Sulphonamido-phosphorus nickel complexes for the selective oligomerisation of olefins: Exploring dissymmetric ligands and supramolecular strategies

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Chapter 1

Oligomerisation of Olefins by Nickel Complexes and Supramolecular Concepts in Homogeneous Catalysis: General Introduction
1 Nickel oligomerisation

1.1 History and general considerations about nickel in organometallic chemistry

Nickel has been used by humanity for thousands of years. The oldest known examples of the employment of nickel come from Syria where bronze artefacts with high nickel contents from around 3500 BC have been found. In China, old manuscripts mention the common use of nickel (as “white silver”) between 1800 and 1500 BC. In the 16th century, miners in the region of Sachsen (Germany) tried to recover copper from a “reddish” ore (they called Kupfernickel), which contained only nickel and arsenic. They did not know that they were about to discover one of the metals which today is of high importance in industrial catalysis. A century later, Cronstedt, a Swedish mineralogist, isolated this metal and named it nickel. J.B. Richter determined its physical properties much later. Nickel is now extracted from ores such as nickelliferrous limonite: (Fe,Ni)O(OH), garnierite: (Ni, Mg)₃Si₂O₅(OH)₄ and pentlandite: (Ni, Fe)₉S₈.

1.1.1 Electronic and atomic properties

Nickel is a late and first row transition metal with symbol Ni and atomic number 28. It has two electronic configurations very similar in energy: \([\text{Ar}]\): 4s² 3d⁸ and \([\text{Ar}]\): 4s¹ 3d⁹ (the first one is generally admitted as the ground state). Nickel is commonly encountered in nature as Ni (II) compounds, but valencies -1, 0 +1, +3 and +4 also exist. The highest coordination number for Ni (0) is 5 (ten electrons required to reach the stable electronic \([\text{Kr}]\) structure) and 6 for Ni²⁺. Nickel has five natural isotopes that are represented below with their natural isotopic abundance.

\[
\frac{58}{26}\text{Ni} (68.08 \%), \frac{60}{26}\text{Ni} (26.23 \%), \frac{61}{26}\text{Ni} (1.14 \%), \frac{62}{26}\text{Ni} (3.63 \%), \frac{64}{26}\text{Ni} (0.93 \%)
\]

1.1.2 Geometries

Three main geometries (based on the valence-bond-theory) are relevant to explain the spatial organisation of nickel complexes: square planar, tetrahedral and octahedral. Besides these geometries trigonal planar, trigonal bipyramidal, trigonal prismatic, square pyramidal and pentagonal bipyramidal have been described.
The geometry of nickel complexes is strongly related to the oxidation number of the metal as shown in Table 1. For a given coordination number and oxidation state, several geometries are sometimes possible.

**Table 1.** Geometry of some Ni complexes as a function of the oxidation state and the coordination number (from Greenwood et al.)[2]

<table>
<thead>
<tr>
<th>Oxidation state</th>
<th>Coordination number</th>
<th>Geometry</th>
<th>Complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>3</td>
<td>-</td>
<td>[Ni₂(CO)₆]⁻²⁻</td>
</tr>
<tr>
<td>0</td>
<td>+</td>
<td>Planar</td>
<td>[Ni{P(OCH₃)₃H₂-2-Me}₃]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tetrahedral</td>
<td>[Ni(CO)₄]</td>
</tr>
<tr>
<td>1</td>
<td>+</td>
<td>Trigonal planar</td>
<td>[Ni(NPH)₂]⁻²⁻</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tetrahedral</td>
<td>[NiBr(PPh₃)₃]</td>
</tr>
<tr>
<td></td>
<td>+</td>
<td>Tetrahedral</td>
<td>[NiCl₂]²⁻</td>
</tr>
<tr>
<td></td>
<td>+</td>
<td>Square planar</td>
<td>[Ni(CN)₄]²⁻</td>
</tr>
<tr>
<td></td>
<td>+</td>
<td>Trigonal pyramidal</td>
<td>[Ni(PPhMe₂)₃(CN)]</td>
</tr>
<tr>
<td>2</td>
<td>+</td>
<td>Square planar</td>
<td>[Ni(CN)₃]³⁻</td>
</tr>
<tr>
<td></td>
<td>+</td>
<td>Octahedral</td>
<td>[Ni(H₂O)₆]²⁺</td>
</tr>
<tr>
<td></td>
<td>+</td>
<td>Trigonal prismatic</td>
<td>Ni₅As (a)</td>
</tr>
<tr>
<td></td>
<td>+</td>
<td>Pentagonal bipyramidal</td>
<td>[Ni(dapbH)₂(H₂O)₂]²⁻ (b)</td>
</tr>
<tr>
<td>3</td>
<td>+</td>
<td>Trigonal bipyramidal</td>
<td>[NiBr₃(PEt₃)₂]</td>
</tr>
<tr>
<td></td>
<td>+</td>
<td>Octahedral</td>
<td>[NiF₆]³⁻</td>
</tr>
<tr>
<td>4</td>
<td>+</td>
<td>Octahedral</td>
<td>[NiF₆]²⁻</td>
</tr>
</tbody>
</table>

(a) Nickeline : P 6₃/mmc (b) dapbH, 2,6-diacylpyridinebis(benzoic acid hydrazone).
Nickel (II) complexes that have 4 coordinated ligands lead either to square planar or to tetrahedral geometries (conformational isomerism). Indeed, both sec-alkylsalicylaldiminato derivatives and the complex \([\text{NiBr}_2(\text{PETPh}_2)_2]\) display an equilibrium between square planar and tetrahedral geometries in non-coordinating solvents. Solvents molecules such as water or bases can also coordinate to metallic centres and change the geometry of the complex. Two molecules of solvent can coordinate to square planar complexes increasing the coordination number up to 6 and leading to octahedral complexes.

A common observation is that reddish and yellowish nickel complexes have a square planar geometry whereas blue and green complexes have any other possible geometry. Square planar complexes are also diamagnetic and observable by NMR whereas paramagnetic complexes generally give rise to broad and undefined signals when using this spectroscopic technique.

1.2 Production of olefins by oligomerisation reactions

1.2.1 General market considerations

Ethylene and propylene are important raw materials in petrochemistry. The market for these first generation olefins is, and should remain in the nearby future, in constant growth (Table 2).[4–6]

<table>
<thead>
<tr>
<th></th>
<th>2011</th>
<th>2035</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>123</td>
<td>273</td>
</tr>
<tr>
<td>Propylene</td>
<td>81</td>
<td>217</td>
</tr>
</tbody>
</table>

Ethylene is a product that is particularly demanded. Indeed, 30% of the products manufactured by the petrochemical industries use ethylene in the process. The United States has the highest production capacity of ethylene with 28 Mt/y in 2011. This production relies on catalytic cracking and vapocracking processes in refineries that convert higher hydrocarbons into ethylene and propylene. More recently, biorefineries aim to produce “bio-ethylene” by dehydration of bio-ethanol. Most of ethylene and propylene produced worldwide is used for the plastics industry. In 2008, 58 % of the global ethylene production was used for HDPE, LLDPE and LDPE whereas 64 % of all propylene was used for polypropylene production.

The higher olefins (>C3) market, especially \(\alpha\)-linear-olefins, is also in constant growth. The demand for LAO (Linear Alpha Olefins) has been increasing to reach
5.1 Mt per year in 2011. Most of these olefins are used as co-monomers in the plastics industry for the production of HDPE and LLDPE (Table 3).\cite{7-9}

**Table 3.** Demand of LAO in 2011 in the industry and importance of the plastics industry (LLDPE, HDPE).

<table>
<thead>
<tr>
<th>Demand 2011 (%)</th>
<th>1-butene</th>
<th>1-hexene</th>
<th>1-octene</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLDPE</td>
<td>78</td>
<td>59</td>
<td>73</td>
</tr>
<tr>
<td>HDPE</td>
<td>14</td>
<td>32</td>
<td>2</td>
</tr>
<tr>
<td>Other</td>
<td>8</td>
<td>9</td>
<td>25</td>
</tr>
</tbody>
</table>

Besides being used in the production of polymers, linear alpha olefins are the starting material for surfactants, lubricants and other chemicals (Table 4). Several routes are used to produce LAO: Fisher-Tropsch synthesis and catalytic cracking and /or paraffin dehydrogenation, olefin metathesis, ethylene oligomerisation and dehydration of alcohols.\cite{10,11} Growth estimations based on the demand for 1-butene (AAGR 2006-2015: 5.2%) and 1-hexene (AAGR 2006-2015: 4.7%) confirm that these short olefins remain key-intermediates for the industry.

**Table 4.** Different uses of alpha-olefins in industry depending on their chain length.

<table>
<thead>
<tr>
<th>Chain length:</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_4^=$</td>
<td>HDPE, LLDPE</td>
</tr>
<tr>
<td>$C_6^=$</td>
<td>PVC/plasticisers</td>
</tr>
<tr>
<td>$C_8^=$</td>
<td>Lubricants</td>
</tr>
<tr>
<td>$C_{10}^=$</td>
<td>Herbicides, plastics</td>
</tr>
<tr>
<td>$C_{12}^=$</td>
<td>Acids, detergents, alcohols</td>
</tr>
<tr>
<td>$C_{14}^=$</td>
<td>Surfactants</td>
</tr>
<tr>
<td>$C_{16}^=$</td>
<td>Lubricant additives</td>
</tr>
<tr>
<td>$C_{18}^=$</td>
<td>Preservatives</td>
</tr>
<tr>
<td>$C_{20}^=$</td>
<td>Antistatics</td>
</tr>
</tbody>
</table>

### 1.2.2 Ethylene oligomerisation processes

Two types of oligomerisation processes produce alpha olefins: processes \textit{on purpose} and \textit{full range}. Processes on purpose target a defined linear alpha olefin ($1-C_4$ or $1-C_6$ or/and $1-C_8$) while full range processes target a broad mixture of linear alpha olefins (from $C_4$ to $C_{22}$ for instance) that generally follows a geometric distribution of products.
1.2.2.1 Full range processes: mixture of linear alpha olefins

One of the initial processes to manufacture mixtures of LAO was the Ziegler (Alfen) process (now replaced) using aluminium for chain growth. After the observation that nickel salts could modify the outcome of AlR₃-catalysed “growth reaction” (Aufbaureaktion) of ethylene⁹¹¹³, this metal was also used as a catalyst to produce mixtures of LAO. Several processes that produce mixtures of LAO are presented in Table 5⁹¹¹⁴¹⁵

Table 5. Characteristics of processes affording linear alpha-olefins not selectively.

