Nickel and palladium complexes of pyridine-phosphine ligands: synthesis, characterization, and ethene oligomerization

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Chapter 1

Introduction
Introduction

Production and applications of olefins

α-Olefins are produced on a megaton scale per year. They can be produced via different routes, of which the best known are oligomerization of ethene, thermal and catalytic cracking of paraffins, dehydrogenation of paraffins, and dehydration of alcohols. Ethene oligomerization is the most important industrial reaction for α-olefins production. This reaction yields products with only even numbers of carbon atoms. The obtained olefins are used in many industrial processes. Depending on their chain length, they find their most important applications in the production of linear low-density polyethylene (LLDPE) [C4-C10], poly-α-olefins (C4, C10), plasticizers (C6-C10), lubricants (C8-C10), lube oil additives (C12-C18), and surfactants (C12-C20).1-7

Traditionally, ethene oligomerization catalysis is performed by systems based on the ‘aufbau’ reaction of alkylaluminum or by transition metal catalysts which are mainly based on titanium, nickel, and zirconium. The commercial Gulf (now Chevron Philips) and Ethyl (now BP Amoco) processes make use of aluminum, while the Shell Higher Olefin Process (SHOP) is based on nickel catalysis.1-3,5,6 In the commercial Alphabutol process (by IFP), ethene is selectively dimerized to 1-butene using a Ti(OR)4 / AlEt3 based system.9-11

In recent years, other metals have also been utilized in olefin oligomerization. For example, pyridinediimine iron complexes were reported to have a very high activity in the oligomerization of ethene.12-14 Selective trimerization to form predominantly 1-hexene was accomplished using titanium and chromium catalysis, and even tetramerization to form mainly 1-octene was achieved using the latter metal.15-17

A complete description of all ethene oligomerization catalysts is beyond the scope of this overview, and we will focus on oligomerization of ethene by systems based on nickel and, to a lesser extent, palladium.

Mechanism of transition metal catalyzed ethene oligomerization

The mechanism of transition metal catalyzed ethene oligomerization is characterized by a few basic steps: initiation, propagation, termination, and (if applicable) isomerization.
Scheme 1. Initiation of active species from different catalyst precursors; $i =$ activation.

An overview of different pathways to start oligomerization is shown in scheme 1. Initiation generates the active metal hydride species. This is usually obtained from an alkylmetal complex, which gives the metal hydride after elimination of an alkene. The alkylmetal species, in turn, can be generated from different species. Activation [$i$ in scheme 1] of a complex $MX_2$, $MXR$, or $MR_2$ (where $X$ is a halide and $R$ is an alkyl or aryl) and subsequent ethene insertion can give this species. This activation can be performed for example by alkylaluminum cocatalysts (like MAO or $\text{EtAlCl}_2$), by halide abstraction from an alkylmetal halide, or by protonation of one $R$ group in $MR_2$. Replacement of a neutral coordinating group (L) by ethene from an aryl- or alkylmetal species and subsequent migratory insertion can also generate the alkylmetal species.$^{18,19}$

Scheme 2. Chain propagation and termination.

Propagation, or chain growth, takes place by subsequent insertions of ethene in the metal hydride complex, thus elongating the chain by two carbons every insertion. Chain termination takes place via $\beta$-hydride elimination and subsequent dissociation of the so formed alkene. This also gives back the starting metal hydride, which can grow another chain [see scheme 2].
Sometimes next to propagation and termination, isomerization takes place, as depicted in scheme 3. After β-hydride elimination, the hydride can re-insert with different regiochemistry resulting in a branched alkyl, coordinated to the metal. This can have an agostic interaction with another β-proton, resulting in β-hydride elimination to give an internal alkene ligated to the metal. Multiple elimination-reinsertion cycles lead to isomerization of the olefin functionality or so-called ‘chain-walking’ of the metal.

