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Synthesis of new zirconium complexes

Par

Ibrahim El-Zoghbi

Département de chimie
Faculté des arts et des sciences

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Présenté par :
Ibrahim El-Zoghbi

A été évalué par un jury composé des personnes suivantes :

Président-rapporteur	Professeur Davit Zargarian
Membre du jury	Professeur Christian Reber
Directeur de recherche	Professeur Frank Schaper

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Résumé

L'étude suivante décrit la synthèse des ligands *nacnac*^{xyl}H, *nacnac*^{Bn}H, *nacnac*^{R,R}H et *nacnac*^{Cy}H en utilisant une méthode générale qui implique des rendements élevés et des coûts raisonnables, la complexation de ces ligands au Zr, la caractérisation de ces complexes et l'investigation de leurs réactivités. Les complexes de zirconium ont été obtenus en utilisant deux méthodes synthétiques principales : la première consiste en traitement du sel de lithium du ligand avec le $ZrCl_4$. La seconde est la réaction du ligand neutre avec les complexes d'alkyl-zirconium(IV) par protonation de l'alkyle coordonné.

Le ligand adopte deux modes de coordination avec le Zr. Une coordination κ^2 est observée dans les complexes octaèdriques contenant un ou deux ligands *nacnac*. En présence d'un autre ligand ayant une coordonnation η^5, par exemple Cp ou Ind, le ligand *nacnac* se trouve en coordination $\eta^{4/5}$ avec le centre métallique de zirconium. En solution, les complexes obtenus de (*nacnac*)$_2$ZrX$_2$ montrent un comportement dynamique via un « Bailar-twist » et les paramètres d'activation de cette isomérisation ont été obtenus. Le complexe octaèdrique (*nacnac*^{Bn})$_2$ZrCl$_2$, **2c**, n'a pas montré de réactivité dans la carbozirconation et son alkylation n'était pas possible par l'échange des chlorures avec les alkyles. L'analogue dimethylé (*nacnac*^{Bn})$_2$ZrMe$_2$, **2d**, peut être préparé par alkylation du $ZrCl_4$ avant la complexation du ligand. Ce dernier a été prouvé aussi de ne pas être réactif dans la carbozirconation.

Mots clés : Zirconium, complexes de *nacnac*, complexes β-diketiminate, hydrozirconation, carbozirconation, « Bailar-twist ».

Abstract

The present study describes the synthesis of ligands *nacnac*^{xyl}H, *nacnac*^{Bn}H, *nacnac*^{R,R}H and *nacnac*^{Cy}H, using a general method of synthesis which affords high yields at affordable costs, the complexation of these ligands to Zr, the characterization of these complexes and the investigation of their reactivities. Zirconium complexes were obtained using two major synthetic routes: The first one consists of treatment of the previously prepared lithium salt of the ligand with $ZrCl_4$. The second is the reaction of the neutral ligand with alkyl-Zr(IV) complexes by protonation of the coordinated alkyl(s).

The *nacnac* ligand adopts two coordination modes with the Zr metal. κ^2-Coordination is observed in octahedral complexes containing one or two *nacnac* ligands. In the presence of another η^5-coordinated ligand, such as Cp or Ind, the *nacnac* ligand is found to be $\eta^{4/5}$-coordinated to the Zr center. The obtained complexes (*nacnac*)$_2$ZrX$_2$ showed a fluxional behavior in solution via a Bailar Twist and the activation parameters of this isomerisation were obtained. The cis octahedral dichloride complex (*nacnac*^{Bn})$_2$ZrCl$_2$, **2c,** showed no reactivity in carbozirconation and its alkylation was not possible by exchange of chlorides with alkyls. The dimethyl analogue (*nacnac*^{Bn})$_2$ZrMe$_2$, **2d**, could be prepared by alkylation of $ZrCl_4$ prior to ligand complexation, but proved as well to be unreactive in carbozirconation.

Key words: Zirconium, *nacnac* complexes, β-diketiminate complexes, hydrozirconation, carbozirconation, Bailar-twist.

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Abbreviations

Acac	acetylacetonate
i-Bu	isobutyl
n-Bu	*n*-butyl
t-Bu	*tert*-butyl
bp	boiling point
bs	broad (singlet)
bm	broad (multiplet)
Bn	benzyl
Cp	cyclopentadienyl (η^5-C_5H_5)
Cp*	pentamethylcyclopentadienyl (η^5-C_5Me_5)
Cy	cyclohexyl
Nacnac	β-diketiminate
d	doublet
dd	doublet of doublets
equiv.	equivalents
Et	ethyl
GC	Gas chromatography
MS	mass spectrometry
Me	methyl
MW	molecular weight

m	multiplet (spectral)
NMR	nuclear magnetic resonance
ppm	part per milliom
Ph	phenyl
i-Pr	iso-propyl
n-Pr	*n*-propyl
q	quadret (NMR)
quin	quintet (NMR)
R	alkyl group
s	singlet
tol	tolyl
TsOH	*para*-toluene sulfonic acid
t	triplet

CHAPTER 1

Introduction

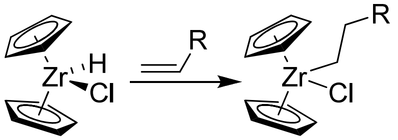
Introduction

Early transition metal alkyl complexes have been involved in many organic synthetic applications, such as Ziegler-Natta polymerization, olefin oligomerization, and carbometallation, where the complex was employed either as a reagent or a catalyst.[1] One important common aspect in all of these reactions is that their application depends eventually on the stability and reactivity of the active early transition organometallic species which is responsible for the utility of each particular process. The fundamental understanding of the stability and reactivity of early transition metal complexes is very important for the improvement of their applications, as well as for the development of new processes.

1.1 Historical overview

Major advances in the field of early transition metal organometallic chemistry followed the discovery of $(C_5H_5)_2Fe$ (ferrocene) by Pauson and Miller in 1951.[2] In 1953, Wilkinson and coworkers reported the synthesis of Cp_2ZrBr_2, Cp_2TiBr_2, and Cp_2VCl_2.[3] Parallel to the discovery of metallocenes, Karl Ziegler and Giulio Natta discovered in 1955 heterogeneous processes using titanium chlorides and aluminum alkyls for the polymerization of olefins.[1a,1b,4]

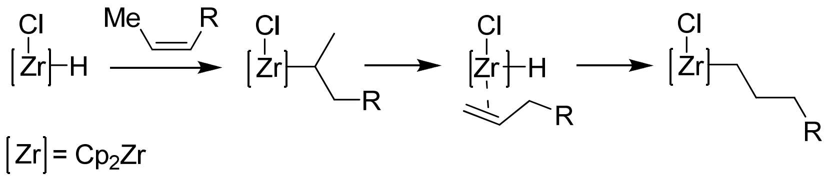
However, it was not until the development of Cp_2ZrHCl (Schwartz' reagent) in 1976 for the hydrozirconation of alkenes and alkynes[5,6] that alkyl zirconium(IV) complexes of the type $(\eta^5\text{-}C_5H_5)_2Zr(Cl)R$ have been shown to be useful intermediates in rational organic syntheses.[7,8,9] Alkylzirconocene derivatives have been involved in the selective cross-coupling via transition metal catalysis with Ni^0 or Pd^0.[10] In the late 1970s, Negishi's contributions expanded the use of organozirconium towards carbozirconation, which (despite the limited success with alkenes) was regarded a valuable synthetic tool.[11] Kaminsky showed that organozirconocene compounds exhibiting no or low polymerization activity became very active catalysts by addition of trialkylaluminum previously treated with water (MAO). [12,13,14]



Scheme 1.1 Hydrozirconation of terminal alkenes

1.2 Hydrozirconation

This reaction transforms alkenes and alkynes into alkyl or alkenyl derivatives of zirconocene. It involves the insertion of an alkene or alkyne into the Zr-H bond of Cp_2ZrHCl (Schwartz' reagent). The latter can be prepared by the reaction of Cp_2ZrCl_2 with various aluminum hydrides. Hydrozirconation involves a *syn* addition placing the Zr generally at the less substituted carbon atom of the double bond. With internal olefins, isomerization by a chain-walking mechanism places the zirconium on a terminal carbon atom.[6] This is believed to occur due to the low energy barrier for β-H eliminations in the zirconocene chloro alkyl complexes.[15]

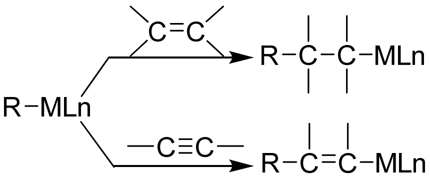


Scheme 1.2 Chain walking after hydrozirconation of an internal alkene

In fact, this *cis*-addition remains one of the most important routes to functionalize non-activated alkenes or alkynes.[16] Hydrozirconation reactions have found many applications, such as ring opening and ring forming reactions.[17]

1.3 Carbozirconation

Also referred to Negishi's carbozirconation,[18] carbozirconation allows the addition of a Zr-C bond to a double or triple bond.



Scheme 1.3 Carbozirconation of alkenes and alkynes

Carbozirconation attracted much attention, since this would introduce a new alkyl group as well as a functional group on a non-activated olefin. Even if Zr itself is relatively inexpensive, zirconocene derivatives may not generally be considered inexpensive chemicals. It is therefore desirable to use them as catalysts. Zr-catalyzed carboalumination of alkynes was discovered and reported in 1978 by Negishi.[19,20] For a facile *syn* carbometallation to take place, the presence or ready availability of a low-lying metal empty orbital is essential.

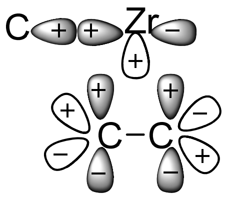
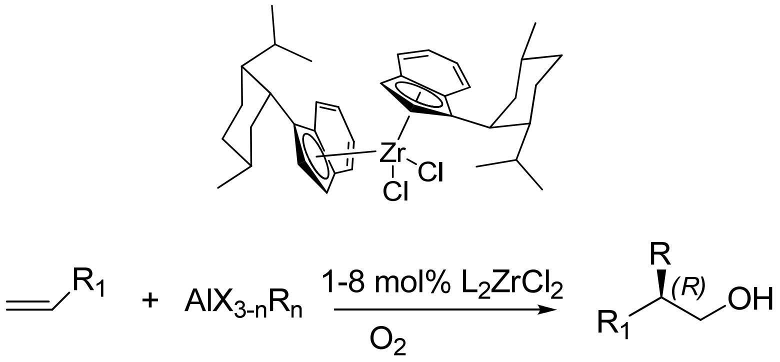


Figure 1.1. Frontier orbital interactions in carbometallation

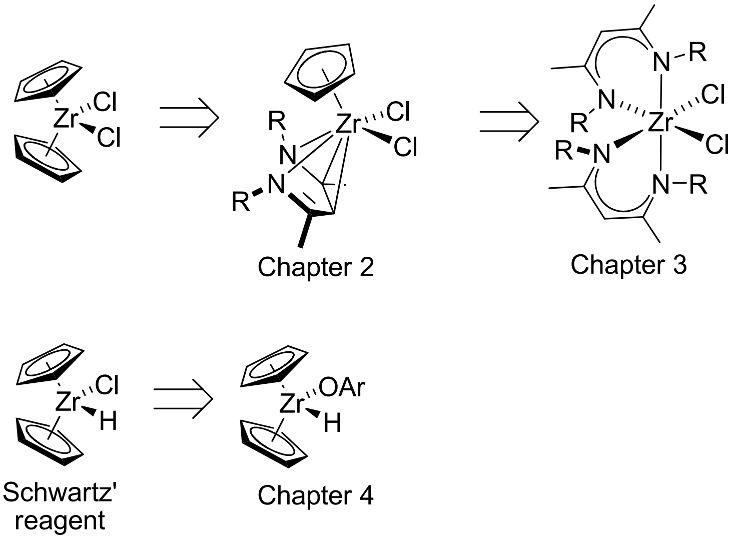
The presence of an aluminum species is crucial to weaken the Zr-Cl bond. Zr-catalyzed carboalumination have been expanded to alkenes, but no reactivity has been observed before Negishi employed Erker's bulky neomenthylindenyl-zirconium dichloride complex, which was believed to suppress the β-H elimination reaction responsible for the very low yields in carboaluminations with unsubstituted zirconocenes. [21,22]



Scheme 1.4 Carbozirconation of alkenes using Erker's catalyst.

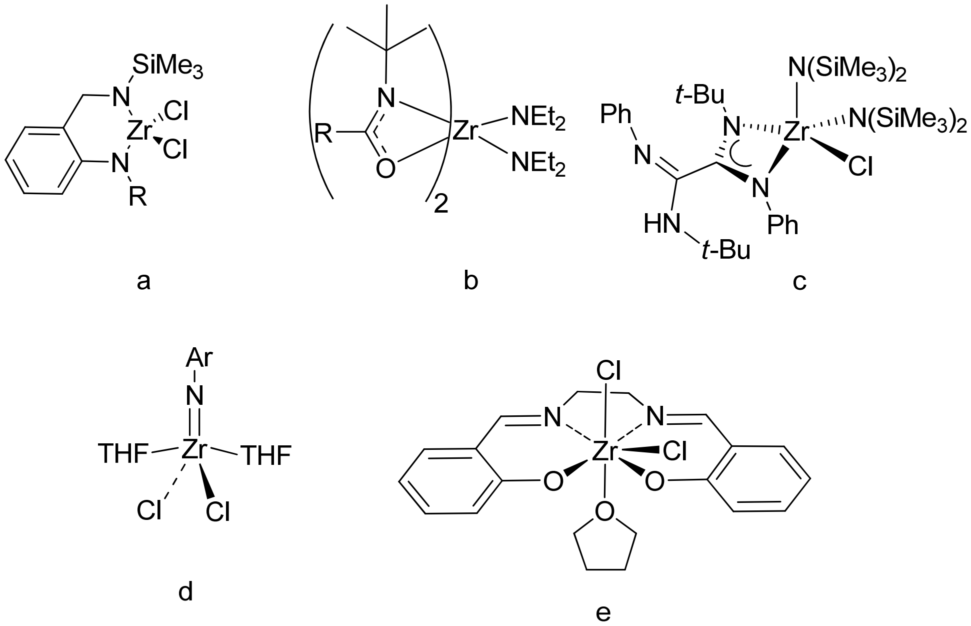
1.4 Aim of the project

It is clear from the above examples that investigations into metallocenes of early transition metals have greatly affected the development of the organometallic chemistry of zirconium. Metallocenes became popular due to their ability to stabilize early transition metals and to their ease of synthesis. The steric and electronic environment of the two Cp ligands in a bent metallocene imparts a special stability on the metal complex and dictates the reactivity of the metal. It is therefore possible to envision that the same metal would behave differently under the influence of a different ligand set. There are two different possibilities to modify the typical Cp_2ZrCl_2 framework: (i) Spectator ligands other than Cp or (ii) ligands other than chloride, if the latter stays attached during the reaction. (**Scheme 1.6**)



Scheme 1.6

Ligands "beyond Cp" might have advantages. Ligands containing Cp has been replaced by amido,[23a] amidato,[23b]amidinato,[23c] imido,[23d] Schiff base ligands[23e] and others. (**Scheme 1.7)**



Scheme 1.7

The general goal of this research project is to synthesize and characterize novel Zr complexes analogous to zirconocene, i. e. with two spectator ligands and two chlorine ligands, which can be replaced by substrate(s) for subsequent reactions. Of particular intrest are ligand frameworks that are of low cost compared to highly substituted Cp/indenyl ligands such as Cp* or neomenthylindenyl[21,22] and have the ability to suppress the β-H elimination reaction during carbozirconation. β-Diketiminates or (*nacnac*) ligands have gained an increasing importance in the last two decades, due to their suitability as spectator ligands, versatility, stability and their ease of synthesis. Zr complexes with β-diketiminate ligands have previously shown to be active catalysts in olefin's polymerization[24,25] and to adopt different geometries dictated, in some cases, by the ligands coordination modes.[25-30] These latter vary between κ^2-coordination and $\eta^{4/5}$-coordination. If only when one cyclopentadienyl is replaced by *nacnac,* Zr retains its pseudotetrahedral geometry. In these types of complexes, the diketiminate displays an out-of-plane "η^5-like"-coordination mode.[31] In chapter 2 we will investigate this coordination mode in detail using *nacnac*$^{\mathrm{Xyl}}$ and test the prepared complexes in potential applications.

When both cyclopentadienyl ligands are replaced by diketiminate ligands, an octahedral geometry is obtained.[25,28] Previous reports show that the bis-*nacnac* species are obtained only when the N-aryl groups are not substituted in the *ortho*-position, such as phenyl or p-tolyl.[27,28] In chapter 3, we will attempt to avoid this obstacle by using N-alkyl substituted diketiminate ligands. In addition, the use of the N-alkyl substituents will allow us to introduce chirality and to explore different sterical and electronic environments. Although Zr-diketiminate complexes could in principle be applied in hydrozirconation or olefin polymerization, only their reactivity in carbozirconation reactions will be investigated in this work.

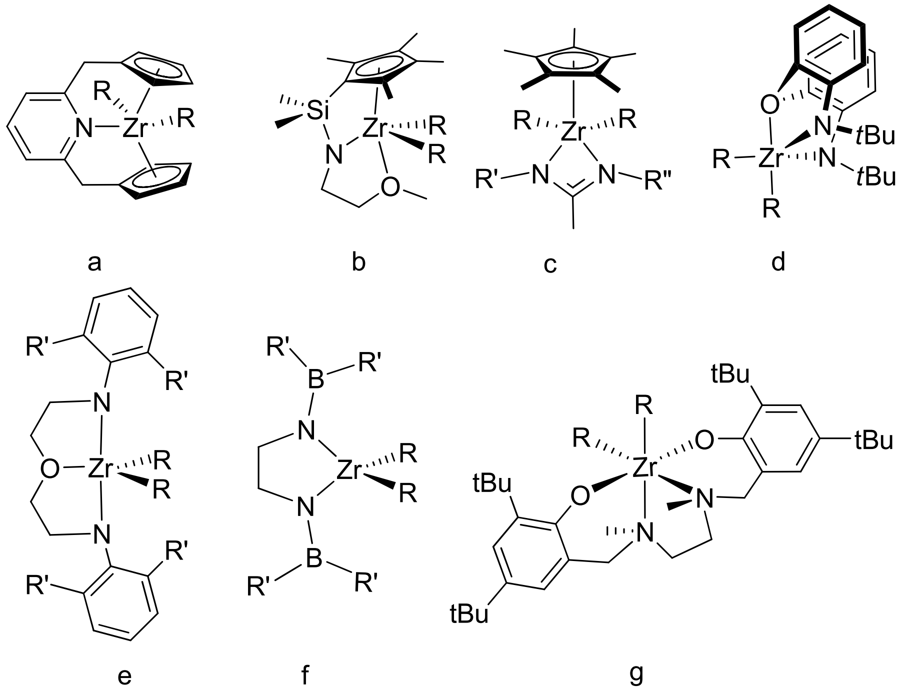
Hydrozirconation with Schwartz' reagent is a typical example where chloride is retained as a ligand during the reaction.[15,32] Hydrozirconation suffers from regioselectivity limitations, especially when the alkenes contain an aromatic or a polar substituent along their chain.[33,34] Previous modifications to Schwartz' reagent were moderately successful to improve solubility and reactivity, but none of them proved to suppress β-H elimination.[35,,36] In chapter four, I present my contribution towards hydrozirconations using aryloxide complexes, $Cp_2ZrH(OAr)$, as an alternative to Schwartz' reagent.

CHAPTER 2

Nacnac zirconium complexes containing ”η^5-like” coordinated ligands

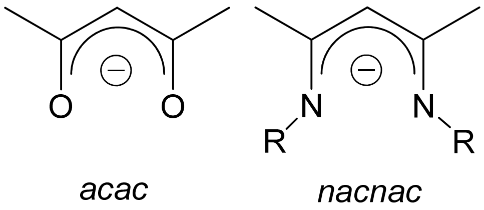
2.1 Introduction

Although zirconocene or monocyclopentadienyl zirconium derivatives have been employed successfully in many synthetic applications,[37,38] a drawback of zircononcene alkyl complexes is their lability towards β-H eliminations. On the other hand, several zirconium alkyl complexes that display stability against β-H elimination have been reported, of which several have a pseudotetrahedral, "half sandwich like" coordination geometry around Zr (Scheme 2.1, b+c). In all cases, ligands coordinated via nitrogen atoms are present.[39] Although attractive targets for carbozirconation reactions, none of these complexes has been investigated for these reactions.



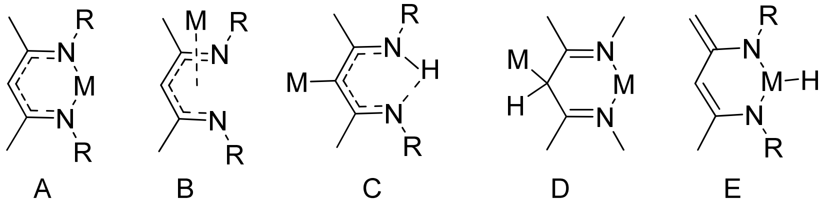
Scheme 2.1. Zirconium dialkyls complexes stabilized by nitrogen coordination against β-H elimination.

A class of nitrogen containing ligands which have not been investigated in this regard are β-diketiminates. While β-diketonate ligands are known as famous chelating systems, the β-diketiminate (*nacnac)* analogs, where oxygen atoms are replaced by two nitrogen atoms, have received increasing attention only in the last decade. Their chemistry is known since 1968 with the first reported synthesis of this ligand[40a] and its metal complexes.[41] Since then, *nacnac* ligands with aromatic N-substituents have received much attention, most likely due to the phenomenal work of Brookhart, which showed the suitability of related α-diketimine ligands for polymerization catalysis.[42,43]



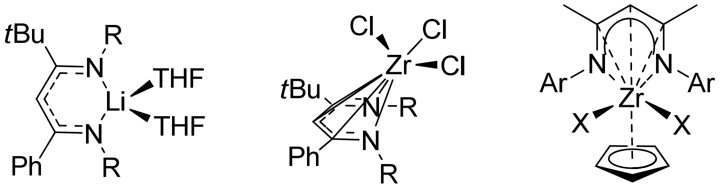
Scheme 2.2 *acac* and *nacnac* ligands.

This system is of interest considering their diversity and their versatility, through the variation of the R groups on nitrogen, which may be hydrogen, alkyl or aryl. β-Diketiminates have been recognized for their role as *spectator ligands*,[44] like cyclopentadienyls, by virtue of their strong metal-ligand bonds and their exceptional and tunable steric demands. Indeed, β-diketiminates are the most used ligands in coordination chemistry for the stabilization of low coordination numbers and low oxidation states of main group or transition elements[40] and are now known to form complexes with a large number of transition metals and with a wide variety of N-substituents on the ligand.[44]



Scheme 2.3 Different modes of coordination for the *nacnac* ligand.[44]

β–Diketiminates display a variety of coordination modes (Scheme 2.3) in their metal complexes.[34] Coordination mode A is best desribed as a κ^2-coordination via nitrogen atoms where the metal is placed in the NCCCN plane. This mode is widely observed in literature. An example of coordination mode A is Li(*nacnac*)(THF)$_2$ reported by Lappert.[27] Here the ligand can be considered a 4 e$^-$ donor, although additional p-d donation cannot be excluded when suitable empty d-orbitals are present. Coordination mode B is less common in literature and best described as an ”η^5-like”-coordination. Here the metal is coordinated to the face of the almost planar NCCCN moiety. Examples are (*nacnac*)ZrCl$_3$, reported by Lappert,[27] and (*nacnac*)Zr(Cp)Cl$_2$, reported by Collins.[28] In these complexes the *nacnac* ligand should be considered a 6 e$^-$ donor.



Scheme 2.4. κ^2- and "η^5-like"-coordination of the *nacnac* ligand.[30,31]

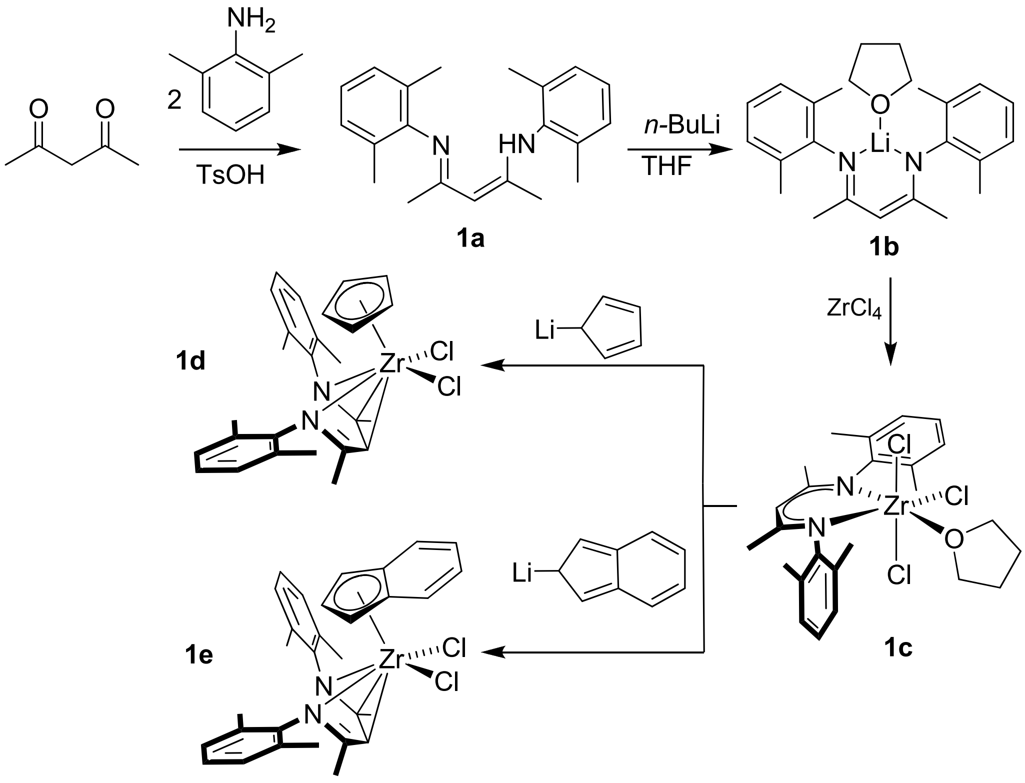
Zirconium complexes with mono and bis *nacnac* ligands have been reported by Kakaliou et al.[26] Lappert and co-workers also described the preparation of some examples of mono substituted complexes (X=Cl): X-ray studies revealed that the coordination mode of the *nacnac* ligand can be described as an "η^5-like"-coordination to the metal, thus highlighting the similarity between these ligands and Cp anions.[27] Collins reported the use of mono- and disubstituted *nacnac* complexes of group 4 in olefin polymerization among which monocyclopentadienyl *nacnac* complexes which showed an "η^5-like"-coordination of the *nacnac* to the metal center.[28]

Given the electronic similarity between *nacnac* ligands and cyclopentadienyl anions, and the steric and electronic versatility of these ligands, we present in this chapter the synthesis and the characterization of a *nacnac* ligand with 2,6-dimethylphenyl substituents on nitrogen, its complexation with Zr in "half-sandwich" like complexes and some preliminary investigations with regard to their application in catalyzed or stoichiometric carbozirconation.

Previous work on this subject has been performed by two summer trainees in our group. During their work, small amounts of crystals, suitable for X-ray diffraction studies, were obtained, but in insufficient quantity for further analyses. While synthetic and spectroscopic results in this chapter are new, the crystal structure data has been published previously and will be commented upon only briefly.

2.2 Results and discussion

2.2.1 Synthesis of 2,6-dimethyl-Phenyl)amino-4-(2,6-dimethyl-phenyl)imino-pent-2-ene, ***nacnac***$^{\mathbf{xyl}}$**H, 1a.**[45]



Scheme 2.5. Synthesis of mononacnac zirconium complexes

Co-condensation of 2 equiv. 2,6-dimethylaniline and acetylacetone was achieved in the presence of 1 equiv. of *p*-toluene sulfonic acid under elimination of water with a Dean-Stark apparatus for 24 h. **1a** was obtained in 51% yield.

2.2.2 Synthesis of κ^2-coordinated complexes

Deprotonation of **1a** by addition of *n*-BuLi at -78 ˚C in a THF gave (*nacnac*^{xyl})Li(THF), **1b**,[41] in high yields of ca. 94%. ^{1}H and ^{13}C NMR spectra showed the presence of THF to complete the sphere of coordination of the Li atom.

Reaction of **1b** with 1 equiv. of $ZrCl_4$ and excess of THF afforded the yellow complex (*nacnac*^{xyl})$ZrCl_3$(THF), **1c**, in high yields (97%) after crystallization from toluene/hexane. NMR data of complex **1c** is consistent with the proposed 1:1 adduct. Elemental analysis of the crystalline material, however, showed low carbon values (Δ1%).

A structural analysis was important for the characterization of this complex, because the anionic *nacnac* ligand can act as either four- or six-electron donor depending on the interaction between the metal and the two nitrogens and central carbon atom. A similar complex using the bulky N,N-(2,6-diisopropylaniline)*nacnac* ligand (*nacnac*$^{\mathrm{biPr}}$) was reported by Jin & Novak.[25] The X-ray structure of (*nacnac*$^{\mathrm{biPr}}$)$ZrCl_3$(THF) shows a κ^2-coordination of the *nacnac* ligand. Coordination of a THF molecule completes the distorted octahedral coordination geometry around Zr. In the absence of THF, however, the same ligand was reported to show an ”η^5-like”-coordination in a distorted tetrahedral (*nacnac*$^{\mathrm{biPr}}$)$ZrCl_3$ complex.[46] (Jin and Novak also reported synthesis of **1c**, but neither synthesis nor characterisation of this complex was provided.) [25]

In our case, complex **1c** crystallizes with one THF molecule coordinated to the zirconium center in an octahedral coordination geometry.[47] The ORTEP diagram of complex **1c** is shown in **Figure 2.1.**

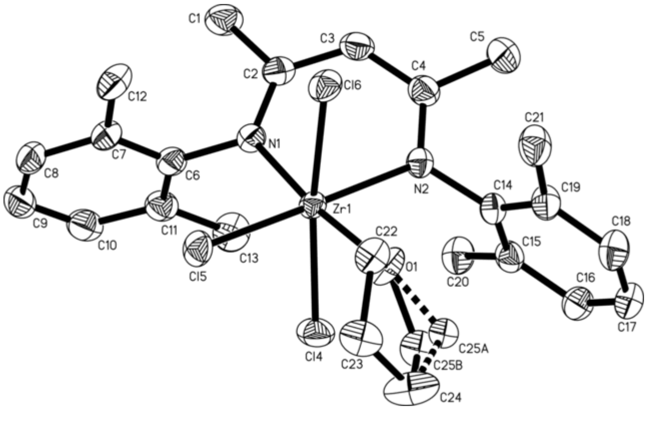


Figure 2.1. Thermal ellipsoid drawing of the title compound. Thermal ellipsoids are shown at 50% probability levels. Hydrogen atoms are omitted for clarity. One carbon atom of the THF molecule was disordered and refined isotropically. Only one of the two independent molecules is shown. For bond lengths and angles see **Table 2.1**.

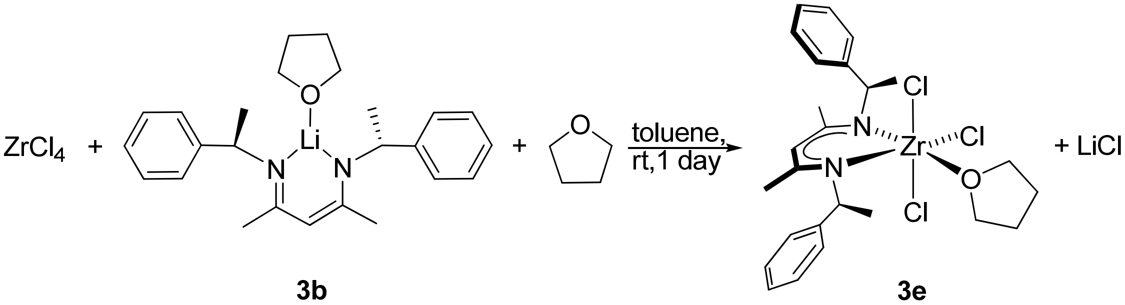
As observed in related complexes[25,28] N1-C4-C3-C2-N1 are coplanar and the relatively equal bond distances among them suggest a strong delocalization of the double bond of this system. The Zr-N2 distance in the title compound is slightly longer than Zr-N1 (2.218(2) and 2.176(2) Å, respectively), in agreement with a stronger *trans* effect of chlorine compared to oxygen. While the crystal structure is close to C_s symmetry, NMR spectra show an apparent C_{2v} symmetry of the complex, indicating that either THF dissociation and reassociation is fast or, more probably, that the complex isomerizes easily (Bailar-Twist).[48]

Table 2.1. Selected bond distances [Å] and bond angles [deg] for **1c**, **1d** and **1e**

	1c[a]	**1d**	**1e**
Zr-N1	2.1759(18) Å	2.1879(19) Å	2.1836(18)
Zr-N2	2.2182(17) Å	2.2944(19) Å	2.2900(17) Å
Zr-C2		2.616(2) Å	2.617(2) Å
Zr-C3		2.620(2) Å	2.825(2) Å
Zr-Cl	2.4316 (6) - 2.4551(5) Å	2.5022 (5) -2.5043 (5) Å	2.4758 (5) - 2.5081(5) Å
N1-C2	1.345(3) Å	1.354(3) Å	1.352(3) Å
N2-C4	1.338(3) Å	1.306(3) Å	1.303(3) Å
C2-C3	1.387(3) Å	1.389(3) Å	1.394(3) Å
C3-C4	1.409(3) Å	1.462(3) Å	1.454(3) Å
N1-Zr1-N2	83.11(7)°	79.32(7)°	80.58(6)°
Cl-Zr-Cl	90.06(2)° - 170.91(2)°	84.33(2)°	84.20(2)°
N1-Zr-X[b]	91.09(5)°- 97.72(5)°	89.10(5)°	88.12(5)°
N2-Zr-X[c]	85.93(5)°- 92.34(5)°	85.52(5)°	85.63(4)°

[a] Only values of one of the two molecules are listed, for the second one, the values are identical within the margin error . [b] X= Cl4 and Cl6 (**1c**), Cl1 (**1d** and **1e**). [c] X= Cl4 and Cl6 (**1c**), Cl2 (**1d** and **1e**).

Similarly, reaction of **3b** (see scheme 2.6 & chapter 3) with 1 equiv. of $ZrCl_4$ and excess of THF afforded the orange complex (*nacnac*^{R,R})$ZrCl_3$(THF), **3e**, in 35% yield. NMR data and elemental analysis of complex **3e** is consistent with the presence of a coordinated THF. Although, no crystals of this compound could have been obtained, its structure is most likely comparable to that of **1c**.



Scheme 2.6 Synthesis of (*nacnac*^{R,R}) $ZrCl_3$(THF), **3e.**

2.2.3 Synthesis of η^x-coordinated complexes

Reactions of **3e** with 1 equiv. of CpLi showed only decomposition products in their NMR spectra. Reaction of **1c**, on the other hand, with 1 equiv of CpLi at room temperature afforded after 3 days **1d** in 35% yield. The main side product obtained is the protonated ligand, *nacnac*^{xyl}H, separated by extraction using a hexane solution. **1c** is not recovered at the end of the reaction, which might indicate the presence of moisture in the reactional medium. Elemental analysis of crystals of this compound are consistent with the proposed 1:1 adducts. X-ray data of this complex have been reported previously by our group.[29]

Smith reported the synthesis of mixed (*nacnac*)CpCr complexes by reaction of Cp_2Cr with the neutral form of the ligand *nacnac*H.[49] In our hands, addition of *nacnac*^{xyl}H to Cp_2ZrCl_2 showed no reaction even at high temperature and with prolongated reaction time. As well, a mixture of $ZrCl_4$, 1 equiv of *nacnac*^{xyl}H and excess of CpLi did not yield the desired product. It seems that deprotonation of *nacnac*^{xyl}H cannot be acchieved by an anionic cyclopentadienyl. This can be attributed either to the rigidity of the zirconocene complex or to the low acidity of *nacnac*^{xyl}H itself.

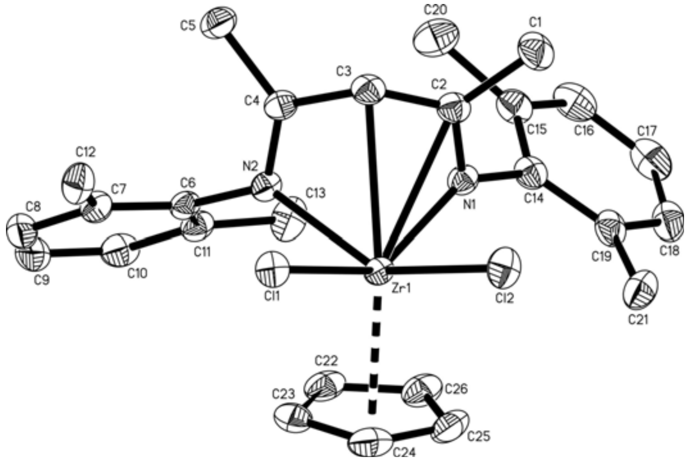


Figure 2.2. *ORTEP* view of compound **1d**. Displacement ellipsoids are shown at the 50% probability level. For bond lengths and angles see **Table 2.1**.

Crystals of this compound were obtained by layering of a toluene solution with hexane in sufficient quality for X-ray analysis.[29] The coordination of the *nacnac* ligand in **1d** differs from the earlier described η^2- or η^5-coordination. The coordination mode of the *nacnac* ligand is an intermediate between κ^2- and ”η^5-like”-coordination, with both N atoms and two C atoms clearly coordinated to the Zr center. A comparable coordination was observed for the *nacnac* ligand in the five-coordinated complexes reported by Basuli et al., where the coordination was described simply as "sandwich-like".[46] However, the *nacnac* coordination is best described as an η^1-imine and an η^3-enaminato coordination of the ligand. Of note is the orientation of the N-aryl substituent. The plane of each of the aniline groups is perpendicular to the plane formed by N1C2C3C4N2 and the two methyl substituents on the phenyl ring are placed above and below the ligand plane, respectively. This will make the two methyl substitutents different because one of them is oriented toward, the other one away from the $ZrCl_2$ fragment. In fact, both methyl groups appear at different displacements in the ^1H NMR (2.66 and 1.69 ppm) and ^{13}C NMR spectra (22.8 and 21.3 ppm), which confirms the difference in the chemical surrounding of these two methyls and that rotation around the N-Ar bond is slow on the NMR time scale. The non-symmetrical coordination of the *nacnac* ligand is not evident in its NMR spetra, which shows an apparent C_s symmetry of the complex. Not surprisingly, haptrotropic rearrangements in the *nacnac* ligand are thus fast at room temperature.

