction of 21 with Na/Hg.

A solution of the 21 (0.054 g, 0.075 mmol) in THF (～3 mL) was prepared. The Na/Hg was prepared in a vial, allowed to cool, and then THF (～2 mL) and a stir bar were added. The solution
of 21 was added to the stirring amalgam. The reaction mixture stirred for 6 h at 23 °C. As the reaction progressed, the color of the solution changed from orange, to purple, to a ruddy brown. After 6 h, the reaction mixture was decanted away from the amalgam, filtered through a plug of Celite on a glass fiber filter, and the filtrate solution was dried under reduced pressure. The resulting brown residue was triturated once with n-hexane (2 mL) and then dried under reduced pressure. The brown solids were dissolved in a solution of hexamethyldisiloxane and deuterated benzene (0.0304 g HMDSO, 3.312 g C₆D₆, 0.0537 M HMDSO, 1.142 g of solution). The ¹H NMR spectrum was collected. A second treatment was performed in a similar manner (21 - 0.052 g, 0.072 mmol, 1.568 g of deuterated benzene solution). From the resonance integrations in the ¹H NMR spectrum, the yield of nitride 17 in the first treatment is 0.050 mmol (66%), and the yield in the second treatment is 0.048 mmol (67%). The other anilide-containing species in the product mixture are the oxo complex ONb(N'[Bu]Ar)₃ and free ligand HN'[Bu]Ar.

3.8.11. Spectroscopic Yield of 17 from the reduction of 22 with Na/Hg.

A solution of 22 (0.047 g, 0.060 mmol) in THF (3 mL) was prepared and added to freshly prepared Na/Hg amalgam (0.015 g Na, 3 g Hg). The reaction mixture was stirred for 7 h. The reaction mixture was decanted away from the amalgam and filtered through a plug of Celite on a glass fiber filter. The filter cake was washed with THF (1 mL). The filtrate was dried under reduced pressure. The resulting brown residue was triturated with n-hexane (2 mL) for 10 min and then dried under reduced pressure to give a light brown powder. The product mixture was extracted into deuterated benzene with HMDSO serving as an internal standard (0.020 g HMDSO, 1.514 g of total stock solution prepared, 1.192 g of solution used for sample). Based on the ratio of peak areas in the ¹H NMR spectrum and known concentration of HMDSO, the concentration of product complex could be determined and from that, the total yield. Yield: 0.048 mmol (79%).

3.8.12. Quantification of CO Produced from Reaction of 21 with Na/Hg via Chemical Trapping with Cp’RuCl(PCy₃).

The sodium/mercury amalgam (0.028 g Na, 5.6 g Hg) was prepared in a 100 mL round-bottom flask and was allowed to cool. Complex 21 (0.100 g, 0.14 mmol) was added, as a solid, to the flask with the sodium amalgam. The Cp’RuCl(PCy₃) (0.074 g, 0.14 mmol) was added to a separate 100 mL round-bottom flask. The two flasks were connected to a Y-shaped adaptor, and this apparatus was fitted with a 24/40 jointed, PTFE valve adapter. The apparatus was removed from the glove box and connected to the diffusion pump line. Approximately 15 mL of THF was vacuum transferred into the round bottom flask containing the 21 and sodium amalgam. The reaction mixture was vigorously stirred upon thawing, and the flask was left under static vacuum.
During the reaction, THF was observed to spontaneously transfer to the flask containing the ruthenium complex. The reduction reaction was stirred for 3 h. At this point the reaction mixture had gone from orange, to purple, to brown in color. The volatile components of the reaction mixture were transferred to the round bottom flask containing the ruthenium complex, which had begun to change from dark blue to orange. The ruthenium complex solution was stirred for one hour. The reaction vessel was taken to dryness under reduced pressure. The ruthenium-containing mixture was analyzed by $^{31}$P NMR spectroscopy. The ratio of Cp*RuCl(PCy$_3$) (40 ppm):Cp*RuCl(PCy$_3$)(CO) (52 ppm) was observed to be 73:27.

3.8.13. Quantification of CO Produced from Reaction of 22 with Na/Hg via Chemical Trapping with Cp*RuCl(PCy$_3$).

The sodium/mercury amalgam (0.030 g Na, 6.0 g Hg) was prepared in a 100 mL round-bottom flask and was allowed to cool. Complex 22 (0.099 g, 0.13 mmol) was added, as a solid, to the flask with the sodium amalgam. The Cp*RuCl(PCy$_3$) (0.070 g, 0.13 mmol) was added to a separate 100 mL round-bottom flask. The two flasks were connected to a Y-shaped adaptor, and this apparatus was fitted with a 24/40 jointed, PTFE valve adapter. The apparatus was removed from the glove box and connected to the diffusion pump line. Approximately 15 mL of THF was vacuum transferred into the round bottom flask containing the 22 and sodium amalgam. The reaction mixture was vigorously stirred upon thawing, and the flask was left under static vacuum. The reaction mixture was moderately cooled by using the evaporation of acetone at 22 °C. The reduction reaction was stirred for 6 h. At this point the reaction mixture had gone from orange, to purple, to brown in color. The volatile components of the reaction mixture were transferred to the round-bottom flask containing the ruthenium complex. The ruthenium complex solution was stirred for one hour. The reaction vessel was taken to dryness under reduced pressure. The ruthenium containing mixture was analyzed by $^{31}$P NMR spectroscopy. The ratio of Cp*RuCl(PCy$_3$):Cp*RuCl(PCy$_3$)(CO) was observed to be 44:56.


A solution of 18 (0.331 g, 0.46 mmol) in THF (5 mL) was prepared and then cooled in the cold well. A solution of Me$_3$SiCl (0.050 g, 0.046 mmol) in THF (3 mL) was prepared and cooled in the cold well. The solutions were removed after freezing, allowed to thaw, and then combined. The reaction mixture was stirred and allowed to warm to room temperature. After stirring for 1 h, the reaction mixture was yellow (no color change observed) with a small amount of precipitate. The reaction mixture was dried under reduced pressure, triturated with $n$-hexane (3 mL), dried under reduced pressure, and then extracted into diethyl ether (8 mL). The heterogeneous mixture was filtered through a plug of Celite on a glass fiber filter. The filtrate solution was dried under
reduced pressure without stirring to give a white crystalline product. Yield: 0.272 g (0.36 mmol, 79%). $^1$H NMR (benzene-$d_6$, 20 ºC, 400 MHz): $\delta$ 6.70 (br, 3 H, $p$-H), 5.97 (s, 6 H, $o$-H), 2.09 (s, 18 H, Ar-$CH_2$), 1.47 (s, 27 H, t-Bu) 0.50 ppm (s, 9 H, Si($CH_3)_3$). $^{13}$C NMR (CDCl$_3$, 20 ºC, 100 MHz): $\delta$ 153.1 (s, NC(O)OSi), 148.0 (s, $ipso$-Ar), 136.9 (s, $p$-Ar), 129.8 (s, $o$-Ar) 127.5 ($m$-Ar), 61.3 (s, NC($CH_3)_3$), 31.8 (s, NC($CH_3)_3$), 21.5 (s, Ar-$CH_2$) 0.11 ppm (s, Si($CH_3)_3$). IR (KBr, thin film): 1650, 1598, 1586 cm$^{-1}$. Elem. anal. Calcd for C$_{40}$H$_{63}$N$_4$NbO$_2$Si: C, 63.81; H, 8.43; N, 7.44%. Found: C, 63.68; H, 8.23; N, 7.43%.

3.8.15. Electrochemical Measurements.

Electrochemical measurements were made using a BAS CV-50W potentiostat with a platinum disk working electrode, platinum wire counter electrode, and a silver wire pseudoreference electrode. Potentials were internally referenced to the ferrocene/ferricenium redox couple at 0 mV. Measurements were made under an atmosphere of N$_2$ using THF solutions of 0.2 M [TBA][BAR$_4$]. The cyclic voltammograms of complexes 21, 22, and 23 were collected at sweep rates of 300 mV/s.

3.8.16. Crystallographic Details.

Low-temperature data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo/K$\alpha$ radiation ($\lambda = 0.71073$ Å), performing $\omega$- and $\varphi$-scans. All structures were solved either by direct or Patterson methods using SHELXS and refined against $F^2$ on all data by full-matrix least squares with SHELXL-97. A semi-empirical absorption correction (SADABS) was applied to the diffraction data for all structures. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the $U$ value of the atoms they are linked to (1.5 times for methyl groups).

Complex 20-C$_7$H$_8$ crystallizes in the space group $P2_1/c$, and the structure was solved using direct methods. Refinement proceeded by assigning atom positions according to the electron-density difference map. Anisotropic displacement parameters for all atoms were restrained using rigid bond restraints. Positional disorder in one 12-crown-4 molecule and the interstitial toluene molecule was refined by constraining total occupancy to unity and allowing the part percentage to refine freely. Stable refinement of both disorders required the use of 1,2- and 1,3-distance similarity restraints. The thermal ellipsoid plot was generated using PLATON.

Complex 21-$\frac{1}{2}$(C$_4$H$_6$O) crystallizes in the space group $P2_1/c$ and the structure was solved using direct methods. Refinement proceeded by assigning atom positions according to the electron-density difference map. A single molecule of THF is disordered about the inversion
center. Anisotropic displacement parameters for the atoms of this molecule of THF were restrained using rigid bond restraints. Additionally, 1,2- and 1,3-distance similarity restraints were applied within the THF molecule. The thermal ellipsoid plot was generated using PLATON.\textsuperscript{44}

Complex 23 crystallizes in the space group $P\overline{1}$ and the structure was solved using Patterson methods. Refinement proceeded by assigning atom positions according to the electron-density difference map. No restraints were used in the refinement. The thermal ellipsoid plot was generated using PLATON.\textsuperscript{44}
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<td>9136 [R(int) = 0.0859]</td>
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Table 3.2. Crystal Data for (tBuC(O)O)(OCN)Nb(N^{Bu}Ar)₃ (23).

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3.9. References


Chapter 4. Binding of CO$_2$ to a Titanium Oxo-anion*

4.1. Introduction

4.1.1. CO$_2$ Activation by Metal Oxides

The thermodynamics of binding CO$_2$ to metal oxide materials (e.g., CaO) has been an area of research for chemists for over a century.$^1$ Such research has received renewed interest in recent years for possible application in carbon capture and sequestration strategies.$^2$ Metal oxides containing lithium have been shown to be very effective at absorbing CO$_2$,$^3$ with lithium silicates and zirconates having received considerable attention for their ability to bind CO$_2$ reversibly at elevated temperatures.$^4$ In addition to sorption studies, the activation of CO$_2$ with photoactive metal oxides such as titania to give reduced carbon fragments has been a growing area of research.$^5$ In most cases, characterization of the CO$_2$ bound species is limited to IR spectroscopy,$^6$ thermogravimetric analysis, and powder X-ray diffraction studies,$^4$ thus limiting a detailed understanding of the bonding and structure in these systems.

Complementing research on heterogeneous systems, there have been numerous examples of discrete molecular systems where metal-oxygen bonds react readily with CO$_2$ to form carbonate moieties. Bridging oxide, alkoxide, and hydroxide ligands have all been shown to be capable of binding CO$_2$ through insertion reactions, and in some cases, this binding is reversible.$^7-13$ In most of these cases, because the binding of the CO$_2$ involves insertion of CO$_2$ into the metal-oxygen bond, the CO$_2$ binding is an intrinsic property of the molecule and cannot be tuned.

4.1.2. Synthesis of the Oxo complex $[(\text{Et}_2\text{O})_2\text{Li}][\text{OTi(N('Bu)Ar)}_3]$

The abstraction of halogen atoms from organic substrates by the titanium(III) complex Ti(N('Bu)Ar)$_3$ (25) is well-documented.$^{14,15}$ This propensity for halogen abstraction can extend to pseudo-halogen moieties as well and provides a viable pathway for the synthesis of unique metal

* Reproduced in part from manuscript accepted for publication: Silvia, J. S., and Cummins, C. C. Chemical Science 2011 DOI:10.1039/C1SC00215E.
complexes. One such example is the synthesis of the formate complex \( \text{HC(O)OTi(N'[Bu]Ar)₃} \) (26) from the reaction of 25 with 'BuOC(O)H, where the tert-butyl radical is expelled from the substrate.\(^{16}\) Mendiratta et al. were able to show that complex 26 reacts readily with LiN'Pr₂ to form the titanium oxo-anion complex \([\text{Et₂O}](\text{Et₂O})\text{Li}[\text{OTi(N'[Bu]Ar)₃}]\) (27) with concomitant formation of HN'Pr₂ and CO (Scheme 4.1).\(^{16}\)

\[
\text{LiN'Pr}_2 \xrightarrow{\text{Et}_2\text{O}} \xrightarrow{-116 \text{ to } 23 \text{ °C}} \xrightarrow{1 \text{ h}} \text{[Et}_2\text{O]} \text{Li} \xrightarrow{60\%} \text{HN'Pr}_2
\]

**Scheme 4.1.** Synthesis of \([\text{Et}_2\text{O}](\text{Et}_2\text{O})\text{Li}[\text{OTi(N'[Bu]Ar)₃}]\) (27).

My interest in complex 27 stems from its structural and electronic similarity with the terminal nitrido complexes of vanadium 2 and niobium 17. It was hypothesized that, as was the case with complexes 2 and 17, the overall negative charge on the oxo complex of 27 would impart enhanced nucleophilicity to the terminal oxo ligand (the oxo moiety can also be thought of as a stabilized oxide ligand). As a result, it was envisioned that 27 would react with CO₂ to give a carbonate ligand κ¹O-bound to the titanium metal center. This carbonato complex was envisioned as a potential platform for transforming CO₂ to CO. Such a system would have the advantage of avoiding the deleterious pathway of cyanate extrusion to form the oxo complex that was observed in the case of 18 (Chapter 3). The intramolecular rearrangement of the carbonate moiety is degenerate, and thus, the active binding platform cannot be lost (Scheme 4.2). With this working hypothesis, the reactivity of 27 with CO₂ was investigated, the results of which investigation are presented herein.
4.2. A Titanium Carbonate Complex

4.2.1. Carboxylation of [(Et₂O)₂Li][OTi(N[′Bu]Ar)₃]

Treatment of 27 in diethyl ether at 0 ºC with one equivalent of CO₂ produces a color change from pale yellow to bright orange in a matter of minutes. After drying the reaction mixture under reduced pressure, the product ([Li][O₂COTi(N[′Bu]Ar)₃])₆ (28), a bright yellow powder, is isolated in 69% yield via vacuum filtration after washing with n-hexane (Scheme 4.3). This simple work-up affords 28 as a pure material, as assayed by both ¹H NMR spectroscopy (Figure 4.1) and elemental analysis. Complex 28 has limited solubility in aliphatic hydrocarbon solvents such as n-hexane, but slightly better solubility in benzene. As isolated, 28 is free of ethereal solvent (e.g., diethyl ether), preliminary evidence that 28 forms an oligomeric structure. The IR spectrum of 28 contains a very broad absorbance at 1590 cm⁻¹, overlapping with stretching modes of the aryl moieties of the ligand and precluding definitive evidence for the carbonate moiety. Definitive identification of the carbonate moiety came from performing a ¹³C labeling study. After repeating the synthesis of 28 with ¹³CO₂, analysis of the reaction mixture by ¹³C NMR spectroscopy revealed a strong resonance at 160 ppm (Figure 4.1), characteristic of carbonates.⁵¹⁷,¹⁸

Scheme 4.2. Intramolecular rearrangements of terminal carbamate (top) and carbonate (bottom) fragments.
Scheme 4.3. Synthesis of [(Li)[O₂COTi(N('Bu)Ar)₃]₆ (28).

