

# Chemistry of Mixed Donor Pincer Ligand Nickel Complexes

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## INTRODUCTION

My C-500 project entailed the synthesis and reactivity of (PNP)NiCl[1]. I was given a list, of potential reactions to assess the reactivity, and instructions to characterize the products through various analytical techniques. The Caulton group has focused on synthesis and reactivity of unsaturated metal complexes. Most transition metal complexes tend to form species to fill their outer electron shell that have 18 valence electrons (saturated), similar to the octet rule for non metal. Unsaturated complexes often have higher reactivity than saturated complexes for this reason.

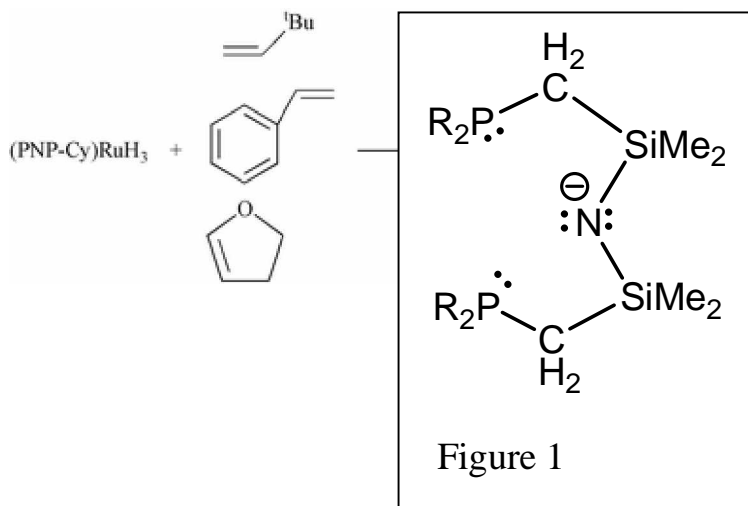
In organometallic chemistry, it is well known that two major factors influence the chemistry of different complexes. First, is the metal-center and its oxidation state. This influence can be seen in several instances when a set of ligands remains the same and the metal or oxidation state of the metal changes. The choice of metal for an organometallic complex is extremely important. It can affect whether or not your complex is paramagnetic or diamagnetic, which dictate techniques of characterization. It can also influence the tendency of certain red-ox reactions because of the preferred oxidation state of the metal and drive the chemistry toward that common oxidation state. Nickel was chosen for its preferred oxidation state of Ni(II) making the starting material [1] simple to achieve. Nickel (0), (I), (III), and (IV) oxidation states are all known though are much less accessible.<sup>[5,7,12]</sup>

In hopes of reaching other oxidation states of Ni we turned to the second major factor of organometallic chemistry, ligand choice and design. It has been well documented that solely changing the ligand on the same metal center in the same oxidation state can

result in drastic changes in reactivity. In recent years, the Caulton group and others have used a tridentate amido phosphine ligand 1,3[bis-(di-tert-butyl-phosphino)-methyl]-tetramethyldisilazane, which is hereafter referred to PNP. This ligand was initially developed by Fryzuk in the early 1980's (Figure 1). In the Caulton group the R groups that are used are <sup>t</sup>butyl. <sup>t</sup>Butyls are used to avoid ligand activation, as is seen when R

groups are cyclohexyl groups<sup>[2]</sup>.

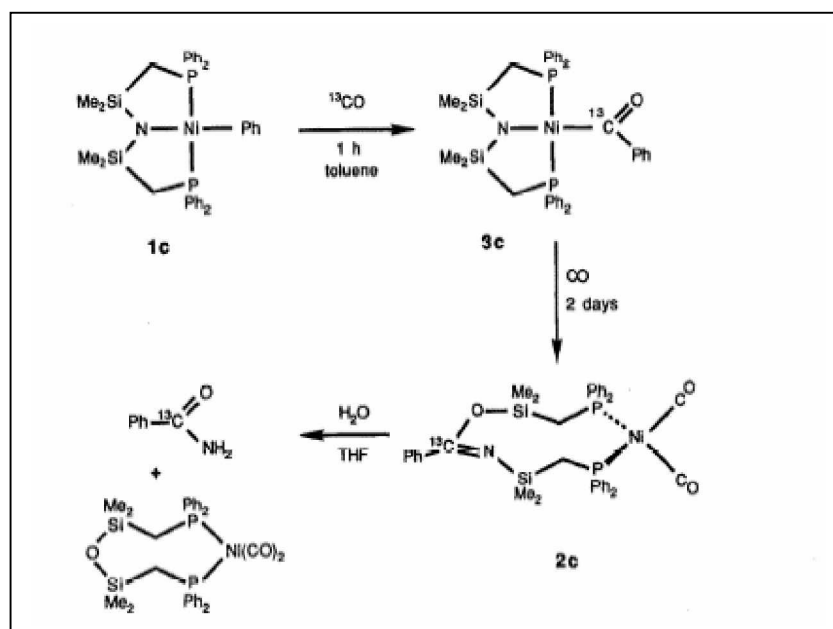
**Scheme 1**<sup>[2]</sup>



Scheme 1 shows an example of ligand activation. The PNP ligand has been chosen for a number of reasons. First, it is a hybrid-type ligand that combines both hard and soft donor atoms to the coordination sphere of the bound metal. This feature helps to unlock unusual electronic properties of the various metals to which it ligates. The sterics of the <sup>t</sup>butyl groups force the phosphorus to be meridonal (usually trans) and push the electron density inductively donated by the <sup>t</sup>butyl groups to the metal center in order to “feed” electron hungry metal centers. The amide nitrogen having a lone pair could possibly donate three electrons (neutral state formalism), allowing for even more electron density donated to the metal center. The sterics of the <sup>t</sup>butyl groups of the phosphorus seemingly dictate reactivity. The ability of this ligand to enable the synthesis of low valent, unsaturated electron complexes has led to isolation of extremely unusual complexes<sup>[1]</sup>.

