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

Boulens, P.A.

Citation for published version (APA):
Chapter 2

Synthesis of Sulphonamido-Based Phosphorus Ligands and their Coordination to Nickel
1 Introduction

The access to a diverse set of functionalised phosphorus ligands is of prime interest in the field of homogeneous catalysis as they allow the generation of easily tunable coordination complexes through self-assembly via the functional groups or by formation of chelate coordination complexes. Recently, sulphonamido based phosphorus compounds were introduced as a new class of ligands.\textsuperscript{[1]} This ligand motif can coordinate by a number of different manners around the metal centre, (i.e. monodentate (P),\textsuperscript{[1–3]} bidentate (P,O),\textsuperscript{[1,3–5]}in neutral (PO)\textsuperscript{[3,5]} or in anionic fashion (PO\textsuperscript{-}, PN\textsuperscript{-})\textsuperscript{[1,3–7]} to a single metal or bridging between metal centres\textsuperscript{[6,7]} giving access to diverse set of complexes with only few ligands. The coordination behaviour of these ligands was notably described with Rh, Ir, Ru and besides, it was successfully used to construct supramolecular systems through hydrogen bonding.\textsuperscript{[3,4]}

Sulphonamido phosphorus-based ligands, known as METAMORPhos, exist in two tautomeric forms: a NH form with trivalent phosphorus and a PH form with pentavalent phosphorus as shown in Scheme 1.\textsuperscript{[1,8]}

The synthesis of METAMORPhos ligands involves the mono addition of a chlorophosphine on a sulphonamide in the presence of a base (Scheme 1). It is a nucleophilic substitution reaction in which the sulphonamide attacks the chlorophosphine and releases a chlorine atom (leaving group) to form HCl, which is captured by the base (NEt\textsubscript{3}). The synthesis is generally performed in THF or diethyl ether to separate the triethylammonium salt from the organic compounds.

Sulphonamides are weak acids with pKa values around 10 (see Table 1 and experimental part) and their acidity may be modulated by the introduction of electron withdrawing groups at the sulphur as –CF\textsubscript{3} (pKa = 6.4). Introducing electron withdrawing phosphine groups, such as P(1,1'-bi(2-naphtol)) (P(Binol)) to the METAMORPhos structures, results in an increase of overall acidity shifting the pKa from 9.2 to 3.8 (Table 2).

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
R= & Ph & 4-Me-Ph & 4-nBu-Ph & 4-MeO-Ph & 4-Br-Ph & Me & CF\textsubscript{3} \\
\hline
pKa & 10.1±0.1 & 10.2±0.1 & 10.2±0.2 & 10.3±0.1 & 9.9±0.1 & 10.9±0.6 & 6.4±0.6 \\
\hline
\end{tabular}
\caption{Calculated pKa values of common sulphonamides R-SO\textsubscript{2}-NH\textsubscript{2} (first acidity) \textendash; from SciFinder.}
\end{table}
Synthesis of Sulphonamido-Based Phosphorus Ligands and their Coordination to Nickel

<table>
<thead>
<tr>
<th>Table 2. Calculated pKa values of some phosphorus N-substituted sulphonamides (METAMORPhos) – from SciFinder.</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Sulphonamido-based phosphorus ligands" /></td>
</tr>
<tr>
<td>10.2±0.1</td>
</tr>
</tbody>
</table>

The decrease of pKa of mono-substituted sulphonamides is expected to lead to competitive formation of mono- and bis-addition of chlorophosphine on the sulphonamide when triethylamine is used as base during the reaction (pKa = 10.6 ± 0.2). Initial studies by Reek and co-workers already indicated that the bis-addition product can form in this reaction, as a side or as the main product. This competitive addition had also been previously reported by the group of Foss et al. who studied the reaction of primary alkylamines and tosylamide with chlorophosphines. They suggested that the competitive addition was in fact the result of two independent reactions as depicted in Scheme 2. The first reaction involves the bis-addition of chlorophosphine on the mono-substituted product, in line with increased nucleophilicity of the mono-addition product (Table 2). The second reaction is a disproportionation equilibrium (“self-condensation”), that is an equilibrium between the mono-addition product and the bis-addition product plus sulphonamide. The same group also established that tosylamides stabilise the bis-addition product under the iminobisphosphines (-N=P-P).

Scheme 2. Side reactions affecting sulphonamido-phosphines: bis addition and self-condensation equilibrium.

In this Chapter we describe the reinvestigation of the synthesis of METAMORPhos ligands by a comprehensive study of the reaction between sulphonamides and chlorophosphines. Based on phosphorus NMR, the formation of METAMORPhos and the by-products was established from the crude mixtures. Also it was possible to
determine the state of the tautomeric equilibrium in solution between the NH and the PH forms. The results from the condensation reactions (mono or di-substitution products, PH or NH tautomers) allowed the identification of the drivers that account for by-product formation but also the relative stability of the tautomeric forms of the ligands. Preliminary coordination studies of METAMORPhos with nickel(II) precursors revealed several possible coordination modes. The reactivity of sulphonamido-phosphine ligands was also transposed to Ni(0) with the aim to generate organometallic nickel species. For this purpose, sulphonyl-iminophosphoranes were introduced as promising pre-ligands for the formation of PO-chelated organometallic nickel complexes.

2 Synthesis and characterisation of tautomeric ligands

The reaction between several sulphonamides and chlorophosphines was explored (Scheme 1), using in all reactions triethylamine as a base. The course of the reaction (products formation) was monitored by unlocked $^{31}$P NMR. This non-destructive technique is a precious asset to get information on the composition of the mixture. From these experiments the change in ratio between the PCl signal (indicative chemical shifts in Table 3) and that of the products was established and used as a measure for the reaction progress.

Table 3. Indicative $^{31}$P chemical shifts for some common chlorophosphines.

<table>
<thead>
<tr>
<th></th>
<th>PPh$_2$Cl</th>
<th>P(iPr)$_2$Cl</th>
<th>P(tBu)$_2$Cl</th>
<th>P(o-tolyl)$_2$Cl</th>
<th>P(Binol)Cl</th>
<th>PEt$_2$Cl</th>
<th>PCy$_2$Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$(ppm)</td>
<td>81</td>
<td>133</td>
<td>146</td>
<td>67</td>
<td>179</td>
<td>118</td>
<td>128</td>
</tr>
</tbody>
</table>

Recording unlocked $^{31}$P{$_{^1}$H} and $^{31}$P NMR allowed to discriminate systems leading to mono-addition, bis-addition or a combination of both. Unlocked NMR easily evidences the tautomer equilibrium PH/NH since the two tautomers display distinct chemical shifts in $^{31}$P{$_{^1}$H} NMR where they appear as singlets. Both tautomers can be distinguished by proton-coupled phosphorus NMR ($^{31}$P NMR) as shown in Figure 1. The PH tautomer has a covalent bond between the phosphorus and the proton leading to large $^{1}$J$_{PH}$ coupling (around 490 Hz) in the phosphorus NMR spectrum. The coupling for the NH tautomer is much smaller (ca. 7 Hz). Similarly, the tautomers also appear distinctly in the $^{1}$H NMR spectra as two independent signals. In a phosphorus-decoupled proton NMR ($^{1}$H{$_{^{31}$P}) NMR, both tautomers appear as singlets while in phosphorus-coupled proton NMR ($^{1}$H NMR) the PH proton appears as a doublet with a large coupling identical to that observed in $^{31}$P NMR. The NH proton splits also but with a much smaller constant. In these NMR experiments, iminobisphosphines, the bis-addition products, were also identified as two doublets.
Synthesis of Sulphonamido-Based Phosphorus Ligands and their Coordination to Nickel

exhibiting $J_{PP}$ couplings around 350 Hz. A quick and comprehensive mixture analysis based on $^{31}P\{^1H\}$ NMR, $^{31}P$ NMR and $^1H$ analyses is displayed in Table 4.

![Figure 1. Tautomeric equilibrium of METAMORPhos ligand and corresponding pattern in $^{31}P$ NMR.](image)

**Figure 1.** Tautomeric equilibrium of METAMORPhos ligand and corresponding pattern in $^{31}P$ NMR.

**Table 4.** Determination grid based on NMR for products stemming from chlorophosphine and sulphonamides in presence of NEt$_3$.

<table>
<thead>
<tr>
<th></th>
<th>$^{31}P{^1H}$</th>
<th>$^{31}P$</th>
<th>$^1H{^{31}P}$</th>
<th>$^1H$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MONO</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-H form</td>
<td>singlet</td>
<td>doublet</td>
<td>singlet</td>
<td>singlet</td>
</tr>
<tr>
<td>P-H form</td>
<td>singlet</td>
<td>doublet</td>
<td>singlet</td>
<td>doublet</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$(2J_{PH}$ ca. 7 Hz)</td>
<td>$(J_{PH}$ ca. 480 Hz)</td>
<td>$(J_{HP}$ ca. 480 Hz)</td>
</tr>
<tr>
<td><strong>BIS</strong></td>
<td>2 doublets</td>
<td>2 doublets</td>
<td>no acidic proton</td>
<td></td>
</tr>
</tbody>
</table>

The reaction involved the dropwise addition of chlorophosphine (1 eq.) to a mixture of sulphonamide (1 eq.) with excess of triethylamine (2.6 eq.) in THF at room temperature. Almost all condensation reactions leading to 1-20 were quick as all the starting material (according to the disappearance of the chlorophosphine) had reacted after 10 minutes at room temperature. Yet, the use of phenyl sulphonamide to form
ligands 6 and 13 resulted in low conversion. The very bulky di-tert-butylichlorophosphine took much longer to react with sulphonamides (15 and 17) and refluxing the mixture was necessary to obtain full conversion.