Definitive structural assignment of carbonate complex 28 came from the determination of its solid-state structure via single-crystal X-ray diffraction techniques (Figure 4.2). Crystals of 28 were grown by slowly concentrating solutions of 28 in benzene at ambient temperatures.
Complex 28 forms a hexamer in the solid state with a hexagonal prismatic core formed from the lithium countercations bridged by oxygen atoms of the carbonate moiety (Figure 4.3). The laddering of carboxylates and heterocarboxylates is a common structural motif. The carbonate ligand adopts a $\kappa'^{1}O$-cooordination mode to the titanium center and a pseudo-$\kappa^{2}O_{2}$-coordination mode to the lithium ion (Figure 4.2). The titanium–oxygen interatomic distance in 28 (1.849(2) Å) is significantly longer than the titanium–oxygen distance found in the oxo complex 27 (1.712(2) Å). This lengthening is likely the result of a significant decrease in the $\pi$-bonding between the titanium and oxygen atom, which is supported by DFT calculations (vide infra). The titanium-oxygen $\pi$-bond in 27 is anti-bonding with respect to the titanium-anilide $\sigma$-bonds, and as expected, the titanium-anilide distance is shorter in 28 (1.930(3) Å) than in 27 (1.990(4) Å). The Ti–O–C angle in the carbonate complex 28 is nearly linear (174.7(2)°). A search of the Cambridge Structural Database reveals that such a linear linkage is rare for carbonate ligands. The only example of a more linear M–O–C linkage is found in the bimetallic complex [Cp²Ti₂][μ-$\kappa^{1}$-$\kappa^{2}$-CO₃] (175.43°). In this example, the steric bulk of the Cp² ligands force the metal centers apart, thus preventing the carbonate ligand from binding $\mu-$-$\kappa^{2}:\kappa^{2}$, as is observed in the parent titanocene derivative [Cp₂Ti₂][μ-$\kappa^{2}:\kappa^{2}$-CO₃].
Figure 4.2. Solid-state structure of the asymmetric unit of ([Li][O_{2}COTi(N^3Bu)]_{6}) (28).

Thermal ellipsoids are drawn at 50% probability, and hydrogen atoms and interstitial molecules of benzene have been omitted for clarity.

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$R_3$

$Z = 18$

$R(F) = 0.0560$

$R_w(F^2) = 0.1485$
Figure 4.3. Solid state structure of \([\text{Li}_6\text{O}_2\text{COTi(N[Bu]Ar)_3}]\_6\) (28). Thermal ellipsoids are drawn at 50% probability, and hydrogen atoms and interstitial molecules of benzene have been omitted for clarity.

4.2.3. Solution-Phase Structure

To determine whether or not the hexameric structure of 28 persists in solution, the solution phase molecular weight was measured using \(^1\text{H}\) DOSY NMR techniques. As was shown by Waldeck et al., the diffusion coefficients of two molecules in the same solvent are proportional to the cube root of the inverse ratio of the molecular weights (Eq. 4.1). Two assumptions are made in deriving this relationship: 1) the Stokes-Einstein theory of diffusion holds for the molecules of interest, and 2) the molecules can be approximated as uniform spheres.
The complex [((12-crown-4)Li)[OTi(N'[Bu]Ar)]_3] (29) was selected as an external reference. The 12-crown-4 ensures that 29 remains monomeric in solution by satisfying the coordination sphere of lithium. A salt was selected to stay as consistent as possible to the nature of the carbonate 28. The diffusion coefficient of 29 was determined to be $6.6 \times 10^{-10}$ m$^2$/s and the diffusion coefficient of 28 was determined to be $3.8 \times 10^{-10}$ m$^2$/s (Figure 4.4). Using the relationship from Eq. 4.1 and the molecular weight of 29 as 775.68 g/mol, the calculated value of the molecular weight of carbonate 28 is 4064 g/mol. This value is very close to the expected value of 3862 g/mol for the molecular weight of the hexamer 28. This is taken as strong evidence that the hexameric structure of 28 observed in the solid state persists in solution in the absence of strongly coordinating agents.

\[
\frac{D_1}{D_2} = \sqrt[3]{\frac{MW_2}{MW_1}} \quad \text{Eq. 4.1}
\]
4.2.4. Functionalization Reactions

Functionalization of 28 can be achieved using select electrophiles. Treatment of 28 with one equivalent of Me$_3$SiOTf in diethyl ether produced a gradual color change of bright orange to red with concomitant formation of a colorless precipitate. Analysis of the crude reaction mixture by $^1$H NMR spectroscopy confirmed formation of a single product assigned as the trimethylsilyl carbonate complex Me$_3$SiOC(O)OTi(N['Bu]Ar)$_3$ (30, Scheme 4.4). Complex 30 was isolated in crystalline form by storing saturated solutions of 30 in diethyl ether at $-35$ °C. The IR spectrum of the isolated material contains a strong absorbance at 1691 cm$^{-1}$ that can be attributed to v$_{CO}$ of the carbonate ligand. The solid-state structure of 30 was determined by X-ray diffraction methods (Figure 4.5). The carbon-oxygen distances in the carbonato ligand are reasonable for the expected carbon-oxygen single and double bonds (1.336(3) and 1.197(3) Å). The titanium-oxygen interatomic distance (1.857(2) Å) is only slightly longer than the titanium-oxygen distance found in the lithium carbonate 28 (1.849(2) Å) indicating little change in the bonding interaction between the titanium and the oxygen upon silylation.
The stability of the carbonate moiety in 28 after functionalization is strongly dependent on the nature of the electrophile. Treatment of 28 with one equivalent of 'BuC(O)Cl in diethyl ether resulted in formation of a white precipitate and an observed color change of yellow to orange. Analysis of the reaction mixture by $^1$H NMR spectroscopy confirmed clean formation of a single anilide-containing product. The IR spectrum of the crude reaction mixture contained a strong absorbance at 1680 cm$^{-1}$, characteristic of a $\nu_{CO}$ stretching mode for a carbonyl moiety. In the case where the salt elimination proceeds without further reaction, it is expected for an anhydride moiety to have two IR active modes, symmetric and antisymmetric stretching. The single IR absorbance in the carbonyl region led to the hypothesis that the reaction proceeds to form the pivalate complex $^’$BuC(O)OTi(N'[Bu]Ar)$_3$ with loss of CO$_2$ (31, Scheme 4.4). This was confirmed through independent synthesis of 4 from the reaction of $^’$BuC(O)Cl with 27. It is not clear when CO$_2$ loss occurs in the reaction of 28 with $^’$BuC(O)Cl, but it is tempting to hypothesize that the expected salt elimination occurs to give an intermediate anhydride complex that then undergoes a rapid intramolecular rearrangement to lose CO$_2$ (Scheme 2). This hypothesis is consistent with the previously observed reaction of organic acid chlorides and acid anhydrides.
with the niobium carbamate complex 18 to give the five-coordinate complexes of the type \((\text{RC(O)O})(\text{OCN})\text{Nb(N'[\text{Bu}]\text{Ar})_3}\) (Chapter 3).

The ultimate goal of these functionalization reactions was to deoxygenate the carbonate position with concomitant production of CO and regeneration of the oxo complex 27, similar to what was developed for the niobium nitride system. Although loss of CO\(_2\) was observed in the reaction of carbonate 28 with pivaloyl chloride, it was thought that it might be possible to intercept the presumed carbonic anhydride intermediate with a reducing agent, as was achieved in the closely related vanadium carbamate system (Chapter 2). Carrying out the treatment of 28 with pivaloyl chloride in the presence of two equivalents of cobaltocene did not alter the course of the reaction, and the pivalate complex 31 formed cleanly.

After observing this result, I attempted to find a suitable oxygen abstraction reagent. The vanadium(III) tris-anilide complex 1 was selected for initial studies given the thermodynamically favorable formation of the oxo complex 5 (V=O BDE: 165 kcal/mol). Treatment of carbonate 28 with 1 in diethyl ether gave no reaction. This is likely the result of the hexameric structure of 28 coupled with the steric bulk of the anilide ligands precluding access to the carbonate moiety.
Attempts to perform the reaction in solvents that would break up the hexameric structure of the carbonate 28 (i.e., THF) suffered from either the loss of CO$_2$ from 28 (vide infra), or if performed under an atmosphere of CO$_2$, unwanted formation of car bamates through insertion of CO$_2$ into the metal-anilide bonds. This type of CO$_2$ insertion reactivity has been observed before in these systems. Specific to the vanadium complex 1, it was discovered that reaction with excess CO$_2$ results in complete conversion of the anilide ligands into carbamate ligands and generation of the tris-carbamate complex V(O$_2$CN[Bu]Ar)$_3$ (32). Complex 32 adopts a dimeric structure in solid state with two bridging carbamate ligands (Figure 4.6).

![Figure 4.6. Solid-state structure of V(O$_2$CN[Bu]Ar)$_3$ (32).](image)

- V1 - O381: 1.985(2) Å
- V1 - O382: 1.929(2) Å
- V1 - O281: 2.032(2) Å
- V1 - O282: 2.056(2) Å
- V1 - V1A: 4.202 Å

C2/c
Z = 8
R(F) = 0.0535
R$_w$(F$^2$) = 0.1552

4.3. Solvent Effects on the Binding of CO$_2$ to Oxo Anion.
4.3.1. Affecting Loss of CO₂ with Addition of 12-crown-4

Having shown that carbonate 28 exists as a hexamer in the solid state and in solutions of benzene, the question of whether 28 could be isolated as a monomeric species arose. Having shown that the vanadium carbamate complex 4 could be induced into a monomeric bonding motif with the introduction of 15-crown-5 to partially complete the coordination sphere of the sodium countercation, it was proposed that 28 could be forced to be monomeric by adding one equivalent of 12-crown-4 to partially sequester the lithium countercation. Treatment of carbonate 28 with one equivalent of 12-crown-4 in diethyl ether at 22 °C resulted in the formation of a bright yellow solution. Upon introduction of dynamic vacuum to the reaction vessel, the color of the solution changed from bright yellow to nearly colorless within a matter of seconds. After drying the material completely, analysis via ¹H NMR spectroscopy revealed a single anilide containing species in the appropriate 1:1 ratio with the 12-crown-4. The IR spectrum of the material revealed that the stretches attributed to the carbonate linkage were no longer present. From this information, it was hypothesized that addition of the 12-crown-4 ether had effected the release of CO₂ from 28 to generate the oxo complex 29, which was confirmed by comparing the spectroscopic signatures of the isolated product to independently synthesized material (Scheme 4.5).

$$\text{Scheme 4.5. Synthesis of } [(12\text{-crown-}4)\text{Li}[\text{OTi(N}[\text{tBu}]\text{Ar}]_3]\text{ (29) from } [(\text{Li})[\text{OCOTi(N}[\text{tBu}]\text{Ar})_3]_6\text{ (28) via loss of CO}_2].$$

The fact that CO₂ loss from carbonate 28 occurs upon the addition of the 12-crown-4 was surprising at first, but could be rationalized in retrospect. The formation of the hexameric structure in 28 results in the generation of several lithium-oxygen interactions. These multiple interactions satisfy the electrophilicity of the lithium cation without the need of external coordinating reagents. When this network of bonds is disrupted and the electrophilicity of the lithium cation is satisfied through coordination by the 12-crown-4, the entropically favored release of CO₂ occurs.
4.3.2. Determination of Thermodynamic Parameters for CO₂ Binding

With qualitative evidence that the binding of CO₂ to the oxo complex 27 is dependent on the solvent composition and coordination environment of the lithium cation, I sought to quantify this dependency. To study this phenomenon, variable temperature ¹H and ¹³C NMR spectroscopy studies of the reaction between ¹³CO₂ and oxo complex 27 were performed in flame-sealed NMR tubes. The equilibrium constant for the reaction could be determined by measuring the concentration of the reactants and products in solution via NMR spectroscopy.

In the case where 27 was dissolved in toluene-ᵈ with no additional additives, the reaction goes to apparent completion at 23 °C within the limits of the sensitivity of the NMR spectrometer. However, when 27 is dissolved in THF-ᵈ, the reactant oxo complex 27 and product carbonate 28 can be observed and resolved in the ¹H NMR spectrum (Figure 4.7). If ¹³CO₂ is used, the presence of free ¹³CO₂ and 28 is also clear in the ¹³C NMR spectrum. When the temperature of the sample is varied, the ratio of reactants and products shifts in a manner consistent with an associative process. After measuring the concentration of the reactants and products in solution, the equilibrium constant could be determined. By plotting \( \ln K \) vs. \( 1/T \), the thermodynamic parameters for the reaction could be calculated (Figure 4.9). The results of the study indicate that the Δ\( H \) of the reaction is small and negative (−9.7 ± 0.3 kcal/mol) and the Δ\( S \) of the reaction is negative (−23 ± 1 cal/mol*K). Changing the coordination sphere of the lithium cation changes the thermodynamic parameters of the reaction. From the treatment of the 12-crown-4 capped oxo 29 with excess CO₂ in toluene-ᵈ, the value of Δ\( H \) for the reaction is −11 ± 0.3 kcal/mol and the Δ\( S \) of the reaction is −31 ± 1 cal/mol*K. A hypothesis to explain this observation is that the nucleophilicity of the terminal oxo ligand is not sufficient to irreversibly bind CO₂, in contrast to the similar nitride materials,²⁷,²⁸ and that the high charge density of the lithium cation is integral for effective binding. Changing the coordination sphere of the lithium perturbs the charge density on the lithium and thus affects the reaction equilibrium.
Figure 4.7. Variable temperature $^1$H NMR spectra for the reaction of excess CO$_2$ with \([\text{Et}_2\text{O}]_2\text{Li}[\text{OTi(N'\text{Bu}Ar)}_3]\) (27). Aliphatic region, 500 MHz, THF-$d_8$.

Figure 4.8. Variable temperature $^1$H NMR spectra for the reaction of excess CO$_2$ with \([\text{(12-crown-4)Li}]_2[\text{OTi(N'\text{Bu}Ar)}_3]\) (29). Aliphatic region, 500 MHz, toluene-$d_8$. 

123
Another factor affecting the equilibrium is the bonding environment of the oxo ligand. In 27, the short titanium-oxygen distance observed in the solid state is taken as evidence for the existence of the titanium-oxygen triple bond. To bind a molecule of CO₂, one likely mechanism is nucleophilic attack by the oxo ligand on the carbon position in CO₂. The lithium cation may serve in a cooperative role and help stabilize the transition state as well as the product. In this process, we hypothesize, with inference from the solid-state structure of 28, that the titanium-oxygen distance elongates significantly and the titanium-oxygen bonding interaction weakens significantly. Although the titanium(IV) center is likely very electrophilic, the combined acidity of the lithium cation and carbon dioxide is great enough to weaken the titanium-oxygen bond, reducing the bond order from a triple bond to a single bond. When 12-crown-4 is present and the electrostatic need of the lithium cation is satisfied, the electrophilicity of the titanium center wins out, and reformation of the oxo ligand and dissociation of CO₂ becomes favorable. Such a structural rearrangement might also result in significant changes in the distribution of charge in the molecule thus accounting for the observed change in the ΔS value when solvents with different dielectric constants are used.