While there have been various papers on the reactivity of these complexes<sup>[8,10]</sup> there is still much we can learn from the combination of this ligand with other metals. There are some possible drawbacks to this ligand, one of which is that the N of the backbone is not always going to be passive and the sterics of the <sup>t</sup>butyl groups might block the majority of substrates that could be useful to our research. Phosphine oxide formation and silicon-nitrogen bond hydrolysis are other possible side reactions that have been observed.

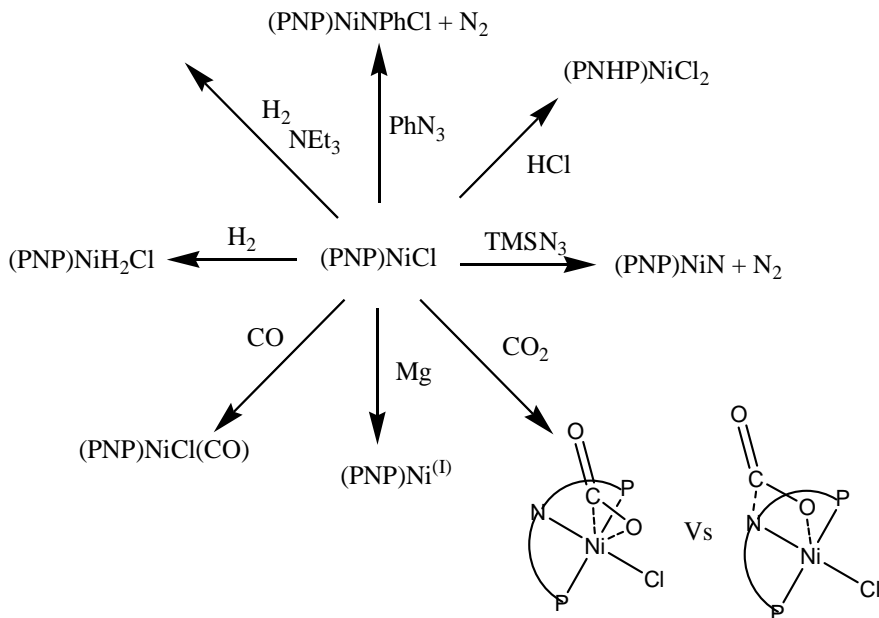
Some work has been done on PNPNiX complexes with different substituents on the phosphine groups. Fryzuk and coworkers using the phenyl derivative of PNP led to a unique carbonylation that has not been seen previous to this system (scheme2).<sup>[9]</sup>



Scheme 2

## PLAN OF ACTION

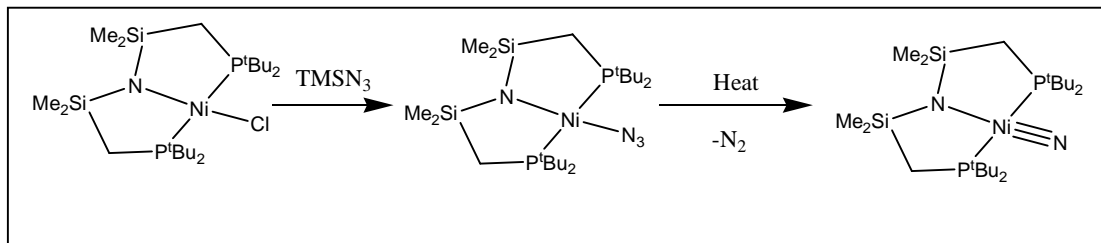
The list of reactions I was given (figure 2), was chosen with specific objectives in mind.



**Figure 2**

The CO reaction was designed to determine the degree of Ni center for back donation to CO. The H<sub>2</sub>-reaction was designed to form an adduct that might activate the dihydrogen bond, or possibly forming a hydride or di-hydride species on the metal accessing uncommon oxidation states of nickel (nickel (III) or (IV)). One possible conclusion of the reaction with H<sub>2</sub> was that an adduct would form in a very low equilibrium, that could not be observed by NMR. To avoid this possibility triethylamine would be added to the reaction in order to facilitate loss of HCl. This reaction would trap the hydride species making it visible and shifting the equilibrium reaction to favor the mono-hydride product. The phenyl-azide reaction was designed with the goal of forming an imido complex. The azide would form an adduct, followed by electron transfer resulting in N<sub>2</sub> being lost. This would produce a Ni(IV) imido complex. Little work has been fruitful in this area of nickel chemistry. It was proposed that our complex might be electron rich enough to