<table>
<thead>
<tr>
<th>Process</th>
<th>«Catalyst»</th>
<th>T (°C)</th>
<th>P (bar)</th>
<th>Product distribution</th>
<th>α-selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP Chem</td>
<td>AlEt₃</td>
<td>180</td>
<td>230</td>
<td>15% C₄= 70% C₆=C₁₈= 15% C₂₀=C₄₀=</td>
<td>Schulz-Flory (94-98%)</td>
</tr>
<tr>
<td>Ineos</td>
<td>AlEt₃/AlR₃ (3 steps)</td>
<td>160-275</td>
<td>135-270</td>
<td>15% C₄= 83% C₆=C₁₈= 2% C₂₀=C₄₀=</td>
<td>Poisson (63-97%)</td>
</tr>
<tr>
<td>SHOP</td>
<td>Ni(P,O)</td>
<td>80-140</td>
<td>70-140</td>
<td>11% C₄= 82% C₆=C₁₈= 7% C₂₀=C₄₀=</td>
<td>Schulz-Flory 96-98%</td>
</tr>
</tbody>
</table>

The first two processes (Chevron-Phillips Chemicals and Ineos) are based on chain growth on aluminium. They are operated under very high pressure. The Chevron-Phillips Chemicals process uses AlEt₃ as catalyst. The chain growth on aluminium (by insertion of ethylene into the Al-C bond) and transfer (R₂Al-CH₂=CH₂-R’ + H₂C=CH₂ → R₂Al-CH₂=CH₃ + R’-CH=CH₂) are performed in the same reactor. The Ethyl process (currently employed by INEOS) is performed in two reactors with different temperatures and pressures. In the first reactor, short alkyl-aluminium species are formed and longer chains are formed in the second reactor. The product formed in this second reactor reacts in a third step with light products from the first reactor (trans-alkylation). The olefins produced follow a statistical Poisson distribution of products.

SHOP (Shell Higher Olefin Process) uses a nickel catalyst prepared in situ from a nickel(II) species associated with a P,O bidentate ligand (Figure 2) by a reduction with sodium borohydride.¹⁶ After the first oligomerisation step, the olefins are readily separated from the catalyst thanks to a biphasic process. The SHOP process is designed to produce mainly C₁₂-C₁₈ olefins. This fraction is first isolated while the
lighter and heavier fractions are subsequently isomerised to internal olefins that are engaged in a metathesis step leading to the desired olefins.

\[ \text{Figure 2. Examples of SHOP ligands used for the } \textit{in situ} \text{ formation of the catalytically active nickel complex in combination with a nickel salt and NaBH}_4. \]

There is currently a growing interest in short linear alpha-olefins. Several processes affording such distributions are commercialised. IFPEN developed the AlphaSelect process, based on a zirconium catalyst that produces α-olefins from 1-butene to 1-decene (selectivity > 93%).\cite{15,17,18} Sabic-Linde developed the Alpha-Sablin process that is currently in the demonstration phase. Idemitsu produces 55000 tons/year of \( \text{C}_4^-\text{C}_{18}^- \) α-linear olefins with the Idemitsu-Linealene process in Japan.\cite{12,17,19}

1.2.2.2 \textbf{On purpose processes: one olefin is produced}

Four commercialised processes are selective towards the production of a single olefin. The main characteristics are outlined in Table 6.\cite{11,20–22}

\begin{table}[h]
\centering
\begin{tabular}{|l|c|c|c|c|}
\hline
Process & Temperature & \text{« Catalytic system »} & Products & α-selectivity \\
\hline
AlphaButol® (Axens) & 45-55°C & \text{Ti}^{IV}, \text{AlR}_3, \text{L} & >90% \text{C}_4^- < 10% \text{C}_6^- & > 99% for \text{C}_4^- \\
\hline
AlphaPlus® 1-Hexene (CP Chem) & ? & \text{Cr}^{III}, \text{AlEt}_3, \text{L} & 1% \text{C}_4^- 93% \text{C}_6^- 6% \text{C}_{10}^- & > 99% for \text{C}_6^- \\
\hline
AlphaHexol™ (Axens) & 120-140°C & \text{Cr}^{III}, \text{AlR}_3, \text{L} & >83% \text{C}_6^- & > 99% for \text{C}_6^- \\
\hline
Sasol & 50-60°C & \text{Cr}^{III}, \text{MMAO}, \text{L} & 30% \text{C}_6^- 60% \text{C}_8^- & > 99% (in \text{C}_8^-) \\
\hline
\end{tabular}
\caption{Characteristics of processes affording linear alpha-olefins selectively.}
\end{table}

These four processes target different LAOs: 1-butene, 1-hexene or 1-octene. AlphaButol® process, licensed by Axens targets selective ethylene dimerisation with a titanium catalyst activated by alkylaluminium.\cite{15} Currently, more than 30 industrial plants use this technology to produce 1-butene which is massively used as a co-monomer for the synthesis of branched polyethylene (HDPE, LLDPE).\cite{23}
The AlphaPlus® 1-hexene process, currently employed by Chevron Phillips Chemicals produces 1-hexene by trimerisation of ethylene. The catalyst is a chromium alkanoate complexed by a pyrrolyle ligand and activated by triethylaluminium\cite{24}. The first plant utilising this technology was set up in Qatar in 2003. Two other plants are in construction in Saudi Arabia and in Texas.

IFPEN discovered in 1998 a new catalytic system, able to trimerise ethylene into 1-hexene with a high selectivity, based on chromium and proprietary ligands. This process has been in commercial use as the AlphaHexol\textsuperscript{TM} process currently employed by Axens since 2010.\cite{25,26}

Sasol, discovered a new catalytic system for the tri- and tetramerisation of ethylene, based on a chromium diphosphinamine ($\text{iPrN(PPh}_3\text{)}_2$) catalyst and methylaluminoxane as cocatalyst. A plant is now in construction on Sasol's site in Louisiana to produce 100 kt/year of 1-hexene and 1-octene.\cite{27,28}

### 1.2.3 Propylene oligomerisation processes

The oligomerisation of propylene catalysed by a nickel compound and an alkylaluminium chloride derivative was first described in a 1955 patent by Lyons et al.\cite{29} In 1966, the group of Wilke gave crucial impetus to this reaction by using a “well-defined” organometallic nickel complex: a cationic $\eta^3$-allylnickel complex $\mathbf{1}$.\cite{30} By this approach, they confirmed the reaction mechanism but also underlined the control by tertiary phosphines on the selectivity of the oligomers formed. Complex $\mathbf{1}$ is only soluble in chlorinated hydrocarbons. Many other systems based on nickel catalyse the dimerisation reaction and have been described in publications and patents.

![Diagram of complex 1](image)

The oligomerisation of propylene consists of the consecutive addition of two or more molecules of propylene to the active species (Ni-H and Ni-C complexes) with subsequent chain elimination (or chain transfer) to regenerate the catalyst and give the oligomer. The formation of olefin dimers predominate in the reaction products due to a high rate of beta-hydrogen elimination. The reaction pathways leading to the formation of all possible propylene dimers is presented in Scheme 1.
Trimers and tetramers, found in smaller proportions, form both by a parallel growing chain reaction and by consecutive reactions of dimers with monomer (co-dimerisation) as seen in Scheme 2. The selectivity in dimers at high conversion (> 80%) strongly depends on the type of reactor used i.e., batch and plug-flow open systems, or semi-batch and one stage well-mixed open systems. Although the type of reactor has no effect on the parallel growing chain reaction it has a strong influence on the consecutive reaction (co-dimerisation).
In absence of additives, the dimerisation of propylene affords an average isomer composition, which hardly depends on the temperature. At 50°C propylene dimers have the following composition: 22 % n-hexenes, 72 % 2-methylpentenes and 6 % 2,3-dimethylbutenes. This reaction is widely used at an industrial scale with the Dimersol™ process licensed by Axens. The catalyst results from the interaction of a nickel organic salt, soluble in a paraffinic hydrocarbon solvent, and an alkylaluminium halide; the active species is formed in situ inside the dimerisation reactor. A simplified process scheme of Dimersol™ is depicted in Figure 3. The reaction takes place at 50°C, without any solvent, in several consecutive reactors (CSTR and plug-flow).[^15]
The presence of bulky and basic phosphine ligands such as triisopropylphosphine or tricyclohexylphosphine drive the propylene dimerisation reaction to high selectivity for the formation of 2,3-dimethylbutenes (2,3-DMB-1 and 2,3-DMB-2).\[^{[31]}\] 2,3-Dimethylbutenes are especially important since they can be used as key starting olefins for fine chemical intermediates. 2,3-DMB-2 is used for the synthesis of Danitol (or Rody)\[^{TM}\], a high performance pyrethroid insecticide invented by Sumitomo in 1976, and to produce other intermediates (Pinacolone, Scheme 3).\[^{[32-35]}\] 2,3-DMB-1 is a key intermediate for the production of musk fragrances (as example: Tonalid\[^{TM}\] commercialised by PFW Aroma Chemicals).
Selective dimerisation of propylene to 2,3-dimethylbutenes (DMBs) is currently operated by Sumitomo and BP Chemicals.\cite{32} In the Sumitomo process, very high selectivity for DMBs (up to 85\%) are obtained at 20-50°C thanks to a sophisticated, highly efficient Ziegler type catalyst system (ten times more efficient than those of conventional catalysts) and by using toluene as a solvent. Isomerisation of 2,3-dimethyl-1-butene (DMB-1) into 2,3-dimethyl-2-butene (DMB-2) takes place directly in the dimerisation reactor in the presence of an acidic component (a chlorinated phenol) coming from the catalyst formula. DMB-2 is easily extracted from the mixture by distillation. The BP Chemicals process operates without any solvent at lower temperature and the catalyst composition is simpler but gives DMB-1 as the main product. DMB-2 is obtained by subsequent isomerisation on an acidic resin catalyst. Many studies have been made on these Ni-phosphine catalytic systems to improve the activity and the selectivity, not only by varying the phosphine ligand, but also by varying the additives. Immobilisation of nickel-based catalysts on a solid support has also been reported.\cite{36} On top of this, fluorinated biphasic systems have been also applied to facilitate the separation of the catalyst from the reaction products, e.g. by modifying nickel β-diketonate complexes with a long perfluorinated alkyl chain. However, the polar character of the Ni active species was not favourable to the non-polar fluorinated layer.\cite{37}

1.3 Activation of nickel complexes for olefin oligomerisation

1.3.1 General considerations

Cationic nickel (II) hydride complexes have been proposed as being the active catalysts for olefin oligomerisation or polymerisation.\cite{38} The stability of these very reactive species is, however, limited and makes nickel (II) hydride complexes very
difficult to handle. To circumvent this problem, a common practice consists of starting from a precatalyst (stable nickel complex). Nickel precatalysts are divided in two groups: single components catalysts that lead to the catalytically active species without activator and the others that require an activator (see Figure 4).

