

Highly hindered monophosphines for isolation and reactivity of low valent nickel complexes

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Abstract

This work falls within the context of the conception of new structures and catalysts based on nickel able to produce, selectively and quantitatively, high quality olefins by ethylene oligomerization.

Based on literature, potential monophosphine ligands were selected, based on their electronegative properties and hindrance. The purpose of this internship was first focused on the synthesis of the desired ligands, when they were not commercially available. We then studied their impact on the metal center stabilization, selectivity, and activity whenever possible.

Keywords: Nickel, monophosphines, oligomerization or ethylene.

1. Introduction

Linear alpha olefins (LAOs) are important intermediates for the petrochemical industry. More than 90% of the LAOs are produced by the reaction of ethylene oligomerization [1]. Concerning homogenous catalytic systems, this reaction dominates the current market, where reactivity and product selectivity are now defined by the combination of transition metal surrounded by different ligands.

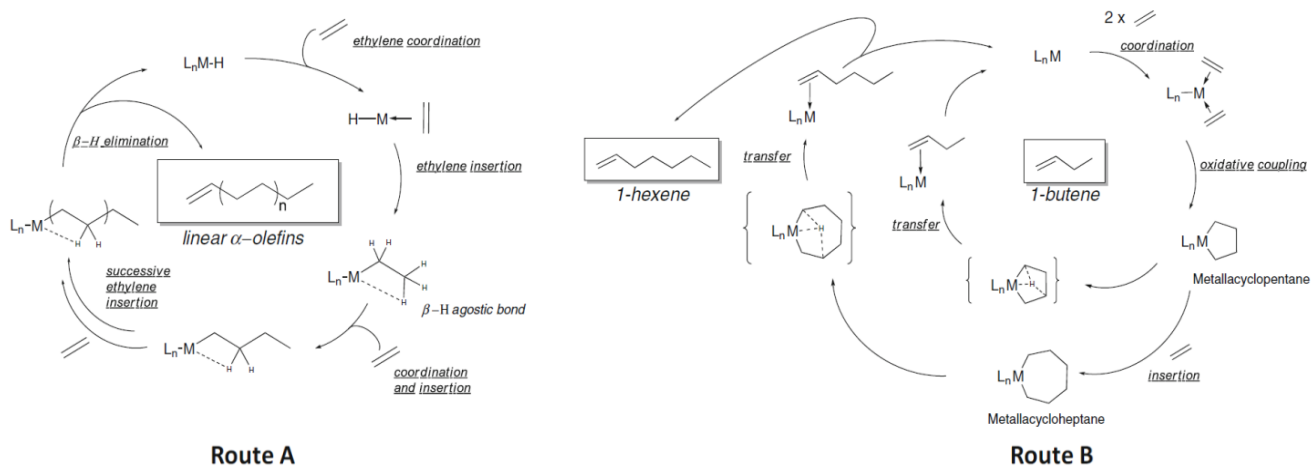
The main applications for short chains LAOs (1-butene, 1-hexene or 1-octene) are as co-monomers for LLDPE and HDPE production, and in poly-alpha-olefins production. It is easy to spot an extra demand in high quality lighter

alpha olefins, due to a larger use as co-monomers. In the meantime, there is a significant shortfall in C₄ fractions caused by refinery industry. The shale gas exploration in North America contributed for the low price, and easy availability, of natural gas [2]. Therefore, a gap between crude oil and natural gas was created, and it made more attractive for companies start to use light feed streams for cracking operations than heavier ones derived from crudes like naphtha. So, if today the principal source of 1-butene supply is refinery, and certainly this is changing, we can expect that, in a close future, a new type of technology can appear to be predominant on selective dimerization of ethylene to 1-butene production.

Nowadays LAOs are produced in *full-range processes* (large distribution of olefins is obtained) and their supply is still led by companies that developed many years ago, such as Chevron Phillips Chemical, Ineos and Shell. In order to explain the large distribution of products, a mechanism it was adjusted: Cossee-Arlman mechanism. It presupposed that, after the insertion of the first ethylene molecule into the active species, the two electrons of the C – H bond in β position will enter in the empty d-orbital of the transition metal creating an agostic interaction. This $\beta - H \cdots M$ agostic bond will allow a successive insertion of several ethylene molecules forming a chain. A classic $\beta - H$ elimination, with a formation of a double bond, will terminate the chain development producing a linear α -olefin and renewing the active catalyst. The renewed catalyst will start a new cycle.

In the meantime, significant progress towards selective production of LAOs has been made and new processes emerged. These *on purpose processes*, based on transition metals for homogeneous catalysis, achieved to produce selectively high quality alpha olefins such as 1-butene, 1-hexene and 1-octene.

