β-DIKETIMINATO NICKEL AND COPPER COMPLEXES IN C-N BOND FORMATION AND N-O BOND ACTIVATION

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ABSTRACT

Carbon-nitrogen bond formation (C-N) is an essential process in synthetic chemistry. The ability to form C-N bonds without traditional functional group manipulations can decrease synthetic steps and chemical byproducts.

A focus of this work is the development of nickel and copper systems for catalytic C-N bond formation. Our approach involves the discovery of stoichiometric transformations, study of mechanistic details, and application of these insights to develop new catalytic protocols for C-N bond formation.

We target nickel-nitrenes [Ni]=NR and nickel-amides [Ni]-NHR as active intermediates in carbodiimide (RN=C=NR’) formation. Chapter 1 describes the use of organoazides RN₃ with the β-diketiminato nickel(I) complex [Me₃NN]Ni(2-picoline) to generate reactive nickel nitrene complexes {{[Me₂NN]Ni}₂(μ-NR). Reaction of [Ni]=NR with isocyanides CNR’ stoichiometrically forms carbodiimides RN=C=NR’. Stoichiometric investigations resulted in [Me₃NN]Ni(2-picoline) as a catalyst for carbodiimide formation. Chapter 2 investigates the use of amines HNR₁R² to prepare nickel(II) amides [Me₃NN]Ni-NR₁R² via acid/base chemistry of a nickel(II) alkoxide {{[Me₂NN]Ni}₂(μ-OBu’). Reactivity studies of these nickel(II) amides with tert-
butylisocyanide identified key features to make these intermediates amenable to carbodiimide formation.

Stoichiometric studies in Chapter 3 identify the three-coordinate β-diketiminato copper(II) amide [Cl\textsubscript{2}NN]Cu-NHAd in the amination of C-H bonds. This C-H functionalization reaction proceeds by hydrogen atom abstraction (HAA) followed by radical combination (RC). Use of the oxidant 'BuOOBu' allows for the generation of [Cl\textsubscript{2}NN]Cu-NR\textsubscript{1}R\textsubscript{2} active intermediates from amines HR\textsubscript{1}R\textsubscript{2}. These studies lead to the first catalytic method to convert unactivated alkyl amines HNR\textsubscript{1}R\textsubscript{2} into C-H functionalized products R-NR\textsubscript{1}R\textsubscript{2}. To examine the influence of the supporting β-diketiminato ligand on this C-H functionalization reactivity, Chapter 4 describes the new electron-deficient catalyst \{[Cl\textsubscript{2}NN\textsubscript{F6}]Cu\}_2(benzene). The electron-deficiency allows the use of a broader range of substrates for catalytic C-N and C-O bond forming reactions.

Chapter 5 reinvestigates [Me\textsubscript{3}NN]Ni=NAd for C-H functionalization. Similar bifunctional reactivity of [Me\textsubscript{3}NN]Ni=NAd with C-H substrates occurs to give new nickel(II) amides.

With relevance to bioinorganic chemistry, Chapter 6 focuses on the activation of the N-O bonds in nitroso compounds ArN=O by β-diketiminato nickel and copper complexes. This study harnesses the reducing power of these complexes to reveal new bonding modes [Ni\textsubscript{2}(μ-η\textsubscript{2}:-η\textsubscript{2}-ONAr)], [Cu\textsubscript{2}(μ-η\textsubscript{2}:-η\textsubscript{1}-ONAr)], and [Cu](η\textsubscript{2}-ONAr) that may foreshadow unknown HNO binding modes.
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RESPECTIVE CONTRIBUTIONS

Dr. Susanne Mossin from Professor Dr. Karsten Meyer’s research group at the University of Erlangen-Nürnberg, Germany acquired some EPR spectra in Chapters 1 and 6 as well as all EPR spectra in Chapter 3. Dr. Mossin also performed the challenging simulation studies of the copper(II)-amide and –alkoxide species reported in Chapter 3. Prof. Jeffrey Peterson of West Virginia University performed EPR analyses of \([\text{Me}_2\text{NN}]\text{Cu}(\kappa^2-\text{O}_2\text{N}_2\text{Ar})\) reported in Chapter 6.

Prof. Tom Cundari and Dr. Jason McAfee at the University of North Texas performed computational investigations of the H-atom abstraction / radical combination pathways discussed in Chapters 3 and 5 regarding the reaction of \([\text{Cl}_2\text{NN}]\text{Cu-}\text{NHAd}\) and \([\text{Me}_3\text{NN}]\text{Ni=NHAd}\) with hydrocarbon substrates R-H.

Professor Timothy H. Warren performed DFT studies of the dinuclear nickel species \({\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{Ar})}\) and \({\{[\text{Me}_2\text{NN}]\text{Ni}\}_2(\mu-\eta^2:\eta^2-\text{ONAr})}\) discussed in Chapters 1 and 6.

XAS spectra of nickel and copper C-nitroso compounds discussed in Chapter 6 were acquired at SLAC by Dr. Stephen Sproules from Professor Dr. Karl Wieghardt’s group at the Max Planck Institute for Bioinorganic Chemistry in Mülheim, Germany. Dr. Neil Tomson of the Wieghardt group has begun to simulate these spectra computationally.
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Chapter 1

Nickel-Catalyzed Nitrene Transfer to Isocyanides

Abstract

The β-diketiminato nickel(I) species [Me₃NN]Ni(2,4-lutidine) and [Me₃NN]Ni(2-picoline) serve as catalysts for carbodiimide (RN=C=NR’) and isocyanate (RN=C=O) formation in the reactions of a range of organoazides N₃R with isocyanides R’NC and carbon monoxide. Stoichiometric reactivity studies indicate that the nickel nitrenes [Ni]₂(µ-NR) and [Ni]=NR serve as intermediates in this catalytic nitrene-transfer reaction with [Me₃NN]Ni(CNR)₂ and {[Me₃NN]Ni}₂(µ-CO)₂ species serving as resting states. Addition of 3,5-dimethylphenylazide (N₃Ar₃,5-Me₂) to 2 equiv. [Me₆NN]Ni(2-picoline) (x = 2 or 3) in Et₂O yields the dinickel nitrenes {[Me₆NN]Ni}₂(µ-NAr₃,5-Me₂) as deep purple, diamagnetic substances which features a Ni-Ni distance of 2.7210(3) Å in the X-ray structure of {[Me₂NN]Ni}₂(µ-NAr₃,5-Me₂). These dinickel nitrenes react stoichiometrically with isocyanides CNR to yield the corresponding carbodiimides RN=C=NAr₃,5Me₂. Other stoichiometric reactions involve the isolation of [Me₃NN]Ni(CN‘Bu)₂ and [Me₃NN]Ni(CNAr₂,6-Me₂)₂ via the addition of tert-butylisocyanide or 2,6-dimethylphenylisocyanide to [Me₁NN]Ni(2-picoline). Addition of N₃Ar₃,5-Me₂ to these isocyanide adducts [Me₃NN]Ni(CNR)₂ delivers the
corresponding carbodiimides RN=C=NAr\(^{3,5}\)Me\(^2\). Based on these stoichiometric results, a catalytic cycle is suggested using [Me\(_3\)NN]Ni(2-picoline) as a pre-catalyst to produce carbodiimides from a family of organoazides and two different isocyanides.

**Introduction**

1.1.a. *Carbodiimide synthesis, applications and possible alternative synthetic routes*

Carbodiimides are commonly used as dehydrating agents in organic syntheses. Peptide synthesis is a very common organic reaction during which a carboxylic acid reacts with an amine to liberate water. Carbodiimides commonly facilitate this reaction as

**Scheme 1.1.** a. Application of carbodiimides. b. Synthetic route to carbodiimides. c. Alternative route to carbodiimides.

---

Disadvantages:
- Phosgene: poisonous gas
- HCl: corrosive byproduct

Examples:
- N=C=N
- DCC
- Cy
- N=C=N
- DHC
- Pr

Possible Synthons:
- N=C=N
- R
- R'
- N=C=N
- R
- +
- N=C=N
- R'
- nitrene
- isocyanide
dehydrating agents adding a water molecule across the nitrogen-carbon-nitrogen unit to give the corresponding urea. Two of the most commonly used dehydrating agents are DCC (dicyclohexyl carbodiimide) and DIC (diisopropyl carbodiimide) (Scheme 1.1a).¹

Carbodiimides are synthesized on an industrial scale using ureas or thioureas and phosgene (COCl₂). A concern in the industrial synthesis of these compounds is the use of phosgene, a poisonous gas used during World War I as a chemical weapon that gives hydrochloric acid as a corrosive byproduct (Scheme 1.1b). These heterocumulenes also serve as important large-scale industrial intermediates and are also used in the synthesis of many specialty chemicals as organic building blocks that possess nucleophilic moieties at the nitrogen atoms and an electrophilic center at the carbon atoms.² For instance, the therapeutic cyanoguanidine derivative N-(3-chloro-5-cyanophenyl)-N’-cyano-N”-tert-pentylguanidine is a vasodilator that acts upon potassium channels with minimum side effects and is synthesized from a carbodiimide (Scheme 1.2).³–⁶

**Scheme 1.2.** Total synthesis of cyanoguanidine derivative.
A number of organic synthetic routes to carbodiimides RN=C=NR’ exist and often involve the reaction between an isocyanate RNCO, an amine R’NH₂, and triphenylphosphine. These reactions proceed via an aza-Wittig type of mechanism during which a phosphaimide Ph₃P=NR’ reacts with an isocyanate to form the corresponding phosphine oxide (Scheme 1.3a,b). Alternatively, urea derivatives can be formed in reactions between amines and isocyanates. They undergo dehydration reactions in the presence of phosphine and base to deliver the corresponding carbodiimide (Scheme 1.3c).

**Scheme 1.3.** Examples of aza-Wittig variations to carbodiimides (a and b). Example of thiourea dehydration to carbodiimide (c).

![Scheme 1.3](image_url)
1.1.b. Alternative routes to carbodiimides not involving metal nitrenes

An alternative route to carbodiimides involves the catalytic reaction of amines and isocyanides using either PdCl₂/Ag₂O\(^{10}\) or solid state Au surface chemistry and O₂ as the oxidant.\(^{11}\) Both of these precious metal catalyst systems react quite differently as compared to the previously mentioned catalysts. The amine and isocyanide react at the metal (Pd or Au) to form a metal bound urea adduct (Scheme 1.4). In the case of Pd, Ag₂O oxidizes the urea moiety releasing the carbodiimide and 1 equiv. water. For Au, O₂ is the oxidant that releases the carbodiimide and produces water as the stoichiometric byproduct (Scheme 1.4)\(^{10,11}\).

**Scheme 1.4.** Pd or Au catalyzed RN=C=NR’ formation with amines.

\[
\text{RNH}_2 + \text{R'NC} \xrightarrow{\text{Au or PdCl}_2(\text{R'NC})} [\text{M}] \xrightarrow{\text{Ag}_2\text{O or O}_2} \text{RN=C=NR'} - \text{H}_2\text{O}
\]

Even though the aforementioned Pd and Au systems allow for reactions between commercially available amines and isocyanides, the cost of the catalyst can be a concern and motivates the development of systems based on less expensive metals such as first row transition metals. In addition, the heterogeneous character of the Au system does not lend itself as readily to detailed structural analysis of intermediates that could provide valuable mechanistic insights.
1.1.c. Metal complexes can stabilize nitrenes

Dissecting the carbodiimide moiety (RN=C=NR’), one can conceptually split one of the nitrogen-carbon double bonds to arrive at a nitrene and isocyanide (Scheme 1.1c). Nitrenes (NR) themselves are highly reactive, unselective electron-deficient species possessing only six valence electrons about the nitrene N atom. Metals can stabilize nitrenes via binding and guide their reactivity in a highly selective fashion. Nitrenes are stabilized by binding to the metal via N->M σ-donation while accepting additional electron density from the metal via π-backbonding (Figure 1.1). Early

![Figure 1.1. σ-donation from N to M. π-backbonding from M to N.](image)

Figure 1.1. Late and early TM interactions with the nitrene moiety.

![Figure 1.2. Late and early TM interactions with the nitrene moiety.](image)
transition metals with d electrons undergo a more complete backbonding interaction due to their higher electropositive nature (high energy d orbitals) giving the NR unit nucleophilic character. Late transition metals undergo a more covalent interaction since the d-electron orbital of the metal and empty orbital on the nitrogen are closer in energy. The smaller metal – nitrogen orbital energy difference arises from the higher electronegativity of the late transition metal vs. an early transition metal. This phenomena provides late M=NR with electrophilic character at the nitrogen (Figure 1.2). Thus early transition metal [M]≡NR compounds are deemed “imides” in which the metal is in a high formal oxidation state while late transition metal [M]=NR species may be called “nitrenes” with the metal in a lower formal oxidation state. This picture suggests similar trends that are observed among Schrock alkylidenes (nucleophlic at C) and Fischer carbenes (electrophilic at C).

1.1.d. Metal nitrenes in reactions with C-H bonds, alkenes, and isocyanides

Metal nitrenes (M=NR) serve as active intermediates in a variety of carbon-nitrogen (C-N) bond forming reactions such as C-H functionalization, alkene aziridination, and carbodiimide formation (Scheme 1.5). C-H functionalization involves the activation of a C-H bond and will be discussed in great detail in later chapters. Aziridination and carbodiimide formation are similar in that they transfer nitrene species to unsaturated organic compounds. This chapter focuses exclusively on carbodiimide and isocyanate formation.
1.1.e. Metal imides and isocyanates in the formation of carbodiimides

Isocyanates RN=O have been used with a number of group 5 and 6 imido complexes to form symmetric via expulsion of carbon dioxide (CO$_2$) (Scheme 1.6). A metal-oxo functionality reacts with 1 equiv. isocyanate to form a four-membered metalloccycle which goes on to expel CO$_2$ to yield a metal-imido intermediate. This

**Scheme 1.5.** Reactivity of metal-nitrenes [M]=NR with organic compounds.

**Scheme 1.6.** M=NR as intermediates in group 5 and 6 facilitated carbodiimide formation.
metal-imido reacts with a second equivalent of isocyanate to form a metallacycle that expels the desired carbodiimide and reforms the metal-oxo.\textsuperscript{13-15} Due to the use of two equiv. isocyanate only symmetric carbodiimides can be formed.

\textbf{1.1.f. Metal nitrenes and isocyanides for carbodiimide formation}

The combination of organoazides and isocyanides has been used in the literature to arrive at the more challenging and valuable unsymmetric carbodiimides. Hillhouse and Mindiola isolated a mononuclear Ni nitrene species (dtbpe)Ni=N(2,6-\textsuperscript{i}Pr\textsubscript{2}C\textsubscript{6}H\textsubscript{3}) (dtbpe = 1,2-bis(di-\textit{tert}-butylphosphino)ethane) by addition of LiNH(2,6-\textsuperscript{i}Pr\textsubscript{2}C\textsubscript{6}H\textsubscript{3}) to the dinuclear nickel(I) chloride complex \{(dtbpe)Ni\textsubscript{2}(\mu-Cl)\textsubscript{2}. (dtbpe)Ni=N(2,6-\textsuperscript{i}Pr\textsubscript{2}C\textsubscript{6}H\textsubscript{3})\textsuperscript{-} reacts with unsaturated small molecules such as benzyl isocyanide (PhCH\textsubscript{2}NC) and carbon monoxide (CO) to give nickel bound carbodiimide or isocyanate adducts. The product carbodiimide or isocyanate is only released from the metal upon addition of excess CO (Scheme 1.7). The use of lithium salts for the synthesis of the nickel imido species (dtbpe)Ni=N(2,6-\textsuperscript{i}Pr\textsubscript{2}C\textsubscript{6}H\textsubscript{3}) along with tight binding of the carbodiimide product prevents this system from being able to readily form carbodiimides and isocyanates in a catalytic manner.\textsuperscript{16,17}
Initial attempts to employ (dtbpe)Ni=NR intermediates from the reaction with organoazides to perform nitrene group transfer to small unsaturated molecules (e.g. CO and CNR) suffered from the competition reaction to form diazenes RN=NR.\textsuperscript{16-20} Hillhouse \textit{et al.} reported a more recent NHC Ni catalyst system (NHC = N-heterocyclic carbene) that activates organoazides in the presence of isocyanides using a dinuclear Ni catalyst (\{(iPr)Ni(μ-Cl)\}_2). Employing a 10 mol% catalyst loading, yields of up to 80% may be obtained for a small range of azide and isocyanide substrates at room temperature (Scheme 1.8).\textsuperscript{21}

While our work was under development, Holland \textit{et al.} demonstrated the use of organoazides RN\textsubscript{3} and isocyanides CNR’ to form carbodiimides RN=C=NR’ via the

\textbf{Scheme 1.8.} Ni catalyzed RN=C=NR’ formation.
dinuclear \(\beta\)-diketiminato iron pre-catalyst \(\{L^1\text{Bu}Fe\}_2(\mu-N_2)\). The reaction conditions require heating of up to 60 °C and a catalyst loading of 5 mol %. This system is able to form carbodiimides for a limited number of substrates in yields of up to 95% (Scheme 1.9). Holland et al. showed spectroscopically that a terminal iron(III) imido \(L^1\text{Bu}Fe=NR\) is the active intermediate.\(^{22}\)

1.1.g. \(\beta\)-Diketiminato Ni imides – stoichiometric reactivity

Warren et al. reported a paramagnetic, singly bridged \(\beta\)-diketiminato dinickel imide \(\{[\text{Me}_2\text{NN}]\text{Ni}\}_2(\mu-\text{NAd})\) that forms from the reaction of \([\text{Me}_2\text{NN}]\text{Ni}(2,4\text{-lutidine})\) and 1-azidoadamantane (AdN\(_3\)).\(^{23}\) A slight steric increase at the para position on the \(\beta\)-diketiminato \(N\)-aryl rings yielded the terminal Ni imide \([\text{Me}_3\text{NN}]\text{Ni}=\text{NAd}\) isolated from the reaction of \([\text{Me}_3\text{NN}]\text{Ni}(2,4\text{-lutidine})\) with AdN\(_3\). Stoichiometric reactivity studies showed imide transfer to unsaturated organics. For instance, reactions between \([\text{Me}_3\text{NN}]\text{Ni}=\text{NAd}\) and \textit{tert}-butylisocyanide (\('\text{BuNC}\)) or CO provide the corresponding carbodiimide (AdN=\(C=\text{N}^\prime\text{Bu}\)) or isocyanate (AdN=\(C=O\)) in good yields. Further reactivity studies revealed complete group transfer to PMe\(_3\) to give Me\(_3\)P=\text{NAd}. Radical character at the imido N atom of \([\text{Me}_3\text{NN}]\text{Ni}=\text{NAd}\) indicated its frozen glass X-band
EPR spectrum \((A_2(^{14}\text{N} = 22\text{ G}))\) was demonstrated via the reaction with cobaltocene (Cp₂Co) to produce the nickel(II)-amide \([\text{Me}_3\text{NN}]\text{Ni-NAAd}(\eta^4\text{-C}_5\text{H}_5)\text{CoCp}\). This radical type reactivity was further substantiated via the hydrogen atom abstraction (HAA) reaction employing \(1,4\)-cyclohexadiene (C-H BDE = 77 kcal/mol)\(^{24}\) that gave \([\text{Me}_3\text{NN}]\text{Ni-NHAd}\) and benzene (Scheme 1.10)\(^{23}\).

The radical character of a related Ni(III) imido species was also observed by Stephan et al. in the reaction of a related \(\beta\)-diketiminato Ni(I) species \([[\text{iPr}_2\text{NN}]\text{Ni}]_2(\eta^6\text{-toluene})\) with 2,6-diisopropylphenylazide or 2,6-dimethyphenylazide (Scheme 1.11)\(^{25}\).

C-C bond coupling reactions were observed via the likely intermediacy of terminal Ni(III)-arylimido species \([[\text{iPr}_2\text{NN}]\text{Ni}=\text{NAr}]\). The Ni(III) imide can also be thought of as a Ni(II)-arylimidyl radical that can dimerize via C-C bond formation at the \textit{para} position. Alternatively, C-N bond formation at the \textit{para} position of the imido N-aryl ring could yield a new Ni(II) amido species occurs via attack of the \([\text{Ni}]=\text{NAr}\) moiety at this position.
It is important to point out that an efficient catalyst for carbodiimide formation and isocyanate formation would activate organoazides and completely transfer the nitrene group to isocyanide and CO without undergoing these C-C and C-N bond forming side-reactions.

Results and Discussion

1.2.a. β-Diketiminato ligand synthesis and catalyst synthesis

The β-diketiminato ligand H[Me₃NN] may be prepared as previously reported by Warren et al.²³ by refluxing 2,4-pentadione with 2 equiv. 2,4,6-trimethylaniline with p-toluenesulfonic acid in toluene for 3 hours provides the tosylate salt of the β-diketimine ligand which upon basic workup with sodium carbonate and crystallization from methanol provides white crystals of the β-diketimine H[Me₃NN] in >95% yield.

(Scheme 1.12). The corresponding potassium salt is formed via addition of KH followed by reaction with thallous acetate to give Tl[NNMe$_3$] as yellow crystals.$^{23}$

**1.2.b. Synthesis of new nickel(I) 2-picoline precursors**

Reaction of Tl[Me$_3$NN] with anhydrous NiI$_2$ and 2-picoline (or 2,4-lutidine) followed by reduction with Na/Hg gives [Me$_3$NN]Ni(2-pic) (1a) in 80% yield and ([Me$_3$NN]Ni(2,4-lut) (1b)$^{23}$ as red crystals from Et$_2$O (Scheme 1.13).

**Scheme 1.13. New nickel(I) precursor synthesis.**

The single crystal X-ray structure of 1a (Figure 1.3) shows a “bent” trigonal planar structure with a N2-Ni-N3 angle of 156.15(8)$^\circ$ that is considerably more obtuse than the N1-Ni-N3 angle of 107.03(8)$^\circ$. These angles are very similar to the angles found in [Me$_2$NN]Ni(2,4-lutidine)$^{23}$ (N1-Ni-N3: 153.58(9)$^\circ$; N2-Ni-N3: 108.78(9)$^\circ$). The Ni-N$_{\beta}$-dik distances of 1.938(2) and 1.896(2) Å and Ni-N$_2$-pic distance of 1.966(2) Å in 1a also compare closely to distances in [Me$_2$NN]Ni(2,4-lutidine)$^{23}$ (Ni-N$_{\beta}$-dik: 1.873(2) and 1.925(2) Å; Ni-N$_2$-lut: 1.946(2) Å)
Measurement of the magnetic moment of 1a in benzene-$d_6$ by the Evans method gives $\mu_{\text{eff}} = 1.55$ B.M. in the presence of a slight excess of 2-picoline. This value is consistent with the presence of one unpaired electron ($\mu_{\text{eff}}(\text{spin-only}) = 1.73$ B.M.) and is analogous to [Me$_2$NN]Ni(2,4-lutidine) which has $\mu_{\text{eff}} = 1.8$ B.M. in the presence of excess 2,4-lutidine.\textsuperscript{23} EPR glass spectra of 1a at 89 K in toluene glass (with a drop of 2-picoline) indicates a rhombic environment with $g_1 = 2.41$, $g_2 = 2.12$ and $g_3 = 2.06$ (Figure 1.5). These values are essentially identical to those seen for [Me$_2$NN]Ni(2,4-lutidine)\textsuperscript{23} ($g_1 = 2.435$, $g_2 = 2.133$ and $g_3 = 2.068$).
Figure 1.3. X-ray crystal structure of [Me₃NN]Ni(2-picoline) (1a). All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ni – N1 1.938(2), Ni – N2 1.896(2), Ni – N3 1.966(2), N1 – Ni – N2 96.77(8), N1 – Ni – N3 107.03(8), and N2 – Ni – N3 156.15(8).
Figure 1.4. X-band EPR spectrum of [Me$_3$NNi(2-picoline) (1a) in toluene at RT $g_{\text{iso}} = 2.21$.

Figure 1.5. X-band EPR spectrum of [Me$_3$NNi(2-picoline) (1a) with excess 2-picoline in toluene at 89 K as frozen glass $g_1 = 2.41$, $g_2 = 2.12$ and $g_3 = 2.06$. 
1.2.c. Initial catalytic reactions

As probed by the commercially available isocyanides CNBu\(^t\) and CNAr (Ar = 2,6-Me\(_2\)C\(_6\)H\(_3\)), the monovalent [Me\(_3\)NN]Ni(2-picoline) (1a) pre-catalyst exhibits broad azide substrate scope (Table 1.1). In our initial screen, we employed a 5 mol % loading of 1a relative to the isocyanide (~0.2 M) and azide (~0.2 M) reactants for 30 min in Et\(_2\)O at RT. The arylazides ArN\(_3\) examined (Ar = 2,4,6-trimethylphenyl, 3,5-bis(trifluoromethyl)phenyl, 2,6-dimethylphenyl and phenyl) in combination with tert-butylisocyanide (\(^t\)BuNC) gave excellent yields (79 – 99%). In contrast, the more electron-poor arylisocyanide Ar’NC in combination with arylazides ArN\(_3\) delivered moderate yields (46 – 84%), with particularly poor performance by the sterically hindered azide MesN\(_3\) (< 5%) (Table 1.1).

Reactions with the arylisocyanide ArNC proceed more sluggishly and require longer reaction times (17 h) to obtain high yields of 73 - 99%. In particular, the reaction between mesityl azide and ArNC requires heating at 60 °C in benzene for 24 h to improve the yield to 73% (Table 1.1).

We also examined the primary aliphatic azide PhCH\(_2\)CH\(_2\)N\(_3\) as well as the electron-deficient sulfonylazide TsN\(_3\) and benzoylazide PhC(O)N\(_3\) that each represent classes of azides that have not been reported for catalytic nitrene transfer to isocyanides. Hillhouse et al. reported the use of TsN\(_3\) for their NHC Ni system but only in the stoichiometric reaction of \{(IPr)Ni(\(\mu\)-Cl)\}_2 with TsN\(_3\) to form \{(IPr)Ni\}_2(Cl)(\(\mu\)-Cl)(\(\mu\)-N\(_\text{I,1-O:NSO}_2\text{Tol}\)).\(^{26}\) Despite the reaction of primary aliphatic azides to form metal imines via \(\alpha\)-H migration,\(^{27}\) PhCH\(_2\)CH\(_2\)N\(_3\) cleanly forms the corresponding
carbodiimides. Tosylazide requires a higher catalyst loading and gives the highest yield with the arylisocyanide (95%). Benzoyl azides are a substrate class that have not been heavily investigated in late metal nitrene chemistry – perhaps due to the thermal Curtius arrangement that gives PhNCO and N₂. Nonetheless we demonstrate high and moderate carbodiimide yields employing this nitrene source with NCBu' and NCAr', respectively (Table 1.1).

**Table 1.1.** Initial and optimized catalytic results for carbodiimide formation employing [Me₃NNi(2-pic) (1a).

![Chemical Structure](image)

<table>
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<tr>
<th>Substrate</th>
<th>N Cooling</th>
<th>N Cooling</th>
<th>Reaction</th>
<th>Reaction</th>
<th>Reaction</th>
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<td>98%</td>
<td>99%</td>
<td>79%</td>
<td>35%</td>
<td>84%</td>
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<td>(1 mol%, 17h)</td>
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<td>99%</td>
<td>41%</td>
<td>4%</td>
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<tr>
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</tr>
<tr>
<td>(17h)</td>
<td>(3%)</td>
<td>(92%)</td>
<td>(99%)</td>
<td>(73%)</td>
<td>(95%)</td>
<td>(87%)</td>
</tr>
</tbody>
</table>

Reaction Conditions: 30 min (17h), Et₂O, RT; ¹H NMR yields using anthracene, naphthalene, or anisole as a standard. [Ni] = [Me₃NNi(2-pic)]; BOLD = best reaction conditions
1.2.d. Synthetic investigations into catalytic mechanism - synthesis and reactivity of isocyanide adduct

To gain more insight into the catalytic process, we performed a series of synthetic investigations involving the catalyst [Me$_3$NN]Ni(2-pic) (1a) and both isocyanide and azide reagents to probe new nickel species that could reasonably participate in the catalytic reactions. The addition of 2.2 equiv. CNBu$^t$ or 3.7 equiv. CNAr to [Me$_3$NN]Ni(2-pic) gives [Me$_3$NN]Ni(CNBu$^t$)$_2$ (2a) or [Me$_3$NN]Ni(CNAr)$_2$ (2b) as brown crystals from pentane in 74% and 34% isolated yield, respectively (Scheme 1.14). The two $\nu_{CN}$ bands observed in the IR spectrum of each isocyanide adduct are consistent with the presence of two coordinated isocyanide ligands owing to symmetric and antisymmetric combinations of the individual C$=$N oscillators. These bands occur at $\nu_{CN} = 2080$ and 2112 cm$^{-1}$ for [Me$_3$NN]Ni(CNBu$^t$)$_2$ (2a) and at $\nu_{CN} = 1997$ and 2025 cm$^{-1}$ for [Me$_3$NN]Ni(CNAr)$_2$ (2b). These bands are lower than their values at 2331 and 2123 cm$^{-1}$ in their free forms of tert-butylisocyanide and 2,6-dimethylphenylisocyanide,

**Scheme 1.14.** Synthesis of isocyanide adducts 2a and 2b.
respectively, indicating that a significant degree of backbonding occurs in the adducts 2a and 2b. EPR glass spectra of 2a at 89 K in toluene glass (with a drop of tBuNC) indicates an axial environment with \( g_1 = 2.32 \) and \( g_2, g_3 = 2.17 \) (Figure 1.7). Similarly, 2b also shows an axial environment at 89 K in toluene glass (with excess ArNC) with \( g_1 = 2.27 \) and \( g_2 = g_3 = 2.17 \) (Figure 1.9). The reason for adding additional isocyanide for the EPR experiments is that EPR spectra of pure 2a and 2b give more complex spectra, likely from a dissociation of one isocyanide from the bis(isocyanide) complex in solution to give a mixture of mono- and bis(isocyanide) complexes.

The X-ray structure of \([\text{Me}_3\text{NN}]\text{Ni(CNAr)}_2\) (2b) (Figure 1.10) shows a distorted tetrahedral coordination at the Ni center with symmetric Ni-CNAr bonds shown by the nearly identical Ni-C_isocyanide bond distances of 1.863(3) and 1.866(3) Å. The Ni-N_{\beta\text{-dik}} bond distances are 1.9563(19) and 1.963(2) Å. The twist angle between N_{\beta\text{-dik}}-Ni-N_{\beta\text{-dik}} and C_isocy-Ni-C_isocy planes is 65.9° which illustrates the distorted tetrahedral geometry at nickel.
Figure 1.6. X-band EPR spectrum of [Me₃NNi(CNBu')]₂ (2a) with excess 'BuNC in toluene at RT. $g_{iso} = 2.20$.

Figure 1.7. X-band EPR spectrum of [Me₃NNi(CNBu')]₂ (2a) with excess 'BuNC in toluene glass at 89 K. $g_1 = 2.32$ and $g_2 = g_3 = 2.17$. 
Figure 1.8. X-band EPR spectrum of [Me$_3$NNi(CNAr)$_2$ (2b) with excess ArNC in toluene at RT. $g_{iso} = 2.20$.

Figure 1.9. X-band EPR spectrum of [Me$_3$NNi(CNAr)$_2$ (2b) with excess ArNC in toluene glass at 89 K. $g_1 = 2.27$ and $g_2, g_3 = 2.17$. 
Figure 1.10. X-ray crystal structure of [Me₃~NN~]Ni(CNAr)₂ (2b). All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ni – C24 1.863(3), Ni – C25 1.866(3), Ni – N1 1.9563(19), Ni – N2 1.963(2), N1 – Ni – C24 131.63(10), N1 – Ni – C25 134.63(10), N2 – Ni – C24 131.14(10), N2 – Ni – C25 99.72(9), C24 – Ni – C25 96.85(11), N1 – Ni – N2 92.72(9).
Table 1.2. Crystallographic data for 1a and 2a.

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<th>Compd.</th>
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<th>2b</th>
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Using $\text{N}_3\text{Ar'}$ ($\text{Ar'} = 3,5-\text{Me}_2\text{C}_6\text{H}_3$) as a representative azide, both $[\text{Me}_3\text{NN}]\text{Ni(CNBu')}_2$ (2a) and $[\text{Me}_3\text{NN}]\text{Ni(CNAr'}^{2,6-\text{Me}})_2$ (2b) react at RT in ether to give the corresponding carbodiimides. In the case of $[\text{Me}_3\text{NN}]\text{Ni(CNBu')}_2$ (2a), reaction with $\text{N}_3\text{Ar'}$ gives $\text{Ar'}\text{N}=\text{C}=\text{NBu'}$ in 97% yield as quantified by $^1\text{H}$ NMR spectroscopy (Scheme 1.15).

**Scheme 1.15.** Stoichiometric carbodiimide formation.

$$[\text{Me}_3\text{NN}]\text{Ni(CNBu')}_2 + 2\text{ eq. } \text{Ar'}\text{N}_3 \xrightarrow{\text{Et}_2\text{O}, \text{rt}} \text{Bu'}\text{N}=\text{C}=\text{NAr'}$$

$\text{Ar'} = 3,5-\text{Me}_2\text{C}_6\text{H}_4, 97\%$ yield

### 1.2.e. Synthesis of new dinickel arylnitrene complexes and their reactivity with isocyanides

To probe the nature of the nickel nitrene species formed upon reaction of 1a with arylazides, we added $\text{N}_3\text{Ar'}$ ($\text{Ar'} = 3,5-\text{Me}_2\text{C}_6\text{H}_4$) to 2 equiv. 1a which gives

**Scheme 1.16.** Dinickel nitrene synthesis.
{{Me}_2NNNi}_2(μ-NAr’) (3a) as substantiated by NMR and elemental analysis (Scheme 1.16). Variable temperature 1H NMR spectra of 3a in toluene-\textit{d}_8 show unusual chemical shifts. For instance, the nitrene \textit{o}-\textit{H} resonance appears at δ 0.159 ppm at 20 °C that shifts upon cooling to δ 2.137 ppm at -60 °C. For the same species, the nitrene \textit{p}-\textit{Ar}-\textit{H} signal shifts much more moderately from δ 8.010 ppm 20 °C to 7.933 ppm at -60 °C. Additionally, the \textit{β}-diketiminate backbone \textit{C}-\textit{H} resonance experiences a downfield shift from δ 4.706 ppm at 20 °C to δ 5.079 ppm at -60 °C.

To better establish the nature of this putative dinickel nitrene species, we sought the crystal structure of 3a. Unfortunately, numerous attempts were unsuccessful which motivated the synthesis of the analogue \{[Me}_2NNNi\}_2(μ(μ-NAr’) (3b) which lacks \textit{p}-Me groups on the \textit{β}-diketiminato \textit{N}-aryl rings. Reaction of 2 equiv. [Me₂NN]Ni(2-pic) with N₃Ar’ (Ar’ = 3,5-MeC₆H₃) in Et₂O results in an immediate color change from red to dark purple. The product \{[Me}_2NNNi\}_2(μ-μ-NAr’) (3b) may be crystallized from Et₂O as dark purple crystals suitable for X-ray diffraction in 80% yield (Scheme 1.16).

The X-ray structure of 3b (Figure 1.11) shows the dinuclear nature of this nitrene species with a Ni-Ni’ bond distance of 2.7120(3) Å (Figure 1.4). More important than the Ni-N_{β-dik} distances of 1.8969(16) and 1.9378(15) Å are the Ni-N_{nitrene} distances of 1.7476(15)-1.7549(15) Å. As a point of comparison, the related dicopper nitrene \{[Me}_3NNCu\}_2(μ-NAr)\textsuperscript{30} shows longer Cu-N_{nitrene} distances of 1.794(5) and 1.808(5) Å as well as a longer Cu-Cu’ separation of 2.911(1) Å.
Figure 1.11. X-ray crystal structure of \([\text{Me}_2\text{NN}]\text{Ni}\)_2(\(\mu\)-\text{NAr}^{3,5-\text{Me}_2}\)) (3b). All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ni – Ni’ 2.7120(3), Ni – N1 1.8969(16), Ni – N2 1.9378(15), Ni – N3 1.7476(15), Ni’ – N3 1.7549(15), N1 – Ni – N2 95.71(7).
We find that $\{[\text{Me}_2\text{NN}]\text{Ni}\}_2(\mu-\text{NAr'})$ (3b) exhibits related, but less dramatic temperature dependent $^1H$ NMR chemical shifts than $\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{NAr'})$ (3a). For instance, the $\beta$-diketiminato C-H backbone $^1H$ NMR resonance in 3b shifts from $\delta$ 4.768 ppm at 20 °C to $\delta$ 5.020 ppm at -60 °C, while the nitrene $o$-H resonance shifts from $\delta$ 1.938 ppm at 20 °C to $\delta$ 2.110 ppm at -60 °C.

DFT studies conducted on a model of $\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{NAr'})$ (3a) obtained through the optimization of the crystal structure of $\{[\text{Me}_2\text{NN}]\text{Ni}\}_2(\mu-\text{NAr'})$ (3b) (Figure 1.12) indicate that the $S = 0$ and $S = 1$ forms are close in energy, favoring the $S = 0$ form by only 0.7 kcal/mol.

Importantly, in the $S = 1$ state spin density is located on the nitrene $o$-C and $p$-C positions which exhibit particularly temperature sensitive $^1H$ NMR resonances. There is excess spin $\alpha$ in the vicinity of the nitrene N-aryl $o$-C atom as well as the $\beta$-diketiminato backbone C-H. On the other hand, there is an excess of spin $\beta$ at the nitrene N-aryl $p$-C at the $\beta$-diketiminato backbone C-H (Figure 1.13). Consistent with the upfield movement of the former two resonances and the downfield movement of the nitrene $o$-H the temperature dependent shift which are most sensitive at these positions are likely due to contact shifts from a very small amount of the $S = 1$ form that increasingly contributes at elevated temperature. Nonetheless, both species show a $\mu_{\text{eff}} = 0.0(1)$ B.M. based on the Evans method at RT suggesting that the ground state is the $S = 0$ form.
Figure 1.12. DFT structures of low-spin (3a – S0) and S = 1 (3a – S1) forms of \{[Me_3NN]Ni\}_2(\mu-\text{Ar'}) (ADF ZORA BP/TZ2P(+)). DFT optimized distances are also collected. At this level of theory and in the gas-phase, the S = 1 form is calculated to be 0.7 kcal/mol higher in electronic energy.

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<th></th>
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Figure 1.13. Spin density plot of 3a – S1 illustrating significant spin density at the nitrene \(\alpha\)-C and \(p\)-C atoms along with the \(\beta\)-diketiminato backbone C-H position (isovalue = 0.001; excess spin \(\alpha\) in blue, excess spin \(\beta\) in red).
Importantly, \{[Me_3NN]Ni\}_2(\mu-\text{NAr}) (3a) and \{[Me_2NN]Ni\}_2(\mu-\text{NAr'}) (3b) react quickly with excess CNBu\textsuperscript{t} to give the carbodiimide 'BuN=C=\text{NAr}' in 88 and 69\% yield, respectively (Scheme 1.17).

**Scheme 1.15.** Stoichiometric carbodiimide formation from dinickel nitrenes

\[
\begin{align*}
\text{[Me}_x\text{NN]Ni} & \quad \text{Ni[NNMe}_x\text{]} \quad \text{CNBu} \quad \text{[Ni]} \\
\text{purple crystals} & \quad \text{N=C=N} \\
& \quad \text{carbodiimide} \\
& \quad \text{if } x = 3 \quad 88\% \text{ yield} \\
& \quad \text{if } x = 2 \quad 69\% \text{ yield}
\end{align*}
\]

1.2.f. **Identification of resting state under catalytic conditions for carbodiimide formation**

In an attempt to determine the resting state of the catalytic system, a representative catalytic reaction was followed by UV-vis spectroscopy at -80 °C. The reason for the temperature difference for the UV-vis analysis as compared to a regular catalytic run (25 °C) is to be able to slow the reaction down and be able to observe a resting state. Mixing 5 mol \% 1a, 1 equiv. 3,5-dimethylarylazide, and 1.2 equiv. \textsuperscript{t}BuNC

**Scheme 1.18.** Proposed catalytic cycle for carbodiimide formation.
in toluene shows a dominant absorbance at $\lambda_{\text{max}} = 441$ nm which suggests the presence of $[\text{Me}_3\text{NN}]\text{Ni(CNBu}^\text{t})_2$ (2b) ($\lambda_{\text{max}} = 475$ nm (910 M$^{-1}$cm$^{-1}$)). Inspection of the UV-vis spectrum of this catalytic mixture does not indicate the presence of any other species. The intensity of the $\lambda_{\text{max}} = 441$ nm signal in this catalytic mixture immediately rises to its maximum which indicates that 80% of all added $[\text{Me}_3\text{NN}]\text{Ni}$ species is in the form of $[\text{Me}_3\text{NN}]\text{Ni(CNBu}^\text{t})_2$ (2b) which slowly decreases over time over 100 minutes (Figure 1.14).

This leads to proposing a catalytic cycle in which $[\text{Me}_3\text{NN}]\text{Ni(CNR)}_2$ is a possible resting. Upon on displacement of one or two isocyanides a Ni nitrene is formed. This Ni nitrene reacts with isocyanide to form the desired carbodiimide product and regenerating the resting state (Scheme 1.18).
1.2.g. Side reactions – formation of metal-azide species

It is curious that the stoichiometric reaction between $[\text{Me}_3\text{NN}]\text{Ni}=\text{NAd}$ and $^1\text{BuNC}$ gave a 76% yield of carbodiimide $\text{AdN}=\text{C}=$NBu$^{123}$ while attempted catalytic synthesis of this carbodiimide with $[\text{Me}_3\text{NN}]\text{Ni}(2\text{-pic})$ in benzene at 60 °C for 24 h showed no observable carbodiimide product. Perhaps the low catalytic reactivity of AdN$_3$ can be explained due the bulkiness of the 1-adamantyl group. It is likely that the
Scheme 1.19. Top: Reactivity of organoazides with [Me$_3$NN]Ni(2-pic) (1a). Middle: Side-on attack to form M=NR. Bottom: Head-on attack to transfer azide functionality.
stERIC bulk of the 1-Ad group makes it difficult to displace at least one of the isocyanides present in the [Me₃NN]Ni(CNR)₂ resting state the catalyst. For instance, in order for the organoazide to become activated for N₂ loss, the N-atom bearing the bulky Ad group needs to coordinate to the metal center. Owing to the poor nucleophilicity of organoazides, particularly at the sterically encumbered N atom, perhaps displacement of an isocyanide ligand is challenging, especially in the presence of excess isocyanide.

As previously mentioned, Holland et al. was able to successfully employ AdN₃ in catalytic carbodiimide formation. The catalyst used was a more electron-rich Fe based catalyst, {L'BuFe}₂(11-N₂) and yields were in excess of 95%. A possible explanation for the success is that the more electron-rich complex provides a higher driving force by making it easier to dissociate isocyanide and also being more nucleophilic to attack the organoazide to form the corresponding iron imido L'BuFe=NAd.²²

Reaction of our catalyst [Me₃NN]Ni(2-picoline) (1a) with trimethylsilyl azide demonstrates an extreme case in which the whole azide functionality is transferred to the metal center. This reaction generates the square planar nickel(II) azide species [Me₃NN]Ni(N₃)(2-pic) (4) in 44% yield as red crystals. The X-ray crystal structure of 4 (Figure 1.16) shows a four-coordinate, pseudo square planar coordination environment at nickel with Ni-Nβ-dik distances of 1.9119(19) and 1.8996(19) Å. The square planar geometry is shown by the slight twist angle between the Nβ-dik-Ni-Nβ-dik and N3-Ni-N4 planes of 17.3° which is nearly identical to 2b’s twist angle of 17.0°. The nickel to azide and 2-picoline are slightly longer with Ni-N₃azide = 1.9230(19) Å and Ni-N₃pic =
1.9392(19) Å. Notably, this species is inactive for organoazide based nitrene transfer catalysis (Scheme 1.19).

[Me₃NN]Ni(N₃)(2-pic) (4) is not stable when redissolved after isolation: excess 2-picoline must be added for spectroscopic characterization. Despite its square planar nature, broad ¹H NMR signals are observed at RT in the range δ -2 – 9 ppm, somewhat out of the normal diamagnetic range for these compounds. Cooling to -80 °C results in sharpening of broad peaks to allow for assignment in which rotation of 2-pic still has not been completely locked out due to appearance of broad o-Me peak. The backbone

**Figure 1.15.** ¹H NMR spectrum (400 MHz, toluene-d₈, -80 °C) of [Me₃NN]Ni(N₃)(pic) (4) with ex. 2-picoline (bound 2-picoline (*#); free 2-picoline
Figure 1.16. X-ray crystal structure of \([\text{Me}_2\text{NN}\text{Ni}]_2\text{(N}_3\text{)(2-picoline)}\) (4). All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ni – N3 1.9392(19) Å, Ni – N4 1.9230(19) Å, Ni – N1 1.9119(19) Å, Ni – N2 1.8996(19) Å.
Table 1.3 Crystallographic data for 3b and 4.

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</table>
methyl moves from a broad peak at -2 ppm at 20 °C to 1.367 ppm at -80 °C. The bound peaks of 2-picoline are non-distinguishable from the baseline at room temperature. At -80 °C aromatic signals are present at δ 6.544, 6.311 and 6.01-5.93 ppm. The Me-group of bound 2-picoline has a chemical shift of δ 4.166 ppm (Figure 1.15).

There are numerous examples of azide functional group transfer from carbon and silicon based organoazides to organometallic complexes. Focusing on the more closely related complexes there are at least three β-diketiminato complexes that show azide group transfer from organoazides to metals.32-34 Holland et al. reported a dinuclear β-diketiminato Fe(II)-hydride complex \{L'BuFe\}_2(μ-H)_2 that undergoes a reaction with TMSN₃ to produce \{L'BuFe\}_2(μ-N₃)_2, a dinuclear Fe(II) complex bridged via two azide-groups in an end-on fashion.32 Noltemeyer et al. reported an Al(I) β-diketiminato complex that undergoes a reaction with the silyl triazide 'BuSi(N₃)₃ to ultimately form a bridged dinuclear species that underwent complete azide functional group transfer to the metal in combination with azide group activation to expel dinitrogen to from NSi'tBu as a bridging motif shown in Scheme 1.20.33 Schulzke et al. reported a mononuclear Ge(II) β-diketiminato hydride complex that reacts with TMSN₃ to produce two new species shown in Scheme 1.20. One product results from complete azide functional group transfer to from a monomeric Ge(II) azide complex while the second structure is a monomeric Ge(IV) diamide formed via a formal insertion of NTMS into the Ge-H bond as well as deprotonation of a backbone CH₃ group by a Ge=NTMS functionality.34
1.2. Scouting experiments with CO – catalytic isocyanate formation with organoazides

Scouting experiments with organoazides RN₃ ad CO unfortunately resulted in only poor yields of the anticipated isocyanates RNCO. Stoichiometric reaction of \{[Me₃NN]Ni\}_2(\mu-CO)₂ with 3,5-dimethylphenylazide resulted in a yield of 13% after 3 h at RT. A catalytic attempt employing 5 mol % [Me₃NN]Ni(2-pic) (1a) as catalyst, 1
equiv. 3,5-dimethylphenylazide, and 6 atm CO in benzene at 60 °C for 24 h resulted in <1% yield. Instead the diazene (ArN=NAr) was observed as the major product via GC/MS. The previously reported stoichiometric reaction of [Me₃NN]Ni=NAd with excess CO resulted in a 76% yield.²³ A catalytic reaction was performed with AdN₃ under similar conditions with no observable product (Scheme 1.21).

The relative difficulty of employing CO in our catalytic protocol may be due to the bridging nature of the likely resting state {[Me₃NN]Ni}₂(µ-CO)₂ which formed upon addition of excess CO to [Me₃NN]Ni=NAd or [Me₃NN]Ni(2,4-lutidine) (1b).²³,³⁵ Coupled with the poor nucleophilicity of AdN₃ and ArN₃, their reaction with a sterically encumbered dinuclear species proves challenging. To enhance reactivity, this bridging structure of the {[Me₃NN]Ni}₂(µ-CO)₂ resting state should be prevented. This can be done via steric modifications of the β-diketiminato ligand. Holland et al. have shown that the more sterically demanding β-diketiminato ligand can form a T-shaped Ni(I) CO complex [iPr₂NN]Ni(CO).³⁶
In conclusion, [Me$_3$NN]Ni(2-pic) (1a) catalyzes nitrene transfer from a wide array of organoazides RN$_3$ to isocyanides CNR’ to give carbodiimides RN=C=NR’ in good to excellent yields. Investigation of the mechanism suggests [Ni](NCR)$_2$ resting states along with the formation of dinickel [Ni]$_2$(μ-NR) species that are reactive towards reaction with isocyanides, perhaps via terminal [Ni]=NR species. Careful investigation of the fate of the nickel catalyst reveals that in isolated cases complete azide transfer to the catalyst takes place such as with TMSN$_3$.

Possible future improvements could incorporate more sterically demanding variations of the β-diketiminato ligand in complexes such as [iPr$_2$NN]Ni. These bulkier
catalysts could enhance the dissociation of isocyanide in the [Ni](CNR)₂ resting state during carbodiimide formation as well as to prevent dimeric CO species that cause sluggish reactivity in isocyanate formation. Bulkier ligands might also favor the formation of terminal nitrene intermediates [Ni]=NR. While this may enhance the rate of nitrene transfer, it could also favor side reactions via radical C-C and C-N reactions involving [Ni]=NAr species observed by Stephan et al.²⁵

Experimental

General Experimental Details

All experiments were carried out in a dry nitrogen atmosphere using an MBraun glovebox and/or standard Schlenk techniques. 4A molecular sieves were activated in vacuo at 180 ºC for 24 h. Diethyl ether and tetrahydrofuran (THF) were first sparged with nitrogen and then dried by passage through activated alumina columns. Pentane was first washed with conc. HNO₃ / H₂SO₄ to remove olefins, stored over CaCl₂ and then distilled before use from sodium/benzophenone. All deuterated solvents were sparged with nitrogen, dried over activated 4A molecular sieves and stored under nitrogen. All column chromatography employed silica (particle size 32-64 m) as the stationary phase. ¹H and ¹³C NMR spectra were recorded on a Mercury Varian 400 MHz spectrometer (400 and 75.4 MHz, respectively). All NMR spectra were recorded at room temperature unless otherwise noted and were indirectly referenced to TMS using residual solvent signals as internal standards. X-band EPR spectra were recorded in toluene at RT or as a frozen glass near 80 K. The EPR measurements were performed
in quartz tubes with J. Young valves. Solution EPR spectra were recorded on a JEOL continuous wave spectrometer JES-FA200 equipped with an X-band Gunn oscillator bridge, a cylindrical mode cavity, and a helium cryostat. Elemental analyses were performed on a Perkin-Elmer PE2400 microanalyzer in our laboratories. GC-MS spectra were recorded on a Varian Saturn 3900.

1.3.a. Synthesis of organoazide reagents – general precautions

Caution must be exercised during the synthesis and workup of organoazides as they could potentially explosively release N$_2$, especially in contact with any strong reductants, high temperatures, or high light fluxes. For instance, when all volatiles are removed during the workup of the organoazides below, the temperature should not exceed 30 °C. Once isolated, the neat organoazides should be stored cold (< -10 °C) and in the dark.

3,5-dimethylphenylazide (N$_3$Ar'). This azide was synthesized according to the procedure of Moses et al.$^{37}$ while the actual compound was previously reported by Sadighi et al.$^{38}$ To a solution of 3,5-dimethylaniline (2.5 g, 0.021 mol) in 40 mL acetonitrile in an ice-bath (0 °C) was added dropwise 1BuONO (3.20 g, 0.0311 mol), followed by TMSN$_3$ (2.84 g, 0.0248 mol). The reaction mixture was allowed to stir for 1 h at RT. All volatiles were removed in vacuo without exceeding 30 °C. The crude product was purified via column chromatography using pentane as the mobile phase; the first yellow layer of the column was collected. All volatiles were removed in vacuo.
without exceeding 30 °C to isolate the product as pale yellow oil in 54% yield (1.64 g, 0.0112 mol). $^1$H NMR (CDCl$_3$, RT, 300 MHz): $\delta$ 6.761 (s, 1H, p-Ar-H), 6.635 (s, 2H, o-Ar-H), 2.289 (s, 6H, CH$_3$); GC/MS: $m/z$ (CI) = 147 (119 for -N$_2$, 239 for Ar’N=NAr’).

**Phenylazide (N$_3$Ph).** This azide was synthesized according to Moses et al.$^{37}$ while the actual compound was previously reported by Luo and Frisbie.$^{39}$ To a solution of aniline (3.00 g, 0.0322 mol) in 40 mL acetonitrile in an ice-bath (0 °C) to was added dropwise $^1$BuONO (4.99 g, 0.0485 mol), followed by TMSN$_3$ (4.43 g, 0.0387 mol). The reaction mixture was allowed to stir for 1 h at RT. All volatiles were removed in vacuo without exceeding 30 °C. The crude product was purified via column chromatography using pentane as the mobile phase; the first yellow layer of the column was collected. All volatiles were removed in vacuo without exceeding 30 °C to isolate the product as pale yellow oil in 47% yield (1.80 g, 0.0151 mol). $^1$H NMR (CDCl$_3$, RT, 300 MHz): $\delta$ 7.328 (t, 2H, m-Ph-H), 7.119 (t, 1H, p-Ph-H), 7.020 (d, 2H, o-Ph-H); GC/MS: $m/z$ (CI) = 119 (91 for -N$_2$, 182 for PhN=NPh).

**2,4,6-trimethylphenylazide (mesitylazide; MesN$_3$).** This azide was synthesized according to the procedure of Sadighi et al.$^{38}$ while the actual compound was reported by Laali et al.$^{40}$ To 2,4,6-trimethylaniline (12.7 g, 0.0943 mol) in a rock salt ice-bath (-10 °C) was added dropwise a solution of 20 mL conc. HCl in 50 mL water. A yellow slurry formed immediately. To this slurry was added a chilled solution of NaNO$_2$ (13.01 g, 0.189 mol) in 30 mL of water. The reaction mixture was allowed to stir for 15 min.
Subsequently, a solution of NaN$_3$ (5.14 g, 0.0791 mol) in 20 mL water was added and the reaction mixture was stirred for 1 h. The crude product was extracted with pentane (3 × 50 mL). The organic layers were combined, dried over MgSO$_4$ and vacuum filtered. All volatiles were removed in vacuo without exceeding 30 °C. The crude product was purified using column chromatography with pentane as the mobile phase; the first yellow layer of the column was collected. All volatiles were removed in vacuo without exceeding 30 °C to isolate the product as pale yellow oil in 51% yield (7.81 g, 0.0485 mol). $^1$H NMR (CDCl$_3$, RT, 300 MHz): $\delta$ 6.818 (s, 2H, m-Ar-H), 2.309 (s, 6H, o-CH$_3$), 2.238 (s, 3H, p-CH$_3$); GC/MS: $m/z$ (CI) = 161 (133 for -N$_2$, 266 for MesN=NMes).

3,5-bis(trifluoromethyl)phenylazide (Ar$_{3,5}$CF$_3$N$_3$). This azide was synthesized as previously reported by Sadighi et al.$^{38}$ To a solution of 3,5-bis(trifluoromethyl)aniline (2.00 mL, 2.96 g, 0.0129 mol) without solvent in a rock salt ice-bath (-10 °C) was added slowly over 30 min trifluoroacetic acid (33.3 mL, 49.28 g, 0.432 mol) and then NaNO$_2$ (1.78 g, 0.0258 mol) as a solid. The reaction mixture was allowed to stir for 30 min during a color change from clear to yellow to green occurred. NaN$_3$ (1.76 g, 0.0271 mol) was then added as a solid over 5 minutes. The reaction mixture was allowed to stir for 90 min. The reaction was quenched with 70 mL water and then allowed to warm to RT. The crude product was extracted with pentane (3 × 50 mL). The combined organic layers were sequentially washed with 80 mL of aqueous saturated sodium bicarbonate, 80 mL brine and 100 mL of water. The organic layer was dried
over MgSO_4 and filtered to remove all Mg salts. All volatiles were removed in vacuo without exceeding 30 °C to isolate the product as yellow oil in 70% yield (2.31, 9.06 mmol). ^1H NMR (CDCl_3, RT, 300 MHz): δ 7.325 (s, 2H, o-Ar-H), 6.782 (s, 1H, p-Ar-H); GC/MS: m/z (CI) = 255 (227 for -N_2, 454 for ArN=NAr).

1-azido-2-phenylethane (PhCH_2CH_2N_3). This azide was synthesized as previously reported by Takaya et al. Under an inert atmosphere, TMSN_3 (2.0 g, 0.0174 mol) was added to PhCH_2CH_2Br, followed by addition of tetrabutylammonium fluoride in THF (17.4 mL, 0.0174 mol, 1 M in THF). The reaction mixture was allowed to stir at RT for 12 h. All volatiles were removed in vacuo without exceeding 30 °C. The resulting residue was taken up in 50 mL pentane and stirred for 90 min to allow for thorough extraction of the product into pentane. The resulting suspension was decanted and vacuum filtered. All volatiles were removed in vacuo without exceeding 30 °C to give the product as yellow oil in 59% yield (1.40 g, 9.52 mmol). ^1H NMR (CDCl_3, RT, 300 MHz): δ 7.331-7.295 (m, 2H, Ar-H), 7.258-7.200 (m, 3H, Ar-H), 3.490 (t, 2H, CH_2), 2.885 (t, 2H, CH_2); GC/MS: m/z (CI) = 147 (119 for -N_2, 239 for Ar’N=NAr’).

Tosylazide (TsN_3). This azide was synthesized according to the procedure reported by McElwee-White and Dougherty. NaN_3 (0.75 g, 0.0115 mol) was dissolved in 5 mL ethanol (95%). To this solution was added p-toluenesulfonyl chloride (2.0 g, 0.0105 mol) in 10 mL acetone. NaCl immediately precipitated out of solution as white powder. The reaction mixture was allowed to stir for 15 min at RT and then vacuum filtered. All
volatiles were removed in vacuo without exceeding 30 °C. The residue was extracted with 20 mL CH₂Cl₂ and washed with 20 mL water. The organic layer was dried over MgSO₄, filtered, and all volatiles were removed in vacuo without exceeding 30 °C to give the product as a clear oil 89% yield (1.845 g, 9.37 mmol). ¹H NMR (CDCl₃, RT, 300 MHz): δ 7.854 (d, 2H, o-Ar-H), 7.420 (d, 2H, m-Ar-H), 2.483 (s, 3H, CH₃); GC/MS: m/z (CI) = 169 for -N₂ (338 for TsN=NTs).

**Benzoylazide (PhC(O)N₃).** This azide was synthesized according to Barrett et al.¹⁴³ and has been previously reported by Platz et al.²⁸ This organoazide is the most thermally sensitive organoazide that we have worked with and extreme caution must be used to ensure that the temperature never rises above 30 °C. It is not recommended to be prepared on a scale greater than 1g. Benzoyl chloride (1.0 g, 7.14 mmol) was dissolved in 10 mL acetone and placed in an ice bath. To this solution was slowly added cold NaN₃ (0.53 g, 8.14 mmol) in 10 mL water. The reaction mixture was allowed to stir for 30 min at 0 °C. The organic layer was separated and dried over MgSO₄, and all volatiles were removed in vacuo without exceeding 30 °C to afford a white solid in 50% yield (0.53 g, 3.57 mmol). PhC(O)N₃ can undergo the Curtius rearrangement to expel N₂ with formation of PhNCO and therefore must be stored cold.²⁸,⁴⁴,⁴⁵ ¹H NMR (CDCl₃, RT, 300 MHz): δ 7.385-7.105 (m, 5H, Ph-H); GC/MS: m/z (CI) = 119 for PhNCO.
1.3.b. General procedure for catalytic formation of carbodiimides and characterization of carbodiimide products

A solution of organoazide (0.843 mmol) along with tert-butylisocyanide (1.2 eq, 1.01 mmol) or 2,6-dimethylphenylisocyanide (1.1 eq, 0.927 mmol) was prepared in 3 mL Et₂O and chilled to -35 °C. A second solution of [Me₃NNi(2-picoline)] (0.0422 mmol = 5 mol% or 0.00843 mmol = 1 mol%) was prepared in 3 mL Et₂O and similarly chilled. The two cooled solutions were added together and allowed to react under the described conditions in Table 1.1, typically at RT for 30 min or 17 h. The reactions were then quenched with 5 mL CH₂Cl₂ to oxidize the catalyst to insoluble {[Me₃NNi]₂(µ-Cl)}₂. All volatiles were removed in vacuo. The remaining oil was taken up in CH₂Cl₂ and filtered through Celite. All volatiles were removed in vacuo. Quantification was performed by addition of 1 equiv. of internal standard (anthracene, naphthalene, or anisole) followed by ¹H NMR analysis in CDCl₃.

**MesN=C=NᵗBu.** ¹H NMR (CDCl₃, RT): δ 6.807 (s, 2, Ar-H), 2.305 (s, 6, m-Me), 2.228 (s, 3, p-Me), 1.346 (s, 9, ¹Bu); ¹³C{¹H} NMR (CDCl₃): δ 134.17, 133.42, 132.10, 128.72, 55.82, 31.28, 20.62, 18.90; IR ν₇C=NCN = 2122 cm⁻¹; m/z (CI mode) = 217 (M+1). NMR standard: Anthracene.

**(3,5-Me)ArN=C=NᵗBu.** ¹H NMR (CDCl₃, RT): δ 6.737 (s, 1, Ar-H), 6.713 (s, 2, Ar-H), 2.266 (s, 6, o-Me), 1.388 (s, 9, ¹Bu);
$^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 140.54, 138.97, 126.40, 120.96, 57.18, 31.56, 21.10; IR $\nu_{\text{NCN}}$ = 2127 cm$^{-1}$; m/z (CI mode) = 203 (M+1). Standard: Anthracene.

**PhN=C=N^t$Bu.** $^1$H NMR (CDCl$_3$, RT): $\delta$ 7.280 (m, 2, Ar-H), 7.101 (m, 3, Ar-H), 1.397 (s, 9, $^t$Bu); $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 140.96, 129.31, 124.54, 123.23, 57.30, 31.56; IR $\nu_{\text{NCN}}$ = 2117 cm$^{-1}$; m/z (CI mode) = 175 (M+1). NMR standard: Anthracene.

(3,5-$^3$CF$_3$)ArNCN$^t$Bu. $^1$H NMR (CDCl$_3$, RT): $\delta$ 7.571 (s, 1, Ar-H), 7.450 (s, 2, Ar-H), 1.433 (s, 9, $^t$Bu); $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 149.49, 143.71, 132.80, 122.94, 117.54, 58.64, 52.11, 31.68; IR $\nu_{\text{NCN, SO}}$ = 2128, 2151 cm$^{-1}$; m/z (CI mode) = 311 (M+1). NMR standard: Anthracene.

TosNCN$^t$Bu. $^1$H NMR (CDCl$_3$, RT): $\delta$ 7.377 (d, 2, Ar-H), 7.317 (d, 2, Ar-H), 2.441 (s, 3, p-Me), 1.366 (s, 9, $^t$Bu); $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 145.40, 131.86, 129.66, 127.13, 59.68, 28.68, 20.62; $\nu_{\text{NCN, SO}}$ = 2357, 2339, 2128 cm$^{-1}$; m/z (CI mode) = 253 (M+1). NMR standard: Anthracene.

PhCH$_2$CH$_2$N=C=N$^t$Bu. $^1$H NMR (CDCl$_3$, RT): $\delta$ 7.292 (m, 2, Ar-H), 7.219 (m, 3, Ar-H), 3.457 (t, 2, Et-H), 2.870 (t, 2, Et-H),
1.193 (s, 9, 'Bu); $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 138.90, 128.75, 128.44, 128.12, 126.40, 55.00, 48.13, 37.82, 31.12; IR $\nu_{\text{NCN}}$ = 2125 cm$^{-1}$; m/z (CI mode) = 203 (M+1). NMR standard: Anthracene.

PhC(O)NCN'tBU. $^1$H NMR (CDCl$_3$, RT): $\delta$ 8.089 (d, 2, o-Ph-$H$), 7.520 (t, 1, p-Ph-$H$), 7.396 (t, 2, m-Ph-$H$), 1.489 (s, 9, 'Bu-$H$); $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 174.77, 134.11, 133.18, 129.87, 129.10, 128.38, 59.14, 31.52; IR $\nu_{\text{N CN}}$, $\nu_{\text{CO}}$ = 2156 cm$^{-1}$; m/z (CI mode) = 203 (M+1). NMR standard: Anisole.

MesNCNAr$^{2,6}$-Me. $^1$H NMR (CDCl$_3$, RT): $\delta$ 6.973 – 6.954 (d, 2H, m-Ar-$H$), 6.705 (s, 2H, m-Ar-$H$), 2.296 (s, 6H, o-Ar-$CH_3$), 2.198 (s, 6H, o-Ar-$CH_3$), 2.127 (s, 3H, p-Ar-$CH_3$); $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 136.31, 132.83, 129.07, 128.53, 20.96, 19.06, 18.24; $\nu_{\text{N CN}}$ = 2160, 2119 cm$^{-1}$; m/z (CI mode) = 264 (M+1). NMR standard: Anisole.

(3,5-Me)ArN=C=NAr$^{2,6}$-Me. $^1$H NMR (CDCl$_3$, RT): $\delta$ 7.137 (d, 2, Ar-$H$), 7.091 (s, 1, Ar-$H$), 6.913 (s, 2, Ar-$H$), 6.867 (s, 1, Ar-$H$), 2.500 (s, 6, CH$_3$), 2.391 (s, 6, CH$_3$); $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 139.62, 139.23, 135.28, 132.99, 128.32, 126.73, 125.38, 125.15, 121.54, 21.25, 19.12; IR $\nu_{\text{N CN}}$ = 2159, 2127 cm$^{-1}$; m/z (CI mode) = 251 (M+1). NMR standard: Naphthalene.
**PhN=C=NAr^{(2,6-Me)}**.  $^1$H NMR (CDCl$_3$, RT): $\delta$ 7.273 (t, 2, Ar-H), 7.152 (d, 2, Ar-H), 7.086 (t, 1, Ar-H), 6.989 (d, 2, Ar-H), 2.361 (s, 6, CH$_3$); $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 139.76, 132.70, 129.36, 128.11, 125.18, 125.05, 124.64, 123.58, 18.89; IR $\nu_{\text{NCN}}$ = 2152 cm$^{-1}$; m/z (CI mode) = 223 (M+1). NMR standard: Naphthalene.

**(3,5-CF$_3$)PhNCNAr^{(2,6-Me)}**.  $^1$H NMR (CDCl$_3$, RT): $\delta$ 7.536 (d, 3, Ar-H), 7.025 (s, 3, Ar-H), 2.365 (s, 6, o-CH$_3$); $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 142.82, 133.34, 128.39, 128.14, 126.19, 125.28, 123.56, 117.78, 18.67; IR $\nu_{\text{NCN}}$, $\nu_{\text{SO}}$ = 2169 cm$^{-1}$; m/z (CI mode) = 359 (M+1). NMR standard: Anthracene.

**TosN=C=NAr^{(2,6-Me)}**.  $^1$H NMR (CDCl$_3$, RT): $\delta$ 7.889 (d, 2, Ar-H), 7.320 (d, 2, Ar-H), 7.061 (s, 1, Ar-H), 7.061 (s, 1, Ar-H), 2.399 (s, 3, p-CH$_3$), 2.248 (s, 6, o-CH$_3$); $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 144.45, 134.67, 130.32, 129.79, 128.33, 128.02, 127.44, 126.73, 125.33, 21.58, 18.71; IR $\nu_{\text{NCN}}$, $\nu_{\text{SO}}$ = 2272, 2176, 2128 cm$^{-1}$; m/z (CI mode) = 301 (M+1). NMR standard: Anthracene.

**PhCH$_2$CH$_2$N=C=NAr^{(2,6-Me)}**.  $^1$H NMR (CDCl$_3$, RT): $\delta$ 7.229 (t, 1, Ar-H), 7.190 (s, 1, Ar-H), 7.172 (t, 2, Ar-H), 6.943 (d,
2, Ar-H), 3.572 (t, 2, CH₂), 2.912 (t, 2, CH₂), 2.234 (s, 6, o-CH₃); \(^{13}\)C\(^{1}\)H\) NMR (CDCl₃): \(\delta\) 138.49, 132.17, 128.67, 128.37, 127.92, 126.41, 126.08, 125.20, 124.01, 47.98, 37.46, 18.72; IR \(\nu_{\text{NCN}} = 2142\) cm\(^{-1}\); m/z (CI mode) = 251 (M+1). NMR standard: Naphthalene.

\[
\text{PhC(O)NCNAr}^{2,6-\text{Me}}. \]
\(\text{H NMR (CDCl₃, RT): } \delta\) 8.054 (d, 2, o-Ar-H), 7.640-7.547 (m, 6, m,p-Ar-H), 2.225 (s, 6H, o-Ar-CH₃); \(^{13}\)C\(^{1}\)H\) NMR (CDCl₃): \(\delta\) 173.73, 135.36, 134.12, 129.90, 129.17, 128.07, 127.87, 127.19, 124.56; IR \(\nu_{\text{NCN, CO}} = 2178\) cm\(^{-1}\); m/z (CI mode) = 251 (M+1). NMR standard: Anisole.

