Introduction

Ziegler Natta catalysts

Ziegler-Natta catalysts are used in the synthesis of polymers of 1-alkenes (α-olefins). It could be either heterogeneous or homogeneous.

Currently three kind are employed:

- Solid and supported catalysts based on titanium compounds. They are used in polymerization reactions in combination with cocatalysts, i.e. organoaluminum compounds such as triethylaluminium, $Al(C_2H_5)_3$.
- Various mono- and bis-metallocene complexes of Ti, Zr or Hf, which are soluble in reactionmedium. They are usually used in polymerization reactions in combination with a different organoaluminum cocatalyst, methylaluminoxane (or methylalumoxane, MAO).
- Soluble post-metallocene catalysts based on complexes of various transition metals with multidentate oxygen- and nitrogen-based ligands. These complexes are also activated with MAO.

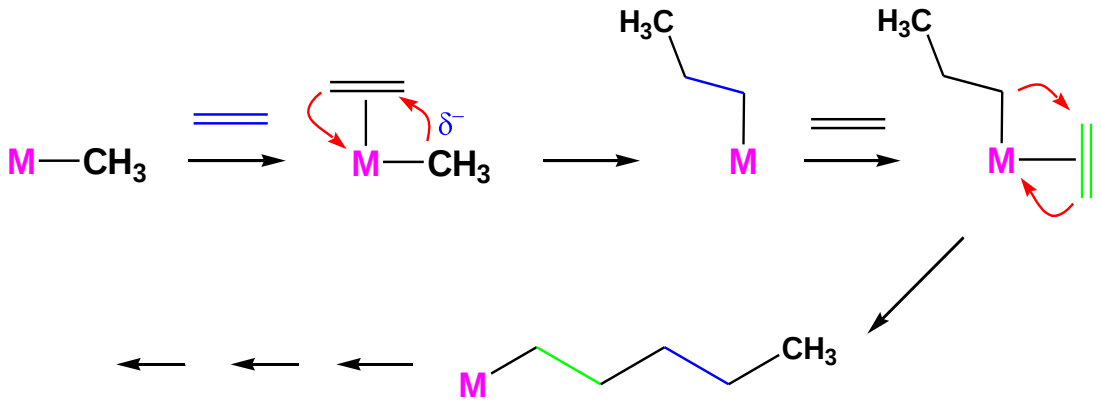
Historically, heterogeneous polymerization catalysts have been the workhorse of the polymer industry. Although these catalysts offer many important advantages, over their homogeneous counterparts, in commercial production, they also have a significant number of drawbacks.

For example, hetereogeneous catalysts typically have multiple active sites, each of which has its own rate constants for monomer enchainment, stereoselectivity, comonomer incorporation, and chain transfer.[1] Therefore a substantial amount of empirical optimization of these catalysts is necessary before polymers of relatively uniform molecular weights, composition, and stereochemistry can be produced.

Mechanism of α-olefin Polymerization

Ziegler-Natta catalysts, are remarkable for their ability to effect the polymerization of olefins to polymers of high molecular weights and highly ordered (stereoregular) structures.[2]

The commonly accepted mechanism for polymer chain growth on a transition metal catalyst is the very simple migratory insertion mechanism initially proposed by Cossee and Arlman (Royal Shell labs) in 1964.[3]



Scheme 1. Cossee-Arlamn mechanism for olefin polymerization.

This mechanism substantially take places in two steps:

- olefin coordination to a vacant site
- alkyl migration of the σ-coordinated growing chain to the π-coordinated olefin. At the end of the reaction, a net migration of the Mt−chain σ-bond to the coordination position previously occupied by the olefin ensures.

The key features of the insertion mechanism are that the active metal center bearing the growing alkyl chain must have an available coordination site for the incoming monomer (the active catalyst are monoalkyl cations), and that insertion happens via chain migration to the closest carbon of the olefin double bond, which undergoes cis opening with formation of the new metal−carbon and carbon−carbon bonds: the new C−C bond is then

on the site previously occupied by the coordinated monomer molecule.

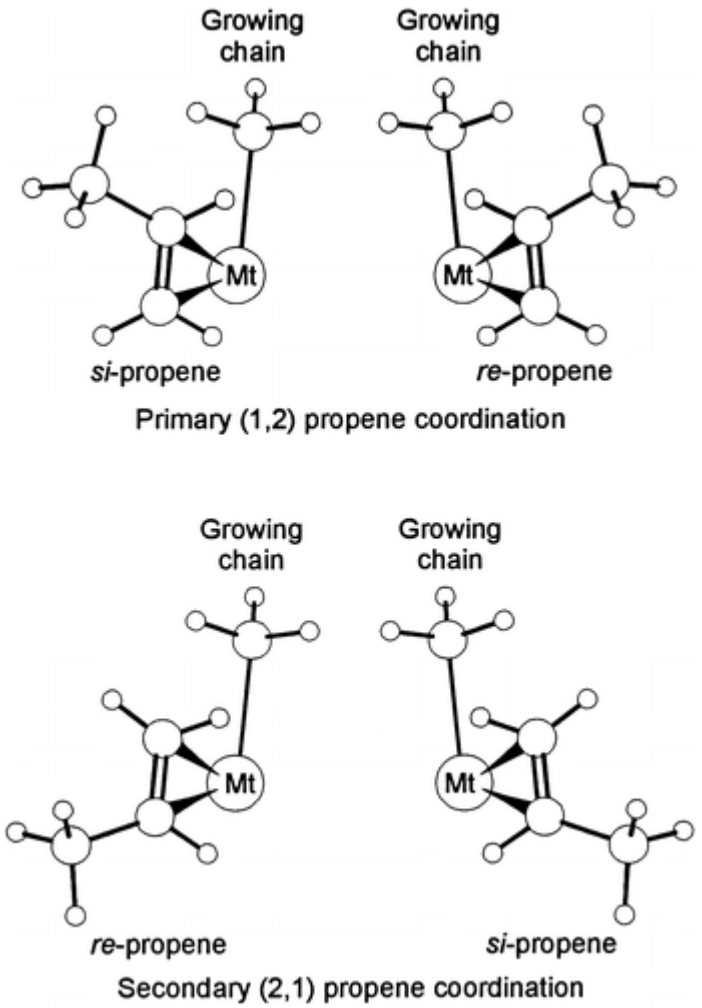
Concerning the organometallic chemistry of olefin insertion,[4] it is now clear that in most cases the active catalytic species for olefin polymerization are coordinatively unsaturated metal alkyls of the formula $[L_nM{-}P]^+[A]^-$, where P is a polymer chain, and A is a weakly coordinating anion. Many convenient methods for generating these species are now available; among the most used are reaction of a metal dihalide $[L_nMX_2]$ with MAO or the reaction of a metal dialkyl $[L_nMR_2]$ with either fluorinated boranes,[5] borate salts,[6] or aluminate salts.[7]

Selectivity in α-olefins polymerization

The polymerization of α-olefins introduces the problems of stereoselectivity (enantioface selectivity or enantioselectivity) and regioselectivity.[8]

In Ziegler−Natta catalysis, and in general in coordination polymerization, a polyolefin is produced by multiple insertion of olefins into a metal−carbon bond. If we consider propene and a metallocene catalyst of general formula L_2MX_2, we have that primary propene insertion occurs when the CH_2 group of the olefin binds to the metal while secondary propene insertion follow when the CH group of the olefin binds to the growing chain.

Whether the olefin insertion is primary or secondary defines the *regiochemistry* of insertion (thus the catalyst *regioselectivity* and the *regioregularity* of the polymer), while the choice of the olefin enantioface (or enantioface selectivity) defines the *stereochemistry* of each insertion (the catalyst *stereoselectivity*). Since α-olefins are prochiral, in principle they can coordinate and insert into a transition metal−carbon bond in four different ways (Scheme 2).



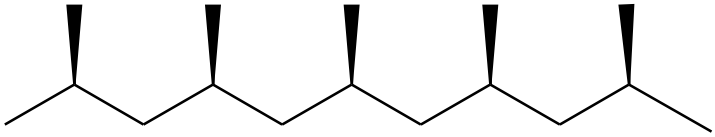
Scheme 2. Possible insertion modes of propene into the Mt-growing chain bond.

Multiple insertions of the same enantioface produce a polymer chain with chiral centers and we could obtain different kind of products, stereoregular or not, depending on the relative stereochemistry of adjacent chiral centers within a macromolecule.

Since every propene insertion, whatever its orientation, creates a new stereogenic center, the catalyst *stereoselectivity* (and the *stereoregularity* or *tacticity* of the polymer) is determined by the stereochemical relationship between the stereogenic carbon atoms in the polymer chain. In fact stereoregular poly(1-alkene) can be isotactic or syndiotactic, depending on the relative orientation of the alkyl groups in polymer chains consisting of units -[CH_2-CHR]-. In the isotactic polymers (A in Scheme 3), all stereogenic centers CHR share the same configuration. Multiple insertions of alternating enantiofaces produce

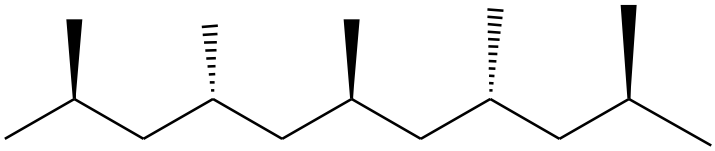
a syndiotactic polymer (B in Scheme 3) chain with chiral centers of alternating configuration. A polymer that lacks any regular arrangement in the position of its alkyl substituents (R) is called atactic (C in Scheme 3).

The regularity of lack of regularity affect their properties by way of large differences in their abilities to crystallize. For example while isotactic and syndiotactic polypropenes are partially crystalline materials with relatively high melting points (up to 160−170°C for *i*-PP, and ~150°C for *s*-PP), atactic polypropene (*a*-PP) is a fully amorphous polymer, since it lacks long-range stereochemical regularity.[9]



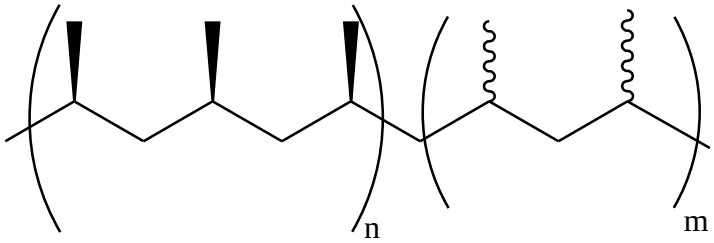
ISOTACTIC POLYPROPYLENE

A



SYNDIOTACTIC POLYPROPYLENE

B



STEREOBLOCK POLYPROPYLENE

C

Scheme 3. Chain segments shown in theirs trans-planar and Fisher projections.

There are some parameters that are used to describe the stereoselectivity of the monomer enchainment process. Two adjacent structural units in a polymer molecule constitute a diad. If the diad consists of two identically oriented units, the diad is called a meso diad

reflecting similar features as a meso compound. If the diad consists of units oriented in opposition, the diad is called a racemo diad as in a racemic compound. In the case of vinyl polymer molecules, a meso diad is one in which the substituent carbon chains are oriented on the same side of the polymer backbone.

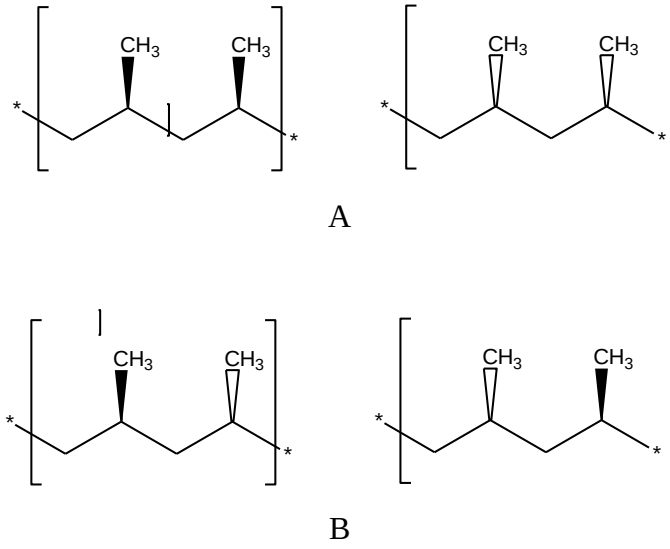


Figure 1. An example of *meso* diads A and *racemo* diads B in a polypropylene molecule.

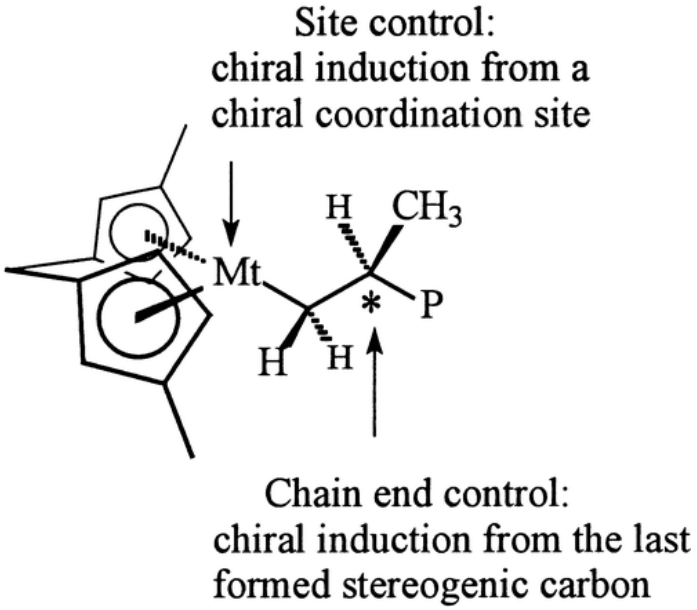
The stereoregularity of the polymer is determined by the catalyst used to prepare it. Once the polymer chain is formed, its stereochemistry does not change.

There are two possible sources of enantioface selectivity in olefin insertion and both the ligand set of a single-site catalyst and the growing polymer chain influence the stereochemistry of the polymerization reaction.[10] It is interesting to note that, unlike the catalytic synthesis of small molecules, during a chain-growth polymerization reaction a polymer chain remains bound to the active metal center during monomer enchainment.

Thus, the stereogenic center from the last enchained monomer unit will have an influence on the stereochemistry of monomer addition, because every monomer insertion generates a new stereogenic center. As a consequence, chiral induction (that is, enantioface preference) can come from the last unit, and this mechanism is referred to as *chain-end control* (Scheme 4).

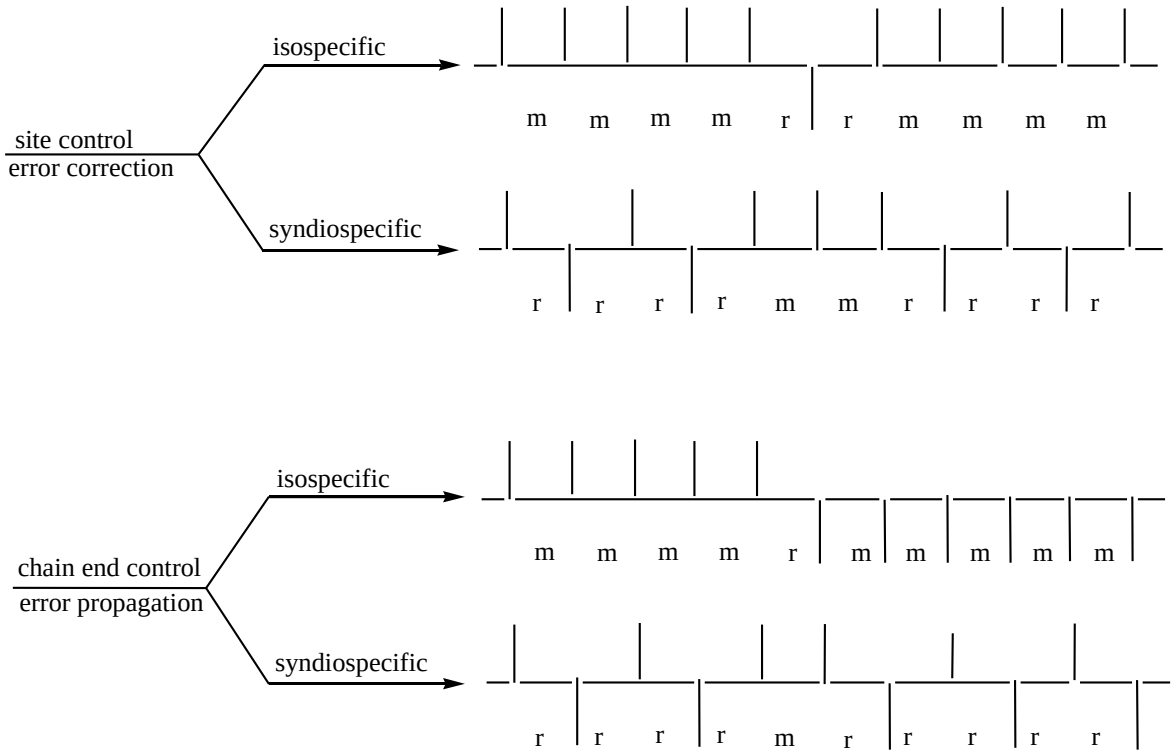
It should be noted that in rare instances more than one stereogenic center of the polymer can play a significant role in stereoregulation. It is the chirality relationship of the two coordination sites of the catalytic complex that determines the stereochemistry of the polymer.

If the ligand set is chiral and overrides the influence of the polymer chain end, the mechanism of stereochemical direction is termed "*enantiomorphic site control*" (Scheme 4). In this case the chiral induction comes from the asymmetry of the reaction site. In the former mechanism, a stereochemical error is propagated, while in the other one a correction occurs since the ligands direct the stereochemical events.



Scheme 4.

Hence, there can be four stereospecific polymerization mechanisms in primary polyinsertion, all of which have been documented with metallocene catalysts (Scheme 5): the two originated by the chiralities of the catalyst active sites, referred to as *enantiomorphic site control* (isospecific[11] and syndiospecific[12,13] site control), can be relatively strong, with differences in activation energy ($\Delta\Delta E$) for the insertion of the two enantiofaces up to 5 kcal/mol.



If the enantiomorphic site control is operative (top-half view), stereoerrors do not propagate, and the corresponding iso- and syndiotactic polymers are characterized by the presence of rr and mm triads, respectively. If chain-end control is operative (bottom-half view), stereoerrors propagate, and the corresponding iso- and syndiotactic polymers are characterized by the presence of isolated r and m diads, respectively.

Scheme 5. Mechanism of stereocontrol in 1-olefin polyinsertion.

Because of the mechanism of enantioface selectivity and the two-site, chain migratory insertion mechanism, the microstructure of a poly(α-olefin) made with a given metallocene is, to a large extent, predictable.

The most important mechanism of stereospecific polymerization is isospecific enantiomorphic site control,[14] which allows today the production of more than 25 million

tons per year of isotactic polypropene and its copolymers, in a wide range of molecular weights and crystallinities.

Polymerization catalysts based on 4 group metal complexes

Starting from metallocenes[15] and geometry-constrained complexes, over the last 25 years a tremendous effort has been made in designing new complexes as potential Ziegler–Natta catalysts for the polymerization and copolymerization of *α-olefins*[16,17]. Various compounds of the Group 3–13 metals with carbon- [18-20] , oxygen-[21-24], and nitrogen- [25-29] based ligands have been described.

Among all catalysts for the linear polymerization of hydrocarbyl olefins, the class of group 4 catalyst-based systems is the only one enabling control over the whole range of molecular weights (from olefin dimers and oligomers, to ultrahigh molecular weight polymers) and microstructures (stereoregularity, regioregularity, comonomer distribution) of polyolefins in a very wide range, making possible the synthesis of improved and new polyolefin materials.

The success of group 4 metallocenes in olefin polymerization[30] arises not only from their intrinsic understandability in terms of "simple" steric effects but also from the challenge they posed in terms of organic and organometallic syntheses: while the heterogeneous catalysts are much more difficult to study in terms of elementary steps than the homogeneous ones, the latter in turn are in general more difficult to synthesize.

The most important progresses in the field, which have largely outpaced those made in heterogeneous Ti-based and Cr-based catalysts, are the understanding of the catalyst structure/polymerization mechanism/polymer structure relationships and, in part as a consequence of it, the synthesis of a large number of novel polyolefin structures, such as random, stereoblock, and syndiotactic polyolefins.

In fact there is a strong correlation between catalyst symmetry and corresponding polymer structure. The stereochemical structure of the polymer is affected by the nature of the transition metal, the substituent of the olefin and the structure of catalyst. In fact in order to produce isotactic polypropylene, C_2 symmetry of the catalyst precursor is necessary.

A family of C_2-symmetric catalysts was designed and synthesized with the intent to polymerize 1-olefine. The catalyst was designed to be C_2-symmetric for the specific goal

that the catalyst would have two identical sites for the propagation of the polymer and therefore eliminate some of the stereoerrors that occur in the propagation of the polymer chain.

Group 4 polymerization catalysts could have tetrahedral and octahedral geometry. Example of tetrahedral 4 group catalysts are the classical metallocene complexes. One of the most successful catalysts for isospecific olefin polymerization is bis cyclopentadienyl zirconium dichloride, a Brintzinger's catalyst for the polymerization of propylene, an *ansa*-zirconocene characterized by a bridging group, which forming a rigid, C_2-symmetric chelating ligand structure[31].

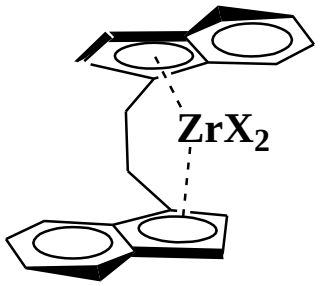


Figure 2. Bis cyclopentadienyl zirconium dichloride.

The explosion of research in this area can be traced to Ewen's 1984 publication that reported the synthesis of moderately isotactic polypropylene using rac-ethylene-bis(1-indenyl)zirconium dichloride (rac- Et[Ind]$_2$ZrCl$_2$), a chiral *ansa*-metallocenes first prepared by Brintzinger[32]

Prior to the mid-1980s, catalysts formed using achiral Cp_2MCl_2 precursors were found to produce only atactic polypropylene (which, incidentally, cannot be obtained in the pure form directly from heterogeneous catalysts).

Ewen first reported the use of metallocene-based catalysts for the isospecific polymerization of propylene. The polymerization of propylene at −45 °C using a Cp_2TiPh_2/MAO catalyst system produced a partially isotactic polymer with a *mmmm*-content of 52% (P_m = 0.85).

Example of octahedral group 4 catalysts are the Fujita complexes. [33] A neutral FI catalyst is an octahedral complex bearing two bidentate phenoxy-imine ligands and two nonspectator X= alogens ligands (Figure 3).

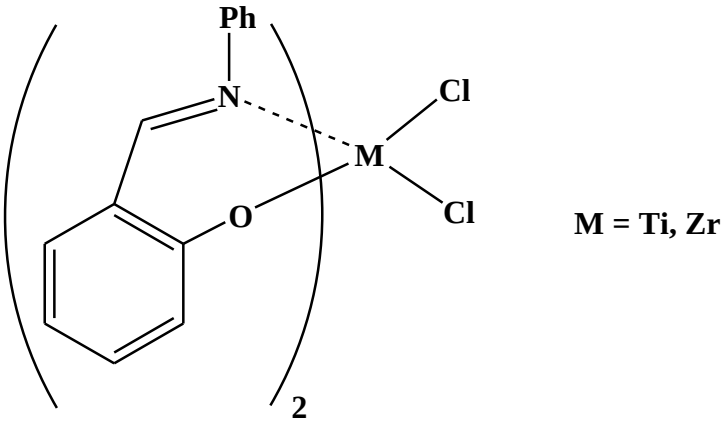


Figure 3. Fujita's catalyst for olefin polymerization.

These compounds are able to produce polyethylene with activities comparable to or exceeding those of metallocene catalyst. In particular, bis(phenoxy)imino zirconium complexes with system i-$Bu_3Al/Ph_3CB(C_6F_5)_4$ produce polypropylene with a high degree of isotacticity.[34]

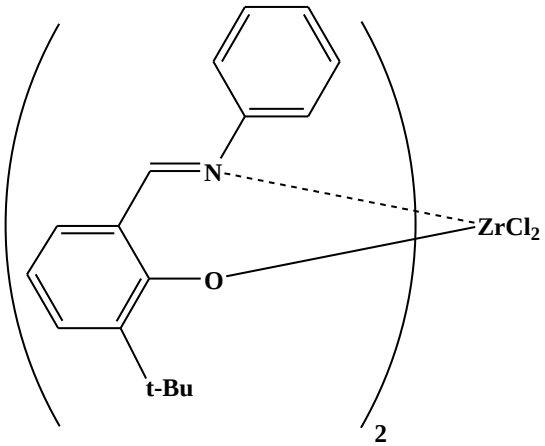


Figure 4. Bis(phenoxy)imino dichloride zirconium complexes

An important feature of FI catalysts is their straightforward synthesis, that is, Schiff base condensation of *ortho*-hydroxy aromatic aldehydes or ketones and primary amines, both of which have numerous synthetic recipes and rich inventories as commercially available

compounds. This feature allows to build enormous and diverse ligand libraries with a variety of substituents, including heteroatom-based functional groups.

During the past 25 years, several different classes of C_2-symmetric catalysts for the isospecific polymerization of α-olefins have been devised, a huge number of different ligand structures have been synthesized, and the substituent effect on polymer properties and catalyst activity is now mastered to a high level. Complexes with octahedral structure, based on monoanionic-bidentate ligands came out as versatile precursors because of their stability, activity and selectivity. [35-36]

Particularly with group 4 metals, the majority of these catalytic precursors contain nitrogen- and/or oxygen- donor ligands such as diamides,[35] benza and alkylamidinates, [36] tetradentate Schiff bases, [37] or alkoxides ligands. [38]

As far as the transition metal is concerned, in polymerization processes, Zr is by far the most active metal used. Research show that stereoregular polymerization of *α*-olefins using octahedral zirconium complexes could be modulate by pressure. These results raise conceptual questions regarding the general applicability of *cis*-octahedral C2-symmetry complexes to the stereospecific polymerization of *a*-olefins.

The interest for this class of compounds encouraged the investigation of new ligands, for instance [N,N], based on nitrogen (amidinate, pyrrolil-aldyminate, pyridil-amido, etc), or [N,O], based on amino or imino group bonded to alkoxo donors. In particular the [N,O] ligands are able to efficiently stabilize the complexes of electropositive group 4 metals: in fact alkoxides are hard, electronegative π-donor ligands, and they offer strong metal-oxygen bonds that are expected to stabilize complexes of electropositive metals.[39]

The synthetic chemistry of early transition metal complexes based on simple alkoxides proved to be, however, often complicated. This is largely due to the high tendency of the relatively more basic alkoxide ligands (as compared to aryloxides) to act as bridging ligands, eventually resulting in (highly) agglomerated structures.
It was observed that also steric and electronic properties of ancillary ligands, strongly influence reactivity of transition metal complexes, producing sometimes highly active olefin polymerization catalysts.

N-heterocyclic carbene ligand

N-heterocyclic carbene [NHC], which are versatile ligands because of their steric and electronic properties, can be suitably tuned in order to stabilize group 4 metal complexes and to obtain compounds having potential catalytic activity.[40]

Since the discovering of the first stable free carbene by Arduengo and relatives stable N-Heterocyclic Carbenes (NHCs, F, Fig. 5) there has been an explosion of interest in this ligand class.

Carbenes reactivity comes mainly from their electronic unsaturation, i.e. carbon as group 14 element has four electrons, four valence orbitals and as carbene two valence bonds. It is therefore left with the choice to place either one electron into each of the two remaining orbitals (thus becoming a triplet carbene) or both electrons into one orbital and leaving the fourth orbital empty (singlet carbene) (see Fig. 5).[41]

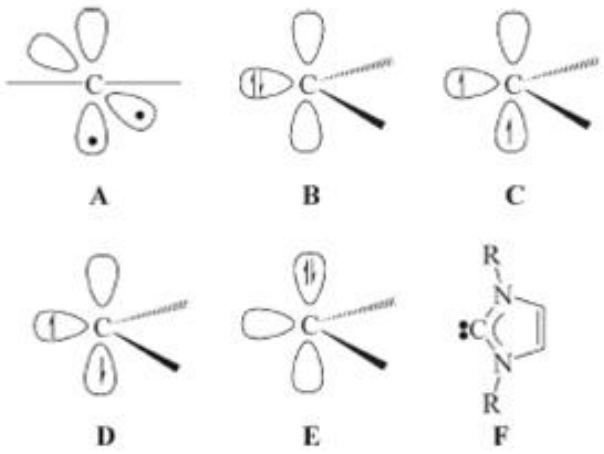


Figure 5. Electronic structures of NHCs

In N-Heterocyclic Carbenes the carbene centre is bent by virtue of its incorporation into a (usually) five-membered ring.

The presence of the two a-amino substituents is very important, bacause play two electronic roles:

- is responsible for the stabilisation of the formally sp^2-hybridised non-bonding lone pair by a s-inductive withdrawing effect.
- cause the destabilisation of the vacant p-orbital by a mesomeric effect, via donation of the α-amino lone pairs into the vacant p-orbital.

This push–push (mesomeric) pull–pull (inductive) arrangement ensures the preservation of electroneutrality at the carbene centre and renders the singlet state dominant.

One of the aspect that has most influenced their spread is the ability of these compounds to replace the classic legand phosphine, catalytic precursors generating much more robust, versatile and high thermal stability of their phosphine congeners.[42]

N.B. *A stable carbene is a carbene that is persistent at ambient temperature (and often does not decompose even at temperatures higher than 200 uC), but requires an inert gas atmosphere and is extremely sensitive to moisture and chlorinated solvents.*

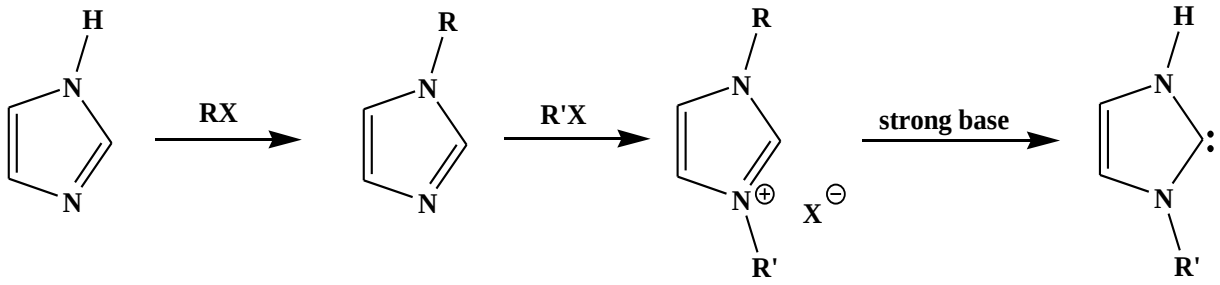
They were found to be more electron-rich ligands than the phosphines they replaced and more firmly bound to the metal catalyst. Both are highly desirable properties and the main reasons for their success in catalytic applications. Now NHCs are increasingly finding use as phosphine ligand replacements in mid- and late- transition metal complexes for homogeneous catalysis.

In fact, although NHCs are very different to phosphines both electronically and in terms of their spatial arrangement of substituents (and thus their steric properties), they both possess a non-bonding singlet lone pair. One more the Addition of the heterocyclic substituents can modulate the effects stereo electronics.

As a consequence of the strongly nucleophilic NHC singlet lone pair, NHCs are suitable for a wide range of metals. That said, although strongly nucleophilic, NHCs are still softer than amides and alkoxides; for a significant expansion into early metal chemistry, functionalised NHCs are required.

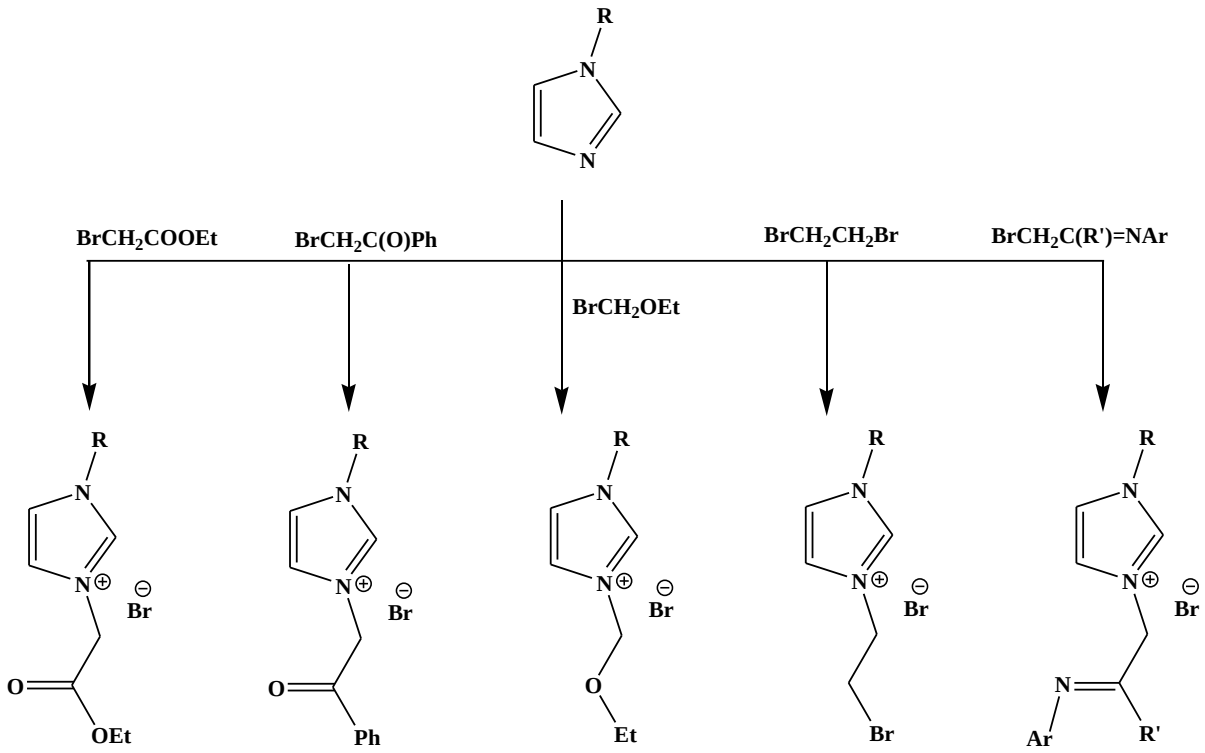
However, whereas phosphines are better suited to mid- and late-transition metals due to their soft nature and involvement in backbonding, NHCs have no necessary requirement for backbonding, although the issue of backbonding to NHCs is still an area of controversy and discussion.

