Chapter 3

A Novel Class of Chelating N-Heterocyclic Carbene Ligands and Their Complexes of Palladium

3.1 Abstract

To address the apparent deactivation of our Ni(sal) catalysts by functionalized olefins such as methyl acrylate, more electron-donating ligands were targeted to make the metal center less oxophilic. The ligand framework we chose to target was a class of chelating N-heterocyclic carbene ligands patterned after the salicylaldimine framework. To access this novel ligand class, a synthesis of unsymmetrically substituted N-heterocyclic carbene ligands was designed. The process is both high yielding and modular, allowing for the synthesis of a wide range of ligands. The success of the ligand synthesis and the viability of the chelating carbene concept are demonstrated by the synthesis of a series of Pd complexes of the new ligands.

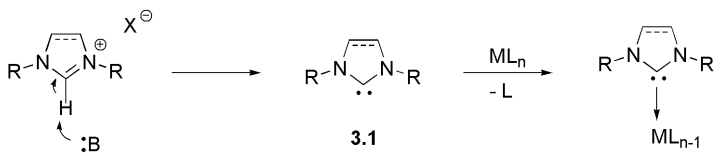
3.2 Introduction

As discussed in Chapter 2, the deactivation of Ni(sal) olefin polymerization catalysts in the presence of vinyl-functionalized olefins is apparently due to the formation of a Ni-enolate chelate that is both inactive toward further polymerization and susceptible to protonolysis. At the end of Chapter 2, it was proposed that the use of a more electron donating ligand than sal might disfavor the formation, or a least weaken the association, of such a chelate by rendering the metal center more electron rich. For this goal, N-heterocyclic carbenes were targeted.

3.3 N-Heterocyclic Carbenes

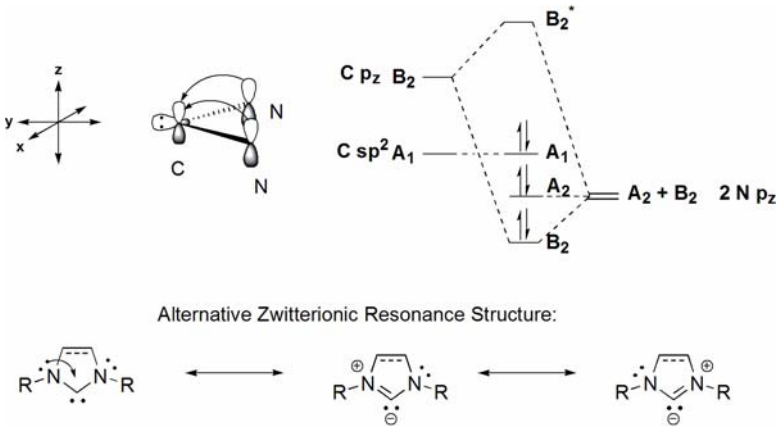
In the last decade there has been a great deal of interest in the development of stable carbenes derived from heterocyclic compounds.[1] The most commonly studied of these are the so-called N-heterocyclic carbenes (NHCs) (**3.1**, Scheme 3.1).[2] These feature a five-member heterocycle derived from a imidazolium or dihydroimidazolium salt. The ease of synthesis of these precursors is one of the chief reasons for the popularity of NHCs. The development of NHCs has had a significant impact on organometallic chemistry because they can act as neutral two-electron donor ligands, commonly replacing similar ligands, such as phosphines, in that role.

Scheme 3.1. N-heterocyclic carbenes and their ligation to metal atoms.



The utility of NHCs comes from their somewhat unusual electronic properties. Examination of the molecular orbital diagram of an NHC (Figure 3.1) reveals that the p_z orbital of the central carbon atom receives significant electron donation from the two adjacent nitrogen atoms (in the B_2 bonding orbital in Figure 3.1). This forces the carbene electrons to occupy the forward-directed carbon sp^2 orbital (the A_1 non-bonding orbital in Figure 3.1). Because the two carbene electrons occupy a single orbital, NHCs are singlet carbenes. This is supported by both crystallographic and computational studies.[1] Indeed, the electron donation from the nitrogen atoms into the empty carbon p_z orbital is so strong that NHCs can also be effectively described by its zwitterionic resonance structure.

Figure 3.1. Molecular orbital diagram of an NHC.



There are interesting chemical consequences of the exceptional electronic properties of NHCs. For example, uncharacteristically for carbenes, NHCs can be isolated and characterized.[2] Furthermore, despite the inherently reactive nature of carbenes, when NHCs are coordinated to metal atoms, they show a low propensity to dissociate to free carbenes. Because NHCs are essentially carbanionic in character, they

are very strong σ-donors. However, unlike analogous σ-donors such as phosphines and CO, NHCs are very weak π-acceptors.[3] Like many of the characteristics of NHCs, this low π-acidity is a consequence of the extensive donation of the nitrogen lone electron pairs into the nominally empty carbon p_z orbital of the carbene, which prevents backbonding from the metal.

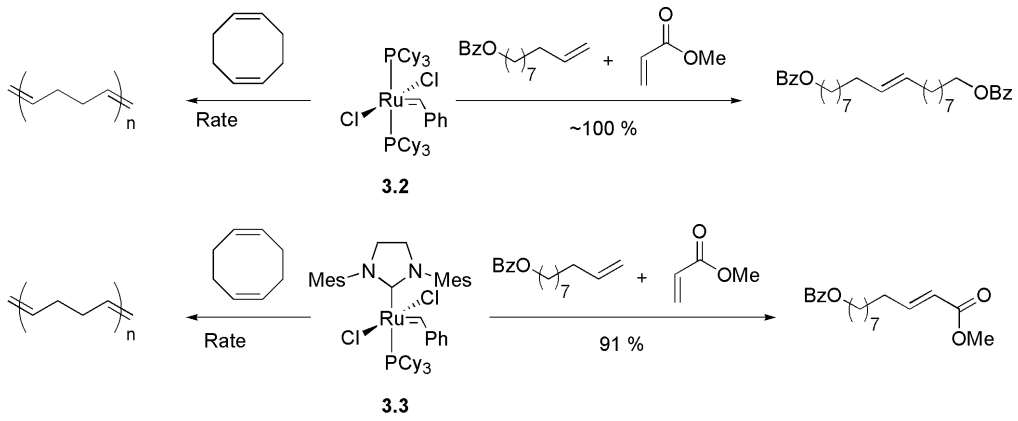
As stated above, the two-carbon backbone of an NHC can be either unsaturated or saturated, depending on whether it is derived from an imidazolium or dihydroimidazolium salt, respectively. Of the two, NHCs with an unsaturated backbone are generally more stable as free carbenes, since the nominally empty p_z orbital is part of an aromatic system, conjugated with the C–C double bond in the backbone.[1] There is, however, little evidence that the aromaticity of an NHC has much bearing on its properties as a ligand for transition metals.[1]

These special electronic properties can sometimes increase the reactivity of transition metal catalysts that feature NHCs in place of more traditional two-electron donor ligands. There can be a number of reasons for this enhancement. For example, catalysts that feature low-coordinate metal atoms are often much more reactive than those with higher-coordinate metal atoms. Because carbenes often are both sterically large and show a low propensity to dissociate, they can sterically shield the environment around low-coordinate, low-valent metal atoms. In addition, the strong σ-donation from an NHC makes a metal center very electron rich and increases its affinity for electron-poor substrates.

Perhaps the most well-known example of enhanced reactivity arising from replacement of a traditional ligand with an NHC has been in the field of Ru-catalyzed

olefin metathesis (Scheme 3.2). In that case, replacement of a single phosphine ligand of Ru carbene **3.2** with an NHC ligand provides a complex (**3.3**) that is, in general, a much more reactive catalyst.[4] For example, in a cross metathesis reaction between an α-olefin and an electron poor olefin such as methyl acrylate, catalyst **3.2** shows no activity toward the electron poor olefin, producing only a homodimer of the α-olefin. (Scheme 3.2). Catalyst **3.3**, however, reacts readily with the electron-deficient olefin to produce the desired heterodimer in excellent yield.[5] In another example, catalyst **3.3** polymerizes cyclooctadiene around 1000 times faster than catalyst **3.2**.[6] This enhancement in reactivity is attributed to the fact that **3.3** displays a greatly increased affinity to bind olefins (10^4x) relative to catalyst **3.2**.[7] Enhanced reactivity has also been observed when NHC ligands are used on Pd catalysts for C–C and C–N coupling reactions.[8]

Scheme 3.2. NHC substitution enhances olefin metathesis activity.



Another attractive feature of NHCs is the wide variety of steric[9] and asymmetric[10] environments that are available through modification of the substituents appended to the NHC nitrogen atoms. Furthermore, through the use of appropriate donor groups on the NHC nitrogen substituents, it is possible to make multidentate NHCs.[10b,11] Such

variability makes possible the synthesis of NHC analogues of many traditional ligands. It was along these lines that we envisioned the synthesis of an NHC analogue of the salicylaldimine framework (Figure 3.2). It was our hope that by replacing the relatively weakly σ-donating imine moiety of the sal framework with an NHC, we could realize some of the reactivity enhancements described above in our neutral Ni catalysts.

Figure 3.2. An NHC analogue of sal ligands.

