Copolymerization of Higher Olefins with Carbon Monoxide by Pd(II) Catalysts and Design of Nickel, Palladium, and Zirconium Complexes with Nitrogen-Based Ligands

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Academic Dissertation

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Abstract

The thesis describes the synthesis and characterization of nitrogen-based ligands and their nickel, palladium and zirconium complexes. The complexation of salicylketimine ligands with trans-(PPh₃)₂Ni(Ph)Cl was studied to broaden understanding of the neutral Ni catalysts that were recently found highly active in olefin polymerization. Several chiral nickel and palladium complexes bearing myrtanyl or bisoxazoline ligands were synthesized for purposes of asymmetric homogeneous catalysis. The versatile coordination chemistry of axially chiral bianiline-based N-donor ligands with Pd(II) and Zr(IV) was studied by preparing the complexes and characterizing their molecular structures. Possible exploitation of their structural features and catalytic behavior in olefin polymerization was examined.

The history and background of polyketone synthesis is briefly discussed. The alternating copolymerization of carbon monoxide and higher olefins by Pd(II) catalysts was found a feasible route to functionalized polyketone materials, which were characterized for their structure and physical properties by IR, NMR, GPC, and DSC. With [(dppp)Pd(NCCH₃)₂](BF₄)₂ as catalyst precursor, olefin functionalities were inserted in the main chain or in side chains by co- and terpolymerization of methylenecycloalkanes and dienes with CO and propene. The stability of polyketone materials against environmental stress could be enhanced by incorporating phenolic antioxidants in the polymer chain as comonomers. Finally, alternating CO/norbornene copolymers were prepared with Pd(II) catalysts based on As∩S heterodonor ligands.
Preface

This work was done in the Laboratory of Inorganic Chemistry at the University of Helsinki between 2000 and 2004. A research period from November 2001 to July 2002 was spent in AG Brintzinger at the University of Konstanz, Germany. Financial support from the Fortum Foundation, the Finnish Cultural Foundation, and Alfred Kordelin Foundation is gratefully acknowledged.

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Helsinki, November 2004

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This thesis is based on the following publications (I-VII), where the experimental details can be found.


**Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Compound/Definition</th>
</tr>
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<tbody>
<tr>
<td>(1R, 2S)-inda-box</td>
<td>3aR-[2(3′aR*,8′aS*),3aβ,8′aβ]-(+)-2,2′-Methylene-bis(3a,8a-dihydro-8H-indenol(1,2-d)-oxazol)</td>
</tr>
<tr>
<td>Anthr</td>
<td>9-Anthracene</td>
</tr>
<tr>
<td>AP-MALDI MS</td>
<td>Atmospheric pressure matrix-assisted laser desorption ion-trap mass spectrometer</td>
</tr>
<tr>
<td>BINAP</td>
<td>2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl</td>
</tr>
<tr>
<td>BIPHEMP</td>
<td>6,6′-Bis(diphenylphosphino)-2,2′-dimethylbiphenyl</td>
</tr>
<tr>
<td>BMDI</td>
<td>N,N′-Bis{(-)-cis-myrtanyl}butylene-2,3-diimine</td>
</tr>
<tr>
<td>COD</td>
<td>1,5-Cyclooctadiene</td>
</tr>
<tr>
<td>DME</td>
<td>1,2-Dimethoxyethane</td>
</tr>
<tr>
<td>dppp</td>
<td>1,3-Bis(diphenylphosphino)propane</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel permeation chromatography</td>
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<tr>
<td>Hp-ol</td>
<td>1,6-Heptadien-4-ol</td>
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<tr>
<td>MAO</td>
<td>Methylaluminoxane</td>
</tr>
<tr>
<td>MCP</td>
<td>Methylene cyclopropane</td>
</tr>
<tr>
<td>MMAO</td>
<td>Modified methylaluminoxane</td>
</tr>
<tr>
<td>MS-EI</td>
<td>Electron ionization mass spectrometer</td>
</tr>
<tr>
<td>nBuLi</td>
<td>n-Buthyllithium</td>
</tr>
<tr>
<td>Od</td>
<td>1,7-Octadiene</td>
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<tr>
<td>Phen</td>
<td>9-Phenanthroline</td>
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<tr>
<td>Ph</td>
<td>phenyl</td>
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<tr>
<td>PE</td>
<td>Polyethylene</td>
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<tr>
<td>P</td>
<td>Propene</td>
</tr>
<tr>
<td>r.t.</td>
<td>Room temperature</td>
</tr>
<tr>
<td>sal</td>
<td>Salicylketiminato</td>
</tr>
<tr>
<td>'Bu₄biphenO₂</td>
<td>3,3′,5,5′-(tert-butyl)₄-1,1′-bi-2-phenolate</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analyzer</td>
</tr>
<tr>
<td>TMEDA</td>
<td>Tetramethylethylenediamine</td>
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1 Introduction

Developments in organometallic chemistry have spurred the homogeneous catalysis industry, and vice versa, ever since the early days of hydroformylation in the late thirties. And, as D. Seebach has stated: “the discovery of truly new reactions is likely to be limited to the realm of transition-metal organic chemistry”.1 The catalytic production of polyolefins for everyday use would not be what it is today without the findings of Karl Ziegler and Giulio Natta in the mid 1950’s.2 Ziegler discovered that TiCl4 together with aluminum alkyls could polymerize ethene, and Natta demonstrated the formation of crystalline isotactic polypropene. The research on early-transition-metal polymerization catalysts evolved significantly after the high activity of metallocenes as soluble and well-defined catalyst precursors was discovered and the step-by-step comparisons of catalyst structure – polymer properties became possible.3 The finding that the structure of a polyolefin can be tailored by small changes in the ligand frame of the metalloocene catalyst in this homogeneous process caused a surge in interest in the synthetic organometallic chemistry and better understanding of catalytic mechanisms.

Unfortunately, the strong oxophilic nature of the early transition metals limits the range of utilizable monomers, and catalysts based on the late transition metals are today pushing to the forefront as alternative elements assisting the way to copolymers of polar and apolar monomers. Despite the reduced activity of the less electrophilic late transition metal centers in olefin insertion reactions, this area of research intensified when Brookhart and coworkers announced the high activity in ethene polymerization by nickel and palladium catalysts bearing bulky diimine ligands.4 Thanks to their better tolerance towards polar functionalities these systems have become the state of the art in alternating copolymerization of carbon monoxide with olefins.5

2 The Scope of the Thesis

Design of nickel, palladium, and zirconium complexes with nitrogen-based ligands. The complexation behavior of salicylketimine ligands with \textit{trans}-(PPh3)2Ni(Ph)Cl was studied (Publication I) to broaden understanding of the neutral Ni catalysts that were recently found highly active in olefin polymerization. New nickel(II) and palladium(II) complexes with chiral myrtillyl- and oxazoline-based diimine ligands were synthesized and characterized for the needs of asymmetric catalytic reactions (Publication II). For the same purpose axially chiral bianiline based N-donor ligands were prepared and their various
complexes with Pd and Zr were characterized and studied in olefin polymerization reactions (Publications III and IV).

**Development of polyketone materials by copolymerizing higher olefins with carbon monoxide using Pd(II) catalyst systems.** The variability of a polyketone backbone can be improved by incorporating other functionalities. With \([(dppp)\text{Pd}(\text{NCCH}_3)_2](\text{BF}_4)_2\] as catalyst precursor, olefin functionalities were inserted in the main chain or in side chains by co- and terpolymerization of methylenecycloalkanes and dienes with CO and propene (Publication V). Since unstabilized polyketones are photodegradable at room temperature and stabilizing agents added to commercially available synthetic polymers may leach or migrate from the polymer matrix with time, this catalyst system was also used to incorporate phenolic stabilizers in the polymer chain as comonomers, and obtain more stable polyketone materials (Publication VI). Finally, alternating CO/norbornene copolymers were prepared with As∩S heterodonor ligand-based Pd(II) catalyst (Publication VII).

The results of the two parts of the study are presented separately in Chapters 3 and 4.

### 3 Catalyst design: synthesis and characterization of nickel, palladium, and zirconium complexes with nitrogen-based ligands

#### 3.1 Ligand synthesis

The condensation of amines with aldehydes or ketones is a simple and effective tool in the hands of an organometallic chemist. Easy work up of the reaction and purification of the product combined with easy availability of a wide spectrum of starting materials give the chemist a fast entrance to imine ligands with easily variable steric and electronic features. Now that these features in the ligand frame have been found important to the catalytic performance of transition metal complexes, and catalysts bearing imine ligands have proved themselves in catalytic reactions, there is a strong call for research in such chemistry. In fact, direct condensation of an amine with carbonyl substrates has been widely used to prepare imine ligands.\(^6\) Reaction with ketones may require more severe conditions, as in the case of salicylketimines.\(^1\) Alternative routes have been introduced. For example, a trimethylaluminum promoted condensation\(^7\) was found effective in the preparation of acenaphthenechinone-based 1,2-diimines from N-hetaryl building blocks.\(^8\) This method achieves the imination through sequential hemiaminal and aminal formation
followed by elimination of tetramethylaluminoxane. In another example, two equivalents of (1R)-(+) -camphor were refluxed with a 1,2-diamine and an excess base such as triethylamine in the presence of TiCl₄ for 46 h to afford the corresponding diimine in moderate yield. Nevertheless, in some cases, such as condensing 2,3-butandione with chiral myrtanylamine, over 50% yield was achieved by stirring in methanol at ambient temperature with formic acid as catalyst. Precipitation of the diimine product from the reaction solution might have been the driving force here.

3.1.1 Synthesis of chiral myrtanyl-based diimine ligands

When 2,3-butandione was stirred with 2 equiv. of enantiomerically pure (-)-cis-myrtanylamine in acidic methanol solution at room temperature, a white precipitate soon formed (Scheme 1). This precipitate was isolated and identified by IR, ¹H and ¹³C NMR and elemental analysis to be the desired N,N’-bis{(-)-cis-myrtanyl}butylene-2,3-diimine (BMDI, 1).

Scheme 1. Synthesis of bismyrtanyldiimine 1 (BMDI).