Usually N-Heterocyclic carbenes are synthesised from imidazole which can be functionalised on both nitrogen atoms (see Scheme 6).



Scheme 6. Synthesis of N-heterocyclic carbenes

Functional groups can be introduced in the imidazole side chain by conventional synthetic methods.[43] The potential of a hydroxyalkyl substituent on the imidazole ring was recognized very early. In fact the hydroxygroup can be converted into an ester or an ether or substituted by a halogen1 and subsequently converted into a phosphine (see Scheme 7).[44]



Scheme 7. Functionalisation of imidazoles

Introduction of an amino sidegroup is equally facile. [45] The main limitation for the introduction of functional groups lies in the method of carbene formation A free NHC is most often synthesised by abstraction of the hydrogen atom bonded to the carbon between the two nitrogen atoms. As this hydrogen atom is not very acidic, a strong base is needed.

Functional groups on the imidazolium ring must therefore be inert to strongly basic conditions, preferably even at elevated temperatures. It comes as no surprise that the first functional groups introduced into NHC were tertiary amines, ethers, and phosphines, but other groups such as primary and secondary amides as well as alcoholates were soon to follow.

N-heterocycle carbene complexes

As a consequence of the strongly nucleophilic NHC singlet lone pair, NHC ligands are suitable for a wide range of metals. They have become established as efficient ancillary ligands for homogeneous catalysis, and over the past decade, an increasing number of catalytic transformations have been carried out using these transition-metal carbene complexes. Such reactions include Heck-type coupling, hydroformylation and hydrogenation, and olefin metathesis.

In particular in the last one research area were obtained an high success with Grubbs' Catalyst [46], a compound that compared to other olefin metathesis catalysts, is able to tolerate other functional groups in the alkene and are compatible with a wide range of solvents. The only difference with the analogous previous complex was the introduction of an NHC ligands intead of PCl_3 group in the structure. For this discovery Grubbs received Nobel Prize recognition.

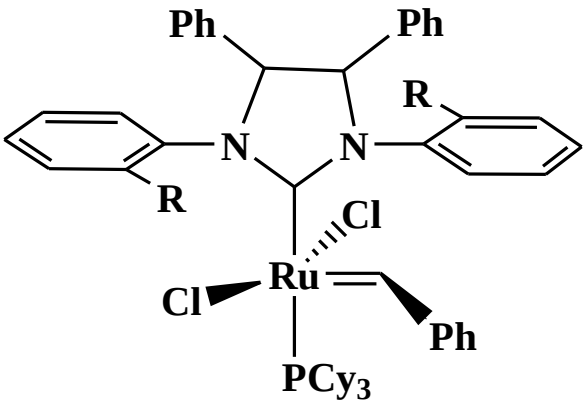


Figure 6. Grubb's catalyst for olefin metathesis polymerization.

With the notable exception of metathesis-based polymerization (Ru−carbene),[47] heterocyclic carbenes have not found widespread application in olefin polymerization. It is interesting to note that, with few exceptions, most examples of these ligands being employed in catalysis have exploited late-transition-metal complexes [48]; early-transition-metal carbene complexes have been sparsely examined in this respect, and reported activities have in general been rather low. [41,49].

This is possibly due in part to the propensity of alkylmetal carbene complexes to decompose via alkyl−imidazolium eliminations.[50] Alkylmetal intermediates are expected to be involved in each step of the polymerization cycle. This reaction has been found to occur for late-transition-metal complexes,[51] and we reasoned that its effect may be attenuated by employing early-transition-metal carbene complexes.

However, early-transition-metal complexes are likewise efficient catalysts for a diverse range of reactions, an example being the ubiquity of these metals in olefin oligomerization and polymerization chemistry.

Recently, functionalized N-heterocyclic carbene [NHC] ligands having a pendant anionic group, have received considerable attention in the organometallic chemistry.[52] The combination of a strong electron-donating ylidene carbon with an anionic group (alcohoxy, phenoxy or amido) generates a chelating ligand abled to give rise to complexes with noticeable stability and having steric rigidity and often chirality. [40]

Kawaguchi described the synthesis of titanium compounds with an aryloxide-NHC hybrid ligands [53], in which the aryloxido group acts as an anchor and reduces the tendency for NHC dissociation.

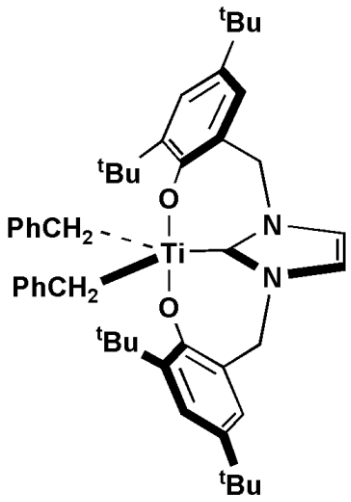


Figure 7. Kawaguchi's catalyst for olefin polymerization.

A problem correlated to this kind of catalysts is due to their low coordination sphere stability. We could resolve it using an high valance early transition metal as strong Lewis acids and specific ligands which including both strong σ-donor atoms and π-donors system. In fact the strong σ-donor property of this ligands is able to generate exceptionally stable Metal-Carbene bonds and give a complex with high thermal and hydrolytic durability.

Another aspect that we have to consider is that introducing into the complex an NHC ligands we destabilize the metal-alkyl bond, which prevents polymerization. To avoid this problem we using an NHC-alkoxy ligand which give more stability to complex.

Here we report the synthesys and charachterization of a new class of post-metallocene catalysts, having bidentate monoanionic [NHC-O] ligands. These compounds are used as active homogeneous catalysts for the polymerization of ethylene and propylene in the present of an alkyl abstractor.

Chapter 1

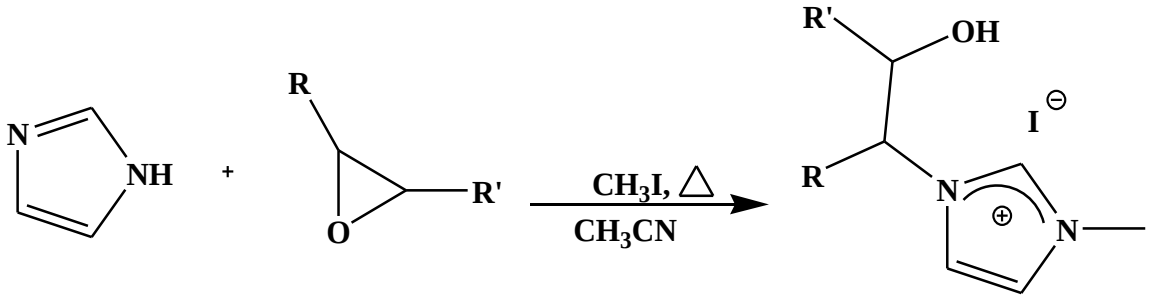
1. Introduction

Synthesis of bis(imidazolidene-N-methyl-N'-alkenyl-2-alkoxy)zirconium-diamide complexes

Recent attention in the catalytic polymerization of olefins has focused on the early transition metals and more particularly on the amido complexes of fourth group elements. [54]

We have prepared a series of NHC-alkoxy derivates to use as proligands to the synthesis of a new class of (imidazolidene-N-methyl-N'-alkenyl-2-alkoxy)zirconium-diamide ([NHC-O]$_2$Zr(NEt$_2$)$_2$) octahedral complexes, by reaction of NHC ligands with Zr(NEt$_2$)$_4$.

For ligands synthesis a particularly convenient and flexible entry point to alkoxidetethered NHCs is through the use of epoxides, which are cheap and can be bought in a chiral, non-racemic form, enabling the synthesis of a library of chiral alkoxy NHCs. The reaction between an epoxide and imidazole affords the ring-opened product, which can then be quaternised with an alkyl halide to afford the corresponding imidazolium pro-ligand (Scheme 8). [41]



Scheme 8. Synthesis of NHC proligand

By this pattern we synthesized 4 proligands:

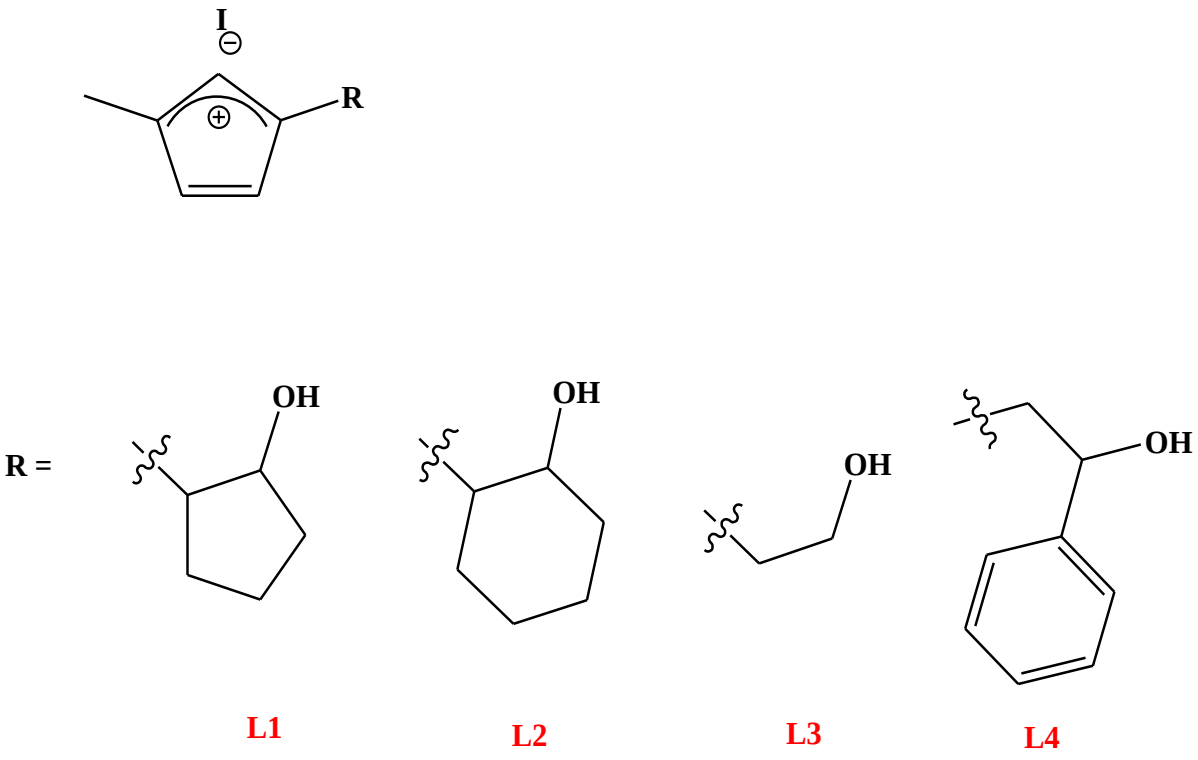


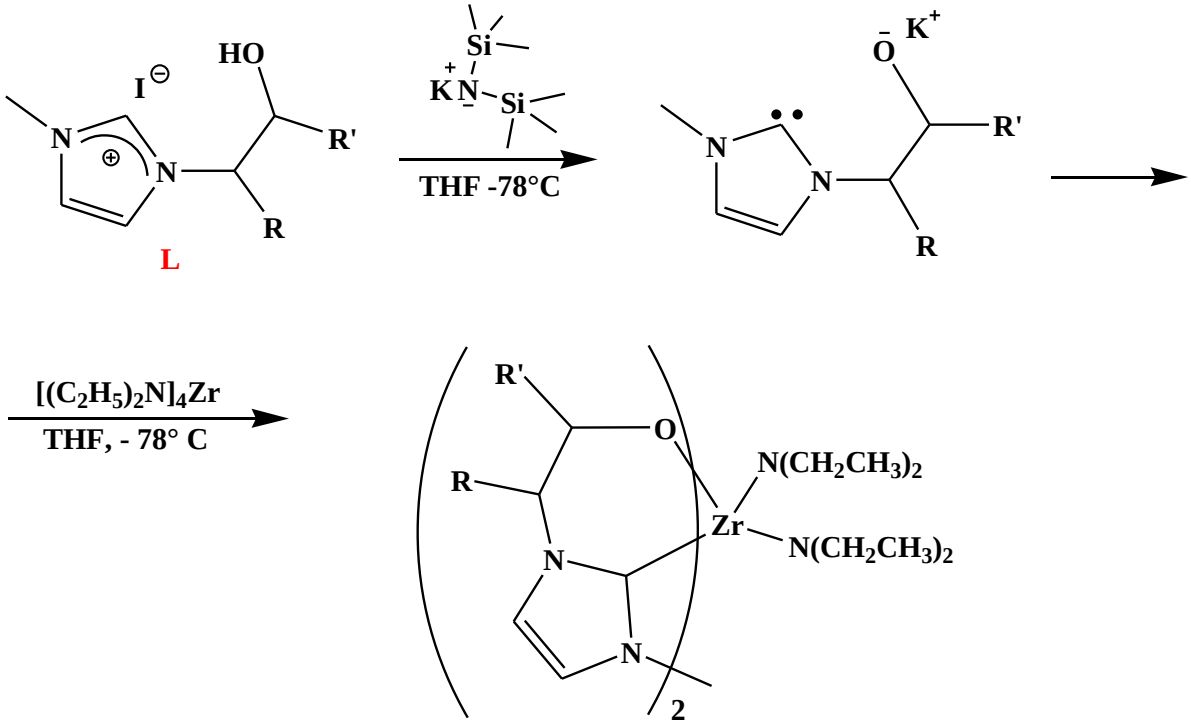
Figure 8. NHC proligands

The proligands are imidazolium salts N,N substituted, where one of the substituents is kept fixed and is the methyl group, while the other one changes both steric hindrance and nature. Respectively L2 is more hindred and L3 is less hindred compared to proligand L1, while in L4 we introduce an aromatic ring in the structure. The aim is to study the effect of these structural variations on complexes properties and catalytic activity in olefins polymerization.

Conversion of the imidazolium pro-ligands to potassium alkoxy NHCs is readily accomplished by sequential deprotonation using two equivalents of bases $KN(SiMe_3)_2$. These potassiumalkoxy NHCs are particularly noteworthy because heavier alkali metal NHCs are usually unstable with respect to a 1,2- alkyl migration reaction.

Potassium alkoxy NHC has proven to be especially effective for the preparation of early metal–NHC complexes. The reaction between potassium alkoxy NHC and $Zr(NEt_2)_4$

afford the final complex.



Scheme 9. Synthesis of complex

The following catalyst were synthesized:

- bis(imidazolidene-N-methyl-N'-cyclopentenyl-2-alkoxy)zirconium-diamide (1)
- bis(imidazolidene-N-methyl-N'-cyclohexenyl-2-alkoxy)zirconium-diamide (2)
- bis(imidazolidene-N-methyl-N'-ethilenyl-2-alkoxy)zirconium-diamide (3)
- bis(imidazolidene-N-methyl-N'-aryl-2-alkoxy)zirconium-diamide (4)

These complexes are characterized by two NHC-alcoxy ligands, bind to complex by the carbenic carbon and the oxygen atom, and with two diamide groups bonded to the same atom. The complexes have different NHC ligand. In general the structure is characterized by an imidazol ring with bearing an alkyl group and an alkoxy group. As we saied before, we changed the structure of alkoxy group, to about concern either the size and the nature.

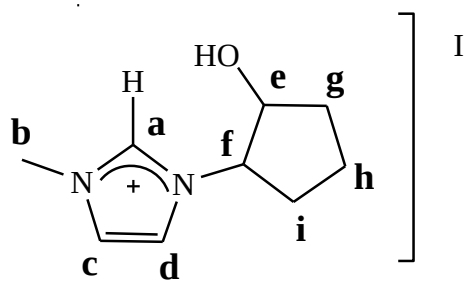
The synthesized complexes, in combination with MAO, were tested in the polymerization of ethylene and propene, obtaining linear polyethylene and isotactic polypropylene, respectively. The NHC amido complexes prepared, being a new class of homogeneous polymerization catalysts, differ from the known NHC complexes in the electron density around the metal center, thus influencing the catalytic activity in the polymerization of α-olefins.

Results and discussion

1.1 Synthesis and characterization of complex bis(imidazolidene-N-methyl-N'-cyclopentenyl-2-alkoxy)zirconium-diamide ($[NHCO]_2Zr(NEt_2)_2$)

Synthesis of bis(imidazolidene-N-methyl-N'-cyclopentenyl-2-alkoxy)zirconium-diamide ($[NHC\text{-}O]_2Zr(NEt_2)_2$) was carried out in good yields by the procedure reported in the scheme x. (For complete synthesis data see experimental section).

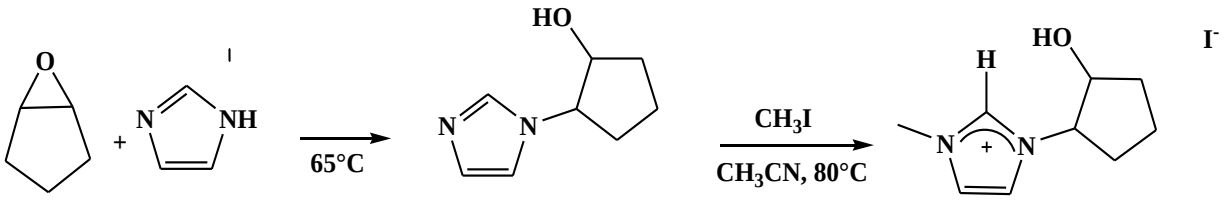
Synthesis of proligand (L1)



(L1)

Figure 9. Imidazolium-N-methyl-N'-cyclopentenyl-2-hydroxy-iodide:

L1 has been prepared according to a procedure described by Arnold and co-workers [41], *i.e.* by reacting cyclopentenoxide with imidazole to form imidazole-N-cyclopentan-2-ol, which was subsequently reacted in acetonitrile with iodomethane.



(L1)

Scheme 10. Synthesis of proligand L1

After distillation of the solvent, the product was purified by crystallization in acetone,

obtaining the imidazolium salt as a white solid in high yield. Elemental analysis (C, H, N) is in agreement with the proposed formulation.

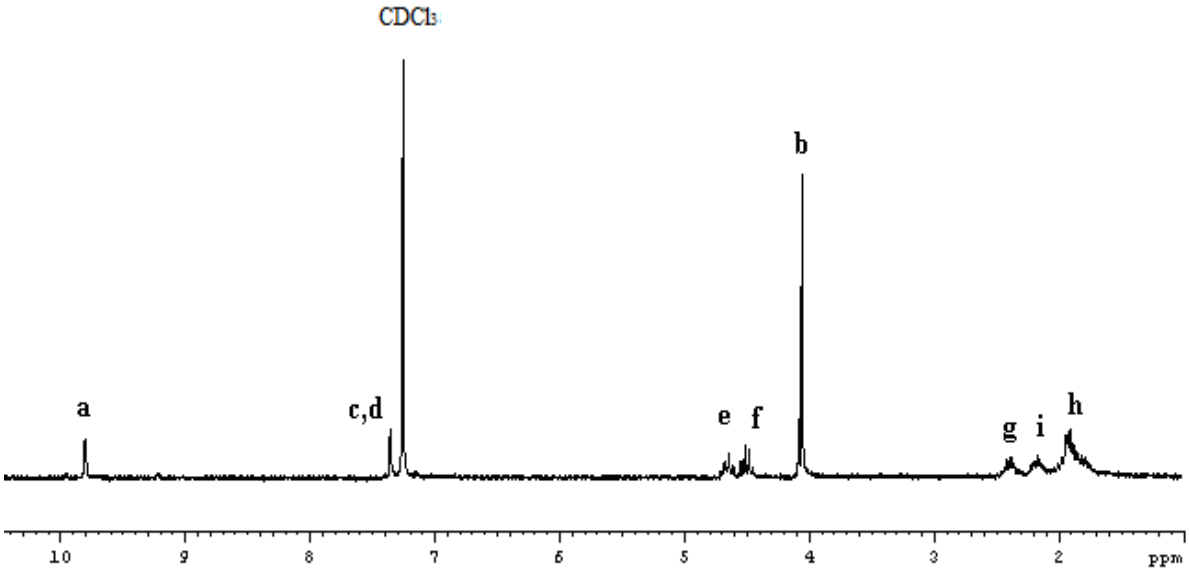


Figure 10. ^{1}H NMR spectrum of L1 in $CDCl_3$

The singlet at 8.71 ppm is assigned to imidazolium H_a, whereas the resonances H_c and H_d of hydrogen atoms of methines of the backbone fall at 7.46 and 7.34 ppm, respectively. The two multiplet at 4.36 and 4.20 ppm were attributed to methine of cyclopentane bonded to heteroatoms, C*H*-O and C*H*-N, respectively, which, obviously, considering the *trans* opening of the epoxide ring, are in *trans* configuration. The protons of the methyl bonded to nitrogen atom give a singlet at 3.80 ppm. The methylene protons of cyclopentane rings give complex multiplets between 2.30 and 1.64 ppm.

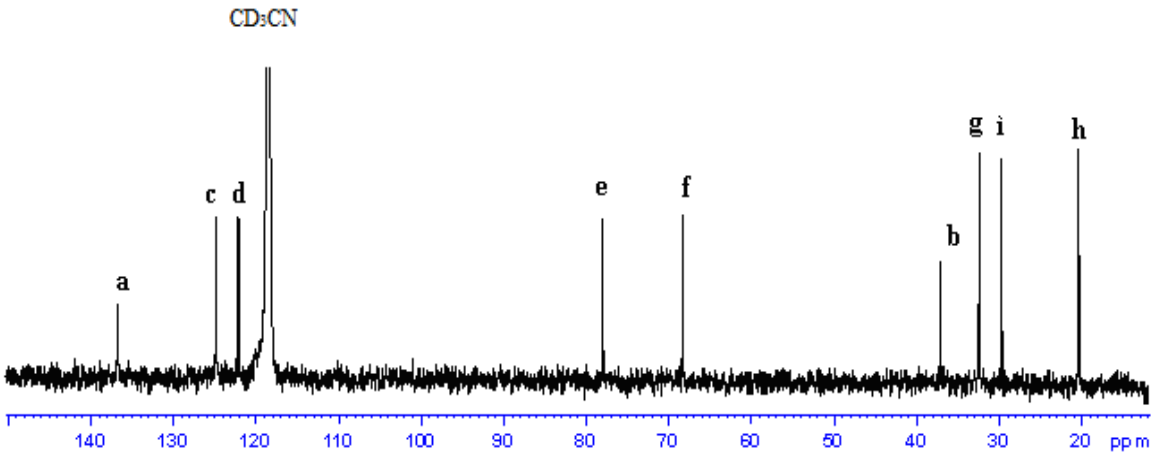
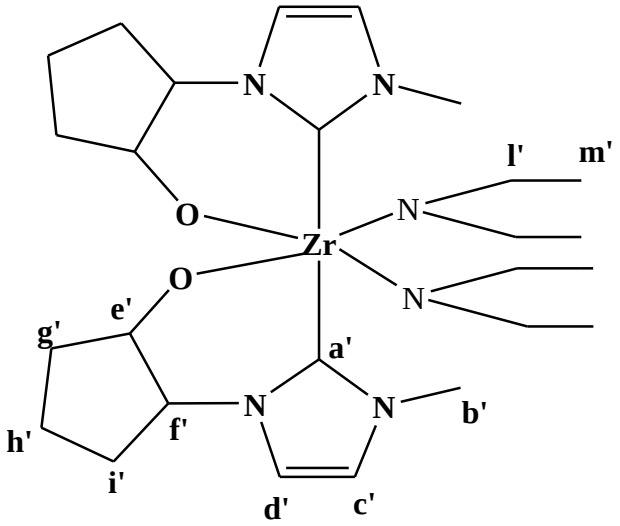


Figure 11.^{13}C NMR spectrum of L1 in CD_3CN

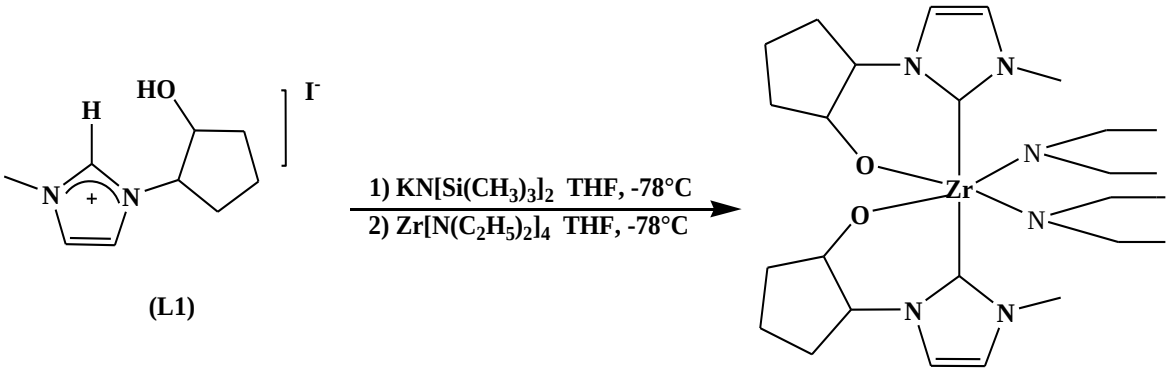
The sp^2 methine carbons give signals at 136.8, 124.9 and 122.1 ppm and they are attributed to C_a, C_c and C_d, respectively. Methine carbons bonded to oxygen and to nitrogen atoms (C_f and C_e) resonate at 77.9 and 68.4 ppm, respectively, whereas the N-methyl carbon (C_b) sound at 37.2 ppm. Methylene carbons of cyclopentane ring give signals at 32.4, 29.7 and 20.4 ppm and are attributed to C_g, C_i and C_h, respectively.

Synthesis of complex (1)



(1)

Figure 12. Bis(imidazolidene-N-methyl-N'-cyclopentenyl-2-alkoxy) diamide –zirconium complex



(L1) **(1)**

Scheme 11. Synthesis of complex 1

Reaction of imidazolium salt (L1) with a slight excess of a strong base (*i.e.* potassium-hexamethyldisilazide) produces potassium alkoxide carbene, that was added to a solution

of $Zr(NEt_2)_4$ to obtain the desired neutral octahedral complex $[NHC\text{-}O]_2Zr(NEt_2)_2$ (1). 1 was isolated as air- and moisture sensitive solids and characterized by ^1H and ^{13}C NMR, elemental analysis and mass spectroscopy. Elemental analyses (C, H, N) of 1 is in agreement with the proposed formulation. The ^1H and ^{13}C NMR spectra could indicate the presence of at least two isomers in solution at RT for complex 1.

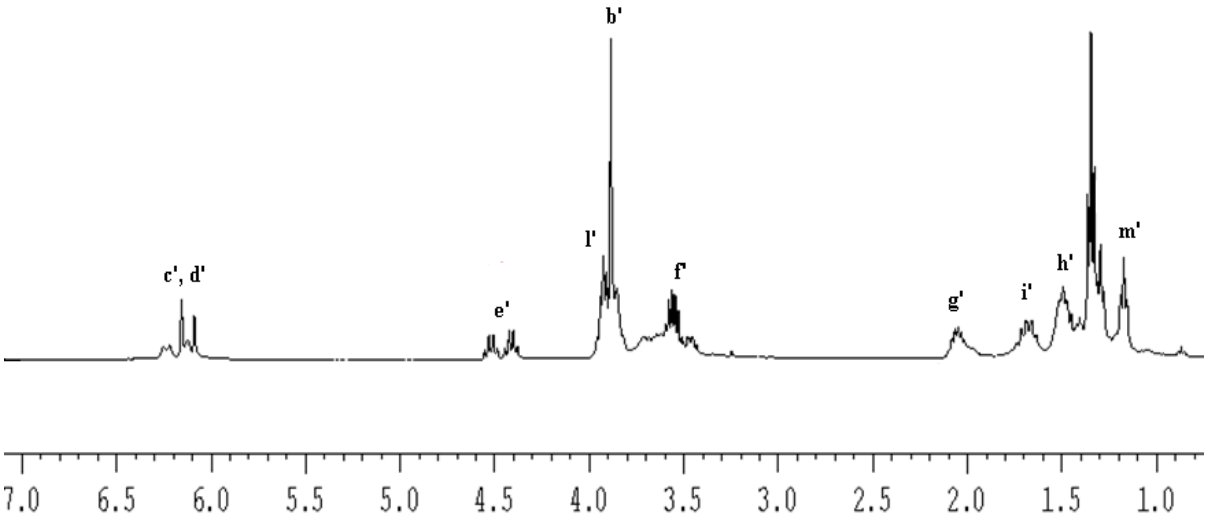


Figure 13. ^1H NMR spectrum of complex 1 in $CDCl_3$

In the ^1H spectrum, two set of peaks for the protons of the unsaturated methine of the backbone of heterocyclic, between 6.26 and 6.10 ppm and two quartet attributable to methine next to alkoxide at 4.52 and 4.43 ppm are detectable. The protons bonded to carbon next to nitrogen atoms, *i.e.* those on the imidazolium N-CH_3 and N-C*H*, as well as those of amide groups N-CH_2CH$_3$, resonate in the range 3.94-3.56. The methylene protons of cyclopentane ring and those of methyl groups of amides show signals between 2.08 and 1.18 ppm.

^{13}C NMR spectrum shows a signal at 196.7 ppm and two less intence resonances at 196.5 and 195.9 ppm attributable to carbene carbons. Moreover, also the signals for other carbons are split and folded at least, and in Fig. it is possible to observe the complete attribution of resonances.

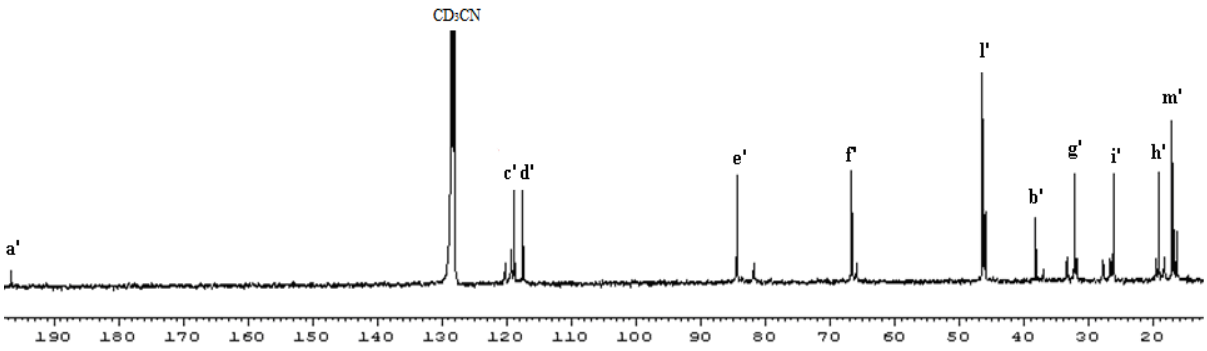


Figure 14. ^{1}H NMR spectrum of 1 in CD_3CN

Variable-temperature (VT) ^{1}H NMR experiments in the range −70 °C < T < 60 °C (see fig.16) show clearly at 0 °C, as well as at -20 °C, six signals in the range 6.4 – 5.9 ppm attributable to protons of the heterocyclic backbone. This fact could is a further proof of the presence of more species in solution.

