SYNTHESIS AND INITIAL REACTIVITY STUDIES OF NICKEL COMPLEXES ON A PINCER SCAFFOLD

by

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ABSTRACT

Catalytic oxidation reactions are prevalent in the chemical industry. The catalysts are often made with expensive metals and the mechanism(s) by which they operate are not well known. Studies of small molecules can lead to better understanding of mechanisms and thus lead to better catalysis design. Work has also been performed in designing catalysts using less costly metals. Nickel is one such metal, as it is a congener of platinum and palladium, two costly metals used widely in catalysis. Ligands can be altered to influence electronic and steric properties of the metal complexes, thus affecting catalytic activity.

This thesis addresses the modification of an SCS pincer ligand and the synthesis of new nickel-SCS pincer complexes. Pincers are tridentate ligands that bind at adjacent coplanar sites. The designation “SCS” refers to the atoms at the coordination sites. The nickel-pincer complexes in this work are built from 2,6-bis(alkylthiomethyl)bromobenzene skeletons, with the alkyl groups being altered. The work presented herein describes the synthesis and characterization of Ni(SCS^{iPr})Br, Ni(SCS^{tBu})Br, Ni(SCS^{Me})OPh, and Ni(SCS^{Me})Me. The reactivity of Ni(SCS^{Me})Me was studied and found to form Ni(SCS^{Me})OPh when reacted with phenol. This showed that Ni(SCS^{Me})Me was able to deprotonate an acidic species to form a new complex. Ni(SCS^{Me})Me was also found to catalyze the oxidation of triphenylphosphine to triphenylphosphine oxide when dry O\textsubscript{2} was introduced. Eight to ten turnovers were observed.
Chapter 1

INTRODUCTION

In the United States, chemical manufacturing is a $720 billion/year industry. Many products are made via catalytic oxidation reactions. They include terephthalic acid, acrylonitrile, and phenol, to name a few. Metal-containing catalysts are keys to some of these reactions. For example, the Wacker process utilizes palladium to convert ethylene into acetaldehyde. The search for more cost-effective catalysts is always continuing. Researchers continue to study the mechanisms involved in catalytic reactions in order to improve or create new, more efficient catalysts. Platinum and palladium complexes are established homogenous catalysts, but are costly. At the time of this writing, platinum costs approximately $1500 per ounce, while palladium costs approximately $600 per ounce. Meanwhile, their congener, nickel, is more abundant and therefore less costly. Bis(1,5-cyclooctadiene)nickel(0), a nickel(0) complex that can be used as a precursor to other nickel complexes, costs approximately $23 per gram.

1.1 Oxidation Catalysis

Olefin epoxidation has been a target of chemists for many years. Several nickel-based catalysts have been previously reported.
1.1.1 Olefin Epoxidation by Ni(II) cyclam

In the late 1980s, Kochi and coworkers published a nickel (II) complex, which catalyzed the epoxidation of olefins. The Ni(II) cyclam complex (cyclam = 1,4,8,11-tetraazacyclotetradecane) was found to epoxidize tetramethylethylene in the presence of iodosylbenzene with 85% yield. Norbornene oxide was also formed from norbornene with 42% yield under similar conditions but with triethylphosphine oxide as a promoter. One proposed mechanism of epoxidation would be the oxygen rebound process, where the metal catalyst would serve as a relay for O-atom transfer. The proposed active intermediate in this reaction is an oxo-nickel (IV) species. This intermediate had not been observed due to its high reactivity. The oxo-nickel (IV) species could subsequently react homolytically with ligands and solvents and/or form a (μ-oxo)nickel(III) dimer.

\[
\begin{align*}
\text{Scheme 1.1} & \quad \text{Scheme of } [\text{Ni(cyclam)}^{+2}] \text{-catalyzed oxidations.}
\end{align*}
\]
1.1.2 Olefin Epoxidation by \( o \)-phenylenebis(\( N' \)-methyloxamidate) Ni(II) complexes

In the late 1990s, Pedro and coworkers published work showing nickel(II) complexes of \( o \)-phenylenebis(\( N' \)-methyloxamidate) and similar ligand systems catalyzed the epoxidation of olefins using pivaldehyde as the reductant.\(^{15}\) In this work, the oxidant was dioxygen. An example of the epoxidation was the formation of \( trans \)-stilbene oxide from \( trans \)-stilbene in 95% yield. Other substrates include \( cis \)-stilbene, \( trans-\beta \)-methylstyrene, 1,2-dihyronaphthalene, indene, and various derivatives of \( \beta \)-citronellol. The proposed mechanism involved the two-electron oxidation of the nickel(II) species by pivaldehyde and dioxygen. The resulting nickel(IV)-oxo would homolytically add to the double bond of the alkene, followed by homolytic cyclization. Once again, the proposed active intermediate was the oxo-nickel species.

