SYNTHESIS OF TRISPYRAZOLYLBORATE-SUPPORTED NICKEL COMPLEXES FOR SMALL MOLECULE ACTIVATION

by

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ABSTRACT

The structure and function of enzymes has been of great interest to the scientific community for many years. In particular, interest lies in the ability of metalloenzymes to catalyze the activation of small molecules. In 1996, a new metal variant of superoxide dismutase was discovered, which contained nickel in the active site. Additionally, of the nine known nickel-containing enzymes, five contain nickel-sulfur bonds including nickel superoxide dismutase (NiSOD), acetyl-coenzyme A synthase/carbon monoxide dehydrogenase (ACS/COdH), [NiFe] hydrogenase, and methyl-coenzyme M reductase (MCR). The discovery of NiSOD and a nickel form of the acireductone dioxygenase sparked interest in nickel-dioxygen chemistry. While numerous synthetic complexes have been prepared in an effort to model the structure and function of these nickel-containing enzymes, very few examples exist that utilize nickel complexes supported by the trispyrazolylborate (Tp) ligand system.

This thesis addresses synthetic model systems by examining the synthesis, characterization, and reactivity profiles of several new nickel-dioxygen, nickel-sulfur, and nickel-selenium species supported by the Tp ligand class. The synthesis and reactivity of \([\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{O}_2)]\) is described and compared to previously reported \([\text{Tp}^{\text{Bu,Me}}\text{Ni}(\text{O}_2)]\). \([\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{O}_2)]\) was found to be more reactive than \([\text{Tp}^{\text{Bu,Me}}\text{Ni}(\text{O}_2)]\) with respect to phosphine oxidation. While \([\text{Tp}^{\text{Bu,Me}}\text{Ni}(\text{O}_2)]\) oxidizes only alkyl
phosphines, \([\text{Tp}^{\text{Me,Me}}]\text{Ni(O}_2\text{)}\) readily oxidizes both aryl and alkyl phosphines. However, \([\text{Tp}^{\text{Ph,Me}}]\text{Ni(O}_2\text{)}\) is not capable of activating weak C-H bonds as readily as \([\text{Tp}^{\text{tBu,Me}}]\text{Ni(O}_2\text{)}\), converting only 9, 10-dihydroanthracene to anthraquinone in low yields. Interestingly, \([\text{Tp}^{\text{Ph,Me}}]\text{Ni(O}_2\text{)}\) deformylates aldehydes in quantitative yields.

The nickel(I) and nickel(II) complexes formed from the synthesis of \([\text{Tp}^{\text{Ph,Me}}]\text{Ni(O}_2\text{)}\) were used in an attempt to prepare \(\{[\text{Tp}^{\text{Ph,Me}}]\text{Ni}\}_2(\mu-S_2)\) and \(\{[\text{Tp}^{\text{Ph,Me}}]\text{Ni}\}_2(\mu-Se_2)\). \([\text{Tp}^{\text{Ph,Me}}]\text{Ni(SCH}_2\text{CH}_2\text{)}\) was formed from the reaction of \([\text{Tp}^{\text{Ph,Me}}]\text{Ni(PP}_3\text{)}\) with ethylene sulfide. This nickel complex possesses a magnetic moment consistent with the expected doublet ground state, \(S = \frac{1}{2}\). In addition, \([\text{Tp}^{\text{Ph,Me}}]\text{Ni(SCH}_2\text{CH}_2\text{)}\) is inert towards reaction with \text{CO}, O\text{\textsubscript{2}}, and PEt\text{\textsubscript{3}}. Reaction with PMe\text{\textsubscript{3}} yielded \([\text{Tp}^{\text{Ph,Me}}]\text{Ni}_2\) and \([\text{PMe}_3\text{Et}\text{]}^+\). Reactions with methyl iodide and \(n\)-butyl lithium did not yield the desired nucleophilic reaction products. Attempts to make the analogous complex, \([\text{Tp}^{\text{tBu,Me}}]\text{Ni(SCH}_2\text{CH}_2\text{)}\), were unsuccessful resulting in rapid decomposition of the product to pyrazole and nickel sulfide. The instability of this complex as compared to \([\text{Tp}^{\text{Ph,Me}}]\text{Ni(SCH}_2\text{CH}_2\text{)}\) indicates that the latter is a uniquely stable nickel(III) complex. As such, the rapid decomposition of \([\text{Tp}^{\text{tBu,Me}}]\text{Ni(SCH}_2\text{CH}_2\text{)}\) supports the proposed nickel(III) mechanistic intermediate in catalytic cross-coupling reactions while also identifying a stable nickel(III) complex whose geometric and electronic properties can be well studied.
In addition, efforts were pursued to synthesize two new Tp-supported nickel-dioxygen species, $[\text{Tp}^{\text{Fc,Me}}\text{Ni}(O_2)]$ and $[\text{Tp}^{\text{Ind,Me}}\text{Ni}(O_2)]$. The series of halide complexes were made for each Tp ligand. However, conventional nickel(I) and nickel(II) routes for synthesizing the dioxygen complexes were unsuccessful. Two new sulfur- and selenium-containing complexes were synthesized using the $[\text{Tp}^{\text{Ind,Me}}]\text{Ni}$ halide complexes, namely $[\text{Tp}^{\text{Ind,Me}}\text{Ni}(\text{SH})]$ and $([\text{Tp}^{\text{Ind,Me}}\text{Ni}]_2(\mu-\text{Se}))$.

Overall, this thesis describes a stable Tp-supported nickel(III) (or Ni(II)L•) complex as well as several new Tp-supported nickel-sulfur and nickel-selenium complexes. A new Tp-supported superoxide complex, $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(O_2)]$, is also described which exhibits a much different reactivity scope than the previously prepared $[\text{Tp}^{\text{tBu,Me}}\text{Ni}(O_2)]$. The difference in reactivity is largely attributed to the more open coordination sphere in $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(O_2)]$ versus $[\text{Tp}^{\text{tBu,Me}}\text{Ni}(O_2)]$. Continued work with Tp$^{\text{Ind,Me}}$ and Tp$^{\text{Fc,Me}}$ ligated nickel complexes to synthesize the corresponding dioxygen complexes could provide for further comparison to $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(O_2)]$ and $[\text{Tp}^{\text{tBu,Me}}\text{Ni}(O_2)]$. These complexes have similar open coordination spheres but will likely exhibit much different reactivity due to the electronic differences of the Tp substitutents as well as the introduction of a redox-active moiety on the ligand.
Chapter 1
INTRODUCTION

1.1 Bioinorganic Nickel Chemistry

1.1.1 Nickel dioxygen chemistry

Dioxygen chemistry is deeply rooted in aerobic biological systems, the advent of which occurred following a major atmospheric shift that occurred 2.4 billion years ago. Prior to that time, the Earth’s atmosphere was predominantly comprised of water vapor and carbon dioxide. The photosynthetic organisms that populated the Earth thrived in this environment, utilizing the carbon dioxide as a carbon source and the water vapor as an electron donor forming oxygen as a byproduct. Eventually, the atmosphere was depleted of carbon dioxide and was converted from a slightly reducing atmosphere to an oxidizing atmosphere that enabled the evolution of animal life as we know it.¹

As a result of this evolution, several cellular mechanisms were developed to effectively utilize atmospheric oxygen through the process of respiration. One key mechanism for this process involved the development of proteins capable of transporting oxygen throughout the organism. The most well-known oxygen-binding proteins for the purpose of oxygen transfer are heme proteins which contain iron
porphyrin cores which can reversibly bind dioxygen. This class of proteins includes hemoglobin, myoglobin, and cytochrome P450. The isolation of hemoglobin in 1840 provided insight into the basic aspects of oxygen in respiration and allowed early chemists to further explore the mechanisms of these oxygen carriers during the respiration process. Lehninger’s work in the 1950s examined the role of oxygen in oxidative phosphorylation in the mitochondria which is the process that utilizes 90-95% of all respired oxygen. The role of the residual oxygen acquired during respiration was illuminated by a 1955 report by Mason and co-workers that presented the ability of oxygen transfer and electron transport by the dioxygen moiety of the phenolase enzyme. This work was a nice complement to the previous work of Fenton in 1894, which described the oxidation of tartaric acid with hydrogen peroxide facilitated by a metal complex.

While heme proteins contain iron as their metal center, this is not the only metal found in biology that is capable of activating dioxygen. Copper and manganese are also found in dioxygen binding and activating proteins. One of the most notable copper-based proteins capable of dioxygen activation is hemocyanin, the binuclear copper oxygen transport protein found in mollusks and some arthropods. More recently, two nickel-containing enzymes that utilize dioxygen have been discovered—aci-reductone dioxygenase (NiARD) and superoxide dismutase (NiSOD)—which have spurred interest in nickel dioxygen chemistry.
1.1.2 Nickel sulfur and nickel selenium chemistry

In addition to nickel-dioxygen chemistry, nickel chemistry with sulfur and selenium has also been of particular interest in recent years. Sulfur and selenium belong to the same family in the periodic table as oxygen known as the chalcogens. As such, many anaerobic enzymes substitute the dioxygen moiety for a sulfur or selenium moiety. Of the nine known nickel containing enzymes, five contain nickel sulfur bonds including nickel superoxide dismutase (NiSOD), acetyl-coenzyme A synthase/carbon monoxide dehydrogenase (ACS/COdH), [NiFe] hydrogenase, and methyl-coenzyme M reductase (MCR). These enzymes are all redox active enzymes indicating that thiolate ligation might be required for the function of these enzymes at physiological redox potentials and for the ability to access higher oxidation state intermediates involved in these catalytic cycles. In the catalytic mechanism of NiSOD, the dioxygen moiety is proposed to bind axially to the nickel center. This allows the nickel-bound oxygen to participate in hydrogen bonding with the backbone nitrogen atoms of an asparagine and cysteine residue while the second oxygen atom participates in hydrogen bonding with a tyrosine residue. The sulfur in the cysteine residue causes the residue to be reducing (-0.340V) which allows, in combination with the other hydrogen bonding residues, for electron transfer between the superoxide and the nickel to occur and to overcome the large redox potential of the Ni(III/II) couple which is approximately 1V. NiSOD is one example of an enzyme that employs
thiolate ligands, a surprising occurrence in nature given the propensity of thiolates to oxidize when exposed to oxidizing agents such as O$_2$ and H$_2$O$_2$ (Figure 1.1).

**Figure 1.1 Proposed enzymatic mechanism for NiSOD**

The existence of selenium in biological systems was discovered in 1973 when two bacterial enzymes, formate dehydrogenase and glycine reductase, were found to contain selenium in the form of selenocysteine.$^{13, 14}$ Subsequently, ten selenocysteine-containing enzymes have been discovered in both prokaryotes and eukaryotes. In addition to decreasing redox potentials down the group, the pKa values of the
chalcogens also decrease down the group. This trend causes the selenol group to be fully dissociated at physiological pH rendering it a better nucleophile in enzyme active sites containing selenocysteine residues. The only nickel containing enzyme that incorporates a selenocysteine residue is nickel-iron-selenium hydrogenase ([NiFeSe] hydrogenase) which performs the reversible oxidation of molecular hydrogen to form two protons and two electrons as a result. The nickel in the nickel-iron-selenium active site is where the reaction occurs and changes in oxidation states ranging from nickel(I) to nickel(III) have been proposed. The iron in this cluster does not change oxidation state during catalysis and is proposed to act as an auxiliary ligand facilitating substrate binding. Additionally, [NiFeSe] hydrogenase exhibits a higher ratio of hydrogen production to hydrogen oxidation compared to its sulfur analogue, which shows the opposite trend. That is, at equilibrium, [NiFeSe] favors the reverse reaction (2H$^+$ + 2e$^-$ $\rightarrow$ H$_2$) while the sulfur analogue favors the forward reaction (H$_2$ $\rightarrow$ 2H$^+$ + 2e$^-$). While the reason for this trend is not solely attributed to the selenocysteine residues replacing the cysteine residues found in [NiFe] hydrogenases, it is clear that this substitution tunes the active site and contributes to the catalytic properties of the enzyme.
1.2 Synthetic Analogues

1.2.1 Nickel dioxygen complexes

To more deeply understand the role of dioxygen in these biological systems, synthetic models have been made that can mimic the steric and electronic properties of the enzymatic sites being studied. First-row transition metal dioxygen species have been the subject of intense investigation. The trispyrazolylborate (Tp) ligand class has proven to be of particular utility in these pursuits. This ligand, developed in the 1960s by Swiatoslaw (Jerry) Trofimenko, has demonstrated to be very useful and versatile for many reasons. First, this ligand is comprised of three pyrazole rings which can bind the metal center such that the metal is coordinated to one of the nitrogen atoms of one, two, or all three of the pyrazole rings. This binding motif is similar to the binding motif of enzyme active sites where the metal is bound to the imidazolyl nitrogens from histidine ligands. Secondly, the synthetic strategy for making these ligands makes it relatively easy for these ligands to be sterically and electronically tuned by changing the substituents at the 3, 4, and 5-positions of the pyrazole rings. In most cases, the first step of the ligand synthesis involves reacting a functionalized ketone enolate with an ester with the desired functionality to form a diketone. Due to the mild reaction conditions of the subsequent steps in the synthesis, the functionality incorporated into the diketone is unaffected and is easily tuned by varying the ketone and ester starting materials. Thirdly, the syntheses are generally high-yielding. Finally, since the steric
and electronic properties of the ligand can be tuned, these ligands can support both low and high metal oxidation states.

There are two main synthetic methods employed for the synthesis of metal dioxygen complexes. The first and most common synthetic approach involves the reaction of a high valent metal salt with hydrogen peroxide. As such, this tends to be the preferred method for the synthesis of nickel-dioxygen complexes since stable and more readily accessible Ni²⁺ salts can be employed. Several important synthetic mimics have been prepared via this route. For example, Kitajima prepared [[Tp/pg/pg]Cu]₂ (μ-η²:η²-O₂) from the reaction of a copper(II) starting material, [Tp/pg/pg]Cu(OH)₂, with hydrogen peroxide. This μ-η²:η² peroxo dicopper(II) complex was shown to accurately model the structure and spectral features of the hemocyanin active site.¹⁹ Using a similar synthetic strategy, Hikichi prepared and fully characterized the first Ni₂(μ-O)₂ core similar to the proposed bis(μ-oxo) intermediate of methane monooxygenase and to explore the effect of the metal on reactivity of the complex.²⁰ ([Tp/me/me]Ni(μ-O₂))₂ was synthesized from the reaction of the nickel(II) hydroxo dimer, ([Tp/me]Ni(OH))₂, with H₂O₂. In this work, Hikichi, et al. determined that the nickel complex showed reactivity 10⁴ times greater than that of the cobalt analogue. In previous work, Hikichi also prepared Tp/pg/pgNi₂(μ-O)₂ by the reaction of 1 equivalent of H₂O₂ in CH₂Cl₂ at low temperatures.²¹ However, this reaction led to rapid decomposition with oxygen functionalization of an isopropyl substituent on each Tp ligand yielding an enolate bridged dimer, Figure 1.2. The synthesis and reactivity of ([Tp/me/me]Ni(μ-O₂))₂ highlighted the hydrogen atom abstraction aptitude and
decomposition route which is a common source of instability in Tp-supported oxometal complexes.

Figure 1.2 Formation of a bis(μ-oxo) complex leading to ligand oxidation.

The second synthetic strategy involves the reaction of a low valent metal complex with dioxygen. To synthesize a nickel-dioxygen complex using this method, a nickel(II) complex is first reduced to nickel(I) before reacting with dioxygen.
Reduction to nickel(I) is necessary since nickel(II) complexes are generally, with few notable exceptions, inert to dioxygen due to the high Ni\(^{3+}/Ni^{2+}\) redox couple (generally >1V). Several examples of first-row transition metal-dioxygen complexes prepared using this synthetic route with Tp ligands have been reported. The first and one of the most notable examples is Theopold’s synthesis of [Tp\(^{\text{tBu,Me}}\)Co(O\(_2\))] from the reaction of [Tp\(^{\text{tBu,Me}}\)Co(N\(_2\))] with dry O\(_2\).\(^{22}\) This complex was the first example of a side-on bound superoxide. However, [Tp\(^{\text{tBu,Me}}\)Co(OH)] is formed as a by-product in significant amounts during the synthesis due to hydrogen atom abstraction from the ligand. This led to proposal of the formation of a [Tp\(^{\text{tBu,Me}}\)Co-O•] intermediate which is suggested to be the reactive species for oxidation by metal dioxygen complexes. Similarly, the less sterically encumbered analogue, [Tp\(^{\text{iPr,Me}}\)Co(O\(_2\))], readily decomposes at room temperature to [Tp\(^{\text{iPr,Me}}\)Co(µ-O\(_2\))Tp\(^{\text{iPr,Me}}\)] as a proposed intermediate before ultimately forming [Tp\(^{\text{iPr,Me}}\)Co(OH)] by hydrogen atom abstraction from the ligand.\(^{23}\) Recently in our laboratory, a highly stable superoxide complex was synthesized utilizing the [Tp\(^{\text{tBu,Me}}\)] ligand. William Green synthesized [Tp\(^{\text{tBu,Me}}\)Ni(O\(_2\))] from the reaction of [Tp\(^{\text{tBu,Me}}\)Ni(CN\(_{\text{tBu}}\))] with excess O\(_2\) in pentane and found the complex to be the first nickel superoxide complex to be thermally stable under ambient conditions in the solid state and in solution.
1.2.2 Nickel sulfur and nickel selenium complexes

Nickel sulfur and nickel selenium complexes may be prepared in similar ways to those of nickel dioxygen complexes. The reported complexes are formed generally from the reaction of a nickel(II) precursor with a sulfur or selenium salt. Much less common is the reaction of a nickel(I) complex with elemental sulfur or selenium. Dreiss et al. successfully synthesized the first isolable nickel superoxide and its supersulfide analogue at low temperatures using a nickel(I) starting material supported by the β-diketiminiate ligand, CH-(CMeN-2,6-iPr$_2$C$_6$H$_3$).$^{24}$ Under the same reaction conditions with elemental selenium, the first structurally characterized complex with a \(\{\text{Ni}^{\text{II}}_2(\mu-\eta^2:\eta^2-\text{Se}_2)\}\) core was synthesized.$^{25}$ This latter complex readily dissociates in solution forming the superselenide complex as supported by $^1$H NMR spectroscopy and high resolution mass spectroscopy.

Using analogous synthetic routes, several nickel sulfide and nickel selenide complexes supported by other ligands have been synthesized in recent years. \(((\text{PhTt}^{\text{Bu}}\text{tBu})\text{Ni})_2(\mu-\eta^2:\eta^2-\text{S}_2)\) was formed from the reaction of \([\text{PhTt}^{\text{Bu}}\text{Ni}(\text{CO})\) with elemental sulfur.$^{26}$ This complex oxidizes PPh$_3$ to S=PPh$_3$ with the resulting metal product, \(((\text{PhTt}^{\text{Bu}}\text{tBu})\text{Ni})_2(\mu-\text{S})\) formed in good yield.$^{27}$ The \(\mu-\eta^2:\eta^2\) disulfide complex was also prepared from the thermal decomposition of \([\text{PhTt}^{\text{Bu}}\text{Ni}(\text{SCPh}_3)\), which likely proceeds via homolysis of the sulfur-carbon bond forming a purported terminal sulfidonickel that subsequently reacted with another terminal sulfidonickel forming \(((\text{PhTt}^{\text{Bu}}\text{tBu})\text{Ni})_2(\mu-\eta^2:\eta^2-\text{S}_2)\). The analogous selenium complex, \(((\text{PhTt}^{\text{Bu}}\text{tBu})\text{Ni})_2(\mu-\eta^2:\eta^2-\text{Se}_2)\)
Se$_2$), was prepared from the salt metathesis of [PhTt$^{Bu}$]Ni(NO$_3$) with Na$_2$Se$_2$.\textsuperscript{28} ([PhTt$^{Bu}$]Ni)$_2$(μ-η$^2$-η$^2$-Se$_2$) oxidizes PPh$_3$ to Se=PPh$_3$ when reacted with excess PPh$_3$.

