EGE UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
(PhD THESIS)

THE SYNTHESIS AND CHARACTERIZATION OF PALLADIUM COMPLEXES CONTAINING PINCER TYPE LIGANDS

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ÖZET

KISKAÇ TİPİ LİGANDLARI İÇEREN PALADYUM KOMPLEKSLERİNİN SENTEZİ VE KARAKTERİZASYONU

YANAR, Selmin

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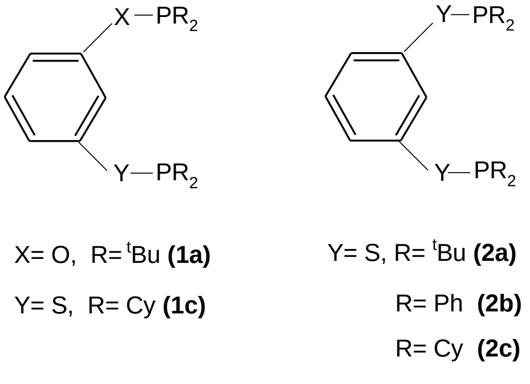
Danışman: Prof. Dr. Sevil İRİŞLİ

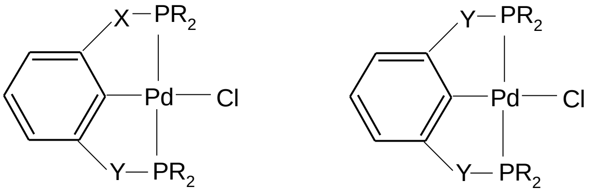
Kasım 2010, 155 sayfa

Bu çalışmada, PCP tipinde beş yeni kıskaç ligand **(1a), (1c), (2a), (2b), (2c)** ve dört yeni kıskaç kompleks **(1a'), (1c'), (2b')** ve **(2c')** sentezlenmiştir. Difenilklorofosfin, disiklohegzilklorofosfin, 3-merkaptofenol, 1,3-benzenditiyol Aldrich firmasından ticari olarak satın alınmıştır. $[PdCl_2(COD)]$ (COD= 1,5-cyclooctadiene), (Chatt et al., 1957) ve $^tBu_2PCl$, literatür bilgilerine göre sentezlenmiştir (Fild et al., 1973). Sentezlenen kıskaç ligandların yapıları aşağıda gösterilmiştir.



Şema 1. POCSP ve PSCSP kıskaç ligandlarının yapısı

Sentezlenen kıskaç ligandlar havaya ve neme karşı oldukça hassas olmalarına rağmen, kıskaç kompleksler havaya ve neme karşı oldukça dayanıklıdırlar. PCP kıskaç kompleksler aşağıdaki tepkime yöntemine göre sentezlenmiştir.



X= O, R= ^{t}Bu **(1a')**

Y= S, R= Cy **(1c')**

Y= S, R= Ph **(2b')**

R= Cy **(2c')**

Şema 2. POCSP ve PSCSP kıskaç komplekslerinin yapısı

Sentezlenen kıskaç ligandlar $^{31}P\{^1H\}$-NMR, ^1H-NMR, $^{13}C\{^1H\}$-NMR ve FT-IR spektroskopisi yöntemleriyle aydınlatılmıştır. Sentezlenen kıskaç kompleksler ise $^{31}P\{^1H\}$-NMR, ^1H-NMR ve FT-IR spektroskopisi yöntemleriyle aydınlatılırken sadece **(1a')** ve **(2c')** komplekslerinin $^{13}C\{^1H\}$-NMR spektrumları alınmıştır. Termal Gravimetrik Analiz (TGA) yöntemini kullanarak **(1a'), (2b')** ve **(2c')** komplekslerinin termal özellikleri incelenmiştir. Ayrıca aynı komplekslerin yüzey karakteristik özellikleri AFM yöntemiyle incelenmiştir.

Komplekslerin Heck ve Suzuki eşleşme tepkimelerindeki katalitik etkinlikleri incelenmiştir.

Anahtar Kelimeler: Kıskaç kompleksler, fosfin ligandları, paladyum, katalitik etkinlik, Suzuki C-C eşleşme tepkimesi, Heck tepkimesi.

ABSTRACT

THE SYNTHESIS AND CHARACTERIZATION OF PALLADIUM COMPLEXES CONTAINING PINCER TYPE LIGANDS

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PhD in Chemistry

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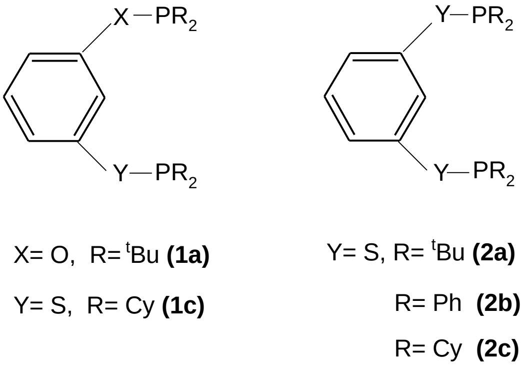
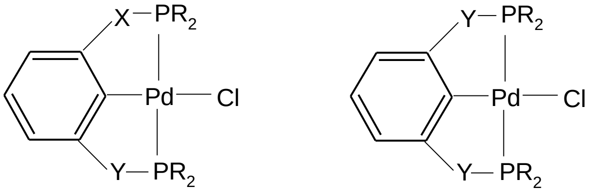
In this study, five new PCP pincer ligands **(1a), (1c), (2a), (2b), (2c)** and four new PCP pincer complexes **(1a'), (1c'), (2b')** and **(2c')** have been synthesized. Diphenylchlorophosphine, dicyclohexylchlorophosphine, 3-mercaptophenol and 1,3-benzenedithiol, were purchased from Aldrich; [$PdCl_2$(COD)] (COD= 1,5-cyclooctadiene), (Chatt et al., 1957) and $^tBu_2PCl$ were synthesized according to the literature (Fild et al., 1973). General reaction route for the synthesis of the pincer ligands was shown below.



Scheme 1. Structure of POCSP and PSCSP pincer ligands

Pincer ligands were very air and moisture sensitive as known and pincer complexes were very stable to air and moisture and could be handled in open air. PCP pincer complexes were synthesized according to the reaction route as shown below.



X= O, R= ^{t}Bu **(1a')**

Y= S, R= Cy **(1c')**

Y= S, R= Ph **(2b')**

R= Cy **(2c')**

Scheme 2. Structure of POCSP and PSCSP pincer complexes.

The identity of the pincer ligands were established by $^{31}P\{^{1}H\}$-NMR, ^{1}H-NMR, $^{13}C\{^{1}H\}$-NMR and FT-IR spectroscopy and the all complexes were established by $^{31}P\{^{1}H\}$-NMR, ^{1}H-NMR and FT-IR but only **(1a')** and **(2c')** were identified by $^{13}C\{^{1}H\}$-NMR spectroscopy, also. The thermal behaviour of pincer complexes **(1a'), (2b'), (2c')** were investigated using thermogravimetry (TGA). Also, AFM measurement of complexes **(1a'), (2b'), (2c')** were investigated for analyses of facile characteristic features.

Catalytic activities of complexes were examined in Suzuki and Heck Cross Coupling Reactions.

Key Words: Pincer complexes, phosphine ligands, palladium, catalytic activity, Suzuki C-C coupling reaction, Heck reaction.

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I would like to present my gratitude to my supervisor, Professor Dr. Sevil İRİŞLİ, for her precious suggestion, support, patience, and for enlightening me via her deep knowledge and experience.

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ABBREVIATIONS

Abbreviations		**Explanations**
Ar	:	Aryl
BINAP	:	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
Bu	:	Butyl
cat.	:	Catalyst
COD	:	1,5-cyclooctadiene
Cy	:	Cyclohexzyl
dba	:	Dibenzylideneacetone
Dppe	:	Diphenylphosphinoethane
Dppm	:	Diphenylphosphinomethane
DMSO	:	Dimethylsulfoxide
DMF	:	Dimethylformamide
Et	:	Ethyl
FTIR	:	Fourier Transform Infrared Spectroscopy
GC	:	Gas Chromatography
Hz	:	Hertz
L	:	Ligand
M	:	Metal
m.p.	:	Melting point
Me	:	Methyl
NMR	:	Nuclear Magnetic Resonance
Np	:	Neopentyl
OAc	:	Acetate
Ph	:	Phenyl
PH_3	:	Phosphine
PPh_3	:	Triphenylphosphine
Pr	:	Propile
R	:	Alkyl
r.t.	:	Room temperature
TFA	:	Trifluoroacetate
THF	:	Tetrahydofurane
TGA	:	Thermal Gravimetric Analysis
AFM	:	Atomic Force Microscopy
s	:	Singlet
d	:	Doublet
t	:	Triplet
i-	:	Iso
t-	:	Tertiary

1. INTRODUCTION

1.1 INFORMATION ABOUT PHOSPHINES

Phosphine, is the compound with the chemical formula PH_3. m.p. -133 ^oC; b.p. -87.7 ^oC; slightly soluble in water. It is a colorless, flammable, toxic gas. Pure phosphine is odourless, but technical grade samples have a highly unpleasant odor like garlic or ratting fish, due to the presence of substituted phosphine and diphosphine (P_2H_4). Phosphine may be preferred by reacting water or dilute acids with calcium phosphide or by reaction between yellow phosphorus and concentrated alkali. Solutions of phosphine are neutral but phosphine does react with same acids to give phosphanium salts containing PH_4^+ ions, analogous to the ammonium ions. Phosphine prepared in the laboratory is usually contamined with diphosphine and is spontaneously flammable but the pure compound is not so. Phosphines, are also a group of organophosphorus compounds with the formula R_3P (R= organic derivative). Organophosphines are important in catalysts where they complex to various metal ions; complexes derived from a chiral phosphine can catalyze reactions to give chiral products.

Ernst von Meyer described the early history of phosphine research thus: The discovery of phosphuretted hydrogen (PH_3) by Gengembre in 1783, and the examination of if by Pelletier (who was the first to prepare it pure), only become fruitful after Humpbry Davy’s investigations; and the last-named elucidated the composition of this gas, and pointed out its analogue to ammonia, this being emphasized still more sharply by H. Rose.

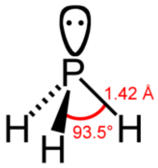


Figure 1.1 Structure of PH_3.

Perhaps because of its strong association with elemental phosphorus, phosphine was once regarded as a gaseous form of the elemental but Lavoiser recognized it as a combination of phosphorus with hydrogen by describing it as “hydroyet of phosphorus, or phosphuret of hydrogen.”

1.1.1. Structure and Properties of Phosphines

PH_3, is a trigonal pyramidal molecule with C_{3V} molecular symmetry. The length of the P-H bond 1,42Å, the H-P-H bond angles are 93,5°. The dipole moment is 0,58 D, which increases with substitution of methyl groups in the series: CH_3PH_2, 1.10D; $(CH_3)_2PH$, 1.23 D; $(CH_3)_3P$, 1.19 D. In contrast, the dipole moments of aminos decrease with substitution, starting with ammonia, which has a dipole moment of 1.47 D. The low dipole moment and almost orthogonal bond angles lead to the conclusion that in PH_3 the P-H bonds are almost entirely pσ (P)- sσ (H) and the lone pair contributes only a little to the molecular orbitals.

The high positive chemical shift of the P atom in $^{31}P\{^1H\}$-NMR spectrum accords with the conclusion that the lone pair electrons occupy the 3s orbital and so are close to the P atom (Fluck, 1973). This electronic structure leads to a lack of nucleophilicity and an inability to form hydrogen bonds.

1.1.2. Applications of Phosphines

Alkyl and aryl derivatives of phosphine are analogous to organic aminos. Common examples include triphenyl phosphine ($(C_6H_5)_3P$) and BINAP, both used as a ligand in homogeneous catalysis or triisopropylphosphine. Phosphine are easily oxidized to phosphine oxides as examplified by the directed synthesis of phosphor-crown, the phosphorus anologue of an aza crown (Edwards et al., 2006), where it is not possible to isolate the phosphine itself.

Phosphine is mainly consumed as an intermediate in organophosphorus chemistry. In an illustrative reaction, formaldehyde adds in the presence of hydrogen chloride to give tetrakis (hydroxymethyl) phosphonium chloride, which is used in textiles. Small amounts of phosphine is used as a dopant in the semiconductor industry, and a precursor for the deposition of compound semiconductors. (Bettermann et al., 2002).

For farm use, pellets of aluminium phosphide, calcium phosphide, or zinc phosphide release phosphine upon contact with atmospheric water or radent's stomach acid. These pellets also contain agents to reduce the potential for ignition or explosion of the released phosphine.

1.2. PHOSPHINE LIGANDS

Phosphine ligands have the general formula PR_3 where R= alkyl, aryl, H, halide etc. Closely related are phophite ligands which have the general formula $P(OR)_3$. Both phosphines and phosphites are neutral two electron donors that bind to transition metals through their lone pairs. There are many examples of polydentate phosphine ligands, same common examples of which are shown below. Furthermore, a variety of chiral phosphine transition metal complexes have been synthesized; these phosphine, metal complexes are stereogenic and can function as stereospecific catalysts. Same typical phosphine ligands are shown below (Figure 1.2).

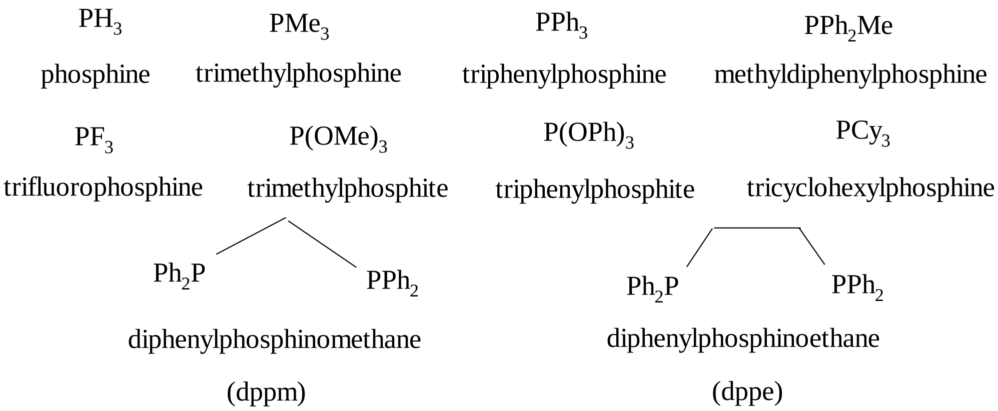


Figure 1.2 Structures of Some Typical Phosphine Ligands.

While phosphine ligands are ubiquitous in transition metal chemistry and afford extremely reactive and versatile homogeneous catalysts, a process called phosphine degradation tends to limit their industrial application. Phosphine degradation typically involves an oxidative addition of the phosphine ligand which deactivates the metal center towards further catalysis.

The use of phosphine ligands in necessary for nearly all homogenous catalysis with precious-metals. The choice of the right ligand can influence

- the solubility of the active species
- the shielding and sterical properties of the catalyst
- the electron-density at the metal atom
- the reactivity of the catalyst in the catalytic cycle
- the lifetime and turnover-numbers of the catalyst
- the enantioselectivity of the reaction (with chiral ligands)

1.2.1. Steric Effects in Phosphine Ligands

Phosphines are easy to synthesize and are excellent ligands for transition metals. As a consequence, the steric attributes of the phosphine ligand are easily controlled. This ability to control the bulk of the ligand permit are to tune the reactivity of the metal complex. For example, if the dissociation of a phosphine ligand is the first step in a reaction, the reaction can be accelerated by utilizing a larger phosphine ligand. Likewise, if dissociation is a problem, than a smaller phosphine can be used.

1.2.2. Electronic Attributes of Phosphine Ligands

The bonding in phosphine ligands, like that of carbonyls can be thought of as having two important components. The primary component is sigma donating of the phosphine lone pair to an empty orbital on the metal. The second component is backdonating from a filled metal orbital to an empty orbital on the phosphine ligand. This empty phosphorus orbital has been described as being either a d-orbital or an antibonding sigma orbital; current consensus is that the latter is more appropriate given the relatively high energy of a phosphorus d-orbital:

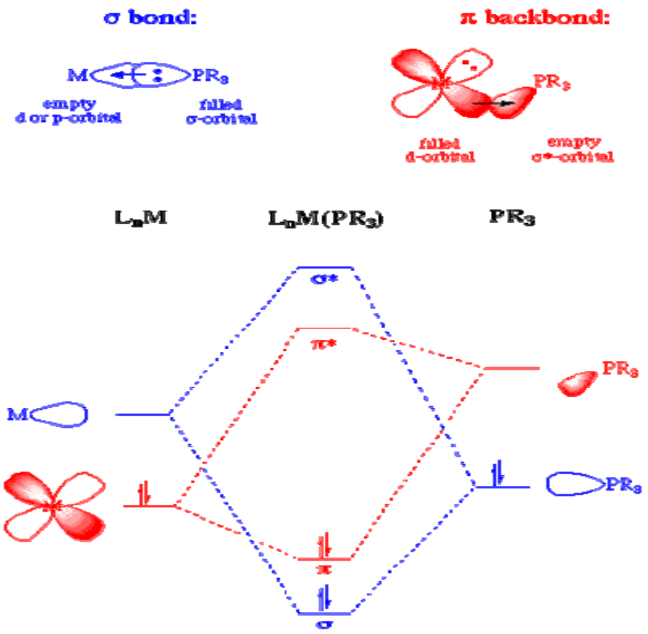


Figure 1.3 Molecule Orbital Energy Diagram of Formation Metal-Phosphorus Bond.

As electron-withdrawing (electronegative) groups are placed on the phosphorus atom, the σ-donating capacity of the phosphine ligand tends to decrease. At the same time, the energy of the Π-acceptor (sigma-*) on phosphorus is lowered in energy, providing an increase in backbonding ability. Therefore, phosphines can exhibit a range of σ-donor and Π-acceptor capabilities, and the electronic properties of a metal center can be tuned by the substitution of electronically different but isosteric phosphines.

A rough ordering of the Π-accepting or σ-donating capabilities of phosphines can be accomplished by synthesizing a series of complexes in which the only difference is the nature of the phosphine ligand. If these complexes contain a carbonyl ligand, the CO stretching frequency can be used as an indicator of electron density at the metal (the lower the value of the CO stretching frequency, the greater the backbonding to the metal and thus the higher the electron density at the metal). Experiments such as this permit us to come up with the following empirical ordering:

$$PMe_3 < PPh_3 < P(OMe)_3 < P(OPh)_3 < P(NR_2)_3 < PCL_3 < CO \approx PF$$

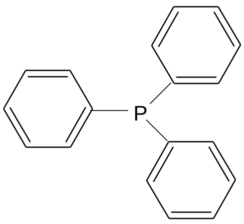
Greater Π-acidity →

← Greater σ-donating

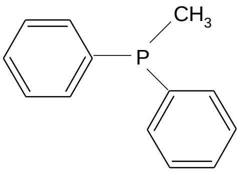
Phosphine-ligands are mainly prepared by two routes, the radical addition of alkenes to phosphines, and the nucleophilic substitution of phosphine-halogenides with Grignard-reagents or organo-lithium compounds. This methods allow to produce a wide variety of phosphine-ligands with different properties.

Some phosphine-ligands with different properties are as follows:

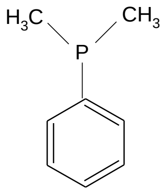
1- Triarylphosphines, mono-and di-aryl- phosphines:



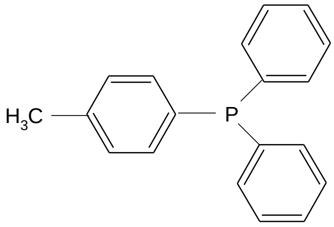
triphenylphosphine



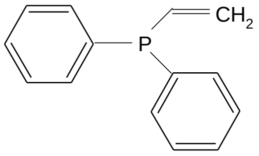
methyldiphenylphosphine



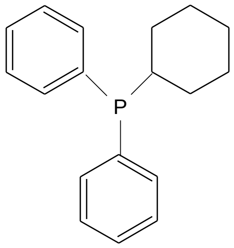
dimethylphenylphosphine



diphenyl(p-tolyl)phosphine

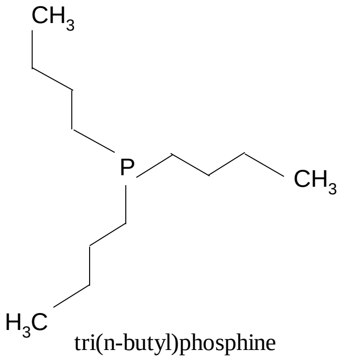


vinyldiphenylphosphine

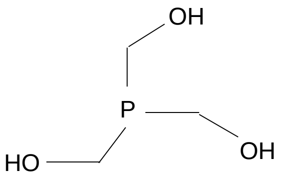


cyclohexyldiphenylphosphine

2- Trialkyl-phosphines:

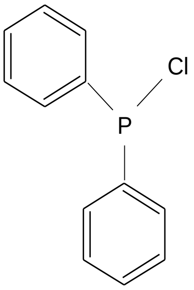


tri(n-butyl)phosphine

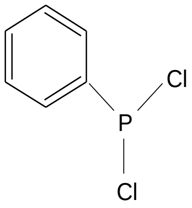


tris(hydroxymethyl)phosphine

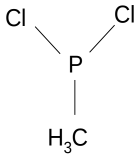
3- Phosphines Halogenides:



chlorodiphenylphosphine



dichlorophenylphosphine

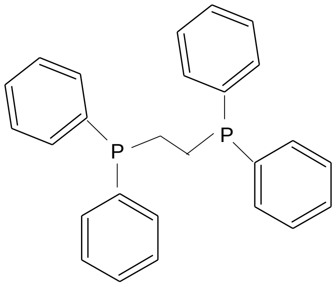


methyldichloro phosphine

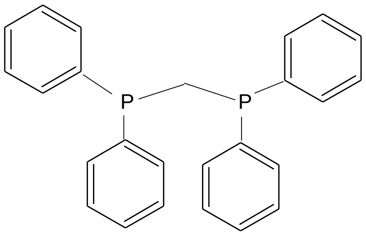
4- Chelating Non-Chiral Phosphine-Ligands:

i. Diphosphines Ligands

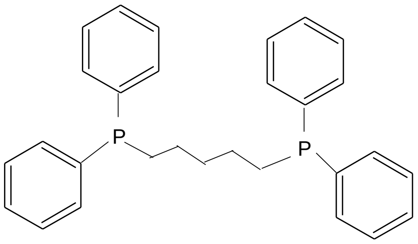
Diphosphines, are a class of compounds used as ligands in inorganic and organometallic chemistry. They are identified by the presence of two phosphine ligands joined by a backbone, and are usually chelating. The most widely used diphosphine ligands are the bis(diphenylphosphino)alkanes, $Ph_2P(CH_2)_nPPh_2$. These can be prepared from $X(CH_2)_nX$ (X= halogen) and $YPPh_2$ (Y= alkali metal) in THF (Wilkinson et al., 1987). Bidentate phosphines with only one bridging group such as dppm tend to promote metal-metal interaction or bond formation because the two donor P atoms are so close together. The use of chelate phosphines with many bridging groups giving long flexible chains has quite a different effect. For example, the chelate phosphine $^tBu_2P(CH_2)_{10}P^tBu_2$ can give complexes that have as many as 72 atoms in a ring (Cotton and Wilkinson, 1980).



1,2-bis(diphenyl-phosphino)ethane

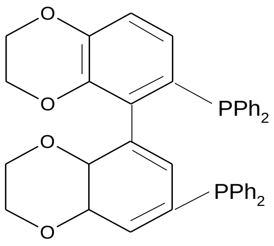


bis(diphenylphosphino) methane

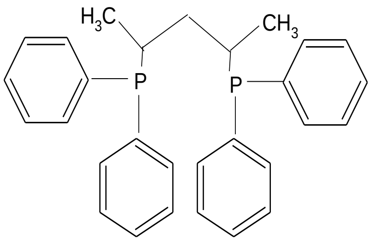


1,5-bis(diphenyl-phosphion)pentane

5- Chiral-Phosphine Ligands:



(R)-[(5,6), (5',6')-Bis (ethylenedioxy)- Biphenyl -2,2'-diyl]-Bis (diphenylphosphine)



(2s,4s)-(-) – 2,4-Bis-(Diphenylphosphino) pentane “S,S-BDPP”

1.3. THE SULPHUR ATOM and ITS CHEMISTRY

Sulphur, with atomic number 16, is the second element of the Group VI B of the Periodic Table. There are ten reported isotopes, four of which are stable, whilst the remaining six are radioactive.

Elemental sulphur has been known and used since antiquity, purified in large quantities since the fifteenth century, and burnt in “lead-houses” into sulphuric acid in ton-quantities since about 1750.

1.3.1. Reaction with trivalent phosphorus compounds

Elemental phosphorus shows great affinity for sulphur and many phosphorus compounds will add sulphur or react with sulphur compounds. The entire field of orgonophosphorus chemistry was reviewed by Kasolapoff in 1950.

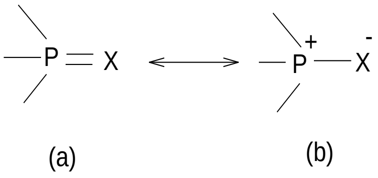
The phosphines, RPH_2, R_2PH and R_3P are generally characterized by marked reactivity towards oxygen, sulphur, halogens, alkyl halides and other reagents, forming numerous compounds and complexes. The reaction at a primary phosphine with sulphur has received very little study. Phenylphosphine react at elevated temperatures with sulphur to form a compound, $C_6H_5PSH_2$, and a small amount of a material having an empirical formula, $(C_6H_5)_3P_3S_2$.

Secondary phosphines, R_2PH, react with sulphur, the viger dependent upon the nature of the R groups, to produce secondary dithiophosphoric acids, R_2PS_2H.

The tertiary phosphines are reactive towards oxygen, sulphur and selenium to form the corresponding oxides, sulfides and selenides.

Tertiary phosphites, $(RO)_3P$, react with elemental sulphur forming the corresponding $(RO)_3PS$.

That known structures, sulphures replace oxygen and selenium. From a correlation between the chemical shifts of the methylene protons and the charge on phosphorus in the $(C_6H_5)_2P(O)\text{-}<(C_6H_5)_2P(S)\text{-}<(C_6H_5)_2P(Se)\text{-}<(C_6H_5)_2PCH_3\text{-}$. Since this is not in the expected order on the basis of the electronegativity of chalcogenes, these data furnish additional corroborative evidence that contribution of the double bond is more important in the case of oxygen than in the case of sulphur and selenium, for which the dipolar form (b) is of greater importance.



1.4. PALLADIUM

The element palladium was isolated and identified by William Wollaston in 1803. It’s name comes from the asteroid Pallas (Pallas was another name for Athena, the Greek goddess of wisdam). Palladium in pure form is not found in nature. The preparation of the element is via a series of reactions. Platinum metal are concentrates (65% of which come from the Merensky Reef in South Africa) are treated with aqua regia (giving copper and nickel as by products). The solutions, containing H_2PdCl_4 with platinum and gold complexes, are treated with $FeCl_2$ and then with excess of NH_4OH followed by HCl to precipitate the impure $[Pd(NH_3)_2Cl_2]$ is ignited to palladium metal.

Palladium metal, like platinum metal, is silvery-white and lustrous and has malleable and ductile properties. It has face-centered cubic crystal structure. It forms a fluoride, PdF_4 (brick-red), and other halides: PdF_2 (pale violet), α-$PdCl_2$ (dark red), $PdBr_2$ (red black), and PdI_2 (black). Pd metal can absorb up to 935 times its own volume of hydrogen molecules. When the composition reaches about $PdH_{0,5}$, the substance becomes a semiconducter.

Palladium can form complexes in a variety of oxidation states. Examples of some oxidation state complexes are shown below:

Oxidation States Complexes:

(0) $K_4[Pd(CN)_4]$ (yelllow)

(I) $[PdCl(CO)]_x$ (reddish-violet)

(II) $Na_2[PdCl_4]$ (yelllow)

(IV) $K_2[PdF_6]$ (bright yellow)

Palladium, is a soft steel-white metal that resembles platinum, doesn't tarnish in air, and is the least dense and has the lowest melting point of the platinum group metals. Palladium is chemically attacked by sulfuric and nitric acid but dissolves slowly in hydrochloric acid. This metal also does react with oxygen at normal temperatures.

Naturally-occurring palladium is composed of six isotopes. The most stable radioisotopes are Pd-107 with a half-life of 6,5 million years, Pd-103 with a half-life of 17 days, and Pd-100 with a half-life of 3,63 days.

When it is finely divided, palladium forms a good catalyst and is used to speed up hydrogenation and dehydrogenation reactions, as well as in petroleum cracking. It is also alloyed and used in jewellry. Other uses;

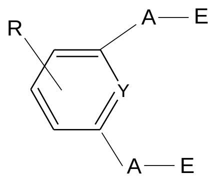
- White gold is an alloy of gold that is decolorized by the addition of palladium.
- Similar to gold, palladium can be beaten into a thin leaf form as thin as 100 nm.
- Hydrogen easily diffuses through heated palladium, thus, it provides a means of purifying the gas.
- Telecommunications switching-system equipment uses palladium.
- Palladium is also used in dentistry, watch making, in aircraft spark plugs and in the production of surgical instruments and electrical contacts.
- It is also used as Palladium-Hydrogen electrodes in electrochemical studies.

In recent years, however, most studies have focused on the use of soluble Pd complexes with various types of P ligands with the aim of increasing the effectiveness of the catalysts (Brase et al., 1998; Beletskaya and Cheprakov, 2000). The palladium catalyzed asymmetric allylic substitution reaction (Kocovsky, 2003; Pfaltz et al., 1994; Frost et al., 1992) has been demonstrated to be useful in the synthesis of valuable small molecules and complex natural products (Trost and Crawley, 2003). A number of chiral ligands have been successful, used in the palladium catalyzed allylic substitutions.

However, the relativity high price of the palladium complex has greatly limited the industrial application of homogeneous Heck reaction, and some of the phosphine ligands are sensitive to air and moisture. The removal of ligands derived from palladium homogenous catalyst often complicates work up and product isolation. In addition, phoshine-free reaction conditions are highly designed due to the environmental effects associated with phosphine (Reefz and de Vries, 2004).

1.5. PINCER LIGANDS and PINCER COMPLEXES

Pincer complexes consist of a metal centre and a pincer skeleton. The pincer skeleton is a tridentate ligand which is connected to the metal via at least one metal-carbon σ bond. The most common type of pincer skeleton is an aryl anion, which is connected to the metal via only one metal-carbon σ bond; substituents ortho-to this σ bond are held in a fixed position and can co-ordinate to the metal site via O, S, N or P donor atoms (Figure 1.4) (Singleton et al., 2003).



E= NR_2, PR_2, $P(OR)_2$, OR, SR, AsR_2, SeR

Y= N, C

A= CH_2, NH(R)O

R= alkyl, aryl

Figure 1. 4 General Structure of Pincer Ligands.

Transition metal pincer complexes using phosphorus as the donor atoms (PCP pincer complexes) were reported in the early 1970s. The term PCP refers to the three atoms directly attached to the metal, phosphorus, carbon and phosphorus. Other common pincer complexes contain the PNP, NCN, SCS, SPS and CNC sekeletons. The CNC skeleton or ligand is slightly different to the other pincer ligands because, whilst being tridentate, it bonds to the metal by two metal-carbon σ bonds. Different types of pincer ligands are shown in (Figure 1.5).

It is the presence of at least one metal-carbon σ bond in a pincer complex that is responsible for many of the desirable properties of these compounds. This linking of the metal to a ligand prevents, at least to a large extent, the metal disassociating from the ligand and gives the complexes a high degree of thermal stability.

The donor atoms and their substituents can control the accessibility of the metal to potential fine tuning of the reactivity of the complex. It is also possible that stereochemical information can be introduced, for example, at the benzylic carbons in the generic pincer complex (Figure 1.4) or by the donor atom substituents, creating potential stereoselective catalysts.

It has been known that; the substituents E can be connected to the central aromatic backbone by different spacers (A), such as methylene groups ($-CH_2-$), amines (-NR-) or oxygen atoms (-O-). The (un)substituted aromatic ring can be either a pyridine ring (Y=N) or a benzene ring (Y=C). As for the lone pair donors E, they were known as amines (NR_2), phosphines (PR_2), phosphites ($P(OR)_2$), ethers (OR), thioethers (SR), and even n-heterocyclic carbenes (NHC) (Benito-Garagorri and Kirchner, 2008).

Among the many ligand systems that can be found in the literatures, pincer ligands and their complexes have attracted increasing interest due to their high stability, activity and variability. In the late 1990s several applications of pincer complexes in the fields of catalysis, molecular recognition, and supramolecular chemistry were discovered, turning this area into an intensively investigated subject in organometallic chemistry. Pincer complexes have been used as catalysts in different transition metal mediated processes, including C-C bond forming reactions, polymerization reactions, transfer hydrogenation and dehydrogenation reactions. Moreover, pincer complexes have been employed as sensors, have been used to investigate C-C, C-H and C-O bond activation processes, or have been serving as building blocks for the synthesis of self-assembled supramolecular structures (Benito-Garagorri and Kirchner, 2008).

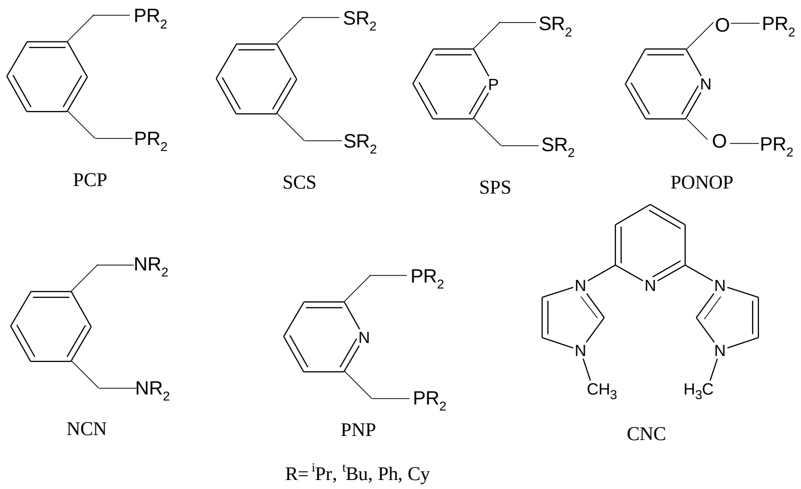


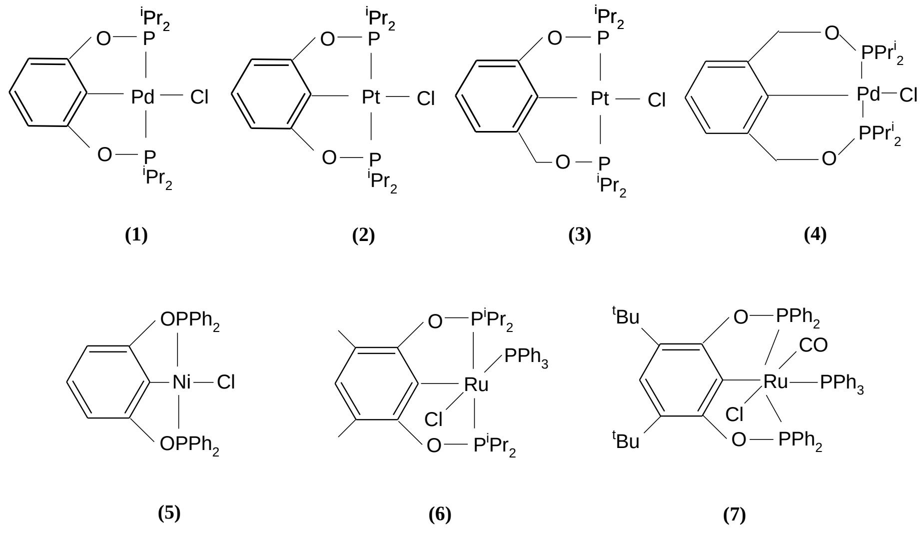
Figure 1.5 Different Types of Pincer Ligands.

1.5.1. PCP Type Pincer Complexes

PCP pincer ligands, monoanionic terdentate ligands with the general formula $[(C_6H_3)(APR_2)_2]^-$ ($A=CH_2,O$), have received great attention since the first example was reported by Moulton and Shaw (Moulton and Shaw, 1976). PCP pincer complexes were found to be active catalysts for a wide range of reactions including dehydrogenation, transfer dehydrogenation (Dani et al., 2000), Heck reaction (Ohff et al., 1997), Suzuki-coupling (Bedford et al., 2000), Nagishi-type coupling (Eberhard et al., 2002) and enantioselective sharpless epoxidations (Gorla et al., 1994). Pincer ligands bond most commonly in the meridional η^3-PCP co-ordination mode to metals, which is the reason for their great air-, temperature-and moisture-stability. Most pincer ligands are based on one-atom linkages between the donor atom P and the aryl-carbon. Thus, upon metal complexation the ligand forms two five-membered metallocycles (Wang et al., 2003).

PCP Type pincer complexes were classified into two groups;

a. Phosphinito PCP type pincer complexes (POCOP type pincer complexes).

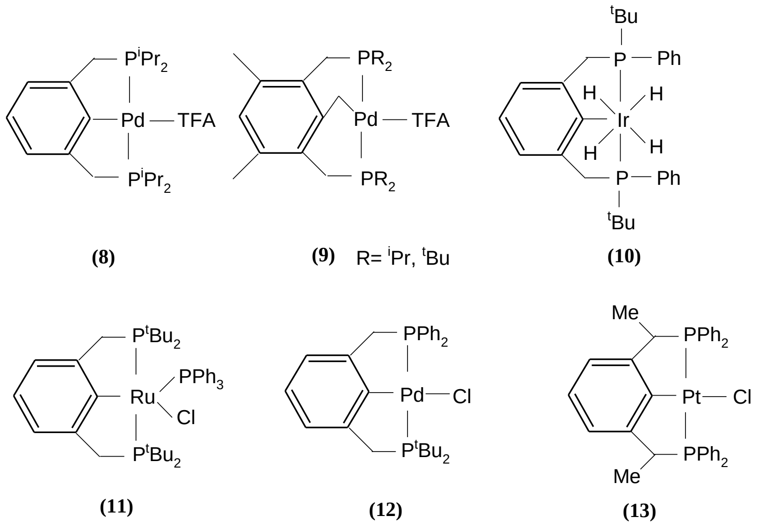


(1) (2) (3) (4)

(5) (6) (7)

Figure 1.6 Examples of Phosphinito PCP Type Pincer Complexes (POCOP Complexes).

b. Phosphino PCP type pincer complexes.

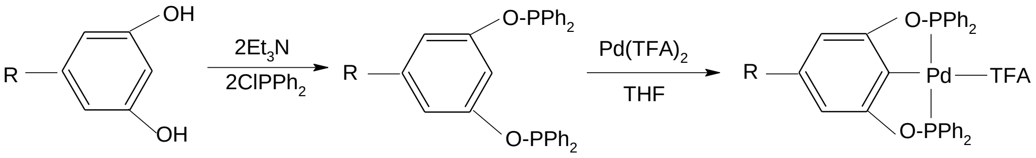


(8) (9) R= ^{i}Pr, ^{t}Bu (10)

(11) (12) (13)

Figure 1.7 Examples of Phosphino PCP Type Pincer Complexes.

Bedford and co-workers have synthesized the ligands **14a** and **14b** in good yields by the reaction of the appropriate aromatic diol with chlorodiphenylphosphine in toluene in the presence of triethylamine (Scheme 1.1) (Bedford et al., 2000). The reactions of these ligands with palladium trifluoroacetate in THF at room temperature gives the POCOP pincer complexes **15a** and **15b** which were shown excellent air and moisture stability.



(14a) R= H

(14b) R= Me

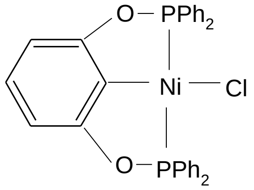
(15a) R= H

(15b) R= Me

Scheme 1.1 General Route for Preparing POCOP Pincer Type Complexes.

It was reported that palladium POCOP pincer complexes can be used as high activity catalysts in the Suzuki reaction and that bis(phosphinite) PCP pincer complexes were ideal catalysts for the coupling of deactivated and sterically hindered aryl bromides as they were inexpensive and very easily synthesized by Bedford et al.

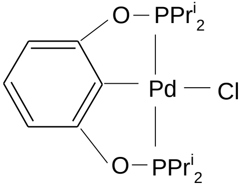
Another example of POCOP pincer complex with two five membered metallocycles was known as $[NiCl\{C_6H_3\text{-}2,6\text{-}(OPPh_2)_2\}]$ (Gomez-Benitez et al., 2006). Gomez-Benitez and co-workers were reported that complex **16** (Figure 1.8) was inexpensive and easy to prepare, and also efficiently catalyzes the thiolation of iodobenzene with a broad scope of disulfides in the presence of zinc.



(16)

Figure 1.8 Structure of POCOP Ni Complex.

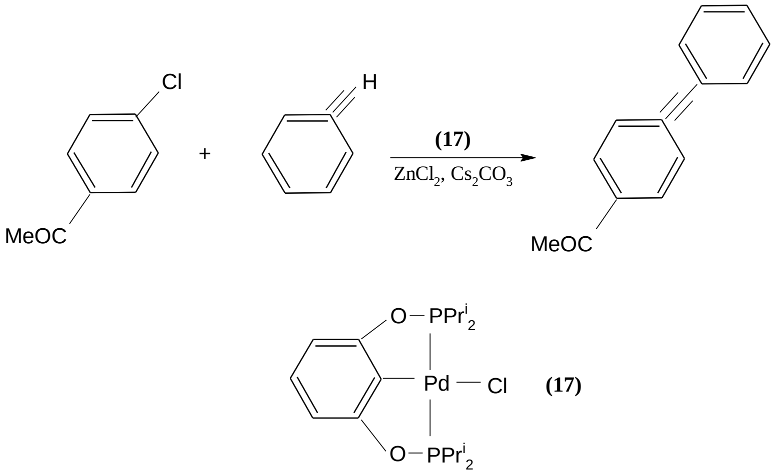
Morales and co-workers have reported the palladium POCOP pincer complex PdCl $\{C_6H_3\text{-}2,6\text{-}(OPPr^i{}_2)_2\}$ **17** (Figure 1.9) (Morales-Morales et al., 2000). The complex was reported as a highly efficient catalyst for the olifinic coupling of aryl bromo and iodo compounds under aerobic conditions.



(17)

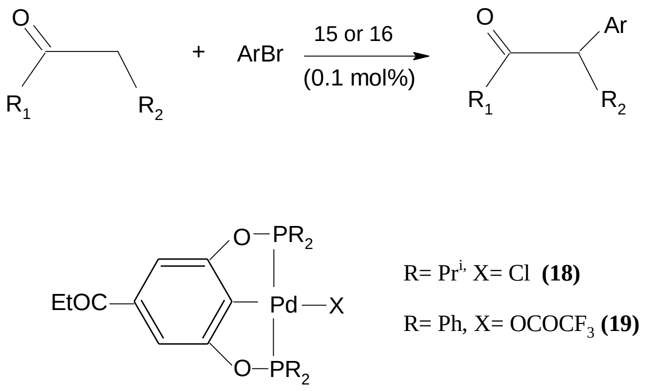
Figure 1.9 Structure of POCOP Pd Complex.

In 2002 Eberhard and co-workers, reported a modified Negishi coupling reaction protocol for the one pot coupling of a wide arroy of aryl chlorides with phenylacetylene in the presence of $ZnCl_2$ using complex **17** as catalyst, achieving yields as high as 91% for the reaction of 4-chloroacetophenone with phenyacetylene at 160°C for 24 h reaction time (Scheme 1.2) (Eberhard et al., 2002).



