

Synthesis and Chemistry of Fluorinated α - Iminocarboxamide Nickel and Zirconium Catalysts

تحضير ودراسة خصائص محفزات الفلوروايمينوكربوكس

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ABSTRACT: Synthesis and investigations of Nickel-based olefin oligomerization and polymerization catalysts, fluorinated α -Iminocarboxamide μ 3-Penzyl(II) Ni Complexes is reported. The synthesis of the above mentioned catalysts by the direct reaction of the potassium salt of the ligand, Ni(COD)₂(bis(1,5-cyclooctadiene)-nickel, and Benzyl halide in THF and starting temperature of -35°C led to the formation of the two isomers: The [N-O] and the [N-N]. Moreover, the complexes di α - fluorinated Iminocarboxamide Zr-dimmed has been synthesized, investigated and tested for ethylene polymerization.

Keywords: Inorganic Chemistry; Organometallic Chemistry; Catalysts; Polymerizations; Isomers.

المستخلص: تم في هذا البحث دراسة وتحضير مركبات النيكل من النوع fluorinated α -Iminocarboxamide μ 3-Penzyl(II) Ni Complexes وهي مركبات محفزة لعملية بلمرة الإيثيلين. وتم تحضير هذه المركبات عن طريق التفاعل المباشر بين ملح البوتاسيوم للجاند والسيكلوبنتاديين النيكل مع البنزيل هاليد في محلول من الـ THF عند درجة حرارة -35 درجة مئوية، وبهذه الطريقة تم الحصول على متماكب من نوع [N-O] وآخر من نوع [N-N]. وكذلك تم تحضير مركبات الزركونيوم من النوع di α - fluorinated Iminocarboxamide Zr-dimmed والتي أبدت جدواها في عملية بلمرة الإيثيلين.

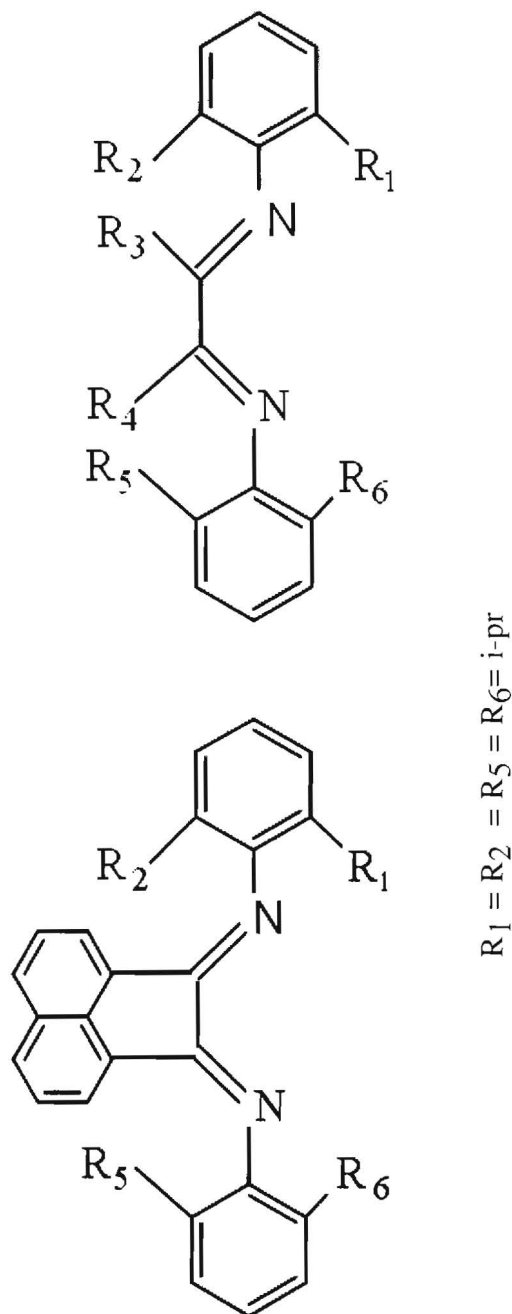
كلمات مدخلية: كيمياء غير عضوية، كيمياء عضو معدنية، محفزات، بلمرة، متماكبات.

