Late Transition Metal Complexes for the Polymerization of Olefins and Vinylic Monomers

Kristian Lappalainen
Laboratory of Inorganic Chemistry
Department of Chemistry
University of Helsinki
Finland

Academic Dissertation

To be presented, with the permission of the Faculty of Science of the University of Helsinki, for public criticism in the Auditorium A110 of Chemicum, A. I. Virtasen aukio on June 8th, 2005 at 12 noon.
Supervisors
Professor Markku Leskelä
and
Docent Timo Repo
Laboratory of Inorganic Chemistry
Department of Chemistry
University of Helsinki
Finland

Professor Adnan Abu-Surrah
Department of Chemistry
Hashemite University
Zarqa, Jordan.

Reviewers
Professor Tuula Pakkanen
Department of Chemistry
University of Joensuu
Finland

Professor Carl-Eric Wilen
Laboratory of Polymer Technology
Åbo Akademi
Finland

Opponent
Professor Reko Leino
Department of Organic Chemistry
Åbo Akademi
Finland

© Kristian Lappalainen 2005
ISBN 952-91-8737-8 (printed version)
ISBN 952-10-2478-X (pdf)
http://ethesis.helsinki.fi
Yliopistopaino
Helsinki 2005
Abstract

The literature part of the thesis reviews results and proposed mechanisms for the polymerization of ethene, norbornene, and acrylate monomers. In the case of ethene, focus is on bis(imino)pyridine iron and cobalt catalysts, while for norbornene polymerization mechanisms and catalyst systems are described. Polymerization of polar monomers, particularly acrylates, is reviewed in the second part.

Eighteen new iron(II) and cobalt(II) complexes with tridentate bis(imino)pyridine ligands, and eleven palladium(II) complexes with bidentate nitrogen, phosphorus, sulfur, and arsenic donor atom ligands, were synthesized and characterized. The iron(II) and cobalt(II) bis(imino)pyridine complexes were formed with seven ketimine and four aldimine ligands bearing bulky aliphatic or aromatic substituents. The palladium(II) complexes were formed with three pyridinylimine and three ethyl-bridged phosphorus, sulfur, and arsenic ligands. As well, five ion pair complexes were investigated.

Iron(II) and cobalt(II) complexes activated with methylaluminoxane (MAO) gave highly active catalysts for the polymerization of ethene and tert-butyl acrylate. Moreover, activities from moderate to high were obtained in preliminary polymerizations of methyl acrylate, acrylonitrile, and n-vinylcarbazole. The palladium(II) complexes were activated for norbornene polymerization either by formation of distinct ion pairs or with MAO. Depending on the ligand structure the obtained activities varied between high and moderate.
Preface

This work was carried out between 1999 and 2005 in the Laboratory of Inorganic Chemistry, University of Helsinki. Financial support from the Academy of Finland, Finnish National Technology Agency (TEKES), and Association of Finnish Chemical Societies is gratefully acknowledged.

I wish to express my deepest gratitude to Professor Markku Leskelä for providing me the opportunity to work in his laboratory and for wise advice, constructive criticism, and lots of encouragement during the years of this work.

I am deeply grateful to Professor Adnan S. Abu-Surrah, Hashemite University, Jordan, who nudged me on my way at the outset of the work. I thank him for his patience in both laboratory investigations and literature studies. Special thanks go to Docent Timo Repo for our many friendly scientific and general discussions.

I wish to express warmest thanks to all my colleagues and friends at the Laboratory of Inorganic Chemistry, for their collaboration, encouragement, and tireless help. While it is impossible to mention everyone who has been of help, I would like to single out a few who have been especially instrumental. It was pleasure to work in the same laboratory with Katarina Yliheikkilä and Ulla Markkanen and a privilege to learn from Mika Kettunen, who found answers to so many of my questions and assisted me with his linguistic skills.

My warmest thanks go to all my friends, especially Mika L., Netta, and Panu, for numerous stimulating discussions and the encouragement needed in life’s difficult moments.

I am deeply grateful to my mother and father for their support and encouragement. Most of all I wish to thank my family– my dear wife Heidi and Maria and little Aaron. They have been endlessly patient and supportive, while reminding me that occasionally there are things more important than chemistry.
LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following publications and manuscript, which are referred to in the text by the Roman numerals I-VII


VII  K. Lappalainen, K. Yliheikkilä, A. S. Abu-Surrah, M. Kalmi, M. Leskelä, T. Repo, α-Olefin-Functionalized Polymers Via 2,6-Bis(imino)pyridine Iron(II)- and Cobalt(II)-Complexes. (manuscript)
Contents

Abstract ...................................................................................................................................... 3

Preface ........................................................................................................................................ 4

Contents ...................................................................................................................................... 6

Abbreviations ............................................................................................................................. 7

Introduction ................................................................................................................................ 9

1. REVIEW OF THE LITERATURE ...................................................................................... 10
  1.1. Alkene Polymerization ................................................................................................. 10
    1.1.1. Ethene polymerization with bis(imino)pyridine complexes ...................................... 11
    1.1.2. Polymerization of norbornene with transition metal catalysts .................................. 15
  1.2. Polar Monomer Polymerization ...................................................................................... 18
    1.2.1. Acrylates ............................................................................................................... 18
    1.2.2. n-Vinyl carbazole and acrylonitrile ......................................................................... 22

2. RESULTS AND DISCUSSION ........................................................................................... 22
  2.1. 2,6-Bis(imino)pyridine complexes of iron(II) and cobalt(II) [IV-VI] ............................... 22
    2.1.1. Ligands ................................................................................................................. 23
    2.1.2. Complexes and solid state structures ....................................................................... 24
  2.2. Palladium Complexes with Nitrogen, Phosphorus, Sulfur and Arsene Donor Atoms ... 25
    2.2.1. Ethyl bridged palladium(II) complexes and solid state structures [I, II, IV] ............. 26
    2.2.2. Pyridinylimine palladium(II) complexes and solid state-structures [III] ................... 27
  2.3. Polymerizations ........................................................................................................... 29
    2.3.1. Polymerization of ethene ........................................................................................ 29
    2.3.2. Polymerization of norbornene and phenylnorbornene ........................................... 31
    2.3.3. Polymerization of polar monomers ......................................................................... 32

3. CONCLUSIONS ................................................................................................................... 36

REFERENCES ......................................................................................................................... 37
## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{13}$C-NMR</td>
<td>Carbon nuclear magnetic resonance spectroscopy</td>
</tr>
<tr>
<td>$^1$H-NMR</td>
<td>Proton nuclear magnetic resonance spectroscopy</td>
</tr>
<tr>
<td>AN</td>
<td>Acrylonitrile</td>
</tr>
<tr>
<td>ATRP</td>
<td>Atom transfer radical polymerization</td>
</tr>
<tr>
<td>BuOH</td>
<td>Butanol</td>
</tr>
<tr>
<td>COD</td>
<td>1,5-Cyclooctadiene</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>EA</td>
<td>Elemental analysis</td>
</tr>
<tr>
<td>EPR</td>
<td>Electron paramagnetic resonance</td>
</tr>
<tr>
<td>EtOH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel permeation chromatography</td>
</tr>
<tr>
<td>GTP</td>
<td>Group transfer polymerization</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared resonance spectroscopy</td>
</tr>
<tr>
<td>MA</td>
<td>Methyl acrylate</td>
</tr>
<tr>
<td>MAO</td>
<td>Methylaluminoxane</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectrometry</td>
</tr>
<tr>
<td>PAN</td>
<td>Polyacrylonitrile</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>PVCZ</td>
<td>Poly($n$-vinylcarbazole)</td>
</tr>
<tr>
<td>RAFT</td>
<td>Reversible addition-fragmentation chain transfer polymerization</td>
</tr>
<tr>
<td>ROMP</td>
<td>Ring-opening metathesis polymerization</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
<tr>
<td>tBA</td>
<td>tert-Butyl acrylate</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
</tbody>
</table>
Introduction

