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

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Chapter 5

Zwitterionic and Nickel Hydride Complexes based on METAMORPhos Ligand: a Parameter Study on their Formation
1 Introduction

Single component and well-defined nickel catalysts are of particular interest for olefins oligomerisation as they do not require an additional activator. These systems greatly simplify the operability of the catalytic reactions. Besides they allow identifying the reaction intermediates (active species). One of the prominent examples is the neutral (PO)-coordinated nickel aryl phosphine complex 1 that affords linear alpha olefins (LAO) and allowed for the development of the SHOP process in the late 70s.[1-5] This single system was extensively reviewed and key structural factors such as phosphorus substituents, ligands and chelate backbone have been identified and linked to performances in oligomerisation reaction.[6-8] In Chapter 4, we disclosed a new class of single component nickel catalysts based on structure 2. These complexes, stabilised by hydrogen bonding, readily oligomerise ethylene with high activity (24 kg_{oligo}/(g_{Ni}·h)) but most importantly possess unprecedented selectivity features. A simple change in phosphorus substituents allows a shift between a broad LAO distribution, (comparable to SHOP) to a more interesting selective 1-butene formation.

![Diagram](image)

We sought to understand the structural parameters allowing the formation of such architectures through self-assembly. We studied the combination of METAMORPhos ligands (Figure 1) with aminophosphines as well as non-functionalised phosphines on the complex formation and stability. We observed the formation of supramolecular assemblies, zwitterionic and hydride complexes. The influence of steric and electronic parameters of both ligands applied on the complex formation is described and a mechanism that accounts for their formation is suggested.
2 Synthesis of the complexes

2.1 Reactivity of the system METAMORPhos / aminophosphine with Ni(COD)$_2$

2.1.1 Access to zwitterionic bis(METAMORPhos) nickel complexes

In the previous Chapter we reported that METAMORPhos ligand 3 or 5 reacted with Ni(COD)$_2$ and the aminophosphine (iPr-NH-PPh$_2$) leading to the corresponding supramolecular complexes 11 and 12. The selective formation of the heterocomplex was interesting, and proposed to be (partly) driven by hydrogen bond formation. Complex formation from two monodentate ligands and a metal, leads (in principle) to the statistical combinations of 2 homocomplexes and the heterocomplex in a 2/3 and 1/3 ratio respectively.

To understand the formation of these complexes and potentially broaden the scope of available single component nickel complexes, we investigated the synthesis of METAMORPhos-based homocomplexes by reacting METAMORPhos ligand (2 eq.) with Ni(COD)$_2$ (1 eq.) according to Scheme 1.
Scheme 1. Reaction of two METAMORPhos ligands with Ni(COD)$_2$ aiming to form bis(METAMORPhos) nickel zwitterionic cationic supramolecular complexes

When two equivalents of METAMORPhos 3 (PH tautomer) were added to a solution of Ni(COD)$_2$ no reaction was observed and therefore the synthesis of the corresponding homocomplex was not possible. In contrast, a quick colour change from yellow to dark greenish was observed when two equivalents of ligand 4 were added to a solution of Ni(COD)$_2$. The complex 13 that formed had a broad peak appearing in the $^{31}$P NMR spectrum at $\delta$: 55 ppm. We suggest that the peak broadness is the result of signal overlap and fast intermolecular proton exchange at room temperature, leading to equivalent ligands at the NMR timescale. Decreasing the temperature should limit the rate of exchange of the proton between the two moieties and therefore should lead to splitting of this broad signal. Indeed, a slow decrease in the temperature (to -80°C) led to disappearance of the original broad signal in $^{31}$P NMR and the appearance of new broad signals at $\delta$(CD$_2$Cl$_2$): 57 and 30 ppm. These chemical shift values are close to those of a phosphine coordinated to nickel and of free ligand 4 respectively (see experimental part). Typical proton signals attributed to the allyl fragment were also observed for 13 and the ligand 4 NH signal at 5.81 ppm (C$_6$D$_6$) was shifted to 9.64 ppm (C$_6$D$_6$) in the complex, suggesting that a hydrogen-bond is present between the two ligand moieties. As a consequence complex 13 is likely to adopt a cis arrangement, as proposed in the structure of Scheme 2.

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1 The crude reaction mixture consisted of the product 13 at 55 ppm (80%) and the other product was a doublet system at $\delta$(ppm): 12 (d, $^2J_{PP} = 17.0$ Hz) and 53 (d, $^2J_{PP} = 17.0$ Hz) for 20% corresponding to the thermal degradation product (see experimental part for further details).
Scheme 2. Synthesis of bis METAMORPhos zwitterionic nickel complex 13 from METAMORPhos ligand 4 and Ni(COD)₂.

METAMORPhos 5 was not very reactive with Ni(COD)₂ but a broad signal observed in ³¹P NMR at 62 ppm suggests that the homocomplex had formed similarly to what observed for ligand 4. The peak broadness also suggests quick proton exchange at RT. Other products observed in ³¹P NMR probably correspond to the decomposition products of the homocomplex (37 and 61 ppm). Unfortunately the homocomplex could not be isolated.

Synthetic access to the heterocomplex (3,4) was also investigated with ligands 3 and 4. NMR analysis of the crude reaction mixture shows that it consists of a mixture of the heterocomplex (3,4), ligand 3 and the homocomplex (4,4) as concluding from broad signals around 90 ppm and 54 ppm. No product could however be isolated.

In summary, the reactivity of METAMORPhos + Ni(COD)₂ to form the homocomplexes depends on the tautomeric form of the ligand. METAMORPhos ligands under the PⅢ coordinating NH tautomer led to homocomplexes (4,4) and (5,5) while ligands under the PH tautomer are not reactive with Ni(COD)₂, whereas when combined with a proper co-ligand, they do form complexes. Therefore, the choice of METAMORPhos in the PH tautomer is a way to supress the formation of the homocomplexes and favour clean hetero-combinations. However a co-ligand (aminophosphine) is required to achieve complex formation. The choice of this co-ligand is crucial as clean formation of the heterocomplex (3,4), using 4 (NH tautomer) as co-ligand, was hampered by competitive side reactions leading to homocomplexes.
2.1.2 Diversification of the aminophosphines of the zwitterionic nickel complexes

The synthesis of homocomplexes, based on METAMORPhos ligands presented above, stresses the importance of the co-ligand properties to prevent the formation of homocomplexes. In order to have a clearer idea of the parameters that rule this selectivity, we studied the influence of several aminophosphine co-ligands (A-F presented in Figure 2) on the synthesis of supramolecular nickel complexes. For this study, METAMORPhos ligands 3, 4, 5 with different electronic contributions have been selected and the experimental conditions followed are presented in Scheme 3.

Nickel complexes will be abbreviated by Ni(X,Y) where X refers to the METAMORPhos under the anionic form and Y corresponds to the neutral co-ligand. In addition to this abbreviation, isolated complexes will be indexed with a number.

**Scheme 3.** General synthetic approach used for the preparation of zwitterionic complexes from METAMORPhos, aminophosphine and Ni(COD)$_2$.

**Figure 2.** Aminophosphine co-ligands A-F used in this study of general formula R$_1$-NH-P(R$_2$)$_2$; they are potentially H-donor moieties.

Using a similar procedure to the one affording Ni(3,B):11 and Ni(5,B):12, the heterocomplexes containing the co-ligand A Ni(3,A):14 and Ni(5,A):15 were formed quantitatively and isolated. The NMR spectra are very similar to those of complexes 11 and 12. Crystal structures were determined for 14 and 15 (see Figure 3 and Figure 4 respectively). The resemblance of both crystal structures with those of 11 and 12,
suggests that an increase of steric bulk on the nitrogen from \((n-Pr\) to \(iPr\)) had little influence on the geometry of the complex. The use of the very bulky aminophosphine \(F\) (\(tBu-NH-PPh_2\)) for the synthesis of \(\text{Ni}(3,F)\) led to a slow reaction and we could not observe clear complex formation by NMR. This suggests that a threshold exists above which too much steric hindrance at the \(R^3\) prevents the formation of supramolecular zwitterionic nickel complexes. Similarly, a decrease of the steric bulk on \(\text{METAMORPhos}\) phosphine \(\text{P}(\text{o-tolyl})_2\) to \(\text{PPh}_2\) led to the formation of complex \(\text{Ni}(4,B)\) in good yields (> 95%). This complex was sensitive to heat and could not be isolated in pure form. This suggests that bulky substituents on \(\text{METAMORPhos}\) phosphorus increase the stability of the heterocomplexes with respect to the homocomplex.

**Figure 3.** ORTEP plot (50% probability displacement ellipsoids) of complex 14. Hydrogen atoms have been omitted for clarity (except for NH moiety). Selected bond lengths (Å) and angles (°): Ni1-P1 2.221(2); Ni1-P2 2.197(2); N2-H2 0.869; N1--H2 2.074; O2--H2 3.033; P1-Ni1-P2 102.44(7).

**Figure 4.** ORTEP plot (50% probability displacement ellipsoids) of complex 15. Hydrogen atoms have been omitted for clarity (except for NH moiety). Selected bond lengths (Å) and angles (°): Ni1-P1 2.2173(9); Ni1-P2 2.2024(9); N2-H1 0.851; N1--H1 3.304; O--H1 2.373; P1-Ni1-P2 106.56(3).
Next, the use of aminophosphine C (Ph-NH-PPh₂) was explored. The phenyl group attached to the nitrogen reduces the electronic density of this aminophosphine at the nitrogen. Moreover, as C is unable to form a zwitterionic homocomplex with Ni(COD)₂ it should favour the formation of heterocomplexes to the same extent as co-ligand A and B with METAMORPhos 3 and 5. The synthesis of Ni(3,C), Ni(4,C), Ni(5,C) led indeed to the respective heterocomplexes in solution, however with limited conversion (up to 66% according to 31P NMR of the crude mixture). A competitive ligand coordination was observed for complex Ni(4,C), (similarly to complex Ni(4,3)) leading to the formation of the homocomplex Ni(4,4). This shows the importance of strong electron donating groups on the nitrogen of the aminophosphine co-ligands (such as A or B) to favour the selective formation of heterocomplexes.

Co-ligands A, B, C, F and 4 used so far, all have in common the -NH–PPh₂ group. Although very similar, a clear difference is noted in their reactivity. This suggests that the substitution at the nitrogen atom affects the H-bonding and probably also the electronic properties at the phosphorus atom. We sought to determine if increasing the electron density on the phosphorus by using directly attached substituents would also lead to the corresponding zwitterionic complexes as shown in Scheme 3. For this, we introduced P-alkyl substituted aminophosphine ligand D and E. The heterocomplex Ni(3,D) was observed (31P and 1H NMR) in solution but the presence of several other products in the crude mixture prevented its isolation. Attempts to form Ni(4,D) led to numerous products. Similarly the heterocomplex Ni(5,E) was observed in solution at very low conversion but could not be isolated. Increasing the electron density on the phosphorus by using directly attached substituents also led to the formation of the heterocomplexes but also by-products were observed in reaction mixtures that probably correspond to degradation products of the cationic complex. In comparison, co-ligands with a diphenyl substituted phosphorus (e.g. A and B) led to more stable nickel heterocomplexes.

In summary, the access to supramolecular zwitterionic heterocomplexes in the reaction of METAMORPhos + aminophosphine + Ni(COD)₂ depends on several parameters. The phosphorus atom at the co-ligand needs to be sufficiently electron-rich for stable coordination to the nickel atom to occur. This was realised by employing phenyl P-substituted aminophosphines having donating groups on the nitrogen. Moreover, hetero-complexes formed selectively when by themselves both ligand and co-ligand did not perform oxidative addition on Ni(COD)₂ and only a mixture of the two formed the desired complex. This was particularly the case for METAMORPhos in the PH tautomer and electron rich aminophosphines (see 11-15). In the case of reactive METAMORPhos (NH), it was important that the co-ligand...
was more electron-donating than METAMORPhos itself to favour pure hetero-combinations. By following this strategy 4 heterocomplexes and 1 homocomplex were synthesised in pure form. This class of complexes was not particularly stable because degradation in solution occurred already at 60°C. The overall stability depends mainly on the nature of the co-ligand. Co-ligands with bulky phosphine substituents such as tBu led to slow complex formation. An increase in the basicity of the phosphorus atom by using directly attached substituents led to complicated mixtures.

2.2 Reactivity of the system METAMORPhos / phosphine (or phosphite) with Ni(COD)$_2$

Aminophosphines and in particular diphenyl P-substituted analogues have been successfully used to selectively form stable zwitterionic heterocomplexes 11, 12, 14, 15. We wondered if other electron-rich ligands would function similarly. Non-functionalised phosphines (and phosphites) were introduced as co-ligands instead of aminophosphines with the aim to further diversify the properties of the complexes. METAMORPhos ligand 3 was selected for this study since it does not form the homocomplex Ni(3,3) by itself in the presence of Ni(COD)$_2$.

2.2.1 Trimethylphosphine (PMe$_3$) as co-ligand

Trimethylphosphine, a strongly electron donating phosphine with limited bulk, was first evaluated as co-ligand in the reaction of ligand 3 with Ni(COD)$_2$ at room temperature according to Scheme 4.

Scheme 4. General procedure used for the preparation of complexes based on different phosphines PR$_3$ and ligand 3.