Additionally, a series of polysulfido dinickel(II) complexes were prepared by Jessica Wallick using a nickel(I) tetramethylcyclohexane complex and were similarly found to oxidize PPh$_3$ to S=PPh$_3$.\textsuperscript{29} The series was synthesized by first reacting [Ni(Me$_4$[12]aneN$_4$)(CO)]PF$_6$ with excess elemental sulfur forming

\{[Ni(Me$_4$[12]aneN$_4$)]$_2$(S$_6$)$^2^+$ followed by reaction with 1, 2, 3, 4, or 5 equivalents of PPh$_3$ producing \{[Ni(Me$_4$[12]aneN$_4$)]$_2$(S$_5$)$^2^+$, \{[Ni(Me$_4$[12]aneN$_4$)]$_2$(S$_4$)$^2^+$, \{[Ni(Me$_4$[12]aneN$_4$)]$_2$(S$_3$)$^2^+$, \{[Ni(Me$_4$[12]aneN$_4$)]$_2$(μ-η$^2$-η$^1$-S$_2$)$^2^+$, or

[Ni(Me$_4$[12]aneN$_4$)SH]$^+$, respectively.\textsuperscript{29} In an analogous experiment involving the reaction of [Ni(Me$_4$[12]aneN$_4$)(CO)]PF$_6$ with elemental selenium, [Ni(Me$_4$[12]aneN$_4$)]$_2$(μ-η$^2$-η$^2$-Se$_2$)(PF$_6$)$_2$ was formed in high yield. This complex activates the C-H bonds of 9,10-dihydroanthracene forming anthracene in 48% yield.\textsuperscript{30} Interestingly, the resulting metal product, [Ni(Me$_4$[12]aneN$_4$)]$_2$(SeH)(PF$_6$), converted back to the starting material, [Ni(Me$_4$[12]aneN$_4$)]$_2$(μ-η$^2$-η$^2$-Se$_2$)(PF$_6$)$_2$, upon reaction with 2,4,6-tri-\textit{tert}-butylphenoxyl radical or TEMPO. The Se-H effective bond dissociation enthalpy (BDE) was determined to be between 50 kcal/mol (average of the 2 C—H BDEs) and 69 kcal/mol (O—H BDE in TEMPO-H). In another report, the reaction of a 17 electron nickel(I) radical [CpNi(IDipp)] with elemental sulfur and elemental selenium resulted in the formation of a 70%/30% mixture of

\{[CpNi(IDipp)]$_2$(μ-S$_2$)$^2^+$ and \{[CpNi(IDipp)]$_2$(μ-S$_3$)$^2^+$ and an 82%/6% mixture of

\{[CpNi(IDipp)]$_2$(μ-Se$_2$)$^2^+$ and \{[CpNi(IDipp)]$_2$(μ-Se$_3$)$^2^+$, respectively.\textsuperscript{31}
There are no examples of Tp-supported nickel disulfide/diselenide motifs nor nickel supersulfido/superselenido complexes. Additionally, few examples of nickel sulfur and nickel selenium complexes supported by a Tp ligand have been reported. Jensen et al. reported the synthesis of five new pseudotetrahedral nickel(II) arylthiolate complexes supported by various 3,5-substituted Tp ligands, [Tp\textsuperscript{R,R}Ni(SAr)]\textsuperscript{32}. These complexes prepared by the metathesis of the corresponding metal chloride complex with the sodium arylthiolate salt in THF were capable of performing electrophilic alkylation using methyl iodide forming the corresponding thioether, MeSR. The proposed dissociative reactivity of the thiolate from the uncharged nickel complexes in low-polarity solvent is reminiscent of the lability of the proximal site in the ACS A-cluster, whose turnover has been proposed to occur through a formally diamagnetic Ni(0)/Ni(II) couple at the proximal nickel. The resting active-site nickel in the ACS A-cluster is also ligated in a tetrahedral geometry by weak field ligands in a divalent, high-spin state analogous to Jensen’s complexes. Sulfur ligands supported by 3,5-substituted Tp nickel complexes have also been utilized to model the enzyme active side of NiSOD. Jensen synthesized a [Tp\textsuperscript{Me,Me}Ni\textsuperscript{33,34}] complex ligated to a dithiocarbamate ligand forming a neutral high-spin pentacoordinate complex with a formally trianionic \(\text{N}_3\text{S}_2\) ligand field similar to that of NiSOD. When the redox properties of the complex were explored, they were found to exhibit a quasi-reversible one-electron redox couple at potentials suitable for SOD activity.
1.3 Summary

The use of metals to activate small molecules, including dioxygen, sulfur, and selenium, has been perfected by Nature. Synthetic analogues are exploring the scope and nature of reactivity of these enzymatic complexes. While significant advances in the study of nickel oxygen motifs have been made in recent years, the study of nickel sulfur and nickel selenium complexes supported by Tp ligands has been largely unexplored. The examination of such systems can afford insight into understanding basic biochemical reactions including those of enzymes such as acetyl CoA and NiSOD. The examples herein demonstrate the importance of structure-function relationships and contribute to understanding how to synthesize future complexes supported by the Tp ligand system. This thesis provides insights into the synthesis of Tp supported nickel sulfur and nickel selenium complexes including the synthesis, characterization, and reactivity of a nickel(III) thiametallacycle, \([\text{Tp}^{\text{Ph,Me}}\text{Ni(SCH}_2\text{CH}_2)]\). In addition, the synthesis of a new nickel superoxide complex, \([\text{Tp}^{\text{Ph,Me}}\text{Ni(O}_2])\) is explored and its reactivity is compared to that of a complex, \([\text{Tp}^{\text{tBu,Me}}\text{Ni(O}_2])\), previously synthesized by William L. Green in the Riordan laboratory.
Chapter 2
EXPERIMENTAL

2.1 Physical Methods

2.1.1 Nuclear Magnetic Resonance Spectroscopy

$^1$H and $^{31}$P NMR spectra were acquired on either a Bruker AV 600 autosampler or a Bruker DRX 400. Both spectrophotometers are outfitted with BBO, BBFO, and BBI probes. Air sensitive samples were prepared in either an Ar or N$_2$-filled glovebox, capped with a septum, and sealed with parafilm. Data processing was performed using Bruker Topspin® software. Chemical shifts (δ) were referenced to residual protons on the deuterated solvent. Abbreviations for NMR spectral features are as follows: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. The $^{31}$P NMR spectra were recorded with proton decoupling and were referenced to phosphoric acid (85% in D$_2$O). Magnetic moments were obtained in the solution state by the Evans Method.$^{35}$

2.1.2 Infrared Spectroscopy

Infrared data were collected on a Nicolet Magna 560 IR Spectrometer. Solid samples were prepared by first flushing the sample chamber with compressed air and completing a background scan to ensure removal of atmospheric gases. In general,
samples were ground to a fine powder with KBr using a mortar and pestle. The solid mixture was then placed in a pellet press. Air sensitive samples were prepared in an N2-filled glovebox.

2.1.3 Mass Spectroscopy

High resolution mass spectra were recorded on Waters GCT mass spectrometer with a liquid injection field desorption ionization (LIFDI) source. The instrument was calibrated using a polyethylene glycol (PEG) standard. A small vial with the sample solution was placed in a larger vial and sealed under inert atmosphere. A sample aliquot was removed with a needle for single injection to limit exposure to either oxygen or moisture.

2.1.4 Electronic Absorption Spectroscopy

Optical spectra were collected on a Varian Cary 50 spectrophotometer in a cell with a 1-cm path length. Optical data were first collected on the corresponding solvent at a given temperature allowing for background correction. The sample cells are custom-made glass vessels constructed to exclude water and oxygen. In a typical experiment, sample solutions were prepared in an N2-filled glovebox. The glass vessel was filled with approximately 5 mL of sample solution, sealed, and removed from the glove box. Temperature control for electronic absorption measurements was maintained using a Unisoku CoolSpek UV cyrostat.
2.1.5 Electron Paramagnetic Resonance Spectroscopy

The X-band (~9.5 GHz) EPR spectrum was collected at Pennsylvania State University in Prof. Michael Green’s laboratory on a Bruker ESP-300 spectrometer equipped with a ER 4102 ST resonator, an Oxford Instruments continuous flow cryostat (ER 4112-HV), and an Oxford Instruments Temperature Controller (ITC 503S). The sample was prepared by dissolving crystalline material in toluene to afford a 5 mM solution. The spectrum was collected at 10 K with a microwave power of 2.040 mW and attenuation of 20 dB.

2.1.6 X-Ray Diffraction

Crystals were mounted using viscous oil onto a plastic mesh and cooled to the data collection temperature. Data were collected on a Bruker-AXS APEX 2 DUO CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å) monochromated with graphite. Unit cell parameters were obtained from 36 data frames, 0.5° ω, from three different sections of the Ewald sphere. The data sets were treated with multi-scan absorption corrections (Apex2 software suite, Madison, WI, 2005). The structures were solved using direct methods and refined with full-matrix least-squares procedures of \( F^2 \). All hydrogen atoms were treated as idealized contributions with the exception of \([\text{Tp}^{\text{Ph,Me}}\text{Ni(SH)}]\). Atomic scattering factors are contained in the SHELXTL 6.12 program library. Crystal data collection and refinement parameters are provided in Table 2.3. Crystallographic data were collected and refined by Dr. Glenn P. A. Yap, Department of Chemistry and Biochemistry, University of Delaware.
2.1.7 Gas Chromatography

Low-resolution mass spectra were recorded on Agilent 5973 GC-MS with autosampler. General parameters used included a 200°C injection temperature and a starting column temperature of 50°C followed by a ramp to 300°C at 10°C/minute.

2.1.8 Combustion Analyses

Combustion analyses were performed by Robertson Microlit Laboratories, Ledgewood, NJ. Samples were crystallized and the resulting crystals were ground to a fine powder. The powder was dried under vacuum for several days. The samples were shipped in a small vial inside of a larger vial and sealed under an inert atmosphere.

2.2 Experimental

All air- and moisture-sensitive reactions were carried out under an inert atmosphere either in a Vacuum Atmospheres glovebox or by using standard Schlenk techniques. Unless described otherwise, reagents were purchased from commercial sources and were used as received. K[Tp\textsuperscript{Ph,Me}] and [Tp\textsuperscript{Ph,Me}]NiCl were prepared according to the literature methods.\textsuperscript{37} CO and O\textsubscript{2} gas was purchased from Keen Gas and were dried via passage through a Drierite column. Solvents were dried by passage through activated alumina, sparged with N\textsubscript{2}, and tested with Na/benzophenone ketal prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories and dried over 4 Å molecular sieves. All materials were handled using nitrile, powder-free gloves and while wearing safety goggles in accordance with the
University of Delaware Environmental Health and Safety guidelines. All chemicals were handled in a chemical fume hood or glovebox. Foul-smelling reagents, such as ethylene sulfide, were oxidized by passage through an aqueous solution of bleach before proper disposal. Mercury was disposed of in its own waste container and was reused after distillation.

2.2.1 Synthesis of [Tp\textsuperscript{Ph,Me}]NiI

[Tp\textsuperscript{Ph,Me}]NiCl (19.4 g, 33.5 mmol) was added to a 1-L round bottom flask and dissolved in ~500 mL of acetone. To this solution was added 4 equiv. of solid NaI (20.0 g, 134 mmol). The addition resulted in an immediate color change from pink-red to a much darker red and was accompanied by the generation of a white precipitate, NaCl. The reaction mixture was stirred overnight, after which the solution was filtered through Celite and the solvent was removed under vacuum. The reddish-black residue was dissolved in toluene, again filtered through Celite and the solvent removed under vacuum to give a dark reddish-black powder. The powder was washed with pentane and dried under vacuum to give [Tp\textsuperscript{Ph,Me}]NiI as a dark red powder. 19.5 g (87%). \textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}, 400 MHz): \(\delta\) 75.1 (4-\textit{Pz}, s, 3H), 8.7 (\textit{m}-\textit{Ph}, s, 6H), 8.1 (\textit{5-Me}, s, 9H), 6.9 (\textit{p}-\textit{Ph}, s, 3H), 3.0 (\textit{o}-\textit{Ph}, br, 6H), ~2.7 (\textit{BH}, br, 1H). UV-vis (toluene), \(\lambda_{\text{max}}\) (\(\varepsilon\), M\textsuperscript{−1}cm\textsuperscript{−1}): 520 (1139) nm, 600 (285) nm, 860 (136) nm, 960 (161) nm. IR (KBr pellet, v/cm\textsuperscript{−1}): 2545 cm\textsuperscript{−1} (B–H). LIFDI-MS (\(m/z\)): Calc 668.08, Found 668.09.
2.2.2 Synthesis of $\text{Tp}^{\text{Ph,Me}}\text{Ni(PPh}_3\text{)}$

$\text{Tp}^{\text{Ph,Me}}\text{NiI}$ (500 mg, 0.75 mmol) and PPh$_3$ (230 mg, 0.87 mmol) were suspended in ~15 mL of toluene. To this mixture was added 5 equivalents of a 0.3% sodium mercury amalgam (Na, 86 mg; Hg, 28.7 g). The reaction mixture was shaken for 8 minutes during which time all of the starting material was drawn into solution and the color changed from dark red to bright yellow. The reaction solution was separated from the amalgam by filtration through Celite, transferred to a 250-mL round bottom flask and layered with ~120 mL of pentane. $\text{Tp}^{\text{Ph,Me}}\text{Ni(PPh}_3\text{)}$ precipitated as a bright yellow, microcrystalline powder over the course of 2 days. The product was collected by filtration and dried under vacuum giving $\text{Tp}^{\text{Ph,Me}}\text{Ni(PPh}_3\text{)}$ as a bright yellow powder, 406 mg (67%). $^1$H NMR (C$_6$D$_6$, 400 MHz): $\delta$ 49.2 (BH, b, 1H), 18.5 (5-Me, s, 9H), 13.9 (4-Pz, s, 3H), 9.0 (3-Ph, s, 3H), 8.2 (Ph, b, 6H), 7.6 (3-Ph, s, 6H), 5.3 (Ph, s, 3H), 4.0 (Ph, s, 6H), -18.15 (3-Ph, s, 6H). UV-vis (toluene), $\lambda_{\text{max}}$ ($\varepsilon$, M$^{-1}$cm$^{-1}$): 391 (3318) nm. IR (KBr pellet, v/cm$^{-1}$): 2542 cm$^{-1}$ (B–H). LIFDI-MS (m/z): Calc 803.27, Found 803.27.

2.2.3 Synthesis of $\text{Tp}^{\text{Ph,Me}}\text{Ni(CO)}$

$\text{Tp}^{\text{Ph,Me}}\text{Ni(PPh}_3\text{)}$ (1.1 g, 1.4 mmol) was added to a 50-mL Schlenk flask and dissolved in ~5 mL of THF. The flask was purged with CO for 2 minutes, followed by stirring for 10 minutes. The addition of CO resulted in a color change from bright yellow to a much paler yellow. The solvent and excess CO was removed under vacuum and the product washed with pentane to remove free PPh$_3$. After washing, the product was dried under vacuum to give $\text{Tp}^{\text{Ph,Me}}\text{Ni(CO)}$ as a pale yellow powder,
600 mg (85%). $^1$H NMR (C$_6$D$_6$, 400 MHz): $\delta$ 32.8 (BH, br, 1H), 19.0 (4-Pz, s, 3H), 16.9 (5-Me, s, 9H), 8.0 (m-Ph, s, 6H), 7.3 (p-Ph, s, 3H), -8.9 (o-Ph, br, 6H). UV-vis (CHCl$_3$), $\lambda_{\text{max}}$ (c, M$^{-1}$cm$^{-1}$): 237 (47,500), 343 (sh, 2600). IR (KBr pellet, v/cm$^{-1}$): 2527 (B–H), 2005 (C≡O). LIFDI-MS (m/z): Calc 569.18, Found 569.18.

2.2.4 Synthesis of [Tp$^{\text{Ph,Me}}$]Ni(O$_2$)

[Tp$^{\text{Ph,Me}}$]NiCO (0.300 g, 0.53 mmol) was suspended in pentane in a scintillation vial equipped with a stir bar and a rubber septum secured with copper wire. O$_2$ was bubbled through the solution for ~1 minute during which time the solution color changed from pale yellow to colorless with a mocha precipitate. The reaction was stirred under 1 atm of O$_2$ for an additional minute before the stirring was ceased and then the precipitate settled. The pentane was decanted off and the precipitate was washed twice with 15 mL portions of pentane. After washing, the product was dried under vacuum to give [Tp$^{\text{Ph,Me}}$]Ni(O$_2$) as a mocha powder, 272 mg (90%). $^1$H NMR (C$_6$D$_6$, 400 MHz): $\delta$ 34.9 (4-Pz, br, 3H), 7.6 (p-Ph, s, 3H), 7.4 (o-Ph, br, 6H), 6.9 (m-Ph, s, 3H), 2.5 (5-Me, s, 9H), -1.8 (BH, br, 1H). $\lambda_{\text{max}}$ (c, M$^{-1}$cm$^{-1}$): 311 (sh, 1550), 874 (150). IR (KBr pellet, v/cm$^{-1}$): 2531 (B–H), 991 (O–O).

2.3 Reaction of [Tp$^{\text{Ph,Me}}$]Ni(O$_2$) with stoichiometric PR$_3$ (R = Me, Et, Cy, Ph)

[Tp$^{\text{Ph,Me}}$]Ni(O$_2$) (0.050 g, 0.088 mmol) was added to 5 mL of a stock solution of PR$_3$ (0.088 mmol) in deuterated benzene in a 20-mL scintillation vial. A few drops of pyridine were added to the solution to preclude OPR$_3$ binding to the paramagnetic nickel product. The reaction was stirred at room temperature for 24 hr during which
time the solution color changed from reddish-brown to bright yellow. Stirring was discontinued and aliquots from both the crude mixture and the stock solution were removed and subjected to $^{31}$P NMR and $^1$H NMR spectroscopy. $^{31}$P NMR spectral analysis was performed directly on the stock and reaction solutions respectively, with a capillary tube containing phosphoric acid (85% H$_3$PO$_4$ in D$_2$O) used as a spectral reference and internal standard. The reactions were found to produce OPR$_3$ in quantitative yields for R = Me, Et and in 66% and 78% yields for R = Cy, Ph, respectively.

2.4 Reaction of [Tp$^{\text{Ph,Me}}$]Ni(O$_2$) with 9, 10-dihydroanthracene

[Tp$^{\text{Ph,Me}}$]Ni(O$_2$) (0.050 g, 0.088 mmol) was added to 5 mL of a stock solution containing 9,10-dihydroanthracene (0.008 g, 0.044 mmol) and hexamethylbenzene (internal standard) dissolved in deuterated toluene in a 20-mL scintillation vial. The reaction was stirred for 24 hr at room temperature during which time the color of the solution changed from reddish-brown to golden brown. Aliquots of the solution were removed for $^1$H NMR and GC-MS analysis which confirmed the presence of 9,10-anthraquinone when compared to spectra of authentic material. The experiment was repeated varying the number of equivalents of [Tp$^{\text{Ph,Me}}$]Ni(O$_2$), temperature, and reaction time. The optimum reaction conditions were found to be 6 equivalents of [Tp$^{\text{Ph,Me}}$]Ni(O$_2$) reacted with 1 equivalent of 9,10-dihydroanthracene at 60°C for 24 hours to yield a 7% conversion of 9,10-dihydroanthracene to 9,10-anthraquinone, Table 2.1.
Table 2.1 Reaction Conditions and Yields for the Oxidation of 9,10-dihydroanthracene by [Tp\textsubscript{Ph,Me}]Ni(O\textsubscript{2}).