The qualitative results at full conversion based on unlocked NMR, are presented in Table 5. Under the applied reaction conditions (see Footnote Table 5), ligands 1 and 2 containing the electron withdrawing and bulky P(Binol) resulted both in selective formation of METAMORPhos. Carrying out the condensation reaction with diphenylchlorophosphine led to the partial formation of iminobisphosphine by-product along with ligands 3-7 (bis-addition product < 50%). However, increasing the steric bulk from phenyl to o-tolyl led to selective formation of the mono-addition product 8. Switching to alkyl phosphines with low steric bulk -P(Et)₂ (Entries 9 and 10) resulted both in the formation of the bis-addition product (quantitative for 10). In contrast, the products 11-14 with the more bulky -P(iPr)₂ were obtained with the bis-addition side-product in much smaller quantity (< 10%). The even bulkier -PCy₂ and -P(tBu)₂ resulted in selective formation of the sulphonamidophosphine 15-20.

The pKa values described in Table 2 show that all the METAMORPhos ligands, regardless of the ligand substituents, have pKa values lower than the sulphonamide. This suggests that whatever the substituents is at the phosphorus, the formation of the bis addition product is favoured. This suggests also that the discrimination between mono or bis addition only relies on the steric hindrance at the phosphorus. The more bulky ligands all resulted in cleaner reactions, suggesting that the side reaction to form the iminobisphosphine is suppressed by steric hindrance at the phosphorus, in line with the observations of groups of Rossknecht[14] and Foss.[9]

Since the scope of available METAMORPhos ligands is limited to very bulky analogues we sought to optimise the reaction conditions to facilitate the extension of the ligand synthesis to less bulky ligand, including diphenylphosphine-based METAMORPhos. For this purpose, the challenging reaction of CH₃-SO₂-NH₂ and PPh₂Cl that produced equimolar ratio of mono- and bis-addition product (Entry 7) was selected. Increasing the reaction temperature to 60°C led to the same product ratio obtained at RT while performing the experiment at -80°C led first to exclusive iminobisphosphine formation which subsequently equilibrated to the usual mixture obtained at room temperature (ratio mono:bis = 1:1, K = 1). Changing the base ratio (2.6 eq. or 1.0 eq.) did not have impact on the product ratio. Finally, the best results were obtained with butyl-lithium (BuLi) and particularly with in 1:1 combination with TMEDA followed by the addition of the chlorophosphine. This protocol, gave selectively the mono-addition product (peak at 35 ppm) according to the unlocked ³¹P NMR of the reaction mixture. However, the product could not be isolated as it
rearranged quickly to the iminobisphosphine upon standing. This rapid rearrangement complies with the self-condensation equilibrium, as described by Foss et al., which also means that the formation of bis-addition product is independent on the mode of preparation.

Table 5. Condensation of chlorophosphines or chlorophosphites with sulphonamides.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Chlorophosphine</th>
<th>Sulphonamide</th>
<th>Product crude</th>
<th>Tautomer in situ</th>
<th>Tautomer isolated</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>P(Binol)Cl</td>
<td>F₃C-SO₂NH₂</td>
<td>mono</td>
<td>NH--NEt₃</td>
<td>NH--NEt₃</td>
</tr>
<tr>
<td>2</td>
<td>P(Binol)Cl</td>
<td>4-nBu-Ph-SO₂NH₂</td>
<td>mono</td>
<td>NH--NEt₃</td>
<td>NH--NEt₃</td>
</tr>
<tr>
<td>3</td>
<td>PPh₂Cl</td>
<td>4-nBu-Ph-SO₂NH₂</td>
<td>mono, bis</td>
<td>NH</td>
<td>NH, PH</td>
</tr>
<tr>
<td>4</td>
<td>PPh₂Cl</td>
<td>F₃C-SO₂NH₂</td>
<td>mono, bis</td>
<td>NH</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>PPh₂Cl</td>
<td>4-Br-Ph-SO₂NH₂</td>
<td>bis</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>PPh₂Cl</td>
<td>Ph-SO₂NH₂</td>
<td>mono, bis</td>
<td>NH</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>PPh₂Cl</td>
<td>H₃C-SO₂NH₂</td>
<td>mono, bis</td>
<td>NH</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>P(o-tolyl)₂Cl</td>
<td>F₃C-SO₂NH₂</td>
<td>mono</td>
<td>NH--NEt₃</td>
<td>NH--NEt₃</td>
</tr>
<tr>
<td>9</td>
<td>P(Et)₂Cl</td>
<td>F₃C-SO₂NH₂</td>
<td>mono, bis</td>
<td>NH</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>P(Et)₂Cl</td>
<td>4-nBu-Ph-SO₂NH₂</td>
<td>bis</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>P(iPr)₂Cl</td>
<td>F₃C-SO₂NH₂</td>
<td>mono</td>
<td>(no 'JPH)</td>
<td>PH</td>
</tr>
<tr>
<td>12</td>
<td>P(iPr)₂Cl</td>
<td>4-Br-Ph-SO₂NH₂</td>
<td>mono, bis</td>
<td>PH, NH</td>
<td>PH</td>
</tr>
<tr>
<td>13</td>
<td>P(iPr)₂Cl</td>
<td>Ph-SO₂NH₂</td>
<td>mono, bis</td>
<td>PH</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>P(iPr)₂Cl</td>
<td>4-MeO-Ph-SO₂NH₂</td>
<td>mono, bis</td>
<td>PH</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>P(tBu)₂Cl</td>
<td>F₃C-SO₂NH₂</td>
<td>mono</td>
<td>(no 'JPH)</td>
<td>PH</td>
</tr>
<tr>
<td>16</td>
<td>P(tBu)₂Cl</td>
<td>Ph-SO₂NH₂</td>
<td>(mono)</td>
<td>PH</td>
<td>-</td>
</tr>
<tr>
<td>17</td>
<td>P(tBu)₂Cl</td>
<td>4-nBu-Ph-SO₂NH₂</td>
<td>mono</td>
<td>PH</td>
<td>PH</td>
</tr>
<tr>
<td>18</td>
<td>P(tBu)₂Cl</td>
<td>4-MeO-Ph-SO₂NH₂</td>
<td>mono, bis</td>
<td>PH</td>
<td>-</td>
</tr>
<tr>
<td>19</td>
<td>PCy₂Cl</td>
<td>F₃C-SO₂NH₂</td>
<td>mono</td>
<td>PH</td>
<td>PH</td>
</tr>
<tr>
<td>20</td>
<td>PCy₂Cl</td>
<td>4-nBu-Ph-SO₂NH₂</td>
<td>mono</td>
<td>PH</td>
<td>PH</td>
</tr>
</tbody>
</table>

General conditions: Sulphonamide (10 mmol, 1 eq.) and triethylamine (26 mmol, 2.6 eq.) dissolved in THF (20 mL), and then chlorophosphine (10 mmol, 1 eq.) is added dropwise to the mixture at RT under vigorous stirring. Reaction time was 16 h, unless completion was noted after unlocked ³¹P NMR after 10 min.

Product purification from the crude mixture by chromatography column was not effective due to the self-condensation equilibrium, and also the similar polarity of
some of the components and their sensitivity on basic alumina complicated such purification procedure. Selective precipitation was nonetheless effective to purify crude mixtures containing no more than 30 % iminobisphosphines such as 3 or 12 (DCM / nC₅ or THF / nC₅ 1:3). Finally, ligands with sufficient steric bulk at the phosphorus (1, 2, 8, 11, 15, 17, 19 and 20) were easily isolated as pure powders with moderate to excellent yields (up to 92%) on the gram scale. Isolated products are presented in Scheme 3 with their predominant tautomer that was present in solution (from CDC₃, C₆D₆ or CD₂Cl₂). The structures of ligands 8 and 11 were confirmed by X-ray diffraction. In the solid state ligand 8 forms a ion pair with triethylamine as shown in Figure 2 (N4--H241 2.063 Å) and a weak interaction with the oxygen of the sulphonamide (O2--H241 2.989 Å). In the solid state, ligand 11 is in the PH tautomeric form, with a short PN bond (1.619 Å). This ligand establishes intermolecular hydrogen bond with another moiety as shown in Figure 3 (O--H bond, 2.477 Å).