Upon addition of trimethylphosphine to a mixture of ligand 3 and Ni(COD)$_2$ a clear brown colour developed and the solution slowly darkened upon stirring. When monitoring the reaction by unlocked $^{31}$P NMR, first the formation of a peak at -23 ppm was observed, which corresponds to Ni(PMe$_3$)$_4$ according to literature.$^{[9]}$ This signal, together with the one of METAMORPhos ligand 3, decreased upon time with the formation of two doublets at 87 ppm and -11 ppm, both having a coupling
constant of 31 Hz. The reaction was complete and neat already after 10 min as evidenced by $^{31}$P NMR.

The isolated product had typical features of previously reported zwitterionic supramolecular complexes: two phosphorus atoms with small $^2J_{pp}$ cis coupling and the allylic protons between 3.5 and 4.4 ppm in the $^1$H NMR spectrum (see Scheme 5 and Figure 5). Further NMR characterisation and proper elemental analysis confirmed the formation of complex 16. The absence of a proton donor moiety in the co-ligand (PMe$_3$) proved that hydrogen bonding was not a crucial element for the formation of the hetero ligated complex.

Scheme 5. Synthesis of zwitterionic cationic complex 16 from METAMORPhos ligand 3, PMe$_3$ and Ni(COD)$_2$

Figure 5. $^{31}$P NMR (121 MHz, C$_6$D$_6$, 300K) spectrum (above) and $^1$H NMR (300 MHz, C$_6$D$_6$, 300K) spectrum (allyl region, below) for complex 16 ($\alpha$: central allylic proton, $\beta$ and $\beta'$: side allylic protons).
Crystals of complex 16 suitable for X-ray diffraction were grown by slow diffusion of pentane in a toluene solution of the complex. The corresponding ORTEP plot is presented in Figure 6. Zwitterionic complex 16 adopts a square planar environment around the metal (sum of angles = 360.7°), which was in line with the diamagnetic nature of this complex and its observation by NMR. Moreover, the solid-state arrangement for zwitterionic complex 16 was very similar to the supramolecular complexes 11-15 (similar angles and bond lengths). This means that replacing aminophosphines by phosphines also has limited effect on the complex geometry.

Figure 6. ORTEP plot (50% probability displacement ellipsoids) of complex 16. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ni1-P2 2.1889 (5); Ni1-P1 2.2127 (5); Ni1-C21 2.0825 (18); Ni1-C22 1.9744 (18); Ni1-C23 2.0864 (17); P1-N1 1.6592 (16); N1-S1 1.5313 (16); S1-O1 1.4482 (17); S1-O2 1.4492 (17); P2-Ni1-P1 100.34 (2); P1-N1-S1 133.88 (11)

By a similar approach we synthesised PMe₃-based zwitterionic complexes 16, 17, 18, 19, 20, 21, 22 based on METAMORPhos ligands 3, 4, 5, 7, 8, 9, 10. Their structures are presented in Figure 7. Complexes 16, 17 and 18 were synthesised on a larger scale and isolated for further analysis and catalytic experiments (see Chapter 6). The clean formation of hetero ligated complex was ensured thanks to the strong basicity and certainly the small size of PMe₃, which for instance prevented the formation of the homocombination 13 (Ni(4,4)), observed in absence of PMe₃ with ligand 4 and Ni(COD)₂.
Figure 7. Zwitterionic complexes based on PMe$_3$ isolated (16, 17, 18) or observed from the crude reaction mixture (19, 20, 21, 22) based on $^{31}$P NMR chemical shifts. Conditions: [METAMORPhos] = [PMe$_3$] = [Ni(COD)$_2$] = 50 mM in toluene, stirring 10 min at RT, almost quantitative reactions.

Crystals of complex 17 were grown by slow vapour diffusion of pentane in a toluene solution of the complex. The corresponding ORTEP plot is presented in Figure 8. According to the crystal structures, both zwitterionic complexes 16 (Figure 6) and 17 adopt a square planar environment around the metal (sum of angles = 360.67° for 16 and 360.03° for 17). Both are diamagnetic with similar characteristics. The P$_{\text{METAMORPhos}}$-Ni bond (P1-Ni1) bond was longer for complex 16 with P(iPr)$_2$ (Ni1-P1 2.2127 (5) Å) than that of complex 17 with PPh$_2$ (Ni1-P2 2.1929 (10) Å). The bite angle (P1-Ni-P2) for complex 16 was 100.34(2)° while the one for 17 is 102.15 (4)°, which is close to that of the supramolecular complex 11 with a value of 103.96(6)°.
The stability of these PMe₃-based complexes is excellent compared to the aminophosphine-based complexes described before as they did not show degradation at room temperature. Heating the complexes was necessary to observe degradation. Indeed, irreversible degradation of 17 started around 80°C in 1-octene (used to mimic ethylene) leading to a new species (quantitatively) as observed by ³¹P NMR at δ(tol-d₈): -40.67 (dd, J = 7.8 and 18.3 Hz), 73.95 (dd, J = 7.8 and 18.4 Hz) in which both phosphines are still coordinated to nickel. The very small coupling constant was similar to the degradation product of supramolecular complex 13 and probably indicates that the decomposition of the complex occurs by loss of the COD moiety.

2.2.1 Tricyclohexylphosphine (PCy₃) as co-ligand

Having studied the behaviour of 3 with PMe₃, we wondered if a diversification of the co-ligand was possible by using other phosphines. In order to have an overview at both sides of the steric range, we evaluated the very bulky PCy₃ (with similar electron donating properties) for this reaction to prepare an analogue of 16. Under similar conditions, the reaction mixture showed almost no conversion after 10 min at RT and only the signals of PCy₃ and ligand 3 were observed by ³¹P NMR at 10 ppm and 40 ppm respectively (Ni(PCy₃)₃ was not observed). After leaving this mixture to stir for 16 h, the colour had changed to brown and unlocked ³¹P (and ³¹P{¹H}) NMR indicated a new set of signals at 37 and 103 ppm with a multiplicity different from zwitterionic complexes (Figure 9). Each signal was a doublet of doublet with a large coupling of 236 Hz, consistent with two phosphorus atoms in a trans position with respect to each other. Next to this, two smaller couplings of 64 Hz and 77 Hz were
observed for the peaks at 37 and 103 ppm, respectively, which would correspond to a cis coupling. Heating the mixture at 60°C for two more hours led to full conversion towards complex 23. The reaction was faster by heating the mixture at 60°C for 3 h as depicted in Scheme 6.

Further characterisation by $^1$H NMR showed that the product contained a hydride, observed at $\delta$(C$_6$D$_6$): -26.8 ppm (dd, $^2$J$_{PH}$ = 64 Hz, $^2$J$_{PH}$ = 78 Hz) (see Figure 10). The similar coupling constant observed for this hydride and the phosphorus signals indicate that this constant corresponds to $^2$J$_{PH}$ coupling between the hydride and phosphines in cis position to nickel. Also the chemical shift for the P(iPr)$_2$ signal was significantly different in both complexes: while the phosphorus signal of P(iPr)$_2$ for zwitterionic complex 16 appears at 87.3 ppm, it is observed at 103.4 ppm for the hydride PO-chelated nickel complex 23. This shows that the change between a zwitterionic diphosphine complex and a PO chelated nickel hydride complex has a direct influence on the chemical shift of the phosphorus.

Scheme 6. Synthesis of hydride complex 23 from METAMORPhos ligand 3, PCy$_3$ and Ni(COD)$_2$.

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The observation of the $^2$J$_{PH}$ coupling in the $^{31}$P{H} NMR spectrum is explained by a limited range of proton decoupling set in routine experiments, which did not include the hydride signal in $^1$H NMR at $\delta$= -26.9 ppm. To decouple efficiently hydrides from $^{31}$P{H} experiments, the O2P frequency and the decoupling range should be modified accordingly.
Figure 9. $^{31}$P NMR (121 MHz, C$_6$D$_6$, 300K) spectrum for complex 23 (the signal at 40 ppm in $^{31}$P NMR corresponds to impurity of ligand 3).

Figure 10. $^1$H NMR (300 MHz, C$_6$D$_6$, 300K) spectrum (hydride region) for complex 23 evidencing the coupling of the hydride with two different phosphorus atoms in cis position.

Crystals suitable for diffraction were grown by slow diffusion of pentane in a toluene solution of complex 23 and the ORTEP plot of the solid state structure is presented in Figure 11. This complex confirms the presence of two phosphines in trans position with respect to one another as well as an hydride being in cis with respect to the phosphines.

The complex has a square planar geometry, as is evident from the sum of angles around nickel (360.0°). A major difference with zwitterionic complex 16 is the formation of a PO anionic chelate, resulting in a neutral complex. This also results in a clear N=S bond (S(1)-N(1) 1.5276(17) Å) and the two single bonds at N-P and S-O (2.2092(6) Å and 1.4867(14) Å respectively).
On the basis of chelated hydride 23, we investigated whether other hydride complexes could be synthesised. METAMORPhos ligands 3, 5, 6 and 7 were used in combination with PCy$_3$ and Ni(COD)$_2$; these combinations all led to the formation of hydride complexes (23, 24, 25 and 26 respectively). These hydrides were remarkably stable as no decomposition occurred in solution below a temperature of 60°C. METAMORPhos ligand 4 (NH tautomer), however, did not lead to the selective formation of the nickel hydride complex when reacted with a mixture of Ni(COD)$_2$ and PCy$_3$. The major product consisted of the homocomplex Ni(4,4) suggesting a competition between the formation of the homo and the heterocomplex. The nickel hydride complexes 23-26 were all diamagnetic and their chemdraw structures are displayed in Figure 12. Complexes 23 and 26 were isolated, whereas 24 and 25 were observed in solution (at high conversion). This extension shows again the potential of METAMORPhos ligands to generate stable hydrides, which are not common in the literature.\cite{10-23}

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**Figure 11.** ORTEP plot (50% probability displacement ellipsoids) of complex 23. Hydrogen atoms (excepted for the Ni-H) have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ni(1)-P(11) 2.1496(6); Ni(1)-P(21) 2.2092(6); Ni(1)-O(11) 1.9953(13); S(1)-O(11) 1.4867(14); S(1)-O(21) 1.4333(15); S(1)-N(1) 1.5276(17); P(11)-N(1) 1.6918(17); Ni(1)-H(1) 1.42(2); P(11)-Ni(1)-P(21) 174.04(2); P(11)-Ni(1)-O(11) 87.76(4); P(21)-Ni(1)-O(11) 98.06(4); S(1)-N(1)-P(11) 115.49(10).

**Figure 12.** Nickel hydride complexes generated from the combination of METAMORPhos, Ni(COD)$_2$ and PCy$_3$.
2.2.2 Extension to other phosphines and phosphites

The structural change at the metal complex caused by a simple change between PMe₃ and PCy₃ (summarised in Scheme 7), led us to investigate the factors that ruled the complex formation. As the co-ligand was obviously the pivotal element, other types of phosphines or phosphites were selected and assessed as co-ligands for this transformation.

![Scheme 7](image)

Scheme 7. Reactivity of METAMORPhos ligand 3 with the system Ni(COD)₂ + PR₃ (R= Me, Cy): Either zwitterionic nickel complex 16 or a neutral nickel hydride complex 23 is formed depending on the phosphine co-ligand used.

The geometry of complexes in solution was determined by recording a ³¹P NMR spectrum of the crude reaction mixture (see Table 1). The results of these experiments (reactivity and chemical shifts from the crude) are summarised in Table 2.

Table 1. Determination grid to distinguish hydride from zwitterionic nickel complexes by ³¹P and ¹H NMR spectroscopy.

<table>
<thead>
<tr>
<th>Zwitterionic complex</th>
<th>Hydride complex</th>
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<tr>
<td>³¹P NMR (unlocked)</td>
<td>Two signals at x ppm and y ppm x and y are doublets with a coupling constant J≈30 Hz</td>
</tr>
<tr>
<td>¹H NMR</td>
<td>Two signals at x ppm and y ppm x and y are doublets of doublets with a great coupling constant (J≈230 Hz) and two smaller (J≈50-70 Hz)</td>
</tr>
<tr>
<td></td>
<td>2 or 3 signals of the allyl in the 4-5 ppm region (no signal &lt; 0 ppm)</td>
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<tr>
<td></td>
<td>One signal (dd) in the hydride region around -36 ppm</td>
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Table 2. Study of the reactivity of the system [ligand 3 + Ni(COD)2 + Phosphine (or phosphite)].

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<th>P(OMe)3</th>
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<th>PCy2H</th>
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<tbody>
<tr>
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<td>no reactivity</td>
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<td>zwiterionic c</td>
<td>zwiterionic c (broad)</td>
<td>zwiterionic c</td>
<td>broad signals</td>
</tr>
<tr>
<td>δ1, δ2 (ppm)</td>
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<td>128°</td>
<td>118°</td>
<td>136°</td>
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<tr>
<td>Electronic parameter (v_{CO}(\text{cm}^{-1}))</td>
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<td>2085.3</td>
<td>2064.1</td>
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<table>
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<th>PCy3</th>
<th>P(tBu)3</th>
<th>P(otolyl)3</th>
<th>P(Mes)3</th>
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<td>Tolman’s cone angle Θ (°)</td>
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<td>165°</td>
<td>194°</td>
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<tr>
<td>Electronic parameter (v_{CO}(\text{cm}^{-1}))</td>
<td>2067.3</td>
<td>2059.2</td>
<td>2066.4</td>
<td>2066.6</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Conditions: Ni(COD)2 (0.1 mmol, 1 eq.), METAMORPhos (0.1 mmol, 1 eq.) and phosphine (0.1 mmol, 1 eq.) are dissolved in toluene (2 mL) under stirring at RT. If no reaction, the mixture was heated at 60°C for at least 10 min. The chemical shifts are indicative and based on unlocked \(^{31}\text{P}\) NMR experiments.* iPrNHPPh2 and (iPr)2NPPh2 approximated from the calculated values of Me2NPPh2 that appear in the table. nd.: not determined, decomp.: decomposition to black nickel.