### 1.3.c. Synthesis of nickel complexes

**[Me₃NN]Ni(2-picoline).** A solution of [Me₃NN]Tl (1.68 g, 3.20 mmol) in 10 mL THF was added to a solution of NiI₂ (1.0 g, 3.20 mmol) and 2-picoline (0.298 g, 3.20 mmol) in 20 mL THF. The solution was allowed to stir for 3 h at RT. The suspension was filtered through Celite. The solution was concentrated to dryness and the resulting solid was crystallized from ether at -35 °C to afford dark green crystals in 90% yield (1.73 g, 2.88 mmol). \(^{1}\)H NMR (C₆D₆, RT): \(\delta\) 47.56 (s, 6, p-Ar-Me), 34.69 (s, 12, o-Ar-Me), 32.72 (s, 4, Ar-H), -11.10 (br, 1, backbone-CH), -46.19 (s, 6, backbone-Me). \(\mu_{\text{eff}}\) (benzene-\(d₆\)) = 2.39 B.M. UV-Vis (Et₂O, 25 °C): \(\lambda_{\text{max}} = 539\) nm (\(\varepsilon = 430\) M\(^{-1}\) cm\(^{-1}\)), 627
54 nm (ε = 570 L mol⁻¹ cm⁻¹), 681 nm (ε = 650 M⁻¹ cm⁻¹). Anal. Calcd for C₂₉H₃₆N₃Ni: C, 56.89; H, 5.93; N, 6.86. Found: C, 56.75; H, 5.66; N, 6.68.

[Me₃NN]Nil(2-picoline) (8.38 g, 0.0143 mol) were suspended in 80 mL Et₂O. To this green suspension was added Na/Hg (0.5 % w/w Na, 82.7 g). The reaction mixture was allowed to stir for 3 hours during which a color change to red occurred. The red solution was decanted and filtered through Celite and finally concentrated to crystallize from Et₂O at -35 °C to afford [Me₃NN]Ni(2-picoline) as a red solid in 78% yield (5.09 g, 0.0112 mol).

[Me₃NN]Ni(2-picoline) (1a). To a solution of Nil₂ (0.595 g, 1.91 mmol) and 2-picoline (0.177 g, 1.91 mmol) in 5 mL THF was added [Me₃NN]Tl (1.0 g, 1.91 mmol). The reaction mixture was allowed to stir for 1 h before it was filtered through Celite to remove insoluble TlI. To the resulting solution was added 11.0 g Na/Hg (0.5% Na by weight) and the solution was allowed to stir for 1 h before it was decanted from the amalgam and filtered through Celite. The solution was concentrated to dryness and the remaining solid was crystallized from pentane to afford red crystals at -35 °C in 80% yield (0.718 g, 1.52 mmol). Recrystallization from ether at -35°C resulted in crystals suitable for single crystal x-ray crystallography. UV-Vis (Et₂O, 25°C): λmax = 523 nm (ε = 1400 M⁻¹ cm⁻¹); μeff (benzene-d6) = 1.55 B.M. (with a drop of 2-pic added). EPR (toluene, frozen glass, 77K) g₁ = 2.41, g₂ = 2.12, g₃ = 2.06 (with drop of 2-pic added); Anal. Calcd for C₂₉H₃₆N₃Ni: C, 71.77; H, 7.48; N, 8.66 Found C, 71.52; H, 7.43; N, 8.33
[Me₃NN]Ni(CNBuᵗ)₂ (2a). A chilled solution of tert-butylisocyanide (0.038 g, 0.458 mmol) in 2 mL Et₂O was added to a chilled solution of [Me₃NN]Ni(2-pic) (0.100 g, 0.206 mmol) in 5 mL Et₂O. The reaction mixture was allowed to stir at RT for 30 min during which time an immediate color change from red to brownish orange took place. All volatiles were removed in vacuo and the resulting crude product was crystallized from pentane at -35 °C. Brown crystals were recovered in 74% yield (0.085 g, 0.152 mmol). ν_{CN} = 2080, 2112 cm⁻¹; µ_{eff} (C₆D₆) = 1.63 B.M.; UV-Vis (Et₂O, 25 °C): λ_{max} = 475 nm (ε = 910 M⁻¹ cm⁻¹); Anal. Calcd for C₃₃H₄₇N₄Ni: C, 70.97; H, 8.48; N, 10.03. Found: C, 70.67; H, 8.35; N, 9.75. EPR of 2a with excess ḳBuNC in toluene frozen glass at 89 K g₁ = 2.32 and g₂ = g₃ = 2.17.

**Figure 1.17.** Beer’s law plot of [Me₃NN]Ni(CNBuᵗ)₂ (2a) in Et₂O at RT λ_{max} = 475 nm (ε = 910 M⁻¹ cm⁻¹)
[Me₃NN]Ni(CNAr²,6-Me₂)₂ (2b). A chilled solution of 2,6-dimethylphenylisocyanide (0.099 g, 0.756 mmol) in 4 mL Et₂O was added to a chilled solution of [Me₃NN]Ni(2-pic) (0.100 g, 0.206 mmol) in 5 mL Et₂O. The reaction mixture was allowed to stir at RT overnight during which time a color change from red to dark brown took place. All volatiles were removed in vacuo and the resulting crude product was crystallized from pentane at -35 °C. Brown crystals were recovered in 34% yield (0.045 g, 0.0692 mmol).

ν_{CN} = 1997, 2025 cm⁻¹; μ_{eff}(C₆D₆)= 1.51 B.M; UV-Vis (Et₂O, 25°C): λ_{max} = 543 nm (ε = 1900 M⁻¹ cm⁻¹); Anal. Calcd for C₄₁H₄₇N₄Ni: C, 75.24; H, 8.48; N, 8.56. Found: C, 75.71; H, 7.41; N, 8.44. EPR of 2b with excess ArNC in toluene frozen glass at 89 K g₁ = 2.27 and g₂ = g₃ = 2.17.

Figure 1.18. Beer’s law plot of [Me₃NN]Ni(CNAr²,6-Me₂)₂ (2b) in Et₂O at RT λ_{max} = 543 nm (ε = 1900 M⁻¹ cm⁻¹)
\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{NAr}^{3,5-\text{Me}_2})\) (3a). To a cold solution of \([\text{Me}_3\text{NN}]\text{Ni}(2\text{-picoline})\) (0.235 g, 0.484 mmol) in 3 mL Et\(_2\)O was added cold a solution of 3,5-dimethylphenylazide (0.036 g, 0.242 mmol) in 2 mL Et\(_2\)O. An immediate color change from red to dark purple took place and gas bubbles evolved. All volatiles were immediately removed in \textit{vacuo}. The remaining residue was taken up in 10 mL pentane and all volatiles were again removed in \textit{vacuo}. This step is necessary to remove as much free 2-picoline as possible to maximize the isolated yield of this substance. The remaining dark purple residue was taken up in cold Et\(_2\)O and filtered through Celite. The resulting solution was concentrated and layered with cold pentane and allowed to crystallize overnight at -35 °C to afford a dark purple solid in 76% yield (0.167 g, 0.185 mmol). \(^1\text{H}\) NMR (toluene-\(d_8\), RT, 400 MHz): \(\delta\) 8.010 (s, 1H, \(p\)-\text{NAr}\text{-}H), 7.546 (s, 8H, \(m\)-\text{Ar}\text{-}H), 4.707 (s, 2H, C-H backbone), 3.411 (s, 12H, \(p\)-\text{Ar}\text{-CH}_3), 3.243 (s, 24H, \(o\)-\text{Ar}\text{-CH}_3), 2.597 (s, 6H, \(m\)-\text{NAr}\text{-CH}_3), 0.159 (s, 2H, \(o\)-\text{NAr}\text{-}H), -0.403 (s, 12H, backbone \text{CH}_3); \(^{13}\text{C}\{^1\text{H}\} (\text{C}_6\text{D}_6; \text{RT, 400 MHz}): \delta 156.61, 146.81, 139.18, 126.67, 110.81, 25.05, 19.21, 15.67.; \mu_{\text{eff}} (\text{C}_6\text{D}_6)= 0.0(2) \text{ B.M.}; \text{UV-Vis (Et}_2\text{O, 25°C): } \lambda_{\text{max}} = 375 \text{ nm (} \varepsilon = 18000 \text{ M}^{-1} \text{ cm}^{-1}) \text{ and 529 nm (} \varepsilon = 4500 \text{ M}^{-1} \text{ cm}^{-1}); \text{Anal. Calcd for C}_{54}\text{H}_{67}\text{N}_{15}\text{Ni}_2: C, 71.78; H, 7.47; N, 7.75 \text{ Found C, 71.58; H, 7.59; N, 8.04.}
Figure 1.19. Beer’s law plot of \({\left[ [\text{Me}_3\text{NN}]\text{Ni} \right]_2(\mu-\text{NAr}^{3,5-\text{Me}})} \) (3a) at 529 nm in Et₂O at 25°C. \( \lambda_{\text{max}} = 375 \text{ nm (} \varepsilon = 18000 \text{ M}^{-1} \text{ cm}^{-1} \) ) and 529 nm ( \( \varepsilon = 4500 \text{ M}^{-1} \text{ cm}^{-1} \) ).

\{[\text{Me}_2\text{NN}]\text{Ni}\}_2(\mu-\text{NAr}^{3,5-\text{Me}}) \) (3b). To a cold solution of [Me₂NN]Ni(2-picoline) (0.490 g, 1.07 mmol) in 8 mL Et₂O was added cold a solution of 3,5-dimethylarylmethyldrazide (0.079 g, 0.536 mmol) in 3 mL Et₂O. An immediate color change from red to dark purple took place and gas bubbles evolved. All volatiles were immediately removed in vacuo. The remaining residue was taken up in 10 mL of pentane and all volatiles were again removed in vacuo. This step is necessary to remove as much free 2-picoline was possible to better yields later on. The remaining dark purple residue was taken up in cold Et₂O and filtered through Celite. The resulting solution was concentrated and layered with cold pentane and allowed to crystallize overnight at -35°C to afford a dark purple solid in 80% yield (0.362 g, 0.428 mmol). \(^1\)H NMR (C₆D₆, RT): \( \delta 7.564 – 7.546 \)
(d, 8H, m-Ar-H), 7.286 (s, 1H, p-Ar-H), 6.578 (t, 4H, p-Ar-H), 4.768 (s, 2H, backbone C-H), 2.791 (s, 24H, o-Ar-CH₃), 2.294 (s, 6H, m-Ar-CH₃), 1.940 (s, 2H, o-Ar-H), 0.341 (s, 12H, backbone CH₃); ¹³C{'¹H} (C₆D₆; RT, 400 MHz): δ 157.05, 147.38, 141.30, 127.65, 122.82, 35.46, 23.50, 17.87; µₑₑₑ(C₆D₆)= 0.0(2); UV-Vis (Et₂O, 25°C): λmax = 408 nm (ε = 11000 M⁻¹ cm⁻¹) and 527 nm (ε = 6900 M⁻¹ cm⁻¹); Anal. Calcd for C₅₀H₅₉N₅Ni₂: C, 70.87; H, 7.02; N, 8.26 Found C, 71.19; H, 7.30; N, 8.18.

Figure 1.20. Beer’s law plot of [{Me₂NN]Ni}₂(µ-NAr₃,5-Me) (3b) at 527 nm in Et₂O at 25 °C. λmax = 408 nm (ε = 11000 M⁻¹ cm⁻¹) and 527 nm (ε = 6900 M⁻¹ cm⁻¹).

[Me₃NN]Ni(N₃)(2-picoline) (4). A chilled solution of [Me₃NN]Ni(2-picoline) (1a) (0.196 g (0.404 mmol) was prepared in 8 mL Et₂O to which a chilled (-35 °C) solution of TMSN₃ (1.0 mL, 0.868 g, 7.53 mmol) was added. The solution was allowed to warm to RT. During this time the red color of the starting material changed hues to a magenta
red. The reaction mixture was allowed to stir for 1 h at RT after which time all volatiles were removed in vacuo. The red solid was taken up in Et₂O and passed through Celite. Then the intense red solution was concentrated to afford red crystals at -35 °C suitable for single crystal X-ray analysis in 44% yield (0.092 g, 0.176 mmol). All NMRs and UV-vis were taken with excess 2-picoline (~10 eq.); otherwise the compound decomposes to a black suspension: ¹H NMR (toluene-d₈, -80 °C): δ 8.543 (s, 5H, free pic-Ar-H), 7.591 (br s, 1H, Ar-H), 7.171 (s, 1H, Ar-H), 7.089 (s, 1H, Ar-H), 6.544 (br s, overlaps with next peak Ar-H), 6.544-6.525 (d, overlaps with previous peak free pic-Ar-H). 6.311 (br s, 1H, bound pic-Ar-H), 5.971 (d, 2H, bound pic-Ar-H), 4.717 (s, 1H, backbone CH), 4.166 (s, 3H, bound pic-CH₃), 2.661 (br, ex. free pic-Ar-CH₃), overlap with previous 2.450 (s, Ar-CH₃), 2.120 (overlapping singlets, Ar-CH₃), 1.367 (s, 6H, backbone CH₃); ¹³C{¹H} NMR (toluene-d₈, -80 °C): δ 158.47, 150.46, 149.50, 148.45, 135.96, 135.50, 133.29, 132.61, 123.00, 120.60, 25.00, 24.67, 24.34, 24.00; µ_eff (C₆D₆ and 100eq. 2-picoline) = 0.814 B.M.; UV-Vis (Et₂O with 100 eq. 2-picoline; 25°C): λ_max = 540 nm (ε = 3800 M⁻¹ cm⁻¹); Anal. Calcd for C₂₉H₃₆N₆Ni: C, 66.05; H, 6.88; N, 15.94 Found C, 66.34; H, 7.19; N, 15.59.
Figure 1.21. Beer’s law plot of $[\text{Me}_3\text{NN}]\text{Ni}(\text{N}_3)(2\text{-picoline})$ (4) in Et$_2$O at 25 °C with $\lambda_{\text{max}} = 540$ nm ($\varepsilon = 3800$ M$^{-1}$ cm$^{-1}$).

1.3.d. Stoichiometric and catalytic reactions for carbodiimide formation

Stoichiometric $^{3,5}\text{-Me}_2\text{ArNCN}^4\text{Bu}$ formation from $\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\text{NAr}^{3,5}\text{-Me}_2)$ and $^1\text{BuNC}$. To a cold solution consisting of $\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(1\text{-NAr}^{3,5}\text{-Me})$ (3a) (0.048 g, 0.0531 mmol) in 5 mL Et$_2$O was prepared was added tert-butylisocyanide (24 µL, 0.018 g, 0.212 mmol). The reaction was allowed to stir at RT for 30 min. The reaction was quenched with 2 mL CH$_2$Cl$_2$. All volatiles were removed in vacuo and the remaining film was taken up in Et$_2$O and passed through Celite. All volatiles were removed in vacuo. To this oil was added 10 eq. of anisole for $^1\text{H}$ NMR quantification (57.7 µL, 0.057 g, 0.531 mmol) to indicate a 88% yield of $^{3,5}\text{-Me}_2\text{ArNCN}^4\text{Bu}$.
Stoichiometric formation of $^{2,6}$-$\text{Me}_2\text{ArN} = \text{C} = \text{NAr}^{3,5}$-$\text{Me}_2$ from $[\text{Me}_3\text{NN}]\text{Ni}$$^{2,6}$-$\text{Me}_2$ and $^{3,5}$-$\text{Me}_2\text{ArN}_3$. $[\text{Me}_3\text{NN}]\text{Ni}$$^{2,6}$-$\text{Me}_2$ (2b) (0.040 g, 0.0611 mmol) was dissolved in 5 mL Et$_2$O and chilled to -35 °C. To this chilled solution was added a chilled solution of 3,5-dimethylphenylazide (0.018 g, 0.122 mmol). This reaction mixture was allowed to stir for 30 min at RT. All volatiles were removed in vacuo. Then the remaining solid was taken up in Et$_2$O and passed through Celite. All volatiles were removed in vacuo and anisole (13.2 µL, 0.013 g, 0.122 mmol) was added as a $^1$H NMR standard. Unfortunately, overlapping peaks did not allow for $^1$H NMR quantification. The product was observed via GC/MS m/z (CI mode) = 251 (M+1).

Stoichiometric formation of $^{t\text{Bu}}\text{N} = \text{C} = \text{NAr}^{3,5}$-$\text{Me}$ from $[\text{Me}_3\text{NN}]\text{Ni}$$^{t\text{Bu}}$ and $^{3,5}$-$\text{Me}_2\text{ArN}_3$. $[\text{Me}_3\text{NN}]\text{Ni}$$^{t\text{Bu}}$ (2a) (0.245 g, 0.439 mmol) of were dissolved in 10 mL Et$_2$O and chilled. To this chilled solution was added a tert-butylisocyanide (129 µL, 0.877 mmol). This reaction mixture was allowed to stir for 30 min at RT after which all volatiles were removed in vacuo. Then the remaining solid was taken up in Et$_2$O and passed through Celite. All volatiles were removed in vacuo and anisole (95.3 µL, 0.095 g, 0.877 mmol) was added as a $^1$H NMR standard. The product was quantified via $^1$H NMR (97% yield) as well as observed via GC/MS: m/z (CI mode) = 251 (M+1).

Stoichiometric formation of $^{3,5}$-$\text{Me}_2\text{ArNCN}^{t\text{Bu}}$ using $\{[\text{Me}_2\text{NN}]\text{Ni}\}_2(\mu-\text{NAr}^{3,5}$-$\text{Me}_2)$ and $^{t\text{BuNC}}$. To a chilled (-35 °C) solution consisting of $\{[\text{Me}_2\text{NN}]\text{Ni}\}_2(\mu-\text{NAr}^{3,5}$-$\text{Me}_2)$ (3b) (0.040 g, 0.0472 mmol) in 5 mL Et$_2$O was added tert-butylisocyanide (10 µL,
0.007 g, 0.0884 mmol). The reaction was allowed to stir at RT for 30 min after which time the reaction was quenched with 2 mL CH$_2$Cl$_2$. All volatiles were removed in vacuo and the remaining film was taken up in Et$_2$O and passed through Celite. All volatiles were removed in vacuo. To this oil was added anisole (51.2 µL; 0.472 mmol) for $^1$H NMR quantification to indicate the formation of $^{3,5}$-Me$_2$ArNCN$^t$Bu in 69% yield.

**Catalytic formation of $^{3,5}$-MeArNCN$^t$Bu from $^{3,5}$-MeArN$_3$ and $^t$BuNC with [Me$_2$NN]Ni(2-picoline) as catalyst.** To a chilled (-35 °C) solution of 3,5-dimethylphenylazide (0.214 g, 1.46 mmol) and tert-butylisocyanide (198 µL, 0.145 g, 1.74 mmol) in 6 mL Et$_2$O was added [Me$_2$NN]Ni(2-picoline) (1.67 mL of 0.0438 M solution in Et$_2$O, 0.033 g, 0.073 mmol). The reaction was allowed to stir at RT for 30 min after which time the reaction was quenched with 2 mL CH$_2$Cl$_2$. All volatiles were removed in vacuo and the remaining film was taken up in Et$_2$O and passed through Celite. All volatiles were removed in vacuo. To this oil was added 1 eq. of anisole (158.7 µL, 0.157 g, 1.46 mmol) for $^1$H NMR quantification to indicate the formation of $^{3,5}$-Me$_2$ArNCN$^t$Bu in 94% yield.

**1.3.e. Stoichiometric and catalytic CO screening reactions**

**Stoichiometric formation of $^{3,5}$-MeArN=C=O from {[Me$_3$NN]Ni)$_2$(µ-CO)$_2$ and $^{3,5}$-MeArN$_3$.** To a chilled (-35 °C) solution of {[Me$_3$NN]Ni)$_2$(µ-CO)$_2$ (0.036 g, 0.0428 mmol) in 10 mL Et$_2$O was added 3,5-dimethylphenylazide (0.0126 g, 0.105 mmol) in 5 mL Et$_2$O. This reaction mixture was allowed to stir for 3 h at RT. All volatiles were
removed in \textit{vacuo}. Then the remaining solid was taken up in Et$_2$O and passed through Celite. All volatiles were removed in \textit{vacuo} and anisole (9.3 µL, 0.009 g; 0.0857 mmol) was added as a GC/MS standard. Commercially available $^{3,5}$-MeArN=C=O was prepared in a 1:1 mixture with anisole to get a retention factor (1.08 +/-0.02). The product was observed via GC/MS m/z (CI mode) = 148 and quantified via GC/MS to reveal to formation of the isocyanate product in 10% yield.

\textbf{Stoichiometric formation of $^{3,5}$-MeArN=C=O from $\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu\text{-CO})_2$ and $^{3,5}$-MeArN$_3$.} To a chilled (-35 °C) solution of $\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu\text{-CO})_2$ (0.046 g, 0.0547 mmol) in 8 mL toluene was added a chilled solution of 3,5-dimethylphenylazide (0.016 g, 0.109 mmol) in 2 mL toluene. This reaction mixture was allowed to stir for 3 h at 80 °C in a sealed tube. All volatiles were removed in \textit{vacuo}. Then the remaining solid was taken up in Et$_2$O and passed through Celite. All volatiles were removed in \textit{vacuo} and anisole (11.8 µL, 0.012 g, 0.109 mmol) was added as a GC/MS standard. Commercially available $^{3,5}$-MeArN=C=O was prepared in a 1:1 mixture with anisole to get a retention factor (1.08 +/-0.02). The product was observed via GC/MS m/z (CI mode) = 148 (M+1) and quantified (13% yield).

\textbf{Catalytic formation of $^{3,5}$-MeArN=C=O from CO and $^{3,5}$-MeArN$_3$ with $[\text{Me}_3\text{NN}]\text{Ni}(2$-pic) as catalyst.} To a chilled (-35 °C) solution of 3,5-dimethylphenylazide (0.185 g, 1.26 mmol) in 8 mL benzene was added a solution of $[\text{Me}_3\text{NN}]\text{Ni}(2\text{-pic})$ (1a) (0.0288 g, 0.0629 mmol) in 1 mL benzene. This reaction mixture was loaded into a vessel and
pressurized with CO to 6 atm and heated to 60 °C for 24 h. The volatiles were removed \textit{in vacuo} and anisole (137 µL, 0.136 g, 1.26 mmol) was added as a GC/MS standard. Commercially available $^{3,5}$-MeArN=C=O was prepared in a 1:1 mixture with anisole to get a retention factor (1.08 +/-0.02). The product was observed via GC/MS m/z (CI mode) = 148 (M+1) and quantified via GC/MS (<1% yield).

**Catalytic carbodiimide formation of $^{3,5}$-MeArN=C=N\textit{t}Bu followed via UV-vis.** A 1.29 mM stock solution of [Me$_3$NN]Ni(2-pic) (1a) in toluene was prepared (0.059 g, 0.129 mmol). From this stock solution, 1.0 mL (0.0129 mmol) was diluted up to 10.0 mL with toluene. A 2.5 mL portion of [Me$_3$NN]Ni(2-pic) (1a) in toluene (0.00323 mmol) was chilled inside the UV-vis cuvette in the UV-vis instrument to -80 °C. Under nitrogen at -80 °C, a solution that was previously chilled to -35 °C consisting of a 0.5 mL solution of 3,5-dimethylphenylazide (0.190 g, 1.29 mmol) and tert-butylisocyanide (174 µL, 1.55 mmol) in toluene was added. The overall nickel concentration in 3 mL of total volume is now 1.075 mM [Ni], 0.430 M 3,5-dimethylphenylazide, and 0.517 M tert-butylisocyanide. The reaction was allowed to proceed at -80°C scanning every 12 seconds. An initial spectrum was taken before the addition of azide and isocyanide substrate to show [Me$_3$NN]Ni(2-pic) (1a) at $\lambda_{max} = 521$ nm. Then, the peak at $\lambda_{max} = 441$ nm was followed which corresponds to [Me$_3$NN]Ni(CN\textit{t}Bu)$_2$ (2a). The absorbance is translated into percentage of total [Ni] to show that at the beginning of the reaction up to 80% of all [Ni] is in the form [Me$_3$NN]Ni(CN\textit{t}Bu)$_2$ (2a).
1.3.f. DFT calculations

The DFT calculations employed the Becke-Perdew exchange correlation functional\textsuperscript{46-48} using the Amsterdam Density Functional suite of programs (ADF 2007.01).\textsuperscript{49-51} Slater-type orbital (STO) basis sets employed for H, C, and N atoms were of triple-\(\zeta\) quality augmented with two polarization functions (ZORA/TZ2P) while an improved triple-\(\zeta\) basis set with two polarization functions (ZORA/TZ2P+) was employed for the Ni atom. Scalar relativistic effects were included by virtue of the zero order regular approximation (ZORA).\textsuperscript{52-54} The 1s electrons of C and N as well as the 1s – 2p electrons of Ni were treated as frozen core. The VWN (Vosko, Wilk, and Nusair) functional was used for LDA (local density approximation).\textsuperscript{55} Somewhat tighter than default convergence (\(\Delta E = 1 \times 10^{-3}\) hartree, max. gradient = \(1 \times 10^{-3}\) hartree / Å, max. Cartesian step = \(1 \times 10^{-2}\) Å) and integration (4 significant digits) parameters were employed for geometry optimizations.

Experimental X-ray coordinates for \{[Me\textsubscript{2}NN]Ni\}\textsubscript{2}(\mu-NAr) (3b) were used as the starting point for the geometry optimization of low-spin \{[Me\textsubscript{3}NN]Ni\}\textsubscript{2}(\mu-NAr) (3a – S0) in a restricted (S = 0) calculation after \(p\)-Me groups were installed on the \(\beta\)-diketiminato N-aryl rings. The geometry optimization for the S = 1 form of \{[Me\textsubscript{2}NN]Ni\}\textsubscript{2}(\mu-NAr) (3b – S1) employed the DFT optimized coordinates for 1a – S0 as a starting point in an unrestricted (S = 1) calculation specifying 2 unpaired electrons (spin \(\alpha\) – spin \(\beta\)). ADFview\textsuperscript{49} was used to prepare the three-dimensional representations of the structures shown in Figure 1.12 as well as the spin density plot shown in Figure 1.13.
References


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Chapter 2

β-Diketimino Nickel(II) Amides: Synthesis, Characterization and Reactivity with Isocyanides

Abstract

The dinuclear β-diketimino nickel(II) alkoxide $\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{OBu}^t)_2$ (1) synthesized from $[\text{Me}_3\text{NN}]\text{Ni}(2\text{-picoline})$ and di-tert-butyliperoxide is a versatile intermediate in the synthesis of a wide range of nickel(II) amides which exhibit diverse bonding modes. $\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{OBu}^t)_2$ reacts with unactivated amines $\text{HN}\text{R}_1\text{R}_2$ and amides $\text{HN}\text{RC(O)}\text{R}'$ to deliver corresponding mono- or dinuclear Ni(II) amido species $[\text{Me}_3\text{NN}]\text{Ni}-\text{NR}_1\text{R}_2$, $\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{NR}_1\text{R}_2)_2$ and $[\text{Me}_3\text{NN}]\text{Ni}(\text{RC(O)}\text{R}')$ including the parent amide $\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{NH}_2)_2$ (8). Addition of isocyanide to these Ni(II) amides can result in square planar species such as $[\text{Me}_3\text{NN}]\text{Ni}(\text{NHA}_{2,4,6-\text{Cl}})(\text{CNBu}^t)$ (10) (Ar$_{2,4,6-\text{Cl}}^2$ = 2,4,6-Cl$_2$C$_6$H$_2$) and $[\text{Me}_3\text{NN}]\text{Ni}(\text{NHC(O)}\text{Ph})(\text{CNBu}^t)$ (11). Alternatively, the secondary mononuclear Ni(II) morpholinide species $[\text{Me}_3\text{NN}]\text{Ni}(\text{morpholine})(\text{N(CH}_2)_2\text{O(CH}_2)_2)$ (7) reacts with tert-butyliisocyanide to give a new adduct $[\text{Me}_3\text{NN}]\text{Ni}(\text{N(CH}_2)_2\text{O(CH}_2)_2)=\text{N}^t\text{Bu})(\text{CNBu}^t)$ (12) in which isocyanide inserted into the Ni-Namide bond. Stoichiometric RN=C=NAr$_{3,5\text{-Me}_2}$ formation was observed upon addition of CNR (R = $^t\text{Bu}$ and Ar$_{2,6\text{-Me}_2}^2$) to $\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{NHA}_{3,5\text{-Me}_2})$.
leading to the investigation of a catalytic protocol involving [Me₃NN]Ni(2-picoline), 'BuOO'Bu, and CNR in the formation of carbodiimides from amines H₂NR’.

**Introduction**

Carbon-nitrogen (C-N) bond forming reactions are of tremendous importance. The pharmaceutical industry faces the challenge of installing C-N bonds into almost all of their pharmaceuticals and possible drug candidates. Streamlining C-N bond forming reactions employing only unactivated amines and carbon hydrogen bond (C-H) in the presence of a metal catalysts allows to avoid functional group manipulations (e.g. hydroxyl to amine) (Scheme 2.1).¹⁻³ This would allow of the minimization of synthetic steps and stoichiometric byproducts, making amine synthesis more atom economic.

**Scheme 2.1.** C-N bond forming reaction – hydroxyl to amine.

Towards the use of amines for C-H functionalization via metal catalysts extremely electron poor nitrenes (M=NR) have been identified as possible active intermediates.⁴⁻⁹ On the other hand, related metal amido (M-NHR and M-NR¹R²) species have shown to provide alternative active intermediates in C-H functionalization.¹⁰⁻¹³ In particular, Chapters 3 and 4 address this important challenge. In this chapter, however, we focus on the synthesis and characterization of a family of
nickel(II) amides along with their reactivity with isocyanides that uncovers pathways for the formation of carbodiimides complementary to those discussed in Chapter 1 which proceed via nickel nitrenes.

2.1.a. Previous examples of nickel amido complexes

Perhaps more so than their early transition metal analogues, nickel(II) amides exhibit rather extensive insertion reactivity with unsaturated substrates such as carbon monoxide and isocyanides. Bergman et al. reported a stable Ni(II) Cp*Ni(acac) complex (acac = $O, O-k^2$-acetylacetonate) synthesized from MgCp*$_2$ and commercially available [Ni(acac)$_2$]$_n$. Cp*Ni(acac) reacts with lithium amides (LiNHR) (R = p-tolyl, phenyl, 2,6-xylyl, and tert-butyl) to result in dimeric Ni(II) amido complexes [Cp*Ni(µ-NHR)]$_2$. The dimeric species [Cp*NiNH(p-tol)]$_2$ proceeds to react with strong coordinating Lewis bases such as carbon monoxide, tert-butylisocyanide, and trimethylphosphine to result in monomeric species Cp*Ni(CO)(C(O)NH(p-tol)), Cp*Ni(CN$^t$Bu)(C(N$^t$Bu)NH(p-tol)), and Cp*Ni(PMe$_3$)(NH(p-tol)), respectively (Scheme 2.2).$^{14,15}$

**Scheme 2.2.** Monomeric Cp*Ni amide and its reactivity.
Other monomeric Ni(II) amido complexes such as \(\text{trans-Ni(Ar)(NHar')}(\text{PMe}_3)\) \(_2\) (Ar = Ph, 2,4,6-\text{Me}_3\text{C}_6\text{H}_2; \text{Ar'} = \text{Ph}, 2,6-\text{iPr}_2\text{C}_6\text{H}_3)\) synthesized from \(\text{trans-Ni(Ar)(Br)}(\text{PMe}_3)\) and KNHar’ exhibit extensive insertion reactivity with the unsaturated substrates carbon dioxide, \(\text{CH}_3\text{O}_2\text{C}==\text{CCO}_2\text{CH}_3\) (DMAD), Ph$_2$CCO, and isocyanates (RNCO; R = Ph, tBu) (Scheme 2.3). Additionally, it reacts with water to give a dimeric Ni(II) hydroxo species \([\text{Ni}(\text{R})(\mu-\text{OH})(\text{PMe}_3)]_2\) with loss of H$_2$NAr.
Less reactive monomeric diamido nickel(II) complexes [Ni{N(R)(8-C9H6N)}2] (R = Me3 or tBuMe2) featuring amides with chelating groups have been reported by Mak et al. by addition of [{Li(OEt2)(L)}2] (L = _N(SiMe3)(8-C9H6N) or _N(Si'tBuMe2)(8-C9H6N)) to NiCl2 (Figure 2.1).  

The metallocyclic Ni(II) amido alkyl complex [(bpy)Ni{N(tol)(CH2)}4] formed via [(bpy)Ni(CH2CMe2-α-C6H4)] with the organoazide TolN3 (Tol = p-MeC6H4) undergoes reductive elimination in the presence of either [(AcCp)2Fe]⁺, O2, I2, or heat to give a heterocyclic amine product (Scheme 2.4).

Using the monoanionic pincer ligand 2,6-bis((diisopropylphosphino)methyl)phenyl (PCP), (PCP)NiBr reacts with NaNH2 to deliver (PCP)Ni-NH2. This monomeric parent amido species reacts with MeOH and H2O under loss of NH3 to give (PCP)Ni-OMe and (PCP)Ni-OH in acid-base reactions. Interestingly, (PCP)Ni-NH2 reacts with benzaldehyde (PhCHO) to give not the insertion

**Scheme 2.4.** Reductive elimination of metallocyclic Ni(II) amide.
Employing a β-diketiminato supporting ligand, we target a family of Ni(II) amido species derived from the acid-base chemistry between a Ni(II) alkoxide \([\text{Ni}-\text{OBu}^t]\) and unactivated amines and organic amides. The family of mono- and dinuclear Ni(II) amides \([\text{Ni}]\text{-NR}^1\text{R}^2\) and \([\text{Ni}]_2(\mu-\text{NR}^1\text{R}^2)_2\) demonstrates a variety of bonding modes that strongly depend on the amido N-substituents. Additionally, we describe their stoichiometric and catalytic reactivity with isocyanides which range from simple adduct formation to catalytic carbodiimide synthesis.

Results and Discussion

2.2.a. Synthesis of \(\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{OBu})_2\) (1)

Addition of 'BuOOBu\(^t\) to a solution of \([\text{Me}_3\text{NN}]\text{Ni}(2\text{-picoline})\) in cold (-35 °C) ether results in the precipitation of the nickel alkoxide \(\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{OBu}')_2\) (1) in 82% yield as a green solid (Scheme 2.6). Solubility issues makes characterization
extremely challenging but slow vapor diffusion of di-tert-butylperoxide into a solution of [Me₃NN]Ni(2-picoline) allows the formation of green crystals suitable for single X-ray diffraction. The preliminary X-ray structure of dinuclear 1 consists of two monomeric [Me₃NN]Ni-OBu units in which the two Ni centers are related via an inversion center with a Ni··Ni separation of 3.067 Å (Figure 2.2). 1 shows a pseudotetrahedral coordination at nickel with twist angles between N-Ni-N and O-Ni-O planes of 83.5° and Ni-O distances of 1.9600(19) and 1.9871(19) Å. 1 is closely related in structure to previously reported {[Me₃NN]Ni}₂(µ-OCy)₂ that was prepared via an oxidative route involving the addition of the O-organonitroso compound CyONO to 2 equiv. [Me₃NN]Ni(2,4-lutidine) which also generates the nickel(0) nitrosyl [Me₃NN]Ni-NO (Scheme 2.7). For comparison, {[Me₃NN]Ni(µ-OCy)}₂ has a twist angle of 81.1° with Ni-O distances of 1.955(2) and 1.994(2) Å with a Ni-Ni separation of 3.050(1) Å.

Scheme 2.7. Literature procedure for reaction of [Me₃NN]Ni(2,4-lutidine) with CyONO.

\[
2 \text{[Me₃NN]Ni(2,4-lutidine)} \xrightarrow{\text{CyONO, toluene, 2,2,4-lut.}} 1/2 \text{[Ni]} + \text{[Me₃NN]Ni(NO)}
\]

{[Me₃NN]Ni}₂(µ-OBu)₂ (1) is a paramagnetic complex but shows ¹H NMR peaks at the unusual chemical shifts δ 27.20 (p-Ar-Me), 25.12 (o-Ar-Me), 2.98 (m-Ar-H) and -37.35 ppm (backbone CH₃) (Figure 2.3). UV-vis spectroscopy in benzene at RT shows absorption maxima at 566 and 636 nm. Due to insolubility molar absorptivity could not be determined accurately.
Figure 2.2. Preliminary X-ray crystal structure of \{[\text{Me}_3\text{NNi}]_2(\mu-\text{OBU})_2\} (1). All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ni-Ni’ 3.067, Ni-N1 2.005(2), Ni-N2 1.983(3), Ni-O 1.9600(19), Ni-O’ 1.9871(19), N1-Ni-N2 91.59(9).
Figure 2.3. $^1$H NMR spectrum (RT, benzene-$d_6$, 400 MHz) of $\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{OBu}^t)_2$ (1).

In an attempt to synthesize a more soluble and possibly more reactive mononuclear Ni(II) alkoxide, we used the more sterically demanding dicumyl peroxide. Addition of dicumyl peroxide to 2 equiv. $[\text{Me}_3\text{NN}]\text{Ni}(2\text{-picoline})$ in Et$_2$O followed by crystallization from Et$_2$O resulted in the isolation of the dinuclear $\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{OCPhMe}_2)(\mu-\text{OEt})$ from pentane at -35 °C as green crystals in 55 % yield (Scheme 2.8). While we do not know the origin of the Et group, we speculate that it came from the solvent Et$_2$O. The X-ray structure of $\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{OCPhMe}_2)(\mu-\text{OEt})$ (Figure 2.4) is similar in form to that of 1. The pseudotetrahedral coordination at the Ni shows a twist angle of the $N_{\beta\text{-dik}}$-Ni-$N_{\beta\text{-dik}}$ and $O_{\text{Cum}}$-Ni-O$_{\text{Et}}$ planes of 88.7° which is very similar
to the twist angle of 83.5° in 1. Characteristic distances are the Ni-Ni separation of 3.051(2) Å and Ni-O distances ranging from 1.9229(19) to 1.994(21) Å.

Despite its dinuclear nature that renders it largely insoluble in common organic solvents (e.g. THF, ether), \{[Me_3NN]Ni\}_2(\mu-OCPhMe_2)(\mu-OEt) (1) reacts readily with aryl amines (3,5-dimethylaniline and 2,4,6-trichloroaniline), acyl substrates (benzamide and acetophenone), primary and secondary alkyl amines (phenethylamine and morpholine), and even ammonia (NH_3) in an acid-base fashion liberating only tert-butanol (tBuOH). The resulting Ni-amides are both mononuclear and dinuclear in nature and exhibit a range of M-amide bonding modes that depend on the nature of the organic amine or amide.
Figure 2.4. X-ray crystal structure of $\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{OCPhMe}_2)(\mu-\text{OEt})$. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ni … Ni 3.051(2), Ni2-O1 1.9228(19), Ni2-O2 1.994(2), Ni2-N4 1.962(2), Ni2-N3 1.9742(19), Ni1-O1 1.942(2), Ni1-O2 1.967(2), Ni1-N1 1.956(2), Ni1-N2 1.967(2), N4-Ni2-N3 92.48(9), N1-Ni1-N2 91.33(9).
2.2.b. Reaction of 1 with aryl amines

\[
\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{OBu})_2 \text{ (1)} \text{ reacts with anilines } \text{H}_2\text{NAr to give two different types of complexes depending on the geometric and electronic structure of the aniline.}
\]

Dinuclear alkoxide 1 reacts with 3,5-dimethylaniline in Et2O at RT to form the dinuclear species \{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{NHAr}^{3,5-\text{Me}_2})_2 \text{ (2)} as maroon crystals in 39\% yield from Et2O at -35 °C (Scheme 2.9). The low yield is due to insolubility that causes product loss during the crystallization procedure.

**Scheme 2.9.** Synthesis of \{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{NHAr}^{3,5-\text{Me}_2})_2 \text{ (2)}.

The X-ray crystal structure of \{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{NHAr}^{3,5-\text{Me}_2})_2 \text{ (2)} (Figure 2.5) exhibits square planar geometry at each Ni. The two Ni centers are related via an inversion center with a Ni···Ni separation of 3.004(2) Å and a twist angle between N1-Ni-N2 and N3-Ni-N3’ planes of 22.0°. The Ni-Namide bond distances are 1.923(2) and 1.955(2) Å. These distance is significantly longer than monomeric Ni-amides that have been isolated such as [Me3NN]Ni-NPh2 (Ni-Namide 1.823(1) Å; low-spin)20, [Pr2NN]Ni-NTMS2 (Ni-Namide 1.873(2) Å; high-spin)21 and [Me3NN]Ni-NHAd (Ni-Namide 1.743(4) Å).22

Based on its square planar geometry at each Ni center, 2 is diamagnetic in solution. The \(^1\)H NMR spectrum of 2 (Figure 2.6) in benzene-\(d_6\) at RT shows a single characteristic \(\beta\)-diketiminato C-H backbone peak at \(\delta 4.51\) ppm. Also, there are two
Figure 2.5. X-ray crystal structure of {[Me$_3$NNi]$_2$(µ-NHAr)$_2$} (2). All hydrogen atoms have been omitted for clarity except of amido H. Selected bond distances (Å) and angles (°): Ni – N1 1.948(2), Ni – N2 1.940(2), Ni – N3 1.923(2), N1 – Ni – N2 93.43(8), Ni···Ni separation 3.004(2).
Table 2.1 Crystallographic data for \{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{OCPhMe}_2)(\mu-\text{OEt}), 1, and 2.

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different signals for the β-diketiminato N-aryl m-Ar-H groups at δ 6.880 and 6.464 ppm. This solution behavior indicates that we observe only a dimeric species in solution. The characteristic amide N-H peak resonates at δ 2.701 ppm.

Figure 2.6. $^1$H NMR spectrum (400 MHz, benzene-$d_6$, RT) of $\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu$-$\text{NHAr}^{3,5-\text{Me}_2})_2$ (2).
In contrast, 2,4,6-trichloroaniline reacts with \([\text{Me}_3\text{NN}]\text{Ni}2(\mu-\text{OBu})2\) (1) in Et\(_2\)O at RT to form a mononuclear species \([\text{Me}_3\text{NN}]\text{Ni}(\text{NHAr})2,4,6-\text{Cl}\) (3) isolated as blue crystals in 43% yield from Et\(_2\)O (Scheme 2.10). During the isolation of \([\text{Me}_3\text{NN}]\text{Ni}(\text{NHAr})2,4,6-\text{Cl}\) (3), \([\text{Me}_3\text{NN}]\text{Ni}2(\mu-\text{OBu})2\) (1) is observed as unreacted starting material. The insolubility of 1 probably prevents a complete conversion but is easily removed by filtration. Longer reaction times do not improve the yield, which could potentially indicate an equilibrium between \([\text{Me}_3\text{NN}]\text{Ni}2(\mu-\text{OBu})2\) (1) and 3.

The X-ray structure of mononuclear \([\text{Me}_3\text{NN}]\text{Ni}(\text{NHAr})2,4,6-\text{Cl}\) (3) (Figure 2.7) reveals a four coordinate nickel center in which one of the N-aryl \(\sigma\)-Cl atoms completes a pseudo-tetrahedral geometry about nickel. The Ni-N\text{amide} distance is 1.8796(15) Å which is considerably shorter than the Ni-N\text{amide} distances in the dimeric Ni(II) amido complex above (Table 2.7). The Ni-N\text{amide}-C\text{ipso} angle of 124.52(12) Å is consistent with \(sp^2\)-hybridization at N. As expected, the Ni-Cl distance of 2.4805(5) Å in \([\text{Me}_3\text{NN}]\text{Ni}(\text{NHAr})2,4,6-\text{Cl}\) (3) is considerably longer than previously reported \(\beta\)-diketiminato nickel(II) chloride complexes \([\text{^1Pr}_2\text{NN}]\text{Ni}2(\mu-\text{Cl})2\) (Ni-Cl: 2.324(1) - 2.349(1) Å),\(^{21}\) \([\text{Me}_2\text{NN}]\text{Ni}2(\mu-\text{Cl})2\) (Ni-Cl: 2.2997(9) - 2.3127(9) Å),\(^{23}\) and \([\text{^1Pr}_2\text{NN-tBu}]\text{Ni-Cl}\) (Ni-Cl: 2.137(2) Å)\(^{24}\) that feature covalent Ni-Cl bonds.
Figure 2.7. X-ray crystal structure of $[\text{Me}_3\text{NN}]\text{Ni(NHAr}^{2,4,6-}\text{Cl})$ (3). All hydrogen atoms have been omitted for clarity except the amido N-H. Selected bond distances (Å) and angles (°): Ni – N1 1.9087(15), Ni – N2 1.8956(14), Ni – N3 1.8796(15), Ni – Cl1 2.4805(5), N2 – Ni – N1 94.98(6), N1 – Ni – Cl1 108.25(4), C24-N3-Ni
As suggested by the tetrahedral geometry and short Ni-Namide distance, this species is paramagnetic in solution and possesses a $\mu_{\text{eff}}$ of 2.40 B.M. in benzene-$d_6$ by the Evans method. Though paramagnetic, it exhibits clearly identifiable $^1$H NMR peaks at $\delta$ 29.62, 28.57, 28.30, and -46.81 ppm in benzene-$d_6$ at RT (Figure 2.8). Integration of these peaks allows for assignment of $\beta$-diketimato $N$-aryl $p$-Me, $o$-Me, and $m$-H resonances at $\delta$ 28.64, 28.57, and 28.30 ppm, respectively. A single upfield peak at $\delta$ -46.81 ppm is ascribed to the $\beta$-diketimino backbone C-H resonance.

![Figure 2.8. $^1$H NMR spectrum (benzene-$d_6$, RT, 400 MHz) of [Me$_3$NN]Ni(NHAr$_{2,4,6}$Cl)](3).
2.2.3. Reaction of 1 with benzamide and acetophenone

To examine the influence of an α-carbonyl group on nickel-amide bonding, we examined the reaction of 1 with benzamide (PhC(O)NH₂) as well as the related ketone acetophenone (PhC(O)CH₃) to explore any differences between Ni-N and Ni-C bonding. \{[Me₃NN]Ni}_{2}(µ-OBu̇)₂ (1) reacts with benzamide or acetophenone in toluene at RT to give the mononuclear species [Me₃NN]Ni(κ²-NHC(O)Ph) (4) as brown crystals from Et₂O in 66% yield and [Me₃NN]Ni(κ³-CH₂C(O)Ph) (5) as yellowish brown crystals from Et₂O in 60% yield, respectively (Scheme 2.11).

\[ \text{[Me₃NN]Ni(κ²-NHC(O)Ph) (4) and [Me₃NN]Ni(κ³-CH₂C(O)Ph) (5) have closely related square planar structures in the solid state (Figures 2.9 and 2.10). An important difference, however, is that the anionic benzamide ligand in 4 (disordered over two sets of positions; preliminary refinement) exhibits κ²-O,N coordination whereas the acetophenone enolate experiences an κ³-interaction with the O,C, and N atoms in the delocalized enolate π-system. The Ni-O distances are very similiar for 4 and 5 at 1.919(9) (major occupancy) and 1.9051(12) Å, respectively. While 4 has a Ni-Namide bond distance of 1.923(7) Å, the related Ni-C₆H₂ bond distance in 5 is 2.0545(18) Å.} \]
Figure 2.9. Preliminary X-ray crystal structure \([\text{Me}_3\text{NN}][\text{Ni}(\text{MeCN})_2\text{NHC(O)Ph}]\) (4). NHC(O)Ph moiety disordered over two positions at 57:43 occupancies – only major shown. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ni-N3A 1.942(8), Ni-OA 1.919(8), Ni-N1 1.847(5), Ni-N2 1.841(5), Ni-C24A 2.348(12), N3A-Ni-OA 66.7(4), N1-Ni-N2 95.97(7). (Further refinement of separate β-diketiminato orientations is necessary.)
Figure 2.10. X-ray crystal structure of [Me₃NNi(η¹-C₂H₅C(O)Ph)] (5). All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ni-N1 1.8617(14), Ni-N2 1.8792(14), Ni-O1 1.9051(12), Ni-C24 2.0545(18), Ni-C25 2.0428(18), N1-Ni-N2 96.06(6).
Table 2.2: Crystallographic data for 3, 4 and 5.

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Å perhaps a reflection of the different sizes of N and C as well as the difference in bonding modes for these two ligands. The Ni-C\textsubscript{carbonyl} distances, however, are markedly different in 4 and 5 at 2.348(12) and 2.0428(18) Å. The twist angles between the $N_{\beta}$-dik-Ni-N$_{\beta}$-dik and $N_{\text{amide}}$-Ni-O planes in 4 is 10.5 and the twist angle between the $N_{\beta}$-dik-Ni-N$_{\beta}$-dik and C\textsubscript{CH2}-Ni-O planes in 5 is 5.2°, each consistent with square planar coordination at Ni.

As judged by their $^1$H NMR spectra in benzene-$d_6$ at RT, each species 4 and 5 is fluxional in solution (Figure 2.11 and 2.12). For instance, [Me$_3$NN]Ni(k$^2$-NHC(O)Ph) (4) and [Me$_3$NN]Ni(i$^3$-CH$_2$C(O)Ph) (5) each shows one set of $\beta$-diketiminato $N$-aryl o-Me and backbone Me resonances at $\delta$ 2.720 and 1.404 ppm and $\delta$ 2.266 and 1.446 ppm, respectively. If the NHC(O)Ph and CH$_2$C(O)Ph ligands were firmly locked in the orientations seen in their crystal structures, one would expect two backbone Me signals rather than one observed in 4 and 5. VT NMR spectra of [Me$_3$NN]Ni(k$^2$-NHC(O)Ph) (4) over the range -80 °C to + 25 °C (Figure 2.11) reveals a coalescence of the backbone Me peaks at $T_c = -47$ °C for which corresponds to an activation barrier $\Delta G^\ddagger$(226 K) = 11.1(2) kcal/mol for this process. VT NMR spectra of [Me$_3$NN]Ni(i$^3$-CH$_2$C(O)Ph) (5) (Figure 2.12) indicates a higher activation barrier $\Delta G^\ddagger$(291 K) = 13.8(4) kcal/mol.
Figure 2.11. VT $^1$H NMR (400 MHz, toluene-$d_8$, -80 °C to +25 °C) spectra of 4.

Figure 2.12. VT $^1$H NMR (400 MHz, toluene-$d_8$, -80 °C to +25 °C) spectra of 5.
2.2.d. Reaction of 1 with alkyl amines

Reaction of \{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-O\text{Bu})_2 (1) with the primary alkyl amine phenethylamine (PhCH₂CH₂NH₂) in Et₂O at RT forms the dinuclear species \{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-N\text{HCH}_2\text{CH}_2\text{Ph}) (5) as red crystals in 60% yield at -35 °C from Et₂O (Scheme 2.12).

**Scheme 2.12.** Synthesis of dinuclear alkylamido complex.

\[
\begin{align*}
\text{Ph} & \quad \text{Et}_2\text{O} \\
\text{H}_2\text{N} & \quad -2\text{HBrOH} \\
\text{Ni} & \quad \text{Ni} \\
\text{N} & \quad \text{N} \\
\text{Bu}^\text{t} & \quad \text{Bu}^\text{t}
\end{align*}
\]

The X-ray structure of \{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-N\text{HCH}_2\text{CH}_2\text{Ph})_2 (6) (Figure 2.13) is closely related to that of \{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-N\text{HAr}_{3,5}\text{-Me}_2)_2 (2). The two Ni centers in 6 are related by inversion symmetry with a Ni...Ni separation of 2.9423(5) Å. The Ni-Namide bond distances of 1.9144(16) and 1.9192(16) Å in \{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-N\text{HCH}_2\text{CH}_2\text{Ph})_2 (6) are slightly shorter than the Ni-Namide bond distances of 1.923(2) and 1.955(2) Å for \{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-N\text{HAr}_{3,5}\text{-Me}_2)_2 (2). The twist angle between the N\beta₅-dik-Ni-N\beta₅-dik and Namide-Ni-Namide planes is 22.8° which shows a similar level of distortion from idealized square planar coordination at Ni as found in 2.

**Scheme 2.13.** Formation of isomers via β-hydride elimination / reinsertion pathway.
Figure 2.13. X-ray crystal structure of $\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{NHCH}_2\text{CH}_2\text{Ph})_2$ (6). All hydrogen atoms have been omitted for clarity except amido H. Selected bond distances (Å) and angles (°): Ni1 – N1 1.9185(15), Ni1 – N2 1.9245(15), Ni1 – N3 1.9144(16), Ni-N3’ 1.9192(16), Ni1 – Ni1’ 2.9423(5), N1 – Ni1 – N2 93.66(6).
$^1$H NMR spectra of 2 in benzene-$d_6$ shows complicated behavior (Figure 2.14). Two prominent signals in the β-diketiminato backbone C-H region (δ 5 to 6 ppm) indicate that there is more than one species in solution. VT $^1$H NMR analysis of these two major backbone C-H signals in the temperature range of -80 to +60 °C shows a temperature dependent shift of relative integration of these signals. At first we believed a dissociation between the dimer and monomer was taken place (Scheme 2.13). Upon van’t Hoff analysis that considers this dimer / monomer equilibrium, however, we determined a nonlinear correlation, which lead us to believe that a more complex process might be occurring. A possible mechanism that would explain the formation of up to four related species is shown in Scheme 2.13 that features β-hydride elimination / reinsertion in the monomeric [Me$_3$NN]Ni-NHCH$_2$CH$_2$Ph species considered (see Chapter 4).
Figure 2.14. VT $^1$H NMR spectra (400 MHz, toluene-$d_8$, -80 to +60 °C) of 6.

2.2.e. Reaction of 1 with ammonia to give $\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{NH}_2)_2$ (7)

$\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{OBU})_2$ (1) dissolved in a small quantity of THF reacts with NH$_3$ via slow vapor diffusion of this volatile amine from a 0.5 M NH$_3$ solution in THF to give orange crystals of $\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{NH}_2)_2$ (7) in 96% yield (Scheme 2.15).

Scheme 2.15. Formation of dinuclear parent amido complex $\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{NH}_2)_2$ (7).
Once formed, \( \{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu\text{-NH}_2)_2 \) (7) is essentially insoluble in common organic solvents which prevents further spectroscopic characterization. Single crystal X-ray diffraction and elemental analysis support the formation of \( \{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu\text{-NH}_2)_2 \) (7) (Figure 2.16). As compared to the other dinuclear amido complexes \( \{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu\text{-NHAr})_2 \) (2; \( \text{Ar} = 3,5\text{-Me}_2\text{C}_6\text{H}_3 \)) and \( \{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu\text{-NHCH}_2\text{CH}_2\text{Ph})_2 \) (6), the parent amide 7 exhibits the shortest Ni-Namide bond distances of 1.899(2) and 1.901(2) Å. Similarly, the Ni···Ni separation of 2.920 Å in \( \{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu\text{-NH}_2)_2 \) (7) is shorter than the Ni···Ni separation in 2 (3.004 Å) and 6 (2.942 Å). The twist angle between the N\( \beta\text{-dik}\)-Ni-N\( \beta\text{-dik} \) and Namide-Ni-Namide planes of 17.0° deviates least from idealized square planar geometry, likely a result of minimal steric demands of the NH\(_2\) ligands.

For comparison, we sought the corresponding hydroxide bridged species which have been reported to form upon reaction of Ni(I) species with \( \text{O}_2 \). Slow reaction of \([\text{Me}_3\text{NN}]\text{Ni}(2\text{-picoline}) \) in toluene with air that enters through a syringe needle slowly forms green crystals of \( \{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu\text{-OH})_2 \) (8) in 93% yield (Scheme 2.16). As with 7, once formed \( \{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu\text{-OH})_2 \) (8) is quite insoluble and resists further spectroscopic characterization. Single crystal X-ray diffraction and elemental analysis support the formation of \( \{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu\text{-OH})_2 \) (8) (Figure 2.17). The Ni-N\( \beta\text{-dik} \) bond distances are 1.8769(19) and 1.8692(19) Å which is considerable shorter than the Ni-N\( \beta\text{-e} \).

**Scheme 2.16.** Ni(II) hydroxide formation from Ni(I) precursor and air.
Figure 2.16. X-ray crystal structure of \{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{NH}_2)_2\, (7)\). All hydrogen atoms have been omitted for clarity except amido H. Selected bond distances (Å) and angles (°): Ni1 – N1 1.902(2), Ni1 – N2 1.895(2), Ni1 – N3 1.899(2), Ni1-N3’ 1.901(2), Ni1 – Ni1’ 2.9196(6), N2 – Ni1 – N1 95.55(10).
dik distances of 1.902(2) and 1.895(2) Å in 7. Similarly, the Ni-O distances of 1.8767(17) and 1.8856(17) Å along with a Ni⋯Ni separation of 2.8935(6) Å are consistently shorter in the Ni(amide) counterpart 7 which has Ni-Namide of 1.899(2) and 1.901(2) Å and a Ni⋯Ni separation of 2.9196(6) Å. The twist angle between the Nβ-dik-Ni-Nβ-dik and O-Ni-O planes is 16.7° which shows a square planar geometry at the nickel, essentially identical to 7’s twist angle of 17.0°. Driess et al. reported a β-diketiminato Ni(II) hydroxide species, \{[^{1}_iPr_2NN]Ni\}_2(\mu-OH)_2^{26} with Ni-O bond distances of 1.861(7), 1.885(7), 1.908(7) and 1.963(7) Å, while Wu et al. reported a similar structure using an electron-poor β-diketiminate, \{[Me_2NN_F_6]Ni\}_2(\mu-OH)_2^{25}, which has all identical Ni-O bond distances of 1.863(2) Å.\textsuperscript{25,26} The IR spectrum for 8 shows a νOH = 3264 cm\textsuperscript{-1}. 
Figure 2.17. X-ray crystal structure of \{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{OH})_2 (8). All hydrogen atoms have been omitted for clarity except for hydroxide. Selected bond distances (Å) and angles (°): Ni1-N1 1.8769(19), Ni1-N2 1.8692(19), Ni1-O1 1.8767(17), Ni1-O1’ 1.8856(17), Ni1…Ni1’ 2.8935(6), N1-Ni1-N2 95.13(8).
**Table 2.4.** Crystallographic data for 6, 7 and 8.

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2.2. Stoichiometric reactivity of nickel amides with isonitriles

The mononuclear nickel amides 3 and 4 react rapidly with strong the electron-rich isocyanide \(^{t}BuNC\) to incorporate this good \(\sigma\)-donor, \(\pi\)-acceptor ligand into new square planar complexes with or without insertion of isocyanide into the Ni-Namide bond.

\[
[\text{Me}_3\text{NN}]\text{Ni(}\text{NHAr}^{2,4,6-}\text{Cl}) \quad (3)
\]
reacts with \(^{t}BuNC\) to give square planar \([\text{Me}_3\text{NN}]\text{Ni(}\text{NHAr}^{2,4,6-}\text{Cl})(\text{CNBu}^t) \quad (9)\) as purple crystals 97\% yield at -35 °C from Et\(_2\)O.

**Scheme 2.17.** Formation of isocyanide adduct 9 from reaction of CNBu\(^t\) with 3.

(Scheme 2.17). Despite poor donating ability of the NHAr\(^{2,4,6-}\text{Cl}\) ligand, coordination of the isocyanide induces square planar coordination with a Ni-Namide distance of 1.9109(19). This compares to \([\text{Me}_3\text{NN}]\text{Ni(}\text{NHAr}^{2,4,6-}\text{Cl}) \quad (3)\) Ni-Namide distance of 1.8796(15) Å. The Ni-C_isocyanide distance is 1.858(2) Å while the Ni-N_{\text{dik}} distances are 1.9104(19) and 1.9249(19) Å (Figure 2.18). The FT-IR spectrum of 9 measured via evaporation of an Et\(_2\)O solution of 9 on a KBr salt plate shows a prominent \(v_{\text{CN}}\) stretch at 2195 cm\(^{-1}\) as compared to free \(^{t}BuNC\) \((v_{\text{CN}} = 2331 \text{ cm}^{-1})\). This difference in frequencies is consistent with a significant amount of backbonding from the d\(^8\) Ni\(^{II}\) center to the isocyanide ligand.

VT \(^1\)H NMR spectra of \([\text{Me}_3\text{NN}]\text{Ni(}\text{NHAr}^{2,4,6-}\text{Cl})(\text{CNBu}^t) \quad (9)\) in toluene-\(d_8\) over the temperature range -65 to +50 °C (Figure 2.19) indicates a fluxional process consistent with the net exchange of positions of the NHAr\(^\text{Cl}\) and CNBu\(^t\) groups within
Figure 2.18. X-ray crystal structure of [Me₃NNi(NHAr²,4,6-Cl')(CNBu')] (9). All hydrogen atoms have been omitted for clarity except for N-H. Selected bond distances (Å) and angles (°): Ni-N1 1.9104(19), Ni-N2 1.9249(19), Ni-N3 1.9109(19), Ni-C30 1.858(2), C30-N4 1.160(3), N3-C24 1.355(3), N1-Ni-N2 93.75(8), Ni-N3-C24 133.96(16)
the coordination wedge of the [Me$_3$NN]Ni fragment. Specifically, the β-diketiminato backbone Me resonances appear at δ 1.573 and 1.384 ppm at -65 °C and coalesces to give a singlet at δ 1.460 ppm at RT.

Figure 2.19. VT $^1$H NMR spectra (400 MHz, toluene-$d_8$, -65 to +50 °C) of [Me$_3$NN]Ni(NHAr$_{2,4,6}$-Cl$^-$)(CNBu$^t$) (9).
To investigate the mechanism of $^1$BuNC exchange, excess CNBu$^t$ ($\sim$0.0448 M) was added to a solution of isolated [Me$_3$NN]Ni(NHar$_{2,4,6}$-Cl)(CNBu$^t$) ($\sim$0.0149 M) in toluene-$d_8$. Notably, the temperature for coalescence of the backbone Me peaks did not change as compared to a sample of 9 without added CNBu$^t$, consistent with a dissociative mechanism in which CNBu$^t$ leaves to generate [Me$_3$NN]Ni(NHar$_{2,4,6}$-Cl) (3). Contribution of an associative mechanism would be expected to exhibit some dependence of the CNBu$^t$ concentration on the rate, being accelerated upon addition of external CNBu$^t$ (Scheme 2.18).

$[\text{Me}_3\text{NN}]\text{Ni}(\text{N}^3\text{HNC(O)Ph})$ (4) reacts with $^1$BuNC to form the $[\text{Me}_3\text{NN}]\text{Ni}(\text{NHC(O)Ph})(\text{CNBu}^t)$ (10) adduct as orange crystals in 59% yield from Et$_2$O at -35 °C (Scheme 2.19). The crystal structure of $[\text{Me}_3\text{NN}]\text{Ni}(\text{NHC(O)Ph})(\text{CNBu}^t)$ (10) (Figure 2.20) shows that the 'NHC(O)Ph moiety is bound through the nitrogen with Ni-
Figure 2.20. X-ray crystal structure of [Me₃NN]Ni(NHC(O)Ph)(CNBu') (10) All hydrogen atoms have been omitted for clarity except for N-H. Selected bond distances (Å) and angles (°): Ni-N1 1.8891(13), Ni-N2 1.9120(14), Ni-N3 1.8913(13), Ni-C31 1.8585(17), C31-N4 1.152(2), C24-O 1.252(2), C24-N3 1.324(2), N3-C24-O 122.72(15), Ni-N3-C24 126.99(11), N1-Ni-N2 93.00(6).
Namide distance of 1.8913(13) Å and a Ni-C_isocyanide distance of 1.8585(17) Å. The Ni-Namide distance in 10 is slightly shorter than in 9 (1.9109(19) Å), while the Ni-C_isocyanide distance in 10 is essentially identical to that in 9 (1.858(2) Å).

The $^1$H NMR spectrum of 10 in benzene-$d_6$ shows a surprisingly symmetric species with single peaks for the β-diketiminato N-aryl o-Me, p-Me and backbone Me resonances at δ 2.570, 2.101 and 1.479 ppm, respectively (Figure 2.21). Thus 10 just like [Me$_3$NNi(NHAr$_{2,4,6}$Cl)(CNBu')] (9) has fluxional NMR behavior owing to rapid symmetrization of the coordination wedge of 10, presumably via facile dissociation of CNBu' from 10. The IR spectrum of 10 reveals $\nu_{CN} = 2207$ cm$^{-1}$ which is closer to free $^t$BuNC ($\nu_{CN} = 2331$ cm$^{-1}$) than complex 9 indicating weaker backbonding in 10.
Figure 2.21. $^1$H NMR (benzene-$d_6$, RT, 400 MHz) of [Me$_3$NN]Ni(NHC(O)Ph)(CNBu')] (10).

2.2.g. One pot reaction to yield [Me$_3$NN]Ni(C(N(CH$_2$)O(CH$_2$)$_2$)=NBu')(CNBu') (11)

In a one-pot reaction, {[Me$_3$NN]Ni}$_2$(μ-OBu)$'_2$ (1) was reacted with 4 equiv. morpholine followed by the addition of 4 equiv. 'BuNC. We hypothesize that a

Scheme 2.20. One-pot synthesis of 11.

proposed intermediate - not isolated

[Ni]$_2$O[O][Ni] + 4 NHC(O)Ph (toluene) $\rightarrow$ 2 [Ni](N(C$_4$H$_9$O))(morpholine) $\rightarrow$ 2 [Ni]CNBu'$'$

orange crystals 75% yield
nickel(II) morpholinide complex forms first that undergoes insertion of CNBu' into the Ni-Namide bond to give \([\text{Me}_3\text{NN}]\text{Ni}(\text{C(N(CH}_2\text{)O(CH}_2\text{)2})=\text{NBu}'\text{(CNBu') (11)}\) as orange crystals in 75% from Et_2O at -35 °C (Scheme 2.20). A similar reaction has been observed for a niobium(V) amido complexes.\textsuperscript{27} For example, \([\text{Nb}^1_1\eta^5-\text{C}_5\text{H}_4\text{SiMe}_2(\eta^1-\text{NBu')})\text{(NBu')Cl}]\) reacts with isocyanide \((\text{CNAr})\) to give \([\text{Nb}^1_1\eta^5-\text{C}_5\text{H}_4\text{SiMe}_2(\text{NBu'})-\eta^2-(\text{C=NAr})\text{(NBu')Cl}]\).\textsuperscript{27}

The X-ray structure of 11 (Figure 2.22) reveals a square planar species in which an isocyanide has been inserted into the Ni-Namide bond. The Ni-C24 distance is 1.924(5) Å, while the C24-N4 and C24-N5 bond distances are 1.293(6) and 1.390(6) Å, respectively. The large difference between the bond distances in C24-N4 and C24-N5 indicates that C24-N4 is a C=N (double) bond and C24-N5 is a C-N (single) bond.

The X-ray structure of 11 also shows a Ni-C_isocyanide distance of 1.804(6) Å for the bound isocyanide with a isocyanide bond distance N-C_isocyanide of 1.165(6). The Ni-C_isocyanide bond in 11 is significantly shorter than in 9 (1.858(2) Å) and in 10 (1.8585(17) Å), while the isocyanide bond in 11 falls in the same range for 10 (1.160(3) Å) and 11 (1.152(2) Å). The imine bond N=C has a bond length of 1.293(6) Å and the C-N_morph is 1.390(6) Å. The Ni-N_β-dik distances are 1.966(4) and 1.924(4) Å (Figure 2.22).

\([\text{Me}_3\text{NN}]\text{Ni}(\text{C(N(CH}_2\text{)O(CH}_2\text{)2})=\text{NBu}')\text{(CNBu') (11)}\) shows a complex \(^1\text{H}\) NMR spectrum in benzene-\(d_6\). Partial assignment of this spectrum shows 4 different \(\alpha\)-Ar-\(Me\) peaks in the range of \(\delta\) 2.576 to 2.393 ppm and four different \(m\)-Ar-\(H\) in the range of \(\delta\) 6.862 to 6.730 ppm. A single backbone C-H peaks is observed at \(\delta\) 5.057 ppm.
Figure 2.22. X-ray crystal structure of [Me$_3$NNiC(N(CH$_2$)O(CH$_2$)$_2$)=NBu')C(NBu') (11). The morpholine unit shows disorder over 2 positions modeled in a 59:31 ratio. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ni – N1 1.966(4), Ni – N2 1.924(4), Ni – C24 1.924(5), Ni – C33 1.804(6), C24 – N5 1.390(6), C24 – N4 1.293(6), C33 – N3 1.165(6), N1 – Ni – N2 94.15(17), N4 – C24 – N5 117.0(4).
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**Table 2.5. Crystallographic data for 9, 10 and 11.**
2.2.h. Reaction of $\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{NHA}r^{3,5-\text{Me}})_2$ (2) with RNC to give carbodiimides

While no reaction between $\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{NHA}r^{3,5-\text{Me}})_2$ (2) and \textsuperscript{1}BuNC takes place in toluene at RT after 24 h, stoichiometric reactions at 80 °C in toluene between $\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{NHA}r^{3,5-\text{Me}})_2$ (2) and \textsuperscript{1}BuNC or ArNC (Ar = \textsuperscript{2,6-Me}Ar) deliver the carbodiimides $^{3,5-\text{Me}_2}\text{ArN}C=\text{NR}$ (R = \textsuperscript{1}Bu or \textsuperscript{2,6-Me}Ar), in 92% and 47% yield, respectively (Scheme 2.21).

**Scheme 2.21.** Stoichiometric carbodiimide formation via Ni(II) amide 2.

Intrigued by these stoichiometric transformations, we attempted a catalytic protocol with 1 equiv. \textsuperscript{1}BuOObu\textsuperscript{1}, 1 equiv. $^{3,5-\text{Me}}\text{ArNH}_2$, and 1.2 equiv. RNC (R = \textsuperscript{1}Bu or \textsuperscript{2,6-Me}Ar) with a 10 mol % catalyst loading of $[\text{Me}_3\text{NN}]\text{Ni}(2\text{-picoline})$ at 80 °C for 24 h in toluene. As monitored by \textsuperscript{1}H NMR spectra, we observe carbodiimide $^{3,5-\text{Me}_2}\text{ArN}C=\text{NR}$ yields of 18% (R = \textsuperscript{1}Bu) and 46% (R = \textsuperscript{2,6-Me}Ar). Use of the bulkier amine MesNH\textsubscript{2} (Mes = \textsuperscript{2,4,6-Me$_3$C$_6$H$_2$}) under the same conditions with \textsuperscript{1}BuNC lowers carbodiimide MesN=C=N\textsuperscript{1}Bu yield to 5%.