In the 1950s, Karl Ziegler and Giulio Natta developed a highly active titanium-based trialkylaluminum-activated catalyst for \(\alpha\)-olefin polymerization, and still today major industrial polymerization processes are based on this discovery.[1] Highly active Ziegler-Natta catalysts facilitate the production of cheap polyethene (PE) and polypropene (PP), which have revolutionary changed the polyolefin industry and our everyday life. Since the fifties catalysts based on early transition metals have dominated the research on polymerization catalysts.

Although the first homogeneous ethene polymerization utilizing Group 4 metallocene catalysts was reported in 1957, the activity was only moderate.[2] It was not until two decades later that the activity of metallocenes was dramatically increased with the introduction of methylaluminoxane (MAO) as an activator.[3, 4] Since then, single-site metallocene catalysts have been the subject of enormous interest and convincing improvements of poly(1-olefin) materials have been achieved.[5] As well, understanding has been gained of the basic reaction mechanisms responsible for the growth of a stereoregular polymer chain at a metal center. Nevertheless, this generation of activated metallocene catalysts are not suitable for all polar monomers. The limitation is due to the sensitivity of early transition metal complexes to electron donating functional groups.[6] Thus, homopolymers of technically important polar monomers and copolymers of these monomers with ethene are today produced exclusively by radical polymerization in high-pressure processes.[7] The development of new families of catalysts that allow copolymerization of a wide variety of different polar monomers, better control of the polymer properties, and a wider selection of materials is thus high on the agenda in catalyst research. Catalysts with improved ability to incorporate polar monomers to the polyethene main chain can be expected to give rise to new high-performance materials with high adhesion, toughness, and dyeability.[8] Such catalysts may also be more tolerant of minor contaminants in ethene polymerization. The demand search for these properties in polymerization catalysts has led to complexes formed with the late transition metals.

In 1995, Brookhart and co-workers[9, 10] turned a new page in the research on transition metal complex catalysts when they announced novel nickel- and palladium-based polymerization catalyst precursors. These complexes, which were highly active in ethene polymerization and produced high molar mass polymers, initiated a period of intensive research on late transition metal catalysis. The aim of the research was the same as in single site-metallocene studies: to understand the relation between catalyst structure and polymer microstructure and so improve
catalyst performance. In 1998 the groups of Gibson\cite{11} and Brookhart\cite{12} discovered the highly active tridentate iron and cobalt complexes.

In the work now reported new iron(II)- and cobalt(II)-based complexes bearing 2,6-bis(imino)pyridine ligands with bulky aromatic and aliphatic terminal groups were synthesized. In the presence of MAO the new complexes were highly active toward the polymerization of ethene, and they initiated polymerization of tert-butyl acrylate, methyl acrylate, acrylonitrile, and n-vinylcarbazole. In addition three bidentate pyridinylimine palladium(II) complexes and ethylene-bridged palladium(II) complexes containing heterodonor atoms such as phosphorus, arsenic, and sulfur were prepared. The catalytic behavior of both the cationic and MAO-activated complexes was investigated in the polymerization of norbornenes such as bicyclo[2.2.1]hept-2-ene and (5-phenylbicyclo[2.2.1]hept-2-ene). Depending on the ligand structure the polymerization activities varied between high and moderate.

1. REVIEW OF THE LITERATURE

The review of the literature relevant to the syntheses and polymerizations of this work fall into two parts. The section on alkene polymerization reviews ethene polymerizations with bis(imino)pyridine iron and cobalt complexes and norbornene polymerizations with late transition metal catalysts. The section on the polymerization of polar monomers deals particularly with acrylates and the mechanisms by which they are polymerized.

1.1. Alkene Polymerization

Ever since the discovery of highly active Ni(II) and Pd(II) olefin polymerization catalysts containing α-diimine ligands by Brookhart and co-workers in 1995,\cite{9,10} extensive studies have been carried out on the synthesis of late transition metal catalysts and their application in alkene polymerization or oligomerization.\cite{13,14} Recent advances in olefin polymerization catalysis relying on group 8 and 9 metals are mainly based on iron and cobalt complexes. This family of catalysts has attracted interest not only in academia but also in industry.\cite{15} In the following, iron(II) and cobalt(II) bis(imino)pyridine complexes in ethene polymerizations are reviewed, and selected catalysts for norbornene polymerization, particularly palladium catalysts are presented.
1.1.1. Ethene polymerization with bis(imino)pyridine complexes

Recent reports on catalysis of olefin polymerization with late transition metal systems mainly describe bis(imino)pyridine ligands with iron(II) and cobalt(II) as metal centers (Scheme 1). In these catalysts both the ligand frame and the metal center have an effect on the polymer properties. In the original discovery, these iron- and cobalt-based catalysts had bis(imino)pyridine ligands with bulky aryl substituents.[12, 11] The most remarkable of these early catalysts was iron(II) ketimine (R’ = Me) complex substituted with 2,6-isopropyl aniline (=R) (Scheme 1), which shows high activities for the production of high molar mass polyethene. The corresponding cobalt complexes are less active than the iron complexes and tend to produce polyethene of lower molar mass.[16] 13C NMR analysis of polyethenes obtained with these iron(II) and cobalt(II) catalysts has revealed linear microstructure with few branches in the polymer chain. The chain end groups obtained with iron ketimine complexes are highly saturated, the ratio of saturated to unsaturated being 2:1, the ratio is somewhat lower with iron aldimine (R’ = H) complexes. With cobalt complexes the ratio of methyl to vinyl end groups is 1:1 regardless of the chelating ligand.[16]

Iron catalysts with only one methyl substituent on the aryl groups (R = 2-methyl aniline, Scheme 1) have significant selectivity for ethene oligomerization to linear α-olefins, yielding chain end groups with nearly 100 % unsaturation.[17, 18] Sterically bulky substituents on the imino nitrogen donors play an essential role in controlling the speed of propagation vs. chain termination, thus controlling both the activity of the polymerization and molar mass of the polymer. Reducing the size of the substituents on the aryl rings in the iron ketimine catalyst increases the activity but decreases the molar mass. Replacing one proton in the ortho-position by tert-butyl group leads to a slight reduction in the activity but doubles the molar mass. A methyl substituent in the para-position increases the activity and reduces the molar mass. In addition to β-hydrogen transfer, chain transfer to aluminum becomes efficient in the presence of high MAO loadings, typically resulting in the formation of polymer with broad and bimodal molar mass distributions.[16] The nature of the pendant imino donor also heavily influences the polymerization activity and polymer properties.