![Scheme of aerobic oxidation with Ni- \( o \)-phenylenebis(\( N' \)-methyloxamidate) complexes.](image)

\[ \begin{align*}
\text{Ni cat.} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{N(CH\text{\textsubscript{3}})} & \quad \text{N(CH\text{\textsubscript{3}})} \\
\text{O} & \quad \text{O}
\end{align*} \]
1.2 Mechanistic insight

In the quest for the terminal oxo-nickel species, possible precursors have been isolated. These include alkylperoxo complexes and superoxo complexes.

1.2.1 \([\text{Ni(II)(OOtBu)(Tp}^{\text{Pr}}])\)

One such precursor is a transition-metal alkylperoxo species. In 2009, Hikichi and coworkers reported the structure and oxidizing activity of \([\text{Ni(II)(OOtBu)(Tp}^{\text{Pr2}}])\) (Tp^{Pr2} = hydrotris(3,5-di-2-propylpyrazolyl)borate).\(^{16}\) This complex was formed via dehydrative condensation of \([(\text{Ni(II)Tp}^{\text{Pr}})_{2}(\mu-\text{OH})_{2}]\) with tert-butylhydroperoxide. The OOtBu ligand was assigned as intermediate between \(\eta^1\) and \(\eta^2\) coordination modes due to the bond distances from the nickel center to the two oxygen atoms as derived by X-ray diffraction analysis. The complex oxidized various substrates. Triphenylphosphine was oxidized to triphenylphosphine oxide in greater than 98% yield. This transformation was proposed to proceed through a bimolecular mechanism. The complex also oxidized carbon monoxide to form a dinuclear nickel (II) \(\mu\)-carbonato complex. Various \(para\)-substituted benzaldehydes were oxidized to produce the corresponding nickel(II) benzoate complexes. In the absence of substrates, \([\text{Ni(II)(OOtBu)(Tp}^{\text{Pr2}}])\) decomposed spontaneously with a decay rate of \(5.41 \times 10^{-5}\) s\(^{-1}\) at 298K in toluene. The decomposition products were a mixture of ligand-oxidized complex and the dinuclear nickel bis(\(\mu\)-alkoxo) complex.

\[
P\text{Ph}_3 + [\text{Tp}^{\text{Pr2}}\text{Ni(OOBu}^t)] \rightarrow \text{O=PPPh}_3
\]

Scheme 1.3  Scheme of triphenylphosphine oxidation by \([\text{Tp}^{\text{Pr2}}\text{Ni(OOBu}^t)].\)
Scheme 1.4  Scheme of carbon monoxide oxidation by $[\text{Tp}^{\text{Pr}_2}\text{Ni(OOBu)}]$.

Scheme 1.5  Scheme of $p$-substituted benzaldehyde oxidation by $[\text{Tp}^{\text{Pr}_2}\text{Ni(OOBu)}]$. $X = \text{OMe, Me, H, Cl}$

A follow-up paper was published in 2010. Hikichi and co-workers brominated the Tp ligand at the 4-position of the pyrazole rings. The modification stabilized the alkylperoxonickel species by decreasing the decay rate to $2.01 \times 10^{-5}$ s$^{-1}$. Structural and spectroscopic characteristics were very similar between the brominated and non-brominated complexes. The oxidizing capability of the new complex was different though. Triphenylphosphine and carbon monoxide were oxidized with similar results to the non-brominated complex, but the substituted benzaldehydes were not. This was due to the electron-withdrawing bromine lowering the electron density on the peroxide moiety, thus resulting in the loss of nucleophilic reactivity.
1.2.2 \([\text{PhTt}^R]\text{NiO}_2\) Complexes

Riordan and coworkers used a different strategy to obtain nickel-oxygen complexes. The phenyl[tris(alkylthiomethyl)]borate (PhTt\(^R\)) ligand system was employed to make nickel(II) complexes.\(^{18,19,20}\) These complexes were subsequently reduced and trapped. Dioxygen was added to the resulting nickel(I) species and the nickel-oxygen complexes were observed. It was found that a bis-\(\mu\)-oxo dinickel(III) dimer was produced when the ligand had \(\text{tert}\)-butyl groups on the thioether arms. This complex displayed limited reactivity with substrates, only oxidizing NO to nitrite to generate the \([\text{PhTt}^{\text{Bu}}]\text{Ni(II)NO}_2\) complex. A mononuclear dioxygen adduct was formed when the \(\text{tert}\)-butyl groups were replaced with 1-adamantyl groups on the thioether arms. Spectroscopic evidence and DFT calculations found the species to be a nickel(II)-superoxo complex with \(\text{O}_2\) coordinated in a side-on fashion. This complex was able to stoichiometrically oxidize triphenylphosphine to triphenylphosphine oxide. It was also able to transform NO to nitrate in producing \([\text{PhTt}^{\text{Ad}}]\text{Ni(NO}_3\)\).