The ethene oligomerization is schematically depicted in scheme 4. The rate of termination ($k_t$) and the rate of propagation ($k_p$) are of the same order of magnitude ($k_p-k_t$). The Schulz-Flory constant ($\alpha$) is often used to describe the ratio between the change of chain termination and chain propagation and is defined as $\alpha = C_{\text{n+2}} / C_{\text{n}}$; where $C_n$ is the amount of product with $n$ carbons in the chain (in mol). This formula only holds if specific criteria are fulfilled. First, the chance of termination of a chain should be independent of the length of this chain, so: $k_{t[n]} = k_{t[n+2]}$. Especially with short chains, this criterion is not always met. Furthermore, the rate of chain isomerization ($k_t$) should be negligible compared to propagation: $k_p >> k_t$.

If the rate of chain isomerization is in the same order of magnitude as chain growth ($k_p - k_t$), the mechanism becomes much more complicated. Scheme 5 shows a simplified overview of possible pathways for the first 3 insertions if isomerization is taken into account. After insertion of two molecules of ethene, next to chain termination or elongation, chain isomerization can take place. As a consequence of this, next to 1-butene also cis- and trans-2-butene are formed. The next ethene molecule can insert in the linear
or in the branched alkylmetal species, and the so formed products can undergo isomerization as well, before chain elongation or termination takes place. For the C6-fraction, no less than nine different products can be formed. Needless to say, the number of possible products increases with each ethene insertion. The simple formula for the Schulz-Flory constant does not hold, as different rates of termination and growth must be accounted for. Even if the chain length or tacticity are not concerned, the rate constants for growth, termination, and isomerization will be different if the metal is attached to a primary, secondary, or tertiary carbon atom. As a consequence of this, a classical Schulz-Flory distribution of the products is not obtained and thus it is incorrect to speak of a Schulz-Flory constant in cases were isomerization is competitive with chain growth.

Scheme 5. Schematic overview of possible pathways for chain growth, termination, and isomerization [up to C6] with rate constants from primary \( k \), secondary \( k' \), and tertiary \( k'' \) metal-carbon complexes if \( k_p - k_i - k_t \).
Nickel and palladium based oligomerization and polymerization catalysts

The last decade, there has been great academic and industrial interest in late transition metal catalyzed ethene and olefin polymerization and oligomerization, and this has extensively been reviewed.\textsuperscript{7,18,20-25} The renewed interest has largely been triggered by the finding of the group of Brookhart that $\alpha$-diimine based nickel and palladium complexes catalyze the polymerization of ethene and $\alpha$-olefins.\textsuperscript{26} In these catalysts, bulky substituents blocking the axial sites of the metal were the key feature to suppress chain transfer and obtain high molecular weight products.\textsuperscript{26-28} Indeed, when these substituents were not present at both aryl groups, chain transfer became competitive with propagation and the complexes functioned as oligomerization catalysts.\textsuperscript{29,30} The high tendency of group 10 metals to give $\beta$-hydride elimination and subsequent chain transfer is the reason that these elements are usually utilized in oligomerization catalysis. Before the report of the Brookhart group,\textsuperscript{26} a few nickel based polymerization catalysts were known to produce linear polyethylene.\textsuperscript{31-37} One of the special features of the diimine systems is that a branched polymer can be obtained from ethene (without the use of co-monomers), and the degree of branching can be varied from nearly linear to hyperbranched.\textsuperscript{38-40} Recently, other highly active nickel based systems yielding branched polyethylene have been reported.\textsuperscript{41-44}