Iron-based aldimine complexes (R’ = H, Scheme 1) typically show an order of magnitude lower activity than their ketimine (R’ = Me) counterparts derived from 2,6-diacetylpyridine.[16] The results obtained with aldimine complexes follow the trends in activities and molecular weights described above for ketimine complexes but with smaller
differences. However, the polydispersities are exceptionally wide. In contrast to ketimine catalysts, a substituent at para-position of the aryl groups in aldimine ligands has no effect on polymer properties.

Complexes with a variety of aryl-imino substituents have been reported as well, but these usually exhibit lower activities than the parent complex.\textsuperscript{[19, 20]} Extending the polymerization time increases the relative amount of the longer chains in the polyethylene. With both iron and cobalt catalysts, the activity increases almost linearly with ethene pressure (0 to 6 bar), accompanied by narrowing polydispersity (PDI). Increase in polymerization temperature (35-70 °C) causes a clear decrease in activity and molar mass.

\begin{center}
\begin{tikzpicture}
\node (R) at (1,0) {$R'$};
\node (R') at (2.5,0) {$R$};
\node (N) at (2,1) {$N$};
\node (M) at (2.5,2) {$M$};
\node (X) at (3,2.5) {$(X)_n$};
\node (N') at (1,2) {$N'$};
\node (R'') at (2.5,2) {$R$};
\draw (R) -- (N) -- (M) -- (X) -- (M) -- (N') -- (R'');
\end{tikzpicture}
\end{center}

\textbf{Scheme 1.} General structure of bis(imino)pyridine complexes.

Only low to moderate ethene polymerization activities were observed when one or both imino functions were replaced by neutral amino donors.\textsuperscript{21} The tetrahedral amino donor affords a different orientation of the aryl substituents from the bis(imino)pyridine complex, perhaps resulting in more hindered access of the monomer and hence lower activity. Various modifications of the original bis(imino)pyridine ligand framework, metal substitution, and detailed polymerization studies have been reported.\textsuperscript{15a} Modifications of the central donor atom have been reported as well, but these lead to a different group of complexes, which are not discussed in this thesis.

The active species for bis(imino)pyridine complexes are not as well known as those for the \(\alpha\)-diimine nickel and palladium catalysts.\textsuperscript{22, 23} The nature of the active species in the Fe(II) and Co(II) systems has most often been investigated with bis(2,6-diisopropylphenylimino)-pyridine ligand. Initially it was assumed that in the case of the Fe(II) system a 14-electron cationic Fe(II) alkyl species is formed upon activation with MAO,\textsuperscript{16, 24} similarly to
metallocene and the nickel and palladium catalysts. Several conclusions were drawn on the basis of this assumption.\textsuperscript{25} Talsi \textit{et al.}\textsuperscript{26} proposed an initiation mechanism \textit{via} neutral Fe(II) complexes containing TMA or MAO in the coordination sphere of the metal center. Electron paramagnetic resonance (EPR) and Mössbauer studies revealed that, upon addition of MAO, the catalyst precursor bis(imino)pyridine Fe(II) is oxidized to an Fe(III) species.\textsuperscript{27} \textsuperscript{1}H-NMR technique showed the existence of neutral Fe(II) bis(imino)pyridine complexes.\textsuperscript{26} Fe(II) and Fe(III) precursors nevertheless produce similar PE with comparable activities, indicating the existence of the same active species – a species whose exact nature remains unclear.\textsuperscript{16}

Britovsek \textit{et al.}\textsuperscript{16} presented a mechanism for bis(imino)pyridine iron(II) and cobalt(II) catalysts, although the initiating species is unknown. Propagation and chain-transfer pathways are shown in Scheme 2. The propagation mechanism is assumed to be of Cossee type (path A, Scheme 2),\textsuperscript{28} involving migratory insertion of ethene into a metal alkyl bond. Three different chain-transfer pathways can be distinguished (Scheme 2): 1) path B, consisting of two kinetically distinct \( \beta \)-H transfers to metal center, 2) \( \beta \)-H transfer to monomer (path C), and 3) chain transfer to aluminum (path D). \( \beta \)-H transfer to metal (path B) is a general chain-transfer route, especially for polymerization with late transition metals. The \( \beta \)-H elimination reaction is unimolecular and does not depend on monomer concentration provided that the following step, the monomer associative transfer of the polymer chain, is fast. \( \beta \)-H transfer to monomer (path C) is kinetically distinguishable from the \( \beta \)-H transfer to metal center. This chain-transfer pathway is bimolecular, and has been proposed earlier for metallocene catalysts.\textsuperscript{29} The chain-transfer reaction to aluminum (path D) also appears with Ziegler-Natta catalysts,\textsuperscript{30} Group 4 metallocenes,\textsuperscript{29a, 31} and lanthanocenes\textsuperscript{32} and it depends on the alkyl aluminum concentration. In general, \( \beta \)-H-transfer reactions to the metal (two types of path B) or the monomer (path C) give one double bond per polymer chain (vinyl end groups), whereas chain transfer to aluminum (path D) gives saturated polymer chains. NMR and computational studies of cobalt complexes by Gibson \textit{et al.}\textsuperscript{33} have shown that \( \beta \)-H chain transfer proceeds via a stepped mechanism involving a cobalt-hydride species (path B).
Scheme 2. A proposed catalytic mechanism for bis(imino)pyridine iron(II) and cobalt(II) catalysts.\textsuperscript{[16]}
Computational studies have been carried out on bis(imino)pyridine cobalt, where a 15-electron cationic Co(II) alkyl complex was assumed to be the active species. Later experimental results showed that Co(I) or Co(III) complexes could be formed at the active site. Addition of excess MAO to bis(imino)pyridine cobalt causes a color change from green to purple in complex solution. The same color change is seen for bis(imino)pyridine cobalt(I) alkyl complexes. These alkyl complexes do not alone polymerize ethene, but after addition of excess MAO, polymerization proceeds as with the MAO-activated bis(2,6-diisopropylphenylimino)pyridine Co(II) complexes, which means that similar active species are present. The bis(imino)pyridine cobalt(I) methyl complex, after activation with B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} under nitrogen atmosphere, gave a dinitrogen complex, which was isolated. In this complex the coordinated ethene starts slow polymerization, and when an excess of ethene is consumed the cationic ethene complex stays in solution. These results show that, after addition of MAO, the bis(imino)pyridine cobalt(II)Cl\textsubscript{2} reduces to Co(I) complex, forming a cationic monoalkyl complex with MAO-based counteranion. A number of pathways for the initiation of the polymerization reaction from bis(imino)pyridine Co(II) complexes are possible. Cationic monochloride bis(imino)pyridine iron and cobalt complexes where acetonitrile coordinates to the metal center and the charge is stabilized by hexafluoroantimonate anion are described in the literature. In combination with MAO or AlMe\textsubscript{3}/B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} these complexes show high ethene polymerization activities and give relatively narrow polydispersities.

1.1.2. Polymerization of norbornene with transition metal catalysts

Bicyclo[2.2.1]hept-2-ene, better known as norbornene, and its derivatives are polymerized by three methods: (Figure 1.), ring-opening metathesis polymerization (ROMP), cationic or radical polymerization, and vinylic polymerization. Each route yields a different polymer structure and properties.