To account for this catalysis, we suggest two possible mechanisms (Scheme 2.22). In mechanism I, a disproportionation of the nickel(II)-amide species $[\text{Ni}]_2(\mu\text{-NHR})$ to the corresponding Ni(III)-imide $[\text{Ni}]=\text{NR}$ and Ni(I)-amine adduct $[\text{Ni}](\text{NH}_2\text{R})$ occurs. As demonstrated in Chapter 1, the nickel(III)-imide may go on to react with
'BuNC to give the observed carbodiimide RN=C=NBu'. An alternative mechanism considers the direct reaction of isocyanides with the nickel(II)-amido species. First, the dinuclear nickel-amide [Ni]₂(μ-NHR)₂ breaks apart into a monomer [Ni](NHR)(CNBu₁) in the presence of 'BuNC. This is followed by insertion of CNBu₁ into the Ni-Namide bond to give a bound carbodiimide adduct similar to 12 isolated for morpholine. β-hydride elimination follows to excrete the carbodiimide and form a Ni-hydride that possibly reacts with 'BuOOBu₁ to form 'BuOH and the Ni alkoxide [Ni]-OBu₁ that reacts with amine to give the dinuclear nickel-amide. Since we were not able to trap any nitrene species as the phospha-imide (R₃P=NR) by heating {[Me₃NN]Ni}₂(μ-NHAr³,⁵-Me₂)₂ in the presence of PMe₃ or PPh₃, we suggest that the second mechanism may be operative. Moreover, we did isolate the nickel(II)-morpholinide insertion product [Me₃NN]Ni(C(N(CH₂)O(CH₂)₂)=N' Bu)('BuNC) (11) because this adduct has no β-hydrogen atom and therefore cannot react further.
2.2.i. Reaction of $[\text{Me}_3\text{NN}]\text{Ni(I)}(2\text{-picoline})$ with LiNHAd

In an attempt to synthesize the monomeric, three-coordinate Ni amido species $[\text{Me}_3\text{NN}]\text{NiNHAd}$ initially prepared via H-atom abstraction of 1,4-cyclohexadiene by $[\text{Me}_3\text{NN}]\text{Ni=NAAd}$,22 we examined a couple of different routes. For instance, $\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{OBu})_2$ (1) does not react with NH$_2$Ad to produce the any new observable products. The reaction mixture seems to remain as unreacted starting materials. As an alternate route we investigated the reaction of $[\text{Me}_3\text{NN}]\text{Ni(I)}(2\text{-picoline})$ with LiNHAd which allowed for the isolation of $[\text{Me}_3\text{NN}]\text{Ni(κ²-picolinide)}$ (12) in 18% yield as brown crystals from pentane at -35 °C (Scheme 2.23). In this reaction, LiNHAd serves as a sterically hindered base that formally deprotonates the benzylic CH$_3$-group of 2-picoline, possibly because NHAd is too bulky to easily coordinate to $[\text{Me}_3\text{NN}]\text{Ni(I)}(2\text{-picoline})$.

Scheme 2.23. Reaction of $[\text{Me}_3\text{NN}]\text{Ni(I)}(2\text{-picoline})$ with LiNHAd.

The X-ray structure of $[\text{Me}_3\text{NN}]\text{Ni(κ²-picolinide)}$ (12) (Figure 2.24) shows Ni-N$_{β\text{-dik}}$ distances of 1.9287(16) and 1.8764(16) Å. The Ni-CH$_2$ (1.959(2)Å) and Ni-N$_{\text{pic}}$ (1.9649(16) Å) distances are short, with a long Ni--C$_{\text{ipso}}$ contact of 2.444(2) Å. Thus, this picolinide species 12 compares relatively closely to benzamide species 4 which also exhibits κ²-bonding of the benzamide ligand.
Figure 2.24. X-ray crystal structure of [Me$_3$NNi(κ$^2$-2-picoline)] (12). All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ni-N1 1.9287(16), Ni-N2 1.8764(16), Ni-N3 1.9649(16), Ni-C29 1.959(2), Ni-C28 2.444(2), N1-Ni-N2 94.56(7), Ni-C29-C28 89.62(13).
$^1$H NMR analysis of 12 in benzene-$d_6$ (Figure 2.23) shows a rigid structure with closely spaced singlets for β-diketiminato N-aryl $o$-Me ($\delta$ 2.650 and 2.620 ppm), $p$-Me ($\delta$ 2.220 and 2.197 ppm) and $m$-Ar-H ($\delta$ 6.855 and 6.812 ppm) groups indicating the static, unsymmetric nature of the [Me$_3$NN]Ni coordination wedge due to the $\kappa^2$-binding the deprotonated 2-picoline ligand.

**Figure 2.23.** $^1$H NMR spectrum (400 MHz, benzene-$d_6$, RT) of [Me$_3$NN]Ni(κ$^2$-2-picolinide) (12).
2.2.j. Reaction of $[\text{Me}_3\text{NN}]\text{Ni}(\eta^2-\text{CH}_2(\text{C}(\text{O})\text{Ph})$ (5) with benzaldehyde

In an effort to use $[\text{Me}_3\text{NN}]\text{Ni}(\eta^3-\text{CH}_2(\text{C}(\text{O})\text{Ph})$ (5) as a precursor in C-C bond formation reactions, benzaldehyde was added to 5. Instead of the expected insertion product $[\text{Me}_3\text{NN}]\text{Ni}(\kappa^2-\text{OCH(Ph)CH}_2\text{C}(\text{O})\text{Ph})$ the delocalized $\beta$-diketonate $[\text{Me}_3\text{NN}]\text{Ni}(\kappa^2-\text{PhC(O)CHC(O)Ph})$ (13) formed (Scheme 2.24).

**Scheme 2.24.** Reaction of 5 with benzaldehyde.

The X-ray structure of 13 (Figure 2.25) shows almost symmetric Ni-N$_{\beta\text{-dik}}$ bonds 1.898(7) and 1.910(7) Å and more unsymmetric Ni-O bonds of 1.873(6) and 1.890(6) Å. The unsymmetric bond length coincides with C24-O1 of 1.292(11) Å and C26-O2 of 1.276(11) Å, while the C24-C25 and C25-C26 are 1.394(12) and 1.421(12) Å, respectively. $^1\text{H}$ NMR in benzene-$d_6$ at RT showed no identifiable peaks, therefore an Evans method was performed, which showed a $\mu_{\text{eff}} = 2.42$ B.M. Thus the structure in solution may be different than in the solid state since square planar species are typically diamagnetic. Therefore, a tetrahedral structure could dominate in solution.
Figure 2.25. X-ray crystal structure of [Me₃NNi(k²-PhC(O)CHC(O)Ph) (13). All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ni-N1 1.898(7), Ni-N2 1.910(7), Ni-O1 1.873(6), Ni-O2 1.890(6), C24-O1 1.292(11), C26-O2 1.276(11), C24-C25 1.394(12), C25-C26 1.421(12), N1-Ni-N2 94.2(3), Ni-O1-C24 128.3(6), Ni-O2-C26 127.6(6).
Table 2.6. Crystallographic data for 12 and 13.

<table>
<thead>
<tr>
<th>Compd.</th>
<th>12</th>
<th>13</th>
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<tbody>
<tr>
<td>formula</td>
<td>C_{29}H_{35}N_{3}Ni</td>
<td>C_{38}H_{40}N_{2}NiO_{2}</td>
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<td>Temp.(K)</td>
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<td>100(2)</td>
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<tr>
<td>crystal description</td>
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<td>block</td>
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<tr>
<td>crystal color</td>
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<tr>
<td>crystal size (mm$^3$)</td>
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<tr>
<td>system</td>
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</tr>
<tr>
<td>Space group</td>
<td>$P2_1/n$</td>
<td>triclinic</td>
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<tr>
<td>$a$ (Å)</td>
<td>13.6035(17)</td>
<td>12.0611(18)</td>
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<tr>
<td>$b$ (Å)</td>
<td>14.7530(19)</td>
<td>12.5847(19)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>14.1577(18)</td>
<td>13.765(2)</td>
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<tr>
<td>$\beta$ (deg)</td>
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<td>$\gamma$ (deg)</td>
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<td>0.0280</td>
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<td>$R_1$ ($I &gt; 2\sigma(I)$)</td>
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<tr>
<td>wR$_2$ (all data)</td>
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</tr>
<tr>
<td>Largest diff. peak and hole e$^-\cdot$Å$^3$</td>
<td>0.412 and -0.357</td>
<td>0.398 and -0.412</td>
</tr>
</tbody>
</table>
**Conclusions**

Mono- and dinuclear β-diketiminato nickel(II) amido species demonstrate a wide variety of binding modes and their Ni-N\text{amide} bonds are listed in Table 2.7. These species may be prepared via the straightforward acid-base chemistry involving the dinuclear nickel(II) alkoide \text{[[Me}_3\text{NN]}\text{Ni}]_2(\text{t}1-\text{OBu})_2 (Scheme 2.25). Square-planar dinuclear species \text{[[Me}_3\text{NN]}\text{Ni}]_2(\text{t}1-\text{NHR})_2 (R = \text{Ar}^{3,5}\text{-Me}_2, \text{CH}_2\text{CH}_2\text{Ph} (6), \text{H} (7)) reflect the high Lewis acidity of the nickel center as do the various bonding interactions that result in four-coordinate geometries in compounds 3, 4, and 5. Reaction of several of these species with the isocyanide \text{CNBu}^+ further illustrates the high affinity of three-coordinate nickel(II)-amides for an additional donor. Interestingly, \text{[[Me}_3\text{NN]}\text{Ni}]_2(\text{t}1-\text{OBu})_2 (1) when reacted first with morpholine undergoes insertion upon addition of

**Scheme 2.25.** Ni alkoide formation and its vast reactivity with amines to form Ni amides.
### Table 2.7. Ni-Namide and Ni-O bond distances in 1 - 11.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Ni-Namide or Ni-O Bond Distances (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>{[Me₃NN]Ni}₂(µ-OBu')₂</td>
<td>1.9600(19) and 1.9871(19)</td>
</tr>
<tr>
<td>{[Me₃NN]Ni}₂(µ-OCPhMe₂)(µ-OEt)</td>
<td>1.9228(19) – 1.994(2)</td>
</tr>
<tr>
<td>{[Me₃NN]Ni}₂(µ-NHar₃,5-Me₂)</td>
<td>1.923(2) and 1.955(2)</td>
</tr>
<tr>
<td>[Me₃NN]Ni(NHar₂,4,6-CI)</td>
<td>1.8796(15)</td>
</tr>
<tr>
<td>[Me₃NN]Ni(κ²-NHC(O)Ph)</td>
<td>1.942(8)</td>
</tr>
<tr>
<td>[Me₃NN]Ni(η¹-CH₂C(O)Ph)</td>
<td>Ni-C₇H₂ 2.0545(18)</td>
</tr>
<tr>
<td>{[Me₃NN]Ni}₂(µ-NH(CH₂)₂Ph)</td>
<td>1.9144(16) and 1.9192(16)</td>
</tr>
<tr>
<td>{[Me₃NN]Ni}₂(µ-NH₂)</td>
<td>1.899(2) and 1.901(2)</td>
</tr>
<tr>
<td>{[Me₃NN]Ni}₂(µ-OH)</td>
<td>1.8767(17) and 1.8856(17)</td>
</tr>
<tr>
<td>[Me₃NN]Ni(NHar₂,4,6-CI)(tBuNC)</td>
<td>1.9109(19)</td>
</tr>
<tr>
<td>[Me₃NN]Ni(NHC(O)Ph)(tBuNC)</td>
<td>1.8913(13)</td>
</tr>
</tbody>
</table>

'tBuNC to form a new N-C bond in 11 (Scheme 2.26). This insertion behavior motivated the examination of stoichiometric carbodiimide formation from {[Me₃NN]Ni}₂(µ-NHar₃,5-Me₂) (2) as well as a catalytic protocol involving primary amines H₂NR’ and isocyanides CNR with 'BuOOBu⁺ as oxidant under catalysis by [Me₃NN]Ni(2-picoline).
Scheme 2.26. Ni(II) amides reactivity with \(^1\text{BuNC}\).

\[
\begin{align*}
\text{[Me}_2\text{NN]}\text{Ni}(\text{NHC}^2\text{Ph}) + 4 \text{BuNC} & \rightarrow \text{[Ni]} \text{NHC}^2\text{Ph} + 4 \text{BuNC} \\
\text{[Me}_2\text{NN]}\text{Ni}(\text{NHC}^2\text{Ph}) + \text{BuNC} & \rightarrow \text{[Ni]} \text{NHC}^2\text{Ph} + \text{BuNC} \\
\text{[Me}_2\text{NN]}\text{Ni}(\text{NNMe}_3) + 4 \text{BuNC} & \rightarrow \text{[Ni]} \text{NNMe}_3 + 4 \text{BuNC}
\end{align*}
\]

Experimental

General Experimental Details

All experiments were carried out in a dry nitrogen atmosphere using an MBraun glovebox and/or standard Schlenk techniques. 4A molecular sieves were activated in vacuo at 180 °C for 24 h. Dry benzene was purchased from Aldrich and was stored over activated 4A molecular sieves. Pentane, diethyl ether and tetrahydrofuran (THF) were first sparged with nitrogen and then dried by passage through activated alumina columns. Pentane was first washed with conc. H\text{NO}_3 / H_2\text{SO}_4 to remove olefins, stored over CaCl\text{2} prior to passage through alumina columns. Benzene, toluene, and ethylbenzene were purchased anhydrous and stored over 4A molecular sieves. All solvents were tested before use with a drop of sodium benzophenone ketyl in THF.
solution. All deuterated solvents were sparged with nitrogen, dried over activated 4A molecular sieves and stored under nitrogen. Celite was dried overnight at 200 °C under vacuum. [Me₃NN]Ni(2-picoline) was synthesized according to literature procedure. All other reagents were obtained commercially unless otherwise noted.

¹H and ¹³C{¹H} NMR spectra were recorded on a Varian 400 MHz spectrometer (400 and 100.47 MHz respectively). All NMR spectra were recorded at room temperature unless otherwise noted and were indirectly referenced to residual solvent signals or TMS as internal standards. UV-Vis spectra were measured on a Varian Cary 50 or 100 spectrophotometer, using cuvettes with screw-cap tops of Teflon stopcocks. GC-MS spectra were recorded on a Varian Saturn 3900 and elemental analyses were performed on a Perkin-Elmer PE2400 microanalyzer at Georgetown. IR measurements were performed on Perkin Elmer Spectrum One FT-IR Spectrometer.

2.3.a. Synthesis of Ni complexes

{[Me₃NN]Ni}₂(µ-OBu')₂ (1). To a chilled solution of [Me₃NN]Ni(2-picoline) (0.500g, 1.03 mmol) in Et₂O was added 10 equiv. di-tert-butylperoxide (1.50 g, 10.3 mmol) previously chilled to -35 °C. The reaction mixture was allowed to stir at RT for 3 h. Throughout this time the color changed from a homogenous red solution to a dark brown solution with green precipitate. The reaction mixture was allowed to settle and the green solid was isolated via filtration and washed with cold pentane to afford a green solid in 82% yield (393 mg; 0.422 mmol). To prepare crystals suitable for single crystal X-ray, [Me₃NN]Ni(2-picoline) was dissolved in 3 mL of benzene inside a small
4 mL vial. This vial was placed inside a larger vial which was filled with 2 mL of di-
tert-butylperoxide. The outer vial was capped tightly and slow evaporation of di-tert-
butylperoxide into the [Me₃NN]Ni(2-picoline) benzene solution to give green crystals
of 1. ¹H NMR (benzene-d₈, RT, 400 MHz) δ 27.200, 25.125, 6.643, 2.975, 2.591, 1.249;
UV-vis (benzene, RT) λ_max = 566 and 642 nm (ε not determined due to insolubility);
Anal. Calcd for C₅₄H₇₆N₄Ni₂O₂: C, 69.70; H, 8.23; N, 6.02. Found: C, 69.51; H, 8.36;
N, 6.02.

[{Me₃NN}Ni(µ-OCumyl)(µ-OEt)]. To a chilled solution of [Me₃NN]Ni(2-picoline)
(0.100 g, 0.206 mmol) in 5 mL of Et₂O was added a chilled solution of di-
cumylperoxide (0.028 g, 0.103 mmol). The reaction mixture was allowed to stir
overnight at RT. Afterwards, all volatiles were removed in vacuo and the remaining
residue was taken up in pentane and filtered through Celite. The brown solution was
concentrated and crystallized from pentane at -35 °C to afford green crystals in 55%
yield (0.055 g, 0.0570 mmol) suitable for single crystal X-ray.

[{Me₃NN}Ni]₂(µ-NHAr₃,5-Me₂)₂ (2). To a chilled solution of [{Me₃NN}Ni]₂(µ-OBu')₂
(0.052 g, 0.0559 mmol) in 5 mL of toluene was added a chilled solution of 3,5-
dimethylaniline (0.013 g, 0.107 mmol) in 3 mL of toluene. The reaction mixture was
allowed to stir at RT for 90 min during which time a color change from green to dark
purple was observed. All volatiles were removed in vacuo to yield a dark maroon solid.
The crude solid was taken up in 15 mL pentane and filtered through Celite.
Concentration and cooling to -35 °C afforded red crystals suitable for single crystal X-ray diffraction in 39% yield (0.023 g; 0.0219 mmol). $^1$H NMR (C$_6$D$_6$, 400 MHz) $\delta$ 8.01 (s, 4, Ar-H), 6.91 (s, 2, Ar-H), 6.88 (s, 4, Ar-H), 6.46 (s, 4, Ar-H), 4.52 (s, 2, backbone C-H), 3.19 (s, 12, Me-H), 2.70 (s, 2, N-H), 2.59 (s, 12, Me-H), 2.33 (s, 12, Me-H), 1.28 (s, 12, backbone Me-H), 1.10 (s, 12, backbone Me-H); $^1$H NMR (C$_6$D$_6$): $\delta$ 158.96, 152.10, 145.77, 136.35, 135.46, 133.89, 133.18, 129.99, 129.74, 126.78, 123.84, 110.79, 99.98, 66.29, 23.63, 21.65, 20.62, 18.77, 15.86; $\nu_{NH} = 3434$ cm$^{-1}$; Anal. Calcd for C$_{62}$H$_{78}$N$_6$Ni$_2$: C, 72.67; H, 7.67; N, 8.20. Found: C, 72.31; H, 7.70; N, 8.25.

$[\text{Me}_3\text{NN}]\text{Ni(NAr}^{2,4,6-\text{Cl}}])$ (3). To a chilled solution of $\{[\text{Me}_3\text{NN}]\text{Ni}_2(\mu-\text{OBu})_2$ (0.140 g, 0.150 mmol) in 10 mL of Et$_2$O was added 2,4,6-trichloroaniline (0.059 g, 0.301 mmol) in 2 mL of Et$_2$O. The reaction mixture was stirred for only 5 min at RT during which an immediate color change from green to blue occurred. All volatiles were removed in vacuo. The remaining solid was taken up in Et$_2$O and passed through Celite and then concentrated to afford blue crystals suitable for single crystal X-ray crystallography in 43% yield (0.075 g; 0.128 mmol). $^1$H NMR (C$_6$D$_6$, 400 MHz) $\delta$ 29.64 (s, 6, p-Me-H), 28.57 (s, 12, o-Me-H), 28.30 (s, 4, m-Ar-H), -46.81 (s, 6, backbone Me-H); $\nu_{NH} = 3381$ cm$^{-1}$; $\mu_{eff} = 2.40$ B.M.; UV-Vis (Et$_2$O, 25 °C) $\lambda_{max} = 598$ nm (4870 M$^{-1}$ cm$^{-1}$); Anal. Calcd for C$_{29}$H$_{32}$Cl$_3$N$_3$Ni: C, 59.27; H, 5.49; N, 7.15. Found: C, 59.24; H, 5.71; N, 7.08.
Figure 2.26. Beer’s law plot of 3 in Et₂O at RT ($\lambda_{\text{max}} = 598$ nm ($\varepsilon = 4870$ M$^{-1}$ cm$^{-1}$)).

$[\text{Me}_3\text{NN}]\text{Ni}(\kappa^2\text{-NHC(O)Ph})$ (4). To a chilled solution of $\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu\text{-OBu})_2$ (0.120 g, 0.129 mmol) in 10 mL of Et₂O was added benzamide (0.031 g, 0.258 mmol) in 2 mL Et₂O. An immediate color change from green to brown occurred and the reaction mixture was stirred for 24 h at RT. After all volatiles were removed in vacuo, the remaining solid was taken up in Et₂O and passed through Celite and then concentrated to afford brown crystals suitable for single crystal X-ray crystallography in 66% yield (0.087 g; 0.170 mmol). $^1$H NMR (benzene-$d_6$, RT, 400 MHz) δ 7.10 (s, 4, m-Ar-H), 6.84 (d, 2, o-Ph-H), 6.76 (t, 1, p-Ph-H), 6.48 (t, 2, m-Ph-H), 4.90 (s, 1, backbone C-H), 2.92 (br s, 1, N-H), 2.72 (s, 12, o-Me-H), 2.09 (s, 6, p-Me-H), 1.40 (s, 6, backbone-Me-H); $^1$H NMR (benzene-$d_6$, RT, 400 MHz): δ 158.50, 146.18, 134.03,
133.43, 131.61, 129.04, 126.14, 99.24, 21.89, 21.50, 19.68; ν\textsubscript{NH} = 3184 cm\textsuperscript{-1}; Anal. Calcd for C\textsubscript{31}H\textsubscript{37}N\textsubscript{3}NiO: C, 70.33; H, 6.89; N, 8.20. Found: C, 70.38; H, 7.28; N, 8.33.

VT \textsuperscript{1}H NMR (toluene-\textit{d}\textsubscript{8}, 400 MHz): T\textsubscript{c} = -47 °C for backbone Me signals at δ 2.189 and 2.090 ppm (measured at -70 °C) to give ΔG\textsuperscript{‡}(226K) = 11.1(3) kcal/ mol.

[Me\textsubscript{3}NN]Ni(\eta\textsuperscript{3}-CH\textsubscript{2}COPh) (5). To a chilled solution of \{[Me\textsubscript{3}NN]Ni\}\textsubscript{2}(\mu-OBu')\textsubscript{2} (0.054 g, 0.0580 mmol) in 10 mL toluene was added a solution of acetophenone (0.014 g, 0.116 mmol) in 2 mL toluene. The reaction mixture was stirred for 90 min during which time a color change from green to a yellowish brown occurred. The volatiles were removed \textit{in vacuo} to yield a yellowish brown solid. The solid was crystallized from pentane to yield yellowish brown crystals in 60% yield (0.063 g, 0.123 mmol) suitable for single crystal X-ray diffraction. \textsuperscript{1}H NMR (toluene-\textit{d}\textsubscript{8}, RT, 400 MHz) δ 7.469 (m, 2H, Ar-H), 7.097 (m, 4H, Ar-H), 6.784 (br, 3H, Ar-H), 4.930 (s, 1H, C-H backbone), 2.842 (s, 2H, CH\textsubscript{2}), 2.366 (br, 12H, o-Ar-CH\textsubscript{3}), 2.177 (s, 6H, p-Ar-CH\textsubscript{3}), 1.446 (br, 6H, CH\textsubscript{3} backbone); \{\textsuperscript{1}H\} NMR (benzene-\textit{d}\textsubscript{6}; RT, 400 MHz): δ 164.25, 131.85, 129.26, 128.83, 128.39, 128.00, 105.65, 98.57, 54.76, 34.86, 22.05, 21.38, 14.65. Anal. Calcd for C\textsubscript{31}H\textsubscript{36}N\textsubscript{2}NiO: C, 72.82; H, 7.10; N, 5.48. Found: C, 73.16; H, 7.47; N, 5.13. VT NMR (toluene-\textit{d}\textsubscript{8}, 400 MHz): T\textsubscript{c} = 18°C for backbone Me signals at δ 1.614 and 1.324 ppm (measured at -70 °C) to give ΔG\textsuperscript{‡}(291K) = 13.8(4) kcal/ mol.

{[Me\textsubscript{3}NN]Ni\textsubscript{2}(\mu-NHCH\textsubscript{2}CH\textsubscript{2}Ph)\textsubscript{2} (6). To a chilled solution of {[Me\textsubscript{3}NN]Ni\textsubscript{2}(\mu-OBu')\textsubscript{2} (0.109 g, 0.117 mmol) in 10 mL of Et\textsubscript{2}O was added phenethylamine (30 µL,
0.028 mg; 0.234 mmol) in 2 mL Et₂O. The reaction mixture was stirred for 1 h at RT during which time a change from a green suspension to brown suspension with brown solid occurred. All volatiles were removed in vacuo. The remaining solid was taken up in Et₂O, the resulting solution passed through Celite and then concentrated and cooled to -35 °C to afford red crystals suitable for single crystal X-ray crystallography in 60% yield (72 mg; 0.0703 mmol). {¹H} NMR (C₆D₆, RT): δ 160.19, 159.61, 158.97, 148.31, 146.38, 141.50, 133.51, 132.63, 131.79, 129.93, 129.53, 126.27, 99.60, 66.33, 50.08, 39.42, 24.25, 23.48, 22.27, 21.06, 19.69, 19.37, 19.08, 16.00; v_NH = 3289 cm⁻¹. Anal. Calcd for C₆₂H₇₈N₆Ni₂: C, 72.67; H, 7.67; N, 8.20. Found: C, 72.35; H, 7.28; N, 7.82.

{[Me₃NN]Ni}(µ-NH₂)₂ (7). {[Me₃NN]Ni}(µ-OBu')₂ (1) (0.050 g, 0.0537 mmol) was dissolved in 5 mL THF. The solution was passed through Celite into a 4 mL vial. This small vial was placed into a larger 22 mL vial that was filled with 5 mL of a 0.5 M NH₃ solution in dioxane. The large vial was capped and crystals formed via vapor diffusion at RT over 5 days. Orange crystals formed in 96% yield (0.042 g, 0.0514 mmol) suitable for single crystal X-ray. Anal. Calcd for C₄₆H₆₅N₇Ni₂ (for {[Me₃NN]Ni}(µ-NH₂)₂(NH₃)): C, 66.29; H, 7.85; N, 11.76. Anal. Calcd for C₄₆H₆₂N₆Ni₂ (for {[Me₃NN]Ni}(µ-NH₂)₂): C, 66.29; H, 7.85; N, 11.76. Found: C, 67.47; H, 7.92; N, 10.94 (not a full equivalent of NH₃). X-ray shows one equivalent of NH₃ per molecule of 7.
{$[\text{Me}_3\text{NN}]\text{Ni}_2(\mu-\text{OH})_2$ (8). Inside a 8 mL vial was prepared a solution of $[\text{Me}_3\text{NN}]\text{Ni}(2\text{-picoline})^{28}$ (0.300 g, 0.618 mmol) in 6 mL of toluene. The vial was sealed with a plastic cap that was punctured a syringe needle to allow slow diffusion of air into the solution. Over several days the red solution turned green/brown forming green/brown crystals in 96 % yield (0.243 g, 0.297 mmol) suitable for single crystal X-ray. UV-vis (benzene, RT) $\lambda_{\text{max}}$ = 636 nm (e not determined due to insolubility); IR (KBr plate) $\nu_{\text{OH}}$ = 3264 cm$^{-1}$; Anal. Calcd. for C$_{46}$H$_{60}$N$_4$Ni$_2$O$_2$: C, 67.51; H, 7.39; N, 6.85. Found: C, 67.62; H, 7.7.41; N, 6.80.

$[\text{Me}_3\text{NN}]\text{Ni(NHAr}^{2,4,6-\text{Cl}}\text{)(CNBu}^t\text{)}$ (9). To a chilled solution of $[\text{Me}_3\text{NN}]\text{Ni(NHAr}^{2,4,6-\text{Cl}}\text{)}$ (3) (0.145 g, 0.247 mmol) in 5 mL Et$_2$O was added tert-butylisocyanide (15 µL, 0.136 mmol). An immediate color change from blue to purple was observed. The reaction mixture was allowed to stir at RT for 10 min. Then all volatiles were removed in vacuo and the remaining purple solid was taken back up in 10 mL Et$_2$O and passed through Celite. This solution was concentrated to afford purple crystals at -35 ºC in 97% yield (91 mg; 0.135 mmol) suitable for single crystal X-ray. $^1$H NMR (C$_6$D$_6$, 400 MHz) $\delta$ 6.969 (s, 2H, Ar-H), 6.711 (s, 3H, Ar-H), 4.984 (s, 1H, CH backbone), 2.566 (s, 9H, $\omega$-Ar-CH$_3$), 2.115 (s, 6H, $p$-Ar-CH$_3$), 1.490 (s, 6H, CH$_3$ backbone), 0.339 (s, 9H, CH$_3$ for $^t$Bu), 0.079 (s, 1H, NH); $^{13}$C {($^1$H} NMR (C$_6$D$_6$): $\delta$ 150.47, 134.13, 134.05, 132.91, 129.17, 127.95, 113.30, 98.29, 28.84, 21.45, 19.53.; UV-Vis (Et$_2$O, 25ºC) $\lambda_{\text{max}}$ = 555 nm (2100 cm$^{-1}$M$^{-1}$); IR: $\nu_{\text{CN}}$ = 2194 cm$^{-1}$ Anal. Calcd for C$_{34}$H$_{42}$Cl$_3$N$_4$Ni: C, 60.79; H, 6.30; N, 8.34. Found: C, 60.59; H, 6.17; N, 8.27.
Figure 2.27. Beer’s law plot of 9 in Et₂O at RT ($\lambda_{\text{max}} = 555$ nm ($\varepsilon = 2100$ M⁻¹ cm⁻¹)).

$[\text{Me}_3\text{NN}]\text{Ni(NHC(O)Ph)(CNBu)}$ (10). A cold (-35 °C) solution of $[\text{Me}_3\text{NN}]\text{Ni}(\kappa^2-$NHCOPh) (6) (0.106 g, 0.207 mmol) was prepared in 5 mL Et₂O. To this solution was added tert-butylisocyanide (26 µL, 0.228 mmol). The solution changed immediately from brown to reddish orange. The mixture was allowed to stir at RT for 3 h. All volatiles were removed in vacuo and the remaining orange solid was taken up in Et₂O and the resulting solution was passed through Celite. Concentrating the Et₂O solution afforded orange crystals in 59% yield (0.072 g, 0.121 mmol). $^1$H NMR (benzene-$d_6$, 400 MHz) δ 7.775 (d, 1H, Ar-H), 7.411 – 7.394 (d, 2H, Ar-H), 7.057 (m, 3H, Ar-H), 6.693 (s, 3H, Ar-H), 5.025 (s, 1H, CH backbone), 2.570 (s, 12H, o-Ar-CH₃), 2.101 (s, 6H, p-Ar-CH₃), 1.479 (s, 6H, CH₃ backbone), 0.712 (s, 9H, CH₃ for tBu); $^1$H NMR (C₆D₆):
δ 171.67, 159.73, 139.69, 133.15, 131.79, 129.39, 127.90, 127.45, 98.52, 29.24, 21.15, 19.68; UV-Vis (Et₂O, 25°C) 503 nm (128 cm⁻¹M⁻¹); IR: ν_{CN} = 2207 cm⁻¹; Anal. Calcd for C₃₅H₄₄N₄NiO: C, 70.60; H, 7.45; N, 9.41. Found: C, 70.62; H, 7.59; N, 9.58.

Figure 2.28. Beer’s law plot of [Me₃NN]Ni(NH(C(O)Ph)(CNBuᵗ) (10) in Et₂O at RT (λ = 503 nm (ε = 128 M⁻¹cm⁻¹)).

[Me₃NN]Ni(C(N(CH₂)O(CH₂)₂)=NᵗBu)(CNBuᵗ) (11). In a one-pot synthesis of [Me₃NN]Ni₂(µ-OBuᵗ)₂ (1) (0.201 g, 0.216 mmol) was suspended in 15 mL toluene. Morpholine (0.075 g, 0.865 mmol) was added and the reaction mixture was allowed to stir for 1 h. All volatiles were removed in vacuo. The remaining solid was taken up in 10 mL Et₂O and tert-butylisocyanide (0.072 g, 0.865 mmol) was added. The reaction mixture was allowed to stir at RT overnight during which it became more orange in appearance. All volatiles were removed in vacuo and the remaining solid was taken up
in Et₂O and the resulting solution was passed through Celite. The solution was concentrated and layered with pentane to afford orange crystals in 75% yield (0.322 g, 0.576 mmol) at -35 °C. ¹H NMR (C₆D₆, RT, 400 MHz) δ 6.862-6.828 (overlapping s, 2H, m-Ar-H), 6.730 (s, 2H, m-Ar-H), 5.047 (s, 1H, backbone CH), 2.576 – 2.517 (d, 5H, Morph-CH₂), 2.393-2.269 (d, 5H, Morph-CH₂), 2.236 (s, 3H, Morph-CH₂), 2.177 (s overlapping, 12H, o-Me-H), 2.146 (s overlapping, 3H, Morph-CH₂), 1.571-1.533 (d, 6H, p-Me-H), 1.102 (s, 6H, backbone CH₃), 0.644 (s, 9H, t-Bu); ¹¹H¹ NMR (C₆D₆): δ 162.23, 161.29, 159.56, 150.56, 150.40, 135.03, 133.38, 132.51, 131.85, 129.78, 129.46, 128.97, 99.59, 67.57, 55.20, 34.65, 31.44, 29.57, 24.49, 23.02, 21.80, 21.20, 21.06, 20.73, 20.31, 20.09; Anal. Calcd for C₃₇H₅₅N₅NiO: C, 68.95; H, 8.60; N, 10.87. Found: C, 68.60; H, 8.57; N, 10.60.

[Me₃NN]Ni(κ²-2-picolinide) (12). To a chilled suspension of [Me₃NN]Ni(I)(2-picoline) (0.541 g, 0.884 mmol) in 8 mL Et₂O was added a chilled suspension of LiNHAd (0.153 g, 0.972 mmol) (previously prepared via deprotonation of H₂NAd with BuLi in pentane) in 4 mL Et₂O. The reaction mixture was allowed to stir for 3 h at RT during which time it turned from green to brown. All volatiles were removed in vacuo. The residue was taken up in pentane and the resulting solution was passed through Celite. The brown solution was concentrated and allowed to crystallize at -35 °C to afford brown crystals in 18% yield (101 mg; 0.159 mmol). ¹H NMR (C₆D₆, 400 MHz) δ 6.855 (d, 4H, Ar-H), 6.542 (t, 1H, 2-picoline-Ar-H), 5.928 (t, 1H, 2-picoline-Ar-H), 5.828 (d, 1H, 2-picoline-Ar-H), 5.333 (d, 1H, 2-picoline-Ar-H), 5.062 (s, 1H, backbone CH), 2.650
(overlapping s, 12H, o-Ar-H), 2.220 (overlapping s, 6H, p-Ar-H), 1.535 (s, 6H, backbone CH$_3$), 0.341 (s, 3H, 2-picoline CH$_3$); $^1$H NMR (C$_6$D$_6$): $\delta$ 173.57, 159.10, 158.97, 150.79, 144.64, 136.81, 129.05, 121.03, 119.06, 97.95, 23.73, 23.06, 21.33, 19.61, 19.44, 2.48; Anal. Calcd for C$_{29}$H$_{35}$N$_3$Ni: C, 71.92; H, 7.28; N, 8.68; Found C, 71.77; H, 7.65; N, 8.50.

[Me$_3$NN]Ni(PhC(O)CHC(O)Ph) (13). To a chilled solution of [Me$_3$NN]Ni(µ$^3$-CH$_2$C(O)Ph) (5) (0.215 g, 0.420 mmol) in 8 mL Et$_2$O was added benzaldehyde (42 µL, 0.045g, 0.420 mmol). The reaction mixture was allowed to stir for 1 h at RT. An immediate color change from yellow brown to reddish brown occurred. All volatiles were removed in vacuo, the residue was taken up in Et$_2$O and the resulting solution passed through Celite, concentrated and cooled to -35 °C to produce reddish brown crystals in 63% yield (0.163 g, 0.264 mmol) suitable for single crystal X-ray. Anal. Calcd for C$_{38}$H$_{41}$N$_2$NiO$_2$: C, 74.04; H, 6.70; N, 4.54; Found C, 73.73; H, 7.05; N, 4.18.

$^1$H NMR in benzene-$d_6$ showed no identifiable peaks. $\mu_{\text{eff}}$ (benzene-$d_6$, RT) = 2.42 B.M. (Evans method).

2.3.b. Stoichiometric and catalytic reactions to form carbodiimides

Stoichiometric formation of $^1$BuN=C=NAr$_{3.5}$Me from $^1$BuNC and [{[Me$_3$NN]Ni}$_2$(µ-NHAr$_{3.5}$Me)$_2$] (2). A chilled of tert-butylisocyanide (0.040 g, 0.482 mmol) 2 mL toluene to a chilled solution of 40 mg (0.0391 mmol) of [{[Me$_3$NN]Ni}$_2$(µ-NHAr$_{3.5}$Me)$_2$] (2) (0.040 g, 0.0391 mmol) in 5 mL toluene inside a pressure vessel. The pressure vessel
was sealed with a Teflon screw cap and heated to 80 °C for 30 min. During the course of the heating the reaction mixture changed from reddish to orange yellow. The desired carbodiimide product was identified by GC/MS analysis. 

$^1$H NMR (benzene-$d_6$) analysis indicated the yield of the carbodiimide to be 92% using naphthalene as an internal standard.

**Catalytic formation of $^1$BuN=C=NAr$_{2,4,6}$-$^1$Me from $^1$BuNC, H$_2$NAr$_{2,4,6}$Me$_3$, and $^1$BuOOBu*. A chilled solution of [Me$_3$NN]Ni(2-picoline) (0.054 g, 0.111 mmol, 10 mol %) in 5 mL toluene was added to a chilled solution of 2,4,6-trimethylaniline (0.150 g, 1.11 mmol), di-tert-butylperoxide (0.195 g, 1.33 mmol), tert-butylisocyanide (0.111 g, 1.33 mmol) and naphthalene (0.142 g, 1.11 mmol; standard) in 10 mL toluene. The reddish reaction mixture was heated to 80 °C in a pressure vessel under nitrogen for 24 h. The reaction mixture was then passed through alumina to remove the catalyst. GC/MS showed the desired carbodiimide. $^1$H NMR (benzene-$d_6$) analysis shows 5% yield compared to the naphthalene standard.

**Catalytic formation of $^1$BuN=C=NAr$_{3,5}$-$^1$Me from $^1$BuNC, H$_2$NAr$_{3,5}$Me$_2$, and $^1$BuOOBu*. A chilled solution of [Me$_3$NN]Ni(2-picoline) (0.060 g, 0.124 mmol, 10 mol %) in 5 mL toluene was added to a chilled solution of 3,5-dimethylaniline (0.150 g, 1.24 mmol), di-tert-butylperoxide (0.217 g, 1.49 mmol), of tert-butylisocyanide (0.123 g (1.49 mmol) and naphthalene (0.157 g, 1.24 mmol; standard) in 10 mL toluene. The reddish reaction mixture was heated to 80 °C in a sealed pressure vessel under
nitrogen for 24 h. Afterwards under nitrogen the reaction mixture was passed through alumina to remove the catalyst. GC/MS showed the desired carbodiimide (\(^3\)BuNCN\(\text{Ar}_{3,5}^\text{-Me}\)). \(^1\)H NMR (400 MHz, benzene-\(d_6\), RT) shows 18% yield as compared to the internal naphthalene standard.

**Stoichiometric formation of \(^3,5\)-Me\(^2\)ArNCN\(\text{Ar}_{2,6}^\text{-Me2}\).** Inside a pressure vessel, a solution consisting of \([[\text{Me}_3\text{NN}]\text{Ni}]_2(\mu-\text{Ar}_{3,5}^\text{-Me}^2)_2\) (0.66 g, 0.0643 mmol) in 3 mL toluene and 2,6-dimethylphenyl isocyanide (0.017 g, 0.129 mmol) in 2 mL toluene were added together. The pressure vessel was sealed and heated to 100 °C for 30 min. The reaction mixture was then allowed to cool, exposed to air, and finally passed through Celite. GC/MS showed the desired carbodiimide. \(^1\)H NMR (benzene-\(d_6\)) analysis shows 47% yield carbodiimide yield against the anthracene internal standard.

**Catalytic formation of \(^3,5\)-Me\(^2\)ArNCN\(\text{Ar}_{2,6}^\text{-Me2}\).** A solution of 3,5-dimethylaniline (0.150 g, 154 \(\mu\)L, 1.24 mmol), di-\text{tert}-butylperoxide (217 mg, 271\(\mu\)L; 1.47 mmol) and diphenylhydrazine (0.162 g, 0.890 mmol) in 5 mL toluene was added to (10 mol %) of [\text{Me}_3\text{NN}]\text{Ni}(2-pic) (0.060 g, 0.124 mmol). The pressure vessel was sealed and heated to 80 °C for 24 h. After 24 h the reaction mixture was allowed to cool and then passed through Celite. GC/MS showed the desired carbodiimide. \(^1\)H NMR (benzene-\(d_6\)) analysis indicated a 46% yield of the carbodiimide against the naphthalene internal standard.
References


Chapter 3

Catalytic C-H Amination with Unactivated Amines via Copper(II) Amides

Abstract

Catalytic C-H amination offers the promise to directly transform ubiquitous C-H bonds into valuable C-N bonds without a pre-functionalization step. A shortcoming of current methods, however, is the requirement that participating amines bear strongly electron-withdrawing groups that would later need to be deprotected and refunctionalized. Such extra steps detract from the atom economic promise of C-H functionalization. We report herein a catalytic system is reported that is compatible with the unactivated amine H$_2$NAd (Ad = 1-adamantyl) as well as others such as cyclohexylamine, phenylamine and morpholine. In the case of 1-adamantylamine, the key intermediate is a three-coordinate, β-diketiminato copper(II) amide [Cl$_2$NN]Cu-NHAd that engages in efficient C-H amination with benzylic substrates. Kinetic and theoretical analysis reveals rate-limiting C-H abstraction by the copper(II) amide to provide a benzylic radical, which is rapidly trapped by an additional equivalent of [Cl$_2$NN]Cu-NHAd to give the C-H functionalized amine product. The active copper-amide intermediate may be generated under catalytic conditions by use of 'BuOOBu' and the amine H$_2$NAd, allowing for catalytic C-H amination of benzylic substrates with this unactivated amine. Good to excellent yields of C-H amination with H$_2$NAd, H$_2$NCy, H$_2$NCH$_2$CH$_2$Ph, and
morpholine may be obtained through this protocol with substrates possessing \( sp^3 \)-hybridized C-H bonds such as indane, ethylbenzene and even cyclohexane.

**Introduction**

Catalytic C-H amination is an attractive strategy to prepare C-N bonds without the need for a pre-functionalized site.\(^2\)-\(^4\) This approach offers substantial opportunities to streamline chemical syntheses by decreasing the number of functional group manipulations such as “hydroxyl to amine”.\(^5\) An appealing feature of this and related catalytic C-H functionalization reactions is that protection steps may not be required for these transformations – the relative inertness of the C-H bond insulates it from many traditional functional group modifications.\(^4,6\) The ability to directly affect the C-H to C-N transformation without the need to isolate, purify, and transform the corresponding oxidized precursors promises reduced cost, energy consumption, and environmental impact.

Some of the earliest C-H amination examples date back to the late 1960’s with work by Kwart and Kahn\(^7\), D. S. Breslow and Sloan\(^8\) as well as Turner et al\(^9\). Kwart and Kahn activated benzenesulfonyl azide via suspended copper powder in the presence of cyclohexene at 84 °C for 14 h with the remarkable formation of several products as shown in Scheme 3.1 a.\(^7\) D. S. Breslow and Sloan found that dichloramine-T and zinc powder in the presence of cyclohexane resulted in the amination of cyclohexane in 80% yield (Scheme 3.1 b).\(^8\) Turner et al. also used copper powder and chloramine-T to functionalize dimethylsulphoxide and 1,4-dioxane in 80 and 78% yield, respectively (Scheme 3.1 c).\(^9\) All of these reactions were believed go via a nitrene intermediate
[M]=NR that was responsible for the C-H amination.\textsuperscript{2,7-9}

\textbf{Scheme 3.1.} Early examples of C-H amination.

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\includegraphics[width=\textwidth]{Scheme_3.1.png}};
\end{tikzpicture}
\end{center}

\textbf{Scheme 3.2.} Early intra- and intermolecular C-H amination with Fe and Rh.

\textit{intra)molecular C-H activation}

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\includegraphics[width=\textwidth]{Scheme_3.2.png}};
\end{tikzpicture}
\end{center}

\textit{intermolecular C-H activation}

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\includegraphics[width=\textwidth]{Scheme_3.2_inter.png}};
\end{tikzpicture}
\end{center}

\begin{itemize}
  \item \textbf{Fe\textsuperscript{III}(porph)} or \textbf{Rh\textsuperscript{II}(OAc)\textsubscript{2}}
  \item \textbf{Phl} = NTs + R-H \rightarrow R-NHTs
  \item \textbf{R-H} = cyclohexane, adamantane and heptane
\end{itemize}
More widely recognized work by R. Breslow and Gellman on intramolecular C-H amination\textsuperscript{10,11} and Mansuy’s work on intermolecular\textsuperscript{12} C-H amination appeared in the 1980’s. Mansuy \textit{et al.} were able to aminate C-H substrates such as cyclohexane, adamantane and heptane in yields of 13 to 56%. Adamantane was selectively aminated to give 1-tosylaminoadamantane while heptane predominately formed 2-toslyaminohexane. These systems used benzenesulfonylimidoiodobenzene derivatives as nitrene precursors in the presence of iron(III) porphyrin or rhodium(II) acetate catalysts for C-H amination (Scheme 3.2).\textsuperscript{2,10-12}

3.1.a. \textit{Rh, Ru and Pd catalyst systems}

There are a growing number of C-H amination catalysts that allow for \textit{sp}\textsuperscript{3}-C-N bond formation compatible with multi-step syntheses of complex molecules.\textsuperscript{2,4,6,13} Typically catalyst systems are based on expensive Rh\textsuperscript{14-16}, Ru\textsuperscript{17,18} and Pd\textsuperscript{19,20} metals. These catalyst system have different mechanisms at work for their respective C-H bond functionalization (e.g. nitrene-based, allylic C-H activation/substitution and cross coupling).

3.1.b. \textit{C-H Amination via nitrene based Rh and Ru catalyst systems}

Du Bois and co-workers developed Rh\textsubscript{2}(esp)\textsubscript{2} (Rh\textsubscript{2}(esp)\textsubscript{2} = Rh\textsubscript{2}(\alpha,\alpha,\alpha’,\alpha’-tetramethyl-1,3-benzenedipropionate)\textsubscript{2}) for the amination of benzylic C-H bonds using electron poor sulfonamides (H\textsubscript{2}NSO\textsubscript{2}R; R = OCH\textsubscript{2}CCl\textsubscript{3}, OCH\textsubscript{2}\textsuperscript{t}Bu, OC\textsubscript{6}H\textsubscript{4}CH\textsubscript{3}, C\textsubscript{6}H\textsubscript{4}CH\textsubscript{3}) and the strong oxidant PhI(O\textsubscript{2}C\textsuperscript{t}Bu)\textsubscript{2}.\textsuperscript{14} Yields for this reaction at 2
mol % catalyst loading and 23 °C span range of yields of 5-80 % (Scheme 3.3.a). Amination proceeds selectively at benzylic C-H bonds and with retention of stereochemistry at the reacting C-H bond (Scheme 3.3.b). Using NHTces (Tces = SO₃CH₂CCl₃) as a nitrogen substrate allows for subsequent deprotection chemistry with Zn(Cu)/HCl to produce primary amines (Scheme 3.3.c). A proposed mechanism in this systems involves a Rh nitrene intermediate that is responsible for C-H amination ([Rh] = Rh₂.esp₂) (Scheme 3.3.d).
Huard and Lebel found that the similarly bulky Dirhodium species \( \text{Rh}_2(\text{tpa})_2 \) (\( \text{Rh}_2(\text{tpa})_2 = \text{Rh}_2(\text{triphenylacetate}) \)) catalyses inter- and intramolecular amination reactions of benzylic and aliphatic C-H bonds. These reactions employ carbamates as nitrogen sources in combination with \( \text{K}_2\text{CO}_3 \) as the oxidant at 25 °C for 6 – 16 h (Scheme 3.4). Deprotection of the Troc moiety can be achieved with Zn and AcOH followed by AcCl, MeOH, and heat (Scheme 3.4.d). The proposed mechanism in Scheme 3.5 features a dinuclear Rh nitrene as the active intermediate for C-H amination.\(^\text{16} \)
A family of cationic Ru$^{II}$pybox complexes acts as catalysts for intramolecular amination reaction of benzylic and allylic C-H bonds. These reactions are performed in an enantioselective fashion using PhI(O$_2$C$t$Bu)$_2$ as an oxidant along with strong electron withdrawing groups on the amine functionality and take place at RT over 1 day and require AgOTf and MgO as additives to deliver yields of 14 to 71 % with ee’s up to 99% (Scheme 4.4). The C-H functionalization is thought to proceed via cationic Ru nitrene intermediates (Scheme 3.6). $^{17}$
**Scheme 3.6.** Cationic Rh(II)pybox catalysts for intramolecular amination.

The following examples by Driver et al. show a [Rh₂(O₂CR)₄] (R = C₃F₇, C₇H₁₅) system along with an Ir system [(cod)Ir(OMe)]₂ that are capable of intramolecular C-H

**Scheme 3.7.** Intramolecular C-H amination via Rh and Ir catalysts.
amination of vinyl- and benzylic aryl C-H bonds using aryl organoazides. Both reactions are believed to involve metal nitrene intermediates via the lost of N₂ which also serve as the active intermediates for intramolecular C-H amination. The Rh systems requires a 5 mol% catalyst loading at 60 °C in toluene and achieves yields of up to 96%. The Ir systems requires lower catalyst loading of only 2 mol% at 25 °C with yields of up to 82% (Scheme 3.7).

3.1.c. Pd catalyzed allylic inter- and intramolecular amination

The combination of Pd(OAc)₂ with a bis-sulfoxide ligand is capable of aminating allylic C-H bonds favoring linear products of E configuration. The amine substrates require strong nitrogen-based electron withdrawing groups (N-C(O)OR) and several additives are required (e.g. 1,4-benzoquinone and N,N-diisopropylethylamine).

Scheme 3.8. Catalytic amination of allylic C-H bonds via an in-situ formed Pd catalyst.
The yields for the reactions at optimized conditions range from 55 – 89 % (Scheme 3.8). The linear product is formed via a formation an allylic Pd complex that undergoes nucleophilic attack.\textsuperscript{19}

A similar Pd system also performs allylic amination in a regio- and stereoselective fashion favoring linear over branched and E over Z isomers. These reactions are performed at a catalyst loading of 10 mol\% with O\textsubscript{2} as the oxidant. Other additives are requires such as maleic anhydride (MA), sodium acetate and molecular sieves which remove the water formed in this reaction. This protocol has the important advantage that it can be performed under aerobic conditions (Scheme 3.9).\textsuperscript{20}

Likely via a similar mechanism, related Pd-based catalysts perform intramolecular allylic C-H amination. Pd(OAc)\textsubscript{2} (10 mol\%) in combination with a bis-

**Scheme 3.9.** Pd catalyzed allylic amination to selectively form linear E-products.

\[
\begin{align*}
\text{R} & + \text{TsHN} & \xrightarrow{\text{Pd(OAc)}_2 (10 \text{ mol\%})} & \text{TsN} \\
\text{O} & & \text{OR} & \xrightarrow{\text{MA (40 mol\%)}} & \text{Ts} & \xrightarrow{\text{NaOAc (25 mol\%)}} & \text{E} > \text{Z} \\
\text{M. S., DMA, O}_2 & & & & & & 53 - 8% \text{ yield}
\end{align*}
\]

**Scheme 3.10.** Pd catalyzed intramolecular allylic C-H amination.

\[
\begin{align*}
\text{Ph} & \xrightarrow{\text{Pd(OAc)}_2 \text{ 10 mol\%}} \text{O} \\
\text{O} & \xrightarrow{\text{quinone (1.05 to 2 eq.)}} \text{NTs} & \text{THF, 45 \text{ \textdegree C, 72 h}}
\end{align*}
\]
sulfoxide ligand (1.05 or 2 equiv.) is capable of intramolecular allylic C-H amination in up to 86% yield in a diastereoselective fashion that favors the *anti* product (Scheme 3.10).\(^{23,24}\)

Another system using Pd(OAc)\(_2\) is capable of controlling the ring size that depends on the specific additives employed. When a mild base is added such as sodium benzoate (NaOBz), 7-membered ring products are formed while without base but employing instead (salen)Cr\(^{III}\)(Cl) results in the formation of a 5-membered ring as major product. Both conditions form the desired products in moderate to excellent yields (41 – 86%) at a Pd(OAc)\(_2\) loading of 10 mol% under aerobic conditions (Scheme 3.11).\(^{25}\)

**Scheme 3.11.** Pd catalyzed Selective 7- or 5-membered ring formation.

\[
\begin{align*}
\text{NaOBz, MA, MS, 70 °C} & \quad \text{Pd(OAc)}_2 \quad 10 \text{ mol%}, \text{O}_2 \\
\text{DMA, O}_2 & \quad \text{(salen)Cr}^{III}\text{Cl} \quad 50 \text{ °C} \\
\end{align*}
\]

3.1.d. Intramolecular C-H amination via sp\(^2\)-C-H activation

Pd(OAc)\(_2\) also serves as a catalyst for intramolecular C-H amination of biaryls bearing an amine functionality in proximity of an aryl C-H bond to deliver carbazoles. PhI(OAc)\(_2\) is the best oxidant for this reaction at RT employing AcOH as an additive with catalyst loadings of 5 – 20 mol % to give yields between 56 – 95% under
optimized conditions. This reaction undergoes a “cross-coupling”-like mechanism featuring an aryl-Pd-N(R)Ar intermediate susceptible to reductive elimination to form the desired carbazole (Scheme 3.11).  

**Scheme 3.11.** Pd(OAc)$_2$ catalyst for the formation of carbazoles.

3.1.e. Fe, Co and Cu catalysts for C-H amination

Earth abundant, inexpensive metals can also perform C-H amination reactions. These catalyst systems employing base metals such as Fe$^{27}$, Co$^{28}$ and Cu$^{29,30}$ FeCl$_2$ can aminate benzylic C-H bonds using amines and NBS ($N$-bromosuccinimide). This air-stable system operates at 50 °C over 3 - 6 h with 10 mol% FeCl$_2$ and 1 equiv. NBS. The proposed mechanism involves bromination of the amine to HN(Br)R$^3$ which acts as a precursor to generate an Fe-imide active intermediate [Fe]=NR. This [Fe]=NR species
then undergoes direct insertion with C-H bonds to produce the desired aminated product with yields varying between 60 – 81% (Scheme 3.12).\(^{27}\)

Co(II) porphyrin complexes (Co(por)) are also capable of facilitating benzylic C-H amination employing bromoamines-T. Such amine sources possess a strongly electron-withdrawing tosyl group (Ts) and the reaction conditions require reaction times of 17 – 20 h with catalyst loadings of 5 mol%. The yields are rather low with only in a few cases delivering yields in the 50 – 75% range (Scheme 3.13).\(^{28}\)

**Scheme 3.12.** FeCl\(_2\) catalyzed benzylic C-H amination employing NBS.

\[
\begin{align*}
R^1 & \quad \text{H or Br} \\
R^2 & \quad \text{CH}_3, \text{C}_6\text{H}_5 \\
R^3 & \quad \text{EWG}
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{N}-\text{R}^3 & \quad \text{BrH}_2\text{N}-\text{R}^3 \\
\text{[Fe]} & \quad \text{[Fe]=NR}^3
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{N}-\text{R}^3 & \quad \text{BrH}_2\text{N}-\text{R}^3 \\
\text{[Fe]} & \quad \text{[Fe]=NR}^3
\end{align*}
\]

**Scheme 3.13.** Co(por) catalyzed benzylic C-H amination using bromamines-T.

\[
\begin{align*}
\text{simplified Co porphyrin} & \quad \text{(not actual catalyst)} \\
\text{Co} & \quad \text{no metal}
\end{align*}
\]

Related porphyrin metal catalysts developed by Zhang et al. are able to perform intra-\(^{31,32}\) and intermolecular\(^{33}\) C-H amination of primary, secondary and tertiary benzylic C-H bonds. The intramolecular systems employ numerous metals such as zinc,
iron, copper, and nickel but cobalt is the most successful being able to aminate in yields of up to 99% using sulfonylazides \((RS(O)\_2N\_3)\)\(^{31}\) and phosphoryl azides \(((RO)\_2P(O)N\_3)\)\(^{32}\). Similarly, Zhang’s intermolecular benzylic C-H amination systems also employed Co porphyrins as the most successful catalysts with sulfonylazide and 2,2,2-trichloroethoxycarbonyl azide \((\text{TrocN}\_3)\) as nitrogen sources.\(^{33}\) The Zhang group recently reported at a national ACS meeting a chiral Co porphyrin system that is capable of intramolecular benzylic C-H bond amination of arylsulfonyl azides in an enantioselective fashion.\(^{34}\)

Building upon Kwart and Kahn’s initial successes with copper, several contemporary Cu-based catalyst systems have been developed for C-H amination. The tri(pyrazolyl)borate Cu complex \(\text{Tp}^{\text{Br}3}\text{Cu(NCMe)}\) has been shown by Pérez and co-

**Scheme 3.14.** C-H amination by a tris(pyrazolyl)borate Cu catalyst.  
(a) aromatic C-H amination.  
(b) benzylic C-H amination.  
(c) alkyl C-H amination.  
(d) product distribution.
workers to serve as a catalyst for benzylic, aromatic, and alkyl C-H bond amination.\(^2^9\) Both PhI=NTs and bromamine-T serve as nitrogen sources with yields of up to 95\% (Scheme 3.14). Reactions of benzylic substrates with more than one kind of benzylic position give distributions among 1° benzylic, 2° benzylic, and primary alkyl functionalized products (Scheme 3.14.d).\(^2^9\)

Use of the commercially available CuBr in combination with NBS can aminate benzylic positions and \(N\)-Me groups of \(N,N\)-dimethylaniline using amides such as benzamide, TsNH\(_2\), \(p\)-nitrobenzamide and \(p\)-fluorobenzamide. NBS is thought to serve a function identical as in the catalyst system FeCl\(_2\)/NBS\(^2^7\) in which NBS is suggested to first \(N\)-brominate the amine or amide which then may serve as a nitrene precursor. The nitrene moiety inserts into the C-H bond delivering yields up to 79\% (Scheme 3.15).\(^3^0\)

**Scheme 3.15.** Amidation of benzylic C-H bonds and C-H bonds of \(N,N\)-dimethylaniline using commercially available CuBr.

\[ \begin{align*}
\text{Scheme 3.15} & \quad \text{Amidation of benzylic C-H bonds and C-H bonds of } N,N\text{-dimethylaniline using commercially available CuBr.} \\
\end{align*} \]

Commercially available Cu(OTf)\(_2\) can also be used an amination catalyst for benzylic C-H bonds. The reaction requires strong electron withdrawing groups (e.g. sulfonyle) on the amine and the peroxide \(^{1}\)BuOOAc as oxidant along with 1,10-phenanthroline as a ligand in the presence of molecular sieves. The reaction takes place at 60 °C for 6 h with yields up to 73\% (Scheme 3.16).
Apparent in every example illustrated above, existing C-H amination methodologies typically employ nitrogen sources bearing powerful electron-withdrawing groups such as H$_2$NSO$_2$R or H$_2$NC(O)OR along with oxidants such as PhI(OAc)$_2$ capable of generating sulfonylnitrene (N-SO$_2$R) or carbamoylnitrene (N-C(O)OR) intermediates in the presence of a transition metal catalyst though in some cases simple organic amides H$_2$NC(O)R may be employed.$^{30}$ In most circumstances, however, inclusion of these approaches in complex molecule synthesis requires $N$-based deprotection of the activating group followed by refunctionalization which detract from the atom economic promise of C-H amination.

**3.1.f. $\beta$-Diketiminate copper nitrenes in C-H amination**

In 2006 Dr. Yosra Badiei reported the dicopper nitrene $\{[\text{Me}_3\text{NN}]\text{Cu}\}_2(-\text{NAr})$ employing a $\beta$-diketiminate supporting ligand to provide the first examples of isolable Cu-nitrene complexes that exhibit nitrene group transfer reactivity.$^{35}$ This dicopper nitrene serves as a nitrene-transfer reagent with $^1$BuNC and PMe$_3$ to form the carbodiimide ArN=C=NBu and phosphoimide Me$_3$P=NAr, respectively. Through use of the copper anilidoimine complex $[\text{Me}_2\text{AI}]\text{Cu}$, evidence for terminal copper nitrenes
[Cu]=NAr was obtained via a crossover experiment with this β–diketiminato analogue (Scheme 3.17).

**Scheme 3.17.** Reactivity of \([\text{Me}_3\text{NN}]\text{Cu}_2(\mu\text{-NAr})\)

\[
\begin{align*}
\text{[Me}_3\text{NN]}\text{Cu} & \quad \text{[Me}_2\text{Al]}\text{Cu} \\
\text{[Me}_3\text{NN]}\text{Cu} & \quad \text{[Me}_2\text{Al]}\text{Cu} \\
\text{[Me}_3\text{NN]}\text{Cu} & \quad \text{[Me}_2\text{Al]}\text{Cu}
\end{align*}
\]

In an attempt to isolate a mononuclear nitrene intermediate through steric bulk at the nitrene N-atom, Dr. Yosra Badiei recently described the isolation of the β–diketiminato dicopper nitrene \(\{\text{[Cl}_2\text{NN}]\text{Cu}_2(\mu\text{-NAd})\}\) from reaction of \(\{\text{[Cl}_2\text{NN}]\text{Cu}_2(\mu\text{-benzene})\}\) with the organoazide \(\text{N}_3\text{Ad}\) (Figure 4.4; Ad = 1-adamantyl). A key discovery is that this species reacts readily with hydrocarbons to formally insert the nitrene moiety NAd into \(sp^3\)-hybridized C-H bonds under both stoichiometric and catalytic conditions (Scheme 3.18). Under stoichiometric conditions the yields are near quantitative with indane, toluene, and even cyclohexane. Under catalytic conditions with only 2.5 mol% catalyst loading at 110 °C for 1 – 48 h, excellent yields of up to 93% yield are achieved.

Two limiting mechanisms have been considered for this C-H amination reactivity (Scheme 3.19). Concerted, direct insertion of the nitrene into a C-H bond could occur incited by an electrophilic N-center that attracts electron density from the
reacting C-H bond. Alternatively, a stepwise mechanism could be operative. H-atom abstraction (HAA) of the reacting C-H bond in R'-H by the copper-nitrene intermediate [Cu]=NR produces a novel Cu(II) amido intermediate [Cu$^{II}$]-NHR which goes on to undergo radical rebound (RR) with the R'• radical generated by HAA. For instance, the

**Scheme 3.19.** Possible mechanisms for C-H functionalization. Top: Direct insertion. Bottom: HAA/RR.
Scheme 3.20. Stepwise amination by [Cl₂NN]Cu=NAd.

closely related β-diketiminato nickel nitrene [Me₃NN]Ni=NAd reacts with 1,4-
cyclohexadiene via HAA to give [Me₃NN]Ni-NHAd.³⁷ {[Cl₂NN]Cu}₂(μ-1-NAd) reacts
with cis-1,4-dimethylcyclohexane to produce cis- and trans-isomers for the aminated
product resulting from reaction at the 3° site.³⁸ This finding is consistent with a stepwise
HAA / RR mechanism since the 3° radical loses its stereochemical information prior to
combination with the newly formed Cu(II)-amide [Cl₂NN]Cu-NHAd to form the
observed cis- and trans aminated products (Scheme 3.20).³⁸

3.1.g. Low-coordinate copper(II) amides

Relatively few Cu(II) amido complexes have been reported in the literature. In
1999, Walsh et al. reported a synthesis of an asymmetric bis(sulfonamide) based
copper(II) complex (Figure 3.1).³⁹ More germane to nitrene-transfer reactions,
however, is the report by Chang et al. that illustrated aziridination of aryl olefins and
electron-deficient amines with PhI(OAc)₂ serving as oxidant. A bis-ligand Cu(II)
complex was isolated and showed to be effective as a catalyst for aziridination. The
Cu(II) amide is in an acid-base equilibrium with a copper(II) imide. This system demands strong electron-withdrawing groups on the amine (Scheme 3.21).40

In 2009 Peters et al. reported a bis(phosphino)borate species [Ph₂BP(tBu)₂]Cu(NTol₂)⁴¹ that could be formulated as Cu(II) amido complex. Based on a series of spectroscopic measurements, however, they describe it as a copper(I) aminyl radical complex. This species is capable of hydrogen atom transfer (HAT) of weak benzylic bonds to form anthracene from 9,10-dihydroanthracene and 2 equiv. copper(I) amine species [Ph₂BP(tBu)₂]Cu(NHTol₂) (Scheme 3.22).⁴¹
Scheme 3.22. Peter’s Cu(I) aminyl radical complex and HAA reactivity.

Herein we describe a synthetic study that targets a copper(II) amide intermediate in C-H amination\textsuperscript{40,42-45} which reveals a bifunctional role for [Cl\textsubscript{2}NN]Cu-NHA\textsubscript{Ad} in stoichiometric C-H functionalization and results in a new system for catalytic intermolecular C-H amination with simple, unactivated alkylamines.\textsuperscript{46} Since N-based activating groups are not required, this method promises substantially broader amine substrate scope than found in contemporary C-H amination systems.

Results and Discussion

3.2.a. [Cl\textsubscript{2}NN]Cu-NHA\textsubscript{Ad} synthesis and characterization

As first described by Dr. Yosra Badiei in her dissertation, the addition of Li[Cl\textsubscript{2}NN] to anhydrous CuCl\textsubscript{2} in THF gives the dinuclear β-diketiminato copper(II) chloride \{[Cl\textsubscript{2}NN]Cu\}\textsubscript{2}(-Cl\textsubscript{2}) (1) in 79% yield as green crystals.\textsuperscript{38,47} Reaction of 1 with the lithium amide LiNHA\textsubscript{Ad} in Et\textsubscript{2}O at -35 °C immediately results in a deep purple solution from which the corresponding copper(II) amide [Cl\textsubscript{2}NN]Cu-NHA\textsubscript{Ad} (2) may be
obtained as thermally sensitive purple crystals from pentane in 50-70% isolated yield (Scheme 3.23).\textsuperscript{38,48}

**Scheme 3.23.** Synthesis of β-diketiminato Cu(II) amide [Cl\textsubscript{2}NN]Cu-NHAd.

The X-ray structure of 2 exhibits a three-coordinate copper center with a relatively short Cu-N\textsubscript{amido} distance of 1.839(9) Å. The Cu-N\textsubscript{amido}-C angle in 2 is 127.6(7)° which indicates \textit{sp}\textsuperscript{2}-hybridization at the amido N atom. The Cu-N\textsubscript{amido} distance is similar to that found in recently reported β-diketiminato copper(II) amide [Me\textsubscript{2}NN]Cu-NPh\textsubscript{2} (1.841(6) Å)\textsuperscript{42} and shorter than in the three-coordinate copper amide κ\textsuperscript{2}-[\{Ph\textsubscript{2}B(CH\textsubscript{2}PBU\textsubscript{2})\textsubscript{2}Cu-N(p-tolyl)\textsubscript{2}\}] (Cu-N = 1.906(2) Å)\textsuperscript{41} which was best described as a copper(I) aminyl radical complex.\textsuperscript{49} The X-ray structure of 2 is distinct from that of the simple amine adduct [Cl\textsubscript{2}NN]Cu(NH\textsubscript{2}Ad) which has longer Cu-N\textsubscript{amine} distance of 1.970(2) Å. Moreover, the Cu-N\textsubscript{amine}-C angle of 117.69(11)° in [Cl\textsubscript{2}NN]Cu(NH\textsubscript{2}Ad) is also consistent with a simple amine coordinated to copper with \textit{sp}\textsuperscript{3}-hybridization at nitrogen (Figure 3.2).
Figure 3.2. X-ray crystal structure of \([\text{Cl}_2\text{NN}]\text{Cu(NH}_2\text{Ad})\). Selected bond distances (Å) and angles (°): Cu-N1 1.9037(15), Cu-N2 2.0119(15), Cu-N3 1.9695(16) N3-C18 1.496(2), N1-Cu-N2 96.79(6), N1-Cu-N3 151.97(7), N2-Cu-N3 111.14(6), Cu-N3-C18 117.69(11).
3.2.b. [Cl₂NN]Cu-NHAd reactivity towards C-H bonds: stoichiometry

While Dr. Yosra Badiei first observed C-H amination of benzylic C-H bonds with 2, important details regarding the stoichiometry, substrate scope, and mechanism of this reaction were unclear.³⁸ Stoichiometric quantification was not reproducible at this early stage due to the thermal instability of 2.³⁸ Optimization of the reaction conditions in this study led to reproducible results giving aminated product yield of 87% yield with the formation of AdNH₂ in 88% yield with 2 equiv. 2 (Scheme 3.24). This exciting reactivity and the 1 to 1 ratio of functionalized product to amine prompted a detailed mechanistic investigation that could potentially reveal insights required to develop a highly desirable catalytic protocol involving copper(II) amides.

**Scheme 3.24.** Stoichiometry and possible mechanism for C-H functionalization.

Reaction of two equiv. 2 with ethylbenzene or indane (100 equiv. in heptane) at room temperature for 24 h results in the formation of PhCH(NHAd)Me or (1-indanyl)NHAd in 87% and 81% yield, respectively, along with one equiv. H₂NAd. The stronger primary benzylic C-H bond of toluene requires heating at 60 °C to provide the corresponding amine PhCH₂NHAd product. The solvent diethyl ether is also aminated
at room temperature to ultimately provide the imine AdN=CHMe in 41% yield upon loss of HOEt from EtOCH(NHAd)Me (Table 3.1).

Table 3.1. Stoichiometric results for C-H amination.

