

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

Tiago João Neves

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Supervisors: Pierre-Alain Breuil

Typhene Michel

Prof. Ana Margarida Martins

Examination Committee

Chairperson: Prof. José Manuel Madeira Lopes

Supervisor: Prof. Ana Margarida Martins

Members of the Committee: Prof. Pedro Teixeira Gomes

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“A book is proof that humans are capable of working magic”

Carl Sagan

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Resumo

O objetivo deste projeto consistiu na concepção de novas estruturas e catalisadores para oligomerização seletiva do etileno.

Para atingir este objetivo, e baseando-nos na literatura disponível, foram selecionadas potenciais monofosfinas ligantes com base nas suas propriedades eletronegativas e de impedimento estereoquímico.

O ligantes desejados foram sintetizados com sucesso, e quando possível adquiridos comercialmente.

Palavras-chave: Níquel, monofosfinas, oligomerização, etileno.

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Abstract

This work fall within the context of the conception of new structures and catalysts for ethylene oligomerization.

Based on literature, potential monophoshines ligands were selected, based on their electronegative properties and hindrance.

The desired ligands were synthesised, with success, when they were not commercially available.

Keywords: Nickel, monophosphines, oligomerisation, ethylene.

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Abbreviations

%	percent	LAO	linear alpha olefins
°C	degree Celsius	LLDPE	linear low density polyethylene
μ	micro	M	molarity (mol/L)
1-C₄	1-butene	MAO	methylaluminoxane
1-C₆	1-hexene	mg	milligram
1-C₈	1-octene	mL	milliliter
Å	angstrom	mmol	millimol
Ar	aryl	nBu	n-butyl
AAGR	average annual growth rate	Ni	nickel
C	carbon	NMR	nuclear magnetic resonance
C₂H₄	ethylene	P	Phosphorus
C₆D₆	deuterated benzene	Ph	phenyl
C₆D₈	deuterated toluene	ppm	parts-per-million
CD₂Cl₂	deuterated dichloromethane	R	any carbon containing group
C_n⁺	oligomers greater than n	RT	room temperature
CH	cyclohexane	SHOP	Shell Higher Olefin Process
COD	cyclooctadiene	Sn	tin
CPC	Chevron Phillips Chemical	SPS	solvent purification system
Cy	cyclohexyl	T	toluene
DEAC	diethylaluminium chloride	tBu	tertbutyl
DFT	Density functional theory	THF	tetrahydrofuran
DME	1,2-dimethoxyethane	US	United States
EADC	ethylaluminium dichloride	vs	versus
EASC	ethylaluminium sesquichloride	XRD	x-ray diffraction
et al.	<i>et alii</i>	Zr	zirconium
g	gram		
GC	gas chromatography		
h	hour		
HDPE	high density polyethylene		
Hz	Hertz		
iPr	isopropyl		
J	coupling constant		

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1 Introduction and Scope

1.1 Context

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. 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.

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. In 2012, the total world production of LAOs was accounted for 3,5 Mt, with an *Average Annual Growing Rate (AAGR)* of 3,5% in high quality olefinic fraction from C₄ to C₁₀ [1]. The LAOs market trend is the following: the demand for short LAOs increases faster than C₁₀⁺ LAOs, consequently solutions favoring the production of short LAOs have to be developed.

Table 1 - Market survey of alpha olefins production [2].

	LAO	1-butene	1-hexene
Demand 2006 (Mt)	4,3	1,1	0,5
AAGR (%)	2006-2020	2006-2020	2006-2020
	3,5	5,3	4,7

Table 2 - Importance of LAO for the plastics industry (LLDPE and HDPE) [3].

Demand 2011 (%)	1-butene	1-hexene	1-octene
LLDPE	78	59	73
HDPE	14	32	2
Other	8	9	25

Table 3 - Different use of alpha olefins in industry depending on their chain length [3].

Chain Length									Applications
C ₄ ⁻	C ₆ ⁻	C ₈ ⁻	C ₁₀ ⁻	C ₁₂ ⁻	C ₁₄ ⁻	C ₁₆ ⁻	C ₁₈ ⁻	C ₂₀ ⁻	
■									LLDPE, HDPE
	■								PVC/plasticizers
		■							Lubricants
			■						Herbicides, plastics
				■					Acids, detergents, alcohols
					■				Surfactants
						■			Lubricant additives
							■		Preservatives
								■	Antistatics

This extra demand of high quality lighter alpha olefins is due to a larger use as co-monomers for LLDPE and HDPE production. 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 [4]. 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.

Several processes have been developed and industrialized to meet market requirements, once it is of prime importance to improve both activity and selectivity of olefin oligomerization to obtain the desired oligomers. These developments have been focusing on catalyst technologies and process development to increase productivity, selectivity and sustainability. It is well known that the adaptation of the architecture and composition of the ligand to the nature of the metal and their mode of activation plays an important role to control all these variables.

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. These three major companies operate with different catalytic systems, the oldest one is from the end of 1960s, based on aluminum; a biphasic system using nickel catalysts (SHOP process) appears in the end of 1970s, and later, just in the 1990s, appeared processes using zirconium(IV) complex. All these process developments made over the years were required by demand and accomplished with great achievements in technology.

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.

Table 4 - *On purpose* processes for selective production of 1-butene, 1-hexene and 1-octene [1].

LAO produced	Process/Company	Catalyst type	Capacity (kt/y) ^a
1-Butene	AlphaButol/Axens	Ti/AlR ₃	708
1-Hexene	CPChem	Cr/ AlR ₃	397
1-Hexene	AlphaHexol/Axens	Cr/ AlR ₃	50 ^b
1-Hexene	Mitsui	Ti/ 'MAO'	30
1-Octene/1-Hexene	Sasol	Cr/ 'MAO'	100

Only commercialized processes are cited here.

^a Includes planned capacities

^b Total capacity for 2 AlphaButol and AlphaHexol units

Although almost all available ethylene comes from petroleum derivatives, there are some new emerging alternative technologies and processes, such as ethylene production from biomass. Starting with bio-ethanol, that has a production of around 100 billion liters per year, it is possible to produce bio-plastics using alumina or silica-alumina based acid catalyst. Besides the big environmental advantages, bio-ethylene is chemically identical and the final cost production will be almost equal to the petrochemical ethylene. Today, bio-ethylene only represents 0,3% of the market, but if all bio-ethanol used in transports sector was used to produce bio-ethylene it would be possible to cover 25% of the demand [5].

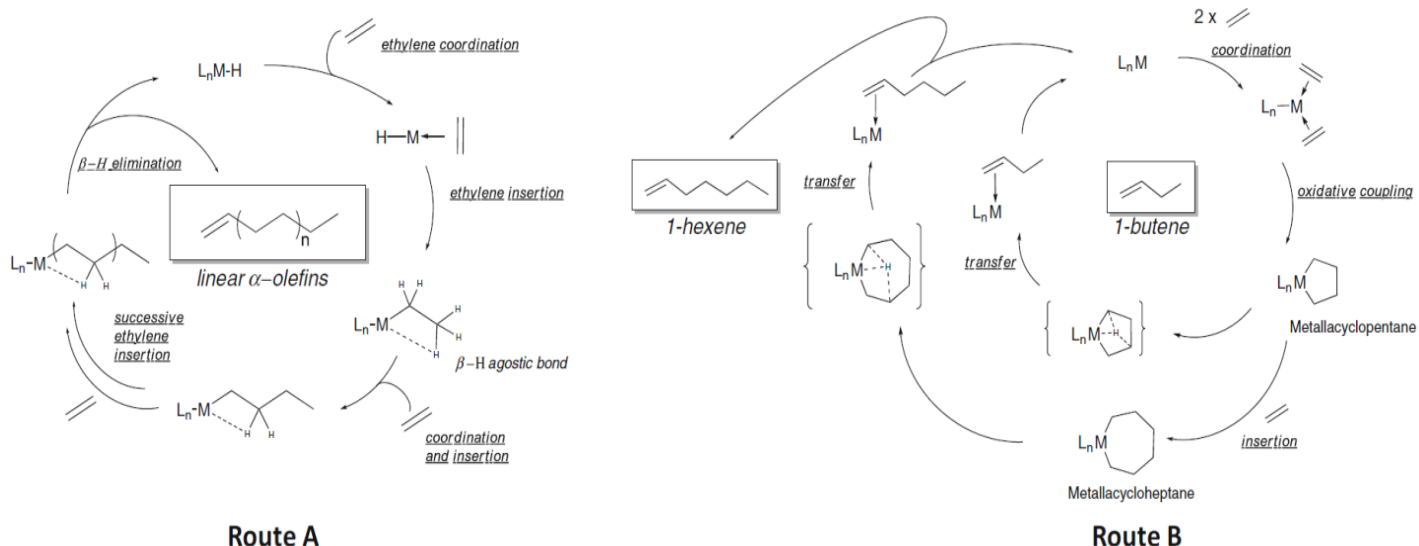
Just to resume, there will be always available ethylene for oligomerization reactions, whether it comes from petrochemical industry or from the renewable emerging sources. To meet the demand in short LAOs, companies have to provide new solutions. The development of new *on purpose processes* will be successful thanks to new scientific breakthroughs. Due to their big flexibility, transition metal catalysts have a great potential to achieve all these new goals.