Scheme 3. Isolated METAMORPhos ligands with predominant tautomer observed in apolar and aprotic organic solvents.
The different isolated METAMORPhos ligands displayed in Scheme 3 exhibit different tautomeric ratios in solution. Ligand 1, with bulky and electron withdrawing Binol moiety, led to exclusive formation of the NH tautomer and formed an ion pair with triethylamine. By keeping the substitution at S identical (-CF₃) but increasing the donating ability of the phosphorus gave ligand 8 (tolyl) that was also in the NH-NEt₃ tautomer. Going from aryl to alkyl phosphines such as -P(iPr)₂, -P(tBu)₂ or -PCy₂ (in 11, 15 or 19), shifted the tautomer from NH to the PH form. Interestingly, ligand 3 displayed both the NH and the PH tautomer in equilibrium. Again, introducing bulkiness and electron donating property on the phosphino group shifted the equilibrium to the PH tautomer (from 3 to 17 or to 20). Changing the sulphonamide substituent with the same phosphine moiety (from 1 to 2, 11 to 12, 15 to 17 or 19 to 20) had no visible impact on the tautomer formed, which was always PH. This strongly suggests that the main driver of the tautomeric equilibrium are the electronic properties of the phosphine. METAMORPhos under the NH form are favoured by phosphines substituted by electron withdrawing groups while METAMORPhos under the PH are stabilised by electron donating phosphines, as alkyl phosphines.
As we anticipated to observe tautomeric behaviour similar to METAMORPhos ligands, we prepared four amidophosphines of general formula \( R^1\text{-CO-NH-P}(R^2)_2 \) with diverse electronic properties introduced either \textit{via} the carbonyl \((R^1)\) or at the phosphorus \((R^2)\) (Scheme 4).\(^{[15]}\) Amidophosphines 21-24 gave rise to three tautomers: NH, OH and PH; NH being the most commonly represented in the literature.\(^{[16]}\) Amidophosphine 21 with electron withdrawing groups \( R^1 = \text{Ph} \) lead preferentially to the NH form (21), while amidophosphines with electron donating groups \( (R^1 = \text{CH}_3) \) favour the OH tautomer, which is still in equilibrium with the NH tautomer for ligands 22 and 23. The OH tautomer was never observed so far for METAMORPhos. Also increasing the donating ability of the phosphine from 22 to 23 led to an increase of this OH tautomer (from 32 % to 77%). The tautomer equilibrium is shifted more towards the PH form as for 24 when \( R^1 \) and \( R^2 \) are electron withdrawing and donating groups, respectively. METAMORPhos ligands 3 (NH/PH) and 11 (PH), display higher proportion of the PH tautomer compared to the analogous amidophosphines 21 (NH) and 24 (NH/PH) as shown in Scheme 4. This shift towards the PH tautomer is also driven by a higher electron withdrawing influence of the sulphonyl group compared to the carbonyl group which certainly also accounts for the absence of the OH tautomer within METAMORPhos.

\[
\begin{array}{|c|c|c|}
\hline
\text{NH} & \text{NH: 100 % (CD}_2\text{Cl}_2) & 21 \\
\text{NH/OH} & \text{NH: 68 % (CD}_2\text{Cl}_2) & 22 \\
\text{NH/OH} & \text{NH: 23% (C}_6\text{D}_6) & 23 \\
\text{NH/PH} & \text{NH: 69 % (CD}_2\text{Cl}_2) & 24 \\
\text{NH/PH} & \text{NH: 86 % (CD}_2\text{Cl}_2) & 3 \\
\text{PH} & \text{PH: 100 % (C}_6\text{D}_6) & 11 \\
\hline
\end{array}
\]

\textbf{Scheme 4.} Four amidophosphines and two METAMORPhos ligands with diverse electronic contributions and their corresponding tautomeric forms.

Besides being affected by the electronic properties of the substituents at P and S, the tautomer equilibrium within METAMORPhos is influenced by the presence of a base or by hydrogen bond acceptor moieties, similar to that reported for secondary
phosphine oxides.\textsuperscript{[17]} Indeed, there is a difference between the tautomeric ratio from the crude reaction mixture compared to that of the isolated product as can be seen in Table 5, which substantiates the influence of triethylamine. The base, present in excess in the reaction mixtures shifts the equilibrium from the PH to the NH as is observed for ligands 3 and 12.

Since the PH and NH tautomers for METAMORPhos originate all from the delocalised P-N-S-O fragment we expected that they would display a pKa in a close range that would be detectable by a single NMR titration of METAMORPhos by a base (Figures 4 and 5). Triethylamine was chosen as a weak base to ensure that it would not deprotonate the ligand. Upon increasing the base concentration in a CDCl\(_3\) solution of ligand 11, the PH doublet in \(^1\)H NMR became broader and its intensity decreased (Figure 4).

**Figure 4.** Titration of ligand 11 by NEt\(_3\) – \(^1\)H NMR study (CDCl\(_3\), relative intensity and chemical shifts corrected on the basis of \(iPr\) signals with no NEt\(_3\) in CDCl\(_3\), initial ligand concentration= 0.1 M).

**Figure 5.** Titration of ligand 11 by NEt\(_3\) – \(^31\)P NMR study (CDCl\(_3\)). Initial, ligand concentration: 0.1 M.
A new sharp peak progressively formed at δ(CDCl₃): 5.28 ppm which was maximal around 20 mol% of triethylamine and decreased upon further increasing the NEt₃ concentration. Finally when the base concentration increased above 62% a very broad peak around δ(CDCl₃): 6.80 ppm appeared, which was the major product even at the highest NEt₃ concentration (260 mol%). There was no trace of triethylammonium proton in the 8-10 ppm range, which suggests that this is more an interaction than a full deprotonation. In parallel to the proton spectrum, the PH signals in ³¹P NMR became broader with triethylamine increasing and merged into one central peak around 50 mol% of NEt₃ (Figure 5). This suggests that triethylamine shifted the original tautomer equilibrium, for which the main form is PH, in favour of other tautomers. However, the proximity between the original doublet and final singlet in ³¹P NMR is surprising considering the chemical shift difference observed for other ligands between the NH and the PH tautomer (for 3: ³¹P NMR (C₆D₆): NH tautomer at δ= 32.75 ppm; PH tautomer at δ= 2.82 ppm). It is likely that the phosphorus remains pentavalent in presence of triethylamine but that the interatomic distance P-H was increased by formation of a hydrogen bond as proposed in Figure 6.

![Figure 6. Possible interaction with triethylamine and METAMORPhos ligand 11.](image)

3 Coordination chemistry of sulphonamido-based phosphorus ligands with nickel precursors

The coordination chemistry of METAMORPhos ligands was first evaluated with nickel (II) precursors. The synthesis was performed in apolar and aprotic solvents to favour possible intermolecular hydrogen bonds between two ligands. We observed that the reaction of ligand 3 and NiCl₂(DME) in a 2:1 ratio in benzene at 60°C was complete after 16 h leading to a red precipitate (Scheme 5). No more ligand was present in the benzene phase according to ³¹P NMR. To ensure full conversion of the precursor, we used a slight excess of ligands that was removed in the end of the reaction by filtration. The precipitate was only slightly soluble in dichloromethane and ³¹P NMR analysis of a saturated sample in CD₂Cl₂ led to a broad signal at
δ(CD₂Cl₂): 34.8 ppm that likely corresponds to the free ligand 3; the complex might be paramagnetic and therefore not visible in ³¹P NMR.

Crystals of complex 25 were obtained from slow vapour diffusion of pentane in a dichloromethane solution of complex and the X-ray structure that was determined from diffraction experiments is presented in Figure 7. Both ligands in this complex are in the NH form and they coordinate via the phosphorus atom in trans with respect to each other. The arrangement around nickel is square planar (sum of angles = 360°). The H-bond between the NH and the chloride that is coordinated to the nickel is very short (2.40(2) Å), constraining the two ligands in a square planar geometry. The geometry of ligand in the complex is very similar to that of the free METAMORPhos ligand with only a slightly shorter PN bond in the complex (ligand 1.720 Å, complex 1.696 Å) and slightly longer NS bond in the complex (ligand 1.624 Å, complex 1.642 Å). Complex 25 was evaluated for ethylene oligomerisation with MAO (300 eq.) as activator. The complex produced at 45°C and 35 bar, mainly butenes (92.5% of oligomers) of which 88.1% accounted for 2-butene. Although the activity was very high at the start with a value of 3.5 10⁶ gₐ( g Ni⁻¹), the complex degraded to black material and turned inactive after 10 min.

Attempts to form coordination complex with ligand 11, which exists exclusively as the PH tautomer, under similar conditions as described for ligand 25 with NiCl₂(DME) did not lead to a clear transformation as no colour change was observed and analysis of the crude by ³¹P NMR showed only the starting material. Supposing that more electrophilic nickel would trigger the tautomer rearrangement with ligand 11 allowing a trivalent phosphorus coordination, we added AgBF₄ in THF as abstracting halide agent. The reaction was also performed with nickel tetrafluoroborate as precursor but no reactivity was noticed.