Besides systems that polymerize ethene, many oligomerization catalysts based on nickel or palladium have been reported. We already mentioned the famous SHOP system, based on a nickel catalyst with an anionic P,O ligand.\textsuperscript{35,45} Its performance is characterized by high linearity (99\%) and $\alpha$-olefin content (98\%) of the product, the most valuable olefins; the industrial application requires low levels of reinsertion and isomerization of the product. The structure-reactivity relationships in this type of catalysts have recently been reviewed,\textsuperscript{25} and studies in this field continue.\textsuperscript{46} A series of related nickel complexes with neutral P,O ligands showed a remarkable high activity for the dimerization of ethene, but selectivity and (thermal) stability were low. The palladium analogues are less active and gave butenes and hexenes as the products.\textsuperscript{47} Anionic N,O ligands have also been applied successfully in ethene oligomerization.\textsuperscript{48-57} Examples of systems with neutral N,N ligands are the aforementioned $\alpha$-diimine systems lacking aryl-substituents,\textsuperscript{29,30} but many more have been reported.\textsuperscript{21,22} On the contrary, only a few P,P bidentate ligands have been reported to form active ethene oligomerization catalysts with nickel.\textsuperscript{58-62} Transition metal complexes bearing hybrid ligands having one nitrogen and one phosphorus donor atom [P,N ligands] have shown their value in many catalytic reactions.\textsuperscript{63-70} Nickel and palladium
complexes derived from these ligands have been used in the formation of olefins from ethene. In the next part, we will focus on the performance of these complexes.

**Nickel complexes with P,N-ligands in ethene oligomerization**

We will give an overview of nickel (table 1) and palladium (table 2) complexes bearing P,N-ligands which have been used as ethene oligomerization catalyst precursor. Their performance is compared despite the differences in many factors that influence the outcome of the reaction like pressure, reaction time, reaction temperature, cooling, solvent, nature and amount of cocatalyst (including quality of MAO), reactor size, and stirring. Turn over frequencies have been converted, where necessary, into the units [mol C₆H₆](mol Ni·h)⁻¹.