Similar to PMe3 and PCy3, the other phosphines (with different steric and electronic properties) reacted in solution with ligand 3 and Ni(COD)2 to generate either the hydride or the zwiterionic nickel complex in solution. The electron-poor P(OPh)3 in combination with ligand 3 and Ni(COD)2 led to two new signals at 131 ppm and 142 ppm, which according to the literature, correspond to Ni(P(OPh)3)4 and most certainly to Ni(P(OPh)3)4(COD).\(^{[9]}\) Ligand 3 did not react, even after 16 h at RT (signal at 40 ppm). Similarly, stirring a solution of P(OMe)3, 3 and Ni(COD)2 only led to the formation of Ni(P(OMe)3)4 as indicated by the presence of a peak at 164 ppm in the \(^{31}\text{P}\) NMR spectrum. Employing the electron rich ligand P(nBu)3 led to a clear brown solution and after 10 min the \(^{31}\text{P}\) NMR signal consisted quantitatively of two doublets at 86.2 and 11.4 ppm with a small coupling (\(2J_{PP} = 28\) Hz) in line with a zwiterionic complex. Using the PCy2H as co-ligand led also to a brown solution with two broad signals at 26.5 and 86.9 ppm, displaying a small coupling (\(2J_{PP} = 29\) Hz).

Changing from alkyl to arylphosphines led to two very broad signals, especially for PPh3Me which formed a zwiterionic species on the basis of the signal integration.
and chemical shifts but for which the coupling constant could not be measured. Triphenylphosphine led to low-intensity broad and undefined signals, which indicates either complex decomposition or the formation of paramagnetic species.

In comparison, P(iPr)$_3$, an alkyl phosphine with higher steric bulk, led to a clear orange solution and after 1 h no P(iPr)$_3$ nickel-based chelates were observed (only the signals of free P(iPr)$_3$ at 19.9 ppm and free METAMORPhos at 40 ppm were observed). After stirring for a longer period of time (16 h at RT) a typical pattern consisting of two doublets of doublets was observed by $^{31}$P NMR, which is characteristic of the hydride complex formation. In a similar way, the use of P(tBu)$_3$ led to a characteristic hydride pattern at 63 and 104 ppm, but heating (60°C) was required to improve the conversion as the reaction was very slow at RT. Neither the very bulky P(o-tolyl)$_3$ nor P(Mes)$_3$ reacted with 3. Indeed, the peaks of both free phosphines were monitored at -30 ppm and -36 ppm, respectively, without any signals of phosphine-nickel chelates. Instead, after a few minutes the reaction mixtures formed black particles, which indicates decomposition of Ni(COD)$_2$. In contrast, the bulky tribenzylphosphine was reactive. However the presence of multiple broad peaks that showed up in the $^{31}$P NMR after a reaction at 60°C revealed that several species had formed.

The Tolman’s cone angle $\Theta$ and Tolman electronic parameter $\nu_{CO}$ (cm$^{-1}$), relative to the phosphine co-ligand, were found to be suitable reactivity descriptors for this study.$^{[24]}$ Regardless of zwitterionic or hydride complexes, the reactivity of the systems was in line with the phosphine basicity represented by the Tolman electronic parameter $\nu_{CO}$. Within the range covered by this study (2056.1 cm$^{-1}$: P(tBu)$_3$ to 2085.3 cm$^{-1}$: P(OMe)$_3$), only phosphines with $\nu_{CO}$ between 2056.1 and 2068.9 cm$^{-1}$ reacted as shown on the Tolman plot, Figure 13. Less basic phosphites such as P(OMe)$_3$ or P(OPh)$_3$ coordinated to nickel without reactivity. Moderately basic phosphines such as PPh$_3$ reacted but led to complicated mixture and broad signals in $^{31}$P NMR and $^1$H NMR hinting at a paramagnetic nature of the formed complexes. Finally very basic and electron rich phosphines reacted quickly and led selectively to the isolation of nickel complexes (zwitterionic or hydride).

Among the reactive systems, steric bulk, as represented by Tolman’s cone angle $\Theta$, was in line with the type of complex formed (zwitterionic or hydride). Phosphines with low steric bulk (118° < $\Theta$ <143°), such as PMe$_3$, P(nBu)$_3$, PMePh$_2$ and PCy$_2$H led selectively to zwitterionic nickel complexes. Phosphines of intermediate size (136° < $\Theta$ <160°) such as PPh$_3$Me, PCy$_2$H, PPh$_3$ and iPr$_2$NPPh$_2$ did not lead to selective complex formation (some paramagnetic species were probably formed during the reaction). Finally, bulky phosphines (160° < $\Theta$ < 182°) generated
selectively nickel hydride complexes. There was no observable reaction with the most bulky phosphines $\text{P(\(\alpha\)-tolyl)$_{3}$}$ and $\text{P(Mes)$_{3}$}$ with $\Theta > 182$.

The aminophosphine co-ligands that led to supramolecular complexes 11-15 can also be ranked within the series of classical phosphines in terms of electronic and steric contribution. Indeed, aminophosphine $\text{iPr-NH-PPh$_{2}$}$ would be comparable to $\text{PPh$_{3}$}$ or to $(\text{iPr})_{2}-\text{N-PPh$_{2}$}$, which are the two closest intermediates for which the Tolman parameters can be calculated (see experimental part for the calculation).

Whereas aminophosphines ($\text{iPr-NH-PPh$_{2}$}$, $\text{nPr-NH-PPh$_{2}$}$ and $4-\text{nBuPh-SO$_{2}$-NH-PPh$_{2}$}$) led to the supramolecular H-bonded complexes 11-15, their electronic and steric equivalents, $\text{PPh$_{3}$}$ and $\text{Ph$_{2}$P-N(iPr)$_{2}$}$, did not lead to isolable complexes. This difference at iso electronic and iso steric suggests an important role for the supramolecular hydrogen bonding in complex stability for arylphosphine-containing co-ligands. This interaction could stabilise the cis configuration leading to zwitterionic complexes.

![Figure 13. Tolman plot of phosphines used in this study and their reactivity towards nickel complex formation with METAMORPhos 3.](image)

The formation of complexes with an allyl nickel moiety on a cyclooctadiene ring has been reported.$^{[9,25,26]}$ Indeed, this moiety was described to exist in two isomers that are in equilibrium: a $\eta^{3}$-allylic form and a 4-enyl form (paramagnetic). Even though the 4-enyl isomer was not detected in the METAMORPhos-based zwitterionic complexes, it could exist as a new type of complex next to zwitterionic and hydride complexes. This hypothesis would fit well with the change in the geometry of the
complex when increasing the Tolman angle. Also it would clarify the situation for the “intermediate” range (136°< Θ <160°) for which no clear formation of hydride or cationic was established due to undefined and broad signals. Therefore, this new species could well exist for co-ligands with a Tolman cone angle: 136°< Θ <160 according to Figure 14.

![Figure 14](image-url)

**Figure 14.** Influence of the Tolman cone angle for PR₃ on the complex geometry based on METAMORPhos 3.

In summary, aiming to create a small library of catalysts derived from complexes 11 and 12 and understanding the effect of the co-ligand on complex stability, we found that aminophosphines could be replaced by more classical phosphine ligands. The formation of zwitterionic complexes with phosphines, free of hydrogen-donors, showed that hydrogen-bonding is not the crucial factor for complex formation. However hydrogen bonding between a H-donor co-ligand and METAMORPhos (with H-acceptor properties) stabilises the complexes and allows their isolation as co-ligands having no H-donor properties lead to complex decomposition. Phosphines used as co-ligand must be sufficiently basic (electron-rich) for the formation of stable complexes to occur. Increasing the steric bulk of the phosphine at iso-basicity resulted in a severe geometry change from a zwitterionic diphosphine complex to a PO-chelated nickel hydride complex. This new class of hydride complexes based on METAMORPhos, is promising as it is a clear extension of the showcase SHOP-type complexes.

### 3 Mechanism of complex formation

#### 3.1 Are zwitterionic and nickel hydride complexes interconvertible?

Through ligand variation of the phosphine in the METAMORPhos / Ni(COD)₂ system (METAMORPhos, co-ligand, nickel = 1:1:1), two classes of complexes with different geometries were obtained via identical synthetic procedure: those with a zwitterionic structure and those containing a metal hydride. We set out to investigate if these two complexes were interconvertible.
Attempts to convert zwitterionic complexes by thermal cleavage of the COD, did not lead to formation of the metal hydride species but led instead to several decomposition products. However, the addition of a five-fold excess of PCy$_3$ to the supramolecular zwitterionic nickel complex 11 (1 eq.) at 60°C in toluene-$d_8$ led to the emergence of two doublets of doublets in the $^{31}$P NMR spectrum at $\delta$(tol-$d_8$, ppm): 36.6 (dd, $^2J_{PP} = 235$ Hz, $^2J_{PH} = 64$ Hz) and 103.0 (dd, $^2J_{PP} = 230$ Hz, $^2J_{PH} = 74$ Hz). Furthermore, in the $^1$H NMR spectrum, a hydride signal was clearly observable at $\delta$(tol-$d_8$): -26.8 ppm alongside with the characteristic signals of unbound 1,3-COD (already reported in Figure 20). All these signals corresponded to those measured for hydride 23 and proved that zwitterionic complex 11 in presence of PCy$_3$ rearranges to the hydride complex 23 by loss of 1,3-COD according to Scheme 8. This experiment proved that the zwitterionic and hydride complexes are two closely-related structures and that the steric bulk of the phosphine co-ligand determines which of the two classes of compounds is formed.

**Scheme 8.** Conversion of zwitterionic cationic complex 11 to hydride 23 mediated by PCy$_3$

We suggest that the formation of 23, starting from 11 involves first the competitive coordination of tricyclohexylphosphine and aminophosphine to the metal centre (by displacement of the aminophosphine). This first step is likely to be directed towards the coordination of the more electron rich PCy$_3$ despite its steric bulk. Once the bulky phosphine is coordinated to nickel, it is likely that it destabilises the allyl moiety to form the enyl (mentioned in Figure 14). In a second step 1,3-COD is released by $\beta$-H elimination to form the hydride. We believe that steric bulk is the main driver of this reaction provided that the phosphine basicity is sufficient (Figure 13). To discriminate the implication of steric bulk from electronics in the complex rearrangement, additional experiments should involve changing PCy$_3$ in Scheme 8 by PMe$_3$ (same basicity, different steric bulk) or P(o-tolyl)$_3$ (same steric bulk, different basicity) and see if the corresponding hydride would form (which we do not expect).

To prove completely that zwitterionic and hydride species are interconvertible, we should also prove that the reverse pathway is possible (hydride to zwitterionic). The
insertion of a hydride into a diene is known, however, this was not investigated for the current system.\cite{9,25,26}

### 3.2 Role of the co-ligand in the mechanism

Developing an overall mechanism to account for the formation of both zwitterionic and hydride complexes formation is challenging. Indeed, it requires identifying which intermediate between the allyl and the hydride would form initially. The transformation of a zwitterionic complex to a non-charged complex appears more facile and is shown experimentally (with PCy$_3$ in Scheme 8). We propose a pathway in which the zwitterionic species forms first and then evolves to a hydride depending on the steric bulk of the co-ligand.

We have already reported in this Chapter that the phosphine (co-ligand) was compulsory for hetero-complexes formation (hydride or zwitterionic). Also, at the start of complex formation, we detected by NMR spectroscopy a peak corresponding to Ni(co-ligand)$_4$, of which the intensity was decreasing in time while complex formation was observed (this was especially clear for the co-ligand PMe$_3$). This is a strong indication that the co-ligand is important for the first step in the mechanism as it coordinates to the nickel centre.

To understand the different interactions between phosphine co-ligand, nickel and 1,5-COD, we synthesised the bright yellow model complex Ni(COD)(PPh$_3$)$_2$ according to the procedure of Maciejewski et al.\cite{27} Dissolved in C$_6$D$_6$, the complex shows in the $^{31}$P NMR spectrum two peaks at $\delta$(C$_6$D$_6$): 22.9 ppm (62 %) and 39.4 ppm (38 %) that we assigned to Ni(PPh$_3$)$_4$ and Ni(COD)(PPh$_3$)$_2$, respectively, according to literature.\cite{27–29} This equilibrium confirmed the occurrence of ligand fast exchange in solution (see Scheme 9).

\[
\text{Ni(COD)(PPh}_3)_2 \xrightleftharpoons{C_6D_6} \text{Ni(COD)}_2 + \text{Ni(PPh}_3)_4 + \text{COD}
\]

**Scheme 9.** Ligand exchange in a system Ni(COD)$_2$ ,PPh$_3$: equilibrium between Ni(COD)(PPh$_3$)$_2$ and Ni(PPh$_3$)$_4$ in C$_6$D$_6$.