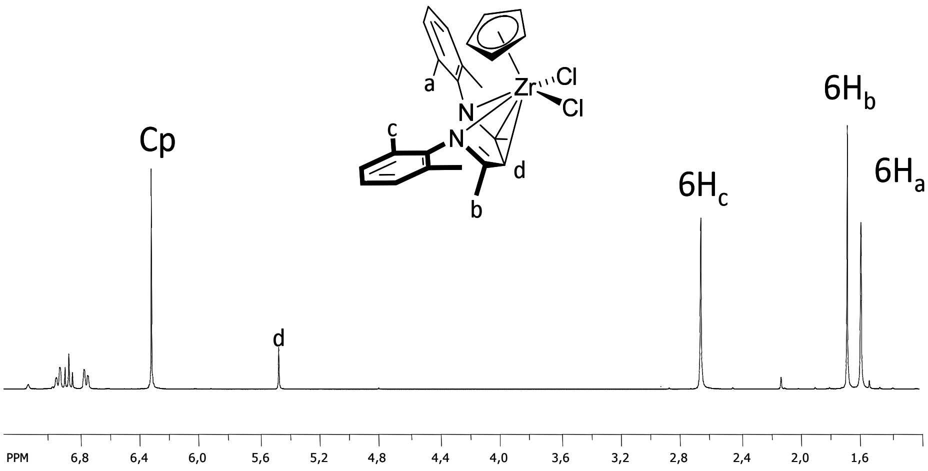


Figure 2.3. ^1H NMR spectra of **1d** in C_6D_6, the rest of the spectrum was omitted for the clarity.

Following the same metathesis procedure as for **1d**, several essays to isolate the desired indenyl complex (*nacnac*^{xyl})Zr(Ind)Cl_2, **1e**, were unsuccessful. Reaction of **1c** with (*nacnac*^{xyl})Li(THF) in toluene, THF and CH_2Cl_2, at room temperature or under refluxing conditions were tried and only gave a mixture of products. ^1H NMR spectra of the reaction mixtures confirmed the presence of **1e** together with starting materials even after prolonged time of reaction at room temperature or at reflux. In the best attempt, 10% of the desired product accompanied by ca. 45% of starting materials and ca. 45% of protonated ligand were obtained. Neither elemental analysis nor ^{13}C NMR experiments could be performed due to lack of purity in the title compound. What has been previously described as “A typical procedure of preparation of zirconocene” was also tried:[50] Reaction of zirconium tetrachloride with 2 equiv. of *n*-BuLi at –78 °C for 1 h followed by subsequent addition of 1 equiv. indene and 1 equiv. *nacnac*^{xyl}H did not yield the desired compound.

An X-ray structure of this compound obtained from an isolated crystal has been previously published by our group.[30] A complex similar to **1e** has been reported by Rahim et al. using the sterically less demanding *nacnac*^{Ph} ligand .[28]

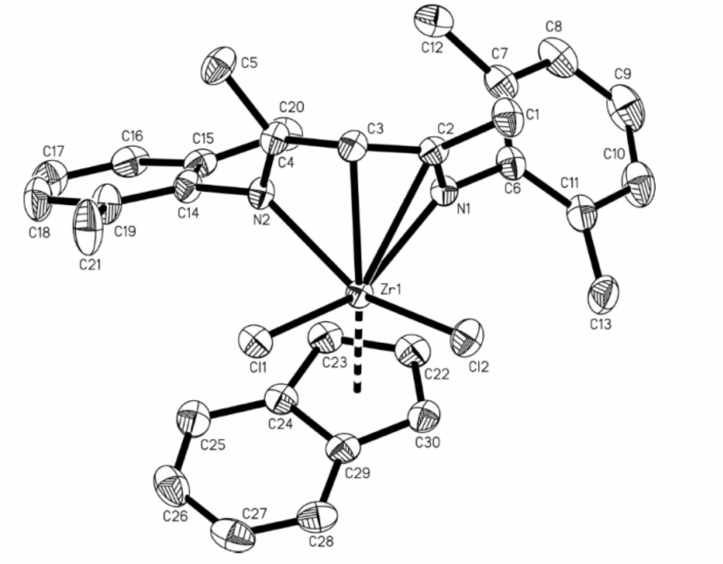
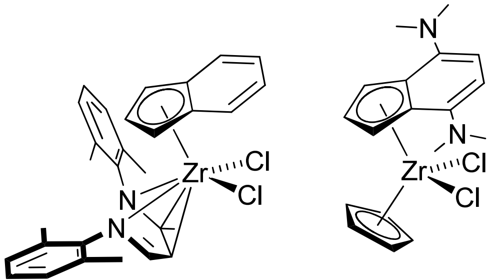


Figure 2.4. Molecular structure of complex **1e** with 50% probability thermal ellipsoids depicted and most H-atoms omitted for clarity. For bond lengths and angles see **Table 2.1**.

Not surprisingly, the compound is nearly isostructural to **1d**. Again, ^{1}H NMR spectroscopy indicates an apparent C_s symmetry and confirms a slow N-Ar rotation. In the crystal structure, the indenyl ligand in **1e** displays only a very slight deviation from ideal η^5-coordination (ΔZr-C = 0.13 Å). The Zr-Ind bond lengths range from (2.475(2)-2.602(2) Å) and are nearly identical to those in Cp(Ind(NMe$_2$)$_2$)ZrCl$_2$[*] (2.477(2)-2.601(2) Å).[51] Both structures adopt pseudotetrahedral geometries. Although, the coordination of the *nacnac*$^{\mathrm{Xyl}}$ ligand can again be described as an "η^5-like"-coordination, Zr-C$_{\mathrm{xyl}}$ and Zr-N distances in **1e** (2.1836(2)-2.825(2) Å) cannot be compared to Zr-C$_{\mathrm{Cp}}$ in Cp(Ind(N-Me$_2$)$_2$)ZrCl$_2$ (2.483(2)-2.537(2) Å).



1e

Scheme 2.7

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[*] Cp(Ind(NMe$_2$)$_2$)ZrCl$_2$ was chosen due to its the similarity to Cp(Ind)ZrCl$_2$, the crystal structure of which is not known.

2.2.4 Reactivity tests

A limited number of reactivity tests have been undertaken with complex **1d**. Reaction of **1d** in catalytic amounts with styrene in a ratio of 1:10 in presence of $AlMe_3$ gave no indications of any insertion taking place. The reaction was also tried in stoichiometric ratios and, again, no reactivity was observed. In order to test our complex's stability against β-H elimination we reacted **1d** with *t*-BuLi in a 1:1 ratio in THF for 1 h at -78˚C and 1 h at room temperature. ^1H NMR showed the presence of protonated ligand and several unidentified products with the absence of the starting material. The same was also observed when 1 equiv. of *n*-BuLi was added to **1c**.

2.3 Conclusion

In summary, haptomeric zirconium complexes **1c** and **1d** have been synthesized and characterized, which show different modes of coordination of the *nacnac* ligand. Our attempts to isolate the (*nacnac*^{xyl})Zr(Ind)Cl_2, **1e**, have failed and the complex was only characterized by ^1H NMR spectroscopy. The reactivity of **1d** has been tested in catalytic and stoicheometric carbozirconation reaction with negative results. The absence of starting materials might indicate that stability of these complexes is not sufficient under carbozirconation conditions.

CHAPTER 3

Synthesis and characterization of new bis-*nacnac* zirconium complexes

3.1 Introduction

Still following our long term goal towards new reagents for the formation of C-C single bonds via carbozirconation reactions, we continued our investigations of *nacnac* zirconium complexes. Taking advantage of its variety of coordination modes, this chapter focusses on (*nacnac*)$_2$ZrX$_2$ complexes, which in general display an octahedral coordination geometry in contrast to the pseudo-tetrahedral geometry observed in the previous chapter. Several features make (*nacnac*)$_2$ZrX$_2$ complexes attractive targets for catalytic applications:

- An octahedral geometry would place the N-substituents of a *cis*-(*nacnac*)$_2$ZrX$_2$ complex in close contact to the reactive coordination sites and would form a classical C$_2$-symmetric catalytic pocket (see Figure 3.0).
- Steric interactions between the N-substituents might disfavour the formation of unreactive *trans*-(*nacnac*)$_2$ZrX$_2$ isomers, which are observed, e. g., for bis(acetylacetonate) complexes.
- Nitrogen coordination might disfavour β-H elimination reactions by π-donation from nitrogen to the Zirconium.
- In addition, steric hindrance by the N-substituents might also suppress the β-H elimination reaction, as observed in carbozirconation reactions.[18]

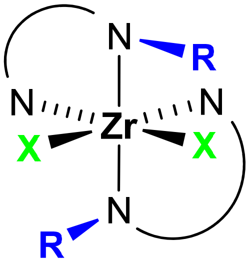


Figure 3.0 Idealized geometry of a *cis*-(*nacnac*)$_2$ZrX$_2$ complex

Our attempts to coordinate a second *nacnac*^{xyl} ligand to complex **1c** to prepare bis(*nacnac*^{xyl})$ZrCl_2$ failed and only the mono-*nacnac* complex **1c** was obtained in reactions with 2 equiv of (*nacnac*^{xyl})Li(THF). Similar reactivity was reported for the *nacnac*^{biPr} ligand containing diisopropylphenyl substituents on nitrogen, which failed to coordinate a second ligand.[46] Rahim et al. reported the synthesis of a bis(*nacnac*) zirconium dichloride complex using a less sterically demanding ligand bearing only Ph as a N,N'-substituents.[28] Along those lines, Kakaliou et al.[26] also reported the synthesis of bis((N,N'-tolyl)*nacnac*) zirconium dichloride. While none of these bis(*nacnac*)$ZrCl_2$ was investigated for carbozirconation reactions, they proved to be moderately active as catalysts in ethylene polymerization.[52]

A concurrent trend observed so far, is that *nacnac* ligands with ortho-substitued phenyl rings on N, which proved so successful in other applications, do not coordinate more than one ligand to Zr. By switching from aromatic to aliphatic N,N'-substituents we intended to modify the steric environment of the ligand to enable the coordination of two ligands to Zr. In addition, alkyl substituents are suitable for inducing chirality on the *nacnac* ligand.

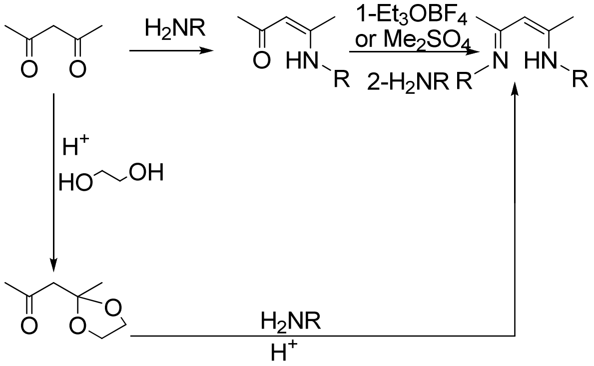
3.2 Results and discussion

3.2.1 Ligand synthesis

The chemistry of *nacnac* ligands has been known for 40 years.[40,41,53] Especially in recent years, N-aryl substituted *nacnac* ligands have received most of the attention, and, although introduced at the same time,[41] only few reports regarding the synthesis and application of N-alkyl *nacnac* ligands have appeared in the literature.

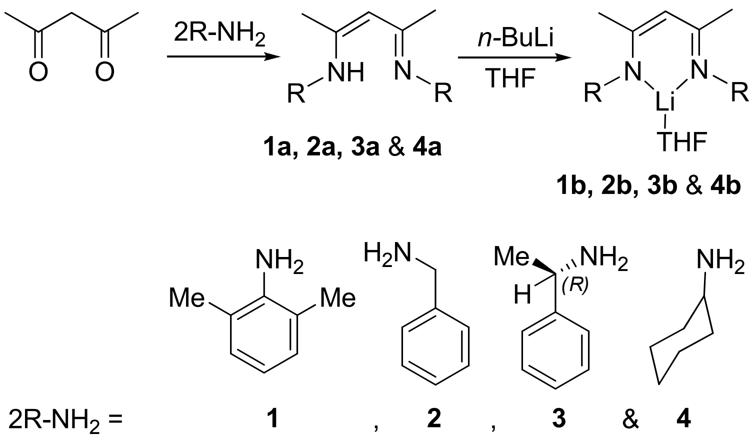
The most common synthetic route to β-diketimine (*nacnac*) ligands is the double condensation of a β-diketone (most often acetylacetone) with two equivalents of amine.

This reaction was first reported in 1968 using Meerwein's salt $[Et_3O][BF_4]$ as an activating agent (Scheme 3.0).[41] The first condensation of the β-diketone with an amine occurs without the presence of an activating agent, while the second condensation does not take place in the absence of an activating agent.[53] The synthetic protocol depends on the propensity of triethyloxonium fluoroborate for O-alkylation of the enamino ketone, which renders the carbon of the original carbonyl function readily susceptible to nucleophilic attack in the resulting vinylogous imino ether. A disadvantage of this method is that the fluoroborate generated must be protected from moisture[41] and that Meerwein's salt is carcinogenic and hardly economic.[54] Bradley et al. recently reported the synthesis of N-alkyl *nacnac* ligands in a two-step reaction in good yields of 75-85% using dimethylsulfate instead of Meerwein's salt to activate oxygen as a leaving group.[55] The use of dimethylsulfate reduced the costs of the reaction, but still requires moisture-free conditions. An alternative synthetic procedure is the conversion of the β-diketone into a ketoketal before condensation with the amine (Scheme 3.0).[40] However, yields of this reaction are low, the synthesis of the monoketal is cumbersome, and the reaction seems to depend strongly on reaction conditions.[56]



Scheme 3.0 Different routes of syntheses for *nacnac* ligands.

More recently, synthesis of *nacnac* ligands with N-aryl substituents have been reported in high yields by using either HCl/EtOH or one equiv. of *p*-toluene sulfonic acid.[57] Following a similar synthetic protocol as outlined for aryl-substituted *nacnac* ligands,[45] we obtained N,N'-di(benzyl)-*nacnac,* **2a,** N,N'-di(*R*-2-phenylethyl)-*nacnac*, **3a**, and N,N'-di(cyclohexyl)-*nacnac,* **4a**, by condensation of two equiv. of amine with acetylacetone in the presence of a stoichiometric equivalent of toluene sulfonic acid with azeotropical removal of water using a Dean-Stark apparatus. For ligands **2a** and **3a** the syntheses reported here are modifications of the original synthesis by Paul Oguadinma in our group.[58] The original protocol introduced all reactands at the same time. Addition of one equiv. of the akylamine and refluxing for 2 hours, followed by addition of the second equiv. of the alkylamine was, however, more effective and lead to improved yields. Yields could further be improved by reducing the amount of toluene solvent.



Scheme 3.1 Ligand synthesis and deprotonation to the lithium salt

Using the improved synthetic protocol, 2-(benzyl)amino-4-(benzyl)imino-pent-2-ene, *nacnac*$^{\mathrm{Bn}}$H, **2a**, was obtained in 90% yield with a reaction time of one day. Previous synthesis via a two-step procedure did not exceed 60% yield.[44] Reactions with secondary amines proceeded more slowly and 2-(2-phenylethyl)amino-4-(4-phenylethyl)imino-pent-

2-ene, was obtained in 67% yield for *nacnac*^{R,R}H, *RR*-**3a,** and 70% yield for *nacnac*^{S,S}H, *SS*-**3a,** after 5 days of reflux. Independently of us, Buch and Harder reported the synthesis of *SS*-**3a** in a two-step procedure via alkylation of the corresponding enaminoketone in 36% yield.[59] 2-(Cyclohexyl)amino-4-(cyclohexyl)imino-pent-2-ene, *nacnac*^{cy}H, **4a**, was obtained in 69% yields after 3 days at reflux using a Dean-Stark apparatus. Previous synthesis using $TiCl_4$ as activator was reported in 23% yield.[60] The ketimine ligand (*R*-2-phenylethyl)aminopent-2-en-4-one, *acnac*^{R}H, **5a**, was prepared by reaction of the enantiomerically pure phenylethylamine with 2,4-pentandione in a 1: 1 ratio in presence of catalytic amounts of TsOH. Elemental analysis of the compound gave unsatisfactory results and ^{1}H NMR spectra of the obtained oil showed 95% of **5a** in addition to 5% of free amines and the 2,4-pentadione. Crystallisation attempts were unsuccessful and no further attempts of purification were undertaken.

3.2.2 Deprotonation of *nacnac*H ligands

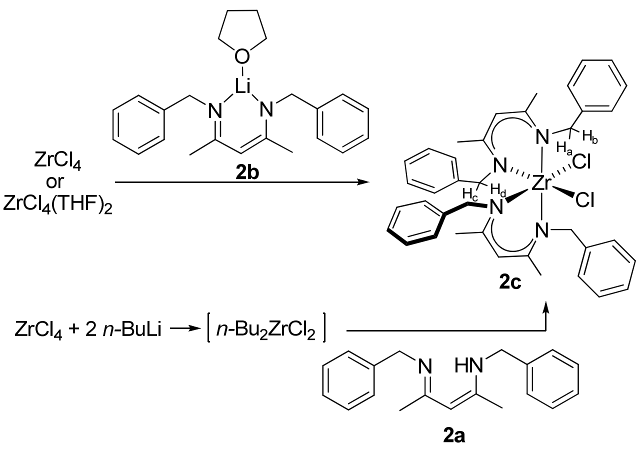
Although it is possible to use the β-diketimine, *nacnac*H, as a ligand source in the preparation of some complexes, the lithium salts of the *nacnac* ligand are the most widely used and the most important transfer agents for this ligand. While deprotonation of *nacnac* ligands can be done with or without a coordinated solvent such as Et_2O or THF,[28,61] we found that deprotonation in THF gives a product easier to characterize by NMR. Lithiation at room temperature surprisingly afforded higher yields and ring-opening of THF by *n*-BuLi[62] did not seem to impede the reaction. Treatment of *nacnac*H ligands **2-5a** with excess *n*-BuLi in THF gave the lithiated compounds **2**-**5b**, respectively, in yields >90 %. ^{1}H and ^{13}C NMR spectra confirmed the presence of one coordinated THF molecule in **2b**, **3b** and **4b**, while for **5b** of ^{1}H and ^{13}C NMR showed the presence of 0.5 equiv. of free, probably cocrystistallized THF. Elemental analysis of this compound confirmed the presence of **5b** and THF in a 2:1 ratio.

3.2.3 Synthesis of (*nacnac*)$_2$ZrCl$_2$ complexes

The optimal synthesis of L_2ZrCl_2 complexes differs significantly from one ligand to another. Different pathways were tried and some were optimized. These methods can be divided in two categories. (i) Transfer of the anionic *nacnac* moiety to the metal by a transmetallation reaction between the lithium salt of the ligand and a Zr salt, usually $ZrCl_4$. (ii) Protonation of Zr-bound amides or alkyls by the neutral ligands *nacnac*H under elimination of amines or alkanes.

3.2.3.1 Synthesis of (*nacnac*^{Bn})$_2$ZrCl$_2$, 2c

Our initial effort focussed on reactions of *nacnac*^{Bn} lithium salts with $ZrCl_4(THF)_2$, as this has been reported to give acceptable yields in the case of the aryl-substituted *nacnac*^{tol}.[26] Indeed, reaction of **2b** with $ZrCl_4(THF)_2$ in a ratio 2:1 in THF afforded the desired product **2c** in moderate yield (35%, Scheme 3.2). Alternatively, *n*-Bu$_2$ZrCl$_2$, generated *in situ* by reaction of zirconium tetrachloride with *n*-BuLi in 1:2 ratio in toluene or hexane for 12 h,[50] and subsequent addition of 2 equiv. of **2b** and refluxing for 2 days, afforded **2c** in high yields (65-75%, Scheme 3.2). The choice of solvents in the latter reaction is limited to non-coordinating solvents, since *n*-Bu$_2$ZrCl$_2$ easily undergoes β-H elimination reactions if the tetrahedral coordination is opened by coordination of a solvent molecule to an octahedral coordination.



Scheme 3.2 Synthesis of complex **2c**

Crystals of this compound were obtained by slow diffusion of hexane into a THF solution of **2c** at 25 °C. Complex **2c** possesses a crystallographically imposed C_2-axis of symmetry (Figure 3.2). The geometry of coordination around the Zr can be characterized as a distorted *cis*-octahedral geometry at the metal, in which the N-Zr-N angles involving the bis(*nacnac*)ligands and the *cis* dichloride group differ significantly from 90^o ($78.0(1)^o$-$97.2(1)^o$, Table 3.1). A somewhat longer Zr-N distance of the N *trans* to Cl might be attributed to the greater trans effect of chloride compared to N. Comparaison to other complexes (*vide infra*) shows, however, that Zr-N bonds *trans* to Cl are comparable to those *trans* to N. In contrast to expectations for a κ^2-coordinated *nacnac* ligand, the diketenimine ligand is no longer planar. The two benzyl substituents and the methyl substituents are bent to one side of the C2/C4/N1/N2 plane, forcing the ligand in a "boat-like" conformation (Figure 3.1), in which the methine atom of the backbone C3 and in particular the Zr atom are significantly bent out of the mean plane of the *nacnac* ligand with a ligand bending angle (angle between the ligand plane (N1, N2, C2, C4) and the plane defined by N1, N2, Zr) of 38°. This *syn* conformation of the N-benzyl substituent is most probably responsible for placing the CH_2 groups in an intermediate position between the two chloride atoms (Figure 3.1, right), instead of above one and below the other as would be expected in an undistorted idealized geometry (Figure 3.1).

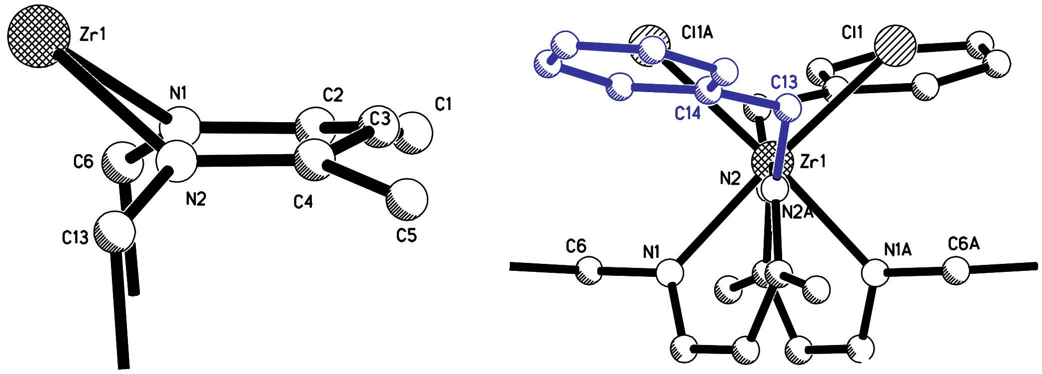


Figure 3.1 ”Boat-like” conformation of the ligand, Zr1 and C3 are bent out of the mean plane of the ligand.

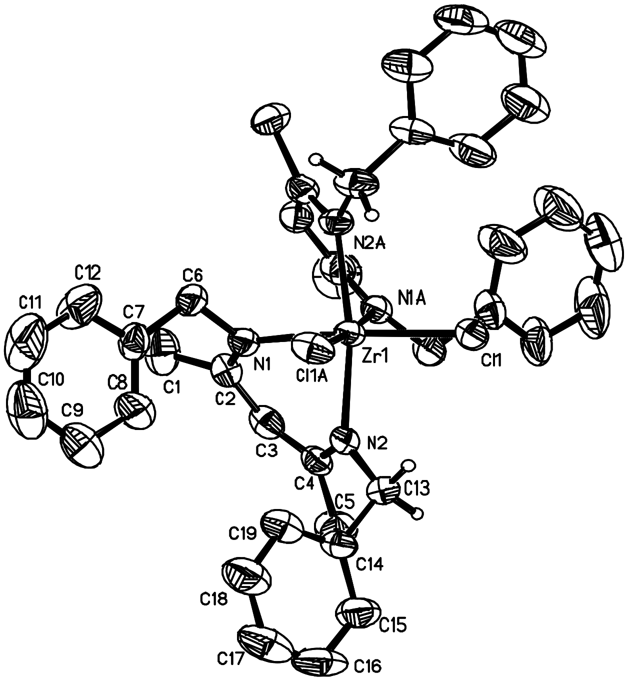


Figure 3.2 Molecular structure of complex **2c** with 50% probability thermal ellipsoids depicted and most H-atoms omitted for clarity. For bond lengths and angles see **Table 3.1**; for crystallographic data see **Table 6.1**

At room temperature, the ^{1}H NMR spectrum of **2c** exhibits two resonances for the CH_2 groups and one large peak for the methyls, which indicates an apparent symmetry of the complex, which is not present in the solid state. To resolve this ambiguity, ^{1}H NMR spectra were mesured at different temperatures. As the temperature was lowered the CH_2 and methyl resonances start to broaden. They separate at 253 K, and at 223 K four separated doublets appears for the CH_2 and 2 singlets for CH_3 resonances (see figure 3.3).

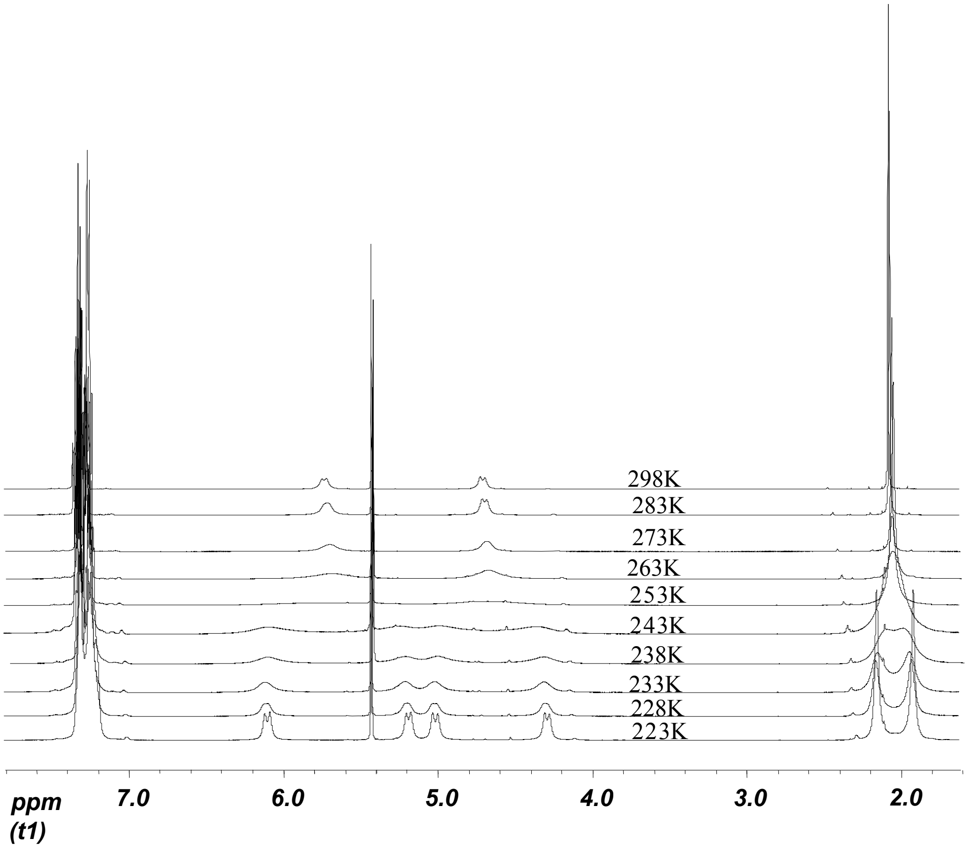


Figure 3.3 Variable temperature ^{1}H NMR of **2c** in $CDCl_3$. Methyl peaks appear around 2 ppm while CH_2 peaks are found from 4.2 to 6.1 ppm. The rest of the spectrum was omitted for clarity.

The low-temperature spectrum is consistent with the C_2-symmetry of the solid state structure. The two CH_2 groups of the same *nacnac*^{Bn} and the protons of each CH_2 group are diastereotopic, as well as the two methyl groups on the backbone of the ligand. The two *nacnac* ligands as a whole are related by a C_2-axis. A fluxional behaviour in NMR spectra has been observed in other $(nacnac)_2ZrX_2$ complexes[26,28] and was explained by a Bailar twist mechanism[48] through which isomerization between the Δ- and Λ-enantiomer is taking place. At room temperature, the two enantiomers interconvert rapidly on the NMR time scale via a C_s-symmetric trigonal-prismatic intermediate. As a consequence of the Bailar twist, groups formerly *trans* to nitrogen end up *trans* to chlorine. Only one signal is observed for the CH group in the ligand backbone at low and high temperature and no broadening of this signal is observed. This is in agreement with a Bailar twist, which symmetrizes each ligand, but retains the equivalence of the two ligands even at low temperature. The appearance of two broadened doublets for the CH_2 groups at high temperature indicates that protons of the same CH_2 remain diastereotopic even in the fast-exchange region. Thus even at high temperatures, a complex with *trans*-chloride ligands, in which all CH_2 protons would be homotopic, is not accessible even as a short-lived intermediate.

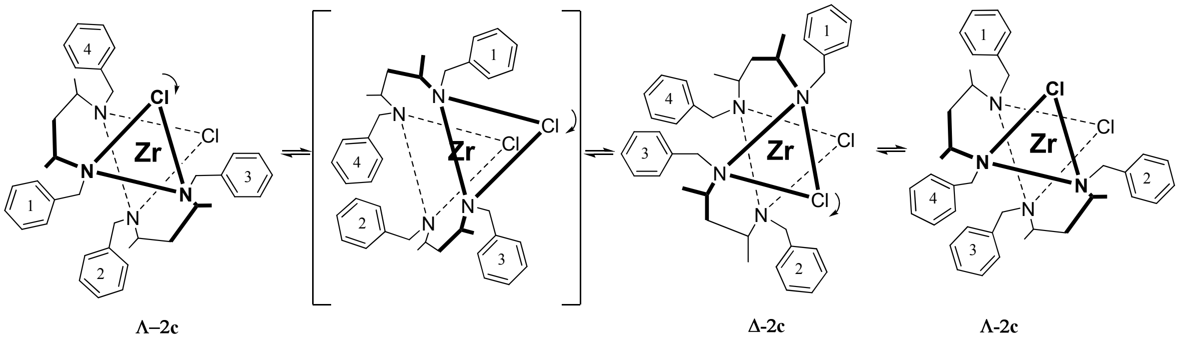
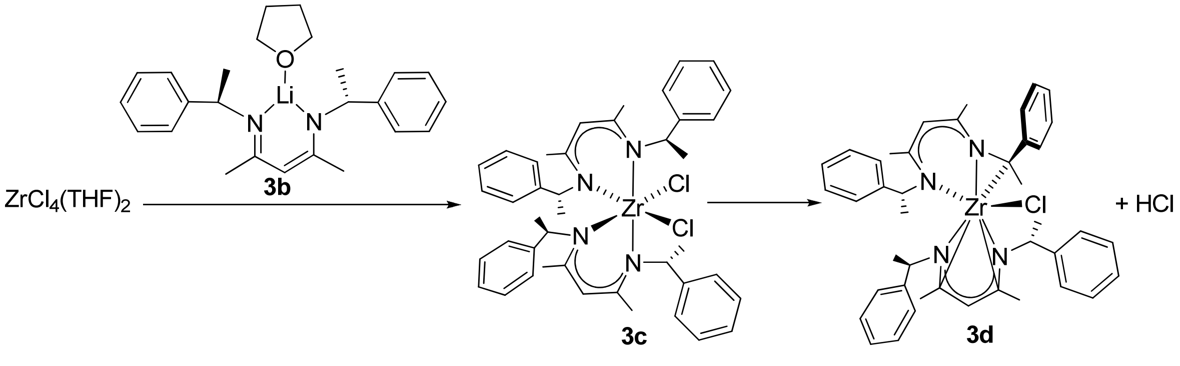


Figure 3.4 Bailar-Twist in an octahedral system

3.2.3.2 Synthesis of (*nacnac*^{R,R})$_2$ZrCl$_2$, 3c

Attempts to generate **3c** from the in situ generated *n*-Bu_2ZrCl_2, failed. Complex **3c** was obtained by reaction of (*nacnac*^{R,R})Li(THF) (**3b**) and $ZrCl_4$ or $ZrCl_4(THF)_2$ in a 2:1 ratio. While only **3c** was recovered from reactions in toluene or dichloromethane, reaction in THF at room temperature for 2 days afforded an orange powder (65%). Recrystallization by slow diffusion of hexane into a toluene solution of the obtained powder gave yellow crystals of **3c**, which were contaminated with small amounts of red crystals of the CH-activation product **3d** (Scheme 3.3).



Scheme 3.3 Synthesis of complex **3c** & **3d**

The chiral complex **3c** crystallizes with two diastereomers (ΔRR and ΛRR) in the asymmetric unit, both with an approximately a C_2-axis of symmetry. Similarly to **2c**, both Λ-**3c** and Δ-**3c** diastereoisomers show a significant bending of the Zr center out of the mean plane of the ligand (bending angles of 36-49°). Due to the chirality of the ligand, the interconversion between Δ/Λ conformations is also accompanied by changes in the conformation of the diketiminate ligand. In the Δ-isomer, the diketiminate ligands retain a C_2-symmetric conformation, placing the phenyl substituents *anti* towards each other and orienting the hydrogen atoms at the chiral carbons to the Zr center. In the Λ-isomer, the two phenyl rings of each diketiminate are placed in a *syn*-orientation, comparable to the C_s-symmetric ligand conformation observed in **2c** (**Figure 3.2**). Consequently, methyl groups C27 and C57 instead of hydrogen atoms are oriented towards the Zr center, causing an increased distortion from octahedral geometry, increased Zr1-Cl distances and a reduced Cl1-Zr1-Cl2 angle in Λ-**3c** compared to Δ-**3c** (**Table 3.1**).

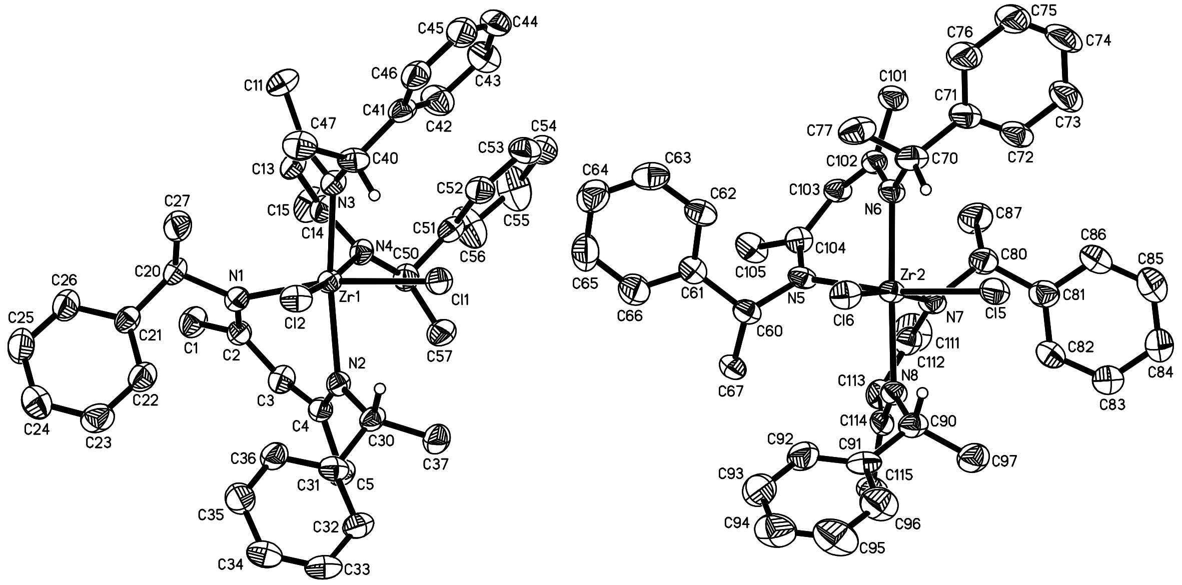
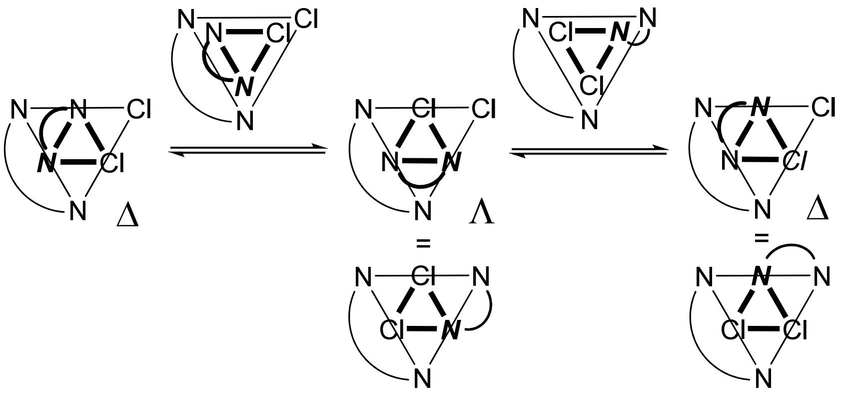


Figure 3.5 Crystal Structures of Λ-**3c** (left) and Δ-**3c** (right), both found in the same asymmetric unit. Thermal ellipsoids are drawn at the 50% probability level. Most hydrogen atoms are omitted for clarity.

As observed for **2c**, **3c** displays evidence of a Bailar-twist mechanism. At room temperature, resonances in ^{1}H and ^{13}C spectra are broadened by isomerisation, but show the presence of two diastereomeric complexes. Upon cooling to 0˚C, resonances of ligand protons sharpen to give two sets of resonances corresponding to two diastereoisomers in a ratio of approximately 2:1 for Δ-**3c** and Λ-**3c**. This is in agreement with the crystal structures obtained for Δ-**RR** and Λ-**RR.** The lack of differentiation between Δ and Λ isomers, caused by the facile N-C rotation, indicates that this ligand will not be rigid enough to impact chirality in a potential catalytic reactions. The Δ/Λ-isomerisation is slower than in **2c**, and coalescence was not observed in $CDCl_3$ or even in toluene-d_8 at 100 °C. For **3c**, coalescence into a fully symmetric spectra requires two different Bailar-twists (**Scheme 3.4**). In the first one, the groups previously *trans* to N in the Δ-isomer (Δ-N) will be exchanged with groups *trans* to Cl in the Λ-isomer (Λ-Cl). In the second Bailar-twist, the groups *trans* to N in the Δ-isomer (Δ-N) will be exchanged with the groups *trans* to Cl in the Δ-isomer (Δ-Cl) (or Λ-N with Λ-Cl, respectively). Since no coalesced spectrum containing 2 sharp methine resonances is obtained, both exchange processes seem to overlap. The lack of coalescence even at higher temperatures is probably due to the high energy that the second twist requires, since this one occurs with the constraint of one diketiminate ligand bridging the two trigonal faces of the prismatic transition state (**Scheme 3.4**). Four C*H*(Me)Ph resonances in the ^{1}H NMR spectrum of **3c** at room temperature (**Figure 3.6**) and two H*C*(=N)$_2$ resonances in its ^{13}C spectrum, indicate that the Δ/Λ-isomerisation is slow on the NMR time scale.