**Table 1. Comparison of P,N-nickel catalysts in ethene oligomerization**

<table>
<thead>
<tr>
<th>Catalyst (precursor)</th>
<th>Conditions</th>
<th>Co-catalyst (equiv)</th>
<th>(max-)imum</th>
<th>Selectivity</th>
<th>Comments</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Complex 1" /></td>
<td>50 µmol cat, 5 bar C₂H₄, 20 mL PhMe, r.t., 16h.</td>
<td>-</td>
<td>very low</td>
<td>traces of low molecular weight linear α-olefins</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td><img src="image2.png" alt="Complex 2" /></td>
<td>50 µmol cat, 28 bar C₂H₄, 150 mL PhMe, 40 °C, 1h</td>
<td>-</td>
<td>12,150</td>
<td>average M₉: 500</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td><img src="image3.png" alt="Complex 3" /></td>
<td>4.6 µmol cat, 28 bar C₂H₄, 100 mL PhCl, 30 °C, 0.3h</td>
<td>EtAlCl₂ (400)</td>
<td>10⁰</td>
<td>butenes</td>
<td>MMAO activation yielded polymer</td>
<td>73</td>
</tr>
<tr>
<td><img src="image4.png" alt="Complex 4" /></td>
<td>20 µmol cat, 30 bar C₂H₄, 20 mL PhMe, 50 °C, 2h</td>
<td>MAO (100)</td>
<td>29,500</td>
<td>(molC₁₀) / (molC₈) = 0.83; linearity C₆: 84%, α-olefin C₆: 49%</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>Catalyst</td>
<td>Reaction Conditions</td>
<td>Molar Yield</td>
<td>Olefin Selectivity</td>
<td>Remarks</td>
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<tr>
<td><img src="image.png" alt="Catalyst 5" /></td>
<td>10 µmol cat, 7 bar C₂H₄, 30 mL PhMe, 25 °C, 0.17h.</td>
<td>Br(C₆F₅)₃ (2.5)</td>
<td>butenes</td>
<td>one catalyst yielded polymer</td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image.png" alt="Catalyst 6" /></td>
<td>50 µmol cat, 1 bar C₂H₄, 50 mL PhMe, 20 °C, 0.5h.</td>
<td>EtAlCl₂ (4.5)</td>
<td>C4: 33,214</td>
<td>corresponding Pd-complexes were inactive</td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image.png" alt="Catalyst 7" /></td>
<td>20 µmol cat, 30 bar C₂H₄, 30 mL PhMe, 25 °C, 0.3h.</td>
<td>MAO (300)</td>
<td>C4: 2,032</td>
<td>alkyl or aryl backbone; 1-butene selectivity: 73%; 1-hexene selectivity: 50%</td>
<td></td>
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</tr>
<tr>
<td><img src="image.png" alt="Catalyst 8" /></td>
<td>0.25 µmol cat, 31 bar C₂H₄, 4 mL PhMe, 30 °C, 2h.</td>
<td>EtAlCl₂ (1000)</td>
<td>C4: 324,500</td>
<td>Ni⁰ precursor, also Ni¹ used</td>
<td></td>
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<tr>
<td><img src="image.png" alt="Catalyst 9" /></td>
<td>0.25 µmol cat, 21 bar C₂H₄, 4 mL PhMe, 30 °C, 1h.</td>
<td>MAO (1000)</td>
<td>C4: 120,600</td>
<td>Ni⁰ precursor; 1-butene selectivity: 77%</td>
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<tr>
<td><img src="image.png" alt="Catalyst 10" /></td>
<td>10 µmol cat, 30 bar C₂H₄, 30 mL CH₂Cl₂, 30 °C, 2h.</td>
<td>MAO (100)</td>
<td>C4: 88,000</td>
<td>Schulz-Flory constant: 0.35; α-olefins 77%</td>
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</tr>
<tr>
<td><img src="image.png" alt="Catalyst 11" /></td>
<td>40 µmol cat, 10 bar C₂H₄, 15 mL PhMe, 30 °C, 0.58h.</td>
<td>EtAlCl₂ (6)</td>
<td>C4: 45,900</td>
<td>maximum C4 selectivity: 67%; maximum 1-butene selectivity: 25%</td>
<td></td>
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<tr>
<td>Compound</td>
<td>Conditions</td>
<td>Activity</td>
<td>C4 Selectivity</td>
<td>C6 Selectivity</td>
<td>C8 Selectivity</td>
<td>1-butene Selectivity</td>
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<tr>
<td>12</td>
<td>40 µmol cat, 10 bar C₂H₄, 15 mL PhMe, 30 °C, 0.58h.</td>
<td>EtAlCl₂ (6)</td>
<td>49,500</td>
<td>C4: 64%</td>
<td>C6: 33%</td>
<td>C8: 3%</td>
</tr>
<tr>
<td>13</td>
<td>20 µmol cat, 20 bar C₂H₄, 150 mL PhMe, 25 °C, 0.5h.</td>
<td>MAO (1000)</td>
<td>42,143</td>
<td>C4: 85%</td>
<td>C6: 9%</td>
<td>≥C8: 5%</td>
</tr>
<tr>
<td>14</td>
<td>20 µmol cat, 34 bar C₂H₄, 50 mL PhMe, 80 °C, 3h.</td>
<td>MAO (500)</td>
<td>33,929</td>
<td>C4: 73%</td>
<td>C6: 27%</td>
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<tr>
<td>15</td>
<td>40 µmol cat, 10 bar C₂H₄, 15 mL PhMe, 30 °C, 0.58h.</td>
<td>EtAlCl₂ (6)</td>
<td>58,100</td>
<td>C4: 65%</td>
<td>C6: 32%</td>
<td>C8: 3%</td>