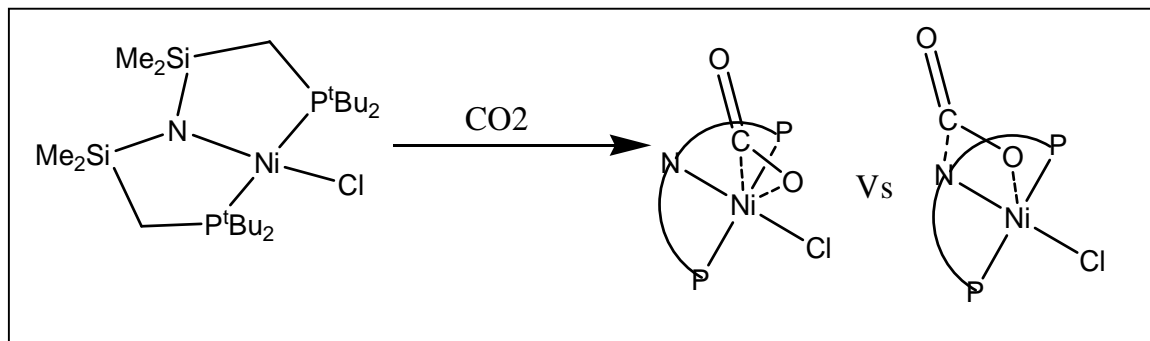
successfully complete this reaction. In an attempt to obtain the nitrido complex a reaction with TMS-azide (Figure 3) was proposed.



**Figure 3**

The theory was that TMS would abstract a Cl from [1] and replace it with an azide (Figure 3). With this complete, I could attempt to evolve N<sub>2</sub> through various methods. The reaction of [1] with HCl was designed to produce PNHPNiCl<sub>2</sub> to better understand if H<sub>2</sub>O contamination in the formation of [1] from [3] would produce the same product.

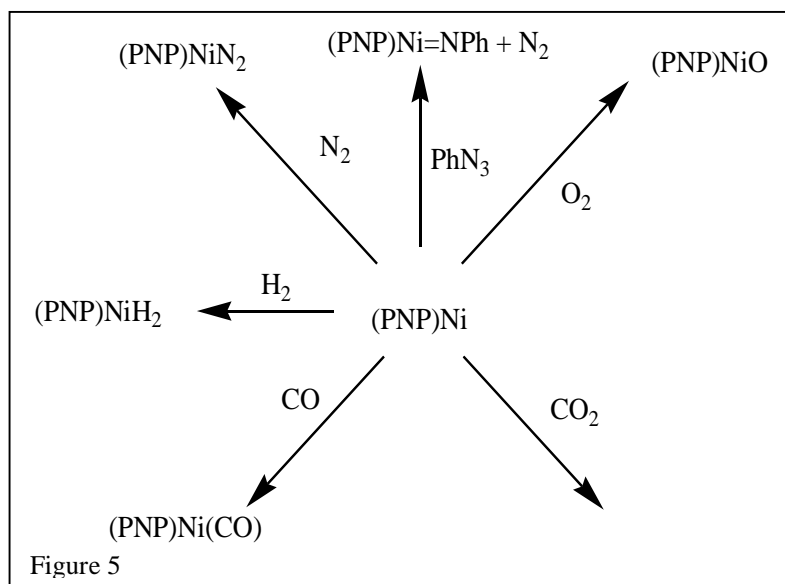
The reaction with CO<sub>2</sub> was designed to determine how innocent the amide of backbone is. The reaction with CO<sub>2</sub> was most likely to form an adduct. It was predicted that it would form one of two adducts shown in figure 4 .



**Figure 4**

By determining which adduct was formed, it could be determined if the reactivity of the nucleophilicity of N in the (PNP) backbone would complicate later research. It had been

shown in previous work in the Caulton lab that the reduction of the metal center of (PNP)CoCl could be accomplished using Mg powder. The product of this reaction was a tri-coordinate Co(I) complex, T-shaped. It was proposed that the same reaction may work for Ni. The Ni(I) complex would have a more reducing metal center. This would allow for more redox reactivity. In addition the tri coordinate complex would have an open reaction site for chemistry. With this compound we would test its reactivity and a scheme of reactions was proposed (Figure 5).

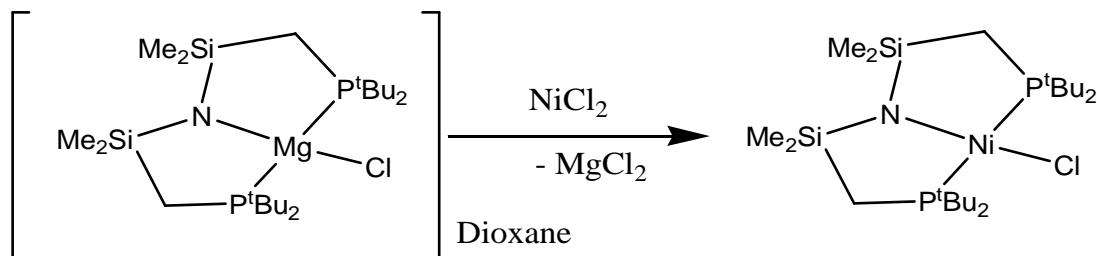


Many reactions were similar to the ones proposed with [1] (Figure 1). The reaction with N<sub>2</sub> (Figure 9) was an attempt to activate the N-N bond with the (PNP)Ni(I)[2] compound.

The reaction of (PNP)Ni[2] with half of an equivalent of O<sub>2</sub> (Figure 9) was designed to produce an oxide or a superoxide. Interestingly enough, even though O<sub>2</sub> is so abundant, reactions with it are difficult especially with the (PNP)M complexes because of the oxidizing power of peroxo and superoxo; it attacks the phosphorus and silicon atoms in addition to the metal center.