The most widely studied is the ROMP, which is commercialized in the Norsorex process. ROMP produces polymer with double bonds in the polymer backbone, which allow crosslinking, or vulcanizing. These crosslinked polynorbornene products are used as an elastomeric material for vibration and sound damping in applications such as engine mounts, shock-proof bumpers, and flexible couplings. As well, porous polynorbornene is used as an absorbent material for oil spills. Ring-opening metathesis polymerization of norbornene is
catalyzed by metals like tungsten, rhenium, molybdenum, titanium, tantalum, ruthenium, osmium, and iridium.\textsuperscript{[41]} The unsaturated polymer (poly(1,3-cyclopentylene vinylene)) contains one double bond per repeating unit\textsuperscript{[42]} and the reaction proceeds via a metal carbene species.\textsuperscript{[38a, 43]}

Cationic\textsuperscript{[44]} or radical\textsuperscript{[45]} polymerization of norbornene is initiated by free radicals or ethylaluminum dichloride and results in a 2,7-linked, bicyclic, low molar mass oligomeric material.

Vinylic polymerization, or addition polymerization, leaves the bicyclic structural unit intact and opens only the double bond of the $\pi$-component. Poly(2,3-bicyclo[2.2.1]heptene) is formed in vinylic polymerization catalyzed by transition metal complexes\textsuperscript{[46]} containing nickel,\textsuperscript{[47]} chromium,\textsuperscript{[48]} titanium,\textsuperscript{[49]} zirconium,\textsuperscript{[50]} cobalt,\textsuperscript{[51]} and palladium.\textsuperscript{[52]} Vinylic polymerization resembles olefin polymerization where the product is fully saturated. The vinylic polymerization method allows both homopolymerization of norbornene and copolymerization with several monomers.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Three different methods and polymer units in the polymerization of norbornene.\textsuperscript{[40]}}
\end{figure}
Vinyl-type polymerized polynorbornene is an extraordinary polymer. It has high glass transition temperature, good adhesion to a variety of films and substrates, thermal stability, high elongation-to-break values, heat resistivity, and transparency. It also offers a cost advantage over related materials. Vinyl polynorbornene is currently being investigated as a UV photoresist and dielectric material for microelectronics purposes. Films made of vinyl polynorbornene are of good transparency and heat resistance and provide stable viscoelastic and electric properties at high temperatures; they make suitable insulating material and cover material for liquid-crystal displays. The B. F. Goodrich Company has commercialized the film under the trademark Avatrel® dielectric polymer. In addition, vinyl polynorbornene has been patented for use in IR, visible, and UV light sources and sensors.

The first palladium(II)-based catalysts for norbornene polymerization catalysts were simple salts or nitrile and phosphine adducts. Polymerizations were time-consuming (21 h) and conversions were moderate (20–40%). In the early eighties Sen et al. developed a cationic palladium catalyst in which the metal center was surrounded by four weakly coordinated neutral alkynitrile ligands, and the charge of the complex was stabilized by two tetrafluoroborate anions. Over 90% conversion was achieved in a few minutes time. An essential part of later work rests on this breakthrough. As well, \( \eta^3 \)-allyl, \( \eta^3 \)-allyl, bulky tertiary diamines, and alkyl-type bicyclo[2.2.1]heptenyl palladium complexes have been studied as catalysts for the polymerization of norbornene.

The mechanism of the vinyl-type norbornene polymerization has not yet been resolved. Initiation of a cationic polymerization of norbornene by electrophilic cleavage of the \( \pi \)-bond has been proposed. At least two publications describe cases in which initiation involves introduction of chloride or nitrile ligands into the polymer chain. In addition, a nucleophilic impurity such as water may initiate polymerization through a coordinated alkene resulting in a metal alkyl complex (Scheme 3). The fact that diaqua complexes show better polymerization activities than diacetonitrile palladium complexes suggests the Wacker-like activation reaction. The chain propagation step in the vinylic polymerization of norbornene is considered to proceed by insertion of the coordinated monomer into the metal–carbon bond (Scheme 3).
Scheme 3. A proposal for Wacker-type activation mechanism relying on palladium aqua complexes.\textsuperscript{[63]}

1.2. Polar Monomer Polymerization

A great deal of attention is currently being paid to polymers containing polar monomers, which may give rise to new high-performance materials with high adhesion and toughness and good dyeing and moisture adsorption properties\textsuperscript{[8]} Metal-based catalysts tolerant of polar functionalities, which perform homopolymerization, and if possible copolymerization with nonpolar olefins, are being sought. Late transition metal complexes look promising because of their lower oxophilicity, and probable tolerance against polar monomers, and against impurities in ethene polymerization. This is a challenging area, offering new avenues in polymerization catalyst research. The polymerization of acrylates, \textit{n}-vinylcarbazole, and acrylonitrile is reviewed below.

1.2.1. Acrylates

Acrylates are polymerized and copolymerized for many different uses including coatings, textiles, adhesives, and paper\textsuperscript{[65]} Commercial poly(methyl methacrylate) has been produced since 1927\textsuperscript{[66]} Like many other polar monomers, acrylates are commonly polymerized by
radical$^{67}$ or anionic$^{68}$ mechanisms. In addition, polymerization of acrylates with late transition metal complexes has been studied.

Radical mechanisms
The classical free radical mechanism is uncontrolled in terms of molar mass and polydispersity. Both atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer mechanism (RAFT)$^{69}$ offer better control over the polymerization. Group transfer polymerization (GTP) also gives good control in acrylate polymerization, but as the mechanism is under dispute this method is discussed under anionic mechanisms, with which it has significant similarities. Recently, polymerization of tert-butyl acrylate (tBA) has been demonstrated by ATRP.$^{70}$ As well as offering good control over polymerization, ATRP tolerates functional groups and impurities, and potential of this method is thus of considerable interest to industry.$^{71}$

Scheme 4. Classical free radical mechanism initiation (a), propagation (b), and termination (c).$^{72}$
The free radical mechanism involves formation of an initiating radical species and addition of the radical to monomer. The monomer quickly inserts to the growing chains and termination occurs through recombination or disproportionation (Scheme 4.) The major difference between the controlled radical polymerization mechanisms and the classical free radical mechanism is in the termination, which occurs in the controlled mechanism in less than a few per cent of the total number of chains. Narrow molar mass distribution is achieved as a result.

ATRP (and living radical polymerization) proceed without side reactions like termination and chain transfer at all, and in this way allow the preparation of polymers with well-defined architectures. Propagation takes place at the same or at lower rate than initiation, which as already noted, leads to narrow molar weight distribution.\[73\]

Anionic mechanisms
Organometallic compounds of group I and II metals generally operate as initiators of acrylate polymerization through anionic mechanism. Polymer architectures and molar masses generated in anionic polymerization depend on both initiator and solvent.\[65\] In nonpolar solvent, for example, acrylates generally yield isotactic polymers, whereas in polar solvent syndiotactic polymers are favored,\[74\] but evidently the size of the counterion plays a role.\[75\] The mechanism that leads to stereoregularity is still unclear.\[76\]

Anionic polymerization mechanism is based on the Michael reaction where the initiating species form a nucleophilic addition to monomer and the resonance of the carbanion stabilizes it (Scheme 5). Propagation occurs by head-to-tail addition of the monomer. Termination reaction with acrylates is a nucleophilic substitution by intramolecular backbiting attack of a propagating carbanion.