INTRODUCTION

In the last two decades, there has been immense interest in the developments of a new types of catalysis, other than Ziegler-Natta type of catalysts, for ethylene polymerization (Park, *et al.* 2005; Branquinho, *et al.* 2005; Park, *et al.* 2004; Braunstein, 2004; Mecking, 2000; Peuckert and Keim, 1983). This interest was generated by the discovery of the so-called Shill Higher Olefin Process (SHOP) catalysts which contain a bidentate ligand [P-O], and the complexes of di α - imine with a transition metal such as Ni and Pd which contain the bidentate ligand [N-N] (Schmidt, *et al.* 2004; Helldorfer, *et al.* 2003a; Helldorfer, *et al.* 2003b).

These type of ligands impart a very desirable property on the catalysts. That is, great heteroatoms tolerance which allows co-polymerization of olefins with other functionalized olefins such as acrylate, vinylactate, and pyrimidone, whereas early transition metal complexes tend to polymerize non-polar olefins.

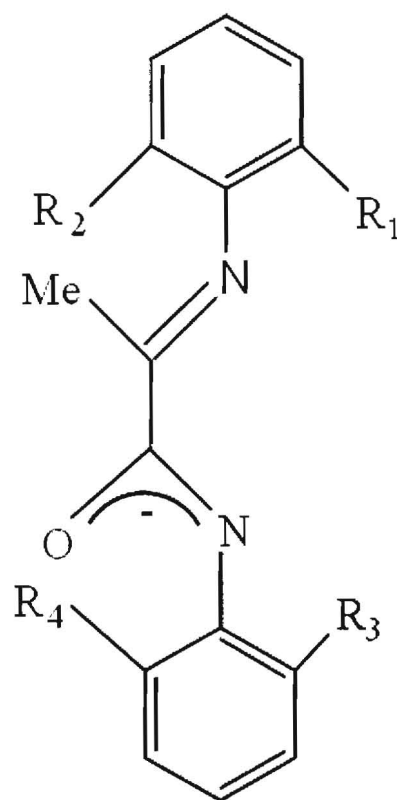
There is a plethora of these types of bidentate ligand as shown in Figure 1, which indicates the research groups in the United State and Europe that are responsible for the major developments of these types of ligands and their corresponding catalytic activities towards ethylene polymerizations (Small, *et al.* 1998; Killian, *et al.* 1996; Johnson, *et al.* 1995).



R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	Group
i-pr	i-pr	H	H	i-pr	i-pr	Killian, <i>et al.</i> 1996
i-pr	i-pr	Me	Me	i-pr	i-pr	
Me ₂	Me ₂	H	H	Me ₂	Me ₂	
Me ₂	Me ₂	Me	Me	Me ₂	Me ₂	
H	X	Me	Et	H	X	Schmidt, <i>et al.</i> 20043
H	X	Et	Et	H	X	

Fig. 1. Examples of some Diimine ligands.

α -Iminocarboxamide ligands are unique in a way that enable the additions of $B(C_6F_5)_3$. Carbonyl coordination to the borane removes electron density from nickel. This "activation" by action of a Lewis acid on a site removed from the monomer is catalytically very attractive. For instant, it eliminates the use of MAO as a co-catalyst. Bazan Group are extensively studying these type of ligand, shown in Figure 2, and synthesizing their formations of the correspondents α -Iminocarboxamide μ_3 -Penzyl(II) Ni complexes, then testing these later compounds activities towards ethylene polymerization (Zachary, *et al.* 2003; Diamanti, *et al.* 2003; Young, *et al.* 2002; Zachary, *et al.* 2002; Lee, *et al.* 2001; Zachary, *et al.* 2000)



Lignad	R1	R2	R4	R3
1	i-pr	i-pr	i-pr	i-pr
2	H	H	i-pr	i-pr
3	i-pr	i-pr	H	H
4	Me	Me	Me	Me
5	Me	i-pr	Me	i-pr
6	Et	Et	Et	Et

Fig. 2. Iminocarboxamide ligand used by Bazan Group.

