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METALLOCYCLIC COMPLEXES WHICH CONTAIN DIFFERENT HETEROATOM AND THEIR CATALITIC APPLICATIONS

Nilgün ARDA

Supervisor: Prof. Dr. Sevil İRİŞLİ

Department of Chemistry

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NİLGÜN ARDA tarafından **YÜKSEK LİSANS** tezi olarak sunulan "**METALLOCYCLIC COMPLEXES WHICH CONTAIN DIFFERENT HETEROATOM AND THEIR CATALITIC APPLICATIONS**" başlıklı bu çalışma E.Ü. Lisansüstü Eğitim ve Öğretim Yönetmeliği ile E.Ü. Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi'nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve 26.11.2010 tarihinde yapılan tez savunma sınavında aday oybirliği/oyçokluğu ile başarılı bulunmuştur.

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Raportör Üye	: **Yrd. Doç. Dr. Bircan DİNDAR**	……………………..
Üye	: **Doç. Dr. Hayati TÜRKMEN**	…………………….

ÖZET

FARKLI HETEROATOM İÇEREN METALLOHALKALI KOMPLEKSLER VE KATALİTİK UYGULAMALARI

ARDA, Nilgün

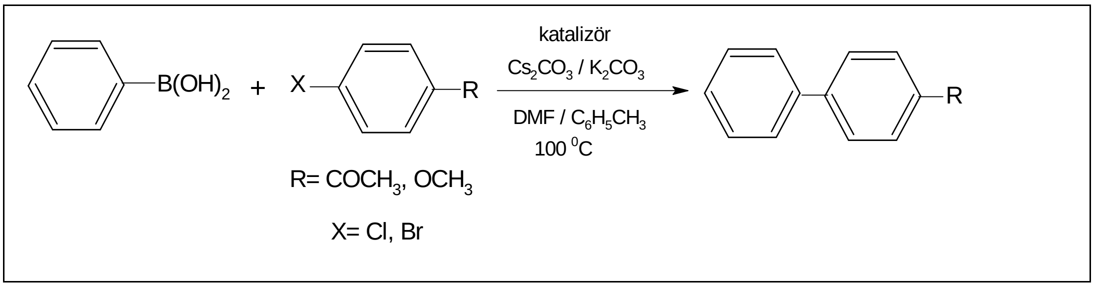
Yüksek Lisans Tezi, Kimya Bölümü
Danışman: Prof. Dr. Sevil İRİŞLİ
Kasım 2010, 135 sayfa

Tez üç bölümden oluşmaktadır. Birinci bölümde fosfinlerin genel özellikleri, belli başlı kıskaç ligandlar ve metal komplekleri, ayrıca katalitik özellikleri ile ilgili çalışmalar özetlenmiştir. İkinci bölümde deneysel çalışmalara yer verilmiştir. Üçüncü bölümde sentezlenen ligand ve komplekslerin karakterizasyonu, katalitik incelemeleri, AFM ve TGA analiz sonuçları sunulmuştur.

Toplamda 4 ligand ve 6 metal kompleksinin sentez ve karakterizasyonu gerçekleştirilmiştir. Ligand **1a**, **1b** ve **3a** yeni sentezlenmiş ligandlar olup, **2c** ligandı literatürde mevcuttur (Bernskoetter et al., 2009). Ligandların yapısal özellikleri $^{31}P\{^{1}H\}$-NMR spektroskopisi ile aydınlatılmış olup, komplekslerin (**1a’**, **1b’**, **1b’’**, **2c’**, **3a’** ve **3a’’**) ve sadece **1b** ligandının yapısal özellikleri $^{31}P\{^{1}H\}$-NMR, ^{1}H-NMR, FT-IR and elementel analiz ile aydınlatılmıştır. Ayrıca **3a’** kompleksinin yapısı X-ray analizi ile de açıklanmıştır.

1b’, **2c’** ve **3a’** kompleksleri Suzuki-Miyaura C-C eşleşme reaksiyonlarında katalizör olarak test edilmi tir. Suzuki-Miyaura C-C e le me reaksiyonlarında en iyi sonuç **1b’** kompleksi ile elde edilmi tir.

Suzuki-Miyaura C-C eşleşme tepkimesi



Anahtar kelimeler: Fosfin ligandları, kıskaç kompleksler, PONOP, Suzuki-Miyaura C-C eşleşme tepkimesi, palladyum, platin.

ABSTRACT

METALLOCYCLIC COMPLEXES WHICH CONTAIN DIFFERENT HETEROATOM AND THEIR CATALITIC APPLICATIONS

ARDA, Nilgün

Master Thesis in Chemistry

Supervisor: Prof. Dr. Sevil İRİŞLİ

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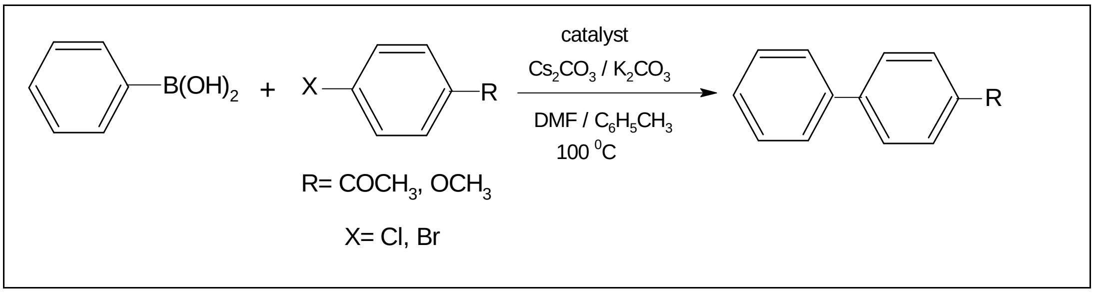
This thesis consists of three parts. The first part is a concise review of general properties of phosphines, well-known pincer ligands and their complexes, also their catalitic applications. In part 2, the experimental details are explained. In part 3, characterization of synthesized ligands and complexes; complexes' catalitic applications, results of AFM and TGA analysis were presented.

Total result for this thesis, we have synthesized and characterizated 4 ligands and 6 metal complexes. Ligand of **1a**, **1b** and **3a** have synthesized recently, but ligand of **2c** has presented in the literature (Bernskoetter et al., 2009). Structural properties of the ligands have explained with $^{31}P\{^{1}H\}$-NMR spectroscopy, the complexes (**1a'**, **1b'**, **1b''**, **2c'**, **3a'** ve **3a''**) and only **1b'**s structural properties have explained with $^{31}P\{^{1}H\}$-NMR, ^{1}H-NMR, FT-IR and elemental analysis. On the other hand, the identity of **3a'** has explained with X-ray analysis, too.

1b', **2c'** and **3a'** complexes have been employed as catalyst for the Suzuki–Miyaura cross coupling reaction. The best result in the Suzuki–Miyaura cross coupling reaction with complex of **1b'** were obtained.

Suzuki-Miyaura cross coupling reaction



Keywords: Phosphine ligands, pincer complexes, PONOP, Suzuki-Miyaura cross coupling reaction, palladium, platinum

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I would like to dedicate this thesis to my dear father Necdet ARDA.

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ABBREVIATIONS

Abbreviations	**Explanations**
L	Ligand
M	Metal
Ar	Aril
R	Alkyl
Me	Methyl
Ar	Aryl
DMAP	4-Dimethylaminopyridine
DMSO	Dimethyl Sulfoxid
Ph	Phenyl
^{t}Bu	terbutyl
^{i}Pr	isopropyl
THF	Tetrahydrofuran
COD	1,5-Cyclooctadien
COE	Cyclooctene
Et	Ethyl
PPh_2Cl	Diphenylcholorophosphine
$^{t}Bu_2PCl$	Ditertbutylcholorophosphine
NMR	Nuclear Magnetic Reconance
FT-IR	Fourier Transform Infrared
GC	Gas Chromatography
NMP	N-methylpyrrolidine
AFM	Atomic Force Microscopy
TGA	Thermal Gravimetric Analysis

ABBREVIATIONS (continue)

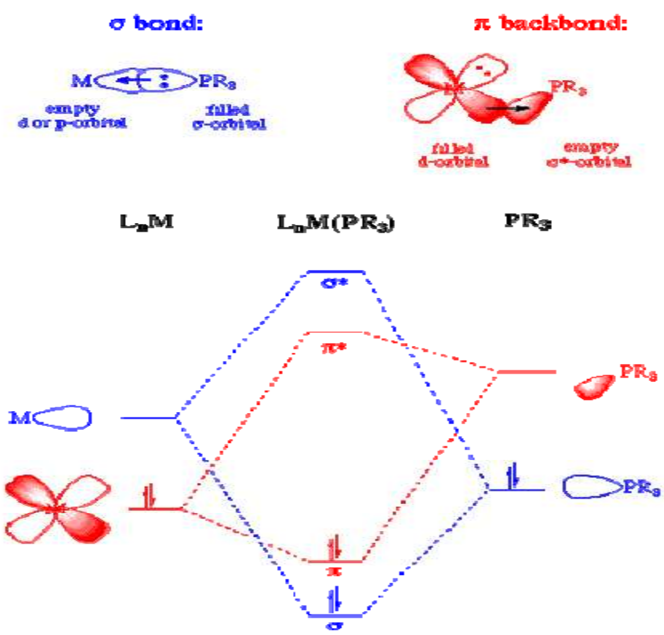
Abbreviations	**Explanations**
TON	Turn Over Number
DMF	Dimethylformamid
m.p	Melting point
cat.	Catalyst
Hz	Hertz
s	Singlet
d	Doublet
t	Triplet
m	Multiplet

1. INTRODUCTION

1.1 INFORMATION ABOUT PHOSPHINES

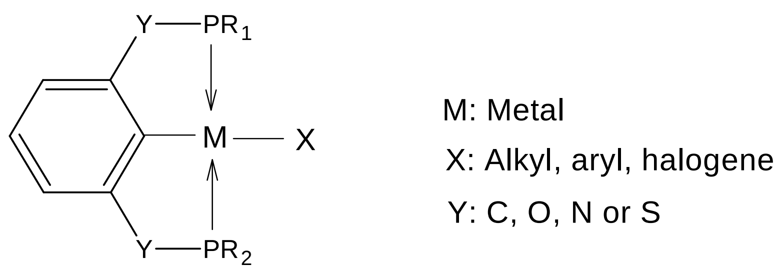
Phosphine is the compound with the chemical formula PH_3. It is a colorless, flammable, toxic gas. Pure phosphine is odourless, but technical grade samples have a highly unpleasant odor like garlic or rotting fish, due to the presence of substituted phosphine and diphosphine (P_2H_4). Phosphines are also a group of organophosphorus compounds with the general formula like PR_3 (R= alkyl, aryl or H). Organophosphines are important in catalysts where they complex to various metal ions. Also, phosphines are one of the most important classes of ligand in chemistry in both the industrial and academic spheres.

Phosphine ligands have a pair of electron to bound to the center atom. With this feature, they are similar to ammonia (NH_3). However, phosphine ligands are not similar to the ammonia because of carrying out π-bond.



Scheme 1.1 Molecule orbital energy diagram of formation metal-phosphorus bond

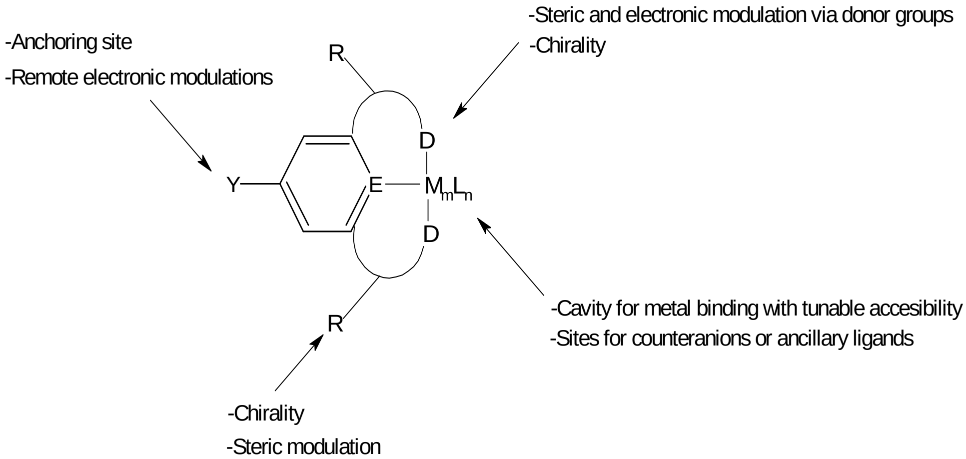
σ* orbitals of P-R bond supply to be acceptor for phosphine ligands in metal complex. Therefore, the most electronegative atom bonds to phosphorus atom. A lot of kind of phosphine ligands have synthesized by taking into consideration of bonds and orbital properties. A group of this type of ligands are called pincer ligands. By using this kind of ligands, lots of metal-phosphine pincer complexes have synthesized. Pincer complexes produce as a metal center and pincer skeleton. Pincer skeleton is three gear ligand that coordinate to metal at least one metal-carbon σ bond (see Scheme 1.2). The most common type of pincer sceleton 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 coordinate to the metal site via O, S, N or P donor atoms.



Scheme 1.2 Skeleton of pincer complex

Too much pincer complexes have been synthesized by changing groups on M(metal), ligand of X whose position is trans to carbon atom and D (donor) atoms. Consequently, many examples of phosphines (Y= CH_2, R_1=R_2= alkyl or aryl), phosphinites (Y=O, R_1=R_2= alkyl or aryl) and phosphites (Y=O, R_1=R_2= O-alkyl or O-aryl) have been synthesized.

In general these compounds have been first synthesized for their potential applications in some organic transformations, fact that has served as motivation for the chemical to include stereochemical centers in their structures and thus making available today a rich variety of chiral pincer species able to perform efficiently enantioselective processes. The pincer ligands have a lot of modification sites that can affect the properties of metal centres, and their complexation with pincer ligands usually occurs with the formation of two five-membered metallacycles to afford complexes [MXn(Y,C,Y)Lm].

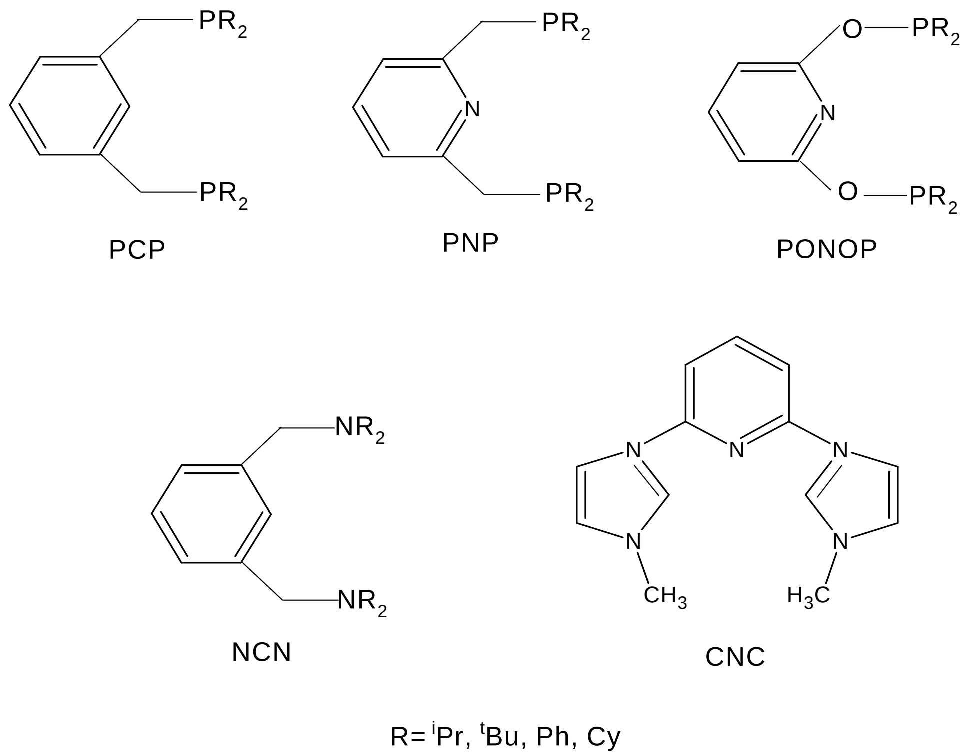


Scheme 1.3 Versatility of the pincer backbone and potential sites for modifications

In such organometallic complexes containing a direct metal−carbon bond, chelation led to the formation of metallacycles through the D → M donor−acceptor bond, which provides additional stabilization of the M−E bond (Scheme 1.3).

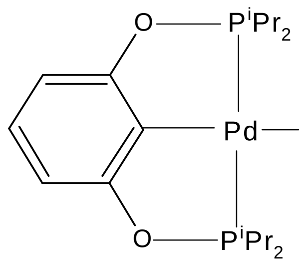
The basic structure incorporates a central ligating atom that carries a formal negative charge which forms a strong σ bond to a given metal center. This is flanked by two ortho-situated chains or rings containing neutral donor groups that datively bind to the metal, effectively forming a claw which ‘pinches’ the metal between its ‘arms’ (see Scheme 1.3).

According to this σ bond, substituents are attending –ortho position and they are coordinated to metal atom from P, O, N or S donor atoms because of with what are generally termed pincer ligands, the central ligating atom is typically carbon and the donors are generally N, P, O, and/or S atoms. So we can showed this type of ligands ‘YCY’ as an abridgement where YCY is typically an PCP, NCN, POCOP anionic six-electron donor ligand and on the other hand we both showed them PNP or PONOP are a well-established family of ligands (see Scheme 1.4) and their organometallic complexes which contain Pd, Pt, Ru, Ir, or Rh, with applications in catalysis, synthesis and materials science.



Scheme 1.4 Different kind of pincer ligands

Most pincer complexes have symmetrical structure (Morales et al., 2000) which is given in structure of complexes **1** and **2**, but on the other hand unsymmetrical pincer complexes have documented (Wang et al., 2003) which is given in structure **3** and **4**.



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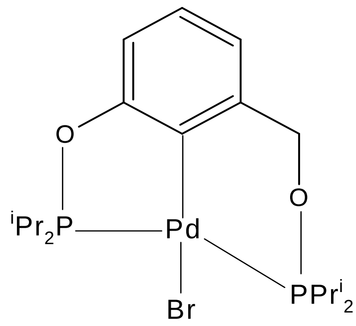

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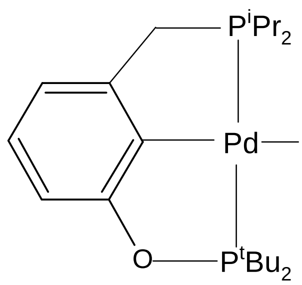

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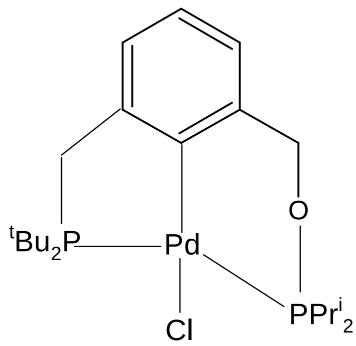

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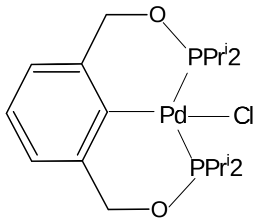
Pincer complexes have many attractive properties because of the presence of least a metal-carbon σ bond at this type of complex. This bond which is between metal atom and ligand, prevents to seperated metal atom from ligand and so that the pincer complex has thermal stability. Donor atoms and substituents can control interaction between metal with ligand and electron intensity around the metal atom. Also, changing donor atoms or substituents, stereospecific catalyst can obtain.

On the other hand, steric and electronic features of phosphine ligands effect that bonding to transition metals. Electronic and steric properties of ancillary ligands are crucial factors for designing functional transition metal complexes. By converting steric and electronic properties of phosphine ligands, their transition metal complexes' catalytic reaction activities and selectivity can increase.

Pincer type of complexes chemistry has been having a steadily increasing interest in homogeneous catalysis due to the high thermal stability that these complexes exhibit and the potential alternative mechanistic routes they follow. These complexes as a catalyst that displays broad functional group tolerance, useful rates and high turn over number. In fact, palladium and platinum PCP, PNP, NCN, CNC and PONOP type of phosphino complexes have been studied Mizoraki-Heck reaction, Suzuki-Miyaura Cross-Coupling reactions or employed in ketone transfer hydrogenation reactions. There are a few samples of pincer complexes as catalyst (Naghipour et al., 2007; Benito-Garagorri et al., 2008; Melaimi et al., 2004) in structure **5, 6** and **7**.



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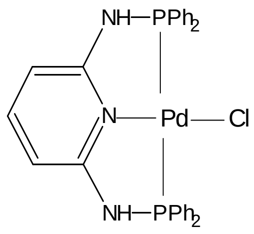

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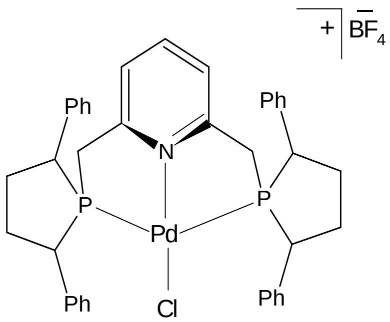

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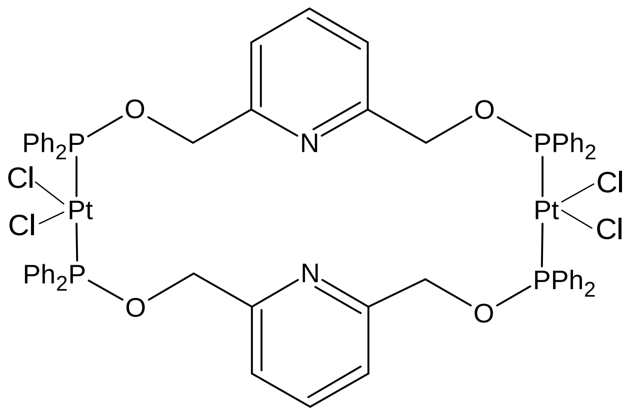
On the other hand, sometimes polydentate ligands like PNP, PONOP, PCP phosphine ligands coordinate metallic ions both pincer and either as chelates like structure **8**, yielding monometallic complexes or as bridges, yielding polynuclear (especially dınuclear)complexes. A few literatures have appeared concerning the electronical and structural factors that govern the formation of monomers or dimers upon coordination of metallic complex. With diphosphines, it was elucidated that chain lenght or the bulkiness of the substituents on phosphorus were of prime importance (Hill et al., 1982).



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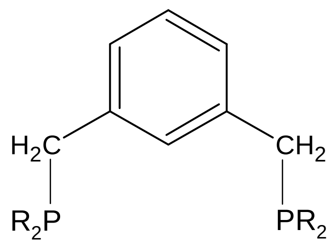
1.2 TYPE OF PCP LIGANDS

PCP pincer ligands (see Scheme 1.5 and Scheme 1.6), were first introduced by Moulton and Shaw in the 1970's (Moulton et al., 1976). It is still a hot and emerging topic covering all aspects of modern organometallic chemistry and touching other fields as well. The first PCP ligands had structure **9**, in which the phosphino donor arms were connected to the central aromatic ring with $–CH_2$ groups. Also, a more newly modifications is the bis(phosphinite) PCP ligands which is given **10** and in which phosphine donor arms are connected to the central aromatic ring with 'O' links and sometimes 'N' links. When we use 'O' donor atom to connect to the central aromatic ring, is named like POCOP and called 'phosphinito'.



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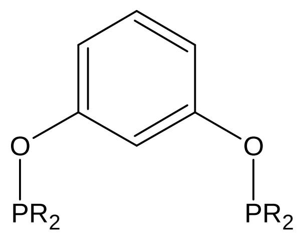

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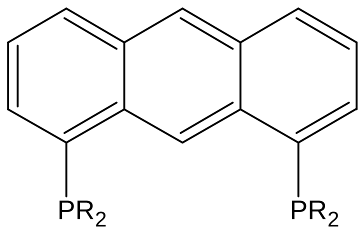

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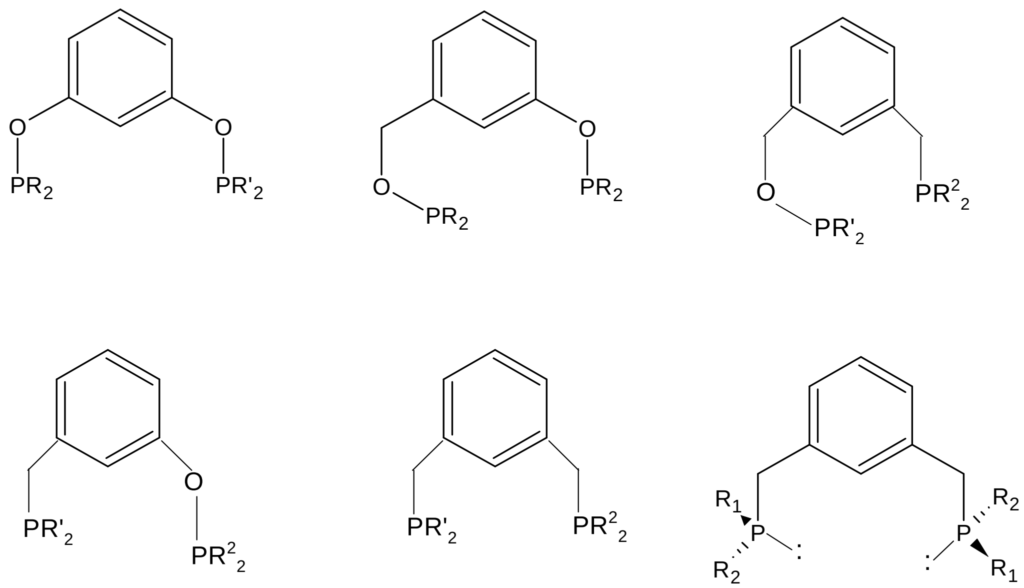
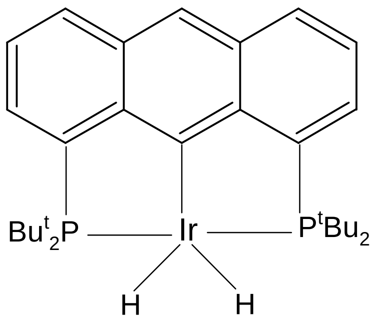
Scheme 1.5 Structure of the most commun types of PCP pincer ligands



Scheme 1.6 Bis-phosphinito and unsymetrical phosphino-phosphinito PCP ligands

PCP pincer ligands like structure **11**, and their metal complexes like structure **12** were just prepared in an effort to generate pincer complexes of even greater thermal stability (Haenel et al., 2001).



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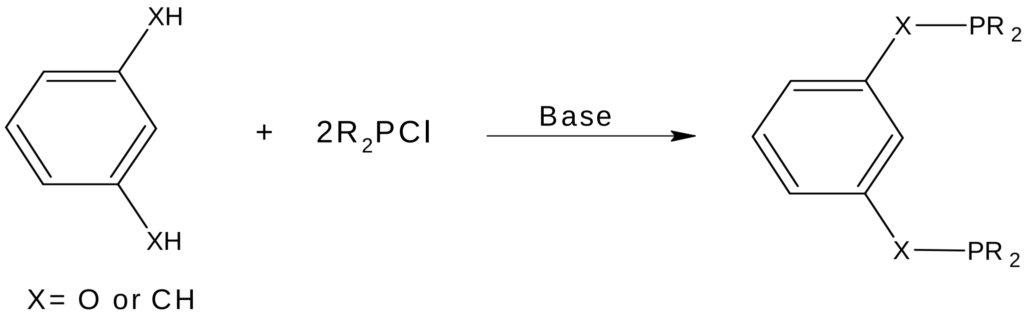
For synthesis of PCP ligands (see Scheme 1.7), can be attained in a very facile manner from the corresponding chlorophosphine and resorcinol (for the most commonly known version of the PCP phosphinite ligands) in the presence of a base.



Scheme 1.7 Synthesis metod of PCP ligands

This procedure has been used successfully for the synthesis of a variety of PCP phosphinite and phosphino ligands (vide infra) and the same method has been probed adequate for the synthesis of other pincer ligands containing in their structures (Eberhard et al., 2003).

Ligand design is one of the most important aspects of organometallic chemistry. The ability to simply and independently vary the steric and electronic impact of a given ligand provides a wealth of opportunities to influence reactivity, stability, catalysis, and other important properties at the metal center. Only certain classes of ligands can fulfill these synthetic requirements and also generate interesting metal complexes. The so-called pincer ligands are a prime example of a simple design that has enabled the development of a broad and diverse research portfolio with complexes containing this motif.

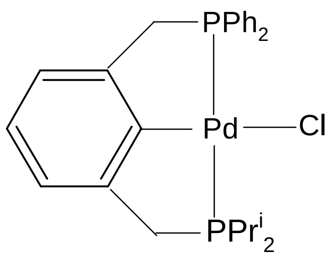
1.2.1 PCP Complexes

Afterwards, interest and activity about synthesis PCP ligands and their transition metal complexes have rapidly increased. For instance, cyclometalated phosphine-based pincer complexes and structurally/electronically related systems are about to become a valuable asset in the formation of functional nanoscale assemblies, while various mechanistic, structural, catalytic, synthetic, theoretical, and coordination studies are ongoing (van der Boom et al., 2003). Pincer-based metal complexes possess an unique balance of stability and reactivity which can be controlled by systematic ligand modifications and/or variation of the metal center, allowing enhancement of metal complex reactivity, stability, reaction selectivity, and simultaneously provide a flurry of new fundamental insight.

Modifications of the benzylic positions and phosphino or phosphinito R groups have been used to 'tune', the steric, electronic and stereochemical properties of these ligands thus their metal complexes (Moulton et al., 1976).

The use of the PCP ligands **9** and **11** opens a large number of interesting research possibilities given the complex reaction chemistry which is not yet fully understood. For instance, how are the physicochemical properties of PCP-based metal complexes influenced by the nature of the metal center (periodic table position, oxidation state), substituents on P and on the aryl and alkyl ligand backbones, ancillary ligands, and coordination geometry.

This class of ligands have attracted a considerable amount of attention. The most important attraction of the PCP ligands (indeed, of many other pincer type of ligands as well) is their ability to give rise to extraordinary robust metal complexes like **13** and **14**. The importance of stability of pincer-ligated metal complexes supplies their use as catalysts under hard conditions (van der Boom et al., 2003). These synthesis PNP complexes which have obtained reaction with transition metals like palladium, platinum, iridium etc. inculude the Heck coupling (Morales-Morales et al., 2000), Suzuki-Miyaura cross coupling (Solono-Prado et al., 2009), alkane dehydrogenation (Liu et al., 1999), transfer hydrogenation (Doni et al., 2000) and Sonagashira coupling (Eberhard et al., 2002) reactions.