## RESULTS

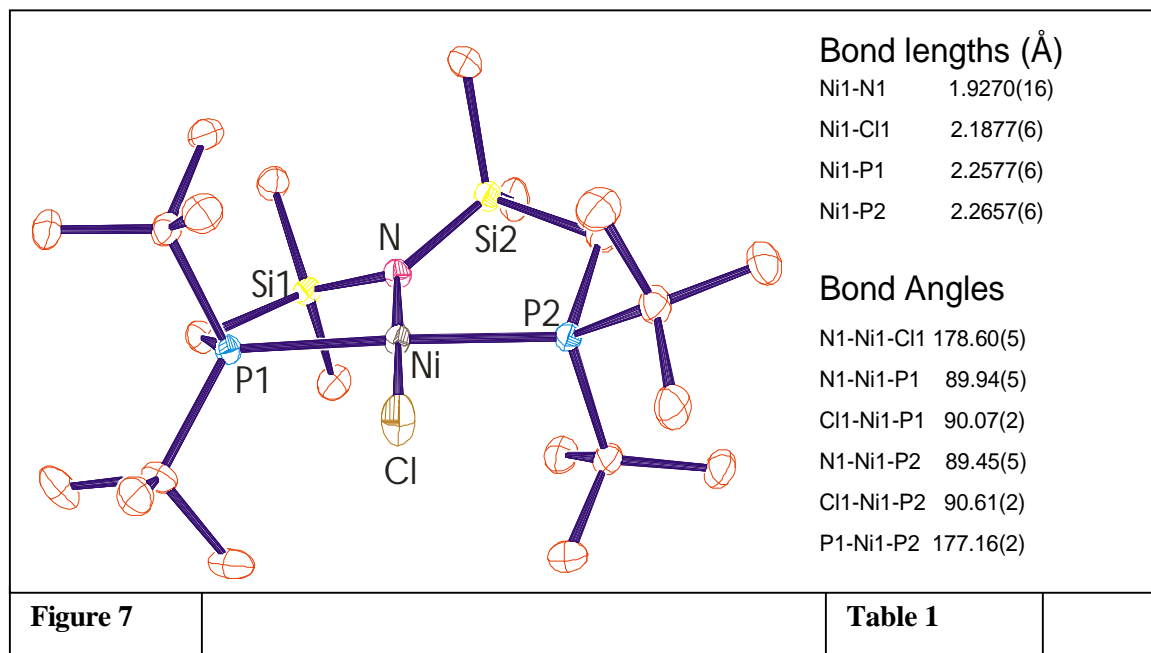
To begin a metathesis reaction was carried out by stirring PNP<sub>Mg</sub>Cl-Dioxane in THF with anhydrous NiCl<sub>2</sub> (figure 6). The solution went from colorless to deep red. X-ray crystallographic data was determined.



**Figure 6**

The data showed the structure to be [1]. Figure 7 shows the ORTEP diagram of the molecular structure (thermal ellipsoids at x0%, hydrogen removed for clarity). The coordination sphere is square planar determined by the bond angles around the metal center totaling 360° (Table 1). The crystallographic data also showed that the silicons of the PNP backbone were puckered out of the plane of the coordination sphere. The HNMR spectrum showed three peaks that indicate a C<sub>2v</sub> symmetric product. With [1] isolated and identified work began on reactivity of this compound.





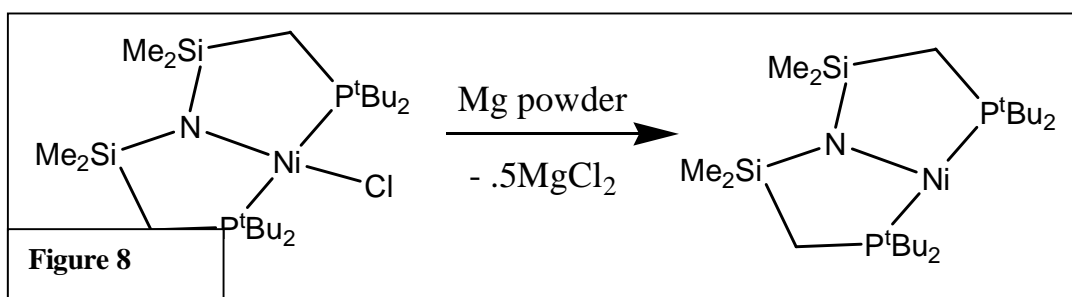
The reaction of CO and [1] yielded no change in color or NMR spectra, and therefore no reaction. The H<sub>2</sub> reaction with [1] showed free H<sub>2</sub> in the HNMR and no change to the starting material. In the triethylamine reaction under an atmosphere of H<sub>2</sub> the peaks indicating un-reacted triethylamine were present as was the free H<sub>2</sub> peak. These reactions showed that [1] did not react with H<sub>2</sub> even in a minute equilibrium. The reaction of [1] with phenyl azide, no color change appeared and the spectra showed free phenyl-azide and starting material. These reactions were carried out in C<sub>6</sub>D<sub>6</sub> at room under 1 atm of gas. This non reaction and that of CO and H<sub>2</sub> showed that no adduct formed for [1].

Upon addition of TMS azide to a solution of [1], the solution darkened slightly and the HNMR showed a new compound growing in. In order to force the reaction using LeChatelier's principle a large excess of TMS azide was then added. The peaks that appeared initially grew slightly and it was concluded that these peaks corresponded to the compound that had replaced the Cl with an azide. From the NMR spectra results it was

hypothesized that it was an equilibrium of the (PNP)NiN<sub>3</sub>[3] vs. [1] (both Ni(II) complexes), and that N<sub>2</sub> was not evolved. This conclusion led to another reaction. If NaN<sub>3</sub> was used then the precipitation of NaCl would force any equilibrium to completion. Upon addition of NaN<sub>3</sub> the solution went from deep red to purple. This reaction confirmed our hypothesis. With the attachment of the azide complete, the next step was to remove N<sub>2</sub>. To remove N<sub>2</sub> a solution of (PNP)NiN<sub>3</sub> was first heated for 24 hours; no reaction occurred. Reduction (the evolution of N<sub>2</sub> being a 2 electron process) of [3] with Mg powder in order to lose N<sub>2</sub> was attempted next. The product of this reaction was identical to the product of [1] with an addition of Mg powder, and will be discussed later herein.

