CYCLOMETALLATED COMPLEXES PROMOTED ASYMMETRIC INSERTION AND HYDROPHOSPHINATION REACTIONS

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Summary

In this thesis chiral cyclometalated-amine template has been used successfully to promote insertion reaction for the synthesis of a series of chiral bi- or tri-metallic complexes and hydrophosphination reaction for for the synthesis of chiral phosphines and their metal complexes.

In Chapter 1, a brief introduction on cyclometallated palladium and platinum complexes, insertion reaction and hydrophosphination reaction, and the objectives of this project is presented.

In Chapter 2, The insertion of alkynes with di(1-propynyl)phenylphosphine ligands into Pd-C bonds of phenylamine palladacycles has been demonstrated. In this study, cyclopalladated and cycloplatinated complexes containing the phenyl and naphthylamine systems have been chosen to promote the reaction to give a series of bi- or tri-metallic compounds. Reactions involving cycloplatinated promoters usually produced two products, in which phosphorus stereogenic center adopting *R* absolute configuration was the major product. Moreover, this major product would perform a series of transformations to generate a new C stereogenic center which always adopts *S* absolute configuration. However, reactions involving cyclopalladated promoters could only obtain one product in which phosphorus stereogenic center always adopt *R* absolute configuration. Similarly, transformed products were also obtained.

Then insertion of alkynes with into Pd-C bonds of naphthyamine palladacycles has been investigated. It was found that, the reaction showed excellent selectivity which lead to the single insertion product. Moreover, this insertion product is very stable and no transformations were observed.

In Chapter 3, the insertion of alkynes with diphenylprop-1-ynylarsine ligands into Pd-C bonds of phenylamine palladacycles has been demonstrated. Cyclopalladated and cycloplatinated complexes containing the phenyl and naphthylamine systems have been chosen to promote the reaction to give a series of bi-metallic compounds. Compared with alkynes with phosphine ligand, insertion reactions with arsine ligand need longer reaction time. However, the yield of the reaction is higher.

Chapter 4 describes the chiral organopalladium template promoted asymmetric hydrophosphination reactions between ethylphenylphosphine and diphenylvinylphosphine, (*E*)- or (*Z*)-diphenyl-1-propenylphosphine, and 2-Vinylpyridine which proceed in high regio- and stereoselectivities under mild conditions. In the absence of the chiral reaction promoter, no reaction was observed. The reactions show high regio- and stereoselectivities under mild reaction conditions, with ethylphenylphosphino group was always added to the β-carbon of the vinylphosphines to form five- or six-membered chelate ring exclusively and the ethylphenylphosphino group occupied a position *trans* to the NMe_2 group of the chiral organopalladium template. The naphthylamine auxiliary can be removed *chemo*-selectively from the template products by treatment with concentrated hydrochloric acid to form the corresponding optically pure neutral dichloro palladium complexes. Subsequently, the dichloro complexes undergo ligand displacement with aqueous cyanide to generate the corresponding optically pure diphosphine ligands in high yields.

Nomenclature

The nomenclature used throughout this thesis conforms to the format adopted by Chemical Abstracts (Chemical Abstracts, 13th Collective index, Index Guide, 1992-1996)

X-Ray Structural Data

The X-ray structural analyses were kindly performed by Dr. Koh Lip Lin and Ms Tan Geok-Kheng at the National University of Singapore (Department of Chemistry), and Dr. Li Yongxin at Nanyang Technological University. Full structural data (listing of crystal and refinement data, bond distances, angles and thermal parameters) are available from Prof. Leung Pak-Hing upon request.

Abbreviations and Symbols

Ar	aryl group
ax	axial
br	broad
ca.	about (Latin *circa*)
conc.	concentrated
d	doublet
dd	doublet of a doublet
ddd	doublet of a doublet of a doublet
dec.	decomposed
dppe	1, 2 – bis(diphenylphosphino)ethane
dq	doublet of a quartet
eq	equatorial
Et	ethyl
et al.	and others (Latin *et alii*)
g	gram(s)
Hz	Hertz
m	multiplet
Me	methyl
mg	milligram(s)
min	minutes
mmol	millimole(s)
mp	melting point
NMR	Nuclear Magnetic Resonance

o	ortho
m	meta
p	para
Ph	phenyl
ppm	parts per million
q	quartet
qn	quintet
R	*rectus* (Latin: right absolute configuration)
S	*sinister* (Latin: left absolute configuration)
s	singlet
t	triplet
THF	tetrahydrofuran
Å	Angstrom(s)
δ	NMR spectroscopy chemical shift in ppm
$[\alpha]_D$	specific optical rotation measures at D line (589nm)

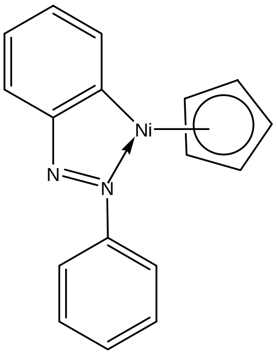
Chapter 1

General Introduction

1.1 Cyclometallated Palladium and Platinum Complexes

Cyclometallated complexes contain a comparatively reactive carbon–metal bond which is stabilized by the additional coordination of the metal (Pd, Pt, Ni, Rh, Ir, Ru, Re, Mn, Sn, etc.) to a heterodonor atom (N, P, S, As, or O) of the same ligand**.**

As early as 1963, the first cyclometallated complexe, azobenzenenickel **1**, was synthesized from dicyclopentadienylnickel and azobenzene by Kleiman and Dubeck.[1] Since then, a number of synthetic approaches have been investigated and an enormous number of cyclometallated compounds have been obtained.[2–12]



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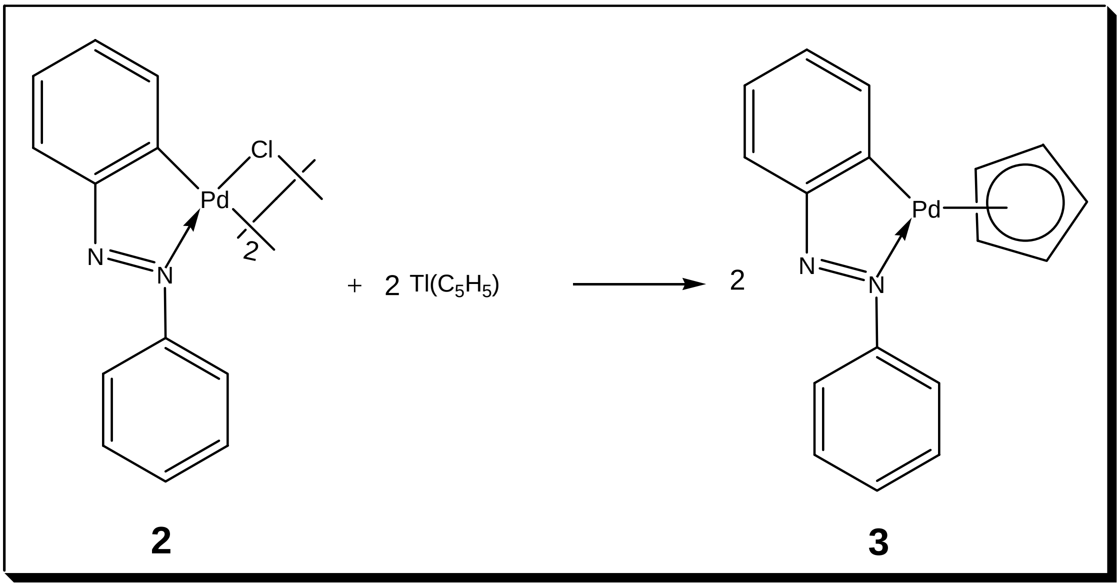
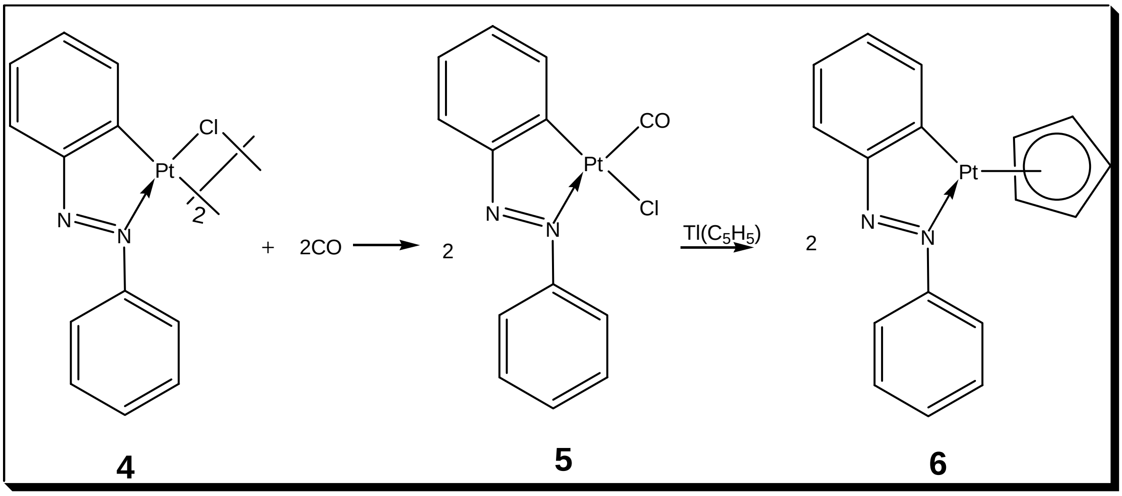
In the past decade, due to their application in different areas, the study of cyclometallated complexes containing palladium or platinum has initiated considerable interest.[13-15] Comparatively, cyclometallated palladium complexes have been studied much more than their platinum counterparts.[16] In general, cyclometallated palladium complexes are chemically more reactive than the corresponding platinum analogies. For example, as shown in

Scheme 1.1, azobenzenepalladium compound **2** readily reacts with cyclopentadienylthalium to give the cyclopentadienylpalladium compound **3**. On the other hand, there is no reaction between azobenzeneplatinum compound **4** and cyclopentadienylthalium under the similar reaction conditions, however, the carbonyl derivative **5**, obtained by treatment of azobenzeneplatinum compound **4** with carbon monoxide, immediately reacts with cyclopentadienylthallium to give cyclopentadienylplatinum compound **6** (Scheme 1.2).[17]



Scheme 1.1 Formation of cyclopentadienylpalladium compound



Scheme 1.2 Formation of cyclopentadienylplatinum compound

1.1.1 Cyclometallated Palladium Complexes

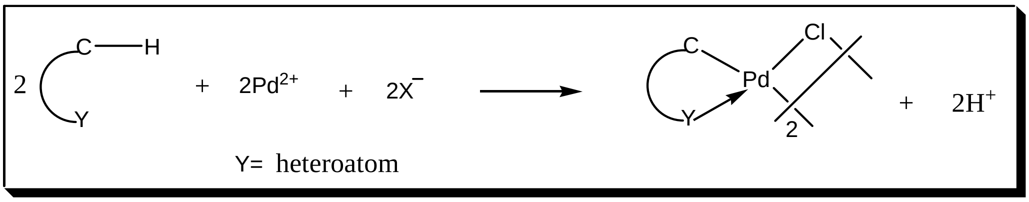
1.1.1.1 Synthesis of Cyclometallated Palladium Complexes

The synthesis of cyclometallated palladium complexes has been examined in great detail in a number of reviews.[2-12] In this part, only general approaches to the synthesis of the cyclometallated palladium complexes used in organic synthesis are briefly described.

1.1.1.1.1 The Direct Palladation Approach

Among all the known methods of synthesis of cyclometallated palladium complexes, the direct palladation of a ligand coordinated via heteroatom is the simplest and most convenient. The sequence is illustrated in Scheme 1.3.

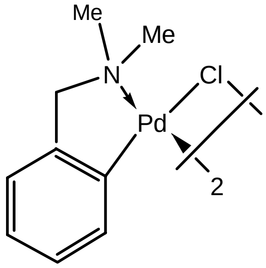
The palladium(II) salts are M_2PdCl_4, M_2PdCl_4–MOAc, and $Pd(OAc)_2$, where M is lithium or sodium. Lithium or sodium tetrachloropalladate(II) is considered as "mildest" metallating agent, while the M_2PdCl_4–alkali metal acetate or amine system is more generally effective. The acetate anion functions as a base which facilitates the dissociation of the C–H bond. Solvents for palladation reactions are methanol, ethanol, acetone, dioxin, chloroform, acetic acid, and aqueous organic mixtures. Usually, this kind of reaction can be conducted smoothly at room temperature, but in many cases heating is necessary.



Scheme 1.3 The direct palladation reaction

"Cyclopalladation" or "*ortho*-palladation" refers to the specific case of cyclometallation involving an *ortho*-carbon atom of an aromatic ring within the ligand.[18, 19] For *ortho*-palladation reactions, it has been suggested that preliminary coordination of the ligand *via* its heteroatom to the metal center is usually the first stage in the cyclopallation process.[19,20-22] Without the preliminary coordination, the formation of a metal–carbon σ-bond by direct metallation takes place in rare cases. For example, the intramolecular cyclopalladation of azobenzene is 4×10^4 times faster than the intermolecular reaction of $PdCl_2$ with benzene.[20]

Another factor that influences the rate and mode of cyclopalladation reactions is the basicity of the ligand. Cope and Friedrich performed *ortho*-palladation reactions by treatment primary, secondary and tertiary benzylamine with $[PdCl_4]^{2-}$ and found that cyclopalladation was unsuccessful when primary and secondary amines were used, only the *ortho*-palladated complex **7** with the tertiary amine was obtained.[19] Base on their study, it has been suggested that the stronger *N*-coordination of the primary and secondary amines compared with the tertiary amine weakens the electrophilic properties of the metal to such extend that this prevents the attack on the aromatic ring.



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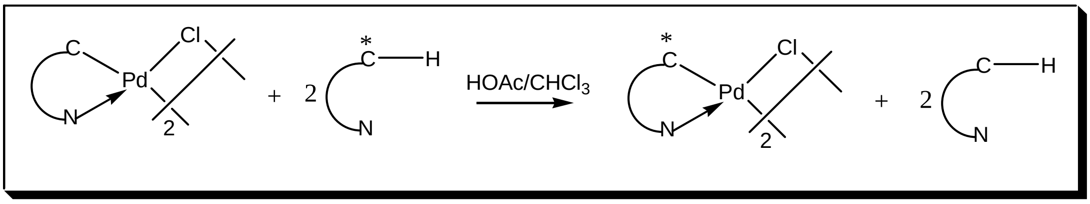
Direct palladation makes it possible to obtain complexes with aromatic, pseudoaromatic, and aliphatic ligands.

1.1.1.1.2 The Ligand Exchange Approach

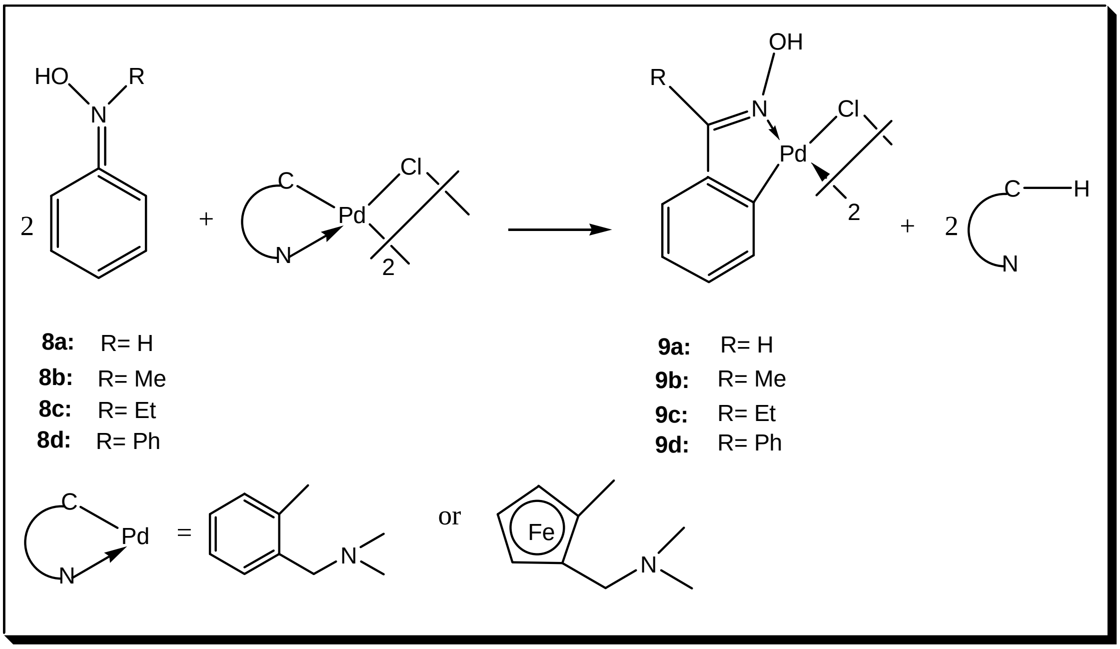
In 1984, Ryabov and Yatsimisky reported a remarkable reaction via ligand exchange involving the interaction of cyclopalladated dimer with a free *N*-donor ligand, which leads to a new palladocycle (Scheme 1.4).[23] This process has permitted the obtaining of cyclopalladated complexes of *N*-donor ligands containing electron-withdrawing substituents which are difficult to prepare by direct palladation reactions since the process occurs by the electrophilic attack of Pd(II) on the ligand ring.



Scheme 1.4 The ligand exchange reaction

The ligand exchange reaction occurs only in the presence of acetic acid as the co-solvent. [24] The method makes it possible to obtain complexes with N and P atoms, but ligands with an O donor do not have similar reactivity.[24, 25]

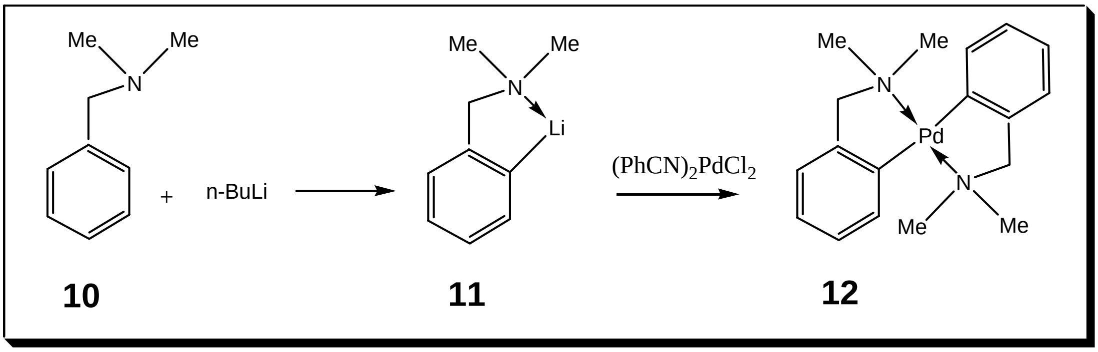
It has been reported that the ligand exchange approach is especially advantageous when a chloro-bridged cyclopalladated dimer is obtained in one step.[23, 25] Moreover, this method is particularly convenient for the synthesis of compounds which can be obtained by the direct palladation of the corresponding ligands. For example, the synthesis of *ortho*-palladated aryl oximes suffers from the presence of byproducts using the reported means [26] if tetrachlopalladate(II) is used as the metallating agent. However, by means of ligand exchange, *ortho*-palladated aryl oximes **9a–9d** can be obtained with slightly higher yields and the lack of by-products containing *N*-coordinated but non-palladated ligands(Scheme 1.5).[27]



Scheme 1.5 Synthesis of *ortho*-palladated aryl oximes *via* ligand exchange reactions

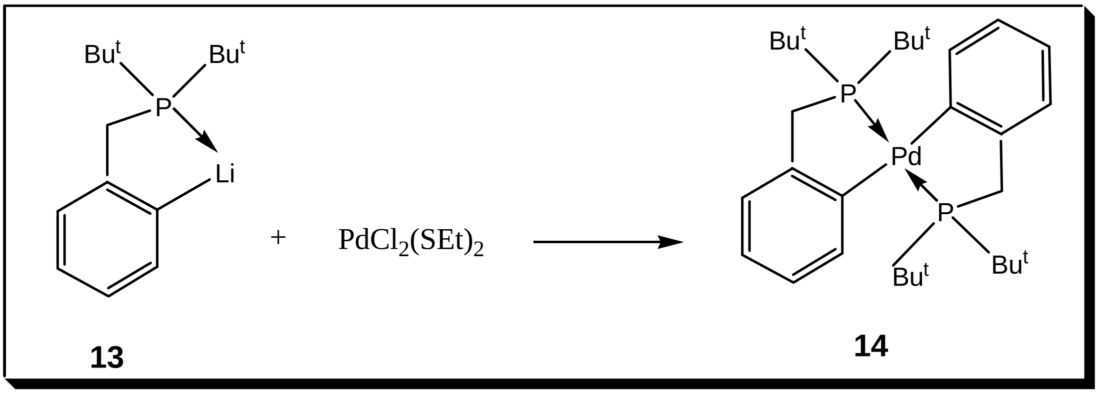
1.1.1.1.3 The Transmetallation Method

In the process of transmetallation reaction, the ligand is first treated with a suitable organolithium compound to afford the litho-derivative. Then the palladium(II) salt, which serves as the source of palladium(II) in the stage of metal exchange, is added. For example, the reaction of *o*-lithio-*N*,*N*-dimethylbenzylamine **11** with bis(benzonitrile)dichloropalladium affords the dimeric compound **12** which has two five-membered rings (Scheme 1.6).[28]



Scheme 1.6 Formation of complex **12** *via* transmetallation

The transmetallation of lithiated phosphines on treatment with palladium(II) coordination complexes is a unique method for the synthesis of phosphapalladacycles.[29,30] For example, the reaction between [$PdCl_2(SEt_2)_2$] coordination complex and *ortho*-lithated ligand **13** leads to the phosphapalladacycle **14**.[29,31]



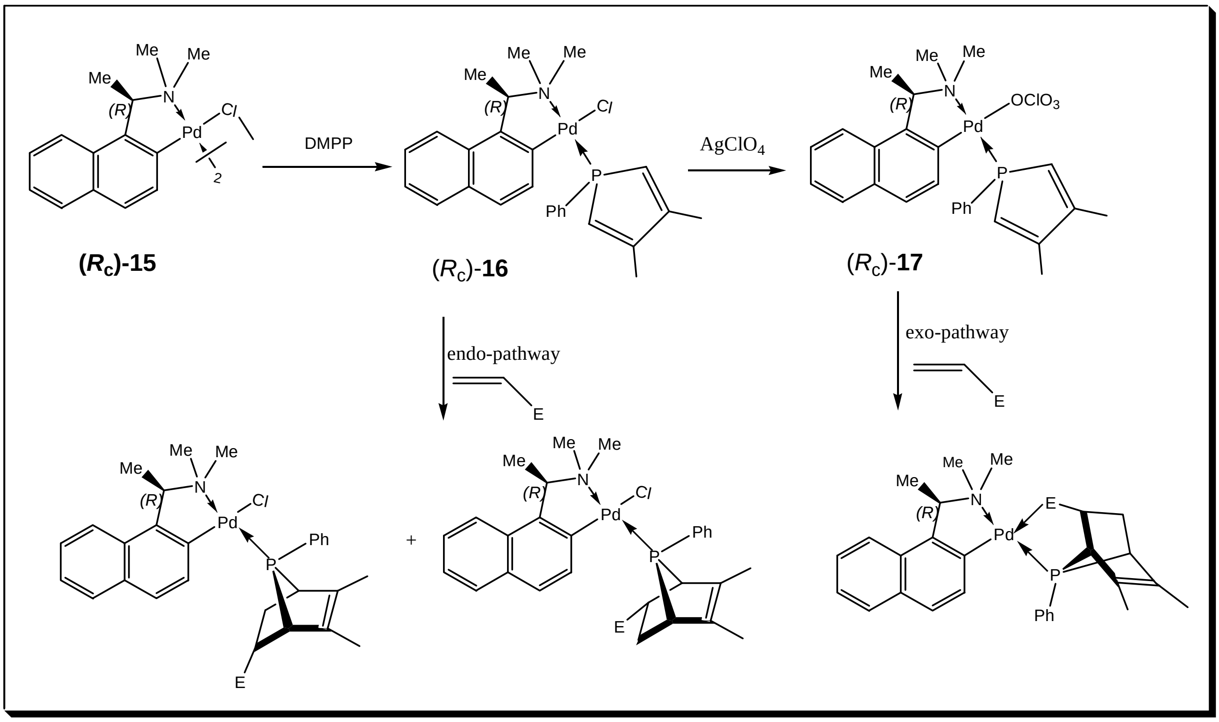
Scheme 1.6 Formation of phosphapalladacycle spiro complex **14**

1.1.1.2 Applications of Cyclometallated Palladium Complexes

The interest in cyclometallated palladium compounds was initially encouraged by obvious perspectives of using the compounds in organic and organometallic synthesis, but very soon these compounds began to be involved with other branches of chemistry including, such diverse areas as catalysis, photochemistry, liquid-crystal materials, the design of new metallomesogenes, and antitumoral drugs. Some of the applications of cyclometallated palladium compounds are briefly describe in the following part.

1.1.1.2.1 Cyclometallated Palladium Complexes in Asymmetric Synthesis

In the field of synthetic chemistry, the asymmetric Diels–Alder reaction is one of the most efficient and elegant methods for the preparation of chiral six-membered rings.[32] Optically–pure phosphines play important roles in homogenous asymmetric catalysis.[33] However, preparations of phosphines have been dependent on resolution of the racemates which is a tedious and often inefficient process. It has been proved that the Diels–Alder reaction offers an efficient way to synthesize functionalized *P*-stereogenic phosphines without classic separation of diastereomers.[34] As shown in Scheme 1.7, the asymmetric [4+2] cycloaddition reactions, which is promoted by the ortho-palladated complex (*R*$_c$)-**15**, has been carried out between 1-phenyl-3,4-dimethylphosphole (DMPP) and various functionalized dieneophiles .[34]



Scheme 1.7 Diels-Alder reaction promoted by cyclometallated palladium complex

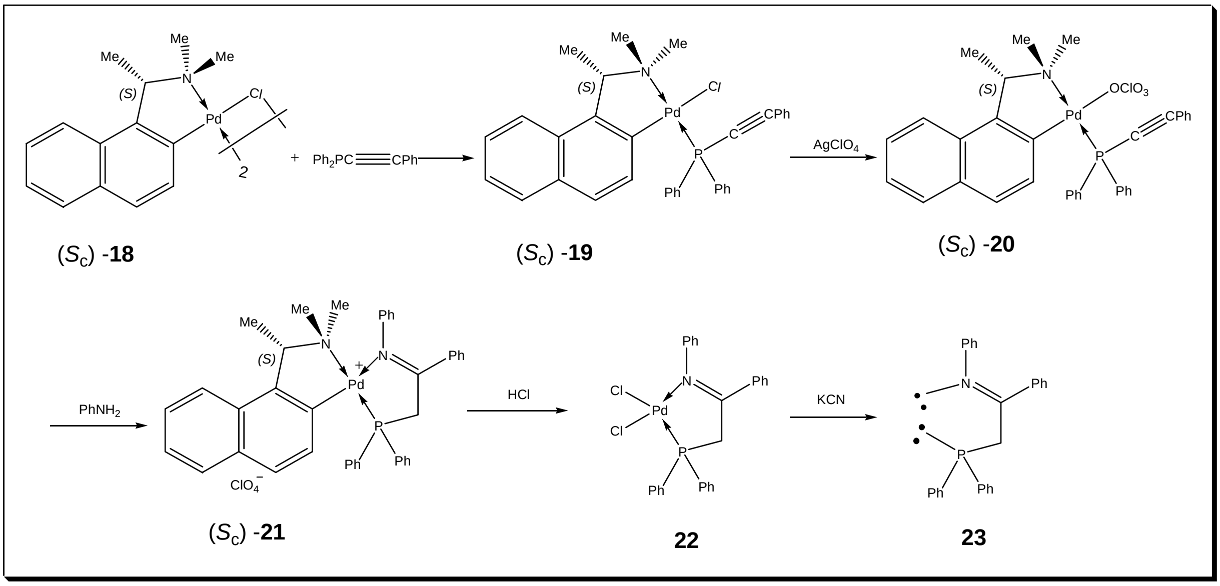
During the course of the Diels–Alder reaction, first the chloro bridges of complex (*R*$_c$)-**15** is split when DMPP coordinates regiospecifically to the position trans to the *N*Me$_2$ moiety to give (*R*$_c$)-**16** as a result of the unique electronic directing effects originating from the strong π-accepting aromatic carbon and the σ-donating nitrogen donor of the organopalladium unit. [35] The coordinated DMPP then undergoes a *endo*-cycloaddition or *exo*-cycloaddition reaction.

In the *endo*-cycloaddition reaction, the Pd–Cl bond in the complex (*R*$_c$)-**16** thermodynamically stable and kinetically inert, which therefore could not be displaced by the reacting dieneophile during the course of the cycloaddition reaction. As a result, the reaction adopts an intermolecular mechanism. Stereochemically, the *endo*-cycloaddition is controlled by the chiral template via only a single and rotatable P–Pd bond. Thus this intermolecular process does not show high stereoselectivity and produces a pair of diastereomeric *endo*-cycloadducts. Whereas in the *exo*-cycloaddition reaction, the kinetically labile perchlorato ligand could be displaced by the reacting dienneophile, therefore, the DMPP and the dieneophile could coordinate simultaneously onto the palladium during the course of reaction and the reaction adopts an intramolecular mechanism.[36]

By this controlled asymmetric cycloaddition method, several diphosphines[37] and functionalized monophosphines bearing functionalities such as sulfinyl and thiolato, [38] sulfonyl, [39] amide, [40] and keto-ester [41] have been efficiently synthesized in their optically pure forms.

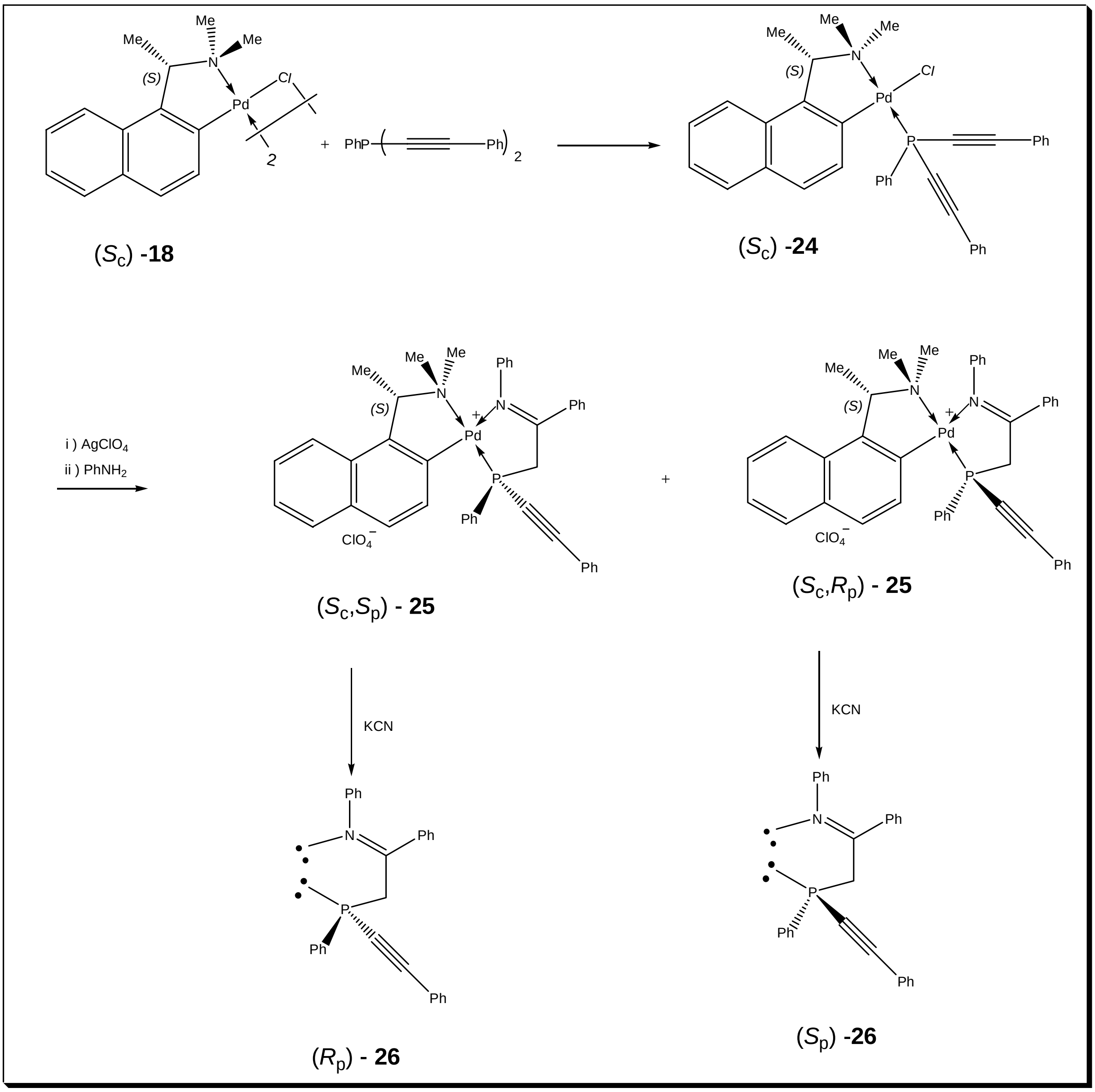
It has been reported that cyclometallated palladium complexes could also be applied to asymmetric hydroamination as an efficient template. As a result of this asymmetric reaction, iminophosphine ligands were generated efficiently.[42] It is noteworthy that iminophosphines are important ligands as potential catalyst supporters. [43]

As illustrated in Scheme 1.8, the reaction initially involved the regiospecific coordination of the phosphinoalkyne ligand onto palladium complex (S_c)-**18** to form the monomeric chloro complex (S_c)-**19**. Then, silver perchlorate was used to remove the chloro ligand so that the aniline could coordinate to the metal to afford complex (S_c)-**21**. Achiral iminophosphine ligand **23** was achieved by treatment of complex **22** with potassium cyanide.



Scheme 1.8 Asymmetric hydroamination of diphenyl(phenylethnyl)phosphine and synthesis of the achiral iminophosphine.

Still using complex (S_c)-**18** as template, asymmetric hydroamination of the prochiral di(phenylethynyl)phosphine led to a pair of diastereomeric complexes containing *P*-chiral iminophosphines (S_c,S_p)-**25** and (S_c,R_p)-**25.** After liberation, two optically pure *P*-chiral iminophosphines (R_p)-**26** and (S_p)-**26** were obtained (Scheme 1.9).[42]

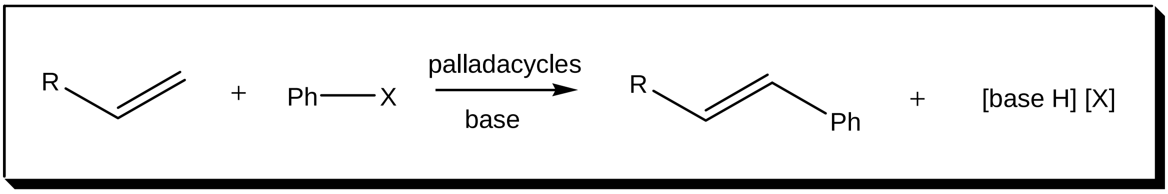


Scheme 1.9 Asymmetric hydroamination of the prochiral phosphinoalkyne and synthesis of the chiral iminophosphines

1.1.1.2.2 Cyclometallated Palladium Complexes in Catalysis

Pfeffer and his co-workers have reported the true potential of cyclometallated palladium complexes in organometallic catalysis: i) the Pd–C bond in the majority of palladacycles is reactive towards a wide range of nucleophilic and electrophilic reagents exploited in catalysis, and ii) the palladacycle can often be recovered unchanged following catalysis and can sometimes even be recycled.[44] Cyclometallated palladium complexes are now emerging as a new family of catalyst precursors for a host of reactions, such as hydrogenations,[45] aldol-type reaction,[46] cyclopropanation,[47] and coupling reactions including Heck,[48,52-64] Suzuki,[49] Sonogashira,[50] and Stille[51] reactions.

In the process of the Heck coupling reaction, for example, the arylation of C=C double bonds is mediated by a variety of Pd(II) and Pd(0) catalysts precursors (Scheme 1.10). In this context, palladacycles containing phosphorus,[52-56] nitrogen,[48b,57-60] and sulfur[61-63] are among the most active catalyst precursors for the promotion of such reactions.



Scheme 1.10 Heck coupling reaction

The mechanism of the Heck reaction involves the in situ generation of a Pd(0) species, which undergoes oxidative addition of the aryl halide to give a Pd(II)–aryl intermediate.[64] Coordination of the olefin and its migratory insertion into the Pd–aryl bond leads to a Pd(II)–aryl complex. β-Hydrogen elimination affords the arylated olefin and a Pd–H species, which through reductive elimination, regenerates the Pd(0) catalytically active species.[65]

1.1.1.2.3 Cyclometallated Palladium Complexes as Liquid Crystal

Liquid crystals or mesogenic compounds, which combine properties of both the crystalline (optical and electrical anisotropy) and the liquid (molecular mobility and fluidity) states, have been defined as “orientationally ordered” liquids or “pssitionally disordered” crystals.[66] This behaviour appears under given conditions when phases that do not correspond to an ordered solid nor to a disordered liquid or solution are formed, and these phases are called *mesophases*. Liquid crystals can be categorized to two different types corresponding to the way of taking a crystal to a mesophase: i) *thermotropic* liquid crystals which can be obtained by heating the crystalline solid or cooling the isotropic liquid; ii) *lyotropic* liquid crystals which can be obtained by dissolving the compound in an adequate solvent under certain concentration and temperature.

The ubiquitous presence of liquid crystal displays (LCD) has made liquid crystals perhaps the most popular and familiar class of advanced materials in modern life. In recent years, these materials have given rise to important technological innovations. The advances extend to fields as diverse as electro-optical displays, temperature sensing devices, high performance polymers, etc.. [67]

Ortho-metallated palladium(II) complexes are by far the most widely studied mesogenic complexes, especially the complexes derived from *ortho*-cyclo-palladated imines[68] and azines,[69] as well as azobenzenes.[70] This class of mesogens is represented by palladium derivatives mainly, due to the formation of stable complexes and the ease of the orthocyclopalladation reaction which produces aromatic core with planar structure, thus leading to the formation of liquid crystalline phase. As a chemical diversity, these complexes offer many opportunities for the formation of novel palladium metal based materials.

For example, cyclometallated palladium(II) imine complexes have received much attention due to: i) their thermal stability; ii) the variety of ligands useful for *ortho*-metallation leading either to calamitic or to discotic mesogens; and iii) the possibility of tuning the mesogenic properties not only by varying the nature or the length of the chains, but also the nature of the bridges in dinuclear complexes. The imine moiety provides the rigid core and flexible chains needed for liquid-crystal behavior, and two of these moieties are fused together upon orthometallation to give a X-bridged dinuclear complex (Figure 1.1).[71, 72]

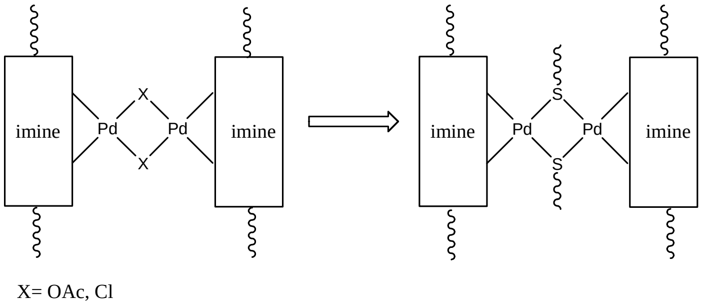


Figure 1.1 Different space-filling efficiencies for cyclopalladated imine complexes having bridges without or with long alkyl chains

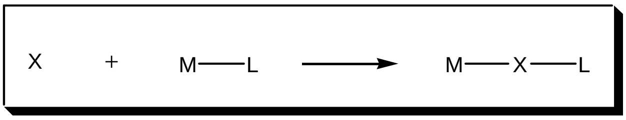
1.1.2 Cyclometallated Platinum Complexes

Cyclometallated platinum complexes have been studied along with their palladium analogy and they are of interest for several reasons including their attractive photochemical and photophysical properties,[73] their potential use as molecular devices,[74] and more generally, for their potential utility in catalysis and organic synthesis.[75] Furthermore, several examples can be found in platinum-phosphine chemistry.[76]

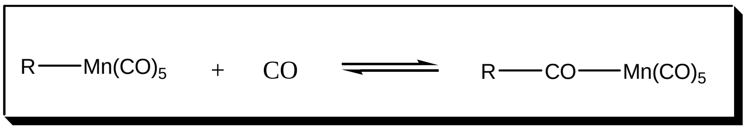
Comparatively, cyclometallated platinum complexes are not as widely studied and readily accomplished as cyclometallated palladium complexes; although there are not rare.[18, 19, 77-79] Usually, cycloplatination reactions require longer reaction times and give poorer yields than the cyclopalladation processes. [78] For example some cycloplatinations required two weeks to complete[19] or relatively strong reaction conditions, such as refluxing in DMF [77]. Some suggestions on the improvement of the reaction efficiency have been reported For example, Anklin and co-workers emphasized the advantage of choosing the starting material complex which i) can increase its extent of coordinative unsaturation and ii) has electrophilic character. Arising from this approach, cycloplatination of quinoline 8-carboxyaldehyde can be facilitated by using $SnCl_2$ or Ag^+ as halogen extracting reagents when the complex has a Pt–Cl bond, thereby achieving i) and ii) simultaneously.[79]

1.2 Insertion Reactions

The concept of ‘insertion’ is widely applicable in chemistry when defined as a reaction wherein any atom or group of atoms is inserted between two atoms initially bound together.[80] The reaction often leads to chain growth. In coordination chemistry, for a metal complex M–L, therefore, we speak of an insertion reaction if the stoichiometric product results from the formation of new bonds by X to both the metal M and the ligand L (Scheme 1.11). The classical example of an insertion reaction is the carbonylation of alkyl(pentacarbony1) manganese by carbon monoxide (Scheme 1.12).[81]

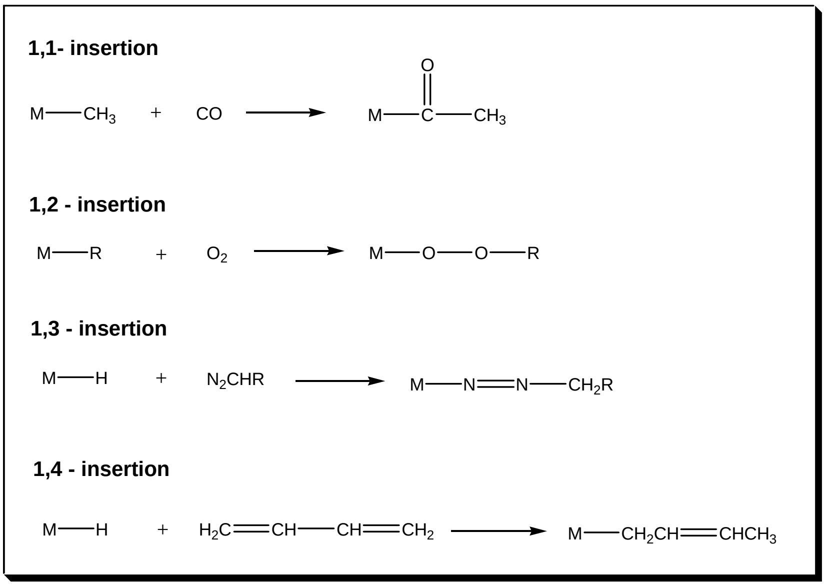


Scheme 1.11 Insertion reaction of M-L by X



Scheme 1.12 Insertion reaction of alkyl(pentacarbony1) manganese by carbon monoxide

The insertion process can proceed intermolecularly (migratory insertion) or intramolecularly. From the synthetic point of view, intermolecular insertion is not generally useful because of low selectivity and competition from intramolecular reactions.[82] Depending on the nature of the inserting ligand and the atom to which the migrating group is transferred, common types of insertion reactions mainly involve 1,1- , 1,2- , 1,3-, and 1,4-insertion reaction, respectively (Scheme 1.13).[83]



Scheme 1.13 Types of insertion reactions

For the insertion reactions described in Scheme 1.11, the species X to be inserted into the M–L bond is by definition “coordinatively unsaturated”, since it increases its coordination number on forming new bonds. Its unsaturation is usually of the p_π–p_π type (CO, SO_2, CO_2, *etc*.). Table 1 summarizes the insertion reactions which have been observed or may, at least in principle, become observable. The inserted group X can function in the end product as a monoatomic (CO, CNR, $SnC1_2$), a diatomic (>C=C<, —C≡C—, O_2), a triatomic (CS_2), or a polyatomic (S_n) bridge. Some of the groups X may be bidentate, *e.g.*, CO_2 and CS_2, which insert into M–NR_2 bonds to give dialkylcarbamato- and dialkyldithiocarbamato complexes, respectively.[84]

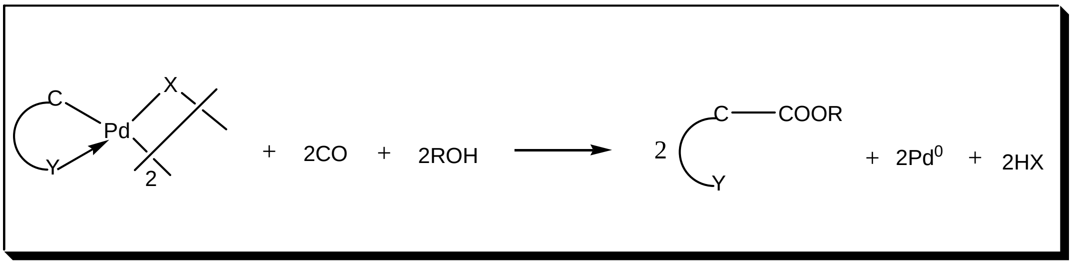
Table 1.1 Experimentally detected and theoretically possible insertions reactions

Metal- ligang bond	Group inserted
M-C	CO, CNR, CR_2, >C=C<, —C≡C—, CO_2, O_2, SO_2, S_n, $SnCl_2$
M-H	CO_2,CNR, >C=C<, RNCO
M-N	CO_2, CS_2
M-O	RNCO, SO_2
M-S	CS_2
M-Cl	CNR, CR_2, $SnCl_2$
M-M	$SnCl_2$

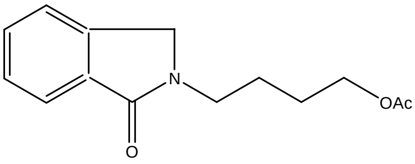
1.2.1 Carbon Monoxide Insertion

Insertion of CO has been the most widely studied of the insertion processes and most of the early investigations have concentrated on organo-metal complexes with monodentate ligands (primarily phosphines). The interest in carbon monoxide insertion reactions resides in the scope they offer for functionalizing hydrocarbons and other substrates to give more valuable organic compounds, such as aldehydes, acids, and esters. Catalytic reactions of this kind are hydroformylation,[85,86] the reaction of methanol with CO to give acetic acid,[87] the double insertion of CO and olefins within the coordination sphere of a metal to give acids or esters in the presence of water or alcohols,[88] the synthesis of hydroquinone by carbonylation of acetylene in the presence of ruthenium catalysts,[89] and the synthesis of acrylic acid from acetylene in the presence of nickel catalysts.[90]

Cyclopalladated complexes play an important role in insertion reactions involving CO, and in particular, the carbonylation of organic substrates is a useful tool for the synthesis of a variety of organic compounds. [91-95] The carbonylation is accompanied by the reduction of palladium (II) to palladium (0). As shown in Scheme 1.14, the most characteristic carbonylation pathway involves the formation of esters from alcohols. By this method, a lot of esters, like complexes **26–31**,[95-99] have been obtained,



Scheme 1.14 Carbonylation pathway of cyclopalladated complexes involving CO



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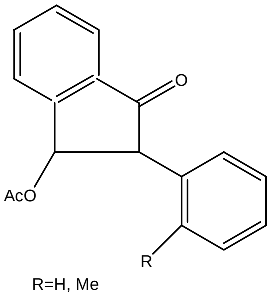

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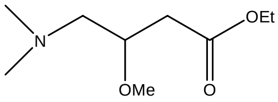

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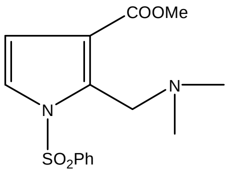

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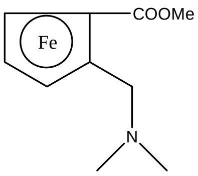

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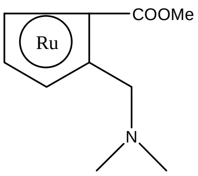
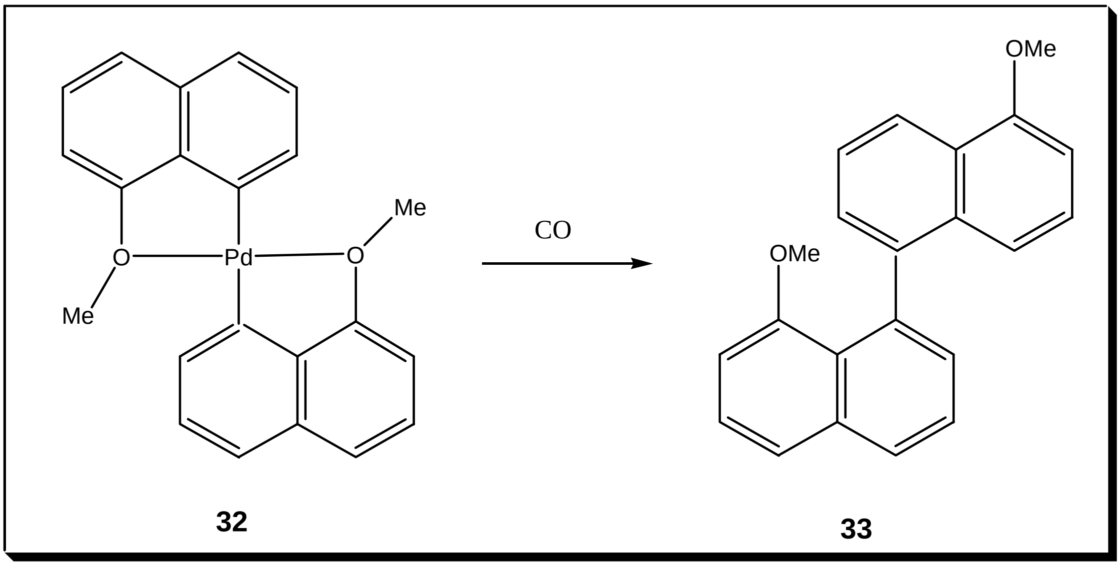


31

In a number of instances the “carbonylation products” of cyclopalladated complexes do not contain carbon monoxide at all. For example, the carbonylation of derivatives of 1-methoxynaphthalene, **26**, results in the quantitative formation of complex **27**, 8,8′-dimethoxy-1,1′-binaphthyl.[100] The study of the interaction of palladated oximes with CO showed that the free ligand is formed under certain conditions.[22,23] This “reductive carbonylation” reaction has served as the basis of a method of synthesis of selectively deuteriated vinyl[101] and aryl[102]oximes.



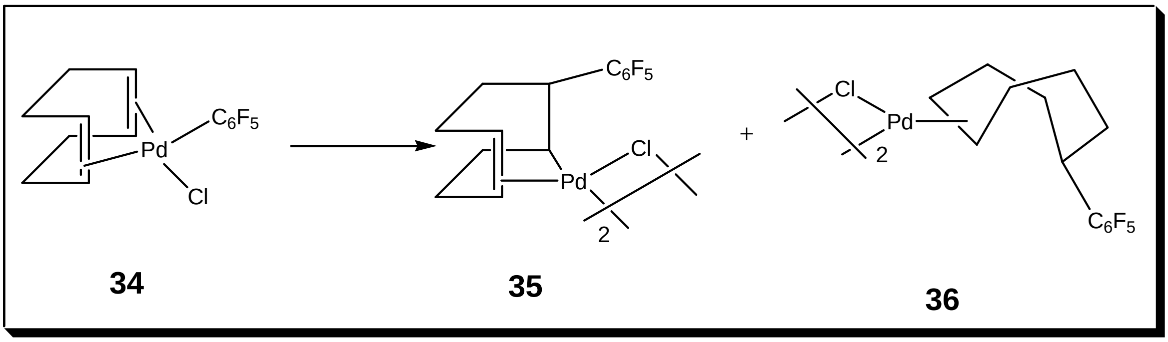
32 **33**

Scheme 1.15 Carbonylation of derivatives of 1-methoxynaphthalene

1.2.2 Alkene Insertion

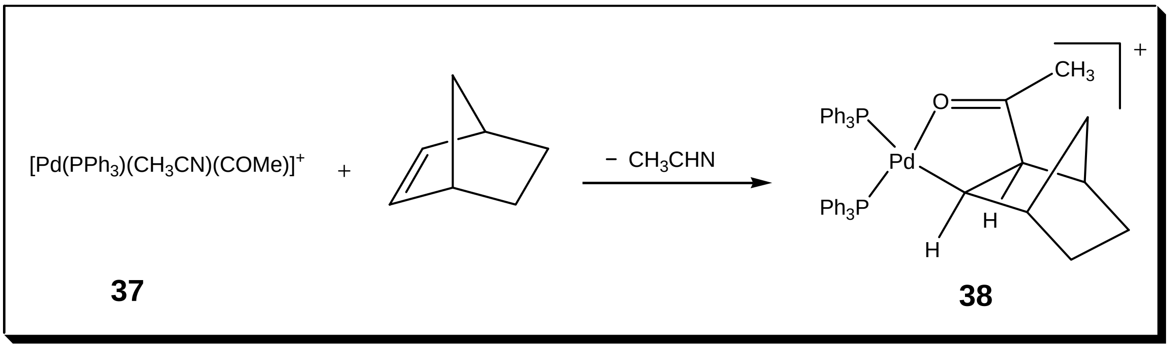
The insertion of a π-coordinated alkene into a *cis* metal-bound hydrocarbyl group is one of the most fascinating topics in organometallic chemistry, for both theoretical and experimental reasons.[103] Thus, the study of the insertion of alkenes into the palladium–carbon bond has attracted a great deal of interest, since it constitutes a key step in very important processes such as the Heck reaction,[104-107] the palladium catalyzed oligo-[108,109] or polymerization of olefins,[110-115] annulation of cyclic and bicyclic alkenes,[116] or double arylation of olefins.[117-119]

Investigations of alkene insertions into metal–carbon bonds are often impeded by difficulties in observing the pre-insertion *cis*-(alkyl–alkene) intermediate and the final inserted product. The reasons are that once the pre-insertion intermediate is formed, insertion is very facile and, likewise, the final inserted product generally has a low energy pathway for decomposition, namely β-elimination. Another problem is to provide a suitable cis coordination site for the alkene prior to insertion. Recently, various approaches have been developed to overcome difficulties in observing these intermediates. For example, Espient and co-workers have structurally characterised the cis–alkylalkene complex **34** [PdCl(C_6F_5)(COD)], and identified two isomeric insertion products resulting from endo attack of the C_6F_5 group on the cyclooctadiene double bond (i.e., the C_6F_5 group and the Pd atom both attach to the same face of the cyclooctadienyl ring) (Scheme 1.16).[120]



Scheme 1.16 Formation of isomers from *endo*-insertion.

