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The method development for synthesizing chiral CCC-NHC Zr pincer complexes

Amarraj Chakraborty

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The method development for synthesizing chiral CCC-NHC Zr pincer complexes

By

Amarraj Chakraborty

A Thesis
Submitted to the Faculty of
Mississippi State University
in Partial Fulfillment of the Requirements
for the Degree of Master of Science
in Chemistry
in the Department of Chemistry

Mississippi State, Mississippi

August 2015

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2015

The method development for synthesizing chiral CCC-NHC Zr pincer complexes

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There are numerous classes of *N*-heterocyclic carbenes (NHCs) that have been synthesized since the discovery of stable NHCs in 1988. Their application as ligands in metal complexes has received much attention because of their strong sigma-donor and poor pi-acceptor properties. Within these NHC metal complexes, we are interested in studying zirconium metal complexes with pincer NHC ligands. Recently, achiral CCC-NHC pincer zirconium complexes were synthesized and their catalytic activity in intramolecular hydroamination of aminoalkenes were reported.

Herein is reported new reaction conditions which yield pure, chiral CCC-NHC Zr pincer mono(amido) dibromo complex. The enantiopure crystal structure of the same complex is reported. Attempts to synthesize chiral CCC-NHC Zr pincer bis- and tris-amido complexes with the iodo salt of the ligand precursor are summarized. Moreover, syntheses of chiral bis(imidazolinium) ligand precursors with different counter anions are reported with optimized reaction conditions.

DEDICATION

I dedicate my thesis to my mother, Mrs. Krishna Chakraborty, my father, Mr. Sasanka Sekhar Chakraborty, my wife, Bhawna and rest of my family. Thank you all for your continuous love, encouragements and patience for these past three years.

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LIST OF ABBREVIATIONS

Å	Angstrom
BOC	t-Butyloxycarbonyl
d	Doublet
DCC	N,N'-Dicyclohexylcarbodiimide
G	Gram
CH ₂ Cl ₂	Dichloromethane
dd	Doublet of doublets
DMSO	Dimethyl sulfoxide
eq	Equivalence
EtOAc	Ethylacetate
Et ₂ O	Diethyl ether
HRMS	High Resolution Mass Spectroscopy
h	Hour(s)
m	Multiplet
mG	Milligram
mL	Milliliter
MHz	Megahertz
NHC	N-heterocyclic carbene

Min	Minute(s)
NMR	Nuclear Magnetic Resonance
ppm	parts per million
rt	Room Temperature
s	Singlet
t	Triplet
TEA	Triethylamine
TFA	Trifluoroacetic Acid
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography

CHAPTER I
INTRODUCTION TO N-HETEROCYCLIC CARBENES

1.1 Carbene

A carbene is a very reactive, neutral chemical species that contains a divalent carbon with only six electrons in its valence shell.¹⁻² There are two main classes of carbenes based on their electronic spin state: singlet and triplet (Fig 1.1) carbene. The singlet carbene possesses a sp^2 hybridized carbon with one p orbital. A non bonded pair of electrons is present in either a sp^2 orbital or p orbital. In a triplet carbene, the carbene carbon is sp or sp^2 hybridized with two unpaired electrons.³

Figure 1.1 Orbital diagram of singlet and triplet carbene

Valence shell electronic arrangements cause great changes in reactivity. This is evident when considering the mechanism of addition of carbenes to double bonds. (Scheme 1.1). The electronic character of singlet and triplet carbenes is fundamentally

different since the former is electrophilic and the later is biradical . Moreover, the reaction mechanisms follows different paths and they different stereochemical outcomes.⁴ The singlet carbene undergoes a one-step reaction yielding a stereospecific product. However, the triplet carbene forms an intermediate that has two unpaired electrons and because of free rotation, it loses its stereocontrol. (Scheme 1.1)

Scheme 1.1 Different reactivity of singlet and triplet carbenes

1.2 Carbenes in organometallic chemistry

Carbenes may also be considered as ligands in metal-carbene complexes. There are multiple types of carbene-metal complexes available. Fischer and Schrock carbenes are two representative examples possessing metal-carbon double bonds (Figure 1.2).

Figure 1.2 The bonding carbene metal complexes

Fischer (a) and Schrock (b)

Fischer carbenes were named after E. Fischer, a 1973 Noble laureate. Schrock carbenes were named after Richard Schrock, a 2005 Noble laureate.

Fischer and Schrock carbenes have fundamentally different bonding characteristics. In Fischer carbene complexes, the lone pair of electrons from a singlet carbene is donated to a late transition metal while π -backbonding occurs synergistically. In addition, the presence of a heteroatom on the α carbon stabilises empty p orbital of carbene by donation of π -electrons through resonance.⁵ On the contrary, Schrock carbene complexes are formed from high oxidation state, early transition metal, and a triplet carbene without any heteroatom substituents and Schrock carbenes form two covalent bonds from unpaired electrons (Figure 1.3).⁶

Figure 1.3 Orbital diagram of the bonding pattern

Fischer (A) and Schrock (B) carbene metal complexes.

1.3 *N*-Heterocyclic carbene (NHC)

In 1988, Bertrand and coworkers reported the first stable, isolable singlet carbene.⁷ Previously, carbenes were perceived as very short lived reaction intermediates (unless they were stabilized with metal centers). Bertrand's carbene became known as the push-pull carbene (Figure 1.4). Arduengo and coworkers then reported the discovery of the push-push diaminocarbene.⁸ Arduengo carbenes are known as a *N*-heterocyclic carbenes (NHCs).

Figure 1.4 First stable carbenes

Bertrand's push-pull (a) and Arduengo's push-push (b) carbene .

Arduengo reported the molecular structure (determined by X-ray crystallography) of *N,N*-diadamantyl-imidazol-2-ylidenes (Scheme 1.2). Both, inductive and resonance effects occurring between the carbene and the two neighboring nitrogen atoms are believed to be the reason for enhanced stability of *N,N*-diadamantyl-imidazol-2-ylidenes (Figure 1.5).²

Scheme 1.2 The first isolation of an NHC reported by Arduengo.

Figure 1.5 The stabilization of *N*-heterocyclic carbene by inductive and resonance effect.

The empty p orbital of the carbene is stabilized by electron donation from the two nitrogen atoms. The lone pair of the carbene on sp^2 hybridized orbital is also stabilized by the inductive effect that occurs from the presence of the electronegative nitrogen atoms. Therefore, *N*-heterocyclic carbenes (NHCs) are more thermodynamically stable in the absence of oxygen and moisture.²

Various NHC's have been designed and synthesized following the isolation of *N*-heterocyclic carbenes (NHC's) from Arduengo (Figure 1.6).⁹⁻¹⁷

Figure 1.6 The structure of various *N*-heterocyclic and acyclic carbenes.

1.4 *N*-heterocyclic carbenes (NHC's) as ligands in organometallic chemistry

Discovery of isolable *N*-heterocyclic carbenes (NHC's) and their ability to coordinate to most metals has opened a new frontier of research in organometallic chemistry.¹⁸⁻²⁰ Because of their stronger σ donor with less π -back bonding than most commonly used phosphine ligands in metal complexes,²¹ *N*-heterocyclic carbenes (NHC's) were found more effective in facilitating oxidative addition of reactants into the metal center of these complexes.²² Moreover, introduction of sterically demanding substituents on NHCs can result in better reductive elimination of product from the metal. Chemical feature of NHC can also be tailored easily by attaching various electronic directing substituents on the NHC backbone. In addition, metal-NHC complexes possess high thermal stability. Because of these advantages, *N*-heterocyclic carbenes (NHC's) are now common ligands in a variety of catalysts in reactions such as hydrogenation^{21, 23-26}, carbon-carbon bond formation²⁷⁻²⁹, carbon-nitrogen bond formation^{28, 30-31} and olefin metathesis.^{3, 32-37}

Chiral NHC complexes are desired because of continuously growing use of the NHC based metal complexes in catalysis. Introducing a chiral center into the backbone and synthesis of a chiral NHC ligand precursor would pave the way to prepare chiral metal complexes for application in asymmetric catalysis.³⁸⁻³⁹

1.5 NHC-Pincer Complexes

Pincer ligands are a class of tridentate ligands, which coordinate to a metal with three bonds in a meridional plane (Fig 1.7).⁴⁰ Conventionally the pincer ligand is named according to the coordinating atoms on the pincer ligand. For instance, a CNC pincer complex would have two carbons and one nitrogen coordinated to the metal center.

D = N, O, C etc

Figure 1.7 Graphical representation of pincer complex

Pincer complexes have drawn considerable attention because of their catalytic activities toward various important transformations such as polymerization of alkene,⁴¹⁻⁴³ C-X bond formation,⁴⁴⁻⁴⁷ activation of CO₂⁴⁸⁻⁴⁹ and N₂⁵⁰. *N*-heterocyclic carbene (NHC) as pincer ligand shows excellent thermal stability with greater bond strength with respect to its other analogues.²

Our group has synthesized bis(imidazolium) salts **6** as carbene ligand precursors and a direct mapping of *N*-heterocyclic carbene (NHC) ligand of the pincer motif is illustrated in Figure 1.8.

Figure 1.8 The design of CCC-NHC pincer complex

In order to prepare CCC-Pincer complexes from bis(imidazolium) salts, activation of the central Ar-H bond and simultaneous deprotonation of the imidazole ring were needed. This feat requires two different types of reagents: a base and an electrophile. We

have found that $\text{Zr}(\text{NMe}_2)_4$ satisfied those requirements as it is basic enough to activate the imidazolium proton, and it is also electrophilic enough (d^0 metal center) to activate the aryl proton (Scheme 1.3).⁵¹⁻⁵² This reaction can be easily monitored by ^1H NMR with disappearance of the highlighted proton peaks as depicted in Fig. 1.9.

Scheme 1.3 Zirconium (IV) metallation on bis(imidazolium) iodo ligand precursor **6**.