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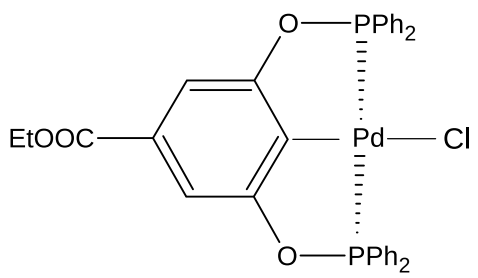

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In the last years, it is important for a catalyst to be a cleaner environmentally friendlier chemistry has led to the development of new heterogeneous catalytic systems and in an opinion, PCP pincer type complexes would constitute excellent condidates for such task. In the recent years, transition metal complexes which containing PCP pincer ligands have been employed in a wide variety of homogeneous and heterogenized (supported) catalytic reactions due to their excellent moisture, air and temperature stability. We can explain that the metal-carbon σ bond is the key to the high stability of PCP pincer complexes. The stability of these complexes to air and moisture, as well their thermal stability, means that they offer considerable advantages over the other catalysts commonly employed in Mizoraki-Heck reactions and the dehydrogenation of alkanes to alkenes. Some Suzuki-Miyaura cross coupling reactions have also been carried out without the need for an inert atmosphere.

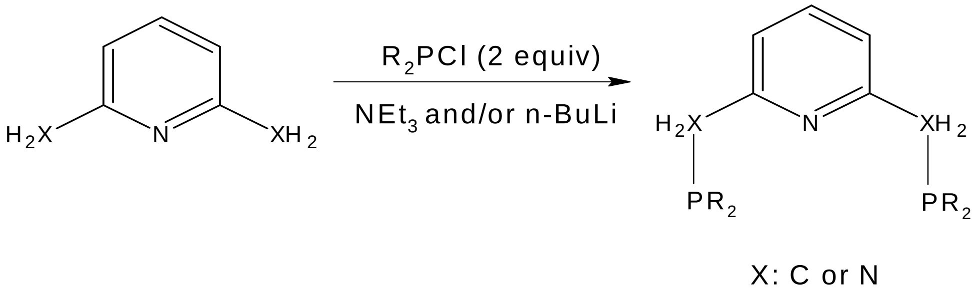
1.3 TYPE OF PNP LIGANDS

Tridentate PNP ligands which the central pyridine-based ring and donor contains substituents in the two ortho positions are fairly employed ligands in transition metal chemistry. Steric, electronic and stereochemical parameters in this kind of ligand can be manipulated of modifications of the benzylic position or the phoshpino R (phenyl, cyclohexil, tert-butyl, isopropyl) groups so as to control the reactivity at the metal center (When we use ‘O’ donor atom to connect to the central aromatic ring, is named like PONOP and called ‘phosphinito’ like POCOP).

Especially, groups of tert-butyl bearing highly electron-donating PNP ligands were sythesized. It is now well established the throle of ancillary phosphine groups in crucial and a fine tuning of the electronic and stereochemical properties of transition metal complexes can be achieved by adjusting the substitution scheme around phosphorus.

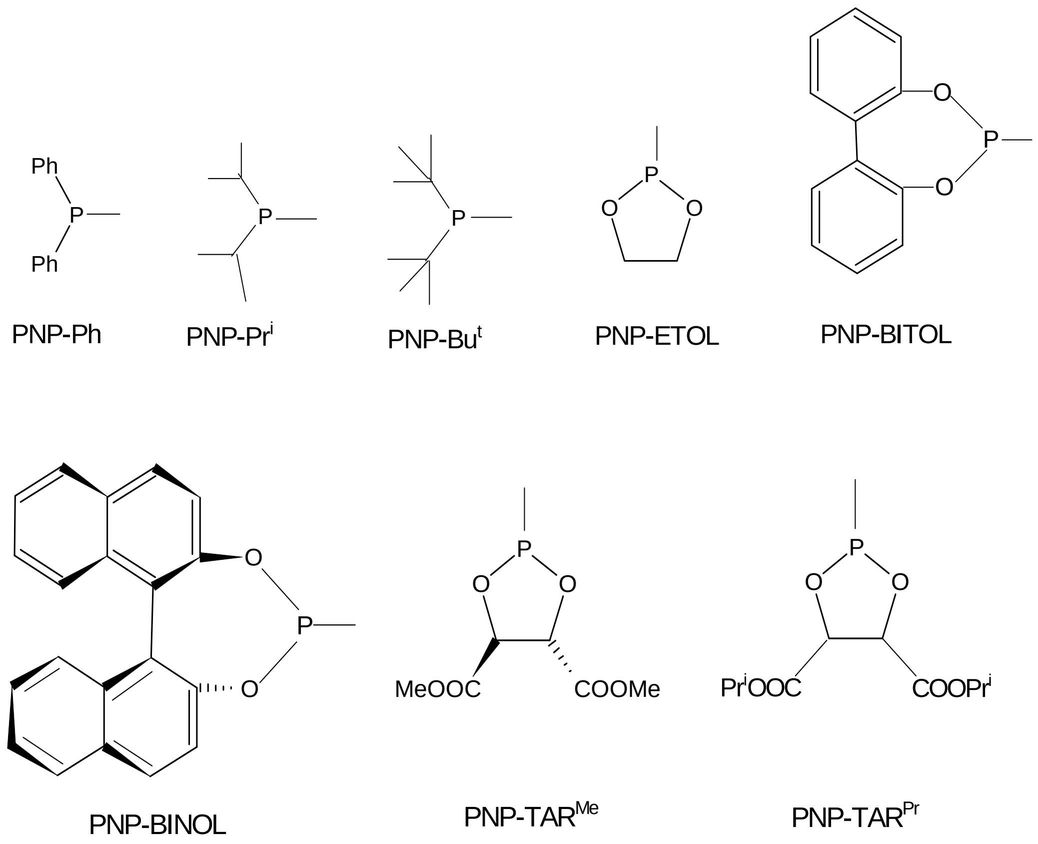
In contrast to the aryl C donor in PCP, amido is a much stronger σ-donor and is a ligand of weaker trans-influence. These factors, inter alia, may lead to significant structural and reactivity differences between PCP- and PNP-supported chemistry. As well, PNP ligands provide a hybrid environment that combines soft phosphine donors and a hard amido donor. Thus, PNP ligands are capable of supporting both the hard early transition metal centers and the soft late transition metal ones. The central pyridine behaves as hemilabile ligand that competes reversibly with chloride, this hemilabile behaviour of PONOP is reminiscent of similar systems reported by Mirkin (Holliday et al., 2001).

Generally, all PNP ligands are thermally robust, air stable in the solid state and in oxygen-free solution. PNP ligands and their complexes based on R_2PCl that contain both bulky and electron-rich dialkyl phosphines. The phosphine fragment is often the most expensive component in the synthesis of the PNP ligands. Therefore, it is prudent to install the phosphine functionality as late as possible in the synthesis. This strategy is also sensible because at least the more basic phosphines (and thus PNP ligands) are air-sensitive and thus require special treatment and transition metal-catalyzed procedures (such as Pd-catalyzed amination) are unlikely to work well with phosphine-containing reagents. Below, there is a kind of way to synthesis PNP ligands (Scheme 1.8).



Scheme 1.8 Schematic representation of synthesis PNP ligands

For functional groups of R;



1.3.1 PNP Pincer Ligand Backbone

The general nature of pincer chemistry has allowed for the very facile synthesis of numerous analogues of tridentate bonding to the central metal atom. One of these arrangements involves the replacement of the sigma bond to the metal with nitrogen, silicon and phosphorus rather than carbon.

The obvious advantage of nitrogen as central atom is the possibility that the lone pair of non-bonded electrons on the nitrogen atom will interact with suitable symmetrical orbitals on the metal atom, thereby decreasing or increasing the electron density (Fryzug et al., 1989; Fryzug et al., 1998). There are normally three bonding modes for metal-substituted amines (Fryzug et al., 1989; Cundari et al., 1992; Fryzug et al., 1986*)*.

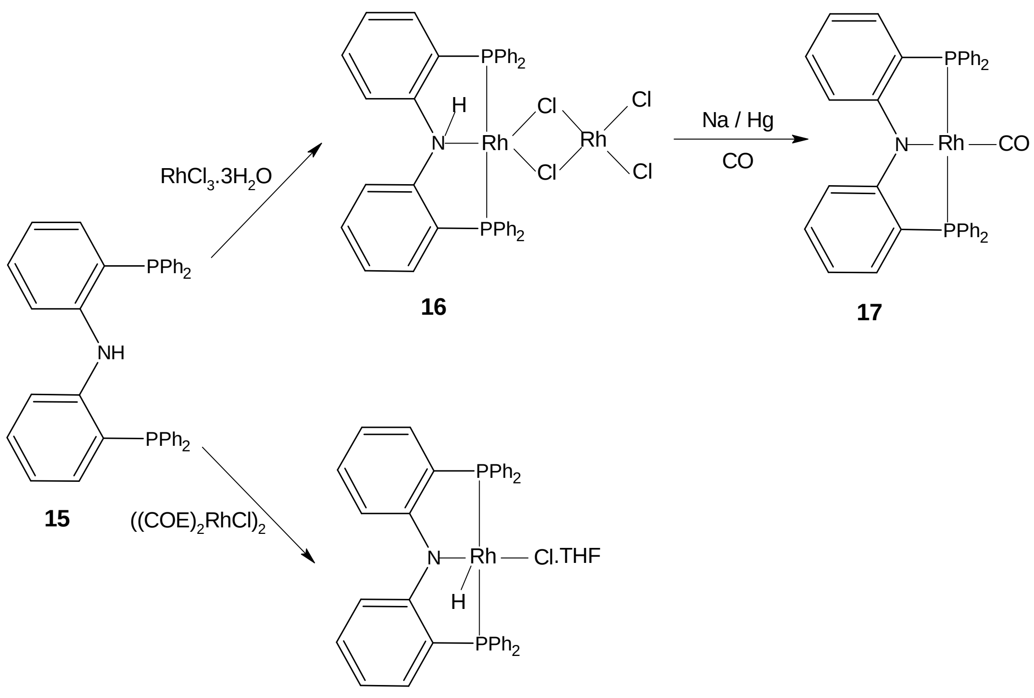
The pincer complexes with nitrogen in the backbone that have been synthesized recently have more or less an almost planar form, which indicates some amount of π-electron interaction (Winter et al., 2003). In the ligand system **15**, the amine is positioned between two diphenylphosphine groups. Thus, the strong metal-binding properties of the phosphines and the chelate effect prevent the dissociation of the highly electron rich amide from the electron-rich low-valent rhodium(I) (**17**) and rhodium(III) (**18**) amide complexes.

The amide complexes **17** and **18** have been synthesized by two different routes. Upon refluxing of $RhCl_3$ trihydrate with **15** in methanol, the air-stable pale-yellow dinuclear complex **16** is formed, which can be converted to the rhodium(I) amide complex **17** by treatment with Na/Hg in the presence of CO in THF. The rhodium(III) amide **18** is obtained by direct reaction between the pincer ligand **15** and $[(COE)_2RhCl]_2$ (COE =cyclooctene) in THF. Interestingly, the latter reaction is a rare instance where a chelate-assisted oxidative addition of N−H bond occurs with rhodium. Moreover, it has been demonstrated recently that the N−H bond of ammonia can be cleaved by intermolecular oxidative addition to a pentamethylenediphosphine pincer iridium(I) complex fragment (Zhao et al., 2005).

There is no clear-cut evidence that there is an appreciable amount of pπ–dπ-bonding in these types of complexes (Ingleson et al., 2006). The experimental Rh−N bond distance of 2.074(9) Å as well as the theoretically calculated values for **17** suggests that this is a single bond. Moreover, the planarity of the rhodium-amide bond does not necessarily confirm whether π-bonding occurs between these fragments.

Liang (Liang et al., 2006; Liang et al., 2005) and Ozerov (Celenligil-Çetin et al., 2005; Ozerov et al., 2004) who have recently studied nitrogen pincer complexes also found that most nitrogen atoms in the backbone of pincer complexes are more or less of the amido type with little π-bonding.

As a result of the rigid backbone and fused five membered ring chelation about the metal center, this PNP ligand should in preference from meridional rather than facial complexes. This will be important for enantioselective reactions, as the number of diastereoisomeric forms of catalytic intermediates will thus be limited and supply greater stereocontrol of the reaction (Whitesell et al., 1989).



15 16 17 18

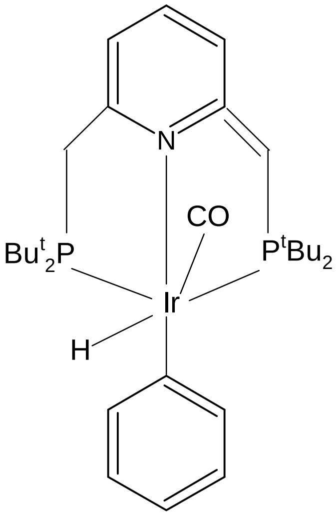
1.3.2 PNP Complexes

The PNP ligands are ideally suited to support a variety of square-planar complexes of the general formula (PNP)MX (M = Ni, Pd, Pt). The usefulness of the PNP ligands extends to both borders of the transition metal series. Such versatility is largely owing to the rigid backbone that pre-arranges the three donor atoms for binding a transition metal and also to the hybrid nature of PNP, incorporating both the hard amido donor and the soft phosphine donors.

The coordination chemistry of the simplest achiral member of this PNP familiy, has been well studied and a few applications of the obtained complexes in catalysis (Steffey et al., 1994).

Especially Pd-PNP pincer complexes, in the catalytic cross-coupling of various aryl halogenes with phenyl boronic acid (in the well-known Suzuki-Miyaura cross-coupling reaction) as a catalyst can be employed and have investigated.

PNP pincer ligation with transition metals like **19** (Iron et al., 2009) and **20** (Zhang et al., 2004) has already shown a broad collage of structural and chemical reactivity. Almost all pincer complexes have unique properties of thermodynamic and kinetic stability along with electron density flexibility on the transition metal atoms. In the future, these types of complexes should be expected to show an unusual array of chemical reactivity, synthetic potential, spectroscopic details and an advance in new material research.



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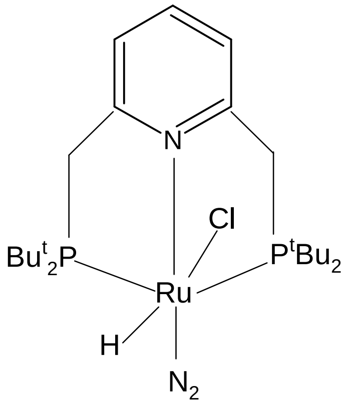


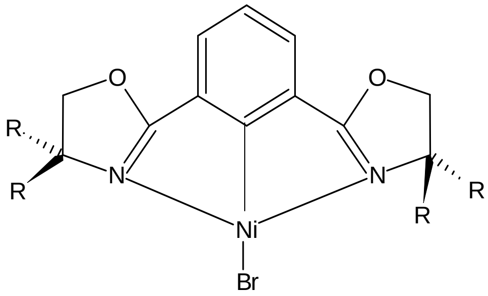
20

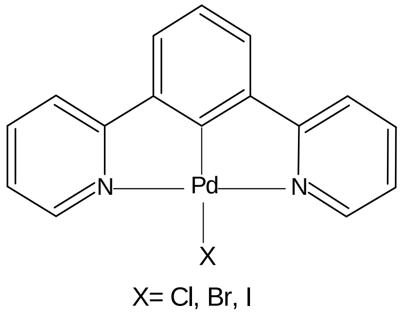
The bulky, tridentate ligand can stabilize coordinatively unsaturated complexes and when this ligand bears strong σ donating groups, reactive unsaturated, electron-rich complexes can be obtained. More electron-rich complexes of PNP type containing alkyl substituents on phosphorus are very rare.

Finally, it is believed that further investigations will give deeper insights into the reactivity and applicability of aminophosphine-based pincer complexes which contains P-N bond in pincer ligands and complexes.

1.4 TYPE OF NCN LIGANDS

The typical designation of a pincer, for instance 'NCN', systems from the presence of two amine or other nitrogen-based donors flanking the central aryl or alkyl C−M bond. The NCN-pincer ligands and their metal complexes like **21** (Lee et al., 2008) and **22** (Soro et al., 2005) are a well-utilized and extremely useful platform for the stabilization and isolation of unique complexes and exploring their utility in a variety of applications. Soro and co-workers prepared pincer complex **22**, in which two pyridines work as the source of N-donor atoms, and reported relatively good results in the Heck reaction between iodobenzene and methyl acrylate.



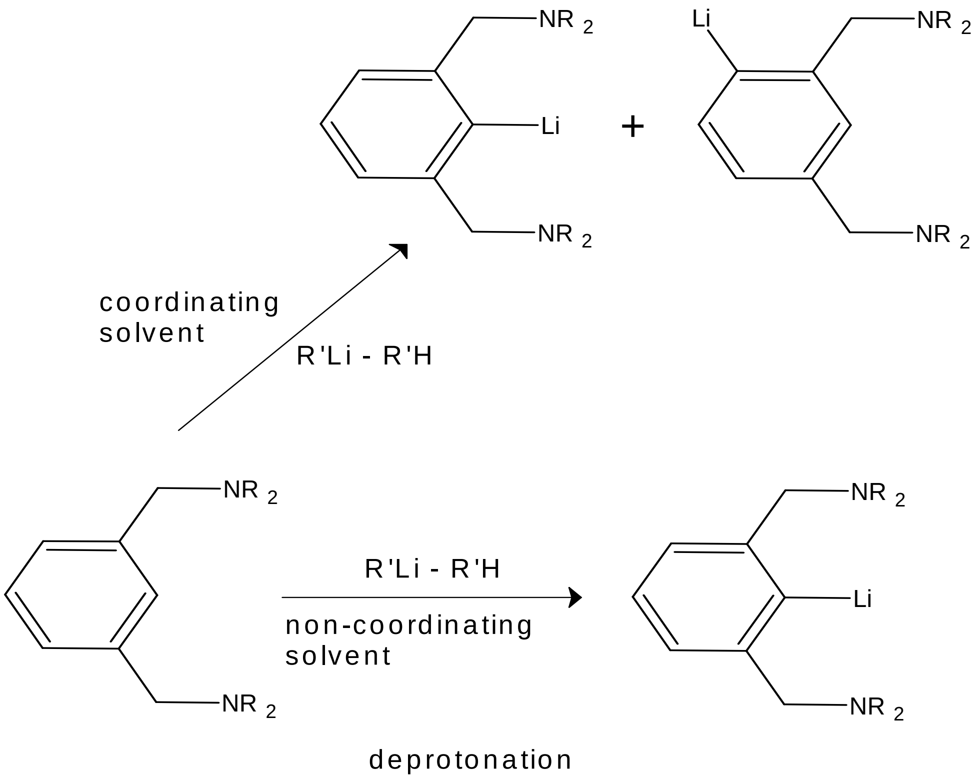


21 **22**

1.4.1 NCN Complexes

The first NCN-type metal complexes, reported by van Koten in 1978, were main group systems incorporating Sn and Li(NCN) species (van Koten et al., 1978). The prototypical Pt(NCN) species was disclosed soon thereafter (van Koten et al., 1978). In addition to the well-developed organometallic chemistry, there is also a relatively rich and diverse variety of main group complexes that have been studied (Rietveld et al., 1997). In terms of impact on organometallic and main group chemistry, complexes containing the NCN motif represent a rather large number of chemical 'firsts.' For example, the first well-characterized organometallic dendrimer applied to catalysis contained Ni(NCN) groups as the active sites (Knapen et al., 1994). Dendritic effects in these systems were also thoroughly explained, a fairly rare occurrence in dendrimer chemistry (Kleij et al., 2000; Kleij et al., 2000).

One of the primary reasons for the quantity and variety of NCN complexes reported to date stems from the availability and well-understood chemistry of a variety of [Li(NCN)] species (see Scheme 1.9). These are truly the workhorse reagents for synthetic methods to generate other transition metal and main group complexes via transmetalation.



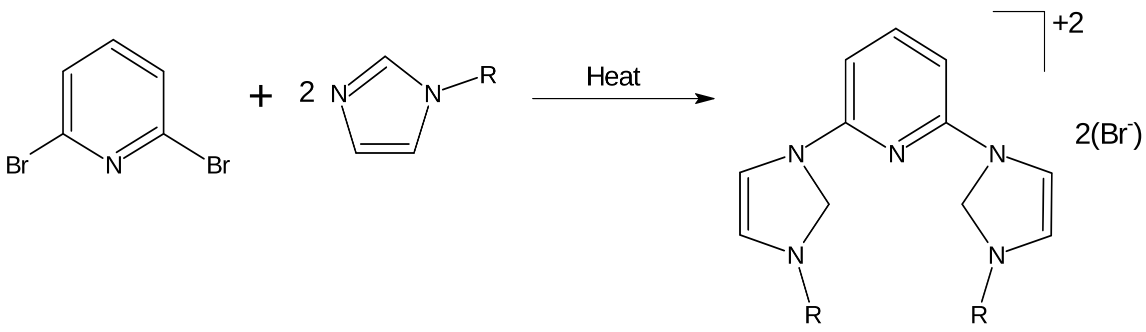
Scheme 1.9 Synthesis of Li[NCN] pincers via deprotonation

The vast majority of metallopincer complexes, NCN-type systems included, incorporate group 10 metals. As such, a number of reviews that cover this area have been reported (van Koten et al. 1989), which detail the interesting catalytic and material properties of these species in conjunction with studies in fundamental bond-making and bond-breaking processes. To a large extent, the viability of M(NCN) (M=Ni, Pd, Pt) complexes for such varied and numerous studies stems from their relatively direct synthesis and high stability. Also, a number of metallo-dendritic complexes have been synthesized that incorporate pincer-ligated Ni, Pd, and Pt, a topic which has also been reviewed (Albrecht et al., 2001). The Pd complexes were tested as aldol catalysts in the synthesis of oxazolines, but no chiral induction was observed.

The NCN motif is the most versatile of the pincer ligands as complexes with almost all transition metals have been generated and also demonstrate the largest variety of binding modes and geometries. On this tour through the periodic table, it was shown that metalated NCN pincers have wide applications in catalysis and mechanistic studies, in the preparation of functional materials and sensors, and in the discovery of new reactivity. The stabilization of unusual metal oxidation states, geometries, and coordination numbers has also been observed.

1.5 TYPE OF CNC LIGANDS

Most CNC-pincer-carbene complexes reported so far are prepared from pyridinebisimidazolium salts. The simplest preparation of these ‘bis-carbene precursors’ consists of the direct reaction between two equivalents of an alkyimidazole and 2,6-dibromopyridine in Scheme 1.10 (Chen et al., 2000).

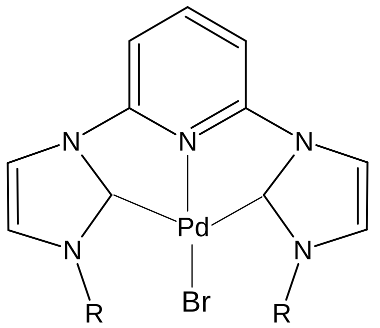


Scheme 1.10 Schematic representation of synthesis CNC ligands

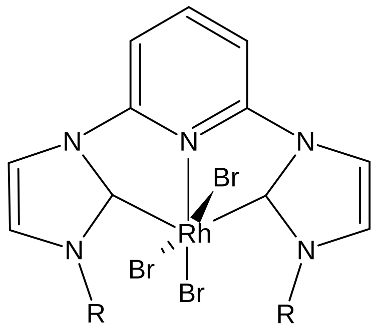
Pincer ligands of the C−N−C type pyridine $(NHC)_2$ have shown high stability which has potential applications in radiopharmaceutical imaging applications. But an even more important application of these highly stable pincer complexes is in the catalytic dehydrogenation of alkanes.

1.5.1 CNC Complexes

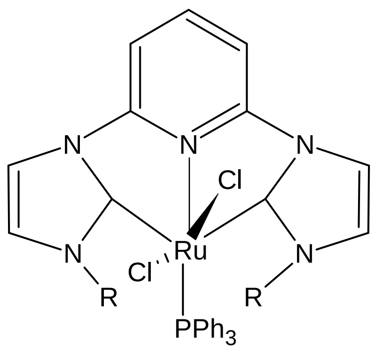
The first palladium pincer carbene complex which was **23**, revealed to be an active catalyst for the Heck reaction was described by Crabtree and co-workers (Peris et al., 2001). Extension of the coordination of pincer-carbene ligands like CNC, Rh (**24**) and Ru (**25**) has afforded new complexes that proved active for several other homogeneous-catalyzed reactions (Poyatos et al., 2003). The rhodium CNC complexes like **24** were tested in the catalytic hydrosilylation of alkynes with hydrosilanes, producing isomers of the alkenylsilanes (Zeng et al., 2005). The first ruthenium CNC-pincer carbene complex (**25**) was obtained by Danopoulos and coworkers in 2002 (Danopoulos et al., 2002)



R: Me, Bu



23 **24**



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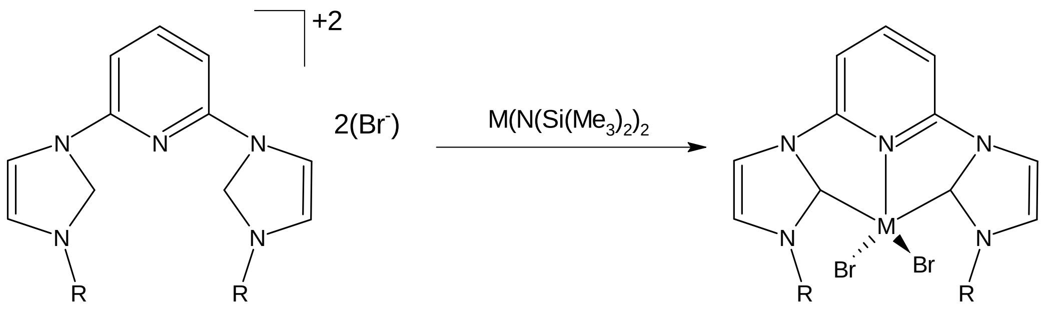
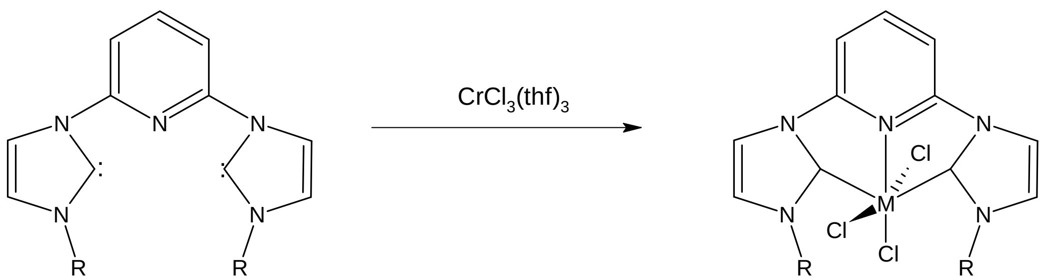
The reaction of the free pyridine-bis(imidazolylidene) and $RuCl_2(PPh_3)_3$ afforded the preparation of the (CNC)-Ru complex **25** in high yield.

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 analogous phosphine complexes. One of the advantages of these systems is 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 special precautions being taken.

Although most of the examples reported so far are from Pd, Rh and Ru, a few examples are known of pincer-carbene complexes of iron **26** (Danopoulas et al., 2004), cobalt **27** (Danopoulas et al., 2004), chromium **28** (McGuinness et al., 2003) and early transition metals (McGuinness et al., 2004).



M: Fe(**26**), Co(**27**)



M: Cr(**28**)

The Fe (**26**) and Co (**27**) complexes were tested for the catalytic polymerization of ethylene, in view of the structural analogies with compounds of the type [bis(imino)pyridine]MCl_2 (M = Co, Fe) which are very active for this reaction (Britovsek et al., 1999).

1.6 PINCER COMPLEXES APPLICATIONS in CATALYSIS

Transition metal complexes are useful tools for any synthetic chemist. Ideally, any metal-mediated process should be fast, clean, efficient, selective and take place in catalytic manner. These criteria are especially important considering that main of the transition metals employed in catalysis are rare and expensive. One of the access of modifying and countrolling the properties of transition metal complexes is the use of appropriate ligand system, such as pincer ligands.

Usually consisting of a central aromatic backbone tethered to two-electron donor groups by different spacers, this class of tridentate ligands have found numerous applications in various areas of chemistry, including catalysis, due to their combination of stability, activity and variability.

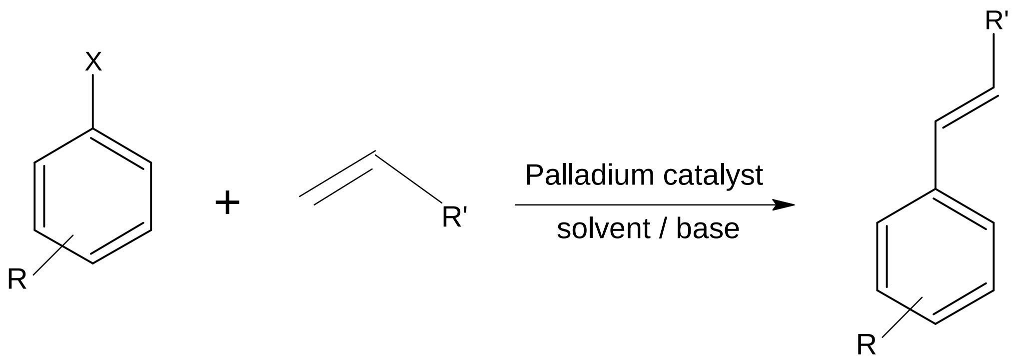
In the resent years the development of complexes which having in its structure pincer type ligands has believed considerable attention. Nowadays, these complexes are designed and synthesized not just for the structural interest but for the great number of potential demonstrations that these compounds may have, including their use as robust catalysts, motifs in molecules that exhibit self assembly arrangements, synthons for their employment in medicinal chemistry and as fundamental components in the synthesis of dendrimeric materials for their potential use in catalyst. The multiple applications that the pincer complexes have had in particular in the area of catalysis and the future perspectives of demonstrations of these compounds in chemistry.

The donor atoms and their substituents can control the electron density around the metal atom and the accessibility of the metal to potential substrates. This allows 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 (see Scheme 1.2) or by the donor atom substituents, creating potential stereoselective catalysts.

Generally pincer complexes are used in Mizoraki-Heck coupling reaction, Suzuki-Miyaura cross coupling reaction, dehydrogenation of alkanes, hydrogen transfer reaction, aldolic condensation, asymmetric allylic alkylation.

1.6.1 Mizoraki-Heck Reaction

Since its discovery in 1960s, the Mizoraki-Heck reaction has turned into a real power tool in organic synthesis, nowaday reaching the status of angular stone in the modern organic synthesis (Heck et al., 1991).