</tr>
<tr>
<td>16</td>
<td>40 µmol cat, 10 bar C₂H₄, 15 mL PhMe, 30 °C, 0.58h.</td>
<td>EtAlCl₂ (6)</td>
<td>61,000</td>
<td>C4: 77%</td>
<td>C6: 22%</td>
<td>C8: 1%</td>
</tr>
<tr>
<td>17</td>
<td>10 µmol cat, 10 bar C₂H₄, 15 mL PhCl, 30 °C, 0.58h.</td>
<td>EtAlCl₂ (6)</td>
<td>207,600</td>
<td>C4: 69%</td>
<td>C6: 30%</td>
<td>C8: 1%</td>
</tr>
<tr>
<td>18</td>
<td>10 µmol cat, 30 bar C₂H₄, 30 mL PhMe, 30 °C, 1.7h.</td>
<td>MAO (100)</td>
<td>9,024</td>
<td>C4: 73%</td>
<td>C6: 23%</td>
<td>C8: 3%</td>
</tr>
<tr>
<td>Catalyst Structure</td>
<td>Reaction Conditions</td>
<td>Yield</td>
<td>C4 Selectivity</td>
<td>1-Butene Selectivity</td>
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<tr>
<td>19</td>
<td>40 µmol cat, 10 bar C2H4, 15 mL PhMe, 30 °C, 0.58h.</td>
<td>EtAlCl2 (6)</td>
<td>56,100</td>
<td>70% C4, 28% C6, 2% C8</td>
<td>with 2 equiv EtAlCl2 C4 selectivity: 92%; 1-butene selectivity: 13%</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>40 µmol cat, 10 bar C2H4, 15 mL PhMe, 30 °C, 0.58h.</td>
<td>EtAlCl2 (6)</td>
<td>49,900</td>
<td>71% C4, 29% C6, 2% C8</td>
<td>maximum C4 selectivity: 92%; maximum 1-butene selectivity: 19%</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>40 µmol cat, 10 bar C2H4, 15 mL PhMe, 30 °C, 0.58h.</td>
<td>EtAlCl2 (6)</td>
<td>57,300</td>
<td>75% C4, 23% C6, 2% C8</td>
<td>maximum C4 selectivity: 92%; maximum 1-butene selectivity: 22%</td>
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<tr>
<td>22</td>
<td>10 µmol cat, 10 bar C2H4, 15 mL PhCl, 30 °C, 0.58h.</td>
<td>EtAlCl2 (6)</td>
<td>150,100</td>
<td>71% C4, 27% C6, 2% C8</td>
<td>maximum C4 selectivity: 97%; maximum 1-butene selectivity: 72%</td>
<td></td>
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<tr>
<td>23</td>
<td>33 µmol cat, 21 bar C2H4, 50 mL PhCl, 0 °C, 1h.</td>
<td>Et2AlCl (70)</td>
<td>56,160</td>
<td>90% C4, 8% C6, 2% C8</td>
<td>maximum C4 selectivity: 97%; maximum 1-butene selectivity: 80%</td>
<td></td>
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<tr>
<td>24</td>
<td>15 µmol cat, 4 bar C2H4, 35 mL PhMe, 25 °C</td>
<td>MAO (500)</td>
<td>4,643</td>
<td>66% C4, 34% C6</td>
<td>reaction time not given</td>
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</tr>
<tr>
<td>25</td>
<td>4 µmol cat, 1 bar C2H4, 50 mL PhMe, 0 °C, 0.5h</td>
<td>MAO (300)</td>
<td>7,321</td>
<td>84% C4, 16% C6</td>
<td>selectivity for 1-butene &gt;99%</td>
<td></td>
</tr>
<tr>
<td>Catalyst</td>
<td>Reaction Conditions</td>
<td>Turnover Frequency</td>
<td>Product Distribution</td>
<td>Notes</td>
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<tr>
<td>MAO (100)</td>
<td>10 µmol cat, 3 bar C₂H₄, 10 mL PhMe, 0 °C, 2h.</td>
<td>9250</td>
<td>Mixture of linear and branched olefins</td>
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</tr>
<tr>
<td>EtAlCl₂ (10)</td>
<td>40 µmol cat, 10 bar C₂H₄, 15 mL PhCl, 30 °C, 0.58h.</td>
<td>61,800</td>
<td>C₄: 54%, C₆: 42%, C₈: 4%</td>
<td>Pyridine or oxazoline heterocycles; maximum C₄ selectivity: 90%; maximum 1-butene selectivity: 31%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EtAlCl₂ (10)</td>
<td>40 µmol cat, 10 bar C₂H₄, 15 mL PhCl, 30 °C, 0.58h.</td>
<td>58,200</td>
<td>C₄: 53%, C₆: 43%, C₈: 4%</td>
<td>Maximum C₄ selectivity: 89%; maximum 1-butene selectivity: 13%</td>
<td></td>
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</tr>
<tr>
<td>EtAlCl₂ (6)</td>
<td>40 µmol cat, 10 bar C₂H₄, 50 mL PhMe, 30 °C, 0.58h.</td>
<td>37,900</td>
<td>C₄: 75%, C₆: 23%, C₈: 2%</td>
<td>Maximum C₄ selectivity: 90%; maximum 1-butene selectivity: 21%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MAO (1000)</td>
<td>5 µmol cat, 1 bar C₂H₄, 30 mL PhMe, 20 °C, 0.5h.</td>
<td>47,857</td>
<td>C₄: 37%, C₆: 26%, ≥C₈: 37%</td>
<td>Maximum linear α-olefin: 99%</td>
<td></td>
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</tr>
<tr>
<td>MAO (500)</td>
<td>5 µmol cat, 1 bar C₂H₄, 30 mL PhMe, 20 °C, 0.5h.</td>
<td>40,714</td>
<td>C₄: 84%, C₆: 10%, ≥C₈: 6%</td>
<td>Maximum linear α-olefin: 98%</td>
<td></td>
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</tr>
</tbody>
</table>

