Sulphonamido-phosphorus nickel complexes for the selective oligomerisation of olefins: Exploring dissymmetric ligands and supramolecular strategies
Boulens, P.A.

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Chapter 4

Self-Assembled Organometallic Nickel Complexes as Catalysts for Selective Oligomerisation of Ethylene
1 Introduction

Since the discovery by Keim and co-workers that nickel complexes can be highly active catalysts for the oligomerisation of ethylene (Figure 1),[1,2] this reaction has been one of the showcase examples of homogeneous catalysis as it led to one of the key industrial processes, Shell Higher Olefin Process (SHOP).[3,4] Due to the commercial success, the nickel-catalysed ethylene oligomerisation reaction was studied in detail at the fundamental level.[5–10] The market for olefins has slowly changed and there is a growing commercial interest in obtaining selectively shorter linear alpha olefins such as 1-butene, which is only a minor product when the traditional nickel catalysts giving a broad Schulz-Flory product distribution are employed. As such, re-exploring nickel-based catalysts with a different approach could be scientifically and commercially rewarding.

Sulphonamido-phosphorus ligands (METAMORPhos) were recently introduced as a family of highly versatile building blocks for late transition metal complexes (Figure 1).[11–16] They display interesting adaptive coordination behaviour as they coordinate in P and P,O chelating form and in both neutral and anionic states of the ligand. Tuning of the substituents on the sulphonamide allows for the optimisation of specific catalytic properties, e.g. a more acidic character of the R\(^1\)SO\(_2\)-NH-R\(^2\) is anticipated to disfavour the reductive elimination reaction leading to the neutral ligand and inactive Ni(0), resulting in an improved catalyst life time. Moreover, these ligands proved to be particularly suited to construct supramolecular bidentate or tridentate complexes through hydrogen bonding. As it is known that the additional PPh\(_3\) ligand coordinated to the SHOP catalyst displayed in Figure 1 has a great influence on catalyst stability and product distribution,[5–7] we anticipated that nickel complexes based on METAMORPhos and aminophosphine ligands would form supramolecular pincer ligands that due to the dynamic nature of the supramolecular complexes would favour the catalyst stability, but at the same time retain the vacant site required for adequate catalytic activity. While self-assembled ligands by hydrogen bonding, metal-ligand, ionic, and stacking interactions have successfully been developed for noble transition metals such as rhodium, palladium and platinum, and have been applied in various catalytic transformations,[17–31] this approach has hardly been applied for first-row transition metals. To the best of our knowledge, the in situ generated Ni(0) complex that was used as catalyst in the hydrocyanation reaction is the only example, reported by Breit et al.[32] Considering the frequent use of nickel for industrial catalytic transformations there is, however, still a lot of potential for the use of self-assembled ligands. We report here such a supramolecular ligand approach for the formation of stable nickel complexes based on hydrogen bonds, by self-assembly of a METAMORPhos and an aminophosphine ligand. The
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Organometallic nickel complexes are remarkably stable and at the same time form very active and selective dimerisation catalysts for ethylene to form 1-butene as the main product.

![Figure 1. Representative anionic P,O ligand that forms the active nickel based SHOP catalyst (left) and a typical coordination mode of METAMORPhos, an adaptive sulphonamido-phosphorus ligand (right).](image)

**2 Discussion**

Mixing equimolar amounts of nickel(0) bis(1,5-cyclooctadiene) (Ni(COD)$_2$), $i$Pr-NH-PPh$_2$ and 1.NEt$_3$ (or 2) in a chlorobenzene solution led to the selective formation of nickel(II) complex 3 (or 4) in which METAMORPhos coordinates as an anionic ligand. During the formation of the complex the COD ligand was converted to the π-allyl (Figure 2). Such complexes can be formed after oxidative addition of the acidic sulphonamide ligand, and subsequent insertion of the hydride in the double bond of the COD fragment. The supramolecular nickel complexes were isolated as yellow powders (yields up to 57 %) and characterised by $^{1}$H, $^{13}$C and $^{31}$P NMR and the molecular structure was confirmed by X-ray analysis (see experimental part).

