Chapter 4

The Synthesis of Nickel Complexes of Chelating N-Heterocyclic Carbene Ligands

4.1 Abstract

Having synthesized a novel class of chelating N-heterocyclic carbene (NHC) ligands modeled after salicylaldimine (sal) ligands, we targeted the synthesis of Ni complexes of these ligands. It was hoped that these new Ni compounds would prove to be active catalysts for both the homopolymerization of ethylene, as well as for the copolymerization of ethylene with methyl acrylate and other functionalized olefins. However, difficulties arose in the synthesis of the desired Ni complexes. Treatment of the new NHC ligands with inorganic Ni sources, *e.g.*, $NiBr_2(PPh_3)_2$ provided almost exclusively bis-ligated complexes, even for very bulky ligands. Treatment of the chelating NHCs with an organometallic Ni source, $NiClPh(PPh_3)_2$, led to a novel NHC ring-opening reaction, apparently resulting from attack of the Ni-bound Ph group on the carbene carbon. It was shown that this reaction could be avoided through the proper choice of ligands on Ni, however, no Ni complex of the chelating NHCs proved to be an effective catalyst for olefin polymerization.

4.2 Introduction

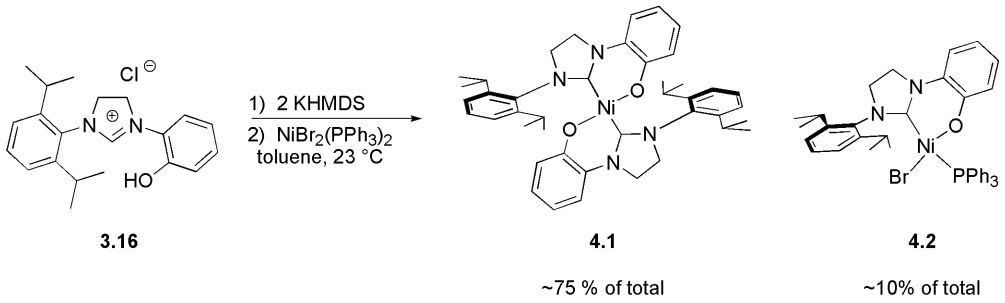
In Chapter 3, the synthesis of a series of chelating N-heterocyclic carbenes and their complexes with Pd was described. As mentioned in Chapter 1, while diimine complexes of both Pd and Ni are active catalysts for olefin addition polymerization, only Ni complexes of salicylaldimine catalysts are viable olefin polymerization catalysts. Therefore, the synthesis of Ni complexes of the chelating carbenes was the most important target for this project.

4.3 Inorganic Nickel Complexes

In order to establish that the novel chelating NHCs were competent ligands for Ni, the synthesis of inorganic complexes was our first target. We reasoned that inorganic complexes would have greater stability relative to organometallic complexes,[1] which could be air- and moisture-sensitive, as well as prone to the unique reductive elimination process described in Chapter 3 (Scheme 3.13).

Treatment of ligand **3.16** (see Scheme 3.7) with two equivalents of KHMDS in toluene, followed by addition of a solution of $NiBr_2(PPh_3)_2$, gave a brown solid upon workup (Scheme 4.1). ^{1}H NMR characterization of this product was made difficult due to paramagnetism from a high-spin Ni(II) species in solution. However, it was found that several types of crystals suitable for X-ray crystallographic analysis could be grown from the reaction mixture. Light pink crystals isolated from the mixture proved to be bis-ligated complex **4.1** (Figure 4.1), making up the bulk (~75%) of the product. The minor product (<10%) proved to be mono-ligated $NiBrPPh_3$(NHC) compound **4.2** (Figure 4.2). Both compounds feature a nearly square planar arrangement of ligands around the Ni atom, with anionic moieties trans to each other.

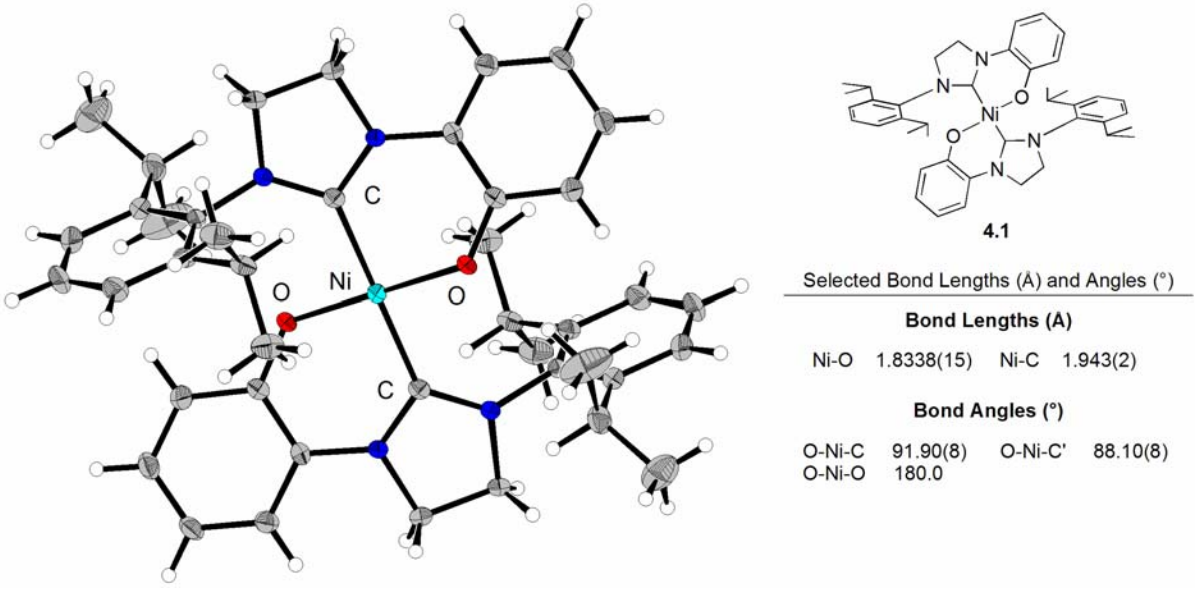
Scheme 4.1. The synthesis of Ni compounds **4.1** and **4.2**.



3.16 **4.1** **4.2**

~75 % of total ~10% of total

Figure 4.1. Molecular structure of Ni complex **4.1**. Atoms are represented by thermal ellipsoids at 50% probability.



4.1

Selected Bond Lengths (Å) and Angles (°)

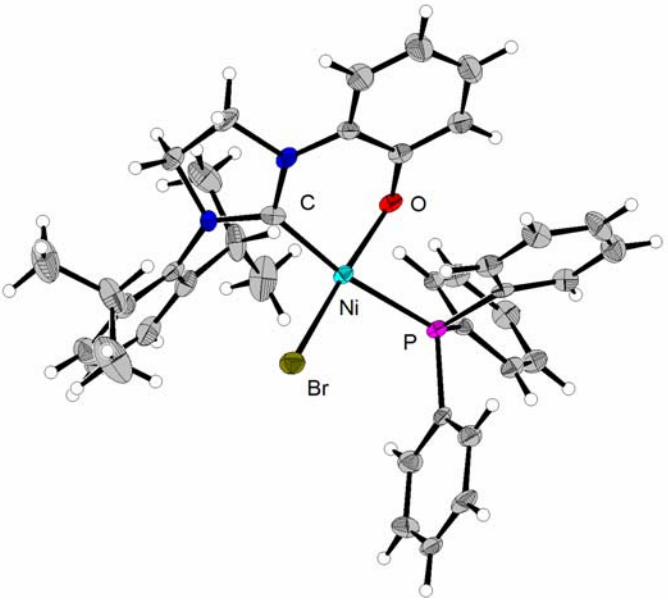
Bond Lengths (Å)

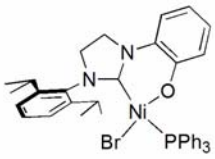
Ni-O	1.8338(15)	Ni-C	1.943(2)

Bond Angles (°)

O-Ni-C	91.90(8)	O-Ni-C'	88.10(8)
O-Ni-O	180.0		

Figure 4.2. Molecular structure of Ni complex **4.2**. Atoms are represented by thermal ellipsoids at 50% probability.