<table>
<thead>
<tr>
<th>Number of Equivalents of [Tp\textsubscript{Ph,Me}]NiO\textsubscript{2}</th>
<th>Reaction Time (hrs)</th>
<th>Temperature (°C)</th>
<th>% Conversion of 9,10-DHA to 9,10-anthraquinone</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>24</td>
<td>25</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>48</td>
<td>25</td>
<td>7</td>
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<tr>
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<td>25</td>
<td>15</td>
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<tr>
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</tr>
<tr>
<td>6</td>
<td>24</td>
<td>60</td>
<td>7</td>
</tr>
</tbody>
</table>

2.5 Reaction of [Tp\textsubscript{Ph,Me}]Ni(O\textsubscript{2}) with 1,4-cyclohexadiene

[Tp\textsubscript{Ph,Me}]Ni(O\textsubscript{2}) (0.050 g, 0.088 mmol) was added to 5 mL of a stock solution containing 1,4-cyclohexadiene (0.004 g, 0.044 mmol) and hexamethylbenzene (internal standard) dissolved in deuterated toluene in a 20-mL scintillation vial. The reaction was stirred for 24 hr at room temperature. Aliquots of the solution were removed for \textsuperscript{1}H NMR spectral and GC-MS analysis, which showed no oxidation of 1,4-cyclohexadiene when compared to spectra of authentic material. The experiment was repeated at a longer reaction time, elevated temperature, and with an excess of 1,4-cyclohexadiene; however, no conversion was observed, Table 2.2.
<table>
<thead>
<tr>
<th>Number of Equivalents of $[\text{Tp}^{\text{Ph,Me}}\text{Ni(O}_2)$</th>
<th>Reaction Time (hrs)</th>
<th>Temperature (°C)</th>
<th>% Conversion of 1,4-CHD to benzene/1,4-cyclohexanedione</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
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</tr>
<tr>
<td>10</td>
<td>48</td>
<td>25</td>
<td>0</td>
</tr>
</tbody>
</table>

### 2.6 Reaction of $[\text{Tp}^{\text{Ph,Me}}\text{Ni(O}_2)$ with styrene

$[\text{Tp}^{\text{Ph,Me}}\text{Ni(O}_2)$ (0.050 g, 0.088 mmol) was added to 5 mL of a stock solution containing styrene (0.005 g, 0.044 mmol) and hexamethylbenzene (internal standard) dissolved in deuterated toluene in a 20-mL scintillation vial. The reaction was stirred for 24 hr at room temperature. Aliquots of the solution were removed for $^1\text{H}$ NMR spectral and GC-MS analysis, which showed no oxidation of styrene when compared to spectra of authentic material. The experiment was repeated at a longer reaction time, specifically 72 hr; however, no conversion was observed.

### 2.7 Reaction of $[\text{Tp}^{\text{Ph,Me}}\text{Ni(O}_2)$ with cyclohexene

$[\text{Tp}^{\text{Ph,Me}}\text{Ni(O}_2)$ (0.050 g, 0.088 mmol) was added to 5 mL of a stock solution containing cyclohexene (0.005 g, 0.044 mmol, 1.8 μL) and hexamethylbenzene (internal standard) dissolved in deuterated toluene in a 20-mL scintillation vial. The reaction was stirred for 24 hr at room temperature. Aliquots of the solution were
removed for $^1$H NMR spectral and GC-MS analysis which showed no oxidation of cyclohexene when compared to spectra of authentic material.

2.8 Aldehyde deformylation using [Tp$^{\text{Ph,Me}}$]Ni(O$_2$)

[Tp$^{\text{Ph,Me}}$]Ni(O$_2$) (0.050 g, 0.088 mmol) was added to 5 mL of a stock solution containing 2-phenylpropionaldehyde (0.010 g, 0.088 mmol) and hexamethylbenzene (internal standard) in deuterated toluene in a 20 mL scintillation vial. The reaction was stirred for 24 hr at room temperature. Aliquots of the solution were removed for $^1$H NMR spectral, GC-MS, and LIFDI-MS analysis. $^1$H NMR spectral and GC-MS analyses confirmed quantitative conversion of 2-phenylpropionaldehyde to acetophenone. The major nickel-containing product was [Tp$^{\text{Ph,Me}}$]Ni(COOH) as confirmed by LIFDI-MS and $^1$H NMR spectroscopy when compared to independently prepared material (vide infra).

2.9 Synthesis of [Tp$^{\text{Ph,Me}}$]Ni(COOH)

To a 20-mL scintillation vial was added [Tp$^{\text{Ph,Me}}$]NiCl (0.010 g, 0.017 mmol) and NaH (0.001 mg, 0.017 mmol). The reactants were dissolved in THF and the vial was equipped with a stir bar before being capped with a rubber septum secured with copper wire. Formic acid (0.001 mg, 0.017 mmol, 1 μL) was added by syringe and the reaction was stirred at room temperature for 24 hr during which time the color changed from magenta to pale green. The solvent was removed and the product was redissolved in toluene, filtered to remove salt by-products, and dried under vacuum to
afford \([\text{Tp}^{\text{Ph,Me}}\text{Ni(COOH)}]\) in quantitative yield. \(^1\text{H}\) NMR (C\(_6\)D\(_6\), 400 MHz): \(\delta\) 67.0 (CO\(_2\)H, s 1H), 8.2 (o-Ph, s, 6H), 7.5 (m-Ph, br, 6H), 7.2 (p-Ph, br, 3H), 6.7 (4-Pz, s, 3H), 3.4 (5-Me, s, 9H), -10.7 (BH, s, 1H). LIFDI-MS (m/z): Calc 586.18, Found 586.18. IR (KBr pellet, \(\nu/\text{cm}^{-1}\)): 2522 (B–H), 2964 (O–H).

\(\text{2.10 Synthesis of } [\text{Tp}^{\text{Ph,Me}}\text{Ni(SCH}_2\text{CH}_2)]\)

To a solution of \([\text{Tp}^{\text{Ph,Me}}\text{Ni(PPh}_3\text{)}]\) (0.03 g, 0.04 mmol) prepared in 10 mL of toluene was added dry, degassed ethylene sulfide (0.003 g, 0.06 mmol) resulting in an immediate color change from bright yellow to dark red. The reaction solution was stirred at 40°C for 24 hr during which time the color deepened to dark reddish brown. The reaction solution was then filtered through Celite and concentrated under vacuum. The product was recrystallized by vapor diffusion of pentane into toluene (Table 2.3). 10 mg, 45% crystalline yield. UV-Vis (toluene): \(\lambda_{\text{max}}\) (\(\epsilon, \text{M}^{-1}\text{cm}^{-1}\)) 285 (23,680) nm, 385 (7,040) nm, 480 (13,120) nm, 1020 (620) nm; IR (KBr pellet, \(\nu/\text{cm}^{-1}\)): 2542 (B–H). \(^1\text{H}\) NMR (C\(_6\)D\(_6\), 400 MHz): \(\delta\) 68.3 (4-Pz, s, 3H), 7.6 (o-Ph, m, 6H), 7.4 (m-Ph, m, 6H), 6.7 (p-Ph, m, 3H), 6.0 (CH\(_2\), t, 4H), 2.2 (5-Me, s, 9H), -11.7 (BH, s, 1H). Combustion analysis (%) calculated for C\(_{32}\)H\(_{32}\)BN\(_6\)NiS: C, 63.82, H, 5.36, N, 13.96; found C, 63.75, H, 5.44, N, 13.83. \(\mu_{\text{eff}} = 1.75(4) \mu_\text{B}\).
2.11 Synthesis of $[\text{Tp}^{\text{Ph,Me}}\text{Ni}]\text{Ni(SH)}$

To a solution of $[\text{Tp}^{\text{Ph,Me}}\text{NiCl]} (0.065g, 0.11 \text{ mmol})$ in toluene was added 1 equiv. of NaSH (0.006g, 0.11 mmol). The reaction was stirred for 24 hr at room temperature during which time the color changed from magenta to red-orange. The precipitate (NaCl) was filtered off and the solvent was removed. The product was recrystallized from toluene/pentane vapor diffusion, Table 2.4. 60 mg, 94% yield. UV-Vis (toluene): $\lambda_{\text{max}} (\varepsilon, \text{M}^{-1}\text{cm}^{-1}) 330 (8130) \text{ nm, 410 (8320) nm, 490 (4370) nm, 910 (250) nm;}$ $^1\text{H NMR (C}_6\text{D}_6, 400 \text{ MHz): } \delta 69.7 (4-\text{Pz, s, 3H}), 9.8 (o-\text{Ph, m, 6H}), 8.2 (m-\text{Ph, m, 6H}), 7.5 (p-\text{Ph, m, 3H}), 3.6 (5-\text{Me, s, 9H}), -1.8 (\text{SH, s, 1H}), -11.7 (\text{BH, s, 1H}).$ LIFDI-MS ($m/\text{z}$): Calc 574.16, Found 574.21.

2.12 Synthesis of $[\text{Tp}^{\text{Ph,Me}}\text{Ni(SCPh}_3\text{)}$

To a solution of $[\text{Tp}^{\text{Ph,Me}}\text{NiCl]} (0.025g, 0.043 \text{ mmol})$ in toluene was added 1 equiv. of NaSCPh$_3$ (0.012g, 0.043 mmol). The reaction was stirred for 24 hr at room temperature during which time the color changed from magenta to dark red. The solution was filtered and the solvent was removed. 30 mg, 86% yield. UV-Vis (toluene): $\lambda_{\text{max}} (\varepsilon, \text{M}^{-1}\text{cm}^{-1}) 485 (18,390) \text{ nm, 925 (750) nm;}$ IR (KBr pellet, $\nu/\text{cm}^{-1}$): 2544 (B–H); $^1\text{H NMR (C}_6\text{D}_6, 400 \text{ MHz): } \delta 63.7 (4-\text{Pz, s, 3H}), 35.1 (o-\text{Ph, SCPh}_3, \text{s, 6H}), 10.1 (m-\text{Ph, SCPh}_3, \text{s, 6H}), 8.9 (p-\text{Ph, SCPh}_3, \text{m, 3H}), 7.2 (m-\text{Ph, m, 6H}), 7.0 (o-\text{Ph, br, 6H}), 6.86 (p-\text{Ph, m, 3H}), 3.6 (5-\text{Me, s, 9H}), -11.7 (\text{BH, s, 1H}).$ LIFDI-MS ($m/\text{z}$): Calc 816.27, Found 816.27.
2.13 Synthesis of [Tp\text{Ph,Me}]Ni(SePh)

To a scintillation vial was added [Tp\text{Ph,Me}]NiCO (0.005g, 0.0087 mmol) and 1 equiv. of Ph$_2$Se$_2$ (0.003g, 0.0087 mmol). The solids were dissolved in toluene resulting in an immediate color change from pale yellow to blue-green. The reaction was stirred overnight at room temperature during which time the color deepened to cobalt blue. The product was recrystallized from toluene and pentane vapor diffusion at -20°C, Figure 2.1 and Table 2.5. 4 mg, 67% yield. UV-Vis (toluene): $\lambda_{\text{max}}$ ($\varepsilon$, M$^{-1}$cm$^{-1}$) 580 (27,920) nm, 945 (100) nm; $^1$H NMR (C$_6$D$_6$, 400 MHz): $\delta$ 68.8 (4-P$_Z$, s, 3H), 22.3 (m-Ph, SePh, s, 2H), 9.6 (o-Ph, m, 6H), 7.8 (m-Ph, m, 6H), 6.9 (p-Ph, m, 3H), 4.9 (5-Me, s, 9H), -8.4 (o-Ph, SePh, s, 2H), -23.1 (BH, br, 1H), -29.7 (p-Ph, SePh, br, 1H). LIFDI-MS (m/z): Calc 699.14, Found 699.14.

2.14 Synthesis of ([Tp\text{Ph,Me}]Ni)$_2$(\mu-Se)

To a scintillation vial was added [Tp\text{Ph,Me}]NiCl (0.023g, 0.0040 mmol) and 1 equiv. of Na$_2$Se (0.005g, 0.0040 mmol). The reactants were dissolved in toluene and allowed to stir overnight at room temperature during which time the solution color changed from magenta to deep purple. The solution was filtered and the solvent removed. 30 mg, 61% yield. UV-Vis (toluene): $\lambda_{\text{max}}$ ($\varepsilon$, M$^{-1}$cm$^{-1}$) 385 (35,000) nm, 520 (7,900) nm; IR (KBr pellet, v/cm$^{-1}$): 2474 (B–H). $^1$H NMR (C$_6$D$_6$, 400 MHz): $\delta$ 8.3(p-Ph, m, 3H), 7.8(o-Ph, m, 6H), 7.6 (m-Ph, m, 6H), 6.7 (o-Ph, m, 6H), 6.6 (m-Ph, m, 6H), 6.3 (p-Ph, m, 3H), 5.5 (BH, br, 1H), 2.4 (5-Me, s, 9H), 2.2 (5-Me, s, 9H). LIFDI-MS (m/z): Calc 1162.28, Found 1162.29.
2.15 Reaction of $[\text{Tp}^{\text{Ph}, \text{Me}}] \text{Ni(SCH}_2 \text{CH}_2]$ with CO

$[\text{Tp}^{\text{Ph}, \text{Me}}] \text{Ni(SCH}_2 \text{CH}_2]$ (0.010 g, 0.017 mmol) was dissolved in 5 mL of toluene in a 20 mL scintillation vial. The vial was equipped with a stir bar and capped with a 14/20 septum secured with copper wire. The solution was cooled to -78°C in a dry ice/acetone bath and was bubbled with CO for 5 minutes. The reaction was stirred at -78°C for 1 hr before warming to room temperature and further stirring overnight. The solvent was transferred by high vacuum line and analyzed by GC-MS; no formation of dihydrothiophen-2(3H)-one was observed. Analysis of the $^1$H NMR spectrum of the residue after vacuum transfer showed solely starting material, $[\text{Tp}^{\text{Ph}, \text{Me}}] \text{Ni(SCH}_2 \text{CH}_2]$.

2.16 Reaction of $[\text{Tp}^{\text{Ph}, \text{Me}}] \text{Ni(SCH}_2 \text{CH}_2]$ with PR$_3$ (R = Me, Et)

$[\text{Tp}^{\text{Ph}, \text{Me}}] \text{Ni(SCH}_2 \text{CH}_2]$ (0.010 g, 0.017 mmol) was added to a stock solution of PR$_3$ in 5 mL of deuterated benzene in a 20 mL scintillation vial. The solution was stirred at room temperature for 24 hrs after which time stirring was discontinued and aliquots from both the crude mixture and the stock solution were removed and subjected to $^{31}$P NMR and $^1$H NMR spectrosopies. $^{31}$P NMR spectral analysis was performed on the stock and reaction solutions respectively, with a capillary tube containing phosphoric acid (85% H$_3$PO$_4$ in D$_2$O) used as a spectral reference and internal standard. No reaction was observed by $^1$H NMR spectroscopy when $[\text{Tp}^{\text{Ph}, \text{Me}}] \text{Ni(SCH}_2 \text{CH}_2]$ was reacted with PEt$_3$; however, reaction with PMe$_3$ was produced the protonated phosphonium salt, $[\text{PMe}_3 \text{Et}]^+$, in quantitative yields which
was confirmed by GC-MS analysis of the reaction solution and by comparison of the \( ^{31}P \) NMR spectrum to that of previously reported spectra of similar alkyl substituted phosphonium cation samples.\(^{38}\) The major metal product of the reaction was \([\text{Tp}^{\text{Ph},\text{Me}}]_2\text{Ni}\) as deduced by \(^1\text{H}\) NMR spectroscopy when compared to spectra of authentic samples.

\section*{2.17 Reaction of \([\text{Tp}^{\text{Ph},\text{Me}}]_2\text{Ni}(\text{SCH}_2\text{CH}_2)\) with O\(_2\)}

\([\text{Tp}^{\text{Ph},\text{Me}}]_2\text{Ni}(\text{SCH}_2\text{CH}_2)\) (0.010 g, 0.017 mmol) was dissolved in 5 mL of deuterated benzene in a 20 mL scintillation vial. The vial was equipped with a stir bar and capped with a rubber septum wired down with copper wire. The solution was bubbled with O\(_2\) for 5 minutes before being left under 1 atm of O\(_2\) for the duration of the reaction. The solution was stirred and monitored by \(^1\text{H}\) NMR spectroscopy. No reaction was observed over the course of 11 days. Analysis of the resulting solution by LIFDI-MS showed no evidence of oxidized sulfur (SO\(_x\)) products.

\section*{2.18 Synthesis of \([\text{Tp}^{\text{Fc},\text{Me}}]\text{NiCl}\)}

To a solution of \([\text{Tp}^{\text{Fc},\text{Me}}]\text{Tl}\) (0.100 g, 0.098 mmol) in THF was added anhydrous NiCl\(_2\) (0.024 g, 0.10 mmol). The solution was stirred at room temperature overnight during which time the color of the solution changed from orange to red. The solution was filtered to remove excess salts (NiCl\(_2\) and TlCl). The solvent was removed from the solution and the resulting red solid was redissolved in
dichloromethane. The product was recrystallized by layering pentane on a concentrated dichloromethane solution affording the product, \([\text{Tp}^{\text{Fc,Me}}]\text{NiCl}\), in 96% yield (105 mg) (Figure 2.2 and Table 2.6). \(^1\)H NMR (C\(_6\)D\(_6\), 400 MHz): \(\delta\) 75.9 (4-P\(_2\), br, 3H), 7.5 (Fc, br, 2H), 6.1 (Fc, s, 2H), 4.7 (Fc, s, 5H), 2.3 (5-Me, s, 9H), -12.4 (BH, br, 1H). \(\lambda_{\text{max}}\) (\(\varepsilon, \text{M}^{-1}\text{cm}^{-1}\)): 480 (10,620), 815 (710), 930 (1,070). IR (KBr pellet, \(\nu/\text{cm}^{-1}\)): 2534 (B–H). LIFDI-MS (\(m/z\)): Calc 900.05, Found 900.05.

2.19 Synthesis of \([\text{Tp}^{\text{Fc,Me}}]\text{NiBr}\)

To a solution of \([\text{Tp}^{\text{Fc,Me}}]\text{Tl}\) (0.100 g, 0.098 mmol) in THF was added anhydrous NiBr\(_2\) (0.026 g, 0.12 mmol). The solution was heated to reflux before cooling and stirring at room temperature overnight during which time the color of the solution changed from orange to red. The solution was filtered to remove excess salts (NiCl\(_2\) and TlCl) producing \([\text{Tp}^{\text{Fc,Me}}]\text{NiBr}\), in 75% yield (77 mg). \(^1\)H NMR (C\(_6\)D\(_6\), 400 MHz): \(\delta\) 74.9 (4-P\(_2\), br, 3H), 5.8 (Fc, br, 2H), 4.9 (Fc, s, 2H), 3.6 (Fc, s, 5H), 3.3 (5-Me, s, 9H), -9.0 (BH, br, 1H). \(\lambda_{\text{max}}\) (\(\varepsilon, \text{M}^{-1}\text{cm}^{-1}\)): 430 (7,376), 825 (505), 935 (615). IR (KBr pellet, \(\nu/\text{cm}^{-1}\)): 2536 (B–H). LIFDI-MS (\(m/z\)): Calc 945.99, Found 945.99.

2.20 Synthesis of \([\text{Tp}^{\text{Fc,Me}}]\text{NiI}\)

To a solution of \([\text{Tp}^{\text{Fc,Me}}]\text{NiCl}\) (0.030 g, 0.027 mmol) in THF was added 4 equivalents of NaI (0.016 g, 0.011 mmol). The solution immediately changed in color from red to deep burgundy. The solution was stirred at room temperature overnight before filtering to remove excess salts (NaCl) affording \([\text{Tp}^{\text{Fc,Me}}]\text{NiI}\) in quantitative
yield (29 mg). ¹H NMR (C₆D₆, 400 MHz): δ 73.4 (4-Pz, br, 3H), 7.9 (Fc, br, 6H), 7.0 (Fc, s, 2H), 4.9 (Fc, s, 2H), 2.5 (5-Me, s, 9H), -3.7 (BH, br, 1H). λₘₚₜ (ε, M⁻¹cm⁻¹): 425 (20,030), 515 (10,827), 860 (962), 965 (1,111). IR (KBr pellet, v/cm⁻¹): 2540 (B–H).

LIFDI-MS (m/z): Calc 991.99, Found 991.99.

2.21 Synthesis of [Tp⁰Ind,Me]NiCl

To a solution of 3 equiv. of NiCl₂•6H₂O (1.86 g, 7.83 mmol) in 1:1 CH₂Cl₂/DMF was added [Tp⁰Ind,Me]Tl (2.00 g, 2.61 mmol). The solution immediately underwent a color change from green to peach-colored with a white precipitate. The reaction was stirred overnight at room temperature before being filtered through Celite. The solvent was removed to yield a red powder, [Tp⁰Ind,Me]NiCl, in 91% yield (1.55 g). The product was recrystallized from CH₂Cl₂/pentane layering (Figure 2.3 and Table 2.6). ¹H NMR (CDCl₃, 400 MHz): δ 14.2 (CH₂, t, 6H), 11.8 (Ph-C₆H, br, 3H), 9.1 (Ph-C₆H, dd, 3H), 7.5 (Ph-C₆H, dd, 3H), 6.8 (Ph-C₆H, ddd, 3H), 6.3 (CH₂, t, 6H), 2.6 (5-Me, s, 9H), -12.9 (BH, br, 1H). λₘₚₜ (ε, M⁻¹cm⁻¹): 350 (12,800), 430 (2,600), 515 (2,200), 550 (sh, 2,200), 820 (500), 945 (900). IR (KBr pellet, v/cm⁻¹): 2548 (B–H).