4.4. **Countercation Effects on the Binding of CO₂**

After observing that only minor changes to the coordination environment of the lithium countercation dramatically effects the ability of 27 to bind CO₂, it became of interest to study the effect of replacing the countercation. The sodium and potassium derivatives of 27, NaOTi(N[3'Bu]Ar)₃ and KOTi(N[3'Bu]Ar)₃ (33 and 34, respectively), can be synthesized from the formate complex 26 in a manner analogous to the original synthesis of the lithium salt 27 with NaN(SiMe₃)₂ or KN(SiMe₃)₂ replacing LiNPr₂ as the external base (Scheme 4.6). Complex 33 was isolated from the reaction mixture as the THF solvate [(THF)Na][OTi(N[3'Bu]Ar)₃] in 97% yield. Complex 34 was isolated from the reaction mixture as a solvate-free dimer [KOTi(N[3'Bu]Ar)₃]₂ in 66% yield, the structure of which has been determined by crystallographic methods (Figure 4.10). In the solid state, the potassium countercations bridge the oxo ligands of two molecules and interact with the aryl moieties of the anilide ligands of both titanium centers. This aryl ring-alkali metal cation interaction is a common structural motif for anionic tris-anilide complexes with basic terminal ligands.²⁹⁻³¹ There is a slight shortening of the Ti–O distance in 34 (1.680(2) Å) when compared with lithium derivative 27 (1.712(2) Å).


The observation that the sodium and potassium hexamethyldisilazides react with the formate complex 26 was somewhat unexpected. The mechanism for the formation of the oxo anion complex is proposed to involve deprotonation of the formate ligand to generate the anion complex [OCOTi(N[3'Bu]Ar)₃]⁻ that then decarbonylates. Given the fact that the pKₐ of hexamethyldisilazane (29.5 in THF) is significantly lower than the pKₐ of di-isopropylamine (35.7 in THF),³² it was surprising that the silazide would be a potent enough base to perform the requisite deprotonation.
4.4.2. CO$_2$ Binding to [Na][OTi(N'Bu)Ar]$_3$ and [K][OTi(N'Bu)Ar]$_3$

Treatment of a solution of the sodium oxo complex 33 in benzene with a slight excess of $^{13}$CO$_2$ (1.5-2 equivalents) results in a rapid color change from pale yellow to orange. Analysis of the reaction mixture in situ reveals that the starting oxo complex is completely consumed. The product displays multiple ligand environments according to both $^1$H and $^{13}$C NMR spectroscopy indicating possible aggregation in solution to form various oligomers or multiple ligand environments as a result of asymmetric ligand orientations that exchange on a timescale slower than that of NMR spectroscopy. Similarly, the $^{13}$C NMR spectrum contains at least two distinct signals that can be attributed to a carbonate moiety (162 and 161 ppm). To definitively confirm the formation of the carbonate complex [Na][O$_2$CTi(N'Bu)Ar]$_3$ (35) in this case, the reaction mixture was subsequently treated with Me$_3$SiCl. As a result, the silyl carbonate complex 30 formed from the in situ generated carbonate complex (>90% conversion) with concomitant formation of NaCl (visible as a white precipitate). The generation of 30 was clear from the diagnostic peaks in the $^1$H NMR spectrum and from a strong resonance at 152 ppm in the $^{13}$C
NMR spectra. Similar results are observed when a solution of the potassium analogue 34 in benzene is treated with $^{13}$CO$_2$. The produced carbonate complex [K][O$_2$COTi[N[Bu]Ar)$_3$] (36) gives rise to multiple, broad signals in the $^1$H NMR spectrum and a broad signal in the $^{13}$C NMR spectrum centered 163 ppm. Treatment of 36 with Me$_3$SiCl in situ again results in formation of the silyl carbonate complex 30 as the major anilide-containing product. Thus, in benzene solutions, the sodium and potassium derivatives of the titanium oxo complex effectively bind CO$_2$.

When benzene is replaced by THF, the binding of CO$_2$ becomes less favorable. Treatment of solutions of 33 or 34 in THF results in a rapid color change from yellow to orange. From the $^1$H NMR spectra, it appears that oxo complexes 33 and 34 form a dynamic equilibrium mixture with the respective carbonate complexes 35 and 36. In these cases, the rate of oxo to carbonate exchange appears to be faster, qualitatively, than was observed in the equilibrium of 27 with 28 in THF on the basis of the breadth of the $^1$H NMR signals. When the sodium complex 33 is treated with $^{13}$CO$_2$ at 22 °C, the resonances of the oxo and carbonate complex are distinct but much broader than the resonances observed when the lithium derivative 27 is treated in a similar manner. This broadening is also observed in the $^{13}$C NMR spectrum for both the carbonate carbon signal at 162 ppm and free CO$_2$ signal at 126 ppm. In the case of the potassium derivative 34, the $^1$H NMR spectrum contains only a single set of peaks attributable to an anilide species. The chemical shift of the resonances is very close to that of pure 34, but the peaks are broader (o-Ar, $\Delta \nu_{1/2} = 6$ Hz for 34 vs. 50 Hz for 36). In the $^{13}$C NMR spectrum, two broad signals centered at 163 ppm and 130 ppm are assigned to the carbonate moiety and free CO$_2$, respectively. The broadening and coalescence of the resonances attributed to the complexes are taken as evidence for a faster rate of CO$_2$ binding and release. Faster rates would be expected if the alkali metal counterion does not interact strongly with the negatively charged oxo or carbonato ligand, as this would facilitate both the binding and release of CO$_2$. The more diffuse positive charge of sodium and potassium would likely give rise to such an effect.

A variable temperature NMR study in THF-d$_8$ was undertaken to provide definitive evidence for the presence of both the oxo and carbonate complexes in these treatments and possibly measure the thermodynamic parameters of the reactions. In the treatment of 33 with $^{13}$CO$_2$ in THF, cooling the sample resulted in a sharpening of the signals and a shift in the equilibrium to favor the formation of 35 (Figure 4.11). However, a locking out of aryl moiety rotation about the ipso-C–N bond complicated the spectral assignment, eventually superseding the sharpening in proton resonances. In the case of the reaction of $^{13}$CO$_2$ with 34, cooling the solution to -40 °C did allow for the observation of two sets of anilide resonances that were attributed to 34 and 36, but their resolution at this temperature was poor (Figure 4.12). For these reasons, the concentration of the reactants and products could not be measured using NMR spectroscopy, thus preventing the determination of the thermodynamic parameters for CO$_2$ binding to 33 and 34. However, the general trend of CO$_2$ binding becoming more favorable at lower temperatures was confirmed.
Figure 4.11. Variable temperature $^1$H NMR spectra of the treatment of [Na][OTi(N[Bu]Ar)$_3$] (33) with $^{13}$CO$_2$. Aliphatic region, 500 MHz, THF-$d_4$.

Figure 4.12. Variable temperature $^1$H NMR spectra of the treatment of [K][OTi(N[Bu]Ar)$_3$] with $^{13}$CO$_2$, Aliphatic region, 500 MHz, THF-$d_6$. 128
Attempts to isolate either 35 or 36 as a pure solid met with varying levels of success. Preparative scale treatments of the potassium salt 34 with CO₂ in toluene at 0 ºC produced the previously observed color change of pale yellow to orange. After removing the solvent under reduced pressure, washing the reaction mixture with n-pentane resulted in formation of a white powder that could be collected via vacuum filtration. Analysis of this material by ¹H NMR spectroscopy revealed this material to be the starting oxo complex 34. Treatments of 34 with CO₂ in diethyl ether met with similar results. Treatments of the sodium salt 33 with CO₂ in diethyl ether at 0 ºC met with more success, but complete consumption of the starting oxo complex could never be achieved. However the carbonate complex 35 could be isolated in the solid state in these treatments as a mixture with 33 as assayed by ¹H NMR spectroscopy. These synthetic observations agree with the trends determined in the NMR studies that CO₂ binding to lithium derivative 27 > sodium derivative 33 > potassium derivative 34.

4.4.3. Synthesis, Solid-State Structure, and Reactivity with CO₂ of [(2,2,2-crypt)K][OTi(N[²Bu]Ar)₃]

To study the effect of removing direct bonding interactions between the countercation and the anionic oxo complex, the alkali metal counter cation was sequestered using a cryptand molecule. Treating 34 with one equivalent of 2,2,2-crypt provides the oxo anion complex [(2,2,2-crypt)K][OTi(N[²Bu]Ar)₃] (37), which has been structurally characterized (Figure 4.13). In the solid-state structure of 37, the Ti–O interatomic distance is short (1.663(1) Å), representing a contraction of about 0.05 Å compared to the Ti–O distance in 27 (1.712(2) Å) and a contraction of about 0.02 Å compared to the Ti–O distance in 34 (1.680(2) Å). This contraction of the Ti–O distance is likely the result of a strengthening of electrostatic interaction between the oxo ligand and the titanium metal center as the electrostatic interaction between the alkali metal countercation and the oxo ligand is no longer present.
When a solution of 37 in THF-$d_8$ is treated with an excess of $^{13}$CO$_2$ (~3 equiv), analysis via $^1$H NMR spectroscopy reveals the proton NMR resonances of the anilide ligands have shifted negligibly (Figure 4.14). The $^{13}$C NMR spectrum contains a diagnostic carbonate peak centered at 168 ppm and substantial amounts of free $^{13}$CO$_2$ is observed (Figure 4.15). The single set of resonances in the $^1$H NMR spectrum is proposed to be the result of signal averaging between a oxo and carbonate complex that are exchanging at a rate on the time scale of NMR spectroscopy, similar to what was observed for the treatment of 34 with CO$_2$ in THF (vide supra).
Figure 4.14. $^1$H NMR spectrum for the treatment of [(2,2,2-crypt)K][OTi(N[Bu]Ar)$_3$] (37) with $^{13}$CO$_2$. 22 °C, 125 MHz, THF-$_2$O. Resonances at 1.30 and 2.15 ppm are attributed to HN[Bu]Ar.

Figure 4.15. $^{13}$C NMR spectrum for the treatment of [(2,2,2-crypt)K][OTi(N[Bu]Ar)$_3$] (37) with $^{13}$CO$_2$. 22 °C, 125 MHz, THF-$_2$O.
4.5. DFT Calculations on CO\textsubscript{2} Binding

4.5.1. Cation Effect on Bonding Geometries and Bonding Energy

To provide insight into energetic effects of the different counterions on CO\textsubscript{2} binding, DFT calculations were performed. The optimized geometry of the lithium carbonate 28 contains a carbonato ligand in a $\kappa^1$O-titanium, $\kappa^2$O-lithium binding motif (Figure 4.16). The titanium-oxygen distance (1.857 Å), titanium-bound oxygen-carbon distance (1.326 Å), and titanium-oxygen-carbon angle (174.34°) all agree well with crystallographically measured values. A vibrational-mode analysis of the optimized geometry predicts the $\nu_{CO}$ stretching band to be observed at 1585 cm\textsuperscript{-1}, in good agreement with the experimentally observed value of 1590 cm\textsuperscript{-1}. Similarly, the chemical shift of the carbonate carbon was predicted to be 162 ppm, in good agreement with the experimentally observed signal at 160 ppm (Table 4.1). The agreement with observed structural and spectroscopic values supports the notion that the simplified monomeric model is sufficiently similar to the hexamer for the purpose of our analysis. The lone pairs of the nitrogen atoms of the anilide ligands dominate the HOMO of the model complex. An analysis of the frontier molecular orbitals from the DFT calculations reveals no clear $\pi$-bonding interactions between the titanium and the bound oxygen atom. Earlier DFT computational studies of the oxo complex 27 had revealed a substantial degree of $\pi$-bonding between the titanium and oxo ligand.\textsuperscript{16} This change in the bonding agrees well with our earlier hypothesis based on the structural data. Bonding to CO\textsubscript{2} likely results in a contraction and lowering in the energy of the $p$-orbitals at the bound oxygen, making the bonding interaction with the titanium much less favorable. Such effects on bonding have been observed previously when terminal oxos were functionalized with Lewis acids.\textsuperscript{33} This apparent weakening of the titanium-oxygen bond contrasts sharply with the analogous niobium nitride system. In that system, the short niobium-nitrogen interatomic distance persists in going from the terminal nitride to the N-bound carbamate complex and was taken as support for assigning the presence of a niobium-nitrogen triple-bond in both the nitride and carbamate complexes.\textsuperscript{28}

<table>
<thead>
<tr>
<th>Table 4.1. Calculated Chemical Shielding Constant and Corrected Chemical Shift for CO\textsubscript{2} and 28.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated Isotropic Chemical Shielding Constant ($\sigma$)</td>
</tr>
<tr>
<td>-------------------------------------------------------------</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
</tr>
<tr>
<td>28</td>
</tr>
</tbody>
</table>

\textsuperscript{a) Reference vs. CO\textsubscript{2} in THF-$d_6$ at 125.69 ppm
When the lithium countercation is replaced with a different alkali metal cation and the geometry reoptimized, small changes in the structural parameters are observed (Table 4.2). The general trend is that the Ti1-O1 distance decreases, the O1-C1 distance increases, and the O21-C1-O22 angle becomes more obtuse in moving down the alkali metal period. Furthermore, the calculated $\Delta E$ associated with going from the free alkali metal cation, CO$_2$, and oxo anion complex to the final carbonate complex increases upon descending the alkali metal group, in good agreement with the empirical evidence (Table 4.3).

![Figure 4.16. Optimized geometry of [Li][O$_2$COTi(N$^{t}$Bu)Ar$_3$].](image)

**Table 4.2.** Optimized metrics for the complex [M][O$_2$COTi(N$^{t}$Bu)Ar$_3$].

<table>
<thead>
<tr>
<th></th>
<th>Li</th>
<th>Na</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti1–O1 (Å)</td>
<td>1.856</td>
<td>1.839</td>
<td>1.818</td>
</tr>
<tr>
<td>O1–C1 (Å)</td>
<td>1.326</td>
<td>1.351</td>
<td>1.360</td>
</tr>
<tr>
<td>C1-O21/O22 (Å, avg.)</td>
<td>1.275</td>
<td>1.268</td>
<td>1.263</td>
</tr>
<tr>
<td>O21–C1–O22</td>
<td>121.91</td>
<td>125.15</td>
<td>126.54</td>
</tr>
</tbody>
</table>
Table 4.3. Calculated $\Delta E$ (kcal/mol) values for the association reaction:

\[ M^+ + CO_2 + [OTi(N'[Bu]Ar)_3]^- \rightarrow [M][O_2COTi(N'[Bu]Ar)_3]. \]

<table>
<thead>
<tr>
<th></th>
<th>Li$^+$</th>
<th>Na$^+$</th>
<th>K$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E$</td>
<td>-138.42</td>
<td>-110.85</td>
<td>-92.25</td>
</tr>
</tbody>
</table>

Interestingly, if the geometry for the carbonate anion [$O_2COTi(N'[Bu]Ar)_3]^- is optimized without an alkali metal cation present, the energy minimum corresponds to complete dissociation of $CO_2$ from the molecule (Figure 4.17). The final coordinates reveal the oxo anion complex with structural parameters in good agreement with the parameters of the structurally characterized oxo anion in 37, and a molecule of $CO_2$ with structural parameters consistent with the reported values of gaseous $CO_2$.

This result further confirms the hypothesis that the alkali metal cation is playing a critical role in the stabilization of the carbonate moiety.

![Figure 4.17. Optimized geometry of $[O_2COTi(N'[Bu]Ar)_3]^-$.](image)

4.6. Additional Oxo Systems

In conjunction with the work presented in this chapter and under the supervision of the author, visiting graduate student Albert Paparo explored the synthesis and reactivity of the titanium oxo anion complex with di- and trivalent countercations. His studies included the synthesis of the magnesium and aluminum salts \([(Et_2O)_2Mg][OTi(N'[Bu]Ar)_3]_2 \text{ and } [Cl_2Al(Et_2O)][OTi(N'[Bu]Ar)_3]\) via salt-metathesis reactions. Albert was also able to synthesize...
the complex [(12-crown-4)Mg][OTi(N[′Bu]Ar)₃]₂. This material reacts very rapidly with CO₂ to form an isolable carbonate species.

