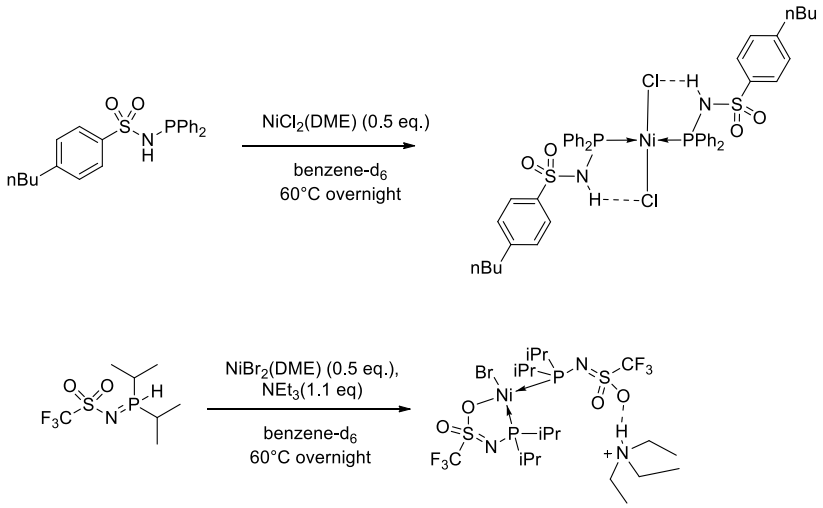
Sulphonamido-Phosporus Nickel Complexes for the Selective Oligomerisation of Olefins. Exploring Disymmetric Ligands and Supramolecular Strategies

P.A. Boulens

Summary

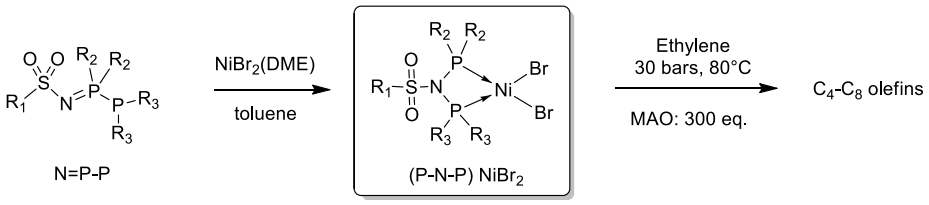
The demand for short Linear Alpha Olefins (LAO) is constantly increasing in the industry, which motivates the search for robust catalysts affording one LAO (1-butene, 1-hexene or 1-octene) selectively. Among the different metals used for ethylene oligomerisation, nickel has certainly the richest history of coordination and organometallic chemistry, documented for over one century now. Phosphine ligands in combination with nickel have shown a strong ability in changing the selectivity of this nickel catalysed reaction. Their robustness permitted their use industrially in the SHOP and Phillips processes for the production of LAOs with broad distribution (Schulz-Flory) or 2-butene. So far, it is still a challenge to find proper nickel complexes to oligomerise selectively ethylene in 1-butene, 1-hexene or 1-octene. For this purpose, we investigated dissymmetric ligands and supramolecular concepts based on sulphonamido-phosphorus ligands aiming for novel, selective nickel catalysts.

In the first part of this thesis, we describe the synthesis of ligand building blocks that facilitate the formation of supramolecular systems based on hydrogen-bonds. A one-step synthesis was developed that allowed the preparation of small libraries of aminophosphines R^1-NH-P(R^2)$_2$, amidophosphines R^1-CO-NH-P(R^2)$_2$, and sulphonamido phosphines (R^1-SO_2-NH-P(R^2)$_2$, known as METAMORPhos). Next to this, we also reported a side reaction that produces iminobisphosphines of formula: R^1-N=P(R^2)$_2$-P(R^2)$_2$. The occurrence of this side reaction strongly depends on the steric parameters at the ligand. Sulphonamido phosphine ligands exist in two different tautomers (NH or PH) while for the amidophosphines three tautomers were observed (NH, PH, OH), a sign of rich electronic variety brought within the ligand library. Coordination chemistry studies of METAMORPhos ligands with Ni(II) revealed the potential of these ligands as at least three different coordination modes with the same type of ligand were observed.