1.2 State of Art

1.2.1 Cossee-Arlman Mechanism vs Metallocycle Mechanism

Focusing on the state of art in the oligomerization reaction, it is observable that numerous transition metals (from group 4 to group 10) led to active catalysts. Besides activity, the selectivity is also crucial, and results from the right combination metal-ligand that must be chosen wisely in order to obtain the desired main product.

Depending on the metal properties, it was adjusted to the type of mechanisms corresponding to one of the two types of processes. It is believed that the *full range processes* occur via degenerate polymerization mechanisms (route A, Cossee-Arlman Mechanism) and the *on purpose processes* follow a selective path that goes through a metallocycle mechanism (route B). The following schemes describe the different routes to the desired products.



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

The adjusted mechanism of *Cossee-Arlman* 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.

Regarding the second mechanism it was assumed 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. This theoretical mechanism explains the results obtained with some metals used on selective ethylene oligomerization.

There are some examples of zirconium catalysts for ethylene oligomerization. Zirconium-based systems, like cyclopentadienyl-based complexes activated by MAO, appeared very early as efficient catalysts but for ethylene and propylene polymerization. In order to maximize the amount of alpha olefins in the co-monomer range, the processes were specially developed to produce mainly C_4 to C_{12} . SABIC-Linde and IFPEN/Axens processes are by far the most widely described and they operate in the liquid phase using a proprietary soluble zirconium-based catalytic system activated *in situ* by an alkylaluminium co-catalyst [1], affording ethylene oligomers with a Schulz-Flory type distribution. A great number of attempts by academia have been quite unsuccessful to selective ethylene oligomerization into 1-butene, 1-hexene and 1-octene with zirconium catalysts. Other metals, like iron, follow the same Cossee-Arlman mechanism [1].

Aiming on selective catalyst examples for selective dimerization and trimerization of ethylene, titanium-based homogenous catalysts proved their high importance. The AlphaButol process was the first commercially viable process for 1-butene production, developed in the 1980 by IFPEN and SABIC. The catalytic system is based on a proprietary titanium(IV) precursor and an alkylaluminum co-catalyst which are both injected in the reactor to generate the active species. Studies were carried out to understand the role of the different species and the mechanisms: the selectivity obtained was first explained with the metallacycle mechanism, but recent studies showed that this system could go through a Cossee-Arlman mechanism (the question is still under debate [6]). Regarding ethylene trimerization to 1-hexene, a large number of researches have focused on the hemilability of the ligand. To give a specific example, the trimerization of ethylene was achieved recently by Fujita *et al.* using titanium complexes bearing phenoxy-imines ligands with pendant aryloxy donors [7].

Chromium systems present the best activity and selectivity in ethylene trimerization, they are also capable of selective tetramerization [1]. It was in the 1960 the first report of chromium complexes to oligomerize selectively ethylene to 1-hexene, since then, many improvements were made. The relevant catalytic systems commercialized work with well-defined alkylaluminum and/or

chloroalkylaluminum co-catalyst; the use of pyrrolide and aryloxide ligands are also reported by CPChem and IFPEN, respectively. These systems, associated with Cr (III), lead to selectivities in 1-hexene over than 99%, and this technology was implanted in several facilities in Qatar, Saudi Arabia and also in Texas [1]. Many new studies in ligand structure and activator compounds are ongoing to improve these systems that follow the metallacycle mechanism.

1.2.2 Catalysts based on Nickel

Among all the available transition metals, this study will be focusing on nickel, as a possible candidate for selective processes.

Nickel is commonly encountered in nature as Ni (II) compounds, but valences $-1, 0, +1, +3$ and $+4$ also exist. Three main geometries (based on the valence-bond-theory) are relevant to explain the special organization of nickel complexes: square planar, tetrahedral and octahedral. Regarding Nickel (II) complexes, that have 4 coordinated ligands, square planar or tetrahedral geometries are described. Square planar complexes are always diamagnetic and observable by NMR, whereas paramagnetic complexes result in undefined signals with a background noise.

It is possible to distinguish two main families of active nickel species, differentiated by the nature of the ligand coordinated on the metal center: *cationic (A)* and *neutral (B) nickel catalysts*.

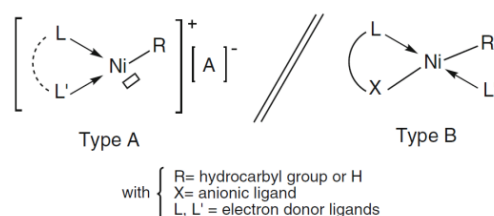
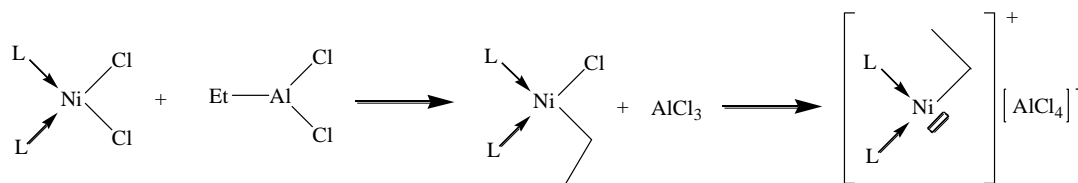


Figure 1- The two main families of Ni active catalysts [1].

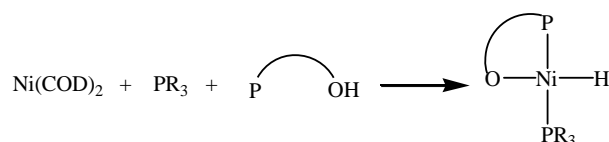
Type A species are electronically unsaturated and highly electrophilic, they incorporate donor monodentate or bidentate ligands and present generally a square planar geometry; they also present high reactivity that makes isolation very difficult, in fact they are formed *in situ* with nickel precursor plus activator. These types of catalysts are highly active homogenous catalysts for ethylene and propylene dimerization. From this first family, were developed two important industrial nickel-catalyzed processes: Dimersol/Difasol Axens (C_3/C_4 to C_6/C_8) and Phillips processes (C_2 to 2-butene).

Also concerning type A compounds, the activation mechanism plays a crucial role to form the active species. An activator agent must be used, the most popular being aluminum-based activators, such as, ethylaluminiumdichloride (EADC), ethylaluminiumsesquichloride (EASC) or methylaluminoxane (MAO). In the scheme bellow, we describe the proposed mechanism of activation: the catalyst, composed by L_2NiX_2 , will be alkylated by the co-catalyst replacing one X ligand, then the second anionic ligand will be captured to form the final active species. It is very important to adapt the molar ratio and the type of co-catalyst to the desired system/conditions.