<table>
<thead>
<tr>
<th>Substrates</th>
<th>BDE = 86 kcal/mol</th>
<th>BDE = 87</th>
<th>BDE = 90</th>
<th>BDE = 93</th>
</tr>
</thead>
<tbody>
<tr>
<td>NHAd</td>
<td>81%</td>
<td>87%</td>
<td>18% (70%)a</td>
<td>44%</td>
</tr>
<tr>
<td>[Cl2NN]Cu-NHAd</td>
<td>15% (15%)a</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.2.c. Mechanistic investigation of C-H amination: kinetics

Based on the stoichiometry of this C-H amination reaction, we considered two mechanistic pathways (Scheme 3.25). First, the copper nitrene \([\{\text{Cl}_{2}\text{NN}\}\text{Cu}\}_{2}(\text{-NAd})\), known to participate in C-H amination,\(^{36}\) could be formed via a disproportionation reaction between two equiv. \(2\) with generation of H2NAd. Alternately, copper amide \(2\) could affect C-H amination in a stepwise fashion. The first molecule of \(2\) abstracts an...
H-atom from the substrate R-H to give copper(I) amine adduct $[\text{Cl}_2\text{NN}]\text{Cu(NH}_2\text{Ad})$ and an organic radical $R\cdot$. In a rapid subsequent step, another equivalent of 2 captures this radical $R\cdot$ to form the product amine $RNH\text{Ad}$ coordinated to copper. Kinetic analysis following the loss of 2 at 25 °C by UV-vis spectroscopy ($\lambda_{\text{max}}$(heptane) = 572 nm (2350 M$^{-1}$cm$^{-1}$)) with excess ethylbenzene or indane (500 – 2000 equiv.) (Figure 3.3) in heptane indicates that the rate law follows: rate = $k_1[2][R-H]$ (Figure 3.4; Table 3.2; Figure 3.5; Table 3.3). Thus, kinetic data support the HAA / radical capture pathway since the disproportionation pathway would require a second order dependence on the reacting 2. Eyring analysis of indane amination (1000 equiv. in heptane) over the temperature range 20 – 50 °C (Figure 3.6) gives activation parameters $\Delta H^\ddagger = 11.4(4)$ kcal/mol and $\Delta S^\ddagger = -38.7(14)$ e.u. with $\Delta G^\ddagger = 22.9(8)$ kcal/mol at 298 K (Figure 3.7). These activation parameters are similar to those in the tosyl-amidation of ethylbenzene by the nitrene species (porph)Ru(=NTs)$_2$ ($\Delta H^\ddagger = 8.9(2)$ kcal/mol and $\Delta S^\ddagger = -39.8(20)$ e.u.) thought to proceed by initial HAA followed by radical capture.$^{50}$ We observe a large primary kinetic isotope effect ($k_H / k_D = 70(9))$ at room temperature in the amination of ethylbenzene, which suggests a tunneling pathway.$^{51}$

**Scheme 3.25.** Possible mechanisms for C-H amination.
Figure 3.3. Consumption of [Cl₂NN]Cu-NHAd (2) as monitored by the loss of its UV-vis absorbance at λ = 572 nm in the presence of 1000 equiv. indane under pseudo first-order conditions in heptane at 25 °C.

Figure 3.4. Kinetic plots of ln(A_t/A_0) vs. time (A = absorbance at λ = 572 nm) for the amination of indane by [Cl₂NN]Cu-NHAd (2) in the presence of 500, 1000, 1500, and 2000 equiv. indane under pseudo first order conditions. The initial concentration of [Cl₂NN]Cu-NHAd (2) was 1.56 mM in each case.
Table 3.2. Observed rate constants for amination of indane by [Cl₂NN]Cu-NHAd (2) under pseudo first order conditions (excess indane).

<table>
<thead>
<tr>
<th>Indane amt</th>
<th>[Indane] (M)</th>
<th>$k_{obs}$ (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 eq</td>
<td>0.776</td>
<td>$9.3(4) \times 10^{-5}$</td>
</tr>
<tr>
<td>1000 eq</td>
<td>1.55</td>
<td>$1.6(1) \times 10^{-4}$</td>
</tr>
<tr>
<td>1500 eq</td>
<td>2.33</td>
<td>$2.2(1) \times 10^{-4}$</td>
</tr>
<tr>
<td>2000 eq</td>
<td>3.10</td>
<td>$2.8(1) \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Figure 3.5. Plot of observed first order rate constant $k_{obs}$ vs. [indane].

Table 3.3. Observed pseudo first order rate constants $k_{obs}$ and second order rate constants $k_{act}$ for the amination of indane (1000 equiv.) by [Cl₂NN]Cu-NHAd (2) in heptane.

<table>
<thead>
<tr>
<th>Temp</th>
<th>$k_{obs}$ (s⁻¹)</th>
<th>$k_{act}$ (M⁻¹s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 °C</td>
<td>$7.1(3) \times 10^{-5}$</td>
<td>$7.6(3) \times 10^{-4}$</td>
</tr>
<tr>
<td>30 °C</td>
<td>$1.4(1) \times 10^{-4}$</td>
<td>$1.5(1) \times 10^{-4}$</td>
</tr>
<tr>
<td>40 °C</td>
<td>$2.6(1) \times 10^{-4}$</td>
<td>$2.8(1) \times 10^{-4}$</td>
</tr>
<tr>
<td>50 °C</td>
<td>$4.8(1) \times 10^{-4}$</td>
<td>$5.1 (1) \times 10^{-4}$</td>
</tr>
</tbody>
</table>
Figure 3.6. Kinetic plots of $\ln(A_t/A_0)$ vs. time ($A = \text{absorbance at } \lambda = 572 \text{ nm}$) for the amination of indane (1000 equiv.) by $[\text{Cl}_2\text{NN}]\text{Cu-NHAd (2)}$ at 20.0 °C, 30.0 °C, 40.0 °C, and 50.0 °C. The initial concentration of $[\text{Cl}_2\text{NN}]\text{Cu-NHAd (2)}$ and indane were 0.94 mM and 0.939 M, respectively.

$\Delta H^\ddagger = 11.4(4) \text{ kcal/mol}$

$\Delta S^\ddagger = -38.7(14) \text{ e.u.}$

$\Delta G^\ddagger_{298K} = 22.9(8) \text{ kcal/mol}$

Figure 3.7. Eyring plot of $\ln(k/T)$ vs. $1/T$ for amination of 1000 equiv. indane (0.939 M) using second order rate constants collected in Table 3 3. Error analysis in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ follows that by Girolami et al. using a assumed temperature error of ± 0.5 °C and assuming an average error of 4% in the absolute values of the rate constants.\textsuperscript{1}
**3.2.d. Computational investigation by collaborator Dr. Tom Cundari**

In collaboration with Dr. Tom Cundari at the University of North Texas, the transition state (TS) in the reaction of 2 with indane was computed using full chemical models and hybrid ONIOM(BP86/6-311+G(d):UFF) methods (Scheme 3.26) with the goal to better understand the rate limiting T.S.\textsuperscript{48} Notably, the calculated activation parameters are remarkably similar to those experimentally obtained and result from a TS with a nearly linear C\textsubscript{indane}–H--N\textsubscript{amide} linkage: $\Delta H^\ddagger = 11.3$ kcal/mol, $\Delta S^\ddagger = -46.8$ e.u. with $\Delta G^\ddagger = 25.2$ kcal/mol. The TS may be viewed as late with a significant degree of N-H bond formation (N-H = 1.284; C-H = 1.417 \textgreek{\AA}). HAA to form [Cl\textsubscript{2}NN]Cu(NH\textsubscript{2}Ad) and the indanyl radical is uphill: $\Delta H = 15.1$ kcal/mol, $\Delta S = +5.2$ e.u., $\Delta G = +13.6$ kcal/mol. Addition of the indanyl radical to 2, however, is considerably downhill to give [Cl\textsubscript{2}NN]Cu(NH(indanyl)Ad): $\Delta G = -17.2$ kcal/mol, $\Delta H = -35.1$ kcal/mol, $\Delta S = -60.0$ e.u (Scheme 2.26; Figure 3.8).
3.2.e. Electronic structure of [Cl₂NN]Cu-NHAd probed by EPR spectroscopy and DFT calculations

To better understand the N-centered HAA and radical capture reactivity of 2 we examined its electronic structure using a combination of EPR spectroscopy and DFT calculations. All EPR spectra were collected and simulated in Erlangen, Germany by Dr. Susanne Mossin in Prof. Dr. Karsten Meyer’s laboratory while the DFT collaborations were done at Georgetown by Prof. Timothy H. Warren. Simulation of the X-band EPR spectra of 2 (Figure 3.9) reveals a nearly axial environment about the Cu center with $g_1 = 2.133(5)$, $g_2 = 2.036(5)$, and $g_3 = 2.031(5)$. These g values, along with the hyperfine coupling constant $A_1$(Cu) = 365(10) MHz, are consistent with three-coordinate copper(II) center. The superhyperfine interactions are best simulated using a 2N (β-diketiminate), 1N (amide), 1H (amide N-H) model in which there is
considerable anisotropy in Cu-N(amido) interaction (Figures 3.9; Figure 3.10). Consistent with the highly directional nature of the 2-center / 3-electron Cu-N\text{amide} \pi interaction which places significant unpaired electron density at the N\text{amide} atom (0.49 e⁻).

![Diagram](image)

**Figure 3.27.** Molecular orbital diagram starting from limiting resonance structures involving a Cu(II)-amide (left) and a Cu(I)-aminyl radical (right).

(figure 3.27; figure 3.11), calculations indicate that the interaction of the unpaired electron with the amido N atom is appreciably more anisotropic ($A_1(N) = 7, A_2(N) = 5, A_3(N) = 61$ MHz) than with the \(\beta\)-diketiminate N donors ($A_{1-3}(N) = 19 - 28$ MHz). Moreover, EPR spectra reveal coupling to the amido N-H \(^1\)H nucleus ($A_{iso} = 34(5)$ MHz; $A_1 = 5, A_2 = 55, A_3 = 34$) as confirmed by spectral changes in EPR spectra of [Cl\(_2\)NN]Cu-N\text{DAd} (2-d) taken at RT and in frozen toluene glass (Figures 3.9 and 3.10). TD-DFT calculations suggest that the strong optical band observed at \(\lambda = 572\) nm for 2 originates from the Cu-N\text{amide} \pi \rightarrow \pi^* transition.
Figure 3.9. X-band EPR spectra and simulations for [Cl₂NN]Cu-NHAd (2) (toluene, RT; 9.000708 GHz, ModWidth = 0.25 mT, Power = 1.00 mW. [Cu]-NDAd sample: 8.987061 GHz, ModWidth = 0.25 mT, Power = 0.25 mW). Simulation ([Cu]-NHAd, 1Cu, 2N, 1N and 1H model) provides $g_{\text{iso}} = 2.067(2)$ with $A_{\text{iso}}(\text{Cu}) = 143(5) \text{ MHz}$, $A_{\text{iso}}(\text{N}) = 23(5) \text{ MHz}$ for 2 N atoms with similar superhyperfine coupling, $A_{\text{iso}}(\text{N}) = 26(5) \text{ MHz}$ for an additional N atom and $A_{\text{iso}}(\text{H}) = 34(5) \text{ MHz}$. For 2-D, $A_{\text{iso}}(\text{D}) = 6 \text{ MHz}$ was used in the simulation owing to the smaller absolute magnitude of the $g_N$ factor for D as compared to H. The linewidth is kept constant between the fittings of 2 and 2-D, the broadening observed in the 2-D spectrum is reproduced in the fittings and is believed to be due to the presence of a comparably low ($\approx 6 \text{ MHz}$) superhyperfine coupling from D which smooths out the superhyperfine features from the nitrogens. Linear A strain $\theta = 6 \times 10^{-6} \text{ mT}^2/\text{MHz}$ was implemented in order to reproduce the copper nuclear quantum number dependence of the linewidth.
Figure 3.10. X-band EPR spectra and simulations for [Cl₂NN]Cu-NHAd (2) (frozen toluene glass, 51 K; 9.020655 GHz, ModWidth = 0.25 mT, Power = 0.50 mW; [Cu]-NDAd sample: 55 K; 8.991828 GHz, ModWidth = 0.25 mT, Power = 1.00 mW). Simulation using a 1Cu, 2N, 1N, 1H model inspired by the DFT calculations for 2-NHAd provides $g_1 = 2.133(5)$, $g_2 = 2.036(5)$, $g_3 = 2.031(5)$ with $A_{1}(Cu) = 365(10)$ MHz, $A_{2}(Cu) = 60(20)$ MHz, $A_{3}(Cu) = 15(10)$ MHz; $A_{1}(N) = 20$ MHz, $A_{2}(N) = 22$ MHz, $A_{3}(N) = 30$ MHz, for 2 N atoms with similar superhyperfine coupling; $A_{1}(N) = 5$ MHz, $A_{2}(N) = 5$ MHz, $A_{3}(N) = 63$ MHz for an additional N atom; $A_{1}(H) = 5$ MHz, $A_{2}(H) = 55$ MHz, $A_{3}(H) = 34$ MHz. For 2-NDAd, $A_{1}(D) = 1$ MHz, $A_{2}(D) = 8$ MHz, $A_{3}(D) = 6$ MHz were used in the simulation owing to the small absolute magnitude of the $g_N$ factor for D as compared to H. The linewidth is kept constant between the fittings of 2 and 2-D.
3.2.f. Rendering stoichiometric C-H amination catalytic

The key copper(II) amide intermediate 2 may be generated under conditions that allow for catalysis. Inspired by the alkoxide-amide exchange that takes place in some variants of the Buchwald-Hartwig amination\textsuperscript{53,54} between [Pd]-OBu\textsuperscript{i} intermediates and amines HNR\textsuperscript{1}R\textsuperscript{2} to form reactive [Pd]-NR\textsuperscript{1}R\textsuperscript{2} species,\textsuperscript{55} we were eager to explore an analogous transformation in this copper-based system (Scheme 3.28).

Dr. Matthew Varonka first synthesized and collected the crystal structure of [Cl\textsubscript{2}NN]Cu-OBu\textsuperscript{i} (3) and Dr. Susanne Mossin collected and simulated EPR spectra of this three-coordinate copper(II)-alkoxide. The reaction of {[Cl\textsubscript{2}NN]Cu\textsubscript{i}.\textsubscript{2} ( benzene) with 'BuOOBu\textsuperscript{i} cleanly provides [Cl\textsubscript{2}NN]Cu-OBu\textsuperscript{i} (3) in 90+% spectroscopic yield
Scheme 3.28. Buchwald-Hartwig amination mechanism.

($
\lambda_{max}\text{(benzene)} = 471 \text{ nm (2950 M}^{-1}\text{cm}^{-1})$) upon reaction in benzene. It may also be isolated in 53% yield as thermally sensitive red crystals from pentane (Scheme 3.29).

X-ray structure analysis of this trigonal species shows a short Cu-O bond (1.785(2) Å) along with shortened Cu-N distances (1.884(2), 1.889(2) Å) relative to 1 or 2 (Figure 3.12). The room temperature EPR spectrum of 3 in toluene consists of a broad signal essentially devoid of hyperfine coupling to $^{63/65}\text{Cu}$ which suggests rapid spin-spin exchange, perhaps via the intermediacy of the dinuclear $\{\text{Cl}_2\text{NN}][\text{Cu}]_2(\mu-\text{OBu})_2$.

Frozen glass EPR spectra of 3 indicate a roughly axial environment ($g_1 = 2.243(5)$, $g_2 = 2.059(5)$, $g_3 = 2.042(5)$) with $A_1(\text{Cu}) = 353(10) \text{ MHz}$ similar to that found in amide 2 (Figures 3.12 and 3.13).

Scheme 3.29. Cu(II) alkoxide formation.

$\{\text{Cl}_2\text{NN}][\text{Cu}]\text{(4-benzene)} + \text{BuOOBu} \xrightarrow{\text{benzene}} 2 \text{[Cl}_2\text{NN}][\text{Cu}−\text{OBu}}$
Figure 3.12. X-ray crystal structure of [Cl₂NN]Cu-OBu⁺ (3). All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Cu-N1 1.884(2), Cu-N2 1.890(2), Cu-O 1.785(2), O-C18 1.425(3), N1-Cu-N2 96.26(9), N1-Cu-O 134.04(9), N2-Cu-O 129.64(9), Cu-O-C18 122.67(15).
### Table 3.4. Crystallographic data for 3 and [Cl$_2$NN]CuNH$_2$Ad.

<table>
<thead>
<tr>
<th>Compd.</th>
<th>3</th>
<th>[Cl$_2$NN]CuNH$_2$Ad</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
<td>C$<em>{21}$H$</em>{22}$Cl$_4$CuN$_2$O</td>
<td>C$<em>{27}$H$</em>{29}$N$_3$Cl$_4$Cu</td>
</tr>
<tr>
<td>Mol. Wt.</td>
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<td>600.87</td>
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<tr>
<td>Temp.(K)</td>
<td>100(2)</td>
<td>100(2)</td>
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<tr>
<td>crystal description</td>
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<td>block</td>
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<tr>
<td>crystal color</td>
<td>red</td>
<td>yellow</td>
</tr>
<tr>
<td>crystal size (mm$^3$)</td>
<td>0.38×0.25×0.15</td>
<td>0.45×0.20×0.12</td>
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<tr>
<td>system</td>
<td>monoclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2$_1$/c</td>
<td>P1bar</td>
</tr>
<tr>
<td>a (Å)</td>
<td>14.1177(18)</td>
<td>7.0922(6)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>8.7210(11)</td>
<td>11.8876(9)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>19.499(3)</td>
<td>16.6455(13)</td>
</tr>
<tr>
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<tr>
<td>β (deg)</td>
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<tr>
<td>γ (deg)</td>
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</tr>
<tr>
<td>R(int)</td>
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<td>0.0236</td>
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<tr>
<td>GOF of F$^2$</td>
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<td>1.072</td>
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<tr>
<td>R$_1$ (I &gt; 2σ(I))</td>
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<td>0.0306</td>
</tr>
<tr>
<td>wR$_2$ (all data)</td>
<td>0.0517</td>
<td>0.0365</td>
</tr>
<tr>
<td>Largest diff. peak and hole e$^-$·Å$^{-3}$</td>
<td>2.075 and -0.817</td>
<td>0.793 and -0.283</td>
</tr>
</tbody>
</table>
Figure 3.13. X-band EPR spectrum and simulation for [Cl₂NN]Cu-OBu¹ (3) (toluene, RT, 8.995625 GHz, ModWidth = 0.2 mT, Power = 0.25 mW). Simulation using an 1Cu, 2N model provides \( g_{iso} = 2.11(1) \) with \( A_{iso}(Cu) = 92(5) \) MHz, \( A_{iso}(N) \) was used from the fit at low temperature. Linewidth broadening at RT is significant resulting in loss of observed \( A_{iso}(Cu) \). It is likely a result of a dynamic exchange of OBu¹ groups between [Cl₂NN]Cu fragments via the dinuclear intermediate \{[Cl₂NN]Cu\}_2(µ-OBu)\_2. The simulation was performed under the assumption of just one spin \( S = 1/2 \) species.

Figure 3.14. X-band EPR spectrum and simulation for [Cl₂NN]Cu-OBu¹ (3) (frozen toluene glass, 58 K, 8.9910940 GHz, ModWidth = 0.2 mT, Power = 0.15 mW). Simulation provides \( g_1 = 2.243(5), g_2 = 2.059(5), g_3 = 2.042(5) \) with \( A_1(Cu) = 353(10) \) MHz, \( A_2(Cu) = 14(10) \) MHz, \( A_3(Cu) = 32(15) \) MHz and \( A_1(N) = 33(15) \) MHz, \( A_2(N) = 29(5) \) MHz, \( A_3(N) = 37(5) \) MHz for 2 N atoms with similar superhyperfine coupling parameters.
3.2.g. Interconversion of [Cl₂NN]Cu-OBu' and [Cl₂NN]Cu-NHAd

Dissolution of 3 in ether followed by the addition of an excess of H₂NAd results in the instantaneous loss of the UV-vis band of 3 centered at λ = 471 nm with growth of a band a λ = 572 nm corresponding to copper(II) amide 2 (Figure 3.14). Quantitative analysis in benzene at 25 °C reveals an equilibrium constant \( K_{eq} = 4(1) \) favoring the amido species 2 (Scheme 3.30). Thus, a rapid acid/base reaction ensues between [Cl₂NN]Cu-OBu' (3) and H₂NAd to generate [Cl₂NN]Cu-NHAd (2).

**Scheme 3.30.** Cu(II) amide formation.

\[
\textit{[Cl}_2\textit{NN})\textit{Cu}^{\text{II}}-\text{O}^{\text{Bu}} + \textit{AdNH}_2 \leftrightarrow \textit{[Cl}_2\textit{NN})\textit{Cu}^{\text{II}}-\text{N}^{\text{Ad}} + ^\text{iBuOH} \]

Thus, at 25°C, \( K_{eq} = 4(1) \) favors the amido species 2 (Scheme 3.30). Thus, a rapid acid/base reaction ensues between [Cl₂NN]Cu-OBu' (3) and H₂NAd to generate [Cl₂NN]Cu-NHAd (2).

**Figure 3.14.** Addition of excess H₂NAd to an ether solution of [Cl₂NN]Cu-OBu' (3) results in the loss of 3 (\( \lambda_{\text{max}} = 471 \)) and the formation of [Cl₂NN]Cu-NHAd (2) (\( \lambda_{\text{max}} = 572 \)) nm as followed by UV-vis spectroscopy.
3.2.h. Catalytic C-H amination with unactivated amines and \( \text{tBuOOBu}^\dagger \)

These individual steps may be tied together in a new protocol for catalytic C-H amination (Scheme 3.31). A mixture of 1 equiv. H₂NAd, 1 equiv. \( \text{tBuOOBu}^\dagger \), and 10 equiv. indane in heptane in the presence of 10 mol% \{[Cl₂NN]Cu\}_2( -benzene) gives a 78% yield of (1-indanyl)NHAd after standing at RT for 5 days. Increasing the reaction temperature to 90 °C allows for increased yields with decreased catalyst loadings (1 mol% mononuclear [Cu]) and reaction times (24 – 72 h). Employing either 10 or 1 equiv. indane in benzene with 1.2 equiv. \( \text{tBuOOBu}^\dagger \) and 1 mol% [Cu] provides the product amine in 83% or 46% yields, respectively. Importantly, in situ UV-vis analysis demonstrates the presence of copper amide 2 in catalytic C-H amination reaction mixtures (10 equiv. indane in benzene; 30, 50 and 75 °C) which builds up to a maximum mol fraction of ca. 0.8 relative to the initial amount of [Cu] employed (Figures 3.14 and 3.15). Consistent with stoichiometric studies that reveal the complete

**Scheme 3.31.** Proposed catalytic cycle for C-H functionalization via a Cu(II) amide. [Cu] = [Cl₂NN]Cu
Figure 3.15. UV-vis spectra taken every 30 s during in-situ analysis of catalytic reaction at 30 °C employing H₂NAd, tBuOOBu', and 10 equiv. indane in benzene. Growth of [Cl₂NN]Cu-NHAd (2) is indicated by the appearance of the band at λ = 572 nm.

Figure 3.16. Mole fraction of [Cl₂NN]Cu-NHAd (2) observed via UV-vis spectroscopy vs. time with respect to total amount of copper catalyst [Cl₂NN]Cu used during in-situ UV-vis analysis of catalytic C-H amination with H₂NAd, tBuOOBu', and 10 equiv. indane at 30, 50, and 75 °C in benzene.
consumption of \([\text{Cl}_2\text{NN}]\text{Cu-OBu}^+ (3)\) in the presence of an excess of \(\text{H}_2\text{NAd}\), alkoxide 3 is not observed in catalytic reactions. Rather, the \(\lambda_{\text{max}} = 572\) nm band of 2 grows in from the initial copper(I) species present (likely \([\text{Cl}_2\text{NN}]\text{Cu(NH}_2\text{Ad})\)) with isosbestic behavior.

**Table 3.5.** Catalytic C-H amination with alkyl amines ([Cu] = [Cl\(_2\)NN]Cu)

\[
\text{R-H} + 2\text{R}{^1}\text{RN-H} + \text{^4\text{BuOO}Bu}^+ \xrightarrow{1 \text{ mol}\% \text{[Cu]}} \text{90\textdegree C, 24h} \quad 2\text{R}{^1}\text{RN-R} + 2\text{^4\text{BuOH}}
\]

<table>
<thead>
<tr>
<th>Substrates</th>
<th>BDE C-H 85.9 kcal/mol</th>
<th>BDE C-H 88.5 kcal/mol</th>
<th>BDE C-H 97.6 kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>neat</td>
<td>10 eq.</td>
<td>1 eq.</td>
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<tr>
<td>(\text{NH}_2)</td>
<td>98</td>
<td>83</td>
<td>46</td>
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<td>(\text{NH}_2)</td>
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<td>65</td>
<td>17</td>
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<td>(\text{NH}_2)</td>
<td>74</td>
<td>59</td>
<td>24</td>
</tr>
<tr>
<td>(\text{NH}_2)</td>
<td>79</td>
<td>40\textsuperscript{a}</td>
<td>19\textsuperscript{a}</td>
</tr>
<tr>
<td>(\text{NH}_2)</td>
<td>55</td>
<td>35\textsuperscript{a}</td>
<td>n/a</td>
</tr>
</tbody>
</table>

\(\text{2}^\circ\) amine products isolated as HCl salts; \(\text{3}^\circ\) amine products isolated as pure substances
\(\text{a}^\circ\) yield by \(^1\text{H}\) NMR; \(\text{b}^\circ\) yield by GC/MS

In collaboration with Raymond Gephart, a brief survey of other unactivated primary (\(\text{H}_2\text{NCy}\) and \(\text{H}_2\text{NCH}_2\text{CH}_2\text{Ph}\)) and secondary (morpholine) alkylamines in this catalytic protocol with indane and ethylbenzene results in the expected secondary or
tertiary amines in good to excellent yields (Table 3.5). The use of morpholine is noteworthy as secondary amines are not amenable to nitrene-based C-H amination protocols. This method also allows for the C-H amination of strong, unactivated $sp^3$-hybridized C-H bonds with primary amines. Using cyclohexane (C-H BDE $\sim$ 97 kcal/mol)$^{56}$ as a solvent, yields of 91 – 61% are obtained. Attempted amination of cyclohexane with morpholine results oxidation of morpholine to the corresponding heterocyclic imine$^{57}$ as the major product.

**Conclusion**

The synthesis of the copper(II) amide $[\text{Cl}_2\text{NN}]\text{Cu-NHAd}$ (2) and its stoichiometric C-H amination chemistry with benzylic substrates serves as a springboard to a new protocol for catalytic C-H amination. $[\text{Cl}_2\text{NN}]\text{Cu-NHAd}$ (2) represents a rare example of a discrete metal-amido complex that engages in H-atom abstraction chemistry with C-H bonds. A recent, related example is $\kappa^2$-[\{Ph$_2$B(CH$_2$PBu)$_2$\}Cu-N(p-tolyl)$_2$]$^{41}$ that exhibits HAA chemistry with the weak C-H bond of 9,10-dihydroanthracene (BDE = 76 kcal/mol)$^{56}$ and Sn-H bond of Bu$_3$Sn-H (BDE = 78 kcal/mol)$^{56}$ though this species is best described as a copper(I) aminyl radical complex.$^{49}$ The copper(II) amide $[\text{Cl}_2\text{NN}]\text{Cu-NHAd}$ (2) reacts with much stronger C-H bonds such as those found in indane and ethylbenzene (BDE = 84 – 87 kcal/mol)$^{56}$ Perhaps the key to heightened reactivity of 2 is the formation of strong N-H bonds upon HAA. The N-H bond strength in free primary alkylamines $\text{H}_2\text{NR}$ is approximately 100-102 kcal/mol,$^{56}$ though this is certainly lower in copper(I) amine
adducts $[\text{Cl}_2\text{NN}]\text{Cu}(\text{NH}_2\text{R})$ estimated by theory at 68 kcal/mol for $[\text{Cl}_2\text{NN}]\text{Cu}(\text{NH}_2\text{Ad})$. Owing to its $N$-based radical character, the amide moiety in $[\text{Cl}_2\text{NN}]\text{Cu}-\text{NHAd}$ (2) exhibits bifunctional reactivity, capable of abstracting H atoms from C-H bonds as well as forming new C-N bonds from carbon-based radicals. The significant amount of unpaired electron density at the N atom contributes to facile C-N bond formation.

Importantly, the key copper amide species 2 that engages in stoichiometric C-H amination may be formed from the free amine $\text{H}_2\text{NAd}$ and $\{[\text{Cl}_2\text{NN}]\text{Cu}\}_2(\mu-\text{benzene})$ through the use of $^\prime\text{BuOOBu}$. The oxidant $^\prime\text{BuOOBu}$ cleanly oxidizes copper(I) catalyst to the three-coordinate $[\text{Cl}_2\text{NN}]\text{Cu}-\text{OBu}$ (3) which engages in acid/base chemistry to generate copper(II) amide intermediates. This ultimately allows for catalytic C-H amination with unactivated amines generating the easily separated HOBu$^\prime$ as the sole stoichiometric principle byproduct. Furthermore, these individual steps illustrate specific roles in which peroxide oxidants may participate in copper-catalyzed C-H functionalization reactions.$^{58-60}$

In contrast to contemporary catalytic C-H amination systems, unactivated primary and secondary alkyl amines may efficiently participate in the intermolecular amination of $sp^3$-hybridized C-H bonds. This method greatly expands the range of amines that may participate in C-H amination and represents a valuable alternative to existing procedures that require $N$-based electron-withdrawing activating groups. For instance, new intramolecular C-H amination variants may be envisioned in which the resulting cyclic amine is devoid of heteroatom activating groups.$^{2,26,61}$ Given the especially encouraging intermolecular reactivity with $1^o$ amines, ammonia ($\text{NH}_3$), the
least expensive and most versatile synthetic source of N atoms, becomes a particularly attractive target for direct use in C-H amination reactions.

**Experimental**

**General Procedures and Instrumentation**

All experiments were carried out in a dry nitrogen atmosphere using an MBraun glovebox and/or standard Schlenk techniques. 4 A molecular sieves were activated *in vacuo* at 180 °C for 24 h. Dry benzene was purchased from Aldrich and was stored over activated 4 A molecular sieves. Diethyl ether and tetrahydrofuran (THF) were first sparged with nitrogen and then dried by passage through activated alumina columns. Pentane was first washed with conc. HNO₃ / H₂SO₄ to remove olefins, stored over CaCl₂ and then distilled before use from sodium/benzophenone. Benzene, toluene, and ethylbenzene were purchased anhydrous and stored over 4 A molecular sieves. All solvents were tested before use with a drop of sodium benzophenone ketyl in THF solution. All deuterated solvents were sparged with nitrogen, dried over activated 4 A molecular sieves and stored under nitrogen. Celite was dried overnight at 200 °C under vacuum.

¹H and ¹³C NMR spectra were recorded on a Varian Unity 300 or 400 MHz Inova Spectrometer (300 and 75.4 MHz; 400 and 100.47 MHz respectively). All NMR spectra were recorded at room temperature unless otherwise noted and were indirectly referenced to residual solvent signals or TMS as internal standards. UV-Vis spectra were measured on a Varian Cary 50 or 100 spectrophotometer, using cuvettes with
screw-cap tops. GC-MS spectra were recorded on a Varian Saturn 3900 and elemental analyses were performed on a Perkin-Elmer PE2400 microanalyzer at Georgetown. IR measurements were performed on Perkin Elmer Spectrum One FT-IR Spectrometer.

All reagents were obtained commercially unless otherwise noted. Ethylbenzene-$d_{10}$ was obtained from Acros and purified by passing it through activated alumina. 1-adamantylamine was purchased from Aldrich. Anhydrous CuCl$_2$ was obtained from Strem Chemicals. H[Cl$_2$NN]$^1$ and {[Cl$_2$NN]Cu}$_2$(μ-$d_{10}$-benzene)$^2$ were prepared by literature methods or may be obtained from Strem Chemicals. Ethylbenzene-$d_{10}$ was obtained from Acros and purified by passing it through activated alumina.$^{36,62}$

### 3.3.a. Synthesis of [Cl$_2$NN]Cu complexes

**Synthesis of {[Cl$_2$NN]Cu}$_2$(μ-Cl)$_2$ (1)**. To a chilled solution of H[Cl$_2$NN] (1.369 g, 3.556 mmol) at -35 °C in 75 mL THF, was added $n$-butyllithium in hexane (2.2 mL of 1.6 M solution, 3.6 mmol) and the mixture was stirred for 30 min. To this solution was added anhydrous CuCl$_2$ (0.478 g, 3.556 mmol) resulting in an immediate color change from yellow to dark green. The mixture was stirred for 3 hours and all volatiles were then removed *in vacuo* to dryness. The green residue was extracted with 50 mL CH$_2$Cl$_2$, and then stirred for 15 min. The solution was then filtered through Celite, and the frit was washed thoroughly (twice) with 5 mL CH$_2$Cl$_2$. The solvent was removed *in vacuo* and a green solid was obtained. The solid was washed with 15 mL of cold pentane on a
frit, dried to give a dark green powder (1.20 g, 70 %) and a second crop was obtained upon crystallization of the mother liquor solution overnight at -35 °C (0.140 g) to give a total yield of 79 % of 1. Crystallization from ether allowed for X-ray characterization.

Anal. Calcd for C_{34}H_{26}Cl_{10}Cu_{2}Na: C, 42.00; H, 2.70; N, 5.76. Found: C, 42.10; H, 2.77; N, 5.73. T_{eff} = 2.63 B.M. UV-vis: λ_{max} = 474 nm (ε = 2700 M^{-1}cm^{-1}). EPR (frozen toluene glass, 4 K, 8.991291 GHz, ModWidth = 0.025 mT, Power = 1.00 mW) g_1 = 2.23(1), g_{2,3} = 2.06(1).

**Synthesis of [Cl_2NN]Cu-NHAd (2).** It is imperative to maintain solutions containing [Cl_2NN]Cu-NHAd at low temperature (-35 °C) whenever possible during the synthesis and workup of this thermally sensitive compound. A suspension of \{[Cl_2NN]Cu\}_2(μ-Cl)_2 (0.400 g, 0.415 mmol) in 10 mL of Et_2O was prepared and cooled to -35 °C. To this chilled suspension was added solid AdNHLi (0.135 g, 0.860 mmol). (LiNHAd was previously prepared by addition of 1 equiv. BuLi to H_2NAd in pentane followed by isolation of the resulting white powder by filtration). The suspension was shaken vigorously for 5 min during which time it turned from dark green to purple. The suspension was chilled again to -35 °C and after standing for 5 min at -35 °C, the suspension was shaken vigorously again. The mixture was then to about 2 mL in vacuo.

To the concentrated suspension was added cold pentane (10 mL) and the sides of the vial were scrapped with a spatula to free any solids sticking on the vial. The suspension was returned to the -35 °C freezer and allowed to settle. A green (unreacted \{[Cl_2NN]Cu\}_2(μ-Cl)_2) and white (LiCl) precipitate was observed at the bottom of a
purple solution. The purple solution was decanted off and filtered through Celite. The remaining solids were extracted another three times with cold pentane following an identical procedure, each time allowing the initially formed suspension to settle at -35 °C. All pentane extracts were combined and concentrated to 1 – 2 mL and allowed to stand overnight at -35 °C to yield sticky purple crystals in 50 – 70% yield. \( \lambda_{\text{max}} \) (heptane) = 572 nm \((\varepsilon = 2350 \text{ M}^{-1}\text{cm}^{-1})\); \( \lambda_{\text{max}} \) (Et\(_2\)O) = 572 nm \((\varepsilon = 2030 \text{ M}^{-1}\text{cm}^{-1})\); \( \lambda_{\text{max}} \) (C\(_6\)H\(_6\)) = 572 nm \((\varepsilon = 2260 \text{ M}^{-1}\text{cm}^{-1})\). EPR (frozen toluene glass, 51 K; 9.020655 GHz, ModWidth = 0.25 mT, Power = 0.50 mW) \( g_1 = 2.133(5), g_2 = 2.036(5), g_3 = 2.031(5) \) (Figure 3.9 and 3.10).

![Figure 3.16](image.png)

**Figure 3.16.** Beer’s Law plot for [Cl\(_2\)NN]Cu-NHAd (2) in Et\(_2\)O at 25 °C.
Figure 3.17. Beer’s Law plot for [Cl₂NN]Cu-NHAd (2) in heptane at 25 °C.

Figure 3.18. Beer’s Law plot for [Cl₂NN]Cu-NHAd (2) in benzene at 25 °C.
Synthesis of $[\text{Cl}_2\text{NN}]\text{Cu(\text{NH}_2\text{Ad})}$. $^1$H NMR data for this compound was reported previously by the addition of 2 equiv. H$_2$NAd to $[[\text{Cl}_2\text{NN}]\text{Cu}]_2(\mu_1\text{-benzene})$\textsuperscript{36}.

To a suspension of $[[\text{Cl}_2\text{NN}]\text{Cu}]_2(\mu_1\text{-benzene})$ (0.200 g, 0.204 mmol) of in 10 mL Et$_2$O was added 1-adamantylamine (0.062 g, 0.408 mmol). The suspension turned bright yellow and was allowed to stir for 3 h at RT. All volatiles were removed in \textit{vacuo}. The remaining solid was extracted with 20 mL Et$_2$O and the suspension was filtered through Celite. The ether solution was concentrated and layered with pentane (final solution ~ 2:1 Et$_2$O : pentane) to afford 0.108 g (44%) yellow crystals suitable for single crystal X-ray diffraction. $^1$H NMR (C$_6$D$_6$): 7.13 (4, d, m-Ar-H), 6.40 (2, t, p-Ar-H), 5.00 (1, s, backbone), 1.87 (6, s, backbone-CH$_3$), 1.70 (2, br, N-H), 1.33 (9, m, Ad-H), 1.01 (6, br, Ad-H). $^{13}$C NMR \{H\} (C$_6$D$_6$): 123.00, 94.71, 36.36, 30.37, 24.12; IR: $\nu_{\text{NH}} = 3274$ and 3218 cm$^{-1}$; Anal. Calcd for C$_{27}$H$_{30}$Cl$_4$CuN$_3$: C, 53.88; H, 5.02; N, 6.98. Found: C, 54.08; H, 5.05; N, 6.96.
Figure 3.19. UV-vis spectrum of [Cl₂NN]Cu(NH₂Ad) in heptane (3.16 mM) at 25 °C (UV-vis silent above 500 nm).

Synthesis of [Cl₂NN]Cu-OBu⁴ (3). Di-tert-butyl peroxide (0.152 g, 4.17 mmol) was added to a stirring suspension of {[Cl₂NN]Cu}₃(μ-benzene) (1.000 g, 1.042 mmol) in ca. 10 mL toluene (-35 °C). The suspension was allowed to stir for ca. 10 minutes at RT and then the solvent was removed in vacuo. The remaining solid was taken up in 10 mL of pentane and allowed to stir for 5 min. Then, the suspension was filtered through Celite and concentrated for crystallization from n-pentane at -35 °C to yield 0.900 g (53%) of red crystals. X-ray quality crystals were obtained from pentane at -35 °C. UV/Vis \( \lambda_{\text{max}} \) (benzene) = 471 nm (\( \varepsilon = 2950 \text{ M}^{-1}\text{cm}^{-1} \)); Anal. Calcd for \( \text{C}_{21}\text{H}_{22}\text{Cl}_{4}\text{CuN}_{2}\text{O} \): C, 48.16; H, 4.23; N, 5.35. Found: C, 47.87; H, 4.31; N, 5.33.
3.3.3b. Stoichiometric C-H amination by [Cl₂NN]Cu-NHAd (2)

Owing to the extreme reactivity of [Cl₂NN]Cu-NHAd (2), it was freshly synthesized from {[Cl₂NN]Cu}₂[t-Cl]₂ prior to each set of stoichiometric reactions.

**General Procedure.** A solution of [Cl₂NN]Cu-NHAd (2) in ca. 5 mL cold (-35 °C) n-heptane was freshly prepared with a known amount of [Cl₂NN]Cu-NHAd (52.5 - 60 mg, 0.0874 – 0.0999 mmol). This solution was added to the appropriate amount of substrate (100 eq. indane, 100 eq. ethylbenzene, 1000 eq. diethyl ether). The reaction mixture was allowed to stir for 24 h at room temperature.
N-(2,3-dihydro-1H-inden-1-aminoadamantane). A solution of [Cl₂NN]Cu-NHAd (2) (60 mg, 0.0999 mmol) in 5 mL of cold heptane was prepared. This solution was added cold to a chilled portion of indane (1.24 mL, 1.20 g, 10.1 mmol). The reaction mixture was allowed warm to RT and stir for 24 hours at RT. The reaction was quenched outside the glovebox by exposing the sealed reaction vessel to air. The solution was allowed to stand in air for about 10 minutes before passing it through Celite. All volatiles were removed in vacuo. To the dried crude product was added 1,2,4,5-tetrachlorobenzene (10.8 mg, 0.0500 mmol) for ¹H NMR (CDCl₃) quantification with a characteristic peak at δ 4.35 ppm (t, 1H, benzylic AdNH-C-H). 81% yield. m/z (EI) = 267. (previously characterized by Badiei et al.)³⁶

N-(1-phenylethyl)-1-aminoadamantane. A solution of [Cl₂NN]Cu-NHAd (2) (52.5 mg, 0.0874 mmol) in 5 mL of cold heptane was prepared. This solution was added cold to a chilled portion of ethylbenzene (1.08 mL, 936 mg, 8.81 mmol). The reaction mixture was allowed warm to RT and stir for 24 hours at RT. The reaction was quenched outside the glovebox by exposing the sealed reaction vessel to air. The solution was allowed to stand in air for about 10 minutes before passing it through Celite. All volatiles were removed in vacuo. To the dried crude product was added 1,2,4,5-tetrachlorobenzene (9.5 mg, 0.0440 mmol) for ¹H NMR (CDCl₃) quantification with a characteristic peak at δ 4.06 ppm (q, 3H, benzylic AdNH-C-H). 87% yield. m/z (EI) = 255. (previously characterized by Badiei et al.)³⁶
**N-Benzyl-1-aminoadamantane and N-benzylidene-1-aminoadamantane.** A solution of [Cl₂NN]Cu-NHAd (2) (60 mg, 0.0999 mmol) in 5 mL of cold heptane was prepared. This solution was added cold to a chilled portion of toluene (1.07 mL, 928 mg, 10.1 mmol). The reaction mixture was allowed warm to RT and stir for 24 hours at RT. The reaction was quenched outside the glovebox by exposing the sealed reaction vessel to air. The solution was allowed to stand in air for about 10 minutes before passing it through Celite. All volatiles were removed in *vacuo*. To the dried crude product was added 1,2,4,5-tetrachlorobenzene (10.8 mg, 0.0500 mmol) for ¹H NMR (CDCl₃) quantification with a characteristic peak at δ 3.78 ppm (br, 2H, benzylic AdNH-C-H) 18% yield of amine; δ 8.26 ppm (s, 1H, AdN=C-H) 15% yield of imine. Amine: m/z (EI) = 241; imine: m/z (EI) = 239.

Using a solution of 2 (105 mg, 0.175 mmol) in 4 mL heptane added to 10 mL toluene (ca. 500 equiv.), this reaction was performed with at elevated temperature of 60 °C for 24 h to increase the yield of the amine product to 70% yield while keeping the imine product at 15% yield. (Both products previously characterized by Badiei et al.)³⁶

**N-adamantylimidoethane.** A solution of [Cl₂NN]Cu-NHAd (2) (60 mg, 0.0999 mmol) in 5 mL of cold heptane was prepared. This solution was added cold to a portion of diethyl ether (10.49 mL, 7.48 g, 101 mmol). The reaction mixture was allowed warm to RT and stir for 24 hours at RT. The reaction was quenched outside the glovebox by exposing the sealed reaction vessel to air. The solution was allowed to stand in air for about 10 minutes before passing it through Celite. All volatiles were removed in *vacuo*.
To the dried crude product was added 10.8 mg (0.0500 mmol) of 1,2,4,5-tetrachlorobenzene for $^1$H NMR (CDCl$_3$) quantification with a characteristic peak at $\delta$ 7.64 ppm (q, 1H, AdN=CHCH$_3$) and $\delta$ 1.95 ppm (d, 3H, AdN=CHCH$_3$) 44% yield of imine. m/z (EI) = 177. This imine has the same spectral characteristics as reported by Pearson et al.$^{63}$

3.3.c. Kinetic analyses monitored by UV-vis spectroscopy

UV-vis Sample Preparation

The solutions for kinetic analysis by UV-Vis spectroscopy were prepared using freshly prepared and crystallized [Cl$_2$NN]Cu-NHAd as described above.

General Procedure. A known amount of [Cl$_2$NN]CuNHAd was dissolved in cold heptane (-35 °C) to a known amount using a volumetric flask. A known portion of this diluted sample (approximate mol amount = $2 \times 10^{-6}$ mol of [Cl$_2$NN]CuNHAd) was taken and added to a 10 mL volumetric flask to which the appropriate amount of cold substrate (-35 °C) (indane or ethylbenzene) was added and diluted up to 10 mL using cold heptane (-35 °C). This sample was used for UV-Vis analysis.
3.3.d. UV-vis kinetics for the amination of ethylbenzene by [Cl$_2$NN]Cu-NHAd - kinetic studies for the amination of ethylbenzene by [Cl$_2$NN]Cu-NHAd (2) in heptane

A 25.0 mL stock solution of [Cl$_2$NN]Cu-NHAd (108 mg, 0.180 mmol) in cold heptane (-35 °C) was prepared from freshly synthesized [Cl$_2$NN]Cu-NHAd. From this stock solution was taken a 1.0 mL portions (7.2 × 10$^{-6}$ mol). To this portion was added 888 µL of ethylbenzene (1000 eq.) and diluted up to 10.0 mL with cold heptane. In a UV-vis experiment, the decreasing concentration of [Cl$_2$NN]Cu-NHAd over time was quantified by UV-vis spectroscopy by monitoring the decrease in intensity of the band due to (3) at $\lambda_{\text{max}}$ = 572 nm at temperature 25.0 °C (Figure 3.3). A plot of ln [A$_i$] vs. time gave a straight lines (Figure 3.4). The uncertainties in reported rate constants was estimated on the basis of inspection of the sensitivity of the fit of the ln [A$_i$] vs. time plots. The concentration of ethylbenzene was 0.724 M. From this plot $k_{\text{act}} = k_{\text{obs}} / 0.724$ M.

At 25 °C: \[ k_{\text{obs}} = 1.6(1) \times 10^{-5} \text{ s}^{-1} \]

Thus \[ k = 2.2(2) \times 10^{-5} \text{ M}^{-1}\text{s}^{-1} \] for rate = $k$[Cu-NHAd][ethylbenzene] assuming first-order dependence on [ethylbenzene] as observed in the amination of indane.

3.3.e. UV-vis kinetics for the stoichiometric amination of indane by [Cl$_2$NN]Cu-NHAd - explicit determination of order in [Cl$_2$NN]Cu-NHAd and indane

A 25.0 mL stock solution of [Cl$_2$NN]Cu-NHAd (116 mg, 0.193 mmol) in cold heptane (-35 °C) was prepared from freshly synthesized [Cl$_2$NN]Cu-NHAd. From this stock solution were taken four 2 mL portions. To each portion was added a different amount
of indane: 500, 1000, 1500, and 2000 equivalents respectively. Then, each portion was diluted up to 10.0 mL with cold heptane. In separate experiments, the decreasing concentration of [Cl₂NN]Cu-NHAd over time was quantified by UV-vis spectroscopy by monitoring the decrease in intensity of the band due to (3) at \( \lambda_{max} = 572 \) nm at temperature 25.0 °C (Figure 3.4). Data were generally taken for ca. 3 half-lives. Temperatures can be deemed accurate ± 0.1 °C. Plots of ln [Aₜ] vs. time gave straight lines (Figure 3.5) with observed rate constants that appear in Table 3.3. Uncertainties in reported rate constants were estimated on the basis of inspection of the sensitivity of the fits of the ln [Aₜ] vs. time plots. The concentrations of indane were 0.776, 1.55, 2.33, and 3.10 M, respectively.

A plot of \( k_{obs} \) vs. [indane] gives slope = 8.06 × 10⁻⁵. The second order rate constant for indane amination at 25 °C is thus: \( k = 8.1(2) \times 10^{-5} \) M\(^{-1}\)s\(^{-1}\) for rate = \( k[\text{Cu-NHAd}][\text{indane}] \). There is a modest non-zero (3.1 × 10⁻⁵) intercept suggesting a decomposition pathway not involving indane.

3.3.f. UV-vis kinetics for the stoichiometric amination of indane by [Cl₂NN]Cu-NHAd - temperature dependence for Eyring analysis

A 25.0 mL stock solution of [Cl₂NN]Cu-NHAd (140 mg, 0.233 mmol) in cold heptane (-35 °C) was prepared from freshly synthesized [Cl₂NN]Cu-NHAd. From this stock solution were taken four 1 mL portions. To each portion was added 1.15 mL of indane and diluted up to 10.0 mL with cold heptane. In separate experiments, the decreasing
concentration of [Cl\textsubscript{2}NN]Cu-NHAd over time was quantified by UV-vis spectroscopy by monitoring the decrease in intensity of the band due to 3 at \( \lambda_{\text{max}} = 572 \) nm at temperatures 20.0, 30.0, 40.0, and 50.0 °C. Temperatures can be deemed accurate ± 0.1 °C. Plots of ln \([A_t]\) vs. time gave straight lines over 3 half-lives with observed rate constants that appear in. Uncertainties in reported rate constants were estimated on the basis of inspection of the sensitivity of the fits of the ln \([A_t]\) vs. time plots. The concentration of indane was 0.939 M in each case, leading to second order rate constants \( k_{\text{act}} = k_{\text{obs}} / 0.939 \) M. Eyring analysis (Figure 3.6 and 3.7) gives \( \Delta H^\ddagger = 11.3(4) \) kcal/mol and \( \Delta S^\ddagger = 38.7(14) \) kcal/mol with \( \Delta G^\ddagger (298 \, \text{K}) = 22.9(8) \) kcal/mol. Error analysis in \( \Delta H^\ddagger \) and \( \Delta S^\ddagger \) follows that by Girolami \textit{et al.} using a assumed temperature error of ± 0.5 °C and assuming an average error of 4% in the absolute values of the rate constants.\textsuperscript{1}

3.3.g. Determination of KIE for amination of ethylbenzene by [Cl\textsubscript{2}NN]Cu-NHAd via competition experiments

A solution of [Cl\textsubscript{2}NN]Cu-NHAd (200 mg, 0.336 mmol) in 9.0 mL of cold heptane (-35 °C) was divided into three equal portions of 3.0 mL each. Three separate solutions of ethylbenzene-\textsubscript{d10} : ethylbenzene were prepared in the ratios 80:1, 50:1, and 20:1. The 80:1 solution consisted of ethylbenzene-\textsubscript{d10} (5.19 g, 0.0447 mol) and ethylbenzene (68.5 L, 59.4 mg, 0.559 mmol). The 50:1 solution consisted of ethylbenzene-\textsubscript{d10} (5.19 g, 0.0447 mol) and ethylbenzene (109.6 L, 95.0 mg, 0.895 mmol). The 20:1 solution consisted of ethylbenzene-\textsubscript{d10} (5.19 g, 0.0447 mol) and ethylbenzene (274 L, 237 mg,
2.24 mmol). One of the equal portions of \([\text{Cl}_2\text{NN}]\text{Cu-NHAd (2)}\) was added to each of the above described ethylbenzene-\(d_{10}\) : ethylbenzene solutions. The three reaction mixtures were allowed to react for 3 days at room temperature and analyzed by GC-MS. The relative yields of AdNHCH(Me)Ph and AdNHC(CD\(_3\))(C\(_6\)D\(_5\)) were determined by GC/MS integration against each other and by applying a response factor based on a previously 1:1 sample of pure compounds (AdNHCH(Me)Ph and AdNHC(CD\(_3\))(C\(_6\)D\(_5\))) to give their relative response factors. Averaging the three different runs gave a value \(k_H/k_D = 70(9)\).

![Sample GC/MS chromatogram (EI mode) illustrating baseline separation of isotopomers AdNHCD(CD\(_3\))(C\(_6\)D\(_5\)) and AdNHCH(Me)Ph.](image)

**Figure 3.21.** Sample GC/MS chromatogram (EI mode) illustrating baseline separation of isotopomers AdNHC(CD\(_3\))(C\(_6\)D\(_5\)) and AdNHCH(Me)Ph.
Determination of GC/MS response factors from a 1:1 molar mixture of AdNHCH(Me)Ph and AdNHCD(CD$_3$)(C$_6$D$_5$).

<table>
<thead>
<tr>
<th>1:1 Ratio</th>
<th>Integration AdNHCH(Me)Ph</th>
<th>Integration AdNHCD(CD$_3$)(C$_6$D$_5$)</th>
<th>Ratio</th>
<th>Avg. +/- St. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 1</td>
<td>2.57×10$^7$</td>
<td>2.28×10$^7$</td>
<td>1.13</td>
<td>1.13 +/- 0.006</td>
</tr>
<tr>
<td>Run 2</td>
<td>1.31×10$^7$</td>
<td>1.15×10$^7$</td>
<td>1.14</td>
<td></td>
</tr>
<tr>
<td>Run 3</td>
<td>1.78×10$^7$</td>
<td>1.57×10$^7$</td>
<td>1.13</td>
<td></td>
</tr>
</tbody>
</table>

The response factor was determined to be 1.13 ± 0.006.

Data from individual competition experiments used to determine KIE for HAA via competition experiments.

(i) 80:1

<table>
<thead>
<tr>
<th>80:1</th>
<th>Integr. 1</th>
<th>Integr. 2</th>
<th>Integr. 3</th>
<th>Integr. 4</th>
<th>Avg. +/- St. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AdNHCH(Me)Ph</td>
<td>72.7</td>
<td>74.6</td>
<td>71.9</td>
<td>71.3</td>
<td>72.6 +/- 1.44</td>
</tr>
<tr>
<td>AdNHCD(CD$_3$)(C$_6$D$_5$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Retention Coefficient Correction:
(72.6+1.44) / 1.13 = 71.16
(72.6-1.44) / 1.13 = 62.97
Avg = 67.1 ± 5.79 (EtB/d-EtB)

(ii) 50:1

<table>
<thead>
<tr>
<th>50:1</th>
<th>Integr. 1</th>
<th>Integr. 2</th>
<th>Integr. 3</th>
<th>Integr. 4</th>
<th>Avg. +/- St. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtB / d-EtB</td>
<td>86.9</td>
<td>94.8</td>
<td>90.4</td>
<td>89.1</td>
<td>90.3 +/- 3.33</td>
</tr>
</tbody>
</table>

Retention Coefficient Correction:
(90.3+3.33) / 1.13 = 82.9
(90.3-3.33) / 1.13 = 77.0
Avg = 80.0 ± 4.17 (EtB/d-EtB)

(iii) 20:1

<table>
<thead>
<tr>
<th>20:1</th>
<th>Integr. 1</th>
<th>Integr. 2</th>
<th>Integr. 3</th>
<th>Integr. 4</th>
<th>Avg. +/- St. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtB / d-EtB</td>
<td>70.5</td>
<td>68.9</td>
<td>71.4</td>
<td>67.9</td>
<td>69.7 +/- 1.57</td>
</tr>
</tbody>
</table>

Retention Coefficient Correction:
(69.7+1.57) / 1.13 = 63.1
(69.7-1.57) / 1.13 = 60.3
Avg = 61.7 ± 1.98 (EtB/d-EtB)
Thus, the average $k_{H} / k_{D} = 70(9)$ for the amination of ethylbenzene / ethylbenzene-$d_{10}$ at RT.

3.3.h. **Generation of $[\text{ClNN}]\text{Cu-NHAd}$ from $[\text{ClNN}]\text{Cu-OBu}'$ – observation by UV-vis**

A solution of $[\text{ClNN}]\text{Cu-O'Bu} (0.015g, 0.029 mmol) was prepared in cold (-35 °C) diethyl ether by dilution to 25 mL using a volumetric flask. 1.00 mL of that solution was diluted to 2 mL using cold diethyl ether in a volumetric flask and transferred to a UV-vis cuvette ($1.15 \times 10^{-6} \text{ mol } [\text{ClNN}]\text{Cu-OtBu}; 0.577 \text{ mM}$). The cuvette was placed in the UV-vis instrument and thermostated to -20 °C after which the UV-vis spectrum of $[\text{ClNN}]\text{Cu-O'Bu}$ was obtained ($\lambda_{\text{max}} = 471 \text{ nm}$). Via syringe, excess adamantylamine (4 eq., 17 mg, 0.115 mmol, 0.115 M solution) was added as a suspension in 1 mL of chilled ether to give $[\text{ClNN}]\text{Cu-NHAd}$ (2) observed by its absorbance at $\lambda = 572 \text{ nm}$ with loss of $[\text{ClNN}]\text{Cu-OBu}' (\lambda = 471 \text{ nm})$.

3.3.i. **Determination of equilibrium constant for alcohol / amine exchange**

$[\text{ClNN}]\text{Cu-NHAd} + \text{HOBu}' \xrightleftharpoons[K_{eq}]{} [\text{ClNN}]\text{Cu-OBu}' + \text{AdNH}_2$

A stock solution of $[\text{ClNN}]\text{Cu-NHAd}$ (2) (0.480 g, 0.799 mmol) was prepared in 100.0 mL of benzene using a volumetric flask, maintaining it just above the freezing point of benzene. Four equal portions were taken from this stock solution of 25 mL each (0.200 mmol of $[\text{ClNN}]\text{Cu-NHAd}$ (2)). 1 eq. of $'\text{BuOH}$ (19 L, 14.8 mg, 0.200 mmol) was added to the first portion. 1.0 mL of that solution was taken and diluted up to 10.0 mL with chilled benzene. To the second portion was added 2 eq. of $'\text{BuOH}$ (38 L, 29.6 mg,
0.400 mmol). From this solution was taken 1.0 mL and diluted up to 10 mL with cold benzene. 3 eq. of tBuOH (57 L, 44.5 mg, 0.600 mmol) were added to the third portion. 1.0 mL of that solution was taken and diluted up to 10.0 mL with cold benzene. And 4 eq. of tBuOH (76 L, 59.3 mg, 0.800 mmol) were added to the fourth portion. 1.0 mL of that solution was taken and diluted up to 10.0 mL with cold benzene. Separate UV-vis experiments were performed on each portion keeping the temperature constant at 25.0 °C. The UV-vis experiment for each portion observed absorbance for the λ\text{max} of [Cl\textsubscript{2}NN]Cu-NHAd (3) and [Cl\textsubscript{2}NN]Cu-O\textsuperscript{t}Bu.

<table>
<thead>
<tr>
<th>tBuOH equiv.</th>
<th>λ\text{max} Cu-NHAd</th>
<th>λ\text{max} Cu-O\textsuperscript{t}Bu</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 eq.</td>
<td>573 nm</td>
<td>493 nm</td>
</tr>
<tr>
<td>2 eq.</td>
<td>572 nm</td>
<td>481 nm</td>
</tr>
<tr>
<td>3 eq.</td>
<td>572 nm</td>
<td>475 nm</td>
</tr>
<tr>
<td>4 eq.</td>
<td>572 nm</td>
<td>473 nm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>[tBuOH]\text{initial}</th>
<th>Abs Cu-\textsuperscript{O}Bu</th>
<th>Cu-NHAd</th>
<th>Abs Cu-NHAd</th>
<th>[Cu-NHAd]\text{obs}</th>
<th>[Cu-O\textsuperscript{t}Bu]\text{obs}</th>
<th>[Cu-NHAd]\text{initial}</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.01×10\textsuperscript{-4} M</td>
<td>0.773</td>
<td>1.07</td>
<td>4.73×10\textsuperscript{-4} M</td>
<td>2.62×10\textsuperscript{-4} M</td>
<td>7.99×10\textsuperscript{-4} M</td>
<td></td>
</tr>
<tr>
<td>1.60×10\textsuperscript{-3} M</td>
<td>0.791</td>
<td>0.798</td>
<td>3.53×10\textsuperscript{-4} M</td>
<td>2.68×10\textsuperscript{-4} M</td>
<td>7.99×10\textsuperscript{-4} M</td>
<td></td>
</tr>
<tr>
<td>2.40×10\textsuperscript{-3} M</td>
<td>0.776</td>
<td>0.625</td>
<td>2.76×10\textsuperscript{-4} M</td>
<td>2.63×10\textsuperscript{-4} M</td>
<td>7.99×10\textsuperscript{-4} M</td>
<td></td>
</tr>
<tr>
<td>3.20×10\textsuperscript{-3} M</td>
<td>0.789</td>
<td>0.541</td>
<td>2.39×10\textsuperscript{-4} M</td>
<td>2.67×10\textsuperscript{-4} M</td>
<td>7.99×10\textsuperscript{-4} M</td>
<td></td>
</tr>
</tbody>
</table>

**Keq Results: (0.26(5))**

Keq = [Cu-O\textsuperscript{t}Bu]\text{obs}[AdNH\textsubscript{2}]\text{act} / [Cu-NHAd]\text{obs}[tBuOH]\text{act}

**Assumptions:**

[tBuOH]\text{act} = [tBuOH]\text{initial} − [Cu-OtBu]\text{obs}

[AdNH\textsubscript{2}]\text{act} = [Cu-NHAd]\text{initial} − [Cu-OtBu]\text{obs}

<table>
<thead>
<tr>
<th>Keq</th>
<th>Keq</th>
<th>Keq</th>
<th>Keq</th>
<th>Avg. +/- St. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.334</td>
<td>0.253</td>
<td>0.232</td>
<td>0.213</td>
<td>0.258 +/- 0.053</td>
</tr>
</tbody>
</table>
Keq for amine – alcohol exchange (reverse reaction: 4(1))

3.3.j. Initial Catalytic C-H Amination Reactions of Indane, Ethylbenzene and Toluene with \( \text{H}_2\text{NAd} \) and \( \text{tBuOOBu} \) – high catalyst loadings (10 mol% \( \{\text{Cl}_2\text{NN}][\text{Cu}\}_{2}(\mu-\text{benzene}) \))

All C-H amination products were identified by comparison of their GC/MS and \( ^1\text{H} \) NMR spectra with those reported by Badiei et al. and/or products obtained in the low catalyst loading experiments. In each case yields were monitored by \( ^1\text{H} \) NMR using an internal standard (1,2,4,5-tetrachlorobenzene; 110 mg, 0.510 mmol) added after the reaction had been deemed complete.\(^{36}\)

\text{N-(2,3-dihydro-1H-inden-1-aminoadamantane).} \ 1\text{-adamantylamine (0.077 g, 0.510 mmol) and 10 equiv. indane (625 L; 0.603 g, 5.10 mmol), di-\text{t}-butylperoxide (93 L, 0.075 g, 0.510 mmol) were added to a solution containing 10 mol\% } \{\text{Cl}_2\text{NN}][\text{Cu}\}_{2}(\text{benzene}) (0.050 g, 0.051 mmol) \text{ in 3 mL heptane. The resultant mixture turned dark purple and was allowed to react at room temperature for 5 days or was transferred to a sealed pressure vessel and heated at 50 °C for 24 hours to give the C-H amination product in 78% or 88% yield, respectively, as monitored by } ^1\text{H} \text{ NMR using an internal standard (1,2,4,5-tetrachlorobenzene) added after the reaction was stopped. m/z + 1\text{H}^+ (\text{Cl}) = 268.} \n
\text{N-(1-phenylethyl)-1-aminoadamantane.} \ 1\text{-adamantylamine (0.077 g, 0.510 mmol) and 10 equiv. ethylbenzene (626 L; 542 mg, 5.10 mmol), di-\text{t}-butylperoxide (93 L,}
0.075 g, 0.510 mmol) were added to a solution containing 10 mol % \([\text{Cl}_2\text{NN}]\text{Cu}\)\(_2\)(benzene) (0.050 g, 0.051 mmol) in 3 mL heptane. The resultant mixture turned dark purple and was allowed to react at room temperature for 5 days or was transferred to a sealed pressure vessel and heated at 50 °C for 24 hours to give the C-H amination product in 55% or 31% yield, respectively, as monitored by \(^1\)H NMR using an internal standard (1,2,4,5-tetrachlorobenzene) added after the reaction was stopped. m/z + 1H\(^+\) (CI) = 256.

**N-Benzyl-1-aminoadamantane and N-benzyldiene-1-aminoadamantane.** 1-adamantylamine (0.077 g, 0.510 mmol) and neat toluene (10 mL), di-\(\tau\)-butylperoxide (93 \(\mu\)L; 0.075 g; 0.510 mmol) were added to a solution containing 10 mol % \([\text{Cl}_2\text{NN}]\text{Cu}\)\(_2\)(benzene) (0.050 g, 0.051 mmol). The resultant mixture turned dark purple and was allowed to react at room temperature for 5 days or was transferred to a sealed pressure vessel and heated at 50 °C for 24 hours. Amine / imine product mixtures were formed. Imine: m/z + 1H\(^+\) (CI) = 240; amine: m/z + 1H\(^+\) (CI) = 242.

3.3.k. Procedures for Catalytic C-H amination at low catalyst loadings

(0.5 mol% \([\text{Cl}_2\text{NN}]\text{Cu}\)\(_2\)(\(\mu\)-benzene) = 1 mol% \[\text{Cl}_2\text{NN}]\text{Cu}\))

**Catalyst stock solution preparation.** A stock solution was prepared by dissolving \([\text{Cl}_2\text{NN}]\text{Cu}\)\(_2\)(benzene) (96.2 mg, 0.100 mmol) in 10 mL of benzene in a volumetric flask to give a 0.01 M solution based on \([\text{Cu}]_2\) or 0.02 M based on mononuclear \([\text{Cu}]\).
Neat C-H substrate (isolation of secondary amine products).

A reaction mixture was prepared inside the glovebox consisting of 1.0 mmol amine (1.0 eq.), 1.2 mmol di-$t$-butyl peroxide (1.2 eq., 292 mg), and neat C-H substrate (20.0 mL). To this reaction mixture was added 1 mol % $[\text{Cl}_2\text{NN}]\text{Cu}$ (0.5 mol% $\{[\text{Cl}_2\text{NN}]\text{Cu}\}_2$ (benzene)) from the catalyst stock solution described above (0.500 mL = 0.005 mmol $\{[\text{Cl}_2\text{NN}]\text{Cu}\}_2$ (benzene)). The reactions were allowed to stir inside a sealed pressure vessel at 90 °C for 24 h. Afterwards the reaction mixture was allowed to cool passed through Celite and all volatiles were removed under vacuum. The remaining oil was taken up in 5 mL of Et$_2$O/CH$_2$Cl$_2$ (1:1 / v:v) and passed through a 1 cm silica filter stick. 5 mL of this solvent mixture were used to push the oil through. All volatiles are then removed under vacuum. To isolate the desired as the HCl salt, the dried oil was taken up in 10 mL of hexanes and 1 eq. (0.5 mL) of 2 M HCl in Et$_2$O was added. The salt precipitates out immediately. The heterogeneous suspension is then placed in an ultrasonic bath for 3 min or until the precipitate breaks up entirely. This suspension is then placed in the freezer overnight. Finally, the HCl salt is isolated on a filter paper and washed with 15 mL of cold pentane.

**3.3.k. 10 eq. C-H substrate and 1 equiv. C-H substrate (isolation of secondary amine products)**

A reaction mixture was prepared inside the glovebox consisting of 1.0 mmol amine (1.0 eq.), 1.2 mmol di-$t$-butyl peroxide (1.2 eq.), 10 mmol C-H substrate (10 eq.) or 1.0 mmol C-H substrate and 5.0 mL benzene. To this reaction mixture was added 1 mol %
[Cl\textsubscript{2}NN]Cu (0.5 mol\% \{[Cl\textsubscript{2}NN]Cu\}_2(benzene)) from the catalyst stock solution described above (0.500 mL = 0.005 mmol \{[Cl\textsubscript{2}NN]Cu\}_2(benzene)). The reactions were allowed to stir inside a sealed pressure vessel at 90 °C for 24 h if 10 equiv. of C-H substrate is used and 72 h if 1 equiv. of C-H substrate was used. Afterwards the reaction mixture was allowed to cool passed through Celite and all volatiles were removed under \textit{vacuo}. The remaining oil was taken up in 5 mL of Et\textsubscript{2}O/CH\textsubscript{2}Cl\textsubscript{2} (1:1 / v:v) and passed through a 1 cm silica filter stick. 5 mL of this solvent mixture were used to push the oil through. All volatiles are then removed under \textit{vacuo}. To isolate the desired as the HCl salt, the dried oil was taken up in 10 mL of hexanes and 1 eq. (0.5 mL) of 2 M HCl in Et\textsubscript{2}O was added. The salt precipitates out immediately. The heterogeneous suspension is then placed in an ultrasonic bath for 3 min or until the precipitate breaks up entirely. This suspension is then placed in the freezer overnight. Finally, the HCl salt is isolated on a filter paper and washed with 15 mL of cold pentane.

\textit{3.3.l. General procedure for recrystallization of amine HCl salts}

The amine HCl salt was dissolved in minimal amount of MeOH using an ultrasound bath with slight heating. The solution was concentrated by evaporating some MeOH. To this saturated solution was added pentane and topped off with Et\textsubscript{2}O (roughly as much Et\textsubscript{2}O as MeOH and 8 mL of pentane; the order of solvents is important to allow for slow crystallization). This solution was then placed in the freezer overnight. The recrystallized amine HCl salt was collected via vacuum filtration and washed with cold pentane.
3.3.m. Neutralizing HCl salts of C-H amination products

The isolated HCl salts of the desired product was added to a biphasic solution of 75 mL saturated sodium bicarbonate and 75 mL CH₂Cl₂. This biphasic mixture is then stirred vigorously for 10 minutes. The organic layer is isolated washed with 50 mL of water and dried over MgSO₄. All volatiles were removed under vacuo to isolate the neutral form of the desired compounds.