3.1.2 Synthesis of axially chiral bianiline based N-donor ligands

Axially chiral bianiline-based tetridentate ligands of this study (2-5) were readily prepared by condensation of 6,6’-dimethyl-bianiline with 2 equiv. of the desired aldehyde in methanol or ethanol at room temperature (Scheme 2). The reaction solvent was evaporated under reduced pressure after 1 h, and the product precipitated cleanly upon stirring of the oily residue overnight in n-pentane. Isolation of this precipitate gave nearly 90% yields and no further purification was needed. Interestingly, while pyridine-2-carboxaldehydes and
furyl-2-carboxaldehydes reacted best in pure ethanol, for pyrrole-2-carboxaldehyde it was necessary to add a few drops of formic acid as catalyst and methanol as solvent.

\[ \text{Scheme 2. Synthesis of bianiline-based diimines.} \]

Study of the effect of sidearm functionalities on their zirconium complexes required that dipyridine diimines were reduced to their diamines to make dianionic ligands accessible to them. Although attempts to reduce the dipyridine diimines with NaBH\(_4\) or LiAlH\(_4\) were unsuccessful or gave low isolated yields, \(^1\)H NMR study showed that complete conversion to the oily products 6\(\text{H}_2\) and 7\(\text{H}_2\), respectively, was achieved by Pd(OH)\(_2\)-catalyzed hydrogenation under H\(_2\) atmosphere at 80 °C (Scheme 3).
3.1.3 Synthesis of salicylketimines

Salicylaldehydes readily react with substituted phenylamines, including sterically hindered 2,6-dialkyl derivatives, to form salicylaldimin es in a direct acid-catalyzed condensation reaction in methanol at room temperature. This method appeared unfavorable for the preparation of salicylketimines, since starting from aromatic ketones requires more severe reaction conditions. The salicylketimine ligands 8-10 were prepared in methanol at 200 °C in a closed steel autoclave in the presence of Na₂SO₄ and a catalytic amount of formic acid (Scheme 4). After purification by column chromatography, ligands 8 and 9 were isolated in nearly 50% yields, but ligand 10 in only 6% yield. No increase of the yield was achieved by varying acid catalyst or solvent (toluene and Dean-Starck equipment) or by performing the reaction without solvent and at different temperatures.

3.2 Neutral salicylketiminato nickel(II) complexes

Until the mid-1990s only a few reports described the use of late transition metal complexes as catalyst precursors for the polymerization of α-olefins. The generally low activities of these catalysts for olefin polyinsertion may explain the lack of interest. In addition, β-hydride elimination steadily competes with the chain growth, resulting in the formation of oligomers. In 1995, however, new nickel(II)- and palladium(II)-based catalysts bearing bulky diimine ligands were reported for ethene polymerization, and a few years later iron(II), too, was successfully applied as a metal center with bis(imino)pyridine ligands. These complexes, after methylaluminoxane (MAO) activation, produced high molecular weight polymers with high activity. Moreover, in view of their tolerance toward polar functionalities, these systems were considered promising alternatives to Ziegler-Natta and metallocene catalysts. By now, the use of late transition metals as olefin polymerization catalysts have been extensively reviewed and their possible application even in acrylate polymerization have been described.

The sensitivity of MAO activated cationic catalysts to polar monomers and solvents has created substantial interest in the development of new, less oxophilic, catalysts for olefin polymerization. The Shell higher olefin process (SHOP) for ethene oligomerization is a good example of the catalytic activity of neutral nickel catalysts, and, recently, researchers at DuPont and Grubbs and coworkers described homo and copolymerization of olefins with novel salicylaldimine-based Ni(II) complexes as catalysts. The most active systems contain either electron-withdrawing nitro substituents on the aromatic ring or bulky substituents at C-3, a 9-anthracenyl group being the most effective [activity of $1.3 \times 10^5$ mol ethene/(mol Ni·h)]. Changing the imine backbone substituent from hydrogen to methyl and inserting halogens on the aromatic ring increases branching and decreases the molecular weight, while maintaining similar polyethene productivity. These complexes work as single-component catalysts, or require only a phosphane scavenger such as [Ni(COD)$_2$] (COD: 1,5-cyclooctadiene) to act as catalysts for homo- and copolymerization of ethene with non-vinyl functionalized monomers such as esters, alcohols, anhydrides, and amides. Surprisingly, MAO turned out to be essential to initiate the homopolymerization of norbornene.

Since the reports of Grubbs and coworkers, numerous studies have been done on neutral Ni(II) catalysts for olefin polymerization. For example, a neutral salicylaldimine-based Ni catalyst was heterogenized during polymerization reaction via an allyl-substituent in the ligand by ‘self-immobilization’ (Figure 1).
In a recent study, salicylaldiminato complexes bearing different substituents were found inactive towards ethene polymerization while being highly active in MMAO-activated norbornene polymerization. In the same study this was noticed for neutral complexes bearing also β-ketiminato and β-diketiminato ligands. Recently, an amido-aldehyde nickel(II) complex (b, Figure 2) was reported to display comparable activity in ethene polymerization to complexes reported earlier by Grubbs and coworkers. Generally common to active catalyst precursors are bulky, ortho-substituted aryl moieties at imine – or diazene – nitrogen protecting the axial sites of the metal center (c, Figure 2). This is supported also by computational studies. Such an effect on polymer productivity has not always been observed, however. Moreover, a recent study has shown that even more remote substituents on the ortho-positioned phenyl rings control the polymer branching and molecular weight of polyethylene in highly active aqueous emulsion polymerization by neutral methylnickel(II) complexes (d, Figure 2). The results suggest that the effect of these remote substituents is related to their electronic properties rather than their steric requirements. Again, theoretical calculations support also the finding that electron-withdrawing ligand substituents increase catalytic activities substantially.

The steric impact was underlined when neutral nickel complexes based on anilinotropone or anilinoperinaphthenone ligands (e and f, Figure 2), structures containing a five-membered chelate were found to afford high-molecular-weight PE with good activities without the use of aluminoxanes as cocatalyst. This polymerization reaction has also been under thorough mechanistic investigation. The catalyst decay process was found to comprise reductive elimination of the free ligand from the hydride Ni(H)(N,O)(PPh3)] and its subsequent reaction with propagating nickel species. The catalyst decay products included mostly the free ligands and bis-ligand complexes.
Figure 2. Structures of selected neutral Ni(II) catalyst precursors reported by working groups of Grubbs (a), Novak (b), Mecking (c, d), and Brookhart (e, f).

Bis(salicylaldiminate)Ni(II) complexes have also been prepared and tested in aluminoxane activated polymerization of ethene (Figure 3), norbornene and methyl methacrylate. For a single component polymerization catalyst, which works without addition of excess aluminoxanes as activator, a bis-(sal) complex is coordinatively too saturated and thus not desired. Bis-ligated complexes appear to be a thermodynamic sink for some nickel(sal) compounds, however.
ligation plays an important role in stability and lifetime of the catalytically active species and represents, therefore, an interesting topic for further study. Recently, it has been found that penta-coordinated iron(II) complexes with tridentate ketimine ligands (2,6-bis(imino)pyridyl derivatives) are an order of magnitude more active as ethene polymerization catalysts than their aldimine analogues. For these reasons, in this work new salicylketimine ligands were prepared and their complexation with \textit{trans-}(PPh$_3$)$_2$Ni(Ph)Cl was studied.

![Diagram of catalytic cycle](image)

\textbf{Figure 3.} Formation of a catalytically active monochelate methyl nickel species from bis(salicylaldiminate)Ni(II) precursor by reaction with MAO under ethene pressure.

3.2.1 Complexation of salicylketimines with \textit{trans-}(PPh$_3$)$_2$Ni(Ph)Cl

The synthesis route of the nickel(II) complexes 11-15 is shown in Scheme 5. After deprotonation of the ligands with an excess of NaH in THF, the corresponding sodium salts were allowed to react with \textit{trans-}[(PPh$_3$)$_2$Ni((Ph)Cl], either by addition of the reaction solvent (benzene) to a solid mixture of the two reactants at temperature close to the solvent’s freezing point or by addition of a solution of the corresponding sodium salt to a suspension of the nickel precursor. The former method favors the formation of monophenyl-nickel(II) complexes 11 and 12, while the latter leads to the formation of the bis(sal)Ni(II) complexes 13-15.
Scheme 5. Synthesis of salicylketiminato Ni(II) complexes.

The formation of the monophenyl complex relative to the bis(sal) complex was followed by $^1$H NMR. In the spectra, the septet due to the CH protons of the isopropyl groups is shifted downfield from that in the spectra of ligands 8 and 9 (2.78 and 2.89 ppm) to 3.84-3.89 ppm in 11 and 12. In the case of the bis-ligated complexes this septet is further shifted to 3.87, 4.08, and 4.60 ppm for 15, 13, and 14, respectively. Characteristic signals of the triphenylphosphane ligand in the $^{31}$P NMR spectra of complexes 11 and 12 are observed at 23.8-24.3 ppm. Other methods used to identify the complexes were IR, MS (EI and AP-MALDI), elemental analysis, and single-crystal X-ray structure determination.

In its isolated form, complex 12 is relatively stable in solution at room temperature. According to $^1$H NMR, no decomposition or transformation to the corresponding bis(sal)-Ni(II) species occurred even after 8 hrs at room temperature, and after 50 hrs the molar ratio of 14 to 12 was 1:15. In the case of the salicylaldimines in nickel phosphane
complexes, the formation of bis(sal)Ni(II) complexes usually requires harsher reaction conditions. However, when salicylaldimines were reacted with (tmeda)NiMe₂ (tmeda = N, N, N', N'-tetramethylethylenediamine) in acetonitrile, the bis-(sal) complex turned out to be thermodynamically favored and the monochelate (sal)Ni(Me)(NCCH₃) could be isolated only when sterically bulky groups (anthracenyl on the ortho-position in the phenoxy ring and diisopropylaryl on the imine moiety) were distributed evenly on both sides of the ligand.