4.7. Conclusions

Building on the work of the related nitrido anion complexes of vanadium and niobium, I have shown that the oxo anion complex of titanium 27 reacts readily with CO₂ to form the carbonate complex 28. Complex 28 adopts a hexameric structure in the solid state centered around a hexagonal prismatic core comprised of the lithium countercations bridged with oxygens from the carbonate group. Using ¹H DOSY NMR spectroscopy, it was shown that this hexameric structure persists in solutions of benzene. Attempts to breakup the hexameric structure of 28 with the introduction of 12-crown-4 resulted in the rapid loss of CO₂ from the system. The solvent dependent nature of the CO₂ binding to 27 was investigated using NMR spectroscopy, and the thermodynamic parameters for the reaction were calculated. Building on this understanding, the synthesis of the oxo anion titanium complex with other countercations was developed. The sodium and potassium derivatives, 33 and 34 respectively, bind CO₂ in weakly coordinating solvents to form the carbonate complexes 35 and 36, but qualitatively, the binding was found to be weaker than in 28. The oxo anion complex ion-pair species 37 was found to react with CO₂ but the rate of CO₂ binding/release was very rapid, faster than the time scale of ¹H NMR spectroscopy. The clear dependence of CO₂ binding on the exact nature of the countercation provides a unique ability to tune the thermodynamics of the system, a feature that many other systems capable of binding CO₂ lack. Further work focused on divalent cations (i.e. Mg²⁺) and trivalent cations (i.e. Al³⁺) will be a welcomed addition to the work focused on the alkali metal cations.

To date, the goal of converting CO₂ to CO using an oxo-anion system remains unachieved. The notable difference between the oxo anion system and the nitrido anion system, the lack of an isolable deoxygenated species like the isocyanate complex 8, requires a different approach to the problem. Rather than perform an -O¹⁻ abstraction from the titanium carbonate complex, oxygen atom abstraction must be investigated. This will require the discovery of an electrophilic reagent capable of the requisite two-electron reduction.

4.8. Experimental Section

4.8.1. General Considerations.

All manipulations were carried out either in a Vacuum Atmospheres model MO-40M glove box under an atmosphere of N₂ or using standard Schlenk techniques. All solvents were degassed and dried using a solvent-purification system provided by Glass Contour. After purification, all
solvents were stored under an atmosphere of N₂ over 4 Å molecular sieves. Deuterated benzene (Cambridge Isotope Labs) was dried by stirring over CaH₂ for 24 h and was subsequently vacuum-transferred onto 4 Å molecular sieves. Deuterated tetrahydrofuran (Cambridge Isotopes Labs) was dried by stirring over sodium metal with a catalytic amount of benzophenone and subsequently vacuum-transferred onto 4 Å molecular sieves. The formate complex 26 and oxo complex 27 were prepared according to literature procedures. All other reagents were used as supplied by the vendor without further purification. Celite 435 (EMD Chemicals), alumina (Aldrich) and 4 Å molecular sieves (Aldrich) were dried prior to use by heating at 200 °C for 48 h under dynamic vacuum. All glassware was oven dried at 220 °C prior to use. NMR spectra were obtained on either a Varian 500 Inova spectrometer equipped with an Oxford Instruments Ltd. superconducting magnet, a Bruker 400-AVANCE spectrometer equipped with a Magnex Scientific superconducting magnet, a Varian Inova 500 spectrometer equipped with an Oxford Instruments Ltd. superconducting magnet, or a Varian Mercury 300 spectrometer equipped with an Oxford Instruments Ltd. superconducting magnet. ¹H NMR spectra were referenced to residual C₆D₅H (7.16 ppm) or residual C₄H₁₀D₁₇O (3.58 ppm).¹³C NMR spectra were referenced internally to naturally abundant ¹³C benzene (128.06 ppm), pyridine (150.35 ppm), or THF (67.21 ppm).¹³C IR spectra were collected on a Perkin-Elmer 2000 FT-IR spectrophotometer. Elemental analysis was performed by Midwest Microlab, Indianapolis, IN.

4.8.2. Computational Studies.

All calculations were carried out using ADF 2008.01 from Scientific Computing and Modeling on a 32-processor Quantum Cube workstation from Parallel Quantum Solutions. The calculations were performed using the OLYP functionals, which are a combination of the OPTX exchange functional of Handy and Cohen used with Lee, Yang, and Parr’s nonlocal correlation function (LYP). In addition, all calculations were carried out using the zero-order regular approximation (ZORA) for relativistic effects. The basis sets used were triple-ζ with a polarization function (TZP) for all non-hydrogen atoms and double-ζ with a polarization function (DZP) for all other calculations, as supplied with ADF. The starting geometry for the calculations was derived from the solid-state structure of the complex Me₃SiOC(O)OTi(N[BU]Ar); the Me₃Si group was removed and the lithium countercation was placed with the carbonate bound in a κ²-fashion. The geometry was then optimized. Starting geometries for the sodium and potassium derivatives were obtained by replacing the lithium cation in the optimized geometry of the lithium derivative. Chemical shielding tensors were calculated for the ¹³C nuclei in the optimized structures by the GIAO method using the ADF package. Frequency calculations were computed using optimized structures as described above.
4.8.3. 1H DOSY NMR Spectroscopy

DOSY spectra were collected using a Bruker 400-AVANCE spectrometer equipped with a Magnex Scientific superconducting magnet. Data collection was performed using a stimulated echo experiment (stepglsld). A gradient length of 3200 µs and a Stejskal-Tanner diffusion delay of 0.1 s were used in the data collection. The gradient ratio was varied from 2% to 95% in 16 steps. The diffusion coefficient was calculated using the Bayesian DOSY Transform as implemented by Mnova NMR.

4.8.4. Synthesis of ([Li][O2COTi(N'[Bu]Ar)3])₆ (28)

A solution of 27 (3.12 g, 4.17 mmol) in diethyl ether (100 mL) was prepared in a 250 mL Schlenk flask fitted with a rubber septum. The flask was removed from the glove box and attached to the Schlenk manifold. The reaction vessel was cooled to 0 °C using an ice bath. The flask was placed under a slight static vacuum by evacuating the hose connected to the Schlenk flask, closing the valve to the vacuum manifold, opening the sidearm valve of the flask, and then closing the sidearm valve of the flask. CO₂ (107 mL, 4.39 mmol, 1.05 equiv) was then introduced to the flask via a syringe and the reaction mixture was stirred vigorously using a magnetic stir bar. The color of the solution changed from yellow to orange as the reaction proceeded. After stirring for 1 h, the reaction mixture was dried under reduced pressure while being kept at 0 °C. The flask was returned to the glove box, and the resulting orange residue was triturated with n-hexane (40 mL) and then dried under reduced pressure. The resulting yellow powder was suspended in n-pentane (20 mL) and collected on a sintered glass frit via vacuum filtration. The powder was dried under reduced pressure. Yield: 1.85 g (2.88 mmol, 69%) Crystals of 28 suitable for single-crystal X-ray diffraction studies were grown by slow evaporation of solutions of 28 in benzene at room temperature. 1H NMR (C₆D₆, 20 °C, 400 MHz): δ 6.75 (s, 3 H, p-H), 6.30 (br, 6 H, o-H), 2.24 (s, 18 H, Ar-CH₃), 1.75 (s, 27 H, NC(CH₃)₃). 13C NMR (THF-d₈, 20 °C, 100 MHz): δ 162.9 (s, O₂CO), 153.3 (s, ipso-Ar), 136.6 (s, o-Ar), 126.6 (s, p-Ar), 62.2 (s, NC(CH₃)₃), 31.4 (s, NC(CH₃)₃), 21.8 ppm (s, Ar-CH3). IR (KBr, thin film): 2963, 2915, 2863, 1598 (vs), 1588 cm⁻¹. Elemental analysis: Calculated for C₃₇H₅₄LiN₅O₃Ti: C, 69.04; H, 8.46; N, 6.53%. Found: C, 68.84; H, 8.39; N, 6.28%.

4.8.5. Synthesis of Me₃SiOC(O)OTi(N'[Bu]Ar)₃ (30).

A suspension of 28 (0.679 g, 1.05 mmol) in diethyl ether (15 mL) was prepared and cooled in the liquid nitrogen bathed cold well of the glove box. A solution of Me₃SiOS(O)₂CF₃ (0.235 g, 1.05 mmol) in diethyl ether (3 mL) was prepared and cooled in the cold well. Both mixtures were frozen, allowed to partially thaw, and then combined. The reaction mixture was allowed to warm to 22 °C while stirring. As the reaction progressed, the originally yellow suspension became a
homogeneous orange mixture. After stirring for 2 h, the reaction mixture was taken to dryness under reduced pressure, triturated with n-hexane, and then dried again. The resulting orange residue was extracted into diethyl ether (~10 mL) and filtered through a pad of Celite on a sintered glass frit. The filtrate solution was concentrated under reduced pressure and then stored at −35 °C. After standing for 24 h, yellow crystals had formed. The crystals were collected on a sintered glass frit via vacuum filtration and then dried under reduced pressure. Yield: 0.469 g (0.66 mmol, 63%). 1H NMR (CD6D, 20 °C, 400 MHz): δ 6.73 (s, 3 H, p-H), 6.13 (br, 6 H, o-H), 2.19 (s, 18 H, Ar-CH3), 1.39 (s, 27 H, NC(CH3)3). 13C NMR (CD6D, 20 °C, 100 MHz): δ 153.2 (s, Me3SiOC(O)O), 152.9 (s, ipso-Ar), 137.0 (s, o-Ar), 127.8 (s, m-Ar), 127.07 (s, p-Ar), 62.8 (s, NC(CH3)3), 30.9 (s, NC(CH3)3), 22.0 (s, Ar-CH3), 0.12 ppm (s, (H3C)3Si). IR (KBr, thin film): 1691 (vs), 1598, 1588 cm−1. Elemental analysis: Calculated for C40H63N3O3SiTi: C, 67.67; H, 8.94; N, 5.92%. Found: C, 67.53; H, 8.84; N, 5.82%.


A suspension of 28 (0.187 g, 0.29 mmol) in diethyl ether (10 mL) was prepared and frozen in the cold well. A solution of pivaloyl chloride (0.035 g, 0.29 mmol) in diethyl ether (2 mL) was prepared and frozen in the cold well. The two mixtures were allowed to thaw and were subsequently combined. The yellow mixture was stirred and allowed to warm to 22 °C. The mixture changed from yellow to orange over the course of 1 h and gas evolution was observed when the cap of the vessel was removed. The reaction mixture was then dried under reduced pressure. The orange residue was extracted into toluene (5 mL). The solution was filtered through a pad of Celite on a glass fiber filter. The filtrate solution was dried under reduced pressure. The orange residue was dissolved in a minimum volume of diethyl ether (~3 mL) and the solution was stored at −35 °C. After standing for 6 h, orange crystals had deposited on the bottom of the vial. The mother liquor was decanted away from the crystals, and these were washed with n-pentane (1 mL). The crystals were dried under reduced pressure. Yield: 0.106 g. A second crop of the material was obtained by concentrating the mother liquor under reduced pressure and storing the solution at −35 °C. 2nd crop: 0.047 g. Total yield: 0.153 g (0.23 mmol, 78%). 1H NMR (CDCl3, 20 °C, 400 MHz): δ 6.76 (s, 3 H, p-H), 6.24 (br, 6 H, o-H), 2.25 (s, 18 H, Ar-CH3), 1.22 (s, 9 H, (O)CC(CH3)3), 1.13 (s, 27 H, NC(CH3)3). 13C NMR (CDCl3, 20 °C, 100 MHz): δ 180.2 (s, OC(O)), 151.2 (s, ipso-Ar), 136.3 (s, o-Ar), 127.3 (s, m-Ar), 126.4 (s, p-Ar), 62.4 (s, NC(CH3)3), 39.9 (s, (O)CC(CH3)3), 30.2 (s, NC(CH3)3), 27.8 (s, (O)CC(CH3)3), 21.6 ppm (s, Ar-CH3). IR (KBr, thin film): 1680 (vs), 1598, 1588 cm−1. Elemental analysis: Calculated for C41H66N3O2SiTi: C, 72.65; H, 9.37; N, 6.20%. Found: C, 72.57; H, 9.39; N, 6.26%.
4.8.7. Synthesis of [(12-crown-4)Li][OTi(N' Bu)Ar]₃ (29)

A solution of 27 (0.256 g, 0.351 mmol) in THF (5 mL) was prepared. A solution of 12-crown-4 (0.062 g, 0.351 mmol) in THF (7 mL) was added to the stirring solution of oxo anion complex 27 at 23 °C. The mixture was stirred for 45 min and then dried under reduced pressure. The yellow residue was triturated with n-hexane (5 mL) and then dried under reduced pressure. The bright yellow solids were suspended in n-hexane, collected on a sintered glass frit via vacuum filtration, and dried under reduced pressure. Yield: 0.220 g (81%).

1H NMR (C₆D₆, 20 °C, 400 MHz): δ 6.81 (s, 3 H, p-H), 6.35 (br, 6 H, o-H), 2.55 (in, 8H, 12-crown-4), 2.25 (in, 8H, 12-crown-4), 2.39 (s, 18 H, Ar-CH₃), 1.78 (s, 27 H, NC(CH₃)₃).

13C NMR (C₆D₆, 20 °C, 125 MHz): δ 156.0 (s, ipso-Ar), 135.6 (s, o-Ar), 130.9 (s, m-Ar), 124.2 (s, p-Ar), 66.3 (s, 12-crown-4), 56.8 (s, NC(CH₃)₃), 33.5 (s, NC(CH₃)₃), 22.1 (s, Ar-CH₃).

Elemental analysis: Calculated for C₄H₇0LiN₃O₅Ti: C, 68.11; H, 9.09; N, 5.41%. Found: C, 66.71; H, 9.15; N, 5.13%.

4.8.8. Synthesis of [(THF)Na][OTi(N' Bu)Ar]₃ (33)

An orange solution of 26 (1.547 g, 2.5 mmol) in THF (20 mL) was cooled in a liquid nitrogen bathed cold well in the glove box. A solution of NaN(SiMe₃)₂ (0.456 g, 2.5 mmol) in THF (10 mL) was prepared and cooled in the cold well. Once frozen, the two solutions were allowed to partially thaw and were subsequently combined. The reaction mixture was stirred and allowed to warm to room temperature. As the reaction progressed, there was an orange to yellow color change. After stirring for 1 h, the reaction mixture was taken to dryness under reduced pressure. The resulting yellow solids were suspended in n-pentane (20 mL), the mixture was cooled to −35 °C. The solids were then collected on a sintered glass via vacuum filtration. The white solids were dried under reduced pressure. Yield: 1.71 g. The 1H NMR was collected. The spectrum reveals clean formation of the oxo complex and about 3/2 equiv of THF present. Thus, as isolated the most correct molecular formula would be [(THF)₃/2Na][OTi(N' Bu)Ar]₃ (1.71 g, 707.82 g/mol, 2.4 mmol, 97%). This material could be recrystallized from the slow diffusion of n-pentane into saturated solutions in diethyl ether:THF 20:1 at 23 °C to give 33. 1H NMR (C₆D₆, 20 °C, 400 MHz): δ 6.81 (s, 6 H, o-H), 6.76 (s, 3 H, p-H), 2.33 (s, 18 H, Ar-CH₃), 1.34 (s, 27 H, NC(CH₃)₃). 13C NMR (pyridine-d₅, 20 °C, 100 MHz): δ 156.6 (s, ipso-Ar), 135.7 (s, o-Ar), 131.1 (s, m-Ar), 124.0 (s, p-Ar), 56.7 (s, NC(CH₃)₃), 33.6 (s, NC(CH₃)₃), 22.4 (s, Ar-CH₃).