Scheme 1.2 Negishi Coupling Reaction.

POCOP type Pd(II) complexes **18** and **19** were prepared by Charruca and co-workers in 2006 (Charruca et al., 2006). Also they have reported on the use of p-alcoxycarbonylated PCP- Pd(II) phosphinite pincer-type complexes **18** and **19** for the α-arylation of ketones. Catalytic activity of complexes **18** and **19** have been tested in several C-C bond-forming reactions and they have shown excellent catalytic properties in Heck, Suzuki and Sonogashira cross-coupling reactions (Scheme 1.3).

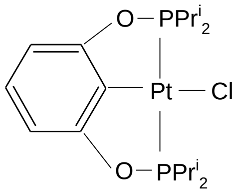


R= $Pr^{i,}$ X= Cl **(18)**

R= Ph, X= $OCOCF_3$ **(19)**

Scheme 1.3 Reaction of the α-arylation of Ketones.

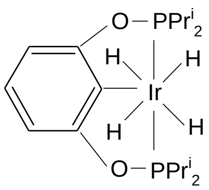
One of the example of POCOP type Pt(II) complex **20**, which is shown below (Figure 1.10) have been explored as catalysts for the hydroxylation of 1-propanol to 1,3-propanediol under mild conditions (Wang et all., 2006).



(20)

Figure 1.10 Structure of POCOP Pt Complex.

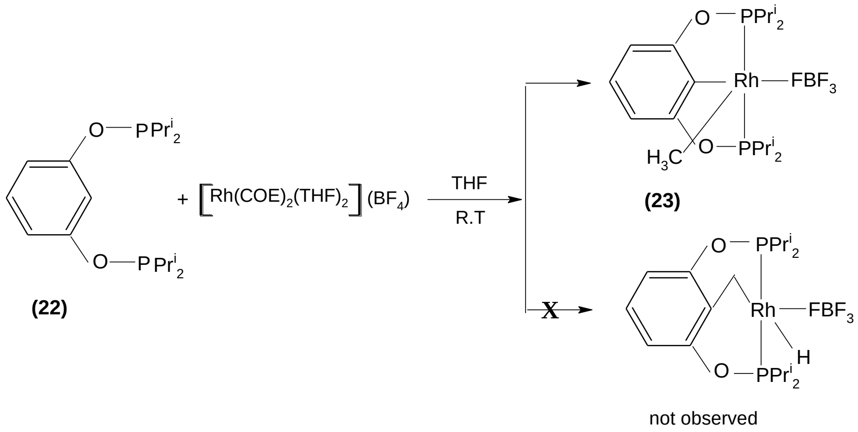
Morales and co-workers have also reported iridium POCOP pincer complex $IrH_4\{C_6H_3\text{-}2,6\text{-}(OPPr^i_2)_2\}$ **21** (Morales et al., 2004) (Figure 1.11). This complex catalyzes the dehydrogenation of linear alkanes to alkenes with efficiencies that are equal to those of iridium POCOP pincer complexes of analogous bis(phosphino) ligands. It has been reported that complex **21** catalyses the dehydrogenation of linear alkanes to alkenes with efficiencies that are equal to those of iridium POCOP pincer complexes of analogues bis(phosphino)ligands. Also, authors have reported that the bis(phosphinito) POCOP ligand can be prepared from relatively inexpensive starting materials with much greater convenience than the bis(phosphino) PCP ligands.



(21)

Figure 1.11 Structure of POCOP Ir Complex.

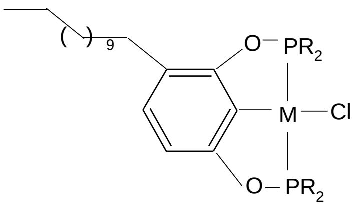
The first rhodium POCOP pincer complexes were synthesized by Milstein and co-workers (Scheme 1.4). The ligand **22** was synthesized in an analogous manner as that of ligand [C_6H_4-1,3-($OPPri_2)_2$] by diphosphination of 2-methyl resorcinol with diisopropylchlorophosphine using 4(dimethylamino) pyridine as base. Reaction of this ligand with $[Rh(COE)_2Cl_2]_2$ resulted in a mixture of compounds. However, the reaction of ligand **22** with the cationic starting material $[Rh(COE)_2(THF)_2]BF_4$ at room temperature led to the immediate formation of the C-C activation product **23** as the main product (Milstein et al., 2006).



Scheme 1.4 Synthesis of the POCOP Rh Complex.

The phosphinite POCOP ligands [4-($nC_{12}H_{25}$)-C_6H_3-1,3-($OPR_2)_2$] R= Ph, Pr^i and their Ni, Pd, Pt complexes **24(a-c)(a'-c')** (Figure 1.12) were synthesized by Solano-Prado et al. (Solano-Prado et al., 2010). It was reported that these complexes may present interesting opticial properties, particularly in the field of liquid crystals, instead of their catalytic applications in Heck and Suzuki reactions. And also, it has been observed that Pd complexes of phosphinite

POCOP ligands were very effective catalysts for the Heck and Suzuki- Miyaura reactions.



(24a) M= Ni ; R= Ph

(24a') M= Ni ; R= Pr^i

(24b) M= Pd ; R= Ph

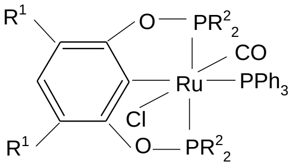
(24b') M= Pd ; R= Pr^i

(24c) M= Pt ; R= Ph

(24c') M= Pt ; R= Pr^i

Figure 1.12 Structure of POCOP Ni, Pd, Pt Complexes.

Although, there were many POCOP type palladium and platinum complexes, ruthenium POCOP complexes were less common. In addition to that, Bedford and co-workers have reported resorcinolbis (phosphinite) ligands readily from ruthenium POCOP pincer complexes **25(a-d)** (Figure 1.13) (Bedford et al., 2006). They have shown that, when steric bulk is introduced onto the resorcinol backbone, in which case the rate of C-H activation is significantly accelerated.



(25a): R^1= H; R^2= Ph

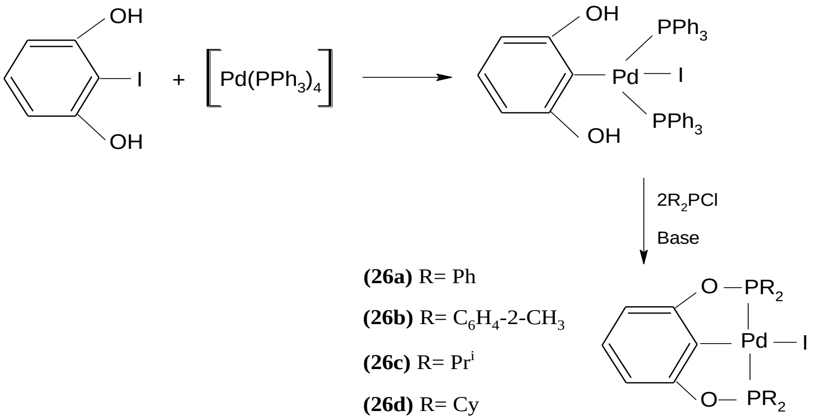
(25b): R^1= H; R^2= ^{i}Pr

(25c): R^1= ^{t}Bu; R^2= Ph

(25d): R$_1$= ^{t}Bu; R^2= ^{i}Pr

Figure 1.13 Structure of POCOP Ru Complex.

A novel method for the synthesis of pincer complexes denominated as the ‘ligand introduction route’ this method being particularly useful for the synthesis of pincer complexes having bulky and / or chemically unstable ligand units has been reported by Kimura et al. (Kimura and Uozumi, 2006). This procedure consists of the oxidative addition reaction of 2-iodoresorcinol to a Pd(0) complex [Pd(PPh$_3$)$_4$]. Hence, once the insertion of the 2-iodoresorcinol on the metal center has taken place the procedure that follows resembles very much the traditional method described above. Thus, the oxidative addition product is than reacted in a 1:2 molar ratio with the corresponding chlorophosphine in the presence of a base, to afford directly the POCOP pincer complex **26(a-d)** (Scheme 1.5). It was reported that, the pincer complexes were active catalysts for the Suzuki Coupling reactions.



(26a) R= Ph

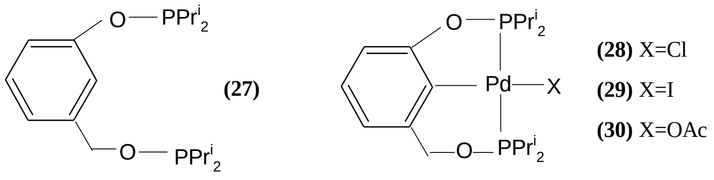
(26b) R= C_6H_4-2-CH_3

(26c) R= Pr^i

(26d) R= Cy

Scheme 1.5 Mechanism of Ligand Introduction Route.

Wang and co-workers have reported the synthesis of the first unsymmetrical POCOP' ligand 1-(^{i}PrPO)-3-(^{i}Pr$_2$POCH$_2$) (C_6H_4) **27** and its palladium (II) complexes: [PdX{(C_6H_3)(OP^{i}Pr$_2$)-2-(CH$_2$OP^{i}Pr$_2$)-2-(CH$_2$OP^{i}Pr$_2$)-6}] **28-30** (Wang et al., 2003) (Figure 1.14). Complexes **28-30** were unusual for pincer complexes in that they were composed of five and six-membered metallocycles. They represent the first examples of pincer complexes with different metallocycle ring sizes.



(27)

(28) X=Cl

(29) X=I

(30) X=OAc

Figure 1.14 Unsymmetrical POCOP Pincer Ligand and Pd Complex.

All complexes **28-30** were compared to complexes derived from the symmetrical pincer analogue 1,3-(^{i}PrPO)$_2$(C_6H_4). These complexes were applied to be active catalysts for the allylic alkylation of cinnomyl acetate with sodium dimethyl malanate. This increase in activity to the introduction of a six membered metallocycle into the pincer complex structure. This in turn leads to a more flexible complex structure and an increase in the P-M-P angle. Moreover, the catalytic activity depends strongly on the presence or absence of co-ordinating anions.

There weren’t many examples on the synthesis and usage of bis (phosphinite) PCP pincer complexes with two six-membered metallocycles. Naghipour and co-workers has been reported 1-3-bis [(di-isopropylphosphinite) methyl] benzene **31** and it’s Pd complex **32** with two six-membered metallocycles (Naghipour et al., 2007) (Figure 1.15). It has been reported that complex **32** exhibited very good catalytic activity with excellent results on the Heck, coupling of iodobenzene with styrene.

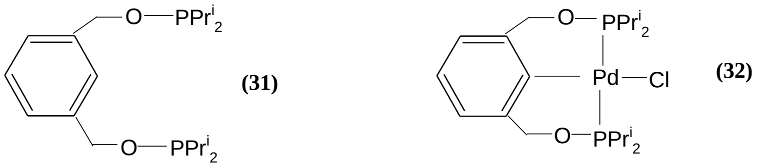
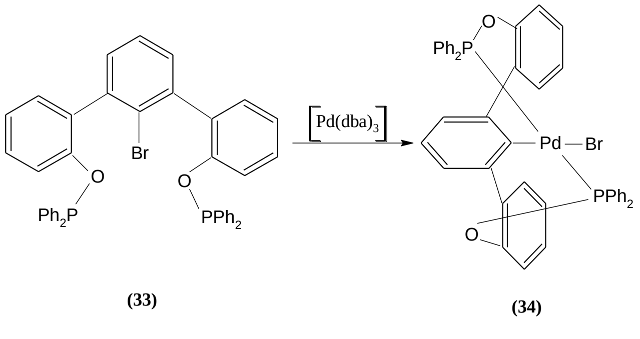


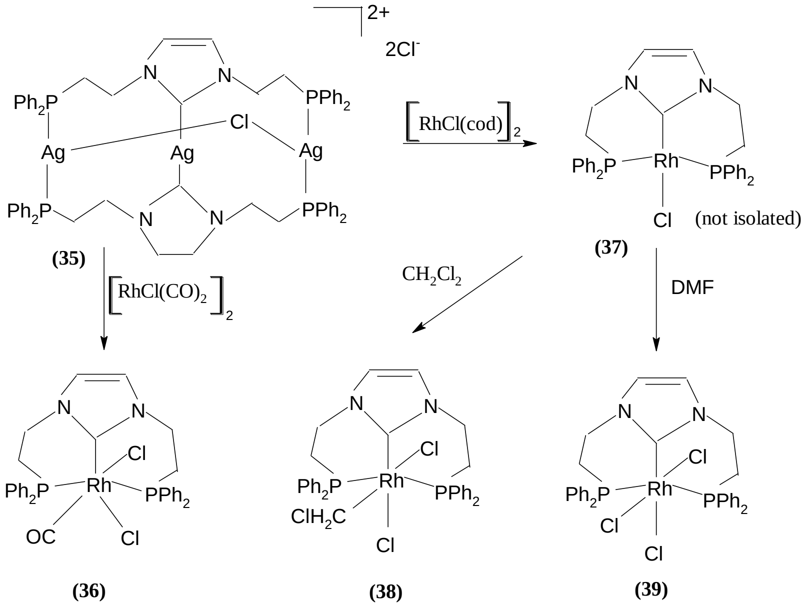
Figure 1.15 Two six membered POCOP Pincer Ligand and Pd Complex.

Protasiewicz and co-workers were reported a new phosphinite pincer-type ligand with the largest ‘twist’ angle so far observed. Ligand **33** reacts with [Pd(dba)$_3$] to yield the pincer complex **34** (Scheme 1.6). It was reported that this new pincer complex is robust and displays great air and heat stabilities and can be easily purified by flash chromatography on silica gel under ambient conditions (Protasiewicz et al., 2006).



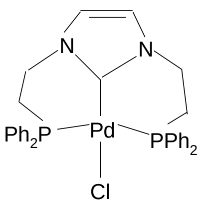
Scheme 1.6 Synthesis of the POCOP Pd Complex.

A series of PCP pincer carbene complexes of Rh(I) and Rh(III) were recently prepared by Zeng and co-workers in 2005 (Zeng et al., 2005) (Scheme 1.7). Transmetallation from the silver-carbene compound **35** to $[RhCl(CO)_2]_2$ provided the pentacoordinate Rh(I) complex **36** with a pincer structure. A similar reaction with $[RhCl(cod)]_2$ was intended to produce the electron-rich complex (PCP)Rh^{I}Cl, **37**, but this compound could not be isolated because it rapidly underwent oxidative addition with solvent CH_2Cl_2 affording the Rh(III) species **38.** The reaction was also tried in DMF to avoid the presence of chlorinated solvents, but the reaction proceed to the Rh(III) species **39** (Scheme 1.7).



Scheme 1.7 Synthesis of the PCP Phosphine Rh Carbene Complexes.

Palladium complexes of similar PCP pincer ligands have been also tested in the Suzuki coupling of aryl bromides with phenylboronic acid (Lee et al., 2004). Application of PCP pincer type palladium complexes **40** and **41** (Figure 1.16) in the Heck and Suzuki coupling reactions has also been reported by the same group and modest activity was observed for these reactions (Lee et al., 2004).



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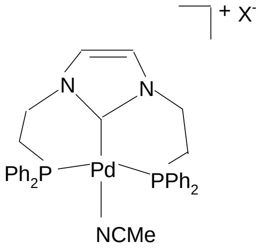
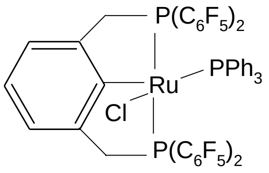


(41)

Figure 1.16 PCP Phosphine Pd Carbene Complexes.

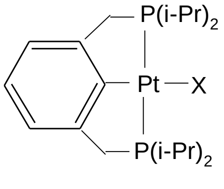
Ru(II) complex **42** (Figure 1.17) containing an electron poor, highly fluorinated PCP^{ArF} pincer ligand has been synthesized by Gagliardo et al. (Gagliardo et al., 2005). PCP-Ru(II) complexes were known as highly active catalysts in the transfer hydrogenation of ketones (Amoroso et al., 2004) and also their interesting redox and photophysical effects (Gagliardo et al., 2004) were reported.



(42)

Figure 1.17 PCP Phosphine Ru Complex.

A series of the first C-coordinated diazoalkane complexes of Pt, **43(a-c)**, (Figure 1.18) based on pincer–type PCP ligands were synthesized and reported (Poverenov et al., 2005). It was demonstrated that the reactivity of C-metallated diazoalkane complexes were strongly dependent on the pincer ligand properties.



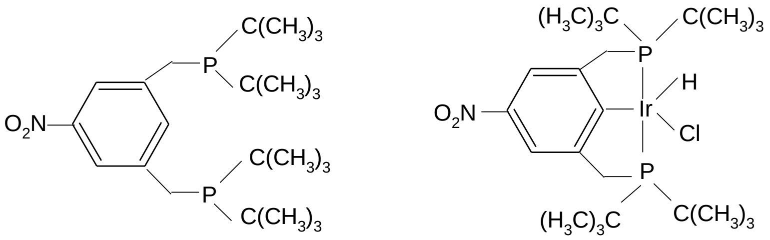
(43a) X= Cl

(43b) X= OTf

(43c) X= Me

Figure 1.18 PCP Phosphine Pt Complex.

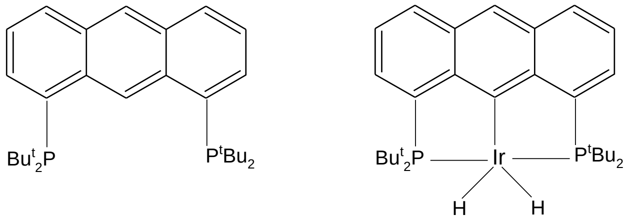
Another example of PCP-Pincer type complexes were synthesized and reported by Grimm and co-workers (Grimm et al., 2000). 3,5-di(bromomethyl)nitrobenzene with di-t-butylphosphine and subsequent treatment with sodium acetate was given the PCP pincer ligand **44.** Heating a isopropanol/ water solution of this ligand with iridium(chloride) resulted in the iridium hydrochloride complex **45** (Figure 1.19).



(44) **(45)**

Figure 1.19 PCP Phosphine Ligand and Ir Complex.

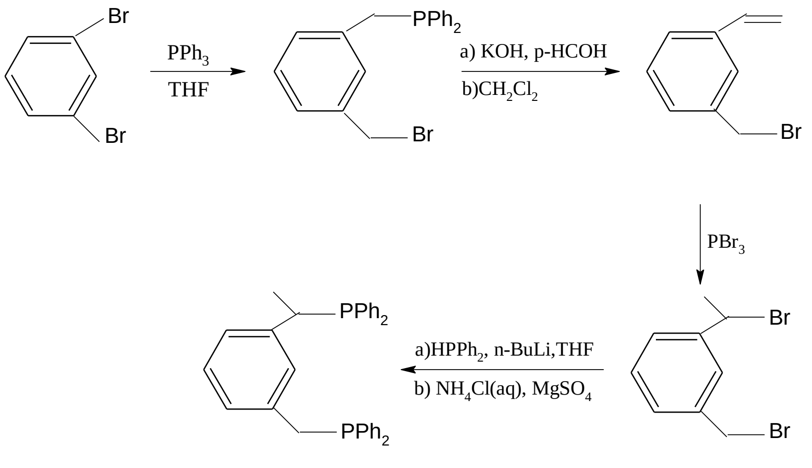
PCP pincer ligands like structure **46**, and their metal complexes like structure **47** (Figure 1.20) were just prepared in an effort to generate pincer complexes of even greater thermal stability (Haenel et al., 2001).



(46) **(47)**

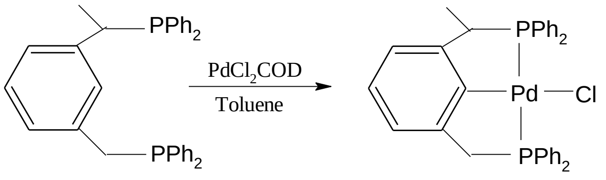
Figure 1.20 PCP Phosphine Ligand and Ir Complex.

One of the example of the asymmetric ligand [C_6H_4-1-(CH_2PPh_2)-3-($CH(CH_3)PPh_2$)] **48** (Scheme 1.8) and its Pd (II) derivative [$PdCl\{C_6H_3$-2-(CH_2PPh_2)-6-(CH_3)-$PPh_2\}$] **49** (Scheme 1.9) have been reported by Naghipour et al. Although, the number of examples of complexes including asymmetric pincer type ligands was limited in comparison with those of their symmetric analogues, complexes bearing asymmetric pincer ligands have shown enhanced and in many cases markedly different reactivities, such as hemilability. This was partly because their preparation was a considerable challenge, which was laborious and requires a series of steps to introduce different groups or donors (Naghipour et al., 2008).



(48)

Scheme 1.8 Synthesis of the Asymmetric PCP Pincer Ligand.



(48) **(49)**

Scheme 1. 9 Synthesis of the Asymmetric PCP Pincer Pd Complex.

Steric and electronic properties of PCP pincer ligands can be modified by varying the substituents on the phosphorus (R^1 and R^2), the atom-linkage X and Y between phosphorus and aryl-ring carbon, and the ring-substituent R^3. Many examples of phosphines, phosphinites, phosphites have been synthesized, there aren't much are examples for PCP' pincer ligands where $R^1 \neq R^2$ (Figure 1.21) such ligands are however of great interest since this would allow greater control over steric and electronic properties and may, for example, influence the activity of complexes in homogenous catalysis. The first examples of mixed phosphino-phosphinito pincer ligands **50, 51** and their Pd complexes **52, 53** (Figure 1.22) have prepared (Eberhard et al., 2003).

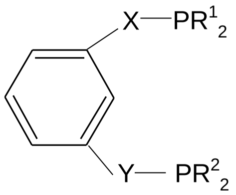
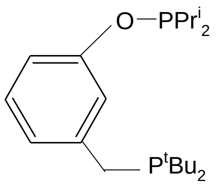
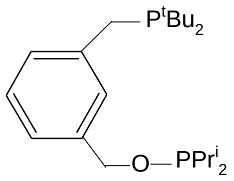


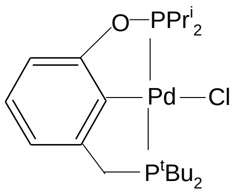
Figure 1.21 Design of PCP Unsymmetrical Ligands.



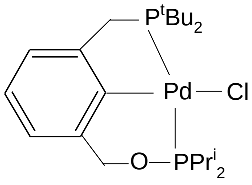
(50)



(51)



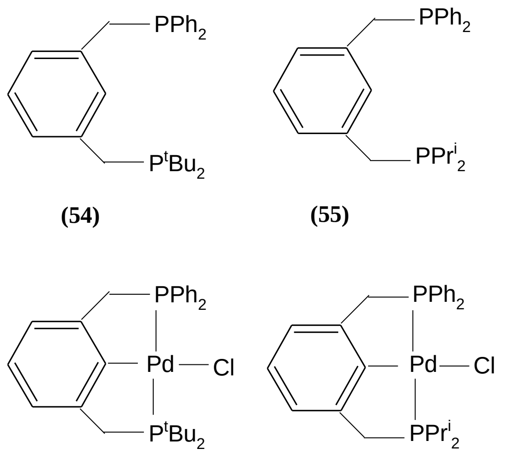
(52)



(53)

Figure 1.22 Unsymmetrical POCP’ Ligands and Pd Complexes.

Similar examples of unsymmetrical phosphino PCP’ pincer ligands **54, 55** and their Pd complexes **56, 57** (Figure 1.23) have been reported by Naghipour et al (Naghipour et al., 2004). It was reported that these complexes were tested as catalysts for the olefination of aryl halides with styrene.

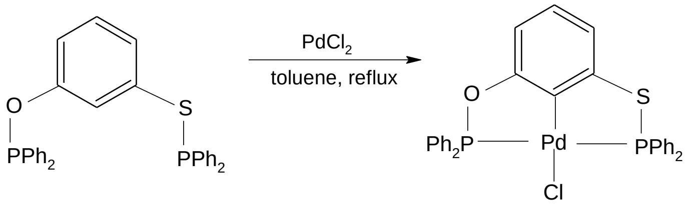


(54) **(55)**

(56) **(57)**

Figure 1.23 Unsymmetrical PCP’ Ligands and Pd Complexes.

It was reported that the number of examples of complexes including non-symmetric pincer type ligands was limited in comparison with those of their symmetric analogs (Serrano-Becerra et al., 2010). A novel non-symmetric Pd(II) phosphinito-thiophosphinito PSCOP pincer complex **59** was synthesized by Serrano and co-workers (Scheme 1.10).



(58) **(59)**

Scheme 1.10 Synthesis of PSCOP Type Ligand and Pd Complex.

1.5.2. SPS and SCS PINCER COMPLEXES

Transition metal chemistry involving sulphur donor groups have a great interest in biology, because of its many industrial applications, and because of its importance in the area of novel complex synthesis (Stiefel, 1995). Sulphur ligated transition metal complexes form the organic parts of the biologically active centres of some metalloproteins and enzymes. Consequently, some of these have found applications in pharmacology (Hille, 1996; Stiefel, 1993), and industrial chemistry (Topsoe et al., 1996). Transition metal thiolate complexes have received special interest because of their ability to adopt different structures and nuclearities (Blower and Dilworth, 1987).

These pincer ligands and their complexes will be presented, have been used in different areas like; coordination chemistry, supramolecular chemistry, catalysis, etc. (Morales-Morales and Jensen, 2007).

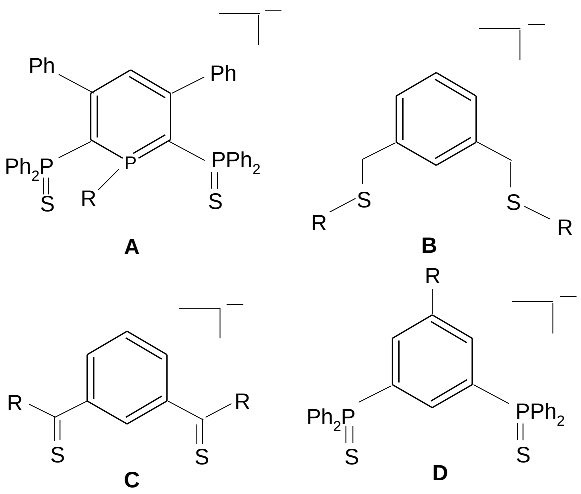


Figure 1.24 Structures of SPS and SCS Pincer Ligands.

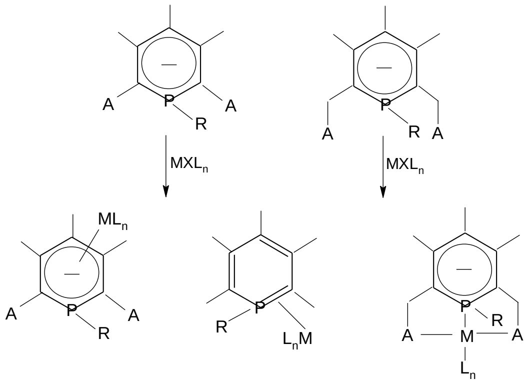
1.5.2.1. SPS PINCER COMPLEXES

Studies on the coordination chemistry of polydentate ligands incorporating both thiolate and tertiary phosphine donor ligands have been increasing. Some of these complexes have been used as models of biologically active centres in metalloproteins such as ferrodoxins, nitrogenase, blue copper proteins and metallothioneins (Franolic et al., 1995) or as models for the design of complexes with potential application as radiopharmaceuticals (Vries et al., 1989). In the specific case of compounds with elements of the groups 8-10, these may be suitable species for catalytic screening. Moreover, the presence of these ligands in the cordination sphere of transition metal complexes may render interesting behaviours in solution as these ligands can be capable of full or partial de-ligation (Dilworth and Weatley, 2000), being able to provide important extra coordination sites for incoming substrates during a catalytic process.

The chemistry of bis(phosphinosulfides)phosphinines was based upon studies on the reactivity of λ^3-phosphinines (Le Flosch, 2001). These heterocycles which are the phosphorus analogues of pyridines display unusual electronic properties which mainly result from the replacement of nitrogen by phosphorus. Thus whereas pyridines show a significant negative charge at nitrogen, phosphinines exhibit the opposite charge distribution because of the lower electronegativity of phosphorus (2.1 for P versus 3.0 for N according to the Pauling scale). This unusual charge distribution and the presence of a low-lying Π*-system make these heterocycles particularly interesting for the stabilization of electron-rich or electron-excessive metal centers (poor σ-donor but strong Π-acceptor ligands) contrary to pyridine ligands which behave as strong σ-donor but only moderate Π-acceptor ligands (Le Flosch, 2006; Mezailles and Le Flosch, 2006; Mezailles et al., 2001). These peculiar electronic properties have been widely exploited in the synthesis of low-valent transition metal complexes with early and late transition metals. Another important consequence of this particular electronic distribution concerns their reactivity toward nucleophiles. Whereas nucleophiles tend to react on the α-carbon atom in pyridines, they react at the electrophilic phosphorus atom of phosphinines to form λ^4

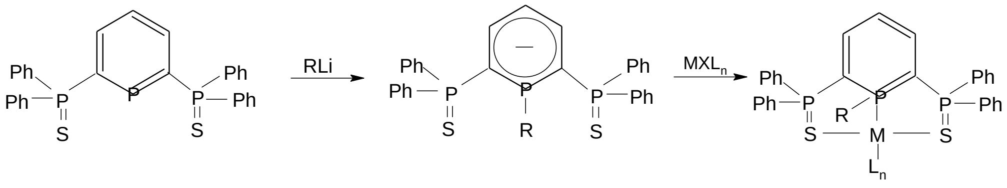
phosphacyclohexadienylanions which do not exhibit aromatic properties. This nucleophilic attack occurs on free ligands as well as on their complexes with transition metals. This cumbersome reactivity has hampered the use of phosphinine as ligands in homogeneous catalysis as the aromatic character of the ring may be disrupted (Carmichael et al., 1993). As a consequence, only a few applications of phosphinines in catalysis have been reported so far.

However, the reactivity of nucleophiles at the phosphorus atom furnishes a straight forward entry in the chemistry of λ^4-phosphacyclohexadienyl anions which display an interesting coordination chemistry. Recent studies have shown that these ligands can behave either as two or six-electron donor ligands depending on the substitution scheme of the ring and the nature of the metal fragment MXL_n (Scheme 1.11) (Morales-Morales and Jensen, 2007).



Scheme 1.11 Structures of SPS Pincer Ligands and SPS Pincer Complex.

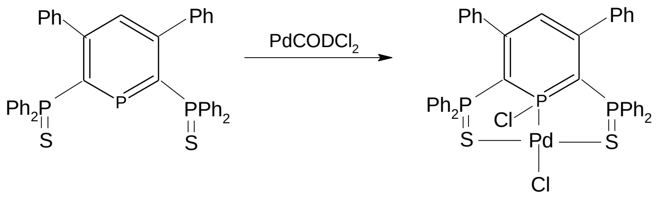
It has been shown that, the synthesis of complexes with these tridentate-based ligands was easily achieved by the reaction of a lithium derivative with a 2,6-(diphenyl phosphino) phosphinine **60** to form anion **61** which can be subsequently trapped with a transition metal fragment (Morales-Morales and Jensen, 2007) (Scheme 1.12).



(60) **(61)** **(62)**

Scheme 1.12 Synthesis of SPS Pincer Complex.

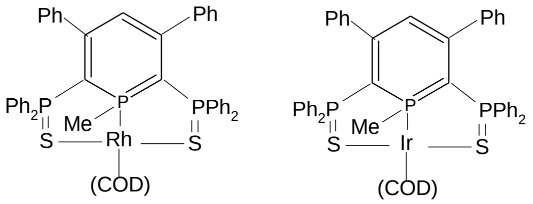
Thus, it was shown that the reaction of the phosphinine ligand **60** with [Pd(COD)Cl_2] affords complex **63** which results from the attack of one chloride ligand on the phosphorus atom (Morales-Morales and Jensen, 2007) (Scheme 1.13).



(60) **(63)**

Scheme 1.13 Synthesis of SPS Pincer Pd Complex.

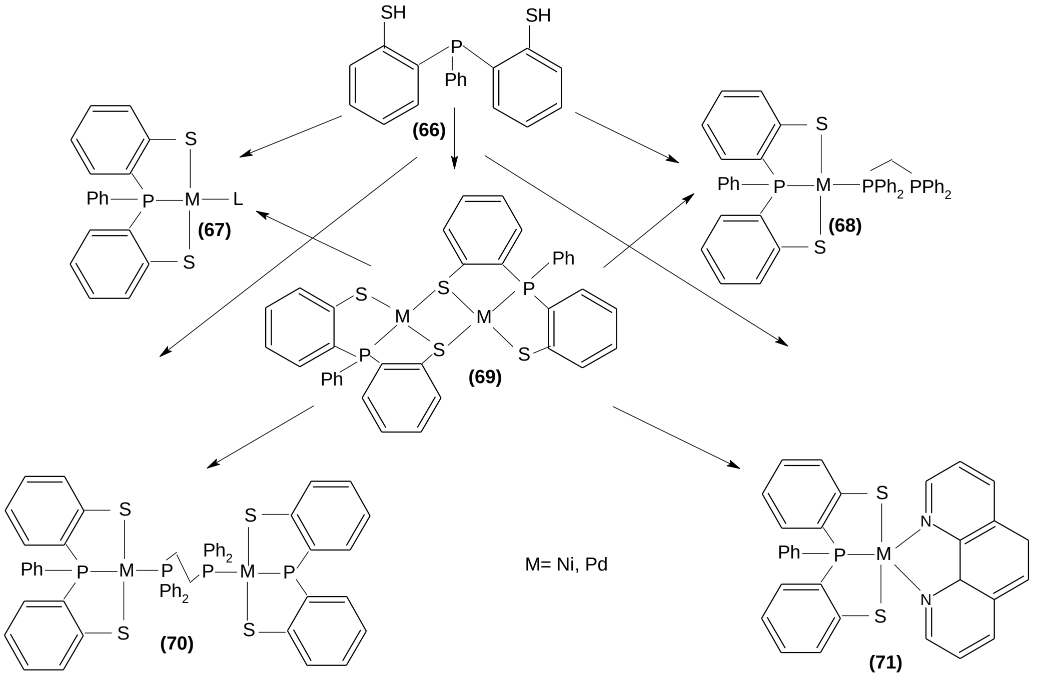
Rh(I) and Ir(I) complexes of the same ligand type were synthesized and reported by Doux et al. SPS type pincer based Rh(I) and Ir(I) complexes **64, 65** (Figure 1.25) was studied by means of DFT calculations. (Doux et al., 2005).



(64) **(65)**

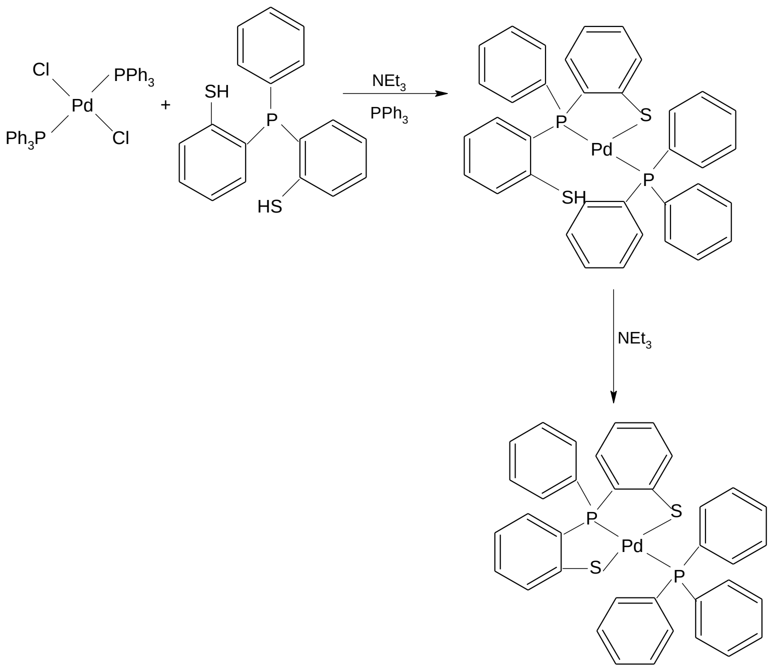
Figure 1.25 Examples of SPS Pincer Rh and Ir Complexes.

Cerrada and co-workers have been synthesized some mono- and dinuclear complexes of Ni(II) and Pd(II) with $PPh(C_6H_4S)_2^{2-}$ acting as a SPS pincer ligand (Cerrada et al., 2002) (Scheme 1.14).



Scheme 1.14 Examples of SPS Pincer Ligand and SPS Pincer Complexes.

It has been reported that, must studies have focused on bidentate ligands such as $R_2PCH_2CH_2SH$ and $R_2P(C_6H_4\text{-}SH\text{-}2)$, while the potentially tridentate proligands $R_2P(CH_2CH_2SH)_2$ and $RP(C_6H_4\text{-}SH\text{-}2)_2$ have received much less attention. New pincer complex **72** with tridentate S-P-S ligand $PhP(C_6H_4\text{-}SH\text{-}2)_2$ have been reported by Gomez-Benitez and co-workers, (Gomez-Benitez et all., 2003) with high thermal stability for potential application in catalytic reactions (Scheme 1.15).



(72)

Scheme 1.15 Proposed Mechanism for the Formation of Complex [Pd(Ph_3PS_2)(PPh_3)].

1.5.2.2. SCS TYPE PINCER COMPLEXES

It was reported that the organometallic chemistry of SCS type pincer complexes was limited to palladium complexes (except one platinum analogue reported in 1992 (Hanan and Kickham, 1992)) until 2002. It was believed that cyclometallation was only possible with Pd(II).

The first efficient method to form new carbon−Pd bonds was known the direct cyclometallation of SC(H)S pincer ligand with a Pd(II) precursor. It has been observed that several factors influence the yield of the desired complex to a very large extent: nature of the R substituent of the sulfur center, nature of the substituent para to the CH moiety and last but not least the palladium precursor (Figure 1.26) (Morales-Morales and Jensen, 2007).

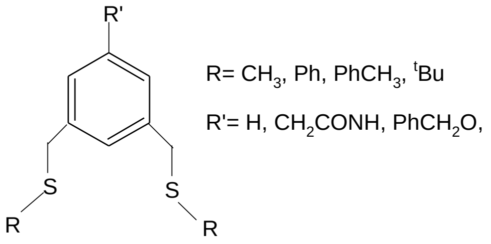
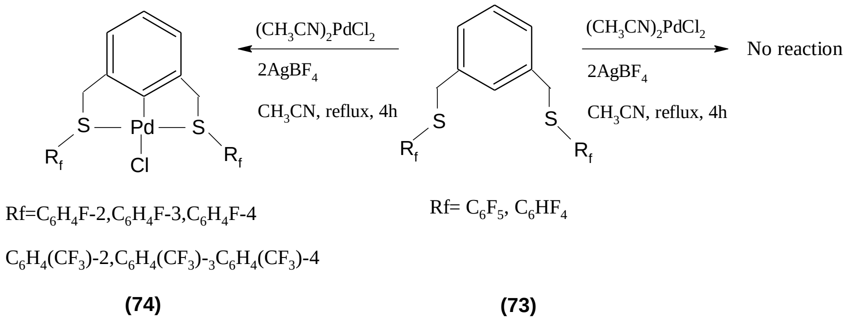


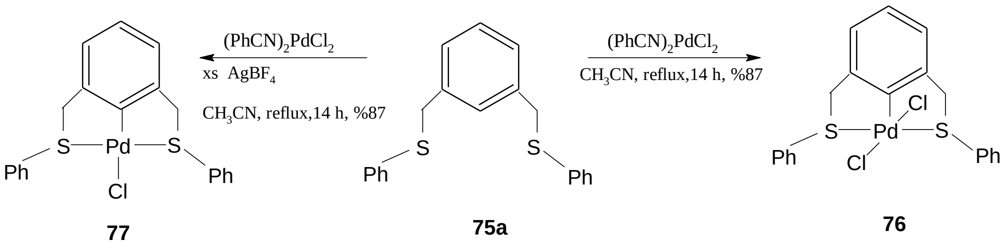
Figure 1.26 Example of SCS Pincer Ligand.

Low yields of complexes were obtained, for small alkyl groups. It has been observed that for phenyl or benzyl groups the insertion was more efficient, for the ^{t}Bu group the insertion required longer heating periods (Morales-Morales and Jensen, 2007). In a very recent article, Torrens and co-workers have studied the influence of the number of fluorine substituents on the phenyl ring bound to the S center on the outcome of the insertion reaction (Cervantes et al., 2006) (Scheme 1.16). They showed that the palladation could only be observed for the substituents with one F atom or one CF_3 moiety.



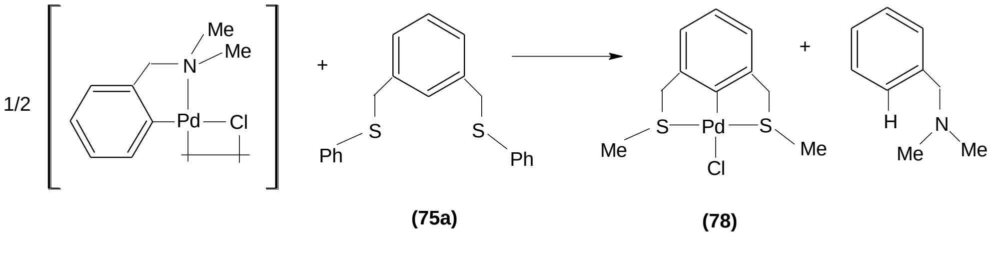
Scheme 1.16 Synthesis of SCS Pincer Pd Complex.

These results are consistent with earlier reports as for the derivative R=Ph, R'=H, insertion could not be achieved with [$(PhCN)_2PdCl_2$] even after prolonged heating in CH_3CN. Only the '$PdCl_2$' adduct **76** was obtained. On the other hand, it was reported that increasing the electrophilicity of the metal center by chloride abstraction led to the desired complex **77** after prolonged refluxing in acetonitrile (Morales-Morales and Jensen, 2007) (Scheme 1.17).



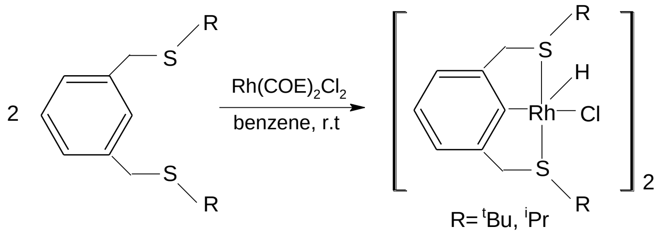
Scheme 1.17 Synthesis of SCS Pincer Pd Complex.

Another way to obtain SMe derivative **78** as shown below (Morales-Morales and Jensen, 2007) (Scheme 1.18) was based on the substitution of one cyclometallated ligand by another.



Scheme 1.18 Synthesis of SCS Pincer Pd Complex.

There is only one complex of the ligand **B** (Figure 1.24) that was reported with a metal center other than palladium. The insertion of a Rh(I) center into the C−H bond was reported by Evans et al. (Evans et al., 2002). In fact, their synthesis led to the formation of a chloride-bridged dimers, which is highly unusual for pincer-type Rh complexes (Scheme 1.19).