Figure 1.9 ^1H NMR probe of metallation on ligand precursor 6 with zirconium tetrakis(dimethylamido)

CHAPTER II

RESULTS AND DISCUSSION

2.1 Synthesis and characterization of chiral imidazolinium salts as N-heterocyclic carbene (NHC) ligands

Our group has reported an efficient method for the synthesis of achiral bis(imidazolium) salts as NHC ligand precursors (Scheme 2.1, **8a-d**). The process involves only two steps and starts with 1,3-dibromobenzene.⁵³

Scheme 2.1 Synthetic scheme of bis(imidazolium) salt as achiral ligand precursor

We were interested in synthesizing chiral ligand precursors. The chiral ligand precursors require a saturated backbone in place of the imidazole ring (Figure 2.1).

Therefore, a significantly different approach was necessary.

Figure 2.1 Achiral bis(imidazolium) ligand precursor **9** and proposed structure of chiral NHC precursor **10**.

A retrosynthetic strategy of chiral bis(imidazolinium) salt was designed previously from *N*-substituted amino acids (Scheme 2.2)⁵⁴ and this chiral bis(imidazolinium) salt **17** would be obtained from cyclization of tetramine **16** in the presence of triethyl orthoformate and ammonium tetrafluoroborate. Tetramine **16** would be synthesized from reduction of the corresponding tetramide **15**. Tetramide **15** would be formed by amidation of diamide **14**. Diamide **14** would be subsequently prepared from BOC-deprotection of diamide-dicarbamate **13** which can be prepared from the coupling reaction of 1,3 phenylenediamine **11** and corresponding *N*-BOC amino acid **12**. The advantage of this synthetic strategy was that any type of alkyl group could be introduced into the side chain of the imidazolinium backbone.

Scheme 2.2 Retrosynthetic strategy for the synthesis of chiral bis(imidazolinium) salts as ligand precursor

Commercially available chiral amino acids were used, which avoid generating the chiral center in the compounds. This strategy was found to be very effective. However, the challenge was to maintain the absolute configuration of the chiral amino acids in every step of the synthesis. After a long trial, the method was standardized as depicted in Scheme 2.3.

Scheme 2.3 Standardized synthetic scheme

N-Boc-L-Valine was first considered for initial exploration as the chiral amino acid (R' group is isopropyl) for two reasons. Firstly, it contains an isopropyl group as the chiral pendant group in the amino acid backbone. This sterically demanding alkyl group on the chiral center would be effective at introducing asymmetric environment. Secondly, it was somewhat cheaper compared to other commercially available chiral enantiopure amino acids. Furthermore, the sterically bulky cyclohexyl group was preferred for the R

group. This results in an increased hindrance in rotation and may result in chiral induction to the ligand and corresponding metal pincer complex. (Fig 2.2)

19

Figure 2.2 Target moiety **19** for screening induction of chirality in metal pincer complex

As per method our group have developed previously⁵⁴, the first step yields 86 % of compound **21**, which was recovered pure as light brown solid. Resultant diamide **21** was transformed to free diamine **22** by Boc-deprotection with TFA in CH₂Cl₂, followed by an aqueous work up with KOH solution. This step gave a 76 % yield of a light brown oil which was dissolved in CH₂Cl₂ and reacted with 10 eq of cyclohexylcarbonyl chloride and 8 eq of TEA, affording tetramide **23** in 85% yield. The overall yield of the last two steps becomes 65 %. Tetramide **23** was reduced with 29 eq. BH₃-THF complex under refluxing condition for two days followed another day of reflux with large excess of MeOH (160 ml per mmol of amide) to yield **24** as a crude light brown oil. The crude liquid **24** was taken forward to cyclization with triethyl orthoformate and ammonium tetrafluoroborate to afford low yield of **25** (52 %). This was followed by an anion exchange reaction with NaI/MeOH giving target compound **19** in 83% yield (Scheme

2.4).

Scheme 2.4 Synthesis of target molecule **19**

In an efficient synthesis, optimization becomes necessary in order to lower the cost. This occurs by reducing the amount of chemicals, developing chemist friendly methods, reducing reaction times and achieving higher yields. Therefore, close monitoring of these reactions was needed. In the first step of amidation, 1,3 phenylene diamine **11** (see scheme 2.6) was reacted with *N*-Boc-L-Valine **20** in the presence of

DCC in CH₂Cl₂ at room temperature. The crude reaction mass was chromatographed on silica gel using ethyl acetate and hexane as an eluent. This process afforded a white solid **21** with a 96 % yield with adequate purity. This result is in contrast to the previously reported 86 % yield. The identity/purity of the product was confirmed by ¹H and ¹³C NMR spectroscopy and specific rotation (-17.6°, C = 0.01g/mL, CHCl₃). In the BOC-deprotection step (second step in scheme 2.5), the reaction was found to be complete in 4 h (in comparison to the previously reported 16 h).⁵⁴ Although previously reported, the use of aqueous KOH to retrieve the resultant free diamine compound (**22**) was found to be very ineffective in terms of percent recovery, even after multiple extraction with 30 % isopropanol-chloroform.⁵⁴ So, it appeared that isolation of the free amine was not necessary and the reaction could be taken forward with the di-TFA salt (**22-TFA**).

Scheme 2.5 Modification in second step of Scheme 2.4

Excess TFA was completely removed with reduced pressure, resulting in a light brown sticky solid. This crude mass was not very soluble in CH₂Cl₂, but as TEA (5.5 eq.) was added dropwise at 0°C to it, it gradually became homogeneous mixture. Dropwise addition of cyclohexylcarbonyl chloride (2.75 eq.) resulted in a cloudy precipitation which was previously thought to be either TEA·TFA or TEA·HCl salt. Later it was found

to be our desired tetraamide **23**. However, as expected, the salts mentioned above were trapped in it, so it had to be washed several times with mixture of CH₂Cl₂ and water. After drying, a pure white solid was obtained in 86 % yield, in contrast to 64.4 % yield with previous method.⁵⁴ However, the solid was insoluble in every solvent except DMSO. This prevented us from obtaining mass and specific rotation data for characterization of the solid.

Since BH₃-THF is very expensive, its use had to be minimized with optimized reaction conditions. A literature search revealed the best conditions where when 4 eq of BH₃-THF complex were used per amide group.⁵⁵ In regards to quenching the reaction, it was found that 2 h at room temperature with 5 ml of MeOH per mmol of diamine would suffice in comparison to refluxing for one day with a large excess of MeOH. Concentration of the reaction mixture down to dryness yielded a crude brownish oil **24**. It was very difficult to purify the very polar tetramine **24**. Therefore, tetramine **24** was taken forward without further purification for cyclization with triethyl orthoformate and ammonium tetrafluoroborate in toluene. The recovery of product **25** was low (52 %) as previously reported.⁵⁴ The modification in work up afforded 75 % as a two-step yield with higher purity. It was found that in the work up process, compound was lost as it stayed dissolved in decanted toluene. Complete evaporation and use of CH₂Cl₂ in place of EtOH as solvent afforded pure **25**. Product was confirmed by ¹H NMR, ¹³C NMR and specific rotation was recorded to be -12.6° (C = 0.01g/mL, CHCl₃). BF₄-salt **25** was transformed to the iodo salt **19** by an anion exchange reaction with NaI in MeOH, followed by purification by column chromatography with MeOH/CH₂Cl₂ as eluent yielding highly pure iodo salt **19** (75 % yield). The product was confirmed by ¹H and ¹³C

NMR spectroscopy. The specific rotation was recorded to be -15.4° ($C = 0.01\text{g/mL}$, CHCl_3).

Scheme 2.6 Modified synthetic route to access iodo salt of chiral NHC ligand precursor 19

This reaction was extended to prepare the corresponding bromo salt **26** using KBr and MeOH under the same reaction conditions (Scheme 2.7). The yield of pure bromo salt **26** was 71 % after column chromatography. The product was confirmed by ^1H and ^{13}C NMR spectroscopy. The specific rotation was recorded to be -22.6° ($C = 0.005\text{g/mL}$, CHCl_3).

Scheme 2.7 Synthesis of bromo salt of chiral NHC ligand precursor **26**.

Figure 2.3 Synthesized iodo **19** and bromo **26** salt of chiral NHC pincer ligand precursor

This optimized new method has been consistent in terms of efficacy with other variable substituents on the imidazolidine ring.

2.2 Method development for chiral CCC NHC Zr pincer complexes.

Our group have previously demonstrated that the achiral bis-amido CCC-NHC Zr pincer complex **7** is a better precatalyst for hydroamination/cyclization than the mono-amido Zr pincer complex.

Figure 2.4 Representation of Zr-CCC NHC pincer complex achiral mono amido (a) and bis amido (b)

Therefore, our initial goal was to synthesize the chiral bis-amido CCC-NHC Zr pincer complex to study its enantioselective catalysis in hydroamination. First, the synthesis was performed at 25 mg scale (¹H NMR scale) with the same method followed for achiral Zr CCC-NHC pincer complex synthesis. In a screw cap NMR tube, ligand precursor **19** was added to a solution of 2.5 equivalent of freshly sublimed tetrakis(dimethylamido) zirconium in d₈-toluene and heated at 160 °C and reaction was monitored by ¹HNMR spectroscopy (Scheme 2.8).

Scheme 2.8 Initial probe on preparing bis amido mono iodo chiral CCC NHC pincer complex **27** with the disappearance of proton (in bold) peaks.

As discussed in the introduction (section 1.5), the first goal was to see the disappearance of the two imidazolium C-H peaks (δ 10.63 ppm for iodo salt) and aromatic C-H peak from benzene part (δ 8.13 ppm) of the molecule. It was observed that after heating at 160 °C for 16h, there was complete disappearance of the above mentioned peaks. There were also two new sets of resonances at δ 6.20 ppm (d) and 6.36 ppm (d) and two sets of corresponding triplets at δ 7.28-7.22 ppm appeared on spectra.