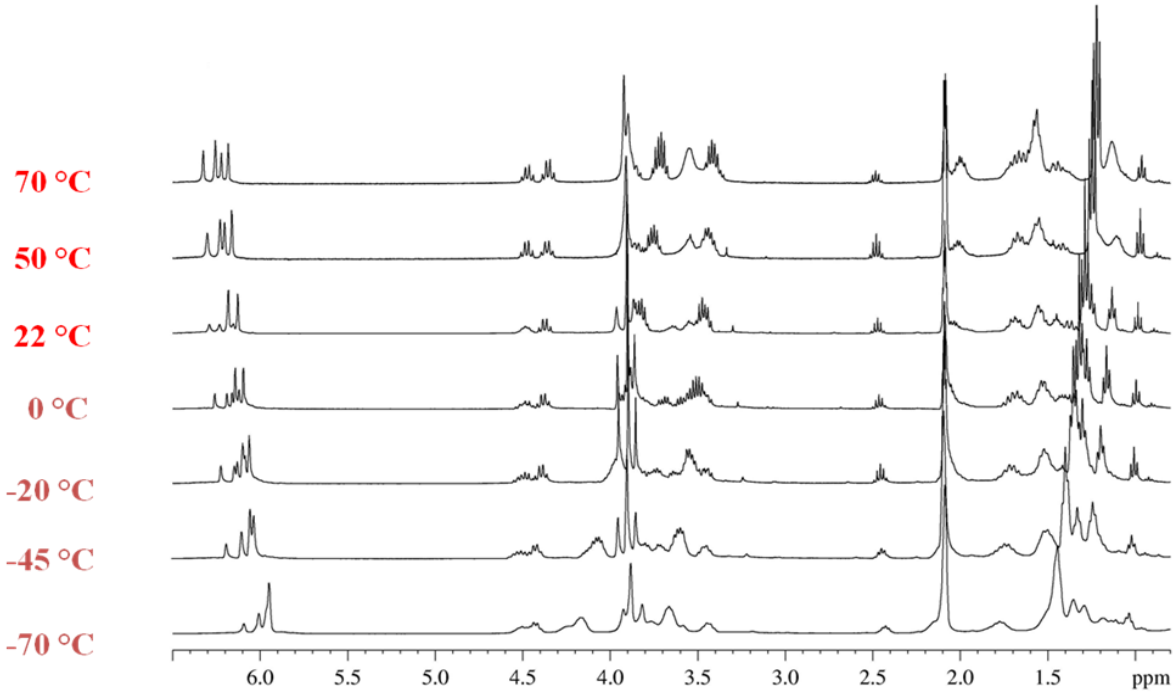
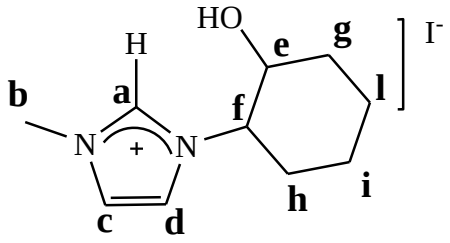


Figure 15. Variable-temperature ^{1}H NMR experiments

Thus, NMR analysis ^{1}H and ^{13}C NMR experiments have allowed a structure determination in solution. Unfortunately, despite all the attempts, we were unable to grow crystals suitable for the X-ray analyses.

1.2 Synthesis and characterization of complex bis (imidazolidene-N-methyl-N'-cyclohexenyl-2-alkoxy)zirconium-diamide ($[NHC\text{-}O]_2Zr(NEt_2)_2$)

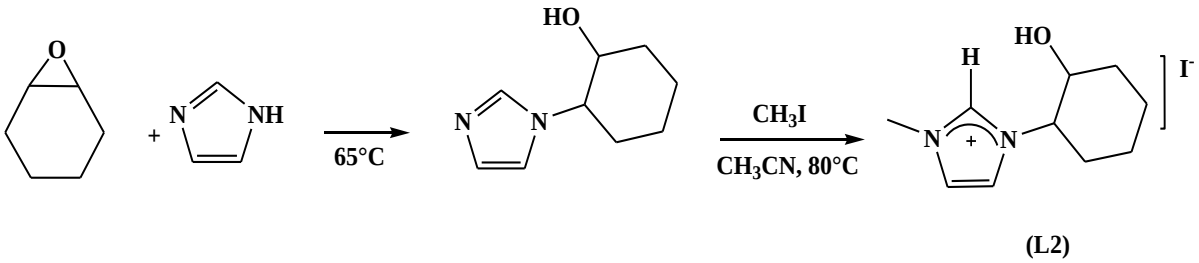
Synthesis of imidazolium salt (L2)



(L2)

Figure 16. Imidazolium-N-methyl-N'-cyclohexenyl-2-hydroxy-iodide

The compound L2 has been prepared according to Arnold and co-workers [41], i.e. by reacting cyclohexenoxide with imidazole to form imidazole-N-cycloexan-2-ol, which was subsequently reacted in acetonitrile with iodomethane.



Scheme 12. Synthesis of proligand L2

After distillation of solvent, the product was purified by crystallization in acetone, obtaining the imidazolium salt as a white solid in good yield.

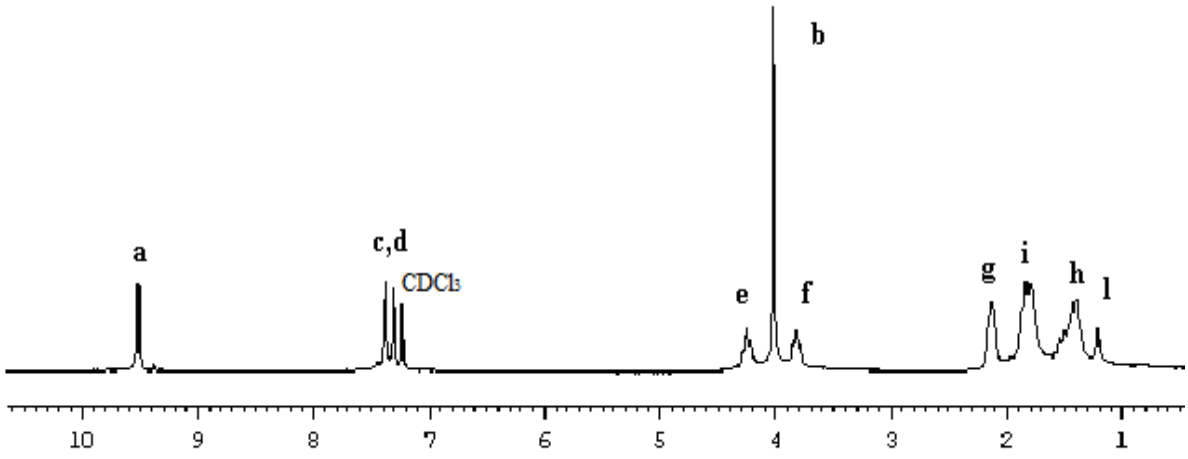


Figure 17. ^{1}H NMR spectrum of L2 in $CDCl_3$

The singlet at 9.48 ppm is assigned to imidazolium H_a, whereas the resonances H_b and H_c of hydrogen atoms of methines of the backbone fall at 7.42 and 7.33 ppm, respectively. The two multiplet at 4.23 and 3.83 ppm were attributed to methine of cycloexane bonded to heteroatoms, CH-O and CH-N, respectively, which, obviously, considering the *trans* opening of the epoxide ring, are in *trans* configuration.

The protons of the methyl bonded to nitrogen atom give a singlet at 4.02 ppm. The methylene protons of cyclohexane rings give complex multiplets between 2.13 and 1.23 ppm.

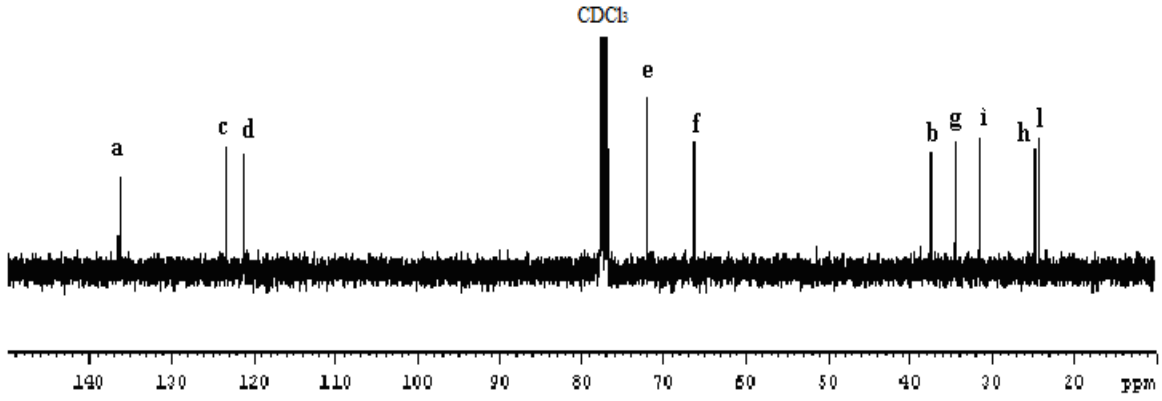
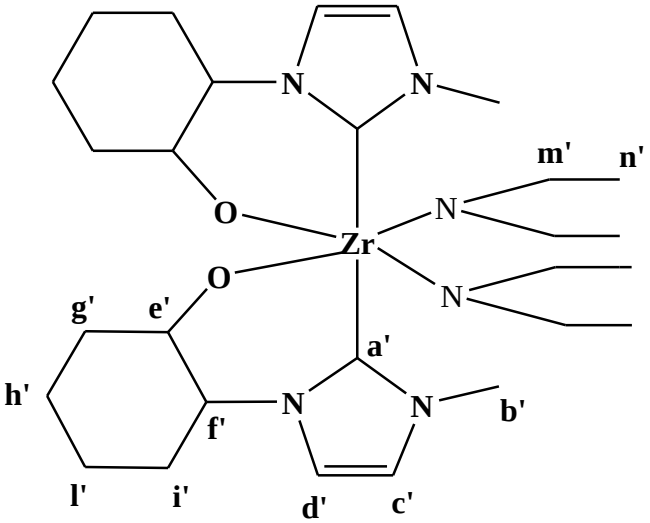


Figure 18. ^{13}C NMR spectrum of L2 in $CDCl_3$

The sp^2 methine carbons give signals at 136.4, 123.3 and 121.2 ppm and they are attributed

to C_a, C_b and C_d, respectively. Methine carbons bonded to oxygen and to nitrogen atoms (C_f and C_e) resonate at 72.0 and 66.3 ppm, respectively, whereas the N-methyl carbon (C_c) have the resonance at 37.5 ppm. Methylene carbons of cyclohexane ring give signals at 34.4, 31.6, 24.8 and 24.2 ppm and are attributed to C_i, C_h, C_l and C_g, respectively.

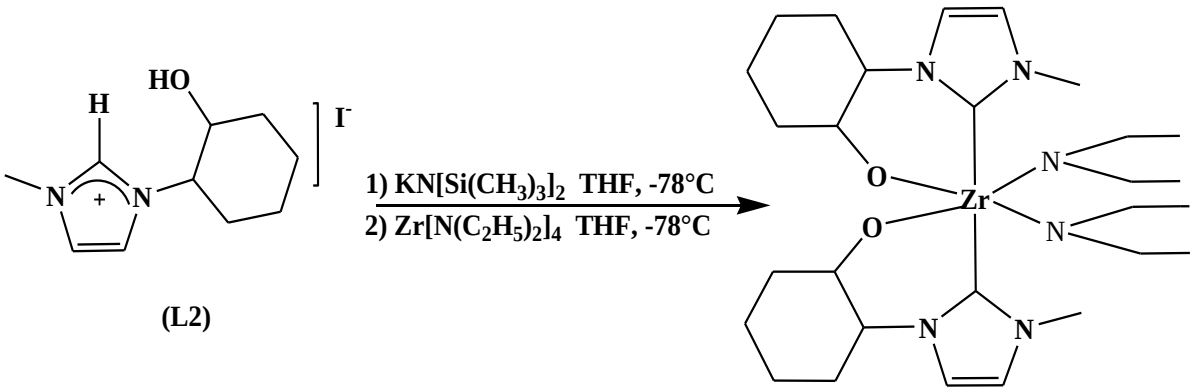
Synthesis of complex (2)



(2)

Figure 19. Bis(imidazolidene-N-methyl-N'-cyclohexenyl-2-alkoxy) diamide –zirconium complex

Reaction of imidazolium salt (L2) with an slight excess of strong base (*i.e.* potassium-hexamethyldisilazide) produce potassium alkoxide carbene, which was added to a solution of $Zr(NEt_2)_4$ to afford the desired neutral octahedral complex $[NHC\text{-}O]_2Zr(NEt_2)_2$ (2).



(L2) **(2)**

Scheme 13. Synthesis of complex 2

It was isolated as air- and moisture sensitive solids and characterized by ^{1}H and ^{13}C NMR.

^{1}H NMR* spectrum show two set of peaks for the protons of the unsaturated methine of the backbone of heterocyclic, between 6.37 and 6.15 ppm and two quartet attributable to methine next to alkoxide at 4.19 and 3.77 ppm, are detectable. In the range 3.86 and 3.38 resonate the protons bonded to carbon next to nitrogen atoms, *i.e.* those on the imidazolium N-C*H*$_3$ and N-C*H*, as well as those of amide groups N-C*H*$_2$CH$_3$, The methylene protons of cycloexane ring and those of methyl groups of amides groups N-CH$_2$*CH*$_3$ show signals between 1.93 and 0.94 ppm.

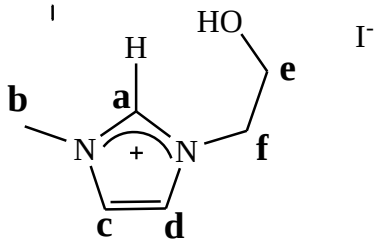
^{13}C NMR spectrum* show signal at 207.93 ppm related the carbon $C_{a'}$ and the backbone carbons give signals at 159.3 ppm Methine carbons bonded to oxygen and to nitrogen atoms ($C_{e'}$ and $C_{f'}$) resonate at 78.8 and 72.3 ppm, respectively, whereas the N-methyl carbon ($C_{b'}$) have the resonance at 54.5 ppm. In the range of 40- 0 ppm sound the methylene protons of cycloexane ring and those of methyl groups of amides show signals between 1.93 and 0.94 ppm.

** Unfortunatelly we are not able to obtained NMR spectra with a good signals resolution, for this reason we prefer don't report it.*

Variable-temperature (VT) ^{1}H NMR experiments in the range −40 °C < T < 80 °C reveal that the complex are quite stable at low temperature, in fact signals of the proton not change significantly with temperature.

1.3 Synthesis and characterization of complex bis(imidazolidene-N-methyl-N'-ethilenyl-2-alkoxy)zirconium-diamide ($[NHC\text{-}O]_2Zr(NEt_2)_2$)

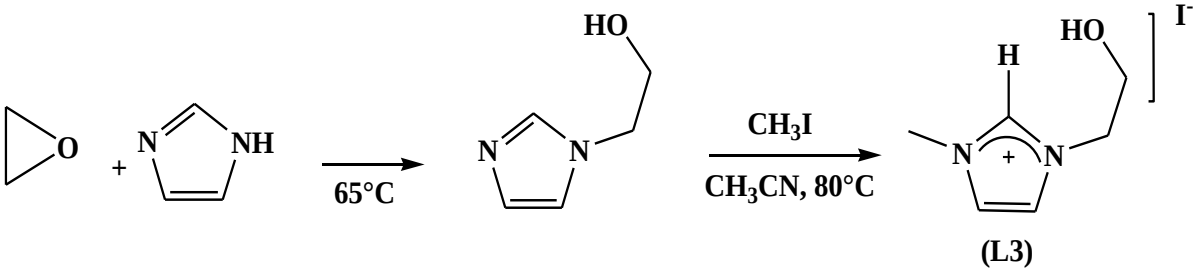
Synthesis of imidazolium salt (L3)



(L3)

Figure 20. Imidazolium-N-methyl-N'-Ethylenyl-2-hydroxy-iodide

The compound L3 has been prepared according to Arnold and co-workers [41], i.e. by reacting ethylenoxide with imidazole to form imidazole-N-ethylen-2-ol, which was subsequently reacted in acetonitrile with iodomethane.



Scheme 14. Synthesis of proligand L3

After distillation of solvent, the product was purified by crystallization in acetone, obtaining the imidazolium salt as a white solid in high yield.

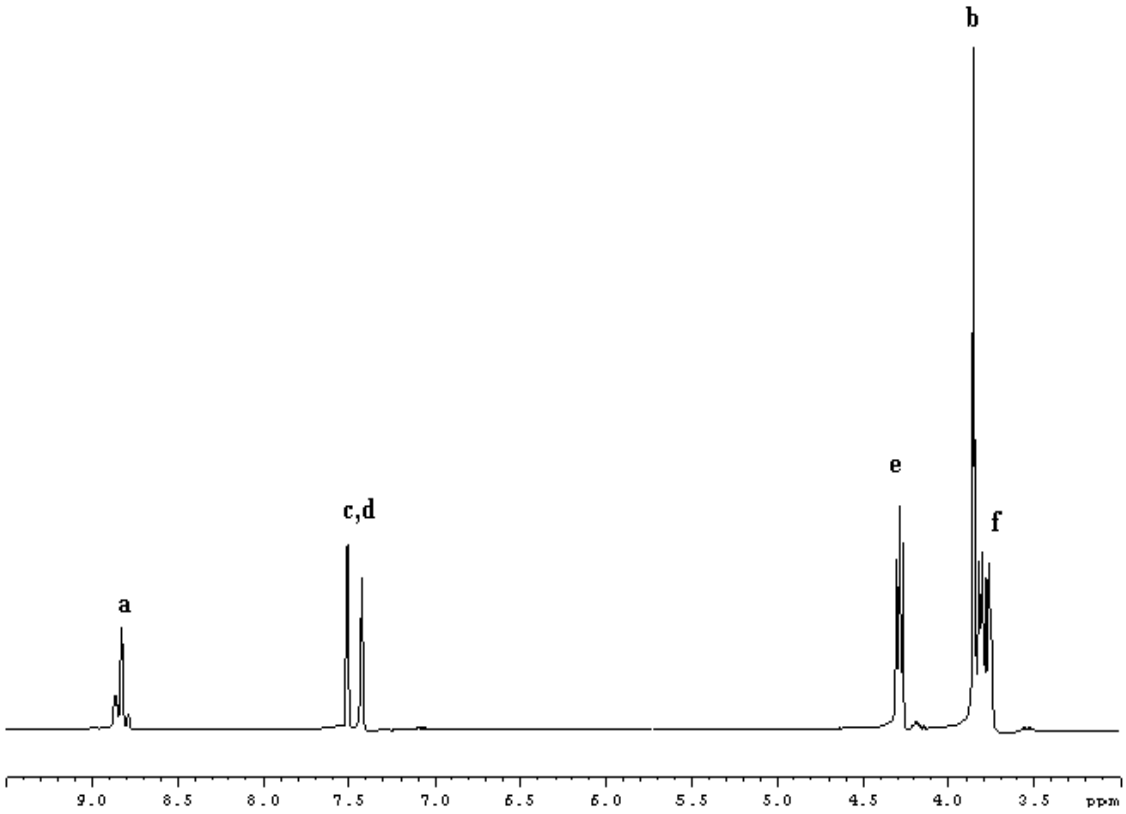


Figure 21. ^{1}HNMR spectrum of L3 in CD_3CN

The singlet at 8.11 ppm is assigned to imidazolium H_a, the resonances H_b and H_c of hydrogen atoms of methines of the backbone fall at 7.51 and 7.42 ppm, respectively. The two multiplet at 4.28 and 3.80 were attributed to methine of ethylene bonded to heteroatoms, CH-O and CH-N, respectively, which, obviously, considering the *trans* opening of the epoxide ring, are in *trans* configuration.

The protons of the methyl bonded to nitrogen atom give a singlet at 3.82 ppm.

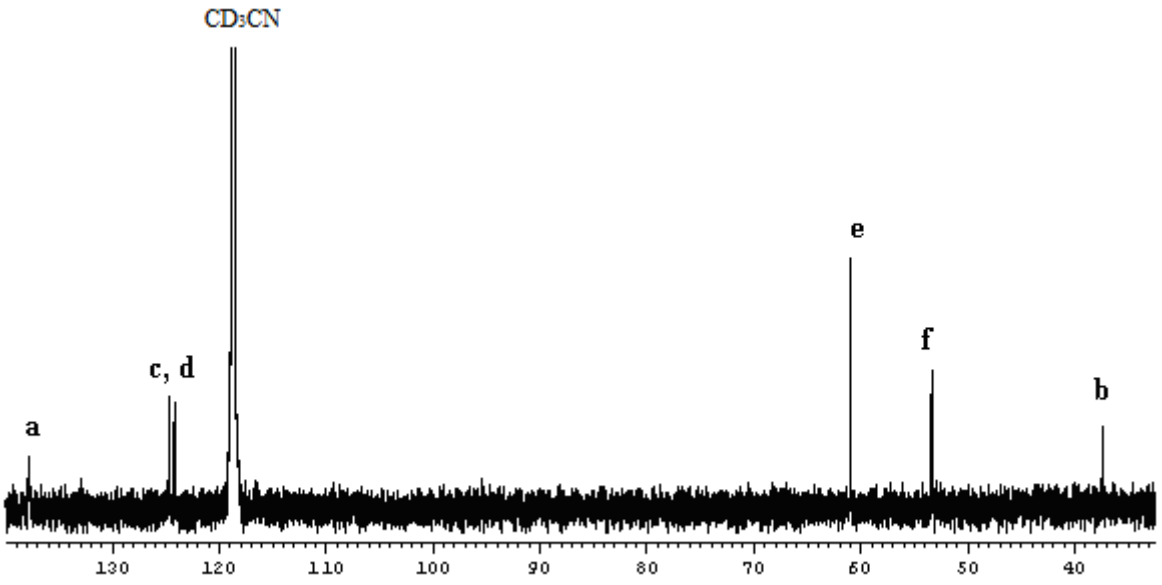
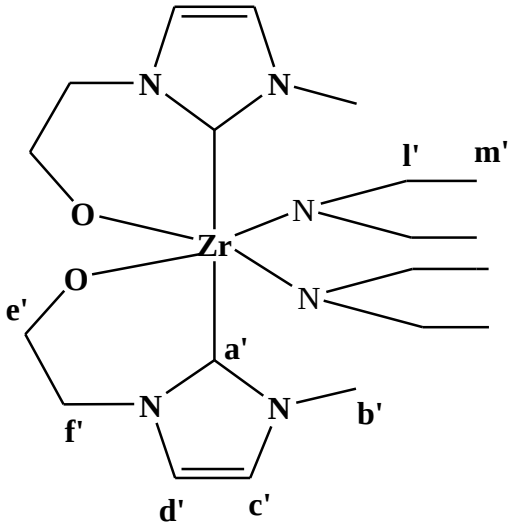


Figure 22. ^{13}CNMR spectrum of L3 in CD_3CN

The signal of C_a carbon sound at 139.8 ppm. The backbone carbons give signals at 124.7 and 124.2 ppm and they are attributed to, C_c and C_d, respectively. Methine carbons bonded to oxygen and to nitrogen atoms (C_e and C_f) resonate at 60.9 and 53.3 ppm, respectively, whereas the N-methyl carbon (C_c) have the resonance at 37.3 ppm.

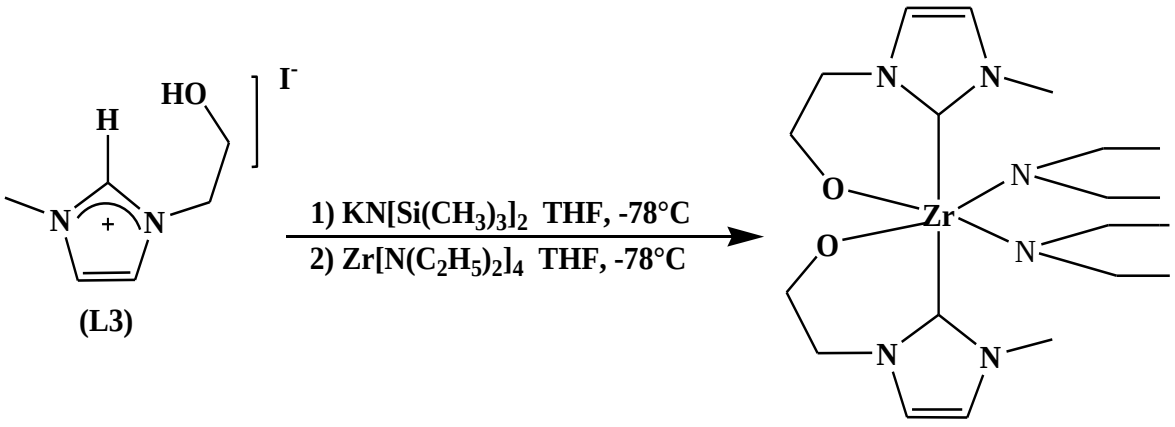
Synthesis of complex (3)



(3)

Figure 23. Bis(imidazolidene-N-methyl-N'-Ethylenyl-2-alkoxy) diamide zirconium complex

Reaction of imidazolium salt (L3) with an slight excess of strong base (*i.e.* potassium-hexamethyldisilazide) produce potassium alkoxide carbene, which was added to a solution of $Zr(NEt_2)_4$ to afford the desired neutral octahedral complex $[NHC\text{-}O]_2Zr(NEt_2)_2$ (3).



(L3) **(3)**

Scheme 15. Synthesis of complex 3

It was isolated as air- and moisture sensitive solids and characterized by ^{1}H and ^{13}C NMR.

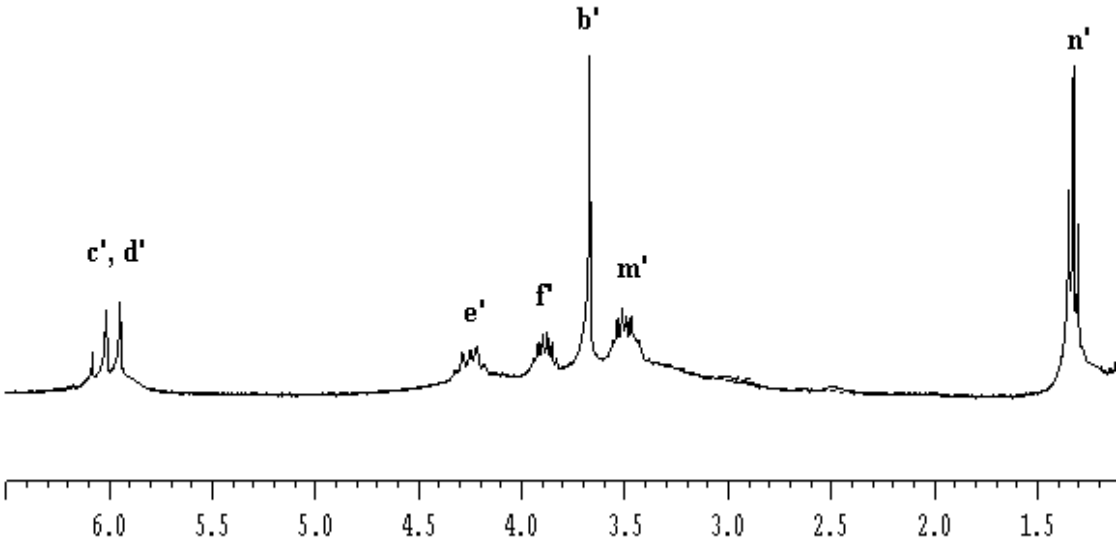


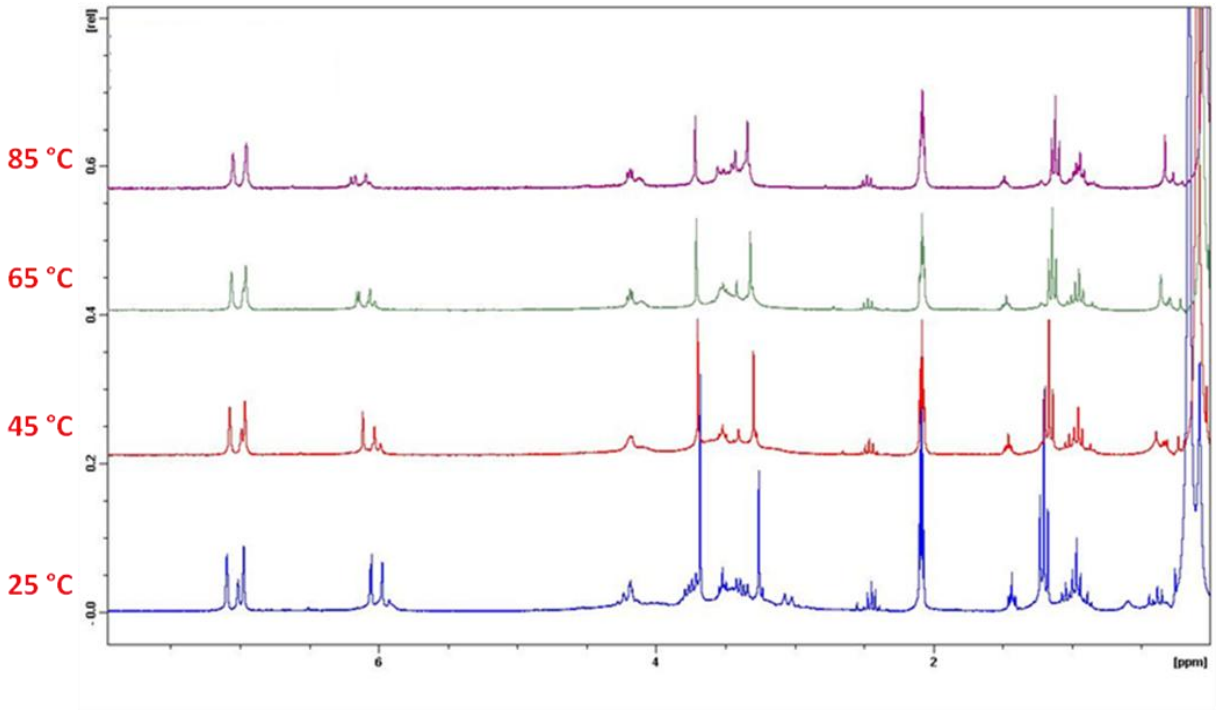
Figure 24. ^{1}H NMR spectrum of complex 3 in $CDCl_3$

^{1}H spectrum show two set of peaks for the protons of the unsaturated methine of the backbone of heterocyclic, between 6.08 and 5.95 ppm and quartet attributable to methine next to alkoxide at 4.28, is detectable. In the range 3.87-3.47 ppm resonate the protons bonded to carbon next to nitrogen atoms, *i.e.* those on the imidazolium N-CH_3 and N-C*H*, as well as those of amide groups N-CH_2CH$_3$, The methylene protons of methyl groups of amides show signals at 1.32.

^{13}C NMR spectrum* show signals at 196.3 ppm related the carbon $C_{a'}$ and the backbone carbons give signals at 120.5 and 118.9 ppm and they are attributed to $C_{c'}$ and $C_{d'}$, respectively. Methine carbons bonded to oxygen and to nitrogen atoms ($C_{e'}$ and $C_{f'}$) resonate at 67.4 and 54.8 ppm, respectively, whereas the N-methyl carbon ($C_{b'}$) have the resonance at 37.8 ppm.

** Unfortunatelly we are not able to obtained a ^{13}C NMR spectrum with a good signals resolution, for this reason we prefer don't report it*.

High temperature experiments



Low temperature experiments

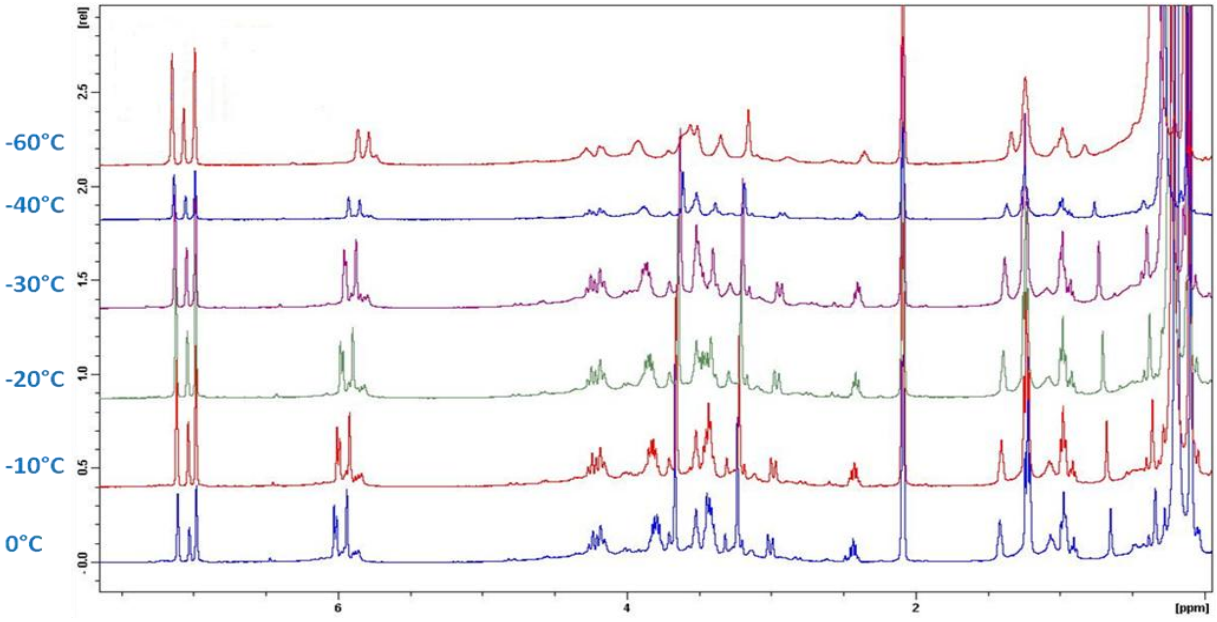
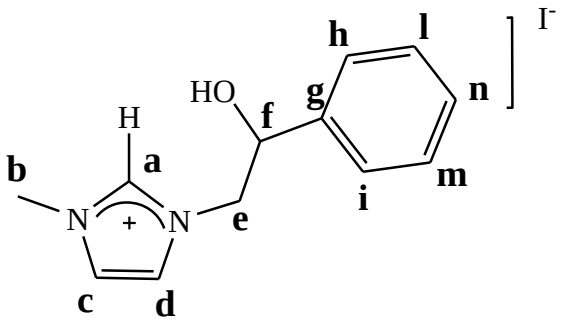


Figure 25. ^{1}H NMR variable temperature experiments in $CDCl_3$

Variable-temperature (VT) ^{1}H NMR experiments in the range −40 °C < T < 85 °C reveal that the complex is quite stable.