![Scheme 5. Synthesis of Ni(METAMORPhos 3)₂Cl₂ complex 25.](image-url)
Next we investigated if the presence of a base during the complexation would activate ligand 11 by inducing a shift in the tautomeric ratio. Complexation of ligand 11 (2 eq.) with NiBr₂(DME) (1 eq.) in benzene and in the presence of triethylamine (4 eq.), immediately led to a brown solution with quick consumption of insoluble NiBr₂(DME). According to $^{31}$P NMR, a new nickel complex 26 formed, in which non-equivalent phosphines are coordinated to nickel as can be seen from two very broad signals shifted downfield (80-100 ppm region).

![Figure 7. ORTEP plot (50% probability displacement ellipsoids) of complex 25. Hydrogen atoms have been omitted for clarity (except for NH moiety). Selected bond lengths (Å) and angles (°): Ni1-Cl1 2.1610(5); Ni1-P1 2.2342(5); P1-N1 1.6964(15); N1-S1 1.6424(15); N1-H1N 0.80(3); S1-O1 1.4308(13); S1-O2 1.4333(16); Cl1-H1N 2.40(2); Cl1-Ni1-P1 86.43(2); Cl1-Ni1-Ni1 180.00; P1-Ni1-P1 180.00.](image)

A crystal of 26 was obtained from slow vapour diffusion of pentane into a dichloromethane crude solution of complex (see Figure 8). The X-ray structure shows some unusual features. The two ligands adopt a cis configuration in the solid state and coordinate in the anionic form. The primary ligand forms a PO chelate containing a double S-N bond, which is significantly shorter than the free ligand 11 (N1-S1 1.5232(15) Å vs. 1.5471(9) Å in the ligand) and two formal single bonds: P-N and S-O (P1-N1 1.6827(14) Å and S1-O1 1.4812(13) Å vs. N1-P1 1.6193(9) Å and S1-O1 1.4402(9) Å for ligand 11). The second ligand is engaged in coordination to nickel but only through the phosphorus. The S-N bond length (N2-S2 1.5215(13) Å) is similar to the other S1-N1 double bond in the PO chelate and still very short compared to the free ligand, suggesting that this involves a double bond. Besides, the P-N and S-O bonds in the second ligand are of intermediate length between single and double, which suggests a delocalised structure on the PNSO moiety. This ligand is also obviously deprotonated by triethylamine as the proton is closer from the
triethylamine than for the original ligand ($N_{NEt^3}$-H 0.83(2) Å and $N_{MET}$-H 2.08(2) Å). It forms an ion pair that resides at the oxygen in the solid state meaning that once coordinated on nickel, METAMORPhos 11 may be deprotonated by triethylamine. These experiments show that sulphonamido-phosphorus based ligands coordinate in several modes to nickel.

![Scheme 6: Synthesis of nickel complex 26 from METAMORPhos 11, NiBr2(DME) and triethylamine.](image)

**Figure 8.** ORTEP plot (50% probability displacement ellipsoids) of complex 26. Hydrogen atoms have been omitted for clarity (except for OH moiety). Selected bond lengths (Å) and angles (°): Ni1-P1 2.2099(4); P1-N1 1.6827(14); N1-S1 1.5232(15); S1-O1 1.4812(13); Ni1-Br1 2.3166(3); Ni1-O1 1.9771(13); Ni1-P2 2.1769(4); P2-N2 1.6579(14); N2-S2 1.5215(13); S2-O3 1.4511(13); S2-O4 1.4458(13); [H-bond: O3-N3 2.8881(19); O3-H3N 2.08(2); N3-H3N 0.83(2)].

The use of single component catalysts in oligomerisation, such as nickel-aryl type complexes, offer active systems that do not need activation before the application in catalytic reaction. The direct preparation of Ni-H or Ni-R (R= aryl, alkyl) complexes based on these METAMORPhos ligands would be interesting as they can be directly used for ethylene oligomerisation catalysis. Indeed, the reaction of carboxymethylphosphoranes (R-CO-CH=PR’$_3$) or amidophosphoranes (R-CO-
N=PR’\_3) with Ni(0) was successfully used to generate a plethora or PCCO\(^-\) (or PCNO\(^-\)) chelated aryl nickel complexes that constitute the basis of SHOP catalyst.\(^{18-22}\) These complexes were demonstrated to be active in ethylene oligomerisation producing linear alpha olefins with a large Schulz-Flory product distribution. By analogy, we thought that sulphonyl-iminophosphoranes of general formula R-SO\(_2\)-N=PR’\_3 or METAMORPhos in the PH tautomeric form R-SO\(_2\)-N=P(R’\_2)H would be good candidates to form similar organometallic arrangements based on a PNSO\(^-\) chelate (Scheme 7).

\[\text{Sulphonyl iminophosphoranes were prepared by condensation of a sulphonamide and a tri-substituted phosphine in the presence of diethylazodicarboxylate (DEAD) in an overnight reaction at room temperature (Scheme 8).}^{[23]} \text{This procedure is more suited than the reaction of sulphonyl azide on PR’\_3 or reaction of N,N’-dibrominated sulphonamides with PR’\_3, which in both cases generated also a lot of phosphine oxide.}^{[24-26]} \text{The approach with DEAD was smooth as the pure product precipitated from THF at the end of the reaction. This strategy afforded sulphonyl iminophosphoranes 27, 28, 29, 30 in moderate yield (isolated up to 40 \%) which were characterised by \text{\(^{31}\)P and \text{\(^1\)H NMR (Scheme 8).}}\]
The ability of this new class of sulphonyl-iminophosphoranes to form organometallic complexes was investigated with Ni(COD)$_2$ in presence of a phosphine (PPh$_3$ or PCy$_3$).[18,27,28] The presence of a coordinating phosphine is mandatory for the reaction to happen and probably relies on the intervention of Ni(PR$_3$)$_n$ intermediates. In the presence of PPh$_3$, the solutions first turned red due to the initial coordination of PPh$_3$ to Ni(0) but no further reactivity was observed with sulphonyl-iminophosphoranes at room temperature. We expected that the low solubility of the ligands would not be limiting, considering that carboxymethylphosphoranes or amidophosphoranes have similar low solubility but dissolve in the course of complex formation.[19] Increasing the reaction temperature to 60°C improved ligand dissolution but led also to complex decomposition, as indicated by the formation of a suspension of black insoluble material and loss of the red colour. In all experiments the sulphonyl-iminophosphoranes were very stable and did not react with the metal complex. Similar experiments performed in the presence of PCy$_3$ led to the formation several compounds as indicated by $^{31}$P NMR that displayed several peaks whereas only a doublet was expected. We suggest that PPh$_3$ is not strongly coordinating to nickel and therefore does not sufficiently stabilise the system.

4 Conclusion

In this Chapter we reported some synthetic aspects in the preparation of METAMORPhos ligands. We found that during the preparation of METAMORPhos, iminobisphosphines, the bis-addition product, form as by products under certain conditions. Iminobisphosphines and METAMORPhos are also in equilibrium via a sort of disproportionation reaction, which is less dependent on the operating conditions. However, this equilibrium is supressed by the use of bulky or alkyl substituents on the phosphorus. As a result, several METAMORPhos ligands could be isolated, depending on the properties of the starting materials. Similarly to amidophosphines and secondary phosphine oxides, METAMORPhos give rise to formation of several tautomers in solution with the PH (P$^{IV}$) and the NH (P$^{III}$) forms being the most
common. The domains of predominance of each tautomer (PH/NH) depend on the electronic properties of the ligand. Systems with electron donating groups on P and electron withdrawing groups at the S favour the PH form. Besides this electronic effect, the presence of a base (or hydrogen-bond acceptor moiety) may also induce a shift in the tautomeric equilibrium. METAMORPhos ligands that are in tautomeric form with the trivalent phosphorus, coordinate to nickel(II) to form square planar bis-METAMORPhos complexes. In contrast, METAMORPhos ligands that are in the pentavalent state did not form coordination complexes when mixed with a nickel(II) precursor. However, the same reaction in the presence of triethylamine as a base, resulted in complex formation in which METAMORPhos acted as anionic PO\textsuperscript{−} ligand. The X-ray structure of this complex confirmed that one such anionic ligand is chelated at the nickel complex, while a second ligand coordinated monotonically \textit{via} the phosphorus. Importantly, a wide variety of METAMORPhos ligands can be prepared and they display interesting coordination behaviour to nickel.