As mentioned above, several research groups such as Alt, Brookhart, Bazan, Alnajjar (Alnajjar, *et al.* 2004) and other groups (Batten, *et al.* 2006; Sun, *et al.* 2004) have widely recognized that changing the electronic environment and the steric hindrance around the single sites catalyst would lead to a different type polyethylene which is an industrial requirement. This observation and previous work by the author contributed to Bazan Group, which concentrated on the direct synthesis of the α -Iminocarboxamide μ 3-Penzyl(II) Ni complexes using the least sterically hindered ligand **3** (see figure 2), has prompted the synthesizing the fluorinated analog of ligand **3**.

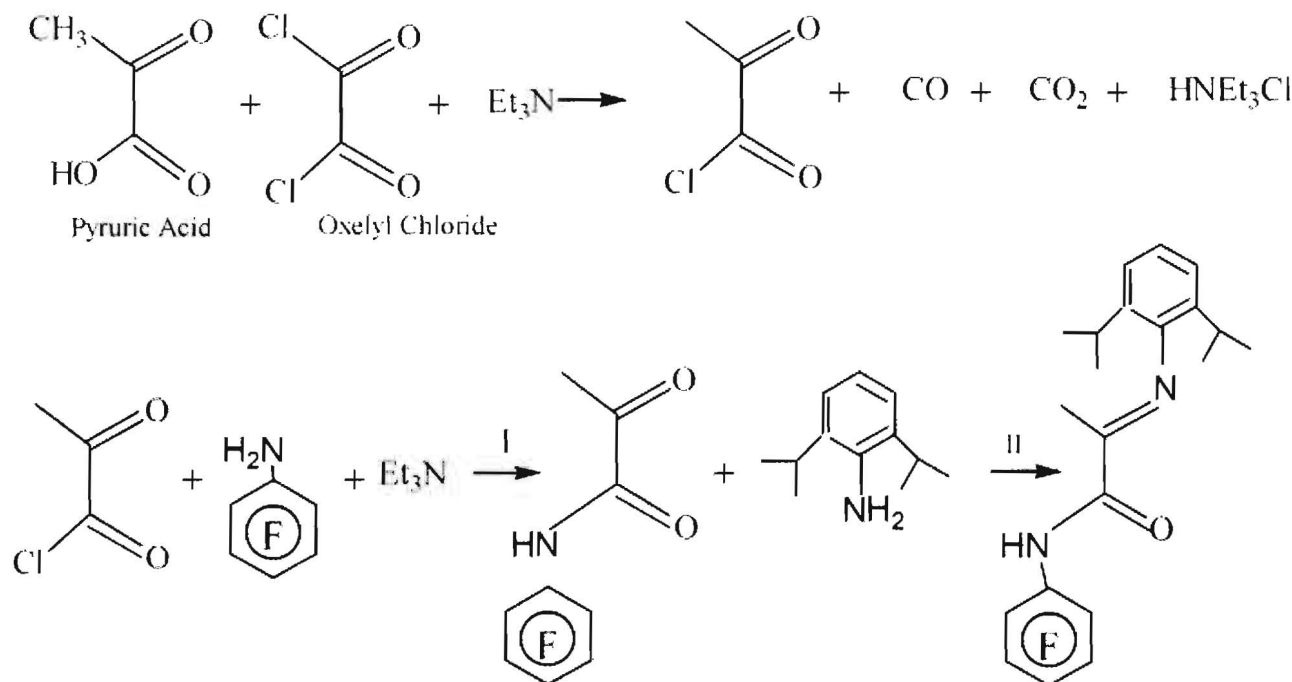
EXPERIMENTAL AND PROCEDURES

All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk techniques. All reagents were used as received from Aldrich unless otherwise specified. Solvents like toluene, THF, hexane, and pentane were distilled from benzophenone ketyl. Purification of the catalysts were made by re-crystallization by slow diffusion of Pentane at -35°C . NMR spectra were obtained using a Varian Unity 400 spectrometer.

Typical Schiff-base condensation of primary fluorinated arylamines with *N*-aryl pyruvamides by reacting oxalyl chloride and pyruvic acid in benzene at room temperature in the presence of triethylamine generating pyruvic acid chloride. Then one equivalent of the fluorinated aniline is added, also, in the presence of an equivalent triethylamine causing a reaction at acid chloride site. Adding one equivalent of 2,4-diisopropyl aniline yielded the fluorinated α -iminocarboxamides (Scheme 1). The ligand was purified by chromatography and characterized by ^1H NMR as shown in Figure 3 (Rojas, *et al.* 2006).