Insertion of strained alkenes or alkenes without β-hydrogens into metal–acyl bonds has also allowed isolation or identification of inserted products. For example, Sen and co-workers have studied the insertion of olefins such as norbornene, norbornadiene and dicyclopentadiene into the platinum–acyl[121] and palladium–acyl [122] bonds of the neutral and cationic complexes $Pd(PPh_3)_2(Cl)(COR)$ and $[M(PPh_3)_2(CH_3CN)(COR)]BF_4^-$. Complex **38** was isolated from the reaction of complex **37** with norbornene (Scheme 1.17).[122]

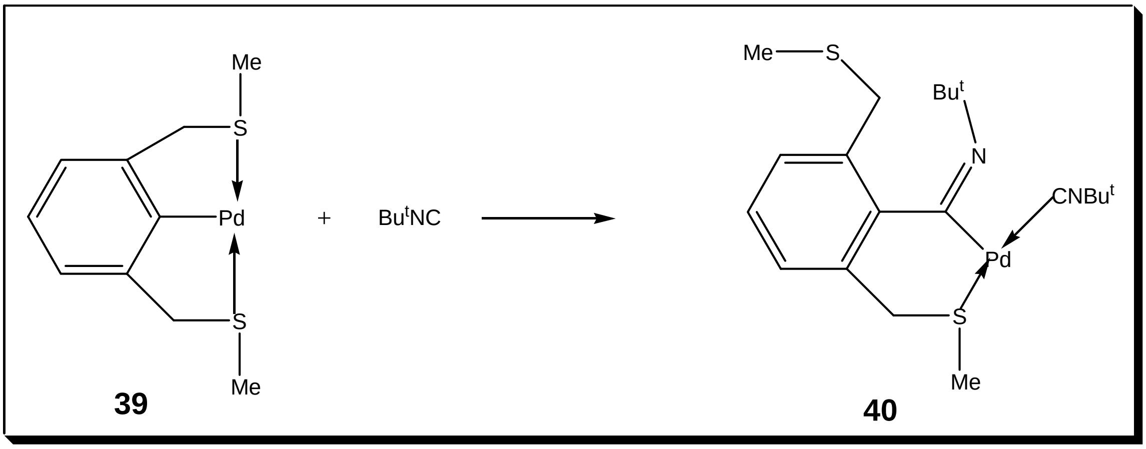


Scheme 1.17 Insertion involving norbornene

1.2.3 Isocyanide Insertion

The reactivity of the isocyanides with respect to the transition metal–carbon bond is in many aspects analogous to that of carbon monoxide, which is isoelectronic with isocyanides. Insertion reactions of isocyanides into Pd–C bonds are involved in the synthesis of aminoisoindolinium salts,[123,124] 3-imino-2-phenylindazolines,[125] 2-cyano-1-arylazonaphthalenes, 3-amino-2-arylbenzoindazoles,[126] ketenimines,[127,128] 2,3-dihydroisoindol-1-ones,[129] and other *N*-heterocycles,[130] or *N*-functionalized arenes.[129,131]

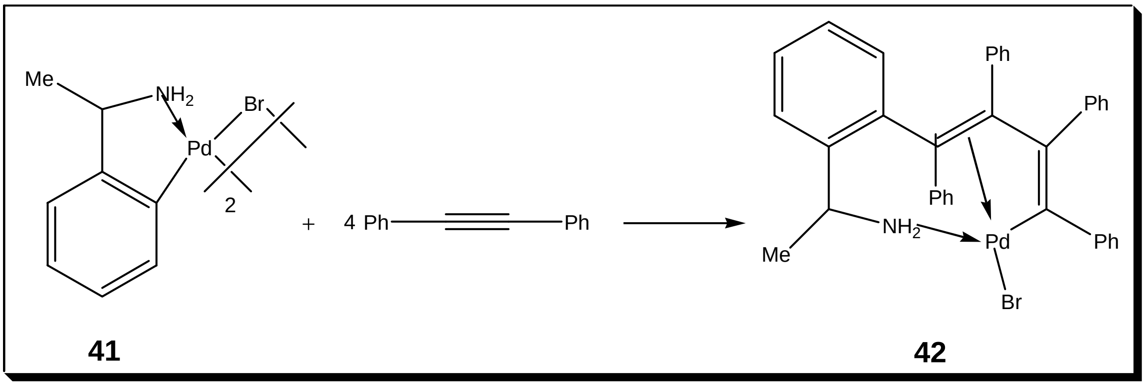
The insertion reactions of isocyanides into the aryl–palladium bond to give iminoacyl complexes are well-known.[132-137] For example, no reaction occurred when complex **39** was treated with 1 equivalent of RNC. However, in the presence of an excess of *t*-butyl isocyanide ([Bu^{t}NC]/[Pd] > 2:l) the insertion of this isocyanide into the Pd–C bond of **39** was observed after *ca.* 2 h in dichloromethane at room temperature to give compound **40** in good yield (Scheme 1.18).[133]



Scheme 1.18 Insertion involving isocyanide

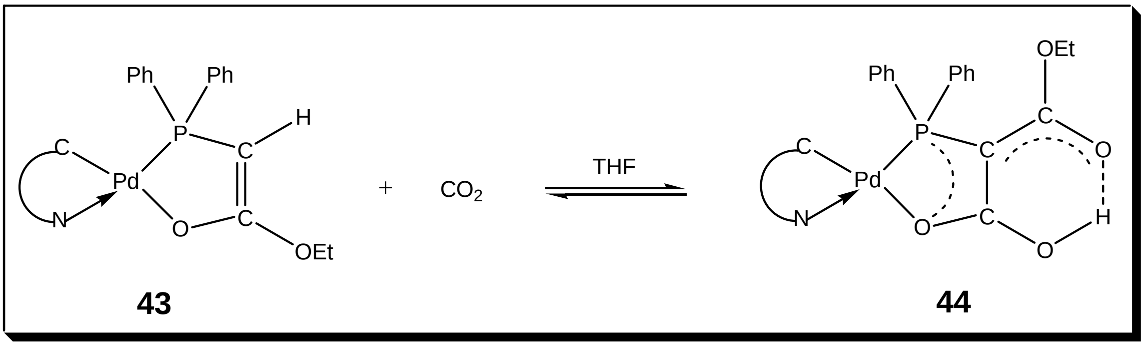
1.2.4 Insertions involving Alkyne and Carbon Dioxide

It is well known that insertion of alkynes into Pd–C$_{sp3}$ and Pd–C$_{sp2}$ bonds of intramolecular coordination systems gives products involving the incorporation of one, two or three alkyne units into the Pd-C bond.[138-142] As illustrated in Scheme 1.19, double insertion product **42** is formed in the interaction of tolane with dimeric palladium(II) complex **41**.[143]



Sheme 1.19 Insertion involving alkyne

CO_2 can undergo insertion into a series of metal–ligand bonds and there are several reviews on the insertion of CO_2 into the M–L bond in the literature.[144-147] The first example of reversible CO_2 insertion into a Pd(I1) complex is shown in Scheme 1.20. Bubbling of dry CO_2 through solutions of complex **43** in THF in for several seconds leads to the insertion of CO_2 in the PC–H bond and the formation of new complex **44** in which chelation via an oxygen atom of the ester has been replaced by chelation via an oxygen atom of carbon dioxide.[148]



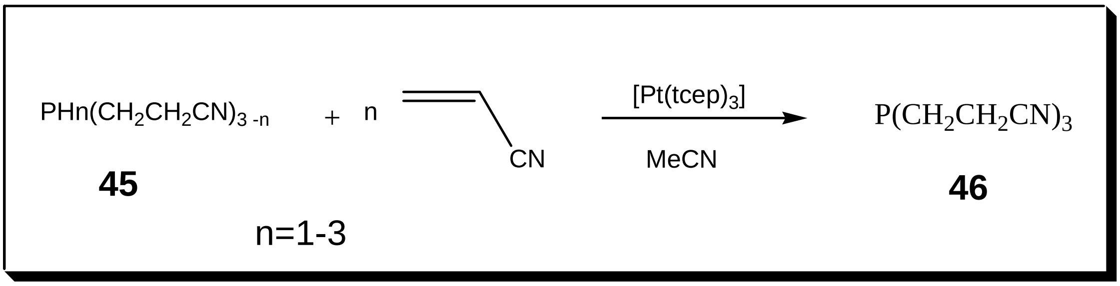
Scheme 1.20 Insertion involving carbon dioxide

1.3 Metal-catalyzed Hydrophosphination

The addition of PH_3, primary or secondary phosphines to unsaturated carbon-carbon bonds is, in terms of synthetic value and atom economy, a very promising process for the construction of C–P bonds. This reaction, known as hydrophosphination, allows the synthesis of highly desirable phosphines, which are ligands of choice for homogeneous catalysis. The reactions are mainly carried out under acidic, basic conditions, or radical activation.[149-151] Compared to the addition of other heteroatom-hydrogen bond (e.g., hydrosilylation,[152] hydroboration,[153] hydrostannation[154]) hydrophosphination has been much less studied. Recently, metal-catalyzed hydrophosphinations of alkenes or alkynes have been reported, allowing a variety of structurally and electronically diverse phosphines to be accessed more easily and efficiently.

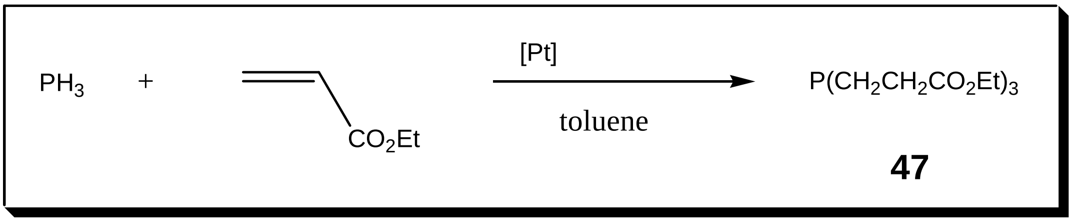
1.3.1 Hydrophosphination of Alkenes

Platinum-catalyzed hydrophosphination of activated olefins (acrylonitrile and acrylate derivatives) is an atom-economical route to functionalized phosphines.[155] The first example of hydrophosphination of an alkene catalyzed by a transition metal was the Pt(0)-catalyzed hydrophosphination of acrylonitrile.[156] The tris(cyanoethyl)phosphine(tcep) has previously been well-studied,[157] and the complex [Pt(tcep)$_3$] was found to catalyse the addition of $PH(CH_2CH_2CN)_2$ to $H_2C=CHCN$ to give **46** (Scheme 1.21). It was later found that other d^8 and d^{10} metal-tcep complexes, including Pd, Ir, and Ni, were also found to catalyze the hydrophosphination of acrylonitrile,[158] but Pt remained the most efficient.



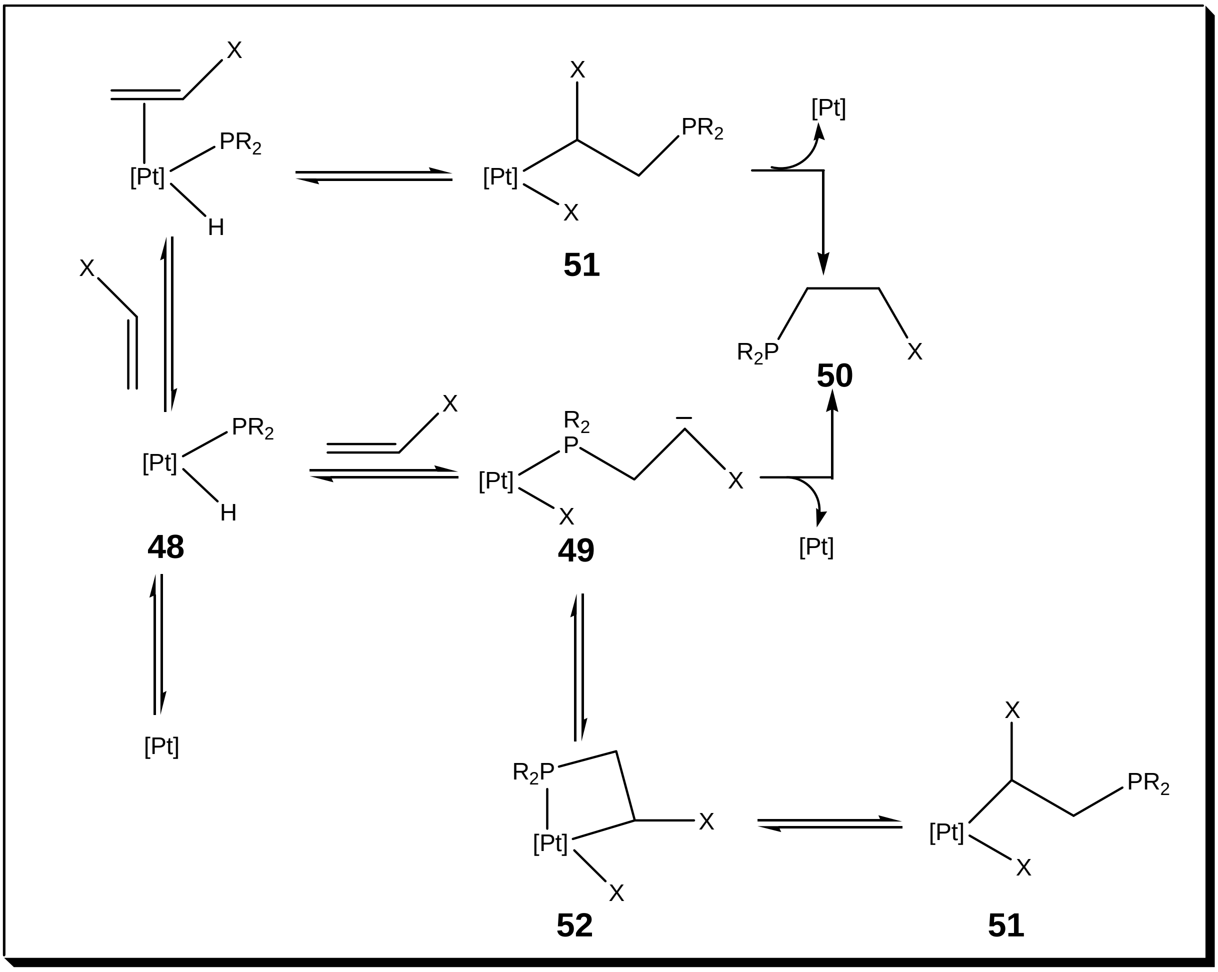
Scheme 1.21 Hydrophosphination of acrylonitrile

Pt can also catalyze the hydrophosphination of ethyl acrylate. For example, it was reported that synthesis of the triester phosphine **47** by the addition of PH_3 to $CH_2=CHCO_2Et$ is catalyszd by platinum(0) complexes of **47** and once again, platinum complexes of the product ligand are effective catalysts for the reaction itself (Scheme 1.22).[159]



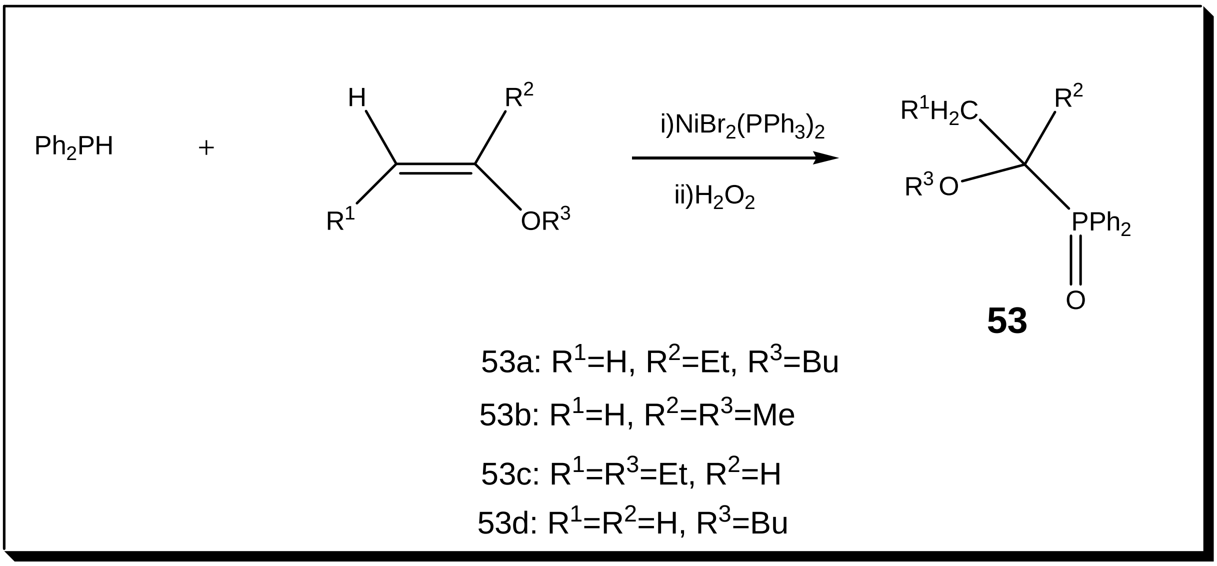
Scheme 1.22 Hydrophosphination of ethyl acrylate.

Recently, a proposed mechanism for platinum-catalyzed hydrophosphination of activated alkenes has been reported, in which P–H oxidative addition yielded intermediate hydride complex [Pt(diphos)(PR_2)-(H)) **48**, then nucleophilic attack of a phosphido ligand in complex **48** on the alkene CH_2=CHX (X = CN or CO_2R) gave the zwitterion Pt(diphos)(H)(PR_2CH_2CHX) **49**, containing a cationic Pt center and a phosphine ligand with a pendent stabilized carbanion. Subsequent C–H bond formation involving the Pt–H and the carbanion would yield the product $R_2PCH_2CH_2X$ **50** and regenerate the catalyst, while attack of the carbanion on another alkene would yield byproducts derived from more than one alkene, such as $R_2P(CH_2CHX)_nCH_2CH_2X$. Alternatively, carbanion attack at platinum, along with Pt-P dissociation, could generate alkyl hydride **51**, perhaps *via* five-coordinate **52** (Scheme 1.23).[160] Several tests of this mechanism and related pathways for product and byproduct formation were investigated.[161]



Scheme 1.23 proposed mechanism for platinum-catalyzed hydrophosphination of activated alkene

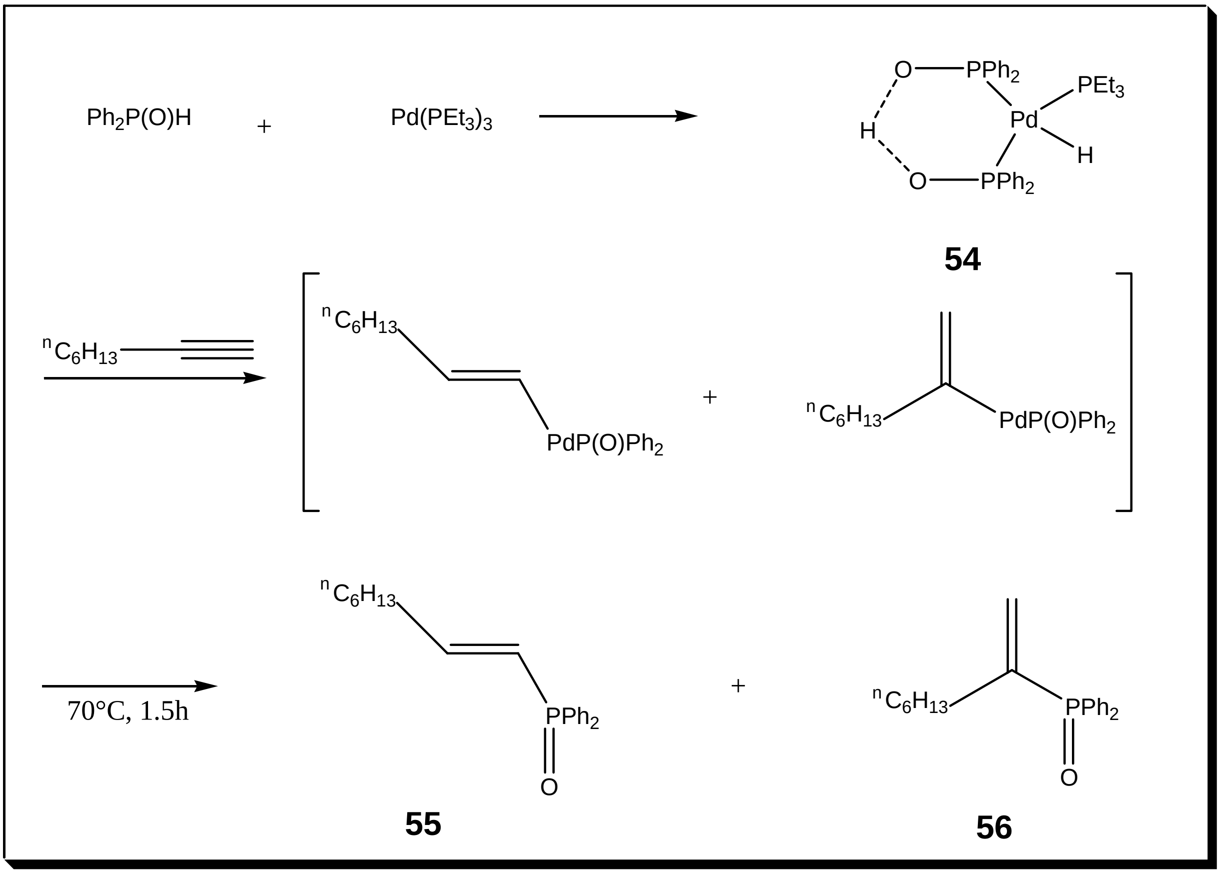
Metal-catalyzed hydrophosphination of slightly activated alkenes has been poorly studied. Only one article involving alkenylalkylethers has been reported.[162] As shown in Scheme 1.24, the hydrophosphination of butylvinylether was performed using diphenylphosphine in the presence of various Pd(II) and Ni(II) complexes. The adducts **53a–e** were fully characterized after oxidation into phosphine oxides.



Scheme 1.24 Hydrophosphination of butylvinylether

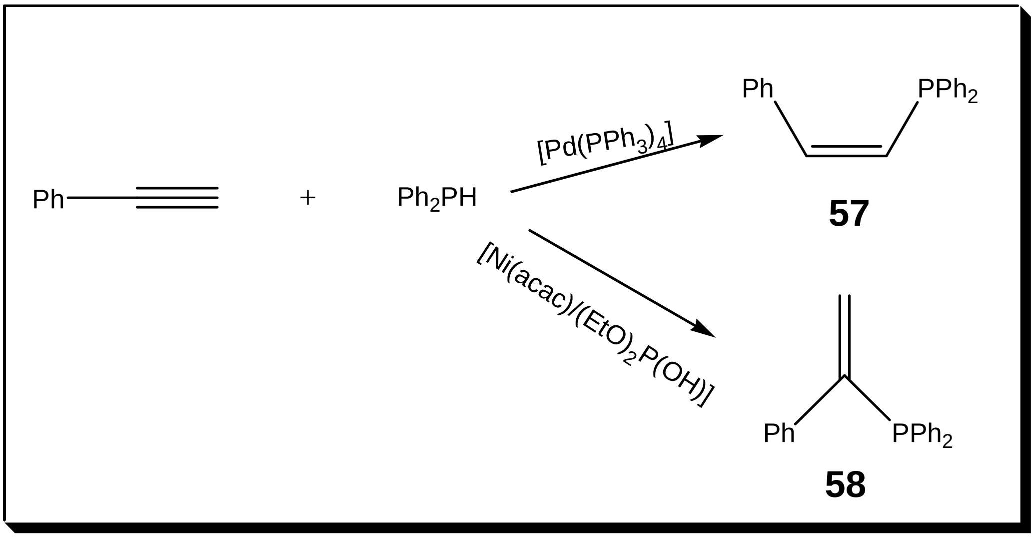
1.3.2 Hydrophosphination of Alkynes

The addition of phosphorus–hydrogen bonds to alkynes is an important reaction leading to functionally substituted olefins. The feasibility of the catalytic hydrophosphination of alkynes via a metal-catalyzed P-H bond activation has been shown in a few recent reports. Tanaka and co-workers reported the first example of hydrophosphination of alkynes in which oxidative addition of $Ph_2P(O)H$ to the compound $[Pd(PEt_3)_3]$ afforded *cis*-$[PdH\{P(O)Ph_2\}\{PPh_2(OH)\}(PEt_3)]$ complexes at room temperature in benzene.[163] As depicted in Scheme 1.25, the Pd(II) complex **54** was found to undergo an insertion reaction with 1-octyne to give (*E*)-1-(diphenylph-osphinyl)oct-1-ene **55** and 2-(diphenylphosphiny-l)oct-1-ene **56** (Scheme 1.25).



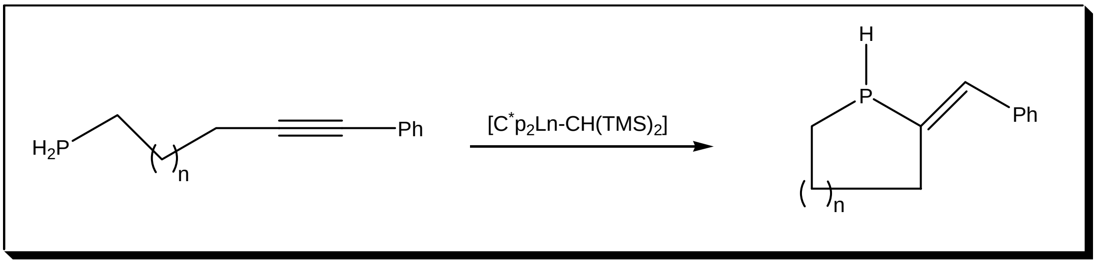
Scheme 1.25 Hydrophosphination of 1-octyne

Nickel was also found to catalyze the addition of phosphine to alkynes. For example, vinylphosphines have recently been prepared by Pd- and Ni-catalyzed direct diphenylphosphine addition to alkynes.[164] An interesting aspect of the reaction is that the regioselectivity depends dramatically on the nature of the catalyst. As shown in Scheme 1.26, β-(*Z*)- and α-alkenylphosphines could be selectively reached *via* catalytic addition of Ph_2PH to phenylacetylene with 5 mol% $[Pd(PPh_3)_4]$ and $[Ni(acac)_2]/(EtO)_2P(O)H$, respectively.[164]



Scheme 1.26 Hydrophosphination catalyzed by Pd and Ni

Organolanthanide complexes have been reported to be able to promote either an intramolecular[165] or an intermolecular[166] hydrophosphination-cyclization process. For example, as shown in Scheme 1.27, catalysts of the type [Cp*$_2$LnCH(TMS)$_2$] promoted the cycliation of primary alkynyl phosphines to yield secondary phospholanes and phosphinanes. However, the products were somewhat unstable and could only be characterized *in situ* by NMR spectroscopy



Scheme 1.27 Hydrophosphination catalyzed by Ln

1.4 Aims of the Present Project

Our research group has previously studied several asymmetric transformations promoted by chiral cyclometallated palladium or platinum complexes, such as the Diels–Alder reaction, the hydroamination reaction, and [2+2] cycloaddition reactions. In order to further explore the activating and stereochemical directing abilities of the chiral cyclometallated complexes, the insertion of alkynes with phosphine ligands or arsine ligands into Pd–C bonds of palladacycles is investigated, respectively. This investigation is attempted to study the reactivity and selectivity of the reaction when the alkyne moiety with the phosphine or arsine ligand is coordinated to cyclometallated complexes containing the phenyl and naphthylamine systems.

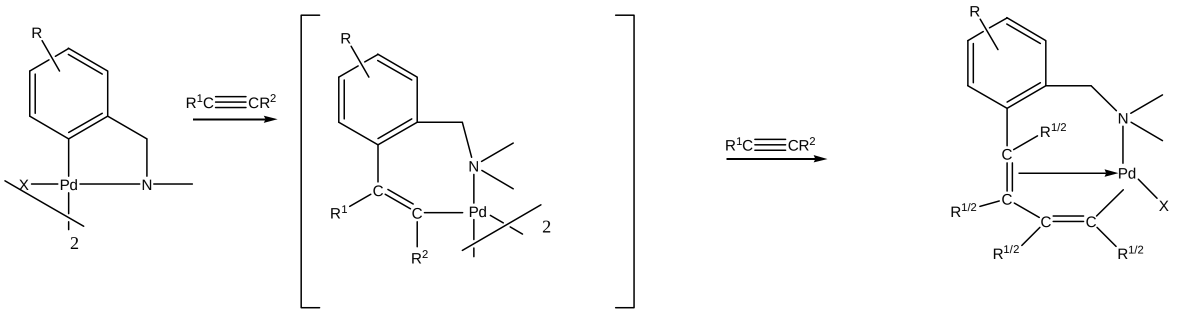
In order to establish the importance of such chiral cyclometallated templates for asymmetric synthesis, another objective of this project is to prepare chiral phosphine ligands by means of hydrophosphination reactions. Various phosphines will be coordinated to cyclopalladated complexes and react with diphenylphosphine or ethylphenylphosphine.

Chapter 2

Insertion of Alkynylphosphine Into the Pd–C bond of Cyclopalladated Complex

2.1 Introduction:

Insertion of alkynes into Pd–C bonds of cyclometallated compounds is one of the representative processes that makes cyclometallated palladium compounds attractive starting materials in organic synthesis.[167–171] In fact, much has been done in terms of synthesis of various and often unique organic and organometallic compounds starting with palladacycles and alkynes since the first report in 1979.[167] As illustrated in Scheme 2.1, all these alkynes insertions have the same key steps, e.g., the insertion of one or two alkynes into the Pd–C bond of cyclometallated palladium complex **65** to yield complexes of **66** or **67**, respectively, depending on the nature of the alkyne.[172] One major asset of these reactions is that the organometallic complex, resulting from the insertion of the alkyne into the Pd–C bond, can be isolated, and these have often been shown to be genuine intermediates in the formation of the organic products.



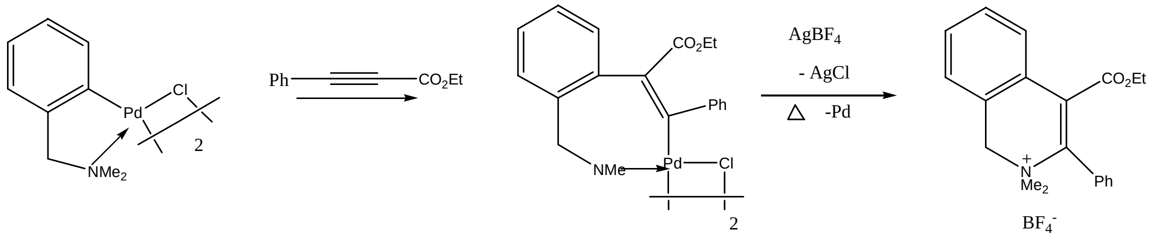
65 **66** **67**

R/X= (a) H/Cl, (b) 4-OMe/Cl,(c) 5-OMe/Cl, (d)5-F/Cl, (e) 5-H/I

R^1/R^2 = Ph/Ph, Ph/C_6H_4-4-NO_2, Ph/C_6H_4-3-CF_3, Et/Et

Scheme 2.1 Insertion of alkynes into Pd-C bonds of cyclometallated compounds

With dissymmetric alkynes, these insertions are usually regioselective and steric factors would appear to have a more dominant influence than electronic effects on the regiochemistry of these reactions (Scheme 2.2).[173]



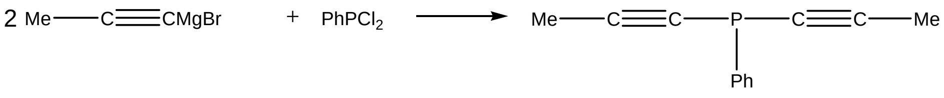
68 **69** **70**

Scheme 2.2

2.2 Results and Discussion

2.2.1 Preparation of Phosphine Ligand 71

Tertiary phosphines can be readily prepared from alkyl(or aryl) magnesium halides and dichlorophenylphosphine. The ligand, di(prop-1-ynyl)phenylphosphine **71** was synthesized as outlined in Scheme 2.3.



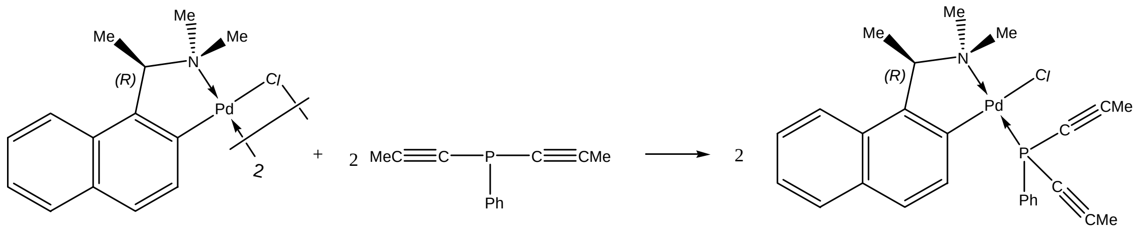
71

Scheme 2.3

After the reaction between dichlorophenyphosphine and the THF solution of 1-propynylmagnesium bromide, the $^{31}P\{^1H\}$ NMR spectrum of the crude product in $CDCl_3$ showed a major peak at δ –60.3 and a very minor singlet at δ –39.0 for the desired phosphine **71** and the phosphine oxide, respectively. Since a small quantity of the phosphine oxide was formed, the crude mixture was distilled to give pure phosphine **71** as a pale yellow oil in yield 44.0%, b.p. 118–120 ℃. It is noteworthy that the phosphine **71** is not air–sensitive. The chemical shift of the phosphine ligand remained unchanged after the NMR sample was left for several days in $CDCl_3$ in the air.

2.2.2 Preparation of Precursor Complexes (R_c)-72 and (R_c)-73

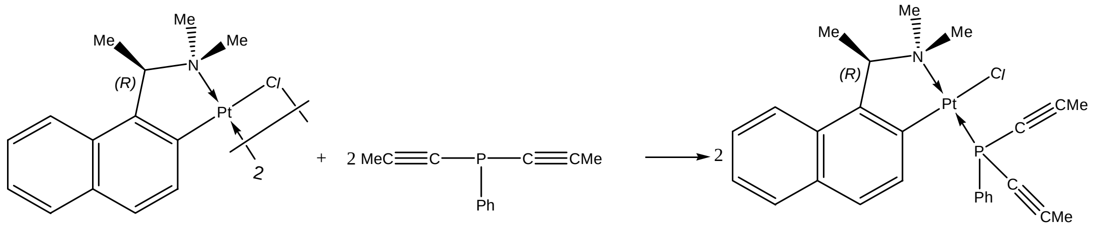
The synthesis of the chiral phosphine complex (R_c)-**72** was achieved by treatment of the di(1-propynyl)phenylphosphine ligand **71** with 0.5 equivalent of the dimeric palladium(II) complex (R_c)-**59** in dichloromethane. The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy and was found to be complete in 2 hours. The $^{31}P\{^1H\}$ NMR spectrum of the crude product in $CDCl_3$ exhibited a sharp singlet at δ –20.5. The complex (R_c)-**72** was recrystallized from dichloromethane–hexane as yellow crystals in 84% yield (Scheme 2.4).



(R_c)-**59** **71** (R_c)-**72**

Scheme 2.4

Similar to the preparation of the palladium complex (R_c)-**72**, the platinum complex (R_c)-**73** was prepared by treatment of the di-(1-propynyl)phenylphosphine ligand **71** with 0.5 equivalent of the dimeric platinum(II) complex (R_c)-**6** in CH_2Cl_2. At room temperature the reaction was complete in 2 h. The ^{31}P {^1H} NMR spectrum of the crude product in $CDCl_3$ exhibited a sharp singlet at δ –39.4 ($^1J_{P-Pt}$ = 4524 Hz). The complex (R_c)-**73** was then recrystallized from dichloromethane–n-hexane as pale yellow crystals in 87% yield (Scheme 2.5).



(R_c)-**60** **71** (R_c)-**73**

Scheme 2.5

2.2.2.1 X-ray Structural Analysis of Complex (R_c)-72

The single X-ray structural analysis of the isolated palladium complex (R_c)-**72** revealed that the phosphorus donor atom is coordinated regiospecifically in the position *trans* to the naphthylamine–*N* donor atom, as shown in Figure 2.1. Such regiospecificity has been invariably observed with heterobidentate complexes containing this cyclopalladated naphthylamine unit and has been attributed to the *trans* electronic influences originating from the σ–donating nitrogen and the strong π–accepting aromatic carbon atoms of the organometallic ring.[174]

The geometry at palladium is a slightly distorted square planar with angles in the ranges of 81.1(1)–93.6(1)°, and 172.9(1)–174.5(1)°, respectively. Selected bond distances and angles for (R_c)-**72** are given in Table 2.1.

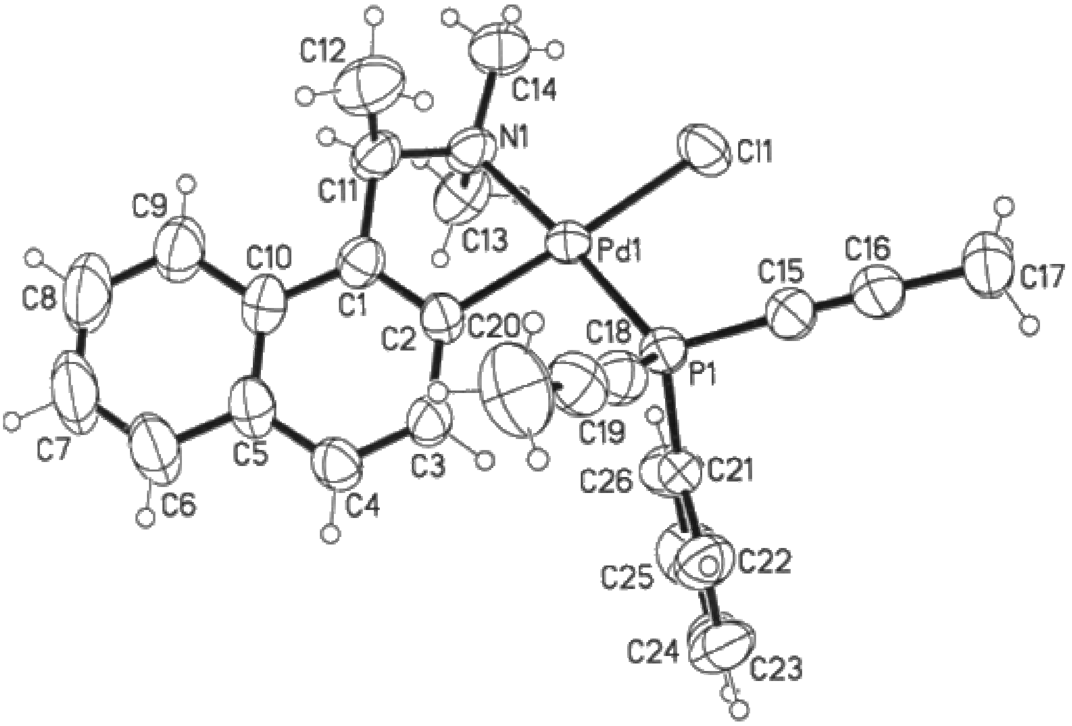


Figure 2.1 Molecular Structure of Complex (R_c)-**72**

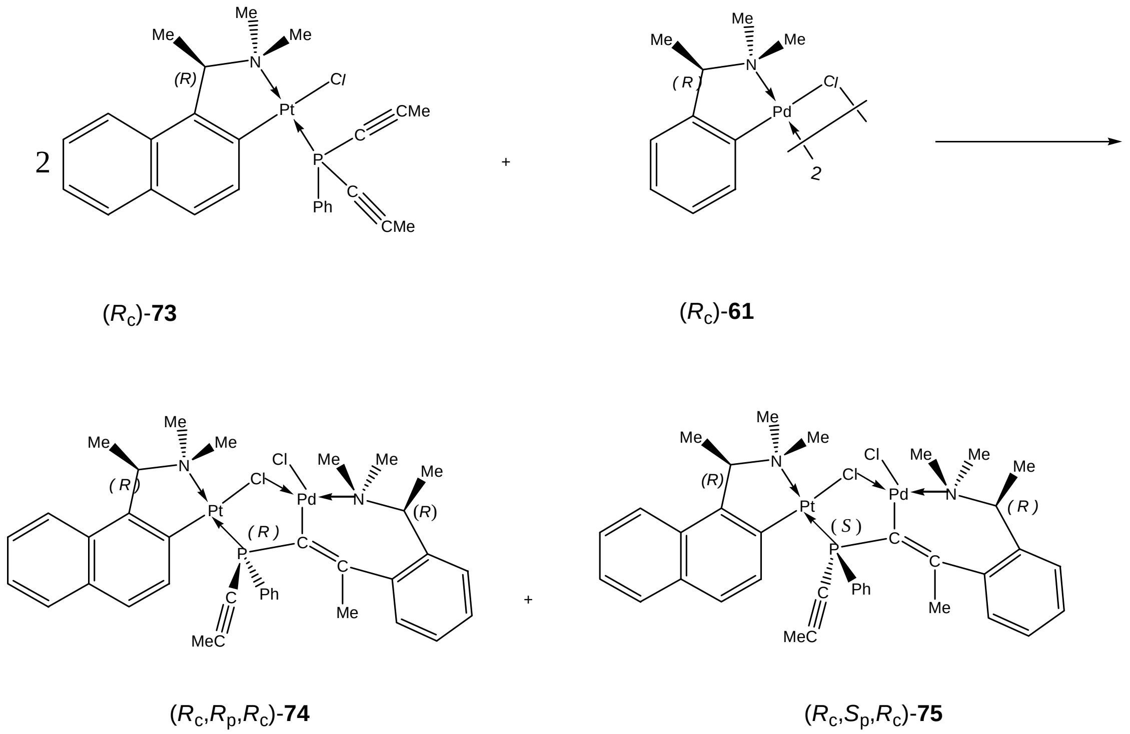
Table 2.1 Selected bond distances (Å) and angles (°) of Complex (R_c)-**72**

Pd(1)–C(2)	2.021(3)	C(18)–C(19)	1.173(5)
Pd(1)–N(1)	2.128(3)	C(2)–Pd(1)–N(1)	81.2(1)
Pd(1)–P(1)	2.229(1)	C(2)–Pd(1)–P(1)	93.6(1)
Pd(1)–Cl(1)	2.371(1)	N(1)–Pd(1)–P(1)	174.5(1)
P(1)–C(15)	1.757(3)	C(2)–Pd(1)–Cl(1)	172.9(1)
P(1)–C(18)	1.759(3)	N(1)–Pd(1)–Cl(1)	92.8(1)
P(1)–C(21)	1.818(3)	P(1)–Pd(1)–Cl(1)	92.6(1)
C(15)–C(16)	1.175(4)		

2.2.3 Synthesis of Complexes (R_c,R_p,R_c)-74, (R_c,S_p,R_c)-75 and (R_c,S_c,R_p,R_c)-76

The insertion reaction between naphthylamine platinum(II) complex (R_c)-**73** and 0.5 equivalent of benzylamine palladium (II) dimer (R_c)-**61** was carried out at room temperature in dichloromethane. This reaction was monitored using $^{31}P\{^1H\}$ NMR spectroscopy, and was found to be complete in 36 hours. The $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture in $CDCl_3$ exhibited 2 sharp singlets at δ –38.2 ($^1J_{P-Pt}$ = 4047 Hz) and δ –35.9 ($^1J_{P-Pt}$ = 3983 Hz) with relative intensities of 4:3, respectively, indicating the formation of 2 distinct stereoisomeric products (Scheme 2.6).

The crude reaction mixture was purified by column chromatography and crystallized from acetone–hexane to give complex (R_c,R_p,R_c)-**74** and complex (R_c,S_p,R_c)-**75** as light yellow crystals. The phosphorus resonance signal at δ –38.2 is assigned to complex (R_c,R_p,R_c) **-74,** while the signal at δ –35.9 is assigned to complex (R_c,S_p,R_c)-**75** in 23% and 19% isolated yield, respectively.

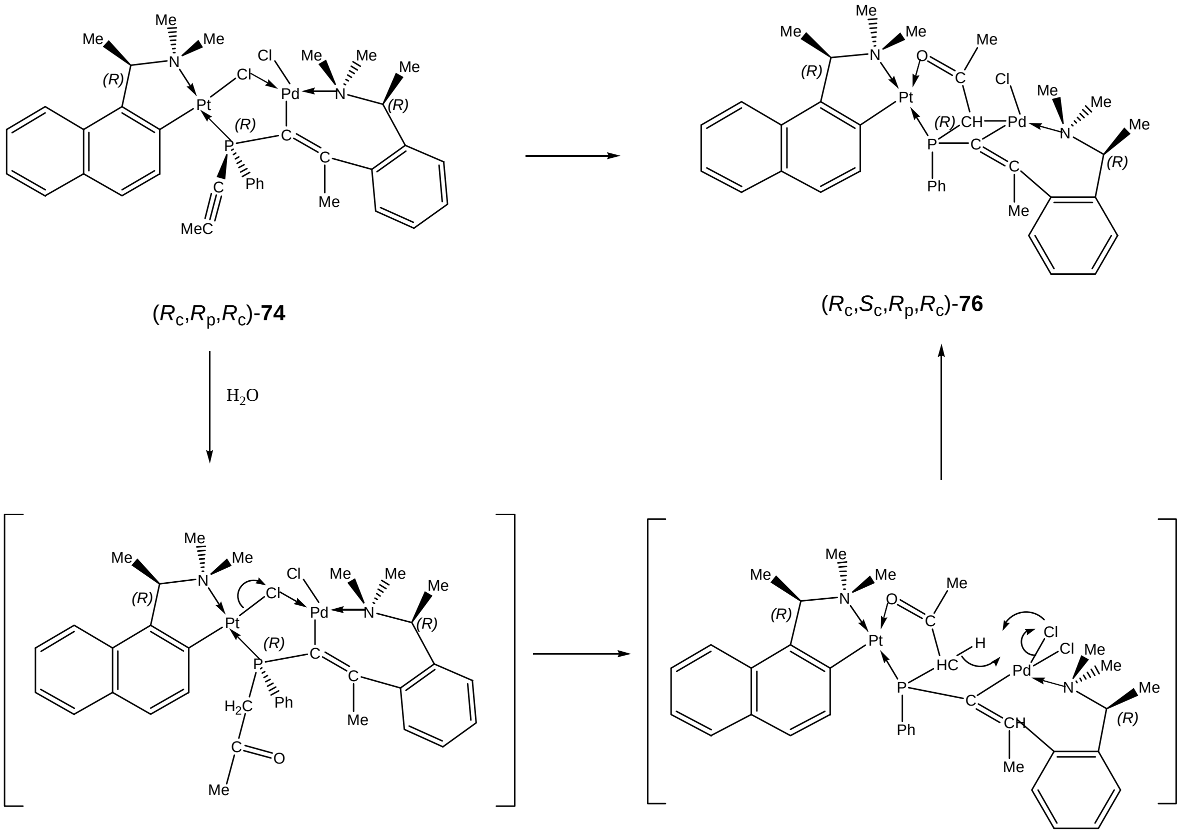


Scheme 2.6

Interestingly, while the two insertion complexes were separated by column chromatography, the ^{31}P{^{1}H} NMR spectrum of the product mixture showed an additional phosphorous resonate signal at δ –2.3. Subsequently, it was found that this new phosphorous signal always re–appeared when the complex (R_{c},R_{p},R_{c})-**74** passing through a silica gel. However, such situation was not observed with complex (R_{c},R_{p},R_{c})-**74** was dissolved in various solvents.

The signal at δ –2.3 later was eventually confirmed as the unexpected new product (R_{c},S_{c},R_{p},R_{c})-**76** after it had been recrystallized from diethyl ether–acetonitrile as light yellow crystals. It was proposed that complex (R_{c},R_{p},R_{c})-**74** underwent a series of transformations while passing through column to give the transformed product (R_{c},S_{c},R_{p},R_{c})-**76**.. As shown in

Scheme 2.7, these transformations included a nucleophilic attack by water followed by a chloride bridge splitting and subsequent coordination of O to Pt center as well as concomitant formation of a new C–Pd bond.



Scheme 2.7

Unlike complex (R_c,R_p,R_c)-**74**, the insertion product (R_c,S_p,R_c)-**74** didn't undergo the transformations while passing through silica gel.

2.2.3.1 X-ray Structural Analysis of Complex (R_c,R_p,R_c)-74

The single crystal X-ray diffraction studies of the complex (R_c,R_p,R_c)-**74** confirmed that the desired insertion product has been generated (Figure 2.2). One of the original carbon–carbon bonds in the alkynylphosphine, bond C(18)–C(19), has been inserted into the palladium

–carbon bond, Pd(1)–C(30), of cyclopalladated complex (*R*$_c$)-**61**, forming a new carbon–carbon bond between C(19) and C(30), together with a new metal–carbon bond between Pd(1) and C(18). A new stereogenic center at phosphorus was generated, which adopts the *R* absolute configuration. The absolute configurations of the two stereocenters at C(11), C(24) remained unchanged. The phosphorus donor atom is coordinated regiospecifically in the position *trans* to the naphthylamine–*N* donor atom.

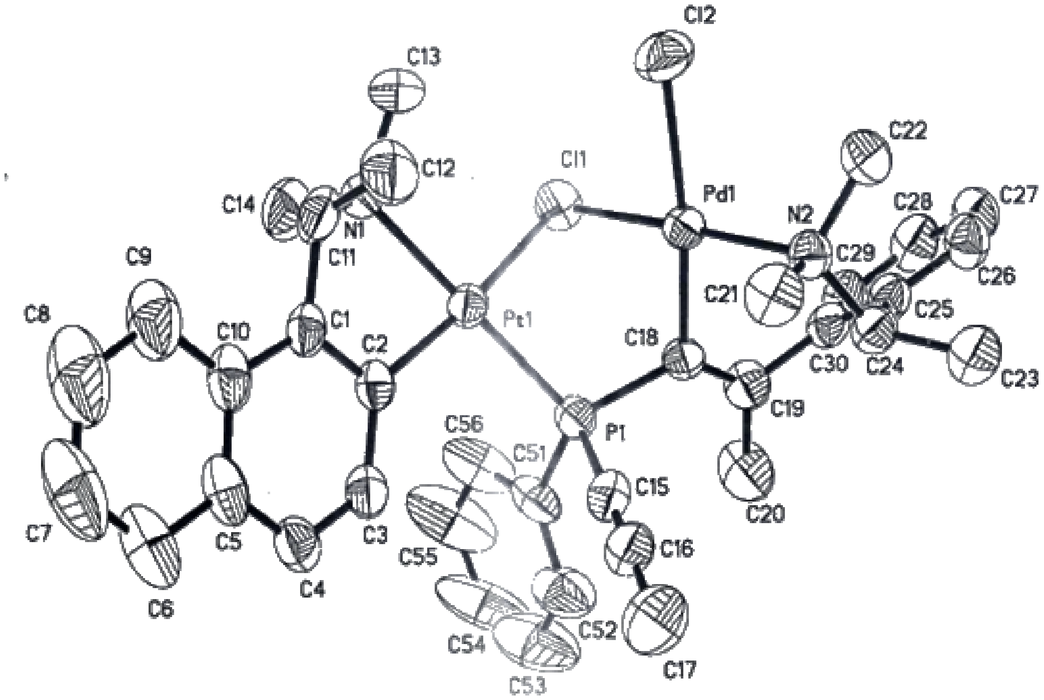


Figure 2.2 Molecular Structure of Complex (*R*$_c$,*R*$_p$,*R*$_c$)-**74**

The geometry at platinum and palladium centers is distorted square planar with bond angles at Pt(1) in the range of 81.0(1)–97.9(1)° and 174.0(1)–178.1 (1)°, while those at Pd(1) ranges from 84.1(1)–93.5(1)° and 172.4(1)–177.3(1)°, respectively. Table 2.2 shows selected bond distances and angles of complex (*R*$_c$,*R*$_p$,*R*$_c$)-**74**.

Table 2.2 Selected bond distances (Å) and angles (°) of Complex $(R_\mathrm{c},R_\mathrm{p},R_\mathrm{c})$-**74**

Pt(1)–C(2)	1.990(4)	C(2)–Pt(1)–N(1)	81.0(1)
Pt(1)–N(1)	2.118(4)	C(2)–Pt(1)–P(1)	97.9(1)
Pt(1)–P(1)	2.216(3)	N(1)–Pt(1)–P(1)	178.2(1)
Pt(1)–Cl(1)	2.419(2)	C(18)–Pd(1)–N(2)	93.5(2)
Pt(1)–Pd(1)	3.222(1)	C(18)–Pd(1)–Cl(1)	84.1(1)
Pd(1)–C(18)	2.002(4)	N(2)–Pd(1)–Cl(1)	177.3(1)
Pd(1)–N(2)	2.120(4)	N(1)–Pt(1)–Cl(1)	93.7(1)
Pd(1)–Cl(1)	2.339(1)	P(1)–Pt(1)–Cl(1)	87.5(1)
Pd(1)–Cl(2)	2.412(1)	C(2)–Pt(1)–Cl(1)	178.1(1)
P(1)–C(15)	1.768(6)	N(2)–Pd(1)–Cl(2)	94.1(1)
P(1)–C(18)	1.809(4)	Cl(1)–Pd(1)–Cl(2)	88.4(1)

2.2.3.2 X-ray Structural Analysis of Complex $(R_\mathrm{c},S_\mathrm{p},R_\mathrm{c})$-75

The molecular structure and absolute stereochemistry of complex $(R_\mathrm{c},S_\mathrm{p},R_\mathrm{c})$-**75** was established by X-ray crystallography (Figure 2.3 and Table2.3). Similar with the formation of complex $(R_\mathrm{c},R_\mathrm{p},R_\mathrm{c})$-**74**, one of the original carbon–carbon bond in the alkynylphosphine, bond C(18)–C(19), has been inserted into the palladinum–carbon bond, Pd(1)–C(30), of cyclopalladated complex (R_c)-**61**, forming a new carbon–carbon bond between C(19) and C(30), together with a new metal–carbon between Pd(1) and C(18). The new generated stereocenter at phosphorus adopts the *S* absolute configuration which is different from complex $(R_{\mathrm{c}},R_{\mathrm{p}},R_{\mathrm{c}})$-**74**. Meanwhile, the absolute configurations of the two stereocenters at C(11), C(24) remained unchanged.

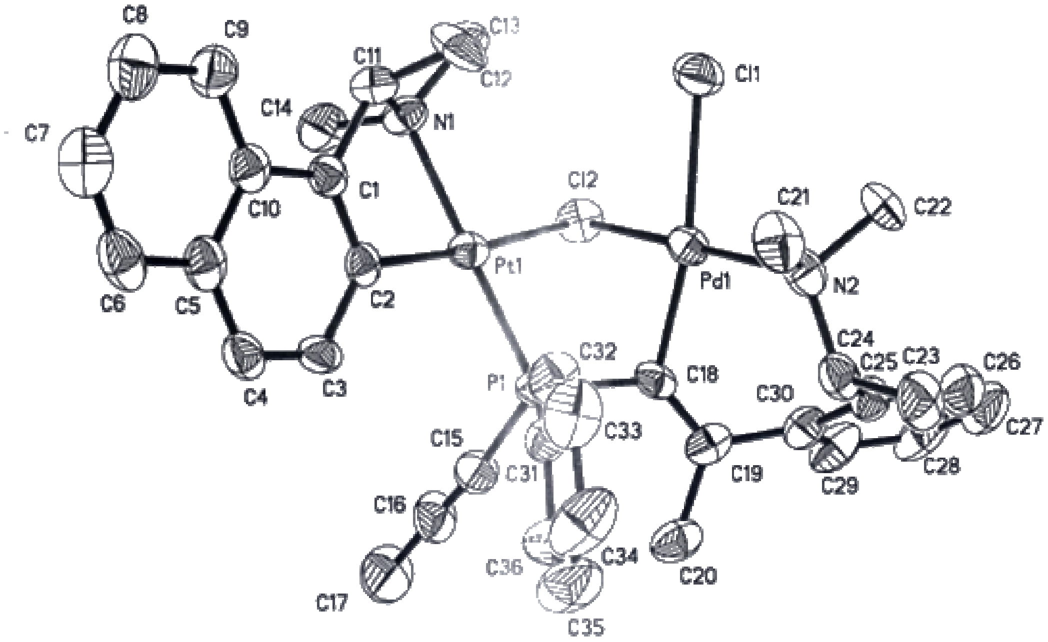


Figure 2.3 Molecular Structure of Complex $(R_{\mathrm{c}},R_{\mathrm{p}},R_{\mathrm{c}})$ – **75**

The geometry at platinum and palladium centers are distorted square planar with bond angles at Pt(1) in the range of 79.7(1)–97.9(1)˚ and 174.9(1)–176.2 (1)˚, while those at Pd(1) ranges from 84.7(1)–94.9(1)˚ and 169.8(1)–173.1(1)˚, respectively. Table 2.3 shows selected bond distances and angles of complex $(R_{\mathrm{c}},S_{\mathrm{p}},R_{\mathrm{c}})$-**75**.