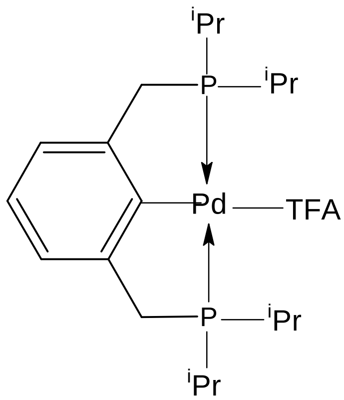
Scheme 1.11 Heck coupling reactions

In general, the Heck reaction consists in the coupling of an aryl iodide or bromide (R-X) with a terminal alkene. Most of the prosesses involving the Heck reaction are catalyzed by Pd(II) or Pd(0) derivatives in the presence of PPh_3. Palladium pincer complexes are still under argument because of the conventional Pd(0) / Pd(II) mechanism(Heck et al., 1991) for Heck coupling is unlikely to apply. The high probability that the Heck reactions catalysed by pincer complexes proceed via different mechanism to the other palladium-catalysed Heck couplings gives rise to potentially different constraints and opportunities.

Unfortunately, the reactions conditions are hard. The reaction intermediates formed during the catalytic reaction are sensitive to oxygen or thermally unstable, hampering the coupling prosess.

1.6.1.1 Phosphino-Palladium PCP Pincer Complexes

Complex of **29** , the first Pd(II)-PCP pincer complexes as catalysts for the Heck reaction, were reported by Milstein and co-workers (Ohff et al., 1997).



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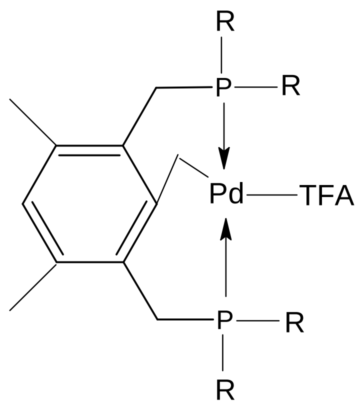


R= ^{i}Pr or ^{t}Bu

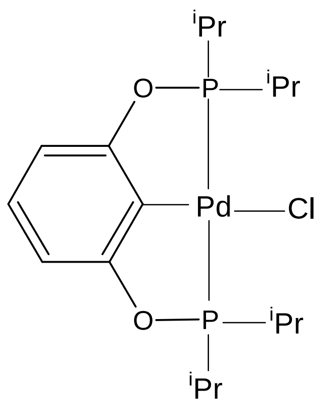
30

These phosphino-palladium PCP pincer complexes are readily prepared by treating Pd(TFA)$_2$ with the corresponding diphosphine in THF at 80 ^{o}C. They were active without decomposition at reaction temperatures as high as 140 ^{0}C over reaction periods of 300 hours or higher. The compounds which were obtained also not sensitive to oxygene or moisture. By using these catalysts which are **29** and **30**, Milstein achieved full conversion in the couplings of iodobenzene with methylacrylate, using NMP as solvent and sodium carbonate as base w;ith a maximum of 500.000 turnover numbers for iodobenzene and up to 132.900 for bromobenzene.

Consequently, these palladium complexes have shown good catalytic activite in Heck reactions.

1.6.1.2 Phosphinito-Palladium PCP Pincer Complexes

Based on the results, Jensen (Morales-Morales et al., 2000) synthesized an analogous PCP pincer type ligand based on phosphinito fragments as P donors. This complex has been found to be a highyl active catalyst in Heck reactions involving aryl chlorides, were shown to be efficient in the coupling of chlorobenzenes, being one of the few examples then known to activate, deactivated or sterically hindered chlorobenzenes.



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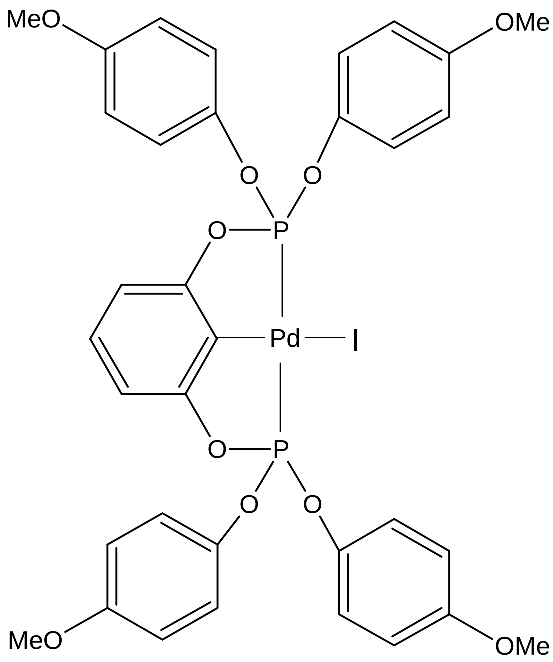
The complex of **31** showed to be as reactive as the PCP phosphino derivative reported previously by Milstein and Jensen. Jensen extended Heck reactions with aryl chlorides generally require a higher catalyst loading than the corresponding aryl bromide reaction. The group of Jensen used 0.67 % mol of their phosphinito catalyst in which **31**, in dioxane at 120 ^{0}C and 1.1 equivalent of base. The system almost exclusively produces the corresponding trans stilbene and is one of the few to show reactivity with electron rich and sterically-hindered aryl chlorides.



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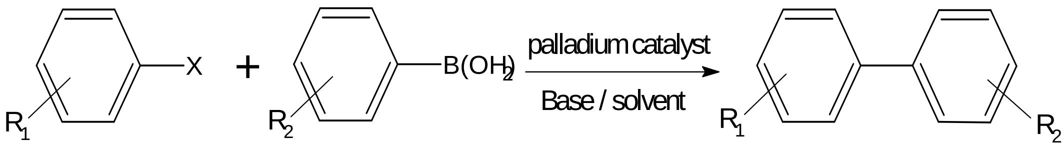
These type of pincer complex, **32**, is reported to be so stable towards air that several of these Heck reactions could be carried out in the absence of an inert atmosphere without any detrimental effect on yield. The catalyst has been shown to be effective in the reaction of iodo- and bromobenzene as well as in that of an aryl chloride with styrene.

Finally, palladium pincer complexes have already become useful catalysts in Heck reaction. These complexes are also be able to catalyse the traditionally diffucult Heck couplings of aryl chlorides or electron-rich aryl compounds.

1.6.2 Suzuki-Miyaura Cross Coupling Reaction

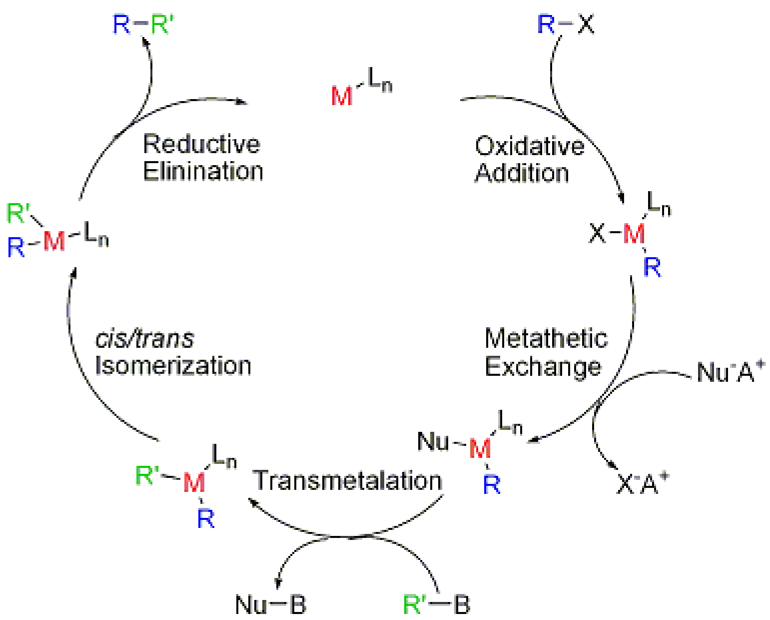
The Suzuki or Suzuki-Miyaura C-C coupling reactions consist in the reaction of a halobenzene with arylboronic acids in the presence of a base. This reaction proceeds by a similar reaction mechanism as that of the Heck reaction, thus most of the catalysts usually employed in the Heck coupling reactions have been succesfully employed in the Suzuki-Miyaura reaction too.



Scheme 1.12 Suzuki-Miyaura coupling reactions

The palladium-catalysed is regarded as one of the most efficient ways of forming a carbon–carbon bond. Unfortunately, substantially high catalyst concentrations and the difficulties and costs associated with the removal of palladium from the product have limited its commercial use.

The preference for the Suzuki-Miyaura reaction above other Pd-catalyzed cross-coupling reactions is not incidental. The key advantages of the Suzuki-Miyaura coupling are the mild reaction conditions and the commercial availability of the diverse boronic acids that are environmentally safer than the other organometallic reagents. The palladium catalysts show a broad tolerance towards various functional groups.

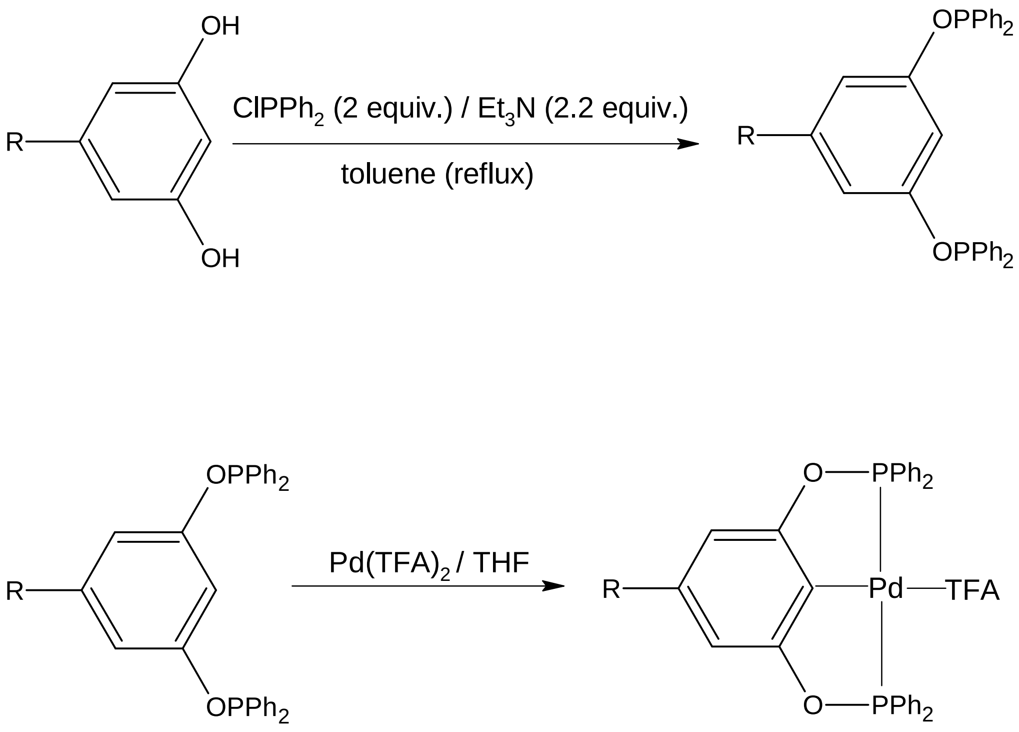


Scheme 1.13 General mechanism of Suzuki coupling reactions

The mechanism of the Suzuki coupling reactions consists of four main steps (Scheme 1.13): 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 (Suzuki, 1999; 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_2 CO_3, KOMe, TiOH and NaOH.

1.6.2.1 Phosphinito-Palladium PCP pincer complexes

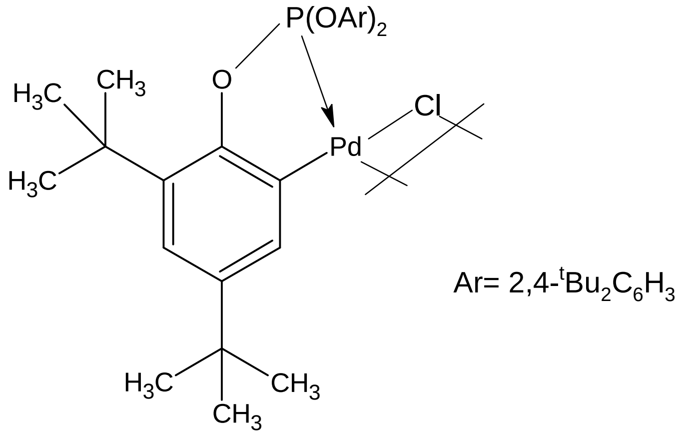
Pd(II) complexes which are having phosphinito PCP pincer ligands have been succesfully used by Bedford (Bedford et al., 2000) in the Suzuki coupling of various aryl halides and phenylboronic acid exhibiting quantitative yields and turn over numbers in the order of 92.000. These complexes are also efficent in the couplings of deactivated and sterically hindered aryl bromides. These catalysts can be easily synthesized from the corresponding diol in good yields (Scheme 1.14) and show no degradation in solutions open to air and in the presence of moisture for up to 10 days.



R= H (**33**) or Me (**34**)

Scheme 1.14 Synthesis of phosphinito-palladium PCP pincer complexes as a catalyst

While other catalysts for Suzuki reactions appear to be more active than the palladium pincer complexes **33** and **34**, e.g. the palladacycle **35**, these are often much more difficult and expensive to synthesize and are far less stable.



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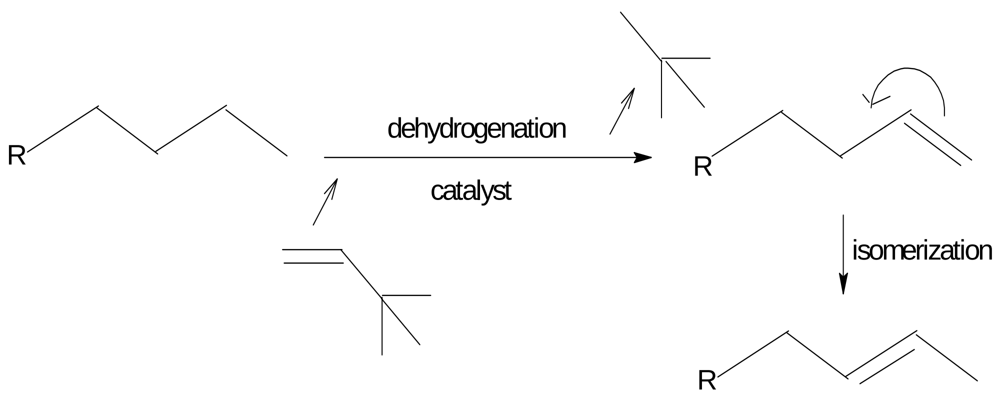
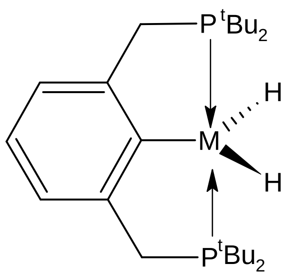
1.6.3 Dehydrogenation of Alkanes

Saturated hydrocarbons represent one of the most abundant and accessible feedstockss in our planet (Jones et al., 2000). However their use has been limited due to the instrinsic lack of reactivity of these compounds (Kakiuchi et al., 1999). An interesting alternative to this problem has been the use of transition metal complexes able to active C-H bonds under mild conditions (Burk et al., 1987). Some of these complexes have shown activity in the dehydrogenation of alkanes to alkenes. Many research groups are currently examining the production of important organic building blocks such as terminal alkenes through the dehydrogenation of readily-available alkanes.

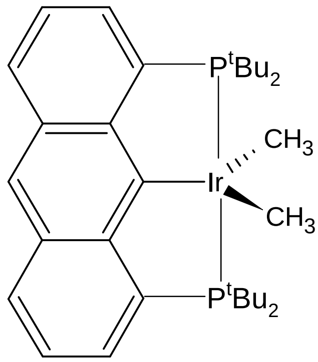


Scheme 1.15 Dehydrogenation reactions

In 1970, Moulton and Shaw were reported for the first time the synthesis of the complex $IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$(**36**) (Moulton et al., 1976).



M= Ir (**36**) or Rh(**37**)



38

These complexes have high thermal stabilities, subliming at a temperature >180 ^{0}C without any decomposition. use of dihydro-PCP pincer complexes (**36**) as potential catalysts for aliphatic dehydrogenations.

They observed that this compound exhibited a high thermal stability, subliming without visible decomposition at temperatures as high as 180 ^{0}C. These results, led independently to the research groups of Jensen (Gupta et al., 1996), Goldman (Wang et al., 1996) and Leitner (Leitner et al., 1997) to the use of derivatives of this complex for its potential application as catalysts in the dehydrogenation of alkanes. At 150 ^{0}C, the dehydrogenation of cyclooctane by the rhodium complex, $RhH_2\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2)$, using tert-butylethylene as sacrificial hydrogen acceptor. This compound has been tested at reaction temperatures as high as 200 ^{0}C, showing to be stable for periods of weeks. However the hydrogenation reaction using this complex only afforded 1.8 turnovers at 200 ^{0}C although decomposition of the catalyst was observed after 24 h (Lee et al., 1998).

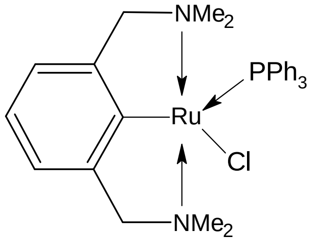
An attractively higher activity was observed using the iridium complex of $IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2P^tBu_2)_2$ (**36**). At 150 ^{0}C, dehydrogenation of cyclooctane preceded at 82 turnovers h^{-1}, while a rate of 720 turnovers h^{-1} was observed at 200 ^{0}C. The iridium complex also shows no decomposition for one week at both temperatures. Further experiments, determine that it was in fact iridium derivative (**36**) and not rhodium complex (**37**) the best hydrogenation catalyst. On the other hand, recently, Kaska and co-workers have reported an iridium PCP type complex (**38**) has demonstrated catalytic activity in the dehydrogenation of alkanes at temperatures as high as 250 ^{0}C without decomposition. Complex **36** do not match the performance of the complex **38** nor in yield of the terminal olefin or in the turn over numbers previously discussed.

Dihydroiridium PCP pincer complexes are highly active, robust catalysts for aliphatic dehydrogenation reactions. The unique nature of the pincer ligand allows the metal centre to react with C–H bonds of the substrate, while remaining unreactive towards the C–C and P–C bonds of the ligand. The high thermal stability of these complexes makes them highly-efficient catalysts for acceptorless dehydrogenations and their high activity provides the opportunity to selectively produce ά-olefins from linear alkanes. The tolerability of other functional groups present during dehydrogenation is still under investigation.

Unfortunately the complexes described are currently of limited practical value due to problems of product inhibition and/or the requirement of a sacrificial hydrogen acceptor. Modified PCP pincer complexes may provide a possibility for the commercial production of organic feedstocks through catalytic aliphatic dehydrogenation, if these problems can be overcome.

1.6.4 Hydrogen Transfer Reactions

Van Koten and co-workers have employed successfully ruthenium NCN (**39**) and PCP (**40** and **41**) pincer complexes to feature hydrogen transfer reactions to reduce ketones to their corresponding alcohols using iso-propanol as source of hydrogen and KOH as co-catalyst (Dani et al., 2000).



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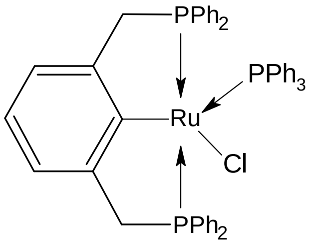

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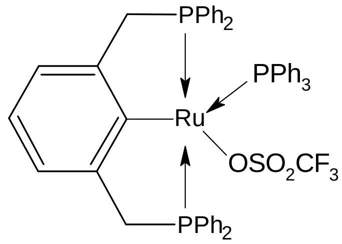

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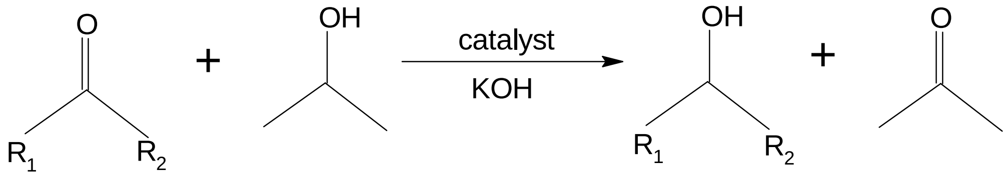
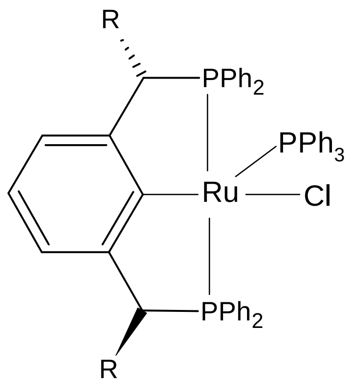


Scheme 1. **16** Hydrogen transfer reactions

Catalysts which are **39**, **40** and **41** were used in the transfer hydrogenation of several ketones. Although both complexes are active catalysts in this process, the best yields and turnover numbers where obtained with the PCP pincer derivatives, for instance, rof cyclohexanone, under reflux conditions, yields of 98% and turnover numbers of 27.000 were obtained, being these numbers the best so far obtained, compared with mono phosphine ruthenium complexes like $[RuCl_2(PPh_3)]$ or $[RuCl(H)(PPh_3)]$ (Naota et al., 1998). Given these results, several attempts have been done with the aim of this proses to obtain enantiomerically pure alcohols, among these the use of chiral ruthenium PCP pincer complexes which one is **41**. However, despite of the fact that complex **42** exhibits catalytic activity comparable to the non-chiral counterparts, the reaction of iso-PrOH and acetophenone only affords 14% (Albrecht et al., 2001).



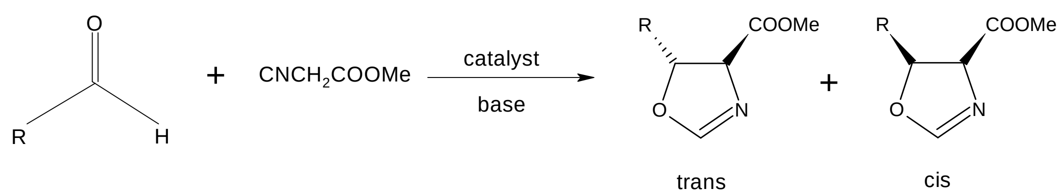
R= Me, Et

42

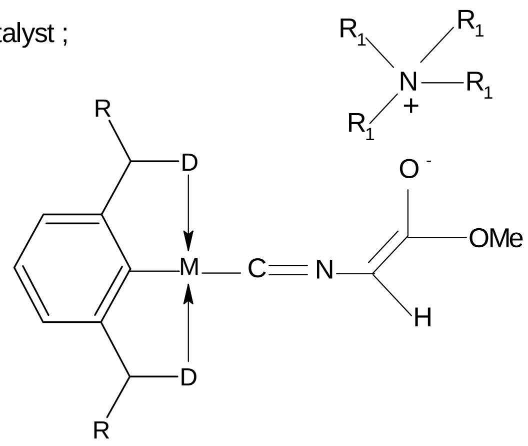
It is quite surprising that pincer complexes have only just begun to be investigated as potential transfer hydrogenation catalysts, for the reduction of ketones.

1.6.5 Aldolic Condensation Reactions

The synthesis of enantiomerically pure oxazolines can be conveniently done through the gold catalyzed (Ito et al., 1986) aldolic condensation reaction between an aldehyde or a ketone with an isocyanate. These kind of compounds are very important, since the consecutive hydrolysis of the oxazolines obtained by this procedure, offers a simple and efficient route for the synthesis of β-hydroxyaminoacids.



catalyst ;

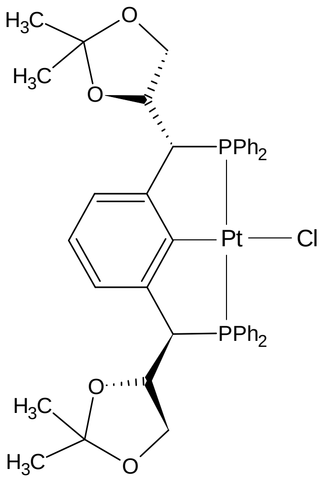


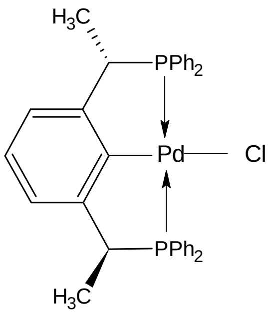
D= donor atom of the pincer complexes

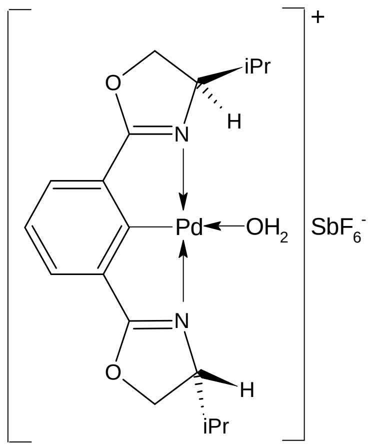
Scheme 1.17 Aldolic condensation reactions

Various platinum and palladium pincer complexes have been found to catalyse the aldol reactions of carbonyl compounds with isocyanates by providing a vacant coordination site for the isocyanoacetate. Before the aldol condensation can occur, the precoordinated isocyanate must be enolised by the addition of a base (Scheme 1.17) and this enolate can then react with the carbonyl compound.

Remarkable, the first enantiomerically pure pincer complexes of PCP type were appraised in this process. The first reported PCP platinum pincer complex (**43**) was designed by Venanzi (Gorla et al., 1994) and co-workers by introducing chiral acetals in the benzylic positions of the PCP ligands.





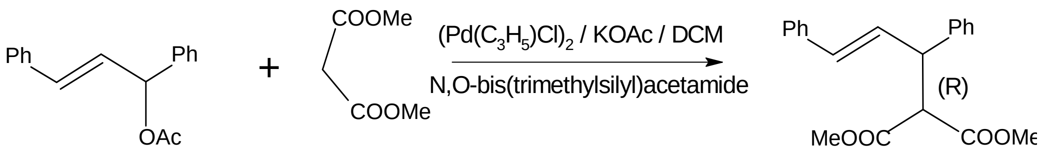


43 **44** **45**

The platinum derivative complex has shown to be active in the asymmetric aldolic addition of methyl-ά-isocyanoacetate with aldehydes to yield moderated enantiomeric yields of 32% and 65% for the corresponding cis and trans oxazolines respectively. Synthesis of this type of platinum complexes is diffucult and tedious, because of this its potential applications has been limited. On the other hand Zhang and co-workers (Zhang et al., 1998) have reported enantiomerically pure PCP pincer palladium complexes (**44**) The use of palladium derivatives in the same reaction reported by Venanzi, affords the formation of oxazolines in high yield, with high enantioselectivity for the formation of the cis-oxazolines. Other chiral pincer type complexes have also been employed (**45**).

1.6.6 Asymmetric Allylic Alkylation

In the recent years, the allylic alkylation reaction in its asymmetric fashion has received considerable interest, prouf of this is the tremendous number (more than a 1000) of chiral diphosphines that have been synthesized for this particular reaction. The complex **45** had originally been used to form the chiral pincer complex which could be used as a catalyst in asymmetric aldol reactions.



Scheme 1.18 Asymmetric allylic alkylation

The reported ease of synthesis of the complex **45** and the promising asymmetric alkylation, is however, encouraging for the further applications of palladium PCP pincer complexes as catalysts for asymmetric synthesis in the future.

2. EXPERIMENTAL

Solvents were dried on suitable drying agents and purified under inert conditions (Jolly, 1970). All synthesis were carried out using standard Schlenk tube techniques under inert atmosphere.

Starting compounds and reagents were obtained from Merck, Aldrich. 2,6-dihydroxypyridine, 3-hydroxypiperidine, diphenylchlorophosphine, triethylamine were purchased from Aldrich; dichloromethane, toluene, diethylether, hexane, pentane, acetone were purchased from Merck. $^{t}Bu_2PCl$ were synthesized according to the literature *(*Fild et al., 1973*)*. The starting complexes, $[PdCl_2(COD)]$ (Chat et al., 1957) and $[PtCl_2(COD)]$ (Komiya, 1997), which are used for preparation of new phosphine complexes were synthesized according to the method given in the literature.

$^{31}P\{^{1}H\}$-NMR, ^{1}H-NMR and ^{13}C-NMR spectras were recorded on a Varian AS 400 MHz spectrometer. As solvent $CDCl_3$ was employed. J values are given in Hz. IR spectra were obtained Perkin-Elmer spectrum used FT-IR spectrometer. Melting points were determined by electrothermal melting point detection apparatus. Elemental analyses were performed by the TÜBİTAK-Ankara Test and Analyse Laboratories. The yields of catalytic experiments were measured by GS (Agilent Technologies 6890N-Thermo-Finnigan on a HP-5 capillary column and with a FID detector)) in Ege University in Faculty of Science at Department of Chemistry. X-Ray data was measured in Ondokuz Mayis University, Turkey, for the use of the STOE IPDS II diffractometer. AFM analyses were performed by using Q SCOPE 250 SCANNING PROBE MICROSCOPE AMBIOS TECH. Thermogravimetric analyses were determined by Perkin Elmer Pyris 6 TGA.

2.1.1 Synthesis of pyridine-2,6-diyl bis[diphenyl(phosphinite)] (1a)

Triethylamine (0.21 g; 0.28 ml; 2.00 mmol) was slowly added to a suspension of 2,6-dihydroxypyridine (0.10 g; 0.68 mmol) in toluene (15 ml). The mixture was then cooled to -78 ^{0}C. Solution of PPh_2Cl (0.30 g; 0.25 ml; 1.36 mmol) in toluene (10 ml) was slowly added by dropwise. After addition, the mixture was stirred at room temperature for 24 h. The suspension was filtered by canula. Toluene was evaporated under vacuum. The product, **1a**, was formed as a white oil. The product was treated with hexane to eliminate the impurity from diphenylchlorophosphine.

2.1.2 Synthesis of pyridine-2,6-diyl bis[diphenyl(phosphinate)] (1b)

The base of triethylamine (0.21 g; 0.28 ml; 2.00 mmol) was slowly added at room temparature to a suspension of 2,6-dihydroxypyridine (0.10 g; 0.68 mmol) in toluene (10 ml). After stirring at room temperature, diphenylchlorophosphine (0.30 g; 0.25 ml; 1.36 mmol) in toluene (10 ml) was slowly added by dropwise at 0 ^{0}C to the mixture and stirred at 0 ^{0}C for 1 hour and then overnight at room temperature. The suspension was filtered by canula. After toluene was evaporated under vacuum, the resulting white oil was washed two times with acetone (20 ml x 2). Ligand **1b** precipitated as a white powder after removing acetone. It could be recrystallized from dichloromethane/ether (v.v = 1:3). Yield: 1.2 g; 94%, m.p= 133-135 ^{0}C, ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{0}C): δ= 7.23 (dd, 2H, -CH-, py^{2,4}), 7.36 (m, 4H, -CH-, ArH^{4}), 7.44 (dd, 1H, -CH-, py^{3}), 7.56 (m, 8H, -CH-, ArH^{3,5}), 7.21 (dd, 8H, -CH-, ArH^{2,6}), ^{31}P{^{1}H)-NMR ($CDCl_3$): 35 ppm, IR, cm^{-1} (CsI): 1149 υ(P=O), Anal. Calc. For $C_{29}H_{23}NO_4P_2$ (Mr=511.44): % C: 68.6, % H: 4.5, % N: 2.7; Found: % C: 66.7, % H: 5.6 , % N: 0.02.