Scheme 2 - Activation mechanism with dichloroethylaluminum.

Type B species are usually composed by anionic L – X type ligands, based on oxygen or nitrogen, and a Ni – C or Ni – H active bond in which the olefin will be inserted to begin the catalytic cycle. In the end of 1970, Keim described and first isolated nickel complexes combining soft phosphorous and hard anionic oxygen atom in a chelate P – O ligand, forming an isolable model of the SHOP type catalysts [8] [9]. The SHOP process operates in a biphasic system (liquid/liquid technology but not aqueous) using 1,4-butanediol as the catalyst solvent, it was the first commercial catalytic process of his kind. In toluene, they produce 99% of linear alpha-olefins, mainly $C_{12}^{\equiv} - C_{18}^{\equiv}$, under 50 bars of ethylene at 50°C with an activity of $60000 g_{C_2H_4}/(mol_{Ni} \cdot h)$ [1].



Scheme 3 - Example of SHOP catalyst formation by Keim.

The SHOP type catalyst had a huge impact in the development of well-defined (pre)catalysts. So, to rationalize the ligand effects Keim *et al.* suggested an analysis of the ligands by fragmentation of the complex in a chelate part and an organo part [10]. The chelate part remains bonded to the metal during the course of the reaction, so it is believed that this fragment has a greater influence on the outcome and selectivity than the organo part. Many studies have focused on this point always attempting to modify the electronic density at the nickel center in order to facilitate β -elimination during the growing chain.

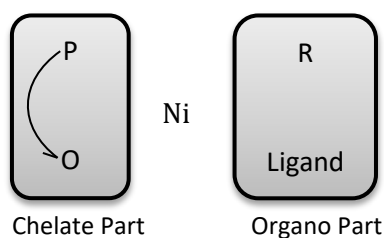


Figure 2 - General form of a typical SHOP catalysts by Keim *et al.*

Many different ligands were developed looking for neutral or cationic nickel active species. They can be divided in different classes like monodentate, bidentate or tridentate ligands bearing P, N, O or S donor atoms. Regarding bidentate ligands there are many arrangements, once it is possible to combine hard donor atoms, like nitrogen or oxygen, with soft donor atoms such as phosphines and sulfur. The most common combination are the α -diimines (N,N) or the diphosphines (P,P) that present some similar properties, and mixed ligands (P,N), (P,O) or (N,O) are also available and were studied scrutiny. All of them present different structures and influence the activity and the selectivity of the oligomerization reaction, for example mixed (P,O) ligands were also extensively studied by Keim *et al.* and they are currently used industrially by SHELL to produce LAOs with a broad Schulz-Flory distribution [3].

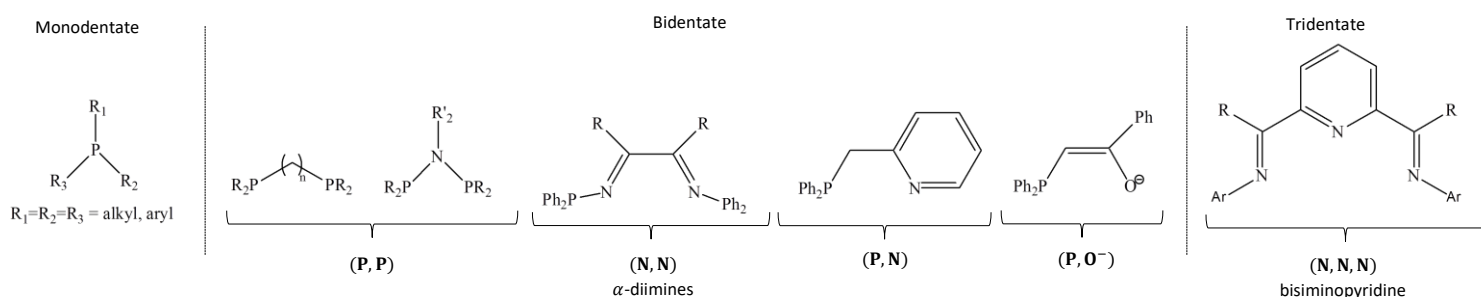


Figure 3 - Some examples of ligands that can coordinate Nickel.

Analyzing the current data on catalytic systems based on nickel, we observe that many variables can be changed, such as ligands, activators and operating conditions, but none of these combinations have been effective for selective oligomerization of ethylene. There is only one exception, described recently by IFPEN, that achieved to obtain 1-butene selectively using zwitterionic nickel complexes [1].

1.3 Aim of the project

In order to produce high quality linear olefins from selective oligomerization of ethylene, nickel-based catalysts were considered.

Moreover, from recent achievements with similar species in this field, a perimeter of potential ligands was identified. These ligands were chosen for their special properties, such 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.

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2 Results and Discussion

Due to their specific properties, ligands always play 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.

2.1 Monophosphine ligands

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 ^{31}P – NMR. Therefore, almost every time, it is possible to follow reactions.

2.1.1 Buchwald Phosphines

Buchwald phosphines are highly hindered and used mainly with palladium for different catalytic transformations [13]. For example, in 2010 P. Leeuwen *et al.* [14] disclosed the telomerization of butadiene with methanol using these complexes.

Some of these Buchwald phosphines, which could be synthesized or are commercially available, were selected and are now presented below:

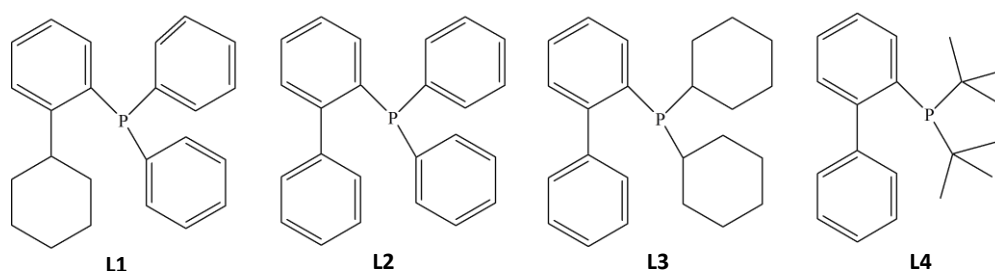
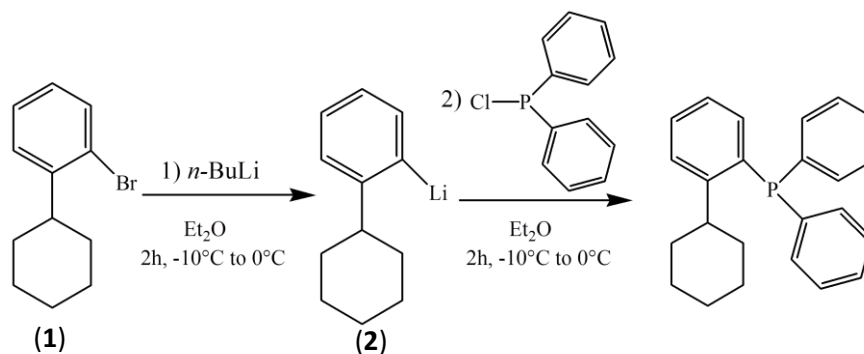


Figure 4 - Selected Buchwald phosphines: **L1** and **L2** synthesized; **L3** and **L4** commercially available.

The phosphines **L1** and **L2**, under inert atmosphere, were synthesized and characterized with success (as described in literature [15]), while **L3** and **L4** were purchased from external suppliers. The synthesis of **L1** made in diethyl ether, consisted in a two steps synthesis.



Scheme 4 - Synthetic route to (2-cyclohexylphenyl)biphenyl-phosphine (**L1**).