Once again a mechanism was adjusted: the metallacycle mechanism. It assumes that two molecules of ethylene must be coordinated to the metal center in order to form a metallacycle through oxidative coupling. After the metallacycle is formed, the insertion of several ethylene molecules is not favored due to the instability of these intermediate species. In fact, the $\alpha - H$ proximity force by the metallacycle, makes easier the hydrogen transfer breaking the cycle in a small olefin (at the same time the catalyst is renewed and starts a new cycle). The nature and architecture of the metal-ligand species allow a short insertion number of ethylene molecules determining the selectivity of the final product. As we can see, the crucial step of this mechanism is the oxidative coupling to form the metallacycle.



Scheme 1 - Ethylene oligomerization mechanisms: degenerative polymerization (route A), metallacycle pathway (route B) [1].

2. Aim of the project

Among all the available transition metals, nickel-based complexes were considered as a possible candidates for selective processes.

Moreover, from recent achievements with similar species in this field, a perimeter of potential ligands was identified. These ligands as metal center stabilization, easy characterization, or even accessible synthesis and isolation.

The aim of this work consists in the synthesis and the full characterisation of several highly hindered phosphine ligands.

3. Results and Conclusions

Due to their specific properties, ligands always plays a crucial role in homogeneous catalysis. Based on literature, a perimeter of potential ligands was defined for the development of original nickel catalysts. Our work focused on the synthesis of the desired ligands, when not commercially available.

To discover the right phosphine structure, the first approach was to map the influence of different phosphines in terms of hindrance, electronegative properties (basicity and charge), in order to find the right conditions of steric inhibition and metal stabilization.

Just to clarify: besides their chemical properties, another advantage of working with phosphines is the capability to isolate and characterize products and intermediate species, they are very easy to characterize by $P31-NMR$. Therefore, almost every times, it is possible to follow reactions.

3.1 Monophosphines Ligands

a) *Buchwald phosphines*: This class of phosphines are highly hindered and used mainly with palladium for different catalytic transformations. For example, in 2010 P. Leeuwen et al. [5] disclosed the telomerization of butadiene with methanol using these complexes. Several types of complexes were used, but the best results were achieved with complexes that presented a structure very close to the desired one, that can lead to the formation of the nickellacycle. Through these results, Buchwald class of phosphine became a strong candidate to test, once that the bis-aryl moiety could stabilize the nickel species thanks to a "weak interaction". In addition, none of these ligands were reported on nickel.

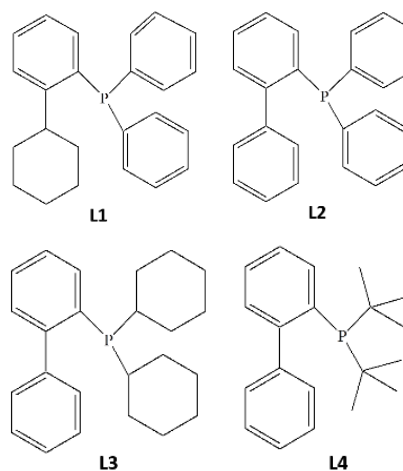


Figure 1 - Selected Buchwald phosphines: L1 and L2 synthesized; L3 and L4 commercially available.

The ligands **L1** and **L2** were synthesized and characterized with success, with purities over than 97%, while the ligands **L3** and **L4** were purchased from external suppliers.

b) *Mixed isopropyl and tertbutyl phosphines*: following the same methodology presented, and based on literature, a second group of

phosphines were selected (figure 2). Some of these phosphines used as ligand in palladium systems, namely Pd(0) and Pd(I), are known to favor the dimerisation of ethylene. Their ability to stabilize the metal centers with rare oxidative state was also demonstrated [6]. The phosphines **L5** and **L7** were obtained from external suppliers, while **L6** was synthesized and characterized with success (96% purity).

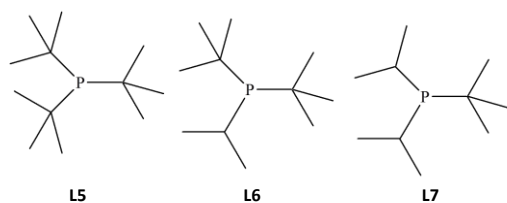


Figure 2 - Second group of selected monophosphines.

c) *Anionic phosphine*: another possible strategy is to use anionic ligands. As it is quite impossible to have a located negative charge on the α -carbon, the strategy is to have a delocalized negative charge on this carbon by forming an aromatic structure. Sheng-Hua Liu et al. [7] synthesized and characterized one type of ligand phosphine, *2-phenylindenyl phosphine* (**L8**), capable to be changed into anionic and to have the mentioned properties. They utilized it in palladium-catalyzed Buchwald/Hartwig amination reactions in DME, but this ligand can also be used to coordinate Ni(0) species, and applied to ethylene oligomerization. In this part, we investigated the influence of the negative charge on the stability and the reactivity of the nickel complex. So, the ligand **L8** was synthesized and characterized with success, 96% of purity, while **L9** was formed *in situ* using **L8** and a common base, as *t*BuONa.