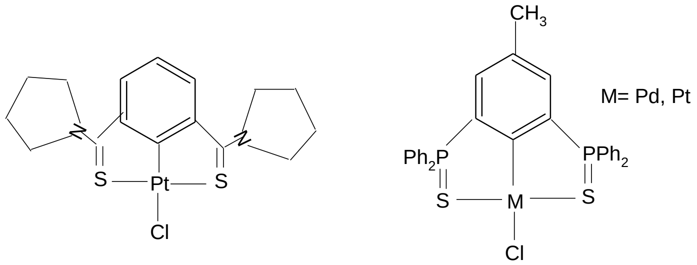
R= **(75b)** ^{t}Bu

(75c) ^{i}Pr

(79)

Scheme 1.19 Synthesis of SCS Pincer Rh Complex.

The platinum complex **80** having the thioamide-based SCS-pincer ligand have been prepared by Kanbara and co-workers (Kanbara et al., 2004). Platinum and palladium complexes **80, 81** that contains phosphine ligands have been synthesized by Kanbara et al. (Kanbara and Yamamoto, 2003) (Figure 1.27). Photoluminescence and light emitting properties of these complexes have been studied and reported by Kanbara et al. (Kanbara et al., 2004; Kanbara and Yamamoto, 2003).



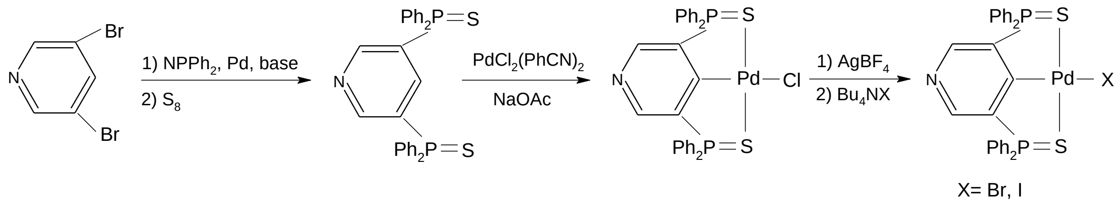
(80)

(81)

Figure 1.27 Examples of SCS Pincer Pt and Pd Complexes.

None of these complexes **80, 81** showed light emission in solution at room temperature, but strong luminescence was observed in the solid state and in the glassy frozen state.

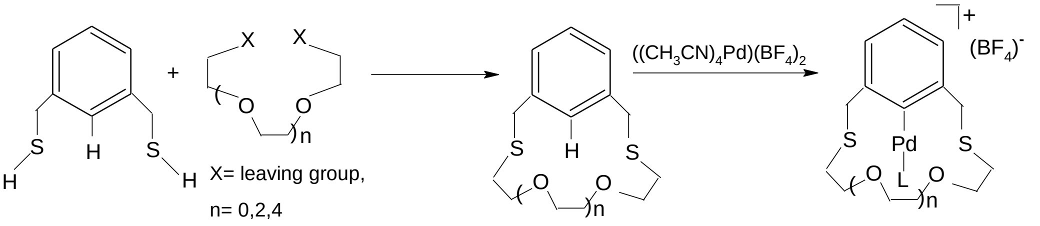
It has been known that examples of pincer ligands with a 3,5-pyridinediyl moiety, have been limited because of the presence of Npy sometimes leads to a number of unexpected coordination modes. It was explained that κ^3 P,C,P-pincer rhodium and palladium complexes of a monoanionic bis (phopshine) pyridine ligand, $[3,5\text{-}(Ph_2\text{-}PCH_2)_2C_5H_2N]^-$, serve as a metalloligand for a second metal center. The preparation of pincer palladium complexes **82, 83** with a centered phonylere-type ligand bearing phosphine sulfide auxiliary ligands at the o-positions as shown in (Scheme 1.20) were reported by Meguro and co-workers (Meguro et al., 2008).



(82) **(83)**

Scheme 1.20 Synthesis of SCS Pincer Pd Complexes.

In the early 1990s, Loeb and co-workers synthesized a range of thiacyclophane ligands **84**–**86** in order for the corresponding cyclometallated palladium complexes **87**–**89** to act as metalloreceptors (Scheme 1.21). One of the major goals was to show that simultaneous first and second sphere coordination would allow a selective recognition of various substrates (Kickham and Loeb, 1994).



(84): n= 0
(85): n= 2
(86): n= 4

(87): n= 0 L= CH_3CN
(88): n= 2
(89): n= 4

Scheme 1.21 Synthesis of Cyclometallated Pd Complexes.

Competition experiments between pyridine and o-aminopyridine or the DNA bases cytosine, guanine, adenine and thymine were performed (Kickham et al., 1993). They showed that the crown ether ligand **85** bearing three oxygen centers provided the best results in terms of recognition. The resulting complex **88** was selective for cytosine over the three other DNA nucleobases.

1.5.3. PNP TYPE PINCER COMPLEXES

Although PNP pincer ligands with a central amido donor were less common, Fryzuk and co-workers have been reported the amido-PNP ligands in the early 1980s. (**B**, albeit they were not originally referred to as ‘pincers’) (Fryzuk, 1992; Fryzuk et. al., 1990; Fryzuk and Montgomery, 1989). PNP ligands **C** with aliphatic backbones were first reported by Edwards and co-workers (Danapoulos and Edwards, 1989; Danapoulos et al., 1989). The use of **C** has been limited to several early transition metal and actinide complexes (Al-Soudani et al., 1994; Coles et al., 1994; Al-Soudani et al., 1995; Coles et al., 1995). Amido-PNP ligands may be viewed as a chelating analog of the ubiquitous *mer*-$Cl(R_3P)_2$ motif. In contrast to the aryl C donor in PCP, amido is a much stronger σ-donor and is a ligand of weaker *trans*-influence. Structural and reactivity differences between PCP- and PNP- supported chemistry because of these factors. Also it has been reported that PNP ligands were provide a hybrid environment that combines soft phosphine donors and a hard amido donor. This provides the PNP ligands to coordinate both the hard early transition metal centers and the soft late transition metal ones (Morales et al., 2007).

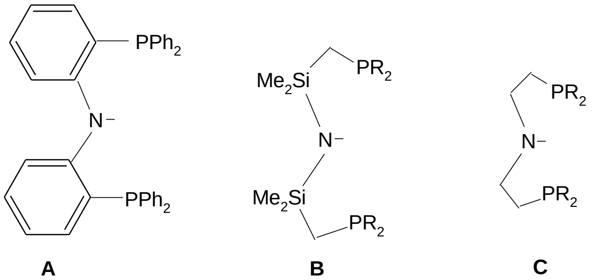
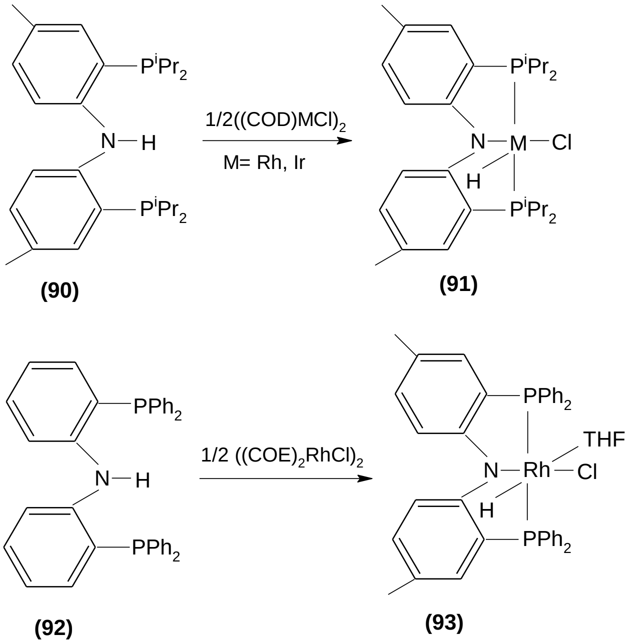


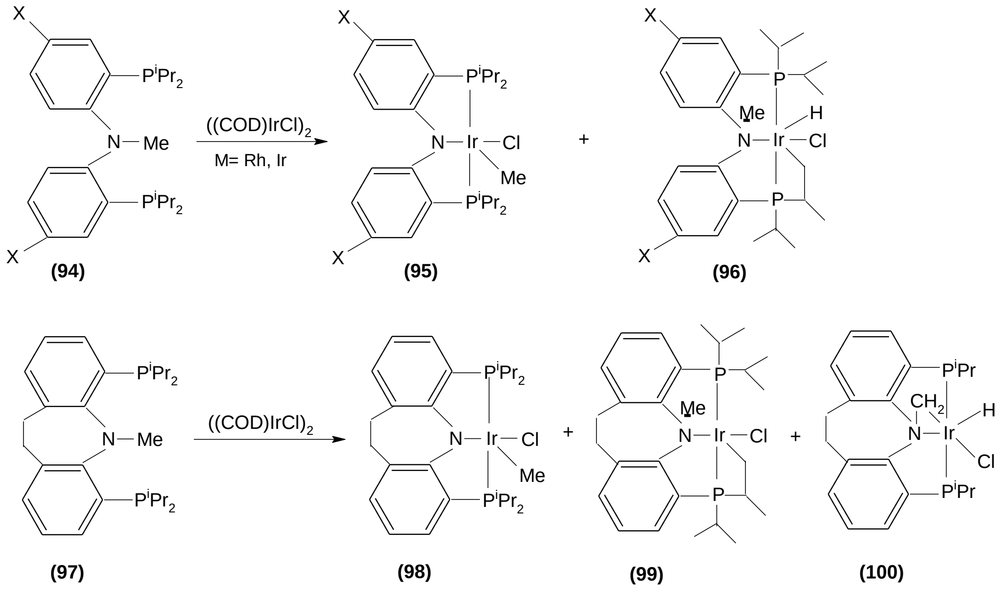
Figure 1.28 Examples of PNP Pincer Ligands.

The phosphine fragment has known as the most expensive component in the synthesis of the PNP ligands. This strategy was also sensible because (a) at least the more basic phosphines (and thus PNP ligands) were air-sensitive and thus require special treatment and (b) transition metal-catalyzed procedures (such as Pd-catalyzed amination) were unlikely to work well with phosphine-containing reagents. The investigations of the oxidative addition reactions of the N−H and N−Me forms of the PNP ligands were inspired by the work of Milstein and co-workers on the topologically similar C−C vs. C−H oxidative addition with PCP ligands (Rybtchinski and Milstein, 1999). The PN(H)P ligand **90** reacts cleanly with RhI and IrI precursors by N−H oxidative addition and formation of deep-green Rh(III) and Ir(III) products **91** (Ozerov et al., 2004). When the PN(H)P ligand **92** also reacts with an RhI source, complex **93** was ocuured in the presence of THF (Winter et al., 2003) (Scheme 1.22).



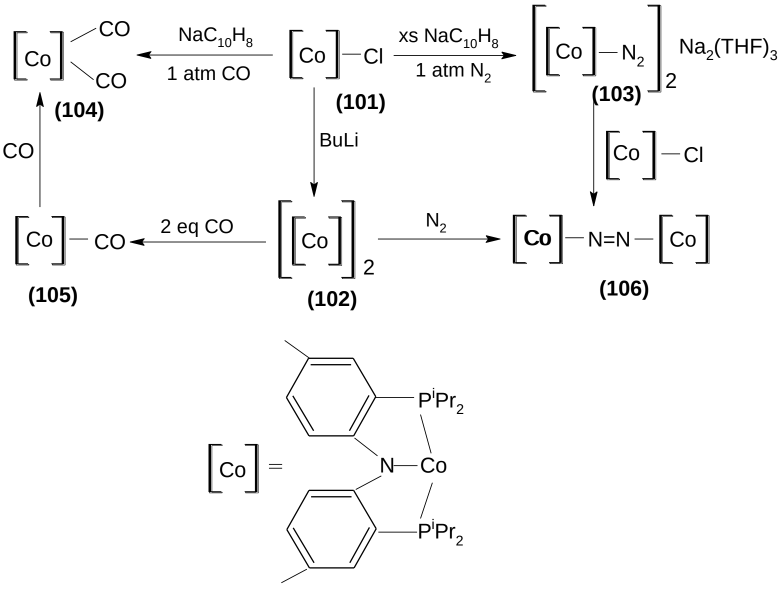
Scheme 1.22 N-H Oxidative Addition to Rh and Ir.

It was reported that complex **95** was synthesized by the reactions of **94** with [(COD)IrCl]$_2$. At the same conditions **97** reacts with [(COD)IrCl]$_2$ to produce **98** and **99**, and also **100** (Morales and Jensen, 2007) (Scheme 1.23).



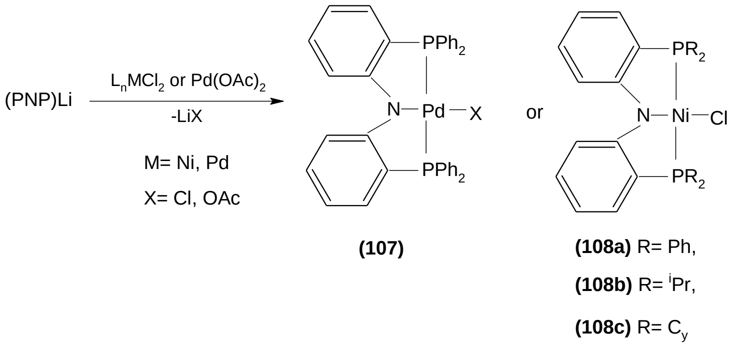
Scheme 1.23 Synthesis of PNP Ir Complexes.

Mindiola and co-workers reported several Co complexes of the PNP ligand with Co in various oxidation states (Scheme 1.24) (Fout et al., 2006). The installation of the PNP ligand is accomplished by salt metathesis of (PNP)Li with $CoCl_2$ to produce **101**. Reduction of **101** under argon leads to the dimeric species **102**. A monomeric three-coordinate (PNP*) Co complex utilizing a Fryzuk-type PNP ligand was recently reported by Caulton and coworkers (Ingleson et al., 2006). Reduction in the presence of excess of CO leads to the 5-coordinate **104**. A monocarbonyl complex **105** can be prepared by reaction of **102** with stoichiometric amount of CO. Reduction of **101** under N_2 leads to the formation of the dimeric anionic N_2 complex of apparently Co^0 **103**. A bridging CoI dinitrogen complex **106** can be accessed via reaction of **102** with N_2.



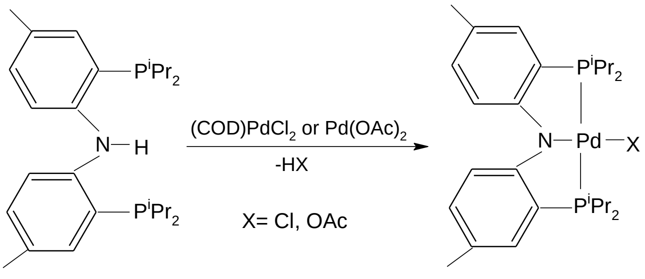
Scheme 1.24 Synthesis of PNP Co Complexes.

A variety of square-planar complexes of the general formula (PNP)MX **108(a-c)** with Ni, Pd or Pt has been reported (Morales and Jensen, 2007). The PNP ligands were ideally suited to support a three forms of the ligand precursor (N−Li, N−H, or N−Me forms) that can be used to introduce the amido-PNP ligand into the coordination sphere of a group 10 metal. The reactions can be separated into four categories.



Scheme 1.25 Salt Metathesis Synthesis of PNP Complexes of Pd and Ni.

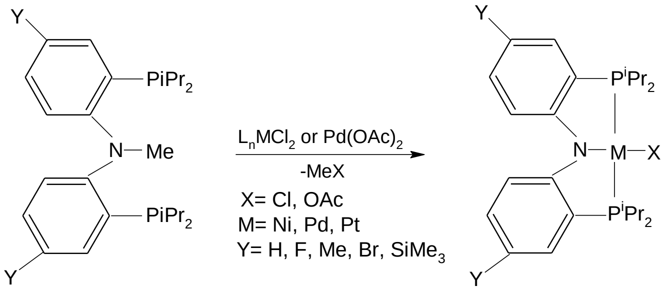
In the first one; salt metathesis between a (PNP)Li derivative and a group 10 metal halide or acetate reliably produces (PNP)MX **107, 108** and LiX as the by-product which is shown in (Scheme 1.25) (Liang et al., 2003; Liang et al., 2006). Secondly, direct reaction of the neutral (PNP)H form of the ligand **90** with the group 10 metal halide or acetate (for Pd) is also possible (Scheme 1.26) (Fan et al., 2004). It was reported that, in the case of $Pd(OAc)_2$, base is not required, and the reaction produces (PNP)PdOAc, with AcOH as the by-product. In the case of $LnMCl_2$ precursors, the HCl by-product of the formation of (PNP)MCl **109** can be removed by addition of a weak base (e.g., Et_3N) or even simply by application of vacuum.



(90) **(109)**

Scheme 1.26 N-H Cleavage by Pd(II).

Another route that was reported is as follows, the methylated form of the ligand (PNP)Me may also be used in a reaction with MX_2 precursors to produce (PNP)MX and MeX as the byproduct (Scheme 1.27). The N−C cleavage reaction works for the PNP ligands bearing PPr^i_2 arms, but not PPh_2 arms (Fan et al., 2004; Weng et al., 2005). It was explained that the exact mechanism of the N−C cleavage here (particularly, whether N−Me oxidative addition to produce M(IV) intermediates is involved) remains unclear, although some pathways were ruled out (Fan et al., 2004).

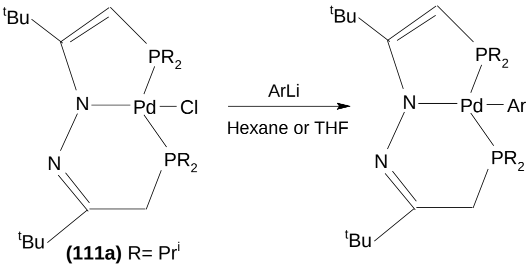


(94) **(110)**

Scheme 1.27 N-C Cleavage by Pd(II).

Square planar palladium(II) aryl-amido complexes **112(a-i)** of diphosphinoazines in monoanionic unsymmetrical PNP' pincer type coordination were prepared by Storch and co-workers (Storch et all., 2008) (Scheme 1.28). It is one of the example of unsymmetrical pincer type that contains both the five and six membered rings.

Cationic palladium(II) starting complexes **111(a-c)** [PdCl{$PR_2CH_2C(Bu^t)=NN=C(Bu^t)CH_2PR_2$}]Cl, where R= Pr^i, cy, Bu^t, were sythesized by the reaction of the corresponding diphosphinoazines with bis(acetonitrile)palladium(II) dichloride (Storch et al., 2004).

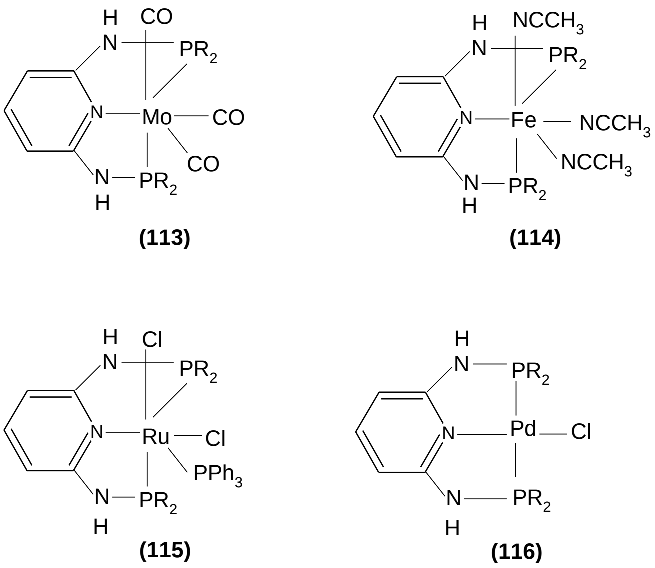


(111a) R= Pr^i
(111b) R= Cy
(111c) R= Bu^t

(112a) R= Pr^i, Ar= Ph
(112b) R= Pr^i, Ar= o-tolyl
(112c) R= Pr^i, Ar= 2,6-dimethylphenyl
(112d) R= Cy, Ar= Ph
(112e) R= Cy, Ar= o-tolyl
(112f) R= Cy, Ar= 2,6-dimethylphenyl
(112g) R= Bu^t, Ar= Ph
(112h) R= Bu^t, Ar= o-tolyl
(112i) R= Bu^t, Ar= 2,6-dimethylphenyl

Scheme 1.28 Synythesis of PNP Pd Complexes.

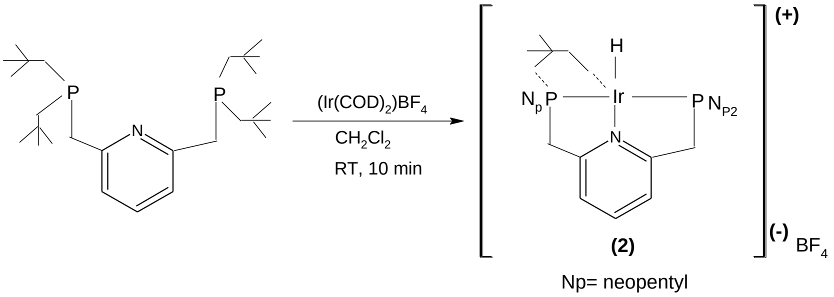
PNP pincer complexes **113-116** including aromatic diamines and chlorophosphines with molybdenum, iron, ruthenium, nickel, palladium and platinum metals were prepared and reported by Benito-Garagorri et al. (Benito-Garagorri and Kirchner, 2008) (Figure 1.29). The use of these ligands with several transition metal precursors has reported in the preparation of new pincer complexes, including the first heptacoordinated molybdenum pincer complexes by using a controlled ligand decomposition pathway. Furthermore, some of these complexes have proven to be effective catalysts in different coupling reactions: Palladium PNP pincer complexes can be used as catalysts in the Suzuki-Miyaura coupling, while iron PNP complexes catalyze the coupling of aromatic aldehydes with ethyl diazoacetate to give selectively 3-hydroxyacrylates, which are otherwise difficult to prepare.



(113) **(114)** **(115)** **(116)**

Figure 1.29 PNP Complexes of Molybdenum, Iron, Ruthenium, Nickel, Palladium and Platinum.

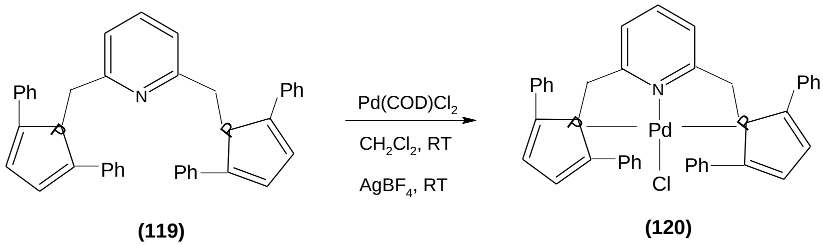
Yamashito and co-workers (Yamashito et al., 2010) were reported an application of neopentyl-substituted pincer iridium complex, **118** (Scheme 1.29), to catalytic dimerization of alkylamines to give dialkylamine via N-H bond cleavege with the highest activity ever reported, where the neopentyl groups may accelerate the reaction because of relatively unhindered space around the central metal (Yamashita et al., 2010).



(117) **(118)**

Scheme 1.29 Synthesis of PNP Ir Complex.

Melaimi and co-workers were reported the synthesis of the cationic palladium complex **120**, was achieved by reacting ligand **119**, with [Pd(COD)Cl$_2$] in the presence of AgBF$_4$ as chloride abstractor in CH$_2$Cl$_2$ at room temperature (Scheme 1.30). The analogous Ni complex was prepared in a similar way by reacting ligand **119** with [$NiBr_2$(DME)] in the presence of $AgBF_4$. Complex **120,** efficiently catalyzes the coupling between pinacolborane and iodo and bromoarenes with good TON (Melaimi et al., 2004).

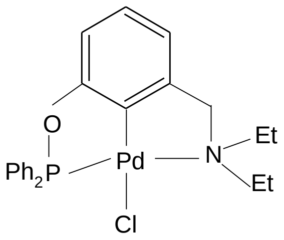


Scheme 1.30 Synthesis of PNP Ir Complex.

1.5.4. PCN TYPE PINCER COMPLEXES

Palladium pincer complexes that contains YCY type ligands have known a great amount of interest, due to their feasible structural modifications with multiple choices of donor atoms and substituents thereon (Y=NR_2, SR, PR_2, OPR_2, etc.) high stability, and remarkable catalytic activities in various C-C coupling reactions (Singleton, 2003). The most common pincer palladacycles were known as NCN (Jung et al., 2003), PCP (Morales et al., 2000) or SCS (Kanbara and Yamamoto, 2003) types, which were symmetrical with two identical donor groups and two equivalent five-membered palladacycles. It was also explained that the nature of the donor group greatly influences the reactivity, stability and catalytic performances of these compounds. For instance, the hardness of the chelating N donor versus the softness of P donor result in the more labile N-Pd coordination and very different behavior of the corresponding NCN and PCP based complexes. Therefore, it can be anticipated that mixed, nonsymmetrical YCY' pincer palladium complexes especially those containing potentially hemilabile hybrid PCN ligands, could benefit from advantages of varied donors and provide unique reactivity. By contrast, there are very few reports on the synthesis and applications of PCN pincer palladium complexes. This is partly because their preparation is a considerable challenge, which is laborious and requires a series of steps to introduce different donors. PCN type pincer palladium (II) complex, **121,** with phophinito group have been reported by

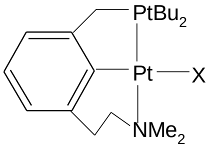
Gong et al. (Figure 1.30). The catalytic activities of these complexes were studied in Suzuki reactions of aryl halides with phenylboronic acid (Gong et al., 2007).



(121)

Figure 1.30 Example of PCN Pd Complex.

Another example of PCN type pincer complex has been synthesized by Poverenov et al. It was known as a long-arm PCN based platinum chloride complex **122(a-c)** (Figure 1.31). It has a less stable six membered ring rather than five membered rings. It was reported that the thermal stability of this complex was surprising, since it has not contain strong Π acceptors that can stabilize the anionic metal center (Poverenov et al., 2004).



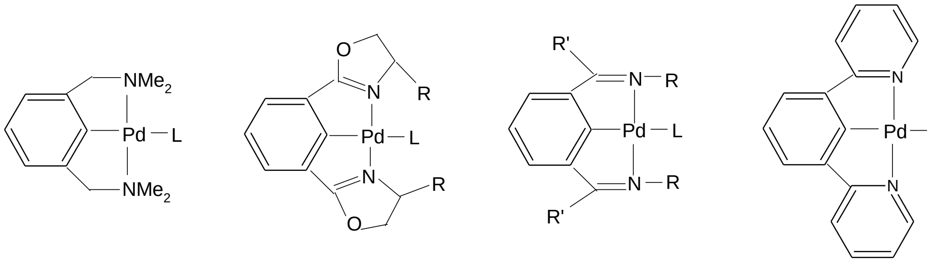
(122a) X= Cl
(122b) X= H
(122c) X= CH_3

Figure 1.31 Examples of PCN Pt Complexes.

1.5.5. NCN TYPE PINCER COMPLEXES

Van Koten and co-workers were first introduced the NCN diamine pincer ligand $[2,6\text{-}(Me_2NCH_2)_2\text{-}C_6H_3]^-$ and its metal complexes in the late 1970's. These pincer complexes were receiving attention for wide range applications such as catalysts for effecting carbon-carbon bond forming reactions transfer hydrogenation reactions (Dani et al., 2000) and even gas sensing elements (Albrecht et al., 2000; Gründemann et al., 2001). Palladium complexes with NCN pincer ligands have been extensively studied in recent years due to their high stability, feasible structural modifications, and remarkable catalytic activities in organometallic catalysis (Rietveld et al., 1997; Albrecht and van Koten, 2001;

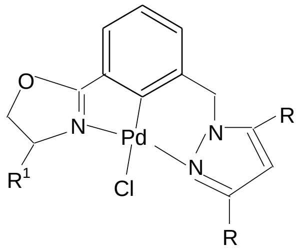
Singleton, 2003; Morales and Jensen, 2007). Much of the research has focused on symmetrical NCN pincer palladium complexes, which are symmetrical with two identical N donors such as amines (Wallner and Szabo, 2004; Kjellgren et al., 2004; Slagt et al., 2004), imines (Takenaka et al., 2005; Fossey et al., 2007), pyridines (Soro et al., 2005, 2006), oxazolines (Stark and Richards, 1997) or other N-containing heterocycles (Jung et al., 2003) and 2 equivalent five-membered palladacycles. Some of the complexes have been succesfully applied as catalysts for stannylation of allyl (Wallner and Szabo, 2004) or propargylic substrates (Kjellgren et al., 2004), Diels-Alder reaction (Stark and Richards, 1997), Heck (Takenaka et al., 2005; Soro et al., 2005; Jung et al., 2003), Suzuki and Sonogashira (Churruca et al, 2005), coupling reactions.



(123) **(124)** **(125)** **(126)**

Figure 1.32 Structures of the Most Common Type of NCN Pd Complexes.

Unsymmetrical, NCN pincer Pd complexes **127(a-d)** (Figure 1.33) has been reported by Hao et al. It was also reported that the Pd complexes **127(a-d)** were unusual in that they not only had different N-heterocyclic donors, but also contained both five- and six- membered metallocycles in the molecules. The obtained Pd complexes were applied to the Suzuki reactions of aryl halides with phenylboronic acid and exhibited good activities (Hao et all., 2010).



(127a) R= CH_3, R'= H

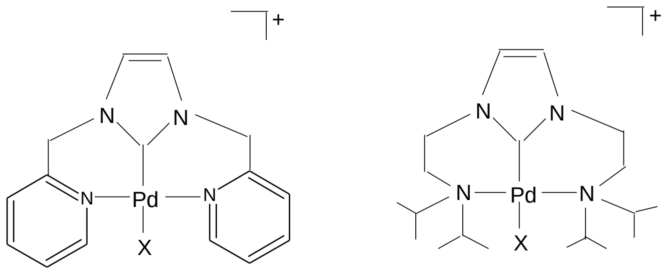
(127b) R= R'= H

(127c) R= CH_3, R'= ^{i}Pr

(127d) R= H, R' ^{i}Pr

Figure 1.33 Examples of NCN Pd Complexes.

Another examples of NCN type pincer Pd(II) compounds **128, 129** (Figure 1.34) were also reported by Cavell and coworkers (Magill et al., 2001). These complexes consist of a pincer tridentate ligand with a central imidazolylidene ring having two wingtip substituents contaning nitrogen donor fragments, such as pyridine.

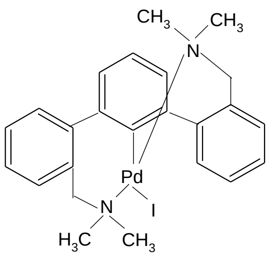


(128) **(129)**

Figure 1.34 Examples of NCN Pd Complexes.

It was reported that the thermal stability of these complexes is lower than that for the CCC and CNC pincer Pd(II) analogs (Morales and Jensen, 2007).

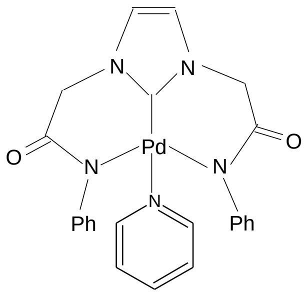
Although NCN pincer ligands have known more stable towards moisture and air than their PCP counterparts but the analogues phosphine pincer ligands $[2,6\text{-}(R_2PCH_2)_2C_6H_3]^-$ have perhaps received more attention (Van der Boom and Milstein, 2003). Such stability makes it easier to modify the NCN pincer platform by changing different functional groups within their multiple anchoring points (Slagt et al., 2004). One example of NCN pincer palladium complex, **130** (Figure 1.35), was sythesized and reported by Ma and co-workers (Ma et al, 2007). This complex has revealed a conventional square planar geometry about the palladium center and a global C_2 symmetric structure.



(130)

Figure 1.35 Example of NCN Pd Complex.

In 2007 Liao et al., reported the pincer-type amido-functionalized Pd(II)-NHC complex **131** (Figure 1.36), under different basic conditons (Liao et al., 2007). The activity of complex in the Suzuki coupling reactions with aryl bromides was low.

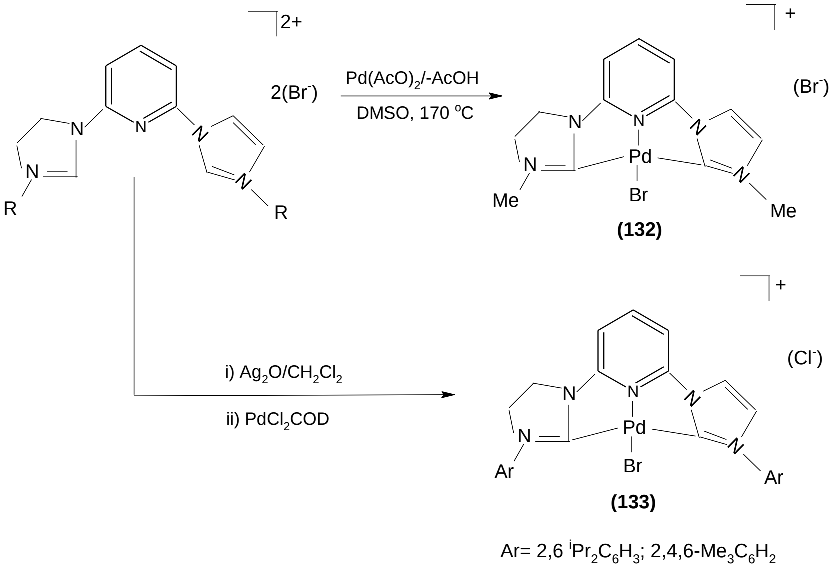


(131)

Figure 1.36 Example of NCN Pd Complex.

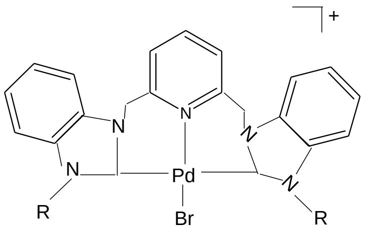
1.5.6. CNC TYPE PINCER COMPLEXES

CNC type pincer complexes **132** and **133** were prepared by the route in (Scheme 1.31) (Morales et al., 2007).



Scheme 1.31 Synthesis of CNC Pd Complexes.

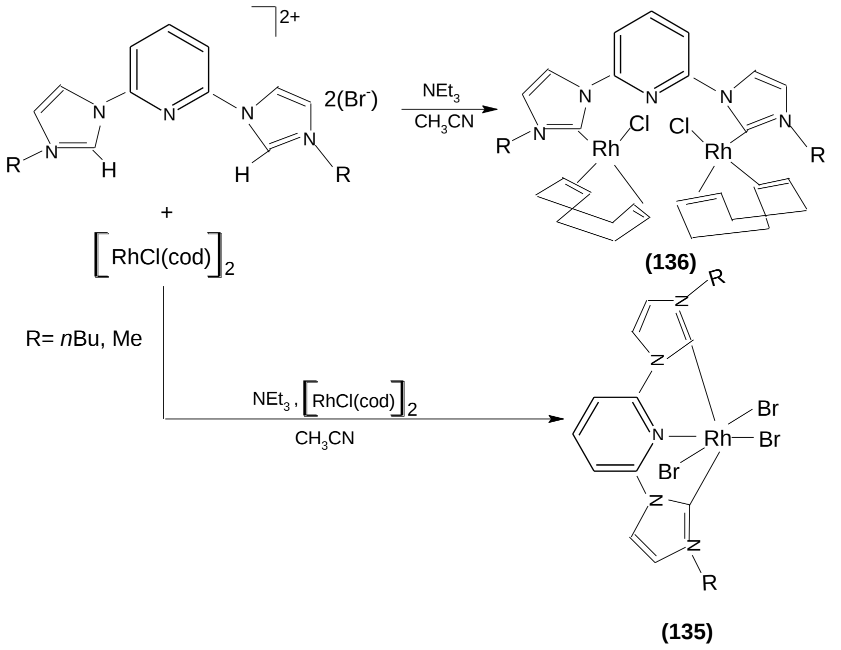
Another example for the CNC pincer type complex is the bis(benzimidozolylidene)analog **134** (Figure 1.37), was described by Hahn and co-workers in 2005(Hahn et al., 2005).



(134)

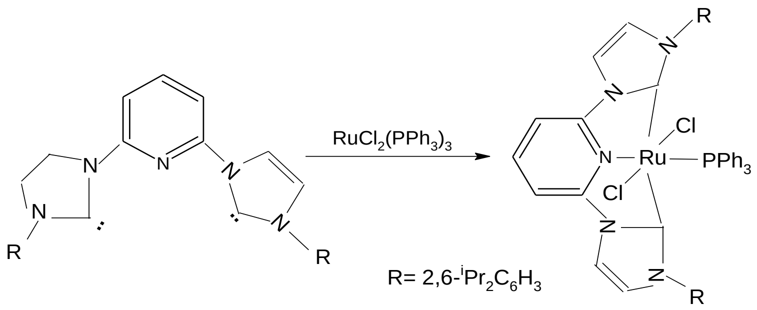
Figure 1.37 Example of CNC Pd Complex.

The preparation of the CNC-Rh(III) complex **135** from the corresponding pyridine-bisimidazolium CNC pro-ligand proceeds through a dimetallic complex of Rh(I), **136**, in which the biscarbene ligand is bridging the two metal units (Scheme 1.32) (Poyatos et al., 2003).



Scheme 1.32 Synthesis of CNC Rh Complexes.

The first ruthenium CNC-pincer carbene complex **137** was obtained by Danapoulos and co-workers in 2002 (Danopoulos et al., 2002) (Scheme 1.33).



(137)

Scheme 1.33 Synthesis of CNC Ru Complex.

It was reported that the coordination of pincer NHC ligands to Rh and Ru afforded a series of complexes that showed similar or even higher catalytic activities than some analogues phosphine complexes. One of the advantages of these systems was expalined that the pincer coordination of the ligand gives the complexes high thermal stability, and in most cases, the catalytic reactions can be carried out in the presence of air without any precautions being taken (Morales et al., 2007).

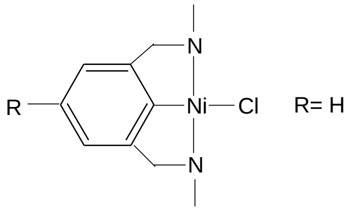
1.6. USES OF PINCER COMPLEXES

1.6.1. Kharasch Additions

1.6.1.1.Nickel-catalysed Kharasch Addition

It has been reported that the nickel NCN pincer complex **138** (Figure 1.40), was found to be an excellent catalyst for the reaction of methyl methacrylate with CCl_4, producing the 1:1 adduct in 90% yield after 15 min. at room temperature by Kuil et al. (Kuil et al., 1997).

The use of bidentate ligands based on the 1,3-[(dimethyl-amino) methly] benzene moiety has been investigated by Gossage et al in the late 1980s. (Gossage et al., 1998). It has been found that lithiation at the 2-position allowed oxidative addition of almost any transition metal, has created the first NCN pincer complexes. The NCN pincer ligands were found to stabilize a variety of metal oxiditation states and the discovery of the very law redox potential ($N:^{II}/N:^{III}$) for nickel NCN pincer complex was thought to make them ideal catalysts for Kharasch additions.

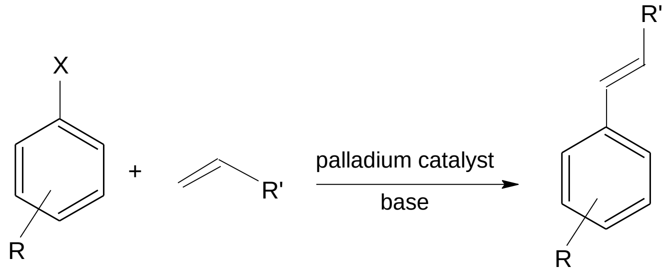


(138)

Figure 1.38 Example of NCN Ni Complex.

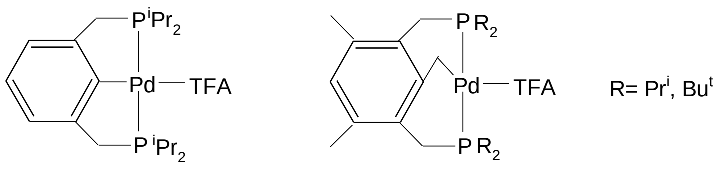
1.6.2. Heck Reactions

After it has been first investigated in the 1960s, the Heck reaction has turned into a real power tool in organic synthesis, now a days reaching the status of angular stone in the modern organic synthesis (Beletskaya and Cheprakov, 2000; Corbet, J. P., Mignani, 2006). In general the Heck reaction consists of the coupling of an α-olefin with a bromo or iodo derivative (Scheme 1.34). Most of the processes involving the Heck reaction are catalyzed by Pd(II) or Pd(0) derivatives in the presence of PPh_3 in excess.



Scheme 1.34 General Route of the Heck Reaction.

Pd(II)-PCP pincer complexes **8, 9** were the first examples which have been used in the Heck coupling reaction by Ohff et al. (Ohff et al., 1997) (Figure 1.39).

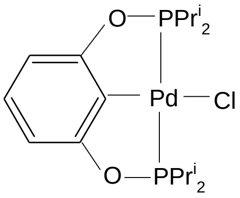


(8) **(9)**

Figure 1.39 Examples of PCP Pd Complexes.

It has been found that, these complexes were active without decomposition at reaction temperatures as high as 140°C, over reaction periods of 300 h or higher. By using these catalysts **8**, **9** Milstein achieved full conversion in the couplings of iodobenzene with methylacrylate, using N-methyl pyrrolidine (NMP) as solvent and sodium carbonate asbase with a maximum of 500 000 turnover numbers (TON) for iodobenzene and up to 132 900 for bromobenzene.

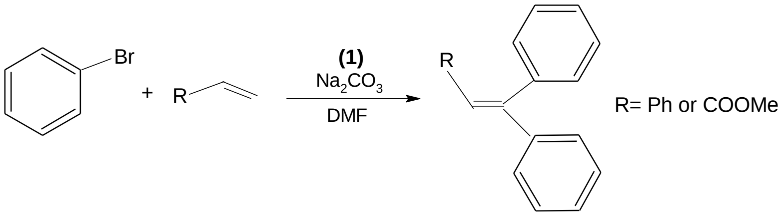
Another example of PCP pincer-type phosphinito ligand and it's palladium derivative **1** (Figure 1.40) has been synthesized by Morales-Morales and Jensen (Morales et al., 2000). It has been reported that, complex **1** was shown to be efficient in the coupling of chlorobenzenes, being one of the few examples than known to activate, deactivated or sterically hindered chlorobenzenes (Morales et al., 2000). Complex **1** showed to be as reactive as the PCP phosphine derivative reported previously by Milstein (Ohff et al., 1997).



(1)

Figure 1.40 Example of POCOP Pd Complex.

The Heck reactions of bromo-benzene, and styrene or methyl acrylate, however, catalysed by complex **1**, surprisingly produced the trisubstituted olefins (Morales et al., 2000) (Scheme 1.35). These trisubstituted olefins are not produced when Milstein's phosphino PCP palladium complexes were used.

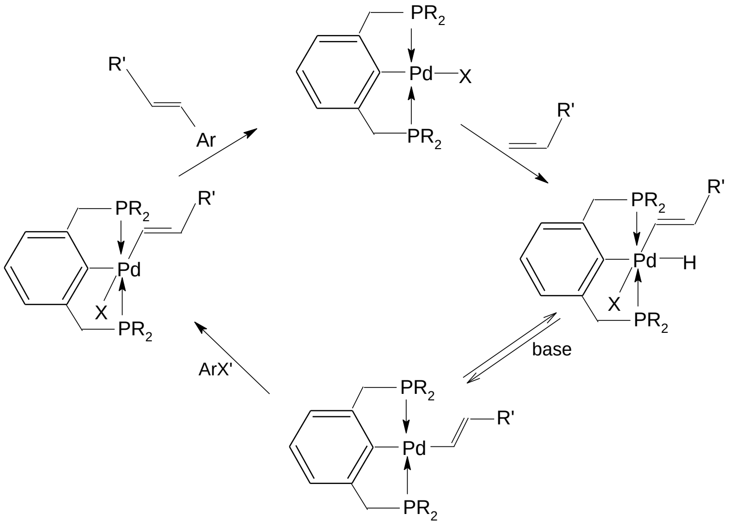


Scheme 1.35 The Heck Reaction of Bromo-Benzene and Styrene.