First, *n*-BuLi was added dropwise slowly into a fresh solution of 1-bromo-2-cyclohexylbenzene at -10°C and then the media was stirred for further 2 hours at 0°C . During this stage, a well known Lithium-Halogen exchange occurs, giving place to a very nucleophilic organolithium species (**2**). In the second step, a solution of chlorodiphenylphosphine was added into the first media yielding a yellow mixture. This addition was made slowly at -10°C , and then stirred further 2 hours at 0°C . During this time the solution color changed to white due to the salt formed. The precipitated salt corresponds to lithium chloride, formed while the nucleophilic lithium species (**2**) reacts with the chlorophosphine. The process was carried at low temperatures to avoid product degradation and secondary reactions. The crude was followed by ^{31}P – NMR until the reaction was complete. After filtration, the solvent was evaporated under vacuum, giving place to a white oily product.

Being afraid of oxidizing the product, we decided to try to crystallize it in dichloromethane instead of ethanol, as suggested in literature [15]. The oily product was very soluble in this solvent, so no crystals were formed. Therefore, we followed again the protocol, and a few quantity of dry ethanol (dried in molecular sieves 3 \AA) was added. The oil was dissolved with some difficulty and was carried into a fridge (6°C) in order to purify the main product by crystallization (Figure 5). A white crystals were obtained in an amount of $1,50 \text{ g}$, with a purity of 98% and a yield of 86%. This yield is higher than the one disclosed on literature, 72%; after analyzing the spectra we saw the presence of grease and diethyl ether, suggesting that the final powder was not dried enough resulting in a higher yield. The chemical shift of the final product is ^{31}P – NMR(CD_2Cl_2 , 300 MHz, 298K): $\delta - 15,9 \text{ ppm}$.

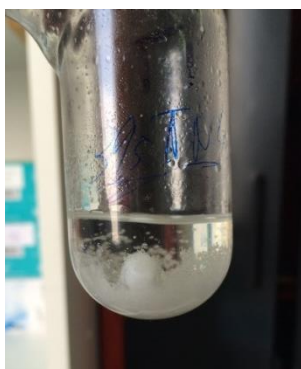
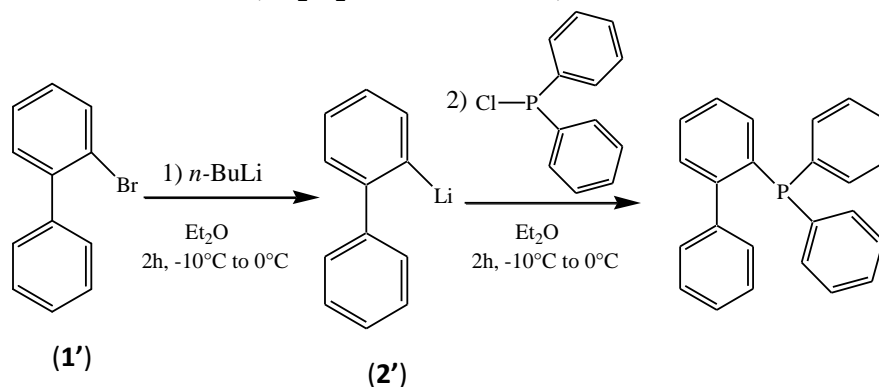


Figure 5 - White crystals of **L1**.

Regarding the synthesis of **L2**, there was no protocol describing its synthesis. So, we developed almost exactly as it is described on the synthesis of **L1** and the same observations were detected. The main difference was that the *n*-BuLi was added to a solution of *2-bromobiphenyl* in order to obtain a complete aromatic compound. Other small alteration occurred during the purification process: when we were aiming for crystallization, the ultrasonic device was used to help dissolve the oil in ethanol, but as soon the oil was dissolving, a white precipitate was formed due to the excessive vibrations. Finally, the **L2** was obtained in an amount of 1,29 g, with a purity of 97% and a yield of 76%. The shift of the final product is ^{31}P – NMR(CD_2Cl_2 , 300 MHz, 298K): δ – 13,6 ppm.



Scheme 5 -Synthetic route to (2-diphenyl)biphenyl-phosphine (**L2**).

Nolan *et al.* [16] presented a general method to determine the steric parameter of organometallic ligands as a function of the percent buried volume. This method was developed first in order to compare phosphine to N-heterocyclic carbene's (NHC). They measured several type of ligands, including the phosphines mentioned above, where it was possible to confirm their hindrance. Another important tool is the Tolman's map (Appendix), in which the different classic phosphines and their relationship between steric hindrance and electronic properties can be observed. Taking into account these characteristics, phosphines **L1** and **L2** present a hindrance very similar to *tri-phenylphosphine* (PPh_3), and the last two phosphines, **L3** and **L4**, are more hindered than *tri-tert-butylphosphine* (PtBu_3). The basicity of the different phosphines will change, depending on the presence of more or less electroattractive groups, where **L3** and **L4** are the most basic followed by **L1** and at last **L2**.

Following the same methodology presented, and based on literature, a second group of phosphines were selected (Figure 6). 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 [17].

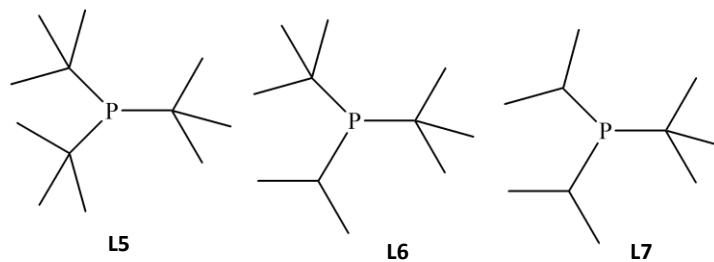
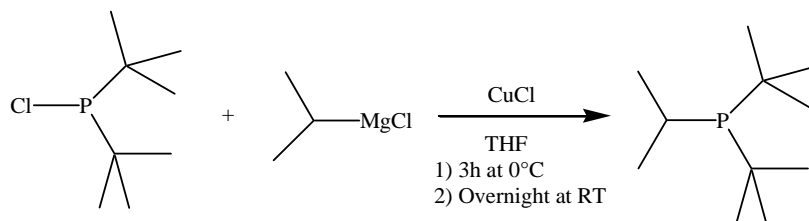


Figure 6 - Second group of selected monophosphines.

Analyzing Tolman's map, all the ligands **L5** to **L7** are very basic analogous to **L5**–PtBu₃, once there are no presence of electroattractive groups. Regarding hindrance, **L5** is the most hindered followed by **L6**. The final selected ligand, **L7**, is between *PiPr*₃ and **L6**.

The phosphines **L5** and **L7** were obtained from external suppliers, while **L6** was synthesized and characterized with success. The synthesis of **L6** [17] consisted on adding a solution of *isopropylmagnesium chloride* into another solution of *di-tert-butylchlorophosphine* and *copper(I) chloride*.



Scheme 6 - Synthetic route to *Di-tert-butylisopropylphosphine* (**L6**).

As seen previously, the nucleophilic species will react with the chlorophosphine in a replacement reaction followed by the formation of MgCl₂. Due to its strong reactivity and exothermicity, the magnesium solution addition was made at 0°C dropwise during 1 hour, after which the resulting media was stirred at the same temperature for further 3 hours, warmed until room temperature and stirred overnight. This addition resulted in color change, the mixture turned instantly to purple, and then it was disappearing with stirring until reaching a light brown color. On the next day, this media was quenched with a saturated solution of NH₄Cl, previously degassed, and with Et₂O, also previously degassed, causing a colorless but cloudy mixture. The aqueous phase was extracted with Et₂O, and then the organic layers were combined and washed with degassed water in order to remove all the NH₄Cl and the MgCl₂ formed during the reaction. This process was carried out until the organic phase was very clean, resulting in a well defined separation line between organic and aqueous phase. Then it was dried over MgSO₄ and filtrated to remove the solid particles. The organic phase was concentrated under vacuum to afford a colorless oil. On the literature they never mention that the species are highly air and moisture sensitive, or how to verify if the product is oxidized. Therefore, we

proceed with extreme careful to avoid contamination, and even so, some oxidized phosphine may have been formed resulting in a light color change to blue. Also in the literature they reported filtration through a short pad of silica gel; we supposed that the purpose of this step was to remove some oxidized phosphine. Thus, the oil was dissolved in pentane and filtrated through activate alumina that has the same effect; the compound was again dried under vacuum to afford a colorless oil, in an amount of around 0,05 g, with a purity of 96%. Once we d not have the precise amount of product the yield was not calculated or compare with literature. The principal chemical shift of the final product is ^{31}P – NMR(C_6D_6 , 300 MHz, 298K): δ 46,0 ppm. This characterization are the same reported by F. Schoenebeck *et al.* [17].