Table 2.3 Selected bond distances (Å) and angles (°) of Complex $(R_{\mathrm{c}},S_{\mathrm{p}},R_{\mathrm{c}})$-**75**

Pt(1)–C(2)	2.009(5)	C(2)–Pt(1)–N(1)	79.7(2)
Pt(1)–N(1)	2.132(4)	C(2)–Pt(1)–P(1)	97.9(2)
Pt(1)–P(1)	2.220(1)	N(1)–Pt(1)–P(1)	172.2(1)

Pt(1)–Cl(2)	2.418(1)	C(2)–Pt(1)–Cl(2)	174.9(2)
Pd(1)–C(18)	2.008(5)	N(1)–Pt(1)–Cl(2)	95.2(1)
Pd(1)–N(2)	2.115(5)	P(1)–Pt(1)–Cl(2)	87.16(5)
Pd(1)–Cl(2)	2.364(2)	C(18)–Pd(1)–N(2)	94.9(2)
Pd(1)–Cl(1)	2.437(2)	C(18)–Pd(1)–Cl(2)	84.7(2)
P(1)–C(15)	1.767(6)	C(2)–Pt(1)–Cl(1)	173.1(1)
P(1)–C(18)	1.819(5)	N(2)–Pd(1)–Cl(2)	169.8(2)
C(15)–C(16)	1.172(8)	C(18)–Pd(1)–Cl(2)	91.0(1)
C(18)–C(19)	1.335(7)	Cl(1)–Pd(1)–Cl(2)	90.4(1)

2.2.3.3 X-ray Structural Analysis of Complex (R_c,S_c,R_p,R_c)-76

The X-ray structural analysis of complexes of (R_c,S_c,R_p,R_c)-**76** revealed that one of the original carbon–carbon triple bonds in the alkynylphosphine, bond C(18)–C(19), has inserted into the Pd(1)–C(21) bond of benzylamine dimer (R_c)-**61**. This carbon–carbon triple bond insertion generated two new bonds, one was a new carbon–carbon bond between C(19) and C(21), another was a metal–carbon bond between Pd(1) and C(18). Furthermore, the remaining carbon–carbon triple bond C(15)–C(16) took part in the hydration reaction to give a carbonyl C=O bond, forming a five-membered platinum chelate via the carbonyl oxygen O(1) and the P(1). In addition, a new metal–carbon bond was formed between Pd (1) and C (15) that resulted in a new four-membered hetero bimetallic ring. Consequently, a new stereocenter at C (15) was generated which adopts the *S* absolute configuration. The absolute configurations at

C(11), P(1) and C(27) stereocenters are *R*, *R*, and *S*, respectively

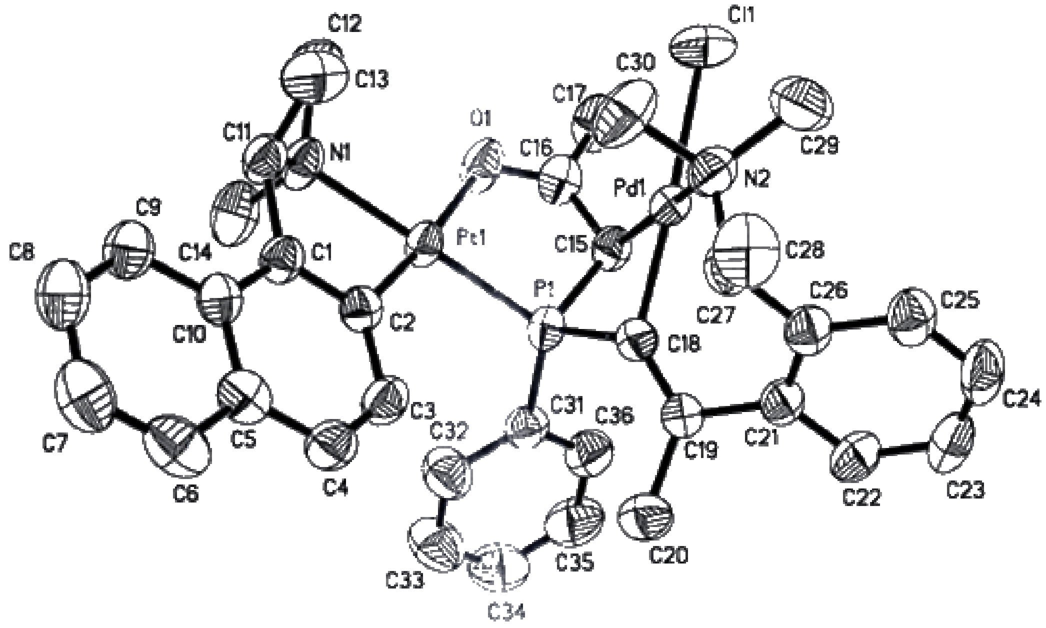


Figure 2.4 Molecular Structure of Complex (*R*$_c$,*S*$_c$,*R*$_p$,*R*$_c$)-76

The geometry at platinum and palladium centers are distorted square planar with bond angles at Pt in the range of 81.1(1)–102.0(1)˚, 173.4(1)–174.9(1)˚**,** while those at Pd(1) ranges from 75.3(1)–96.4 (1)˚, 168.4(1)–171.7(1)˚**,** respectively. The selected bond distances and angles in the complex (*R*$_c$,*S*$_c$,*R*$_p$,*R*$_c$)-**76** are shown in Table 2.4.

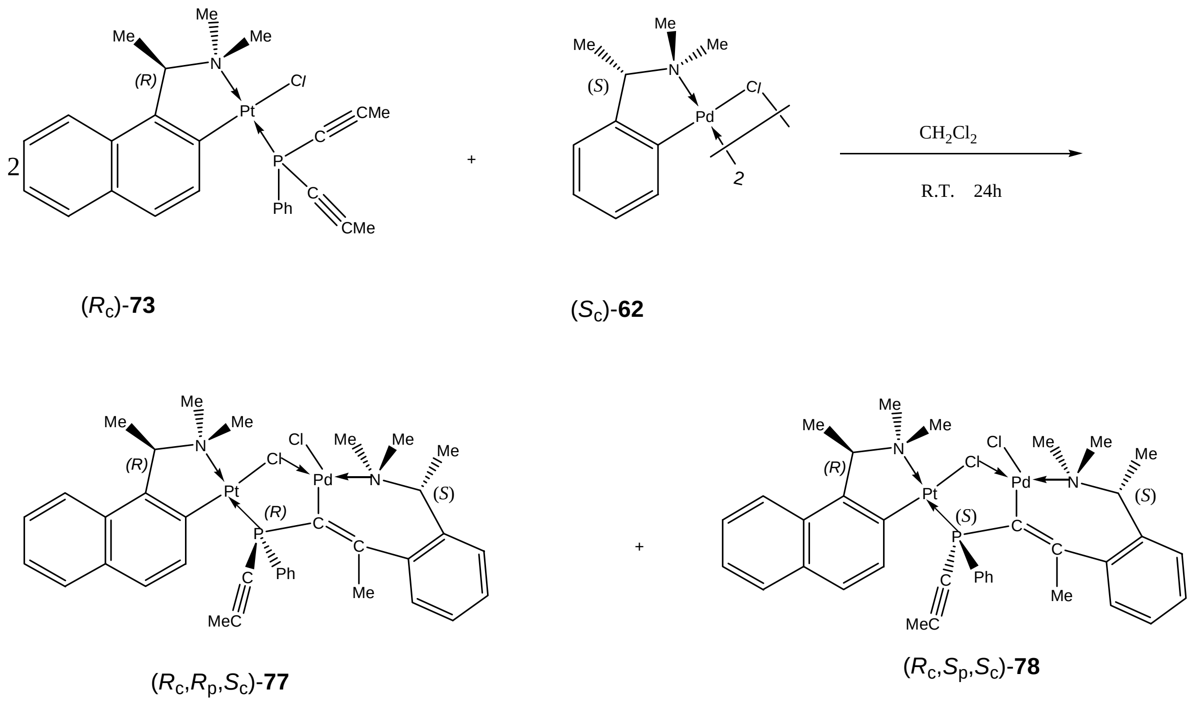
Table 2.4 Selected bond distances (Å) and angles (°) of Complex (*R*$_c$,*S*$_c$,*R*$_p$,*R*$_c$)-**76**

Pt(1)–C(2)	1.976(4)	N(1)–Pt(1)–O(1)	94.3(1)
Pt(1)–N(1)	2.121(4)	C(2)–Pt(1)–P(1)	102.0(1)
Pt(1)–O(1)	2.126(3)	N(1)–Pt(1)–P(1)	174.9(1)
Pt(1)–P(1)	2.212(1)	O(1)–Pt(1)–P(1)	82.9(1)
Pd(1)–C(18)	1.994(5)	C(18)–Pd(1)–C(15)	75.3(2)

Pd(1)–C(15)	2.139(4)	N(1)–Pt(1)–P(1)	174.9(1)
Pd(1)–N(2)	2.178(4)	C(18)–Pd(1)–N(2)	96.3(1)
Pd(1)–Cl(1)	2.406(1)	C(15)–Pd(1)–N(2)	168.4(2)
C(15)–C(16)	1.431(7)	C(18)–Pd(1)–Cl(1)	171.7(1)
C(18)–C(19)	1.339(6)	C(15)–Pd(1)–Cl(1)	96.4(1)
C(2)–Pt(1)–N(1)	81.1(2)	N(2)–Pd(1)–Cl(1)	92.1(1)
C(2)–Pt(1)–O(1)	173.4(2)	C(16)–O(1)–Pt(1)	117.9(3)

2.2.4 Synthesis of Complex (R_c,R_p,S_c)-77 and (R_c,S_c,R_p,S_c)-79

In the insertion reaction described in **2.2.3**, an unexpected insertion product, complex (R_c,S_c,R_p,R_c)-**76**, was obtained. This product was not observed in the original reaction mixture, but it always coexisted with another insertion product, complex (R_c,R_p,R_c)-**74**, during the purification process via silica gel. In order to establish that the transformation from complex (R_c,R_p,R_c)-**74** to complex (R_c,S_c,R_p,R_c)-**76** is a general phenomenon, the insertion reaction was repeated with naphthylamine platinum(II) complex (R_c)-**73** and 0.5 equivalent of benzylamine palladium (II) dimer (S_c)-**62** in dichloromethane at room temperature. This analogue reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy and was found to be complete in 24 hours. The $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture in $CDCl_3$ exhibited 2 sharp singlets at δ –9.3 ($^1J_{P\text{–}Pt}$ = 4203 Hz) and δ –28.6 ($^1J_{P\text{–}Pt}$ = 4046 Hz) with relative intensities of 2:1, respectively (Scheme 2.8).



(R_c)-**73**

(S_c)-**62**

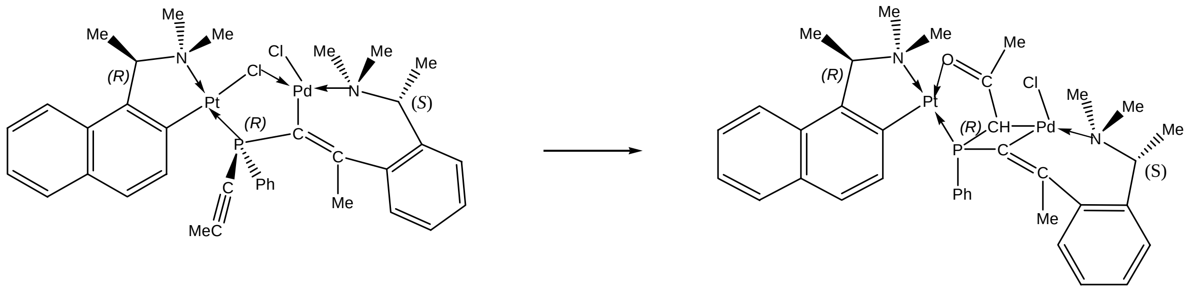
(R_c,R_p,S_c)-**77**

(R_c,S_p,S_c)-**78**

Scheme 2.8

Similar to the insertion reaction described in **2.2.3**, the purification of the crude reaction mixture by silica gel column chromatography gave three light yellow solids in 31%, 20% and 9.5% yields, respectively. The phosphorus resonance signal at δ –9.3 of the major product is assigned to complex (R_c,R_p,R_c)-**77**, while the signal at δ –28.6 of the second major product is assigned to complex (R_c,S_p,R_c)-**78**.

As expected, a transformed product, complex (R_c,S_c,R_p,R_c)-**79**, was always observed when complex (R_c,R_p,S_c)-**77** was purified by column chromatography (Scheme 2.9). The ^{31}P{^{1}H} NMR spectrum of complex (R_c,S_c,R_p,S_c)-**79** in CDCl$_3$ exhibited a sharp singlet at δ –7.1($^1J_{P-Pt}$ = 3883 Hz). Complex (R_c,R_p,S_c)-**77** and complex (R_c,S_c,R_p,S_c)-**79** were recrystallized from acetone–hexane as light yellow crystals, respectively.



(R_c,R_p,S_c)-**77**

(R_c,S_c,R_p,S_c)-**79**

Scheme 2.9

Unfortunately, single crystals of complex (R_{c},S_{p},S_{c})-**78** suitable for X–ray structural analysis could not be produced, despite many attempts to crystallize it using a wide variety of different solvent systems.

2.2.4.1 X-ray Structural Analysis of Complex (R_{c},R_{p},S_{c})-77

X-ray crystallagraphy confirmed the structure of complex (R_{c},R_{p},S_{c})-**77** (Figure 2.5). One of the original carbon–carbon triple bond in the alkynylphosphine, bond C(18)–C(19), has been inserted into the palladium–carbon, bond Pd(1)–C(19), of cyclopalladated complex (S_{c})-**62**, forming a new carbon–carbon bond between C(19) and C(30), together with a new metal–carbon between Pd(1) and C(18). A new stereogenic center at phosphorus was generated, which adopts the *R* absolute configuration, while the absolute configurations of the two stereocenters at C(11), C(24) remaine unchanged. The phosphorus donor atom is coordinated regiospecifically in the position *trans* to the naphthylamine–*N* donor atom.

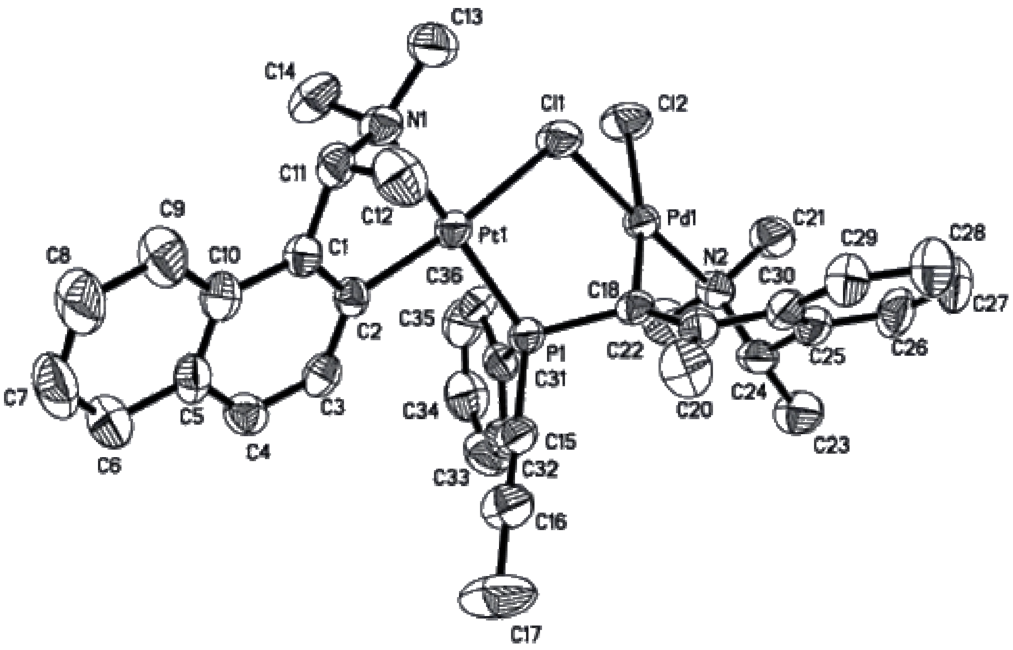


Figure 2.5 Molecular Structure of Complex (R_c,R_p,S_c)-**77**

The geometry at platinum and palladium centers are distorted square planar. The bond angles at the platinum center are in the range of 79.9(2)–98.2(1)˚, 173.5(2)–174.3(1)˚. And the bond angles at palladium center ranges from 85.0(1)–93.9(2)˚, 170.2(1)–176.9(1)˚. Table 2.5 shows selected bond distances and angles of complex (R_c,R_p,S_c)-**77**.

Table 2.5 Selected bond distances (Å) and angles (°) of complex (R_c,R_p,S_c)-**77**

Pt(1)–C(2)	1.993(4)	C(2)–Pt(1)–P(1)	98.2(1)
Pt(1)–N(1)	2.137(4)	N(1)–Pt(1)–P(1)	174.3(1)
Pt(1)–P(1)	2.210(1)	C(2)–Pt(1)–Cl(1)	173.5(2)
Pt(1)–Cl(1)	2.414(1)	N(1)–Pt(1)–Cl(1)	95.4(1)
Pd(1)–C(18)	1.997(5)	P(1)–Pt(1)–Cl(1)	86.9(1)
Pd(1)–N(2)	2.102(4)	C(18)–Pd(1)–N(2)	93.9(2)

Pd(1)–Cl(1)	2.361(1)	C(18)–Pd(1)–Cl(1)	85.0(1)
Pd(1)–Cl(2)	2.418(1)	N(2)–Pd(1)–Cl(1)	176.9(1)
C(15)–C(16)	1.174(7)	C(18)–Pd(1)–Cl(2)	170.2(1)
C(18)–C(19)	1.349(1)	N(2)–Pd(1)–Cl(2)	93.6(1)
C(2)–Pt(1)–N(1)	79.9(2)	Cl(2)–Pd(1)–Cl(2)	87.9(1)

2.2.4.2 X-ray Structural Analysis of Complex ($\boldsymbol{R_c,S_c,R_p,S_c}$)-79

The X-ray structural analysis of complexes of (R_c,S_c,R_p,S_c)-**79** revealed that one of the original carbon–carbon triple bonds in the alkynylphosphine, bond C(18)–C(19), has been inserted into the Pd(1)–C(21) bond of benzylamine dimer (R_c)-**8** (Figure 2.6). As a result, two new bonds were formed and they are the C(19)–C(21) and Pd(1)–C(18) bond. Furthermore, another alkynyl carbon–carbon triple bond C(15)–C(16) underwent hydration reaction to yield a carbonyl C=O bond. A five-membered platinum chelate was generated via the carbonyl oxygen O(1) and the phosphorous. In addition, a new bond was generated between Pd(1) and C(15) that resulted in a new 4-membered hetero bimetallic ring. Consequently, a new stereocenter at C (15) was generated which adopts the *S* absolute configuration. The absolute configurations at C(11), P(1) and C(27) stereocenters are *R*, *R*, and *S*, respectively.

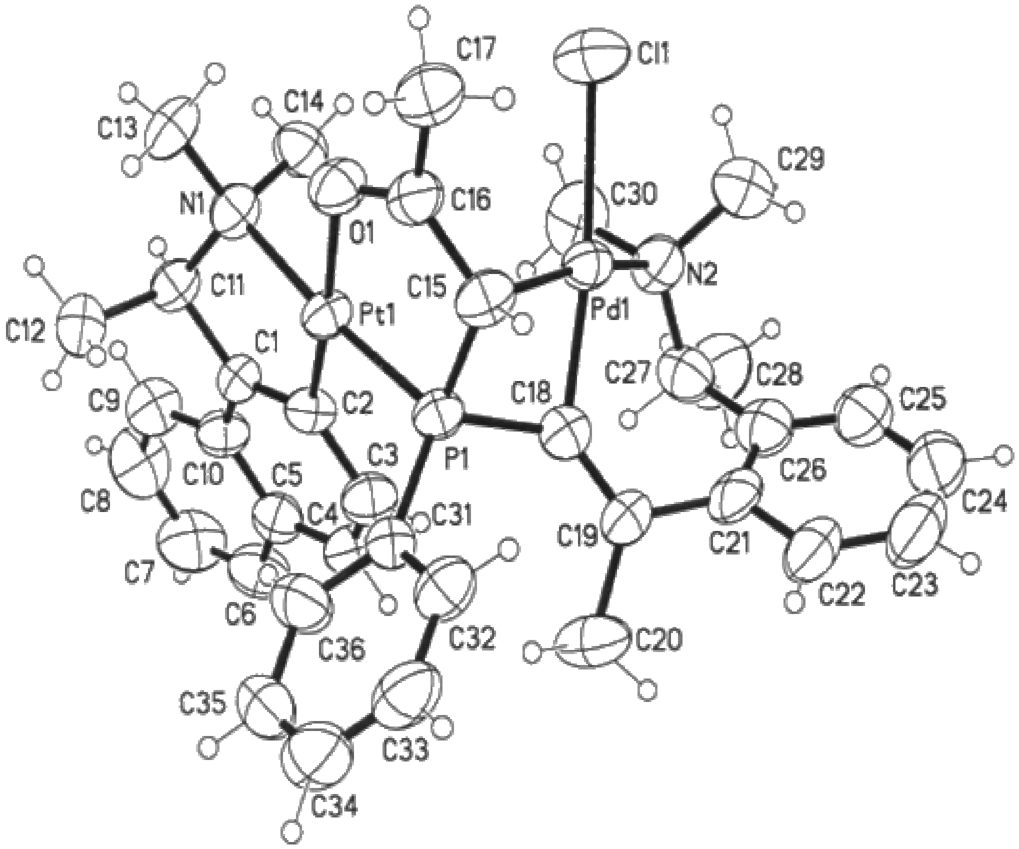


Figure 2.6 Molecular Structure of Complex (R_c,S_c,R_p,S_c)-**79**

The geometry at both platinum and palladium centers are slightly distorted square planar with bond angles at Pt(1) recorded in the range of 81.6(3)–92.2(2)° and 173.8(2)–174.6(2)°, while those at Pd(1) are found to be 74.7(1)–97.2(2)° and 166.5(3)–171.5(2)°. Table 2.6 shows selected bond distances and angles of complex (R_c,S_c,R_p,S_c)-**79**.

Table 2.6 Selected bond distances (Å) and angles (°) of complex (R_c,S_c,R_p,S_c)-**79**

Pt(1)–C(2)	1.979(2)	C(2)–Pt(1)–O(1)	173.8(2)
Pt(1)–N(1)	2.111(5)	N(1)–Pt(1)–O(1)	92.2(2)
Pt(1)–O(1)	2.134(5)	C(2)–Pt(1)–P(1)	102.4(2)

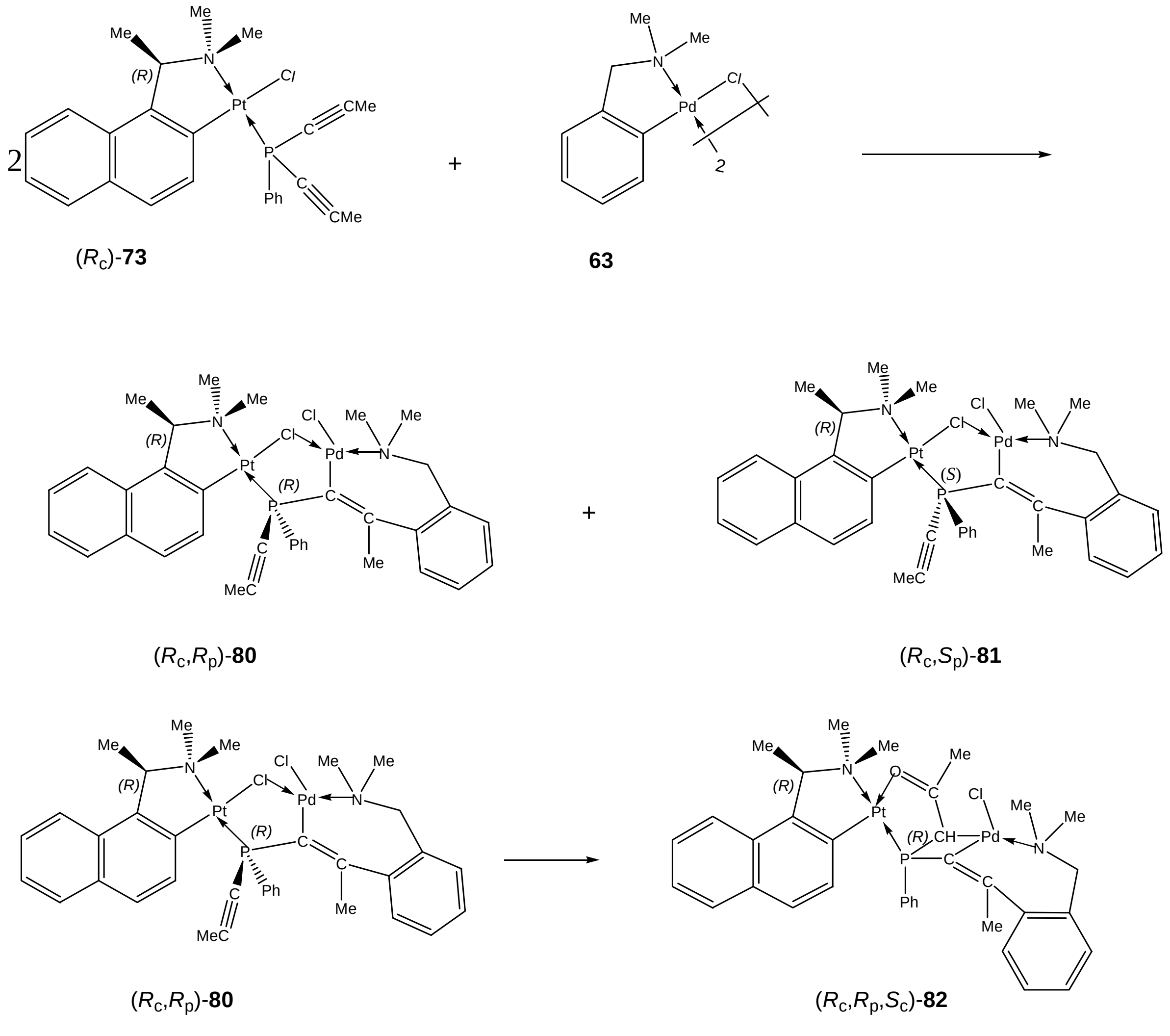
Pt(1)–P(1)	2.225(2)	N(1)–Pt(1)–P(1)	174.6(2)
Pd(1)–C(18)	1.990(8)	O(1)–Pt(1)–P(1)	83.7(1)
Pd(1)–N(2)	2.163(7)	C(18)–Pd(1)–N(2)	94.6(3)
Pd(1)–C(15)	2.168(8)	C(18)–Pd(1)–C(15)	74.7(3)
Pd(1)–Cl(1)	2.420(2)	N(2)–Pd(1)–Cl(1)	166.5(3)
O(1)–C(16)	1.277(9)	C(18)–Pd(1)–Cl(1)	171.5(2)
C(15)–C(16)	1.421(1)	N(2)–Pd(1)–Cl(1)	93.0(2)
C(18)–C(19)	1.315(1)	C(15)–Pd(1)–Cl(1)	97.2(2)
	81.6(3)	C(16)–O(1)–Pt(1)	116.9(5)

2.2.5 Synthesis of Complex (R_{c},S_{p})-81

In order to investigate the origin of the stereoselectivity in the previous insertion reaction, the process was repeated by using the achiral dimeric cyclopalladated benzylamine complex **63** and the enantiomerically pure naphthylamine. This reaction was monitored by $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectroscopy and was found to be complete in 1 day. The $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectrum of the crude reaction mixture in $CDCl_3$ exhibited 2 sharp singlets at δ –35.5 ($^{1}J_{P\text{–}Pt}$ = 3971 Hz) and δ –37.9 ($^{1}J_{P\text{–}Pt}$ = 4058 Hz) with relative intensities of 5:4, respectively (Scheme 2.10). The phosphorus resonance signal at δ –35.5 is assigned to complex (R_{c},R_{p})-**80**, and the signal at δ –37.9 is assigned to complex (R_{c},S_{p})-**81**.

As previously observed, complex (R_{c},R_{p})-**80** underwent a series of transformations in a silica gel column to generate a small amount of the transformed product (R_{c},S_{c},R_{p})-**82,** which showed a $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR signal at δ –3.7.

Unfortunately, only complex (R_c,S_p)-**81** could be induced to crystallize as light yellow crystals from acetone–hexane. Single crystals of complex (R_c,R_p)-**80** and complex (R_c,S_c,R_p)-**82** that were suitable for X-ray structural analysis could not be produced, despite numerous attempts to crystallize them using a wide variety of solvent systems.



Scheme 2.10

2.2.5.1 X-ray Structural Analysis of Complex (R_c,S_p)-81

The molecular structure and absolute stereochemistry of complex (R_c,S_p)-**81** was confirmed by X-ray crystallography(Figure 2.7). As expected, one of carbon–carbon triple bonds of the original alkynylphosphine, bond C(18)–C(19), had inserted into the Pd(1)–C(29) bond of benzylamine dimer 13. This resulted in a new carbon–carbon bond between C(19) and C(29) together with a new metal–carbon bond between Pd(1) and C(18). The phosphorus donor atom is coordinated regiospecifically in the position *trans* to the naphthylamine–*N* donor atom. A new stereogenic center adopting the *S* absolute configuration was formed at P(1) while the absolute configuration of the stereocenter at C(11) remained unchanged.

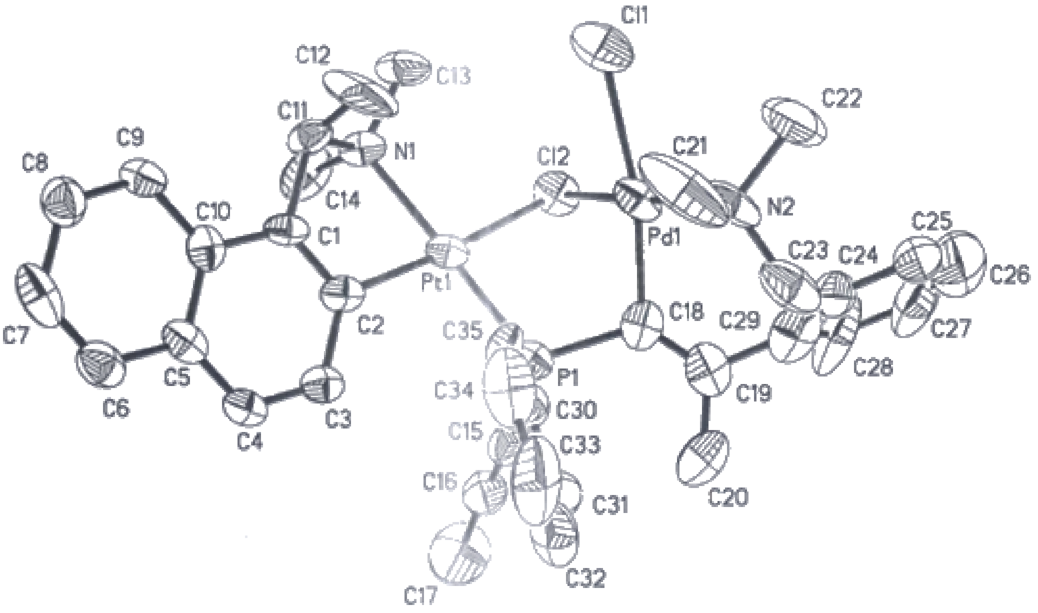


Figure 2.7 Molecular Structure of Complex (R_{c},$S_{\text{p,}}$)-**81**

The geometry at platinum and palladium centers are distorted square planar with bond angles at Pt(1) in the range of 78.9(1)–97.9(3)˚ and 174.4(3)–175.9(3)˚, while those at Pd(1) ranges from 84.5(3)–94.9(5)˚ and 169.0(4)–171.8(4)˚, respectively. Table 2.7 shows selected bond distances and angles of complex ($R_{\text{c,}}S_{\text{p,}}$)-**81**.

Table 2.7 Selected bond distances (Å) and angles (°) of complex (R_c,$S_\mathrm{p,}$)-**81**

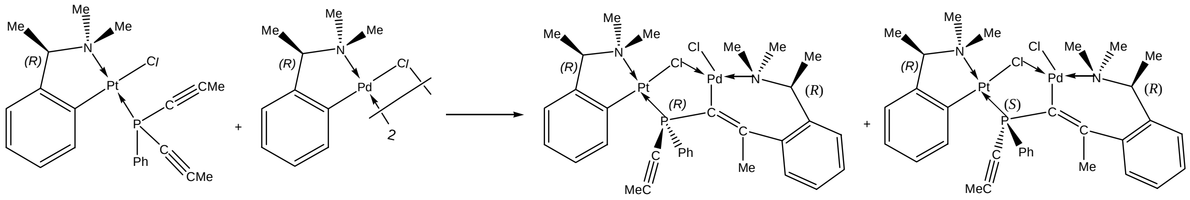
Pt(1)–C(2)	2.017(11)	C(2)–Pt(1)–P(1)	97.9(3)
Pt(1)–N(1)	2.158(10)	N(1)–Pt(1)–P(1)	175.9(3)
Pt(1)–P(1)	2.215(3)	C(2)–Pt(1)–Cl(2)	174.4(3)
Pt(1)–Cl(2)	2.406(3)	N(1)–Pt(1)–Cl(2)	95.5(3)
Pd(1)–C(18)	1.988(14)	P(1)–Pt(1)–Cl(2)	87.7(1)
Pd(1)–N(2)	2.118(11)	C(18)–Pd(1)–N(2)	94.9(5)
Pd(1)–Cl(2)	2.402(3)	C(18)–Pd(1)–Cl(2)	84.5(3)
Pd(1)–Cl(1)	2.417(5)	N(2)–Pd(1)–Cl(2)	171.8(4)
C(15)–C(16)	1.169(19)	C(18)–Pd(1)–Cl(1)	169.0(4)
C(18)–C(19)	1.33(2)	N(2)–Pd(1)–Cl(1)	90.6(4)
C(2)–Pd(1)–N(1)	78.9(4)	Cl(1)–Pd(1)–Cl(2)	91.4(1)

2.2.6 Insertion Reactions Promoted by Different Organometallic Templates

To study the reactivity and the selectivity of palladium–carbon bond of cyclopalladated benzylamine dimer toward the insertion reaction of carbon–carbon triple bond when phosphine ligand, dipropynylphenylphosphine **71**, was coordinated to different organometallic templates, several insertion reactions were investigated.

2.2.6.1 Synthesis of Complex (R_c,R_p,R_c)-83, (R_c,S_p,R_c)-84

Insertion reaction between benylamine platinum(II) complex (R_c)-**82** and 0.5 equivalent of benzylamine palladium(II) dimer (R_c)-**61** was carried out at room temperature using dichloromethane as solvent(Scheme 2.11). This reaction was monitored by the ^{31}P{^{1}H} NMR spectroscopy and was found to be complete in 20 hours. The $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture in $CDCl_3$ exhibited 2 sharp singlets at δ –24.9 ($^1J_{P-Pt}$ = 4166 Hz) and δ –35.8 ($^1J_{P-Pt}$ = 4016 Hz) with relative intensities of 3:2, respectively.



(R_c)-**82** (R_c)-**61** (R_c,R_p,R_c)-**83** (R_c,S_p,R_c)-**84**

Scheme 2.11

The two products were separated by column chromatography as light yellow solid in 30% and 23% yields. The phosphorus resonance signal at δ –24.9 is assigned to complex (R_c,R_p,R_c)-**83**, while the signal at δ –35.8 is assigned to complex (R_c,S_p,R_c)-**84**, respectively. Both complexes were crystallized from dichloromethane–hexane as light yellow crystals.

It should be noted that during the purification of the product via silica gel chromatography, several extra phosphorus resonance signals were observed in the $^{31}P\{^1H\}$ NMR spectrum. However, none of the new compounds could be isolated as they decomposed very rapidly.

2.2.6.1.1 X-ray Structural Analysis of Complexes (R_c,R_p,R_c)-83 and (R_c,S_p,R_c)-84

The X-ray structural analysis of the two complexes confirmed that the desired insertion products had been formed (Figure 2.8, 2.9). The phosphorus donor atoms were coordinated regiospecifically in the position *trans* to the phenylamine–*N* donor atom. The newly formed stereogenic centers at P adopt *R* and *S* absolute configuration for complex (R_c,R_p,R_c)-**83** and (R_c,S_p,R_c)-**84,** respectively, while the absolute configuration of the stereocenter at the carbon remained unchanged for the two compounds.

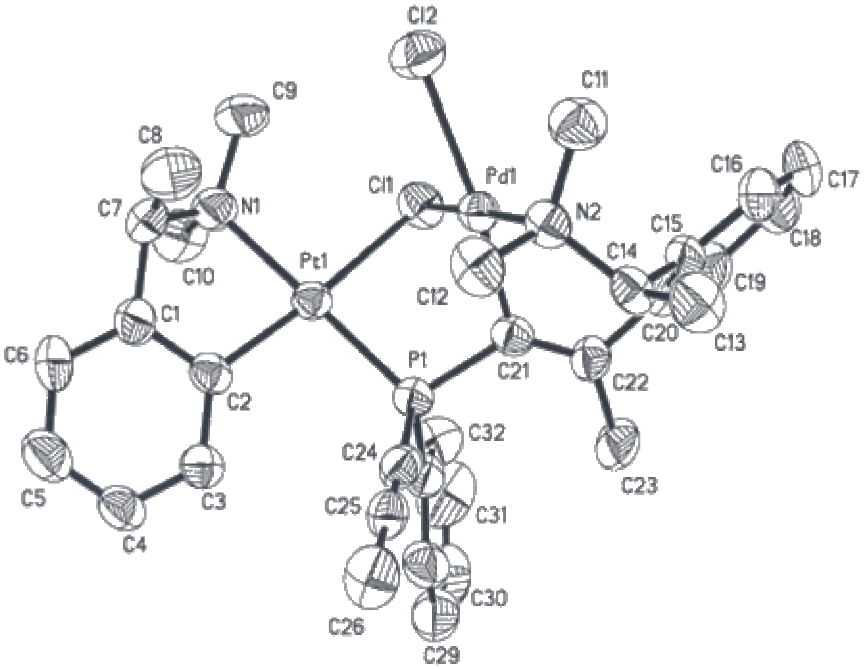


Figure 2.8 Molecular Structure of Complex (R_c,R_p,R_c)-**83**

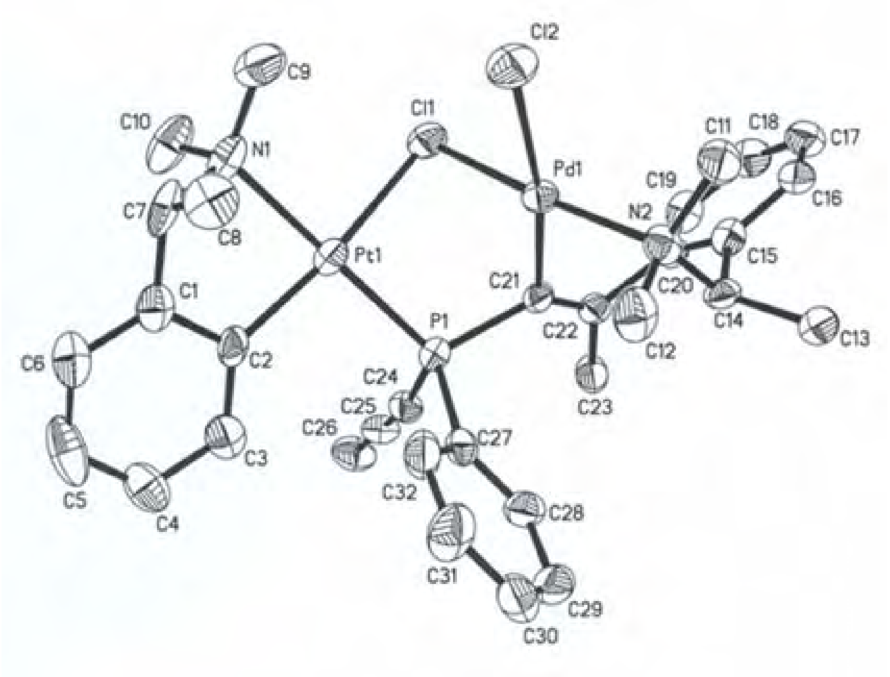


Figure 2.9 Molecular Structure of Complex (R_c,S_p,R_c)-**84**

The molecular structure of complex (R_c,R_p,R_c)-**83** showed that one of carbon–carbon triple bonds of alkynylphosphine, bond C(21)–C(22), had inserted into the Pd(1)–C(20) bond of benzylamine dimer (R_c)-**8**, while another carbon–carbon bond remained unreacted. As the result of this insertion, two new bonds were generated, and they are C(22)–C(20) and Pd(1)–C(21). The platinum and palladium metal centers are connected by Cl(1) to give a 5-membered bimetallic heterocycle. Except the fact that the stereogenic centers at C and P adopt different absolute configuration for the three complexes, complex (R_c,S_p,R_c)-**84** and (R_c,R_p,S_c)-**85** have the same molecular connectivity and differ in the bond lengths and angles.

The geometry at both platinum and palladium centers are distorted square planar. The bond angles at Pt(1) are in the range of 80.5(2)–98.3(2)° and 174.7(2)–178.2(1)° for complex (R_c,R_p,R_c)-**83**; 81.7(3)–97.6(2)° and 171.2(2)–176.9(2)° for complex (R_c,S_p,R_c)-**84**; respectively. While the bond angles at Pd(1) ranges from 83.5(2)–92.7(2)° and 171.9(2)–175.0(1)° for complex (R_c,R_p,R_c)-**83**; 84.3(2)–93.8(2)° and 170.0(2)–172.4(2)° for complex (R_c,S_p,R_c)-**84**; respectively. Table 2.8 shows selected bond distances and angles of complex (R_c,R_p,R_c)-**83**, (R_c,S_p,R_c)-**84**.

Table 2.8 Selected bond distances (Å) and angles (°) of complex (R_c,R_p,R_c)-**83,** (R_c,S_p,R_c)-**84**

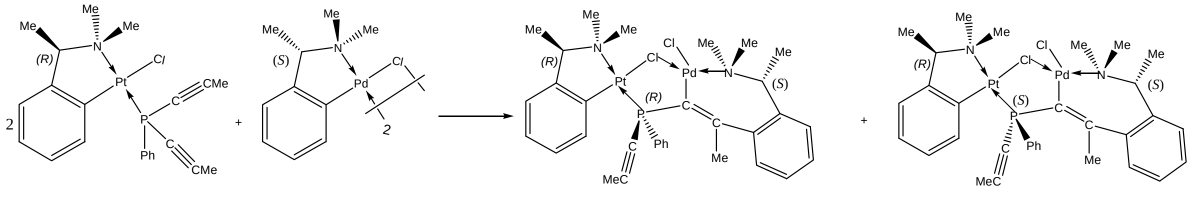
	Complex (R_c,R_p,R_c)-83	**Complex (R_c,S_p,R_c)-84**
Pt(1)–C(2)	1.998(5)	1.997(7)
Pt(1)–N(1)	2.145(5)	2.151(6)
Pt(1)–P(1)	2.218(2)	2.222(2)
Pt(1)–Cl(1)	2.429(1)	2.424(2)

Pd(1)–C(21)	1.993(5)	2.009(6)
Pd(1)–N(2)	2.137(5)	2.125(6)
Pd(1)–Cl(1)	2.363(2)	2.343(2)
Pd(1)–Cl(2)	2.440(2)	2.409(2)
C(21)–C(22)	1.318(7)	1.321(9)
C(2)–Pt(1)–N(1)	80.5(2)	81.7(3)
C(2)–Pt(1)–P(1)	98.3(2)	97.6(2)
N(1)–Pt(1)–P(1)	178.2(1)	176.9(2)
C(2)–Pt(1)–Cl(1)	174.8(1)	171.2(2)
N(1)–Pt(1)–Cl(1)	94.2(1)	92.6(2)
P(1)–Pt(1)–Cl(1)	87.1(1)	88.5(1)
C(21)–Pd(1)–N(2)	92.7(2)	93.8(2)
C(21)–Pd(1)–Cl(1)	83.5(2)	84.3(2)
N(2)–Pd(1)–Cl(1)	175.0(1)	172.4(2)
C(21)–Pd(1)–Cl(2)	171.9(2)	170.0(2)
N(2)–Pd(1)–Cl(2)	94.8(1)	93.5(2)
Cl(1)–Pd(1)–Cl(2)	89.2(1)	89.3(1)
Pd(1)–Cl(1)–Pt(1)	83.3(1)	86.4(1)

2.2.6.2 Synthesis of Complex (R_{c},R_{p},S_{c})-85

In an attempt to identify the origin of the stereoselectivity, another similar insertion reaction was performed between benzylamine platinum(II) complex (R_{c})-**82** and 0.5 equivalent of benzylamine palladium(II) dimer (S_{c})-**62** at room temperature in dichloromethane. This reaction was monitored by ^{31}P{^{1}H} NMR spectroscopy and was found to be complete in 1 day.

The $^{31}P\{^{1}H\}$ NMR spectrum of the crude reaction mixture in $CDCl_3$ exhibited 2 sharp singlets at δ –15.6 ($^{1}J_{P-Pt}$ = 4215 Hz) and δ –33.9 ($^{1}J_{P-Pt}$ = 4036 Hz) with relative intensities of 2:1, respectively (Scheme 2.12).



(R_c)-**82** (S_c)-**62** (R_c,R_p,S_c)-**85** (R_c,R_p,S_c)-**86**

Scheme 2.12

The crude reaction mixture was purified by column chromatography to give two light yellow solids in 37% and 21% yield. Complex (R_c,R_p,S_c)-**85** was crystallized from acetone–hexane as light yellow crystals. Unfortunately, single crystals of complex (R_c,S_p,S_c)-**86** suitable for X–ray structural analysis could not be produced, despite many attempts to crystallize it using a wide variety of different solvent system. The phosphorus resonance signal at δ –15.6 is assigned to complex (R_c,R_p,S_c)-**85**, while the signal at δ –33.8 is assigned to complex (R_c,S_p,S_c)-**86**, respectively. Similarly, new phosphorus resonance signals were observed on $^{31}P\{^{1}H\}$ NMR spectrum when column chromatography was performed to separate the products, however, none of them was isolated as they decomposed very rapidly.

2.2.6.2.1 X-ray Structural Analysis of Complex (R_c,R_p,S_c)-85

The X-ray structural analysis of the complex (R_c,R_p,S_c)-**85** confirmed the formation of the desired insertion products (Figure 2.10). The phosphorus donor atoms were coordinated regiospecifically in the position *trans* to the benzylamine–*N* donor atom. The newly formed stereogenic center at P adopts the *S* absolute configuration. And the absolute configuration of the stereocenter at carbon remained unchanged.

From the molecular structure of complex (R_{c},R_{p},S_{c})-**85,** it could be concluded that except the fact that the stereogenic centers at C and P adopt different absolute configuration from complex (R_{c},R_{p},R_{c})-**83**, they havethe same molecular connectivity and differ in the bond lengths and angles.

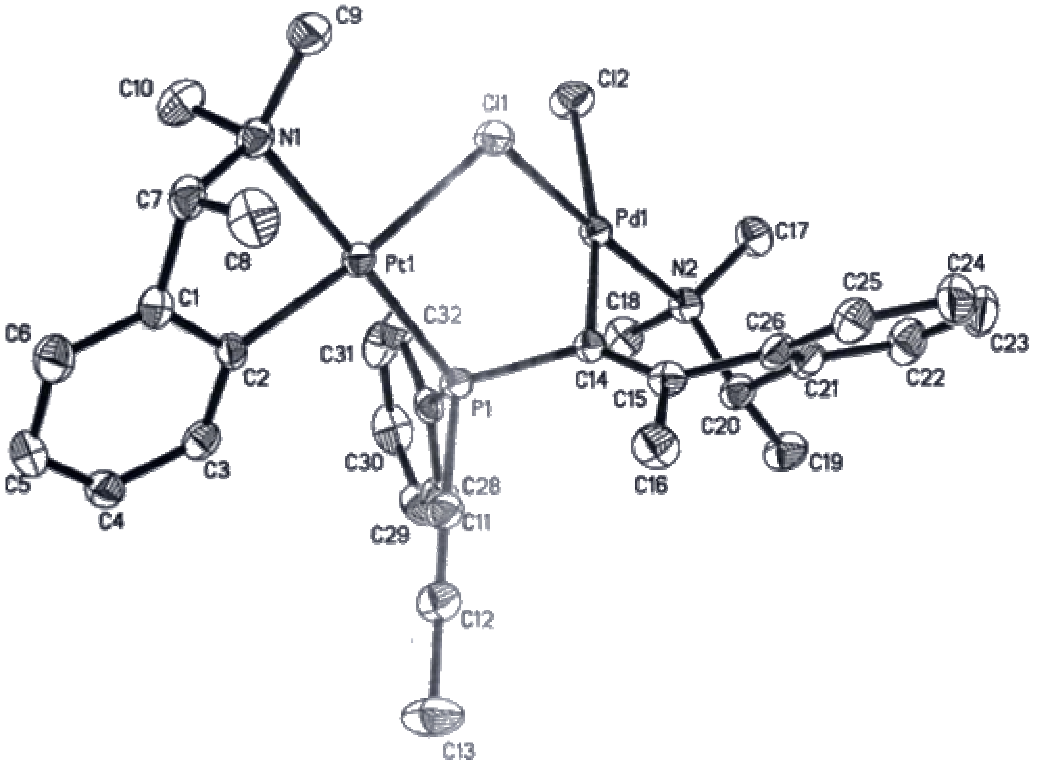


Figure 2.10 Molecular Structure of Complex (R_{c},R_{p},S_{c})-**85**

The geometry at both platinum and palladium centers are distorted square planar. The bond angles at Pt (1) are in the range of 80.7(1)–97.1(1)˚ and 173.8(1)–176.1(1)˚,respectively. While the bond angles at Pd(1) ranges from 85.2(1)–94.0(1)˚ and 169.6(1)–176.6(1)˚**,** respectively. Table 2.10 shows selected bond distances and angles of complex (R_{c},R_{p},S_{c})-**85**,

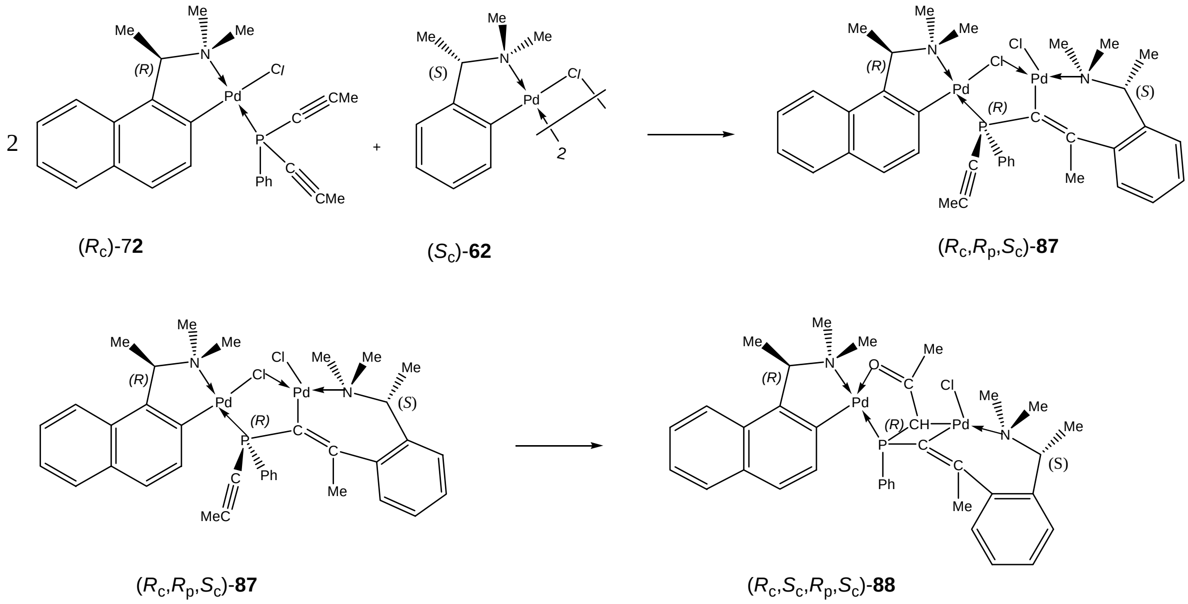
Table 2.10 Selected bond distances (Å) and angles (°) of complex (R_{c},R_{p},S_{c})-**85**

Pt(1)–C(2)	1.992(3)	N(1)–Pt(1)–P(1)	176.2(1)
Pt(1)–N(1)	2.139(3)	C(2)–Pt(1)–Cl(1)	173.8(1)
Pt(1)–P(1)	2.211(1)	N(1)–Pt(1)–Cl(1)	95.6(1)
Pt(1)–Cl(1)	2.422(1)	P(1)–Pt(1)–Cl(1)	87.0(3)
Pd(1)–C(14)	1.997(3)	C(14)–Pd(1)–N(2)	94.0(1)
Pd(1)–N(2)	2.106(3)	C(14)–Pd(1)–Cl(1)	85.2(1)
Pd(1)–Cl(1)	2.363(1)	N(2)–Pd(1)–Cl(1)	176.6(1)
Pd(1)–Cl(2)	2.4061(1)	C(14)–Pd(1)–Cl(2)	169.6(1)
C(14)–C(15)	1.341(4)	N(2)–Pd(1)–Cl(2)	93.1(1)
C(2)–Pt(1)–N(1)	80.7(1)	Cl(1)–Pd(1)–Cl(2)	88.1(1)
C(2)–Pt(1)–P(1)	97.1(1)	Pd(1)–Cl(1)–Pt(1)	106.7(1)

2.2.6.3 Synthesis of Complexes (R_{c},R_{p},S_{c})-87 and (R_{c},S_{c},R_{p},S_{c})-88

In order to study the subtle metal template effects arising from the benzylamine and naphthylamine auxiliary, a set of insertion reactions were conducted.

Insertion reaction between naphthylamine palladium(II) complex (R_{c})-**72** and 0.5 equivalent of benzylamine palladium(II) dimer (S_{c})-**62** was carried out at room temperature using dichloromethane as solvent (Scheme 2.13). This reaction was monitored the ^{31}P{^{1}H} NMR spectroscopy and was found to be complete in 3 days. Prior to isolation, the ^{31}P{^{1}H} NMR spectrum of the crude reaction mixture in $CDCl_3$ exhibited a major sharp singlet at δ –16.9 together with several minor resonance signals.



Scheme 2.13

After the crude reaction mixture was purified by silica gel column chromatography, major product (R_c,R_p,S_c)-**87** was obtained as yellow solid in 28% yield. In addition to the major signal at δ –16.9, the $^{31}P\{^1H\}$ NMR spectrum of the isolated product in $CDCl_3$ showed an extra phosphorus resonance signal at δ –10.9. Indeed the new phosphorus resonance signal always re–appeared when complex (R_c,R_p,S_c)-**87** was purified by column chromatography. It was subsequently conformed that complex (R_c,R_p,S_c)-**87** was unstable when it was being passed through a column. As a result, a new transformed product, complex (R_c,S_c,R_p,S_c)-**88** was obtained. Complex (R_c,R_p,S_c)-**87** and (R_c,S_c,R_p,S_c)-**88** could be crystallized from acetone–hexane as yellow crystals.

It is noteworthy that unlike the insertion reactions discussed before, the insertion reaction between naphthylamine palladium(II) complex and benzylamine palladium(II) dimer only formed one kind of insertion product.

2.2.6.3.1 X-ray Structural Analysis of Complex (*R*$_c$,*R*$_p$,*S*$_c$)-87

The X-ray structural analysis of the complexes (*R*$_c$,*R*$_p$,*S*$_c$)-**87** confirmed that the desired insertion products has been formed (Figure 2.11). The phosphorus donor atoms were coordinated regiospecifically in the position *trans* to the naphthylamine *N* donor atom. The newly formed stereogenic centers at P adopts the *R* absolute configuration. The absolute configuration of the stereocenter at carbon remained unchanged.