*Turn over frequency in [mol C₂H₄]·[mol Ni·h]⁻¹; if similar catalysts were tested or different conditions were applied, the highest activity is reported.

The only nickel complexes with anionic P,N ligands that have been utilized in ethene oligomerization are 1 and 2. This is rather surprising, as the SHOP catalyst is based on an
anionic ligand. Complex 1 is hardly active, while complexes of type 2 show a good activity, forming mainly internal olefins with an average degree of polymerization between 10 and 35.

Different type of P,N ligands with imine functionalities have been used. Type 3 complexes showed a very high activity for dimerization of ethene when activated with EtAlCl₂, but polyethene was obtained when MMAO (modified MAO) was used as activator. A series of phosphine-imine ligands 4 have been used in palladium (see below) and nickel catalyzed oligomerization. The activity dropped when ligand flexibility or steric shielding were increased. Catalyst 5 coordinates an anionic ligand, but this ligand has neutral donors; the negative charge is located away from the metal center. While most complexes dimerized ethene, high molecular weight material was obtained with the complex having bulky iso-propyl substituents. Type 6 complexes showed a moderate activity to form isomeric mixtures of butenes and hexenes, the selectivity was dependant on the exact catalyst used. The corresponding palladium complexes proved to be inactive towards ethene. Very high dimerization activities were obtained with complexes 7, but this was accompanied with short catalyst lifetimes and low thermal stability. Complexes 8 and 9 are examples where the metal is in the unusual oxidation states Ni¹ or Ni⁰. Because of the use of large amounts of alkylaluminum cocatalysts, though, the oxidation state of the active species might be different.

Complex 10 has an amine donor functionality. After activation, it has a low activity to form mainly butenes. This suggests that a nitrogen donor with better π-acceptor properties (like imines) is the better choice for this type of catalysis.

The group of Braunstein has published a number of reports on ethene oligomerization using nickel complexes with P,N ligands, and this has been reviewed.⁷ Complexes 11 and 12 are examples with an oxazoline N-donor, combined with a phosphine (11) or phosphinite (12) P-donor. The complexes show a good activity with only very small amounts of EtAlCl₂ as activator, even as low as 2 equivalents. Another example of a ligand with an oxazoline functionality is 13. The activity at atmospheric pressure was somewhat lower than that at 20 bars. Remarkably, the activity at 1 bar increased when 2-4 equivalents of PPh₃ were added.