5 Experimental part

5.1 General

All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. Sulphonamides, di(o-toly)chlorophosphate, ditertbutylchlorophosphate, diethylchlorophosphate, dicyclohexylchlorophosphate were purchased from commercial suppliers and used without further purification. Diphenylchlorophosphate and diisopropylchlorophosphine were distilled trap to trap under reduced pressure. THF, pentane and Et\textsubscript{2}O were distilled from sodium benzophenone. CH\textsubscript{2}Cl\textsubscript{2} and triethylamine were distilled from CaH\textsubscript{2}, toluene from sodium, under nitrogen. Alternatively solvents from SPS (Solvent Purification System, MBraun) were used. NMR solvents were degassed by freeze-pump-thaw cycling under argon and stored over activated 3 Å molecular sieves. NMR spectra (\textit{\textit{1}}\textsuperscript{H}, \textit{\textit{3}}\textsuperscript{1}P, \textit{\textit{3}}\textsuperscript{1}P\{\textit{\textit{1}}\textsuperscript{H}\} and \textit{\textit{1}}\textsuperscript{3}C\{\textit{\textit{1}}\textsuperscript{H}\}) were measured on a BRUKER 300 MHz spectrometer at 25°C. Analysis of liquid phases was performed on a GC Agilent 6850 Series II equipped with a PONA column. The gas phase for ethylene oligomerisation were analysed by gas GC on HP 6890. Elemental analyses were performed by Stephen Boyer (London Metropolitan University). Values of pKa for sulphonamides and related compounds were gathered from Scifinder (06/2014) and correspond to the value of the first acidity at 25°C, calculated using ACD/Labs Software (© 1994-2014).

5.2 Synthesis of ligands METAMORPhos

\textbf{Synthesis of (R)-1,1′-Bi-2-naphtol-PCI (Binol PCI)}

(R)-Binaphtol (11.05 g, 38.60 mmol, 1.00 eq.) was weighted in a 1000 mL round bottom flask and suspended in dry toluene (20 mL) stirred for 5 min at RT and then evaporated under vacuum. This operation was repeated twice. Then the solid was suspended in toluene (20 mL), phosphorus trichloride (50.00 mL, 78.70 g, 573 mmol, 14.80 eq.) and N-methylpyrrolidone (21 drops, acts as a catalyst). The mixture was heated at 60°C until complete dissolution of the (R)-binaphtol leading to a clear solution (15 min). Then toluene and phosphorus trichloride were evaporated. The resulting oil was co-
evaporated twice with toluene (2 x 50 mL) and triturated in pentane to give a powder (12.58 g, isolate yield: 93%). The product was in accordance with the literature, contained no oxide and displayed a singlet in $^{31}$P NMR (121 MHz, C$_6$D$_6$, 300K): δ(ppm): 177.

**Ligand 1**

![Ligand 1](image)

(R)-1,1'-Bi-2-naphtol-PCl (4.10 g, 11.70 mmol, 1.00 eq.) was dissolved in 20 mL of dry THF leading to an orange solution. In another Schlenk, commercially available 4-butylbenzene-1-sulphonamide (2.49 g, 11.70 mmol, 1.00 eq.) and triethylamine (9.80 mL, 70.20 mmol, 6.00 eq.) were dissolved in THF (30 mL). The phosphine was transferred to the sulphonamide solution by cannula under strong stirring leading to a white precipitate. The suspension was then filtered under argon atmosphere and the resulting clear solution was evaporated to sticky oil. The product was then washed with 30 mL of toluene/hexanes (1:2), and then with 30 mL Et$_2$O. The product was obtained as a white powder (2.21 g, isolated yield: 33%). The NMR analysis of the product was in accordance with the literature, contained no sulphonamide residue, and displayed a singlet in aromatic region, 12 CH$_a$; 8.60 (br s, 1H, NH).

**Ligand 2**

![Ligand 2](image)

(R)-1,1'-Bi-2-naphtol-PCl (4.10 g, 11.70 mmol, 1.00 eq.) was dissolved in 20 mL of dry THF leading to an orange solution. In another Schlenk, commercially available 4-butylbenzene-1-sulphonamide (2.49 g, 11.70 mmol, 1.00 eq.) and triethylamine (9.80 mL, 70.20 mmol, 6.00 eq.) were dissolved in THF (30 mL). The phosphine was transferred to the sulphonamide solution by cannula under strong stirring leading to a white precipitate. The suspension was then filtered under argon atmosphere and the resulting clear solution was evaporated to sticky oil. The oil was dissolved in dichloromethane (15 mL) and evaporated, followed by a trituration in toluene (20 mL) leading to a solid. The solid was washed with toluene (2 x 20 mL) leading to a white solid. This solid was dried under vacuum to yield a powder (5.36 g, isolated yield: 73%). The NMR analysis of the product was in accordance with the literature, contained no sulphonamide residue, and displayed a singlet in aromatic region, 16H; 6.78 (br s, NH, 1H).

**Ligand 3**

Commercially available 4-butylbenzene-1-sulphonamide (2.38 g, 11.14 mmol, 1.00 eq.) was placed in a Schlenk flask under argon. 3 mL of toluene was dropped on it leading to a blurred suspension which was stirred at room temperature for 5 minutes. The solvent was then evaporated. The process was repeated twice. The compound was then dissolved in THF (20 mL) and triethylamine (4.20 mL, 30.00 mmol, 2.70 eq.), leading to a clear colourless solution. Distilled chlorodiphenylphosphine (2 mL, 11.14
mmol, 1.0 eq.) was added dropwise under strong magnetic stirring at room temperature. The immediate formation of salt was observed as a white suspension. The suspension was left to stir overnight at room temperature. The suspension was then filtered under argon atmosphere and the resulting clear solution was evaporated to a white solid (87% of METÁMORPhos and 13% iminobisphosphine). The solid was dissolved in 10 mL of THF and filtered over a short alumina gel column which was washed twice with 10 mL of THF. Evaporation of the solvent led to pure product in 53% yield. The NMR analysis of the product was in accordance with the literature. 

\(^{31}\text{P}\{^1\text{H}\} \text{ NMR (121 MHz, } C_6D_6, 300K) : \delta (ppm): 2.82 (s, PH); 32.75 (s, NH); ratio NH/PH = 18.9; \text{H NMR (300 MHz, } C_6D_6, 300K) ; \delta (ppm): 8.14 (d, 1H, \text{J}_{HP} = 490 Hz, tautomer PH), 8.10-6.5 (aromatic region : tautomer NH and PH), 5.82 (d, 1H, \text{J}_{HP} = 7 Hz, NH tautomer NH), 2.34-2.14 (m, (C_3H_2)-CH_2-Ar : tautomer NH and PH), 1.27 (m, 2H, (C_2H_5)-CH_2-CH_2-Ar : tautomer PH), 1.16-1.02 (m, CH_3-CH_2-(C_3H_4)-Ar, 2H tautomer NH and 2H tautomer PH), 0.84-0.77 (m, CH_3-(C_3H_5)-Ar, 3H tautomer PH).

### Ligand 8

Trifluoromethanesulfonamide (1.2 g, 8.0 mmol, 1 eq.) was dried azeotropically tree times by suspending the powder in toluene (3 mL), stirring for 5 min at RT and removing the solvent under vacuum. After that, the dry trifluoromethanesulfonamide was mixed with anhydrous triethylamine (2.1 g, 20 mmol, 2.6 eq., 3.0 mL) and dissolved in dry THF (20 mL). Di(o-tolyl)chlorophosphine was dissolved in another Schlenk without stirring for 5 min at RT and removing the solvent under vacuum. After 10 minutes, a \(^{31}\text{P}\{^1\text{H}\} \text{ NMR indicated complete conversion of the chlorophosphine towards two tautomers at 15.77 ppm (NH—NEt_3, 70%) and 22.6 ppm (PH, \text{J}_{PH} = 472.6 Hz, 30%). The mixture was filtered by cannula to remove the triethylammonium salt and the filtrate was washed twice with THF leading to a white thick precipitate. The oil was heated to 50°C under vacuum to remove traces of volatile products and diethyl ether (20 mL) was finally added to the oil leading to a white thick precipitate. The oil was washed 3 x 5 mL of diethyl ether (solubilizing the PH tautomer only) and finally dried under vacuum to give the product under the NH—NEt_3 tautomer (isolated yield : 2.43 g, yield : 66%). Analyses were performed on the NH—NEt_3 tautomer.

