

Synthesis and Behavior of α -Iminocarboxamide Nickel and Zirconium Catalysts Towards Olefin Polymerization

Abdulhamid Ahmad Alsaygh

King Abdulaziz Military Academy, Riyadh,

P.O.BOX 58898, Riyadh, 11515, KSA

asaygh@yahoo.com

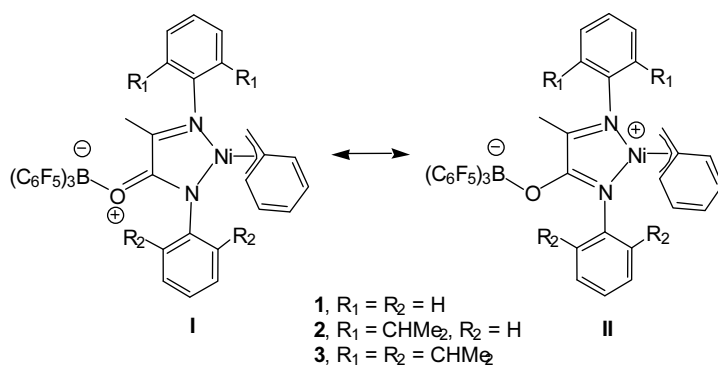
Abstract. Synthesis and investigations of Nickel-based olefin oligomerization and polymerization catalysts, α -Iminocarboxamide μ -3-Benzyl Ni(II) Complex(2) is reported. The attempt to improve the yield of the synthesis of the above mentioned catalysts by the direct reaction of the potassium salt of the ligand, Ni(COD)₂(bis(1,5-cyclooctadiene)-nickel, and Benzyl halide in THF and starting temperature of -35°C. Led instead to disclose that the less hindered N-aryl moieties on the diimine complexes the more difficult to synthesize the ethylene polymerization catalyst, Instead, yielding the di α -Iminocarboxamide Ni-complex(5) which is inactive towards ethylene polymerization. This promoted us to synthesize the complex di α -Iminocarboxamide Zr-complex(6) which is activated by MAO for ethylene polymerization.

Introduction

Since the discovery of the new metallocene-based type, Ziegler-Nata, catalysts^[1], there has been an immense interest in the developments of new types of catalysts such as the utilization of the Nickel catalysts that are used for ethylene polymerization and oligomerization Shell Higher Olefin Process (SHOP)^[2-4]. These types of catalysts have generated lots of research in the area of late transition metals catalysts with the emphasis on the influence of the legend structure on catalysts activity towards ethylene polymerization^[5,6].

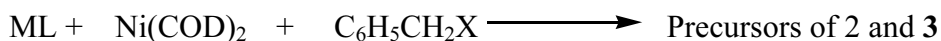
Brookhart and others have demonstrated that (α -diimine) Nickel dihalides complexes catalyze the polymerization of ethylene in the presence of an activating agent or co-catalyst: Methylaluminoxane (MAO)^[7,8].

Bazan *et al.* have discovered that the reactivity of a new type of catalysts α -Iminocarboxamide μ^3 -Benzyl Ni(II) Complex, increases considerably upon addition 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 insertion trajectory prompted our attention^[9]. The metal activation by formation of carbonyl adducts creates a new basis for designing novel nickel olefin polymerization and oligomerization catalysts. Compounds **1-3** were recently prepared in Bazans' labs and exemplify the group strategy. Resonance structures **I** and **II** illustrate the loss of electron density at nickel upon coordination to $B(C_6F_5)_3$ ^[11].