In the GTP method, which in some ways resembles the anionic mechanisms, backbiting reaction rates are much lower than propagation rates,\[77\] Usually organosilicon compounds initiate polymerization in the presence of an anionic or a Lewis acid catalyst.\[78\]
Late transition metal-mediated polymerization of acrylates

Late transition metal-mediated vinyl polymerization of acrylates is an area of great current interest because of the control over polymer microstructure, molecular weight, and polydispersity that such systems are expected to provide.[79][13] Recently, iron, cobalt, nickel, and copper based polymerizations of acrylates have been described.[80] Some of these MAO-activated polymerizations have been carried out with radical traps to hinder the radical polymerization,[67b, 81] though at least one report has suggested that radical traps are irrelevant in the presence of MAO.[82] Moreover, radical traps may react with and deactivate metal-based systems via coordination.[83] Use of radical traps assumes that reaction occurs only via radical species, and the traps are only hindering radical polymerization while leaving other species unaffected. In palladium and copper-based systems, however polymerization reaction occurs with low activity. More research on late transition metal-assisted polymerization of vinyl monomers is needed before firm conclusions can be drawn about mechanism.
1.2.2. n-Vinyl carbazole and acrylonitrile

Poly(n-vinylcarbazole) (PVCZ) has been a focus of study because of its uses in photoconductors,[84] electroluminescent devices,[85] and photo-refractive materials.[86] Known polymerization mechanisms for PVCZ include free radical, conventional cation (protonic acids, Lewis acids, carbocations), photo-initiation, Ziegler-Natta, charge-transfer electrochemical, vapor deposition, and solid state.[87]

Polyacrylonitrile (PAN) and related copolymers are produced commercially by radical polymerization method. PAN has also been polymerized by controlled radical polymerization. [88, 89] Several metal complexes have been studied for the polymerization of AN. Some of the processes are known to be anionic, while others are of unclear mechanisms.[90] AN polymerized by radical mechanism is normally completely linear, whereas anionic polymerization generates low molar mass branched PAN.[91]

2. RESULTS AND DISCUSSION

The focus of this research was the synthesis of catalyst precursors and the use of these precursors in the polymerization of ethene, norbornene, and some polar monomers. All reactions were carried out under dry argon using standard Schlenk techniques, and hydrocarbon solvents were purified by refluxing over sodium or lithium aluminum hydride, methanol was treated with sodium methoxide/dimethyl terephthalate followed by distillation under argon.[1-VI] Synthesized precursors were characterized by ¹H and ¹³C nuclear magnetic resonance spectroscopy (NMR), elemental analysis (EA), infrared resonance spectroscopy (IR), mass spectrometry (MS), melting point analysis, and magnetic susceptibility measurement. Polymers were characterized by gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA).

2.1. 2,6-Bis(imino)pyridine complexes of iron(II) and cobalt(II)[IV-VI]

Late transition metal-catalyzed polymerization is an area of considerable interest because of the expectation that these catalysts can tolerate polar monomers and are robust against impurities in the polymerization reaction. Also, correlations have been established between
catalyst structure and polymer microstructure, molar mass, and polydispersity. Iron and cobalt complexes are particularly good candidates because they are cheap, abundant, and relatively easy to handle during the preparation. As noted in the introduction, iron and cobalt complexes bearing tridentate bis(imino)pyridine ligands possess high activities in ethene polymerization and this ligand family was further explored here.[V]

2.1.1. Ligands

Tridentate ligands (1-11) were prepared by imine Schiff-base condensation reaction, where two equivalents of primary amine were reacted with 2,6-diacylpyridine (ketimine) or 2,6-pyridinedicarboxaldehyde (aldimine) (Figure 2). The products were yellow or white, aromatic amines usually forming yellow and aliphatic amines white bis(imino)pyridine compounds. Polar solvent (MeOH) was used in the reactions, and formic acid to catalyze all the ketimine condensation reactions and some of the aldimine reactions (Figure 2). Reaction temperature ranged from room temperature to 50 °C, and reaction time was from 4 h to three days.

The reactions can be followed by IR for the strong aldehyde and ketone peaks disappear and new peaks appear between 1620 and 1642 cm⁻¹ due to the imine (C=N) bond. In ¹³C-NMR spectra the tridentate ligands exhibit a singlet signal at about 160-169 ppm, which can be assigned to the imine (C=N) carbon. The ketimine ligands also show a singlet at 13.9 - 17.5 ppm, which can be ascribed to the methyl groups in the backbone of the ligand.

![Figure 2. Synthesis of the 2,6-bis(imino)pyridine ligands.[V-VI]](image_url)
2.1.2. Complexes and solid state structures

The pentacoordinated iron(II) and cobalt(II) complexes (12-29, Figure 3) were synthesized by reaction of FeCl₂ or CoCl₂ with 2,6-bis(imino)pyridine ligands in THF (Figure 2). Reaction time varied between 3 and 24 h and complexes were isolated in moderate to high yields. The complexes were brown, green, or blue.

Figure 3. 2,6-Bis(imino)pyridine complexes prepared in this work. [V-VI]
The crystal structure of the complex 17 was solved in this work. Complex 17 crystallized with two discrete cobalt(II) complexes and one solvent molecule in the asymmetric unit cell. The coordination sphere around the cobalt can be roughly classified as distorted trigonal bipyramid in which the imino nitrogens of the ligand occupy the axial positions, and two chlorines and the nitrogen atom of the pyridine form the trigonal plane. Trigonal bipyramid describes well the C$_2$-symmetry of this molecule when the pyridine nitrogen and the cobalt atom are chosen for as the rotation axis.

The solid state structure of 17 is closely related to the structure described by Britovsek et al. for the 2,6-bis[(2,6-diisopropylphenylimino)ethyl]pyridine cobalt(II) complex (BPEP-Co(II)).\[^{16}\] A clear difference in the geometry of the two complexes is the location of the cobalt in respect of the N$_3$-plane. In the Co complex of reference [16], the cobalt deviates from the plane by 0.56 Å, whereas in 17 the corresponding deviations are only 0.0706(3) Å and 0.0278(3) Å. We assume that this difference is due to the change of the imino substituents from aromatic to aliphatic. In addition, the ligand framework of 17 is twisted, as can be seen in the side-view presented in Figure 4. The imino nitrogens are shifted to opposite sides of the mean plane, established by the pyridine and the cobalt center.