\(^{31}\text{P}\{^1\text{H}\} \text{ NMR (121 MHz, } CD_2Cl_2): \delta (ppm) = 26.4 \text{ (broad s)}; \text{J}_{PH} = 490 Hz, \text{ tautomer PH), 8.10-6.5 (aromatic region : tautomer NH and PH), 5.82 (d, 1H, \text{J}_{HP} = 7 Hz, NH tautomer NH), 2.34-2.14 (m, (C_3H_2)-CH_2-Ar : tautomer NH and PH), 1.27 (m, 2H, (C_2H_5)-CH_2-CH_2-Ar : tautomer PH), 1.16-1.02 (m, CH_3-CH_2-(C_3H_4)-Ar, 2H tautomer NH and 2H tautomer PH), 0.84-0.77 (m, CH_3-(C_3H_5)-Ar, 3H tautomer PH).}

### Crystal data

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>C_{15}H_{14}F_{3}NO_{2}PS·C_{6}H_{16}N</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M_r)</td>
<td>462.51</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Orthorhombic, (P2_12_12_1)</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>200</td>
</tr>
<tr>
<td>(a, b, c \text{ (Å)})</td>
<td>8.854 (1), 14.840 (2), 18.005 (2)</td>
</tr>
</tbody>
</table>
Synthesis of Sulphonamido-Based Phosphorus Ligands and their Coordination to Nickel

<table>
<thead>
<tr>
<th>$V$ (Å³)</th>
<th>2365.7 (5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Z$</td>
<td>4</td>
</tr>
<tr>
<td>Radiation type</td>
<td>Mo Kα</td>
</tr>
<tr>
<td>m (mm⁻¹)</td>
<td>0.25</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>$0.43 \times 0.26 \times 0.21$</td>
</tr>
</tbody>
</table>

Data collection

<table>
<thead>
<tr>
<th>Diffractometer</th>
<th>Xcalibur, Atlas, Gemini ultra diffractometer</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{\text{min}}, T_{\text{max}}$</td>
<td>0.864, 0.924</td>
</tr>
<tr>
<td>No. of measured, independent and observed $</td>
<td>I &gt; 2.0\sigma(I)$ reflections</td>
</tr>
<tr>
<td>$R_{\text{int}}$</td>
<td>0.047</td>
</tr>
<tr>
<td>$(\sin \theta/\lambda)_{\text{max}}$ (Å⁻¹)</td>
<td>0.693</td>
</tr>
</tbody>
</table>

Refinement

| $R[F^2 > 2\sigma(F^2)], wR(F^2), S$ | 0.043, 0.080, 0.99 |
| No. of reflections | 5692 |
| No. of parameters | 273 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta^>_\text{max}, \Delta^>_\text{min}$ (e Å⁻³) | 0.44, -0.54 |
| Absolute structure | Flack (1983), 3610 Friedel-pairs |
| Absolute structure parameter | 0.05 (9) |

Ligand 11

Commerially available trifluoromethyl sulphonamide (5.62 g, 37.70 mmol, 1.00 eq.) was placed in a 100 mL Schlenk. The powder was suspended in toluene (3 mL), stirred for 5 min and evaporated under vacuum. This operation was repeated twice (co-evaporation). Then, the sulphonamide was dissolved in dry THF (40 mL). Distilled chlorodiisopropylphosphine (6.00 mL, 37.70 mmol, 1.00 eq.) was added to the solution leading to a slightly blurred solution). To this solution was added dropwise triethylamine (13.10 mL, 98.30 mmol, 2.60 eq.) leading to a white precipitate. After stirring the suspension for 20 min at room temperature, unlocked $^{31}\text{P}$ NMR showed complete conversion of the chlorophosphine to a singlet at 40 ppm. The suspension was then filtered under argon atmosphere and the resulting clear solution was evaporated leading to a white powder (9.20 g, isolated yield: 92%). Crystals were grown from slow vapour diffusion of pentane in a toluene/
dichloromethane solution of the ligand. The NMR analysis of the product were in accordance with the literature. The NMR analysis of the product were in accordance with the literature. 

\[ \text{1}^3\text{P}\{^1\text{H}\} \text{ NMR (121 MHz, CDCl}_3, 300 K): \delta (\text{ppm}): 42.32 (s); \]

\[ \text{3}^1\text{H} \text{ NMR (300 MHz, CDCl}_3, 300 K): \delta (\text{ppm}): 42.32 (\text{d}, ^1\text{J}_{\text{PH}} = 451.7 \text{ Hz}); \]

\[ \text{1}^3\text{P NMR (121 MHz, CDCl}_3, 300 K): \delta (\text{ppm}): 36.5 (\text{dd}, ^1\text{J}_{\text{PH}} = 443.8 \text{ Hz}, ^2\text{J}_{\text{PH}} = 28.9 \text{ Hz}, ^3\text{J}_{\text{PH}} = 9.5 \text{ Hz}); \]

\[ \text{1}^3\text{H} \text{ NMR (300 MHz, CDCl}_3, 300 K): \delta (\text{ppm}): 1.36 (\text{d}, ^1\text{J}_{\text{HP}} = 17.3 \text{ Hz}, \text{CH}_3\text{Bu}, 18 \text{H}); 6.13 (\text{d}, ^1\text{J}_{\text{HP}} = 441.3 \text{ Hz}, \text{PH}, 1 \text{H}); \]

\[ \text{1}^9\text{F} \text{ NMR (282 MHz, CDCl}_3, 300 K): \delta (\text{ppm}): 78.76 (s). \]

Ligand 17

Commercially available 4-butylbenzene-1-sulphonamide (2.00 g, 9.37 mmol, 1.00 eq.) was dissolved in dry triethylamine (10 mL, 71.77 mmol, 7.70 eq.) and THF (2 mL). Distilled chloroditerbutylphosphine (1.78 mL, 9.37 mmol, 1.00 eq.) was added dropwise under strong magnetic stirring at room temperature. The mixture was then heated at 60°C for 3 days until the conversion reached a
plateau at 84% according to NMR. The suspension was then filtered under argon atmosphere and the resulting clear solution was evaporated to a white solid. The solid was suspended in diethyl ether (10 mL) causing a solid to crash out. This solid was further washed with diethyl ether (4 x 20 mL) and dried under vacuum to yield a white powder (660 mg, isolated yield: 20%). The low yield may be explained by partial solubility of the product in diethyl ether. Using pentane instead of diethyl ether may increase yield. \(^{31}\)P \(\{^1\}H\) NMR (121 MHz, tol-\(d_8\), 300 K): \(\delta\) (ppm): 42.23 (s); \(^{31}\)P NMR (121 MHz, tol-\(d_8\), 300 K): \(\delta\) (ppm): 42.23 (dm, \(J_{PH} = 432.5\) Hz, \(J_{PH} = 16.4\) Hz); \(^1\)H NMR (300 MHz, tol-\(d_8\), 300K): \(\delta\) (ppm): 0.86 (t, \(J_{HH} = 7.3\) Hz, -CH\(_2\)-CH\(_3\)); 0.97 (d, \(J = 16.3\) Hz, -CH\(_3\)-buta, 1H); 1.21 (qd, \(J_{HH} = 7.8\) Hz, -CH\(_2\)-CH\(_2\)-, 2H); 1.42 (m, -CH\(_2\)-CH\(_2\)-CH\(_3\), 2H); 2.40 (t, \(J_{HH} = 7.8\) Hz, -CH\(_2\)-Ar, 2H); 6.09 (d, \(J_{HP} = 435.5\) Hz, PH, 1H); 6.99 (d, \(J_{HH} = 8.2\) Hz, CH\(_2\)-Ar, 2H); 8.08 (d, \(J_{HH} = 8.2\) Hz, CH\(_2\)-Ar, 2H); \(^{13}\)C NMR (75 MHz, tol-\(d_8\), 300K): \(\delta\) (ppm): 11.14 (-CH\(_2\)-CH\(_3\)); 22.65 (-CH\(_2\)-CH\(_3\)); 26.05 (d, \(J_{CP} = 1.6\) Hz, -CH\(_3\)-buta); 33.39 (C\(^\text{iv}_{-}\text{buta}\)); 33.68 (-CH\(_2\)-CH\(_2\)-CH\(_3\)); 34.18 (C\(^\text{iv}_{\text{buta}}\)); 35.68 (-CH\(_2\)-Ar); 126.49 (CH\(_2\)-Ar, 2C); 128.27 (CH\(_2\)-Ar, 2C); 144.97 (C\(^{\text{iv}}_{\text{C-buta}}\)); 144.55 (C\(^{\text{iv}}_{\text{C-SO}_2}\)).

**Ligand 19**

Commercially available trifluoromethyl sulphonamide (1.01 g, 6.79 mmol, 1.00 eq.) was placed in a 100 mL Schlenk and suspended THF (20 mL) and triethylamine (2.50 mL, 17.60 mmol, 2.60 eq.). Chlorodi(cyclohexyl)phosphine (1.5 mL, 6.79 mmol, 1 eq.) was added dropwise and under strong stirring to the sulphonamide at RT. After stirring the mixture for 10 min at RT, all the chlorophosphine had reacted to give the product along with 12% of iminobisphosphine. The suspension was then filtered under argon atmosphere and the resulting clear solution was evaporated leading to a white powder. The powder was washed with pentane (3 x 10 mL). Finally the product was dissolved in a minimum of dichloromethane and precipitated with pentane. The solid was dried under vacuum to give a white powder (1.3 g, isolated yield: 55%). \(^{31}\)P \(\{^1\}H\) NMR (121 MHz, CD\(_2\)Cl\(_2\), 300 K): \(\delta\) (ppm): 35.33 (s); \(^{31}\)P NMR (121 MHz, CD\(_2\)Cl\(_2\), 300 K): \(\delta\) (ppm): 50.61 (d, \(J_{PH} = 450.9\) Hz); \(^1\)H NMR (300 MHz, CD\(_2\)Cl\(_2\), 300K): \(\delta\) (ppm): 1.2-2.2 (m, Cy, 22H); 3.05 (dd, \(J_{HP} = 14.9\) Hz & \(J_{HH} = 7.4\) Hz, P-CH, 2H); 6.30 (dt, \(J_{HP} = 451.4\) Hz & \(J_{HH} = 3.9\) Hz, PH, 1H). \(^{13}\)F NMR (282 MHz, CD\(_2\)Cl\(_2\), 300K): \(\delta\) (ppm): -79.22.