2.1.3 Synthesis of pyridine-2,6-diyl bis[di-tert-butyl(phosphinite)] (2c)

This ligand has been synthesized before (Bernskoetter et al., 2009). In this study, we have succeed an alternative synthesis process by changing reaction conditions.

Triethylamine (1.02 g; 1.45 ml; 10 mmol) was added to a suspension of 2,6-dihydroxypyridine (0.50 g; 3.39 mmol) in toluene (10 ml). The mixture was stirred at room temperature 30 minutes. The temperature was decreased to 0 ^{0}C and then di-tert-butylchlorophosphine (0.74 g; 0.78 ml; 4.0 mmol) in toluene (10 ml) was slowly added dropwise to the mixture and a white precipitate was formed. Stirring was continued at room temperature overnight. The solvent was evaporated under vacuum and a white oil was formed, **2c**. The impurity from phosphine couldn't be eliminated because of the solubility of phosphine ligand isn't different from the solubility of di-tert-butylchlorophosphine. $^{31}P\{^1H\}$-NMR ($CDCl_3$): 157 ppm

2.1.4 Synthesis of 1-(diphenylphosphino)piperidine-3-yl diphenyl phosphinite (3a)

To a suspension of 3-hydroxypiperidine (0.05 g; 0.53 mmol) in toluene (10 ml) was added Et_3N (0.20 g; 0.20 ml; 1 mmol). The mixture was then cooled to -78 ^{0}C. A solution of PPh_2Cl (0.22 g; 1 mmol; 0.19 ml) in toluene (10 ml) was slowly added dropwise and stirred at -78 ^{0}C for 1 h and the temperature was raised to 0 ^{0}C. Stirring was maintained at 0 ^{0}C for 1 h and then at room temperature for 30 min. By the reason of oxidation, the solution wasn't filtered.

2.1.5 Synthesis of chloro{pyridine-2,6-diylbis[diphenyl(phosphinite)]} Pd(II) chloride (1a')

$PdCl_2$(COD) (0.11 g; 0.39 mmol) was added to a stirred solution in toluene (10 ml) of ligand **1a** (0.18 g, 0.39 mmol). Then 10 ml of toluene was added to the mixture. The mixture was heated at 110 ^{0}C and stirred 4 hours. Orange precipitate was formed. Than solution was removed under vacuum. The resulting orange powder, **1a'**, was washed with pentane (2x5 ml) to eliminate impurity of ligand. And than dried under vacuum. Yield: 0.22 g; 89%, m.p= 181-182 ^{0}C, ^{1}H NMR (400 MHz, $CDCl_{3,}$ 25 ^{0}C): δ= 7.25 (s, 2H, -CH-, py^{2,4}), 7.34 (m, 4H, -CH-, ArH^{4}), 7.43 (dd, 1H, -CH-, py^{3}), 7.45 (m, 8H, -CH-, ArH^{3,5}), 7.72 (dd, 8H, -CH-, ArH^{2,6}), IR, cm^{-1} (CsI): 286 υ (Pd-Cl), $^{31}P\{^1H\}$-NMR ($CDCl_3$)= 183 ppm.

2.1.6 Synthesis of chloro{pyridine-2,6-diyl bis[diphenyl(phosphinate)]} Pd(II) chloride (1b')

Suspension of **1b** (0.23 g; 0.34 mmol) in toluene (20 ml) was slowly added at room temperature to $PdCl_2$(COD) (0.10 g; 0.35 mmol). After addition the mixture was heated to 110 ^{0}C and stirred overnight. The solvent was removed under vacuum. After concentration of the solution and addition of pentane (10 ml x 2) to eliminate of impurities, complex **1b'** was precipitated as a light yellow powder. Yield: 0.18 g; 64%, m.p= 238 ^{0}C (decomposed), ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{0}C): δ= 7.24 (dd, 2H, -CH-, py^{2,4}), 7.34 (m, 4H, -CH-, ArH^4), 7.44 (dd, 1H, -CH-, py^3), 7.56 (m, 8H, -CH-, ArH^{3,5}), 7.79 (dd, 8H, -CH-, ArH^{2,6}), IR, cm^{-1} (CsI): 1108 υ(P=O), 492 υ(Pd-N), 434 υ(Pd-O), 333 υ(Pd-Cl), ^{31}P{^{1}H)-NMR ($CDCl_3$)= 79 ppm, Anal. Calc. For $C_{29}H_{23}ClNO_4P_2Pd$ (Mr= 546.89): % C:50.5, % H:3.4; Found: % C:52.6, % H:3.9) .

2.1.7 Synthesis of chloro{pyridine-2,6-diyl bis[diphenyl(phosphinate)]} Pt(II) chloride (1b'')

This complex has been prepared analogously to **1b'** with $PtCl_2$(COD) (0.10 g; 0.26 mmol) and **1b** (0.14 g; 0.27 mmol) as the starting materials. The product was precipitated as a white powder, **1b''**. Yield: 0.17, 91%; m.p= 175-179 ^{0}C, ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{0}C): δ= 7.23 (dd, 2H, -CH-, py^{2,4}), 7.34 (m, 4H, -CH-, ArH^4), 7.32 (dd, 1H, -CH-, py^3), 7.52 (m, 8H, -CH-, ArH^{3,5}), 7.71 (dd, 8H, -CH-, ArH^{2,6}), IR, cm^{-1} (CsI): 1109 υ(P=O), 499 υ(Pt-N), 454 υ(Pt-O), 337 υ(Pt-Cl), ^{31}P{^{1}H)-NMR ($CDCl_3$)= 50 ppm, Anal. Calc. For $C_{29}H_{23}ClNO_4P_2Pt$ (Mr=741.97): % C:44.8, % H:3.0; Found: % C:44.8, % H:3.4) .

2.1.8 Synthesis of chloro{pyridine-2,6-diyl bis[di-tert-butyl(phosphinite)]} Pd(II) chloride (2c')

Ligand of **2c** (0.13 g; 0.34 mmol) was dissolved in toluene (20 ml). Then $PdCl_2$(COD) (0.09 g; 0.34 mmol) was added to the stirring mixture. The solution was heated to reflux temperature for 10 hours. After 10 hours the resulting solution was cooled to room temperature. The precipitate was eliminated. The solvent was removed under vacuum. The remaining dark-yellow solid was washed with pentane (10 ml x 2). Then, the dark-yellow powder (**2c'**) was formed. Yield: 0.91, 87%, m.p= 156-158 ^{0}C, , ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{0}C): δ= 1.59 (vt, 36 H, P-$C(CH_3)$)), 6.55 (d, 2H, m-C_6H_3N), 7.69 (t, 1H, p-C_6H_3N), IR, cm^{-1} (CsI): 286 υ(Pd-Cl), ^{31}P{^{1}H)-NMR ($CDCl_3$)= 198 ppm.

2.1.9 Synthesis of dichloro{1-(diphenylphosphino)piperidine-3-yl diphenylphosphinite} Pd(II) (3a')

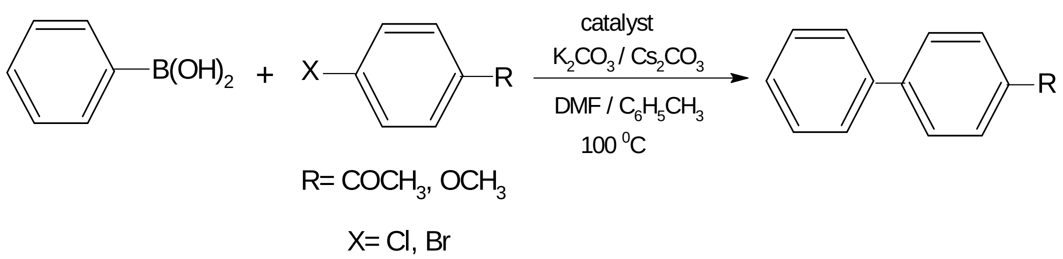
PdCl$_2$(COD) (0.14 g; 0.50 mmol) was added to mixture of ligand **3a** (0.23 g; 0.53 mmol) in toluene (20 ml) . The reaction mixture was heated to reflux temperature and was stirred for 4 hours leading to a colour change from white to yellow. The solvent was removed under vacuum. The product, **3a'**, was precipitated with acetone, water and Et_2O and then dried under vacuum. It could be recrystallized from dichloromethane/ether (v:v = 1:3). Yield: 0.25 g, 88%; m.p= 218-220 ^{0}C, ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{0}C): δ= 1.64 (dd, 2H, -CH_2-, piperidine), 2.99 (m, 2H, -CH_2-, piperidine), δ= 3.25 (q, 2H, N-CH_2-, piperidine), 3.60 (m, 2H, -CH_2-N, piperidine), 4.58 (t, 1H, CH-O, piperidine), 7.19-8.07 (m, 20H, ArH), IR, cm^{-1} (CsI): 283, 306 υ(Pd-Cl), ^{31}P{^{1}H) NMR ($CDCl_3$): δ= 91 ppm (P-N), 99 ppm (P-O), ^{13}C{^{1}H) NMR (400 MHz, $CDCl_3$): δ= 19.27 (s, -CH_2-, piperidine), 28.95 (s, -CH_2-, piperidine), 46.48 (s, N -CH_2-, piperidine), 52.07 (s, -CH_2-N, piperidine), 70.78 (d, -CH-O, piperidine), 126.74-134.26 (m, Ar), Anal. Calc. For $C_{29}H_{29}Cl_2NOP_2Pd$ (Mr= 540.39): %C 57.07, %H 4.62; Found: %C 57.76, %H 4.68,.

2.1.10 Synthesis of dichloro{1-(diphenylphosphino)piperidine-3-yl diphenyl phosphinite} Pt(II) (3a'')

This complex (**3a''**) has been prepared analogously to **3a'** with PtCl$_2$(COD) (0.15 g; 0.40 mmol) and **3a** (0.19 g; 0.41 mmol) as the starting materials. Yield: 0.23 g; 87%; m.p= 184-185 ^{0}C, ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{0}C): δ= 1.93 (dd, 2H, -CH_2-, piperidine), 2.99 (m, 2H, -CH_2-, piperidine), δ= 3.16 (q, 2H, N-CH_2-, piperidine), 3.69 (m, 2H, -CH_2-N, piperidine), 5.03 (t, 1H, CH-O, piperidine), 7.23-8.21 (m, 20H, ArH), IR, cm^{-1} (CsI): 285, 309 υ(Pt-Cl), ^{31}P{^{1}H)-NMR ($CDCl_3$): δ= 65 ppm (P-N), 71 ppm (P-O), ^{13}C NMR (400 MHz, $CDCl_3$): δ= 19.06 (s, -CH_2-, piperidine), 29.14 (s, -CH_2-, piperidine), 44.89 (s, N -CH_2-, piperidine), 51.91 (s, -CH_2-N, piperidine), 70.51 (d, -CH-O, piperidine), 127.17-134.63 (m, Ar), Anal. Calc. For $C_{29}H_{29}Cl_2NOP_2Pt$ (Mr= 735.47): %C 47.36, %H 3.97; Found: %C 46.11, %H 4.19.

2.2 Catalytic Experiments

2.2.1 General procedure for the Suzuki coupling reactions



In a typical run, a two-necked 25 mL flask fitted with a reflux condenser and septum was charged with aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), Cs_2CO_3 (1.5 mmol) or K_2CO_3 , diethyleneglycol di-*n*-butyl ether (0.6 mmol, internal standard) and the palladium-phosphine catalyst (1mol%) in 3 mL of DMF or toluene was added. The flask was placed in a preheated oil bath (100 ^{0}C) under an argon atmosphere. The conversion was monitored by gas chromatography.

2.3 Thermal Stability (TGA) of 1b’, 2c’ and 3a’

Thermal stability of complexes were measured method of TGA-DTG. By using this results the gradient of the TGA-DTG for complex **1b**’, **2c’** and **3a’**.

2.4 AFM Analysis of 1b', 2c' and 3a'

For conducting of catalytic experiments of Suzuki-Miyaura cross coupling reactions comprehensively, we decided to investigate of new synthesis complexes' surface properties. Exquisite film of compounds had obtained by metod of removing solvents from compound on a glass material to view by using Q SCOPE 250 SCANNING PROBE MICROSCOPE AMBIOS TECH (use of 20 micron tool and modal of non-contact).

2.5 X-ray Crystal Structures of Complex 3a'

Light yellow, single crystals of compound **3a'** were obtained by a slow diffussion of a dichloromethane/diethylether system (v:v = 1:3) at room temperature. A crystal dimensions 0.47 x 0.25 x 0.04 mm was used for data collection. Intensity data for complex **3a'** were collected on a STOE IPDS II diffractometer using graphite-monochromated Mo Kά radiation (λ= 0.71073 Å). A total of 8224 reflections having I>2\s(I) were regarded as observed and used in the structure analysis. The pertinent details of data collection and the final cell dimensions are given in Table 3.1. All positional and thermal parameters were refined by using SHELXL-97 program. The hydrogen atoms could have been identified but were not included in the refinement process. Atomic coordinates, bond lengths and angles have been deposited with the Cambridge Crystallographic Data Center as 793538, 12 Union Road, Cambridge CB2 1EZ, U.K. Selected bond distances and angles are listed in Table 3.2.

3. RESULTS AND DISCUSSION

All pincer ligands, amidophosphine-phosphinite ligand and phosphine-phosphinite complexes exhibit very good solubility in most organic solvents as toluene, THF, dichloromethane, chloroform etc. Phosphine complexes are cleanly in good isolated yields. All palladium and platinum complexes which are new synthesis are thermally stable and also that are stable moisture, to air both in the solid state and in oxygen-free solution.

The identity of the ligands and complexes were established by $^{31}P\{^1H\}$-NMR and also ligand **1b** and the complexes were established by ^1H-NMR, ^{13}C-NMR spectroscopy, FT-IR and by elemental analysis, too.

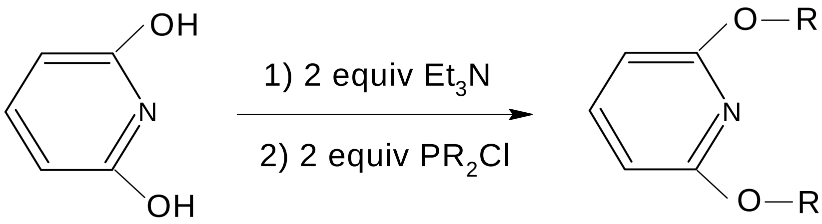
Also, single crystals of complex **3a'** suitable for X-ray diffraction were obtained by slow diffussion of a dichloromethane/diethylether system (v:v = 1:3) at room temperature. Therefore the identity of **3a'** was established by X-Ray crystallography. Structural view of **3a'** is showed in Figure 3.25, with selected geometric data is depicted in Table 3.1. Moleculer structure of new palladium complex display the usual square planar coordination around the palladium center with the two chlorine atoms in cis positions.

3.1 Synthesis and Characterization of PONOP Ligands

Metallosupramolecules of pincer complexes, the introduction of several functional groups at the para-position of the centered arene ring of pincer ligands (see Scheme 1.4) has been achieved (Albrecht et al., 2001; Steenwinkel et al., 1998; Back et al., 2001; Gagliardo et al., 2007). Mechanistic investigations evidenced that the methylene groups on the PNP ligands play an important role in the reactivity of the metal complexes (Rahmouni et al., 1998; Zhang et al., 2006; Zhang et al., 2005). These CH_2 groups are susceptible to deprotonation by external base or the transition metal itself resulting in dearomatization of the ligand (Feller et al., 2006; Ben-Ari et al., 2006).

In addition to factors that could change the thermodynamics and kinetics of C-H activation reactions, the PONOP ligands offers the advantage of enchanging the reactive $–CH_2$- sites on PNP for an –O- linking unit which avoids the posibility of ligand deprotonation. Also P-O bonds can be made more dependably than the P-C bonds (Ozerov et al., 2006). An analogous species of the PNP ligand would obtain new types of pincer ligands 2,6-bis(di-tert-butylphosphinito)pyridine, 2,6-bis(di-tert-butylphosphinate)pyridine which are called PONOP.

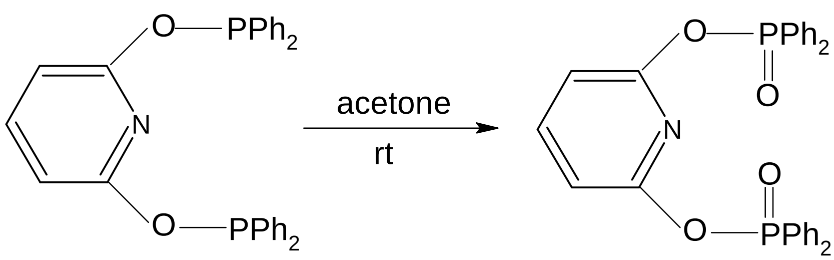
The neutral, tridentate PONOP ligands **1a** and **2c** have been easily synthesized in one step from 2,6-dihydroxypyridine hydrochloride. The alcohol functions were first deprotonated with 2 equiv triethylamine, and the resulting compound reacted with 2 equiv diphenylchlorophosphine (**1a**) or di-tert-butylchlorophosphine (**2c**) at 0 ^{0}C than stirred 24 hours at room temperature (Scheme 3.1). Both ligands were formed as a colourless oil in good yields. Both phosphorus atoms are equivalent, the chemical shift of their $^{31}P\{^{1}H\}$-NMR signal, for **1a**, we expected a singlet signal but there were three signals at 121, 137 and 136 ppm (Figure 3.1) that the same length. We couldn’t bet which signal was our complex’s. Also by purification, the ligand was oxidized. So we hadn’t made further purification and synthesized complex of **1a’** by using one pot metod. For complex **2c** a singlet at 157 ppm (Bernskoetter et al., 2009) that lies in the normal range for a phosphinite ligand (Salem et al., 2009*).* For each ligands, the ^{1}H-NMR spectrum indicates the presence of impurities, which gives rise to peaks in the aromatic and aliphatic regions. Removal of the impurities by recrystallization was not succesfully by the reason of oxidation. These ligands are too sensitive to oxygen, thus can’t be handled in the open air. The diffuculty with route is separation of the ligands from the generated impurities due to similar solubilities. Only since these are reasons for couldn’t carried out further purification. Therefore, for these ligands have been afforded only $^{31}P\{^{1}H\}$-NMR signals, couldn’t afford ^{1}H-NMR signals.



R= PPh_2 (**1a**), P^tBu_2 (**2c**)

Scheme 3.1 Synthesis of PONOP ligands, **1a** and **2c**

On the other hand, when ligand **1a** washed with acetone 24 hours at room temperature, a white solid precipitated and gives ligand of **1b** (see Scheme 3.2) such as pure type, in high yield, %94. It was isolated as a white powder, stable in air and moisture, also characterized by $^{31}P\{^1H\}$-NMR, ^1H-NMR, FT-IR and elemental analysis. The $^{31}P\{^1H\}$-NMR spectrum of **1b** displays a singlet at 35 ppm (Figure 3.2). The value of the $^{31}P\{^1H\}$-NMR spectrum has featured that the ligand was oxidized and P=O bond was formed. *(*Bhattacharyya et al., 1995; Balakrıshna et al., 1993*).* The ^1H-NMR spectrum (Figure 3.3) exhibits a doublet at 7.23 ppm and triplet at 7.44 ppm assigned to the aromatic protons of the pyridine. The presence of $\upsilon_{P=O}$ signal at 1149 cm^{-1} in the IR spectrum (Figure 3.4) of **1b** is characteristic for P=O (Cao et al., 2009). Also this structure is supported with events of elemental analysis, too.

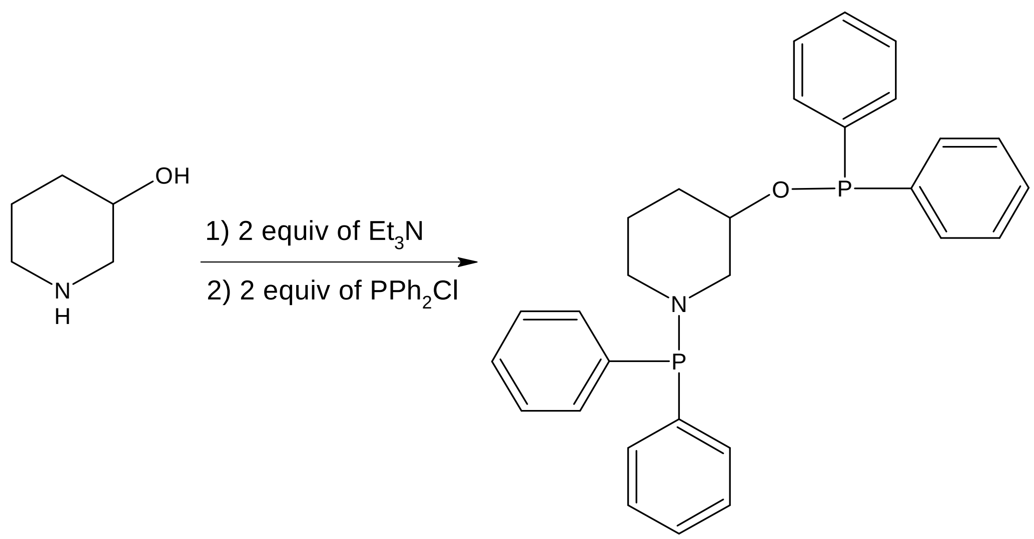


1a **1b**

Scheme 3.2 Synthesis of PONOP ligand, **1b**

Organophosphorus ligands such as tertiary phosphine oxides chalcogenide bearing O donor atom have got much attention due to its coordination chemistry, extractive metallurgy, catalytic properties and structural chemistry (Lobana et al., 2002; Andrews et al., 1989). Transition metal complexes, as palladium or platinum complexes featuring phosphine oxide auxiliary ligands are comparatively rare.

On the other hand in this study we have sythesised a kind of amidophosphine-phosphinite ligand (**3a**) which starting material is 3-hydroxy piperidine. The sythesis of this ligand could be achieved, via one-step procedure. First, addition of 2 equiv of Et_3N to 3-hydroxypiperidine, than 2 equiv of PPh_2Cl at -78 ^{0}C in the presence of toluene and stirred 2 hours at 0 ^{0}C (Scheme 3.3). We tried to eliminate and purificate the ligand but it isn’t stable in air or in solution. Also, when the solvent removed by vacuum, the ligand was oxidized; because of this, there were lots of peaks in the $^{31}P\{^1H\}$-NMR spectrum. So it couldn’t be characterized any spectroscopic metods.

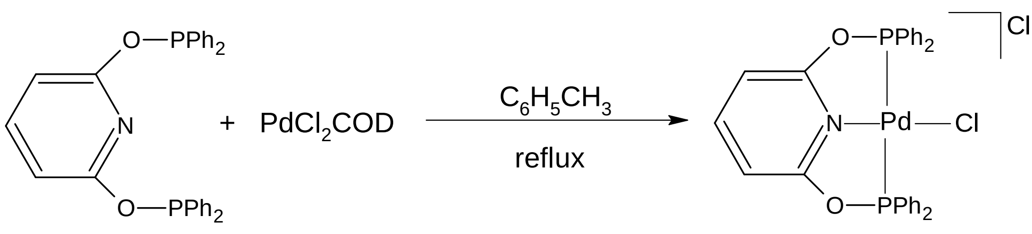


3a

Scheme 3.3 Synthesis of amidophosphine-phosphinite ligand, **3a**

3.2 Synthesis and Characterization of PONOP Palladium and Platinum Complexes

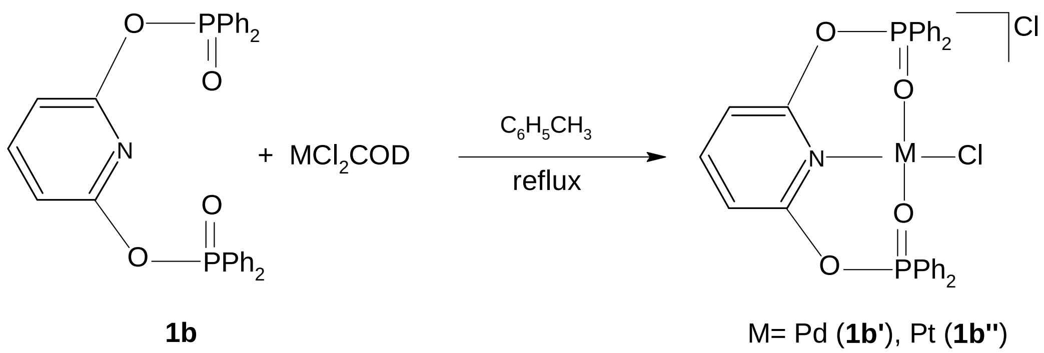
Pyridine-2,6-diyl bis[diphenyl(phosphinite)] PONOP ligand (**1a**) was converted into the complex [PdCl $(PONOP)^{Ph}$] (**1a'**) in thundering yields 89%, by reaction with 1 equiv of $PdCl_2$(COD) in toluene at reflux temperature for 4 hours (Scheme 3.4). The resulting compound was isolated from the corresponding reaction mixture as orange powders, that was stable off in solids, water and 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 (Figure 3.5) at 183 ppm, indicative of both phosphorus being equivalent. For ^{1}H-NMR spektrum (Figure 3.6) reveals this complex, exhibiting signals concerning to the aromatic rings of phenyl groups and pyridine group for the phosphinite complex at 7.25-7.72 ppm. The presence of Pd-Cl bond is indicated by IR spectroscopy (Figure 3.7) which shows a strong υ(Pd-Cl) at 286 cm^{-1}, is an argument for bonding to N in pyridine ring and be consisted of [PdCl $(PONOP)^{Ph}$] (**1a'**) pincer complex. On the other hand this reaction was attempted with $PtCl_2$COD to make [PtCl$(PONOP)^{Ph}$] pincer complex but it couldn't be synthesized. By changing reaction conditions, synthesis platinum-PONOP complex was experienced. Unfortunately we weren't be successful.



1a **1a'**

Scheme 3.4 Synthesis of [PdCl $(PONOP)^{Ph}$] complex, **1a'**

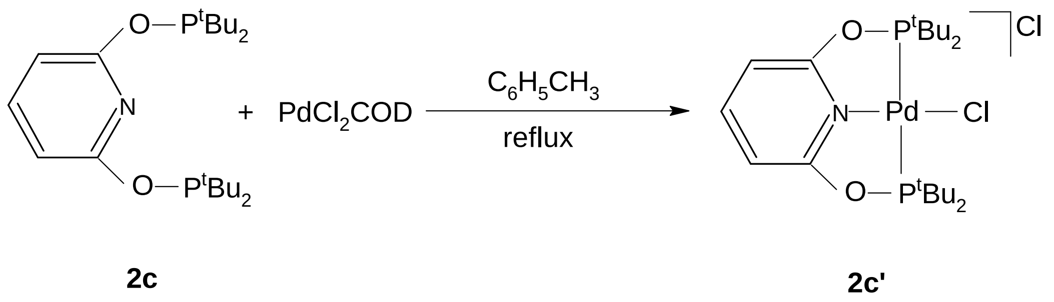
Metal complexes of phosphine chalcogenides particularly sulfides, oxides and selenides are reported (Dutta et al., 2006; Dutta et al., 2006; Chutia et al., 2004). But, to our knowledge, there is no report of palladium or platinum complexes which contain pyridine structure with oxide phosphine as chalcogen donor ligands. In this study, we have synthesized a new type of palladium (**1b'**) and platinum (**1b''**) phosphinate complexes. Their synthesis processes were very similar. The ligand of **1b** was stirred with 1 equiv of MCl_2(COD) (M= Pd (**1b'**), Pt (**1b''**)) at 110 ^{0}C, nearly 24 hours, than washed with pentane, complex of **1b'** was precipitated as a light yellow powder in tolerable yield, 64% and complex of **1b''** was precipitated as a white powder in good yield, 91% (Scheme 3.5). The chemical structures of **1b'** and **1b''** were confirmed by $^{31}P\{^1H\}$-NMR, ^1H-NMR spectroscopy, FT-IR and elemental analysis. In the $^{31}P\{^1H\}$-NMR (Figure 3.8) of **1b'** displays a singlet at 79 ppm lies in the normal range for a phosphinate (Meguro et al., 2008). ^1H-NMR spectrum (Figure 3.9) of **1b',** the signals assigned to the 2H at 7.24 ppm and 1H at 7.44 ppm of the pyridine ring, was observed and multiplet resonances 7.34 ppm, 7.56 ppm, 7.79 ppm which is attributable to the three equivalent phenylic protons. The IR spectrum (Figure 3.10) of the complex **1b'** shows υ(P=O) bands in the region 1108 cm^{-1} (Cao et al. 2009). υ(Pd-N) and υ(Pd-O) values are 492 cm^{-1} and 434 cm^{-1} respectively (Nakamoto, 1986). υ(Pd-Cl) bands in the region of 333 cm^{-1}. Also this structure is supported with events of elemental analysis.



Scheme 3.5 Synthesis of Palladium (**1b'**)/Platinum(**1b''**) phosphinate complexes

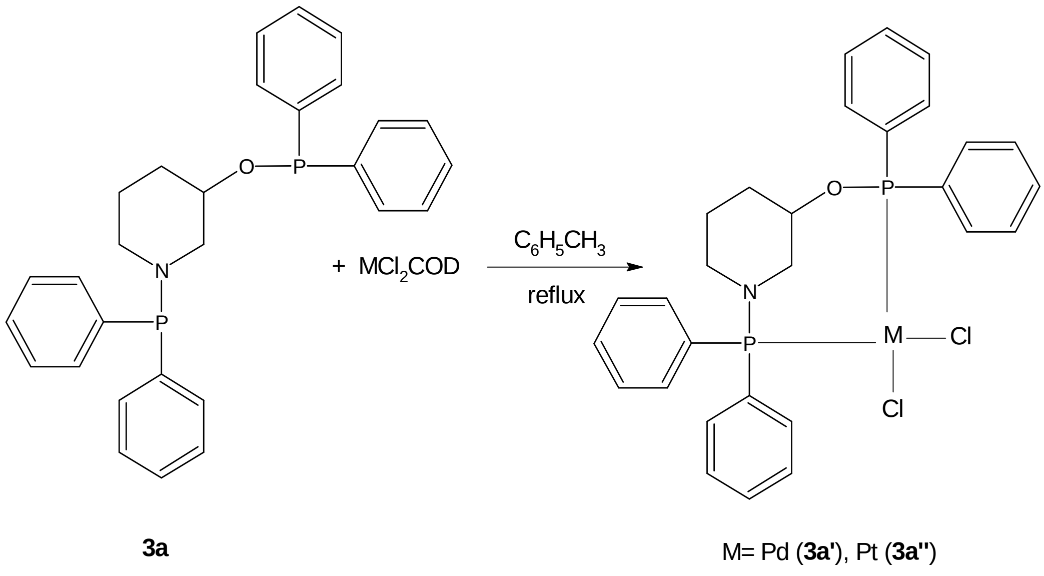
For the $^{31}P\{^1H\}$-NMR (Figure 3.11) signal of complex **1b''** at 50 ppm as a singlet and this upfield shift, value of $^1J_{P\text{-}Pt}$ (4090) is charecteristic. ^1H-NMR spectrum (Figure 3.12) of **1b''** the signals assigned to the 2H at 7.23 and 1H at 7.32 ppm of the pyridine ring, was observed and multiplet resonances 7.34 ppm, 7.52 ppm, 7.71 ppm which is attributable to the three equivalent phenylic protons. The IR spectrum (Figure 3.13) of the complex **1b''** shows υ(P=O) bands in the region 1109 cm^{-1}. υ(Pt-N) and υ(Pt-O) values are 499 cm^{-1} and 454 cm^{-1} respectively (Nakamoto, 1986). υ(Pt-Cl) bands in the region of 337 cm^{-1}. Also this structure is supported with events of elemental analysis, too. However all of this spectroscopic analysis, we aren't be sure that these complexes bond as a pincer type because we couldn't obtained suitable, single crystals for X-ray analysis. But the structure is most probably like this.