2.1.2 Anionic phosphines

Another possible strategy in order to achieve the synthesis of a ligand with high electron donor properties able to stabilize the metal center, 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.* [18] synthetized and characterized one type of ligand phosphine, *2-phenylindenyl phosphine*, 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 study, both neutral and anionic ligands are investigated in order to observe the influence of the negative charge on the stability and the reactivity of the nickel complex.

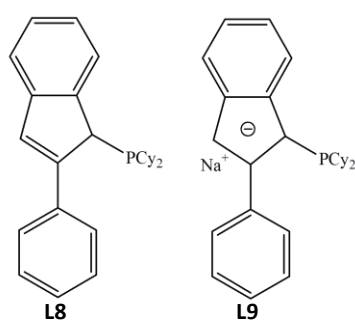
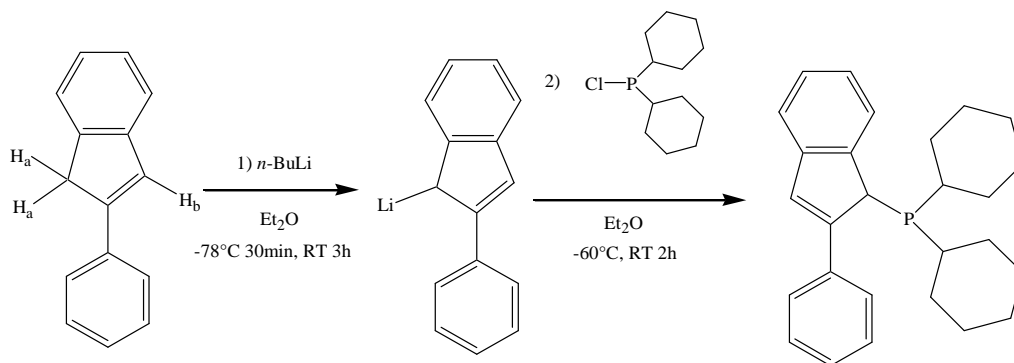


Figure 7 - (2-phenylindenyl)dicyclohexylphosphine (neutral L8; anionic L9) [18].

The neutral phosphine was synthetized and characterized with success based on literature [18] but without isolate the phosphine under the form of a salt.



Scheme 7 - Synthetic route to (2-phenylindenyl)dicyclohexylphosphine.

First, 2-phenylindene was dissolved in diethyl ether and cooled to -78°C in a bath of dry ice and acetone. Then, a solution of *n*-BuLi was added slowly, affording a brown mixture, that was stirred at the same temperature for 30 minutes. This media reached room temperature and was stirred for further 3 hours. In this step, working at the described conditions, the strong base (*n*-BuLi) deprotonates the phenylindene (H_a more acid than H_b) to form the nucleophilic organolithium species that can react with the chlorophosphine as before. Therefore, the second step consisted in the addition of chlorodicyclohexylphosphine. It was added slowly at -60°C (dry ice only), then warmed until room temperature and stirred for additional 2 hours. After stirring, a yellow mixture and a white precipitate (lithium chloride) were obtained. The solid was removed by filtration over a pad of Celite under argon atmosphere. As we said before, to isolate the final product, the procedure described by Sheng-Hua Liu *et al.* [18] was not followed: instead of getting a salt using HBF_4 , the final product was obtained by crystallization. First, ether was removed by evaporation under vacuum, giving a light yellow solid that was dissolved in the minimum amount of toluene. This media was taken into the fridge (-18°C) in which a white crystal was obtained in an amount of 0,50 g, with a purity of 96% and a yield of 30%. The process of purification can be improved to obtain a higher yield, but the principal aim in all synthesis reported is to reach pure compounds. It is crucial for a good characterization and minimization of secondary products in complexation reactions. The yield reported on literature was 43%, of course this process was optimized and we followed a different procedure at the end, but our yield was not so lower. The principal chemical shift of the final product is ^{31}P – NMR(CD_2Cl_2 , 300 MHz, 298K): δ 9,91 ppm.

Regarding the synthesis of the anionic phosphine (**L9**), due to the few amount obtained in the synthesis of **L8**, and the not detailed description on literature, it was decided not to try to isolate the phosphine. The anionic transformation was thus done *in situ* during the complexation reaction in nickel.

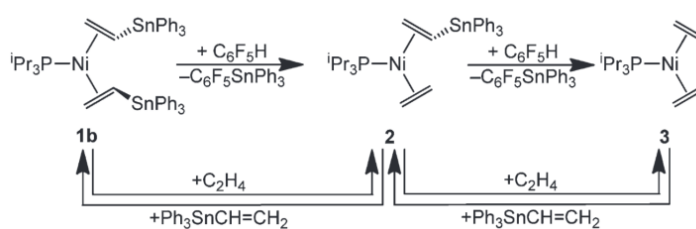
Therefore, the first approach was to study the transformation into an anionic species by adding *t*BuONa. Following the reaction in ^{31}P NMR, two parameters were studied: solvent and quantity of *t*BuONa added. Toluene and dichloromethane were tried and no difference was observed; and, four essays adding 1, 2, 3 and 4 equivalents of *t*BuONa were preformed, in which the results are similar but with better performance in the last one, affording the appearance of a new signal in a quantity of 68%. The time of exposure to the added base was analyzed, in which no influence on the conversion was observed for small or big times.

Our observation differs from the literature at this point. Liu et al. reported [18] that after the addition of one equivalent of *t*BuONa into the phosphinium salt, the appearance of a new signal, $\delta_p = -17,17 \text{ ppm}$, and with more three equivalents, making a total of four, a new signal at $\delta_p = -13,15 \text{ ppm}$ corresponding to the anionic phosphine was observed. In all our essays, when the number of equivalents were changed, the results were always the same, a chemical signal at $\delta_p = -17,45 \text{ ppm}$ was observed. This difference, between the results, may be due to the fact that they used a phosphinium salt in DME instead of the isolated phosphine dissolved in toluene.

To conclude, the ligand **L8** was synthesized and isolated with success, it can be manipulated in further reactions in this form. The ligand **L9** was not isolated and the characterization results were a bit different from literature.

2.2 Silicon and Tin moieties

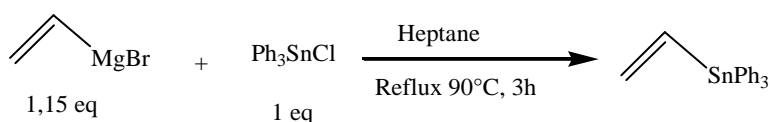
Two new potential tin structures were found thanks to the studies made by Hatnean *et al.* [19] on carbon-hydrogen stannylation. They were able to isolate and characterize Ni(0) complex coordinated by monophosphine, like the complex $(iPr_3P)Ni(\eta^2-Bu_3SnCH=CH_2)_2$, that are active species for catalytic stannylation of partially fluorinated aromatics. The important point here is not the fluorinated final species, but the path they took to achieve them. With more profound analysis of Scheme 8 it is possible to note that the two olefinic ligands structured by tin are both easily replaced by the ethylene molecules making the coupling.