![Figure 4](image.png)

**Figure 4.** Solid state structure of 17. The second cobalt complex and the solvent molecule and hydrogen atoms are omitted for clarity. \[^{[VI]}\]

2.2. **Palladium Complexes with Nitrogen, Phosphorus, Sulfur and Arsene Donor Atoms**

Palladium(II) complexes with symmetrical bidentate P- or N-donor ligands are well-known and their catalytic activity has been widely investigated.\[^{8}\] At the same time, research on asymmetrical complexes with mixed donor atoms *e.g.*, ligands bearing P and S or N as donor atoms, has been insignificant. A general feature of the coordination chemistry of complexes
that carry mixed donor ligands is that a stronger donor group, such as an aryl phosphine, can stabilize the metal ion in low oxidation states, and a weakly coordinating site having an S or N atom can be substituted with a π-acceptor ligand.\[92\]

2.2.1. Ethyl bridged palladium(II) complexes and solid state structures\[I,II,IV\]

Asymmetrical palladium(II) complexes \([\text{Pd}(\text{P} \cap \text{P})\text{Cl}_2]\) (33), \([\text{Pd}(\text{S} \cap \text{P})\text{Cl}_2]\) (34) and \([\text{Pd}(\text{S} \cap \text{As})\text{Cl}_2]\) (35) were prepared by stirring the ligands 30, 31, and 32, respectively, with \(\text{Pd(NCPh)}\text{Cl}_2\) in acetone. Ligands were prepared by the reaction of \(\text{Na}^+\text{P(CH}_3\text{)}_2\) or \(\text{Na}^+\text{As}^-(\text{C}_6\text{H}_5)_2\) with 2-chloroethylmethyl sulfide.\[93\] Chloride abstraction from the complexes 33, 34, and 35 with \(\text{AgBF}_4\) afforded the solvated diacetonitrile derivatives 36, 37, and 38, respectively (Figure 5). The complexes were characterized by elemental analysis and \(^1\text{H}\) NMR and IR spectroscopy.

\[30, 31, 32\]: \(X = \text{P}; Y = \text{P Ph}_2\)

\[31, 34, 37\]: \(X = \text{P}; Y = \text{S-CH}_3\)

\[32, 35, 38\]: \(X = \text{As}; Y = \text{S-CH}_3\)

\[\text{Pd(PhNC)}_2\text{Cl}_2\] Acetone \(\text{R.T}\) \([\text{Pd}(\text{P} \cap \text{P})\text{Cl}_2]\) \([\text{Pd}(\text{S} \cap \text{P})\text{Cl}_2]\) \([\text{Pd}(\text{S} \cap \text{As})\text{Cl}_2]\) \(\text{Cl}^-\) abstraction \(\text{AgBF}_4\) \(\text{NCCH}_3\) \(\text{NCCH}_3\) \(\text{NCCH}_3\) \(\text{Cl}^-\) abstraction \(\text{AgBF}_4\)

**Figure 5.** Preparation of palladium(II) complexes containing hetero donor atoms and corresponding ion-pair complexes.\[II,IV\]

Crystal structures of complexes 34 and 35 were determined from crystals obtained by recrystallization from acetone. Both complexes crystallized in the monoclinic space group and, as expected, the Pd atoms have square-planar coordination sphere.
Figure 6. Crystal structures of the ethyl-bridged palladium(II) complexes $34^1$ and $35^{II}$

The Pd-Cl1 and Pd-C12 bonds are shorter in the complexes $34$ and $35$ than in the corresponding symmetrical bisphosphine complexes [Pd- (P-P)Cl$_2$].$^{[94]}$ Furthermore, the metal–halide bond trans to the S atom is shorter than that trans to the P or As atom. This could be due to the stronger trans influence$^{[95]}$ of the P and As donor atoms than the S atom. The longer Pd-Cl bond when P is the trans group is in agreement with previous NMR investigations carried out on the corresponding mono- and dialkyl complexes.$^{[96]}$

2.2.2. Pyridinylimine palladium(II) complexes and solid state-structures$^{[III]}$

The pyridinylimine palladium(II) complexes ($42$, $43$, and $44$) were prepared in good yields (55–77%) by stirring the ligands $39$, $40$, and $41$, respectively, with [(COD)PdCl$_2$] in dichloromethane. Chloride abstraction from compounds $42$ and $43$ with AgBF$_4$ afforded the solvated diacetonitrile complexes $45$ and $46$ (Figure 7) although the reaction to the cationic species proved to be somewhat complicated. In the case of the dimethylphenylamine complex $44$, chloride abstraction led to decomposition, and the corresponding ion-pair compound was not obtained. The complexes $42$, $43$, and $44$ were characterized by elemental analysis and $^1$H NMR spectroscopy.
Figure 7. Synthesis of the pyridinylimine palladium(II) complexes and corresponding counterion complexes.\[^{[III]}\]

Crystal structures of complexes 43 and 44 are presented in Figure 8. Crystals were obtained by recrystallization from acetone (43) and a mixture of acetone and pentane (1:1). The asymmetric unit of 44 contains two independent, closely similar molecules, whereas only one molecule is present in the asymmetric unit of complex 43. Both palladium compounds have square-planar coordination spheres consisting of two chlorine atoms (Cl1 and Cl2) and two nitrogen atoms of the ligand (N1 and N8). As in related pyridinylimine\[^{[97]}\] and bipyridine\[^{[98]}\] complexes, in both cases the square structure is slightly deformed as a result of the narrow nitrogen–palladium–nitrogen angle.
2.3. Polymerizations

Iron(II) and cobalt(II) complexes were studied in the polymerization of ethene and tert-butyl acrylate and palladium(II) complexes in the polymerization of norbornene.

2.3.1. Polymerization of ethene

Ethene polymerizations were carried out in a 1 L Büchi glass reactor. In a typical polymerization experiment, the reactor was charged with 200 ml toluene and the system was pressurized with ethene up to the desired concentration; the appropriate amount of the complex and MAO, previously mixed together, were then introduced. Pressure, inside temperature, and the consumption of ethene were recorded as a function of time online with Advantech GENIE® runtime software. The mechanical stirrer was run at 1800 rpm for all experiments to avoid diffusion controlled polymerization reactions. After the preferred polymerization time, the polymerization was stopped by quenching with methanol containing 2% HCl. Polymers were washed with methanol and dried overnight at 70 °C. Molar mass and molar mass distributions were measured by gel permeation chromatography (GPC) relative to polystyrene standards.

Of the series of catalyst precursors prepared in this work the most active complex was 26 [(BBzEP)FeCl₂], which produced polyethene up to 40860 kg PE/(mol cat. h) (Table 1 entry 6). The catalyst is formed with a ketimine ligand where the ligand bears one benzyl substituent on each phenyl group. Better understanding of the influence of benzyl substituents was sought by preparing iron(II) complexes of the ligands 2,6-bis[(1-phenylimino)ethyl]pyridine (21) and 2,6-bis[(1-(cis)-myrtanylimino)ethyl]pyridine (14) and some corresponding aldimine complexes for comparison. The activity of these complexes very low, however, and no convincing reason was found for the high activity of complex 26.
Table 1. Results of ethene polymerizations with selected catalyst precursors