Scheme 2.9 Generation of two new sets of peaks on ^1H NMR probe

The metallation reaction may be an equilibrium reaction which can lead to more than one products before making pincer complexes. Therefore, it was decided to continue

this reaction at 160 °C even after 16 h and monitor it every 24 hrs. Over time the peak integration ratio between δ 6.2 ppm and δ 6.36 ppm increased (Figure. 2.5).

Later, we changed the solvent to C_6D_6 for two reasons. It was difficult to monitor the reaction in d_8 -toluene as it has four sets of peaks which populate the region of NMR spectra we are interested in. Additionally, toluene- d_8 is much more expensive than d_6 -benzene. Fortunately, we found no difference in the course of reaction in terms of the peak patterns.

Figure 2.5 Initial 1H NMR probing of metallation reaction with 2.5 eq. $Zr(NMe_2)_4$ at 160 °C

The excess of $\text{Zr}(\text{NMe}_2)_4$ may be a problem, so the same reaction with 1.5 eq of $\text{Zr}(\text{NMe}_2)_4$ in C_6D_6 at 160°C was tried (Scheme 2.10) and monitored with ^1H NMR spectroscopy. A very clean metallation was seen on ^1H NMR which was found to be mono(amido) diiodo Zr CCC-NHC complex **28** (Fig 2.6 and Fig. 2.7).

Scheme 2.10 Synthesis of chiral mono(amido) diiodo zirconium pincer complex

Figure 2.6 ^1H NMR of in situ formation of chiral mono amido-di iodo zirconium pincer complex **28**

Figure 2.7 Assignment of peaks of interest on ^1H NMR for chiral mono(amido) diiodo zirconium pincer complex **28**

Based on the latest finding (Scheme 2.9 and Figure 2.5), the two sets of proton peaks in aromatic and 6.4-6.2 ppm region were from mixture of mono amido **28** and bis-amido **27**. With heating at 160°C, the integration ratio of **27** to **28** was increasing. These data were consistent with the bis-amido **27** converting into the mono amido **28** over time. This result led us to plan our next experiment with 2.5 eq of $\text{Zr}(\text{NMe}_2)_4$ at room temperature. This room temperature reaction was closely monitored with ^1H NMR spectroscopy (Figure 2.8) and temperature was raised step wise according to reaction course (Table **2.1**)

Scheme 2.11 Probing temperature dependence of metallation reaction

Figure 2.8 ^1H NMR probing of reaction progress to synthesize bisamido mono iodo Zr pincer complex **27** at variable temperature.

Table 2.1 Optimization of temperature to synthesize bis(amido) monoiodo Zr pincer complex

Time at temperature stated (Total reaction time)	Temp (°C)	Observations from ¹ HNMR spectroscopy
10min (10 min)	rt	No formation of 28 , Formation of 27 (peak at 6.36 ppm) is observed along with other peaks (May be multiple coordination sphere)
1 h (1 h)	rt	No change
0.5 h Sonication (1.5 h)	rt	No change
14.5h (16h)	40	Formation of 27 with other peaks without 28
3h (19h)	100	27 is formed majorly, no 28 formation
6h (22h)	100	85% of 27 is formed
16h (32h)	110	27:28 85:15
1h (33h)	130	27:28 80:20

It was very evident that this reaction is temperature sensitive and temperatures beyond 100°C are giving mostly mono amido product **28**. It was decided to try different equivalents of Zr(NMe₂)₄ with the optimized temperature at 100 °C. Unfortunately, all reactions had the disadvantage of having excess Zr(NMe₂)₄ present which ruined the products purity (Figure 2.9).

Table 2.2 Optimization of equivalence of Zr(NMe₂)₄ usage in the synthesis of bis(amido) monoiodo Zr pincer complex

Zr(NMe ₂) ₄ (eq)	Temp (°C)	Time	Bis amido complex 27 / Mono amido complex 28 / Unidentified complex
3.5	RT	10 min	50%/ Not observed/50%
	100	1 h	85%/ Not observed/15%
	100	3 h	95%/ Not observed/5%
5	RT	10 min	50%/ Not observed/50%
	100	1 h	80%/ Not observed/20%
	100	3 h	90%/ Not observed/10%
	100	16 h	98%/ Not observed/2%
2	100	3 h	57%/43% mono/Not observed
	100	6 h	50%/50%/Not observed
2.5	100	3 h	98%/2%/Not observed

Figure 2.9 ^1H NMR of in situ formation of bis(amido) moniodo Zr pincer complex **27**

Figure 2.10 Assignment of peaks of interest on ^1H NMR for chiral bis amido mono iodo zirconium pincer complex **27**.

Based on data discussed above, it became clear that we have to minimize the $\text{Zr}(\text{NMe}_2)_4$ equivalence in order to get a pure product. We considered metallating the chiral ligand precursor first to the mono(amido) Zr pincer complex **28**. This product can be converted into the bis(amido) Zr pincer complex **27** with another 0.25 eq of $\text{Zr}(\text{NMe}_2)_4$. After several trials, the optimized condition for synthesizing mono(amido) was found to use 1.2 eq of $\text{Zr}(\text{NMe}_2)_4$ with heating at 130 °C for 4 hours in benzene (Figure 2.11).

Figure 2.11 Strategy to access pure bis(amido) monoiodo Zr pincer complex

- i) 1.2 eq $\text{Zr}(\text{NMe}_2)_4$, benzene, 130 °C, 4 h
- ii) 1 eq $\text{Zr}(\text{NMe}_2)_4$, rt, 10 min

But surprisingly, the second step required a full equivalence of $\text{Zr}(\text{NMe}_2)_4$ to convert the mono-amido **28** to bis-amido **27** (Figure 2.11). This requirement made this approach unsuccessful at accessing an efficient synthesis of bis-amido Zr complex **27**. The crude reaction mixture was concentrated to dryness in reduced pressure and washed with hexane to provide a purer product. However, ^1H NMR spectrum showed formation of mono amido, which was indicative towards reversibility.

As we had a good method to make the monoamido Zr complex **28**, it was decided to explore the efficacy of this method on the bromo analog **26**. The reaction was monitored by ^1H NMR.

Scheme 2.12 Synthesis of chiral mono(amido) dibromo Zr CCC-NHC pincer complex **29**

X-Ray quality pale yellow block like crystals formed out of the reaction solution as it was allowed to cool slowly to room temperature. The crystal sample was studied using single crystal X-ray diffraction by Dr. Oliver Allen at the University of Notre Dame. An ORTEP® figure of complex **29** is illustrated in Figure 2.12. The geometry of the Zr center is found to be slightly distorted octahedron. The pincer ligand is in a meridional plane attached to zirconium. The Zr-C_{carbene} bond distances are found to be Zr1-C10 2.392(3) Å, Zr1-C1 2.407(3) Å respectively and Zr-C_{Aryl} is Zr1-C5 2.292(3) Å which is consistent with other Zr-Phenyl complexes.⁵⁶ The axial Zr-Br(1) distance is 2.6760(5) Å, which is almost same as the equatorial Zr-Br (2) bond distance (2.6769(5) Å). The Zr-N5 distance is 2.036(3) Å. Additional bond distances can be found in the Appendix. Isolated yield of this reaction was found to be 50 %.

Figure 2.12 Molecular structure of complex **29** determined by X-ray crystallography.

Thermal ellipsoids are shown at 50% probability. Hydrogen atoms have been omitted for clarity.

From the crystal structure, we observed the expected absolute configuration of S at chiral carbons (C11 and C2). This is significant as this configuration is consistent with the absolute configuration of the amino acid starting material (N-Boc L-Valine). This result provides a strong evidence of non racemization during metallation.

Figure 2.13 New chiral Zr CCC-NHC pincer complex **29** synthesized

2.3 An attempt to make bis(amido) monoiodo Zr CCC-NHC pincer complex **27**

With the iodo salt in hand, it was decided to explore the scope for LiNMe_2 as a potential dimethylamido source in an effort to convert mono-amido **28** to bis-amido **27** without having excess $\text{Zr}(\text{NMe}_2)_4$. As per our previous assumption,⁵⁷ this reaction is reversible (see scheme 2.13). Therefore, it is challenging to convert all of the mono amido **28** to bis amido **27**. Moreover, purification was problematic as it instigates reversibility. This problem was overcome with crystallization method in case of unsaturated pincer complex **7**. But, the chiral NHC's are much more soluble, even in non polar solvent like benzene, which has made crystallization unsuccessful for bis-amido, in particular. So, the next reaction was strategized to break the equilibrium once it forms the mono amido **28** with 1.2 equivalence of $\text{Zr}(\text{NMe}_2)_4$.

Scheme 2.13 The strategy to synthesize chiral bis(amido) monoiodo Zr CCC-NHC pincer complex **27**

The reaction was performed on a very small ^1H NMR (25 mg) scale, and more than exactly 1 eq of LiNMe_2 was added in situ as a result of manual error. Fortunately, along with the desired bis-amido Zr pincer complex **27**, resonances attributed to the tris-amido complex **30** were seen in the ^1H NMR spectrum. Scale of the reaction was increased to 100 mg and experimented with two reaction conditions. In two separate reactions, 1 eq and 2 eq of LiNMe_2 were added and in 30 min it was transformed to bis- and tris-amido Zr pincer complexes respectively (Figure 2.14 and 2.15). ^1H NMR of tris-amido **30** were studied and it was found that resonance of peaks of interest are significantly different from what we have already observed with mono-amido **28** and bis-amido **27** (Figure 2.16).

Figure 2.14 Attempted synthesis of bis(amido), monoiodo Zr CCC NHC pincer complex **27**

Figure 2.15 Attempted synthesis of tris(amido) Zr CCC NHC pincer complex **30**

A

B

Figure 2.16 Comparative ^1H NMR study on relative positions of peaks of interest in monoamido **28**, diamido **27** and triamido Zr pincer complexes **30**.