![Figure 2. Synthesis of supramolecular nickel complexes 3 and 4.](image)
Crystals of complexes 3 and 4 suitable for X-ray analysis were obtained by slow diffusion of pentane in a toluene solution of the complex. The complexes 3 and 4, displayed in Figures 3 and 4, adopt a square planar coordination geometry, with the phosphorus ligands in cis-position with respect to one another. The nickel atom is formally cationic, whereas the negative charge is delocalised on the NSO fragment of the METAMORPhos ligand, as is also clear from the P-N and N-S bond lengths (intermediate between single and double bond) and the S-N-P angles (typically between sp² or sp¹ hybridised nitrogen, 131.0° for 3 and 134.17° for 4). The anionic NSO site forms a good hydrogen bond acceptor, and indeed there is a hydrogen bond formed with the NHP of the adjacent ligand. Interestingly, for complex 3 the hydrogen bond distance is significantly longer (2.994 Å) compared to that found in complex 4 (N2-H---N1 bond of 2.190 Å, consistent with literature), suggesting that there is a weaker interaction between the ligands in complex 3. The difference in steric bulk between the two METAMORPhos ligands likely accounts for this. Inspection of the solid state structures reveals that in complex 4 the two isopropyl substituents are transversal to the coordination plane, whereas in complex 3 the o-tolyl substituents are opposite to the allyl moiety. The latter geometry results in a rotation of the sulphonamido fragment, increasing the distance to the hydrogen bond donor. This geometry difference in the two complexes is further supported by the switch of the dihedral angle P-Ni-P-N\textsubscript{METAMORPhos} from 28.5° for 4 to 79.3° for 3.

**Figure 3.** ORTEP plot (50% probability displacement ellipsoids) of complex 3. Hydrogen atoms have been omitted for clarity (except for NH moiety). Selected bond lengths (Å) and angles (°): Ni1-P1 2.222(2); Ni1-P2 2.206(2); N2-H2 0.859; N1--H2 2.994; O1--H2 2.844; P2-Ni1-P1 104.55(9).

**Figure 4.** ORTEP plot (50% probability displacement ellipsoids) of complex 4. Hydrogen atoms have been omitted for clarity (except for NH moiety). Selected bond lengths (Å) and angles (°): Ni1-P1 2.2165(17); Ni1-P2 2.2007(13); N2-H2 0.852; N1--H2 2.190; O1--H2 2.588; P2-Ni1-P1 103.96(6).
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These diamagnetic complexes also form in solution as is clear from the $^{31}$P NMR and $^1$H NMR spectra. The two doublets observed in $^{31}$P NMR are shifted downfield with respect to the corresponding ligands and the small coupling constant is in agreement with cis-geometries ($^2J_{PP} = 30$ Hz) as seen in Figure 5. In the $^1$H NMR spectra the signals for the π-allyl fragment are clearly observed at δ(ppm, C$_6$D$_6$): 3.71 (2H) and 5.09 (1H) for complex 3 and 3.36 (1H), 4.19 (1H) and 4.48 (1H) for complex 4 (Figure 6 and Figure 7, respectively). Moreover the NH proton of the co-ligand iPr-NH-PPh$_2$, initially appearing at 1.56 ppm (in C$_6$D$_6$) was shifted to 2.85 ppm for complex 3 and to 5.85 ppm for complex 4 in agreement with a H-bonding interaction between the two ligands.

**Figure 5.** $^{31}$P NMR (121 MHz, C$_6$D$_6$) spectrum of complex 3 showing two doublets with small coupling constants ($^2J_{PP} = 23$ Hz) attributed to a cis arrangement of phosphines around nickel.

**Figure 6.** $^1$H NMR (300 MHz, C$_6$D$_6$) of complex 3 showing two signals of the allyl moiety (the 2 lateral allylic protons are overlapping).
These complexes were evaluated as catalysts in the ethylene oligomerisation at 40°C under an ethylene atmosphere with a pressure of 30 bar in the absence of any additional activator. High selectivity for the formation 1-butene (up to 84% / all products) and good productivity (24 kg_{oligo}/(g_{Ni}•h)) were obtained with steady ethylene uptake over a period of 90 minutes for complex 3 (Table 1 and Figure 8). Based on these results, we formed a new class of nickel complexes which are, to our knowledge, the most robust and efficient organometallic nickel catalyst for 1-butene formation.[5–7,33–40] The high selectivity for short terminal olefins (1-C_4 > 99.0%), i.e. little isomerisation, was also observed when complex 4 was applied as the catalyst. A lower productivity and a clear shift in selectivity to a larger alpha-olefin distribution (Schulz-Flory with K_{SF} = 0.45) were, however, observed. In comparison, the representative industrial benchmark complex (Ref, Figure 1), at higher concentration, required a slightly higher temperature for activation (50°C) and led to a very large Schulz-Flory distribution with a low productivity under equal reaction conditions (K_{SF} > 0.90).