A number of ligands with pyridine donor functionalities have been used in nickel catalyzed ethene oligomerization. The largest number of papers is from the group of Braunstein.⁷ Complexes 14-19 bear similar ligands with a pyridine and a phosphine donor. They all show
good activities to from mainly butenes. Complexes 15-17 and 19 required only small amounts of cocatalyst. Complex 18 is the only one with a trisalkyl phosphine, and shows a relatively low activity. In 20-22, the P-donor is a phosphinite. The catalytic behavior is similar to that of the related complexes 14-19 bearing a phosphine donor. Using a pyridine-phosphole ligand, 23 forms a catalyst with a high selectivity for 1-butene. Complexes with a quinoline and a phosphine (24), phosphinite, or pyrrolidinephosphine (25) donor were less active than the pyridine complexes. Complex 26, a nickel-allyl complex with a pyridylphosphine ligand, showed low activity without any activator, but the activity increased when MAO activation was applied.

Complexes 27-31 with tridentate ligands have been utilized in ethene oligomerization. It is unclear, though, if the ligand still behaves as a tridentate in the active species. The hemilability of multitdentate ligands have been reviewed. The activity is similar to related complexes with bidentate ligands, implying that the third donor does not compete for coordination with ethene. This suggests a pentacoordinated active species, like its dihalide precursors.

**Palladium complexes with P,N-ligands in ethene oligomerization**

Palladium complexes with P,N ligands have been applied less often in ethene oligomerization than their nickel counterparts. The activity is usually lower than that of nickel complexes. This, combined with the higher price of palladium, makes them less attractive for this purpose. An advantage is that often they can be converted easily into species that do not require a cocatalyst, in contrast to the corresponding nickel complexes. Indeed, as can be seen from table 2, none of the reported systems makes use of an alkylaluminum cocatalyst. Also, the higher tolerance towards polar comonomers or impurities might be an advantage of palladium based systems, but to date, there are no reports in which this advantage has been utilized in ethene oligomerization.
<table>
<thead>
<tr>
<th>catalyst (precursor)</th>
<th>conditions</th>
<th>TOF(a)</th>
<th>comments</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Catalyst Image 1" /></td>
<td>0.1 mmol Pd(OAc)(_2), 0.11 mmol ligand, 0.21 mmol TsOH, 20 bar C(_2)H(_4), 50 mL MeOH, 100 °C, 5h.</td>
<td>220</td>
<td>C6: 22%; C8: 25%; C10: 22%; C12: 16%; &gt;C12: 15%; C4 not measured</td>
<td>96</td>
</tr>
<tr>
<td><img src="image2.png" alt="Catalyst Image 2" /></td>
<td>50 µmol cat, 30 bar C(_2)H(_4), 20 mL CH(_2)Cl(_2), 70 °C, 2h</td>
<td>1034</td>
<td>(molC10) / (molC8) = 0.74; linearity C6 = 97%, (\alpha)-olefin C6 = 52%</td>
<td>74</td>
</tr>
<tr>
<td><img src="image3.png" alt="Catalyst Image 3" /></td>
<td>10 µmol cat, 28 bar C(_2)H(_4), 100 mL PhMe, 80 °C, 3h.</td>
<td>510</td>
<td>Mn: 350</td>
<td>73</td>
</tr>
<tr>
<td><img src="image4.png" alt="Catalyst Image 4" /></td>
<td>47 µmol cat, 34 bar C(_2)H(_4), 30 mL PhCl, 70 °C, 24h</td>
<td>1.7</td>
<td></td>
<td>97</td>
</tr>
<tr>
<td><img src="image5.png" alt="Catalyst Image 5" /></td>
<td>50 µmol cat, 50 µmol NaBAR(_4), 60 bar C(_2)H(_4), 30 mL CH(_2)Cl(_2)</td>
<td>active system reported, but activity not specified</td>
<td></td>
<td>98</td>
</tr>
<tr>
<td><img src="image6.png" alt="Catalyst Image 6" /></td>
<td>14 bar 30 - 60 °C</td>
<td>very low</td>
<td>complex decomposes under catalytic conditions</td>
<td>84</td>
</tr>
<tr>
<td><img src="image7.png" alt="Catalyst Image 7" /></td>
<td>9.7 µmol cat, 14 bar C(_2)H(_4), 100 mL CH(_2)Cl(_2), 50 °C, 1h.</td>
<td>15,760</td>
<td>Schulz-Flory constant: 0.35</td>
<td>99</td>
</tr>
</tbody>
</table>