The synthesis of palladium complex **2c'** was achieved by reacting ligand **2c** with 1 equiv $PdCl_2(COD)$ in toluene 10 hours at reflux temperature (Scheme 3.6). Complex **2c'** was isolated in good yields, 87%, as an air stable, dark-orange solids after purification. The complex of **2c'** contains two five-membered metallacycles. Though the structure of the intermediary complex was investigated in details. Both phosphorus atoms are equivalent. The singlet peak observed in the $^{31}P\{^1H\}$-NMR spektrum (Figure 3.14) which is giving signal at 198 ppm suggests that ligand **2c** is coordinated to palladium, lies in the normal range for a phosphinite complex (Eberhard et al., 2003), and a symmetrical complex **2c'** is formed. On the other hand, at the ^1H-NMR spectrum (Figure 3.15), coordination of the pyridine moiety evidenced by a significant downfield shift of the H aromatic signals which are doublet at 6.55 ppm and triplet at 7.69 ppm. Further support comes from the IR spectrum (Figure 3.16) which shows one distinct υ(Pd-Cl) stretches at 286 cm^{-1}.



Scheme 3.6 Synthesis of Pd-PONOP^{ter} complex, **2c'**

New amidophosphine-phosphinite complexes **3a'** and **3a''** were easily prepared from 1-(diphenylphosphino)piperidine-3-yl diphenyl phosphinite **(3a)** ligand by a one pot amidophosphine-phosphinite palladium and platinum sequence, according to procedures similar to described in the literature (Assen et al., 2008; Ozerov et al., 2006).



Scheme 3.7 Synthesis of amidophosphine-phosphinite complexes, **3a'** and **3a''**

The ligand is later on treated with the $PdCl_2(COD)$ and $PtCl_2(COD)$ at 110 ^0C, 24 hours, by using toluene as solvent, to yield destination complexes **3a’** and **3a’’** (see Scheme 3.7). In contrast to the free ligand **3a**, which is quite air sensitive, complexes **3a’** and **3a’’** are stable off in solids, water and can be stored in air over long periods of time. When acetone was used as solvent, a yellow precipitate of complex **3a’** was formed in good yields, 88% and besides by using acetone as solvent, a white precipitate of complex **3a’’** was gradually formed in good yields, 87% too. The new complexes of **3a’** and **3a’’** are for the first time synthesis. They have been characterized by $^{31}P\{^1H\}$-NMR, ^1H-NMR, ^{13}C-NMR, FT-IR and elemental analysis. Also this structure is supported with events of elemental analysis, too. Although the identity of **3a’** was established by X-ray crystallography.

For the palladium complex **3a’**, $^{31}P\{^1H\}$-NMR spectrum (Figure 3.17) revealed significant shifts of the doublets for 91 ppm, P(N) and 99 ppm, P(O) assigned to the diphenylphosphino groups coordinated to nitrogen and oxygen (Cesarotti et al., 1989) and palladium respectively, thus confirming that the two phosphorus atoms aren’t magnetically equivalent and that the structure isn’t symmetric. On the other hand in the ^1H-NMR spectrum (Figure 3.18) there is a triplet at 4.58 ppm for CH-O proton. At 3.60 ppm and 3.25 ppm, there are multiplets for piperidine protons which can’t be bond to palladium. Also exhibiting signals concerning to the aromatic rings of phenyl groups between at 7.19-8.07 ppm. In ^{13}C-NMR spectrum (Figure 3.19), the signals of phenyl carbons are between 134 ppm and 126 ppm. The carbon atom signal between CH-O and N is at 52.07 ppm and also CH-O carbon atom signal is at 70.75 ppm. Further support comes from the IR spectrum (Figure 3.20) 283 and 306 cm^{-1} that υ(Pd-Cl).

For the platinum complex **3a’’**, $^{31}P\{^1H\}$-NMR spectrum (Figure 3.21), shows two signals as doublets for 65 ppm and 71 ppm for the $–NPPh_2$ and $–OPPh_2$ resonances which ^{195}Pt satellites are 4204 Hz (^{1}JPt,P(N)) and 4050 Hz (^{1}JPt,P(O)) respectively. The value of the signals are responsively seven-membered platinum complexes (Naili et al., 1995; Agbossou et al., 1995). ^1H-NMR spectrum (Figure 3.22) there is a triplet at 5.03 ppm for CH-O proton. At 3.69 ppm and 3.42 ppm, there are multiplets for piperidine protons which can’t be bond to platinum. Also exhibiting signals concerning to the aromatic rings of phenyl groups between at 7.23-

8.21 ppm. There are signals which are phenyl carbons are between 134 ppm and 127 ppm in ^{13}C- NMR spectrum (Figure 3.23) of the complex **3a''**. The carbon atom signal between CH-O and N is at 51.91 ppm and also CH-O carbon atom signal is at 70.51 ppm. IR spectrum (Figure 3.24) (CsI, pellet) shows two distinct υ(Pt-Cl) stretches at 285 and 309 cm^{-1} consistent with a cis-$PtCl_2$ geometry (Bhattacharyya et al., 1996*).* Also this structure is supported with events of elemental analysis, too.

3.3 X-ray Diffraction Studies for the Palladium Complex of 3a'

Crystalline, single, yellow crystals of **3a'** grown by slow diffusion from a dichloromethane-diethylether (v:v =1:3) solvent system in diffussion. The details of the structure determination are given in Table 3.1 and selected bond lengths and angles are listed in Table 3.2. A view of the molecule is depicted in Figure 3.25 together with the numbering scheme adopted. Analysis of the coloured crystals reveals the palladium center to be located into a lightly distorted square planar environment with angles of $98.99(4)^0$ for P(1)-Pd(1)-P(2); $84.78(4)^0$ for P(2)-Pd(1)-Cl(2); $92.84(4)^0$ for Cl(2)-Pd(1)-Cl(1); $84.72(4)^0$ for Cl(1)-Pd(1)-P(1), respectively. The metal-phosphorus bonds as Pd-P(O)= 2.2487(12) Å; Pd-P(N)= 2.2585(13). Å expect that the Pd-P(O) bond is somewhat shortened than Pd-P(N) bond.

Table 3.1 Crystal data and structure refinement for the complex **3a'**

Empirical formula	$C_{29}\,H_{29}\,Cl_2\,N\,O\,P_2\,Pd$
Formula weight	646.77
Crystal colour	Light yellow
T (K)	296
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	H-M 'P 21/c'
Description	prism
Unit cell dimension	
	a= 20.5304(12) Å, α= 90.00°
	b=14.4110(5) Å, β= 120.557(4)°
	c= 22.1063(15) Å, γ= 90.00°
Z	8
D_{calc} (Mg/m^3)	1.526
Volume, Å^3	5632.1(5)
Crystal size, mm^3	0.47 x 0.25 x 0.04
Theta range, ^{0}	1.41 to 27.33^0
F (000)	2624
Independent reflections (R_{int})	76053 (0.0688)
R1, all data	0.0866
R1, [I >2σ(I)]	0.0514
Max. / min transmission	0.87 / 0.70
Detector distance, mm	120

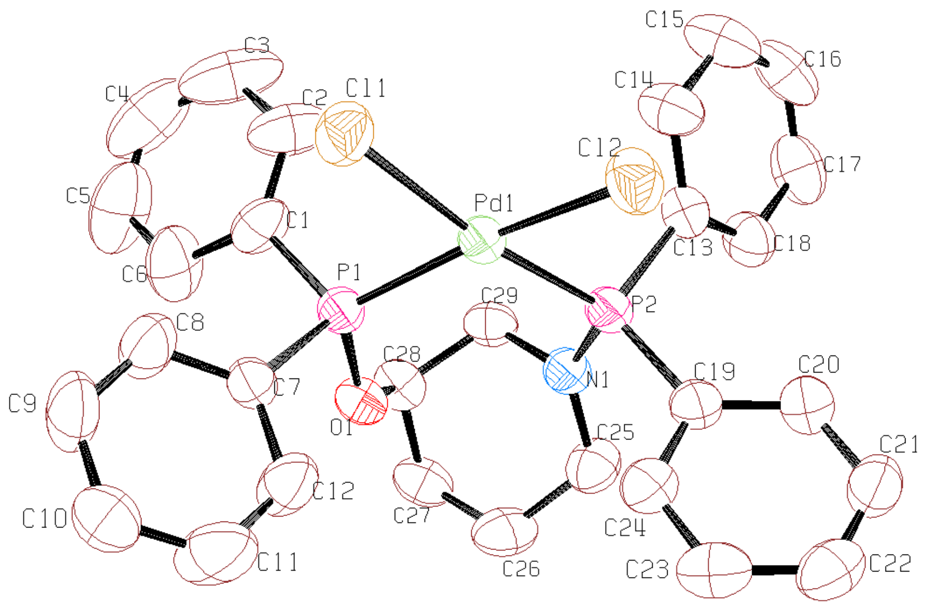


Figure 3.25 Moleculer structure of **3a'** complex

As we see the moleculer view of compound **3a'**, the palladium atom is coordinated to two chlorine atoms, the phosphorus atoms of a diphenylphosphine ligand in usual square planar geometry.

Expectedly, the Pd-Cl bond length (2.3499 (11)) which trans to $–OPPh_2$ groups are slightly but significantly shorter than the Pd-Cl bond length (2.3750 (12)) which trans to $–NPPh_2$ groups.

The P1-Pd1-P2 angle and Cl2-Pd2-Cl1 angle in complex **3a'** like $98.99(4)^0$ and $92.84(4)^0$, respectively are close to expected value of 90^0.

Table 3.2 Selected Bond Distances (Å) and Angles (^{0}) for Complex **3a'**

P1-Pd1	2.2427(11)
P2-Pd1	2.2489(12)
Cl1-Pd1	2.3750(12)
Cl2-Pd1	2.3499(11)
N1-P2	1.666(4)
O1-P1	1.611(3)
O1-C28	1.460(5)
O1-P1-Pd1	119.52(12)
N1-P2-Pd1	117.16(14)
P1-Pd1-P2	98.99(4)
P2-Pd1-Cl2	84.78(4)
P1-Pd1-Cl1	84.72(4)
Cl2-Pd1-Cl1	92.84(4)

3.4 Thermal Analysis of Complex 2c', 3a' and 3a''

The thermal behaviour of new synthesis compounds was investigated using thermogravimetry (TGA/DTG). The complex **2c'** for example, decomposes between 180 and 450 ^{0}C in a two step process (Figure 3.26). The first step observed in temperature range 180 ºC with a total mass loss of 8%, which can be assigned to the removal of chlor atom or –CH_3 group, perhaps fregmented organic compounds. The second step takes place between 280 and 450 ^{o}C with the 85 % weight loss. The total weight loss is 93%. The observed mass loss may be due to the elimination of molecules like H_2O, ter-butyl group, pyridine, Cl etc. Formed from decomposed moieties of the metal complex **2c'**.

The complex **3a'** is stabilized approximately at 200 ^{0}C. The first mass loss was observed between 200 and 330 ^{0}C, there is a total mass loss of about 30%. Than, it was indicated that as the gradient of TGA/DTG curve was being high the disintegration of complex was accelerated (see Figure 3.27). The observed mass loss may be due to the elimination of molecules like H_2O, Cl, CO, CO_2, phenyl, piperidine ring etc. Formed from decomposed moieties of the metal complex **3a'**.

For the complex **3a''**, there was no mass losses nearly to temperature 130 ^{0}C. The same as **3a',** it is stabilized approximately at 200 ^{0}C. A main mass loss between 230 and 350 ^{0}C. Because of the many groups that could be easily cleaved in the structure, as CO, CO_2, phenyl etc, during by increasing temperature, it has observed distinct curves (Figure 3.28). In the temperature range between 230 and 400 ^{0}C with a mass loss of approximately 50%.

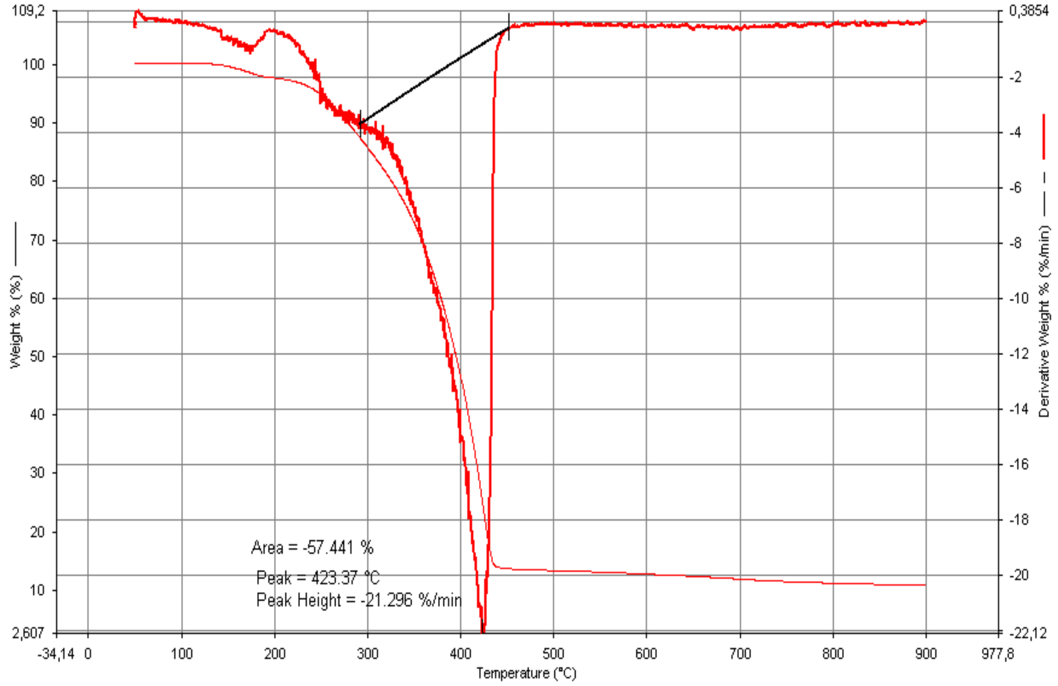


Figure 3.26 The TGA/DTG Curve of Complex **2c’**

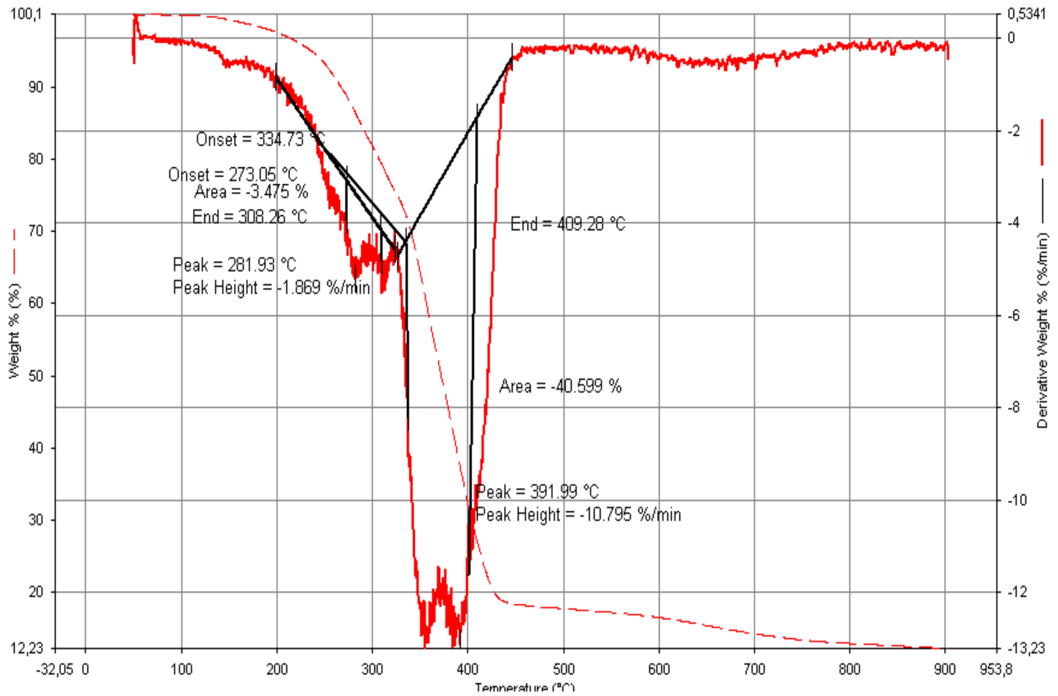


Figure 3.27 The TGA/DTG Curve of Complex **3a’**

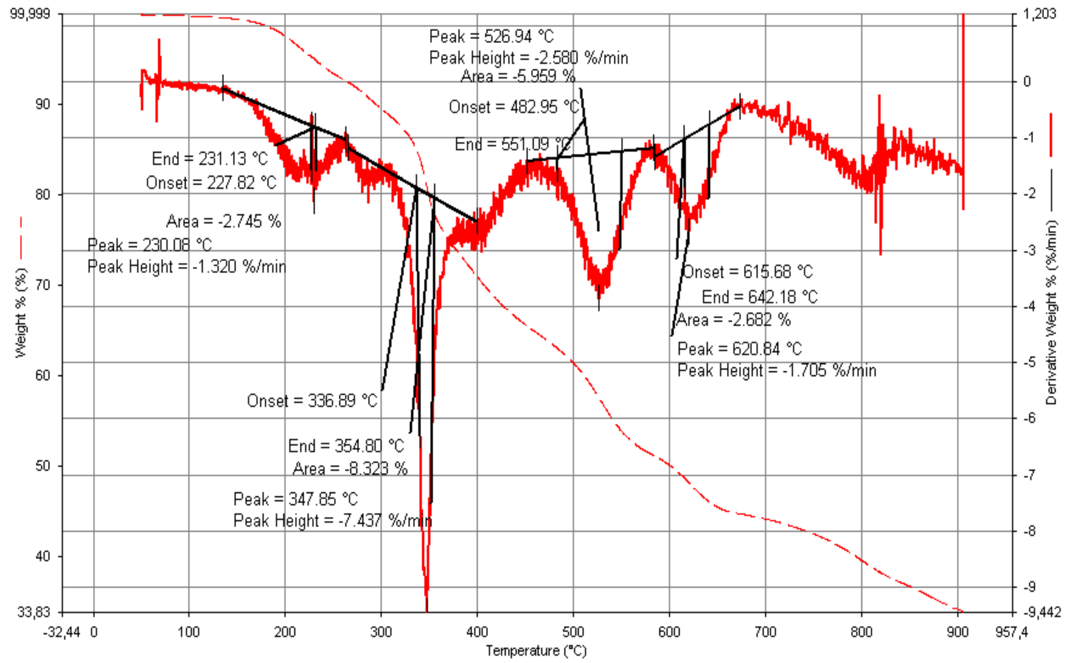


Figure 3.28 The TGA/DTG Curve of Complex **3a’’**

3.5 Results of the AFM for Complexes 2c’, 3a’ and 3a’’

AFM measurement of complexes **2c’**, **3a’** and **3a’’** was investigated for analyses of facile characteristic features. The result of these measurement is given in Figure 3.29 for complex **2c’**, Figure 3.30 for complex **3a’** and Figure 3.31 for complex **3a’’**. Based on this results, we may say that their surfaces were regular (Senthılarasu et al., 2003). Besides, due to interaction of metal-metal or metal ligand, molecules of complexes were aggregated, especially complex of **3a’’** in such a case.

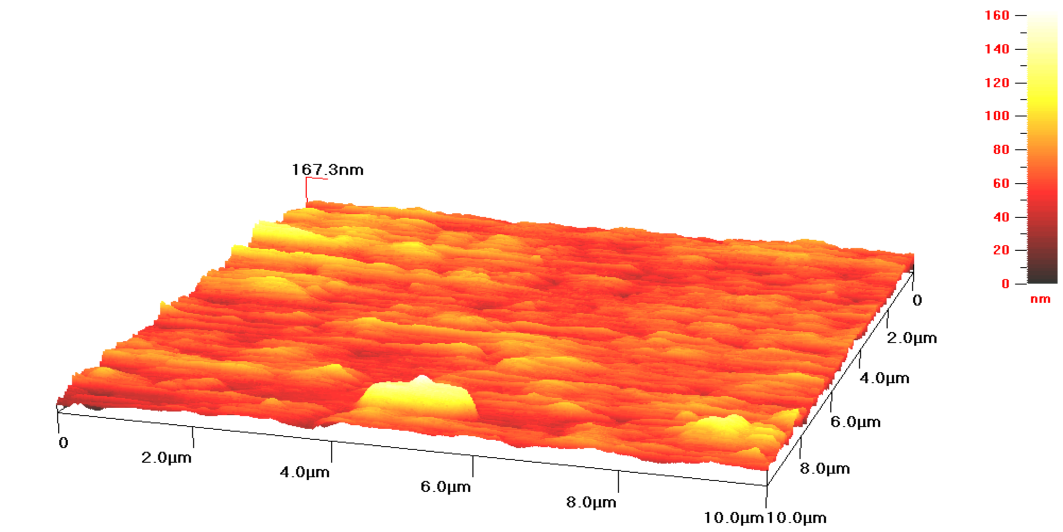


Figure 3.29 AFM image of the complex **2c'**

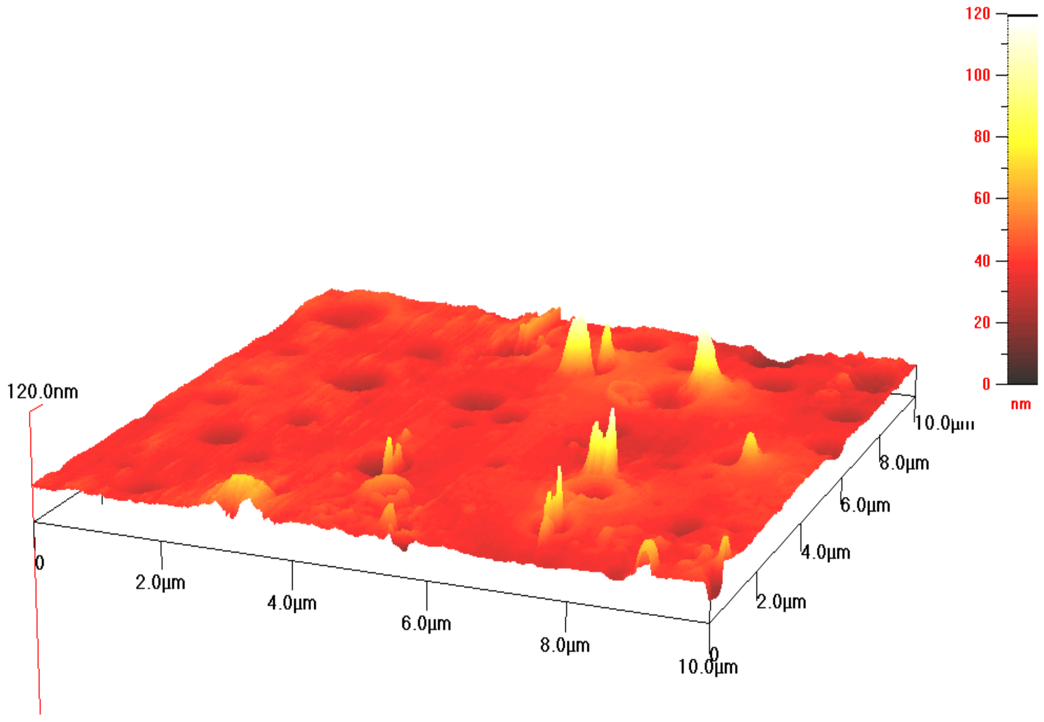


Figure 3.30 AFM image of the complex **3a'**

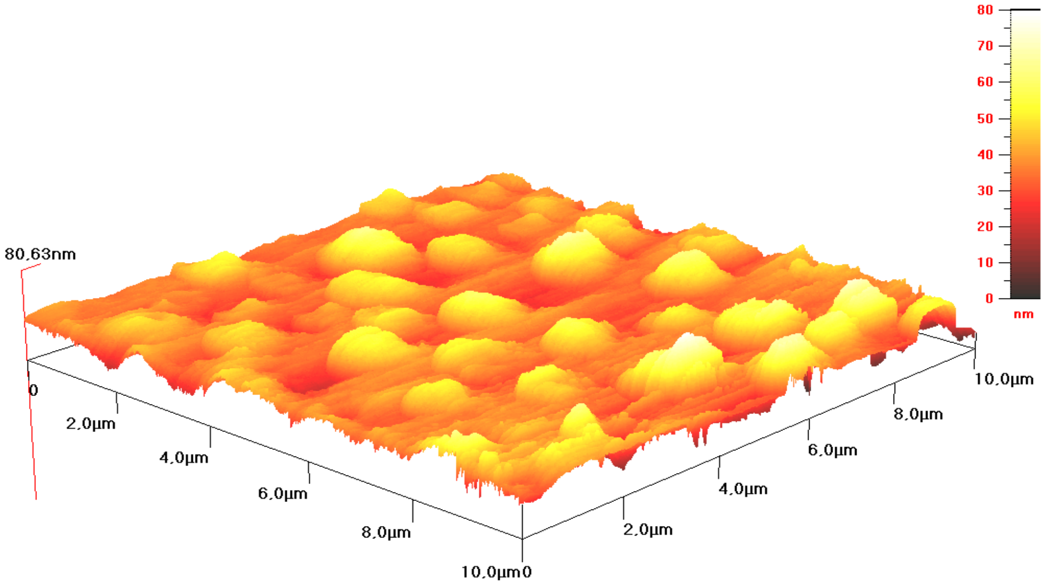
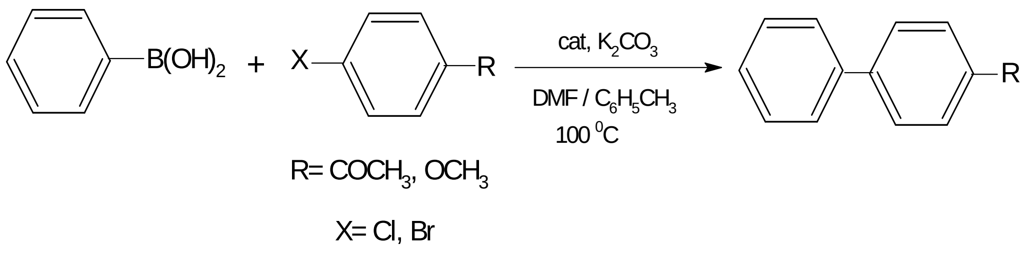


Figure 3.31 AFM image of the complex **3a''**

3.6 Results of Catalytic Experiments for Suzuki-Miyaura Coupling Reaction

The palladium-catalyzed cross-coupling of arylboronic acids with aryl halides (bromoacetophenone, chloroacetophenone, bromoanisole, chloroanisole) 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 (Suzuki, et al., 1999). The reactions are usually carried out homogeneously in the presence of a base under inert atmosphere. The reactivity of the aryl halide component decreases drastically in the order X = Br > Cl. This optimized coupling reaction conditions used for catalytic experiments.

We investigated the activity of complexes **1b'**, **2c'** and **3a'** as catalysts for the coupling of various aryl bromides and chlorides with phenyl boronic acid. The results of this study are summarized in Table 3.3 and Table 3.4. The conditions employed for the catalytic experiments are depicted on Scheme 3.8. Palladium complexes in which synthesis in this study, **1b'**, **2c'** and **3a'**, are excellent catalysts for the Suzuki-Miyaura cross coupling reactions. In general, complexes of **1b'** and **2c'** exhibits higher activity than the previously reported ones (Benito et al., 2007; Aydemir et. al., 2008; Borhade et. al., 2008). In all our experiments, the platinum complexes 1b’’ and 3a’’ showed no activity.



Scheme 3.8 Suzuki-Miyaura coupling reaction

Aryl Halogen	Catalyst	Time (h)	Base	Solvent	Yield (%)	TON
4-bromoacetophenone	**2c’**	2	Cs_2CO_3	DMF	>99	99
4-bromoacetophenone	**2c’**	2	K_2CO_3	DMF	93.8	93,8
4-bromoacetophenone	**2c’**	24	Cs_2CO_3	Toluen	87	87
4-chloroacetophenone	**2c’**	6	Cs_2CO_3	DMF	53	53
4-chloroacetophenone	**2c’**	2	K_2CO_3	DMF	>99	99
4-chloroacetophenone	**2c’**	24	Cs_2CO_3	Toluen	100	100
4-bromoacetophenone	**1b’**	2	Cs_2CO_3	DMF	>99	99
4-bromoacetophenone	**1b’**	2	K_2CO_3	DMF	>99	99
4-bromoacetophenone	**1b’**	4	Cs_2CO_3	Toluen	89	89
4-chloroacetophenone	**1b’**	6	Cs_2CO_3	DMF	19	19
4-chloroacetophenone	**1b’**	2	K_2CO_3	DMF	77.8	77.8
4-chloroacetophenone	**1b’**	24	Cs_2CO_3	Toluen	94.4	94.4

Table 3.3 The Suzuki coupling reaction of aryl halides with phenylboronic acid of catalysts **1b’** and **2c’**

Aryl Halogen	Catalyst	Time (hour)	Base	Solvent	Yield(%)	TON
4-chloroacetophenone	**3a’**	24	K_2CO_3	DMF	53	53
4-chloroanisole	**3a’**	24	K_2CO_3	DMF	41	41
4-bromoacetophenone	**3a’**	1	K_2CO_3	DMF	>99	99
4-bromoanisole	**3a’**	2	K_2CO_3	DMF	89	89
4-chloroacetophenone	**3a’**	3	K_2CO_3	toluen	78	78
4-chloroanisole	**3a’**	24	K_2CO_3	toluen	40	40
4-bromoacetophenone	**3a’**	2	K_2CO_3	toluen	98	98
4-bromoanisole	**3a’**	24	K_2CO_3	toluen	60	60

Table 3.4 The Suzuki coupling reaction of aryl halides with phenylboronic acid of catalyst **3a’**

Results of the Suzuki-Miyaura cross coupling reactions obtained are presented in Table 3.3 and Table 3.4. Generally the best performance is expected from bromo derivatives.