Table 1. Catalytic evaluation of 3, 4 and benchmark complex Ref.

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<th>Complex</th>
<th>n_{Ni} (µmol)</th>
<th>T(°C)</th>
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Test conditions: 30 bar C_2H_4, solvent: toluene (55 mL), 90 min, [a] productivity in kg_{oligo}/(g_{Ni}•h), [b] in wt. %, determined by GC, [c] 1-C_4 wt. % in C_4 fraction, determined by GC.
Self-assembled organometallic nickel complexes as catalysts for selective oligomerisation of ethylene

More information on the active species was obtained from in situ NMR, revealing the rearrangement of both complexes under ethylene pressure. Indeed, at room temperature and under 5 bar of ethylene, the original complex 3 solution turned from orange to green and a new complex formed with two phosphines in trans position as evidenced by the large coupling observed in $^{31}$P NMR (55.5 ppm (d, $J = 271$ Hz); 69.2 ppm (d, $J = 271$ Hz)) illustrated in Figure 9. In the $^1$H NMR no hydride was observed. Similar reactivity was observed with complex 4 leading to a new species (53.5 ppm (d, $J = 275$ Hz); 89.8 ppm (d, $J = 275$ Hz)) illustrated in Figure 10. GC and GC/MS analyses of the NMR solution revealed the presence of short chain olefins (butenes and hexenes) and vinylcyclooctene. These experiments suggest ethylene insertion in catalyst precursor 3 (and 4) with subsequent beta-H elimination or beta-H transfer with ethylene leading to vinylcyclooctene and the nickel-ethyl complex as the resting state (see Figure 11). Concomitantly, the rearrangement of the METAMORPhos ligand under the monoanionic P,O chelating ligand is proposed.

Figure 8. Ethylene uptake for catalysts 3,4 and Ref during the oligomerisation reaction. Initial uptake corresponds to the dissolution of ethylene into the solvent (ca. 13 g of ethylene).
Figure 9. High pressure $^{31}$P NMR (131 MHz, C$_6$D$_6$, 300 K) NMR experiment on complex 3 under 5 bar of ethylene. Above: complex 3 with ethylene (5 bar) immediately after introduction, below complex 3 with ethylene (5 bar) after 45 min.

Figure 10. High pressure $^{31}$P NMR (131 MHz, C$_6$D$_6$, 300 K) NMR experiment on complex 4 under 5 bar of ethylene: complex 4 without ethylene, below complex 4 with ethylene (5 bar) after 45 min.
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3 Conclusion

In conclusion, we report the synthesis and detailed characterisation of stable nickel complexes supported by supramolecular bidendate ligands based on sulphonamido-phosphorus and aminophosphine ligands. The hydrogen-bond between the ligands in the zwitterionic nickel complexes was unambiguously proven in two X-ray structures. Importantly, this novel class of complexes reveals highly active and selective catalyst for ethylene oligomerisation with up to 84 wt. % of 1-butene compared to all products formed. This high selectivity for short linear alpha olefins is interesting considering the change in the market towards such products, and as such these results may renew the interest in the development of a new generation of nickel catalysts. *In situ* NMR experiments under ethylene pressure show the rearrangement of these structures to the proposed monoanionic P,O-P nickel complex as the resting state, that may explain the specific properties displayed by the catalyst. This provides a good starting point for further development and detailed understanding of this new class of nickel catalysts.

4 Experimental part

4.1 General

All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. The trifluoromethanesulphonamide, 1,5-cyclooctadiene, di(o-
tolyl)chlorophosphine and diisopropylchlorophosphine were purchased from commercial suppliers and used without further purification. The ligand 2 and benchmark complex Ref were prepared according to known literature procedure.\cite{1,16} THF, pentane and Et₂O were distilled from sodium / benzophenone. CH₂Cl₂, chlorobenzene and triethylamine were pre-dried and distilled with CaH₂, toluene from sodium, under nitrogen. Alternatively solvents from Solvent Purification System (M-Braun SPS 800) 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 at 25°C with C₆D₆ as solvent. The calibration of the spectrum was performed on NMR solvent signal (C₆D₅H for proton at \(\delta = 7.16\) ppm and C₆D₆ carbon at \(\delta = 128.06\) ppm). Analysis of liquid phase was performed on a GC Agilent 6850 Series II equipped with a PONA column. The gas phase for ethylene oligomerisation was analysed by GC on a HP 6890.