4.2

Selected Bond Lengths (Å) and Angles (°)

Bond Lengths (Å)

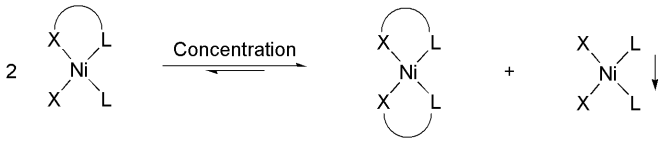
Ni-O	1.852(3)	Ni-P	2.2447(11)
Ni-C	1.902(4)	Ni-Br	2.2932(6)

Bond Angles (°)

O-Ni-C	87.26(14)	O-Ni-Br	173.05(9)
O-Ni-P	83.18(8)	C-Ni-Br	94.25(12)
C-Ni-P	170.24(13)	P-Ni-Br	95.02(3)

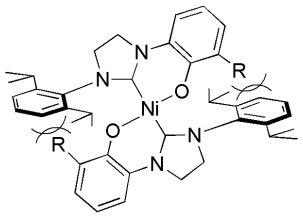
As discussed in Chapter 2, bis-ligation of [L,X]-chelating ligands is favorable for Ni(II).[2] Therefore, the formation of **4.1** in high yield from the reaction between **3.16** and $NiBr_2(PPh_3)_2$ was not surprising. The driving force for bis-ligation is likely thermodynamic in most cases. For instance, in the formation of complex **4.1**, the desired product, mono-ligated **4.2** is likely formed first. However, upon concentration of the reaction solvent or attempted crystallization, disproportionation of two molecules of **4.2** leads to one molecule of **4.1** and one molecule of $NiBr_2(PPh_3)_2$ (Scheme 4.2). The relatively insoluble $NiBr_2(PPh_3)_2$ precipitates, or crystallizes, leaving **4.1** behind, which then crystallizes on its own, as was observed in the crystal mixture that yielded both **4.1** and **4.2**. That this should happen to an NHC complex such as **4.2** is not surprising, since the NHC exhibits a strong trans effect on the triphenylphosphine ligand, leading to the phosphine dissociation that is a likely prerequisite for disproportionation.

Scheme 4.2. The likely cause of bis-ligation.



Bis-ligation is undesirable for Ni(II) polymerization catalysts, since, as discussed in Chapter 2, bis-ligated complexes are not catalytically active. Although even the bulkiest ligands bis-ligate on Ni under forcing conditions, the use of a large ligand can disfavor bis-ligation.[3] This approach seemed particularly promising upon examination of the structure of complex **4.1**. In this structure, the protons in positions ortho to the O atom point directly at the diisopropylphenyl groups on the opposing ligand (Figure 4.1). Therefore, it seemed likely that the presence of any group larger than a proton would make the formation of a bis-ligated structure similar to **4.1** impossible (Figure 4.3).

Figure 4.3. Destabilizing interactions between 2,6-diisopropylphenyl groups and ortho substituents in complex **4.1**.



4.1

To test this hypothesis, *tert*-butyl substituted **3.21** (see Scheme 3.8) was treated with two equivalents of KHMDS, followed by $NiBr_2(PPh_3)_2$, in toluene (Scheme 4.3), which afforded a dark brown paramagnetic solid upon workup. Yellow crystals were obtained from the product mixture; X-ray crystallographic analysis of this compound revealed bis-ligated structure **4.3** (Figure 4.4).[4] Examination of the structure of **4.3**

reveals that the ligands around Ni exhibit a nearly square planar arrangement, in which the anionic substituents are cis to each other (as are the neutral) in contrast to **4.1**, in which the anionic substituents (and the neutral) are mutually trans.

Scheme 4.3. Synthesis of bis-ligated compound **4.3**.

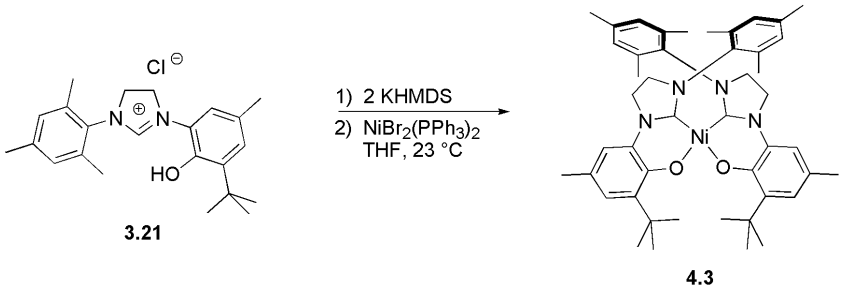
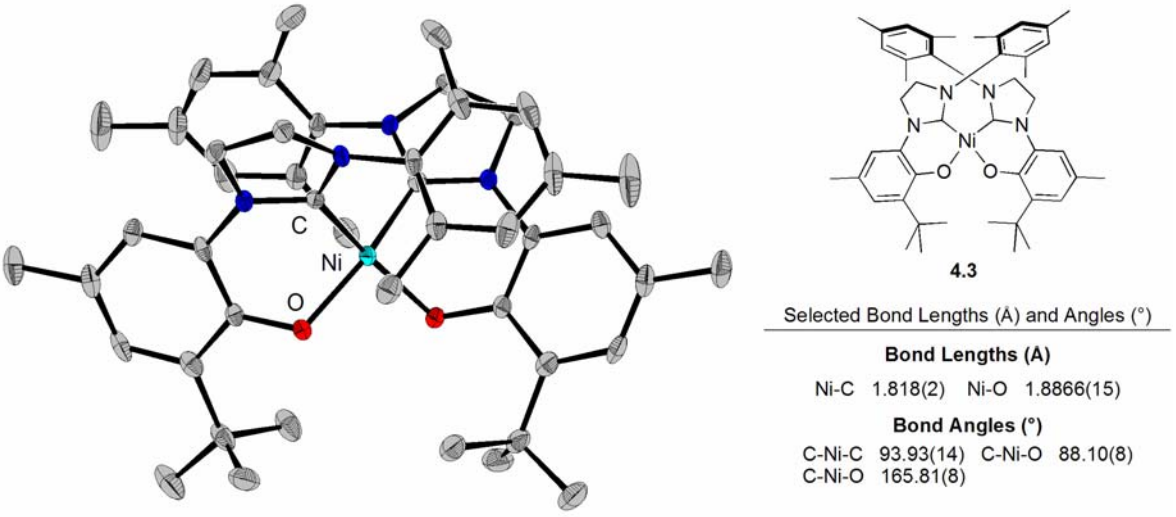


Figure 4.4. Molecular structure of Ni complex **4.3** (hydrogen atoms have been omitted for clarity). Atoms are represented by thermal ellipsoids at 50% probability.



Thus, the hypothesis depicted in Figure 4.3 was correct. The complex avoids placement of the *tert*-butyl group ortho to the O atom in direct opposition to the mesityl group on the other ligand. However, this does not prevent bis-ligation. Instead, the complex accommodates the bulkier ligands by altering the coordination geometry.

Remarkably, in spite of this accommodation of the two ligands around the Ni atom, the complex still displays a very close (~4.03 Å) interaction between the *tert*-butyl groups of the two ligands – a testament to the highly favored status of bis-ligation. It should be noted that, although a mono-ligated complex of ligand **3.21** was not obtained, it is likely that this compound was formed initially, and it was only upon concentration and crystallization that **4.3** was formed (see Scheme 4.2).

Upon examination of the structure of **4.3**, with the opposing *tert*-butyl groups in such close proximity, it was postulated that the placement of any larger group in that position would likely prevent coordination of two ligands around the metal center. With this in mind, the synthesis of a Ni complex from adamantyl substituted **3.24** (see Scheme 3.9) and $NiBr_2(PPh_3)_2$ was targeted (Scheme 4.4). Similar to the first two cases, from a paramagnetic brown solid were obtained air-stable yellow crystals, which proved to be bis-ligated complex **4.4** (Figure 4.5).[5] Like the structure of *tert*-butyl substituted **4.3**, complex **4.4** features a square planar arrangement around the Ni atom. The anionic moieties are mutually cis (as are the neutral moieties), and the two adamantyl groups are oriented in very close proximity (~3.81 Å).

Scheme 4.4. Synthesis of bis-ligated compound **4.4**.

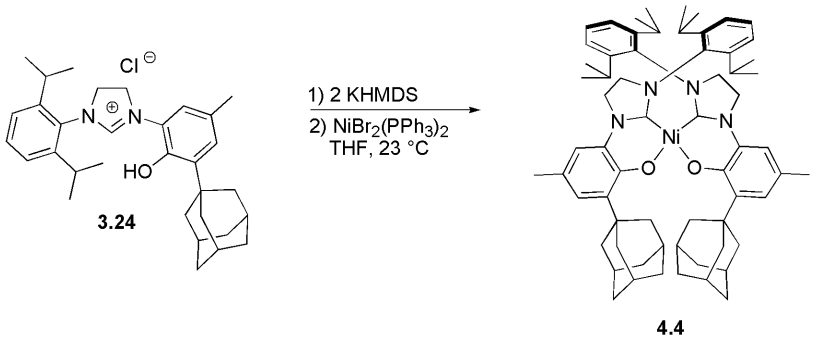
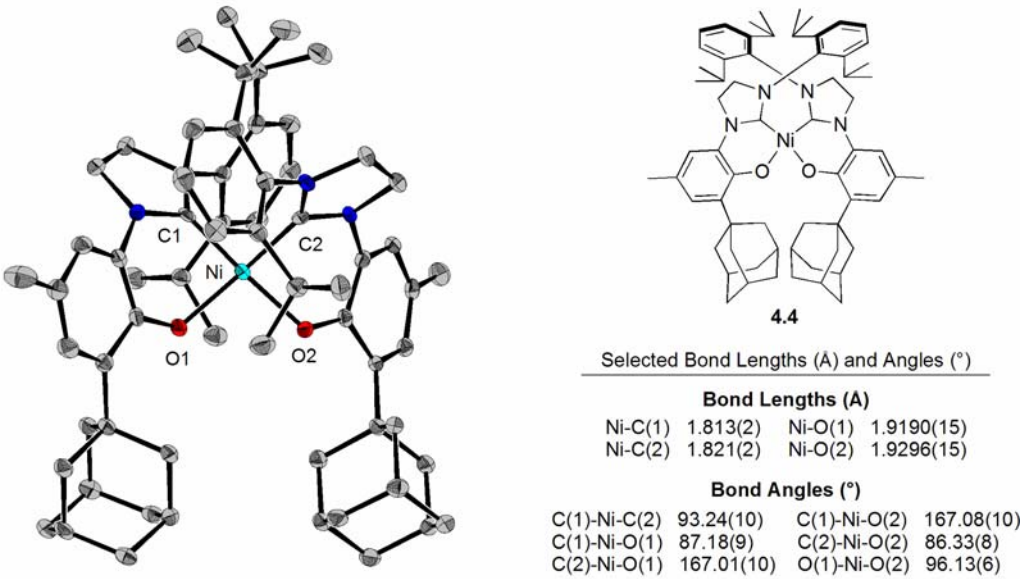


Figure 4.5. Molecular structure of Ni complex **4.4** (hydrogen atoms have been omitted for clarity). Atoms are represented by thermal ellipsoids at 50% probability.