1.6.2.1. Mechanism using palladium (II) pincer complexes

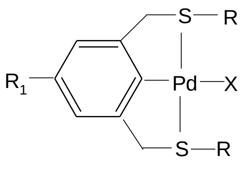
The mechanism for Heck coupling reactions involving palladium pincer complexes is currently under debate, as the palladium in the pincer complexes is Pd(II) and it is unlikely to be reduced to Pd(O). This means that the conventional Pd(O)/Pd(II) mechanism for Heck couplings is unlikely to apply. The current theory is that the reaction proceeds via a mechanism involving Pd(II)/Pd(IV) oxidation states (Scheme 1.36).

It has been seem that the sequence could be initiated by oxidative addition of the aryl halide to the metal, as this would produce a stable 18-electron complex, which would not be expected to undergo further reaction. The reaction is therefore initiated by the alkene co-ordinating to the complex, followed by the loss of HCI. Oxidative addition of the arly halide would lead to formation by subsequent reductive elimination regenerating the catalyst. The high probability that the Heck reactions catalysed by pincer complexes proced via different mechanisms to the other palladium-catalysed Heck couplings gives rise to potentially different constraints and opportunities (Singleton et al., 2003).



Scheme 1.36 The Mechanism for Heck Coupling Reactions.

Another alternative to the phosphine pincer complexes are the tridentate SCS palladium complex **139** (Figure 1.41) developed by Bengbreiter and co-workers (Bergbreiter et al., 1999).



R= ^{t}Bu or Ph

R_1= H, CH_3CONH or $PhCH_2O$

X= Cl or CF_3CO_2

X= Cl, R= Ph, R_1= AcNH

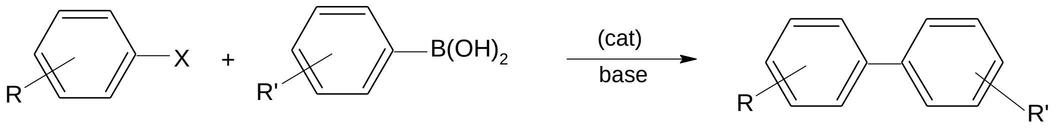
(139)

Figure 1.41 Examples of SCS Pincer Pd Complexes.

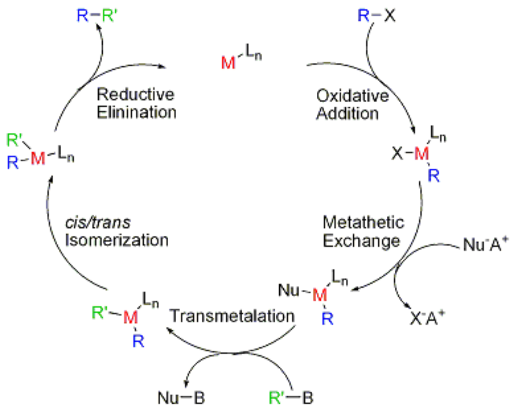
It has been reported that the most stable of these catalysts is **139**. Catalytic reaction of **139** using various aryl iodides and alkenes have been conducted in DMF or NMP at 105-110°C using 1 equiv. of triethylamine or sodium carbonate as the base, without the need for an inert atmosphere.

1.6.3. Suziki Couplings

The Suziki reaction (Scheme 1.37) is regarded as one of the most efficient ways of forming a carbon-carbon bond. Palladium complexes were used as catalysts in the coupling of an aryl halide with an organoboran compound. Unfortunately, fairly high catalyst concentrations and the difficulties and costs associated with the removal of palladium from the product have limited its commercial use (Singleton, 2003).



Scheme 1.37 The Mechanism of Suzuki-Miyaura Coupling Reactions.



Scheme 1.38 General Mechanism of Suzuki Coupling Reactions.

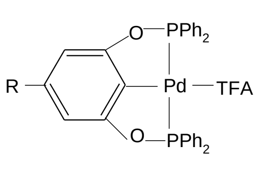
The mechanism of the Suzuki coupling reactions consists of four main steps (Scheme 1.38). Oxidative addition of aryl halides to palladium catalyst; transmetallation of aryl borate to form trans-diaryl palladium complex; trans-cis isomerization of this palladium complex; reductive elimination of the biaryl to regenerate the catalyst. Several parameters effecting the Suzuki-Miyaura coupling reactions are considered. These factors are; solvents effect, substitution group effects, base effect, halogen and ligand effect. Solvents are the most important parameters in organic reactions; appropriately chosen solvent system strongly favors the cross-coupling pathway. In literature dioxane, THF, different DMF/H_2O and EtOH/H_2O ratios, toluene and benzene have been used as solvents in Suzuki-Miyaura coupling reactions. The halogen type determines the activity of aryl halide towards the Suzuki-Miyaura coupling reaction. The reactivity of aryl halide component decreases drastically in the order X = I > Br > Cl and electron-withdrawing substituents R are required for the chlorides to react (Gibson et al., 2001; Bedford et al., 2002). Suzuki coupling reactions proceeds via transmetallation in the presence of bases. This procedure does not take place under natural conditions. This is characteristic feature of boron chemistry which is different from that of other organometallic reagents. The most commonly used base in Suzuki cross coupling reaction is Na_2CO_3 but this is often ineffective with sterically demanding substrates. In such instance, $Ba(OH)_2$ or K_3PO_4 has been used the generate good yields of the cross-coupling products. Other bases utilized in the Suzuki cross-coupling reaction include Cs_2CO_3, K_2CO_3, KOMe, TiOH and NaOH.

1.6.3.1. Palladium PCP Pincer Complexes

Instead of the successful application of pincer complexes as catalysts in the Heck reactions, their use in Suzuki couplings have investigated by several groups. Many palladium complexes have known efficient catalysts in Suzuki coupling reactions, but many of them suffer from poor thermal stability, as well as poor stability towards air and moisture.

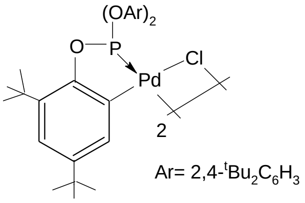
The PCP-palladium complexes **15a** and **15b** (Figure 1.42) were synthesized by Bedford et al. in 2000. It has been reported that these complexes show good catalytic activity in the Suzuki coupling of phenylbaronic acid with standard substrates such as 4-bromocetophenone (Bedford et al., 2000). Also, these complexes have good catalytic activity in the reactions of phenylboronic acid with deactivated or sterically-bindered aryl bromides.

It has been reported that, the palladacycle **140** was more active than the palladium pincer complexes **15a** and **15b**. But also, it has known that, complex **140** was often much more difficult and expensive to synthesize and were far less stable (Singleton, 2003).



(15a) R= H

(15b) R= Me

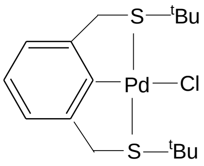


(140)

Figure 1.42 Examples of POCOP Pd Complexes.

1.6.3.2. Palladium SCS Pincer Complexes

One example of the SCS palladium pincer complex **141** (Figure 1.43) has been found to catalyse the Suzuki coupling of p-bromotoluene and phenyl boronic acid. It has been reported that, the catalyst loadings (typically, 1 mol %) were higher than the phosphine-based pincer complexes, but a respectable 69% yield of phenytolune has been achieved (Gruber et al., 2000).



(141)

Figure 1.43 Example of SCS Pd Complex.

1.6.4. Dehydrogenation reactions

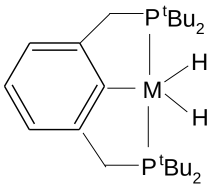
The use of soluble transition metal complexes in the stoichiometric convension of alkanes to alkenes has been reported by Crabtree and co-workers.

After than, many groups have joined this area using transition metal complexes such as rhodium or iridium as catalysts in the following years (Singleton, 2003).

1.6.4.1. Iridium and ruthenium PCP pincer complexes

Moulton and Shaw have reported mono-hydrido iridium and ruthenium complexes **142, 143** (Figure 1.44) containing phosphine-based pincer ligands MClH [2,6-$(CH_2P^tBu_2)_2$-C_6H_3] in the mid 1970s (Singleton, 2003).

These complexes have high thermal stabilities, subliming at a temperature > 180^{o}C without any decomposition. The possibility that the complexes could be adapted to create dehydrogenation catalysts led to work by the groups of Gupta et al. (Gupta et al., 1996), Wang et al. (Wang et al., 1996) and Leitner et al. (Leitner et al., 1997). All three groups began separate investigations into the synthesis and use of dihydro-PCP pincer complexes as potential catalysts for aliphatic dehydrogenations.



(142) M= Rh

(143) M= Ir

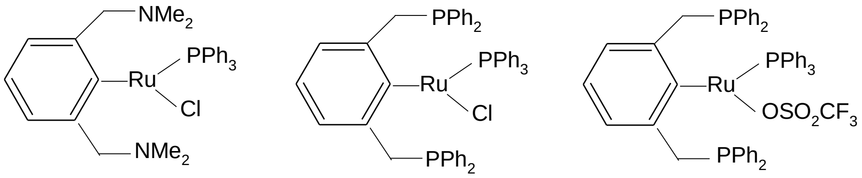
Figure 1.44 Examples of PCP Rh and Ir Complexes.

1.6.5. Transfer Hydrogen Reactions

1.6.5.1. Hydrogenation of ketones to alcohols

Although, a large amount of work on the dehydrogenation of alkanes with pincer complexes and sacrificial hydrogen acceptors such as the, which is essentially the transfer hydrogenation of tert-butylethene, pincer complexes have only just began to be investigated as potential transfer hydrogenation catalysts, for the reduction of ketones.

Three ruthenium pincer complexes **144-146** which was shown below have been reported as active catalysts in the transfer hydrogenation of several ketones by Dani and co-workers (Dani et al., 2000).



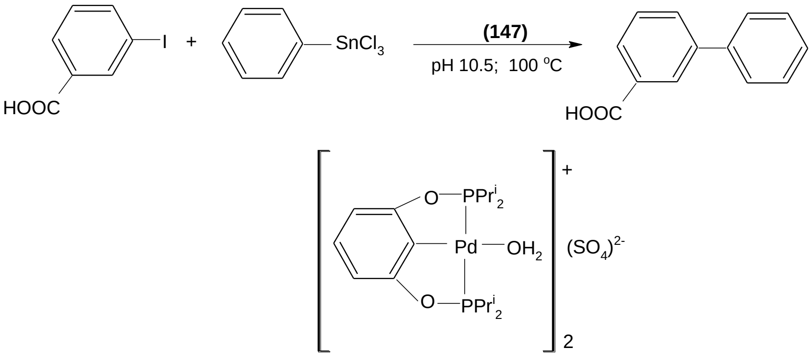
(144) **(145)** **(146)**

Figure 1.45 Examples of NCN and PCP Ru Complexes.

1.6.6. Stille Coupling Reactions

The Stille coupling reactions were known as a C−C bond-forming reactions between stannanes and halides or pseudohalides, with very few limitations on the R-groups (Singleton, 2003). In general the Suzuki coupling reactions were preferred to the Stille couplings thus avoiding the drawbacks of using tin compounds.

The only report of Stille coupling using pincer complexes of any type is provided by Ogo and co-workers, using complex **147** (vide supra) for the coupling of PhSnCl$_3$ with 3-iodobenzoic acid in water at a pH of 10.5, achieving modest yields (42%) and TON of 2100 at 100°C (Ogo et al., 2006) (Scheme 1.39).

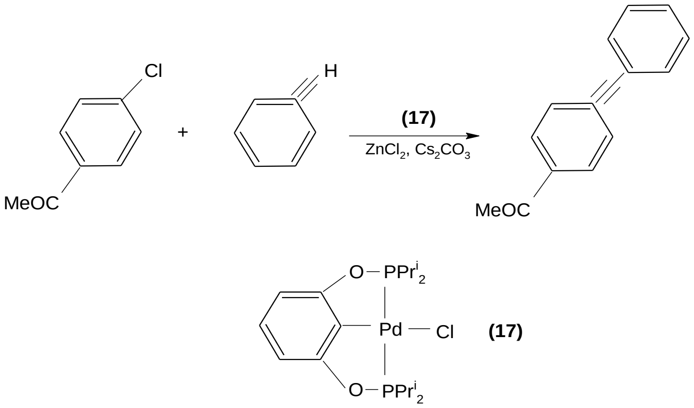


(147)

Scheme 1.39 The Route of Stille Coupling Reaction.

1.6.7. Negishi Coupling Reactions

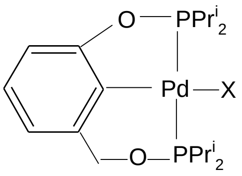
One modified Negishi coupling reaction protocol for the one-pot coupling of a wide array of aryl chlorides with phenylacetylene in the presence of $ZnCl_2$ using complex **17** as catalyst, achieving yields as high as 91% for the reaction of 4-chloroacetophenone with phenylacetylene at 160°C for 24 h reaction time has been reported by Eberhard and co-workers (Eberhard et al.,2002).



Scheme 1.40 Negishi Coupling Reaction Route.

1.6.8. Allylic Alkylation

Unsymmetrical POCOP pincer ligand and its palladium derivatives were found to be active in the allylic alkylation of cinnamyl acetate with sodium dimethyl malonate, showing little isomerization activity affording exclusively the linear product (Wang et al., 2003).



(28) X= Cl

(29) X= I

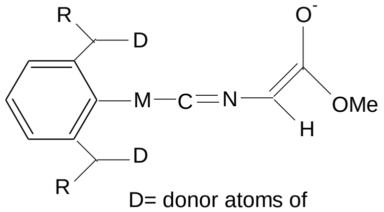
(30) X= OAc

Figure 1.46 Examples of POCOP Pd Complexes.

Reactivity of complexes **28–30** as compared with compound **17** is due to the introduction of a six-membered metallacycle into the pincer complex structure, thus making these species more flexible and increasing the P−M−P bite angle. Moreover, the catalytic activity resulted to be strongly dependent on the anion coordinated to the palladium center, hence the activity of the complexes increases when the metal is more easily available, the more active specie being that having the less coordinating ligand (OAc) complex **30**.

1.6.9. Aldol Reactions

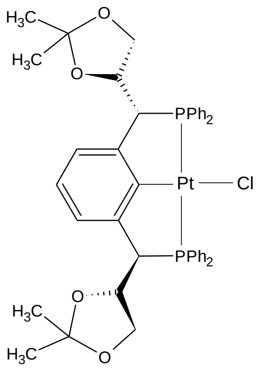
Several platinum and palladium pincer complexes have been found to catalyse the aldol reactions of carbonyl compounds with isorganates by providing a vacant coordination site for the isocyanoacetate. Before the aldol condensation can occur, the prec-ordinated isocynate must be enolised by the addition of a base and this enolate can than react with the carbonyl compound (Singleton, 2003).



D= donor atoms of
pincer complexes

1.6.9.1. Asymmetric Aldol Reactions Catalysed by PCP Pincer Complexes

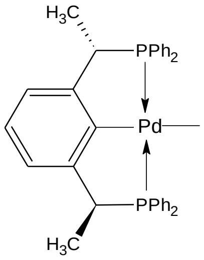
The use of a chiral PCP platinum pincer complex **148**, in the aldol condensations of various aldehydes with methyl isocyonate has been reported by Gorla and co-workers (Gorla et al., 1994) (Figure 1.47).



(148)

Figure 1.47 Example of PCP Pt Complex.

The synthetic route to this platinum pincer complex **148** was long and difficult, which detracts from this system's utility. A simpler palladium pincer complex **149** was developed by Zhang et al. for the same aldol condensations (Zhang et al., 1998). The results published indicate that the palladium catalyst **149** produces a higher enontioselectivity for cis oxozolines, but a lower enontioselectivity for trans oxazolines, when compared with the platinum catalysts **148.**



(149)

Figure 1.48 Example of PCP Pd Complex.

1.6.9.2. SCS Pincer Complex-Catalysed Aldol Reactions

The use of SCS palladium pincer complexes as both homogenous and heterogeneous catalysts in various aldol reactions have been investigated in 2001 (Gimenez et al., 2001).

Three homogenous catalysts **150, 151** and **152** were synthesized; **150** and **151** are binuclear complexes cantaining a chiral spacer derived from o-isopropylidiere-1- threitol and it was hoped that such complexes could act as effective asymmetric catalysts in aldol reactions.

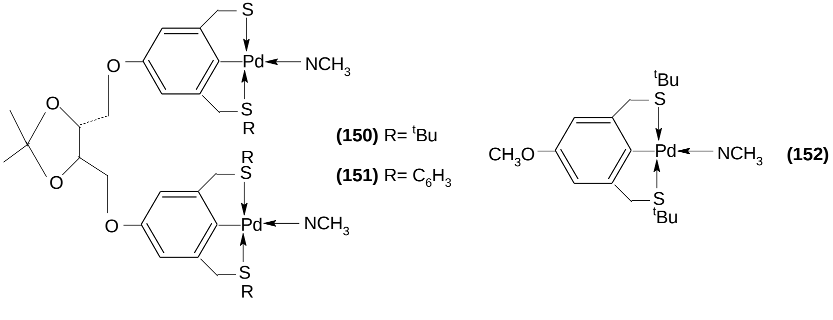
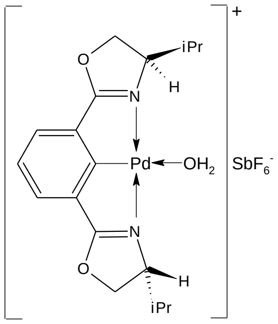


Figure 1.49 Examples of SCS Pd Complexes.

1.6.10. Michael Reactions

The use of the palladium NCN pincer complex **153** (Figure 1.50) as a potential catalyst in other reactions were reported in 1997 (Stark et al., 1997).

Catalyst **153** was shown for example, to increase the rate of the Diels-Alder reaction of cyclopentadiene with methacrolein, but, as the increase was very marginal and with no change in the exo/endo ratio of the products, this area of research was curtailed. It was reported that in the case of ethyl cyanoacetate, the double Michael addition adduct was formed when catalyst **153** has been used.



(153)

Figure 1.50 Example of NCN Pd Complex.

2. EXPERIMENTAL

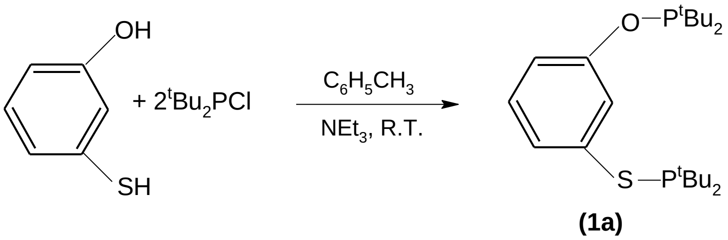
Schlenk-type flask under argon atmosphere and high vacuum-line techniques were used for the reactions involving air sensitive components. In order to remove oxygen and moisture all of the glass equipments were heated under vacuum. Solvents were dried on suitable drying agents and purified under inert conditions (Jolly, W., 1970).

Dicholoromethane, toluene, diethylether, hexane, tetrahydrofuran, Et_3N were purchased from Merck. Diphenylchlorophosphine, dicyclohexylchlorophosphine, 3-mercaptophenol and 1,3-benzenedithiol, were purchased from Aldrich; $[PdCl_2(COD)]$ (COD= 1,5-cyclooctadiene), (Chatt et al., 1957) and $^tBu_2PCl$ were synthesized according to the literature (Fild et al., 1973).

^{31}P-{^1H}-NMR, ^1H-NMR and ^{13}C-NMR spectras were recorded on a Varian AS 400 MHz spectrometer. J values are given in Hz. IR spectras were obtained Perkin-Elmer 1600 series FT-IR spectrometer by using KBr and CsI discs. Melting points were determined by electro thermal melting point detection apparatus. The measurements for catalytic experiments performed by Thermo Electron Corporation Trace GC Ultra in Ege University Department of Chemistry. AFM analyses were performed by using Scanning Probe Microscope SCOPE 250 SCANNING PROBE MICROSCOPE AMBIOS TECH. TGA and DTG curves were determined by Perkin Elmer device.

2.1. Synthesis of PCP Pincer Ligands Derivatives

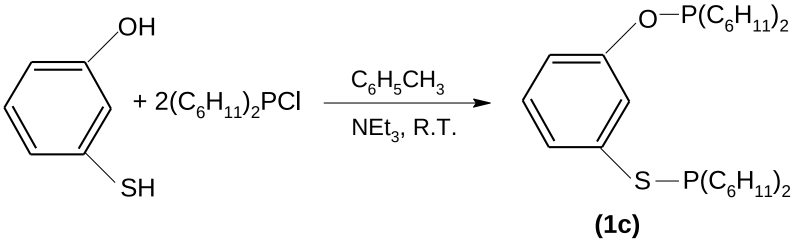
2.1.1. Synthesis of 3[(di-tert-butylphosphino)thio]phenyl di-tert-butylphosphinite (1a).



Scheme 2.1 Reaction route for the synthesis of (1a).

3-mercaptophenol (1.00 mmol) was dissolved in toluene (20 mL) and then Et_3N (2.00 mmol) was added and stirred. After 10 minutes, dropwise a solution of $^tBu_2PCl$ (2.00 mmol) in toluen (20 mL) was added at 0°C. The reaction mixture stirred for 72 h. at room temperature. The mixture was filtered with cannula to seperate Et_3NHCl salt. The solvent was removed in vacuum. It was ended a yellow oil. The ligand was characterized by FT-IR and NMR spectra. Yield % 78. ^{31}P-{^{1}H}-NMR: δ= 84.12 and 164.17 ppm. FT-IR: υ (P-S) 774.82, υ(P-O) 1174.82 cm^{-1}. ^{1}H-NMR (400 MHz, DMSO): δ= 1.09-1.41 ppm (m, 36 H, $C(CH_3)_3$), δ= 6.49-7.23 ppm (m, 4H, Ar-H). ^{13}C-NMR (400 MHz, DMSO): δ= 118.14, 126.17, 128.85, 138.18, 158.23 ppm (Ar-C), δ= 26.50, 30.06, 33.78, 35.46 ppm ($C(CH_3)_3$).

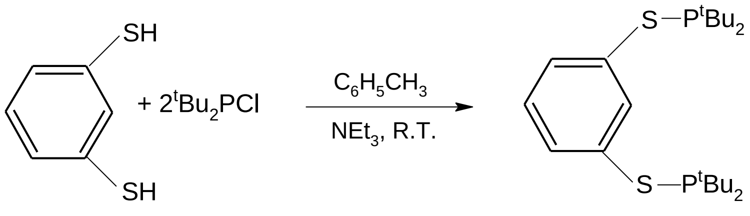
2.1.2. Synthesis of 3-[(dicyclohexylphosphino)thio]phenyl dicyclohexylphosphinite (1c).



Scheme 2.2 Reaction route for the synthesis of (1c).

The formation of pincer ligand from the reaction of 3-mercaptophenol (0.98 mmol) and Et_3N (1.96 mmol) with $(Cy)_2PCl$ (1.96 mmol) was obtained under the same conditions. The reaction was end up a cream oil. The product was controlled by TLC. There was no further purification. The ligand was characterized by FT-IR and NMR spectra. Yield % 80, $^{31}P-\{^1H\}$-NMR : δ= 67.97 and 147.59 ppm., ^1H-NMR (400 MHz, DMSO): δ= 1.16-2.48 ppm (m, 44 H, Cy), δ= 6.55-7.23 ppm (m, 4H, Ar-H), ^{13}C-NMR (400MHz, $CDCl_3$): δ= 114.02, 118.35, 122.21, 128.86, 130.33, 158.20 ppm (Ar-C), δ= 25.21-35.12 ppm (Cy), FT-IR: υ (P-S) 705.42 cm^{-1}; υ (P-O) 1265.52 cm^{-1}.

2.1.3. Synthesis of 1,3-phenylene bis[di-tert-butyl(phosphinothioite)] (2a).

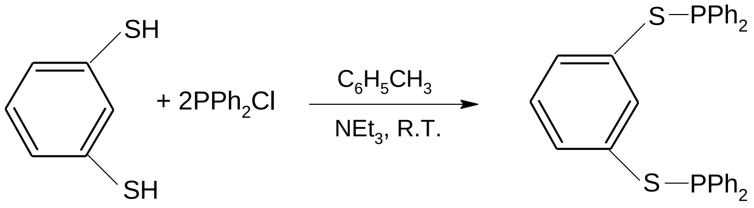


(2a)

Scheme 2.3 Reaction route for the synthesis of (2a).

$^tBu_2PCl$ (1.54 mmol) in toluen (20 mL) was added to the solution of 1,3-benzeneditihiol (0.77 mmol) and Et_3N (1.54 mmol) in toluen at 0°C under argon atmosphere and stirred 1 h. After cooling to room temperature, the reaction mixture stirred 2 days at room temperature. The solvent was removed in vacuum. It was ended a cream oil. The ligand was characterized by FT-IR and NMR spectra. Yield % 70, $^{31}P-\{^1H\}$-NMR : δ= 85.45 and 86.76 ppm. ^1H-NMR (400 MHz, $CDCl_3$): δ= 1.20-1.40 ppm (m, 36 H, $C(CH_3)_3$), δ= 7.00-7.60 ppm (m, 4H, Ar-H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ=125.98, 128.87, 129.57, 138.21 ppm (Ar-C), δ= 27.00, 29.87, 30.01, 35.59 ppm ($C(CH_3)_3$). FT-IR: υ (P-S) 693.66 cm^{-1}.

2.1.4. Synthesis of 1,3-phenylene bis[diphenyl(phosphinothioite)] (2b).

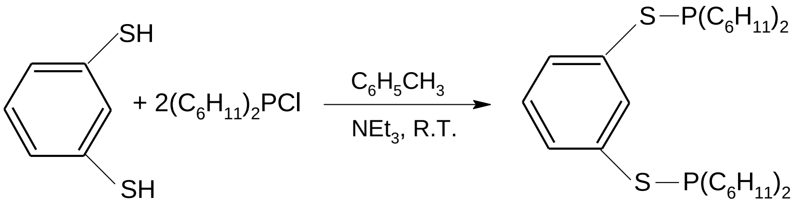


(2b)

Scheme 2.4 Reaction route for the synthesis of (2b).

1,3-benzeneditihiol (0.77 mmol) was dissolved in toluene (20 mL) and then Et$_3$N (1.54 mmol) was added to the solution and stirred. After 10 minutes, dropwise a solution of Ph$_2$PCl (2.00 mmol) in toluen (20 mL) was added at 0^{o}C. The reaction mixture stirred for 36 h. at room temperature. The mixture was filtered with cannula to seperate Et$_3$NHCl salt. The solvent was removed in vacuum. It was ended a yellow-cream oil. The ligand was characterized by FT-IR and NMR spectra. Yield % 82, ^{31}P-{^{1}H}-NMR : δ= 32.15 ppm., ^{1}H-NMR (400 MHz, CDCl$_3$): δ= 7.40-7.56 ppm (m, 4H, ArH), δ= 7.11- 7.22 ppm (m, 16 H, Ph), ^{13}C-NMR(400 MHz, CDCl$_3$): δ= 129.77, 132.07, 134.99, 136.32 ppm (Ar-C), δ= 128.87, 129.56, 129.65, 131.58 ppm (P-Ar-C), FT-IR: υ (P-S) 774.80 cm^{-1}.

2.1.5. Synthesis of 1,3-phenylene bis[dicyclohexyl(phophinothioite)] (2c).



(2c)

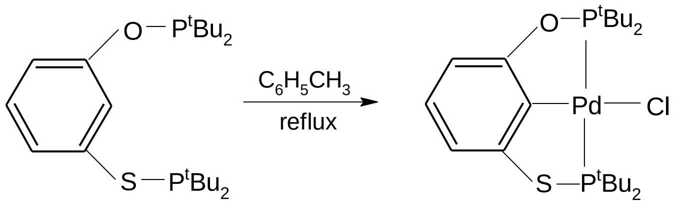
Scheme 2.5 Reaction route for the synthesis of (2c).

Cy$_2$PCl (1.55 mmol) was added to the solution of 1,3-benzeneditihiol (0.77 mmol) and Et$_3$N (1.55 mmol) in toluen at 0^{o}C under argon atmosphere and stirred 1 h. After cooling to room temperature, the reaction mixture stirred 2 days at room temperature. The solvent was removed in vacuum. It was ended a yellow oil. The

The ligand was characterized by FT-IR and NMR spectra. Yield %71. ^{31}P-{^{1}H}-NMR : δ= 69.14 ppm., ^{1}H-NMR (400 MHz, DMSO): δ= 6.84-7.73 ppm (m, 4H, Ar-H), δ= 1.20-2.33 ppm (m, 44 H, Cy), ^{13}C-NMR (400 MHz, DMSO): δ= 125.37, 128.41, 131.24, 134.49 ppm (Ar-C), δ= 25.19, 33.74, 39.23 ppm (Cy), FT-IR: υ (P-S) 807.73 cm^{-1}.

2.2. Synthesis of PCP Pincer Palladium Complexes

2.2.1. 3[(di-tert-butylphosphino)thio]phenyl di-tert-butylphosphinite Pd(II) Complex (1a').

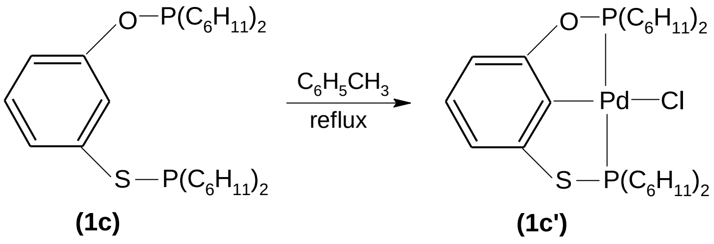


(1a) **(1a')**

Scheme 2.6 Reaction route for the synthesis of (1a').

To the toluene solution (10 mL) of 3[(di-tert-butylphosphino)thio]phenyl di-tert-butylphosphinite, (0.36 mmol), $PdCl_2COD$ (0.36 mmol) suspension in toluene (10 mL) was added and stirred under reflux for 24 h. After 24 h. the mixture was filtered with cannula to seperate the product. After filtration a red solid was remained. In order to obtain pure complex, the residue was washed with dichloromethane to remove the ligand and $PdCl_2COD$ impurity. The red powder was obtained after treating with dichloromethane. The product was characterized by ^{31}P-{^{1}H}-NMR, ^{1}H-NMR and FT-IR spectrums. Yield % 75., m.p.= 283-285 °C(decomposed), ^{31}P-{^{1}H}-NMR : δ= 178.77 and 189.16 ppm. ^{13}C-NMR (400 MHz, DMSO): δ= 114.38, 116.17, 117.97, 120.07, 130.58, 158.45 ppm, (Ar-C), δ= 39.60-46.19 ppm (^{t}Bu), FT-IR: υ (Pd-Cl) 321.75 cm^{-1}.

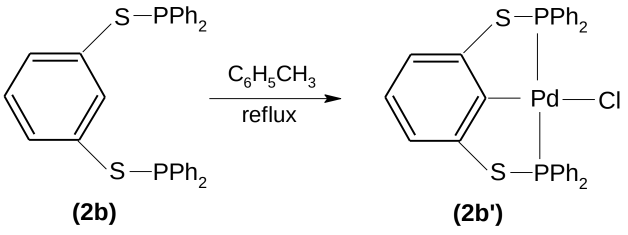
2.2.2. 3-[(dicyclohexylphosphino)thio]phenyl dicyclohexylphosphinite Pd(II) Complex (1c’).



Scheme 2.7 Reaction route for the synthesis of (1c’).

This compound was prepared in the same manner as 2.2.2 using 3-[(dicyclohexylphosphino)thio]phenyl dicyclohexylphosphinite (0.26 mmol) and $PdCl_2COD$ (0.26 mmol). The reddish solid was obtained. Same purification was done for this product with dichloromethane. The product was characterized by ^{31}P-{^{1}H}-NMR, ^{1}H-NMR and FT-IR spectrums. Yield % 80, m.p.= 280-282 °C (decomposed), ^{31}P-{^{1}H}-NMR : δ= 110.87 and 159.11ppm., ^{1}H-NMR (400 MHz, DMSO): δ= 6.34-7.25 ppm (m, 4H, Ar-H); δ= 1.22-2.51 ppm (m, 44 H, Cy), FT-IR: υ (Pd-Cl), 275.9 cm^{-1}.

2.2.3. 1,3-phenylene bis[diphenyl(phosphinothioite)] Pd(II) Complex (2b’).

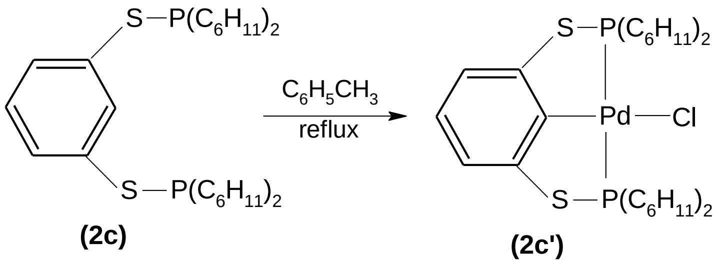


Scheme 2.8 Reaction route for the synthesis of (2b’).

1,3-phenylene bis[diphenyl(phosphinothioite)] (0.24 mmol) was dissolved in toluene (10 mL). Toluene suspension (10 mL) of $PdCl_2COD$ (0.24 mmol) was added and stirred under reflux for 24 h. After then, in order to seperate the product, the mixture was filtered with cannula. The residue was as a red-brown powder, it was washed with dichloromethane to remove the ligand and $PdCl_2COD$

impurity. The product was characterized by ^{31}P-{^{1}H}-NMR, ^{1}H-NMR and FT-IR spectrums. Yield % 72, m.p.=280-283°C (decomposed), ^{31}P-{^{1}H}-NMR : δ= 54.08 ppm., ^{1}H-NMR (400 MHz, DMSO): δ= 7.05-7.84 ppm (Ar-H), FT-IR: υ (Pd-Cl) 293.88 cm^{-1}.

2.2.4. 1,3-phenylene bis[dicyclohexyl(phophinothioite)] Pd(II) Complex (2c').



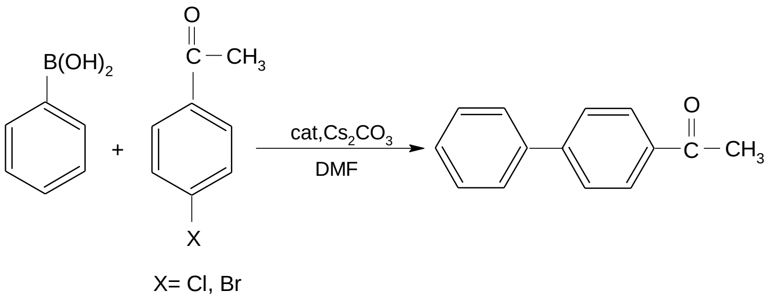
Scheme 2.9 Reaction route for the synthesis of (2c').

This compound was prepared in the same manner as 2.2.2 using 1,3-phenylene bis[dicyclohexyl(phophinothioite)] (0.35 mmol) and PdCl$_2$COD (0.35 mmol). The red-brown solid was obtained. The product was washed with dichloromethane and diethylether to remove ligand and PdCl$_2$COD impurity. The product was characterized by ^{31}P-{^{1}H}-NMR, ^{1}H-NMR and FT-IR spectrums. Yield % 75, m.p.= 178-180 °C (decomposed), ^{31}P-{^{1}H}-NMR: δ= 89.91 ppm., ^{1}H-NMR (400 MHz, DMSO): δ= 6.72-7.27 ppm (m, 4H, Ar-H), δ= 1.22-2.38 ppm (m, 44 H, Cy), ^{13}C-NMR (400 MHz, DMSO): δ= 119.63, 125.47, 126.57, 129.61 ppm (Ar-C), δ= 25.01, 26.67, 27.94, 36.52 ppm (Cy), FT-IR: υ (Pd-Cl) 267.02 cm^{-1}

2.3. Catalytic Experiments

2.3.1. General Procedure for the Suzuki Coupling Reactions

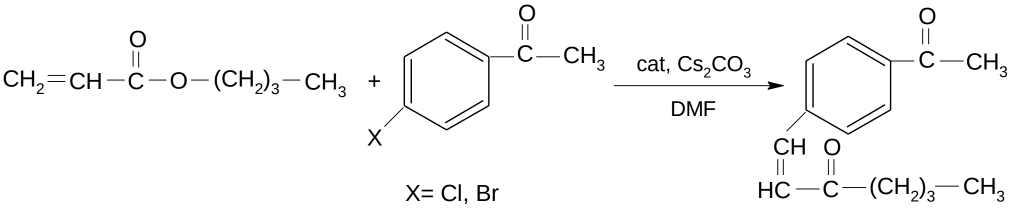
Under nitrogen atmosphere, a mixture of benzeneboronic acid (1.50 mmol), 1.00 mmol 4-bromoacetophenone / 4-chloroacetophenone, 1.50 mmol Cs_2CO_3/K_2CO_3, %1 mmol catalyst, in the presence of diethyleneglycoldibutylether, in 3.00 mL of DMF was refluxed at 100°C with stirring for 48 hours. At the conclusion the solution was allowed to cool, extracted with CH_2Cl_2 and the organic phase seperated. Yields were determined by gas chromatography for an every two hours.



Scheme 2.10 General route for the Suzuki Coupling Reactions.

2.3.2. General Procedure for the Heck Coupling Reactions

Butylacrilate (0.75 mmol), 4-bromoacetophenone / 4-chloroacetophenone (0.50 mmol), 1.50 mmol Cs_2CO_3/K_2CO_3, %1 mmol catalyst, in the presence of diethyleneglycoldibutylether, in 3.00 mL of DMF was refluxed at 140°C with stirring for 48 hours under nitrogen atmosphere. At the conclusion the solution was allowed to cool, extracted with CH_2Cl_2 and the organic phase seperated. The progress of the reaction was monitored by GC for an every two hours.



Scheme 2.11 General route for the Heck Coupling Reactions.

2.4. TGA Analyses

Thermal stability of the complexes (1a’and 2c’) TGA, DTG methods were measured with the help of these results TGA and DTG curves were drawn by Perkin Elmer device.

2.5. AFM Analyses

These studies were carried out to determine the characterization of the surface of the complexes (1a’and 2c’) which were aimed to use as a catalysts for Suzuki and Heck reactions. Thin film of the complexes which obtained from the method of solvent removal on a glass material were examined using the AFM instrument (Q SCOPE 250 SCANNING PROBE MICROSCOPE AMBIOS TECH).

3. RESULTS AND DISCUSSION

Polydentate ligands featuring different heteroatoms as binding sites are currently attracting great attention both in coordination chemistry and in catalysis. Indeed, it is well recognized that the combination of very different electronic and steric effects can lead to subtle changes in the coordinating behavior of ligands as well as the reactivity of their respective complexes. Modulation of these electronic effects were found to play an important role in many catalytic processes. Among different possible combinations only litte attention has been paid to mixed P-S ligands. However, some P-S based catalytic systems, even operating at high temperature with low-valent metals, already proved to be efficient catalysts (Doux et al., 2005). With the help of this information, we have synthesized PCP pincer ligands that contain O and S heteroatoms, and their palladium complexes. Although, pincer ligands are very air and moisture sensitive, pincer complexes are very stable to air and moisture and can be handled in open air.

The identity of the ligands were established by $^{31}P\{^1H\}$-NMR, ^1H-NMR, $^{13}C\{^1H\}$-NMR and FT-IR spectroscopy and the all complexes were established by $^{31}P\{^1H\}$-NMR, ^1H-NMR and FT-IR but only **(1a')** and **(2c')** were identified by $^{13}C\{^1H\}$-NMR spectroscopy, also.

Because the ligands were in oily form and they can not be handled in open air, elemental analysis was impossible for them.

The thermal behaviour of pincer complexes **(1a'), (2b'), (2c')** were investigated using thermogravimetry (TGA). Also, AFM measurement of complexes **(1a'), (2b'), (2c')** were investigated for analyses of facile characteristic features.

Catalytic activities of complexes were examined in Suzuki and Heck Cross Coupling Reactions.

3.1. Characterization of PCP Pincer Ligands Derivatives

The tridentate PCP bis(phosphinite) and bis(phosphine) ligands **(1a, 2a, 2b, 1c, 2c)** have been easily synthesized in one step from 3-mercaptophenol and 1,3-benzenedithiol. –OH and –SH protons were first deprotonated with 2 equivalents of triethylamine, and the resulting compounds reacted with 2 equivalents of ditertbutylchlorophosphine, diphenylchlorophosphine and dicyclohexylchlorophosphine at 0°C, than the mixtures were set to stirred at room temperature. Ligands were formed as a colourless oil and they can not be handled in open air because of their air and moisture sensitivity.

3.1.1. Characterization of 3[(di-tert-butylphosphino)thio]phenyl di-tert-butylphosphinite (1a)

The reaction of the 3-mercaptophenol with two equivalent of ditertbutylchlorophosphine in dry toluene with triethylamine as a base yields the unsymmetrical bis(phosphinite)ligand **(1a)** as a colourless oil.

The $^{31}P\{^1H\}$-NMR experiment is very illustrating showing two signals in the spectra which are in accordance with the presence of two different phosphorus nuclei; one located at 84.12 ppm due to the presence of the thiophosphinito fragment (Serrano- Becerra et al., 2010; Boldovino-Pantaleon et al., 2005), and the other at 164.17 ppm due to the phosphinito moiety (Wang et al., 2003; Morales-Morales et al., 2004; Bedford et al., 2006). Analysis by ^1H-NMR reveal the presence of the aromatic groups at 6.49-7.23 ppm (m, 4H, ArH) and methyls of the ^{t}Bu groups in the P moiety between 1.09-1.41 ppm (m, 36 H, $C(CH_3)_3$). Results obtained from the analysis of this ligand by $^{13}C\{^1H\}$-NMR, the signals observed for the aromatic carbons in the usual region at 118.14, 126.17, 128.85, 138.18, 158.23 ppm, and the signals for the ^{t}Bu groups observed at 26.50, 30.06, 33.78, 35.46 ppm, respectively. Analysis by FTIR spectroscopy reveal the disapperance of the S-H vibrations at 2560 cm^{-1} which was observed in the FTIR spectrum of 3-mercaptophenol. Also, P-S and P-O single bond vibrations were observed at 774.82 cm^{-1} and 1174.82 cm^{-1} (Bellamy, 1975). This PCP pincer ligand is very sensitive to oxygen and moisture, thus it can not be handled in the open air. Also, it was used in the next step without any further purifications.

