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Zirconium Complexes of a New Schiff Base Ligand Having Pyrrole Units

Pirol Birimleri İçeren Yeni Bir Schiff Bazı Ligandı ve Zirkonyum Kompleksleri

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ABSTRACT

The design and synthesis of new transition-metal catalyst precursors is a very important subject that can provide high catalytic activity with low cocatalyst-to-catalyst precursor (pre-catalyst) ratios and allows unprecedented control over the polymer microstructure, producing new polymers with improved polymer properties. The catalytic activity of transition metal Schiff base complexes became compelling in synthesis of commercially important polymers. Schiff base complexes of especially early transition metal ions (Ti, Zr, Hf) are efficient catalysts both in homogeneous and heterogeneous reactions, the activity of these complexes varied with the type of ligands, coordination sites and metal ions. The non-metallocene complexes of zirconium and hafnium so called “post-metallocene” complexes, such as the zirconium and hafnium phenoxyimine complexes, bisimido pyridyl complexes and recently some Schiff Base complexes bearing heterocycle donors such as furan, thiophene and pyrrole are showing high efficiency in olefin polymerization.

In this study, perfluorophenyl ethylenediamine was synthesized by reacting hexafluorobenzene with ethylenediamine in pyridine.

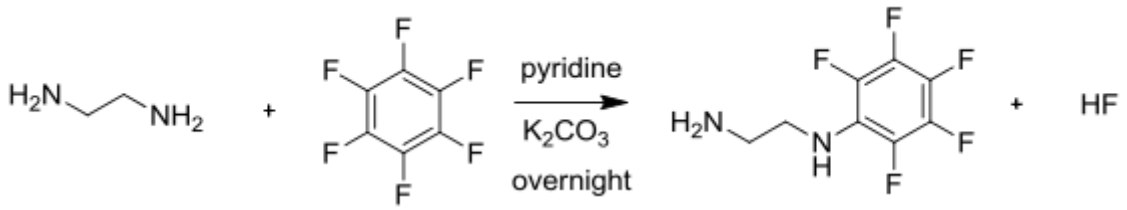


Figure 1. Preparation of the primary amine with the reaction between ethylene diamine and hexafluorobenzene.

The new Schiff base ligand was synthesized by the reaction between pyrrole-2-carboxaldehyde and perfluoroethylene diamine in chloroform.

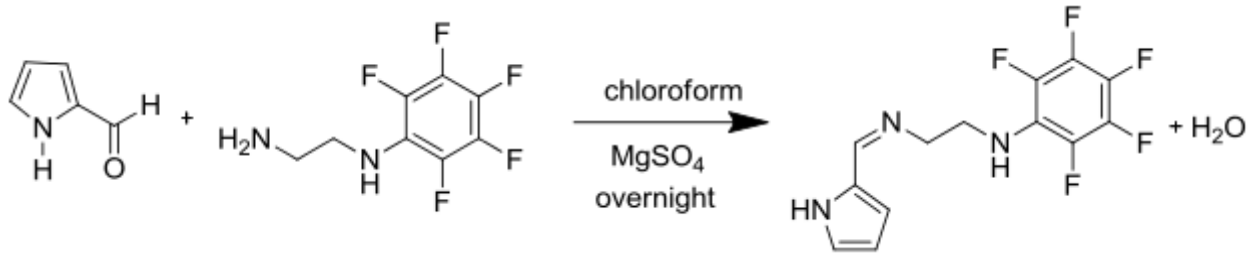


Figure 2. Formation of the Schiff base between aldehyde and primary amine.

The synthesis of novel zirconium complex of Schiff base derivative of pyrrole was achieved by the reaction of the Schiff base with THF adducts of zirconium tetrachloride.