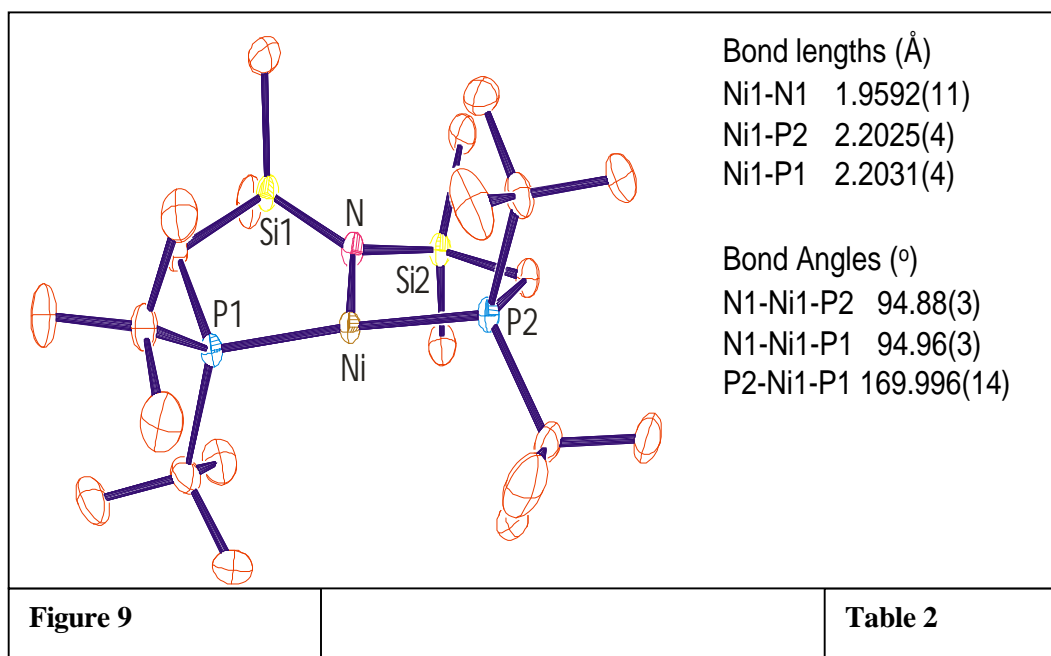
When [1] is reacted with one equivalent or excess HCl the solution color changes to bright blue and only one product is visible in the NMR. It was hypothesized that the product was the (PHNP)NiCl<sub>2</sub> complex, which was still Ni(II) and was not bonded to the N of the backbone.

In the reaction of [1] and Mg powder (figure 8) the solution gradually went from



dark red to a pale yellow color. The H NMR showed a paramagnetic product with identical color and <sup>1</sup>H NMR to the product from the reduction of [3] by Mg powder. Pale yellow block like crystals were grown. These crystals were submitted for x-ray

crystallography and the resulting structure is shown in Figure 9, confirming reduction and formation of [2]. The angles of the coordination sphere around the Ni center added up to approximately 360° (Table 2) showing that the coordination sphere is still planar. The P1-Ni-P2 bond angle is approximately 170°.



This tells us that the coordination sphere is approximately T-shaped as was demonstrated in (PNP)Co chemistry. An Evans method<sup>[11]</sup> magnetic moment calculation revealed a moment of 2.07 $\mu_B$  (at 298 K). Although this value is a little high for the theoretical value of 1.7, this nevertheless shows that our compound is a  $d^9$ , Ni(I) complex. It is interesting to note, that while the Ni-N distance lengthens in the three coordinate complex the Ni-P bonds shorten. One way of explaining the Ni-N distance is that the  $d_{x^2-y^2}$  orbital, (the HOMO/SOMO), plays the key factor in bonding. In the [1] complex, the lobes of the  $d_{x^2-y^2}$  orbital are pointed directly at the attached ligand of the coordination sphere.

This orbital is 1) protected from attack and 2) anti-bonding to the PNP ligand. The  $d_{x^2-y^2}$  orbital of [1] is not filled thus allowing a little more donation from the lone pair of the nitrogen backbone while the [2] orbital is half filled. The half occupancy does not permit any N lone pair to donate to the Ni center because of the excess electron density in the SOMO. While this goes some way to explaining the Ni-N bond length change, it does very little to explain the Ni-P bond lengths. However, Ni(I) complexes tend to form more numerous dative bonds than Ni(II)<sup>[13]</sup> species which could allow for stronger interaction between the Ni center and the phosphorus of the ligand. In conclusion, the reduction of [1] to [2] gives us not only a more electron rich Ni core but also gives us a sterically open reaction site for chemistry to occur. There is only a single occupied d orbital left for reactivity.