A. Full spectra, B. Aromatic region and C. Dimethylamido peak region

C

Figure 2.16 (Continued)

These results were significant as the formation of a tris-amido Zr complex **30** has been previously unreported in the CCC-NHC Zr pincer literature.⁵⁸⁻⁵⁹ These are the initial proof in support of formation of tris(amido) Zr CCC-NHC pincer complex **30**. As it is observed on the ^1H NMR spectra (Figure 2.13 and 2.14), the biggest advantage of this methodology is absence of any $\text{Zr}(\text{NMe}_2)_4$ peaks but ^1H NMR spectra of these isolated compounds are not very clean and optimization of equivalence of LiNMe_2 needed to be developed.

2.4 Conclusion and future work

In this study, we described optimization of synthetic route to access chiral ligand precursor and reported synthesis and characterization of novel bromide salt precursor. We summarized our approaches to synthesize mono-, bis- and tris-amido Zr CCC-NHC pincer complexes with iodo salt ligand precursor and reported successful synthesis,

isolation and characterization of novel mono(amido) dibromo Zr CCC-NHC pincer complex.

We have evaluated LiNMe₂ as a potential source of dimethylamido ligand source to replace excess use of Zr(NMe₂)₄ and it was found to be very effective. Based on our initial findings, protocols to access pure bis- and tris-amido Zr pincer complexes has to be optimized and crystallization condition of these complexes has to be explored.

Moreover, catalytic activity of novel mono(amido) di(bromo) CCC-NHC Zr pincer complex has to be evaluated to find any enantioselectivity it induces in intramolecular hydroamination.

CHAPTER III

EXPERIMENTAL PROCEDURE

3.1 General Procedures

All reactions in the making of chiral ligand precursors were performed using oven-dried glassware under inert atmosphere (Ar or N₂) using standard Schlenk techniques. All reactions involving zirconium were performed in the glove box under Ar atmosphere using silylated and dried glassware. General reactions were monitored by TLC using Millipore silica gel 60 TLC plates (UV 254). Metallation reactions with zirconium were monitored with ¹H-NMR. Column chromatography was performed on silica gel (230-400 mesh). Solvents were purchased from BDH and used as received. Anhydrous solvents like tetrahydrofuran, dichloromethane, chloroform, heaxene, acetonitrile, diethyl ether were procured directly from the in-house LC solvent system. All reagents for the preparation of ligand precursors were purchased from Aldrich, Acros and TCI and used as received. Tetrakis(dimethylamido) Zirconium for the synthesis of metal complexes was purchased from Aldrich and sublimed before it was used. The ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker- Avance 300 MHz or a Bruker-Avance 600 MHz instrument. CDCl₃, CD₂Cl₂, d₈-Tol, C₆D₆ were purchased from Cambridge Isotopes Laboratories and dried with activated basic alumina prior to use. The chemical shift values are recorded in δ units (parts per million) relative to tetramethylsilane as an internal standard. Specific rotation of ligand precursors was

recorded on Rudolph automatic polarimeter IV. The X-Ray crystal structure was analyzed by Dr. Allen Oliver of the University of Notre Dam. Electrospray MS (m/z) was done with Bruker MicrOTOF-Q II ESI standard sprayer.

3.2 2-(S)-tert-Butyloxycarbonylamino-3-methyl-butanoic acid-N-[3-(2-(S)-tert-butyloxycarbonylamino-3-methyl-butanoylamino)-phenyl]-amide, **21**

Scheme 3.1 Synthesis of compound **21**.

To a stirred solution of N-(tert-butoxycarbonyl)-L-valine (7.2 g, 33.02 mmol, 2.1 eq.) in CH₂Cl₂, N,N'-dicyclohexylcarbodiimide (7.14 g, 34.60 mmol, 2.2 eq.) was added in several portions at 0 °C, and followed by addition of 1,3-diaminobenzene (1.70 g, 15.73 mmol, 1 eq.) under same condition. The mixture was stirred for 16 h while allowing it to warm to room temperature. The mixture was filtered to remove the white precipitate, and the filtrate was concentrated to yield a crude product (10.5 g) which was chromatographed on a silica plug using ethyl acetate/hexane as eluent to afford a white crystalline solid (7.7 g, 97 %). ¹H NMR (CDCl₃, 600MHz) : δ 8.78 (s, 2H), 7.51 (s, 1H), 7.1 (d, J = 7.2 Hz, 2H), 6.93 (s, 1H), 5.45 (d, J = 7.8 Hz, 2H), 4.15 (m, 2H), 2.1 (q, J = 6.6 Hz, 2H), 1.45 (s, 18H), 1.00 (d, J = 6.5 Hz, 12H). ¹³C (¹H) (150MHz, CDCl₃): δ 170.9, 156.9, 138.3, 128.9, 115.1, 110.9, 80.2, 61.0, 31.0, 28.5, 19.3, 18.8. MS C₂₆H₄₂N₄O₆ (M⁺ + Na) Calc. 529.2997, Obtnd. 529.3018. [α]²²D = -17.6° (C=0.01g, CHCl₃).

3.3 2-(S)-Cyclohexanecarbonylamino-3-methyl-butanoic acid-N-[3-(2-(S)-cyclohexanecarbonylamino-3-methyl-butanoylamino)-phenyl]-amide, 23

Scheme 3.2 Synthesis of compound **23**.

To a solution of 2-(S)-tert-butyloxycarbonylamino-3-methyl-butanoic acid-N-[3-(2-(S)-tert-butyloxycarbonylamino-3-methyl-butanoylamino)-phenyl]-amide (4.76 g, 9.39 mmol, 1 eq.) in CH₂Cl₂ (200ml), trifluoroacetic acid (14.5 ml, 188.0 mmol, 20 eq.) was added drop wise at room temperature. The mixture was stirred for 4 h before it was concentrated under reduced pressure affording crude Boc-deprotected di-TFA salt, which was taken forward without further purification. To a suspension of resultant crude di-TFA salt of amine in CH₂Cl₂ (200 ml), triethylamine (7.2 ml, 51.67 mmol, 5.5 eq.) was added drop wise at 0 °C, followed by slow addition of cyclohexanecarbonyl chloride (3.46 ml, 25.8 mmol, 2.75 eq.). The mixture formed a white colloidal precipitate immediately after cyclohexanecarbonyl chloride addition and remained this way thorough out the reaction course for 8 h at room temperature. The precipitate was collected and the white solid was washed with CH₂Cl₂ (100 ml X 5) and water (100ml X 10) in sequence and dried in reduced pressure (4.28 g, 86 %, two step yield). ¹H NMR (600 MHz, d₆-DMSO): δ 10.02 (s, 2H), 7.9 (s, 1H), 7.8 (d, J = 7.2 Hz, 2H), 7.28 (s, 2H),

7.19 (s, 1H), 4.26 (s, 2H), 2.29 (s, 2H), 1.99 (s, 2H), 1.60-1.63 (m, 10H), 1.13-1.38 (m, 10H), 0.88 (s, 12H). ^{13}C (^1H) (150 MHz, DMSO- d_6): δ 175.5, 170.5, 139.1, 128.8, 114.5, 110.5, 58.4, 43.5, 30.6, 29.7, 28.9, 25.5, 25.4, 25.2, 19.2, 18.4.

3.4 1,3-Bis(1-cyclohexanemethyl-5-(S)-iso-propyl-imidazolinium)benzene bis(tetrafluoroborate), **25**

Scheme 3.3 Synthesis of compound **25**.

To an ice cold suspension of 2-(S)-cyclohexanecarbonylamino-3-methyl-butanoic acid-N-[3-(2-(S)-cyclohexanecarbonylamino-3-methyl-butanoylamino)-phenyl]-amide (4.2 g, 7.97 mmol, 1 eq.) in dry THF (200 ml), THF solution of BH_3 (1.0 M, 127.6 ml, 127.6 mmol, 16 eq.) was added drop wise. The mixture was heated to reflux at 100°C for two days. After cooling to room temperature, the resultant solution was concentrated to dryness under reduced pressure. MeOH (40 ml) was added drop wise at 0°C to the reaction mass and stirred for 2 h at room temperature, and concentrated to dryness to afford a crude brown oil which was taken forward without further purification. To a stirred solution of the obtained crude product in dry toluene (100 mL) triethyl orthoformate (26.5 ml, 159.5 mmol, 20 eq.) and ammonium tetrafluoroborate (6.7 g, 63.8 mmol, 8 eq.) were added at room temperature before heating to reflux at 130°C for 16 h.

The reaction mixture was cooled to room temperature and concentrated to dryness under reduced pressure, CH₂Cl₂ was added and the mixture was filtered through fritted glass filter to remove impurities. The filtrate was concentrated and precipitated from EtOH/Et₂O and recrystallized from EtOH to afford off-white solid (3.98 g, 75 % two step yield). ¹H NMR (600 MHz, CDCl₃): δ 8.91 (s, 2H), 7.42 (s, 1H), 7.28 (s, 3H), 4.55 (t, J = 11.7 Hz, 2H), 4.4 (m, 2H), 4.14 (t, J = 9.3 Hz, 2H), 3.64 (dd, J = 10.9 and 12.7 Hz, 2H), 3.33 (d, J = 11.9 Hz, 2H), 2.25 (s, 2H), 1.72-1.64 (m, 12H), 1.27-1.13 (m, 6H), 1.04-0.97 (m, 10H), 0.87 (d, J = 6.6 Hz, 6H). ¹³C (¹H) (150 MHz, CDCl₃): δ 153.8, 137.1, 132.1, 115.9, 106.8, 65.2, 52.5, 48.5, 35.1, 30.5, 29.8, 27.2, 25.9, 25.6, 25.3, 17.6, 13.7. MS C₃₂H₅₂N₄B₂F₈ (M⁺ -BF₄) Calc. 579.4221, Obtnd. 579.4241. [α]^{22.2}_D = -12.6° (C=0.01, CHCl₃).

3.5 1,3-Bis(1-cyclohexanemethyl-5-(S)-iso-propyl-imidazolinium)benzene di(iodide), **19**.