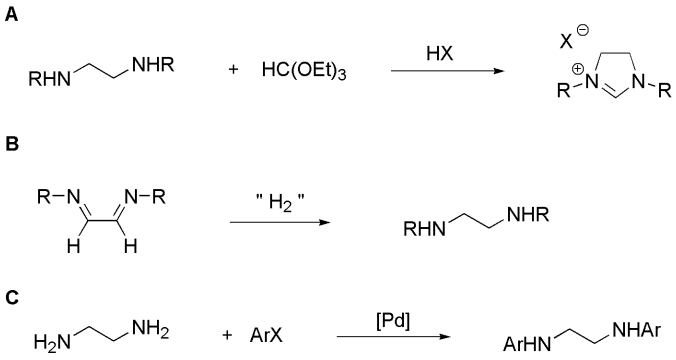
Salicylaldimine framework

Proposed chelating carbene

3.4 Ligand Synthesis

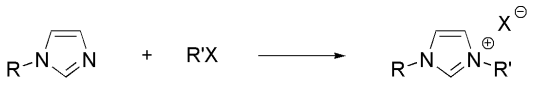
The synthesis of the proposed ligand framework was not trivial. One of then main difficulties we foresaw was the introduction of unsymmetrical *N,N´*-substitution. Often, *N,N´*-diaryl saturated NHC precursors are synthesized by condensation of a formic acid equivalent with an *N,N´*-diaryl ethylenediamine (Scheme 3.3A). Such ethylenediamines are typically easy to synthesize; for example, they can be formed by reduction of a diimine (Scheme 3.3B) or Pd-catalyzed coupling of ethylenediamine with appropriate aryl halides (Scheme 3.3C). Although the synthesis of symmetrically substituted diamines is simple enough, it was anticipated that making them unsymmetrical would be relatively difficult using these approaches.

Scheme 3.3. Traditional approaches to the synthesis of saturated NHCs.



Unsymmetrically substituted NHCs have been successfully synthesized via nucleophilic attack of a 1-alkylimidazole on an alkyl halide (Scheme 3.4).[8] However, nucleophilic attack on an aryl ring by an imidazole is difficult, making *N*,*N*´-diaryl substitution unattainable by this approach. This is problematic because our aim was to reproduce as nearly as possible the steric environment created by sal ligands, and *N*,*N*´-diaryl substitution was considered important. Therefore, because none of the previously reported approaches seemed compatible with the synthesis of unsymmetrically substituted *N*,*N*´-diaryl NHC precursors, we realized that it was necessary to develop a new route.

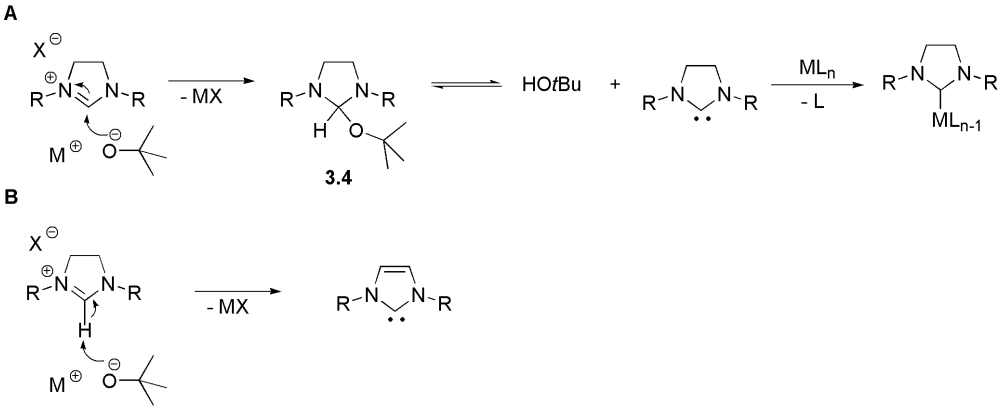
Scheme 3.4. Attack of an imidazole on an alkyl electrophile can provide an unsaturated NHC precursor.



In addition to difficulties in the synthesis of our proposed NHC precursors, we also foresaw potential difficulties in generating the corresponding carbenes. The

generation of NHCs from imidazolium and dihydroimidazolium precursors can be described as a deprotonation. However, that characterization is not always strictly accurate. Certainly, non-nucleophilic bases such as sodium hydride and butyllithium directly deprotonate NHC precursors to give NHCs. If, however, an alkoxide base is used, *e.g. t*-butoxide, dihydroimidazolium NHC precursors instead form an adduct (**3.4**) with the alkoxide base. This adduct provides the desired NHC upon elimination of the corresponding alcohol (Scheme 3.5A),[12] which is likely reversible. In the presence of a transition metal, the NHC binds to the metal, thus driving the reaction forward. Incidentally, imidazolium NHC precursors are directly deprotonated by alkoxide bases, since formation of an adduct analogous to **3.4** would disrupt the aromaticity of the imidazolium ring (Scheme 3.5B).

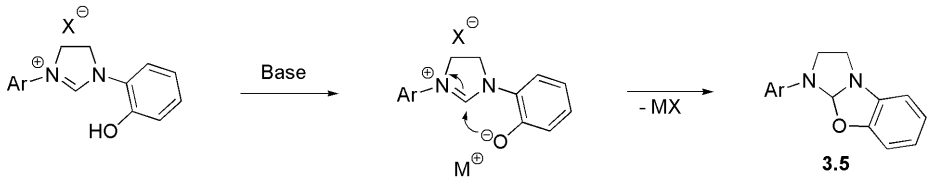
Scheme 3.5. A: Formation of saturated NHCs by treatment with an alkoxide base.
B: Formation of unsaturated NHCs by treatment with an alkoxide base.



Because the formation of adducts with alkoxide bases was known, it was anticipated that there could be difficulty forming an NHC with an adjacent phenoxide moiety (Scheme 3.6). Since the phenol is expected to be more acidic than the dihydroimidazolium salt, it should be deprotonated first. Given the proximity of the

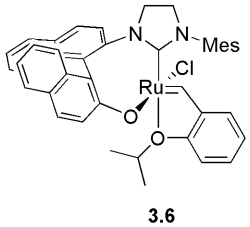
phenoxide unit, and the fact that cyclization leads to a five-member ring, it was feared that cyclization might produce an adduct (**3.5**) that would not undergo the elimination necessary to form the NHC, or would do so only transiently, thus preventing coordination to a metal atom.

Scheme 3.6. Anticipated formation of a cyclized product.



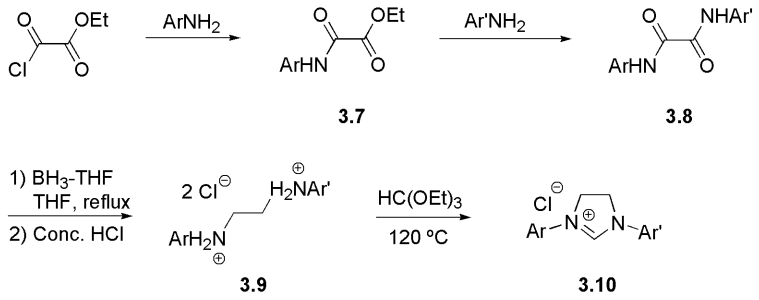
Despite the difficulties envisioned in the synthesis of our proposed NHC ligands, we were encouraged by the example of a Ru complex reported by Hoveyda and coworkers for asymmetric olefin metathesis (**3.6**, Figure 3.3).[10b] This complex features an unsymmetrically substituted *N*,*N*´-diaryl NHC ligand with a chelating phenoxide moiety, thereby proving that the problems that we foresaw with our framework could be overcome. Unfortunately, the synthesis of this ligand is somewhat lengthy. Thus, a simpler and more general approach needed to be sought.

Figure 3.3. Hoveyda's example of an *N*,*N*´-diaryl substituted chelating NHC.



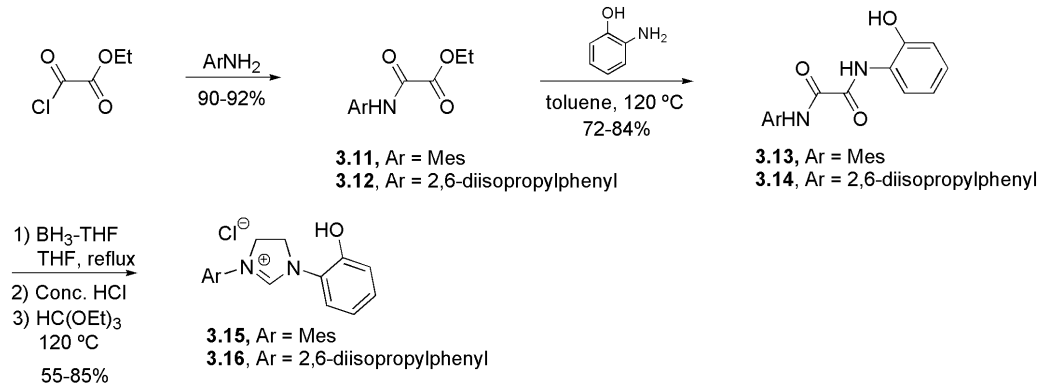
After some consideration, the general protocol for the synthesis of unsymmetrically substituted NHCs illustrated in Scheme 3.7 was developed.[13] Because unsymmetrically substituted diamines seemed relatively easy to synthesize, it was decided that it would be simpler to develop an approach to saturated NHC precursors. To begin the synthesis, ethyl chlorooxoacetate is treated with an aniline in the presence of triethylamine to give oxanilic acid ester **3.7** (Scheme 3.7). Reaction with the appropriate aminophenol under varying conditions provides oxalamide **3.8**. Reduction of **3.8** with borane-THF complex forms an ethylenediamine. Formation of the hydrochloride salt of this ethylenediamine (**3.9**), followed by condensation with triethylorthoformate gives NHC precursor **3.10**.