Scheme 1.6  Scheme of the syntheses \([\text{PhTt}^R]\text{Ni dioxygen complexes}\)
1.3 Pincer Compounds

Pincers are tridentate ligand systems that bind metals at three adjacent coplanar sites. Studies of pincer-type metal complexes have increased in the past few decades. “ECE” is the designation used when describing pincers, with each letter denoting the atom that coordinates to the metal. There are many variations of this type of pincer system found in the literature. The “E” groups on the pendant arms range from phosphorous-based donors to nitrogen-based donors to sulfur-based donors. These donor groups can be altered for steric and electronic purposes. Another attractive characteristic of such complexes is the stable metal-carbon σ-bond.

In the literature, there are several examples of nickel pincer complexes with nitrogen-based and phosphorus-based donors. However, there are very few with sulfur-based donors. One is a pincer containing thioamide donor arms and the other is the basis for the work reported in this thesis. This thesis reports work which expands upon the previously reported Ni(SCS\text{Me})Br, on which reactivity studies have not been reported.

1.3.1 Ni(NCN\text{Me})Br

Metallopincer complexes have been shown to have interesting reactivity and catalytic activities. A Ni(NCN\text{Me})\text{Br} metallopincer has been shown to be an excellent catalyst for the Kharasch addition. The Kharasch addition is the reaction of a polyhalogenated alkane with an alkene to form a 1:1 adduct. A new carbon-carbon bond is formed and a halide substituent is added. This addition requires a metal catalyst or a free radical precursor as a promoter. The Ni(NCN\text{Me})\text{Br} metallopincer
had been previously reported as an active catalyst for the Kharasch addition with many terminal alkenes (e.g. styrene, 1-octene, and methyl methacrylate) and various polyhalogenated alkanes (e.g. CBr₄, CCl₄, and CF₃CCl₃). The proposed mechanism for this catalyzed addition was a radical, nonchain-mechanism. The proposed catalytic cycle consisted of three steps. In the first step, the polyhalogenated alkane reacts with the catalyst to transfer a halogen from the alkane to the metal center. The metal center also transfers an electron to the alkane, forming a radical adduct. The second step involves the introduction of the alkene. The third step involves the addition of the alkane radical to the alkene and halogen transfer from the metal center to the alkene. The catalyst is then regenerated.

Scheme 1.7  Scheme of Ni(NCNMe₂)Br-catalyzed Kharasch addition.

1.3.2 Ir(PCP₉)H₂

Jensen, Goldman, and coworkers reported an iridium pincer that catalyzed the dehydrogenation of n-octane to form 1-octene. This pincer complex contained iso-
propyl groups on the pendant arms. The reaction required the use of a hydrogen acceptor, such as norbornene, \( t \)-butylethene, or 1-decene. With the exception of trials with \( t \)-butylethene, 1-octene constituted at least 90% of the octene product initially. As the reaction continued, a mix of 1- and 2-octenes was observed due to olefin isomerization. When the pincer complex was modified to have \textit{tert}-butyl groups on the pendant arms and 1-decene was the acceptor, the best regioselectivity and 1-octene yield (97 turnovers) was observed. The proposed mechanism involved the iridium complex donating both hydrogens to the hydrogen acceptor, leaving two open coordination sites. The \( n \)-octane would then oxidatively add to the complex, followed by \( \beta \)-hydrogen elimination to form the 1-octene. Further modification of reaction conditions may lead to higher yields.

![Scheme 1.8](image)

**Scheme 1.8**  Scheme of Ir(PCP\textsuperscript{R})H\textsubscript{2}-catalyzed \( n \)-octane dehydrogenation to 1-octene (\( R = i \text{Pr, tBu} \))
1.3.3 Ru(NCN) and Ru(PCP) Complexes

van Koten and coworkers reported three ruthenium pincer complexes that were catalysts for the reduction of various ketones to the corresponding alcohols. These complexes, in the presence of isopropanol and potassium hydroxide, were observed to convert cyclohexanone, acetophenone, benzophenone, and 2-pentanone to their respective alcohols. In most trials with varying catalysts and substrates, the conversions were 90% or greater. The proposed active catalysts involved ruthenium hydride complexes, based on NMR evidence.

Figure 1.1 Ruthenium pincer catalysts for the reduction of ketones to alcohols.

Scheme 1.9 Scheme for the ruthenium pincer-catalyzed reduction of ketones to alcohols.
1.4 Summary

The chemical industry utilizes inorganic complexes as catalysts in chemical production. The search continues for more cost-efficient and cost-effective catalysts, especially those that use inexpensive substrates and catalysts. One such substrate is dioxygen for oxidation reactions. Another cost-saving development would be the use of a less expensive metal, such as nickel, instead of platinum or palladium. There is still much to learn about catalytic oxidation reactions. Many mechanisms are still unknown. Catalyst stability and activity can be modified to produce better, more efficient catalysis. Many proposed active intermediates have yet to be isolated and characterized. Work has been done on nickel-containing complexes that perform catalytic oxidation reactions. It has been proposed that, in numerous cases, the active intermediate is a terminal oxo-nickel species. This species has yet to be isolated and characterized. There have been many attempts at isolating active intermediates in catalytic oxidation reactions. This thesis addresses several new and some previously reported ligands and nickel complexes which may lead to new nickel-oxygen species. These ligands are designed electronically and sterically for the synthesis of low-valent (i.e. nickel(I)) nickel-oxygen precursors as well as mononuclear nickel-oxygen complexes.
2.1 Physical Methods