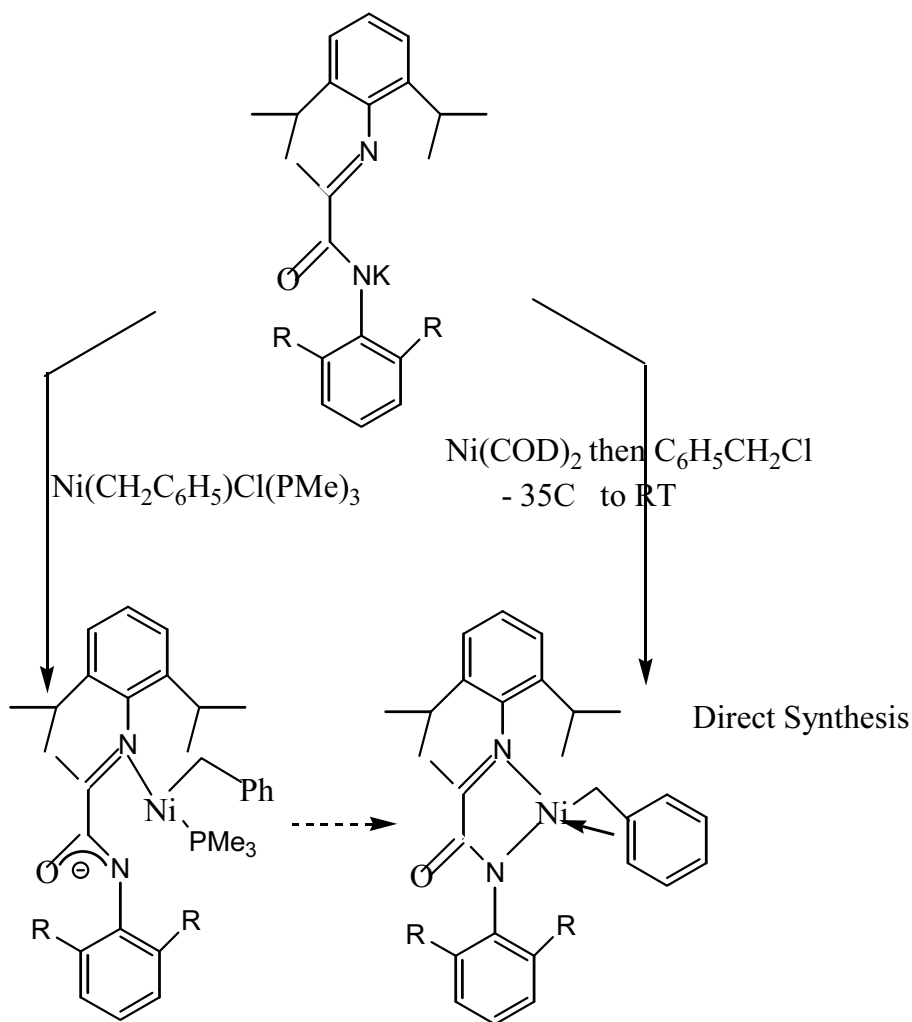


α -Iminocarboxamide ligands were chosen because they can be readily prepared and because the size of the nitrogen aryl groups can be varied to modulate steric effects. Of interest to us was to control the size of the substituents on the pseudo axial sites, since blocking these sites in other nickel catalysts reduces chain transfer to monomer. Incorporation of the μ^3 -benzyl fragment was selected, instead of the more frequently used methallyl, because it displays faster rates of initiation^[12-16].

Bazan group were having a great success in synthesizing the precursors of compounds **2** and **3** as shown in Scheme 1. But the yields are very close to 1% for the direct synthesis of **2** that is for the reaction:



Since the α -Iminocarboxamide μ 3-Penzyl Ni(II) Complex is least sterically hindered, it promises to produce a high molecular weight polyethylene. Therefore; I investigated and tried to understand the best conditions for the reaction, which would help elucidating all these types of reactions and eventually, providing the industry with a very practical catalysts.



Scheme 1. Synthesis of α -Iminocarboxamide μ 3-Penzyl Ni(II) Complex.

Experimental and Procedures

All manipulations were performed under an inert atmosphere using standard glove box 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 done by recrystallization via slow diffusion of Pentane at -35°C . NMR spectra were obtained using a Varian Unity 400 spectrometer. Elemental analysis was performed at physics department at UCSB.

Typical Schiff-base condensation of primary arylamines with *N*-aryl pyruvamides yields α -iminocarboxamides^[5,6]. As shown in Scheme 1, carboxamide deprotonation with 1.0 equiv KH, followed by reaction with $\text{Ni}(\text{COD})_2$ and benzyl chloride^[13,14].