Examination of the structure of **4.4** makes it hard to imagine that any bulkier group could be accommodated in the position ortho to the O atom. However, the attempted synthesis of compounds with larger and larger ligands to prevent bis-ligation was becoming a tedious exercise. It was now well established that bis-ligation occurs for even the bulkiest NHC ligands that we had made. However, the fact that bis-ligation can occur does not necessarily mean that it will be an insurmountable problem, as evidenced

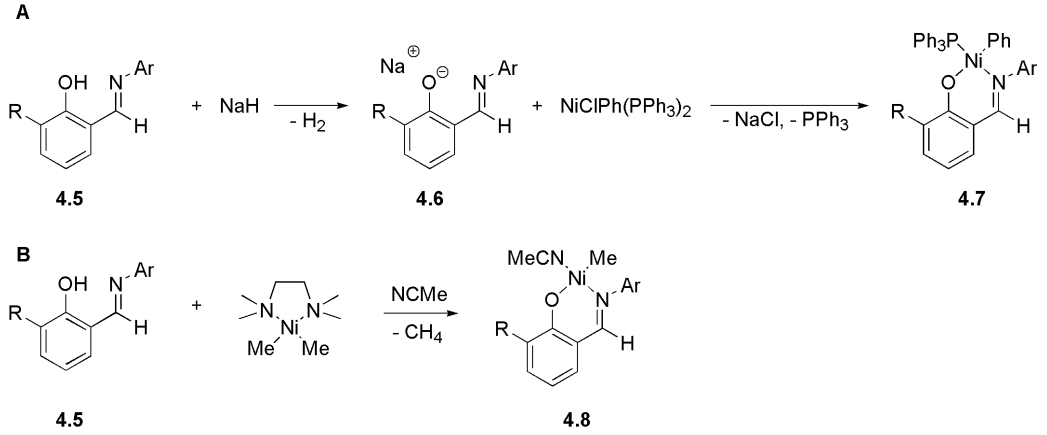
by the existence of Ni(sal) catalysts for ethylene polymerization. It was therefore decided to attempt the synthesis of organometallic complexes of Ni, as any potential polymerization catalyst would necessarily feature a Ni-alkyl bond.

4.4 Organometallic Nickel Complexes

Because the formation of bis-ligated complexes typically depends upon the formation of an insoluble inorganic salt, *e.g.*, NaCl, KBr, or an inorganic metal complex, *e.g.*, $NiBr_2(PPh_3)_2$, it was expected that the use of organometallic Ni sources, which are less prone to lose a ligand through metathesis, would provide the desired mono-ligated complex. In addition, the synthesis of an olefin addition polymerization catalyst requires a Ni-bound alkyl group. Thus, in spite of the somewhat discouraging results from the reaction of inorganic Ni precursors with chelating NHCs, organometallic Ni complexes were targeted.

Previously in our group, Ni(sal) catalysts have been synthesized using two basic approaches. The first route begins with deprotonation of sal precursor **4.5**, typically by NaH, to form its sodium phenoxide salt **4.6** (Scheme 4.5A). Treatment of this salt with the appropriate Ni precursor, *e.g.*, $NiClPh(PPh_3)_2$, results in the formation of free PPh_3, NaCl and the desired Ni(sal) complex (**4.7**). The other approach to the synthesis of Ni(sal) catalysts features the use of a basic Ni source to deprotonate the sal precursor (Scheme 4.5B). In this case, (tmeda)$NiMe_2$ (tmeda = *N*,*N*,*N´*,*N´*-tetramethyl ethylenediamine) is mixed with sal precursor (**4.5**) in acetonitrile to provide Ni(sal) complex **4.8** along with CH_4 and free tmeda.

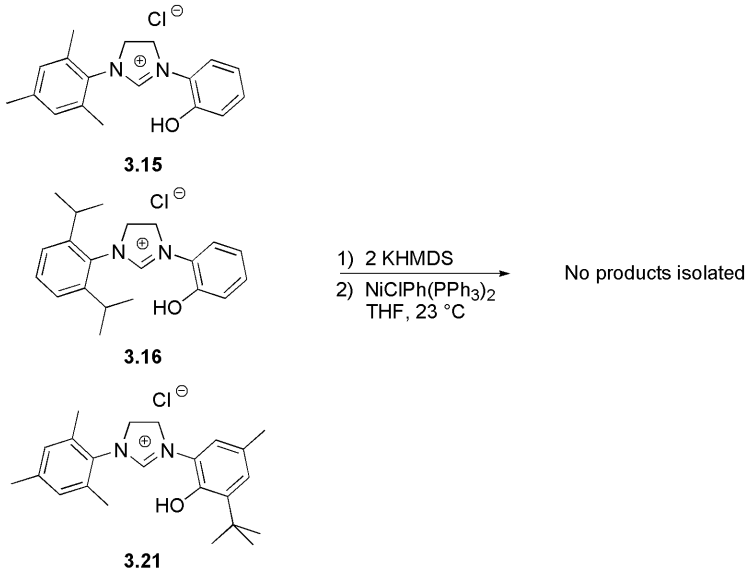
Scheme 4.5. The synthesis of Ni(sal) complexes.



In planning the synthesis of Ni complexes of chelating carbenes, the above described syntheses of Ni(sal) complexes were taken into consideration. Because the generation of our chelating carbenes requires the use of two equivalents of base – one to deprotonate the phenol, the other to deprotonate the dihydroimidazolium ring – the use of monobasic (tmeda)$NiMe_2$ did not seem a viable approach. Therefore, our first approach was to deprotonate the NHC precursors with two equivalents of a Brønsted base – the same method used to generate the Pd complexes described in Chapter 3 and the Ni complexes (**4.1-4.4**) described above.

It was also decided that $NiClPh(PPh_3)_2$ would be the first Ni source used. This was the favored Ni starting material in the synthesis of Ni(sal) complexes, and is easy to prepare and fairly robust to air and moisture. As a first experiment, NHC precursor **3.15** was treated with two equivalents of KHMDS, and then with a single equivalent of $NiClPh(PPh_3)_2$ in THF (Scheme 4.6). This reaction mixture yielded no characterizable products. Similar results were obtained with ligands **3.15** and **3.24** as well.

Scheme 4.6. Attempted synthesis of a Ni complex of ligand **3.16**.



The synthesis of a Ni complex of adamantyl substituted NHC precursor **3.24** was attempted next (Scheme 4.7). Upon workup, the procedure this time afforded a dark green, air-sensitive solid with an unfamiliar ^{1}H NMR spectrum. Crystals of this product were grown and analyzed with X-ray diffraction crystallography. The structure obtained from this analysis provided a surprising structure (**4.9**, Figure 4.6).

Scheme 4.7. Synthesis of ring-opened compound **4.9**.