With the salicylketimine ligands, the formation of the bis(sal) complexes may take place spontaneously even if more strongly coordinating phosphanes are used with Ni(II). Moreover, in the reaction of Na-10 with trans-[(PPh₃)₂Ni(Ph)Cl], the bis(sal)Ni(II) complex (15) was the predominant product. Evidently the presence of the phenyl group on the ketimine carbon of the ligand increased the tendency to form a bis(sal) complex. The reason for this particular behavior remains unclear, but it could be related to the trans influence of the ketimine site, allowing a faster dissociation of the second PPh₃ ligand. Thus, in addition to fine tuning of the reaction conditions, also different substituents on the ketimine carbon may affect the complexation behavior of these salicylketimine ligands.

The nickel complex containing a labile acetonitrile ligand, (2-anthracen-9-yl-6-((2,6-diisopropylphenyl)iminomethyl)phenoxide)NiMe(MeCN), is more active in ethene polymerization than the corresponding triphenylphosphane adduct. In the light of this observation and of the easier dissociation of the pendant triphenylphosphane ligand in the salicylketimine complex than in salicylaldimine complexes, it was surprising that the monophenyl salicylketiminato based Ni(II) complexes 11 and 12 turned out to be catalytically inactive in homopolymerization of ethene or norbornene when [Ni(COD)₂] or BF₃ were applied as phosphane scavengers, even at elevated temperatures (up to 60 °C) and pressures (up to 40 bar). Possibly, formation of a bis-sal complex might have prevented the polymerization.

### 3.2.2 Solid state structures

For further investigation of structural features, crystals of complexes 11 and 12 suitable for X-ray structure determination were grown from 1:5 benzene/n-pentane mixture at -20 °C, and crystals of complexes 13-15 were obtained at ambient temperature. The coordination geometry of complex 12 was found to be similar to that of 11 (Figure 4). The coordination geometries of bis(sal)Ni(II) complexes 13, 14, and 15 (Figure 5) were found to be alike.
In the solid state, complex 11 has a square-planar geometry. The Ni-O1, Ni-N1, and Ni-C21 bond distances and bond angles are similar to those for known nickel complexes. The Ni-P1 bond distance (2.185(1) Å) is only slightly longer than that in Grubbs’ nickel-based complex (2.172(2) Å) and in Cavell’s [Ni(PPh₃)(o-tolyl)(N-O)] complexes with N-O bidentate pyridinecarboxylate ligands (2.1653(2) Å). It is clearly shorter, however, than that in nickel(II) salicylaldiminato complexes bearing naphthyl instead of phenyl group cis to PPh₃ (2.200(1) Å and 2.198(2) Å). Nevertheless, these naphthyl complexes are active in
norbornene polymerization with only MAO as cocatalyst. Thus, care should be taken in drawing conclusions from solid-state structures about the lability and ease of removal of the phosphane ligand from Ni in the polymerization solution. The bis(sal) complexes 13, 14, and 15 form a square planar coordination geometry with nickel in the symmetry center of the molecule and thus in the plane of the four donor atoms. Their bond angles and distances are alike, the average Ni-O distance (1.808 Å) being somewhat shorter and the Ni-N distance (1.926) somewhat longer than the distances in the bis(salicylaldiminato) complexes reported by Jordan et al. (Ni-O 1.846 Å, Ni-N 1.899 Å)\[^{34b}\] and Knoch et al. (1.856, 1.899 Å).\[^{34a}\]

![Molecular structure of bis(salisylketiminato) nickel(II) complex 16.](image)

**Figure 6.** Molecular structure of bis(salisylketiminato) nickel(II) complex 16.

It should be mentioned that caution is required when applying such harsh reaction conditions (stirring overnight in a closed vessel at 200 °C) in the synthesis of salicylketimine ligand. This was demonstrated when a prolonged reaction time was applied in an attempt to increase the yield of the 2-[(2,6-diisopropylphenylimino)-(phenyl)methyl]phenol. After the isolated product was reacted with *trans*-(PPh\(_3\))\(_2\)Ni(Ph)Cl, one of the orange crystals from the product was taken for single-crystal X-ray diffraction measurement. The structure (Figure 6) of the obtained bis(sal)Ni(II) complex 16 resembled that of complex 15, except that in one of the arylimine moieties one of the isopropyl groups (C46-C48) was displaced from ortho to para position. Indication of this displacement was also seen in the \(^1\)H NMR spectrum recorded from the ligand before complexation, as weaker signals were observed slightly downfield from the parent peaks due to the isopropyl groups on the ortho positions. Such rearrangement is uncommon and its mechanism remains unclear.
3.3 Chiral nickel(II) and palladium(II) complexes with myrtanyl and oxazoline based diimine ligands

Late transition metal complexes with phosphane ligands have been extensively studied in catalytic processes. Catalysts containing nitrogen ligands are also suitable for many of these processes. These include C-C cross-coupling reaction, hydrogenation, allylic alkylation and the Heck reaction, where catalysts bearing nitrogen ligands may perform even better than those with soft Lewis-base phosphorus ligands.\textsuperscript{36} Although phosphane complexes still play the main role in industrial applications, catalysts based on nitrogen ligands are of considerable interest.\textsuperscript{37}

The coordination chemistry of Schiff-base ligands has played an essential role in the development of transition metal complexes for biological applications, catalysis and materials science.\textsuperscript{38} Furthermore, chiral and achiral Pd(II) and Ni(II) complexes bearing bidentate nitrogen donors have attracted interest as catalysts for homo- and copolymerization of linear and cyclic olefins with carbon monoxide\textsuperscript{11,14a,39} and for polymerization of functionalized olefins.\textsuperscript{40} The attractiveness of nitrogen donors is enhanced by their good availability from the ‘chiral pool’.\textsuperscript{41} For example, the chiral and $C_2$-symmetric bisoxazoline ligands have been applied in transition metal-catalyzed reactions such as enantioselective C-C bond forming reactions,\textsuperscript{42} allylic alkylation,\textsuperscript{43} oxidation,\textsuperscript{44} reduction,\textsuperscript{45} and carbonylation of alkenes.\textsuperscript{36a} As part of this interest, new chiral diimine-palladium(II) and nickel(II) complexes containing bis(myrtanyl)diimine (BMDI) or a commercially available bisoxazoline ((1\textsuperscript{R}, 2\textsuperscript{S})-inda-box)\textsuperscript{46} were to be synthesized and characterized.

3.3.1 Synthesis and characterization of complexes

The complexes (BMDI)PdCl\textsubscript{2} (17) and (BMDI)NiBr\textsubscript{2} (18) were prepared by the reaction of BMDI (1) at ambient temperature with Pd(PhCN)\textsubscript{2}Cl\textsubscript{2} in acetone or with Ni(DME)Br\textsubscript{2} in CH\textsubscript{2}Cl\textsubscript{2}, (Scheme 6). The same procedure with (1\textsuperscript{R}, 2\textsuperscript{S})-inda-box allowed the isolation of the corresponding complexes 19 and 20 (Scheme 7).
Scheme 6. Synthesis of Pd(II) and Ni(II) complexes of bis(myrtanyl)diimine (BMDI).

A solvent stabilized cationic monoalkyl Pd(II) complex was synthesized for the purposes of preparing a single-component catalyst for CO/alkene copolymerization.\(^{47}\) (1R, 2S)-inda-box was reacted with (TMEDA)PdMeCl, followed by chloride abstraction with NaB(Ar)\(_4\) in
the presence of acetonitrile to yield 21 (Scheme 7). The \( C_2 \)-symmetry for the palladium complexes 17, 19, and 21 was confirmed in solution by NMR and in solid state for 19 by single-crystal X-ray diffraction. The corresponding dibromo nickel complexes were poorly soluble in common organic solvents and therefore no solution NMR could be obtained. Copolymerization of 4-(tert-butyl)-styrene with carbon monoxide by 21 as catalyst under the conditions described by Brookhart and coworkers gave reasonable amounts of white powder, the IR and \(^{13}\text{C} \) NMR spectra of which, while ruling out the presence of a polyketone, were not assignable to any plausible polymer structure.\(^{48} \)

3.4 Coordination chemistry of axially chiral bianiline-based ligands

The importance of axially chiral ligands in catalytic asymmetric reactions is well seen in the development of stereoselective hydrogenation of olefins. The low enantiomeric excess induced by the first chiral monodentate phosphane ligands in the 1960s\(^{49} \) was soon enhanced by chelating bisphosphanes.\(^{50} \) Axially chiral ligands were first reported in hydrogenation reaction in 1977 and have gained ground ever since.\(^{51} \) In addition to the biaryl backboned bisphosphanes BINAP (2,2’-bis(phenylphosphino)-1,1’-binaphthyl)\(^{52} \) and BIPHEMP (6,6’-bis-(phenylphosphino)-2,2’-dimethylbiphenyl),\(^{53} \) derivatives of the corresponding diamines (g and h, Figure 7) have performed successfully in many asymmetric catalytic reactions.\(^{54} \) These include stereoselective polymerizations of methacrylate\(^{55} \) and lactate\(^{56} \) and numerous enantioselective modifications of olefins such as epoxidation,\(^{57} \) aziridination,\(^{58} \) cyclopropanation,\(^{59} \) hydrogenation,\(^{60} \) hydrosilylation,\(^{61} \) and hydroformylation\(^{62} \) in addition to the trimethylsilylcyanation of aldehydes,\(^{63} \) Diels-Alder reaction,\(^{64} \) and allylic substitution.\(^{65} \)

![Figure 7](image)

**Figure 7.** Structures of some axially chiral ligands.\(^{66} \)
With a structurally rigid 6,6'-disubstituted biaryl ligand backbone, the configuration of the ligand is fixed and its axial chirality can efficiently be transmitted to the stereotopicity of the active site. In general, biphenyl-bridged ligands form mononuclear complexes, but binuclear complexes have also been reported, e.g., with Cu(II). Tetradentate N₃P₂, N₂O₂, and N₄ ligands are known to form both mono- and binuclear Pd(II) complexes, but only a few of these have chiral biaryl backbones.