Furthermore, upon addition of co-ligand B (iPr-NH-PPh$_2$) (2 eq.) to Ni(COD)$_2$ in $d_8$-toluene at RT, two signals appeared in the $^{31}$P NMR spectrum at 63 ppm and 79 ppm in a ratio of 1 : 0.3. The same procedure in 1,5-COD led to a ratio of 1 : 2.2, suggesting that the signal at 79 ppm corresponds to a complex containing COD. Also, the difference in chemical shift between the two signals of 16 ppm fits with the hypothesis that both Ni(COD)(B)$_2$ (79 ppm) and Ni(B)$_4$ (63 ppm) are formed when B
is added to a solution containing Ni(COD)$_2$. Based on the above, we propose a pathway (Scheme 10) that summarises the different pathways that lead to the formation of either zwitterionic or nickel hydride complexes.

Depending on the relative basicity of METAMORPhos and PR$_3$, there is a competitive coordination between phosphorus ligands to nickel. A complex of type Ni(COD)(METAMORPhos)$_2$ could form initially in the absence of PR$_3$ (see Ni(4,4) or Ni(5,5)) or if the METAMORPhos ligand is more electron rich than PR$_3$ (see the synthesis of Ni(4,C) leading to complex formation Ni(4,4)). This competition could happen at the start but also probably at the end of the reaction.

Starting from NiP$_2$(COD) (I), METAMORPhos can coordinate by exchange with a co-ligand to form (II). Then, by intramolecular oxidative addition of METAMORPhos, a zwitterionic nickel (II) hydride complex (III), with a negatively charged METAMORPhos fragment can form. This intermediate could lead to the hydride complex by loss of 1,5-COD and coordination of a bulky co-ligand (PCy$_3$ for example). Alternatively, the migratory insertion of the hydride in the coordinated 1,5-COD double bond could generate (IV). The 1,4-enyl form, which upon isomerisation will lead to the zwitterionic complex. Two different pathways can explain the experiment displayed in Scheme 8 (zwitterionic to hydride): a) ZW – (V) – HY or b) ZW – (V) – (IV) – (III) – HY. In pathway a) the system would release 1,3-COD by β-H elimination while pathway b) it would release 1,5-COD. Given the observation of 1,3-COD by $^1$H NMR at the end of the reaction, pathway a) is most likely. However, given that nickel hydrides are also considered as isomerisation catalysts, it is possible that the free 1,3-COD observed by NMR come from the isomerisation of free 1,5-COD to the conjugated diene.
Scheme 10. Proposed mechanism leading to zwitterionic or nickel hydride complexes by oxidative addition of METAMORPhos ligand on zerovalent nickel phosphine COD complex. P: co-ligand and RSO₂N=PH: METAMORPhos ligand.

4 Conclusion

By the evaluation of different combinations of aminophosphines, we have identified that the formation of zwitterionic and cationic supramolecular nickel complexes is favoured when METAMORPhos ligands and bulky phosphines are involved. Also basic aminophosphines of type alkyl-NH-PPh₂ leads to such complexes. The high selectivity of the reaction towards the heterocomplex was ensured by a difference in basicity between the two ligands. Homocomplexes form when METAMORPhos ligand is present in the NH or the NH—NEt₃ tautomer. More conventional and unsubstituted phosphines were introduced and in combination with METAMORPhos and Ni(COD)₂ they also lead to the formation of zwitterionic heterocomplexes. By modulating the electronic and steric properties of the co-ligand, we found that this phosphine was crucial for the formation of the complex. We established that the basicity of the phosphine, described by the Tolman Electronic Parameter ($ν_{CO}$) has to be above a certain threshold for the complex formation to take place ($ν_{CO} < 2068.9$
cm$^{-1}$). Also, the steric bulk of the phosphine (described by the Tolman cone angle \( \theta \)) has an influence on the geometry of the complex. Electron rich phosphines with limited steric bulk lead to zwitterionic nickel complexes, whereas more bulky phosphines lead to the formation of \( \textit{trans-}(PO,P) \) chelated nickel hydride complexes. These two types of complexes are interrelated as a zwitterionic complex may be converted to a hydride complex. A mechanism leading to either a zwitterionic complex or a hydride complex was proposed. It most certainly involves the oxidative addition of a METAMORPhos ligand to a Ni(COD)(ligand)$_2$ intermediate, which is only realised when the co-ligand brings sufficient electron density to the metal. The discrimination between zwitterionic and hydride complex certainly happens in a second step and is directed by the steric bulk of the co-ligand.

## 5 Experimental part

### 5.1 General

All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. Phosphines, sulphonamides, 1,5-cyclooctadiene, di(o-tolyl)chlorophosphine were purchased from commercial suppliers and used without further purification. The benchmark complex Ref was prepared according to known literature procedure and NMR analysis was confirm.[5] Chlorophosphines were distilled trap to trap under reduced pressure. THF, pentane and Et$_2$O were distilled from sodium benzophenone. CH$_2$Cl$_2$ and chlorobenzene were distilled from CaH$_2$, 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 ($^1$H, $^1$H, $^{31}$P, $^{31}$P, $^{31}$P/$^1$H and $^{13}$C/$^1$H) were measured on a BRUKER 300 MHz spectrometer. Elemental analyses were performed by Stephen Boyer (London Metropolitan University).

### 5.2 Ligand synthesis

METAMORPhos ligands 3-10 were synthesised according to literature procedure described in chapter 2.
The ligand N-isopropyl-1,1-diphenylphosphinamine (31) (iPr-NH-PPh₂) was synthesised in Chapter 5. The synthesis of ligands amidophosphines (27, 28, 29, 30) were reported in Chapter 2.

**Ligand A (N-propyl-1,1-diphenylphosphinamine)**

\[
\text{N} \quad \text{PPh}_2
\]

\[\text{n-propylamine (3.00 mL, 36.70 mmol, 3.00 eq.) was placed in a Schlenk in THF (10 mL). Chlorodiphenylphosphine was then added dropwise (2.00 mL, 11.14 mmol, 1.00 eq.) to this mixture. The mixture was then stirred for 10 min at room temperature and the precipitate formed was filtered off. The filtrate was submitted to vacuum to give a colourless oil. Isolated yield 2.3 g (85%).}\]

\[\text{^31}P\{^1H\} NMR (121 MHz, CDCl}_3, 300K): \delta(ppm): 41.05 (s); ^1H NMR (300 MHz, CDCl}_3, 300K): \delta(ppm): 0.91 (t, \ J_{HH} = 7.5 Hz, CH$_3$, 3H); 1.51 (sext, \ J_{HH} = 7.2 Hz, CH$_2$-CH$_3$, 2H); 1.95 (d, \ J_{HP} = 5.0 Hz, NH, 1H); 2.93 (quint., \ J_{HH} = 7.6 Hz, CH$_2$-N, 2H); 7.0-7.8 (m, H$_{Ar}$, 10H).\]

\[\text{^13}C NMR (75 MHz, CDCl}_3, 300K): \delta(ppm): 11.5 (s, CH$_3$); 26.22 (d, \ J_{CP} = 6.1 Hz, CH$_2$-CH$_3$); 48.3 (d, \ J_{CP} = 14.0 Hz, CH$_2$-N); 128.3 (d, \ J_{CP} = 6.3 Hz, C$_{Ar}$); 128.46 (s, C$_{Ar}$); 131.4 (d, \ J_{CP} = 19.5 Hz); 141.9 (d, \ J_{CP} = 12.6 Hz, C$_{Ar}$).\]

**Ligand B (prepared in Chapter 4)**

**Ligand C (N,1,1-triphenylphosphinamine)**

\[
\text{N} \quad \text{PPh}_2
\]

\[\text{Dry aniline (6.00 mL, 5.22 g, 66.0 mmol, 3.0 eq.) was dissolved in a first Schlenk in THF (30 mL). In another Schlenk chlorodiphenylphosphine (4 mL, 4.92 g, 22 mmol, 1.0 eq.) was dissolved in THF (10 mL). Then the solution of chlorophosphine was added dropwise under strong stirring to the aniline solution leading to the formation of a white solid. After stirring the mixture for 10 min, unlocked ^31P NMR indicated that the reaction was complete. The precipitate that formed was filtered off and the filtrate evaporated under vacuum to an oil. This oil was submitted to vacuum and heated to 50°C to remove the excess of aniline leading to a white precipitate. The powder was then dissolved in a minimum amount of dichloromethane and n-pentane was added dropwise leading to a white precipitate. The solvent was then syringed out and the solid washed with n-pentane (3 x 20 mL) and finally dried under vacuum to give a white powder (isolated yield: 2.0 g, 33%).}\]

\[\text{^31}P\{^1H\} NMR (121 MHz, CDCl}_2, 300K): \delta(ppm): 27.45 (s); ^1H NMR (300 MHz, CDCl}_2, 300K): \delta(ppm): 4.53 (d, \ J_{HP} = 7.5 Hz, NH, 1H); 6.81 (t, \ J_{HH} = 7.7 Hz, C$_{Ar}$, 1H); 6.93-7.05 (m, C$_{Ar}$, 2H); 7.08-7.18 (m, C$_{Ar}$, 2H).\]

**Ligand D (1,1-dicyclohexyl-N-phenylphosphinamine)**

\[
\text{N} \quad \text{PCy}_2
\]

\[\text{Dry aniline (1.00 mL, 1.04 g, 11.3 mmol, 2.5 eq.) was dissolved in THF (10 mL). To this solution was added chlorodicyclohexylphosphine (1 mL, 1.05 g, 4.5 mmol, 1 eq.) dropwise under strong stirring leading to a thick precipitate. The mixture was stirred at RT for 10 min and ^31P unlocked NMR indicated full conversion to the product. The precipitate that formed was filtered off and the filtrate evaporated under vacuum to form a white powder (isolated yield 1.24 g, 96%).}\]

\[\text{^31}P\{^1H\} NMR (121 MHz, CDCl}_2, 300K): \delta(ppm): 41.01 (s); ^1H NMR (300 MHz, CDCl}_2, 300K): \delta(ppm): 0.52-1.97 (m, CH$_{Cy}$, 22H); 3.34 (d, \ J_{HP} = 10.5 Hz, NH, 1H); 6.61-6.83 (m, C$_{Ar}$, 1H); 6.93-7.05 (m, C$_{Ar}$, 2H); 7.08-7.18 (m, C$_{Ar}$, 2H).\]
Ligand E (1,1-diisopropyl-N-(trimethylsilyl)phosphinamine)

Chlorodiisopropylphosphine (4.00 mL, 3.84 g, 25.1 mmol, 1 eq.) was added dropwise to a HMDS (Hexamethyldisilazane) solution in toluene (5.25 mL, 4.06 g, 25.1 mmol, 1 eq. in 20 mL of toluene). The mixture was left to stir for 3 days at RT. Unlocked NMR of the crude mixture indicated complete conversion of the chlorophosphine but that two peaks formed at 47.3 ppm (monoaddition product 54%) and 66.4 ppm (bis addition product, 46%). The solvent and TMSCl were then removed under static vacuum leading to an oily residue. This residue was distilled under reduced pressure to give an oil (yield 45%).

\[^{31}P\{^1\text{H}\} \text{NMR (121 MHz, } C_6D_6, 300K): \delta (ppm): 48.4 (s); \]^1H NMR (300 MHz, C_6D_6, 300K): δ(ppm): 0.16 (s, (CH_3)_3Si, 9H); 0.92 (dd, \(^3J_{HH} = 6.9 \text{ Hz and } ^3J_{HP} = 10.1 \text{ Hz, CH}_3iPr, 6H); 0.98 (dd, \(^3J_{HH} = 7.0 \text{ Hz and } ^2J_{HP} = 1.4 \text{ Hz, CH}_3iPr, 2H), \text{NH not observed.}]

Ligand F (N-tert-butyl-1,1-diphenylphosphinamine)

Dry tert-butyl amine (1.76 mL, 1.22 g, 16.7 mmol, 3 eq.) was dissolved in THF (10 mL). To this solution was added chlorodiphenylphosphine dropwise (1 mL, 1.23 g, 5.57 mmol, 1 eq.) leading to a white precipitate. The mixture was left to stir for 16 h at room temperature. The precipitate that formed was filtered off and the filtrate evaporated under vacuum to form a white solid soluble in pentane (isolated yield: 2.45 g, 85 %). \[^{31}P\{^1\text{H}\} \text{NMR (121 MHz, } C_6D_6, 300K): \delta (ppm): 22.5 (s); \]^1H NMR (300 MHz, C_6D_6, 300K): δ(ppm): 1.13 (s, CH_3tBu, 9H); 1.82 (d, \(^2J_{PH} = 11.5 \text{ Hz, NH, 1H); 6.69-7.17 (m, CH}_Ar, 3H); 7.43 (ddd, J = 8.1 Hz, 3.2 Hz and 1.5 Hz, CH_Ar, 2H).

5.3 In situ approach for complex synthesis

In situ approaches described in the first part of this Chapter were first assessed by means of unlocked NMR to evaluate several combinations quickly. We focussed mainly on doublets systems with couplings around 30 Hz or greater to distinguish cationic complexes from hydride complexes. The values of the chemical shifts obtained without field locking were generally good with a reproducibility of ± 2 ppm, sufficient for a first screening of ligands combinations (with Ni(COD)_2). The results of the screening are summarised in Table 3. Grey entries correspond to isolated compounds.