With bromoacetophenone as aryl halides in cross coupling reactions, the catalysts of **1b’** and **2c’** were much more active than with chloroacetophenone as aryl halides. Either complexes, middle of DMF and also using Cs_2CO_3 as a base, were featured the most higher activities. Also, the activities of **1b’** and **2c’** with chloroacetophenone as aryl halides were tolerable values. Performance order of complexes is given as: **1b’**> **2c’**. This reactivity trend suggests that both the stronger donating ability and steric demand of the PR_2 substituents make the complexes more electron-rich and render catalyst, **2c’** less active. Value of the conversion thus TON, obtained with complex **1b’** as catalyst were the highest one.

There aren’t any literatures about amidophosphine-phosphinite type palladium complexes. In this study, we synthesized a kind of amidophosphine-phosphinite palladium complex, **3a’** and compared its catalytic activity in Suzuki-Miyaura cross coupling reaction.

The catalyst of **3a’** that including amidophosphine-phosphinite ligand, was an active catalyst for Suzuki-Miyaura cross coupling reaction with tolerable yields and TON values. In the reaction of 4-bromoacetophenone with phenylboronic acid to yield biphenyl, no complete conversion was observed. For catalyst of **3a’**, the coupling of 4-bromoacetophenone with phenylboronic acid proceeds with 99% isolated yield with a catalyst loading of 0.001 mol, while the electronically deactivated and thus more challenging substrate 4-bromoanisole can be efficiently coupled with 99% isolated yield with a catalyst loading of 0.001%. But, for other yields, better performances can be obtained by changing the reaction conditions.

Finally, so far the catalyst described here are ideal to catalyze the coupling of electronically deactivated substrate aryl bromides and chlorides as they are comperatively inexpensive and can be used to give high conversion at low concentrations of catalysts.

3.7 Conclusion

We have shown that new ligands are easily prepared from commercially available and inexpensive 2,6-dihydroxypyridine and 3-hydroxypiperidine, and related precursors, which can be varied in modular fashion by choosing monochlorophosphine, R_2PCl (R= ^tBu, Ph). In conjunction with transition metal fragments such as $PdCl_2$(COD) and $PtCl_2$(COD), stable PONOP complexes are formed and characterized with spectroscopic metods. Some of these compounds, especially palladium derivatives, are catalytically active in C-C bond-forming reactions such as Suzuki-Miyaura cross coupling reactions.

The formation of the palladium(II) and platinum(II) aminophosphine-phosphinite complexes (**3a'** and **3a''**) of unsymetrical 1-(diphenylphosphino)piperidine-3-yl diphenyl phosphinite ligand described in this study can be readily and cleanly achieved. These complexes, which are very stable under ordinary conditions, have been synthesised and charecterized. The identity of **3a'** as cis-complex has been confirmed by X-ray diffraction. Also this palladium complex has been found to be active catalyst for Suzuki-Miyaura cross coupling reaction. The complex **3a'** showed slightly better activities with 4-bromoasetofenon or 4-bromoanisol than 4-kloroasetofenon or 4-kloroanisol.

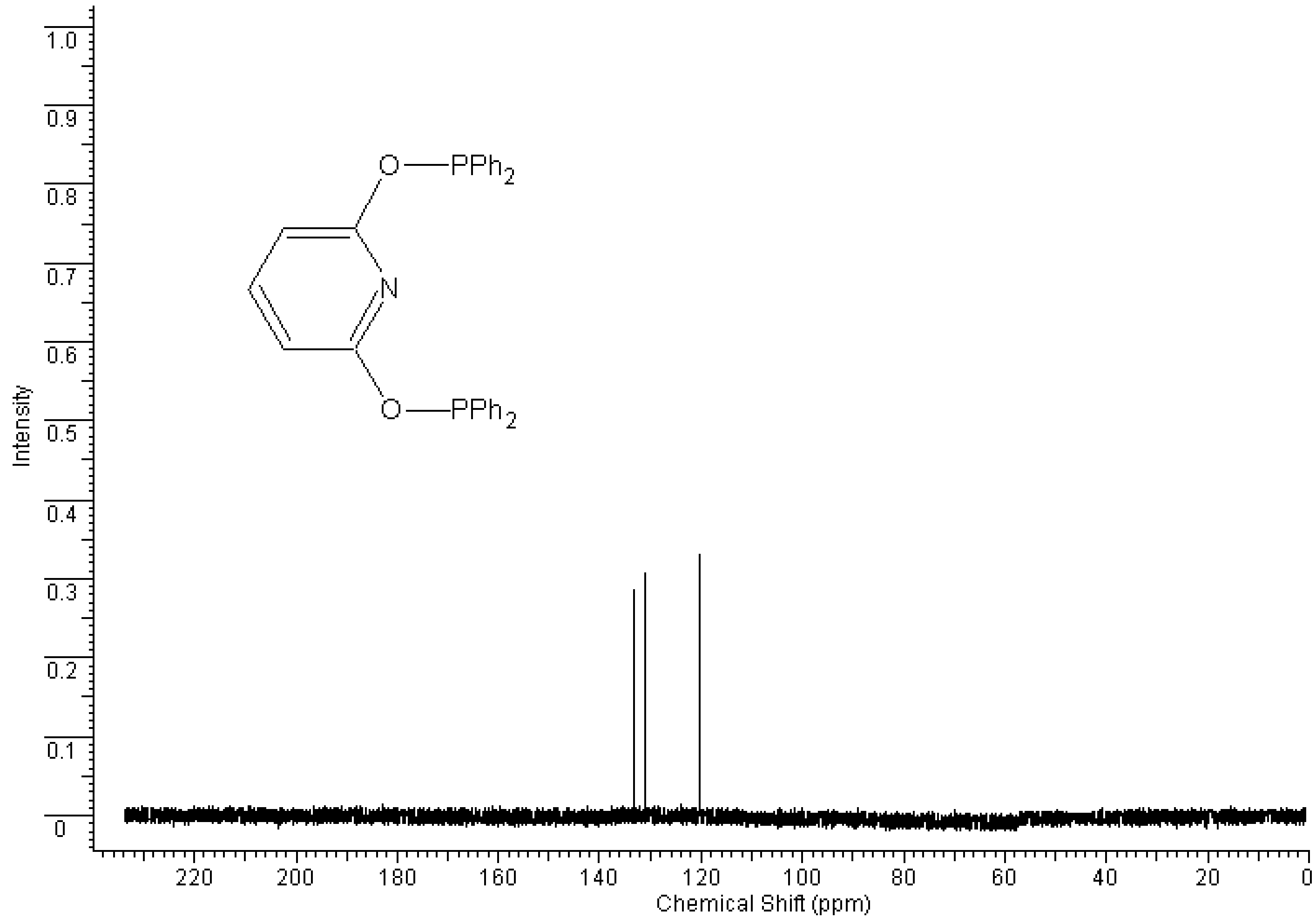


Figure 3.1 $^{31}P\{^{1}H\}$-NMR Spektrum of Ligand **1a**

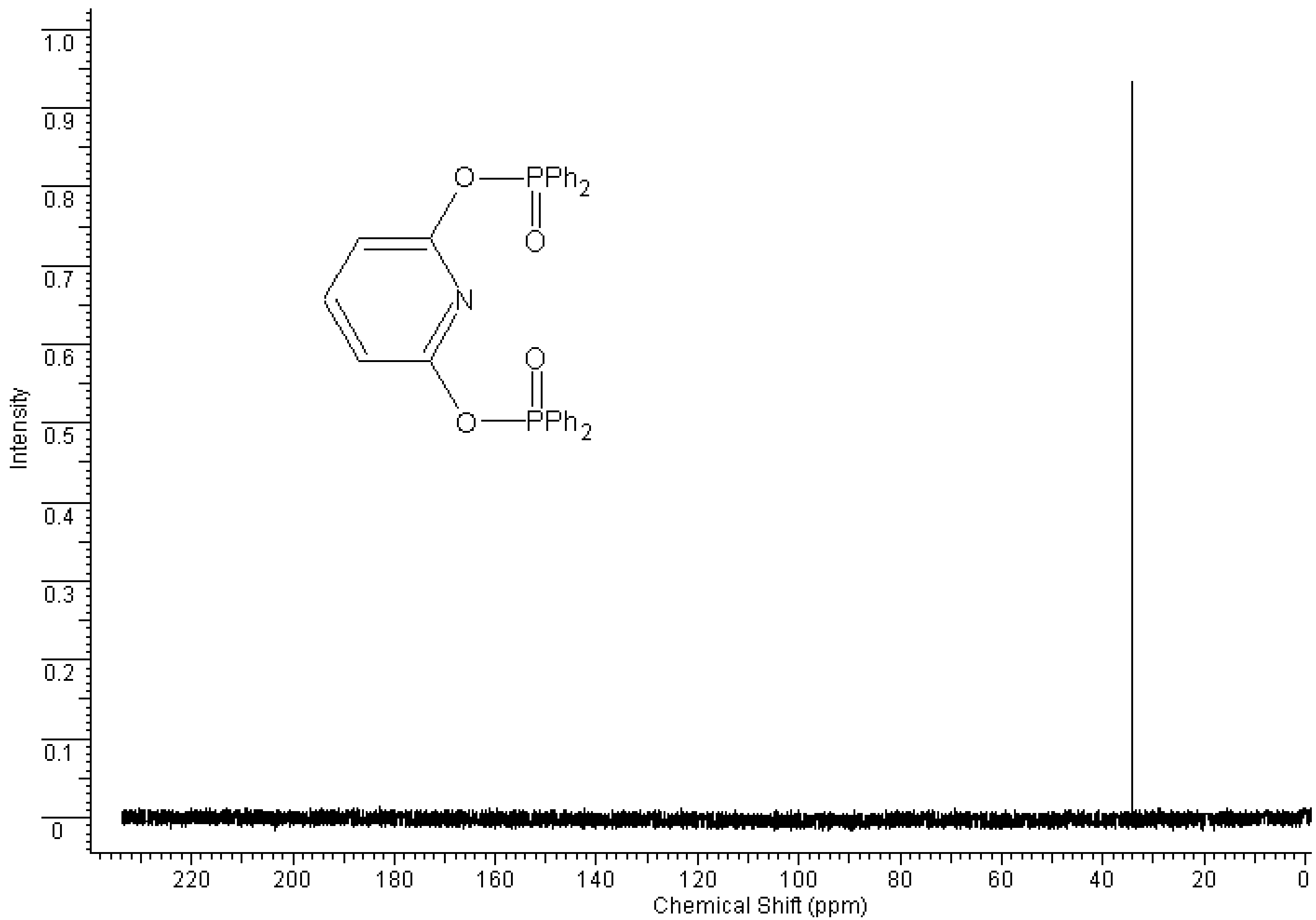


Figure 3.2 $^{31}P\{^{1}H\}$-NMR Spektrum of Ligand **1b**

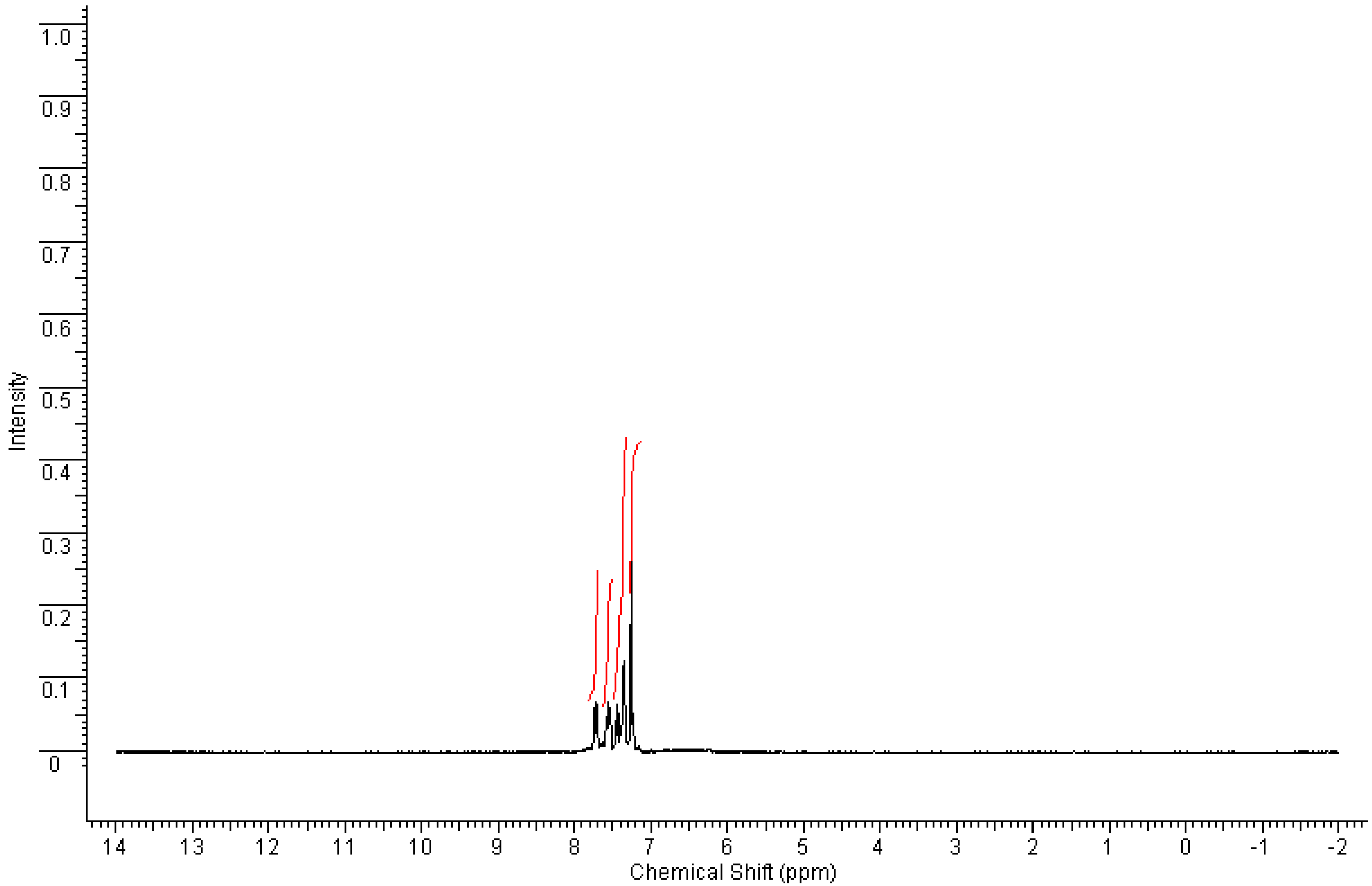


Figure 3.3 ^{1}H-NMR Spektrum of Ligand **1b**

Figure 3.4 FT-IR Spectrum of Ligand **1b**

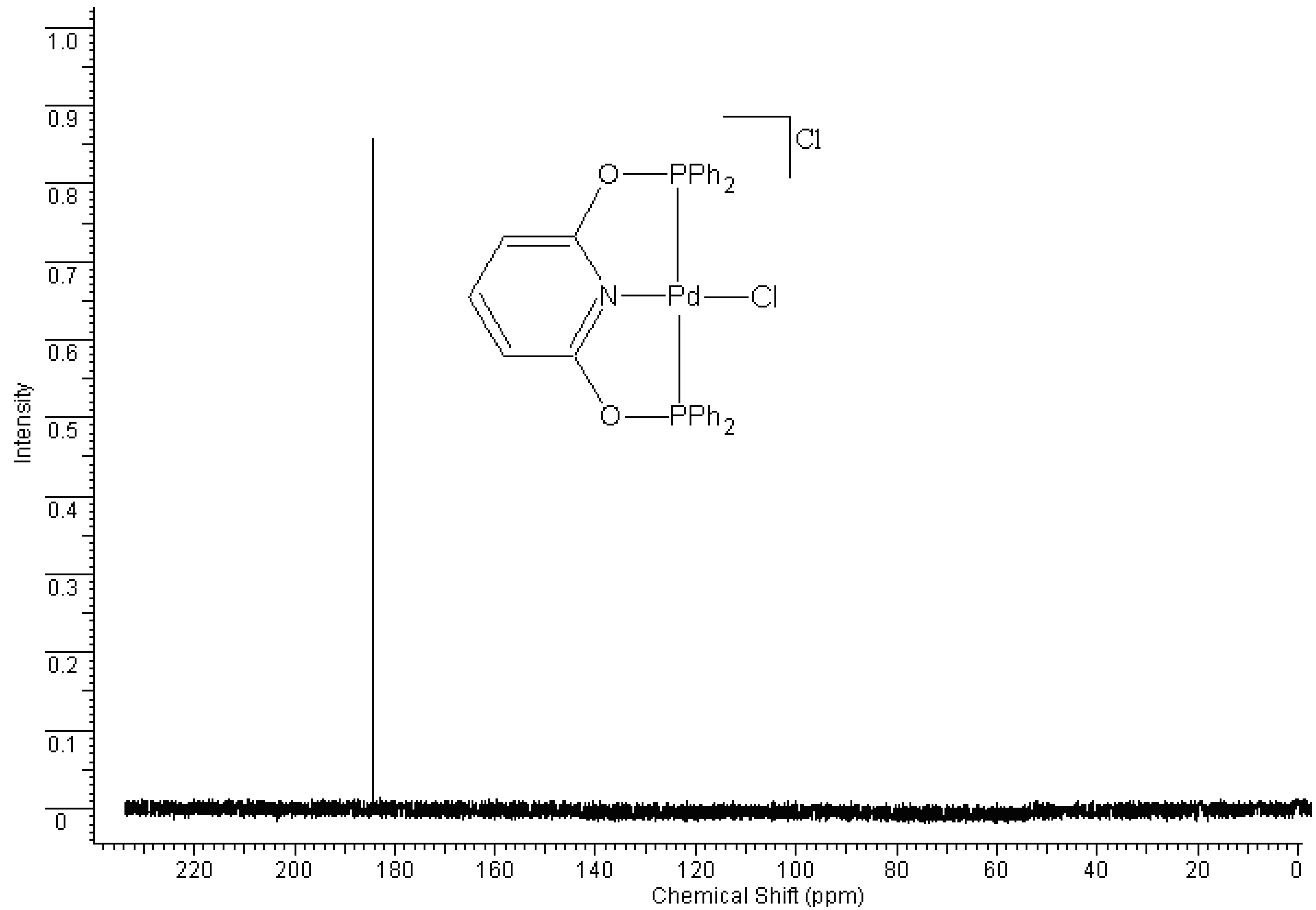


Figure 3.5 $^{31}P\{^{1}H\}$-NMR Spectrum of Complex **1a'**

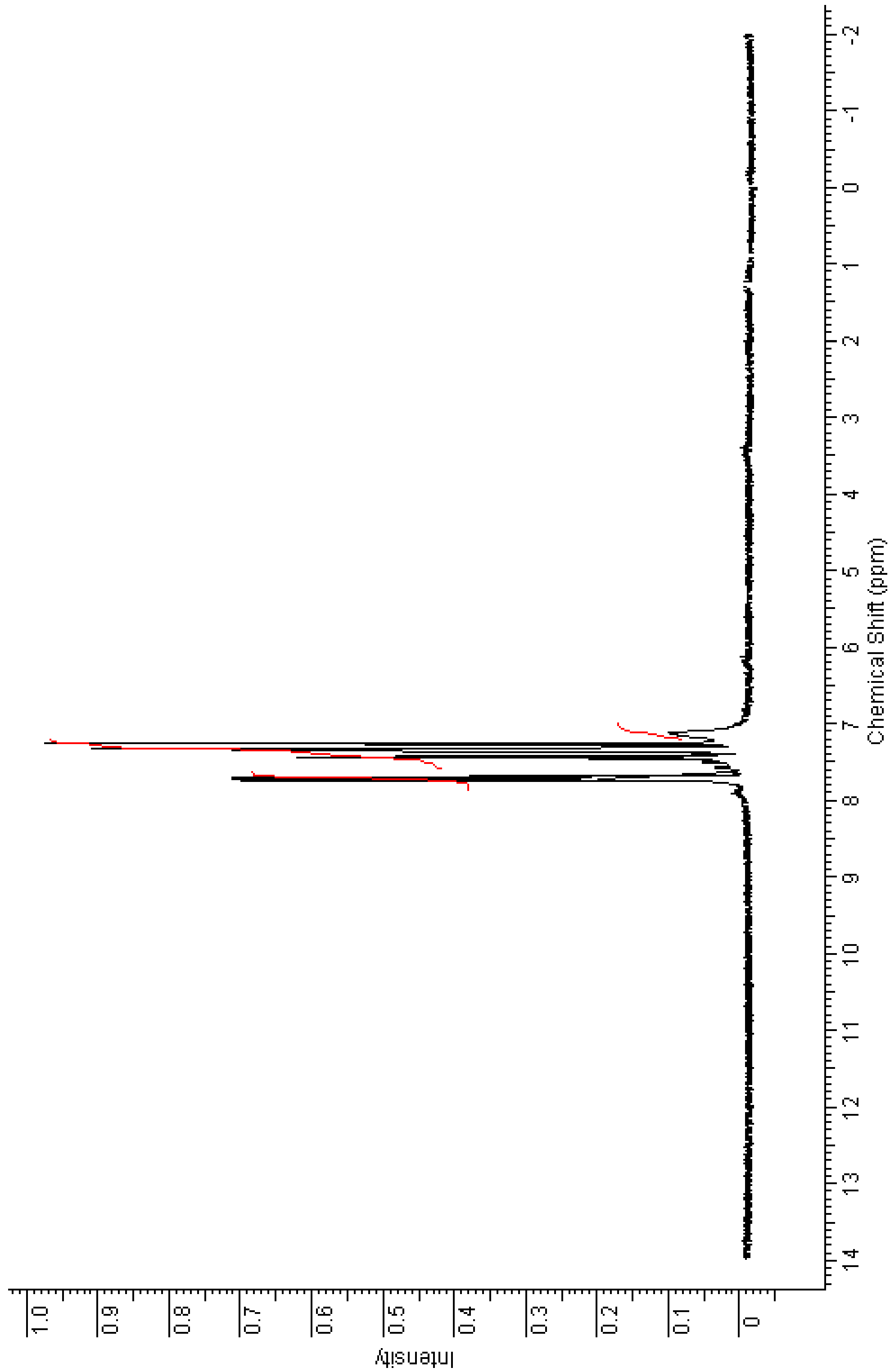


Figure 3.6 : ^{1}H-NMR Spektrum of Complex **1a'**

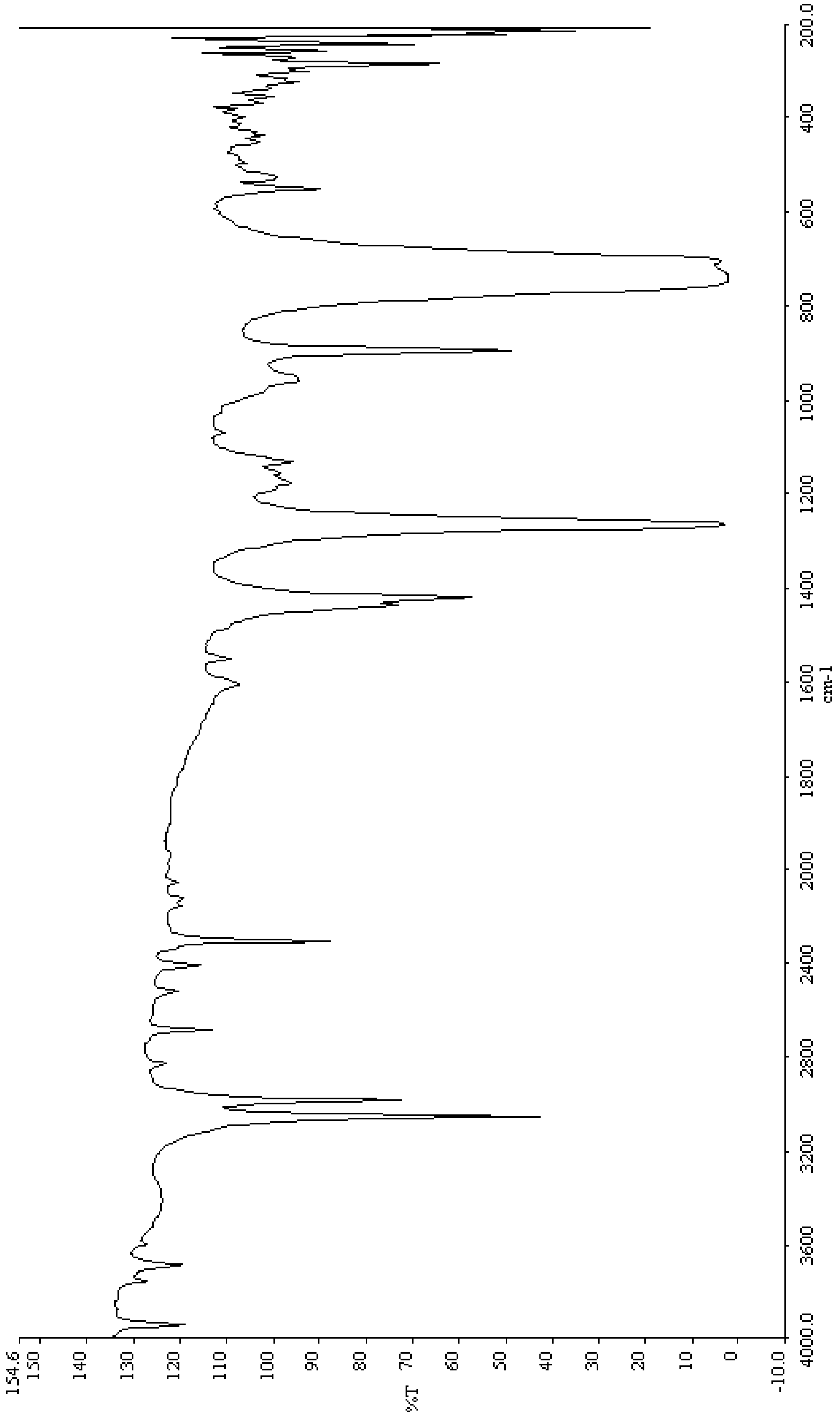


Figure 3.7 FT-IR Spectrum of Complex **1a'**

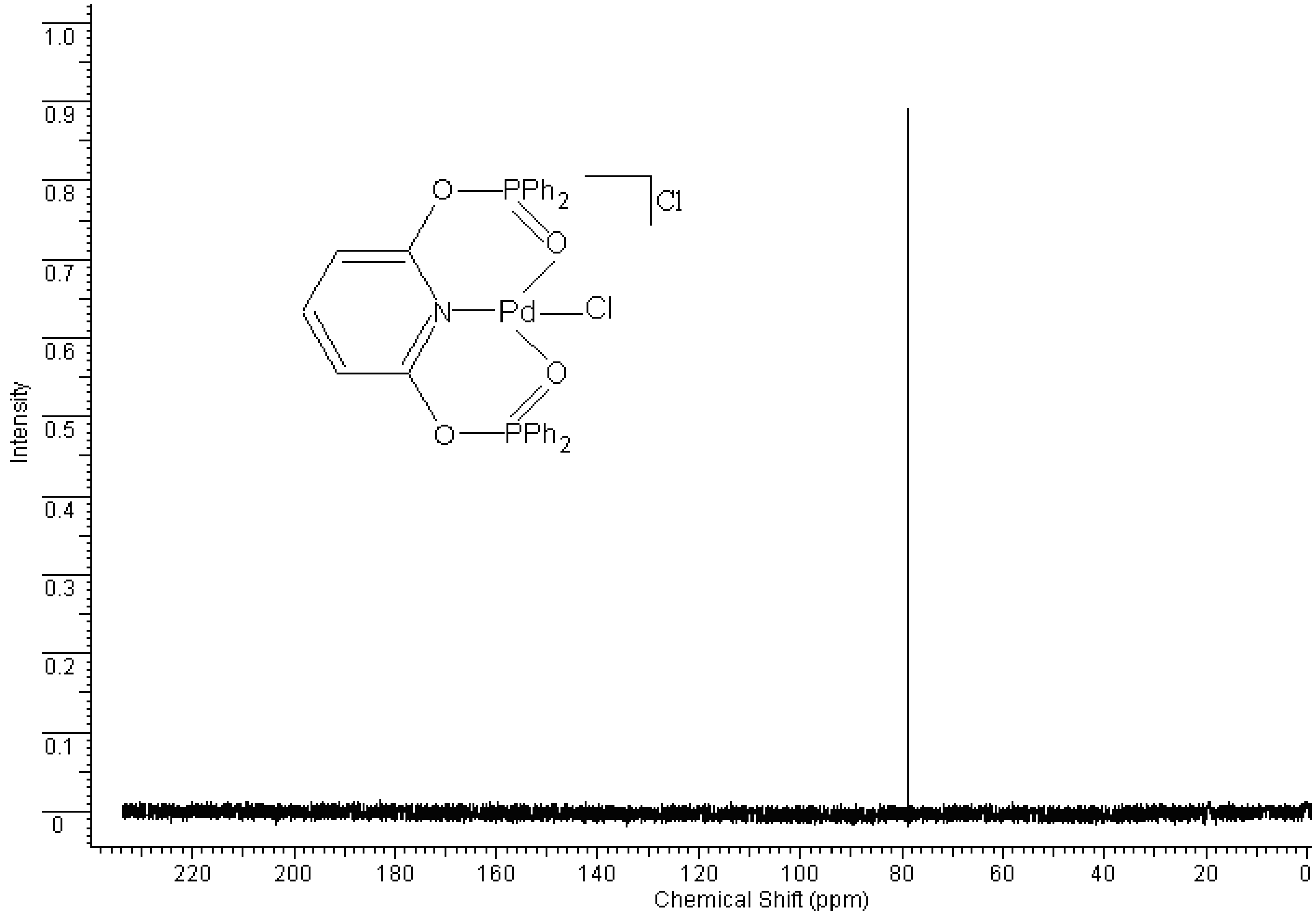


Figure 3.8 $^{31}P\{^{1}H\}$-NMR Spectrum of Complex **1b'**

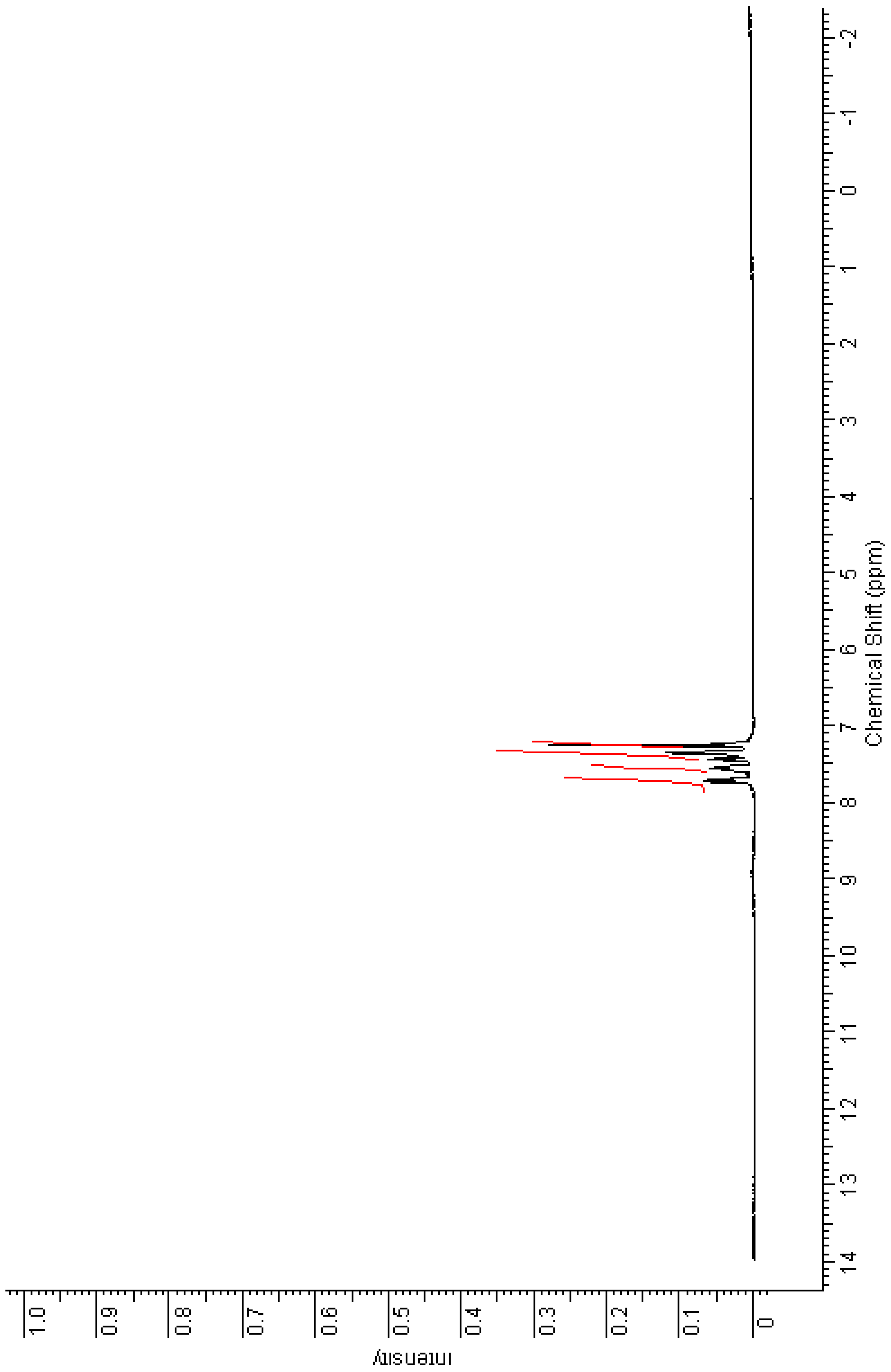


Figure 3.9 ^{1}H-NMR Spektrum of Complex **1b**'