2.1.1 Nuclear Magnetic Resonance Spectroscopy

$^1$H and $^{13}$C NMR spectra were acquired on either a Bruker AV400 NMR spectrometer equipped with an auto sampler or a Bruker DRX400 spectrometer. The AV400 spectrometer is outfitted with a QNP probe. The DRX400 spectrometer is outfitted with a BBO probe. Air sensitive samples were prepared in either an Ar- or N$_2$-filled glovebox, capped with a septum, and sealed with Parafilm. Samples taken in C$_6$D$_6$ were referenced to residual solvent $^1$H and $^{13}$C peaks for the respective spectra. Samples taken in CDCl$_3$ were referenced to TMS. $^{31}$P NMR spectra were referenced to an internal standard of 85% H$_3$PO$_4$ in D$_2$O. NMR solvents were purchased from Cambridge Isotope Laboratories.
2.1.2 Electronic Absorption Spectroscopy

Optical spectra were collected on a Varian Cary 50 spectrophotometer, using a 1 cm path length cell. Optical data were first collected on solvent at a given temperature to allow for background correction.

2.1.3 X-Ray Diffraction

Crystals were mounted and solved by Dr. Glenn P. A. Yap, University of Delaware. Data was collected on a Bruker-AXS APEX CCD diffractometer with 0.7107 Å Mo Kα radiation. Absorption correction was done using SADABS. SHELXTL 6.12 provided information regarding systematic absences, allowing structures to be solved in the appropriate space groups.

2.2 Experimental Details

All solvents were purchased at reagent grade or higher. The following were used as received from commercial sources: 2-bromo-\textit{m}-xylene, azobisisobutyronitrile, 2-propanethiol, 2-methyl-2-propanethiol, sodium hydroxide, sodium hydride, 1,5-bis(cyclooctadiene)nickel(0), phenol, methylmagnesium bromide, and triphenylphosphine. N-bromosuccinimide was recrystallized from hot deionized water prior to use. Activated alumina columns were used to dry solvents. Air sensitive samples were prepared in either an Ar or N\textsubscript{2}-filled glovebox.
Sodium phenoxide was prepared under N\textsubscript{2}. To a THF solution of phenol, 1.05 equivalents of sodium hydride were added and the solution was stirred overnight. The mixture was filtered through a Celite plug and the solvent removed under vacuum. The solid (~90% yield) was washed with pentane and dried under vacuum prior to usage.

### 2.2.1 Synthesis of 2,6-bis(bromomethyl)-1-bromobenzene

2,6-bis(bromomethyl)-1-bromobenzene was prepared according to the following procedure, which was adapted from literature procedures\textsuperscript{37,38}. 2-bromo-\textit{m}-xylene (3.0 mL, 0.021 mol) was dissolved in chloroform (~100 mL). N-bromosuccinimide (8.925 g, 0.050 mol) and a catalytic amount of azobisisobutyronitrile were added. The mixture was refluxed under a 90W lamp for 16 h. The solvent was removed, leaving an orange/tan solid. The solid was extracted twice with boiling hexanes (~250 mL each extraction). The filtrate was collected in a flask immersed in a dry ice/acetone bath. The white solid product was recovered. Yield = 50-60% \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) \(\delta = 4.65\) (s, CH\textsubscript{2}, 4H), 7.29 (t, 4-aryl-\textit{H}, 1H), 7.42 (d, 3,5-aryl-\textit{H}, 2H). \textsuperscript{13}C-NMR (400 MHz, CDCl\textsubscript{3}) \(\delta = 33.92\) (CH\textsubscript{2}Br), 126.69 (1-aryl-C), 128.08 (4-aryl-C), 131.45 (3,5-aryl-C), 138.52 (2,6-aryl-C).
2.2.2 Synthesis of 2,6-bis("iso-propylthiomethyl")-1-bromobenzene