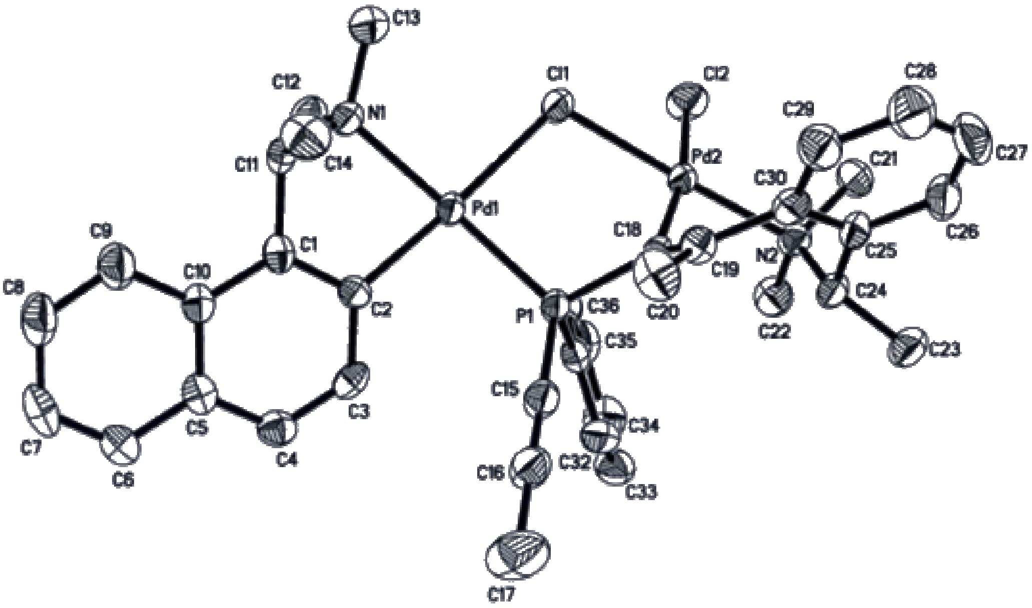


Figure 2.11 Molecular Structure of Complex (*R*$_c$,*R*$_p$,*S*$_c$)-**87**

The molecular structure of complex (*R*$_c$,*R*$_p$,*S*$_c$)-**87** revealed that one of original carbon–carbon triple bonds in the alkynylphosphine, bond C(18)–C(19), has inserted into the Pd(2)–C(30) bond of benzylamine dimer (*S*$_c$)-**62**, while another original carbon–carbon bond, bondC(15)–C(16), remained unchanged. As a result, two new bonds were generated, and they are bond C(19)–C(30) and bond Pd(2)–C(18). The two palladium metal centers are connected by Cl(1) to give a 5-membered bimetallic heterocycle.

The geometry at both palladium centers are distorted square planar. The bond angles at Pd(1) are in the range of 81.1(2)–96.2(1)° and 173.2(1)–174.4(1)°; While the bond angles at Pd(2) ranges from 85.2(1)–93.9(2)° and 173.2(1)–174.4(1)°. Table 2.11 shows selected bond distances and angles of complex (R_c,R_p,S_c)-**87**.

Table 2.11 Selected bond distances (Å) and angles (°) of complex (R_c,R_p,S_c)-**87**

Pd(1)–C(2)	1.986(4)	N(1)–Pd(1)–P(1)	173.2(1)
Pd(1)–N(1)	2.138(4)	C(2)–Pd(1)–Cl(1)	174.4(1)
Pd(1)–P(1)	2.228(1)	N(1)–Pd(1)–Cl(1)	96.1(1)
Pd(1)–Cl(1)	2.416(1)	P(1)–Pd(1)–Cl(1)	87.2(1)
Pd(2)–C(14)	1.994(4)	C(18)–Pd(2)–N(2)	93.9(2)
Pd(2)–N(2)	2.099(3)	C(18)–Pd(1)–Cl(1)	85.2(1)
Pd(2)–Cl(1)	2.355(1)	N(2)–Pd(2)–Cl(1)	176.9(1)
Pd(2)–Cl(2)	2.414(1)	C(18)–Pd(2)–Cl(2)	170.4(1)
C(18)–C(19)	1.343(6)	N(2)–Pd(2)–Cl(2)	93.4(1)
C(2)–Pd(1)–N(1)	81.1(2)	Cl(1)–Pd(2)–Cl(2)	87.8(1)
C(2)–Pd(1)–P(1)	96.2(1)	Pd(2)–Cl(1)–Pd(1)	108.4(1)

2.2.6.3.2 X-ray Structural Analysis of Complex (R_c,S_c,R_p,S_c)-88

The X-ray structural analysis of complexes (R_c,S_c,R_p,S_c)-**88** revealed that one of original carbon–carbon triple bonds in the alkynylphosphine, bond C(18)–C(19), has inserted into the Pd(1)–C(21) bond of benzylamine dimer (S_c)-**62** (Figure 2.12). As a result, two new bonds were formed and they are the C(19)–C(21) and Pd(1)–C(18) bond. Furthermore, another alkynyl carbon–carbon triple bond, bond C(15)–C(16), underwent hydration reaction to yield a carbonyl C=O bond. A five-membered palladium chelate was generated via the carbonyl oxygen O(1) and phosphorous P(1). In addition, a new bond was generated between Pd(2) and C(15) that resulted in a new 4-membered hetero bimetallic ring. The absolute configuration at C(11), P(1) and C(27) stereocenters are *R*, *R*, and *S*, respectively.

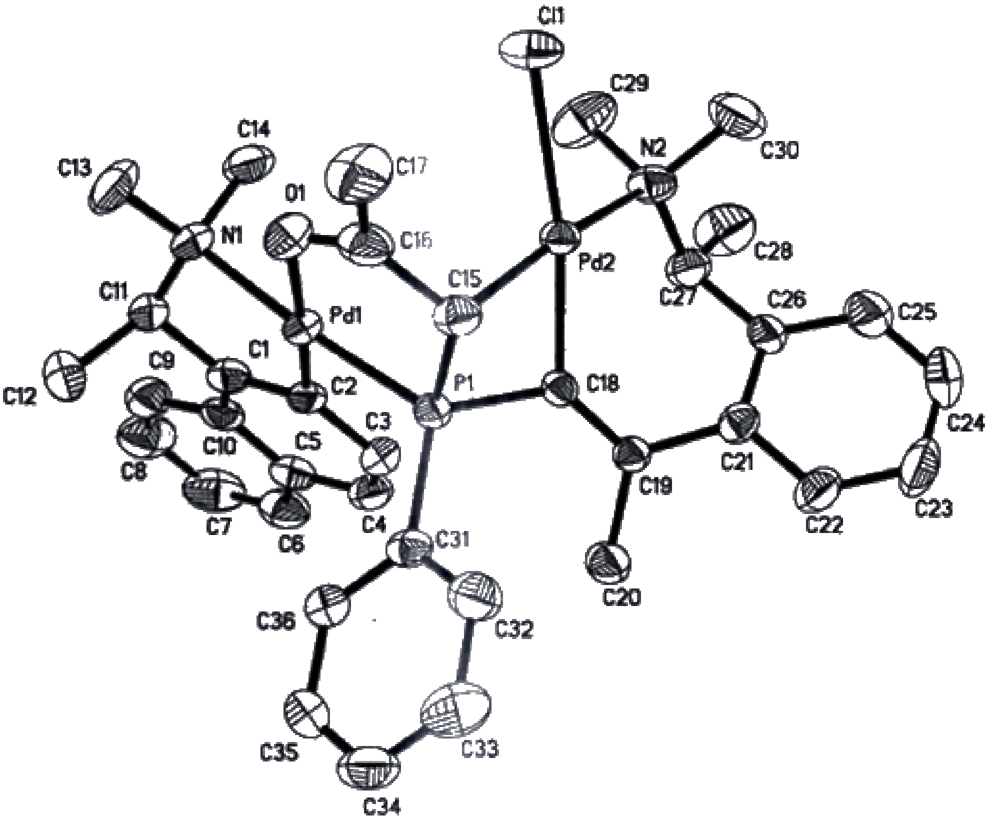


Figure 2.12 Molecular Structure of Complex (R_c,S_c,R_p,S_c)-**88**

The geometry at both palladium centers are slightly distorted square planar with bond angles at Pd(1) in the range of 82.0(2)–99.8(2)° and 175.6(1)–176.1(2)°, while those at Pd(2) ranges from 92.4(1)–96.6(2)° and 170.0(2)–171.1(2)°, respectively. Table 2.12 shows selected bond distances and angles of complex $(R_{\mathrm{c}},S_{\mathrm{c}},R_{\mathrm{p}},S_{\mathrm{c}})$-**88**.

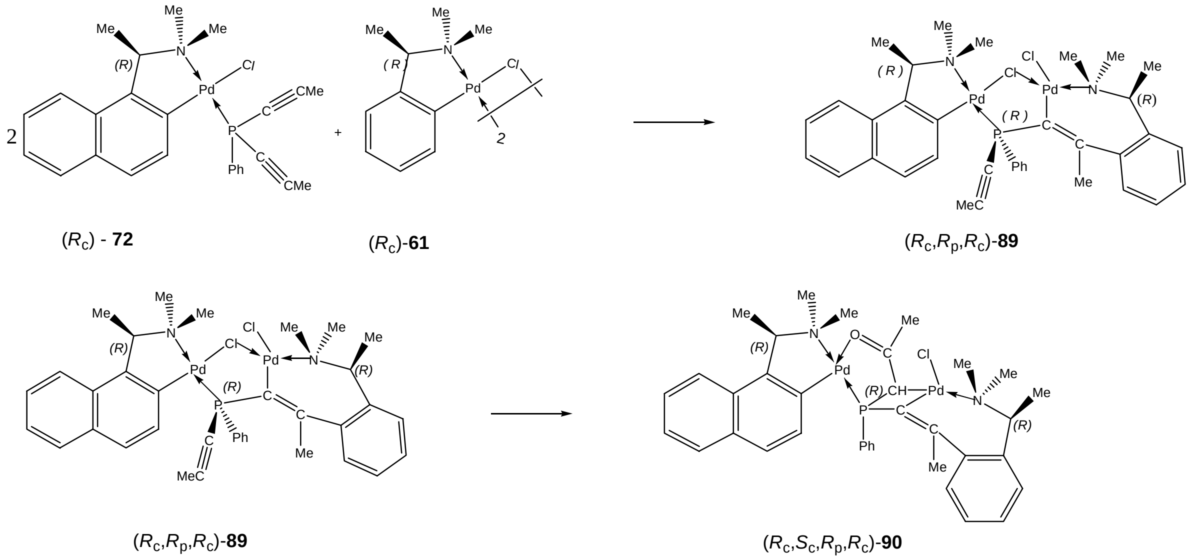
Table 2.12 Selected bond distances (Å) and angles (°) of complex $(R_{\mathrm{c}},S_{\mathrm{c}},R_{\mathrm{p}},S_{\mathrm{c}})$-**88**

Pd(1)–C(2)	1.971(6)	C(2)–Pd(1)–O(1)	176.1(2)
Pd(1)–N(1)	2.120(4)	N(1)–Pd(1)–O(1)	94.1(2)
Pd(1)–O(1)	2.138(4)	C(2)–Pd(1)–P(1)	99.8(2)
Pd(1)–P(1)	2.234(1)	N(1)–Pd(1)–P(1)	175.6(2)
Pd(2)–C(18)	1.991(5)	O(1)–Pd(1)–P(1)	84.1(1)
Pd(2)–N(2)	2.153(5)	C(18)–Pd(2)–N(2)	96.6(2)
Pd(2)–C(15)	2.130(5)	C(18)–Pd(2)–C(15)	75.5(2)
Pd(2)–Cl(1)	2.428(1)	N(2)–Pd(2)–Cl(1)	92.4(1)
O(1)–C(16)	1.254(7)	C(18)–Pd(2)–Cl(1)	170.0(2)
C(15)–C(16)	1.434(8)	N(2)–Pd(2)–Cl(1)	92.4(1)
C(18)–C(19)	1.350(7)	C(15)–Pd(2)–Cl(1)	95.4(1)
	82.0(2)	C(16)–O(1)–Pd(1)	116.9(4)

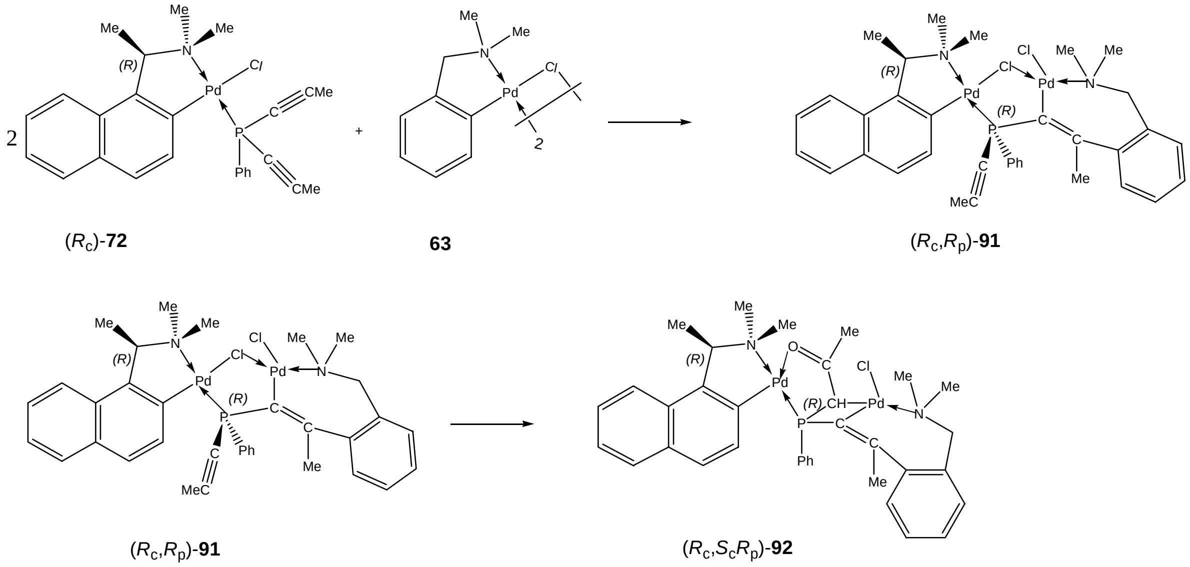
From the above reaction, it was confirmed that the dialkynyl phosphine remained coordinated on the naphthylamine template through the insertion reaction. Therefore, ligand distribution between the naphthylamine and benzylamine orthopalladate templates appears to be insignificant.

2.2.6.4 Synthesis of Complexes (*R*$_c$,*R*$_p$,*R*$_c$)-89 and (*R*$_c$,*R*$_p$)-91

To understand the origin of the stereoselectivity, the naphthylamine palladium(II) complex (*R*$_c$)-**72** was choose to react separately with the *R* enantiomer benzylamine palladium(II) dimer (*R*$_c$)-**8** and its achiral analogue benzylamine palladium(II) dimer **63** (Scheme 2.14 and Scheme 2.15, respectively).



Scheme 2.14



Scheme 2.15

After separation by column chromatography, both reactions generated one single insertion product. It should be noted that for each reaction, during the purification of the product via silica gel an extra phosphorus resonance signal was observed which assigned to the transformed product. However, only the original insertion products complex (R_c,R_p,R_c)-**89** and (R_c,R_p)-**91** could be crystallized from acetone–hexane or dichloromethane– hexane as yellow crystals. The ^{31}P{^{1}H}NMR spectrum of complex (R_c,R_p,R_c)-**89** exhibited a sharp singlet at δ –16.9, that of complex (R_c,R_p)-**91** at δ –16.4.

2.2.6.4.1 X-ray Structural Analysis of Complexes (R_c,R_p,R_c)–89 and (R_c,R_p)–91

The X-ray structural analysis of the two complexes confirmed that the desired insertion products have been formed (Figures 2.13 and 2.14). The phosphorus donor atoms were coordinated regiospecifically in the position *trans* to the naphthylamine–*N* donor atom. The newly formed stereogenic centers at P adopt *R* absolute configuration for both complexes, while the absolute configurations of the stereocenters at the benzylic carbons remained unchanged for both compounds.

The molecular structure of complex (R_c,R_p,R_c)-**89** revealed that one of the original carbon–carbon triple bonds in the alkynylphosphine, bond C(18)–C(19), has inserted into the Pd(2)–C(30) bond of benzylamine dimer (R_c)-**61**, while another carbon–carbon bond, C(15)–C(16), remained unchanged. As the result of this insertion, two new bonds were generated, and they are C(19)–C(30) and Pd(2)–C(18). The two palladium metal centers are connected by Cl to give a 5-membered bimetallic heterocycle. Except the fact that the stereogenic centers at benzylic carbon adopt different absolute configuration for the two complexes, they have the same molecular connectivity, and only differ in the bond lengths and angles.

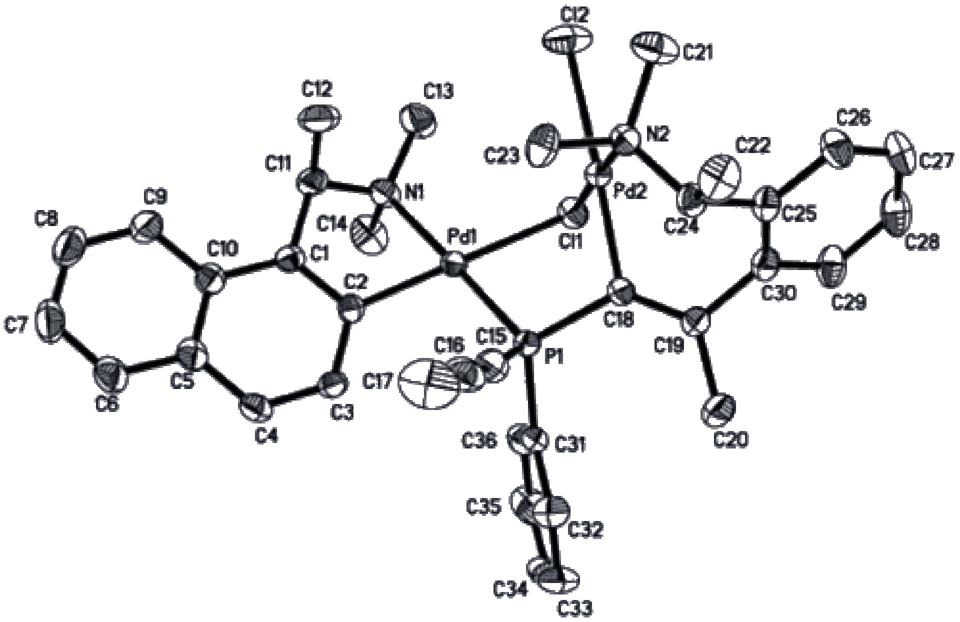


Figure 2.13 Molecular Structure of Complex ((R_c,R_p,R_c))-**89**

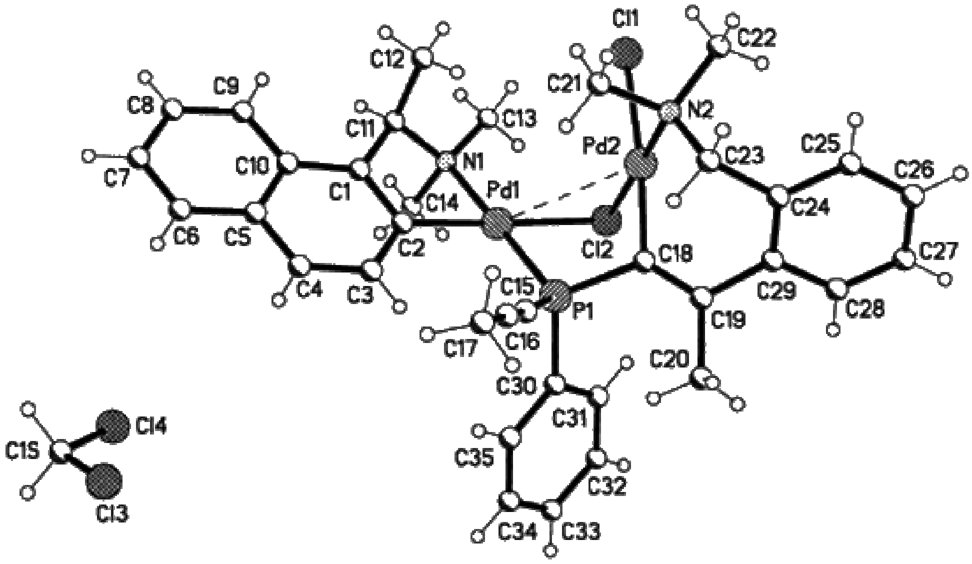


Figure 2.14 Molecular Structure of Complex ((R_c,R_p))-**91**

The geometry at both palladium centers are distorted square planar. The bond angles at Pd(1) are in the range of 81.3(1)–96.0(7)° and 174.9(1)–176.8(1)° for complex (R_{c},R_{p},R_{c})-**89**; 81.2(2)–99.6(2)° and 177.4(2)–177.7(2)° for complex (R_{c},R_{p})-**91**, respectively. While the bond angles at Pd(2) ranges from 84.0(1)–93.8(2)° and 170.0(2)–172.4(2)° for complex (R_{c},R_{p},R_{c})-**89**; 85.0(2)–92.7(3)° and 173.5(2)–176.5(2)° for complex (R_{c},R_{p})-**91**, respectively. Table 2.13 and 2.14 show selected bond distances and angles of complex (R_{c},R_{p},R_{c})-**89** and complex (R_{c},R_{p})-**91**.

Table 2.13 Selected bond distances (Å) and angles (°) of complex (R_{c},R_{p},S_{c})-**89**

Pd(1)–C(2)	1.992(3)	N(1)–Pd(1)–P(1)	176.76(8)
Pd(1)–N(1)	2.123(2)	C(2)–Pd(1)–Cl(1)	174.86(8)
Pd(1)–P(1)	2.2421(6)	N(1)–Pd(1)–Cl(1)	95.70(7)
Pd(1)–Cl(1)	2.4338(7)	P(1)–Pd(1)–Cl(1)	87.15(2)
Pd(2)–C(14)	2.003(3)	C(18)–Pd(2)–N(2)	93.52(9)
Pd(2)–N(2)	2.123(2)	C(18)–Pd(1)–Cl(1)	84.03(7)
Pd(2)–Cl(1)	2.3395(7)	N(2)–Pd(2)–Cl(1)	177.53(6)
Pd(2)–Cl(2)	2.4057(8)	C(18)–Pd(2)–Cl(2)	172.32(7)
C(18)–C(19)	1.337(4)	N(2)–Pd(2)–Cl(2)	94.16(6)
C(2)–Pd(1)–N(1)	81.26(10)	Cl(1)–Pd(2)–Cl(2)	88.30(3)
C(2)–Pd(1)–P(1)	96.01(7)	Pd(2)–Cl(1)–Pd(1)	83.10(2)

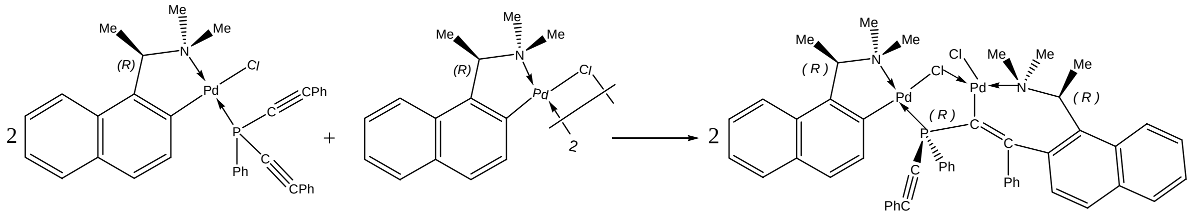
Table 2.14 Selected bond distances (Å) and angles (°) of complex (R_c,R_p)-**91**

Pd(1)–C(2)	1.999(6)	N(1)–Pd(1)–P(1)	177.66(16)
Pd(1)–N(1)	2.134(5)	C(2)–Pd(1)–Cl(2)	177.38(19)
Pd(1)–P(1)	2.2491(18)	N(1)–Pd(1)–Cl(2)	96.20(14)
Pd(1)–Cl(2)	2.4506(18)	P(1)–Pd(1)–Cl(2)	83.05(6)
Pd(2)–C(18)	1.987(6)	C(18)–Pd(2)–N(2)	92.7(3)
Pd(2)–N(2)	2.100(6)	C(18)–Pd(2)–Cl(2)	84.97(18)
Pd(2)–Cl(2)	2.358(2)	N(2)–Pd(2)–Cl(2)	176.53(17)
Pd(2)–Cl(1)	2.414(2)	C(18)–Pd(2)–Cl(1)	173.48(19)
C(18)–C(19)	1.336(9)	N(2)–Pd(2)–Cl(1)	92.5(2)
C(2)–Pd(1)–N(1)	81.2(2)	Cl(2)–Pd(2)–Cl(1)	89.69(8)
C(2)–Pd(1)–P(1)	99.58(19)	Pd(2)–Cl(2)–Pd(1)	80.13(6)

2.2.7 Synthesis of Complexes (R_c,R_p,R_c)-95 and (R_c,R_p,R_c)-96

The earlier insertion reactions have demonstrated the flexibility of insertion an alkyne into the Pd–phenyl bond. In order to explore if the insertion reaction could be induced into the analogous Pd–naphthyl complexes, the two precursor complexes (R_c)-**93** and (R_c)-**94** were prepared and reacted separately with the chiral naphthylamine palladium(II) complex (R_c)-**59** (Scheme 2.16 and 2.17).

The reaction between naphthylamine palladium(II) complex (R_c)-**93** and 0.5 equivalent of naphthylamine palladium(II) dimer (R_c)-**59** was carried out in refluxing 1,2-dichloroethane (Scheme 2.16). This reaction was monitored by the ^{31}P{^{1}H} NMR spectroscopy and was found to be complete in 10 hours. Unlike other insertion reactions described earlier, the $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture in $CDCl_3$ exhibited only one sharp singlet at δ 16.5 and no other NMR signals were observed in the $^{31}P\{^1H\}$ NMR spectrum.

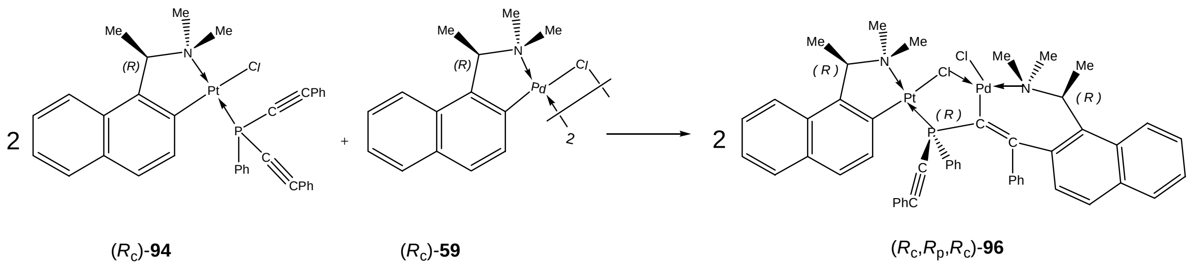


(R_c)-**93** (R_c)-**59** (R_c,R_p,R_c)-**95**

Scheme 2.16

The crude reaction mixture was purified by column chromatography to give complex (R_c,R_p,R_c)–**95** as yellow solid in 23% yield. No new phosphorus resonance signal was observed in the $^{31}P\{^1H\}$ NMR spectrum throughout the purification. Complex (R_c,R_p,R_c)–**95** was recrystallized from acetone–hexane as yellow crystals.

Using a similar procedure as illustrated in Scheme 2.14, another insertion reaction was carried out between naphthylamine platinum(II) complex (R_c)-**94** and 0.5 equivalent of naphthylamine palladium (II) dimer (R_c)-**59** in 1,2-dichloroethane (Scheme 2.17). As monitored by the $^{31}P\{^1H\}$ NMR spectroscopy this reaction was found to complete after being refluxed 24 hours. Only one sharp singlet at δ 1.3 ($^1J_{P\text{–}Pt}$ = 4275 Hz) was observed in the $^{31}P\{^1H\}$NMR. After being purified by column chromatography, complex (R_c,R_p,R_c)-**96** was obtained as yellow solid in 20% yield. The insertion product could be crystallized from acetone–hexane as yellow crystals.



Scheme 2.17

2.2.7.1 X-ray Structural Analysis of Complexes ($\boldsymbol{R_c,R_p,R_c}$)-95 and ($\boldsymbol{R_c,R_p,R_c}$)-96

The X-ray structural analysis of complex (R_c,R_p,R_c)-**95** and (R_c,R_p,R_c)-**96** confirmed that the desired insertion products have been formed (Figure 2.16 and 2.17). The phosphorus donor atoms were coordinated regiospecifically in the position *trans* to the naphthylamine–*N* donor atom. The newly formed stereogenic centers at P adopt *R* absolute configuration for the two complexes, while the absolute configuration of the stereocenter at C remained unchanged for them.

The molecular structure of complex (R_c,R_p,R_c)-**95** showed that one of carbon–carbon triple bonds of alkynylphosphine, bond C(23)–C(24), has inserted into the Pd(2)–C(27) bond of naphthylamine dimer (R_c)-**59**, while another carbon–carbon bond, C(25)–C(26), remained unchanged. As the result of this carbon–carbon insertion, two new bonds were generated, and they are C(24)–C(27) and Pd(2)–C(23). The two palladium metal centers are connected by Cl to give a 5-membered bimetallic heterocycle. Apart from the fact that the two complexes contain different metal centers, complex (R_c,R_p,R_c)-**95** and complex (R_c,R_p,R_c)-**96** have similar molecular structureand differ slightly in the bond lengths and angles.

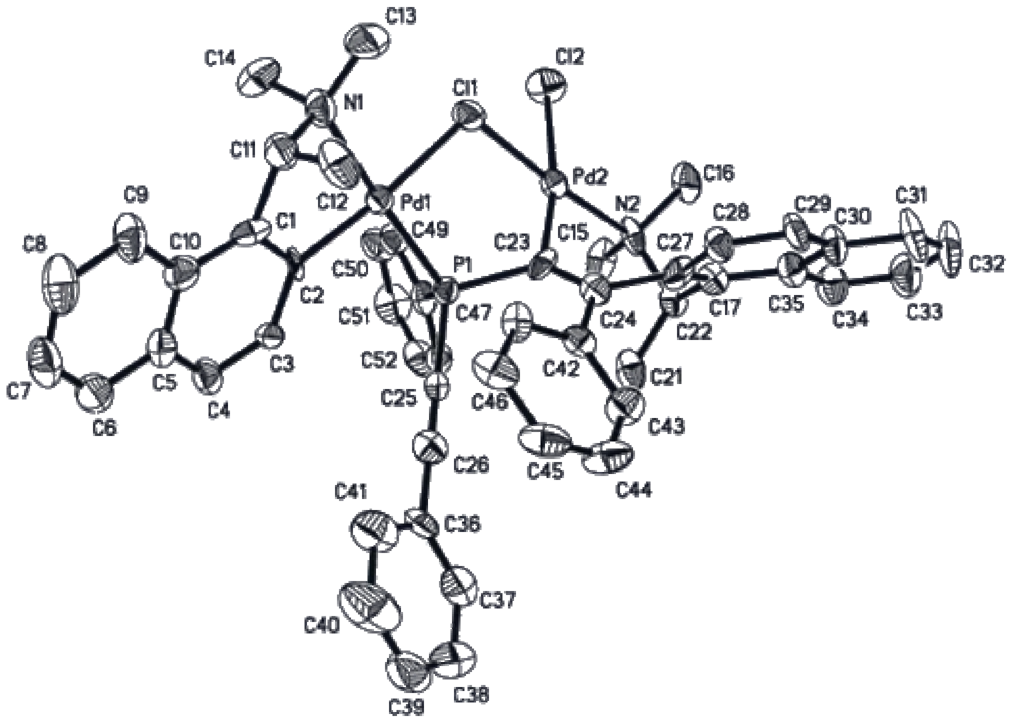


Figure 2.15 Molecular Structure of Complex (R_c,R_p,R_c)-**95**

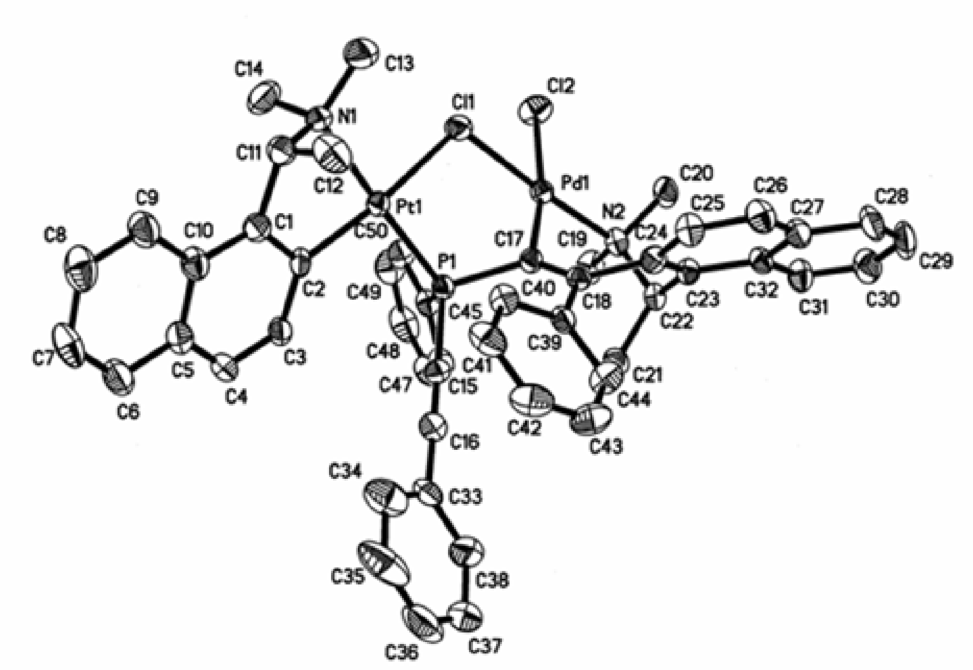


Figure 2.16 Molecular Structure of Complex (R_c,R_p,R_c)-**96**

The geometry at the platinum and palladium centers are both distorted square planar for complexe (R_c,R_p,R_c)-**95** and (R_c,R_p,R_c)-**96**. For complex (R_c,R_p,R_c)-**95** the bond angles at the Pd(1) center range from 81.7(3)–99.0(3)˚, 174.2(3)–174.3(3)˚ and at Pd(2) from 85.3(2)–94.7(3)˚, 169.8(3)–174.6(2)˚**,** respectively. For complex (R_c,R_p,R_c)-**96** the bond angles at the Pd(1) center are in the range of 85.4(1)–93.8(1)˚, 170.9(1)–175.4(1)˚ and at Pt(1) range from 81.5 (2)–99.7(1)˚, 174.2(1)–174.9 (1)˚**,** respectively. Table 2.15 and 2.16 show selected bond distances and angles of complexes (R_c,R_p,R_c)-**95** and (R_c,R_p,R_c)-**96**, respectively.

Table 2.15 Selected bond distances (Å) and angles (°) of complex (R_c,R_p,R_c)-**95**

Pd(1)–C(2)	1.969(8)	N(1)–Pd(1)–P(1)	174.3(3)
Pd(1)–N(1)	2.134(9)	C(2)–Pd(1)–Cl(1)	174.2(3)
Pd(1)–P(1)	2.242(2)	N(1)–Pd(1)–Cl(1)	94.5(2)
Pd(1)–Cl(1)	2.401(2)	P(1)–Pd(1)–Cl(1)	85.2(1)
Pd(2)–C(23)	1.979(10)	C(23)–Pd(2)–N(2)	94.7(3)
Pd(2)–N(2)	2.069(8)	C(23)–Pd(2)–Cl(1)	85.3(2)
Pd(2)–Cl(1)	2.361(2)	N(2)–Pd(2)–Cl(1)	174.6(2)
Pd(2)–Cl(2)	2.436(3)	C(23)–Pd(2)–Cl(2)	169.8(3)
C(23)–C(24)	1.342(13)	N(2)–Pd(2)–Cl(2)	94.2(2)
C(2)–Pd(1)–N(1)	81.7(3)	Cl(1)–Pd(2)–Cl(2)	86.3(1)
C(2)–Pd(1)–P(1)	99.0(3)	Pd(2)–Cl(1)–Pd(1)	110.7(1)

Table 2.16 Selected bond distances (Å) and angles (°) of complex ($R_{\mathrm{c}},R_{\mathrm{p}},R_{\mathrm{c}}$)-**96**

Pt(1)–C(2)	1.988(4)	N(1)–Pt(1)–P(1)	174.9(1)
Pt(1)–N(1)	2.124(3)	C(2)–Pt(1)–Cl(1)	174.2(1)
Pt(1)–P(1)	2.218(1)	N(1)–Pt(1)–Cl(1)	94.4(1)
Pt(1)–Cl(1)	2.411(1)	P(1)–Pt(1)–Cl(1)	84.8(1)
Pd(1)–C(17)	1.985(4)	C(17)–Pd(1)–N(2)	93.8(1)
Pd(1)–N(2)	2.091(3)	C(17)–Pd(1)–Cl(1)	85.4(1)
Pd(1)–Cl(1)	2.365(1)	N(2)–Pd(1)–Cl(1)	175.4(1)
Pd(1)–Cl(2)	2.432(1)	C(17)–Pd(1)–Cl(2)	170.9(1)
C(17)–C(18)	1.342(5)	N(2)–Pd(1)–Cl(2)	93.7(1)
C(2)–Pt(1)–N(1)	81.5(2)	Cl(1)–Pd(1)–Cl(2)	87.5(1)
C(2)–Pt(1)–P(1)	99.7(1)	Pd(1)–Cl(1)–Pt(1)	110.9(1)

2.3 Conclusions

The insertion of alkynes with di-(1-propynyl)phenylphosphine ligands into Pd–C bonds of phenylamine palladacycles has been demonstrated. In this study, cyclopalladated and cycloplatinated complexes containing the benzyl and naphthylamine systems have been chosen to promote the reaction to give a series of bi- or tri-metallic compounds. Reactions involving cycloplatinated promoters usually produced two products, in which phosphorus stereogenic center adopting *R* absolute configurationwas the major product. Moreover, this major product would perform a series of transformations to generate a new C stereogenic center which always adopts *S* absolute configuration. However, reactions involving cyclopalladated promoters could only obtain one product in which phosphorus stereogenic center always adopt *R* absolute configuration. Similarly, transformed products were also obtained.

Then insertion of alkynes with into Pd–C bonds of naphthyamine palladacycles has been investigated. It was found that, the reaction showed excellent selectivity which lead to the single insertion product. Moreover, this insertion product is very stable and no transformations were observed.

2.4 Experimental

Reactions involving air–sensitive compounds were performed under a positive pressure of purified nitrogen. Bruker ACF 300 spectometer was used to record the ^{1}H (300 MHz) and ^{31}P{^{1}H} (121 MHz) NMR spectra. Optical retations were measured on the specified solution in 1–dm cell at 25℃ with a Perkin–Elmer 341 polarimetrer. Melting points were determined on a Bϋchi melting point B–540. Elemental analyses were performed by the Elemental Analysis Laboratory of the Department of Chemistry at the National University of Singapore and Division of Chemistry and Biological Chemistry at the Nanyang Technological University.

The dimeric benzylamine palladium(II) complexes (R_c)-**61**, (S_c)-**62** and **63**,[176] dimeric naphthylamine palladium(II) complex (R_c)-**59**[177,178] and dimeric naphthylamine pllatium(II) (R_c)-**60**[179] were prepared according to standard literature methods.

Synthesis of diprop-1-ynylphenylphosphine, **71**

Dichlorophenylphosphine(5.09 mL d = 1.319, 0.0375 mol) was added to 150 mL 1–propynylmagnesium bromide (suspended in THF, 0.5M) at –30℃. Then the reaction mixture was left to stir overnight.

THF was removed using distillation. Saturated ammonium chloride solution was then added slowly to the remaining reaction mixture and left to stir for 30 minutes. The resulting mixture was extracted with degassed dichloromethane (3×100 mL). The organic layer was put together and dried with anhydrous magnesium sulfate. Then the mixture was filtered and dichloromethane was removed using distillation. The crude product was purified using microdistillation to give a slightly yellowish and viscous liquid, **71**, 3.08 g (44% yield). (The procedure was performed under nitrogen.) b.p. 118–120℃ at 0.85 mmHg. $^{31}P\{^1H\}$NMR ($CDCl_3$) δ –60.2 (s); ^1H NMR ($CDCl_3$) δ 2.01 (s, 3H), 2.02 (s, 3H), δ 7.4–7.8 (m, 5H, *aromatics*).

Synthesis of chloro{(*R*$_c$)-1-[1-(dimethylamino)ethyl]naphthyl-*C*^{2},*N*}{diprop-1-ynylphenylphosphine}palladium(II), (*R*$_c$)-72

Phosphine ligand diprop–1–ynylphenylphosphine **3** **(**1.06 g, 5.69 mmol) was dissolved in dichloromethane. Complex (*R*$_c$)–**5** (1.94 g, 2.85 mmol) was then added to this solution. The reaction was then left to stir at room temperature. This reaction was monitored using $^{31}P\{^1H\}$NMR spectroscopy, and was found to be complete in 2 hours. The complex (*R*$_c$)–5 was crystallized from dichloromethane–hexane as yellow crystals: m.p. 225–227℃; $[\alpha]_D$ –130°(c 0.5, CH_2Cl_2) ; 2.49g (83.5% yield). Anal. Calcd . for $C_{26}H_{27}ClNPdP$: C, 59.33; H, 5.17; N, 2.66. Found: C,59.76; H, 5.44; N, 2.53. $^{31}P\{^1H\}$NMR ($CDCl_3$) δ –20.5(s).^1H NMR (CDCl3): δ 1.97(d, 3H, $^3J_{HH}$ = 6.4 Hz, CH*Me*), 2.01(d, 3H, $^4J_{PH}$ = 3.2 Hz,≡C*Me*), 2.1(d, 3H, $^4J_{PH}$ = 3.6,≡C*Me*), 2.71(d, 3H, $^4J_{PH}$ = 2.0 Hz, N*Me*), 2.96 (d, 3H, $^4J_{PH}$ = 4.0 Hz, N*Me*), 4.4

(qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 13.2 Hz,C*H*Me), 7.27~7.44 (m, 11H, aromatics).

Synthesis of (R_c,R_p,R_c)–74, (R_c,S_p,R_c)–75, and (R_c,S_c,R_p,R_c)–76

Complex (R_c)–73 (0.50 g, 0.81 mmol) was dissolved in dichloromethane (100 mL). This solution then was treated with phenylamine palladium (II) dimer (R_c)–**61** (0.24 g, 0.41mmol). The mixture was stirred at room temperature for 36 hours. Upon completion, the solvent was removed to give dark brown residue which was purified by column chromatography (with an eluting gradient starting from hexane: acetone 6:1) give the products as light yellow solids.

***μ*-chloro{{(R_c)-1-[1-(dimethylamino)ethyl]naphthyl-*C*^{2},*N*}platinum(II){(R_c,R_p)-1-[1-(di-methylamino)ethyl]-2-[(*Z*)-1-(phenylprop-1-ynylphosphino)prop-1-en-2-yl-*C*^{1})]phenyl-*N*} chloro palladium(II)}, (R_c,R_p,R_c)-74,** was crystallized from hexane–acetone as light yellow crystals: 0.17 g (23% yield); m.p.212~214℃ (dec) ; [α]$_D$ +208°(c 0.3, CH_2Cl_2). Anal. Calcd. for $C_{36}H_{41}Cl_2N_2PPdPt$: C, 47.8; H, 4.6; N, 3.1. Found: C, 46.1; H, 4.5; N, 2.9. ^{31}P {^{1}H}NMR($CDCl_3$): δ –38.2 (s, $^1J_{Pt–P}$ = 4074 Hz, 1P); ^{1}H NMR (CDCl3): δ 1.03(d, 3H, $^3J_{HH}$ = 6.8 Hz, CH*Me'*), 2.03(s, 3H, N*Me'*), 2.17(d, 3H, $^4J_{PH}$ = 2.8 Hz, =C*Me*), 2.20(d, 3H, $^3J_{HH}$ = 5.6 Hz, CH*Me*), 2.52(s, 3H, N*Me'*), 2.72(d, 3H, $^4J_{PH}$ = 2.0 Hz, N*Me*$_{ax}$), 2.78 (d, 3H, $^4J_{PH}$ = 2.0 Hz, ≡C*Me*), 3.29 (d, 3H, N*Me*$_{eq}$,$^4J_{PH}$ = 3.2Hz), 3.56 (q, 1H, $^3J_{HH}$ = 6.8 Hz, C*H'*Me),4.58 (dq, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.4 Hz, C*H*Me), 7.13~8.23 (m, 15H, aromatics).

***μ*-chloro{{(R_c)-1-[1-(dimethylamino)ethyl]naphthyl-*C*^{2},*N*}platinum(II){(R_c,S_p)-1-[1-(di-methylamino)ethyl]-2-[(*Z*)-1-(phenylprop-1-ynylphosphino)prop-1-en-2-yl-*C*^{1})]phenyl-*N*} chloro palladium(II)}, (R_c,S_p,R_c)-75** was crystallized from hexane–acetone as light yellow crystals: 0.14 g (19% yield); m.p. 178~180℃ (dec)； Anal. Calcd . for $C_{36}H_{41}Cl_2N_2PPdPt$: C, 47.8; H, 4.6; N, 3.1. Found: C, 45.5; H, 5.1; N, 3.1. $^{31}P\ \{^1H\}$NMR($CDCl_3$): δ –35.9 (s, $^1J_{Pt–P}$ = 3983 Hz, 1P); ^{1}H NMR (CDCl3): δ 1.33(d, 3H, $^3J_{HH}$ = 7.2 Hz, CH*Me*'), 1.59(d, 3H, $^4J_{PH}$ = 2.4 Hz, =C*Me*), 2.05(d, 3H, $^3J_{HH}$ = 3.6 Hz, CH*Me*), 2.22 (d, 3H, $^4J_{PH}$ = 6.4 Hz, ≡C*Me*), 2.59(brs,3H, NMe_{ax}), 2.73(s,3H, N*Me*'), 3.24 (s, 3H, N*Me*'), 3.36(d, 3H, $^4J_{PH}$ = 3.6Hz, NMe_{eq}), 4.25 (q, 1H, $^3J_{HH}$ = 6.8 Hz,C*H*'Me), 4.50 (dq, 1H, $^3J_{HH}$ = 6.8 Hz, $^4J_{PH}$ = 6.4 Hz, C*H*Me), 7.32~8.19 (m, 15H, aromatics).

(R_c,R_p,R_c)-76 was crystallized from diethyl ether–acetonitrile as light yellow crystals. m.p. 208–210℃ (dec)； $[\alpha]_D$ +67°(c 0.3, CH_2Cl_2). Anal. Calcd. for $C_{36}H_{42}ClN_2OPPdPt$: C, 48.7; H, 4.8; N, 3.2. Found: C, 48.4; H, 4.8; N, 3.6. $^{31}P\ \{^1H\}$NMR($CDCl_3$): δ –2.3 (s, $^1J_{Pt–P}$ = 3872 Hz, 1P); ^{1}H NMR (CDCl3): δ 1.17(d, 3H, $^3J_{HH}$ = 7.2 Hz, CH*Me*'), 1.92(d, 3H, $^3J_{HH}$ = 1.6 Hz, CH*Me*), 1.95(d, 3H, $^4J_{PH}$ = 6.8 Hz, =C*Me*), 2.27(d, 3H, $^4J_{PH}$ = 2.0 Hz, O=C*Me*), 2.49(s, 3H, N*Me*'), 2.56(s, 1H, PC*H*), 3.06(d, 3H, $^4J_{PH}$ = 1.6 Hz, NMe_{ax}), 3.09(s, 3H, N*Me*'), 3.31 (d, 3H, NMe_{eq}, $^4J_{PH}$ = 2.8 Hz), 4.05 (q, 1H, $^3J_{HH}$ = 6.4 Hz, C*H*'Me), 4.84 (dq, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.4 Hz, C*H*Me), 7.12~8.01 (m, 15H, aromatics).

Synthesis of (R_c,R_p,S_c)-77, (R_c,S_c,R_p,S_c)-79

Complex (R_c)-**73** (0.50 g, 0.81 mmol) was dissolved in dichloromethane (100 mL). This solution then was treated with phenylamine palladium (II) dimer (S_c)-**62** (0.24 g, 0.41mmol). The mixture was stirred at room temperature for 24 hours. Upon completion, the solvent was removed to give dark brown residue which was purified by column chromatography (with an eluting gradient starting from hexane: acetone 6:1) give the products as light yellow solids.

***μ*-chloro{{(R_c)-1-[1-(dimethylamino)ethyl]naphthyl-*C*^{2},*N*}platinum(II){(S_c,R_p)-1-[1-(dimethylamino)ethyl]-2-[(*Z*)-1-(phenylprop-1-ynylphosphino)prop-1-en-2-yl-*C*^{1})]phenyl-*N*} chloro palladium(II)}, (R_c,R_p,S_c)-77** was crystallized from hexane – acetone as light yellow crystals: 0.23 g (31% yield); m.p. 197–199℃ (dec); $[\alpha]_D$ –77°(*c* 0.3, CH_2Cl_2). Anal. Calcd. for $C_{36}H_{41}Cl_2N_2PPdPt$: C,47.7; H, 4.6; N, 3.1. Found: C, 47.5; H, 5.1; N, 3.1. ^{31}P {^1H}NMR($CDCl_3$): δ –9.3 (s, $^1J_{Pt–P}$ = 4207 Hz, 1P)

^1H NMR (CDCl3): δ 1.19(d, 3H, $^3J_{HH}$ = 6.8 Hz, CH*Me'*), 1.81(s, 3H, N*Me'*),1.88(d, 3H, $^3J_{HH}$ = 6.0 Hz, CH*Me*), 1.97(d, 3H, $^4J_{PH}$ =3.6 Hz, =C*Me*), 2.45(s, 3H, N*Me'*), 2.63(d, 3H, J_{PH} = 1.6 Hz, ≡C*Me*), , 2.84(s, 3H, NMe_{ax},$^4J_{PH}$ = 2.0 Hz), 3.13 ((d, 3H, NMe_{eq},$^4J_{PH}$ = 2.8 Hz), 4.09 (q, 1H, $^3J_{HH}$ = 6.8 Hz, C*H'*Me), 4.53 (qn, 1H, $^3J_{HH}$ = 6.4Hz, $^4J_{PH}$ = 6.8 Hz, C*H*Me), 7.32~8.19 (m, 15H, aromatics).

(R_c,S_c,R_p,S_c)-79 was crystallized from hexane–acetone as light yellow crystals: m.p. 180–182℃ (dec); $[\alpha]_D$ –26°(c 0.2, CH_2Cl_2). Anal. Calcd. for $C_{36}H_{42}ClN_2OPPdPt$: C, 48.7; H, 4.8; N, 3.2. Found: C, 48.9; H, 4.8; N, 3.2. ^{31}P {^1H}NMR($CDCl_3$): δ –7.2 (s, $^1J_{Pt–P}$ = 3887 Hz, 1P); ^1H NMR (CDCl3): δ 1.25(d, 3H, $^3J_{HH}$ = 6.8 Hz, CH*Me'*), 1.88(d, 3H, $^3J_{HH}$ = 6.4 Hz, CH*Me*), 1.95(d, 3H, $^4J_{PH}$ =1.6 Hz, =C*Me*), 2.32(d, 3H, $^4J_{PH}$ =1.6 Hz, O=C*Me*), 2.53(s, 3H, N*Me'*), 2.83(s, 1H, PC*H*), 3.02(d, 3H, $^4J_{PH}$ = 1.6Hz, NMe_{ax}), 3.08(s, 3H, N*Me'*), 3.27 (d, 3H, NMe_{eq}, $^4J_{PH}$ = 2.8 Hz), 4.31 (q, 1H, $^3J_{HH}$ =7.2 Hz, C*H'*Me), 4.79 (dq, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.8 Hz, C*H*Me), 7.19~7.78 (m, 15H, aromatics).

Synthesis of *μ*-chloro{{(R_c)-1-[1-(dimethylamino)ethyl]naphthyl-*C*^{2},*N*} platinum(II){[(S_p)-1-(dimethylamino)methyl-2-[(*Z*)-1-(phenylprop-1-ynylphosphino)prop

-1-en-2-yl-*C*^{1})]phenyl-*N*}chloro palladium(II)}, (*R*$_c$,*S*$_p$)-81

Complex (*R*$_c$)-**73** (0.60 g, 0.98 mmol) was dissolved in dichloromethane (100 mL). This solution then was treated with non–chiral dimeric cyclopaladated phenylamine complex **63** (0.27 g, 0.49mmol). The mixture was stirred at room temperature for 24 hours. Upon completion, the solvent was removed to give dark brown residue which was purified by column chromatography (with an eluting gradient starting from hexane: acetone 6:1) give the products as light yellow solids. Crystallization from acetone–hexane gave (*R*$_c$,*S*$_p$)-**81** as light yellow crystals: 0.19 g (22% yield); m.p. 197–198℃（dec）; $[\alpha]_D$ +162°(*c* 0.1, CH_2Cl_2). Anal. Calcd . for $C_{35}H_{39}Cl_2N_2PPdPt$: C, 47.2; H, 4.4; N, 3.1. Found: C, 47.2; H, 4.1; N, 3.3. $^{31}P\{^1H\}$NMR($CDCl_3$): δ –37.9 (s, $^1J_{Pt-P}$ = 4063 Hz, 1P); ^{1}H NMR (CDCl3): δ 1.59(d, 3H, $^4J_{PH}$ = 6.4 Hz, =C*Me*), 1.68(d, 3H, $^3J_{HH}$ = 3.2 Hz, CH*Me*), 2.29(d, 3H, $^4J_{PH}$ = 6.4 Hz, ≡C*Me*), 2.72(d, 3H, $^4J_{PH}$ = 2.0 Hz, N*Me*$_{ax}$), 2.81(s, 3H, N*Me'*), 2.92(d,1H, $^2J_{HH}$ = 10.8 Hz, C*H*H), 3.25(s, 3H, N*Me'*), 3.30(d, 3H, N*Me*$_{eq}$,$^4J_{PH}$ = 3.6 Hz), 4.0(d,1H, $^2J_{HH}$ = 10.8 Hz, C*H*H), 4.58 (dq 2H, $^3J_{HH}$ = $^4J_{PH}$ = 6.4 Hz, C*H*Me), 7.04~8.23 (m, 15H, aromatics).

Synthesis of (*R*$_c$,*R*$_p$,*R*$_c$)-83 and (*R*$_c$,*S*$_p$,*R*$_c$)-84,

Complex (*R*$_c$)-**82** (0.50 g, 0.89 mmol) was dissolved in dichloromethane (100 mL). This solution then was treated with half – mole equivalent of phenylamine palladium(II) dimer (*R*$_c$) **-61** (0.26 g, 0.44mmol). The mixture was stirred at room temperature for 20 hours. Upon completion, the solvent was removed to give dark brown residue which was purified by column chromatography (with an eluting gradient starting from hexane: acetone 5:1) give the products as light yellow solids.

μ-chloro {{(R_c)-1-[1-(dimethylamino)ethyl]phenyl-C^2,N} platinum(II) {(R_c,R_p)-1-[1-(dimethylamino)ethyl]-2-[(Z)-1-(phenylprop-1-ynylphosphino)prop-1-en-2-yl-C^1)]phenyl-N}chloro palladium(II)}, (R_c,R_p,R_c)-83 was crystallized from dichloromethane –hexane as light yellow crystals: 0.22 g (30% yield); m.p. 211–212℃（dec）; [α]$_D$ +68° (c 0.2, CH_2Cl_2). Anal. Calcd. for $C_{32}H_{39}Cl_2N_2PPdPt$: C,44.9; H, 4.6; N, 3.3. Found: C, 43.6; H, 4.4; N, 3.0. ^{31}P {^{1}H}NMR($CDCl_3$): δ –24.9 (s, $^1J_{Pt–P}$ = 4166 Hz, 1P); ^{1}H NMR (CDCl3): δ 1.10(d, 3H, $^3J_{HH}$ = 7.0 Hz, CH*Me'*), 1.46(d, 3H, $^3J_{HH}$ = 6.5 Hz, CH*Me*), 1.56 (brs, 3H, =C*Me*), 1.83(brs, 3H, ≡C*Me*), 1.99 (s, 3H, N*Me'*), 2.53(s, 3H, N*Me'*), 2.68(brs,3H, N*Me*$_{ax}$), 3.34 (brs, 3H, N*Me*$_{eq}$), 3.87 (dq, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.49 Hz , C*H*Me), 4.42 (q, 1H, $^3J_{HH}$ = 6.7 Hz, C*H'*Me), 6.45~8.10 (m, 13H, aromatics).