Synthesis of fluorinated α -Iminocarboxamide μ 3-Penzyl(II) Ni Complex.

Potassium salt of the fluorinated α -Iminocarboxamide was prepared by deprotonation of the ligand with 1.0 equivalent KH and stirred overnight in THF to give the yellow crystalline product after evaporating the solvent and washing with pentane (77% yield). The above product is followed by reaction with $\text{Ni}(\text{COD})_2$ and benzyl chloride in THF at starting temperature of -35°C . Minimizing light exposure gave products **7** and **8**, which is apparent from the ^1H NMR spectrum (Figure 4).



Scheme 1. Procedure for the synthesis of fluorinated α -iminocarboxamides. I) Benzene, 25°C and 2h; II) Toluene, 110°C , p-toluenesulfonic acid, 24h.

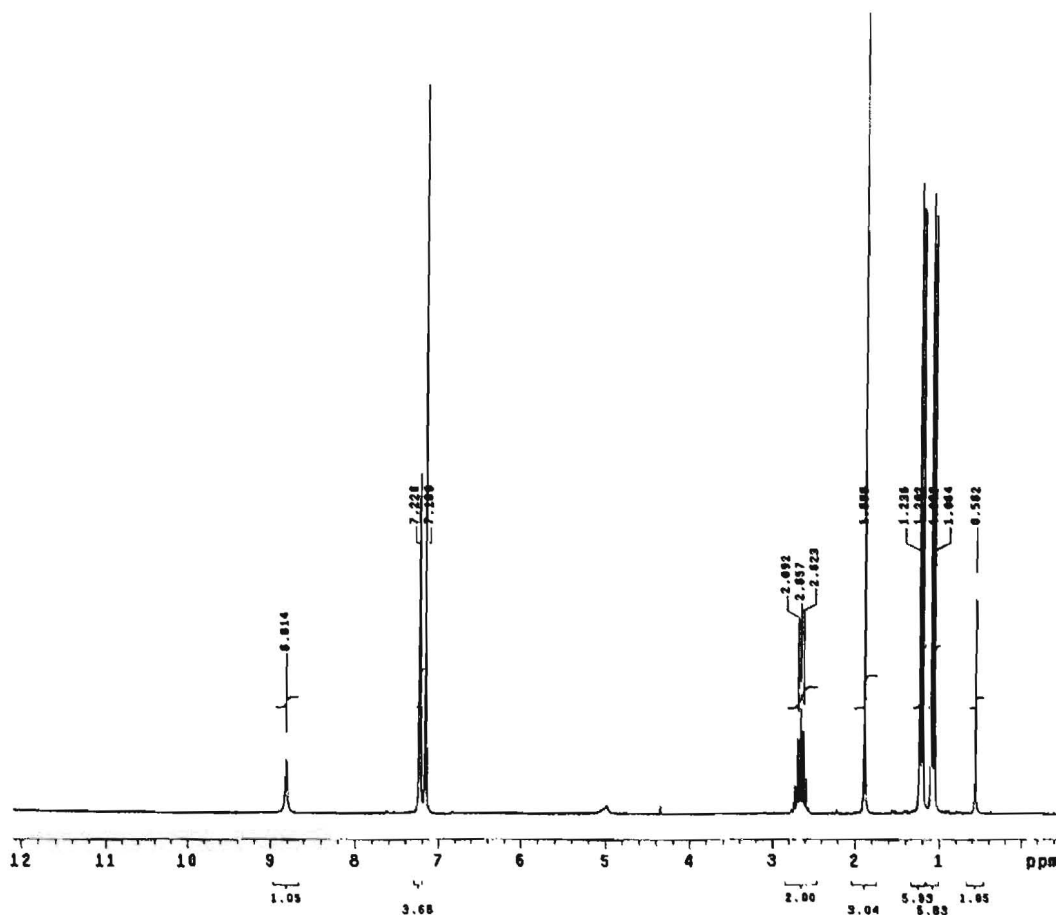


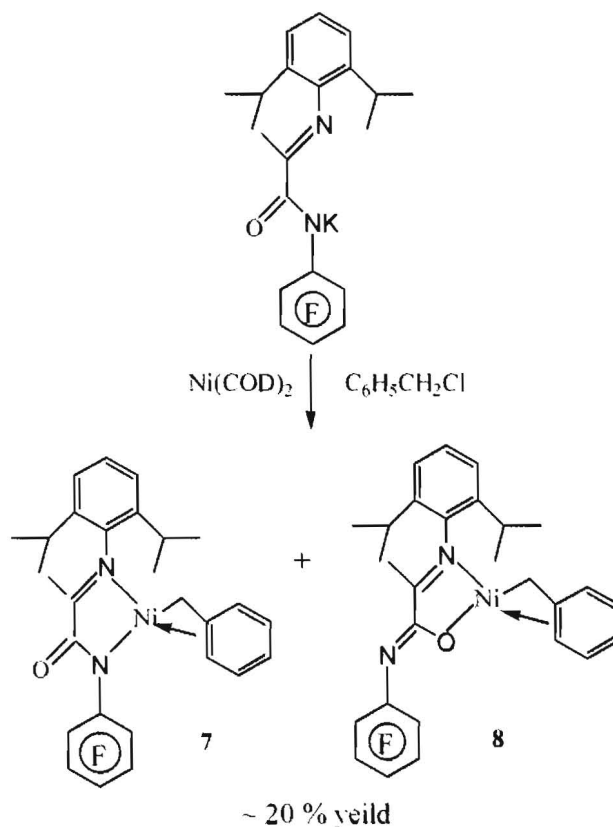
Fig. 2. ^1H NMR, in C_6D_6 , spectrum of the fluorinated α -iminocarboxamides.

Synthesis of the fluorinated (α -iminocarboxamides) $_2$ Zr complex.