2,6-bis("iso-propylthiomethyl")-1-bromobenzene was prepared according to a modified literature procedure. In an ice bath, 2-propanethiol (3.6 mL, 0.039 mol) was dissolved in THF (~150 mL). Sodium hydride (1.030 g, 0.043 mol) was added to the solution as well as a small amount of ethanol. The mixture was stirred for 30 min. 2,6-bis(bromomethyl)-1-bromobenzene (6.070 g, 0.018 mol) was dissolved in THF (100 mL) and added to the thiolate mixture. This mixture was stirred for 16 h. Diethyl ether (100 mL) and 1M NaOH (100 mL) solution were added and the mixture was stirred for 30 min. The mixture was extracted with diethyl ether (2 x 300 mL) and the organic layer dried over magnesium sulfate. The magnesium sulfate was filtered off and the solvent removed, leaving an off-white oil. Yield = 90-95%. \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta = 1.29\) (d, \(CH_3\), 12H), 2.91 (m, \(CH\), 2H), 3.91 (s, \(CH_2\), 4H), 7.20 (t, 4-aryl-\(H\), 1H), 7.28 (d, 3,5-aryl-\(H\), 2H). \(^13\)C-NMR (400 MHz, CDCl\(_3\)) \(\delta = 23.38\) (CH\(_3\)), 35.13 (CH), 36.29 (CH\(_2\)), 126.52 (1-aryl-C), 127.00 (4-aryl-C), 129.20 (3,5-aryl-C), 139.17 (2,6-aryl-C).
2.2.3 Synthesis of 2,6-bis(tert-butylthiomethyl)-1-bromobenzene

2,6-bis(tert-butylthiomethyl)-1-bromobenzene was prepared according to a modified literature procedure. In an ice bath, 2-methyl-2-propanethiol (5.4 mL, 0.0479 mol) was dissolved in THF (~200 mL). Sodium hydride (1.26 g, 0.0525 mol) was added to the solution as well as a small amount of ethanol. The mixture was stirred for 30 min. 2,6-bis(bromomethyl)-1-bromobenzene (3.277 g, 0.00956 mol) was dissolved in THF (100 mL) and added to the thiolate mixture. This mixture was stirred for 16h. Diethyl ether (100 mL) and 1M NaOH (100 mL) solution were added and the mixture was stirred for 30 min. The mixture was extracted with diethyl ether (2 x 300mL) and the organic layer dried over magnesium sulfate. The magnesium sulfate was filtered off and the solvent removed, leaving an off-white oil. Yield = 90-95%.

$\text{H-NMR (400MHz, CDCl}_3\text{)} \delta = 1.38 (s, CH}_3\text{, 18H), 3.91 (s, CH}_2\text{, 4H), 7.17 (t, 4-aryl-H, 1H), 7.28 (d, 3,5-aryl-H, 2H).}$

$\text{C-NMR (400MHz, CDCl}_3\text{)} \delta = 30.86 (CH}_3\text{), 34.42 (CH}_2\text{), 43.21 (tBu C), 126.48 (1-aryl-C), 127.20 (4-aryl-C), 129.59 (3,5-aryl-C), 138.81 (2,6-aryl-C).$
2.2.4 Synthesis of Ni(SCS\textsuperscript{iPr})Br

Ni(SCS\textsuperscript{iPr})Br was prepared according to a modified literature procedure.\textsuperscript{31} 2,6-bis(\textit{iso}-propylthiomethyl)-1-bromobenzene (3.178 g, 0.00953 mol) was dried under vacuum overnight. Under a nitrogen atmosphere, 1,5-bis(cyclooctadiene)nickel(0) (2.401 g, 0.00873 mol) was dissolved in THF (100 mL) and the solution cooled to -78°C. The 2,6-bis(\textit{iso}-propylthiomethyl)-1-bromobenzene was also dissolved in THF (50 mL) and this solution was transferred to the Ni(COD)\textsubscript{2} solution via cannula. The solution was stirred overnight and slowly warmed to room temperature. The solvent was then removed, leaving a dark residue. The residue was extracted with benzene (500 mL) and filtered through a plug of Celite. The resulting red solution was concentrated under vacuum. Cold hexanes (-78°C, 200 mL) were added. The precipitate was collected while cold. This isolation procedure was repeated a minimum of 3 to 4 times. Yield = 30-40%. \textsuperscript{1}H-NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}) \(\delta = 1.22\) (b s, CH\textsubscript{3}, 12H), 3.35 (s, CH\textsubscript{2}, 4H), 3.67 (m, CH, 2H), 6.58 (d, 3,5-aryl-H, 2H), 6.90 (t, 4-aryl-H, 1H). \textsuperscript{13}C-NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}) \(\delta = 21.92\) (CH\textsubscript{3}), 40.35 (CH\textsubscript{2}), 40.79 (CH), 121.50 (3,5-aryl-C), 149.00 (2-aryl-C).
aryl-C), 124.94 (4-aryl-C), 151.20 (2,6-aryl-C), 156.57 (1-aryl-C). UV-Vis (MeCN) λ = 449 nm (ε = 540 M⁻¹ cm⁻¹), 296 nm (sh, ε = 7120 M⁻¹ cm⁻¹).

Scheme 2.4  Scheme of Ni(SCS⁻Pr)Br synthesis.