Scheme 3.4 Exchange of Δ-Cl first with Λ-N, then with Δ-N.

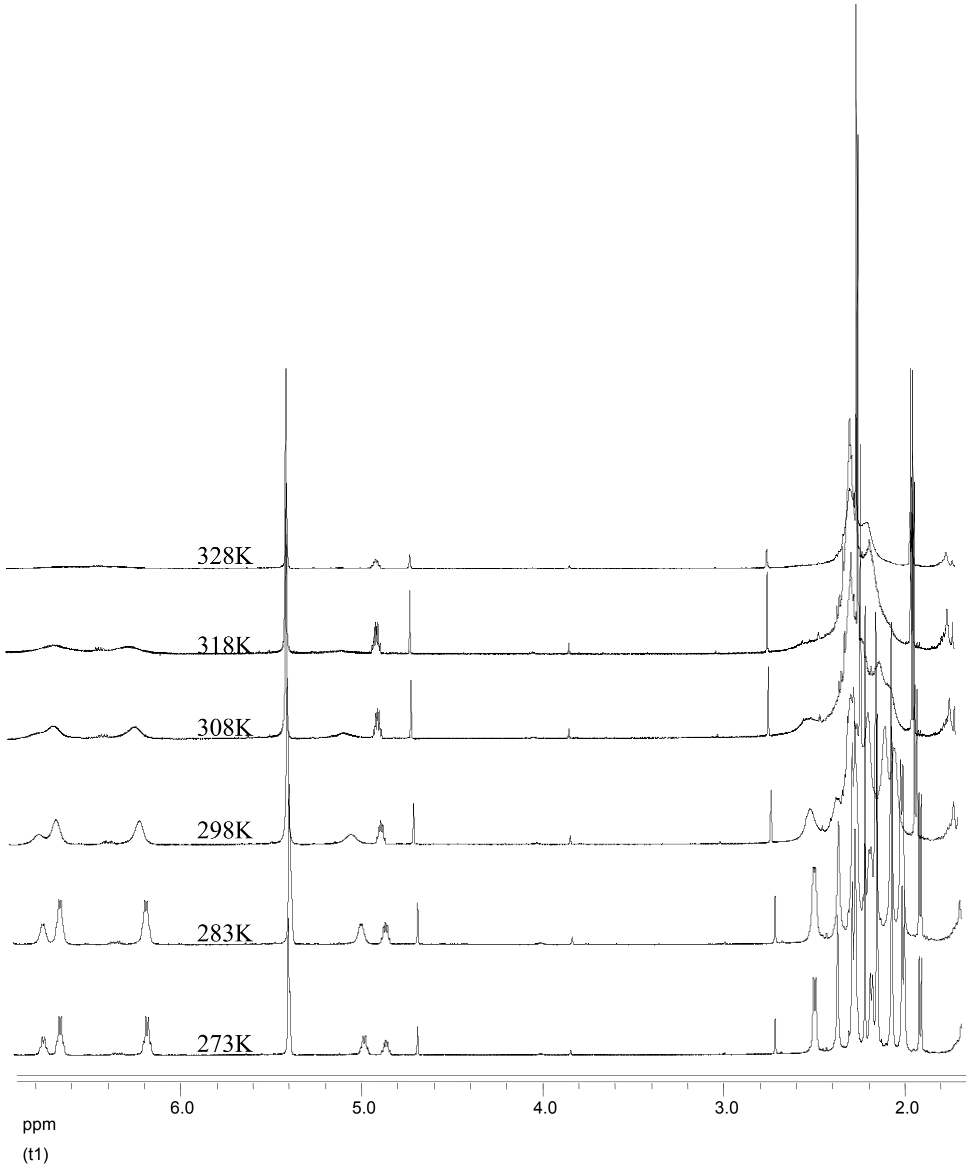


Figure 3.6. Variable temperature ^{1}H NMR of **3c** in $CDCl_3$, only showing the resonance from 6.9 to 1.2 ppm the rest of the spectrum was omitted for clarity.

The red crystals of the CH-activation product **3d** could not be obtained in sufficient quantity for a full characterization, but allowed an X-ray structure determination. The complex is non-symmetric and its geometry best described as a distorted square pyramidal with N1 and C27 sharing the apical position. The two *nacnac* ligands are coordinated differently. In the first ligand, the atoms Zr1, N1, N2, C22, C23, C24, C25, C26 & C27 are all in the same plane and the two phenyl rings have an anti-orientation. In the second ligand, Zr is found to be bent quite strongly out of the mean ligand plane, with an angle between the ligand plane (N3, N4, C2, C4) and the plane formed by N3, N4 & Zr of 62°. Zr-C distances to the ligand backbone are significantly smaller in the second *nacnac*-ligand than observed in CH-activated ligand (Zr-C2 & Zr-C4 = 2.835(2) & 2.819(2) Å, vs. Zr-C23 & Zr-C25 = 3.4 & 3.2 Å; Zr-C3 = 2.9 Å, vs. Zr-C24 = 3.7 Å) or even than those in **3e**. It is difficult to judge if the closer coordination of the ligand backbone is indeed a coordinative interaction or simply a result of the increased bending of the Zr out of the ligand's mean plane.

The formation of **3d** as a result of formal HCl elimination was surprising and only observed with this ligand. Treatment of the analogous complexes **2c** or **4c** (*vide supra*) with excess (1-2 equiv.) of bases, such as NaO*t*-Bu, Et_3N, pyridine, $Na(NSiMe_3)_2$ or *n*-BuLi showed no reaction. This suggests that this conversion from **3c** to **3d** is not a deprotonation reaction, but most probably a C-H activation caused by the constraint of the ligand and placing the H close to Cl.

Table 3.1 Selected bond distances [Å] and bond angles [deg] for **2c, 3c**, **4c**, **2d** and **2e**. [a]

	2c	**4c**	**Λ-3c**	**Δ-3c**	**2d**	**2e**
Zr-N1 [b]	2.201(3)	2.235(2)	2.181(2) & 2.205(2)	2.177(3) & 2.183(2)	2.203(3) & 2.217(3)	2.288(2)-2.305(2)
Zr-N2 [c]	2.190(2)	2.197(2)	2.213(3) & 2.246(3)	2.221(3) & 2.247(3)	2.289(3) & 2.295(3)	2.225(2)-2.232(2)
Zr-X [d]	2.455(1)	2.483(1)	2.499(1) & 2.516(1)	2.483(1) & 2.487(1)	2.290(4) & 2.297(4)	1.939(2)-1.954(2)
N1-C2/ N2-C4	1.325(4) & 1.339(4)	1.339(3) & 1.331(2)	1.321(4) - 1.357(4)	1.328(4) - 1.348(4)	1.328(5)-1.338(5)	1.314(3)-1.336(3)
C2-C3/ C3-C4	1.410(5) & 1.388(5)	1.397(3) & 1.410(3)	1.394(5) - 1.408(4)	1.398(4) - 1.413(4)	1.380(6)-1.403(5)	1.388(4)-1.416(4)
Complex bending [e]	37	34	47-49	36-42	31	32-34
N1-Zr-N2 [f]	78.06(9)	80.52(6)	83.71(9) & 85.46(9)	82.28(9) & 82.44(9)	74.56(11) & 74.81(11)	76.65(7)-77.52(8)
N-Zr-N [g]	86.71(13)-87.28(9)	86.7(1)-89.2(1)	91.32(9)-106.81(9)	91.31(9)-98.60(9)	77.31(11)-127.20(12)	83.20(7)-87.37(8)
X1-Zr-X2	93.58(5)	93.36(3)	88.52(3)	90.59(3)	116.36(15)	97.12(7) & 98.72(7)
N-Zr-X [d]	90.11(7)-97.54(7)	90.07(5)-95.48(4)	83.53(6)-92.51(7)	88.95(7)-91.41(7)	78.34(13)-94.59(12)	87.78(7)-102.55(8)

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[a] Atom numeration according to **2c**. Values were provided for analogous atoms in other structures, *independent of the numeration in the respective complex.* [b] Nitrogen atoms *trans* to Cl, numeration differs between complexes. [c] Nitrogen atoms *trans* to N, numeration differs between complexes. [d] X = Cl (**2c** - **4c**), C (**2d**), O (**2e**). [e] Angle(s) between the least-square planes defined by N1,N2,C2-C4 and Zr1,N1,N2 in **2c** or respective atoms in other complexes. [f] *Cis*-angle(s) between nitrogen atoms of the same ligand. [g] *Cis*-angle(s) between nitrogen atoms of different ligands.

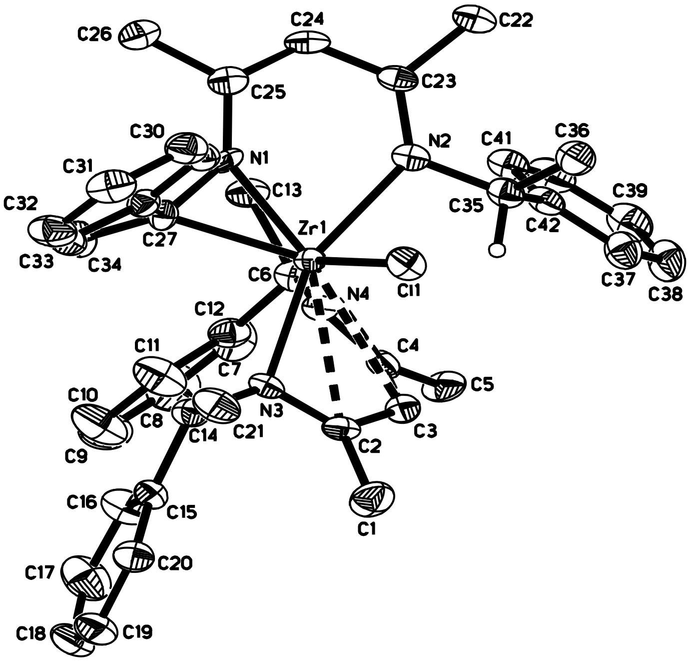


Figure 3.7 Molecular structure of complex **3d** with 50% probability thermal ellipsoids depicted and most H-atoms omitted for clarity. For bond lengths and angles see **Table 3.2**; for crystallographic data see **Table 6.1.**

Table 3.2. Selected bond distances [Å] and bond angles [deg] for **3d**

Zr-N1	2.031(3)	Zr-C4	2.819(5)	N4-C4	1.302(6)	N1-Zr-N4	109.11(16)°
Zr-N2	2.318(4)	Zr-C27	1.410(7)	C2-C3	1.423(7)	N4-Zr-N3	83.50(13)°
Zr-N3	2.230(3)	N1-C27	1.410(7)	C3-C4	1.404(7)	N1-Zr-C27	37.29(18)°

3.2.3.3 Synthesis of (*nacnac*^{Cy})$_2$ZrCl$_2$, 4c

While the reaction of **4b** and ZrCl$_4$ in THF at room temperature afforded **4c** in moderate yields (35%), reaction of **4a** with the *in situ* generated intermediate *n*-Bu$_2$ZrCl$_2$ showed a mixture of ligand and products that were not identified. It seems that *nacnac* ligands with secondary alkyl substituents on N, such as **3a** and **4a**, do not react fast enough and the low stability of n-Bu$_2$ZrCl$_2$ towards reductive elimination[46] impedes the success of this pathway. The crystal structure of **4c** is isostructural to **2c**: the complex has a distorted octahedral geometry, with a "boat-like" distortion of the ligand and an out-of-plane bending angle of the metal of 34°. The cyxlohexyl ring is oriented in an intermediate position between the two chlorides, with close H-Cl distances of 2.86 Å.

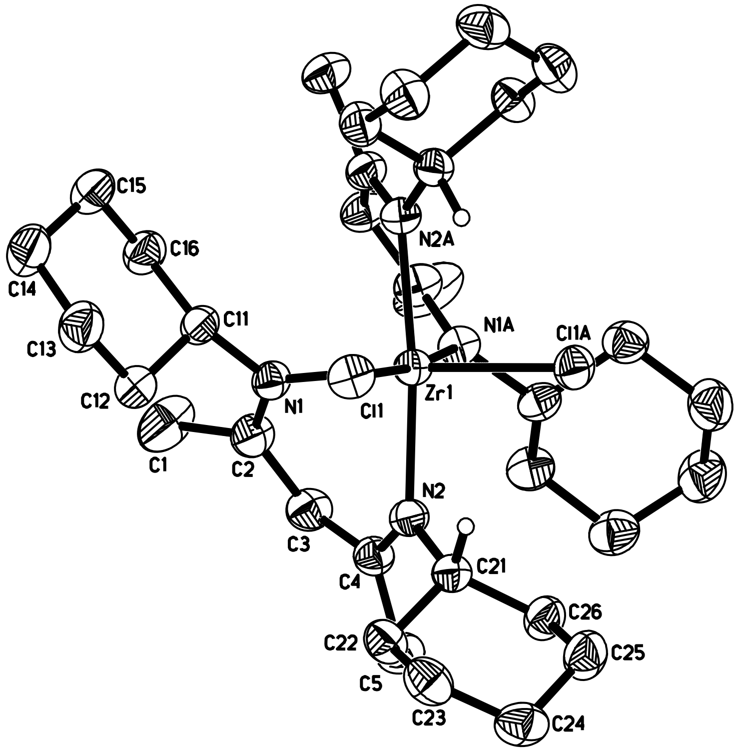


Figure 3.8 Molecular structure of complex **4c** with 50% probability thermal ellipsoids depicted and most H-atoms omitted for clarity. For bond lengths and angles see **Table 3.1**; for crystallographic data see **Table 6.1**

Overall, the complex has a C_2 symmetry and the observation of two broadened ^{1}H NMR signals for the methine groups of the cyclohexyl rings at room temperature can be attributed to the rapid interconversion between two enantiomers of the complex via a Bailar twist. Variable temperature studies showed coalescence of peaks at 328 K and complete decoalescence of peaks at 223 K, where the two enantiomers interconvert slowly on the NMR time scale, suggesting a structure consistent with the solid state one. Identical observations are made for the ^{13}C NMR signals of the cyclohexyl ring, which are broadened at room temperature. At temperatures above the coalescence temperature, the ^{13}C spectra still showed 6 resonances for the cyclohexyl ring; thus again indicating the inaccessibility of the *trans* isomer.

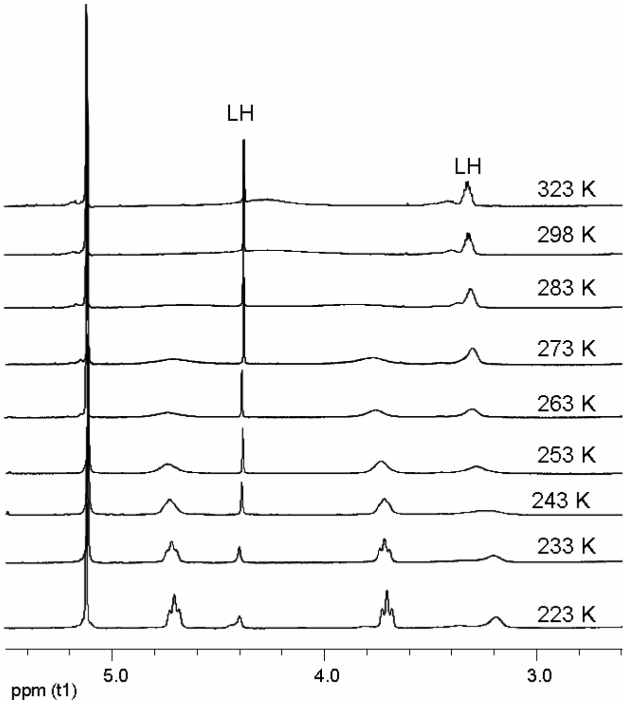


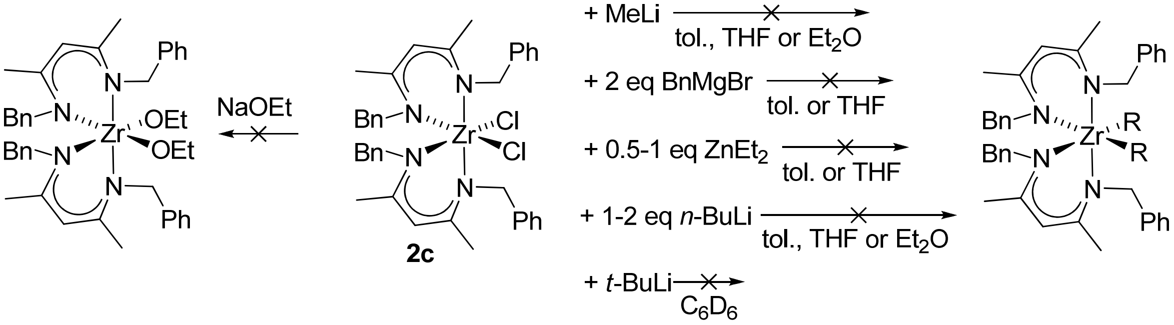
Figure 3.9 Variable temperature ^{1}H NMR spectra of **4c** in $CDCl_3$, showing only the resonances of the CH_{Cy} from 5.5 to 2.6 ppm. The rest of the spectrum was omitted for clarity.

3.2.4 Reactivity in carbozirconation reactions

Following the experimental protocol for Negishi's carbozirconation reaction,[63] reactions of styrene with $AlCl_{3-x}Me_x$ in the presence of catalytic or stoichiometric amounts of **2c** in polar or apolar solvents showed no evidence for methylation of the alkene (NMR, GC-MS).

Using Wipf's modified procedure[64] to generate the more active cocatalyst MAO by water addition likewise did not yield any activity of our complexes.

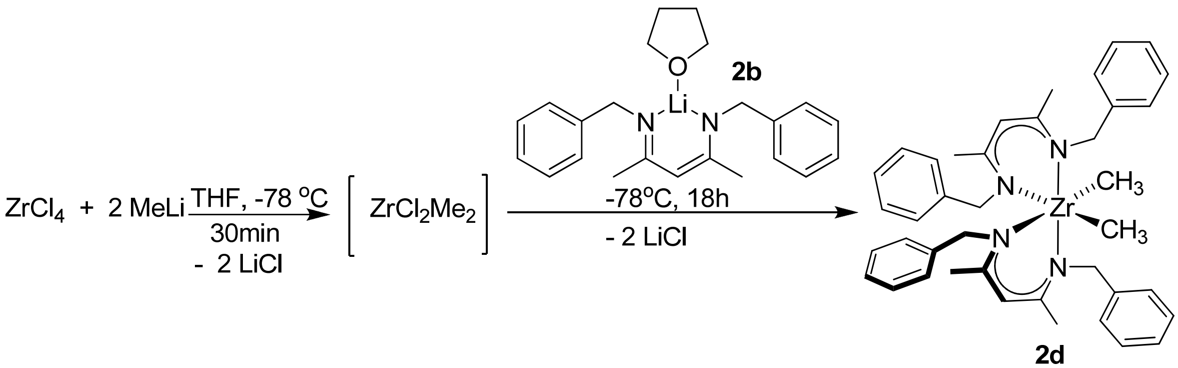
We thus decided to investigate these reactions in more detail, starting from the alkylated complexes. Unfortunately, our attempts to prepare alkyl derivatives of (*nacnac*^{Bn})$_2$ZrCl$_2$ using alkylating agents such as MeLi, MeMgBr, BnMgBr, ZnEt$_2$, *t*-BuLi or *n*-BuLi did not meet with success (Scheme 3.5). NMR spectra of reaction products showed only the presence of the **2c** or – under forcing conditions such as prolonged heating – decomposition products. Exchange of the chloride ligands against ethanolate ligands also failed. These reactions showed that the chloride ligands in **2c** are inaccessible for alkylation via transmetallation, most probably due to steric hindrance around the Zr metal center.



Scheme: 3.5 Reactivity tests of **2c**

3.2.5 Synthesis and reactivity of (*nacnac*^{Bn})$_2$ZrMe$_2$, 2d

Since alkylation seemed not possible after complexation of the *nacnac* ligand, we decided to introduce the methyl group prior to complexation. Indeed, the dimethyl analogue **2d** was obtained in high yields (60%) by reaction of ZrCl$_4$ first with 2 equiv of MeLi at -78˚C for 30-40 min and then with the lithium salt, **2b** for 16 hrs at -78˚C to room temperature. Only complex **2d** was accessible by this pathway. As observed for the synthesis of the dichloride complexes, ligands with secondary alkyls on N did not react fast enough to compete with the decomposition of the zirconium alkyl chloride complex.



Scheme 3.6 Synthesis of complex **2d.**

While complex **2d** also shows an octahedral cis-geometry, the deviation from the ideal geometry is significantly more pronounced, as evidenced by N-Zr-X angles of 78-95°, while the bending angle of 31° is the smallest observed so far.

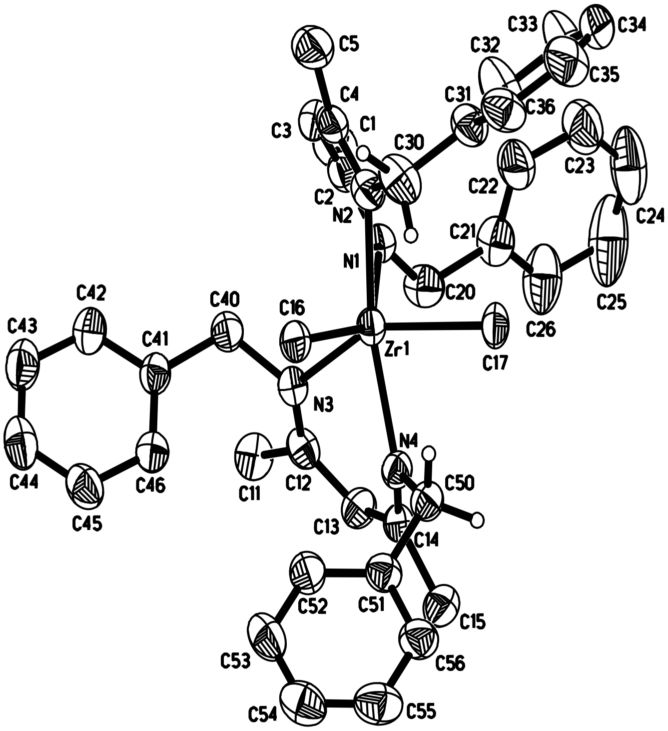
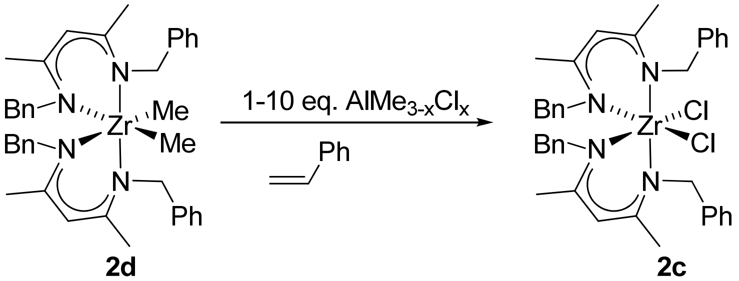


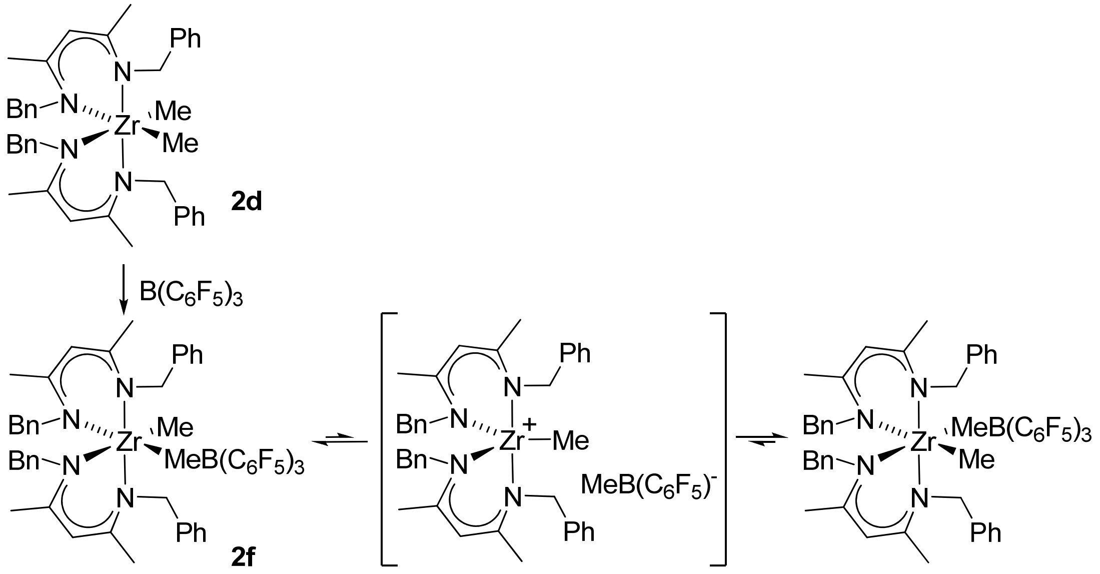
Figure 3.10 Molecular structure of complex **2d** with 50% probability thermal ellipsoids depicted and most H-atoms omitted for clarity. For bond lengths and angles see **Table 3.1**; for crystallographic data see **Table 6.1**

Having complex **2d** in hand, the latter was investigated in several NMR experiments with regard to stoichiometric carbozirconation. A solution of **2d** and 1 equiv. of styrene was reacted with 1 equiv. of $AlMe_xCl_{3-x}$ ($AlCl_3$, $AlMeCl_2$ and $AlMe_2Cl$). No insertion of styrene into Zr-Me was observed in any case in the ^1H NMR spectra of the reaction mixture. Instead, the *cis*-dichloride analogue **2c** was obtained in all cases (for $AlMeCl_2$ in a 1:1 mixture with **2d**). Reactions with an excess (up to 10 equiv) of $AlMe_xCl_{3-x}$ also yielded only **2c**.



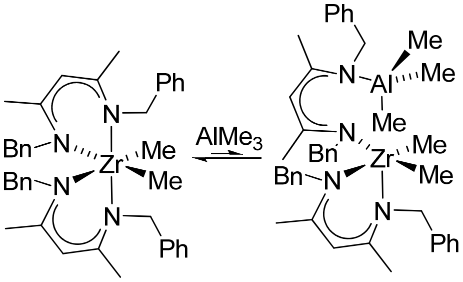
Scheme 3.7 Reaction of **2d** with $AlMe_{3-x}Cl_x$ in presence of styrene

Similar to the activation by MAO, we tried to activate the complex towards styrene insertion by cationization with tris(pentafluorophenyl)borane. While direct reaction of **2d** and $B(C_6F_5)_3$ in C_6D_6 gave unidentified mixtures, slow addition of a C_6D_6 solution of **2d** in portions of 0.1 equiv. every 5 min to a C_6D_6 solution of $B(C_6F_5)_3$ yielded clear spectra of a product assigned as [(*nacnac*^{Bn})$_2$ZrMe][MeB(C_6F_5)$_3$], **2f**. The resonances of the *nacnac* ligands, while slightly broadened, are highly symmetric. In ^{1}H and ^{13}C spectra, only one resonance each is observed for all CH_2, CH, or Me groups, while two resonances appear for the Zr-bound methyl groups. This suggests that the complex isomerizes by $MeB(C_6F_5)_3^-$ dissociation and re-association rather than by Me-B bond breakage. The ion-pair is only meta-stable in solution and rapidly separates as a red oil. Reaction of styrene with a C_6D_6 solution of **2f** or addition of $B(C_6F_5)_3$ to a solution containing **2d** and styrene, again did not yield any styrene insertion products.



Scheme 3.8 Dissociation and re-association of Me

While the lack of reactivity in carbozirconation was unfortunate but in line with the inaccessibility of the Zr-bound ligands indicated by the failed alkylation attempts, the fast exchange of methyl against chloride in the presence of aluminium chlorides seems to contradict this lack of reactivity. To investigate this further, a C_6D_6 solution of **2d** was titrated with $AlMe_3$ (0.2, 0.5, 0.5, 0.75, 1.0, and 1.5 equiv $AlMe_3$ in total after addition). A ^1H NMR spectrum was immediately registered after each addition. Only one resonance was observed for the Zr- and Al-bound methyl groups, which shifted from 0.32 to -0.23 ppm as the concentration of $AlMe_3$ increased. No change in the ligand peaks was observed. Exchange of methyl groups between Al and Zr centers is thus occurring fast on the NMR time scale, in contradiction with the problems encoutered in alkylating these complexes. An explanation for this contradiction would be that alkylation of (*nacnac*)$_2$ZrCl$_2$ is a thermodynamic rather than a kinetic problem, which seems unlikely. Another possible explanation would be a loosening of the *nacnac* coordination by interaction of the nitrogen lone pairs with the aluminum center.

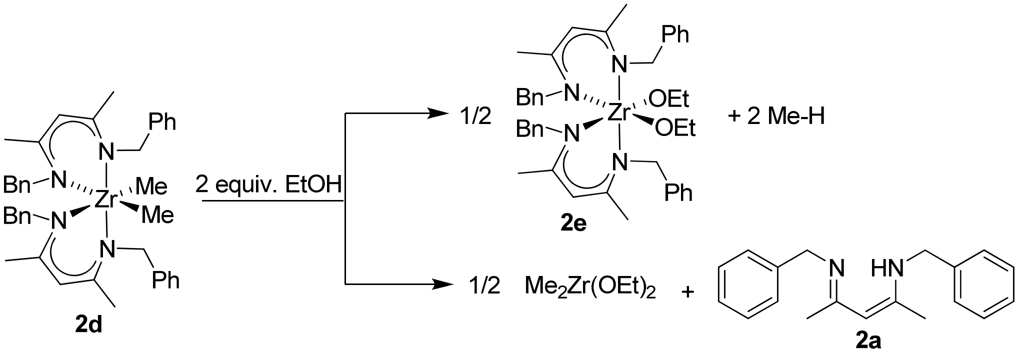


Scheme 3.9 Reaction of **2d** with $AlMe_3$

3.2.6 Synthesis of $(\text{nacnac}^{\text{Bn}})_2\text{Zr(OEt)}_2$ and application in lactide polymerization

Although methyl as a ligand is sterically comparable to chloride, synthesis of the dialkoxy compound **2e** proved to be possible by reaction of **2d** with 2 equiv. of ethanol. The formation of the ligand **2a** in a ratio of 1:1 with **2e**, indicates that the protonation of the Zr-Me groups is competitive with the protonation of the anionic *nacnac* ligand.

Recrystallization in ethanol at -20°C gave only crystals of **2e**. This complex has a structure similar to the dichlorides **2-4c.** The presence of a Bailar twist isomerization process was again confirmed by variable temperature NMR spectra. At room temperature, the ^{1}H NMR spectrum exhibits the same behaviour as observed with **2c**, i. e. two resonances for the CH_2 peaks and one large peak for the methyl groups, which separate at 223 K into 4 doublets for the CH_2 and 2 singlets for the methyl groups. In addition, we observe decoalescence of the CH_2O group into two quadruplets at low temperature.



Scheme 3.10 Reaction of **2d** with EtOH

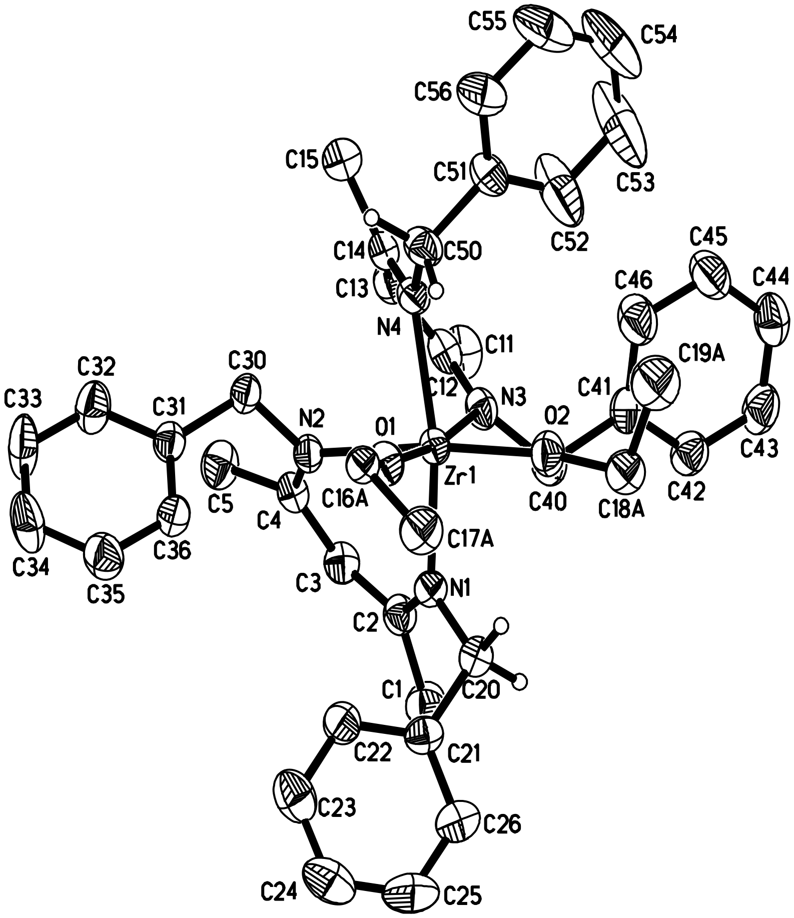


Figure 3.11 Molecular structure of complex **2e** with 50% probability thermal ellipsoids depicted and most H-atoms omitted for clarity. Only one of the two molecules is shown. The minor occupancy of the OEt disorder was omitted. For bond lengths and angles see **Table 3.1**; for crystallographic data see **Table 6.1**

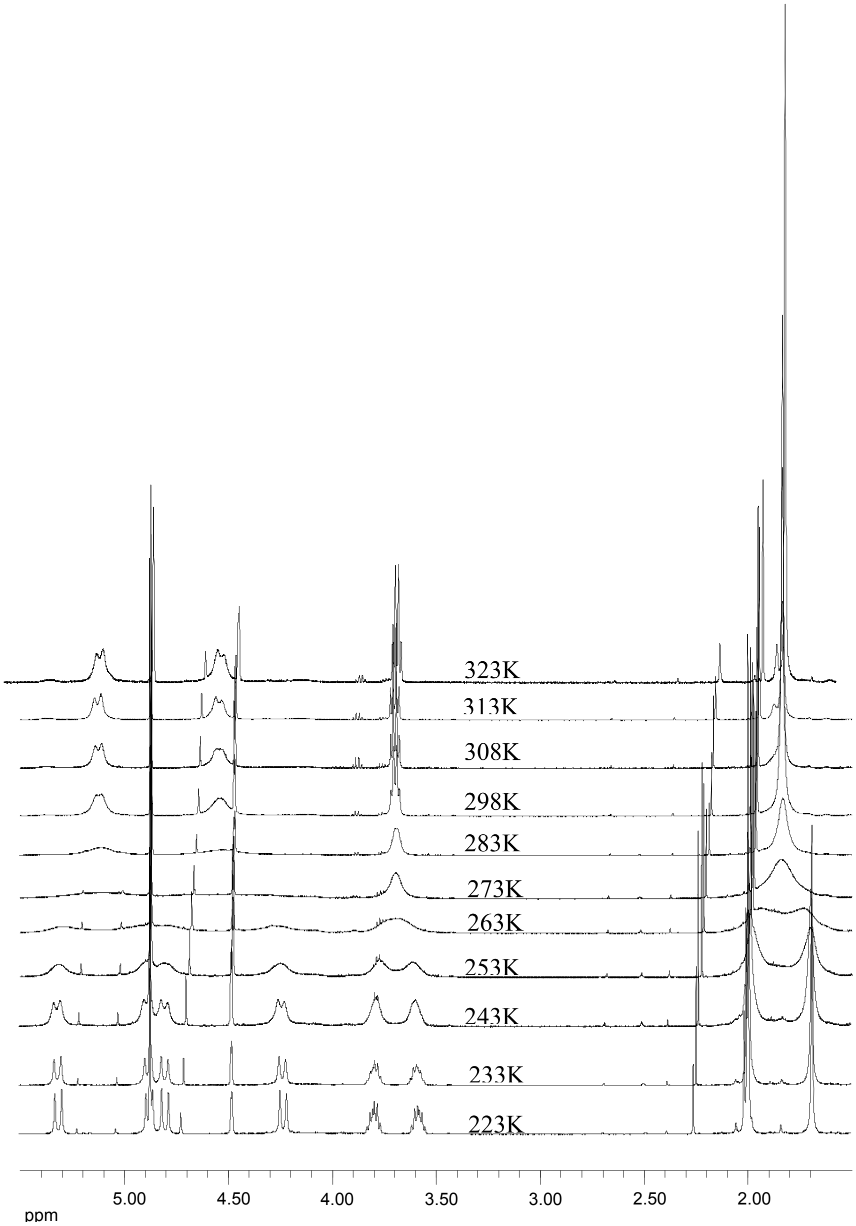


Figure 3.12: Variable temperature ^{1}H NMR of **2e** in $CDCl_3$, only showing the resonance from 5.5 to 1.5 ppm the rest of the spectrum was omitted for clarity

Given the C_2 symmetric structure of $(nacnac)_2ZrX_2$ complexes, they might be interesting targets for stereoselective polymerisations, if the chain propagation is faster than complex epimerisation. We tested **2f** thus as catalyst for the polymerisation of *rac*-lactide. Literature reports indicate that zirconium dialkoxide complexes are suitable initiators for solvent free polymerization at elevated temperatures, but not at low temperatures in diluted solutions.[65] Polymerisations were thus performed at 130 ˚C for 0.5 h with a monomer: initiator ratio of 200:1. After quenching with excess methanol, the resulting solid was dissolved in deuterated chloroform. Integration of the remaining *rac*-lactide resonances indicated a nearly quantitative conversion to polylactide of 98%. The polymer microstructure was analysed by ^{13}C NMR. The carbonyl carbon region shows three characteristic peaks of the polylactide, of different stereochemistry. In the methine region of the spectrum, 2 pics of the polylactide appear at 69.1 (*mrm)* and at 68.9 ppm, corresponding to 4 other tetrads. From the relative intensity of the *mrm* tetrad of 30%, a probablity for isotactic insertion of $P_m = 0.6$ is calculated, using pair-addition Bernoullian statistics.[66] Complex **2f** seems thus to be unselective in the polymerisation of *rac*-lactide, with a slight syndiotactic preference which might be attributed to chain-end control. The lack of selectivity is not that surprising, considering that the epimerisation of the complex is already fast at room temperature.