Scheme 3.4 Synthesis of compound **19**.

To a stirred solution of 1,3-bis(1-cyclohexanemethyl-5-(S)-iso-propyl-imidazolinium)benzene bis(tetrafluoroborate) (1.0 g, 1.5 mmol, 1 eq.) in MeOH (200 mL), sodium iodide (6.75 g, 45 mmol, 30 eq.) was added at room temperature and heated

to reflux at 110°C. After 16 h the reaction was cooled to room temperature and concentrated to dryness. CH₂Cl₂ (100 ml) was added and the mixture was filtered through a celite plug. The filtrate was concentrated under reduced pressure to yield a crude yellow solid (1.4 g) which was purified with column chromatography (silica, 230-400 mesh, MeOH/CH₂Cl₂) affording a light yellowish amorphous solid (0.84 g, 75 %). ¹H NMR (600MHz, CDCl₃): δ 10.62 (s, 2H), 8.13 (s, 1H), 7.59 (d, J = 7.8 Hz, 2H), 7.36 (t, J = 8.1 Hz, 1H), 4.89 (t, J = 11.7 Hz, 2H), 4.48 (t, J = 9 Hz, 2H), 4.28 (dd, J = 11.4 Hz and 8.4 Hz, 2H), 4.06 (dd, J = 13.2 Hz and 10.8 Hz, 2H), 3.34 (dd, J = 3.6 Hz and 10.2 Hz, 2H), 2.27 (m, 2H), 1.6-1.8 (m, 12H), 1.06-1.31 (m, 10H), 1.11 (d, J = 6.6 Hz, 6H), 0.92 (d, J = 6.6 Hz, 6H). ¹³C (¹H) (150 MHz, CDCl₃): δ 154.1, 137.05, 132.1, 116.2, 107.4, 65.2, 52.2, 50.2, 35.4, 30.5, 30.1, 27.5, 25.8, 25.6, 25.3, 18.3, 14.3. MS C₃₂H₅₂N₄I₂ (M⁺ -I) Calc. 619.3231, Obtnd. 619.3259. [α]^{22.4}_D = -15.4° (C=0.01, CHCl₃).

3.6 1,3-Bis(3'-(1'-cyclohexylmethyl-5'-(S)isopropylimidazolinium))benzene dibromide, **26**

Scheme 3.5 Synthesis of compound **26**.

To a stirred solution of 1,3-bis(1-cyclohexanemethyl-5-(S)-iso-propyl-imidazolinium)benzene bis(tetrafluoroborate) (0.5 g, 0.75 mmol, 1 eq.) in MeOH

To a clear, colorless solution of tetrakis(dimethylamido) zirconium (28.7 mg, 0.11 mmol, 1.4 eq.) and dry toluene (0.5 mL), 1,3-bis(1-cyclohexanemethyl-5-(S)-iso-propyl-imidazolinium)benzene dibromide **24** (50 mg, 0.08 mmol, 1 eq.) was added and heated at 160 °C. After 8 h, from the reaction mixture, mother liquor was decanted off to separate solid residue, collected solution gradually cooled to room temperature and crystal was grown during cooling process. Crystals were recovered and dried under reduced pressure in a glovebox to afford yellow solid (30.4 mg, 50 %). ¹H NMR (600MHz, CD₂Cl₂): δ 7.07 (t, J = 7.8 Hz, 1H), 6.26 (d, J = 7.8 Hz, 2H), 4.2-4.16 (m, 2H), 4.09 (dd, J = 9.6 Hz and 13.8 Hz , 2H), 3.82 (t, J = 11.1 Hz, 2H), 3.64 (s, 2H), 3.23 (dd, J = 5.4 Hz and 13.8 Hz, 2H), 3.04 (s, 6H), 2.24 (m, 2H), 1.77-1.68 (m, 12H), 1.3-1.07 (m, 10H), 0.98 (d, J = 7.2 Hz, 6H), 0.92-0.75 (m, 6H) ¹³C (¹H) (150 MHz, CD₂Cl₂): δ 214.8, 213.6, 161.8, 149.3, 129.4, 105.3, 67.5, 53.8, 45.0, 44.5, 36.99, 31.3, 30.8, 27.9, 27.0, 26.8, , 26.7, 26.4, 26.2, 18.5, 14.3.

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APPENDIX A

X-RAY CRYSTAL DATA AND STRUCTURE REFINEMENTS FOR

C₃₄H₅₇BR₂N₅ZR (29)

Identification code	msu1501	
Empirical formula	C ₃₄ H ₅₅ Br ₂ N ₅ Zr	
Formula weight	784.87	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2₁2₁2₁	
Unit cell dimensions	<i>a</i> = 9.5276(6) Å	$\alpha = 90^\circ$
	<i>b</i> = 11.1579(8) Å	$\beta = 90^\circ$
	<i>c</i> = 33.887(2) Å	$\gamma = 90^\circ$
Volume	3602.4(4) Å ³	
<i>Z</i>	4	
Density (calculated)	1.447 g.cm ⁻³	
Absorption coefficient (μ)	2.553 mm ⁻¹	
<i>F</i> (000)	1616	
Crystal color, habit	yellow, block	
Crystal size	0.143 × 0.111 × 0.083 mm ³	
θ range for data collection	1.922 to 27.208°	
Index ranges	-12 ≤ <i>h</i> ≤ 8, -14 ≤ <i>k</i> ≤ 14, -43 ≤ <i>l</i> ≤ 43	
Reflections collected	59640	

Independent reflections	8023 [Rint = 0.0504]
Completeness to $\theta = 25.242^\circ$	100.0 %
Absorption correction	Numerical
Max. and min. transmission	0.9984 and 0.9465
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8023 / 0 / 385
Goodness-of-fit on F ²	1.000
Final R indices [I>2 σ (I)]	R1 = 0.0258, wR2 = 0.0503
R indices (all data)	R1 = 0.0343, wR2 = 0.0525
Absolute structure parameter	0.006(3)
Extinction coefficient	n/a
Largest diff. peak and hole	0.441 and -0.464 e ⁻ .Å ⁻³

Table A.1 Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for msu1501.

	x	y	z	U(eq)
Zr(1)	0.53101(3)	0.72850(3)	0.36982(2)	0.016(1)
Br(1)	0.33240(4)	0.69464(4)	0.42457(2)	0.039(1)
Br(2)	0.38194(4)	0.91763(3)	0.34531(2)	0.030(1)
N(1)	0.3555(3)	0.5934(2)	0.29204(8)	0.019(1)
N(2)	0.5684(3)	0.6451(2)	0.27912(8)	0.019(1)
N(3)	0.8284(3)	0.8659(2)	0.37067(8)	0.018(1)
N(4)	0.7418(3)	0.9121(2)	0.42742(8)	0.017(1)
N(5)	0.6377(3)	0.5825(2)	0.38975(8)	0.023(1)
C(1)	0.4694(4)	0.6416(3)	0.30717(9)	0.018(1)
C(2)	0.3678(4)	0.5689(3)	0.24880(9)	0.020(1)
C(3)	0.5241(4)	0.5904(3)	0.24192(9)	0.022(1)
C(4)	0.6957(3)	0.7042(3)	0.28654(9)	0.019(1)
C(5)	0.7028(4)	0.7573(3)	0.32344(9)	0.019(1)
C(6)	0.8265(4)	0.8152(3)	0.33248(9)	0.020(1)
C(7)	0.9394(4)	0.8249(3)	0.30644(10)	0.022(1)
C(8)	0.9248(4)	0.7714(3)	0.26988(10)	0.024(1)
C(9)	0.8059(4)	0.7086(3)	0.25943(10)	0.023(1)
C(10)	0.7158(3)	0.8535(3)	0.39410(9)	0.016(1)
C(11)	0.8833(3)	0.9678(3)	0.42876(9)	0.017(1)
C(12)	0.9412(4)	0.9366(3)	0.38765(9)	0.021(1)
C(13)	0.2303(4)	0.5651(3)	0.31433(10)	0.021(1)
C(14)	0.2166(4)	0.4318(3)	0.32412(10)	0.022(1)
C(15)	0.3429(4)	0.3835(3)	0.34569(10)	0.024(1)
C(16)	0.3243(4)	0.2526(3)	0.35660(10)	0.031(1)
C(17)	0.1937(4)	0.2342(4)	0.38105(11)	0.037(1)
C(18)	0.0655(4)	0.2808(4)	0.35956(11)	0.037(1)
C(19)	0.0831(4)	0.4118(3)	0.34801(11)	0.031(1)
C(20)	0.2726(4)	0.6521(3)	0.22465(10)	0.021(1)
C(21)	0.2975(4)	0.7838(3)	0.23356(10)	0.027(1)
C(22)	0.2889(4)	0.6255(3)	0.18072(10)	0.029(1)
C(23)	0.6467(3)	0.9165(3)	0.46074(9)	0.019(1)
C(24)	0.6103(4)	1.0426(3)	0.47393(9)	0.019(1)
C(25)	0.5130(4)	1.0376(3)	0.50924(11)	0.030(1)
C(26)	0.4735(5)	1.1625(3)	0.52354(12)	0.039(1)
C(27)	0.4150(4)	1.2386(4)	0.49065(13)	0.044(1)
C(28)	0.5122(4)	1.2420(3)	0.45557(12)	0.036(1)
C(29)	0.5468(4)	1.1169(3)	0.44090(11)	0.028(1)
C(30)	0.9702(4)	0.9229(3)	0.46300(9)	0.021(1)
C(31)	1.1161(4)	0.9811(3)	0.46213(11)	0.029(1)
C(32)	0.9800(4)	0.7868(3)	0.46365(11)	0.031(1)

Table A.1 (Continued)