Catalytic systems working with an activator are evaluated in catalysis with an in situ approach. The reaction between the precatalyst and the activator to generate the active species takes place in the reactor. Although this approach is often considered as a “black box” (the active species that forms is not well defined and parallel reactions may happen), it is preferred in the industry for the robustness of the components and a facile synthetic access.

In contrast, single component catalysts are well defined catalysts that are organometallic nickel complexes (having a Ni-H or a Ni-C bond). They activate readily under an atmosphere of ethylene to give the active catalytic species. Since these single component catalysts work by themselves, they offer the possibility to understand the catalytic elementary steps by using in situ or in operando high-pressure NMR or IR spectroscopy. These type of single component catalysts is however less robust than catalytic systems working with an activator.

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**Figure 4.** Activation of nickel precatalysts: single component catalysts (generally organometallic species are directly active in ethylene oligomerisation while other precatalysts need an activation step by using a co-catalyst (also called activator).
Several nickel complexes that have been described in ethylene oligomerisation (single-component catalysts and precatalyst / activator systems) are presented in this Chapter with their synthetic pathway and their activation mode. The aim of this part is to understand which type of activation is needed for a given nickel complex and its impact on activity and selectivity. As oligomerisation and polymerisation are closely related reactions, some polymerisation systems are also included. Indeed, a simple change of solvent (toluene to heptane) may turn a system for oligomerisation into one for polymerisation. \[^{[39]}\]

### 1.3.2 Aryl nickel complexes

Aryl-nickel complexes are organometallic compounds that are easily isolable. Most of them crystallise easily and adopt a square planar fashion giving diamagnetic complexes, observable by NMR spectroscopy. \[^{[40-42]}\] These complexes are activated under an ethylene atmosphere (40-50 bars of ethylene) and heating is generally required. Some aryl-nickel complexes used in ethylene oligomerisation (or polymerisation) are presented in Figure 5.

![Figure 5](image)

**Figure 5.** Selected examples of nickel-aryl complexes described for ethylene oligomerisation.

Several synthetic pathways lead to the formation of aryl-nickel complexes. On the track of SHOP process, Keim’s group discovered that the reaction of the phosphorus ylide (benzoylmethylene)triphenylphosphorane (Ph\(_3\)P=CH\(_2\)C(=O)Ph) with Ni(COD)\(_2\) and in the presence of a coordinating phosphine led to the nickel aryl complex 2. The mechanism of this reaction is most likely an oxidative addition on the P-Ph bond followed by a rearrangement (Scheme 4). Aryl-nickel complexes may
also be formed by reaction of the precursor phenyllnickelbromide bis(triphenylphosphine) with a base or reducing agents.\textsuperscript{[43–48]}

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\textbf{Scheme 4.} Synthesis of SHOP catalyst from a phosphorus ylide, Ni(COD)\textsubscript{2} and PR\textsubscript{3} with the synthetic rearrangement proposed by Keim \textit{et al.} \textsuperscript{[39]}};
\end{tikzpicture}
\end{center}

Nickel complex 2, with a PO chelate is the showcase example of the SHOP catalyst.\textsuperscript{[39,40]} This complex is activated under 50 bar of ethylene pressure at 50°C and a small induction time is required before ethylene uptake starts. In toluene, this complex produces olefins of which 99% are linear and 98% are alpha-olefins with activity of 1 000 g\textsubscript{C2H4}/(g\textsubscript{Ni}.h). Using hexanes instead of toluene leads only to linear polyethylene (PE) highlighting the importance of the solvent for the selectivity of the reaction.\textsuperscript{[49,50]}

Nickel-aryl complexes with NO chelates received significantly less attention than those based on PO chelates. Cavell’s group described NO-chelated nickel-aryl complexes of general formula 3 (see Figure 5) which under mild conditions (80°C, 40 bars), also affords oligomers with linearity above 84% and alpha linear products above 51 \%.\textsuperscript{[51]} By using an iminopyrrole chelate, Gomes \textit{et al.} synthesised a NN-chelated nickel-aryl complex 4 (see Figure 5) which under 2 bars of ethylene pressure and between 20 and 50°C gave only liquid oligomers.\textsuperscript{[52]} These three examples show that aryl-nickel complexes are directly active and that oligomerisation activity does not appear to depend on a specific chelate since PO, NO and NN based complexes are active catalysts.

Wheareas the above mentioned complexes are single component catalysts that are directly active under ethylene, these complexes have been sometimes evaluated in catalysis in combination with alkylaluminiums. Zhao \textit{et al.}, for example combined
ligand 5 (of Figure 5) with MAO or AlEt₃ producing very short oligomers C₄ - C₈, with a system significantly more active (up to 550 kg_{oligomers}/(g_{Ni}.h)) than SHOP catalyst 2. Aryl-nickel bromide complex 6 (of Figure 5), activated by 300 eq. or MAO, also displays high activity but low alpha-selectivity. The presence of labile moieties (phosphines) or a vacant site at proximity of the aryl group seems to be an important requirement to observe catalytic activity for aryl-nickel complexes.

When aryl-nickel complexes are brought into contact with ethylene at a suitably high temperature for activation to occur, styrene is released. This observation supports the ethylene insertion into the nickel-phenyl bond and the formation of a potentially active nickel-hydride by β-H elimination (or a nickel-ethyl by chain transfer). For systems NiBrRL₂, one or more insertions of ethylene may occur before the generation of the hydride (Scheme 5). Multiple insertions of ethylene in the Ni-R bond appear for highly substituted R groups (2,4,6-Me₃-C₆H₂, C₆Cl₅) in the presence of a monodentate phosphine (PPh₃, PMe₂Ph, P(CH₂-Ph)₃), in that case kᵢ² > kᵢ¹ and kᵢ² > kᵢ³.

![Scheme 5. Activation of aryl-nickel complexes of type [NiBrRL₂] compounds under ethylene. There may be several consecutive insertions of ethylene in the Ni-Ar bond.]

**1.3.3 Allyl and cyclopentadienyl nickel complexes**

Allylic nickel complexes have appeared in the pioneering work of Wilke in 1966 on nickel chemistry. Similarly to nickel-aryl complexes, allyl-nickel complexes are activated thermally in situ under an ethylene atmosphere.

**1.3.3.1 Preparation of η³ and η⁵ bound nickel complexes**

The chemistry of Ni-allyl complexes and their synthetic access was particularly developed by the group of Bogdanovic. Bis-(π-allyl) nickel compounds [(allyl)₂Ni] are synthesised from NiBr₂ and two equivalents of the corresponding π-allyl Grignard reagent. Nickel (II) allyl precursors of formula [(allyl)Ni(halide)]₂ are readily prepared by the reaction of a nickel(0) precursor (e.g. Ni(COD)₂ or Ni(CO)₄)
with the corresponding allyl halide or hydration of [(allyl)$_2$Ni] with anhydrous hydrogen halide.$^{[30]}$ They are now commercially available.

Cationic complexes of type [(allyl)NiL$_2$]$^+$ are formed by abstraction of the halide from [(allyl)Ni(halide)]$_2$. This operation is generally performed with thallium salts (TlBF$_4$, TIOEt, TIPF$_6$, TlSbF$_6$, TlBAR$_4^-$, silver and sodium salts have also been reported) in the presence of two equivalents of a monodentate ligand L or one equivalent of a bidentate ligand L$_2$.$^{[43,62]}$ Based on the showcase example of SHOP nickel-aryl complex 2, the group of Keim prepared in 1986, PO-chelated nickel allyl complexes by reacting (benzoylmethylene) triphenylphosphorane with bis allylnickel (II) precursors (Scheme 6).$^{[40]}$ In this synthesis there is no change in the oxidation state of the nickel between the precursor and the final PO-chelated complex and organic side products containing the allyl fragment substituted by a phenyl group (from the PPh$_3$) are observed. Similar complexes may be synthesized using phosphine ligand of general formula Ph$_2$P-(CH$_2$)$_n$-COOH and bis allylnickel (II).$^{[67]}$

**Scheme 6.** Preparation of η$^3$ and η$^5$ allylnickel complexes by Keim *et al.* starting from Ni(II) bis allyl precursors and (benzoylmethylene) triphenylphosphorane (the side product observed for the nickellacyclopentane results from the Diels-Alder condensation of two monomers).
1.3.3.2 Activation of allyl nickel halide complexes

Allyl nickel halide dimer precursors of general formula [(allyl)NiX]₂ are not directly active for ethylene oligomerisation. An activation step consisting of halide abstraction is required for the formation of a cationic nickel complex and the creation of a vacant site. The halide atoms from the dimer can be abstracted by a Lewis acid such as an aluminium halide or alkylaluminiums to form (non-isolable) active complexes in situ of formula (allyl)Ni⁺(AlR₃X₃₋ₙ)⁻ with a vacant site which serves for ethylene coordination. Performing the abstraction in the presence of chelating agents lead to stable and isolable complexes (see 7 with COD as chelating agent).

The halogen atom may alternatively be replaced by non-coordinating anions such as BF₄⁻ or PF₆⁻ by anion exchange (see above). The resulting cationic nickel complexes with a vacant site are active in oligomerisation (25°C, 10 bars, up to 2 000 g oligo/(gNi·h) for 8) producing a mixture of ethylene dimers and short oligomers. The dimer fraction consists mainly of 2-butenes and the trimer fraction of 3-methylpentene and 2-methylpentene as well as a minor amount of n-hexenes.