3.2.7 Variable-Temperature NMR Spectroscopy.

As noted previously, the ^{1}H NMR spectra of bis(*nacnac*)Zr complexes **2c**, **2d**, **2e**, **3c** and **4c** revealed a fluxional behavior in solution. Simulation of the ^{1}H NMR spectrum using the DNMR71 program[67] allowed us to determine the exchange rates (k_{obs}) at different temperatures. Activation parameters were obtained from Eyring plots.[68] While satisfactory linear plots and identical values from different pairs of exchanging nuclei were obtained for **2c**, **2e** and **4c**, a short observable temperature window and difficulties in determination of the exchange constants made the obtained values for **3c** rather unreliable. Two Bailar-twists are present in **3c** (*vide supra)*, but data between 0 °C (no isomerization) and 50 °C, i. e. the activation parameters obtained in **Table 3.3**, describe only the first interconversion mechanism between Δ- and Λ-isomers, which is comparable to **2c, 2e** and **4c.**

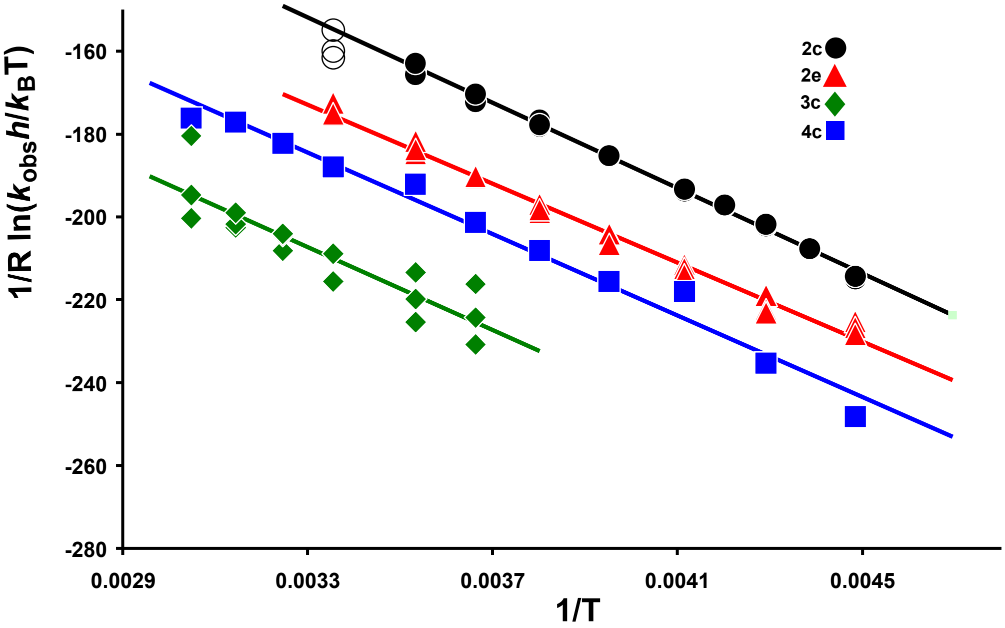


Figure 3.13: Eyring plot for interconversion of the two enantiomers of complexes (**2c**, **2e**, **3c** and **4c**)

Eyring's equation: $1/R \ln(k_{obs}h/k_BT) = -\Delta H^{\ddagger}/T + \Delta S$

R = Universal Gas Constant = 8.3145 J/mol K

$\Delta S^{\ddagger}$ = Activation entropy [$J \cdot mol^{-1} \cdot K^{-1}$]

$\Delta H^{\ddagger}$ = Activation enthalpy [$kJ \cdot mol^{-1}$]

k_B = Boltzmann's constant [$1.381 \cdot 10^{-23}$ $J \cdot K^{-1}$]

T = absolute temperature in Kelvin (K)

h = Planck's constant [$6.626 \cdot 10^{-34}$ $J \cdot s$]

k_{obs} is the rate constant of the observed exchange.

Plotting $1/R \ln(k_{obs}h/k_BT)$ versus 1/T yielded a line with the slope $-\Delta H^{\ddagger}$ and the interception with the y-axis is $\Delta S^{\ddagger}$. The obtained values are comparable to those previously reported with octahedral *nacnac* complexes.[26,28] The negative values of $\Delta S^{\ddagger}$, with the exception of compound **2c,** indicate a highly ordered (or sterically congested) transition state and are also consistent with an ordered exchange *via* a Bailar twist mechanism as opposed to ligand dissociation. Although variations of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ between the complexes is slight and barely significant considering the margin of error, their trends agree with expectations: (i) Complexes with different ligands show a correlation between the loss of entropy in the transition state and the increase in steric bulk of the N-substituent ($\Delta S^{\ddagger}$: **2c** > **4c** > **3c**). (ii) Although $\Delta H^{\ddagger}$ was not remarkably affected when chlorides are replaced with ethoxides in $(nacnac^{Bn})_2ZrX_2$, isomerisation of **2e** is significantly slower at room temperature due to a loss in entropy in the transition state of **2e** vs. **2c** ($\Delta\Delta S^{\ddagger}$ = 34 J/(mol·K)), which might be attributed to a hindered rotation of the alkoxy groups in the transition state.

Table 3.3 Calculated activation parameters

Complex	R/X	$\Delta H^{\ddagger}$ (kJ·mol^{-1})	$\Delta S^{\ddagger}$ (J·mol^{-1}·K^{-1})	k_{298K} (x 10^3 s^{-1})
2c	Bn/Cl	51(1)	18 (3)	62
2d	Bn/Me	----	----	Very fast
2e	Bn/OEt	48(1)	-16 (6)	3.5
3c	R*/Cl	50 (4)	-42 (13)	0.07
4c	Cy/Cl	46 (2)	-33 (8)	10

3.3 Conclusion

In summary, *nacnac*H ligands with aliphatic N-substituents have been synthesized in one pot synthesis and in excellent yields using TsOH as an activating agent. Their complexation with zirconium was effected by salt metathesis or by protonation of n-Bu_2ZrCl_2. X-ray structures of the complexes showed a *cis* conformation and indicated a strong distortion of the *nacnac* ligand, most likely caused by the interaction of the N-alkyl substituent with the chloride ligands. All complexes showed dynamic behavior in solution attributed to a Bailar twist and studied by variable temperature ^{1}H NMR. The rate of exchange between the interconverting *cis*-enantiomers correlated with the steric effect of the N-alkyl substituents of the ligand. The dichloride complexes showed no reactivity in carbozirconation of alkenes under Negishi's conditions, nor could they be alkylated using standard conditions. This is probably due to the steric hindrance around the $ZrCl_2$ fragment introduced by the N-substituents, which was observed in the structural studies.

While an alternative synthetic route to obtain the dimethyl analog was successful, its reactivity again seemed to be very limited and insertion of styrene was not observed even after activation with trispentafluorophenyl borane. However, preliminary tests showed a possible insertion of C=O into Zr-Me. The ethoxy analogue **2e** showed satisfactory activity, but no selectivity in the polymerization of *rac*-lactides.

In conclusion, the chemistry of (*nacnac*)$_2$ZrX$_2$ complexes seems to suffer from two essential setbacks: The steric hindrance around the ZrX_2 fragment reduces the accessibility to these coordination sites and isomerization reactions are slow enough to make NMR spectroscopy difficult, but fast enough to loose the chirality of the metal center for catalytic applications.

CHAPTER 4

Replacing chloride by alkoxide: $Cp_2Zr(H)OR$, searching for alternatives to Schwartz' reagent

This chapter is part of an article by

Philippe Perrotin, Ibrahim El-Zoghbi, Paul O. Oguadinma and Frank Schaper,

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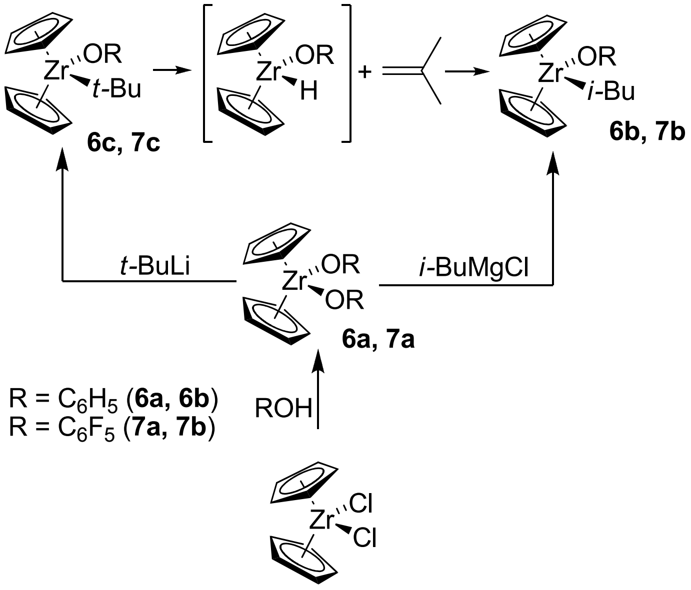
4.1 Introduction

Hydrozirconation using Schwartz' reagent, CpZr(H)Cl,[32] is still regarded as one of the most successful applications of transition metals to functionalize non-activated alkenes and alkynes.[32,33] Although the reaction normally generates primary functionalized alkyls,[33,69] mixtures of secondary and primary alkyl zirconocenes were obtained, when the alkenes contained an aromatic or a polar substituent along their chain.[34,69,70,71]

Several modifications of Schwartz' reagent, have been reported previously, mainly to increase solubility, reactivity, and/or selectivity.[35,36,72-73] Modifications consisted in substitution of the Cp ligands or by replacing chloride with other groups such as bromides or sulfonates.[71] Our group is interested in the modification of Schwartz' reagent by replacing chloride with an alkoxide to yield $Cp_2Zr(H)OR$, with the main goals of suppressing β-H eliminations and the possibility to control the hydrozirconation reaction. Attempts to isolate $Cp_2Zr(H)OR$ complexes have failed and these complexes seem to undergo a disproportionation into Cp_2ZrH_2 and $Cp_2Zr(OR)_2$. However, $Cp_2Zr(H)OC_6H_5$ and $Cp_2Zr(H)OC_6F_5$ have been generated *in situ* either via a β-H elimination from $Cp_2Zr(t\text{-}Bu)OAr$ or by ligand exchange between Cp_2ZrH_2 and $Cp_2Zr(OAr)_2$.

The *tert*-butyl complexes $Cp_2Zr(t\text{-}Bu)(OAr)$ were surprisingly stable against β-H elimination at room temperature. At 60-70 °C, they isomerized within 3 h-3 d to the *iso*-butyl complexes **6b** and **7b**, respectively. A similar complex, $Cp_2Zr(i\text{-}Bu)Cl$,[74] has been reported to react as a hydrozirconation reagent.[75] Due to the forcing conditions of the isomerisation, **6b** and **7b** could not be isolated from the decomposition products formed. To confirm the NMR assignment of the *iso*-butyl complexes, we decided to prepare them independently, providing a general synthesis of this compound with complete characterization. We will also present the hydrozirconation of terminal alkenes using the *in situ* generated zirconocene alkoxide complexes.*



Scheme 4.1 Synthesis of *i*sobutyl complexes

4.2 Results and discussion

4.2.1 Syntheses of isobutyl complexes

Reaction of Cp_2ZrCl_2 with phenol in the presence of triethylamine according to literature procedures yielded the desired zirconocene diphenoxide, $Cp_2Zr(OPh)_2$, **6a**,[76] with NMR spectral data identical to literature. Analogously, **7a**, is obtained by reaction of C_6F_5OH, with Cp_2ZrCl_2 in the presence of aniline.[77]

Addition of 1 equiv of *i*-BuMgCl to an ethereal solution of **6a** at -78°C for 1 h, followed by stirring for 2 h at room temperature afforded yellow-orange oil in moderate yields. NMR spectra showed the presence of ca. 30% **6b**, together with impurities, the most common being unreacted **6a**. Addition of *i*BuMgCl at 25°C followed by stirring for 2 h gave a

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[*] Part of these syntheses has been undertaken together with a French summer trainee, Marie Theillard.

mixture of unidentified products with 45% purity in **6b**. NMR spectra also showed complete consumption of **6a**. On the other hand, reaction at 0 °C followed by stirring for another two hours at room temperature showed to be the best conditions with yields of 65-70% of **6b**, still contaminated by unidentified products (signals at 5.95 ppm and at 1.01 ppm). Increasing the temperature to 0 °C can be considered as a compromise between the increase of reactivity of **6a** and reduced reaction control.

Several attempts to purify the product by cristallization of the oil at -20°C failed and showed decomposition products upon standing for long periods. Crystals of this compound were only obtained from a saturated hexane solution after two weeks at -20°C. Elemental analysis of crystalline material, however, showed low carbon values ($\Delta = 1.5\%$). This low value is probably due to contamination of these crystals with the decomposed oil.

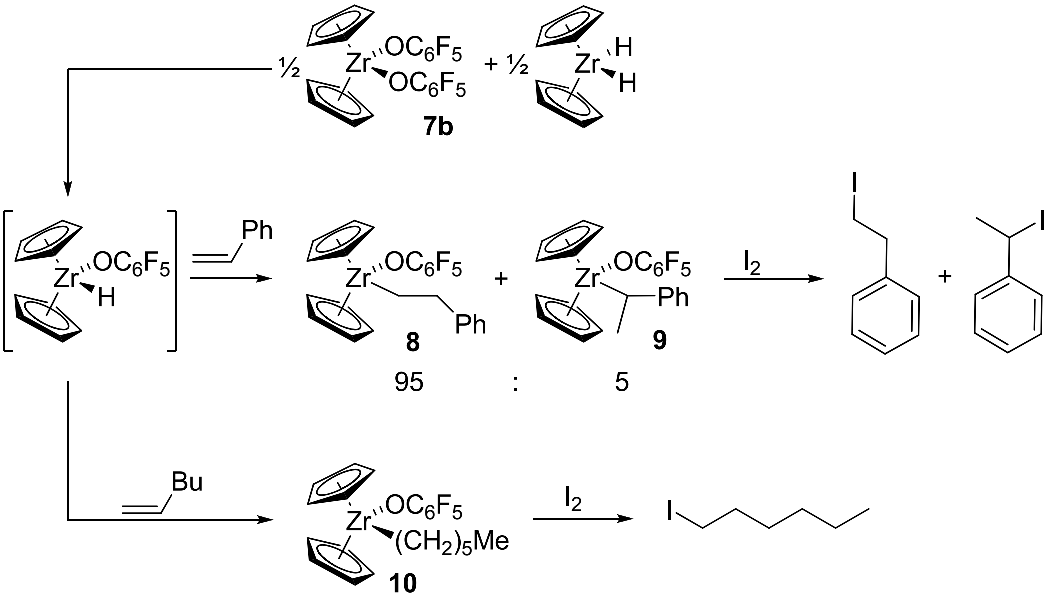
Similarly, the electron-poor analog of **6b,** the pentafluorophenolate derivative $Cp_2Zr(i\text{-}Bu)OC_6F_5$, **7b**, was also prepared.[78] Synthesis of **7b** was optimized by changing the temperature from -78°C to 0°C. Addition of 1 equiv. of *i*-BuMgCl to a cooled (0 °C) solution of **7a** in Et_2O, stirring for 2 h at 0 °C and finally for 2 h at room temperature afforded **7b** in a yield of ca. 60%. NMR spectra showed **7b** (60%) and a decomposition product identified as $\{Cp_2Zr(OC_6F_5)\}_2(\mu\text{-}O)$ (25%, 5.98 ppm) and an unidentified product showing two multiplets in the alkyl region (1.01 and 1.20 ppm).

Attempts to purify **7b** by recrystallization upon standing or to grow crystals from a hexane solution have failed. In both cases, ^1H NMR showed the disappearance of **7b** and appearance of unidentified products. Elemental analysis of this compound was not performed due to its lack of purity.

While the compounds could not be obtained in pure form, they show identical ^1H and ^{13}C NMR spectra to **6b** and **7b** obtained in the isomerization of the tert-butyl complexes, thus confirming their assignment.

4.2.2 Syntheses of phenyl-ethyl-complexes and olefin hydrozirconation

Our group's previous investigations showed the possibility to generate the hydrido compound $Cp_2Zr(H)OR$ *in situ*. Generation of $Cp_2Zr(H)(OC_6F_5)$ in the presence of styrene by reaction of the zirconocene dihydride with $Cp_2Zr(OC_6F_5)_2$ gave the insertion product, $Cp_2Zr(OC_6F_5)(CH_2CH_2Ph)$, **8**, in moderate yields (51%), accompanied by **7a** and minor amounts of decomposition or side products, such as $\{Cp_2Zr(OC_6F_5)\}_2(\mu\text{-}O)$ (Scheme 4.2). ^1H NMR has shown also the presence of a compound in smaller concentrations, which was putatively assigned to be the 2,1-insertion product of styrene $Cp_2Zr(OC_6F_5)CH(Me)(Ph)$, **9**. The ratio of **8:9** was approximately 95:5.[†]



Scheme 4.2 Olefin's hydrozirconation

[†] This part is earlier work by Philippe Perrotin in our group.

To confirm the assignment of **8**, the compound was independently synthesized by reaction of **7a** with $PhCH_2CH_2MgBr$. While the NMR spectra were identical to those of **8** obtained by hydrozirconation, reactions yielded again viscous oils of 60-80% purity, which could not be crystallized despite several attempts. Thus to further confirm the assignment of **8** as the hydrozirconation product, **8** was derivatized after hydrozirconation by reaction of the benzene-d_6 solution with I_2. ^1H NMR and GC-MS analyses showed the formation of 1-iodo-2-phenylethane in 50% yield (determined by NMR relative to initial olefin). 1-iodo-1-phenylethane (expected upon reaction of **9** with iodine) was not identified in the obtained reaction mixtures, although a minor, iodine-containing compound was observed in GC-MS analyses, which showed identical fragmentation patterns and similar retention times as 1-iodo-2-phenylethane. Hydrozirconation product **8** was also obtained in 30% yield (NMR) by reaction of Cp_2ZrH_2 and C_6F_5OH in the presence of styrene.

Following the same procedure, evidence of *in situ* formation of $Cp_2Zr(H)(OC_6F_5)$ has also been obtained by insertion of 1-hexene into the Zr-H bond. The only insertion product obtained is $Cp_2Zr(OC_6F_5)(CH_2(CH_2)_4CH_3)$, **10**.[†] Assignment of **10** was confirmed by repetition of the hydrozirconation reaction and subsequent derivatization. Thus, reaction of a benzene-d_6 solution of Cp_2ZrH_2 with C_6F_5OH in the presence of 1-hexene for 3 h at 60 °C gave the compound **10**, which was immediately reacted with excess I_2. ^1H NMR and GC-MS analyses confirmed the formation of 1-iodohexane in 90% yield (from NMR, relative to initial olefin).

4.3 Conclusion

In summary, isolation of the pure compounds **6b** and **7b** was not possible. Their NMR spectra, however, were identical to those of the compounds obtained by hydrozirconation/isomerisation. Characterization of hydrozirconation products was accomplished by derivatization reactions using I_2, which also confirmed the regioselectivity towards the 1,2-insertion of styrene. We are planning to investigate the reactivities and selectivities of these hydrozirconations in general and in particular the conflicting evidence with regard to β-H elimination, as well as the suitability of other alcohols than the "pseudo-halogen" C_6F_5OH.

CHAPTER 5

Concluding Statements and Future Work

5.1 Summary and conclusion

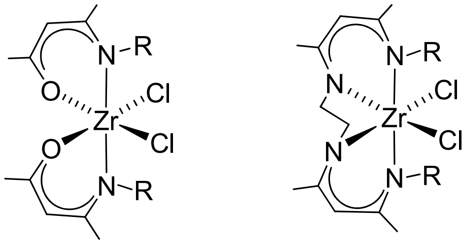
Using *nacnac* ligands with different frameworks, new zirconium complexes were synthesized via different synthetic routes and characterized. The study of their mode of coordination, their structural characteristics, their stability and their reactivity has been realized.

As our structural investigations showed, the *nacnac* ligand displays two modes of coordination to Zr metal. While an κ^2-coordination mode is observed with octahedral complexes having one or two *nacnac* ligands the presence of another η^5- coordinated ligand such as Cp or Ind forces the metal to adopt a pseudo-tetrahedral geometry where the *nacnac* ligand is found to be in an η^x-coordination to the Zr metal center. Although *nacnacs* can coordinate similar to cyclopentadienyl, they most often do not and cannot be considered their analogs.

In solution, an important dynamic isomerizing behavior via a Bailar twist was observed for the $(nacnac)_2ZrX_2$ complexes. The reactivity of these complexes is still ambiguous, but no reactivity has been observed in carbozirconation of alkenes or in alkylation reactions. This is most probably due to the steric crowding blocking the access towards the active coordination sites of the metal complex and thus prohibiting the exchange of the chlorides with other reagents. The observed C-H activation of the *nacnac*^{R,R} is most likely a consequence of this steric congestion.

5.2 Future work

Based on the results we obtained regarding the reactivity of the (*nacnac)*$_2$ZrX$_2$, future work will focus on the modification of the ligand. Although they increase the number of possible coordination isomers, unsymmetrical ligands might prove helpful in reducing steric congestion. One example of a less sterically demanding ligand, are *acnac* ligands, where only one keto group is exchanged versus imine, might be useful.



Scheme 5.1 Future work

Another approach would be the bridging of the two *nacnac* ligands, e. g. by an ethylene bridge. The presence of the bridge, in particular in the case of cyclic bridges, might slow the isomerisation via the Bailar twist. Bridiging the ligands might also be helpful to decrease the steric encumbrance around the reactive coordination sites by a "backbending" of the ligand. We are currently investigating the synthesis of these ligands using different types of aliphatic amines.

In hydrozirconation, we intend to use the developed in situ generation of the reagent to screen other alcohols than C_6F_5OH and to test the reactivity towards other alkenes.

CHAPTER 6

Experimental

6.1 General experimental:

All reactions were carried out under an inert atmosphere using Schlenk and glove box techniques under a purified N_2 atmosphere.. $ZrCl_4(THF)_2$,[79] CpLi, IndLi,[80] *nacnac*^{xyl}H, *nacnac*^{xyl}Li(THF),[45] $Cp_2Zr(OPh)_2$[77] and $Cp_2Zr(OC_6F_5)_2$[78] were prepared according to literature procedures. $ZrCl_4$, Cp_2ZrCl_2, Cp_2ZrH_2, and others chemicals were purchased from common commercial suppliers. ^1H and ^{13}C NMR spectra were acquired on a Bruker AMX 300 or Bruker AV 400 spectrometer. ^{19}F NMR spectra were acquired on a Bruker Avance 300. Chemical shifts were referenced to the residual signals of the deuterated solvents (C_6D_6: ^1H: δ 7.16 ppm, ^{13}C: δ 128.38 ppm; $CDCl_3$: ^1H: δ 7.26 ppm, ^{13}C: δ 77.00 ppm and C_7D_8: ^1H: δ 2.09 ppm, ^{13}C: δ 20.40 ppm). THF was distilled from sodium/benzophenone, all others solvents were dried by passage through activated aluminum oxide (MBrown SPS) and de-oxygenated by repeated extraction with nitrogen. C_6D_6 was dried over sodium, $CDCl_3$ was dried over CaH_2 and both were distilled under reduced pressure, and then degassed by three freeze-pump-thaw cycles. Styrene, ethanol and 1-hexene were evacuated under vacuum and dried over 4Å molecular sieves. Low-temperature NMR spectra were recorded using a Bruker AV 500 spectrometer in $CDCl_3$ solution using a toluene solution in $CDCl_3$ for calibration purposes. The ^1H NMR spectra were fed into the DNMR71 program.[59] The exchange rate was obtained by comparaison of experimental and simulated spectra. Activation parameters were obtained from the Eyring plots and listed in table 3.3.

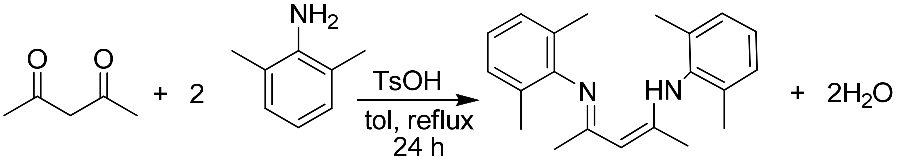
GC/MS analyses were obtained using an Agilent 6890 N spectrometer at Davit Zargarian laboratory (Université de Montréal).

Elemental analyses were performed by the Laboratoire d'analyse élémentaire (Université de Montréal).

Diffraction data for complexes **2c** was recorded on a Bruker Smart APEXII (Mo radiation) diffractometer using the APEX2 software package.[81] For complexes **2d**, **2e**, **3c** and **3d** were measured on a Bruker Proteum X8/Microstar diffractometer equipped with Cu radiation (APEX2). For **4c** was recorded on a Bruker Smart 6000 equipped with a Cu rotating Anode**.** Data reduction was performed with SAINT, the structure was solved with direct methods (SHELXTL2001). All non-hydrogen atoms were refined anisotropically using full-matrix least-squares on F^2 and hydrogen atoms refined with fixed isotropic U using a riding model (SHELXL97).[82] For **4c,** the co-crystallized solvent was identified as a disordered hexane (in agreement with NMR data), but could not be resolved and thus suppressed by application of SQUEEZE.[83]

6.2 Chapter 2

2,6-dimethyl-phenylamino-4-(2,6-dimethyl-phenyl)imino-pent-2-ene, *nacnac*^{Xyl}H, 1a.[45]



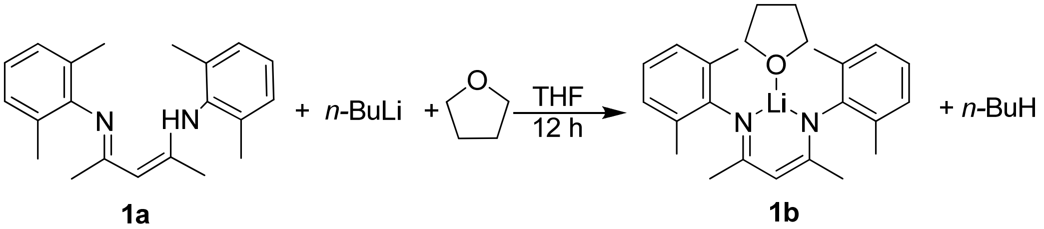
1a

Scheme 6.2.1 synthesis of *nacnac*^{Xyl}H, **1a**

Acetylacetone (12.4 g, 0.12 mol), TsOH (22.8 g, 0.12 mol) and 2,6-dimethylaniline (30 g, 0.24 mol) were combined with toluene (350 mL). The reaction mixture was then refluxed for 24 h with the help of a Dean-Stark apparatus to afford a yellow suspension. On cooling to room temperature, a white precipitate appeared. The precipitate was dissolved in 200 mL ether and 200 mL of distilled water. Then K_2CO_3 was added to neutralize the medium. The organic phase was extracted with ether, dried over Na_2SO_4 concentrated using a rota-vap and gave a brown oil. The addition of methanol followed by sonicator agitation yielded colorless crystals (18.7 g, 51%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ12.21 (bs, 1H, NH), 7.04-7.26 (m, 6 H, $Me_2C_6H_3$), 4.90 (s, 1H, $CH(C=N)_2$), 2.18 (s, 12 H, $Me_2C_6H_3$), 1.71 (s, 6H, $Me(C=N)$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 76 MHz): δ160.7 (C=N), 143.7 (*ipso* $Me_2C_6H_3$), 132.1 (*ortho* $Me_2C_6H_3$), 127.7 *(meta* $Me_2C_6H_3$*)*, 124.2 (*para* $Me_2C_6H_3$), 93.3 ($CH(C=N)_2$), 20.3 (Me(C=N)), 18.3 ($Me_2C_6H_3$). Anal. Calcd. for $C_{21}H_{26}N_2$: C, 82.31; H, 8.55; N, 9.15. Found: C, 81.67; H, 8.38; N, 9.14.

(*nacnac*^{Xyl})Li(THF), 1b.[45]



Scheme 6.2.2 synthesis of *nacnac*^{Xyl}Li(THF), 1b

To a yellow THF solution of **1a** (7.8 g, 20 mmol) a hexane solution of *n*-BuLi (2.9 M, 28 mmol) was added gradually at -78˚C. The solution becomes orange and the reaction medium was allowed to return to room temperature and was stirred for 12 h. The brown orange solution was evaporated to dryness, to give an off-white solid, which was washed with hexane to remove excess *n*-BuLi. Drying at vacuum line yielded an off-white powder (9.0 g, 94%), which was used without further purification.

^{1}H NMR (C_6D_6, 400 MHz): δ 6.90-7.1 (m, 6 H, $Me_2C_6H_3$), 4.95 (s, 1H, $CH(C{=}N)_2$), 2.89 (bm, 4H, CH_2O), 2.20 (s, 12 H, $Me_2C_6H_3$), 1.80 (s, 6H, $Me(C{=}N)$), 0.90 (bm, 4H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$ 101 MHz): δ186.1 (C=N), 157.1 (*ipso* $Me_2C_6H_3$), 128.2 (*ortho* $Me_2C_6H_3$), 127.7 (*meta* $Me_2C_6H_3$), 127.4 (*para* $Me_2C_6H_3$), 93.4 ($CH(C{=}N)_2$), 67.9 (CH_2O), 25.5 ($Me_2C_6H_3$), 18.5 ($Me(C{=}N)$), 18.3 (CH_2).

Lithium cyclopentadienide, CpLi.[80]

In a 250 mL flask equipped with a magnetic stirrer and with a fractionnal distillation apparatus, dicyclopentadiene (40 g, 0.43 mol) was heated up to 160°C. After 4 h of cracking we obtained 35 g of the colorless cyclopentadiene monomer (88%).

The obtained monomer (4.05 g, 61 mmol) was mixed with 50 mL of hexane and deprotonated by slow addition of a hexane solution of *n*-BuLi (2.89 M, 23 mL, 67 mmol).

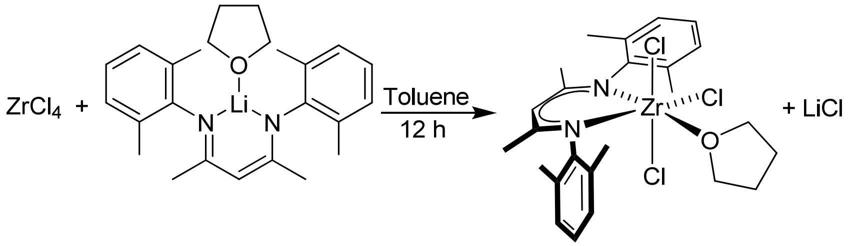
The obtained white mixture was allowed to stir for 2 h, filtered, washed with 15 mL of hexane, dried under vacuum gave a white powder (4.15 g, 98%).

^{1}H NMR (DMSO, 300 MHz): 5.32 (s, 5H, Cp).

Lithium indenide, IndLi.[80]

To a 100 mL hexane solution of indene (12.5 g, 0.19 mol), a hexane solution of *n*-BuLi (2.89 M, 6.5 ml, 0. 19 mol) were added over 25 min at -78°C. The obtained creamy mixture was allowed to return to room temperature while stirring. The obtained mixture was filtered, washed with 15 mL of hexane and dried under vacuum to yield a colorless powder (9.5 g, 70%).

(*nacnac*$^{\mathrm{Xyl}}$)ZrCl$_3$(THF), 1c



1b **1c**

Scheme 6.2.3 synthesis of (*nacnac*$^{\mathrm{Xyl}}$)ZrCl$_3$(THF), **1c**

ZrCl$_4$ (1.0 g, 2.6 mmol) and **1b** (0.60 g, 2.6 mmol) were mixed together with 30 mL of dry toluene. To the obtained mixture 4 mL of anhydrous THF were added slowly at room temperature. The obtained yellow mixture was allowed to stir for 24 h. The reaction mixture was then filtered and the yellow filtrate was concentrated to half of its volume, layered with an equal volume of hexane allowed to precipitate for 48 h. The slow evaporation of solvent gave a mixture of a yellow powder and crystals (1.43 g, 97%).

Crystals of this compound were used for X-ray structure determination and for elemental analyses

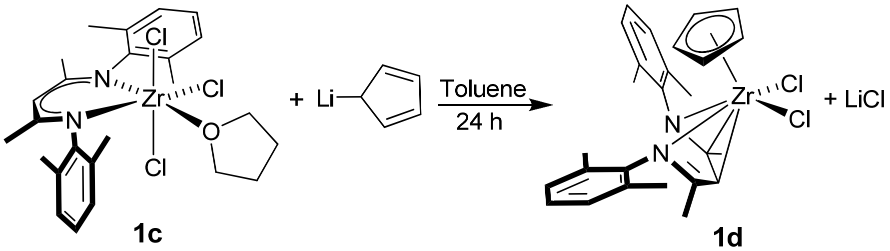
^{1}H NMR (C_6D_6, 300 MHz): δ 6.94 (m, 6 H, $Me_2C_6\mathit{H_3}$), 5.55 (s, 1H, C*H*(C=N)$_2$), 3.80 (bm, 4H, CH_2O), 2.44 (s, 12 H, $\mathit{Me_2}C_6H_3$), 1.45 (s, 6H, *Me*(C=N)), 1.01 (bm, 4H, CH_2).

^{1}H NMR ($CDCl_3$, 300 MHz) : δ 7.09 (m, 6H, $Me_2C_6\mathit{H_3}$), 5.90 (s, 1H, CH(C=N)), 3.95 (bm, 4H, THF), 2.33 (s, 12H, $\mathit{Me_2}C_6H_3$), 1.81 (bm, 4 H, CH_2O), 1.76 (s, 6H, *Me*(C=N))

^{13}C{^{1}H} NMR (C_6D_6, 76MHz): δ168.9 (C=N), 145.2 (*ipso* $Me_2\mathit{C_6}H_3$), 134.1 (*ortho* $Me_2C_6\mathit{H_3}$), 129.1 *(meta* $Me_2\mathit{C_6}H_3$*)*, 126.7 (*para* $Me_2\mathit{C_6}H_3$), 107.2 (CH(C=N)$_2$), 77.6 (*C*H_2O), 25.5 (CH_2), 24.26 (*Me*(C=N)), 19.9 ($\mathit{Me_2}C_6H_3$).

Anal. Calcd. for $C_{25}H_{33}Cl_3ZrN_2O$: C, 52.21; H, 5.78; N, 4.87. Found: C, 51.20; H, 5.45; N, 4.46.

(nacnac$^{\mathrm{Xyl}}$**)ZrCl$_2$(Cp), 1d**



1c **1d**

Scheme 6.2.4 synthesis of *nacnac*$^{\mathrm{Xyl}}$Zr(Cp)Cl_2 (THF), **1d**

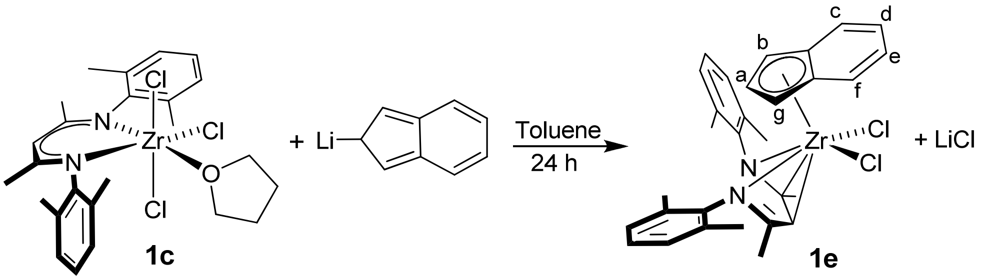
1c (0.50 g, 0.87 mmol) and CpLi (70 mg, 0.96 mmol) were combined together in a Schlenk flask. 30 mL of toluene were added resulting in a red mixture. The reaction was allowed to stirr for 24 h during which time a brown precipitate appeared. The resulting mixture was filtered over dried celite and the brown precipitate was washed with 3 x 5 mL of toluene. The toluene fractions were combined, concentrated to half their volume and then layered with a double volume of hexane. After 3 days a precipitate formed at the bottom and some crystals appeared on the wall of the Schlenk flask. Crystals of this compound were used for X-ray structure determination and for elemental analysis. The precipitate was separated by decantation, washed with 3 x 5 mL of hexane and dried on a vacuum line (0.15 g, 33%).

^{1}H NMR (C_6D_6, 300 MHz): δ 6.93-6.75 (m, 6H, $Me_2C_6\mathit{H_3}$), 6.33 (s, 5H, Cp), 5.35 (s, 1H, $CH(C{=}N)_2$), 2.66 (s, 6H, $\mathit{Me_2}C_6H_3$), 1.69 (s, 6H, $\mathit{Me_2}C_6H_3$), 1.59 (s, 6 H, *Me*(C=N)).

$^{13}C\{^1H\}$ NMR (C_6D_6, 76 MHz): δ 165.3 (C=N), 147.1 (*ipso* $Me_2\mathit{C_6}H_3$), 130.5 (*para* $Me_2\mathit{C_6}H_3$), 128.8 (*meta* $Me_2\mathit{C_6}H_3$), 126.1 (*ortho* $Me_2\mathit{C_6}H_3$), 118.1(Cp), 92.4 (*C*H(C=N)$_2$), 22.8 ($\mathit{Me_2}C_6H_3$), 21.3 ($\mathit{Me_2}C_6H_3$), 19.9 (*Me*(C=N)).

Anal. Calcd. for $C_{26}H_{30}N_2Cl_2Zr$: C, 58.47; H, 5.99; N, 5.07; Found: C, 58.60; H, 5.60; N, 5.30.

nacnac^{Xyl} ZrCl$_2$Ind, 1e



Scheme 6.2.5 synthesis of *nacnac*^{xyl}Zr(Ind)Cl$_2$ (THF), **1e**

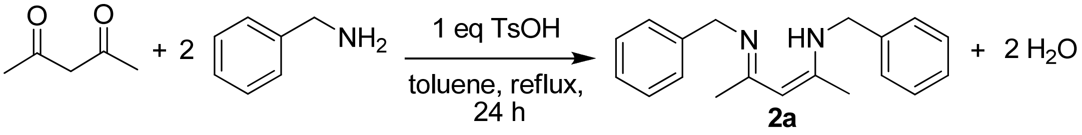
1c (0.19 g. 0.87 mmol) and IndLi (0.043 g, 0.36 mmol) were combined together in a Schlenk flask. 30 mL of toluene were added to the mixture resulting in a red mixture. The reaction was allowed to stir for 24 h during which time an orange precipitate appeared. The resulting mixture was filtered over dried celite and the brown precipitate was washed with 3 x 5 mL of toluene. The toluene fractions were combined and concentrated to half their volume then layered with a double volume of hexane. After 3 days a precipitate formed at the bottom and some crystals appeared on the wall of the Schlenk flask. Crystals of this compound were used for X-ray structure determination. The precipitate was separated by decantation, washed with 3 x 5 mL of hexane and dried on a vacuum line (20 mg, 10%).

^{1}H NMR (C_6D_6, 300 MHz): 7.34 (m, 4H, $H_{d\text{-}g}$Ind), 6.93 (m, 6H, $Me_2C_6\mathit{H_3}$), 6.61 (t, *J* = 2 Hz, 1H, H_aInd), 6.42 (d, *J* = 2 Hz, 2H, H_b & H_cInd), 5.20 (s, 1H, C*H*(C=N), 2.68 (s, 6H, $\mathit{Me_2}C_6H_3$), 1.66 (s, 6H, $\mathit{Me_2}C_6H_3$), 1.58 (s, 6H, *Me(*C=N)).