A 0.46 g (10 mmol, 2 equivalents) of the potassium salt of the fluorinated ligand was placed in 50 mL vial with 26 mL THF. A 0.46 g (5 mmol) of ZrCl_4 was added to the mixture and the reaction mixture was stirred for four hours. Then, the resultant yellow solution was filtered through a fritted glass, the solvent was pulled off and the yellow solid was purified by washing with pentane, and re-crystallization from toluene gave products **9** and **10**, which is apparent from the ^1H NMR spectrum (Figure 5).

RESULTS AND DISCUSSION

The reaction of potassium salt of the fluorinated ligand with $\text{Ni}(\text{COD})_2$ and benzyl chloride to form the α -Iminocarboxamide μ -3-Benzyl(II) Ni complex (Scheme 2; Alsaygh, 2008). ^1H NMR spectra confirmed that there are definitely two separable isomers: The [N-O] and the [N-N], which are apparent from the two characteristic doublets: δ 5.82 and 6.010 (Figure 4).



Scheme 2. The formation of the two isomers of the fluorinated α -Iminocarboxamide μ -3-benzyl(II) Ni complexes.

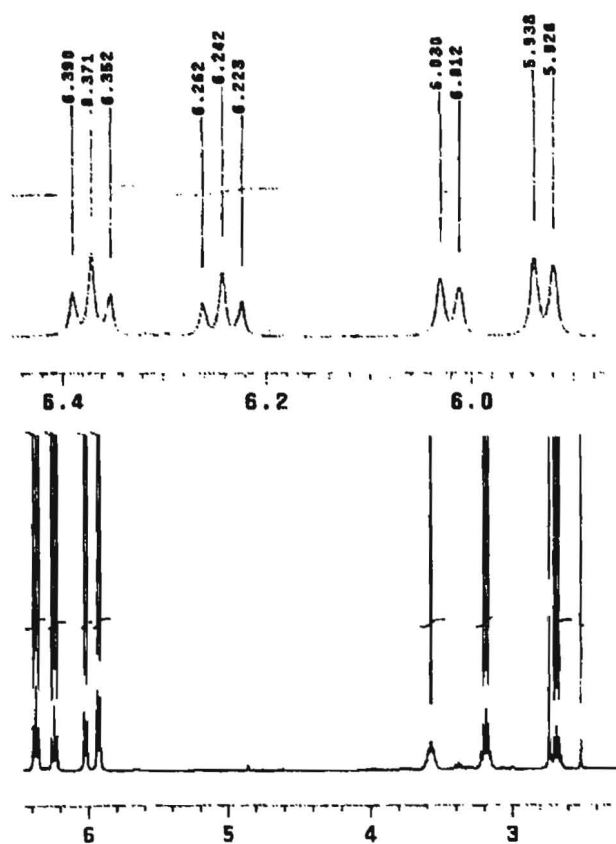


Fig. 4. ^1H NMR, in C_6D_6 , of the μ_3 region of the two isomers of the reaction of scheme 2.