LIFDI-MS (m/z): Calc 654.20, Found 654.18.

2.22 Synthesis of [Tp⁰Ind,Me]NiI

To a scintillation vial was added [Tp⁰Ind,Me]NiCl (0.400 g, 0.610 mmol) and 4 equivalents of NaI (0.366 g, 2.44 mmol). The reactants were dissolved in CH₂Cl₂ and
stirred overnight at room temperature. The solution was filtered through Celite and the solvent removed from the filtrate to afford the product, $[^\text{Tp}\text{Ind,Me}]\text{NiI}$, as a dark red powder (0.173 g, 38%). The product was recrystallized by layering pentane on a concentrated CH$_2$Cl$_2$ solution, Figure 2.4 and Table 2.7. $^1$H NMR (CDCl$_3$, 400 MHz): \(\delta\) 15.4 (CH$_2$, t, 6H), 10.2 (Ph-CH, br, 3H), 7.3 (Ph-CH, dd, 3H), 6.6 (Ph-CH, dd, 3H), 5.9 (Ph-CH, ddd, 3H), 5.3 (CH$_2$, t, 6H), 1.2 (5-Me, s, 9H), -2.6 (BH, br, 1H). \(\lambda_{\text{max}}\) (\(\varepsilon\), M$^{-1}$cm$^{-1}$): 370 (5.760), 415 (sh, 3.645), 560 (1.441), 850 (328), 955 (411). IR (KBr pellet, \(\nu$/cm$^{-1}$): 2548 (B–H). LIFDI-MS (m/z): Calc 746.13, Found 746.14.

### 2.23 Synthesis of $[^\text{Tp}\text{Ind,Me}]\text{NiBr}$

$\text{NiBr}_2$ (0.852 g, 3.90 mmol) was left standing on the benchtop to absorb ambient water over the course of a few days before dissolving in methanol. To this solution was added a chloroform solution of $[^\text{Tp}\text{Ind,Me}]\text{Tl}$ (1.00 g, 1.30 mmol). The reaction solution turned dark red immediately and a white precipitate formed. After stirring overnight at room temperature, the solution was filtered through Celite. The solvent was removed yielding a dark red powder, $[^\text{Tp}\text{Ind,Me}]\text{NiBr}$, in quantitative yield (0.890 g). The product was recrystallized from chloroform/pentane layering (Figure 2.5 and Table 2.8). $^1$H NMR (CDCl$_3$, 400 MHz): \(\delta\) 14.8 (CH$_2$, t, 6H), 9.6 (Ph-CH, s, 3H), 8.6 (Ph-CH, dd, 3H), 7.2 (Ph-CH, dd, 6H), 6.5 (CH$_2$, t, 6H), 2.0 (5-Me, s, 9H), -7.9 (BH, br, 1H). \(\lambda_{\text{max}}\) (\(\varepsilon\), M$^{-1}$cm$^{-1}$): 335 (2.660), 425 (343), 525 (364), 830 (75), 950 (114). IR (KBr pellet, \(\nu$/cm$^{-1}$): 2547 (B–H). LIFDI-MS (m/z): Calc 700.15, Found 700.14.
Table 2.3 Crystallographic Data for $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{SCH}_2\text{CH}_2)]$.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Identification code</td>
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<td>Formula Weight</td>
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<tr>
<td>Crystal System</td>
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<tr>
<td>Space Group</td>
<td>$\text{P2}_1/n$</td>
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<td>$a$, Å</td>
<td>9.452(2)</td>
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<td>$b$, Å</td>
<td>15.980(4)</td>
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<tr>
<td>$c$, Å</td>
<td>19.385(5)</td>
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<tr>
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<tr>
<td>$\beta$, deg</td>
<td>95.880(4)</td>
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<td>$\gamma$, deg</td>
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<tr>
<td>$V$, Å$^3$</td>
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<td>$\lambda$, Å (Mo, Kα)</td>
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</tr>
<tr>
<td>$Z$</td>
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<tr>
<td>Density, g/cm$^3$</td>
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<td>R(F), Rw(F)</td>
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Table 2.4 Crystallographic Data for $[\text{Tp}^{\text{Ph,Me}}]\text{NiSH}$.

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<tr>
<td>Space Group</td>
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<td>$c$, Å</td>
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<tr>
<td>$\gamma$, deg</td>
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Figure 2.1 Crystal structure of $[\text{Tp}^{\text{Ph},\text{Me}}]\text{Ni(SePh)}$. Thermal ellipsoids drawn at 30%. Hydrogen atoms omitted.
Table 2.5 Crystallographic Data for $[\text{Tp}^{\text{Ph,Me}}\text{Ni(SePh)}]$. 

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<td>$\gamma$, deg</td>
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Figure 2.2 Crystal structure of [Tp\textsuperscript{Fe,Me}]NiCl. Thermal ellipsoids drawn at 30%. Hydrogen atoms omitted.
Table 2.6 Crystallographic Data for \([\text{Tp}^{\text{Fc,Me}}]\text{NiCl}\).

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<th>([\text{Tp}^{\text{Fc,Me}}]\text{NiCl})</th>
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<tr>
<td>Formula Weight</td>
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<td>Crystal System</td>
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Figure 2.3 Crystal structure of $[^{\text{Ind,Me}}\text{Tp}^\text{NiCl}]$. Thermal ellipsoids drawn at 30%. Hydrogen atoms omitted.
Table 2.7 Crystallographic Data for [Tp\textsuperscript{Ind,Me}]NiCl.

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<th>[Tp\textsuperscript{Ind,Me}]NiCl</th>
</tr>
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<td>c, Å</td>
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Figure 2.4 Crystal structure of $[\text{Tp}^{\text{Ind,Me}}]\text{NiI}$. Thermal ellipsoids drawn at 30%. Hydrogen atoms omitted.
Table 2.8 Crystallographic Data for $[\text{Tp}^\text{Ind,Me}]\text{NiI}$.

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Figure 2.5 Crystal structure of $[\text{Tp}^{\text{Ind,Me}}]\text{NiBr}$. Thermal ellipsoids drawn at 30%. Hydrogen atoms omitted.
Table 2.9 Crystallographic Data for [Tp\textsuperscript{Ind,Me}]NiBr.

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Chapter 3
SYNTHESIS AND REACTIVITY OF [Tp\textsubscript{Ph,Me}]Ni(O\textsubscript{2})

3.1 Synthesis of [Tp\textsubscript{Ph,Me}]Ni(O\textsubscript{2})

The synthesis of a superoxide complex supported by the [Tp\textsubscript{tBu,Me}] ligand has been previously reported by William Green in the Riordan laboratory.\textsuperscript{39} This complex was synthesized by first preparing [Tp\textsubscript{tBu,Me}]NiBr from the reaction of K[Tp\textsubscript{tBu,Me}] and NiBr\textsubscript{2} in THF over the course of 5 days.\textsuperscript{40} The resulting purple solid was then reduced to [Tp\textsubscript{tBu,Me}]Ni(CN\textsubscript{tBu}) using a 0.3% sodium-mercury amalgam in the presence of tert-butyl isocyanide as a trapping agent. This nickel(I) complex was converted to the superoxide complex by purging a cold solution (\(-78^\circ\text{C}\)) of [Tp\textsubscript{tBu,Me}]Ni(CN\textsubscript{tBu}) in pentane with dry O\textsubscript{2} for several minutes followed by stirring under O\textsubscript{2} for 20 minutes.

This synthetic route was taken from the synthesis of [Tp\textsubscript{Ph,Me}]Ni(O\textsubscript{2}) developed by W. L. Green. [Tp\textsubscript{Ph,Me}]NiI was used as the nickel(II) starting material for reduction to the nickel(I) precursor. In this case, [Tp\textsubscript{Ph,Me}]NiI was chosen as the nickel(II) starting material since it showed faster and more efficient reduction than either the chloride or bromide analogues. [Tp\textsubscript{Ph,Me}]NiI was synthesized by a halide exchange reaction using [Tp\textsubscript{Ph,Me}]NiCl and 4 equivalents of NaI in acetone. The reaction solution was filtered to remove the NaCl salts as well as any [Tp\textsubscript{Ph,Me}]\textsubscript{2}Ni formed during the
previous reaction to synthesize $[\text{Tp}^{\text{Ph,Me}}]\text{NiCl}$. The solvent was removed and the residue was taken up in toluene before being filtered a second time to remove any remaining salt contaminants. After the toluene was removed, the resulting reddish-brown powder was washed with pentane and dried overnight.

$^1$H NMR spectra showed features characteristic of a Tp-supported nickel(II) complex with the pyrazole protons shifted far downfield to 75.1 ppm and the proton on the boron atom shifted upfield to -2.7 ppm (Figure 3.1).

![Figure 3.1](image)

**Figure 3.1** $^1$H NMR spectrum of $[\text{Tp}^{\text{Ph,Me}}]\text{NiI}$ recorded in C$_6$D$_6$. * indicates residual solvent signals. Inset shows diamagnetic region.

Electronic absorption spectroscopy of the nickel(II) complex shows an intense band at 520 nm ascribed to a LMCT transition in addition to a much less intense
ligand field transition at 960 nm consistent with a Tp-supported nickel(II) halide complex.

![UV-visible spectrum of [Tp\textsubscript{Ph,Me}]NiI recorded in toluene.](image)

**Figure 3.2** UV-visible spectrum of [Tp\textsubscript{Ph,Me}]NiI recorded in toluene.

[Tp\textsubscript{Ph,Me}]NiI was reduced in a similar manner to [Tp\textsubscript{tBu,Me}]NiBr; however, PPh\textsubscript{3} was used as the trapping ligand instead of tert-butyl isocyanide due to steric considerations. To a solution of [Tp\textsubscript{Ph,Me}]NiI and 1.2 equivalents of PPh\textsubscript{3} in toluene was added a 0.3% sodium-mercury amalgam. The reaction mixture was shaken for 8-10 minutes during which time a color change from dark red to bright yellow was observed. \textsuperscript{1}H NMR spectral analysis showed features characteristic of a Tp-supported nickel(I) complex as compared to the Tp\textsubscript{tBu,Me} complexes previously prepared. The pyrazole protons are paramagnetically shifted downfield to 13.9 ppm and the proton on the boron atom is shifted far downfield to 49.2 ppm, Figure 3.3. In addition, the
protons on the ortho position of the 3-phenyl substituent are shifted far upfield to -18.2 ppm consistent with an electron-rich low-valent nickel complex.

![Figure 3.3](image)

**Figure 3.3** $^1$H NMR spectrum of $[\text{Tp}^{\text{Ph,Me}}]\text{Ni(PPh}_3\text{)}$ recorded in C$_6$D$_6$. * indicates residual solvent signals.

$[\text{Tp}^{\text{Ph,Me}}]\text{Ni(PPh}_3\text{)}$ was then converted to $[\text{Tp}^{\text{Ph,Me}}]\text{Ni(CO)}$. This complex was sought for the synthesis of the superoxide complex since reaction of $[\text{Tp}^{\text{Ph,Me}}]\text{Ni(PPh}_3\text{)}$ with dry O$_2$ would likely oxidize the PPh$_3$ ligand interfering with formation of the desired complex. To prepare $[\text{Tp}^{\text{Ph,Me}}]\text{Ni(CO)}$, a solution of $[\text{Tp}^{\text{Ph,Me}}]\text{Ni(PPh}_3\text{)}$ in THF was purged with CO for several minutes followed by 10-20 minutes of stirring. The solution color changed from a bright yellow-orange (the orange tint due to the coordination of the THF to the metal center) to pale yellow. The $^1$H NMR spectrum showed features characteristic of a Tp-supported nickel(I) complex, similar to those
observed for [Tp^{Ph,Me}]Ni(PPh\textsubscript{3}). The resonance for the proton on the boron was shifted far downfield to 32.8 ppm while protons on the \textit{ortho} position of the 3-phenyl substituent were shifted upfield to -8.9 ppm, Figure 3.4.

![Figure 3.4](image)

**Figure 3.4** \textsuperscript{1}H NMR spectrum of [Tp^{Ph,Me}]Ni(CO) recorded in C\textsubscript{6}D\textsubscript{6}. * indicates residual solvent signals.

[Tp^{Ph,Me}]Ni(O\textsubscript{2}) was prepared from [Tp^{Ph,Me}]Ni(CO) by suspending the nickel(I) complex in pentane and purging the reaction vessel with dry O\textsubscript{2} for several minutes causing a color change from pale yellow to colorless with a mocha precipitate. After decanting off the pentane and washing the solid with several aliquots of pentane, a \textsuperscript{1}H NMR spectrum was obtained with spectral features similar to that of the spectrum for [Tp^{Bu,Me}]Ni(O\textsubscript{2}) and to that of the nickel(II) halide starting material, [Tp^{Ph,Me}]NiI, Figure 3.5. The pyrazole protons are paramagnetically shifted far
downfield to 34.9 ppm while the proton on the boron atom is shifted upfield to -1.8 ppm.

![Figure 3.5 1H NMR spectrum of [Tp^{Ph,Me}]Ni(O_2) recorded in C_6D_6. * indicates residual solvent signals.](image)

**Figure 3.5** 1H NMR spectrum of [Tp^{Ph,Me}]Ni(O_2) recorded in C_6D_6. * indicates residual solvent signals.

### 3.2 Thermal Stability and Decomposition Products of [Tp^{Ph,Me}]Ni(O_2)

The thermal stability of [Tp^{Ph,Me}]Ni(O_2) was assessed. While the complex was found to be stable for at least months in the solid state, it readily decomposed over the course of two days at room temperature in solution. When the solution temperature was elevated to 60°C, the complex fully decomposed after 24 hours, Figure 3.6. The decomposition products were identified as the oxygen metallacycle complex,
[Tp^{Ph,Me}_2]Ni, and a third product proposed to be the hydroxo complex, ([Tp^{Ph,Me}_2]Ni(μ-OH))_2, based on the previous work with [Tp^{tBu,Me}_2]Ni(O_2), which showed the decomposition products of that system to be the oxygen metallacycle complex and [Tp^{tBu,Me}_2]Ni(OH).^{41} ([Tp^{Ph,Me}_2]Ni(μ-OH))_2 is proposed to be a dinuclear complex based on a previously reported hydroxo complex prepared with a ligand of similar steric demands, namely Tp^{iPr,iPr}.^{42}

Figure 3.6 ¹H NMR spectra of [Tp^{Ph,Me}_2]Ni(O_2) after stirring in C_6D_6 at 60°C for (a) 0 hrs, (b) 1 hr, (c) 2 hrs, (d) 3 hrs, (e) 4 hrs, (f) 5 hrs, (g) 6 hrs, (h) 7 hrs, and (i) 24 hrs.
To aid in identifying ([Tp^{Ph,Me}]Ni(μ-OH))$_2$ among the decomposition products, the solution of decomposed [Tp^{Ph,Me}]Ni(O$_2$) was reacted with 2 equivalents of phenol forming the phenoxide complex, [Tp^{Ph,Me}]Ni(OPh). The reaction formed a product with spectral features perhaps consistent with that of the phenoxide complex, [Tp^{Ph,Me}]Ni(OPh), when compared to the independently prepared phenoxide complex, Figure 3.7. The signals in the $^1$H NMR spectrum of the reaction mixture were significantly shifted when compared to the independently prepared [Tp^{Ph,Me}]Ni(OPh) possibly due to the interaction of the metallacycle with the phenoxide complex, e.g. forming a [Tp^{Ph,Me}]Ni(OO)PhNi[Tp^{Ph,Me}] dimer. Additionally, LIFDI-MS confirmed the presence of [Tp^{Ph,Me}]Ni(OPh) in the reaction mixture along with the oxygen metallacycle and [Tp^{Ph,Me}] as the products, Figure 3.8.
Figure 3.7 $^1$H NMR spectra of (bottom to top) [Tp$^{\text{Ph,Me}}$]Ni(O$_2$) decomposition products, reaction of decomposition products with phenol, and independently prepared [Tp$^{\text{Ph,Me}}$]Ni(OPh) recorded in C$_6$D$_6$.

Figure 3.8 LIFDI-MS of reaction of [Tp$^{\text{Ph,Me}}$]Ni(O$_2$) decomposition products with phenol. Isotope patterns correspond to [Tp$^{\text{Ph,Me}}$] (541.2), oxygen metallacycle (556.1), and [Tp$^{\text{Ph,Me}}$]Ni(OPh) (634.2). Calculated spectrum for [Tp$^{\text{Ph,Me}}$]Ni(OPh) is shown in green.

In an effort to even further confirm the presence of ([Tp$^{\text{Ph,Me}}$]Ni(μ-OH))$_2$ as a decomposition product and to fully characterize it, several pathways to its independent synthesis were explored. [Tp$^{\text{Ph,Me}}$]NiCl was reacted with 1.2 equivalents of NaOH in anhydrous methanol. This reaction caused decomposition to free pyrazole ligand. When the same reaction was conducted in toluene, the nickel-containing product was [Tp$^{\text{Ph,Me}}$]$_2$Ni. Similarly, when tetrabutylammonium hydroxide was used in the reaction instead of NaOH, the reaction yielded metallacycle and [Tp$^{\text{Ph,Me}}$]$_2$Ni.
Since $[\text{Tp}^{\text{Ph,Me}}]\text{Ni(OPh)}$ had been prepared previously by a reaction of the presumed hydroxo complex in the decomposition solution with phenol, an attempt to reverse this reaction by hydrolyzing $[\text{Tp}^{\text{Ph,Me}}]\text{Ni(OPh)}$ with 1.1 equivalents of water was explored. This reaction resulted in the sole formation of $[\text{Tp}^{\text{Ph,Me}}]_2\text{Ni}$. A similar reaction with a substituted phenoxide complex, $[\text{Tp}^{\text{Ph,Me}}]\text{Ni(O-2,6-Me}_2\text{C}_6\text{H}_3)$, yielded identical results. Analogous hydrolysis reactions were attempted with the trityl alkoxide complex, $[\text{Tp}^{\text{Ph,Me}}]\text{Ni(OCPh}_3)$. Reacting $[\text{Tp}^{\text{Ph,Me}}]\text{Ni(OCPh}_3)$ with 1.1 equivalents of water resulted in the formation of $[\text{Tp}^{\text{Ph,Me}}]_2\text{Ni}$, similar to the results obtained for the phenoxide complexes.

Reaction of $[\text{Tp}^{\text{Ph,Me}}]\text{NiCl}$ with 1 equivalent of TIOH resulted in the formation of a new product with $^1\text{H NMR}$ spectral features not consistent with either the oxygen metallacycle or $[\text{Tp}^{\text{Ph,Me}}]_2\text{Ni}$. When the reaction solution was exposed to air, a rapid color change from pale yellow to green occurred and the $^1\text{H NMR}$ spectrum of the resulting green complex confirmed the rapid formation of $[\text{Tp}^{\text{Ph,Me}}]_2\text{Ni}$. Additionally, when the product from the reaction of $[\text{Tp}^{\text{Ph,Me}}]\text{NiCl}$ with TIOH was reacted with phenol, a spectrum was obtained with peaks similar to, but slightly shifted from, those of $[\text{Tp}^{\text{Ph,Me}}]\text{Ni(OPh)}$, Figure 3.9.
Figure 3.9 $^1$H NMR spectra of (bottom to top) [Tp$^{\text{Ph,Me}}$]NiCl, the reaction of [Tp$^{\text{Ph,Me}}$]NiCl with TIOH, the reaction of the product with phenol, and the reaction of the product with air recorded in C$_6$D$_6$.

3.3 Reactivity of [Tp$^{\text{Ph,Me}}$]Ni(O$_2$)

Previous work with [Tp$^{\text{tBu,Me}}$]Ni(O$_2$) showed that the compound can efficiently perform electrophilic oxidations as expected for metal-superoxo complexes.$^{43}$

[Tp$^{\text{tBu,Me}}$]Ni(O$_2$) readily oxidizes alkyl phosphines (PR$_3$, R = Me, Et, Cy) to the corresponding phosphine oxide resulting in the formation of [Tp$^{\text{tBu,Me}}$]NiOH as the metal product. Additionally, the reaction of 6 equivalents of [Tp$^{\text{tBu,Me}}$]Ni(O$_2$) with 9,10-dihydroanthracene oxidized the substrate to anthraquinone at elevated temperatures (60$^\circ$C) in 80-90% yield with a metal product ratio of 1:1 oxygen metallacycle and [Tp$^{\text{tBu,Me}}$]NiOH. Alternatively, the reaction of 2 equivalents of [Tp$^{\text{tBu,Me}}$]Ni(O$_2$) with 1,4-cyclohexadiene also resulted in the oxidation of the substrate.
at elevated temperatures (60°C) forming benzene, as opposed to the quinone, in 65-70% yield with a product ratio of 6:1 oxygen metallacycle to [Tp^{tBu,Me}NiOH].