2.2.5  Synthesis of Ni(SCS⁻Bu)Br

Ni(SCS⁻Bu)Br was prepared according to a modified literature procedure.³¹ 2,6-bis(tert-butylthiomethyl)-1-bromobenzene (0.266 g, 0.000736 mol) was dried under vacuum overnight. Under a nitrogen atmosphere, 1,5-bis(cyclooctadiene)nickel(0) (0.200 g, 0.000727 mol) was dissolved in THF (100 mL) and cooled to -78°C. The 2,6-bis(tert-butylthiomethyl)-1-bromobenzene was also dissolved in THF (50 mL) and this solution was transferred to the Ni(COD)₂ solution via cannula. The solution was stirred overnight and slowly warmed to room temperature. Solvent was then removed, leaving a dark residue. The residue was extracted with benzene (500 mL) and filtered through a plug of Celite. The orange-red solution was concentrated under vacuum. Hexanes (~200 mL) were added and the solution cooled to -30°C. Red crystals were collected after 2 d. Crystalline yield = 10-15%. ¹H-NMR (400 MHz, CDCl₃) δ = 1.61 (s, CH₃, 18H), 4.03 (s, CH₂, 4H), 6.76 (d, 3,5-aryl-H, 2H), 6.89 (t, 4-aryl-H, 1H). ¹³C-
NMR (400 MHz, CDCl$_3$) δ = 31.06 (CH$_3$), 43.29 (CH$_2$), 51.35 (tBu C), 120.68 (3,5-aryl-C), 124.98 (4-aryl-C), 151.47 (2,6-aryl-C). UV-Vis (MeCN) λ = 463 nm (ε = 83.5 M$^{-1}$ cm$^{-1}$), 297 nm (ε = 6310 M$^{-1}$ cm$^{-1}$).

Scheme 2.5  Scheme of Ni(SCS$^{tBu}$)Br synthesis.

2.2.6  Synthesis of Ni(SCS$^{Me}$)OPh

Ni(SCS$^{Me}$)Br was prepared following a literature procedure.$^{31}$ Ni(SCS$^{Me}$)Br (0.150 g, 0.447 mmol) was dissolved in dry THF (100 mL). NaOPh (0.057 g, 0.000491 mol) was added to the solution. The mixture was stirred for 3 days under N$_2$. The mixture was filtered through a Celite plug and solvent removed in vacuo. The solid was collected. Yield = 90-95%. $^1$H-NMR (400 MHz, C$_6$D$_6$) δ = 1.80 (s, CH$_3$, 6H), 3.21 (s, CH$_2$, 4H), 6.45 (d, 3,5-aryl-H), 6.79 (t, 4-OPh-H), 6.85 (t, 4-aryl-H), 7.37 (t, 3,5-OPh-H), 7.56 (d, 2,6-OPh-H). $^{13}$C-NMR (400 MHz, C$_6$D$_6$) δ = 19.99 (CH$_3$), 47.78 (CH$_2$), 114.51 (4-OPh-C), 121.01 (2,6-OPh-C), 121.90 (3,5-aryl-C), 125.25 (4-aryl-C), 129.93 (3,5-OPh-C), 150.64, 151.71, 169.74 (1-aryl-C). UV-Vis (CHCl$_3$) λ = 452 nm (ε = 174 M$^{-1}$ cm$^{-1}$).
2.3 Results and Discussion

2.3.1 Ni(SCS^{iPr})Br

The $^1$H-NMR spectrum of Ni(SCS^{iPr})Br showed only one peak each for the $i$Pr methyl and methine protons as well as the methylene protons between the S and the phenyl ring. This would imply that both arms of the ligands were chemically equivalent. By looking at the crystal structure, this would appear to be the case for Ni(SCS^{iPr})Br, since the $i$Pr groups were oriented in a $syn$ fashion. However, this may be more reflective of the fluxional nature of the ligand in solution. Bond distances were obtained from the X-ray crystal structure. The average Ni-S bond distance of Ni(SCS^{iPr})Br was longer than the average Ni-S bond length in the previously reported Ni(SCS^{Me})Br (2.1624(2) Å vs. 2.1604(2) Å). In the crystal structure of Ni(SCS^{iPr})Br, one Ni-S bond was actually shorter than the Ni-S bonds in Ni(SCS^{Me})Br. This could be due to lateral movement of the Ni atom between the two coordinating S atoms.
Figure 2.1 $^1$H-NMR spectrum of Ni(SCS$^{iPr}$)Br in C$_6$D$_6$. 
Figure 2.2  Molecular structure of Ni(SCS$^{iPr}$)Br as determined by X-ray diffraction. Thermal ellipsoids drawn at 30%. Hydrogen atoms not shown.

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Table 2.1  Select bond distances and angles from the X-ray structure of Ni(SCS$^{iPr}$)Br.