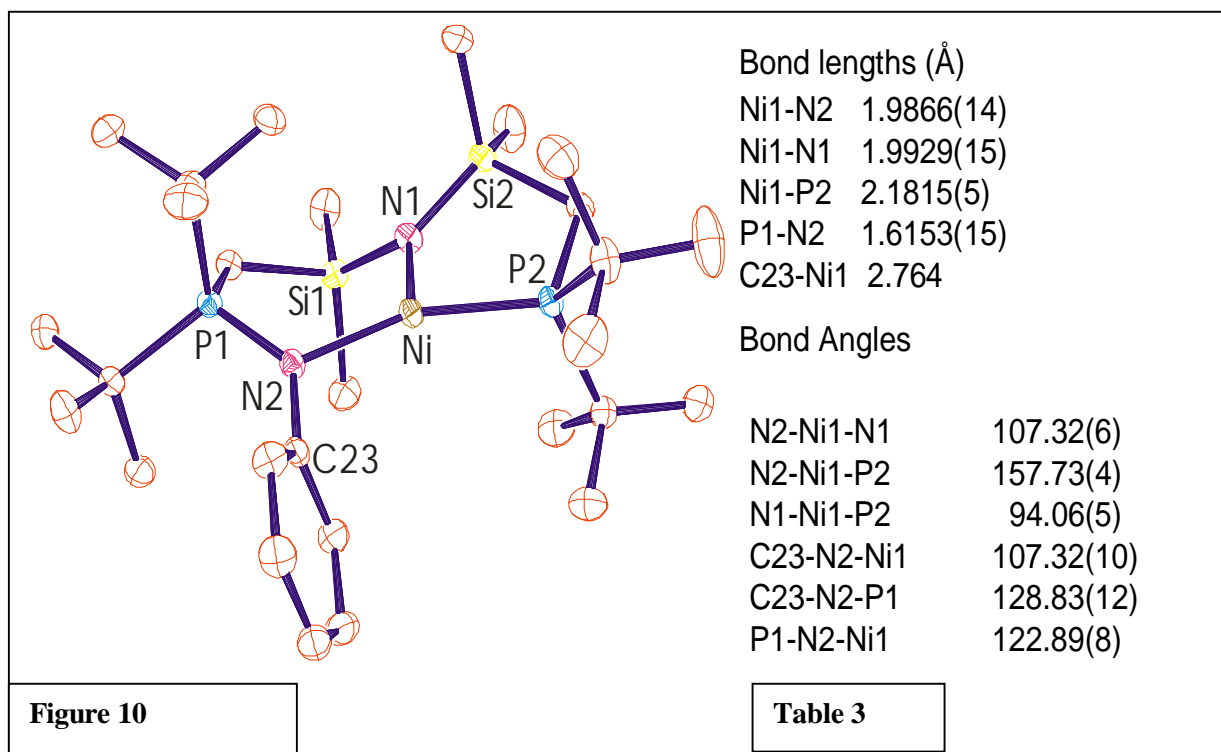
When [2] was reacted with one equivalent of CO the solution darkened to a yellow brown. The H NMR showed some un-reacted starting material and one broad peak growing in. In order to completely react all starting material an excess of CO was added. The color turned to brown and the H NMR showed only one very broad peak. The IR spectra showed a peak that could be considered a carbonyl stretch. It was hypothesized that this product could be (PNP)NiCO.

In order to possibly obtain higher oxidation states of Ni (Ni (III) or (II)), H<sub>2</sub> was added to a solution of [2]. The color stayed the same. The NMR data showed a peak indicating free H<sub>2</sub> and no indication of change to the starting material.

Under 1 atm of [2] with N<sub>2</sub> in benzene, the color of [2] stayed the same and the NMR spectra showed no change.

In the reaction with  $\frac{1}{2}$  an equivalent of  $O_2$  I found several new paramagnetic peaks growing in the H NMR, yet starting material remained. After the second addition, of  $\frac{1}{2}$  an equivalent the starting material was completely gone, and all of the new peaks had gained intensity. The solution color changed from pale yellow to dark brown.

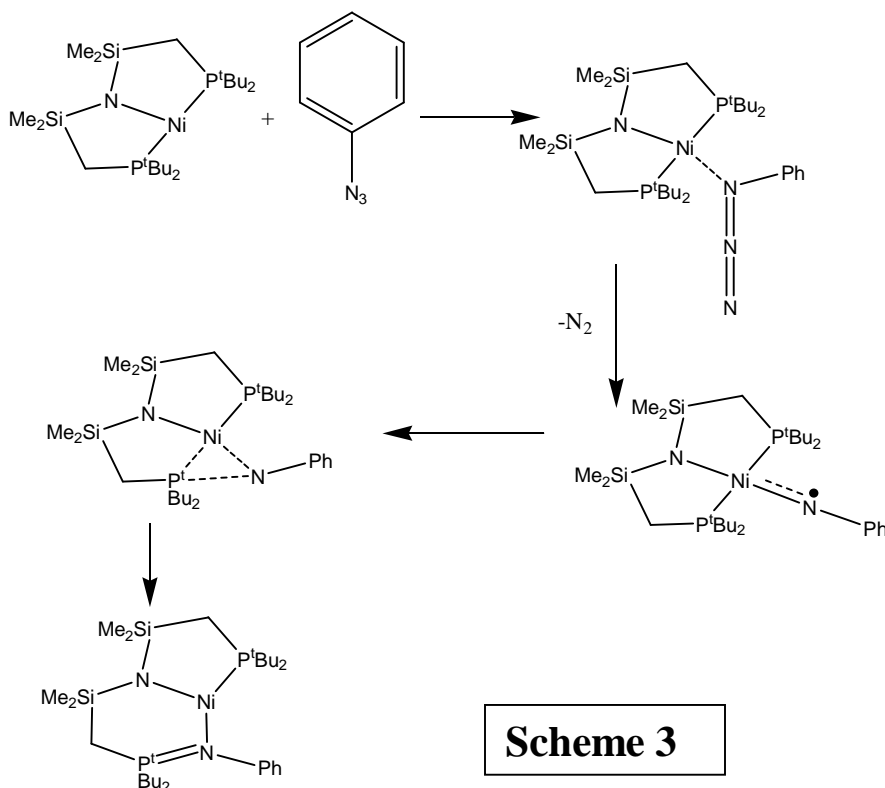
Upon addition of  $PhN_3$  to a solution of [2] the color immediately turned from yellow to a brown-yellow and  $N_2$  evolution was evident. Light yellow crystals were formed and they were submitted for x-ray diffraction. Figure 10 and table 3 show the data received from the diffraction study. As can be seen from the figure 10, the N-Phenyl has inserted into a nickel