Moreover, the reaction of two equivalents of the fluorinated Potassium salt of the ligand with

Zirconium tetrachloride (as shown in scheme 3), gave two isomers: the equatorial and the axial isomers: complex **9** and **10**, respectively, characterized by ^1H NMR, as shown in Figure 5. The two isomers could be confirmed by noticing that there are two sets of a multiplets (that correspond to two singlets (for the two methyl) and eight doublets for the two sets of isopropyl group (four for each isomer)).

CONCLUDING REMARKS

As reported previously (Alsaygh, 2008), that synthesizing the μ_3 - complexes with the less steric hindered Iminocarboxyamide by the direct method was unsuccessful. Whereas in the fluorinated form, the yield of the α -Iminocarboxyamide μ_3 -Penzyl(II) Ni complexes increased, which open up an opportunity for further research in this area.

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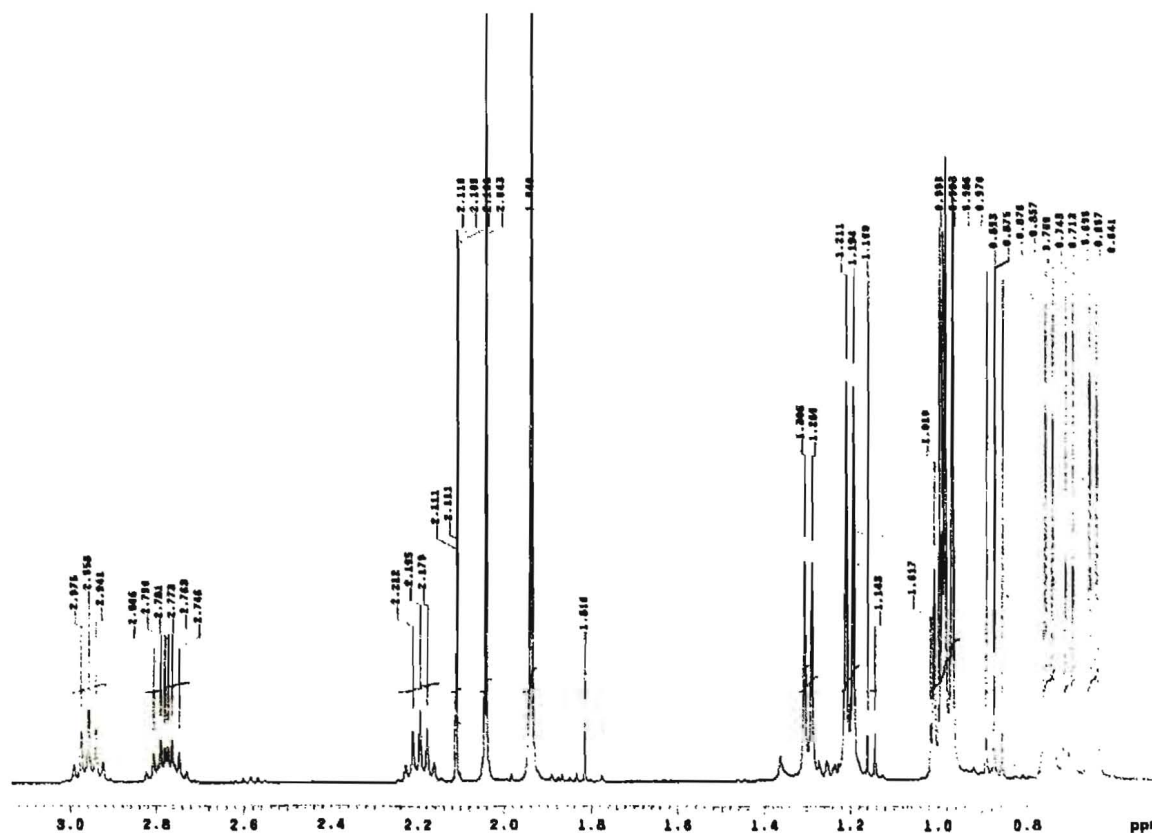
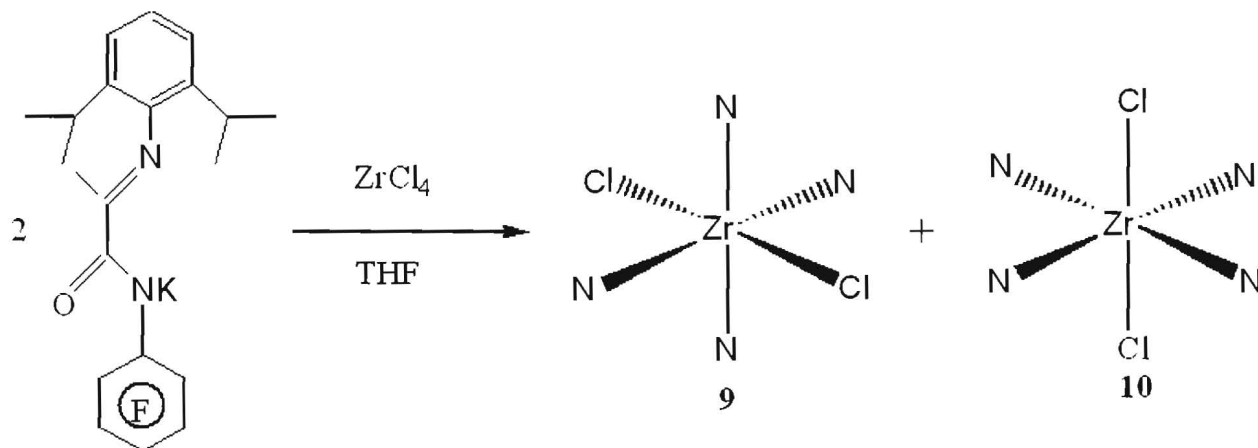