^{1}H NMR ($CDCl_3$, 300 MHz) **:** δ 7.13 (m, 4H, $H_{d\text{-}g}$Ind), 7.02 (m, 6H, $Me_2C_6\mathit{H_3}$), 6.68 (t, *J* = 2 Hz, 1H, H_aInd), 6.42 (d, *J* = 2 Hz, 2H, H_b & H_cInd), 5.64 (s, 1H, C*H*(C=N), 2.61 (s, 6H, *Me*Ph), 2.05 (s, 6H, $\mathit{Me_2}C_6H_3$), 1.94 (s, 6H, *Me(*C=N)).

6.3 Chapter 3

2-(Benzyl)amino-4-(benzyl)imino-pent-2-ene, *nacnac*^{Bn}H, 2a



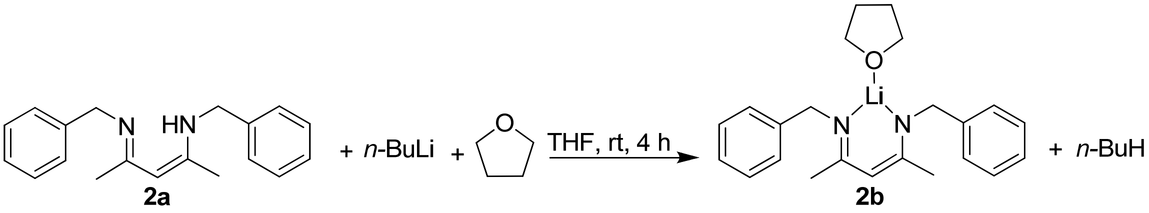
Scheme 6.3.1 synthesis of *nacnac*^{Bn}H, **2a**

Acetylacetone (2.62 g, 26.2 mmol), TsOH (5.00 g, 26.2 mmol) and benzylamine (2.92 g, 26.2 mmol) were combined with toluene (250 mL). The resulting white suspension was refluxed for 3 h with the help of a Dean-Stark apparatus to afford a yellow solution. After cooling to room temperature, a second equivalent of benzylamine (2.92 g, 26.2 mmol) was added. The reaction mixture was then refluxed for 24 h. Upon cooling to room temperature, an orange precipitate appeared which was separated by filtration and dissolved into a mixture of ether and water then the medium was neutralised by K_2CO_3 (3.6 g, 26.2 mmol). The organic phase was extracted with ether, dried over Na_2SO_4 and separated by filtration. Evaporation of the solvent gave brown oil, which was dissolved in EtOH (10 mL). Colourless crystals formed at –20 °C after 1 day (6.0 g, 82%). Spectral data matched previous reports, the compound is pure according to NMR.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.49 (bs, 1H, N*H*), 7.22-7.30 (m, 10H, Ph), 4.64 (s, 1H, C*H*(C=N)$_2$), 4.46 (s, 4H, C*H*$_2$), 1.95 (s, 6H, *Me* (C=N)).

^{13}C{H} NMR ($CDCl_3$, 101 MHz): δ 161.1 (*C*=N), 140.8 (*ipso* Ph), 128.3 (*ortho* Ph), 127.2 (*para* Ph), 126.4 (*meta* Ph), 95.1 (*C*H(C=N)$_2$), 50.7(C*H*$_2$), 19.6 (*Me*(C=N)).

nacnac^{Bn}Li(THF), 2b.



Scheme 6.3.2 synthesis of *nacnac*^{Bn}Li(THF), **2b**

A hexane solution of *n*-BuLi (1.36 mL, 2.9 M, 3.95 mmol) was added over 25 minutes at room temperature to a yellow THF solution of **2a** (1.0 g, 3.6 mmol). The yellow orange solution was allowed to stir for 4 hrs. The volatiles were removed and the remaining solid was washed with 2 x 5 mL of hexane. The solid was dried under reduced pressure to yield a colorless powder (1.25 g, 90%) and used without further purification.

^{1}H NMR ($CDCl_3$,400 MHz): δ 7.22-7.30 (m, 10H, Ph), 4.54 (s, 1H, C*H*(C=N)$_2$), 4.42 (s, 4H, C*H*$_2$Ph), 3.74 (m, 4H, THF), 1.93 (s, 6H, *Me*(C=N)), 1.83 (m, 4H, THF).

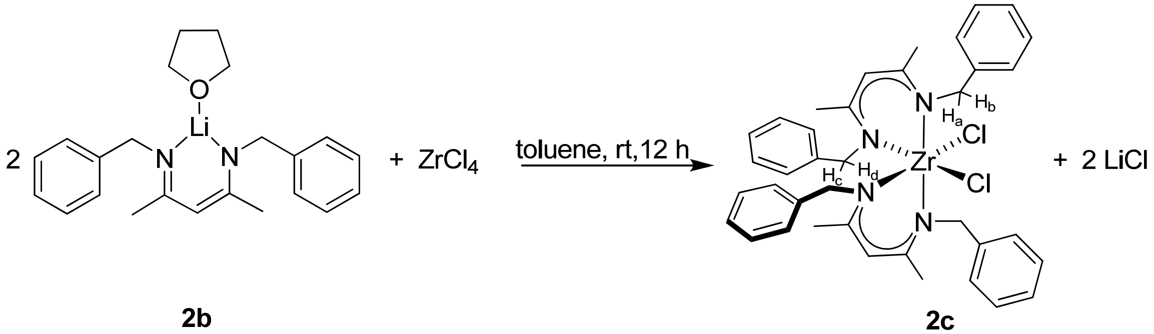
^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 161.0 (C=N), 140.9 (*ipso* Ph) 128.3 (*ortho*Ph), 127.2 (*para* Ph), 126 (*meta* Ph), 95.1 (*C*H(C=N)$_2$), 67.9 (THF), 50.7 (*C*H$_2$(Ph)), 25.6 (THF), 19.6 (*Me*(C=N)).

^{1}H NMR (C_6D_6,400 MHz): δ 7.00-7.30 (m, 10H, Ph), 4.82 (s, 1H, C*H*(C=N)$_2$), 4.60 (s, 4H, C*H*$_2$Ph), 2.86 (m, 4H, THF), 2.09 (s, 6H, *Me*(C=N)), 0.98 (m, 4H, THF).

^{13}C{^{1}H} NMR (C_6D_6, 101 MHz): δ 165.8 (C=N), 145.4 (*ipso* Ph) 128.5 (*ortho*Ph), 127.5 (*para* Ph), 126.0 (*meta* Ph), 93.8 (*C*H(C=N)$_2$), 67.5 (THF), 50.7 (*C*H$_2$(Ph)), 25.1 (THF), 22.0 (*Me*(C=N)).

(*nacnac*$^{\mathrm{Bn}}$)$_2$ZrCl$_2$, 2c.

Method 1:



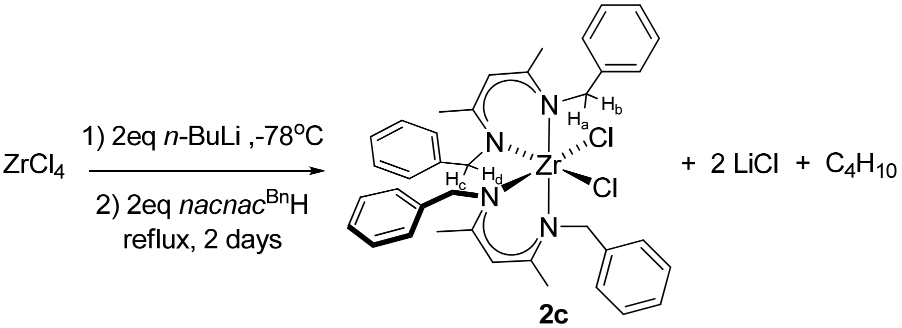
2b

2c

Scheme 6.3.3 Synthesis of (*nacnac*$^{\mathrm{Bn}}$)$_2$ZrCl$_2$, **2c.**(*Method1)*

In a dry schlenk ZrCl$_4$ (0.34 g, 1.4 mmol) and **2b** (1.0 g, 2.8 mmol) were mixed together, to which we added 10 mL of toluene under stirring. After 24 hours of stirring at room temperature the obtained orange mixture was filtered. The yellow filtrate was concentrated to half its volume and the desired product was precipitated by addition of 15 mL of hexane. The yellow precipitate was separated by filtration and dried on a vacuum line to yield **2c** (0.35 g, 0.50 mmol, 35%).

Method 2:



2c

Scheme 6.3.4 Synthesis of (*nacnac*$^{\mathrm{Bn}}$)$_2$ZrCl$_2$, **2c.**(*Method2)*

A hexane solution of *n*-BuLi (2.9 M, 5.4 mmol) was added to a toluene suspension of $ZrCl_4$ (0.62 g, 2.7 mmol) at -78°C. The mixture was allowed to warm to room temperature and then stirred for another 12 h. To the obtained brown mixture, 15 mL of a toluene solution of **2a** (5.4 mmol, 1.5 g) were gradually added. The mixture was refluxed for 2 days under reduced pressure at a temperature of 90˚C. The obtained yellow mixture was cooled to room temperature, 20 mL of dichloromethane were added and the mixture was filtered. The combined volatiles were removed under vacuum, yielding a yellow powder **2c** (1.5 g, 75%).

^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.20-7.30 (m, 20H, Ph), 5.65 (bs, 2H, CH_2Ph), 5.62 (bs, 2H, CH_2Ph), 5.32 (s, 2H, $CH(C{=}N)_2$), 4.61(bs, 2H, CH_2Ph), 4.56 (bs, 2H, CH_2Ph), 1.92 (s,12H, *Me*(C=N)).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz**,** 298 K): δ 167.1 (C=N), 139.5 (*ipso* Ph), 128.2 (*ortho* Ph), 127.2 (*para* Ph), 126.5 (*meta* Ph), 108.1 ($CH(C{=}N)_2$), 54.9 (CH_2Ph), 23.2 (*Me*(C=N)).

Anal. Calcd for $C_{38}H_{42}ZrN_4Cl_2$: C, 63.66; H, 5.91; N, 7.82. Found: C, 63.00; H, 6.19; N, 7.69.

Variable temperature NMR studies

At -50 ˚C the exchange between the two *cis* enantiomers of this complex is slow enough to see the separation of the broadened peaks.

^1H NMR (500 MHz, $CDCl_3$, 223K): δ 7.20-7.30 (m, 20H, *Ph,*), 6.06 (bd, 2H, H_a), 5.37 (s, 2H, $CH(C{=}N)_2$), 5.14 (bd, 2H, H_b), 4.96 (bd, 2H, H_c), 4.23 (bd, 2H, H_d), 2.05 (s, 6H, *Me*(C=N)), 1.80 (s, 6H, *Me*(C=N)).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz, 223 K): δ 168.0 (*C*=N), 165.5 (*C*=N), 139.4 (*ipso* Ph), 135.1 (*ipso* Ph), 128.8 (*ortho* Ph), 128.4 (*ortho* Ph), 128.1 (*para* Ph), 127.3 (*para* Ph), 126.8 (*meta* Ph), 126.4 (*meta* Ph), 108.3 (CH(C=N)$_2$), 54.3 (CH$_2$Ph), 24.4 (CH$_2$Ph), 22.7 (*Me*(C=N)), 22.3 (*Me*(C=N)).

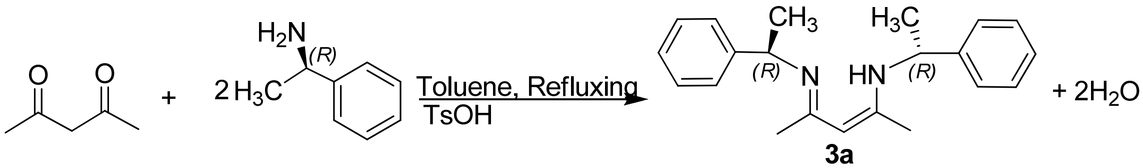
Crystals of this compound were obtained by slow diffusion of hexane into a THF solution of the complex at 25 °C

Table 6.1 Details of X-ray Diffraction Studies

	2c	**4c**	**3c**	**3d**	**2d**	**2e**
Formula	$C_{38}H_{42}Cl_2N_4Zr$	$C_{34}H_{58}Cl_2N_4Zr$	$C_{42}H_{50}Cl_2N_4Zr$	$C_{42}H_{49}ClN_4Zr$	$C_{40}H_{48}N_4Zr$	$C_{42}H_{52}N_4O_2Zr$
M_w (g/mol); F(000)	716.88; 1488	684.96; 1456	772.98; 1616	736.52; 772	676.04; 1424	736.10; 3104
Crystal color and form	yellow block	colorless block	yellow fragment	red plate	yellow plate	colorless plate
Crystal size (mm)	0.12x0.06x0.03	0.60x0.28x0.10	0.10x0.08x0.04	0.06x0.06x0.04	0.06x0.05x0.02	0.06x0.04x0.02
T (K); wavelength	200; 0.71073	150; 1.54178	150; 1.54178	150; 1.54178	150; 1.54178	150; 1.54178
Crystal System	Tetragonal	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space Group	$P4_32_12$	C2/c	$P2_1$	$P2_1$	$P2_1/n$	$P2_12_12_1$
Unit Cell: a (Å)	8.7244(5)	20.2320(8)	13.6460(3)	13.5011(18)	15.2045(13)	11.6079(9)
b (Å)	8.7244(5)	9.0276(4)	20.5189(5)	9.1289(11)	9.6321(8)	15.7760(12)
c (Å)	47.453(6)	22.539(1)	14.4588(4)	15.1108(18)	24.0981(19)	42.516(3)
β (°)	90	91.250(2)	108.891(1)	95.413(7)	97.213(4)	90
V (Å^3); Z; $d_{\text{calcd.}}$ (g/cm^3)	3611.9(6); 4;1.318	4115.7(3); 4; 1.105 [a]	3830.41(16);4; 1.340	1854.1(4); 2; 1.319	3501.3(5); 4; 1.283	7785.8(10); 8; 1.256
θ range (°); completeness	1.7-27.6; 1.0	3.9-72.3; 0.99	3.2-58.0; 0.99	2.9-68.1; 0.98	3.3-67.5; 1.0	2.1-67.9; 1.0
collected reflections; R_σ	99235; 0.070	53603; 0.021	60497; 0.025	27516; 0.082	54484; 0.063	137856; 0.027
unique reflections; R_{int}	4177; 0.144	4013; 0.036	10532; 0.046	6510; 0.079	6282; 0.116	14075; 0.060
μ (mm^{-1}); Abs. Corr.	0.484; multi-scan	3.554; multi-scan	3.893; multi-scan	3.348; multi-scan	2.813; multi-scan	2.611; multi-scan
R1(F); wR(F^2) (I > 2σ(I))	0.039; 0.069	0.034; 0.098	0.025; 0.064	0.050; 0.127	0.045; 0.101	0.027; 0.072
R1(F); wR(F^2) (all data)	0.075; 0.078	0.034; 0.098	0.027; 0.065	0.058; 0.131	0.076; 0.117	0.029; 0.073
GoF(F^2)	0.920	1.113	1.029	0.793	1.013	1.026
Residual electron density	0.28 e$^-$/Å^3	0.40 e$^-$/Å^3	0.53 e$^-$/Å^3	1.28 e$^-$/Å^3	0.88 e$^-$/Å^3	0.31 e$^-$/Å^3

[a] co-crystallized solvent removed with SQUEEZE

2-(*R*-2-phenylethyl)amino-4-(*R*-4-phenylethyl)imino-pent-2-ene, *nacnac*^{R,R}H, 3a.



Scheme 6.3.5 Synthesis of *nacnac*^{R,R}H, **3a.**

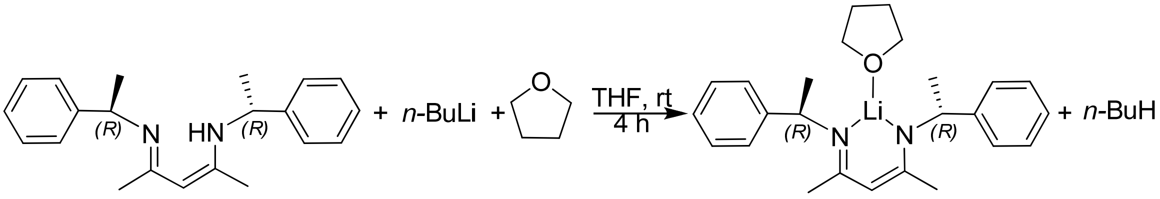
Acetylacetone (2.6 mL, 25 mmol), TsOH (4.7 g, 25 mmol) and *R*-Ph(Me)CHNH$_2$ (3.0 g, 25 mmol) were combined with toluene (250 mL). The resulting white suspension was refluxed for 3 h with the help of Dean-Stark apparatus to afford a yellow solution. After cooling to room temperature, a second equivalent of *R*-Ph(Me)CHNH$_2$ (3.0 g, 25 mmol) was added. The reaction mixture was then refluxed for 5 days. On cooling to room temperature, a brown precipitate appeared. The suspension was added to an aqueous KOH solution (5.0 g, 0.45 M) and stirred for 30 min. The phases were separated and the aqueous phase extracted twice with toluene (400 mL). The combined organic phases were dried over Na$_2$SO$_4$. Filtration and evaporation of the solvent gave brown oil, which was dissolved in EtOH (10 mL). Colourless crystals formed at –20 °C after 1 day (5.2 g, 70%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 11.89 (bs, 1H, NH), 7.20-7.35 (m, 10H, Ph), 4.68 (q, 2H, *J* = 7 Hz, C*H*(Me)Ph), 4.48 (s, 1H, C*H*(C=N)$_2$), 1.82 (s, 6H, *Me*(C=N)), 1.49 (d, 6H, *J* = 7 Hz CH(*Me*)Ph). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz) δ 159.7 (C=N), 146.9 (*ipso* Ph), 128.4 (*ortho* Ph), 126.3 (*para* CH(Me)*Ph),* 126.2 (*meta* Ph) 95.2 (*C*H(C=N)$_2$), 55.9 (*C*H(Me)Ph), 25.8 (*Me*(C=N)), 19.5 (CH(*Me*)Ph). Anal. Calcd. for C$_{21}$H$_{26}$N$_2$: C, 82.31; H, 8.55; N, 9.15. Found: C, 81.67; H, 8.38; N, 9.14. Mp. 43.0-43.8 °C.

2-(*S*-2-phenylethyl)amino-4-(*S*-4-phenylethyl)imino-pent-2-ene, *nacnac*^{S,S}H, *SS*-3a.

Following the same procedure as for the *R*-enantiomer, ***SS*-3a** was obtained in 67% yield.

Anal.Calcd. for $C_{21}H_{26}N_2$: C, 82.31; H, 8.55; N, 9.15. Found: C, 81.99; H, 8.68; N, 9.07.

***nacnac*$^{(R,R)}$-Li(THF), 3b.**



3a **3c**

Scheme 6.3.6 Synthesis of *nacnac*^{R,R} Li(THF), **3b.**

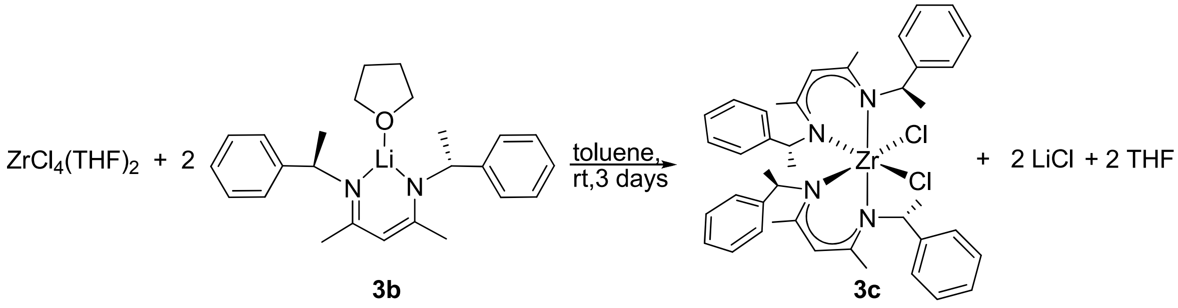
A solution of *n*-BuLi in hexane (2.9 M, 0.9 mmol) was added gradually over 10 minutes to a yellow THF solution of **3a** (0.25 g, 0.82 mmol). The yellow orange solution was allowed to stir for 4 hours at room temperature, volatiles were evaporated and a brown oil is obtained (0.30 g, 92%), which was used without further purification.

^{1}H NMR (400 MHz, C_6D_6): δ 7.16-7.42 (m, 10H, *Ph*), 4.81 (q, 2H, *J*= *7*, C*H*(Me)Ph), 4.71 (s, 1H, C*H*(C=N)$_2$),3.00(m, 4H, THF), 2.07 (s, 6H, *Me*(C=N)), 1.44 (d, 6H, *J*=7, CH(*Me*)Ph), 0.97 (m, 4H, THF).

^{13}C{^{1}H} NMR (C_6D_6, 101 MHz): δ 161.0 (C=N), 150.2 (*ipso* Ph), 128.4 (*ortho* Ph), 126.6 (*para Ph*), 125.8 (*meta* Ph), 93.7 (*C*H(C=N)$_2$), 67.6 (*C*H(Me)Ph), 57.2 (THF), 25.5 (THF), 24.6 (CH(*Me*)Ph), 22.3 (*Me*(C=N)).

Anal. Calcd. for $C_{25}H_{33}LiN_2O$: C, 78.10; H, 8.65; N, 7.29. Found: C, 72.99; H, 8.79; N, 7.61.

($nacnac^{R,R}$)$_2$ZrCl$_2$, 3c.



Scheme 6.3.7 Synthesis of ($nacnac^{R,R}$)$_2$ZrCl$_2$, **3c.**

To a mixture of $ZrCl_4(THF)_2$ (0.77 g, 2.04 mmol) and (1.57 g, 4.08 mmol) of **3b** toluene was added under stirring. The obtained orange mixture was allowed to react for 3 days at room temperaturre. The mixture was filtered and the orange filtrate was concentrated to half its volume and the desired product was precipitated by addition of 15 mL of hexane. The crystallization of the product by slow diffusion of hexane into a saturated toluene solution of the product gave by mainly yellow (I) and few red crystals (II). (1.1 g, 65%)

Analysis on yellow crystals of **3c** was performed by removing the red crystals, **3d**, by hand. The red crystals, **3d,** could not be obtained in sufficient quantity for a full characterization but allowed only X-ray structure determination.

For **3c**: (Peaks are severely broadened. both diastereomers *a* and *b* are present, see crystal structure and low temperature NMR)

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.08-7.4 (m, 20H, *Ph*), 6.74 (bm, 2H, *b* C*H*(Me)Ph), 6.64 (bm, 2H, *a* C*H*(Me)Ph), 6.14 (bm, 2H, *a* C*H*(Me)Ph), 5.26 (bs, *a*+*b* C*H*(C=N)$_2$), 4.48 (bm, 2H, *b* C*H*(Me)Ph), 2.15-1.63 (m, 24H, Me). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, 298 K): δ 168.1 (C=N), 167 (C=N), 162.9 (C=N), 143.9 (*ipso* Ph), 143.4 (*ipso* Ph), 110.8 (*C*H(C=N)$_2$), 104.3 (*C*H(C=N)$_2$), 62 (*C*H(Me)Ph), 59.4 (*C*H(Me)Ph), 57.6 (*C*H(Me)Ph), 27.2 (CH(*Me*)Ph), 25.3 (CH(*Me*)Ph), 19.8 (*Me*(C=N)), 18.2 (*Me*(C=N)), 17 (*Me*(C=N)).

Anal. Calcd. for $C_{42}H_{50}N_2ZrCl_2$: C, 65.26; H, 6.52; N, 7.01. Found: C, 64.93; H, 6.70 ; N, 7.13.

^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 7.08-7.4 (m, 20H, *Ph*), 6.45-6.43 (bm, 2H, C*H*(Me)Ph), 4.88 (bs, 2H, C*H*(C=N)$_2$), 4.74 (bm, 2H, C*H*(Me)Ph), 2.07-1.42 (m, 24H, Me).

^{1}H NMR (toluene-*d*$_8$, 400 MHz, 298 K): δ 7.08-7.8 (m, 20H, *Ph*), 6.37 (bm, 1H, C*H*(Me)Ph), 6.28 (bm, 1H, C*H*(Me)Ph), 4.79 (bs, 2H, C*H*(C=N)$_2$), 4.68 (bm, 2H, C*H*(Me)Ph), 2.05-1.44 (m, 24H, Me). ^{13}C{^{1}H} NMR (toluene-*d*$_8$, 101 MHz, 298K): δ 132.7 (*ipso* Ph), 124.6 (*ortho* Ph), 123.7 (*para* Ph), 121.7 (*meta* Ph), 103.6 (*C*H(C=N)$_2$), 91.5, 55.6, 55.1, 30.2 (*C*H(Me)Ph), 27.3 (CH(*Me*)Ph), 20.1, 18.1 (*Me*(C=N)).

^{1}H NMR (toluene-*d*$_8$, 400 MHz, 373 K): δ 6.96-7.41 (m, 20H, *Ph*), 4.70-6.38 (bm, 4H, C*H*(Me)Ph), 4.79 (bs, 2H, C*H*(C=N)$_2$), 1.82-1.44 (m, 24H, Me). ^{13}C{^{1}H} NMR (toluene-*d*$_8$, 101 MHz, 373K): δ 205.1 (C=N), 132.7 (*ipso* Ph), 124.6 (*ortho* Ph), 123.7 (*para* Ph), 121.7 (*meta* Ph), 107.1 (*C*H(C=N)$_2$), 100.7 (*C*H(Me)Ph), 27.3 (CH(*Me*)Ph), 18.9 (*Me*(C=N)).

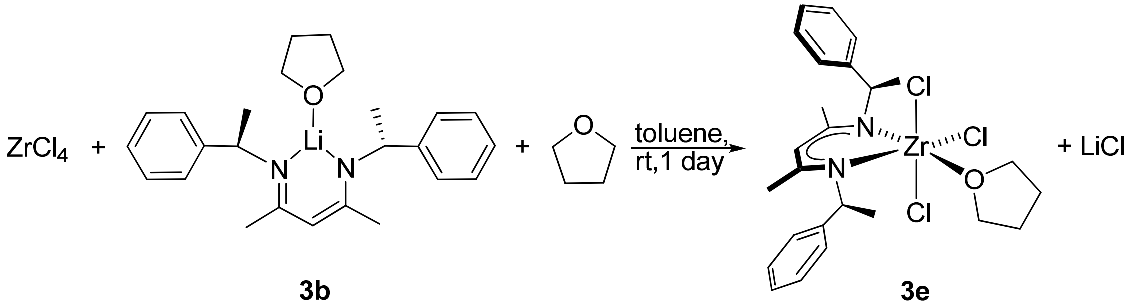
Low temperature NMR at -50 ˚C was performed to identify the two diastereoisomers *a* (67%) and *b* (33%) of this product.

^{1}H NMR (500 MHz, $CDCl_3$, 223 K), stereoisomer *a*: δ 7.85-7.07 (m, 20H, *Ph*), 6.65(q, *J* = 7 Hz, 2H, C*H*(Me)Ph,), 6.12 (q, *J* = 7 Hz, 1H, C*H*(Me)Ph), 5.29 (s, 2H, C*H*(C=N)$_2$), 1.92 (d, *J* = 7 Hz, 6H, CH(*Me*)Ph,), 1.77 (s, 6H, *Me*(C=N), 1.69 (s, 6H, *Me*(C=N), 1.61 (d, *J* = 7 Hz, 6H, CH(*Me*)Ph). Stereoisomer *b:* δ 7.85-7.07 (m, 20H, Ph), 6.74 (q, *J* = 7 Hz, 1H, C*H*(Me)Ph,), 5.28 (s, 1H, C*H*(C=N)$_2$), 4.83 (q, *J* = 7 Hz, 0.5H, C*H*(Me)Ph), 2.15 (d, *J* = 7

Hz*,* 3H, CH(*Me*)Ph), 2.01 (s, 3H, *Me*(C=N), 1. 90 (s, 3H, *Me*(C=N), 1.80 (d, *J* = 7 Hz*,* 3H, CH(*Me*)Ph*)*.

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz, 223 K) for both a and b 168.2, 167 (C=N), 143.9, 143.6, 143.2, 128.4, 127.9, 127.7, 127.5, 126.9, 126.8, 126.5, 126.3, 126.2, 126.1, 126.0, 125.9 (Ph), 111.1 (*C*H(C=N)$_2$), 104.2 *(C*H(C=N)$_2$), 62.33, 59.5, 59.2, 57.5 (*C*H(Me)Ph), 27.3, 26.7, 25.6, 25.3, 25.2, 19.5, 17.9, 17.1 (*Me*(C=N)).

(*nacnac*^{R,R})ZrCl$_3$(THF), 3e.



Scheme 6.3.8 Synthesis of (*nacnac*^{R,R}) ZrCl$_3$(THF), **3e.**

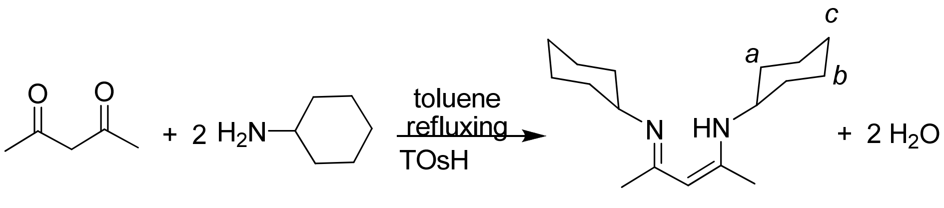
A toluene suspension of $ZrCl_4$ (0.30 g, 2.6 mmol) was added to a mixture of a red toluene solution of **3b** (0.5 g in 20 mL, 2.6 mmol) and 3 mL of THF. The obtained orange mixture was allowed to react for 1 day at room temperature. The brown mixture was filtered and the precipitate was extracted with 2 x 5 mL of toluene. The volatiles were removed and a brown precipitate is obtained (0.45 g, 35%).

^1H NMR (400 MHz, $CDCl_3$): δ 7.01-7.17 (m, 10H, *Ph*), 6.94 (bm, 2H, C*H*(Me)Ph), 5.56 (s, 1H, C*H*(C=N)$_2$), 3.18 (m, 4H, THF), 2.45 (s, 6H, *Me*(C=N), 1.46 (d, 6H, *J* = 7 Hz, CH(*Me*)Ph), 1.03 (m, 4H, THF).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 144.9 (C=N), 143.6 (*ipso* Ph), 128.4 (*ortho* Ph), 127.6 (*para Ph*), 126.8 (*meta* Ph), 86.6 (*C*H(C=N)$_2$), 59.4 (*C*H(Me)Ph), 57.5 (THF), 25.5 (THF), 25.3 (CH(*Me*)Ph), 25.1 (*Me*(C=N)).

Anal. Calcd. for $C_{25}H_{33}N_2ZrCl_3O$: C, 52.21.14; H, 5.84; N, 4.87. Found: C, 51.52; H, 5.78 ; N, 4.68.

2-(cyclohexyl)amino-4-(cyclohexyl)imino-pent-2-ene, *nacnac*^{cy}H, 4a.



4a

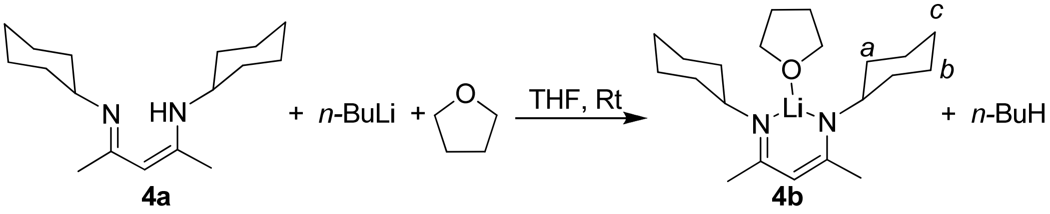
Scheme 6.3.9 Synthesis of *nacnac*^{Cy}H, **4a.**

Acetylacetone (1.00 g, 10 mmol), TsOH (1.9 g, 10 mmol) and cyclohexylamine (1.0 g, 10 mmol) were combined with toluene (100 mL). The resulting white suspension was refluxed for 3 h with the help of Dean-Stark apparatus to afford a colorless solution. After cooling to room temperature, a second equivalent of cyclohexylamine (1.0 g, 10 mmol) was added. The reaction mixture was then refluxed for 3 days. Upon cooling to room temperature, a colorless precipitate appeared which was separated by filtration and mixed with 100 mL ether and 100 mL of an aqueous solution of KOH (5.6 g, 100 mmol). The organic phase was extracted with ether, dried by adding Na_2SO_4 and concentrated using the rota-vap. The obtained yellow liquid was allowed to cool down slowly to room temperature to yield colorless crystals (1.8 g, 69%). The spectral data agreed with literature and the compound was used without further purification.

^{1}H NMR (CDCl$_3$, 400 MHz, 298 K): δ 11. 72 (bs, 1H, NH), 4.44 (s, 1H, CH(C=N)$_2$), 3.32-3.35 (m, 2H,CH(Cy)), 1.90 (s, 6H, Me(C=N)), 1.80-1.35 (m, 20H, Cy).

^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, 298 K): δ 158.4 (*C*=N), 93.7(*C*H(C=N)$_2$), 54.1 (*C*H$_{Cy}$), 34.6 (*C*H$_{2a}$), 25.7 (*C*H$_{2b}$), 25.7 (*C*H$_{2c}$), 18.8 (*C*H$_3$).

***nacnac*^{Cy}Li(THF), 4b.**



Scheme 6.3.10 Synthesis of *nacnac*^{Cy}Li(THF), **4b.**

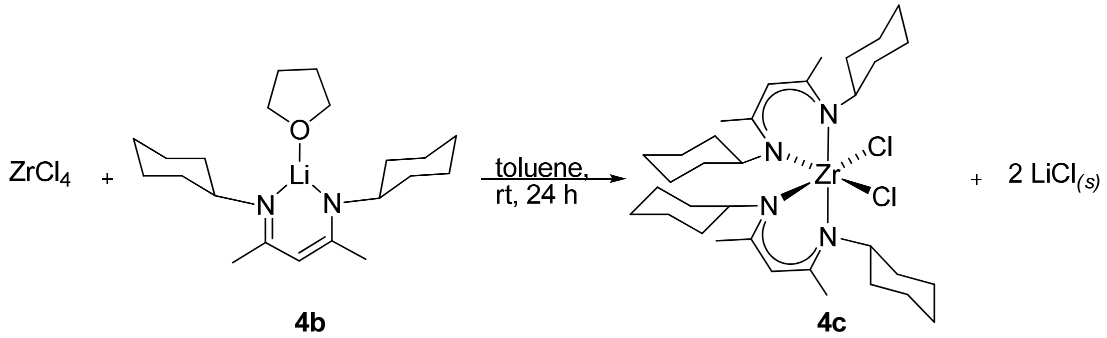
To a yellow THF solution of **4a** (1.5 g, 5.8 mmol) a hexane solution of *n*-BuLi (2 mL, 2.9 M, 5.8 mmol) was added gradually at room temperature. After 4 hours of stirring the solution turns orange. The volatiles were removed under reduced pressure to yield a yellow solid which when dried gave (1.9 g, 96%) of **4b**, used without further purification.

^{1}H NMR (C$_6$D$_6$, 400 MHz, 298 K): δ 4.56 (s, 1 H, C*H*(C=N)$_2$), 3.40-3.44 (m, 6 H, Cy C*H* & C*H$_2$*O), 2.16 (s, 6 H, C*H$_3$*), 1.77-1.3 (m, 24 H, THF & Cy C*H*$_2$)

^{13}C{^{1}H} NMR (C$_6$D$_6$, 101 MHz, 298 K): δ 158.0 (*C*=N), 95.0 (*C*H(C=N)$_2$), 54.6 (THF), 54.4 (Cy *C*H), 34.6 (*C*H$_{2a}$), 25.7 (*C*H$_{2b}$), 25.7 (*C*H$_{2c}$), 24.5 (THF), 18.8 (*C*H$_3$).

Anal. Calcd. for C$_{21}$H$_{37}$LiN$_2$O: C, 74.08; H, 10.95; N, 8.23. Found: C, 72.10; H, 10.85; N, 8.14.

(*nacnac*^{cy})$_2$ZrCl$_2$, 4c.



Scheme 6.3.11 Synthesis of (*nacnac*^{cy})$_2$ZrCl$_2$, **4c.**

In a dry schlenk ZrCl$_4$ (0.34 g, 1.5 mmol) and **4b** (1.0 g, 3.0 mmol) were mixed together, to which we added 10 mL of toluene under stirring. After 24 hours of stirring at room temperaturre the obtained orange mixture was filtered. The red filtrate was concentrated to half its volume and the desired product was precipitated by addition of 15 mL of hexane. The white precipitate was separated by filtration and dried on a vacuum line to yield (0.35 g, 0.52 mmol, 35%). Anal. Calcd for $C_{34}H_{58}ZrN_4Cl_2$: C, 59.62; H, 8.53; N, 8.18. Found: C, 58.98; H, 8.75; N, 7.71.

^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ 5.16 (bm, 2H, Cy C*H*), 4.95 (s, 2H, C*H*(C=N)$_2$), 4.05 (bm, 2H, Cy C*H*), 2.75 - 1.01 (m, 52H, CH$_3$ & Cy)

^{1}H NMR (CDCl$_3$, 500 MHz, 298 K): δ 5.15 (s, 2H, C*H*(C=N)$_2$), 4,75 (bm, 2H, Cy C*H*), 3.84 (bm, 2H, Cy C*H*), 1.91 (bs, 12H, CH$_3$**)**, 2.16- 1.19 (m, 40 H, Cy CH$_2$)

^{13}C{^{1}H} NMR (CDCl$_3$, 76 MHz**,** 298 K): δ 162.6 (C=N)), 111.8 (*C*H(C=N)$_2$), 35.4, 32.4, 28.1, 27.2, 26.3 (Cy *C*H), 26.5 (CH$_3$).

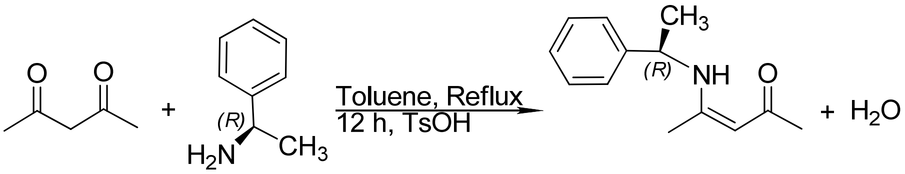
Low temperature NMR at -50 ˚C.