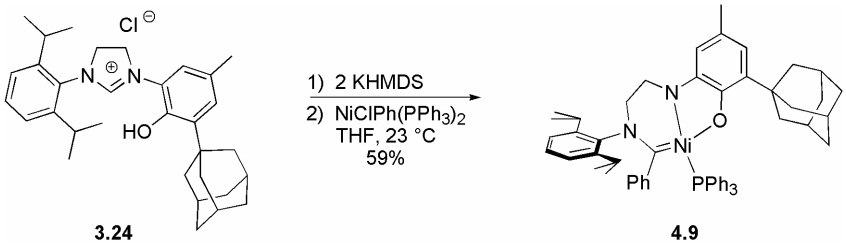
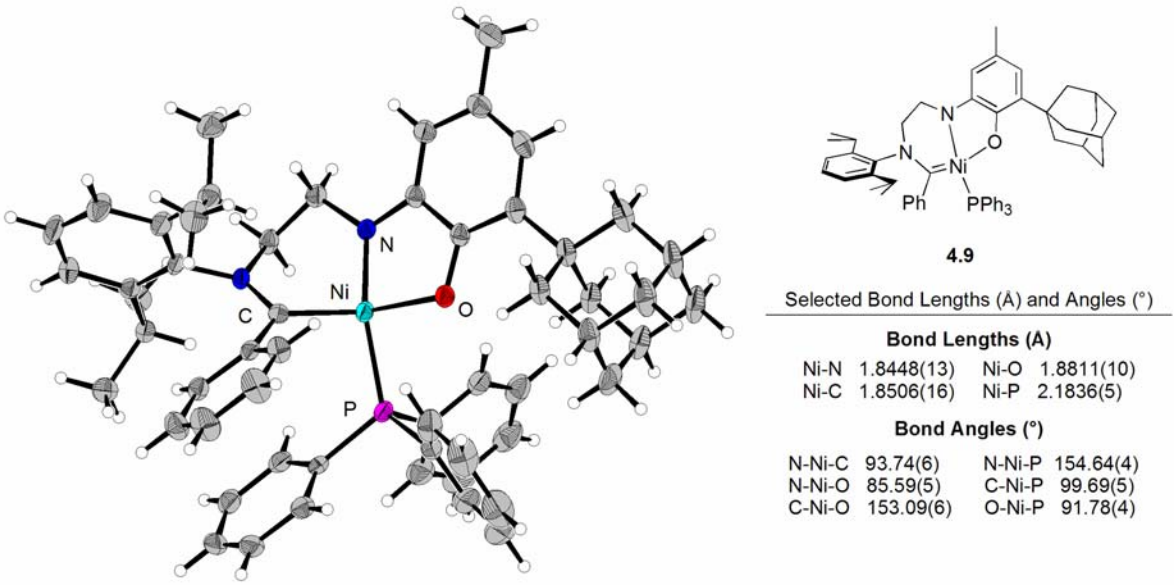


Figure 4.6. Molecular structure of Ni complex **4.9**. Atoms are represented by thermal ellipsoids at 50% probability.

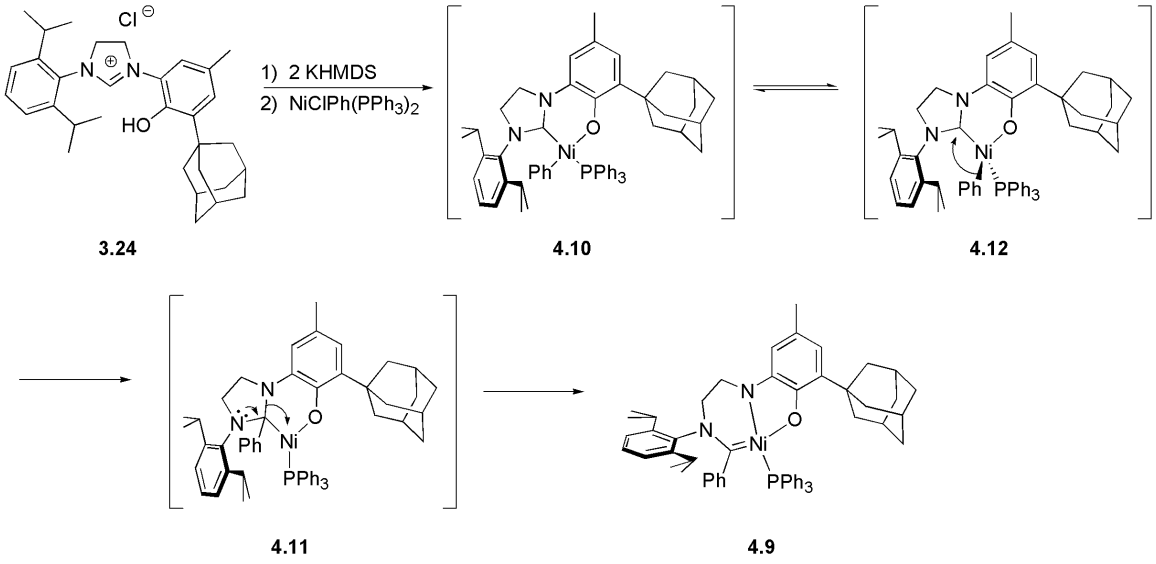


The X-ray crystallographic structure of **4.9** reveals that N–C bond cleavage of the dihydroimidazole ring of ligand **3.24** has occurred to yield a novel tridentate ligand that features carbene, amide and phenoxide moieties which are arranged in a distorted square planar geometry around the Ni atom. In addition, the phenyl group that was ligated to Ni in the starting material has been transferred to the ligand at the carbene carbon. This type of reactivity – the ring opening of an NHC ligated to a metal center – has, to the best of our knowledge, not been reported before. Thus, this otherwise undesirable reaction represents a new example of the occasionally unusual behavior of NHCs.[6]

Based on the fate of the originally Ni-bound phenyl group, now part of the ligand framework of complex **4.9**, we propose that the unique reductive elimination described in Scheme 3.13 plays a role in the formation of **4.9**. As a first attempt at explanation, a tentative mechanism for this process is proposed (Scheme 4.8). The expected product of reaction between ligand **3.24** and $NiClPh(PPh_3)_2$ is structure **4.10**. Following formation

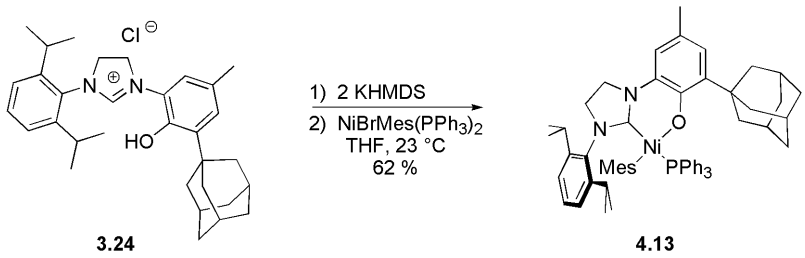
of **4.10**, attack of the phenyl group on the carbene carbon, reminiscent of the reductive elimination of NHC ligands and alkyl groups from group 10 metals described in Chapter 3, leads to chelate complex **4.11**. Interestingly, this behavior is not observed for Pd-methyl complexes **3.25-3.28**. The stability of these Pd complexes is attributed to the fact the NHC ligands are chelating, and are therefore incapable of rotating into the proper orientation for attack by the metal-bound alkyl group of the square planar Pd complexes. It may be that the propensity of Ni to attain a tetrahedral arrangement of ligands[7] (**4.12**) allows the phenyl group to attain the necessary orbital overlap to attack the carbene carbon without rotation along the Ni-NHC bond. Proposed complex **4.11** features a sterically congested trisubstituted alkyl center bound directly to Ni. This arrangement would be highly unstable, and therefore should exist only transiently. C–N bond cleavage and ligation of the resultant amide to Ni leads to **4.9**.

Scheme 4.8. A proposed mechanism for the formation of **4.9**.



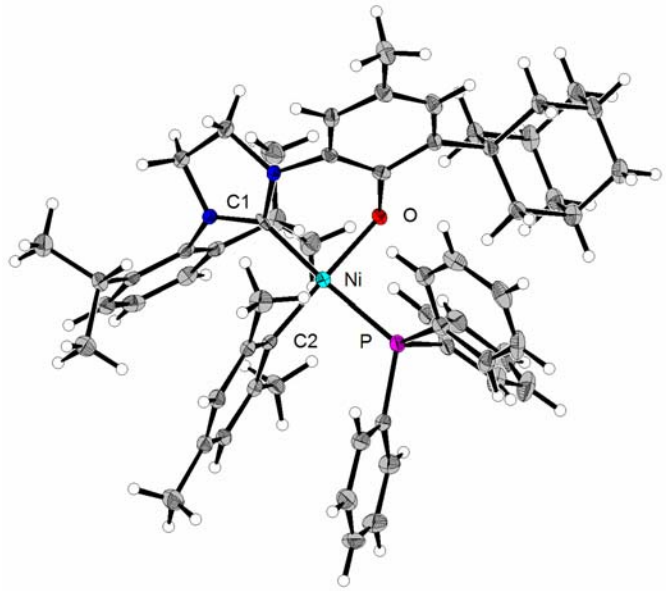
Upon consideration of the proposed mechanism for the formation of **4.9**, it was reasoned that attack on the relatively crowded NHC carbon might be prevented through the use of a bulkier alkyl group on the Ni starting material.[8] For this purpose, we chose $NiBrMes(PPh_3)_2$. Treatment of this Ni source to an activated solution of ligand **3.24** in THF gave a yellow solid (Scheme 4.9). The ^1H NMR spectrum of this compound suggested that the structure corresponded to the desired complex of chelating NHC ligand (**4.13**). Final confirmation was obtained through X-ray crystallographic analysis of a single crystal grown from THF/pentane (Figure 4.7).

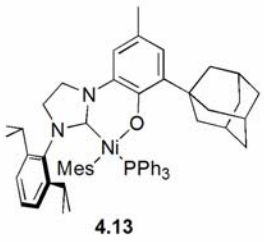
Scheme 4.9. Synthesis of Ni-mesityl complex **4.13**.