**Ligand 20**

Commercially available 4-butylbenzene-1-sulphonamide (834 mg, 4.00 mmol, 1.00 eq.) and triethylamine (571 \(\mu\)L, 4.10 mmol, 1.03 eq.) were dissolved in dry THF (20 mL) and commercial Chlorodicyclohexylphosphine (880 \(\mu\)L, 4.00 mmol, 1.00 eq.) was added dropwise under strong magnetic stirring at room temperature leading to a white precipitate. The mixture was stirred until no more chlorophosphine was seen by \(^{31}\)P NMR (20 h). The suspension was then filtered under argon atmosphere and the resulting clear solution was evaporated to sticky oil. Diethyl ether was added to the oil (10 mL) and the mixture stirred for 5 min at RT after which the solvent was evaporated. This operation was repeated twice leading to a white solid. Diethyl ether (10 mL) and pentane (10 mL) were added to the powder and the solvents were syringed out. The solid was washed again with pentane (2 x 10 mL) and dried under vacuum to give a white powder (isolated yield: 980 mg, 60%). \(^{31}\)P \(\{^1\}H\) NMR (121 MHz, CD\(_2\)Cl\(_2\), 300 K): \(\delta\) (ppm): 28.84 (s); \(^{31}\)P NMR (121 MHz, CD\(_2\)Cl\(_2\), 300 K): \(\delta\) (ppm): 28.84 (s, \(J_{PH} = 433.0\) Hz); \(^1\)H NMR (300 MHz, CD\(_2\)Cl\(_2\), 300K): \(\delta\) (ppm): 0.91 (t, \(J_{HH} = 7.4\) Hz, -CH\(_3\), 3H); 1.1-2.1 (m, signals of the Cy and the -CH\(_2\)-CH\(_2\)-CH\(_3\), 22H); 2.64 (t, \(J_{HH} = 7.5\) Hz, Ar-CH\(_2\)-, 2H); 6.28 (dt, \(J_{HP} = 441.4\) Hz, \(J_{PH} = 3.7\) Hz, PH, 1H); 7.23 (d, \(J_{HH} = 8\) Hz, CH\(_2\)-Ar, 2H); 7.72 (d, \(J_{HH} = 8.1\) Hz, CH\(_2\)-Ar, 2H).

**Ligand 21** (according to the procedure of Woolins et al.\(^{30,31}\))
Benzamide (3.00 g, 24.76 mmol, 1.00 eq.) and 4-DMAP (187 mg, 1.55 mmol, 0.06 eq.) were placed in a Schlenk and degassed. To this Schlenk were added THF (90 mL) and triethylamine (6.80 mL, 49.20 mmol, 2.00 eq.). To this solution was added dropwise chlorodiphenylphosphine (4.44 mL, 24.76 mmol, 1 eq.) under strong magnetic stirring, causing a white solid to form. Immediately after addition, the crude product consisted only of iminobisphosphine at -16.3 (d, \( J_{PP} = 280 \) Hz) and 23.8 (d, \( J_{PP} = 280 \) Hz). The mixture was refluxed for 16 h which led to improved conversion to the monosubstituted product (85% of crude by \( ^{31}P \) NMR). The mixture was filtered under inert argon atmosphere and the filtrate evaporated to a white viscous powder. The powder was washed with diethyl ether (2 x 40 mL) and dried under vacuum to give a white solid. The solid was crystallised from dichloromethane / diethyl ether to give white needles. (Isolate yield 2.48 g, 33 %).

**Ligand 22** (According to the procedure of Braunstein and co-workers.\[^{15,32}\])

![Ligand 22](image)

N(trimethylsilyl)-acetamide (1.46 g, 11.10 mmol, 1.00 eq.) was dissolved in toluene (20 mL). To this solution was added chlorodiphenylphosphine (1.00 mL, 6.28 mmol, 1.00 eq.). The mixture was then heated at 60°C for 1 h under dynamic bubbling of argon to remove TMSCl formed in the reaction mixture and an important precipitate formed. The solid that precipitated was filtered and washed with pentane (3 x 10 mL) and dried under vacuum. (Isolated yield: 2.2 g, 82 %). \( ^{31}P \) \{\(^1H\)\} NMR (121 MHz, CD\(_2\)Cl\(_2\), 300 K): \( \delta(\text{ppm}) \): 22.8 (s, NH form, 68 %); 30.3 (s, OH form, 32 %). \(^1H\) NMR (300 MHz, C\(_6\)D\(_6\), 300K): \( \delta(\text{ppm}) \): 2.13 (s, -CH\(_3\), 3H); 2.31 (s, 1H); 6.04 (br s, 1H); 7.43 (m, CH\(_{Ar}\), 10H).

**Ligand 23** (According to the procedure of Braunstein and co-workers.\[^{15,32}\])

![Ligand 23](image)

N(trimethylsilyl)-acetamide (824 mg, 6.28 mmol, 1.00 eq.) was dissolved in toluene (20 mL). To this solution was added chlorodiisopropylphosphine (1.00 mL, 6.28 mmol, 1.00 eq.) dropwise. The mixture was then heated at 70°C for 2 h under dynamic bubbling of argon to remove TMSCI formed in the reaction mixture. The solvent was removed to give a colourless solid in a quantitative yield. \( ^{31}P \) \{\(^1H\)\} NMR (121 MHz, C\(_6\)D\(_6\), 300 K): \( \delta(\text{ppm}) \): 49.7 (s, NH form, 14 %); 56.14 (s, OH form, 86 %). Only the signals of the major tautomer were reported. \(^1H\) NMR (300 MHz, C\(_6\)D\(_6\), 300K): \( \delta(\text{ppm}) \): 0.85 (dd, \( J_{HH} = 16.2 \) Hz, \( J_{HP} = 7.0 \) Hz, -CH\(_3\) \(_{iPr}\), 6H); 0.94 (dd, \( J_{HH} = 11.0 \) Hz, \( J_{HP} = 6.9 \) Hz, -CH\(_3\) \(_{iPr}\), 6H); 1.58 (br s, -CH\(_3\) \(_{iPr}\), 2H); 2.16 (d, \( J_{HP} = 2.4 \) Hz, H\(_3\)C=O, 3H); 4.86 (weak signal tautomer OH, OH); 7.38 (br s, NH, 1H).

**Ligand 24** (adapted from Woolins et al.\[^{30,31}\])

![Ligand 24](image)

Trifluoroacetamide (2.80 g, 24.70 mmol, 1.00 eq.) and 4-(dimethylamino)pyridine (DMAP, 187 mg, 1.55 mmol, 0.006 eq.) were placed in a 100 mL Schlenk. The powders were co-evaporated twice with toluene to remove residual water (2 x 3 mL). The powders were then dissolved in THF (25 mL) and triethylamine, (3.78 mL, 27.20 mmol, 1.10 eq.) followed by the dropwise addition of diisopropylchlorophosphine (3.77 g, 3.93 mL, 24.70 mmol, 1.00 eq.) under strong magnetic stirring, leading to a white precipitate. Unlocked \( ^{31}P \) NMR, measured immediately after addition showed the formation of 59% of
iminosobisphosphine and 41 % of amidophosphine. The mixture was refluxed for 16h which led to 85 % of amidophosphine in the crude. The suspension was then filtered under argon atmosphere and the resulting clear solution was evaporated leading to an orange solid. The solid was dissolved in diethyl ether (20 mL) and precipitated with pentane (40 mL). The solvents were syringed out and the solid was washed with pentane (3 x 10 mL) and dried under vacuum to give a yellowish powder (1.5 g, isolated yield: 26%). ^{31}P$ \{^{1}H\}$ NMR (121 MHz, CD$_{2}$Cl$_{2}$, 300 K): δ (ppm): 40.1 (s, PH tautomer, 31%P); 56.9 (s, NH tautomer, 69%P); ^{31}P NMR (121 MHz, CD$_{2}$Cl$_{2}$, 300 K): δ (ppm): 40.1 (d, PH tautomer, $^{1}J_{PH} = 447.2$ Hz); 56.9 (s, NH tautomer); ^{1}H NMR (300 MHz, CD$_{2}$Cl$_{2}$, 300K): δ (ppm): 1.0-1.2 (m, CH$_{3}$-iPr, NH tautomer, 12H); 1.22-1.44 (m, CH$_{3}$-iPr, PH tautomer, 12H); 1.96 (sept d, $^{3}J_{HH} = 5.3$ Hz, $^{2}J_{HP} = 1.7$ Hz, CH$_{3}$-iPr, NH tautomer, 2H); 2.40 (sept, $^{3}J_{HH} = 3.2$ Hz, CH$_{3}$-iPr, PH tautomer, 2H); 6.05 (br s, NH, 1H); 6.46 (dt, $^{1}J_{HP} = 440$ Hz, $^{3}J_{HH} = 3.8$ Hz, PH, 1H). Signals of the residue from 4-DMAP at 3.2 ppm (-CH$_{3}$, 6H), 6.7 and 8.2 ppm.