^{1}H NMR (CDCl$_3$, 500 MHz, 223 K): δ 5.11 (s, 2H, C*H*(C=N)$_2$), 4.70 (bm, 2H,CH_{Cy}), 3.70 (bm, 2H,CH_{Cy}), 2.16 (bs, 6H, CH_{3b}**)**, 1.91(bs, H, CH_{3a}**)**, 1.89- 1.57 (m, 40 H, Cy)

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz, 223 K): δ 162.7 (C=N)), 162.0(C=N)), 112.4 (*C*H(C=N)$_2$), 61.6, 59.9 (Cy *C*H), 34.8, 33.8, 32.2, 31.2, 30.7 (Cy *C*H$_2$), 27.5(*Me*(C=N)), 27.1, 26.4, 25.9, 25.6, 25.1 (Cy CH$_2$), 24.0 (*Me*(C=N)).

Crystals of this compound were obtained by slow diffusion of hexane into a THF solution of the complex at 25 °C.

2-(*R*-2-phenylethyl)aminopent-2- en-4-one, *acnac*^{R}, 5a.



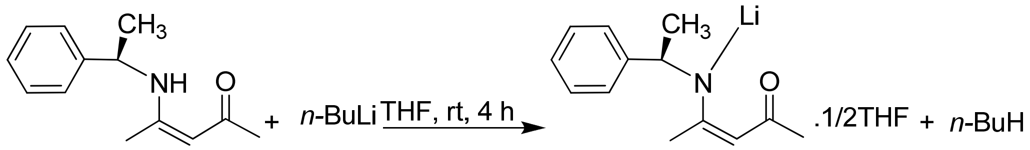
Scheme 6.3.12 Synthesis of *acnac*^{R}, **5a.**

Using a Dean-Stark apparatus, we introduce: TsOH (0.98 g, 5.1 mmol), 2,4-pentandione (5.1g, 51 mmol), (+)1-phenylethylamine (5.9 g, 51 mmol) in 150 mL of dry toluene. The yellow mixture was heated to reflux for 12 h. To the obtained mixture we added 100 mL of ether, 100mL of water. The organic phase was extracted with ether, dried by adding $MgSO_4$, separated by filtration, concentrated using the rota-vap. The desired product is a yellow liquid (10.3 g, 95%).

^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 11.29 (bs, 1H, C=NH), 7.24-7.34 (m, 6H, *Ph*), 4.99 (s, 1H, C*H*(C=N), 4.66 (qt, *J* = *7* Hz, 1H,, C*H*(Me)Ph), 2.05 (s, 3H, *Me*(C=O)), 1.77(s, 3H, (*Me*(C=N)).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 MHz, 298 K): δ 194.9 (C=O), 162.3 (C=N), 144.1 (*ipso* Ph), 128.6 (*ortho* Ph), 126.9 (*para* Ph), 125.2 (*meta* Ph), 95.6 (*C*H(C=N)) 52.8 (*C*H(Me)Ph), 28.7 (C*H*(Me)Ph), 24.5 (*Me*(C=O)), 18.9 (*Me*(C=N)).

(*acnac*^{R})Li.1/2THF, 5b



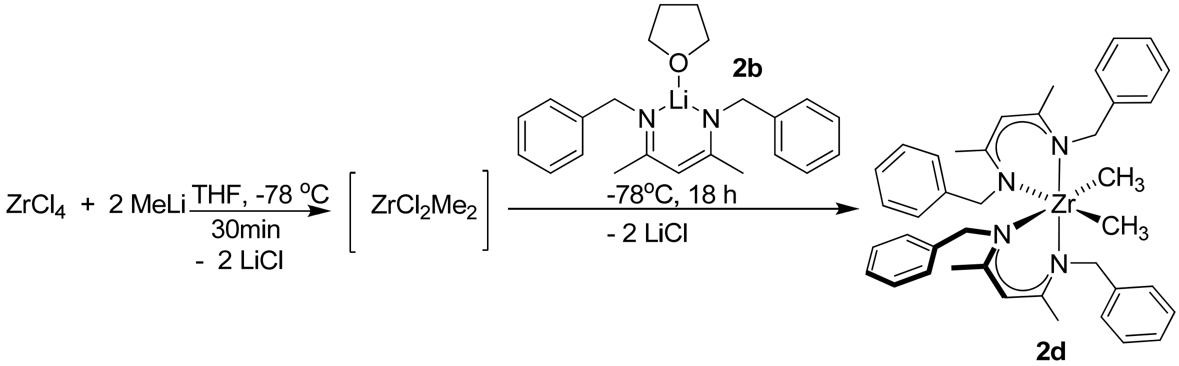
Scheme 6.3.13 Synthesis of *acnac*^{R} Li. ½ (THF), **5b**

To a yellow THF solution of **5b** (1.0 g, 4.9 mmol) we added (2.9 M, 1.8 mL, 4.9 mmol) of *n*-BuLi over 25 min. The obtained orange solution was evaporated to dryness and an off-white solid is obtained (1.1 g, 100%). Anal. Calcd for $C_{13}H_{16}LiNO.1/2(C_4H_8O)$: C, 73.46; H, 8.22; N, 5.71. Found: C, 73.09; H, 8.22; N, 6.09**.** (Presence of 0.5 equiv. of free THF is confirmed by NMR)

^{1}H NMR (CDCl$_3$, 400 MHz, 298 K): δ 7.24-7.34 (m, 6H, *Ph*), 4.61 (s, 1H, C*H*(C=N), 4.60 (m, 1H, C*H*(Me)Ph), 3.76 (m, 2H, THF), 1.85 (bm, 2H, THF), 1.72 (bs, 3H, *Me*(C=O)), 1.55 (bs, 6H, *Me*(C=N)CH(*Me*)Ph).

^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, 298 K): δ 173.4 (C=O), 169.4 (C=N)), 146.1(*ipso* Ph), 128.3 (*ortho* Ph), 126.9 (*para* Ph), 125.2 (*meta* Ph), 99.8 (CH(C=N)), 68.1 (THF), 58.7 (*C*H(Me)Ph), 28.6 (*Me*(C=O)), 26.4 (THF), 25.5(CH(*Me*)Ph), 22.1(*Me*(C=N)).

(*nacnac*^{Bn})$_2$Zr(Me)$_2$, 2d



Scheme 6.3.14 Synthesis of (*nacnac*^{Bn})$_2$Zr(Me)$_2$, **2d**

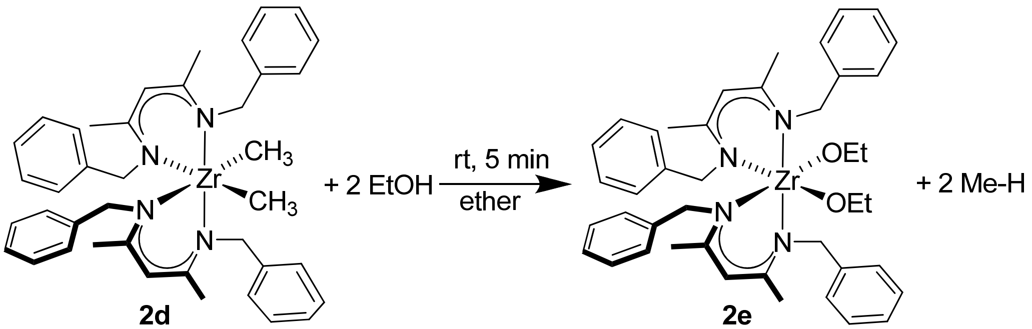
$ZrCl_4$ (0.42 g, 1.8 mmol) was dissolved in 60 mL of THF in a 250 mL schlenk covered with aluminum foil. The resulting colorless solution was cooled to -78˚C to which we added an ether solution of MeLi (2.5 mL, 1.6 M, 4.0 mmol). The obtained white suspension was allowed to stir for 30 min in order to generate. To the obtained mixture deprotonated (*nacnac*^{Cy}*)* ligand (1.28 g, 3.6 mmol) was added giving a yellow suspension. The mixture was allowed to warm up to room temperature during 18 h giving a red solution. Volatiles were evaporated under reduced pressure gave a yellow solid film, the product was extracted with 20 mL of CH_2Cl_2 and the resulting red solution was evaporated to dryness to yield a yellow powder (0.7 g, 63%). Anal. Calcd for $C_{40}H_{48}N_4Zr$: C, 71.06; H, 7.16; N, 8.29. Found: C, 71.59; H, 7.28; N, 8.29.

^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 7.60-7.06 (m, 20 H, Ph), 4.94 (s, 2H, C*H*(C=N)$_2$), 4.77 (bs, 8 H, C*H$_2$*), 1.76 (s, 12 H, *Me*(C=N)), 0.32 (s, 6H, *Me*-Zr).

^{13}C{^{1}H} NMR (C_6D_6, 101 MHz, 298 K): δ 163.5 (C=N), 140.2 (*ipso* Ph), 128.1 (*ortho* Ph), 126.6 (*para* Ph), 126.1 (*meta* Ph), 100.5 (CH(C=N)), 52.1 (*C*H$_2$Ph), 41.2 (*Me*-Zr), 21.4 (*Me*(C=N)).

Crystals of this compound were obtained by slow diffusion at -20˚C of hexane into a saturated toluene solution of this complexe.

(*nacnac*^{Bn})$_2$Zr(OEt)$_2$, 2e



Scheme 6.3.15 Synthesis of (*nacnac*^{Bn})$_2$Zr(OEt)$_2$, **2e.**

Ethanol (37.5 mg, 0.81 mmol) were added to a yellow ether solution of **2d** (250 mg, 0.37 mmol), upon which gas formation (CH_4) was observed. The yellow solution was evaporated to dryness and the obtained yellow solid, was extracted with 15 mL of hexane solution which was evaporated to dryness to yield a colorless powder. ^{1}H NMR analysis showed a 1:1 mixture of 2e and the protonated ligand **2a.** Recrystallization of **2e** from a saturated ethanol solution at -20˚C gave colorless crystals (136 mg, 50%). Anal. Calcd for $C_{42}H_{48}N_4O_2Zr$: C, 68.53; H, 7.12; N, 7.61. Found: C, 68.13; H, 7.45; N, 7.68.

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.30-7.06 (m, 20H, Ph), 5.10 (bs, 4 H, C*H$_2$*), 4.86 (s, 2H, C*H*(C=N)$_2$), 4.54 (bs, 4H, C*H$_2$*), 3.69 (q, 4H, CH_2O), 1.83 (bs, 12H, *Me*(C=N)), 0.72 (s, 6H, *Me*-CH_2O).

^{1}H NMR ($CDCl_3$, 400 MHz, 223 K): δ 7.30-7.06 (m, 20H, Ph), 5.30 (bd, *J* = 7 Hz, 2H, C*H$_2$*), 4.87 (bd, *J* = 7 Hz, 2H, C*H$_2$*), 4.86 (s, 1H, C*H*(C=N)$_2$), 4.75 (bd, *J* = 7 Hz, 2H, C*H$_2$*), 4.23 (bd, *J* = 7 Hz, 2H, C*H$_2$*), 3.80 (m, 2H, CH_2O), 3.60 (m, 2H, CH_2O), 1.99 (bs, 12H, *Me*(C=N)), 1.68 (bs, 12H, *Me*(C=N)), 0.72 (t, *J* = 7 Hz, 6H, *Me*-CH_2O).

$^{13}C\{^1H\}$ NMR (C_6D_6, 400 MHz, 298 K): δ 163.5 (C=N), 142.1 (*ipso* Ph), 127.9 (*ortho* Ph), 127.2 (*para* Ph), 125.8 (*meta* Ph), 102.7 (CH(C=N)), 64.7 (CH_2O), 53.6 (*C*H_2Ph), 22.2 (*Me*-CH_2O), 19.8 (*Me*(C=N)).

[(*nacnac*$^{\mathbf{Bn}}$)$_2$Zr(Me)]$^+$[B(C_6F_5)$_3$(Me)]$^-$, 2f

To a red C_6D_6 solution of $B(C_6F_5)_3$ (7.5 mg, 0.0148 mmol), in a J.Young NMR tube, 0.5 mL of a yellow C_6D_6 solution of **2d** (2.96 10^{-3} M, 0.0148 mmol) was added in portions of 0.1 mL every 5 min, to yield a red oil and a yellow floating solution.

^1H NMR (C_6D_6, 400 MHz, 298 K): δ 7.37-7.06 (m, 20 H, Ph), 4.89 (bs, 2 H, C*H*(C=N)$_2$), 4.54 (bs, 8 H, C*H*$_2$), 1.77 (bs, 12 H, *Me*(C=N)), 0.43 (s, 3H, $B(C_6F_5)_3$*(Me)*), 0.19 (s, 3H, *Me*-Zr)

$^{13}C\{^1H\}$ NMR (C_6D_6, 101 MHz, 298 K): δ 191.0 (C=N), 136.9 (*ipso* Ph), 129.3 ($B(C_6F_5)_3$) 128.3 ($B(C_6F_5)_3$), 128.1 (*ortho* Ph*),* 128.05 (*para* Ph), 127.9(*meta* Ph), 126.9 ($B(C_6F_5)_3$), 93.2 (*C*H(C=N)), 31.9 (*C*H_2Ph), 23.0 (*Me*($B(C_6F_5)_3$)), 21.4 (*Me*(C=N)), 14.4 (*Me*-Zr).

***rac*-Lactide polymerization using $L_2Zr(OEt)_2$:**

In a well closed J.Young NMR tube, **2e** (1.5 mg, 2.1 x 10^{-3} mmol) and *rac*-lactide (60 mg, 0.42 mmol) were heated up to 130 ˚C for half an hour. To the obtained mixture 0.1 mL of methanol were added, followed by addition of C_6D_6 (0.5 mL). Yield was determined from ^1H NMR by comparaison to remaining lactide: 98%

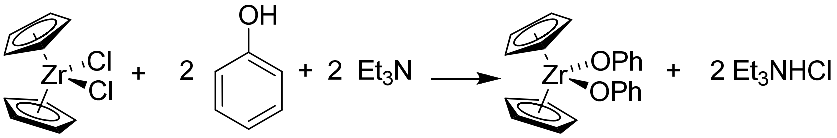
^1H NMR ($CDCl_3$, 400 MHz, 298 K): *δ* 5.15-5.01 (m, polylactide CH), 3.49 (bs, *Me*OH), 1.52-1.42 (m, polylactide CH_3).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz, 298 K) *δ:* 169.5 (polylactide C=O, *siiis, iiiis, iiiii, siiii*), 169.3 (polylactide C=O, *iiisi*), 169.25 (polylactide C=O, *isiii, iisii, sisii*), 169.1 (polylactide

C=O, *iisis, sisis*), 69.1 (polylactide CH, *isi*), 68.9 (polylactide CH, *iii, iis, sii, sis*), 49.9 (*Me*OH), 16.6 (polylactide *Me*), 16.5 (polylactide *Me*), 16.4 (polylactide *Me*)

6.4 Chapter 4

$Cp_2Zr(OPh)_2$, 6a.[77]

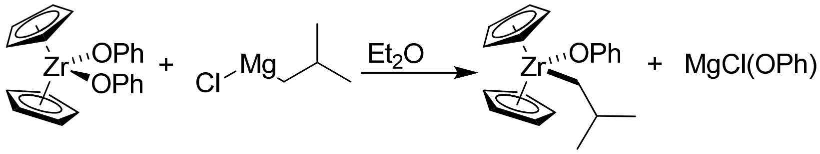


Scheme 6.4.1 Synthesis of $(Cp)_2Zr(OPh)_2$, **6a**

20 mL of toluene was added to Schlenk flask containing Cp_2ZrCl_2 (2.75 g, 9.42 mmol) and PhOH (1.77 g, 18.86 mmol). The solution was allowed to stir 30 min at room temperature, during which time a white precipitate appeared. The reaction mixture was then cooled with an ice bath and Et_3N (3.10 mL, 21.9 mmol) was added over 5 min. The reaction is slightly exothermic. A large amount of precipitate appeared and the reaction was vigorously stirred overnight (16 hrs). The resulting reaction mixture was filtered, and the white precipitate extracted with toluene (3 x 10 mL). The toluene fractions were combined and evaporated to dryness. The resulting white residue was washed with hexane (3 x 10 mL) to afford **5a** as a white powder (3.18 g, 82%).

^{1}H NMR (300 MHz, C_6D_6): δ 7.26 (t, 4H, J = 8 Hz, *meta* OPh), 6.89 (t, J = 7 Hz, 2H, *para* OPh), 6.79 (d, J = 8 Hz, 4H, *ortho* OPh), 5.95 (s, 10H, C5*H*5) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 76 MHz): δ 166.4 (*ipso* OPh), 130.1 (*ortho* OPh), 119.9 (*para* OPh), 119.0 (*meta* OPh), 113.6 (C_5H_5).

Cp_2Zr(*i*Bu)OPh, 6b.



Scheme 6.4.2 Synthesis of $(Cp)_2Zr$(*i*Bu)OPh, **6b**

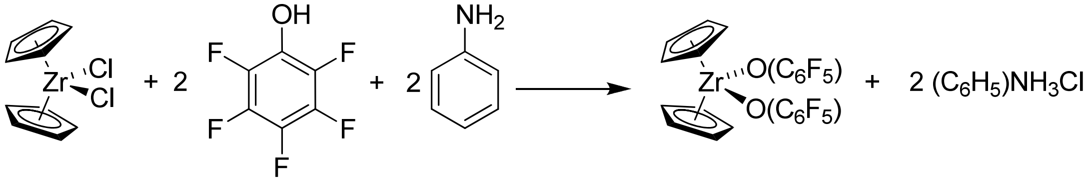
$Cp_2Zr(OPh)_2$ (171 mg, 0.42 mmol) was dissolved in 40 mL Et_2O yielding a colorless solution. Upon cooling to 0 ˚C the solution turns brown. To this cooled solution, *i*BuMgCl (0.21 mL, 0.42 mmol, 2 M solution in Et_2O) was added dropwise with a syringe. After 2 h at 0 °C, the colorless solution was allowed to warm up to room temperature and stirred additional 2 h. The solution turned yellow with formation of some precipitate. The solvent was removed under reduced pressure yielding a yellow solid, to which 10 mL of hexane were added, stirred, and removed under vacuum to facilitate removal of the volatiles. The resulting yellow brown residue was then dried for 2 h under vacuum. Addition of 10 mL hexane, subsequent filtration and evaporation of the filtrate to dryness yielded yellow oil that turned brown upon standing (at room temperature or -20 °C). (150 mg, purity estimated from NMR 70%). Several attempts to recrystallize this product, gave crystals from a saturated hexane solution at -20˚C. Anal. Calcd for $C_{20}H_{24}O_2Zr$: C, 64.64; H, 6.51. Found: C, 62.45; H, 6.71.

Elemental analysis of these crystals was non consistent, most probably due to contamination of the crystals with the decomposed oil.

^{1}H NMR (300 MHz, C_6D_6): δ 7.19 (t, 2H, J = 7 Hz, *meta* OPh), 6.85 (t, 1H, J = 7 Hz, *para* OPh), 6.58 (d, 2H, J = 8 Hz, *ortho* OPh), 5.75 (s, 10H, C_5H_5), 2.21 (m, 1H, CH_2CH), 1.15 (d, 6H, J = 7 Hz, $CH(CH_3)_2$), 1.06 (d, 2H, J = 7 Hz, $ZrCH_2$).

$^{13}C\{^1H\}$ NMR (C_6D_6, 76 MHz): δ 165.8 (*ispo* OPh), 130.0 (*ortho* OPh), 120.0 (*para* OPh), 118.7 (*meta* OPh), 111.5 (C_5H_5), 56.0 ($CH(CH_3)_2$), 33.2 ($ZrCH_2$), 28.8 ($CH(CH_3)_2$).

$Cp_2Zr(OC_6F_5)_2$, 7a.[79]

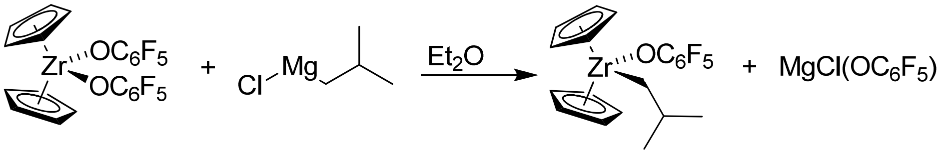


Scheme 6.4.3 Synthesis of $(Cp)_2Zr$ $Cp_2Zr(OC_6F_5)_2$, **7a**

80 mL of Et_2O were added to Schlenk flask containing Cp_2ZrCl_2 (1.00 g, 3.42 mmol) and C_6F_5OH (1.26 g, 6.85 mmol). To the obtained suspension aniline (0.92 g, 9.87 mmol) was added drop by drop and the mixture was allowed to stir for 30 min at room temperature, during which time a white precipitate appeared. The resulting reaction mixture was filtered, and the filtrate was evaporated to dryness to give a white solid which was washed with hexanes (3 x 10 mL) to afford a white powder (1.83 g, 91%).

^1H NMR (C_6D_6, 300 MHz)*:* δ 5.82 (s, 10H, C_5H_5). ^{19}F (300 MHz, C_6D_6) δ -164.90 (d, *ortho* C_6F_5), δ -165.90 (t, *meta* C_6F_5), δ -170.50 (td, *para* C_6F_5).

$Cp_2Zr(i\text{-}Bu)OC_6F_5$, 7b.



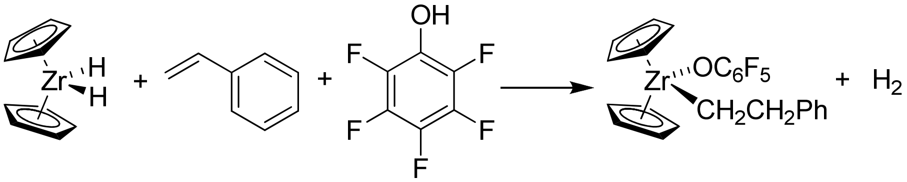
Scheme 6.4.4 Synthesis of $Cp_2Zr(iBu)OC_6F_5$, **7b.**

An Et_2O (35 mL) solution of **7a** (507 mg, 0.86 mmol) was cooled to 0 °C. Isobutyl magnesium chloride (465 μL, 2.0 M solution in Et_2O) was added dropwise to the cooled reaction mixture and the solution was stirred for 2 h at 0 °C, then 2 h at room temperature, yielding a bright yellow solution with a white precipitate. The volatiles were removed under vacuum and the yellow residue dried for additional 15 min. Hexane (10 mL) was added, stirred and evaporated. The product was extracted with hexane (30 mL), filtrated and evaporated to dryness affording thick yellow oil (241 mg, purity of **7b** was estimated by NMR 60%).

^{1}H NMR (C_6D_6, 300 MHz): δ 5.72 (s, 10H, C_5H_5), 2.17 (m, 1H, C*H*), 1.11 (d, *J* = 7 Hz, 2H, CH_2), 1.06 (d, *J* = 7 Hz, 6H, *Me*). $^{13}C\{^1H\}$ NMR(C_6D_6, 76 MHz): : δ 112.5 (C_5H_5), 61.2 (s, CH_2), 33.7 (s, 1H, *C*H), 28.4 (*Me*).^{19}F (C_6D_6, 282 MHz): δ 166.18 (m, *ortho* C_6F_5), –167.50 (m, *meta* C_6F_5), –174.22 (m, *para* C_6F_5).

Cp₂Zr(CH₂CH₂Ph)OC₆F₅, 8.

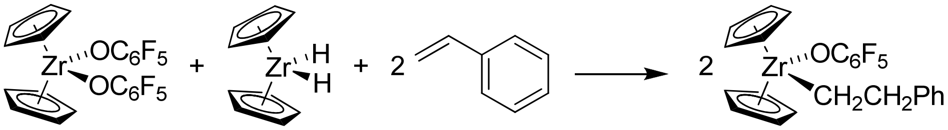
Method 1:



Scheme 6.4.5 Synthesis of $Cp_2Zr(CH_2CH_2Ph)OC_6F_5$, **8**.(*Method 1*)

In a nitrogen filled glovebox, a J. Young NMR tube was charged with Cp_2ZrH_2 (8.0 mg, 0.036 mmol), styrene (7.5 mg, 0.072 mmol), C_6F_5OH (6.6 mg, 0.036 mmol), and 0.6 mL of benzene-*d*$_6$. The NMR tube was closed and heated up to 70 ˚C for 3 h during which the obtained mixture becomes brown in color. The ^{1}H NMR displayed signals for **8** and **Cp₂Zr(OC₆F₅)₂** (yield of **8** was determined by NMR 30%)

Method 2:



Scheme 6.4.6 Synthesis of $Cp_2Zr(CH_2CH_2Ph)OC_6F_5$, **8**.(*Method 2*)

In a nitrogen filled glovebox, a J. Young NMR tube was charged with Cp_2ZrH_2 (14.4 mg, 0.064 mmol), $Cp_2Zr(OC_6F_5)_2$ (37.8 mg, 0.060 mmol), styrene (26.7 mg, 0.26 mmol) and 0.6 mL of benzene-d_6. The NMR tube was closed and heated up to 70˚C for 90 min during which the obtained mixture becomes brown in color. The ^1H NMR displayed signals for **8** (50%) and signals assigned to the 2,1-insertion product, **9** (2%), unreacted **7a** (20%), the dimere $\{Cp_2Zr(OC_6F_5)_2\}O$ (10%) and styrene (used in excess).

^1H NMR (C_6D_6, 300 MHz): δ 7.32 (m, 7H, Ph(**8**) & Ph(**9**)), 5.84 (s, 5H, ($Cp_2Zr(OC_6F_5))_2O$), 5.73 (s, 5H, Cp(**9**)), 5.69 (s, 10H, C_5H_5(**8**)), 2.90 (m, 2H, CH_2Ph(**8**)), 1.55 (m, 1H, CH_2Ph (**9**)), 1.43 (m, 2H, $ZrCH_2$(**8**)), 1.29 (m, 1H, $ZrCH_2$(**9**).

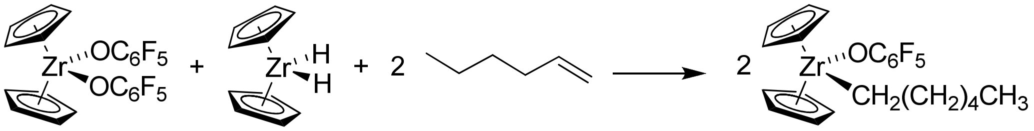
Evidence of the insertion was confirmed by addition of I_2 (32.7 mg, 0.13 mmol). The obtained red solution was then mixed with 5 mL of aqueous solution of $Na_2S_2O_3$ (57mg, 0.36 mmol), the colorless organic phase was separated by decantation and passed through a silica column to remove Zr residues, which yielded the 1-iodo-2-phenylethane, (***a****;* 95%), ,signals assigned to 2-iodo-2-phenylethane, (***b****; 5%*), in addition to styrene (used in excess). Yield of insertion was determined from ^1H NMR spectra (51% relative to initial olefin) and the presence of 1-iodo-2-phenylethane was confirmed by GC-MS analyses.

^1H NMR (C_6D_6, 300 MHz): δ 7.30-7.10 (m, 5H, Ph (***a***)), 2.80 (m, 2H, CH_2Ph (***a***)), 1.55 (m, 1H, CH_2Ph (***a***)).

^1H NMR (C_6D_6, 300 MHz): δ 7.30-7.10 (m, 5H, Ph (***b***)), 1.43 (m, 2H, ICH_2 (***b***)), 1.29 (m, 2H, CH_2Ph (***b***)).

GC-MS showed the presence a mixture of products, listed by their increasing order of their retention time: styrene (m/z: 103), the ambiguous product, (***b***) (m/z: 254) and 1-iodo-2-phenylethane, (***a***) (m/z: 254).

$Cp_2Zr(OC_6F_5)(CH_2)_5CH_3$, 10.



Scheme 6.4.7 Synthesis of $Cp_2Zr\ (OC_6F_5)(CH_2)_5CH_3$, **10**.

A J. Young tube was charged with Cp_2ZrH_2 (7.5 mg, 0.067 mmol), $Cp_2Zr(OC_6F_5)_2$ (13.0 mg, 0.048 mmol), 1-hexene (7.8 mg, 0.18 mmol) and 0.6 mL of benzene-d_6. The NMR tube was closed and allowed to heat up to 70 ˚C for 90 min. NMR analysis showed that the obtained solution contains a mixture of products $\{Cp_2Zr(OC_6F_5)\}_2O$ (10%), **9** (90%) and 1-hexene (used in excess).

^{1}H NMR (C_6D_6, 300 MHz): δ 5.73 (s, 10H, C_5H_5), 1.66 (m, 2H, $ZrCH_2CH_2$), 1.47 (m, 6H, $(CH_2)_3$Me), 1.23 (m, 2H, $ZrCH_2$), 1.02 (m, 2H, CH_3) ppm.

Evidence of the insertion was confirmed by addition of I_2 (45.2 mg, 0.18 mmol). The obtained red solution was then mixed with an aqueous solution of $Na_2S_2O_3$ (56.6 mg, 0.356 mmol), the colorless organic phase was separated by decantation and passed through a silica column to remove Zr residues, which yielded the 1-iodohexane. ^{1}H NMR and GC-MS analyses showed the formation of 1-iodohexane, 90% yield (relative to initial olefin).

^{1}H NMR (C_6D_6, 300 MHz): δ 2.69 (t, 2H, ICH_2), 1.43-1.23 (m, 6H, $(CH_2)_3$Me), 1.10 (m, 2H, I-CH_2CH_2), 0.90 (m, 3H, CH_3) ppm.

Gc-Ms showed the presence a mixture of products, listed by their increasing order of their retention time of 1-hexene (m/z: 85) and 1-iodohexane (m/z: 212)

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Annexe
Tables of bond distances (Å) and bond angles (°)

```
saida4 (2c)   P43212       R = 0.04          : Aug 24 10:42:03 2009
         ===========================================
         S U P P L E M E N T A R Y   M A T E R I A L
         ===========================================
         B E L O N G I N G   TO   T H E   P A P E R
                           b y
                     C o n t e n t s
                     ===============
Table A-1 - Bond Distances (Angstrom)
           for: saida4(2c)  P43212       R = 0.04


Table A-2- Bond Angles    (Degrees)
           for: saida4(2c)  P43212       R = 0.04
```

Table A-1 - Bond Distances (Angstrom)
for: saida4(**2c**) P43212 R = 0.04

Zr1	-Cl1	2.4547(9)	C16	-C17	1.355(7)
Zr1	-N1	2.202(3)	C17	-C18	1.367(6)
Zr1	-N2	2.190(2)	C18	-C19	1.390(6)
Zr1	-Cl1_a	2.4547(9)	C1	-H1A	0.9800
Zr1	-N1_a	2.202(3)	C1	-H1B	0.9800
Zr1	-N2_a	2.190(2)	C1	-H1C	0.9800
N1	-C2	1.325(4)	C3	-H3A	0.9500
N1	-C6	1.480(4)	C5	-H5A	0.9800
N2	-C4	1.340(4)	C5	-H5B	0.9800
N2	-C13	1.478(4)	C5	-H5C	0.9800
C1	-C2	1.502(5)	C6	-H6A	0.9900
C2	-C3	1.411(5)	C6	-H6B	0.9900
C3	-C4	1.388(5)	C8	-H8A	0.9500
C4	-C5	1.514(5)	C9	-H9A	0.9500
C6	-C7	1.509(5)	C10	-H10A	0.9500
C7	-C8	1.362(5)	C11	-H11A	0.9500
C7	-C12	1.362(6)	C12	-H12A	0.9500
C8	-C9	1.387(6)	C13	-H13A	0.9900
C9	-C10	1.364(7)	C13	-H13B	0.9900
C10	-C11	1.336(7)	C15	-H15A	0.9500
C11	-C12	1.375(7)	C16	-H16A	0.9500
C13	-C14	1.513(4)	C17	-H17A	0.9500
C14	-C15	1.378(5)	C18	-H18A	0.9500
C14	-C19	1.374(6)	C19	-H19A	0.9500
C15	-C16	1.387(5)			

Table A-2 - Bond Angles (Degrees)
for: saida4(**2c**) P43212 R = 0.04

Cl1	-Zr1	-N1	173.57(7)	N1	-C6	-C7	115.3(2)
Cl1	-Zr1	-N2	96.22(7)	C6	-C7	-C8	123.8(3)
Cl1	-Zr1	-Cl1_a	93.58(4)	C6	-C7	-C12	118.8(3)
Cl1	-Zr1	-N1_a	90.11(7)	C8	-C7	-C12	117.4(4)
Cl1	-Zr1	-N2_a	97.53(7)	C7	-C8	-C9	121.8(4)
N1	-Zr1	-N2	78.06(9)	C8	-C9	-C10	119.4(4)
Cl1_a	-Zr1	-N1	90.11(7)	C9	-C10	-C11	119.0(5)
N1	-Zr1	-N1_a	86.71(10)	C10	-C11	-C12	121.7(4)
N1	-Zr1	-N2_a	87.28(9)	C7	-C12	-C11	120.8(4)
Cl1_a	-Zr1	-N2	97.53(7)	N2	-C13	-C14	114.8(3)
N1_a	-Zr1	-N2	87.28(9)	C13	-C14	-C15	121.1(3)
N2	-Zr1	-N2_a	159.86(10)	C13	-C14	-C19	120.5(3)
Cl1_a	-Zr1	-N1_a	173.57(7)	C15	-C14	-C19	118.2(3)
Cl1_a	-Zr1	-N2_a	96.22(7)	C14	-C15	-C16	120.9(4)
N1_a	-Zr1	-N2_a	78.06(9)	C15	-C16	-C17	120.3(4)
Zr1	-N1	-C2	122.8(2)	C16	-C17	-C18	119.7(4)
Zr1	-N1	-C6	117.79(19)	C17	-C18	-C19	120.3(4)
C2	-N1	-C6	118.3(3)	C14	-C19	-C18	120.6(4)
Zr1	-N2	-C4	123.5(2)	C2	-C1	-H1A	109.00
Zr1	-N2	-C13	117.47(19)	C2	-C1	-H1B	109.00
C4	-N2	-C13	118.3(3)	C2	-C1	-H1C	109.00
N1	-C2	-C1	121.7(3)	H1A	-C1	-H1B	109.00
N1	-C2	-C3	121.8(3)	H1A	-C1	-H1C	110.00
C1	-C2	-C3	116.4(3)	H1B	-C1	-H1C	109.00
C2	-C3	-C4	126.3(3)	C2	-C3	-H3A	117.00
N2	-C4	-C3	121.4(3)	C4	-C3	-H3A	117.00
N2	-C4	-C5	121.4(3)	C4	-C5	-H5A	109.00
C3	-C4	-C5	117.2(3)	C4	-C5	-H5B	109.00
C4	-C5	-H5C	109.00	C7	-C12	-H12A	120.00
H5A	-C5	-H5B	109.00	C11	-C12	-H12A	120.00
H5A	-C5	-H5C	109.00	N2	-C13	-H13A	109.00
H5B	-C5	-H5C	109.00	N2	-C13	-H13B	109.00
N1	-C6	-H6A	108.00	C14	-C13	-H13A	108.00
N1	-C6	-H6B	108.00	C14	-C13	-H13B	109.00
C7	-C6	-H6A	108.00	H13A	-C13	-H13B	108.00
C7	-C6	-H6B	108.00	C14	-C15	-H15A	120.00
H6A	-C6	-H6B	107.00	C16	-C15	-H15A	119.00
C7	-C8	-H8A	119.00	C15	-C16	-H16A	120.00
C9	-C8	-H8A	119.00	C17	-C16	-H16A	120.00
C8	-C9	-H9A	120.00	C16	-C17	-H17A	120.00
C10	-C9	-H9A	120.00	C18	-C17	-H17A	120.00
C9	-C10	-H10A	121.00	C17	-C18	-H18A	120.00
C11	-C10	-H10A	120.00	C19	-C18	-H18A	120.00
C10	-C11	-H11A	119.00	C14	-C19	-H19A	120.00
C12	-C11	-H11A	119.00	C18	-C19	-H19A	120.00

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saida15(3c)   P21          R = 0.02          : Aug 24 10:47:00 2009
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         S U P P L E M E N T A R Y   M A T E R I A L
         ===========================================
         B E L O N G I N G   TO   T H E   P A P E R
                             b y
                     C o n t e n t s
                     ===============
Table A-3 - Bond Distances  (Angstrom)
            for: saida15(3c)   P21          R = 0.02
Table A-4 - Bond Angles     (Degrees)
            for: saida15(3c)   P21          R = 0.02

Table A-3 - Bond Distances  (Angstrom)
            for: saida15(3c)   P21          R = 0.02
Zr1    -Cl1       2.5156(8)      C1     -C2          1.517(4)
Zr1    -Cl2       2.4987(8)      C2     -C3          1.396(4)
Zr1    -N1         2.205(2)      C3     -C4          1.408(4)
Zr1    -N2         2.247(2)      C4     -C5          1.513(4)
Zr1    -N3         2.213(2)      C11    -C12         1.522(5)
Zr1    -N4         2.181(2)      C12    -C13         1.408(4)
Zr2    -N6         2.221(3)      C13    -C14         1.394(5)
Zr2    -N7         2.178(3)      C14    -C15         1.516(4)
Zr2    -N8         2.247(2)      C20    -C21         1.514(4)
Zr2    -N5         2.183(2)      C20    -C27         1.526(4)
Zr2    -Cl5       2.4831(8)      C21    -C26         1.376(4)
Zr2    -Cl6       2.4873(9)      C21    -C22         1.382(4)
N1     -C2         1.348(4)      C22    -C23         1.384(5)
N1     -C20        1.507(4)      C23    -C24         1.372(6)
N2     -C30        1.497(4)      C24    -C25         1.362(6)
N2     -C4         1.321(4)      C25    -C26         1.386(5)
N3     -C12        1.324(4)      C30    -C37         1.527(4)
N3     -C40        1.487(4)      C30    -C31         1.535(4)
N4     -C14        1.357(4)      C31    -C32         1.392(4)
N4     -C50        1.501(4)      C31    -C36         1.381(4)
N5     -C104       1.340(4)      C32    -C33         1.387(5)
N5     -C60        1.506(4)      C33    -C34         1.364(6)
N6     -C70        1.499(4)      C34    -C35         1.373(4)
N6     -C102       1.341(4)      C35    -C36         1.384(4)
N7     -C80        1.489(4)      C40    -C47         1.536(5)
N7     -C112       1.347(4)      C40    -C41         1.519(4)
N8     -C114       1.328(4)      C41    -C42         1.377(5)
N8     -C90        1.485(4)      C41    -C46         1.396(5)
C42    -C43        1.392(6)      C23    -H23A          0.9300
C43    -C44        1.395(5)      C24    -H24A          0.9300
C44    -C45        1.354(5)      C25    -H25A          0.9300
C45    -C46        1.372(4)      C26    -H26A          0.9300
C50    -C51        1.509(4)      C27    -H27A          0.9600
C50    -C57        1.522(5)      C27    -H27B          0.9600
C51    -C52        1.377(4)      C27    -H27C          0.9600
C51    -C56        1.383(5)      C30    -H30A          0.9800
C52    -C53        1.376(5)      C32    -H32A          0.9300
C53    -C54        1.367(6)      C33    -H33A          0.9300
C54    -C55        1.377(6)      C34    -H34A          0.9300
C55    -C56        1.368(6)      C35    -H35A          0.9300
C1     -H1A          0.9600      C36    -H36A          0.9300
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Table A-3 - Bond Distances (Angstrom) (continued)
for: saida15(**3c**) P21 R = 0.02