Elemental analysis: Calculated for C₄₀H₇₀LiN₃O₂Ti: C, 69.85; H, 9.09; N, 6.11%. Found: C, 69.97; H, 8.99; N, 5.99%.

4.8.9. Synthesis of [K][OTi(N' Bu)Ar]₃ (34)

A solution of 26 (2.10 g, 3.38 mmol) in THF (25 mL) was prepared and cooled in the liquid nitrogen bathed cold well in the glove box. A solution of KN(SiMe₃)₂ (0.674 g, 3.38 mmol) in

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THF (10 mL) was prepared and cooled in the liquid nitrogen bathed cold-well. After freezing, the two solutions were allowed to partially thaw and were then combined. The reaction mixture was stirred and allowed to warm to 23 °C. The color of solution changed from dark orange to bright yellow as the reaction proceeded. After stirring for 1 h, the reaction mixture was taken to dryness under reduced pressure. The resulting yellow foam was triturated with n-hexane (10 mL) and then dried under reduced pressure. The yellow solids were extracted into a 5:1 mixture of diethyl ether:toluene (20 mL) and then filtered through a bed of Celite on a sintered glass frit. The filtrate solution was dried under reduced pressure and the resulting yellow solids were suspended in n-pentane. The solids were collected on a sintered glass frit via vacuum filtration and then dried under reduced pressure. The filtrate solution could be dried, the solids again suspended in n-pentane, and then collected for a second crop. Yield: 1.418 g (2.24 mmol 66%). ^1H NMR (C₆D₆, 20 °C, 400 MHz): δ 6.94 (s, 6 H, o-H), 6.65 (s, 3 H, p-H), 2.32 (s, 18 H, Ar-CH₃), 1.38 (s, 27 H, NC(CH₃)₃). ^13C NMR (C₆D₆, 20 °C, 100 MHz): δ 157.9 (s, ipso-Ar), 137.1 (s, o-Ar), 129.2 (s, m-Ar), 124.0 (s, p-Ar), 57.5 (s, NC(CH₃)₂), 32.8 (s, NC(CH₃)₂), 22.0 (s, Ar-CH₃). Elemental analysis was collected on material obtained by recrystallizing [K][1] from saturated solutions in diethyl ether at −35 °C: Calculated for C₅₄H₆₀KN₂O₇Ti: C, 68.44; H, 8.61; N, 6.65%. Found: C, 68.07; H, 8.49; N, 6.59%.

4.8.10. Synthesis of [(2,2,2-crypt)K][OTi(N[13u]Ar)₃]

A solution of the 2,2,2-crypt (0.165 g, 0.44 mmol) in benzene (1 mL) was prepared. A solution of 34 (0.256 g, 0.44 mmol) in benzene (5 mL) was prepared. The solution of 34 was layered on top of the solution of the cryptand. The layering was allowed to stand for 12 h. After standing, a thin layer of oil had formed in the bottom of the vessel. Agitation of the reaction vessel resulted in the gradual crystallization of the product. The solids were collected on a sintered glass frit via vacuum filtration. The white solids were washed with n-pentane and then dried under reduced pressure. Yield: 0.292 g (0.31 mmol, 69%). ^1H NMR (THF-d₈, 20 °C, 400 MHz): δ 6.29 (s, 3 H, p-H), 5.83 (s, 6 H, o-H), 3.61 (s, 12 H, OCH₂CH₂O), 3.57 (t, 12 H, OCH₂CH₂N), 2.58 (t, 12 H, OCH₂CH₂N), 2.03 (s, 18 H, Ar-CH₃), 1.35 (s, 27 H, NC(CH₃)₃). ^13C NMR (THF-d₈, 20 °C, 100 MHz): δ 157.6 (s, ipso-Ar), 135.9 (s, o-Ar), 131.0 (s, m-Ar), 122.6 (s, p-Ar), 71.5 (s, OCH₂CH₂O), 68.7 (s, OCH₂CH₂N), 56.4 (s, NC(CH₃)₂), 55.0 (s, OCH₂CH₂N), 33.9 (s, NC(CH₃)₂), 22.2 (s, Ar-CH₃). Elemental analysis: Calculated for C₅₄H₆₀KN₂O₇Ti: C, 64.32; H, 9.00; N, 6.95%. Found: C, 63.29; H, 8.78; N, 6.82%.

4.8.11. CO₂ Binding Studies

In the glove box, a sample of 27, 33, 34, or 37 was placed in an NMR tube fitted with a PTFE valve. The solvent of choice was added and the complex was dissolved. The solution was
degassed using three freeze-pump-thaw cycles. The PTFE valve adaptor was then fitted with a rubber septum. The tube was removed from the glove box, and CO₂ was added to the NMR tube via a syringe by piercing the rubber septum and then opening the valve. The partial vacuum in the NMR tube drew the CO₂ into the headspace. The valve was closed and the tube was flame sealed at reduced temperatures. The ratio of carbonate:oxo complex was assayed using 'H NMR spectroscopy, and the ratio of carbonate:CO₂ was assayed using ¹³C NMR spectroscopy.


A solution of the 1 (0.030 g, 0.052 mmol) in toluene (4 mL) was prepared in a 25 mL PTFE sealed reaction vessel. The vessel was removed from the glove box and attached to the Schlenk line. The flask was evacuated, and the headspace was backfilled with CO₂. The color of the solution changed from dark green-yellow to dark orange-brown upon the addition of CO₂. The reaction mixture was allowed to stir for 12 h at 21 °C. After stirring, the reaction mixture was a dark olive green color. The reaction mixture was dried under reduced pressure on the Schlenk line, and the vessel was returned to the glove box. The reaction mixture was dried under reduced pressure and the product extracted into a 1:1 mixture of toluene:n-hexane (2 mL). The solution was stored in the freezer to afford the product as a pale green crystalline material. 'H NMR (CD₆, 20 °C, 400 MHz): δ 6.54 (s, 3 H, p-H), 6.23 (br, 6 H, o-H), 2.27 (s, 18 H, Ar-CH₃), 0.50 (s, 27 H, NC(CH₃)₃). IR (thin film, KBr): 1600 (s), 1450 cm⁻¹ (s).

4.8.13. Crystallographic Details

Low-temperature data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo/Kα radiation (λ = 0.71073 Å), performing ω- and φ-scans, or on a Bruker X8 four circle diffractometer coupled to a Bruker Apex II CCD detector with graphite monochromated Cu/Kα radiation (λ = 1.54178 Å). All structures were solved either by direct or Patterson methods using SHELXS and refined against F² on all data by full-matrix least squares with SHELXL-97. A semi-empirical absorption correction (SADABS) was applied to the diffraction data for all structures. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups).

Complex 28 • 1.33 (C₆H₆) crystallizes in the space group R3, and the structure was solved using direct methods. Refinement proceeded by assigning atom positions according to the electron-density difference map. Four molecules of interstitial benzene are each disordered over three positions that are related by a crystallographic three-fold axis. Each benzene molecule was
constrained to a third occupancy in each possible position. Similarity restraints on the 1,2- and 1,3-distances were applied. The anisotropic displacement parameters of the benzene molecules were restrained assuming rigid bond behavior. The thermal ellipsoid plot was generated using PLATON.50

Complex 30 crystallizes in the space group Pbca, and the structure was solved using direct methods. Refinement proceeded by assigning atom positions according to the electron-density difference map. No restraints were used in the refinement. The thermal ellipsoid plot was generated using PLATON.50

Complex 34 crystallizes in the space group Pǐ, and the structure was solved using direct methods. Refinement proceeded by assigning atom positions according to the electron-density difference map. No restraints were used in the refinement. The thermal ellipsoid plot was generated using PLATON.50

Complex 37 crystallizes in the space group P2₁/n, and the structure was solved using direct methods. Refinement proceeded by assigning atom positions according to the electron-density difference map. No restraints were used in the refinement. The thermal ellipsoid plot was generated using PLATON.50

Complex 32 • C7H8 crystallizes in the space group C2/c and the structure was solved using direct methods. Refinement proceeded by assigning atoms positions according to the electron-density difference map. The bridging carbamate ligand suffers from a positional disorder that was refined freely over two positions while constraining the total occupancy to unity. An interstitial molecule of toluene suffers from positional disorder about an inversion center and was refined by modeling one of the positions at half-occupancy without symmetry elements. 1,2- and 1,3-distance similarity restraints were applied to the disordered portions. Anisotropic displacement parameters were restrained assuming rigid bond behavior. The thermal ellipsoid plot was generated using PLATON.50
Table 4.4. Crystal data for \([\text{Li}[\text{O}_2\text{COTi(N}[\text{Bu}\text{Ar}]_3)]_6\) (28) and \(\text{Me}_3\text{SiOC(O)Ti(N}[\text{Bu}\text{Ar}]_3\) (30).

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<td>10068/819847</td>
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<td>100(2) K</td>
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<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>(\overline{R}^3)</td>
<td>(\text{Pbc}a)</td>
</tr>
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<td>(b = 19.171(2) , \text{Å}, \beta = 90^\circ)</td>
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<td>(Z)</td>
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<td>8</td>
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<td>100%</td>
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Table 4.5. Crystal data for [K][OTi(N[\text{Bu}]Ar)₃] (34) and [(2,2,2-crypt)K][OTi(N[\text{Bu}]Ar)₃] (37).

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4.9. References

(20) Cambridge Structural Database, 2010, v5.32.
Appendix A. Synthesis of Vanadium Nitrile Complexes

A.1. Introduction

As part of an ongoing collaboration with Prof. Carl Hoff of the University of Miami and Prof. Elena Rybak-Akimova of Tufts University, I briefly investigated the interaction of nitriles with the vanadium(III) tris-anilide complex 1. The related molybdenum(III) complex Mo(N['Bu]Ar)₃ reacts with nitriles to form the four-coordinate complexes (RCN)Mo(N['Bu]Ar)₃. The β-carbon position of the nitrile ligand possesses a large amount of unpaired electron density, and as a result, the complexes react readily with radicals and radical precursors.¹ The investigations into the reactivity of nitriles with the vanadium complex 1 were undertaken to explore the possibility of imparting carbene character onto the β-carbon position using the vanadium(III)/(V) redox couple. Presented herein is the synthesis of vanadium(III) and vanadium(IV) nitrile complexes.

A.2. (η¹-RCN)V(N['Bu]Ar)₃ complexes

A.2.1. Synthesis and Structure

When V(N['Bu]Ar)₃ (1) is dissolved in diethyl ether, the color of solution is a dark green brown. When benzonitrile was added to the reaction mixture, the color of solution immediately changed to a deep purple color (Scheme A 1). The product PhCNV(N['Bu]Ar)₃ (38) was isolated as purple crystals by drying the reaction mixture, extracting the product into n-hexane, and storing the solution at −35 °C for two days. Repeated attempts to obtain crystals suitable for X-ray diffraction studies were met without success. Thus, other nitrile complexes were prepared.
The complex (2,6-F$_2$C$_6$H$_3$CN)V(N[‘Bu]Ar)$_3$ (39) was synthesized in a similar manner as 38 (Scheme A 1). The complex displays the same intense purple color as 38 in solution, and this color persists in the solid state. Although, the difluorobenzonitrile has a lower binding enthalpy than benzonitrile to 1, crystals of 39 suitable for single-crystal X-ray diffraction studies could be grown with ease from concentrated diethyl ether solutions (vide infra).

Me$_2$NCN has been shown to bind to Mo(N[‘Bu]Ar)$_3$ in an η$_2$-fashion, so it was of interest to see if the vanadium system would display the same preference in reactivity. When 1 is treated with Me$_2$NCN in diethyl ether, the color of solution became deep blue-purple. The product (Me$_2$NCN)V(N[‘Bu]Ar)$_3$ (40) was isolated as a cerulean blue solid by precipitation from n-pentane. Crystals of 40 suitable for X-ray diffraction studies could be grown from concentrated solutions of 40 in a 1:1 mixture of toluene:diethyl ether at −35 °C. This confirmed the assignment of the Me$_2$NCN ligand bound in an η’-fashion (vide infra). This was somewhat of unexpected given that DFT calculations of the system had indicated that the η$_2$-isomer of 40 should be energetically favored (vide infra). Furthermore, the η$_2$-isomer should be diamagnetic. Hypothesizing that the nitrile be might in a rapid-equilibrium process between the η’- and η$_2$-forms, we looked to confirm formation of the η$_2$-complex of 40 at low temperatures via $^1$H NMR spectroscopy. At −80 °C in toluene-$d_8$, no diamagnetic species were observed.

The $^1$H NMR spectra of 38, 39, and 40 were collected in deuterated benzene revealing that all three complexes were paramagnetic. The IR spectrum of 38, 39, and 40 contain the expected absorbance for the $\nu_{CN}$ mode, with only slight shifts between free and bound species, thus providing little evidence for significant activation of the carbon-nitrogen bond of the nitrile ligand.

The solid-state structure of 39 contains a vanadium metal center in a distorted trigonal-monopyramidal coordination geometry (N$_{amidide}$–V–N$_{nitrile}$ 96.10(7)° avg., N$_{amidide}$–V–N$_{amidide}$ 118.89(7)° avg., Figure A 1). The V–N$_{nitrile}$ interatomic distance (2.044(2) Å) is longer than the V–N$_{amidide}$ distances. (1.943(2) Å avg.). The amidide ligands adopt a one-down, two-up arrangement probably due to steric effects. Furthermore, there is a deviation from linearity in the angle V–N–C.
One possible rationalization for this is that there may be a π-stacking interaction between the aryl residue on the nitrile and the aryl substituent on one of the anilides bound to vanadium. Such an interaction has been previously observed in the ketimide complex (Ph(H)C=N)Mo(N[Bu]Ar)$_3$.\textsuperscript{3}

![Structure diagram](image)

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<tr>
<td>N4 - V1</td>
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<td>V1-N$_{anilide}$ avg.</td>
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$\rho$1

$Z = 2$

$R(F) = 0.0483$

$R_w(F^2) = 0.1288$

**Figure A 1.** Solid-state structure of (2,6-F$_2$C$_6$H$_3$CN)V(N[Bu]Ar)$_3$ (39). Thermal ellipsoids are drawn at 50% probability, and hydrogen atoms have been omitted for clarity.

The solid-state structure of 40 as determined by X-ray crystallography shows that the cyanamide ligand binds to the vanadium metal center in an η$^1$-fashion (Figure A 2). The anilide ligands adopt a crystallographically imposed three-fold symmetric arrangement, markedly different than the arrangement in 39. The V–N$_{nitrile}$ interatomic distance (2.037(3) Å) in 40 is on par with the V–N$_{nitrile}$ distance observed in 39. Compared with other known vanadium(III) η$^1$-nitrile complexes,\textsuperscript{45} 39 and 40 show typical structural features. Interestingly, vanadium(III) has been shown to be competent at binding nitriles in an η$^2$-fashion,\textsuperscript{6} and we hypothesize that the steric encumbrance of the anilide ligands precludes this from occurring in our system.
A.2.2. Reactivity of $\eta^1$-nitrile Complexes

With regard to reactivity, there is a stark difference between the $(\eta^1\text{-RCN})V(\text{N}'\text{Bu}\text{Ar})_3$ complexes and the analogous adducts in the Mo(\text{N}'\text{Bu}\text{Ar})_3 system. The Mo(\text{N}'\text{Bu}\text{Ar})_3 nitrile complexes have been found to possess significant unpaired electron density on the carbon position of the nitrile ligand. As a result, the complexes were shown to undergo bimolecular coupling reactions and were efficiently trapped by common radical sources.\(^\text{7}\) In contrast, inner-sphere, one-electron oxidants react at the vanadium metal center to give vanadium(IV) products. Similarly, inner-sphere, two-electron oxidants, such as oxygen atom sources, react with at the metal center to give the vanadium(V) products. It appears that the on-off equilibrium of the nitrile binding allows for the vanadium complex 1 to be the dominant reactant in solution under the conditions tested. Attempts to shift the equilibrium in favor of the nitrile complexes, e.g., by using excess nitrile or by cooling the reaction mixtures, gave similar results.