3.3.n. Neat C-H substrate (isolation of morpholine-based tertiary amine products) developed in collaboration with Raymond Gephart

A reaction mixture was prepared inside the glovebox consisting of 1.0 mmol morpholine (1.0 equiv. = 96.2 μL, 87.1 mg), 1.2 mmol di-t-butylperoxide (1.2 eq., 292 mg), and neat C-H substrate (20.0 mL). To this reaction mixture was added 1 mol % [Cl₂NN]Cu (0.5 mol% [[Cl₂NN]Cu]₂(benzene)) from the catalyst stock solution described above (0.500 mL = 0.005 mmol [[Cl₂NN]Cu]₂(benzene)). The reactions were allowed to stir inside a sealed pressure vessel at 90 °C for 24 h. Afterwards the reaction mixture was allowed to cool passed through Celite and all volatiles were removed under vacuo. The resulting oil was dissolved in CH₂Cl₂ and passed through a short silica column. After the silica column has been washed through with 200 mL of CH₂Cl₂, the solvent is changed to MeOH. This drives the product off the column with 200 mL of MeOH. The MeOH was removed under vacuo to yield the pure product.
3.3.o. 10 equiv. C-H substrate and 1 equiv. C-H substrate (1H NMR yields of morpholine-based tertiary amine products)

A reaction mixture was prepared inside the glovebox consisting of 1.0 mmol amine (1.0 eq.), 1.2 mmol of di-t-butyl peroxide (1.2 eq., 292 mg), 10 mmol C-H substrate (10 eq.) or 1.0 mmol C-H substrate, 1.0 mmol 1,2,4,5-tetrachlorobenzene (1.0 eq.) and 5.0 mL of benzene. To this reaction mixture was added 1 mol % \([\text{Cl}_2\text{NN}]\text{Cu}\) (0.5 mol% \([\text{Cl}_2\text{NN}]\text{Cu}\)_2(benzene)) from the catalyst stock solution described above (0.500 mL = 0.005 mmol \([\text{Cl}_2\text{NN}]\text{Cu}\)_2(benzene)). The reactions were allowed to stir inside a sealed pressure vessel at 90 °C for 72 h. Afterwards the reaction mixture was allowed to cool passed through Celite and all volatiles were removed under \textit{vacuo}. Afterwards the reaction mixture was allowed to cool, passed through Celite and all volatiles were removed under \textit{vacuo}. Yields were characterized by 1H NMR by comparison to 1,2,4,5-tetrachlorobenzene in CDCl₃.

3.3.p. Characterization of new C-H amination products

(All C-H amination products with H₂NAd have been previously characterized as HCl salts by Badiei \textit{et al.}³⁶)

\[ \text{N-Benzyl-1-aminocyclohexane: HCl salt.} \] (neat C-H substrate: 73% yield; 10 eq. C-H substrate: 52% yield; 1 eq. C-H substrate: 15% yield)

1H NMR (CDCl₃, 400 MHz) \( \delta \) 9.87 (br s, 1, N-H), 9.58 (br s, 1, N-H), 7.66 (d, 2, Ar-H), 7.43-7.33 (m, 3, Ar-H), 4.36 (br s, 1, benzylic-CH), 2.54 (m, 1, CH), 2.31 (br, 1, CH), 1.77-1.51 (m, 8, CH), 1.16 (m, 4, CH); 13C\{1H\} NMR (CDCl₃): \( \delta \) 136.73, 129.63,
N-(2,3-dihydro-1H-inden-1-aminocyclohexane): HCl salt. (neat C-H substrate: 73% yield; 10 eq. C-H substrate: 52% yield; 1 eq. C-H substrate: 17% yield) $^1$H NMR (CDCl$_3$, 400 MHz) δ 9.64 (br s, 1, N-H), 9.15 (br s, 1, N-H), 7.72 (d, 2, Ar-H), 7.19 (br, 2, Ar-H), 4.65 (br s, 1, benzylic-CH), 3.58-3.51 (m, 1, CH), 2.95 (br, 1, CH), 2.86-2.80 (m, 1, CH), 2.35-2.31 (m, 2, CH), 2.17 (t, 2, CH), 1.78 (br s, 1, CH), 1.65-1.58 (m, 3, CH) (overlaps with the previous peak), 1.24-1.71 (m, 3, CH), 0.86 (m, 1, CH); $^{13}$C{$^1$H} NMR (CDCl$_3$): δ 145.93, 136.57, 129.83, 127.14, 126.80, 125.53, 59.59, 56.07, 30.98, 29.69, 29.67, 29.14, 25.10, 25.06, 24.94. Anal. Calcd for C$_{16}$H$_{28}$ClN: C, 71.55; H, 10.46; N, 5.19. Found: C, 70.89; H, 10.67; N, 5.15.

N-Cyclohexyl-1-aminoadamantane: HCl salt. (neat C-H substrate: 91% yield) $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.85 (br s, 2, N-H), 3.07 (br, 1, C-H), 2.21-2.15 (br, 10, C-H), 1.70-1.60 (m, 10, C-H), 1.28-1.06 (m, 10, C-H); $^{13}$C{$^1$H} NMR (CDCl$_3$): δ 59.09, 52.91, 38.99, 35.81, 32.97, 29.36, 25.47, 25.04. Anal. Calcd for C$_{16}$H$_{28}$ClN: C, 71.21; H, 10.46; N, 5.19. Found: C, 70.89; H, 10.67; N, 5.15.

N-phenethylcyclohexanamine: HCl salt. (neat C-H substrate: 61% yield) $^1$H NMR (CDCl$_3$, 400 MHz) δ 9.61 (br s, 2, N-H), 7.28-7.21 (m, 5, Ar-H) (overlaps with CDCl$_3$ peak), 3.30-3.29 (m, 2, Et-H), 3.17-3.13 (m, 2, Et-H), 2.96 (br t, 1, C-H), 2.27 (d, 2, C-H), 1.82 (br, 2, C-H), 1.63 (br, 2, C-H), 1.23 (br, 3, C-
$^1$H NMR (CDCl$_3$): $\delta$ 137.08, 129.06, 128.92, 57.76, 46.25, 32.63, 29.50, 25.02, 24.78. Anal. Calcd for C$_{14}$H$_{22}$ClN: C, 70.13; H, 9.25; N, 5.84. Found: C, 69.95; H, 9.15; N, 5.94.

**Dicyclohexylamine: HCl salt.** (neat C-H substrate: 70% yield) $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 9.09 (br s, 2, N-H), 3.05 (br, 2, C-H), 2.21 (d, 4, C-H), 1.81-1.62 (m, 10, C-H), 1.22-1.19 (m, 6, C-H); $^{13}$C $\{$$^1$H\} NMR (CDCl$_3$): $\delta$ 54.01, 29.49, 25.05. Anal. Calcd for C$_{12}$H$_{24}$ClN: C, 66.18; H, 11.11; N, 6.43. Found: C, 65.82; H, 11.46; N, 6.52.

**N-phenethyl-1-phenylethanamine: HCl salt:** (neat C-H substrate: 81% yield; 10 eq. C-H substrate: 49% yield) $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 10.46 (br s, 1, N-H), 10.08 (br s, 1, N-H), 7.60 (d, 2, Ar-H), 7.40 (t, 2, Ar-H), 7.35 (d, 1, Ar-H), 7.21 (m, 2, Ar-H), 7.09 (d, 2, Ar-H), 4.23 (br, 1, benzylic-CH), 3.37-3.29 (m, 2, ethyl-CH), 3.25-3.17 (m, 2, ethyl-CH), 2.89 (br, 2, benzylic-CH$_2$), 1.93 (d, 3, CH$_3$); $^{13}$C $\{$$^1$H\} NMR (CDCl$_3$): $\delta$ 136.99, 136.15, 129.71, 129.61, 128.94, 128.92, 128.01, 127.17, 59.43, 47.43, 32.54, 20.97. Anal. Calcd for C$_{16}$H$_{20}$ClN: C, 73.41; H, 7.70; N, 5.35. Found: C, 73.06; H, 7.61; N, 5.32.

**N-phenethyl-2,3-dihydro-1H-inden-1-amine: HCl salt:** (neat C-H substrate: 74% yield; 10 eq. C-H substrate: 59% yield; 1 eq. C-H substrate: 24% yield) $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 10.22 (br d, 2, N-H), 7.91 (t, 1, Ar-H), 7.35-7.22 (m, 8, Ar-H) (overlaps with CDCl$_3$ peak), 4.72 (br, 1, benzylic-
$C\text{H}$, 3.42 (qnt, 1, indan-$C\text{H}$), 3.33-3.19 (m, 2, indan-$C\text{H}$), 3.10-3.03 (br m, 1, indan-$C\text{H}_2$), 3.01-2.94 (br, m, ethyl-$C\text{H}_2$) (overlaps with previous peak) 2.53-2.48 (m, 2, benzyl-$C\text{H}_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl$_3$): $\delta$ 145.32, 137.11, 136.02, 130.14, 129.04, 128.95, 127.30, 127.18, 126.92, 125.49, 62.44, 45.86, 32.61, 31.02, 28.46. Anal. Calcd for C$_{17}$H$_{20}$ClN: C, 74.57; H, 7.36; N, 5.12. Found: C, 74.29; H, 7.53; N, 5.10.

**$N$-(1-phenylethyl)-1-aminoadamantane HCl salt:** (Neat C-H substrate: 93% yield; 10 eq. substrate C-H: 65% yield) $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 9.38 (br s, 2, N-H), 7.76 (d, 2, Ar-H), 7.40-7.32 (m, 3, Ar-H), 4.46 (m, 1, benzyl-$C\text{H}$), 2.09-1.95 (m, 9, Ad-$C\text{H}$), 1.85 (d, 3, CH$_3$), 1.55 (br s, 6, Ad-$C\text{H}_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl$_3$, 400 MHz) $\delta$ 139.38, 129.14, 128.70, 127.65, 60.14, 54.73, 39.47, 35.38, 29.24, 23.51.$^1$

**$N$-(2,3-dihydro-1$H$-inden-1-aminoadamantane) HCl salt:** (Neat C-H substrate: 98% yield; 10 eq. substrate C-H: 83% yield) $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 9.60 (br s, 1, N-H), 8.70 (br s, 1, N-H), 7.78 (d, 1, Ar-H), 7.24-7.16 (m, 3, Ar-H), 4.65 (br s, 1, benzyl-$C\text{H}$), 3.50 (qnt, 1, indane-$C\text{H}$), 2.86-2.79 (m, 1, indan-$C\text{H}_2$), 2.70-2.65 (m, 1, indan-$C\text{H}$), 2.37-2.27 (m, 1, indan-$C\text{H}_2$), 2.03 (br s, 3, Ad-$C\text{H}_2$), 2.00 (br s, 6, Ad-$C\text{H}_2$) (overlaps with previous peak), 1.61 (br s, 6, Ad-$C\text{H}_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl$_3$, 400 MHz) $\delta$ 144.97, 136.87, 129.13, 127.92, 126.34, 124.29, 59.37, 56.99, 38.35, 35.43, 31.21, 30.94, 29.17.$^1$
4-(2,3-dihydro-1H-inden-1-yl)morpholine: (Neat C-H substrate: 77% yield; 10 eq. substrate 40% yield) $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.37 (tr, 1, Ar-H), 7.22 (m, 3, Ar-H), 4.31 (tr, 1, benzylic-CH), 3.72 (m, 4, morpholine-CH$_2$), 2.95 (m, 1, indan-CH$_2$), 2.83 (m, 1, indan-CH$_2$), 2.54 (m, 4, morpholine-CH$_2$), 2.11 (m, 2, benzylic-CH$_2$); $^{13}$C{$_1^1$H} NMR (CDCl$_3$, 400 MHz) δ 144.15, 142.28, 127.48, 126.04, 125.42, 124.62, 70.07, 67.39, 49.09, 30.87, 24.56; Anal Calcd for C$_{13}$H$_{17}$NO: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.42; H, 8.23; N, 6.72.

4-(1-Phenylethyl)-morpholine: (Neat C-H substrate: 53% yield; 10 eq. substrate 40% yield) $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.31 (m, 4, Ar-H), 7.23 (m, 1, Ar-H), 3.69 (tr, 4, morpholine-CH$_2$), 3.30 (q, 1, benzylic-CH$_2$), 2.47 (m, 2, morpholine-CH$_2$), 2.37 (m, 2, morpholine-CH$_2$), 1.35 (d, 3, CH$_3$); $^{13}$C{$_1^1$H} NMR (CDCl$_3$, 400 MHz) δ 143.89, 128.25, 127.59, 126.93, 67.20, 65.37, 51.28, 19.80. Previously characterized by Tillack et al.$^{64}$

4-cyclohexylmorpholine: (neat C-H substrate 2% yield). Independent synthesis for identification and quantification by GC/MS followed procedure by Alinezhad et al.$^{65,66}$ With a mortar and pestle, silica-gel-supported sulfuric acid (SSA) (4.0 g), cyclohexanol (1.96 g, 20.0 mmol), morpholine (1.74 g, 20.0 mmol), and sodium borohydride (757 mg, 20.0 mmol) were ground together for 3 min. Then a solvent mixture consisting of hexanes/ethyl acetate (10:1) was used to extract the crude material from the solid via vacuum filtration. All volatiles were removed in vacuo and
the crude oil was loaded onto a silica column. First 250 mL of CH$_2$Cl$_2$ were used to wash through the column, followed by 250 mL of MeOH to extract the desired product. All volatiles were removed in vacuo and the remaining slightly yellow oil was passed through a filter stick with 1 cm of silica gel using 10 mL of CH$_2$Cl$_2$ as the mobile phase. After removing all volatiles in vacuo a colorless oil resulted in 10% yield (348 mg, 2.06 mmol). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 3.68 (t, 4, Morph-H), 2.52 (t, 4, Morph-H), 2.17-2.12 (m, 1, Cy-H), 1.86-1.84 (m, 4, Cy-H), 1.61-1.58 (m, 1, Cy-H), 1.26-1.06 (m, 5, Cy-H); $^{13}$C{$^1$H} NMR (CDCl$_3$, 400 MHz) $\delta$ 67.70, 63.95, 49.93, 29.11, 26.50, 25.93.

Silica-gel-supported sulfuric acid (SSA) was prepared according to Lakouraj and Akbari: 66 30.0 grams of silica gel and 2 mL of sulfuric acid (conc. H$_2$SO$_4$) in 30 mL MeOH were added together and stirred for 20 min. The slurry was dried under vacuo at 45 - 50 °C for 4 h to produce a white solid.

3.3.q. In-situ UV-vis analysis of catalytic reaction

Emulating the initial concentrations of substrates and catalyst in the catalytic reactions described above, a stock solution was prepared consisting of 1-adamantylamine (219 mg, 1.45 mmol), di-t-butylperoxide (318 L, 1.74 mmol), indane (1.78 mL, 14.5 mmol), [Cl$_2$NN]Cu(C$_6$H$_6$)$_{0.4}$ (7 mg from a stock solution in benzene) in 25.0 mL benzene. Approximately 3 mL was transferred to an air-tight UV-vis cell which was thermostated at either 30 °C, 50 °C, or 75 °C for 250 min. UV-vis spectra taken every 30 s shows isosbestic growth of [Cl$_2$NN]Cu-NHAd (2) from the anticipated [Cl$_2$NN]Cu(NH$_2$Ad) resting state. This solution was kept at -35 °C prior to use. Based
on the extinction coefficient of [Cl₂NN]Cu-NHAd in benzene, the mole fraction of the initially used [Cl₂NN]Cu as [Cl₂NN]Cu-NHAd was plotted.

3.3.r. Comparison of concentrations for catalytic C-H amination and spectroscopy

General catalytic reactions (10 equiv. substrate in benzene): 1.0 mmol amine (0.05 M), [Cu] $1.0 \times 10^{-5}$ mol (0.0005 M; [Cu] = [Cl₂NN]Cu), 1.2 mmol tBuOOBu (0.06 M), 10.0 mmol C-H substrate (0.5 M); each initially in 20.0 mL benzene.

UV-vis reaction: 1.45 mmol amine (0.058 M), [Cu] $1.45 \times 10^{-5}$ mol (0.00058 M), 1.74 mmol tBuOOBu (0.070 M), 14.5 mmol C-H substrate (0.58 M); each initially in 25.0 mL benzene.

3.3.s. DFT calculation details – electronic structure

Electronic structure, TD-DFT and EPR calculations on [Cl₂NN]Cu-NHAd (2) employed the Becke-Perdew exchange correlation (XC) functional using the Amsterdam Density Functional suite of programs (ADF 2007.01). The LDA (local density approximation) portion of the XC functional was that of VWN (Vosko, Wilk, and Nusair) functional. Slater-type orbital (STO) basis sets employed for H, C, and N atoms were of triple-$\zeta$ quality augmented with two polarization functions (ZORA/TZ2P) while an improved triple-$\zeta$ basis set with two polarization functions (ZORA/TZ2P+) was employed for the Cu atom. Scalar relativistic effects were included by virtue of the zero order regular approximation (ZORA). The 1s electrons of C and N as well as the 1s – 2p electrons of Cu were frozen. Mostly default
convergence ($\Delta E = 1 \times 10^{-4}$ Hartree (default = $1 \times 10^{-3}$ hartree), max. gradient = $1 \times 10^{-2}$ Hartree / Å, max. Cartesian step = $1 \times 10^{-2}$ Å) and integration (4 significant digits) parameters were employed for geometry optimizations. 

Experimental X-ray coordinates for [Me₂NN]Cu-NHAd (2) were used as the starting point for the geometry optimization of [Me₂NN]Cu-NHAd in an unrestricted (S = 1/2) calculation specifying 1 unpaired electron (spin $\alpha$ – spin $\beta$). ADFview\textsuperscript{72} was used to prepare the three-dimensional representations of the structures as well as to render the Kohn-Sham MOs.

3.3.t. EPR Spectra collected and simulated by Dr. Susanne Mossin

General X-Band EPR Details. The EPR measurements were performed in quartz tubes with J. Young valves. Solution EPR spectra were recorded on a JEOL continuous wave spectrometer JES-FA200 equipped with an X-band Gunn oscillator bridge, a cylindrical mode cavity, and a helium cryostat. For all samples, a modulation frequency of 100 kHz and a time constant of 0.1 s were employed.(ref to paper) Spectral simulation was performed using the program QCMP 136 by Prof. Dr. Frank Neese from the Quantum Chemistry Program Exchange as used by Neese et al.\textsuperscript{77}.

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Chapter 4

Synthesis and Exploratory Reactivity of an Electron-Deficient Copper β-
Diketiminato Catalyst

Abstract

We prepared the electron-deficient β-diketiminato copper(I) catalyst 
{[Cl₂NN₆]Cu₂(μ-benzene)}₂ (2) from copper(I) tert-butoxide and the free β-diketimine 
H[Cl₂NN₆] which was synthesized in an aza-Wittig reaction involving 2 equiv. 
phosphaimide Me₃P=NArCl² (ArCl² = 2,6-Cl₂C₆H₃) and 2,4-pentanedione. This new 
electron-deficient catalyst 2 shows promising results in the catalytic C-H amination of 
unactivated amines with broadened substrate scope. In particular, the electron-
withdrawing nature of the β-diketiminate ligand renders the [Cl₂NN₆]Cu fragment 
much more stable than [Cl₂NN]Cu towards mildly acidic substrates such as organic 
amides and alcohols. Unprecedented C-H activation via β-diketiminato systems of 
aromatic C-H was observed when alcohols were employed to form cyclized products. 
During screening of 2 as a C-H amination catalyst in conjunction with ⁴BuOO⁴Bu as 
oxidant, the electron-deficient amine ³,⁵-CF₃ArNH₂ (³,⁵-CF₃Ar = 3,5-(CF₃)₂C₆H₃) showed 
promising results by being able to functionalize primary C-H bonds in ethylbenzene. 
Newly synthezised {[Cl₂NN₆]Cu}₂(benzene) (2) can be reacted with excess ⁴BuOOBu⁴ to 
yield Cu(II) alkoxide [Cl₂NN₆]Cu-OBu⁴ (5). Preliminary reactions targeting Cu(II)
amides via acid/base chemistry of $[\text{Cl}_2\text{NNF}_6]\text{Cu-OBu}^1$ (5) and amines resulted in isolation of the corresponding Cu(I) amine complexes $[\text{Cl}_2\text{NNF}_6]\text{Cu(NH}_2\text{Mes)}$ (6) and $[\text{Cl}_2\text{NNF}_6]\text{Cu(NH(Et)Ph)}$ (7).

**Introduction**

4.1. Development of a 2nd generation $\beta$-diketiminato copper(I) catalyst

To further enhance the driving force for HAA from C-H bonds by copper(II)-amides $[\text{Cu}^{II}]\text{-NR}_1\text{R}_2^2$ we targeted a $\beta$-diketiminate that possesses backbone CF$_3$ groups in place of the backbone Me groups of $[\text{Cl}_2\text{NN}]$. Furthermore, increased electron deficiency can potentially broaden the substrate scope to more acidic substrates (e.g. amides and alcohols) since the corresponding $\beta$-diketiminate anion would not be expected to be as susceptible to protonolysis resulting in its loss from the metal center.

Che et al. have shown that electron deficient porphyrin Ru catalysts enhance the rate of C-H abstraction in related nitrene species (porph)$\text{Ru(=NSO}_2\text{R)}_2$ (Scheme 4.1).$^{1,2}$ Reaction of PhI=NTs with Ru(II) complexes (TMP)$\text{Ru}^{II}(\text{CO})$ and (F$_{20}$-TPP)$\text{Ru}^{II}(\text{CO})$ resulted in the formation of the corresponding Ru(IV) bis-imido complexes (TMP)$\text{Ru}^{IV}(\text{=NTs)}_2^1$ and (F$_{20}$-TPP)$\text{Ru}^{IV}(\text{=NTs)}_2$, respectively. To demonstrate the electron-withdrawing effect of fluorinated analogue, these two closely related complexes were investigated via cyclic voltammetry (CV) against an internal Cp$_2$Fe standard in CH$_2$Cl$_2$ containing 0.1 M [NBu$_4^+$]PF$_6$. The electron-rich (TMP)$\text{Ru}^{IV}(\text{=NTs)}_2$ shows two reduction peaks at -0.38 and -1.54 V and an oxidation at 0.62 V as compared to the electron-poor (F$_{20}$-TPP)$\text{Ru}^{IV}(\text{=NTs)}_2$ which exhibits reduction peaks at -0.12 and -
1.12 V and its oxidation peak at 1.18 V. Thus the more electron-deficient fluorinated complex \((\text{F}_{20}^{20-}\text{TPP})\text{Ru}^{\text{IV}}(=\text{NTs})_2\) is both easier to reduce and harder to oxidize.\(^1\,^2\) The benefit of an electron-deficient supporting ligand was demonstrated in a stoichiometric C-H bond amination reaction with ethylbenzene (Scheme 4.2). The second order rate constant in the amination of ethylbenzene for \((\text{F}_{20}^{20-}\text{TPP})\text{Ru}^{\text{IV}}(=\text{NTs})_2\) was \(k = 13.8(7) \times 10^3 \text{ M}^{-1} \text{s}^{-1}\) which is ca. 42 times faster than the same reaction using \((\text{TMP})\text{Ru}^{\text{IV}}(=\text{NTs})_2\) \((k = 0.33(02) \times 10^3 \text{ M}^{-1} \text{s}^{-1})\).\(^2\) Given that the anticipated direct product of C-H amination is the Ru(IV) species \((\text{porph})\text{Ru}^{\text{IV}}(=\text{NTs})(\text{NH}(\text{R})\text{Ts})\). Thus ligands that allow for more

**Scheme 4.1.** Example of enhanced reactivity via electron-deficient catalyst.

\[
\begin{align*}
\begin{array}{c}
\text{Me} & \text{Me} \\
\text{Me} & \text{Me} \\
\text{Me} & \text{Me} \\
\text{Me} & \text{Me} \\
\text{Me} & \text{Me} \\
\text{Me} & \text{Me} \\
\end{array}
\quad & 
\begin{array}{c}
\text{F} & \text{F} \\
\text{F} & \text{F} \\
\text{F} & \text{F} \\
\text{F} & \text{F} \\
\text{F} & \text{F} \\
\text{F} & \text{F} \\
\end{array}
\]
\begin{align*}
\text{NSO}_2\text{R} & \quad + 
\text{C} & \quad \text{NH} \\
\text{NSO}_2\text{R} & \quad \text{SO}_2\text{R}
\end{align*}
\end{align*}
\]

\[(\text{porph})\text{Ru}(=\text{NSO}_2\text{R}) + \text{C}-\text{H} \rightarrow \text{C}-\text{NH} \quad \text{SO}_2\text{R}
\]

*Enhance rate of \((\text{F}_{20}^{20-}\text{TPP})\text{Ru}(=\text{NSO}_2\text{R})\) over \((\text{TMP})\text{Ru}(=\text{NSO}_2\text{R})\)*

**Scheme 4.2.** Reactivity of \((\text{porph})\text{Ru}^{\text{IV}}\) imido complexes with C-H bonds.

\[
\begin{align*}
\begin{array}{c}
\text{Me} & \text{Me} \\
\text{Me} & \text{Me} \\
\text{Me} & \text{Me} \\
\text{Me} & \text{Me} \\
\text{Me} & \text{Me} \\
\text{Me} & \text{Me} \\
\end{array}
\quad & 
\begin{array}{c}
\text{F} & \text{F} \\
\text{F} & \text{F} \\
\text{F} & \text{F} \\
\text{F} & \text{F} \\
\text{F} & \text{F} \\
\text{F} & \text{F} \\
\end{array}
\]
\begin{align*}
\text{NSO}_2\text{R} & \quad + 
\text{C} & \quad \text{H} \\
\text{NSO}_2\text{R} & \quad 
\end{align*}
\]

\[(\text{porph})\text{Ru}^{\text{IV}}(=\text{NTs})_2 + \text{R} \rightarrow (\text{porph})\text{Ru}^{\text{IV}}(=\text{NTs})(\text{NH}(\text{R})\text{Ts})
\]
facile reduction of the Ru(VI) species (porph)Ru\textsuperscript{IV}(=NTs)\textsubscript{2} are expected to promote C-H amination.

Pierpont and Cundari reported a computational investigation into C-H amination of methane by simple \(\beta\)-diketiminato model complexes [M]=NR (M = Fe, Co, Ni) which demonstrated a decrease in the endothermicity of HAA by [M]=NR upon substitution of electron-withdrawing groups onto the backbone as well as \(N\)-substitutents of the simplified \(\beta\)-diketiminate ligands (Scheme 4.3). Focusing on modifications of the \(\beta\)-diketiminato backbone, they compared hydrogen (H) versus trifluoromethyl (CF\textsubscript{3}). The calculated enthalpies for HAA decrease upon fluorination from 18.6 kcal/mol to 18.0 kcal/mol while enhancing the exothermicity of radical recombination (RR) of the methyl radical with the nickel(II)-amide thus formed from -44.2 kcal/mol to -49.0 kcal/mol. Thus, the overall C-H functionalization reaction is also favored for the fluorinated species (\(\Delta H\) (overall) = -21.6 and -31.0 kcal/mol). \(\Delta H\textsuperscript{\Delta H} \) calculations for

**Scheme 4.3.** Computational investigation into electron-withdrawing effect of the \(\beta\)-diketiminate ligand L\textsubscript{n}. Values correspond to enthalpies in kcal/mol.

\[
\begin{array}{ccc}
\text{HAA}: & \Delta H: & 18.6 (\Delta H_\text{act} = 26.5) \quad 18.0 (\Delta H_\text{act} = 26.1) \\
\text{RR}: & \Delta H: & -44.2 \quad -49.0 \\
\text{Overall}: & \Delta H: & -21.6 \quad -31.0
\end{array}
\]

*increased exothermicity if L\textsubscript{n} is electron-deficient*

**HHA:** \(L_n\text{M}=\text{NR} + \text{CH}_4 \rightarrow L_n\text{M}-(\text{N(H)}\text{R}) + \cdot \text{CH}_3\)

**RR:** \(L_n\text{M}-(\text{N(H)}\text{R}) + \cdot \text{CH}_3 \rightarrow L_n\text{M}(\text{CH}_3\text{N(H)}\text{R})\)

**Overall:** \(L_n\text{M}=\text{NR} + \text{CH}_4 \rightarrow L_n\text{M}(\text{CH}_3\text{N(H)}\text{R})\)
HHA also slightly favored the fluorinated species (26.5 and 26.1 kcal/mol) thus showing a smaller activation barrier for HHA for the electron-deficient complex.\(^3\) Thus, both experimental and theoretical precedent argues for both greater kinetic and thermodynamic C-H functionalization reactivity at metal centers supported by electron-deficient ligands.

**Results and Discussion**

4.2.\(a\). *Synthesis of electron-deficient [Cl\(_2\)NN\(_F_6\)]Cu catalyst*

The ligand H[Cl\(_2\)NN\(_F_6\)] (1) that features backbone CF\(_3\) groups in place of the Me groups present in H[Cl\(_2\)NN] (Scheme 4.4) requires a different synthetic route than typical condensation methods used for \(N\)-aryl \(\beta\)-diketimines.\(^4\)-\(^1\)\(^2\)\(^1\)\(^3\) While a TiCl\(_4\) assisted condensation route has been used to successfully prepare \(\beta\)-diketimimates with backbone CF\(_3\) groups and electron-rich \(N\)-aryl groups (e.g. \(\sigma\)-Me, \(\sigma\)-\(i\)Pr),\(^1\)\(^3\),\(^1\)\(^4\) we find that

**Scheme 4.4.** Literature protocols for the synthesis of CF\(_3\)-backbone.
this route only results in formation of the ketoimine “half-ligand” CF₃C(=N(2,6-
Cl₂C₆H₃))CH₂C(O)CF₃. Instead, we followed an aza-Wittig route employing the
phosphaimide (Ph₃P=N(2,6-Cl₂C₆H₃)) with hexafluoroacetylacetone in a manner first
described by Sadighi for the synthesis of β-diketiminate ligands with backbone CF₃
groups.¹⁵

Reaction of 2,6-dichloroaniline with tert-butylnitrite and trimethylsilylazide in
MeCN gives 2,6-dichlorophenylazide (ArCl₂N₃; ArCl₂ = 2,6-Cl₂C₆H₃) in 67% yield as a
pale yellow oil after column chromatography. Under air-free conditions the Staudinger
reaction of this arylazide with a THF solution of trimethylphosphine quickly gives the
corresponding phosphaimide Me₃P=NArCl₂ which is used without further purification
after removal of the volatiles in vacuo. Reaction of 2 equiv. Me₃P=NArCl₂ with

**Scheme 4.5.** Synthesis of electron-deficient Cu catalyst [Cl₂NNF₆]Cu (2).
hexafluoroacetlyacetone in toluene at 100 °C in a sealed tube for 4 ½ days followed by flash chromatography of the mixture and crystallization from methanol provides H[Cl₂NNF₆] (1) as bright yellow crystals 56% yield (Scheme 4.5). Since this synthetic route employs the arylazides ArCl₂N₃, H[Cl₂NNF₆] is most conveniently performed on ~2-3 g scale. In benzene-d₆ H[Cl₂NNF₆] (1) shows a characteristic ¹H NMR C-H backbone peak at δ 6.10 ppm and the bridging N-H-N at δ 11.50 ppm (Figure 1, top).

H[Cl₂NNF₆] (1) can also be prepared under microwave conditions by loading a microwave pressure vessel under inert atmosphere with 2 equiv. Me₂P=NArCl₂ and 1 equiv. hexafluoroacetlyacetone in toluene. The reactions conditions require microwave settings of 150 °C, 100 Watts and 275 psi with a reaction time of only 5 h and a yield of 42%. Even though this method allows a much shorter reaction time the general protocol only yields ~300 mg due to the reduced size of glassware conveniently employed in the microwave.

Reaction of H[Cl₂NNF₆] (1) with slight excess of copper(I) tert-butoxide with several equiv. benzene in THF affords the desired complex {[Cl₂NNF₆]Cu}₂(benzene) (2) in 75% yield as an orange solid. This species is formulated based on the X-ray structure of {[Cl₂NN]Cu}₂(benzene)¹⁶ as well as a recent X-ray structure obtained by Dan Seidenberg from recrystallization of this substance from methanol. The ¹H NMR spectrum of 1 in benzene-d₆ shows a characteristic C-H backbone peak at δ 6.095 ppm
Figure 4.1. $^1$H NMR spectrum (benzene-$d_6$, 400 MHz, 25°C) of H[Cl$_2$NN$_6$F$_6$] (1) (top) and {[Cl$_2$NN$_6$F$_6$]Cu}$_2$(benzene) (2) (bottom).
and the free ligand N-H-N peak at δ 11-12 ppm is conspicuously absent (Scheme 4.5 and Figure 4.1 bottom).

4.2.b. Assessing electronic effect of backbone CF₃ groups

To begin to quantify the electron-deficiency of [Cl₂NNF₆]Cu relative to [Cl₂NN]Cu, we synthesized two very similar complexes [Cl₂NN]Cu(CNAr²,6-Me²) (3a) and [Cl₂NNF₆]Cu(CNAr²,6-Me²) (3b) that employs the 2,6-dimethylphenylisocyanide ligand CNAr²,6-Me². Addition of CNAr²,6-Me² to {[Cl₂NN]Cu}₂(η-C₆H₆) or {[Cl₂NNF₆]Cu}₂(η-C₆H₆) (2) in Et₂O gives [Cl₂NN]Cu(CNAr²,6-Me²) (3a) or [Cl₂NNF₆]Cu(CNAr²,6-Me²) (3b) each in 64% yield as yellow and orange crystals from Et₂O at -35 °C, respectively (Scheme 4.6). X-ray structures of 3a and 3b (Figures 4.3 and 4.4) reveal three-coordinate metal centers with Cu-N[β-dik] distances of 1.9359(13) and 1.9340(13) Å for 3a that are somewhat longer at 1.9728(12) and 1.9567(12) Å in 3b. The Cu-C_isocyanide distances are very close at 1.8202(16) and 1.8246(15) Å for 3a and 3b respectively, while C-N triple-bond distance of the isocyanide moiety are essentially identical at 1.157(2) and 1.156(2) Å. These complexes are similar in form to other [β-dik]Cu(CNAr) adducts such as [Me₃NN]Cu(CNAr²,6-Me²).¹⁷

Scheme 4.6. Synthesis of copper(I) isocyanide complexes 3a and 3b.

\[
\begin{align*}
\text{Et}_2\text{O}, \text{Ih} 
\end{align*}
\]
[Cl(Me₂NN)]Cu(CNAr\(^{2,6-\text{Me}2}\))\(^{18}\) and [Me₂NN]Cu(CNAr\(^{2,6-\text{Me}2}\))\(^{19}\). Importantly, IR spectroscopy shows the CN stretch at 2141 cm\(^{-1}\) for \(3a\) as compared to 2158 cm\(^{-1}\) for \(3b\). The increased stretching frequency for \(3b\) is consistent with less backbonding from the more electron-deficient Cu center in \(3b\) relative to \(3a\).

Table 4.1. IR Stretches and bond distance of CN for Cu isocyanide

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR (\nu)(CN) (cm(^{-1}))</th>
<th>CN bond distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cl(_2)NN]Cu(CNAr(^{2,6-\text{Me}2})) (3a)</td>
<td>2141</td>
<td>1.157(2)</td>
</tr>
<tr>
<td>[Cl(_2)NN(_F_6)]Cu(CNAr(^{2,6-\text{Me}2})) (3b)</td>
<td>2158</td>
<td>1.156(2)</td>
</tr>
<tr>
<td>[Me(_3)NN]Cu(CNAr(^{2,6-\text{Me}2}))</td>
<td>2121</td>
<td>1.159(2)</td>
</tr>
<tr>
<td>[Cl(Me(_2)NN)]Cu(CNAr(^{2,6-\text{Me}2}))</td>
<td>2128</td>
<td>n/a</td>
</tr>
<tr>
<td>[Me(_2)NN]Cu(CNAr(^{2,6-\text{Me}2}))</td>
<td>2123</td>
<td>1.157(3)</td>
</tr>
<tr>
<td>free CNAr(^{2,6-\text{Me}2})</td>
<td>2119</td>
<td>n/a</td>
</tr>
</tbody>
</table>
Figure 4.3. X-ray crystal structure of [Cl₂NN]Cu(CNAr²,6-Me₂) (3a). All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Cu-N1 1.9359(13), Cu-N2 1.9340(13), Cu-C18 1.8202(16), C18-N3 1.157(2), N1-Cu-N2 96.95(5).
Figure 4.4. X-ray crystal structure of [Cl₂NN₆]Cu(CNAr²,₆-Me₂) (3b). All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Cu-N1 1.9728(12), Cu-N2 1.95667(12), Cu-C18 1.8246(15), C18-N3 1.156(2), N1-Cu-N2 94.38(5).
### Table 4.2. Crystallographic data for 3a and 3b.

<table>
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<tr>
<th>Compd.</th>
<th>3a</th>
<th>3b</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
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<td>C_{26}H_{16}Cl_{4}F_{6}N_{3}Cu</td>
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<td>Mol. Wt.</td>
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</tr>
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<td>100(2)</td>
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<td>crystal description</td>
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<td>brick</td>
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<tr>
<td>crystal color</td>
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<td>crystal size (mm$^3$)</td>
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<td>monoclinic</td>
</tr>
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<td>Space group</td>
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<td>P21/c</td>
</tr>
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<td>a (Å)</td>
<td>13.3741(13)</td>
<td>7.4116(6)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>10.6530(11)</td>
<td>23.0415(18)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>18.8303(19)</td>
<td>15.8438(12)</td>
</tr>
<tr>
<td>α (deg)</td>
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<td>90.00</td>
</tr>
<tr>
<td>β (deg)</td>
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<td>97.5170(10)</td>
</tr>
<tr>
<td>γ (deg)</td>
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<td>90.00</td>
</tr>
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<td>4</td>
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<td>unique reflns</td>
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<td>1.043</td>
</tr>
<tr>
<td>R$_1$ (I &gt; 2σ(I))</td>
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<td>0.0208</td>
</tr>
<tr>
<td>wR$_2$ (all data)</td>
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<td>0.0237</td>
</tr>
<tr>
<td>Largest diff. peak and hole e$^-\cdot Å^{-3}$</td>
<td>0.371 and -0.376</td>
<td>0.389 and -0.312</td>
</tr>
</tbody>
</table>
4.2.c. Enhanced stability of \( \{\text{Cl}_2\text{NNF}_6\} \text{Cu} \) towards organic amides

Sofi Bahgat, a previous student in the Warren group, showed via \( ^1\text{H} \) NMR experiments in benzene-\( d_6 \) that exposure of \( \{\text{[Cl}_2\text{NN}]\text{Cu}\}_2(\text{11-benzene}) \) to organic amides such as benzamide and 2-pyrrolidione results in protonation of the \( \beta \)-diketiminate ligand to release \( \text{[Cl}_2\text{NN}]\text{H} \) along with some insoluble Cu-containing material, presumably \( \text{[Cu(amide)]} \). Under the same conditions

**Scheme 4.7.** Synthesis of \( \text{[Cl}_2\text{NNF}_6\} \text{Cu}((\kappa^1-O-2\text{-pyrrolidinone}) (4).

\[
\begin{align*}
\{\text{[Cl}_2\text{NNF}_6\} \text{Cu}_2\text{(benzene) + 2} &\rightarrow 2 \text{[Cl}_2\text{NNF}_6\} \text{Cu} \\
\text{(1-O-2-pyrrolidinone)} &\rightarrow 4 \\
\text{Et}_2\text{O} &\rightarrow \text{Et}_2\text{O}
\end{align*}
\]

The X-ray structure of 4 shows that 2-pyrrolidinone is coordinated through

**Figure 4.5.** Related pyrrolidinone structures for X-ray comparison.
its oxygen with a Cu-O distance of 1.965(5) Å, while the O-C18 distance is 1.261(10) Å and C18-N3 distance is 1.310(10) Å (Figure 4.6). For comparison, the related free pyrrolidinones 3-(iodomethyl)pyrrolidin-2-one and 5-(2-methyloxiran-2-yl)pyrrolidin-2-one possess C-O bond distances of 1.24(1) and 1.239(5) Å, respectively, along with C_carbonyl-N distances of 1.35(2) and 1.341(6) Å, respectively. Thus copper adduct 4 shows a shortening of the C-N bond and an elongation of C-O bond indicating a zwitterionic resonance structure of the pyrrolidinone moiety (Scheme 4.7 and Figure 4.5). The Cu-Nβ-dik distances of 1.962(6) and 1.970(7) Å are just slightly different than in [Cl2NNF6]Cu(CNAr2,6-Me2) (3b) (1.9728(12) and 1.9567(12) Å) (Figure 4.4).
Figure 4.6. X-ray crystal structure of $[\text{Cl}_2\text{NNF}_6]\text{Cu}(\kappa^1-O-2$-pyrroldione) (4). All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Cu-N1 1.962(6), Cu-N2 1.9707(7), Cu-O 1.965(5), O-C18 1.261(10), C18-N3 1.310(10), N1-Cu-N2 99.6(3).
4.2.d. Synthesis of $[\text{Cl}_2\text{NNF}_6]\text{Cu-OBu}^\dagger$ (5)

To investigate the potential for $[[\text{Cl}_2\text{NN}]\text{Cu}]_2$ (benzene) (2) to serve as a catalyst for amination and amidation reactions employing $^t\text{BuOOBun}^\dagger$ as oxidant, we targeted the synthesis of the corresponding copper(II)-alkoxide $[\text{Cl}_2\text{NNF}_6]\text{Cu-OBu}^\dagger$ (5). Addition of a chilled solution of 8.55 equiv. $^t\text{BuOOBun}^\dagger$ in pentane to a cold solution (-35 °C) of $[[\text{Cl}_2\text{NN}]\text{Cu}]_2$ (benzene) (2) in pentane results in an immediate coloration to dark red. After allowing the reaction mixture to stand an additional 90 min at RT, $[\text{Cl}_2\text{NNF}_6]\text{Cu-OBu}^\dagger$ (5) can be isolated as red crystals in 34% yield from pentane at -35 °C. The X-ray structure of 5 shows Cu-N\text{dik} distances of 1.905(4) and 1.904(4) Å and a Cu-O bond distance of 1.765(4) Å (Figure 4.7). Substance 5 shows a strong absorbance at $\lambda_{\text{max}} = 520$ nm ($\varepsilon = 3750$ M$^{-1}$ cm$^{-1}$) in benzene solution.

**Scheme 4.8.** Cu alkoxide synthesis 5.

$$[[\text{Cl}_2\text{NNF}_6]\text{Cu}]_2$(benzene) + 8.55 eq. $^t\text{BuOOBun}^\dagger$ $\xrightarrow{\text{pentane}} 2 [\text{Cl}_2\text{NNF}_6]\text{Cu-OBu}^\dagger 5 \text{34\% yield}$

The X-ray structure of $[\text{Cl}_2\text{NNF}_6]\text{Cu-OBu}^\dagger$ (5) compares well to the closely related $[\text{Cl}_2\text{NN}]\text{Cu-OBu}^\dagger$23, though the fluorinated species has a slightly shorted Cu-O distance of 1.767(2) vs. 1.785(2) Å in $[\text{Cl}_2\text{NN}]\text{Cu-OBu}^\dagger$. The electron-poor species exhibits longer Cu-N\text{dik} distances of 1.903(3) and 1.903(2) Å vs. 1.884(2) and 1.889(2) Å in $[\text{Cl}_2\text{NN}]\text{Cu-OBu}^\dagger$. 

239
Figure 4.7. Preliminary X-ray crystal structure of [Cl$_2$NN$_6$]Cu-OBu$^t$ (5). All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): N1-Cu 1.903(3), N2-Cu 1.903(3), Cu-O 1.767(2), N1-Cu-N2 95.58(11), O-Cu-N2 132.22(11) and O-Cu-N1 132.17(11).
Table 4.3. Crystallographic data for 4 and 5.

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<tr>
<th>Compd.</th>
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<th>5</th>
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<td>( \text{C}<em>{21}\text{H}</em>{16}\text{Cl}_4\text{CuF}_6\text{N}_2\text{O} )</td>
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<td>( \text{P1bar} )</td>
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</tr>
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<td>( \beta ) (deg)</td>
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<td>( \gamma ) (deg)</td>
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<td>( R_1 ) ( ( I &gt; 2\sigma(I) ))</td>
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<td>( wR_2 ) (all data)</td>
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<td>Largest diff. peak and hole ( e^{-\cdot \text{Å}^{-3}} )</td>
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<td>0.331 and -0.214</td>
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</table>
4.2.e. Attempts to isolate copper(II) amide complexes

In analogy to the alkoxide-amide exchange described employing [Cl₂NN]Cu-OBu' with amines HNR₁R₂ to generate [Cl₂NN]Cu-NR₁R₂, we began to scout related reactions with [Cl₂NN₆]Cu-OBu' (5). Addition of 2,4,6-trimethylaniline and N-ethylaniline to [Cl₂NN]Cu-OBu' (5) in pentane at -35 °C resulted in the isolation of the corresponding copper(I)-amine adducts [Cl₂NN₆]Cu(NH₂Mes) (6) and [Cl₂NN₆]Cu(NH(Et)Ph) (7) from pentane as red crystals in 75% and 80% yield, respectively (Scheme 4.9). [Cl₂NN]Cu-OBu' (5) plus 2,4,6-trimethylaniline undergoes an immediate color change from red to greenish blue. This greenish blue solution produces red crystals of [Cl₂NN₆]Cu(H₂NMes) (6) (Figure 4.8). [Cl₂NN]Cu-OBu' (5) plus N-ethylaniline immediately changes from red to brown without any other colors observed and red crystals of [Cl₂NN₆]Cu(HN(Et)Ph) (7) (Figure 4.9). Copper(I) amine adducts 6 and 7 show slightly different Cu-Namine distances 1.9810(16) and 1.960(3) Å,

**Scheme 4.9.** Formation of observed Cu-amines and alternative synthetic route.

\[
\begin{align*}
\text{[Cl}_2\text{NN}_6\text{Cu}-\text{OBu'} + \text{NH}_2\text{Mes} & \xrightarrow{\text{pentane, -35 °C, BuOH}} \text{[Cl}_2\text{NN}_6\text{Cu} \text{H}_2\text{NMes}} \\
\text{[Cl}_2\text{NN}_6\text{Cu}-\text{OBu'} + \text{HN(Et)Ph} & \xrightarrow{\text{pentane, -35 °C, BuOH}} \text{[Cl}_2\text{NN}_6\text{Cu} \text{HN(Et)Ph}}
\end{align*}
\]

*alternative route*

\[
\begin{align*}
\text{[Cl}_2\text{NN}_6\text{Cu}_X + \text{R}_1^1\text{R}_2^2\text{NLi} & \xrightarrow{\text{UV/vis, cold, LiX}} \text{[Cl}_2\text{NN}_6\text{Cu}_X \text{NR}_1^1\text{R}_2^2}
\end{align*}
\]
respectively. The bond angle for Cu-N3-C18 are consistent with $sp^3$-hybridized amines coordinated at copper for [Cl$_2$NN$_{F6}$]Cu(NH$_2$Mes) (6) 113.76(11)$^\circ$ and for [Cl$_2$NN$_{F6}$]Cu(NH(Et)Ph) (7) 108.7(2)$^\circ$. The sum of the angles about N3 in 6 and 7 is 360 and 347$^\circ$ compared to 360$^\circ$ if each N atom was $sp^3$-hybridized.

A possible explanation for isolation Cu(I)-amine products rather than the expected copper(II)-amides is that the later may quickly decompose via some HAA pathway due to their high reactivity. Future studies should observe these exchange reactions in situ by UV-vis at low temperature. In addition, their potential syntheses should be examined from a halide species such as {[Cl$_2$NN$_{F6}$]Cu}$^\text{2}$([t-X])$_2$ and LiNR$_1$R$_2$ (Scheme 4.9). Under these conditions it should be possible to observe new copper(II)-amide species that would allow mechanistic study of HAA reactivity resulting in the formation of the corresponding copper(I) amine adducts.
Figure 4.8. X-ray crystal structure of \([\text{Cl}_2\text{NNF}_6]\text{Cu(NH}_2\text{Mes})\) (6). All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Cu-N1 1.9459(15), Cu-N2 1.9628(15), Cu-N3 1.9810(16), N1-Cu-N2 98.53(6), and C18-N3-Cu 113.76(11).
Figure 4.9. X-ray crystal structure of [Cl₂NNF₆]Cu(NH(Et)Ph) (7). All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Cu-N1 1.927(3), Cu-N2 1.969(2), Cu-N3 1.960(3), C18-N3 1.444(4), C24-N3 1.389(4), C24-C25 1.492, N1-Cu-N2 98.59(10) and C18-N3-Cu 108.7(2), C18-N3-C24 117.9(3), C24-N3-Cu 120.7(2) and C18-N3-Cu 108.7(2).
### Table 4.4. Crystallographic data for 6 and 7.

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<th>Compd.</th>
<th>6</th>
<th>7</th>
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<td>formula</td>
<td>$\text{C}<em>{35}\text{H}</em>{30}\text{Cl}_4\text{CuF}_6\text{N}_4$</td>
<td>$\text{C}<em>{25}\text{H}</em>{18}\text{Cl}_4\text{CuF}_6\text{N}_3$</td>
</tr>
<tr>
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<td>679.76</td>
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<td>100(2)</td>
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<td>needle</td>
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<td>$P21/c$</td>
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<tr>
<td>$b$ (Å)</td>
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<td>22.328(7)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
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</tr>
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<td>$\beta$ (deg)</td>
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<td>93.739(4)</td>
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<td>$\gamma$ (deg)</td>
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</tr>
<tr>
<td>$Z$</td>
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<td>Largest diff. peak and hole e$^{-} \cdot $Å$^{-3}$</td>
<td>0.0612 and -0.352</td>
<td>0.699 and -0.533</td>
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</tbody>
</table>
4.2.f. Preliminary investigation of C-H amination with \([\text{Cl}_2\text{NNF}_6]\text{Cu}\)

To examine the utility of \([[\text{Cl}_2\text{NNF}_6]\text{Cu}]_2(\text{benzene})\) (2) in C-H amination catalysis, we briefly screened a few sample amines with ethylbenzene (Scheme 4.10). In our initial screen, we employed 10 mol% \([[\text{Cl}_2\text{NNF}_6]\text{Cu}]_2(\text{benzene})\) (2), neat ethylbenzene (20 mL), and 1.0 equiv. \('\text{BuOOBu}'\) at 80 °C for 16 h along with amines of interest. The use of mesitylamine (H₂NMes) led to the aminated ethylbenzene product in 18% yield along with MesN=NMes in 17% yield. Unfortunately, this screen also indicated that 56% of MesNH₂ remained. At 1 mol% catalyst loading with 3,5-fluoromethylaniline, neat ethylbenzene (20 mL) and 5 equiv. \('\text{BuOOBu}'\) at 80 °C for 16 h yielded the expected product PhCH(NHar₃.₅-CF₃)Me in 67% yield. A second product of the same m/z with a different retention time than the secondary benzylic product was observed. At this point we hypothesize the new product to be the result of amination at the primary position with an estimated yield of 10% based on GC/MS (total ion count) (Scheme 4.10). Amination at this position would be quite interesting, since the primary C-H bond is much stronger (BDE = 98 kcal/mol) than the secondary benzylic C-H bond (BDE = 87 kcal/mol).
Preliminary screens under these conditions with other amines (e.g. aniline, 2,4,6-trimethylaniline, morpholine and 1-adamantylamine) were carried out as well (10 mol% catalyst loading) in neat (10 mL) and 5 equiv. C-H substrate (diluted with 10 mL benzene) (Scheme 4.11). In each case the expected C-H amination product was observed by GC/MS but not quantified since mostly starting material was observed via GC/MS. Decreasing the catalyst loading to 1 mol % did not improve any of the reaction yields under otherwise identical reaction conditions. Also no evidence for primary aminated products was observed. Since these yields and conditions did not seem to compete with the 1st generation catalyst \([\{\text{Cl}_2\text{NN}_{F_6}\}2\text{Cu}\}\text{ (benzene)}\), we turned our attention to other substrates. It is possible that turnover is slow due to the difficulty of activating \(\text{BuOOBu}^+\) to give \([\text{Cl}_2\text{NN}_{F_6}\]Cu-\text{OBu}^+\) if amines bind tightly to the \([\text{Cl}_2\text{NN}_{F_6}\]Cu.
4.2.g. Catalytic C-H amidation with organic amides

Sofi Bahgat showed that under catalytic conditions employing 10 mol\% \(\{\text{Cl}_2\text{NN}_{6}\text{Cu}\}_2\text{(benzene)}\) (2) (20 mol \% [Cu]) amidates ethylbenzene as well as cyclohexane in yields of >90\% for benzamide and 2-pyrrolidinone using \(^{1}\text{BuOOBu}^+\) as the oxidant.\(^{20}\) These results were reproduced with extremely clean GC/MS spectra of only one product and no starting material. 2,2,2-trifluoro-N-phenylacetamide in neat ethylbenzene was able to undergo amidation at appreciable yield of 24\% to the corresponding 2,2,2-trifluoro-N-phenyl-N-(1-phenylethyl)acetamide (Scheme 4.12). These preliminary screening results lead to screening of the two most promising amides, benzamide and 2-pyrrolidinone with allylic C-H bond 1-octene. Varying C-H substrate concentration (neat, 10 equiv., 1 equiv.) and varying catalyst loading (10 mol \% and 1 mol \%) did not result in measurable yields.

4.2.h. Intramolecular C-H oxidative cyclization of alcohols

Given the greater stability against protolytic loss of the \(\beta\)-diketiminate ligand that \([\text{Cl}_2\text{NN}_{6}\text{Cu}]\) enjoys compared to \([\text{Cl}_2\text{NN}_{6}\text{Cu}]\), we examined alcohol substrates for the potential of intramolecular C-H oxidative cyclization to form new C-O bonds. Ideally, we envisioned the oxidative functionalization of \(sp^3\)-hybridized C-H bonds in
an intramolecular manner (Scheme 4.13). We felt that the entropic advantage of an intramolecular H-atom abstraction might just allow such a C-O bond forming process take place; up to now we have not observed any productive C-O bond formation via [CuII]-OR intermediates. We also reasoned that a phenyl ring could serve as a directing group as it would provide weaker secondary benzylic C-H bonds more prone to HAA.

Employing a 1 mol% catalyst loading of [Cl2N3F6]Cu in the presence of 1.2
equiv. 'BuOOBu' and 5 mL benzene as the solvent at 80 °C for 20 h, 4-phenyl-1-butanol and 5-phenyl-1-pentanol were cyclized to 2,3,4,5-tetrahydrobenzo[b]oxepine and 3,4,5,6-tetrahydro-2H-benzo[b]oxocine in 22% and 25% yield, respectively (Scheme 4.14). Shorter chain length substrates that would result in 5- and 6-membered cyclized products yielded no new products (Scheme 4.14).

The cyclized products shown in the top two reactions in Scheme 4.14 were identified via 1D and 2D ¹H NMR spectra of the crude mixtures. Following the reactions via ¹H NMR in benzene-đ6, a new triplet grows in at δ 3.90 ppm that corresponds to O-CH2 resonance of the newly formed cyclized products. Selectively irradiating the respective triplets in a 1D TOCSY experiment produces splitting patterns consistent with the cyclized products were observed. Identifying the same peaks in a 2D HSQC experiment showed them to be sp3 CH2. GHMBC showed long range coupling partners of O-CH2 and O-Cipso of δ 3.901 to 172.48 ppm for 2,3,4,5-tetrahydrobenzo[b]oxepine and δ 3.904 to 172.49 ppm for 3,4,5,6-tetrahydro-2H-benzo[b]oxocine. The two products were not isolated but simply analyzed as the crude mixture. Higher catalyst loadings or longer reaction times did not improve the yields.

The heterocycle 2,3,4,5-tetrahydrobenzo[b]oxepine may be prepared in a cross-coupling pathway from the corresponding aryl halide in 73 – 74% yield but the reaction

**Scheme 4.15.** Alcohol cyclization via Pd(OAc)2.
requires halogens ortho to the alkyl chain (Scheme 4.15). The larger 8-membered ring structure, 3,4,5,6-tetrahydro-2H-benzo[b]oxocine, was not reported via this route.

Perhaps more insight into the mechanism could be obtained by considering previous reactions of such phenyl-subsituted alkyl alcohols Ph(CH₂)ₓOH (x = 2 – 5) with strong oxidants such as cerium(IV) nitrate or lead(IV) acetate (Scheme 4.16a). These oxidants essentially remove H• (radical) to produce an oxygen based radical that reacts further by attacking the benzene ring and upon losing a second H• (radical) forming the cyclized product. Alternatively, hypervalent iodanes (PhI(OH)BF₄ and PhI(OC(O)CF₃)₂), another strong oxidant, are thought of to undergo a different mechanism (Scheme 4.16b) by first forming a phenyl cation via oxidation, which then undergoes intramolecular OH attack to first give a 5-membered ring with loss of H⁺ and e⁻. 1,2-C or 1,2-O reorganization produces a 6-membered cationic ring. Finally loss of H⁺ gives the final product. Both of these mechanisms favor 6-membered rings.

**Scheme 4.16.** Two proposed C-O cyclization reactions for strong oxidants.
Conclusions

Switching to a more electron-deficient catalyst has not as of now shown dramatically enhanced catalytic C-H amination reactivity with unactivated amines but opens up a broader substrate scope by being stable towards more acidic substrates such as amides and alcohols. While the copper(II) tert-butoxide \([\text{Cl}_2\text{NNF}_6]\text{Cu-OBu}^t\) has been isolated, careful low-temperatures UV-vis studies are required with amines \(\text{HNR}^1\text{R}^2\) to assess the relative reactivity of the expected \([\text{Cl}_2\text{NNF}_6]\text{Cu-NR}^1\text{R}^2\) species. It is possible that the more electron-poor \([\text{Cl}_2\text{NNF}_6]\text{Cu}\) catalyst coordinates the amine substrates \(\text{HNR}^1\text{R}^2\) more strongly than \([\text{Cl}_2\text{NN}]\text{Cu}\), hampering reaction with \(\text{tBuOOBu}^t\) to give \([\text{Cl}_2\text{NN}]\text{Cu-OBu}^t\) necessary for the formation of \([\text{Cl}_2\text{NN}]\text{Cu-NR}^1\text{R}^2\) intermediates required for C-H amination. Perhaps alternative oxidants such as \(\text{tBuOOC(O)Ph}\) may prove easier to activate and thus enhance the C-H amination activity of \([\text{Cl}_2\text{NNF}_6]\text{Cu}\). Importantly, a new C-H functionalization reaction in which aromatic C-O bonds may be catalytically prepared has been discovered through the use of long chain alcohols possessing pendant phenyl rings were employed to form 7- and 8-membered heterocycles.

Experimental

General Procedures and Instrumentation

All experiments were carried out in a dry nitrogen atmosphere using an MBraun glovebox and/or standard Schlenk techniques. 4A molecular sieves were activated \textit{in vacuo} at 180 °C for 24 h. Dry benzene was purchased from Aldrich and was stored
over activated 4A molecular sieves. Diethyl ether and tetrahydrofuran (THF) were first sparged with nitrogen and then dried by passage through activated alumina columns. Pentane was first washed with conc. HNO$_3$ / H$_2$SO$_4$ to remove olefins, stored over CaCl$_2$ and then distilled before use from sodium/benzophenone. Benzene, toluene, and ethylbenzene were purchased anhydrous and stored over 4A molecular sieves. All solvents were tested before use with a drop of sodium benzophenone ketyl in THF solution. All deuterated solvents were sparged with nitrogen, dried over activated 4A molecular sieves and stored under nitrogen. Celite was dried overnight at 200 °C under vacuum.

$^1$H and $^{13}$C NMR spectra were recorded on a Varian 400 MHz Inova Spectrometer (400 and 100.47 MHz, respectively). All NMR spectra were recorded at room temperature unless otherwise noted and were indirectly referenced to residual solvent signals or TMS as internal standards. $^{19}$F NMR spectra were referenced to fluorobenzene (C$_6$F$_6$) at δ -164.901 ppm. UV-Vis spectra were measured on a Varian Cary 50 or 100 spectrophotometer, using cuvettes with screw-cap tops. GC-MS spectra were recorded on a Varian Saturn 3900 and elemental analyses were performed on a Perkin-Elmer PE2400 microanalyzer at Georgetown. IR measurements were performed on Perkin Elmer Spectrum One FT-IR Spectrometer.

All reagents were obtained commercially unless otherwise noted. Ethylbenzene-$d_{10}$ was obtained from Acros and purified by passing it through activated alumina. 1-adamantylamine was purchased from Aldrich. Anhydrous CuCl$_2$ was obtained from Strem Chemicals. H[Cl$_2$NN]$^1$ and {[Cl$_2$NN]Cu}$_2$(μ-$t$-benzene)$^2$ were prepared by
literature methods or may be obtained from Strem Chemicals. CuOBu\(^1\) was prepared according to the procedure published by Badiee et al.\(^{10,29}\)

### 4.3.a. Preparation of compounds

\(2,6\text{-Cl}^2\text{ArN}_3\) (\(2,6\text{-Cl}^2\text{Ar} = 2,6\text{-Cl}_2\text{C}_6\text{H}_3\)). This compound was synthesized via the protocol described by Moses et al.\(^{30}\) but this exact compound was previously reported Zanardi and Meazza\(^{31}\) and by Nitsche et al.\(^{32}\). In air, a solution of 2,6-dichloroaniline (6.41 g, 0.0395 mol) in 50 mL MeCN was cooled to 0 °C in an ice bath. Chilled tert-butylnitrite (6.10 g, 0.0592 mol) was added followed by chilled trimethylsilyl azide (5.45 g, 0.0474 mol). The reaction mixture was allowed to stir for 3 h at RT. Afterwards all volatiles were removed in *vacuo*, making sure that the temperature of the rotary evaporation bath did not exceed 35 °C. The resulting crude oil was purified via column chromatography using pentane, collecting the first yellow fraction to give the substance as a yellow oil in 67% yield (4.99 g, 0.0265 mol). \(^1\)H NMR (benzene-\(d_6\), 25°C, 400 MHz): \(\delta\) 6.689 (d, 2, \(m\)-Ar-H), 6.189 (t, 1, \(p\)-Ar-H); m/z (CI mode) = 161 (\(2,6\text{-Cl}^2\text{ArN}_3 – \text{N}_2\)).

\(2,6\text{-Cl}^1\text{ArN=PMe}_3\). Under a nitrogen atmosphere a chilled solution of \(2,6\text{-Cl}^1\text{ArN}_3\) (4.99 g, 0.0265 mol) in 10 mL THF was added slowly to a chilled THF solution of 1 M trimethylphosphine (26.5 mL, 26.5 mmol, 1M in THF). Rapid gas evolution was observed. The yellow solution was allowed to react for 20 min at RT. All volatiles were removed from the crude product in *vacuo*. The product was used without additional
purification in the subsequent step. $^1$H NMR (benzene-$d_6$, 25°C, 400 MHz): $\delta$ 7.264 (d, 2, $m$-Ar-H), 6.333 (t, 1, $p$-Ar-H), 1.000 (s, 9, Me); m/z (CI mode) = 237.

$[\text{Cl}_2\text{N}_6\text{F}_6]\text{H}$ (1). This new $\beta$-diketiminato ligand was synthesized following an aza-Wittig protocol first published by Sadighi et al.$^{15}$

**Thermal conditions.** Under inert atmosphere, $\text{Me}_3\text{P}=\text{NAr}^{2,6\text{Cl}_2}$ (0.458 g, 1.94 mmol) in 3 mL toluene and 1,1,1,5,5,5-heaxafluoropentadione (0.201 g, 0.966 mmol) in 3 mL toluene were heated for 108 h at 100 °C inside a sealed pressure vessel. The brown reaction mixture was concentrated to remove all volatiles. The brown remaining oil was purified via column chromatography using 30:1 hexanes to toluene as the mobile phase. The first bright yellow fraction was collected. Crystallization from methanol at -7 °C afforded bright yellow crystals in 56% yield (0.269 g, 0.543 mmol). $^1$H NMR (benzene-$d_6$, 25 °C, 400 MHz): $\delta$ 11.50 (s, 1H, N-H) $\delta$ 6.83 (d, 4H, meta-Ar-H), $\delta$ 6.30 (t, 2H, para-Ar-H), $\delta$ 6.10 (s, 1.00, backbone-C-H); $^{13}$C NMR (benzene-$d_6$): $\delta$ 153.07, 152.76, 138.62, 131.18, 128.50, 127.98, 121.04, 118.19, 89.82; $^{19}$F NMR (C$_6$F$_6$ in C$_6$D$_6$): -69.712; m/z (CI mode) = 497. EA Calc C. 41.16; H. 1.63; N. 5.65; Found C. 40.94; H. 1.64; N. 5.39.

**Microwave conditions.** Under inert atmosphere $\text{Me}_3\text{P}=\text{NAr}^{2,6\text{Cl}_2}$ (0.620 g, 2.63 mmol) and 1,1,1,5,5,5-heaxafluoropentadione (0.273 g, 1.31 mmol) in 4 mL of toluene were loaded inside a microwave pressure vessel which was then sealed. The microwave heated the reaction mixture for 5 h at 150 °C, 100 Watts, and 275 psi. All volatiles were removed from the crude product in vacuo. The crude product was purified via column chromatography using silica and hexanes: toluene (30:1) and a bright yellow oil was
collected as the first compound off the column. Crystallization from pentane at -35 °C afforded bright yellow crystals in 42% yield (0.273 g, 0.551 mmol). $^{19}$F NMR (C$_6$F$_6$ in C$_6$D$_6$): $\delta$ -67.512 ppm. m/z (Cl mode) = 497.

{[Cl$_2$NN$_{F_6}$]Cu}$_2$(benzene) (2). Under an inert atmosphere, [Cl$_2$NN$_{F_6}$]H (2.38 g, 4.79 mmol) was added to a stirring suspension of CuOBu$^+$ (0.786 g, 5.75 mmol) in 6 mL benzene and 50 mL THF. The reaction mixture was allowed to stir for 3 h at room temperature. All volatiles were removed under vacuo and the remaining solid was washed with cold pentane to afford an orange solid in 75% yield (2.15 g, 1.79 mmol).

$^1$H NMR (benzene-$d_6$, 25°C, 400 MHz): $\delta$ 6.993 (d, 4H, meta-Ar-H), $\delta$ 6.401 (t, 2H, para-Ar-H), $\delta$ 6.095 (s, 1.00, backbone-C-H); $^{19}$F NMR (C$_6$F$_6$ in benzene-$d_6$): -67.512.

[Cl$_2$NN]Cu(CNAr$_{2,6-Me_2}$) (3a). To a suspension of {[Cl$_2$NN]Cu}$_2$(benzene) (0.150 g, 0.311 mmol) in 10 mL Et$_2$O was added 2,6-dimethylphenylisocyanide (0.041 g, 0.311 mmol). The reaction mixture was allowed to stir for 1 h at RT. The reaction mixture immediately changed colors to a bright yellow. All volatiles were removed in vacuo and the remaining solid was taken up in Et$_2$O and passed through Celite. Finally the yellow solution was concentrated to afford yellow crystals at -35 °C in 64% yield (0.115 g, 0.199 mmol) suitable for single crystal X-ray. $^1$H NMR (benzene-$d_6$, 25°C, 400 MHz): $\delta$ 7.124 (d, 3H, Ar-H), 6.617 (t, 1H, p-Ar-H), 6.424 (t, 4H, Ar-H), 5.076 (s, 1H, backbone C-H), 1.878 (s, 6H, backbone CH$_3$), 1.660 (s, 6H, o-Ar-CH$_3$); $^{13}$C {$^1$H} NMR (benzene-$d_6$, 25°C, 400 MHz): $\delta$ 164.84, 149.49, 135.41, 130.96, 128.89, 127.89, 123.85, 96.34,
23.40, 18.58. FT-IR: ν_{CN} = 2141 cm\(^{-1}\); EA Calc for C\(_{26}\)H\(_{22}\)Cl\(_4\)CuN\(_3\): C, 53.67; H, 3.81; N, 7.22; Found C, 53.61; H, 3.95; N, 7.40.

\[\text{[Cl}_2\text{NN}_6\text{]}\text{Cu(CNAr}^{2,6-\text{Me}}\text{)}\quad (3b)\]. To a suspension of \{[Cl\(_2\)NN\(_6\)]Cu\}\(_2\) (benzene) (0.120 g, 0.204 mmol) in 10 mL Et\(_2\)O was added 2,6-dimethylphenylisocyanide (0.028 g, 0.204 mmol). The reaction mixture was allowed to stir for 1 h at RT. The mixture changed immediately to a dark reddish brown color. All volatiles were removed in vacuo and the remaining solid was taken up in Et\(_2\)O and passed through Celite. The solution was concentrated to afford bright orange crystals at -35 °C suitable for single crystal X-ray in 64% yield (0.090 g, 0.130 mmol). \(^1\)H NMR (benzene-\(d_6\), 25°C): δ 7.020 (d, 3H, Ar-H), 6.613 (t, 1H, p-Ar-H), 6.384 (t, 4H, Ar-H), 6.293 (s, 1H, backbone C-H), 1.553 (s, 6H, o-Ar-CH\(_3\)); \(^{13}\)C \{\(^1\)H\} NMR (benzene-\(d_6\), 25°C, 400 MHz): δ 154.25, 146.67, 135.61, 129.68, 125.35, 122.63, 119.78, 86.41, 18.28. FT-IR: ν_{CN} = 2158 cm\(^{-1}\); EA Calc for C\(_{26}\)H\(_{16}\)Cl\(_4\)CuF\(_6\)N\(_3\): C, 45.27; H, 2.34; N, 6.09; Found C, 45.54; H, 2.51; N, 6.08.

\[\text{[Cl}_2\text{NN}_6\text{]}\text{Cu(\kappa}^1\text{-O-2-pyrrolidinone)}\quad (4)\]. To a suspension of \{[Cl\(_2\)NN\(_6\)]Cu\}\(_2\) (benzene) (0.150 g, 0.255 mmol) (2) in 10 mL Et\(_2\)O was added 2-pyrrolidinone (19.4 L, 0.022 g, 0.255 mmol). The reaction mixture was allowed to stir for 3 h at RT. An immediate color change to brighter yellow occurred. All volatiles were removed in vacuo and the remaining solid was taken up in Et\(_2\)O and filtered through Celite and finally
concentrated to crystallize at -35°C to afford brown crystals 48% yield (0.078 g, 0.121 mmol) suitable for single crystal X-ray.

\[ \text{[Cl}_2\text{NN}_6\text{F}_6\text{]}\text{Cu-OBu}^+ \text{ (5).} \text{ A chilled solution of di-tert-buty]peroxide (0.141 g, 0.967 mmol) in 2 mL pentane was added to a chilled solution of \{[Cl}_2\text{NN}_6\text{Cu}\}_2(\text{benzene}) \text{ (0.135 g, 0.113 mmol) in 3 mL pentane. The reaction mixture was allowed to stir at room temperature for 90 min and changed color from orange/yellow to purple/maroon. All volatiles were removed under vacuo and the remaining solid was taken up in 20 mL of pentane and filtered through Celite and concentrated for crystallization at -35 °C to afford red crystals in 34% yield (0.050 g, 0.0791 mmol). UV-Vis: (benzene, 25°C) } \lambda_{\text{max}} = 520 \text{ nm (3750 M}^{-1}\text{ cm}^{-1}). \]

**Figure 4.10.** Beer’s law plot of [Cl\text{2NN}_6\text{F}_6\text{]}\text{Cu-OBu}^+ \text{ in benzene at 25 °C (} \lambda_{\text{max}} = 520 \text{ nm (3750 M}^{-1}\text{ cm}^{-1}). \)**
[Cl\textsubscript{2}NN\textsubscript{F\textsubscript{6}}]Cu(NH\textsubscript{2}Mes) (6). To a chilled solution of [Cl\textsubscript{2}NN\textsubscript{F\textsubscript{6}}]Cu-OBu\textsuperscript{t} (0.187 g, 0.296 mmol) in 10 mL pentane was added a chilled solution of mesitylaniline (0.040 g, 0.296 mmol) in 5 mL pentane. All volatiles were immediately removed in vacuo while a color change from red to greenish brown was observed. The resulting solid was taken up in pentane and passed through Celite and concentrated and allowed to crystallize at -35 °C. A greenish/blue solution produced red crystals in 75% yield (0.154 g, 0.222 mmol) suitable for single crystal X-ray diffraction. [Cl\textsubscript{2}NN\textsubscript{F\textsubscript{6}}]Cu(NH\textsubscript{2}Mes)•NH\textsubscript{2}Mes EA Calc for C\textsubscript{35}H\textsubscript{33}Cl\textsubscript{4}CuF\textsubscript{6}N\textsubscript{4}: C, 50.71; H, 4.01; N, 6.76; Found C, 50.33; H, 4.18; N, 6.65.