As mentioned above, late transition metal complexes with nitrogen-based ligands have found a wide range of applications in homogeneous catalysis. Dendrimeric pyridylimine-Pd(II) complexes and binuclear Pd(II) complexes with long aliphatic spacers have recently been described as effective catalyst precursors for Heck coupling and ethene polymerization, respectively. Moreover, palladium complexes with chiral bidentate bis(oxazoline) ligands have been found efficient in asymmetric allylic alkylation. Palladium-catalyzed enantioselective transformations have recently been reviewed.

Research on group IV metallocenes as diverse and effective homogeneous polymerization catalysts peaked in the 1980s, but the interest in non-metallocene catalysts has been increasing in recent years. In addition to late transition metal catalysts with their attractive functional group tolerance, a new generation of early transition metal catalysts evolved, in part to avoid the growing jungle of patents in group IV cyclopentadienyl systems. Various complexes with two bidentate N,N ligands, O,N ligands, or a tetradeinate O,N,N,O ligand have been applied in MAO-activated olefin polymerization catalysis, some with marked success. Recently, good results have been obtained even without MAO activation. Nevertheless, the polymerization activities for MAO-activated titanium and zirconium complexes with Schiff-base O,N,N,O ligands containing a chiral bianiline backbone, prepared by Scott and coworkers, have been reported only once. Complexes containing ligands with N donor atoms only, including amidinato, diamido, triamidoamine, diamido-diamine, and tetraaza-macrocyclic ligands, have been prepared but not always tested in polymerization. Among those are chiral zirconium complexes containing bidentate and tetradeinate diamido ligands with a bianiline backbone.

The Pd(II) chemistry of 6,6'-dimethyl-bianiline-based tetradeinate ligands was here expanded to chiral zirconium complexes derived from their dianionic deprotonation products, and their structures and properties as precatalysts for olefin polymerization were studied.
3.4.1 Binuclear late transition metal complexes as catalysts

Binuclear organometallic compounds are especially interesting in view of the expectation that their reactivity in synthesis and catalysis may differ significantly from that of analogous mononuclear species. Additional oxidation states might also be accessible to binuclear complexes as a result of stabilizing metal-metal interactions. Interactions between closely adjacent metal centers might cause increased reaction rates or transformations not occurring with monometallic species, as was recently shown for copolymerization of styrene and ethene by binuclear titanocene complexes. In particular, the distance between two metal centers and their orientation to each other may be important for catalytic performance, as has been noted for palladium complexes that catalyze hydration reactions and for binuclear rhodium hydroformylation catalysts (Figure 8).

The dirhodium complex showed over 40% higher activity and enhanced regioselectivity (28:1 linear-to-branched aldehyde) in hydroformylation of 1-hexene, whereas compounds with longer spacers between rhodium centers, and , as well as the mononuclear complex, were barely active. The Rh…Rh distance in is 5.5 Å.

Figure 8. Different active (i) and inactive (j, k) dirhodium hydroformylation catalysts.

Ligtenbarg et al. synthesized mono- and binuclear Pd(II) complexes of P$_2$N$_2$ ligands with a chiral biaryl backbone and obtained only complexes with geometries A and C (Figure 9). For A, the distance between the two Pd nuclei was observed to be in the range of 7.2 to 8.7 Å. A complex like B, with a syn-folded geometry, they suggest, would have metal centers closer to each other and the two nuclei would be more prone to co-operate in catalysis. In fact, as shown below, such orientation B becomes possible with some modification in the ligand, and then the two Pd nuclei are 3.38 Å apart from each other. By way of comparison, the interatomic spacing in palladium metal is 2.75 Å.
Figure 9. Possible coordination geometries of mono- and binuclear complexes with a biaryl ligand.\textsuperscript{72c}

3.4.2 Preparation of Pd(II) complexes

Reaction of N,N\textsuperscript{'}-(6,6\textsuperscript{'}-dimethylbiphenyl-2,2\textsuperscript{'}-diyl)bis(2-pyridylmethyl)diimine (2) with one equivalent of Pd(COD)Cl\textsubscript{2} at 0\textdegree C gave 2-PdCl\textsubscript{2}, which precipitated from the reaction mixture in almost quantitative yield (Scheme 8). When the reaction was repeated in an NMR tube, starting at 0\textdegree C and continuing at room temperature, the reaction was found to be quite fast; 95\% of the Pd(COD)Cl\textsubscript{2} was consumed after 30 minutes. Ligand 3 likewise reacted readily with Pd(COD)Cl\textsubscript{2} under similar reaction conditions, but 3-PdCl\textsubscript{2} was isolated in lower yield than 2-PdCl\textsubscript{2} owing to its higher solubility. In solution, 2-PdCl\textsubscript{2} and 3-PdCl\textsubscript{2} both appear to contain a Pd-coordinated and an uncoordinated ligand moiety as judged from their \textsuperscript{1}H NMR spectra. A single-crystal X-ray structure analysis of 2-PdCl\textsubscript{2} (Figure 10) confirms an approximately square-planar coordination of the Pd(II) \textit{cis}-dichloro unit to one of the pyridylimine moieties of ligand 2, which thus forms a five-membered pyridylimine chelate with palladium. In the solid state, the non-coordinated pyridylimine moiety lies on the backside of the biphenyl bridge, pointing away from the PdCl\textsubscript{2} unit.
Figure 10. Crystal structure of complex 2-PdCl₂.

With ligand 4, where the side-arm pyridyl groups are replaced by furyl rings, a significantly longer reaction time (20h) was required for complex formation with Pd(COD)Cl₂ (Scheme 9). CDCl₃ solutions of 4-PdCl₂ give ¹H NMR spectra indicative of a $C_2$-symmetric geometry, as is also shown by the crystal structure (Figure 11). Ligand 4 is bound again in a bidentate manner, but this time the two imino nitrogens form a seven-membered chelate with the cis-dichloro Pd(II) unit to give an approximately square-planar, $C_2$-symmetric geometry. Both furyl rings are uncoordinated, located at non-bonding distances of 4.8 and 5.2 Å from the Pd center, from which the side arms are pointing away. Owing to the dihedral angle of 71° between the phenyl rings of the biphenyl bridge, the ligand plane at the Pd center is somewhat distorted, with an angle of 10.7(2)° spanned by the planes Cl1-Pd-N1 and Cl2-Pd-N2. The preference of the Pd center for N over O ligand atoms clearly overrides its preference for 5-membered over 7-membered chelate rings to such an extent that a $C_2$-symmetric geometry becomes favored for 4-PdCl₂ over the $C_1$-symmetric structures of 2-PdCl₂ and 3-PdCl₂.

Figure 11. Pd(II) complexes of ligand 4 (two structures of 4-PdCl$_2$ (dashed line) and one of [4-Pd(NCCH$_3$)$_2$](BF$_4$)$_2$ (solid line)) in one presentation, showing the different orientations of the furyl side-arms in the solid state.
Since in 2-PdCl₂ only one half of ligand 2 is bound to PdCl₂, its other half remains available for further coordination and open a door for the preparation of bimetallic complexes. Indeed, the dipalladium complex 2-(PdCl₂)₂ was isolated in 97% yield when ligand 2 was reacted with two equivalents of Pd(COD)Cl₂ at room temperature (Scheme 8). As confirmed by the solid-state structure (Figure 12), one PdCl₂ unit is coordinated to each of the biphenyl-bridged pyridylimine moieties of binuclear 2-(PdCl₂)₂. The biaryl backbone, with its dihedral angle of 69°, holds the two metal centers Pd(1) and Pd(2) at a fairly short distance of 3.38 Å. Their tetragonal coordination planes are stacked under an angle of 7.40(2)°. Viewed along the Pd-Pd axis, the two PdCl₂ units are rotated by an angle of 104.9° relative to each other.

![Figure 12. Molecular structure of a binuclear complex 2-(PdCl₂)₂.](image)

While the cis-PdCl₂ unit favors formation of a five-membered pyridylimine chelate over that of a seven-membered diimine chelate, complexes such as 2-PdCl₂ and 3-PdCl₂ possess C₁ symmetry. In order to generate C₂-symmetric complexes, which fully exploit the axial symmetry inherent in the biaryl backbone and would thus be more suitable for asymmetric catalysis,⁹⁶ tetradentate coordination of ligand 2 was induced through use of one equiv. of the electron-deficient Pd precursor [Pd(NCCH₃)₄](BF₄)₂. Reaction in acetonitrile at room temperature gave the ion pair [2-Pd]²⁺(BF₄⁻)₂ in high yield (Scheme 8). The expected tetradentate coordination of ligand 2 was verified by a single-crystal structure determination (Figure 13). Owing to the dihedral angle of 71° in the 2,2’-dimethyl-substituted biphenyl backbone, the square-planar coordination at the Pd atom is tetrahedrally distorted, such that the planes N1-Pd-N2 and N3-Pd-N4 span an angle of 12.9(5)°.
When ligand 4 was reacted with [Pd(NCCH₃)₄](BF₄)₂ in acetonitrile solution, the reaction proceeded fast and with high yield to give the bis-acetonitrile adduct [4-Pd(NCCH₃)₂](BF₄)₂ (Scheme 9). The coordinated NCCH₃ molecules are observed in ¹H NMR spectra as a signal at 2.08 ppm. In the crystal structure of [4-Pd(NCCH₃)₂](BF₄)₂, ligand 4 again forms only one 7-membered chelate ring with the Pd center and the imine nitrogens (Figure 11). Unlike in 4-PdCl₂, where the furyl oxygen atoms point away from the Pd center, they are now turned toward the center and lie rather close to it, in “axial” positions at Pd-O distances of 3.0 Å. Some (presumably weak) coordination or dipolar attraction of the furyl oxygen atoms to the Pd(II) center thus appears to be stabilized by the cationic nature of the latter. According to available literature, a solid state structure of a Pd complex with furyl oxygen atoms coordinated to Pd from oxygen has not been reported so far.