2.3.2  Ni(SCS$^{tBu}$)Br

Similar to the $^1$H-NMR spectrum of Ni(SCS$^{tBu}$)Br, the $t$Bu methyl and methylene protons of Ni(SCS$^{tBu}$)Br appeared to be chemically similar in both pendant arms. The Ni-S bond distance was longer than that in Ni(SCS$^{Me}$)Br (2.2015(6) Å vs. 2.1601(5) Å and 2.1606(5) Å). The X-ray crystal structure showed the $t$Bu groups on the pendant arms to be oriented in an anti fashion. However, the complex may be fluxional in solution.
Figure 2.3 \(^1\text{H-NMR}\) spectrum of Ni(SCS\(^{\text{tPr}}\))Br in CDCl\(_3\).

Figure 2.4 Molecular structure of Ni(SCS\(^{\text{tBu}}\))Br as determined by X-ray diffraction. Thermal ellipsoids drawn at 30\%. Hydrogen atoms not shown.
## Table 2.2 Select bond distances and angles from the X-ray structure of Ni(SCS\textsuperscript{tBu})Br.

### 2.3.3 Ni(SCS\textsuperscript{Me})OPh

Proton assignments in the \(^1\)H-NMR spectrum were made using correlation spectroscopy (COSY). Carbon assignments in the \(^{13}\)C-NMR spectrum were made using heteronuclear multiple quantum coherence (HMQC) spectroscopy. The Ni-O bond distance of 1.903(2) Å correlated well with a previously published square planar Ni-OPh complex (\textit{trans}-NiH(OPh)(PBz\textsubscript{3})\textsubscript{2}·HOPh, Ni-O bond distance 1.949(7) Å).\textsuperscript{39} The C-Ni-O bond angle was quite different from the published angle (174.71(10)° vs. 123.0(4)°). This was due to the literature structure containing a phenol in the lattice that was hydrogen-bonding to the phenolate group in the complex.
Figure 2.5  $^1$H-NMR spectrum of Ni(SCS$^{Me}$)OPh in C$_6$D$_6$.

Figure 2.6  Molecular structure of Ni(SCS$^{Me}$)OPh as determined by X-ray diffraction. Thermal ellipsoids drawn at 30%. Hydrogen atoms not shown.
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**Table 2.3** Select bond distances and angles from the X-ray structure of Ni(SCS\textsuperscript{Me})OPh.
Chapter 3

Ni(SCS<sup>Me</sup>)Me SYNTHESIS AND REACTIVITY

This section details the synthesis of a new nickel-alkyl complex and initial reactivity studies performed on it.

3.1 Synthesis of Ni(SCS<sup>Me</sup>)Me

Ni(SCS<sup>Me</sup>)Br was prepared following a literature procedure.<sup>31</sup> Ni(SCS<sup>Me</sup>)Me was prepared according to a modified literature procedure.<sup>26</sup> Ni(SCS<sup>Me</sup>)Br (1.357 g, 4.040 mmol) was dried overnight under vacuum. Me<sub>2</sub>Mg was prepared in situ by adding MeMgBr (2.01 mL, 3 M in Et<sub>2</sub>O) to 1,4-dioxane (~25 mL). The Me<sub>2</sub>Mg mixture was cooled to -78°C. Ni(SCS<sup>Me</sup>)Br was dissolved in dry THF (~150 mL) and transferred to the Me<sub>2</sub>Mg mixture. This mixture was stirred and allowed to warm up slowly overnight. Subsequently, the solvent was removed in vacuo. The residue was extracted with pentanes (~500 mL) and filtered through a Celite plug. Solvent was removed in vacuo and the light yellow solid collected. Yield = 30-40%. <sup>1</sup>H-NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ = -0.55 (s, Ni-CH<sub>3</sub>, 3H), 1.89 (s CH<sub>3</sub>, 6H), 3.77 (s, CH<sub>2</sub>, 4H), 6.90 (d, J = 7Hz, 3,5-aryl-H, 2H), 7.06 (t, J = 7Hz, 4-aryl-H, 1H). <sup>13</sup>C-NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ = -15.11 (Ni-CH<sub>3</sub>), 19.89 (CH<sub>3</sub>), 55.81 (CH<sub>2</sub>), 120.40 (3,5-aryl-C), 124.41 (4-aryl-C), 147.69 (2,6-aryl-C), 176.36 (1-aryl-C). UV-Vis (THF) λ = 387 nm (ε = 688 M<sup>-1</sup> cm<sup>-1</sup>).
Scheme 3.1  Scheme of Ni(SCS^{Me})Me synthesis.

Figure 3.1  $^1$H-NMR spectrum of Ni(SCS^{Me})Me in C$_6$D$_6$. 
Figure 3.2  Molecular structure of Ni(SCS\textsuperscript{Me})Me as determined by X-ray diffraction. Thermal ellipsoids drawn at 30%. Hydrogen atoms shown only for Ni-CH\textsubscript{3}.

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Table 3.1  Select bond distances and angles from the X-ray structure of Ni(SCS\textsuperscript{Me})Me.