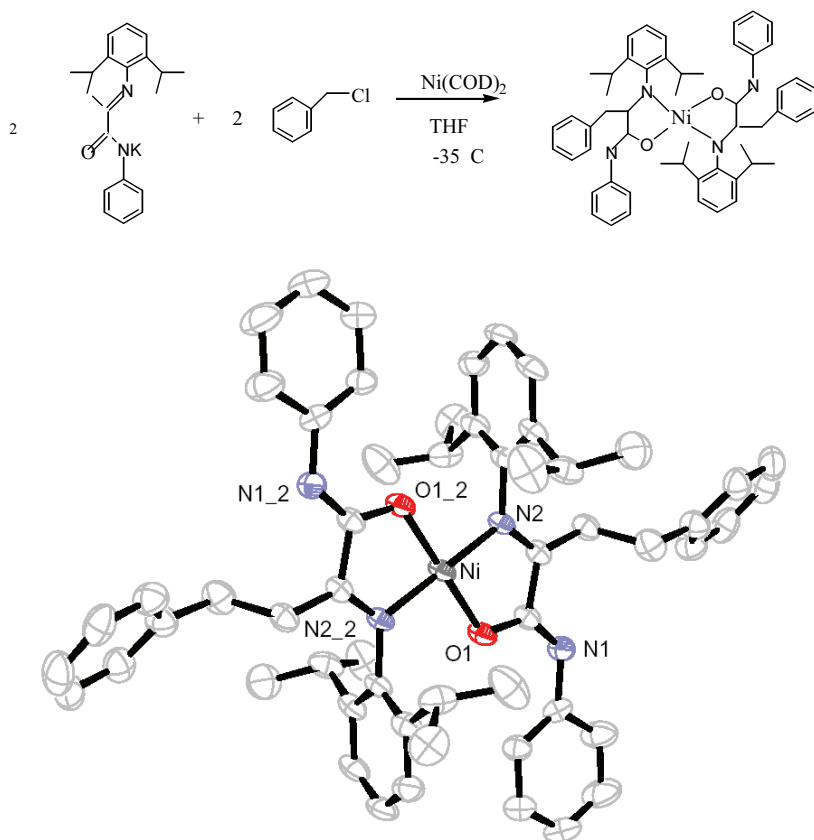


Fig. 1. X-ray structure of Nickel dimer(4).

Synthesis of (α -iminocarboxamides)₂ Ni complex, 5.

0.36g (10 mmol) of the potassium salt of the ligand was placed in 50 ml vile with 26 ml THF. To it, 0.33g (10mmol) of DMENiBr₂, was added and the reaction mixture was stirred for four hours, then, the resultant red brown was filtered through a fritted glass, the solvent was pulled off and the red brown solid purified by washing with pentan and recrystallization from toluene and characterized by ¹H NMR and Its' crystal structure was obtained as shown in Fig. 2.

Synthesis of (α -iminocarboxamides)₂ Zr complex, 6.

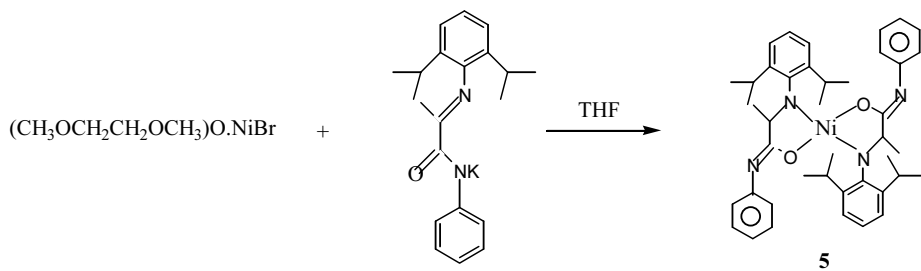
0.36g (10 mmol) of the potassium salt of the ligand was placed in 50 ml vile with 26 ml THF. To it, 0.46g (5mmol) of ZrCl₄, was added and the reaction mixture was stirred for eight hours, then, the resultant yellow solution was filtered through a fritted glass, the solvent was pulled off and the yellow solid purified by washing with pentane and recrystallization from toluene characterized by ¹H NMR as shown in Fig. 3. Anal. : C₄₂H₅₀N₄O₂Cl₂Zr, Theory: C, 60.8%; H, 6.22%; N, 6.96%. Found: C, 60.75; H, 6.13; N, 6.48.