Scheme 3.7. General protocol for the synthesis of unsymmetrically substituted NHCs.



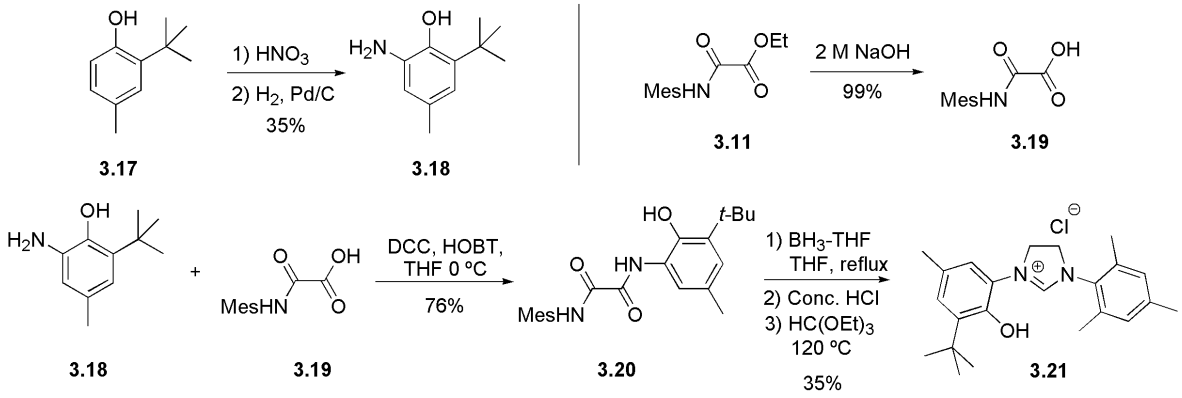
For each specific ligand, a different approach was required to append an aminophenol in the second step. For instance, treatment of **3.11** and **3.12** with 2-aminophenol in refluxing toluene provided bis-amides **3.13** and **3.14** (Scheme 3.8). Reduction of these bis-amides with borane, followed by salt formation and condensation provided the desired NHC precursors **3.15** and **3.16**.

Scheme 3.8. Synthesis of NHC precursors **3.15** and **3.16**.



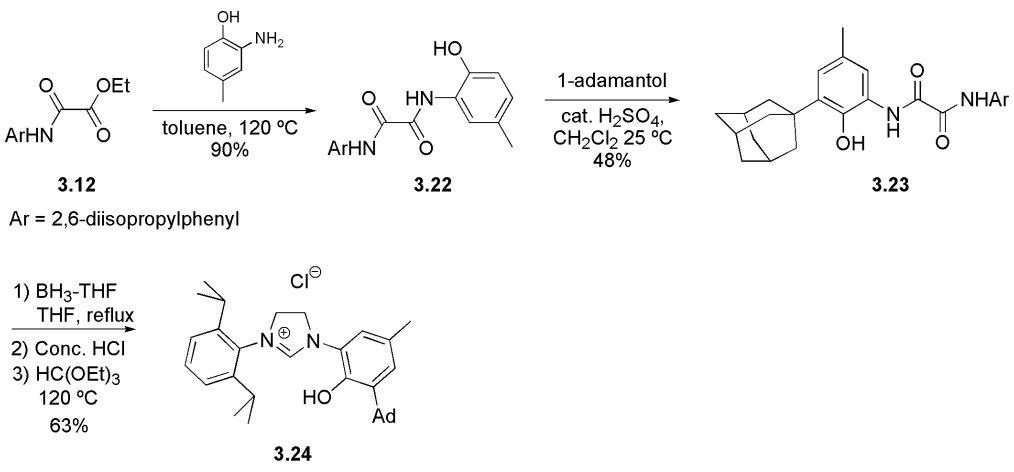
As discussed in Chapter 1, it is well established that late metal olefin addition polymerization catalysts must feature a bulky ligand set to display good reactivity and stability. With this in mind, a chelating NHC ligand that featured a sterically large moiety ortho to the phenoxide was targeted (Scheme 3.9). Nitration of 2-*tert*-butyl-4-methyl phenol (**3.17**), followed by nitro reduction by H_2 over Pd/C yielded 2-*tert*-butyl-4-methyl-6-aminophenol (**3.18**). The placement of the methyl group para to the phenol served to block nitration at that position. Aminophenol **3.18** proved too bulky to react in a manner similar to that employed in the syntheses of **3.13** and **3.14** (Scheme 3.8). Therefore, peptide coupling of **3.18** with oxanilic acid **3.19** (made by saponification of **3.11**) was employed to form bis-amide **3.20**. From this point, reduction and cyclization with triethyl orthoformate provided NHC precursor **3.21**.

Scheme 3.9. Synthesis of NHC precursor **3.21**.



An even bulkier NHC precursor was prepared by the introduction of an adamantyl group in the position ortho to the phenol (Scheme 3.10). This was accomplished by treatment of **3.12** with 2-amino-4-methylphenol in refluxing toluene to provide bis-amide **3.22**. Again, the purpose of the methyl group para to the phenol was to block substitution at that position. Reaction of **3.22** with 1-adamantol and catalytic sulfuric acid afforded bis-amide **3.23**. From this point, reduction and cyclization with triethyl orthoformate provided dihydroimidazolium NHC precursor **3.24**.

Scheme 3.10. Synthesis of NHC precursor **3.24**.



NHC precursors **3.15**, **3.16**, **3.21** and **3.24** are white, air and moisture tolerant, crystalline solids that display good to moderate solubility in a range of organic solvents. The successful synthesis of this small class of NHC precursors demonstrates the usefulness and variability of this approach. Unlike the previously described routes to NHCs (Scheme 3.3), this modular approach appends the nitrogen atom substituents in separate steps involving orthogonal reaction conditions. This allows for the synthesis of unsymmetrically substituted NHCs limited only by the imagination and the availability of the starting amines.

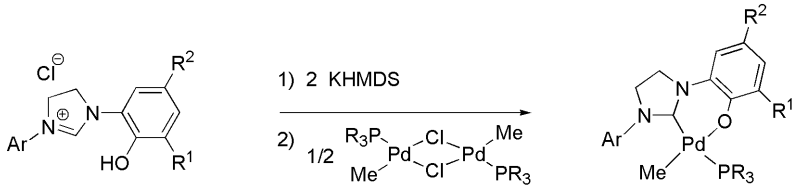
3.5 Synthesis and Characterization of Pd Complexes

Although the synthesis of Ni complexes of chelating NHCs was the primary goal of this project, Pd complexes were targeted first. As discussed in Chapter 1, sal complexes of Pd are not active catalysts for olefin addition polymerization. However, Pd tends to form more stable complexes than Ni. Therefore, as a first test of the viability of the novel ligand framework, it was decided that Pd complexes of the novel ligands would be targeted, although any Pd complexes of chelating NHCs that were synthesized would certainly be tested for polymerization activity.

As discussed above, there was some uncertainty as to whether it would be possible to generate NHCs from a dihydroimidazolium precursor with an adjacent phenolic moiety (see Scheme 3.6). Gratifyingly, it was found that simple treatment of the NHC precursors with two equivalents of potassium hexamethyldisilazide (KHMDS) at room temperature in toluene or THF, followed by mixing with a suitable Pd compound proved to be an adequate method for generation of the desired Pd/chelating NHC complexes (Scheme 3.11).[14] KHMDS was chosen for its high basicity and low

nucleophilicity. In other words, it would be expected to directly deprotonate a saturated NHC precursor, rather than form an adduct similar to **3.4** (Scheme 3.5). Treatment of a solution of deprotonated NHC with monophosphine methyl palladium chloro-bridged dimers $((PR_3)PdMeCl)_2$ (R = Et, Ph), resulted in the formation of the targeted Pd carbene complexes of the type $(NHC)PdMe(PR_3)$ (R = Et, Ph) in good yields (Scheme 3.11).[11] Complexes **3.25** and **3.28** were structurally characterized by X-ray crystallography (Figures 3.4 and 3.5). They possess square-planar geometry with the anionic donors (methyl and phenoxide) *trans* to each other.

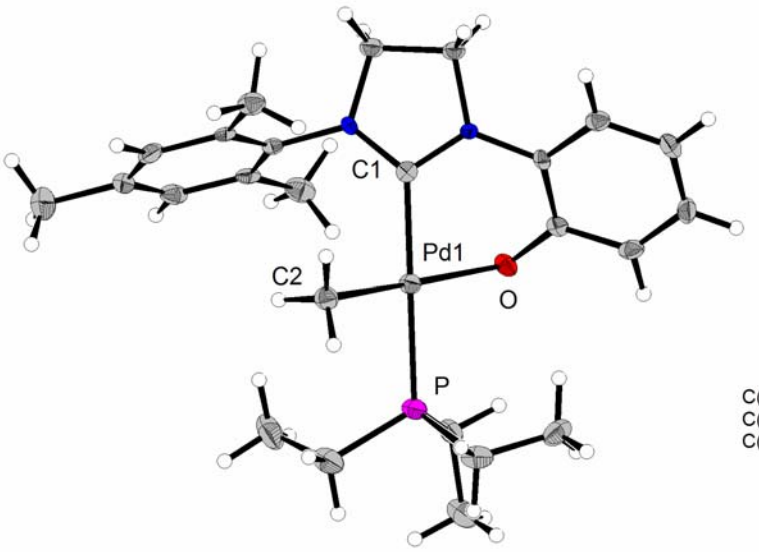
Scheme 3.11. Synthesis of Pd complexes of chelating NHCs.