Since two nitrogen ligand atoms are sufficient for the formation of a cationic di-acetonitrile complex, ligand 2 was reacted with two equivalents of [Pd(NCCH₃)₄](BF₄)₂ to prepare the binuclear cationic complex [2-[Pd(NCCH₃)₂]₂](BF₄)₄ (Scheme 8). The reaction yielded an oily product, the elemental analysis and ¹H NMR spectrum of which indicated formation of the expected binuclear complex.
### 3.4.3 Preparation of Zr(IV) complexes

The pyrrole rings of ligand \(5H_2\) were easily deprotonated with NaH in THF, and the disodium salt \(5Na_2\) thus formed was reacted with \(ZrCl_4(THF)_2\) in THF at room temperature to give complex \(5-ZrCl_2(THF)\) (Scheme 10). The coordinated THF was not removable in vacuo at 100 °C or by co-evaporation with toluene.

#### Scheme 10. Synthesis of Zr(IV) complex bearing biaryl-bridged bis(pyrroleimine) ligand.

A more soluble complex was sought by reacting \(5-\)Na\(_2\) with \(\text{tBu}_4\text{biphenO}_2\)ZrCl\(_2\)(THF)\(_2\) and the biphenolate complex \(5-Zr(\text{tBu}_4\text{biphenO}_2)\) was obtained (Scheme 11). Apparently, the bulky biphenolate ligand, which necessarily must occupy two cis-coordination sites, does not allow the coordination of an extra THF ligand molecule.

#### Scheme 11. Synthesis of a biphenoxy derivative of a Zr(IV) complex bearing biaryl-bridged pyrroleimine ligand.
The effects of different side-arm functionalities on structures and reactivities of these bianiline-based complexes were studied by replacing the pyrrole with pyridyl moieties and reducing the diimine dipyridine ligands to the corresponding diamines $6H_2$ and $7H_2$. However, deprotonation followed by complexation reaction of these diamines proved more difficult than for $5H_2$. While attempts with NaH were unsuccessful, the use of $^n$BuLi led to the isolation of a few crystals of $7-ZrCl_2$ (Scheme 12) allowing structural characterization by single-crystal X-ray diffraction. The reaction with zirconium amine, ($^t$Bu$_4$biphenO$_2$)Zr(NMe$_2$)$_2$, in an attempt to prepare a biphenolate complex was equally scarce (Scheme 13).

**Scheme 12.** Preparation of a Zr(IV) dichloro complex bearing biaryl-bridged pyridylimine ligand.

**Scheme 13.** Preparation of a biphenolate derivative of Zr(IV) complex bearing biaryl-bridged pyridylimine ligand.

The best route to Zr(IV) complexes for these dipyridine diimine ligands turned out to be reaction with Zr(CH$_2$Ph)$_4$. Acceptable yields of $6$-$Zr$(CH$_2$Ph)$_2$ and $7$-$Zr$(CH$_2$Ph)$_2$ were obtained after stirring at room temperature for a long time (Scheme 14). All the Zr(IV)
complexes containing ligands 5, 6, or 7 gave room-temperature NMR spectra in accord with a structure of time-averaged $C_2$-symmetry. NMR patterns of AB type were observed for the diastereotopic N-CH$_2$ and Zr-CH$_2$ protons of 6-Zr(CH$_2$Ph)$_2$ and 7-Zr(CH$_2$Ph)$_2$, in accord with the chiral geometry of these complexes.

![Scheme 14](image)


3.4.4 Solid-state structures

In comparison with the versatile coordination behavior of Pd(II), which prefers square-planar coordination to these ligands, it was of interest to study the coordination of Zr(IV), which is known to prefer an octahedral geometry. The molecular structures of 5-ZrCl$_2$(THF), 7-ZrCl$_2$, 7-Zr(CH$_2$Ph)$_2$ and 6-Zr(Bu$_4$biphenO$_2$) were determined (Figures 14-17).

![Figure 14](image)

Figure 14. Molecular structure of 5-ZrCl$_2$(THF).
Figure 15. Molecular structure of $7$-$\text{ZrCl}_2$.\textsuperscript{IV}

Figure 16. Molecular structure of $7$-$\text{Zr(CH}_2\text{Ph)}_2$.\textsuperscript{IV}
As can be seen from the structures in Figures 14-16, in the bianiline-bridged ligands in complexes of the type ZrN$_4$X$_2$ all four N ligand atoms tend to be almost in plane with the metal. The same was observed in the structure of palladium cation in [2-Pd]$^{2+}$(BF$_4$)$^-_2$ (Figure 13). This plane bisects the rather large X-Zr-X angle so that the two X ligands occupy axial-type positions. The striking structural similarity of these four Zr complexes suggests that the interchange of anionic and neutral N ligand atoms between the inner and outer positions of the coordination base plane in 5-ZrCl$_2$(THF) and 7-ZrCl$_2$ has only a small effect on the overall coordination geometries. A similar conclusion can be drawn from change in the ligand X from chloride to benzyl. Owing to the rather short distance between the bianiline N atoms, associated with rather small dihedral angles of 62 – 67° between the two phenyl rings, the four N atoms leave a relatively large open space in the equatorial plane, opposite to the bridging biphenylene unit. This position, which corresponds to an equatorial corner of a distorted pentagonal bipyramid, can either be occupied by an additional ligand molecule, as in 5-ZrCl$_2$(THF), or remain open, as in the sterically congested complexes of the type 7-ZrX$_2$ (X=Cl, benzyl). While repulsive contacts (3.6 Å) between the methyl groups at the pyridyl rings might stabilize the large N(pyridyl)-Zr-N(pyridyl) angles, they are evidently not sufficient to displace the two pyridyl ligands from their positions close to the molecular mid-plane into axial positions.

Figure 17. Molecular structure of 6-Zr(′Bu$_4$biphenO$_2$).$^\text{IV}$
Scheme 15. Cis- (A) and trans-configurations (B) of $\text{6-ZrCl}_2$ (R=H) and $\text{7-ZrCl}_2$ (R=CH$_3$).

The accessibility of complex configurations with monodentate ligands in cis-position was investigated by calculating the relative energies of trans-$\text{6-ZrCl}_2$ (B, Scheme 15) and of hypothetical cis-$\text{6-ZrCl}_2$ (A, Scheme 15) using molecular mechanics models. Interestingly, for our model complexes, the cis-configuration turned out to be less stable than the trans-configuration by only 4 kJ/mol. One can conclude from this that isomerization into a cis-coordinated complex is feasible during polymerization with $\text{6-ZrX}_2$ as a precatalyst. For cis-$\text{7-ZrCl}_2$, on the other hand, a much greater energy difference of 23 kJ/mol relative to trans-$\text{7-ZrCl}_2$ was found.

A structure with axially placed pyridyl ligands is brought about by the biphenolate ligand in $\text{6-Zr(}^1\text{Bu}_4\text{biphenO}_2\text{)}$, in which the O ligand atoms must necessarily occupy cis-coordination positions (Figure 17). This complex adopts a slightly distorted octahedral geometry, with an N(pyridyl)-Zr-N(pyridyl) angle of 162° and N-Zr-N, N-Zr-O and O-Zr-O angles all close to 90°. Remarkably, the dihedral angle between the two phenyl rings in the bianiline backbone, 61°, is even smaller than in complexes where all 4 N-ligand atoms are in equatorial positions. By analogy, one could assume that the bis-pyrrole complex $\text{5-Zr(}^1\text{Bu}_4\text{biphenO}_2\text{)}$ discussed above likewise has an octahedral geometry with pyrrole rings in axial positions.
4 Polymerization

4.1 Alternating co- and terpolymerization of carbon monoxide and higher olefins

The search for new polymers with high content of heteroatom functionalities that can provide materials with interesting engineering properties continues unabated ever since the rise of polyolefin production and of the plastics made from them for daily use. Alternating copolymerization of alkenes like ethene or propene with carbon monoxide has become an attractive option due to the readily available and inexpensive starting materials. Moreover, the resulting polymer, poly(1,4-ketone), has potential photo- and biodegradable properties owing to the repeating carbonyl units, which lend themselves to further chemical modifications. The use of a chiral and enantiomerically pure catalyst allows the preparation of optically active polymers from prochiral monomers.

Whereas alternating ethene/CO copolymers are white crystalline high-melting solids ($T_m=260 \, ^\circ \text{C}$), only poorly soluble and difficult to process, the corresponding terpolymers containing small amount of propene/CO units (5-10%) show reduced melting transitions and more favorable behavior in blow-molding or extrusion applications. This thermoplastic material was commercialized by Shell under the trade name Carilon in the nineties. Although Shell has now announced the closure of their plant for Carilon production, research on polyketones prepared with late transition metal catalysts continues in academic and industrial laboratories around the world. It has been comprehensively reviewed.

4.1.1 Polyketone synthesis

The synthesis of copolymers of carbon monoxide and olefins can be initiated with free radicals, induced by $\gamma$-rays or catalyzed by transition metal complexes. While the free-radical initiated and $\gamma$-ray induced copolymerizations require harsh reaction conditions and produce polymers with a variable CO content in a non-alternating fashion, the transition metal catalyzed copolymerization proceeds in an alternating fashion at ambient temperature and under significantly lower pressures. In the first free-radical-initiated copolymerizations, peroxides, hydroperoxides, and $\text{O}_2$ were used as initiators, and the comonomers included ethene, propene, butadiene, tetrafluoroethene, or vinylic monomers such as vinyl chloride. Pressures up to 1000 atm and temperatures of 135-200 $^\circ \text{C}$ were required and, depending on the reaction conditions, ethene/CO copolymer with less than 50% CO content and molecular weight up to 8000 was obtained. When $\gamma$-ray irradiation
was applied, somewhat higher CO contents and molecular weights were obtained at lower temperature.\textsuperscript{103}

The alternating copolymerization of alkene and carbon monoxide was discovered in 1950 by Reppe and Magin.\textsuperscript{104} The catalyst $\text{K}_2[\text{Ni(CN)}_4]$ produced, in water and at high temperature, oligomers of ethene and CO in addition to propionic acid and diethyl ketone. Since then, new nickel catalysts have been reported to produce high molecular weight ethene/CO copolymers.\textsuperscript{105} Among other group VIII metals, besides Pd, which has been most studied, also Co\textsuperscript{106} and Rh\textsuperscript{107} have shown activity in turning ethene and CO into low molecular weight alternating polyketone or oligomer products. Interestingly, rhodium carbonyl cluster catalyst was found to copolymerize norbornadienes with CO under water gas shift reaction conditions but only to oligomerize norbornene.\textsuperscript{108}