μ-chloro{{(R_c)-1-[1-(dimethylamino)ethyl]phenyl-C^2,N}platinum(II){(R_c,S_p)-1-[1–(dimethylamino)ethyl]-2-[(Z)-1-(phenylprop-1-ynylphosphino)prop-1-en-2-yl-C^1)]phenyl-N}chloro palladium(II)}, (R_c,S_p,R_c)-84 was crystallized from dichloromethane –hexane as light yellow crystals: 0.28 g (23% yield); m.p. 210–212℃（dec）; [α]$_D$ +62.0° (c 0.5, CH_2Cl_2). Anal. Calcd. for $C_{32}H_{39}Cl_2N_2PPdPt$: C,44.9; H, 4.6; N, 3.3. Found: C, 44.6; H, 4.6; N, 3.3. ^{31}P {^{1}H}NMR($CDCl_3$): δ –35.5 (s, $^1J_{Pt–P}$ = 4016 Hz, 1P); ^{1}H NMR (CDCl3): δ 1.35(d, 3H, $^3J_{HH}$ = 6.9 Hz, CH*Me'*), 1.59(d, 3H, $^4J_{PH}$ = 1.4 Hz, =C*Me*), 2.05(d, 3H, $^3J_{HH}$ = 6.5 Hz, CH*Me*), 2.11 (d, 3H, $^4J_{PH}$ = 3.7 Hz, ≡C*Me*), 2.61(brs,3H, N*Me*$_{ax}$), 2.73(s, 3H, N*Me'*),3.20 (d, 3H, N*Me*$_{eq}$,$^4J_{PH}$ = 3.3 Hz), 3.27(s, 3H, N*Me'*), 3.72 (dq, 1H, $^3J_{HH}$ = 6.0 Hz, $^4J_{PH}$ = 6.4 Hz , C*H*Me), 4.27 (q, 1H, $^3J_{HH}$ = 6.5 Hz, C*H'*Me), 7.32~8.19 (m, 13H, aromatics).

Synthesis of μ-chloro {{(R_c)-1-[1-(dimethylamino)ethyl]phenyl-C^2,N} platinum(II)

{(S_c,S_p)-1-[1-(dimethylamino)ethyl]-2-[(*Z*)-1-(phenylprop-1-ynylphosphino)prop-1-en-2-yl -C^1)]phenyl-*N*}chloro palladium(II)}, (R_c,R_p,S_c)-85

Complex (R_c)-**82** (0.50 g, 0.89 mmol) was dissolved in dichloromethane (100 mL). This solution then was treated with half – mole equivalent of phenylamine palladium (II) dimer (S_c)-**62** (0.26 g, 0.44mmol). The mixture was stirred at room temperature for 24 hours. Upon completion, the solvent was removed to give dark brown residue which was purified by column chromatography (with an eluting gradient starting from hexane: acetone 7:1) give the products as light yellow solids. Crystallization from acetone–hexane gave (R_c,R_p,S_c)-**85** as light yellow crystals: 0.28 g (37.1% yield); m.p. 213~215℃（dec）; $[\alpha]_D$–74° (*c* 0.2, CH_2Cl_2). Anal. Calcd. for $C_{32}H_{39}Cl_2N_2PPdPt$: C, 45.0; H, 4.6; N, 3.3. Found: C, 45.2; H, 5.5; N, 3.3. $^{31}P\{^1H\}$NMR($CDCl_3$): δ –15.6 (s, $^1J_{Pt–P}$ = 4215 Hz, 1P); ^1H NMR (CDCl3): δ 1.16(d, 3H, $^3J_{HH}$ = 6.8 Hz, CH*Me′*), 1.68(d, 3H, $^4J_{PH}$ =6.4 Hz, =C*Me*), 1.84(s, 3H, N*Me′*), 2.03(d, 3H, $^3J_{HH}$ = 3.2 Hz, CH*Me*), 2.45(s, 3H, N*Me′*), 2.66 (d, 3H, $^4J_{PH}$ = 2.0 Hz, ≡C*Me*), 2.90(d, 3H, $^4J_{PH}$ = 2.8 Hz, NMe_{ax}), 2.92 (d, 3H, NMe_{eq},$^4J_{PH}$ = 2.4 Hz), 3.90 (dq, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.4 Hz, C*H*Me), 3.96 (q, 1H, $^3J_{HH}$ = 7.2 Hz, C*H′*Me), 6.69~8.64 (m, 13H, aromatics).

Synthesis of (R_c,R_p,S_c)-87 and (R_c,S_c,R_p,S_c)-88,

Complex (S_c)-**72** (0.28 g, 0.47mmol) was added to the solution of complex (S_c)-**62** (0.50 g, 0.95 mmol) in dichloromethane (100 mL). The mixture was stirred at room temperature for 3 days. Upon completion, the solvent was removed to give dark brown residue which was purified by column chromatography (hexane: acetone 5:1) give the products as yellow solids.

***μ*-chloro{{(R_c)-1-[1-(dimethylamino)ethyl]naphthyl-C^2,*N*}{(S_c,R_p)-1-[1-(dimethylamino)**

ethyl]-2-[(*Z*)-1-(phenylprop-1-ynylphosphino)prop-1-en-2-yl-*C*^{1})]phenyl-*N*}chloro dipalladium(II)}, (*R*$_c$,*R*$_p$,*S*$_c$)-87, was crystallized from hexane–acetone as yellow crystals: 0.22 g (28% yield); m.p. 198–200 ℃（dec）; [α]$_D$ –61°(*c* 0.29, CH_2Cl_2). Anal. Calcd. for $C_{36}H_{41}Cl_2N_2PPd_2$: C, 52.9; H, 5.1; N, 3.4. Found: C, 52.9; H, 5.5; N, 3.4. ^{31}P {^{1}H}NMR($CDCl_3$): δ 8.7 (s); ^{1}H NMR (CDCl3): δ 1.22(d, 3H, $^3J_{HH}$ = 7.2 Hz, CH*Me*′), 1.58(d, 3H, $^4J_{PH}$ = 2.0 Hz, =C*Me*), 1.90(brs, 3H, ≡C*Me*), 1.97(d, 3H, $^3J_{HH}$ = 2.0 Hz, CH*Me*), 2.47 (s, 3H, N*Me*′), 2.59(d, 3H, $^4J_{PH}$ = 1.6 Hz, N*Me*$_{ax}$), 2.76 (s, 3H, N*Me*′), 2.90 (d, 3H, $^4J_{PH}$ = 2.8 Hz, N*Me*$_{eq}$),4.1 (q, 1H, $^3J_{HH}$ = 20.5 Hz, C*H*′Me), 4.3 (dq, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 12.8 Hz,C*H*Me), 7.24~8.84 (m, 15H, aromatics)

(*R*$_c$,*S*$_c$,*R*$_p$,*S*$_c$)-88, was crystallized from hexane–acetone as yellow crystals: m.p. 202–204℃（dec）; [α]$_D$ +50°(*c* 0.2, CH_2Cl_2). Anal. Calcd. for $C_{36}H_{42}ClN_2OPPd_2$: C, 54.2; H, 5.3; N, 3.5. Found: C, 52.7; H, 5.1; N, 3.4.

^{31}P {^{1}H}NMR($CDCl_3$): δ 10.9; ^{1}H NMR (CDCl3): δ 1.26(d, 3H, $^3J_{HH}$ = 6.8 Hz, CH*Me*′), 1.85(d, 3H, $^3J_{HH}$ = 1.6 Hz, CH*Me*), 1.99(d, 3H, $^4J_{PH}$ =6.4 Hz, =C*Me*), 2.27(d, 3H, $^4J_{PH}$ =1.2 Hz, O=C*Me*), 2.54(s, 3H, N*Me*′), 2.74(d, 1H,$^2J_{PH}$ =4.0 Hz, PC*H*), 2.97(brs, 3H, N*Me*$_{ax}$), 3.03(d, 3H, N*Me*$_{eq}$, $^4J_{PH}$ =3.2 Hz), 3.07(s, 3H, N*Me*′), 4.35 (q, 1H, $^3J_{HH}$ =7.2 Hz, C*H*′Me), 4.79 (dq, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 5.6 Hz, C*H*Me), 7.21~7.80 (m, 15H, aromatics).

Synthesis of *μ*-chloro{{(*R*$_c$)-1-[1-(dimethylamino)ethyl]naphthyl-*C*^{2},*N*}{(*R*$_c$, *R*$_p$)-1-[1-(dimethylamino)ethyl]-2-[(*Z*)-1-(phenylprop-1-ynylphosphino)prop-1-en-2-yl-*C*^{1})]phenyl-*N*}chloro dipalladium(II)}, (*R*$_c$,*R*$_p$,*R*$_c$)-89

Complex (*R*$_c$)-**72** (0.28 g, 0.47mmol) was added to the solution of complex (*R*$_c$)-**61** (0.50

g, 0.95 mmol) in dichloromethane (100 mL). The mixture was stirred at room temperature for 2 days. Upon completion, the solvent was removed to give dark brown residue which was purified by column chromatography (with an eluting gradient starting from hexane: acetone 3:2) give the products as yellow solids. Crystallization from acetone–hexane gave (R_c,R_p,R_c)-**27** as yellow crystals: 0.17 g (22% yield); m.p. 203–205℃（dec）; $[\alpha]_D$ +163°(*c* 0.3, CH_2Cl_2). Anal. Calcd. for $C_{36}H_{41}Cl_2N_2PPd_2$: C, 53.0; H, 5.0; N, 3.4. Found: C, 51.2; H, 4.6; N, 3.1. $^{31}P\{^1H\}$NMR($CDCl_3$): δ–16.9; ^1H NMR (CDCl3): δ 1.33(d, 3H, $^3J_{HH}$ = 7.2 Hz, CH*Me*'), 1.64(d, 3H, $^4J_{PH}$ = 2.9 Hz, =C*Me*), 2.02(d, 3H, $^3J_{HH}$ = 3.6 Hz, CH*Me*), 2.31 (d, 3H, $^4J_{PH}$ = 6.4 Hz, ≡C*Me*), 2.54(d, 3H, $^4J_{PH}$ =1.2 Hz, NMe_{ax}), 2.76(s, 3H, N*Me*'), 3.13(d, 3H, NMe_{eq},$^4J_{PH}$ = 4.4 Hz), 3.23(s, 3H, N*Me*'), 4.23~ 4.32 (dq and q, 2H, $^3J_{HH}$ = 8.0 Hz, C*H*Me and C*H*'Me), 7.29~8.23 (m, 15H, aromatics).

Synthesis of *μ*-chloro{{(R_c)-1-[1-(dimethylamino)ethyl]naphthyl-C^2,*N*}{(R_p)-[1-(dimethylamino)methyl-2-[(*Z*)-1-(phenylprop-1-ynylphosphino)prop-1-en-2-yl-C^1)] phenyl–*N*}chloro dipalladium(II)}, (R_c,R_p)-91,

Complex **63** (0.08 g, 0.14mmol) was added to the solution of complex (R_c)-**72** (0.15 g, 0.28 mmol) in chloroform (50 mL). The mixture was stirred at room temperature for 1 day. Upon completion, the solvent was removed to give dark brown residue which was purified by column chromatography (with an eluting gradient starting from hexane: acetone 3:2) give the products as yellow solids. Crystallization from dichloromethane – hexane gave (R_c,R_p)-**29** as yellow crystals: 0.05 g (20% yield); m.p. 201–203℃（dec）; $[\alpha]_D$ +126°(*c* 0.2, CH_2Cl_2). $^{31}P\{^1H\}$NMR($CDCl_3$): δ –16.4; ^1H NMR (CDCl3): δ 1.59(d, 3H, $^4J_{PH}$ = 6.4 Hz, =C*Me*), 2.01(d, 3H,

$^3J_{HH}$ = 2.8 Hz, CH*Me*), 2.32(d, 3H, $^4J_{PH}$ = 6.4 Hz, ≡C*Me*), 2.55(s, 3H, N*Me'*), 2.78(d,1H, $^2J_{HH}$ = 10.8 Hz, C*H*H), 2.83(s, 3H, N*Me'*), 3.15(d, 6H, NMe_{ax} and NMe_{eq}), 3.88(d,1H, $^2J_{HH}$ = 10.8 Hz, C*H*H), 4.27 (dq 2H, $^3J_{HH}$ = $^4J_{PH}$ = 5.6 Hz, C*H*Me), 7.14~8.19 (m, 15H, aromatics)

Synthesis of *μ*-chloro {{(*R*$_c$)-1-[1-(dimethylamino)ethyl]naphthyl-*C*^{2},*N*} {(*R*$_{c,}$ *R*$_p$)-1-[1-(dimethylamino)ethyl]-2-[(*Z*)-1-phenyl(phenylethynyl)phosphino-2-phenylethen-2-yl-*C*^{1})] naphthyl-*N*}chloro dipalladium(II)}, (*R*$_c$,*R*$_p$,*R*$_c$)-95

Complex (*R*$_c$)-**59** (0.19 g, 0.28mmol) was added to the solution of complex complex (*R*$_c$)-**93** (0.30 g, 0.57 mmol) in 1, 2–dichloroethane (50 mL). The reaction mixture was refluxed for 10 hours. Upon completion, the solvent was removed to give dark brown residue which was purified by column chromatography (hexane: acetone 3:2) give the products as yellow solids. Crystallization from dichloromethane–hexane gave (*R*$_{c,}$*R*$_{p,}$*R*$_c$)–**95** as yellow crystals: 0.11 g (23% yield); m.p. 198–200℃（dec）; [α]$_D$ +209°(*c* 0.4, CH_2Cl_2). Anal. Calcd. for $C_{50}H_{47}Cl_2N_2PPd_2$: C, 62.6; H, 4.9; N, 2.9. Found: C, 59.9; H, 4.6; N, 3.3. ^{31}P {^{1}H}NMR($CDCl_3$): δ 16.5 (s). ^{1}H NMR (CDCl3): δ 1.73(d, 3H, $^3J_{HH}$ = 6.8 Hz, CH*Me'*), 2.03 (s, 3H, N*Me'*), 2.16(d, 3H, $^3J_{HH}$ = 6.0 Hz, CH*Me*), 2.69 (s, 3H, N*Me'*), 2.81 (d, 3H, $^4J_{PH}$ = 1.6 Hz, NMe_{ax}), 3.07(d, 3H, $^4J_{PH}$ = 2.8 Hz, NMe_{eq}), 4.39 (dq, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.4 Hz, C*H*Me),4.48 (q, 1H, $^3J_{HH}$ = 7.2 Hz,C*H'*Me), 6.87~8.93 (m, 25H, aromatics).

Synthesis of *μ*-chloro {{(*R*$_c$)-1-[1-(dimethylamino)ethyl]naphthyl–*C*^{2},*N*} platinum(II){(*R*$_c$,*R*$_p$)-1-[1-(dimethylamino)ethyl-2-[(*Z*)-1-phenyl(phenylethynyl)phosphino -2-phenylethen-2-yl-*C*^{1})] naphthyl-*N*} chloro dipalladium(II)}, (*R*$_c$,*R*$_p$,*R*$_c$)-96

Complex (*R*$_c$)-**59** (0.14 g, 0.20mmol) was added to the solution of complex complex (*R*$_c$)-

94 (0.30 g, 0.41 mmol) in 1, 2–dichloroethane (50 mL). The reaction mixture was refluxed for 24 hours. Upon completion, the solvent was removed to give dark brown residue which was purified by column chromatography (with an eluting gradient starting from hexane: acetone 3:2) give the products as yellow solids. Crystallization from dichloromethane – hexane gave (R_c,R_p,R_c)-**96** as yellow crystals: 0.088 g (20.1% yield); m.p. 198–200℃（dec）; $[\alpha]_D$ +112°(c 0.5, CH_2Cl_2). Anal. Calcd. for $C_{50}H_{47}Cl_2N_2PPdPt$: C, 57.3; H, 4.5; N, 2.7. Found: C, 59.9; H, 4.6; N, 3.3. ^{31}P {^1H}NMR($CDCl_3$): δ 1.3 (s, $^1J_{Pt-P}$ = 4275 Hz, 1P); ^1H NMR (CDCl3): δ 1.72(d, 3H, $^3J_{HH}$ = 6.0 Hz, CH*Me'*), 2.01 (s, 3H, N*Me'*), 2.10(d, 3H, $^3J_{HH}$ = 6.0 Hz, CH*Me*), 2.69 (s, 3H, N*Me'*), 2.85 (d, 3H, $^4J_{PH}$ = 2.0 Hz, NMe_{ax}), 3.31(d, 3H, $^4J_{PH}$ = 3.2 Hz, NMe_{eq}), 4.51 (q, 1H, $^3J_{HH}$ = 6.8 Hz, C*H'*Me), 4.59 (dq, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.6 Hz, C*H*Me), 6.87~8.89 (m, 25H, aromatics).

Chapter 3

Insertion of Alkynylarsine Into the Pd–C bond of Cyclopalladated Complexes

3.1 Introduction:

Compared with phosphorus, arsenic is a weaker σ donor and π acceptor, therefore, arsenic will form weaker bonds with metal centers than phosphorus.[34] The field of organoarsenic chemistry is small by comparison with that of organophosphorous chemistry and the chemical reason for this is yet unclear, although the ^{31}P NMR spectroscopy is a powerful technique in the phosphorus chemistry development. However, arsenic has many advantages over phosphorus when it comes to the synthesis of organic derivatives. For instance, arsines like $AsR^1R^2R^3$ have reduced air–sensitivity, increased pyramidal stability and easier recovery from arsonium salts and metal complexes compared with their phosphine analogue.[180] Due to the toxicity of organoarsenic compounds in general, they are prime candidates for immobilization onto a polymer support so that they can be easily recovered and reused.[181]

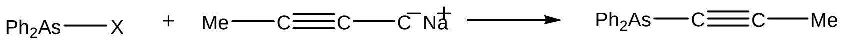
It has been known that tertiary arsines are powerful ligands for metals in a range of oxidation states a feature that makes them particularly suitable for the design of complexes for catalysis. For example, triphenylarsine has been found to be useful as a ligand for palladium in a variety of palladium catalyzed cross–coupling reactions,[182] including the Suzuki–Miyaura coupling[183,184] of boronic acids with aryl and vinyl halides.[185,186] Triphenylarsine is also useful for the generation of arsonium ylides, which are more nucleophilic than the corresponding phosphonium ylides.[187–189]

Insertion of a carbon–carbon triple bond into a transition metal–carbon bond is an important reaction of organotransition metal complexes involved in various synthetic organic reactions. Our research group has previously studied the reactivity of the alkyne moiety with phosphine ligands. It is believed that the P→M bond is responsible for the activation of the insertion process. The alkynl insertion reaction reported in this thesis is however the first attempt to study the reactivity with arsine ligands.

3.2 Results and Discussion:

3.2.1 Preparation of diphenylprop-1-ynylarsine Ligand, 97

Diphenylprop-1-ynylarsine **97** was previously synthesized by the pathway shown in Scheme 3.1.[190] However, the starting material, Ph_2AsCl cannot be purchased and is difficult to synthesize. Moreover, this chloroarsine is highly toxic, corrosive and difficult to handle as it causes skin burn on contact.[191] Therefore, this pathway was not feasible. [190]

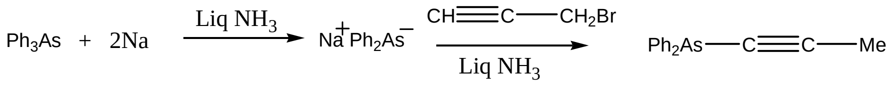


X= Cl or Br

97

Scheme 3.1

It was reported that $Ph_2P{\equiv}CMe$ had been successfully synthesized via a rearrangement mechanism (Scheme 3.2).[192] This pathway gives reasonably high yields (78%) for the phosphine and the starting materials are easily purchased. As the chemistry of phosphorus and arsenic is expected to be similar, the synthesis of diphenylprop-1-ynylarsine **97** was attempted by making modification to the literature method[192] (Scheme 3.2). In this pathway Ph_2As^- acted as the nucleophile and there are two possible reaction mechanisms proposed for this rearrangement pathway of the phosphors analog.[192] Since the chemistry of phosphorus and arsenic is expected to be similar, the mechanisms are expected to be quite similar as well.



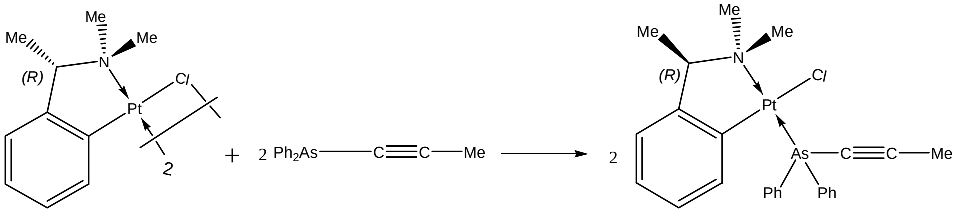
97

Scheme 3.2

After micro distillation diphenylprop-1-ynylarsine, **97**, was obtained as slightly yellowish liquid in 42% yield. The ^{1}H NMR and IR spectra of the ligand were recorded before and after it was left exposed to air for a day. The spectra remained unchanged and this indicated this arsine ligand **97** is quite air stable.

3.2.2 Synthesis of Complexes (R_c,R_c)-99 and (R_c, S_c)-100

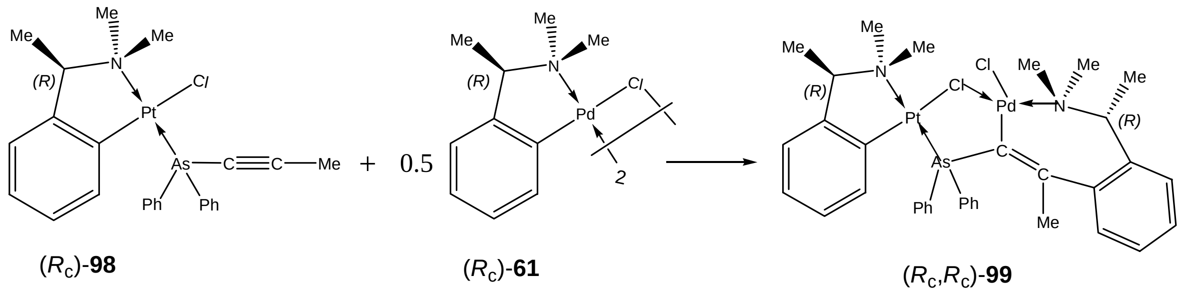
By the treatment of the diphenylprop-1-ynylarsine, **97**, with a half equivalent of the dimeric platinum(II) complex (R_c)-**64** in dichloromethane for 4 hours, the precursor complex (R_c)-**98** was obtained and isolated as a yellow solid in quantitative yield. (Scheme 3.3).



(R_c)-**64** **97** (R_c)-**98**

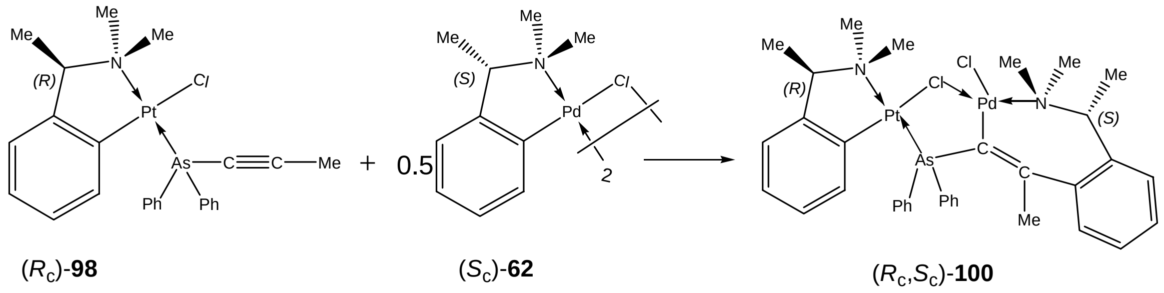
Scheme 3.3

The precursor complex (R_c)-**98** was then treated with half equivalent of phenylamine palladium (II) dimer (R_c)-**61** at room temperature in dichloromethane (Scheme 3.4). This reaction was monitored using thin layer chromatography (TLC) and was found to be complete in 4 days. The crude reaction mixture was purified by column chromatography and subsequently crystallized from dichloromethane–hexane to give complex (R_c,R_c)-**99** as yellowish orange crystals in 67% yield.



Scheme 3.4

A similar insertion reaction was performed between complex (R_c)-**98** and half equivalent of the enantiomeric benzylamine palladium(II) dimer (S_c)-**62** at room temperature in dichloromethane (Scheme 3.5). The formation of the dimeric product (R_c,S_c)-**100** was found to be slower than its (R_c,R_c)-**99** diastereomer. Using thin layer chromatography (TLC) this reaction was found to be complete in 5 days. After purifying by column chromatography yellowish orange solids were obtained. Crystallization from dichloromethane–hexane gave (R_c,S_c)-**100** as yellowish orange crystals in 88% yield.



Scheme 3.5

3.2.2.1 X-ray Structural Analysis of Complexes (*R*$_c$,*R*$_c$)-99 and (*R*$_c$,*S*$_c$)-100

The X-ray structural analysis of the complex (*R*$_c$,*R*$_c$)–**99** and (*R*$_c$,*S*$_c$)–**100** confirmed that the desired insertion diasteremeric products have been formed (Figure 3.1 and 3.2). In both complexes, the arsenic donor atoms were coordinated regiospecifically in the position *trans* to the benzylamine–*N* donor atom. Moreover, as expected, the absolute configuration of the stereocenters at C (7) and C (17) remained unchanged for the two complexes.

The molecular structure of complex (*R*$_c$,*R*$_c$)-**99** showed that the carbon–carbon triple bonds of alkynylarsine, bond C(11)–C(12), had inserted into the Pd(1)–C(23) bond of benzyl amine dimer (*R*$_c$)-**5**. As the result of this insertion, two new bonds, C(22)–C(20) and Pd(1)–C(21) were generated, while the bond C(11)–C(12) was changed from C≡C to C=C . The platinum and palladium metal centers are connected by Cl to give a 5–membered bimetallic heterocycle. Complex (*R*$_c$,*S*$_c$)-**100** has the same molecular connectivity with complex (*R*$_c$,*R*$_c$)-**99**, and only differ in the bond lengths and angles.

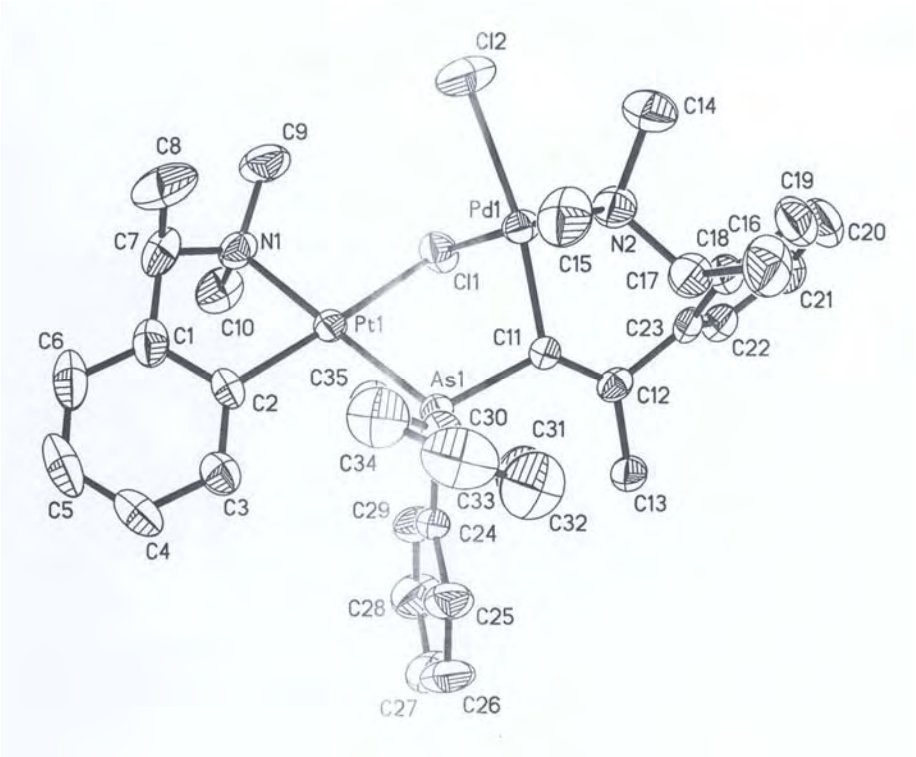


Figure 3.1 Molecular Structure of Complex ($R_{c,}R_{c}$)-**99**

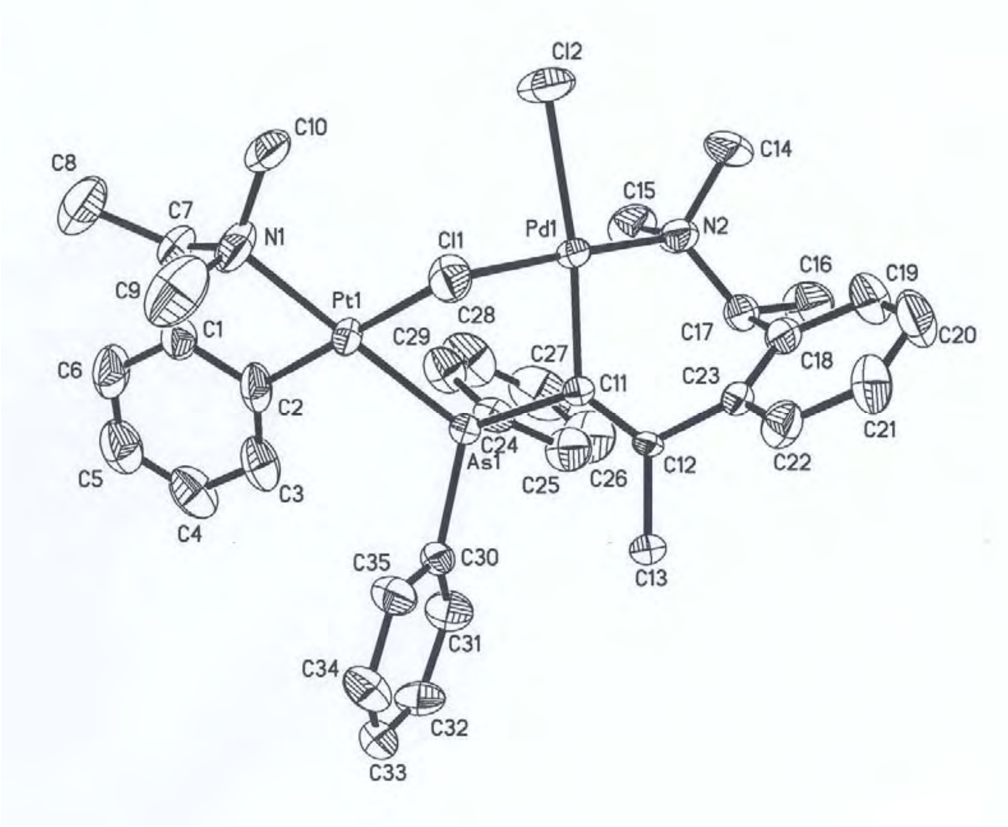


Figure 3.2 Molecular Structure of Complex ($R_{c,}$ S_{c})–**100**

The geometry at platinum and palladium centers is slightly distorted square planar for complex (R_c,R_c)-**99** and (R_c,S_c)-**100**. The bond angles at Pt(1) are in the range of 82.1(2)–98.3(2)° and 172.7(2)–179.5(2)° for complex (R_c,R_c)-**99**; 81.5(3)–97.1(2)° and 172.3(2)–177.4(2)° for complex (R_c, S_c)-**100**. While the bond angles at Pd(1) ranges from 83.1(1)–95.8(1)° and 169.7(1)–173.5(1)° for complex (R_c,R_c)-**99**; 84.7(2)–95.5(2)° and 171.1(1)–178.2(2)° for complex (R_c,S_c)-**100**. The C(11)–C(12) bond distances in (R_c,R_c)-**99** [1.324(5)] and in complex (R_c,S_c)-**100** [1.338(9)] clearly indicate that they are C=C bonds. Table 3.1 shows selected bond distances and angles of complex (R_c,R_c)-**99** and (R_c, S_c)-**100**.

Table 3.1 Selected bond distances (Å) and angles (°) of complex (R_c,R_c)-**99** and (R_c, S_c)-**100**

	Complex (R_c,R_c)-99	**Complex (R_c, S_c)-100**
Pt(1)–C(2)	1.987(4)	2.026(7)
Pt(1)–N(1)	2.122(3)	2.109(6)
Pt(1)–As(1)	2.3342(4)	2.332(1)
Pt(1)–Cl(1)	2.407(1)	2.416(2)
Pd(1)–C(11)	1.994(3)	1.998(5)
Pd(1)–N(2)	2.123(4)	2.130(6)
Pd(1)–Cl(1)	2.348(2)	2.328(2)
Pd(1)–Cl(2)	2.433(2)	2.417(2)
C(11)–C(12)	1.324(5)	1.338(9)
C(2)–Pt(1)–N(1)	82.1(2)	81.5(3)
C(2)–Pt(1)–As(1)	98.3(2)	97.1(2)

N(1)–Pt(1)–As(1)	179.5 (2)	177.4(2)
C(2)–Pt(1)–Cl(1)	172.7(2)	172.3(2)
N(1)–Pt(1)–Cl(1)	92.8 (2)	95.3(2)
As(1)–Pt(1)–Cl(1)	86.7(1)	86.3(1)
C(11)–Pd(1)–N(2)	93.2(2)	93.4(2)
C(11)–Pd(1)–Cl(1)	83.1(2)	84.7(2)
N(2)–Pd(1)–Cl(1)	173.5(2)	178.2(2)
C(11)–Pd(1)–Cl(2)	169.7(2)	171.1(2)
N(2)–Pd(1)–Cl(2)	95.8(2)	95.5(2)
Cl(1)–Pd(1)–Cl(2)	88.3(1)	86.4(1)
Pd(1)–Cl(1)–Pt(1)	92.8(1)	96.3(1)

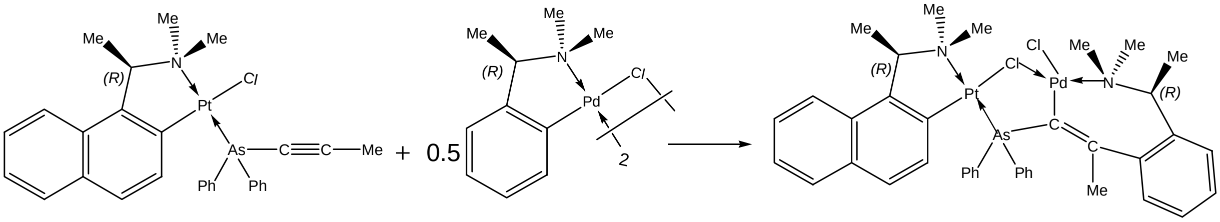
3.2.3 Insertion Reactions Promoted by Different Organometallic Templates

In order to check the reactivity of palladium–carbon bond of cyclopalladated benzylamine dimer toward the insertion reaction of carbon–carbon triple bond when arsine ligand, diphenylprop-1-ynylarsine **97** was coordinated to different organometallic templates, several insertion reactions were investigated.

3.2.3.1 Synthesis of Complexes ((R_c,R_c))-102 and ((R_c,S_c))-103

Complex (R_c)-**101** was prepared quantitatively as a yellow solid by treatment of the diphenylprop-1-ynylarsine **97** with half equivalent of the dimeric naphthylamine platinum(II) complex (R_c)-**60** in dichloromethane for 4 hours.

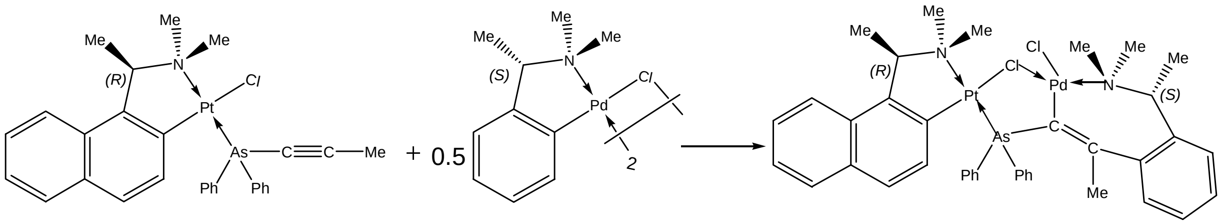
Insertion reaction between naphthylamine platinum(II) complex (R_c)-**101** and half equivalent of benzylamine palladium(II) dimer (R_c)-**61** was carried out at room temperature using dichloromethane as solvent (Scheme 3.6). This reaction was monitored by thin layer chromatography (TLC) and was found to be complete in 5 days. The crude reaction mixture was purified by column chromatography and subsequently crystallized from dichloromethane–hexane to give complex (R_c,R_c)-**102** as yellowish orange crystals in 86% yield.



(R_c)-**101**　(R_c)-**61**　(R_c,R_c)-**102**

Scheme 3.6

A similar insertion reaction was performed between naphthylamine platinum(II) complex (R_c)-**101** and half equivalent of benzylamine palladium(II) dimer (S_c)-**62** at room temperature using dichloromethane as solvent (Scheme 3.7). This reaction was monitored by running thin layer chromatography (TLC) and was found to be complete in 6 days. The crude reaction mixture was then purified by column chromatography and yellow solids were thus obtained. Unfortunately, single crystals of complex (R_c,S_c)-**103** suitable for X-ray structural analysis could not be produced, despite many attempts to crystallize it using a wide variety of different solvent systems.



(R_c)-**101**

(S_c)-**62**

(R_c,S_c)-**103**

Scheme 3.7

3.2.3.1.1 X-ray Structural Analysis of Complex (*R*c,*R*c)-102

The X-ray structural analysis of the complex (R_c,R_c)-**102** indicated that the expected insertion product had been formed (Figure 3.3). The arsenic donor atom was coordinated regiospecifically in the position *trans* to the benzylamine–*N* donor atom. Moreover, as expected, the absolute configuration of the stereocenters at C (11) and C (21) remained unchanged.

The molecular structure of complex (R_c,R_c)–**102** showed that carbon–carbon triple bonds of alkynylarsine, bond C(15)–C(16), has inserted into the Pd(1)–C(27) bond of benzyl amine dimer (S_c)-**62**. As the result of this insertion, two new bonds, C(16)–C(27) and Pd(1)–C(15) were generated, while bond C(15)–C(16) was changed from C≡C to C=C . The platinum and palladium metal centers are connected by Cl to give a 5–membered bimetallic heterocycle.

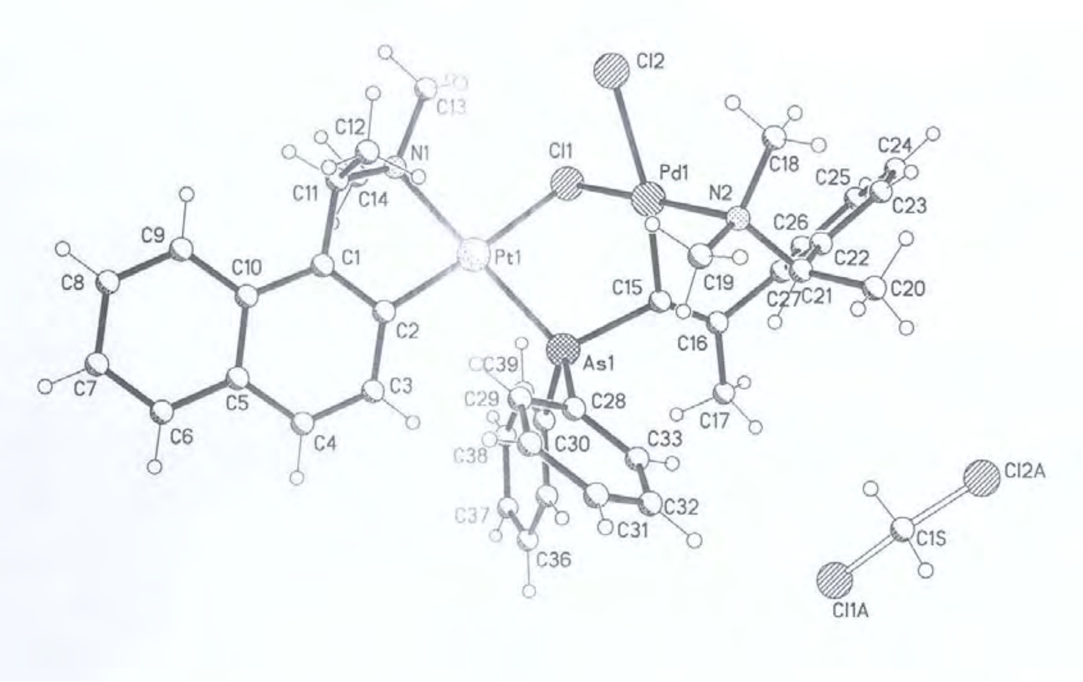


Figure 3.3 Molecular Structure of Complex (R_c,R_c)-**102**

The geometry at the platinum and palladium centers is slightly distorted square planar for complex (R_c,R_c)-**102**. The bond angles at Pt(1) are in the range of 82.4(2)–98.8(2)˚ and 171.8(2)–178.0(2)˚, while the bond angles at Pd(1) ranges from 83.5(2)–94.8(2)˚ and 170.7(2)– 173.2(2)˚. The C(15)–C(16) bond distance in (R_c,R_c)-**102** [1.339(9)] clearly indicates that it is a C=C bonds. Table 3.2 shows selected bond distances and angles of complex (R_c,R_c)–**102**.

Table 3.2 Selected bond distances (Å) and angles (°) of complex (R_c,R_c)-**102**

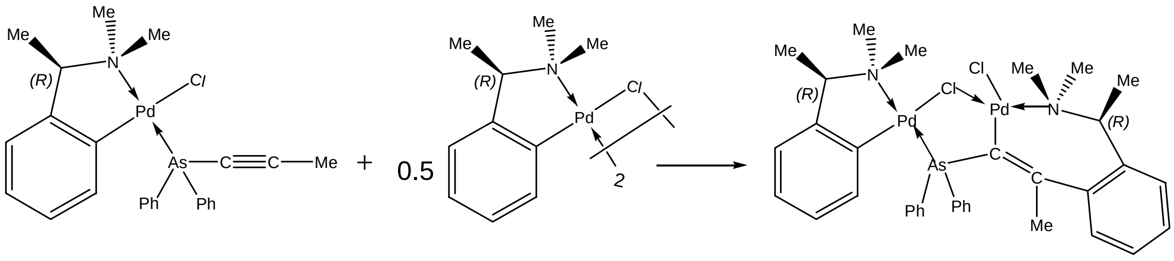
Pt(1)–C(2)	1.987(6)	N(1)–Pt(1)–As(1)	178.0(2)
Pt(1)–N(1)	2.105(6)	C(2)–Pt(1)–Cl(1)	171.8(2)
Pt(1)–As(1)	2.339(1)	N(1)–Pt(1)–Cl(1)	93.6(2)
Pt(1)–Cl(1)	2.405(2)	As(1)–Pt(1)–Cl(1)	86.4(1)
Pd(1)–C(15)	1.977(6)	C(15)–Pd(1)–N(2)	92.5(2)

Pd(1)–N(2)	2.123(6)	C(15)–Pd(1)–Cl(1)	83.5(2)
Pd(1)–Cl(1)	2.355(2)	N(2)–Pd(1)–Cl(1)	173.2(2)
Pd(1)–Cl(2)	2.405(2)	C(15)–Pd(1)–Cl(2)	170.7(2)
C(15)–C(16)	1.339(9)	N(2)–Pd(1)–Cl(2)	94.8(2)
C(2)–Pt(1)–N(1)	81.4(2)	Cl(1)–Pd(1)–Cl(2)	89.8(1)
C(2)–Pt(1)–As(1)	98.8(2)	Pd(1)–Cl(1)–Pt(1)	88.3(1)

3.2.3.2 Synthesis of Complexes (R_{c},R_{c})-105 and (R_{c},S_{c})-106

By treatment of the diphenylprop-1-ynylarsine **97** with a half equivalent of the dimeric phenylamine palladium(II) complex in dichloromethane for 4 hours, complex (R_{c})-**104** was obtained quantitatively as a yellow solid.

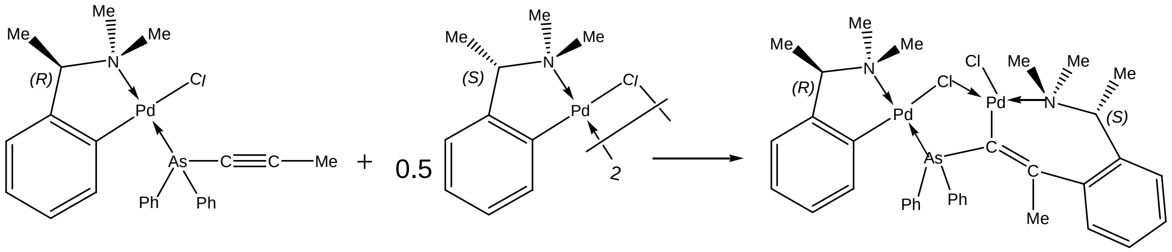
Insertion reaction was then carried out between complex (R_{c})-**104** and half equivalent of benzylamine palladium(II) dimer (R_{c})-**61** at room temperature in dichloromethane (Scheme 3.8). This reaction was monitored using thin layer chromatography (TLC) and was found to be complete in 6 days. The crude reaction mixture was purified by column chromatography and subsequently crystallized from acetone–hexane to give complex (R_{c},R_{c})-**105** as yellowish orange crystals in 68% yield.



(R_{c})-**104** (R_{c})-**61** (R_{c},R_{c})-**105**

Scheme 3.8

Using the similar procedure another insertion reaction was then performed between complex (R_c)-**104** and half equivalent of benzylamine palladium(II) dimer (S_c)- **62** at room temperature in dichloromethane (Scheme 3.9). This reaction was found to be complete in 4 days by monitoring with TLC. After purification by column chromatography, complex (R_c, S_c)-**106** was crystallized from acetone–hexane as yellowish orange crystals in 90% yield.



(R_c)-**104** (S_c)-**62** (R_c,S_c)-**106**

Scheme 3.9

3.2.3.2.1 X-ray Structural Analysis of Complexes (R_c,R_c)-105 and (R_c, S_c)-106

Figure 3.4 and 3.5 show the molecular structures of complex (R_c,R_c)-**105** and (R_c, S_c) **-106,** which indicated that the desired insertion products had been formed. For both of them the arsenic donor atoms are coordinated regiospecifically in the position *trans* to the benzylamine–*N* donor atom. Moreover, as expected, the absolute configurations of the stereocenters at C (7) and C (17) remained unchanged for the two complexes.

The molecular structure of complex (R_c,R_c)-**105** showed that carbon–carbon triple bonds of alkynylarsine, bond C(11)–C(12), has inserted into the Pd(2)–C(23) bond of benzyl amine dimer (R_c)-**5**. As a result of this insertion, two new bonds, C(22)–C(20) and Pd(2)–C(21) were generated, while bond C(11)–C(12) was changed from C≡C to C=C . The two palladium metal centers are connected by Cl to give a 5–membered bimetallic heterocycle. Complex (R_c,

S_c)-**106** has the same molecular connectivity as complex (R_c,R_c)-**105**, and only differs in the bond lengths and angles.

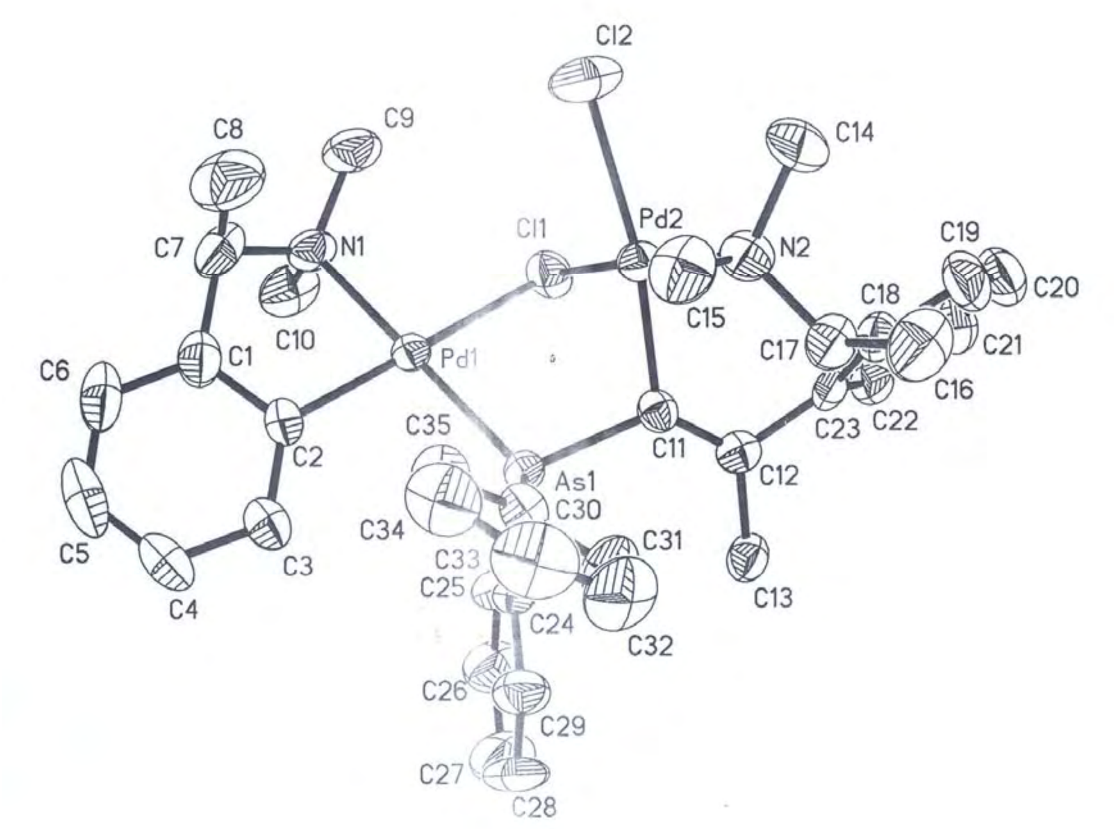


Figure 3.4 Molecular Structure of Complex (R_c,R_c)-**105**

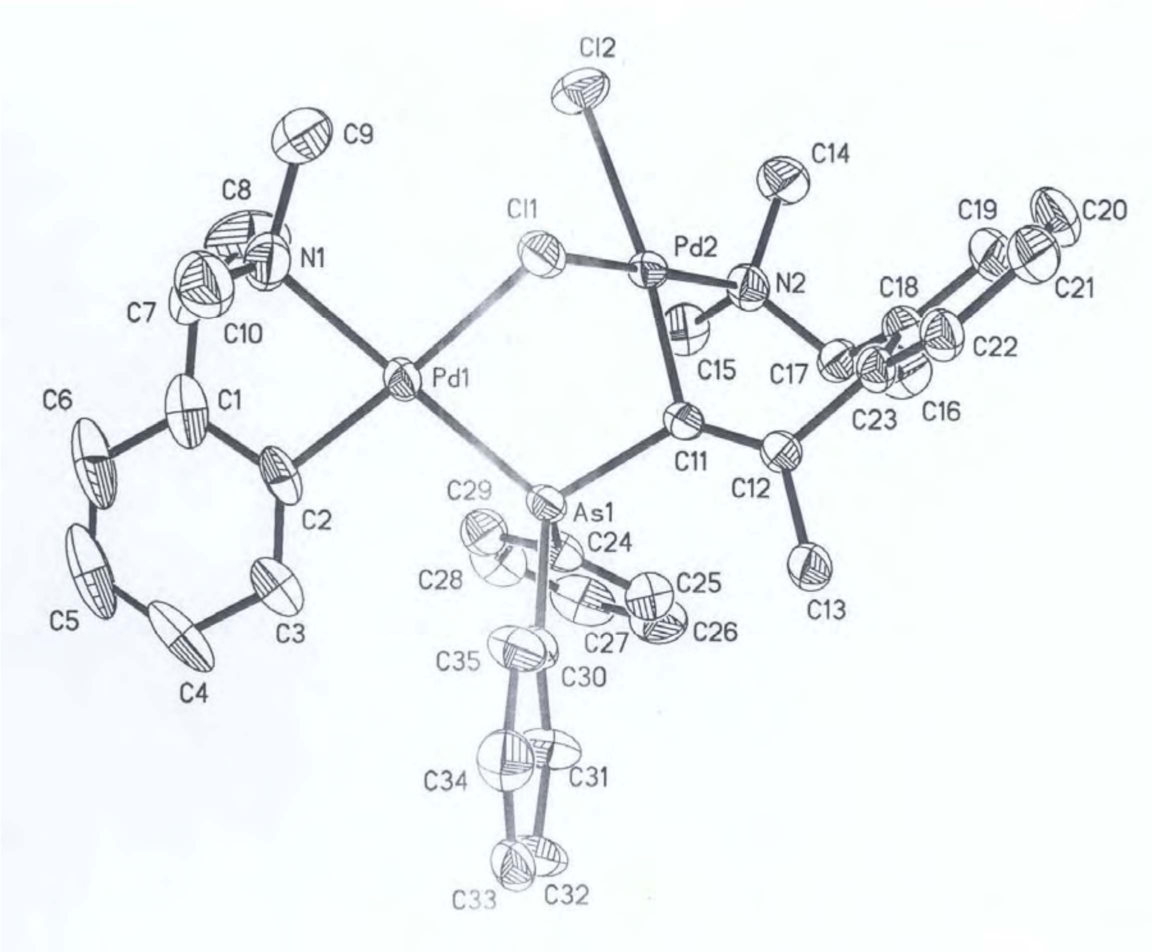


Figure 3.5 Molecular Structure of Complex (R_c, S_c)-**106**

The geometry at both palladium centers is slightly distorted square planar for complex (R_c,R_c)-**105** and (R_c,S_c)-**106** . The bond angles at Pd(1) are in the range of 82.5(2)–97.0(2)° and 172.4(2)–179.5(2)° for complex (R_c,R_c)-**105**; 82.4(2)–97.0(2)° and 173.33(2)–177.8(2)° for complex (R_c,S_c)-**106**. While the bond angles at Pd(1) ranges from 83.4(2)–95.7(2)° and 169.8(2)–172.4(2)° for complex (R_c,R_c)-**105**; 83.4(2)–95.6(2)° and 171.0(1) –173.8(2)° for complex (R_c,S_c)-**106**. The C(11)–C(12) bond distances in (R_c,R_c)-**105** [1.319(5)] and in complex (R_c,S_c)-**106** [1.325(7)] clearly indicate that they are C=C bonds. Table 3.3 shows selected bond distances and angles of complex (R_c,R_c)-**105** and (R_c,S_c) -**106**.