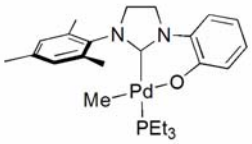


	Ar	R^1,R^2	L
3.25	Mes	$R^1 = R^2 = H$	PEt_3
3.26	DIPP	$R^1 = R^2 = H$	PPh_3
3.27	Mes	R^1 = *t*-Bu, R^2 = Me	PPh_3
3.28	DIPP	R^1 = Ad, R^2 = Me	PPh_3

DIPP = 2,6-diisopropylphenyl

Figure 3.4. Molecular structure of Pd complex **3.25**. Atoms are represented by thermal ellipsoids at 50% probability.





3.25

Selected Bond Lengths (Å) and Angles (°)

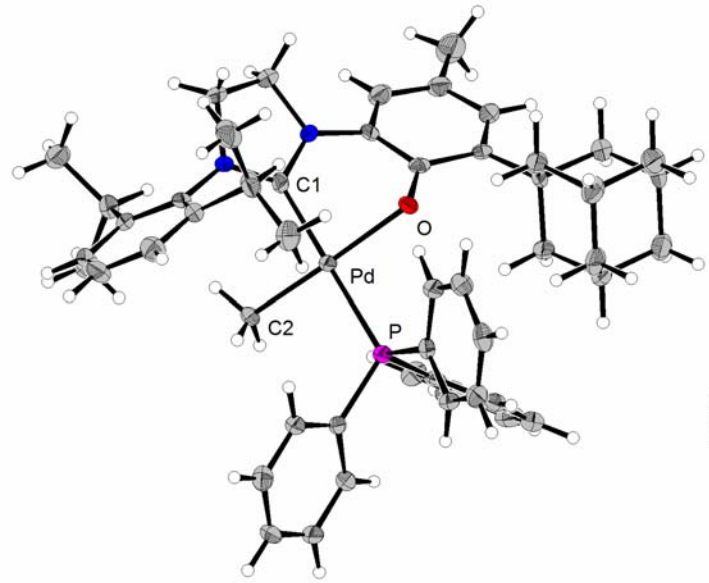
Bond Lengths (Å)

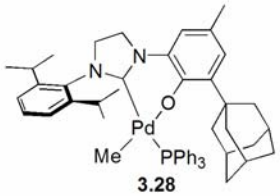
Pd-C(1)	2.030(3)	Pd-O	2.1182(19)
Pd-C(2)	2.041(3)	Pd-P	2.2858(9)

Bond Angles (°)

C(1)-Pd-C(2)	93.37(12)	C(1)-Pd-P	175.26(8)
C(1)-Pd-O	84.61(10)	C(2)-Pd-P	90.02(9)
C(2)-Pd-O	172.65(10)	O(1)-Pd-P	92.44(6)

Figure 3.5. Molecular structure of Pd complex **3.28**. Atoms are represented by thermal ellipsoids at 50% probability.





3.28

Selected Bond Lengths (Å) and Angles (°)

Bond Lengths (Å)

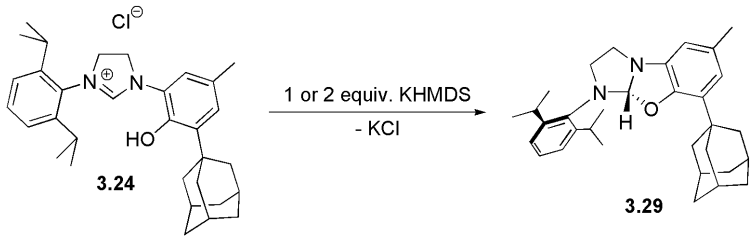
Pd-C(1)	2.009(3)	Pd-O	2.1332(18)
Pd-C(2)	2.042(3)	Pd-P	2.2987(8)

Bond Angles (°)

C(1)-Pd-C(2)	91.65(11)	C(1)-Pd-P	174.92(8)
C(1)-Pd-O	85.47(9)	C(2)-Pd-P	90.26(9)
C(2)-Pd-O	173.07(11)	O(1)-Pd-P	93.14(5)

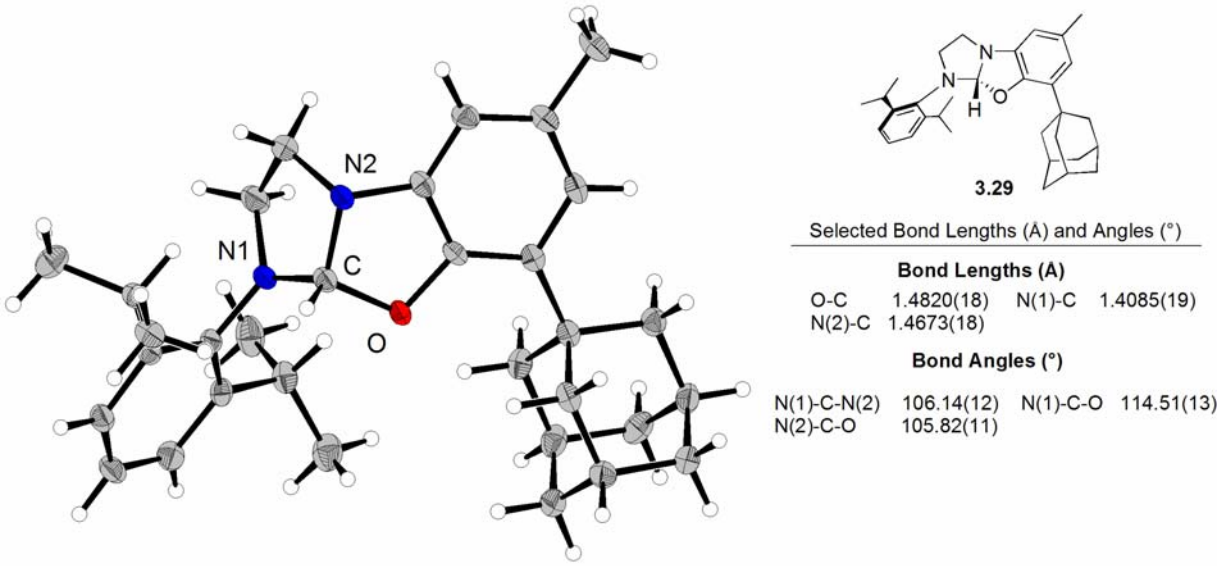
In the syntheses of Pd complexes **3.25-3.28**, the anticipated problem arising from formation of a cyclized product such as **3.5** had been avoided (see Scheme 3.6). However, examination of the ^{1}H NMR spectrum of **3.24** when treated with two equivalents of KHMDS suggested that a cyclized product (**3.29**) was indeed formed. The spectrum of this was very similar to that of NHC precursor **3.24**. However, the two signals representing the backbone protons of the dihydroimidazolium ring had shifted downfield, indicating that the ring was no longer cationic. In addition, a new singlet had appeared (δ 6.76 ppm, 300 MHz, C_6D_6). This represented the proton on the C atom situated between the two N atoms. Treatment of **3.24** with a single equivalent of KHMDS resulted in a nearly identical ^{1}H NMR spectrum, suggesting that only a single equivalent of KHMDS had been consumed in the first reaction (Scheme 3.12).

Scheme 3.12. Synthesis of cyclized product **3.29** by reaction of **3.24** with KHMDS.



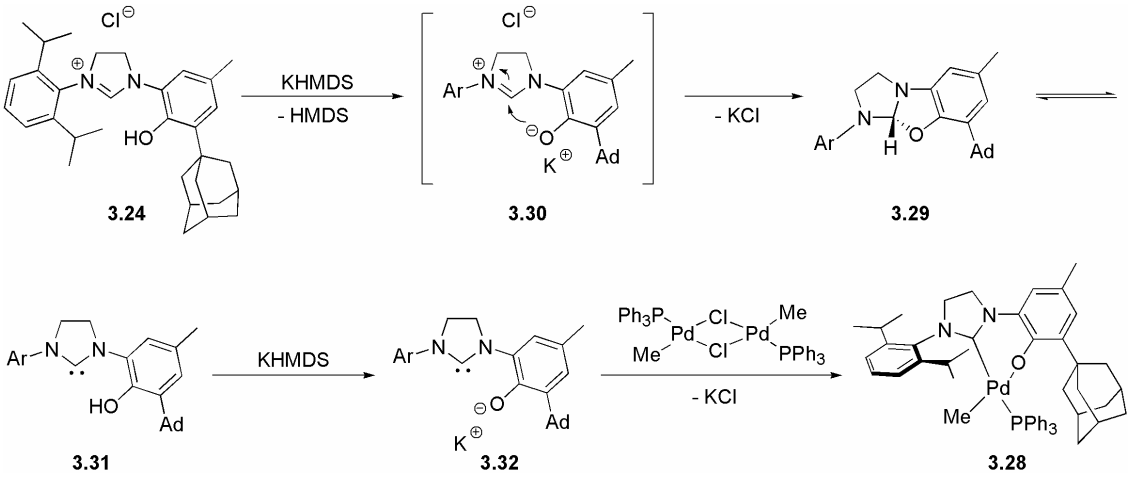
The product from the reaction with a single equivalent of KHMDS was examined by X-ray crystallography and was indeed found to be structure **3.29** (Figure 3.6).

Figure 3.6. Molecular structure of cyclized product **3.29**. Atoms are represented by thermal ellipsoids at 50% probability.