Crystals of [Tp^{Ph,Me}Ni(O_2)] were grown by vapor diffusion of pentane into toluene. X-ray diffraction of the crystals and analysis of the bond lengths in the resulting structure led to conjecture about the reactivity of [Tp^{Ph,Me}Ni(O_2)] as compared to [Tp^{tBu,Me}Ni(O_2)]. Figure 3.10. Specifically, the O—O bond distance in [Tp^{tBu,Me}Ni(O_2)] (1.278 Å) is shorter than that of [Tp^{Ph,Me}Ni(O_2)] (1.330 Å).

Additionally, the nickel-oxygen bond lengths differ between the complexes. While the Ni—O bond distances are approximately the same in [Tp^{tBu,Me}Ni(O_2)] (Ni—O1 = 1.872 Å, Ni—O2 = 1.859 Å), one of the nickel-oxygen bond distances is shorter than the second nickel-oxygen bond distance in [Tp^{Ph,Me}Ni(O_2)] (Ni—O1 = 1.815 Å, Ni—O2 = 1.8708 Å). These bond distances are suggestive of a more reduced, and therefore, perhaps more reactive dioxygen moiety in [Tp^{Ph,Me}Ni(O_2)] as compared to [Tp^{tBu,Me}Ni(O_2)].
Figure 3.10 Structures of $[\text{Tp}^{\text{Bu,Me}}]\text{Ni(O}_2\text{)}$ and $[\text{Tp}^{\text{Ph,Me}}]\text{Ni(O}_2\text{)}$ with selected bond lengths as determined by X-ray diffraction.

3.3.1 Reactivity of $[\text{Tp}^{\text{Ph,Me}}]\text{Ni(O}_2\text{)}$ with PR$_3$ ($R = \text{Me, Et, Cy, Ph}$)

$[\text{Tp}^{\text{Ph,Me}}]\text{Ni(O}_2\text{)}$ was reacted with a series of alkyl and aryl phosphines. When $[\text{Tp}^{\text{Ph,Me}}]\text{Ni(O}_2\text{)}$ was reacted with triphenylphosphine, triphenylphosphine oxide was formed in 78% yield. Similarly, $[\text{Tp}^{\text{Ph,Me}}]\text{Ni(O}_2\text{)}$ oxidized tricyclohexylphosphine to tricyclohexylphosphine oxide in 66% yield. Smaller alkyl phosphines, trimethylphosphine and triethylphosphine, were oxidized to the corresponding phosphine oxides in quantitative yields, Figure 3.11. The major metal products from
these reactions were identified by $^1$H NMR spectroscopy as the oxygen metallacycle and $[\text{Tp}^{\text{Ph,Me}}]_2\text{Ni}$, Figure 3.12.

Figure 3.11 $^{31}$P NMR spectra of (bottom to top) PPh$_3$ stock solution, PPh$_3$ oxidation products, PCy$_3$ stock solution, PCy$_3$ oxidation products, PEt$_3$ stock solution, PEt$_3$ oxidation products, PMe$_3$ stock solution, PMe$_3$ oxidation products.
Figure 3.12 $^1$H NMR spectra of (bottom to top) paramagnetic metal products from the oxidation of PMe$_3$, PEt$_3$, PCy$_3$, and PPh$_3$ recorded in C$_6$D$_6$.

3.3.2 C-H Bond Activation by [Tp$^{Ph,Me}$]Ni(O$_2$)

The ability of [Tp$^{Ph,Me}$]Ni(O$_2$) to activate weak C-H bonds was explored through a series of experiments with substrates containing weak C-H bonds. [Tp$^{Ph,Me}$]Ni(O$_2$) was reacted with 0.5 equivalents of 9,10-dihydroanthracene at room temperature resulting in oxidation to anthraquinone in 4% yield and decomposition of [Tp$^{Ph,Me}$]Ni(O$_2$). The experiment was repeated at longer time intervals (48 and 144 hr).
at room temperature with an increase in yields to 7% and 15%, respectively. Since the optimum stoichiometry for the reaction of $\text{[Tp}^{\text{tBu,Me}}\text{Ni(O}_2\text{)}$ with 9,10-dihydroanthracene was deduced to be 6:1, the experiment with $\text{[Tp}^{\text{Ph,Me}}\text{NiO}_2\text{]}$ was repeated with 6 equivalents of $\text{[Tp}^{\text{Ph,Me}}\text{Ni(O}_2\text{)}$. When the reaction was conducted at room temperature, 9,10-dihydroanthracene was oxidized to anthraquinone in 2% yield. However, when the reaction temperature was increased to 60°C, the yield was increased to 7%, Figures 3.13 and 3.14.

Figure 3.13 Reaction of $\text{[Tp}^{\text{Ph,Me}}\text{Ni(O}_2\text{)}$ with 9,10-dihydroanthracene with reaction conditions (from bottom to top) 2 equivalents of $\text{[Tp}^{\text{Ph,Me}}\text{Ni(O}_2\text{)}$ for 144 hr at room temperature, 6 equivalents of $\text{[Tp}^{\text{Ph,Me}}\text{Ni(O}_2\text{)}$ for 96 hr at room temperature, 6 equivalents of $\text{[Tp}^{\text{Ph,Me}}\text{Ni(O}_2\text{)}$ for 24 hr at 60°C.
Figure 3.14 GC-MS of reaction products from the reaction of 2 equivalents of [Tp\textsubscript{Ph,Me}]Ni(O\textsubscript{2}) with 9,10-dihydroanthracene at room temperature for 24 hr. Top spectrum is 9,10-dihydroanthracene stock solution, bottom spectrum is solution after reaction showing peaks for both 9,10-dihydroanthracene and anthraquinone.

[Tp\textsubscript{Ph,Me}]Ni(O\textsubscript{2}) was reacted with 0.5 equivalents of 1,4-cyclohexadiene at room temperature for 24 hours. No reaction was forming either benzene or 1,4-cyclohexanedione as the oxidized product. Similar results were obtained when 0.5 equivalents of 1,4-cyclohexadiene was reacted with [Tp\textsubscript{Ph,Me}]Ni(O\textsubscript{2}) at 60°C, Figure 3.15. Additionally, reaction of 10 equivalents of 1,4-cyclohexadiene with [Tp\textsubscript{Ph,Me}]Ni(O\textsubscript{2}) afforded the same results as the reactions with 0.5 equivalents of 1,4-
cyclohexadiene. Reaction of \([\text{Tp}^{\text{Ph,Me}}\text{Ni(O}_2\text{)}] \) with the internal and terminal olefins, cyclohexene and styrene, did not result in oxidation of these unsaturated substrates.

![Figure 3.15](image)

**Figure 3.15** \(^1\text{H NMR spectra of reaction of [Tp}^{\text{Ph,Me}}\text{Ni(O}_2\text{)} \) with 0.5 equivalents of 1,4-cyclohexadiene recorded in toluene-d8. From bottom to top: 1,4-cyclohexadiene stock solution, reaction solution after 24 hrs at r.t., reaction solution after 24 hours at 60°C.

Analysis of the metal products from the C-H activation reactions showed similar product formation with varying ratios of products (Figure 3.16). The major products in all of the reactions were the oxygen metallacycle complex along with \(([\text{Tp}^{\text{Ph,Me}}\text{Ni(μ-OH)}])_2\). For the reaction of \([\text{Tp}^{\text{Ph,Me}}\text{Ni(O}_2\text{)}] \) with 9,10-dihydroanthracene, the product ratio is approximately 2:1 oxygen metallacycle to \(([\text{Tp}^{\text{Ph,Me}}\text{Ni(μ-OH)}])_2\) when the reaction was performed at room temperature with 2
equivalents of $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{O}_2)]$ and 6 equivalents of $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{O}_2)]$, respectively. This ratio shifts to approximately 1:1 when the reaction was conducted with 2 equivalents of $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{O}_2)]$ at 60°C. A similar trend is observed for the reaction of $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{O}_2)]$ with 1,4-cyclohexadiene. When the reaction was performed at room temperature with 2 equivalents of $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{O}_2)]$, the product ratio was approximately 3:1 oxygen metallacycle to $([\text{Tp}^{\text{Ph,Me}}\text{Ni}(\mu-\text{OH})])_2$. However, at 60°C with the same stoichiometry, the product ratio shifted to approximately 1:1. The product ratio for the reaction of $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{O}_2)]$ with cyclohexene and styrene was identical to that observed in the thermal decomposition of $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{O}_2)]$ consistent with the assertion that these substrates do not influence the thermal decomposition.
Figure 3.16 $^1$H NMR spectra of paramagnetic products from C-H bond activation reactions with $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{O}_2)]$ recorded in $\text{C}_6\text{D}_6$. From bottom to top: reaction with 1 eq. styrene, reaction with 1 eq. cyclohexene, reaction with $\frac{1}{2}$ equivalent of 1,4-cyclohexadiene at 60°C, reaction with $\frac{1}{2}$ equivalent of 1,4-cyclohexadiene at room temperature, reaction with $\frac{1}{2}$ equivalent of 9,10-dihydroanthracene at 60°C, reaction with 1/6 equivalent of 9,10-dihydroanthracene at room temperature, reaction with $\frac{1}{2}$ equivalent of 9,10-dihydroanthracene

3.3.3 Aldehyde Deformylation by $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{O}_2)]$

Since metal-peroxo complexes are most often considered nucleophilic, they have been shown to effectively promote aldehyde deformylation. Thus, the
deformylation of 2-phenylpropionaldehyde by $[\text{Tp}^{\text{Ph,Me}}\text{NiO}_2$ was explored.\textsuperscript{44} When the reaction was performed at room temperature for 24 hr, quantitative formation of acetophenone was observed by $^1\text{H}$ NMR spectroscopy, Figure 3.17. Additionally, the predominant metal product was identified as $[\text{Tp}^{\text{Ph,Me}}\text{Ni(COOH)}$ by comparison to the $^1\text{H}$ NMR spectrum of the independently prepared complex. The deprotonated starting material coordinated to the metal center, $[\text{Tp}^{\text{Ph,Me}}\text{Ni[CH}_3\text{(Ph)(COH)}$, was also eliminated as a possible product by $^1\text{H}$ NMR spectral comparison to the independently prepared complex, Figure 3.18.

![Figure 3.17](image-url)

**Figure 3.17** $^1\text{H}$ NMR spectra of the reaction of $[\text{Tp}^{\text{Ph,Me}}\text{Ni(O}_2$ with 2-phenylpropionaldehyde recorded in C\textsubscript{6}D\textsubscript{6}. From bottom to top: 2-phenylpropionaldehyde stock solution, reaction solution, acetophenone standard.
3.4 Summary

[Tp^{Ph,Me}]Ni(O_2) was synthesized using an analogous route to that developed by W. L. Green for the synthesis of [Tp^{Bu,Me}]Ni(O_2). The former complex was formed by the reaction of nickel(I) ([Tp^{Ph,Me}]Ni(CO)) with dry O_2. This nickel(I) starting material was synthesized by the reduction of a nickel(II) halide, [Tp^{Ph,Me}]NiI, using 0.3% sodium-mercury amalgam and PPh_3 as the trapping agent followed by the reaction of the resulting complex, [Tp^{Ph,Me}]Ni(PPh_3), with CO. Based on the X-ray crystal structure, [Tp^{Ph,Me}]Ni(O_2) was proposed to be more reactive than [Tp^{Bu,Me}]Ni(O_2).
since the O—O bond distance is longer indicating a more reduced oxygen moiety. Additionally, the O$_2$ binding pocket is more open in [Tp$^{\text{Ph,Me}}$]Ni(O$_2$) versus [Tp$^{\text{tBu,Me}}$]Ni(O$_2$) suggesting the former has increased reactivity since, from a steric consideration, the openness allows for a wider range of substrates to access the O$_2$ ligand.

[Tp$^{\text{Ph,Me}}$]Ni(O$_2$) is more reactive than [Tp$^{\text{tBu,Me}}$]Ni(O$_2$) for electrophilic oxidation of aryl and alkyl phosphines. While [Tp$^{\text{Ph,Me}}$]Ni(O$_2$) oxidizes PPh$_3$ in 78% yield, PCy$_3$ in 66% yield, and quantitatively in the cases of PMe$_3$ and PEt$_3$, [Tp$^{\text{tBu,Me}}$]Ni(O$_2$) oxidizes only alkyl phosphines (PEt$_3$, PMe$_3$, and PCy$_3$) in high yields. However, [Tp$^{\text{tBu,Me}}$]Ni(O$_2$) is much more efficient at activating weak C—H bonds than [Tp$^{\text{Ph,Me}}$]Ni(O$_2$). Under the same reaction conditions for the oxidation of 9,10-dihydroanthracene, reaction with [Tp$^{\text{tBu,Me}}$]Ni(O$_2$) results in 80-90% conversion to anthraquinone while reaction with [Tp$^{\text{Ph,Me}}$]Ni(O$_2$) results in only 15% conversion. Similarly, for reaction with 1,4-cyclohexadiene under the same reaction conditions, reaction with [Tp$^{\text{tBu,Me}}$]Ni(O$_2$) results in 65-70% conversion to benzene whereas reaction with [Tp$^{\text{Ph,Me}}$]Ni(O$_2$) did not result in any oxidation of 1,4-cyclohexadiene.

[Tp$^{\text{Ph,Me}}$]Ni(O$_2$) is incapable of oxidizing internal or terminal olefins. Both systems form the oxygen metallacycle and hydroxo complexes as the metal products and similar ratios are observed for the reaction of the superoxide complexes with 9,10-dihydroanthracene under the same reaction conditions (1:1).

[Tp$^{\text{Ph,Me}}$]Ni(O$_2$) is capable of aldehyde deformylation, a reaction typically attributed to metal-peroxo species.$^{44}$ [Tp$^{\text{Ph,Me}}$]Ni(O$_2$) quantitatively converts 2-
phenylpropionaldehyde to acetophenone at room temperature with the metal product identified as \([\text{Tp}^{\text{Ph,Me}}\text{Ni(COOH)}]\) by comparison of its spectroscopic features to an independently prepared sample. Overall, \([\text{Tp}^{\text{Ph,Me}}\text{Ni(O_2)}]\) presents an interesting reactivity profile that is similar to that of \([\text{Tp}^{\text{Bu,Me}}\text{Ni(O_2)}]\) in the electrophilic oxidation of phosphines yet differs on reactivity with weak C—H bonds as well as aldehyde deformylation. This result suggests that these reactions are dependent on ligand electronics to activate the O—O bond rather than the size of the binding pocket as determined by the steric bulk of the ligand.
Chapter 4

SYNTHESIS AND REACTIVITY OF $[\text{Tp}^{\text{Ph,Me}}\text{Ni}](\mu-\text{S}_2)$

4.1 Synthesis and Characterization of $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{SCH}_2\text{CH}_2)]$

While several Tp-supported metal dioxygen complexes are known, there are no nickel disulfide or nickel diselenide complexes reported employing the Tp ligand. As such, given the successful synthesis of $[\text{Tp}^{\text{Ph,Me}}\text{Ni}]^+$ and $[\text{Tp}^{\text{Ph,Me}}\text{Ni}]^{\text{II}}$ complexes, several synthetic routes were envisioned to prepare $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\mu-\text{S}_2)]$ and $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\mu-\text{Se}_2)]$. Reaction of $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{CO})]$ with $\frac{1}{4}$ equivalents of elemental sulfur ($\text{S}_8$) resulted in the formation of $[\text{Tp}^{\text{Ph,Me}}\text{Ni}]_2$ as determined by $^1\text{H}$ NMR spectroscopy. Similarly, reaction of $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{CO})]$ with $1/2$ equivalents of elemental selenium resulted in the formation of $[\text{Tp}^{\text{Ph,Me}}\text{Ni}]_2$.

Since the nickel(I) synthetic routes were unsuccessful, nickel(II) routes were explored using $[\text{Tp}^{\text{Ph,Me}}\text{Ni}]$ as the nickel(II) source. Reaction with 1 equivalent of either $\text{Na}_2\text{S}_2$ or $\text{Na}_2\text{Se}_2$ resulted in the formation of $[\text{Tp}^{\text{Ph,Me}}\text{Ni}]_2$ in both cases. However, reaction of $[\text{Tp}^{\text{Ph,Me}}\text{Ni}]$ with 2 equivalents of $\text{Na}_2\text{Se}$ resulted in the formation of $([\text{Tp}^{\text{Ph,Me}}\text{Ni}])_2(\mu-\text{Se})$. The formation of $([\text{Tp}^{\text{Ph,Me}}\text{Ni}])_2(\mu-\text{Se})$ was supported by diamagnetic features in the $^1\text{H}$ NMR spectrum due to spin coupling of
the nickel centers through the selenium bridge, Figure 4.1. Analogous features were observed in the synthesis of ([Tp\textsuperscript{Ph,Me}]Ni)\textsubscript{2}(μ-S) through a similar synthetic route using Na\textsubscript{2}S, Figure 4.2. The identity of the former product was further confirmed by electronic absorption spectroscopy which showed an intense LMCT band at 520 nm (ε = 7900 M\textsuperscript{-1}cm\textsuperscript{-1}) similar to that observed for [Ni(Me\textsubscript{4}[12]aneN\textsubscript{4})\textsubscript{2}(μ-Se)]\textsuperscript{2+} (525 nm) and by LIFDI-MS, which showed a parent ion peak at m/z=1162 and an isotope pattern consistent with the parent ion.\textsuperscript{29}

\textbf{Figure 4.1} \textsuperscript{1}H NMR spectrum of ([Tp\textsuperscript{Ph,Me}]Ni)\textsubscript{2}(μ-Se) recorded in C\textsubscript{6}D\textsubscript{6}.
Figure 4.2 $^1$H NMR spectrum of ([Tp$_{\text{Ph,Me}}$]Ni)$_2$(μ-S) recorded in C$_6$D$_6$. 
Figure 4.3 LIFDI-MS of ([Tp$^{Ph,Me}$]Ni)$_2$(μ-Se) (top: experimental, bottom: calculated)
In previous reports, decomposition of a trityl thiolate metal complex led to formation of a bridging disulfide complex.\textsuperscript{26,53} This synthetic strategy was employed in the present case by reacting $[\text{Tp}^{\text{Ph,Me}}]\text{NiI}$ with NaSCPh\textsubscript{3} forming $[\text{Tp}^{\text{Ph,Me}}]\text{Ni(SCPH}_3\text{).}$ The resulting product was characterized; its electronic absorption spectrum compares well to that of Cho’s trityl thiolate, $[\text{PhTt}^{\text{tBu}}]\text{Ni(SCPH}_3\text{).}$\textsuperscript{4}

Electronic absorption spectroscopy of $[\text{PhTt}^{\text{tBu}}]\text{Ni(SCPH}_3\text{)}$ showed bands at 391 nm and 510 nm assigned to charge transfer bands along with a band at 855 nm assigned to a ligand field transition. $[\text{Tp}^{\text{Ph,Me}}]\text{Ni(SCPH}_3\text{)}$ shows similar bands at 485 nm and 925 nm assigned to a charge transfer band and ligand field transition, respectively.