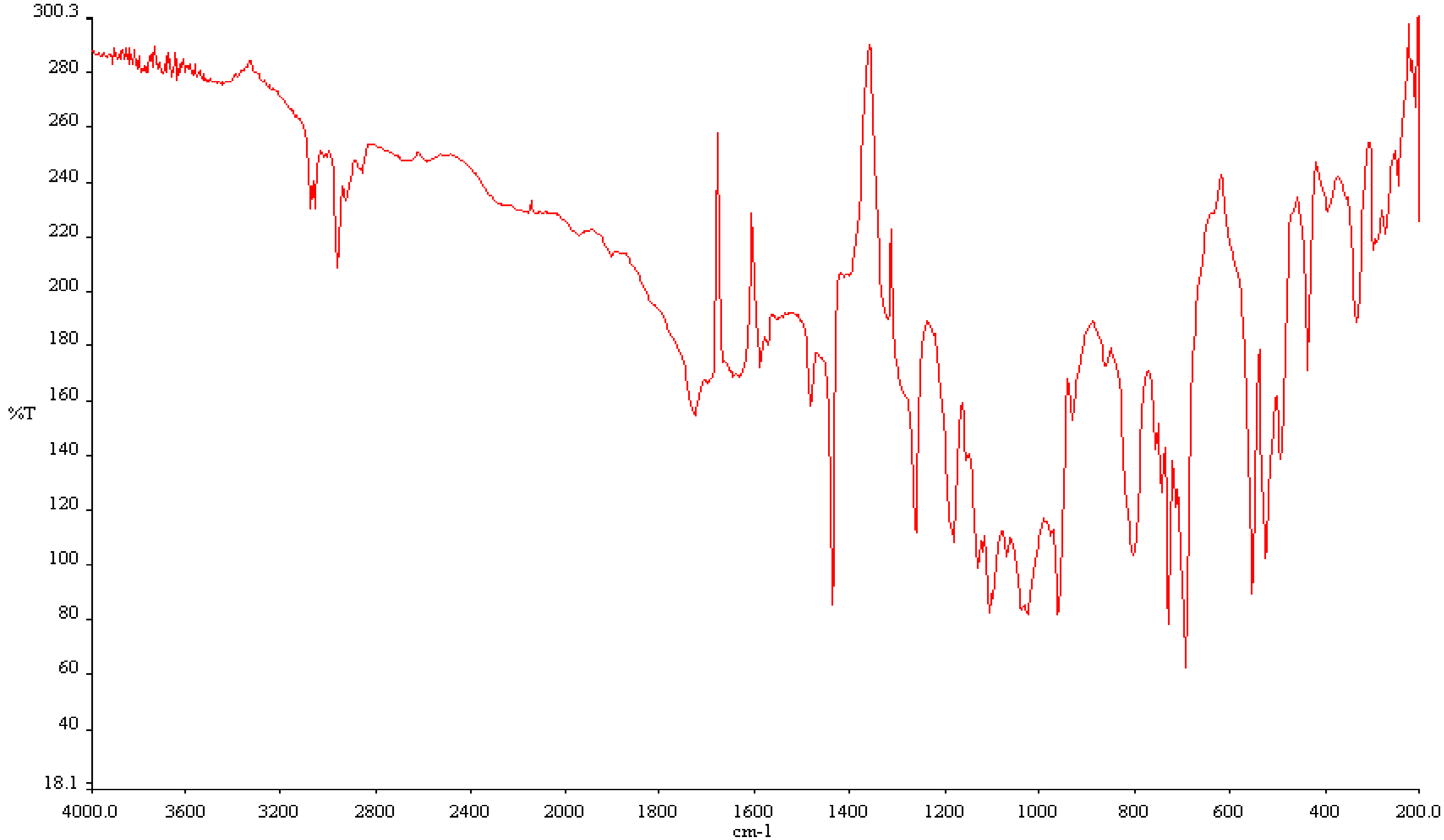


Figure 3.10 FT-IR Spectrum of Complex **1b'**

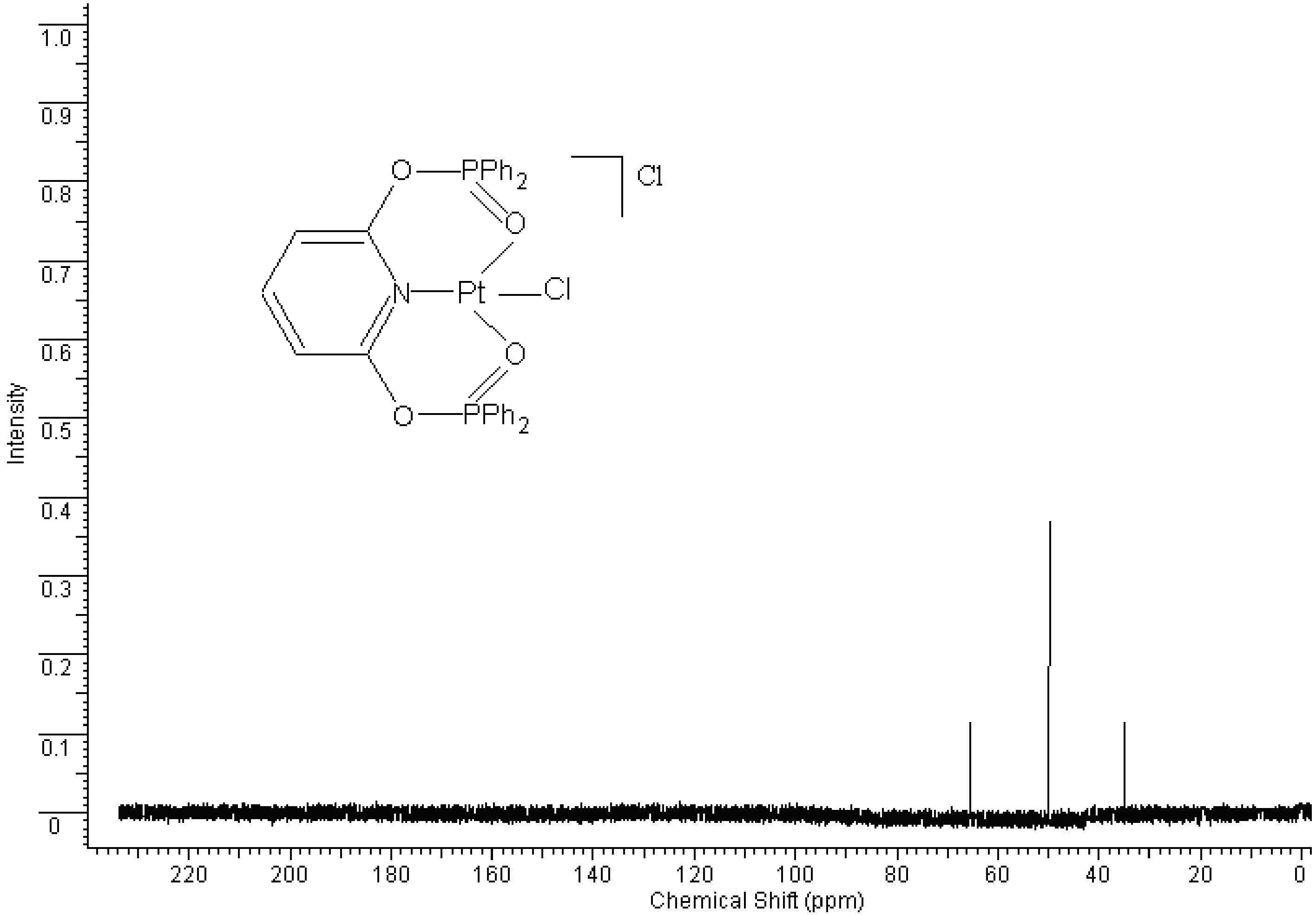


Figure 3.11 $^{31}P\{^{1}H\}$-NMR Spectrum of Complex **1b''**

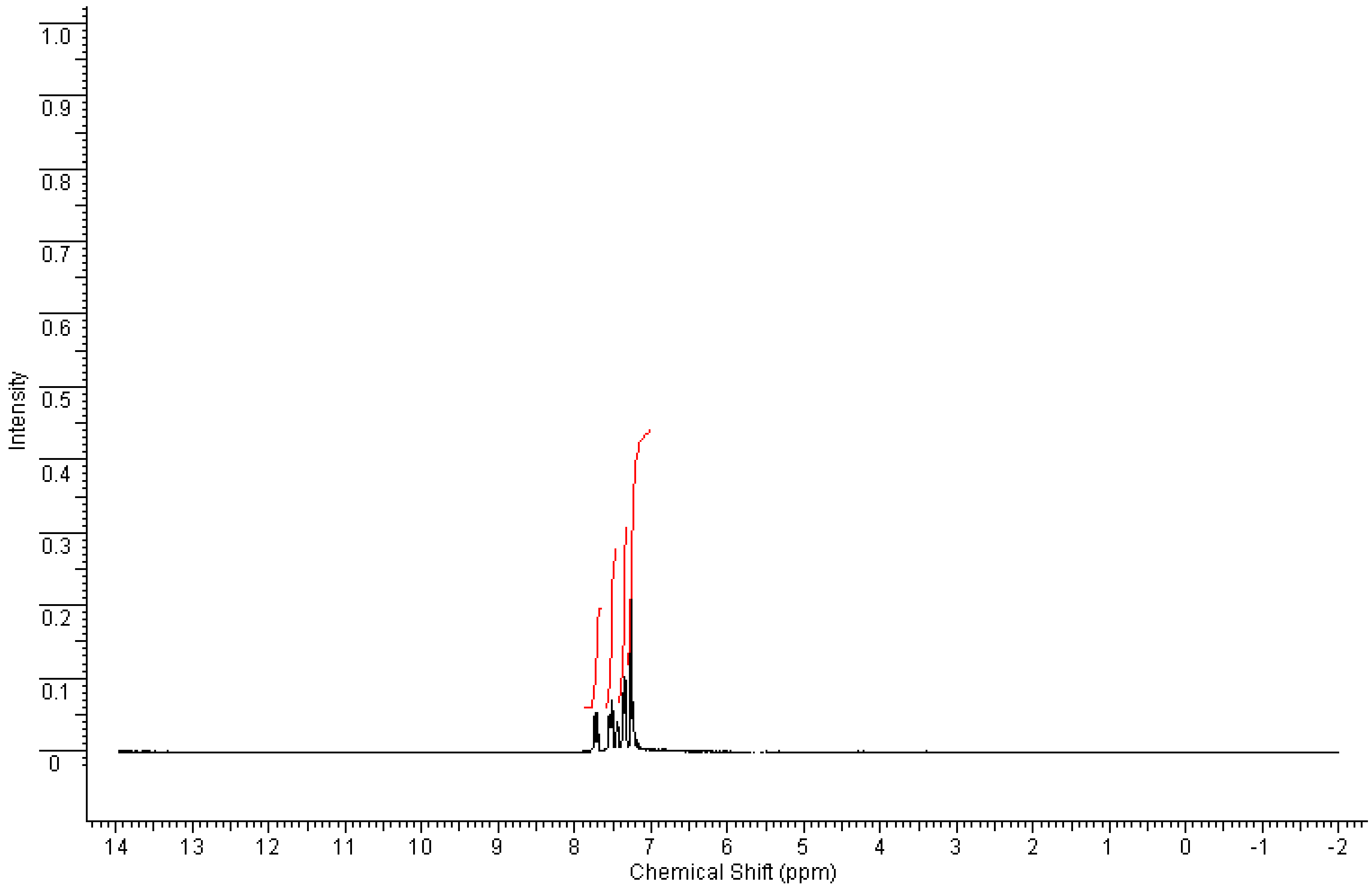


Figure 3.12 ^{1}H-NMR Spektrum of Complex **1b''**

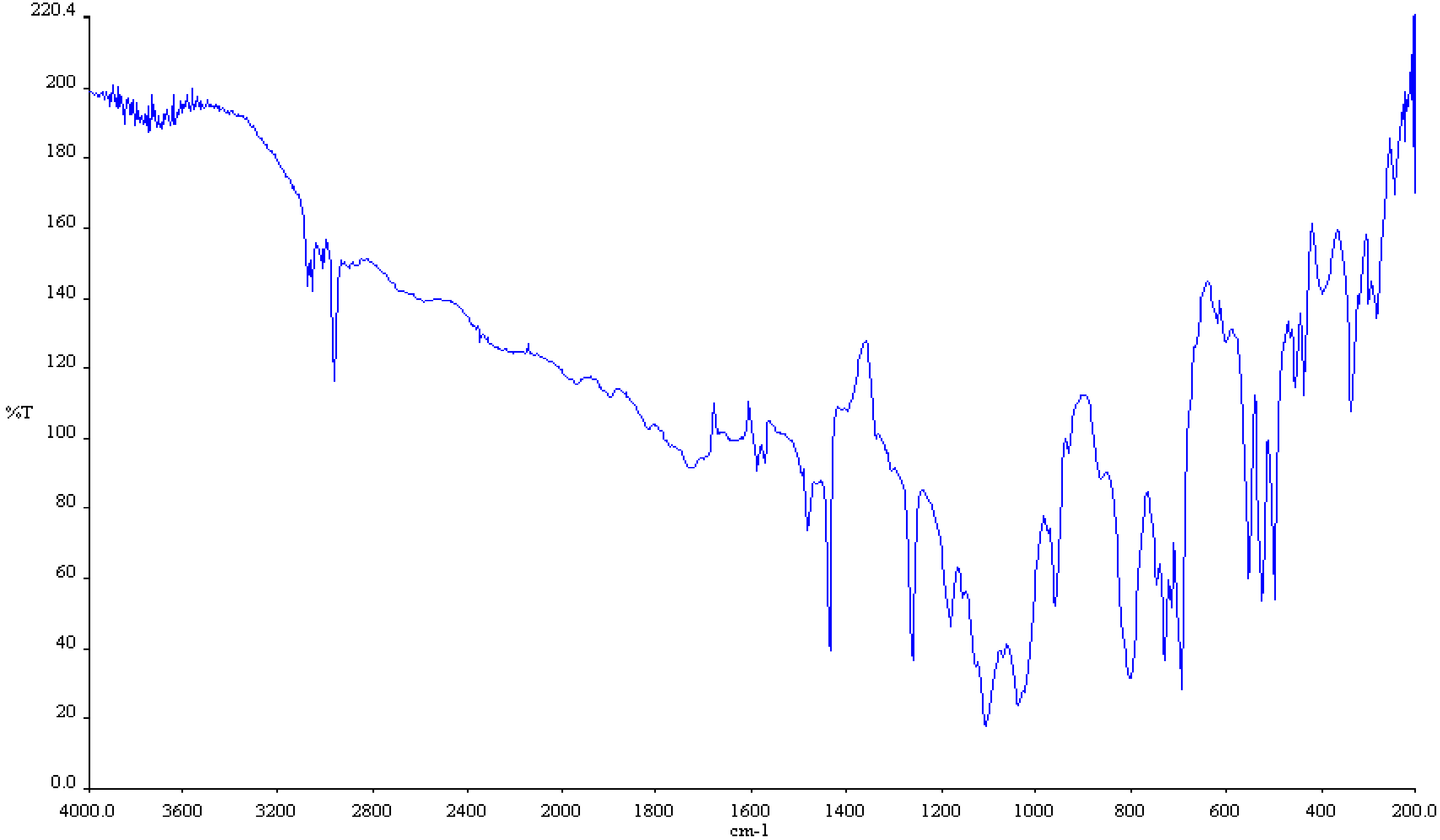


Figure 3.13 FT-IR Spectrum of Complex **1b''**

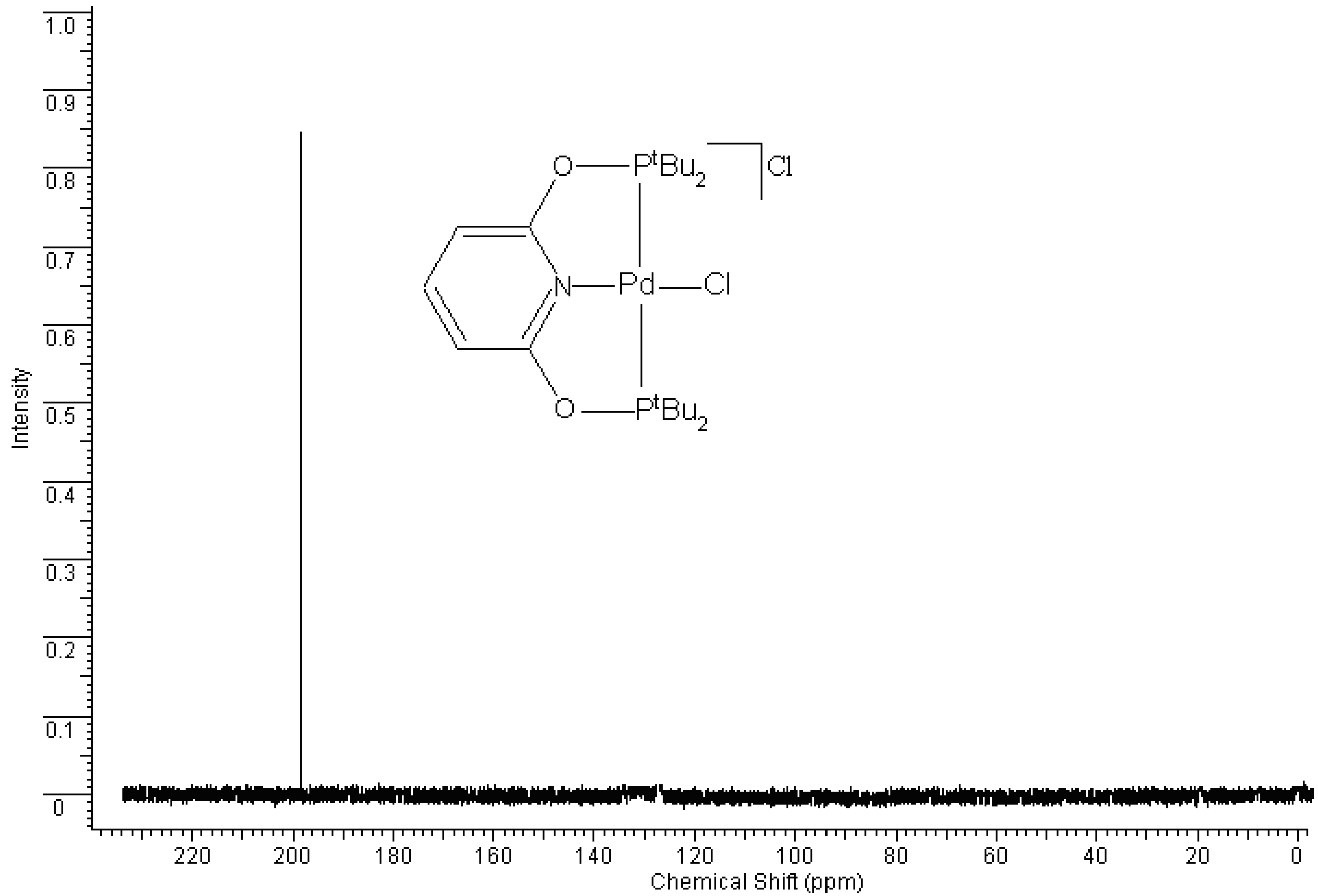


Figure 3.14 $^{31}P\{^1H\}$-NMR Spectrum of Complex **2c'**

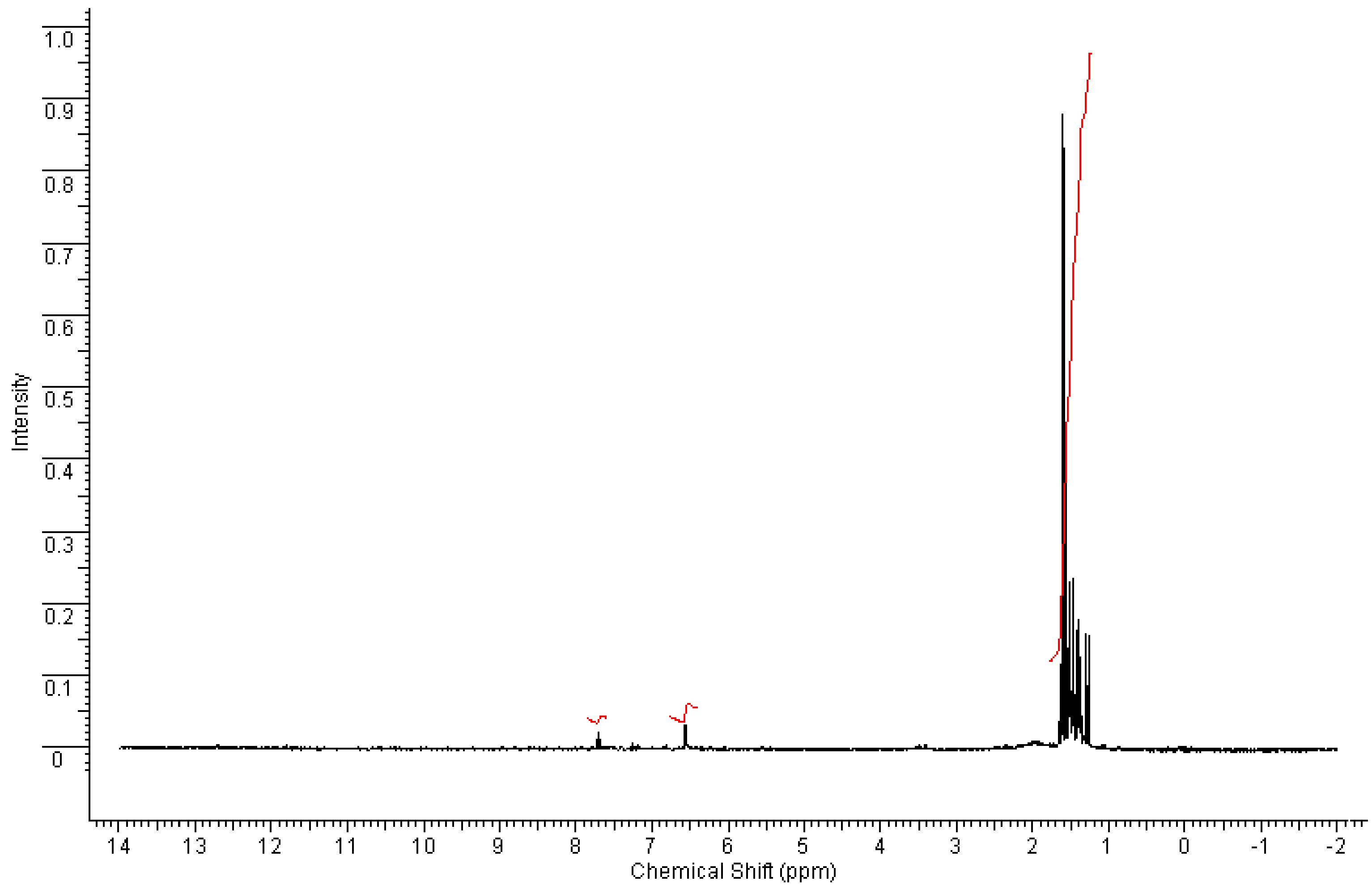


Figure 3.15 ^{1}H-NMR Spektrum of Complex **2c'**

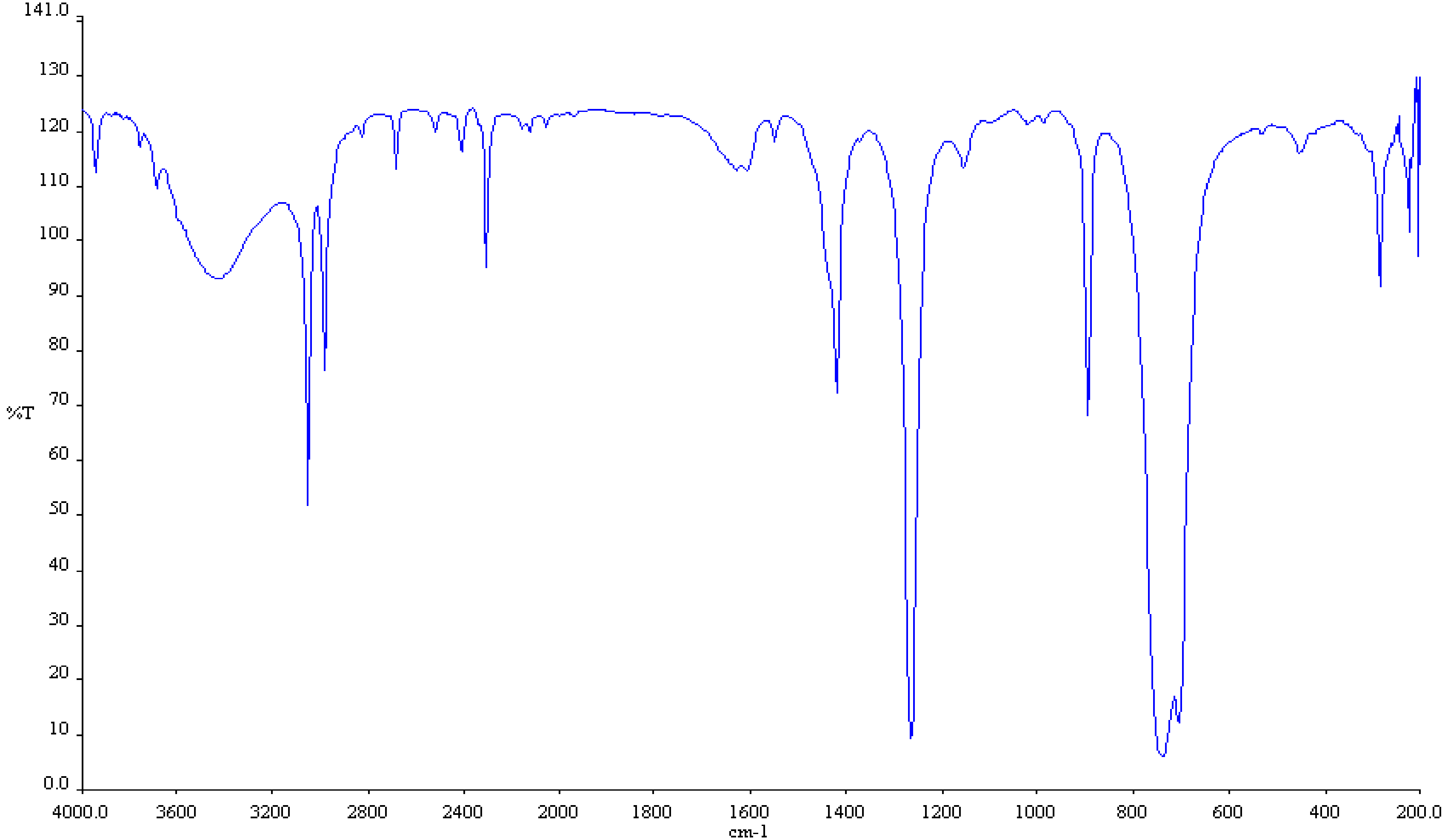


Figure 3.16 FT-IR Spectrum of Complex **2c'**

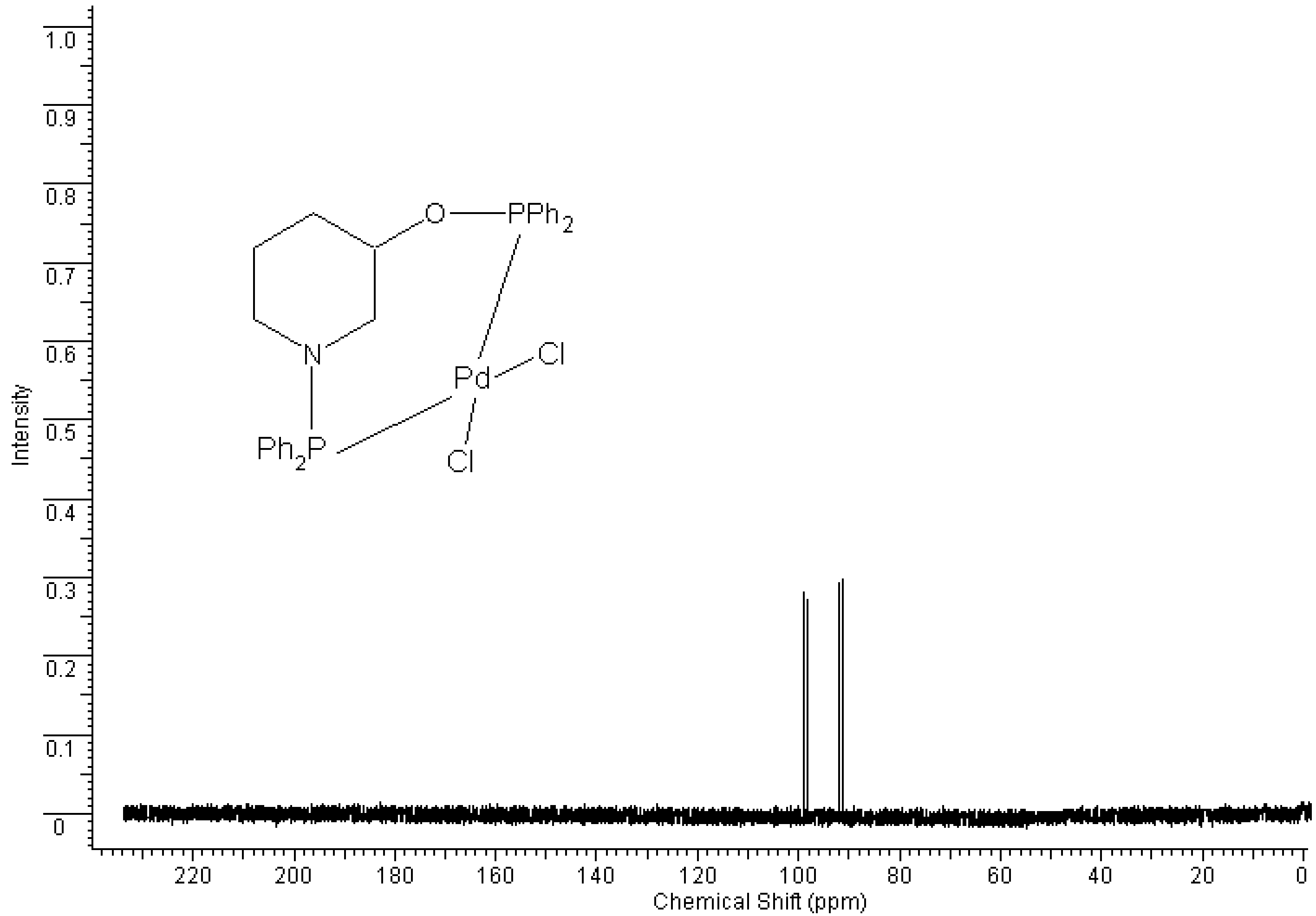


Figure 3.17 $^{31}P\{^1H\}$-NMR Spectrum of Complex **3a'**

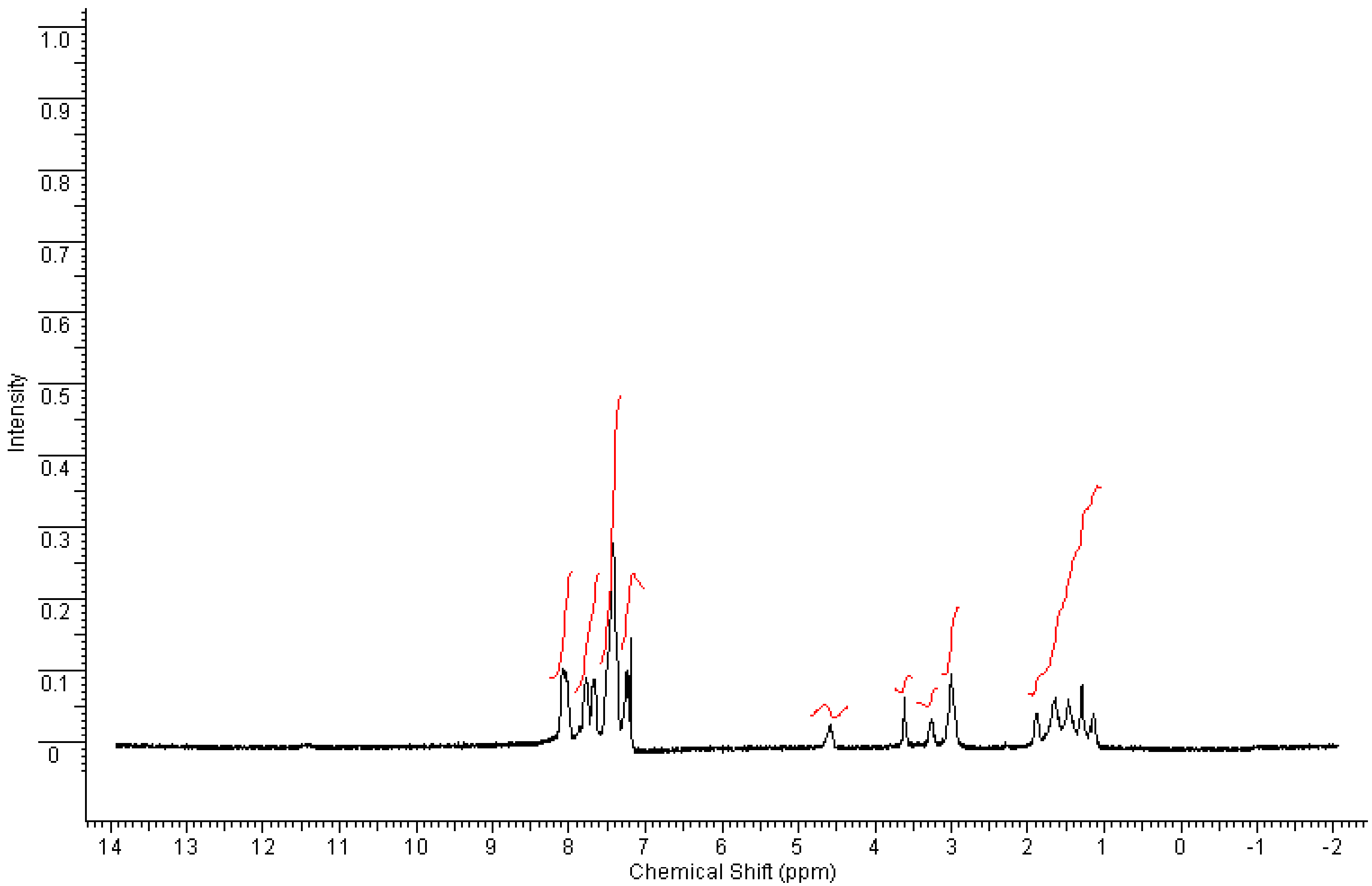


Figure 3.18 ^{1}H-NMR Spektrum of Complex **3a**'

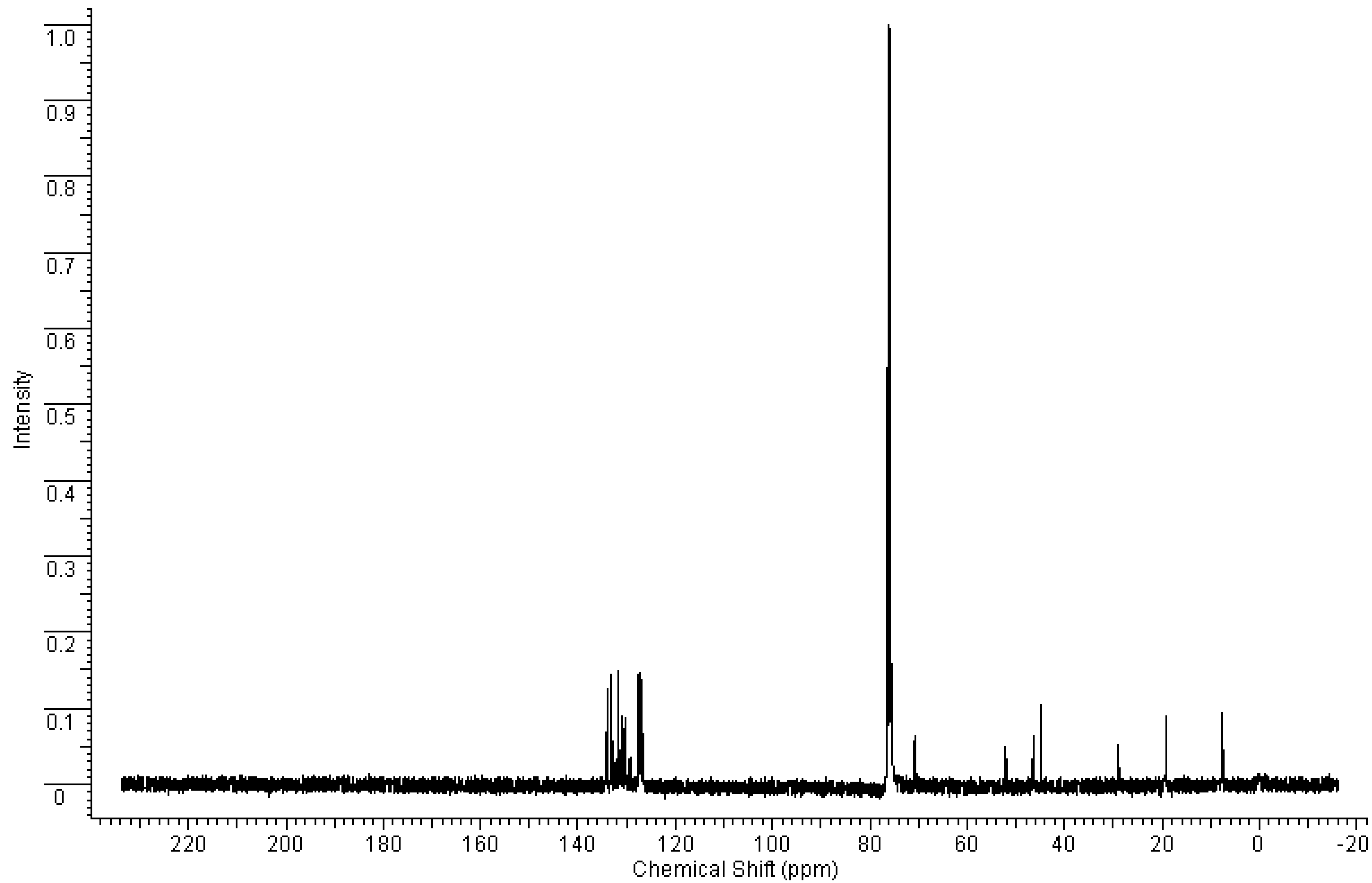


Figure 3.19 ^{13}C-NMR Spectrum of Complex **3a'**