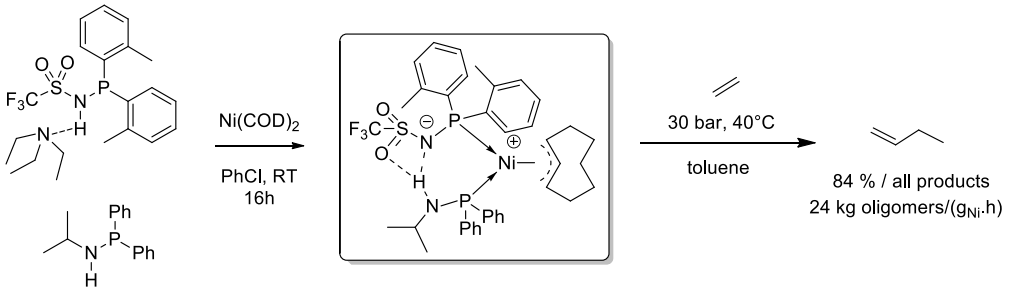


The evaluation of the use of bidentate diphosphine ligands in nickel (II) catalysed oligomerisation has so far been limited to symmetrical ligands, mainly because the synthesis to dissymmetrical ligands is more tedious. We anticipated that dissymmetrical diphosphine ligands with two different phosphine contributions could control elementary steps in the catalysis and favour termination over propagation. We found that iminobisphosphines, in the presence of a nickel (II) precursor, rearranged to form

dissymmetrical diphosphine chelated nickel complex of structure $((R^2)_2P\text{-}N(R^1)\text{-}P(R^3)_2)NiBr_2$ that were isolated and characterised. The rearrangement involves the cleavage of the P-P bond mediated by the nickel complex. Nickel complexes with both symmetrical and dissymmetrical, bidentate ligands were explored in ethylene oligomerisation and when activated with MAO they were active producing short oligomers. The complexes were also active in propylene oligomerisation for which the dissymmetrical nature of the complexes had a direct impact on outcome of the reaction: arylphosphines favoured high selectivity for the dimer while basic phosphines gave high yields of 2,3-dimethylbutenes, a valuable chemical intermediate. The same strategy transposed to chromium did not lead to selective ethylene transformation.

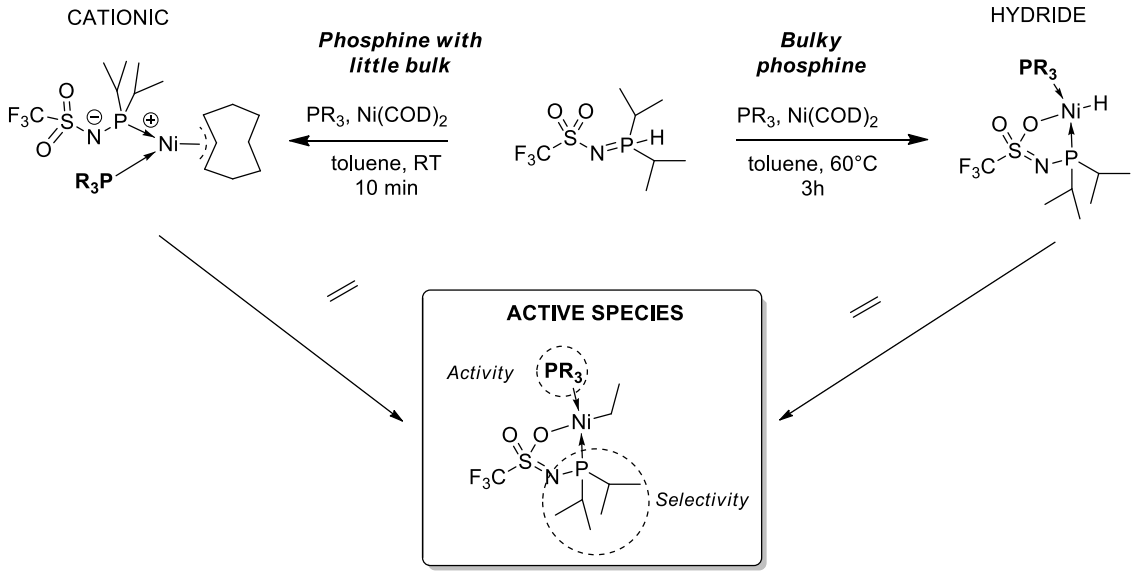


Based on coordination studies of METAMORPhos ligand with nickel, we disclosed a new synthetic approach, based on Ni(0) to generate supramolecular nickel (II) complexes based on the interaction between a sulphonamido phosphine and an additional aminophosphine. The presence of an intramolecular hydrogen-bond in this assembly was unambiguously proven by crystal structures and in solution by NMR analysis of the complexes. This new class of zwitterionic organometallic and supramolecular nickel complexes showed good chemical and thermal stability. Most importantly, these complexes oligomerised ethylene, even in the absence of any co-catalysts, and displayed high activity (up to 24 $kg_{oligo}/(g_{Ni}.h)$). In addition, complexes based on aryl P-substituted METAMORPhos ligands displayed exceptional selectivity for 1-butene, which is currently a highly demanded olefin for polyethylene industry.

