



STUDY THE SYNTHESIS OF EARLY TRANSITION METAL BISPHENOLATE COMPLEXES AND THEIR USE AS OLEFIN POLYMERIZATION CATALYSTS

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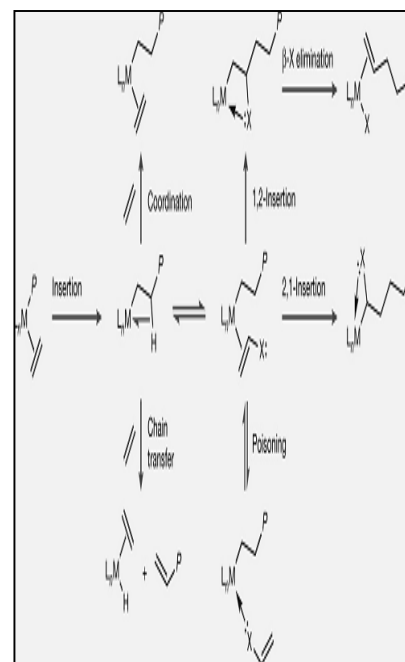
ABSTRACT

Bisphenolate ligands with pyridine- and benzene-diyl linkers have been synthesized and metalated with group 4 and 5 transition metals. The solid state structures of some of the group 4 complexes have been solved. The titanium, zirconium, hafnium, and vanadium complexes were tested for propylene polymerization and ethylene/1-octene copolymerization activities with methylaluminoxane as co-catalyst. The vanadium (III) precatalyst is the most active for propylene polymerization and shows the highest 1-octene incorporation for ethylene/1-octene copolymerization. The zirconium (IV) precatalyst was the most active for propylene polymerization of the group 4 precatalysts. Titanium and zirconium (IV) precatalysts with pyridine-diyl linkers provided mixtures of isotactic and atactic polypropylene while titanium (IV) precatalysts with benzene-diyl linkers gave atactic polypropylene only. The hafnium (IV) precatalyst with a pyridine-diyl linker generated moderately isotactic polypropylene.

KEYWORD: Bisphenolate ligand, isotactic polypropylene, zirconium (IV) precatalyst etc.

INTRODUCTION

Polymers are ubiquitous materials with applications in household products, biomedicine and transportation. The polymerizations of ethylene, propylene, and styrene with Ziegler-Natta catalysts represent important processes that have grown to a worldwide production exceeding 100 billion pounds per year. Understanding the influence of catalyst structure on polymer composition and microstructure allows for the development of polymer architectures with various applications. Single-site catalysts are amenable to these types of studies such that an enormous number of metallocene and non-metallocene catalysts have been synthesized in the last thirty years. Metallocene catalysts are well understood with respect to the relationship between catalyst symmetry and polymer microstructure (Figure 1). However, non-metallocene catalysts



represent a less understood sector of polymerization catalysts with respect to catalyst symmetry-polymer microstructure relationships

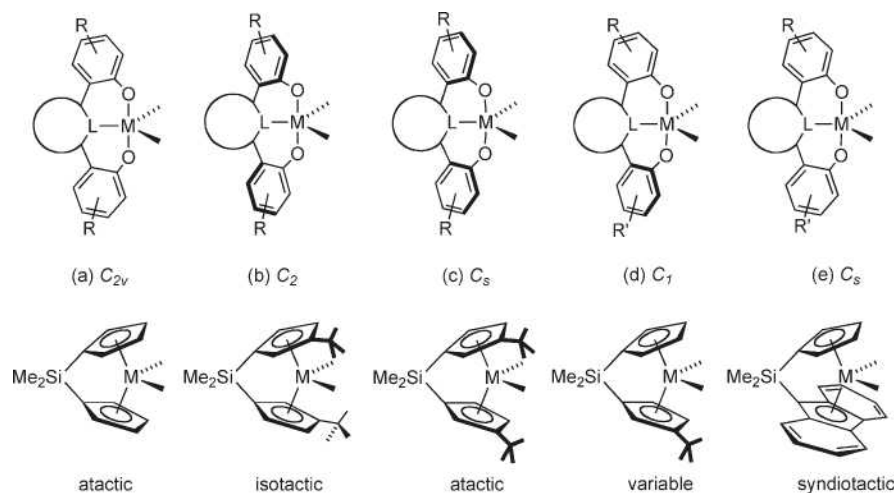


Figure 1. Relationship between catalyst geometry and anticipated polymer microstructure where R = alkyl, linker = pyridine-diyl or benzene-diyl, and L = N (neutral) or C (neutral or anionic).

Given the promising ability of non-metallocene catalysts to control polymer tacticity, we found it desirable to synthesize a new type of ligand for detailed study. This non-metallocene ligand framework features a bidentate or tridentate moiety with two anionic donors positioned around a central atom or donor connected at the *ortho* position *via* semi-rigid $sp-sp$ linkages (see Figure 1). To explore the polymerization activities and selectivities of group 4 complexes with these ligands. Herein we disclose the synthesis of bisphenolate pyridine- and benzene-diyl linked ligands. Group 4 and 5 complexes supported by these ligands have been prepared and their utility as polymerization catalysts has been examined, including their influence on molecular weight and ability to control polymer tacticity.