Phosphine ligands have the ability to break the dimer structure of [(allyl)NiX]₂ to give two stable monomers (allyl)NiX(PR₃) where the vacant site is occupied by the phosphine (such as 9). Halide abstraction from this monomer (with AlCl₃, AlBr₃ or chloroalkylaluminium) gives “phosphine-modified catalysts” that are isolable. The phosphine ligand has a pronounced influence on both activity and selectivity of the complex as is clear from Table 7. Nickel catalysts with a sterically demanding phosphine, such as tricyclohexylphosphine, produce mainly 2,3-dimethyl-1-butene in the propylene oligomerisation. Related complexes with a less sterically demanding phosphine will lead to n-hexenes and methylpentenes (2,3-dimethyl-1-butene is only a side product).
Table 7. Influence of the phosphine ligand on propylene oligomerisation for “phosphine modified catalysts”: [(π-allylnickelchloride)+ phosphine + AlCl₃] at -20°C, 1 bar, (from Bogdanovic et al.)[63]

<table>
<thead>
<tr>
<th>Phosphine</th>
<th>hexenes (%)</th>
<th>methyl-pentenes (%)</th>
<th>2,3-dimethylbutenes</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPh₃</td>
<td>21.6</td>
<td>73.9</td>
<td>4.5</td>
</tr>
<tr>
<td>PPh₂(CH₂Ph)</td>
<td>19.2</td>
<td>75.5</td>
<td>5.1</td>
</tr>
<tr>
<td>Ph₂P-(CH₂)₂-PPh₂</td>
<td>20.0</td>
<td>73.3</td>
<td>6.6</td>
</tr>
<tr>
<td>Ph₂P-CH₂-PPh₂</td>
<td>12.2</td>
<td>83.0</td>
<td>4.7</td>
</tr>
<tr>
<td>PMe₃</td>
<td>9.9</td>
<td>80.3</td>
<td>9.8</td>
</tr>
<tr>
<td>PPh₂(iPr)</td>
<td>14.4</td>
<td>73.0</td>
<td>12.6</td>
</tr>
<tr>
<td>PEt₃</td>
<td>9.2</td>
<td>69.7</td>
<td>21.1</td>
</tr>
<tr>
<td>P(nBu)₃</td>
<td>7.1</td>
<td>69.6</td>
<td>23.3</td>
</tr>
<tr>
<td>P(CH₃Ph)₃</td>
<td>6.7</td>
<td>63.6</td>
<td>29.2</td>
</tr>
<tr>
<td>P(NEt₂)₃</td>
<td>5.5</td>
<td>51.4</td>
<td>43.0</td>
</tr>
<tr>
<td>PCy₃</td>
<td>3.3</td>
<td>37.9</td>
<td>58.8</td>
</tr>
<tr>
<td>P(iPr)₃</td>
<td>1.8</td>
<td>30.3</td>
<td>67.9</td>
</tr>
<tr>
<td>PMe(tBu)₂</td>
<td>1.2</td>
<td>24.5</td>
<td>74.0</td>
</tr>
<tr>
<td>PPh(tBu)₂</td>
<td>0.6</td>
<td>22.3</td>
<td>77.0</td>
</tr>
<tr>
<td>P(iPr)(tBu)₂</td>
<td>0.6</td>
<td>70.1</td>
<td>29.1</td>
</tr>
</tbody>
</table>

1.3.3.3 Activation of allyl and cyclopentadienyl nickel complexes

The activation of allyl and cyclopentadienyl nickel complexes with a vacant site (that may be chelated) is realised under an ethylene atmosphere. The mechanism is similar to nickel aryl complexes, according to the observation of by-products. Indeed, the formation of a product containing C_{allyl} + 2 carbon atoms (see Scheme 7) suggests that ethylene inserts in the Ni-C bond of the allyl with subsequent β-H elimination or chain transfer to ethylene. The observation of this organic fragment is likely to result from the joint formation of the active species: a nickel-hydride (or ethyl) complex. The activation temperature of this class of complexes differs with the nature of the allyl group as seen in Scheme 7. The activation of the allyl complex (a) is realised at 40°C whereas the complex with a cyclopentadienyl group (b) is activated at 130°C (both under 70 bars of ethylene pressure).[66]
Scheme 7. Activation of SHOP-type P,O complexes bearing η³ or η⁵ moieties by insertion of ethylene in the Ni-allyl bond with subsequent cleavage of a vinyl-allyl group (here the β-H elimination pathway is considered).

The activation temperature is also dependant on the chelate part. Starting from a phosphanylphenolate ligand for instance, the corresponding nickel Cp complex has to be activated at 190°C (as indicated by the loss of cyclopentadiene fragment observed by DTA) in order for the polymerisation of ethylene to commence.[50]

Methallyl complexes are also activated under ethylene pressure at different temperatures. The structure of the by-product (leaving group) gives insight in the formation of the active species, presumably a nickel hydride according to Keim et al. (Scheme 8).[67]

Scheme 8. Suggested mechanism for the activation of nickel-allyl complexes with insertion of ethylene and release of an dienyl compound and a nickel hydride. (I): ethylene coordination to nickel, (II) migratory insertion of ethylene in the Ni-Ci,vl bond and coordination of another ethylene molecule, (III) β-H elimination and release of the nickel hydride complex and the diene compound (PO = Ph₂P-(CH₂)ₙ-C(=O)O)
The activation of the simplest allylnickel $\eta^3$-propenyl nickel complex was reported to be more difficult than the other allylic analogues. Interestingly the $\eta^3$-propenyl nickel complexes in Scheme 9 (top) is inactive, whereas the same ligand reacted with Ni(COD)$_2$ gives two isomers. One is an excellent catalyst for 1-butene dimerisation and ethylene oligomerisation, the other $\eta^3$-octenyl is inactive.$^{[66]}$ Keim suggested that $\eta^3$-propenyl nickel complex is in equilibrium with the system propylallene / nickel hydride and that, due to the high reactivity of this allene, the equilibrium is pushed towards the $\eta^3$-propenyl nickel complex. This supposition is in contrast with other systems that lead first to ethylene insertion and then elimination.

Scheme 9. Reactivity of $\eta^3$-propenyl nickel complexes vs. Ni(COD) complexes in olefins oligomerisation (from Keim et al.).

To bypass the drastic operating conditions relative to the activation of the Ni-Cp complexes (high temperature, 70 bar)$^{[66]}$, Matt et al. used successfully a stoichiometric amount of NaBH$_4$ and activated complexes 10 and 11 in situ under reduced ethylene pressure (< 40 bars)$^{[68]}$. Complex 10 + NaBH$_4$ gave linear $\alpha$-olefins with a selectivity of 98% whereas 11 + NaBH$_4$, under the same reaction conditions led to high proportions of polyethylene (Mn = 479). They interpret this striking difference by the greater ability of 11 to form a Ni-H bond due to the competition between the leaving groups and ethylene insertion.
The elevated pressure and temperature conditions required to activate allyl nickel complexes reveal that the allyl fragment has a strong binding affinity for nickel which in turns lowers the reactivity towards oligomerisation/polymerisation. Based on the same NN ligand and in similar conditions (0°C and 1 bar), the methallyl-nickel complex 12 is inactive whereas complex 13, the original Brookhart Ni-Me catalyst system is highly active (activity estimated to 34 000 g\_C2H4/(g\_Ni.h)). This difference may also come from other parameters such as the presence of Et2O.\textsuperscript{[69,70]}

1.3.4 Alkyl nickel complexes

Alkyl-nickel complexes are generally air and moisture sensitive complexes that are difficult to handle. The addition of bidentate ligands has been reported to stabilise these systems. Nickel-alkyl species are organometallic complexes that and they should not require any co-catalyst to perform olefin oligomerisation.

Bauers and Mecking isolated and characterised compound 14 by mixing salicylaldimine ligand and pyridine with one equivalent of [(tmeda)Ni(CH\_3)_2].\textsuperscript{[71]} When this complex was brought under an ethylene atmosphere in a water based
medium, polymer was formed with a moderate activity of 600 g
C2H4/(gNi·h). The analogue complex bearing a phenyl group instead of -CH3 and a PPh3 adduct exhibits in the presence of a phosphine scavenger [Rh(CH2=CH2)2(acac)] the same reactivity.

Similarly to SHOP-type catalysts, Klabunde and Ittel reported the synthesis of the five coordinated (P,O) methyl-nickel complex 15 (18 valence electrons) that was active for ethylene polymerisation in toluene without an induction period, showing that ethylene insertion in the Ni-methyl bond is quick in this complex. The corresponding phosphanylphenolato nickel complexes of general structure 16 were synthesised and characterised (NMR, IR, element analysis, nickel precursor: [NiMe(PMe3)(µ-MeO)]2) and these yielded ethylene oligomers with a large distribution of products (Schulz Flory, C4-C50). Complexes bearing two (PMe3) tend to give a narrower olefin distribution.

Interestingly most of Ni-Me complexes tend to oligomerise ethylene into long chain olefins. The use of nickel complexes with longer alkyl chains (ethyl, propyl, butyl…) was not reported in the literature. This may be explained by the fact that alkyl chains with more than 2 carbons lead to potential agostic interactions between the proton in beta position of the nickel and the nickel atom, which leads to the equilibrium nickel-alkyl / nickel hydride + olefin.

Dimethyl nickel complexes were not reported as being active in ethylene oligomerisation. Brookhart and co-workers showed that such complexes could, however, be activated by methyl abstraction (see Scheme 10). Strong acids such as [H(OEt)+][BAR4−] protonate the [(α-diimine)Ni(Me)2] complex resulting in the loss of methane and formation of the monomethyl nickel complex with a diethyl ether adduct. These complexes produce high molecular weight polymer when using ethylene, propylene or 1-hexene as monomers.

\[
\text{Scheme 10. Activation of a Ni-dimethyl complex by protonation of a methyl group by a Brønsted acid.}
\]
1.3.5 Nickel hydrides and related complexes

1.3.5.1 Oxidative addition on zerovalent nickel

Nickel hydride is regarded as being the active species in ethylene oligomerisation. It forms by β-H elimination starting from e.g. conventional nickel aryl or nickel allyl complexes. Nickel hydrides can also be prepared by reacting zerovalent nickel with protic species. Ni(COD)$_2$ for instance, reacts with ligands bearing a Brønsted acid moiety, presumably by oxidative addition.