Results and Discussions

As shown in Scheme 1, the direct rout of the synthesis is very delicate process; since Ni(COD)₂ is very light sensitive, the reaction is done under dark condition to prevent it from decomposing before it reacts with the salt of the ligend. Moreover, the order of addition of reaction agents is very important, that is we established that after mixing Ni(COD)₂ with ligand salt, the benzyl chloride is added drop wise at 35°C in THF.

By varying the reaction conditions, solvents types (toluene or THF), Halides types (benzyl halides), and the salts (potassium or Sodium) of the ligand. Following the reaction product by ¹H NMR, we were able to detect traces of the product with a mixture of the dimmers and some other complex (complex 4) that is determined by X-ray structure as shown in Fig. 1. In this latter complex it appeared that the benzyl group activated the carbon of methyl group of the α -iminocarboxamides ligand! This is thought of, as a side product of the direct method.

This led to substituting DME for Ni(COD)₂, as follow:



Scheme 2. Synthesis of $(\alpha\text{-iminocarboxamides})_2$ Ni complex.

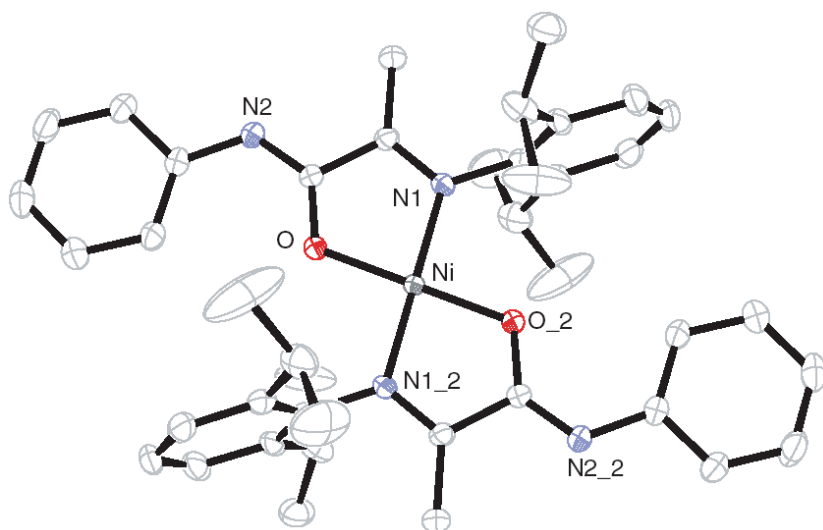
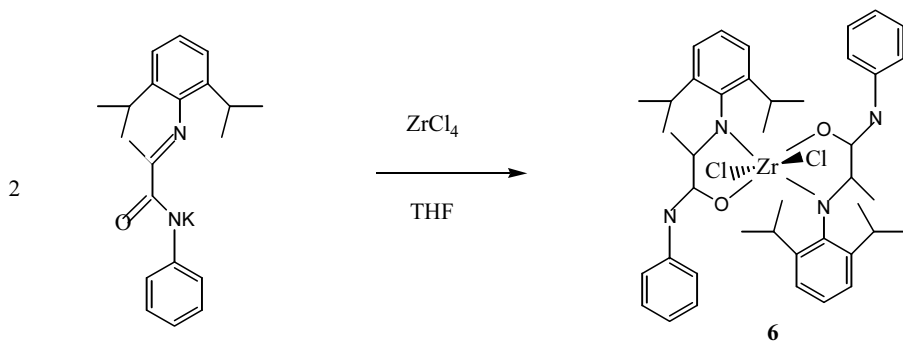


Fig. 2. X-ray structure of Nickel dimer(5) the product of Scheme 2.