1.4 Synthesis and characterization of complex bis(imidazolidene-N-methyl-N'-aryl-2-alkoxy)zirconium-diamide ($[NHC\text{-}O]_2Zr(NEt_2)_2$)

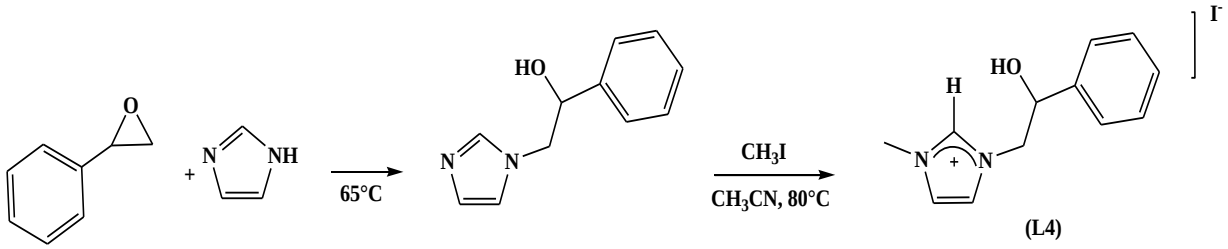
Synthesis of imidazolium salt (L4)



(L4)

Figure 26. Imidazolium-N-methyl-N'-aryl-2-hydroxy-iodide

The compound L4 has been prepared according to Arnold and co-workers [41], i.e. by reacting aryloxide with imidazole to form imidazole-N-aryl-2-ol, which was subsequently reacted in acetonitrile with iodomethane.



Scheme 16. Synthesis of proligand 4

After distillation of solvent, the product was purified by crystallization in acetone, obtaining the imidazolium salt as a white solid in high yield.

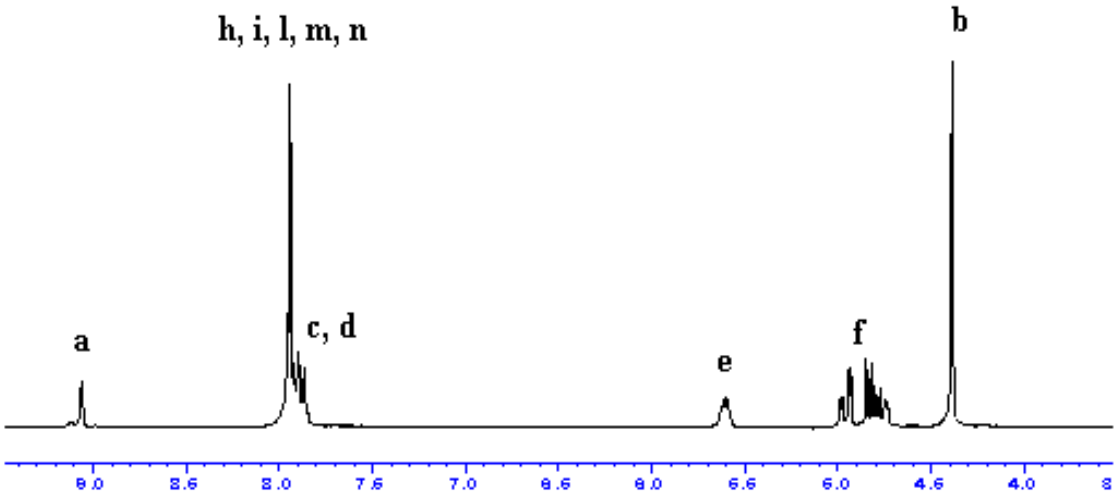


Figure 27. ^{1}HNMR spectrum of L4 in DMSO

The singlet at 9.12 ppm is assigned to imidazolium H_a, whereas the resonances H_b and H_c of hydrogen atoms of methines of the backbone fall at 7.87 and 7.85 ppm, respectively. The signal of aromatic ring fall at 7.79 ppm. The two multiplet at 5.57 and 4.80 ppm were attributed to methine of aryl ring bonded to heteroatoms, CH-O and CH-N, respectively, which, obviously, considering the *trans* opening of the epoxide ring, are in *trans* configuration.

The protons of the methyl bonded to nitrogen atom give a singlet at 3.79 ppm.

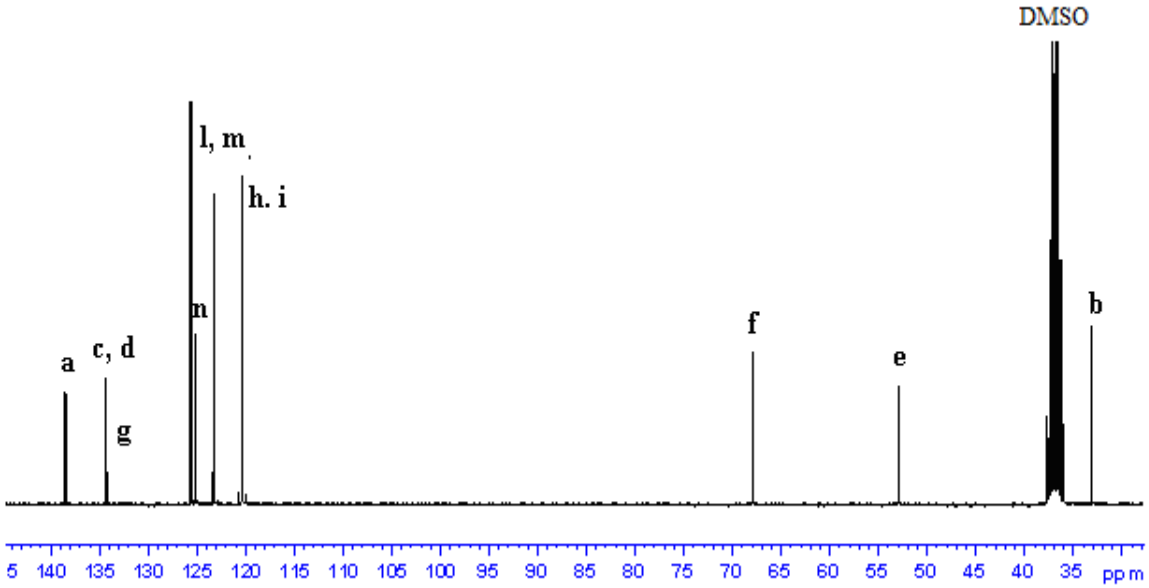
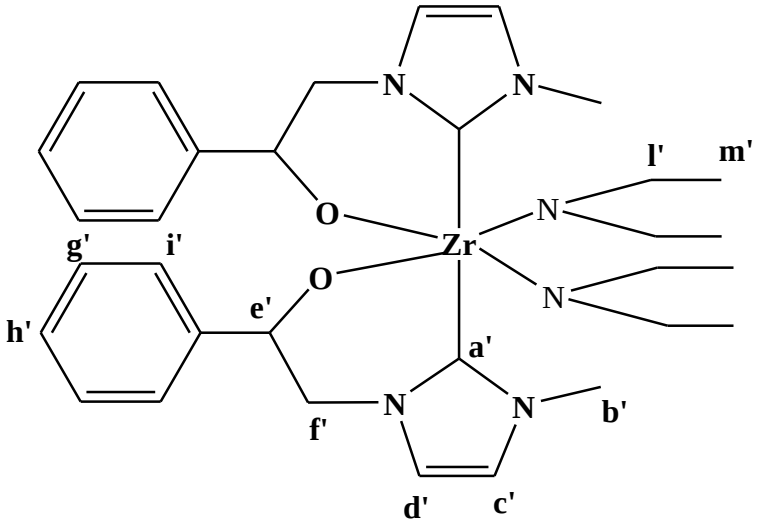


Figure 28. ^{13}CNMR spectrum of L4 in DMSO-d-

Signal 138.5 is assigned to imidazolium C_a and 134.3 ppm is the signal of two carbons of Imidazolium backbone. Aromatic carbons sound at 134.2 (C_g) , 125.1 ($C_{l,m}$), 123.2 (C_n), 120.3 ($C_{h,i}$). Methine carbons bonded to oxygen and to nitrogen atoms (C_f and C_e) resonate at 66.7 and 52.9 ppm, respectively, whereas the N-methyl carbon (C_b) have the resonance at 33.1 ppm.

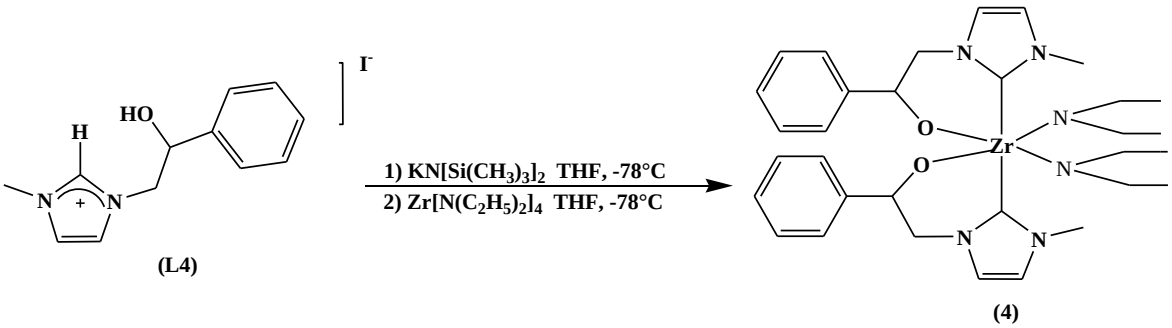
Synthesis of complex (4)



(4)

Figure 29. bis(imidazolidene-N-methyl-N'-aryl-2-alkoxy)zirconium-diamide

Reaction of imidazolium salt (L4) with an slight excess of strong base (*i.e.* potassium-hexamethyldisilazide) produce potassium alkoxide carbene, which was added to a solution of $Zr(NEt_2)_4$ to afford the desired neutral octahedral complex $[NHC\text{-}O]_2Zr(NEt_2)_2$ (4).



Scheme 17. Synthesis of complex 4

It was isolated as air- and moisture sensitive solids and characterized by ^{1}H and ^{13}C NMR.

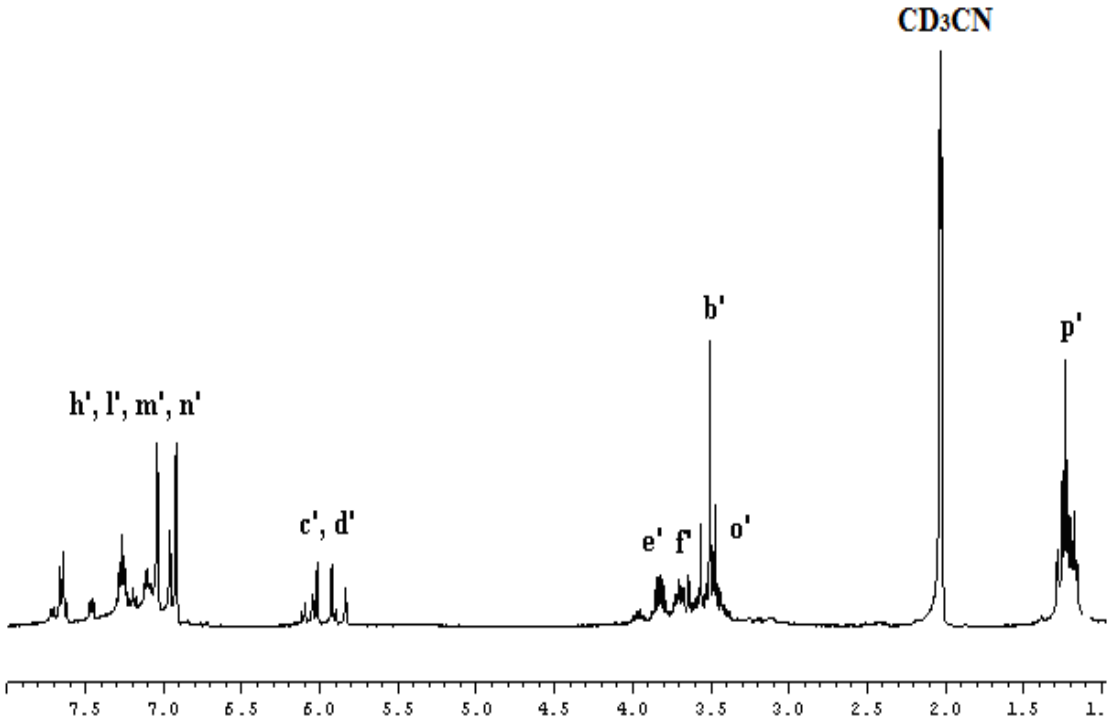


Figure 31. ^{1}HNMR spectra of complex 4 in CD_3CN

^{1}H spectrum show more set of peaks for the protons of the unsaturated methine of aromatic ring between 7.65 and 6.92, and we have the same situation for the backbone proton of heterocyclic, between 6.01 and 5.83 ppm. Two multiplet, attributable to methine next to alkoxide at 3.80 ppm and next to nitrogen at 3.66 ppm, are detectable. At 3.48 ppm resonate the protons bonded to carbon next to nitrogen atoms, *i.e.* those on the imidazolium N-CH_3 and N-CH_2 of amide groups N-CH_2CH$_3$, and at 1.19 we found the signal of N-CH_3 of amide groups N-CH_2CH$_3$.

In ^{13}C spectrum* we found the same situation of proton spectrum, and all the signal are splitting.

Signal 196.9 is assigned to imidazolium $C_{a'}$, while 121.7 ($C_{c',d'}$) is the signal of two carbons of Imidazolium backbone. Aromatic carbons sound at 118.6 ($C_{l',m'}$), 116.7 ($C_{h',l'}$), 115.3 ($C_{n'}$) and 112.6 ($C_{g'}$) ppm. Methine carbons bonded to oxygen and to nitrogen atoms ($C_{f'}$ and $C_{e'}$) resonate at 79.6 and 66.0 ppm, respectively, whereas the N-methyl carbon ($C_{b'}$) have the resonance at 47.4 ppm. At 25.9 and 17.4 ppm there are signals of N-CH_2 and N-CH_2CH$_3$of amide groups N-CH_2CH$_3$.

** Unfortunatelly we are not able to obtained a* ^{13}C *NMR spectrum with a good signals resolution, for this reason we prefer don't report it*.

Polymerization studies

1.5 Polymerization reactions of ethylene and propylene carried out using complex bis(imidazolidene-N-methyl-N'-cyclopentenyl-2 alkoxy)zirconium-diamide ($[NHC\text{-}O]_2Zr(NEt_2)_2$)

Compound (1) was tested in the polymerization of ethylene after activation by methylaluminoxane (MAO). The reactions were performed in a glass autoclave at 50 °C under a ethylene pressure of 6 bar.

Data reported in the Table 2 show that the complex is able to polymerize ethylene, producing linear polyethylenes having a melting point higher than 135 °C and a high molecular weight ($Mw > 6 \cdot 10^5$ dalton).

The molecular weight distribution is in some cases larger than 2 and occasionally bimodal, revealing that the polymer are not produced by a single site catalyst. The activities of the catalysts have been correlated to Al/Zr mole ratio and, as one can see from the figure 2, the activities increase increasing the mole ratio of Al/Zr, reaching a maximum for a mole ratio ≈ 2500 and subsequently decrease.

Usually the activity of the catalyst increases by increasing the MAO/Zr molar ratio, possibly because the equilibrium of formation of the active specie is more shifted to right, thus enhancing the average rate constants:

$$(L)_2ZrX_2 + MAO \rightleftharpoons [(L)_2ZrCH_3]^+ + [MAOX_2]^-$$

Our results are not necessarily in conflict with the previous statement, because they could be explained by considering that MAO may compete with the monomer for coordination at catalytic zirconium cation. In fact, it is generally accepted that the coordination of monomer is a preliminary step with respect to insertion into the catalytic zirconium-carbon bond. In this case, probably, at high concentration of MAO, association phenomena might

occur between oppositely charged ions, effectively reducing the concentration of active sites.

It is worth noting that the molecular weight of the polymers is only poorly affected by this molar ratio, probably because the termination reaction, involving the transfer of the growing chain from zirconium to aluminum, is not relevant in our conditions.

Table 1. Polymerizations of ethylene in the presence of the catalytic system 1/MAO

Run [a]	**[Al]/[Zr]**	**Activity** [b] **(10^3)**	**M_W** [c] **(10^5)**	**M_W/M_n** [c]
1	500	4.1	12.1	2.9
2	800	5.5	7.5	2.5
3	1000	5.6	6.7	1.6
4	1500	9.5	37	2.3
5	2000	17.9	8.9	2.5
6	2500	28.6	11	3.4
7	3000	10.1	16	3.0
8	5000	6.6	6.3	2.0

[a] Polymerization conditions: room temperature, solvent toluene, total volume 150 ml; complex = 8.0×10^{-6} mol; cocatalyst: MAO (based on Al); ethylene concentration in the feed = 1.05×10^{-3} mol/l; [b]Activity in Kg polymer/ [complex] x time (h) x [monomer]; [c]Molecular weight and polydispersity index (M_w/M_n) determined by gel permeation chromatography versus polystyrene standard.

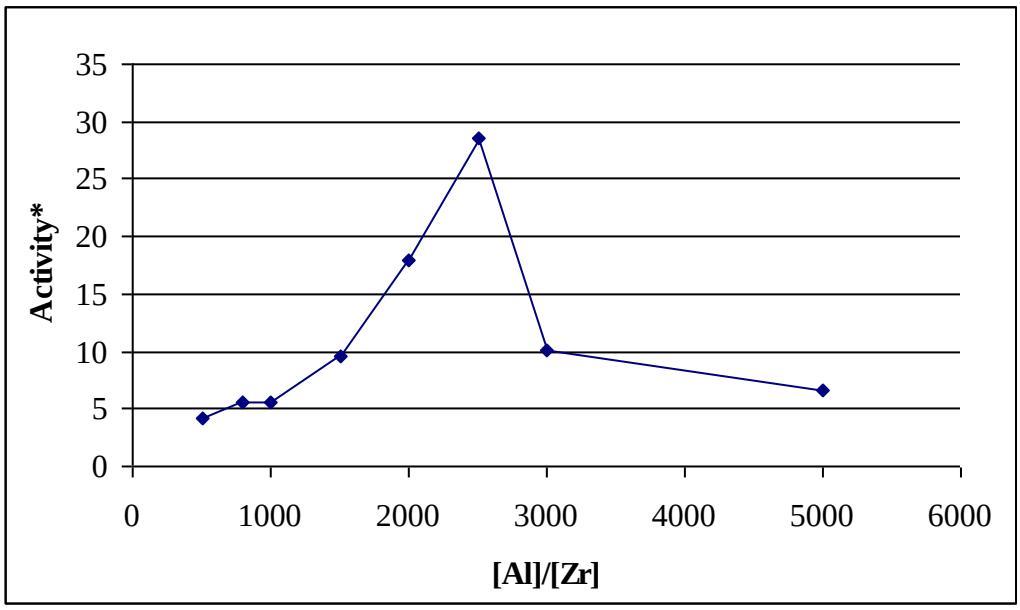


Figure 32. Plot of the activity in ethylene polymerization of complex 1 versus mole ratio [Al]/[Zr].

*Activity in Kg polymer/ [complex] x time (h) x [monomer] $*10^3$

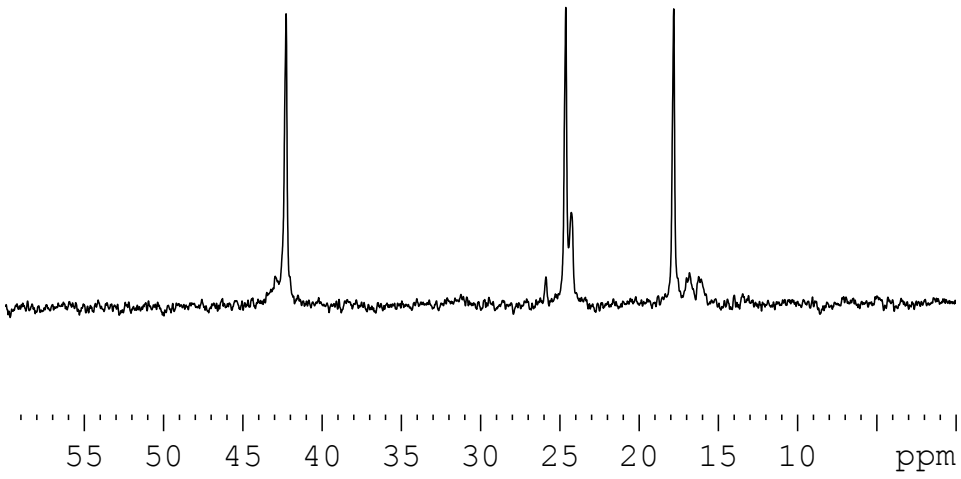
The gel permeation chromatography analysis shows that molecular weights distributions of polymers is rather broad (< 2), suggesting the possible existence of more of one active specie in the reaction mixture. In fact we could be in presence of three complexes having C_2 symmetry, or, alternatively, one complex with C_2 symmetry, together with a complex having C_1 symmetry. This result is consistent with the fact that performing polymerization of propylene at 50 °C under a pressure of 6 bar we obtained a mixer of prodouct.

Table 2. Polymerizations of propylene in the presence of catalytic system 1/MAO

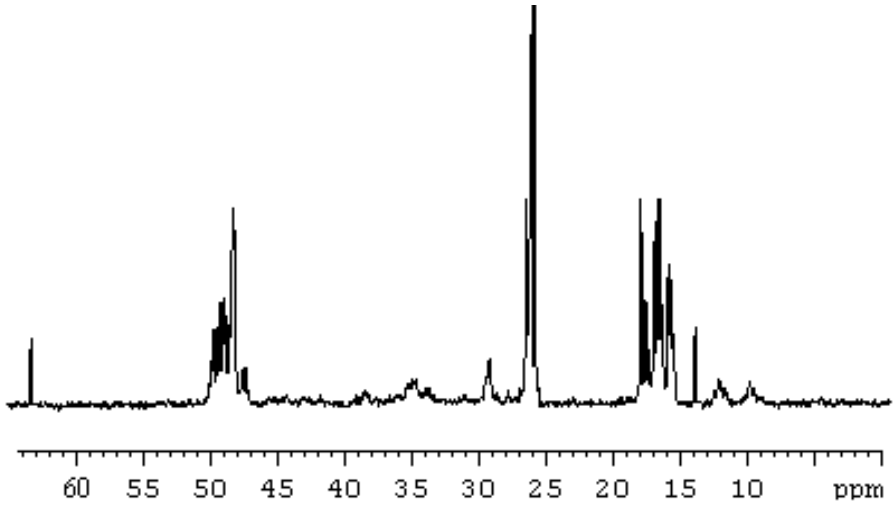
Run [a]	**Al/Zr (mol)**	**Activity** [b]	**M_W** [c] **(10^5)**	**M_W/M_n** [c]
9	250	0.007	12	2.0
10	1000	29	7.3	1.7
11	2000	38	3.8	5.7

[a] Polymerization conditions: room temperature, solvent toluene, total volume 150 ml; complex = 8.0 $x10^{-6}$ mol; cocatalyst: MAO (based on Al); propylene concentration in the feed = 5.48 $x10^{-3}$ mol/l; [b]Activity in Kg polymer/ [complex] x time (h) x [monomer]; [c]Molecular weight and polydispersity index (M_w/M_n) determined by gel permeation chromatography versus polystyrene standard; Molecular weight and polydispersity index of hexane insoluble fraction.

The obtained polypropylene was fractionated, by exhaustive extraction with boiling hexane, in atactic polypropylene (30% w/w hexane soluble fraction) and in highly isotactic polypropylene (70% w/w hexane insoluble fraction). ^{13}C NMR spectra of the two fractions obtained by sample 10 are reported in Fig 32. The kind of prodouct obtained suggest the presence in solution of two species able to give polymerization, one which prodouce atactic polypropylene and other one which produce isotactic polypropylene.



A



B

Figure 33. ^{13}C NMR spectra of hexane soluble fraction (A) and hexane insoluble fraction (B) of polypropylene obtaining with complex 1.

GPC analysis of hexane soluble and hexane insoluble fraction showed high molecular weight (>7.0 x10^5) and narrow MDI (< 2). The latter data is also indicative of the fact that only one aspecific and only one stereospecific catalytic species are present in the reaction mixture.

1.5.a Molecular modeling studies on complex 1

Polymerization results suggest that at least two catalytic species are responsible for the production of the obtained polymer. Furthermore, the previous NMR characterization of the Zr based catalyst showed the presence of more the one isomer.

In order to shed light on the species possibly involved in the polymerization, the different diastereoisomers of the alkylated Zr complex $[NHC\text{-}O]_2Zr(CH_3)_2$* were modeled by DFT calculations both in gas phase and in benzene.

*We replaced the amide group with a methyl group to simplify the structure.

NHC-O proligand L1 present two stereogenic centers that can be *SS* or *RR*, due to the non-selective trans ring opening of the epoxide relative to the synthesis reported in Scheme 10.

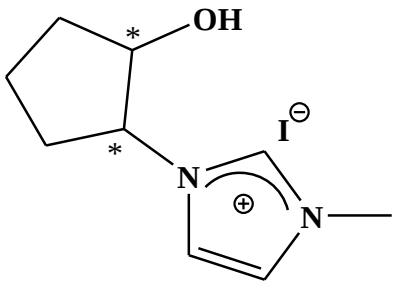
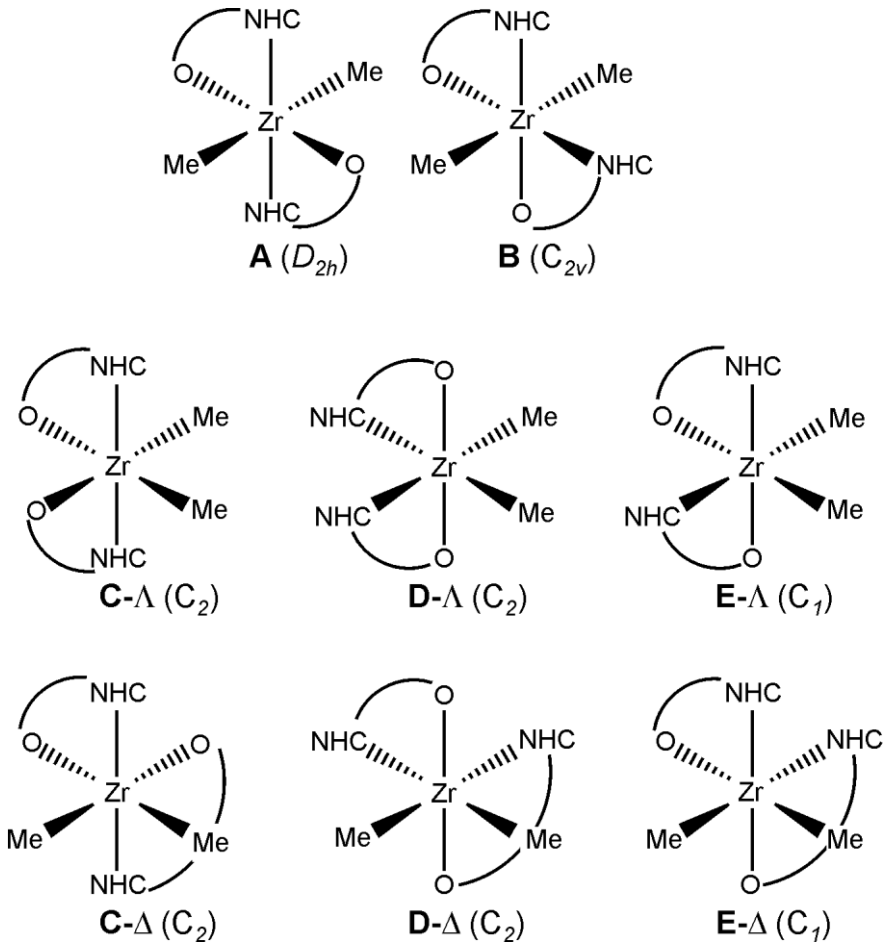


Figure 34. Imidazolium-N-methyl-N'-cyclopentenyl-2-hydroxy-iodide

Hence, complexes presenting two NHC-O ligands could have a combination of *SSSS*, *SSRR*, *RRSS* and *RRRR* stereogenic centers. Indepentenly from the stereogenic centers, for an octahedral complex with two chelating ligands of the type of NHC-O and two methyl groups, five diastereoisomers with different symmetries are in principle possible (A-E in Scheme 18).



Scheme 18. Possible diastereoisomers of complex 1

In particular, diastereoisomers **C**-**E** can have Λ or the corresponding Δ configuration, and are the only diastereoisomers that can be responsible for the polymerization, having *cis* alkyl groups. Taking in account the chirality of the ligands, 32 possible structures can be drawn. Among them, there are 18 couples of enantiomers (for example **C**-***SSSS***-**Λ** and **C**-***RRRR***-**Δ** are enantiomers, as well as **C**-***SSRR***-**Λ** and **C**-***RRSS***-**Δ**).

In summary, due to the symmetry, 14 possible diastereoisomeric structures (8 generated by the *SSSS* ligand combination and 6 by the *SSRR* ligand combination) have to be considered. In Table 3 internal and free energies, in gas phase and benzene, of all structures have been reported.

Table 3. Internal and free energies in gas phase and benzene of minimum energy structures relative to $[NHC\text{-}O]_2Zr(CH_3)_2$.

	E(gas)[a]	G(gas)[a]	E(benz)[a]	G(benz)[a]
A-*SSRR*	0	0	0	0
B-*SSRR*	6,1	6,6	5,3	5,7
C-*SSRR*-Λ	3,2	4,3	3,0	4,5
D-*SSRR*-Λ	5,1	3,3	4,6	3,9
E-*SSRR*-Λ	3,6	3,6	3,0	3,4
E-*SSRR*-Δ	7,1	6,7	6,4	6,1
A-*SSSS*	0,0	0,0	0,1	0,1
B-*SSSS*	2,1	3,7	1,8	3,2
C-*SSSS*-Λ	7,1	7,4	6,7	9,6
C-*SSSS*-Δ	-1,5	0,7	1,9	-0,2
D-*SSSS*-Λ	-	-	-	-
D-*SSSS*-Δ	3,0	2,1	2,3	2,2
E-*SSSS*-Λ	6,4	6,5	5,5	6,0
E-*SSSS*-Δ	5,6	5,7	5,0	5,6

[a]Internal and free energies are in kcal/mol..

Minimum energy structures in gas phase are shown in Figure 36 and 37, for *SSRR* and *SSSS* structures, respectively. For the sake of clarity, hydrogen atoms on the cyclopentane ring have not been shown.

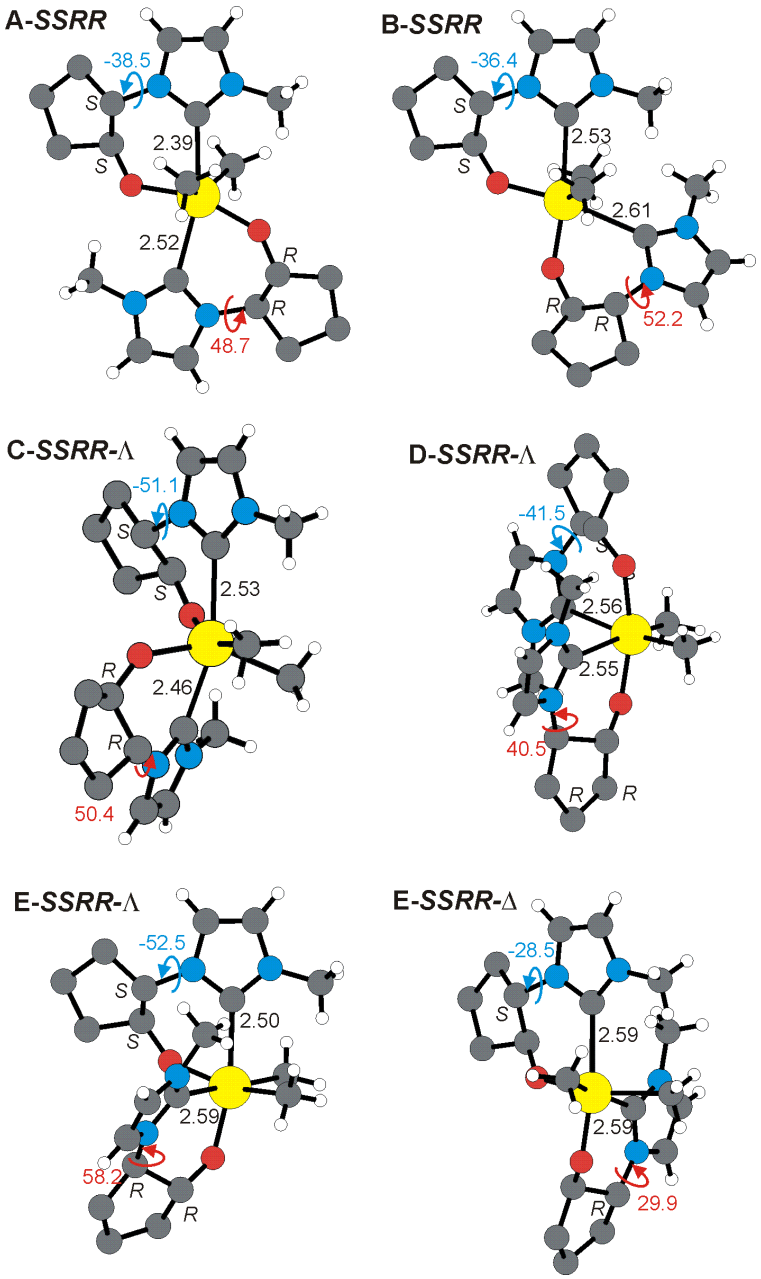


Figure 36. Minimum energy structures of $[NHC\text{-}O]_2Zr(CH_3)_2$ with a *SSRR* chirality combination of the NHC-O coordinated ligands. Zr-C distances (in black) between the metal and the NHC are in Å.