<table>
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<th>B</th>
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<td>82 (br)</td>
<td>nd</td>
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<td>92 (32)</td>
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<tr>
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<td>nd</td>
<td>nd</td>
<td>60 (27)</td>
<td>44 (27)</td>
<td>43 (28)</td>
<td>55 (28)</td>
</tr>
<tr>
<td>5</td>
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<td>52 (25)</td>
<td>65 (25)</td>
<td>53 (23)</td>
<td>59 (24)</td>
</tr>
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</table>

Table 3. Chemical shifts of the supramolecular complexes resulting from the coupling of two aminophosphines with Ni(COD)_2 on the basis of unlocked \[^{31}P\] NMR. The values correspond to the chemical shift and the numbers between parentheses are the coupling constant. Grey entries correspond to isolated and characterised complexes (see expt. part). nd: not determined, no reac.: no reactivity, br: broad signals, slow dec. slow synthesis leading to decomposition products.
Ni(3,4):
Formation of several combinations Ni(4,4), Ni(3,3) and Ni(3,4).

Ni(3,C), Ni(4,C), Ni(5,C)

Unlike co-ligands A and B, aminophosphine C reacted promptly with Ni(COD)_2 in toluene forming a yellow insoluble compound that likely consisted of neutral chelates of proposed formula Ni(C)_4 or [Ni(C)_2]_2. To counteract the formation of these complexes, the solvent was then replaced by a mixture of chlorobenzene / 1,5-COD (10:1) favouring precursor solubility and dissociation.

The synthesis of Ni(3,C) was very slow compared to Ni(3,B). For any significant complexation to occur, the temperature of the reactant solution had to be increased to 60°C. The zwitterionic complex was observed by NMR at δ(ppm): 56 (d, \(^{2}J_{PP} = 28\) Hz); 82 (d, \(^{2}J_{PP} = 29\) Hz). However, the integration of the complex signals constituted only in 47 %P of the crude and the presence of black particles suggested that the complex decomposed in solution.

The synthesis of Ni(4,C) led to the expected product, found in \(^{31}\)P NMR at δ(ppm): 43 (d, \(^{2}J_{PP} = 28\) Hz); 55 (d, \(^{2}J_{PP} = 28\) Hz) for 66 %P. Surprisingly, the other products consisted of the homocomplex Ni(4,4) at 53 ppm (br s) and its decomposition product at δ(ppm): 14 (d, \(^{2}J_{PP} = 17\) Hz); 42 (d, \(^{2}J_{PP} = 17\) Hz) see Figure 15. The presence of the homocomplex and its degradation product substantiated a competitive coordination behaviour of co-ligands 4 and C, as already observed in the synthesis of Ni(4,3). It also underlined that 4 and C had resembling basicity at the phosphorus and therefore a comparable ability to bind to nickel. In contrast, the co-ligand B with an electron donating group at R had a stronger binding ability, as supported by the selective formation of Ni(4,B).

\(^{4}\) bright yellow solid; \(^{31}\)P NMR at δ(CD_2Cl_2): 52.4 ppm (sharp s), DEPT135 aromatic signals at 120-140 ppm, no allyl and no CH_3 (expected in the 20-35 ppm): absence of COD in the structure. Postulated: Ni(C)_4 or a dimer [Ni(C)_2]_2 yet a clear resolution of this structure was not investigated.
Figure 15. Crude $^{31}$P NMR recorded after reacting an equimolar mixture of Ni(COD)$_2$, METAMORPhos 4 and co-ligand C (0.1 mmol) in toluene. Above after 1 h at RT, below 1h at RT followed by 1h at 60°C.

The synthesis of Ni(5,C) led after 16 h to the expected product as shown by $^{31}$P NMR (CD$_2$Cl$_2$) at δ(ppm) 52.64 (d, $^2J_{PP}$ = 23.4 Hz); 58.58 (d, $^2J_{PP}$ = 23.7 Hz). Also in this case, many black particles were formed. The product was isolated as a yellow powder which was poorly soluble in toluene; however, this complex was not pure enough to be used in catalysis.

Ni(3,D)
When 3 and D were added to a solution of Ni(COD)$_2$ at room temperature, no complexation was observed. The formation of Ni(3,D) was apparent when the same mixture was heated to 60°C; this led to two broad signals in the NMR spectrum at δ(C$_6$D$_6$): 84.2 ppm and 101.7 ppm but also a characteristic signal for the allyl was observed by $^1$H NMR at δ(C$_6$D$_6$): 4.71 ppm (t, $^3J_{HH} = 8.2$ Hz) in the range of reported signals. These data are in good agreement with the generation of a zwitterionic complex. Further isolation, however, was not attempted due to the formation of many other complexes in the crude reaction mixture.

Ni(5,E)
Ligand E also generated a lot of products when reacted with Ni(COD)$_2$ and 5 according to NMR in which a doublet system was observed at 53 ppm (d, $J_{PP}$ = 26 Hz) and 75 ppm (d, $J_{PP}$ = 23 Hz), suggesting zwitterionic complex formation. However no selective complex formation was evidenced.

PMe$_3$-based METAMORPhos zwitterionic complexes
Since PMe$_3$ showed very quick and quantitative conversion for the synthesis of zwitterionic complex 16, the METAMORPhos ligands were tested according to the procedure depicted in Scheme 11.
Scheme 11. General procedure adopted to evaluate the influence of different METAMORPhos on the synthesis on the zwitterionic and cationic PMe₃-based nickel complexes.

Chemical shifts (ppm) and coupling constant (Hz) for PMe₃-based complexes 19-22 (the other PMe₃-based complexes were isolated, see following section for experimental details)

The reaction of METAMORPhos ligands 9 and 10, having a chiral centre with Ni(COD)₂ and PMe₃ led to the formation of the corresponding zwitterionic complexes with however a “splitting” of each signal in the NMR spectrum in a 1:1 ratio as shown in Figure 16.

Figure 16. Phosphorus NMR spectrum of complex 21 (in situ) and respective chemical shifts for both diastereoisomers (a) and (b).

This splitting of signals, observed upon the insertion of a chiral element in the complex structure, suggested that two diastereoisomers had formed and consequently that the
zwitterionic complex itself had its own source of chirality expressed in a 1:1 ratio. The origin of this chirality probably resulted in the position of the COD. Indeed on the basis of the crystal structures that were presented in Chapter 4, we observed that the 5 methylene groups of the COD could point either above or below the coordination plane compared with the two phosphines as shown in Figure 17.

Figure 17. Position of the COD in the complexes that can be located above or below the \( P_1, Ni, P_2 \) coordination plane according to the solid state crystal structures of zwitterionic cationic nickel complexes.

**PCy\(_3\)**-based **METAMORPhos** zwitterionic complexes
The reaction conditions presented in Scheme 12 were adopted as a general procedure for the screening of the synthesis of **PCy\(_3\)**-based **METAMORPhos** zwitterionic complexes.

![Scheme 12. General procedure adopted for screening of different **METAMORPhos** ligands with **PCy\(_3\)** and **Ni(COD)\(_2\)**](image)

METAMORPhos 4 (NH tautomer with \( R^1 = 4-\text{tBu-Ph} \) and \( R_2 = \text{Ph} \)) was very reactive with **Ni(COD)\(_2\)** and **PCy\(_3\)** producing several decomposition products, suggesting complex instability. A small peak in \(^1\text{H NMR} \) spectrum of the mixture could be observed at – 26 ppm, which signals that a hydride had formed. However this product only accounted for a small fraction of the total yield of products and **Ni(4,4)** was also observed. The presence of **Ni(4,4)** suggested that there was a competitive reaction between hydride or zwitterionic complex formation. This competition was mainly directed towards **Ni(4,4)** which can be explained by the easier formation of the less bulky **Ni(4,4)** complex compared with the **PCy\(_3\)**-based hydride.

METAMORPhos ligands 5 and 6 (PH tautomer) bearing bulky phosphines **PCy\(_2\)** and \( P(\text{t-Bu})\(_2\) \) reacted very slowly with **Ni(COD)\(_2\)** and **PCy\(_3\)** to form hydride complexes 26 and 25, respectively. Full conversion of ligand 5 to hydride 26 was possible by heating the reaction mixture to 60°C for 16 h. The resulting complex was stable and soluble in toluene but precipitated in pentane. Analysis of the isolated product by NMR and elemental analysis also confirmed that complex 26 formed. Unfortunately no crystals could be obtained from these complexes.

Increasing again the steric bulk on the P atom (\( R^1 = \text{CF}_3, R^2 = \text{tBu} \)), going through the tert-butyl substituted **METAMORPhos** ligand 6 decreased again system reactivity since the
system had to be heated up to 90°C for one hour; this led to the formation of a typical hydride pattern in the $^{31}$P NMR spectrum (doublets of doublets) with good conversion (85 %).

We investigated the reactivity of the analogue METAMORPhos 7 ($R^1 = \text{CF}_3$, $R^2 = \text{Cy}$) with the bulky cyclohexyl group on P. In the conditions of Scheme 12, already after 1 h ligand 7 had converted for 73 % to doublets of doublets in the $^{31}$P NMR spectrum. Surprisingly leaving this mixture in toluene for one week led to an orange precipitate which was insoluble in toluene or benzene and that we could not identify because of its low solubility. The higher reactivity of 7 (reaction at RT) compared with 3, 5 and 6 suggests that less electron withdrawing groups on the METAMORPhos led to easier complex formation.

Chemical shifts observed for the hydride species:

<table>
<thead>
<tr>
<th>Structure</th>
<th>Chemical Shifts</th>
</tr>
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<tbody>
<tr>
<td><img src="image1.png" alt="" /></td>
<td><img src="image2.png" alt="" /></td>
</tr>
<tr>
<td>23 (C$_6$D$_6$):</td>
<td>36.1 (dd, $J = 236$ &amp; 64 Hz); 103.4 (dd, $J = 236$ &amp; 77 Hz)</td>
</tr>
<tr>
<td>26 (unlocked):</td>
<td>36.6 (dd, $J = 236$ &amp; 67 Hz); 78.6 (dd, $J = 237$ &amp; 82 Hz)</td>
</tr>
<tr>
<td>25 (C$_6$D$_6$):</td>
<td>40.4 (dd, $J = 235$ &amp; 69 Hz); 120.7 (dd, $J = 235$ &amp; 68 Hz)</td>
</tr>
<tr>
<td>24 (tol-d8):</td>
<td>40.42 (dd, $J = 242$ &amp; 74 Hz); 63.27 (dd, $J = 242$ &amp; 64 Hz)</td>
</tr>
<tr>
<td>see isolated for further details</td>
<td>see isolated for further details</td>
</tr>
</tbody>
</table>

Extension to amidophosphines $+ (\text{PMe}_3/\text{Ni(COD)}_2)$ or $+ (\text{PCy}_3/\text{Ni(COD)}_2)$.

Because different METAMORPhos ligands allowed for the facile formation of either hydride or zwitterionic complexes as seen in Figure 7 and Figure 12, we wondered if changing METAMORPhos ligands for the more common amidophosphines would display equivalent reactivity under similar conditions. Zwitterionic or hydride complexes based on these ligands have not been reported to date with nickel. However, nickellacycles with P-N-C-O atoms have been described by Keim for Ni-aryl complexes suggesting the apparent stability of this arrangement.$^{[30]}$ This motivated our investigations into the synthesis of amidophosphine based zwitterionic of hydride complexes according to Scheme 13.$^5$

$^5$ Amidophosphine ligands 27-31 were described and synthesised in Chapter 2 and they are represented under the NH tautomer for simplicity.
The reaction of amidophosphine 27 (the direct carbonyl analogue of METAMORPhos ligand 3) with PMe₃ and Ni(COD)₂ led to a clear brown solution. The PMe₃ signal observed initially at -62 ppm in the ³¹P NMR spectrum had disappeared completely and several multiplet structures were observed at δ(ppm): -21 (s); -26.3 (d, \( J_{PP} = 28.9 \) Hz); 110 (br s); 115.5 (d, \( J_{PP} = 30.3 \) Hz); 116.4 (br s). The two small doublets at -26.3 ppm and 115.5 ppm corresponded to the resonances of two phosphorus atoms in cis position to a nickel centre (small value of \( J_{PP} \)). Heating this mixture to 60°C did not lead to any appreciable change in the product ratio, suggesting that a ligand equilibrium established between Ni(0), PMe₃ and 27 without formation of the zwitterionic complex.

Through the same general procedure, the compounds 28-31 led to simple metal coordination without oxidative addition. This coordination was particularly visible for ligands 29 and 30 which generated in the ³¹P NMR spectrum in the -20 ; -30 ppm region simultaneously, a singlet, a doublet, a triplet and a quadruplet δ(ppm): -21.6 (s, Ni(PMee)₄); -22.8 (d, \( J_{PP} = 33 \) Hz, Ni(29)(PMe₃)₃); -24.9 (dd, \( J_{PP} = 35 \) Hz Ni(29)₂(PMee)₂); -28.0 (dd, \( J_{PP} = 40 \) Hz Ni(29)₃(PMee). A similar pattern was also observed downfield (around 65 ppm). These signals accounted for all the possible chelates combinations containing PMe₃ and 29, according to Wilke for Ni(PMee)ₙ(PPh₃)₄₋ₙ.[9]

Subsequently, we explored the second reaction, that is, the reactivity of several amidophosphines with Ni(COD)₂ and PCy₃. Ligands 27 and 28 with a basic diisopropylphosphine, converted quickly at RT to hydrides 32 and 33, respectively, as confirmed by NMR. These amidophosphine-based hydrides were not isolated but their chemical shifts and coupling constants very close to those of METAMORPhos-based complexes 32 and 23 suggested that they had identical structure structures based on a PO chelate and two phosphines in trans position. Amido(aryl)phosphines 29 and 30 showed formation of the expected complexes when subjected to the general reaction conditions but also a number of by-products were formed according to ³¹P NMR, suggesting fast degradation. The aminophosphine 31 did not form hydrides even upon prolonged heating.