C(33)	0.6582(4)	0.5621(3)	0.43143(11)	0.035(1)
C(34)	0.7110(5)	0.4923(4)	0.36734(12)	0.041(1)
H(2)	0.3440	0.4832	0.2432	0.024
H(3A)	0.5745	0.5142	0.2370	0.026
H(3B)	0.5399	0.6453	0.2194	0.026
H(7)	1.0226	0.8665	0.3135	0.027
H(8)	0.9992	0.7782	0.2513	0.029
H(9)	0.7992	0.6696	0.2346	0.027
H(11)	0.8729	1.0568	0.4309	0.020
H(12A)	0.9592	1.0098	0.3719	0.026
H(12B)	1.0290	0.8895	0.3896	0.026
H(13A)	0.1470	0.5905	0.2990	0.025
H(13B)	0.2312	0.6115	0.3392	0.025
H(14)	0.2072	0.3868	0.2987	0.026
H(15A)	0.3583	0.4310	0.3700	0.029
H(15B)	0.4270	0.3922	0.3288	0.029
H(16A)	0.3178	0.2039	0.3322	0.037
H(16B)	0.4072	0.2250	0.3717	0.037
H(17A)	0.2038	0.2767	0.4065	0.044
H(17B)	0.1816	0.1477	0.3867	0.044
H(18A)	-0.0179	0.2724	0.3768	0.044
H(18B)	0.0496	0.2322	0.3355	0.044
H(19A)	0.0864	0.4617	0.3722	0.037
H(19B)	0.0010	0.4376	0.3322	0.037
H(20)	0.1734	0.6334	0.2320	0.026
H(21A)	0.2804	0.7989	0.2616	0.040
H(21B)	0.2334	0.8328	0.2177	0.040
H(21C)	0.3947	0.8047	0.2271	0.040
H(22A)	0.2160	0.6682	0.1659	0.044
H(22B)	0.2794	0.5391	0.1762	0.044
H(22C)	0.3816	0.6522	0.1718	0.044
H(23A)	0.6897	0.8731	0.4832	0.022
H(23B)	0.5589	0.8741	0.4536	0.022
H(24)	0.6991	1.0827	0.4825	0.023
H(25A)	0.5596	0.9934	0.5309	0.036
H(25B)	0.4267	0.9933	0.5020	0.036
H(26A)	0.4028	1.1557	0.5448	0.047
H(26B)	0.5577	1.2021	0.5347	0.047
H(27A)	0.3230	1.2061	0.4824	0.052
H(27B)	0.4000	1.3212	0.5004	0.052
H(28A)	0.6001	1.2835	0.4630	0.044
H(28B)	0.4675	1.2882	0.4340	0.044
H(29A)	0.6139	1.1221	0.4187	0.033

Table A.1 (Continued)

H(29B)	0.4603	1.0776	0.4312	0.033
H(30)	0.9227	0.9488	0.4879	0.025
H(31A)	1.1649	0.9578	0.4378	0.044
H(31B)	1.1705	0.9541	0.4850	0.044
H(31C)	1.1062	1.0684	0.4630	0.044
H(32A)	0.8857	0.7526	0.4662	0.047
H(32B)	1.0376	0.7614	0.4861	0.047
H(32C)	1.0230	0.7586	0.4391	0.047
H(33A)	0.7589	0.5578	0.4371	0.053
H(33B)	0.6134	0.4864	0.4390	0.053
H(33C)	0.6163	0.6281	0.4464	0.053
H(34A)	0.6920	0.5037	0.3392	0.062
H(34B)	0.6789	0.4126	0.3755	0.062
H(34C)	0.8121	0.4993	0.3721	0.062

$U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table A.2 Anisotropic displacement parameters (Å²) for msu1501.
$$-2\pi^2[h2a^*2U11 + \dots + 2hka^*b^*U12]$$

	U11	U22	U33	U23	U13	U12
Zr(1)	0.0154(2)	0.0177(1)	0.0137(1)	-0.0004(1)	0.0022(1)	-0.0010(1)
Br(1)	0.0336(2)	0.0475(3)	0.0360(2)	0.0096(2)	0.0185(2)	0.0062(2)
Br(2)	0.0328(2)	0.0236(2)	0.0324(2)	0.0060(2)	0.0007(2)	0.0063(2)
N(1)	0.0203(16)	0.0202(14)	0.0153(13)	-0.0022(11)	-0.0007(12)	-0.0005(12)
N(2)	0.0192(17)	0.0240(15)	0.0146(14)	-0.0036(11)	0.0009(12)	-0.0014(12)
N(3)	0.0150(15)	0.0212(13)	0.0185(14)	-0.0010(12)	0.0010(13)	-0.0027(11)
N(4)	0.0156(15)	0.0183(13)	0.0176(14)	-0.0004(12)	0.0029(12)	-0.0012(12)
N(5)	0.0236(17)	0.0206(14)	0.0257(15)	0.0046(13)	0.0036(13)	0.0007(13)
C(1)	0.0198(18)	0.0152(15)	0.0193(16)	0.0025(12)	0.0009(16)	0.0007(15)
C(2)	0.024(2)	0.0184(16)	0.0179(16)	-0.0028(13)	-0.0020(15)	-0.0006(15)
C(3)	0.0228(19)	0.0261(17)	0.0170(16)	-0.0036(14)	-0.0008(16)	0.0032(17)
C(4)	0.0170(19)	0.0226(18)	0.0171(16)	0.0018(13)	-0.0002(14)	0.0027(14)
C(5)	0.0188(19)	0.0219(18)	0.0148(16)	0.0021(13)	0.0003(14)	-0.0004(14)
C(6)	0.0190(19)	0.0212(16)	0.0183(17)	0.0023(13)	0.0010(15)	-0.0002(15)
C(7)	0.016(2)	0.0264(18)	0.0247(18)	-0.0007(14)	0.0030(15)	0.0006(15)
C(8)	0.0169(19)	0.0360(19)	0.0200(16)	0.0033(16)	0.0045(14)	0.0046(16)
C(9)	0.023(2)	0.031(2)	0.0142(16)	0.0004(14)	0.0022(15)	0.0048(16)
C(10)	0.0144(18)	0.0170(16)	0.0181(17)	0.0009(13)	0.0010(15)	0.0013(13)
C(11)	0.0153(17)	0.0160(15)	0.0193(17)	0.0016(13)	0.0010(15)	-0.0023(13)
C(12)	0.018(2)	0.0263(18)	0.0196(16)	-0.0005(14)	-0.0001(15)	-0.0048(14)
C(13)	0.0172(19)	0.0254(19)	0.0202(17)	-0.0028(15)	0.0000(15)	0.0009(15)
C(14)	0.022(2)	0.0234(18)	0.0186(17)	-0.0025(14)	0.0019(15)	-0.0044(15)
C(15)	0.027(2)	0.0242(17)	0.0216(18)	0.0006(14)	0.0049(17)	0.0032(15)
C(16)	0.042(2)	0.026(2)	0.0248(18)	0.0030(14)	0.0045(18)	0.0010(17)
C(17)	0.046(3)	0.034(2)	0.030(2)	0.0063(17)	0.0083(19)	-0.011(2)
C(18)	0.035(2)	0.043(2)	0.033(2)	0.0027(18)	0.0096(18)	-0.0164(19)
C(19)	0.021(2)	0.042(2)	0.029(2)	0.0002(18)	0.0051(17)	-0.0037(17)
C(20)	0.0171(19)	0.0241(18)	0.0232(19)	0.0012(14)	-0.0027(16)	-0.0010(15)
C(21)	0.027(2)	0.0250(19)	0.0280(19)	0.0057(16)	0.0024(16)	0.0039(16)
C(22)	0.032(2)	0.033(2)	0.0219(19)	-0.0004(15)	-0.0068(17)	-0.0005(17)
C(23)	0.0191(19)	0.0199(16)	0.0165(16)	-0.0009(14)	0.0025(14)	-0.0026(14)
C(24)	0.0159(18)	0.0210(16)	0.0207(17)	-0.0048(13)	0.0009(16)	-0.0027(14)
C(25)	0.028(2)	0.0325(19)	0.029(2)	-0.0103(16)	0.0086(18)	-0.0032(17)
C(26)	0.029(2)	0.045(2)	0.043(2)	-0.0255(19)	0.013(2)	-0.005(2)
C(27)	0.023(2)	0.038(2)	0.070(3)	-0.028(2)	-0.005(2)	0.0069(18)
C(28)	0.034(2)	0.025(2)	0.050(2)	-0.0044(17)	-0.010(2)	0.0052(17)
C(29)	0.029(2)	0.0231(18)	0.031(2)	-0.0020(14)	-0.0058(18)	0.0030(16)
C(30)	0.0202(18)	0.0243(16)	0.0190(16)	0.0032(14)	-0.0012(16)	-0.0014(16)
C(31)	0.023(2)	0.037(2)	0.027(2)	0.0033(16)	-0.0056(18)	-0.0078(17)

Table A.2 (Continued)

C(32)	0.026(2)	0.028(2)	0.039(2)	0.0105(16)	-0.0021(18)	0.0052(17)
C(33)	0.045(3)	0.028(2)	0.032(2)	0.0051(16)	-0.006(2)	0.0023(18)
C(34)	0.043(3)	0.043(2)	0.038(2)	0.002(2)	0.005(2)	0.018(2)

The anisotropic displacement factor exponent takes the form

Table A.3 Bond lengths [$\text{\AA}$] for msu1501.