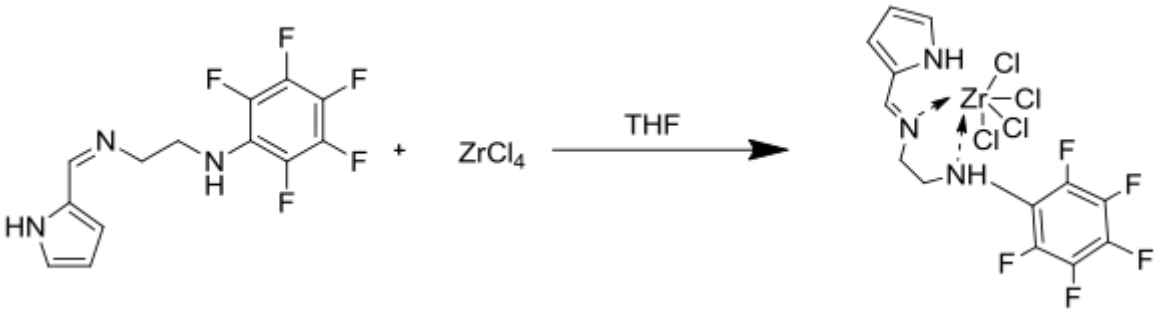


Figure 3. Synthesis of the zirconium complex with the reaction between the schiff base and zirconium tetrachloride.

Later, starting from this new ligand a sodium salt and its zirconium complex were synthesized.

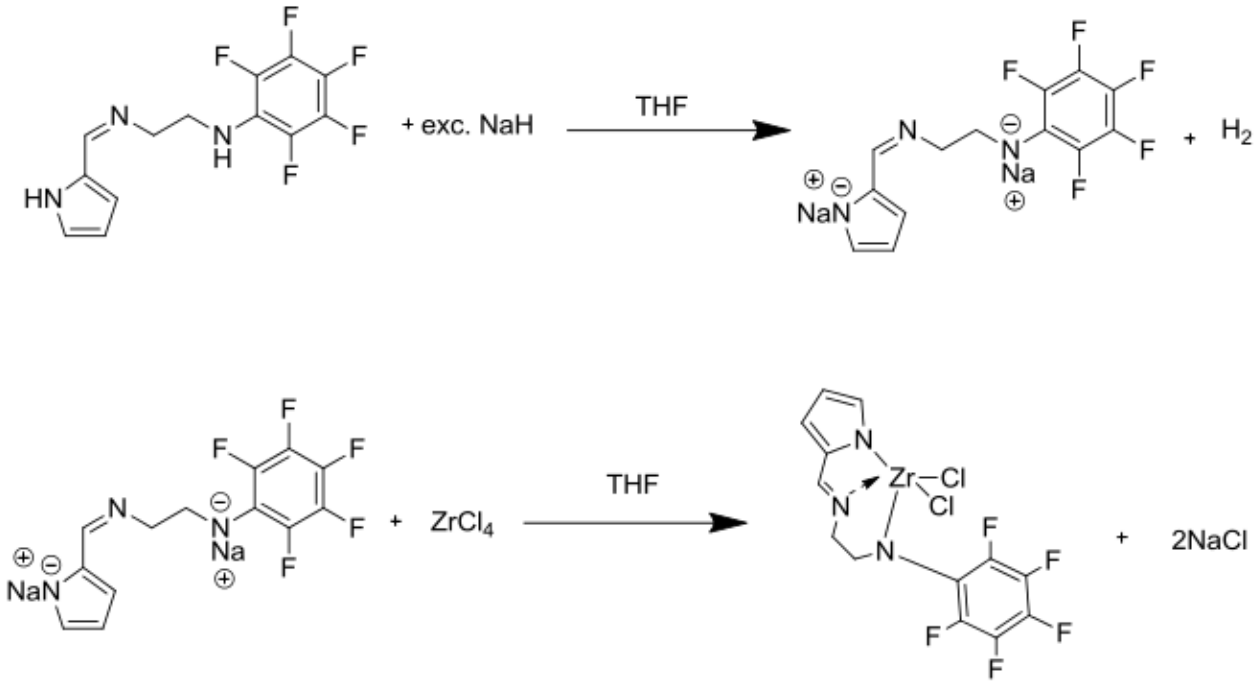


Figure 4. The reaction yielding zirconium complex and salt by the action of the disodium salt of the pyrrole-containing schiff base and zirconium tetrachloride.