Similarly, the features in the $^1$H NMR spectrum are assignable to that of $[\text{Tp}^{\text{Ph,Me}}]\text{Ni(SCPH}_3\text{)}$ and analogous to those of Cho’s complex. The $\alpha$-phenyl protons on the SCPH\textsubscript{3} moiety are shifted to 30.2 ppm and the $m$-phenyl and $p$-phenyl protons are shifted to 8.6 ppm in the $^1$H NMR spectrum for $[\text{PhTt}^{\text{tBu}}]\text{Ni(SCPH}_3\text{)}$ while the same protons are shifted to 35.1 ppm, 10.1 ppm, and 8.9 ppm, respectively, in the $^1$H NMR spectrum for $[\text{Tp}^{\text{Ph,Me}}]\text{Ni(SCPH}_3\text{)}$. The product was confirmed by LIFDI-MS analysis which showed a parent ion peak at $m/z = 816$ with the expected isotope pattern, Figure 4.4.
Figure 4.4 $^1$H NMR spectrum of $[\text{Tp}^{\text{Ph,Me}}]\text{Ni(SCPh}_3\text{)}$ recorded in C$_6$D$_6$. 
Figure 4.5 LIFDI-MS of \([\text{Tp}^{\text{Ph,Me}}\text{Ni(SCPH}_3)]\) (top: calculated, bottom: experimental)

\([\text{Tp}^{\text{Ph,Me}}\text{Ni(SCPH}_3]\) was heated in deuterated benzene for 24 hr at various temperatures and monitored by \(^1\text{H} \) NMR spectroscopy. After heating at 40°C for 24 hr, minimal decomposition was observed and the new features were consistent with the formation of \([\text{Tp}^{\text{Ph,Me}}\text{Ni}]_2\). Similar decomposition was observed at 60°C after 24 hr with a few new paramagnetic features observed, specifically at \(\delta=72\) and 75. After heating at 80°C for 24 hr, 50% of the complex had decomposed into \([\text{Tp}^{\text{Ph,Me}}\text{Ni}]_2\) as
well as a mixture of other, unidentified paramagnetic products, Figure 4.6. LIFDI-MS showed the formation of a number of sulfur-containing complexes, including

\[ \text{[Tp}^{\text{Ph,Me}}\text{]}_2\text{Ni(S}_2\text{)}, \text{[Tp}^{\text{Ph,Me}}\text{]}_2\text{Ni(S)}, \text{and [Tp}^{\text{Ph,Me}}\text{]}\text{Ni(S}_2\text{)}, \text{Figure 4.7.} \]

**Figure 4.6** \(^1\text{H}\) NMR spectra of the thermal decomposition of \([\text{Tp}^{\text{Ph,Me}}\text{]}\text{Ni(SCPh}_3\text{)}\) in \(\text{C}_6\text{D}_6\). From top to bottom, spectra of \([\text{Tp}^{\text{Ph,Me}}\text{]}\text{Ni(SCPh}_3\text{)}\), \([\text{Tp}^{\text{Ph,Me}}\text{]}\text{Ni(SCPh}_3\text{)}\) after heating for 40°C at 24 hr, \([\text{Tp}^{\text{Ph,Me}}\text{]}\text{Ni(SCPh}_3\text{)}\) after heating for 60°C at 24 hr, \([\text{Tp}^{\text{Ph,Me}}\text{]}\text{Ni(SCPh}_3\text{)}\) after heating for 80°C at 24 hr.
Figure 4.7 LIFDI-MS of thermal decomposition products of $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{SCPh}_3)]$ after heating at 80°C for 24 hr.

In previous work conducted by Jessica Wallick in the Riordan laboratory, $[\text{Ni}(\text{Me}_4[12\text{aneN}_4]\text{SeH})(\text{PF}_6)]$, was converted to $[\text{Ni}(\text{Me}_4[12\text{aneN}_4])_2(\mu-\eta^2:\eta^2-\text{Se}_2)](\text{PF}_6)_2$, by reaction with the 2,4,6-tri-tert-butylphenoxy radical. A similar strategy was undertaken to synthesize $[[\text{Tp}^{\text{Ph,Me}}\text{Ni}]_2(\text{S}_2)]$. $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{SH})]$ was prepared from the reaction of $[\text{Tp}^{\text{Ph,Me}}\text{NiI]}$ with 2 equivalents of NaSH in toluene. The resulting solution was filtered and the product was crystallized by vapor diffusion of pentane into toluene. The $^1\text{H}$ NMR spectrum contained features consistent with a nickel(II) complex, Figure 4.8. Electronic absorption spectra displayed features at 330 nm ($\epsilon = 8130 \text{ M}^{-1}\text{cm}^{-1}$), 410 nm ($\epsilon = 8320 \text{ M}^{-1}\text{cm}^{-1}$), 490 nm ($\epsilon = 4370 \text{ M}^{-1}\text{cm}^{-1}$), and 910 nm ($\epsilon = 250 \text{ M}^{-1}\text{cm}^{-1}$). LIFDI-MS confirmed the identity of the product with the
parent ion peak found at \( m/z = 574 \) and an isotope pattern consistent with the
elemental composition, Figure 4.9. Single crystal X-ray diffraction revealed a structure
with a distorted tetrahedral geometry \( (\tau_4 = 0.587) \), Figure 4.10. The \( \text{Ni}^-\text{S} \) bond
distance is \( 2.2137(5) \) Å, similar to that of previously reported high-spin nickel(II)
complexes. 29, 32, 33, 45

Figure 4.8 \(^1\text{H NMR spectrum of \([Tp^{\text{Ph,Me}}]\text{Ni(SH)}\) recorded in C\(_6\)D\(_6\).}
Figure 4.9 LIFDI-MS of $[\text{Tp}^{\text{Ph,Me}}]\text{Ni(SH)}$ (top: experimental, bottom: calculated).
Figure 4.10 Molecular structure of [Tp^{Ph,Me}]NiSH. Thermal ellipsoids drawn at 30%. Hydrogen atoms omitted except for S—H.

Synthesis of [Tp^{Ph,Me}]Ni(S₂) from the S-atom donor, ethylene sulfide, was attempted. When [Tp^{Ph,Me}]Ni(PPh₃) was reacted with one equivalent of ethylene sulfide at 40°C for 24 hr, an immediate color change from yellow to dark red was observed and a paramagnetic product feature appeared at 68 ppm in the ¹H NMR spectrum along with features consistent with [Tp^{Ph,Me}]Ni(PPh₃). When reacted with 3 equivalents of ethylene sulfide under the same conditions, complete conversion to the paramagnetic product was observed, Figure 4.11. Additionally, reaction of [Tp^{Ph,Me}]Ni(CO) with 3 equivalents of ethylene sulfide under the same conditions led
to the product in similar yields. Single crystal X-ray diffraction showed the product to be $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{SCH}_2\text{CH}_2)]$ with $\tau_5=0.645$ indicating a distorted trigonal bipyramidal geometry, Figure 4.12. Interestingly, the $^1\text{H NMR}$ spectral features are similar to a nickel(II) complex despite the product perhaps being assigned as nickel(III). The magnetic moment of $\mu_{\text{eff}} = 1.75 \mu_\text{B}$ is consistent with one unpaired electron, i.e. $S = \frac{1}{2}$, doublet state. Low-temperature optical cryostat experiments did not reveal intermediates during the course of the reaction as evidenced by the decrease in the starting material feature at 410 nm followed by the increase of the product features at 385 nm and 480 nm, Figure 4.13.

**Figure 4.11** $^1\text{H NMR}$ spectrum of $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{SCH}_2\text{CH}_2)]$ recorded in C$_6$D$_6$.  

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Figure 4.12 Molecular structure of $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{SCH}_2\text{CH}_2)]$. Thermal ellipsoids drawn at 30%. Hydrogen atoms omitted.
Figure 4.13 Low-temperature optical cryostat experiment to monitor the reaction of [Tp^Ph,Me]Ni(PPh3) with ethylene sulfide from -90°C to -40°C over the course of 5 hr recorded in toluene.

Electrochemical studies of [Tp^Ph,Me]Ni(SCH2CH2) showed a quasi-reversible reduction peak at -2.0 V (vs. ferrocene/ferrocenium) as well as a smaller non-reversible reduction peak at -1.5 V. Similarly, a non-reversible oxidation peak was observed at 0.44 V, Figure 4.14. The very negative reduction potential suggests a highly stable nickel(III) species that is relatively inert to reduction.
Figure 4.14 Cyclic voltammogram of $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{SCH}_2\text{CH}_2)]$ measured in THF with 0.1M NBu$_4$PF$_6$ as the supporting electrolyte. Scan rate: 100 mV/s. Ferrocene/ferrocenium was used as the internal reference.

Electron paramagnetic resonance (EPR) spectral experiments were conducted to further aid in elucidating the electronic structure of the complex. The spectrum of $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{SCH}_2\text{CH}_2)]$ at 10K showed an isotropic signal centered at 3385 G with $g = 1.98$. This signal shape is much different than the anisotropic signals typically observed for Ni-based paramagnets.\textsuperscript{27,56} The $g$-value associated with this spectrum is also lower than those previously reported for Ni(III) complexes. This data suggests an alternative electronic structure with a ligand-based radical, for example, Ni(II)$'$S$^\cdot$. 

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Further studies, including temperature-dependent EPR measurements and DFT calculations, are needed to confirm this assignment.

Figure 4.15. EPR spectrum of $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{SCH}_2\text{CH}_2)]$ recorded at 10 K and 20 dB.

Due to the success of the ring opening of ethylene sulfide by $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{PPh}_3)]$, an analogous reaction was performed with tetrahydrothiophene. When $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{CO})]$ was reacted with 3 equivalents of tetrahydrothiophene for 24 hr at room temperature, partial decomposition to pyrazole was observed along with features consistent with starting material, Figure 4.16. When $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{CO})]$ was reacted with 3 equivalents of tetrahydrothiophene for 48 hr at room temperature, decomposition to pyrazole was observed. When the reaction was conducted at elevated temperatures, total decomposition to the same product was observed in less than 24 hours.
The results of the experiments with tetrahydrothiophene indicated that ring strain is likely a dominant driving force in the ring opening reaction forming $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{SCH}_2\text{CH}_2)]$. To explore the effects of sterics on the reaction, $[\text{Tp}^{\text{Ph,Me}}\text{Ni(CO)}]$ and $[\text{Tp}^{\text{Ph,Me}}\text{Ni(PPh}_3)]$ were reacted with 3 equivalents of propylene sulfide for 24 hr at room temperature. In both cases, complete conversion was observed showing similar features to those of $[\text{Tp}^{\text{Ph,Me}}\text{Ni(SCH}_2\text{CH}_2)]$ in the $^1\text{H}$ NMR spectrum, Figure 4.17. A broadened feature was detected at 4.3 ppm which is ascribed
to the methyl protons of the methyl group on the thiametallacycle group due to an integration of 3H.

**Figure 4.17** $^1$H NMR of [Tp$^{\text{Ph,Me}}$]NiS(CH$_2$)$_2$CH$_3$ recorded in C$_6$D$_6$.

The electronic absorption spectra of [Tp$^{\text{Ph,Me}}$]Ni(SCH$_2$CH$_2$) and [Tp$^{\text{Ph,Me}}$]Ni(SCH$_2$CH$_2$CH$_3$) contain very similar features. [Tp$^{\text{Ph,Me}}$]Ni(SCH$_2$CH$_2$) shows charge transfer bands at 290 nm ($\varepsilon = 23,680$ M$^{-1}$cm$^{-1}$), 385 nm ($\varepsilon = 7,040$ M$^{-1}$cm$^{-1}$), and 475 nm ($\varepsilon = 13,120$ M$^{-1}$cm$^{-1}$) as well as a ligand field transition at 1020 nm ($\varepsilon = 620$ M$^{-1}$cm$^{-1}$). Similarly, [Tp$^{\text{Ph,Me}}$]Ni(SCH$_2$CH$_2$CH$_3$) shows charge transfer bands at 285 nm ($\varepsilon = 33,210$ M$^{-1}$cm$^{-1}$), 385 nm (6,740 M$^{-1}$cm$^{-1}$), and 475 nm (13,950 M$^{-1}$cm$^{-1}$) as
well as a ligand field transition at 1020 nm (780 M$^{-1}$cm$^{-1}$). IR spectra show B-H stretches for [Tp$^{\text{Ph,Me}}$]Ni(SCH$_2$CH$_2$) and [Tp$^{\text{Ph,Me}}$]Ni(SCH$_2$CH$_2$CH$_3$) at 2542 cm$^{-1}$ and 2549 cm$^{-1}$, respectively. Surprisingly, and in stark contrast to [Tp$^{\text{Ph,Me}}$]Ni(SCH$_2$CH$_2$), [Tp$^{\text{Ph,Me}}$]Ni(SCH$_2$CH$_2$CH$_3$) decomposed in solution to nickel sulfide and pyrazole readily over 24 hrs. Efforts to isolate single crystals of [Tp$^{\text{Ph,Me}}$]Ni(SCH$_2$CH$_2$CH$_3$) suitable for X-ray diffraction analysis proved unsuccessful. The $^1$H NMR spectral data are consistent with formation of a single regio isomer, namely the one with the methyl group attached to the β-carbon. In this isomer, the thermodynamically stronger Ni—C(primary) vis-à-vis Ni—C(secondary) bond is formed. Further studies are warranted to unequivocally deduce the identity of the regio isomer.

The ring opening reaction was also explored with [Tp$^{\text{Bu,Me}}$]Ni(CN$^\text{Bu}$) and [Tp$^{\text{Bu,Me}}$]Ni(CO) to assess the effect of the labile ligand on the reaction. The reactions of [Tp$^{\text{Bu,Me}}$]Ni(CN$^\text{Bu}$) and [Tp$^{\text{Bu,Me}}$]Ni(CO) with excess (10 equivalents) ethylene sulfide resulted in the formation of product after reaction at 60°C for 3 days. However, $^1$H NMR spectroscopy showed two features in the paramagnetic region at 76 ppm and 80 ppm, consistent with two products, Figure 4.18. The reactions of [Tp$^{\text{Bu,Me}}$]Ni(CN$^\text{Bu}$) and [Tp$^{\text{Bu,Me}}$]Ni(CO) with excess (10 equivalents) propylene sulfide under the same conditions resulted in similar products as identified by $^1$H NMR spectroscopy, Figure 4.19. These products are less stable than [Tp$^{\text{Ph,Me}}$]Ni(SCH$_2$CH$_2$CH$_3$), readily decomposing in solution in less than 24 hr to nickel
sulfide and pyrazole, even at low temperatures. The products could not be definitively identified. However, the results of these reactions show that not only does the increased steric bulk of the ligand destabilize the product, it also slows the reaction rate.

**Figure 4.18** $^1$H NMR spectrum recorded in C$_6$D$_6$ of product(s) from reaction of [Tp$_{tBu,Me}$]Ni(CN$_{tBu}$) with ethylene sulfide. * indicates unreacted [Tp$_{tBu,Me}$]Ni(CN$_{tBu}$).
Figure 4.19 $^1$H NMR spectrum recorded in C$_6$D$_6$ of product from reaction of [Tp$^{Bu,Me}$]Ni(CN$^{Bu}$) and propylene sulfide.

Since the Tp supported nickel(I) complexes inserted into 3-membered cyclic thioethers, the analogous reaction was explored with an epoxide. However, attempts to ring open styrene oxide with [Tp$^{Ph,Me}$]Ni(CO) under analogous conditions were unsuccessful, resulting only in the decomposition of [Tp$^{Ph,Me}$]Ni(CO) to pyrazole along with a number of unidentified paramagnetic products, Figure 4.20. Similarly disappointing results were obtained when [Tp$^{Ph,Me}$]Ni(CO) was reacted with 1,4-dioxane. Reactions conducted with cyclic ethers rather than cyclic thioethers are presumed not to proceed since the bond strength of C—O bonds is much higher than that of C—S bonds (91 kcal/mol versus 80 kcal/mol).
Figure 4.20 $^1$H NMR spectra of (from bottom to top) $[\text{Tp}^{\text{Ph,Me}}\text{Ni(CO)}]$, the reaction of $[\text{Tp}^{\text{Ph,Me}}\text{Ni(CO)}]$ with 3 equivalents of styrene oxide at room temperature for 24 hours, and the reaction of $[\text{Tp}^{\text{Ph,Me}}\text{Ni(CO)}]$ with 3 equivalents of 1,4-dioxane at room temperature for 24 hours.
4.2 Reactivity of $\text{[Tp}^{\text{Ph,Me}}\text{Ni(SCH}_2\text{CH}_2\text{]}$)

4.2.1 Reactivity of $\text{[Tp}^{\text{Ph,Me}}\text{Ni(SCH}_2\text{CH}_2\text{]}$ with CO

Thianickelacycles have been reported by Hillhouse and coworkers in the reaction of [(bpy)Ni(cod)] with ethylene sulfide, propylene sulfide, or thietane.$^{46}$ These thianickelacycles were shown to undergo CO insertion followed by reductive elimination forming the corresponding thiolactone analogous to the biosynthesis of acetyl coenzyme A.$^{54}$

$\text{[Tp}^{\text{Ph,Me}}\text{Ni(SCH}_2\text{CH}_2\text{]}$ was reacted with excess CO with the objective of forming the $\alpha$-lactone. A solution of $\text{[Tp}^{\text{Ph,Me}}\text{Ni(SCH}_2\text{CH}_2\text{]}$ was chilled to -78$^\circ$C and purged with CO for several minutes. The solution was then warmed to room temperature and stirred under 1 atm of CO for 24 hr. The $^1$H NMR spectrum showed several new paramagnetic features consistent with the formation of $\text{[Tp}^{\text{Ph,Me}}\text{Ni} \text{SCH}_2\text{CH}_2\text{]}$ (54 ppm) and another unidentified paramagnetic product, Figure 4.21. There was no evidence for formation of either $\text{[Tp}^{\text{Ph,Me}}\text{Ni(CO)}$ or the $\alpha$-lactone.
4.2.2 Reaction of $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{SCH}_2\text{CH}_2)]$ with Phosphines

Since the sulfur atom is attached to a nickel(III) center, it is likely to be more electron deficient and thus, electrophilic as it transfers its electron density to the nickel. As such, this sulfur is anticipated to react with small alkyl phosphines forming the corresponding phosphine sulfide. $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{SCH}_2\text{CH}_2)]$ was reacted with $\text{PEt}_3$ in deuterated benzene and the reaction progress was monitored by $^{31}\text{P}$ and $^1\text{H}$ NMR spectroscopies. After 24 hr at room temperature, no reaction was observed. However, under the same reaction conditions, $\text{PMe}_3$ was converted to the protonated
phosphonium salt, [PMe$_3$Et]$^+$ in quantitative yields as deduced by $^{31}$P NMR spectroscopy, Figure 4.22. The identity of the organic product was confirmed by GC-MS ($m/z = 105$), Figure 4.23. This reaction occurs presumably as a result of the phosphine attacking the nucleophilic carbon adjacent to the sulfur atom leading to ring opening followed by rapid decomposition to nickel sulfide and pyrazole.

**Figure 4.22** $^{31}$P NMR spectra of (bottom to top) PMe$_3$ stock solution and reaction of [Tp$^{Ph,Me}$]Ni(SCH$_2$CH$_2$) with PMe$_3$ recorded in C$_6$D$_6$.  

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Figure 4.23 GC-MS of reaction of $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{SCH}_2\text{CH}_2)]$ with PMe$_3$. Parent ion peak for $[\text{PMe}_3\text{Et}]^+$ is found at $m/z = 105$.

Alternatively, reaction of $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{SCH}_2\text{CH}_2)]$ with methyl iodide would result in the formation of the ring opened product, $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{CH}_2)_2\text{SCH}_3]$, due to the nucleophilic character of the sulfur. When 1 equiv. of methyl iodide was reacted with $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{SCH}_2\text{CH}_2)]$, a color change from red to blue-green was observed. The $^1$H NMR spectrum of the solution showed the formation of $[\text{Tp}^{\text{Ph,Me}}]\text{Ni}_2$ (54 ppm) as well as a few other unidentified paramagnetic products, Figure 4.24. LIFDI-MS showed no evidence of the target product, Figure 4.25.
Figure 4.24 $^1$H NMR spectra of (bottom to top) $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{SCH}_2\text{CH}_2)]$ and the reaction of $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{SCH}_2\text{CH}_2)]$ with methyl iodide recorded in C$_6$D$_6$. 
In an analogous reaction, \(^{n}\text{BuLi}\) is expected to open the thianickelacycle at the carbon atom adjacent to the nickel forming \([\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{SCH}_2\text{CH}_2)]\). When \([\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{SCH}_2\text{CH}_2)]\) was reacted with 1 equiv. of \(^{n}\text{BuLi}\) for 24 hr at room temperature, the solution bleached and a dark precipitate formed. Based on previously published work, it is conjectured that the precipitate could be the nickel dimer,
[Ni(S(CH$_2$)$_2$)$_2$Bu]$_2$, given the multiplet seen at 1.75 ppm and singlet at 1.07 ppm with integrations consistent with the CH$_2$ groups adjacent to the sulfur atom and the CH$_3$ group at the end of the chain, respectively.$^{47}$ The $^1$H NMR spectrum showed a major product to be Li[Tp$^{\text{Ph,Me}}$], Figure 4.26.

Figure 4.26 $^1$H NMR spectra of (bottom to top) [Tp$^{\text{Ph,Me}}$]Ni(SCH$_2$CH$_2$)$_2$ and the reaction of [Tp$^{\text{Ph,Me}}$]Ni(SCH$_2$CH$_2$)$_2$ with $^n$BuLi.