The evolution of palladium-based catalysts began in 1967 when Gough described a Pd(II)chloride complex stabilized with monodentate tertiary phosphanes that yielded alternating polyketone under drastic reaction conditions (250 °C and 2000 bar).\textsuperscript{109} The activity was very low, however. When Sen and coworkers modified the catalyst to a cationic complex $[\text{Pd(PR}_3)_2(\text{NCCH}_3)_2](\text{BF}_4)_2$ by replacing the chlorides with non-coordinating tetrafluoroborates in the presence of weakly coordinating acetonitriles, it produced ethene/CO copolymers under much milder conditions.\textsuperscript{110} Yields and molecular weights were still low. High molecular weight was obtained, together with high activity (6 kg/g Pd/h), when Drent in 1984 replaced the monodentate phosphane ligands with chelating diphosphanes.\textsuperscript{111} The catalyst system patented by Shell was formed by the combination of palladium acetate with a diphosphane ligand, a Brönstedt acid and an oxidating agent in methanol. It produced ethene/CO copolymers with high activities under relatively mild reaction conditions (90 °C, 40-60 bar). It was found later that a highly active catalyst can be obtained with palladium tetrakisacetonitrile tetrafluoroborate, a diphosphane ligand, and methanol as cocatalyst.\textsuperscript{112}

All these findings have encouraged many research groups to pursue different ligand and catalysts structures, reaction conditions, and comonomer selections with the aim of achieving better understanding of catalyst – polymer structure relations and reaction mechanisms.\textsuperscript{5, 14a, 101} The most thoroughly studied comonomers are ethene and propene, for which Pd complexes based on phosphane ligands have been by far the most widely used precatalysts. Among the higher olefins, styrene has gained most attention as comonomer, and most of the results with styrene have been obtained with catalysts based on nitrogen chelates. Also linear higher aliphatic $\alpha$-olefins have been incorporated into the polyketone backbone and their effect on the physical properties of the resulting material has been studied.\textsuperscript{14a} Reports on copolymerizing functional monomers with carbon monoxide are
fewer, although the resultant highly functionalized materials are likely to be of practical importance given the varied applications of the presently known functional polymers. One advantage of using late transition metals such as Pd(II) as catalyst for olefin polymerization instead of the highly active group IV metallocene catalysts, is that they are less prone to be poisoned by polar functionalities present in the reaction system. This has allowed the preparation of the new functional polyketones described below.

4.1.2 Mechanism

Several possible initiation and termination reactions have been proposed for the copolymerization of carbon monoxide with 1-alkenes by Pd(II) catalyst (Figure 18). The initiation step (Eqs. 1-3) is proposed to take place through the insertion of an alkene into a Pd-hydride bond or of carbon monoxide into a Pd-acyl bond formed by reaction with an activator such as methanol or water. It has also been proposed, however, that the initiation is a Wacker-analogous reaction, where the initial Pd-C bond results from the nucleophilic attack of an HOR group (R = H, CH₃) on a coordinated olefin or carbon monoxide.

In addition to the role as an initiator, excess methanol can act as a chain termination agent by protonolysis (Eq. 5) or methanolysis (Eqs. 6 and 7). Thus, an amount of methanol that achieves the highest molecular weight was used in the present work. Another likely termination mechanism is β-hydrogen elimination (Eq. 4).
The chain propagation involves the alternating insertion of carbon monoxide into the Pd-alkyl bond and of the alkene into the Pd-acyl bond (Figure 19). The reasons for the perfect alternation of the comonomers were found in the thermodynamically disfavored double carbon monoxide insertion and in the low coordination ability of ethene with respect to carbon monoxide combined with a more rapid insertion of the latter in the alkyl intermediates.
Figure 19. Formation of alternating CO/1-alkene copolymers by successive migratory insertion reactions of carbon monoxide and an alkene.\textsuperscript{14a}

Alkene insertion is the rate-determining step in the CO/alkene copolymerization reaction,\textsuperscript{117, 119} and the preceding coordination of the olefinic double bond is likely to depend on the steric characteristics of the alkene.\textsuperscript{120} Propene and higher olefins can react with the catalytically active metal-acyl species by either 1,2- or 2,1-insertion. The regioselectivity of the catalyst thus determines the regiochemical structure of the resulting copolymer by allowing either a mixture of these two insertions and the formation of a regioirregular polymer or only one of them and the formation of a regioregular (H-T) polymer (Figure 20). Each of these structural units gives characteristic carbonyl signals in the $^{13}$C NMR spectrum of the polymer. While achiral Pd complexes such as $\text{[Pd(dppp)(NCCH}_3\text{)_2](BF}_4\text{)_2}$ are known to produce regioirregular polyketone, chiral diphosphane or diimine ligand can give not only regioregular but also stereoregular, isotactic, and optically active polyketones.\textsuperscript{99}

![Figure 20](image)

Figure 20. Regioregular (head-tail, H-T) and regioirregular (head-head, H-H, and tail-tail, T-T) structural units in propene/CO copolymer.

Soon after the first synthesis of propene/CO copolymers, they were also found to exist in the isomeric poly-spiroketal structure (Figure 21).\textsuperscript{121} The relative stability of the two
structures seems to be determined by entropic factors. Increase in size of the olefin substituent\textsuperscript{99a,122} or the number of substituents (e.g. norbornene)\textsuperscript{123} leads to the stabilization of the spiroketal structure. The polyketone structure seems to be thermodynamically more stable, however, as it is obtained from the spiroketal structure produced in a highly regio- and stereoselective propene/CO copolymerization after treatment of the spiroketal product with hexafluoroisopropanol.\textsuperscript{124} It is noteworthy that the spiroketal structure usually requires a regio- and stereoregular copolymerization and it was not detected in the irregular polymerizations of this study.

![Figure 21. Possible structures of olefin/carbon monoxide copolymers.](image)

### 4.2 Preparation of olefin-functionalized polyketones

All polymerizations were carried out in CH\textsubscript{2}Cl\textsubscript{2} (100 ml) at room temperature and 60 bar pressure using [Pd(dppp)(NC\textsubscript{3})\textsubscript{2}](BF\textsubscript{4})\textsubscript{2} (50 mg) as catalyst precursor and a minimum amount of methanol (0.25 ml) as activator.

#### 4.2.1 Co- and terpolymerization of methylenecycloalkanes with CO and propene

A pathway toward olefin-functionalized polyketones seemed feasible by applying methylenecycloalkanes as monomers. The results of polymerization of methylenecyclobutane mediated by zirconocenes have demonstrated that ring-opening with \(\beta\)-alkyl shift represents an efficient propagation pathway for the synthesis of \textit{exo}-methylene functionalized polyolefins.\textsuperscript{125} With this in mind, co- and terpolymers of methylenecyclopropane with carbon monoxide and propene were prepared (Scheme 16).
Scheme 16. Terpolymerization of methylenecyclopropane (MCP) with carbon monoxide and propene. V

The resulting materials were insoluble in most of the organic solvents and were analyzed by IR and solid state $^{13}$C NMR. The analyses showed the polyketone to consist of both ring-opened and cyclic structures. On the bases of these results and those of Marks and coworkers, 125 a possible reaction scheme for the ring-opening in the copolymerization reaction was drawn (Scheme 17). Recently, this mechanism was confirmed by the alternating copolymerization of CO with $^{13}$C enriched methylenecyclopropane containing aryl substituents. 126 In that case, the product contained exclusively ring-opened structures. Evidently, this reaction efficiently implants methylene functionalities directly in the polyketone backbone. Highly unsaturated polyketones have also been obtained by copolymerizing 3,3-dimethylallene with CO. 127 In this method to put pendant vinylic functionalities in conjugation with backbone keto groups, monodentate phosphane ligands were more efficient than their bidentate chelates. This is in contrast to the general trend in polyketone synthesis and implies a different mechanism. Various arylallenes have also been copolymerized with CO using Rh-based catalysts. 128

4.2.2 Co- and terpolymerization of dienes with CO and propene

Another approach to the preparation of unsaturated polyketones is to place olefin functionalities in the side chains. A way to do this was achieved in the present work by the co- and terpolymerization of aliphatic linear dienes (Scheme 18). All the carbon monoxide/diene copolymers and terpolymers with propene were soluble in chlorinated solvents, such as dichloromethane, and were characterized by IR, GPC, DSC, and $^1$H and $^{13}$C NMR. When 1,5-hexadiene was used as comonomer, it underwent a regioirregular cyclocopolymerization, forming 5- and 6-membered-ring ketones, but the use of higher dienes, 1,7-octadiene or 1,6-heptadien-4-ol, did not lead to cyclic structures. Instead, a second double bond was found in the end of the side chain and detected by IR ($\nu$(C=C) $\equiv$ 1640 cm$^{-1}$) and $^{13}$C-NMR (resonances at 138 and 118 ppm). Although the copolymers are soluble in chlorinated solvents, a certain amount of cross linking appears to be present. According to $^1$H NMR analysis the amounts of monomer units with intact double bonds in the polymers are 60% and 40% for Oc/CO and Hp-ol/CO copolymers, respectively.
When these higher dienes, in which the double bonds are spaced with at least three carbon atoms apart, were terpolymerized with propene, the incorporation of diene/CO units rose to 23 mol-% in the terpolymers, keeping the unsaturation high. In the case of 1,5-hexadiene, introducing propene as a termonomer in the polymerization system did not prevent the ring formation and no sign of unsaturated resonances was found in spectral analyses. These results confirm the formation of ring structures in 1,5-hexadiene/CO copolymerization, as was also observed by Borkowski and Waymouth. They concluded that the six-membered rings are probably due to an initial 1,2-insertion of the hexadiene followed by 1,2-insertion of the second double bond into the preformed Pd-acyl species, whereas five-membered rings are formed by initial 2,1-insertion. As expected for higher dienes, the reinsertion of the same monomer (1,7-octadiene) into the Pd-acyl species to form 7-, 8-, and 9-membered ring polyketone seems to be prohibited by an energetically unfavorable metallacyclic intermediate.