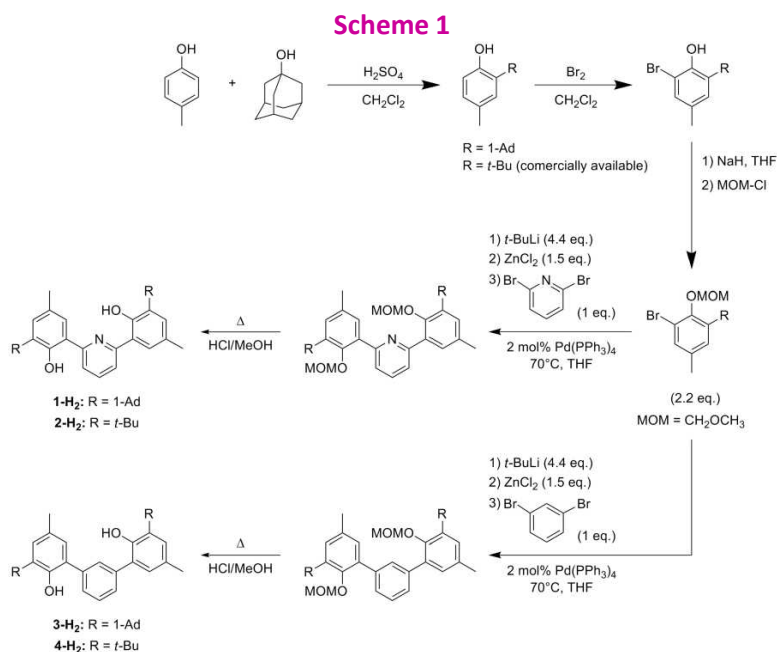
REVIEW OF LITERATURE

The discovery of the polymerisation activity of titanium and zirconium complexes resulted from an investigation by Karl Ziegler and co-workers into the multiple insertion of ethene into aluminium alkyl bonds to give long chain aluminium alkyls. Interest in the effects of transition metals on this insertion process was stimulated by an observation that small amounts of nickel inhibit the insertion/polymerisation reaction. This discovery not only led to nickel being developed as an ethene oligomerisation catalyst, but also to an extensive study into the effects of other transition metals on the insertion of ethene into aluminium alkyl bonds. These studies led to the discovery that certain transition metal complexes (e.g. zirconium acetylacetonate) can, in the presence of an aluminium alkyl (e.g. $AlEt_2Cl$), catalyse polymerisation of ethene under mild conditions (e.g. $50^\circ C/10\ atm$). This result contrasted starkly with radical polymerisation processes available at the time, which typically required pressures in excess of 1000 atm and temperatures of the order of $200^\circ C$. By 1952, Giulio Natta extended Ziegler's work to the polymerisation of higher α -olefins.

MATERIAL AND METHODS

The ligands (1- H_2 , 2- H_2 , 3- H_2 , and 4- H_2) were synthesized with overall yields ranging from 20% to 60% (Scheme 1). The acid-promoted alkylation of p-cresol with 1-adamantanol was previously reported. Both ortho-

bromination and deprotonation with sodium hydride followed by protection with chloromethyl methylether (MOM-Cl) occur in high yield. In the case of the adamantyl substituted species, the deprotonation/protection reaction produced an unidentifiable byproduct which was removed by Kuglerrohr distillation. The coupling reaction of the protected bromo-phenol with either 2,6-dibromopyridine or 1,3-dibromobenzene was achieved through lithium-halogen exchange followed by transmetalation using ZnCl_2 and palladium-catalyzed Negishi cross-coupling. The protecting group (MOM) was removed by treatment with acidic methanol at 65°C . Simple filtration of the methanol solution afforded the adamantyl substituted ligands (1- H_2 and 3- H_2). The *t*-butyl substituted ligands (2- H_2 and 4- H_2) were obtained by solvent removal. The identity of the ligands was confirmed by ^1H NMR spectroscopy, ^{13}C NMR spectroscopy, and HRMS.