atom-atom	distance	atom-atom	distance
Zr(1)-N(5)	2.036(3)	Zr(1)-C(5)	2.292(3)
Zr(1)-C(10)	2.392(3)	Zr(1)-C(1)	2.407(3)
Zr(1)-Br(2)	2.6760(5)	Zr(1)-Br(1)	2.6769(5)
N(1)-C(1)	1.315(4)	N(1)-C(13)	1.447(4)
N(1)-C(2)	1.495(4)	N(2)-C(1)	1.340(4)
N(2)-C(4)	1.403(4)	N(2)-C(3)	1.463(4)
N(3)-C(10)	1.342(4)	N(3)-C(6)	1.413(4)
N(3)-C(12)	1.453(4)	N(4)-C(10)	1.328(4)
N(4)-C(23)	1.449(4)	N(4)-C(11)	1.486(4)
N(5)-C(34)	1.441(5)	N(5)-C(33)	1.444(4)
C(2)-C(3)	1.526(5)	C(2)-C(20)	1.535(5)
C(2)-H(2)	1.0000	C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900	C(4)-C(5)	1.385(4)
C(4)-C(9)	1.396(5)	C(5)-C(6)	1.378(5)
C(6)-C(7)	1.396(5)	C(7)-C(8)	1.382(5)
C(7)-H(7)	0.9500	C(8)-C(9)	1.378(5)
C(8)-H(8)	0.9500	C(9)-H(9)	0.9500
C(11)-C(30)	1.511(4)	C(11)-C(12)	1.538(4)
C(11)-H(11)	1.0000	C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900	C(13)-C(14)	1.530(5)
C(13)-H(13A)	0.9900	C(13)-H(13B)	0.9900
C(14)-C(15)	1.507(5)	C(14)-C(19)	1.524(5)
C(14)-H(14)	1.0000	C(15)-C(16)	1.517(5)
C(15)-H(15A)	0.9900	C(15)-H(15B)	0.9900
C(16)-C(17)	1.509(5)	C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900	C(17)-C(18)	1.514(6)
C(17)-H(17A)	0.9900	C(17)-H(17B)	0.9900
C(18)-C(19)	1.522(5)	C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900	C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900	C(20)-C(21)	1.519(5)
C(20)-C(22)	1.526(5)	C(20)-H(20)	1.0000
C(21)-H(21A)	0.9800	C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800	C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800	C(22)-H(22C)	0.9800
C(23)-C(24)	1.517(4)	C(23)-H(23A)	0.9900
C(23)-H(23B)	0.9900	C(24)-C(25)	1.515(5)
C(24)-C(29)	1.518(5)	C(24)-H(24)	1.0000
C(25)-C(26)	1.523(5)	C(25)-H(25A)	0.9900
C(25)-H(25B)	0.9900	C(26)-C(27)	1.508(6)
C(26)-H(26A)	0.9900	C(26)-H(26B)	0.9900
C(27)-C(28)	1.507(6)	C(27)-H(27A)	0.9900
C(27)-H(27B)	0.9900	C(28)-C(29)	1.518(5)

Table A.3 (Continued)

C(28)-H(28A)	0.9900	C(28)-H(28B)	0.9900
C(29)-H(29A)	0.9900	C(29)-H(29B)	0.9900
C(30)-C(32)	1.522(5)	C(30)-C(31)	1.535(5)
C(30)-H(30)	1.0000	C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800	C(31)-H(31C)	0.9800
C(32)-H(32A)	0.9800	C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800	C(33)-H(33A)	0.9800
C(33)-H(33B)	0.9800	C(33)-H(33C)	0.9800
C(34)-H(34A)	0.9800	C(34)-H(34B)	0.9800
C(34)-H(34C)	0.9800		

Symmetry transformations used to generate equivalent atoms:

Table A.4 Bond angles [°] for msu1501.

atom-atom-atom	angle	atom-atom-atom	angle
N(5)-Zr(1)-C(5)	89.04(11)	N(5)-Zr(1)-C(10)	89.14(11)
C(5)-Zr(1)-C(10)	68.19(11)	N(5)-Zr(1)-C(1)	95.28(11)
C(5)-Zr(1)-C(1)	68.02(12)	C(10)-Zr(1)-C(1)	135.88(11)
N(5)-Zr(1)-Br(2)	177.72(8)	C(5)-Zr(1)-Br(2)	93.19(8)
C(10)-Zr(1)-Br(2)	92.16(8)	C(1)-Zr(1)-Br(2)	85.09(8)
N(5)-Zr(1)-Br(1)	90.57(8)	C(5)-Zr(1)-Br(1)	179.41(8)
C(10)-Zr(1)-Br(1)	111.36(8)	C(1)-Zr(1)-Br(1)	112.46(9)
Br(2)-Zr(1)-Br(1)	87.207(15)	C(1)-N(1)-C(13)	124.5(3)
C(1)-N(1)-C(2)	113.1(3)	C(13)-N(1)-C(2)	122.4(3)
C(1)-N(2)-C(4)	119.7(3)	C(1)-N(2)-C(3)	113.3(3)
C(4)-N(2)-C(3)	126.9(3)	C(10)-N(3)-C(6)	119.4(3)
C(10)-N(3)-C(12)	114.4(3)	C(6)-N(3)-C(12)	126.2(3)
C(10)-N(4)-C(23)	124.2(3)	C(10)-N(4)-C(11)	113.7(3)
C(23)-N(4)-C(11)	122.0(3)	C(34)-N(5)-C(33)	109.8(3)
C(34)-N(5)-Zr(1)	128.8(2)	C(33)-N(5)-Zr(1)	121.2(2)
N(1)-C(1)-N(2)	108.5(3)	N(1)-C(1)-Zr(1)	135.2(2)
N(2)-C(1)-Zr(1)	116.2(2)	N(1)-C(2)-C(3)	101.4(3)
N(1)-C(2)-C(20)	111.4(3)	C(3)-C(2)-C(20)	113.6(3)
N(1)-C(2)-H(2)	110.1	C(3)-C(2)-H(2)	110.1
C(20)-C(2)-H(2)	110.1	N(2)-C(3)-C(2)	102.4(3)
N(2)-C(3)-H(3A)	111.3	C(2)-C(3)-H(3A)	111.3
N(2)-C(3)-H(3B)	111.3	C(2)-C(3)-H(3B)	111.3
H(3A)-C(3)-H(3B)	109.2	C(5)-C(4)-C(9)	122.8(3)
C(5)-C(4)-N(2)	113.9(3)	C(9)-C(4)-N(2)	123.3(3)
C(6)-C(5)-C(4)	116.3(3)	C(6)-C(5)-Zr(1)	121.6(2)
C(4)-C(5)-Zr(1)	121.6(2)	C(5)-C(6)-C(7)	123.7(3)
C(5)-C(6)-N(3)	113.7(3)	C(7)-C(6)-N(3)	122.5(3)
C(8)-C(7)-C(6)	117.1(3)	C(8)-C(7)-H(7)	121.4
C(6)-C(7)-H(7)	121.4	C(9)-C(8)-C(7)	122.2(3)
C(9)-C(8)-H(8)	118.9	C(7)-C(8)-H(8)	118.9
C(8)-C(9)-C(4)	117.8(3)	C(8)-C(9)-H(9)	121.1
C(4)-C(9)-H(9)	121.1	N(4)-C(10)-N(3)	107.6(3)
N(4)-C(10)-Zr(1)	135.8(2)	N(3)-C(10)-Zr(1)	116.4(2)
N(4)-C(11)-C(30)	112.4(3)	N(4)-C(11)-C(12)	101.7(2)
C(30)-C(11)-C(12)	115.1(3)	N(4)-C(11)-H(11)	109.1
C(30)-C(11)-H(11)	109.1	C(12)-C(11)-H(11)	109.1
N(3)-C(12)-C(11)	102.5(3)	N(3)-C(12)-H(12A)	111.3
C(11)-C(12)-H(12A)	111.3	N(3)-C(12)-H(12B)	111.3
C(11)-C(12)-H(12B)	111.3	H(12A)-C(12)-H(12B)	109.2
N(1)-C(13)-C(14)	113.3(3)	N(1)-C(13)-H(13A)	108.9
C(14)-C(13)-H(13A)	108.9	N(1)-C(13)-H(13B)	108.9
C(14)-C(13)-H(13B)	108.9	H(13A)-C(13)-H(13B)	107.7
C(15)-C(14)-C(19)	110.9(3)	C(15)-C(14)-C(13)	112.6(3)
C(19)-C(14)-C(13)	109.2(3)	C(15)-C(14)-H(14)	108.0
C(19)-C(14)-H(14)	108.0	C(13)-C(14)-H(14)	108.0
C(14)-C(15)-C(16)	111.6(3)	C(14)-C(15)-H(15A)	109.3

Table A.4 (Continued)