### 4.2 Synthesis of N-isopropyl-1,1-diphenylphosphinamine

![N-Isopropyl-1,1-diphenylphosphinamine](image)

Isopropylamine (1.8 mL, 22.3 mmol, 2.0 eq.) and triethylamine (4.7 mL, 33.4 mmol, 3.0 eq.) were placed in a Schlenk with 10 mL of dry THF. To this mixture was added chlorodiphenylphosphine dropwise (2.0 mL, 11.1 mmol, 1.0 eq.). The mixture was stirred for 10 min at room temperature and the precipitate which formed was filtered off. The filtrate was submitted to vacuum to give a colourless oily liquid. Trituration of the oil in pentane led to a white powder which was washed with pentane (2 x 10 mL). A pure compound was obtained by distillation of the solid under reduced pressure with an isolated yield of 2.1 g (77%). The product was stored at -18°C. \(^{31}\)P\{\(^1\)H\} NMR (121 MHz, C₆D₆): \(\delta(ppm) = 34.94\); \(^1\)H NMR (300 MHz, C₆D₆): \(\delta(ppm) = 0.95\) (s, -CH₃, 3H); 0.97 (s, -CH₃, 3H); 1.56 (m, NH, 1H); 3.22 (m, CH, 1H); 7.0-7.22 (m, CHAr, 6H); 7.4-7.6 (m, CHAr, 4H). \(^{13}\)C (C₆D₆): \(\delta(ppm) = 26.17\) (d, \(J_{CP} = 6.7\) Hz, CH₃, 2C); 48.72 (d, \(J_{CP} = 23.1\) Hz, CH, 1C); 128.4 (m, CHAr, 6C); 131.53 (d, \(J_{CP} = 20\) Hz, CHAr, 4C), CIV not observed.

### 4.3 Synthesis of ligand 1

![Trifluoromethanesulphonamide](image)

Trifluoromethanesulphonamide (2.4 g, 16.1 mmol, 1 eq.) and triethylamine (5.8 g, 41.8 mmol, 6.0 mL 2.6 eq.) were dissolved in dry THF (30 mL). Di(o-tolyl)chlorophosphine was dissolved in another Schlenk in 10 mL of THF. The chlorophosphine solution (4.0 g, 16.1 mmol, 1.0 eq.) was added dropwise to the sulphonamide solution leading to a white precipitate. After 20 minutes, the mixture was filtered to remove the salt and the filtrate was rinsed twice with 10 mL of THF. The liquid phase was evaporated under reduced pressure to give a colorless oil. A white powder was obtained by addition of diethyl ether (20 mL) to the oil. This powder was washed with diethyl ether (3 x 5 mL) and finally dried under vacuum to give the product (isolate yield : 2.5 g, yield : 34%). \(^{31}\)P\{\(^1\)H\} NMR (121 MHz, C₆D₆): \(\delta(ppm) = 15.77\) (s, PH form 12%); 22.62 (broad s, NH-NEt₃ form, 88%); \(^{31}\)P NMR (121 MHz, C₆D₆) \(\delta(ppm) = 15.77\) (d,
Self-assembled organometallic nickel complexes as catalysts for selective oligomerisation of ethylene