By mixing Ni(COD)$_2$ with a phosphanyl alcohol in situ, Keim and co-workers observed the formation of a hydride signal in $^1$H NMR but this very reactive system could not be isolated. The same system reacted in the presence of ethylene to form LAO with a broad Schulz-Flory distribution (C$_4$-C$_{30}$) and a good activity (2 400 g$_{C_2H_4}$/g$_{Ni}$.h). The addition of PCy$_3$ to this system blocked the catalytic activity but allowed to trap and characterise a nickel hydride 17 (Scheme 11). In the presence of ethylene, 17 reacted to form a Ni-ethyl species.$^{[38]}$ These observations likely support the mechanism of degenerate polymerisation proposed by Cossee and Arlmann, based on the nickel-hydride active species.$^{[75-77]}$ 

![Scheme 11. Formation of a (P,O) chelated nickel hydride complex, by oxidative addition of a phosphanylalcool in Ni(COD)$_2$ in presence of PCy$_3$. This type of complex (without PCy$_3$) is considered as the active species for the oligomerisation of olefins.](image)

Ni(COD)$_2$ reacts also with Phosphinocarboxylic acid but no hydride was detected by NMR. A mixture of two (P,O) chelated nickel complexes appeared instead in which the nickel is attached to a cyclooctene ring (see Figure 12). This cycle with 8 carbons likely comes from the 1,5-cyclooctadiene of the nickel precursor. The presence of only one insaturation (double bond) in the complexes suggest that a nickel hydride complex formed (upon mixing the the acid and the Ni(COD)$_2$) that instantly reacts with one of the cyclooctadiene double bond to give an -enyl or -allyl nickel complex. The resulting nickel complex mixture presented Scheme 12 is moderately active in ethylene oligomerisation ($\pm$ 2 000 g$_{C_2H_4}$/g$_{Ni}$.h), affording a mixture of linear alpha olefins (C$_4$-C$_{24}$, $\alpha\% > 99\%$, linearity > 99%).$^{[78]}$ This work was completed recently: the structure of the complex was confirmed by MS, IR, $^1$H, $^{13}$C and $^{31}$P NMR.$^{[79]}$
The equilibrium depicted in Scheme 12 between a 4-enynickel and a \(^3\eta\)-allyl nickel might be the result of an isomerisation reaction due to a Ni-H species. Interestingly, changing the PO chelate to an (O,O) chelate led to the formation of the same two isomers which did not presented any equilibrium between each other and could be isolated. \(^{[80]}\) The first one (4-enynickel) is an excellent catalyst for 1-butene oligomerisation while the other (\(^3\eta\)-allyl nickel) is inactive. \(^{[39,49,78,81]}\)

In the course of the catalytic reaction with the 4-enynickel complex, the group of Keim observed the formation of hexahydropentalene.\(^{[80]}\) This molecule suggests the formation of the active Ni-hydride from the 4-enynickel (Scheme 13). In contrast, they explained that the other isomer was inactive because it was unable to release a Ni-H by elimination of hexahydropentalene.

Phosphanylphenols, which are stronger Brønsted acids than phosphanylalcohols also react with Ni(COD)\(_2\).\(^{[50,82]}\) The reaction of 18(a) with Ni(COD)\(_2\) gives a system which reacts with ethylene and forms linear polymer and a small amount of linear oligomers. In contrast, 18(b) under the same conditions shows less activity (3.5% conversion) but lead to short oligomers (C\(_4\) 68%, C\(_6\) 24%, C\(_8\) \(\pm\) 8%). The basicity and the steric bulk of the phosphine are certainly responsible for this behaviour.
Oxidative addition was also reported for N-H bonds (such as Phosphanyl ureas 19 or carbamylmethylphosphines). Under ethylene pressure, the system 19(a) + Ni(COD)$_2$ produces a high content of LAO (75% α-C$_4$, 10% C$_6$, 5% C$_8$, activity = 2 900 g$_{C_2H_4}$/g$_{Ni}$/h). In comparison, the system 19(b) + Ni(COD)$_2$ is more active (7 200 g$_{C_2H_4}$/g$_{Ni}$/h) affording mainly n-hexenes of which 65% are branched. A change in the phosphine substitution induces major changes in catalysis.

When the chelating ligand is not acidic, the addition of a strong Brønsted acids (e.g. [H(OEt)$_2$][B(C$_6$F$_5$)$_4$]) leads to similar protonation of nickel. Carpentier et al. reported precatalysts of the type (PNP)Ni$^{0}$(cod) which, once activated by [H(OEt)$_2$][B(C$_6$F$_5$)$_4$], polymerise at room temperature ethylene into low molecular weight, moderately branched, polyethylene. NMR studies and ESI-MS data show that protonation occurs at the cyclooctadiene moiety affording a cationic nickel-allyl species. They postulate the structure (PNP)Ni(codH)$^+$ presented in Scheme 14.

![Scheme 14](image)

Scheme 14. Protonation of a Ni$^{0}$(PNP(COD)) complex by [H(OEt)$_2$][B(C$_6$F$_5$)$_4$].

1.3.5.2 In situ hydride formation

Nickel hydride has been postulated to be the active species for ethylene oligomerisation reaction. As this class of compounds is very reactive and the corresponding complexes are not very stable, Heinicke et al. attempted to form a PO chelated nickel hydride complex in situ similar to 17 by using a mixture of NiBr$_3$(DME), NaH and an ortho-phosphanylphenol. This mixture, together with gaseous ethylene led to linear polyethylene with low catalytic activity and poor selectivity (compared to activation with Ni(COD)$_2$: see 18(a)). This suggests that a
nickel-hydride complex forms according to Scheme 15. Besides, an increase in the
phosphine basicity of the ligand (e.g. 2-dialkylphosphanylphenols) led to complex
inactivity (compared to the Ni(COD)_2 analogues).

Scheme 15. In situ generation of nickel-hydride complexes by using a mixture of phosphanylphenol,
NiBr_2(DME) and sodium hydride.

The use of sodium borohydride has also been reported to activate a mixture of
potassium phosphinoacetate and NiCl_2 (Scheme 16). The mixture has activity
similar to the systems presented above [phosphinoacetic acid + Ni(COD)_2] and
certainly forms a nickel-hydride intermediate. This reaction has been extensively
studied and is the heart of the industrial SHOP process.

Scheme 16. Typical composition of the catalytic mixture used in the SHOP process.

1.3.6 Di-halide nickel complexes

Nickel halides complexes are among the easiest accessible and stable nickel
compounds. They are generally obtained by mixing one or two equivalents of ligand
with NiBr_2(DME) or other nickel precursors.

In order to become catalysts for ethylene oligomerisation, nickel di-halide complexes
require an activation step with an aluminium activator that abstracts the halide and
acts as an alkylating agent (Scheme 17). In this case, the nature of the anion greatly
influences the activity of the catalytic system.

Scheme 17. Activation of a Ni dihalide complexes by chlorodialkylaluminium: general mechanism.
The co-catalysts used are generally chloroalkylaluminium compounds and since the 1990s also aluminoxanes. Alkyl aluminium activators are avoided because they reduce complexes to Ni(0) species which are not active in oligomerisation.\[87,88]\n
The ability of chloroalkylaluminiums to activate nickel di-halide complexes is related to their Lewis acidity (potential to abstract Cl) but also their alkylation potential. Only a small number of chloroalkylaluminiums are used in practice, with a variable Cl/Al ratio. De Souza et al. observed that the activity of a complex was proportional to the Lewis acidity of the co-catalyst (see Figure 6).\[89]\n
Interestingly, AlCl$_3$, which has the most pronounced Lewis acid character despite having no alkylation potential, would be the best halide abstractor. Although this candidate is not soluble in organic media, its properties were investigated in combination with ionic liquids at IFPEN for the activation of nickel methallyl nickel chloride dimer.\[33]\n
<table>
<thead>
<tr>
<th>Ratio Cl/Al</th>
<th>AI$\text{Et}_3$</th>
<th>DEAC</th>
<th>EASC</th>
<th>EADC</th>
<th>AlCl$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lewis acidity</td>
<td>0</td>
<td>1</td>
<td>1.5</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Activity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 6.** Some commonly used chloroalkylaluminium for nickel complexes activation ranked by increasing Lewis acidity and activity in the transformation (correlation proposed by De Souza et al.)\[89].

In industry, the Dimersol process (1977) uses the more Lewis acidic reagent EADC to activate NiX$_2$ whereas the Phillips process uses it to activate NiX$_2$L$_2$ (L = P(nBu)$_3$). In this process ethylene selectively converts into 2-butene.

The use of aluminoxanes has started relatively recently and originates from the polymerisation research on group IV transition metals. In the late ‘90, BP and DuPont (Gibson, Brookhart and co-workers) developed bis-imino ligands (known as Versipol®). The related nickel complex 20, activated by 100 eq. of MMAO (modified MAO) gave linear olefins with a broad Schulz Flory distribution (activity: 57 000 g$_{C2H4}$/g$_{Ni}$.h, α-selectivity: 94% with possibility to reach 110 000 g$_{C2H4}$/g$_{Ni}$.h with an α-selectivity of 80%).\[70,90,91]\n
Although MAO significantly reduces isomerisation, a large excess of this activator is generally required (Al/Ni > 100 and 1000 in some cases) and activation by MAO generally shows a significantly diminished activity in comparison with chloroalkylaluminium activators. The reaction of MAO and its analogues with nickel halide complexes leads to the formation of bulky counter ions that prevent ligand migration from nickel to aluminium. The proposed structures of MAO vary between one-dimensional linear chain, two-dimensional structures, three-dimensional clusters, cyclic and cage structures (Figure 7).\[92]\n
The MAO structure cannot be directly elucidated because of different equilibria between the conformers. MAO is produced
by partial hydrolysis of trimethylaluminium (TMA) and so the commercial product always holds a small quantity of residual TMA (around 5%).

![Chemical structures](image)

**Figure 7.** Suggested structure for methylaluminoxane (from Sinn et al.\[92\]).

Due to the easy synthesis of NiCl₂ chelated complexes, many groups have been working on the synthesis of bidentate or tridentate ligands combining oxygen, nitrogen, sulphur or phosphorus.\[7,93\] Based on this work, Sun et al. extended the scope to several other (N,N) complexes of type imino-pyridinyl. They found that complex 21, after activation with 400 eq. of EASC is highly active as an ethylene oligomerisation catalyst (150 000 g\(_{C_2H_4}/(g_{Ni}.h)) producing short α-olefins (C\(_4\)-C\(_6\), α-\(C_4/C_4\)>99%).\[94–96\] In the same way, many bidentate and tridentate ligands (22, 23) have been developed and were found to be active in ethylene oligomerisation.\[93\]

![Chemical structures](image)

In industry, nickel halides are replaced by nickel(2-ethylhexanoate) (also called nickel octoate) with a similar activation procedure (alkylaluminium or aluminoxanes). This nickel precursor with long alkyl chains is very soluble in aliphatic solvents, including olefin feeds, and is therefore preferred for continuous oligomerisation processes.
1.4 Mechanistic considerations

1.4.1 Nickel hydrides and the degenerated polymerisation mechanism

Thanks to a careful observation of several precatalyst side products (Figure 8), Ni-H or Ni-C based complexes have been identified as the active species for olefins oligomerisation.