[Cl\textsubscript{2}NN\textsubscript{F\textsubscript{6}}]Cu(NH(Et)Ph) (7). To a chilled solution of [Cl\textsubscript{2}NN\textsubscript{F\textsubscript{6}}]Cu-OBu\textsuperscript{t} (0.080 g, 0.127 mmol) in 3 mL pentane was added a chilled solution of N-ethylaniline (15.9 µL, 0.015 g, 0.127 mmol) in 2 mL pentane. An immediate color change from red to brown was observed. All volatiles were removed in vacuo and the remaining solid was taken up in pentane and passed through Celite. The resulting brown solution was concentrated and allowed to crystallize at -35 °C to afford red needles in 80% yield (0.069 g, 0.102 mmol) suitable for single crystal X-ray diffraction. Calc for C\textsubscript{35}H\textsubscript{18}Cl\textsubscript{4}CuF\textsubscript{6}N\textsubscript{3}: C, 44.53; H, 2.88; N, 5.97; Found C, 44.17; H, 2.67; N, 6.18.
4.3.b. Experimental details for catalytic amination, amidation and cyclization reactions

**2,4,6-trimethyl-N-(1-phenylethyl)aniline.** To a solution of mesitylamine (104. L, 0.100 g, 0.741 mmol), iBuOObBu (136. L, 0.108 g, 0.741 mmol), and 20 mL ethylbenzene was added 1 mol% 2 (1.33 mL of 5.61 mM in benzene). The reaction mixture was sealed inside a pressure vessel and heated to 80 °C for 16 h. GC/MS m/z (CI) = 240 (diazene MesN=NMes m/z (CI) = 267; MesNH₂ m/z (CI) = 136).

**N-(1-phenylethyl)-3,5-bis(trifluoromethyl)aniline.** To a solution of 3,5-fluoromethylaniline (231. L, 1.48 mmol), iBuOObBu (1.36 mL, 7.4 mmol), and 20 mL of ethylbenzene was added 1 mol% 2 (2.66 mL of 5.61 mM in benzene). The reaction mixture was sealed inside a pressure vessel and heated to 80 °C for 16 h. GC/MS m/z (CI) = 334 (two peaks). N-(1-phenylethyl)-3,5-bis(trifluoromethyl)aniline quantified via use of 1,2,4,5-tetrachlorobenzene standard δ 7.500 ppm (s, 2H, Ar-H) by ¹H NMR 400 MHz, benzene-d₆, RT) showed 67% yield of N-(1-phenylethyl)-3,5-bis(trifluoromethyl)aniline 4.201 ppm (quintet, 1H, benzylic-CH).

**2,2,2-trifluoro-N-phenyl-N-(1-phenylethyl)acetamide.** To a solution of 2,2,2-trifluoro-N-phenylacetamide (0.189 g, 1.0 mmol),
'BuOObu' (219 L, 0.176 g, 1.2 mmol), 10 mL ethylbenzene was added 1 mol% 2 (1.64 mL of 6.11 mM in benzene). The reaction mixture was sealed inside a pressure vessel and heated to 80 °C for 24 h. GC/MS m/z (CI) = 294 (starting material m/z (CI) = 190). 2,2,2-trifluoro-N-phenyl-N-(1-phenylethyl)acetamide was quantified via use of 1,2,4,5-tetrachlorobenzene standard δ 7.500 ppm (s, 2H, Ar-H) by 1H NMR 400 MHz, benzene-d₆, RT) showed 24% yield of 2,2,2-trifluoro-N-phenyl-N-(1-phenylethyl)acetamide 6.170 ppm (quartet, 1H, benzylic-CH).

**2,3,4,5-tetrahydrobenzo[b]oxepine.** To a solution of 4-phenyl-1-butanol (153 L, 1.0 mmol), 'BuOObu' (219 L, 1.2 mmol), 5 mL benzene was added 1 mol% of 2 (2.5 mL of 4.0 mM in benzene). The reaction mixture was heated to 80 °C for 20 h inside a pressure vessel. 1H NMR (benzene-d₆, RT, 400 MHz): δ 3.900 ppm (t, 2H, CH₂), 2.321 (t, 2H, Ar-CH₂), 1.348 (m, 4H, CH₂); 13C {¹H} NMR (benzene-d₆, 25°C, 400 MHz): δ 27.55, 35.10, 63.58, 126.25, 141.77 and 172.48 ppm; GC/MS m/z (CI) = 147.1, 148.1 and 149.1. 2,3,4,5-tetrahydrobenzo[b]oxepine was quantified via use of 1,2,4,5-tetrachlorobenzene standard δ 7.500 ppm (s, 2H, Ar-H) by 1H NMR (400 MHz, benzene-d₆, RT) showed 22% yield of 2,3,4,5-tetrahydrobenzo[b]oxepine employing the resonance at δ 3.901 ppm (t, 2H, O-CH₂).

**1D TOCSY** (benzene-d₆, 400 MHz, RT): Irradiation at δ 3.901 (CH₂ (1)) gives following signals: δ 3.901 ppm (t, 1-H), 2.321 (t, 4-H) and 1.348 (m, 2-H and 3-H).
GCOSY (benzene-$d_6$, 400 MHz, RT) $\delta$ 3.901 (1-H) / 1.348 (2-H); 2.321 (4-H) / 1.348 (3-H); 1.348 (2-H, 3-H) / 3.901 (1-H); 1.348 (2-H, 3-H) / 2.321 (4-H).

GHSQC (benzene-$d_6$, 400 MHz, RT) $\delta$ 3.901 (1-H) / 63.58 (1-C); 2.321 (4-H) / 35.10 (4-C); 1.348 (2-H, 3-H) / 27.55 (2-C, 3-C).

GHMBC (benzene-$d_6$, 400 MHz, RT) $\delta$ 3.904 (1-H) / 27.55 (2-C); 3.904 (1-H) / 172.48 (10-C); 2.321 (4-H) / 27.55 (3-C); 2.321 (4-H) / 126.25 (6-C); 2.321 (4-H) / 141.77 (5-C).

**3,4,5,6-tetrahydro-2H-benzo[b]oxocine.** To a solution of 5-phenyl-1-pentanol (169 µL, 1.0 mmol), $t$BuOOBu$^t$ (219 µL, 1.2 mmol), 5 mL benzene was added 1 mol% of 2 (2.5 mL of 4.0 mM in benzene). The reaction mixture was heated to 80 °C for 20 h inside a pressure vessel. 3,4,5,6-tetrahydro-2H-benzo[b]oxocine was quantified via use of 1,2,4,5-tetrachlorobenzene standard $\delta$ 7.500 ppm (s, 2H, Ar-H) by $^1$H NMR (400 MHz, benzene-$d_6$, RT) showed 25% yield of 3,4,5,6-tetrahydro-2H-benzo[b]oxocine using the resonance at $\delta$ 3.904 ppm (t, 2H, O-CH$_2$). $^1$H NMR (benzene-$d_6$, RT, 400 MHz): $\delta$ 3.900 (t, 2H, O-CH$_2$), 2.347 (t, 2H, Ar-CH$_2$), 1.351 (m, 4H, CH$_2$), 1.090 (m, 2H, CH$_2$); $^{13}$C $\{^1$H$\}$ NMR (benzene-$d_6$, 25°C, 400 MHz): $\delta$ 25.25, 28.32, 30.73, 35.49, 63.71, 128.21, 142.05 and 172.49. GC/MS m/z (Cl) = 163.

**1D TOCSY (benzene-$d_6$, 400 MHz, RT):** Irradiation at $\delta$ 3.904 (CH$_2$ (1)) gives following signals: $\delta$ 3.904 (t, 2H, 1-H), 2.347 (t, 2H, 5-H), 1.354 (m, 4H, 2-H and 4-H), 1.094 (m, 2H, 3-H).
**GCOSY** (benzene-$d_6$, 400 MHz, RT) $\delta$ 3.904 (1-H) / 1.354 (2-H); 2.347 (5-H) / 1.354 (4-H); 1.354 (2-H) / 3.904 (1-H); 1.354 (2-H, 4-H) / 1.094 (3-H); 1.354 (4-H) / 2.347 (5-H); 1.094 (3-H) / 1.354 (2-H, 4-H).

**GHSQC** (benzene-$d_6$, 400 MHz, RT) $\delta$ 3.904 (1-H) / 63.71 (1-C); 2.347 (5-H) / 35.49 (5-C); 1.354 (2-H, 4-H) / 30.73 and 28.32 (2-C, 4-C); 1.094 (3-H) / 25.25 (3-C).

**GHMBC** (benzene-$d_6$, 400 MHz, RT) $\delta$ 3.904 (1-H) / 25.25 (3-C); 3.904 (1-H) / 28.32 (2-C); 3.904 (1-H) / 172.49 (11-C); 2.347 (5-H) / 25.25 (3-C); 2.347 (5-H) / 30.73 (4-C); 2.347 (5-H) / 128.21 (7-C); 2.347 (5-H) / 142.05 (6-C); 1.354 (3-H) / 142.05 (6-C).

**References**


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Chapter 5

Bifunctional Reactivity of a Ni(III)-Imide in C-H Functionalization

Abstract

Reinvestigation of Ni(III) imido species [Me₃NN]Ni=NAd (1) showed surprising reactivity with C-H substrates. Reaction of 1 with ethylbenzene forms the new Ni(II) amido species [Me₃NN]Ni-N(Ad)CH(Me)Ph (2). Similarly, reaction of 1 with toluene results in a Ni(II) aminoalkyl product [Me₃NN]Ni(η²-CH(Ph)NHAd) (3) which may be considered a tautomer of the secondary nickel(II) amide [Me₃NN]Ni-N(Ad)CH₂Ph related by β-H elimination / reinsertion. Based on these products a H-atom abstraction / radical combination (HAA / RC) mechanism is proposed in which [Me₃NN]Ni=NAd (1) first abstracts a H-atom from the C-H substrate R-H followed by RC of a second equiv. of 1 with the newly formed organic radical R•. Kinetic analysis were performed on the reaction of [Me₃NN]Ni=NAd (1) with excess toluene, ethylbenzene and indane. The overall free energies of activation track with bond dissociation enthalpies (BDE) of the reacting C-H bonds – lower barriers are observed with weaker C-H bonds. Surprising was the decrease in ΔH‡ (with increase in ΔS‡) with increasing BDE. In collaboration with Prof. Tom Cundari and Dr. Jason McAfee of the University of North Texas, we suggest that the more sterically hindered substrates assume a looser, more disordered transition state (TS) that increases ΔH‡ for these reactions. Indicating that
other reaction pathways may be operative, a bridged dinickel nitrene \{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{NAd})_2 (4) is isolated from the reaction of 1 with excess indane. This finding led to two additional mechanistic proposals: (a) HAA followed by radical combination of \( \text{R}^\bullet \) with nickel(II) amide \([\text{Me}_3\text{NN}]\text{Ni-NHAd}\) to give the nickel(I) amine \([\text{Me}_3\text{NN}]\text{Ni(NH(Ad)R)}\) or (b) direct insertion of \([\text{Me}_3\text{NN}]\text{Ni=NAd}\) (1) into the \( \text{R-H} \) bond to give \([\text{Me}_3\text{NN}]\text{Ni(NH(Ad)R)}\).

**Introduction**

As discussed in the introduction to Chapter 3, C-H amination is an attractive, emerging strategy to introduce N atoms into organic molecules. While metal-nitrene intermediates \([\text{M}]=\text{NR}\) attract the most attention, we have also discovered that the discrete copper(II)-amide \([\text{Cl}_2\text{NN}]\text{Cu-NHAd}\) can engage in a H-atom abstraction / radical capture sequence (HAA/ RC) functionalize C-H bonds (Scheme 5.1).

**Scheme 5.1.** HHA and RC mechanism for stoichiometric reaction.

\[
\begin{align*}
[\text{Cu}^\text{II}]=[\text{Cl}_2\text{NN}]\text{Cu-NHAd} &\rightarrow \text{R-H} & [\text{Cu}^\text{II}][\text{NH}_2\text{Ad}]
\end{align*}
\]

In this light we became interested in the possibility of related bifunctional reactivity by the nickel(III)-imide \([\text{Me}_3\text{NN}]=\text{NAd}\) (1). For instance, \([\text{Me}_3\text{NN}]\text{Ni=NAd}\) reacts with 1,4-cyclohexadiene via hydrogen atom abstraction (HAA) to form \([\text{Me}_3\text{NN}]\text{Ni-NHAd}\) and \( \frac{1}{2} \) equiv. benzene (Scheme 5.2). Additionally, \([\text{Me}_3\text{NN}]\text{Ni=NAd}\) undergoes reaction with substrates such as \( \text{Cp}_2\text{Co} \) that exhibit C-
based radical character to form $[\text{Me}_3\text{NN}]\text{Ni-NAd}(\eta^4\text{-C}_5\text{H}_5)\text{CoCp}$ featuring a new N-C bond (Scheme 5.2).²

**Scheme 5.2.** Bifunctional reactivity of $[\text{Me}_3\text{NN}]\text{Ni=NAd}$.

Furthermore, the nickel(III)-imide $[\text{Me}_3\text{NN}]\text{Ni=NAd}^2$ and copper(II)-amide $[\text{Cl}_2\text{NN}]\text{Cu-NHAd}^1$ possess related electronic structures (Figure 5.1). Each exhibits incomplete $\pi$-bonding owing to the presence of an additional electron that results in a 2-center, 3-electron $\pi$-interaction. Both species have resonance structures that can place the radical at either the metal center or the nitrogen of the imido or amido group. The net result is a significant amount of unpaired electron density at the imide (0.57 e)$^2$ or amide (0.49 e)$^1$ as predicted by DFT. EPR spectroscopy of $[\text{Me}_3\text{NN}]\text{Ni=NAd}$ and $[\text{Cl}_2\text{NN}]\text{Cu-NHAd}$ experimentally supports this electronic structure in which the
interaction of the unpaired electron in these $S = \frac{1}{2}$ species with the N atom is both significant and highly anisotropic. For example, X-band EPR data collected at 77K in frozen glass (toluene) of $[\text{Me}_3\text{NN}]\text{Ni} = \text{NAd}$ showed a rhombic environment with $g_1 = 2.162$, $g_2 = 2.038$ and $g_3 = 1.937$. The $g$-value at $g = 2.038$ shows a hyperfine splitting pattern that is a 1:1:1 triplet ($A_2(N) = 63 \text{ MHz}$) which is consistent with the involvement of the imido nitrogen ($^{14}\text{N}; I = 1$) in the single occupied molecular orbital of this low-spin species. Similarly, the X-band EPR spectrum of $[\text{Cl}_2\text{NN}]\text{Cu} = \text{NHAd}$ at 55 K in toluene glass shows a nearly axial environment with $g_1 = 2.133(5)$, $g_2 = 2.036(5)$ and $g_3 = 2.031(5)$ with a highly anisotropic interaction with the amido N atom ($A_1(N) = 5$; $A_2(N) = 5$; $A_3(N) = 63 \text{ MHz}$). Combined with the hyperfine coupling constant $A_1(\text{Cu}) =
365(10) MHz these values are also consistent with the involvement of the amido nitrogen in the singly occupied molecular orbital.¹

Based on these strong similarities between [Me₃NN]Ni=NAd and [Cl₂NN]Cu-NHAd, we became interested in examining the possibility of a related HAA / radical capture sequence that would result in the formation of new C-N bonds employing simple hydrocarbons R-H (Scheme 5.3). Drawing close analogy to that which we have established for [Cl₂NN]Cu-NHAd, we envision a rate limiting first step in which the nickel(III) imido abstracts a hydrogen atom from a C-H substrate R-H followed by rapid capture of the radical R• by an additional equivalent of [Me₃NN]Ni=NAd.

**Scheme 5.3.** Proposed sequential HAA / radical capture reactivity of [Me₃NN]Ni=NAd.

```latex
\begin{align*}
\text{Step I: } & \quad [\text{Me}_3\text{NN}]\text{Ni}=\text{NAd} + \text{R-H} \xrightarrow{\text{RDS}} [\text{Me}_3\text{NN}]\text{Ni-NHAd} + \text{R}\cdot \\
\text{Step II: } & \quad [\text{Me}_3\text{NN}]\text{Ni}=\text{NAd} + \text{R}\cdot \quad \longrightarrow \quad [\text{Me}_3\text{NN}]\text{Ni}-\begin{array}{c}\text{Ad} \\
\text{R}
\end{array}
\end{align*}
```

**Overall reaction**


---

**Results and Discussion**

**5.2.a. Stoichiometric reaction of [Me₃NN]Ni=NAd with ethylbenzene**

The stoichiometric reaction of [Me₃NN]Ni=NAd (1) with 100 equiv. ethylbenzene in Et₂O at RT yielded the Ni(II) secondary amido species [Me₃NN]Ni-
Scheme 5.3. Stoichiometric reaction of 1 with ethylbenzene.

\[
2 \text{[Me}_3\text{NN]}\text{Ni=NA}_\text{d} + \text{Et}_2\text{O} \rightarrow \text{[Me}_3\text{NN]}\text{Ni=NA}_\text{d} \quad \text{(2)}
\]
N(Ad)CH(Me)Ph (2) as brown crystals isolated in 49% yield upon crystallization from Et₂O at -35 °C (Scheme 5.3).

The X-ray structure of the three-coordinate Ni(II)-amide 2 reveals a short Ni-Namido distance of 1.794(5) Å along with relatively short Ni-Nβ-dik distances of 1.877(5) and 1.874(5) Å (Figure 5.2). These parameters may be compared to those found in the related Ni(II)-amido species [Me₃NN]Ni-NA₅(C₅H₅)CoCp₂ with a Ni-Namido distance of 1.812(3) Å along with Ni-Nβ-dik distances of 1.881(3) and 1.879(3) Å. The two Ni-Namido-C angles of 122.5(4) and 123.7(5)° are both consistent with sp²-hybridized Namido donor further supported by the sum of the angles about Namido of 359.4° which indicates an essentially planar environment at this N atom.

The ¹H NMR spectrum of 2 in benzene-*_d*_6 (Figure 5.3) shows a diamagnetic species with characteristic C-H backbone peak at δ 4.709 ppm. The asymmetric spectrum due to the newly formed chiral center at the benzylic position shows a set of two peaks for the β-diketiminato o-Ar at δ 1.818 and 1.508 ppm, while the m-Ar and backbone Me groups at δ 2.189 and 1.241 ppm, respectively. Importantly, the newly formed benzylic CH appears as a quartet at δ 2.580 ppm coupled to the CHMe group which appears as a doublet at δ 1.626 ppm.
Figure 5.2. X-ray crystal structure of [Me₃NN]Ni-N(Ad)CH(Me)Ph (2). All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ni-N1 1.877(5), Ni-N2 1.874(5), Ni-N3 1.794(5), N3-C24 1.489(8), N3-C40 1.505(8), N1-Ni-N2 93.6(2), Ni-N3-C24 122.5(4), Ni-N3-C40 123.7(5), C24-N3-C40 113.2(5), C24-N3-C40 113.2(5).
[Me₃NN]Ni-N(Ad)CH(Me)Ph (2) can also be synthesized by forming [Me₃NN]Ni=NAd (1) *in situ* from the corresponding organoazide in the presence of ethylbenzene. Reaction [Me₃NN]Ni(2-picoline) with 1-azidoadamantane (AdN₃) in a solution of 1:1 ethylbenzene:Et₂O yields 2 in 49% yield as brown crystals when crystallized from Et₂O at -35 °C (Scheme 5.4).

**Scheme 5.4.** *In situ* formation of [Me₃NN]Ni=NAd (2) for the reaction with ethylbenzene.
Based on the proposed HAA / RC mechanism (Scheme 5.3), we set out to further investigate the proposed mechanism via quantification of [Me$_3$NN]Ni-NHAd. Theoretically, [Me$_3$NN]Ni-NHAd should account for the missing 50% yield of this reaction considering that [Me$_3$NN]Ni-N(Ad)CH(Me)Ph (2) is isolated in 49% yield. A reaction mixture initially containing [Me$_3$NN]Ni=NAd (1) in neat ethylbenzene was hydrolyzed after 24 h and analyzed against an internal standard. Observed via GC/MS were the organic molecules AdNH$_2$ and NH(Ad)CH(Me)Ph in 43(10)% and 69(10)% yields, respectively. These results are in agreement with the hypothesis that [Me$_3$NN]Ni-NHAd and [Me$_3$NN]Ni-NH(Ad)CH(Me)Ph were formed in a nearly 1:1 ratio prior to hydrolysis. More ideal would be the direct detection of [Me$_3$NN]Ni-NHAd which has thus far proven somewhat elusive.

5.2.b. Kinetic analysis of the reaction of [Ni]=NAd (1) with ethylbenzene

Using UV-vis spectroscopy, we monitored the reaction of [Me$_3$NN]Ni=NAd (1) with excess ethylbenzene to gain insight into the conversion of 1 to 2. In a typical reaction of 1 (2.32 mM) with ethylbenzene (4.64 M) with benzene as the (co)solvent at 45 °C, we followed the loss 1 as monitored by its $\lambda_{\text{max}} = 596$ nm band (Figure 5.4).

Scheme 5.5. Proposed mechanism consistent with kinetic data.

\[
\begin{align*}
\text{Step I: } [\text{Me}_3\text{NN}]\text{Ni}=\text{NAd} + & \quad \text{[Me}_3\text{NN}]\text{Ni-NHAd} + \quad \text{[Me}_3\text{NN}]\text{Ni}-\text{N(Ad)CH(Me)Ph} \\
\text{Step II: } [\text{Me}_3\text{NN}]\text{Ni}=\text{NAd} + & \quad \text{[Me}_3\text{NN}]\text{Ni}\text{N-Ad}_{\text{CH(CH}_3)\text{Ph}} \\
\text{rate} = 1.04(3) \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1} \quad [\text{Ni}=\text{NAd}]^{-1} [\text{ethylbenzene}]^{-1}
\end{align*}
\]
Plots of $\ln(A-A_{\text{inst}})$ vs. time yielded straight lines, indicating that the reaction is 1st order in [Me$_3$NN]Ni=NAd (1). Varying the ethylbenzene concentration (2.48, 3.71, 4.95, and 6.19 M) while keeping the [Me$_3$NN]Ni=NAd (1) concentration constant (2.47 mM) in benzene at 25 °C yielded observed rate constants $k_{\text{obs}}$ that varied linearly with [ethylbenzene] (Figure 5.5 and Table 5.1) indicating first order behavior in ethylbenzene as well. From this data, we arrived at the rate expression: rate = $k_1$ [Ni=NAd]$^1$ [ethylbenzene]$^1$ with $k_1 = 1.04(3) \times 10^{-5}$ M$^{-1}$ s$^{-1}$ at 25 °C (Figure 5.6 and Table 5.2). Varying the temperature (25, 35, 45, 55 °C) employing uniform initial concentrations of [Me$_3$NN]Ni=NAd (1) (2.47 mM) and ethylbenzene (4.95 M) allowed the determination of second order rate constants $k_1$ at these temperatures from which an Eyring plot was constructed (Figure 5.7 and 5.8). This analysis yielded activation parameters $\Delta H^\ddagger = +11.6(7)$ kcal/mol, $\Delta S^\ddagger = -42(2)$ cal/mol•K, $\Delta G^\ddagger_{(298K)} = +24.2(25)$ kcal/mol). Comparison of observed rate constants in the reaction of [Me$_3$NN]Ni=Ad (1) (2.41 mM) with either ethylbenzene or ethylbenzene-$d_{10}$ (each 4.82 M) at 35 °C in benzene led to the primary kinetic isotope effect $k_H/k_D = 4.6$ (4) (Figure 5.9). Thus, the rate determining step (or steps leading to it) involve a significant amount of C-H bond cleavage.
Figure 5.4. Consumption of $[\text{Me}_3\text{NN}]\text{Ni=NAd}$ (1) as monitored by the loss of its UV-vis absorbance at $\lambda = 596$ nm in the presence of 2000 equiv. ethylbenzene under pseudo first-order conditions in benzene at 45 °C. Scan interval = 300 s.

Figure 5.5. Kinetic plots of $\ln(A_t/A_0)$ vs. time ($A$ = absorbance at $\lambda = 596$ nm) for the C-H abstraction from ethylbenzene by $[\text{Me}_3\text{NN}]\text{Ni=NAd}$ (1) in the presence of 1000, 1500, 2000 and 2500 equiv. ethylbenzene under pseudo first order conditions. The initial concentration of $[\text{Me}_3\text{NN}]\text{Ni=NAd}$ (1) was 2.48 mM in each case.
Table 5.1. Observed rate constants for C-H abstraction of ethylbenzene by [Me₃NN]Ni=NAd (I) under pseudo first order conditions (excess ethylbenzene).

<table>
<thead>
<tr>
<th>ethylbenzene amt</th>
<th>[ethylbenzene] (M)</th>
<th>k_{obs} (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 equiv.</td>
<td>2.48</td>
<td>3.5(1) × 10⁻⁵</td>
</tr>
<tr>
<td>1500 equiv.</td>
<td>3.71</td>
<td>4.4(1) × 10⁻⁵</td>
</tr>
<tr>
<td>2000 equiv.</td>
<td>4.95</td>
<td>6.0(1) × 10⁻⁵</td>
</tr>
<tr>
<td>2500 equiv.</td>
<td>6.19</td>
<td>7.3(1) × 10⁻⁵</td>
</tr>
</tbody>
</table>

Figure 5.6. Plot of observed first-order rate constant k_{obs} vs. [ethylbenzene].

Table 5.2. Observed pseudo first order rate constants k_{obs} and second order rate constants k₁ for the C-H abstraction of ethylbenzene (2000 equiv.) by [Me₃NN]Ni=NAd (I) in benzene.

<table>
<thead>
<tr>
<th>Temp</th>
<th>k_{obs} (s⁻¹)</th>
<th>k₁ (M⁻¹s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 °C</td>
<td>7.2(1) × 10⁻⁵</td>
<td>1.4(2) × 10⁻⁵</td>
</tr>
<tr>
<td>35 °C</td>
<td>1.1(1) × 10⁻⁴</td>
<td>2.4(2) × 10⁻³</td>
</tr>
<tr>
<td>45 °C</td>
<td>2.1(1) × 10⁻⁴</td>
<td>4.4(2) × 10⁻⁵</td>
</tr>
<tr>
<td>55 °C</td>
<td>4.1(1) × 10⁻⁴</td>
<td>8.2(2) × 10⁻⁵</td>
</tr>
</tbody>
</table>
Figure 5.7. Kinetic plots of $\ln(A_t/A_0)$ vs. time ($A =$ absorbance at $\lambda = 596$ nm) for the C-H abstraction of ethylbenzene (2000 equiv.) by [Me$_3$NNi=NAd (1) at 25 °C, 35 °C, 45 °C and 55 °C. The initial concentration of [Me$_3$NNi=NAd (1) and ethylbenzene were 2.48 mM and 4.96 M, respectively.
Figure 5.8. Eyring plot of ln(k/T) vs. 1/T for C-H abstraction of 2000 equiv. ethylbenzene (4.95 M) using second order rate constants collected in Table 5.2. Error analysis in H and S follows that by Girolami et al. using a assumed temperature error of +/- 0.5 C and assuming an average error of 4% in the absolute values of the rate constants.³

![Eyring plot of ln(k/T) vs. 1/T for C-H abstraction](image)

\[ \Delta H^\ddagger = +11.6(7) \text{ kcal/mol} \]
\[ \Delta S^\ddagger = -42(2) \text{ e.u.} \]
\[ \Delta G^\ddagger_{298K} = +24.2(25) \text{ kcal/mol} \]

Figure 5.9. First order decay of [Me₃NN]Ni=NAd (1) (2.41 mM) (monitored at 596 nm) with excess ethylbenzene (4.82 M; red) or excess ethylbenzene-\text{d}_{10} (4.82 M; blue) in benzene at 35 °C. KIE = 4.6(4).

![First order decay of [Me₃NN]Ni=NAd (1)](image)
5.2.c. Stoichiometric reaction of [Me$_3$NN]Ni=NAd (1) with toluene

The stoichiometric reaction of [Me$_3$NN]Ni=NAd (1) with neat toluene at RT yielded the Ni(II) secondary alkyl species [Me$_3$NN]Ni(η$^2$-CH(Ph)NHAd) (3) as brown crystals in 38% yield from Et$_2$O at -35 °C (Scheme 5.6). The connectivity of this species was determined by X-ray crystallography that revealed a Ni-C bonded species possessing an η$^2$-aminoalkyl group likely formed via the tautomerization of [Me$_3$NN]Ni-N(Ad)CH$_2$Ph via a β-H elimination / reinsertion sequence (Scheme 5.7).

Scheme 5.6. Stoichiometric reaction of 1 with toluene.

\[
2 \text{[Me}_3\text{NN]Ni=NAd} + \text{toluene} \rightarrow \text{[Me}_3\text{NN]Ni=CH}_2\text{NHAd} \rightarrow \text{[Me}_3\text{NN]Ni=CH}_2\text{Ph} \rightarrow \text{[Me}_3\text{NN]Ni=NAd} \text{Ph} \text{38% yield}
\]

Scheme 5.7. Proposed mechanism for tautomerization to 3.

The X-ray structure of 3 (Figure 5.10) reveals a four-coordinate Ni(II)-aminoalkyl species 3 that shows Ni-C$_{\text{alkyl}}$ bond distance of 1.895(5) Å and Ni-N$_{\text{amine}}$ bond distance of 1.920(4) Å along with a highly acute Ni-C$_{\text{alkyl}}$-N$_{\text{alkyl}}$ angle of 69.4(3)$^\circ$. The Ni-N$_{\beta-\text{dik}}$ distances are 1.920(4) and 1.875(4) Å. Such unsymmetric Ni-N$_{\beta-\text{dik}}$ bond distances were also observed in the related β-agostic alkyl complex [Me$_2$NN]Ni-CH$_2$CH$_3$. The weak donation of the β-agostic interaction (relative to the covalent σ-bond to C) allows the trans-Ni-N$_{\beta-\text{dik}}$ distance to be shorter. Similarly in complex 3, the
elongated Ni-Nβ-dik distance is trans to the Ni-Namine donor in the β-diketiminato coordination wedge.

The 1H NMR spectrum of 3 in benzene-d6 at RT shows a diamagnetic species with a characteristic C-H backbone peak at δ 4.145 ppm (Figure 5.11). The o-Ar, p-Ar and backbone Me groups appear at δ 2.666, 2.250 and 1.575 ppm, respectively. The fact that we observe only a single resonance for each of these three sets of peaks indicates the presence of a fast fluxional process in which the NHAd group dissociates from nickel to allow free rotation about the Ni-Calkyl bond. Alternatively, the symmetric NMR could also be caused by a fast interchange of the two isomers shown in Scheme 5.6.

Based on the proposed HAA / RC discussed above, we set out to further investigate the proposed mechanism via quantification of [Me3NN]Ni-NHAd that we anticipate forms. Theoretically, [Me3NN]Ni-NHAd should account for 50% yield of this reaction; [Me3NN]Ni(I2-CH(Ph)NHAd) (3) is isolated in 38% yield. The reaction mixture of [Me3NN]Ni=NAd (2) in neat toluene was hydrolyzed after 48 h and analyzed by GC/MS using an internal standard to show AdNH2 and NH(Ad)CH2Ph in 36(10)% and 40(10)% yield, respectively. These results support the formation of [Me3NN]Ni-NHAd and [Me3NN]Ni(I2-CH(Ph)NHAd) (3) in a nearly 1:1 ratio prior to hydrolysis.
Figure 5.10. X-ray crystal structure of $[\text{Me}_3\text{NN}]\text{Ni}[	ext{Ph}_2\text{CH}](\text{Ph})\text{HAd}$ (3). All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ni-N1 1.920(4), Ni-N2 1.875(4), Ni-N3 1.920(4), Ni-C34 1.895(5), N3-C24 1.502(5), N3-C34 1.423(7), N1-Ni-N2 96.80(18), Ni-N3-C24 127.3(3), Ni-N3-C34 67.0(3), C24-N3-C34 120.2(5), N2-Ni-C34 104.7(2), Ni-C34-N3.
5.2.d. Kinetics analysis of the reaction of [Ni]=NAd (1) with toluene

Using UV-vis spectroscopy, we monitored the reaction of [Me₃NN]Ni=NAd (1) with excess toluene to gain insight into the conversion of 1 to 3 (Scheme 5.8). In a

Scheme 5.8. Proposed mechanism for formation of 3.

Step I: [Me₃NN]Ni=NAd + \[\begin{array}{c} \text{C} \\ \text{H}_2 \text{Ph} \end{array} \]  \xrightarrow{k_1} [Me₃NN]Ni-NHAd + \[\begin{array}{c} \text{C} \\ \text{H}_2 \text{Ph} \end{array} \]

Step II: [Me₃NN]Ni=NAd + \[\begin{array}{c} \text{C} \\ \text{H}_2 \text{Ph} \end{array} \]  \xrightarrow{\text{taut.}} [Me₃NN]Ni-NAd \[\begin{array}{c} \text{C} \\ \text{H}_2 \text{Ph} \end{array} \]

Step III: [Me₃NN]Ni-NAd \[\begin{array}{c} \text{C} \\ \text{H}_2 \text{Ph} \end{array} \]  \xrightarrow{\text{taut.}} [Me₃NN]Ni-CH \[\begin{array}{c} \text{Ph} \end{array} \]

Figure 5.11. $^1$H NMR spectrum (400 MHz, benzene-$d_6$, RT) of [Me₃NN]Ni(η²-CH(Ph)NHAd (3)).
reaction of $1$ (2.32 mM) with toluene (4.64 M) with benzene as the (co)solvent at 45 °C, we followed the loss $1$ as monitored by its $\lambda_{\text{max}} = 596$ nm band (Figure 5.12). Plots of $\ln(A-A_{\text{inf}})$ vs. time yielded straight lines, indicating that the reaction is 1st order in $[\text{Me}_3\text{NN}]\text{Ni}=\text{NAd} \ (1)$. Varying the temperature (35, 45, 55, 65 °C) employing uniform initial concentrations of $[\text{Me}_3\text{NN}]\text{Ni}=\text{NAd} \ (1) \ (2.41 \text{ mM})$ and toluene (7.23 M) allowed the determination of second order rate constants $k_1$ at these temperatures from which an Eyring plot was constructed (Figure 5.13 and Table 5.3). This analysis yielded activation parameters $\Delta H^\ddagger = +10.0(10) \text{ kcal/mol}$, $\Delta S^\ddagger = -50(3) \text{ cal/mol} \cdot \text{K}$ and $\Delta G^\ddagger_{298\text{K}} = +25.1(13) \text{ kcal/mol}$. 
Figure 5.12. Consumption of [Me₃NN]Ni=NAd (1) as monitored by the loss of its UV-vis absorbance at \( \lambda = 596 \) nm in the presence of 2000 equiv. toluene under pseudo first order conditions in benzene at 45 °C. Scan interval = 300 sec.

\[ \Delta H^\ddagger = +10.0(10) \text{ kcal/mol} \]
\[ \Delta S^\ddagger = -50(3) \text{ e.u.} \]
\[ \Delta G^\ddagger_{298K} = +25.1(13) \text{ kcal/mol} \]

Figure 5.13. Eyring plot of ln(k/T) vs. 1/T for C-H activation of 3000 eq. toluene (0.482 M) using second order rate constants collected in Table 5.3. Error analysis in \( \Delta H^\ddagger \) and \( \Delta S^\ddagger \) follows that by Girolami et al. using an assumed temperature error of +/- 0.5 °C and assuming an average error of 4% in the absolute values of the rate constant.⁵
Table 5.3. Observed first order rate constants $k_{\text{obs}}$ and second order rate constants $k_1$ for the C-H activation of toluene (3000 equiv.) by $\left[\text{Me}_3\text{NN}\right]\text{Ni}=\text{NAd} \ (1)$ in benzene.

<table>
<thead>
<tr>
<th>Temp</th>
<th>$k_{\text{obs}} \ (s^{-1})$</th>
<th>$k_1 \ (M^{-1}s^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>35 °C</td>
<td>$3.2(1) \times 10^{-5}$</td>
<td>$4.5(2) \times 10^{-6}$</td>
</tr>
<tr>
<td>45 °C</td>
<td>$4.9(1) \times 10^{-5}$</td>
<td>$6.8(2) \times 10^{-6}$</td>
</tr>
<tr>
<td>55 °C</td>
<td>$7.9(1) \times 10^{-5}$</td>
<td>$1.1(2) \times 10^{-5}$</td>
</tr>
<tr>
<td>65 °C</td>
<td>$1.5(1) \times 10^{-4}$</td>
<td>$2.1(2) \times 10^{-5}$</td>
</tr>
</tbody>
</table>

5.2.e. Stoichiometric reaction of $[\text{Me}_3\text{NN}]\text{Ni}=\text{NAd} \ (1)$ with indane

In the stoichiometric reaction of $[\text{Me}_3\text{NN}]\text{Ni}=\text{NAd} \ (1)$ and neat indane (100 equiv.) at RT we did not observe the expected Ni(II) secondary amido species $[\text{Me}_3\text{NN}]\text{Ni}-\text{N(Ad)}(1\text{-indanyl})$. Instead, the dinickel nitrene $\{[\text{Me}_3\text{NN}]\text{Ni}\}_2(\mu-\text{NAd}) \ (4)$ was isolated as brown crystals in 26% yield from Et$_2$O at -35 °C, identified by X-ray crystallography (Scheme 5.9).

Scheme 5.9. Proposed stoichiometric reaction of 1 with indane to account for 4.

The X-ray structure of 4 (Figure 5.14) shows Ni-$N_{\text{nitr}}$e distances of 1.738(3) and 1.758(3) Å along with a Ni-Ni distance of 2.4873(7) Å. This species is nearly identical in structure to the previously reported $\{[\text{Me}_2\text{NN}]\text{Ni}\}_2(\mu-\text{NAd})^2$ which possesses Ni-$N_{\text{nitr}}$e bond distances of 1.732(4) and 1.752(4) Å and a Ni-Ni distance of 2.5057(12) Å.$^2$ These dinickel adamantyl nitrene complexes may be directly compared against their copper analogue $\{[\text{Me}_3\text{NN}]\text{Cu}\}_2(\mu-\text{NAd})^5$ which has Cu-$N_{\text{nitr}}$e bond distances of 1.785(6) and 1.821(5) Å along with a much longer Cu···Cu separation of 2.901(2) Å.
Based on the proposed stoichiometric reaction, we set out to further investigate possible mechanisms via quantification of NH(Ad)(1-indanyl) that we anticipate forms. Theoretically, \{[\text{Me}_3\text{NN}][\text{Ni}]_2(\mu-\text{NAd})\} (4) should account for 50% yield of this reaction; \{[\text{Me}_3\text{NN}][\text{Ni}]_2(\mu-\text{NAd})\} (4) is isolated in 26% yield. The reaction mixture of [\text{Me}_3\text{NN}][\text{Ni}=\text{NAd} (2) in neat indane was hydrolyzed after 48 h and analyzed by GC/MS using an internal standard to show AdNH\textsubscript{2} and NH(Ad)(1-indanyl) in 17(10)% and 46(10)% yield, respectively. A possible explanation for not observing a 1:1 ratio between AdNH\textsubscript{2} and NH(Ad)(1-indanyl) is that\{[\text{Me}_3\text{NN}][\text{Ni}]_2(\mu-\text{NAd})\} (4) does not readily hydrolyze to AdNH\textsubscript{2}. In a separate experiment [\text{Me}_3\text{NN}][\text{Ni}=\text{NAd} (1) was hydrolyzed via the same procedure as above to show a yield of AdNH\textsubscript{2} via analogues GC/MS of only 55%, presumably the dinuclear nickel nitrene, \{[\text{Me}_3\text{NN}][\text{Ni}]_2(\mu-\text{NAd})\} (4), will hydrolyze even less readily. These preliminary results still need further attention to unambiguously determine the stoichiometry of this reaction.
Figure 5.14. X-ray crystal structure of \([\text{[Me}_3\text{NN]}\text{Ni}]_2(\mu-\text{NAd})\) (4). All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ni1-N1 1.948(3), Ni1-N2 1.922(3), Ni2-N4 1.951(3), Ni2-N5 1.933(3), Ni1-N3 1.738(3), Ni2-N3 1.758(3), Ni1-Ni2 2.4873(7), N1-Ni1-N2 93.74(12), N4-Ni2-N5 92.93(12).
### Table 5.4. Crystallographic data for 2, 3 and 4.

<table>
<thead>
<tr>
<th>Compd.</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
<td>C$<em>{41}$H$</em>{53}$N$_3$Ni</td>
<td>C$<em>{44}$H$</em>{61}$N$_3$NiO</td>
<td>C$<em>{60}$H$</em>{84}$N$_5$Ni$_2$O</td>
</tr>
<tr>
<td>Mol. Wt.</td>
<td>646.57</td>
<td>706.67</td>
<td>1008.74</td>
</tr>
<tr>
<td>Temp.(K)</td>
<td>100(2)</td>
<td>100(2)</td>
<td>100(2)</td>
</tr>
<tr>
<td>crystal description</td>
<td>brick</td>
<td>plate</td>
<td>brick</td>
</tr>
<tr>
<td>crystal color</td>
<td>brown</td>
<td>brown</td>
<td>brown</td>
</tr>
<tr>
<td>crystal size (mm$^3$)</td>
<td>0.40×0.29×0.25</td>
<td>0.38×0.21×0.12</td>
<td>0.35×0.24×0.10</td>
</tr>
<tr>
<td>system</td>
<td>orthorhombic</td>
<td>monoclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P21212$</td>
<td>$P21/n$</td>
<td>$P1\bar{1}$</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>16.670(3)</td>
<td>9.810(3)</td>
<td>11.4076(14)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>24.497(4)</td>
<td>16.118(4)</td>
<td>12.7225(16)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>9.2897(14)</td>
<td>24.663(7)</td>
<td>19.095(2)</td>
</tr>
<tr>
<td>$\alpha$ (deg)</td>
<td>90.00</td>
<td>90.00</td>
<td>89.664(2)</td>
</tr>
<tr>
<td>$\beta$ (deg)</td>
<td>90.00</td>
<td>90.508(4)</td>
<td>88.036(2)</td>
</tr>
<tr>
<td>$\gamma$ (deg)</td>
<td>90.00</td>
<td>90.00</td>
<td>84.121(2)</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>$\Theta$ range (deg)</td>
<td>1.48-26.00</td>
<td>1.51-26.00</td>
<td>1.61-26.00</td>
</tr>
<tr>
<td>measd reflns</td>
<td>30102</td>
<td>22411</td>
<td>28628</td>
</tr>
<tr>
<td>unique reflns</td>
<td>7477</td>
<td>7632</td>
<td>10748</td>
</tr>
<tr>
<td>R(int)</td>
<td>0.0903</td>
<td>0.1026</td>
<td>0.0767</td>
</tr>
<tr>
<td>GOF of $F^2$</td>
<td>1.139</td>
<td>1.008</td>
<td>0.939</td>
</tr>
<tr>
<td>$R_1$ ($I &gt; 2\sigma(I)$)</td>
<td>0.0763</td>
<td>0.0762</td>
<td>0.0521</td>
</tr>
<tr>
<td>$wR_2$ (all data)</td>
<td>0.1058</td>
<td>0.1575</td>
<td>0.1169</td>
</tr>
<tr>
<td>Largest diff. peak and hole e$^-\cdot$Å$^{-3}$)</td>
<td>1.578 and -0.565</td>
<td>0.790 and -0.646</td>
<td>0.857 and -0.773</td>
</tr>
</tbody>
</table>
A possible route for the formation 4 is the direct insertion of [Me₃NN]Ni=NAd (1) into the C-H bond of indane giving the new secondary amine HN(Ad)indanyl and one equivalent of the [Me₃NN]Ni fragment that combines with a second equivalent of [Me₃NN]Ni=NAd (1) to form {[Me₃NN]Ni}₂(µ-NAd) (4). {[Me₃NN]Ni}₂(µ-NAd) (4) was independently synthesized by adding 1 equiv. AdN₃ to 2 equiv. [Me₃NN]Ni(2-picoline) in Et₂O at -35 °C followed by immediate workup. After crystallization from Et₂O at -35 °C brown crystals of {[Me₃NN]Ni}₂(µ-NAd) (4) were isolated in 78% yield (Scheme 5.10).

Scheme 5.10. Independent synthesis of 4.

\[
\begin{align*}
[\text{Me}_{3}\text{NN}]\text{Ni(2-pic)} + \text{AdN}_{3} & \xrightarrow{\text{Et}_{2}\text{O}} \text{N}_{2} \xrightarrow{-2\text{-pic}} [\text{Me}_{3}\text{NN}][\text{Ni}^{-}\text{Ni}[\text{NNMe}_{3}]} \\
\end{align*}
\]

78% yield

5.2.f. Kinetic analysis of the reaction of [Ni]=NAd (1) with indane

Using UV-vis spectroscopy, we monitored the reaction of [Me₃NN]Ni=NAd (1) with excess toluene to gain insight into the conversion of 1 to 3. In a reaction of 1 (2.32 mM) with indane (4.64 M) with benzene as the (co)solvent at 45 °C, we followed the loss 1 as monitored by its \( \lambda_{\text{max}} = 596 \) nm band (Figure 5.15). Plots of ln(A-A_{inf}) vs. time yielded straight lines, indicating that the reaction is 1ˢᵗ order in [Me₃NN]Ni=NAd (1). Varying the temperature (35, 45, 55, 65 °C) employing uniform initial concentrations of [Me₃NN]Ni=NAd (1) (2.41 mM) and toluene (0.482 M) allowed the determination of second order rate constants \( k_1 \) at these temperatures from which an Eyring plot was
constructed (Figure 5.16 and Table 5.5). This analysis yielded activation parameters

\[
\Delta H^\ddagger = +13.5(13) \text{ kcal/mol}, \quad \Delta S^\ddagger = -31(2) \text{ cal/mol•K} \quad \text{and} \quad \Delta G^\ddagger_{298K} = +23.0(23) \text{ kcal/mol}.
\]

Figure 5.15. Consumption of [Me$_3$NN]Ni=NAd (1) as monitored by the loss of its UV-vis absorbance at $\lambda = 596$ nm in the presence of 2000 equiv. indane under pseudo first order conditions in benzene at 45 $^\circ$C. Scan interval = 60 s
Figure 5.15. Eyring plot of ln(k/T) vs. 1/T for C-H activation of 2000 eq. indane (0.482 M) using second order rate constants collected in Table 5.5 Error analysis in ΔH‡ and ΔS‡ follows that by Girolami et al. using an assumed temperature error of +/- 0.5 °C and assuming an average error of 4% in the absolute values of the rate constant.

Table 5.5. Observed first order rate constants \(k_{\text{obs}}\) and second order rate constants \(k_{\text{act}}\) for the C-H activation of indane (200 equiv.) by [Me₃NNi=NAd (I) in benzene.

<table>
<thead>
<tr>
<th>Temp</th>
<th>(k_{\text{obs}}) (s⁻¹)</th>
<th>(k_{\text{act}}) (M⁻¹s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35 °C</td>
<td>1.0(1) × 10⁻⁴</td>
<td>2.1(2) × 10⁻⁴</td>
</tr>
<tr>
<td>45 °C</td>
<td>1.7(1) × 10⁻⁴</td>
<td>3.4(2) × 10⁻⁴</td>
</tr>
<tr>
<td>55 °C</td>
<td>4.0(1) × 10⁻⁴</td>
<td>8.4(2) × 10⁻⁴</td>
</tr>
<tr>
<td>65 °C</td>
<td>7.5(1) × 10⁻⁴</td>
<td>1.6(2) × 10⁻³</td>
</tr>
</tbody>
</table>
5.2.g. Discussion of H-atom abstraction of benzylic substrates by [Ni]=NAd (1).

The activation parameters in the reactions of [Me₃NN]Ni=NAd (1) with the C-H substrates ethylbenzene, toluene and indane are summarized in Table 5.6. The overall free energies of activation track with the bond dissociation enthalpies of the reacting C-H bond – lower overall barriers are observed with weaker C-H bonds. Strikingly, however, is the decrease in ΔH‡ (with increase in ΔS‡) with increasing BDE.

Table 5.6. Experimental kinetic results and BDE^6 for C-H substrates.

<table>
<thead>
<tr>
<th>Substrates</th>
<th>BDE^6 (kcal/mol)</th>
<th>ΔH‡ (kcal/mol)</th>
<th>ΔS‡ (cal/mol)</th>
<th>ΔG^‡(298K) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>indane</td>
<td>85.9</td>
<td>+13.5(13)</td>
<td>-32(2)</td>
<td>+23.0(23)</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>85.4 ± 1.5</td>
<td>+11.6(7)</td>
<td>-42(2)</td>
<td>+24.2(25)</td>
</tr>
<tr>
<td>toluene</td>
<td>88.5 ± 1.5</td>
<td>+10.0(10)</td>
<td>-50(3)</td>
<td>+25.1(13)</td>
</tr>
</tbody>
</table>

A possible explanation is that the entropy of activation has an effect on the enthalpy of activation. It is possible that the TS becomes more ordered as the BDE increases, especially considering that the size of the C-H substrate decreases with increasing C-H bond strength. Indane has the weakest C-H bond (85.9 kcal/mol)^6 but is the most hindered substrate and apparently trades optimal positioning between [Me₃NN]Ni=NAd and indane for HAA in its TS (least negative ΔS‡ = -32(2) cal/mol*K) to avoid unfavorable steric interactions. Thus, the more disordered TS requires higher energy to break the C-H bond which is consistent with the higher ΔH‡ = +13.5(13) kcal/mol. Moving to the slightly less sterically hindered ethylbenzene, the trend is consistent. The smaller size of ethylbenzene allows greater order in its TS (ΔS‡ = -42(2) cal/mol*K) which decreases the enthalpic input required to break the C-H bond (ΔH‡ =
+11.6(7) kcal/mol. Completing the series is toluene, the least sterically hindered substrate with the highest BDE (88.5 ± 1.5 kcal/mol). Toluene has the most ordered TS (ΔS‡ = -50(3) cal/mol•K) which assists the activation of the C-H bond to give the lowest enthalpy of activation ΔH‡ = +10.0(10) kcal/mol.

In the case of indane as a C-H substrate, we were not able to isolate the anticipated Ni(II) amido species [Me₃NN]Ni-N(Ad)(1-indanyl). Instead we isolated bridged nitrene species {[Me₃NN]Ni}₂(μ-NAd) (4) which is not accounted for in our

**Scheme 5.11. Proposed mechanisms for C-H activation by [Me₃NN]Ni=NAd (1).**

*Mechanism I - HAA by [Ni]=NAd / RC by [Ni]=NAd*

<table>
<thead>
<tr>
<th>Step Ia</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₃NNNi=NAd + R-H</td>
<td>→</td>
<td>Me₃NNNi-NAd + R•</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Step Ib</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₃NNNi=NAd + R•</td>
<td>→</td>
<td>Me₃NNNi-N(Ad)R</td>
</tr>
</tbody>
</table>

*Mechanism II - HAA by [Ni]=NAd / RC [Ni]-NHAd*

<table>
<thead>
<tr>
<th>Step IIa</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₃NNNi=NAd + R-H</td>
<td>→</td>
<td>Me₃NNNi-NHAd + R•</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Step IIb</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₃NNNi-NHAd + R•</td>
<td>→</td>
<td>NH(Ad)R + Me₃NNNi</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Step IIc</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₃NNNi=NAd + Me₃NNNi</td>
<td>→</td>
<td>{[Me₃NN]Ni}₂(μ-NAd)</td>
</tr>
</tbody>
</table>

*Mechanism III - Concerted insertion of [Ni]=NAd into R-H*

<table>
<thead>
<tr>
<th>Step IIIa</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₃NNNi=NAd + R-H</td>
<td>→</td>
<td>NH(Ad)R + Me₃NNNi</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Step IIIb</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₃NNNi=NAd + Me₃NNNi</td>
<td>→</td>
<td>{[Me₃NN]Ni}₂(μ-NAd)</td>
</tr>
</tbody>
</table>
original proposed mechanism. Therefore, alternative mechanisms must be considered.

Shown in Scheme 5.11 are three possible mechanisms for the net reduction of $\text{[Me}_3\text{NN]}\text{Ni=NAd}$ (1) to $\{\text{[Me}_3\text{NN]}\text{Ni}\}_2(\mu{-}\text{NAd})$ (4) by indane. Mechanism I represents the original pathway proposed in which 1 equiv. $\text{[Me}_3\text{NN]}\text{Ni=NAd}$ (1) performs HAA to form a carbon radical $R^\bullet$ which subsequently combines with a second equiv. 1 to form a Ni(II) amido species $\text{[Me}_3\text{NN]}\text{Ni-N(Ad)}R$. Mechanism II also features rate-limiting HAA by 1, but instead considers combination of the radical $R^\bullet$ with $\text{[Me}_3\text{NN]}\text{Ni-NHAd}$ to give the nickel(I) species $\text{[Me}_3\text{NN]}\text{Ni(NH(Ad))R}$. Finally, Mechanism III illustrates a concerted direct insertion of 1 into $R-H$ to give $\text{[Me}_3\text{NN]}\text{Ni(NH(Ad))R}$. Both Mechanism II and III ultimately account for the formation of $\{\text{[Me}_3\text{NN]}\text{Ni}\}_2(\mu{-}\text{NAd})$ (4) by dissociating NH(Ad)R from the monovalent species $\text{[Me}_3\text{NN]}\text{Ni(NH(Ad))R}$ to provide an equivalent of $\text{[Me}_3\text{NN]}\text{Ni}$ which can combine with a second equiv. of 1 to give 4. We suspect that dinuclear $\{\text{[Me}_3\text{NN]}\text{Ni}\}_2(\mu{-}\text{NAd})$ (4) is both kinetically and thermodynamically passivated towards HAA relative to the terminal species $\text{[Me}_3\text{NN]}\text{Ni=NAd}$.

As the BDE of the reacting C-H substrate $R-H$ becomes lower, Mechanisms II and III could potentially contribute to a greater extent with respect to the overall reaction between $\text{[Me}_3\text{NN]}\text{Ni=NAd}$ and $R-H$. With a decreased R-H BDE, $\text{[Me}_3\text{NN]}\text{Ni-NHAd}$ could be generated more quickly, enhancing the concentration of this nickel(II) amido species allowing for combination with the corresponding $R^\bullet$ that possesses a greater lifetime owing to its greater stability. Alternatively, the decrease in the R-H BDE might simply cause 1 to directly insert in the R-H bond over HAA / RC.
To begin to assess the possibility of different pathways that could result in different ratios of [Ni]-NHAd and [Ni]-N(Ad)R in the reaction of [Ni]=NAd with R-H, we have collaborated with Prof. Tom Cundari and Dr. Jason McAfee of the University of North Texas who have computationally examined this system.

**Table 5.7.** Theoretical activation energies for HAA by [Me₃NN]Ni=NAd.

<table>
<thead>
<tr>
<th>Substrates Comp</th>
<th>BDE⁶ (kcal/mol)</th>
<th>ΔH‡ (kcal/mol)</th>
<th>ΔS‡ (cal/mol)</th>
<th>ΔG‡(298K) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>indane</td>
<td>85.9</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>85.4 ± 1.5</td>
<td>+9.5</td>
<td>-56.0</td>
<td>+26.3</td>
</tr>
<tr>
<td>toluene</td>
<td>88.5 ± 1.5</td>
<td>+9.6</td>
<td>-61.0</td>
<td>+27.9</td>
</tr>
</tbody>
</table>

The trends in their computational investigation are very similar (Table 5.7). Our collaborators examined these trends by comparing the N-H and C-H bond distances in the transition state. The calculated N-H and C-H distances in the toluene TS are 1.279 and 1.361 Å, respectively. For ethylbenzene the N-H distance increases to 1.305 Å and the C-H distance contracts to 1.346 Å. The shorter bonds in the case of toluene support the hypothesis that the toluene TS is more ordered as compared to the ethylbenzene TS which leads to the observed trends in ΔH‡ and ΔS‡. Alternatively, the toluene TS may be viewed as a later, more highly ordered TS in this bimolecular reaction.

**Scheme 5.12.** Radical capture of R• by [Me₃NN]Ni=NAd (1).

![Scheme 5.12](image)

Radical capture of R• by [Me₃NN]Ni=NAd (1) becomes less favored as the stability of the radical R• increases which coincides with a decrease in the R-H BDE (Scheme 5.12). Toluene has the strongest C-H bond and the capture of PhCH₂• by 1 possesses a very exothermic enthalpy of -46.0 kcal/mol which becomes less favorable as for the corresponding ethylbenzene and 1-indanyl radicals with enthalpies of -41.3
and -40.8 kcal/mol. Further theoretical studies are underway to examine the corresponding enthalpies for the related addition of these radicals \( R^* \) to the nickel(II) amido species \([\text{Me}_3\text{NN}]-\text{NHAd}\) to give the nickel(I) amide adducts \([\text{Me}_3\text{NN}]\text{Ni}(\text{NH(Ad)R})\).

**Conclusion**

\([\text{Me}_3\text{NN}]\text{Ni}=\text{NAd} \ (1)\) exhibits bifunctional behavior, capable of HAA of relatively strong C-H bonds in substrates R-H in addition to readily forming new nickel(II) amido species \([\text{Me}_3\text{NN}]\text{Ni}-\text{N(Ad)}R\) upon capture of the resulting radical \( R^* \). Reaction of 1 with ethylbenzene gave the new Ni(II) amido species \([\text{Me}_3\text{NN}]\text{Ni}-\text{N(Ad)}\text{CH(Me)}\text{Ph} \) (2), while similar reaction of 1 with toluene gave the Ni(II) alkylamine species \([\text{Me}_3\text{NN}]\text{Ni}(\text{2-CH(Ph)NHAd}) \) (3) likely formed via tautomerization of initially formed \([\text{Me}_3\text{NN}]\text{Ni}-\text{N(Ad)CH}_2\text{Ph}\). Employing UV-vis spectroscopy, we investigated the kinetics of the reaction of \([\text{Me}_3\text{NN}]\text{Ni}=\text{NAd}\) with toluene, ethylbenzene and indane and determined the respective activation parameters \( \Delta H^\ddagger \), \( \Delta S^\ddagger \) and \( \Delta G^\ddagger \) (298K). The overall free energy of activation tracks with the BDE of the reacting C-H bonds – lower overall barriers are observed with weaker C-H bonds. More interesting was the finding of a decrease in \( \Delta H^\ddagger \) (with increase in \( \Delta S^\ddagger \)) with increasing BDE. In collaboration with Prof. Tom Cundari and Dr. Jason McAfee, we hypothesized that the steric of the C-H substrate affect the TS in such a way that more sterically hindered C-H substrate adopt a loser TS shown by a increase in \( \Delta S^\ddagger \) which in turns makes HAA enthalpically more challenging.
Experimental

General Procedures and Instrumentation

All experiments were carried out in a dry nitrogen atmosphere using an MBraun glovebox and/or standard Schlenk techniques. 4 A molecular sieves were activated in vacuo at 180 °C for 24 h. Dry benzene was purchased from Aldrich and was stored over activated 4 A molecular sieves. Diethyl ether and tetrahydrofuran (THF) were first sparged with nitrogen and then dried by passage through activated alumina columns. Pentane was first washed with conc. HNO₃ / H₂SO₄ to remove olefins, stored over CaCl₂ and then distilled before use from sodium/benzophenone. Benzene, toluene, and ethylbenzene were purchased anhydrous and stored over 4 A molecular sieves. All solvents were tested before use with a drop of sodium benzophenone ketyl in THF solution. All deuterated solvents were sparged with nitrogen, dried over activated 4 A molecular sieves and stored under nitrogen. Celite was dried overnight at 200 °C under vacuum.

¹H and ¹³C NMR spectra were recorded on a Varian Unity 300 or 400 MHz Inova Spectrometer (300 and 75.4 MHz; 400 and 100.47 MHz respectively). All NMR spectra were recorded at room temperature unless otherwise noted and were indirectly referenced to residual solvent signals or TMS as internal standards. UV-Vis spectra were measured on a Varian Cary 50 or 100 spectrophotometer, using cuvettes with screw-cap tops. GC-MS spectra were recorded on a Varian Saturn 3900 and elemental analyses were performed on a Perkin-Elmer PE2400 microanalyzer at Georgetown. IR measurements were performed on Perkin Elmer Spectrum One FT-IR Spectrometer.
All reagents were obtained commercially unless otherwise noted. [Me$_3$NN]Ni=NAd (1)$^2$ were prepared by literature methods. Ethylbenzene-$d_{10}$ was obtained from Cambridge Isotope Laboratories, Inc.

5.3.a. **Synthesis and characterization of Ni complexes**

[Me$_3$NN]Ni(N(Ad)CH(Me)Ph) (2). To a chilled solution of [Me$_3$NN]Ni=NAd (1) (0.169 g, 0.312 mmol) in 4 mL Et$_2$O was added 8 mL of a 50:50 mixture of Et$_2$O/ethylbenzene. The reaction mixture was allowed to stir at RT for 3 h during which a color change from green to brown occurs. All volatiles were removed in vacuo and the remaining solid was taken up in Et$_2$O, passed through Celite and concentrated to afford brown crystals from Et$_2$O at -35 °C in 49% yield (0.098 g, 0.153 mmol). Partial assignment of $^1$H NMR (C$_6$D$_6$, 400 MHz, RT): $\delta$ 7.041 - 7.005 (t, 1H, p-Ar-H), 6.938 - 6.901 (t, 2H, m-Ar-H), 6.763 - 6.749 (overlapping s, 4H, m-Ar-H), 6.138-6.119 (d, 2H, o-Ar-H), 4.709 (s, 1H, backbone C-H), 3.068 - 3.051 (d, 3H, Ad-H), 2.900 - 2.803 (overlapping m, 16H, Ad-H and benzylic C-H), 2.188 (s, 6H, p-Ar-CH$_3$), 1.654 - 1.625 (d, 3H, CH$_3$), 1.507 (s, 9H, o-Ar-CH$_3$), 1.240 (s, 6H, backbone CH$_3$); $^{13}$C $^{1}$H NMR (C$_6$D$_6$): $\delta$ 156.31, 145.92, 134.01, 133.90, 133.50, 129.58, 129.31, 127.33, 125.74, 102.50, 67.94, 65.42, 43.47, 37.33, 30.90, 22.36, 21.24, 19.55; Anal. Calcd for C$_{41}$H$_{53}$N$_3$Ni: C, 76.16; H, 8.26; N, 6.50 Found C, 76.44; H, 8.26; N, 6.55.
One-pot Synthesis of $[\text{Me}_3\text{NN}]\text{Ni}(\text{N(Ad)CH(Me)Ph})$ (2) from $[\text{Me}_3\text{NN}]\text{Ni}(2\text{-pic})$ and $\text{N}_3\text{Ad}$. To a chilled solution of $[\text{Me}_3\text{NN}]\text{Ni}(2\text{-picoline})$ (0.240 g, 0.494 mmol) in 4 mL Et$_2$O and 4 mL ethylbenzene was added cold a solution of 1-azidoadamantane (0.088 g, 0.494 mmol) in 2 mL Et$_2$O. This reaction mixture was allowed to react at RT for 1 h. Bubbles evolved immediately and the reaction mixture changed from red to green to brown. All volatiles were removed in vacuo and remainder was taken up in Et$_2$O and passed through Celite. This brown solution was concentrated and allowed to crystallize at -35 °C to afford brown crystals in 49% yield (0.159 g, 0.245 mmol) suitable for single crystal X-ray analysis.

$[\text{Me}_3\text{NN}]\text{Ni}(\eta^2\text{-CH(Ph)NHAd})$ (3). $[\text{Me}_3\text{NN}]\text{Ni=NAd}$ (1) (0.375 g, 0.693 mmol) was dissolved in 8 mL toluene and allowed to stir at RT for 72 h. All volatiles were removed in vacuo and the remaining solid was taken up in 10 mL Et$_2$O and all volatiles were removed in vacuo again. The remaining solid was taken up in Et$_2$O again and passed through Celite, concentrated, and allowed to crystallize at -35 °C to afford brown crystals in 38% yield (0.165 g, 0.261 mmol) suitable for single crystal X-ray analysis. Partial assignment of $^1$H NMR (C$_6$D$_6$, 400 MHz, RT): $\delta$ 7.890 (d, 1H, Ph-H), 7.451 (d, 2H, Ph-H), 7.242 (t, 2H, Ph-H), 6.596 (s, 4H, $m$-Ar-H), 4.145 (s, 1H, backbone C-H), 2.666 (s, 12H, o-Ar-CH$_3$), 2.250 (s, 6H, $p$-Ar-CH$_3$), 1.575 (s, 6H, backbone CH$_3$).

$\{[\text{Me}_3\text{NN}]\text{Ni}\}$_2(\mu-\text{NAd})$ (4) – from $[\text{Me}_3\text{NN}]\text{Ni}(2\text{-picoline})$. To a chilled solution of $[\text{Me}_3\text{NN}]\text{Ni}(2\text{-picoline})$ (0.107 g, 0.234 mmol) in 4 mL Et$_2$O was added a chilled
solution of 1-azidoadamantane (0.021 g, 0.117 mmol) in 2 mL Et₂O. The reaction mixture immediately changed colors from red to brown. All volatiles were immediately removed in vacuo. The remaining solid was taken back up in 5 mL of pentane and all volatiles were immediately removed in vacuo again. The remaining solid was taken up in Et₂O passed through Celite, concentrated and layered with pentane to afford brown crystals in 78% yield (0.085 g, 0.09 mmol) suitable for single crystal X-ray analysis. Anal. Calcd for C₅₆H₇₃N₅Ni₂: C, 72.04; H, 7.88; N, 7.50 Found C, 71.91; H, 7.51; N, 7.18.

{[Me₃NN]Ni}₂(µ-NAd) (4) – from [Me₃NN]Ni=NAd and indane. [Me₃NN]Ni=NAd (1) (0.375 g, 0.693 mmol) was dissolved in 8 mL indane. The reaction mixture was allowed to stir at RT for 24 h during which a color change from green to brown occurred. All volatiles were removed in vacuo by adding toluene. The remaining solid was taken up in Et₂O, filtered through Celite, and concentrated to afford brown crystals in 26% yield (0.157 g, 0.179 mmol).

5.3.b. UV-vis studies of [Me₃NN]Ni=NAd reactivity with C-H substrates

Determination of kinetic order in [Me₃NN]Ni=NAd (1) for ethylbenzene, indane, and toluene. A stock solution of [Me₃NN]Ni=NAd (1) (0.063 g, 0.116 mmol) in 10.0 mL cold benzene was prepared using a volumetric flask. To a 2 mL aliquot from this stock solution (0.0116 M, 0.0232 mmol) was added a chilled portion of 2000 equiv. of the appropriate C-H substrate (ethylbenzene: 5.66 mL, 0.0464 mol; toluene: 4.93 mL,
0.0464 mol; indane: 5.68 mL, 0.0464 mol). This new solution was diluted up to 10.0 mL with benzene using a volumetric flask to produce three solutions consisting of 2.32 mM [Me3NN]Ni=NAd (1) and 4.64 M C-H substrate. The three reactions were followed via UV-vis at 45 °C via the gradual decrease of a peak at 596 nm corresponding to [Me3NN]Ni=NAd (1).