Scheme 18. Alternating copolymerization of 1,5-hexadiene, 1,7-octadiene and 1,6-heptadiene-4-ol with carbon monoxide.
4.3 Preparation of phenol-containing polyketones

All organic materials, including polyolefins and especially polyketones, are susceptible to autoxidation. This is an irreversible degradation process that leads ultimately to discoloration and loss of physical properties. Primary antioxidants, known as radical scavengers, are designed to interfere with the autoxidation, and prevent it from becoming autocatalytic. With time, stabilizing agents added to commercial polymers may leach out or migrate from the polymer matrix. Incorporating these stabilizers directly in the polymer main chain using transition metal-based catalysts would represent a new approach to stabilizing organic polymers against degradation caused by high temperatures, ultraviolet light, and other environmental stress.

Stabilizing polymers in the polymerization phase is a cost-efficient approach, and at the same time one achieves an even distribution of the stabilizer in the polymer matrix, so that the amount of stabilizing compounds can be minimized. In packaging applications where the film comes in direct contact with food, the covalent binding of all components of the polymer film in the polymer chain is an additional advantage of these materials. Moreover, previous work on stabilizing polyolefin materials has shown that polymers with covalently bound antioxidants in the polymer main chain possess improved oxidation stability over polymers admixed with commercial antioxidants.

In view of the capability of the early transition metal based catalyst systems to copolymerize the functional stabilizer agents, it was attractive to test the less electrophilic Pd(II) catalyst system for copolymerization with carbon monoxide. The capability of palladium(II)-based catalysts to copolymerize ethene or propene with readily available acrylic monomers to branched, high molecular weight products was particularly encouraging. Recently, [Pd(dppp)(NCCH₃)₂][BF₄]₂ has been found active in co- and terpolymerization of substituted allylbenzenes with CO and propene by Rieger’s group. Since unstabilized polyketones are photodegradable at room temperature, the approach of the present contribution is to apply [Pd(dppp)(NCCH₃)₂][BF₄]₂ for the copolymerization of phenol-containing stabilizing agents. This should increase industrial interest towards Pd-catalyzed carbon monoxide/olefin copolymers.
4.3.1 Stabilization of polyketones by co- and terpolymerization of phenolic antioxidants with CO and propene

This part describes co- and terpolymerization reactions of phenolic vinylsubstituted antioxidants – 6-\textit{tert}-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol (A), o-allylphenol (B), 4-methylstyrene-2,6-di-\textit{tert}-butylphenol (C), and 2,6-di-\textit{tert}-butyl-4-allyl-phenol (D) – with propene and carbon monoxide and the properties of the resulting polymer materials, including molar mass, stability, glass transition temperature, and elastic behavior. All the polymers (Scheme 19, Table 1) were isolated as flexible transparent films, except the copolymer of B, which appeared in powder-like form. Polymer was also obtained, although in a lower yield, when methanol was not used as a cocatalyst, which means that these phenolic monomers, although bulkier than methanol, can also take part in the initiation mechanism.

**Table 1. Co- and terpolymerization\(^a\) of propene, vinyl substituted phenolic antioxidant functionalized \(\alpha\)-olefin, and carbon monoxide.\(^b\)**

<table>
<thead>
<tr>
<th>Run</th>
<th>Co- or Terpolymer</th>
<th>Amount of stabilizer (in feed) (g)</th>
<th>Yield(^b) (g)</th>
<th>Activity g(poly)/mol(pd)(^c)×h</th>
<th>M(_w) (10(^3) g/mol)</th>
<th>Content of stabilizer mol(%)(^d)</th>
<th>T(_g) ((^\circ)C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A/CO</td>
<td>1.84</td>
<td>1.0</td>
<td>217</td>
<td>3.60</td>
<td>50</td>
<td>n.d.</td>
</tr>
<tr>
<td>2</td>
<td>A/CO/propene</td>
<td>0.97</td>
<td>4.0</td>
<td>868</td>
<td>108</td>
<td>0.3</td>
<td>17</td>
</tr>
<tr>
<td>3(^e)</td>
<td>A/CO/propene</td>
<td>0.70</td>
<td>1.0</td>
<td>217</td>
<td>5.60</td>
<td>0.6</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>C/CO/propene</td>
<td>1.00</td>
<td>10.2</td>
<td>2170</td>
<td>92.9</td>
<td>1.1</td>
<td>14</td>
</tr>
<tr>
<td>5</td>
<td>B/CO</td>
<td>5.77</td>
<td>4.0</td>
<td>868</td>
<td>11.5</td>
<td>50</td>
<td>41</td>
</tr>
<tr>
<td>6</td>
<td>B/CO/propene</td>
<td>3.32</td>
<td>5.4</td>
<td>1170</td>
<td>25.6</td>
<td>12</td>
<td>48</td>
</tr>
<tr>
<td>7</td>
<td>D/CO/propene</td>
<td>5.06</td>
<td>4.0</td>
<td>868</td>
<td>87.4</td>
<td>1.8</td>
<td>33</td>
</tr>
</tbody>
</table>

\(^a\) Catalyst [Pd(dpdp)(NCCH\(_3\))\(_2\)](BF\(_4\))\(_2\); MeOH (activator)/Pd(II) mol ratio, 250; propene 40 g, CO pressure 5.52 Mpa, solvent CH\(_2\)Cl\(_2\) 100 ml, time of polymerization 72 h.
\(^b\) Isolated yield after purification of the polymer.
\(^c\) Measured by GPC (Relative to polystyrene standards).
\(^d\) Calculated from \(^1\)H NMR spectrum by comparing the integral values of the aromatic versus aliphatic regions of the spectra, except entries 1 and 5 which are based on the molecular structure.
\(^e\) No MeOH was used.
Scheme 19. Terpolymerization of propene, carbon monoxide and the α-olefin with stabilizer functionality, CH$_2$=CH-R (6-tert-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol (A), α-allylphenol (B), 4-methylstyrene-2,6-di-tert-butylphenol (C), and 2,6-di-tert-butyl-4-allyl-phenol (D)).

The IR spectra of the isolated polymers show an absorbance at 1705 cm$^{-1}$, which is the characteristic area for carbonyl group incorporated in poly(1,4-ketone) and at 3401 cm$^{-1}$, which is due to the phenolic hydroxyl groups. The absorbance due to the hydroxyl groups was not seen for the B/CO copolymer; instead, absorption at 1489 cm$^{-1}$ assignable to the C-O-C group was observed. Formation of cyclic ethers might be due to the ketone-hemiketal equilibrium that may exist between hydroxyl groups in the ortho position and the carbonyl groups in the main chain of the polymer (Scheme 20). Such equilibrium was not observed in the co- and terpolymers of the other incorporated stabilizers (A, C and D), where only resonances of linear polymers were detected by IR and NMR. One reason for this result might be steric hindrance of the OH by neighboring $t$-Bu groups.
Scheme 20. Ketone-hemiketal equilibrium between hydroxyl and carbonyl groups in the main chain of 2-allylphenol (B)/carbon monoxide co- and terpolymers.\textsuperscript{VI}

Although the stabilizer content in the terpolymers was low, less than 2 mol-% except for B/CO/propene (12%), it nevertheless appears to have an effect on the physical properties of the parent copolymer. The copolymer B/CO and the terpolymers B/CO/propene and D/CO/propene show glass transition temperatures ($T_g$) at 41, 48 and 33 °C, respectively, which are higher than that reported for alternating propene/CO thermoplastic elastomer (23 °C).\textsuperscript{136} The stress-strain curve determined for D/CO/propene is comparable to that measured for P/CO, but appears at higher level (Figure 22). Incorporation of the vinyl-substituted phenolic comonomer evidently makes the polymer more rigid.

![Figure 22. Stress-strain behavior of D/CO/P, compared to elastic propene/CO copolymer (PCO) and propene/ethene/CO terpolymers (EPCO), extension ratio ($\lambda$); nominal stress ($\sigma_N$, MPa).\textsuperscript{VI}](image-url)
Molar masses of the resulting terpolymers were measured immediately after polymerization and again after samples were kept in the dark for about 24 months at ambient temperature. All terpolymers showed higher molar masses than the respective fresh samples. For example, the molecular weights of the terpolymers prepared with stabilizers A (run 2), C (run 4) and D (run 7) had increased by $30.8 \times 10^3$, $67.3 \times 10^3$ and $20.3 \times 10^3$ g/mol, respectively. The unstabilized copolymer meanwhile underwent a severe degradation, as indicated by the reduction of its molar mass from $2.3 \times 10^5$ to $7.95 \times 10^3$ g/mol in just 12 months. Increase in the molar mass of the terpolymers could be due to partial intramolecular cross-linking that probably took place between phenolic hydroxyl and ketone sites similar to that observed in o-allylphenol/CO/P terpolymer.

### 4.4 Preparation of alternating carbon monoxide/norbornene copolymer

A cationic palladium(II) complex where the classical diphosphane chelate is replaced by arsenic and sulphur donors (Scheme 21) was prepared. With weaker donor atoms in the chelate, the activity of the complex in norbornene homopolymerization was lower than that of the corresponding phosphane complexes and a catalyst with potential for the copolymerization of norbornene with carbon monoxide was in hand. Under the same reaction conditions as used for other higher olefins in this study, norbornene/CO copolymer was isolated and found to have a high molecular weight ($1.42 \times 10^4$ g/mol) relative to the oligomer obtained with monodentate phosphane ligands. Unlike the norbornene homopolymer obtained with this catalyst, which was of amorphous nature, the norbornene/CO copolymer was crystalline with a glass transition temperature of 161 °C, which is very high for a polyketone material.