Nickel (II) hydride species are generally considered as the active species coming from the degenerate polymerisation mechanism. This mechanism, presented in Figure 9, consists of the successive insertion of ethylene in the metal-hydride (I) or metal-alkyl bond (II and III). Linear α-olefins are subsequently released by β-H elimination of the metal-alkyl intermediate (IV). The isomerisation process is responsible for internal and/or branched olefins.
General Introduction

Figure 9: Postulated mechanism for degenerated polymerisation including isomerisation and co-dimerisation pathways.
The distribution of olefins in this mechanism relies on two parameters: the propagation and termination constants (resp. \( k_p \) and \( k_t \)). If the ratio \( k_p/k_t = 1 \), the system will produce olefins following a broad Schulz-Flory distribution.\textsuperscript{[97]} For \( k_p/k_t << 1 \), the system will afford short olefins (1-butene, 1-hexene, 1-octene) as shown in Figure 10. This distribution is modelled by the Schulz Flory constant,\textsuperscript{[10]} \( K_{SF} \) (also called growing factor), calculated from the oligomers product distribution (% weight) determined from GC and averaged on the \( C_8-C_{18} \) oligomers. The general formula for the calculation of \( K_{SF} \) is given by eq. 1, in which \( p \) corresponds to the number of monomer units (for ethylene \( p = \) number of carbons / 2, for propylene \( p = \) number of carbons / 3) and \( Cte \) is a constant.

\[
\log \left( \frac{\% weight \ of \ p}{p} \right) = (\log K_{SF \ p})(p - 1) + Cte
\]

In practice, the determination of the \( K_{SF(p)} \) constant at the degree \( p \) is calculated between \( p \) and the consecutive oligomer \( p+1 \) and the previous equation is simplified as seen in eq. 2.

\[
K_{SF(p)} = \left( \frac{\% weight \ C_{p+1}}{\% weight \ C_p} \right) \cdot \left( \frac{p}{p + 1} \right)
\]

**Figure 10.** Schulz-Flory olefin distribution

This geometric oligomer distribution has been applied to describe many nickel-based oligomerisation systems. It fitted particularly well with SHOP-type complexes that
produced exclusively LAO, thus enabling the determination of a good structure-selectivity relationship.\textsuperscript{[98,99]}

1.4.2 Towards other mechanisms

Although the most frequently encountered mechanism for ethylene oligomerisation by nickel is the degenerate polymerisation described by Cossee and Arlman, certain systems show exceptional selectivity for one LAO and in particular 1-butene. Mukherjee \textit{et al.} reported a nickel oxime complex 24, which in combination with EADC, produces 77 \% ethylene dimers comprising 99.5\% of 1-butene.\textsuperscript{[100]} As another example, the phosphanyl-urea ligand system 25 + Ni(COD)\textsubscript{2} is reported to afford 75\% butenes of which 1-butene is predominant.\textsuperscript{[83]}

![Chemical Structures](image)

High contents of 1-butene for nickel catalysts are surprising considering a degenerate polymerisation mechanism, which usually gives rise to a geometric mixture of long oligomers (Schulz-Flory). This hints at other oligomerisation mechanisms at work, such as metallacyclic pathways.

Early transition metals such as titanium or chromium oligomerise ethylene with a very high selectivity towards a single LAO. This ability lies in the possibility of a concerted coupling mechanism (Figure 11).\textsuperscript{[101]} In this approach, two molecules of ethylene coordinate to the metal in a coplanar fashion. Oxidative coupling of this system leads to a metallacyclopentane. Depending on its stability, this intermediate evolves according to two pathways:

- the metallacyclopentane is stable and an extra molecule of ethylene coordinates, inserts and forms a metallacycloheptane,
- the metallacyclopentane is unstable and releases a molecule of 1-butene by intramolecular hydrogen transfer.
During the catalytic loop the metal is oxidised and reduced between a valence state of $n$ and $n+2$.

These observations lead to the important question if this concerted coupling mechanism applies to nickel oligomerisation. Although metallacycles are common in chromium and titanium chemistry, literature examples of nickellacycles are extremely scarce. The only example is from Grubbs et al. who managed to synthetically create a nickellacyclopentane stable at low temperature. Depending on the type of phosphine attached to the metal, the elimination step triggered by increasing the temperature leads to the formation of cyclobutane, ethylene or 1-butene. The presence of ethylene in the degradation products could indicate that the reverse reaction (oxidative coupling) is possible$^{[102,103]}$.

This example shows that nickellacyclopentane may be stable (at low temperature), however oxidative coupling of ethylene to Ni(0) and formation of a nickellacyclopentane has not been reported so far. The work of Grubbs was later supported by a DFT investigation showing that ethylene could in theory oxidatively couple to a nickel(0)bisphosphine complex (Figure 31)$^{[104]}$. The pathway calculated in Figure 12 suggests that two molecules of ethylene coordinate around the metallic centre ($M_2$). When a third free molecule of ethylene is added, energy is required to reach the transition state ($TS_1$) in which the extra molecule is in weak anti-interaction with coordinated ethylene to subsequently form a new C-C bond ($M_3$). A rotation

![Figure 11. Mechanism of concerted coupling: affords one olefin selectively.](image-url)
along the newly created C-C bond lowers the energy ($\text{M}_4$) putting the two radicals in proximity. In this situation the two electrons couple to form the new Ni-C bond (metallacycle $\text{M}_5$) and release the coordinating ethylene.

![Energy profile diagram](image)

**Figure 12.** Energy profile describing the attack of an ethylene molecule on the $\text{M}_2$ complex; r.c. 2: reaction coordinates leading to the formation of the $\text{M}_5$ biradical: the formation of a nickellacyclopentane is energetically favoured (extracted from Bernardi et al.\textsuperscript{[104]}).

These studies suggest that a metallacyclic pathway could take place with nickel catalyst forming 1-butene. Furthermore, this leads to the question if higher olefins (such as 1-hexene or 1-octene) are reachable by this pathway.

Recently Alt et al. showed the possibility of activating a nickel dihalide complex in the absence of any alkylating agent. The metal species in the presence of a weak Lewis acid and dissolved in chloroaluminate buffered ionic liquids yielded under an ethylene atmosphere alpha-olefins with high selectivity. The absence of an alkylating agent or the presence of a group with the ability to generate an hydride species contradicts the degenerate polymerisation mechanism and opens the way to a
possible concerted coupling mechanism or a new pathways.\textsuperscript{[105–107]} The reduction of Ni(II) to the unusual oxidative state Ni(I) would be a natural consequence of this pathway.

### 1.4.3 The potential of Ni(I)

While nickel (II) and nickel (0) complexes are widely reported in the literature, less is known about the oxidative states (I) and (III). Some studies in heterogeneous catalysis by Che et al. have demonstrated the potential of Ni(I) immobilised on silica for ethylene oligomerisation without generating nickel hydride or nickel alkyl intermediates.\textsuperscript{[108]} Compounds of Ni(I) are paramagnetic and their observation relies exclusively on EPR, elemental analysis, mass spectroscopy or single crystal diffraction. Due to this unusual oxidative state, Ni(I) can accommodate a greater number of coordinating ligands. Olivier et al. showed that a coordination number up to five was possible (when immobilised on silica) which renders a metallaacyclic pathway possible to account for the formation of 1-butene.\textsuperscript{[109]} A catalytic pathway involving Ni(I), however, is not generally accepted. Go et al. suggested that the activity of Ni(I) relies on a disproportionation leading to Ni(0) and Ni(II).\textsuperscript{[110]}

Some complexes of Ni(I) can be isolated and thus their catalytic ethylene oligomerisation activity can be investigated. Bogdanovic reported that complex 26 in presence of AlCl\textsubscript{3} or BF\textsubscript{3}.OEt\textsubscript{2} is moderately active.\textsuperscript{[63,110]}

![Complexes 26-29](image)

Complexes of monovalent nickel are obtained by the reduction of (PR\textsubscript{3})\textsubscript{2}NiX\textsubscript{2} complexes using sodium sand,\textsuperscript{[111]} zinc,\textsuperscript{[112]} or sodium borohydride.\textsuperscript{[113]} Other procedures mention a comproportionation pathway that leads to Ni(I) species by reacting a cationic nickel (II) species with a phosphine nickel (0) complex (comproportionation: Ni(II) + Ni(0) \rightarrow Ni(I)).\textsuperscript{[114]} Bigorgne et al. reported a way to form nickel (I) hydride complexes upon the reaction of triisopropylaluminium with Ni(acac)\textsubscript{2} in the presence of triethylphosphine.\textsuperscript{[115]} This species may be formed first by alkylation followed by β-H elimination.
The group of Saraev also devoted a lot of attention to Ni(I) complexes and studied them by EPR spectroscopy. They isolated and characterised complexes 27 and 28. Furthermore, in addition to the well-known formation of the metal hydride, when strong Bronsted acids oxidatively adds to zeroidal nickel, they observed by EPR the formation of Ni(I) complex 29, which is active in ethylene oligomerisation. They claim that Ni(II) hydrides are not active in oligomerisation but that they rearrange (comproportionation) in presence of Ni(0) to the potentially active Ni(I) species.  

Similar species are formed with the system (PPh₃)₄Ni / BF₃-OEt₂. The cationic system forms (PPh₃)₂NiBF₄ which upon phosphine decoordination leads to catalytically active (PPh₃)₂Ni(OEt₂)BF₄. In contact with ethylene, oligomerisation starts, the bis ethylene intermediate (PPh₃)Ni(C₂H₄)₂BF₄ forms but quickly disappears towards a species not visible in EPR. This compound is considered to be the active oligomerisation species and may be either a dimer or an oxidised / reduced version of (PPh₃)Ni(C₂H₄)₂BF₄. However, more experimental data is required to claim the role of Ni(I) in ethylene oligomerisation reactions.

2 Major families of catalysts

A nickel based (pre)catalyst used in catalytic ethylene can consist in a wide variety of different ligands around the metallic centre. These ligands have a profound influence on the activity and the selectivity of the oligomerisation reaction. In order to rationalise the ligands effects, Keim et al. suggested an analysis of the ligands (based on the SHOP-complexes) by fragmentation of the complex in a chelate part and an organo part (see Figure 13).

![Figure 13](image.png)

**Figure 13.** Fragmentation of a typical SHOP catalysts by Keim et al. into functional groups. The chelate part and the organo part both have an influence on the activity and selectivity.

Many studies have focussed on the role of the chelate part. This fragment, which remains bonded to the metal during the course of the reaction, is supposed to have a greater influence on the outcome and selectivity than the organo part. A great
deal of ligands have been synthesised and chelated to the nickel centre in order to control the reactivity and the selectivity of the oligomerisation reaction. Some commonly employed ligand classes are discussed below.