Table 3.3 Selected bond distances (Å) and angles (°) of complex (R_c,R_c)-**105** and (R_c,S_c)-**106**

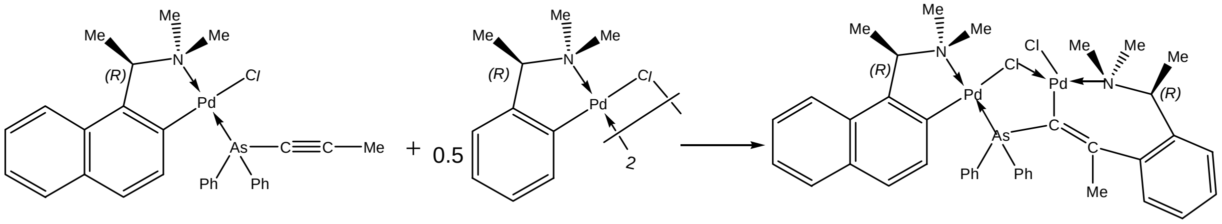
	Complex (R_c,R_c)-105	**Complex (R_c, S_c)-106**
Pd(1)–C(2)	1.992(4)	2.004(6)
Pd(1)–N(1)	2.122(3)	2.134(5)
Pd(1)–As(1)	2.355(1)	2.355(1)
Pd(1)–Cl(1)	2.411(2)	2.404(2)
Pd(2)–C(11)	1.994(4)	1.993(5)
Pd(2)–N(2)	2.123(4)	2.131(5)
Pd(2)–Cl(1)	2.347(2)	2.344(2)
Pd(2)–Cl(2)	2.432(2)	2.428(2)
C(11)–C(12)	1.319(5)	1.325(7)
C(2)–Pd(1)–N(1)	82.5(2)	82.4(2)
C(2)–Pd(1)–As(1)	97.0(2)	97.0(2)
N(1)–Pd(1)–As(1)	179.5(2)	177.8(2)
C(2)–Pd(1)–Cl(1)	172.4(2)	173.3(2)
N(1)–Pd(1)–Cl(1)	93.5(2)	93.6(2)
As(1)–Pd(1)–Cl(1)	86.9 (1)	87.3(1)
C(11)–Pd(2)–N(2)	92.8(2)	92.8(2)
C(11)–Pd(2)–Cl(1)	83.4(2)	83.4(2)
N(2)–Pd(2)–Cl(1)	172.4(2)	173.8(2)
C(11)–Pd(2)–Cl(2)	169.8(2)	171.0(2)
N(2)–Pd(2)–Cl(2)	95.7(2)	95.5(2)
Cl(1)–Pd(2)–Cl(2)	88.8(1)	95.6(2)

Pd(2)–Cl(1)–Pd(1)	91.1(1)	88.5(1)

3.2.3.3 Synthesis of Complex (R_c,R_c)-108 and (R_c,S_c)-109

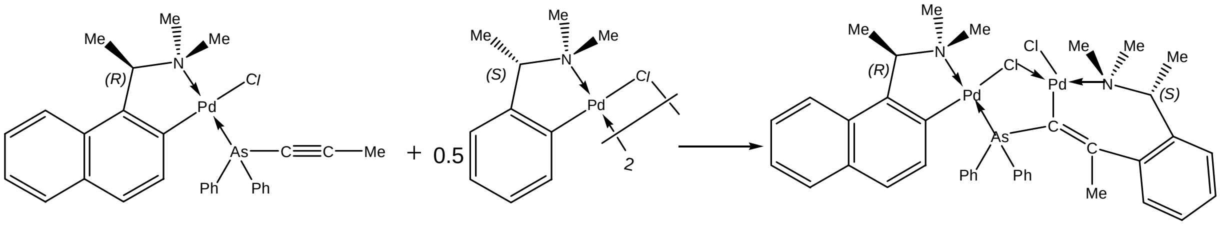
By treatment of the diphenylprop-1-ynylarsine **97** with a half equivalent of the dimeric naphthylamine palladium(II) complex in dichloromethane for 4 hours, complex (R_c)-**107** was obtained as a yellow solid quantitatively.

As illustrated in Scheme 3.10 and 3.11, complex (R_c)-**107** was then treated with half equivalent of benzylamine palladium(II) dimer (R_c)-**61** and (S_c)-**62** at room temperature in dichloromethane, separately. Monitored by thin layer chromatography (TLC), these two insertion reactions were found to be complete in 3 and 2 days, respectively. After purification by column chromatography and crystallized from acetone–hexane, complex (R_c,R_c)-**108** and (R_c,S_c)-**109** were obtained as yellowish orange crystals in 90% and 92% yields, respectively . However, single crystals suitable for X-ray structural analysis could not be produced for both of the products, despite many attempts to crystallize them using a wide variety of different solvent systems.



(R_c)-**107** (R_c)-**61** (R_c,R_c)-**108**

Scheme 3.10



(R_c)-**107**

(S_c)-**62**

(R_c,S_c)-**109**

Scheme 3.11

3.3 Conclusions

The insertion of alkynes with diphenylprop-1-ynylarsine ligands into Pd–C bonds of benzylamine palladacycles has been demonstrated. In this study, cyclopalladated and cycloplatinated complexes containing the benzyl and naphthylamine systems have been chosen to promote the reaction to give a series of bi-metallic compounds.

Compared with alkynes with phosphine ligand, insertion reactions with arsine ligand need longer reaction time. However, the yield of the reaction is higher.

3.4 Experimental

Reactions involving air-sensitive compounds were performed under a positive pressure of purified nitrogen. Bruker ACF 300 spectometer was used to record the ^{1}H (300 MHz) and ^{31}P{^{1}H} (121 MHz) NMR spectra. Optical rotations were measured on the specified solution in 1–dm cell at 25℃ with a Perkin–Elmer 341 polarimetrer. Melting points were determined on a Büchi melting point B–540. Elemental analyses were performed by the Elemental Analysis Laboratory of the Department of Chemistry at the National University of Singapore.

Complex (R_c)-**98** , (R_c)-**101**, (R_c)-**104** and (R_c)-**107** were prepared by a similar pathway as (R_c)-**72**. he dimeric benzylamine palladium(II) complexes (R_c)-**61**, (S_c)-**62** and **63**,[3] dimeric naphthylamine palladium(II) complex (*R*$_c$)-**59**[4,5] and dimeric naphthylamine pllatium(II) (*R*$_c$)-**60**[6] were prepared according to standard literature methods.

Synthesis of diphenylprop-1-ynylarsine Ligand, 97

Triphenylarsine (59.20g ,97%, 0.19mol)was dissolved in 500mL of liquid ammonia at –78℃. Then sodium (9.30 g, 0.40mol) was added slowly during 20 minutes and the color of the solution became reddish brown. The reaction mixture was allowed to stir for 3 hours.

Ammonium chloride (10.02 g, 0.19mol) was then added slowly to the reaction mixture and left to stir for 30 minutes. A solution of propaagyl bromide (13.96 g, 0.19mol) in diethyl ether (10 mL) was added dropwise during 15 minutes. The color of the solution became dark red. The ammonia was allowed to evaporate off overnight.

The resulting mixture was extracted with diethyl ether (3 × 150mL) and water (150mL). The reddish ether exacts were dried with anhydrous magnesium sulphate and the ether was removed at atmospheric pressure. The crude product was purified using microdistillation to give a slightly yellowish and viscous liquid, **3**, 21.4g (42% yield). b.p. 132–34℃ at 0.85 mmHg. ^{1}H NMR ($CDCl_3$) δ 2.09 (s, 3H), δ 7.33–7.66 (m, 10H, *aromatics*). ν (C≡C) medium 2179 cm^{-1}.

Synthesis of *μ*-chloro{{(*R*$_c$)-1-[1-(dimethylamino)ethyl]phenyl-*C*^{2},*N*}platium(II) {(*R*$_c$)-1-[1-(dimethylamino)ethyl]-2-[(*Z*)-1-(diphenylarsino)prop-1-en-2-yl-*C*^{1})]phenyl-*N*} chloro palladium(II)}, (*R*$_c$,*R*$_c$)-99

Complex (*R*$_c$)-**98** (0.50 g, 0.77 mmol) was dissolved in dichloromethane (50 mL). This solution then was treated with dimeric cyclopalladated benzylamine complex (*R*$_c$)-**61**

(0.22 g, 0.39mmol). The mixture was stirred at room temperature for 4 days. Upon completion, the solvent was removed to give brown residue which was purified by column chromatography (with an eluting gradient starting from hexane: acetone 5:1) give the products as yellowish orange solids. Crystallization from dichloromethane –hexane gave (*R*$_c$,*R*$_c$)-**99** as yellowish orange crystals: 0.48 g (67% yield); m.p. 223–224℃（dec）; $[\alpha]_D$ +167°(*c* 0.5, CH_2Cl_2).Anal. Calcd. for $C_{35}H_{41}Cl_2N_2AsPdPt$: C, 44.5; H, 4.4; N, 3.0. Found: C, 44.9; H, 4.5; N, 3.1. ^{1}H NMR (CDCl3): δ 1.07 (d, 3H, $^3J_{HH}$ = 6.8Hz, CH*Me'*), 1.84 (s, 3H, =C*Me*), 2.00 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CH*Me*), 2.04 (s, 3H, N*Me'*), 2.54 (s, 3H, N*Me'*), 2.78 (s, 3H, N*Me*$_{ax}$), 3.21 (s, 3H, N*Me*$_{eq}$,), 3.75 (q, 1H, $^3J_{HH}$ = 6.4Hz, C*H'*Me), 3.81 (q, 1H, $^3J_{HH}$ = 7.2 Hz, C*H*Me), 6.43~8.02(m, 18H, aromatics).

Synthesis of *μ*-chloro{{(*R*$_c$)-1-[1-(dimethylamino)ethyl]phenyl-*C*^{2},*N*}platium(II) {(*S*$_c$)-1-[1-(dimethylamino)ethyl]-2-[(*Z*)-1-(diphenylarsino)prop-1-en-2-yl-*C*^{1})]phenyl-*N*} chloro palladium(II)}, (*R*$_c$, *S*$_c$)-100

Complex (*R*$_c$)-**98** (0.25 g, 0.39 mmol) was dissolved in dichloromethane (50 mL). This solution then was treated with dimeric cyclopaladated benzylamine complex (*S*$_c$)-**62** (0.11 g, 0.19mmol). The mixture was stirred at room temperature for 5 days. Upon completion, the solvent was removed to give brown residue which was purified by column chromatography (with an eluting gradient starting from hexane: acetone 5:1) give the products as yellowish orange solids. Crystallization from dichloromethane–hexane gave (*R*$_c$,*S*$_c$)-**100** as yellowish orange crystals: 0.32 g (87% yield); m.p. 216℃（dec）; $[\alpha]_D$ －175°(*c* 0.5, CH_2Cl_2). Anal. Calcd. for $C_{35}H_{41}Cl_2N_2AsPdPt$: C, 44.5; H, 4.4; N, 3.0. Found: C, 44.8; H, 4.5; N, 3.2. ^{1}H NMR

(CDCl3): δ 1.07 (d, 3H, $^3J_{HH}$ = 7.1Hz, CH*Me*′), 1.86 (s, 3H, =C*Me*), 2.08 (s, 3H, N*Me*′), 2.11 (d, 3H, $^3J_{HH}$ = 6.5 Hz, CH*Me*), 2.57 (s, 3H, N*Me*′), 2.68(s, 3H, NMe_{ax}), 3.01 (s, 3H, NMe_{eq},), 3.55 (q, 1H, $^3J_{HH}$ = 6.4Hz, C*H*′Me), 3.81 (q, 1H, $^3J_{HH}$ = 7.2 Hz, C*H*Me), 6.15~7.95 (m, 18H, aromatics).

Synthesis of *μ*-chloro{{(*R*$_c$)-1-[1-(dimethylamino)ethyl]naphthyl-*C*^{2},*N*} platium(II){(*R*$_c$)-1-[1-(dimethylamino)ethyl]-2-[(*Z*)-1-(diphenylarsino) prop - 1-en-2-yl-*C*^{1}] phenyl-*N*}chloro palladium(II)}, (*R*$_c$,*R*$_c$)-102

Complex (*R*$_c$)-**101** (0.50 g, 0.72 mmol) was dissolved in dichloromethane (50 mL). This solution then was treated with half–mol dimeric cyclopaladated benzylamine complex (*R*$_c$) **-61** (0.21 g, 0.36mmol). The mixture was stirred at room temperature for 5 days. Upon completion, the solvent was removed to give brown residue which was purified by column chromatography (with an eluting gradient starting from hexane: acetone 5:1) give the products as yellowish orange solids. Crystallization from acetone–hexane gave (*R*$_c$,*R*$_c$)-**102** as yellowish orange crystals: 0.61 g (86% yield); m.p. 229–231℃（dec）; $[\alpha]_D$ +175°(*c* 0.5, CH_2Cl_2). Anal. Calcd. for $C_{39}H_{43}Cl_2N_2AsPdPt$: C, 47.5; H, 4.4; N, 2.8. Found: C, 47.2; H, 4.4; N, 3.1. ^{1}H NMR (CDCl3): δ 1.06 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH*Me*′), 1.87 (s, 3H, =C*Me*), 2.03 (s, 3H, N*Me*′), 2.21 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CH*Me*), 2.55 (s, 3H, N*Me*′), 2.76 (s, 3H, NMe_{ax}), 3.36 (s, 3H, NMe_{eq},), 3.80 (q, 1H, $^3J_{HH}$ = 6.8 Hz, C*H*′Me), 4.58 (q, 1H, $^3J_{HH}$ = 6.8 Hz, C*H*Me), 6.79~7.95 (m, 20H, aromatics).

Synthesis of *μ*-chloro{{(*R*$_c$)-1-[1-(dimethylamino)ethyl]phenyl-*C*^{2},*N*}{(*R*$_c$)-1-[1-(dimethylamino)ethyl]-2-(*Z*)-1-[(diphenylarsino)prop-1-en-2-yl-*C*^{1})]phenyl-*N*} chloro dipalladium(II)}, (*R*$_c$,*R*$_c$)-105

Complex (*R*$_c$)-**104** (0.50 g, 0.89 mmol) was dissolved in dichloromethane (50 mL). This solution then was treated with half–mol dimeric cyclopaladated benzylamine complex (*R*$_c$) **-61** (0.26 g, 0.45mmol). The mixture was stirred at room temperature for 6 days. Upon completion, the solvent was removed to give brown residue which was purified by column chromatography (with an eluting gradient starting from hexane: acetone 5:1) give the products as yellowish orange solids. Crystallization from acetone–hexane gave (*R*$_c$,*R*$_c$)-**105** as yellowish orange crystals: 0.51 g (68% yield); m.p. 198–199℃（dec）; $[\alpha]_D$ +73°(*c* 0.5, CH_2Cl_2). Anal. Calcd. for $C_{35}H_{41}Cl_2N_2AsPd_2$: C, 49.6; H, 4.9; N, 3.3. Found: C, 49.5; H, 4.8; N, 3.6. ^{1}H NMR (CDCl3): δ 1.07 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH*Me'*), 1.85 (s, 3H, =C*Me*), 2.09 (s, 3H, N*Me'*), 2.11 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CH*Me*), 2.57 (s, 3H, N*Me'*), 2.68 (s, 3H, N*Me*$_{ax}$), 3.01 (s, 3H, N*Me*$_{eq}$,), 3.55 (q, 1H, $^3J_{HH}$ = 6.4 Hz, C*H'*Me), 3.81 (q, 1H, $^3J_{HH}$ = 7.2 Hz, C*H*Me), 6.49~7.95 (m, 18H, aromatics).

Synthesis of *μ*-chloro{{(*R*$_c$)-1-[1-(dimethylamino)ethyl]phenyl-*C*^{2},*N*}{(*S*$_c$)-1-[1-(dimethylamino)ethyl]-2-[(*Z*)-1-(diphenylarsino)prop-1-en-2-yl-*C*^{1})]phenyl-*N*} chloro dipalladium(II)}, (*R*$_c$,*S*$_c$)-106

Complex (*R*$_c$)-**104** (0.50 g, 0.89 mmol) was dissolved in dichloromethane (50 mL). This solution then was treated with half–mol dimeric cyclopaladated benzylamine complex (*S*$_c$) **-62** (0.26 g, 0.45mmol). The mixture was stirred at room temperature for 4 days. Upon completion, the solvent was removed to give brown residue which was purified by column chromatography (with an eluting gradient starting from hexane: acetone 5:1) give the products as yellowish orange solids. Crystallization from acetone–hexane gave (R_c,S_c)**-106** as yellowish orange crystals: 0.68 g (90% yield); m.p. 183~185℃（dec）; $[\alpha]_D$ –151°(*c* 0.5, CH_2Cl_2). Anal. Calcd. for $C_{35}H_{41}Cl_2N_2AsPd_2$: C, 49.6; H, 4.9; N, 3.3. Found: C, 48.1; H, 4.8; N, 3.4. ^{1}H NMR (CDCl3): δ 1.07 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH*Me'*), 1.85 (s, 3H, =C*Me*), 2.08 (s, 3H, N*Me'*), 2.11 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH*Me*), 2.56 (s, 3H, N*Me'*), 2.68 (s, 3H, NMe_{ax}), 3.01 (s, 3H, NMe_{eq},), 3.55 (q, 1H, $^3J_{HH}$ = 6.4 Hz, C*H'*Me), 3.81 (q, 1H, $^3J_{HH}$ = 6.8 Hz, C*H*Me), 6.49~8.05(m, 18H, aromatics).

Synthesis of *µ*-chloro{{(*R*$_c$)-1-[1-(dimethylamino)ethyl]naphthyl-*C*^{2},*N*}{(*R*$_c$)-1-[1-(dimethylamino)ethyl]-2-[(*Z*)-1-(diphenylarsino)prop-1-en-2-yl-*C*^{1})]phenyl-*N*} chloro dipalladium(II)}, (*R*$_c$,*R*$_c$)-108

Complex (R_c)**-107** (0.50 g, 0.82 mmol) was dissolved in dichloromethane (50 mL). This solution then was treated with half–mol dimeric cyclopaladated benzylamine complex (R_c) **-61** (0.24 g, 0.41mmol). The mixture was stirred at room temperature for 3 days. Upon completion, the solvent was removed to give brown residue which was purified by column chromatography (with an eluting gradient starting from hexane: acetone 5:1) give the products as yellowish orange solids. Crystallization from acetone–hexane gave (R_c,R_c)**-108** as yellowish orange crystals: 0.67 g (90% yield); m.p. 176–177℃ （dec）; $[\alpha]_D$ +38°(*c* 0.5, CH_2Cl_2). Anal. Calcd. for $C_{39}H_{43}Cl_2N_2AsPd_2$: C, 52.1; H, 4.8; N, 3.1. Found: C, 51.1; H, 4.8; N, 3.2. ^{1}H NMR (CDCl3): δ 1.06 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH*Me'*), 1.89 (s, 3H, =C*Me*), 2.07 (s, 3H, N*Me'*), 2.32

(d, 3H, $^{3}J_{HH}$ = 6.4 Hz, CH*Me*), 2.58 (s, 3H, N*Me*'), 2.68 (s, 3H, N*Me*$_{ax}$), 3.14 (s, 3H, N*Me*$_{eq}$,), 3.80 (q, 1H, $^{3}J_{HH}$ = 6.8 Hz, C*H*'Me), 4.34 (q, 1H, $^{3}J_{HH}$ = 6.0 Hz, C*H*Me), 6.48~7.93 (m, 20H, aromatics).

Synthesis of *μ*-chloro{{(*R*$_c$)-1-[1-(dimethylamino)ethyl]naphthyl-*C*^{2},*N*} {(*S*$_c$)-1-[1-(dimethylamino)ethyl]-2-[(*Z*)-1-(diphenylarsino)prop-1-en-2-yl-*C*^{1})]phenyl-*N*} chloro dipalladium(II)}, (*R*$_c$, *S*$_c$)-109

Complex (*R*$_c$)-**107** (0.50 g, 0.82 mmol) was dissolved in dichloromethane (50 mL). This solution then was treated with half–mol dimeric cyclopaladated benzylamine complex (*S*$_c$) **-62** (0.24 g, 0.41mmol). The mixture was stirred at room temperature for 2 days. Upon completion, the solvent was removed to give brown residue which was purified by column chromatography (with an eluting gradient starting from hexane: acetone 5:1) give the products as yellowish orange solids. Crystallization from acetone–hexane gave (*R*$_c$,*S*$_c$)-**109** as yellowish orange crystals: 0.68 g (92% yield); m.p. 180–181℃ （dec）; $[\alpha]_D$ –142°(*c* 0.5, CH_2Cl_2). Anal. Calcd. for $C_{39}H_{43}Cl_2N_2AsPd_2$: C, 52.1; H, 4.8; N, 3.1. Found: C, 51.9; H, 4.9; N, 2.8. ^{1}H NMR (CDCl3): δ 1.07 (d, 3H, $^{3}J_{HH}$ = 7.2 Hz, CH*Me*'), 1.79 (s, 3H, =C*Me*), 2.09 (s, 3H, N*Me*'), 2.11 (d, 3H, $^{3}J_{HH}$ = 6.4 Hz, CH*Me*), 2.57 (s, 3H, N*Me*'), 2.68 (s, 3H, N*Me*$_{ax}$), 3.01 (s, 3H, N*Me*$_{eq}$,), 4.00 (q, 1H, $^{3}J_{HH}$ = 6.8 Hz, C*H*'Me), 4.36 (q, 1H, $^{3}J_{HH}$ = 6.0 Hz, C*H*Me), 6.49~8.43 (m, 20H, aromatics).

Chapter 4

Asymmetric Hydrophosphination Reactions Promoted by Cyclometallated Palladium(II) Complexes

4.1 Introduction

Since the efficiency and the selectivity of a catalyst can be affected significantly by stereoelectronic nature of its associated ligand, there is a great interest in the design and the synthesis of new ligands (amines, aminoalcohols, thioethers, phosphines, etc). From all of them, phosphine derivatives are the most widely used with transition metal catalysts. Phosphines are valuable organometallic ligands and are important in catalysts for stereoselective organic reactions.

Traditionally, phosphines are mainly prepared by one of the following methods: reaction of halophosphines with organometallic reagents, reaction of phosphides with halides, addition of RR′PH to C–C multiple bonds, Friedel–Crafts reactions, and reduction of phosphine oxides.[193] A greener way to phosphines is hydrophosphination–the addition of a P–H bond to a multiple bond, since no atom loss is observed (atom economy concept).[194] These reactions are mainly carried out in the presence of radical initiators or under basic conditions.[195–198] Acidic and neutral media were also proposed.[199,200] A few recent examples reported the use of a metal activation.[201–204] However, metal complex activated asymmetric addition of P–H moiety to carbon–carbon unsaturated compounds are relatively rare and are limited to the synthesis of chiral monophosphines with moderate stereoselectivities.[205–207]

Our group has previously reported the application of chiral cyclometallated–amine complexes as efficient chiral auxiliaries to promote the oxidative coupling reaction between vinylphosphines and imines to get imino–phosphine ligands;[208] asymmetric Diels–Alder reactions to give functionalized *P*–chiral phosphines [34,209] and asymmetric hydroamination reactions to obtain *P*–chiral iminophosphines.[42] In this chapter, our studies focuses on asymmetric hydrophosphination reactions promoted by chiral cyclopalladated–amine template.

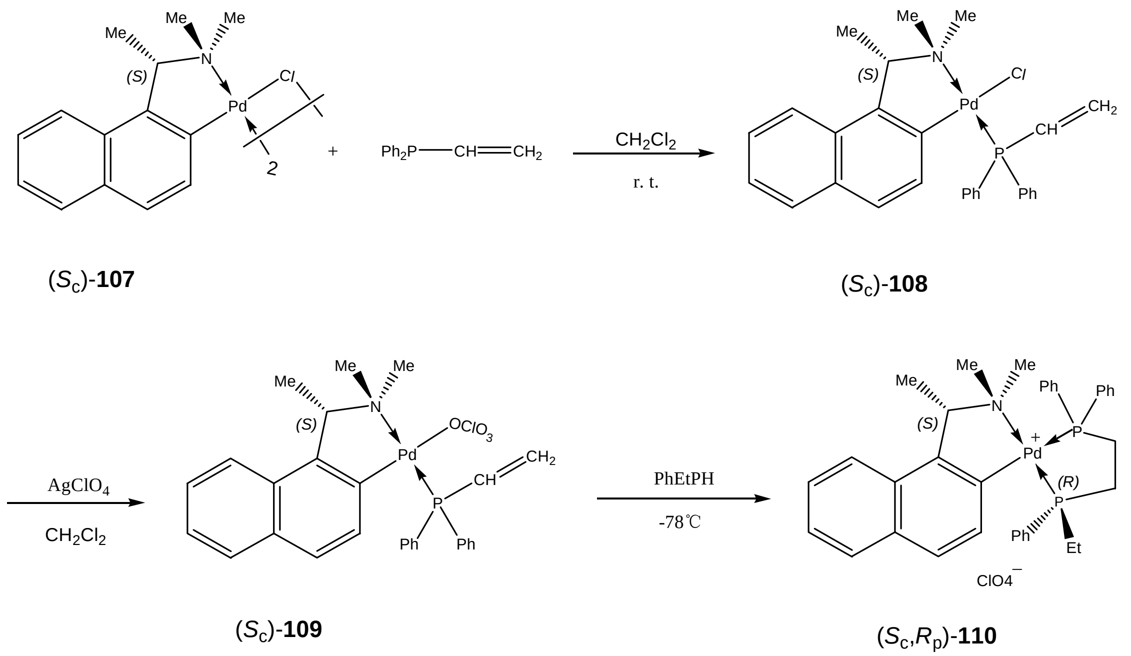
4.2 Results and Discussion

4.2.1 Hydrophosphination of Diphenylvinylphosphine

4.2.1.1 Synthesis of Complex (S_c,R_p)-110

Our group has previously used complex (S_c)-**108** as the chiral template to promote the asymmetric cycloaddition reaction between diphenylvinylphosphine and DMPP,[197] and oxidative coupling reaction between diphenylvinylphosphine and a series of imines.[198] By treatment of the diphenylvinylphosphine with a half molar equivalent of the dimeric palladium(II) complex (S_c)-**107** in dichloromethane for 2 hours, the precursor complex (S_c)-**108** was obtained as a yellow solid quantitatively.

As experienced from earlier analogous reactions, there was no reaction occurred between the PhEtPH and free diphenylvinylphosphine despite under strong reaction conditions. It has been well established that the Pd–Cl bond in the chiral complex (S_c)-**108** is thermodynamically and kinetically stable. In general, the anionic ligand is inert to ligand exchange reactions, even in the presence of strong ligands such as phosphines and arsines. In contrast, the perchlorato complex (S_c)-**109** is labile and readily replaced by most donor atoms. Therefore, as illustrated in Scheme 4.1, the stable chloro ligand in (S_c)-**108** was firstly removed quantitatively by standard treatment with silver perchlorate to generate the reactive complex (S_c)-**109**. Then perchlorato complex (S_c)-**109** was then reacted with an equivalent of PhEtPH in dichloromethane at –78℃.



(S_c)-**107**

(S_c)-**108**

(S_c)-**109**

(S_c,R_p)-**110**

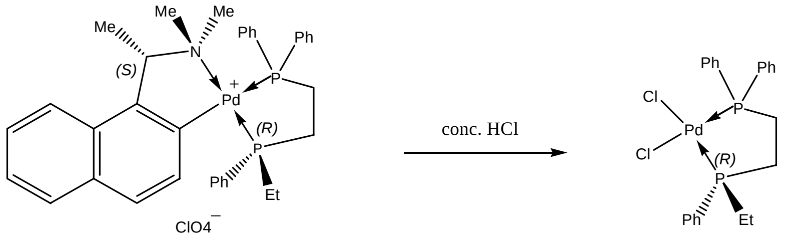
Scheme 4.1

The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy and was found to be complete in 18 h. Prior to purification, the $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture showed two pairs of doublets at δ 68.4 (d, J_{PP} = 26.6 Hz), 42.7 (d, J_{PP} = 22.8 Hz) and 61.7 (d,1P, J_{pp}= 18.4 Hz), 40.2 (d,1P, J_{pp}= 18.4 Hz) in the ratio of 14:1, respectively, indicating that a pair of diastereomeric complexes have been produced. After purified by chromatography, only the major product (S_c,R_p)-**110** was obtained as white solid in 20% yield. Recrystallization of the crude product from acetone–hexane gave pure (S_c, R_p)-**110** as white crystals.

It is important to note that, in theory, PhEtPH is a chiral molecule. However, as typical secondary phosphine, the inversion barrier for PhEtPH is low at room temperature. Thus the chiral template is able to control the stereoselectivity in the product formation despite the fact that the racemic form of PhEtPH is used as the starting material.

4.2.1.2 Removal of the Chiral Auxiliary

As showed in Scheme 4.2, the chiral naphthylamine auxiliary in (S_c,S_p)-**110** can be removed *chemo*selectively from palladium templates by treatment with concentrated hydrochloric acid in dichloromethane. The chiral auxiliary was recovered quantitatively from the mother liquor after treatment with base. On the other hand, the neutral dichloro complex (*R*$_p$)-**111** was obtained efficiently as stable white crystals in 89.1% yields. The $^{31}P\{^1H\}$ NMR spectrum of the dichloro complex (*R*$_p$)-**111** in $CDCl_3$ exhibited a pair of doublets at δ 73.7 (d, 1P, J_{pp}= 11.4 Hz) and 63.8 (d, 1P, J_{pp}= 11.4 Hz).



(*S*$_c$,*R*$_p$)-**110**

(*R*$_p$)-**111**

Scheme 4.2

4.2.1.3 X-ray Structural Analysis of Complex (*R*$_p$)-111

The single crystal X-ray diffraction analysis showed that the isolated compound from the treatment of complex (*S*$_c$,*R*$_p$)-**110** with concentrated hydrochloric acid is the expected dichloro complex (*R*$_p$)-**111** (Figure 4.1). The stereogenic center at P(1) adopts the *R* absolute configuration.

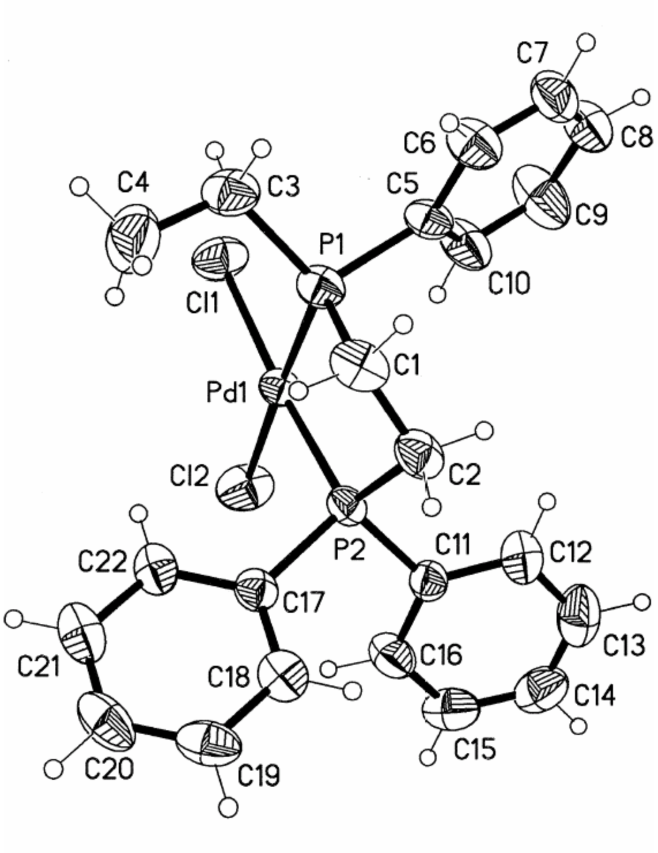


Figure 4.1 Molecular Structural Analysis of Complex (R_p)-**111**

The geometry at the palladium ion coordination sphere is distorted square planar. Bond angles at the palladium centre are in the ranges of 85.8 (6)–93.9(6)˚ and 174.7(6)–176.9 (7)˚. The bond lengths of Pd–P (1) and Pd–P (2) are 2.237 (2) and 2.229(2) Å respectively. The diphosphine coordinates on the palladium as a bidentate ligand *via* the two phosphorous atoms. Selected bond distances and angles of complex (R_p)-**111** are given in Table 4.1.

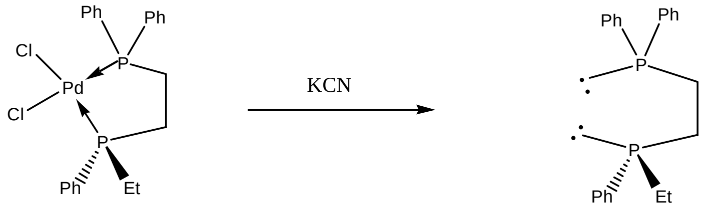
Table 4.1 Selected bond distances (Å) and angles (°) of complex (R_p)-**111**

Pd(1)–P(1)	2.238(3)	P(2)–Pd(1)–Cl(1)	174.7(6)
Pd(1)–P(2)	2.229(2)	P(1)–Pd(1)–Cl(1)	89.1 (6)
Pd(1)–Cl(1)	2.348(2)	P(2)–Pd(1)–Cl(2)	91.2(6)
Pd(1)–Cl(2)	2.357 (2)	P(1)–Pd(1)–Cl(2)	176.9 (7)
P(1)–C(1)	1.83 (6)	Cl(1)–Pd(1)–Cl(2)	93.9(6)

P(2)–C(2)	1.83 (6)	C(2)–P(2)–Pd(1)	108.7(2)
C(1)–C(2)	1.51(8)	C(2)–C(1)–P(1)	109.1(4)
C(18)–C(19)	1.53(6)	C(1)–C(2)–P(2)	108.1(4)
P(2)–Pd(1)–P(1)	85.8 (6)		

4.2.1.4 Liberation and Optical Purity of (*S*$_p$)-112

As shown in Scheme 4.3, the optically pure diphosphine ligand (*S*$_p$)-**112** can be liberated from the dichloro complex (*R*$_p$)-**111** by treatment with saturated aqueous potassium cyanide in dichloromethane. The free ligand (*S*$_p$)-**112** was obtained as white solid in 83% yield, $[\alpha]_D$ = –98.7° (c 0.2, CH_2Cl_2). The $^{31}P\{^1H\}$ NMR spectrum of the free diphosphine ligand (*S*$_p$)-**112** in CDCl3 exhibited a pair of doublets at δ –12.1 (d,1P, J_{pp}= 27.8 Hz) and –15.2 (d,1P, J_{pp}=27.8 Hz). It should be noted that the apparent inversion of configuration that takes place at the phosphorus stereogenic center when the diphosphine ligand is liberated from the complex is merely a consequence of the Cahn–Ingold–Prelog (CIP) sequence rule.[211]



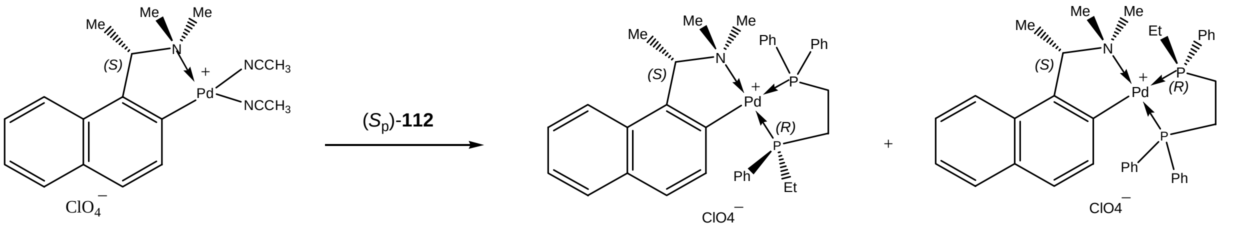
(*R*$_p$)-**111**

(*S*$_p$)-**112**

Scheme 4.3

The optical purity of the liberated ligand (*S*$_p$)-**112** could be determined by subsequent re–complexation to the bis(acetonitrile) complex (*S*$_c$)-**113** (Scheme 4.4). The ^{31}P NMR spectrum of the crude recomplexation product mixture in $CDCl_3$ exhibited two pairs of doublets at δ 68.4 (d, J_{PP}=26.6 Hz), 42.7 (d, J_{PP}= 22.8 Hz) and 61.7 (d,1P, J_{pp}= 18.4 Hz), 40.2

(d,1P, J_{pp}= 18.4 Hz) in the ratio of 11:7, respectively. The resonance signals at δ 68.4 and 42.7 are identical to those observed for the major product (*S*$_c$,*R*$_p$)-**110** in the original hydrophosphination reaction, while the signals at δ 61.7 and 40.2 matches the minor signals seen in the original reaction mixture and are assigned to the major product's regioisomer (*S*$_c$,*R*$_p$) **-114**.



(*S*$_c$)-**113** (*S*$_c$,*R*$_p$)-**110** (*S*$_c$,*R*$_p$)-**114**

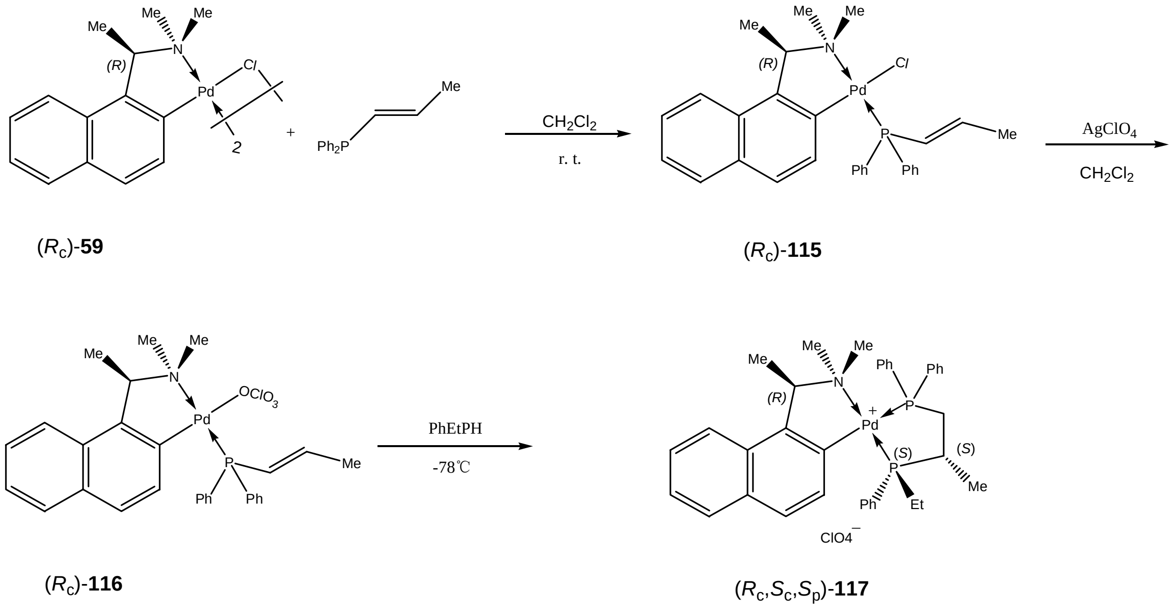
Scheme 4.4

Formation of regioisomers during the recoordination of liberated ligands to the naphthylamine auxiliary is well established. Therefore, it could be confirmed that the liberated (*S*$_p$)**-112** retains the same molecular structure in complex(*S*$_c$, *R*$_p$)**-114** as the diphosphine ligand in complex (*S*$_c$, *R*$_p$)**-110**. The re-coordination step also assists in identifying the minor regioisomeric complex generated directly from the hydrophosphination reaction.

4.2.2 Hydrophosphination of (*E*)-Diphenyl-1-propenylphosphine

4.2.2.1 Synthesis of Complex (*R*$_c$,*S*$_c$,*S*$_p$)-117

In the absence of the metal template, there is no reaction between ethylphenylphosphine, PhEtPH, and (*E*)-diphenyl-1-propenylphosphine under ambient conditions. As illustrated in Scheme 4.4, (*E*)-diphenyl-1-propenylphosphine was first coordinated to (*R*$_c$)**-59** regioselectively to form the neutral complexes (*R*$_c$)**-115**.[209] However, no reaction between complex (*R*$_c$)**-115** and PhEtPH, either. Therefore, the kinetically stable chlorine–palladium bond was cleaved by treatment with silver perchlorate to give the kinetically labile perchlorato complex (*R*$_c$)**-116.** Complexe (*R*$_c$)**-116** was not isolated, but was subsequently treated with PhEtPH in dichloromethane at −78 ℃ for 12 hours.



Scheme 4.5

Prior to purification, the $^{31}P\{^{1}H\}$NMR spectrum of crude reaction mixture in $CDCl_3$ exhibited three pairs of doublets at δ 69.7 (d, 1P, J_{pp}= 34.2 Hz), 30.0 (d, 1P, J_{pp}= 34.2 Hz); 52.3 (d, 1P, J_{pp}= 30.4 Hz), 44.4 (d, 1P, J_{pp}= 30.4 Hz); 53.4 (d, 1P, J_{pp}= 30.4 Hz), 42.5 (d, 1P, J_{pp}= 30.4 Hz) in the ratio of 9.5:1:1, respectively. After purified by silica gel column chromatography (acetone–hexane 1:6), only the major product (R_c,S_c,S_p)-**117** was obtained. Complex (R_c,S_c,S_p)-**117** then crystallized from dichlomethane–diethylether as light yellow crystals in 60% yield (Scheme 4.4).

4.2.2.2 X-ray Structural Analysis of Complex (R_c,S_c,S_p)-117

The single crystal X-ray diffraction analysis of the complex (R_c,S_c,S_p)-**117** revealed that the expected five–membered diphosphine chelate has been formed (Figure 4.2). Two new stereogenic centers at P (1) and C (18) were generated respectively, both which adopt the *S* absolute configuration. While the absolute configuration of the stereocenters at C(11) remained unchanged. The X-ray analysis also showed that this hydrophosphination reaction is highly regioselective, as the ethylphenylphosphino group was added to the *β*–carbon of the vinylphosphines to form five–membered chelate ring exclusively.

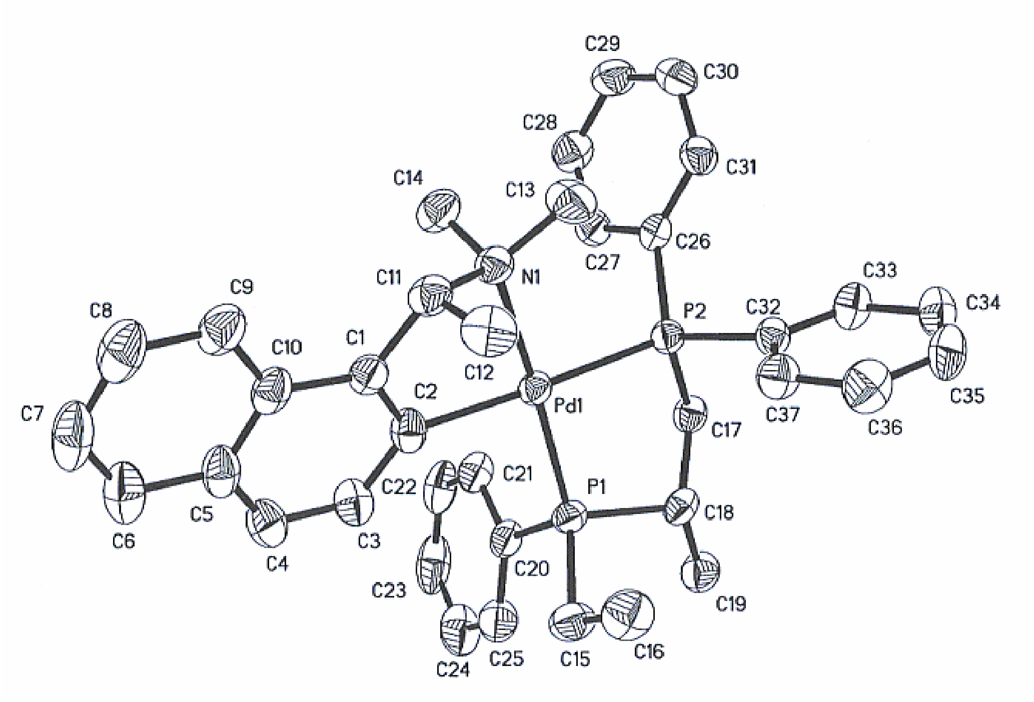


Figure 4.2 Molecular Structure of Complex (R_c,S_c,S_p)-**117**

The geometry at palladium is distorted square planar with angles at palladium in the ranges 80.6(2)–99.0(1) and 175.3 (1)–175.5(1)˚. The Pd–P(1) and Pd–P(2) bond distances are 2.248 (1) and 2.340(1) Å respectively, with the bond trans to the carbon of the naphthylamine auxiliary being longer by 0.0916 Å. This indicates that the phosphorous atoms have quite different donor abilities.[212] Selected bond distances and angles of complex (R_c,S_c,S_p)-**117** are given in Table 4.2.

Table 4.2 Selected bond distances (Å) and angles (°) of complex (R_c,S_c,S_p)-**117**

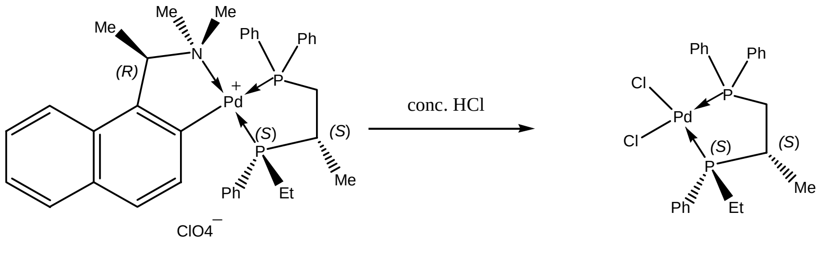
Pd(1)–C(2)	2.047(4)	C(2)–Pd(1)–P(1)	95.6 (1)
Pd(1)–N(1)	2.134(3)	N(1)–Pd(1)–P(1)	175.5(1)
Pd(1)–P(1)	2.248 (1)	C(2)–Pd(1)–P(2)	175.3 (1)
Pd(1)–P(2)	2.340(1)	N(1)–Pd(1)–P(2)	99.0(1)

P(1)–C(18)	1.86 (4)	P(1)–Pd(1)–P(2)	85.0 (4)
P(2)–C(17)	1.83 (4)	C(18)–P(1)–Pd(1)	108.8(1)
C(17)–C(18)	1.53 (6)	C(17)–P(2)–Pd(1)	105.6 (1)
C(18)–C(19)	1.53(6)	C(17)–C(18)–P(1)	107.7(3)
C(2)–Pd(1)–N(1)	80.6(2)	C(18)–C(17)–P(2)	107.5(3)

4.2.2.3 Removal of the Chiral Auxiliary

Removal of the naphthylamine auxiliary of a template complex by treatment with strong acid has been a standard method which leads to the formation of the corresponding neutral dichloro palladium(II) complex.

As showed in Scheme 4.6, the chiral naphthylamine auxiliary in (R_c,S_c,S_p)-**117** can be removed chemoselectively from the palladium template by treatment with concentrated hydrochloric acid in dichloromethane. The chiral auxiliary was recovered quantitatively from the mother liquor after treatment with base. On the other hand, the neutral dichloro complex (S_c,S_p)-**118** was obtained efficiently as stable white crystals in 88% yields. The ^{31}P{^{1}H} NMR spectrum of the dichloro complex (S_c,S_p)-**118** in $CDCl_3$ exhibited a pair of doublets at δ 80.3 (d, 1P, J_{pp}= 5.9 Hz) and 50.5 (d, 1P, J_{pp}= 6.5 Hz).



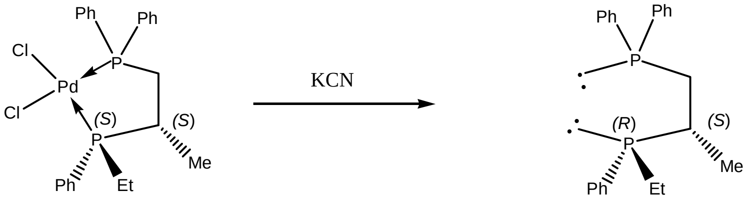
(R_c,S_c,S_p)-**117**

(S_c,S_p)-**118**

Scheme 4.6

4.2.2.4 Liberation and Optical Purities of (*S*c,*R*p)-119

The optically pure diphosphine ligand (*S*c,*R*p)-**119** can be liberated from the dichloro complex (*S*c,*S*p)-**118** by treatment the dichloro complex with saturated aqueous potassium cyanide in dichloromethane at room temperature for 2 h(Scheme 4.7). The free ligand (*S*c,*R*p)-**119** was obtained as white solid in 80% yield, $[\alpha]_D = -118.4°$ (c 0.2, CH_2Cl_2). The $^{31}P\{^1H\}$ NMR spectrum of the free diphosphine ligand (*S*c,*R*p)-**119** in CDCl3 exhibited a pair of doublets at δ –0.66 (d,1P, J_{pp}= 22.1 Hz) and -19.7 (d,1P, J_{pp}= 20.2 Hz).

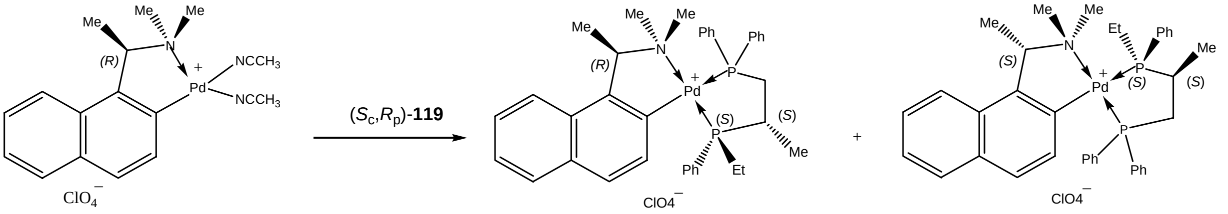


(*S*c,*S*p) -**118**

(*S*c,*R*p) -**119**

Scheme 4.7

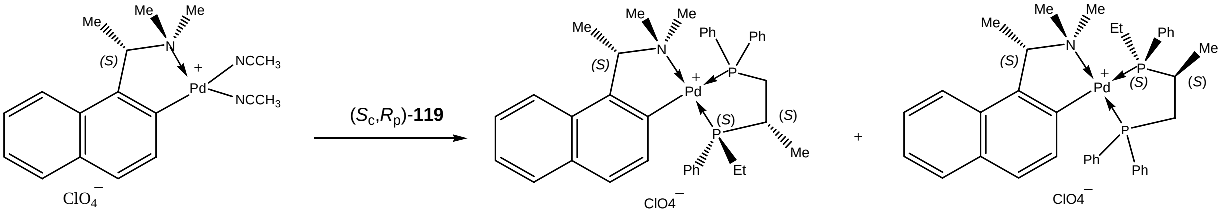
In order to confirm the optical purity of the liberated ligand and to establish the identity of the hydrophosphination product, free ligand (*S*c,*R*p)-**119** was re–coordinated to bis(acetonitrile) complex (*R*c)-**120** and (*S*c)-**113** separately. When the liberated ligand (*S*c,*R*p)-**119** was recomplexed to the bis(acetonitrile) complex (*R*c)-**120** (Scheme 4.7), the ^{31}P NMR spectrum of the crude recomplexation product mixture in $CDCl_3$ exhibited two pairs of doublets at δ 52.3 (d, 1P, J_{pp}= 30.4 Hz), 44.4 (d, 1P, J_{pp}= 30.4 Hz); 69.7 (d, 1P, J_{pp}= 34.2 Hz), 30.0 (d, 1P, J_{pp}= 34.2 Hz) in the ratio of 2:1, respectively. The resonance signals at δ 69.7 and 30.0 are identical to those observed for the major product (*R*c,*S*c,*S*p)-**117** in the original hydrophosphination reaction, while the signals at δ 52.3 and 44.4 match one of the minor signals seen in the original reaction mixture and are assigned to the major product's regioisomer (*R*c,*S*c,*S*p)-**121**. Interestingly, in this re–complexation reaction, the regioisomer (*R*c,*S*c,*S*p)-**121** was the major product, while the major product (*R*c,*S*c,*S*p)-**117** in the original hydrophosphination reaction was observed to be the minor product.



(R_c)-**120** (R_c,S_c,S_p)-**117** (R_c,S_c,S_p)-**121**

Scheme 4.8

When the liberated ligand (S_c,R_p)**-119** was recomplexed to the bis(acetonitrile) complex (S_c)**-113** (Scheme 4.8), the ^{31}P NMR spectrum of the crude recomplexation product mixture in $CDCl_3$ exhibited two pairs of doublets at δ 44.9 (d, 1P, J_{pp}= 35.0 Hz), 28.8 (d, 1P, J_{pp}= 35.0 Hz); 47.1 (d, 1P, J_{pp}= 33.1 Hz), 26.1 (d, 1P, J_{pp}= 33.1 Hz) in the ratio of 1.5 : 1, respectively. However, none of them matches the resonance signals observed in the original hydrophosphination reaction.



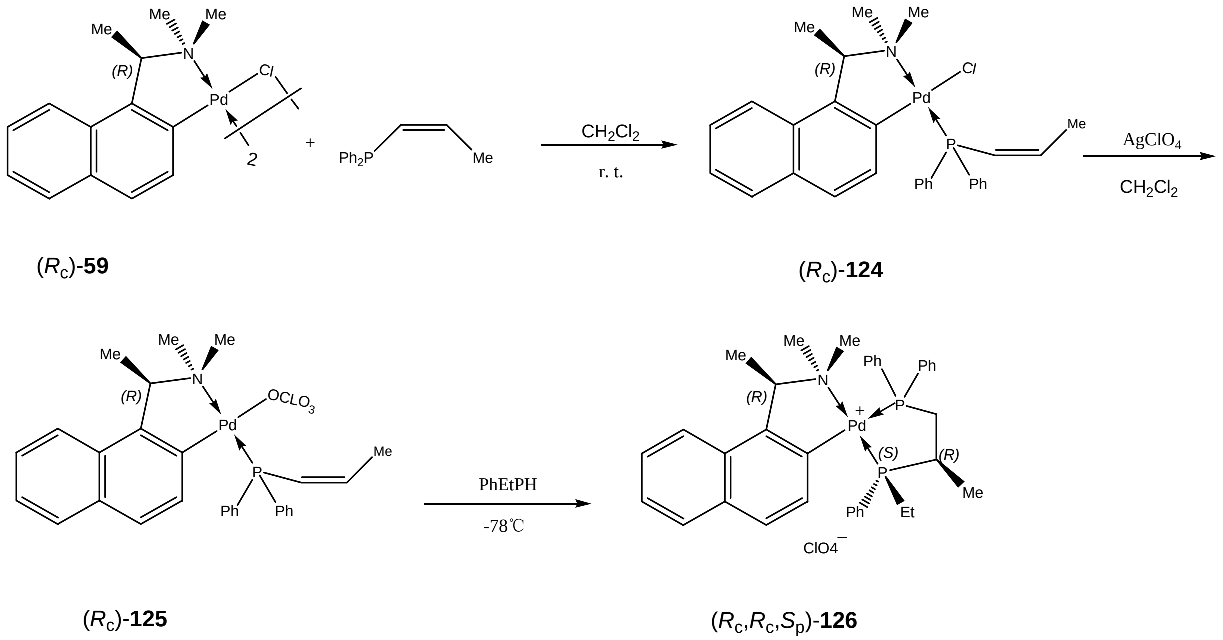
(S_c)-**113** (S_c,S_c,S_p)-**122** (S_c,S_c,S_p)-**123**

Scheme 4.9

4.2.3 Hydrophosphination of (*Z*)-Diphenyl-1-propenylphosphine

4.2.3.1 Synthesis of Complex (R_c,R_c,S_p)-126

As illustrated in Scheme 4.10, (*Z*)-diphenyl-1-propenylphosphine was first coordinated to (R_c)**-59** regioselectively to form the neutral complexes (R_c)**-124**.[197] When the chloro complex (R_c)**-124** was used, no hydrophosphination reaction was detected and no reaction between the free (*Z*)-diphenyl-1-propenylphosphine and PhEtPH was observed, either. Therefore, the kinetically stable chlorine-palladium bond of complex (R_c)**-124** was cleaved by treatment with silver perchlorate to give the kinetically labile perchlorato complex (*R*$_c$)-**125.** Complexes (*R*$_c$)-**125** was not isolated, but was subsequently treated with PhEtPH at −78 ℃ for 12 hours.



Scheme 4.10

Prior to purification, the $^{31}P\{^1H\}$NMR spectrum of crude reaction mixture in $CDCl_3$ exhibited three pairs of doublets at δ 67.7 (d, 1P, J_{pp}= 26.6 Hz), 34.9 (d,1P, J_{pp}=26.6 Hz); 71.1 (d, 1P, J_{pp}= 30.4 Hz), 34.4 (d, 1P, J_{pp}= 30.4 Hz); 51.7 (d, 1P, J_{pp}= 30.4 Hz), 45.6 (d, 1P, J_{pp}= 30.4 Hz); 65.8 (d, 1P, J_{pp}= 30.4 Hz), 30.4 (d, 1P, J_{pp}= 30.4 Hz) in the ratio of 24:13:2:1, respectively. After purified by silica gel column chromatography (acetone–hexane 1:6), only the major product (*R*$_c$,*R*$_c$,*S*$_p$)-**126** was obtained. Complex (*R*$_c$,*R*$_c$,*S*$_p$)-**126** then crystallized from dichlomethane–diethylether as light yellow crystals in 40% yield (Scheme 4.9)

4.2.3.2 X-ray Structural Analysis of Complex (*R*$_c$,*R*$_c$,*S*$_p$)-126

The single crystal X-ray diffraction analysis of the complex (*R*$_c$,*R*$_c$,*S*$_p$)-**126** revealed that the expected five–membered diphosphine chelate had been formed (Figure 4.3). Two new stereogenic centers at P (1) and C (17) were generated, which adopt the *S* and *R* absolute configuration respectively. While the absolute configuration of the stereocenters at C(11) remained unchanged. The X-ray analysis also showed that this hydrophosphination reaction is highly regioselective, as the ethylphenylphosphino group was added to the *β*–carbon of the vinylphosphines to form five–membered chelate ring exclusively.