4.2.3 Reactivity of [Tp$^{\text{Ph,Me}}$]Ni(SCH$_2$CH$_2$)$_2$ with O$_2$

Since [Tp$^{\text{Ph,Me}}$]Ni(SCH$_2$CH$_2$)$_2$ contains nickel(III), it is unlikely to undergo further metal-based oxidation. However, the sulfur atom of the thianickelacycle could possibly be oxidized thereby opening the thianickelacycle resulting in the formation of
an oxidized sulfur product either bound or unbound to the metal center. To test this hypothesis, \([Tp^{Ph,Me}]\text{Ni(SCH}_2\text{CH}_2)\) was reacted with dry O\(_2\) over the course of several days. The starting material remained along with some decomposition products (Figure 4.26). Interestingly, a feature consistent with \([Tp^{Ph,Me}]\text{Ni(O}_2\) (35 ppm) were observed after reaction for 24 hr and persisted even over the course of 11 days. No sulfur oxidation products were observed by LIFDI-MS, Figure 4.27.

**Figure 4.27** 
\(^1\text{H NMR spectra of (from bottom to top) }[Tp^{Ph,Me}]\text{Ni(SCH}_2\text{CH}_2)\text{, reaction of }[Tp^{Ph,Me}]\text{Ni(SCH}_2\text{CH}_2)\text{ with O}_2\text{ after 24 hours at room temperature, reaction of }[Tp^{Ph,Me}]\text{Ni(SCH}_2\text{CH}_2)\text{ with O}_2\text{ after 2 days at room temperature, reaction of }[Tp^{Ph,Me}]\text{Ni(SCH}_2\text{CH}_2)\text{ with O}_2\text{ after 4 days at room temperature, and reaction of }[Tp^{Ph,Me}]\text{Ni(SCH}_2\text{CH}_2)\text{ with O}_2\text{ after 11 days at room temperature recorded in C}_6\text{D}_6.\)
Figure 4.28 LIFDI-MS of low mass species from the reaction of 
\([\text{Tp}^{\text{Ph,Me}}\text{Ni(SCH}_2\text{CH}_2])\) with \(O_2\) (top: experimental, bottom: calculated spectrum of \(H_2SO_4\)).

4.3 Summary

Attempts to synthesize \([\text{Tp}^{\text{Ph,Me}}\text{Ni(S}_2])\) and \([\text{Tp}^{\text{Ph,Me}}\text{Ni(Se}_2])\) were undertaken to provide sulfur and selenium analogs of \([\text{Tp}^{\text{Ph,Me}}\text{Ni(O}_2])\). Conventional nickel(I) routes and nickel(II) metathesis routes proved unproductive. Reaction of \([\text{Tp}^{\text{Ph,Me}}\text{Ni(PPh}_3])\)
with an S-atom donor, ethylene sulfide, resulted in the formation of a ring opened adduct, $\text{[Tp}^{\text{Ph,Me}}\text{Ni(SCH}_2\text{CH}_2\text{)}$]. This novel complex shows interesting properties including a magnetic moment and redox properties consistent with a nickel(III) complex, while exhibiting a $^1\text{H}$ NMR spectrum consistent with previously reported nickel(II) complexes supported by Tp ligand. The EPR signal recorded at 10K is suggestive of a ligand-based radical and thus, a Ni(II)S• formulation must be considered. Reaction with propylene sulfide resulted in the formation of $\text{[Tp}^{\text{Ph,Me}}\text{Ni(SCH}_2\text{CH}_2\text{)}$CH$_3\text{)}$, which showed similar spectral properties to $\text{[Tp}^{\text{Ph,Me}}\text{Ni(SCH}_2\text{CH}_2\text{)}$. However, the former complex was unstable in solution, readily decomposing after 24 hr to pyrazole and nickel sulfide. Attempts to synthesize the corresponding thianickelacycle using tetrahydrothiophene were unsuccessful indicating that ring strain is a crucial driving force in the reaction of $\text{[Tp}^{\text{Ph,Me}}\text{Ni(PPh}_3\text{)}$ with ethylene sulfide and propylene sulfide. Reaction of $\text{[Tp}^{\text{Bu,Me}}\text{Ni(CN}^\text{Bu})$ and $\text{[Tp}^{\text{Bu,Me}}\text{Ni(CO)$ with ethylene sulfide and propylene sulfide showed slow formation of two paramagnetic products. However, the lack of stability of these products in solution, even at low temperatures, precluded definitive characterization. The slow reaction rate and the lack of stability of the products implicate the effects of the steric bulk of the ligand on the reaction leading to thianickelacycle.

$\text{[Tp}^{\text{Ph,Me}}\text{Ni(SCH}_2\text{CH}_2\text{)}$ was incapable of forming the corresponding α-lactone by CO insertion followed by reductive elimination, a reaction common to similar
nickel(II) complexes reported by Hillhouse. Indeed, $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{SCH}_2\text{CH}_2)]$ does not react with CO. However, reaction of PMe$_3$ with $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{SCH}_2\text{CH}_2)]$ revealed the formation of the phosphonium, $[\text{PMe}_3\text{Et}]^+$. When the same reaction was performed with PEt$_3$, no reaction was observed indicating that the size of the PR$_3$ substrate with this particular complex is crucial to the course of the reaction. When $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{SCH}_2\text{CH}_2)]$ was reacted with methyl lithium or $^n$BuLi in an effort to open the thianickelacycle at the carbon atom adjacent to the nickel center, the reactions resulted only in decomposition. Reaction of $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{SCH}_2\text{CH}_2)]$ with dry O$_2$ did not result in oxidation of the thianickelacycle. However, features consistent with $[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{O}_2)]$ were observed during the decomposition of the complex in the presence of O$_2$ indicating a ligand exchange of $\text{S(CH}_2\text{)_2}$ and O$_2$ in solution.

$[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{SCH}_2\text{CH}_2)]$, a novel nickel(III) complex has a wide range of applications to understanding nickel chemistry, including serving as a model for catalytic cross-coupling reactions.$^{49}$ Further reactivity studies with this complex could provide insight into a possible substrate scope for reaction with the thianickelacycle to synthesize novel organic and organometallic products.
Chapter 5

SYNTHESIS OF [Tp\textsuperscript{Fc,Me}]\textbf{AND} [Tp\textsuperscript{Ind,Me}]-SUPPORTED NICKEL COMPLEXES

5.1 Synthesis of [Tp\textsuperscript{Fc,Me}]Ni Halide Complexes

Certain Tp ligands undergo ligand activation when used to form metal dioxygen complexes.\textsuperscript{19, 20, 21} Recently, a ferrocenyl-substituted trispyrazolylborate ligand was synthesized by Eric Sirianni in the Theopold group in an attempt to preclude such decomposition pathways.\textsuperscript{50} Subsequently, Daniel Cummins in the Theopold group has performed initial experiments to metallate this ligand with cobalt and iron. Further, reduction of the resulting complexes to their M(I) forms is being pursued in an effort to form dioxygen complexes supported by this new ligand.

Due to the success of the recent work, an analogous synthetic route to that of the [Tp\textsuperscript{Ph,Me}]NiX complexes was undertaken in an effort to synthesize the halide complexes, [Tp\textsuperscript{Fc,Me}]NiCl, [Tp\textsuperscript{Fc,Me}]NiBr, and [Tp\textsuperscript{Fc,Me}]NiI. [Tp\textsuperscript{Fc,Me}]NiCl was synthesized from the reaction of [Tp\textsuperscript{Fc,Me}]Tl with 1.2 equivalents of anhydrous NiCl\textsubscript{2} in THF at room temperature for 24 hr. The reaction solution underwent a distinct color change from orange to red. \textsuperscript{1}H NMR spectral features were consistent with the formation of the nickel(II) halide complex, Figure 5.1. The electronic absorption
spectrum of the complex contained a band at 480 nm ascribed to a LMCT transition in addition to bands at 815 nm and 930 nm ascribed to a ligand field transition and charge transfer from the ferrocenyl group to the ligand, respectively, Figure 5.2.

Figure 5.1 $^1$H NMR spectrum of $[\text{Tp}^{\text{Fc},\text{Me}}]\text{NiCl}$ recorded in $\text{C}_6\text{D}_6$. Insets show downfield and upfield regions.
[Tp\textsuperscript{Fc,Me}]NiCl recorded in THF.

[Tp\textsuperscript{Fc,Me}]NiBr was synthesized in an analogous manner to that of [Tp\textsuperscript{Fc,Me}]NiCl. [Tp\textsuperscript{Fc,Me}]Tl was added to a solution containing 1.2 equivalents of anhydrous NiBr\textsubscript{2} in THF. The solution was heated to reflux before cooling to room temperature and stirred overnight. \textsuperscript{1}H NMR spectral features were consistent with the formation of the nickel(II) halide complex, Figure 5.3. Electronic absorption spectroscopy of the complex showed a band at 430 nm ascribed to a LMCT transition in addition to bands at 825 nm and 935 nm ascribed to a ligand field transition and a charge transfer transition from the ferrocenyl group to the ligand, respectively, Figure 5.4.
Figure 5.3 $^1$H NMR spectrum of [Tp$^{Fc,Me}$]NiBr recorded in C$_6$D$_6$.

Figure 5.4 Electronic absorption spectrum of [Tp$^{Fc,Me}$]NiBr recorded in THF.
[Tp\textsubscript{Fc,Me}]\textsubscript{2}NiI was formed from the reaction of [Tp\textsubscript{Fc,Me}]\textsubscript{2}NiCl with 4 equivalents of sodium iodide in THF. The reaction went to completion after stirring at room temperature for 24 hours. \textsuperscript{1}H NMR spectral features were consistent with the formation of the nickel(II) halide complex, Figure 5.5. Electronic absorption spectra showed bands at 425 nm and 515 nm ascribed to LMCT transitions in addition to bands at 860 nm and 965 nm ascribed to a ligand field transition and charge transfer from the ferrocenyl group to the ligand, respectively, Figure 5.6.

Figure 5.5 \textsuperscript{1}H NMR spectrum of [Tp\textsubscript{Fc,Me}]\textsubscript{2}NiI recorded in C\textsubscript{6}D\textsubscript{6}. 
In an attempt to synthesize a dioxygen complex supported by this ligand, reduction of the nickel(II) complexes to nickel(I) species was undertaken. Since the dinitrogen complexes, [Tp\textsuperscript{Fc,Me}]Co(N\textsubscript{2}) and [Tp\textsuperscript{Fc,Me}]Fe(N\textsubscript{2}), had been synthesized for use in the formation of [Tp\textsuperscript{Fc,Me}]Co(O\textsubscript{2}) and [Tp\textsuperscript{Fc,Me}]Fe(O\textsubscript{2}), an attempt was made at synthesizing the nickel analogue, [Tp\textsuperscript{Fc,Me}]Ni(N\textsubscript{2}). To a scintillation vial containing a solution of [Tp\textsuperscript{Fc,Me}]NiBr in toluene was added a 1\% Na/Hg amalgam (1.2 equivalents of Na) under nitrogen. The resulting solution was filtered to yield a black precipitate and a colorless solution. \textsuperscript{1}H NMR spectroscopy showed production of the sodium salt of the ligand, [Tp\textsuperscript{Fc,Me}]Na, Figure 5.7, with the black precipitate, presumed to be nickel metal. Experiments under the same conditions with 0.1\% and 0.5\% Na/Hg amalgams yielded analogous results.

Figure 5.6 Electronic absorption spectrum of [Tp\textsuperscript{Fc,Me}]NiI recorded in THF.
Since the preparation of a nickel(I) dinitrogen complex was unsuccessful, a different synthetic strategy was pursued. Previous PhTt-supported CO complexes have been prepared using the reaction of the halide complex with methyl lithium in the presence of CO\textsuperscript{51}. In an analogous reaction, [Tp\textsuperscript{Fc,Me}]NiCl was reacted with 1.1 equivalents of methyl lithium in the presence of excess CO at low temperature, -78°C. After 3 hours, the solution was warmed to room temperature and stirred overnight before a \textsuperscript{1}H NMR spectrum of the product was obtained. The spectrum showed a number of paramagnetic features consistent with the formation of multiple products along with starting material, Figure 5.8.
Figure 5.8 $^1$H NMR spectrum of [Tp$^{\text{Fc,Me}}$]NiCl (bottom) and the reduction of [Tp$^{\text{Fc,Me}}$]NiCl (top) using 1.1 equivalents of CH$_3$Li under 1 atmosphere of CO

A similar experiment was conducted with [Tp$^{\text{Fc,Me}}$]NiI as the halide source instead of [Tp$^{\text{Fc,Me}}$]NiCl. In this case, the $^1$H NMR spectrum of the resulting solution after reaction showed the formation of fewer paramagnetic products than that of the reaction with [Tp$^{\text{Fc,Me}}$]NiCl along with remaining starting material, Figure 5.9. In addition, LIFDI-MS of the product solution showed formation of the desired CO complex, [Tp$^{\text{Fc,Me}}$]Ni(CO) ($m/z = 991.28$), along with the formation of a few additional unidentified products, Figure 5.10. However, attempts to isolate [Tp$^{\text{Fc,Me}}$]Ni(CO) were unsuccessful.
Figure 5.9 $^1$H NMR spectra of [Tp$^{Fc,Me}$]NiI (bottom) and the reduction of [Tp$^{Fc,Me}$]NiI (top) using 1.1 equivalents of CH$_3$Li under 1 atmosphere of CO.

Figure 5.10 LIFDI-MS of the reaction solution of the reduction of [Tp$^{Fc,Me}$]NiI using 1.1 equivalents of CH$_3$Li under 1 atmosphere of CO.
Since the previous two strategies were unsuccessful, one last strategy was employed. [Tp^{Fc,Me}]NiI was reacted with 1% Na/Hg amalgam in the presence of 1.1 equivalents of CN^{tBu} as a trapping ligand instead of N₂, similar to the synthetic method for synthesizing [Tp^{tBu,Me}]Ni(CN^{tBu}). After stirring the reaction for 4 hr, the solution was filtered and a \(^1\)H NMR spectrum of the filtrate was obtained. The spectrum showed the formation of [Tp^{Fc,Me}]Na as the predominant product along with a few minor, unidentified paramagnetic species, Figure 5.11.

**Figure 5.11** \(^1\)H NMR spectrum of [Tp^{Fc,Me}]NiI (top) and the reduction of [Tp^{Fc,Me}]NiI (bottom) using a 1% Na/Hg amalgam in the presence of 1.1 equivalents of CN^{tBu}.

### 5.2 Synthesis of [Tp^{Ind,Me}]Ni Halide Complexes

Since the [Tp^{Ph,Me}] and [Tp^{tBu,Me}] ligand systems afforded stable nickel superoxide complexes with interesting reactivity, a different version of the [Tp^{Ph,Me}]
ligand was employed to synthesize an additional nickel superoxide species for comparison. This ligand, [Tp\textsuperscript{Ind,Me}], contains a fused dihydronaphthalene ring bound to the 3- and 4-positions on the pyrazole.\textsuperscript{52} While the steric properties of this ligand are similar to that of the [Tp\textsuperscript{Ph,Me}] ligand, the electronic properties are expected to differ due to the fused, electron-rich cyclohexane group between the pyrazole and the phenyl group.

[Tp\textsuperscript{Ind,Me}]NiCl was synthesized in an analogous procedure used for [Tp\textsuperscript{Ph,Me}]NiCl. To a solution of NiCl\textsubscript{2} in a 1:1 mixture of dimethylformamide and dichloromethane was added [Tp\textsuperscript{Ind,Me}]Tl. The addition resulted in an immediate color change from green to a peach-colored solution with formation of a white precipitate (thallium chloride). The solution was stirred overnight at room temperature before being filtered. The \textsuperscript{1}H NMR spectrum showed the formation of clean product in near quantitative yields, Figure 5.12. The electronic absorption spectrum showed several bands ascribed to LMCT transitions, 350 nm, 430 nm, 515 nm, and 550 nm, along with two bands assigned to ligand field transitions, 820 nm and 945 nm, Figure 5.13.
Figure 5.12 $^1$H NMR spectrum of $[\text{Tp}^{\text{Ind,Me}}\text{NiCl}]$ recorded in CDCl$_3$. 
Figure 5.13 Electronic absorption spectrum of $[Tp^{\text{Ind,Me}}]\text{NiCl}$ recorded in dichloromethane.

$[Tp^{\text{Ind,Me}}]\text{NiI}$ was synthesized by the halide exchange reaction of $[Tp^{\text{Ind,Me}}]\text{NiCl}$ with 4 equivalents of sodium iodide in THF. Addition of NaI to a solution of $[Tp^{\text{Ind,Me}}]\text{NiCl}$ in THF resulted in an immediate deepening of the color of the solution to a dark red. The solution was filtered after stirring overnight at room temperature and the solvent was removed to yield the product as a dark red solid. The $^1\text{H}$ NMR spectrum showed similar features to that of the $^1\text{H}$ NMR spectrum of $[Tp^{\text{Ind,Me}}]\text{NiCl}$,
Figure 5.14. Additionally, the electronic absorption spectrum was almost identical to that of $[\text{Tp}^{\text{Ind,Me}}\text{NiCl}]$, Figure 5.15.

**Figure 5.14** $^1$H NMR spectrum of $[\text{Tp}^{\text{Ind,Me}}\text{NiI}]$ recorded in CDCl$_3$.
[Tp^{Ind,Me}]NiBr was prepared in a similar manner to that of [Tp^{Ind,Me}]NiCl. Three equivalents of anhydrous NiBr\textsubscript{2} was weighed into a vial and left uncapped for several days on the benchtop so that the solid could become surface wet, which could be determined by the color change from yellow-orange to blue-green. Once the NiBr\textsubscript{2} had absorbed ambient water, the solid was dissolved in methanol. To this solution was added a solution of [Tp^{Ind,Me}]Tl in chloroform. The addition of the chloroform solution of the ligand resulted in an immediate color change from blue-green to dark red with a white precipitate (thallium bromide). After stirring overnight, filtering, and removing the solvent, the resulting dark red powder was characterized. $^1$H NMR analysis

Figure 5.15 Electronic absorption spectrum of [Tp^{Ind,Me}]NiI recorded in dichloromethane.
showed an analogous spectrum to those of [Tp\textsuperscript{Ind,Me}]NiCl and [Tp\textsuperscript{Ind,Me}]NiI, Figure 5.16. Additionally, electronic absorption spectroscopy showed several bands ascribed to LMCT transitions along with two bands ascribed to ligand field transitions similar to those found in the electronic absorption spectra of [Tp\textsuperscript{Ind,Me}]NiCl and [Tp\textsuperscript{Ind,Me}]NiI, Figure 5.17.

![Figure 5.16](image)

**Figure 5.16** \textsuperscript{1}H NMR spectrum of [Tp\textsuperscript{Ind,Me}]NiBr recorded in CDCl\textsubscript{3}.  

\textsuperscript{1}H NMR spectrum of [Tp\textsuperscript{Ind,Me}]NiBr recorded in CDCl\textsubscript{3}.
Figure 5.17 Electronic absorption spectrum of $[\text{Tp}^{\text{Ind},\text{Me}}]\text{NiBr}$ recorded in dichloromethane.

5.2.1 Reaction of $[\text{Tp}^{\text{Ind},\text{Me}}]\text{Ni}$ Complexes with Chalcogens

Since the halide complexes were successfully synthesized, a nickel(II) synthetic route for making $[\text{Tp}^{\text{Ind},\text{Me}}]\text{Ni}(O_2)$ was attempted using these halide complexes. $[\text{Tp}^{\text{Ind},\text{Me}}]\text{NiCl}$ was reacted with 1 equivalent of potassium superoxide in the presence of 18-crown-6 to aid in the solubility of potassium superoxide in toluene. The $^1\text{H}$ NMR spectrum of the resulting solution showed a significant number of features consistent with the formation of multiple products that could not be identified, Figure 5.18.
Figure 5.18 $^1$H NMR spectra of (from bottom to top) $\text{[Tp}^{\text{Ind,Me}}\text{]}\text{NiCl}$ and the reaction of $\text{[Tp}^{\text{Ind,Me}}\text{]}\text{NiCl}$ with KO$_2$ recorded in C$_6$D$_6$.

As the nickel(II) route did not yield clean, isolable product, a nickel(I) route was attempted analogous to the routes used to synthesize $[\text{Tp}^{\text{Ph,Me}}\text{]}\text{Ni(O}_2\text{)}$ and $[\text{Tp}^{\text{Bu,Me}}\text{]}\text{Ni(O}_2\text{)}$. To a solution of $[\text{Tp}^{\text{Ind,Me}}\text{]}\text{NiI}$ and 1.1 equivalents of triphenylphosphine in THF was added 1 equivalent of sodium naphthalide. The reaction was stirred for 2 days at room temperature. No reaction was observed by $^1$H
NMR spectroscopy under these conditions, nor in the presence of excess sodium naphthalide under similar reaction conditions, Figure 5.19.