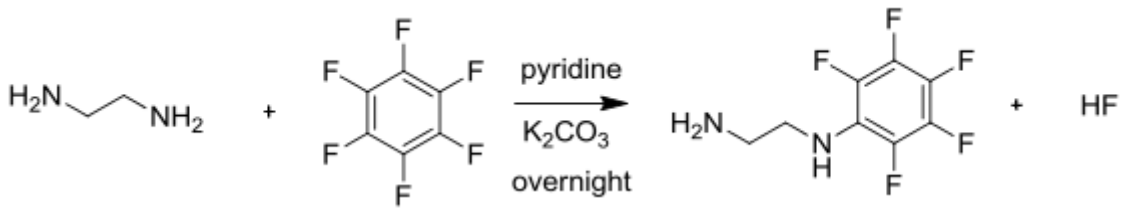
Keywords

Schiff bases, zirconium complexes, perfluorophenylethylene diamine.

ÖZET

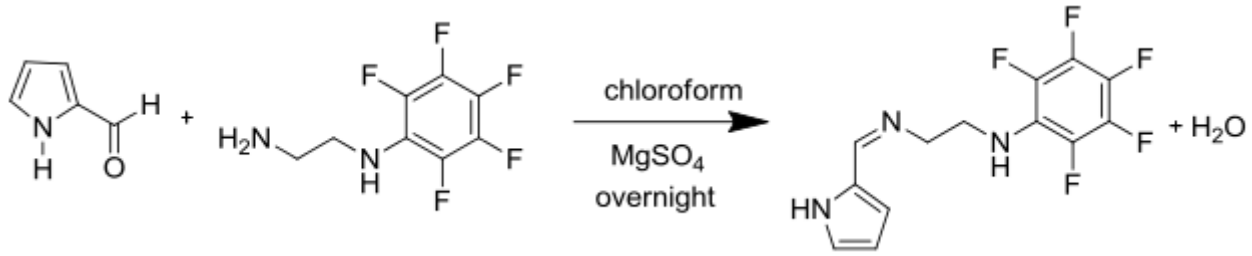
Yeni geçiş metal katalizör öncüllerinin tasarımı ve sentezi, düşük yan katalizör/katalizör öncülü (ön katalizör) oranları veren yüksek katalitik aktivite sağlayabilir ve polimer mikro-yapısı üzerinde tahmin edilmeyecek bir kontrol sağlayarak gelişmiş polimer özelliklerine sahip yeni polimerler oluşturabilir. Geçiş metal Schiff metal komplekslerinin katalitik aktiviteleri, ticari olarak önemli polimerlerin sentezinde cazip bir hale gelmiştir. Özellikle ilk geçiş metal iyonları (Ti, Zr, Hf) için Schiff bazı kompleksleri homojen ve heterojen tepkimelerde etkili katalizörlerdir, bu komplekslerin aktivitesi ligandların türüyle, koordinasyon bölgeleriyle ve metal iyonlarıyla değişiklik gösterir. Zirkonyum ve hafniyumun “post-metalosen” kompleksleri gibi metalosen kökenli olmayan kompleksler, örnek olarak zirkonyum ve hafniyumun fenoksiimin kompleksleri, bisimido piridil kompleksleri ve son zamanlarda furan, tiyofen ve pirol gibi heterohalka donörleri bulunduran bazı Schiff bazı kompleksleri olefin polimerleşmesinde yüksek etkinlik göstermektedir.

Bu çalışmada, heksafluorobenzen piridin içinde etilendiamin ile tepkimeye sokularak perfluorofeniletilen diamin sentezlenmiştir.



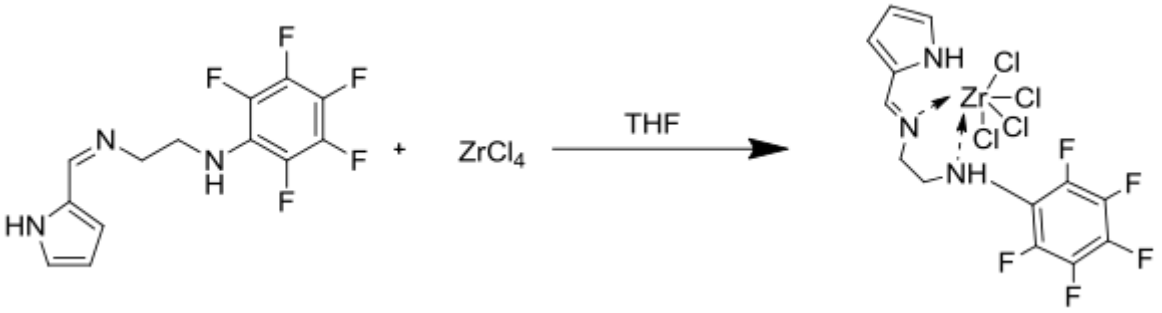
Şekil 1. Perfluorofeniletilen diamin bileşiğinin sentezi.