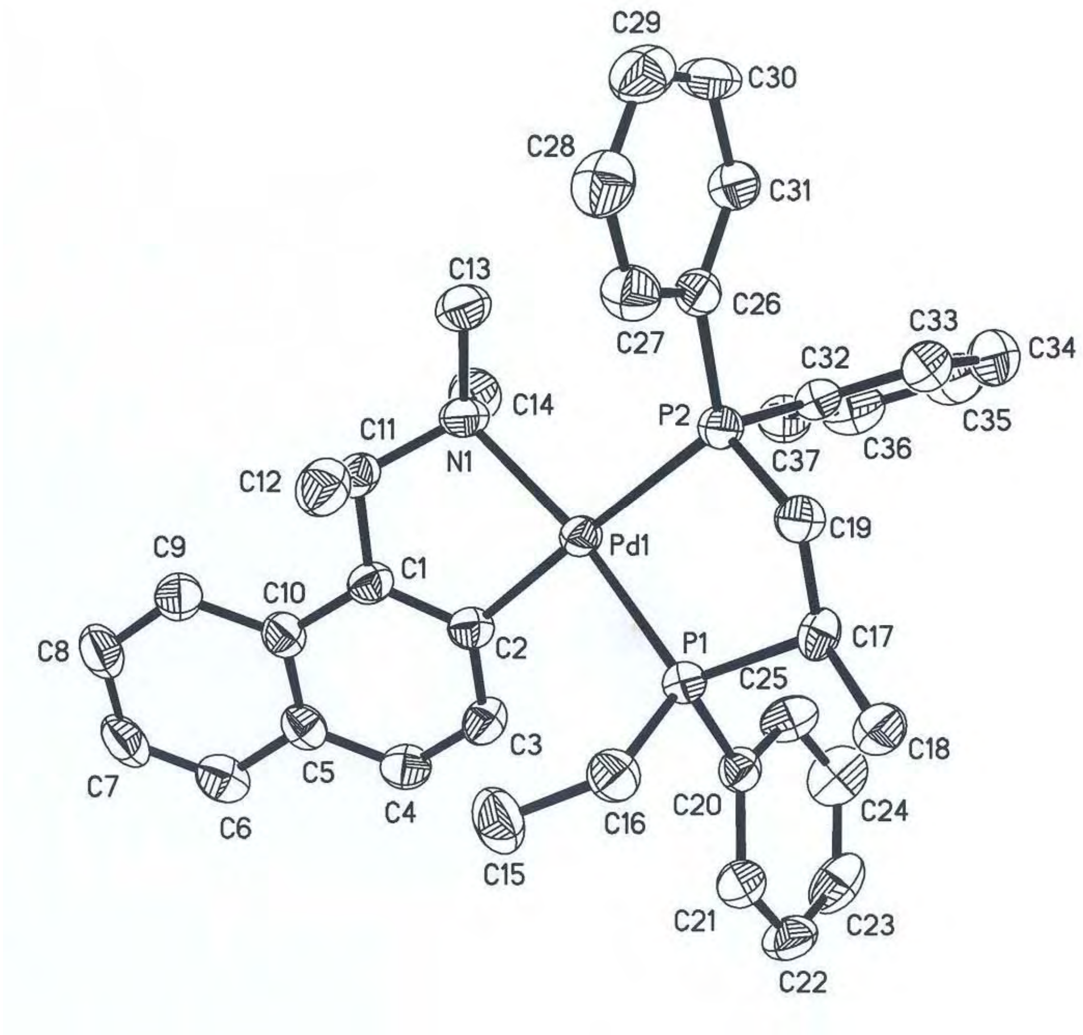


Figure 4.3 Molecular Structure of Complex (R_c,R_c,S_p)-**126**

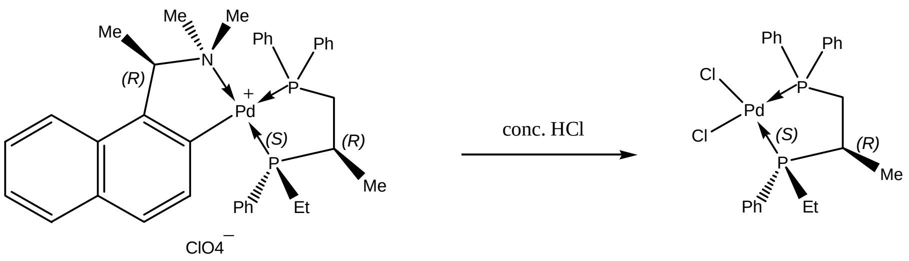
The geometry at palladium is distorted square planar with angles at palladium in the ranges 79.2 (2)–102.1(9) and 170.3(1)–177.1(1)˚. The Pd–P(1) and Pd–P(2) bond distances are 2.265(1) and 2.346 (1) Å respectively, with the bond trans to the carbon of the naphthylamine auxiliary being longer by 0.081 Å. This indicates that the phosphorous atoms have quite different donor abilities.[212] Selected bond distances and angles of complex (R_c,R_c,S_p)-**126** are given in Table 4.3.

Table 4.3 Selected bond distances (Å) and angles (°) of complex (R_c,R_c,S_p)-**126**

Pd(1)–C(2)	2.053(4)	C(2)–Pd(1)–P(1)	95.2 (2)
Pd(1)–N(1)	2.139(3)	N(1)–Pd(1)–P(1)	170.3(1)
Pd(1)–P(1)	2.265(1)	C(2)–Pd(1)–P(2)	177.1(1)
Pd(1)–P(2)	2.346 (1)	N(1)–Pd(1)–P(2)	102.1(9)
P(1)–C(17)	1.857(4)	P(1)–Pd(1)–P(2)	83.9 (4)
P(2)–C(19)	1.827(4)	C(17)–P(1)–Pd(1)	110.5(1)
C(17)–C(19)	1.526(6)	C(19)–P(2)–Pd(1)	106.9(1)
C(17)–C(18)	1.537(6)	C(19)–C(17)–P(1)	109.5(3)
C(2)–Pd(1)–N(1)	79.2 (2)	C(17)–C(19)–P(2)	108.8(3)

4.2.3.3 Removal of the Chiral Auxiliary

As showed in Scheme 4.11, the chiral naphthylamine auxiliary in (R_c,S_c,S_p)-**126** can be removed chemoselectively from the palladium template by treatment with concentrated hydrochloric acid in dichloromethane. The chiral auxiliary was recovered quantitatively from the mother liquor after treatment with base. On the other hand, the neutral dichloro complex (R_c,S_p)-**127** was obtained efficiently as stable white crystals in 89.5% yields. The $^{31}P\{^1H\}$ NMR spectrum of the dichloro complex (S_c,S_p)-**127** in $CDCl_3$ exhibited a pair of doublets at δ 80.8 (d, 1P, J_{pp}= 6.0 Hz) and 58.9 (d, 1P, J_{pp}= 6.6 Hz).

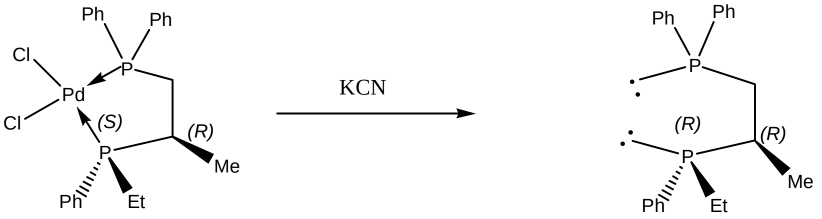


(R_c,R_c,S_p)-**126** (R_c,S_p)-**127**

Scheme 4.11

4.2.3.4 Liberation and Optical Puritiy of (R_c,R_p)-128

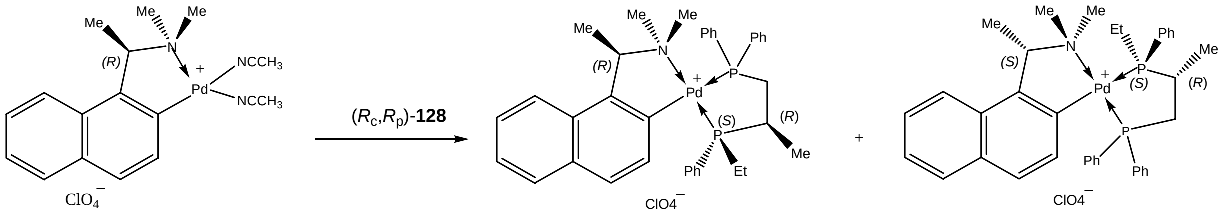
By treatment of the dichloro complex (R_c,R_p)**-127** with saturated aqueous potassium cyanide in dichloromethane at room temperature for 2 hours, the optically pure diphosphine ligand (R_c,R_p)**-128** was liberated successfully (Scheme 4.12). The free ligand (R_c,R_p)**-128** was obtained as white solid in 84% yield, $[\alpha]_D$ = +92.6° (c 0.2., CH_2Cl_2). The $^{31}P\{^1H\}$ NMR spectrum of the free diphosphine ligand (R_c,R_p)**-128** in CDCl3 exhibited a pair of doublets at δ –0.38 (d, 1P, J_{pp}= 18.4 Hz) and –20.5 (d, 1P, J_{pp}=18.4 Hz).



(R_c,S_p)-**127** (R_c,R_p)-**128**

Scheme 4.12

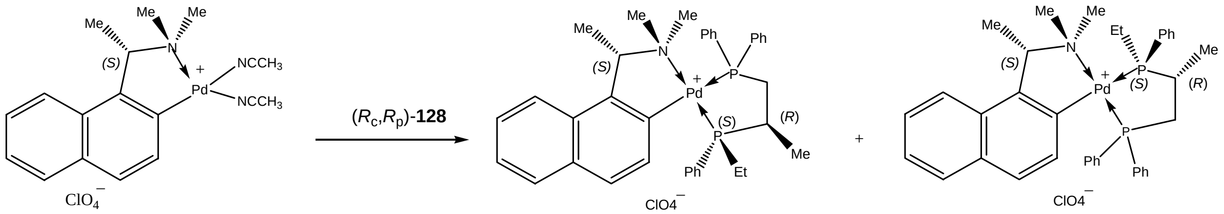
The optical purity of the liberated ligand (R_c,S_p)**-128** was established by subsequent re–complexation to the bis(acetonitrile) complex (R_c)**-120** (Scheme 4.13). The ^{31}P NMR spectrum of the crude recomplexation product mixture in $CDCl_3$ exhibited two pairs of doublets at δ 51.7 (d, 1P, J_{pp}= 30.4 Hz), 45.6 (d, 1P, J_{pp}= 30.4 Hz); 67.7 (d, 1P, J_{pp}= 26.6 Hz), 34.9 (d, 1P, J_{pp}= 26.6 Hz) in the ratio of 2 : 1, respectively. The resonance signals at δ 67.7 and 34.9 are identical to those observed for the major product (R_c,R_c,S_p)**-126** in the original hydrophosphination reaction, while the signals at δ 51.7 and 45.6 match one of the minor signals seen in the original reaction mixture and are assigned to the major product's regioisomer (*R*$_c$,*R*$_c$,*S*$_p$)**-129**.



(*R*$_c$)-**120** (*R*$_c$,*R*$_c$,*S*$_p$)-**126** (*R*$_c$,*R*$_c$,*S*$_p$)-**129**

Scheme 4.13

When the liberated ligand (*R*$_c$,*R*$_p$)**-128** was recomplexed to the bis(acetonitrile) complex (*S*$_c$)**-113** (Scheme 4.14), the ^{31}P NMR spectrum of the crude recomplexation product mixture in CDCl$_3$ exhibited two pairs of doublets at δ 53.2 (d, 1P, J_{pp}= 29.3 Hz), 43.4 (d, 1P, J_{pp}= 29.3 Hz); 65.8 (d, 1P, J_{pp}= 30.4 Hz), 30.4 (d, 1P, J_{pp}= 30.4 Hz) in the ratio of 2 : 1, respectively. The resonance signals at 65.8, 30.4 are identical to one of those observed minor products in the original hydrophosphination reaction. It is noteworthy that in absence any chiral NMR solvent the NMR spectra of enantiomers should exhibit identical resonance signals. Therefore, the minor product at 65.8, 30.4 in the original hydrophosphination reaction should be the enantiomer of re–coordination product (*S*$_c$,*R*$_c$,*S*$_p$)**-129** or (*S*$_c$,*R*$_c$,*S*$_p$)**-130.**



(*S*$_c$)-**113** (*S*$_c$,*R*$_c$,*S*$_p$)-**129** (*S*$_c$,*R*$_c$,*S*$_p$)-**130**

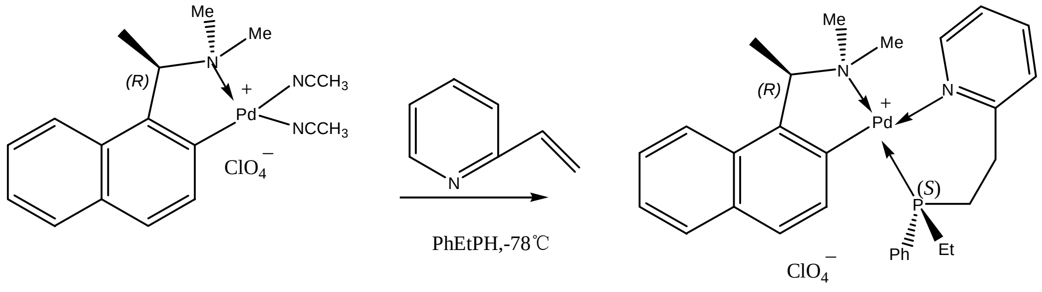
Scheme 4.14

The re–coordination step therefore proves the optical purity of the liberated ligand (*R*$_c$,*R*$_p$) **-128** and also assists in identifying the minor isomeric complexes generated directly from the hydrophosphination reaction.

4.2.4 Hydrophosphination of 2-Vinylpyridine

4.2.4.1 Synthesis of Complex (R_c, S_p)-131

As shown in Scheme 4.15, bis(acetonitrile) palladium complex (R_c)-**120** was allowed to dissolve in dichloromethane first, following by treatment with PhEtPH and 2-Vinylpyridine at –78℃ for 1 day. Prior to purification, the ^{31}P{^{1}H}NMR spectrum of crude reaction mixture in $CDCl_3$ exhibited two singlet at δ 33.0, 34.3 in the ratio 7:5.8. After purified by silica gel column chromatography (acetone–hexane 1:6), only the major product (R_c, S_p)-**131** was obtained. Complex (R_c, S_p)-**131** then crystallized from dichlomethane–diethylether as white crystals in 49.5％yield .



(R_c)-**120**

(R_c,S_p)-**131**

Scheme 4.15

4.2.4.2 X-ray Structural Analysis of Complex (R_c,S_p)-131

The single crystal X-ray diffraction analysis of the complex (R_c,S_p)-**131** revealed that the expected hydrophosphination product with six–membered chelate has been formed (Figure 4.4). The phosphorus donor atom is coordinated regiospecifically in the position *trans* to the naphthylamine–*N* donor atom. A new stereogenic center adopting *S* absolute configuration was formed at P(1) while absolute configuration of the stereocenter at C(11) remained unchanged. The X–ray analysis also showed that this hydrophosphination reaction is highly regioselective, as the ethylphenylphosphino group was added to the *β*–carbon of the vinylphosphines to form six–membered chelate ring exclusively.

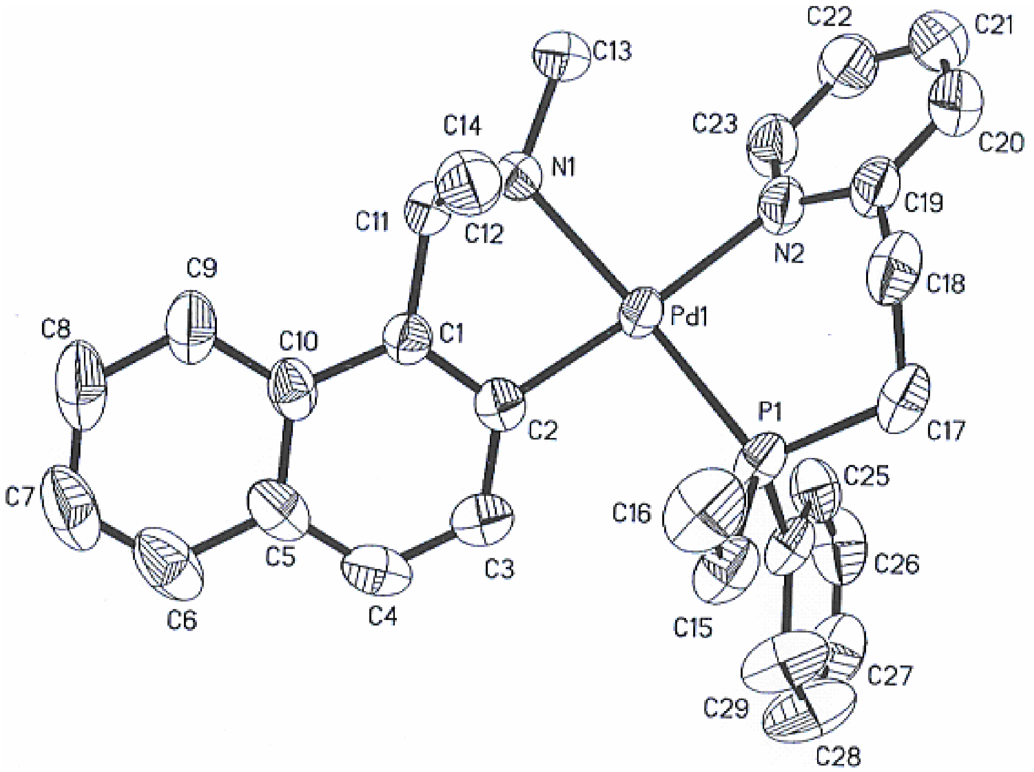


Figure 4.4 Molecular Structure of Complex (R_{c}, S_{p})-**131**

The geometry at palladium is distorted square planar with angles at palladium in the ranges 80.9(1)–95.0 (1) and 167.8(8)–175.5(1)°. The newly formed Pd–N(2) bond distance [2.143(3)] Å is typical. Table 4.4 shows selected bond distances and angles of complex ($R_{\mathrm{c},}S_{\mathrm{p},}$)-**131**.

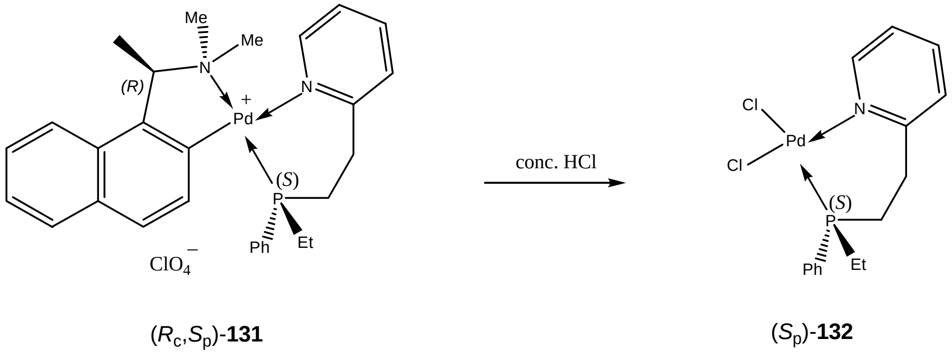
Table 4.4 Selected bond distances (Å) and angles (°) of complex (R_{c}, S_{p})-**131**

Pd(1)–C(2)	1.994(3)	N(2)–Pd(1)–N(1)	95.0 (1)
Pd(1)–N(1)	2.144(3)	C(2)–Pd(1)–P(1)	93.5(1)
Pd(1)–N(2)	2.143(3)	N(2)–Pd(1)–P(1)	90.9 (8)
Pd(1)–P(1)	2.241 (8)	N(1)–Pd(1)–P(1)	167.8(9)
P(1)–C(17)	1.829(4)	C(17)–P(1)–Pd(1)	106.5(1)
C(17)–C(18)	1.552(6)	C(19)–N(2)–Pd(1)	121.5(3)

C(18)–C(19)	1.484(6)	C(18)–C(2)–P (1)	113.2(2)
C(2)–Pd(1)–N(2)	175.5(1)	C(19)–C(18)–C(17)	110.9(3)
C(2)–Pd(1)–N(1)	80.9(1)	N(2)–C(19)–C(18)	117.5(3)

4.2.4.3 Removal of the Chiral Auxiliary

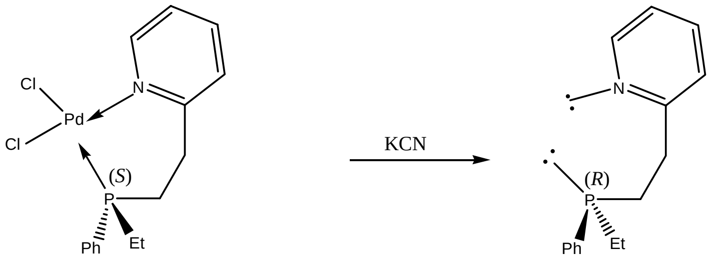
The chiral naphthylamine auxiliary in (*R*$_c$,*S*$_p$)-**131** can be removed chemoselectively from the palladium templates by treatment with concentrated hydrochloric acid in dichloromethane (Scheme 4.16). The neutral dichloro complex (*S*$_p$)-**132** was obtained efficiently as stable yellow crystals in 90% yields. The $^{31}P\{^1H\}$ NMR spectrum of the dichloro complex (*S*$_p$)-**132** in $CDCl_3$ exhibited singlet at δ 31.1.



Scheme 4.16

4.2.3.4 Liberation and Optical Purities of (*R*$_p$)-133

By treatment the dichloro complex (*S*$_p$)-**132** with saturated aqueous potassium cyanide in dichloromethane at room temperature for 1 hour, the optically pure diphosphine ligand (*R*$_p$)-**133** can be liberated successfully (Scheme 4.14). The free ligand (*R*$_p$)-**133** was obtained as air sensitive white solid in 80.5% yield, $[\alpha]_D$ = –26.1° (c 0.2, CH_2Cl_2). The $^{31}P\{^1H\}$ NMR spectrum of the free diphosphine ligand (*R*$_p$)-**133** in $CDCl_3$ exhibited a singlet at δ –18.5.

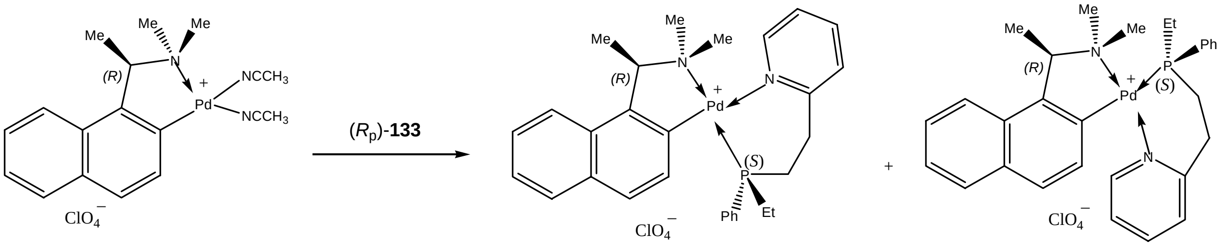


(S_p) - **132**

(R_p) - **133**

Scheme 4.17

In order to confirm the optical purity of the liberated ligand and to establish the identity of the hydrophosphination products, free ligand (R_p)-**133** was re–coordinated to bis(acetonitrile) complex (R_c)-**120** and (S_c)-**113** separately. When free ligand (R_p)-**133** was re–complexed to bis(acetonitrile) complex (R_c)-**120**, the ^{31}P NMR spectrum of the crude reaction mixture showed two sharp singlets at δ 33.0 and 25.1 in the ratio 5:1. The resonance signals at δ 33.0 is identical to that recorded for the major product (R_c, S_p)-**131** in the original hydrophosphination reaction. However, the signals at δ 25.1 is not present in the original hydrophosphination reaction and is assigned to the major product's regioisomer (R_c, S_p)-**134** (Scheme 4.18).



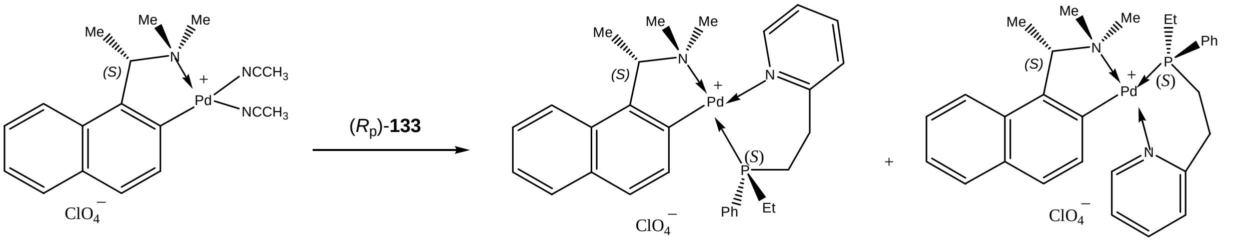
(R_c)-**120**

(R_c,S_p)-**131**

(R_c,S_p)-**134**

Scheme 4.18

When liberated ligand (R_p)-**133** was re–complexed to bis(acetonitrile) complex (S_c)-**113** (Scheme 4.19), the ^{31}P NMR spectrum of the crude reaction mixture showed only one singlet at δ 34.3, which matches that resonance signal of minor product observed in the original hydrophosphination reaction. In the absence of any chiral NMR solvent, the NMR spectra of enantiomers should exhibit identical resonance signals. Therefore, the minor product in the original hydrophosphination reaction should be the enantiomer of re–coordination product (S_c,S_p)-**135** or (R_c,S_p)-**136.**



(S_c)-**113**

(S_c,S_p)-**135**

(S_c,S_p)-**136**

Scheme 4.19

The re–coordination step therefore proves the optical purity of the liberated ligand (R_p) **-130** and also assists in identifying the minor isomeric complex generated directly from the hydrophosphination reaction.

4.3 Conclusions

In summary, in this chapter the chiral organopalladium template promoted asymmetric hydrophosphination reactions between different vinylphosphines and ethylphenylphosphine has been demonstrated. Four optically pure phosphine ligands were obtained. The reactions show high regio– and stereoselectivities under mild reaction conditions, with ethylphenylphosphino group was always added to the *β*–carbon of the vinylphosphines to form five– or six–membered chelate ring exclusively and the ethylphenylphosphino group occupied a position *trans* to the NMe_2 group of the chiral organopalladium template.

It is important to note that, in theory, PhEtPH is a chiral molecule. However, as typical secondary phosphine, the inversion barrier for PhEtPH is low at room temperature. Thus the chiral template is able to control the stereo selectivity in the product formation despite the fact that the racemic form of PhEtPH is used as the starting material.

4.4 Experimental

Reactions involving air sensitive compounds were performed under a positive pressure of purified nitrogen. NMR spectra were recorded at 25 ^{o}C on Bruker ACF 300 and AMX500 spectrometers. Optical rotations were measured on the specified solution in a 0.1dm cell at 25 ^{o}C with a Perkin–Elmer Model 341 polarimeter. Melting points were determined on a Büchi melting point B–540. Elementary analyses were performed by the Elemental Analysis Laboratory of the Department of Chemistry at the National University of Singapore.

Synthesis of {(S_c)-1-[1-(dimethylamino)ethyl]naphthyl-C^2,N}[(R_p)-1-ethylphenylphosphino-2-diphenylphosphinoethane-P^1,P^2]palladium(II)perchlorate, (S_c,R_p) -110

To a solution of the complex (S_c)-**108** (0.1 g, 0.181 mmol) in dichloromethane, silver perchlorate (0.045 g, 0.217 mmol) in water (5mL) was added and stirred vigorously at room temperature for 30 minutes. The mixture was filtered through celite, washed with water and dried with magnesium sulphate. The mixture was then degassed and cooled to -78℃. After that ethylphenylphosphine (0.025 g, 0.181 mmol) was added and the reaction mixture was stirred for 18h.

Upon completion, the solvent was removed to give dark brown residue which was purified by column chromatography (with an eluting gradient starting from hexane: acetone 8:1) give the products as white solids. Recrystallization of the crude product from acetone–hexane gave pure (S_c, R_p)-**110** as white crystals: m.p. 267℃ ; $[\alpha]_D$ +161°(c 0.5, CH_2Cl_2); 0.027 g (20% yield).Anal. Calcd. for $C_{36}H_{40}ClNO_4P_2Pd$: C, 57.3; H, 5.3; N, 1.9. Found: C, 57.2; H, 5.3; N, 1.8. $^{31}P\{^1H\}$ NMR($CDCl_3$): δ 68.4 (d, J_{PP} = 26.6 Hz), 42.7 (d, J_{PP} = 22.8 Hz).

Synthesis of [(*R*$_p$)-dichloro-(1-ethylphenylphosphino-2-diphenylphosphino) ethane-*P*^{1},*P*^{2}] palladium(II), (*R*$_p$)-111

Concentrated hydrochloric acid (5 mL) was added to a solution of (*S*$_c$,*S*$_p$)-**110** (0.1 g, 0.133 mmol) in dichloromethane (15 mL). The reaction mixture was stirred vigorously at room temperature for 16 h, washed with water (3 × 20 mL), and dried ($MgSO_4$). Crystallization of the crude product from dichloromethane–diethyl ether gave the dichloro complex as white crystals: m.p. 253℃;$[\alpha]_D$ +43°(c 0.2, CH_2Cl_2); 0.063 g (89% yield). Anal. Calcd. for $C_{22}H_{24}Cl_2P_2Pd$: C, 50.1; H, 4.6. Found: C, 50.0; H, 4.4. $^{31}P\{^1H\}$ NMR($CDCl_3$): δ 73.7 (d,1P, J_{pp}= 11.4Hz), 63.8 (d,1P, J_{pp}=11.4Hz); ^1H NMR (CDCl3): δ 1.28 (dt, 3H, $^3J_{PH}$ = 20.5 Hz, $^3J_{HH}$ = 7.4 Hz, CH$_2$*Me*), 1.88–2.01(m, 1H, PhEtP*CHH′*), 2.15–2.23 (m, 1H, PhEtP*CH*H′), 2.27–2.40 (m, 2H, *CH*$_2$Me), 2.50–2.80(m, 2H, Ph$_2$P*CH*$_2$), 7.36–7.64(m, 15H, aromatics).

Liberation of (S)-1-ethylphenylphosphino-2-diphenylphosphino ethane, (*S*$_p$)-112

A solution of (*R*$_p$)-**111** (0.03 g, 0.056 mmol) in dichloromethane (10 mL) was stirred vigorously with a saturated aqueous solution of potassium cyanide (1 g) for 2 h. The organic layer was separated, washed with water (3 × 10 mL), and dried ($MgSO_4$). Upon removal of solvent, white solid was obtained: $[\alpha]_D$ –98.7°(c 0.2, CH_2Cl_2); 0.017 g (83% yield). $^{31}P\{^1H\}$NMR ($CDCl_3$): δ –12.1 (d, 1P, J_{pp}= 27.8 Hz), –15.2 (d, 1P, J_{pp}=27.8 Hz).

Hydrophosphination of (*E*) Diphenyl-1-propenylphosphine

Synthesis of {(*R*$_c$)-1-[1-(dimethylamino)ethyl]naphthyl-*C*^{2},*N*} [(*S*$_c$,*S*$_p$)-1-ethylphenylphosphino-1-methyl-2-diphenylphosphinoethane-*P*^{1},*P*^{2}]palladium(II) perchlorate, (*R*$_c$,*S*$_c$,*S*$_p$)-117

A solution of complex (*R*$_c$)-**115** (0.1 g, 0.177 mmol) in dichloromethane was treated with aqueous silver perchlorate (0.044 g, 0.212mmol) for 30 mins. The reaction mixture was subsequently washed with water (3×20 ml) and dried with magnesium sulphate. The mixture was then degassed and cooled to –78℃. After that ethylphenylphosphine (0.025 g, 0.181 mmol) was added and the reaction mixture was stirred for 12 h.

Upon completion, the solvent was removed to give dark brown residue which was purified by column chromatography (with an eluting gradient starting from hexane: acetone 6:1) give the products as white solids. Recrystallization of the crude product from acetone–hexane gave pure (R_c,S_c,S_p)-**117** as light yellow crystals. m.p. 239℃; $[\alpha]_D$ –8.6° (c 0.2, CH_2Cl_2); 0.082 g (60% yield). Anal. Calcd. for $C_{37}H_{42}ClNO_4P_2Pd$: C, 57.8; H, 5.5; N, 1.8. Found: C, 57.7; H, 5.3; N, 1.7. $^{31}P\{^1H\}$ NMR($CDCl_3$): δ 69.7(d,1P, J_{pp}= 34.2 Hz), 30.0(d,1P, J_{pp}= 34.2Hz); ^1H NMR (CDCl3): δ 1.09 (dd, 3H, $^3J_{PH}$ = 11.1 Hz, $^3J_{HH}$ = 6.0 Hz, PCH*Me*), 1.18 (dt, 3H, $^3J_{PH}$ =13.9 Hz, $^3J_{HH}$ = 7.4 Hz, CH_2*Me*), 2.03 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH*Me*), 2.07–2.13 (m, 1H, C*HH′*), 2.29–2.39 (m, 1H, C*HH′*), 2.45 (d, 3H, $^4J_{PH}$ = 0.81 Hz, NMe_{ax}), 2.48–2.59 (m, 2H, CH_2Me), 2.69 (dd, 3H, $^4J_{PH}$ =3.0 Hz , $^4J_{HH}$ = 2.6 Hz, NMe_{eq}), 4.51 (qn, 1H, $^4J_{PH}$ = $^3J_{HH}$ = 6.1 Hz, *CH*Me), 6.73–6.80 (m, 1H, P*CH*Me), 7.35–8.01 (m, 21H, aromatics).

Synthesis of [(S_c,S_p)-dichloro-(1-ethylphenylphosphino-1-methyl-2- diphenylphosphino) ethane-P^1,P^2] palladium(II), (S_c, S_p)-118

A solution containing mixture of complexes (R_c,S_c,S_p)-**117** (0.1 g, 0.189 mmol) in dichloromethane was stirred vigorously with excess concentrated hydrochloric acid for 16h. The reaction mixture was then washed with water (3 × 10 mL), and dried ($MgSO_4$). Crystallization of the crude product from dichloromethane–diethyl ether gave the dichloro complex (S_c, S_p)-**118** as white crystals: m.p. 221℃; $[\alpha]_D$ –100°(c 0.2., CH_2Cl_2); 0.091 g (88% yield). Anal. Calcd. for $C_{23}H_{26}Cl_2P_2Pd$: C, 51.0; H, 4.8. Found: C, 50.9; H, 4.6. $^{31}P\{^1H\}$ NMR($CDCl_3$): δ 68.4(d, J_{PP} = 26.6 Hz), 42.7(d, J_{PP} = 22.8 Hz); ^1H NMR (CDCl3): δ 1.13 (dd, 3H, $^3J_{PH}$ = 9.2 Hz, $^3J_{HH}$ = 6.1 Hz, CH*Me*), 1.40 (dt, 3H, $^3J_{PH}$ = 18.2 Hz, $^3J_{HH}$ = 7.5 Hz, CH_2*Me*), 2.11–2.31 (m, 2H, CH_2Me), 2.39–2.49 (m, 1H, C*HH′*), 2.59–2.67 (m, 1H, C*H*H′), 2.76–2.93

(m, 1H, *CH*Me), 7.43–8.13 (m, 15H, aromatics).

Liberation of (S_c,R_p)-1-ethylphenylphosphino-1-methyl-2-diphenylphosphinoethane, (S_c,R_p)-119

To the solution of dichloro complex (S_c,S_p)-**118** (0.03g, 0.055mmol) in dichloromethane (10mL), an aqueous solution of potassium cyanide (1 g) was added, and the resulting solution was stirred vigorously for 2h. The organic layer was separated, washed with water (3 × 20 mL), and dried ($MgSO_4$). Upon removal of solvent, white solid was obtained: $[\alpha]_D$ –118.4°(c 0.2, CH_2Cl_2); 0.016 g (80% yield). $^{31}P\{^1H\}$ NMR($CDCl_3$): δ –0.66 (d,1P, J_{pp}= 22.1 Hz), –19.7 (d,1P, J_{pp}= 20.2 Hz).

Hydrophosphination of (*Z*)-Diphenyl-1-propenylphosphine

Hydrophosphination of (*Z*)-Diphenyl-1-propenylphosphine was performed similarly with Hydrophosphination of (*E*)-Diphenyl-1-propenylphosphine.

Synthesis of {(R_c)-1-[1-(dimethylamino)ethyl]naphthyl-C^2,*N*}[(R_c,S_p)-1-ethylphenylphosphino-1-methyl-2-diphenylphosphinoethane-P^1,P^2]palladium(II)perchlor-ate, (R_c,R_c,S_p)-126

light yellow crystals: m.p. 243℃ ; $[\alpha]_{365}$ +172°(c 0.25, CH_2Cl_2); 0.028 g, (40% yield). Anal. Calcd. for $C_{37}H_{42}ClNO_4P_2Pd$: C, 57.8; H, 5.5; N, 1.8. Found: C, 56.6; H, 5.2; N, 1.7. $^{31}P\{^1H\}$ NMR($CDCl_3$): δ 67.7 (d,1P, J_{pp}= 26.6 Hz), 34.9 (d,1P, J_{pp}= 26.6 Hz); ^1H NMR (CDCl3): δ 1.25 (dd, 3H, $^3J_{PH}$ =14.1 Hz, $^3J_{HH}$ = 7.7 Hz, PCH*Me*), 1.31 (dt, 3H, $^3J_{PH}$ =15.1 Hz, $^3J_{HH}$ = 7.7 Hz, CH_2*Me*), 1.87 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH*Me*), 2.20-2.33 (m, 2H, PCH_2), 2.44 (dd, 3H, $^4J_{PH}$ = 3.3 Hz, $^4J_{HH}$ = 3.2 Hz, NMe_{eq}), 2.56–2.72 (m, 2H, CH_2Me), 2.77 (br, 3H, NMe_{ax}), 4.42 (qn, 1H, $^4J_{PH}$ = $^3J_{HH}$ = 5.9 Hz, *CH*Me), 6.71–6.78 (m, 1H, P*CH*Me), 7.22–7.94 (m, 21H, aromatics).

Synthesis of [(R_c,S_p)-dichloro-(1-ethylphenylphosphino-1-methyl-2- diphenylphosphino) ethane-P^1,P^2] palladium(II), (R_c, S_p)-127

white crystals: m.p. 220；[α]$_D$ +140° (c 0.2, CH_2Cl_2); 0.06 g (90% yield). Anal. Calcd. for $C_{23}H_{26}Cl_2P_2Pd$: C, 51.0; H, 4.8. Found: C, 50.5; H, 4.5. $^{31}P\{^1H\}$ NMR($CDCl_3$): δ 80.8(d,1P, J_{pp}= 6.0 Hz) and 58.9(d,1P, J_{pp}= 6.6 Hz); ^1H NMR (CDCl3): δ 1.22 (dd, 3H, $^3J_{PH}$ = 14.6 Hz, $^3J_{HH}$ = 7.1 Hz, CH*Me*), 1.41 (dt, 3H, $^3J_{PH}$ = 11.3 Hz, $^3J_{HH}$ = 7.7 Hz, CH_2*Me*), 2.38–2.57 (m, 2H, CH_2Me), 2.59–2.68 (m, 2H, PCH_2), 2.70–2.80 (m, 1H, *CH*Me), 7.38–7.99 (m, 15H, aromatics).

Liberation of (*R*$_c$,*R*$_p$)-1-ethylphenylphosphino-1-methyl-2-diphenylphosphino ethane, (*R*$_c$,*R*$_p$)-128

white solid: [α]$_D$ +92.6°(c 0.2, CH_2Cl_2); 0.017 g (84% yield). $^{31}P\{^1H\}$ NMR($CDCl_3$): δ –0.38 (d, 1P, J_{pp}= 18.4 Hz), –20.5 (d, 1P, J_{pp}=18.4 Hz).

Hydrophosphination of 2-Vinylpyridine

Synthesis of {(*R*$_c$)-1-[1-(dimethylamino)ethyl]naphthyl-*C*^{2},*N*} [(*S*$_p$)-1-ethylphenylphosphino-2- (2-pyridine) ethane -*N*,*P*] palladium(II) perchlorate, (*R*$_c$, *S*$_p$)-131

To the solution of bis(acetonitrile) palladium complex (*R*$_c$)-**120** (0.6 g, 1.56 mmol) in dichloromethane, PhEtPH (0.2151 g, 1.56 mmol) and 2-Vinylpyridine (0.168 mL, 1.56 mmol) were added subsequently. The reaction mixture then was stirred at –78℃ for 1 day. Upon completion, the solvent was removed to give dark brown residue which was purified by column chromatography (with an eluting gradient starting from hexane: acetone 6:1) give the products as white solids. Recrystallization of the crude product from acetone–hexane gave pure (*R*$_c$, *S*$_p$)-**131** as white crystals: m.p. 257℃； [α]$_D$ –11.2° (c 0.2, CH_2Cl_2); 0.5 g (50％yield). Anal. Calcd. for $C_{29}H_{34}ClN_2O_4PPd$: C, 53.8; H, 5.3; N, 4.3. Found: C, 53.5; H, 5.2; N, 4.0. $^{31}P\{^1H\}$ NMR($CDCl_3$): δ 33.0; ^1H NMR (CDCl3): δ 1.07 (dt, 3H, $^3J_{PH}$ = 12.2 Hz, $^3J_{HH}$ = 7.7 Hz, CH_2*Me*), 1.83–1.96 (m, 1H, *CHH′*), 2.08 (d, 3H, $^4J_{PH}$ = 6.2 Hz, N*Me*), 2.23–2.33 (m, 2H, P*CH₂*), 2.49 (d, 3H, $^4J_{PH}$ = 2.8Hz, N*Me′*), 2.57–2.69 (m, 1H, *CH*H′), 3.36–3.70 (m, 2H, *CH₂*Me), 4.44 (qn, 1H, $^4J_{PH} = {}^3J_{HH}$ = 6.2Hz, *CH*Me), 7.04–7.98 (m, 15H, aromatics).

Synthesis of {(S_p)-dichloro-[1-ethylphenylphosphino-2-(2-pyridine)ethane]} palladium(II), (S_p)-132

A solution containing mixture of complexes (R_c, S_p)-**131** (0.1 g, 0.154 mmol) in dichloromethane was stirred vigorously with excess concentrated hydrochloric acid for 16h. The reaction mixture was then washed with water (3 ×10 mL), and dried ($MgSO_4$). Crystallization of the crude product from dichloromethane–diethyl ether gave the dichloro complex (S_p)-**131** as white crystals: m.p. 235℃ ; $[\alpha]_D$ –196.7°(c 0.31, CH_2Cl_2); 0.059 g (90% yield). Anal. Calcd. for $C_{15}H_{18}Cl_2NPPd$: C, 42.8; H, 4.3; N, 3.3 Found: C, 42.7; H, 4.3; N, 3.4. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 31.1; ^1H NMR (CDCl3): δ 1.34 (dt, 3H, $^3J_{PH}$ = 12.4 Hz, $^3J_{HH}$ = 7.2 Hz, CH_2*Me*), 1.77–1.91 (m, 1H, *CHH′*), 2.16–2.38 (m, 2H, P*CH₂*), 2.62–2.78 (m, 1H, *CH*H′), 3.34–3.54 (m, 2H, *CH₂*Me), 7.21–7.82 (m, 9H, aromatics).

Liberation of (R_p)-[1-ethylphenylphosphino-2-(2-pyridine)] ethane, (R_p)-133

A solution of (S_p)-**132** (0.03 g, 0.071 mmol) in dichloromethane (10 mL) was stirred vigorously with a saturated aqueous solution of potassium cyanide (1 g) for 2 h. The organic layer was separated, washed with water (3 × 10 mL), and dried ($MgSO_4$). Upon removal of solvent, white solid was obtained:. $[\alpha]_D$ –26.1°(c 0.2., CH_2Cl_2); 0.017 g (81% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ –18.5.

APPENDICES

Table A1–1. Crystal data and structure refinement for (*R*$_c$)-72.

Empirical formula	$C_{26}H_{27}ClNPPd$	
Formula weight	526.31	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 12.6734(5) Å	α = 90°.
	b = 12.7251(5) Å	β = 90°.
	c = 15.6035(7) Å	γ = 90°.
Volume	2516.38(18) $Å^3$	
Z	4	
Density (calculated)	1.389 Mg/m^3	
Absorption coefficient	0.919 mm^{-1}	
F(000)	1072	
Crystal size	0.14 x 0.26 x 0.40 mm^3	
Theta range for data collection	2.07 to 27.49°.	
Index ranges	–16<=h<=16, –15<=k<=16, –20<=l<=16	
Reflections collected	17628	
Independent reflections	5750 [R(int) = 0.0287]	
Completeness to theta = 27.49°	99.8 %	
Absorption correction	Sadabs (Sheldrick, 2001)	
Max. and min. transmission	0.9756 and 0.2616	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	5750 / 0 / 276	
Goodness–of–fit on F^2	1.066	
Final R indices [I>2sigma(I)]	R_1= 0.0326, wR_2 = 0.0710	
R indices (all data)	R_1 = 0.0355, wR_2 = 0.0722	
Absolute structure parameter	0.00(2)	
Largest diff. peak and hole	0.653 and –0.234 e.$Å^{-3}$	

Table A1–2. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for (R_c)-72. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Pd(1)	6152(1)	1180(1)	8665(1)	39(1)
P(1)	7126(1)	381(1)	7670(1)	42(1)
Cl(1)	7533(1)	2358(1)	9027(1)	57(1)
N(1)	5118(2)	1820(1)	9640(1)	49(1)
C(1)	4097(2)	376(2)	9039(2)	45(1)
C(2)	4852(2)	319(2)	8400(2)	42(1)
C(3)	4605(2)	–236(2)	7644(1)	47(1)
C(4)	3651(2)	–722(2)	7537(2)	51(1)
C(5)	2886(2)	–698(2)	8180(2)	55(1)
C(6)	1913(3)	–1238(4)	8140(3)	80(1)
C(7)	1191(3)	–1213(4)	8740(4)	105(2)
C(8)	1363(3)	–628(5)	9482(4)	101(2)
C(9)	2307(3)	–107(3)	9597(3)	72(1)
C(10)	3099(2)	–133(2)	8947(2)	52(1)
C(11)	4387(3)	945(3)	9850(2)	52(1)
C(12)	4896(4)	168(3)	10478(3)	78(1)
C(13)	4506(3)	2656(3)	9173(3)	63(1)
C(14)	5595(3)	2305(4)	10370(3)	76(1)
C(15)	8489(3)	635(3)	7682(2)	52(1)
C(16)	9378(3)	894(3)	7657(2)	63(1)
C(17)	10487(3)	1221(5)	7608(3)	95(2)
C(18)	7084(3)	–998(3)	7743(2)	51(1)
C(19)	6994(3)	–1894(3)	7905(3)	59(1)
C(20)	6830(4)	–2290(3)	8135(4)	91(2)
C(21)	6797(2)	707(2)	6568(2)	42(1)
C(22)	7010(3)	54(3)	5896(2)	63(1)
C(23)	6815(3)	373(4)	5069(3)	80(1)
C(24)	6416(3)	1333(4)	4913(3)	77(1)
C(25)	6165(4)	1993(4)	5569(3)	83(1)
C(26)	6355(3)	1683(3)	6411(3)	66(1)

Table A2–1. Crystal data and structure refinement for (*R*$_c$,*R*$_p$,*R*$_c$)-74.

Empirical formula	$C_{36}H_{41}Cl_2N_2PPdPt$	
Formula weight	963.15	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 11.8696(5) Å	α = 90°.
	b = 14.7315(6) Å	β = 90°.
	c = 22.5613(7) Å	γ = 90°.
Volume	3945.0(3) $Å^3$	
Z	4	
Density (calculated)	1.622 Mg/m^3	
Absorption coefficient	4.205 mm^{-1}	
F(000)	1904	
Crystal size	0.34 x 0.20 x 0.10 mm^3	
Theta range for data collection	1.65 to 27.50°.	
Index ranges	–15<=h<=10, –18<=k<=19, –28<=l<=29	
Reflections collected	28009	
Independent reflections	9062 [R(int) = 0.0338]	
Completeness to theta = 27.50°	100 %	
Absorption correction	Sadabs (Sheldrick, 2001)	
Max. and min. transmission	0.6785 and 0.3289	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	9062 / 0 / 434	
Goodness–of–fit on F^2	0.954	
Final R indices [I>2sigma(I)]	R_1= 0.0310, wR_2 = 0.0624	
R indices (all data)	R_1 = 0.0361, wR_2 = 0.0641	
Absolute structure parameter	0.001(4)	
Largest diff. peak and hole	1.462 and –0.328 e.$Å^{-3}$	

Table A2–2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for (*R*$_c$, *R*$_p$, *R*$_c$)-74. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pt(1)	2453(1)	3410(1)	3104(1)	36(1)
Pd(1)	4359(1)	3499(1)	2089(1)	35(1)
P(1)	4186(1)	3609(1)	3444(1)	38(1)
Cl(1)	3228(1)	2305(1)	2423(1)	49(1)
Cl(2)	3201(4)	3575(1)	1212(1)	68(1)
N(1)	790(3)	3266(3)	2776(2)	52(1)
N(2)	5448(3)	4558(2)	1812(2)	40(1)
C(1)	611(4)	4520(3)	3469(2)	42(1)
C(2)	1663(4)	4248(3)	3657(2)	38(1)
C(3)	2034(4)	4565(3)	4216(2)	44(1)
C(4)	1426(4)	5153(3)	4549(2)	49(1)
C(5)	376(5)	5475(3)	4348(2)	54(1)
C(6)	–237(6)	6138(4)	4664(3)	77(2)
C(7)	–1244(7)	6453(5)	4456(4)	101(3)
C(8)	–1653(6)	6156(6)	3930(4)	107(3)
C(9)	–1107(5)	5504(5)	3600(3)	82(2)
C(10)	–52(4)	5147(4)	3801(2)	53(1)
C(11)	247(4)	4189(4)	2866(2)	55(1)
C(12)	617(5)	4866(4)	2387(2)	69(2)
C(13)	690(5)	2970(5)	2143(3)	85(2)
C(14)	175(5)	2581(4)	3139(3)	70(2)
C(15)	4559(4)	4740(4)	3620(2)	48(1)
C(16)	4758(4)	5501(4)	3726(2)	53(1)
C(17)	4985(6)	6463(4)	3862(3)	79(2)
C(18)	5166(3)	3323(3)	2859(2)	39(1)
C(19)	6204(4)	2948(3)	2985(2)	49(1)
C(20)	6828(5)	2695(5)	3455(3)	83(2)
C(21)	4925(4)	5405(3)	2031(3)	54(1)
C(22)	5495(5)	4598(4)	1154(2)	59(1)
C(23)	7469(5)	5184(3)	1875(2)	57(1)
C(24)	6623(4)	4445 (5)	2067(2)	44(1)

C(25)	7051(4)	3502(3)	1937(2)	43(1)
C(26)	7685(4)	3317(3)	1423(2)	53(1)
C(27)	8057(5)	2445(4)	1302(3)	59(1)
C(28)	7848(4)	1760(4)	1691(3)	62(2)
C(29)	7265(4)	1935(3)	2214(3)	55(1)
C(30)	6848(4)	2799(3)	2335(2)	45(1)
C(51)	4425(5)	3008(4)	4136(2)	53(1)
C(52)	5178(6)	3297(5)	4571(3)	79(2)
C(53)	5371(9)	2774(7)	5068(3)	116(3)
C(54)	4813(10)	1984(6)	5139(3)	126(4)
C(55)	3993(9)	1697(4)	4733(3)	122(4)
C(56)	3847(7)	2210(4)	4228(3)	83(2)

Table A3–1. Crystal data and structure refinement for (*R*$_c$,*S*$_p$,*R*$_c$)-75.

Empirical formula	$C_{36}H_{41}Cl_2N_2PPdPt$	
Formula weight	963.15	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 12.4087(5) Å	α = 90°.
	b = 15.0921(6) Å	β = 90°.
	c = 20.0822(7) Å	γ = 90°.
Volume	3760.9(3) Å^3	
Z	4	
Density (calculated)	1.701 Mg/m^3	
Absorption coefficient	4.411 mm^{-1}	
F(000)	1904	
Crystal size	0.36 x 0.22 x 0.20 mm^3	
Theta range for data collection	1.93 to 27.50°.	
Index ranges	–14<=h<=16, –19<=k<=9, –26<=l<=25	
Reflections collected	26889	
Independent reflections	8610 [R(int) = 0.0441]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Sadabs (Sheldrick, 2001)	
Max. and min. transmission	0.4724 and 0.2996	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	8610 / 0 / 434	
Goodness–of–fit on F^2	0.932	
Final R indices [I>2sigma(I)]	R_1= 0.0346, wR_2 = 0.0678	
R indices (all data)	R_1 = 0.0411, wR_2 = 0.0699	
Absolute structure parameter	0.005(4)	
Largest diff. peak and hole	1.527 and –0.476 e.Å^{-3}	

Table A3–2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for (R_c,S_p,R_c) -74. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pt(1)	3186(1)	6471(1)	1353(1)	31(1)
Pd(1)	1250(1)	5173(1)	1673(1)	33(1)
P(1)	2859(1)	6261(1)	2428(1)	32(1)
Cl(1)	1236(1)	4521(1)	563(1)	50(1)
Cl(2)	1260(4)	6611(1)	1205(1)	41(1)
N(1)	3565(4)	6595(3)	321(2)	38(1)
N(2)	1039(4)	3911(3)	2112(2)	39(1)
C(1)	5243(4)	6095(4)	796(3)	32(1)
C(2)	4799(4)	6355(3)	1386(3)	31(1)
C(3)	5489(4)	6513(4)	1942(2)	38(1)
C(4)	6562(4)	6372(3)	1896(3)	41(1)
C(5)	7038(4)	6061(4)	1302(3)	39(1)
C(6)	8144(5)	5853(4)	1252(3)	48(2)
C(7)	8578(7)	5506(5)	690(4)	53(2)
C(8)	7923(5)	5371(4)	142(3)	52(2)
C(9)	6842(5)	5574(4)	151(3)	45(1)
C(10)	6365(4)	5924(4)	733(3)	35(1)
C(11)	4484(5)	5962(4)	220(3)	38(1)
C(12)	4127(5)	5005(4)	186(3)	54(2)
C(13)	2654(5)	6416(5)	–148(3)	52(2)
C(14)	3955(6)	7511(5)	193(3)	55(2)
C(15)	3035(5)	7253(4)	2882(3)	44(2)
C(16)	3140(6)	7958(4)	3118(3)	52(2)
C(17)	3270(8)	8815(5)	3434(4)	77(2)
C(18)	1514(4)	5804(3)	2538(3)	33(1)
C(19)	863(5)	5852(4)	3066(3)	38(1)
C(20)	1121(5)	6386(5)	3688(3)	49(1)
C(21)	2011(5)	3376(4)	1951(3)	50(2)
C(22)	94(5)	3496(5)	1779(3)	51(2)
C(23)	913(6)	3000(4)	3166(3)	53(1)
C(24)	865(5)	3929 (4)	2859(3)	41(1)

C(25)	–164(5)	4420(4)	3024(3)	41(1)
C(26)	–1132(5)	3963(5)	3107(3)	57(2)
C(27)	–2060(5)	4391(6)	3254(3)	63(1)
C(28)	–2061(5)	5298(6)	3334(3)	62(2)
C(29)	–1111(5)	5770(5)	3278(3)	56(2)
C(30)	–147(5)	5340(4)	3103(3)	40(1)
C(31)	3690(5)	5439(4)	2846(3)	37(1)
C(32)	4080(5)	4749(4)	2492(3)	46(2)
C(33)	4637(6)	4059(5)	2793(4)	60(2)
C(34)	4780(6)	4092(6)	3464(3)	65(2)
C(35)	4423(6)	4802(7)	3825(3)	73(2)
C(36)	3868(6)	2210(4)	4228(3)	83(2)

Table A4–1. Crystal data and structure refinement for (*R*$_c$,*S*$_c$,*S*$_p$,*R*$_c$)-76.