3.1.2. Characterization of 3-[(dicyclohexylphosphino)thio]phenyl dicyclohexylphosphinite (1c)

3-[(dicyclohexylphosphino)thio]phenyl dicyclohexylphosphinite **(1c)** was synthesized in one step from 3-mercaptophenol, 2 equivalents of Et_3N and 2 equivalents of $(Cy)_2PCl$ as a colourless oil in %80 yield. The $^{31}P\{^1H\}$-NMR experiment is very illustrating showing two signals in the spectra which are in accordance with the presence of two different phosphorus nuclei; one located at 67.97 ppm due to the presence of the thiophosphinito fragment (Serrano- Becerra et al., 2010; Boldovino-Pantaleon et al., 2005), and the other at 147.59 ppm due to the phosphinito moiety (Wang et al., 2003; Morales-Morales et al., 2004; Bedford et al., 2006). When we compare ligand (1c) to ligand (1a), we have seen that $^{31}P\{^1H\}$-NMR values were changed by the electron attractive properties of the R groups which were bonded to phosphorus atoms. Electron attractive groups reduce the density of electrons on the phosphorus atoms and so, $^{31}P\{^1H\}$-NMR values were shifted to high field. In (1a), R groups were ^{t}Bu groups which were less electron attractive than Cy groups in (1c). So, we have obtained the phosphorus signal of the thiophosphinito fragment in (1a) at 84.12 ppm and in (1c) at 67.97 ppm. And also, the phosphinito fragment in (1a) at 164.17 ppm and in (1c) at 147.59 ppm. Analysis by ^1H-NMR reveal the presence of the aromatic groups at 6.55-7.23 ppm (m, 4H, ArH) and protons of the Cy groups in the P moiety between 1.16-2.48 ppm (m, 44 H, Cy). The ^1H-NMR spectrum indicates the presence of starting compounds impurities at 9.48 ppm. Unfortunately, removal of the impurities was not succesfully due to the similar solubilities. Also, signals of the DMSO protons at 3.30 ppm was seen in the spectrum. Although we removed the solvent molecule in the vacuum, because of the oily form of this molecule it absorbs the solvent, and we can see the signals of the $C_6H_5CH_3$ at 5.64 ppm. Results obtained from the analysis of this ligand by $^{13}C\{^1H\}$-NMR, the signals observed for the aromatic carbons in the usual region at 114.02, 118.35, 122.21, 128.86, 130.33, 158.20 ppm., and the signals for the Cy groups observed between 25.21-35.12 ppm.,respectively. Analysis by FTIR spectroscopy also has shown us the coordination of $(C_6H_{11})_2PCl$ to 1,3-benzenedithiol, by the disapperance of the S-H vibrations at 2560 cm^{-1} which was observed in the FTIR spectrum of 3-mercaptophenol. And also, at 705.42 cm^{-1}, P-S single bond vibrations and at 1265.52 cm^{-1} P-O single bond vibrations were observed (Bellamy, 1975). This PCP pincer ligand is very sensitive to oxygen and moisture, thus it can not be handled in the open air. Also, it was used in the next step without any further purifications.

3.1.3. Characterization of 1,3-phenylene bis[di-tert-butyl(phosphinothioite)] (2a)

1,3-phenylene bis[di-tert-butyl(phosphinothioite)] **(2a)** has been conveniently synthesized from the reaction of one amount of 1,3-benzenedithiol and two amounts of ditertbutylchlorophosphine in the presence of triethylamine as a base. This compound was obtained as a colorless oil. The analysis by $^{31}P\{^{1}H\}$-NMR spectrum was more informative, showing two signals at 85.45 and 86.76 ppm (Baldavino-Panteleon et al., 2005). But the $^{31}P\{^{1}H\}$-NMR spectrum of this ligand exhibits a single absorption as expected for equivalent phosphorus nuclei. This multiplicity being the result of the interaction of the phosphorus due to sulfur groups in connection with the geometry. Thus, P-P coupling constants are between 55-450 Hz for trivalent phosphorus and the splitting values are nearly 330 Hz (Verkade, 1987). Analysis by ^{1}H-NMR reveal the presence of the aromatic groups between 7.00-7.60 ppm (m, 4H, ArH) and the signals of the ^{t}Bu groups between 1.20-1.40 ppm (m, 36 H, $C(CH_3)_3$), as respectively. The ^{1}H-NMR spectrum indicates the presence of starting compound, 1,3-benzenedithiol impurities at 3.46 ppm. Unfortunately, removal of the impurities was not succesfully due to the similar solubilities. Results obtained from the analysis of this ligand by $^{13}C\{^{1}H\}$-NMR, the signals observed for the aromatic carbons in the usual region at 125.98, 128.87, 129.57, 138.21 ppm., and the signals for the ^{t}Bu groups observed at 27.00, 29.87, 30.01, 35.59 ppm. respectively. Analysis by FTIR spectroscopy reveal the disapperance of the S-H vibrations at 2560 cm^{-1} which was observed in the FTIR spectrum of 1,3 benzenedithiol. Also, P-S single bond vibrations were observed at 693.66cm^{-1} (Bellamy, 1975).

3.1.4. Characterization of 1,3-phenylene bis[diphenyl(phosphinothioite)] (2b)

The reaction of the 1,3-benzenedithiol with two equivalent of diphenylchlorophosphine in dry toluene with triethylamine as a base yields the thiophosphinito ligand **(2b)** as a colourless oil in %82 yield. The $^{31}P\{^1H\}$-NMR spectrum is very informative, showing a single signal at 32.15 ppm indicative of equivalent phosphorus nuclei. This value is in accordance with the analogues of this ligand which was reported by Serrano-Becerra et al. (Serrano-Becerra et al., 2010). 1,3-phenylene bis[diphenyl(phosphinothioite)] (2b) exhibits signals in the ^1H-NMR due to the presence of the phenyl groups in the thiophosphinito moiety (7.40-7.56 ppm) and the aromatic ring (7.11-7.22) ppm. As observed for ligand 2a; the ^1H-NMR spectrum of ligand 2b, indicates the presence of starting compound, 1,3-benzenedithiol impurities at 3.46 ppm., but removal of the impurities was not succesfully due to the similar solubilities. $^{13}C\{^1H\}$-NMR, where besides the signals observed for the aromatic carbons of the aryl group in the usual region at 129.77, 132.07, 134.99, 136.32 ppm, signals to the aromatic carbons of the phenyl groups observed at 128.87, 129.56, 129.65, 131.58 ppm (P-Ar-C). Analysis by FTIR spectroscopy also has shown us the coordination of PPh_2Cl to 1,3-benzenedithiol, by the disapperance of the S-H vibrations at 2560 cm^{-1} which was observed in the FTIR spectrum of 1,3 benzenedithiol. And also, at 774.80 cm^{-1}, P-S single bond vibrations were observed (Bellamy, 1975). All of these analyses also reveals the ligand to be pure enough to be used in the following process, the metallation step.

3.1.5. Characterization of 1,3-phenylene bis[dicyclohexyl(phophinothioite)] (2c)

The reaction of the 1,3-benzenedithiol with two equivalent of dicyclohexylchlorophosphine in dry toluene with triethylamine as a base yields the thiophosphinito ligand **(2c)** as a colourless oil. The $^{31}P\{^1H\}$-NMR spectrum is very informative, showing a single signal at 69.14 ppm indicative of equivalent phosphorus nuclei. This value is accordance with the analogues of this ligand which was reported by Serrano-Becerra et al. (Serrano-Becerra et al., 2010; Boldovino-Pantaleon et al., 2005). Electron attractive properties of the R groups which were bonded to phosphorus atoms varies according to the following order: Ph > Cy > ^{t}Bu. It was expected to see the $^{31}P\{^{1}H\}$-NMR values of the ligand **(2a)** was shifted to downfield and the ligand **(2b)** was shifted to high field. When we compare the $^{31}P\{^{1}H\}$-NMR results we have seen that the values of the thiophosphinito fragments in all three ligands were in accordance with each other; in ligand **(2b)** at 32.15 ppm, in **(2c)** at 69.14 ppm, in **(2a)** at 85.45 ppm.

Analysis by ^{1}H-NMR reveal the presence of the aromatic groups at 6.84-7.73 ppm (m, 4H, ArH) and protons of the Cy groups in the P moiety between 1.20-2.33 ppm (m, 44 H, Cy). Also, signals of the DMSO protons at 3.50 ppm was seen in the spectrum. $^{13}C\{^{1}H\}$-NMR, where besides the signals observed for the aromatic carbons of the aryl group in the usual region at 125.37, 128.41, 131.24, 134.49 ppm, signals to the cyclohexyl groups observed at 25.19, 33.74, 39.23 ppm. Analysis by FTIR spectroscopy also has shown us the coordination of $(C_6H_{11})_2PCl$ to 1,3-benzenedithiol, by the disapperance of the S-H vibrations at 2560 cm^{-1} which was observed in the FTIR spectrum of 1,3 benzenedithiol. In additon to that, we have seen P-S single bond vibrations at 807.73 cm^{-1} (Bellamy, 1975). Similarly to other ligand derivatives, **(2c)** is very sensitive to oxygen and moisture, thus it can not be handled in the open air. Also, it was used in the next step without any further purifications.

3.2. Characterization of PCP Pincer Palladium Complexes

PCP pincer palladium complexes **(1a’, 2b’, 1c’ and 2c’)** were obtained in moderate yields from the reactions of the pincer ligands **(1a, 2b, 1c** and **2c)** and an equimolar amounts of $PdCl_2COD$ in toluene under reflux. Although, all pincer ligands were air and moisture sensitive, pincer complexes were very stable to air and moisture and can be handled in open air. PCP pincer complexes **(1a’, 2b’, 1c’** and **2c’)** have been fully identified by spectroscopic techniques. Catalytic activities of complexes were examined in Suzuki and Heck Cross Coupling Reactions. Unfortunately, single crystals of these complexes can not be obtained because of the low- solubility.

3.2.1. Characterization of 3[(di-tert-butylphosphino)thio]phenyl di-tert-butylphosphinite Pd(II) Complex (1a')

3[(di-tert-butylphosphino)thio]phenyl di-tert-butylphosphinite Pd(II) Complex **(1a')** has been synthesized by the reaction of $PdCl_2COD$ with one equivalent of the PCP pincer ligand **(1a)** under reflux in toluene for 72 h. The resulting compound **(1a')** was isolated from the corresponding reaction mixture as a deep red powder, that was stable in air. $^{31}P\{^{1}H\}$-NMR spectroscopy reveals similar patterns as observed for the free ligand **(1a).** The $^{31}P\{^{1}H\}$-NMR spectrum of complex **(1a')** exhibits signals at 178.77 ppm (Serrano-Becerra et al., 2010) and 189.16 ppm (Wang et al., 2003; Morales-Morales et al., 2004; Bedford et al., 2006) ppm for the thiophosphinito and the phosphinito moiety. The $^{31}P\{^{1}H\}$-NMR spectrum, passing from 84.12 and 164.17 in the free ligand **(1a)** to 178.77 and 189.16 ppm in the metallated complex **(1a')** for the thiophosphinito and the phosphinito moiety. $^{31}P\{^{1}H\}$-NMR values of the free ligand were shifted to down field by complexation, and this was in accordance with the literatures (Morales-Morales et al., 2000; Morales-Morales et al., 2004). Results obtained from the analysis of this complex by $^{13}C\{^{1}H\}$-NMR, the signals observed for the aromatic carbons in the usual region at 114.38, 116.17, 117.97, 120.07, 130.58, 158.45 ppm, and the signals for the ^{t}Bu groups observed between 39.60- 46.19 ppm respectively. The presence of Pd-Cl bond is indicated by FT-IR spectroscopy, which shows a strong υ(Pd-Cl) at 321.75 cm-^{1}(Bellamy, 1975).

3.2.2. Characterization of 3-[(dicyclohexylphosphino)thio]phenyl dicyclohexylphosphinite Pd(II) Complex (1c')

The direct reaction of 3-[(dicyclohexylphosphino)thio]phenyl dicyclohexylphosphinite **(1c)** with $PdCl_2COD$ in refluxing toluene for 24 hours affords the non-symmetric phosphinito-thiophosphinito PSCOP pincer complex **(1c').** Complex **(1c')** was obtained as a reddish solid which is stable in air. However, is the $^{31}P\{^{1}H\}$-NMR analysis that provides fundamental information about the structure of the complex. Thus, the spectrum of **(1c')** shows two signals at 110.87 and 159.11 ppm for the thiophosphinito (Boldovino-Pantaleon et al., 2005) and the phosphinito (Wang et al., 2003; Morales-Morales et al., 2004;

Bedford et al., 2006) moiety. When we compare **(1a')** to **(1c'),** we have seen that $^{31}P\{^1H\}$-NMR values were changed by the electron attractive properties of the R groups which were bonded to phosphorus atoms. When we have been discussing the properties of the pincer ligands we have seen that R groups electron attractive properties varies according to the following order, like that; Ph > Cy > ^{t}Bu. The same order was seen for these pincer complexes. Electron attractive groups reduce the density of electrons on the phosphorus atoms and so, $^{31}P\{^1H\}$-NMR values were shifted to high field. In **(1a'),** R groups were ^{t}Bu groups which were less electron attractive than Cy groups in **(1c').** So we have obtained the phosphorus signal of the thiophosphinite fragment in **(1a')** at 178.77 ppm and in **(1c')** at 110.87 ppm. And also, the phosphinito fragment in **(1a')** at 189.16 ppm and in **(1c')** at 159.11 ppm. Results obtained from the analysis of this complex by ^1H-NMR, the signals observed for the protons of aromatic carbons between 6.34-7.25 ppm and the protons of Cy groups between 1.22-2.51 ppm. Complex **(2c')** could not identified by $^{13}C\{^1H\}$-NMR spectroscopy because of the low solubility. We could not be successfull in crystallization also because of this reason. The presence of Pd-Cl bond is indicated by FT-IR spectroscopy, which shows a strong υ(Pd-Cl) at 275.9 cm-^{1} (Bellamy, 1975).

3.2.3. Characterization of 1,3-phenylene bis[diphenyl(phosphinothioite)] Pd(II) Complex (2b')

Reaction of $PdCl_2COD$ with one equivalent of the PCP pincer ligand **(2b)** under reflux in toluene for 24 h., yields the complex **(2a')** as a red-brown powder. The NMR spectra of complex exhibit the signal corresponding to the presence of the substituents in the P moieties. Analysis by $^{31}P\{^1H\}$-NMR exhibits a singlet signal in spectrum at 54.08 ppm, indicative of both phosphorus being equivalent. This value was consisted with the similar complex which was reported in the literature (Serrano-Becerra et al., 2010). $^{31}P\{^1H\}$-NMR value of the free ligand was shifted to down field by the coordination to metal atom. This was in accordance with the literatures (Morales-Morales et al., 2000; Morales-Morales et al., 2004). The ^1H-NMR spectrum exhibits signals concerning to the aromatic rings of phenyl groups between 7.05-7.84 ppm. Unfortunately, we can see the signals of the $C_6H_5CH_3$ at 5.64 ppm. Also, signals of the DMSO protons at 3.54

ppm was seen in the spectrum. We could not be successfull in crystallization because of the low solubility. Complex **(2b')** could not identified by $^{13}C\{^1H\}$-NMR spectroscopy because of the low solubility also. The presence of υ (Pd-Cl) signal at 293.88 cm^{-1} in the FT-IR spectrum of **(1b')** is characteristic for Pd-Cl (Bellamy, 1975).

3.2.4. Characterization of 1,3-phenylene bis[dicyclohexyl(phophinothioite)] Pd(II) Complex (2c')

Reaction of $PdCl_2COD$ with one equivalent of the PCP pincer ligand **(2c)** under reflux in toluene for 24 h., yields the complex **(2c')** as a red-brown powder which is stable in air. The NMR spectra of complex exhibit the signal corresponding to the presence of the substituents in the P moieties. Analysis by $^{31}P\{^1H\}$-NMR exhibits a singlet signal in spectrum at 89.91 ppm, indicative of both phosphorus being equivalent. The $^{31}P\{^1H\}$-NMR spectrum, passing from 69.14 in the free ligand **(2c)** to 89.91 in the metallated complex **(2c')** for the thiophosphinito moiety. $^{31}P\{^1H\}$-NMR values of the free ligand were shifted to down field by complexation, and this was in accordance with the literatures (Morales-Morales et al., 2000; Morales-Morales et al., 2004). The ^1H-NMR spectrum exhibits signals concerning to the cyclohexyl groups between 1.22-2.38 ppm and the protons of aromatic group between 6.72-7.27 ppm. respectively. $^{13}C\{^1H\}$-NMR, where besides the signals observed for the aromatic carbons of the aryl group in the usual region at 119.63, 125.47, 126.57 and 129.61 ppm, signals to the cyclohexyl groups observed at 25.01, 26.67, 27.94 and 36.52 ppm. Analysis by FTIR spectroscopy also has shown us the coordination of the **(2c)** to $PdCl_2COD$, by the signal of Pd-Cl at 267.02 cm^{-1}(Bellamy, 1975). We could not be successfull in crystallization also because of the low solubility similar to the previous complexes.

3.3. Results of the AFM for Complexes (1a'), (2b') and (2c')

The AFM is a form of scanning probe microscope developed in the mid 1980s. It works by scanning an extremely fine probe on the end of a cantilever across the surface of a material, profiling the surface by measuring the deflection of the cantilever. This allows a 3D profile of the surface to be produced at magnifications over one million times, giving much more topographical information than optical or scanning electron microscopes. Its limitation is that the surface to be observed needs to be very flat or the tip will crash into the 'hills' as it is scanned.

AFM measurements of the complexes **(1a'), (2b')** and **(2c')** were investigated for analyses of facile characteristic features. The results of these measurements were given in Figure 3.1 for complex **(1a'),** Figure 3.2 for complex **(2b')** and Figure 3.3 for complex **(2c').** According to these results, we could say that the surfaces of the pincer complexes which we have been synthesized were regular (Senthilarasu et al.,, 2003).

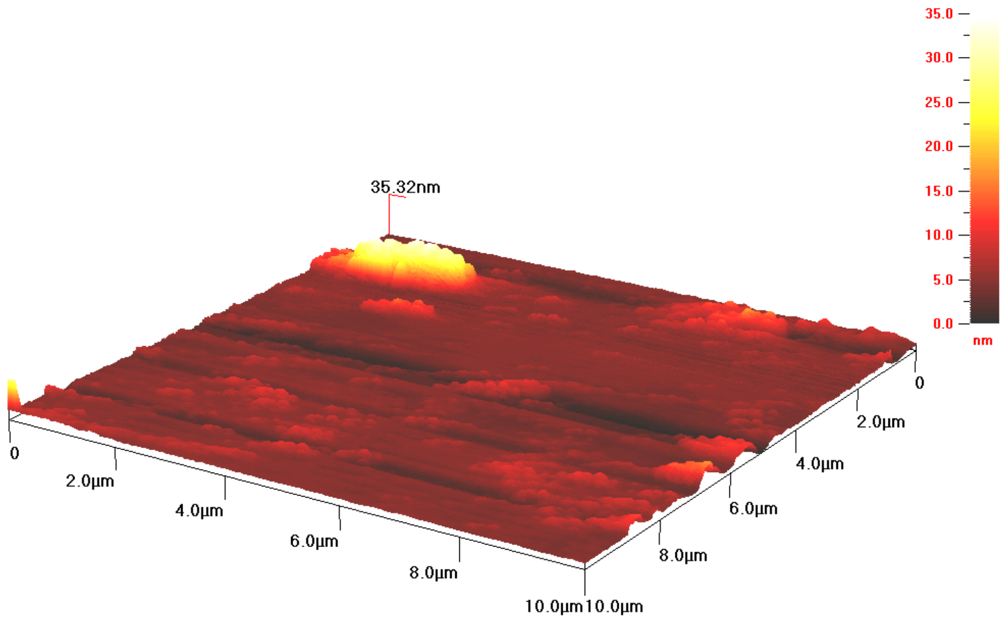


Figure 3.1 : The AFM image of the **(1a').**

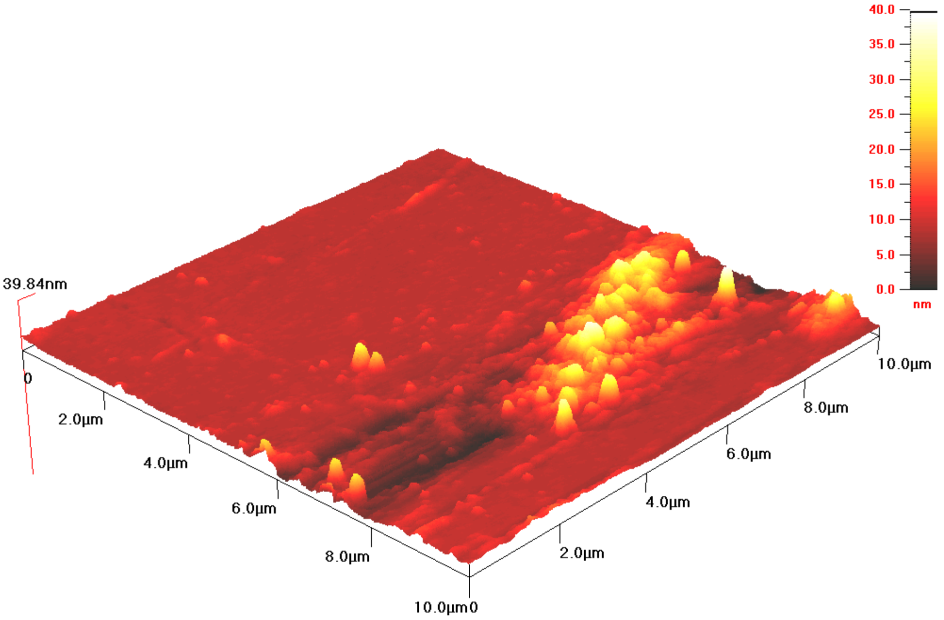


Figure 3.2 : The AFM image of the **(2b').**

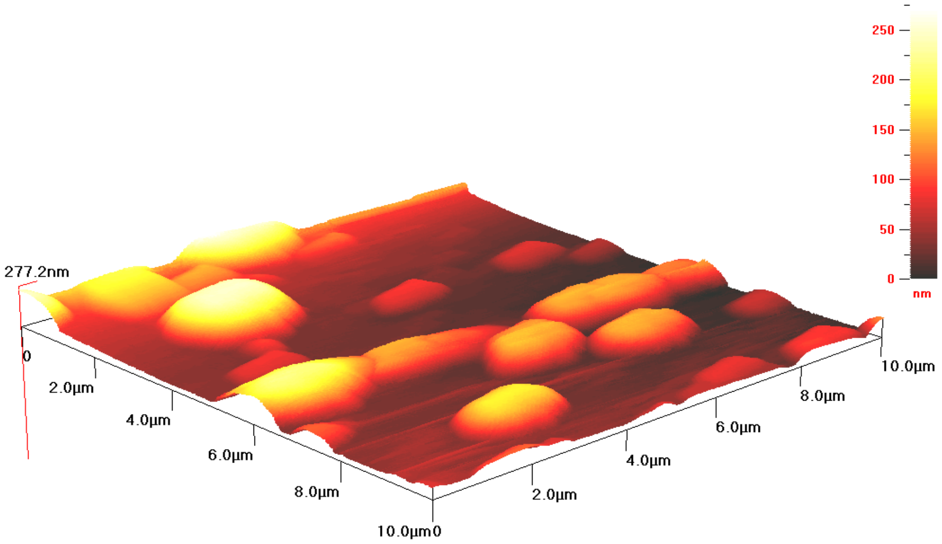


Figure 3.3 : The AFM image of the **(2c').**

3.4. Thermal Analysis of the Complexes (1a’), (2b’) and (2c’)

The thermal behaviour of the complexes were investigated using thermogravimetric analysis (TGA). The complex **(1a’)** decomposes in a three step process (Figure 3.4). The first step observed in temperature range between 150 ºC and 330 ºC with a total mass loss of % 55. The second step takes place between 330- 460 ºC with the % 75 weight loss.

Similar to **(1a’), (2b’)** decomposes in a three step process, too. The first mass loss was observed between 125-220 ºC. The second step takes place up to 360 ºC and the total mass loss of %32. The last step starts at 360 ºC and ends at 550 ºC with a total mass loss of %42.

For the complex **(2c’),** with a loss of moisture at nearly 100 ºC, the decomposition takes place between 285-610 ºC. The total weight loss is approximately %50.

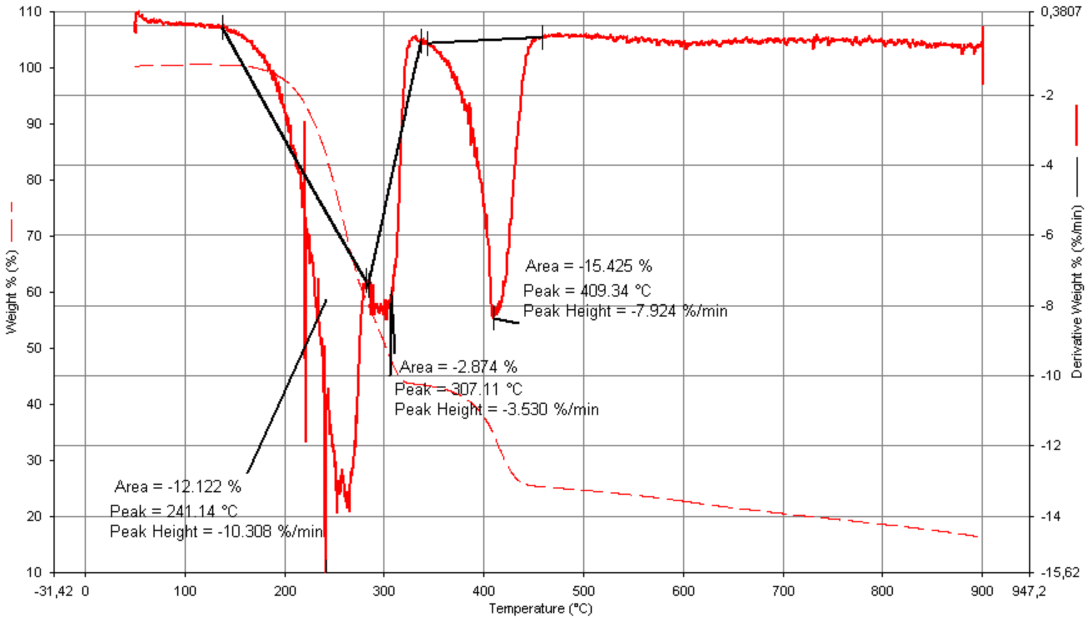


Figure 3.4 : The TGA and DTG curves of the **(1a’).**

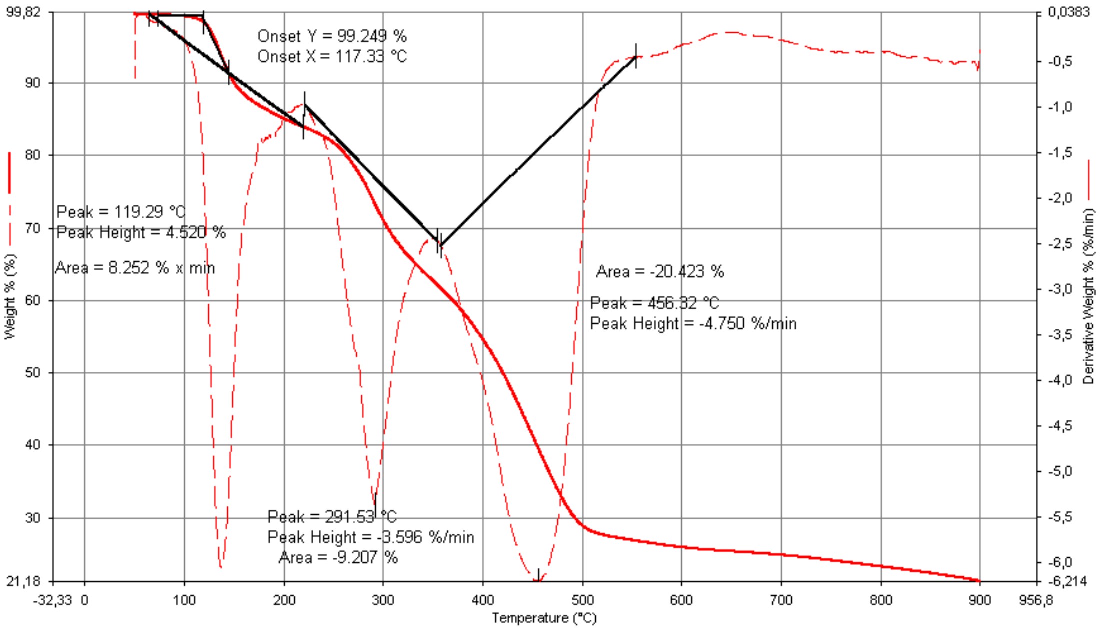


Figure 3.5: The TGA and DTGcurves of the **(2b').**

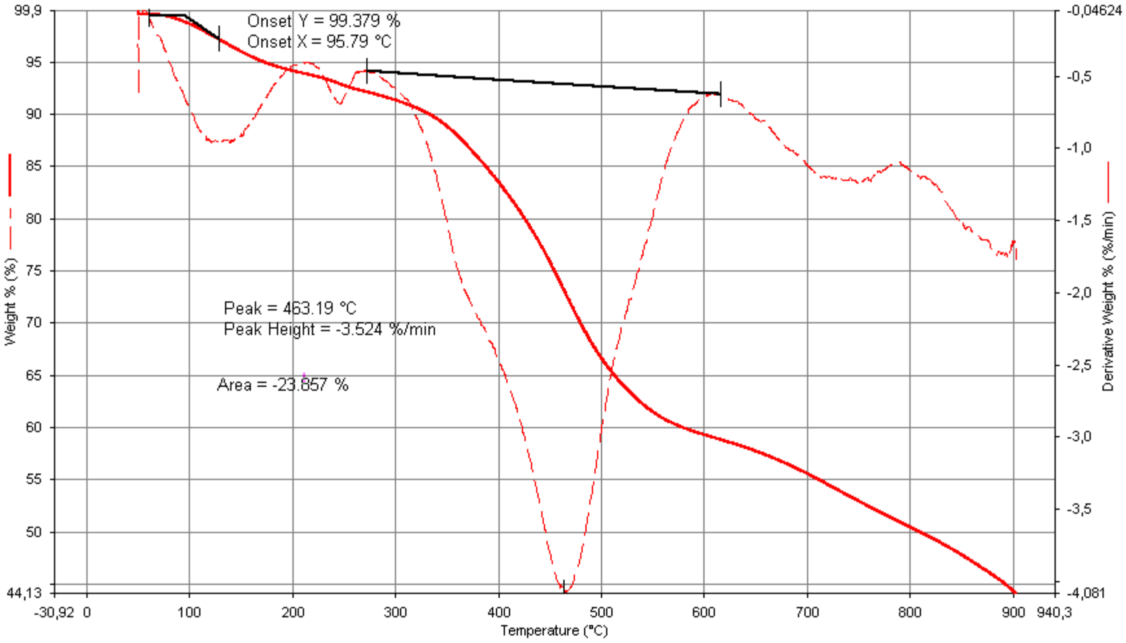


Figure 3.6: The TGA and DTG curves of the **(2c').**

3.5. Catalytic Experiments

Metal complexes based on pincer framework are an appealing target because of their unique balance of stability versus reactivity, which can provide enhanced reactivity and catalytic performances. In particular there has been an increased interest in the use of PCP pincer complexes in homogenous catalysis due to their excellent moisture-, air-, and temperature- stability (Churruca, F., et al., 2006).

PCP pincer complexes were found to be active catalysts for a wide range of reactions including dehydrogenation, transfer dehydrogenation (Dani et al., 2000), Heck reaction (Ohff et al., 1997), Suzuki-coupling (Bedford et al., 2000), Nagishi-type coupling (Eberhard et al., 2002) and enantioselective sharpless epoxidations (Gorla et al., 1994).

Beller and Zapf discovered that Heck coupling reaction mixtures containing phosphinites in place of phosphines have remarkably enhanced catalytic activities (Beller and Zapf, 1998).

The size of chelate rings was important for the catalytic properties of the pincer complexes. The pincer complexes which have six membered palladacycle rings increase the flexibility and have higher activity than the five membered complexes (Naghipour et.al., 2007).

The Suziki reaction is regarded as one of the most efficient ways of forming a carbon-carbon bond. Unfortunately, fairly high catalyst concentrations and the difficulties and costs associated with the removal of palladium from the product have limited its commercial use (Singleton, 2003). Similarly to the Heck reactions, phosphinites PCP pincer complexes have shown high activity in Suzuki coupling reactions than the phosphine pincer complexes (Bedford et al., 2000).

Several parameters effecting the Suzuki-Miyaura coupling reactions are considered. These factors are; solvents effect, substitution group effects, base effect, halogen and the ligand effects. Solvents are the most important parameters in organic reactions; appropriately chosen solvent system strongly favors the cross-coupling pathway. In literature dioxane, THF, different DMF/H_2O and EtOH/H_2O ratios, toluene and benzene have been used as solvents in Suzuki-Miyaura coupling reactions. The halogen type determines the activity of aryl halide towards the

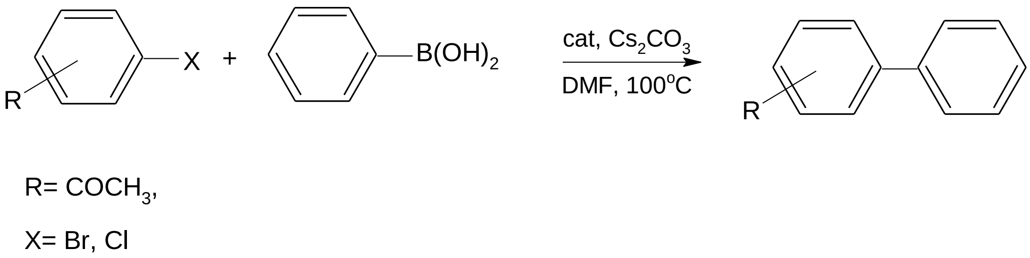
Suzuki-Miyaura coupling reaction. The reactivity of aryl halide component decreases drastically in the order X = I > Br > Cl and electron-withdrawing substituents R are required for the chlorides to react (Gibson et al., 2001; Bedford et al., 2002). Suzuki coupling reactions proceeds via transmetallation in the presence of bases. This procedure does not take place under natural conditions. This is characteristic feature of boron chemistry which is different from that of other organometallic reagents. The most commonly used base in Suzuki cross coupling reaction is Na_2CO_3 but this is often ineffective with sterically demanding substrates. In such instance, $Ba(OH)_2$ or K_3PO_4 has been used the generate good yields of the cross-coupling products. Other bases utilized in the Suzuki cross-coupling reaction include Cs_2CO_3, K_2CO_3, KOMe, TiOH and NaOH.

3.5.1. Results of Catalytic Experiments for Suzuki- Miyaura Coupling Reactions

The palladium-catalyzed cross-coupling of arylboronic acids with aryl halides has been shown the proceed under a variety of conditions; a wide range of bases and solvents, as well as catalysis, have been employed with varying degrees of success according to the substrates.

Although, PCP pincer phosphino and phosphinito complexes have been reported as highly active catalysts for the Heck and Suzuki Coupling Reactions, there has been any report including PCP pincer complexes containing S donor atoms.

We examined the activity of the complexes 1a’, 1c’, 2b’ and 2c’ for Suzuki-Miyaura Coupling Reactions with aryl bromides and chlorides and phenyl boronic acid. Reactions were performed in DMF with Cs_2CO_3 under argon atmosphere (Scheme 3.1). The results of our studies of the catalytic activity of all complexes are presented in Table 3.1. In order to optimize the efficiency of the catalytic system, we initially examined the coupling of aryl halides and phenyl boronic acid by these complexes under a variety of reaction times and analyzed the product mixture through gas chromatography.



Scheme 3.1 The mechanism of Suzuki- Miyaura Coupling Reaction.

The catalysts show high activity in the coupling of aryl bromides; however low activity was observed with aryl chlorides (Table 3.1). In view of the results summarized in Table 3.1, catalytic activity of the pincer complexes **1a’, 1c’, 2b’** and **2c’** were varies depending on the R groups which were bonded to the phosphorus atoms. The reactivity of the R groups decrease in the following order: C_6H_5- > C_6H_{11}- > $(CH_3)_3C$- for the reaction between 4-bromoacetophenone and phenyl boronic acid.

Table 3.1 The Suzuki Coupling Reactions of aryl halides with phenyl boronic acid of catalysts **1a’, 1c’, 2b’** and **2c’**

Entry	**Aryl Halogen**	**Catalyst**	**Time (h)**	**Base**	**Solvent**	**Yield (%)**
1	4-chloroacetophenone	**1a’**	-	Cs_2CO_3	DMF	-
2	4-chloroacetophenone	**1c’**	6	Cs_2CO_3	DMF	18.5
3	4-chloroacetophenone	**2b’**	6	Cs_2CO_3	DMF	20.9
4	4-chloroacetophenone	**2c’**	6	Cs_2CO_3	DMF	20.1
5	4-bromoacetophenone	**1a’**	6	Cs_2CO_3	DMF	93
6	4-bromoacetophenone	**1c’**	6	Cs_2CO_3	DMF	95
7	4-bromoacetophenone	**2b’**	6	Cs_2CO_3	DMF	>99
8	4-bromoacetophenone	**2c’**	6	Cs_2CO_3	DMF	98

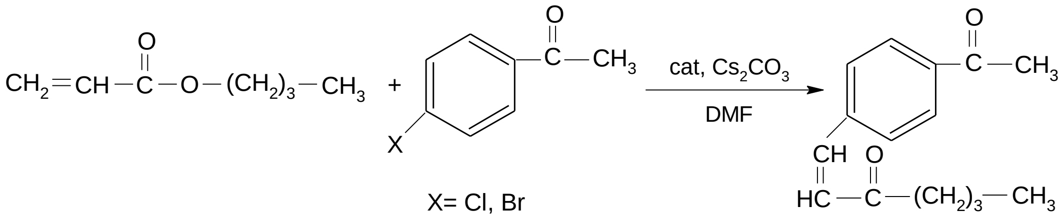
Genarally, the best performance were obtained from the reactions of 4-bromoacetophenone. In accordance with the above order, the performance order of complexes obtained as **2b’**>**1c’**(or **2c’**) >**1a’** for both the reactions of 4-

bromoacetophenone and 4-chloroacetophenone. With 4-bromoacetophenone as aryl halides in cross coupling reactions, the catalysts of **2b'** was the most active catalyst with the yield more than 99%. **1c'** and **2c'** have shown nearly the same activity in the same reaction. The activity of at least has **1a'** for the reactions of 4-bromoacetophenone with the yield of 93%, but the same catalyst 1a' has shown any activity for the reactions of 4-chloroacetophenone. Unfortunately, the catalysts **1c', 2b'** and **2c'** were less active for the reactions of 4-chloroacetophenone.

In conclusion, PSCOP and PSCSP pincer complexes have proved to be highly active catalysts in Suzuki Coupling Reactions with 4-bromoacetophenone as aryl halides. As shown in Table 3.1, when the reaction was conducted in DMF at 100 °C for 6 hours, Cs_2CO_3 as a base gave excellent yields, > 90%.

3.5.2. Results of Catalytic Experiments for Heck Reactions

We examined the activity of the complexes **1a', 1c', 2b'** and **2c'** for Heck Reactions with aryl bromides and chlorides and butylacrilate. Reactions were performed in DMF with Cs_2CO_3 under argon atmosphere (Scheme 3.2). The results of our studies of the catalytic activity of all complexes are presented in Table 3.2. In order to optimize the efficiency of the catalytic system, we initially examined the coupling of aryl halides and phenyl boronic acid by these complexes under a variety of reaction times and analyzed the product mixture through gas chromatography.



Scheme 3.2 The mechanism of Heck Coupling Reactions.

Table 3.2 The Heck Coupling Reactions of aryl halides with phenyl boronic acid of catalysts **1a’, 1c’**, **2b’** and **2c’**

Entry	**Aryl Halogen**	**Catalyst**	**Time (h)**	**Base**	**Solvent**	**Yield (%)**
1	4-chloroacetophenone	**1a’**	2	Cs_2CO_3	DMF	20.9
3	4-chloroacetophenone	**1c’**	2	Cs_2CO_3	DMF	-
2	4-chloroacetophenone	**2b’**	2	Cs_2CO_3	DMF	21.8
4	4-chloroacetophenone	**2c’**	2	Cs_2CO_3	DMF	-
5	4-bromoacetophenone	**1a’**	2	Cs_2CO_3	DMF	32.4
6	4-bromoacetophenone	**1c’**	2	Cs_2CO_3	DMF	-
7	4-bromoacetophenone	**2b’**	2	Cs_2CO_3	DMF	15.0
8	4-bromoacetophenone	**2c’**	2	Cs_2CO_3	DMF	-

In view of the results summarized in Table 3.2, very low activity was found for the pincer complexes **1a’** and **2b’.** In addition to that no activity was observed for **1c’**and **2c’**.

3.6. CONCLUSION

Pincer ligands and their complexes have become more and more important due to the fact that they exhibit the same characteristics of robustness and thermal stability and, as will be shown in further sections of this chapter, enhanced reactivity compared with their phosphine counterparts (Morales-Morales and Jensen, 2007).

Modulation of some electronic effects were found to play an important role in many catalytic processes. The most efficient catalysts in these processes are PCP, NCN and SCS type of pincer complexes characterized by the following structural and electronic features: (1) There is a strong ligand–metal interaction preventing ligand exchange processes; (2) As three of the coordination sites of palladium are kept engaged by the terdentate coordination, there is only one free site available for external ligands; and (3) Under ambient conditions, the oxidation state of palladium is largely restricted to +2 (Morales-Morales and Jensen, 2007).

Pincer ligands and their complexes, involving sulfur donor groups, have been used in different areas like; coordination chemistry, supramolecular chemistry, catalysis, etc. (Morales-Morales and Jensen, 2007). With the help of this information, we have synthesized PCP pincer ligands that contain O and S heteroatoms, and their palladium complexes. Although, pincer ligands are very air and moisture sensitive, pincer complexes are very stable to air and moisture and can be handled in open air.

We have been synthesized five different PCP pincer ligands, two of them contains both S and O heteroatoms, three of them contains only S heteroatoms. We have been synthesized pincer complexes of these ligands using $PdCl_2COD$. The identity of the ligands were established by $^{31}P\{^1H\}$-NMR, ^1H-NMR, $^{13}C\{^1H\}$-NMR and FT-IR spectroscopy and the all complexes were established by $^{31}P\{^1H\}$-NMR, ^1H-NMR and FT-IR but only **(1a')** and **(2c')** were identified by $^{13}C\{^1H\}$-NMR spectroscopy, also. Because of the low solubility, complexes **(1c')** and **(2b')** could not be characterized by $^{13}C\{^1H\}$-NMR spectroscopy.

Because the ligands were in oily form and they can not be handled in open air, elemental analysis was impossible for them.

The thermal behaviour of pincer complexes **(1a'), (2b'), (2c')** were investigated using thermogravimetry (TGA). TGA analyses have shown that, all these complexes were stable up to high temperatures. Also, AFM measurement of complexes **(1a'), (2b'), (2c')** were investigated for analyses of facile characteristic features. According to these results, we could say that the surfaces of the pincer complexes which we have been synthesized were regular (Senthilarasu et al.,, 2003).