In contrast, the nitrile complexes react with outer-sphere oxidants to the give the cationic nitrile complexes $[\eta^1\text{-RCN}]V(\text{N}'\text{Bu}\text{Ar})_3^+$. For example, when a solution of 38 in diethyl ether was added to a stirring suspension of $[(\text{C}_3\text{H}_5)_2\text{Fe}]\text{B}(3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3)_4$ (FcBArF\(_4\)) in diethyl ether,
the color of solution changed to a dark green color. The product [PhCNV(N[′Bu]Ar)₂][BAr₅CF₃]₄ (41) could be crystallized from the reaction mixture by storing the solution at −35 °C for 1 d. The IR spectrum for 5 contains an intense absorbance at 2249 cm⁻¹, which is attributed to the νCN stretching mode. This is at a significantly higher frequency than the νCN observed in the neutral nitrile complex 38 (2218 cm⁻¹). The solid-state structure of the complex was determined using single-crystal X-ray diffraction methods and reveals a four-coordinate vanadium center with an η¹-nitrile ligand (Figure A 3). The vanadium-nitrogen distance in 5 is slightly longer than that of either complex 3 or 4. As in 3, two of the aryl moieties of the anilides are positioned in close proximity to the phenyl group of the nitrile ligand. The third anilide ligand is rotated ~90° with respect to the other anilide ligands; this is typical for vanadium (IV) complexes and is attributed as a Jahn-Teller distortion from the expected C₃ symmetry.

C41 - N4 = 1.144(3) Å
N4 - V1 = 2.059(2) Å
V1-N_anilide avg. = 1.872(2) Å
C41 - N4 - V1 = 172.9(2)°

Figure A 3. Solid-state structure of [PhCNV(N[′Bu]Ar)₂][BAr₅CF₃]₄ (41). Thermal ellipsoids drawn at 50% probability, and hydrogen atoms, the [BAr₅CF₃]⁴⁻ counteranion, and an interstitial molecule of diethyl ether have been omitted for clarity.
A.3. Experimental Details

A.3.1. General Considerations.

All manipulations were carried out either in a Vacuum Atmospheres model MO-40M glove box under an atmosphere of N2 or using standard Schlenk techniques. All solvents were degassed and dried using a solvent-purification system provided by Glass Contour. After purification, all solvents were stored under an atmosphere of N2 over 4 Å molecular sieves. Deuterated benzene (Cambridge Isotope Labs) was dried by stirring over CaH2 for 24 h and was subsequently vacuum-transferred onto 4 Å molecular sieves. Complex 1 was prepared according to literature methods.9 FcBARCF3 was prepared according to literature methods.10 All other reagents were used as supplied by the vendor without further purification. Celite 435 (EMD Chemicals), alumina (Aldrich) and 4 Å molecular sieves (Aldrich) were dried prior to use by heating at 200 °C for 48 h under dynamic vacuum. All glassware was oven dried at 220 °C prior to use. NMR spectra were obtained on either a Varian 500 Inova spectrometer equipped with a Oxford Instruments Ltd. superconducting magnet, a Bruker 400-AVANCE spectrometer equipped with a Magnex Scientific superconducting magnet, or a Varian Mercury 300 spectrometer equipped with an Oxford Instruments Ltd. superconducting magnet. Proton NMR spectra were referenced to residual C6D6H (7.16 ppm).11 13C NMR spectra were referenced internally to naturally abundant 13C benzene (128.06 ppm).11 IR spectra were collected on a Perkin-Elmer 2000 FT-IR spectrophotometer. Elemental analysis was performed by Midwest Microlab, Indianapolis, IN.


A solution of 1 (0.692 g, 1.2 mmol) in diethyl ether (~10 mL) was prepared. A solution of PhCN in diethyl ether (~2 mL) was prepared. The solution of PhCN (0.123 g, 1.2 mol) was added to the stirring solution of 1 in a drop wise manner. The color of solution changed from dark green-brown to a dark purple color. The reaction mixture was dried under reduced pressure. The resulting dark solids were extracted into n-hexane and the resulting solution filtered through a sintered glass frit. The filtrate solution was concentrated under reduced pressure (~5 mL) and the solution was stored at −35 °C. After standing for 2 d, crystals had formed on the bottom of the vial. Decanting the mother liquid away from the crystals allowed for their isolation. These were washed with n-hexane (~1 mL) and then dried under reduced pressure. Yield: 0.642 g of dark purple crystals (682.91 g/mol, 0.94 mmol, 78%). 1H NMR (C6D6, 300 MHz, 20 °C): δ 24.7 (br), 13.9 (br), 3.5 (br), 1.01 (br), −1.47 (br), −31.1 ppm (br). IR: νCN(solid)= 2218 cm−1; UV-Vis(toluene): λmax=480, 687 nm. Elemental analysis: Calculated for C43H58N4V: %C 75.63, %H 8.71, %N 8.20. Found: %C 75.82, %H 8.70, %N 8.04.
A.3.3. Synthesis of 2,6-F$_2$C$_6$H$_3$CNV(N$^{[13]u}$Ar)$_3$ (39).

A solution of 1 (0.913 g, 1.57 mmol) in diethyl ether (∼8 mL) was prepared. A solution of the 2,6-F$_2$C$_6$H$_3$CN (0.219 g, 1.57 mmol) in diethyl ether (∼2 mL) was prepared. The solution of the nitrile was added to the stirring solution of 1 at 23 °C. The reaction mixture became deep purple in color. The reaction mixture was stirred for 1 h before the volatile components of the mixture were removed under reduced pressure. The purple residue was extracted into a 5:1 mixture of diethyl ether:n-pentane (∼10 mL), filtered through a plug of Celite on a glass fiber filter, and then stored at −35 °C. After standing for 12 h, a small amount of crystalline material had precipitated from solution. The mother liquid was decanted away from the crystals that were then washed with n-pentane (1 mL). The crystals were dried under reduced pressure. The mother liquid was concentrated under reduced pressure (∼5 mL) to effect the precipitation of the product. The mixture was then layered with n- pentane and stored at −35 °C. After standing for 48 h, the product was isolated as a purple powder on a sintered glass frit via vacuum filtration. The solids were dried under reduced pressure. Yield: 0.700 g (718.89 g/mol, 0.97 mmol, 62%). $^1$H NMR (C$_6$D$_6$, 400 MHz, 20 °C): δ 31.0 (br), 14.2 (br), 1.12 (br), 0.77 ppm (br); IR: \(v_{CN}(solid)= 2220 \text{ cm}^{-1}\) (weak); UV-Vis(toluene): \(\lambda_{max}= 525, 687 \text{ nm}\). Elemental analysis: Calculated for C$_{43}$H$_{57}$F$_2$N$_4$V: %C 71.84, %H 7.99, %N 7.79. Found: %C 71.51, %H 7.86, %N 7.72.

A.3.4. Synthesis of Me$_2$NCNV(N$^{[Bu]}$Ar)$_3$ (40).

A solution of Me$_2$NCN (0.079 g, 1.13 mmol) in diethyl ether (2 mL) was prepared. A solution of 1 (0.0653 g, 1.13 mmol) in diethyl ether (10 mL) was prepared. The cyanamide solution was added to the stirring solution of 1 at 23 °C via a pipette. The color of solution immediately changed from dark green to dark purple. After stirring for 30 min, the reaction mixture was concentrated to a volume of ∼3 mL. Solids that had precipitated upon concentrating were dissolved by adding ∼4 mL of a 5:1 mixture of diethyl ether:toluene solution to the reaction vessel. The reaction mixture was filtered through a plug of Celite on a glass fiber filter. The purple solution was allowed to stand at −35 °C. After standing for 12 h, a dark, microcrystalline material had deposited on the bottom of the vial. The mother liquid was decanted away from the solids, and these were washed with 1 mL of n-pentane. The solids were dried under reduced pressure. Yield: 0.088 g. The mother liquid was dried under reduced pressure. The resulting blue solids were triturated with n-pentane (3 mL) to give a blue suspension. A bright blue powder was collected on a sintered glass frit and washed with n-pentane (2 x 1 mL). The solids were dried under reduced pressure. Yield: 0.518 g (649.88 g/mol, 0.93 mmol, 83% from both crops). $^1$H NMR (C$_6$D$_6$, 400 MHz, 20 °C): δ 28.39 (br), 12.74 (br), 1.36 (br), 0.42 ppm (br); IR: $v_{CN}(solid)= 2263 \text{ cm}^{-1}$ (intense); UV-Vis: \(\lambda_{max}(toluene) = 560, 705 \text{ nm}\); Elemental analysis of
microcrystalline material: Calculated for C_{59}H_{60}N_{5}V: %C 72.079; %H 9.306; %N 10.776. Found: %C 71.90; %H 9.16; %N 10.40.


A solution of PhCN (0.030 g, 0.29 mmol), 1 (0.169 g, 0.29 mmol) in diethyl ether (3 mL) was prepared and cooled to −35 °C. A suspension of FcBArCF₃ in diethyl ether (3 mL) was prepared and cooled to −35 °C. The solution of PhCN and 1 were subsequently added to the stirring suspension of FcBArCF₃. The reaction mixture was allowed to warm to room temperature while stirring. The color of the solution changed from purple to dark green as the reaction progressed. After stirring at room temperature for 2 h, the reaction mixture was filtered through a plug of Celite on a glass fiber filter. The filter cake was washed with diethyl ether (1 mL). The filtrate solution was concentrated to a total volume of 2 mL and stored at −35 °C for 24 h. Dark green crystals could be isolated by decanting the mother liquor away, washing with n-pentane, and then drying under reduced pressure. Yield: 0.179 g (1546.14 g/mol, 0.11 mmol, 40%). ¹H NMR (C₆D₆, 400 MHz, 20 °C): δ 1.0 ppm (br); IR: νCN(Nujol) = 2249 cm⁻¹ (s); Elemental analysis of microcrystalline material: Calculated for C_{75}H_{71}BF₂N₄V: %C 58.26; %H 4.63; %N 3.62. Found: %C 58.58; %H 4.83; %N 3.57.

A.3.6. Crystallographic Details

Low-temperature data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo/Kα radiation (λ = 0.71073 Å), performing o- and φ-scans. All structures were solved either by direct or Patterson methods using SHELXS and refined against F² on all data by full-matrix least squares with SHELXL-97.¹² A semi-empirical absorption correction (SADABS) was applied to the diffraction data for all structures.¹³ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups).

Complex 39 crystallizes in the space group P1̅1, and the structure was solved using direct methods. Refinement proceeded by assigning atoms positions according to the electron-density difference map. No restraints were used in the refinement process. The thermal ellipsoid plot was generated using PLATON.³²

Complex 40 crystallizes in the space group P2₃a, and the structure was solved using direct methods. Refinement proceeded by assigning atoms positions according to the electron-density difference map. The Me₂NCN ligand is located on a crystallographic three-fold element. Refining one position of the three-part positional disorder at a constrained 33% occupancy and allowing
the symmetry element to generate the other positions effectively modeled this. 1,2- and 1,3-
distance similarity restraints were applied to the Me$_2$NCN group, and the anisotropic
displacement parameters for the Me$_2$NCN group were restrained assuming rigid bond behavior.
The thermal ellipsoid plot was generated using PLATON.$^{32}$

Complex 41 crystallizes in space group $P\bar{1}$, and the structure was solved using direct
methods. Refinement proceeded by assigning atoms positions according to the electron-density
difference map. The CF$_3$ groups are positionally disordered about the C–C bond and were
modeled over two positions whose ratio was allowed to refine freely while the total occupancy
was constrained to unity. 1,2- and 1,3-distance similarity restraints were applied. The anisotropic
displacement parameters were restrained assuming rigid bond behavior. An aryl moiety in one of
the anilide ligands suffers from positional disorder, and this was modeled by allowing the ratio of
the two positions to refine freely while constraining the total occupancy to unity. 1,2- and 1,3-
distance similarity restraints were applied. The anisotropic displacement parameters were
restrained assuming rigid bond behavior. The thermal ellipsoid plot was generated using
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Table A. 2. Crystal data for [(PhCN)\(V(N'\text{Bu})\text{Ar})_3]\[\text{BAr}^{\text{CF}_3}_4\]

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<td>Completeness to (\theta_{\text{max}})</td>
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<td>Absorption correction</td>
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<td>(R) indices (all data)</td>
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A.4. References


Appendix B. Preparative Synthesis of

Ti(N[\text{Bu}]_{3,5-}\text{Me}_{2}\text{C}_6\text{H}_3)_3

B.1. Introduction

Ti(N[\text{Bu}]_{3,5-}\text{Me}_{2}\text{C}_6\text{H}_3)_3 is a potent halogen atom abstraction reagent that is useful for the one-electron reduction of metal halide complexes and for the generation of organic radicals from halogen containing molecules. This reactivity has been exploited to access previously unobtainable, low-valent metal complexes, such as mer-\text{Cl}_3\text{W(THF)}_3, to create synthons for the preparation of metal-ligand multiply bonded complexes, to generate radical intermediates important to organic transformations, and to synthesize phosphines directly from elemental phosphorus.

B.2. Procedure

All manipulations were carried out in a Vacuum Atmospheres model MO-40M glove box under an atmosphere of N\text{\textsubscript{2}}. All glassware was dried at 200 °C for 24 h prior to use. Celite 435 (EMD Chemicals), alumina (Aldrich), and 4 Å molecular sieves (Aldrich) were dried prior to use by heating at 200 °C for 48 h under dynamic vacuum. All solvents were degassed and dried using a solvent-purification system provided by Glass Contour (http://www.glasscontoursolventsystems.com/). After purification, all solvents were stored under an atmosphere of N\text{\textsubscript{2}} over 4 Å molecular sieves. TiCl\textsubscript{3}(THF)\textsubscript{3} was prepared using the method of Arnold and co-workers, rather than first producing TiCl\textsubscript{3} and subsequently complexing with THF. The lithium salt (Et\textsubscript{2}O)Li(N[\text{Bu}]_{3,5-}\text{Me}_{2}\text{C}_6\text{H}_3) was prepared according to literature procedures. TMEDA was dried by distilling from CaH\textsubscript{2} and then filtering through a plug of activated alumina in the glove box.