Yeni Schiff bazı ligandı pirol-2-karboksaldehit ile perfluoroetilen diaminin kloroformda tepkimeye sokulması ile elde edilmiştir.



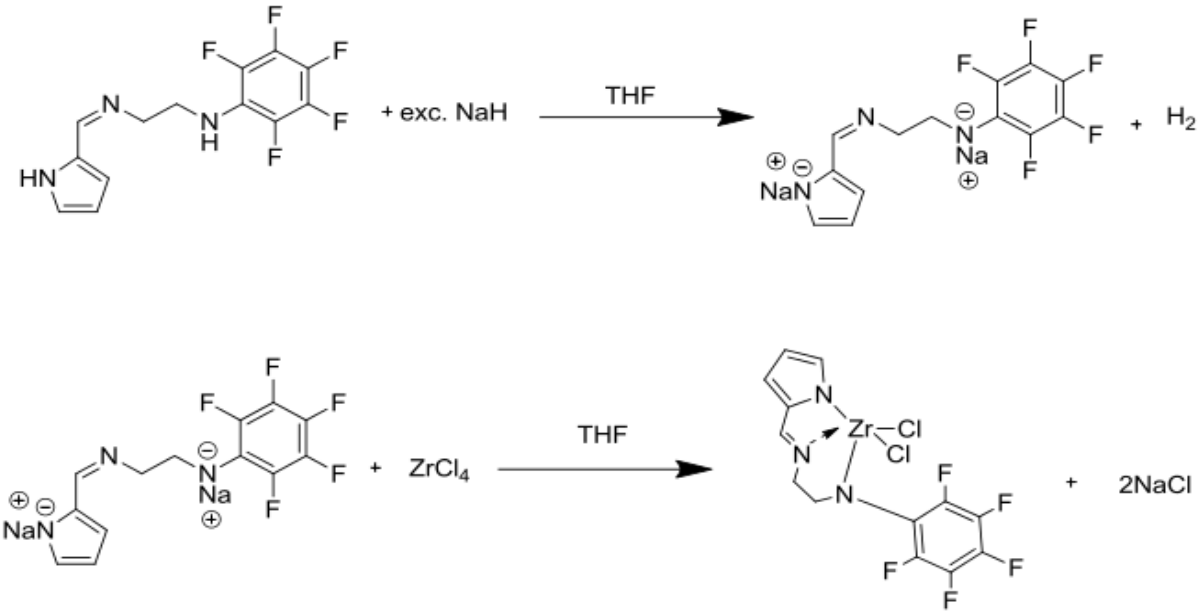
Şekil 2. Aldehit ve primer aminden Schiff bazının oluşumu.

Pirolün Schiff baz türevinin yeni zirkonyum kompleksinin sentezi zirkonyum tetraklorürün THF katılma ürünleri ile Schiff bazı arasındaki tepkime ile gerçekleştirildi.



Şekil 3. Schiff bazı ile zirkonyum tetraklorür arasındaki tepkimeden zirkonyum kompleksinin oluşması.

Daha sonraki aşamada, bu yeni liganddan yola çıkarak sodyum tuzu ve zirkonyum kompleksi oluşturan bir tepkime daha gerçekleştirildi.



Şekil 4. Pirol içeren Schiff bazının sodyum tuzu üzerinden zirkonyum tetraklorür ile tuz çıkışı içeren tepkimesi.

Anahtar Kelimeler

Schiff bazları, zirkonyum kompleksleri, perfluoroetilen diamin.