5.3 Synthesis of sulphonyl-iminophosphoranes

**Sulphonyl iminophosphorane 27**

Tosylamide (856 mg, 5.00 mmol, 1.00 eq.) and triphenylphosphine (1.31 g, 5.00 mmol, 1.00 eq.) were placed in a 50 mL Schlenk with dry THF (10 mL). The solution was cooled to 0°C and diethylazodicarboxylate (solution at 45 mol% in toluene, 1.43 mL, 5.00 mmol, 1.00 eq.) was added dropwise to the solution. The orange DEAD solution immediately turned colourless in solution. After addition, the mixture was left to react at room temperature for 16h. A white precipitate formed which was filtered and washed with diethyl ether (2 x 5 mL) and dried under vacuum. The product was conforming to the literature, isolated yield: 790 mg, 36%.

**Sulphonyl iminophosphorane 28**

4-n-butyl phenyl sulphonamide (1.07 mg, 5.00 mmol, 1.00 eq.) and triphenylphosphine (1.31 g, 5.00 mmol, 1.00 eq.) were placed in a 50 mL Schlenk with dry THF (10 mL). The solution was cooled to 0°C and diethylazodicarboxylate (solution at 45 mol% in toluene, 1.43 mL, 5.00 mmol, 1.00 eq.) was added dropwise to the solution. The orange DEAD solution immediately turned colourless in solution. After addition, the mixture was left to react at room temperature for 16h. A white precipitate formed which was filtered and washed with diethyl ether (2 x 5 mL) and dried under vacuum. The product contained traces of carbamate from the DEAD. It was recrystallised from hot ethanol to give colourless crystals (isolated yield: 1.06 g, 45%). ^{31}P$ \{^{1}H\}$ NMR (121 MHz, CDCl$_{3}$, 300K): δ(ppm): 14.46 (s); ^{31}P NMR (121 MHz, CDCl$_{3}$, 300K): δ(ppm): 14.46 (br s); ^{1}H NMR (300 MHz, CDCl$_{3}$, 300K): δ(ppm): 2.29 (s, -CH$_{3}$, 3H); 7.01 (d, $^{3}J_{HH} = 8.6$ Hz, H$_{Ar}$, 2H), 7.36-7.62 (m, CH$_{Ar}$, 8H); 7.52-7.62 (m, H$_{Ar}$, 3H); 7.67-7.86 (m, CH$_{Ar}$, 6H).

**Sulphonyl iminophosphorane 29**

Trifluoromethane sulphonamide (746 mg, 5 mmol, 1 eq.) and triphenylphosphine (1.31 g, 5.00 mmol, 1.00 eq.) were placed in a 50 mL Schlenk with dry THF (10 mL). The solution was cooled to 0°C and diethylazodicarboxylate (solution at 45 mol% in toluene, 1.43 mL, 5 mmol,
(1 eq.) was added dropwise to the solution. The orange DEAD solution immediately turned colourless in solution. After addition, the mixture was left to react at room temperature for 16h. A white precipitate formed which was filtered and washed with diethyl ether (2 x 5 mL) and dried under vacuum. The product was recrystallised from ethanol / dichloromethane to give colourless crystals (isolated yield: 765 mg, 39%). $^3$P{$^1$H} NMR (121 MHz, CDCl$_3$) $\delta$(ppm) = 21.05 (s); $^3$P NMR (121 MHz, CDCl$_3$, 300K): $\delta$: 21.05 (br s); $^1$H NMR (300 MHz, CDCl$_3$, 300K): $\delta$(ppm): 7.38-7.52 (m, H$_{Ar}$, 6H); 7.52-7.62 (m, H$_{Ar}$, 3H); 7.67-7.82 (m, H$_{Ar}$, 6H).

Sulphonyl iminophosphorane 30

Trifluoromethane sulphonamide (746 mg, 5.00 mmol, 1.00 eq.) and tricyclohexylphosphine (1.40 g, 5.00 mmol, 1.00 eq.) were placed in a 50 mL Schlenk with dry THF (10 mL). The solution was cooled to 0°C and diethylazodicarboxylate (solution at 45 mol% in toluene, 1.43 mL, 5.00 mmol, 1.00 eq.) was added dropwise to the solution. The orange DEAD solution immediately turned colourless in solution. After addition, the mixture was left to react at room temperature for 16h. A white precipitate formed which was filtered and washed with diethyl ether (2 x 5 mL) and dried under vacuum. The product was recrystallised from ethanol / dichloromethane to give colourless crystals (isolated yield: 728 mg, 34%). $^3$P{$^1$H} NMR (121 MHz, CDCl$_3$, 300K): $\delta$(ppm): 44.40 (s); $^3$P NMR (121 MHz, CDCl$_3$, 300K): $\delta$: 44.39 (br s); $^1$H NMR (300 MHz, CDCl$_3$, 300K): $\delta$(ppm): 1.16-1.40 (m, Cy, 9H); 1.42-1.64 (m, Cy, 6H); 1.66-1.82 (m, Cy, 3H); 1.82-2.04 (m, Cy, 12H); 2.24 (qt, $^2$J$_{HP}$ = 12.2 Hz and $^3$J$_{HH}$ = 2.8 Hz, Cy, 3H), $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$(ppm) = -79.05.

5.4 Synthesis of complexes

Complex 25

METAMORPhos ligand 3 (123 mg, 0.31 mmol, 2.20 eq.) and NiCl$_2$(DME) (31 mg, 0.14 mmol, 1.00 eq.) were placed in a Schlenk with toluene (3 mL). The mixture was stirred for 16h at 60°C to give a dark red insoluble solid. The toluene was syringed out and the solid washed again with toluene to get rid of the ligand excess. The solid was dried under vacuum and dissolved in dichloromethane (10 mL). This solution was filtered through a syringe disc filter to remove traces of unreacted NiCl$_2$ (pore diameter 0.15 μm) and the resulting liquid evaporated to give a red powder in almost quantitative yield. We were not able to analyse properly this complex by NMR, since only br signals attributed to the free ligand could be observed in $^3$P and $^1$H NMR.

Complex 26

METAMORPhos ligand 11 (82 mg, 0.31 mmol, 2.20 eq.) and triethylamine (100 μL, 0.74 mmol, 5.30 eq.) were dissolved in a Schlenk with toluene (2 mL). In another Schlenk NiBr$_2$(DME) (43 mg, 0.14 mmol, 1.00 eq.) was suspended in toluene (2 mL). The ligand mixture was added to the nickel suspension by cannula under strong stirring leading to an orange solution which progressively darkened to brown. The solution was heated at 60°C overnight and the solvents were evaporated to give a bright red powder. Crystals were obtained from slow vapour diffusion of.
pentane in a toluene solution of the complex. NMR analyses were realised on the crude product with equimolar quantity of NEt₃·HBr. $^{31}$P NMR (121 MHz, CD₂Cl₂, 300K): δ(ppm): 88.9 (br s) and 106.57 (br d, $^{2}J_{PP}$ ca. 75 Hz).

### 5.5 Procedure for unlocked NMR

As a general procedure, oven-dried NMR tubes were placed in a NMR tube holder connected to the Schlenk line, and purged. Then a portion of the reaction mixture was transferred under circulation of argon to the NMR tube via a cannula (or with a glass pipette); the tube was then sealed and analysed by NMR.

### 5.6 Procedure for ligand titration

The ligand was dissolved in CDCl₃ (5 mL, 0.1 M) in a Schlenk. Triethylamine was added to this Schlenk by small portions (approx. 0.05 mmol). The mixture was shaken and a portion was transferred to a NMR tube under argon. Both $^{31}$P and $^1$H NMR were recorded and the content of the tube was replaced in the Schlenk. The operation was repeated several times with different concentrations of base. The exact molar ratio of base vs. ligand was determined from the relative integration of the CH₃ signals of the triethylamine vs. the CH₃ signals of the ligand.

### 5.7 Procedure for catalytic experiment

The reactor of 50 mL was dried under vacuum at 100°C for 2 hours and then filled at room temperature with ethylene at 1.4 bar. Catalyst solutions were injected through a septum (10 µmol in 8mL of toluene) and methylaluminoxane (2mL, 10% in toluene, 300 eq.) were injected. The temperature and pressure were set to 45°C and 35 bars. The reaction started with stirring and ethylene uptake and temperature were monitored. The reaction was stopped after 1 h. The reactor was cooled down to room temperature and the gas phase evacuated under stirring. The liquid was neutralised with aqueous H₂SO₄ (20%) and the organic phase was analysed by GC.

### 6 References


85


[29] F. G. Terrade, Nature Inspired Catalytic Systems Using Sulfonamido-Phosphorus Based Complexes, University of Amsterdam, **2014**.