We examined the activity of the complexes **(1a'), (1c'), (2b')** and **(2c')** for Suzuki- Miyaura Coupling Reactions with aryl bromides and chlorides and phenyl boronic acid. Reactions were performed in DMF with Cs_2CO_3 under argon atmosphere (Scheme 3.1). The results of our studies of the catalytic activity of all complexes are presented in Table 3.1. In order to optimize the efficiency of the catalytic system, we initially examined the coupling of aryl halides and phenyl boronic acid by these complexes under a variety of reaction times and analyzed the product mixture through gas chromatography. The catalysts show high activity in the coupling of aryl bromides; however low activity was observed with aryl chlorides (Table 3.1). In view of the results summarized in Table 3.1, catalytic activity of the pincer complexes **(1a'), (1c'), (2b')** and **(2c')** were varies depending on the R groups which were bonded to the phosphorus atoms. The reactivity of the R groups decrease in the following order: $C_6H_5^-$ > $C_6H_{11}^-$ > $(CH_3)_3C^-$ for the reaction between 4-bromoacetophenone and benzeneboronic acid. Genarally, the best performance were obtained from the reactions of 4-bromoacetophenone. In accordance with the above order, the performance order of complexes obtained as **2b'>1c'**(or **2c') >1a'** for both the reactions of 4-bromoacetophenone and 4-chloroacetophenone. With 4-bromoacetophenone as aryl halides in cross coupling reactions, the catalysts of **(2b')** was the most active catalyst with the yield more than 99%. **(1c')** and **(2c')** have shown nearly the same activity in the same reaction. The activity of at least has **(1a')** for the reactions of 4-bromoacetophenone with the yield of 93%, but the same catalyst 1a' has shown any activity for the reactions of 4-chloroacetophenone. Unfortunately, the catalysts **(1c'), (2b')** and **(2c')** were less active for the reactions of 4-chloroacetophenone.

We examined the activity of the complexes **(1a'), (1c'), (2b')** and **(2c')** for Heck Reactions with aryl bromides and chlorides and butylacrilate. Reactions were performed in DMF with Cs_2CO_3 under argon atmosphere (Scheme 3.2). The results of our studies of the catalytic activity of all complexes are presented in Table 3.2. In view of the results summarized in Table 3.2, very low activity was found for the pincer complexes **(1a')** and **(2b').** In addition to that no activity was observed for **(1c')** and **(2c').**

In conclusion, PSCOP and PSCSP pincer complexes have proved to be highly active catalysts in Suzuki Coupling Reactions with 4-bromoacetophenone as aryl halides as shown in Table 3.1. But, for the Heck reactions, our complexes have not been found active catalysts as shown in Table 3.2.

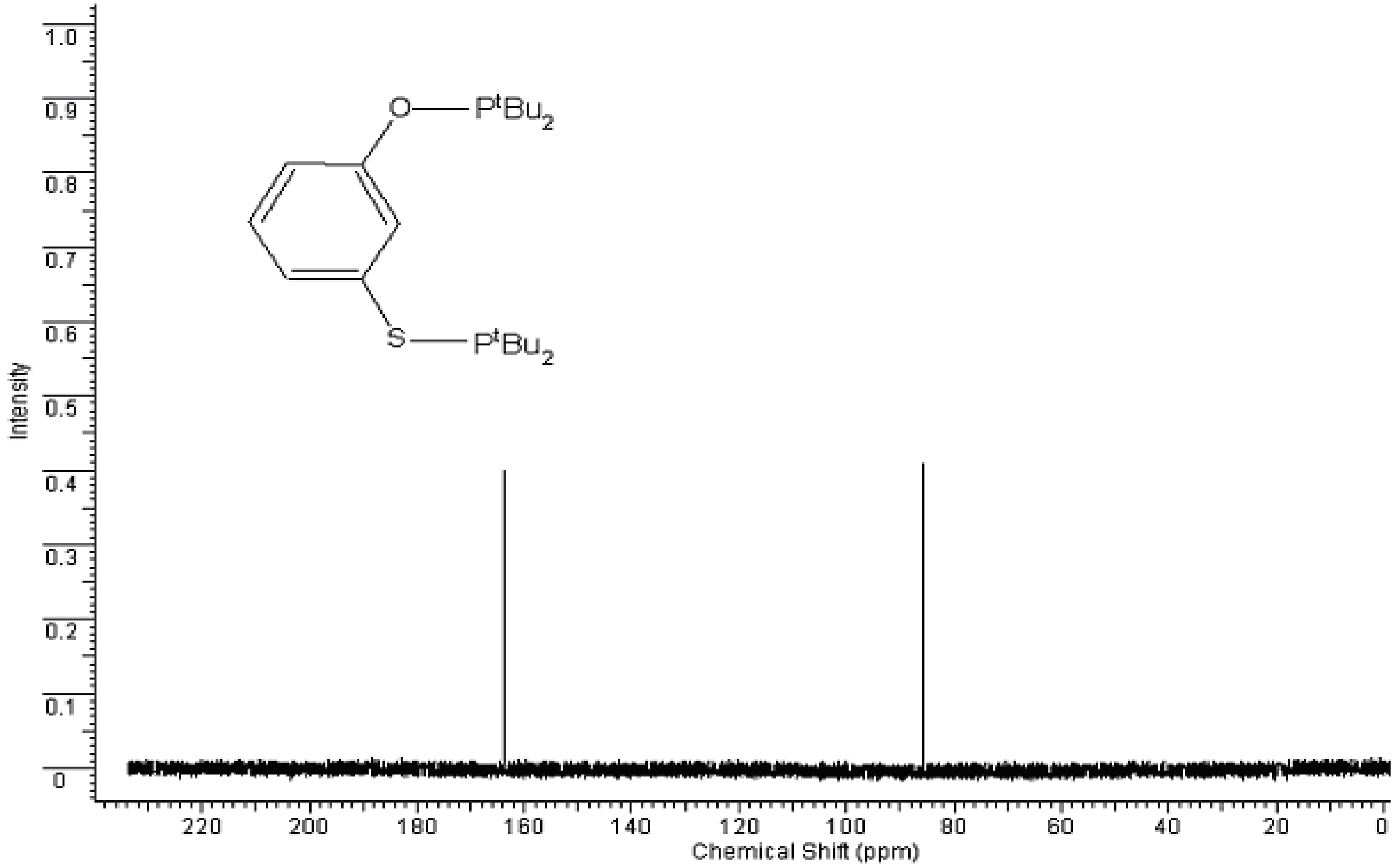


Figure 3.7 $^{31}P\{^1H\}$-NMR spectrum of 3[(di-tert-butylphosphino)thio]phenyl di-tert-butylphosphinite **(1a)**

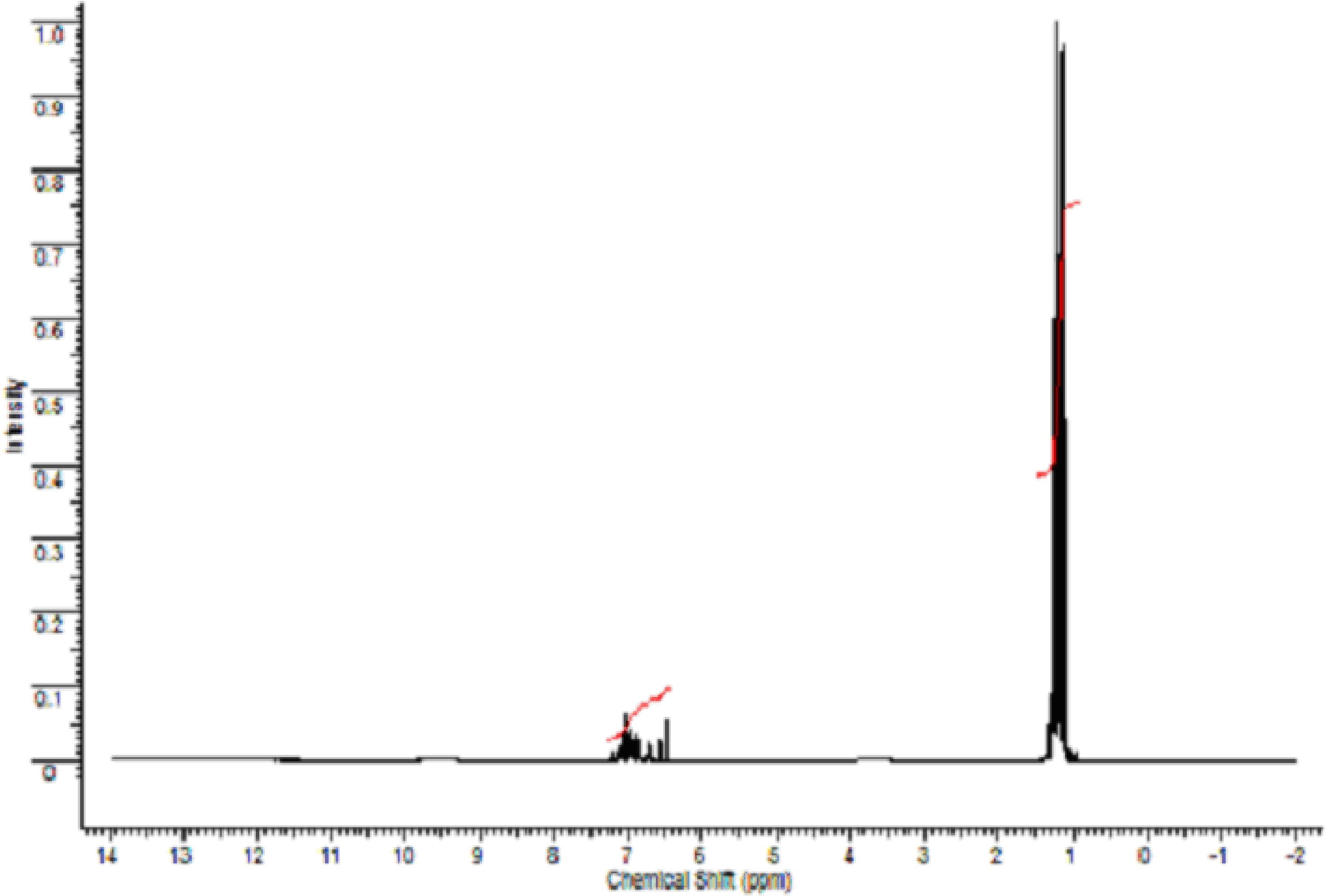


Figure 3.8 ^{1}H-NMR spectrum of 3[(di-tert-butylphosphino)thio]phenyl di-tert-butylphosphinite **(1a)**

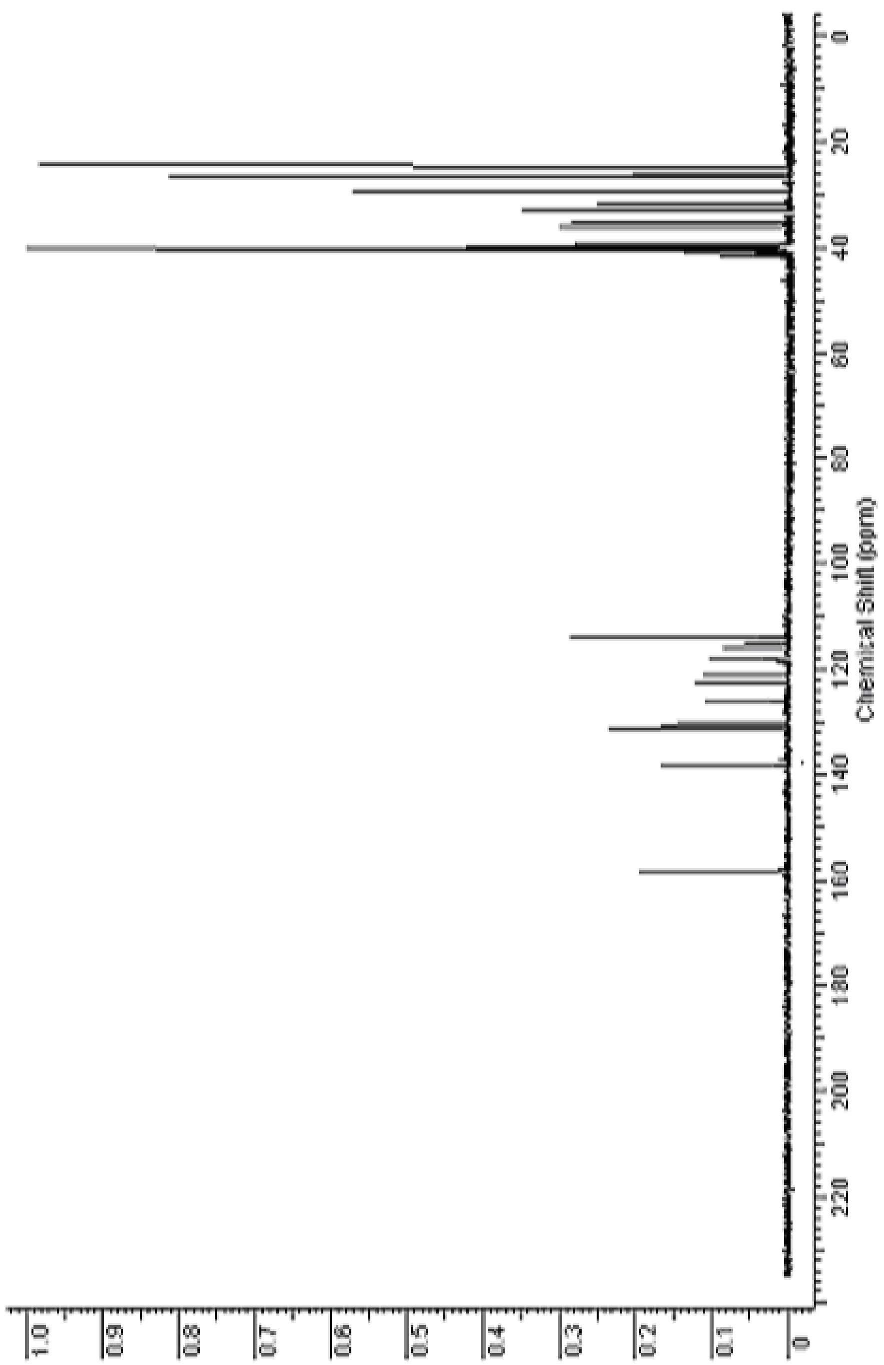


Figure 3.9 $^{13}C\{^{1}H\}$-NMR spectrum of 3[(di-tert-butylphosphino)thio]phenyl di-tert-butylphosphinite (**1a**)

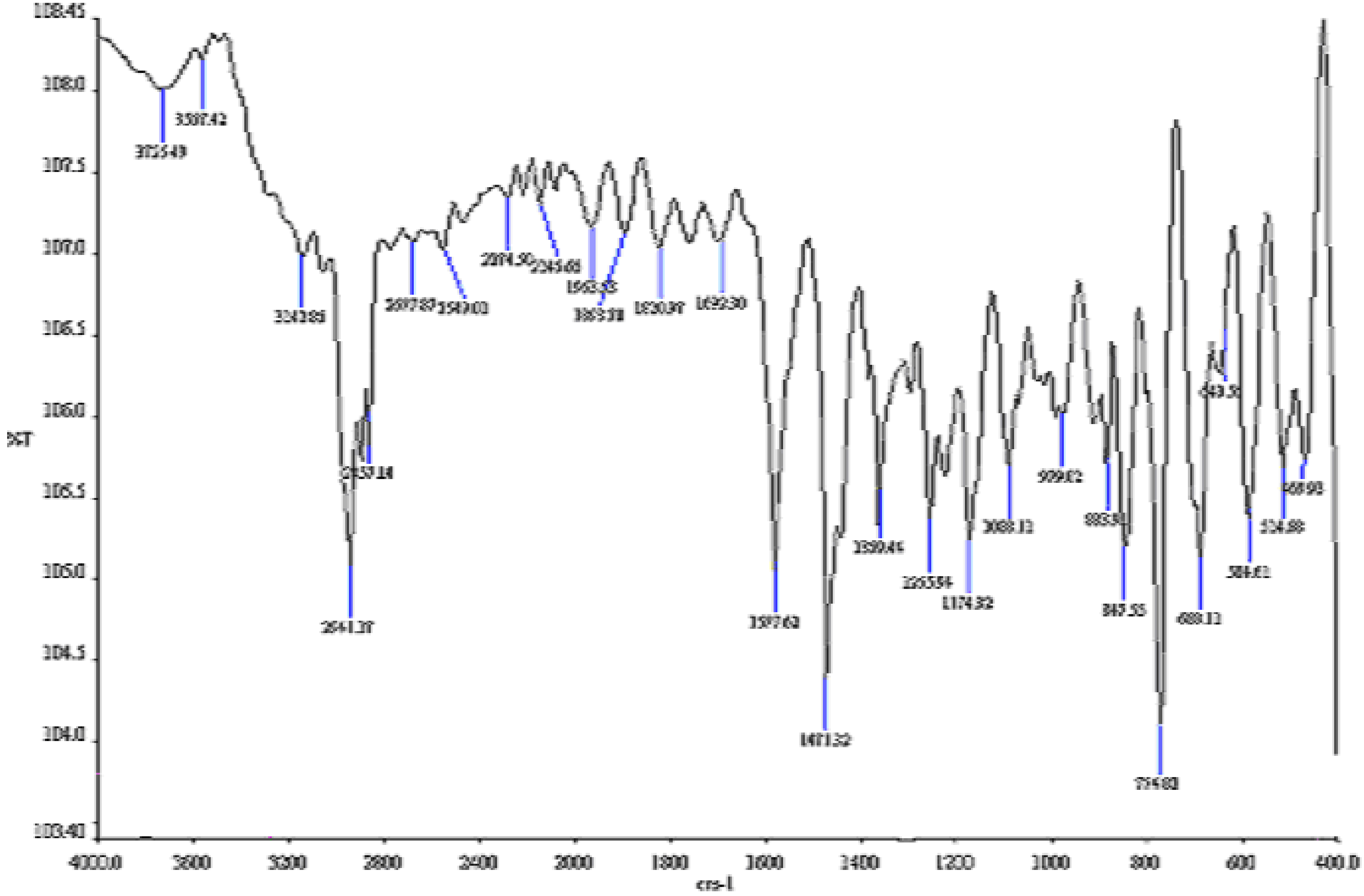


Figure 3.10 FTIR spectrum of 3[(di-tert-butylphosphino)thio]phenyl di-tert-butylphosphinite **(1a)**

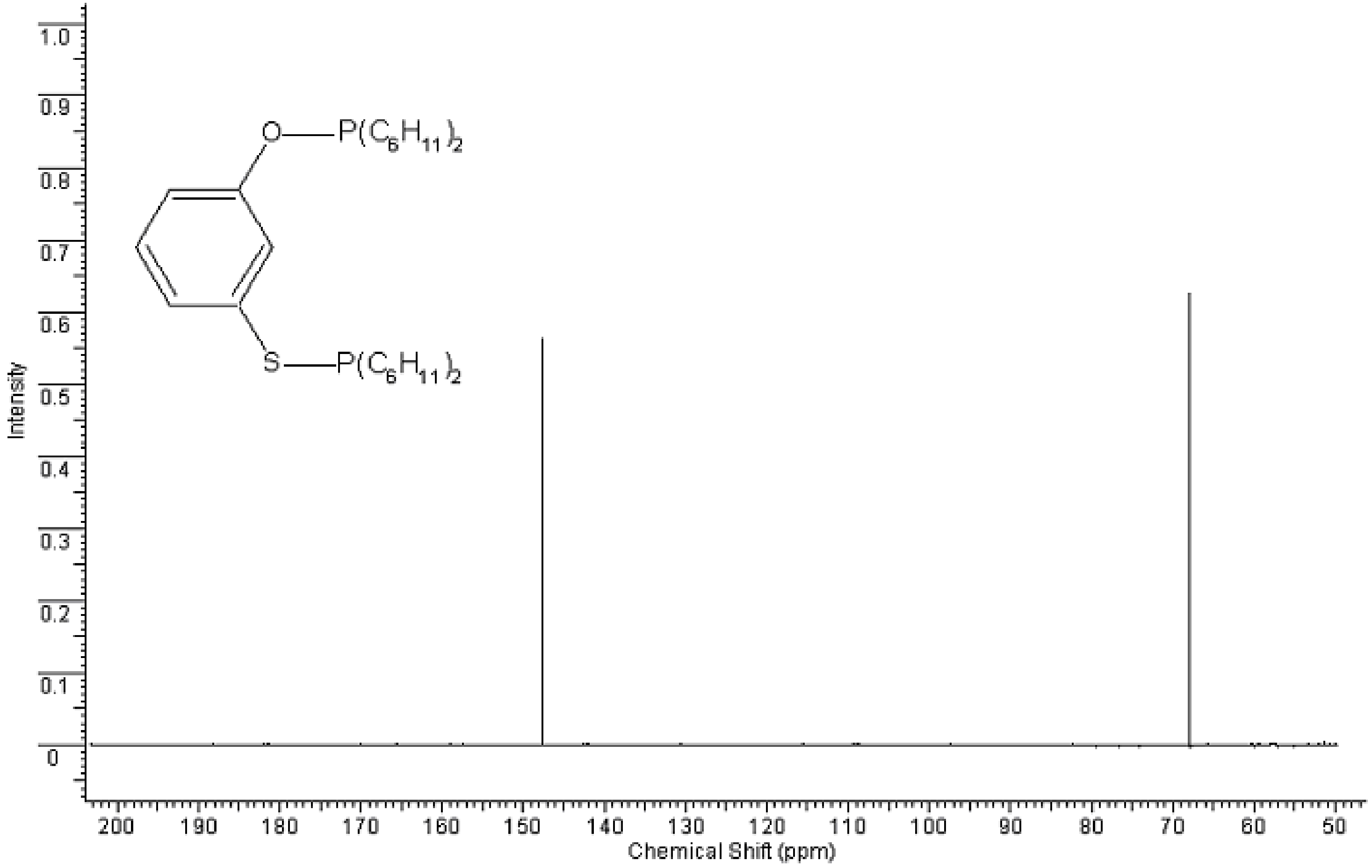


Figure 3.11 $^{31}P\{^{1}H\}$-NMR spectrum of 3-[(dicyclohexylphosphino)thio]phenyl dicyclohexylphosphinite **(1c)**

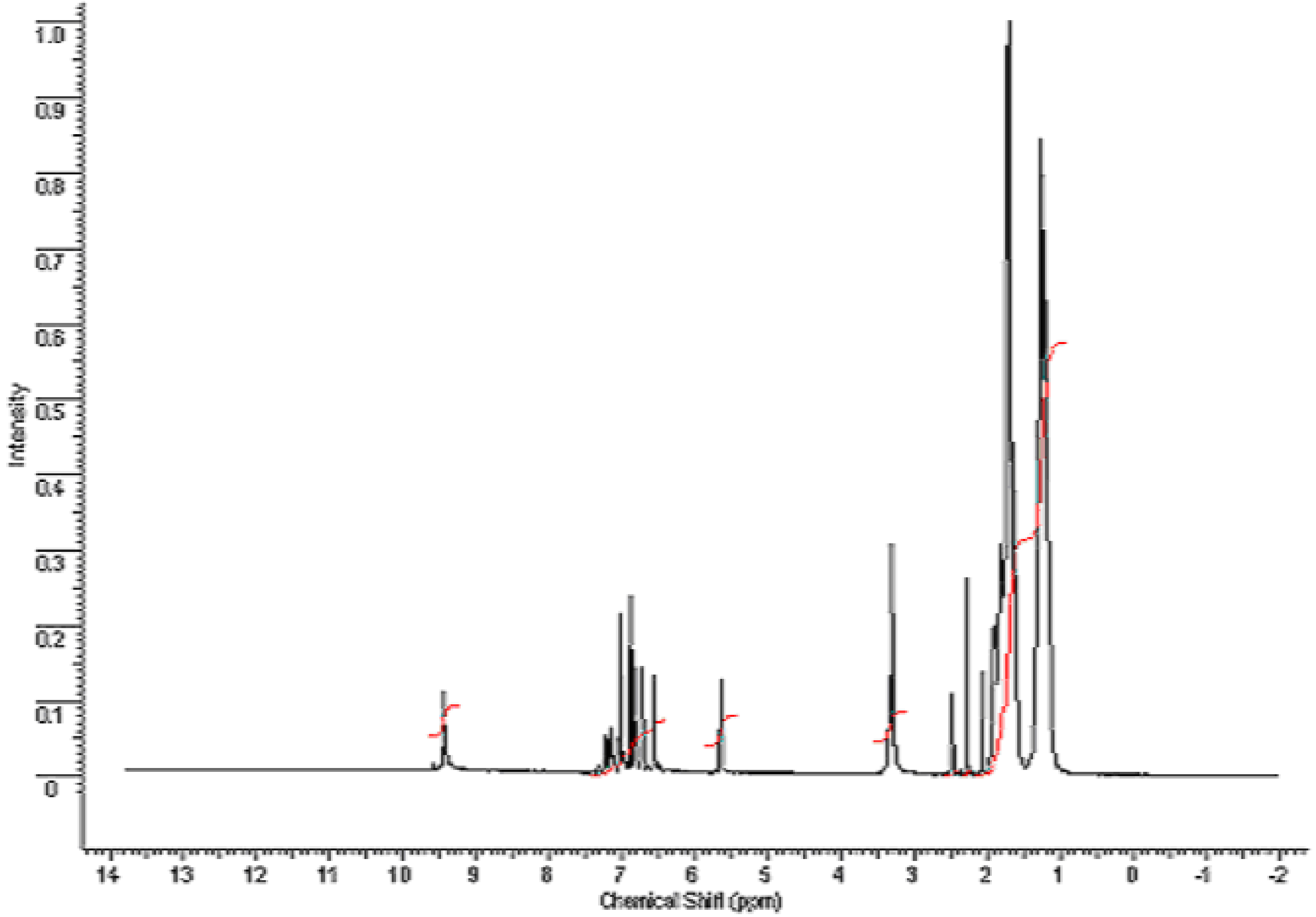


Figure 3.12 ^{1}H-NMR spectrum of 3-[(dicyclohexylphosphino)thio]phenyl dicyclohexylphosphinite **(1c)**

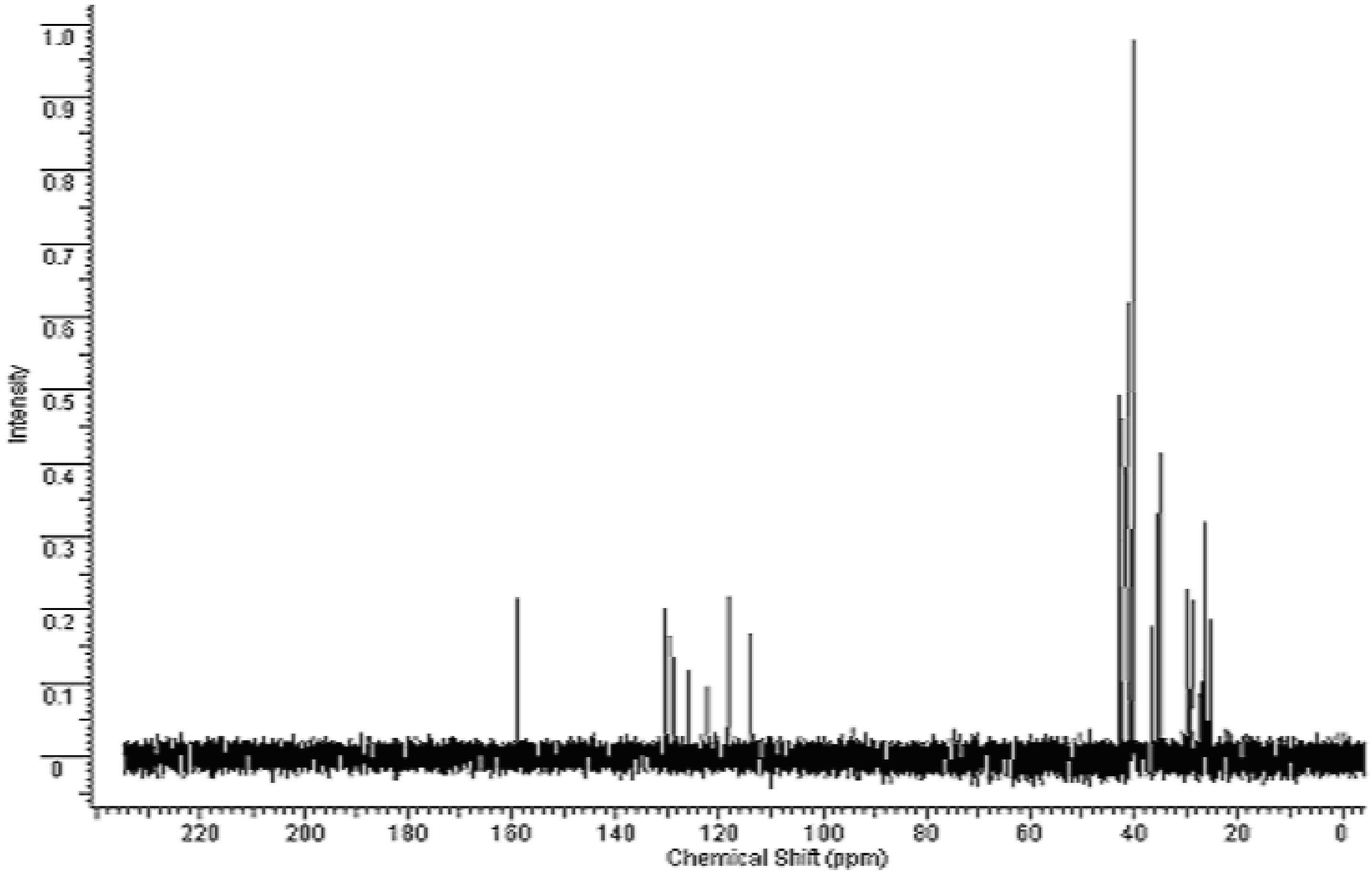


Figure 3.13 $^{13}C\{^{1}H\}$-NMR spectrum of 3-[(dicyclohexylphosphino)thio]phenyl dicyclohexylphosphinite **(1c)**

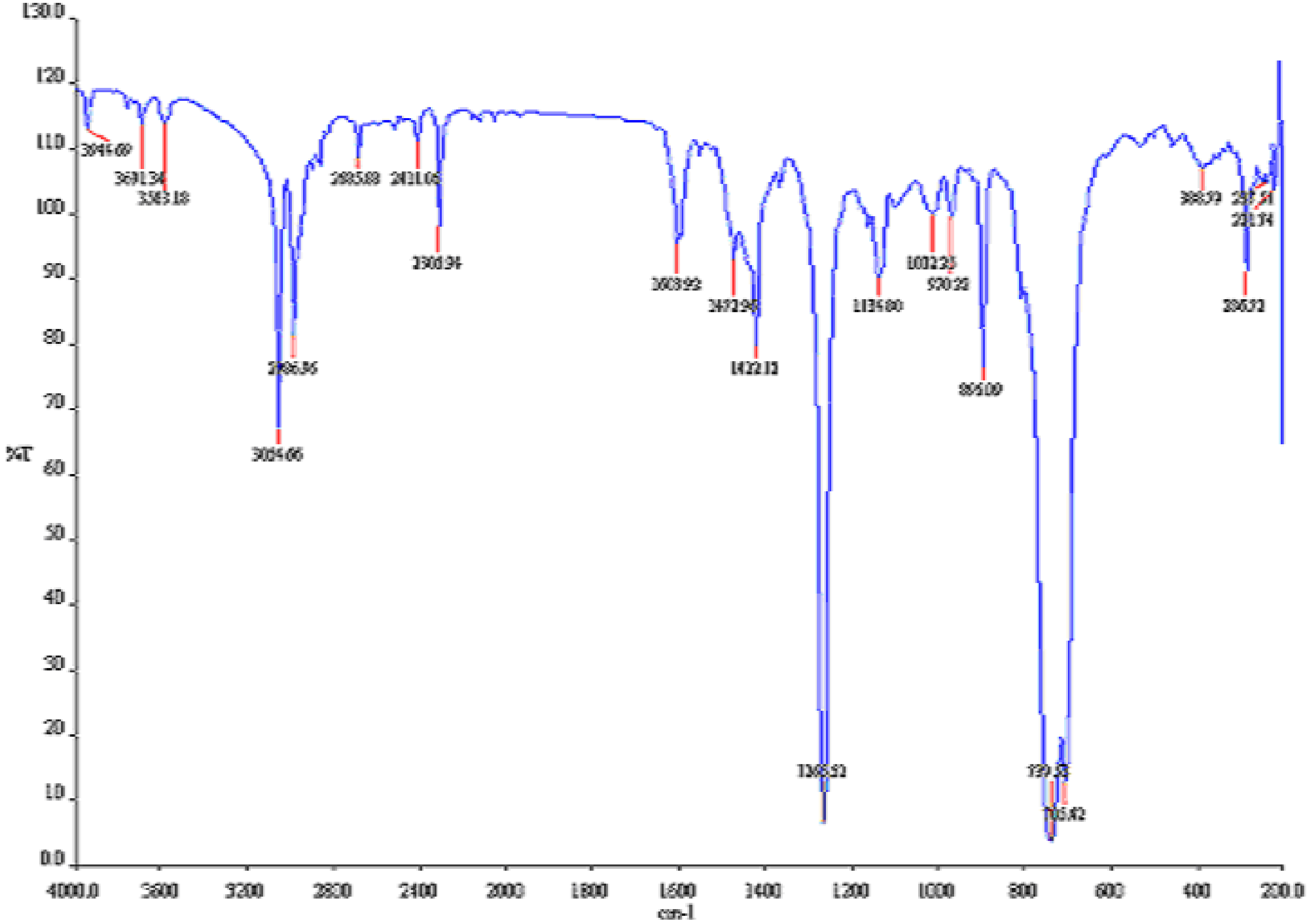


Figure 3.14 FTIR spectrum of 3-[(dicyclohexylphosphino)thio]phenyl dicyclohexylphosphinite **(1c)**

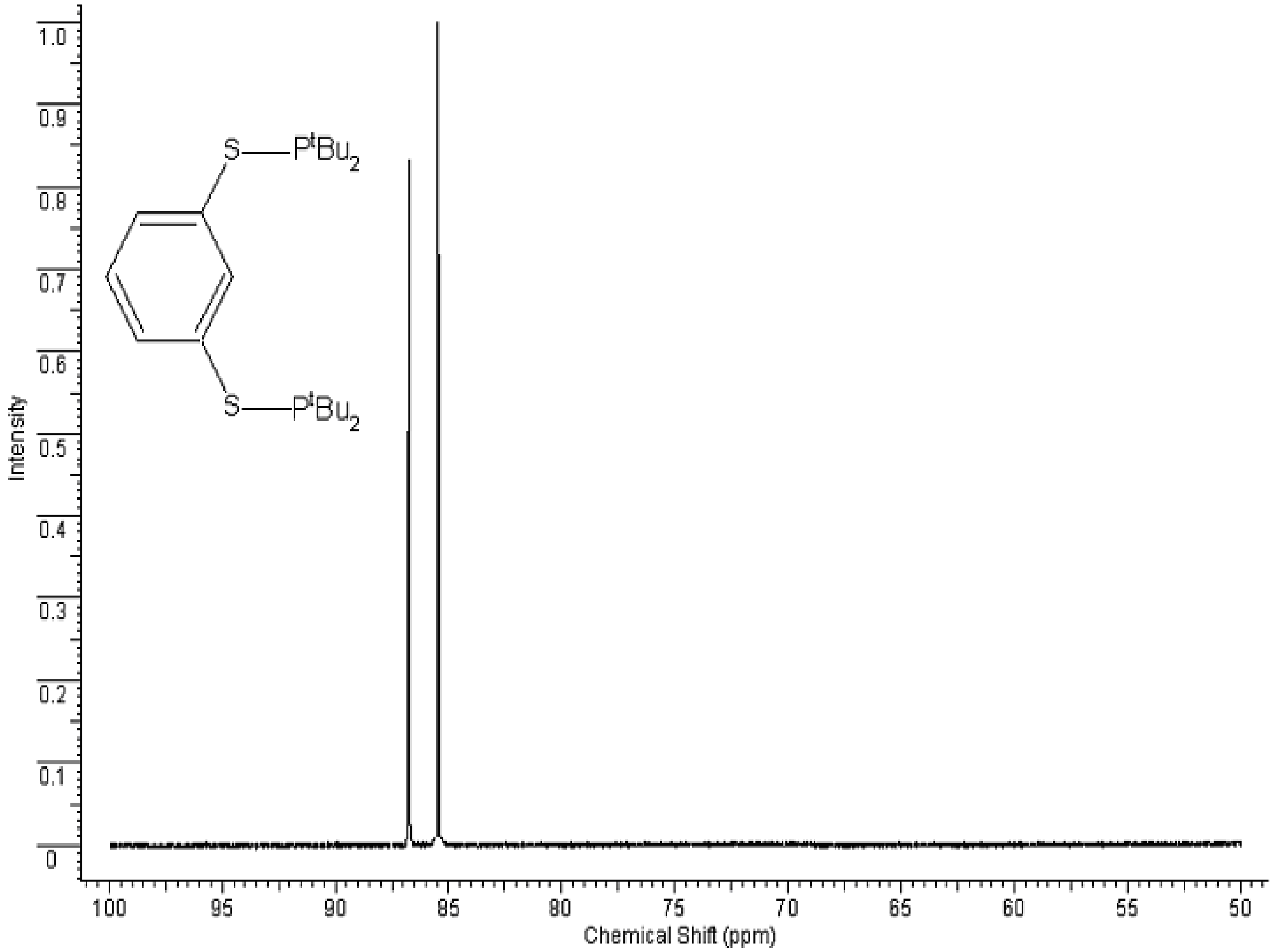


Figure 3.15 $^{31}P\{^1H\}$-NMR spectrum of 1,3-phenylene bis[di-tert-butyl(phosphinothioite)] **(2a)**

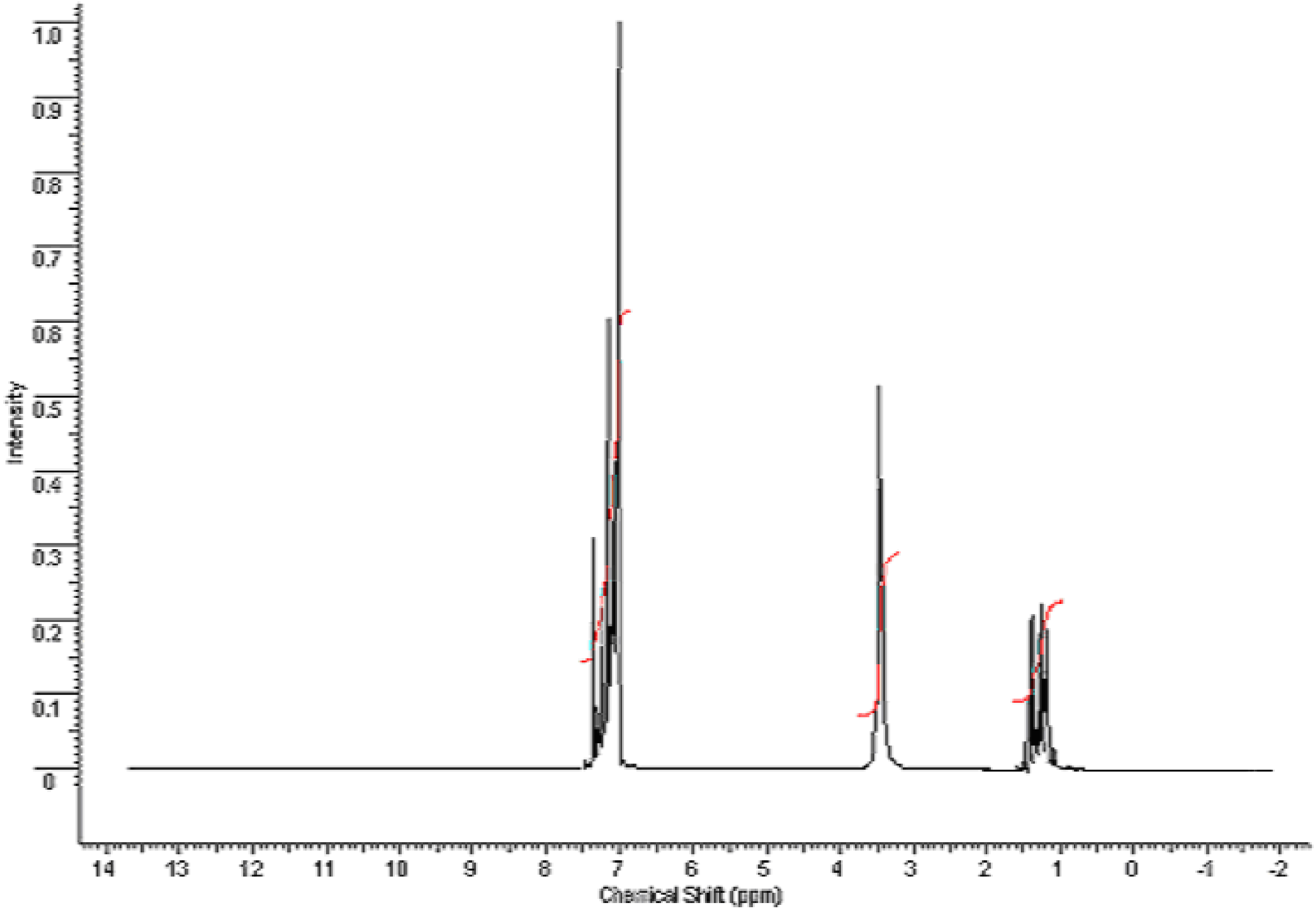


Figure 3.16 ^{1}H-NMR spectrum of 1,3-phenylene bis[di-tert-butyl(phosphinothioite)] **(2a)**

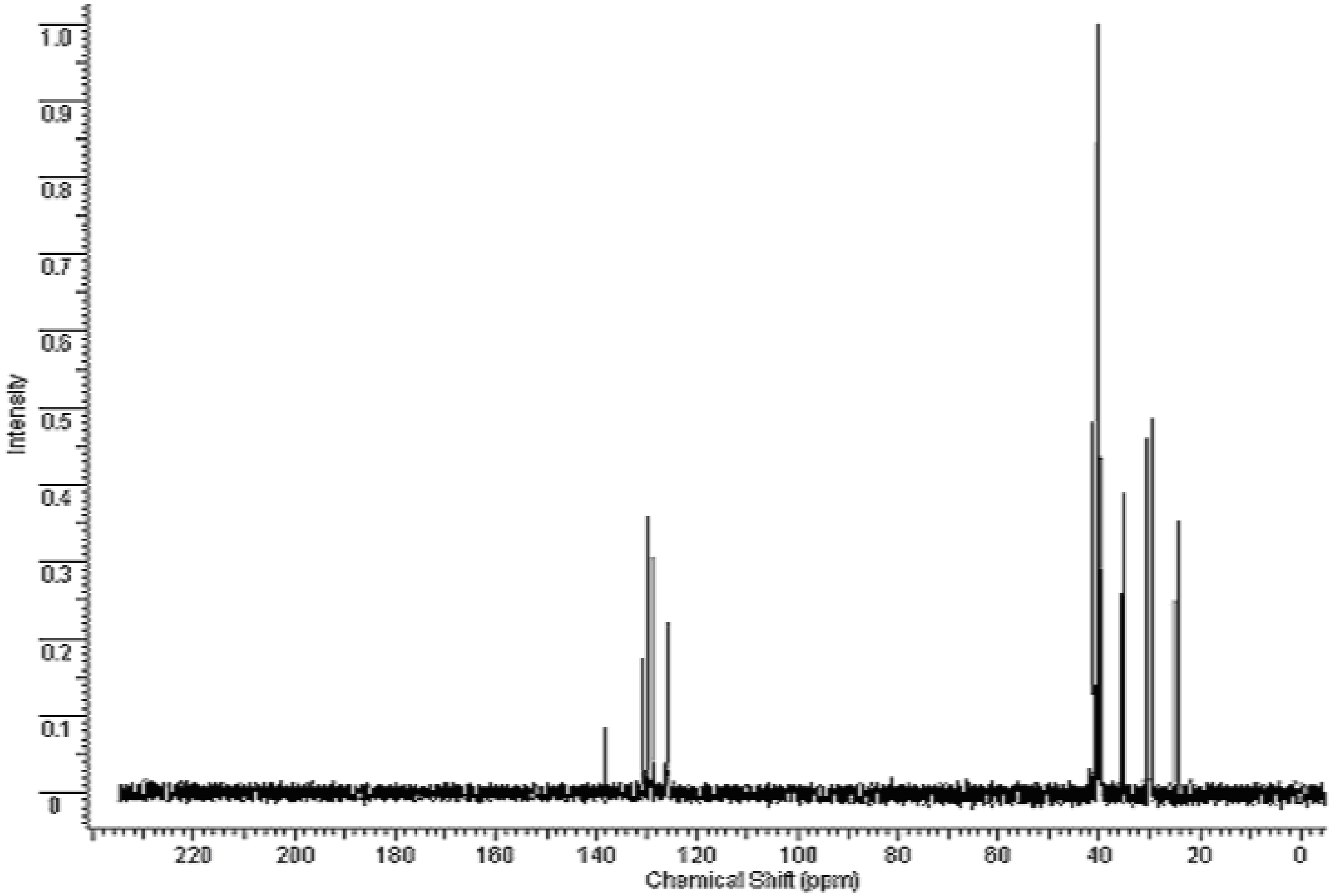


Figure 3.17 $^{13}C\{^{1}H\}$-NMR spectrum of 1,3-phenylene bis[di-tert-butyl(phosphinothioite)] **(2a)**