PH form, \( ^1J_{HH} = 472.6 \text{ Hz} \); 22.62 (broad s); \(^{19}F \text{ NMR} (282 \text{ MHz, } C_6D_6) \delta(\text{ppm}) = -77.57. \(^1H \text{ NMR} (300 \text{ MHz, } C_6D_6): \delta(\text{ppm}) = \) only the signals of the NH-NEt3 form are reported \( \delta(\text{ppm}) = 0.66 \) (m, CH\(_3\)-CH\(_2\)-N, 9H); 2.14 (q, \(^3J_{HH} = 7.4 \text{ Hz, } CH_3-CH_2-N, 6H) ; 2.36 \) (br s, -CH\(_3\) tolyl, 6H) ; 6.7-7.1 (m, H\(_{Ar}\), 6H) ; 7.5-8.0 (m, H\(_{Ar}\), 2H) ; 8.94 (br s, N-H^{=\cdots}N, 1H). \(^{13}C \text{ NMR} (75 \text{ MHz, } C_6D_6): \) only the signals of the NH-NEt3 form are reported : \( \delta(\text{ppm}) = 8.51 \) (CH\(_3\) NEt\(_3\)) ; 20.75 (d, \(^3J_{CP} = 19.5 \text{ Hz, } CH_3 tolyl\) ) ; 45.83 (-CH\(_2\)-N) ; 122.40 (q, \(^1J_{CP} = 326 \text{ Hz, } CF_3\) ) ; 126.03 (d, \( J = 3.0 \text{ Hz, } CH_{Ar}\) ) ; 129.54 (br s, CH\(_{Ar}\) ) ; 130.57 (d, \( J_{CP} = 4.8 \text{ Hz, } CH_{Ar}\) ) ; 131.65 (br s, CH\(_{Ar}\) ) ; 141.45 (d, \( J = 2.5 \text{ Hz and } 24.3 \text{ Hz, } C^\text{IV}, C_{Ar-CH_3}, 2C\) ).