![Scheme 21](image)

**Scheme 21.** Copolymerization of norbornene and carbon monoxide by Pd(II) catalyst.
4.5 Olefin polymerization with transition metal catalysts bearing bianiline-based ligands

4.5.1 Zirconium(IV)-catalyzed polymerization of ethene, propene, and 1-hexene

Despite the structural characterization of the Zr precatalysts (Sect. 3.4.4), which in the solid state appear to have the monodentate ligands in trans positions, some preliminary olefin polymerization tests were run. After activation with MAO, 5-ZrCl₂(THF) was indeed found to catalyze the polymerization of ethene (6.17 kg/mol·h·bar) and of propene (7.76 kg/mol·h·bar), as well as the copolymerization of 1-hexene with ethene (1.49 kg/mol·h·bar) under non-optimized conditions (Table 2).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Activator</th>
<th>Monomer</th>
<th>Activity a</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-ZrCl₂(THF) b</td>
<td>MAO</td>
<td>Ethene</td>
<td>6.17</td>
</tr>
<tr>
<td>5-ZrCl₂(THF) c</td>
<td>MAO</td>
<td>Propene</td>
<td>7.76</td>
</tr>
<tr>
<td>5-ZrCl₂(THF) d</td>
<td>MAO</td>
<td>Ethene/1-hexene</td>
<td>1.49</td>
</tr>
<tr>
<td>6-Zr(CH₂Ph)₂ e</td>
<td>[PhNMe₂H][B(C₆F₅)₄]</td>
<td>Propene</td>
<td>0.44</td>
</tr>
</tbody>
</table>

a given as kg polymer/[mol(catalyst)·h·bar]. b In toluene (100 ml) at 50 °C for 1h, Al/Zr = 1000, p(ethene) = 20 bar. c In toluene (500 ml) at 50 °C for 2h, Al/Zr = 1500, p(propene) = 2 bar. d In a solution of 10 ml of 1-hexene in 100 ml of toluene at 50 °C for 1h, Al/Zr = 1000, p(ethene) = 5 bar. e In toluene (500 ml) at 50 °C for 2h, anilinium borate/Zr = 1, p(propene) = 2 bar, Al(⁻Bu)₃ added as scavanger.

13C NMR spectra (in C₂D₂Cl₄) of the ethene/hexene copolymer revealed a hexene content of 2.2 mol-%. However, the true copolymer nature of the product was not further investigated for example, by attempts to separate a possible polymer blend by extraction. Tetradentate chiral Zr or Ti complexes with an ethylenediamine-linked bispyrrolidine ligand have recently been reported to incorporate no 1-hexene in ethene polymerization. The polypropene obtained with 5-ZrCl₂(THF)/MAO was found to be partially isotactic with 55% mmmm pentads, in distinction to the atactic polypropene obtained with a chiral zirconium complex containing a bidentate bianiline-diamido ligand. After activation with [PhNMe₂H][B(C₆F₅)₄], complex 6-Zr-(CH₂Ph)₂ catalyzed the polymerization of propene with rather low activity (0.44 kg/mol·h·bar). Complex 7-Zr(CH₂Ph)₂, however, showed no propene polymerization activity at all when activated with [PhNMe₂H][B(C₆F₅)₄]. This result is in agreement with molecular modeling studies. One explanation for the lack of
activity of 7-Zr(CH₂Ph)₂ in polymerization may be that this complex is unable to adopt the cis-configuration required for the insertion reaction.

The preliminary results presented above indicate that species of the type 5- or 6-Zr(pol)(olefin)⁺ are generated in these reaction systems, and in these species the growing polymer chain and the olefin substrate occupy cis-coordination sites. This position requires that the heterocyclic N ligands adopt a screw-like trans orientation similar to that observed for 6-Zr(Bu₄biphenO₂), and might thus be suitable to induce a preferential orientation of the last-inserted polymer-chain segment and/or the entering olefin substrate. This would explain the preference for isotactic enchainment observed in these reaction systems.

4.5.2 Palladium(II) catalyzed polymerization of norbornene

The neutral palladium(II) chloro complexes 2-PdCl₂, 2-(PdCl₂)₂, 3-PdCl₂, and 4-PdCl₂ were activated with MAO and their activity, as well as the activity of the dicationic complexes (2-Pd)(BF₄)₂ and [4-Pd(NCCH₃)₂](BF₄)₂, toward the polymerization of norbornene was studied at room temperature (Table 3). The polymers obtained from runs 1-4 with the chloro complexes, isolated in 38-71% yield, were insoluble in organic solvents such as trichlorobenzene, even at elevated temperatures. When the cationic catalyst [4-Pd(NCCH₃)₂](BF₄)₂ was used instead (run 6), polymer with good solubility in toluene and chloroform was isolated in moderate yield. The molecular weight of this sample was found to be 33 800 g/mol with a PDI of 1.26. Complex (2-Pd)(BF₄)₂, in which the tetradentate ligand is bound to Pd from all four N atoms, was inactive in polymerization of norbornene at room temperature.

The decomposition of the polymers was followed by TGA and found to occur at an exceptionally high temperature of about 450 °C. This is more than 100 °C higher than for the polymer obtained with [Pd(NCCH₃)₄](BF₄)₂ (335 °C),³⁶f which suggests that a certain degree of stereoregularity may be present in the polymer due to the chiral ligand. The decomposition temperature of polynorbornene was raised to 415 °C in a similar system bearing an enantiomerically pure (1R, 2R)-(−)-N,N’-di(quinoline-2-methylene)-diiminocyclohexane backbone.⁷⁰b No clear glass transition was detected in DSC analysis. Unfortunately, despite several attempts at pressures up to 10 bar and temperatures up to 60 °C, no ethene was polymerized or oligomerized with these complexes when activated with MAO.
Table 3. Polymerization of norbornene with Pd(II) complexes bearing bianiline based ligands.

<table>
<thead>
<tr>
<th>Run</th>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Activity (kg/mol*h)</th>
<th>TGA (°C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2-PdCl₂/MAO</td>
<td>64</td>
<td>67</td>
<td>455</td>
</tr>
<tr>
<td>2</td>
<td>2-(PdCl₂)₂/MAO</td>
<td>56</td>
<td>59</td>
<td>452</td>
</tr>
<tr>
<td>3</td>
<td>3-PdCl₂/MAO</td>
<td>71</td>
<td>75</td>
<td>447</td>
</tr>
<tr>
<td>4</td>
<td>4-PdCl₂/MAO</td>
<td>38</td>
<td>40</td>
<td>448</td>
</tr>
<tr>
<td>5</td>
<td>(2-Pd)(BF₄)₂</td>
<td>No polymer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td><a href="BF%E2%82%84">4-Pd(NCCH₃)₂</a>₂</td>
<td>44</td>
<td>14</td>
<td>438</td>
</tr>
</tbody>
</table>

runs 1-4 were made in toluene and the catalyst precursor was activated with MAO (molar ratio Al:catalyst = 1000). Norbornene/catalyst molar ratio was 1100. Runs 5-6 were made in CH₂Cl₂/PhCl/nitrobenzene with norbornene/catalyst molar ratio of 340. Reaction mixtures were stirred at room temperature for 1 h.

5 Conclusions

This work shows that various different transition metal complexes can be prepared in a controlled manner by careful fine-tuning of the reaction conditions and work-up. For example, the reaction of sodium salts of salicylketimines with trans-[(PPh₃)₂Ni(Ph)Cl] produced either (sal)Ni(Ph)(PPh₃) or Ni(sal)₂ depending on how the reaction was run. The former product was preferred when the reaction solvent (benzene) was added to a solid mixture of the two reactants at a temperature close to the solvent’s freezing point. Ni(sal)₂ was formed more readily from salicylketimines than salicylaldimines. The formation of Ni(sal)₂ in the polymerization solution can be one reason for the observed inactivity of the monophenyl complexes 11 and 12 in the polymerization of ethene or norbornene when only phosphane scavengers such as Ni(COD)₂ or BF₃ were used as cocatalyst.

As a second example, the biphenyl-bridged diimino ligands with additional pyridyl or furyl side arms were found highly versatile in Pd(II) complex formation. Depending on the Pd precursors and reaction conditions, a variety of mono- or binuclear, C₁ or C₂ symmetric Pd(II) complexes were obtained in a controlled way. Bis(pyridylimine) ligand 2 can be reacted with Pd(COD)Cl₂ to form either mononuclear 2-PdCl₂ or binuclear 2-(PdCl₂)₂ in high yield depending on the reaction temperature. The catalytic behavior of the (2-4)-Pd(II) complexes in norbornene polymerization were found to vary from totally inactive to fairly active, and polynorbornenes ranging from soluble to insoluble materials stable up to 455 °C was produced.
The coordination chemistry of Zr to the chiral biphenyl-bridged bis(pyridylamido) ligands was studied and found to be heavily influenced by the coligands. The solid-state structural analysis showed that the tetradentate ligand occupies the square plane of the octahedral coordination sphere around Zr leaving the monodentate ligands trans to each other. Regardless, the preliminary polymerization results indicated that species of the type $5^{-}$ or $6^{-}$-Zr(pol)(olefin)$^+$ where the growing polymer chain and the coordinated olefin occupy cis-positions, are generated in the reaction system. In this way the heterocyclic N ligands adopt a screw-like trans orientation and the chiral cage formed around Zr might be responsible for the isotactic enchainment observed in the polypropene produced (55% mmmm pentads).

The work demonstrates two different routes for the preparation of olefin-functionalized polyketones by Pd(II)-catalyzed copolymerization of carbon monoxide. Ring-opening copolymerization of methylenecyclopropane with CO yielded polyketone with methylene functionalities attached to the polymer main chain, whereas use of higher linear dienes with seven or more carbon atoms as comonomers gave polymers with olefin functionalities in the side chains. These comonomers were present to a good extend in the terpolymers with propene, changing the physical properties of propene/CO copolymer. Furthermore, the ability of the [Pd(dppp)(NCCH$_3$)$_2$](BF$_4$)$_2$ catalyst system also to incorporate olefins with polar functionalities in the polyketone material was exploited as a means of stabilizing the polyketone material in the polymerization phase. With this method, phenolic stabilizers can be added to the polymer main chain as comonomers, and even a small incorporation (< 2%) significantly changed the stability and physical properties of the parent material.
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