A light blue suspension of TiCl\textsubscript{3}(THF)\textsubscript{3} (3.09 g, 8.34 mmol) in diethyl ether (100 mL) and TMEDA (13.3 mmol, 1.6 equivalents) in a 250 mL round-bottom flask charged with a magnetic stir bar is cooled in the glove box using a liquid nitrogen bathed cold well until the diethyl ether begins to freeze. The flask is removed from the cold well at this point and stirring is commenced immediately upon thawing. A portion of (Et\textsubscript{2}O)Li(N[\text{Bu}]_{3,5-}\text{Me}_{2}\text{C}_6\text{H}_3) (4.30 g, 16.7 mmol, 2
equivalents) is added to this stirring suspension. The reaction mixture is stirred and allowed to warm to ambient temperature. As the reaction proceeds, the color of the suspension changes from light blue, to light green, to yellow, to dark brown. When the reaction mixture begins to change to dark brown (~30 min), the second portion of (Et₂O)Li[N[‘Bu]3,5-Me₂C₆H₃) (2.15g, 8.34 mmol) is added to the reaction vessel. The reaction mixture is stirred at room temperature for 3 h. During this time, the color of the reaction mixture becomes a deep forest green. The reaction mixture is then taken to dryness under reduced pressure in the reaction vessel to give a bright green residue. n-Hexane (30 mL) is added to the reaction vessel, the resulting slurry is stirred for 15 minutes, and then the mixture is dried under reduced pressure. This procedure is repeated. The product is extracted from the resulting green residue with portions of n-pentane (~20 mL) and the solution is filtered through a bed of Celite on a coarse porosity sintered glass fritted funnel into a 125 mL filter flask until complete extraction is achieved (~4 portions). The filtrate solution is stored at ~35 °C for 24 h. The product will crystallize as dark green square crystals on the bottom of the flask. The product is isolated via vacuum filtration on a medium porosity sintered glass fritted funnel, washed with n-pentane (10 mL) that has been cooled to ~35 °C, and then dried under reduced pressure. The filtrate solution can be concentrated to half the original volume and a second crop collected in a similar manner. Yield: 3.88 g (80.7%).


Dark green Ti[N[‘Bu]3,5-Me₂C₆H₃)₃ is soluble in most non-polar, non-halogenated organic solvents. It reacts rapidly with chlorinated, brominated, and iodinated solvents to give the bright yellow titanium(IV) halide complexes. It is a very sensitive compound that should only be handled under inert atmospheres. It reacts violently with air. As a result of its paramagnetic nature, the ‘H NMR spectrum in C₆D₆ exhibits a single broad resonance centered at δ = 4.5 ppm, ~8 ppm in width. If stored in a well-sealed container in the glove box, the compound is stable for months.

Appendix C. Structurally Characterized Bidentate Anilide Complexes of Niobium

C.1. Introduction

In the course of studies, an initial foray into developing an alternative nitride anion platform was undertaken. The initial idea was to circumvent the ability of the metal center to expand its coordination sphere by increasing the coordination number of the ancillary ligand set. Thus, the synthesis of metal complexes with the bidentate anilide ligand \( \text{R} \text{ArL} \) were pursued. Presented herein is a brief survey of the complexes that were synthesized in the course of these investigations and have been structurally characterized.

C.2. Synthesis and Structure

C.2.1. \((\text{Ph}_2\text{C}_2)\text{Nb(N[R]ArL})\text{Cl}_2\)

Originally working in collaboration with Erik Townsend, a visiting Amgen Scholar, the synthesis of the diphenylacetylene complex \((\text{Ph}_2\text{C}_2)\text{Nb(N[R]ArL})\text{Cl}_2\) (42) was prepared through the salt-metathesis reaction of \((\text{Ph}_2\text{C}_2)\text{NbCl}_3(\text{THF})_2\) and the lithiated anilide \((\text{Et}_2\text{O})\text{Li(N[R]ArL})\) (Scheme \(C\ 1\)). Treatment of a thawing solution of \((\text{Ph}_2\text{C}_2)\text{NbCl}_3(\text{THF})_2\) in diethyl ether with one equivalent of the lithiated anilide resulted in a gradual color change from yellow to orange. After stirring for three hours at ambient conditions and working up the reaction mixture to remove the lithium chloride byproduct, complex 42 was obtained as a bright orange powder by precipitating it from \(n\)-pentane. Crystals of the complex could be grown from saturated solutions of 42 in methylene chloride and the solid-state structure has been determined via single crystal X-ray diffraction methods (Figure \(C\ 1\)).

This method also works to produce the hexyne derivative \((\text{Et}_2\text{C}_2)\text{Nb(N[R]ArL})\text{Cl}_2\) (43) when starting from \((\text{Et}_2\text{C}_2)\text{NbCl}_3(\text{DME})\).

**Figure C 1.** Solid-state structure of (Ph₂C₂)Nb(N[R]Ar)L (42). Thermal ellipsoids are drawn at 50% probability level, and hydrogen atoms have been omitted for clarity.

C.2.2. (Ph₂C₂)Nb(N[R]Ar)(ODipp)Cl

The synthesis of the 2,6-diisopropylphenoxide ([ODipp]⁻) complex is achieved through a salt-metathesis reaction of KODipp with 42 to produce (Ph₂C₂)Nb(N[R]Ar)(ODipp)Cl (44, Scheme C 2). Treatment of a thawing solution of 42 in THF with a thawing solution of KODipp resulted in no color change, but a fine white precipitate forms as the reaction mixture is allowed to warm to ambient conditions. Following a standard workup to remove the potassium chloride byproduct, complex 44 was isolated in 58% yield as an orange crystalline material by storing saturated solutions of 44 in toluene layered with n-hexane at -35 °C for three days. The ¹H NMR spectrum assignment of the isolated material is complicated by two factors. In this synthesis, two isomers of complex 44 are isolated. It is proposed that the two isomers differ in the positioning of
the chloride and (ODipp)\textsuperscript{-} ligands. One isomer has the chloride in the axial position and the other has the (ODipp)\textsuperscript{-} in the axial position. Furthermore, there is hindered rotation about the niobium-oxygen bond of the (ODipp)\textsuperscript{-} ligand. This gives rise to two distinct methyne resonances and four distinct methyl resonances attributed to the \textsuperscript{181}Pr moieties. The solid-state structure of complex 44 has been determined using single-crystal X-ray diffraction techniques (Figure C 2).

This method also works to produce the hexyne derivative \((\text{Et}_2\text{C}_2)\text{Nb}(\text{N}[\text{R}]\text{Ar}_1)(\text{ODipp})\text{Cl} (45)\) in 74\% yield from precursor complex 43.

```
\begin{align*}
\text{Scheme C 2. Synthesis of } & (\text{R}_2\text{C}_2)\text{Nb}(\text{N}[\text{R}]\text{Ar}_1)(\text{ODipp})\text{Cl (44 and 45).} \\
\text{KODipp} & \text{THF} \\
3\text{h, } 22\text{ °C} & \rightarrow \\
& -\text{KCl} \\
\text{R' = Ph, 58\%} & \text{R' = Et, 74\%}
\end{align*}
```

![Scheme C 2. Synthesis of (R₂C₂)Nb(N[R]Ar₁)(ODipp)Cl (44 and 45).](image)

```
\begin{align*}
\text{Figure C 2. Solid-state structure of } & (\text{Ph}_2\text{C}_2)\text{Nb}(\text{N}[\text{R}]\text{Ar}_1)(\text{ODipp})\text{Cl (44).} \\
\text{Thermal ellipsoids are drawn at 50\% probability, and hydrogen atoms have been omitted for clarity.}
\end{align*}
```

\begin{align*}
\text{Nb1 - N1} & \quad 2.018(2) \text{ Å} \\
\text{Nb1 - N2} & \quad 2.352(2) \text{ Å} \\
\text{Nb1 - O3} & \quad 1.881(2) \text{ Å} \\
\text{N1 - Nb1 - N2} & \quad 74.23(7)°
\end{align*}

```
\begin{align*}
P2_1/c & \\
Z & = 4 \\
R(F) & = 0.0377 \\
R_w(F^2) & = 0.0898
\end{align*}
```

C.2.3. \((\text{Et}_2\text{C}_2)\text{Nb}(\text{N}[\text{R}]\text{Ar}_1)(\text{ODipp})\text{N}_3\)

With the goal of installing a nitride functionality in mind, the azide complex \((\text{Et}_2\text{C}_2)\text{Nb}(\text{N}[\text{R}]\text{Ar}_1)(\text{ODipp})\text{N}_3\) was synthesized. By installing the azide functionality, it was thought that nitride installation could be achieved with loss of alkyne. In effect, the azide would oxidize the niobium-carbon bonds.
Treatment of complex 45 in THF with excess sodium azide resulted in no observable color change, but the anticipated salt-metathesis reaction proceeded as confirmed by $^1$H NMR and IR spectroscopy. After 12 h of stirring and following workup to remove excess sodium azide and the byproduct sodium chloride, the azide complex (Et$_2$C$_2$)Nb(N[R]Ar$_L$)(ODipp)N$_3$ (46) was isolated by precipitation from $n$-hexane (Scheme C 3). The solid-state structure of complex 46 was determined using single-crystal X-ray diffraction techniques (Figure C 3).


Figure C 3. Solid-state structure of (Et$_2$C$_2$)Nb(N[R]Ar$_L$)(ODipp)N$_3$ (46). Thermal ellipsoids are drawn at 50% probability level, and hydrogen atoms have been omitted for clarity.

C.2.4. [NNb(N[R]Ar$_L$)(ODipp)]$_2$

With the azide complex 46 isolated, photolysis studies were undertaken. Complex 46 was advantageous for this purpose since the volatility of 3-hexyne would allow for easy separation of the products. Irradiation of a solution of 46 in THF in a quartz reaction vessel over the course of
12 h, results in complete consumption of the starting material with a concomitant color change of bright orange to dark red-orange. Crystals of the product were grown by dissolving the crude reaction mixture in a minimum volume of a 10:1 mixture of n-pentane:THF and storing the solution at −35 °C for several days. In the solid state, the product is confirmed to be the bridging nitride species \([\text{NNb(N[R]Ar)}_2(\text{ODipp})]\) (47, Scheme C 4 Figure C 4).

**Scheme C 4.** Synthesis of \([\text{NNb(N[R]Ar)}_2(\text{ODipp})]\) (47).

**Figure C 4.** Solid-state structure of \([\text{NNb(N[R]Ar)}_2(\text{ODipp})]\) (47). Thermal ellipsoids are drawn at 50% probability level, and hydrogen atoms have been omitted for clarity.
C.2.5. **Cl₂Nb(N[R]ArL)₂**

In seeking multiple routes to new niobium starting materials, the salt-metathesis reaction of Li(N[R]Ar₉) with NbCl₃(DME) was investigated. Treatment of a solution of NbCl₃(DME) in a mixture of toluene and diethyl ether with two equivalents of Li(N[R]Ar₉) resulted in a gradual color change from a dark brown suspension to a homogeneous dark brown solution with a white precipitate. After working up the reaction mixture to remove the precipitated lithium chloride, the product was isolated as a rust orange solid via precipitation from n-hexane. The product is paramagnetic, but unexpectedly, it gives rise to two distinct resonances in the $^2$H NMR spectrum, implying inequivalent ligand environments. Crystals of the product suitable for X-ray diffraction studies were grown from concentrated solutions in toluene at $-35 \ ^\circ$C, which allowed for identification of the product as the niobium(IV) complex Cl₂Nb(N[R]Ar₉)₂ (48, Figure C 5). Based on this formulation, the product is isolated in 37% yield. The change in oxidation state of the niobium center implies a disproportionation mechanism is involved in the metallation reaction.

![Figure C 5. Solid-state structure of Cl₂Nb(N[R]Ar₉)₂ (48). Thermal ellipsoids are drawn at 50% probability level, and hydrogen atoms have been omitted for clarity.](image)

\[
\begin{align*}
\text{Nb1 - N1} & \quad 2.052(2) \ \text{Å} \\
\text{Nb1 - N2} & \quad 2.503(2) \ \text{Å} \\
\text{Nb1 - N3} & \quad 2.042(2) \ \text{Å} \\
\text{Nb1 - N4} & \quad 2.429(2) \ \text{Å} \\
\text{N1 - Nb1 - N2} & \quad 72.21(6)^o \\
\text{N3 - Nb1 - N4} & \quad 73.17(6)^o \\
\end{align*}
\]

$P\bar{1}$

\[
\begin{align*}
Z & = 2 \\
R(F) & = 0.0353 \\
R_w(F^2) & = 0.0717 \\
\end{align*}
\]
C.3. Experimental Details

C.3.1. General Considerations

All manipulations were carried out either in a Vacuum Atmospheres model MO-40M glove box under an atmosphere of N₂ or using standard Schlenk techniques. All solvents were degassed and dried using a solvent-purification system provided by Glass Contour. After purification, all solvents were stored under an atmosphere of N₂ over 4 Å molecular sieves. Deuterated benzene (Cambridge Isotope Labs) was dried by stirring over CaH₂ for 24 h and was subsequently vacuum-transferred onto 4 Å molecular sieves. The lithium salt (Et₂O)Li(N[R]Ar₅) was synthesized according to literature procedures.¹ The niobium complexes (Ph₂C₂)NbCl₃(THF)₂ and (Et₂C₂)NbCl₃(DME) were prepared according to literature procedures.² The complex NbCl₃(DME) was prepared according to literature procedures.³ All other reagents were used as supplied by the vendor without further purification. Celite 435 (EMD Chemicals), alumina (Aldrich) and 4 Å molecular sieves (Aldrich) were dried prior to use by heating at 200 °C for 48 h under dynamic vacuum. All glassware was oven dried at 220 °C prior to use. NMR spectra were obtained on either a Varian 500 Inova spectrometer equipped with a Oxford Instruments Ltd. superconducting magnet, a Bruker 400-AVANCE spectrometer equipped with a Magnex Scientific superconducting magnet, or a Varian Mercury 300 spectrometer equipped with an Oxford Instruments Ltd. superconducting magnet.¹ H NMR spectra were referenced to residual CD₅H (7.16 ppm) or CDCl₃ (7.24 ppm).² ²H NMR were reference to internally to naturally abundant ²H resonances from solvent. IR spectra were collected on a Perkin-Elmer 2000 FT-IR spectrophotometer. Elemental analysis was performed by Midwest Microlab, Indianapolis, IN.

C.3.2. Synthesis of (Ph₂C₂)Nb(N[R]Ar₅)Cl₂ (42)

A solution of (Et₂O)Li(N[R]Ar₅) (0.2.51 g, 8.6 mmol) in diethyl ether (200 mL) was prepared and frozen in the cold well. Upon partially thawing, (Ph₂C₂)NbCl₃(THF)₂ (4.48 g, 8.6 mmol) was added directly as a solid to the reaction vessel. The reaction mixture was stirred and allowed to warm to 22 °C. After stirring for 2 h, the reaction mixture was filtered through a sintered glass frit. The filtrate solution was dried under reduced pressure. The dark red orange residue was dissolved in a minimum volume of dichloromethane (25 mL). To this solution, n-pentane (100 mL) was added to precipitate the product as a bright orange powder. The solids were collected on a sintered glass frit and dried under reduced pressure. Yield: 2.38 g (50%).¹ H NMR (CDCl₃, 400 MHz, 22 °C): δ 3.25 (br, 3H, NMe₂), 2.75 (br, 3H, NMe₂), 2.43 (s, 3H, ArMe), 1.27 ppm (m, 3H, R).

C.3.3. Synthesis of (Et₂C₂)Nb(N[R]Ar₅)Cl₂ (43)

Solutions of (Et₂O)Li(N[R]Ar₅) (0.821 g, 2.9 mmol) and (Et₂C₂)NbCl₃(DME) (1.088g, 2.9 mmol) in THF (10 mL each) were frozen in the cold well of the glove box. The solutions were
allowed to partially thaw and were subsequently combined. The reaction mixture was stirred and
allowed to warm to 22 °C. After stirring for 3 h, the reaction mixture was dried under reduced
pressure. The mixture was triturated with toluene (5 mL) and subsequently dried under reduced
pressure. The reaction mixture was extracted into diethyl ether and filtered through a bed of
Celite on a sintered glass frit. The filtrate solution was dried under reduced pressure to give a
tacky orange residue. The residue was washed with n-hexane (10 mL) to give an orange
suspension. The orange solids were collected on a sintered glass frit, washed with n-hexane (3
mL), and then dried under reduced pressure. Yield: 0.832 g (63%). \(^1\)H NMR (C\(_6\)D\(_6\), 400 MHz, 22
°C). δ 3.35 (br, 3H, NMe\(_2\)), 2.83 (br, 3H, NMe\(_2\)), 2.00 (s, 3H, ArMe), 1.27 ppm (s, 3H, R).