3.24 **4.13**

Figure 4.7. Molecular structure of Ni-mesityl complex **4.13**. Atoms are represented by thermal ellipsoids at 50% probability.





4.13

Selected Bond Lengths (Å) and Angles (°)

Bond Lengths (Å)

Ni-C(1)	1.874(2)	Ni-O	1.9544(15)
Ni-C(2)	1.905(2)	Ni-P	2.2274(7)

Bond Angles (°)

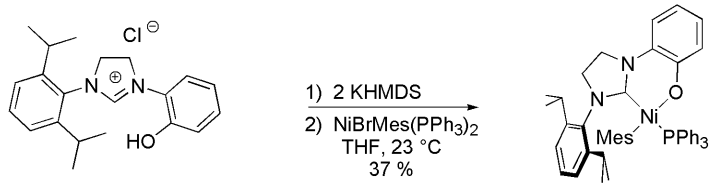
C(1)-Ni-C(2)	93.11(10)	C(1)-Ni-P	172.89(7)
C(1)-Ni-O	87.85(8)	C(2)-Ni-P	89.17(7)
C(2)-Ni-O	176.90(8)	O-Ni-P	89.54(5)

The successful synthesis of **4.13** was gratifying, both because the synthesis of such a complex was the primary goal of this project and because its existence seems to support at least one aspect of the hypothetical mechanism presented in Scheme 4.8: attack of the NHC carbon by the Ni-bound alkyl group precedes ring opening. This also confirms that the steric bulk of the two ortho methyl groups of the mesityl ligand is sufficient to prevent the attack. Alternatively, it may be that the presence of the ortho methyl groups on the mesityl ligand prevents isomerization of square planar **4.13** to the tetrahedral geometry necessary for carbene attack (see Scheme 4.8). Nonetheless, it is clear that the size of the mesityl group prevents a ring-opening reaction similar to the one that provides compound **4.9**.

Having established that Ni complexes of our chelating carbene ligands featuring a phenyl ligand are susceptible to attack on the NHC carbon by the phenyl group, the original reaction between unsubstituted ligand **3.16** and $NiClPh(PPh_3)_2$ (Scheme 4.6) was

revisited. This time, as in the synthesis of compound **4.13**, $NiBrMes(PPh_3)_2$ was used as the Ni source. Under the standard reaction conditions (activation of the ligand precursor with 2 equiv of KHMDS, followed by treatment with the Ni source), compound **4.14**, the analogue of **4.13** featuring ligand **3.16**, was synthesized.

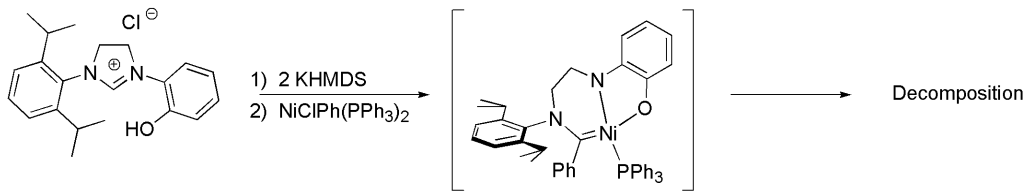
Scheme 4.10. Synthesis of Ni-mesityl complex **4.14**.



3.16 **4.14**

The formation of ring-opened product **4.9** suggests that in the reaction between NHC precursor **3.16** and $NiClPh(PPh_3)_2$ (Scheme 4.6), phenyl migration to the NHC carbon may also have occurred. The fact that no products were isolated from reaction of **3.16** (and other ligands) and $NiClPh(PPh_3)_2$ may be due to the fact that ligand **3.16** is relatively small. Whereas the bulky ortho adamantyl group of **3.24** may shield the Ni atom in ring opened complex **4.9**, the smaller ligand **3.16** does not provide adequate protection of the potentially reactive metal center of hypothetical ring-opened product **4.15** (Scheme 4.11).

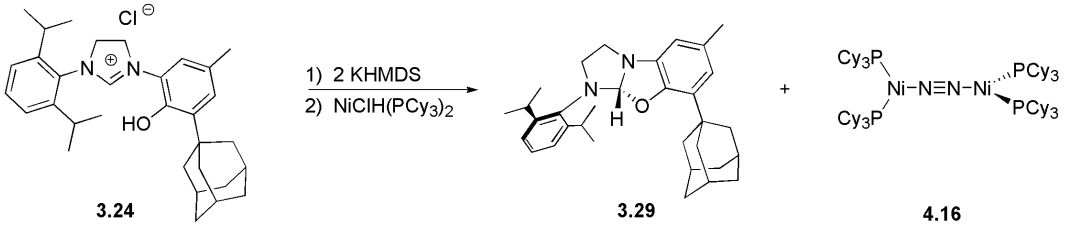
Scheme 4.11. Ligand **3.16** cannot protect the reactive metal center of **4.15**.



3.16 **4.15**

It was decided to further probe the mechanism of the ring opening reaction by observing the reaction of NHC **3.24** with another Ni source. In particular, it was anticipated that hydride, which is small and has a high propensity to participate in migration, would be a good ligand for further study. To this effect, a solution of activated ligand **3.24** was mixed with $NiClH(PCy_3)_2$ in THF (Scheme 4.12).[9] The ^1H NMR spectrum of the resulting red solid suggested the presence of compound **3.29**, the cyclized product of reaction between NHC precursor **3.24** and a single equivalent of KHMDS (see Scheme 3.11). Furthermore, from the red solid, red crystals were obtained which were determined to be $((PCy_3)_2Ni)_2N_2$ (**4.16**) by X-ray crystallographic analysis. This compound, while interesting, is well known.[10]

Scheme 4.12. Reaction of **3.24** with a Ni-hydride.

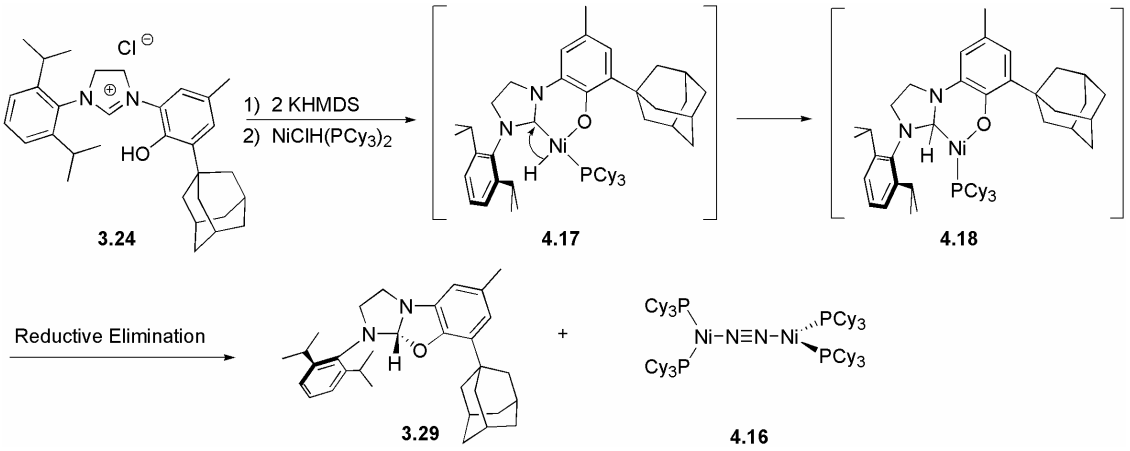


3.24 **3.29** **4.16**

Based on the occurrence of products **3.29** and **4.16**, it appeared that the case for the mechanism proposed in Scheme 4.8 had been strengthened. One could propose formation of a similar three-coordinate intermediate similar to hypothetical complex **4.11** (see Scheme 4.8) en route to both **3.29** and **4.16** (Scheme 4.13). Upon treatment of $NiClH(PCy_3)_2$ with activated ligand **3.24**, Ni-hydride **4.17** is formed initially. However, **4.17** rapidly undergoes attack by the hydride on the NHC carbon to yield intermediate **4.18**, similar to **4.11**, the initial product of phenyl attack on the NHC C atom proposed in Scheme 4.8. It was reasoned that because **4.18** would feature a disubstituted carbon atom

ligated to Ni, the ring-opening reaction does not occur, as it does for **4.11**, which features a trisubstituted carbon ligand on Ni. Instead, reductive elimination occurs to give cyclized product **3.29** and $Ni(PCy_3)_2$, which attains a molecule of N_2 during crystallization in the glovebox to yield **4.16**.

Scheme 4.13. First mechanism proposed for the formation of **3.29** and **4.16**.