**Determination of the order in ethylbenzene for reaction of [Me₃NN]Ni=NAd (1) with ethylbenzene.** A stock solution consisting of [Me₃NN]Ni=NAd (1) (0.134 g, 0.247 mmol) in 10.0 mL benzene was prepared using a volumetric flask. To four 1 mL portions of this stock solution (0.0247 mmol) was added cold an appropriate amount of excess ethylbenzene (1000, 1500, 2000, 2500 equiv.) and each was diluted up to 10.0 mL using benzene. The resulting four reaction mixture consisted of 2.47 mM of 1 and the following concentrations and amounts of ethylbenzene: 1000 equiv.: 2.48 M (3.03 mL, 0.0248 mol); 1500 equiv.: 3.71 M (4.55 mL, 0.0371 mol); 2000 equiv. 4.95 M (6.06 mL, 0.0495 mol); 2500 equiv.: 6.19 M (7.58 mL, 0.0619 mol). The four reactions were followed via UV-vis at 25 °C via the gradual decrease of a peak at 596 nm corresponding to [Me₃NN]Ni=NAd (1). Figure 5.4 shows the gradual loss of [Me₃NN]Ni=NAd (1) corresponding to a peak at 596 nm. Figure 5.5, Table 5.1 and Figure 5.6 illustrate 1st order in ethylbenzene.

**Eyring analysis for reaction of [Me₃NN]Ni=NAd (1) with ethylbenzene.** A stock solution consisting of [Me₃NN]Ni=NAd (1) (0.134 g, 0.247 mmol) in 10.0 mL benzene
was prepared using a volumetric flask. To four 1 mL portions of this stock solution (0.0247 mmol) was added 2000 equiv. cold ethylbenzene (6.06 mL, 0.0495 mol) and each was diluted up to 10.0 mL using benzene to produce four reaction mixtures consisting of the same concentrations of \( \text{I} \) (2.47 mM) and ethylbenzene (4.95 M). The four reactions were followed via UV-vis spectroscopy at 25, 35, 45, 55 °C via the gradual decrease of a peak at \( \lambda = 596 \) nm corresponding to \([\text{Me}_3\text{NN}]\text{Ni}=\text{NAd} \) (I). Figure 5.7, Figure 5.8 and Table 5.2 show Eyring analysis for \([\text{Me}_3\text{NN}]\text{Ni}=\text{NAd} \) (I) in ethylbenzene.

**KIE for \([\text{Me}_3\text{NN}]\text{Ni}=\text{NAd} \) (I) and ethylbenzene.** A stock solution consisting of \([\text{Me}_3\text{NN}]\text{Ni}=\text{NAd} \) (I) (0.163 g, 0.301 mmol) in 10.0 mL benzene was prepared using a volumetric flask. Two 400 µL portions of this \([\text{Me}_3\text{NN}]\text{Ni}=\text{NAd} \) (I) solution (0.0121 mmol I) were taken. To one portion, 2000 equiv. cold ethylbenzene (2.95 mL, 0.0241 mol) was added and diluted up to 5 mL with benzene using a volumetric flask to give final concentrations of 2.42 mM for I and 4.82 M for ethylbenzene. To the second portion of I, 2000 equiv. cold ethylbenzene-\(d_{10} \) (3.23 mL, 0.0241 mol) was added and diluted up to 5 mL with benzene using a volumetric flask. The two reactions were followed via UV-vis at 35 °C via the gradual decrease of a peak at \( \lambda = 596 \) nm corresponding to \([\text{Me}_3\text{NN}]\text{Ni}=\text{NAd} \) (I). A KIE of 4.6(4) was observed. Figure 5.9 shows the relative rates of ethylbenzene vs. ethylbenzene-\(d_{10} \).
Eyring analysis for [Me$_3$NN]Ni=NAd (1) and toluene. A stock solution consisting of [Me$_3$NN]Ni=NAd (1) (0.163 g, 0.301 mmol) in 10.0 mL benzene was prepared using a volumetric flasks. To four 800 µL portions of this stock solution (0.0241 mmol) was added 3000 eq. of cold toluene (7.68 mL, 0.0723 mol) and each was diluted up to 10.0 mL using benzene to produce four reaction mixtures consisting of the same concentrations of 1 (2.41 mM) and toluene (7.23 M). The four reactions were followed via UV-vis at 35, 45, 55, 65 °C via the gradual decrease of a peak at 596 nm corresponding to [Me$_3$NN]Ni=NAd (1) (Figure 5.12). Figure 5.13 and Table 5.3 show Eyring analysis for [Me$_3$NN]Ni=NAd (1) in toluene.

Eyring analysis for [Me$_3$NN]Ni=NAd (1) and indane. A stock solution consisting of [Me$_3$NN]Ni=NAd (1) (0.163 g, 0.301 mmol) in 10.0 mL benzene was prepared using a volumetric flasks. To four 800 µL portions of this stock solution (0.0241 mmol) was added 200 equiv. of cold indane (590 µL, 4.82 mmol) and each was diluted up to 10.0 mL using benzene to produce four reaction mixtures consisting of the same concentrations of 1 (2.41 mM) and indane (0.482 M). The four reactions were followed via UV-vis at 35, 45, 55, 65 °C via the gradual decrease of a peak at 596 nm corresponding to [Me$_3$NN]Ni=NAd (1) (Figure 5.15). Figure 5.16 and Table 5.5 show Eyring analysis for [Me$_3$NN]Ni=NAd (1) in indane.
5.3.c. Reaction stoichiometry via GC/MS analyses for [Me$_3$NN]Ni=NAd (1) with ethylbenzene, toluene and indane

**GC/MS analysis of [Me$_3$NN]Ni=NAd (1) plus ethylbenzene.** To a solution of [Me$_3$NN]Ni=NAd (1) (0.080 g, 0.148 mmol) in 2 mL benzene was added 3 mL of ethylbenzene. The reaction mixture was allowed to stir at RT for 72 h. Afterwards the reaction mixture was exposed to air and 0.5 mL water were added. The biphasic solution was stirred vigorously for 3 h after which MgSO$_4$ was added and the resulting suspension was filtered through Celite. The Celite plug was extracted with 10 mL CH$_2$Cl$_2$. All organic layers were combined and all volatiles were removed in vacuo. The remaining oil was taken back up in CH$_2$Cl$_2$ and transferred to a vial containing 1 equiv. of 1,2,4,5-tetrachlorobenzene (0.032 g, 0.148 mmol) as a standard for GC/MS analysis. An aliquot of this mixture was analysis via GC/MS in EI mode because 1,2,4,5-tetrachlorobenzene ionizes only poorly in CI mode. The observed peaks for AdNH$_2$ and NH(Ad)CH(CH$_3$)Ph were integrated against 1,2,4,5-tetrachlorobenzene and corrected for their respective retention factor. The retention factor was determined via 1:1 mixtures of AdNH$_2$: 1,2,4,5-tetrachlorobenzene and 1:1 mixture of NH(Ad)CH(CH$_3$)Ph: 1,2,4,5-tetrachlorobenzene. NH(Ad)CH(CH$_3$)Ph was independently synthesized using a literature procedure by Warren *et al.*

(i) 1:1 AdNH$_2$ / 1,2,4,5-tetrachlorobenzene (Std.) and 1:1 NH(Ad)CH(CH$_3$)Ph (amine) / 1,2,4,5-tetrachlorobenzene (Std.)

<table>
<thead>
<tr>
<th></th>
<th>Integr. 1</th>
<th>Integr. 2</th>
<th>Integr. 3</th>
<th>Avg. ± St. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AdNH$_2$/ Std.</td>
<td>0.715</td>
<td>0.779</td>
<td>0.861</td>
<td>0.785 ± 0.08</td>
</tr>
<tr>
<td>Amine / Std.</td>
<td>1.90</td>
<td>1.95</td>
<td>2.08</td>
<td>1.98 ± 0.09</td>
</tr>
</tbody>
</table>
Thus the retention factor for AdNH$_2$ is 0.785 ± 0.08 and for NH(Ad)CH(CH$_3$)Ph is 1.98 ± 0.09.

(ii) Reaction mixture for [Ni]=NAd in ethylbenzene

<table>
<thead>
<tr>
<th>Reaction Mixture</th>
<th>Integr. 1</th>
<th>Integr. 2</th>
<th>Integr. 3</th>
<th>Avg. ± St. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AdNH$_2$/ Std.</td>
<td>0.346</td>
<td>0.340</td>
<td>0.325</td>
<td>0.337 ± 0.009</td>
</tr>
<tr>
<td>Amine / Std.</td>
<td>1.39</td>
<td>1.38</td>
<td>1.35</td>
<td>1.37 ± 0.02</td>
</tr>
</tbody>
</table>

Thus, for AdNH$_2$ 0.337 ± 0.009 / 0.785 ± 0.08 = 0.43 which corresponds to 43 ± 10% yield.

Thus, for NH(Ad)CH(CH$_3$)Ph 1.37 ± 0.02 / 1.98 ± 0.09 = 0.69 which corresponds to 69 ± 10% yield.

**GC/MS analysis of [Me$_3$NN]Ni=NAd (1) plus toluene.** To a solution of [Me$_3$NN]Ni=NAd (1) (0.080 g, 0.148 mmol) in 2 mL benzene was added 5 mL of toluene. The reaction mixture was allowed to stir at RT for 72 h. Afterwards the reaction mixture was exposed to air and 0.5 mL water were added. The biphasic solution was stirred vigorously for 3 hours after which MgSO$_4$ was added and the resulting suspension was filtered through Celite. The Celite plug was extracted with 10 mL CH$_2$Cl$_2$. All organic layers were combined and all volatiles were removed in vacuo.

The remaining oil was taken back up in CH$_2$Cl$_2$ and transferred to a vial containing 1 equiv. of 1,2,4,5-tetrachlorobenzene (0.032 g, 0.148 mmol) as a standard for GC/MS analysis. An aliquot of this mixture was analysis via GC/MS in EI mode because 1,2,4,5-tetrachlorobenzene ionizes only poorly in CI mode. The observed peaks for AdNH$_2$ and NH(Ad)CH$_2$Ph were integrated against 1,2,4,5-tetrachlorobenzene and corrected for their respective retention factor. The retention factor was determined via 1:1 mixtures of AdNH$_2$ : 1,2,4,5-tetrachlorobenzene and 1:1 mixture of NH(Ad)CH$_2$Ph :
1,2,4,5-tetrachlorobenzene. NH(Ad)CH₂Ph was independently synthesized using a literature procedure by Warren et al.⁵

(i) 1:1 AdNH₂ / 1,2,4,5-tetrachlorobenzene (Std.) and 1:1 NH(Ad)CH₂Ph (amine2) / 1,2,4,5-tetrachlorobenzene (Std.)

<table>
<thead>
<tr>
<th></th>
<th>Integr. 1</th>
<th>Integr. 2</th>
<th>Integr. 3</th>
<th>Avg. ± St. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AdNH₂/ Std.</td>
<td>0.719</td>
<td>0.708</td>
<td>0.720</td>
<td>0.716 ± 0.008</td>
</tr>
<tr>
<td>Amine2 / Std.</td>
<td>1.80</td>
<td>2.02</td>
<td>1.90</td>
<td>1.91 ± 0.11</td>
</tr>
</tbody>
</table>

Thus the retention factor for AdNH₂ is 0.716 ± 0.008 and for NH(Ad)CH₂Ph is 1.91 ± 0.11.

(ii) Reaction mixture for [Ni]=NAd in toluene

<table>
<thead>
<tr>
<th>Reaction Mixture</th>
<th>Integr. 1</th>
<th>Integr. 2</th>
<th>Integr. 3</th>
<th>Avg. ± St. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AdNH₂/ Std.</td>
<td>0.250</td>
<td>0.260</td>
<td>0.260</td>
<td>0.26 ± 0.005</td>
</tr>
<tr>
<td>Amine2 / Std.</td>
<td>0.67</td>
<td>0.67</td>
<td>0.67</td>
<td>0.67 ± 0.01</td>
</tr>
</tbody>
</table>

Thus, for AdNH₂ 0.26 ± 0.005 / 0.716 ± 0.008 = 0.36 which corresponds to 36 ± 10% yield.
Thus, for NH(Ad)CH(CH₃)Ph 0.67 ± 0.01 / 1.91 ± 0.11 = 0.32 which corresponds to 32 ± 10% yield.

**GC/MS analysis of [Me₃NN]Ni=NAd (1) plus toluene.** To a solution of [Me₃NN]Ni=NAd (1) (0.080 g, 0.148 mmol) in 2 mL benzene was added 1 mL of indane. The reaction mixture was allowed to stir at RT for 72 h. Afterwards the reaction mixture was exposed to air and 0.5 mL water were added. The biphasic solution was stirred vigorously for 3 hours after which MgSO₄ was added and the resulting suspension was filtered through Celite. The Celite plug was extracted with 10 mL CH₂Cl₂. All organic layers were combined and all volatiles were removed in vacuo. The remaining oil was taken back up in CH₂Cl₂ and transferred to a vial containing 1 equiv. of 1,2,4,5-tetrachlorobenzene (0.032 g, 0.148 mmol) as a standard for GC/MS analysis.
An aliquot of this mixture was analysis via GC/MS in EI mode because 1,2,4,5-tetrachlorobenzene ionizes only poorly in CI mode. The observed peaks for AdNH$_2$ and NH(indanyl)(Ad) were integrated against 1,2,4,5-tetrachlorobenzene and corrected for their respective retention factor. The retention factor was determined via 1:1 mixtures of AdNH$_2$ : 1,2,4,5-tetrachlorobenzene and 1:1 mixture of NH(indanyl)(Ad) : 1,2,4,5-tetrachlorobenzene. NH(indanyl)(Ad) was independently synthesized using a literature procedure by Warren et al.$^5$

(i) 1:1 AdNH$_2$ / 1,2,4,5-tetrachlorobenzene (Std.) and 1:1 NH(indanyl)(Ad) (amine3) / 1,2,4,5-tetrachlorobenzene (Std.)

<table>
<thead>
<tr>
<th></th>
<th>Integr. 1</th>
<th>Integr. 2</th>
<th>Integr. 3</th>
<th>Avg. ± St. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AdNH$_2$/ Std.</td>
<td>0.715</td>
<td>0.779</td>
<td>0.861</td>
<td>0.785 ± 0.08</td>
</tr>
<tr>
<td>Amine3 / Std.</td>
<td>2.30</td>
<td>2.05</td>
<td>2.27</td>
<td>2.21 ± 0.16</td>
</tr>
</tbody>
</table>

Thus the retention factor for AdNH$_2$ is 0.716 ± 0.008 and for NH(Ad)CH$_2$Ph is 1.91 ± 0.11.

(ii) Reaction mixture for [Ni]=NAd in indane

<table>
<thead>
<tr>
<th>Reaction Mixture</th>
<th>Integr. 1</th>
<th>Integr. 2</th>
<th>Integr. 3</th>
<th>Avg. ± St. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AdNH$_2$/ Std.</td>
<td>0.131</td>
<td>0.142</td>
<td>0.136</td>
<td>0.136 ± 0.005</td>
</tr>
<tr>
<td>Amine3 / Std.</td>
<td>0.955</td>
<td>1.03</td>
<td>1.04</td>
<td>1.01 ± 0.04</td>
</tr>
</tbody>
</table>

Thus, for AdNH$_2$ 0.136 ± 0.005 / 0.785 ± 0.08 = 0.17 which corresponds to 17 ± 10% yield.

Thus, for NH(indanyl)(Ad) 1.01 ± 0.04 / 2.21 ± 0.16 = 0.46 which corresponds to 46 ± 10% yield.

**GC/MS analysis of [Me$_3$NN]Ni=NAd (1).** A solution of [Me$_3$NN]Ni=NAd (1) (0.098 g, 0.181 mmol) in 5 mL benzene was prepared. The solution was exposed to air and 0.5 mL water were added. The biphasic solution was stirred vigorously for 3 hours after which MgSO$_4$ was added and the resulting suspension was filtered through Celite. The Celite plug was extracted with 10 mL CH$_2$Cl$_2$. All organic layers were combined and all
volatiles were removed in vacuo. The remaining oil was taken back up in CH$_2$Cl$_2$ and transferred to a vial containing 1 equiv. of 1,2,4,5-tetrachlorobenzene (0.039 g, 0.181 mmol) as a standard for GC/MS analysis. An aliquot of this mixture was analysis via GC/MS in EI mode because 1,2,4,5-tetrachlorobenzene ionizes only poorly in CI mode. The observed peak for AdNH$_2$ was integrated against 1,2,4,5-tetrachlorobenzene and corrected its retention factor. The retention factor was determined via 1:1 mixtures of AdNH$_2$ : 1,2,4,5-tetrachlorobenzene.

(i) 1:1 AdNH$_2$ / 1,2,4,5-tetrachlorobenzene (Std.)

<table>
<thead>
<tr>
<th></th>
<th>Integr. 1</th>
<th>Integr. 2</th>
<th>Integr. 3</th>
<th>Integr. 4</th>
<th>Avg. ± St. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AdNH$_2$/ Std.</td>
<td>0.619</td>
<td>0.583</td>
<td>0.607</td>
<td>0.584</td>
<td>0.598 ± 0.01</td>
</tr>
</tbody>
</table>

Thus the retention factor for AdNH$_2$ is 0.598 ± 0.01.

(ii) Reaction mixture for [Ni]=NAd

<table>
<thead>
<tr>
<th>Reaction Mixture</th>
<th>Integr. 1</th>
<th>Integr. 2</th>
<th>Integr. 3</th>
<th>Integr. 4</th>
<th>Avg. ± St. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AdNH$_2$/ Std.</td>
<td>0.325</td>
<td>0.365</td>
<td>0.313</td>
<td>0.319</td>
<td>0.331 ± 0.03</td>
</tr>
</tbody>
</table>

Thus, for AdNH$_2$ 0.331 ± 0.03 / 0.598 ± 0.01= 0.55 which corresponds to 55 ± 10% yield.

References

(3) Morse, P. M.; Spencer, M. D.; Wilson, S. R.; Girolami, G. S. 
Organometallics 1994, 13, 1646.
2004, 126, 11984-11994.

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Nitric Oxide Reductive Nitrosylates Ni(I) and Cu(I) C-Organonitroso Adducts

Abstract

Monovalent nickel and copper β-diketiminato complexes react with ArN=O (Ar = 3,5-Me₂C₆H₃ or Ph) to give C-nitroso adducts which exhibit three different modes of bonding with varying degrees of N-O bond activation. The addition of ArNO to 2 equiv. [Me₂NN]Ni(2,4-lutidine) ([Me₂NN]⁻ = 2,4-bis-(2,6-dimethylphenylimido)pentyl) gives {[Me₂NN]Ni}₂(μ-ν²:ν¹-ONAr) (1a and 1b) which exhibit symmetrical bonding of the ArN=O moiety between two [Me₂NN]Ni fragments with a significantly lengthened N-O bond distance of 1.440(4) Å in 1a compared to free C-organonitroso compounds (1.13 – 1.29 Å). [Me₂NN]Cu(NCMe) reacts with 0.5 equiv. ArNO in ether to give the dinuclear adducts {[Me₂NN]Cu}₂(μ-ν²:ν¹-ONAr) (2a and 2b) that exhibit ν²- and ν¹-bonding of the ArN=O moiety with separate [Me₂NN]Cu fragments possessing N-O distances of 1.375(6) Å (2a) and 1.368(2) Å (2b). In arene solvents, one β-diketiminato copper(I) fragment dissociates from 2 to give [Me₂NN]Cu(ν²-ONAr) (3a and 3b) which may be isolated by the addition of 1 equiv. ArNO to [Me₂NN]Cu(NCMe). The X-ray structures of 3a and 3b are similar to related Cu(I) alkene adducts with N-O distances in the narrow range 1.333(4) - 1.338(5) Å. IR spectra of the nitrosobenzene adducts 1b, 2b, and 3b exhibit ν(NO) stretching frequencies at 915, 1040, and 1113 cm⁻¹, respectively, following the decreasing degree of N=O.
activation observed in the X-ray structures of species 1, 2, and 3. Both 1a and 3a react with anaerobic NO\textsubscript{gas} to give the corresponding $N$-aryl-$N$-nitrosohydroxylaminato complexes $[\text{Me}_2\text{NN}]M(\kappa^2-\text{O}_2\text{N}_2\text{Ar})$ ($M = \text{Ni}$ (4) and Cu (5)). In the reaction of dinuclear 1a with NO, one $[\text{Me}_2\text{NN}]\text{Ni}$ fragment is trapped as the nickel-nitrosyl $[\text{Me}_2\text{NN}]\text{Ni}(\text{NO})$. Reaction of the monovalent $[\text{Me}_2\text{NN}]\text{Cu}(\kappa^2-\text{O}_2\text{N}_2\text{Ar})$ with NO\textsubscript{gas} to give the divalent $[\text{Me}_2\text{NN}]\text{Cu}(\kappa^2-\text{O}_2\text{N}_2\text{Ar})$ represents an example of oxidative nitrosylation. Exposure of $[\text{Me}_2\text{NN}]\text{Ni}(2\text{-picoline})$ to air forms $[[\text{Me}_2\text{NN}]\text{Ni}]_2(\mu-\text{OH})_2$ which reacts with $N$-phenylhydroxylamine to deliver the Ni(II) nitroxide $[\text{Me}_2\text{NN}]\text{Ni}(\kappa^2-\text{ON}\text{HPh})$ that serves as a bona fide nickel(II) complex with $\kappa^2$-ON ligation. While 1 - 3 are formally nitrosoarene adducts of the monovalent fragments $[\text{Me}_2\text{NN}]\text{Ni}$ and $[\text{Me}_2\text{NN}]\text{Cu}$, XAS studies suggest that these may be formulated as Ni(II), Cu(III/I), and Cu(III) complexes, respectively, in which considerable backbonding to the nitrosoarene takes place.

**Introduction**

During the early 1980’s nitric oxide (NO), a simple diatomic molecule, was simply considered to be a toxic gas connected to acid rain, smog, and tobacco smoke. In

![Figure 6.1. Biological functions of nitric oxide (NO).](image)
the late 1980’s, however, NO was discovered to be an important signaling molecule in smooth muscle relaxation, thus responsible for vasodilation.\textsuperscript{1-4} NO has since generated enormous biochemical and biomedical interest and is linked to several physiological processes including immune function, hypertension, male impotence, septic shock, insulin-dependent diabetes mellitus, macrophage mediated destruction of oncogenic cells, and various nervous system activities (Figure 6.1).\textsuperscript{5,6}

NO’s short lifetime\textsuperscript{2} in the blood of 3-5 s requires that it be generated near the site of action. Arginine is oxidized in (at least) a two-step reaction by fully constituted nitric oxide synthase (NOS) isoforms. Under normal conditions this produces relatively low (less than 1 \( \mu \)M) local concentrations of NO.\textsuperscript{7,8} The best understood step is the heme-promoted oxidation of arginine to \( N \)-hydroxyarginine (NHA) by dioxygen and NADPH. Not as well understood are the mechanistic details for the oxidation of NHA to citrulline with formation of NO.\textsuperscript{8} NOS does not oxidize all NHA present; instead up to 30\% of all NOS products exist in the form of NHA at steady-state concentrations.\textsuperscript{1,8-10} During this process NOS produces NH\(_2\)OH as an endogenous, substoichiometric sideproduct,\textsuperscript{11} but NOS is not the only endogenous source of NH\(_2\)OH.\textsuperscript{8}

\begin{center}
\textbf{Scheme 6.1.} NO production in the body.
\end{center}

\begin{center}
\begin{tikzpicture}
  \node [label=left:L-arginine] (A) at (0,0) {\includegraphics{arginine}};
  \node [label=right:N-\text{hydroxyl-L-arginine (NHA)}] (B) at (2,0) {\includegraphics{NHA}};
  \node [label=right:L-citrulline] (C) at (4,0) {\includegraphics{citrulline}};
  \node [label=right:H\(_2\)NOH (byproduct)] (D) at (6,0) {\includegraphics{NH2OH}};
  \node [label=right:NO\(_2\) \((g)\)] (E) at (8,0) {\includegraphics{NO2}};

  \draw[->] (A) -- (B) node [midway, above] {NOS NADPH \( \text{O}_2 \)};
  \draw[->] (B) -- (C) node [midway, above] {CuZn-SOD required} node [midway, below] {-H\(_2\)O} node [midway, below] {NOS NADPH \( \text{O}_2 \)};
  \draw[->] (C) -- (D) node [midway, above] {\( \text{H}_2\text{NOH} \)};
  \draw[->] (D) -- (E) node [midway, above] {\( \text{NO} \)};

\end{tikzpicture}
\end{center}
The exact NO species produced at the heme site responsible for arginine oxidation remains unclear and is subject of debate.\textsuperscript{8,11,12} In a key study, purified NOS lacking the CuZnSOD co-factor gave no NO formation.\textsuperscript{11} The co-factor tetrahydrobiopterin (H\textsubscript{4}B) was also found to be necessary for NO formation - in its absence HNO was generated.\textsuperscript{13,14} It is also clear that the addition of CuZnSOD enhances formation of NO from L-arginine by NOS,\textsuperscript{15} though perhaps by enhancing NO formation at an alternative location by scavenging of O\textsubscript{2} whose reaction with NO rapidly leads to peroxynitrite.\textsuperscript{12} Oxygen and oxygen containing enzymes react with NO to form nitrates and nitrites (Scheme 6.1).\textsuperscript{16}

NO has a rich biochemistry with metalloenzymes, though targets for NO incorporation are not limited to the metal centers themselves.\textsuperscript{17-19} For instance, copper ions are required to induce the S-nitrosation of the two Cys\textsubscript{93} residues of oxyhemoglobin with NO\textsubscript{3};\textsuperscript{20-22} oxyhemoglobin exhibits a higher affinity for NO than its deoxy form.\textsuperscript{23} Redox active metal ions may assist in the nitrosation of organic substrates such as alcohols, amines, and thiols (eq 1).\textsuperscript{24} In such reductive nitrosylation reactions, nitric oxide is formally oxidized to NO\textsuperscript{+} by the metal ion which is reduced by one electron.

\[
\text{NO} + \text{M}^{n+} + \text{E-H} \xrightleftharpoons{E = \text{RO}, \text{R}_{2}\text{N}, \text{RS}} \text{E-NO} + \text{M}^{(n-1)+} + \text{H}^+ \quad (1)
\]

6.1.a. HNO is a redox relative of nitric oxide

Nitroxy (HNO; pK\textsubscript{A} \textasciitilde 11.4)) is a one electron, one proton redox partner of nitric oxide (Scheme 5.2). HNO has common physiological effects as NO such as
vasorelaxation, neurotransmission, antiplatelet action, and immune function but also has its own different reactivity such as resistance to superoxide (O$_2^-$) scavenging, enhanced myocardiological activity, and high thiol reactivity. HNO has an even shorter lifetime than NO in biological environments due to its high reactivity, mainly due to facile dimerization ($k = 8 \times 10^6$ M$^{-1}$s$^{-1}$ in water) to give N$_2$O and H$_2$O (Scheme 6.2). Endogeneous production of HNO in mammalian systems is not completely understood due to the difficulty in detecting HNO. Some researchers believe that HNO is formed via an analogues route as NO and actually serves as a precursor to NO upon oxidation by Cu$^{II}$ZnSOD (Scheme 6.1).

**Scheme 6.2.** Redox partners NO and HNO and dimerization of HNO.

**Scheme 6.3.** Angeli’s salt conversion to HNO.

**Scheme 6.4.** Isopropylamine NONOate’s conversion to HNO.

Since HNO rapidly dimerizes, HNO must be generated prior to studying its reactions. Several molecules that serve as HNO donors are known. Perhaps the best known and most utilized is Angeli’s salt (AS; Na$_2$N$_2$O$_3$). This is an oxide
diazeneiumdiolate dissociates at physiological pH and temperature with a half-life $\sim 2.5$ minutes to give HNO and NO$_2^-$ (Scheme 6.3).\textsuperscript{6} Isopropylamine NONOate (IPA/NO) a primary amine diazeniumdiolate also dissociates at physiological pH and temperature with a half-life $\sim 2.3$ minutes to give HNO and RNNO$^-$ (Scheme 6.4).\textsuperscript{6} Piloty’s acid a N-hydroxysulphenamide decomposes to HNO under basic conditions (Scheme 6.5).\textsuperscript{6} Cyanamide (H$_2$NCN) is an anti-alcoholism drug that first converts to N-hydroxycyanamide via the reaction with catalase and hydrogen peroxide (H$_2$O$_2$). N-hydroxycyanamide further reacts to HNO and cyanide byproduct (Scheme 6.6).\textsuperscript{6} Finally, acyloxy C-nitroso compounds react with nucleophiles such as H$_2$O (or OH$^-$ under basic conditions) to give HNO and carboxylic acid byproducts (Scheme 6.7).\textsuperscript{6}

Scheme 6.5. Piloty’s acid conversion to HNO.

\[ \text{PhO}_2\text{S} - \text{N} - \text{OH} \xrightarrow{\text{OH}} \text{PhSO}_2^- + \text{HNO} \]

Scheme 6.6. Cyanamide conversion to HNO.

\[ \text{H}_2\text{NCN} \xrightarrow{\text{catalase}} \text{HO} \text{-CN} \xrightarrow{\text{H}_2\text{O}_2} \text{HNO} + \text{CN}^- + \text{H}^+ \]

Scheme 6.7. Acyloxy nitroso conversion to HNO.

\[ \text{acyloxy nitroso} \xrightarrow{\text{H}_2\text{O}} \text{HNO} + \text{HO} - \text{R'} + \text{HO} - \text{R''} \]
**6.1.b. Alternative sources of NO – C-nitroso compounds**

Organic derivatives of nitric oxide $E$-NO in many cases can serve as sources of NO (Scheme 6.8). Homolytic cleavage of $E$-NO to form $E\cdot$ and $\cdot$NO$_{\text{gas}}$. Alternatively, 1-electron reduction is required to formally generate the $E^-$ anion and $\cdot$NO$_{\text{gas}}$ which is especially important process for the $S$, $N$, and $O$-nitroso compounds. This study focuses on $C$-nitroso compounds.

**Scheme 6.8.** Alternative NO sources and NO formation. This study focuses on $C$-

\[
\begin{array}{cccc}
E^- + \cdot\text{NO}_{\text{gas}} & \overset{e^-}{\longleftarrow} & E - \text{NO} & \overset{\text{homolytic cleavage}}{\longrightarrow} E\cdot + \cdot\text{NO}_{\text{gas}} \\
E = RO, RS, R_2N \\
\end{array}
\]

$C$-nitroso compounds tend to be more stable than their $N$, $O$, and $S$ counterparts.

Arguably, the decreased reactivity observed with $C$-nitroso compounds may be due to the increased difficulty in generating $C$-based anions (Scheme 6.8). This provides great opportunity to observe the binding of $C$-nitroso compounds at metal centers due to inherently higher stability of resulting complexes. This also allows for the indirect study of highly reactive species such as NO and HNO since these $C$-NO species can be used to foreshadow binding modes of parent HNO species.
6.1.c. C-Nitroso compounds – syntheses

There are several synthetic routes to C-nitroso compounds (RNOs) that have been reviewed over the last thirty years by Coombes (1979), Williams (1988) and Richter-Addo et al. (2002) that summarize synthetic pathways to C-nitroso compounds as well as their spectroscopic and structural properties.

Scheme 6.9. Conversion of amines, C-nitro compounds and hydroxylamines to C-nitroso, and their conversions to C-nitroso.

\[
\begin{align*}
\text{R-NH}_2 & \xrightarrow{[O]} \text{R-N} = \text{O} \\
\text{R-NHOH} & \xrightarrow{\text{FeCl}_3, \text{L}_6\text{Mo(IV)}\text{(O}_2\text{)}} \xrightarrow{\text{CuCl}_2, \text{H}_2\text{O}} \text{R-N} = \text{O} \\
\text{FeCl}_3 & \xrightarrow{\text{L}_6\text{Mo(IV)}\text{(O}_2\text{)}} \xrightarrow{\text{CuCl}_2, \text{H}_2\text{O}} \text{R-N} = \text{O}
\end{align*}
\]

Amines RNH₂, hydroxylamines RNHOH, and C-nitro compounds RNO₂ can be converted to the corresponding C-nitroso compound RNO. A common class of oxidizing agents for the conversion of amines to C-nitroso compounds is peroxo acids, others include hydrogen peroxide with catalyst, and potassium permanganate. N-substituted hydroxylamines RNOH can be oxidized to the corresponding RNO species using oxidizing agents such as Mo(VI), Fe(III), and Cu(II). Specifically, aromatic RNOs have been synthesized via oxidation of hydroxylamines with ferric chloride, pyridinium chlorochromate in THF, or tert-butyl hypochloride in diethyl ether or THF. Alternatively, amalgams of magnesium, zinc, or aluminium can reduce C-nitro compounds RNO₂ to C-nitroso compounds RNO. In biological environments C-nitroso compounds RNO are known to form via the oxidation of amines RNH₂ as well as the reduction of corresponding nitro compounds RNO₂ (Scheme 6.9).
Aromatic \( C \)-nitrosation can be achieved using various sources of the nitrosonium cation (\( \text{NO}^+ \)) such as \( \text{NOBF}_4 \), other nitrogen oxides (\( \text{N}_x\text{O}_y \)), or sodium nitrite in acid media (e.g. \( \text{NaNO}_2 / \text{HClO}_4 \)).\(^{25-27,43}\) For example anisole (\( \text{C}_6\text{H}_5\text{OMe} \)) undergoes nitrosation with \( \text{NOBF}_4 \) to yield \( p\)-\( \text{ONC}_6\text{H}_4\text{OMe} \) (Scheme 5.10).\(^{25,44,45}\) An additional nitrosating agent for the formation of \( C \)-nitroso compounds are alkyl nitrites (\( \text{RONO} \)) when reacted with phenolate ions (e.g. \( \text{C}_6\text{H}_5\text{O}^- \)) (Scheme 6.10).\(^{25,46}\) Other methodologies for the syntheses of \( C \)-nitroso compounds employ organometallic reagents such as Grignards and alkylithiums in combination with nitrosating agents (Scheme 6.11).\(^{25-27,47}\)

Alkenes also serve as reagents for nitrosation reactions with nitrosyl halides (\( \text{XNO} \)) in which \( \text{XNO} \) is added across the \( \text{C} = \text{C} \) double bond (Scheme 6.12).\(^{25}\) Additionally, alkanes can react with \( \text{XNO} \) (e.g. \( \text{ClNO} \)) under photochemical initiation to produce \( \text{Cl}^- \) and \( \text{NO}^- \) radicals that proceed to initiate the production of carbon radicals (\( \text{R}^- \)) that combine with \( \text{NO}^- \) to yield the desired RNOs (Scheme 6.13).\(^{25,48,49}\)

**Scheme 6.10.** Synthesis of aromatic \( C \)-nitroso syntheses.

\[
\begin{align*}
\text{R} & \quad \text{NO}^+ \quad \text{R} \\
\text{R} = \text{OMe}, \text{amine} & \quad \text{NaNO}_2 \quad \text{HClO}_4 \quad \text{R}
\end{align*}
\]

**Scheme 6.11.** Reaction of organometallic reagents.

\[
\{(\text{H}_3\text{C}(\text{H}_2\text{C})_2\text{C})\equiv\text{C}\}_2\text{Hg} + 2 \text{ClNO} \quad \rightarrow \quad 2 \text{H}_3\text{C}(\text{H}_2\text{C})_2\text{C}\equiv\text{CNO}
\]
6.1.d. C-nitroso compounds – chemical properties

C-nitroso compounds are typically colorless in the solid state as dimers but show blue (aliphatic) or green (aromatic) color when in their monomeric form in solution due to a weak $n \to \pi^*$ transition at 630 – 790 nm.\textsuperscript{25,26} Dimerization proceeds via reversible nitrogen-nitrogen bond formation that forms cis and trans isomers of bis-nitroso compounds (e.g. bis-nitrosobenzyl). Aliphatic trans-dimers have a $\pi \to \pi^*$ transition at in the range 276-291 nm, while this transition in cis-dimers occurs in the range 265-271 nm (Scheme 6.14).\textsuperscript{25,26,50}


\begin{align*}
\text{Scheme 6.12. Reaction of alkenes with nitrosylhalides.} \\
\begin{array}{c}
\text{R} \\
\text{= aliphatic (blue)} \\
\text{aromatic (green)} \\
\text{\lambda = 630 - 790 nm} \\
\text{v_{NO} (aromatic) = 1488 - 1513 cm}^{-1}
\end{array}
\end{align*}

Nitrosobenzene has been structurally characterized as the cis-dimer via single crystal X-ray diffraction with the following distances (Å) and angles (°): N-N 1.321(5), C-N 1.454(5) and 1.463(5), N-O 1.268(4) and 1.261(4) Å, C-N-O 120.4(2) and
This N-N distance in the nitrosobenzene dimer is longer than that in azobenzene (PhN=Ph; N-N = 1.237(2) Å) indicating that the O-atoms certainly participate in this delocalized π-system. Aromatic monomers (ArNO) display typical IR stretches $v_{\text{NO}}$ in the range 1488 – 1513 cm$^{-1}$. For instance, nitrosobenzene’s IR stretch is at $v_{\text{NO}} = 1506$ cm$^{-1}$. Aromatic trans-dimers exhibit strong $v_{\text{NO}}$ IR bands in the region 1253 – 1299 cm$^{-1}$ while cis-dimers generally show two $v_{\text{NO}}$ bands between 1389 – 1409 cm$^{-1}$. A NMR study on substituted nitrosobenzenes showed that at ambient temperature, the monomer is favored in solution (e.g. CD$_2$Cl$_2$ and CD$_3$OD) while upon cooling the dimer becomes more dominant with the cis-dimer being favored over the trans-dimer. The dissociation energy for these species falls in the range of $\Delta H^0 = 9 – 13$ kcal/mol for the cis-dimer and $\Delta H^0 \approx 6 – 10$ kcal/mol for the trans-dimer.$^{25,53,54}$

### 6.1.e. Biological properties

While nitrosobenzene and other C-nitroso compounds may be generally considered non-hazardous reagents with low toxicity in humans,$^{55}$ in the presence of both NADH and Cu(II) ions, nitrosobenzene elicits oxidative DNA damage through the intermediacy of the phenylhydronitroxide radical PhNHO•.$^{56}$ This nitroxide has also been identified as a metabolic product of PhNO,$^{57-59}$ (as well as PhNH$_2$, PhNHOH, and PhNO$_2$)$^{60}$ which also participates in the oxidation of thiol residues within red blood cells.$^{60}$ Nitrosobenzene penetrates red blood cells upon prolonged exposure and converts to N-phenylhydroxylamine.$^{55}$ More generally, nitrosarenes (ArNOs) can be produced \textit{in vivo} through $N$-oxygenation of aromatic amines or reduction of nitro
aromatics. ArNOs target cellular thiols such as glutathione (γ-L-glutamyl-L-cysteinylglycine, GSH). Glutathione exposed to nitrosoaromatics causes rapid excretion of the nitroso compound by the liver in conjunction with lowering of GSH levels and alteration of bile flow.\textsuperscript{61}

Exposure of nitrosoarenes ArNO to blood alter ferrihemoglobin formation.\textsuperscript{61} Oxyhemoglobin binding to nitrosobenzene also shows a displacement of O\textsubscript{2}. Oxyhemoglobin’s binding affinity for nitrosobenzene is 6 times higher than for O\textsubscript{2}, while deoxygenated hemoglobins’ binding affinity is 10 times higher for nitrosobenzene than O\textsubscript{2}.\textsuperscript{62} This nitrosobenzene poisoning has long been observed in the literature. The nitrosobenzene hemoglobin adduct forms a violet pigment that was first reported in 1878.\textsuperscript{62,63} Nitrosobenzene binding is largely influenced by its size. Substitutions on the benzene ring can have a large effect on the binding affinity. For example, substitutions in \textit{ortho}-position generally have a negative effect on the binding affinity, while \textit{meta-} and \textit{para}-substitutions with halogens can increase the binding affinity.\textsuperscript{64}

\textit{C}-nitroso compounds including nitrosobenzene are a class of stable compounds that inhibit hepatic mitochondrial aldehyde dehydrogenase (A1DH) without having to be bioactivated. Aldehyde oxidation is an important metabolic pathway in which aldehydes are oxidized to carboxylic acids by aldehyde dehydrogenase enzyme. The resulting carboxylic acids can now leave the liver to be metabolized by muscles and the heart.\textsuperscript{65}
6.1.f. C-Nitroso compounds - metal complexes

A wide variety of [M](RNO), [M]_2(RNO), and [M]_4(RNO) bonding modes in transition metal C-nitroso complexes are known that involve varying degrees of RN=O bond activation.\(^{25}\) For example, CpCo(PPh\(_3\))(\(\text{t}^1\)-N(O)Me)\(^{66}\) exhibits an IR stretch \(\nu_{\text{NO}} = 1310\) cm\(^{-1}\) that indicates significant backbonding from the d\(^8\) Co(I) center since this stretch occurs at 1506 cm\(^{-1}\) for free, monomeric nitrosobenzene. As illustrated in Figure 6.2, increasing degrees of backbonding occur as additional metal fragments interact with a single C-nitroso compound RNO with N-O distances spanning the range 1.13(2).

![Diagram](image)

**Figure 6.2.** Various C-NO binding modes in metal complexes.

**Scheme 6.15.** Complete reductive cleavage of ArN=O bond.
An extreme example of backbonding occurs in the 4-electron reductive cleavage of \( \text{ArN=O} \) (\( \text{Ar} = 3,5\text{-Me}_2\text{C}_6\text{H}_3 \)) by the electron-rich, \( \text{Co(I)} \) \( \beta \)-diketiminate \([\text{Me}_2\text{NN}]\text{Co(1-toluene)}\) to give the oxo-imido complex \{[\text{Me}_2\text{NN}]\text{Co}\}_2(\mu-O)(\mu-\text{NAr})\) (Scheme 6.15).^69

**6.1.g. Synthesis and reactivity of metal-nitroso compounds**

Bergman mechanistically studied C-NO bond formation in the ligand-induced migratory insertion of \( \text{Cp}^*\text{Co(NO)(R)} \) to \( \text{Cp}^*\text{Co(N(O)R)PR}_3 \) (\( \text{R} = \text{Me, Et} \)) (Scheme 6.16).^66,70 This behavior may be contrasted with double NO insertion into metal alkyls \( \text{M-R} \) to give \( \text{N-alkyl-N-nitrosohydroxylaminato species} \) \( \text{M}(\kappa^2\text{-O}_2\text{N}_2\text{R}) \) (Scheme 6.17).^53,71,72 On the other hand, addition of nitrosonium \( \text{(NO}^+\text{)} \) to \( \text{C-organonitroso adducts} \) \([\text{Pt(ArNO)(PPh}_3)_2]\) (\( \text{Ar} = \text{Ph or o-MeC}_6\text{H}_4 \)) gave the diazeniumdiolate cations

Scheme 6.16. C-NO bond formation.

\[
\begin{align*}
\text{Na/Hg, Et}_2\text{O} & \quad \text{Na}^+ [\text{CpCoNO}]^- \\
\text{R} = \text{Me, Et} & \quad \text{CpCoR_3} + \text{PPh}_3 \quad \text{CpCoPPh}_3
\end{align*}
\]

Scheme 6.17. Double NO insertion into M-R.

\[
\begin{align*}
\text{Cp}_2\text{ZrR}_2 & \quad 2 \text{NO} \\
\text{R} = \text{CH}_2\text{Ph} & \quad \text{Cp}_2\text{Zr} - \text{O} \quad \text{N} - \text{R} \\
\text{Cp}_2\text{Zr} & \quad \text{O} \quad \text{N} - \text{R} \\
\text{CpW} & \quad 2 \text{NO} \\
\text{R} = \text{CH}_2\text{SiMe}_3, \text{t-Bu} & \quad (\text{ON})(\text{R})\text{CpW} - \text{O} \\
\text{O} & \quad \text{N} - \text{R} \\
\text{CpW} & \quad \text{O} \quad \text{N} - \text{R}
\end{align*}
\]

Scheme 6.18. NO\(^+\) addition to C-organonitroso.

\[
\begin{align*}
\text{Ph}_3\text{P} & \quad \text{Pt} - \text{O} \\
\text{Ph}_3\text{P} & \quad \text{N} \quad \text{Ar} \\
\text{Ar} = \text{Ph, o-MeC}_6\text{H}_4 & \quad (\text{Ph}_3\text{P})_2\text{Pt} - \text{O} \\
\text{O} & \quad \text{N} - \text{Ar} \\
\text{Ph}_3\text{P} & \quad \text{N} \quad \text{Ar}
\end{align*}
\]
Motivated by the appreciably greater affinity of hemoglobin for nitrosobenzene (PhNO) over dioxygen ($O_2$), a number of heme model complexes have been prepared. Typically, $\kappa^1$-$N$ bonding of the nitroarene is observed in ferrous complexes, though $\kappa^1$-$O$ bonding was observed in the ferric para-amino substituted nitroarene adduct $[(TPP)Fe(ONAr)_2]^+$ (TPP = meso-tetraphenylporphyrinato; Figure 6.3).}

**Scheme 6.19.** C-H functionalization, isocyanate, and carbodiimide formation.

**Figure 6.3.** $[M](ONAr)$ bonding modes in representative mononuclear C-nitroso complexes.
Additionally, organonitroso compounds ArNO serve as reagents in copper-catalyzed C-N bond forming reactions\textsuperscript{75,76} as well as nickel-catalyzed nitrene transfer reactions (Scheme 6.19).\textsuperscript{77} Srivastava showed that allylic C-H bonds undergo amination in moderate yield by ArNO or ArNHOH under catalysis by copper(I) ions.\textsuperscript{75} As part of mechanistic studies, the trigonal tris(nitrosoarene)copper(I) adduct $[\text{Cu}(\kappa^1\text{N}(\text{O})\text{Ar})_3]^+$ ($\text{Ar}' = p$-NE$_2$C$_6$H$_4$) was structurally characterized.\textsuperscript{75} Catalyzed by Ni(CN$^t$Bu)$_4$, nitrene group transfer reactions from PhNO take place with CN$^t$Bu, leading to $^t$BuNCO and PhN=C=$^t$Bu among other products.\textsuperscript{77} Ni($^2$-ONPh)(CN$^t$Bu)$_2$ whose bonding mode was assigned by IR spectroscopy ($v_{\text{NO}} = 1032$ cm$^{-1}$) was suggested as an active intermediate based on its stoichiometric decomposition to PhNHC(O)NH$^t$Bu in the presence of trace water.\textsuperscript{77}

To systematically explore the effect of the metal ion on ArN=O activation, we report herein the synthesis and structure of $\beta$-diketiminato Ni(I) and Cu(I) nitrosoarene adducts as well as their reactivity with NO to give divalent NONOates\textsuperscript{78} $[\text{Me}_2\text{NN}]M(\text{I}^2\text{-O}_2\text{N}_2\text{Ar})$. Additionally, we describe the formation of a nickel(II) nitroxide intermediate $[\text{Me}_2\text{NN}]\text{Ni}(\text{I}^2\text{-ONPh})$ that serves as a model in the study employing hydroxylamines as redox partners of HNO. In collaboration with Prof. Karl Wieghardt’s group at the Max Planck Institute for Bioinorganic Chemistry in Mülheim, Germany, we also discuss preliminary XAS data that give insight into the true oxidation states of these formally monovalent nitrosoarene adducts.
Results and Discussion

6.2.a. Syntheses of nickel and copper precursors to nitrosarene adducts

[Me₂NN]Ni(2-picoline) was synthesized analogously to the previously reported [Me₂NN]Ni(2,4-lutidine) (Scheme 6.20). Reaction of the thallium β-diketiminate Tl[Me₂NN] with NiCl₂(2-picoline)₂ in THF provides dark green [Me₂NN]Ni(2-picoline)Cl which is not isolated. Following filtration of TlCl that is generated, the reductant sodium amalgam is added and a color change to red takes place signaling the formation of [Me₂NN]Ni(2-picoline). This nickel(I) complex is isolated by first filtering the reaction mixture followed by crystallization from pentane to afford red crystals.

The increased volatility of 2-picoline over 2,4-lutidine increases the ease of isolation of [Me₂NN]Ni(2-picoline) over that of [Me₂NN]Ni(2,4-lutidine). Low temperature EPR of [Me₂NN]Ni(2-picoline) in the presence additional 2-picoline in frozen toluene glass at 90 K shows a rhombic spectrum with \(g₁ = 2.41\), \(g₂ = 2.12\), and \(g₃ = 2.06\) (Figure 6.4).

The previously reported copper(I) β-diketiminate [Me₂NN]Cu(MeCN) was prepared via the reaction of the free β-diketimine ligand [Me₂NN]H with copper(I) tert-butoxide (CuOBu'). CuOBu' was synthesized via the reaction of potassium tert-butoxide and copper(I) iodide CuI in THF, isolated by filtration and removal of all volatiles in vacuo (Scheme 6.20).
**Scheme 6.20.** Synthesis of monovalent $\beta$-diketiminato nickel and copper complexes employed in the preparation of nitrosoarene adducts.

**Figure 6.4.** X-band EPR spectrum of $[\text{Me}_2\text{NN}]\text{Ni}(2\text{-picoline})$ with a small amount of added 2-picoline in frozen toluene glass (90 K).
6.2.b. Nickel nitrosoarene adducts

Pooja Kapoor in the Warren group first synthesized and characterized \{[Me₂NN]Ni\}_2(μ-η²:η¹⁻²ONAr) (1a), a member of nitrosoarene adducts under study in this work. Addition of the nitrosoarene ArN=O (Ar = 3,5-Me₂C₆H₃) to 2 equiv. [Me₂NN]Ni(2,4-lutidine)\(^{79}\) in ether allows for the isolation of green crystals of \{[Me₂NN]Ni\}_2(μ-η²:η¹⁻²ONAr) (1a) in 42% yield (Scheme 6.21). Single crystal X-ray analysis revealed a symmetric, butterfly-shaped [Ni]_2(ONAr) core with a pseudo-mirror plane containing the ArNO ligand relating the two Ni fragments (Figure 6.5). The Ni-Ni separation is 3.171(2) Å and the Ni-O bond distances are 1.881(3) and 1.932(3) Å with Ni-N bond distances of 1.921(3) and 1.879(3) Å. The N-O distance of 1.440(4) Å is similar to that in [(Cp*Rh)_2(μ-Cl)(μ-η²:η¹⁻²ONPh)](BF₄) (N-O = 1.422(4) Å)\(^{84}\) which also exhibits a significant reduction in N-O bond order relative to free C-nitroso compounds which possess N-O distances in the range of 1.13-1.29 Å.\(^{25}\)
Figure 6.5. X-ray crystal structure of the solid-state structure of \{[Me₂NN]Ni\}_2(μ-\text{η}^2:\text{η}^2\text{-ONAr}) (1a) (all H atoms omitted). Selected bond distances (Å) and angles (deg): N5-O 1.440(4), Ni1-N5 1.879(3), Ni2-N5 1.921(3), Ni1-O 1.932(3), Ni2-O 1.881(3), Ni1-N1 1.859(3), Ni1-N2 1.868(3), Ni2-N3 1.869(3), Ni2-N4 1.868(3), N1-Ni1-N2 94.88(14), N3-Ni2-N4 96.36(15), N5-Ni1-O 44.37(12), N5-N2-O 44.48(12), Ni1-N5-Ni2 113.09(16), Ni1-O-Ni2 112.52(14), O-N5-C43 112.8(3).
To employ IR spectroscopy to assess the degree of N-O bond activation upon coordination of nitrosoarenes, we prepared complexes of the parent nitrosobenzene PhNO. The commercial availability of Ph$_{15}$NH$_2$ allows for the ready preparation of Ph$_{15}$NO via oxidation of $^{15}$N-labelled aniline. The addition of PhNO or Ph$_{15}$NO to 2 equiv. [Me$_2$NN]Ni(2-picoline) allows for the isolation of \{[Me$_2$NN]Ni$_2$(µ-η$^2$:η$^2$-ONPh)\} (1b and 1b-$^{15}$N) (Scheme 6.21) which possess closely related $^1$H NMR spectra to 1a. Coordination of nitrosobenzene to two [Me$_2$NN]Ni$^i$ fragments markedly reduces the PhNO $v_{NO}$ stretching frequency to 915 cm$^{-1}$ (901 cm$^{-1}$ for 1b-$^{15}$N) (Figure 6.6) relative to free, monomeric PhNO at 1506 cm$^{-1}$.$^{25,85}$

![Solid state IR spectra](image)

**Figure 6.6.** Solid state IR spectra of \{[Me$_2$NN]Ni$_2$(µ-η$^2$:η$^2$-ONPh)\} (1b) and \{[Me$_2$NN]Ni$_2$(µ-η$^2$:η$^2$-O$^{15}$NPh)\} (1b-$^{15}$N) (film from ether on KBr). Difference spectra have $^{14}$N peaks down, $^{15}$N peaks up.
While the diamagnetic $^1$H NMR chemical shifts of 1a are otherwise unremarkable, the backbone-$CH$ and backbone-$Me$ signals are mildly temperature dependent in toluene-$d_8$. Over the temperature range -70 to +25 °C, each of these signals shift upfield from $\delta$ 4.66 to 3.48 ppm and $\delta$ 1.01 to 0.49 ppm, respectively. These observations suggest contact shifts from a minute contribution of a higher spin state in solution. DFT studies on 1a (gas phase) identify an $S = 1$ excited state ca. 12 kcal/mol higher in electronic energy bearing similar metrical parameters to the $S = 0$ ground state (Figure 6.7). In the $S = 1$ state, there is significant unpaired electron density (spin-$\alpha$) on the $\beta$-diketiminato central C-atom (Figure 6.8). Variable temperature solid state magnetic susceptibility measurements of 1a performed by Prof. Karsten Meyer’s laboratory in Erlangen, Germany by give a steadily increasing magnetic moment that reaches 2.6 B.M. at 300 K near the spin-only value of 2.8 B.M. expected for an $S = 1$ system.
\[
\{[\text{Me}_2\text{NN}]\text{Ni}\}_2 (\mu-\eta^2:\eta^2-\text{ONAr})
\]

(1a – S0) \hspace{1cm} 0.0 \text{ kcal/mol} \hspace{1cm} (1a – S1) \hspace{1cm} +12.0 \text{ kcal/mol}

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**Figure 6.7.** DFT structures of low-spin (1a – S0) and S = 1 (1a – S1) forms of \{[\text{Me}_2\text{NN}]\text{Ni}\}_2 (\mu-\eta^2:\eta^2-\text{ONAr}) (ADF ZORA BP/TZ2P(+)). DFT optimized distances are also collected. At this level of theory and in the gas-phase, the S = 1 form is calculated to be 12.0 kcal/mol higher in electronic energy.
6.2.c. Dinuclear and mononuclear copper nitrosoarene adducts

\{[\text{Me}_2\text{NN}]\text{Cu}\}_2(\mu-\eta^2:\eta^1\text{-ONAr}) (2a) was first synthesised and characterized by Pooja Kapoor. Reaction of the Cu(I) \(\beta\)-diketiminate [Me\(_2\)NN]Cu(NCMe)\(^{81}\) with 0.5 equiv. ArNO (Ar = 3,5-Me\(_2\)C\(_6\)H\(_3\) or Ph) in Et\(_2\)O results in the formation of a very dark solution from which crystals of \{[\text{Me}_2\text{NN}]\text{Cu}\}_2(\mu-\eta^2:\eta^1\text{-ONAr}) (2a) may be isolated in

**Scheme 6.22.** Synthesis of Cu(I) nitrosoarene adducts 2 and 3.

\[
\begin{align*}
\text{O=NAS} & \xrightarrow{\text{Et}_2\text{O}} \quad \{[\text{Me}_2\text{NN}]\text{Cu}\}_2(\mu-\eta^2:\eta^1\text{-ONAr}) \\
2 \text{[Me}_2\text{NN}]\text{Cu(NCMe)} & \xrightarrow{\text{benzene-d}_6} \quad \text{[Me}_2\text{NN}]\text{Cu(benzene)} \\
\text{O=NAS} & \xrightarrow{\text{toluene}} \quad \{[\text{Me}_2\text{NN}]\text{Cu}\}_2(\mu-\eta^2:\eta^1\text{-ONAr}) \\
2 \text{[Me}_2\text{NN}]\text{Cu(NCMe)} & \xrightarrow{\text{benzene-d}_6} \quad \text{[Me}_2\text{NN}]\text{Cu(benzene)}
\end{align*}
\]

Figure 6.8. Spin density plot of 1a (S = 1). Blue indicates excess spin-\(\alpha\); red indicates excess spin-\(\beta\) (isospin value = 0.001).
Figure 6.9. X-ray crystal structure of $\{[\text{Me}_2\text{NN}]\text{Cu}_2(\mu-\eta^2:\eta^1\text{-ONAr}) (2a) \cdot \frac{1}{2} \text{ether} \}$ (all H atoms omitted; major occupancy (55%) of disordered β-diketiminato N-aryl ring at N2 shown; ether of solvation omitted). Selected bond distances (Å) and angles (deg): N5-O 1.375(6), Cu1-N5 2.040(5), Cu2-N5 1.879(5), Cu1-O 1.843(4), Cu2-O 2.786, Cu1-N1 1.891(5), Cu1-N2 1.891(5), Cu2-N3 1.984(5), Cu2-N4 1.907(5), N1-Cu1-N2 99.9(2), N3-Cu2-N4 100.16(19), N5-Cu1-O 41.10(18), Cu1-N5-Cu2 140.2(3), O-N5-C43 110.3(5).
Figure 6.10. X-ray crystal structure \([\text{[Me}_2\text{NN}]\text{Cu}_2\{\text{[1-\eta}^2;\eta^1\text{-ONPh}\}\}\) (2b) (all H atoms omitted; thermal ellipsoids represented at the 50% probability level). Selected bond distances (Å) and angles (deg): N5-O 1.368(2), Cu1-N5 2.013(2), Cu2-N5 1.900(2), Cu1-O 1.840(2), Cu2-O 2.797, Cu1-Cu2 3.668, Cu1-N1 1.900(2), Cu1-N2 1.883(2), Cu2-N3 1.969(2), Cu2-N4 1.900(2), N1-Cu1-N2 100.40(7), N3-Cu2-N4 100.49(7), N5-Cu1-O 41.28(7), Cu1-N5-Cu2 139.22(10), O-N5-C43 113.0(2).
modest yield from ether (Scheme 6.22). Unlike in 1a, the nitroarene ligand in 2a is \( \eta^2 \)-bound to one Cu center with Cu1-O and Cu1-N5 distances of 1.843(4) and 2.040(5) Å and only bound through the N atom to the other Cu center with a Cu2-N5 distance of 1.879(5) Å (Figure 6.9). The N-O bond is less activated than in 1a with a N-O distance of 1.375(6) Å. The related \([\text{Me}_2\text{NN}]\text{Cu}_{2}(\mu-\eta^2: \eta^1)\cdot\text{ONPh}\) (2b) possesses similar metrical parameters (N5-O: 1.368(2), Cu1-O: 1.840(2), Cu1-N5: 2.013(2), Cu2-N5 1.900(2) Å; Figure 6.10) and shows a \(\nu_{\text{NO}}\) stretch at 1040 cm\(^{-1}\) (1029 cm\(^{-1}\) for 2b-\(^{15}\text{N}\)) (Figure 6.11).

This asymmetry suggested that one [Me\(_2\)NN]Cu fragment of 2a may be labile in solution. Dissolution of crystals of 2a in benzene-\(d_6\) results in the quantitative formation of mononuclear [Me\(_2\)NN]Cu(\(\eta^2\)-ONAr) (3a) with formation of the solvento species [Me\(_2\)NN]Cu(benzene)\(^{87,88}\) (Scheme 6.22).

[Me\(_2\)NN]Cu(\(\eta^2\)-ONAr) (3a) was first synthesized on a preparative scale and characterized by Pooja Kapoor. Reaction of [Me\(_2\)NN]Cu(NCMe) with 1 eq. ArNO in toluene allows for the isolation of mononuclear 3a (Scheme 6.22) possessing nearly symmetric \( \eta^2 \)-NO bonding with Cu-N3 and Cu-O bond distances of 1.886(3) and 1.851(3) Å, respectively (Figure 6.12). [Me\(_2\)NN]Cu(\(\eta^2\)-ONAr) (3a) possesses the least activated ArN=O bond with a N-O bond distance of 1.333(4) Å, lower than the range of 1.386(3) – 1.432(6) Å established for other mononuclear \( \eta^2 \)-ONR compounds.\(^{25}\) The X-ray structure of the corresponding nitrosobenzene adduct [Me\(_2\)NN]Cu(\(\eta^2\)-ONPh) (3b) possesses two independent molecules of 3b with similar metrical parameters (N3-O: 1.338(5), 1.334(5); Cu-N3: 1.932(4), 1.935(3); Cu-O: 1.853(3), 1.855(3) Å; Figures
6.10. Consistent with the lowest degree of N-O bond activation inferred by N-O bond lengths, this mononuclear nitrosobenzene adduct exhibits the highest $\nu_{\text{NO}}$ at 1113 cm$^{-1}$ (1093 cm$^{-1}$ for $3b$-$^{15}\text{N}$) among $1b$, $2b$, and $3b$ (Table 6.1).

(a) $\{[\text{Me}_2\text{NN}]\text{Cu}\}_2(\mu-\eta^2:\eta^1$)-ONPh

(b) $\{[\text{Me}_2\text{NN}]\text{Cu}\}_2(\mu-\eta^2\cdot\eta^1$)-O$^{15}\text{N}$Ph

(c) Difference Spectrum

\[ \begin{array}{c}
\text{NO-stretch [Cu]} \\
1093 \rightarrow 1029 \\
1114 \rightarrow 1040 \\
\end{array} \]

Figure 6.11. Solid state IR spectrum of $\{[\text{Me}_2\text{NN}]\text{Cu}\}_2(\mu-\eta^2:\eta^1$)-ONPh) (2b) ([Cu]$_2$) and $\{[\text{Me}_2\text{NN}]\text{Cu}\}_2(\mu-\eta^2\cdot\eta^1$)-O$^{15}\text{N}$Ph) (2b-$^{15}\text{N}$) ([Cu]) (film from ether on KBr). $\nu$(NO) stretches at 1114/1093 cm$^{-1}$ due to $[\text{Me}_2\text{NN}]\text{Cu}(\text{ONPh})$ (3b) / $[\text{Me}_2\text{NN}]\text{Cu}(O^{15}\text{NPh})$ (3b-$^{15}\text{N}$). Difference spectra have $^{14}\text{N}$ peaks down, $^{15}\text{N}$ peaks up.
Figure 6.12. X-ray crystal structure of the solid-state structure of [Me₂NN]Cu(η²-ONAr) (3a) (all H atoms omitted). Selected bond distances (Å) and angles (deg): N3-O 1.333(4), Cu-N3 1.936(4), Cu-O 1.851(3), Cu-N1 1.886(3), Cu-N2 1.884(3), N3-C22 1.441(6), N3-Cu-O 41.14(14), N1-Cu-N2 99.96(15), N1-Cu-O 106.69(14), N2-Cu-N3 112.92(15).
Figure 6.13. X-ray crystal structure of $[\text{Me}_2\text{NN}]\text{Cu}(\eta^2\text{-ONPh})$ (3b – molecule 1) (all H atoms omitted; thermal ellipsoids represented at the 50% probability level). Selected bond distances (Å) and angles (deg): N3-O1 1.338(5), Cu1-N3 1.932(4), Cu1-O1 1.853(3), Cu1-N1 1.893(3), Cu1-N2 1.892(3), N3-C22 1.442(6), N3-Cu1-O1 41.35(14), N1-Cu1-N2 99.97(14), N1-Cu1-O1 106.62(14), N2-Cu-N3 112.1(2).
Table 5.1. Crystallographic data for 2b and 3b.

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<th>3b formula</th>
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<td>(P2_1/n)</td>
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<td>(\gamma) (deg)</td>
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<td>1.426 and -0.548</td>
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Despite the larger size of N compared to O, the N-O distance in 3a is significantly shorter than the O-O distances of 1.392(12) and 1.392(3) Å found in Tolman’s side-on copper dioxygen complexes [Cu]($\eta^2$-O$_2$) supported by $\beta$-diketiminato and anilidoimine ligands.$^{89-91}$ Both of these considerations suggest modest backbonding from the

**Table 6.1.** ArN=O distances and $\nu$(NO) stretching frequencies in organonitroso adducts 1 – 3. (*a* average of two independent distances).

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<th>Compound</th>
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<th>$\nu$(14NO) / $\nu$(15NO) (cm$^{-1}$)</th>
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<td>1a</td>
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<td></td>
</tr>
<tr>
<td>1b</td>
<td>n/a</td>
<td>915 / 901</td>
</tr>
<tr>
<td>2a</td>
<td>1.375(6)</td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td>1.368(2)</td>
<td>1040 / 1029</td>
</tr>
<tr>
<td>3a</td>
<td>1.333(4)</td>
<td></td>
</tr>
<tr>
<td>3b</td>
<td>1.336(6)$^a$</td>
<td>1113 / 1093</td>
</tr>
</tbody>
</table>
[Me₂NN]Cu fragment to the nitrosoarene. Indeed, the \( \eta^2 \)-ArN=O binding mode in 3 is reminiscent of \( \eta^2 \)-coordination of an alkene to Cu(I). Variable temperature NMR spectra of 3a recorded by Pooja Kapoor reveal a modest activation barrier \( \Delta G^\ddagger = 11.4(2) \text{ kcal/mol} \) at -44(2) °C for rotation about the Cu-ArNO moiety similar to the value of 10.7(3) kcal/mol observed for [Me₂NN]Cu(\( \eta^2 \)-styrene).

6.2.d. Reactivity with nitric oxide

First demonstrated by Pooja Kapoor, the Ni(I) and Cu(I) nitrosoarene adducts 1a and 3a react with NO\(_\text{gas}\) under anaerobic conditions (Scheme 6.23). Addition of 2.1 equiv. NO to a benzene-\( d_6 \) solution of 1a results in the quantitative formation of the diamagnetic [Me₂NN]Ni(\( \kappa^2 \)-O₂N₂Ar)\(^94 \) (4) and [Me₂NN]Ni(NO)\(^94 \) identified by \( ^1\text{H} \) NMR spectroscopy. It should be noted that 4 quickly forms upon addition of ArNO to nickel- nitrosyl [Me₂NN]Ni(NO)\(^94 \) Perhaps more surprising is the uptake of NO by [Me₂NN]Cu(\( \eta^2 \)-ONAr) (3a) to give red crystals of [Me₂NN]Cu(\( \kappa^2 \)-O₂N₂Ar) (5) in 80% yield when 3a is exposed to a slight excess of NO (2 equiv.). The X-ray structure of 5 (Figure 6.15) shows square planar coordination at Cu as found in the structures of Cu(\( \kappa^2 \)-O₂N₂R)\(_2 \) (R = Ph\(^95 \) Cy\(^96 \)). The EPR spectrum of 5 in toluene at room
Figure 6.15. X-ray crystal structure of the solid-state structure of [Me₂NN]Cu(κ²-O₂N₂Ar) (5) (all H atoms omitted). Selected bond distances (Å) and angles (deg): Cu-O₁ 1.957(2), Cu-O₂ 1.949(2), Cu-N₁ 1.931(3), Cu-N₂ 1.929(3), O₁-N₃ 1.323(3), O₂-N₄ 1.306(3), N₃-N₄ 1.282(4), N₁-Cu-N₂ 95.59(12), O₁-Cu-O₂ 79.23(10), N₁-Cu-O₁ 93.19(11), N₂-Cu-O₂ 92.33(10).
temperature collected by Prof. Jeffrey Peterson of West Virginia University is consistent with a Cu(II) ion in a square-planar environment with two N donors ($g_{iso} = 2.10$, $A_{Cu} = 79$ G, $A_{N} = 13$ G) (Figure 6.16).

In contrast to typical reductive nitrosylation reactions in which the metal center is reduced with concomitant oxidation of the organic fragment, the reaction between $[\text{Me}_2\text{NN}]\text{Cu}(\kappa^2\text{-O}_2\text{N}_2\text{Ar})$ and NO may formally proceed through oxidation of the copper complex to $\{[\text{Me}_2\text{NN}]\text{Cu}(\eta^2\text{-ONAr})\}^+$ and reduction of NO to NO$^-$. The high oxidation potential for $[\text{Me}_2\text{NN}]\text{Cu}(\eta^2\text{-ONAr})$ ($E_{1/2} \approx +1.1$ V vs. NHE)$^{80}$ as well as the high reduction potential for NO to NO$^-$ (estimated at -0.8 V vs. NHE for 1 M NO$_{aq}$)$^{97}$ however, strongly suggests inner-sphere attack of NO on $[\text{Me}_2\text{NN}]\text{Cu}(\eta^2\text{-ONAr})$. 

**Figure 6.16.** X-band EPR spectrum of $[\text{Me}_2\text{NN}]\text{Cu}(\kappa^2\text{-O}_2\text{N}_2\text{Ar})$ (5) at room temperature in toluene.
6.2.e. Targeting nitroxide intermediates M-ONHPPh

As previously mentioned, PhNO metabolises to the nitroxide radical PhNHO• which is responsible for oxidation of thiol residues within red blood cells.\textsuperscript{60} Furthermore, nitrosobenzene’s mechanism for DNA damage is thought of to proceed via one-electron reduction to this radical in the presence of Cu\textsuperscript{II} and NADH.\textsuperscript{56-59} Thus, the synthesis of [M\textsuperscript{II}](ONHPPh) species would be of biological interest as well as providing a bone fide example of a divalent complex that is structurally similar to the nitrosoarene adducts for further spectroscopic study.