<table>
<thead>
<tr>
<th>entry</th>
<th>Cat.</th>
<th>Loading (µmol)</th>
<th>Pressure (bar)</th>
<th>Yield (g)</th>
<th>Activity $10^3$ (kg PE/mol. cat. h)</th>
<th>Mw$^a$ $x10^3$ (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24</td>
<td>(BNaEP)FeCl$_2$</td>
<td>3.0</td>
<td>3.0</td>
<td>28.5</td>
<td>9.50</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>(BNaEP)CoCl$_2$</td>
<td>3.0</td>
<td>3.0</td>
<td>2.02</td>
<td>0.673</td>
</tr>
<tr>
<td>3</td>
<td>28</td>
<td>(BPyEP)FeCl$_2$</td>
<td>3.0</td>
<td>3.0</td>
<td>33.7</td>
<td>13.48</td>
</tr>
<tr>
<td>4</td>
<td>29</td>
<td>(BPyEP)CoCl$_2$</td>
<td>3.0</td>
<td>3.0</td>
<td>0.31</td>
<td>0.103</td>
</tr>
<tr>
<td>5</td>
<td>26</td>
<td>(BBzEP)FeCl$_2$</td>
<td>3.0</td>
<td>3.0</td>
<td>44.0</td>
<td>11.00</td>
</tr>
<tr>
<td>6</td>
<td>26</td>
<td>(BBzEP)FeCl$_2$</td>
<td>1.0</td>
<td>2.0</td>
<td>20.43</td>
<td>40.86</td>
</tr>
<tr>
<td>7</td>
<td>26</td>
<td>(BBzEP)FeCl$_2$</td>
<td>1.1</td>
<td>1.0</td>
<td>3.25</td>
<td>2.96</td>
</tr>
<tr>
<td>8</td>
<td>27</td>
<td>(BBzEP)CoCl$_2$</td>
<td>3.0</td>
<td>3.0</td>
<td>0.22</td>
<td>0.073</td>
</tr>
<tr>
<td>9</td>
<td>14</td>
<td>(BMyEP)FeCl$_2$</td>
<td>3.0</td>
<td>3.0</td>
<td>0.1</td>
<td>0.033</td>
</tr>
<tr>
<td>10</td>
<td>21</td>
<td>(BPhEP)FeCl$_2$</td>
<td>3.0</td>
<td>3.0</td>
<td>0.19</td>
<td>0.063</td>
</tr>
</tbody>
</table>

Conditions: Cat/MAO, 1:1000 (entry 7, 1:300); Solvent (toluene, 200 mL); Polymerization time 60 min (entry 6, 30 min); Temperature, 30 °C.

$^a$ Molecular weight data reported against polystyrene standards.

$^b$ n.d.: not determined.

The possibility to control polymer microstructures through choice of ligand was demonstrated by $^{13}$C-NMR analysis. 2,6-Bis[1-(2-benzylphenylimino)ethyl]pyridine (26) produces linear polyethene, whereas 2,6-bis[(1-naphthylimino)ethyl]pyridine (24) and 2,6-bis[(1-pyrenylimino)ethyl]pyridine (28) produce branched polymers. Catalysts containing bulkier pyrenyl groups produce less branched polymers. GPC measurements showed that the polymers contain both high and low molar mass fractions. A wide molar mass distribution is typical for this kind of MAO-activated catalyst. According to differential scanning calorimetry (DSC), the polymer samples exhibit melting temperatures ($T_m$) ranging from 90 to 129 °C.
2.3.2. Polymerization of norbornene and phenylnorbornene

Norbornene polymerizations were carried out with MAO-activated palladium(II) chloride complexes (33-35 and 42-44) in toluene or by utilizing the self-activated dicationic species (36-38 and 45-46) in a reaction medium consisting of a mixture of dichloromethane, 1,2-dichlorobenzene, and nitrobenzene. The amorphous, transparent polymer products consist of 2,3-linked norbornene units. Monomer conversion up to 100% were achieved with the right choice of ligand and catalyst system. Highest polymer yields (100%) were obtained with use of the MAO-activated N∩N-PdCl₂ complex in Pd: MAO ratio of 1:1000. When the ratio was lowered to 1:200, yields were clearly smaller than in other MAO polymerizations, but polydispersity was slightly narrower. Given the low yield in this system, the ratio 1:200 can be considered too low. At high monomer conversions neither low solubility or high viscosity of the polynorbornene had an effect on the activity in polymerizations in toluene. Single-component Pd(II) catalysts and MAO-activated Pd(II) catalysts with S∩P and P∩P ligands showed considerably higher activity than the corresponding Pd(II) complex with S∩As ligand under similar reaction conditions (Table 2 entries 1-3).

**Table 2.** Results obtained in the homopolymerization of norbornene with catalyst precursors containing N, P, S and As donor atoms.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>Catalyst</th>
<th>Monom./Pd (mol ratio)</th>
<th>Al/Pd (mol ratio)</th>
<th>Time (h)</th>
<th>Mₘ (g/mol) x10³</th>
<th>Mₘ/Mₙ</th>
<th>Yield (g)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S∩As</td>
<td>38</td>
<td>808</td>
<td>2</td>
<td>3.89</td>
<td>1.59</td>
<td>3.67</td>
<td>63.8</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>S∩P</td>
<td>37</td>
<td>808</td>
<td>2</td>
<td>5.71</td>
<td>1.87</td>
<td>5.48</td>
<td>89.5</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>P∩P</td>
<td>36</td>
<td>808</td>
<td>2</td>
<td>4.73</td>
<td>1.91</td>
<td>5.0</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>N∩N</td>
<td>45</td>
<td>800</td>
<td>2</td>
<td></td>
<td></td>
<td>0.21</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>N∩N</td>
<td>46</td>
<td>800</td>
<td>2</td>
<td></td>
<td></td>
<td>Trace</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>S∩As</td>
<td>35</td>
<td>500</td>
<td>200</td>
<td>0.15</td>
<td>1.65</td>
<td>0.77</td>
<td>15.8</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>S∩P</td>
<td>34</td>
<td>500</td>
<td>200</td>
<td>2.86</td>
<td>1.81</td>
<td>2.29</td>
<td>42.6</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>P∩P</td>
<td>33</td>
<td>500</td>
<td>200</td>
<td>2.82</td>
<td>1.34</td>
<td>2.56</td>
<td>62.6</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>N∩N</td>
<td>42</td>
<td>800</td>
<td>1000</td>
<td></td>
<td></td>
<td>4.22</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>N∩N</td>
<td>44</td>
<td>800</td>
<td>1000</td>
<td></td>
<td></td>
<td>4.74</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>N∩N</td>
<td>43</td>
<td>800</td>
<td>1000</td>
<td></td>
<td></td>
<td>4.11</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>
Palladium(II) complexes with \( \text{N} \cap \text{N} \) ligands have very much lower activity under the same polymerization conditions (Table 2 entries 4, 5). A reason for the lower activity with \( \text{N} \cap \text{N} \) ligands has been presented in the literature: palladium alkyl species and direct metal–carbon bond are essential for activation and insertion of the first monomer. The role of the metal–carbon bond was also studied with cationic palladium complexes containing alkyl-type norbornyl ligands.

The polymerization of phenylnorbornene (5-phenylbicyclo[2.2.1]hept-2-ene) was carried out for comparison, because phenylnorbornene is a bulky monomer with two chiral forms, endo / exo. Only the exo form in the phenylnorbornene mixture is polymerized, as was easily verified from absorption of the polymer in the IR region between 600 and 800 cm\(^{-1}\). The isolated poly(phenylnorbornene)s showed strong absorption at 697 cm\(^{-1}\), which can be ascribed to the exo structure. Polymer yields were low partly because the monomer mixture contained only 20% of the exo form.

Thermogravimetric analysis (TGA) carried out under nitrogen atmosphere showed most of the polynorbornenes to be stable up to 330 °C. Polynorbornenes polymerized by complexes containing phosphorus atom were exceptional in their stability and only began to decompose at temperatures above 425 °C. Phenylnorbornenes, in turn began to decompose at 300 °C.