C(16)-C(15)-H(15A)	109.3	C(14)-C(15)-H(15B)	109.3
C(16)-C(15)-H(15B)	109.3	H(15A)-C(15)-H(15B)	108.0
C(17)-C(16)-C(15)	111.2(3)	C(17)-C(16)-H(16A)	109.4
C(15)-C(16)-H(16A)	109.4	C(17)-C(16)-H(16B)	109.4
C(15)-C(16)-H(16B)	109.4	H(16A)-C(16)-H(16B)	108.0
C(16)-C(17)-C(18)	110.7(3)	C(16)-C(17)-H(17A)	109.5
C(18)-C(17)-H(17A)	109.5	C(16)-C(17)-H(17B)	109.5
C(18)-C(17)-H(17B)	109.5	H(17A)-C(17)-H(17B)	108.1
C(17)-C(18)-C(19)	111.4(3)	C(17)-C(18)-H(18A)	109.3
C(19)-C(18)-H(18A)	109.3	C(17)-C(18)-H(18B)	109.3
C(19)-C(18)-H(18B)	109.3	H(18A)-C(18)-H(18B)	108.0
C(18)-C(19)-C(14)	111.6(3)	C(18)-C(19)-H(19A)	109.3
C(14)-C(19)-H(19A)	109.3	C(18)-C(19)-H(19B)	109.3
C(14)-C(19)-H(19B)	109.3	H(19A)-C(19)-H(19B)	108.0
C(21)-C(20)-C(22)	111.5(3)	C(21)-C(20)-C(2)	112.8(3)
C(22)-C(20)-C(2)	110.0(3)	C(21)-C(20)-H(20)	107.4
C(22)-C(20)-H(20)	107.4	C(2)-C(20)-H(20)	107.4
C(20)-C(21)-H(21A)	109.5	C(20)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5	C(20)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5	H(21B)-C(21)-H(21C)	109.5
C(20)-C(22)-H(22A)	109.5	C(20)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5	C(20)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5	H(22B)-C(22)-H(22C)	109.5
N(4)-C(23)-C(24)	113.9(3)	N(4)-C(23)-H(23A)	108.8
C(24)-C(23)-H(23A)	108.8	N(4)-C(23)-H(23B)	108.8
C(24)-C(23)-H(23B)	108.8	H(23A)-C(23)-H(23B)	107.7
C(25)-C(24)-C(23)	109.8(3)	C(25)-C(24)-C(29)	111.0(3)
C(23)-C(24)-C(29)	112.3(3)	C(25)-C(24)-H(24)	107.8
C(23)-C(24)-H(24)	107.8	C(29)-C(24)-H(24)	107.8
C(24)-C(25)-C(26)	111.6(3)	C(24)-C(25)-H(25A)	109.3
C(26)-C(25)-H(25A)	109.3	C(24)-C(25)-H(25B)	109.3
C(26)-C(25)-H(25B)	109.3	H(25A)-C(25)-H(25B)	108.0
C(27)-C(26)-C(25)	111.8(3)	C(27)-C(26)-H(26A)	109.3
C(25)-C(26)-H(26A)	109.3	C(27)-C(26)-H(26B)	109.3
C(25)-C(26)-H(26B)	109.3	H(26A)-C(26)-H(26B)	107.9
C(28)-C(27)-C(26)	111.7(3)	C(28)-C(27)-H(27A)	109.3
C(26)-C(27)-H(27A)	109.3	C(28)-C(27)-H(27B)	109.3
C(26)-C(27)-H(27B)	109.3	H(27A)-C(27)-H(27B)	107.9
C(27)-C(28)-C(29)	111.6(3)	C(27)-C(28)-H(28A)	109.3
C(29)-C(28)-H(28A)	109.3	C(27)-C(28)-H(28B)	109.3
C(29)-C(28)-H(28B)	109.3	H(28A)-C(28)-H(28B)	108.0
C(28)-C(29)-C(24)	110.3(3)	C(28)-C(29)-H(29A)	109.6
C(24)-C(29)-H(29A)	109.6	C(28)-C(29)-H(29B)	109.6
C(24)-C(29)-H(29B)	109.6	H(29A)-C(29)-H(29B)	108.1

Table A.4 (Continued)

C(11)-C(30)-C(32)	112.1(3)	C(11)-C(30)-C(31)	109.9(3)
C(32)-C(30)-C(31)	111.5(3)	C(11)-C(30)-H(30)	107.7
C(32)-C(30)-H(30)	107.7	C(31)-C(30)-H(30)	107.7
C(30)-C(31)-H(31A)	109.5	C(30)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5	C(30)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5	H(31B)-C(31)-H(31C)	109.5
C(30)-C(32)-H(32A)	109.5	C(30)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5	C(30)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5	H(32B)-C(32)-H(32C)	109.5
N(5)-C(33)-H(33A)	109.5	N(5)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5	N(5)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33C)	109.5	H(33B)-C(33)-H(33C)	109.5
N(5)-C(34)-H(34A)	109.5	N(5)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5	N(5)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5	H(34B)-C(34)-H(34C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table A.5 Torsion angles [$^{\circ}$] for msu1501.

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle
C(13)-N(1)-C(1)-N(2)	174.4(3)	C(2)-N(1)-C(1)-N(2)	-5.1(4)
C(13)-N(1)-C(1)-Zr(1)	-9.1(5)	C(2)-N(1)-C(1)-Zr(1)	171.5(2)
C(4)-N(2)-C(1)-N(1)	173.3(3)	C(3)-N(2)-C(1)-N(1)	-2.9(4)
C(4)-N(2)-C(1)-Zr(1)	-4.0(4)	C(3)-N(2)-C(1)-Zr(1)	179.8(2)
C(1)-N(1)-C(2)-C(3)	10.3(4)	C(13)-N(1)-C(2)-C(3)	-169.2(3)
C(1)-N(1)-C(2)-C(20)	-110.8(3)	C(13)-N(1)-C(2)-C(20)	69.7(4)
C(1)-N(2)-C(3)-C(2)	9.1(4)	C(4)-N(2)-C(3)-C(2)	-166.8(3)
N(1)-C(2)-C(3)-N(2)	-10.6(3)	C(20)-C(2)-C(3)-N(2)	109.0(3)
C(1)-N(2)-C(4)-C(5)	-1.7(4)	C(3)-N(2)-C(4)-C(5)	174.0(3)
C(1)-N(2)-C(4)-C(9)	177.8(3)	C(3)-N(2)-C(4)-C(9)	-6.5(5)
C(9)-C(4)-C(5)-C(6)	-0.5(5)	N(2)-C(4)-C(5)-C(6)	179.1(3)
C(9)-C(4)-C(5)-Zr(1)	-172.3(2)	N(2)-C(4)-C(5)-Zr(1)	7.2(4)
C(4)-C(5)-C(6)-C(7)	1.8(5)	Zr(1)-C(5)-C(6)-C(7)	173.7(2)
C(4)-C(5)-C(6)-N(3)	-179.0(3)	Zr(1)-C(5)-C(6)-N(3)	-7.2(4)
C(10)-N(3)-C(6)-C(5)	0.5(4)	C(12)-N(3)-C(6)-C(5)	-177.0(3)
C(10)-N(3)-C(6)-C(7)	179.7(3)	C(12)-N(3)-C(6)-C(7)	2.2(5)
C(5)-C(6)-C(7)-C(8)	-0.9(5)	N(3)-C(6)-C(7)-C(8)	180.0(3)
C(6)-C(7)-C(8)-C(9)	-1.4(5)	C(7)-C(8)-C(9)-C(4)	2.6(5)
C(5)-C(4)-C(9)-C(8)	-1.7(5)	N(2)-C(4)-C(9)-C(8)	178.8(3)
C(23)-N(4)-C(10)-N(3)	-178.0(3)	C(11)-N(4)-C(10)-N(3)	-1.6(4)
C(23)-N(4)-C(10)-Zr(1)	-2.5(5)	C(11)-N(4)-C(10)-Zr(1)	173.8(2)
C(6)-N(3)-C(10)-N(4)	-177.8(3)	C(12)-N(3)-C(10)-N(4)	0.0(4)
C(6)-N(3)-C(10)-Zr(1)	5.7(3)	C(12)-N(3)-C(10)-Zr(1)	-176.5(2)
C(10)-N(4)-C(11)-C(30)	-121.2(3)	C(23)-N(4)-C(11)-C(30)	55.3(4)
C(10)-N(4)-C(11)-C(12)	2.4(3)	C(23)-N(4)-C(11)-C(12)	178.9(3)
C(10)-N(3)-C(12)-C(11)	1.5(4)	C(6)-N(3)-C(12)-C(11)	179.1(3)
N(4)-C(11)-C(12)-N(3)	-2.2(3)	C(30)-C(11)-C(12)-N(3)	119.7(3)
C(1)-N(1)-C(13)-C(14)	-102.2(4)	C(2)-N(1)-C(13)-C(14)	77.2(4)
N(1)-C(13)-C(14)-C(15)	55.6(4)	N(1)-C(13)-C(14)-C(19)	179.2(3)
C(19)-C(14)-C(15)-C(16)	54.9(4)	C(13)-C(14)-C(15)-C(16)	177.6(3)
C(14)-C(15)-C(16)-C(17)	-56.6(4)	C(15)-C(16)-C(17)-C(18)	56.5(4)
C(16)-C(17)-C(18)-C(19)	-55.6(4)	C(17)-C(18)-C(19)-C(14)	54.6(4)
C(15)-C(14)-C(19)-C(18)	-53.9(4)	C(13)-C(14)-C(19)-C(18)	-178.6(3)
N(1)-C(2)-C(20)-C(21)	54.3(4)	C(3)-C(2)-C(20)-C(21)	-59.5(4)
N(1)-C(2)-C(20)-C(22)	179.4(3)	C(3)-C(2)-C(20)-C(22)	65.7(4)
C(10)-N(4)-C(23)-C(24)	-125.3(3)	C(11)-N(4)-C(23)-C(24)	58.6(4)
N(4)-C(23)-C(24)-C(25)	-178.9(3)	N(4)-C(23)-C(24)-C(29)	57.0(4)
C(23)-C(24)-C(25)-C(26)	-180.0(3)	C(29)-C(24)-C(25)-C(26)	-55.2(4)
C(24)-C(25)-C(26)-C(27)	53.3(5)	C(25)-C(26)-C(27)-C(28)	-53.2(5)
C(26)-C(27)-C(28)-C(29)	55.2(4)	C(27)-C(28)-C(29)-C(24)	-56.7(5)
C(25)-C(24)-C(29)-C(28)	56.6(4)	C(23)-C(24)-C(29)-C(28)	180.0(3)
N(4)-C(11)-C(30)-C(32)	53.8(4)	C(12)-C(11)-C(30)-C(32)	-62.0(4)
N(4)-C(11)-C(30)-C(31)	178.5(3)	C(12)-C(11)-C(30)-C(31)	62.7(4)

Symmetry transformations used to generate equivalent atoms.

Figure A.1 Spectra for compounds synthesized for this thesis

Figure A.1 (Continued)

Figure A.1 (Continued)

Figure A.2 ESI-MS Spectrum of compound **21**. A. Obtained mass and B. Calculated mass,

Figure A.2 (Continued)

Figure A.2 (Continued)

Figure A.2 (Continued)

Figure A.3 ESI-MS Spectrum of compound **25**. A. Obtained mass and B. Calculated mass,

Figure A.3 (Continued)

Window Display Report

Figure A.3 (Continued)

Figure A.4 ESI-MS Spectrum of compound **19**. A. Obtained mass and B. Calculated mass,

Figure A.4 (Continued)

Window Display Report

Figure A.4 (Continued)

Figure A.5 1H NMR Spectrum of compound **26**. A. Obtained mass and B. Calculated mass.

Figure A.5 (Continued)