Scheme 8 - Catalytic stannylation of fluorinated aromatics [19].

In this work, only two types of tin ligands mentioned by Hatnean were used, which are: *tributylvinyltin* (tbvt) and *triphenylvinyltin* (tpvt).

The first one, tbvt, is commercially available and it was obtained from external suppliers. The second compound, tpvt, was synthesized and isolated with success (based on literature [20]). The synthesis is based on a Grignard reaction between *vinylmagnesium bromide* and *triphenyltin chloride*.



Scheme 9 - Synthetic route to *triphenylvinyltin* (tpvt).

First, the triphenyltin chloride was dissolved in heptane and heated until 70°C , then a solution of vinylmagnesium bromide in THF was added for 1 hour, once this compound is very reactive. The resultant media was taken up to 90°C and stirred under reflux during 3 hours. First, a white solid appeared (chloride and bromide salt), that with time became dark brown, and the liquid phase became clear. During this period the nucleophilic vinylmagnesium bromide attacked the tin replacing chloro by the vinyl moiety in a typical Grignard mechanism. After taking the mixture until room temperature, the reaction was quenched with a solution of HCl (1M) and water in order to neutralize the remaining species. The solid disappeared and more heptane was added to extract the aqueous phase. The organic phase, after being washed and separated, was filtrated through celite, and then the heptane was

evaporated under vacuum affording a white oil. A few quantity of dry ethanol was added, in order to dissolve the oil, and the media was taken into the fridge (-18°C), in which white crystals were obtained (Figure 8). After dry the final product, a total mass of 3,34 g was obtained, with a purity of 97% and a yield of 68%. Rosenberg *et al.* [20] disclosed a yield of 79% for an developed synthesis and our results are not so far away. Of course our procedure can be improved, especially the liquid-liquid decantation. Concerning characterization, the three protons from the vinyl part are characterized by two double duplets and one quadruplet with characteristic constant couplings between them. So, the principal chemical shifts of the final product are: ^1H – NMR (300MHz) in 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).



Figure 8 - White powder of tpvt after dried.

3 Experimental Part

Numerous synthesis and essays were performed trying to understand and improve the experimental conditions in order to have the best success. This chapter is dedicated to all experimental part, but only for the synthesis that allowed us to have clean and isolated products.

3.1 General procedures

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), Sigma Aldrich (2) and Strem Chemicals (3). These compounds are:

- 1) *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.*
- 2) *n-butyllithium; (2-biphenyl)dicyclohexylphosphine (L3); isopropylmagnesium chloride; copper(I) chloride and 2-phenylindene.*
- 3) *tri-tert-butylphosphine (L5); chlorodicyclohexylphosphine; vinylmagnesium bromide.*

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.

The liquid phases, from the catalytic test reactor and NMR studies, were analyzed on a Agilent Technologies 6890N GC oligomerization sequence.

3.2 Ligands Synthesis

- **Synthesis of (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 (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) a white crystals were formed in ethanol (previously dried in 3 Å sieves to afford a content around 60 ppm of H_2O). After dried under vacuum, the white powder was obtained with a yield of 86% (1,50 g).

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

1H – NMR (300MHz) in CD_2Cl_2 , δ : $1,14 - 1,79$ (m, 10H, CH_2 (Cy)); $3,24 - 3,38$ (m, 1H, CH (Cy)); $6,82 - 7,36$ (m, 14H, aromatics).

- **Synthesis of (2-diphenyl)biphenyl-phosphine (L2)**

This reaction was performed exactly as the synthesis of (2-cyclohexylphenyl)biphenyl-phosphine with two exception: a different solution of bromo precursor, 2-bromobiphenyl (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) in CD_2Cl_2 , δ : $-13,65$ ppm.

1H – NMR (300MHz) in CD_2Cl_2 , δ : $7,03 - 7,44$ ppm (m, 19H, aromatics).

Traces of diethyl ether δ : $1,15$ (t); $3,42$ (q)ppm

- **Synthesis of *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 NH₄Cl (5 ml), previously degassed, and with Et₂O (5 ml), also previously degassed. The aqueous phase was extracted with Et₂O (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 MgSO₄ 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.

³¹P – NMR (300MHz) in C₆D₆, δ: 46,33 ppm.

¹H – NMR (300MHz) in C₆D₆, δ: 1,18 – 1,34(m, 24H, CH₃); 3,24 – 3,38(sep, 1H, CH).

- **Synthesis of *(2-phenylindenyl)dicyclohexylphosphine* (L8)**

The *2-phenylindene* (1,55 g; 7,8 mmol; 1,0 equivalent) was dissolve 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 a white crystals were obtained with a yield of 30% (0,50 g).

³¹P – NMR (300MHz) in C₆D₆, δ: 11,03 ppm.

¹H – NMR (300MHz) in C₆D₆, 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).

- **Synthesis of triphenylvenyltin**

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 warmed 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 the 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 dried under vacuum, the final product was obtained with yield of 68% (3,34 g).

^1H – NMR (300MHz) in 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) in 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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4 Conclusion

Based on literature, a perimeter of potential ligands was defined for the development of original nickel catalysts. These ligands were chosen for their special properties, such as hindrance and electronegative properties (basicity and charge) in order to achieve the synthesis of ligands with high electron donor properties able to stabilize the metal center. Moreover, monophosphine are known for their accessible synthesis, isolation and characterization.

The aim of this work was to synthesize and study highly hindered monophosphine ligands. (Table 5 and 6)

Table 5 - Structure and purity of the synthesized ligands.

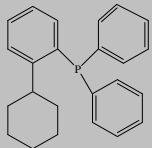
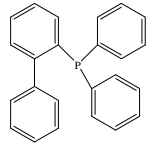
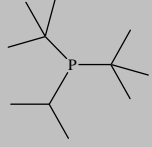
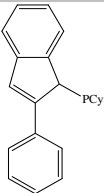
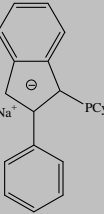
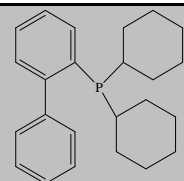
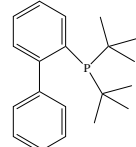
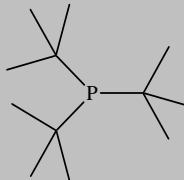
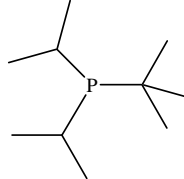
Ligand	Structure	Purity (%)
L1		98
L2		97
L6		96
L8		96
L9		<i>in situ</i>

Table 6 - Structure of the commercial ligands.

Ligand	Structure
L3	
L4	
L5	
L7	

All the aimed monophosphine ligands were, thus, synthesized and characterized with success, following the literature and sometimes by doing the necessary alterations. Triphenylvinyltin was also synthesized and characterized with success. All these ligands could then be applied in complexation reactions with nickel.