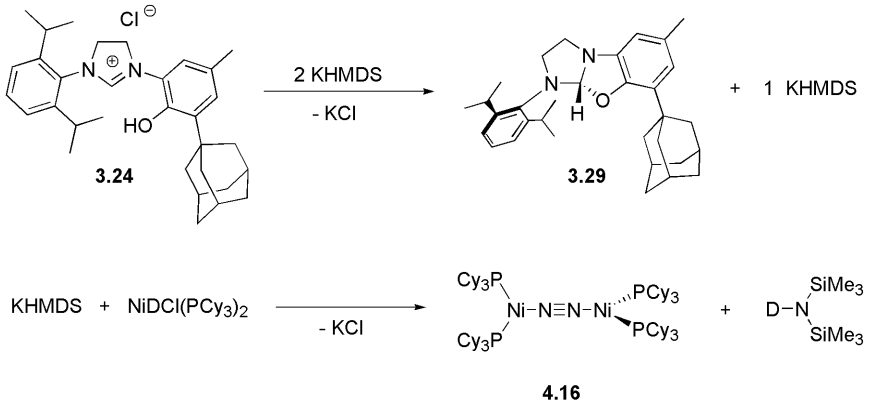


With the results of this experiment, it seemed like a clear mechanistic picture of the behavior of our chelating NHC ligands on Ni had emerged. To confirm that this was the case, the same experiment was conducted using $NiClD(PCy_3)_2$ in place of the Ni-hydride starting material. If the mechanism proposed in Scheme 4.13 were correct, then one would expect that the deuterium label would appear in **3.29**, the cyclized product of the reaction. However, upon treatment of activated NHC ligand **3.24** with $NiClD(PCy_3)_2$, the ^2H NMR spectrum did not show deuterium incorporation at the expected position, while the ^1H spectrum suggested that the position was fully protonated.

If our conclusions from the results of the ^2H experiment are correct, it is difficult to connect the above described syntheses of ring-opened product **4.9** and cyclized

product **3.29** with the same mechanism. An alternate mechanism for the formation of **3.29** is presented in Scheme 4.14. This mechanism is based on the findings reported in Chapter 3 on the ligation of ligand **3.24** to Pd – namely that formation of cyclized product **3.29** precedes ligation to the metal atom (Scheme 3.12). In that case, treatment of NHC precursor **3.24** with two equivalents of KHMDS leads to the formation of **3.29** and leaves an equivalent of KHMDS in solution. To this solution is added $NiClH(PCy_3)_2$, which, instead of reacting with **3.29**, is deprotonated by the remaining equivalent of KHMDS to provide $Ni(PCy_3)_2$, the Ni^0 complex which forms **4.16** upon crystallization.[11]

Scheme 4.14. Revised mechanism for the formation of **3.29** and **4.16**.



4.5 N-Heterocyclic Carbene Ring Opening

As stated above, to the best of our knowledge, the C–N bond cleavage and NHC ring opening that leads to the formation of **4.9** has not been reported before. However, a very similar example of NHC ring opening was discovered in our own laboratory in the course of the development of a [C,P]-chelating NHC/phosphine ligand for Ru-catalyzed olefin metathesis (**4.19**, Scheme 4.15).[12] The planned synthesis of this ligand involved late stage appendage of the phosphine moiety to the carbene precursor (**4.20**). In order to

work with this precursor without premature generation of the carbene, chloroform adduct **4.21** was synthesized by treatment of iodide **4.20** with chloroform under basic conditions. Such chloroform adducts are relatively stable compounds which give the corresponding NHC upon loss of chloroform under mild heating.[13]

Chloroform adduct **4.21** was treated with *n*-BuLi, followed by $PClPh_2$ at –78 °C, with the intended result of Li-halogen exchange with the iodide to provide lithiated intermediate **4.22**. Nucleophilic displacement on $PClPh_2$ would generate phosphine **4.23**, which would then presumably give NHC **4.19** upon loss of chloroform (Scheme 4.15). However, X-ray crystallographic analysis of the product of reaction between lithiated **4.22** and $PClPh_2$ revealed an unexpected product (**4.24**, Figure 4.8).[14] Comparison of this product to the previously described Ni complex **4.9** reveals that they feature the same NHC-derived core (Figure 4.9). The fact that such similar products were obtained from fairly unrelated starting materials in an unrelated reaction suggests that the ring scission may be a general process. Currently, however, the mechanism of the formation of **4.24** is not understood.

Scheme 4.15. Planned synthesis for NHC ligand **4.19**.

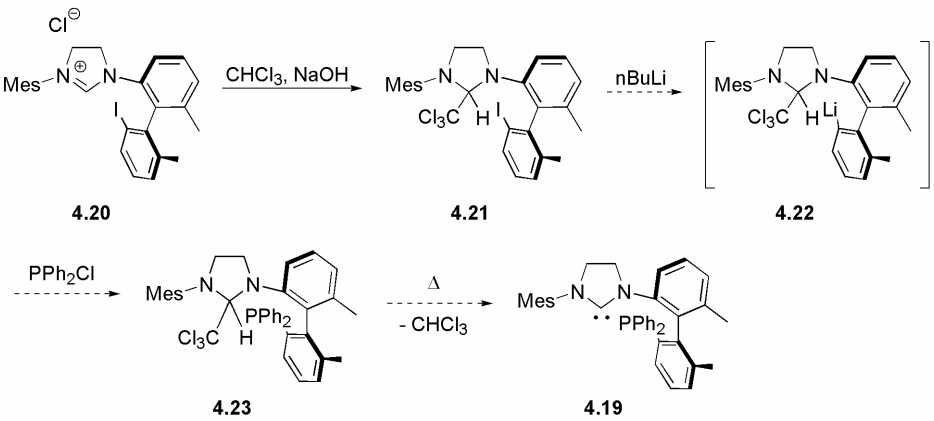


Figure 4.8. Molecular structure of compound **4.24** (chloride ion has been omitted for clarity). Atoms are represented by thermal ellipsoids at 50% probability.

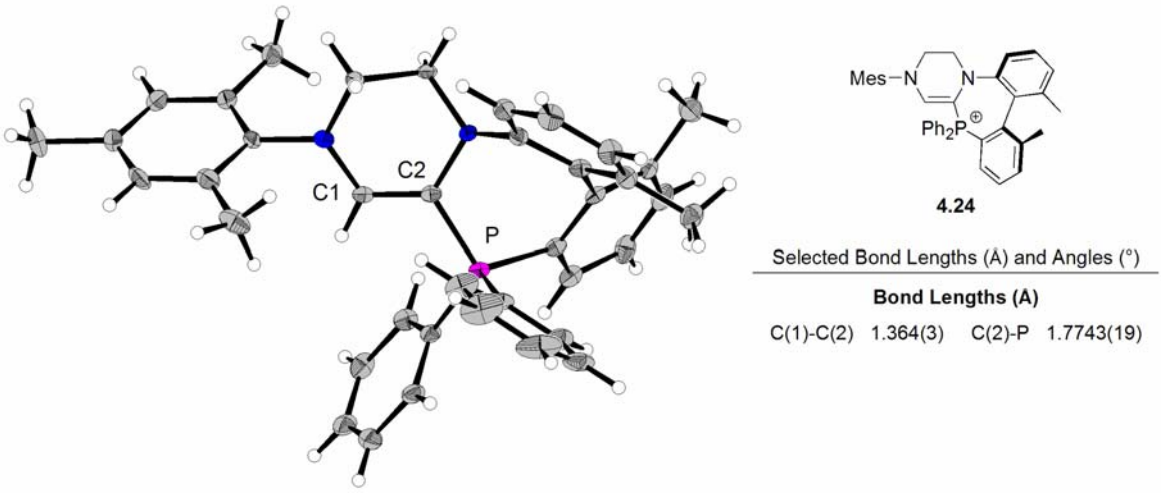
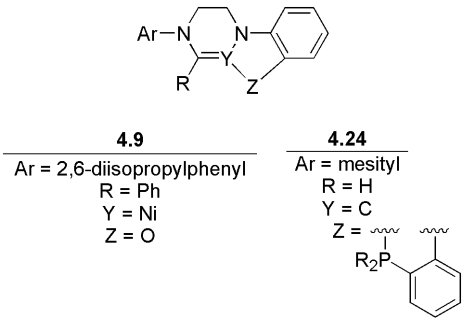


Figure 4.9. Comparison between complexes **4.9** and **4.24**.



4.6 Polymerization Activity

With a suite of stable Ni and Pd complexes of the novel chelating NHC ligands in hand, the next step was to test their activity as catalysts for ethylene polymerization, and hopefully ethylene/polar olefin copolymerization. Unfortunately, the complexes that had been synthesized by that point were less than ideal as polymerization catalysts. As discussed in Chapter 1, Pd complexes of sal are not active for ethylene polymerization, and thus it was not clear whether the NHC complexes would be either. Furthermore, the only successfully synthesized organometallic Ni complex of the novel carbene ligands was Ni-mesityl complex **4.13**, which was stable because of the use of a bulky mesityl ligand on Ni. During the course of a polymerization, this mesityl group would be replaced with much smaller groups, such as hydride and the growing polymer chain, which could conceivably take part in the ring-opening reaction.

Nonetheless, ethylene polymerization and ethylene/polar olefin copolymerization was attempted with all Ni-NHC complexes described above, as well as Pd-NHC complexes **3.25** and **3.28**. Unfortunately, none were found to be effective catalysts for ethylene polymerization. When used without additives, only complex Ni-mesityl complex **4.13** produced any polymeric product, and then only a trace amount (~5 mg). It is not clear why the catalytic activity of this complex is so low. It may be because the size of the mesityl ligand severely curtails ethylene insertion. Polymerizations of ethylene with the polar olefins methyl acrylate and methyl methacrylate were also attempted with the aforementioned catalysts. In all cases, no polymer was obtained.