Amidophosphines did not lead to zwitterionic complexes with PMe₃ while in the presence of PCy₃, bulky ligands led to hydride complex formation. This suggested that the sulphonyl group in METAMORPhos offered a better stabilisation of zwitterionic complexes on the delocalised PNSO backbone, compared with the PNCO system. Moreover we anticipated that
other ligands such as P-NH-P=O\textsuperscript{31} could function similarly to sulphonamides based analogues and would produce zwitterionic or nickel hydride complexes.

5.4 Synthesis and characterisation of supramolecular complexes 11-15

Complexes 11 and 12 have been described previously (chapter 4)

Complex 13

The synthesis of this complex was first performed in toluene and at RT. The reaction mixture quickly turned from yellow to dark greenish. The corresponding \textsuperscript{31}P NMR of the crude mixture stirred overnight consisted in majority of a broad peak (complex 13) at $\delta$: 55 ppm (80%) and in minority (20%) of a double doublet system at $\delta$ (ppm): 12 (d, $^2J_{PP} = 17.0$ Hz) and 53 (d, $^2J_{PP} = 17.0$ Hz) attributed to the thermal degradation product of complex 13: see Figure 18. The minor product was removed quantitatively by selective precipitation of a green solid from the crude mixture, by careful addition of pentane to a toluene solution of the crude. The main product in solution was obtained by evaporation of the solution.

Figure 18. Unlocked \textsuperscript{31}P NMR spectrum of the crude mixture during the synthesis of 13 with broad signals of the complex and the decomposition product at 12 and 53 ppm (values slightly differ in C$_6$D$_6$: $\delta$ (C$_6$D$_6$): 54.0 ppm for the main product, by-product at $\delta$(C$_6$D$_6$): 12.6 ppm (d, $^2J_{PP}$=17.0 Hz) and 52.6 ppm (d, $^2J_{PP}$ =17.0 Hz)
Changing toluene for chlorobenzene as the solvent for the synthesis did not change the product ratio. Surprisingly when 1,5-bis(cyclooctadiene) (1,5-COD) was used as reaction solvent, only the signal at 54 ppm was observed by $^{31}$P NMR. Via this optimised procedure, described below the pure product 13 was isolated with no decomposition product.

METAMORPhos ligand 4, 4-nBuPh-SO$_2$-NH-PPh$_2$ (397 mg, 1.00 mmol, 2.00 eq.) and Ni(COD)$_2$ (138 mg, 0.50 mmol, 1.00 eq.) were dissolved in dry 1,5-cyclooctadiene (10 mL) and stirred overnight. The solvent was evaporated under reduced pressure to yield a greenish oil. The resulting oil was co-evaporated several times with pentane to get rid of the traces of cyclooctadiene. The oil was extracted several times with heptane/toluene mixtures (4:1) and the liquid fractions collected and evaporated to dryness to give an orange powder. The powder was dried and washed twice with 10 mL of pentane, to give an orange powder (131 mg). Isolate yield 27%.

$^{31}$P{$^1$H} NMR (121 MHz, C$_6$D$_6$, 300K): δ(ppm): 54.06; $^1$H NMR (300 MHz, C$_6$D$_6$, 300K): δ(ppm): 0.82 (t, $^3$J = 7.2 Hz, CH$_3$, 6H); 1.15 (sex, $^3$J = 7.5 Hz, CH$_2$-CH$_3$, 4H); 1.34 (q, $^3$J = 7.7 Hz, CH$_2$-CH$_2$-CH$_3$, 4H); 2.30 (t, $^3$J = 7.8 Hz, CH$_2$-Ar, 4H); 1.04 (m, CH$_2$-COD, 4H); 1.45 (m, CH$_2$-COD, 4H); 1.94 (m, CH$_2$-COD, 2H); 3.95 (dd, $^3$J = 17.2 & 8.6 Hz, CH COD allyl β, 2H); 4.85 (t, $^3$J = 8.6 Hz, CH COD allyl α, 1H); 6.85 (d, $^2$J ortho = 8.1 Hz, CH Ar-SO$_2$, 4H); 7.01 (broad s, CH PPh$_2$, 12H); 7.96 (broad s, CH PPh$_2$, 8H); 8.04 (d, $^3$JHH = 7.99 Hz, CH Ar-SO$_2$, 4H); 9.64 (br s, NH, 1H); $^{13}$C NMR (75 MHz, C$_6$D$_6$, 300K): δ(ppm): 14.07 (CH$_3$, 2C); 22.54 (CH$_2$-CH$_3$, 2C); 23.09 (CH$_2$-COD, 1C); 27.05 (CH$_2$-COD, 2C); 29.95 (CH$_2$-COD, 2C); 33.54 (CH$_2$-CH$_2$-CH$_3$, 2C); 35.65 (Ar-CH$_2$, 2C); 82.12 (CH COD allyl β, 2C); 110.08 (CH COD allyl α); 127.34 (CH Ar-SO$_2$, 4C); 128.2 (m, CH PPh$_2$ meta, 8C); 128.46 (CH Ar-SO$_2$, 4C); 129.75 (CH PPh$_2$ para, 4C); 132.26 (m, CH PPh$_2$ ortho, 8C); 136.58 (m, C$^{IV}$ PPh$_2$ ipso, 4C); 143.14 (C$^{IV}$ nBu, 2C); 146.06 (C$^{IV}$ C-SO$_2$, 2C). EA (th): C: 64.17 (64.94); H: 6.64 (6.29); N: 3.15 (2.91).

**Figure 19.** Low temperature $^{31}$P NMR (121 MHz, tol-$d_8$) experiment on complex 13 in tol-$d_8$. From top to bottom: 30°C, -10°C, -40°C, -80°C and back to 30°C.
Thermal stability of complex 13

Given the stability improvement induced by 1,5-COD in the course of the synthesis of 13, we suspected that one possible degradation pathway for these complexes could be the loss of COD of the allyl moiety by beta-H elimination. To check this hypothesis, we tested the effect of a reaction temperature increase on the structure of complex 13. Already at 60°C, a solution of complex 13 in toluene went from yellow to green and we observed by $^{31}$P NMR a decrease of the signals of 13 with an increase of signals of the by-product at 12.6 ppm and 52.6 ppm. Simultaneously the signals of the allyl fragment disappeared from $^1$H NMR and new signals appeared at 5.6-6.2 ppm (see Figure 20), corresponding to free 1,3-COD according to the simulated $^1$H NMR pattern. However, we could not formally determine this degradation product structure and did not observe any hydride formation.

Figure 20. $^1$H NMR (300MHz, C$_6$D$_5$Cl) spectrum of complex 13 at 80°C, detail of the characteristic 1,3-COD signals between 5.5 and 6.1 ppm corresponding to one of the thermal degradation product of the complex.

In the absence of COD in the reaction mixture (replacing Ni(COD)$_2$ by Ni(PPh$_3$)$_4$) there was no signal at 54 ppm and only the two doublet system at 12.6 and 52.6 ppm and corresponding to the side-product were formed.
**Chapter 5**

**Complex 14**

METAMORPhos ligand 3, $\text{F}_3\text{C}-\text{SO}_2\text{-N}=(\text{iPr})_2$ (265 mg, 1.00 mmol, 1.00 eq.) was placed in a Schlenk and dissolved in toluene (5 mL). In another Schlenk, Ni(COD)$_2$ (275 mg, 1.00 mmol, 1.00 eq.), and propyl-1,1-diphenylphosphinamine (244 mg, 1.00 mmol, 1.00 eq.) and some 1,5-cyclooctadiene (0.5 mL for complex stabilisation) were dissolved in toluene (10 mL) in an ice bath. Both solutions were cooled to 0°C and the solution of METAMORPhos ligand 3 was added dropwise to the other Schlenk. The mixture was left to stir for 5h30 at room temperature leading to a brown solution. The solvents were evaporated under vacuum to give a dark yellow solid. This solid was washed and triturated (ultrasound bath) with pentane (2 x 10 mL) to give a yellow powder. It was finally washed with cold diethyl ether (2 x 10 mL) to give a bright yellow solid. The solid was dried under vacuum. To get rid of Et$_2$O traces, the solid was suspended in toluene (5 mL) and the solvent evaporated under vacuum (co-evaporation). This operation was repeated once to give a yellow powder. The solid was then dissolved in dichloromethane (5 mL) to give an orange solution. This solution was passed through a syringe filter to eliminate residual solids or black nickel. The resulting solution was finally evaporated to an oil which is submitted to co-evaporation with toluene (2 x 5 mL). A yellow solid was obtained (isolate yield: 325 mg, 47 %). Due to a very low solubility in aromatic hydrocarbons the NMR was recorded in CD$_2$Cl$_2$. $^3\text{P}$ [H] NMR (121 MHz, CD$_2$Cl$_2$, 300K): $\delta$(ppm): 64.55 (d, $^2J_{PP} = 31.5$ Hz); 92.16 (d, $^2J_{PP} = 31.6$ Hz); $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 300K): $\delta$(ppm): 0.45-2.30 (COD signals of CH$_2$, 10H); 0.86 (t, $^3J_{HH} = 7.4$ Hz, CH$_3$-CH$_2$, 3H); 1.10-1.30 (m, CH$_3$-ipr$_{ar}$, 6H); 1.38 (dd, $^3J_{HH} = 6.7$ Hz, $^4J_{CP} = 13.4$, 3H, CH$_3$-ipr$_{b}$ and CH$_2$-CH$_3$, 5H); 2.20 (m, CH$_3$-ipr$_{b}$, 1H); 2.53 (m, CH$_2$-N, 2H); 3.07 (m, CH$_3$-ipr$_{a}$, 1H); 3.90 (quint, $^3J_{HH} = 8.5$ Hz, CH COD allyl $\beta$, 1H); 4.76 (quint., $^2J_{HH} = 7.4$ Hz, CH COD allyl $\beta$, 1H); 5.05 (t, $^3J_{HH} = 8.5$ Hz, CH COD allyl $\alpha$, 1H); 5.45 (m, NH, 1H); 7.46 (m, H$_{Ar}$ ortho, para, 6H); 7.62 (m, H$_{Ar}$ meta, 4H); $^{19}$F NMR (282 MHz, CD$_2$Cl$_2$, 300K): $\delta$(ppm): -79.79 (s); $^1$C NMR (75 MHz, Cd$_6$D$_6$, 300K): $\delta$(ppm): 11.8 (CH$_2$-CH$_2$); 17.3 (d, $^2J_{CP} = 4.5$ Hz, CH$_3$-ipr$_{b}$); 18.2 (d, $^2J_{CP} = 2.0$ Hz, CH$_3$-ipr$_{a}$); 19.0 (d, $^2J_{CP} = 5.0$ Hz, CH$_3$-ipr$_{a}$); 20.6 (d, $^2J_{CP} = 4.0$ Hz, CH$_3$-ipr$_{a}$); 22.9 (CH$_2$-COD); 25.0 (d, $^2J_{CP} = 8.7$ Hz, CH$_2$-CH$_3$); 27.3 (d, $^2J_{CP} = 4.2$ Hz, CH$_2$-COD); 28.1 (d, $^2J_{CP} = 4.7$ Hz, CH$_2$-COD); 29.4 (d, $^2J_{CP} = 22.7$ Hz, CH$_3$-ipr$_{a}$); 29.9 (d, $^2J_{CP} = 1.9$ Hz, CH$_2$-COD); 31.5 (d, $^2J_{CP} = 17.4$ Hz, CH$_3$-ipr$_{b}$); 31.7 (CH$_2$-COD); 45.5 (d, $^2J_{CP} = 12.3$ Hz, CH$_2$-N); 72.3 (d, $^2J_{CP} = 19.2$ Hz, $^2J_{CP} = 5.6$ Hz, CH COD allyl $\beta$); 82.7 (dd, $^2J_{CP} = 18.3$ Hz, $^2J_{CP} = 4.0$ Hz, CH COD allyl $\beta$); 110.9 (CH COD allyl $\alpha$); 120.98 (qd, $^2J_{CP} = 322.4$ Hz, $^2J_{CP} = 4.2$ Hz); 128.6 (m, CH$_{Ar}$ ortho 4C); 130.5 (d, $^2J_{CP} = 1.8$ Hz, CH$_{Ar}$ para); 130.9 (d, $^2J_{CP} = 1.9$ Hz, CH$_{Ar}$ para); 132.6 (d, $^2J_{CP} = 10.8$ Hz, CH$_{Ar}$ meta, 2C); 133.3 (d, $^2J_{CP} = 13.1$ Hz, CH$_{Ar}$ meta, 2C); 134.6 (d, $^2J_{CP} = 55.6$ Hz, C$^\text{IV}$-PPh$_2$ ipso); 134.9 (d, $^2J_{CP} = 36.9$ Hz, C$^\text{IV}$-PPh$_2$ ipso). EA (th): C : 53.45 (53.35); H : 6.61 (6.72); N : 3.86 (4.15). Crystals suitable for diffraction obtained from a cold saturated solution of the complex 14 in toluene.