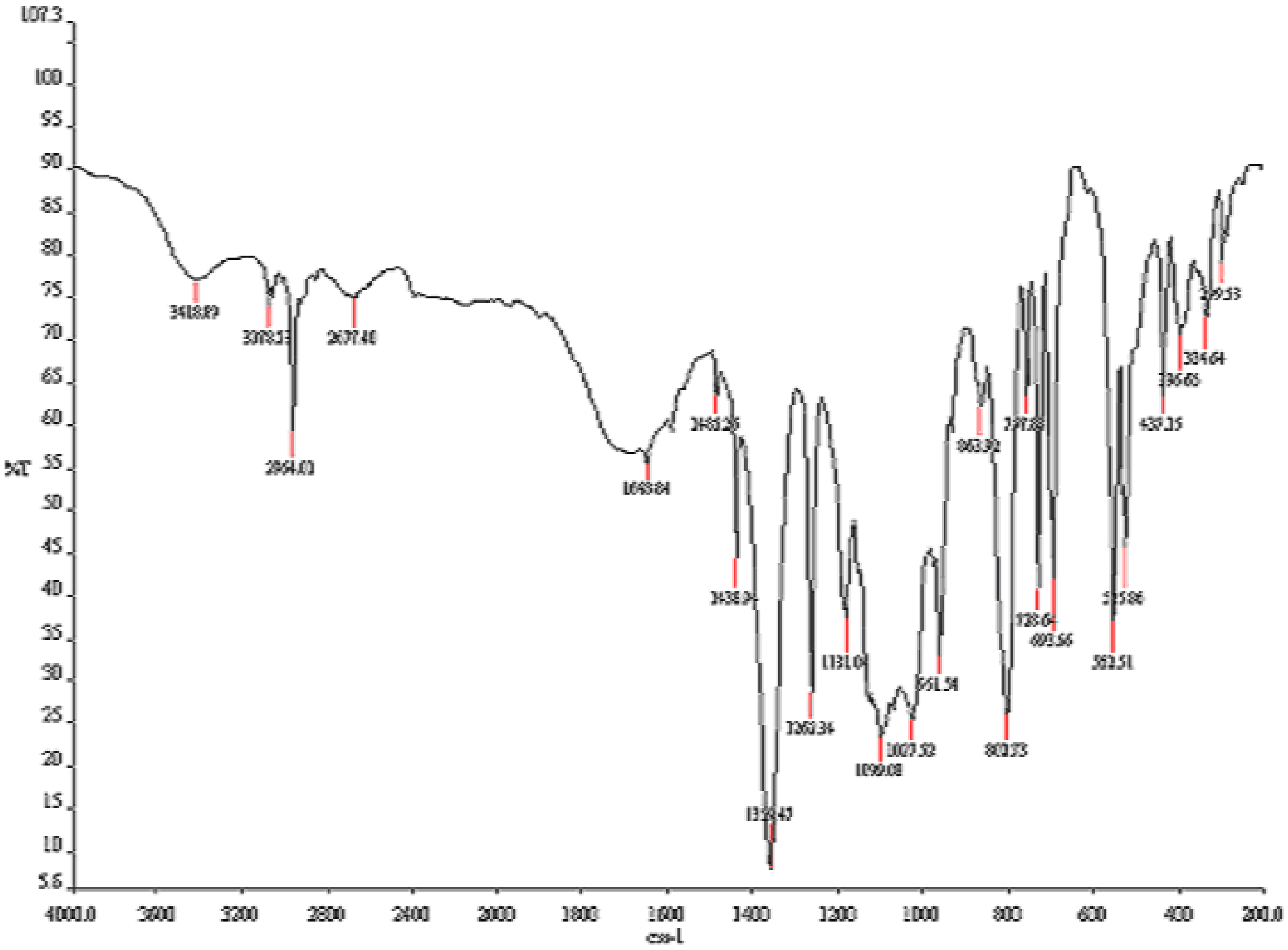


Figure 3.18 FTIR spectrum of1,3-phenylene bis[di-tert-butyl(phosphinothioite)] **(2a)**

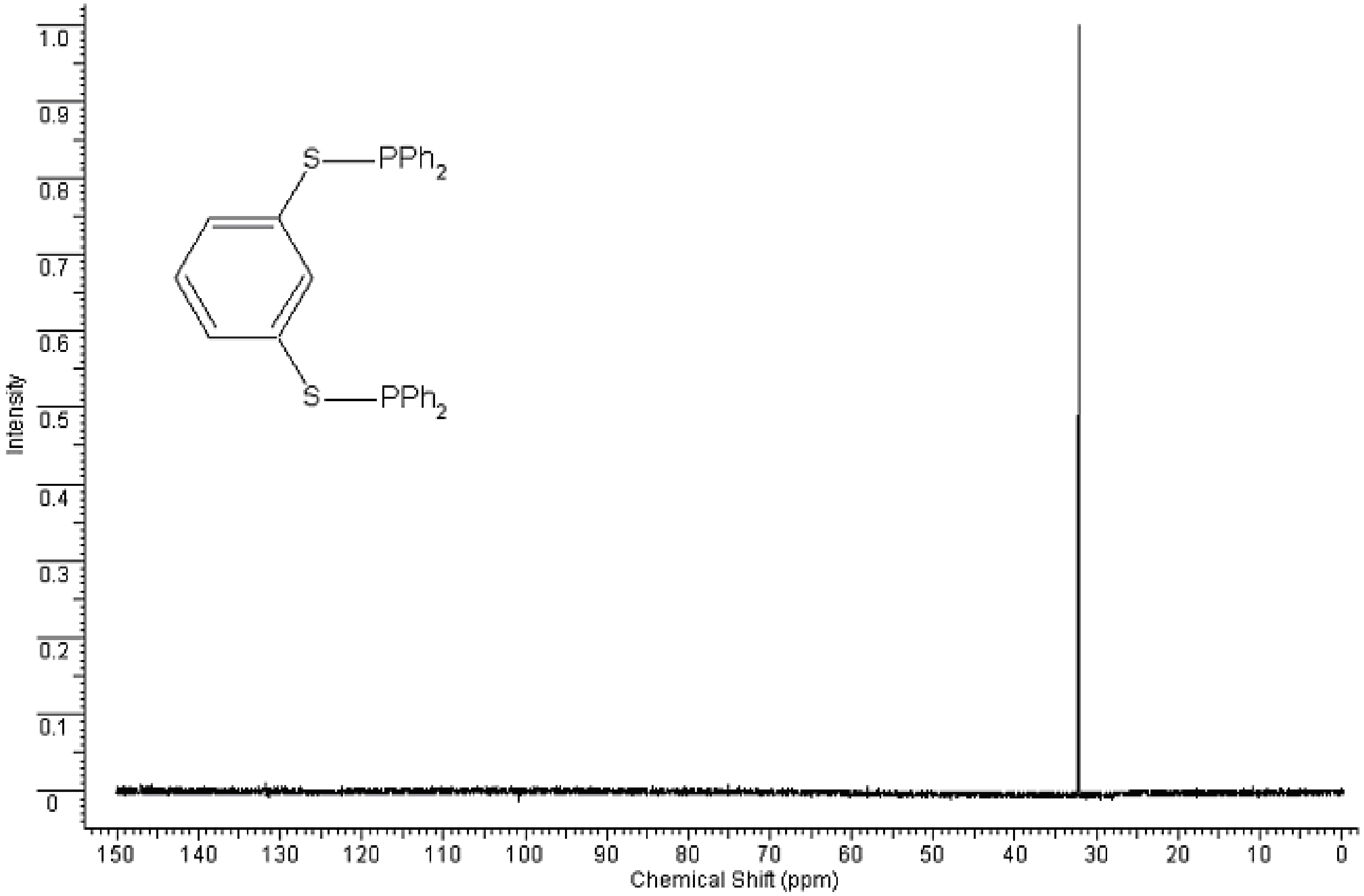


Figure 3.19 $^{31}P\{^1H\}$-NMR spectrum of 1,3-phenylene bis[diphenyl(phosphinothioite)] **(2b)**

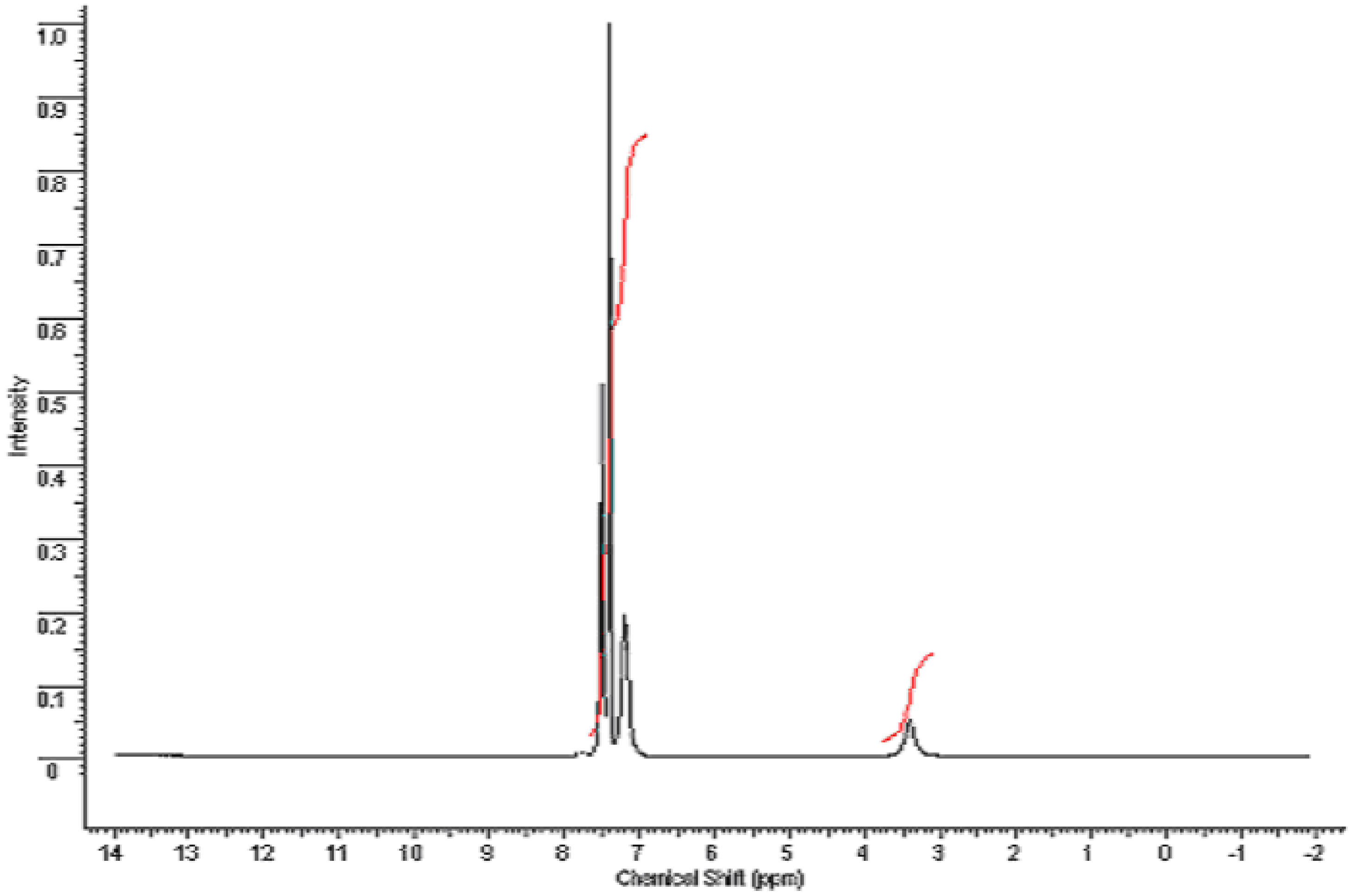


Figure 3.20 ^{1}H-NMR spectrum of 1,3-phenylene bis[diphenyl(phosphinothioite)] **(2b)**

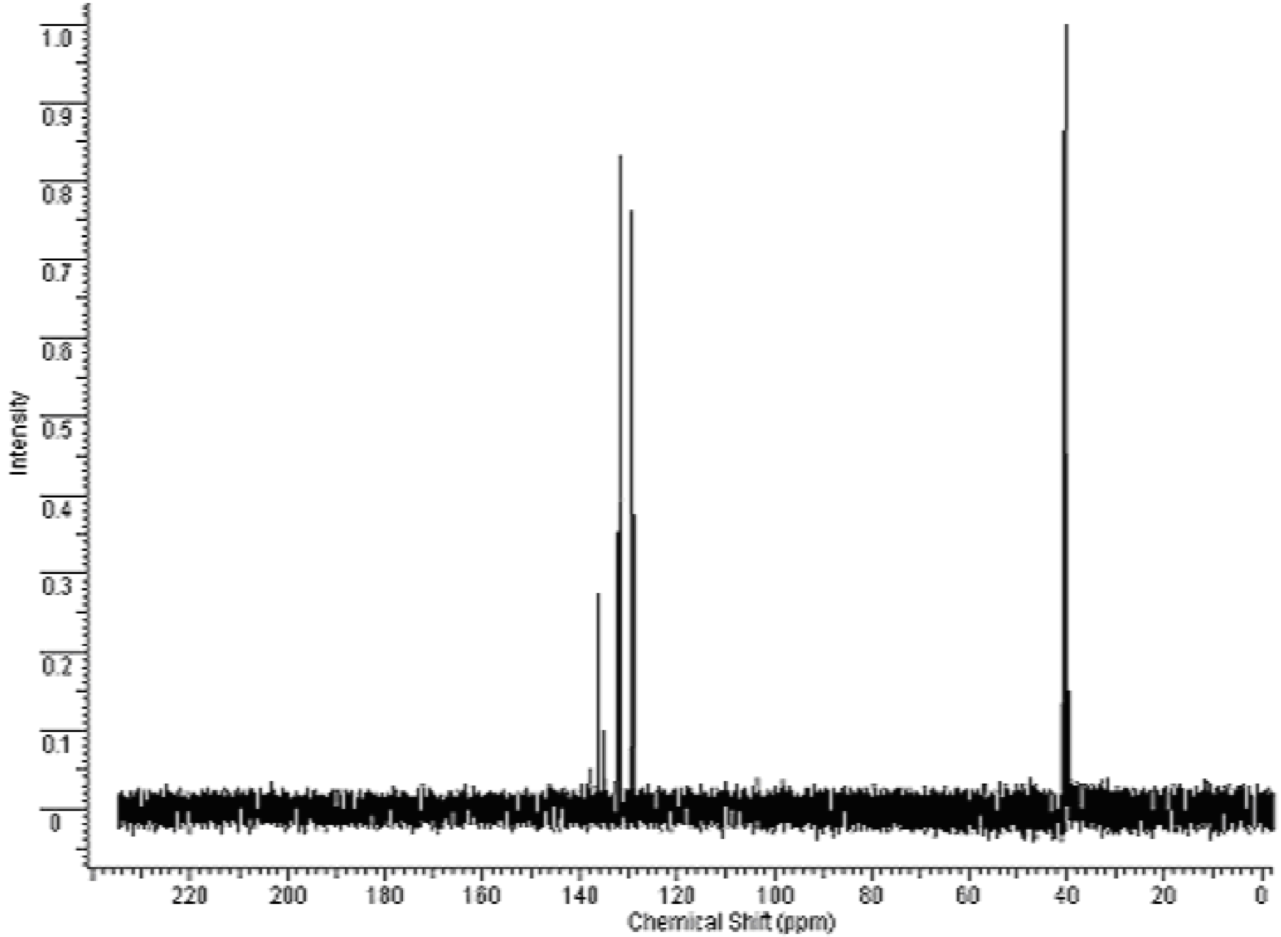


Figure 3.21 $^{13}C\{^{1}H\}$-NMR spectrum of 1,3-phenylene bis[diphenyl(phosphinothioite)] **(2b)**

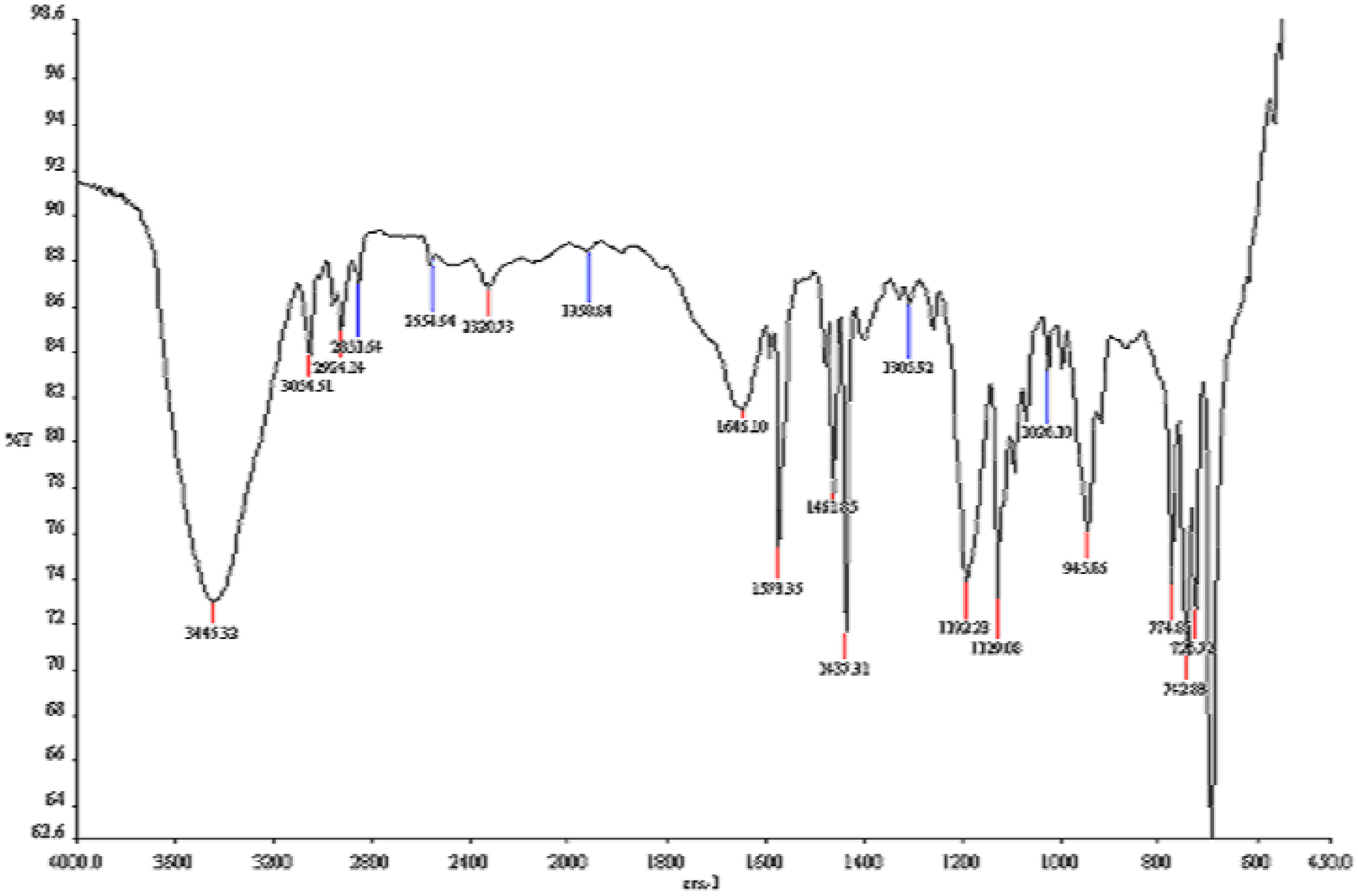


Figure 3.22 FTIR spectrum of 1,3-phenylene bis[diphenyl(phosphinothioite)] **(2b)**

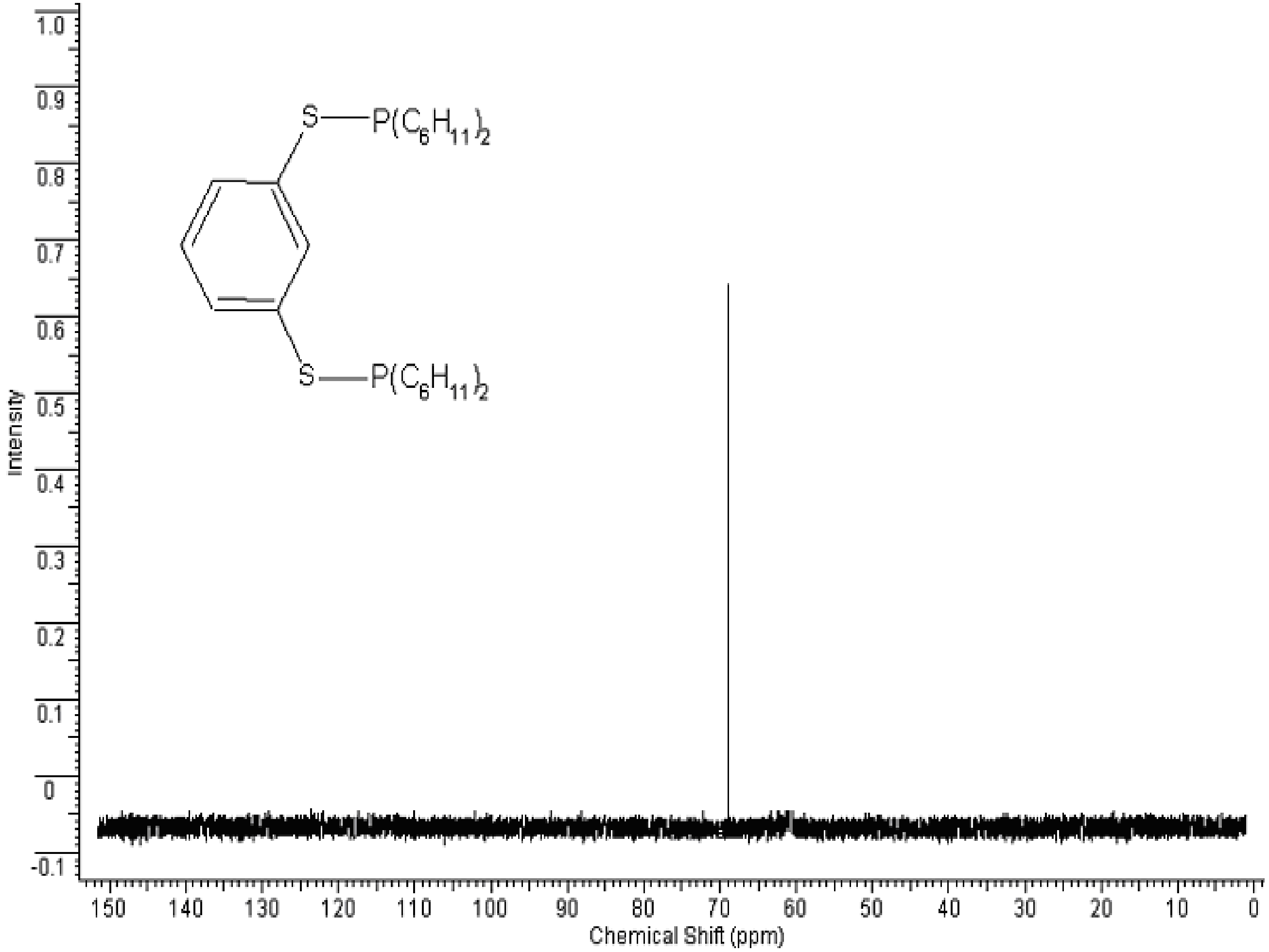


Figure 3.23 $^{31}P\{^{1}H\}$-NMR spectrum of 1,3-phenylene bis[dicyclohexyl(phophinothioite)] **(2c)**

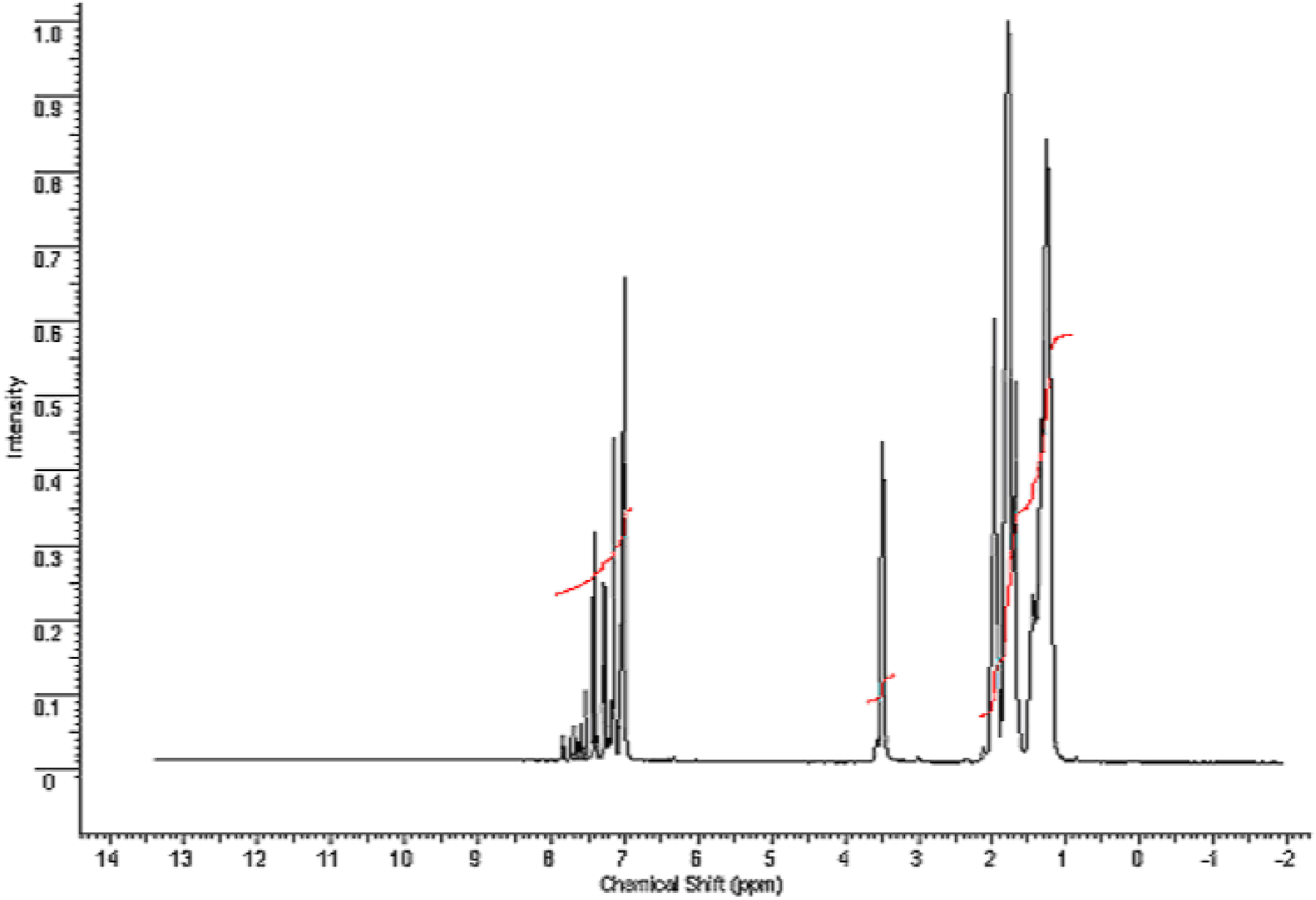


Figure 3.24 ^{1}H-NMR spectrum of 1,3-phenylene bis[dicyclohexyl(phophinothioite)] **(2c)**

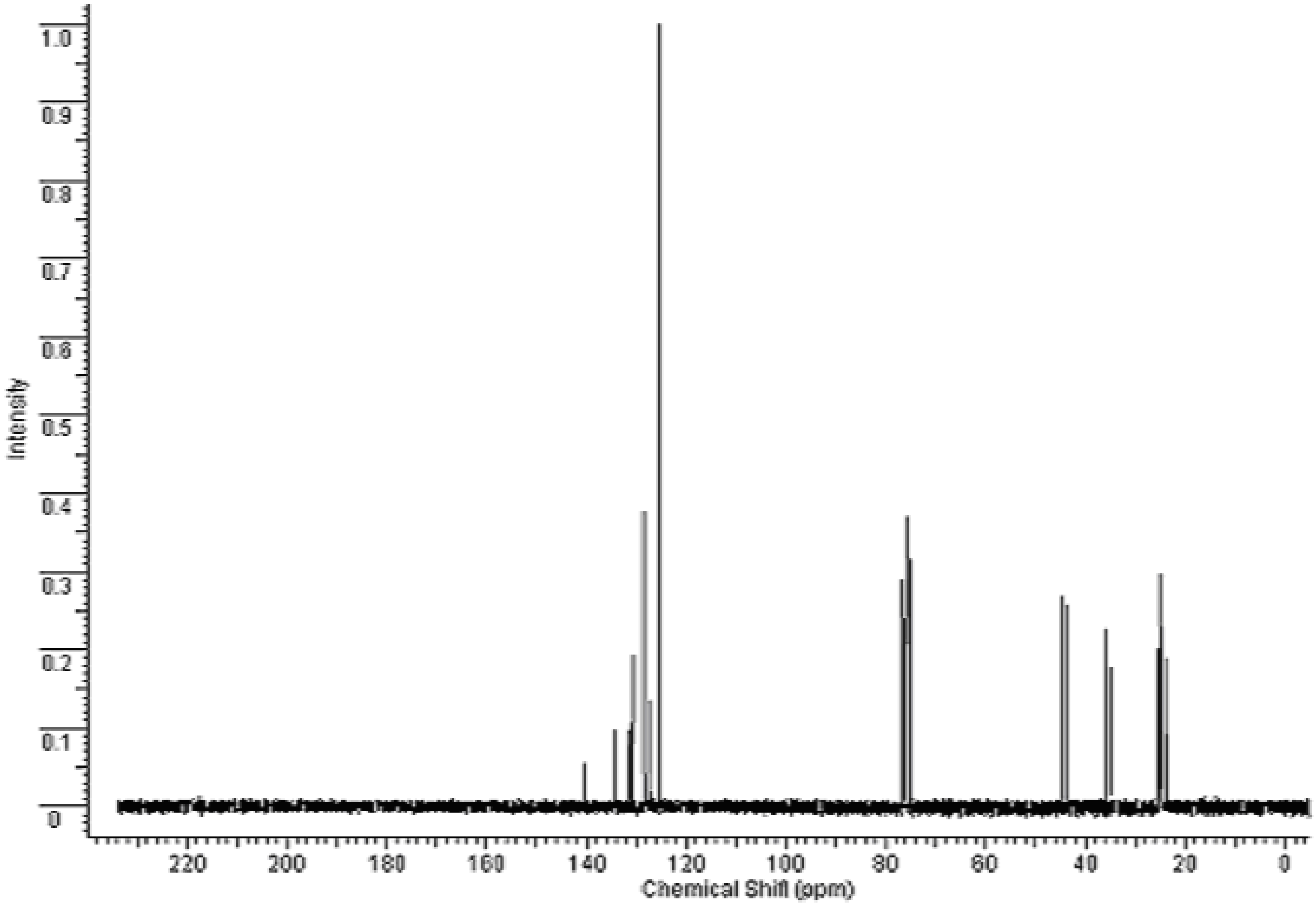


Figure 3.25 $^{13}C\{^1H\}$-NMR spectrum of 1,3-phenylene bis[dicyclohexyl(phophinothioite)] **(2c)**

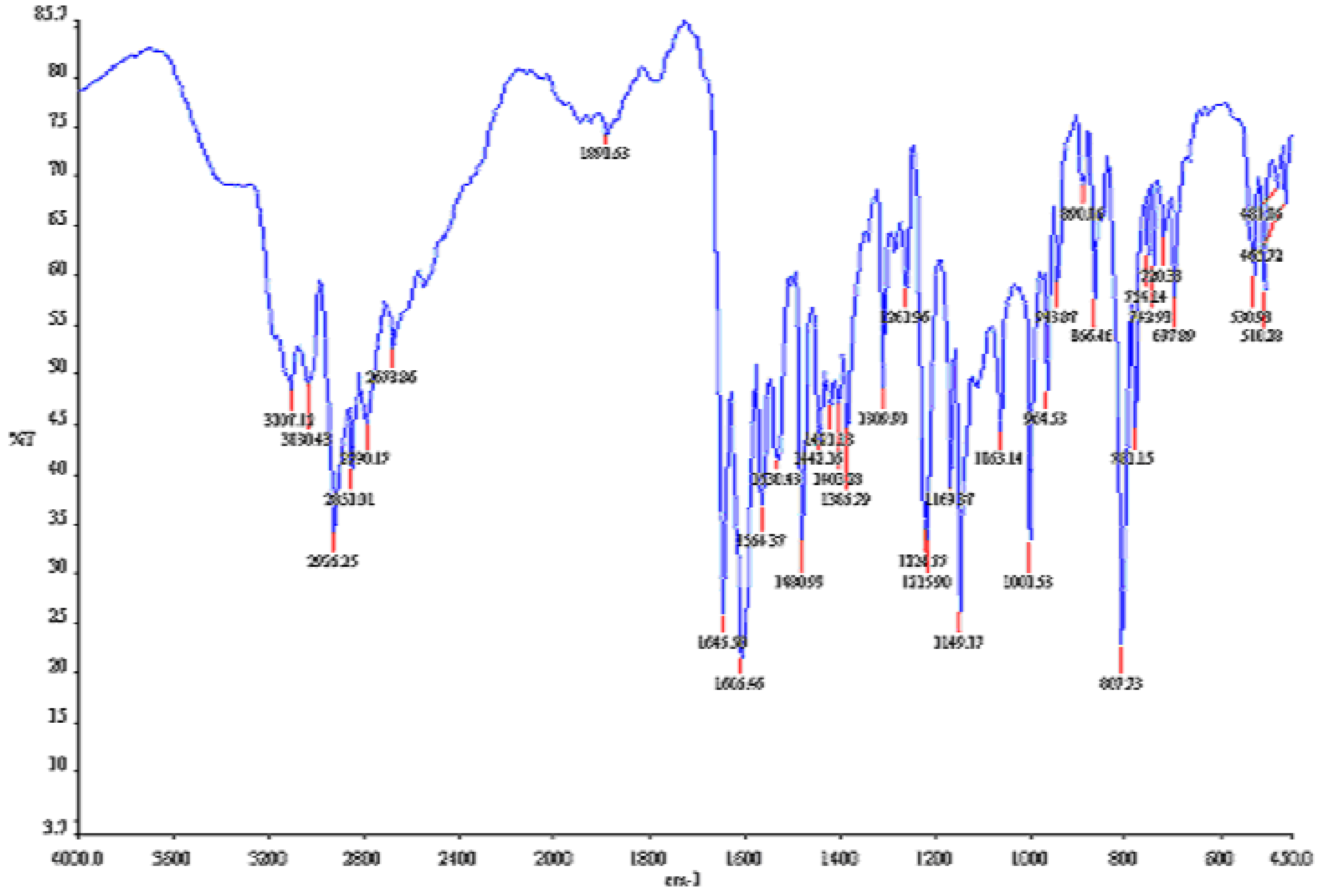


Figure 3.26 FTIR spectrum of 1,3-phenylene bis[dicyclohexyl(phophinothioite)] **(2c)**

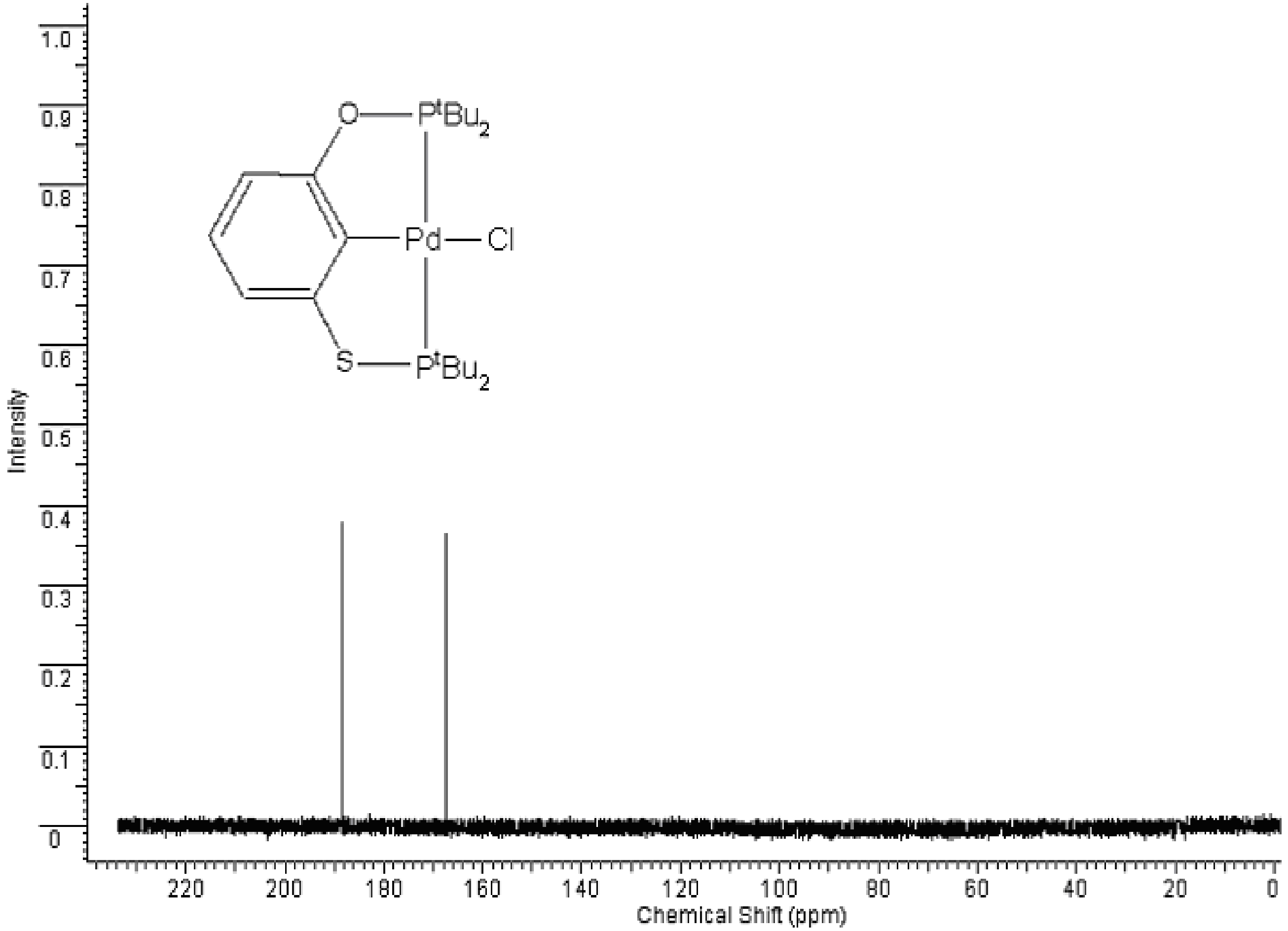


Figure 3.27 $^{31}P\{^1H\}$-NMR spectrum of 3[(di-tert-butylphosphino)thio]phenyl di-tert-butylphosphinite Pd(II) Complex **(1a')**

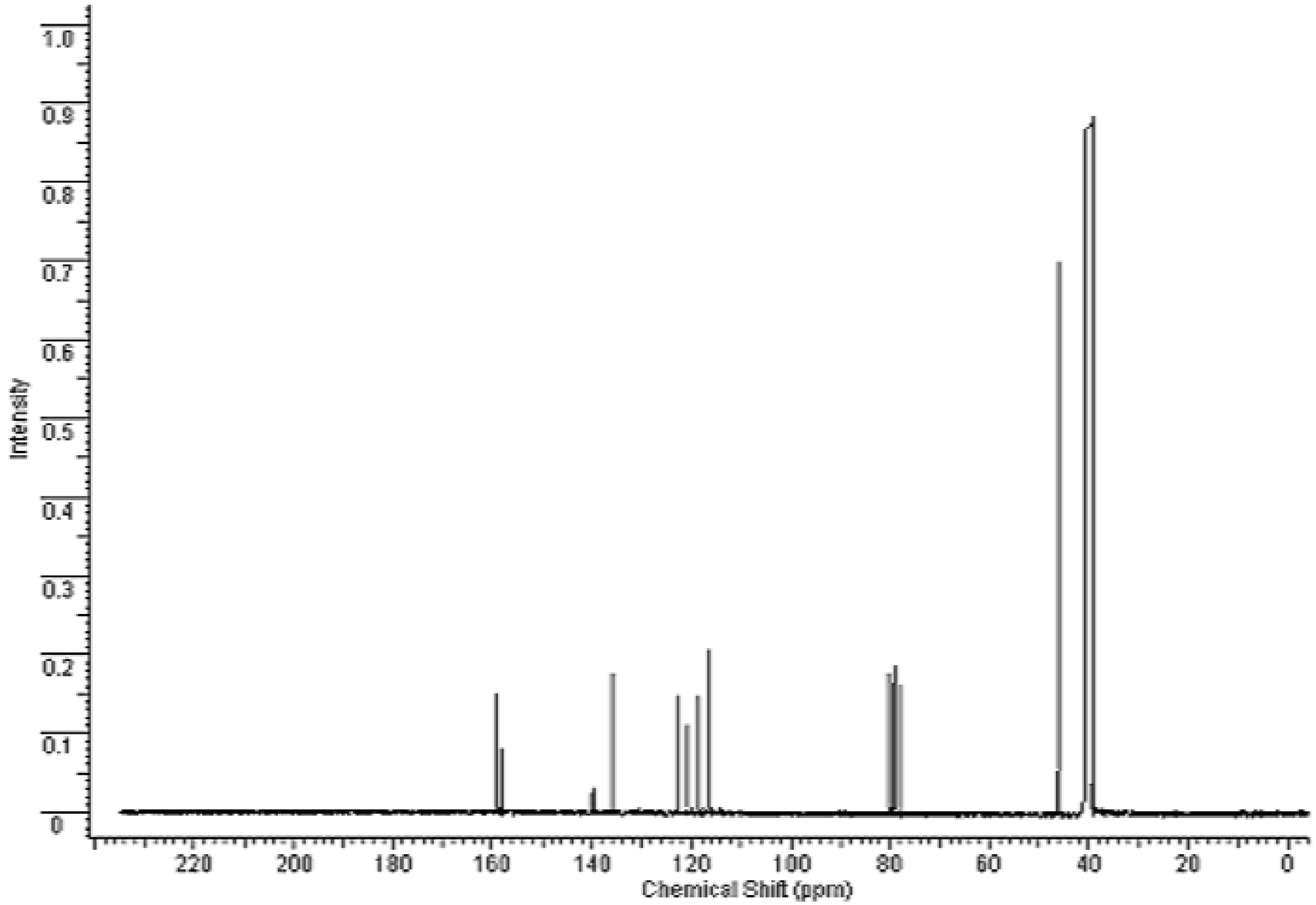


Figure 3.28 $^{13}C\{^{1}H\}$-NMR spectrum of 3[(di-tert-butylphosphino)thio]phenyl di-tert-butylphosphinite Pd(II) Complex **(1a')**