The Ni-CH\textsubscript{3} bond distance was comparable to a previously published pincer Ni-CH\textsubscript{3} complex (2.031(2) Å vs. 1.994(2) Å and 1.997(2) Å).\textsuperscript{26} The C-Ni-C bond angles were also very similar (177.05(8)° vs. 179.07(6)° and 177.67(7)°).
3.2 Reactivity of Ni(SCS$^{Me}$)Me

All reactions were performed under an inert atmosphere, typically under N$_2$. Oxygen was Ultra High Purity Grade 4.4 and dried by passing through a column of anhydrous calcium sulfate.

3.2.1 Reaction of Ni(SCS$^{Me}$)Me with triphenylphosphine under O$_2$

Ni(SCS$^{Me}$)Me was found to catalyze the oxidation of triphenylphosphine. In an NMR scale reaction, Ni(SCS$^{Me}$)Me (0.010 g, 0.0369 mmol) and triphenylphosphine (0.194 g, 0.738 mmol) were dissolved in deuterated benzene. Dry O$_2$ was added to the NMR tube via needle. $^{31}$P NMR spectra were taken before and immediately after O$_2$ addition. Comparison of the integrations of the free triphenylphosphine peak and the triphenylphosphine oxide peaks vs. the H$_3$PO$_4$ standard allowed for the determination of turnover number. The reaction was found to have 8 to 10 turnovers. The mechanism and active intermediate have yet to be determined. It is possible that the oxygenation of Ni(SCS$^{Me}$)Me forms a transient Ni(I)-oxygen or Ni(0)-oxygen species. When Ni(SCS$^{Me}$)Me was oxygenated in the absence of triphenylphosphine, a black precipitate was observed forming as the dioxygen diffused through the solution. This precipitate was unable to be characterized due to its insolubility in common organic solvents. This precipitate was possibly some type of nickel-oxide.
Scheme 3.2  Scheme of Ni(SCS<sub>Me</sub>)Me catalyzed triphenylphosphine oxidation.

3.2.2  Reaction of Ni(SCS<sub>Me</sub>)Me with Phenol

Ni(SCS<sub>Me</sub>)Me reacted with phenol to produce Ni(SCS<sub>Me</sub>)OPh. Ni(SCS<sub>Me</sub>)Me (0.080 g, 0.295 mmol) was dissolved in THF (75 mL). Dry phenol (0.0286 g, 0.304 mmol) was added to the solution and stirred for 1 day. The solution was filtered through a Celite plug and the solvent was removed in vacuo. Ni(SCS<sub>Me</sub>)OPh crystals deposited from the resulting reaction mixture.

Scheme 3.3  Scheme of Ni(SCS<sub>Me</sub>)Me reacting with phenol to form Ni(SCS<sub>Me</sub>)OPh.

The formation of Ni(SCS<sub>Me</sub>)OPh from Ni(SCS<sub>Me</sub>)Me and phenol showed that the Ni(SCS<sub>Me</sub>)Me complex was able to deprotonate an acid with a pK<sub>a</sub> of 9, and presumably more acidic substrates. Ni(SCS<sub>Me</sub>)Me did not react with deionized water.
to from Ni(SCS\textsuperscript{Me})OH. This was not surprising, given that Pandarus and Zargarian reported that their Ni(POCOP)Me did not react with water.\textsuperscript{26}

### 3.3 Conclusion

The study of organometallic complexes has led to many useful catalytic compounds. The search continues for deeper understanding of catalytic mechanisms and for more cost-efficient catalysts. Herein, pincer ligands were synthesized with the goals of supporting nickel-oxygen complexes. These ligands were previously unknown and led to new nickel complexes supported by pincer ligands with sulfur donors. Less work has been done with nickel complexes with sulfur-based pincer ligands than with phosphorus-based or nitrogen-based pincers. The sulfur-donors may yield interesting nickel chemistry and stabilize different nickel complexes. The synthesized nickel-oxygen precursors may allow for a nickel(I) complex to be formed, which could lead to a nickel-superoxo or nickel-peroxo species. This work shows some evidence of catalytic activity with the nickel-alkyl species, possibly via a nickel-alkylperoxo species or other unknown mechanism. This pincer ligand system shows promise for supporting reactive nickel complexes.
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38. Bibal, C., Mazières, S., Gornitzka, H., Couret, C., Polyhedron 2002, 21,
    2827.
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APPENDIX

CRYSTALLOGRAPHIC DATA

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<tr>
<td><strong>GOF ($F^2$)</strong></td>
<td>1.061</td>
<td>1.031</td>
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<tr>
<td>Reflections Collected</td>
<td>15515</td>
<td>19709</td>
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<tr>
<td>Unique Reflections</td>
<td>2963</td>
<td>3789</td>
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<tr>
<td>$R$(int)</td>
<td>0.0372</td>
<td>0.0792</td>
</tr>
<tr>
<td>$R1$</td>
<td>0.0292</td>
<td>0.0412</td>
</tr>
<tr>
<td>w$R2$</td>
<td>0.0762</td>
<td>0.0836</td>
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