Dr. Ela Kogut had noticed previously that exposure of [Me\textsubscript{2}NN]Ni(2,4-lutidine) to air yielded {[Me\textsubscript{2}NN]Ni}\textsubscript{2}(μ-OH).\textsuperscript{79} We thought that acid/base chemistry between a metal hydroxide [M]-OH and N-phenylhydroxylamine (PhNHOH) could represent a viable synthetic pathway to a metal bound nitroxide [M](ONHPPh). A high purity sample of green {[Me\textsubscript{2}NN]Ni}\textsubscript{2}(μ-OH)\textsubscript{2} (6) was prepared by allowing air to slowly diffuse via a syringe needle into an otherwise sealed vial that contained [Me\textsubscript{2}NN]Ni(2-picoline) in toluene (Scheme 6.24).

Scheme 6.24. Synthesis of {[Me\textsubscript{2}NN]Ni}\textsubscript{2}(μ-OH)\textsubscript{2} (6)

\[
2 \text{[Me}_2\text{NN}]{\text{Ni}}(2\text{-picoline}) + \text{air} \xrightarrow{\text{toluene}} \text{[Me}_2\text{NN}]{\text{Ni}}\text{2}(\mu\text{-OH})_2 \quad (6)
\]

The X-ray structure of {[Me\textsubscript{2}NN]Ni}\textsubscript{2}(μ-OH)\textsubscript{2} (6) (Figure 6.17) is related in structure to previously reported {[Me\textsubscript{2}NN]Cu}\textsubscript{2}(μ-OH)\textsubscript{2}\textsuperscript{93} but with different M-O and M-M distances (Cu-Cu’ 3.0581(3) Å and Cu-O 1.9142(11) Å). 6 shows a shorter metal to metal distance of Ni1-Ni1’ 2.900(4) Å. Nickel to oxygen distances are also shorter Ni-O 1.8625(18) Å. The nickel ligand distances are Ni-N\textsubscript{β-dik} 1.8691(18) Å and
1.8740(17) Å. The twist angle between the $N_{\beta\text{-dik}}$-Ni-$N_{\beta\text{-dik}}$ and O-Ni-O planes is only 1.4° showing a nearly perfectly flat, square planar geometry about the nickel.

$\{[\text{Me}_2\text{NN}]\text{Ni}\}_2(\mu\text{-OH})_2$ (6) is green colored compound with characteristic UV-vis absorptions at 508 and 639 nm in THF at 25 °C and an IR stretch of $\nu_{\text{OH}} = 3616$ cm$^{-1}$ while the related Cu complex $\{[\text{Me}_2\text{NN}]\text{Cu}\}_2(\mu\text{-OH})_2$ shows an IR stretch of $\nu_{\text{OH}} = 3646$ cm$^{-1}$.

Due to the poor solubility of 6 in common organic solvents, its molar absorptivity and magnetic susceptibility could not be accurately determined in solution.

.
Figure 6.17. X-ray crystal structure of [Me₂NN]Ni⁺₂(µ-OH) (6) (all H atoms omitted). Selected bond distances (Å) and angles (deg): Ni1-Ni1’ 2.900(4), Ni1-O1 1.8625(18), Ni1-N1 1.8691(18), Ni1-N2 1.8740(17), N1-Ni1-N2 94.69(7), O1-Ni1-N1 93.56(8), O1-Ni1-O1’ 77.91(9), Ni1-O1-Ni1’ 102.09(9).
Reaction of \{[\text{Me}_2\text{NN}]\text{Ni}\}_2(\mu\text{-OH})_2 (6) and PhNHOH in the presence of 4A molecular sieves in THF results in swift formation of \{[\text{Me}_2\text{NN}]\text{Ni}(\eta^2\text{-ONPh})\} (7) as orange/brown crystals in 77\% yield. It is essential that \{[\text{Me}_2\text{NN}]\text{Ni}\}_2(\mu\text{-OH})_2 (6) is of high purity to isolate 7 in high yield (Scheme 6.25).

**Scheme 6.25.** Synthesis of Ni(II) nitroxide.

$$\{[\text{Me}_2\text{NN}]\text{Ni}\}_2(\mu\text{-OH})_2 + 2 \text{THF M.S.} \rightarrow [\text{Me}_2\text{NN}]\text{Ni}(\eta^2\text{-ONPh})$$

The X-ray structure of \{[\text{Me}_2\text{NN}]\text{Ni}(\eta^2\text{-ONPh})\} (7) (Figure 6.18) shows relatively short nickel to ligand bond distances of Ni-N_{\beta\text{-dik}} 1.845(3) and 1.853(3) Å. The nitroxide Ni-N3 and Ni-O bond distances of 1.872(4) and 1.859(3) Å along with an acute Ni-O-N3 angle of 68.69(18)° clearly indicate \eta^2-bonding of the nitroxide. The nitroxide O-N3 bond distance of 1.387(4) Å that shows a single bond between the O-N indicating that it is a nitroxide anion. In comparison, free TEMPO nitroxide anion has a N-O bond distance of 1.433(2) to 1.4447(14) Å.98 Another relevant comparison is the structure \{[\text{Me}_2\text{NN}]\text{Cu}(\eta^2\text{-TEMPO})\} that Kamille Williams obtained upon reaction of TEMPO with \{[\text{Me}_2\text{NN}]\text{Cu(MeCN)}\}.27 This nitroxide adduct has a N-O distance of 1.4104(15) Å indicating its formulation as a copper(II) complex of a nitroxide anion.

$^1$H NMR spectra of 7 benzene-$d_6$ at RT (Figure 6.19) shows a static solution behavior. The nitroxide anion does not dissociate or rotate in solution based on the four unique $\omega$-Me groups of the diketiminate aryl rings which appear as singlets at $\delta$ 2.829, 2.758, 2.706 and 1.750 ppm. Other characteristic peaks are the two Me-backbone peaks.
Figure 6.18. X-ray crystal structure of [Me₂NNi(η⁵-ONHPh) (7) (only H shown on N3). Selected bond distances (Å) and angles (deg): Ni-N1 1.845(3), Ni-N2 1.853(3), Ni-N3 1.872(4), Ni-O 1.859(3), O-N3 1.387(4), N1-Ni-N2 96.42(15), N1-Cu-O 109.35(14), N1-Ni-N3 110.62(15).
Table 6.3. Crystallographic data for 6 and 7.

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<td>1.178 and -0.121</td>
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Figure 6.19. $^1$H NMR (400 MHz) of 7 in benzene-$d_6$ at RT.

at $\delta$ 1.482 and 1.272 ppm. The N-H peak has a chemical shift of 4.471 ppm, while the backbone C-H shift is at 4.892 ppm.

6.2.e. Metal oxidation state of nitrosoarene adducts – XAS studies

There are at least two different possibilities to assign the oxidation state of the metal centers in compounds 1, 2, 3 as well as to describe the C-nitroso ligands. Each of the aforementioned complexes displays various degrees of N-O bond activation. The values of N-O bond distance and IR stretching frequency for compounds 1, 2, and 3 collected in Table 6.1 may be compared against the corresponding ranges of 1.13 – 1.29
Å and 1488 – 1513 cm\(^{-1}\) for free ArN=O species.\(^{25}\) One explanation for the increased N-O bond activation observed in 3 (monomeric Cu) to 2 (dimeric Cu) to 1 (dimeric Ni) considers \(\pi\)-backbonding from the formally monovalent [Me\(_2\)NN]M (M = Cu or Ni) metal fragments. The higher orbital energies of Ni vs. Cu would suggest stronger backbonding by Ni\(^{1}\) vs. Cu\(^{1}\), borne out by both crystallographic and IR spectroscopic studies of the dinuclear adducts 1 and 2. For instance, \{[Me\(_2\)NN]Ni\}_2(\mu-\eta^2:\eta^2\text{-ONAr}) (1a) has a longer N-O bond distance of 1.440(4) Å as compared to the N-O bond distance of 1.375(6) Å in \{[Me\(_2\)NN]Cu\}_2(\mu-\eta^2:\eta^1\text{-ONAr}) (2a). This is consistent with the decreased \(\nu_{\text{NO}}\) stretching frequency in the analogous dinickel nitrosobenzene adduct 1b (915 cm\(^{-1}\)) as compared to the dicopper species 2b (1040 cm\(^{-1}\)). Moreover, the dinuclear copper nitrosoarene adduct 2 benefit from backbonding from two copper centers, not just one as in compounds 3, resulting in more activated N-O bonds in 2 as compared to 3. For instance, the shortest N-O bond distance of 1.333(4) Å in the series 1a – 3a is observed for 3a and the highest \(\nu_{\text{NO}}\) stretching frequency of 1113 cm\(^{-1}\) in the series 1b – 3b is seen for compound 3b.

An alternative bonding scenario considers complete backbonding from Ni or Cu to the nitrosoarene moiety in which the nitrooxide dianion [ONAr]\(^{2-}\) formally coordinates two [Me\(_2\)NN]M (M = Ni or Cu) fragments in compounds 1 – 3 (Figure 6.20). In this formalism, compound 1 would possess two divalent [Me\(_2\)NN]Ni\(^{III}\) fragments and compound 3 would possess a trivalent [Me\(_2\)NN]Cu\(^{III}\) fragment. Compound 2 would have two possibilities, either as a [Cu\(^{II}\)] / [Cu\(^{II}\)] species or as a [Cu\(^{III}\)] / [Cu\(^{I}\)] species (Figure 6.20).
In collaboration with Prof. Dr. Karl Wieghardt’s group at the Max-Planck-Institute for Bioinorganic Chemistry in Mülheim, Germany, XAS data was collected on the above mentioned complexes. To allow for better interpretation, XAS spectra of structurally related compounds such as \([\text{Me}_2\text{NN}]\text{Cu}(\text{MeCN})\) that possess unambiguously monovalent metal centers were also collected (Scheme 6.26).

In addition, we prepared two types of copper-diazene complexes originally reported in Dr. Xuliang Dai’s thesis by addition of azobenzenes ArN=NAr to \([\text{Me}_2\text{NN}]\text{Cu}(\text{MeCN})\).

\[
\{[\text{Me}_2\text{NN}]\text{Cu}\}_2(\text{trans-1},2\text{-PhN=NPh})
\]

**Scheme 6.26.** Synthesis of Cu styrene compounds

\[\text{Ph}\ [\text{Me}_2\text{NN}]\text{Cu}(\text{MeCN}) \xrightarrow{\text{Et}_2\text{O}} \text{MeCN} \rightarrow [\text{Me}_2\text{NN}]\text{Cu} \text{yellow crystals} \]

82% yield
\textbf{Scheme 6.27.} Syntheses of reference compounds for XAS.

\[
\begin{align*}
\text{R}^2\text{NNCu(MeCN)}_{\text{Et}_2\text{R}} & \rightarrow \text{R}^2\text{NNCu}\text{Cu[NNMe}_2] \quad \text{green crystals} \\
\text{R} = \text{Ph, Tol} \\
\text{N}^2\text{NNCu} \quad \text{R}^2\text{NNCu} \quad \text{green crystals} \\
\text{N} = \text{N}^2\text{NNCu} \quad \text{R}^2\text{NNCu} \quad \text{brown crystals} \\
\text{N}^1\text{NNCu} \quad \text{R}^1\text{NNCu} \quad \text{brown crystals}
\end{align*}
\]

\{[\text{Me}_2\text{NN}]\text{Cu}\}_2(\text{trans}-\text{1t}-1,2\text{-TolN}=\text{NTol}) can be isolated as green crystals in 78 and 53 % yield, respectively, via the addition of PhN=NPh or TolN=NTol (Tol = \(p\)-MeC\(_6\)H\(_4\)) to 2 equiv. [Me\(_2\text{NN}\)]Cu(MeCN) in Et\(_2\)O (Scheme 6.27). Significant disorder in the X-ray structure of \{[\text{Me}_2\text{NN}]\text{Cu}\}_2(\text{trans}-\text{1t}-1,2\text{-PhN}=\text{NPh}) observed by Dr. Dai as well as in this study prompted the use of the \(p\)-substituted analogue \{[\text{Me}_2\text{NN}]\text{Cu}\}_2(\text{trans}-\text{1t}-1,2\text{-TolN}=\text{NTol}). Little evidence of significant backbonding is apparent from the diazene N-N distance in the X-ray structure of \{[\text{Me}_2\text{NN}]\text{Cu}\}_2(\text{trans}-\text{1t}-1,2\text{-TolN}=\text{NTol}) which has a long Cu\textsuperscript{+}Cu separation of 4.736 Å (Figure 6.21). The diazene N-N distance in \{[\text{Me}_2\text{NN}]\text{Cu}\}_2(\text{trans}-\text{1t}-1,2\text{-TolN}=\text{NTol}) of 1.280(2) Å is just a little longer than the N-N distance in free trans-azobenzene (1.247(2) Å\textsuperscript{52} or trans-TolN=NTol (1.262(3) Å).\textsuperscript{99} In addition, the Cu-N\(\beta\)-dik distances of 1.940(4) and 1.911(4) Å are also typical for copper(I) species; Cu-N\(\beta\)-dik distances in three-coordinate species shorter than 1.90 Å are more commonly associated with higher oxidation state.\textsuperscript{100}

A mononuclear adduct of the extremely electron-poor diazene Ar\(^F\)N=NAr\(^F\) (Ar\(^F\) = 3,5-(CF\(_3\))\(_2\)C\(_6\)H\(_5\)) may be prepared by combination of an equimolar amount of
[Me₂NN]Cu(MeCN) and ArF=N=NArF in Et₂O to give [Me₂NN]Cu(η²-ArF=N=NArF) as orange brown crystals in 84% yield. Previous X-ray characterization confirmed the η²-coordination of this electron-poor azobenzene with Cu-N distances of 1.893(3) and 1.892(3) Å with an extremely activated N-N distance of 1.351(3) Å.¹⁰¹ This N-N distance is considerably longer than that of the free trans-azobenzene (N-N 1.247(2) Å)⁵² indicating significant backbonding. Despite the high degree of activation of the ArF=N=NArF unit upon coordination, ¹H NMR spectra of [Me₂NN]Cu(η²-ArF=N=NArF) in benzene-d₆ indicate free ArF=N=NArF as well as [Me₂NN]Cu(benzene).⁸⁷ Solution behavior of [Me₂NN]Cu(η²-ArF=N=NArF) shows that the electron poor diazene easily dissociates from the metal. Therefore, ¹H NMR spectra were taken in THF-d₈ at RT which still showed broad peaks at δ 3.267 and 1.325 ppm that correlate to o-Me and CH₃-backbone groups of the β-diketiminato ligand. The broad peaks indicate an exchange of the diazene in solution.
Figure 6.21. X-ray crystal structure diagram of \([\text{Me}_2\text{NN}]\text{Cu}_2(\text{trans-}\mu-1,2-\text{TolN=NTol})\) (all H atoms omitted). Selected bond distances (Å) and angles (deg): Cu-N1 1.940(4), Cu-N2 1.911(4), Cu-N3 1.884(5), N3-N3' 1.280(2), N1-Cu-N2 98.89(18).
Table 6.4. Crystallographic data for \{[\text{Me}_2\text{NN}]\text{Cu}\}_2(\text{trans-}1,2\text{-TolN=NTol})

<table>
<thead>
<tr>
<th>Compd.</th>
<th>{[\text{Me}_2\text{NN}]\text{Cu}}_2(\text{trans-}1,2\text{-TolN=NTol})</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
<td>\text{C}<em>{27}\text{H}</em>{30}\text{CuN}_3</td>
</tr>
<tr>
<td>Mol. Wt.</td>
<td>460.08</td>
</tr>
<tr>
<td>Temp.(K)</td>
<td>100(2)</td>
</tr>
<tr>
<td>crystal description</td>
<td>plate</td>
</tr>
<tr>
<td>crystal color</td>
<td>green</td>
</tr>
<tr>
<td>crystal size (mm³)</td>
<td>0.39×0.17×0.08</td>
</tr>
<tr>
<td>system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>\text{P21/n}</td>
</tr>
<tr>
<td>(a) (Å)</td>
<td>13.1187(13)</td>
</tr>
<tr>
<td>(b) (Å)</td>
<td>12.8709(13)</td>
</tr>
<tr>
<td>(c) (Å)</td>
<td>14.9449(15)</td>
</tr>
<tr>
<td>(\alpha) (deg)</td>
<td>90.00</td>
</tr>
<tr>
<td>(\beta) (deg)</td>
<td>106.0230(10)</td>
</tr>
<tr>
<td>(\gamma) (deg)</td>
<td>90.00</td>
</tr>
<tr>
<td>(Z)</td>
<td>4</td>
</tr>
<tr>
<td>(\varnothing) range (deg)</td>
<td>1.83-26.00</td>
</tr>
<tr>
<td>measd reflns</td>
<td>18871</td>
</tr>
<tr>
<td>unique reflns</td>
<td>4765</td>
</tr>
<tr>
<td>(R) (int)</td>
<td>0.0325</td>
</tr>
<tr>
<td>GOF of (F^2)</td>
<td>1.036</td>
</tr>
<tr>
<td>(R_1) ( (I &gt; 2\sigma(I)))</td>
<td>0.0331</td>
</tr>
<tr>
<td>(wR_2) (all data)</td>
<td>0.0443</td>
</tr>
<tr>
<td>Largest diff. peak and hole (e^{-} \cdot \text{Å}^{-3})</td>
<td>0.996 and -0.061</td>
</tr>
</tbody>
</table>
X-ray absorption spectroscopy (XAS) is a powerful technique to infer metal oxidation states. K-edge spectra are particularly sensitive and originate from the promotion of a 1s electron to a higher energy, valence level that is not completely filled. K-edge spectra may possess pre-edge and rising edge features. If the 3d shell is not completely filled, XAS spectra of copper compounds can show a pre-edge feature that corresponds to a 1s to 3d transition that has low intensity due to being dipole (Laporte) forbidden but is quadrupole allowed. The most dominant feature is the rising-edge which arises from 1s to 4p transition(s) and is more intense since it is Laporte allowed. Focusing on the rising edge feature, a shift to higher energy is directly related to a higher oxidation state - promotion of a core 1s electron to the valence shell becomes harder as the oxidation state of the metal is increased. These features make it possible to compare structurally related compounds and obtain metal oxidation state information for ambiguous cases by comparing the rising edge energies of known compounds with unambiguous oxidation states.

The K-edge XAS spectra of \{[\text{Me}_2\text{NN}]\text{Ni}\}_2(\mu-\eta^2:\eta^2-\text{ONAr}) \ (\text{1a}), \{[\text{Me}_2\text{NN}]\text{Ni}\}_2(\mu-\eta^2:\eta^2-\text{ONPh}) \ (\text{1b}) \text{ and } [\text{Me}_2\text{NN}]\text{Ni}(\eta^2-\text{ONPH}) \ (7) \ (\text{Figure 6.22}) \text{ are quite similar with rising edge absorption energies of } 8337.9, 8337.4 \text{ and } 8336.6 \text{ eV, respectively, and pre-edge absorption energies of } 8331.5, 8331.6 \text{ and } 8331.9 \text{ eV, respectively. Thus the electronic environment of the the Ni center in each is quite similar, indicating a Ni(II) oxidation state based on the genuine Ni(II) species } [\text{Me}_2\text{NN}]\text{Ni}(\eta^2-\text{ONPh}) \ (7) \ (\text{Table 6.5}). \text{ The only important difference is the slightly higher intensity of the 1s } \rightarrow \text{ 4p rising edge band in } [\text{Me}_2\text{NN}]\text{Ni}(\eta^2-\text{ONPH}) \ (7) \text{ which}
The XAS spectra of copper species reveal interesting features relating to their electronic structure. Considering the rising edge energies, $[\text{Me}_2\text{NN}]\text{Cu}(\eta^2-\text{ONAr})$ (3a) (8985.7 eV) and $[\text{Me}_2\text{NN}]\text{Cu}(\eta^2-\text{ONPh})$ (3b) (8985.7 eV) are closely related to $[\text{Me}_2\text{NN}]\text{Cu}(\eta^2-\text{ArN=NAr})$ (8985.6 eV) whereas the bona fide copper(I) complex $[\text{Me}_2\text{NN}]\text{Cu}(\eta^2-\text{CH}_2=\text{CHPh})$ exhibits its rising edge peak at considerably lower energy (8984.5 eV) consistent with a higher oxidation state for the former three species. This can lead to the conclusion that 3a and 3b are more likely to be Cu$^{\text{III}}$ (Table 6.5).

**Figure 6.22.** XAS K-edge spectra for selected Ni complexes 1 and 7.
Each of the dinuclear Cu nitroarene species \{[\text{Me}_2\text{NN}]\text{Cu}\}_2(\mu-\eta^2-\eta^1-\text{ONAr})\ (2a, 2b) has two distinguishable rising edge XAS peaks at 8983.8 and 8985.0 eV which are close to those of \[\text{Me}_2\text{NN}]\text{Cu}(\eta^2-\text{ONAr})\ (3) (8985.7 eV) and \[\text{Me}_2\text{NN}]\text{Cu}(\eta^2-\text{CH}_2=\text{CHPh})\ (8984.5 eV). Thus, this species possesses K-edge XAS spectra consistent with a mixed valence \([\text{Cu}^{\text{III}}]/[\text{Cu}^{\text{I}}]\) species shown in Figure 6.20 and Table 6.5.

Interestingly, the \[[\text{Me}_2\text{NN}]\text{Cu}\]_2(\text{trans}-\mu-1,2-\text{PhN=NPh}) exhibits a unique XAS spectrum which both the 8984.4 and 8988.0 eV. The maximum at 8984.4 eV XAS

**Figure 6.23.** Normalized absorption data for selected Cu complexes. Black lines are actual data – red lines are simulated data by Dr. Neil Tomson at MPI for the rising edge bands of the XAS spectra of selected Cu compounds.
feature is nearly coincident with \([\text{Me}_2\text{NN}]\text{Cu}(\text{C}^2=\text{CH}_2=\text{CHPh})\) (8984.5 eV) suggesting a copper(I) oxidation state for this dinuclear diazene adduct (Table 6.5). This would also be consistent with the modest lengthening of the N-N bond (1.280(2) Å in \([\text{Me}_2\text{NN}]\text{Cu}_2(\text{trans-1,2-TolN=N Tol})\) as compare to the free trans-diazene (trans-TolN=N Tol N-N distances: 1.262(3) Å)\(^99\).

Figure 6.24. Normalized XAS spectra of copper compounds in this study.

These XAS data are relevant to the conceptual description of the reaction of \([\text{Me}_2\text{NN}]\text{Ni}_2(\mu-\text{I}^2:\text{I}^2-\text{ONAr})\) (1a) and \([\text{Me}_2\text{NN}]\text{Cu}(\text{I}^3-\text{ONAr})\) (3a) with NO\(_{\text{gas}}\). We initially considered these as simple nitrosoarene adducts of the monovalent \(\beta\)-diketiminato nickel and copper fragments \([\text{Me}_2\text{NN}]\text{M}\) (M = Ni or Cu) describing their reaction to form \([\text{Me}_2\text{NN}]\text{M}(\kappa^2-\text{O}_2\text{NAr})\) species as oxidative nitrosylation. If the \([\text{Me}_2\text{NN}]\text{Cu}(\text{I}^2-\text{ONAr})\) species is best described as a copper(III) species, however, reaction with NO\(_{\text{gas}}\) would be a more common case of reductive nitrosylation.\(^{103}\)
Table 6.5. XAS rising-edge values.

<table>
<thead>
<tr>
<th>Compound</th>
<th>XAS Rising-Edge Peak (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>{[Me$_2$NN]Ni$_2$(µ-η$^2$:η$^1$-ONAr)} (1a)</td>
<td>8337.9</td>
</tr>
<tr>
<td>{[Me$_2$NN]Ni$_2$(µ-η$^2$:η$^1$-ONPh)} (1b)</td>
<td>8337.4</td>
</tr>
<tr>
<td>[Me$_2$NN]Ni(η$^1$-ONPh) (7)</td>
<td>8336.6</td>
</tr>
<tr>
<td>{[Me$_2$NN]Cu$_2$}{trans-µ-1,2-PhN=NPh}</td>
<td>8984.3</td>
</tr>
<tr>
<td>[Me$_2$NN]Cu(η$^2$-CH$_2$=CHPh)</td>
<td>8984.5</td>
</tr>
<tr>
<td>[Me$_2$NN]Cu(η$^2$-ArF=NArF)</td>
<td>8985.6</td>
</tr>
<tr>
<td>{[Me$_2$NN]Cu$_2$(µ-η$^2$:η$^1$-ONAr)} (2a)</td>
<td>8983.8, 8985.0</td>
</tr>
<tr>
<td>{[Me$_2$NN]Cu$_2$(µ-η$^2$:η$^1$-ONPh)} (2b)</td>
<td>8983.8, 8985.2</td>
</tr>
<tr>
<td>[Me$_2$NN]Cu(η$^2$-ONAr) (3a)</td>
<td>8985.7</td>
</tr>
<tr>
<td>[Me$_2$NN]Cu(η$^2$-ONAr) (3b)</td>
<td>8985.7</td>
</tr>
</tbody>
</table>

Conclusions

The two-coordinate, monovalent fragments [Me$_2$NN]M (M = Ni, Cu) favor π-interactions with the ArN=O bond of C-nitroso compounds which provide to the best of our knowledge the first X-ray structures of Ni and Cu C-nitroso adducts in which the NO functionality is not κ$^1$N bound.$^{25,75}$ We note that a recent theoretical study suggested that η$^2$-ONPh coordination in copper(I) β-diketiminate may be slightly
favored over $\kappa^1$-N bonding\textsuperscript{104} while IR data suggest side-on nitrosobenzene coordination in the zerovalent Ni(ONPh)(CNBu\textsuperscript{1})\textsubscript{2}.\textsuperscript{77}

The dinuclear $\{[\text{Me}_2\text{NN}]\text{Ni}\}_2(\mu-\eta^2:\eta^2$-ONAr) (1) are conceptually related to the dinuclear toluene adduct $\{[\text{Nacnac}]\text{Ni}\}_2(\mu-\eta^3:\eta^3$-toluene) of a related $[\beta$-diketiminato]$\text{Ni}^1$ fragment which possesses $o$-$\text{Pr}$ $N$-aryl substituents.\textsuperscript{105} The monovalent, mononuclear $[\text{Me}_2\text{NN}]\text{Ni}(\eta^2$-ONAr) fragment likely possesses a significant amount of unpaired electron density on the $\eta^2$-ON moiety as found on the $\eta^2$-O\textsubscript{2} ligand in the square planar superoxide complex $[\text{Nacnac}]\text{Ni}(\eta^2$-O\textsubscript{2}).\textsuperscript{106} Thus, the mononuclear species $[\text{Me}_2\text{NN}]\text{Ni}(\eta^2$-ONAr) would be a ready target for the less sterically hindered $[\text{Me}_2\text{NN}]\text{Ni}$ metalloradical to give 1. Perhaps more unusual is the unsymmetrical metal-organonitroso interaction in $\{[\text{Me}_2\text{NN}]\text{Cu}\}_2(\mu-\eta^2:\eta^1$-ONAr) (2) in which the $\kappa^1$-N interaction is readily displaced by benzene to give $[\text{Me}_2\text{NN}]\text{Cu}(\eta^2$-ONAr) (3) and $[\text{Me}_2\text{NN}]\text{Cu}$(benzene).

The C-nitroso adducts reported herein are capable of incorporating an equivalent of NO into the coordinated ONAr ligand to form diazeniumdiolates $[\text{M}]($$\kappa^2$-O\textsubscript{2}N\textsubscript{2}Ar$)$ - oxidatively nitrosylating the formally monovalent $[\text{Me}_2\text{NN}]\text{Cu}(\eta^2$-ONAr). XAS data supported by the synthesis and characterization of additional compounds such as $\{[\text{Me}_2\text{NN}]\text{Cu}\}_2(\text{trans-}\mu-1,2$-PhN=NPh), $\{[\text{Me}_2\text{NN}]\text{Cu}\}_2(\text{trans-}\mu-1,2$-TolN=NTol), $[\text{Me}_2\text{NN}]\text{Cu}(\eta^2$-Ar$^F$N=NAr$^F$) and $[\text{Me}_2\text{NN}]\text{Cu}(\eta^2$-CH\textsubscript{2}=CHPh), however, paint a picture perhaps more consistent with reductive nitrosylation in the reaction of a copper(III) species $[\text{Me}_2\text{NN}]\text{Cu}(\eta^2$-ONAr) with NO.
The $\eta^2$:ONAr binding modes and reactivity observed in the organonitroso complexes $\{[\text{Me}_2\text{NN}]\text{Ni}\}_2(\mu-\eta^2:\eta^1$-ONAr) (1), $\{[\text{Me}_2\text{NN}]\text{Cu}\}_2(\mu-\eta^2:\eta^1$-ONAr) (2) and $[\text{Me}_2\text{NN}]\text{Cu}(\eta^2$-ONAr) (3) may foreshadow possibilities in related “parent” HNO$^6$-$^{107}$$^{109}$ adducts. For instance, aromatic nitroso compounds ArNO have been considered as $N$-substituted nitroxyls$^{110}$ and PhNO rapidly reacts with HNO (but not NO) to give cupferron (HON(Ph)N=O)$^{110}$ the conjugate acid of the diazeniumdiolate anion [O$_2$N$_2$Ph]. Thus far, synthetic examples of [M](HNO) complexes exhibit $\kappa^1$-N bonding and have been limited to substitutionally inert, low-spin d$^6$ octahedral complexes$^{111}$ such as the crystallographically characterized OsCl$_2$(CO)(HNO)(PPh$_3$)$_2$,$^{112}$ [Re(CO)$_3$(PPh$_3$)$_2$(HNO)]OTf$^{113}$ and [Ru(HNO)(py$_{bush}$S$_4$)]Br$^{114}$ (Figure 6.25). Nonetheless, in comparing [M](ArNO) species to the parent [M](HNO) complexes one must bear in mind HNO’s distinct acid/base behavior (pKa = 11.4)$^{97,115}$ facile oxidation (HNO/NO,H$^+$ = +0.5 to +0.6 V at pH = 7)$^{97,115}$ H-atom transfer (BDE (H-NO) $\approx 50$ kcal/mol)$^{116,117}$ and rapid, irreversible dimerization (k = $8 \times 10^6$ M$^{-1}$s$^{-1}$ in aqueous solution)$^{115}$ chemistry.

![Figure 6.25. Crystallographically characterized HNO complexes.](image)
Experimental Section

General Considerations

All experiments were carried out in a dry nitrogen atmosphere using an MBraun glovebox and/or standard Schlenk techniques. 4A molecular sieves were activated in vacuo at 180 °C for 24 h. Diethyl ether and tetrahydrofuran (THF) were first sparged with nitrogen and then dried by passage through activated alumina columns. Pentane was first washed with conc. HNO₃ / H₂SO₄ to remove olefins, stored over CaCl₂ and then distilled before use from sodium/benzophenone. All deuterated solvents were sparged with nitrogen, dried over activated 4A molecular sieves and stored under nitrogen. ¹H and ¹³C NMR spectra were recorded on a Varian 300 MHz or 400 MHz spectrometer (300 or 400 and 75.4 or 100.4 MHz, respectively). All NMR spectra were recorded at room temperature unless otherwise noted and were indirectly referenced to TMS using residual solvent signals as internal standards. X-band EPR spectra were recorded by Prof. Jeffrey Petterson at West Virginia University in toluene at RT in a quartz tube using a Bruker EMX-A spectrometer control system equipped with a Bruker B-E2549 10-inch magnet and a built-in microwave frequency meter or by Dr. Susanne Mossin at University of Erlangen, Germany. The EPR measurements were performed in quartz tubes with J. Young valves. Solution EPR spectra were recorded on a JEOL continuous wave spectrometer JES-FA200 equipped with an X-band Gunn oscillator bridge, a cylindrical mode cavity, and a helium cryostat. For all samples, a modulation frequency of 100 kHz and a time constant of 0.1 s were employed.
All spectra were obtained on freshly prepared solutions (1-10 mM in toluene) of at least 2 independently synthesized batches and were checked carefully for reproducibility. Background spectra were obtained on clean solvents at the same measurement conditions. Elemental analyses were performed on a Perkin-Elmer PE2400 microanalyzer in our laboratories.

The nitrosoarene ArN=O (Ar = 3,5-Me2C₆H₃), [Me₂NN]Ni(2,4-lutidine), [Me₂NN]Cu(MeCN), and Tl[Me₂NN] were synthesized according to literature procedures. ¹⁵N-labelled aniline (Ph¹⁵NH₂) was purchased from Cambridge Isotope Laboratories.

6.3.a. Preparation of compounds

¹⁵N-Nitrosobenzene (Ph¹⁵NO). Prepared by the analogous procedure used for 3,5-dimethylnitrosobenzene.⁶⁹ To a solution of ¹⁵N-labelled aniline (1.00 g, 10.8 mmol) in a 1:1 pentane and dichloromethane mixture (100 mL) was added Na₂WO₄·2H₂O (0.171 g, 0.52 mmol), tetrabutylammonium chloride (0.043 g, 0.15 mmol), and 30 % aqueous hydrogen peroxide (5 mL). The mixture was vigorously stirred for 18 h at RT (room temperature). The organic layer was separated and washed with 0.01 M HCl (50 mL) followed by water (50 mL). The organic layer was then dried over anhydrous MgSO₄. The organic layer was concentrated to dryness and the resulting oil was crystallized using pentane and dichloromethane (1:1) to afford a 60% yield (0.70 g, 6.48 mmol) of the product as brown crystals. ¹H NMR (C₆D₆, RT): δ 7.596 (m, 2, Ar-H), 6.976 (m, 3,
Ar-H); $\text{^{13}C\{^1H\}}$ NMR ($\text{C}_6\text{D}_6$): $\delta$ 166.13, 165.97, 135.06, 129.22, 120.69, 120.63. IR $\nu_{\text{NO}}$ = 1353 cm$^{-1}$ (from PhNO dimer).

$[\text{Me}_2\text{NN}]\text{Ni}(2\text{-picoline})$. A solution of $\text{NiCl}_2(2\text{-picoline})_2$ (2.00 g, 6.33 mmol) (prepared analogously to $\text{NiCl}_2(2,4\text{-lutidine})_2$) in 30 mL THF was added to a solution of $\text{Tl}[\text{Me}_2\text{NN}]$ (3.22 g, 6.33 mmol) in 50 mL THF. The reaction mixture was allowed to stir for 1 h after which it was passed through Celite. To the reaction mixture was added Na/Hg (38.7 g, 0.5% Na w/w) and a color change to red was observed after vigorous shaking. The solution was stirred for an additional 3 h after which the solution was decanted off and passed through Celite. All volatiles were removed in vacuo. The remaining solid was recrystallized from Et$_2$O at -35 °C to afford a 49% yield (1.40 g, 3.10 mmol) red crystals which were dried in vacuo. UV-Vis (Et$_2$O): $\lambda_{\text{max}}$ = 522 nm ($\varepsilon$ = 1000 M$^{-1}$ cm$^{-1}$); EPR (X-band, toluene glass, 90 K – with small amount of added 2-picoline, in collaboration with Dr. Susanne Mossin): $g_1$ = 2.41, $g_2$ = 2.12, $g_3$ = 2.06. Anal. Calcd for $\text{C}_{27}\text{H}_{32}\text{N}_3\text{Ni}$: C, 70.92; H, 7.05; N, 9.19. Found: C, 70.73; H, 7.46; N, 9.20.

$\{[\text{Me}_2\text{NN}]\text{Ni}\}_2(\mu-\eta^2:\eta^2\text{-ONAr})$ (1a). A solution of 3,5-dimethylnitrosobenzene (0.015 g, 0.11 mmol) in ether (3 mL) was slowly added with stirring to a solution of $[\text{Me}_2\text{NN}]\text{Ni}(2,4\text{-lutidine})$ (0.108 g, 0.23 mmol) in ether (10 mL). After stirring for 1 h, the solution was filtered through Celite and the filtrate was concentrated and cooled to -35 °C. The green crystals which had formed were separated from the solution, washed
with cold pentane and dried in vacuo to afford a 42% yield (0.042 g, 0.0462 mmol) of product. Recrystallization from pentane afforded green crystals suitable for X-ray diffraction. $^1$H NMR (C$_6$D$_6$, RT): δ 7.095 (d, 4, m-Ar-H), 6.887 (d, 4, m-Ar-H), 6.509 (s, 1, p-ArNO-H), 6.456 (t, 6, p-Ar-H + o-ArNO-H), 3.476 (s, 2H, backbone-CH), 3.029 (s, 1, p-ArNO-H), 2.279 (s, 12, o-Ar-Me), 2.192 (s, 6, ArNO-Me), 0.485 (s, 12, backbone-Me); $^{13}$C{$^1$H} NMR (C$_6$D$_6$): δ 162.82, 160.46, 159.82, 136.42, 132.00, 122.02, 102.48, 98.21, 24.00, 21.08, 16.86 (2 signals obscured); UV-Vis (Et$_2$O): $\lambda_{max} =$ 615 nm ($\varepsilon =$ 1100 M$^{-1}$cm$^{-1}$); Anal. Calcd for C$_{50}$H$_{59}$O$_{1}$N$_{5}$Ni$_{2}$: C, 69.55; H, 6.88; N, 8.11. Found: C, 69.60; H, 6.97; N, 8.34.

$\{[$Me$_2$NN]$\text{Ni}_2\}($µ-η$^2$:η$^2$-ONPh) (1b). A solution of nitrosobenzene (0.024 g, 0.22 mmol) in toluene (3 mL) was slowly added with stirring to a solution of [Me$_2$NN]Ni(2-picoline) (0.203 g, 0.44 mmol) in ether (10 mL). After stirring for 1 h, the solution was concentrated to dryness, taken up in ether (10 mL) and filtered through Celite. The filtrate was concentrated and cooled to −35 °C. The green crystals were isolated to afford a 30% (0.109 g, 0.066 mmol) of product. $^1$H NMR (C$_6$D$_6$, RT): δ 7.083 (d, 5, Ar-H), 6.870 (m, 7, Ar-H), 6.452 (t, 5, Ar-H), 5.210 (br, 1, p-PhNO-H), 3.495 (2, backbone-CH), 3.010 (s, 12, o-Ar-Me), 2.264 (s, 12, o-Ar-Me), 0.487 (s, 12, backbone-Me); $^{13}$C{$^1$H} NMR (C$_6$D$_6$): δ 164.39, 152.37, 151.06, 150.38, 147.26, 137.68, 137.40, 136.23, 126.85, 126.57, 125.02, 122.73, 106.30, 65.89, 27.37, 26.69, 19.18, 18.22, 17.32, 15.58. IR ν$_{\text{NO}} =$ 915 cm$^{-1}$ (901 cm$^{-1}$ for 1b-$^{15}$N); UV-Vis (Et$_2$O): $\lambda_{max} =$ 583 nm ($\varepsilon$
= 2000 M\(^{-1}\) cm\(^{-1}\)). RT \(^1\)H NMR spectra of \(1a\) and \(1b\) are nearly superimposable with the exception of ONAr and ONPh signals.

\[
{[\text{Me}_2\text{NN}]\text{Cu}}_2(\mu-\eta^2:\eta^1-\text{ONAr}) \quad (2a).
\]

A solution of ArNO (0.046 g, 0.34 mmol) in ether (5 mL) was slowly added with stirring to a solution of [Me\(_2\)NN]Cu(MeCN) (0.290 g, 0.68 mmol) in ether (15 mL). The solution turned dark immediately. After stirring for 30 min., the solution was filtered through Celite and the filtrate was concentrated and cooled to -35 °C. Black crystals were separated from the solution, washed with cold pentane and dried in \textit{vacuo} to afford a 30% yield (0.094 g, 0.204 mmol) of the product.

This dinuclear species dissociates in benzene-\(d_6\) to give [Me\(_2\)NN]Cu(\(\eta^2\)-ONAr) \((3)\) and [Me\(_2\)NN]Cu(benzene).\(^{87,88}\)

\(^1\)H NMR (C\(_6\)D\(_6\)): \(\delta\) 7.11-6.96 (m, 12, Ar-H), 6.751 (s, 1, \(p\)-ArNO-H \((3))\), 6.596 (s, 2, \(\text{o}\)-ArNO-H \((3))\), 4.771 (s, 2, backbone-CH (both \(3\) and \([\text{Cu}](\text{benzene})\)), 2.174 (br, 12 \(\text{o}\)-Ar-Me \((3))\), 2.046 (s, 6, \(m\)-ArNO-Me \((3))\), 2.012 (s, 6, \(\text{o}\)-Ar-Me \(([[\text{Cu}](\text{benzene}))\), 1.629 (s, 6, backbone-Me \(([[\text{Cu}](\text{benzene}))\), 1.445 (s, 6, backbone-Me \((3))\); \(^{13}\)C\({^1}\)H] NMR (C\(_6\)D\(_6\)): \(\delta\) 163.24, 162.43, 160.88, 150.56, 147.90, 138.61, 132.08, 130.61, 129.77, 128.44, 125.00, 123.13, 118.28, 95.81, 93.07, 23.13, 22.87, 21.01, 18.83, 18.50; UV-Vis (Et\(_2\)O): \(\lambda_{\text{max}} = 582\) nm (\(\varepsilon = 1400\) M\(^{-1}\)cm\(^{-1}\)), 791 nm (\(\varepsilon = 2000\) M\(^{-1}\)cm\(^{-1}\)); Anal. Calcd for C\(_{50}\)H\(_{59}\)O\(_3\)N\(_5\)Cu\(_2\): C, 68.78; H, 6.81; N, 8.02. Found: C, 68.50; H, 6.82; N, 7.90.

Molar absorptivities approximate - the higher energy band at \(\lambda = 582\) nm corresponds to [Me\(_2\)NN]Cu(\(\eta^2\)-ONAr) \((3b)\) from dissociation of a [Me\(_2\)NN]Cu fragment in dilute solution.
\{[\text{Me}_2\text{NN}]\text{Cu}_2\}(\mu-\eta^2:\eta^1\text{-ONPh})\text{ (2b)}. A solution of PhNO\ (0.036\ g, 0.34\ mmol) in ether\ (5\ mL) was slowly added with stirring to a solution of \([\text{Me}_2\text{NN}]\text{Cu(MeCN)}\)\ (0.279\ g, 0.68\ mmol) in ether\ (10\ mL). The solution turned dark immediately. After stirring for 1\ h, the solution was filtered through Celite and the filtrate was concentrated to dryness. Crystallization from pentane at \(-35\ ^\circ\text{C}\) afforded 67\% yield (0.199\ g, 0.204\ mmol) of dark crystals as the product. This dinuclear species dissociates in benzene-\(d_6\) to give \([\text{Me}_2\text{NN}]\text{Cu(\eta}^2\text{-ONPh) and [Me}_2\text{NN}]\text{Cu(benzene)}\).\n
\(\text{\H{} NMR (C}_6\text{D}_6\ \text{RT}):\ \delta\ 7.026\ (m, 15, \text{Ar-H}), 6.840\ (d, 2, \text{Ar-H}), 6.755\ (t, 3, \text{Ar-H}), 4.772\ (s, 1, \text{backbone-CH for [Me}_2\text{NN}]\text{Cu(benzene)}), 4.762\ (s, 1, \text{backbone-CH for [Me}_2\text{NN}]\text{Cu(\eta}^2\text{-ONPh)}), 2.127\ (\text{br}, 12, \text{o-Ar-Me for [Me}_2\text{NN}]\text{Cu(\eta}^2\text{-ONPh)}), 2.012\ (s, 12, \text{Me}), 1.630\ (s, 6, \text{backbone-Me for [Me}_2\text{NN}]\text{Cu(\eta}^2\text{-ONPh)}), 1.433\ (s, 6, \text{[Me}_2\text{NN}]\text{Cu(benzene)}); \text{\textsuperscript{13}C {\text{\{}\text{H} NMR (C}_6\text{D}_6)}: \delta\ 163.28, 162.44, 160.50, 160.39, 150.62, 147.86, 132.18, 130.63, 129.36, 128.60, 128.24, 125.12, 123.16, 120.13, 95.88, 93.11, 23.15, 22.54, 18.84, 18.52, 14.27.\text{IR }\nu_{\text{NO}} = 1038\ \text{cm}^{-1};\ \text{UV-Vis (Et}_2\text{O): }\lambda_{\text{max}} = 580\ \text{nm (}\epsilon = 2100\ \text{M}^{-1}\ \text{cm}^{-1}), 781\ \text{nm (}\epsilon = 3300\ \text{M}^{-1}\ \text{cm}^{-1}).\text{ Anal. Calcd for C}_{48}\text{H}_{55}\text{Cu}_2\text{N}_5\text{O: C, 68.22; H, 6.56; N, 8.29. Found: C, 67.87; H, 6.78; N, 8.33.}

UV-vis molar absorptivities approximate - the higher energy band at \(\lambda = 580\ \text{nm}\) corresponds to \([\text{Me}_2\text{NN}]\text{Cu(\eta}^2\text{-ONAr)}\)\ (3b) from dissociation of a \([\text{Me}_2\text{NN}]\text{Cu}\) fragment in dilute solution.
[Me$_2$NN]Cu(η$^2$-ONAr) (3a). A solution of ArNO (0.067 g, 0.49 mmol) in ether (5 mL) was slowly added to the solution of [Me$_2$NN]Cu(MeCN) (0.204 g, 0.49 mmol) in ether (15 mL). The solution turned greenish black immediately and this was let to stir for 30 min. at room temperature. The solution was then filtered through Celite and the filtrate was concentrated and cooled to -35 °C. The mauve crystals were isolated from the solution, washed with cold pentane and dried in vacuo which afforded 60% yield (0.150 g, 0.294 mmol) of the isolated product.$^1$H NMR (C$_6$D$_6$): δ 7.058 (d, 4, m-Ar-H), 6.974 (t, 2, p-Ar-H), 6.790 (s, 1, p-ArNO-H), 6.587 (s, 2, o-ArNO-H), 4.772 (s, 1, backbone-CH), 2.161 (br, 12, o-Ar-Me), 2.046 (s, 6, ArNO-Me), 1.447 (s, 6, backbone-Me).$^{13}$C{$^{1}$H} NMR (C$_6$D$_6$): 163.25, 160.90, 138.63, 132.09, 129.78, 128.45, 125.00, 118.27, 95.82, 22.48, 21.00, 18.49; UV-Vis (Et$_2$O): $\lambda_{\text{max}} = 583$ nm ($\varepsilon = 550$ M$^{-1}$cm$^{-1}$); Anal. Calcd for C$_{29}$H$_{34}$N$_3$OCu: C, 69.09; H, 6.79; N, 8.33. Found: C, 68.90; H, 6.81; N, 8.24.

[Me$_2$NN]Cu(η$^2$-ONPh) (3b). A solution of nitrosobenzene (0.049 g, 0.49 mmol) in toluene (5 mL) was slowly added with stirring to a solution of [Me$_2$NN]Cu(MeCN) (0.205 g, 0.49 mmol) in toluene (10 mL). After stirring for 30 min., the solution was concentrated to dryness, taken up in pentane (10 mL) and filtered through Celite. The filtrate was concentrated and cooled to –35 °C. The brown crystals were isolated in 82% yield (0.191 g; 0.400 mmol).$^1$H NMR (C$_6$D$_6$, RT): δ 7.026 (t, 2, m-PhNO-H), 6.838 (d, 2, o-PhNO-H), 6.753 (t, 1, p-PhNO-H), 4.762 (s, 1, backbone-CH), 2.143 (br, 12, o-Ar-Me), 1.434 (s, 6, backbone-Me); $^{13}$C{$^{1}$H} NMR (C$_6$D$_6$): δ 163.26, 160.44, 147.86, 132.16, 129.32, 128.57, 125.08, 120.10, 95.89, 95.82, 22.50, 18.48. IR $\nu_{\text{NO}} = 1113$ cm$^{-1}$
(1092 cm\(^{-1}\) for 3b\(^{15}\)N); UV-Vis (Et\(_2\)O): \(\lambda_{\text{max}} = 588\) nm (\(\varepsilon = 1000\) L mol\(^{-1}\) cm\(^{-1}\)). Anal. Calcd for C\(_{27}\)H\(_{30}\)CuN\(_3\)O: C, 68.11; H, 6.35; N, 8.83. Found: C, 68.20; H, 6.61; N, 8.72.

**Addition of NO to \{[Me\(_2\)NNi]\(_2\)(\(\mu\)-\(\eta^2\):\(\eta^2\)-ONAr)\} (1a) to form [Me\(_2\)NNi(\(\kappa^2\)-O\(_2\)N\(_2\)Ar) (4) and [Me\(_2\)NNi(NO).** Using a syringe, NO gas (2.0 mL @ 300 K and 1 atm., 0.078 mmol) was slowly bubbled into a solution of \{[Me\(_2\)NNi]\(_2\)(\(\mu\)-\(\eta^2\):\(\eta^2\)-ONAr)\} (0.032 g, 0.037 mmol) in 5 mL C\(_6\)D\(_6\). The color of the solution changed instantaneously from dark green to yellow green. \(^1\)H NMR analysis of the reaction mixture indicated a 1:1 mole ratio of [Me\(_2\)NNi(\(\kappa^2\)-O\(_2\)N\(_2\)Ar)]\(^{94}\) (4) and [Me\(_2\)NNi(NO)]\(^{94}\). \(^1\)H NMR (C\(_6\)D\(_6\)): \(\delta 7.192\) (d, 4, \(m\)-Ar-H, ([Ni][NO])), 7.04-7.00 (m, 8, \(p\)-Ar-H ([Ni][NO]), all Ar-H [Ni](O\(_2\)N\(_2\)Ar)), 6.556 (s, 2, \(o\)-ArNO-H), 6.410 (s, 1, \(p\)-ArNO-H), 4.883 (s, 1, backbone-\(CH\) [Ni](O\(_2\)N\(_2\)Ar)), 4.351 (s, 1, backbone-\(CH\) ([Ni][NO])), 2.693 (s, 12, \(o\)-Ar-Me [Ni](O\(_2\)N\(_2\)Ar)), 2.568 (s, 12, \(o\)-Ar-Me ([Ni][NO])), 1.825 (s, 6, ArNO-Me [Ni](O\(_2\)N\(_2\)Ar)), 1.460 (s, backbone-Me ([Ni][NO]) 1.433 (s, 6, backbone-Me [Ni](O\(_2\)N\(_2\)Ar)).

**Addition of NO to [Me\(_2\)NNCu(\(\eta^2\)-ONAr) (3a) to form [Me\(_2\)NNCu(\(\kappa^2\)-O\(_2\)N\(_2\)Ar) (5).** Using a syringe, NO gas (5.7 mL at 300 K and 1 atm., 0.23 mmol) was slowly bubbled into a solution of [Me\(_2\)NNCu(\(\eta^2\)-ONAr) (0.056g, 0.11 mmol) in 5 mL pentane. The color changed instantaneously from green to red. Volatiles were removed in vacuo and the residue was extracted with pentane and the extracts filtered through Celite. The filtrate was concentrated and crystallized at -35 \(^\circ\)C to afford 80% yield (0.046 g, 0.0911 mmol) of the product. EPR (toluene, RT – Dr. Pettersen) \(g_{\text{iso}} = 2.10\) (\(A_{\text{Cu}} = 79\) G; \(A_N = 13\) G); UV-Vis (Et\(_2\)O): \(\lambda_{\text{max}} = 573\) nm (\(\varepsilon = 450\) M\(^{-1}\)cm\(^{-1}\)), 768 nm (\(\varepsilon = 180\) M\(^{-1}\)cm\(^{-1}\)).
1); Anal. Calcd. for C_{25}H_{34}N_{4}O_{2}Cu: C, 65.20; H, 6.41; N, 10.49. Found: C, 64.98; H, 6.44; N, 10.54.

6.3.b. Preparation of $^{15}$N-labeled PhNO adducts

$\{[Me_2NN]Ni_2\}(\mu-\eta^2:\eta^1$-$O^{15}NPh)$ (1b-$^{15}$N). A solution of $^{15}$N-labelled nitrosobenzene (0.024 g, 0.22 mmol) in toluene (3 mL) was slowly added with stirring to a solution of $[Me_2NN]Ni(2$-picoline) (0.201 g, 0.44 mmol) in ether (10 mL). After stirring for 1 h, the solution was concentrated to dryness, taken up in ether (10 mL) and filtered through Celite. The filtrate was concentrated and cooled to $\sim$35 °C. The green crystals were isolated to afford a yield of 67% (0.122 g, 0.147 mmol) of product. IR $\nu_{^{15}NO}$ = 901 cm$^{-1}$. $^1$H NMR spectrum identical to that of 1b.

$\{[Me_2NN]Cu_2\}(\mu-\eta^2:\eta^1$-$O^{15}NPh)$ (2b-$^{15}$N). A solution of Ph$^{15}$NO (0.036 g, 0.34 mmol) in ether (5 mL) was slowly added with stirring to a solution of $[Me_2NN]Cu(MeCN)$ (0.281 g, 0.68 mmol) in ether (10 mL). The solution turned dark immediately. After stirring for 1 h, the solution was filtered through Celite and the filtrate was concentrated to dryness and crystallized from pentane at $\sim$35 °C to afford a yield of 75% (0.224 g, 0.255 mmol) of dark crystals. This dinuclear species dissociates in benzene-$d_6$ to give $[Me_2NN]Cu(\eta^2$-ONPh) and $[Me_2NN]Cu(benzene)$. IR $\nu_{^{15}NO}$ = 1028 cm$^{-1}$. $^1$H NMR spectrum identical to that of 2b.
[Me₂NN]Cu(η²-O¹⁵NPh) (3b-¹⁵N). A solution of ¹⁵N-labelled nitrosobenzene (0.053 g, 0.49 mmol) in toluene (5 mL) was slowly added with stirring to a solution of [Me₂NN]Cu(MeCN) (0.203 g, 0.49 mmol) in toluene (10 mL). After stirring for 30 min., the solution was concentrated to dryness, taken up in pentane (10 mL) and filtered through Celite. The filtrate was concentrated and cooled to −35 °C. The brown crystals were isolated in 83% yield (0.193 g, 0.407 mmol). IR ν₁₅NO = 1092 cm⁻¹. ¹H NMR spectrum identical to that of 3b.

6.3.c. Syntheses of additional compounds for XAS study

{[Me₂NN]Cu}_2(trans-µ-1,2-PhN=NPh). To a solution of of [Me₂NN]Cu(NCMe) (0.198 g, 0.483 mmol) in 10 mL Et₂O was added a solution of azobenzene (0.044 g, 0.241 mmol) in 2 mL of Et₂O. The solution was allowed to stir for 3 hours and changed colors immediately to blue. Then, all volatiles were removed in vacuo. The crude solid was taken up in 10 mL of Et₂O and stirred for an additional hour. The crude solid was taken up in 10 mL of Et₂O and passed through Celite and then concentrated down for crystallization from Et₂O at -35°C to afford crystals in 78% yield (0.173 g 0.188 mmol). ¹H NMR (C₆D₆, 400 MHz) δ 8.032 (d, 4, Ar-H), 7.114 (d, 8, Ar-H), 7.015 (m, 6, Ar-H), 4.781 (s, 2, backbone-CH), 2.021 (s, 24, Ar-CH₃), 1.639 (backbone-CH₃). Anal. Calcd for C₅₄H₆₀Cu₂N₆: C, 70.48; H, 6.57; N, 9.13. Found: C, 70.22; H, 6.51; N, 8.97. UV-vis (Et₂O, 25°C) = 466 nm (ε = 1998 M⁻¹ cm⁻¹) and 665 nm (ε = 3873 M⁻¹ cm⁻¹).
\{\text{Me}_2\text{NN} \text{Cu}\}_2(\text{Ph}^{15}\text{N} =^{15}\text{NPh}). \text{ To a solution of } \text{Me}_2\text{NN} \text{Cu(NCMe)} (0.266 g, 0.649 mmol) in 10 mL Et}_2\text{O was added a solution of } ^{15}\text{N} , ^{15}\text{N}-\text{azobenzene (0.060 g, 0.324 mmol) in 2 mL of Et}_2\text{O. The solution was allowed to stir for 3 hours and changed colors immediately to blue. Then, all volatiles were removed in vacuo. The crude solid was taken up in 10 mL of Et}_2\text{O and stirred for an additional hour. The crude solid was taken up in 20 mL of Et}_2\text{O and passed through Celite and then concentrated down for crystallization from Et}_2\text{O at } -35 \degree \text{C to afford green crystals in 67\% yield (201 mg; 0.218 mmol).}

\text{Me}_2\text{NN} \text{Cu}(\eta^2-\text{Ar}^{\text{F}}\text{N} = N\text{Ar}^{\text{F}}). \text{ To a solution of } \text{Me}_2\text{NN} \text{Cu(NCMe)} (0.213 g, 0.519 mmol) in 10 mL of Et}_2\text{O was added a solution of } \text{Ar}^{\text{F}}\text{N} = N\text{Ar}^{\text{F}} (\text{Ar}^{\text{F}} = 3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3) (0.236 g, 0.519 mmol) in 2 mL of Et}_2\text{O. The solution changed colors immediately to orange and was allowed to stir for 3 h. Then, all volatiles were removed in vacuo. The crude solid was taken up in 10 mL of Et}_2\text{O and stirred for an additional hour. The crude solid was taken up in 10 mL of Et}_2\text{O and passed through Celite and then concentrated down for crystallization from Et}_2\text{O at } -35 \degree \text{C to afford brown crystals in 84\% yield (359 mg; 0.436 mmol). Anal. Calcd for C}_{37}\text{H}_{31}\text{CuF}_{12}\text{N}_4: C, 53.98; H, 3.80; N, 6.81. Found: C, 54.02; H, 3.83; N, 6.76. UV-vis (Et}_2\text{O, 25\degreeC}) = 421 \text{ nm ( 2200 M}^{-1}\text{ cm}^{-1}).

^{\text{F}}\text{Ar}^{15}\text{N}_3. \text{ Under inert atmosphere trifluoromethylaniline (0.839 g, 3.66 mmol) and trifluoroacetic acid (9.46 mL) were cooled to } -10 \degree\text{C. Over 15 minutes solid sodium nitrite (0.51 g, 7.39 mmol) were slowly added. The reaction mixture was allowed to stir}
for 30 minutes. Then solid singly labeled $^{15}$N-labelled sodium azide (0.5 g, 7.35 mmol) was added over 5 minutes. This reaction mixture was allowed to stir for 2 hours. The reaction was quenched with 40 mL of water and allowed to warm to room temperature. The mixture was extracted 3 times with 50 mL of pentane. All organic layers were combined and washed with 100 mL of water, 80 mL of aqueous sodium bicarbonate and 80 mL of brine. The organic layer was dried over MgSO$_4$, then vacuum filtered and finally all volatiles were removed in vacuo. The resulting product is a 1:1 mixture of Ar$^{15}$N=N=N and Ar$^{14}$N=N=^{15}N).

**FAr$^{15}$NH$_2$.** The resulting oil form the above reaction was used without further purification. FAr$^{15}$N$_3$ (0.5 g, 3.36 mmol) was dissolved in 10 mL of ethyl acetate and 10 mL of methanol. To this solution was added 100 mg of Pd/C suspended in 5 mL of anhydrous ethanol. The reaction mixture was placed in a reduction apparatus brought to 100 psi with H$_2$ and reacted for 2 hours. Afterwards the suspension was vacuum filtered and all volatiles were removed in vacuo. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.195 (s, 1H, p-Ar-H), 7.009 (s, 1H, o-Ar-H), 4.046 (br, 2H, N-H). It is likely that $\frac{1}{2}$ of this sample is Ar$^{15}$NH$_2$ and $\frac{1}{2}$ is Ar$^{14}$NH$_2$.

$^{15}$N labeled $^{15}$ArN=NAr$^{15}$N. The following synthesis was adopted from Shine et al.$^{119}$ The above product was used for this synthetic step without further purification. Under nitrogen and inside a pressure vessel $^{15}$N-enriched FArNH$_2$ (0.635 g, 2.76 mmol) was dissolved in 10 mL benzene. Active manganese(IV) oxide (1.30 g, 0.0183 mol) and
crushed molecular sieves were added. The pressure vessel was sealed and heated to 65 °C for 18 h. Then the reaction mixture was allowed to cool carefully exposed to air, vacuum filtered and all volatiles were removed in vacuo. The resulting oil was taken up in pentane and crystallized at -7 °C overnight to yield 39 % (0.485 g, 1.06 mmol) of brown solid. NMR (CDCl₃, 400 MHz, RT) δ 8.021 (s, 4H, o-Ar-H), 7.755 (s, 2H, p-Ar-H).

$^{15}$N-enriched [Me₂NN]Cu(FArN=NArF). [Me₂NN]Cu(MeCN) (0.156 g, 0.381 mmol) were dissolved in 8 mL Et₂O. To this solution was added a solution of $^{15}$N-enriched FArN=NAr (0.174 g, 0.381 mmol) in 3 mL Et₂O. The reaction mixture was allowed to stir for 3 h during after an immediate color change to dark yellow brown occurred, All volatiles were removed in vacuo. The remaining solid was taken up in Et₂O and passed through Celite. This brown solution was concentrated and layered with pentane to crystallize at -35 °C overnight to afford brown crystals in 40 % yield (0.126 g, 0.153 mmol).

TolN=NTol. This compound was synthesized according to Shine et al.¹¹⁹ Under inert atmosphere a pressure vessel was loaded with manganese(IV) oxide 5.03 g (0.0709 mol), p-toluidine (1.15 g, 10.7 mmol), crushed molecular sieves and 10 mL benzene. The pressure vessel was sealed and heated to 65 °C for 6 h. The resulting suspension was passed through Celite. The remaining residue was taken up in pentane and crystallized from pentane to afford bright orange crystals in 55% yield (0.616 g, 2.93
mmol). $^1$H NMR ($\text{C}_6\text{D}_6$, 400 MHz) δ 8.050 (d, 4H, Ar-\(H\)), 7.018 (d, 4H, Ar-\(H\)), 2.042 (s, 6H, p-Ar-CH\(_3\)). $^{13}$C \{\(^1\)H\} ($\text{C}_6\text{D}_6$, 400 MHz) δ 151.98, 141.83, 130.36, 129.84, 123.69, 121.27, 21.61.

\{[\text{Me}_2\text{NN}]\text{Cu}\}_2(\text{trans-\(\mu\)-1,2-TolN=NTol}). To a solution of [\text{Me}_2\text{NN}]\text{Cu}(\text{MeCN}) (0.330 g, 0.805 mmol) in 8 mL Et\(_2\)O was added a solution of TolN=NTol (0.085 g, 0.402 mmol) of in 2 mL Et\(_2\)O. The reaction mixture turned blue immediately and was allowed to stir for 1 h. All volatiles were removed in vacuo and the remaining solid was taken up in Et\(_2\)O and passed through Celite. The remaining blue solution was concentrated to crystallize from Et\(_2\)O at -35 °C to afford dark crystals 53% yield (0.201 g, 0.212 mmol) suitable for single crystal X-ray. UV-vis (Et\(_2\)O, 25°C) = 474 nm (1767 M\(^{-1}\) cm\(^{-1}\)) and 780 nm (for direct comparison with \{[\text{Me}_2\text{NN}]\text{Cu}\}_2(\text{trans-\(\mu\)-1,2-PhN=NPh}). UV-Vis (Et\(_2\)O): \(\lambda_{\text{max}}\) = 665 nm (\(\varepsilon\) = 4260 M\(^{-1}\) cm\(^{-1}\)); $^1$H NMR ($\text{C}_6\text{D}_6$, 400 MHz, RT) δ 7.956 (d, 4, Ar-\(H\)), 7.363-7.096 (m, 16, Ar-\(H\)), 4.890 (s, 2, backbone-\(CH\)), 2.288 (s, 6H, p-Ar-\(Me\)), 2.029 (s, 24, Ar-\(CH_3\)), 1.841 (backbone-\(CH_3\)); $^{13}$C \{\(^1\)H\} ($\text{C}_6\text{D}_6$, 400 MHz, RT) δ 162.85, 151.97, 151.03, 141.61, 131.18, 130.36, 123.69, 123.52, 93.55, 23.52, 21.62, 19.22. Anal. Caled for C\(_{56}\)H\(_{66}\)Cu\(_2\)N\(_6\): C, 70.93; H, 6.80; N, 8.86. Found: C, 71.28; H, 7.02; N, 8.89.

\{[\text{Me}_2\text{NN}]\text{Ni}\}_2(\text{\(\mu\)-OH})_2 (6). A solution of (0.200 g, 0.437 mmol) [\text{Me}_3\text{NN}]\text{Ni}(2-picoline) in 20 mL of toluene was prepared and tightly sealed inside a vial. This vial was pumped outside the glovebox and punctured with a syringe needle to allow for slow
diffusion of air into the vial via the syringe needle. The red solution was allowed to
stand for 3-5 d during which it turned to a dark green solution with green/brown crystals
at RT suitable for single crystal X-ray in 77% yield (0.128 g, 0.168 mmol). IR ν_{OH} =
3616 cm⁻¹ (prepared via ground up crystals in mineral oil on KBr plate); UV-vis (THF,
25°C) λ_{max} = 508 and 639 nm (molar absorptivity could not be determined due to
extreme insolubility); Anal. Calcd. for C_{42}H_{52}N_{4}Ni_{2}O_{2}: C, 66.18; H, 6.88; N, 7.35.
Found: C, 66.21; H, 6.95; N, 7.23.

[Me_{2}NN]Ni(η²-ONPh) (7). To a chilled suspension of \{[Me_{2}NN]Ni\}_2(µ-OH)_{2} (6)
(0.024 g, 0.0316 mmol) in 10 mL THF and crushed 4A molecular sieves was added a
chilled solution of N-phenylhydroxylamine (0.008 g, 0.0733 mmol) in 3 mL of THF.
The reaction mixture was allowed to stir overnight during which it turned darker brown.
All volatiles were removed in vacuo and the remaining solid was taken up in Et₂O and
passed through Celite. The resulting brown solution was concentrated and layered with
pentane to afford orange/brown crystals at -35 °C suitable for single crystal X-ray in
72% yield (0.021 g 0.0453 mmol). \(^1\)H NMR (C₆D₆): δ 7.069 (m, 2H, Ar-H), 6.959 (t,
1H, Ph-H), 6.845 (m, 2H, Ar-H), 6.730 (t, 1H, Ar-H), 6.568 (d, 1H, Ar-H), 6.381 (d,
2H, Ar-H), 4.892 (s, 1H, backbone C-H), 4.471 (s, 1H, N-H) 2.758 (3 closely spaced s,
9H, o-Ar-CH₃), 1.750 (s, 3H, o-Ar-H), 1.482 (s, 3H, backbone CH₃), 1.272 (s, 3H,
backbone CH₃); \(^{13}\)C{}\(^{1}\)H NMR (C₆D₆): δ (Anal. Calcd. for C_{27}H_{31}N_{3}NiO: C, 68.67; H,
6.62; N, 8.90. Found: C, 68.51; H, 6.70; N, 8.85.
6.3.d. DFT calculation details

The DFT calculations employed the Becke-Perdew exchange correlation functional\textsuperscript{120-122} using the Amsterdam Density Functional suite of programs (ADF 2007.01).\textsuperscript{123,124} Slater-type orbital (STO) basis sets employed for H, C, and N atoms were of triple-\(\zeta\) quality augmented with two polarization functions (ZORA/TZ2P) while an improved triple-\(\zeta\) basis set with two polarization functions (ZORA/TZ2P+) was employed for the Ni atom. Scalar relativistic effects were included by virtue of the zero order regular approximation (ZORA).\textsuperscript{125-127} The 1s electrons of C and N as well as the 1s – 2p electrons of Ni were treated as frozen core. The VWN (Vosko, Wilk, and Nusair) functional was used for LDA (local density approximation).\textsuperscript{128} Default convergence (\(\Delta E = 1 \times 10^{-3}\) hartree, max. gradient = \(1 \times 10^{-2}\) hartree / Å, max. Cartesian step = \(1 \times 10^{-2}\) Å) and integration (4 significant digits) parameters were employed for geometry optimizations.

Experimental X-ray coordinates for \{[Me\textsubscript{2}NN]Ni\}_\textsubscript{2}([\textmu-\eta^2:\eta^2]-ONAr) (1a) were used as the starting point for the geometry optimization of low-spin \{[Me\textsubscript{2}NN]Ni\}_\textsubscript{2}([\textmu-\eta^2:\eta^2]-ONAr) (1a – S0) in a restricted (S = 0) calculation. The geometry optimization for the S = 1 form of \{[Me\textsubscript{2}NN]Ni\}_\textsubscript{2}([\textmu-\eta^2:\eta^2]-ONAr) (1a – S1) employed the DFT optimized coordinates for 1a – S0 as a starting point in an unrestricted (S = 1) calculation specifying 2 unpaired electrons (spin \(\alpha\) – spin \(\beta\)). ADFview\textsuperscript{129} was used to prepare the spin density plot in Figure 6.8, the three-dimensional representations of the structures shown in Figure 6.7 as well as the frontier Kohn-Sham MOs.
6.3.e. X-ray structure refinement details

Single crystals of each compound were mounted under mineral oil on glass fibers and immediately placed in a cold nitrogen stream at $-100(2)$ °C or $-173(2)$ °C (for all X-ray structures in this chapter) on a Bruker SMART CCD system. Either full spheres (triclinic) or hemispheres (monoclinic or higher) of data were collected (0.3° ω-scans; $2θ_{\text{max}} = 56°$; monochromatic Mo Ka radiation, $\lambda = 0.7107$ Å) depending on the crystal system and integrated with the Bruker SAINT program. Structure solutions were performed using the SHELXTL/PC suite\textsuperscript{130} and XSEED.\textsuperscript{131} Intensities were corrected for Lorentz and polarization effects and an empirical absorption correction was applied using Blessing’s method as incorporated into the program SADABS.\textsuperscript{132} Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in idealized positions. The β-diketiminato N-aryl ring in 2a attached to N2 exhibited positional disorder and was modeled isotropically with two sets of positions of 55% and 45% occupancies. Additionally, the X-ray structure of 2a possesses a disordered molecule of ether in which the O atom is on an inversion center. The ether C atoms were modeled with a 70 : 30 site occupancy for atoms 51A : 51B and 52A : 52B. The A-site was modeled anisotropically while the B-site was refined isotropically. Thermal ellipsoids in all ORTEP plots are represented at the 50% probability level.

References


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