### 2.1 Monodentate ligands

In early work on nickel catalysed oligomerisation, monodentate ligands were the most widely used. Monodentate neutral ligands resulting in neutral or cationic nickel (II) complexes have an influence on the outcome of the reaction. Noticeable examples of “phosphine modified catalysts” using phosphine ligands [30] were developed by Wilke *et al.* for propylene dimerisation (see 1.3.3.2.) [60] Besides phosphines, monodentate phosphites [31] were also used by the Mitsubishi Chemical Corporation for the Ni-catalysed dimerisation of *trans*-2-butene. [124]

### 2.2 Bidentate ligands

Bidentate ligands offer the possibility to combine hard donor atoms (such as nitrogen, oxygen) with soft donor atoms (such as phosphorus, sulphur). The most common class of bidentate ligands are the α-diimines (N,N) introduced by Brookhart (32). [70,90,91,125] It is noteworthy that nickel α-diimines complexes can be used both for the polymerisation and the oligomerisation of ethylene. If R is a bulky group the system produces polyethylene whereas oligomers are formed in the absence of steric hindrance. The group of Sun developed ligands based on the same “α-diimines”
backbone (21). Variations on this template include the 1,2-diiminophosphoranes based nickel complexes (33) leading to active systems in ethylene oligomerisation. Those complexes show a tetrahedral geometry around nickel and are therefore paramagnetic. The activity is generally high, especially for the Sun system (167 000 $g_{C_2H_4}/(g_{Ni}.h)$). They produce, under an ethylene atmosphere, a short ($C_4-C_6$) to broad distribution of oligomers ($C_4-C_{30}$) with a high content of LAO. Mukherjee et al. reported nickel oxime complexes 24, which is the association of two (N,N) bidentate ligands described before.

![Diagram of nickel complexes](image)

Diphosphines ($P,P$) present some similarities to $\alpha$-diimines ($N,N$), however, they give generally less active complexes (by a factor 10). The diarylphosphinomethane ligand 34 in combination with by Ni(COD)$_2$ and BAr$_F$ produces a broad distribution of oligomers when the ligand is not very bulky ($R=H$ or $CH_3$). For more bulky groups ($iPr$, $CF_3$), polymer is produced. Bianchini et al. showed that DPPE (diphenylphosphinoethane) 35 is active and they optimised the structure to a phosphine tetrasubstituted cyclobutane analogue, that give complexes with higher activity and robustness. Campora et al. found that the length of the backbone and therefore the bite angle in 36 is in direct correlation with the $\beta$-hydrogen elimination and the switch between polymerisation and oligomerisation. With the number $n$ of methylene increasing, the activity decreases and low molecular weight polyethylene is formed for $n=1$ and $n=2$, while $n=3$ produces oligomers. (PNP) ligands with consecutive donor atoms enter in the ($P,P$) category because, according to crystal structures, the nitrogen does not have the ability to coordinate. The group of Wu synthesised (PNP) Ni(II) complexes (based on 37) which, activated by MAO or DEAC, produces dimers and trimers with moderate activity (10 200 $g_{C_2H_4}/(g_{Ni}.h)$).
Such systems were also reported as polymerisation catalysts by the groups of Carpentier (38) and Rosenthal (39).\textsuperscript{[40]}

Mixed (P,N) ligands combine a soft and hard donor atom. Modification of the steric bulk attached to the phosphine or the nitrogen influences the coordination chemistry and the catalysis. A large number of this type of complexes has been described.\textsuperscript{[93,132]}

![Complexes 40-43](image)

Complexes 40-43 activated by MAO (400 or 800 eq.) or by EADC oligomerise ethylene into olefins with low molecular weight (C\textsubscript{4}-C\textsubscript{8}) and high activities (up to 23 500 g\textsubscript{C\textsubscript{2}H\textsubscript{4}}/(g\textsubscript{Ni}.h) (EADC)) are obtained in the same range as diphosphines (P,P).\textsuperscript{[93]} The LAO content is not very high (even with MAO), probably because of isomerisation. Kamer et al. synthesised various pyridylphosphine analogues and found that increasing the bite angle leads to a higher activity but also more pronounced isomerisation.\textsuperscript{[133]}

Mixed (P,O-) ligands were extensively studied by Keim et al. as they are currently used industrially by SHELL to produce LAO with a broad Schulz-Flory type product distribution. A square planar geometry seems to be a prerequisite for good activity and selectivity of these catalysts.\textsuperscript{[67]} Much research effort has been directed towards the elucidation of the structure activity pattern of catalyst 44.\textsuperscript{[98,99]}

![Complexes 44-47](image)

The properties of these catalysts depend strongly on the donor properties of the P and O atoms, which are ruled by the C\textsubscript{1} and C\textsubscript{2} substitution (complex 45). Strong withdrawing groups on C\textsubscript{1} particularly favour the formation of shorter oligomers by lengthening the O-Ni-C(Ph) bonds and therefore increasing the rate of termination step.\textsuperscript{[56]} Mercier et al. showed in 46 that artificially lowering the electron density on the oxygen by means of a intramolecular hydrogen bond results in formation of LAO of lower molecular weight.\textsuperscript{[58]} Other factors such as the basicity and the steric
hindrance of the phosphines $P(R_2)_3$ or $P(R_1)_2$ in 44 affect the activity (inactive to active) or the formation of polymer. These effects are generally interdependent and related to the backbone.\cite{59,122,123} Matt et al. studied and reviewed these systems in depth.\cite{98,99}

Keim et al. also studied the $(O,O')$ ligands and particularly the acetylacetonate fragment (which is also an electron delocalised ring system based on 6 atoms).\cite{80,134} The allylic COD complexes depicted as 47 were studied in 1-butene dimerisation; they produce dimers with a good selectivity only if $R$ is a CF$_3$. Acetylacetonate nickel itself is inactive.\cite{66,80}

$(N,O)$ ligands have been extensively investigated.\cite{135} One major breakthrough is the discovery of salicylaldimine-based nickel(II) complexes (such as 48) by the group of Grubbs that perform ethylene polymerisation without co-catalyst with activities up to 51 000 $g_{PE}/(g_{Ni} \cdot h)$ under very mild conditions.\cite{136} By modifying the chelate backbone, the group of Bazan found that system 49, with 2 eq. of B(C$_6$F$_5$)$_3$, is able to produce internal olefins with very high activity 93 000 $g_{C_2H_4}/(g_{Ni} \cdot h)$.\cite{137} Other modifications on Grubbs original catalyst led to bis NO chelate-type 50, which, activated by EASC, dimerises ethylene into butenes with activities up to 49 000 $g_{C_2H_4}/(g_{Ni} \cdot h)$.\cite{138}

Catalyst 51 developed by Braunstein et al has a bimetallic structure via bridging Cl with hexacoordinated nickel. Activated by 6 eq. of EADC it produces mostly 1-butene with an activity of 83 000 $g_{C_2H_4}/(g_{Ni} \cdot h)$.\cite{139,140}
2.3 Tridentate ligands

Tridentate ligands have also been used with the potential advantage of offering an even wider diversity of nickel based catalysts. One strategy consists of introducing an additional donor group on bidentate ligands. Tridentate ligands favour new types of geometries with a coordination number of 5 (trigonal pyramidal, square pyramidal).

Carpentier et al. developed nickel tridentates with different central atoms (NNN, NON, NSN). Activated by MAO, the catalytic systems oligomerise ethylene with very high activities (60 000 g\textsubscript{C\textsubscript{2}H\textsubscript{4}}/(g\textsubscript{Ni}.h)) producing exclusively butenes of which 87% is 1-butene. NSN complexes are more active than NNN or NON complexes but they also produce larger amounts of internal olefins.\textsuperscript{[141]} 2-quinoxalinyl-6-iminopyridines-based nickel complexes, reported by the group of Sun and activated by EADC, gave dimers and trimers with high activity (32 000 g\textsubscript{C\textsubscript{2}H\textsubscript{4}}/(g\textsubscript{Ni}.h)).\textsuperscript{[142]} Tetradentates have not been used in the field of nickel oligomerisation.

3  Supramolecular catalysis

3.1 From Nature to supramolecular catalysis

Enzymes are maybe the most beautiful example of the supramolecular catalysts in Nature. They are linear assemblies of aminoacids (primary structure) that fold by weak interactions to adopt a three dimensional structure containing an active site (secondary and tertiary structures). In the course of the catalytic reaction, there is a molecular recognition between the substrate and the enzyme’s active site leading to very quick and selective chemical transformations.

The key to the high activity and selectivity is the geometry of the binding pocket in which the substrate is accommodated by host-guest interactions. This complementarity has been a source of inspiration for chemists who created different techniques at the molecular level to confine molecules in space (e.g. cages and capsules as in Figure 14) leading to higher selectivity compared to traditional non-confined systems.\textsuperscript{[143–151]} More recently, based on a molecular recognition and the use
of co-factors, the ligand that is binding to the metal also pre-organises polar substrates inside the cavity, leading to highly selective transformations (DIMPhos as an example in Figure 15)[152–154]

Supramolecular catalysis was introduced as a new approach to design catalysts and in particular, creating supramolecular bidentate ligands.[157–159] Indeed, starting from two monodentate ligands, it is possible to create a supramolecular bidentate assembly as depicted in Figure 16. This system with a flexible weak interaction in its backbone differs from traditional bidentate ligands having a rigid backbone such as BINAP, DIOP, DIPAMP, JOSIPHOS or XANTPHOS among others. Moreover, the synthesis of diphosphine ligands, which was long and tedious, is achieved more simply just by mixing two monophosphine building blocks.
In the rest of this Chapter, we will focus on bidentate supramolecular ligands and we will explore the different type of supramolecular interactions used to pre-organise the different building blocks.

### 3.2 Ligand metal interaction

In traditional catalysis metals are the active site. In supramolecular chemistry they are also used for the assembly process. Generally, the metal is anchored to one building block and does not interact with the active (P,P) binding site. From this principle, Reek et al. developed SUPRAPhos 54, a new bidentate supramolecular assembly of a Zn-porphyrin functionalised by a phosphorus atom and a pyridine-phosphine. The weak interaction takes place between the Zn atom (from the porphyrin) and the pyridine moiety. The selective formation of this assembly lies in a stronger affinity of the Zn-porphyrins for N atoms than for phosphorus. On the same principle Takacs et al. reported the Pd complex 55 performing allylic amination with good yields and selectivity.

![54](image1)

![55](image2)

The power of this approach has been demonstrated by the preparation of a library of 20 building blocks based on the porphyrins and 20 building blocks with a pyridyl, leading to a library of 400 supramolecular bidentate ligands. Preparation and screening different catalysts is therefore much easier and faster than with traditional catalysts. Metal ligand interaction are also used to create tree dimensional cages in which the substrate is encapsulated and reacts with unprecedented yield and selectivity.