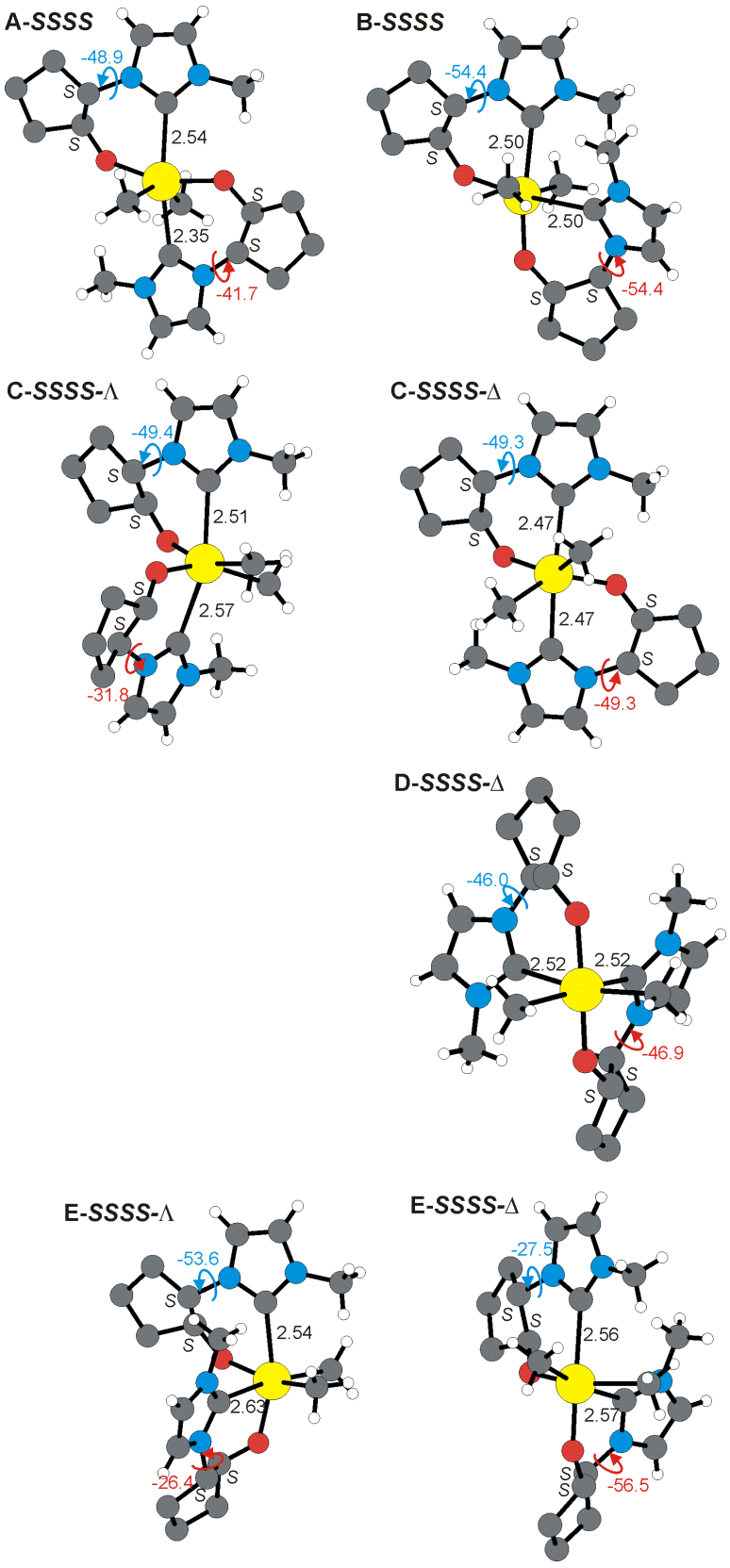


Figure 37. Minimum energy structures of $[NHC\text{-}O]_2Zr(CH_3)_2$ with a SSSS chirality combination of the NHC-O coordinated ligands. Zr-C distances (in black) between the metal and the NHC are in Å.

Most important parameters as the Zr-C distance between the metal and the NHC (in black) and the dihedral angles between the cyclopentane ring and the NHC ring (in blue and red) are depicted on the structures. The energies and the structure of **D-*SSSS*-Λ** were not reported, since any attempt to obtain such a minimum energy structure led to **C-*SSSS*-Δ**.

A-*SSRR* and A-*SSSS*, where the steric interaction between the two NHC-O ligands are minimized, present very similar energies and are two of the most stable species. All *SSRR* structures are quite unfavored with respect to A-*SSRR*.

Lower energy stereoisomers among them are **C-*SSRR*-Λ** and **E-*SSRR*-Λ**, which, in fact, show dihedral angles between the cyclopentane ring and the NHC ring closer to the ideal 60° of a gauche conformation. It is worth noting that only 6 diastereoisomeric *SSRR* species have to be considered, because **C-*SSRR*-Λ** and **C-*SSRR*-Δ** are enantiomers, as well as **D-*SSRR*-Λ** and **D-*SSRR*-Δ**.

Lowest energy structures, with respect to **A-*SSRR*** and **A-*SSSS***, presenting an *SSSS* ligand combination, are **B-*SSSS***, **C-*SSSS*-Δ** and **D-*SSSS*-Δ**. In particular, **C-*SSSS*-Δ** shows slightly higher free energy in gas phase and even lower in benzene, with respect to **A-*SSRR***, and can be described as a highly distorted octahedral where Me-Zr-Me is 79°, Me-Zr-NHC angles are both 77° and O-Zr-O angle is 121°. Nevertheless, it is a very stable and highly symmetrical C_2 species, which could be responsible for the formation of isotactic polypropilene.

According to our computational data, it is not possible to indicate the origin of the atactic polypropylene production. In fact, apparently the most stable alkylated species are only three, one could be responsible for the isotactic propylene polymerization and the other two are not suitable for the polymerization. Nevertheless, one could speculate that the atactic polypropylene can arise:

- from a strong modification of one of the A structure after the cationization with MAO,
- from the formation of a new species with only one NHC-O ligand,
- from one of the other calculated structures, even at very low concentrations.

1.6 Polymerization reactions of ethylene and propylene carried out using complex bis(imidazolidene-N-methyl-N'-cyclohexenyl-2-alkoxy)zirconium-diamide($[NHC\text{-}O]_2Zr(NEt_2)_2$)

Compound (2) was tested in the polymerization of ethylene after activation by methylaluminoxane (MAO). The reactions were performed in a glass autoclave at 50 °C under a ethylene pressure of 6 bar.

Data reported in the Table 4 show that the complex is able to polymerize ethylene, producing linear polyethylenes having a melting point higher than 135 °C and a high molecular weight ($\approx 8 \cdot 10^5$ dalton).

The molecular weight distribution is quite large (from 2 to 5) and quite always bimodal, revealing that the polymer are not generate by single site catalyst. The activities of the catalysts have been correlated to Al/Zr mole ratio and, as one can expect (see figure 38), the activities increase increasing the mole ratio of Al/Zr. Evidently, in this case increasing the concentration of MAO, the equilibrium

$$(L)_2ZrX_2 + MAO \rightleftharpoons [(L)_2ZrCH_3]^+ + [MAOX_2]^-$$

of formation of the active specie shift obviously to right, and association phenomena of the catalytic specie with MAO are not relevant.

Table 4. Polymerizations of ethylene in the presence of catalytic system 2/MAO

Run [a]	[Al]/[Zr]	Activity [b] (10^3)	M_W [c] (10^5)	M_W/M_n [c]
12	500	0.3	23	2.1
13	1000	1.5	7.6	4.3
14	2000	4.1	12	3.5
15	3000	7.3	10	5.2
16	5000	23	15	4.1

[a] Polymerization conditions: temperature 50 °C, solvent toluene, total volume 150 ml; complex = 8.0 $x10^{-6}$ mol; cocatalyst: MAO (based on Al); [b]ethylene concentration in the feed = 1.05 $x10^{-3}$ mol/l; [b]Activity in Kg polymer/ [complex] x time (h) x [monomer]; [c]Molecular weight and polydispersity index (M_w/M_n) determined by gel permeation chromatography versus polystyrene standard.

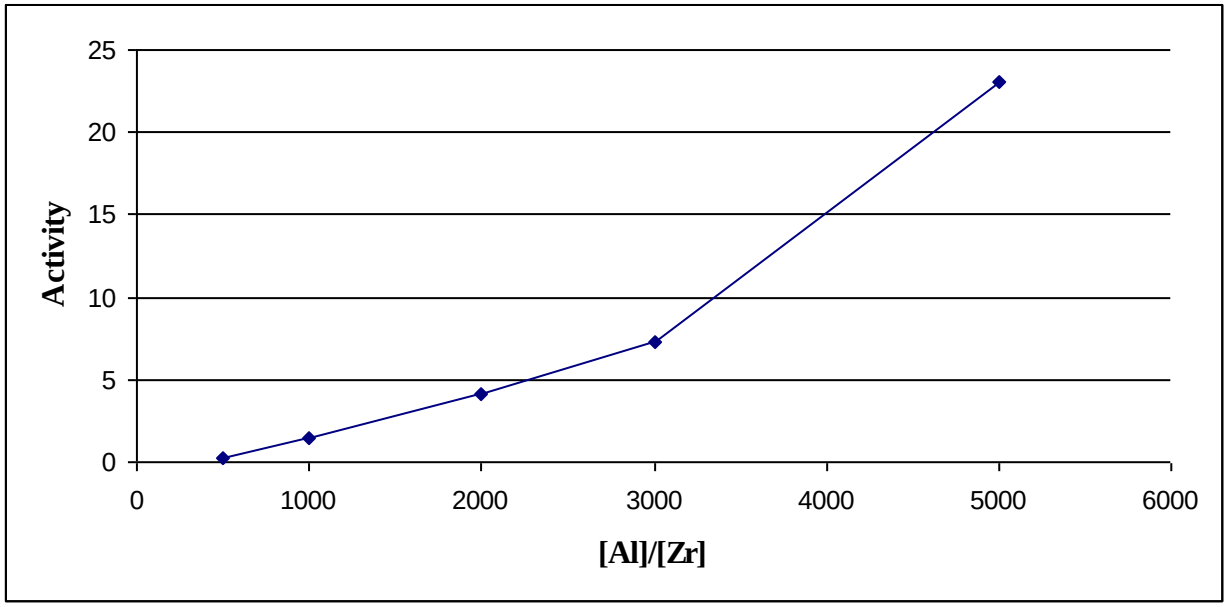


Figure 38: Plot of the activity in ethylene polymerization with complex 2 versus mole ratio Al/Zr.

Activity in Kg polymer/ [complex] x time (h) x [monomer] *10^3

Also in this case gel permeation chromatography analysis of prodoucts suggest the presence of more than one catalytic active site, and the presence of, at least, two species

catalytically active species can be hypotisized also in the polymerization of propylene at 50 °C under a pressure of 6 bar. In fact the polypropylene produced was fractionated, by exhaustive extraction with boiling hexanes, in atactic polypropylene (hexanes soluble fraction) and in highly isotactic polypropylene (hexanes insoluble fraction).

Table 5. Polymerizations of propylene in the presence of 2 based catalyst.

Run [a]	**[Al]/[Zr]**	**Activity** [b]	$\mathbf{M_W}$ [c] **(10^5)**	$\mathbf{M_W/M_n}$ [c]
17	1000	3	3.1	7.2
18	2000	31	2.8	8.2

[a] Polymerization conditions: temperature 50 °C, solvent toluene, total volume 150 ml; complex = 8.0×10^{-6} mol; cocatalyst: MAO (based on Al); propylene concentration in the feed = 5.48×10^{-3} mol/l; [b]Activity in Kg polymer/ [complex] x time (h) x [monomer]; [c]Molecular weight and polydispersity index (M_w/M_n) determined by gel permeation chromatography versus polystyrene standard; Molecular weight and polydispersity index of hexane insoluble fraction.

The activities decrease increasing the mole ratio of Al/Zr. GPC analysis of hexane soluble and hexane insoluble fraction showed high molecular weight ($\approx 7.0 \times 10^5$).

1.6.a Polymerization reactions of ethylene at 80 °C carried out using complex 1 and 2.

In order to evaluate the importance of temperature in polymerizations test in presence of complex 1 and 2, we carried out ethylene polymerization also at 80 °C, using the ratio [MAO]/[Zr] = 1000.

Table 6. Polymerizations of ethylene at differente temperature with catalytic system

Complex	Activity at 50 °C [a] (10^3)	Activity at 80 °C [a] (10^3)
1	5.6	3.5
2	1.5	5.9

[a] Polymerization conditions: solvent toluene, total volume 150 ml; complex = 8.0 x10^{-6} mol; cocatalyst: MAO (based on Al); ethylene concentration in the feed = 1.05 x10^{-3} mol/l; Activity in Kg polymer/ [complex] x time (h) x [monomer]; Molecular weight and polydispersity index (M_w/M_n) determined by gel permeation chromatography versus polystyrene standard.

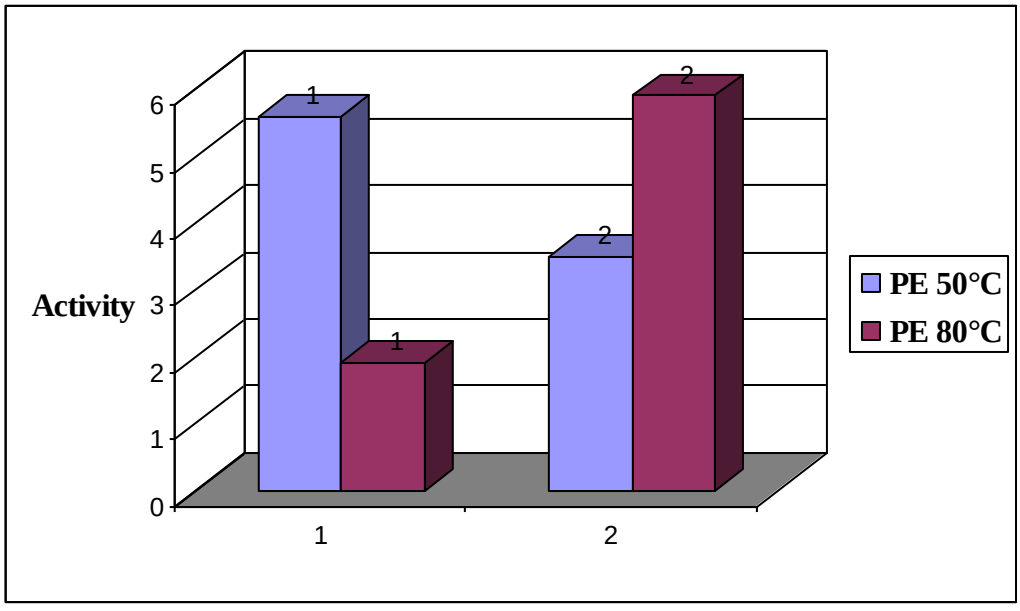


Figure 39. Comparison of activity of complexs 1 and 2 in ethylene polymerization at different temperature. Activity in Kg polymer/ [complex] x time (h) x [monomer] *10^3

Results show that activity at 80 °C respect to that one observed at 50 °C decrease for system 1, while increase for system 2. That result could indicate that complex 1 is more temperature sensible compared with complex 2. This fact is concord with variable temperature H NMR experiments, with show, at high temperature, that complex 1 signals change significantly, while complex 2 signals results quite stable until 80 °C.

1.7 Polymerization reaction of ethylene and propylene carried out using complex bis(imidazolidene-N-methyl-N'-ethylenyl-2-alkoxy)zirconium-diamide ($[NHC\text{-}O]_2Zr(NEt_2)_2$)

Compound (3) was tested in the polymerization of ethylene after activation by methylaluminoxane (MAO). The reactions were performed in a glass autoclave at 50 °C under a ethylene pressure of 6 bar.

Data reported in the Table 6 show that the complex is able to polymerize ethylene, producing linear polyethylenes having high molecular weight (≈ $12.6 \cdot 10^5$ dalton).

Table 7. Polymerizations of ethylene in the presence of catalytic system complex 3/MAO.

Run [a]	[Al]/[Zr]	Activity [b] (10^3)	M_W [c] (10^5)	M_W/M_n [c]
19	600	1.2	6.2	2.2
20	1000	4.3	5.9	7.0
21	1500	4.1	7.9	3.7
22	2000	4.0	20	1.1
23	3000	8.2	12.6	2.4

[a] Polymerization conditions: temperature 50 °C, solvent toluene, total volume 150 ml; complex = 8.0×10^{-6} mol; cocatalyst: MAO (based on Al); [b]ethylene concentration in the feed = 1.05×10^{-3} mol/l; [b]Activity in Kg polymer/ [complex] x time (h) x [monomer]; [c]Molecular weight and polydispersity index (M_w/M_n) determined by gel permeation chromatography versus polystyrene standard.

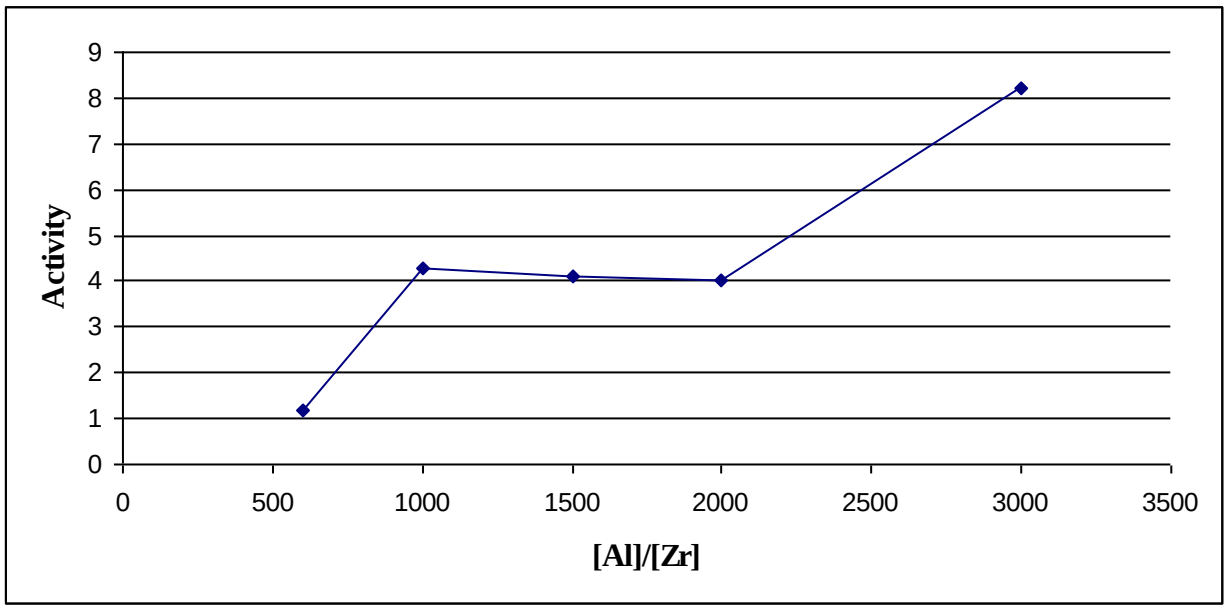


Figure 40. Plot of the activity in ethylene polymerization with complex 3 versus mole ratio [Al]/[Zr].
Activity in Kg polymer/ [complex] x time (h) x [monomer] $*10^3$

The molecular weight distribution is larger than 2 and monomodal. The gel permeation chromatography analysis suggest the presence of more than one catalytic active site and the NMR investigation showed that synthesis of 3 produced more isomers of the compound.

The presence of, at least, two species catalytically active was further confirmed by performing polymerization of propylene at 50 °C under a pressure of 6 bar. The polypropylene produced was fractionated, by exhaustive extraction with boiling hexane, in atactic polypropylene (hexane soluble fraction) and in highly isotactic polypropylene (hexane insoluble fraction).

Table 8. Polymerizations of propylene in the presence of catalytic system 3/MAO.

Run [a]	**Al/Zr**	**Activity** [b]	$\mathbf{M_W}$ [c] **(10^5)**	$\mathbf{M_W/M_n}$ [c]
24	600/1	0.3	4.7	18
25	1000/1	1	5.9	9.6

[a] Polymerization conditions: temperature 50 °C, solvent toluene, total volume 150 ml; complex = 8.0 $x10^{-6}$ mol; cocatalyst: MAO (based on Al); propylene concentration in the feed = 5.48 $x10^{-3}$ mol/l; [b]Activity in Kg polymer/ [complex] x time (h) x [monomer]; [c]Molecular weight and polydispersity index (M_w/M_n) determined by gel permeation chromatography versus polystyrene standard; Molecular weight and polydispersity index of hexane insoluble fraction.

The activities increase increasing the mole ratio of Al/Zr. GPC analysis of hexane soluble and hexane insoluble fraction showed high molecular weight (≈ 6 $x10^5$).

1.8 Polymerization reaction of ethylene and propylene carried out using complex bis(imidazolidene-N-methyl-N'-aryl-2-alkoxy)zirconium-diamide ($[NHC\text{-}O]_2Zr(NEt_2)_2$)

Compound (4) was tested in the polymerization of ethylene after activation by methylaluminoxane (MAO). The reactions were performed in a glass autoclave at 50 °C under a ethylene pressure of 6 bar.

Table 9. Polymerizations of ethylene in the presence of catalytic system 4/MAO.

Run [a]	[Al]/[Zr]	Activity [b] (10^2)	M_W [c] (10^5)	M_W/M_n [c]
26	500	1.1	n.d.	n.d.
27	1000	2.4	7.5	1.7
28	2000	10.4	7.9	2.3

[a] Polymerization conditions: temperature 50 °C, solvent toluene, total volume 150 ml; complex = 8.0 $x10^{-6}$ mol; cocatalyst: MAO (based on Al); ethylene concentration in the feed = 1.05 $x10^{-3}$ mol/l; [b]Activity in Kg polymer/ [complex] x time (h) x [monomer]; [c]Molecular weight and polydispersity index (M_w/M_n) determined by gel permeation chromatography versus polystyrene standard.

Compound (4) was also tested in the polymerization of propylene after activation by methylaluminoxane (MAO). The reactions were performed in a glass autoclave at 50 °C under a ethylene pressure of 6 bar, with a mole ratio of Al/Zr =1000/1 for 70 h. We obtain only few mg of product.

Conclusions

The synthesis and characterization of 4 new ligands and corresponding octahedral zirconium complexes, having two alkoxide funtionalized N-heterocyclic carbene ligands [NHC-O] and two amides group, and their behaviour as catalyst in the polymerization of ethylene and propylene, have been reported.

The new ligands are diazosubstituted N heterocycle carbene alkoxy derivativesdiazo, where one of the substituents is fixed and is represented by the methyl group, while the other substituent is varied both in size (L1-L3) and in nature (L4). The following catalyst were synthesized:

- bis(imidazolidene-N-methyl-N'-cyclopentenyl-2-alkoxy)zirconium-diamide (1)
- bis(imidazolidene-N-methyl-N'-cyclohexenyl-2-alkoxy)zirconium-diamide (2)
- bis(imidazolidene-N-methyl-N'-ethilenyl-2-alkoxy)zirconium-diamide (3)
- bis(imidazolidene-N-methyl-N'-aryl-2-alkoxy)zirconium-diamide (4)

In particular we have focused our attention on bis(imidazolidene-N-methyl-N'-cyclopentenyl-2-alkoxy)zirconium-diamide complex (1), on with where also carried out modeling calculations. NMR analysis allowed the full characterization of the complex, showing that more diastereoisomers cold be obtained during the synthesis.

Complex 1, after activation by MAO, is able to polymerize ethylene giving rise to a linear polyethylene with high molecular weight ($Mw \approx 6.10^5$), $Mw/Mn > 2$ and often bimodal.

In accord with hypothesis of precence of multiple species in solution, the polymerization of propylene has led to obtaining a mixture of products. Extraction with boyling hexane gave a highly isotactic fraction and an atactic fraction. Gel permeation chromatography analyses of isotactic fraction give molecular weight distribution < 2. This result is indicative of the presence of at least two catalytically active species, one able to give isotactic polypropylene and the other one able to produce atactic polypropylene.

If we consider this fact, togheter with NMR analysis results, we could assume in solution

the presence of three complexes having C_2 symmetry, or, alternatively, one complex with C_2 symmetry, together with a complex having C_1 symmetry.

In order to shed light on the species possibly involved in the polymerization, the different diastereoisomers, of the alkylated Zr complex $[NHC\text{-}O]_2Zr(CH_3)_2$, were modeled by DFT calculations. Most stable diastereoisomeric species showed to be A-*SSRR*, A-*SSSS* and C-*SSSS*-□̃

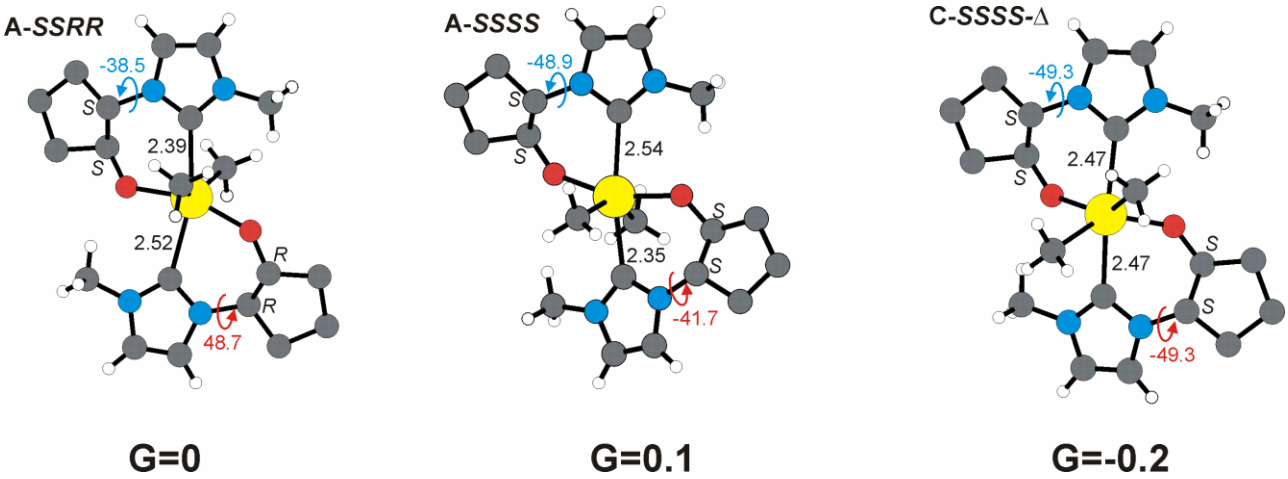


Figure 41. Most stable diastereoisomeric speciesof complex 1, G = free energie, in Kcal/mol

A-*SSRR* and A-*SSSS* structures present trans methyl groups and, as a consequence, are not suitable for the polymerization, whereas C-*SSSS*-Δ is a highly symmetrical C_2 structure with cis methyl groups, that could be responsible for the polymerization of olefins (ethene or propene) and, in particular, for formation of isotactic polypropilene.

Atactic polypropylene could rise from complex having high energy structure and therefore in very low concentration or by modification of one of the calculated structure after reaction with MAO.

Alike complex 1, complexes 2, 3 and 4 were characterized by NMR analysis and tested in polymerization of ethylene and propylene. Complex 2 is quite similar to complex 1: infact inside a cyclopentenyl ring, we have a cyclohexenyl ring.

On this complex modeling calculations were not performed, but if we consider the structural similarity with compound 1, and the NMR analysis results, it is easy to deduce that also in this case we have the formation of multiple species in solution. Moreover complex 2 results more temperature stable compared to complex 1. Polymerization activity of this system is of the same order of 1.

As we saw, there is more of one species that could derivates from complexes synthesis. In order to reduce the number of these possible species, we synthesized complexes 3 and 4. In fact proligand L4 has a single stereogenic center, while proligand L3 has none.

Unfortunately, in these case we have a lower of the catalytic acticity in polymerization of propylene, probably due to the less rigid structure, this impacts negatively on the polymerization of propylene. In fact, as can be seen from the data, the activity decreased significantly for complex 3, and in the case of complex 4, are completely void. In this last case probably the aromatic substituent is too big, and prevent monomer coordination.

In conclusion, among 4 systems synthesized, complex 1 results the specie which has increased catalytic activity in the olefins polymerization. The comparation of this system with other complex, shows that the rigidity of the complex structure is essential for the polymerization reaction. A less in rigidity results in a lower of activity.

Chapter 2

2. Introduction

Synthesis of complexes with N-heterocyclecarbene and Benzyl ligands of Zr(IV) and Ti(IV)

As we saw in introduction, heterocyclic carbenes have not found widespread application in olefin polymerization This is possibly due in part to the propensity of alkylmetal carbene complexes to decompose via alkyl-imidazolium eliminations.[50] Alkylmetal intermediates are expected to be involved in each step of the polymerization cycle. This reaction has been found to occur for late-transition-metal complexes,[51] and we reasoned that its effect may be attenuated by employing early-transition-metal carbene complexes.

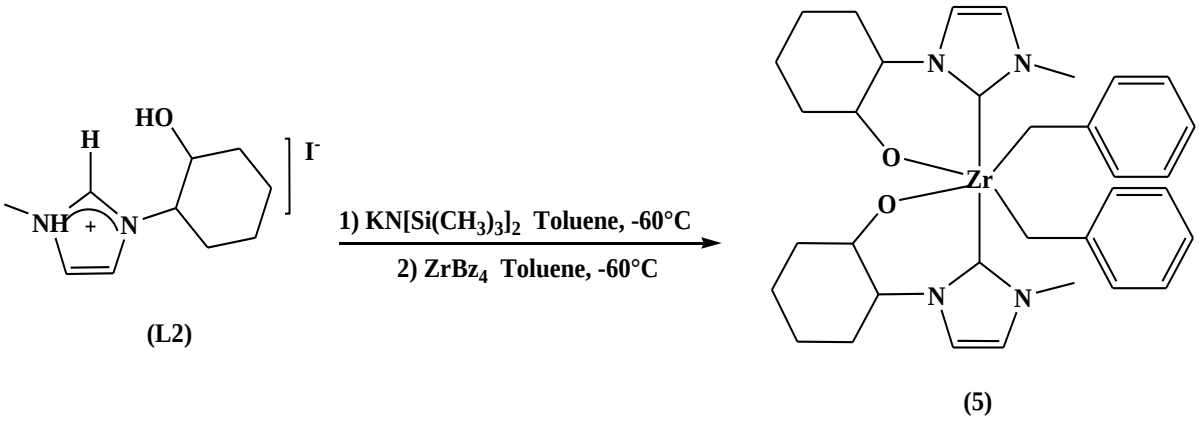
Moreover, alkhyl metal complexes having NHC ligand show a low stability, because strong σ-donation effect of carbene. Considering these two aspects, we desume that NHC-O ligands could give more stability to complex, so we synthesized octahedral complexes with two NHC alkoxy ligands and two alkyl ligands with early transition metals.

We synthesized complexes:

- (Imidazolidene-N-methyl-N'-cyclopentenyl-2-alkoxy)Zirconium-Benzyl (5).
- (Imidazolidene-N-methyl-N'-cyclopentenyl-2-alkoxy)Titanium-Benzyl (6)

These complexes are characterized by two NHC-alcoxy ligands (L2) bind to central cationic metal by the carbenic carbon and the anionic oxygen atom, and two benzyl groups bonded to the same atom. We use L2 ligand, because complex 2 is more temperature stable compared other synthesized systems. These complexes, in combination with MAO, were tested in the polymerization of ethylene and propylene.

2.1 Synthesis of complex bis(imidazolidene-N-methyl-N'-cyclohexenyl-2-alkoxy)Zirconium-dibenzyl ($[NHC\text{-}O]_2ZrBz_2$)



Scheme 19. Synthesis of complex 5

Synthesis of complex (5)

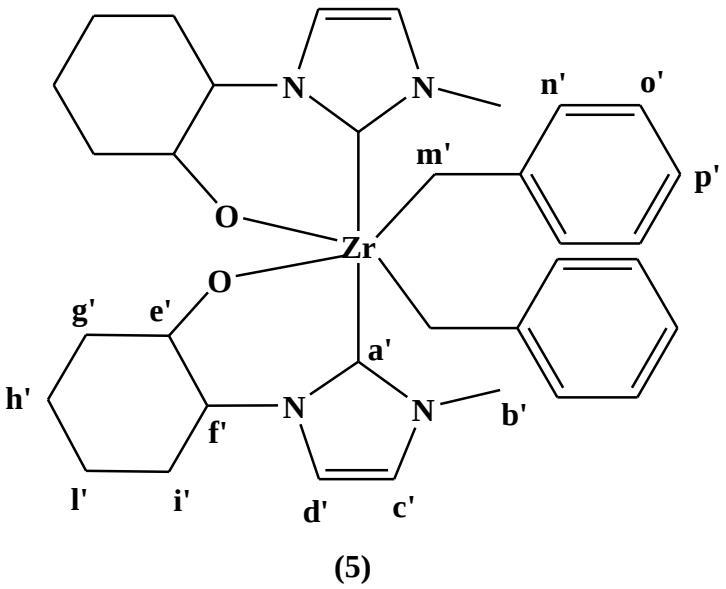


Figure 42. Bis (imidazolidene-N-methyl-N'-cyclopentenyl-2-alkoxy) dibenzyl Zirconium complex

Reaction of imidazolium salt (L2) (see pag 34) with a slight excess of strong base (*i.e.* potassium-hexamethyldisilazide) produce potassium alkoxide carbene, which was added to a solution of $ZrBz_4$ to afford the desired neutral octahedral complex $[NHC\text{-}O]_2ZrBz_2$ (5). It was isolated as air- and moisture sensitive solids and characterized by ^{1}H and ^{13}C NMR analysis.