**4.4 Synthesis and characterisation of complex 3**

A solid mixture of ligand 1 (463 mg, 1.0 mmol, 1.0 eq.), N-isopropyl-1,1-diphenylphosphinamine (244 mg, 1.0 mmol, 1.0 eq.) and Ni(COD)\(_2\) (275 mg, 1.0 mmol, 1.0 eq.) was dissolved in chlorobenzene (20 mL) at 0°C. This mixture was left to stir for 16 h at room temperature, leading to a dark solution. Then the solvents were removed under reduced pressure leading to a dark oil. This oil was triturated in diethylether (10 mL) and the solvent evaporated under vacuum. This operation was repeated twice until a solid formed. The solid was washed with diethyl ether (2 x 10 mL) until the solution became clear. The solid was finally dried under reduced pressure to give the product (isolated yield 190 mg, 25%). A second fraction might be recovered from the ether filtrate. Crystals suitable for X-Ray diffraction analysis were obtained by slow evaporation of a concentrated benzene solution containing complex 3. \(^{31}P\{^1H\} \text{ NMR} (121 \text{ MHz, } C_6D_6): \delta(\text{ppm}) = 52.13 \) (d, \(^2J_{PP} = 23.1 \text{ Hz} \) ); 62.82 (d, \(^2J_{PP} = 23.3 \text{ Hz} \) ); \(^{19}F \text{ NMR} (282 \text{ MHz, } C_6D_6): \delta(\text{ppm}) = -77.70 \text{ ppm} \); \(^1H \text{ NMR} (300 \text{ MHz, } C_6D_6): \delta(\text{ppm}) = 0.41 \) (m, CH\(_3\)-ipr, 3H) ; 0.52 (m, CH\(_2\)-C\(_6\)H\(_5\), 1H) ; 0.93 (m, CH\(_2\)-C\(_6\)H\(_5\)-5H) ; 1.01 (m, -CH\(_3\)-ipr, 3H) ; 1.36 (m, CH\(_2\)-C\(_6\)H\(_5\)-1H) ; 1.61 (m, CH\(_2\)-C\(_6\)H\(_5\)-1H) ; 1.81 (m, CH\(_2\)-C\(_6\)H\(_5\)-1H) ; 2.05 (s, CH\(_3\)-tolyl, 3H) ; 2.23 (m, CH\(_2\)-C\(_6\)H\(_5\)-1H) ; 2.57 (s, CH\(_3\)-tolyl, 3H) ; 2.85 (t, \(^2J_{HH} = 10.1 \text{ Hz, } NH, 1H\) ) ; 2.92 (m, CH\(_3\)-ipr, 1H) ; 3.71 (m, CH\(_{allyl}\) COD\(_{β}\), 2H) ; 5.09 (t, \(^1J_{HH} = 8.4 \text{ Hz, } CH_{allyl}CODα, 1H\) ) ; 6.53 (m, H\(_{toly} \)) ; 6.75 (d, \(^3J_{HP} = 3.9 \text{ Hz, } H_{toly} 4b, 1H\) ) ; 6.77 (d, \(^3J_{HP} = 4.0 \text{ Hz, } H_{toly} 4a, 1H\) ) ; 6.87 (m, H\(_{toly} 3b, 1H\) ) ; 7.02 (m, H\(_{toly} 3a, 1H\) ) ; 7.17 (m, HPPPh\(_2\), 6H) ; 7.20 (m, H\(_{toly} 2a, 1H\) ) ; 7.81 (m, HPPPh\(_2\), 4H) ; 8.04 (m, H\(_{toly} 1b, 1H\) ) ; 8.78 (m, H\(_{toly} 1a, 1H\) ). \(^{13}C \text{ NMR} (75 \text{ MHz, } C_6D_6): \delta(\text{ppm}) = 21.7 \) (CH\(_3\) tolyl) ; 22.1 (CH\(_3\) tolyl) ; 22.9 (CH\(_2\)-C\(_6\)H\(_5\) ; 24.9 (CH\(_3\)-ipr) ; 25.5 (CH\(_3\)-ipr) ; 26.5 (2 CH\(_2\)-C\(_6\)H\(_5\) ; 26.2 (2 CH\(_2\)-C\(_6\)H\(_5\)) ; 46.9 (d, \(^2J_{CP} = 12.2 \text{ Hz, } CH_{ipr}\) ) ; 79.3 (d, \(^2J_{CP} = 18.6 \text{ Hz, } CH_{allyl}CODb\) ) ; 86.4 (d, \(^2J_{CP} = 20.6 \text{ Hz, } CH_{allyl}CODb\) ) ; 110.9 (CH\(_{allyl}\) COD\(_{α}\)) ; 122.0 (qd, \(^1J_{CP} = 322.0 \text{ Hz & } ^2J_{CP} = 6.0 \text{ Hz, } CF_3\)) ; 123.68 (d, \(^1J_{CP} = 11.9 \text{ Hz, } CH_{toly} 2b)\) ; 125.69 (m, CH\(_{toly} 2a)\) ; 128.31 (m, 3C, CHPPPh\(_2\) ) ; 129.9 (d, \(^1J_{CP} = 22 \text{ Hz, } CH_{toly} 3a\) ) ; 130.2 (d, \(^1J_{CP} = 22 \text{ Hz, } CH_{toly} 3b\) ) ; 131.1 (m, CH\(_{toly} 4a\) ) ; 131.6 (m, CH\(_{toly} 1a\) ) ; 132.2 (m, CH\(_{toly} 4a\) ) ; 134.2 (m, CHPPPh\(_2\), 4C) ; 135.0 (m or d, C\(_{toly} COD\)) ; 136.9 (d, \(^1J_{CP} = 48.1 \text{ Hz, } C^\text{IV}\) PPh\(_2\) ipso, 2C) ; 138.3 (m, C\(_{toly} 1C\)) ; 139.6 (d, \(^1J_{CP} = 48.6 \text{ Hz, } C^\text{IV}\) toly ipso) ; 143.6 (m, C\(_{toly} C-Me\) ).
X-Ray structure of complex 3 (see text for picture)

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Data collection

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Refinement

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Hydrogen-bond geometry (Å, °)

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<tr>
<th>( D-H \cdots A )</th>
<th>( D-H \cdots A )</th>
<th>( D-H \cdots A )</th>
<th>( D-H \cdots A )</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2—H2...N1</td>
<td>0.859</td>
<td>2.995</td>
<td>3.775</td>
</tr>
<tr>
<td>N2—H2...O2</td>
<td>0.859</td>
<td>2.844</td>
<td>3.481</td>
</tr>
</tbody>
</table>
4.5 Synthesis and characterisation of complex 4