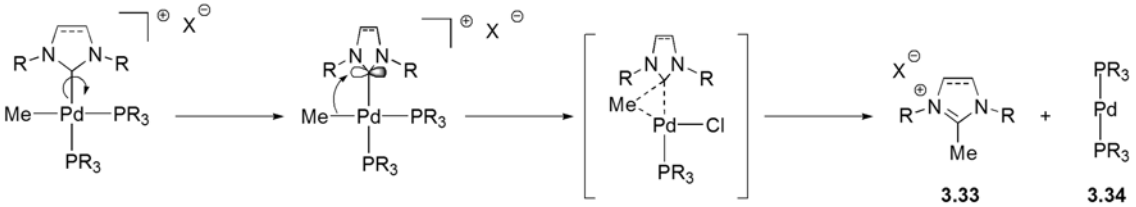
Having established that cyclized products such as **3.29** can and do form, it is possible to propose a mechanism for the formation of Pd complex **3.28** (Scheme 3.13). Upon treatment of **3.24** with two equivalents of KHMDS, the more acidic phenolic moiety is deprotonated, leading to transient formation of phenoxide **3.30**. This quickly cyclizes to give **3.29**. From here, it is likely that cyclized **3.29** and NHC **3.31** are in equilibrium. The equilibrium constant of this process is not known. Eventually, the free phenoxide is deprotonated by the remaining equivalent of KHMDS to give carbene/phenoxide **3.32**. This intermediate then reacts with $((PPh_3)PdMeCl)_2$ with loss of KCl to give Pd complex **3.28**.

Scheme 3.13. Proposed mechanism for the ligation of chelating NHCs to Pd.



There have been, hitherto, relatively few examples of stable group 10 metal/alkyl complexes of N-heterocyclic carbenes.[15] This is partially due to the tendency of such complexes to quickly decompose to a 2-alkylimidazolium salt (**3.33**) and reduced metal (**3.34**, Scheme 3.14).[16] This is attributed to the fact that the nominally empty p_z orbital of the NHC carbon is susceptible to attack by a cis coordinated alkyl group. In order for this attack to occur, the NHC must rotate about the carbene-metal bond.[17] Once the empty orbital is directed toward the metal-bound alkyl group, the metal complex can undergo a unique type of reductive elimination.

Scheme 3.14. Decomposition of group ten alkyl/NHC complexes.



It has been demonstrated previously that Pd/alkyl complexes of NHCs are much more stable when the NHC ligand is chelated.[18] Presumably, this prevents rotation of the carbene to attain the orientation necessary for attack by the alkyl group bound to the metal on the carbene p-orbital. This rationale seems to hold true for Pd complexes **3.25-3.28** as well. The palladium complexes presented in this work are quite stable. For example, the ^{1}H NMR spectra of **3.25** and **3.28** are unchanged after one week at room temperature in C_6D_6.

3.6 Conclusion

A simple, high-yielding and modular protocol for the synthesis of bidentate diaryl N-heterocyclic carbenes (and unsymmetrically substituted carbenes in general) and their effectiveness as stable ligands for Pd have been established. In the next chapter, the unexpected behavior of the novel chelating NHCs as ligands for Ni will be described.

3.7 Acknowledgments

This work was supported by the Rohm and Haas corporation. Steven Goldberg provided the conceptual framework for the synthesis of unsymmetrical NHCs. Larry Henling and Mike Day performed the X-ray crystallographic analysis of compounds **3.25**, **3.28** and **3.29**.

3.8 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. ICN silica gel (particle size 0.032-0.063 mm) was used for flash column chromatography. Organic reagents were purchased from Sigma-Aldrich and metal salts were obtained from Strem. Palladium complexes $((PEt_3)PdMeCl)_2$ and $((PPh_3)PdMeCl)_2$ were synthesized according to literature procedure.[19] ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian Mercury 300 spectrometer (at 300 MHz, 75 MHz and 121 MHz respectively) and are reported relative to Me_4Si (δ 0.0) for ^1H 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. Quantitative analysis was carried out by Desert Analytics Laboratory, Tuscon, AZ.

N-(Mesityl)-oxanilic acid ethyl ester (3.11). 2,4,6-Trimethylaniline (20.0 mL, 142 mmol, 1.00 equiv) and triethylamine (20.0 mL, 143 mmol, 1.00 equiv) were dissolved in dry THF (~150 mL). This solution was cooled to 0 °C, and ethyl chlorooxoactetate (15.3

mL, 142 mmol, 1.00 equiv) was added slowly via syringe. Precipitation of a white solid occurred immediately upon addition. The mixture was allowed to stir overnight and slowly warm to 23 °C. At this point, the solid was filtered off, and the filtrate washed with 2 M HCl solution (2 x ~100 mL). The aqueous layer was washed with ethyl acetate, and the combined organic layers were washed with brine (~100 mL), dried over $MgSO_4$ and filtered. The solvent was then removed under reduced pressure, leaving a yellowish solid. This was recrystallized from hexanes/EtOAc (9:1) to produce a white crystalline solid (30.15 g, 128 mmol, 90% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.34 (s, 1H), 6.92 (s, 2H), 4.43 (q, *J* = 7.2 Hz, 2H), 2.28 (s, 3H), 2.20 (s, 6H), 1.45 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ161.2, 154.9, 138.0, 134.9, 129.7, 129.3, 63.8, 21.2, 18.6, 14.3. Anal. Calc'd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.56; H, 7.15; N, 6.04.

N-(2,6-Diisopropylphenyl)-oxanilic acid ethyl ester (3.12). This compound was prepared in a fashion similar to that for compound **3.11** using 2,6-diisopropylaniline. The product was obtained as a white solid in 92% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.36 (s, 1H), 7.34 (t, *J* = 7.1 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 2H), 4.45 (q, *J* = 7.2 Hz, 2H), 3.01 (septet, *J* = 7.2 Hz, 2H), 1.47 (t, *J* = 7.2 Hz, 3H), 1.21 (d, *J* = 6.6 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.3, 156.1, 146.1, 129.6, 129.2, 124.0, 63.9, 29.1, 23.9, 14.2. Anal. Calc'd for $C_{16}H_{23}NO_3$: C, 69.29; H, 8.36; N, 5.05. Found: C, 69.31; H, 8.13; N, 5.10.

N-(Mesityl)-N'-(2-hydroxyphenyl)-oxalamide (3.13). N-(Mesityl)-oxanilic acid ethyl ester (**3.11**) (5.23 g, 24.4 mmol, 1.00 equiv) and 2-aminophenol (2.67 g, 24.4 mmol, 1.00 equiv) were dissolved in toluene (~50 mL). To this suspension was added triethylamine

(6.8 mL, 50 mmol, 2.0 equiv). The suspension was heated to reflux, causing the solids to dissolve. After heating at reflux overnight, the product precipitated. At this point, ethyl acetate was added until the solid redissolved. The solution was washed with 2 M HCl solution (2x~100 mL). The aqueous layer was then washed with ethyl acetate, and the combined organic layers were washed with brine (~100 mL), and dried over $MgSO_4$. The solvent was then removed under reduced pressure, leaving a yellowish solid. This was recrystallized from toluene, producing a white crystalline solid (5.26 g, 17.7 mmol, 72.4% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.69 (s, 1H), 8.84 (s, 1H), 8.11 (s, 1H), 7.51 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.14 (ddd, *J* = 1.5, 8.1, 7.2 Hz, 1H), 6.92 (m, 3H), 2.30 (s, 3H), 2.22 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.2, 157.9, 148.2, 138.2, 134.9, 129.5, 129.4, 127.7, 124.3, 122.2, 121.1, 118.9, 21.2, 18.6. Anal. Calc'd for $C_{17}H_{18}N_2O_3$: C, 68.44; H, 6.08; N, 9.39. Found: C, 68.50; H, 5.96; N, 9.44.

N-(2,6-Diisopropylphenyl)-N'-(2-hydroxyphenyl)-oxalamide (3.14). This compound was prepared in a fashion similar to that for compound **3.13** using **3.12**. The product was obtained as a white solid in 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.67 (s, 1H), 8.84 (s, 1H), 8.12 (s, 1H), 7.50 (dd, *J* = 8.25, 1.8 Hz 1H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.16 (dt, *J* = 7.7, 1.5 Hz, 1H), 6.95 (comp m, 2H), 3.03 (septet, *J* = 6.6 Hz, 2H), 1.22 (d, *J* = 6.9, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.9, 158.2, 148.2, 146.1, 129.4, 127.9, 124.2, 124.0, 122.3, 121.2, 119.1, 29.2, 23.9. Anal. Calc'd for $C_{20}H_{24}N_2O_3$: C, 70.56; H, 7.11; N, 8.23; O, 14.10. Found: C, 34.90; H, 4.64; N, 5.79.

N-(Mesityl)-oxanilic acid (3.19). N-(Mesityl)-oxanilic acid ethyl ester (**3.11**) (1.99 g, 8.50 mmol) was dissolved in THF (~50 mL). To this solution was added 1M NaOH solution (~40 mL), and the mixture was stirred for 2 hours. Diethyl ether (~25 mL) was

added, and the layers were separated. The organic layer was washed with 1M NaOH solution (~40 mL). The aqueous layer was then acidified with 2M HCl until precipitation occurred. This was then extracted with ethyl acetate (2x~50 mL). The ethyl acetate was washed with brine (~50 mL), and then dried over $MgSO_4$. Removal of the solvent under reduced pressure provided the product as a white solid (1.74 g, 8.40 mmol, 99.0% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.51 (s, 1H), 6.93 (s, 2H), 2.29 (s,3H), 2.19 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.0, 156.1, 138.6, 134.7, 129.5, 128.9, 21.2, 18.5. Anal. Calc'd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32; N, 6.76. Found: C, 63.59; H, 6.32; N, 6.79.