Fig. 5. ^1H NMR, in C_6D_6 , of the aliphatic region of the two isomers of the reaction of Scheme 3.



Scheme 3. The formation of the two isomers of the fluorinated α -iminocarboxamide Zirconium dimmers (only the hetero-atoms are shown for clarity).

REFERENCES

- Alnajjar, I, Alsaygh, A, Bahattab, M, and Almusawi, M** (2004) The Role of Bulky Substituents in the Polymerization of Ethylene using Late Transition Metal Catalysts. In: *Proceedings of the Symposium and Exhibition on Catalysts Applications in the GCC*. Sharjah, UAE.
- Alsaygh, A** (2008) Synthesis and behavior of α -iminocarboxamide Nickel and Zirconium catalysts towards Olefin polymerization. *Journal of King Abdulaziz University: Science* **21** (1): (Publication in progress)
- Batten, MP, Canty, AJ, Cavell, KJ, R  ther, T, Skelton, BW, and White, AH** (2006) Synthesis of Nickel(II) complexes containing neutral N, N⁻ and anionic N,O⁻ bidentate ligands, and their behaviour as chain-growth catalysts; structural characterisation of complexes containing (mim)₂CO, mimCO₂⁻, and mimCPh₂O⁻ (mim = 1-methylimidazol-2-yl). *Inorganica Chimica Acta* **359**: 1710-1724.
- Branquinho, R, Fernandes, AC, Chien, JCW, Singh, RP, and Marque, MM** (2005) Highly active new α -diimine Nickel catalyst for the polymerization of α -olefins. *J. Organomet. Chem.* **690**: 1314-1323.
- Braunstein, P** (2004) Functional ligands and complexes for new structures, homogeneous catalysts and nanomaterials. *J. Organomet. Chem.* **689**: 3953-3967.
- Diamanti, SJ, Ghosh, P, Shimizu, F, and Bazan, GC** (2003) Ethylene Homo-polymerization and Co-polymerization with functionalized 5-Norbornen-2-yl Monomers by a Novel Nickel Catalyst System. *Macromolecules* **36**: 9731-9735.
- Helldorfer, M, Backhaus, J, and Alt, HG** (2003) The influence of the ligand structure on the properties of (α -diimine) Nickel catalysts in the polymerization and oligomerization of ethylene. *Inorganica Chimica Acta* **351** (1): 34-42.
- Helldorfer, M, Backhaus, J, Wolfgang, M, and Alt, HG** (2003) (α -Diimine) Nickel(II) complexes containing chloro substituted ligands as catalyst precursors for the oligomerization and polymerization of ethylene. *J. Molecular Catalysis: A Chemical* **193** (1): 59-70.
- Johnson, LK, Killian, CM, and Brookhart, M** (1995) New Pd(II)- and Ni(II)-Based Catalysts for Polymerization of Ethylene and α -Olefins. *J. Am. Chem. Soc.* **117**: 6414-6415.
- Killian, CM, Tempel, DJ, Johnson, LK, and Brookhart, M** (1996) Living Polymerization of α -Olefins Using Ni^{II}-Diimine Catalysts. Synthesis of New Block Polymers Based on α -Olefins. *J. Am. Chem. Soc.* **118**: 11664-11665.
- Lee, BY, Bazan, GC, Vela, J, Zachary, JA and Xianhui, Bu K** (2001). α -Iminocarboxamidato-Nickel(II) Ethylene Polymerization Catalysts. *J. Am. Chem. Soc.* **123**: 5352-5353.
- Mecking, S** (2000) Cationic Nickel and palladium complexes with bidentate ligands for the C