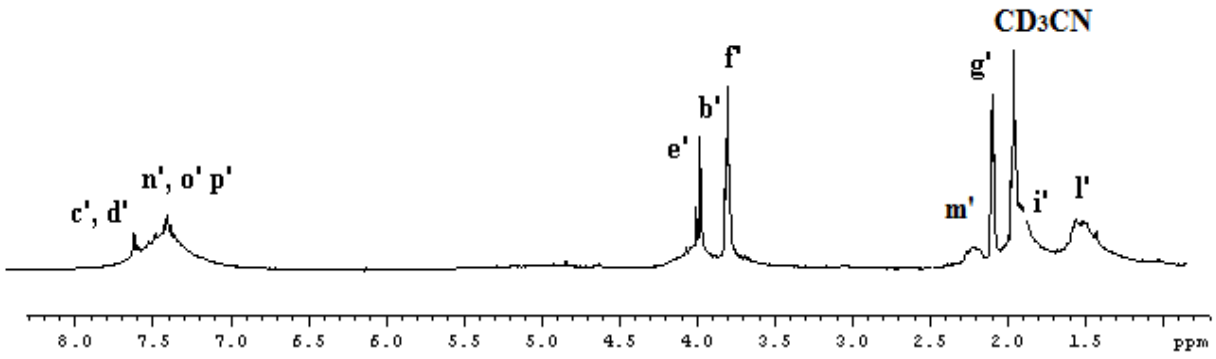
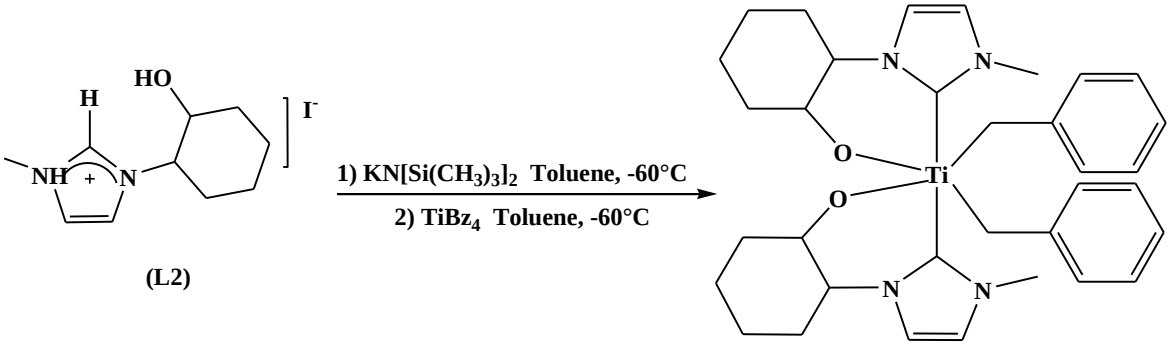


Figure 43. ^{1}HNMR spectra of complex 5 in CD_3CN

^{1}H spectrum show that peaks of aromatic groups fall between 7.39 and 7.24 ppm , while peaks of unsaturated protons of the heterocyclic backbone sound at 7.49 and 7.47ppm. Methine next to alkoxide is at 4.01 ppm, and near, at 3.94 ppm there is signal of N-CH_3 .
At 3.86 resonate the proton bonded to carbon next to nitrogen atoms. The methylene protons of cycloexane ring show signals between 2.36 and 1.48 ppm.

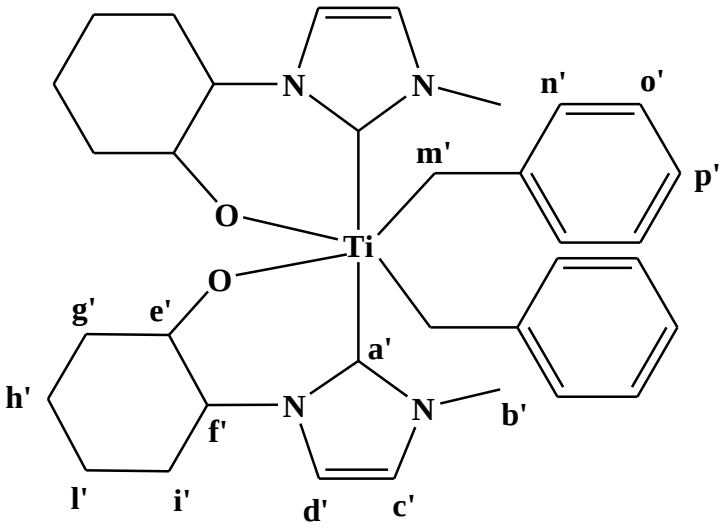
* *Unfortunatelly we are not able to obtained a* C^{13} *NMR spectrum with a good signals resolution, for this reason we prefer don't report it*.

2.2 Synthesis of complex bis(imidazolidene-N-methyl-N'-cycloexenyl-2-alkoxy)Titanium-dibenzyl ([NHC-O]$_2$TiBz$_2$)



Scheme 20. Synthesis of complex 6

Synthesis of complex (6)



(6)

Figure 44. Bis(imidazolidene-N-methyl-N'-cyclopentenyl-2-alkoxy)Titanium dibenzyl complex

Reaction of imidazolium salt (L2) (see pag 34) with an slight excess of strong base (*i.e.* potassium-hexamethyldisilazide) produce potassium alkoxide carbene, which was added to a solution of TiBz$_4$ to afford the desired neutral octahedral complex [NHC-O]$_2$TiBz$_2$ (2).

It was isolated as air- and moisture sensitive solids and characterized by ^{1}H and ^{13}C NMR analysis.

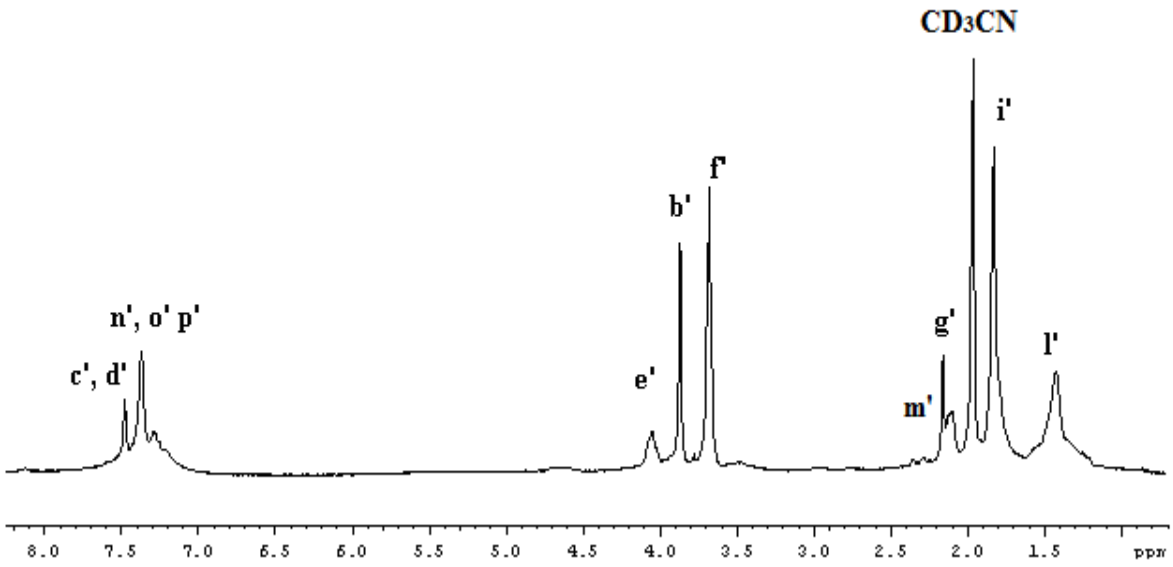


Figure 45. ^{1}HNMR spectra of complex 6 in CD_3CN

^{1}H NMR spectrum show that peaks of benzyl groups fall in the range of 7.38-7.21 ppm, the protons of the unsaturated methine of the backbone of heterocyclic at 7.48 ppm and methine next to alkoxide at 4.05 ppm. At 3.88 resonate the protons bonded to carbon next to nitrogen atoms, *i.e.* those on the imidazolium N-CH_3 and N-C*H*. The methylene protons of cycloexane ring and methyl of benzyl group show signals between 2.11 and 1.31 ppm.

^{13}C NMR* spectrum show signals at 211.9 ppm attributable to carbene carbon , while 123.5($C_{b',c'}$) is the signal of two carbons of Imidazolium backbone. Aromatic carbons sound at 128.5. Methine carbons bonded to oxygen and to nitrogen atoms resonate at 67.7 and 24.7 ppm, respectively, whereas the N-methyl carbon have the resonance at 36.1 ppm. Between 31.6 and 19.5 ppm there are signals of cyclohexane ring and methyl of benzyl group.

** Unfortunatelly we are not able to obtained a C^{13} NMR spectrum with a good signals resolution, for this reason we prefer don't report it.*

2.3 Polymerization reactions of ethylene and propylene carried out using complex bis(imidazolidene-N-methyl-N'-cyclohexenyl-2-alkoxy)zirconium-dibenzyl ($[NHC\text{-}O]_2ZrBz_2$)

Compound (5) was tested in the polymerization of ethylene after activation by methylaluminoxane (MAO). The reactions were performed in a glass autoclave at 50 °C under a ethylene pressure of 6 bar, with a mole ratio of Al/Zr =1000/1 for 48 h. We obtained 110 mg of product. (Activity in Kg polymer/ [complex] x time (h) x [monomer] = 38). Product has a molecular weight of $4.5*10^5$ and a Mw/Mn > 12.

Compound (5) was also tested in the polymerization of propylene after activation by methylaluminoxane (MAO). The reactions were performed in a glass autoclave at 50 °C under a propylene pressure of 6 bar, with a mole ratio of Al/Zr =1000/1 for 72 h. Unfortunately we are able to obtain only 10 mg of product. (Activity in Kg polymer/ [complex] x time (h) x [monomer] = 0.8). Product has a molecular weight of $3.2*10^5$ and a Mw/Mn > 5.6.

2.4 Polymerization reactions of ethylene and propylene carried out using complex bis(imidazolidene-N-methyl-N'-cyclohexenyl-2-alkoxy)Titanium-dibenzyl ($[NHC\text{-}O]_2TiBz_2$)

Compound (6) was tested in the polymerization of ethylene after activation by methylaluminoxane (MAO). The reactions were performed in a glass autoclave at 50 °C under a ethylene pressure of 6 bar, with a mole ratio of Al/Zr =2000 for 2.5 h. We obtained 2g of product. (Activity in Kg polymer/ [complex] x time (h) x [monomer] = 12820). Product has a molecular weight of $5.8*10^5$ and a Mw/Mn = 1.8.

Compound (6) was also tested in the polymerization of propylene after activation by methylaluminoxane (MAO). The reactions were performed in a glass autoclave at 50 °C under a propylene pressure of 6 bar, with a mole ratio of Al/Zr =1000/1 for 72 h. We obtain 313 mg of product (Activity in Kg polymer/ [complex] x time (h) x [monomer] = 13). The polypropylene produced was fractionated, by exhaustive extraction with boiling hexanes, in atactic polypropylene (hexanes soluble fraction 41 %) and in highly isotactic polypropylene (hexanes insoluble fraction 59 %). The soluble fraction has a molecular weight of $5.6*10^5$ and a Mw/Mn > 5, while insoluble fraction is not detectable.

Conclusions

McGuinness report that alkylmetal carbene complexes show a tendence to decompose via alkyl-imidazolium eliminations. [50] In order to demonstrate the stability of the [NHC-O]complexes with amide ligands synthesized in our labs, we carried out the synthesis of octahedral [NHC-O]complexes with alkyl ligands.

We have synthesized two bis[NHC-O]dialkyl zirconium (5) and titanium (6) complexes:

- (Imidazolidene-N-methyl-N'-cyclopentenyl-2-alkoxy)Zirconium-Benzyl (5).
- (Imidazolidene-N-methyl-N'-cyclopentenyl-2-alkoxy)Titanium-Benzyl (6).

These complexes results stable at room temperature. They were tested in olefins polymerization reaction. Complex 6 show a good activities either in polyethylene polymerization, while the corresponding zirconium one doesn't show polymerization activities. To about concern complex 5, it is not stable at high temperature.

Chapter 3

3. Introduction

Synthesis of complexes with N-heterocyclecarbene ligands of Y(III) and Sc(III)

Investigation of efficient catalyst systems for the olefins polymerization to afford polymers with desired properties has been a fascinating and challenging subject for decades. Exploration of new catalyst systems based on rare earth metals and other elements to provide more controllable selective polymerization with respect to molecular weight and molecular weight distribution and microstructure is obviously challengeable and attractive.

Thermally stable N-heterocyclic carbene (NHC) compounds have garnered upsurge in interest in the past decade and become versatile ligands to stabilize and activate metal centers in quite different key catalytic steps. Thus, examples in the polymerization of olefins remain scarce, and only few of that are on NHC complexes with Y and Sc [50,55].

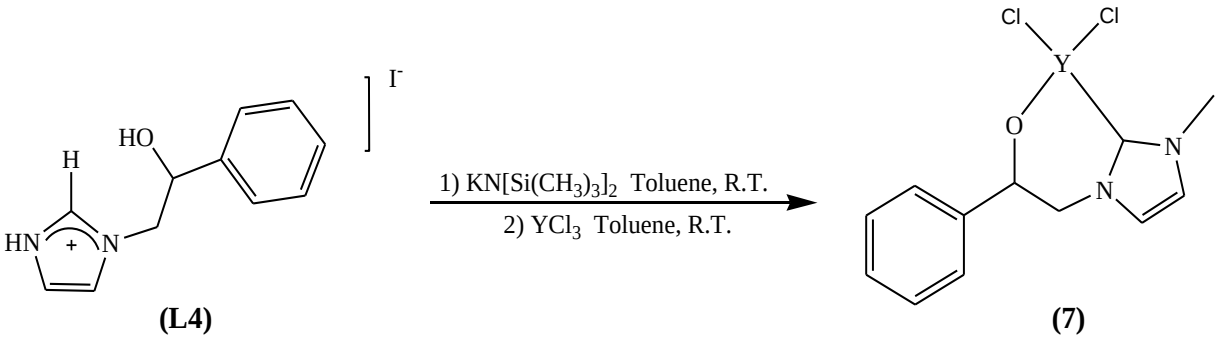
In this project we extended the use of ligands created in our labs to the rare earth metals complexes synthesis, by combination of [NHC-O] proligands with a strong base, and subsequentally reaction with YCl_3 and $ScCl_3$.

The following catalyst were synthesized:

- (imidazolidene-N-methyl-N'-aryl-2-alkoxy)-Yttium-dichloride (7)
- (imidazolidene-N-methyl-N'-cycloexenyl-2-alkoxy)-Scandium-dichloride (8)

These tetracoordinated complexes were characterized by one NHC-alcoxy ligand, bind to complex by the carbonic carbon and the oxygen atom, and with two chloride bonded to the same atom.

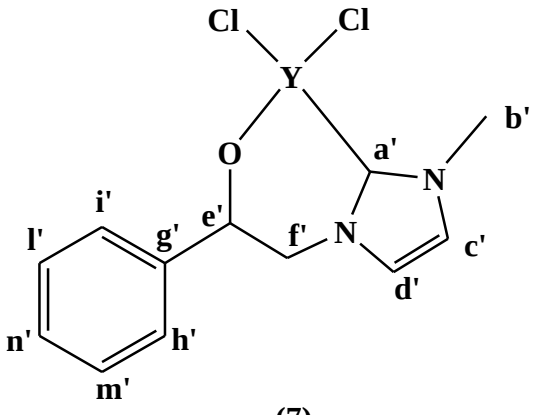
3.1 Synthesis of complex (imidazolidene-N-methyl-N'-aryl-2-alkoxy)-Yttrium-dichloride [(NHC-O)YCl_2



(L4) **(7)**

Scheme 21. Synthesis of complex 7

Synthesis of complex (7)



(7)

Figure 46. (imidazolidene-N-methyl-N'-aryl-2-alkoxy)-Yttium-dichloride

Reaction of imidazolium salt (L4) (see pag 55) with an slight excess of strong base (*i.e.* potassium-hexamethyldisilazide) produce potassium alkoxide carbene, which was added to a solution of YCl_3 to afford the desired neutral tetrahedral complex [NHC-O]YCl_2 (7).

It was isolated as air- and moisture sensitive solids and characterized by ^{1}H and ^{13}C NMR, elemental analysis and mass spectroscopy. Elemental analyses (C, H, N) of 7 agree with the proposed formulation.

^{1}H spectrum show that peaks of aryl groups falls at 7.89 and 7.76 ppm, while peak for the protons of the unsaturated methine of the backbone of heterocyclic sound at 5.53 ppm. Methine next to alkoxide at and that one next to nitrogen are at 4.37 and 4.58 ppm. methyl protons bonded to nitrogen atoms falls at 3.86 ppm. There are other signals, it could indicate the presence of more species in solution. We try to separate this species, but unfortunately our trials to obtain compound 7 pure not had success.

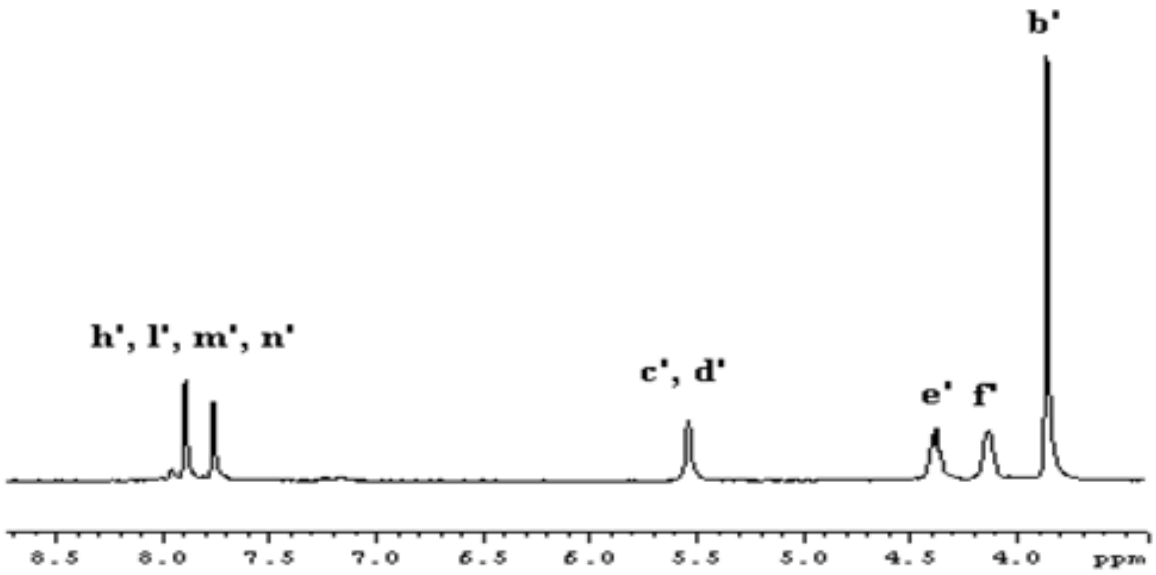


Figure 47. ^{1}HNMR spectra of complex 7 in CD_3CN

^{13}C NMR spectrum show signal at 197.7 ppm attributable to carbene carbons. In Fig.42 it is possible to observe the complete attribution of resonances, and just like on the proton spectra, we could note the presence of other signal.

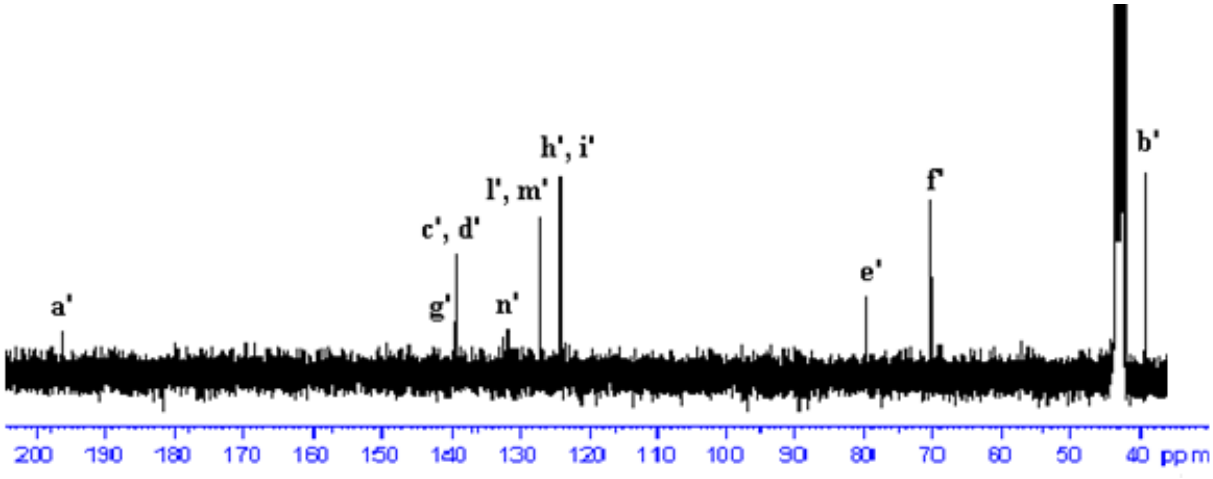
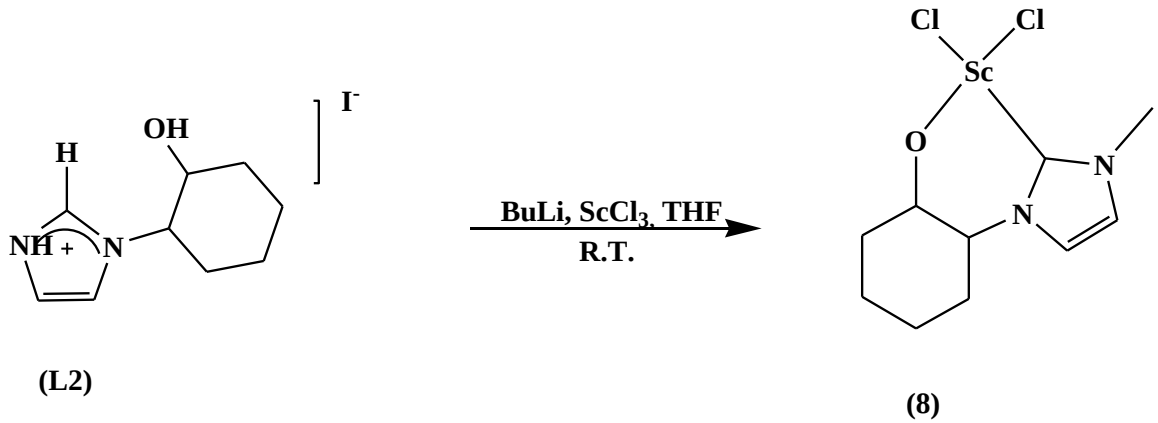


Figure 48. ^{13}CNMR spectra of complex 7 in DMSO-d-

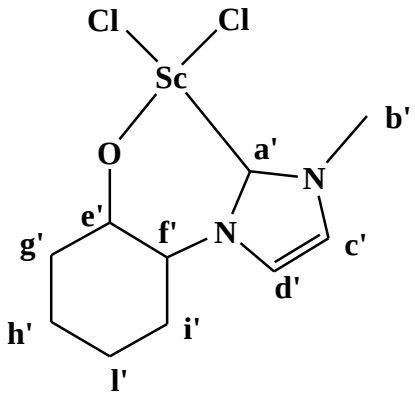
3.2 Synthesis of complex (imidazolidene-N-methyl-N'-cyclohexenyl-2-alkoxy) Scandium-dichloride [(NHC-O)$ScCl_2$]



(L2) **(8)**

Scheme 22. Synthesis of complex 8

Synthesis of complex (8)



(8)

Figure 49. (Imidazolidene-N-methyl-N'-cyclohexenyl-2-alkoxy) Scandium dichloride complex

Reaction of imidazolium salt (L2) (see pag 34) with an slight excess of strong base (*i.e.* potassium-hexamethyldisilazide) produce potassium alkoxide carbene, which was added to a solution of $ScCl_3$ to afford the desired neutral tetrahedral complex [NHC-O]$ScCl_2$ (8).

It was isolated as air- and moisture sensitive solids and characterized by ^{1}HNMR analysis.

^{1}H NMR* spectrum show two set of peaks for the protons of the unsaturated methine of the backbone of heterocyclic, between 7.00 and 6.62 ppm and two multiplet attributable to methine next to alkoxide at 3.59 and 3.37 ppm, are detectable. At 3.39 ppm resonate the protons bonded to carbon next to nitrogen atoms N-CH_3. The methylene protons of cycloexane ring show signals between 1.75 and 0.88 ppm.

3.3 Polymerization reactions of ethylene and propylene carried out using complex (imidazolidene-N-methyl-N'-aryl-2-alkoxy)-Yttrium-dichloride [(NHC-O)YCl_2]

Compound (7) was tested in the polymerization of ethylene after activation by methylaluminoxane (MAO). The reactions were performed in a glass autoclave at 50°C under a ethylene pressure of 6 bar, with a mole ratio of Al/Zr =500/1 for 72 h. Unluckily we are able to obtain only 38 mg of product. (Activity in Kg polymer/ [complex] x time (h) x [monomer] = 95).

Compound (7) was also tested in the polymerization of propylene after activation by methylaluminoxane (MAO). The reactions were performed in a glass autoclave at 50 °C under a ethylene pressure of 6 bar, with a mole ratio of Al/Zr =1000/1 for 72 h. Unfortunately we are not able to obtain any product.

3.4 Polymerization reactions of ethylene and propylene carried out using complex (imidazolidene-N-methyl-N'-cyclohexenyl-2-alkoxy)Scandium-dichloride [(NHC-O)$ScCl_2$]

Compound (8) was tested in the polymerization of ethylene after activation by methylaluminoxane (MAO). The reactions were performed in a glass autoclave at 50 °C under a ethylene pressure of 6 bar, with a mole ratio of Al/Zr =1000. After 48 h we obtained 70 mg of product (Activity in Kg polymer/ [complex] x time (h) x [monomer] = 0.9). Product has a molecular weight of $6.8*10^5$ and a Mw/Mn > 1.7.

Conclusion

We have synthesized some new of tetracoordinated early transition metall [NHC-O] dichloride complexes.

The following catalyst were synthesized:

- (imidazolidene-N-methyl-N'-aryl-2-alkoxy)-Yttium-dichloride (7)
- (imidazolidene-N-methyl-N'-cycloexenyl-2-alkoxy)-Scandium-dichloride (8)

These complexes show a very low activity in ethylene polymerization, and no activity in propylene polymerization. That could be connected to the very law stability of this compounds.

Chapter 4

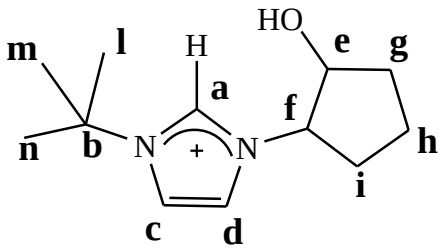
4. Introduction

Synthesis of [NHC-O] ligands

Given the promising results obtained with these catalytic systems, we decided to synthesize sterically bulky ligands that permit us to obtain a single species.

Enough as L1-L3 ligands have shown catalytic activity in aldol reactions, where fundamental is the role of the counter-ion, we tested the possibility of changing the counter-ion on binding by direct reaction with an appropriate alkyl halide (L9)

4.1 Synthesis of imidazolium salt (L 5)



(L 5)

Figure 50. Imidazolium-N-t-Buthyl-N'-cycloepentenyl-2-hydroxy-iodide

The compound L5 has been prepared according to Arnold and co-workers[7], i.e. by reacting cyclopentenoxide with imidazole to form imidazole-N-cyclopentan-2-ol, which was subsequently reacted in acetonitrile with t-Buthyliodide. After distillation of solvent, the product was purified by crystallization in acetone, obtaining the imidazolium salt as a white solid in high yield.

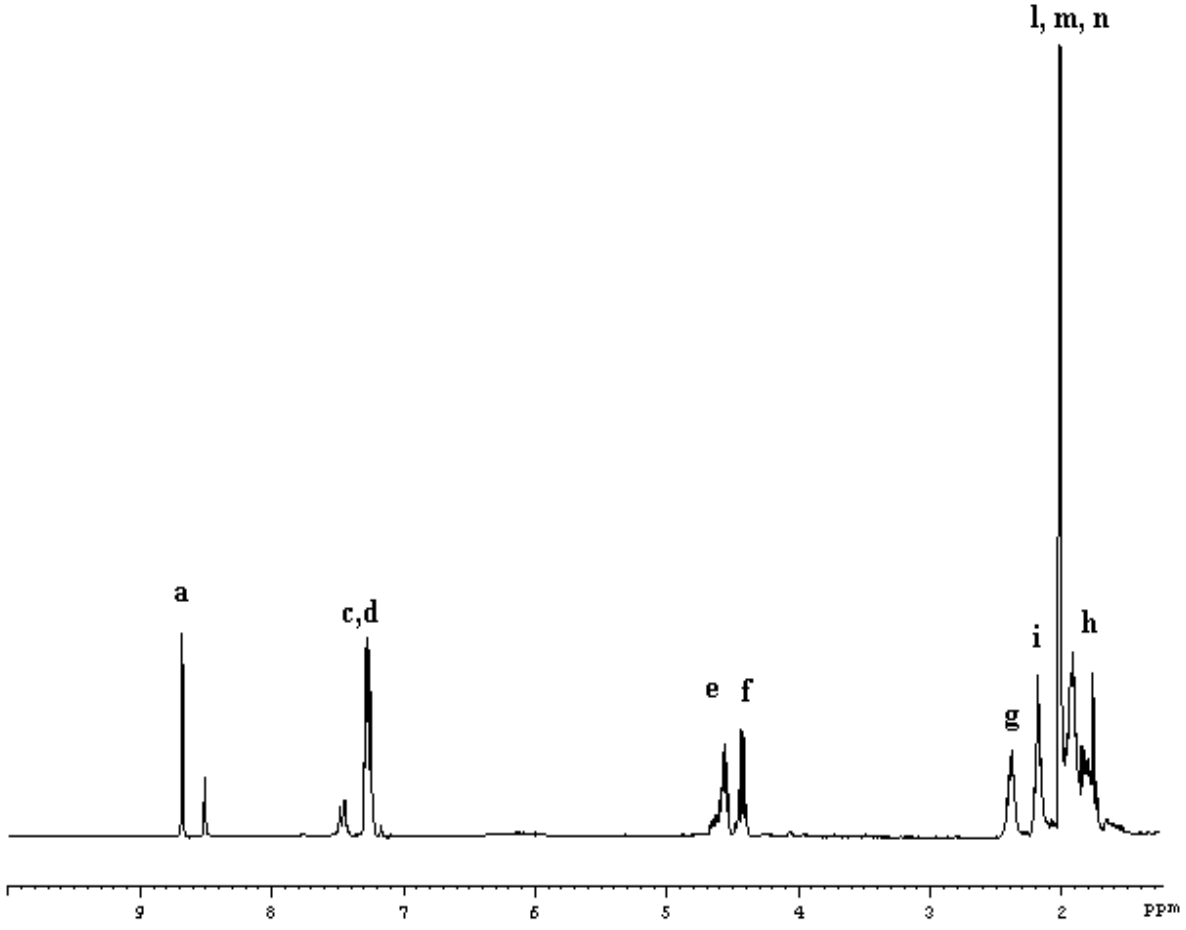
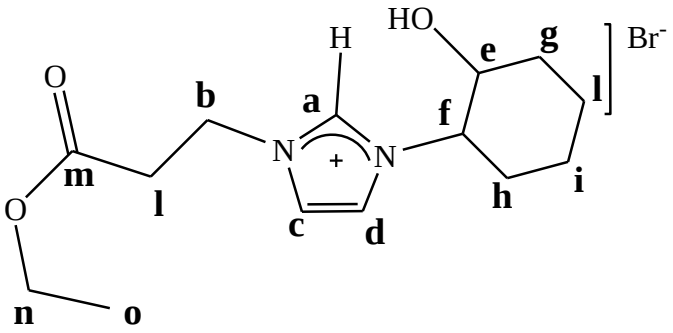


Figure 51. ^{1}HNMR spectra of L5 in $CDCl_3$

The singlet at 8.68 ppm is assigned to imidazolium H_a, whereas the resonances H_b and H_c of hydrogen atoms of methines of the backbone fall at 7.25 ppm, respectively. The two multiplet at 4.56 and 4.42 ppm were attributed to methine of cyclopentane bonded to heteroatoms, CH-O and CH-N, respectively, which, obviously, considering the *trans* opening of the epoxide ring, are in *trans* configuration.

The methylene protons of cyclopentane rings give complex multiplets between 2.37and 1.75 ppm. t-Bu fall at 2.03 ppm.

4.2 Synthesis of imidazolium salt (L 6)



(L6)

Figure 52. Imidazolium-N-ethylenyl acetate-N'-cyclohexenyl-2-hydroxy-bromide

The compound L 6 has been prepared by reacting cyclohexenoxide with imidazole to form imidazole-N-cycloexan-2-ol, which was subsequently reacted in acetonitrile with propyl 2-bromoacetate. After distillation of solvent, the product was purified by crystallization in acetone, obtaining the imidazolium salt as a yellow solid.