**Data crystal**

C$_{30}$H$_{53}$F$_{12}$Ni$_2$O$_2$P$_2$S

$M_e = 675.38$

$D_x = 1.225$ Mg m$^{-3}$

Orthorhombic, Fdd2

Mo Kα radiation, $\lambda = 0.7107$ Å

Hall symbol: F 2 -2d

Cell parameters from 5994 reflections

$a = 37.938$ (3) Å

$0 = 4.4–28.5^\circ$

$b = 37.593$ (6) Å

$\mu = 0.72$ mm$^{-1}$

$c = 10.2721$ (8) Å

$T = 150$ K

$V = 14650$ (3) Å$^3$

Needle, yellow

$Z = 16$

0.58 × 0.21 × 0.18$ mm
Zwitterionic or Nickel Hydride Complexes: a Parameter Study

Data collection

| Xcalibur, Atlas, Gemini ultra diffractometer | 8782 independent reflections |
| Radiation source: Enhance (Mo) X-ray Source | 7121 reflections with $I > 2.0\sigma(I)$ |
| graphite | $R_{int} = 0.000$ |
| Detector resolution: 10.4685 pixels mm$^{-1}$ | $\theta_{max} = 29.8^\circ, \theta_{min} = 3.0^\circ$ |
| $\omega$ scans | $h = 0 \rightarrow 51$ |
| $k = 0 \rightarrow 51$ |
| $T_{min} = 0.728, T_{max} = 0.899$ |
| 46638 measured reflections |

Refinement

| Refinement on $F^2$ | Hydrogen site location: difference Fourier map |
| Least-squares matrix: full | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.074$ | Method = Modified Sheldrick $w = 1/\sigma^2(F^2) + (0.1P)^2 + \ast\ast\ast\ast\ast\ast P$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$ |
| $wR(F^2) = 0.218$ | $(\Delta/\sigma)_{max} = 0.001$ |
| $S = 1.00$ | $\Delta>_{max} = 0.94 e \text{ Å}^{-3}$ |
| 8770 reflections | $\Delta>_{min} = -1.34 e \text{ Å}^{-3}$ |
| 380 parameters | Absolute structure: Flack (1983), 3773 Friedel-pairs |
| 15 restraints | Flack parameter: 0.01 (2) |
| Primary atom site location: structure-invariant direct methods |

Complex 15

METAMORPhos ligand 5, F$_3$C-SO$_2$-NH-P(o-tolyl)$_2$, NEt$_3$ (462 mg, 1.00 mmol, 1.00 eq.) was placed in a Schlenk and dissolved in chlorobenzene (5 mL). In another Schlenk, Ni(COD)$_2$ (275 mg, 1.00 mmol, 1.00 eq.), and propyl-1,1-diphenylphosphinamine (244 mg, 1.00 mmol, 1.00 eq.) and some 1,5-cyclooctadiene (0.5 mL) were dissolved in chlorobenzene (10 mL) in an ice bath. Both solutions were cooled to 0°C and the solution of METAMORPhos ligand was added dropwise to the other Schlenk. The mixture was left to stir for 4 h at room temperature leading to a dark brown solution. The solvents were evaporated under vacuum to give an oily solid. This residue was triturated with pentane (2 x 10 mL) to give a powder which was washed with pentane (5 x 5 mL) giving a dark yellow powder. This solid was washed with cold diethylether (0°C, 3 x 10 mL) resulting in a yellow powder. In order to remove traces of diethyether, the powder was suspended in toluene (3 mL) and the toluene was evaporated under vacuum (co-evaporation). This operation was repeated 3 times to give the expected product as a bright yellow powder (isolate yield: 280 mg, 36%). The product was not very soluble in aromatic hydrocarbons and the NMR was recorded in CD$_2$Cl$_2$. $^{31}$P{$_1^1$H} NMR (121 MHz, CD$_2$Cl$_2$, 300K): δ(ppm): 52.33 (d, $^2J_{PP} = 24.7$ Hz); 65.09 (d, $^2J_{PP} = 24.5$ Hz). $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 300K): δ(ppm):
0.45 (t, J_HH = 7.4 Hz, CH_3 propyl, 3H); 0.40-0.65 (m, CH_2 COD, 1H); 1.02 (sext, CH_2-CH_3, 2H); 1.00-1.95 (m, CH_2 COD, 9H); 1.99 (s, CH_3 tolyl b, 3H); 2.34 (s, CH_3 tolyl a, 3H); 2.38 (m, CH_2-NH, 1H); 2.60 (m, CH_2-NH, 1H); 3.68 (m, J_HH = 5.9 Hz, J_HP = ?, CH COD allyl b, 1H); 4.16 (m, J_HH = 7.0 Hz, J_HP = 8.3 Hz, CH COD allyl a, 1H); 6.59 (m, CH tolyl 2a, 1H); 7.01 (m, CH tolyl 4a and CH tolyl 4b, 2H); 7.12 (m, CH tolyl 3a, 1H); 7.29 (m, CH tolyl 3b and CH tolyl 2b, 2H); 7.41 (m, CH PPPh_2, 3H); 7.58 (m, CH PPPh_2, 5H); 7.70 (m, CH tolyl 1a, 1H); 7.73 (m, CH PPPh_2, 2H); 8.20 (m, CH tolyl 1b, 1H). ^13^C NMR (75 MHz, C6D_6, 300K): δ(ppm): 11.1 (CH_3Me); 21.4 (CH_3 tolyl a); 22.3 (d, J_Cp = 9.1 Hz, CH_3 tolyl b); 23.0 (CH_2 COD); 24.7 (d, J_Cp = 5.8 Hz, CH_2-CH_3); 26.8 (m, CH_2 COD, 2C); 29.4 (CH_2 COD); 46.5 (d, J_Cp = 11.3 Hz, CH_2-NH); 80.1 (d, J_Cp = 17.5 Hz, CH COD allyl b); 86.6 (d, J_Cp = 18.6 Hz, CH COD allyl b); 111.5 (CH COD allyl a); 121.2 (qd, J_Cp = 322 Hz, J_Cp = 6.5 Hz, -CF_3); 124.0 (d, J_Cp = 15.7 Hz, CH_2a); 125.5 (d, J_Cp = 8.1 Hz, CH_3b); 128.5 (d, J_Cp = 9.5 Hz, CH PPPh_2, 2C); 129.0 (d, J_Cp = 9.9 Hz, CH PPPh_2, 2C); 129.9 (s, CH_2b); 130.2 (s, CH PPPh_2); 130.7 (CH_3a); 131.2 (m, CH_1b+4b+PPPh_2, 3C); 131.9 (d, J_Cp = 5.9 Hz, CH_4a); 132.8 (d, J_Cp = 11.2 Hz; CH PPPh_2, 2C); 133.5 (d, J_Cp = 13.0 Hz, CH PPPh_2, 2C); 134.7 (d, J_Cp = 47.5 Hz, C^IV tolyl a, CP); 135.4 (d, J_Cp = 52.4 Hz, C^IV PPPh_2, CP); 136.0 (d, J_Cp = 40.7 Hz, C^IV PPPh_2, CP); 138.9 (m, C tolyl b, C-Me, C tolyl b, C-P, 2C); 142.9 (m, C tolyl a, C Me). EA (th): C: 50.49 (59.16); H: 7.41 (5.88); N: 3.65 (3.63).

C_{13}H_{45}Sn_2NiO_2P_2S  \quad F(000) = 1616

M_r = 771.50  \quad D_2 = 1.422 \text{ Mg m}^{-3}

Monoclinic, P2_1/n  \quad \text{Mo K} \alpha \text{ radiation, } \lambda = 0.7107 \text{ Å}

Hall symbol: -P 2yn  \quad \text{Cell parameters from 36314 reflections}

a = 11.2995 (5) Å  \quad 0 = 3.9–29.4°

b = 19.119 (1) Å  \quad \mu = 0.74 \text{ mm}^{-1}

c = 16.8177 (9) Å  \quad T = 150 \text{ K}

β = 97.401 (5)°  \quad \text{Block, yellow}

V = 3602.9 (3) Å³  \quad 0.53 \times 0.38 \times 0.28 \text{ mm}

Z = 4

Data collection

Xcalibur, Atlas, Gemini ultra diffractometer  \quad 9847 independent reflections

Radiation source: Enhance (Mo) X-ray Source  \quad 7468 reflections with I > 2.0σ(I)

graphite  \quad R_{int} = 0.098

Detector resolution: 10.4685 pixels mm\(^{-1}\)  \quad \theta_{max} = 29.8°, \theta_{min} = 3.0°

ω scans  \quad \theta = -15\rightarrow 15


k = -26\rightarrow 26

T_{min} = 0.969, T_{max} = 0.982  \quad I = -23\rightarrow 22

138950 measured reflections

Refinement

Refinement on F^2  \quad \text{Primary atom site location: structure-invariant direct methods}

Least-squares matrix: full  \quad \text{Hydrogen site location: difference Fourier map}

R[F^2 > 2\sigma(F^2)] = 0.051  \quad \text{H-atom parameters constrained}

wR(F^2) = 0.118  \quad \text{Method, part 1, Chebychev polynomial, (Watkin, 1994, Prince, 1982) [weight] = 1.0|A_n|T_n(x) + A_{n-1}|T_{n-1}(x)|}
5.5 Synthesis and characterisation of phosphine-based zwitterionic complexes

Complex 16

METAMORPhos ligand 3 (212 mg, 0.80 mmol, 1.00 eq.) and trimethylphosphine (1M toluene solution, 1.00 mL, 1.00 mmol, 1.25 eq.) were placed in a Schlenk with toluene (30 mL). In another Schlenk Ni(COD)$_2$ (2200 mg, 0.80 mmol, 1.00 eq) was dissolved in toluene (20 mL). Both solutions were cooled in an ice bath and the solution containing phosphines was added via a cannula to the Ni(COD)$_2$ solution at 0°C. The mixture was left to stir overnight. The solvent was then evaporated to give a yellowish powder.

This crude product was co-evaporated with 5 mL of pentane and washed with 3x10 mL of pentane to give a yellow powde.
Chapter 5

\[ b = 15.2866 \ (7) \ \text{Å} \]
\[ c = 12.7410 \ (5) \ \text{Å} \]
\[ \beta = 95.353 \ (4)^\circ \]
\[ T = 150 \ \text{K} \]
\[ V = 2368.91 \ (17) \ \text{Å}^3 \]
\[ Z = 4 \]

**Data collection**

- **Xcalibur, Atlas, Gemini ultra diffractometer**: 6233 independent reflections
- **Radiation source**: Enhance (Mo) X-ray Source
- **Detector resolution**: 10.4678 pixels mm\(^{-1}\)
- **Graphite**: \( R_{int} = 0.046 \)
- **Absorption correction**: analytical
- **CrysAlis PRO, Agilent Technologies, Version 1.171.36.28 (release 01-02-2013 CrysAlis171.NET) (compiled Feb 1 2013,16:14:44)**
- **Method, part 1, Chebychev polynomial, (Watkin, 1994, Prince, 1982) [weight] = 1.0/[A_0*T_0(x) + A_1*T_1(x) \cdots + A_{n-1}*T_{n-1}(x)]**
- **A_i** are the Chebyshev coefficients listed below and \( x = F / F_{max} \)
- **Method = Robust Weighting (Prince, 1982)**
- **W** = [weight] * [1- (\( \delta F / 6*\sigma F \))^2]^2
- **A_i** are: 300, 454, 232, 62.0
- **S = 0.98**
- **(Δ/σ)_{max} = 0.001**
- **6220 reflections**
- **Δ\( ^> \)max = 1.89 e Å\(^{-3}\)**
- **253 parameters**
- **Δ\( ^< \)min = -0.51 e Å\(^{-3}\)**
- **0 restraints**

**Refinement**

- **Primary atom site location: structure-invariant direct methods**
- **Hydrogen site location: difference Fourier map**
- **H-atom parameters constrained**

**Complex 17**

METAMORPhos ligand 4 (390 mg, 1.00 mmol, 1.00 eq.) and trimethylphosphine (1 M toluene solution, 1.00 mL, 1.00 mmol, 1.00 eq.) were placed in a Schlenk with toluene (30 mL). In another Schlenk Ni(COD)\(_2\) (270 mg, 1.00 mmol, 1.00 eq) was dissolved in toluene (20 mL). Both solutions were cooled in an ice bath and the phosphine solution was added via a cannula to the Ni(COD)\(_2\) solution at 0°C. After addition, the mixture was slowly brought to RT, stirred for 20 min and heated to 60°C for 1h to give a brownish mixture. The solvent was evaporated to give an orange powder (isolate yield: 39%).