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Appendix I - Tolman's map

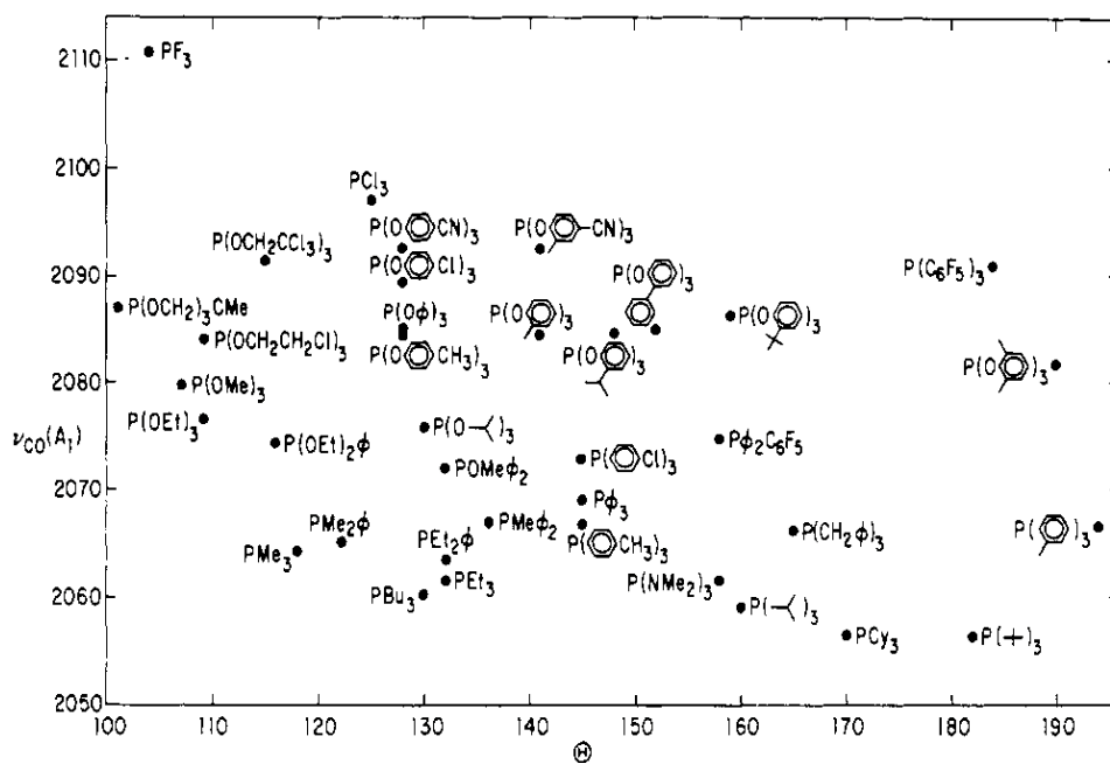


Figure I. 1 - Tolman's map: electronic and steric effects of common P-donor ligands.

Appendix II –Ligands Spectra

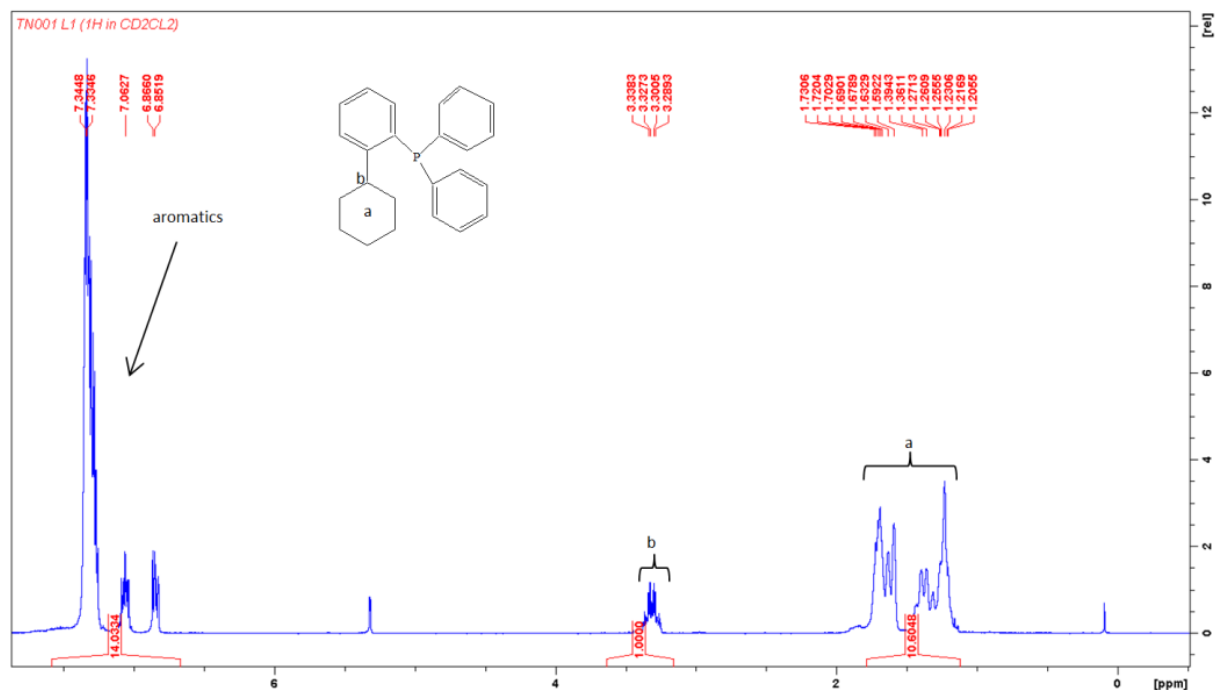


Figure II. 1 – ^1H -NMR spectrum in CD_2Cl_2 of ligand L1.

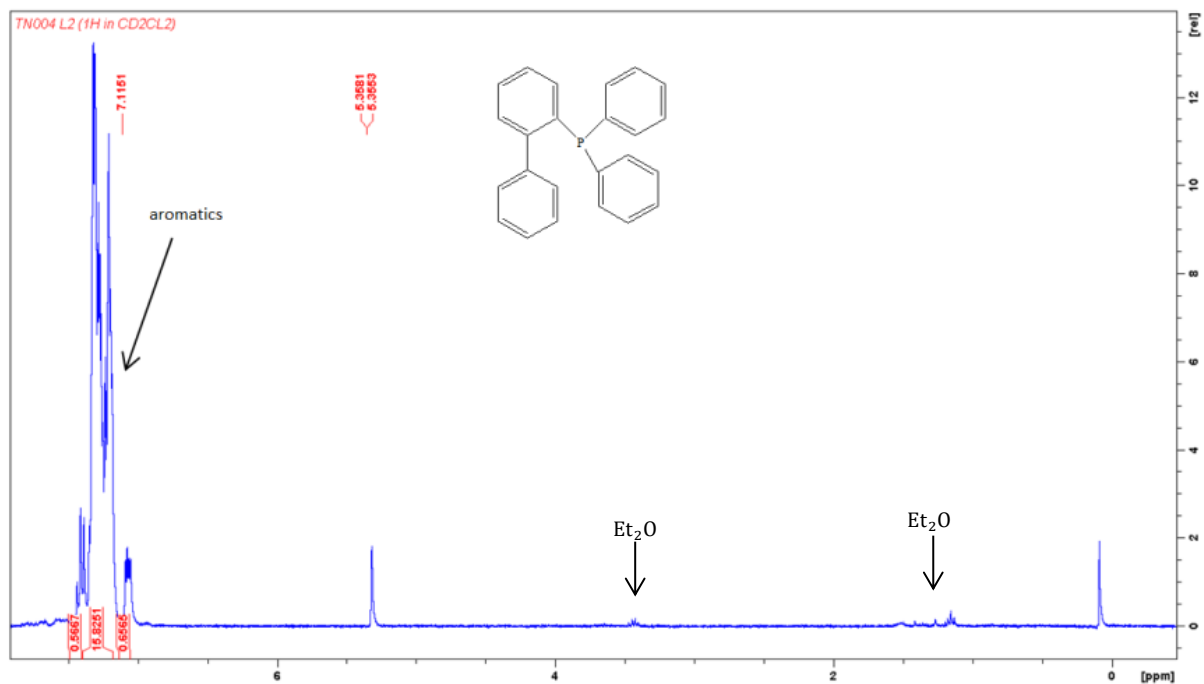


Figure II. 2 - ^1H -NMR spectrum in CD_2Cl_2 of ligand L2.