2-Amino-4-methyl-6-*tert*-butylphenol (3.18).[20] 2-*tert*-Butyl-4-methylphenol (**3.17**) (20.0 g, 122 mmol, 1.00 equiv) is dissolved in AcOH (~200 mL) and cooled to 0 °C. To this solution was added a solution of concentrated nitric acid (7.73 mL, 122 mmol, 1.00 equiv) in an equal volume of acetic acid. Upon addition, the solution turned yellow. After addition was complete, it was allowed to stir at 0 °C for 2.5 hours. At this time, some needles of product began to grow. Deionized water (~25 mL) was added, causing a great deal of precipitation. This was filtered, and water was again added to the filtrate, causing more precipitate that was again filtered. More precipitation/filtration cycles did not yield substantial amounts of product. The orange/yellow solid obtained from the filtrations (13.1 g, 62.4 mmol, 51.2% yield) was dried overnight by vacuum. ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.40 (s, 1H), 7.77 (d, J = 1.5 Hz, 1H), 7.37 (d, J = 2.1 Hz, 1H), 2.31 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.3, 140.4, 136.3, 128.8, 122.5, 35.7, 29.6, 20.0. Anal. Calc'd for $C_{11}H_{15}NO_3$: C, 63.14; H, 7.23; N, 6.69. Found: C, 64.52; H, 7.69; N, 5.89. The resulting product, 2-amino-4-methyl-6-*tert*-butylphenol (4.13 g, 20.0 mmol, 1.00 equiv) was added to an oven dried, two-necked flask, and Pd

(10% on charcoal) (1.05 g, 1.00 mmol Pd, 0.050 equiv) was added. The flask was evacuated, and filled with argon, and then dry, degassed methanol (~50 mL) was added. A balloon of hydrogen gas was placed over the reaction, and it was allowed to stir for 16 hrs. The solution was then filtered through Celite, removing the Pd. It should be noted that although the product is stable in inert atmosphere, it rapidly oxidizes in solution when exposed to air. Therefore, the clear Pd/C suspension turns immediately to a red solution upon filtration on the benchtop. The methanol is evaporated under reduced pressure, leaving a dark red solid. This can then be recrystallized from hexane to yield a whitish solid (2.41 g, 13.4 mmol, 68.4 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.67 (d, *J* = 1.5 Hz, 1H), 6.61 (d, *J* = 1.8 Hz, 1H), 5.57 (bs, 1H), 3.20 (bs, 2H), 2.22 (s, 3H), 1.40 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.1, 135.5, 133.4, 129.3, 120.7, 119.2, 34.6, 30.0, 21.2.

N-(Mesityl)-N'-(2-hydroxy-3-tert-butyl-5-methylphenyl)-oxalamide (3.20). N-(Mesityl)-oxanilic acid (**3.19**) (2.15 g, 10.4 mmol, 1.00 equiv) and 1-hydroxybenzotriazole (2.39 g, 15.6 mmol, 1.50 equiv) were added to an oven dried, two-necked flask. THF (~100 mL) was added and the solution was cooled to 0 °C. To this was then added 1,3-dicyclohexylcarbodiimide (1 M in CH_2Cl_2) (12.5 mL, 12.5 mmol, 1.20 equiv). It was allowed to stir at 0° for 1 hr. During this time, a white precipitate formed. At this point, 2-amino-4-methyl-6-*tert*-butylphenol (**3.18**) (1.86 g, 10.4 mmol, 1.00 equiv) was added to the suspension. It was allowed to stir overnight. The next day, the solvent was removed under reduced pressure, and ethyl acetate was added to make a suspension which was then filtered to remove the solid. The filtrate was washed with 10% citric acid solution (2x~50 mL), 5% $NaHCO_3$ (2x~50 mL) and brine (~50 mL). It

was dried over $MgSO_4$, and the solvent was removed under reduced pressure, leaving a solid which was recrystallized from hexane to give the product as a white solid (2.92 g, 7.90 mmol, 76.8% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.55 (s, 1H), 8.77 (s, 1H), 7.84 (s, 1H), 7.05 (d, *J* = 1.8 Hz, 1H), 6.92 (m, 3H), 2.30 (s, 3H), 2.28 (s, 3H), 2.22 (s, 6H), 1.45 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.5, 157.4, 146.2, 140.6, 138.1, 134.9, 129.9, 129.6, 129.4, 126.9, 124.9, 121.4, 35.3, 30.0, 21.2, 21.0, 18.5. Anal. Calc'd for $C_{22}H_{28}N_2O_3$: C, 71.71; H, 7.66; N, 7.60. Found: C, 72.01; H, 8.03; N, 7.36.

N-(2,6-Diisopropylphenyl)-N'-(2-hydroxy-5-methylphenyl)-oxalamide (3.22). N-(2,6-Diisopropylphenyl)-oxanilic acid ethyl ester (**3.12**) (5.14 g, 18.5 mmol, 1.00 equiv) and 2-amino-5-methylphenol (2.28 g, 18.5 mmol, 1.00 equiv) were dissolved in toluene (~50 mL). To this suspension was added triethylamine (2.6 mL, 19 mmol, 1.0 equiv). The suspension was heated to reflux, causing the solids to dissolve. After heating at reflux overnight, the product precipitated. At this point, ethyl acetate was added until the solid redissolved. The solution was washed with 2 M HCl solution (2x~100 mL). The aqueous layer was then washed with ethyl acetate, and the combined organic layers were washed with brine (~100 mL), and dried over $MgSO_4$. The solvent was then removed under reduced pressure, leaving a yellowish solid. This was recrystallized from toluene, producing a white crystalline solid (5.90 g, 16.6 mmol, 90.3% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.58 (s, 1H), 8.81 (s, 1H), 7.92 (s, 1H), 7.37 (t, *J* = 7.8 Hz 1H), 7.27 (d, *J* = 0.9 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 2H), 6.97 (dd, *J* = 8.1, 2.1 Hz, 1H), 6.90 (d, *J* = 8.1 Hz, 1H), 3.02 (septet, *J* = 6.6, 2H), 2.29 (s, 3H), 1.22 (d, *J* = 7.2, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.8, 158.2, 146.0, 130.7, 129.4, 128.7, 124.0, 123.8, 122.6, 119.1, 29.2, 23.9, 20.7. Anal. Calc'd for $C_{21}H_{26}N_2O_3$: C, 71.16; H, 7.39; N, 7.90. Found: C,

70.85; H, 7.68; N, 7.73.

N-(2,6-Diisopropylphenyl)-N'-(2-hydroxy-3-(adamant-1-yl)-5-methylphenyl)-oxalamide (3.23). N-(2,6-Diisopropylphenyl)-N'-(2-hydroxy-5-methylphenyl)-oxalamide (**7**) (5.59 g, 15.5 mmol, 1.00 equiv) and 1-adamantol (2.83 g, 18.6 mmol, 1.20 equiv) were dissolved in CH_2Cl_2 (~150 mL). To this suspension was added conc. H_2SO_4 (1 mL). After addition of the acid, the solids eventually went into solution. After stirring at room temperature for 24 hours, the TLC (9:1 hexanes:ethyl acetate, visualized by UV) showed that most of the starting material had gone to product. At this point, the solvent was removed under reduced pressure, and the resulting solids were redissolved in ethyl acetate (~100 mL). This solution was washed with sat. $NaHCO_3$ (3x~50 mL, gas is evolved), and brine, then dried over $MgSO_4$. The solvent was removed under reduced pressure, and the resulting solid was purified via column chromatography to give a light yellow solid (3.68 g, 7.50 mmol, 48.2 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.51 (s, 1H), 8.77 (s, 1H), 7.84 (s, 1H), 7.37 (t, *J* = 7.2 Hz 1H), 7.23 (d, *J* = 7.5 Hz, 2H), 7.00 (d, *J* = 2.1 Hz, 1H), 6.94 (d, *J* = 1.8 Hz, 1H), 3.01 (septet, *J* = 6.9, 2H), 2.29 (s, 3H), 2.18 (bs, 6H), 2.10 (bs, 3H), 1.80 (bs, 6H), 1.22 (d, *J* = 6.9, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.3, 158.2, 146.2, 145.8, 140.6, 129.9, 129.2, 129.2, 126.8,, 124.7, 123.8, 120.9, 40.7, 37.3, 37.1, 29.1, 29.0, 23.6, 20.8. Anal. Calc'd for $C_{31}H_{40}N_2O_3$: C, 76.19; H, 8.25; N, 5.73. Found: C, 75.89; H, 8.42; N, 5.37.

1-(Mesityl)-3-(2-hydroxyphenyl)-4,5-dihydro-imidazolium chloride (3.15) N-(Mesityl)-N'-(2-hydroxyphenyl)-oxalamide (**3.13**) (1.47 g, 4.90 mmol, 1 equiv) was weighed into an oven-dried round-bottom flask. To this was added BH_3–THF (1M in

THF) (39 mL, 39 mmol, 8.0 equiv). A great deal of bubbling resulted, as the solution turned bright orange. It was allowed to reflux overnight. The next day, the solution had turned clear. It was allowed to cool to room temperature, and then methanol was added very slowly, until all bubbling ceased. Conc. HCl solution (~1.5 mL) was then added, and the solvent was removed under reduced pressure. The resulting solid was dissolved in methanol, and then the solvent was again removed under reduced pressure. This process was repeated twice more. In this way, the remaining boron was removed as $B(OMe)_3$. The resulting solid material was the dihydrochloride salt of the diamine. This was not isolated or characterized. To this solid was added triethylorthoformate (~15 mL). The resulting suspension was heated to 100 °C. As it heated, the solid slowly went into solution. After ~ 1 min at high temperature, a white solid precipitated. It was allowed to stir for five more minutes, and was then filtered. The resulting solid was washed with ether, to provide the desired product as a white powder (.85 g, 2.7 mmol, 55% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.43 (s, 1H), 8.84 (s, 1H), 7.54 (dd, *J* = 8.25, 1.2 Hz, 1H), 7.05 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.92 (m, 2H), 6.73 (dt, *J* = 7.7, 0.9 Hz 1H), 4.80 (t, *J* = 11.4 Hz, 2H), 4.37 (t, *J* = 11.7 Hz, 2H), 2.33 (s, 3H), 2.29 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.4, 150.0, 141.0, 135.3, 130.7, 130.3, 128.8, 122.8, 120.4, 119.9, 118.8, 51.0, 50.4, 21.3, 18.2. Anal. Calc'd for $C_{18}H_{21}ClN_2O$: C, 68.24; H, 6.68; N, 8.84. Found: C, 67.86; H, 6.92; N, 8.52.