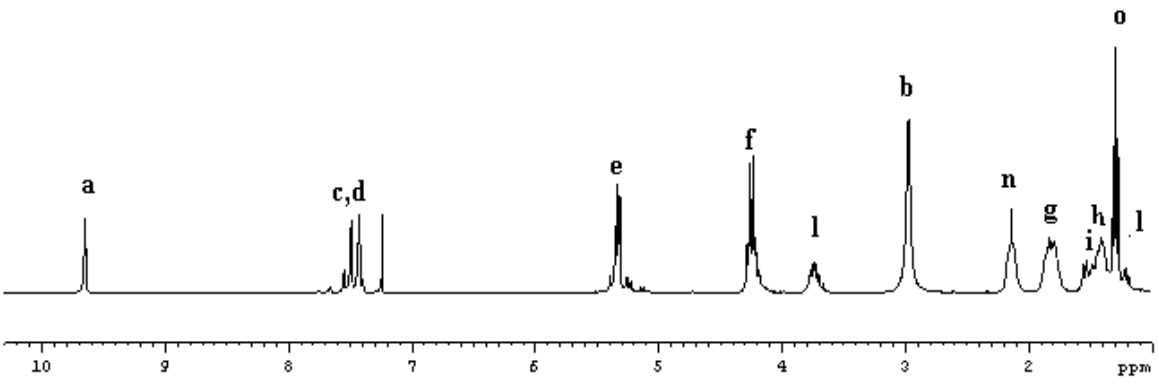
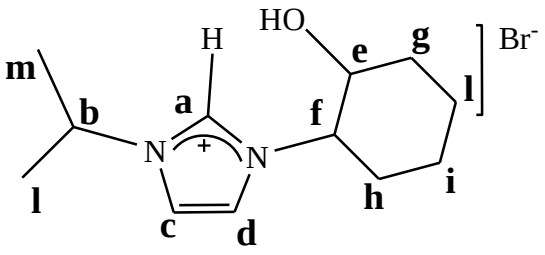


Figure 53. ^{1}HNMR spectra of L6 in $CDCl_3$

The singlet at 9.65 ppm is assigned to imidazolium H_a, whereas the resonances H_b and H_c of hydrogen atoms of methines of the backbone fall at 7.49 and 7.40 ppm, respectively. The two multiplet at 5.33 and 4.23 ppm were attributed to methine of cyclohexane bonded to heteroatoms, CH-O and CH-N, respectively, which, obviously, considering the *trans* opening of the epoxide ring, are in *trans* configuration.

At 3.74 ppm there is the signal of CH_2-O, while at 2.97 that one of CH_2-N. Protons of CH_2CH_3 group fall at 2.14 ppm (CH_2CH_3) and 1.29 ppm (CH_2CH_3). The methylene protons of cyclohexane rings give complex multiplets between 1.83 and 1.31 ppm.

4.3 Synthesis of imidazolium salt (L 7)



(L7)

Figure 54. Imidazolium-N-valerate-N'-cyclohexenyl-2-hydroxy-bromide salt

The compound L 7 has been prepared by reacting cyclohexenoxide with imidazole to form imidazole-N-cycloexan-2-ol, which was subsequently reacted in acetonitrile with Ethylbromide. After distillation of solvent, the product was purified by crystallization in acetone, obtaining the imidazolium salt as a white solid.

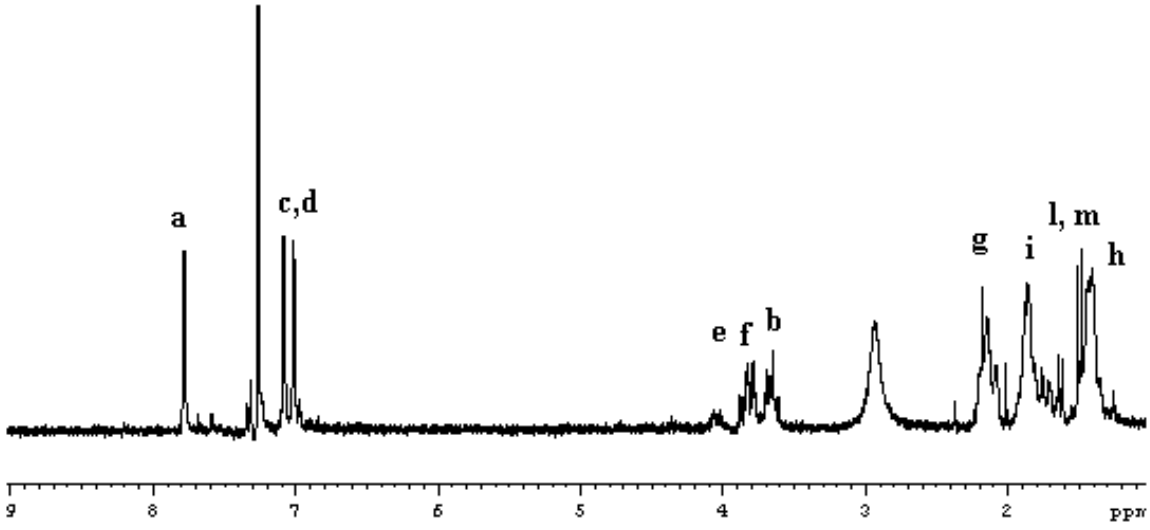
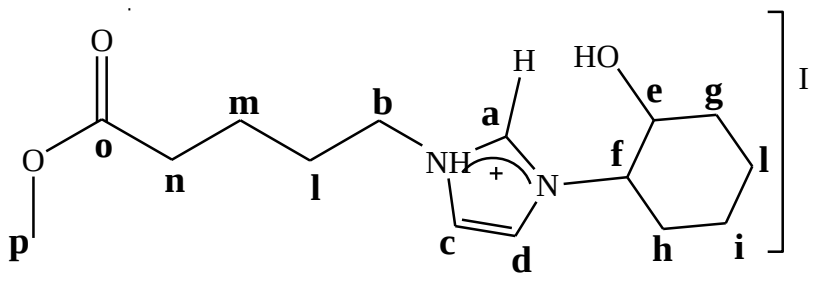


Figure 55. ^{1}HNMR spectra of L7 in $CDCl_3$

The singlet at 7.78 ppm is assigned to imidazolium H_a, whereas the resonances H_b and H_c of hydrogen atoms of methines of the backbone fall at 7.08 and 7.01 ppm, respectively. The two multiplet at 4.01 and 3.82 ppm were attributed to methine of cyclohexane bonded to heteroatoms, CH-O and CH-N, respectively, which, obviously, considering the *trans* opening of the epoxide ring, are in *trans* configuration.

Protons of CH_3 group fall at 1.43 ppm, that one of CH of isobutyle group sound at 3.78 ppm. The methylene protons of cyclohexane rings give complex multiplets between 1.86 and 1.41 ppm.

4.4 Synthesis of imidazolium salt (L 8)



(L 8)

Figure 56. Imidazolium-N-valerate-N'-cyclohexenyl-2-hydroxy-bromide salt

The compound L8 has been prepared by reacting cyclohexenoxide with imidazole to form imidazole-N-cycloexan-2-ol, which was subsequently reacted in acetonitrile with methyl 5-iodovalerate. After distillation of solvent, the product was purified by crystallization in acetone, obtaining the imidazolium salt as a yellow solid.

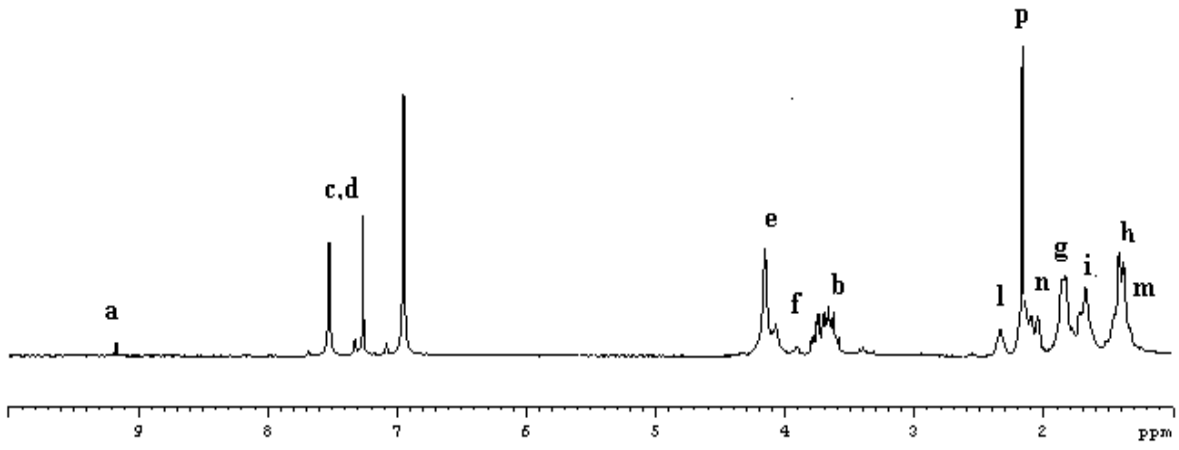
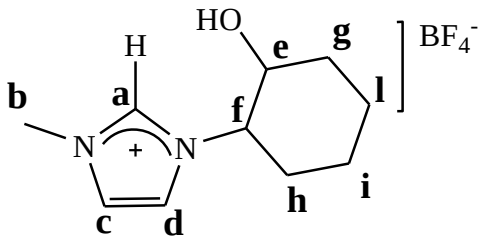


Figure 57. ^{1}HNMR spectra of L8 in $CDCl_3$

The singlet at 9.17 ppm is assigned to imidazolium H_a, whereas the resonances H_c and H_d of hydrogen atoms of methines of the backbone fall at 7.68 and 7.32 ppm, respectively. The two multiplet at 4.34 and 3.39 ppm were attributed to methine of cyclohexane bonded to heteroatoms, CH-O and CH-N, respectively, just like the methine H_b of CH_2-N at 3.66 ppm

At 2.33 ppm there is the signal of CH_2C-O, while other methine fall in the range of 2.16 – 1.38 ppm , the same range of the methylene protons of cyclohexane rings.

4.5 Synthesis of imidazolium salt (L 9)



(L9)

Figure 58. Imidazolium-N-methyl-N'-cyclohexenyl-2-hydroxy tetrafluoroborate

The compound L9 has been prepared by reacting L2 with ammonium tetrafluoroborate in Acetonitrile for 16 h. After distillation of solvent, the product was purified by extraction with chloroform, obtaining the imidazolium salt as a white solid.

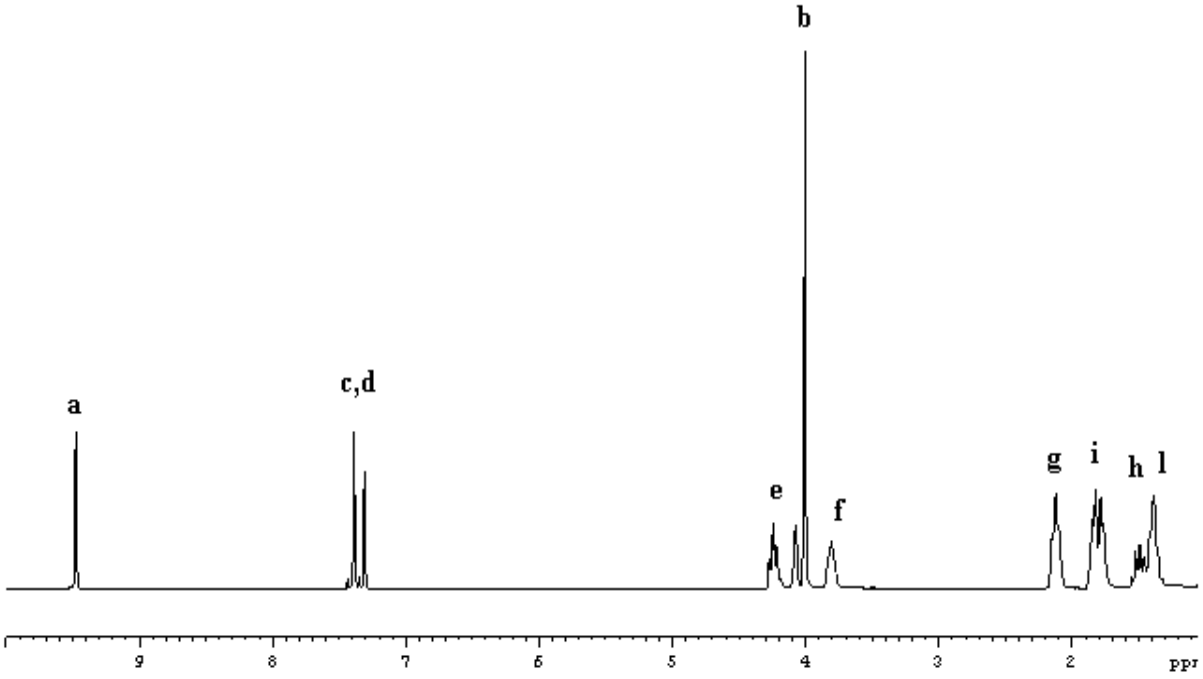


Figure 59. ^{1}HNMR spectra of L9 in $CDCl_3$

The singlet at 9.47 ppm is assigned to imidazolium H_a, whereas the resonances H_b and H_c of hydrogen atoms of methines of the backbone fall at 7.38 and 7.34 ppm, respectively. The two multiplet at 4.24 and 3.81 ppm were attributed to methine of cycloexane bonded to heteroatoms, CH-O and CH-N, respectively, which, obviously, considering the *trans* opening of the epoxide ring, are in *trans* configuration.

The protons of the methyl bonded to nitrogen atom give a singlet at 4.03 ppm. The methylene protons of cyclohexane rings give complex multiplets between 2.12 and 1.39 ppm.

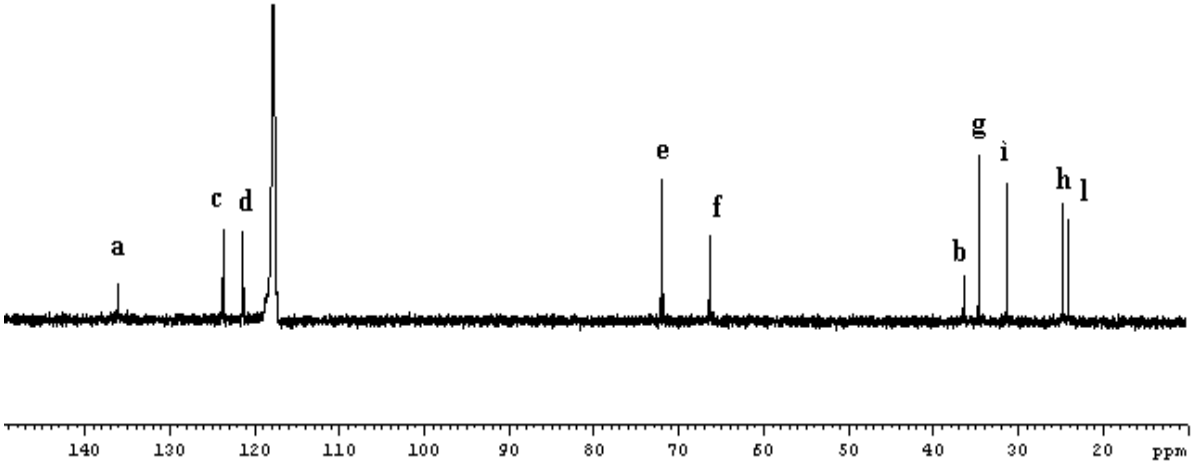


Figure 60. ^{13}CNMR spectra of L9 in CD_3CN

The sp^2 methine carbons give signals at 135.4, 123.5 and 120.9 ppm and they are attributed to C_a, C_b and C_d, respectively. Methine carbons bonded to oxygen and to nitrogen atoms (C_e and C_f) resonate at 71.5 and 65.3 ppm, respectively, whereas the N-methyl carbon (C_c) have the resonance at 37.5 ppm. Methylene carbons of cyclohexane ring give signals at 36.3, 34.1, 30.8 and 24.2 ppm and are attributed to C_i, C_h, C_l and C_g, respectively.

The Boron spectra show a signal at 4.46 ppm, while the fluorine spectra swhow a signal at -152.11 ppm.

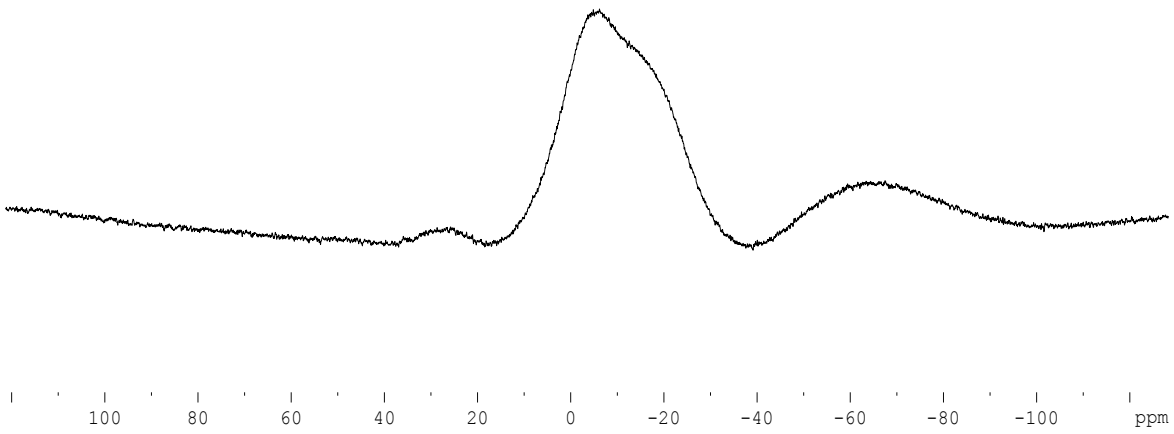


Figure 61. ^{11}BNMR spectra of L9 in CD_3CN

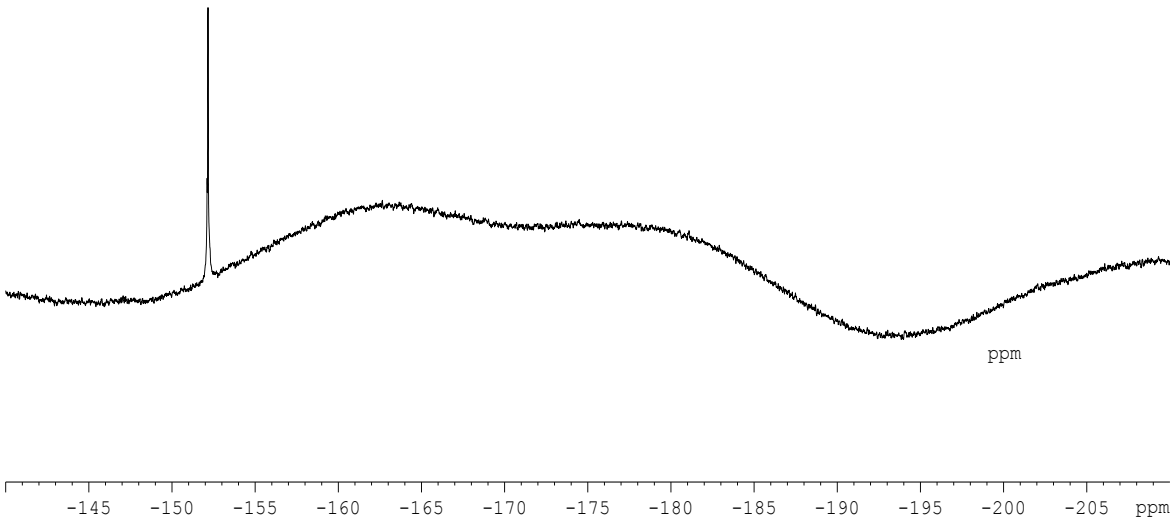


Figure 62. ^{19}FNMR spectra of L9 in CD_3CN

Conclusion

We have synthesized some new NHC-alkoxy ligands, and we demostre to be able to introduce in our proligands a seriers of subtituents, and also to change the counterions. This is very important to development of this class of complexes.

Experimental part

General Procedure

All reactions involving metal complexes were conducted in oven-dried glassware under nitrogen atmosphere with anhydrous solvents, using standard Schlenk techniques and glovebox techniques. Toluene and THF were distilled from sodium/benzophenone. CH_2Cl_2 and Et_2O were dried on CaH_2 and freshly distilled before use.

All chemical products were purchased from Sigma-Aldrich Company and were reagent quality.

These products were used without further purification. Flash column chromatography of organic compounds was performed using silica gel 60 (230-400 mesh). Silica gel for the purification of organometallic complexes was obtained from TSI Scientific, Cambridge, MA (60 Å, 230-400 mesh, pH 6.5-7.0).

Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 precoated plates (0.25 mm thickness) with a fluorescent indicator. Visualization of TLC plates was performed by UV light and $KMnO_4$ or I_2 stains.

Enantiomeric excesses were determined by chiral GC (Chiraldex G-TA, 30 m × 0.25 mm) and were compared to racemic samples. All deuterated solvents were degassed under an N_2 flow and stored over activated molecular sieves (4 Å) in a glovebox prior to use.

NMR spectra were recorded on a Bruker AM300 and a Bruker AVANCE 400 operating at 300 and 400 MHz for ^1H, respectively. The ^1H and ^{13}C NMR chemical shifts are referenced to $SiMe_4$ (δ = 0 ppm) using the residual protio impurities of the deuterated solvents as internal standard. ^{31}P NMR spectra were referenced using H_3PO_4 (δ = 0 ppm) as an external standard.

Spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling costant (Hz), and integration. Multiplicities were abbreviated as follows: singlet (s), doublet (d), triplet

(t), quartet (q), multiplet (m), and broad (br). The ^{13}C NMR assignments were confirmed by two-dimensional correlation experiments (HSQC).

Polymerization

Polymerizations of ethylene were performed in a 250 mL glass-autoclave introducing the amount of catalyst and cocatalyst dissolved in 125 mL of toluene, as reported in Table 1. The mixtures was fed with the monomer and kept under magnetic stirring over the runs. The autoclave was vented and the polymerization mixture was poured in acidified ethanol, the polymers were recovered by filtration, washed with fresh ethanol and dried *in vacuo* at 60°C.

Polymerizations of propylene were performed in a 250 mL glass-autoclave introducing the amount of catalyst and cocatalyst dissolved in 125 mL of toluene, as reported in Table 1. The mixtures was fed with the monomer and kept under magnetic stirring over the runs. The autoclave was vented and the polymerization mixture was poured in acidified ethanol, the polymers were recovered as usual.

Fractionations

Polypropylenes were fractionated by exhaustive extractions with boiling hexane in a Kumagawa extractor

(Imidazolidene-N-methyl-N'-cyclopentenyl-2-alkoxy)Zirconium-diamide complex

Imidazolium-N-methyl-N'-cyclopentenyl-2-hydroxy-iodide

An high pressure ampoule was charged with 0.1 mol of cyclopentene oxide (10 mL, FW=84.12 , d=0.971) and 1.0 mol equiv. of imidazole (7.8 g, FW=68.08). The resulting mixture was stirred at 60°C for 12h. Acetonitrile (28mL) and Iodomethane (1.0 mol equiv, 7.2 mL, FW=141.94, d=2.28)) were added and the mixture remained stirring at 80°C for 5h. The solvent was then concentrated to yield the product as a pale yellow oil, and the product precipitated as a white solid from acetone.

(13.6g, FW= 294,02 g/mol, 46mmol, yield 40 %)
Elemental analysis: found (%):Calc. for $C_9H_{15}IN_2O$ (%): C36.77, H 5.10, I 43.15, N 9.52, O 5.44.

^{1}H NMR (300 MHz, $CDCl_3$, 298 K): 8.68 (s, 1H, NC*H*N), 7.40 (s,1H, NC*H*CH), 7.32 (s, 1H, NCHC*H*), 4.37 (m, 1H, OC*H*), 4.34 (m, 1H, NC*H*), 3.78 (s, 3H, NCH_3), 2.25 (m, 2H, OCHCH_2), 2.01 (m, 2H, NCHCH_2), 1.64 (m, 2H, $CH_2CH_2CH_2$).

^{13}C NMR (75 MHz, CD_3CN, 298K): 136.6 (N*C*HN), 125.6 (N*C*HCH,) 121.7 (NCH*C*H), 77.4 (OCH), 67.3 (N*C*H), 46.3 (NCH_3),32.0 (OCHCH_2), 26.8 (NCHCH_2), 19.3 ($CH_2CH_2CH_2$).

Bis(imidazolidene-N-methyl-N'-cyclopentenyl-2-alkoxy)zirconium-diamide:

In an Schlenk ampoule, under an inert atmosphere, imidazolium salt (1) (4.0 mmol) was charged and next, THF (35mL) at –78°C was added. With the same procedure we prepare a solution of potassium hexamethyldisilazide (8 mmol) in 15 mL of THF, and then we added this solution to the other one to obtain the potassium alkoxide-carbenes. The mixture was allowed to slowly warm to room temperature and stirred for 2 h. After this time, the solution was added to a suspension of zirconium tetra-amide (2.0 mmol) in 15 mL of THF at –78°C. The resulting mixture was allowed to slowly warm to room temperature and stirred for 12 h, then filtered through celite, and washed with hexane. The solvent was removed under reduced pressure to yield the zirconium complex $[NHC\text{-}O]_2Zr(NEt_2)_2$

(0.9 g, FW= 566.28, 1.6 mmol, 40% yield)
Elemental analysis: found (%):Calc. for $C_{26}H_{46}N_6O_2Zr$ (%): C 55.22, H 8.13, N 14.85, O 5.66, Zr 16.13.

^{1}H NMR (300 MHz, $CDCl_3$, 298 K): 6.17(s, 1H, NCHCHN), 6.10 (s, 1H, NC*H*CHN), 4.55-4.42 (q, 1H, OC*H*), 3.94-3.88 (m, 1H, NC*H*), 3.90 (s, 3H, NCH_3), 3.58-3.56 (m, 2H, NCH_2CH_3), 2.09 (m, 2H, $OCHCH_2$), 1.68 (m, 2H, $NCHCH_2$), 1.50 (m, 2H, $CH_2CH_2CH_2$), 1.33-1.21 (m, 3H, NCH_2CH_3).

^{13}C NMR (75 MHz, CD_3CN, 298K): 197.5 (N*C*N), 119.9 (N*C*HCH), 117.4(N*C*HCH), 84.4 (OCH), 66.8 (N*C*H), 46.3 (NCH_2), 38.2 (NCH_3), 32.4 ($OCHCH_2$), 26.3 ($NCHCH_2$), 19.2 ($CH_2CH_2CH_2$), 46.3 (NCH_2 CH_3).

Synthesis of complex (imidazolidene-N-methyl-N'-cyclohexenyl-2-alkoxy)Zirconium-diamide

Imidazolium-N-methyl-N'-cyclohexenyl-2-hydroxy-iodide

An high pressure ampoule was charged with 58 mmol of cycloesene oxide (5.7 ml, FW=98.15, d=0.971) and 1 equiv. of imidazole (4g, 58 mmol, FW=68.08).
The resulting mixture was stirred at 50°C for 18h. Acetonitrile (16mL) and Iodomethane (1.0 mol equiv, 3.6 ml, FW=141.94, d=2.28)) were added and the mixture remained stirring at 80°C for another 2h. The solvent was then concentrated to yield the product as a yellow oil, and the prodouct recrystallised as a pale yellow solid from acetone.

(8.4 g, FW=308.04, 27 mmol, 47% yield)
Elemental analysis: Calc. for $C_{10}H_{17}IN_2O$ (%): C 38.9, H 5.56, I 41.2, N 9.09, O 5.19.

^{1}H NMR (300 MHz, $CDCl_3$, 298 K): 9.48 (s, 1H, NC*H*N), 7.42 (s,1H, NC*H*CH), 7.33 (s, 1H, NCHC*H*), 4.23 (m, 1H, OC*H*), 3.83(m, 1H, NC*H*), 4.02 (s, 3H, NCH_3), 2.13 (m, 2H, OCHCH_2), 1.96 (m, 2H, NCHCH_2), 1.45(m, 2H, $CH_2CH_2CH_2$), 1.23 (m, 2H, $CH_2CH_2CH_2$).

^{13}C NMR (400 MHz, $CDCl_3$, 298K): 136.4 (N*C*HN), 123.3 (N*C*HCH), 121.2 (N*C*HCH), 72.0 (OCH), 66.3 (N*C*H), 37.5 (NCH_3), 34.4 (OCHCH), 31.6 (OCHCH_2), 24.8 ($CH_2CH_2CH_2$), 24.2 ($CH_2CH_2CH_2$).

Bis(imidazolidene-N-methyl-N'-cyclohexenyl-2-alkoxy)zirconium-diamide

In glove box a Schlenk ampoule under a nitrogen atmosphere was charged with imidazolium salt (2 g, 6.5 mmol, FW=308.04) and then, under an inert atmosphere, THF (20mL) at –50°C was added. With the same procedure we prepare a solution of potassium hexamethyldisilazide (2.6 g, 2 equiv., 13 mmol, FW=199.49) in 10 mL of THF, and we added this solution to the other one to obtain the potassium alkoxide-carbenes.
Then the mixture was allowed to slowly warm to room temperature and was stirred for 2 h. After this time, this solution was added to a suspension of Zirconium salt (1.25 g, 3.3 mmol, 0.5 equiv. FW=379.7) in 10 mL of THF at –70°C. The resulting mixture was allowed to slowly warm to room temperature and was stirred for 12 h, then filtered through celite, and washed with hexane. The solvent was removed under reduced pressure to yield the zirconium complex.

(1.99 g, 3.4 mmol, FW=593.31, 51 % yield)
Elemental analysis: Calc. for $C_{28}H_{50}N_6O_2Zr$ (%): C 56.6 H 8.48, N 14.1, O 5.39, Zr 15.4.

^{1}H NMR (300 MHz, C_6D_6, 298 K): 6.37 (s, 1H, NCHCHN), 6.15 (s, 1H, NC*H*CHN), 4.19-3.77 (q, 1H, OC*H*), 3.45-3.38 (m, 1H, NC*H*), 3.86 (s, 3H, NCH_3), 3.77-3.61 (m, 2H, NCH_2CH_3), 1.93 (m, 2H, $OCHCH_2$), 1.69 (m, 2H, $NCHCH_2$), 1.51 (m, 2H, $CH_2CH_2CH_2$), 1.10-0.94 (m, 3H, NCH_2CH_3).

^{13}C NMR (400 MHz, DMSO-d-, 298K): 207.93 (N*C*N), 159.3 (N*C*HCH), 78.8 (OCH), 72.3 (N*C*H), 54.5 (NCH_3), 34.8 (OCHCH), 31.4 ($OCHCH_2$), 25.2 ($CH_2CH_2CH_2$), 24.8 ($CH_2CH_2CH_2$), 13.3 (NCH_2CH_3), 6.3 (NCH_2 CH_3).

Synthesis of complex (imidazolidene-N-methyl-N'-ethylenyl-2-alkoxy)Zirconium-diamide

Imidazolium-N-methyl-N'-ethylenyl-2-hydroxy-iodide

At -10°C an high pressure ampoule was charged with 0.1 mol of ethylene oxide (5.2 g, FW = 44.05) and 1 equiv. of imidazole (FW=68.08). The solution was allowed to slowly warm to 70°C and was stirred at 70°C for 12 h. Acetonitrile (20mL) and Iodomethane (1 equiv, 0.1 mol, 7.34 ml, FW=141.94, d=2.28)) were added and the mixture remained stirring at 80°C for another 12 h. The solvent was then concentrated to yield the product as a pale yellow oil, and the imidazolium salt was recuperated as a yellow wax from extraction of acetone.

(13.8 g, 54 mmol, FW=253.99, 54 % yield)
Elemental analysis: Calc. for $C_6H_{11}IN_2O$ (%): C 28.4, H 4.36, I 49.9, N 11.0, O 6.30.

^{1}H NMR (300 MHz, CD_3CN, 298 K): 8.11 (s, 1H, NC*H*N), 7.51 (s,1H, NC*H*CH), 7.42 (s, 1H, NCHC*H*), 4.28 (m, 1H, OC*H*), 3.80 (m, 1H, NC*H*), 3.82 (s, 3H, NCH_3).

^{13}C NMR (400 MHz, CD_3CN, 298K): 139.8 (N*C*HN), 124.7 (N*C*HCH), 124.2 (N*C*HCH), 60.9 (OCH), 53.3 (N*C*H), 37.3 (NCH_3).

Bis(imidazolidene-N-methyl-N'-ethilenyl-2-alkoxy)zirconium-diamide

In glove box a Schlenk ampoule under a nitrogen atmosphere was charged with imidazolium salt (0.48g, 1.9 mmol, FW=254) and then, under an inert atmosphere, THF (20 mL) at –50°C was added. With the same procedure we prepare a solution of potassium hexamethyldisilazide (0.76 g, 2 equiv., 3.8 mmol, FW=199.49) in 10 mL of THF at –50°C, and we added this solution to the other one to obtain the potassium alkoxide-carbenes.

Then the mixture was allowed to slowly warm to room temperature and was stirred for 2 h. After this time, this solution was added to a suspension of Zirconium salt (0.36g, 0.5 equiv. 0.95 mmol, FW=379.7) in 10 mL of THF at –50°C. The resulting mixture was allowed to slowly warm to room temperature and was stirred for 12 h, then filtered through celite, and washed with hexane. The solvent was removed under reduced pressure to yield the zirconium complex.