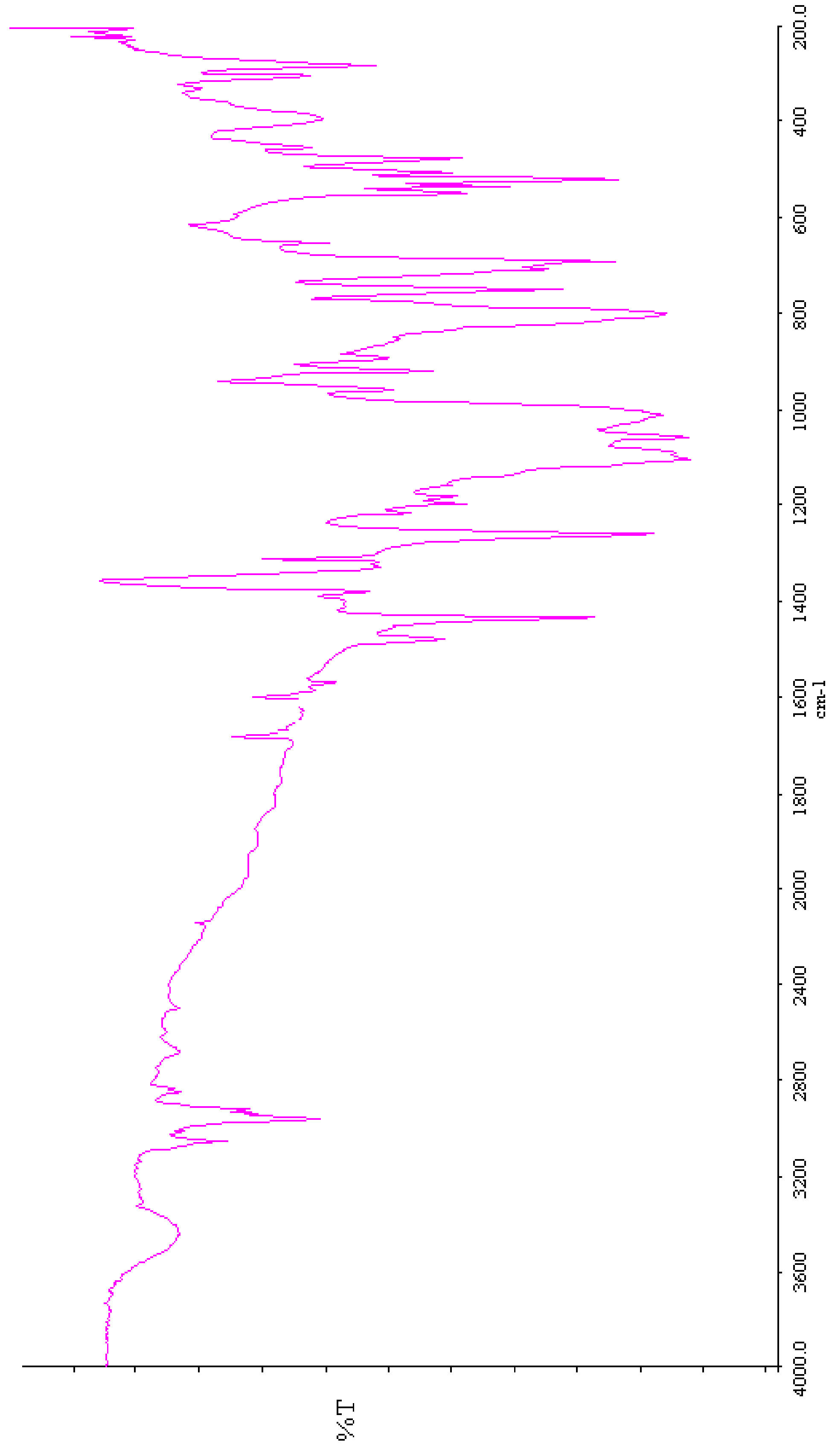


Figure 3.20 FT-IR Spectrum of Complex **3a'**

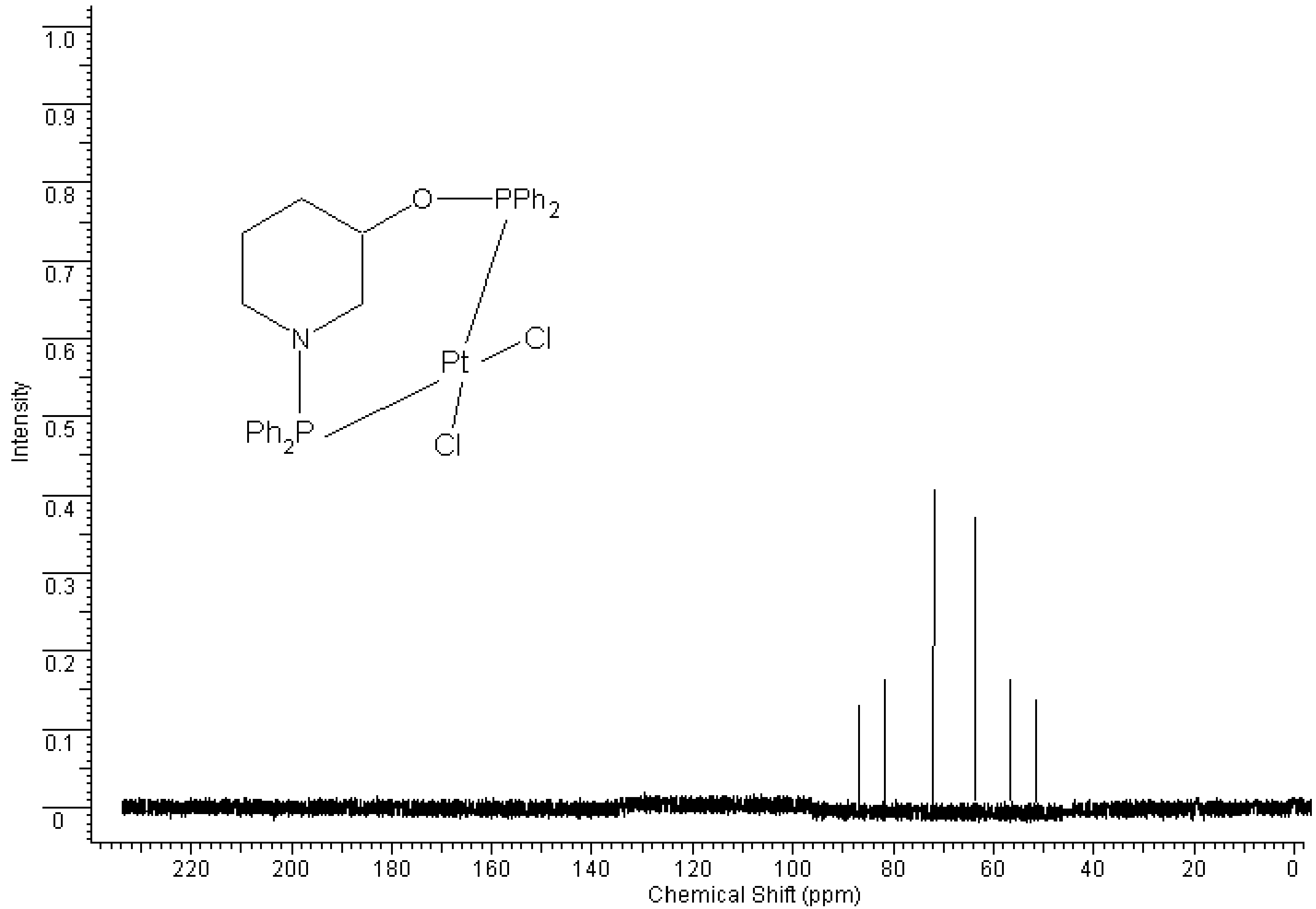


Figure 3.21 $^{31}P\{^{1}H\}$-NMR Spectrum of Complex **3a''**

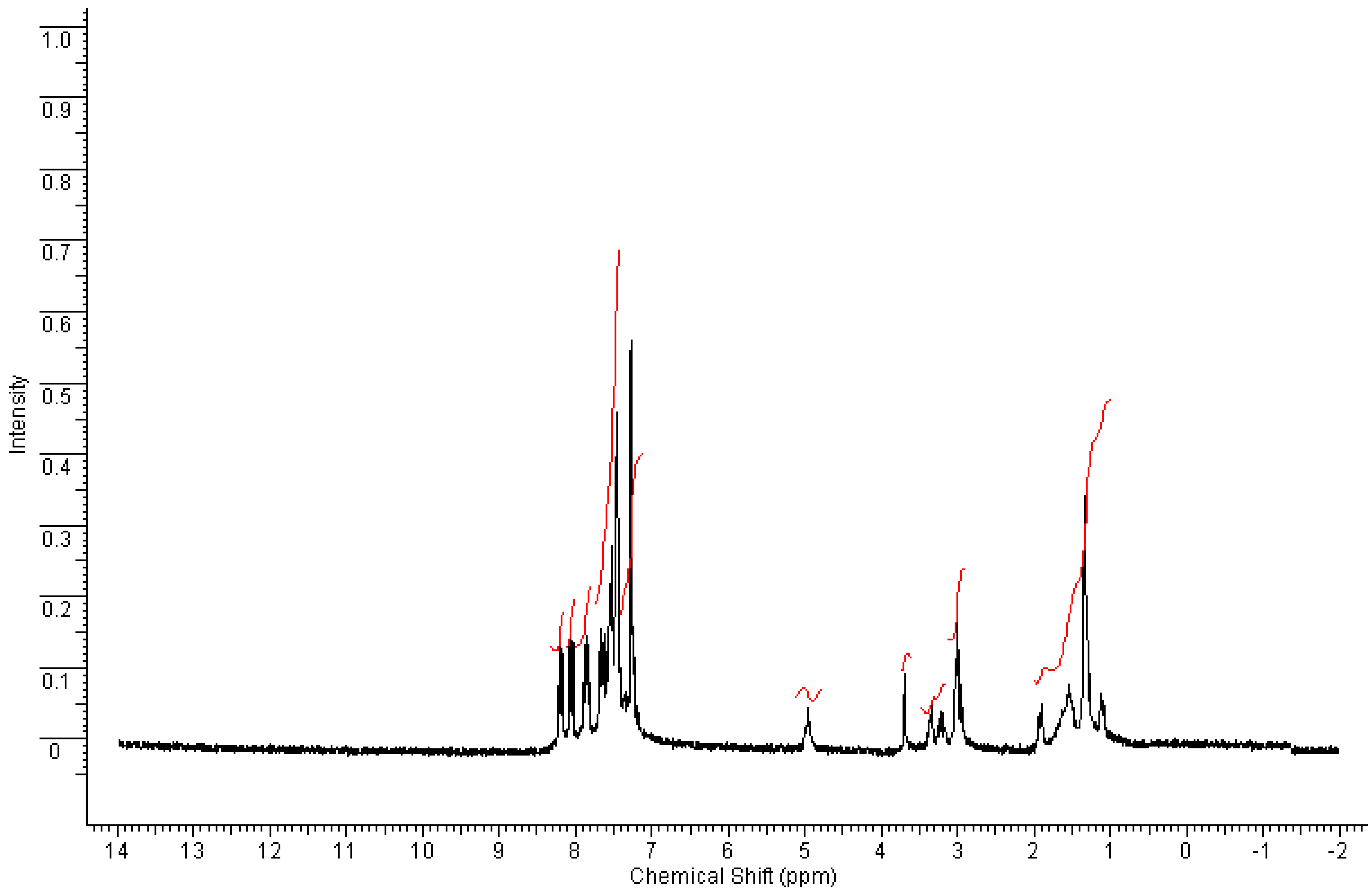


Figure 3.22 ^{1}H-NMR Spektrum of Complex **3a**''

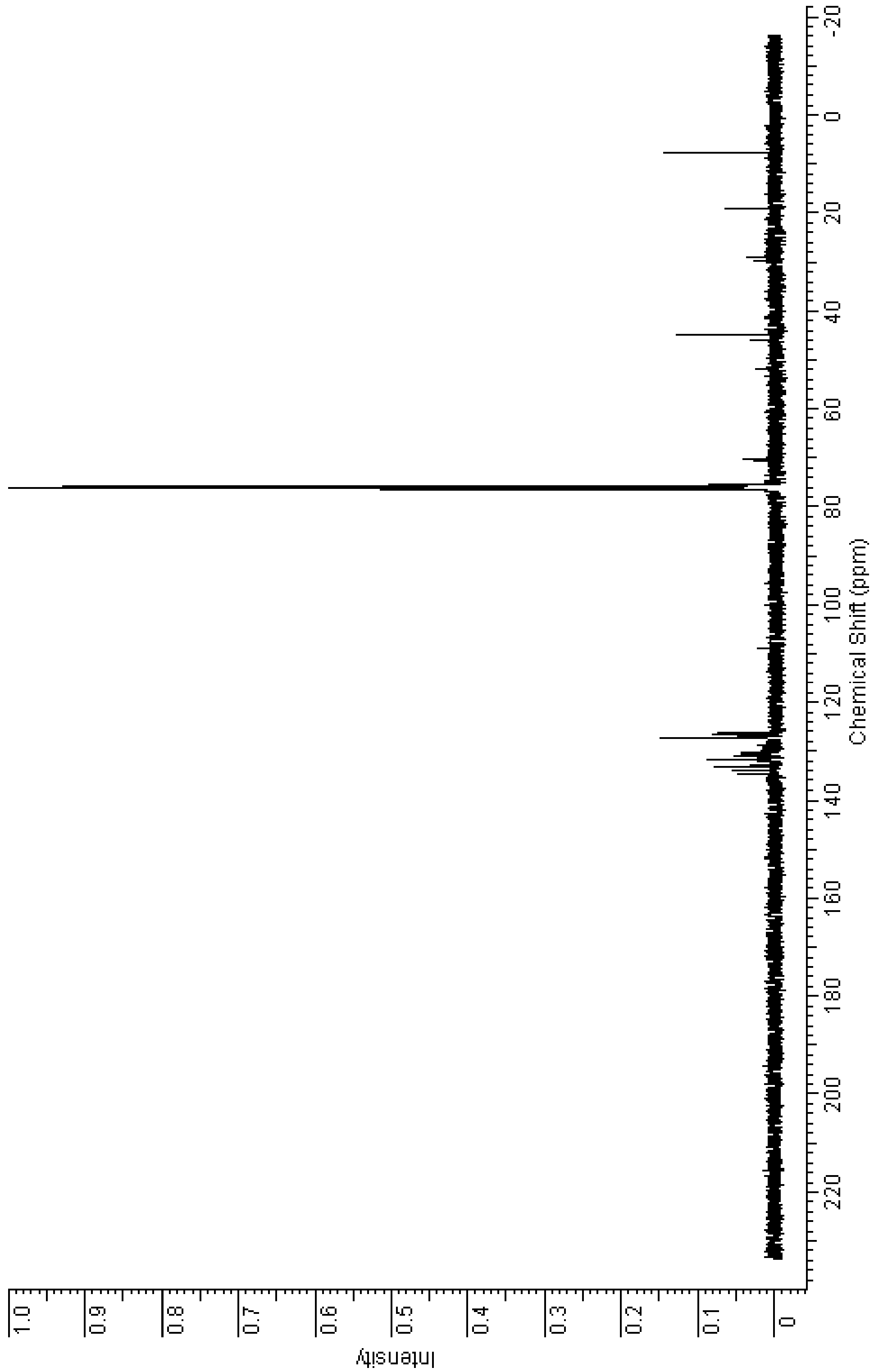


Figure 3.23 ^{13}C-NMR Spectrum of Complex **3a''**

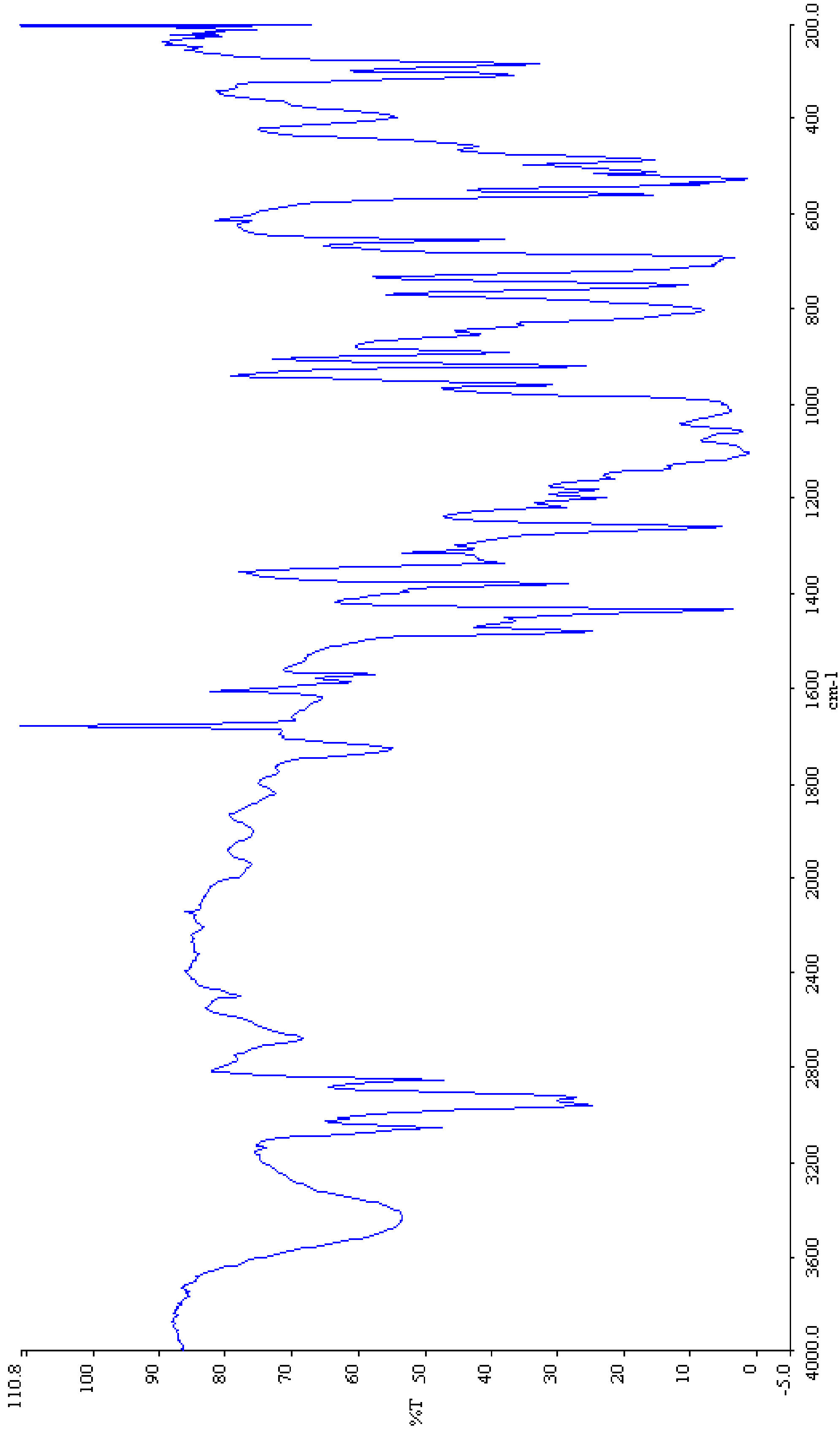


Figure 3.24 FT-IR Spectrum of Complex **3a''**

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CURRICULUM VITAE

Name- Surname : Nilgün ARDA

Date/Place of Birth : 04.08.1986 / Bursa, TURKEY

Nationality : T.C

Marital State : Single

Language : English

: Turkish (mother language

Adress : Ege University, Faculty of Science

Department of Chemistry

Phone Number : 05053824004 (cell)

E-mail : nilgunarda-86@hotmail.com

EDUCATIONAL BACKGROUND

B. S in Chemistry, 2008, Ege University, İzmir-TURKEY

M.S in Chemistry, 2010, Ege University, İzmir-TURKEY