1-(2,6-Diisopropylphenyl)-3-(2-hydroxyphenyl)-4,5-dihydro-imidazolium chloride (3.16) This compound was prepared in a fashion similar to that for compound **3.15** using **3.14**. The product was obtained as a white solid in 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.04 (s, 1H), 7.57 (dd, *J* = 8.9, 1.2 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.22 (d, *J*

= 7.8 Hz, 2H), 7.15 (d, *J* = 6.6 Hz, 1H), 6.97 (dt, *J* = 7.8, 1.8 Hz, 1H), 6.78 (dt, *J* = 8.3, 0.9 Hz, 1H), 4.88 (t, *J* = 11.4 Hz, 2H), 4.44 (t, *J* = 11.1, 2H), 2.95 (septet, *J* = 6.6 Hz, 2H), 1.25 (d, *J* = 7.2 Hz, 6H), 1.16 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.0, 149.8, 146.6, 131.6, 130.0, 128.7, 125.1, 122.6, 120.3, 120.0, 118.6, 52.7, 51.1, 28.9, 25.0, 24.3. Anal. Calc'd for $C_{21}H_{27}ClN_2O$: C, 70.28; H, 7.58; N, 7.81. Found: C, 70.32; H, 7.76; N, 7.63.

1-(Mesityl)-3-(2-hydroxy-3-*tert*-butyl-5-methylphenyl)-4,5-dihydro-imidazolium chloride (3.21) This compound was prepared in a fashion similar to that for compound **3.15** using **3.20**. The product was obtained as a white solid in 35% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.42 (s, 1H), 7.10 (d, *J* = 1.5 Hz, 1H), 6.96 (s, 2H), 6.80 (s, 1H), 4.79 (t, *J* = 11.1 Hz, 2H), 4.43 (t, *J* = 9.6 Hz, 2H), 2.47 (s, 6H), 2.30 (s, 3H), 2.27 (s, 3H), 1.41 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.7, 148.1, 144.2, 140.7, 135.8, 130.8, 130.6, 130.3, 128.9, 127.5, 121.6, 52.3, 51.6, 35.6, 30.1, 21.2, 21.1, 18.6. Anal. Calc'd for $C_{23}H_{31}ClN_2O$: C, 71.39; H, 8.07; N, 7.24. Found: C, 72.01; H, 8.03; N, 7.36.

1-(2,6-Diisopropylphenyl)-3-(2-hydroxy-3-(adamant-1-yl)-5-methylphenyl)-4,5-dihydro-imidazolium chloride (3.24) This compound was prepared in a fashion similar to that for compound **3.15** using **3.23**. The product was obtained as a white solid in 63% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.45 (t, *J* = 8.1 Hz, 1H), 7.27 (d, *J* = 8.1 2H), 7.04 (s, 1H), 6.80 (s, 1H), 4.88 (t, *J* = 10.8 Hz, 2H), 4.45 (t, *J* = 11.7 Hz, 2H), 3.41 (septet, *J* = 6.6 Hz 2H), 2.28 (s, 3H), 2.13 (bs, 6H), 2.04 (bs, 3H), 1.74 (m, 6H), 1.34 (d, *J* = 6.9 Hz, 6H), 1.29 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.4, 148.3, 147.3, 144.4, 131.4, 130.8, 130.2, 128.8, 127.8, 125.2, 121.1, 54.0, 52.4, 40.8, 37.8, 37.2, 29.2, 28.8, 25.5, 24.4, 21.1. Anal. Calc'd for $C_{32}H_{43}ClN_2O$: C, 75.78; H, 8.55; N, 5.52.

Found: C, 74.78; H, 8.64; N, 5.44.

1-(Mesityl)-3-(2-hydroxyphenyl)-4,5-dihydro-imidazolyl methyl triethylphosphine palladium(II) (3.25) 1-(Mesityl)-3-(2-hydroxyphenyl)-4,5-dihydro-imidazolium chloride (**3.15**) (75 mg, 0.24 mmol, 1.0 equiv) and potassium hexamethyldisilazide (99 mg, 0.50 mmol, 2.1 equiv) were weighed together in a vial in the glovebox. THF (~5 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 suspension of $((PEt_3)PdMeCl)_2$ (65 mg, 0.12 mmol, 0.50 equiv) in THF (~5 mL) was added. The resulting yellow suspension quickly turned to a light yellow solution with a light precipitate. It was allowed to stir at room temperature for 1 hr, then filtered through Celite. The solvent was then removed under reduced pressure until ~ 1 mL remained. To this was added pentane, and the resulting suspension was allowed to sit at –40 °C overnight. The next day, the product, an off-white solid, was collected by filtration (39 mg, 0.08 mmol, 32% yield). Crystals suitable for X-ray crystallographic analysis were obtained by layering pentane over a saturated methylene chloride solution of **3.25** and storing this solution at –40 °C. ^{1}H NMR (300 MHz, C_7D_8): δ 7.12 (m, 2H), 6.78 (s, 2H), 6.64 (m, 2H), 3.31 (t, *J* = 10.2 Hz, 2H), 3.02 (t, *J* = 10.2, 2H), 2.44 (s, 6H), 2.12 (s, 3H), 1.41 (apparent quintet, *J* = 8.1 Hz, 6H), 0.93 (ddd, *J* = 15.3, 7.8 Hz, 9H), -50 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, C_7D_8): δ 197.7, 162.7, 137.2, 136.3, 129.4, 126.0, 120.9, 118.8, 111.4, 51.3, 51.2, 19.0, 13.8, 13.5, 8.2, –17.4, –17.6; ^{31}P NMR (121 MHz, C_7D_8): δ 18.29.

1-(2,6-Diisopropylphenyl)-3-(2-hydroxyphenyl)-4,5-dihydro-imidazolyl methyl

triphenylphosphine palladium(II) (3.26) This compound was prepared in a fashion similar to that for compound **3.25** using **3.16** and $((PPh_3)PdMeCl)_2$. The product was obtained as an off-white solid in 63% yield. ^{1}H NMR (300 MHz, C_6D_6): δ 7.74 (m, 6H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 7.01 (bs, 9H), 6.92 (t, *J* = 7.8 Hz, 1H), 6.80 (dd, *J* = 1.8, 7.8 Hz 1H), 6.9 (t, *J* = 7.2 Hz, 1H), 6.63 (d, *J* = 8.1 Hz, 1H), 3.47 (septet, *J* = 6.9 Hz, 2H), 3.38 (t, *J* = 9 Hz, 2H), 3.25 (t, *J* = 9.3, 2H), 1.57 (d, *J* = 6.6, 6H), 1.12 (d, *J* = 6.9, 6H), –0.32 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6): δ 147.6, 135.6, 135.5, 130.1, 130.1, 129.3, 128.6, 128.5, 126.6, 124.9, 122.3, 119.2, 112.1, 54.6, 49.1, 29.1, 26.7, 25.0, 3.0, –9.6, –9.7; ^{31}P NMR (121 MHz, C_6D_6): δ 26.27.

1-(Mesityl)-3-(2-hydroxy-3-*tert*-butyl-5-methylphenyl)-4,5-dihydro-imidazolyl methyl triphenylphosphine palladium(II) (3.27) This compound was prepared in a fashion similar to that for compound **3.25** using **3.21** and $((PPh_3)PdMeCl)_2$. The product was obtained as an off-white solid in 58% yield. ^{1}H NMR (300 MHz, C_6D_6): δ 7.80 (m, 6H), 7.02 (s, 9H), 6.64 (m, 4H), 3.39 (t, *J* = 10.8 Hz, 2H), 3.02 (t, *J* = 10.5 Hz, 2H), 2.49 (s, 6H), 2.47 (s, 3H), 2.11 (s, 3H), 1.42, (s, 9H), –0.36 (d, *J* = 8.1 Hz, 6H); ^{13}C NMR (75 MHz, C_6D_6) δ 199.2, 197.4, 159.2, 140.1, 137.8, 136.8, 136.3, 135.4, 135.2, 133.6, 133.1, 132.9, 129.7, 129.3., 128.1, 124.1, 118.6, 118.3, 51.0, 50.9, 49.8,49.8, 35.5, 29.9, 29.8, 21.3, 20.9, 19.0, –9.4, –9.6; ^{31}P NMR (121 MHz, C_6D_6): δ 24.90.