C1	-H1C	0.9600	C37	-H37C	0.9600
C1	-H1B	0.9600	C37	-H37A	0.9600
C3	-H3A	0.9300	C37	-H37B	0.9600
C5	-H5C	0.9600	C40	-H40A	0.9800
C5	-H5A	0.9600	C42	-H42A	0.9300
C5	-H5B	0.9600	C43	-H43A	0.9300
C11	-H11C	0.9600	C44	-H44A	0.9300
C11	-H11A	0.9600	C45	-H45A	0.9300
C11	-H11B	0.9600	C46	-H46A	0.9300
C13	-H13A	0.9300	C47	-H47C	0.9600
C15	-H15C	0.9600	C47	-H47A	0.9600
C15	-H15A	0.9600	C47	-H47B	0.9600
C15	-H15B	0.9600	C50	-H50A	0.9800
C20	-H20A	0.9800	C52	-H52A	0.9300
C22	-H22A	0.9300	C53	-H53A	0.9300
C54	-H54A	0.9300	C84	-C85	1.371(6)
C55	-H55A	0.9300	C85	-C86	1.371(6)
C56	-H56A	0.9300	C90	-C91	1.534(5)
C57	-H57C	0.9600	C90	-C97	1.531(4)
C57	-H57A	0.9600	C91	-C92	1.391(6)
C57	-H57B	0.9600	C91	-C96	1.373(5)
C60	-C61	1.525(4)	C92	-C93	1.392(5)
C60	-C67	1.517(4)	C93	-C94	1.378(6)
C61	-C62	1.385(4)	C94	-C95	1.362(8)
C61	-C66	1.389(5)	C95	-C96	1.386(6)
C62	-C63	1.386(6)	C101	-C102	1.503(5)
C63	-C64	1.382(6)	C102	-C103	1.414(4)
C64	-C65	1.354(6)	C103	-C104	1.397(4)
C65	-C66	1.387(6)	C104	-C105	1.509(4)
C70	-C71	1.521(5)	C111	-C112	1.503(5)
C70	-C77	1.513(5)	C112	-C113	1.402(5)
C71	-C72	1.371(5)	C113	-C114	1.409(5)
C71	-C76	1.404(6)	C114	-C115	1.499(5)
C72	-C73	1.390(5)	C60	-H60A	0.9800
C73	-C74	1.380(6)	C62	-H62A	0.9300
C74	-C75	1.373(7)	C63	-H63A	0.9300
C75	-C76	1.364(7)	C64	-H64A	0.9300
C80	-C81	1.527(4)	C65	-H65A	0.9300
C80	-C87	1.541(5)	C66	-H66A	0.9300
C81	-C82	1.375(5)	C67	-H67A	0.9600
C81	-C86	1.383(5)	C67	-H67B	0.9600
C82	-C83	1.391(6)	C67	-H67C	0.9600
C83	-C84	1.380(6)	C70	-H70A	0.9800
C72	-H72A	0.9300	C94	-H94A	0.9300
C73	-H73A	0.9300	C95	-H95A	0.9300
C74	-H74A	0.9300	C96	-H96A	0.9300
C75	-H75A	0.9300	C97	-H97A	0.9600
C76	-H76A	0.9300	C97	-H97B	0.9600
C77	-H77A	0.9600	C97	-H97C	0.9600
C77	-H77B	0.9600	C101	-H10A	0.9600
C77	-H77C	0.9600	C101	-H10B	0.9600
C80	-H80A	0.9800	C101	-H10C	0.9600
C82	-H82A	0.9300	C103	-H10D	0.9300
C83	-H83A	0.9300	C105	-H10E	0.9600

Table A-3 - Bond Distances (Angstrom) (continued)
for: saida15(**3c**) P21 R = 0.02

C84	-H84A	0.9300	C105	-H10F	0.9600
C85	-H85A	0.9300	C105	-H10G	0.9600
C86	-H86A	0.9300	C111	-H11D	0.9600
C87	-H87A	0.9600	C111	-H11E	0.9600
C87	-H87B	0.9600	C111	-H11F	0.9600
C87	-H87C	0.9600	C113	-H11G	0.9300
C90	-H90A	0.9800	C115	-H11H	0.9600
C92	-H92A	0.9300	C115	-H11I	0.9600
C93	-H93A	0.9300	C115	-H11J	0.9600

Table A-4 - Bond Angles (Degrees)
for: saida15 P21(**3c**) R = 0.02

Cl1	-Zr1	-Cl2	88.52(3)	N6	-Zr2	-N7	96.29(10)
Cl1	-Zr1	-N1	169.65(7)	N6	-Zr2	-N8	178.46(9)
Cl1	-Zr1	-N2	86.13(7)	Zr1	-N1	-C2	111.13(19)
Cl1	-Zr1	-N3	83.54(7)	Zr1	-N1	-C20	132.62(19)
Cl1	-Zr1	-N4	89.09(7)	C2	-N1	-C20	114.9(2)
Cl2	-Zr1	-N1	92.51(7)	Zr1	-N2	-C4	115.54(19)
Cl2	-Zr1	-N2	84.89(6)	Zr1	-N2	-C30	121.60(18)
Cl2	-Zr1	-N3	86.10(6)	C4	-N2	-C30	122.0(2)
Cl2	-Zr1	-N4	171.43(7)	Zr1	-N3	-C12	114.00(19)
N1	-Zr1	-N2	83.71(9)	Zr1	-N3	-C40	123.24(17)
N1	-Zr1	-N3	106.81(9)	C12	-N3	-C40	121.6(2)
N1	-Zr1	-N4	91.32(9)	Zr1	-N4	-C14	108.77(19)
N2	-Zr1	-N3	166.44(9)	Zr1	-N4	-C50	134.59(18)
N2	-Zr1	-N4	103.16(9)	C14	-N4	-C50	115.0(2)
N3	-Zr1	-N4	85.46(9)	C60	-N5	-C104	119.8(2)
N7	-Zr2	-N8	82.44(9)	Zr2	-N5	-C60	123.16(18)
Cl5	-Zr2	-Cl6	90.59(3)	Zr2	-N5	-C104	116.9(2)
Cl5	-Zr2	-N5	171.86(7)	Zr2	-N6	-C70	119.6(2)
Cl5	-Zr2	-N6	89.61(7)	Zr2	-N6	-C102	118.21(19)
Cl5	-Zr2	-N7	88.95(8)	C70	-N6	-C102	122.2(3)
Cl5	-Zr2	-N8	89.50(7)	Zr2	-N7	-C80	118.0(2)
Cl6	-Zr2	-N5	90.25(7)	Zr2	-N7	-C112	119.7(2)
Cl6	-Zr2	-N6	91.41(7)	C80	-N7	-C112	122.2(3)
Cl6	-Zr2	-N7	172.29(7)	C90	-N8	-C114	121.6(2)
Cl6	-Zr2	-N8	89.86(6)	Zr2	-N8	-C90	117.72(17)
N5	-Zr2	-N6	82.28(9)	Zr2	-N8	-C114	120.5(2)
N5	-Zr2	-N7	91.30(10)	C1	-C2	-C3	115.9(3)
N5	-Zr2	-N8	98.60(9)	N1	-C2	-C3	123.6(3)
N1	-C2	-C1	120.5(3)	C30	-C31	-C36	120.0(3)
C2	-C3	-C4	129.8(3)	C31	-C32	-C33	120.0(3)
C3	-C4	-C5	115.3(3)	C32	-C33	-C34	121.3(3)
N2	-C4	-C3	122.3(3)	C33	-C34	-C35	119.1(3)
N2	-C4	-C5	122.4(2)	C34	-C35	-C36	120.4(3)
N3	-C12	-C11	123.6(3)	C31	-C36	-C35	121.1(3)
N3	-C12	-C13	121.3(3)	N3	-C40	-C47	112.7(3)
C11	-C12	-C13	115.1(2)	C41	-C40	-C47	114.2(3)
C12	-C13	-C14	130.5(3)	N3	-C40	-C41	114.1(2)
C13	-C14	-C15	115.6(3)	C40	-C41	-C46	120.3(3)
N4	-C14	-C13	123.9(3)	C42	-C41	-C46	117.2(3)
N4	-C14	-C15	120.5(3)	C40	-C41	-C42	122.4(3)
N1	-C20	-C27	112.5(2)	C41	-C42	-C43	121.7(3)
C21	-C20	-C27	108.5(2)	C42	-C43	-C44	118.9(4)

Table A-4 - Bond Angles (Degrees) (continued)
for: saida15 P21(**3c**) R = 0.02

N1	-C20	-C21	112.0(2)	C43	-C44	-C45	120.2(4)
C20	-C21	-C22	122.6(3)	C44	-C45	-C46	120.3(3)
C20	-C21	-C26	119.3(3)	C41	-C46	-C45	121.8(3)
C22	-C21	-C26	117.9(3)	C51	-C50	-C57	108.7(3)
C21	-C22	-C23	120.8(3)	N4	-C50	-C51	111.5(2)
C22	-C23	-C24	120.2(3)	N4	-C50	-C57	113.1(2)
C23	-C24	-C25	119.7(4)	C50	-C51	-C56	119.4(3)
C24	-C25	-C26	119.9(4)	C52	-C51	-C56	117.5(3)
C21	-C26	-C25	121.4(4)	C50	-C51	-C52	122.8(3)
N2	-C30	-C31	113.2(2)	C51	-C52	-C53	121.0(3)
N2	-C30	-C37	114.1(2)	C52	-C53	-C54	120.8(4)
C31	-C30	-C37	114.9(2)	C53	-C54	-C55	118.8(4)
C32	-C31	-C36	118.1(3)	C54	-C55	-C56	120.4(4)
C30	-C31	-C32	121.7(3)	C51	-C56	-C55	121.5(4)
H1B	-C1	-H1C	109.00	N1	-C20	-H20A	108.00
H1A	-C1	-H1B	109.00	C21	-C20	-H20A	108.00
H1A	-C1	-H1C	110.00	C27	-C20	-H20A	108.00
C2	-C1	-H1A	109.00	C21	-C22	-H22A	120.00
C2	-C1	-H1B	109.00	C23	-C22	-H22A	120.00
C2	-C1	-H1C	109.00	C24	-C23	-H23A	120.00
C2	-C3	-H3A	115.00	C22	-C23	-H23A	120.00
C4	-C3	-H3A	115.00	C25	-C24	-H24A	120.00
C4	-C5	-H5B	109.00	C23	-C24	-H24A	120.00
C4	-C5	-H5A	109.00	C24	-C25	-H25A	120.00
H5B	-C5	-H5C	109.00	C26	-C25	-H25A	120.00
C4	-C5	-H5C	109.00	C25	-C26	-H26A	119.00
H5A	-C5	-H5B	110.00	C21	-C26	-H26A	119.00
H5A	-C5	-H5C	109.00	C20	-C27	-H27C	110.00
C12	-C11	-H11A	110.00	H27A	-C27	-H27B	109.00
C12	-C11	-H11B	110.00	H27A	-C27	-H27C	109.00
C12	-C11	-H11C	109.00	H27B	-C27	-H27C	110.00
H11B	-C11	-H11C	109.00	C20	-C27	-H27A	109.00
H11A	-C11	-H11B	109.00	C20	-C27	-H27B	109.00
H11A	-C11	-H11C	109.00	N2	-C30	-H30A	104.00
C14	-C13	-H13A	115.00	C37	-C30	-H30A	104.00
C12	-C13	-H13A	115.00	C31	-C30	-H30A	104.00
C14	-C15	-H15B	109.00	C31	-C32	-H32A	120.00
C14	-C15	-H15C	110.00	C33	-C32	-H32A	120.00
C14	-C15	-H15A	109.00	C32	-C33	-H33A	119.00
H15B	-C15	-H15C	109.00	C34	-C33	-H33A	119.00
H15A	-C15	-H15B	110.00	C33	-C34	-H34A	120.00
H15A	-C15	-H15C	109.00	C35	-C34	-H34A	120.00
C36	-C35	-H35A	120.00	H47A	-C47	-H47C	110.00
C34	-C35	-H35A	120.00	C51	-C50	-H50A	108.00
C35	-C36	-H36A	120.00	C57	-C50	-H50A	108.00
C31	-C36	-H36A	119.00	N4	-C50	-H50A	108.00
C30	-C37	-H37C	109.00	C51	-C52	-H52A	120.00
C30	-C37	-H37A	110.00	C53	-C52	-H52A	119.00
C30	-C37	-H37B	110.00	C54	-C53	-H53A	120.00
H37B	-C37	-H37C	109.00	C52	-C53	-H53A	120.00
H37A	-C37	-H37B	109.00	C53	-C54	-H54A	121.00
H37A	-C37	-H37C	109.00	C55	-C54	-H54A	121.00
C41	-C40	-H40A	105.00	C54	-C55	-H55A	120.00

Table A-4 - Bond Angles (Degrees) (continued)
for: saida15 P21(**3c**) R = 0.02

C47	-C40	-H40A	105.00	C56	-C55	-H55A	120.00
N3	-C40	-H40A	105.00	C55	-C56	-H56A	119.00
C41	-C42	-H42A	119.00	C51	-C56	-H56A	119.00
C43	-C42	-H42A	119.00	C50	-C57	-H57C	110.00
C44	-C43	-H43A	121.00	H57A	-C57	-H57B	109.00
C42	-C43	-H43A	121.00	H57A	-C57	-H57C	110.00
C43	-C44	-H44A	120.00	H57B	-C57	-H57C	109.00
C45	-C44	-H44A	120.00	C50	-C57	-H57A	109.00
C46	-C45	-H45A	120.00	C50	-C57	-H57B	109.00
C44	-C45	-H45A	120.00	N5	-C60	-C61	112.6(2)
C41	-C46	-H46A	119.00	N5	-C60	-C67	114.1(2)
C45	-C46	-H46A	119.00	C61	-C60	-C67	114.2(2)
C40	-C47	-H47A	109.00	C60	-C61	-C62	121.0(3)
H47B	-C47	-H47C	109.00	C60	-C61	-C66	121.0(3)
C40	-C47	-H47B	109.00	C62	-C61	-C66	117.9(3)
C40	-C47	-H47C	109.00	C61	-C62	-C63	120.7(4)
H47A	-C47	-H47B	109.00	C62	-C63	-C64	120.5(4)
C63	-C64	-C65	119.1(4)	C90	-C91	-C92	122.1(3)
C64	-C65	-C66	121.1(4)	C90	-C91	-C96	120.4(4)
C61	-C66	-C65	120.6(4)	C92	-C91	-C96	117.5(3)
N6	-C70	-C71	115.6(3)	C91	-C92	-C93	120.6(3)
N6	-C70	-C77	109.1(2)	C92	-C93	-C94	120.7(4)
C71	-C70	-C77	115.1(3)	C93	-C94	-C95	118.8(4)
C70	-C71	-C72	120.8(3)	C94	-C95	-C96	120.7(4)
C70	-C71	-C76	121.9(3)	C91	-C96	-C95	121.7(4)
C72	-C71	-C76	117.3(3)	N6	-C102	-C101	122.3(3)
C71	-C72	-C73	122.3(4)	N6	-C102	-C103	121.5(3)
C72	-C73	-C74	118.8(4)	C101	-C102	-C103	116.2(3)
C73	-C74	-C75	119.8(4)	C102	-C103	-C104	129.1(3)
C74	-C75	-C76	120.9(6)	N5	-C104	-C103	122.2(3)
C71	-C76	-C75	120.8(5)	N5	-C104	-C105	121.7(3)
N7	-C80	-C81	113.2(3)	C103	-C104	-C105	116.1(3)
N7	-C80	-C87	118.1(3)	N7	-C112	-C111	123.4(3)
C81	-C80	-C87	110.3(3)	N7	-C112	-C113	121.6(3)
C80	-C81	-C82	124.5(3)	C111	-C112	-C113	115.0(3)
C80	-C81	-C86	117.2(3)	C112	-C113	-C114	128.7(3)
C82	-C81	-C86	118.3(3)	N8	-C114	-C113	122.7(3)
C81	-C82	-C83	120.6(4)	N8	-C114	-C115	123.5(3)
C82	-C83	-C84	120.6(4)	C113	-C114	-C115	113.8(3)
C83	-C84	-C85	118.2(4)	N5	-C60	-H60A	105.00
C84	-C85	-C86	121.5(4)	C61	-C60	-H60A	105.00
C81	-C86	-C85	120.8(4)	C67	-C60	-H60A	105.00
N8	-C90	-C91	115.3(2)	C61	-C62	-H62A	120.00
N8	-C90	-C97	110.1(3)	C63	-C62	-H62A	120.00
C91	-C90	-C97	115.3(3)	C62	-C63	-H63A	120.00
C64	-C63	-H63A	120.00	C70	-C77	-H77C	109.00
C63	-C64	-H64A	120.00	H77A	-C77	-H77B	109.00
C65	-C64	-H64A	120.00	H77A	-C77	-H77C	110.00
C64	-C65	-H65A	119.00	H77B	-C77	-H77C	109.00
C66	-C65	-H65A	119.00	N7	-C80	-H80A	105.00
C61	-C66	-H66A	120.00	C81	-C80	-H80A	105.00
C65	-C66	-H66A	120.00	C87	-C80	-H80A	105.00
C60	-C67	-H67A	109.00	C81	-C82	-H82A	120.00

Table A-4 - Bond Angles (Degrees) (continued)
for: saida15 P21(**3c**) R = 0.02

C60	-C67	-H67B	109.00	C83	-C82	-H82A	120.00
C60	-C67	-H67C	110.00	C82	-C83	-H83A	120.00
H67A	-C67	-H67B	109.00	C84	-C83	-H83A	120.00
H67A	-C67	-H67C	109.00	C83	-C84	-H84A	121.00
H67B	-C67	-H67C	110.00	C85	-C84	-H84A	121.00
N6	-C70	-H70A	105.00	C84	-C85	-H85A	119.00
C71	-C70	-H70A	105.00	C86	-C85	-H85A	119.00
C77	-C70	-H70A	105.00	C81	-C86	-H86A	120.00
C71	-C72	-H72A	119.00	C85	-C86	-H86A	120.00
C73	-C72	-H72A	119.00	C80	-C87	-H87A	110.00
C72	-C73	-H73A	121.00	C80	-C87	-H87B	109.00
C74	-C73	-H73A	121.00	C80	-C87	-H87C	109.00
C73	-C74	-H74A	120.00	H87A	-C87	-H87B	109.00
C75	-C74	-H74A	120.00	H87A	-C87	-H87C	110.00
C74	-C75	-H75A	119.00	H87B	-C87	-H87C	109.00
C76	-C75	-H75A	120.00	N8	-C90	-H90A	105.00
C71	-C76	-H76A	120.00	C91	-C90	-H90A	105.00
C75	-C76	-H76A	120.00	C97	-C90	-H90A	105.00
C70	-C77	-H77A	110.00	C91	-C92	-H92A	120.00
C70	-C77	-H77B	109.00	C93	-C92	-H92A	120.00
C92	-C93	-H93A	120.00	C104	-C103	-H10D	115.00
C94	-C93	-H93A	120.00	C104	-C105	-H10E	109.00
C93	-C94	-H94A	121.00	C104	-C105	-H10F	110.00
C95	-C94	-H94A	121.00	C104	-C105	-H10G	109.00
C94	-C95	-H95A	120.00	H10E	-C105	-H10F	109.00
C96	-C95	-H95A	120.00	H10E	-C105	-H10G	109.00
C91	-C96	-H96A	119.00	H10F	-C105	-H10G	110.00
C95	-C96	-H96A	119.00	C112	-C111	-H11D	109.00
C90	-C97	-H97A	109.00	C112	-C111	-H11E	109.00
C90	-C97	-H97B	109.00	C112	-C111	-H11F	109.00
C90	-C97	-H97C	109.00	H11D	-C111	-H11E	110.00
H97A	-C97	-H97B	109.00	H11D	-C111	-H11F	109.00
H97A	-C97	-H97C	109.00	H11E	-C111	-H11F	109.00
H97B	-C97	-H97C	109.00	C112	-C113	-H11G	116.00
C102	-C101	-H10A	109.00	C114	-C113	-H11G	116.00
C102	-C101	-H10B	110.00	C114	-C115	-H11H	109.00
C102	-C101	-H10C	109.00	C114	-C115	-H11I	109.00
H10A	-C101	-H10B	110.00	C114	-C115	-H11J	110.00
H10A	-C101	-H10C	109.00	H11H	-C115	-H11I	110.00
H10B	-C101	-H10C	109.00	H11H	-C115	-H11J	109.00
C102	-C103	-H10D	115.00	H11I	-C115	-H11J	109.00

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        Saida21(3d)   P21          R = 0.02          : Aug 24 10:47:00 2009
                 ==========================================
                 S U P P L E M E N T A R Y   M A T E R I A L
                 ==========================================
                 B E L O N G I N G   TO   T H E   P A P E R
                                   b y
                             C o n t e n t s
                             ===============
        Table A-5 - Bond Distances  (Angstrom)
                    for: saida21(3d)   P21          R = 0.02
        Table A-6 - Bond Angles     (Degrees)
                    for: saida21(3d)   P21          R = 0.02
Table A-5 - Bond Distances (Angstrom)
for: saida21 (3d)     P21          R = 0.05
        Zr1    -Cl1      2.4766(13)     C15    -C16        1.371(8)
        Zr1    -N1         2.031(3)     C15    -C20        1.393(7)
        Zr1    -N2         2.317(3)     C16    -C17        1.381(9)
        Zr1    -N3         2.230(3)     C17    -C18        1.381(9)
        Zr1    -N4         2.196(4)     C18    -C19       1.376(10)
        Zr1    -C27        2.305(5)     C19    -C20        1.381(8)
        N1     -C25        1.331(5)     C22    -C23        1.512(7)
        N1     -C27        1.411(6)     C23    -C24        1.437(7)
        N2     -C23        1.324(6)     C24    -C25        1.365(7)
        N2     -C35        1.486(7)     C25    -C26        1.501(8)
        N3     -C2         1.302(7)     C27    -C28        1.498(7)
        N3     -C14        1.489(6)     C27    -C34        1.532(7)
        N4     -C4         1.302(6)     C28    -C29        1.383(7)
        N4     -C6         1.469(7)     C28    -C33        1.410(7)
        C1     -C2         1.519(8)     C29    -C30        1.392(8)
        C2     -C3         1.422(7)     C30    -C31        1.391(7)
        C3     -C4         1.404(7)     C31    -C32        1.363(8)
        C4     -C5         1.534(6)     C32    -C33        1.398(8)
        C6     -C7         1.526(7)     C35    -C36        1.527(7)
        C6     -C13        1.536(7)     C35    -C42        1.531(6)
        C7     -C8         1.397(8)     C37    -C38        1.403(8)
        C7     -C12        1.387(8)     C37    -C42        1.386(7)
        C8     -C9        1.368(10)     C38    -C39        1.369(9)
        C9     -C10       1.391(11)     C39    -C40        1.369(9)
        C10    -C11       1.372(10)     C40    -C41        1.404(8)
        C11    -C12       1.375(10)     C41    -C42        1.391(7)
        C14    -C15        1.534(7)     C1     -H1A          0.9800
        C14    -C21        1.506(8)     C1     -H1B          0.9800
        C1     -H1C          0.9800     C22    -H22B         0.9800
        C3     -H3A          0.9500     C22    -H22C         0.9800
        C5     -H5A          0.9800     C24    -H24A         0.9500
        C5     -H5B          0.9800     C26    -H26A         0.9800
        C5     -H5C          0.9800     C26    -H26B         0.9800
        C6     -H6A          1.0000     C26    -H26C         0.9800
        C8     -H8A          0.9500     C29    -H29A         0.9500
        C9     -H9A          0.9500     C30    -H30A         0.9500
        C10    -H10A         0.9500     C31    -H31A         0.9500
        C11    -H11A         0.9500     C32    -H32A         0.9500
        C12    -H12A         0.9500     C33    -H33A         0.9500
        C13    -H13A         0.9800     C34    -H34A         0.9800
        C13    -H13B         0.9800     C34    -H34B         0.9800
        C13    -H13C         0.9800     C34    -H34C         0.9800
        C14    -H14A         1.0000     C35    -H35A         1.0000
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Table A-5 - Bond Distances (Angstrom) (continued)
for: saida21 (**3d**) P21 R = 0.05

C16	-H16A	0.9500	C36	-H36A	0.9800
C17	-H17A	0.9500	C36	-H36B	0.9800
C18	-H18A	0.9500	C36	-H36C	0.9800
C19	-H19A	0.9500	C37	-H37A	0.9500
C20	-H20A	0.9500	C38	-H38A	0.9500
C21	-H21A	0.9800	C39	-H39A	0.9500
C21	-H21B	0.9800	C40	-H40A	0.9500
C21	-H21C	0.9800	C41	-H41A	0.9500
C22	-H22A	0.9800			

Table A-6 - Bond Angles (Degrees)
for: saida21(**3d**) P21 R = 0.05

Cl1	-Zr1	-N1	110.45(11)	N3	-C2	-C3	121.4(4)
Cl1	-Zr1	-N2	83.89(11)	C1	-C2	-C3	114.8(4)
Cl1	-Zr1	-N3	87.06(13)	C2	-C3	-C4	128.0(4)
Cl1	-Zr1	-N4	136.64(12)	N4	-C4	-C3	124.3(4)
Cl1	-Zr1	-C27	108.27(13)	N4	-C4	-C5	121.3(4)
N1	-Zr1	-N2	76.61(14)	C3	-C4	-C5	114.3(4)
N1	-Zr1	-N3	126.50(16)	N4	-C6	-C7	112.2(4)
N1	-Zr1	-N4	109.10(15)	N4	-C6	-C13	111.9(4)
N1	-Zr1	-C27	37.30(15)	C7	-C6	-C13	108.7(4)
N2	-Zr1	-N3	156.89(16)	C6	-C7	-C8	121.2(5)
N2	-Zr1	-N4	88.58(13)	C6	-C7	-C12	120.9(5)
N2	-Zr1	-C27	113.53(15)	C8	-C7	-C12	117.8(5)
N3	-Zr1	-N4	83.50(11)	C7	-C8	-C9	120.8(6)
N3	-Zr1	-C27	89.50(16)	C8	-C9	-C10	120.8(7)
N4	-Zr1	-C27	113.84(17)	C9	-C10	-C11	118.6(7)
Zr1	-N1	-C25	143.0(3)	C10	-C11	-C12	120.9(6)
Zr1	-N1	-C27	82.0(2)	C7	-C12	-C11	121.1(6)
C25	-N1	-C27	133.9(4)	N3	-C14	-C15	111.1(4)
Zr1	-N2	-C23	131.4(3)	N3	-C14	-C21	113.6(4)
Zr1	-N2	-C35	107.2(2)	C15	-C14	-C21	115.8(4)
C23	-N2	-C35	121.0(4)	C14	-C15	-C16	120.1(5)
Zr1	-N3	-C2	103.6(3)	C14	-C15	-C20	122.1(5)
Zr1	-N3	-C14	128.3(3)	C16	-C15	-C20	117.7(5)
C2	-N3	-C14	123.0(4)	C15	-C16	-C17	122.3(5)
Zr1	-N4	-C4	104.5(3)	C16	-C17	-C18	119.3(6)
Zr1	-N4	-C6	133.7(3)	C17	-C18	-C19	119.7(6)
C4	-N4	-C6	118.9(4)	C18	-C19	-C20	120.3(6)
N3	-C2	-C1	123.8(5)	C15	-C20	-C19	120.8(5)
N2	-C23	-C22	124.0(4)	C40	-C41	-C42	119.3(5)
N2	-C23	-C24	121.9(4)	C35	-C42	-C37	116.6(4)
C22	-C23	-C24	114.1(4)	C35	-C42	-C41	124.2(5)
C23	-C24	-C25	126.1(4)	C37	-C42	-C41	119.2(4)
N1	-C25	-C24	120.7(5)	C2	-C1	-H1A	109.00
N1	-C25	-C26	118.2(4)	C2	-C1	-H1B	109.00
C24	-C25	-C26	121.1(4)	C2	-C1	-H1C	109.00
Zr1	-C27	-N1	60.7(2)	H1A	-C1	-H1B	109.00
Zr1	-C27	-C28	116.8(3)	H1A	-C1	-H1C	109.00
Zr1	-C27	-C34	119.7(4)	H1B	-C1	-H1C	110.00
N1	-C27	-C28	115.6(4)	C2	-C3	-H3A	116.00
N1	-C27	-C34	116.7(4)	C4	-C3	-H3A	116.00
C28	-C27	-C34	115.8(4)	C4	-C5	-H5A	109.00
C27	-C28	-C29	121.5(4)	C4	-C5	-H5B	110.00
C27	-C28	-C33	121.7(4)	C4	-C5	-H5C	110.00

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Table A-6 - Bond Angles    (Degrees)    (continued)
            for: saida21 (3d)    P21           R = 0.05
C29    -C28    -C33          116.8(4)  H5A    -C5     -H5B            109.00
C28    -C29    -C30          121.8(5)  H5A    -C5     -H5C            109.00
C29    -C30    -C31          120.7(5)  H5B    -C5     -H5C            109.00
C30    -C31    -C32          118.3(5)  N4     -C6     -H6A            108.00
C31    -C32    -C33          121.6(5)  C7     -C6     -H6A            108.00
C28    -C33    -C32          120.7(5)  C13    -C6     -H6A            108.00
N2     -C35    -C36          114.7(4)  C7     -C8     -H8A            120.00
N2     -C35    -C42          115.5(4)  C9     -C8     -H8A            120.00
C36    -C35    -C42          112.9(4)  C8     -C9     -H9A            120.00
C38    -C37    -C42          121.0(5)  C10    -C9     -H9A            120.00
C37    -C38    -C39          118.9(5)  C9     -C10    -H10A           121.00
C38    -C39    -C40          121.1(5)  C11    -C10    -H10A           121.00
C39    -C40    -C41          120.4(5)  C10    -C11    -H11A           120.00
C12    -C11    -H11A           120.00  C23    -C22    -H22A           109.00
C7     -C12    -H12A           119.00  C23    -C22    -H22B           109.00
C11    -C12    -H12A           119.00  C23    -C22    -H22C           109.00
C6     -C13    -H13A           110.00  H22A   -C22    -H22B           109.00
C6     -C13    -H13B           109.00  H22A   -C22    -H22C           109.00
C6     -C13    -H13C           109.00  H22B   -C22    -H22C           110.00
H13A   -C13    -H13B           109.00  C23    -C24    -H24A           117.00
H13A   -C13    -H13C           110.00  C25    -C24    -H24A           117.00
H13B   -C13    -H13C           109.00  C25    -C26    -H26A           109.00
N3     -C14    -H14A           105.00  C25    -C26    -H26B           110.00
C15    -C14    -H14A           105.00  C25    -C26    -H26C           109.00
C21    -C14    -H14A           105.00  H26A   -C26    -H26B           110.00
C15    -C16    -H16A           119.00  H26A   -C26    -H26C           109.00
C17    -C16    -H16A           119.00  H26B   -C26    -H26C           109.00
C16    -C17    -H17A           120.00  C28    -C29    -H29A           119.00
C18    -C17    -H17A           120.00  C30    -C29    -H29A           119.00
C17    -C18    -H18A           120.00  C29    -C30    -H30A           120.00
C19    -C18    -H18A           120.00  C31    -C30    -H30A           120.00
C18    -C19    -H19A           120.00  C30    -C31    -H31A           121.00
C20    -C19    -H19A           120.00  C32    -C31    -H31A           121.00
C15    -C20    -H20A           120.00  C31    -C32    -H32A           119.00
C19    -C20    -H20A           120.00  C33    -C32    -H32A           119.00
C14    -C21    -H21A           109.00  C28    -C33    -H33A           120.00
C14    -C21    -H21B           110.00  C32    -C33    -H33A           120.00
C14    -C21    -H21C           109.00  C27    -C34    -H34A           109.00
H21A   -C21    -H21B           109.00  C27    -C34    -H34B           109.00
H21A   -C21    -H21C           109.00  C27    -C34    -H34C           109.00
H21B   -C21    -H21C           109.00  H34A   -C34    -H34B           109.00
```