(0.7 g, 1.4 mmol, FW= 484.21, 76 % yield)

Elemental analysis: Calc. for $C_{20}H_{38}N_6O_2Zr$ (%): C 49.4, H 7.88, N 17.3, O 6.59, Zr 18.8.

^{1}H NMR (300 MHz, $CDCl_3$, 298 K): 6.08 (s,1H, NC*H*CH), 5.95 (s, 1H, NCHC*H*), 4.28 (m, 1H, OC*H*), 3.87 (m, 1H, NC*H*), 3.67 (s, 3H, NCH_3), 3.47 (m, 2H, NCH_2CH_3), 1.32 (m, 2H, NCH_2CH_3).

^{13}C NMR (400 MHz, C_6D_6, 298K): 196.3 (N*C*N), 120.5 (N*C*HCH), 118.9 (N*C*HCH), 67.4 (OCH), 54.8 (N*C*H), 37.8 (NCH_3). 32.8 (NCH_2CH_3), 23.1 (NCH_2CH_3).

Synthesis of complex (imidazolidene-N-methyl-N'-aryl-2-alkoxy)Zirconium-diamide ($[NHC\text{-}O]_2Zr(NEt_2)_2$)

Imidazolium-N-methyl-N'-aryl-2-hydroxy-iodide

At -10°C an high pressure ampoule was charged with 0.12 mol of styrene oxide (13.4 mL, FW=120.15, d=1.054) and 1.0 mol equiv. of imidazole (8g, FW=68.08). The solution was allowed to slowly warm to 70°C and was stirred at 50°C for 24 h. Acetonitrile (20mL) and Iodomethane (1 equiv, 0.12 mol, 7.5 mL, FW=141.94, d=2.28)) were added and the mixture remained stirring at 80°C for another 2 h. The solvent was then concentrated to yield the product as a yellow oil, and the final salt recrystallised as a pale yellow solid from acetone.

(20.8 g, 0.063 mol, FW=330.02, 53 % yield)
Elemental analysis: Calc. for $C_{12}H_{15}IN_2O$ (%): C 43.6, H 4.58, I 38.4, N 8.48, O 4.85.

^{1}H NMR (300 MHz, CD_3CN, 298 K): 9.12 (d, 1H, NC*H*N), 7.79 (aromatic ring), 7.87 (d, 1H, NC*H*CH), 7.85 (d, 1H, NCHC*H*), 5.57 (m, 1H, OC*H*4.80 (m, 1H, NC*H*), 3.79 (s, 3H, NCH_3).

^{13}C NMR (400 MHz, DMSO-d-, 298K): 138.5 (N*C*HN), 134.3 (N*C*HCH), 134.2 (*C*HCH), 125.1 (*C*HCH), 123.2 (*C*HCH), 120.3 (CH*C*H), 66.7 (OCH), 52.9 (N*C*H), 33.1 (NCH_3).

Bis(imidazolidene-N-methyl-N'-aryl-2-alkoxy)zirconium-diamide

In glove box a Schlenk ampoule under a nitrogen atmosphere was charged with imidazolium salt (2 g, 6.06 mmol, FW=330) and then, under an inert atmosphere, THF (40 mL) at –60°C was added. With the same procedure we prepare a solution of potassium hexamethyldisilazide (2.42 g, 2 equiv., 0.12 mol, FW=199.49) in 10 mL of THF at –60°C, and we added this solution to the other one to obtain the potassium alkoxide-carbenes.
Then the mixture was allowed to slowly warm to room temperature and was stirred for 12 h. After this time, this solution was added to a suspension of Zirconium salt (1.14 g, 3.03 mmol, 0.5 equiv. FW=379.7) in 10 mL of THF at –50°C. The resulting mixture was allowed to slowly warm to room temperature and was stirred for 12 h, then filtered through celite, and washed with exane. The solvent was removed under reduced pressure to yield the zirconium complex.

(1.2 g, 2 mmol, FW= 636.27, 29 % yield)
Elemental analysis: Calc. for $C_{32}H_{46}N_6O_2Zr$ (%): C 60.2, H 7.27, N 13.2, O 5.02, Zr 14.3

^{1}H NMR (300 MHz, CD_3CN, 298 K): 7.65-6.92 (m, 1H, aromatic ring), 6.01 (s,1H, NC*H*CH), 5.83 (s, 1H, NCHC*H*), 3.80 (m, 1H, OC*H*), 3.66 (m, 1H, NC*H*), 3.56 (s, 3H, NC*H*$_3$), 3.48 (m, 2H, NCH_2CH_3), 1.19 (m, 2H, NCH_2CH_3).

^{13}C NMR (400 MHz, CD_3CN, 298K): 196.9 (N*C*N), 121.7 (N*C*HCH), 118.6 (*C*HCH), 116.7 (CH*C*H), 115.3 (*C*HCH), 112.6 (*C*HCH), 79.6 (OCH), 66.0 (N*C*H), 47.3 (NCH_3), 25.9 (NCH_2CH_3), 17.4 (NCH_2CH_3).

Synthesis of complex (imidazolidene-N-methyl-N'-cyclohexenyl-2-alkoxy)Zirconium-Benzyl ($[NHC\text{-}O]_2ZrBz_2$)

Bis(imidazolidene-N-methyl-N'-cycloexenyl-2-alkoxy)zirconium-dibenzyl

*I*n an Schlenk ampoule, under an inert atmosphere, imidazolium salt (2) (1g, 3 mmol, FW=308.04) was charged and next, THF (30 mL) at –78°C was added. With the same procedure we prepare a solution of potassium hexamethyldisilazide (0.65 g, 1 equiv., 3mmol, FW=199.49) in 30 mL of THF, and then we added this solution to the other one to obtain the potassium alkoxide-carbenes. The mixture was allowed to slowly warm to room temperature and stirred for 24 h. After this time, the solution was added very slowly to a suspension of zirconium tetra-benzyl (0.68 g, 0.5 equiv., 1.5 mmol, FW=454.12) in 30 mL of THF at –78°C. The resulting mixture was allowed to slowly warm to room temperature and stirred for 24 h, then filtered through celite, and washed with hexane. The solvent was removed under reduced pressure to yield the zirconium complex $[NHC\text{-}O]_2ZrBz_2$

(0.5 g, FW= 602.21, 0.8 mmol, 28 % yield)
Elemental analysis: found (%):Calc. for $C_{32}H_{40}N_4O_2Zr$ (%): C 63.64, H 6.68, N 9.28, O 5.30, Zr 15.11.

^{1}H NMR (300 MHz, CD_3CN, 298 K): 7.39-7.24 (m, aromatic ring), 7.49 (s,1H, NC*H*CH), 3.86 (m, 1H, OC*H*), 3.66 (m, 1H, NC*H*), 3.84 (s, 3H, NCH_3), 1.96 (m, 2H, CH_2CH_2 CH_2), 1.82 (m, 2H, CH_2CH_2 CH_2), 1.38 (m, 2H, CH_2 CH_2CH_2).

Synthesis of complex (imidazolidene-N-methyl-N'-cyclohexenyl-2-alkoxy)Titanium-Benzyl ($[NHC\text{-}O]_2ZrBz_2$)

Bis(imidazolidene-N-methyl-N'-cycloexenyl-2-alkoxy)titanium-dibenzyl

*I*n an Schlenk ampoule, under an inert atmosphere, imidazolium salt (L2) (1g, 3 mmol, FW=308.04) was charged and next, THF (30 mL) at –78°C was added. With the same procedure we prepare a solution of potassium hexamethyldisilazide (0.65 g, 1 equiv., 3 mmol, FW=199.49) in 30 mL of THF, and then we added this solution to the other one to obtain the potassium alkoxide-carbenes. The mixture was allowed to slowly warm to room temperature and stirred for 24 h. After this time, the solution was added very slowly to a suspension of zirconium tetra-benzyl (0.68 g, 0.5 equiv., 1.5 mmol, FW=410.82) in 30 mL of THF at –78°C. The resulting mixture was allowed to slowly warm to room temperature and stirred for 24 h, then filtered through celite, and washed with hexane. The solvent was removed under reduced pressure to yield the Titanium complex $[NHC\text{-}O]_2TiBz_2$.
(0.16 g, FW= 560.26, 0.3 mmol, 10 % yield)
Elemental analysis: found (%):Calc. for $C_{32}H_{40}N_4O_2Ti$ (%): C 68.57, H 7.19, N 9.99, O 5.71, Zr 8.54.

^{1}H NMR (300 MHz, CD_3CN, 298 K): 7.38-7.21 (m, aromatic ring), 7.48 (s,1H, NC*H*CH), 4.05 (m, 1H, OC*H*), 3.63 (m, 1H, NC*H*), 3.88 (s, 3H, NCH_3), 2.11 (m, 2H, CH_2CH_2 CH_2), 1.83 (m, 2H, CH_2CH_2 CH_2), 1.31 (m, 2H, CH_2 CH_2CH_2).

^{13}C NMR (400 MHz, CD_3CN, 298K): 211.9 (N*C*N), 123.5 (N*C*HCH), 128.5 (aromatic ring), 67.7 (OCH), 24.7 (N*C*H), 36.1 (NCH_3), 31.6 ($CH_2CH_2CH_2$), 23.8 ($CH_2CH_2CH_2$), 19.5 (CH_2CH_2 CH_2).

Synthesis of complex (imidazolidene-N-methyl-N'-aryl-2-alkoxy)-Yttrium-dichloride [(NHC-O)YCl_2

In an Schlenk ampoule, under an inert atmosphere, imidazolium salt (4) (0.6 g, 2 mmol, FW=330.02) was charged and next, Toluene (10 mL) at room temperature was added. With the same procedure we prepare a solution of potassium hexamethyldisilazide (0.8 g, 2 equiv., 4 mmol, FW=199.49) in 25 mL of THF, and then we added this solution to the other one to obtain the potassium alkoxide-carbenes. The mixture was stirred for 1 h. After this time, the solution was added very slowly to a suspension of yttrium chloride (0.5 g, 1 equiv., 2 mmol, FW=195.26) in 10 mL of THF at room temperature. The resulting mixture was stirred for 3 h, then filtered through celite and washed with hexane. The solvent was removed under reduced pressure to yield the yttrium complex [NHC-O] YCl_2.

(0.2 g, FW= 359.94, 0.3 mmol, 27 % yield)

Elemental analysis: found (%):Calc. for $C_{12}H_{13}Cl_2N_2OY$ (%): C 39.92, H 3.63, Cl 19.64, N 7.76, O 4.43, Y 24.62.

^{1}H NMR (300 MHz, CD_3CN, 298 K): 7.89-7.76 (m, aromatic ring), 5.53 (s,1H, NC*H*CH), 4.58 (m, 1H, OC*H*), 4.37 (m, 1H, NC*H*), 3.86 (s, 3H, NCH_3).

^{13}C NMR (400 MHz, DMSO-d-, 298K): 197.8 (N*C*N), 139.4 (N*C*HCH), 140-124.2 (aromatic ring), 79.6 (OCH), 70.3 (N*C*H), 39.1 (NCH_3).

Synthesis of complex (imidazolidene-N-methyl-N'-cycloexenyl-2-alkoxy)Scandium dichloride ([NHC-O] $ScCl_2$)

In an Schlenk ampoule, under an inert atmosphere, imidazolium salt (2) (0.21 g, 0.7 mmol, FW=308.04) and Scandium chloride (0.1 g, 1 equiv, 0.7 mmol, FW=149.86)was charged and next, THF (30 mL) at room temperature was added. After the complete dissolution of the powder to this solution was added very slowly 1.43 mL of a solution of nBuLi in hexane (2.5 M) at room temperature. The resulting mixture was stirred for an half of an hour, and then filtered through celite and washed with toluene. The solvent was removed under reduced pressure to yield a powder that was allowed to crystalize in THF. After 24 fall down a pale yellow powder, the scandium complex [NHC-O] $ScCl_2$.
(0.05 g, FW= 294.01, 0.018 mmol, 24 % yield)
Elemental analysis: found (%):Calc. for $C_{10}H_{15}Cl_2N_2OSc$ (%): C 40.70, H 5.12, Cl 24.03, N 9.49, O 5.42, Sc 15.23.

^{1}H NMR (300 MHz, DMSO-d-, 298 K): 7.00-6.62 (2H, NC*H*CH), 3.59 (m, 1H, OC*H*), 3.37 (m, 1H, NC*H*), 3.39 (s, 3H, NCH_3), 1.75 (m, 2H, CH_2CH_2 CH_2), 1.57 (m, 2H, CH_2CH_2 CH_2), 0.88 (m, 2H, CH_2 CH_2CH_2).

Synthesis of salt Imidazolium-N-t-Buthyl-N'-cycloepentenyl-2-hydroxy-iodide:

An high pressure ampoule was charged with 14 mmol of cyclopentene oxide (1.8 mL, FW=84.12 , d=0.971) and 1 equiv. of imidazole (1g, FW=68.08, 14 mmol). The resulting mixture was stirred at 60°C for 24h. Acetonitrile (8mL) and 2-Iodo-2-methyl propane (1 equiv, 1.7 mL, FW=184.02, d=1.54)) were added and the mixture remained stirring at 80°C for 5h. The solvent was then concentrated to yield the product as a pale yellow oil, and the product precipitated as a white solid from acetone.
(1.2, FW= 336.06 g/mol, 3.8 mmol, yield 27 %)
Elemental analysis: Calc. for $C_{12}H_{21}IN_2O$ (%): C 42.87, H 6.30, I 37.73, N 8.33, O 4.76.

^{1}H NMR (300 MHz, $CDCl_3$, 298 K): 8.68 (s, 1H, NC*H*N), 7.25 (s,1H, NC*H*CH), 4.56 (m, 1H, OC*H*), 4.42 (m, 1H, NC*H*), 2.37 (m, 2H, $OCHCH_2$), 1.96 (m, 2H, $NCHCH_2$), 2.03 (s, 9H, $C(CH_3)_3$), 1.94 (m, 2H, $CH_2CH_2CH_2$), 1.75 (m, 2H, $CH_2CH_2CH_2$).

Synthesis of salt Imidazolium-N-ethyl acetate-N'-cyclohexenyl-2-hydroxy-bromide:

An high pressure ampoule was charged with 7.3 mmol of cyclohesene oxide (0.7 ml, FW=98.15, d=0.971) and 1 equiv. of imidazole (500 mg, 7.3 mmol, FW=68.08).

The resulting mixture was stirred at 50°C for 18h. Acetonitrile (8 mL) and Ethyl bromoacetate (1 equiv, 0.8 ml, FW=167.00, d=1.50) were added and the mixture remained stirring at 80°C for another 5 h. The solvent was then concentrated to yield the product as a yellow oil, and the prodouct recrystallised as a pale yellow solid from acetone.

(460 mg, FW=308.04, 27 mmol, 47% yield)

Elemental analysis: Calc. for $C_{14}H_{21}BrN_2O_3$ (%): C 48.42, H 6.68, Br 23.01, N 8.07, O 13.82.

^{1}H NMR (300 MHz, CD_3CN, 298 K): 7.78 (s, 1H, NC*H*N), 7.08 (s,1H, NC*H*CH), 7.01 (s, 1H, NCHC*H*), 4.01 (m, 1H, OC*H*), 3.82 (m, 1H, NC*H*), 3.78 (d, 1H, NC*H*$(CH_3)_2$), 1.43 (m, 6H, NC*H*$(CH_3)_2$), 2.14 (m, 2H, CH_2CH_3), 1.29 (m, 3H, CH_2CH_3), 1.86 (m, 2H, $CH_2CH_2CH_2$), 1.69 (m, 2H, $CH_2CH_2CH_2$), 1.41 (m, 2H, $CH_2CH_2CH_2$).

Synthesis of salt Imidazolium-N-valerate-N'-cyclohexenyl-2-hydroxy-bromide:

An high pressure ampoule was charged with 3 mmol of cyclohexene oxide (0.3 ml, FW=98.15, d=0.971) and 1 equiv. of imidazole (200 mg, 3 mmol, FW=68.08).
The resulting mixture was stirred at 50°C for 18h. Acetonitrile (6 mL) and Methyl- 5-iodovalerate (1 equiv, 0.72 g, FW=242.58) were added and the mixture remained stirring at 80°C for another 24 h. The solvent was then concentrated to yield the product as a yellow oil, and the prodouct recrystallised as a pale yellow solid from acetone.
(9 mg, FW=360.10, 0.02 mmol, 7 % yield)
Elemental analysis: Calc. for $C_{15}H_{25}BrN_2O_3$ (%): C 49.87, H 6.97, Br 22.12, N 7.75, O 13.29.

^{1}H NMR (300 MHz, $CDCl_3$, 298 K): 9.17 (s, 1H, NC*H*N), 7.68 (s,1H, NC*H*CH), 7.32 (s, 1H, NCHC*H*), 4.34 (m, 1H, OC*H*), 3.39 (m, 1H, NC*H*), 3.66 (m, 2H, NCH_2), 2.33 (m, 2H, CH_2C-O), 2.16 (m, 2H, NC$H_2CH_2CH_2$), 2.04 (s, 3H, OCH_3), 1.71 (m, 3H, NC$H_2CH_2CH_2$), 1.68 (m, 2H, $CH_2CH_2CH_2$), 1.42 (m, 2H, $CH_2CH_2CH_2$), 1.38 (m, 2H, $CH_2CH_2CH_2$).

Synthesis of salt Imidazolium (Imidazolium-N-methyl-N'-cyclohexenyl-2-hydroxy-tetrafluoroborate:

An high pressure ampoule was charged with 0.65 mmol of salt L 18 (0.2 g, FW = 308.04, 27) and 5 mL of CH_3CN. After the complete dissolution of the salt we added 68 mg of ammonium tetrafluoroborate and the resulting mixture was stirred at room temperature for 16 h. The solvent was then concentrated and $CHCl_3$ (~ 60 mL anidryficate on basic alumina) was added. Then we filtred and concentrated the solution to yeald the product as a white powder.

(141 mg, FW=268.13, 0.5 mmol, 81 % yield)

Elemental analysis: Calc. for $C_{10}H_{17}BF_4N_2O$ (%): C 44.81, H 6.39, B 4.03, F 28.35, N 10.45, O 5.97.

^{1}H NMR (300 MHz, $CDCl_3$, 298 K): 9.47 (s, 1H, NC*H*N), 7.38 (s,1H, NC*H*CH), 7.34 (s, 1H, NCHC*H*), 4.24 (m, 1H, OC*H*), 3.81(m, 1H, NC*H*), 4.03 (s, 3H, NCH_3), 2.12 (m, 2H, OCHCH_2), 1.94 (m, 2H, NCHCH_2), 1.39 (m, 2H, $CH_2CH_2CH_2$), 1.20 (m, 2H, $CH_2CH_2CH_2$).

^{13}C NMR (400 MHz, $CDCl_3$, 298K): 135.4 (N*C*HN), 123.5 (N*C*HCH), 120.9 (N*C*HCH), 71.5 (OCH), 65.3 (N*C*H), 37.5 (NCH_3), 36.3 (OCHCH), 34.1 (OCHCH_2), 30.8 ($CH_2CH_2CH_2$), 24.2 ($CH_2CH_2CH_2$).

RIFERIMENTI

1. P. Pino, R. Mu¨ lhaupt, *Angew. Chem., Int. Ed. Engl.* **1980**, *19*,857-875
2. G. Natta, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Mazzanti, G. Moraglio, *J. Am. Chem. Soc.* **1955**, *77*, 1708-1710
3. (a) P. Cossee, *J. Catal*. **1964,** 3, 80.(b) E.J. Arlman, P. Cossee, *J. Catal.* **1964 ,** 3, 99
4. (a) G. Hlatky, *Chem. Rev.* **2000**, *100*, 4, 1167–1168. (b) T. J. Marks, *Chem. Rev.* **2000**, *100*, 4, 1391–1434
5. (a) X. Yang, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1991**, *113*, 3623-3625. (b) Y. X. Chen, C. L. Stern, S. T. Yang, T. J. Marks, *J. Am. Chem.Soc.* **1996**, *118*, 12451-12452. (c) Y. X. Chen, M. V. Metz, L. T. Li, C. L. Stern, T. J. Marks, *J.Am. Chem. Soc.* **1998**, *120*, 6287-6305. (d) L. T. Li, T. J. Marks, *Organometallics* **1998**, *17*, 3996-4003. (e) L. Luo, T. J. Marks, *Top. Catal.* **1999**, *7*, 97-106.
6. (a) R. F. Jordan, W. E. Dasher, S. F. Echols, *J. Am. Chem. Soc.* **1986**, *108*, 1718-1719. (b) M. Bochmann, L. M. Wilson, *J. Chem. Soc., Chem. Commun.* **1986**, 1610-1611. (c) R. Taube, L. Krukowka, *J. Organomet. Chem.* **1988**, *347*, C9- C11. (d) H. W. Turner, *Chem. Abstr.* **1989**, *110*, 58290. (e) Precise Control of Polyolefin Stereochemistry Chemical Reviews, **2000**, 100, 4, 1247. (f) J. C. W. Chien, W. M. Tsai, M. D. Rausch, *J. Am. Chem. Soc.* **1991**, *113*, 8570-8571. (g) J. A. Ewen, M. J. Elder, *Chem. Abstr*. **1992**, *115*, 136988.
7. Y. X. Chen, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1997**, *119*, 2582-2583.
8. (a) A. D. Jenkins, *Pure Appl. Chem.* **1981**, *53*, 733. (b) P. Muller, *Pure Appl. Chem.* **1994**, 66, 1077.
9. L. Resconi, L. Cavallo, A. Fait, F.Piemontesi *Chem. Rev.* **2000,** 100, 1253-1345
10.
11. J. A. Ewen, *J. Am. Chem. Soc.* **1984**, 106, 6355.
12. J. A. Ewen, R. L. Jones, A. Razavi, J. Ferrara, *J. Am. Chem.Soc.* **1988**, 110, 6255.
13. J.A. Ewen, M. J. Elder, R. L. Jones, S. Curtis, H. N. Cheng, Catalytic Olefin Polymerization, Studies *in Surface Scienceand Catalysis*; Keii, **1990**, 439
14. R. A. Shelden, T. Fueno, T. Tsunetsugu, J. Furukawa, *J.Polym. Sci., Polym. Lett. Ed.* **1965**, *3*, 23.

15. (a). J. Cardin, M. F. Lappert, C. L. Raston, *Chemistry of Organo-Zirconium and - Hafnium Compounds* Wiley: New York, 1986. (b) R. L. Halterman, *Chem. Rev.* **1992**, 92, 965. (c) R. L. Halterman, *Metallocenes: synthesis reactivity applications*, **1998**, 455.
16. S.D. Ittel, L.K. Johnson, M. Brookhardt, *Chem Rev*, **2000,** 100, 1169.
17. G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew Chem Int Ed, **1999,** 38, 428.
18. M. Bochmann, S.J. Lancaster Organometallics **1993,** 12, 663.
19. S. W. Ewart, M. J. Sarsfield, D. Jeremic, T. L. Tremblay, E. F. Williams, M. C. Baird, *Organometallics*, **1998,** 17, 1502.
20. C. Pellecchia, A. Immirzi, A. Grassi, A. Zambelli, Organometallics, **1993,** 12, 4473.
21. R. R. Shrock, R. Baumann, S. M. Reid, J. T. Goodman, R. Stumpf, W. M. Davis, Organometallics, **1999,** 18, 3649.
22. H. Mack, M. S. Eisen, *J Chem Soc Dalton Trans*, **1998,** 917
23. E. E. Gielens, J. Y. Tiesnitsch, B. Hessen, J. H. Teuben, *Organometallics* **1998,** 17, 1652.
24. Y. X. Chen, P. F. Fu, C. L. Stern, T. J. Marks, *Organometallics*, **1997,** 16, 5958.
25. R. Kempe, *Angew Chem Int Ed*, **2000,** 39, 468.
26. J. T. Goodman, R. R. Schrock, Organometallics, **2001,** 20, 5205.
27. R. R. Schrock, P. J. Bonitatebus, Y. Schrodi, *Organometallics*, **2001,** 20, 1056.
28. P. E. O'Connor, D. J. Morrison, S. Steeves, K. Burrage, D. J. Berg, *Organometallics*, **2001,** 20, 1153.
29. Y. Yoshida, S. Matsui, Y. Takagi, M. Mitani, T. Nakano, H. Tanaka, N. Kasiwa, T. Fujita, *Organometallics*, **2001,** 20, 4793.
30. (a) G. M. Benedikt, B. L. Goodall, *Metallocene-Catalyzed Polymers: Materials, Properties, Processing and Markets*; Eds.; Plastics Design Library: New York, **1998**. (b) V. C. Gibson, S. K. Spitzmesser, *Chem. Rev*. **2003**, 103, 283
31. . F. R. Wild, L. Zsolnai, G. Huttner, H. H. Brintzinger, *J. Organomet. Chem.* **1982**, 232, 233-247.
32. J. A. Ewen, *J. Am. Chem. Soc.* **1984**, *106*, 6355-6364.
33. T. Fujita, Y. Tohi, M. Mitani, S. Matsui, J. Saito, M. Nitabaru, K. Sugi, H. Makio,and T. Tsutsui, Eur. Patent 0874005, **1998**.

34. (a) Matsui, S.; Tohi, Y.; Mitani, M.; Saito, J.; Makio, H.; Tanaka, H.; Nitabaru, M.; Nakano, T.; Fujita, T. *Chem. Lett.* **1999,** 1065. (b) Matsui, S.; Mitani, M.; Saito, J.; Tohi, Y.; Makio, H.; Tanaka, H.; Fujita, T. *Chem. Lett.* **1999**, 1263. Y.Nakayama, H. Bando, Y. Sonobe, T. Fujita, *Journal Of Molecular Catalysis A*, **2004,** 213, 141;

35. (a) M. Aizenberg, L. Turculet, W. M. Davis, F. Schattenmann, R. R. Schrock, *Organometallics* **1998**, *17*, 4795; (b) R. R. Schrock, F. Schattenmann, M. Aizenberg, W. M. Davis, *Chem. Commun*. **1998**, 199; (c) J. D. Scollard, D. H. McConville, *J. Am. Chem. Soc*. **1996**, *118*, 10008.

36. (a) J. C Flores, J. C. W. Chien, M. D. Rausch, *Organometallics* **1995**, *14*, 1827; (b) A. Littke, N. Sleiman, C. Bensimon, D. S. Richeson, G. P. A. Yap, S. J. Brown, *Organometallics* **1998**, *17*, 446; (c) D. Herskovics-Korine, M. S. Eisen, *J. Organomet. Chem*. **1995**, *503*, 307.

37. (a) E. B. Tjaden, D. C. Swenson, R. F. Jordan, *Organometallics* **1995**, *14*, 371; (b) L. Lee, D. J. Berg, J. W. Bushnell, *Organometallics* **1997**, *16*, 2556; (c) L. Lee, D. J. Berg, F. W. Einstein, R. J. Batchelor, *Organometallics* **1997**, *16*, 1819.

38. (a) T. Tsukahara, D. C. Swenson, R. F. Jordan, *Organometallics* **1997**, *16*, 3303; (b) X. Bei, D. C. Swenson, R. F. Jordan, *Organometallics* **1997**, *16*, 3282; (c) I. Kim, Y. Nishihara, R. D. Rogers, A. L. Rheingold, G. P. A. Yap, R. F. Jordan, *Organometallics* **1997**, *16*, 3314.

39. (a) D. C. Bradley, R. M. Mehrotra, I. P. Rothwell, A. Singh, *Alkoxo and Aryloxo Deri*V*ati*V*es of Metals*; Academic Press: London, **2001**. (b) R. M. Mehrotra, A. Singh, *Prog. Inorg. Chem.* **1997**, *46*, 239. (c) L. G. Hubert- Pfalzgraf, *Coord. Chem. Re*v. **1998**, 967, *178-180*. (d) W. E. Piers, D. J. Emslie, *Coord. Chem. Re*v. **2002**, *131*, 233–234. (e) F. T. Edelmann, D. M. Freckmann, H. Schumann, *Chem. Re*v. **2002**, *102*, 1851.

40. (a) S. T.Liddle, I. S. Edworthy, P. L. Arnold, *Chem. Soc. Rev*., **2007**, 36, 1732–1744. (b) W. A. Herrmann, *Angew. Chem.*, **2002**, 114, 1342. (c) W. A. Herrmann, T. Weskamp, V. P. Bo¨hm, *Adv. Organomet. Chem.*, **2001**, 48, 1. (d) W. A. Herrmann, *Angew. Chem., Int. Ed*., **2002**, 41, 1290. (e) P. L. Arnold, *Heteroat. Chem*., **2002**, 13, 534. (f) O. Ku¨ hl,; *Chem. Soc. Rev.*, **2007**, 36, 592. (g) S. T.

Liddle, P. L. Arnold, *Chem. Commun*., **2006**, 3959. (h) P. L. Arnold, M. Rodden, K. Davis, A. C. Scarisbrick, A. J. Blake, C. Wilson, *Chem. Commun*., **2004**, 1612.

41. S. T. Liddle, I. S. Edworthy, P.L. Arnold, *Chem. Soc. Rev*., **2007**, 36, 1732–1744
42. (a) W. A. Herrmann, K. O¨ fele, D. V. Preysing and S. K. Schneider, *J. Organomet. Chem.*, **2003**, 687, 229. (b) K. J. Cavell, D. S. McGuinness, *Coord. Chem. Rev.*, **2004**, 248,671. (c) C. M. Crudden, D. P. Allen, *Coord. Chem. Rev*., **2004**, 248,2247. (d) W. A. Herrmann, C. Ko¨ cher, *Angew. Chem., Int. Ed. Engl*.,**1997**, 36, 2162. (e) W. A. Herrmann, T. Weskamp V. P. W. Bo¨hm, *Adv.Organomet. Chem.*, **2001**, 48, 1. (f) W. A. Herrmann, Angew. *Chem., Int. Ed*., **2002,** 41, 1290. (h) P. L. Arnold, *Heteroat. Chem*., **2002**, 13, 534.
43. W. A. Herrmann, *Angew. Chem.*, **2002**, 114, 1342.
44. O. Ku¨hl, *Chem. Soc. Rev*., **2007**, 36, 592–607
45. M. Frøseth, K. A. Netland, K. W. To¨rnroos, A. Dhindsa, M. Tilset, *Dalton Trans.*, **2005,** 1664 and references therein.
46. C. W. Bielawski, R. H. Grubbs, *Angew. Chem., Int. Ed.* **2000**, *39*, 2903.
47. (a) T.Weskamp, W. C. Schattenmann, M. Spiegler, W. A. Herrmann, *Angew. Chem., Int. Ed.* **1998**, *37*, 2490. (b) L.Ackermann, A. Fürstner, T. Weskamp, F. J. Kohl, W. A. Herrmann, *Tetrahedron Lett.* **1999**, *40*, 4787. (d) J. Haung, H-J. Schanz, E. D. Stevens, S. P. Nolan, *Organometallics* **1999**, *18*, 5375.
48. (a) A. Döhring, J. Göhre, P. W. Jolly, B. Kryger, J. Rust, G. P. Verhovnik, *Organometallics* **2000**, *19*, 388. (b) K.-J. Jens, M. Tilset, H. Voges, R. Blom, M. Froseth, WO 0001739, (*Borealis*), **2000.** (c) M. Tilset, O. Andell, A. Dhindsa M., Froseth, WO 0249758, (*Borealis*), **2002**. (d) M. Niehues, G. Kehr, G. Erker, B. Wibbeling, R. Fröhlich, O. Blacque, H. Berke, *J. Organomet. Chem.* **2002**, *663*, 192.
49. L.P. Spencer, M.D. Fryzuk, J.Organomet.Chem. 690,2005, 5788–5803
50. D. S. McGuinness, N. Saendig, B. F. Yates, K. J. Cavell, J. Am. Chem. Soc. 2001, 123, 4029.
51. K. J. Cavell, D. S. McGuinness, Coord. Chem. Rev. 2004, 248, 671
52. (a) W. A. Herrmann, T. Weskamp, V. P. Bo¨hm, Adv. Organomet. Chem., 2001, 48, 1. (b) W. A. Herrmann, *Angew. Chem., Int. Ed*., **2002**, 41, 1290. (c) P. L.

Arnold, *Heteroat. Chem.*, **2002**, 13, 534. (d) O. Ku¨ hl,; *Chem. Soc. Rev.*, **2007**, 36, 592.

53. H. Aihara, T. Matsuo, H. Kawaguchi, *Chem. Commun.*,, 2003, 2204–2205
54. (a) C.H. Lee, Y.-H. La, J.W. Park, *Organometallics*, **2000,** 19, 344. (b) R.R. Schrock, A.L. Casado, J.T. Goodman, L.-C. Liang, P.J. Bonitatebus, W.M. Davis, *Organometallics,* **2000**, 19, 5325; (d) S. Daniele, P.B. Hitchcock, M.F. Lappert, P.G. Merle, *J. Chem. Soc., Dalton Trans.*, **2001,** 13. (e) J.D. Scollard, D. McConville, N.C. Payne, J.J. Vittal, *Macromolecules,* **1996,** 29, 5241.
55. (a) B. Wang, D. Cui, K. Lv, *Macromolecules* **2008**, *41*, 1983-1988 (b) X. Wang, S. Liu, G. Jin, *Organometallics* **2004**, *23*, 6002-6007. (b) D. McGuiness, V. Gibson, J. Steed, *Organometallics* **2004**, *23*, 6288-6292. (c) J. Ca´mpora, O. de la Tabla, P. Palma, E. AÄ lvarez, F. Lahoz, K. Mereiter, *Organometallics.* **2006**, *25*, 3314-3316.