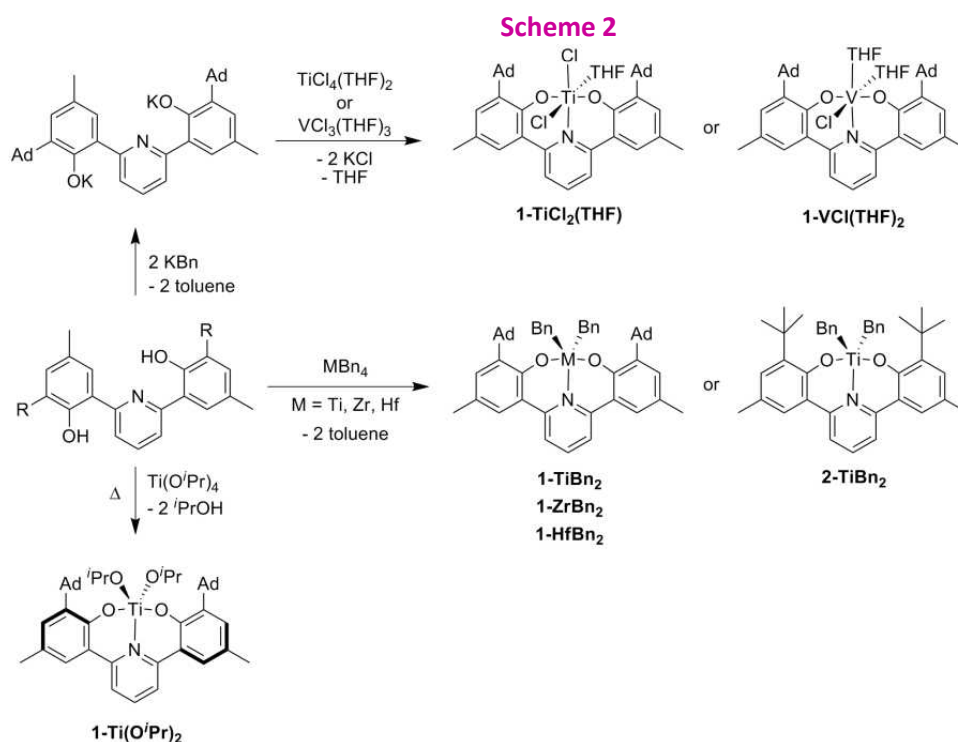
RESULTS AND DISCUSSION

The ligands (or their dianions) were treated with the appropriate early transition metal precursors ($\text{TiCl}_4(\text{THF})_2$, $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$, $\text{Ti}(\text{CH}_2\text{C}_6\text{H}_5)_4$, $\text{Zr}(\text{CH}_2\text{C}_6\text{H}_5)_4$, $\text{Hf}(\text{CH}_2\text{C}_6\text{H}_5)_4$, or $\text{VCl}_3(\text{THF})_3$ where $\text{OCH}(\text{CH}_3)_2 = \text{O}^i\text{Pr}$ and $\text{CH}_2\text{C}_6\text{H}_5 = \text{Bn}$) to give the desired products. The salt metathesis reaction with $\text{TiCl}_4(\text{THF})_2$ or $\text{VCl}_3(\text{THF})_3$ involved initial deprotonation of the ligand with potassium benzyl. The KCl byproduct was removed by filtration. Repeated attempts using the salt metathesis routes with $\text{ZrCl}_4(\text{THF})_2$ or $\text{HfCl}_4(\text{THF})_2$ proved unsuccessful because substantial amounts of the bis-ligated species formed under a variety of conditions. (The bis-ligated species was identified by ^1H NMR spectroscopy data from independent synthesis using an excess of ligand with ZrBn_4 .) The alcohol elimination reaction with $\text{Ti}(\text{O}^i\text{Pr})_4$ lead to the desired product only when heated at 80°C overnight. Alkane elimination reactions were successfully employed with the tetrabenzyl derivatives of the entire group 4 series. All metal complexes were characterized by NMR spectroscopy with the exception of the paramagnetic vanadium complex (vide infra). Further confirmation was obtained through elemental analysis, and in some

cases, X-ray quality crystals were grown.

these complexes display different solution-state geometries (C_{2v} , C_s , C_2 , or C_1) that may, in principle, be assigned by ^1H NMR spectroscopy through analysis of the benzyl protons: (1) C_{2v} geometry is expected to lead to a singlet, (2) C_s geometry should give two singlets, (3) C_2 geometry makes the $[\text{CH}_2]$ protons diastereotopic, which should lead to two doublets, and (4) C_1 geometry would make all four benzylic protons different, appearing as four doublets. All complexes with pyridine-diyl linkers (1-TiBn₂, 2-TiBn₂, 1-ZrBn₂, and 1-HfBn₂) featured one singlet between 3.1 and 4.1 ppm integrating as four benzyl protons, implying either a C_{2v} geometry or dynamic equilibration of methylene hydrogens for a lower symmetry structure to give a singlet on the NMR timescale. The complexes with benzene-diyl linkers (3-TiBn₂ and 4-TiBn₂) showed two singlets between 1.9 and 3.7 ppm with each signal attributed to two benzyl protons, indicating (time-averaged) C_s geometry. These geometry assignments were corroborated by X-ray crystallography data.

The orange/brown solid of 1-VCl(THF)₂ was paramagnetic and showed very broad peaks in the ^1H NMR spectrum. The solution magnetic susceptibility was determined using the Evans Method to give a $p_{\text{eff}} = 2.90(2)$ p b. This matches the predicted value ($p_{\text{eff}}(\text{spin only}) = 2.82$) for two unpaired electrons in trivalent vanadium complexes. The presence of two coordinated THF molecules was confirmed by elemental analysis.



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