### 3.3 Hydrogen bond interaction

Hydrogen bonding is a powerful tool for the construction of bidentate P,P ligands. The use of H-bond in catalysis was initiated by B. Breit et al. who developed complementary ligands based on DNA bases pairs Adenine-Thymine such as 6-
diphenylphosphanyl-2-pyridone (6-DPPON, see Scheme 18), which in the presence of a metal rearrange to form two hydrogen bonds. This chemistry requires most of the time the use of non-coordinating and aprotic solvents to favour H-bonds between the constituents.

Scheme 18. The two tautomeric forms of the 6-diphenylphosphanyl-2-pyridone (6-DPPON) and metal-induced rearrangement to a diphosphine supramolecular complex. The weak interaction consists of two hydrogen bonds: OH—O and NH—N which resembles DNA complementary bases (adenine-thymine, cytosine-guanine)

This work has been extended to new classes of donor/acceptor ligands and libraries of ligands have been generated and studied in hydroformylation and hydrogenation of alkenes. Some of these assemblies are even stable in protic conditions. Interestingly, nickel (Ni(COD)$_2$) has been used in these systems to perform alkene hydrocyanation. On the same strategy, the group of Reek developed UREAPhos ligands that give rhodium complexes that are active and selective in asymmetric hydrogenation. These systems are based on a hydrogen-bond interaction between the carbonyl of the urea (H acceptor) and the two NH of the urea (H-donors) as seen in Scheme 19.

Scheme 19. Synthesis of UREAPhos Pd complex by using the complementarity between two urea moieties.

The same group developed the METAMORPhos ligand which exists in two different tautomeric forms, which will be discussed further in detail in this thesis.
The hydrogen bond, which is a structure element in a supramolecular approach, was also reported in the domain of nickel-catalysed ethylene oligomerisation. Mercier et al., based on SHOP catalysts, developed systems that lower the electron-density at the nickel in 56 and 57, by means of an intramolecular H-bond. This results in a shift of the olefin distribution towards shorter linear alpha olefins.\[42,174\]

![Diagram 56 and 57]

3.4 Ionic interaction

Ionic interactions are used as a tool to join two ligand building blocks in a supramolecular way. The most common strategy consists of the creation of an ion pair. For example monosulphonated triphenylphosphine sodium salt and 3-(diphenylphosphanyl)anilide hydrochloride are reported to react together (Scheme 20) with \([\text{PtCl}_2(\text{COD})]\) to form a supramolecular complex.\[175,176\]

![Scheme 20]

Scheme 20. Creation of an ionic interaction between a sodium sulphonate and an amine hydrochloride moieties resulting in a bidentate diphosphine ligand.

Based on the extensive work in the area of rotaxanes, a bidentate (or tridentate) supramolecular ligand (Scheme 21) was based on two molecules that are interlocked. These complexes were also used in asymmetric hydrogenation with rhodium.\[177,178\]
3.5 Pi stacking interaction

Pi-Pi interactions have also been used to assemble two ligand building blocks. This type of electronic interaction relies on dipole-dipole interactions (Van der Waals) between an electron-rich motif (anthracene, anisoles), and an electron-deficient substituent (2,4,7-trinitrofluoren-9-one, pentafluorobenzene,). The previous motifs have been substituted by phosphorus donor groups which can coordinate to metals (Scheme 22).[179,180] However, there is no proof that such type of interaction is sufficiently strong to have effects in catalysis.

4 Aim and outline of the thesis

Linear alpha olefins are of significant importance in the chemical and petrochemical industry and they represent a constantly growing market. Several processes have been developed leading to high selectivity in LAO formation, but a central issue still needs to be addressed at both academic and industrial levels: the control of the chain length and therefore the development of catalytic systems that are able to produce selectively 1-butene, 1-hexene, 1-octene.

One of the limitations encountered with most catalysts is the Schulz-Flory distribution obtained that highlight the limited selectivity that can be obtained for the different “light” products LAO (C4-C6) which are the most demanded on the market.
However, a more limited number of catalysts were successfully used to induce selective dimerisation. Nickel catalysts were not much reported for selective oligomerisation of ethylene. Among bidentate ligands, two types of chelates have emerged: PO anionic ligands such as used in the SHOP process or the N,N diimine ligands, both being very robust and transposable to industrial scale or pilot plants. Substituting these non-selective systems to selective ones represent a strong challenge.

By using a supramolecular strategy we aimed to construct supramolecular bidentate complexes by the assembly of two monodentate ligands connected by a hydrogen bond, as shown in Figure 17. Although this approach has been successfully used for transition metals such as Rh, Pd and Pt, research on nickel is limited to one example in situ that described the application of these complexes to the hydrocyanation of alkenes.\textsuperscript{[181]}

![Figure 17. Nickel oligomerisation precatalysts and their possible supramolecular equivalents. The wavy bond indicates a supramolecular interaction.](image)

Recently, Reek’s group reported a supramolecular rhodium complex (Figure 18, bottom right) bearing two METAMORPhos ligands in close interaction by means of a hydrogen bond. Besides being supramolecular, this complex has a particular chelation mode (PO anionic ligand + phosphine), which is similar to the structure of the SHOP nickel catalyst used industrially for olefin production (Figure 18, top left). We therefore expected that the combination of METAMORPhos ligands with nickel complexes would form active systems for olefin oligomerisation.
We hypothesised that the presence of a hydrogen bond in PO-chelated nickel complexes would lower the electron density of the coordinating O of the PO chelate and would, in the case of nickel complexes, favour the β-elimination step over the propagation leading to shorter carbon chains (C₄-C₈). In a nickel system based on METAMORPhos ligands, the strength of the intermolecular hydrogen bond and thus the electron density on the oxygen atom can easily be tuned by modifying one or both ligands (see work of Mercier et al. and Figure 18, top right).[42,58,174]

**Figure 18.** Analogy between a supramolecular Rh complex and SHOP Ni catalyst.

Apart from the hydrogen bond, SHOP type catalysts are tuneable by substituents at different positions offering a wide diversity of complexes for employment in catalytic reactions. Heinicke et al.[123] reported that increasing the basicity of the labile PR₃ phosphine (and consequently its ability to coordinate to the metal) leads to shorter α-olefins, and a decrease of the activity. They explained this observation by a potential competition between ethylene and the phosphine. The substrate coordination is suggested to favour the propagation and the chain growth, while the
phosphine coordination would favour the β-elimination step and the chain termination. Matt et al.\cite{98} also proposed that the chain termination involves a β-hydrogen transfer to the coordinated olefin of an 18-electron species. Additionally, the extra ligand is necessary to avoid deactivation of the catalyst by disproportionation, leading to the formation of the inactive bis(PO) chelate.

The positive effect expected using the aminophosphine ligands is the use of the dynamic character of supramolecular assemblies. As mentioned above the distribution in LAO is related to the coordination ability of the phosphine. With the additional hydrogen bond interaction between the phosphorus ligand and the chelate, being in the range of 2-10 kcal/mol, we put forward the hypothesis that the presence of this hydrogen bond strengthens the coordination ability of the additional ligand favouring the formation of short oligomers.

This concept of pre-organised supramolecular assemblies can be extended to discover new classes of ligands. Several ligands formed by cheap and versatile building blocks such as phosphinamide, hydroxyphosphine, aminopyridine or amidopyridine can be used for this purpose.

In this thesis we explore in Chapter 2 the synthesis of a library of phosphorus ligands with H-acceptor and H-donor moieties and in particular the synthesis of amidophosphines and sulphonamide phosphorus ligands (METAMORPhos). Several METAMORPhos ligands that exist as a mixture of tautomers (PH or NH), with diverse electronic and steric properties have been isolated and characterised by NMR. We also report how the tautomeric equilibrium is influenced by the substituents on the nitrogen and the phosphorus atoms. A side “self-condensation” reaction was identified, that converts METAMORPhos ligands into iminobisphosphines (bis-addition product). The rate of this transformation could be reduced and even suppressed by choosing suitable substituents on the phosphorus. Some nickel complexes of these ligands have been studied by NMR and X-Ray diffraction.

In Chapter 3, we employ iminobisphosphines, which serendipitously formed as by-product, and were used as ligands. We could prepare symmetrical and non-symmetrical ligands of general formula $R^1$-N=P(R$^2$)$_2$-P(R$^3$)$_2$ with good yields. In the presence of NiBr$_2$(DME) the ligands rearranged to PNP complexes of general formula (R$^2$)$_2$P-NR$_1$-P(R$^3$)$_2$NiX$_2$. This rearrangement is likely due to the P-P bond cleavage caused by the NiBr$_2$(DME). The complexes were evaluated in ethylene oligomerisation activated by MAO. They display a high productivity, and an unusual product distribution of butenes along with oligomers (C$_6$ and C$_8$+). The complexes also possess a good activity for propylene oligomerisation producing mainly dimers.
and more specifically 2,3-dimethylbutenes when basic phosphines were used. Moreover the rearrangement was applied to chromium ethylene oligomerisation aiming to feature the PNP ligands developed by Sasol.

In Chapter 4 we report the synthesis and detailed characterisation of stable zwitterionic nickel complexes supported by supramolecular bidendate ligands based on sulphonamido-phosphorus and aminophosphine ligands. This novel class of complexes appears to be highly active and selective as catalysts for ethylene oligomerisation with up to 84 wt.% of 1-butene. This high selectivity for short linear alpha olefins is interesting considering the change in the market demand towards such products. *In situ* NMR experiments under ethylene pressure show the rearrangement of these structures to the proposed monoanionic P,O,P nickel complex as the resting state, a stable supramolecular pincer complex that could explain the specific properties displayed by the catalyst.

In Chapter 5 we identified that the electron density on the aminophosphine is the determining factor leading to the formation of stable nickel zwitterionic cationic heterocomplexes. The introduction of more conventional unsubstituted phosphines in the place of aminophosphines indicates that there is a threshold in the phosphine basicity above which complex formation occurs. Moreover there is a steric control in complex formation: phosphines with limited steric bulk lead to the formation of zwitterionic complexes whereas bulky phosphines lead to *trans-(PO,P)* nickel hydride complexes. A mechanism to account for the formation of both related complexes is proposed.

In Chapter 6, the catalytic performances of zwitterionic cationic nickel complexes and nickel hydride complexes were evaluated in the ethylene oligomerisation reaction. Both systems are active, either producing selectively 1-butene or a distribution of higher molecular weight oligomers. According to ethylene high-pressure NMR experiments, cationic zwitterionic and nickel hydride complexes both react under ethylene leading to the same proposed active species. The catalytic activity and selectivity of the nickel complexes were correlated to the electronic parameters of the complexes allowing fine-tuning of the catalytic system.

5 References


General Introduction


Chapter 1


Chapter 1