It became clear to us that the following reaction is attainable:



Scheme 3. Synthesis of $(\alpha\text{-iminocarboxamides})_2$ Zr complex.

Complex 6 is obtained with a good yield and it was characterized by elemental analysis and ^1H NMR, see Fig. 3. It showed good activity towards ethylene polymerization if activated by MAO.

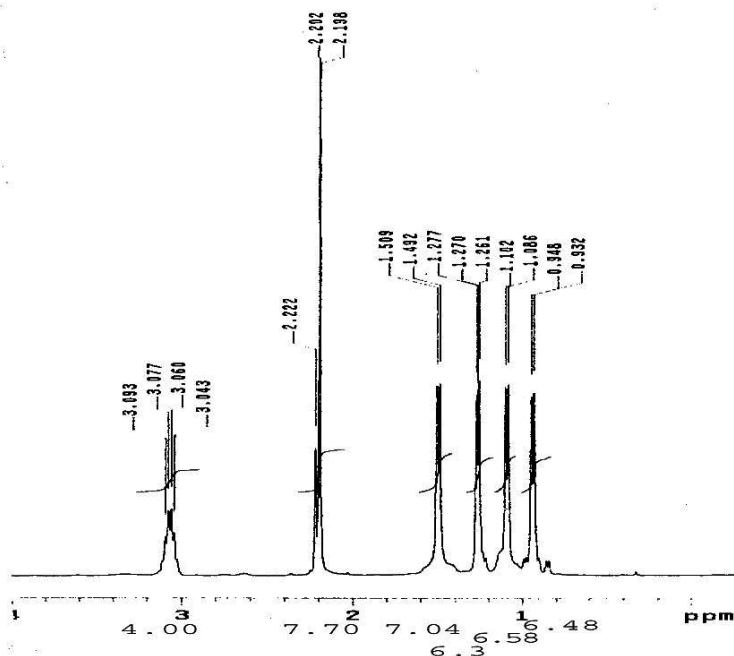


Fig. 3. ^1H NMR, in C_6D_6 , of the aliphatic region of the Zirconium dimer(6) from Scheme 3.

Concluding Remarks

The less sterically hindered Iminocarboxamide, the more sensitive the catalyst synthesis to any minor changes in the procedure which opens up an opportunity for further research in this area^[17]. The difficulties of synthesizing complex 2 by the direct method, Led to preparing new compounds 4, 5 and 6.

Acknowledgments

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تحضير ودراسة مركبات ألفا أمينوكربوكسيل أميد لعنصر النيكل والزركونيوم لاستخدامها كمحفزات لبلمرة الإيثلين

عبد الحميد أحمد الصايغ

كلية الملك عبدالعزيز الحربية،

الرياض، المملكة العربية السعودية

asaygh@yahoo.com

المستخلص. أجريت محاولات تحضير دراسة مركبات النيكل والمستخدم كمحفزات في تحضير البلمرات ذات الأوزان الجزيئية المنخفضة، وكذلك العادية، كالمركب (٢) μ 3-Penzyl Ni(II) Iminocarboxyamide. محاولاتنا لتحسين الناتج لتحضير هذا المركب عن طريق التفاعل المباشر بين ملح البوتاسيوم للجاند و $Ni(COD)_2$ (bis(1,5-cyclooctadiene)-nickel والبنزيل هاليد في الـ THF عند درجة حرارة $-35^\circ C$ ، قادتنا إلى معرفة أنه كلما كان مركب الداي أمين غير متفرع، كلما صعب تحضير هذا المركب بهذه الطريقة، والتي أدت إلى الحصول على المركب (٥) α -di Iminocarboxyamide Nickel complex والذي يعتبر غير نشيط بالنسبة لتحفيز بلمرات الإيثلين. مما حدا بنا لتحضير المركب (٦) α -di Iminocarboxyamide Zirconium complex والذي يعتبر محفزاً جيداً لبلمرة الإيثلين، وخاصة عند وجود نسبة قليلة من مركب MAO.