4.7 Conclusion

The path to compound **4.13**, the only organometallic Ni compound of our chelating NHC ligands successfully synthesized, was unexpectedly arduous. The use of successively bulkier ligands led to the discovery that bis-ligation is highly favorable, even when the ligands feature extremely bulky substituents. A novel NHC ring-opening reaction was discovered, which, while certainly an interesting process, assured that the targeted Ni compound would be difficult, if not impossible, to synthesize. When an organometallic Ni complex of the novel NHC ligands was finally synthesized using a mesityl group on the metal (**4.13**), it proved inactive for ethylene homopolymerization and for ethylene/polar olefin copolymerization. Although copolymerization of ethylene with vinyl-functionalized olefins remains elusive, the primary goal of the project – the synthesis of Ni complexes of [C,O]-chelating NHCs – was attained. Furthermore, a deeper understanding of the reactive properties of NHCs was reached, and the somewhat mercurial nature of Ni was once again revealed. However, in the next chapter, a success story about the novel NHC ligands will be told.

4.8 Acknowledgments

This work was supported by the Rohm and Haas Corporation. Lester McIntosh (Rohm and Haas) assisted with olefin polymerizations and polymer analysis. All work on **4.24** and related compounds was done by Tobias Ritter. Larry Henling and Mike Day performed the X-ray crystallographic analysis of compounds **4.1**, **4.2**, **4.3**, **4.4**, **4.9**, **4.19**, **4.16** and **4.24**.

4.9 Experimental Details

Materials and Methods. All reactions involving metal complexes were conducted in oven-dried glassware under a nitrogen atmosphere using standard glovebox techniques. Solvents were prepared by passage through alumina. All commercially obtained reagents were used as received. Organic reagents were purchased from Sigma-Aldrich and metal salts obtained from Strem. $NiClPh(PPh_3)_2$,[15] $NiBrMes(PPh_3)_2$,[16] $NiClH(PCy_3)_2$ and $NiClD(PCy_3)_2$[17] were prepared according to literature procedures. ^1H, ^2H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian Mercury 300 spectrometer (at 300 MHz, 46 MHz, 75 MHz and 121 MHz respectively) or a Varian Inova 500 spectrometer (at 500 MHz, 77 MHz, 125 MHz and 203 MHz respectively) and are reported relative to Me_4Si (δ 0.0) for ^1H, ^2H and ^{13}C, and H_3PO_4 (δ 0.0) for ^{31}P. Data for ^1H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. Data for ^{13}C and ^{31}P NMR spectra are reported in terms of chemical shift.

Bis(1-(2,6-diisopropylphenyl)-3-(2-hydroxyphenyl)-4,5-dihydro-imidazolyl) nickel(II) (4.1). 1-(2,6-Diisopropylphenyl)-3-(2-hydroxyphenyl)-4,5-dihydro-imidazolium chloride (**3.16**) (174 mg, 0.490 mmol, 1.00 equiv) and potassium

hexamethyldisilazide (213 mg, 1.03 mmol, 2.10 equiv) were weighed together in a vial in the glovebox. Toluene (~10 mL) was added to the mixture of solids, providing a light yellow solution with a light precipitate. This suspension was added to a round-bottomed flask and allowed to stir for 10 min. At this point, a solution of $NiBr_2(PPh_3)_2$ (361 mg, 0.490 mmol, 1.00 equiv) in THF (~5 mL) was added, resulting in a dark solution with precipitate. The mixture was allowed to stir at 23 °C for 1 hr. The flask was then taken from the box and the solution filtered. Solvent was removed from the filtrate under reduced pressure. The resulting brown solid was returned to the box and redissolved in a small amount of toluene (~1 mL). This was layered with pentane (~ 5 mL), and the resulting suspension was allowed to sit at –40 °C. Over the course of a week, at least three types of crystals grew from the solution. A set of pink crystals from the mixture, representing ~75% of the bulk proved to be compound **4.1**.

1-(2,6-Diisopropylphenyl)-3-(2-hydroxyphenyl)-4,5-dihydro-imidazolyl chloro triphenylphosphine nickel(II) (4.2). From the mixture of crystals from which **4.1** was obtained, dark green crystals of **4.2** were obtained as well, representing ~10% of the bulk.

Bis(1-(mesityl)-3-(2-hydroxy-3-*tert*-butyl-5-methylphenyl)-4,5-dihydro-imidazolyl) nickel(II) (4.3). This complex was synthesized in a manner analogous to that for **4.1**, using 1-(mesityl)-3-(2-hydroxy-3-*tert*-butyl-5-methylphenyl)-4,5-dihydro-imidazolium chloride (**3.21**). Yellow crystals of **4.3** were obtained by layering pentane over a THF solution and storing at –40 °C overnight.

Bis(1-(2,6-diisopropylphenyl)-3-(2-hydroxy-3-(adamant-1-yl)-5-methylphenyl)-4,5-dihydro-imidazolyl) nickel(II) (4.4) This complex was synthesized in a manner

analogous to that for **4.1**, using 1-(2,6-diisopropylphenyl)-3-(2-hydroxy-3-(adamant-1-yl)-5-methylphenyl)-4,5-dihydro-imidazolium chloride (**3.24**) in THF. Yellow crystals of **4.4** were obtained from slow evaporation of a concentrated THF solution at 23 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.24 (m, 2H), 7.02 (d, *J* = 7 Hz, 1H), 6.59 (s, 1H), 5.89 (s, 1H), 3.94 (m, 1H), 3.89 (m, 1H), 3.45 (m, 1H), 3.40 (m, 2H), 3.13 (septet, *J* = 6.5 Hz, 1H), 2.20 (s, 3H), 2.04 (m, 6H), 1.94 (bs, 3H), 1.67 (m, 6H), 1.49 (dd, *J* = 6.5 Hz, 33.5 Hz, 6 H), 1.25 (d, *J* = 6.5 Hz, 3 H), 0.87 (d, *J* = 6.5 Hz); ^{13}C NMR (125 MHz, CD_2Cl_2): δ 191.9, 158.3, 150.0, 146.4, 139.1, 136.9, 131.8, 129.5, 126.3, 123.6, 123.3, 118.2, 118.2, 52.1, 41.9, 38.0, 29.9, 29.5, 28.7, 27.5, 27.2, 23.9, 23.6, 20.8; HRMS: Calcd for $C_{64}H_{82}N_4O_2Ni$ (M^+): 996.5791. Found 996.5785.

***N*-(2,6-Diisopropylphenyl)-*N*-benzylidene-*N´*-(2-hydroxy-3-(adamant-1-yl)-5-methylphenyl)-ethylene diimine triphenylphosphine nickel(II) (4.9).** 1-(2,6-Diisopropylphenyl)-3-(2-hydroxy-3-(adamant-1-yl)-5-methylphenyl)-4,5-dihydro-imidazolium chloride (**3.24**) (162 mg, 0.320 mmol, 1.00 equiv) and potassium hexamethyldisilazide (134 mg, 0.670 mmol, 2.10 equiv) were weighed together in a vial in the glovebox. THF (~10 mL) was added to the mixture of solids, providing a light yellow solution with a light precipitate. This was added to a round-bottomed flask and allowed to stir for ten minutes. At this point, a solution of $NiClPh(PPh_3)_2$ (223 mg, 0.320 mmol, 1.00 equiv) in THF (5 mL) was added, giving a dark green solution with precipitate. This solution was allowed to stir at room temperature for 1 hr and then was filtered through Celite. The solvent was removed under reduced pressure until ca. 2 mL remained. Pentane (~15 mL) was added and the solution was allowed to sit at –40 °C overnight, yielding a dark green solid (163 mg, 0.190 mmol, 58.7% yield). Crystals

suitable for X-ray crystallography were grown by layering pentane over a concentrated solution of **4.9** in THF and storing this layered solution at –40 °C for two days. The ^{1}H NMR spectrum of **4.13** showed some broad peaks attributed to a fluxional process on the NMR timescale. This is most likely due to restricted rotation of the diisopropylphenyl and phenyl moieties, which are adjacent in the X-ray crystallographic structure. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.56 (t, *J* = 9 Hz, 6 H), 7.32 (td, *J* = 1.5 Hz, 7.5 Hz, 2H), 7.23 (td, *J* = 1.5 Hz, 7.5 Hz, 6H), 7.16 (t, *J* = 7.5 Hz, 1H), 6.78 (t, *J* = 7 Hz, 1H), 6.4 (d, *J* = 1 Hz, 1H), 6.24 (d, *J* = 1 Hz, 1H), 4.76 (bs, 1H), 4.16 (bs, 1H), 3.38 (bs, 1H), 2.92 (bs, 2H), 2.26 (s, 3H), 1.92 (bs, 6H), 1.60 (bs, 3H), 1.38 (d, *J* = 11 Hz, 3H), 1.24 (bs, 12 H), 1.19 (d, *J* = 11.5 Hz, 3H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ 143.5, 135.1, 135.0, 134.9, 133.6, 133.3, 130.1, 130.0, 129.2, 128.5, 128.4, 128.2, 123.1, 113.4, 107.6, 68.0, 45.2, 41.3, 37.7, 36.6, 30.0, 21.8; ^{31}P NMR (121 MHz, C_6D_6): δ 22.6; HRMS: Calc'd. for $C_{56}H_{61}N_2ONi$ (M^+): 866.3875. Found 866.3835.