- and unknown C linkage of olefins. *Coordination Chemistry Reviews* **203**(1): 325–351.
- Park, S, Han, Y, Seong, KK, Lee, J, Hwa, KK, and Do Y** (2004) Non-Cp type homogeneous catalytic systems for olefin polymerization. *J. Organomet. Chem.* **689**: 4263 - 4276.
- Peuckert, M, and Keim, W** (1983) A new Nickel complex for the oligomerization of ethylene. *Organometallics* **2**: 594.
- Rojas, RS, Wasilke, JC, Wu, G, Ziller, JW, and Bazan, GC** (2005) -Iminocarboxamide Nickel Complexes: Synthesis and uses in Ethylene polymerization. *Organometallic* **24**(23): 5644-5653.
- Schmidt, R, Welch, MB, Knudsen, RD, Gottfriedc, S, and Alt, HG** (2004) a) N, N, N-Tridentate iron(II) and vanadium(III) complexes: Part I. Synthesis and characterization. b) N, N, N-Tridentate iron(II) and vanadium(III) complexes: Part II: Catalytic behavior for the oligomerization and polymerization of ethene and characterization of the resulting products. *Journal of Molecular Catalysis A: Chemical* **222** (1) : 9–15&17-25.
- Small, BL, Brookhart, M, and Bennett, AMA** (1998) Highly active Iron and Cobalt catalysts for the polymerization of Ethylene. *J. Am. Chem. Soc.* **120**: 4049.
- Sun, WH, Tang, X, Gao, T, Wu, B, Zhang W, and Ma, H** (2004) Synthesis, Characterization, and Ethylene Oligomerization and Polymerization of Ferrous and Cobaltous 2-(Ethylcarboxylato)-6-iminopyridyl Complexes. *Organometallics* **23** (21): 5037-5047.
- Young, HK, Tae, HK, Lee, BY, Woodmansee, D, Xianhui, Bu K, and Bazan, GC** (2002) -Iminoenamido Ligands: A Novel Structure for Transition-Metal Activation. *Organometallics* **21**: 3082-3084
- Zachary, JA, Xianhui, Bu K, Bazan, GC, and Fang, C** (2003) Boron trifluoride activation of ethylene oligomerization and polymerization catalysts. *Inorganica Chimica Acta.* **345**: 95 - 102.
- Zachary, JA, Xianhui, Bu K, and Bazan, GC** (2000) Synthesis of Butene-Ethylene and Hexene-Butene-Ethylene Copolymers from Ethylene via Tandem Action of Well-Defined Homogeneous Catalysts. *J. Am. Chem. Soc.* **122**: 1830-1831.
- Zachary, JA, Xianhui, Bu K, Diamond, GM, Leclerc, MK, Murphy, V, Okazaki, M, and Bazan, GC** (2002) Triple Tandem Catalyst Mixtures for the Synthesis of Polyethylenes with Varying Structures. *J. Am. Chem. Soc.* **124**: 15280-15285.

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