```
    saida3 (4c)                R = 0.07          : Aug 24 10:48:18 2009
             ===========================================
             S U P P L E M E N T A R Y   M A T E R I A L
             ===========================================
             B E L O N G I N G   T O   T H E   P A P E R
                               b y
                         C o n t e n t s
                         ===============
    Table A-7 - Bond Distances (Angstrom)
                for: saida3 (4c)                 R = 0.07
    Table A-8 - Bond Angles    (Degrees)
                for: saida3 (4c)                 R = 0.07
```

Table A-7 - Bond Distances (Angstrom)
for: saida3 (**4c**) R = 0.07

Zr1	-Cl1	2.4827(13)	C1	-H1C	0.9800
Zr1	-N1	2.236(4)	C3	-H3A	0.9500
Zr1	-N2	2.192(4)	C5	-H5A	0.9800
Zr1	-Cl1_a	2.4827(13)	C5	-H5B	0.9800
Zr1	-N1_a	2.236(4)	C5	-H5C	0.9800
Zr1	-N2_a	2.192(4)	C11	-H11A	1.0000
N1	-C2	1.334(7)	C12	-H12A	0.9900
N1	-C11	1.489(6)	C12	-H12B	0.9900
N2	-C4	1.334(7)	C13	-H13A	0.9900
N2	-C21	1.496(7)	C13	-H13B	0.9900
C1	-C2	1.517(8)	C14	-H14A	0.9900
C2	-C3	1.411(7)	C14	-H14B	0.9900
C3	-C4	1.394(7)	C15	-H15A	0.9900
C4	-C5	1.529(8)	C15	-H15B	0.9900
C11	-C12	1.534(7)	C16	-H16A	0.9900
C11	-C16	1.536(7)	C16	-H16B	0.9900
C12	-C13	1.538(8)	C21	-H21A	1.0000
C13	-C14	1.524(10)	C22	-H22A	0.9900
C14	-C15	1.525(9)	C22	-H22B	0.9900
C15	-C16	1.535(7)	C23	-H23A	0.9900
C21	-C22	1.536(7)	C23	-H23B	0.9900
C21	-C26	1.534(6)	C24	-H24A	0.9900
C22	-C23	1.521(8)	C24	-H24B	0.9900
C23	-C24	1.524(10)	C25	-H25A	0.9900
C24	-C25	1.522(9)	C25	-H25B	0.9900
C25	-C26	1.519(8)	C26	-H26A	0.9900
C1	-H1A	0.9800	C26	-H26B	0.9900
C1	-H1B	0.9800			

Table A-8 - Bond Angles (Degrees)
for: saida3(**4c**) R = 0.07

Cl1	-Zr1	-N1	90.04(10)	N1	-C11	-C12	111.9(4)
Cl1	-Zr1	-N2	95.43(11)	N1	-C11	-C16	119.6(4)
Cl1	-Zr1	-Cl1_a	93.36(4)	C12	-C11	-C16	110.0(4)
Cl1	-Zr1	-N1_a	174.01(11)	C11	-C12	-C13	109.8(5)
Cl1	-Zr1	-N2_a	94.34(12)	C12	-C13	-C14	111.0(6)
N1	-Zr1	-N2	80.41(15)	C13	-C14	-C15	111.3(5)
Cl1_a	-Zr1	-N1	174.01(11)	C14	-C15	-C16	110.8(5)
N1	-Zr1	-N1_a	87.01(14)	C11	-C16	-C15	108.4(4)
N1	-Zr1	-N2_a	89.23(15)	N2	-C21	-C22	113.4(4)
Cl1_a	-Zr1	-N2	94.34(12)	N2	-C21	-C26	116.7(4)
N1_a	-Zr1	-N2	89.23(15)	C22	-C21	-C26	112.1(4)
N2	-Zr1	-N2_a	165.74(17)	C21	-C22	-C23	109.9(5)
Cl1_a	-Zr1	-N1_a	90.04(10)	C22	-C23	-C24	112.1(5)
Cl1_a	-Zr1	-N2_a	95.43(11)	C23	-C24	-C25	111.3(5)
N1_a	-Zr1	-N2_a	80.41(15)	C24	-C25	-C26	111.6(5)
Zr1	-N1	-C2	121.7(3)	C21	-C26	-C25	109.1(4)
Zr1	-N1	-C11	115.7(3)	C2	-C1	-H1A	109.00
C2	-N1	-C11	122.6(4)	C2	-C1	-H1B	109.00
Zr1	-N2	-C4	123.8(3)	C2	-C1	-H1C	109.00
Zr1	-N2	-C21	113.2(3)	H1A	-C1	-H1B	110.00
C4	-N2	-C21	123.1(4)	H1A	-C1	-H1C	109.00
N1	-C2	-C1	121.8(5)	H1B	-C1	-H1C	110.00

Table A-8 - Bond Angles (Degrees) (continued)
for: saida3(**4c**) R = 0.07

N1	-C2	-C3	123.1(5)	C2	-C3	-H3A	116.00
C1	-C2	-C3	115.2(5)	C4	-C3	-H3A	117.00
C2	-C3	-C4	127.1(5)	C4	-C5	-H5A	109.00
N2	-C4	-C3	121.9(4)	C4	-C5	-H5B	110.00
N2	-C4	-C5	123.1(4)	C4	-C5	-H5C	109.00
C3	-C4	-C5	115.1(5)	H5A	-C5	-H5B	109.00
H5A	-C5	-H5C	109.00	C15	-C16	-H16B	110.00
H5B	-C5	-H5C	110.00	H16A	-C16	-H16B	108.00
N1	-C11	-H11A	105.00	N2	-C21	-H21A	104.00
C12	-C11	-H11A	105.00	C22	-C21	-H21A	104.00
C16	-C11	-H11A	105.00	C26	-C21	-H21A	104.00
C11	-C12	-H12A	110.00	C21	-C22	-H22A	110.00
C11	-C12	-H12B	110.00	C21	-C22	-H22B	110.00
C13	-C12	-H12A	110.00	C23	-C22	-H22A	110.00
C13	-C12	-H12B	110.00	C23	-C22	-H22B	110.00
H12A	-C12	-H12B	108.00	H22A	-C22	-H22B	108.00
C12	-C13	-H13A	109.00	C22	-C23	-H23A	109.00
C12	-C13	-H13B	109.00	C22	-C23	-H23B	109.00
C14	-C13	-H13A	109.00	C24	-C23	-H23A	109.00
C14	-C13	-H13B	109.00	C24	-C23	-H23B	109.00
H13A	-C13	-H13B	108.00	H23A	-C23	-H23B	108.00
C13	-C14	-H14A	109.00	C23	-C24	-H24A	109.00
C13	-C14	-H14B	109.00	C23	-C24	-H24B	109.00
C15	-C14	-H14A	109.00	C25	-C24	-H24A	109.00
C15	-C14	-H14B	109.00	C25	-C24	-H24B	109.00
H14A	-C14	-H14B	108.00	H24A	-C24	-H24B	108.00
C14	-C15	-H15A	109.00	C24	-C25	-H25A	109.00
C14	-C15	-H15B	110.00	C24	-C25	-H25B	109.00
C16	-C15	-H15A	109.00	C26	-C25	-H25A	109.00
C16	-C15	-H15B	109.00	C26	-C25	-H25B	109.00
H15A	-C15	-H15B	108.00	H25A	-C25	-H25B	108.00
C11	-C16	-H16A	110.00	C21	-C26	-H26A	110.00
C11	-C16	-H16B	110.00	C21	-C26	-H26B	110.00
C15	-C16	-H16A	110.00	C25	-C26	-H26A	110.00
C25	-C26	-H26B	110.00	H26A	-C26	-H26B	108.00

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saida23 (2d)   P21/n        R = 0.05          : Aug 24 10:48:50 2009
         ===========================================
         S U P P L E M E N T A R Y   M A T E R I A L
         ===========================================
         B E L O N G I N G   TO   T H E   P A P E R
                           b y
                     C o n t e n t s
                     ===============
Table A-9 - Bond Distances    (Angstrom)
            for: saida23(2d)   P21/n        R = 0.05
Table A-10 - Bond Angles       (Degrees)
            for: saida23(2d)   P21/n        R = 0.05

Table A-9 - Bond Distances   (Angstrom)
            for: saida23(2d)   P21/n        R = 0.05
Zr1    -N1          2.203(3)     C25    -C26        1.390(9)
Zr1    -N2          2.290(3)     C30    -C31        1.520(6)
Zr1    -N3          2.217(3)     C31    -C32        1.379(6)
Zr1    -N4          2.295(3)     C31    -C36        1.370(6)
Zr1    -C16         2.298(4)     C32    -C33        1.376(7)
Zr1    -C17         2.290(4)     C33    -C34        1.362(7)
N1     -C2          1.340(5)     C34    -C35        1.367(7)
N1     -C20         1.463(5)     C35    -C36        1.376(6)
N2     -C4          1.338(5)     C40    -C41        1.519(5)
N2     -C30         1.462(5)     C41    -C42        1.391(5)
N3     -C12         1.328(5)     C41    -C46        1.383(5)
N3     -C40         1.471(5)     C42    -C43        1.384(6)
N4     -C14         1.332(5)     C43    -C44        1.374(7)
N4     -C50         1.471(5)     C44    -C45        1.372(6)
C1     -C2          1.499(6)     C45    -C46        1.394(6)
C2     -C3          1.381(6)     C50    -C51        1.507(6)
C3     -C4          1.394(6)     C51    -C52        1.382(5)
C4     -C5          1.502(7)     C51    -C56        1.383(6)
C11    -C12         1.511(5)     C52    -C53        1.385(6)
C12    -C13         1.382(5)     C53    -C54        1.386(7)
C13    -C14         1.403(5)     C54    -C55        1.363(7)
C14    -C15         1.512(6)     C55    -C56        1.384(6)
C20    -C21         1.516(6)     C1     -H1A           0.9600
C21    -C22         1.373(6)     C1     -H1B           0.9600
C21    -C25         1.363(7)     C1     -H1C           0.9600
C22    -C23         1.383(7)     C3     -H3A           0.9300
C23    -C24         1.355(9)     C5     -H5A           0.9600
C24    -C26        1.354(11)     C5     -H5B           0.9600
C5     -H5C           0.9600     C30    -H30A          0.9700
C11    -H11A          0.9600     C30    -H30B          0.9700
C11    -H11B          0.9600     C32    -H32A          0.9300
C11    -H11C          0.9600     C33    -H33A          0.9300
C13    -H13A          0.9300     C34    -H34A          0.9300
C15    -H15A          0.9600     C35    -H35A          0.9300
C15    -H15B          0.9600     C36    -H36A          0.9300
C15    -H15C          0.9600     C40    -H40A          0.9700
C16    -H16A          0.9600     C40    -H40B          0.9700
C16    -H16B          0.9600     C42    -H42A          0.9300
C16    -H16C          0.9600     C43    -H43A          0.9300
C17    -H17A          0.9600     C44    -H44A          0.9300
C17    -H17B          0.9600     C45    -H45A          0.9300
C17    -H17C          0.9600     C46    -H46A          0.9300
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Table A-9 - Bond Distances (Angstrom) (continued)
for: saida23(**2d**) P21/n R = 0.05

C20	-H20A	0.9700	C50	-H50A	0.9700
C20	-H20B	0.9700	C50	-H50B	0.9700
C22	-H22A	0.9300	C52	-H52A	0.9300
C23	-H23A	0.9300	C53	-H53A	0.9300
C24	-H24A	0.9300	C54	-H54A	0.9300
C25	-H25A	0.9300	C55	-H55A	0.9300
C26	-H26A	0.9300	C56	-H56A	0.9300

Table A-10 - Bond Angles (Degrees)
for: saida23 (**2d**) P21/n R = 0.05

N1	-Zr1	-N2	74.57(11)	N1	-C2	-C3	121.0(3)
N1	-Zr1	-N3	77.30(11)	C1	-C2	-C3	119.0(4)
N1	-Zr1	-N4	126.07(11)	C2	-C3	-C4	125.7(4)
N1	-Zr1	-C16	137.71(13)	N2	-C4	-C3	122.5(4)
N1	-Zr1	-C17	94.25(14)	N2	-C4	-C5	120.8(4)
N2	-Zr1	-N3	127.20(11)	C3	-C4	-C5	116.7(4)
N2	-Zr1	-N4	155.37(10)	N3	-C12	-C11	120.6(4)
N2	-Zr1	-C16	78.35(14)	N3	-C12	-C13	121.7(3)
N2	-Zr1	-C17	87.24(14)	C11	-C12	-C13	117.7(4)
N3	-Zr1	-N4	74.82(10)	C12	-C13	-C14	125.6(3)
N3	-Zr1	-C16	94.60(12)	N4	-C14	-C13	122.7(3)
N3	-Zr1	-C17	138.83(14)	N4	-C14	-C15	120.5(3)
N4	-Zr1	-C16	89.95(13)	C13	-C14	-C15	116.8(3)
N4	-Zr1	-C17	78.58(14)	N1	-C20	-C21	114.6(4)
C16	-Zr1	-C17	116.36(15)	C20	-C21	-C22	123.5(4)
Zr1	-N1	-C2	130.1(2)	C20	-C21	-C25	118.5(4)
Zr1	-N1	-C20	109.4(2)	C22	-C21	-C25	118.0(4)
C2	-N1	-C20	119.6(3)	C21	-C22	-C23	120.9(5)
Zr1	-N2	-C4	126.4(3)	C22	-C23	-C24	120.4(5)
Zr1	-N2	-C30	114.9(2)	C23	-C24	-C26	119.5(5)
C4	-N2	-C30	118.1(3)	C21	-C25	-C26	120.8(6)
Zr1	-N3	-C12	130.0(2)	C24	-C26	-C25	120.3(7)
Zr1	-N3	-C40	108.5(2)	N2	-C30	-C31	114.2(3)
C12	-N3	-C40	120.0(3)	C30	-C31	-C32	123.5(4)
Zr1	-N4	-C14	126.3(2)	C30	-C31	-C36	119.3(4)
Zr1	-N4	-C50	115.2(2)	C32	-C31	-C36	117.2(4)
C14	-N4	-C50	117.5(3)	C31	-C32	-C33	121.4(4)
N1	-C2	-C1	120.0(4)	C32	-C33	-C34	120.7(5)
C33	-C34	-C35	118.7(4)	C4	-C3	-H3A	117.00
C34	-C35	-C36	120.6(4)	C4	-C5	-H5A	109.00
C31	-C36	-C35	121.5(4)	C4	-C5	-H5B	110.00
N3	-C40	-C41	115.3(3)	C4	-C5	-H5C	109.00
C40	-C41	-C42	118.8(3)	H5A	-C5	-H5B	110.00
C40	-C41	-C46	123.1(3)	H5A	-C5	-H5C	109.00
C42	-C41	-C46	118.2(3)	H5B	-C5	-H5C	109.00
C41	-C42	-C43	121.2(4)	C12	-C11	-H11A	109.00
C42	-C43	-C44	119.7(4)	C12	-C11	-H11B	110.00
C43	-C44	-C45	120.1(4)	C12	-C11	-H11C	109.00
C44	-C45	-C46	120.2(4)	H11A	-C11	-H11B	110.00
C41	-C46	-C45	120.6(4)	H11A	-C11	-H11C	109.00
N4	-C50	-C51	114.2(3)	H11B	-C11	-H11C	110.00
C50	-C51	-C52	121.0(4)	C12	-C13	-H13A	117.00
C50	-C51	-C56	121.0(4)	C14	-C13	-H13A	117.00
C52	-C51	-C56	117.9(4)	C14	-C15	-H15A	109.00

Table A-10 - Bond Angles (Degrees) (continued)
for: saida23 **(2d)** P21/n R = 0.05

C51	-C52	-C53	121.5(4)	C14	-C15	-H15B	110.00
C52	-C53	-C54	119.7(4)	C14	-C15	-H15C	109.00
C53	-C54	-C55	119.2(4)	H15A	-C15	-H15B	109.00
C54	-C55	-C56	121.1(4)	H15A	-C15	-H15C	109.00
C51	-C56	-C55	120.7(4)	H15B	-C15	-H15C	109.00
C2	-C1	-H1A	110.00	Zr1	-C16	-H16A	109.00
C2	-C1	-H1B	109.00	Zr1	-C16	-H16B	109.00
C2	-C1	-H1C	109.00	Zr1	-C16	-H16C	109.00
H1A	-C1	-H1B	109.00	H16A	-C16	-H16B	109.00
H1A	-C1	-H1C	109.00	H16A	-C16	-H16C	109.00
H1B	-C1	-H1C	109.00	H16B	-C16	-H16C	110.00
C2	-C3	-H3A	117.00	Zr1	-C17	-H17A	109.00
Zr1	-C17	-H17B	109.00	C34	-C33	-H33A	120.00
Zr1	-C17	-H17C	110.00	C33	-C34	-H34A	121.00
H17A	-C17	-H17B	110.00	C35	-C34	-H34A	121.00
H17A	-C17	-H17C	109.00	C34	-C35	-H35A	120.00
H17B	-C17	-H17C	109.00	C36	-C35	-H35A	120.00
N1	-C20	-H20A	109.00	C31	-C36	-H36A	119.00
N1	-C20	-H20B	109.00	C35	-C36	-H36A	119.00
C21	-C20	-H20A	109.00	N3	-C40	-H40A	108.00
C21	-C20	-H20B	109.00	N3	-C40	-H40B	108.00
H20A	-C20	-H20B	108.00	C41	-C40	-H40A	109.00
C21	-C22	-H22A	120.00	C41	-C40	-H40B	108.00
C23	-C22	-H22A	120.00	H40A	-C40	-H40B	107.00
C22	-C23	-H23A	120.00	C41	-C42	-H42A	119.00
C24	-C23	-H23A	120.00	C43	-C42	-H42A	119.00
C23	-C24	-H24A	120.00	C42	-C43	-H43A	120.00
C26	-C24	-H24A	120.00	C44	-C43	-H43A	120.00
C21	-C25	-H25A	120.00	C43	-C44	-H44A	120.00
C26	-C25	-H25A	120.00	C45	-C44	-H44A	120.00
C24	-C26	-H26A	120.00	C44	-C45	-H45A	120.00
C25	-C26	-H26A	120.00	C46	-C45	-H45A	120.00
N2	-C30	-H30A	109.00	C41	-C46	-H46A	120.00
N2	-C30	-H30B	109.00	C45	-C46	-H46A	120.00
C31	-C30	-H30A	109.00	N4	-C50	-H50A	109.00
C31	-C30	-H30B	109.00	N4	-C50	-H50B	109.00
H30A	-C30	-H30B	108.00	C51	-C50	-H50A	109.00
C31	-C32	-H32A	119.00	C51	-C50	-H50B	109.00
C33	-C32	-H32A	119.00	H50A	-C50	-H50B	108.00
C32	-C33	-H33A	120.00	C51	-C52	-H52A	119.00
C53	-C52	-H52A	119.00	C54	-C55	-H55A	119.00
C52	-C53	-H53A	120.00	C56	-C55	-H55A	120.00
C54	-C53	-H53A	120.00	C51	-C56	-H56A	120.00
C53	-C54	-H54A	120.00	C55	-C56	-H56A	120.00
C55	-C54	-H54A	120.00				

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saida30 (2e)   P212121      R = 0.03          : Aug 24 10:49:14 2009
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         S U P P L E M E N T A R Y   M A T E R I A L
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         B E L O N G I N G   TO   T H E   P A P E R
                           b y
                     C o n t e n t s
                     ===============
Table A-11  - Bond Distances   (Angstrom)
             for: saida30(2e)   P212121      R = 0.03
Table A-12 - Bond Angles       (Degrees)
             for: saida30(2e)   P212121      R = 0.03

Table A-11 - Bond Distances    (Angstrom)
            for: saida30 (2e)  P212121      R = 0.03
Zr1    -O1       1.9536(18)     N11    -C120       1.472(4)
Zr1    -O2       1.9500(18)     N12    -C104       1.326(3)
Zr1    -N1       2.2253(18)     N12    -C130       1.464(3)
Zr1    -N2       2.2882(18)     N13    -C112       1.320(4)
Zr1    -N3       2.3045(19)     N13    -C140       1.464(4)
Zr1    -N4       2.2295(19)     N14    -C114       1.330(3)
Zr2    -N11        2.225(2)     N14    -C150       1.477(4)
Zr2    -N12        2.305(2)     C1     -C2         1.508(3)
Zr2    -N13        2.314(2)     C2     -C3         1.396(3)
Zr2    -N14        2.232(2)     C3     -C4         1.410(3)
Zr2    -O11      1.9522(19)     C4     -C5         1.506(4)
Zr2    -O12      1.9393(18)     C11    -C12        1.510(4)
O1     -C16B       1.421(7)     C12    -C13        1.415(3)
O1     -C16A      1.349(12)     C13    -C14        1.388(3)
O2     -C18A       1.429(9)     C14    -C15        1.512(3)
O2     -C18B       1.391(7)     C16A   -C17A      1.512(19)
O11    -C27A      1.393(11)     C16B   -C17B      1.491(10)
O11    -C27B      1.402(10)     C18A   -C19A      1.534(12)
O12    -C37        1.395(4)     C18B   -C19B      1.528(10)
N1     -C2         1.337(3)     C20    -C21        1.520(4)
N1     -C20        1.472(3)     C21    -C26        1.390(4)
N2     -C30        1.476(3)     C21    -C22        1.385(3)
N2     -C4         1.319(3)     C22    -C23        1.390(4)
N3     -C12        1.314(3)     C23    -C24        1.367(5)
N3     -C40        1.463(3)     C24    -C25        1.379(5)
N4     -C14        1.332(3)     C25    -C26        1.379(5)
N4     -C50        1.474(3)     C30    -C31        1.512(4)
N11    -C102       1.332(3)     C31    -C36        1.385(3)
C31    -C32        1.391(4)     C11    -H11C         0.9600
C32    -C33        1.371(4)     C13    -H13A         0.9300
C33    -C34        1.378(4)     C15    -H15A         0.9600
C34    -C35        1.391(5)     C15    -H15B         0.9600
C35    -C36        1.376(4)     C15    -H15C         0.9600
C40    -C41        1.523(4)     C16A   -H16B         0.9700
C41    -C46        1.387(4)     C16A   -H16A         0.9700
C41    -C42        1.381(3)     C16B   -H16C         0.9700
C42    -C43        1.372(4)     C16B   -H16D         0.9700
C43    -C44        1.376(4)     C17A   -H17A         0.9600
C44    -C45        1.364(5)     C17A   -H17C         0.9600
C45    -C46        1.395(4)     C17A   -H17B         0.9600
C50    -C51        1.518(4)     C17B   -H17F         0.9600
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Table A-11 - Bond Distances (Angstrom) (continued)
for: saida30 (**2e**) P212121 R = 0.03

C51	-C52	1.360(5)	C17B	-H17D	0.9600
C51	-C56	1.363(4)	C17B	-H17E	0.9600
C52	-C53	1.384(5)	C18A	-H18B	0.9700
C53	-C54	1.352(7)	C18A	-H18A	0.9700
C54	-C55	1.352(7)	C18B	-H18D	0.9700
C55	-C56	1.404(5)	C18B	-H18C	0.9700
C1	-H1A	0.9600	C19A	-H19C	0.9600
C1	-H1B	0.9600	C19A	-H19A	0.9600
C1	-H1C	0.9600	C19A	-H19B	0.9600
C3	-H3A	0.9300	C19B	-H19F	0.9600
C5	-H5A	0.9600	C19B	-H19D	0.9600
C5	-H5B	0.9600	C19B	-H19E	0.9600
C5	-H5C	0.9600	C20	-H20A	0.9700
C11	-H11A	0.9600	C20	-H20B	0.9700
C11	-H11B	0.9600	C22	-H22A	0.9300
C23	-H23A	0.9300	C101	-C102	1.505(4)
C24	-H24A	0.9300	C102	-C103	1.409(4)
C25	-H25A	0.9300	C103	-C104	1.399(3)
C26	-H26A	0.9300	C104	-C105	1.509(4)
C30	-H30B	0.9700	C111	-C112	1.508(4)
C30	-H30A	0.9700	C112	-C113	1.412(4)
C32	-H32A	0.9300	C113	-C114	1.393(4)
C33	-H33A	0.9300	C114	-C115	1.516(4)
C34	-H34A	0.9300	C120	-C121	1.508(4)
C35	-H35A	0.9300	C121	-C122	1.411(4)
C36	-H36A	0.9300	C121	-C126	1.375(4)
C40	-H40B	0.9700	C122	-C123	1.379(4)
C40	-H40A	0.9700	C123	-C124	1.378(5)
C42	-H42A	0.9300	C124	-C125	1.363(5)
C43	-H43A	0.9300	C125	-C126	1.384(4)
C44	-H44A	0.9300	C27A	-H27B	0.9700
C45	-H45A	0.9300	C27A	-H27A	0.9700
C46	-H46A	0.9300	C27B	-H27D	0.9700
C50	-H50B	0.9700	C27B	-H27C	0.9700
C50	-H50A	0.9700	C28A	-H28A	0.9600
C52	-H52A	0.9300	C28A	-H28B	0.9600
C53	-H53A	0.9300	C28A	-H28C	0.9600
C54	-H54A	0.9300	C28B	-H28F	0.9600
C55	-H55A	0.9300	C28B	-H28E	0.9600
C56	-H56A	0.9300	C28B	-H28D	0.9600
C27A	-C28A	1.523(10)	C130	-C131	1.520(4)
C27B	-C28B	1.500(17)	C131	-C136	1.393(4)
C37	-C38	1.467(5)	C131	-C132	1.383(4)
C132	-C133	1.387(4)	C105	-H10G	0.9600
C133	-C134	1.381(4)	C105	-H10E	0.9600
C134	-C135	1.378(4)	C111	-H11F	0.9600
C135	-C136	1.382(4)	C111	-H11D	0.9600
C37	-H37A	0.9700	C111	-H11E	0.9600
C37	-H37B	0.9700	C113	-H11G	0.9300
C38	-H38B	0.9600	C115	-H11J	0.9600
C38	-H38C	0.9600	C115	-H11H	0.9600
C38	-H38A	0.9600	C115	-H11I	0.9600
C140	-C141	1.508(4)	C120	-H12B	0.9700
C141	-C142	1.373(5)	C120	-H12A	0.9700

Table A-11- Bond Distances (Angstrom) (continued)
for: saida30 (**2e**) P212121 R = 0.03

C141	-C146	1.399(4)	C122	-H12C	0.9300
C142	-C143	1.392(4)	C123	-H12D	0.9300
C143	-C144	1.370(5)	C124	-H12E	0.9300
C144	-C145	1.380(5)	C125	-H12F	0.9300
C145	-C146	1.372(5)	C126	-H12G	0.9300
C150	-C151	1.502(4)	C130	-H13B	0.9700
C151	-C152	1.377(4)	C130	-H13C	0.9700
C151	-C156	1.390(4)	C132	-H13D	0.9300
C152	-C153	1.367(6)	C133	-H13E	0.9300
C153	-C154	1.376(6)	C134	-H13F	0.9300
C154	-C155	1.370(5)	C135	-H13G	0.9300
C155	-C156	1.380(5)	C136	-H13H	0.9300
C101	-H10C	0.9600	C140	-H14A	0.9700
C101	-H10B	0.9600	C140	-H14B	0.9700
C101	-H10A	0.9600	C142	-H14C	0.9300
C103	-H10D	0.9300	C143	-H14D	0.9300
C105	-H10F	0.9600	C144	-H14E	0.9300
C145	-H14F	0.9300	C153	-H15G	0.9300
C146	-H14G	0.9300	C154	-H15H	0.9300
C150	-H15E	0.9700	C155	-H15I	0.9300
C150	-H15D	0.9700	C156	-H15J	0.9300
C152	-H15F	0.9300			

Table A-12 - Bond Angles (Degrees) (continued)
for: saida30(**2e**) P212121 R = 0.03

O1	-Zr1	-O2	97.12(7)	O11	-Zr2	-N11	98.65(8)
O1	-Zr1	-N1	100.82(7)	O11	-Zr2	-N12	89.07(8)
O1	-Zr1	-N2	89.84(7)	Zr1	-O1	-C16B	157.2(3)
O1	-Zr1	-N3	172.15(7)	Zr1	-O1	-C16A	168.9(4)
O1	-Zr1	-N4	96.24(7)	Zr1	-O2	-C18B	172.6(3)
O2	-Zr1	-N1	94.70(7)	Zr1	-O2	-C18A	169.0(4)
O2	-Zr1	-N2	170.39(7)	Zr2	-O11	-C27A	166.2(4)
O2	-Zr1	-N3	87.79(7)	Zr2	-O11	-C27B	163.1(4)
O2	-Zr1	-N4	102.52(7)	Zr2	-O12	-C37	176.78(18)
N1	-Zr1	-N2	77.42(7)	Zr1	-N1	-C2	126.14(15)
N1	-Zr1	-N3	84.81(7)	Zr1	-N1	-C20	114.95(14)
N1	-Zr1	-N4	154.00(7)	C2	-N1	-C20	118.44(19)
N2	-Zr1	-N3	86.04(7)	Zr1	-N2	-C30	116.04(14)
N2	-Zr1	-N4	83.20(7)	Zr1	-N2	-C4	124.28(16)
N3	-Zr1	-N4	76.66(7)	C4	-N2	-C30	118.28(19)
O11	-Zr2	-N13	169.80(8)	Zr1	-N3	-C12	124.40(16)
O11	-Zr2	-N14	94.33(8)	Zr1	-N3	-C40	116.01(15)
O12	-Zr2	-N11	92.92(8)	C12	-N3	-C40	118.9(2)
O12	-Zr2	-N12	168.49(8)	Zr1	-N4	-C50	114.77(15)
O12	-Zr2	-N13	89.13(8)	C14	-N4	-C50	118.9(2)
O12	-Zr2	-N14	102.55(8)	Zr1	-N4	-C14	125.78(15)
N11	-Zr2	-N12	77.45(8)	C102	-N11	-C120	118.5(2)
N11	-Zr2	-N13	87.37(8)	Zr2	-N11	-C102	126.62(17)
N11	-Zr2	-N14	158.05(8)	Zr2	-N11	-C120	114.59(18)
N12	-Zr2	-N13	84.19(7)	Zr2	-N12	-C130	116.95(15)
N12	-Zr2	-N14	85.18(8)	C104	-N12	-C130	118.2(2)
N13	-Zr2	-N14	77.52(8)	Zr2	-N12	-C104	124.45(17)
O11	-Zr2	-O12	98.72(9)	Zr2	-N13	-C112	124.91(17)
Zr2	-N13	-C140	115.76(16)	C22	-C23	-C24	120.3(3)
C112	-N13	-C140	119.0(2)	C23	-C24	-C25	119.7(3)
Zr2	-N14	-C114	125.49(17)	C24	-C25	-C26	120.4(3)
C114	-N14	-C150	118.8(2)	C21	-C26	-C25	120.7(3)
Zr2	-N14	-C150	114.62(17)	N2	-C30	-C31	115.4(2)
N1	-C2	-C3	122.5(2)	C30	-C31	-C32	120.1(2)
C1	-C2	-C3	117.0(2)	C30	-C31	-C36	121.1(2)
N1	-C2	-C1	120.5(2)	C32	-C31	-C36	118.6(2)
C2	-C3	-C4	126.9(2)	C31	-C32	-C33	120.7(3)
N2	-C4	-C3	122.5(2)	C32	-C33	-C34	120.7(3)
N2	-C4	-C5	121.3(2)	C33	-C34	-C35	119.0(3)
C3	-C4	-C5	116.3(2)	C34	-C35	-C36	120.3(3)
C11	-C12	-C13	115.9(2)	C31	-C36	-C35	120.7(2)
N3	-C12	-C13	123.0(2)	N3	-C40	-C41	115.1(2)
N3	-C12	-C11	121.1(2)	C40	-C41	-C46	122.9(2)
C12	-C13	-C14	125.7(2)	C40	-C41	-C42	119.2(2)
N4	-C14	-C15	119.9(2)	C42	-C41	-C46	118.0(2)
C13	-C14	-C15	117.1(2)	C41	-C42	-C43	121.7(2)
N4	-C14	-C13	123.1(2)	C42	-C43	-C44	120.3(2)
O1	-C16A	-C17A	104.7(11)	C43	-C44	-C45	119.1(3)
O1	-C16B	-C17B	113.9(5)	C44	-C45	-C46	121.0(3)
O2	-C18A	-C19A	107.7(7)	C41	-C46	-C45	120.0(3)
O2	-C18B	-C19B	108.7(5)	N4	-C50	-C51	112.7(2)
N1	-C20	-C21	114.1(2)	C50	-C51	-C52	120.2(2)
C20	-C21	-C22	121.4(2)	C52	-C51	-C56	118.8(3)
C22	-C21	-C26	118.3(2)	C50	-C51	-C56	121.0(2)

Table A-12 - Bond Angles (Degrees) (continued)
for: saida30(**2e**) P212121 R = 0.03

C20	-C21	-C26	120.3(2)	C51	-C52	-C53	120.9(4)
C21	-C22	-C23	120.7(2)	C52	-C53	-C54	120.5(5)
C53	-C54	-C55	119.4(4)	C14	-C15	-H15A	109.00
C54	-C55	-C56	120.3(4)	C14	-C15	-H15B	109.00
C51	-C56	-C55	120.0(3)	H15B	-C15	-H15C	109.00
H1A	-C1	-H1C	109.00	C17A	-C16A	-H16B	111.00
C2	-C1	-H1A	109.00	H16A	-C16A	-H16B	109.00
C2	-C1	-H1B	109.00	C17A	-C16A	-H16A	111.00
C2	-C1	-H1C	110.00	O1	-C16A	-H16B	111.00
H1A	-C1	-H1B	109.00	O1	-C16A	-H16A	111.00
H1B	-C1	-H1C	109.00	O1	-C16B	-H16D	109.00
C2	-C3	-H3A	117.00	O1	-C16B	-H16C	109.00
C4	-C3	-H3A	117.00	H16C	-C16B	-H16D	108.00
C4	-C5	-H5B	110.00	C17B	-C16B	-H16D	109.00
C4	-C5	-H5C	110.00	C17B	-C16B	-H16C	109.00
H5A	-C5	-H5B	109.00	C16A	-C17A	-H17C	109.00
C4	-C5	-H5A	109.00	H17B	-C17A	-H17C	109.00
H5A	-C5	-H5C	109.00	H17A	-C17A	-H17C	109.00
H5B	-C5	-H5C	109.00	C16A	-C17A	-H17A	109.00
H11B	-C11	-H11C	109.00	C16A	-C17A	-H17B	109.00
H11A	-C11	-H11B	110.00	H17A	-C17A	-H17B	110.00
H11A	-C11	-H11C	110.00	H17D	-C17B	-H17F	109.00
C12	-C11	-H11A	109.00	C16B	-C17B	-H17D	109.00
C12	-C11	-H11B	109.00	H17D	-C17B	-H17E	110.00
C12	-C11	-H11C	109.00	H17E	-C17B	-H17F	109.00
C12	-C13	-H13A	117.00	C16B	-C17B	-H17E	109.00
C14	-C13	-H13A	117.00	C16B	-C17B	-H17F	109.00
H15A	-C15	-H15C	109.00	C19A	-C18A	-H18A	110.00
C14	-C15	-H15C	110.00	O2	-C18A	-H18A	110.00
H15A	-C15	-H15B	110.00	O2	-C18A	-H18B	110.00
H18A	-C18A	-H18B	109.00	C25	-C24	-H24A	120.00
C19A	-C18A	-H18B	110.00	C23	-C24	-H24A	120.00
O2	-C18B	-H18C	110.00	C24	-C25	-H25A	120.00
H18C	-C18B	-H18D	108.00	C26	-C25	-H25A	120.00
C19B	-C18B	-H18C	110.00	C25	-C26	-H26A	120.00
C19B	-C18B	-H18D	110.00	C21	-C26	-H26A	120.00
O2	-C18B	-H18D	110.00	C31	-C30	-H30A	108.00
H19B	-C19A	-H19C	109.00	C31	-C30	-H30B	108.00
H19A	-C19A	-H19C	109.00	H30A	-C30	-H30B	108.00
C18A	-C19A	-H19B	110.00	N2	-C30	-H30A	108.00
H19A	-C19A	-H19B	109.00	N2	-C30	-H30B	108.00
C18A	-C19A	-H19A	109.00	C31	-C32	-H32A	120.00
C18A	-C19A	-H19C	109.00	C33	-C32	-H32A	120.00
C18B	-C19B	-H19F	110.00	C32	-C33	-H33A	120.00
C18B	-C19B	-H19D	110.00	C34	-C33	-H33A	120.00
C18B	-C19B	-H19E	109.00	C35	-C34	-H34A	120.00
H19E	-C19B	-H19F	109.00	C33	-C34	-H34A	121.00
H19D	-C19B	-H19E	110.00	C36	-C35	-H35A	120.00
H19D	-C19B	-H19F	109.00	C34	-C35	-H35A	120.00
N1	-C20	-H20B	109.00	C31	-C36	-H36A	120.00
C21	-C20	-H20A	109.00	C35	-C36	-H36A	120.00
C21	-C20	-H20B	109.00	C41	-C40	-H40A	108.00
H20A	-C20	-H20B	108.00	N3	-C40	-H40A	109.00
N1	-C20	-H20A	109.00	C41	-C40	-H40B	108.00

Table A-12 - Bond Angles (Degrees) (continued)
for: saida30(**2e**) P212121 R = 0.03

C21	-C22	-H22A	120.00	H40A	-C40	-H40B	108.00
C23	-C22	-H22A	120.00	N3	-C40	-H40B	109.00
C22	-C23	-H23A	120.00	C41	-C42	-H42A	119.00
C24	-C23	-H23A	120.00	C43	-C42	-H42A	119.00
C42	-C43	-H43A	120.00	N11	-C102	-C103	122.4(2)
C44	-C43	-H43A	120.00	C102	-C103	-C104	126.6(2)
C45	-C44	-H44A	120.00	N12	-C104	-C105	120.3(2)
C43	-C44	-H44A	120.00	C103	-C104	-C105	116.5(2)
C44	-C45	-H45A	120.00	N12	-C104	-C103	123.2(2)
C46	-C45	-H45A	119.00	N13	-C112	-C111	121.5(3)
C41	-C46	-H46A	120.00	N13	-C112	-C113	122.5(2)
C45	-C46	-H46A	120.00	C111	-C112	-C113	116.0(3)
H50A	-C50	-H50B	108.00	C112	-C113	-C114	127.1(3)
N4	-C50	-H50A	109.00	N14	-C114	-C113	123.1(2)
C51	-C50	-H50B	109.00	C113	-C114	-C115	116.4(2)
C51	-C50	-H50A	109.00	N14	-C114	-C115	120.5(2)
N4	-C50	-H50B	109.00	N11	-C120	-C121	114.5(2)
C51	-C52	-H52A	120.00	C120	-C121	-C122	118.5(2)
C53	-C52	-H52A	120.00	C122	-C121	-C126	117.4(3)
C52	-C53	-H53A	120.00	C120	-C121	-C126	124.2(2)
C54	-C53	-H53A	120.00	C121	-C122	-C123	120.5(3)
C55	-C54	-H54A	120.00	C122	-C123	-C124	120.5(3)
C53	-C54	-H54A	120.00	C123	-C124	-C125	119.6(3)
C54	-C55	-H55A	120.00	C124	-C125	-C126	120.4(3)
C56	-C55	-H55A	120.00	C121	-C126	-C125	121.7(3)
C55	-C56	-H56A	120.00	C28A	-C27A	-H27B	109.00
C51	-C56	-H56A	120.00	H27A	-C27A	-H27B	108.00
O11	-C27A	-C28A	110.2(7)	O11	-C27A	-H27A	110.00
O11	-C27B	-C28B	110.6(8)	O11	-C27A	-H27B	110.00
O12	-C37	-C38	111.4(3)	C28A	-C27A	-H27A	110.00
N11	-C102	-C101	120.7(2)	C28B	-C27B	-H27D	110.00
C101	-C102	-C103	117.0(2)	O11	-C27B	-H27C	110.00
H27C	-C27B	-H27D	108.00	H37A	-C37	-H37B	108.00
O11	-C27B	-H27D	110.00	C37	-C38	-H38C	109.00
C28B	-C27B	-H27C	109.00	C37	-C38	-H38B	109.00
C27A	-C28A	-H28B	110.00	H38A	-C38	-H38B	110.00
C27A	-C28A	-H28A	110.00	C37	-C38	-H38A	109.00
C27A	-C28A	-H28C	109.00	H38A	-C38	-H38C	109.00
H28A	-C28A	-H28B	109.00	H38B	-C38	-H38C	110.00
H28A	-C28A	-H28C	109.00	N13	-C140	-C141	115.3(2)
H28B	-C28A	-H28C	109.00	C142	-C141	-C146	117.6(3)
C27B	-C28B	-H28E	109.00	C140	-C141	-C142	123.6(2)
C27B	-C28B	-H28D	109.00	C140	-C141	-C146	118.8(3)
H28D	-C28B	-H28E	109.00	C141	-C142	-C143	120.9(3)
C27B	-C28B	-H28F	110.00	C142	-C143	-C144	120.4(3)
H28E	-C28B	-H28F	109.00	C143	-C144	-C145	119.6(3)
H28D	-C28B	-H28F	110.00	C144	-C145	-C146	119.8(3)
N12	-C130	-C131	114.9(2)	C141	-C146	-C145	121.6(3)
C130	-C131	-C136	120.3(2)	N14	-C150	-C151	115.0(2)
C130	-C131	-C132	121.3(2)	C150	-C151	-C152	118.0(3)
C132	-C131	-C136	118.3(2)	C150	-C151	-C156	124.3(3)
C131	-C132	-C133	121.0(3)	C152	-C151	-C156	117.7(3)
C132	-C133	-C134	120.0(3)	C151	-C152	-C153	121.4(3)
C133	-C134	-C135	119.7(3)	C152	-C153	-C154	120.7(3)

Table A-12 - Bond Angles (Degrees) (continued)
for: saida30(**2e**) P212121 R = 0.03

C134	-C135	-C136	120.2(3)
C131	-C136	-C135	120.8(3)
C38	-C37	-H37A	109.00
O12	-C37	-H37B	109.00
O12	-C37	-H37A	109.00
C38	-C37	-H37B	109.00
C102	-C101	-H10B	109.00
C102	-C101	-H10C	109.00
H10A	-C101	-H10B	109.00
C104	-C103	-H10D	117.00
C102	-C103	-H10D	117.00
C104	-C105	-H10E	110.00
C104	-C105	-H10F	110.00
H10F	-C105	-H10G	109.00
C104	-C105	-H10G	109.00
H10E	-C105	-H10F	109.00
H10E	-C105	-H10G	109.00
C112	-C111	-H11D	110.00
C112	-C111	-H11E	110.00
C112	-C111	-H11F	109.00
H11E	-C111	-H11F	109.00
H11D	-C111	-H11E	109.00
H11D	-C111	-H11F	109.00
C114	-C113	-H11G	116.00
C112	-C113	-H11G	116.00
C114	-C115	-H11I	110.00
C114	-C115	-H11J	109.00
C114	-C115	-H11H	110.00
H11H	-C115	-H11J	109.00
H11I	-C115	-H11J	109.00
H11H	-C115	-H11I	110.00
N11	-C120	-H12A	109.00
C121	-C120	-H12A	109.00
C121	-C120	-H12B	109.00
C141	-C140	-H14A	109.00
H14A	-C140	-H14B	107.00
C141	-C140	-H14B	108.00
N13	-C140	-H14A	108.00
C141	-C142	-H14C	119.00
C143	-C142	-H14C	120.00
C144	-C143	-H14D	120.00
C142	-C143	-H14D	120.00
C143	-C144	-H14E	120.00
C145	-C144	-H14E	120.00
C146	-C145	-H14F	120.00
C144	-C145	-H14F	120.00
C141	-C146	-H14G	119.00
C145	-C146	-H14G	119.00
C151	-C150	-H15E	109.00
C153	-C154	-C155	118.8(3)
C154	-C155	-C156	120.7(3)
C151	-C156	-C155	120.6(3)
C102	-C101	-H10A	109.00
H10B	-C101	-H10C	110.00
H10A	-C101	-H10C	109.00
N11	-C120	-H12B	109.00
H12A	-C120	-H12B	108.00
C121	-C122	-H12C	120.00
C123	-C122	-H12C	120.00
C124	-C123	-H12D	120.00
C122	-C123	-H12D	120.00
C125	-C124	-H12E	120.00
C123	-C124	-H12E	120.00
C126	-C125	-H12F	120.00
C124	-C125	-H12F	120.00
C121	-C126	-H12G	119.00
C125	-C126	-H12G	119.00
C131	-C130	-H13B	109.00
H13B	-C130	-H13C	107.00
N12	-C130	-H13C	109.00
C131	-C130	-H13C	109.00
N12	-C130	-H13B	109.00
C131	-C132	-H13D	119.00
C133	-C132	-H13D	120.00
C134	-C133	-H13E	120.00
C132	-C133	-H13E	120.00
C135	-C134	-H13F	120.00
C133	-C134	-H13F	120.00
C136	-C135	-H13G	120.00
C134	-C135	-H13G	120.00
C131	-C136	-H13H	120.00
C135	-C136	-H13H	120.00
N13	-C140	-H14B	108.00
H15D	-C150	-H15E	107.00
N14	-C150	-H15E	109.00
C151	-C150	-H15D	108.00
N14	-C150	-H15D	109.00
C151	-C152	-H15F	119.00
C153	-C152	-H15F	119.00
C152	-C153	-H15G	120.00
C154	-C153	-H15G	120.00
C155	-C154	-H15H	121.00
C153	-C154	-H15H	121.00
C156	-C155	-H15I	120.00
C154	-C155	-H15I	120.00
C151	-C156	-H15J	120.00
C155	-C156	-H15J	120.00