phosphorus bond. This was an unexpected outcome. The nickel center remains at oxidation state (I). As can be seen from table 3 the nitrogen that inserted into the Ni-P bond is still  $sp^2$  hybridized. The corresponding angles surrounding this nitrogen add up to

approximately  $360^\circ$  thus showing planar conformation. It can also be seen that the angles surrounding the nickel center also add up to approximately  $360^\circ$ . It is interesting to note that the angle between the N2-Ni-P2 is approximately  $160^\circ$ , which is about 10 degrees different from the [2] complex, thus making it more Y-shaped but still considerably T-shaped in the coordination sphere. The bond length indicates that the P1-N2 is a double bond. Important to note is the Ni-N2-C23 bond angle

$107^\circ$



**Scheme 3**

whereas the P1-N2-C23 bond angle is  $128^\circ$ . This shows a 13 degree distortion of ideal  $sp^2$  geometry. The C23-Ni distance is  $2.7\text{\AA}$  (Table 3) (which is much larger than the  $1.9\text{\AA}$  bond length for a Ni-C single bond precluding any interactions). This distortion can be

explained through steric effects from the <sup>t</sup>butyl groups on P1 pushing the phenyl ring. A hypothesized mechanism for this reaction can be seen in scheme 3.

## CONCLUSION

In conclusion, the goals of my C-500 project were to synthesize [1], probe its reactivity and attempt to reach unusual oxidation states of nickel or lower valent compounds. [1] has been successfully synthesized, and it has been determined that it is fairly stable for a sixteen electron compound as are other 16 e<sup>-</sup> Pt group complexes. However, by using magnesium powder to reduce the nickel of the [1], an uncommon oxidation state of Ni, Ni(I) has been accessed. [1] did show some reactivity towards transfer reagents, it undergoes metathesis to form [3]. In addition to my principal goals, probing the reactivity of the [1], it has been found that the [2] reacts with oxidizing agents such as O<sub>2</sub>, and phenyl-azide. [2] also shows some reactivity with CO which with further study might assess its back donation capabilities. From the reaction of [2] with phenyl azide, it has been concluded that the phosphorus in the PNP backbone is not always innocent. An uncommon oxidation state of nickel (Ni(I)) has been accessed with possibility in future research of obtaining a rarer oxidation state of nickel (Ni(III), Ni(IV)). These nickel compounds that have been synthesized are low valent. I have probed the reactivity of these and have found an uncommon Ni(I) T-shaped complex, and an interesting insertion by phenyl azide. I have gained experience in inorganic chemistry methods e.g. the use of dry box, schlenk line, gas line and many other techniques. This experience has helped me to increase my understanding of chemistry dramatically.

## FUTURE

Future research with [1] might include exchange of the chloride with a non-coordinating anion such as triflate (OTf). With this exchange the reactivity could greatly increase because it would be more easily lost.

The reaction of [1] with CO<sub>2</sub> has yet to be carried out due to a lack of CO<sub>2</sub> that is not contaminated with water. This experiment could yield desired information in the future.

In the reaction of [2] with CO the result has left us considering a variable temperature NMR in order to see if it will resolve the one peak into more peaks.

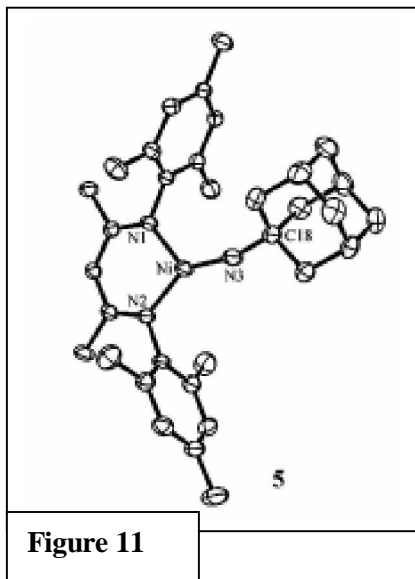
With the unexpected result of no reactivity, from all reactions with H<sub>2</sub> (both with triethylamine, without, and with the Ni(I) complex) it was decided that in order to get the hydride, a different H donor units, such as Bu<sub>3</sub>SnH and 1,4 cyclohexadiene should be used.

The results of the reaction of [2] with O<sub>2</sub> has left us lacking sufficient evidence to conclude anything definite. In order to better understand the reaction with O<sub>2</sub> it has been proposed that other O donors should be used. A few that have been proposed are N<sub>2</sub>O, PhI=O, and Me<sub>3</sub>NO.