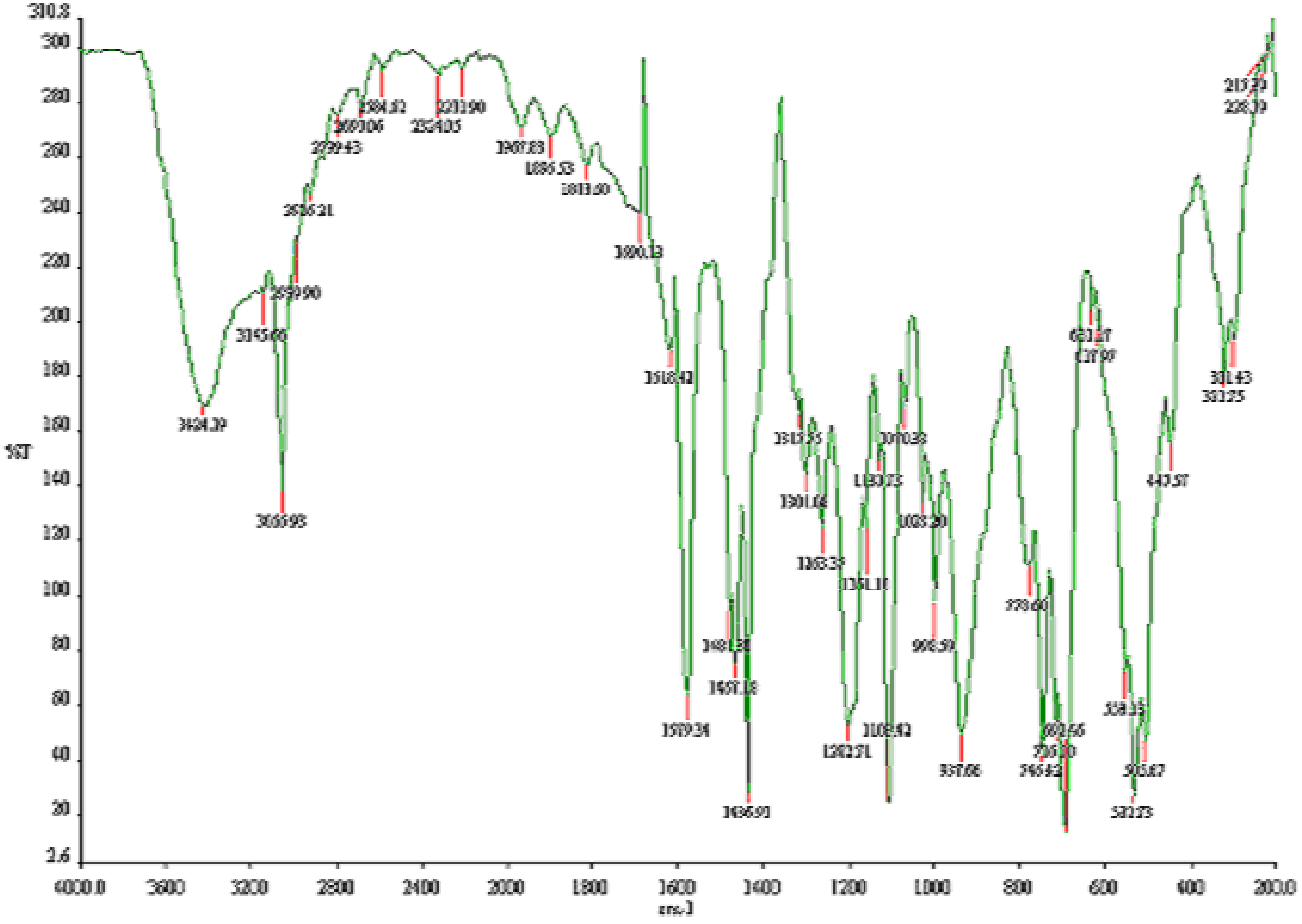


Figure 3.29 FTIR spectrum of 3[(di-tert-butylphosphino)thio]phenyl di-tert-butylphosphinite Pd(II) Complex **(1a’)**

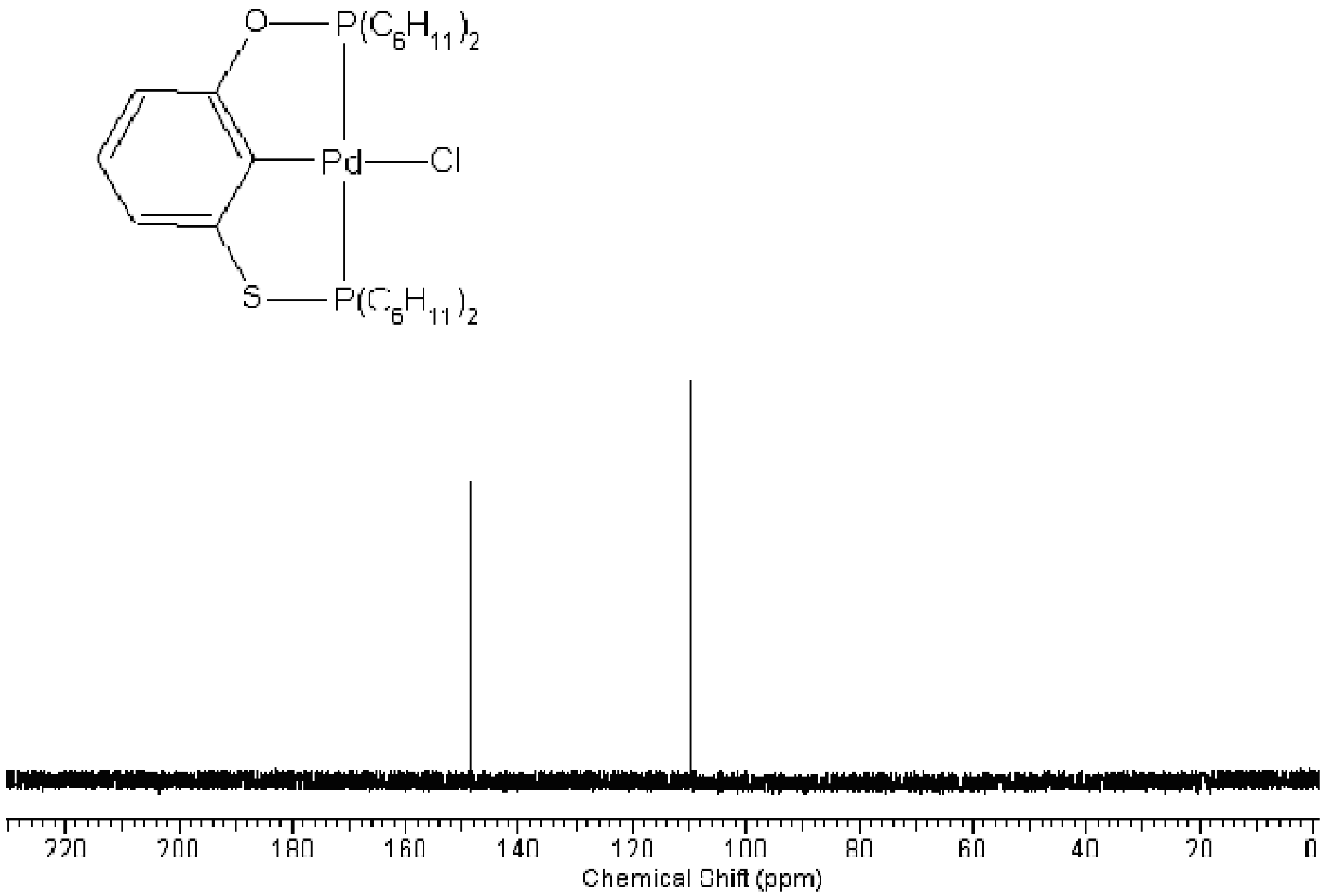


Figure 3.30 $^{31}P\{^{1}H\}$-NMR spectrum of 3-[(dicyclohexylphosphino)thio phenyl dicyclohexylphosphinite Pd(II) Complex (**1c'**)

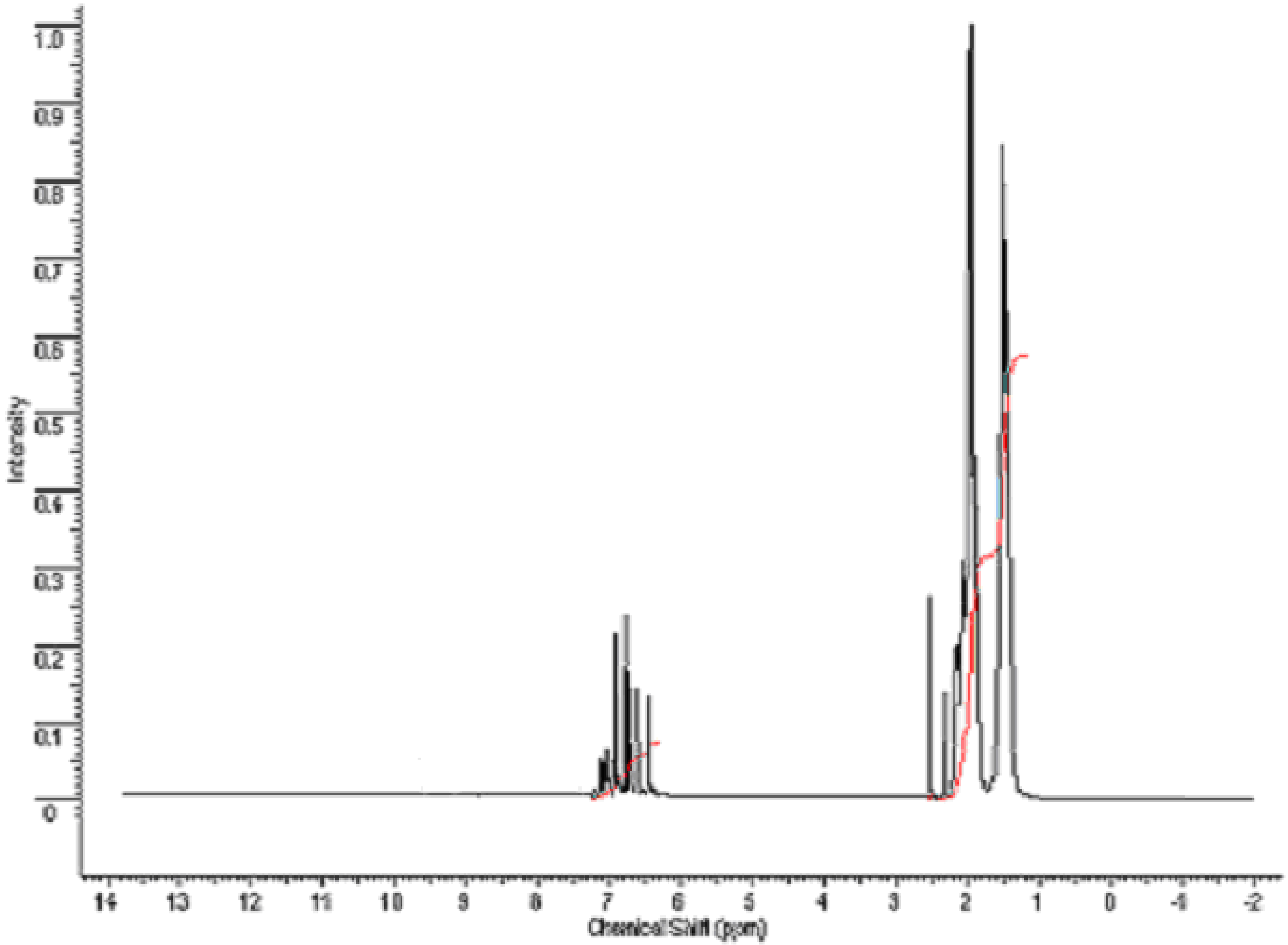


Figure 3.31 ^{1}H-NMR spectrum of 3-[(dicyclohexylphosphino)thio] phenyl dicyclohexylphosphinite Pd(II) Complex **(1c')**

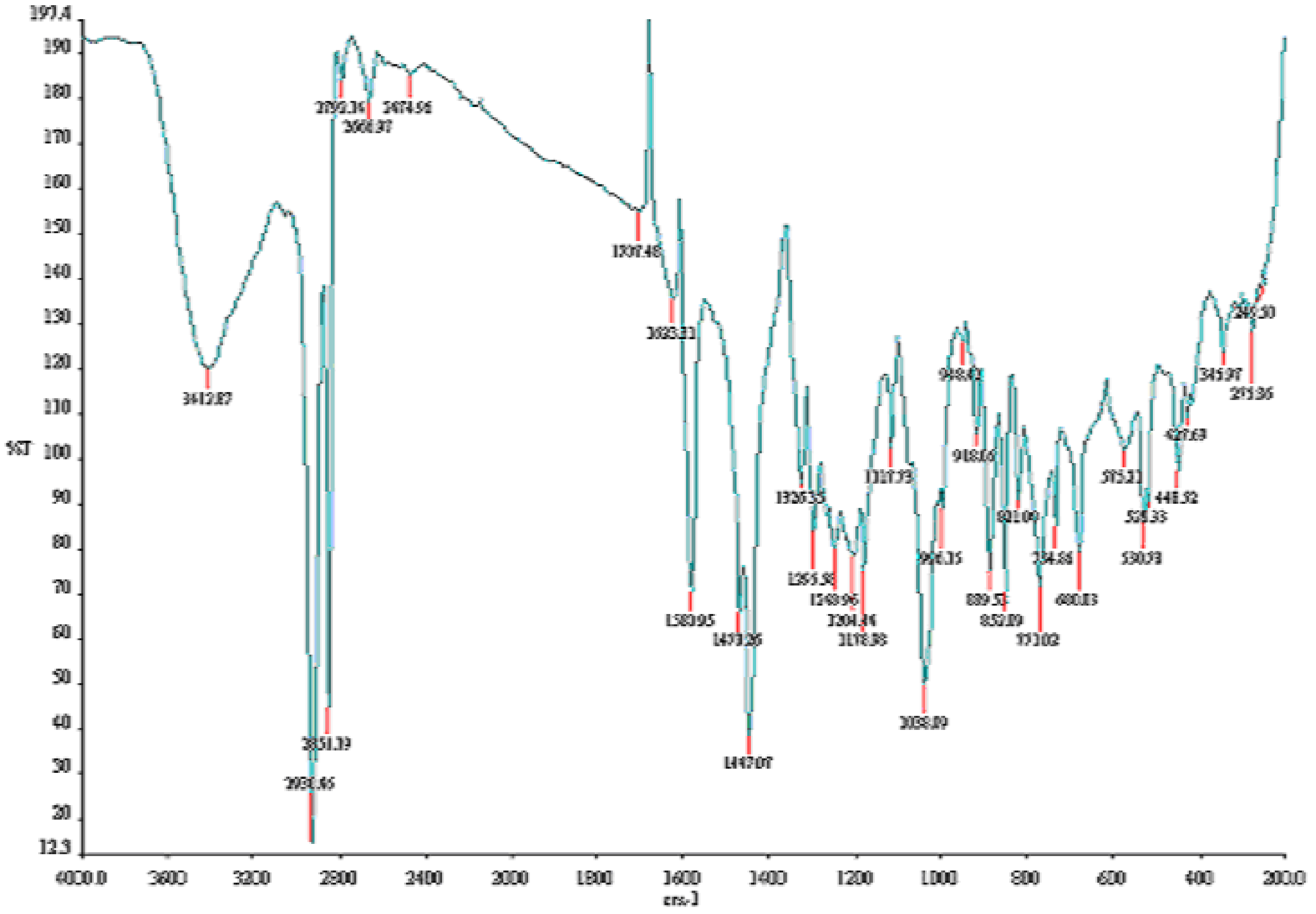


Figure 3.32 FTIR spectrum of 3-[(dicyclohexylphosphino)thio] phenyl dicyclohexylphosphinite Pd(II) Complex **(1c')**

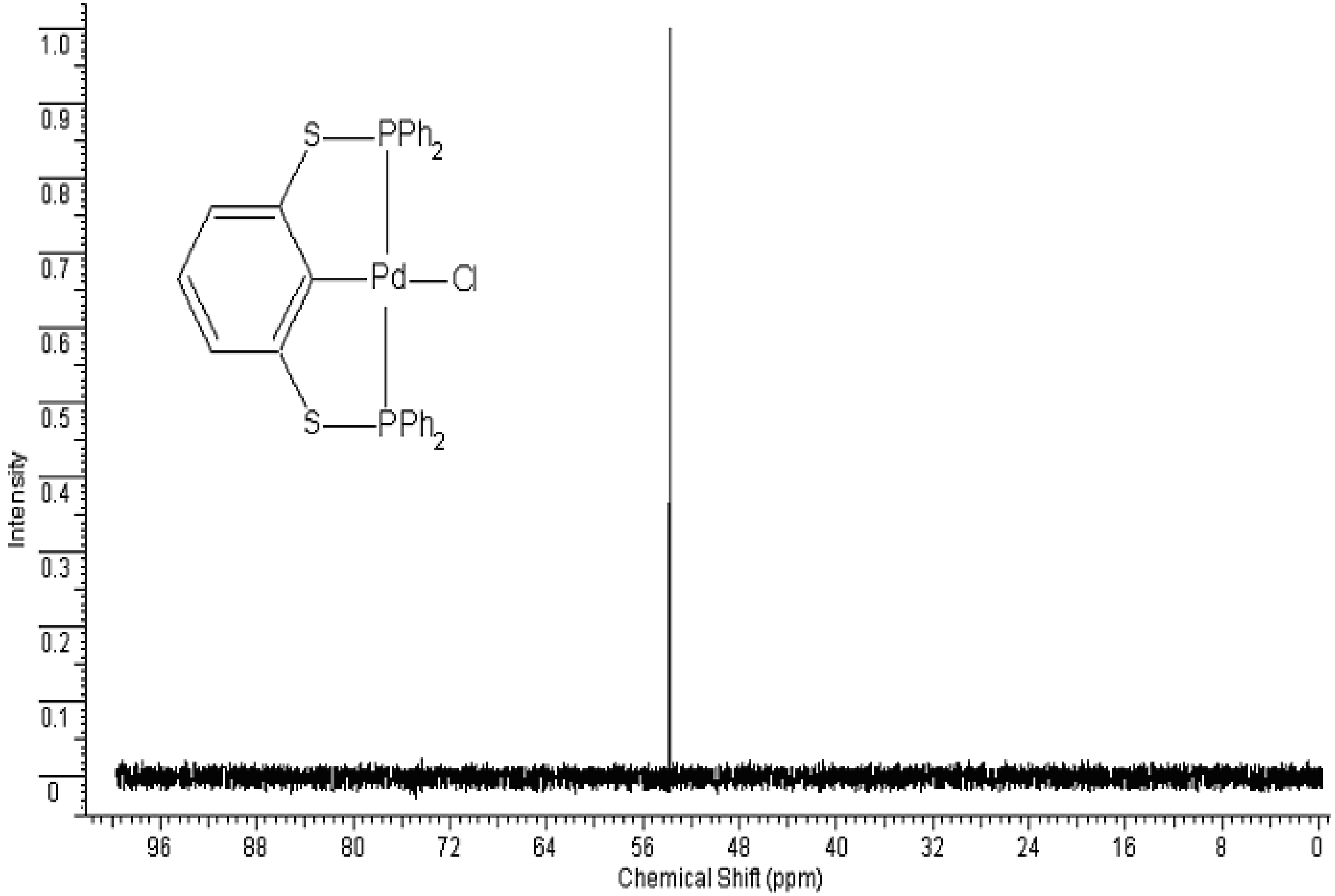


Figure 3.33 $^{31}P\{^{1}H\}$-NMR spectrum of 1,3-phenylene bis[diphenyl(phosphinothioite)] Pd(II) Complex **(2b')**

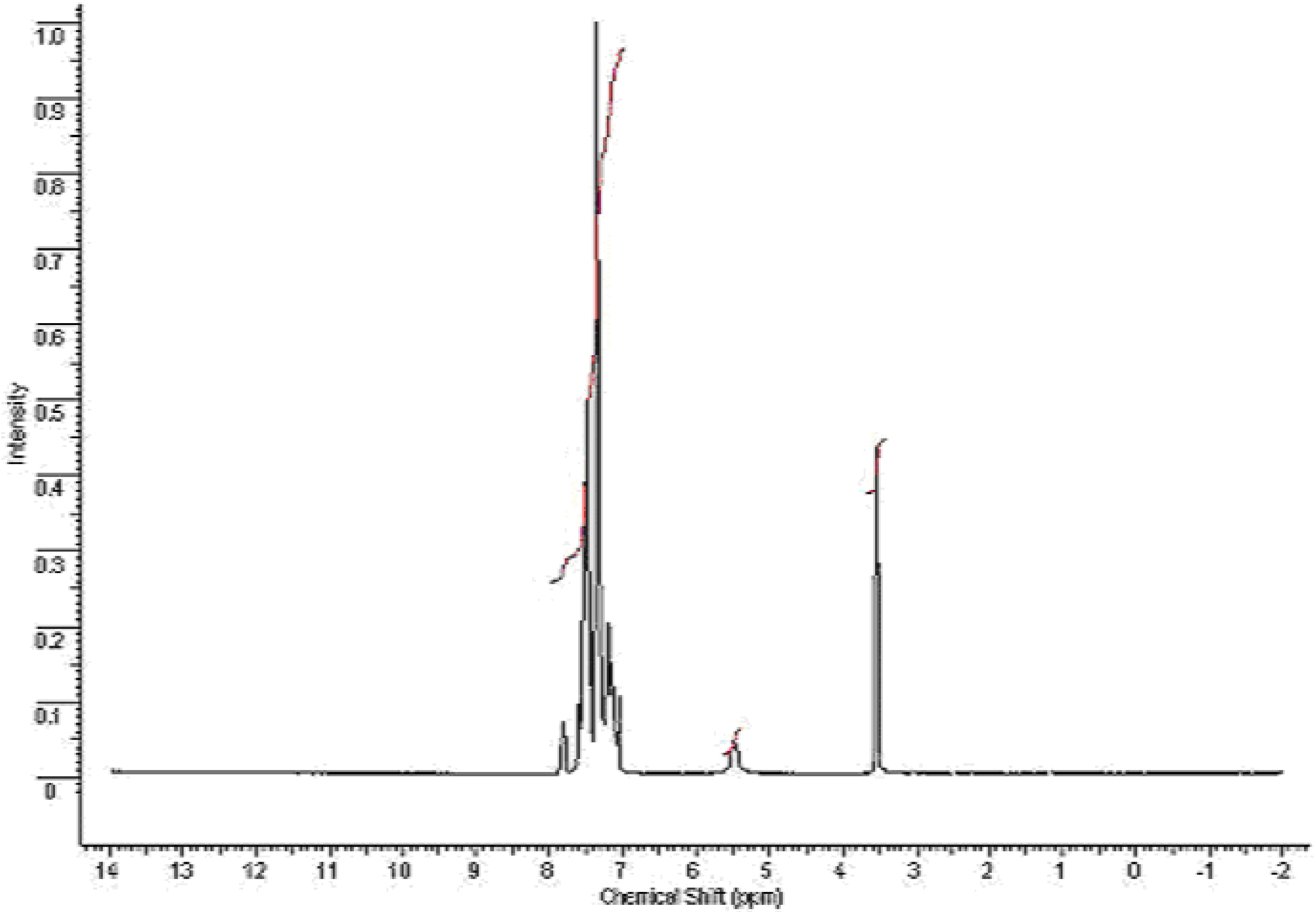


Figure 3.34 ^{1}H-NMR spectrum of 1,3-phenylene bis[diphenyl(phosphinothioite)] Pd(II) Complex **(2b')**

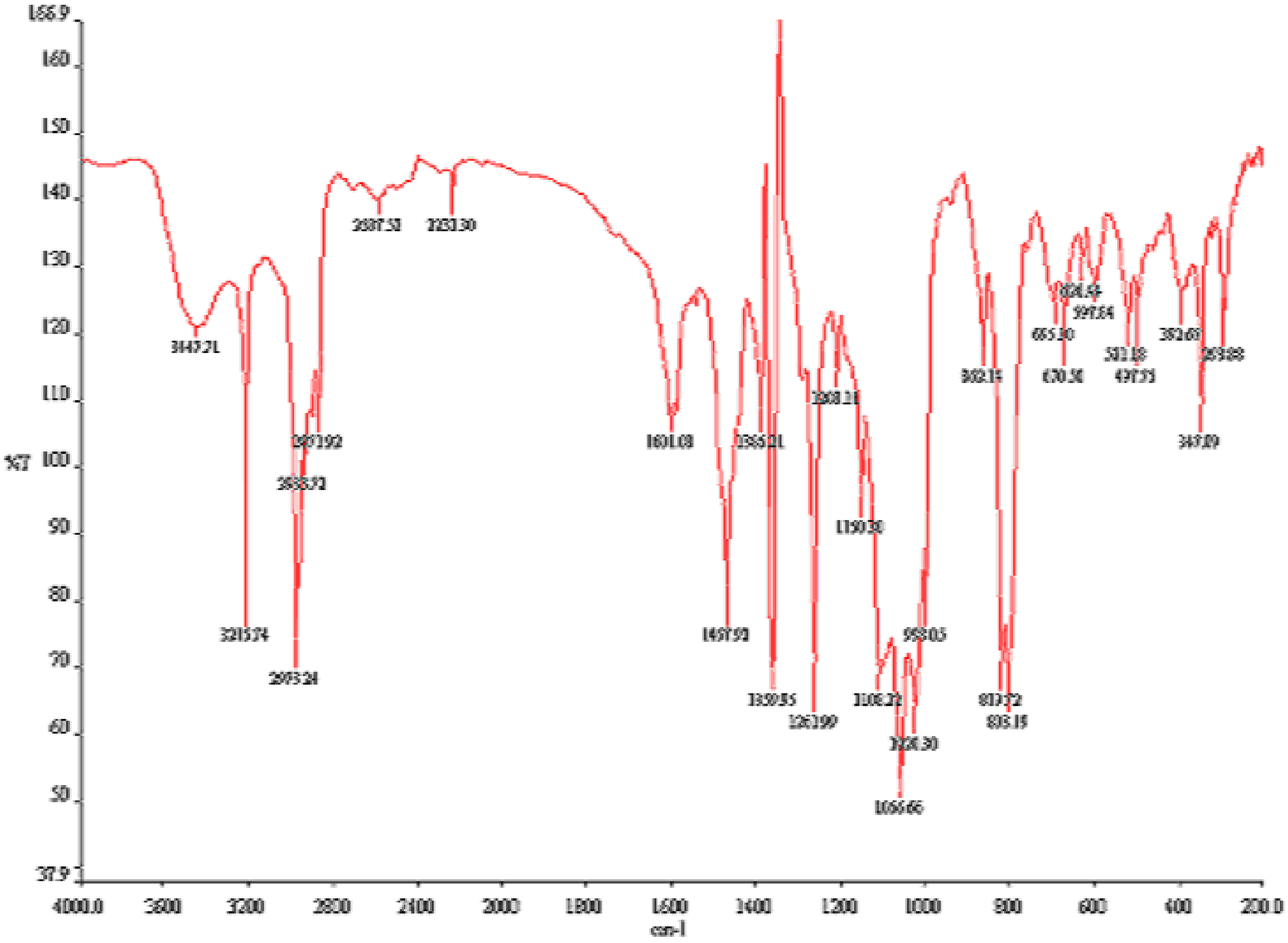


Figure 3.35 FTIR spectrum of 1,3-phenylene bis[diphenyl(phosphinothioite)] Pd(II) Complex **(2b')**

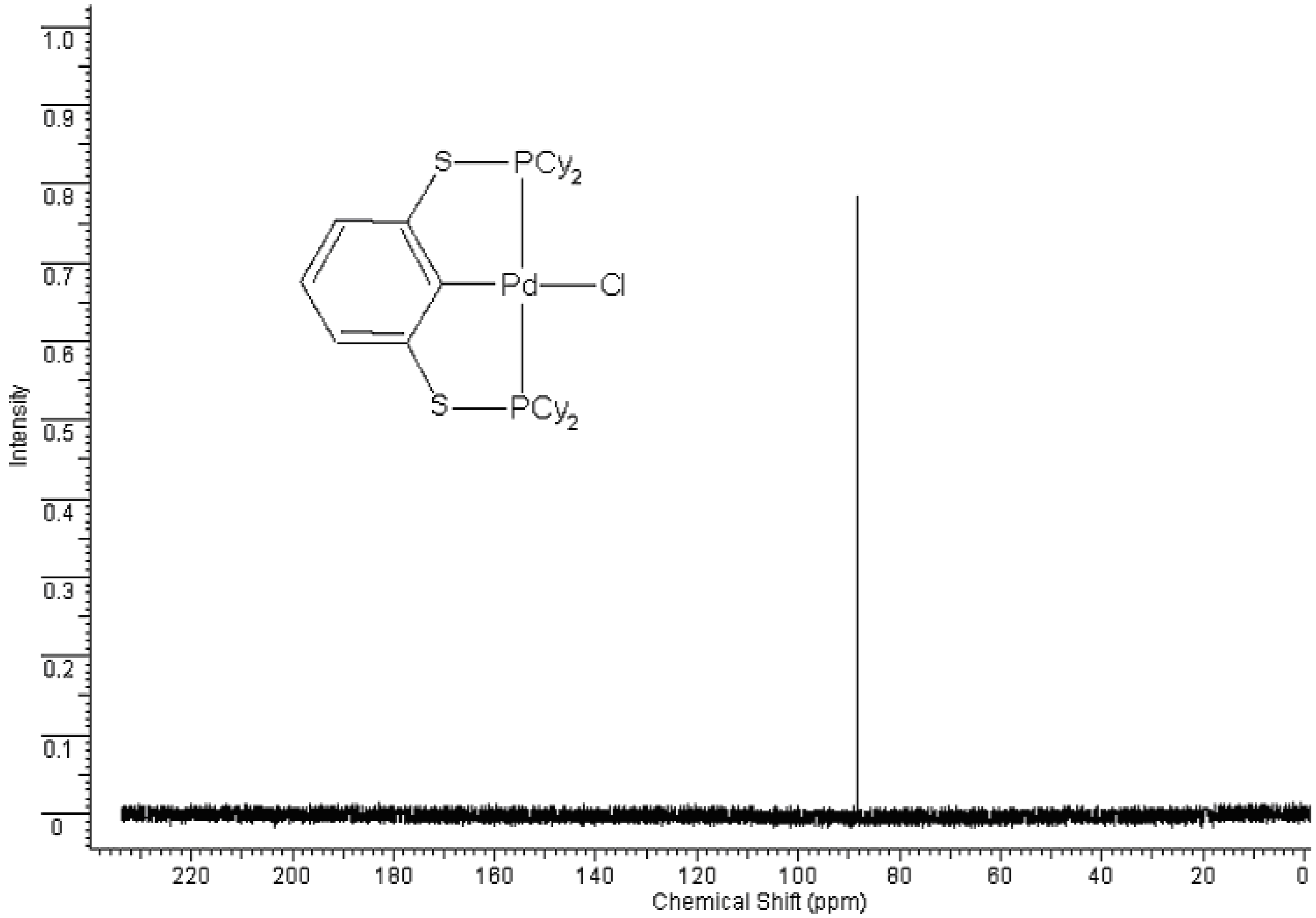


Figure 3.36 $^{31}P\{^1H\}$-NMR spectrum of 1,3-phenylene bis[dicyclohexyl(phophinothioite)] Pd(II) Complex **(2c')**

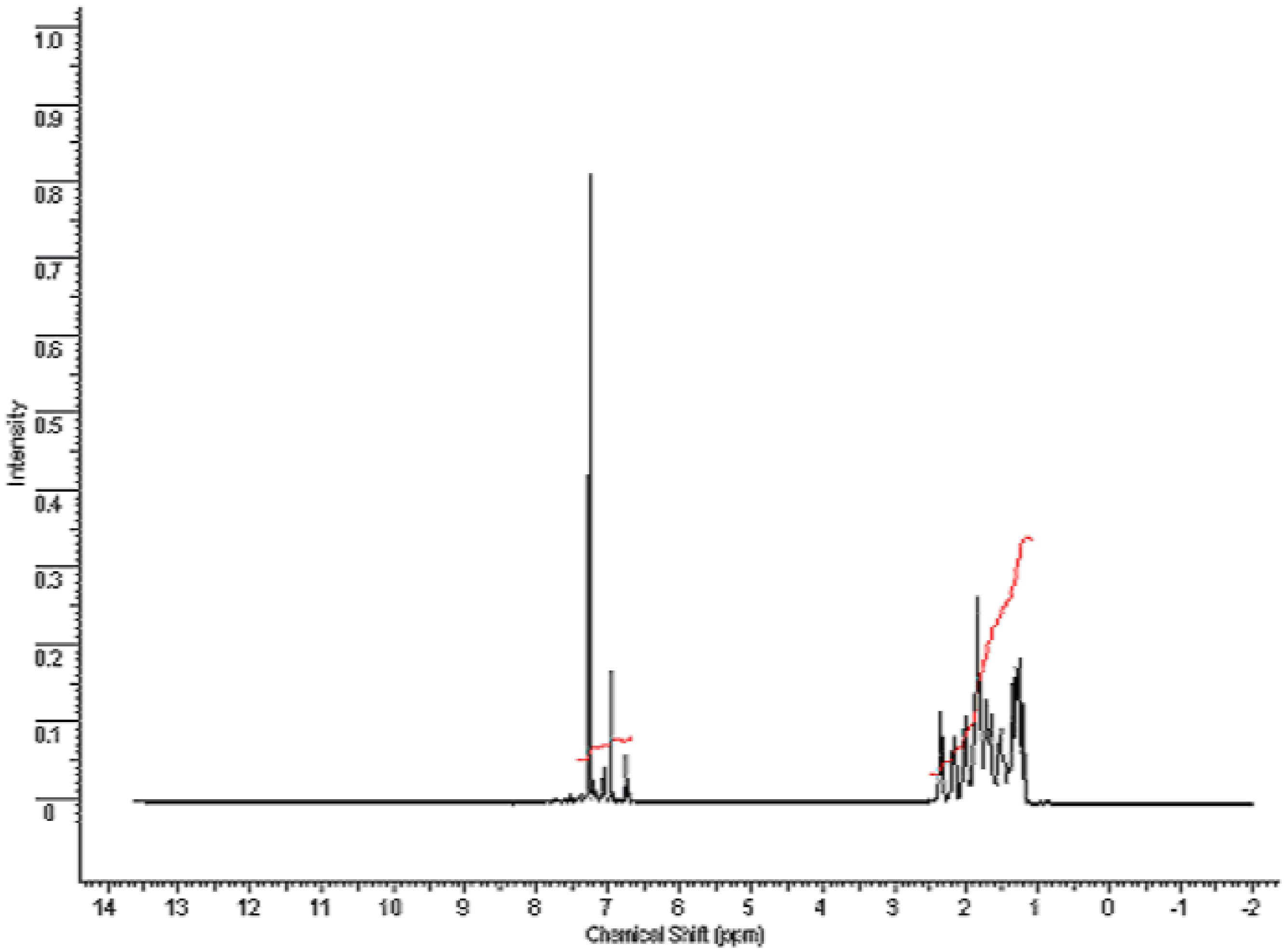


Figure 3.37 ^{1}H-NMR spectrum of 1,3-phenylene bis[dicyclohexyl(phophinothioite)] Pd(II) Complex **(2c')**

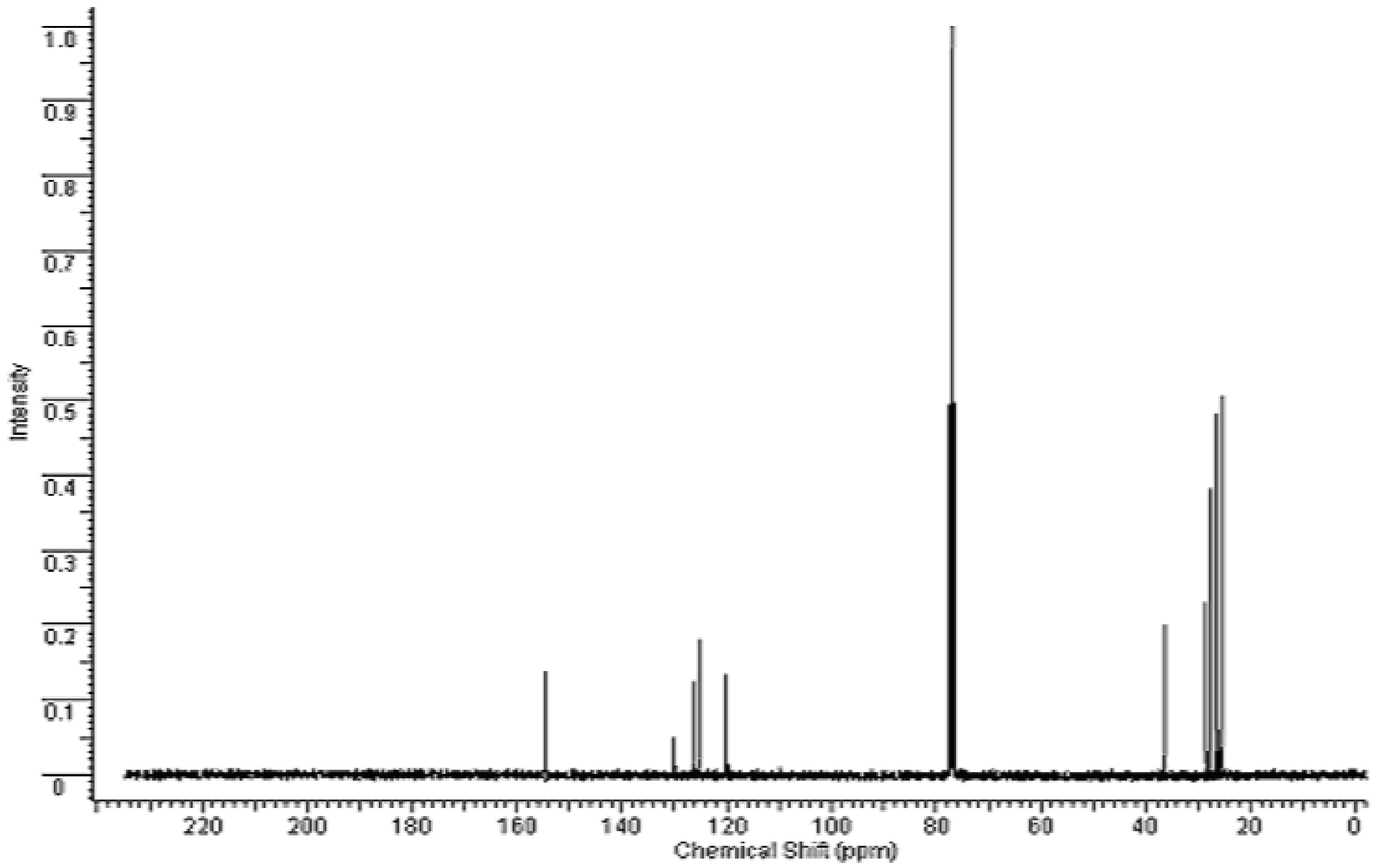


Figure 3.38 $^{13}C\{^1H\}$-NMR spectrum of 1,3-phenylene bis[dicyclohexyl(phophinothioite)] Pd(II) Complex **(2c')**

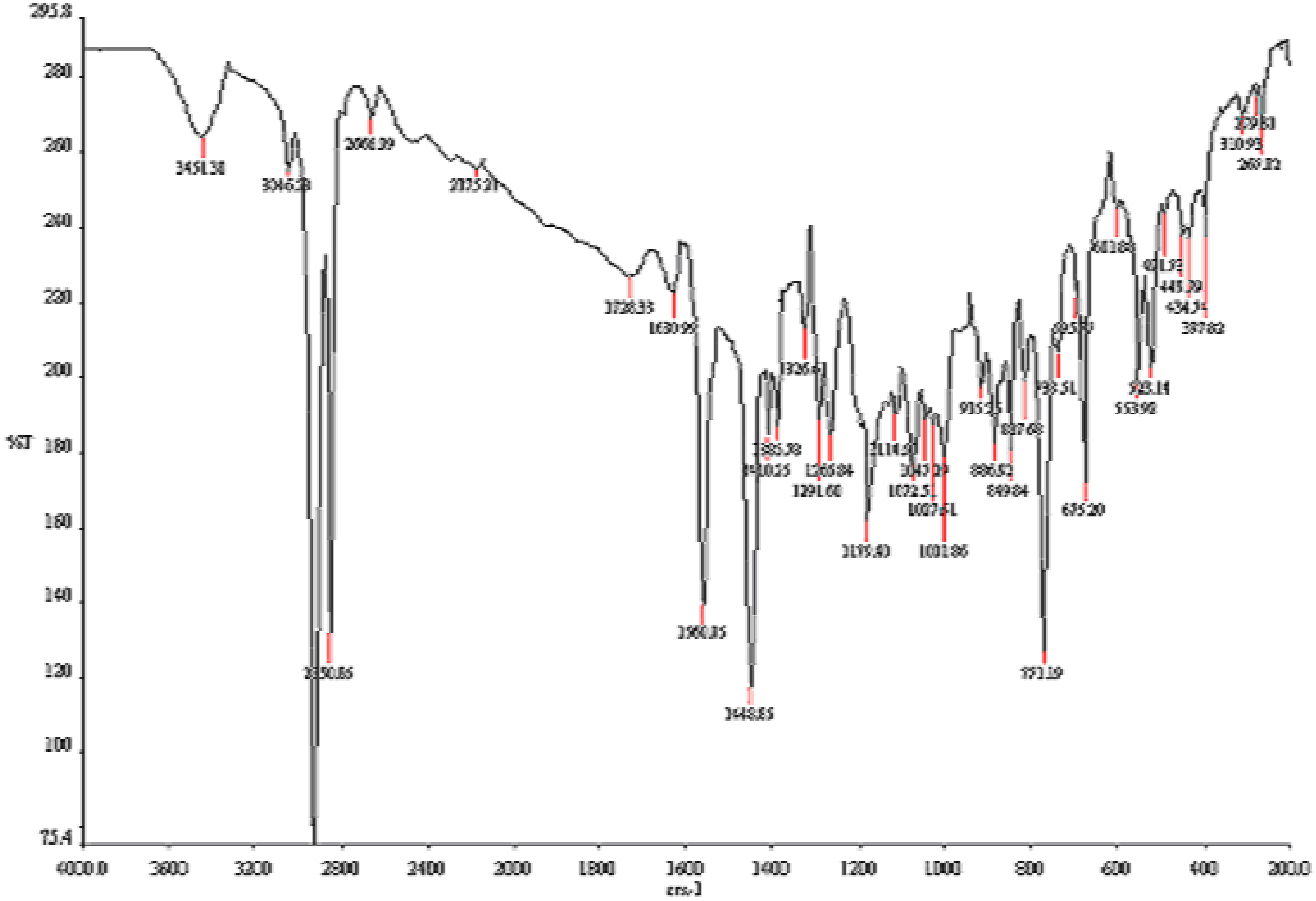


Figure 3.39 FTIR spectrum of 1,3-phenylene bis[dicyclohexyl(phophinothioite)] Pd(II) Complex **(2c')**

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