Ligand 2 (395 mg, 1.5 mmol, 1.0 eq.), N-(diphenylphosphino)isopropylamine (365 mg, 1.5 mmol, 1.0 eq.) and Ni(COD)₂ (415 mg, 1.5 mmol, 1.0 eq) were placed in a Schlenk with toluene (30 mL) and 4 drops of 1,5-cyclooctadiene. Upon dissolution, the mixture turned red. To reach completion, the solution was heated to 50°C for 20 minutes. The solvents were then evaporated to give a sticky solid. This oily solid was co-evaporated twice with 10 mL of pentane to give a solid which was washed with pentane (3 x 10 mL). The powder was re-dissolved in toluene and this solution was filtered to remove solid residue. The filtrate was evaporated and the solid residue submitted to co-evaporation with pentane (2 x 10 mL) followed with washing with pentane (2 x 10 mL). The solid was finally dried under reduced pressure to give a yellow powder (isolated: 574 mg, yield: 57%). Crystals suitable for X-ray diffraction were obtained from slow vapour diffusion of pentane in a toluene solution of 4. ³¹P{¹H} NMR (300 MHz, C₆D₆): δ(ppm) = 85.76 (d, JPP = 30.9 Hz); 60.22 (d, JPP = 31.3 Hz); ³¹F NMR (282 MHz, C₆D₆): δ(ppm) = -78.04 (s); ¹H NMR (300 MHz, C₆D₆): δ(ppm) = 0.8-1.9 (region of -CH₂COD, 10H); 0.99 (dd, J = 5.9 & 14.4 Hz, -CH₃iPrA, 3H); 1.05 (d, J = 5.9 Hz, CH₃iPrC, 3H); 1.19 (d, J = 6.1 Hz, -CH₃iPrC, 3H); 1.34 (dd, J = 16.6 & 6.6 Hz, -CH₃iPrA, 3H); 1.52 (m, -CH₃iPrB, 6H); 2.19 (sept., J = 6.7 Hz, -CH₂iPrC, 1H); 2.90 (m, -CH₂iPrC, 1H); 3.36 (m, CHallylCOD β, 1H); 4.19 (m, CHallylCOD β, 1H); 4.48 (t, JHH = 7.9 Hz, CHallylCOD α, 1H); 5.85 (dd, J = 10.5 & 18.2 Hz, NH, 1H); 7.09 (m, CHAr-m, 6H); 7.62 (m, CHAr-o, 2H); 7.72 (m, CHAr-o, 2H). ¹³C NMR (75 MHz, C₆D₆): δ(ppm) = 18.35 (CH₃B); 18.50 (CH₃A); 19.43 (CH₃A); 19.99 (CH₃B); 22.64 (CH₂COD); 24.75 (CH₃C); 25.25 (CH₃C); 26.92 (CH₂COD); 27.71 (CH₂COD); 29.92 (CH₂COD); 30.72 (d, JCP = 19.2 Hz, CHiPrA); 31.37 (CH₂COD); 32.74 (d, JCP = 19.1 Hz, CHiPrB); 46.78 (d, JCP = 12.4 Hz, CHiPrC); 72.86 (d, J = 15.7 Hz, CHallyl); 81.42 (d, J = 18.2 Hz, CHallyl); 91.50 (CHallylα); 110.50 (CHallylβ); 111.9 (q, J = 323.32 Hz, CF₃); 127.58 (CHAr-m); 128.52 (CHAr-m); 130.44 (d, J = 26.0 Hz, CHAr-p); 132.90 (d, J = 12.05 Hz, CHAr-o); 136.08 (dd, J = 32.3 & 43.0 Hz, CHAr-ips). X-Ray structure determination of complex 4 (see text for picture)
Chapter 4

Xcalibur, Eos, Nova diffractometer  7365 independent reflections
Radiation source: Mova (Mo) X-ray Source  5943 reflections with $I > 2.0\sigma(I)$
mirror  $R_{int} = 0.080$
Detector resolution: 15.9897 pixels mm$^{-1}$  $\theta_{max} = 29.8^\circ$, $\theta_{min} = 3.2^\circ$
$\omega$ scans


$T_{min} = 0.846$, $T_{max} = 0.910$
16282 measured reflections

Refinement

Refinement on $F^2$ Hydrogen site location: difference Fourier map
Least-squares matrix: full H-atom parameters constrained

$R[F^2 > 2\sigma(F^2)] = 0.070$

Method, part 1, Chebychev polynomial, (Watkin, 1994, Prince, 1982) [weight] = 1.0/[A_0*T_0(x) + A_1*T_1(x)+ ... A_n]*T_n(x)]
where $A_i$ are the Chebychev coefficients listed below and $x = F / F_{max}$ Method = Robust Weighting (Prince, 1982) $W = [\text{weight}] * [1-(\Delta/F/6*\sigma(F))^2]^2$ $A_i$ are: 227.285.102.