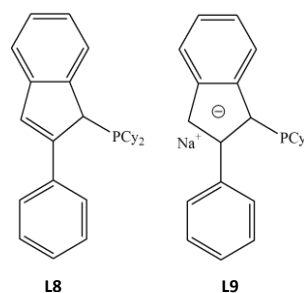


Figure 1 - (2-phenylindenyl)dicyclohexylphosphine (neutral **L8**; anionic **L9**) [7].

d) *Silicon and Tin moieties*: Two new potential tin structures were found thanks to the studies made by Hatnean *et al.* [8] on carbon-hydrogen stannylation. They were able to isolate and characterize Ni(0) complex coordinated by monophosphine, like the complex $(iPr_3)Ni(\eta^2-Bu_3SnCH=CH_2)_2$, that are active species for catalytic stannylation of partially fluorinated aromatics. The important point here is not the fluorinated final species, but the path they took to achieve them. It was possible to note that the two olefinic ligands structured by tin, that they handled, are both easily replace by the ethylene molecules making the coupling.

Taking into account this great achievements, we decided to use this moieties, which the *tributylvinyltin* (tbvt) was commercially available while we synthesized and characterized with success the *triphenylvinyltin* (tpvt).

4. Experimental part

All reaction and sensitive samples were carried and handled under argon atmosphere, using schlenk techniques, or in the glove box. All solvents used on sensitive synthesis came from a SPS solvent system. Several starting materials

were acquired from three main external suppliers: Alfa Aesar (*1-bromo-2-cyclohexylbenzene*; *chlorodiphenylphosphine*; *2-bromobiphenyl*; *2-biphenyl-di-tert-butylphosphine* (**L4**); *di-tert-butylchlorophosphine*; *tert-butyl-diisopropylphosphine* (**L7**); *tributylvinyltin* (tbvt) and *triphenyltin chloride*), Sigma Aldrich (*n-butyllithium*; *(2-biphenyl)dicyclohexylphosphine* (**L3**); *isopropylmagnesium chloride*; *copper(I) chloride* and *2-phenylindene*) and Strem Chemicals (*tri-tert-butylphosphine* (**L5**); *chloro-dicyclohexylphosphine*; *vinylmagnesium bromide* and *bis(1,5-cyclooctadiene)nickel*).

NMR spectra were recorded on a Bruker 300 MHz spectrometer, where chemical shifts are reported in ppm and coupling constants (*J*) are expressed in Hertz. All the solvents used were previously deuterated by freeze pump technique.

4.1 Ligands syntheses

(2-cyclohexylphenyl)biphenyl-phosphine (L1) - A solution of *n-butyllithium* (3,13 ml; 5,0 mmol) was transferred dropwise via a cannula to a freshly prepared solution of *1-bromo-2-cyclohexylbenzene* (1,20 g; 0,93 ml; 5,0 mmol) in diethyl ether (15 ml) at -10°C (salted ice bath) and then let it warmed until 0°C . The bright mixture was stirred for 2 hours at this temperature, after which a solution of *chlorodiphenylphosphine* (1,10 g; 0,92 ml; 5,0 mmol) in diethyl ether (10 ml) was added slowly at -10°C . The addition colored the reaction mixture, first to light yellow and finally white. Stirring was continued for further 2 hours at 0°C . After, slow warming to room temperature, in which some solid material precipitated (inorganic salts). Solid and liquid layers were separated by cannula filtration and the solvent was removed under vacuum. A light yellow crude was obtained; after one night in

the fridge (6°C), white crystals were formed in ethanol (previously dried in 3 \AA sieves to afford a content around 60 ppm of H_2O). After filtration and removal of the solvent under vacuum, the white powder was obtained with a yield of 86% (1,50 g).

^{31}P NMR (300MHz, CD_2Cl_2) δ : $-15,92$ ppm.

^1H NMR (300MHz, CD_2Cl_2) δ : 1,14 – 1,79(*m*, 10H, $\text{CH}_2(\text{Cy})$); 3, –3,38(*m*, 1H, $\text{CH}(\text{Cy})$); 6,82 – 7,36 (*m*, 14H, aromatics).

(2-diphenyl)biphenyl-phosphine (L2) - This reaction was performed exactly as the synthesis of *(2-cyclohexylphenyl)biphenyl-phosphine* with two exceptions: a different solution of bromo precursor, *2-bromobiphenyle* (1,17 g; 0,85 ml; 5,0 mmol); and the purification process: instead of recrystallization in ethanol, the white powder was obtained by precipitation after the oily product, in dried ethanol, was taken into the ultrasonic device. After solvent removal, the white powder was isolated with a yield of 76% (1,29 g).