2.3.3. Polymerization of polar monomers

All \emph{tert-}butyl acrylate (a), acrylonitrile (b), methyl acrylate MA (c), and \emph{n-}vinylcarbazole (d) polymerization experiments were performed under dry argon atmosphere with the standard Schlenk technique. The desired amount of complex (2 \( \mu \)mol) and dry toluene (0.0–5.5 mL) were added to a Schlenk tube. The suspension was stirred at room temperature, and after MAO (30% volume concentration of MAO, 0.1 mL) treatment the complex dissolved and a monomer was introduced. The polymerization solution was stirred at the desired temperature for 24 h. Under these conditions, rapid formation of a gel was observed. After the desired reaction time, hexane (20 mL) was poured into the Schlenk tube followed by 20 mL of 2 M HCl solution. After 10 min of vigorous stirring, 20 mL of tetrahydrofuran (THF) and 20 mL of methanol were added. The solution was maintained under vigorous stirring at room temperature until all solid material had disappeared. The organic solvents were then evaporated under reduced pressure, and the polymers were precipitated in the water phase (Figure 9). After filtration, the polymer was rinsed with water to remove traces of acid and...
dried in the oven at 60 °C until constant weight was obtained. Conversions were determined gravimetrically.

**Figure 9.** Polymers formed in the polymerization of polar monomers were (a) poly(tert-butyl acrylate), (b) poly(acrylonitrile), (c) poly(methyl acrylate) and (d) poly(n-vinylcarbazole).

Fe(II)–, and Co(II)– 2,6-bis(imido)pyridine complexes were investigated for the polymerization of tert-butyl acrylate after MAO activation. It emerged from this study that the choice of metal strongly influences the activity of the initiation system as well as the molar mass of the polymer. Polymerization results showed that the iron(II) complexes to be more active and to produce poly(t-BA) with significantly higher molar mass than their cobalt analogues (Figure 10).

**Figure 10.** Comparison of conversions and molar masses with selected iron (12, 16) and cobalt (13, 17) complexes.

Complexes bearing bulky aliphatic substituents exhibited highest activities in t-BA polymerizations, while activity with the aromatic substituted complexes is as generally at a lower level. Influence of the polymerization conditions is also significant; molar mass of the
polymers increased with monomer concentration, and polymers from low to ultra high (3 000 000 g/mol) molar masses could be prepared (Figure 11).

Figure 11. Molar mass of poly-\textit{t}-butyl acrylate as a function of monomer concentration in 24 h polymerization at RT.\textsuperscript{[VI]}

MAO–activated complex 20 was also tested for polymerization of acrylonitrile, methyl acrylate, and \textit{n}-vinylcarbazole (Table 3). Conversion was a bit slower in the polymerization of methyl acrylate (MA) (d), than in the polymerization of \textit{t}-BA (62%) under similar conditions (Table 3, entry 3). The molar mass of the MA polymer was significantly lower (178 kg/mol) than the molar mass obtained for \textit{t}-BA (1260 kg/mol). Polymerization of the acrylonitrile with 20/MAO proceeded slowly and white insoluble polymeric material was isolated. On the basis of DSC, IR, and elemental analysis, the material was identified as polyacrylonitrile. Desired catalyst control of the polymerization of \textit{n}-vinylcarbazole was introduced by applying similar polymerization conditions to those described for \textit{t}-BA. The results showed the polymerization of \textit{n}-vinylcarbazole to be highly efficient and well controlled as polymers with high molar mass and narrow polydispersity were obtained.
Table 3. Polymerization results for selected monomers with catalyst 20 activated with MAO.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Monomer</th>
<th>c</th>
<th>Conversion\textsuperscript{a}</th>
<th>(M_n)\textsuperscript{b}</th>
<th>(M_n/M_n)\textsuperscript{b}</th>
<th>(T_g)\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(mol/L)</td>
<td>(%)</td>
<td>(\times 10^3) (g/mol)</td>
<td></td>
<td>(°C)</td>
</tr>
<tr>
<td>1</td>
<td>acrylonitrile</td>
<td>b</td>
<td>1.1</td>
<td>33</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>(n)-vinylcarbazole</td>
<td>c</td>
<td>1.1</td>
<td>95</td>
<td>128.1</td>
<td>1.7</td>
</tr>
<tr>
<td>3</td>
<td>methyl acrylate</td>
<td>d</td>
<td>5</td>
<td>52</td>
<td>173.8</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Polymerization conditions: room temperature; solvent toluene (constant volume 6 mL), polymerization time 24 hours
\textsuperscript{a}Determined gravimetrically
\textsuperscript{b}Determined by GPC relative to polystyrene standards
\textsuperscript{c}Determined by DSC
3. CONCLUSIONS

The discovery of tridentate 2,6-bis(imino)pyridine iron and cobalt complexes for olefin polymerization in 1998 sparked an intense worldwide investigation. The study described here represents part of this investigation, expanding the use of these catalysts to the polymerization of polar vinyl monomers. As well, palladium complexes containing nitrogen, phosphorus, arsenic, and sulfur donor atoms were developed for polymerization of norbornene.

Tridentate 2,6-bis(imino)pyridine ligands were synthesized by imine condensation reaction. An acid catalyst is essential with diacetyl pyridine, but is less important for a good yield in the reaction with pyridine dicarboxaldehyde. Complexations were achieved by direct reaction of the ligand with iron(II) and cobalt(II) dichloride. 2,6-Bis(imino)pyridine iron catalysts produced polyethylene with good activity and high molar mass, while cobalt analogues exhibited lower activities and produced polyethylene with lower molar mass.

Both iron and cobalt complexes were active in the polymerization of tert-butyl acrylate. But again the iron complexes were more active. The use of MAO-activated 2,6-bis(imino)pyridine iron initiator in the homopolymerization of various polar monomers was demonstrated. Preliminary polymerization experiments indicated that these catalysts are also active in the polymerization of acrylonitrile, methyl acrylate, and n-vinylcarbazole. Activity varied significantly depending on the monomer.

Bidentate palladium complexes were synthesized by ligand exchange from solvent adduct-type precursors, which afforded the corresponding ethyl bridge or pyridinylimine complexes. In the solid state, palladium compounds have square-planar coordination around the metal. In ethyl bridge complexes trans-influence was seen for P, As, and S atoms. Activity in the MAO-activated polymerization of norbornene was good with all of these catalysts. Pyridinylimine single component catalyst gave unsatisfactory results in norbornene polymerization, while ethyl-bridged single-component catalysts exhibited higher activities under similar conditions. Polymerization of phenylnorbornene with these catalysts under the same reaction conditions yielded only low conversions.
REFERENCES


56. L. F. Rhodes, A. Bell, R. Ravikiran, J. C. Foniran, S. Jayaraman, B. L. Goodall, R. A
   518. (c) J. P. Mathew, A. Reinmuth, J. Melia, N. Swords, W. Risse Macromolecules 29
   173.
   385.
65. R. W. Novak in Kirk-Othmer Encyclopedia of Chemical Technology ( Eds.: J. I.
   pp.314-343.
66. E. Penzel in Ullmann’s Encyclopedia of Industrial Chemistry (Eds.:B. Elvers, S. Hawkins,
67. (a) V. C. Gibson, E. L. Marshall in Comprehensive Coordination Chemistry II (Eds.: J. A.
   29. (b) G. Tian, H. W. Boone, B. M. Novak Macromolecules 34 (2001) 7656. (c) C. Elia,
   S: Elyashiv-Barad, A. Sen Organometallics 21 (2002) 4249. (d) A. C. Albéniz, P.
   Espinet, R. López-Fernández Organometallics 22 (2003) 4206. (e) E. Polo, A. Barbieri,