C.3.4. Synthesis of (Ph\(_2\)C\(_2\))Nb(N[R]ArL)(ODipp)Cl (44)

Solutions of complex 42 (0.553 g, 1 mmol) and KODipp (0.217 g, 1 mmol) in THF (10 mL
each) were prepared and frozen in the cold well. Upon partially thawing, the solutions were
combined, stirred and warmed to 22 °C. The reaction mixture was stirred for 3 h and
subsequently dried under reduced pressure. The resulting orange residue was extracted into
toluene and then filtered through a bed of Celite on a sintered glass frit. The filtrate solution was
concentrated under reduced pressure to a volume of 5 mL and the solution was layered with n-
hexane (10 mL). The solution was stored at −35 °C for three days to afford an orange crystalline
material. The crystals were isolated by decanting away the mother liquid, washing them with n-
pentane (2 mL), and then drying them under reduced pressure. Yield: 0.403 g (58%).
C.3.5. Synthesis of (Et$_2$C$_2$)Nb(N[R]Ar$_L$)(ODipp)Cl (45)

A suspension of KODipp (0.535 g, 3.5 mmol) in diethyl ether (100 mL) was prepared and then frozen in the cold well. Upon thawing, the niobium complex 43 was added to the stirring suspension as a solid. The reaction mixture was allowed to warm to 22 °C. The reaction mixture was stirred for five hours. The reaction mixture was filtered through a bed of Celite on a sintered glass frit. The filtrate solution was dried under reduced pressure to give an orange residue. The mixture was triturated with n-hexane (20 mL) and dried under reduced pressure. The orange solids were washed with n-pentane to give a suspension. Yellow solids were collected on a sintered glass frit and dried under reduced pressure (0.778 g). The filtrate solution was dried under reduced pressure. The resulting residue was taken up in a 1:1 mixture of diethyl ether:methylene chloride (2 mL) and stored at –35 °C for 24 h to give yellow crystals. The mother liquid was decanted away from the crystals, which were then washed with cold diethyl ether and dried under reduced pressure (0.324 g). Yield from both collections: 1.102 g (74%).

Figure C 6. $^1$H NMR Spectrum of (Ph$_2$C$_2$)Nb(N[R]Ar$_L$)(ODipp)Cl (44). CDCl$_3$, 400 MHz, 22 °C.

A solution of complex 45 (1.262 g, 2.1 mmol) in THF (50 mL) was prepared. Sodium azide (0.411 g, 6.3 mmol) was added to the stirring solution at 22 ºC. The reaction mixture was stirred for 12 h. The reaction mixture was dried under reduced pressure. The resulting residue was taken up into toluene and subsequently filtered through a bed of Celite on a sintered glass frit. The filtrate solution was dried under reduced pressure. The residue was washed with $n$-hexane to give an orange suspension, which was cooled to −35 ºC and then filtered through a sintered glass frit to collect the solids. The orange powder was dried under reduced pressure. Yield: 0.556 g (44%). IR (thin film, KBr): 2075 cm$^{-1}$. 

Figure C 7. $^1$H NMR spectrum of (Et$_2$C$_2$)Nb(N[R]Ar$_l$)(ODipp)Cl (45). CDC$_3$, 400 MHz, 22 ºC.
Figure C 8. $^1$H NMR spectrum of (Et$_2$C$_2$)Nb(N[R]Ar$_L$)(ODipp)N$_3$ (46).


A solution of complex 46 (0.355 g, 0.6 mmol) in THF (10 mL) was prepared in a PTFE-valve sealed quartz reaction vessel. The headspace of the flask was evacuated and left under static vacuum. The reaction mixture was irradiated with a broad band of UV/Vis radiation. After irradiating for 12 h, the color of the solution had changed from bright orange to dark red-orange. The flask was returned to the glove box where the reaction mixture was taken to dryness under reduced pressure. The resulting solids were dissolved in a 10:1 n-pentane:THF mixture (3 mL), which was then filtered through a plug of Celite on a glass fiber filter. The filtrate solution was concentrated to a volume of 1 mL and stored at $-35 \degree C$ for 12 h to afford dark red crystals. The mother liquid was decanted away from the crystals, which were washed with n-pentane (1 mL) and then dried under reduced pressure. Yield: 0.150 g (53%).

C.3.8. Synthesis of Cl$_2$Nb(N[R]Ar$_L$)$_2$ (48)

A suspension of NbCl$_3$(DME) (0.600 g, 2.1 mmol) in toluene (12 mL) was prepared. A solution of (Et$_2$O)Li(N[R]Ar$_L$) (1.15 g, 4.2 mmol) in diethyl ether (40 mL) was prepared. Both mixtures were frozen in the cold well. After being allowed to partially thaw, the two mixtures
were combined. The reaction mixture was allowed to warm to 22 °C with stirring. After stirring for 18 h, the reaction mixture was filtered through a bed of Celite on a sintered glass frit. The filtrate solution was dried under reduced pressure. The resulting solids were triturated with n-hexane (10 mL) and then dried under reduced pressure. The resulting orange solids were suspended in n-hexane, collected on a sintered glass frit via vacuum filtration, and then dried under reduced pressure. Yield: 0.437 g (37%). 

\[ ^{2}H \text{NMR (C}_6\text{H}_6, 61.42 \text{ MHz, 20 °C): } \delta 11.86 \text{ (br), 7.16 (br).} \]

C.3.9. Crystallographic Details

Low-temperature data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo/Kα radiation (λ = 0.71073 Å), performing o- and φ-scans. All structures were solved either by direct or Patterson methods using SHELXS and refined against \( F^2 \) on all data by full-matrix least squares with SHELXL-97. A semi-empirical absorption correction (SADABS) was applied to the diffraction data for all structures. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the \( U \) value of the atoms they are linked to (1.5 times for methyl groups).

Complex 42 crystallizes in the space group \( P2_1/n \) and the structure was solved using direct methods. Refinement proceeded by assigning atom positions according to the electron-density difference map. No restraints were used in the refinement. The thermal ellipsoid plot was generated using PLATON.

Complex 44 crystallizes in the space group \( P2_1/c \), and the structure was solved using direct methods. Refinement proceeded by assigning atom positions according to the electron-density difference map. The diphenylacetylene ligand and a single \(^{3}\text{Pr} \) moiety suffered from positional disorder. This was refined by allowing the ratio of the two positions to refine freely while constraining the total occupancy to unity. 1,2- and 1,3-distance similarity restraints were applied to the disordered portions of the molecule and identical related functional groups in the molecule. Anisotropic displacement parameters for the entire molecule were restrained assuming rigid bond behavior. The anisotropic displacement parameters for one of the \(^{3}\text{Pr} \) groups were restrained to be isotropic. The thermal ellipsoid plot was generated using PLATON.

Complex 46 crystallizes in the space group \( P2_1/n \), and the structure was solved using direct methods. Refinement proceeded by assigning atom positions according to the electron-density difference map. No restraints were used in the refinement. The thermal ellipsoid plot was generated using PLATON.

Complex 47 crystallizes in the space group \( P\overline{1} \), and the structure was solved using direct methods. Refinement proceeded by assigning atom positions according to the electron-density difference map. One of the anilide ligands and one of the aryloxide ligands suffer from a positional disorder. This was refined by allowing the ration of the two positions to refine freely.
while constraining the total occupancy to unity. 1,2- and 1,3-distance similarity restraints were applied to the disordered portions of the molecule and identical related functional groups in the molecule. Anisotropic displacement parameters for the entire molecule were restrained assuming rigid bond behavior. The thermal ellipsoids plot was generated using PLATON.\textsuperscript{7}

Complex 48 crystallizes in the space group $P\bar{1}$, and the structure was solved using direct methods. Refinement proceeded by assigning atom positions according to the electron-density difference map. No restraints were used in the refinement. Thermal ellipsoids plot was generated using PLATON.\textsuperscript{7}
Table C. 1. Crystal data for (Ph₂C₂)Nb(N[R]Ar)Cl₂ (42) and (Ph₂C₂)Nb(N[R]ArL)(ODipp)Cl (44).

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<td>P2₁/c</td>
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<tr>
<td>Unit cell dimensions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>9.9493(1) Å, a = 90°</td>
<td>23.207(2) Å, a = 90°</td>
</tr>
<tr>
<td>b</td>
<td>17.782(2) Å, β =</td>
<td>8.7159(8) Å, β =</td>
</tr>
<tr>
<td>c</td>
<td>108.684(2)°, c =</td>
<td>110.507(2)°, c =</td>
</tr>
<tr>
<td></td>
<td>15.429(2) Å, γ = 90°</td>
<td>18.468(2) Å, γ = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>2585.8(6) Å³</td>
<td>3498.8(6) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.406 g/cm³</td>
<td>1.308 g/cm³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.689 mm⁻¹</td>
<td>0.453 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>1128</td>
<td>1448</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.60 × 0.60 × 0.19 mm³</td>
<td>0.18 × 0.15 × 0.15 mm³</td>
</tr>
<tr>
<td>Theta range for collection</td>
<td>1.80 to 28.7°.</td>
<td>0.94 to 27.55°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-13 ≤ h ≤ 13, -22 ≤ k ≤ 24, -20 ≤ l ≤ 20</td>
<td>-30 ≤ h ≤ 28, -11 ≤ k ≤ 11, -23 ≤ l ≤ 23</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>50265</td>
<td>59579</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>6678 [R(int) = 0.0648]</td>
<td>8068 [R(int) = 0.0826]</td>
</tr>
<tr>
<td>Completeness to θmax</td>
<td>100%</td>
<td>99.8%</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Multi-scan (SADABS)</td>
<td>Multi-scan (SADABS)</td>
</tr>
<tr>
<td>Max. and min.</td>
<td>0.8802 and 0.6826</td>
<td>0.9352 and 0.9230</td>
</tr>
<tr>
<td>transmission</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>6678 / 0 / 295</td>
<td>8068 / 1022 / 563</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.019</td>
<td>1.009</td>
</tr>
<tr>
<td>Final R indices [I &gt; 2σ(I)]</td>
<td>R₁ = 0.0308, wR₂ = 0.0665</td>
<td>R₁ = 0.0377, wR₂ = 0.0777</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.0449, wR₂ = 0.0729</td>
<td>R₁ = 0.0635, wR₂ = 0.0898</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.502 and -0.497 e Å⁻³</td>
<td>0.437 and -0.528 e Å⁻³</td>
</tr>
</tbody>
</table>
Table C. 2. Crystal data for and (Et₂C₂)Nb(N[R]Ar₅)(ODipp)N₃ (46) and [NNb(N[R]Ar₅)(ODipp)]₂ (47).

<table>
<thead>
<tr>
<th>Property</th>
<th>46</th>
<th>47</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reciprocal Net # / CCDC #</td>
<td>10258/XX</td>
<td>09481/XX</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C₃H₅N₅NbO</td>
<td>C₂H₈N₆Nb₂O₃</td>
</tr>
<tr>
<td>Formula weight</td>
<td>599.65 g/mol</td>
<td>1053.11 g/mol</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁/n</td>
<td>P₁</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 9.5098(6) Å, α = 90°</td>
<td>a = 9.108(3) Å, α = 92.197(8)°</td>
</tr>
<tr>
<td></td>
<td>b = 16.438(1) Å, β = 93.391(1)°</td>
<td>b = 14.895(5) Å, β = 97.18(1)°</td>
</tr>
<tr>
<td></td>
<td>c = 19.961(1) Å, γ = 90°</td>
<td>c = 20.785(7) Å, γ = 101.772(8)°</td>
</tr>
<tr>
<td></td>
<td>a = 9.108(3) Å, α = 92.197(8)°</td>
<td>b = 14.895(5) Å, β = 97.18(1)°</td>
</tr>
<tr>
<td></td>
<td>c = 20.785(7) Å, γ = 101.772(8)°</td>
<td></td>
</tr>
<tr>
<td>Volume</td>
<td>3114.9(3) Å³</td>
<td>2733(2) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.279 g/cm³</td>
<td>1.280 g/cm³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.417 mm⁻¹</td>
<td>0.465 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>1272</td>
<td>1116</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.27 × 0.20 × 0.20 mm³</td>
<td>0.40 × 0.05 × 0.05 mm³</td>
</tr>
<tr>
<td>Theta range for collection</td>
<td>1.61 to 27.52°</td>
<td>0.99 to 25.35°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>−12 ≤ h ≤ 12, −21 ≤ k ≤ 21, −25 ≤ l ≤ 25</td>
<td>−10 ≤ h ≤ 10, −17 ≤ k ≤ 17, −25 ≤ l ≤ 25</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>59641</td>
<td>42993</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>7166 [R(int) = 0.0501]</td>
<td>9977 [R(int) = 0.0946]</td>
</tr>
<tr>
<td>Completeness to θ_max</td>
<td>99.9%</td>
<td>100%</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Multi-scan (SADABS)</td>
<td>Multi-scan (SADABS)</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9213 and 0.8957</td>
<td>0.9771 and 0.8539</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>7166 / 0 / 335</td>
<td>9977 / 1778 / 911</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.088</td>
<td>1.006</td>
</tr>
<tr>
<td>Final R indices [I &gt; 2σ(I)]</td>
<td>R₁ = 0.0274, wR₂ = 0.0672</td>
<td>R₁ = 0.0489, wR₂ = 0.1000</td>
</tr>
<tr>
<td></td>
<td>R₁ = 0.0343, wR₂ = 0.0720</td>
<td>R₁ = 0.0945, wR₂ = 0.1200</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.785 and −0.613 e Å⁻³</td>
<td>0.603 and −0.741 e Å⁻³</td>
</tr>
</tbody>
</table>
**Table C.3.** Crystal data for Cl₂Nb(N[R]Ar)₂ (48).

<table>
<thead>
<tr>
<th>Reciprocal Net # /CCDC #</th>
<th>09357/XX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₂₆H₄₂Cl₂N₆Nb</td>
</tr>
<tr>
<td>Formula weight</td>
<td>574.45 g/mol</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>pT</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>9.6080(6) Å, α = 92.009(1)°</td>
</tr>
<tr>
<td>b</td>
<td>10.289) Å, β = 105.230(1)°</td>
</tr>
<tr>
<td>c</td>
<td>15.8935(1) Å, γ = 116.091(1)°</td>
</tr>
<tr>
<td>Volume</td>
<td>1340.8(1) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.423 g/cm³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.670 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>602</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.25 × 0.25 × 0.10 mm³</td>
</tr>
<tr>
<td>Theta range for collection</td>
<td>1.35 to 27.46°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -20 ≤ l ≤ 20</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>26527</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>6133 [R(int) = 0.0431]</td>
</tr>
<tr>
<td>Completeness to θmax</td>
<td>99.7%</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Multi-scan (SADABS)</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9316 and 0.8504</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>6133 / 0 / 310</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.037</td>
</tr>
<tr>
<td>Final R indices [I &gt; 2σ(I)]</td>
<td>R₁ = 0.0289, wR₂ = 0.0680</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.0353, wR₂ = 0.0717</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.488 and -0.344 e Å⁻³</td>
</tr>
</tbody>
</table>
C.4. References