The reaction of [2] with PhN<sub>3</sub> had interesting results. In order to give more credit to the proposed reaction scheme the imido complex needs to be observed. Two methods of observation have been suggested. First a low temperature NMR might show different peaks that could be assigned to the imido complex. Second from the distortion of the sp<sup>2</sup> orbitals around the N it is proposed that a bulkier organic azide (1,3 di-isopropylphenyl azide) could trap the imido intermediate. Also of interest, would be reacting [2] with two



more equivalents of phenyl azide to see if a second insertion of a nitrogen into a phosphorus nickel bond or if the second equivalent makes an imido complex. In a recent article by Warren et al.<sup>[6]</sup>, they found that a Ni (III) NACNAC imido complex (figure 11) with 57% radical character on the imido-nitrogen.



A (PNP)Ni-imido species, not only would we have an unusual oxidation state of Nickel, but we might also be able to probe for any radical character of the imido nitrogen and the amido nitrogen.

## EXPERIMENTAL

All Reactions were done using a J-Young NMR tube and 15mg of starting PNP material in C<sub>6</sub>D<sub>6</sub> unless otherwise indicated. Gas reactions were carried out on a gas line with the solution being first degassed and 2ml of headspace assumed. All reactions were carried out at room temperature 22° C unless otherwise stated.

**[[('Bu<sub>2</sub>PCH<sub>2</sub>SiMe<sub>2</sub>)<sub>2</sub>N]NiCl]**[1]** Preparation of (PNP<sup>tBu</sup>)Mg-dioxane**[4]** was accomplished following published synthesis (Watson et al). 199mg of **[4]** was added to 20ml of THF (dried and distilled over Na metal) in a schlenk flask. To this solution 44mg of anhydrous NiCl<sub>2</sub> (99% ordered from STREM) was added. The solution was left to stir for 24 hours. The color went from colorless to deep red and all NiCl<sub>2</sub> dissolved. The solution was stripped to dryness. 15 ml of pentane was added, the solution was filtered and then stripped to dryness again. The solid was dissolved in minimal pentane and cooled to -40° C in a freezer. Deep red block crystals formed suitable for x-ray diffraction study. The solution was decanted and the crystals were washed with cold pentane then dried by vacuum. Note: when the reaction was done with impure NiCl<sub>2</sub> two other products also formed one was violet and one was blue. The blue is thought to be (PNP)NiCl<sub>2</sub> while the violet product is still undetermined.**

<sup>1</sup>H NMR: 1.48 ppm (t, 36), 0.5 ppm (t, 4) , 0.28 (s, 12)

<sup>31</sup>P{<sup>1</sup>H} NMR: 32.8 ppm (s)

**[[('Bu<sub>2</sub>PCH<sub>2</sub>SiMe<sub>2</sub>)<sub>2</sub>N]NiN<sub>3</sub>]**[3]** 1.9mg(1 equivalent) of NaN<sub>3</sub> was added to the C<sub>6</sub>D<sub>6</sub> solution of **[1]** The solution immediately changed from red to purple. The solution was filtered. The solution was then analyzed by NMR spectroscopy.**

<sup>1</sup>H NMR: 1.36 ppm (t), 0.38 ppm (t), 0.22 ppm (s)

<sup>31</sup>P{<sup>1</sup>H} NMR: 40.5 ppm (s)

**[[('Bu<sub>2</sub>PCH<sub>2</sub>SiMe<sub>2</sub>)<sub>2</sub>NH]NiCl<sub>2</sub>]**[2]** To a solution of **[1]** excesses 1M HCl in diethylether was added. The solution went from deep red in color to bright blue.**

<sup>1</sup>H NMR: 5.12 ppm (bs, 1), 3.26 ppm (d, 36), 0.97 ppm (d, 4), 0.29 ppm (s, 12)

$^{31}\text{P}\{^1\text{H}\}$ NMR: 17.72 ppm (s).

$\{[(^t\text{Bu}_2\text{PCH}_2\text{SiMe}_2)_2\text{N}]\text{Ni}\}$ [4] 15mg of [1], or [3] was added to 20ml of THF (dried and distilled over Na metal) in a schlenk flask. A fifty fold excess of Mg powder was then added and the solution was left to stir for 24 hours. The solution went from deep red to pale yellow and was stripped to dryness. 15ml of pentane was added, the solution was filtered and then stripped to dryness again.. Re dissolved in toluene and the toluene allowed to slowly evaporate under reduced pressure. Pale yellow crystals formed suitable for x-ray diffraction study.

$^1\text{H}$  NMR: 8.5 ppm (vbs, 36), 6.5 ppm (vbs, 12), -13.57 ppm (vbs, 4)

$^{31}\text{P}\{^1\text{H}\}$ NMR: NONE

$\{[(^t\text{Bu}_2\text{PCH}_2\text{SiMe}_2)\text{N}(\text{SiMe}_2\text{CH}_2^t\text{Bu}_2\text{P})\text{NPh}]\text{Ni}\}$ [5] to a solution of [4] 3  $\mu\text{l}$  of  $\text{PhN}_3$  was added.the solution went from pale yellow to a yellow brown. The solution was stripped to dryness. The solid was dissolved in minimal pentane and cooled to  $-40^\circ\text{C}$  in a freezer. Yellow crystals formed suitable for x-ray diffraction study. The solution was decanted and the crystals were washed with cold pentane then dried by vacuum.

$^1\text{H}$  NMR: 16.8 ppm (vbs), 8.84 ppm (vbs), 4.6 ppm (vbs),

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