^{31}P NMR (300MHz, CD_2Cl_2) δ : $-13,65$ ppm.

^1H NMR (300MHz, CD_2Cl_2) δ : 7,03 – 7,44(*m*, 19H aromatics).

di-tert-butylisopropylphosphine (L6) - A solution of *isopropylmagnesium chloride* (2M in THF; 2,4 ml; 4,7 mmol; 1,5 equivalents) was added, at 0°C (ice bath) dropwise during 1 hour, into another solution, of *di-tert-butylchlorophosphine* (0,57 ml; 3,1 mmol; 1,0 equivalents) and *copper(I) chloride* (10 mg; 0,10 mmol; 0,03 equivalents) in THF (5 ml). After the addition was completed, the reaction media was further stirred for 3 h at 0°C . The resultant media was warmed until room temperature and stirred overnight. The reaction mixture was quenched with a saturated solution of NH_4Cl (5 ml), previously degassed, and with Et_2O (5 ml), also previously degassed. The aqueous phase was extracted with Et_2O (10 ml), and then the organic layers were combined and washed with degassed water (20 ml). When the organic phase was transparent, the phases were separated, and the organic was dried over MgSO_4 and filtrated via cannula to remove the solid particles. This medium was concentrated under vacuum to afford a colorless oil. This oily product was

dissolved in pentane and filtrated through activate alumina; the compound was again dried under vacuum to afford a colorless oil, in an amount of around 0,05 g.

^{31}P NMR (300MHz, C_6D_6) δ : 46,33 ppm.

^1H NMR (300MHz, C_6D_6) δ : in, δ : 1,18 – 1,34 (m, 24H, CH_3); 3,24 – 3,38(sep, 1H, CH).

(2-phenylindenyl)dicyclohexylphosphine (L8) -

The 2-phenylindene (1,55 g; 7,8 mmol; 1,0 equivalent) was dissolved in diethyl ether (50 ml) and cooled to -78°C in a bath of dry ice in acetone. A solution of *n*-BuLi (1,6M in hexane; 5,0 ml; 8,0 mmol) was added dropwise. The mixture was stirred at the same temperature for 30 minutes, and then for further 3 hours at room temperature. Then, the resulting media was cooled again until -60°C (dry ice only), and a solution of chlorodicyclohexylphosphine (1,8 g; 7,8 mmol; 1,76 ml) was added slowly. The final mixture was warmed until room temperature and stirred for additional 2 hours. After stirring, the white precipitate (lithium chloride) was removed by filtration over a Pad of Celite under schlenk conditions. The solvent was removed by evaporation under vacuum, affording a light yellow solid, that was dissolved in the minimum amount of toluene. This media was taken into the fridge (-18°C) in which white crystals were obtained with a yield of 30% (0,50 g).

^{31}P NMR (300MHz, C_6D_6) δ : 11,03 ppm.

^1H NMR (300MHz, C_6D_6) δ : 0,66 – 2,06(m, 20H, Cy); 2,14(d, 1H, CH(Cy)); 2,36(d, 1H, CH(Cy)); 4,54(s, H, CHP); 7,16 – 7,72(m, 10H, aromatics).

triphenylvinyltin - First, the triphenyltin chloride (5,0 g; 13,0 mmol; 1,0 equivalent) was dissolved in heptane (20 ml) and heated until 70°C . Then a solution of vinylmagnesium bromide (1M in THF; 15 ml; 1,15 equivalents) was added during 1 hour. The resultant media was taken up to 90°C and stirred under reflux during 3 hours. After the mixture was cooled until room temperature, the reaction was quenched with a solution of HCl (1M) and water in order to neutralize the remaining start material. The aqueous phase was extracted with heptane. The organic phase, after being washed

and separated, was filtrated through celite, and then heptane was evaporated under vacuum affording a white oil. The minimum quantity of dry ethanol (~ 60 ppm) was added, in order to dissolve the oil, and the media was taken into the fridge (-18°C), in which white crystals were obtained. After filtration and removal of the solvent under vacuum, the final product was obtained with yield of 68% (3,34 g).

^1H NMR (300MHz, CD_2Cl_2) δ : 5,97(dd, 1H, $J_1 = 2,96\text{Hz}$); 6,5(dd, 1H, $J_2 = 13,34\text{Hz}$); 6,84(q, 1H, $J_{31} = 20,71\text{Hz}$); 7,35 – 7,67(m, 15H, aromatics).

^{13}C - NMR (300MHz, CD_2Cl_2) δ : 128,54(C - meta); 129,04(C - para); 134,95($\text{CH}_2 = \text{CH}$); 136,98(C - ortho); 137,33(C - Sn); 138,15($\text{CH} = \text{CH}_2$).

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