1-(2,6-Diisopropylphenyl)-3-(2-hydroxy-3-(adamant-1-yl)-5-methylphenyl)-4,5-dihydro-imidazolyl methyl triphenylphosphine palladium(II) (3.28) This compound was prepared in a fashion similar to that for compound **3.25** using **3.24** and $((PPh_3)PdMeCl)_2$. The product was obtained as an off-white solid in 46% yield. Crystals

suitable for X-ray crystallographic analysis were obtained by layering pentane over a saturated THF solution of **3.28** and storing this solution at –40 °C. ^{1}H NMR (300 MHz, C_6D_6): δ 7.80 (m, 6H), 7.11 (m, 2H), 7.01 (m, 11H), 6.67 (d, *J* = 1.8 Hz, 1H), 3.51 (m, 6H), 3.22 (t, *J* = 10.2 Hz, 2H), 2.53 (s, 3H), 2.14 (s, 6H), 1.67 (bs, 3H), 1.54 (d, *J* = 6.9 Hz, 6H), 1.43 (m, 6H), 1.09 (d, *J* = 6.6, 6H), –0.44 (d, *J* = 7.8 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6): δ 197.4, 149.5, 147.5, 136.2, 136.1, 134.0, 133.5, 132.8, 130.3, 124.9, 124.7, 118.7, 54.2, 41.2, 38.2, 37.8, 30.5, 30.2, 29.0, 26.8, 25.1, 23.1, 21.9, 14.6; ^{31}P NMR (121 MHz, C_6D_6): δ 27.01.

8-Adamantan-1-yl-1-(2,6-diisopropyl-phenyl)-6-methyl-1,2,3,9a-tetrahydro-benzo[d]imidazo[2,1-b]oxazole (3.29) NHC precursor **3.24** (71 mg, 0.14 mmol, 1.0 equiv) was suspended in THF (~10 mL). To this was added a solution of potassium hexamethyldisilazide (28 mg, 0.14 mmol, 1.0 equiv.) in THF, resulting in a light yellow solution with precipitate. This was allowed to stir at 23 °C for 1 hr, and then was filtered through Celite. Upon removal of the solvent under reduced pressure, a white solid was obtained (58 mg, 0.12 mmol, 87% yield). Crystals suitable for X-ray crystallography were grown by slow evaporation of a benzene solution. ^{1}H NMR (300 MHz, C_6D_6): δ 7.23 (m, 2H), 7.14 (m, 3H), 6.80 (s, 1H), 6.76 (s, 1H), 6.66 (s, 1H), 3.51 (septet, *J* = 6.3 Hz, 2H), 3.37 (t, *J* = 5.7 Hz, 2H), 3.06 (t, *J* = 6.0 Hz, 2H), 2.37 (bs, 3H), 2.28 (bs, 6H), 2.10 (bs, 3H), 1.81 (bs, 6H), 1.30 (d, *J* = 6.3 Hz, 6H), 1.19 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (75 MHz, C_6D_6): δ 150.1, 148.6, 141.7, 139.4, 132.3, 129.6, 124.8, 121.1, 114.8, 113.4, 55.9, 51.0, 41.4, 37.7, 36.6, 29.8, 28.8, 25.8, 24.6, 22.0.

3.9 References

[1] Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39–92 and references therein. Though NHCs are currently a popular subject of research, they have been known for some time: (a) Wanzlick, H. W.; Kleiner, H. J. *Angew. Chem.* **1961**, *73*, 493. (b) Wanzlick, H. W. *Angew. Chem., Int. Ed.* **1962**, *1*, 75. (c) Wanzlick, H. W.; Esser, F.; Kleiner, H. J. *Chem. Ber.* **1963**, *96*, 1208.

[2] Arduengo III, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361–363.

[3] Green, J. C.; Scurr, R. G.; Arnold, P. L.; Cloke, F. G. N. *Chem. Commun.* **1997**, 1963–1964.

[4] (a) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953–956. (b) Morgan, J. P.; Grubbs, R. H. *Org. Lett.* **2000**, *2*, 3153–3155. (c) Fürstner, A.;

Ackermann, L.; Gabor, B.; Goddard, R.; Lehmann, C. W.; Mynott, R.; Stelzer, F.; Thiel, O. R. *Chem. Eur. J.* **2001**, *7*, 3236–3253.

[5] Chatterjee, A. K.; Morgan, J. P.; Scholl, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 3783–3784.

[6] (a) Weskamp, T.; Kohl, F. J.; Hieringer, W.; Gleich, D.; Herrmann, W. A. *Angew. Chem. Int. Ed.* **1999**, *38*, 2416–2419. (b) Huang, J.; Schanz, H.-J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 5375–5380. (c) Bielawski, C. W.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2000**, *39*, 2903–2906.

[7] Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543–6554.

[8] (a) Viciu, M. H.; Kissling, R. M.; Stevens, E. D.; Nolan, S. P. *Org. Lett.* **2002**, *4*, 2229–2231. (b) Viciu, M. S.; Germaneau, R. F.; Nolan, S. P. *Org. Lett.* **2002**, *4*, 4053–4056. (c) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290–1309. (d) McGuinness, D. S.; Cavell, K. J. *Organometallics* **1999**, *18*, 1596–1605. (e) McGuinness, D. S.; Cavell, K. J. *Organometallics* **2000**, *19*, 741–748. (f) Schwarz, J.; Böhm, V. P. W.; Gardiner, M. G.; Grosche, M.; Herrmann, W. A.; Hieringer, W.; Raudaschl-Sieber, G. *Chem. Eur. J.* **2000**, *6*, 1773–1780.

[9] Ma, Y.; Song, C.; Jiang, W.; Wu, Q.; Wang, Y; Liu, X.; Andrus, M. B. *Org. Lett.* **2003**, *5*, 3317– 3319.

[10] (a) Seiders, T. J.; Ward, D. W.; Grubbs, R. H. *Org. Lett.* **2001**, *3*, 3225–3228. (b) Van Veldhuizen, J. J.; Garber, S. B.; Kingsbury, J. S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 4954–4955.

[11] (a) Herrmann, W. A.; Gooßen, L. J.; Spiegler, M. *J. Organomet. Chem.* **1997**, *547*, 357–366. (b) Herrmann, W. A.; Gooßen, L. J; Spiegler, M. *Organometallics* **1998**, *17*,

2162–2168. (c) Tulloch, A. A. D.; Danopoulos, A. D.; Tooze, R. P; Cafferkey, S. M, Kleinhenz, S.; Hursthouse, M. B. *Chem. Commun.* **2000**, 1247–1248. (d) Arnold, P. L; Scarisbrick, A. C.; Blake, A. J.; Wilson, C. *Chem. Commun.* **2001**, 2340–2341. (e) Mas-Marzá, E.; Poyatos, M; Sanaú, M.; Peris, E. *Organometallics* **2004**, *23*, 323–325. (f) Wang, X.; Liu, S.; Jin, G.-J. *Organometallics* **2004**, *23*, 6002–6007. (g) Aihara, H.; Matsuo, T.; Kawaguchi, H. *Chem. Commun.* **2003**, 2204–2205. (h) Arnold, P. L.; Rodden, M.; Wilson, C. *Chem. Commun.* **2005**, 1743–1745. (i) Ketz, B. E.; Cole, A. P.; Waymouth, R. M. *Organometallics* **2004**, *23*, 2835–2837.

[12] 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.

[13] Waltman, A. W.; Grubbs, R. H. *Organometallics* **2004**, *23*, 3105–3107. During the course of our research, two NHC syntheses very similar to this one were reported independently: (a) Dinger, M. B.; Nieczypor, P.; Mol, J. C. *Organometallics* **2003**, *22*, 5291–5296. (b) Clavier, H.; Coutable, L.; Guillemin, J.-C.; Maudit, M. *Tetrahedrom Asymmetry* **2005**, *16*, 921–924. See also: (c) Lambert, J. B.; Huseland, D. E.; Wang, G.-T. *Synthesis* **1986**, 657–658.

[14] NHCs have also been generated by treatment of the imidazolium or dihydroimidazolium salt with a basic silver salt, *e.g.* Ag_2O, Ag_2CO_3. Because of the initial success with standard Brönsted bases, this approach was not explored in our system, though it likely would be a valid approach to the generation of the desired NHCs. See Appendix 1, as well as: (a) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972–975. (b) McGuinness, D. S.; Cavell, K. J. *Organometallics*, **2000**, *19*, 741–748. (c) Reference 10b.

[15] (a) Douthwaite, R. E.; Green, M. L. H.; Silcock, P. J.; Gomes, P. T. *J. Chem. Soc., Dalton Trans.* **2002**, 1386–1390. (b) Marshall, W. J.; Grushin, V. V. *Organometallics* **2003**, *22*, 1591–1593 (c) Ding, Y. Q.; Goddard, R.; Porschke, K. R. *Organometallics* **2005**, *24*, 439–445..

[16] (a) McGuinness, D. S.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Organometallics* **1999**, *18*, 1596–1605. (b) McGuinness, D. S.; Cavell, K. J. *Organometallics* **2000**, *19*, 4918–4920.

[17] Danopoulos, A. A.; Tsoureas, N.; Green, J. C.; Hursthouse, M. B. *Chem Commun.* **2003**, 756 – 757.

[18] (a) McGuiness, D. S.; Saendig, N.; Yates, B. F.; Cavell, K. J. *J. Am. Chem. Soc.* **2001**, *123*, 4029–4040. (b) Nielsen, D. J.; Magill, A. M.; Yates, B. F.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Chem. Commun.* **2002**, 2500–2501.

[19] Ladipo, F.T.; Anderson, G.K. *Organometallics* **1994**, *13*, 303-306.

[20] Albert, H. E. *J. Am. Chem. Soc.* **1954**, *76*, 4985–4988.