1-(2,6-Diisopropylphenyl)-3-(2-hydroxy-3-(adamant-1-yl)-5-methylphenyl)-4,5-dihydro-imidazolyl mesityl triphenylphosphine nickel(II) (4.13). This complex was synthesized in a manner similar to that for **4.9**, using $NiBrMes(PPh_3)_2$ as the nickel source (62.2% yield). Crystals suitable for X-ray crystallography were grown by layering pentane over a concentrated solution of **4.13** in THF and storing this layered solution at –40 °C for two days. The ^{1}H NMR spectrum of **4.13** showed some broad peaks attributed to a fluxional process on the NMR timescale. This is most likely due to restricted rotation of the diisopropylphenyl and mesityl moieties, which are adjacent in the X-ray crystallographic structure. Upon warming a C_6D_6 solution of **4.13** to 70 °C in the NMR spectrometer, the broad peaks began to coalesce. However, they did not

become well-defined. ^{1}H NMR (500 MHz, C_6D_6): δ 8.47 (bs, 1H), 7.93 (bs, 1H), 7.76 (dd, *J* = 8 Hz, 11.5 Hz, 1H), 7.41-7.38 (m, 2H), 7.20 (t, *J* = 8 Hz, 2H), 7.06-6.98 (m, 6H), 6.94 (dd, *J* = 2 Hz, 8 Hz, 6H), 6.70 (bs, 1H), 6.47 (bs, 2H), 6.20 (bs, 2H), 6.12 (bs, 1H), 5.68 (bs, 1H), 4.42 (bs, 1H), 3.68 (bs, 1H), 3.38 (bs, 1H), 3.21 (bs, 1H), 2.99 (bs, 3H), 2.64 (s, 3H), 2.21 (bs, 3H), 2.06 (bs, 3H), 1.98 (s, 3H), 1.82 (bs, 6H), 1.71 (s, 3H), 1.53 (dd, *J* = 11.5 Hz, 27 Hz, 6H), 1.12 (bs, 3H), 0.58 (bs, 3H); ^{1}H NMR (500 MHz, C_6D_6): δ 195.4, 194.6, 158.2, 147.9, 144.5, 144.3, 141.1, 138.5, 136.8, 136.7, 135.8, 134.6, 134.5, 132.8, 132.8, 131.9, 131.3, 131.3, 129.2, 129.1, 129.0, 128.8, 123.9, 119.3, 117.8, 54.7, 54.7, 50.8, 41.2, 38.0, 37.7, 30.0, 21.9, 20.7; ^{31}P NMR (203 MHz, C_6D_6): δ 19.6; HRMS: Calcd for $C_{59}H_{67}N_2ONi$ (M^+): 908.4345. Found 908.4390.

1-(2,6-Diisopropylphenyl)-3-(2-hydroxyphenyl)-4,5-dihydro-imidazolyl mesityl triphenylphosphine nickel(II) (4.14). This complex was synthesized in a manner similar to that for **4.9**, using 1-(2,6-diisopropylphenyl)-3-(2-hydroxyphenyl)-4,5-dihydro-imidazolium chloride (**3.16**) (37.2% yield). ^{1}H NMR (300 MHz, C_6D_6): δ 7.47-7.37 (m, 6H), 7.04-6.96 (m, 12H); 6.89 (t, *J* = 7.8 Hz, 1H), 6.79 (t, *J* = 8.1 Hz, 1H) 6.26 (dd, *J* = 4.8 Hz, 7.8 Hz, 1H), 6.14 (bs, 1H), 3.39 (t, *J* = 10.5 Hz, 2H), 3.18 (t, *J* = 10.5 Hz, 2H), 3.06 (septet, *J* = 6.3 Hz, 2H), 2.51 (s, 6H), 2.14 (s, 3H), 1.29 (d, *J* = 6.6 Hz, 4H), 0.94 (dd, *J* = 1Hz, 6.6 Hz, 4H); ^{31}P NMR (121 MHz, C_6D_6): δ 19.0

Reaction between 3.24 and $NiClH(PCy_3)_2$: 1-(2,6-Diisopropylphenyl)-3-(2-hydroxy-3-(adamant-1-yl)-5-methylphenyl)-4,5-dihydro-imidazolium chloride (**3.24**) (157 mg, 0.310 mmol, 1.00 equiv) and potassium hexamethyldisilazide (129 mg, 0.620 mmol, 1.20 equiv) were weighed together in a vial in the glovebox. THF (~10 mL) was added to the mixture of solids, providing a light yellow solution with a light precipitate. To this

solution was added a solution of $NiHCl(PCy_3)_2$ (203 mg, 0.310 mmol, 1.00 equiv) in THF (~5 mL), giving a dark red solution with precipitate. The reaction mixture was allowed to stir at room temperature for 1 hr, then filtered through Celite. The solvent was removed under reduced pressure. The ^1H NMR spectrum of the resulting red solid revealed the presence of **3.29** and another product. Dark red crystals suitable for X-ray analysis were grown by slow evaporation from THF. These crystals proved to be $((PCy_3)_2Ni)_2N_2$ (**4.16**). This was confirmed by matching the ^1H NMR spectrum of this known compound.[17]

Ethylene polymerization studies – general protocol. All polymerization studies were performed using an Argonaut Endeavor automated parallel multi-reactor synthesizer. A measured amount of a standard solution of catalyst in toluene (such that 5 μmol are used) was added to each reaction vessel. The desired pressure of ethylene was introduced to each vessel, and each vessel was allowed to warm to the desired temperature. At this point, any activator and/or comonomer that was to be used was added via syringe to each vessel. After this, stirring was begun. The ethylene uptake was monitored remotely. After the prescribed reaction interval, the reaction was terminated by venting the ethylene. The samples were removed from the glovebox and any polymer that formed was precipitated from solution by addition of methanol. Excess Al activator was quenched by the addition of 3 M HCl solution. After stirring each sample overnight, any polymer that had precipitated was collected by filtration, and dried in a vacuum oven overnight.

4.10 References

[1] In this chapter and others, organometallic complexes are distinguished from inorganic as "those having a traditional metal-carbon bond." Of course, all complexes of NHC ligands feature a metal-carbon bond, but for ease of discussion, that bond will be disregarded, and only the other ligands of the complex will be considered.

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[4] From this crystallization were also obtained crystals of the Ni byproducts $NiCl_2(PPh_3)_2$ and $NiCl(PPh_3)_3$. Presumably, the chloride ions came from the ligand precursor. The appearance of $NiCl_2(PPh_3)_2$ is in accordance with the mechanism suggested in Scheme **4.2**. As for $NiCl(PPh_3)_3$, we have frequently encountered such Ni(I) complexes during attempted crystallizations of Ni compounds.

[5] It is somewhat interesting that compound **4.4**, featuring very bulky adamantyl-substituted NHC ligands is air-stable. Most $Ni(sal)_2$ complexes are air-stable save for the one resulting from bis-ligation of the very bulky *ortho*-anthracenyl ligand. It is presumed that the great steric encumbrance of two bulky ligands around a small Ni center labilizes the ligand, making the complex susceptible to reaction with oxygen or moisture. It is therefore surprising that complex **4.4**, which features ligands of comparable size to the *ortho*-anthracenyl sal ligands is stable in air (indefinitely).

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[8] McGuinness, D. S.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Organometallics* **1999**, *18*, 1596–1605.

[9] For the sake of consistency, $NiClH(PPh_3)_2$ should have been used; however, that compound cannot be synthesized. Therefore, $NiHCl(PCy_3)_2$ was used.

[10] Jolly, P. W.; Jonas, K.; Krueger, C.; Tsay, Y. H. *J. Organomet. Chem.* **1971**, *33(1)*, 109–122.

[11] Indeed, treatment of $NiHCl(PCy_3)_2$ with KHMDS leads to the deprotonation of the Ni-hydride, as observed with ^1H NMR.

[12] Ritter, T.; Grubbs, R. H., unpublished results.

[13] (a) Arduengo III, A. J.; Calabrese, J. C.; Davidson, F.; Dias, H. V. R.; Goerlich, J. R.; Krafczyk, R.; Marshall, W. J.; Tamm, M.; Schmutzler, R. *Helv. Chim. Acta* **1998**, *82*, 2348–2364. (b) Trnka, T. M.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl. M.; Choi, T.-L.; Ding, S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 2546–2558. (c) Nyce, G. W.; Csihony, S.; Waymouth, R. M.; Hedrick, J. L. *Chem. – Eur. J.* **2004**, *10*, 4073–4079.

[14] The corresponding product was also obtained with the use of PCy_2Cl.

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