\(a\)turn over frequency in [mol C\(_2\)H\(_4\)·mol Ni·h]\(^{-1}\).
As can be seen from table 2, palladium catalysts are indeed generally much less active than nickel based systems. An exception to this is complex 38, which was recently reported by the group of Brookhart. In this complex, an axial Pd···H interaction was proposed as an explanation for the activity for oligomerization instead of dimerization.

The advantage of palladium complexes that they do not need alkylaluminum cocatalysts as activators also has a drawback. To stabilize the pre-activated complex, an ancillary ligand is used, which competes for coordination with ethene. This might explain partly the lower activity of palladium catalysts in this reaction.

Using complexes with phosphine-imine ligands of type 33, a lower activity than with their nickel counterparts 4 and a similar dependence on ligand backbone variation was observed. In contrast to the corresponding nickel complexes 3, palladium complexes 34 gave oligomers with an average $M_n$ of 350 to 660 depending on the exact catalyst structure. Phosphine-imine ligand 32 was used with in-situ complexation of the metal. The labile nature of the ether donor in 35 is reported to assist the complex in catalyzing the oligomerization of ethene. The activity, though, is very low. Two examples of application of palladium complexes with phosphine-pyridine ligands in ethene oligomerization are known. Whereas 37 shows only a very low activity, 36 was reported to be active. Unfortunately, no quantitative data on the activity were given.

**Aim and outline of this thesis**

As can be concluded from the preceding paragraph, there is still little knowledge of the relation between ligand properties and catalytic activity. We wanted to obtain nickel and palladium complexes bearing related pyridine-phosphine ligands and compare the properties of the ligands as well as their behavior in ethene oligomerization.

*Chapter 2* describes the nickel and palladium complexes of five known pyridine-phosphine ligands. In some cases, a new synthetic procedure for the ligands was developed. The paramagnetic nickel and diamagnetic palladium complexes of the ligands were characterized by different techniques. A relation between the bite angle of the ligand and the catalytic behavior of the complex was observed.

The new developed ligands in *chapter 3* have a bulky aryl substituent on the pyridine donor of the ligand, which gives rise to unique coordination behavior in their palladium complexes. The four complexes are all binuclear, with two ligands spanning two palladium
centers. Depending on the ligand’s substituents and the synthetic procedure, the surrounding of the substituents at these centers can be *cis-cis*, *trans-trans*, or even *trans-cis*, despite the fact that both centers are surrounded by the same ligands.

*Chapter 4* continues the studies on the ligands and complexes from the preceding chapter. Furthermore, a ligand related to the ones from the preceding chapter but with a ferrocenyl substituent at the ligand, was obtained. This ligand did not give a single neutral palladium complex, but an undefined mixture. In contrast to their precursors, all corresponding cationic complexes obtained from the neutral complexes appeared as well-defined, monomeric species. The nickel complexes were obtained for all ligands, which did not show unexpected coordination behavior. This, combined with the catalytic behavior of the nickel complexes, showed the influence of the ligand’s substituents to be most prominent in complexes with a square planar surrounded metal center.

*Chapter 5* describes the synthesis and characterization of new pyridine-phosphine ligands with different aryl groups at the phosphorus atom and their nickel and palladium complexes. These different substituents showed their influence in for example the dynamic behavior of the palladium complexes in NMR studies and the catalytic performance of the nickel complexes in ethene oligomerization.

**References**