\(^{31}\)P{\(^1\)H} NMR (121 MHz, C\(_6\)D\(_6\), 300K): \( \delta \) ppm: 60.25 (d, \(^3\)J\(_{PP}\)-cis=26.7 Hz); -0.11 (d, \(^3\)J\(_{PP}\)-cis= 26.7 Hz), \(^1\)H NMR (300 MHz, C\(_6\)D\(_6\), 300K): \( \delta \) ppm: 0.81 (t, \(^3\)J\(_{HH}\) = 7.1 Hz 3H, CH\(_2\)-CH\(_3\));
Zwitterionic or Nickel Hydride Complexes: a Parameter Study

0.945 (d, $^2J_{HP} = 8.8$ Hz, 9H, CH$_3$PMe$_3$); 1.18 (m, 2H, CH$_2$-CH$_3$); 1.20-1.35 (m, 4H, CH$_2$COD); 1.40 (m, 2H, CH$_2$-CH$_2$-CH$_3$); 1.45-1.95 (m, 4H, CH$_2$COD); 2.07 (m, 2H, CH$_2$COD); 2.38 (t, $^3J_{HH} = 7.6$ Hz, 2H, Ar-CH$_2$-CH$_2$); 3.81 (m, 2H, CHCOD allyl $\beta$); 4.98 (t, $^3J_{HH} = 8.7$ Hz; 1H, CHCOD allyl $\beta$); 7.03 (m, 5H, CH$_2$PPh$_2$); 7.04 (d, $^3J_{HH} = 8.05$ Hz, CH$_{Ar-SO_2}$, 2H); 7.91 (dd, $J = 7.27$ & $9.62$ Hz, CH$_2$PPh$_2$, 5H); 8.47 (d, $^3J_{HH} = 8.12$ Hz, CH$_{Ar-SO_2}$, 2H). $^{13}$C NMR (75 MHz, C$_6$D$_6$, 300K): δ(ppm): 14.12 (CH$_2$-CH$_3$); 16.23 (dd, $^1J_{CP} = 26.4$ Hz & $^3J_{CP} = 1.6$ Hz, P-CH$_3$, 3C); 22.57 (CH$_2$-CH$_3$); 23.46 (CH$_2$COD); 27.71 (CH$_2$COD); 27.94 (CH$_2$COD); 29.48 (CH$_2$COD); 31.06 (CH$_2$COD); 33.69 (CH$_2$-CH$_2$-CH$_3$); 35.70 (Ar-CH$_2$); 76.73 (d, $^2J_{CP} = 8.6$ Hz, CH$_{COD allyl\beta}$) 81.67 (d, $^2J_{CP} = 19$ Hz, CH$_{COD allyl\beta}$); 109.57 (CH$_{COD allyl\alpha}$); 126.63 (CH$_{Ar-SO_2}$, 2C); 128.01 (d, $^2J_{CP} = 26.4$ Hz, P-CH$_3$, 3C); 128.29 (CH$_{Ar-SO_2}$, 2C); 128.59 (CH$_{PPh_2\ para}$); 129.38 (CH$_{PPh_2\ para}$); 130.83 (d, $^2J_{CP} = 43.8$ Hz, CH$_{PPh_2 ortho\ 2C}$); 130.99 (d, $^2J_{CP} = 44.3$ Hz, CH$_{PPh_2 ortho\ 2C}$); 143.97 (d, $^2J_{CP} = 117$ Hz, C$_{IV\ C-\ nBu}$); 144.64 (d, $^2J_{CP} = 117$ Hz, C$_{IV\ C-\ SO_2}$).

Crystal data

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<th>2(C$<em>{33}$H$</em>{45}$NNiO$_2$P$_2$S)·C$<em>5$H$</em>{12}$</th>
<th>Z = 1</th>
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<tr>
<td>$M_r$ = 1352.95</td>
<td>F(000) = 722</td>
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<tr>
<td>Triclinic, $P$ 1</td>
<td>$D_x = 1.286$ Mg m$^{-3}$</td>
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<td>Hall symbol: -P 1</td>
<td>Mo Kα radiation, $\lambda = 0.7107$ Å</td>
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<td>$a = 8.6911$ (7) Å</td>
<td>Cell parameters from 13849 reflections</td>
</tr>
<tr>
<td>$b = 10.7717$ (7) Å</td>
<td>$\theta = 3.4$–29.2°</td>
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<tr>
<td>$c = 18.951$ (1) Å</td>
<td>$\mu = 0.74$ mm$^{-1}$</td>
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<tr>
<td>$\alpha = 92.304$ (5)°</td>
<td>$T = 150$ K</td>
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<tr>
<td>$\beta = 95.894$ (6)°</td>
<td>Block, yellow</td>
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<tr>
<td>$\gamma = 97.395$ (6)°</td>
<td>$0.47 \times 0.22 \times 0.16$ mm</td>
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<td>$V = 1747.5$ (2) Å$^3$</td>
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Data collection

| Xcalibur, Atlas, Gemini ultra diffractometer | 8989 independent reflections |
| Radiation source: Enhance (Mo) X-ray Source | 6924 reflections with $I > 2.0\sigma(I)$ |
| graphite | |
| Detector resolution: 10.4685 pixels mm$^{-1}$ | $\theta_{max} = 29.7°$, $\theta_{min} = 2.8°$ |
| $\omega$ scans | $\mu = -12 \rightarrow 11$ |
| Absorption correction: analytical | |
| $T_{min} = 0.781$, $T_{max} = 0.909$ | $I = -25 \rightarrow 25$ |
| 47377 measured reflections | |
Chapter 5

Refinement

<table>
<thead>
<tr>
<th>Refinement on F²</th>
<th>Primary atom site location: structure-invariant direct methods</th>
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</thead>
<tbody>
<tr>
<td>Least-squares matrix: full</td>
<td>Hydrogen site location: difference Fourier map</td>
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<tr>
<td>R[F² &gt; 2σ(F²)] = 0.065</td>
<td>H atoms treated by a mixture of independent and constrained refinement</td>
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<tr>
<td>wR(F²) = 0.138</td>
<td>Method, part 1, Chebychev polynomial, (Watkin, 1994, Prince, 1982) [weight] = 1.0/[A₀<em>ΣT₀(x) + A₁</em>ΣT₁(x) + ... + Aₙ<em>ΣTₙ(x)] where Aᵢ are the Chebychev coefficients listed below and x = F/Fmax Method = Robust Weighting (Prince, 1982) W = [weight] * [1-(deltaF/6</em>sigmaF)]² Aᵢ are: 0.145E + 04 0.214E + 04 0.114E + 04 306.</td>
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<tr>
<td>S = 0.99</td>
<td>(Δσ)max = 0.013</td>
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<tr>
<td>8971 reflections</td>
<td>Δ&gt;max = 1.80 e Å⁻³</td>
</tr>
<tr>
<td>397 parameters</td>
<td>Δ&gt;min = -1.03 e Å⁻³</td>
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<tr>
<td>32 restraints</td>
<td></td>
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Symmetry code: (i) -x+1, -y, -z+1.

Hydrogen-bond geometry (Å, °)

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<tr>
<th>D—H···A</th>
<th>D—H</th>
<th>D···A</th>
<th>D—H···A</th>
</tr>
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<tbody>
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<td>C20—H201···O6&quot;</td>
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<td>2.51</td>
<td>3.386 (8)</td>
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</table>

Symmetry code: (ii) x, y+1, z.

Complex 18

A mixture of solid METAMORPhos (o-tolyl) 5 (463 mg, 1.00 mmol, 1.00 eq.), Ni(COD)₂ (275 mg, 1.00 mmol, 1.00 eq.) was dissolved in chlorobenzene (20 mL). To this solution was rapidly added trimethylphosphine (1M in toluene, 1.00 mL, 1.00 mmol, 1.00 eq.). The mixture was left to stir for 15 min, leading to a very dark solution. The solvent was removed under reduced pressure leading to a dark solid. This solid was triturated in 20 mL of pentane leading to a powder and a solvent phase coloured in purple which was syringed out. This operation was repeated 5 times with 5 mL of pentane until a yellow solid was obtained and the pentane phase was no longer purple. The powder was dried under vacuum to give a yellow solid (isolated: 320 mg, yield: 53%). 3¹P{¹H} NMR (121 MHz, C₆D₆, 300K): δ(ppm): -15.10 (d, 2Jₚₚ = 25.8 Hz); 54.75 (d, 3Jₚₚ = 25.8 Hz); ¹H NMR (300 MHz, C₆D₆, 300K): δ(ppm): 0.83-2.28 (signals of CH₃ of COD); 1.00 (d, 2J_HP = 8.5 Hz, CH₃_PMe₃, 9H); 1.76 (s, CH₃_toly, 3H); 2.48 (s, CH₃_toly, 3H); 3.54 (qd, 3J_HH = 8.5 Hz & 2J_HP = 8.5 Hz, CH COD allyl β, 1H); 3.70 (qd, 3J_HH = 8.5 Hz & 3J_HH = 8.5 Hz, CH COD allyl β, 1H); 4.78 (t, 3J_HH = 8.5 Hz, CH COD allyl α, 1H); 6.64-6.87 (m, CH Ar 4a,4b,3b, 3H); 6.96 (t, 3J_HH = 6.9 Hz, CH Ar 2b, 1H); 7.03 (t, 3J_HH = 7.0 Hz, CH Ar 2a, 1H); 7.25 (t, 3J_HH = 7.2 Hz, 1H, CH Ar 3a); 7.62 (dd, 2J_HH = 7.1 Hz & 2J_HH = 17.6 Hz, CH Ar 1a, 1H); 8.84 (d, 2J_HH = 12.0 Hz & 3J_HP = 12.0 Hz, 1H, CH Ar 1a); ¹³C NMR (75 MHz, C₆D₆, 300K): δ(ppm): 16.58 (dd, 2J_CP = 27.1 Hz, 1J_CP = 1.8 Hz, CH₃_PMe₃, 3C); 21.15 (d, 1J_CP = 2.8 Hz-CH₃ tolyl, 1C); 22.55 (d, 1J_CP = 7.4 Hz, -CH₃ tolyl, 1C); 23.03 (s, CH₃ COD); 26.96 (d, 1J_CP = 4.6 Hz, CH₂ COD); 76.20 (dd, 2J_CP = 19.2 Hz & 1J_CP = 4.3 Hz; CH COD allyl β); 85.50 (d, 2J_CP = 17.2 Hz, CH COD allyl β); 109.67 (s, CH COD allyl α); 121.78 (qd, 1J_CP = 322.2 Hz, 1J_CP = 6.5 Hz, C⁺₁V CF₃); 123.26 (d, 1J_CP = 16.9 Hz, CH Ar 3); 125.83 (d, 1J_CP = 8.4 Hz, CH Ar 3); 129.78 (s, CH Ar 2); 130.62 (CH Ar 2); 131.13 (d, 1J_CP = 8.8 Hz, CH Ar 4); 132.18 (d, 1J_CP = 6.5 Hz, CH Ar 1); 132.71 (d, 1J_CP = 5.8 Hz, CH Ar 4); 135.73 (d, 1J_PP = 50 Hz, C⁺₂V ipso).
136.60 (d, $^2J_{CP} = 37.5$ Hz, CH$_{Ar}$); 137.98 (d, $^2J_{CP} = 16.4$ Hz, C$_{Ar}$); 139.50 (d, $^1J_{CP} = 52$ Hz, C$_{ipso}$); 143.97 (s, C$_{C_{Ar}}$).

**5.6 Synthesis and characterisation of hydride complexes 23, 26**

**Complex 23**

![Complex 23 diagram]

METAMORPhos ligand 3: F$_3$C-SO$_2$N=P(iPr)$_2$H (796 mg, 3.00 mmol, 1.00 eq.), tricyclohexylphosphine (825 mg, 3.00 mmol, 1.00 eq.) and Ni(COD)$_2$ (840 mg, 3.00 mmol 1.00 eq.) were placed in a Schlenk and dissolved in toluene (20 mL). The mixture was stirred at 60°C for 16 h leading to an orange solution. Then the solvents were evaporated under reduced pressure to give a solid that was washed with pentane (3 x 10 mL) and dried under vacuum to give a yellow powder (isolated yield: 694 mg, yield: 38 %). Crystals suitable for diffraction were obtained from slow vapour diffusion of pentane in a toluene solution of the complex. $^{31}$P NMR (121 MHz, C$_6$D$_6$, 300K): δ(ppm): 36.1 (dd, $^2J_{PP} = 236$ Hz, $^2J_{PH} = 64$ Hz); 103.4 (dd, $^2J_{PP} = 236$ Hz, $^2J_{PH} = 77$ Hz); $^1$H NMR (300 MHz, C$_6$D$_6$, 300K): δ(ppm): -26.87 (dd, $^2J_{PH} = 77.9$ Hz, Ni-H, 1H); 0.50-2.50 m, signals of Cy and iPr, 47 H). $^{19}$F NMR (282 MHz, C$_6$D$_6$, 300K): δ(ppm): -76.34. E.A. (% th): C: 43.10 (50.21); H: 6.00 (8.43); N: 1.11 (3.66). The product holds inorganic material probably Ni(0).

**Complex 26**

![Complex 26 diagram]

METAMORPhos ligand 7 (F$_3$C-SO$_2$N=PCy$_2$H) (518 mg, 1.50 mmol, 1.00 eq.), tricyclohexylphosphine (420 mg, 1.50 mmol, 1.00 eq.) and Ni(COD)$_2$ (412 mg, 1.50 mmol 1.00 eq.) were placed in a Schlenk and dissolved in toluene (20 mL). The mixture was stirred and heated at 60°C for 16 h. Then the solvents were evaporated under reduced pressure to give a solid that was washed with pentane (3 x 10 mL) and dried under vacuum to give a yellow powder (isolated yield: 465 mg, yield: 45 %). $^{31}$P NMR (121 MHz, C$_6$D$_6$, 300K): δ(ppm): 36.6 (dd, $^2J_{PP} = 236$ Hz, $^2J_{PH} = 67$ Hz); 78.6 (dd, $^2J_{PP} = 236$ Hz, $^2J_{PH} = 82$ Hz); $^1$H NMR (300 MHz, C$_6$D$_6$, 300K): δ(ppm): -26.91 (dd, $^2J_{PH} = 77.4$ Hz, Ni-H, 1H); 0.50-2.50 m, signals of Cy and iPr, 55H). $^{19}$F NMR (282 MHz, C$_6$D$_6$, 300K): δ(ppm): -76.21. E.A. (% th): C: 54.50 (54.40); H: 8.38 (8.25); N: 2.14 (3.66). The product holds inorganic material probably Ni(0).

**6 References**