$wR(F^2) = 0.116$  $(\Delta/\sigma)_{max} = 0.0001$
$S = 0.99$  $\Delta>_{max} = 2.41$ e Å$^{-3}$
7365 reflections  $\Delta>_{min} = -1.81$ e Å$^{-3}$
371 parameters
1 restraint
Primary atom site location: structure-invariant direct methods

Flack parameter: 0.03 (2)

Hydrogen-bond geometry (Å, °)

$$
\begin{array}{ccc}
D—\cdots H & D—H & H—\cdots A \\
N2—H2···N1 & 0.85 & 2.19 \\
N2—H2···O1 & 0.85 & 2.59 \\
\end{array}
$$

Symmetry code: (i) -x, y+1/2, -z.

4.6 High pressure ethylene NMR experiments

For NMR experiments, ca. 20 mg of complex were charged in a high pressure NMR tube in the glove box under argon and dissolved in 0.6 mL of dry, degassed C$_6$D$_6$. The tube was closed and connected outside of the glove box to ethylene supply by the screw cap. The line was purged 5 times (vacuum / ethylene) to get rid of residual oxygen. The ethylene pressure was set at 5 bars and then the screw cap was gently opened to pressurise the tube which was then closed, disconnected and vigorously shaken. All these operations were repeated twice to ensure saturation of ethylene inside the solution contained in the NMR tube.
4.7 Procedure for the oligomerisation of ethylene (semi-batch)

The reactor of 250 mL was dried under vacuum at 100°C for 2 hours and then pressurised to 5 bar of ethylene. The ethylene supply was closed and the reactor was cooled down at room temperature. Ethylene inside the reactor was evacuated, maintaining however a slight over pressure inside the reactor (1.4 bar). The solvent used for catalysis (toluene, 50 mL) was injected and then heated to 40°C (or 50°C) under magnetic stirring (1000 rpm). When the temperature inside the reactor was stabilised, stirring was stopped and the catalyst solution (10 or 50 µmol in toluene: 5 mL) was injected. Then the reactor was pressurised to 30 bar of ethylene and the pressure maintained by connection to an ethylene supply cylinder (80 bar) positioned on a balance (semi-batch). The reaction started (t=0) with magnetic stirring (1000 rpm) and the test ran for 90 min with a regular monitoring the ethylene uptake by the mass reduction of the ethylene supply cylinder. The reaction was stopped by closing the ethylene supply and cooling the reactor to 25°C (250 rpm). The gas phase was evacuated, quantified through a flowmeter and collected in a 30L plastic drum by water displacement (stirring the liquid phase to 1000 rpm was necessary to degas completely the liquid phase). The plastic drum containing the gas phase was shaken with residual water to homogenise the gas and a portion of this gas phase was collected in a glass ampulla and injected in GC. After all the gas fraction had been evacuated, stirring was stopped and the reactor was carefully opened. The liquid phase was transferred with a plastic pipette to a glass bottle cooled to 0°C (to minimise butene losses). The liquid phase was quantified by mass and a cold sample injected directly in GC.

Catalytic reactions were carried out to have significant ethylene uptake, therefore complexes 3 and 4 were run at 10 µmol of nickel while the less active benchmark complex Ref was evaluated at 50 µmol of nickel. Moreover catalytic reaction for Ref requested to be run at 50°C to trigger catalyst activation, as seen by ethylene consumption. Ethylene uptake was monitored as function of time during the catalytic reaction. Dissolution occurs at the start (0-5 min), followed by a linear uptake. In the test conditions (30 bar and 40°C, 50 mL toluene) complex 3 led to an uptake of 48.6 g of ethylene, which corresponds to 21.0 g of oligomers formed, the mass difference being unreacted ethylene. Complex 4, in the same conditions led to an uptake of 30.5 g of ethylene which correspond to 10.2 g of oligomers, the rest consisting of unreacted ethylene. The benchmark complex (Ref) at 30 bar and 50°C, and n_{Ni} = 50 µmol (five times more concentrated than 3 and 4) led to an uptake of 47.9 g of ethylene which corresponds to 32 g of oligomers and waxes and unreacted ethylene. The Schulz-Flory constant (K_{SF}) was established based on the mass percentage of C_{8}-C_{18} cuts.
5 References

Self-assembled organometallic nickel complexes as catalysts for selective oligomerisation of ethylene