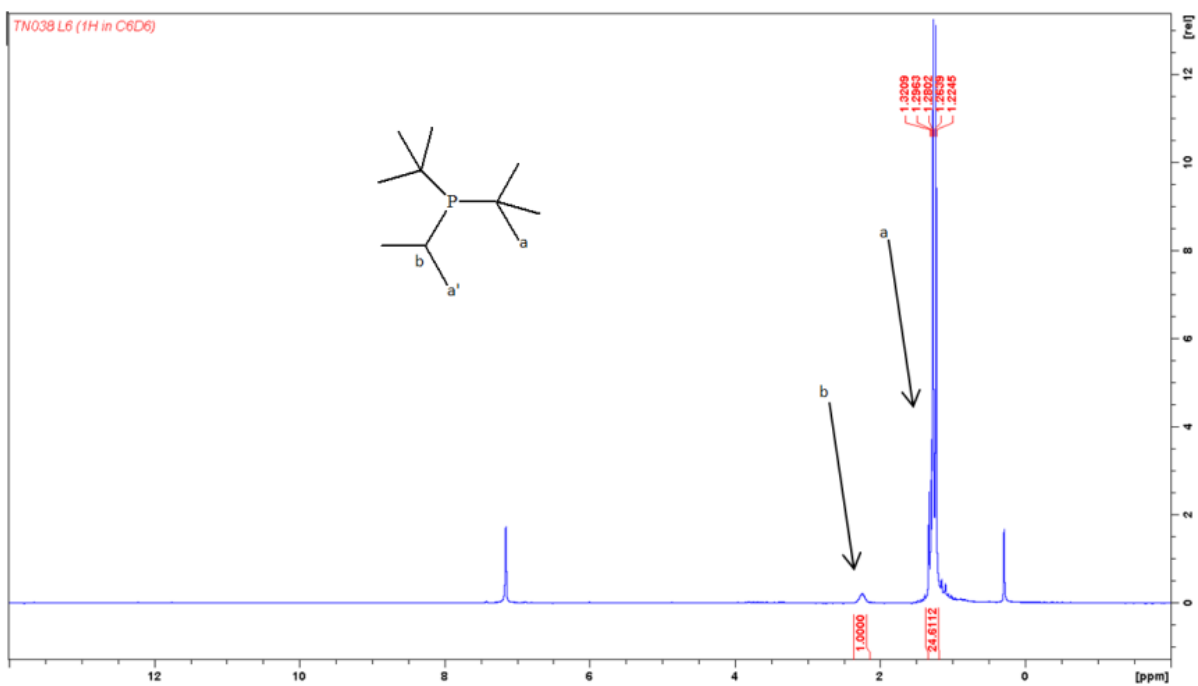


Figure II. 3 - ^1H -NMR spectrum in C_6D_6 of ligand L6.

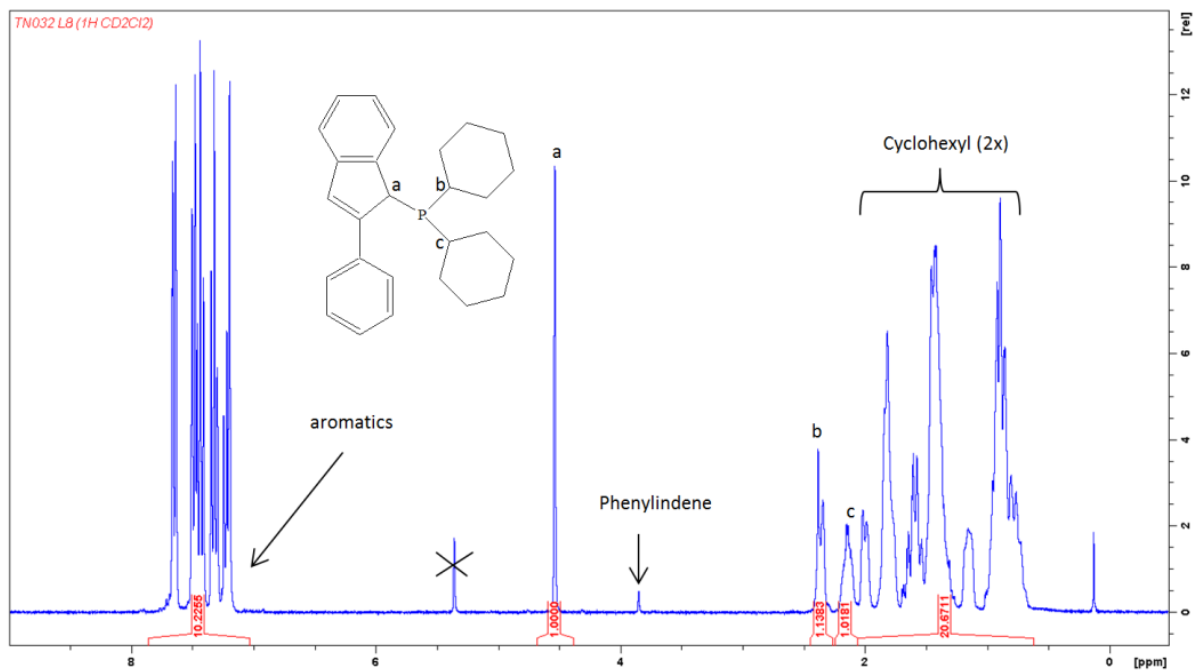


Figure II. 4 - ^1H -NMR Spectrum in CD_2Cl_2 of ligand L8.

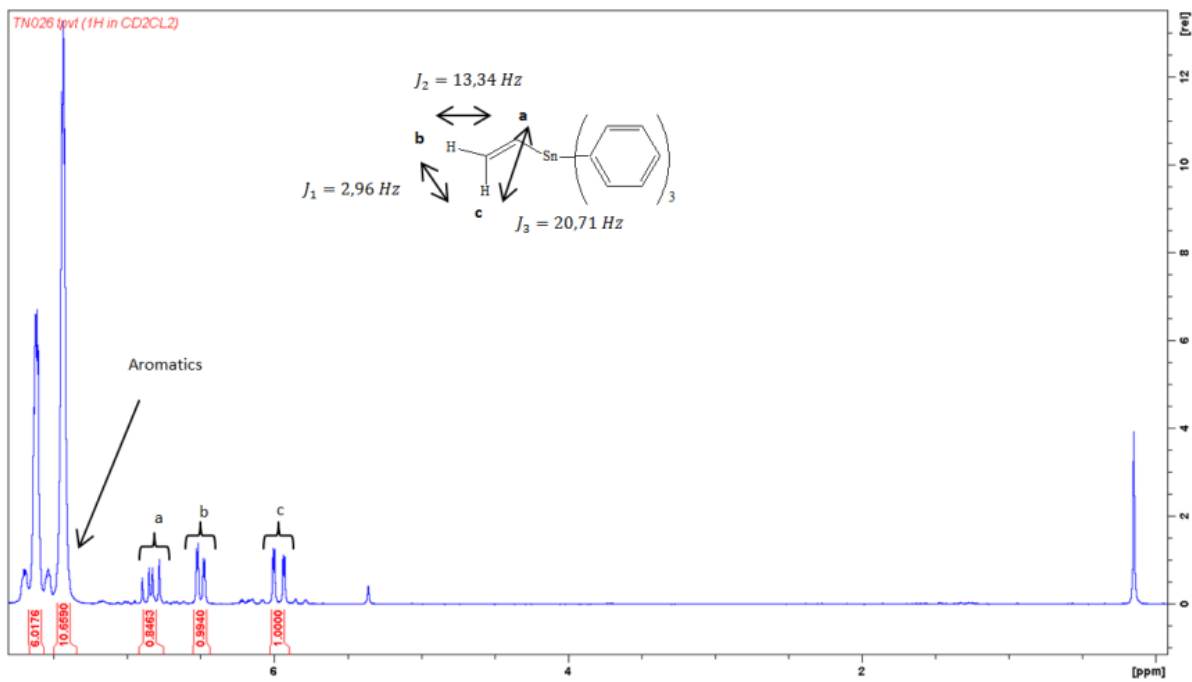


Figure II. 5 - ¹H-NMR spectrum in CD₂Cl₂ of tpvt.