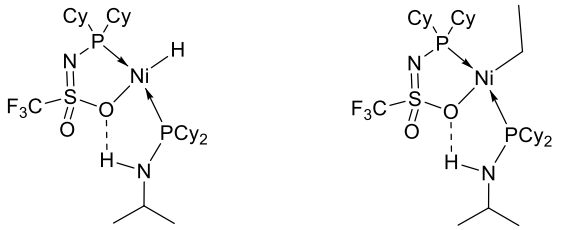


To have a better understanding of this system, we extended this concept to diverse combinations of METAMORPhos ligands with different co-ligands. The formation of a relatively large set of complexes was confirmed by unlocked ^{31}P NMR. We found that bulky co-ligands such as PCy_3 could transform a zwitterionic diphosphine nickel complex to a neutral PO chelated nickel hydride complex. A few nickel hydride complexes were thus isolated using bulky phosphines (PCy_3, $P(t\text{Bu})_3$, $P(i\text{Pr})_3$). Under high-pressure of ethylene, both complexes (zwitterionic and hydride) led to *trans*-(PO,P)Ni-ethyl complex, assigned as the active species. Isolated zwitterionic and hydride catalysts were both active in ethylene oligomerisation, and some complexes gave high selectivity in the formation of 1-butene. By a careful analysis of the structural parameters, we also established that METAMORPhos was responsible for selectivity while the co-ligand regulated activity. We also identified a strong supramolecular control of the stability of the complex. While aminophosphines with a proton donor moiety in combination with the hydrogen acceptor properties of the METAMORPhos ligands

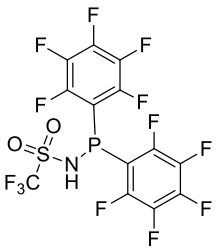
generated zwitterionic complexes that were very stable, complexes with co-ligands with identical electronic and steric parameter that did not have a H-donor, led only to complex decomposition.

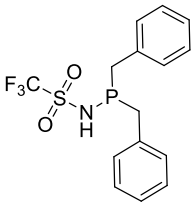


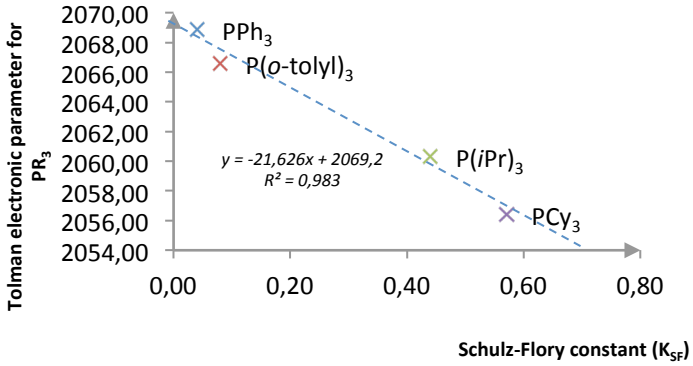
A first perspective for the work described in this thesis is about the mechanism. What is exact role of the hydrogen-bond during the mechanism, and how does the *cis* to *trans* rearrangement under ethylene play a role? Proving that there is a H-bond cannot be easily established by NMR *via in situ* spectroscopy. Isolating the active species or using a characterisation "*in operando*" (IR, NMR …) in combination with DFT calculations could bring new information. Maybe using very basic and bulky aminophosphine co-ligands (in presence of ethylene) could lead to supramolecular hydride complexes with two phosphines in *trans* (or to the corresponding ethyl complex). The nature of the binding of the oxygen atom to the nickel should also be further explored to know what type of interaction exist during catalysis.



A second perspective is about tuning and simplifying the catalyst. We have shown in this thesis that by an efficient ligand tailoring, including the application of hydrogen bonds, we could shift the selectivity in the nickel-catalysed ethylene oligomerisation to produce a distribution of LAO with controlled length (K_{SF}), or even 1-butene selectively. Preliminary insights in the role of each fragment of the nickel complex has been obtained, which highlighted the importance of the METAMORPhos ligand as the key of achieve high selectivity. Also, a tentative correlation was established between the Tolman electronic parameter of the phosphine ligands used and the oligomer distribution modelled by the Schulz-Flory constant (K_{SF}). This approach should be confirmed by using more experimental data points, i.e. by developing METAMORPhos ligands substituted on phosphorus by benzyl groups or by pentafluorophenyl groups. The latter has a value of Tolman electronic parameter of 2090.9 cm^{-1} and therefore is on the edge of the current experimental graph, suggesting that nickel complexes based on this ligand should lead to a complete control of selectivity.






Tolman electronic parameter for PR3
2070,00
2068,00
2066,00
2064,00
2062,00
2060,00
2058,00
2056,00
2054,00
PPh3
P(o-tolyl)3
y = -21,626x + 2069,2
R² = 0,983
P(iPr)3
PCy3
0,00
0,20
0,40
0,60
0,80
Schulz-Flory constant (KSF)