**Figure 5.19** $^1$H NMR spectra of [Tp$^{\text{Ind,Me}}$]NiI (top) and the reaction of [Tp$^{\text{Ind,Me}}$]NiI with PPh$_3$ (bottom) in the presence of sodium naphthalide recorded in C$_6$D$_6$.

In an analogous reaction to that of the synthesis of [Tp$^{\text{tBu,Me}}$]Ni(CO), a solution of [Tp$^{\text{Ind,Me}}$]NiBr in toluene was cooled to -78°C under 1 atmosphere of CO before 1.1 equivalents of KC$_8$ was added to the solution. The $^1$H NMR spectrum of the product
mixture showed new features, possibly consistent with the formation of $[\text{Tp}^{\text{Ind,Me}}\text{Ni(CO)}]$, Figure 5.20. However, IR spectroscopy did confirm the presence of this product in the reaction solution, Figure 5.21.

\textbf{Figure 5.20} $^1$H NMR spectra of $[\text{Tp}^{\text{Ind,Me}}\text{NiBr}]$ (top) and the reaction of $[\text{Tp}^{\text{Ind,Me}}\text{NiBr}]$ with CO (bottom) in the presence of KC$_8$ recorded in C$_6$D$_6$. 
Figure 5.21 IR spectra of (from top to bottom) $[\text{Tp}^{\text{Ind,Me}}\text{NiBr}]$ and the reaction of $[\text{Tp}^{\text{Ind,Me}}\text{NiBr}]$ with CO in the presence of KC$_8$. A very weak CO stretch at 1994 cm$^{-1}$ is shown on the red spectrum.

As the efforts to synthesize $[\text{Tp}^{\text{Ind,Me}}\text{Ni(O}_2\text{)}]$ were unsuccessful, attempts were made at synthesizing sulfur and selenium complexes. $[\text{Tp}^{\text{Ind,Me}}\text{NiI}]$ was reacted with 2 equivalents of NaSH in THF for 24 hours at room temperature forming $[\text{Tp}^{\text{Ind,Me}}\text{Ni(SH)}]$. The $^1$H NMR spectrum showed the formation of a new product, Figure 5.22. Electronic absorption spectroscopy confirmed the presence of the new product with bands similar to that of the halide complexes, but shifted to lower wavelengths and at similar energies to those of $[\text{Tp}^{\text{Ph,Me}}\text{Ni(SH)}]$, Figure 5.23. The
presence of the desired product was further confirmed by LIFDI-MS which revealed $[\text{Tp}^{\text{Ind,Me}}\text{Ni}(\text{SH})$ as the predominant feature in solution ($m/z = 652.25$), Figure 5.24.

![Figure 5.22](image)

**Figure 5.22** $^1$H NMR spectra of $[\text{Tp}^{\text{Ind,Me}}\text{Ni}]$ (top) and the reaction of $[\text{Tp}^{\text{Ind,Me}}\text{Ni}]$ with NaSH (bottom) recorded in C$_6$D$_6$. 
Figure 5.23 Electronic absorption spectrum of \([\text{Tp}^{\text{Ind,Me}}\text{Ni(SH)}]\) with electronic absorption spectra of \([\text{Tp}^{\text{Ph,Me}}\text{Ni(SH)}]\) and \([\text{Tp}^{\text{Ph,Me}}\text{NiI}]\) for comparison recorded in toluene.
In a similar reaction, [Tp\textsuperscript{Ind,Me}]NiI was reacted with 2 equivalents of Na\textsubscript{2}Se in a 1:1 solution of THF and toluene. The \textsuperscript{1}H NMR spectrum showed a diamagnetic product consistent with the formation of ([Tp\textsuperscript{Ind,Me}]Ni)\textsubscript{2}(\mu-Se), Figure 5.25. The electronic absorption spectrum showed several bands similar to that of [Tp\textsuperscript{Ind,Me}]Ni(SH) and ([Tp\textsuperscript{Ph,Me}]Ni)\textsubscript{2}(\mu-Se), Figure 5.26. LIFDI-MS confirmed ([Tp\textsuperscript{Ind,Me}]Ni)\textsubscript{2}(\mu-Se) as the predominant feature in the mass spectrum (m/z = 1318.37), Figure 5.27.
Figure 5.25 $^1$H NMR spectra of $[\text{Tp}^{\text{Ind,Me}}\text{NiI}]$ (bottom) and the reaction of $[\text{Tp}^{\text{Ind,Me}}\text{NiI}]$ with $\text{Na}_2\text{Se}$ (top) recorded in $\text{C}_6\text{D}_6$. 
Figure 5.26 Electronic absorption spectrum of ([Tp^{Ind,Me}\text{Ni})_2(\mu-\text{Se}) with electronic absorption spectrum of ([Tp^{Ph,Me}\text{Ni})_2(\mu-\text{Se}) for comparison. Spectra recorded in toluene.
Interestingly, under the same reaction conditions, these reactions did not proceed when [Tp\textsuperscript{Ind,Me}]NiCl was used as the starting material instead of [Tp\textsuperscript{Ind,Me}]NiI as deduced by \textsuperscript{1}H NMR spectroscopy, Figure 5.28.
Figure 5.28 $^1$H NMR spectra of (from bottom to top) $[\text{Tp}^\text{Ind,Me}]\text{NiCl}$, the reaction of $[\text{Tp}^\text{Ind,Me}]\text{NiCl}$ with NaSH, and the reaction of $[\text{Tp}^\text{Ind,Me}]\text{NiCl}$ with Na$_2$Se recorded in C$_6$D$_6$.

5.3 Summary

A series of $[\text{Tp}^\text{Fc,Me}]\text{NiX}$ and $[\text{Tp}^\text{Ind,Me}]\text{NiX}$ (X = Cl, Br, I) halide complexes were synthesized and fully characterized. Attempts to reduce $[\text{Tp}^\text{Fc,Me}]\text{NiX}$ to $[\text{Tp}^\text{Fc,Me}]\text{Ni(PPh}_3\text{)}$, $[\text{Tp}^\text{Fc,Me}]\text{Ni(N}_2\text{)}$, $[\text{Tp}^\text{Fc,Me}]\text{Ni(CN}_\text{Bu})$, or $[\text{Tp}^\text{Fc,Me}]\text{Ni(CO)}$ using proven Na/Hg reduction methods were unsuccessful. Similarly, attempts to form $[\text{Tp}^\text{Fc,Me}]\text{Ni(CO)}$ from the reaction of $[\text{Tp}^\text{Fc,Me}]\text{NiX}$ with methyl lithium under an atm
of CO were unsuccessful. Synthetic methods to form $[\text{Tp}^{\text{Ind,Me}}\text{Ni}(O_2)]$ from nickel(I) and nickel(II) precursors were not successful. However, two new complexes, $[\text{Tp}^{\text{Ind,Me}}\text{Ni}(\text{SH})]$ and $([\text{Tp}^{\text{Ind,Me}}\text{Ni}](\mu-\text{Se}))_2$, were prepared from metathesis reactions with NaSH and Na$_2$Se, respectively. These complexes could provide insight into steric and electronic effects of Tp ligand systems on nickel-sulfur and nickel-selenium complexes and prove useful models for the active sites of nickel-sulfur and nickel-selenium containing enzymes.
REFERENCES


Appendix

CHECK CIF FILES

1. $[\text{Tp}^{\text{Ph,Me}}]\text{Ni(SCH}_2\text{CH}_2)$

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</tr>
<tr>
<td>Space group</td>
<td>P 21/n</td>
<td>P 21/n</td>
</tr>
<tr>
<td>Hall group</td>
<td>(-P 2yn)</td>
<td>(-P 2yn)</td>
</tr>
<tr>
<td>Moiety formula</td>
<td>C36 H33 B N6 Ni Se</td>
<td>?</td>
</tr>
<tr>
<td>Sum formula</td>
<td>C36 H33 B N6 Ni Se</td>
<td>C36 H33 B N6 Ni Se</td>
</tr>
<tr>
<td>(M_r)</td>
<td>698.14</td>
<td>698.16</td>
</tr>
<tr>
<td>(D_x, g \ cm^{-3})</td>
<td>1.415</td>
<td>1.415</td>
</tr>
<tr>
<td>(Z)</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>(M_u \ (mm^{-1}))</td>
<td>1.738</td>
<td>1.738</td>
</tr>
<tr>
<td>(F(000))</td>
<td>2864.0</td>
<td>2864.0</td>
</tr>
<tr>
<td>(F(000)')</td>
<td>2866.65</td>
<td></td>
</tr>
<tr>
<td>(h,k,l_{max})</td>
<td>25,14,39</td>
<td>25,14,38</td>
</tr>
<tr>
<td>(N_{ref})</td>
<td>15080</td>
<td>15000</td>
</tr>
<tr>
<td>(T_{min}, T_{max})</td>
<td>0.628,0.698</td>
<td>0.636,0.746</td>
</tr>
<tr>
<td>(T_{min}')</td>
<td>0.482</td>
<td></td>
</tr>
</tbody>
</table>

Correction method= # Reported T Limits: Tmin=0.636 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.995 Theta(max)= 27.506

R(reflections)= 0.0455( 9900) \(wR2\)(reflections)= 0.1169( 15000)

\(S = 1.015\) \(N_{par} = 817\)
### Alert level G

<table>
<thead>
<tr>
<th>Alert Code</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLAT332_ALERT_2_G Hirshfeld Test Diff (M-X) Se1 -- Ni1</td>
<td>6.7 su</td>
</tr>
<tr>
<td>PLAT332_ALERT_2_G Hirshfeld Test Diff (M-X) Se2 -- Ni2</td>
<td>9.0 su</td>
</tr>
<tr>
<td>PLAT330_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Motley</td>
<td>C30 Check</td>
</tr>
<tr>
<td>PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Th(Min)</td>
<td>3 Report</td>
</tr>
<tr>
<td>PLAT912_ALERT_4_G Missing # of FCF Reflections Above 3Th/L=</td>
<td>0.600 75 Note</td>
</tr>
</tbody>
</table>

0 ALERT level A = Most likely a serious problem - resolve or explain
0 ALERT level B = A potentially serious problem, consider carefully
0 ALERT level C = Check. Ensure it is not caused by an omission or oversight
5 ALERT level G = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

---

![Diagram](image-url)

Z = 33  char=359  P = 21/n  A = 0.05  RES= 0  -36 X
4. \([\text{Tp}^{\text{Fc,Me}}]\text{NiCl}\)

**checkCIF/PLATON report**

Structure factors have been supplied for datablock(s) char407

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No syntax errors found. CIF dictionary Interpreting this report

**Datablock: char407**

<table>
<thead>
<tr>
<th>Bond precision: C-C</th>
<th>Wavelength=0.71073</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>alpha=107.084(1) beta=110.019(1) gamma=107.725(1)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature: 200 K</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Calculated</th>
<th>Reported</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume 1855.4(3)</td>
<td>1855.4(3)</td>
</tr>
<tr>
<td>Space group P -1</td>
<td>P -1</td>
</tr>
<tr>
<td>Hall group -P 1</td>
<td>-P 1</td>
</tr>
<tr>
<td>Moiety formula C42 H40 B C1 Fe3 N6 Ni</td>
<td>?</td>
</tr>
<tr>
<td>Sum formula C42 H40 B C1 Fe3 N6 Ni</td>
<td>C42 H40 B C1 Fe3 N6 Ni</td>
</tr>
<tr>
<td>Mr 901.30</td>
<td>901.32</td>
</tr>
<tr>
<td>D, g cm(^{-3}) 1.613</td>
<td>1.613</td>
</tr>
<tr>
<td>Z 2</td>
<td>2</td>
</tr>
<tr>
<td>Mu (mm(^{-1})) 1.762</td>
<td>1.762</td>
</tr>
<tr>
<td>F000 924.0</td>
<td>924.0</td>
</tr>
<tr>
<td>F000' 927.22</td>
<td></td>
</tr>
<tr>
<td>h,k,lmax 16,17,17</td>
<td>16,17,17</td>
</tr>
<tr>
<td>Nref 8573</td>
<td>8555</td>
</tr>
<tr>
<td>Tmin,Tmax 0.542,0.809</td>
<td>0.649,0.746</td>
</tr>
<tr>
<td>Tmin' 0.532</td>
<td></td>
</tr>
</tbody>
</table>

Correction method= # Reported T Limits: Tmin=0.649 Tmax=0.746 |
AbsCorr = MULTI-SCAN

Data completeness= 0.998 | Theta(max)= 27.566 |
R(reflections)= 0.0331( 6759) | wR2(reflections)= 0.0815( 8555) |
S = 1.003 | Npar= 490
Alert level G

PLAT154_ALERT_1_G The sm's on the Cell Angles are Equal ............ 0.00100 Degree

PLAT912_ALERT_4_G Missing # of FCF Reflections Above Sth/L= 0.600 18 Note

0 ALERT level A = Most likely a serious problem - resolve or explain
0 ALERT level B = A potentially serious problem, consider carefully
0 ALERT level C = Check. Ensure it is not caused by an omission or oversight
2 ALERT level G = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
0 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check
checkCIF/PLATON report

Structure factors have been supplied for datablock(s) char523

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: char523

Bond precision: \( C-C = 0.0040 \) Å  \( \text{Wavelength}=0.71073 \)

\[
\begin{array}{ccc}
\text{Cell:} & a=9.9102(9) & b=15.9573(13) & c=19.9679(17) \\
\text{alpha}=90 & \text{beta}=90 & \text{gamma}=90 \\
\text{Temperature:} & \text{200 K} \\
\text{Volume} & \text{Calculated} & \text{Reported} \\
\text{Space group} & P 21 21 21 & P 21 21 21 \\
\text{Hall group} & P 2ac 2ab & P 2ac 2ab \\
\text{Molety formula} & C36 H34 B Cl N6 Ni & ? \\
\text{Sum formula} & C36 H34 B Cl N6 Ni & C36 H34 B Cl N6 Ni \\
\text{Mr} & 655.64 & 655.66 \\
\text{Dx,g cm}^{-3} & 1.383 & 1.383 \\
\text{Z} & 4 & 4 \\
\text{Mu (mm}^{-1}) & 0.738 & 0.738 \\
\text{F000} & 1368.0 & 1368.0 \\
\text{F000'} & 1370.28 & \\
\text{h,k,lmax} & 12,20,25 & 12,20,25 \\
\text{Nref} & 7270 \{ 4065 \} & 7230 \\
\text{Tmin,Tmax} & 0.698,0.775 & 0.667,0.746 \\
\text{Tmin'} & 0.679 & \\
\end{array}
\]

Correction method= # Reported T Limits: Tmin=0.667 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 1.78/0.99  \( \text{Theta(max)}= 27.559 \)

R(reflections) = 0.0307( 6669)  \( \text{wR2(reflections)} = 0.0756( 7230) \)

\( S = 1.015 \)  \( \text{Npar}= 410 \)
Alert level C
PLAT090_ALERT_3_C Poor Data / Parameter Ratio (Zmax > 18) ........ 9.88 Note

Alert level G
PLAT091_ALERT_4_G Flack x Value Deviates > 2*sigma from zero ..... 0.236 Note
PLAT912_ALERT_4_G Missing # of PFC Reflections Above Sth/Ith 0.600 14 Note

0 ALERT level A = Most likely a serious problem - resolve or explain
0 ALERT level B = A potentially serious problem, consider carefully
1 ALERT level C = Check. Ensure it is not caused by an omission or oversight
2 ALERT level G = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
0 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check
checkCIF/PLATON report

Structure factors have been supplied for datablock(s) char524

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: char524

Bond precision: C-C = 0.0119 A Wavelength=0.71073

Cell: a=10.016(4) b=16.029(7) c=20.070(7)

alpha=90 beta=90 gamma=90

Temperature: 200 K

Volume 3222 (2) 3222 (2)
Space group P 21 21 21 P 21 21 21
Hall group P 2ac 2ab P 2ac 2ab

Moleity formula C36 H34 B I N6 Ni

Sum formula C36 H34 B I N6 Ni

Mr 747.09 747.11

Dx, g cm-3 1.540 1.540

Z 4 4

M (nm-1) 1.596 1.596

F000 1512.0 1512.0

F000’ 1511.83

h,k,lmax 13,20,26 12,20,26

Nref 7451 [ 4166] 7305

Tmin,Tmax 0.771,0.901 0.671,0.746

Tmin’ 0.771

Correction method= # Reported T Limits: Tmin=0.671 Tmax=0.746

AbsCorr = MULTI-SCAN

Data completeness= 1.75/0.98 Theta(max) = 27.570

R(reflections)= 0.0476 ( 4411) wR2(reflections) = 0.0966 ( 7305)

S = 0.872 Npar= 409
Alert level C
PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds ............. 0.0119 Ang.
PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STH/Im = 0.600 2 Report

Alert level G
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) I1 -- Nil .. 15.0 su
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Molely .... C36 Check
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STH/Im = 0.600 46 Note

0 ALERT level A = Most likely a serious problem - resolve or explain
0 ALERT level B = A potentially serious problem, consider carefully
0 ALERT level C = Check. Ensure it is not caused by an omission or oversight
0 ALERT level G = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
1 ALERT type 2 Indicator that the structure model may be wrong or deficient
2 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

NOMOVE FORCED

Prob = 50
Temp = 200
7. $[\text{Tp}^{\text{Ind,Me}}] \text{NiBr}$

**checkCIF/PLATON report**

Structure factors have been supplied for datablock(s) char241

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No syntax errors found. CIF dictionary Interpreting this report

**Datablock: char241**

<table>
<thead>
<tr>
<th>Bond precision: C-C</th>
<th>0.0070 Å</th>
<th>Wavelength</th>
<th>0.71073</th>
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</thead>
<tbody>
<tr>
<td>Cell:</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>a=9.911(3)</td>
<td>b=16.023(4)</td>
<td>c=19.962(6)</td>
<td></td>
</tr>
<tr>
<td>alpha=90</td>
<td>beta=90</td>
<td>gamma=90</td>
<td></td>
</tr>
<tr>
<td>Temperature:</td>
<td>200 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume</td>
<td>3170.0(16)</td>
<td>3170.2(15)</td>
<td></td>
</tr>
<tr>
<td>Space group</td>
<td>P 21 21 21</td>
<td>P 21 21 21</td>
<td></td>
</tr>
<tr>
<td>Hall group</td>
<td>P 2ac 2ab</td>
<td>P 2ac 2ab</td>
<td></td>
</tr>
<tr>
<td>Moiety formula</td>
<td>C36 H34 B Br N6 Ni</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>Sum formula</td>
<td>C36 H34 B Br N6 Ni</td>
<td>C36 H34 B Br N6 Ni</td>
<td></td>
</tr>
<tr>
<td>M∞</td>
<td>700.09</td>
<td>700.12</td>
<td></td>
</tr>
<tr>
<td>Dx, g cm⁻³</td>
<td>1.467</td>
<td>1.467</td>
<td></td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>μ (nm⁻¹)</td>
<td>1.909</td>
<td>1.909</td>
<td></td>
</tr>
<tr>
<td>F000</td>
<td>1440.0</td>
<td>1440.0</td>
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</tr>
<tr>
<td>F000'</td>
<td>1440.56</td>
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<td></td>
</tr>
<tr>
<td>h,k,lmax</td>
<td>1220,26</td>
<td>1220,26</td>
<td></td>
</tr>
<tr>
<td>Nref</td>
<td>7447(4163)</td>
<td>7405</td>
<td></td>
</tr>
<tr>
<td>Tmin,Tmax</td>
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<td>0.673,0.746</td>
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</tr>
<tr>
<td>Tmin'</td>
<td>0.633</td>
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</table>

Correction method: # Reported T Limits: Tmin=0.673 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness = 1.78/0.99 θ(max) = 27.763

R(reflections) = 0.0441(5317) wR²(reflections) = 0.0873(7405)

S = 1.001 Npar = 409
Alert level C
PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds ............... 0.0070 Ang.

Alert level G
PLAT342_ALERT_4_G Missing # of PEF reflections Above 3σ/λ  0.660 17 note

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1 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

Z 26  char241  P 21 21 21  R = 0.34  RES = 0  -6 X

Prob = 50
temp = 200