Empirical formula	$C_{39}H_{42}ClN_2OPPdPt$	
Formula weight	948.21	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 10.0183(6) Å	α = 76.251(2)°.
	b = 11.9462(9) Å	β = 81.5450(10)°.
	c = 18.5051(11) Å	γ = 65.2690(10)°.
Volume	1951.1(2) $Å^3$	
Z	2	
Density (calculated)	1.614 Mg/m^3	
Absorption coefficient	4.185 mm^{-1}	
F(000)	938	
Crystal size	0.40 x 0.20 x 0.18 mm^3	
Theta range for data collection	1.91 to 30.04°.	
Index ranges	–14<=h<=14, –16<=k<=16, –25<=l<=25	
Reflections collected	28300	
Independent reflections	20428 [R(int) = 0.0198]	
Completeness to theta = 30.04°	95.0%	
Absorption correction	Sadabs (Sheldrick, 2001)	
Max. and min. transmission	0.5196 and 0.2853	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	20428 / 3 / 874	
Goodness–of–fit on F^2	0.710	
Final R indices [I>2sigma(I)]	R_1= 0.0295, wR_2 = 0.0651	
R indices (all data)	R_1 = 0.0340, wR_2 = 0.0674	
Absolute structure parameter	0.000(2)	
Largest diff. peak and hole	1.424 and –0.426 e.$Å^{-3}$	

Table A4–2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for (R_c,S_c,S_p,R_c)-76. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pt(1)	8395(1)	8843(1)	1370(1)	40(1)
Pd(1)	8520(1)	5732(1)	1358(1)	38(1)
Cl(1)	6115(1)	6005(2)	1085(1)	71(1)
P(1)	9411(1)	6968(1)	2096(1)	39(1)
N(1)	7329(4)	10696(4)	762(2)	49(1)
N(2)	9497(4)	5100(4)	319(2)	47(1)
O(1)	6405(4)	8699(3)	1866(2)	56(1)
C(1)	9799(5)	10074(4)	206(2)	41(1)
C(2)	10130(5)	9055(4)	799(2)	39(1)
C(3)	11644(5)	8286(4)	908(3)	47(1)
C(4)	12735(5)	8546(4)	483(3)	49(1)
C(5)	12414(5)	9598(5)	–106(3)	48(1)
C(6)	13537(6)	9910(6)	–548(4)	61(2)
C(7)	13209(7)	10933(6)	–1111(3)	63(2)
C(8)	11725(7)	11699(5)	–1247(3)	61(1)
C(9)	10629(6)	11439(5)	–846(3)	51(1)
C(10)	10910(5)	10384(4)	–246(2)	42(1)
C(11)	8200(5)	10801(4)	37(3)	47(1)
C(12)	7809(7)	10281(7)	–539(4)	72(2)
C(13)	5744(6)	11067(6)	661(4)	78(2)
C(14)	7397(7)	11588(5)	1195(4)	69(2)
C(15)	7831(5)	6567(4)	2324(2)	43(1)
C(16)	6468(5)	7642(5)	2213(3)	49(1)
C(17)	5042(6)	7540(5)	2517(3)	65(1)
C(18)	10372(5)	5599(4)	1719(2)	40(1)
C(19)	11707(5)	4665(4)	1817(2)	41 (1)
C(20)	12949 (6)	4734(5)	2140(4)	63(1)
C(21)	11985(4)	3442(4)	1618(3)	41(1)
C(22)	12492(5)	2349(4)	2173(3)	52(1)
C(23)	12644(6)	1217(5)	2055(3)	60(1)
C(24)	12325(6)	1119(5)	1379(4)	62(2)

C(25)	11884(6)	2159(5)	823(3)	51(1)
C(26)	11673(5)	3348(4)	930(3)	44(1)
C(27)	11166(6)	4482(4)	317(3)	47(1)
C(28)	11922(7)	4203(6)	–442(3)	69(2)
C(29)	8891(7)	4270(6)	143(4)	73(2)
C(30)	9002(8)	6305(6)	–217(3)	77(2)
C(31)	10156(5)	6966(4)	2937(3)	45(1)
C(32)	10739(7)	7833(6)	2947(3)	64(1)
C(33)	11296(8)	7808(7)	3598(4)	77(2)
C(34)	11257(7)	6975(7)	4230(3)	76(2)
C(35)	10634(7)	6123(7)	4235(3)	74(2)
C(36)	10104(6)	6121(5)	3584(3)	60(1)

Table A5–1. Crystal data and structure refinement for (R_c,R_p,S_c)-77.

Empirical formula	$C_{36}H_{41}Cl_2N_2PPdPt$	
Formula weight	976.57	
Temperature	295.2(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 12.6359(6) Å	α = 90°.
	b = 16.2412(7) Å	β = 90°.
	c = 19.1060(9) Å	γ = 90°.
Volume	3922.1(3) $Å^3$	
Z	4	
Density (calculated)	1.654 Mg/m^3	
Absorption coefficient	4.296 mm^{-1}	
F(000)	1924	
Crystal size	0.60 x 0.14 x 0.10 mm^3	
Theta range for data collection	1.65 to 27.49°.	
Index ranges	–16<=h<=16, –21<=k<=16, –24<=l<=24	
Reflections collected	27827	
Independent reflections	8793 [R(int) = 0.0394]	
Completeness to theta = 27.49°	100.0 %	
Absorption correction	Sadabs (Sheldrick, 2001)	
Max. and min. transmission	0.6733 and 0.1825	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	8973 / 9 / 436	
Goodness–of–fit on F^2	0.916	
Final R indices [I>2sigma(I)]	R_1= 0.0321, wR_2 = 0.0627	
R indices (all data)	R_1 = 0.0410, wR_2 = 0.0655	
Absolute structure parameter	–0.003(4)	
Largest diff. peak and hole	1.244 and –0.316 e.$Å^{-3}$	

Table A5–2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for (R_c,R_p,S_c)-77. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pt(1)	5747(1)	5894(1)	6433(1)	37(1)
Pd(1)	4910(1)	5762(1)	4487(1)	38(1)
P(1)	4347(1)	6454(1)	5929(1)	37(1)
Cl(1)	6062(1)	5201(1)	5335(1)	58(1)
Cl(2)	6407(4)	5838(1)	3702(1)	62(1)
N(1)	6992(3)	5287(3)	6987(2)	42(1)
N(2)	3837(3)	6201(2)	3733(2)	41(1)
C(1)	6144(4)	6063(3)	7884(2)	36(1)
C(2)	5664(4)	6480(3)	7347(2)	34(1)
C(3)	5239(4)	7247(3)	7474(2)	40(1)
C(4)	5291(4)	7623(3)	8125(3)	45(1)
C(5)	5741(4)	7195(3)	8696(2)	45(1)
C(6)	5769(5)	7537(4)	9377(3)	59(1)
C(7)	6187(6)	7099(5)	9910(3)	77(2)
C(8)	6610(6)	6328(5)	9808(3)	76(2)
C(9)	6613(5)	5985(4)	9162(3)	58(2)
C(10)	6171(4)	6401(3)	8581(3)	44(1)
C(11)	6619(4)	5242(3)	7728(3)	42(1)
C(12)	5809(6)	4558(3)	7857(3)	62(2)
C(13)	7279(5)	4461(4)	6727(3)	63(2)
C(14)	7956(4)	5802(4)	6962(3)	62(2)
C(15)	3299(4)	6725(3)	6496(3)	44(1)
C(16)	2613(5)	6937(4)	6869(3)	57(2)
C(17)	1753(6)	7187(5)	7325(4)	98(3)
C(18)	3845(4)	5772(3)	5259(2)	35(1)
C(19)	3045(4)	5227(3)	5323(3)	43(1)
C(20)	2546(6)	4993(4)	6012(3)	63(2)
C(21)	4037(5)	5773(4)	3056(3)	60(2)
C(22)	4073(5)	7091(3)	3642(3)	61(2)
C(23)	1892(5)	6534(4)	3469(3)	67(2)
C(24)	2695(4)	6090(3)	3947(3)	46(1)

C(25)	2438(4)	5192(4)	4066(3)	47(1)
C(26)	1969(4)	4734(4)	3522(3)	62(2)
C(27)	1698(5)	3934(4)	3592(4)	74(2)
C(28)	1883(6)	3532(4)	4223(4)	78(2)
C(29)	2343(5)	3966(4)	4757(3)	61(2)
C(30)	2639(4)	4795(3)	4698(3)	45(1)
C(31)	4584(4)	7429(3)	5478(2)	40(1)
C(32)	3824(5)	8039(3)	5456(3)	53(1)
C(33)	4010(6)	8771(4)	5105(3)	65(2)
C(34)	4949(6)	8889(4)	4776(3)	68(2)
C(35)	5707(6)	8287(4)	4783(3)	62(2)
C(36)	5535(4)	7569(4)	5144(3)	48(1)

Table A6–1. Crystal data and structure refinement for (*R*$_c$,*S*$_c$,*R*$_p$,*S*$_c$)-79.

Empirical formula	$C_{36}H_{42}ClN_2OPPdPt$	
Formula weight	915.67	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.4355(12) Å	α = 90°.
	b = 16.2493(18) Å	β = 90°.
	c = 43.211(5) Å	γ = 90°.
Volume	7327.2(14) Å^3	
Z	8	
Density (calculated)	1.660 Mg/m^3	
Absorption coefficient	4.454 mm^{-1}	
F(000)	3616	
Crystal size	0.48 x 0.38 x 0.30 mm^3	
Theta range for data collection	1.57 to 27.50°.	
Index ranges	–13<=h<=11, –21<=k<=20, –51<=l<=56	
Reflections collected	51882	
Independent reflections	16794 [R(int) = 0.0560]	
Completeness to theta = 27.50°	99.8 %	
Absorption correction	Sadabs (Sheldrick, 2001)	
Max. and min. transmission	0.6733 and 0.1825	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	16794 / 29 / 827	
Goodness–of–fit on F^2	1.055	
Final R indices [I>2sigma(I)]	R_1= 0.0482, wR_2 = 0.0940	
R indices (all data)	R_1 = 0.0608, wR_2 = 0.0979	
Absolute structure parameter	0.012(4)	
Largest diff. peak and hole	1.597 and –0.627 e.Å^{-3}	

Table A6–2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for (R_c, S_c, R_p, S_c) – 79. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pt(1)	968(1)	7867(1)	3829(1)	40(1)
Pd(1)	–183(1)	9219(1)	4393(1)	42(1)
P(1)	1211(2)	7850(1)	4341(1)	40(1)
Cl(1)	–2308(2)	9522(2)	4199(1)	70(1)
O(1)	–968(5)	7555(3)	3936(1)	49(1)
N(1)	571(6)	7941(4)	3351(1)	44(2)
N(2)	506(7)	10449(4)	4297(1)	52(2)
C(1)	2889(7)	8119(5)	3368(2)	41(2)
C(2)	2700(7)	8178(5)	3684(2)	41(2)
C(3)	3720(8)	8498(5)	3868(2)	51(2)
C(4)	4869(8)	8713(5)	3733(2)	52(2)
C(5)	5071(8)	8623(5)	3415(2)	49(2)
C(6)	6295(9)	8807(6)	3279(2)	67(2)
C(7)	6478(10)	8695(7)	2968(2)	82(3)
C(8)	5499(10)	8410(7)	2784(2)	79(3)
C(9)	4321(9)	8248(6)	2908(2)	60(2)
C(10)	4069(8)	8330(5)	3228(2)	47(2)
C(11)	1802(7)	7747(5)	3180(2)	43(2)
C(12)	1996(10)	6819(5)	3151(2)	62(2)
C(13)	–512(8)	7416(5)	3252(2)	53(2)
C(14)	226(9)	8804(5)	3280(2)	55(2)
C(15)	–436(7)	7903(5)	4446(2)	45(2)
C(16)	–1323(8)	7643(5)	4217(2)	46(2)
C(17)	–2709(8)	7467(6)	4287(2)	60(2)
C(18)	1508(7)	8799(5)	4535(2)	42(2)
C(19)	2336(8)	9060(5)	4742(2)	46(2)
C(20)	3587(9)	8630(6)	4816(2)	70(3)
C(21)	2052(8)	9824(6)	4918(2)	53(2)
C(22)	2023(9)	9774(6)	5241(2)	64(2)
C(23)	1729(11)	10456(8)	5420(2)	82(3)
C(24)	1554(10)	11179(8)	5279(3)	84(3)

C(25)	1593(10)	11264(7)	4961(3)	77(3)
C(26)	1816(8)	10589(6)	4777(2)	56(2)
C(27)	1825(8)	10629(5)	4429(2)	58(2)
C(28)	2386(12)	11449(6)	4322(3)	90(4)
C(29)	–442(10)	11071(6)	4402(2)	76(3)
C(30)	556(11)	4795(3)	4402(2)	72(3)
C(31)	2037(7)	6981(4)	4517(2)	40(2)
C(32)	1789(9)	6758(5)	4822(2)	53(2)
C(33)	2419(10)	6109(6)	4950(2)	66(3)
C(34)	3340(12)	5704(6)	4788(2)	80(3)
C(35)	3604(10)	5917(6)	4489(2)	68(2)
C(36)	2964(9)	6547(5)	4349(2)	60(2)

Table A7–1. Crystal data and structure refinement for (*R*$_c$,*S*$_p$)-81.

Empirical formula	$C_{35}H_{39}Cl_2N_2PPdPt$	
Formula weight	963.15	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 12.3147(12) Å	α = 90°.
	b = 15.0529(15) Å	β = 90°.
	c = 19.642(2) Å	γ = 90°.
Volume	3641.1(6) $Å^3$	
Z	4	
Density (calculated)	1.678 Mg/m^3	
Absorption coefficient	4.551 mm^{-1}	
F(000)	1808	
Crystal size	0.40 x 0.20 x 0.20 mm^3	
Theta range for data collection	1.70 to 27.50°.	
Index ranges	–15<=h<=16, –19<=k<=19, –12<=l<=25	
Reflections collected	25256	
Independent reflections	8298 [R(int) = 0.0434]	
Completeness to theta = 27.50°	99.8 %	
Absorption correction	Sadabs (Sheldrick, 2001)	
Max. and min. transmission	0.4630 and 0.2633	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	8298 / 0 / 410	
Goodness–of–fit on F^2	1.214	
Final R indices [I>2sigma(I)]	R_1= 0.0635, wR_2 = 0.1482	
R indices (all data)	R_1 = 0.0685, wR_2 = 0.1502	
Absolute structure parameter	0.056(11)	
Largest diff. peak and hole	2.317 and –3.250 e.$Å^{-3}$	

Table A7–2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for (R_c,S_p)-81. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pt(1)	6999(1)	6470(1)	3582(1)	35(1)
Pd(1)	8917(1)	5174(1)	3156(1)	48(1)
P(1)	7284(2)	6319(2)	2475(2)	36(1)
Cl(1)	8917(4)	4400(3)	4234(3)	70(1)
Cl(2)	8935(3)	6591(2)	3719(2)	50(1)
N(1)	6630(8)	6548(7)	4655(5)	42(2)
N(2)	9141(11)	3959(7)	2630(7)	59(4)
C(1)	4914(10)	6093(7)	3566(6)	34(2)
C(2)	5364(9)	6390(7)	3566(6)	34(2)
C(3)	4689(10)	6616(7)	2999(6)	36(3)
C(4)	3609(9)	6536(8)	3050(6)	37(3)
C(5)	3124(10)	6184(7)	3636(7)	40(3)
C(6)	1986(13)	6015(8)	3676(7)	49(3)
C(7)	1535(11)	5649(10)	4245(10)	60(4)
C(8)	2186(11)	5417(9)	4786(8)	49(3)
C(9)	3272(10)	5575(9)	4793(7)	41(3)
C(10)	3786(10)	5969(7)	4206(7)	36(3)
C(11)	5673(10)	5917(9)	4739(6)	43(3)
C(12)	5988(16)	4971(13)	4685(13)	106(9)
C(13)	7531(12)	6279(11)	5102(8)	60(4)
C(14)	6271(16)	7453(10)	4832(8)	65(5)
C(15)	7072(14)	7344(9)	2063(7)	52(3)
C(16)	6838(13)	8043(9)	1851(8)	56(4)
C(17)	6600(20)	8820(12)	1562(13)	105(9)
C(18)	8633(11)	5883(8)	2321(7)	42(3)
C(19)	9283(12)	6005(9)	1790(9)	52(4)
C(20)	9023(14)	6599(10)	1213(7)	63(4)
C(21)	8183(16)	3400(11)	2769(14)	112(10)
C(22)	10121(18)	3506(15)	2953(10)	94(7)
C(23)	9410(15)	4074(10)	1894(10)	69(5)
C(24)	10368(9)	4601(7)	1763(6)	63(4)

C(25)	11347(12)	4151(8)	1693(6)	81(6)
C(26)	12301(9)	4623(13)	1580(6)	123(11)
C(27)	12275(7)	5544(12)	1537(6)	113(10)
C(28)	11295(10)	5994(8)	1608(6)	107(9)
C(29)	10342(7)	5522(7)	1721(6)	72(5)
C(30)	6435(11)	5522(9)	2053(7)	45(3)
C(31)	6211(13)	5555(13)	1353(9)	67(4)
C(32)	5608(13)	4947(16)	1059(10)	81(7)
C(33)	5259(15)	4213(15)	1387(13)	91(7)
C(34)	5455(13)	4152(11)	2054(12)	72(5)
C(35)	6047(10)	4796(7)	2436(6)	33(2)

Table A 8–1. Crystal data and structure refinement for (*R*$_c$,*R*$_p$,*R*$_c$)-83.

Empirical formula	$C_{32}H_{39}Cl_2N_2PPdPt$	
Formula weight	526.31	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	P4(3)2(1)2	
Unit cell dimensions	a = 15.3153(3) Å	α = 90°.
	b = 15.3153(3) Å	β = 90°.
	c = 29.1763(12) Å	γ = 90°.
Volume	6843.5(3) Å^3	
Z	8	
Density (calculated)	1.742 Mg/m^3	
Absorption coefficient	4.915 mm^{-1}	
F(000)	3512	
Crystal size	0.30 x 0.26 x 0.24 mm^3	
Theta range for data collection	1.93 to 27.50°.	
Index ranges	–19<=h<=18, –19<=k<=19, –34<=l<=37	
Reflections collected	48817	
Independent reflections	7864 [R(int) = 0.0838]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Sadabs (Sheldrick, 2001)	
Max. and min. transmission	0.3851 and 0.3203	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	7864 / 12 / 413	
Goodness–of–fit on F^2	1.048	
Final R indices [I>2sigma(I)]	R_1= 0.0430, wR_2 = 0.0826	
R indices (all data)	R_1 = 0.0526, wR_2 = 0.0854	
Absolute structure parameter	0.005(6)	
Largest diff. peak and hole	1.217 and –0.664 e.Å^{-3}	

Table A8–2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ × 10^3) for (R_c,R_p,R_c)-83. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pt(1)	2601(1)	9613(1)	810(1)	29(1)
Pd(1)	980(1)	8306(1)	1047(1)	26(1)
P(1)	2532(1)	8378(1)	413(1)	26(1)
Cl(1)	2613(1)	8800(1)	1485(1)	35(1)
Cl(2)	67(1)	9386(1)	1408(1)	45(1)
N(1)	2604(4)	10834(4)	1176(2)	40(2)
N(2)	–83(4)	7703(4)	702(2)	32(1)
C(1)	3095(5)	11260(5)	410(3)	36(2)
C(2)	3101(5)	10364(5)	316(2)	31(2)
C(3)	3572(5)	10118(5)	–76(3)	40(2)
C(4)	3958(5)	10735(6)	–354(3)	49(2)
C(5)	3907(6)	11616(6)	–294(4)	61(3)
C(6)	3454(5)	11869(6)	134(3)	47(2)
C(7)	2491(5)	11523(4)	808(3)	41(2)
C(8)	1524(5)	11591(6)	674(3)	46(2)
C(9)	1942(6)	10912(6)	1538(3)	51(2)
C(10)	3494(6)	10976(6)	1389(3)	56(3)
C(11)	–898(5)	7751(5)	987(3)	40(2)
C(12)	–227(5)	8183(6)	275(3)	45(2)
C(13)	–654(5)	6265(5)	374(3)	38(2)
C(14)	112(4)	6759(4)	591(2)	27(2)
C(15)	480(4)	6286(4)	1005(2)	30(2)
C(16)	–45(5)	5836(5)	1313(2)	36(2)
C(17)	284(6)	5331(5)	1657(3)	44(2)
C(18)	1162(5)	5254(5)	1710(3)	42(2)
C(19)	1703(5)	5707(5)	1418(3)	37(2)
C(20)	1387(5)	6233(4)	1069(3)	32(2)
C(21)	1884(4)	7581(4)	725(2)	28(2)
C(22)	2000(4)	6731(5)	775(2)	27(2)
C(23)	2699(5)	6169(5)	552(3)	41(2)
C(24)	3585(5)	7968(5)	290(2)	31(2)

C(25)	4328(5)	7763(5)	264(2)	32(2)
C(26)	5239(5)	7480(6)	247(3)	44(2)
C(27)	2006(4)	8418(5)	–145(2)	31(2)
C(28)	1950(5)	7684(5)	–407(2)	36(2)
C(29)	1499(5)	7690(6)	–822(3)	51(2)
C(30)	1094(6)	8441(7)	–970(3)	56(3)
C(31)	1131(6)	9177(6)	–711(3)	54(2)
C(32)	1590(5)	9186(5)	–294(3)	43(2)

Table A 9–1. Crystal data and structure refinement for (*R*$_c$,*S*$_p$,*R*$_c$)-84.

Empirical formula	$C_{32}H_{39}Cl_2N_2PPdPt$	
Formula weight	526.31	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 14.2178(6) Å	α = 90°.
	b = 15.2875(6) Å	β = 90°.
	c = 16.4991(7) Å	γ = 90°.
Volume	3586.2(3) $Å^3$	
Z	4	
Density (calculated)	1.741 Mg/m^3	
Absorption coefficient	4.766 mm^{-1}	
F(000)	1840	
Crystal size	0.20 x 0.12 x 0.10 mm^3	
Theta range for data collection	1.82 to 27.50°.	
Index ranges	–18<=h<=18, –19<=k<=19, –21<=l<=16	
Reflections collected	25298	
Independent reflections	8222 [R(int) = 0.0449]	
Completeness to theta = 27.50°	100.0 %	
Absorption correction	Sadabs (Sheldrick, 2001)	
Max. and min. transmission	0.6742 and 0.4491	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	8222 / 0 / 387	
Goodness–of–fit on F^2	0.926	
Final R indices [I>2sigma(I)]	R_1= 0.0351, wR_2 = 0.0668	
R indices (all data)	R_1 = 0.0453, wR_2 = 0.0699	
Absolute structure parameter	–0.001(4)	
Largest diff. peak and hole	1.301 and –0.375 e.$Å^{-3}$	

Table A8–2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for (R_c,S_p,R_c)-84. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pt(1)	9483(1)	9618(1)	9528(1)	39(1)
Pd(1)	10598(1)	9624(1)	7852(1)	38(1)
P(1)	8613(1)	9270(1)	8460(1)	38(1)
Cl(1)	10139(1)	10788(1)	8708(1)	51(1)
Cl(2)	12188(1)	9729(1)	8399(1)	63(1)
N(1)	10337(4)	9911(3)	10565(3)	55(1)
N(2)	10933(3)	8620(3)	6999(3)	43(1)
C(1)	9632(5)	8534(4)	10933(3)	50(2)
C(2)	9014(4)	8699(4)	10288(3)	41(1)
C(3)	8176(4)	8233(4)	10279(3)	46(1)
C(4)	7966(4)	7632(4)	10879(4)	52(2)
C(5)	8586(5)	7487(5)	11505(4)	64(2)
C(6)	9394(6)	7941(4)	11537(4)	61(2)
C(7)	10539(5)	9035(4)	10920(4)	59(2)
C(8)	11277(5)	8534(5)	10441(5)	80(2)
C(9)	11208(5)	10412(5)	10383(5)	81(2)
C(10)	9770(5)	10437(5)	11151(4)	74(2)
C(11)	11923(4)	8706(5)	6745(4)	62(2)
C(12)	10828(4)	7781(4)	7443(4)	55(2)
C(13)	10525(5)	7961(4)	5607(4)	62(2)
C(14)	10291(4)	8650(3)	6261(3)	42(1)
C(15)	10261(4)	9573(4)	5921(3)	42(1)
C(16)	10848(4)	9850(4)	5306(3)	50(2)
C(17)	10818(5)	10679(4)	4993(4)	60(2)
C(18)	10160(5)	11254(4)	5265(4)	63(2)
C(19)	9519(5)	10989(4)	5861(4)	55(2)
C(20)	9573(4)	10153(3)	6197(3)	43(1)
C(21)	9239(3)	9613(4)	7554(3)	41(1)
C(22)	8900(4)	9894(4)	6857(3)	44(1)
C(23)	7877(4)	9969(5)	6610(4)	66(2)
C(24)	8427(4)	8148(4)	8304(3)	45(1)

C(25)	8342(4)	7381(4)	8228(3)	43(1)
C(26)	8247(5)	6431(4)	8121(4)	62(2)
C(27)	7431(4)	9718(5)	8497(3)	48(1)
C(28)	6632(4)	9224(5)	8392(4)	62(2)
C(29)	5754(5)	9614(7)	8413(4)	82(2)
C(30)	5680(6)	10496(8)	8514(5)	92(3)
C(31)	6458(7)	10999(6)	8612(5)	91(3)
C(32)	7339(5)	10609(4)	8619(5)	71(2)

Table A 10–1. Crystal data and structure refinement for (*R*$_c$,*R*$_p$,*S*$_c$)-85.

Empirical formula	$C_{32}H_{39}Cl_2N_2PPdPt$	
Formula weight	526.31	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 12.7415(6) Å	α = 90°.
	b = 14.9281(7) Å	β = 90°.
	c = 18.3478(8) Å	γ = 90°.
Volume	3489.9(3) Å^3	
Z	4	
Density (calculated)	1.738 Mg/m^3	
Absorption coefficient	4.748 mm^{-1}	
F(000)	1800	
Crystal size	0.40 x 0.40 x 0.26 mm^3	
Theta range for data collection	1.76 to 27.50°.	
Index ranges	–16<=h<=16, –18<=k<=19, –23<=l<=16	
Reflections collected	24341	
Independent reflections	7882 [R(int) = 0.0259]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Sadabs (Sheldrick, 2001)	
Max. and min. transmission	0.3715 and 0.2525	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	7882 / 0 / 398	
Goodness–of–fit on F^2	0.817	
Final R indices [I>2sigma(I)]	R_1= 0.0195, wR_2 = 0.0454	
R indices (all data)	R_1 = 0.02063, wR_2 = 0.0457	
Absolute structure parameter	0.002(3)	
Largest diff. peak and hole	1.575 and –0.401 e.Å^{-3}	

Table A10–2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for (R_c,R_p,S_c)-85. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pt(1)	4373(1)	4006(1)	1639(1)	18(1)
Pd(1)	5177(1)	4486(1)	–340(1)	18(1)
P(1)	5810(1)	3562(1)	1068(1)	18(1)
Cl(1)	4055(1)	4977(1)	604(1)	26(1)
Cl(2)	3666(1)	4425(1)	–1125(1)	34(1)
N(1)	3046(2)	4450(2)	2255(2)	23(1)
N(2)	6218(2)	4127(2)	–1182(1)	22(1)
C(1)	3898(3)	3440(2)	3090(2)	22(1)
C(2)	4473(2)	3163(2)	2477(2)	19(1)
C(3)	4907(3)	2303(2)	2497(2)	23(1)
C(4)	4810(3)	1768(2)	3107(2)	27(1)
C(5)	4291(3)	2063(2)	3717(2)	31(1)
C(6)	3817(3)	2907(2)	3700(2)	31(1)
C(7)	3372(3)	4342(2)	3044(2)	24(1)
C(8)	4107(3)	5078(2)	3292(2)	35(1)
C(9)	2672(3)	5369(2)	2095(2)	32(1)
C(10)	2140(3)	3833(2)	2118(2)	34(1)
C(11)	6870(2)	3211(2)	1617(2)	24(1)
C(12)	7602(3)	2963(2)	1956(2)	28(1)
C(13)	8510(3)	2667(3)	2375(2)	44(1)
C(14)	6271(2)	4411(2)	437(2)	18(1)
C(15)	7072(2)	4982(2)	531(2)	21(1)
C(16)	7650(3)	5132(3)	1243(2)	31(1)
C(17)	5974(3)	4665(2)	–1848(2)	29(1)
C(18)	5988(3)	3165(2)	–1353(2)	29(1)
C(19)	8129(3)	3820(3)	–1518(2)	33(1)
C(20)	7366(2)	4229(2)	–969(2)	24(1)
C(21)	7598(3)	5198(2)	–790(2)	25(1)
C(22)	8019(3)	5756(3)	–1325(2)	34(1)
C(23)	8262(3)	6642(3)	–1192(2)	39(1)
C(24)	8095(3)	6991(3)	–508(2)	38(1)

C(25)	7705(3)	6455(2)	34(2)	30(1)
C(26)	7439(2)	5557(2)	–87(2)	23(1)
C(27)	5610(3)	2559(2)	509(2)	21(1)
C(28)	6406(3)	1937(2)	394(2)	28(1)
C(29)	6232(3)	1190(2)	–42(2)	36(1)
C(30)	5257(3)	1072(3)	–365(2)	40(1)
C(31)	4466(3)	1683(2)	–253(2)	34(1)
C(32)	4633(3)	2423(2)	186(2)	28(1)

Table A 11–1. Crystal data and structure refinement for (*R*$_c$,*R*$_p$,*S*$_c$)-87.

Empirical formula	$C_{39}H_{48}Cl_2N_2OPPd_2$	
Formula weight	875.46	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 12.5436(5) Å	α = 90°.
	b = 16.2505(7) Å	β = 90°.
	c = 19.1199(8) Å	γ = 90°.
Volume	3897.4(3) $Å^3$	
Z	4	
Density (calculated)	1.492 Mg/m^3	
Absorption coefficient	1.133 mm^{-1}	
F(000)	1780	
Crystal size	0.44 x 0.16 x 0.14 mm^3	
Theta range for data collection	1.64 to 27.50°.	
Index ranges	–14<=h<=16, –21<=k<=20, –18<=l<=24	
Reflections collected	27806	
Independent reflections	8957 [R(int) = 0.0419]	
Completeness to theta = 27.50°	100.0 %	
Absorption correction	Sadabs (Sheldrick, 2001)	
Max. and min. transmission	0.8575 and 0.6356	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	8957 / 25 / 432	
Goodness–of–fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R_1= 0.0396, wR_2 = 0.0890	
R indices (all data)	R_1 = 0.0465, wR_2 = 0.0921	
Absolute structure parameter	–0.01(3)	
Largest diff. peak and hole	0.866 and –0.590 e.$Å^{-3}$	

Table A11–2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for (R_c,R_p,S_c)-87. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	10783(1)	884(1)	1424(1)	27(1)
Pd(2)	9936(1)	779(1)	–3520(1)	27(1)
P(1)	9352(1)	1453(1)	930(1)	27(1)
Cl(1)	11109(1)	217(1)	315(1)	42(1)
Cl(2)	11436(1)	877(1)	–1307(1)	45(1)
N(1)	12026(3)	271(2)	1983(2)	31(1)
N(2)	8850(3)	1218(2)	–1266(2)	30(1)
C(1)	11141(3)	1063(3)	2876(2)	28(1)
C(2)	10660(3)	1474(3)	2330(2)	26(1)
C(3)	10235(3)	2275(3)	2461(2)	31(1)
C(4)	10285(3)	2623(3)	3109(2)	34(1)
C(5)	10719(4)	2196(3)	3679(2)	33(1)
C(6)	10731(4)	2524(3)	4367(3)	43(1)
C(7)	11147(5)	2100(4)	4911(3)	52(2)
C(8)	11597(6)	1324(4)	4794(3)	60(2)
C(9)	11610(4)	974(3)	4143(2)	45(1)
C(10)	11160(3)	1393(3)	3572(2)	30(1)
C(11)	11634(4)	238(3)	2724(2)	29(1)
C(12)	10809(4)	–447(3)	2839(3)	45(1)
C(13)	12327(4)	–555(3)	1728(3)	48(1)
C(14)	12998(4)	802(4)	1967(3)	48(1)
C(15)	8295(3)	1717(3)	1486(2)	34(1)
C(16)	7592(4)	1927(3)	1863(3)	42(1)
C(17)	6726(5)	2182(5)	2310(3)	76(2)
C(18)	8866(3)	770(2)	252(2)	27(1)
C(19)	8073(4)	219(3)	312(2)	32(1)
C(20)	7552(5)	–14(4)	994(3)	46(1)
C(21)	9055(4)	814(3)	–1952(2)	43(1)
C(22)	9074(4)	2120(3)	–1342(3)	42(1)
C(23)	6883(4)	1534(3)	–1529(3)	45(1)
C(24)	7690(3)	1095(3)	–1044(2)	32(1)

C(25)	7456(3)	191(3)	–945(2)	32(1)
C(26)	6985(4)	–254(3)	–1491(3)	45(1)
C(27)	6724(4)	–1079(4)	–1407(3)	54(2)
C(28)	6918(4)	–1469(4)	–808(3)	56(2)
C(29)	7380(4)	–1048(3)	–262(3)	43(1)
C(30)	7658(3)	–219(3)	–310(2)	34(1)
C(31)	9590(3)	2434(3)	490(2)	30(1)
C(32)	8835(4)	3050(3)	479(3)	39(1)
C(33)	9027(5)	3776(3)	130(3)	45(1)
C(34)	9985(5)	3901(3)	–213(3)	52(1)
C(35)	10741(4)	3288(3)	–210(3)	44(1)
C(36)	10568(3)	2557(3)	141(3)	37(1)
O(1S)	4405(8)	2137(8)	2958(5)	218(5)
C(1S)	4824(9)	1335(3)	3893(3)	104(3)
C(2S)	4291(7)	1996(6)	3575(4)	121(4)
C(3S)	3664(6)	2614(5)	3790(6)	105(3)

Table A 12–1. Crystal data and structure refinement for (*R*c,*S*c,*R*p,*S*c)-88.

Empirical formula	$C_{36.50}H_{43}Cl_2N_2OPPd_2$	
Formula weight	840.40	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.4539(17) Å	α = 90°.
	b = 16.178(3) Å	β = 90°.
	c = 42.663(8) Å	γ = 90°.
Volume	7215(2) $Å^3$	
Z	8	
Density (calculated)	1.547 Mg/m^3	
Absorption coefficient	1.220 mm^{-1}	
F(000)	3400	
Crystal size	0.40 x 0.36 x 0.20 mm^3	
Theta range for data collection	1.58 to 27.50°.	
Index ranges	–11<=h<=13, –16<=k<=21, –50<=l<=55	
Reflections collected	51067	
Independent reflections	16567 [R(int) = 0.0560]	
Completeness to theta = 27.50°	100.0 %	
Absorption correction	Sadabs (Sheldrick, 2001)	
Max. and min. transmission	0.7924 and 0.6411	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	16567 / 0/ 818	
Goodness–of–fit on F^2	1.102	
Final R indices [I>2sigma(I)]	R_1= 0.0497, wR_2 = 0.0938	
R indices (all data)	R_1 = 0.0582, wR_2 = 0.0965	
Absolute structure parameter	–0.01(2)	
Largest diff. peak and hole	0.755and –0.535 e.$Å^{-3}$	

Table A12–2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for (R_c,S_c,R_p,S_c)-88. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	6176(1)	5436(1)	1447(1)	29(1)
Pd(2)	7163(1)	6751(1)	2095(1)	25(1)
P(1)	7981(1)	5493(1)	1727(1)	26(1)
O(1)	5348(4)	5016(2)	1877(1)	41(1)
Cl(1)	5234(1)	6856(1)	2409(1)	46(1)
N(1)	4408(4)	5457(3)	1204(1)	36(1)
N(2)	7222(4)	8064(3)	2015(1)	35(1)
C(1)	5950(5)	5706(3)	796(1)	32(1)
C(2)	6824(5)	5815(3)	1038(1)	31(1)
C(3)	8001(5)	6223(4)	965(1)	36(1)
C(4)	8292(5)	6453(4)	671(1)	37(1)
C(5)	7439(6)	6327(4)	418(1)	38(1)
C(6)	7749(7)	6549(4)	110(2)	49(2)
C(7)	6916(7)	6419(5)	–131(2)	62(2)
C(8)	5722(7)	6050(5)	–71(2)	65(2)
C(9)	5390(6)	5828(5)	225(2)	51(2)
C(10)	6230(5)	5962(3)	481(1)	36(1)
C(11)	4713(5)	5277(4)	869(1)	37(1)
C(12)	4830(6)	4349(4)	809(2)	52(2)
C(13)	3420(5)	4895(4)	1337(2)	53(2)
C(14)	3927(6)	6324(4)	1228(2)	45(2)
C(15)	7276(5)	5438(3)	2115(1)	31(1)
C(16)	6013(6)	5092(4)	2120(1)	39(1)
C(17)	5464(6)	4791(4)	2424(2)	53(2)
C(18)	8642(5)	6465(3)	1821(1)	23(1)
C(19)	9834(5)	6771(3)	1783(1)	25(1)
C(20)	10793(5)	6374(4)	1570(1)	40(1)
C(21)	10292(5)	7494(3)	1961(1)	29(1)
C(22)	11506(5)	7446(4)	2103(2)	41(2)
C(23)	12004(6)	8068(5)	2277(2)	54(2)
C(24)	11320(7)	8790(5)	2305(2)	67(2)

C(25)	10146(7)	8864(4)	2168(2)	58(2)
C(26)	9605(5)	8233(3)	1991(1)	33(1)
C(27)	8335(5)	8350(4)	1818(2)	36(1)
C(28)	8188(7)	9244(4)	1698(2)	59(2)
C(29)	6011(6)	8246(5)	1849(2)	60(2)
C(30)	7185(7)	8480(4)	2327(2)	58(2)
C(31)	9171(5)	4680(3)	1668(1)	28(1)
C(32)	10054(6)	4509(4)	1899(1)	43(2)
C(33)	10947(6)	3883(4)	1852(2)	55(2)
C(34)	10939(6)	3433(4)	1575(2)	52(2)
C(35)	10064(6)	3606(4)	1349(2)	52(2)
C(36)	9176(5)	4227(4)	1393(1)	38(1)
C(1S)	1667(8)	8853(5)	1319(2)	77(3)
Cl(1S)	3052(2)	8350(2)	1415(1)	95(1)
Cl(2S)	718(3)	8283(2)	1066(1)	142(1)

Table A 13–1. Crystal data and structure refinement for (*R*$_c$,*R*$_p$,*R*$_c$)-89.

Empirical formula	$C_{39}H_{47}Cl_2N_2OPPd_2$	
Formula weight	874.46	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 11.7272(5) Å	α = 90°.
	b = 14.7760(6) Å	β = 90°.
	c = 22.3321(9) Å	γ = 90°.
Volume	3869.7(3) Å^3	
Z	4	
Density (calculated)	1.501 Mg/m^3	
Absorption coefficient	1.141 mm^{-1}	
F(000)	1776	
Crystal size	0.20 x 0.14 x 0.10 mm^3	
Theta range for data collection	1.65 to 27.50°.	
Index ranges	–14<=h<=15, –19<=k<=19, –29<=l<=16	
Reflections collected	27546	
Independent reflections	8872 [R(int) = 0.0268]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Sadabs (Sheldrick, 2001)	
Max. and min. transmission	0.8945 and 0.8040	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	8872 / 25 / 434	
Goodness–of–fit on F^2	1.061	
Final R indices [I>2sigma(I)]	R_1= 0.0267, wR_2 = 0.0604	
R indices (all data)	R_1 = 0.0284, wR_2 = 0.0611	
Absolute structure parameter	–0.014(18)	
Largest diff. peak and hole	0.657 and –0.336 e.Å^{-3}	

Table A13–2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for (R_c,R_p,R_c)-89. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	2703(1)	8495(1)	6905(1)	21(1)
Pd(2)	817(1)	8548(1)	7920(1)	21(1)
P(1)	918(1)	8556(1)	6549(1)	23(1)
Cl(1)	2017(1)	7370(1)	7615(1)	28(1)
Cl(2)	2006(1)	8732(1)	8789(1)	47(1)
N(1)	4406(2)	8514(2)	7228(1)	29(1)
N(2)	–310(2)	9611(1)	8161(1)	24(1)
C(1)	4396(2)	9721(2)	6490(1)	24(1)
C(2)	3374(2)	9338(2)	6305(1)	23(1)
C(3)	2959(2)	9560(2)	5729(1)	26(1)
C(4)	3496(2)	10174(2)	5374(1)	28(1)
C(5)	4496(2)	10619(2)	5567(1)	28(1)
C(6)	5008(3)	11318(2)	5230(1)	38(1)
C(7)	5958(3)	11759(2)	5436(2)	46(1)
C(8)	6421(3)	11534(3)	5987(2)	45(1)
C(9)	5967(3)	10857(2)	6327(2)	38(1)
C(10)	4967(2)	10379(2)	6133(1)	28(1)
C(11)	4818(2)	9457(2)	7103(1)	30(1)
C(12)	4381(3)	10132(2)	7565(1)	42(1)
C(13)	4559(3)	8262(3)	7868(1)	45(1)
C(14)	5083(3)	7858(2)	6867(2)	43(1)
C(15)	398(2)	9624(2)	6331(1)	29(1)
C(16)	85(3)	10373(2)	6231(1)	36(1)
C(17)	–285(4)	11303(2)	6115(2)	57(1)
C(18)	–25(2)	8265(2)	7162(1)	24(1)
C(19)	–1056(2)	7879(2)	7153(1)	26(1)
C(20)	–1676(3)	7546(2)	6602(2)	41(1)
C(21)	–345(3)	9737(2)	8824(1)	40(1)
C(22)	–2360(3)	10200(2)	8081(2)	37(1)
C(23)	185(3)	10440(2)	7897(2)	37(1)
C(24)	–1510(2)	9456(2)	7920(1)	26(1)

C(25)	–1909(2)	8522(2)	8101(1)	26(1)
C(26)	–2515(2)	8385(2)	8632(1)	33(1)
C(27)	–2876(3)	7529(2)	8800(2)	40(1)
C(28)	–2675(3)	6805(2)	8432(2)	42(1)
C(29)	–2108(2)	6930(2)	7898(2)	35(1)
C(30)	–1697(2)	7778(2)	7725(1)	26(1)
C(31)	777(2)	7864(2)	5876(1)	29(1)
C(32)	–48(3)	8003(2)	5437(2)	43(1)
C(33)	–124(3)	7426(3)	4948(2)	55(1)
C(34)	632(4)	6725(2)	4891(2)	58(1)
C(35)	1469(3)	6596(2)	5304(2)	51(1)
C(36)	1552(3)	7161(2)	5801(1)	36(1)
O(1S)	–714(3)	9329(3)	4131(2)	97(1)
C(1S)	192(4)	9645(3)	4273(2)	63(1)
C(2S)	1279(4)	9166(3)	4143(2)	64(1)
C(3S)	301(4)	10531(4)	4583(2)	82(1)

Table A 14–1. Crystal data and structure refinement for (*R*$_c$,*R*$_p$)-91.

Empirical formula	$C_{36}H_{41}Cl_4N_2PPd_2$	
Formula weight	887.28	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.7184(8) Å	α = 90°.
	b = 11.5844(9) Å	β = 90°.
	c = 30.599(3) Å	γ = 90°.
Volume	3799.4(5) Å^3	
Z	4	
Density (calculated)	1.551 Mg/m^3	
Absorption coefficient	1.297 mm^{-1}	
F(000)	1784	
Crystal size	0.18 x 0.16 x 0.10 mm^3	
Theta range for data collection	1.33 to 27.50°.	
Index ranges	–12<=h<=13, –15<=k<=11, –38<=l<=39	
Reflections collected	27216	
Independent reflections	8716 [R(int) = 0.0751]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Sadabs (Sheldrick, 2001)	
Max. and min. transmission	0.8945 and 0.8040	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	8716 / 2 / 401	
Goodness–of–fit on F^2	0.988	
Final R indices [I>2sigma(I)]	R_1= 0.0575, wR_2 = 0.1091	
R indices (all data)	R_1 = 0.0860, wR_2 = 0.1185	
Absolute structure parameter	–0.01 (4)	
Largest diff. peak and hole	0.812 and –0.704 e.Å^{-3}	

Table A14–2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for (R_c,R_p)-91. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	8161(1)	1095(1)	1300(1)	36(1)
Pd(2)	8507(1)	–1558(1)	1309(1)	41(1)
P(1)	6978(2)	190(2)	799(1)	35(1)
Cl(1)	9845(3)	–1629(2)	1943(1)	94(1)
Cl(2)	9810(2)	–136(2)	999(1)	53(1)
N(1)	9321(5)	1992(5)	1755(2)	39(1)
N(2)	7255(6)	–2758(5)	1577(2)	55(2)
C(1)	7261(5)	2631(5)	1961(2)	35(2)
C(2)	6874(6)	2130(5)	1565(2)	35(1)
C(3)	5690(6)	2445(6)	1401(2)	38(2)
C(4)	4969(6)	3239(6)	1610(2)	45(2)
C(5)	5344(6)	3771(6)	1999(2)	43(2)
C(6)	4617(7)	4624(7)	2205(3)	56(2)
C(7)	5007(8)	5147(7)	2585(3)	62(2)
C(8)	6154(8)	4837(7)	2769(3)	61(2)
C(9)	6873(7)	4005(6)	2581(2)	52(2)
C(10)	6513(6)	3451(5)	2183(2)	39(2)
C(11)	8521(6)	2243(6)	2136(2)	41(2)
C(12)	8342(7)	1214(6)	2434(2)	55(2)
C(13)	10486(6)	1411(7)	1887(3)	59(2)
C(14)	9689(7)	3117(6)	1554(3)	59(2)
C(15)	5331(6)	92(6)	864(2)	39(2)
C(16)	4287(7)	–31(6)	931(2)	48(2)
C(17)	2940(6)	–202(9)	1013(3)	83(3)
C(18)	7449(5)	–1309(5)	784(2)	34(2)
C(19)	7141(6)	–2068(6)	474(2)	39(2)
C(20)	6378(9)	–1788(7)	67(3)	73(3)
C(21)	6525(10)	–2097(8)	1904(3)	85(3)
C(22)	7924(9)	–3710(7)	1809(3)	79(3)
C(23)	6394(6)	–3298(6)	1262(3)	54(2)
C(24)	7041(6)	–3914(6)	892(2)	47(2)

C(25)	7216(7)	–5115(6)	915(3)	56(2)
C(26)	7806(8)	–5687(7)	582(3)	69(3)
C(27)	8215(8)	–5086(7)	218(3)	66(2)
C(28)	8014(7)	–3936(6)	194(2)	51(2)
C(29)	7429(6)	–3310(6)	526(2)	40(2)
C(30)	7165(6)	904(6)	268(2)	44(2)
C(31)	8245(8)	717(7)	28(3)	65(2)
C(32)	8418(10)	1272(9)	–362(3)	88(3)
C(33)	7512(14)	2044(10)	–517(4)	108(4)
C(34)	6473(12)	2222(8)	–286(3)	82(3)
C(35)	6385(8)	1655(6)	103(3)	62(2)
C(1S)	1584(9)	6647(10)	1224(5)	140(5)
Cl(3)	729(4)	5583(4)	1025(2)	184(2)
Cl(4)	3102(3)	6574(5)	1183(2)	232(3)

Table A 15–1. Crystal data and structure refinement for (*R*$_c$,*R*$_p$,*R*$_c$)-95.

Empirical formula	$C_{50.50}H_{50}Cl_3N_2OPPd_2$	
Formula weight	1051.05	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.3124(8) Å	α = 90°.
	b = 12.0908(9) Å	β = 90°.
	c = 39.938(3) Å	γ = 90°.
Volume	4979.7(7) Å^3	
Z	4	
Density (calculated)	1.402 Mg/m^3	
Absorption coefficient	0.952 mm^{-1}	
F(000)	2132	
Crystal size	0.60 x 0.50 x 0.22 mm^3	
Theta range for data collection	1.02 to 27.49°.	
Index ranges	–9<=h<=13, –15<=k<=13, –51<=l<=51	
Reflections collected	34547	
Independent reflections	11403 [R(int) = 0.0346]	
Completeness to theta = 27.49°	99.7 %	
Absorption correction	Sadabs (Sheldrick, 2001)	
Max. and min. transmission	0.8180 and 0.5990	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	11403 / 2 / 560	
Goodness–of–fit on F^2	1.233	
Final R indices [I>2sigma(I)]	R_1= 0.0738, wR_2 = 0.1862	
R indices (all data)	R_1 = 0.0742, wR_2 = 0.1865	
Absolute structure parameter	0.11 (6)	
Largest diff. peak and hole	1.023 and –1.137 e.Å^{-3}	

Table A15–2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for (R_c,R_p,R_c)-95. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	7370(1)	3912(1)	4036(1)	26(1)
Pd(2)	8321(1)	5141(1)	3162(1)	27(1)
P(1)	8331(2)	5527(2)	3916(1)	24(1)
Cl(1)	7394(3)	3612(2)	3441(1)	36(1)
Cl(2)	9264(3)	3795(3)	2779(1)	47(1)
N(1)	6274(9)	2456(8)	4142(2)	37(2)
N(2)	8970(7)	6494(8)	2893(2)	32(2)
C(1)	6550(11)	3341(7)	4691(3)	36(2)
C(2)	7406(9)	4000(8)	4528(2)	35(1)
C(3)	5690(6)	2445(6)	1401(2)	32(2)
C(4)	8209(10)	4591(8)	5074(2)	36(2)
C(5)	7243(10)	3947(9)	5241(2)	35(2)
C(6)	7119(10)	3951(10)	5595(3)	42(2)
C(7)	6282(13)	3295(11)	5745(3)	52(3)
C(8)	5485(13)	2623(13)	5568(3)	56(3)
C(9)	5546(11)	2600(11)	5221(3)	46(3)
C(10)	6432(10)	3293(8)	5052(3)	38(2)
C(11)	5586(11)	2725(9)	4472(3)	39(2)
C(12)	4378(11)	3384(12)	4422(3)	49(3)
C(13)	5413(15)	2108(11)	3887(3)	59(4)
C(14)	7178(13)	1527(9)	4200(3)	52(3)
C(15)	10423(10)	6541(10)	2913(3)	46(3)
C(16)	8618(11)	6308(10)	2538(2)	42(3)
C(17)	7015(8)	7688(8)	2945(2)	30(2)
C(21)	9030(11)	8162(10)	3298(3)	43(3)
C(22)	8495(8)	7666(8)	2975(2)	29(2)
C(23)	7603(9)	6029(7)	3534(2)	30(2)
C(24)	6634(10)	6765(8)	3510(2)	31(2)
C(25)	8289(11)	6596(7)	4221(2)	32(2)
C(26)	8137(10)	7257(9)	4428(3)	37(2)
C(27)	6186(9)	7270(7)	3186(3)	33(2)

C(28)	4823(9)	7235(8)	3133(2)	32(2)
C(29)	4291(11)	7722(9)	2861(2)	38(2)
C(30)	5077(10)	8258(9)	2623(3)	37(2)
C(31)	4497(12)	8808(13)	2350(3)	57(4)
C(32)	5202(13)	9363(13)	2115(4)	68(4)
C(33)	6586(15)	9398(11)	2158(3)	60(3)
C(34)	7168(10)	8871(10)	2422(3)	44(2)
C(35)	6423(10)	8258(9)	2663(2)	35(2)
C(36)	7825(11)	8053(9)	4690(2)	40(2)
C(37)	8239(18)	9123(11)	4675(3)	71(4)
C(38)	7830(20)	9854(12)	4926(4)	91(6)
C(39)	7050(18)	9528(14)	5176(4)	83(6)
C(40)	6592(17)	8466(17)	5192(4)	84(5)
C(41)	6991(12)	7703(12)	4956(3)	55(3)
C(42)	5900(9)	7204(8)	3807(2)	29(2)
C(43)	5619(11)	8309(9)	3841(3)	42(2)
C(44)	4917(12)	8674(9)	4123(3)	50(3)
C(45)	4489(12)	7951(10)	4356(3)	48(3)
C(46)	4759(10)	6811(10)	4329(3)	41(2)
C(47)	5417(8)	6468(8)	4052(2)	30(2)
C(48)	10077(9)	5412(8)	3838(2)	31(2)
C(49)	10564(10)	4381(9)	3743(3)	34(2)
C(50)	11915(11)	4274(10)	3679(3)	45(3)
C(51)	12705(9)	5175(11)	3713(3)	48(3)
C(52)	12212(10)	6174(11)	3805(3)	47(3)
C(53)	10887(9)	6316(8)	3867(2)	33(2)
Cl(1S)	5470(30)	580(20)	3115(7)	283(15)
Cl(2S)	7880(50)	1186(17)	2994(8)	380(30)
C(2S)	6960(30)	590(40)	3321(9)	117(15)
O(1W)	360(30)	1833(19)	3343(5)	100(10)
O(2W)	3290(30)	1830(20)	3245(6)	106(9)

Table A 16–1. Crystal data and structure refinement for (*R*$_c$,*R*$_p$,*R*$_c$)-96.

Empirical formula	$C_{53..50}H_{54}Cl_3N_2OPPdPt$	
Formula weight	1179.80	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.2664(6) Å	α = 90°.
	b = 12.3061(7) Å	β = 90°.
	c = 39.800(2) Å	γ = 90°.
Volume	5028.3(5) Å^3	
Z	4	
Density (calculated)	1.558 Mg/m^3	
Absorption coefficient	3.367 mm^{-1}	
F(000)	2348	
Crystal size	0.40 x 0.36 x 0.28 mm^3	
Theta range for data collection	1.73to 27.50°.	
Index ranges	–12<=h<=13, –15<=k<=15, –39<=l<=51	
Reflections collected	50067	
Independent reflections	11499 [R(int) = 0.0387]	
Completeness to theta = 27.50°	100.0 %	
Absorption correction	Sadabs (Sheldrick, 2001)	
Max. and min. transmission	0.4524 and 0.3461	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	11499 / 34 / 583	
Goodness–of–fit on F^2	1.059	
Final R indices [I>2sigma(I)]	R_1= 0.0288, wR_2 = 0.0663	
R indices (all data)	R_1 = 0.0305, wR_2 = 0.0669	
Absolute structure parameter	0.007 (3)	
Largest diff. peak and hole	1.578 and –0.521 e.Å^{-3}	

Table A16–2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for (*R*$_c$,*R*$_p$,*R*$_c$)-96. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	1718(1)	4903(1)	8157(1)	22(1)
Pt(1)	2649(1)	6083(1)	9043(1)	23(1)
P(1)	1662(1)	4535(1)	8915(1)	22(1)
Cl(1)	2673(1)	6384(2)	8445(1)	32(1)
Cl(2)	820(1)	6217(1)	7763(1)	39(1)
N(1)	3754(4)	7497(3)	9156(1)	29(1)
N(2)	1023(3)	3563(3)	7888(1)	25(1)
C(1)	3493(4)	6655(3)	9707(1)	29(1)
C(2)	2585(4)	5995(3)	9542(1)	25(1)
C(3)	1686(4)	5408(3)	9743(1)	28(1)
C(4)	1742(5)	5418(3)	10083(1)	34(1)
C(5)	2708(4)	6029(3)	10256(1)	31(1)
C(6)	2817(5)	6022(4)	10608(1)	41(1)
C(7)	3704(6)	6658(5)	10769(1)	47(1)
C(8)	4525(5)	7336(5)	10584(1)	47(1)
C(9)	4467(5)	7346(4)	10243(1)	38(1)
C(10)	3571(5)	6692(4)	10064(1)	32(1)
C(11)	4455(5)	7251(4)	9486(1)	32(1)
C(12)	5671(5)	6582(5)	9439(1)	43(1)
C(13)	4703(5)	7803(4)	8897(1)	42(1)
C(14)	2855(6)	8418(4)	9210(1)	45(1)
C(15)	1692(4)	3484(3)	9217(1)	28(1)
C(16)	1836(5)	2806(3)	9426(1)	32(1)
C(17)	2386(4)	4005(3)	8534(1)	23(1)
C(18)	3335(4)	3258(3)	8516(1)	23(1)
C(19)	–428(4)	3590(4)	7903(1)	39(1)
C(20)	1417(5)	3734(4)	7531(1)	35(1)
C(21)	889(4)	1959(4)	8303(1)	32(1)
C(22)	1500(4)	2415(3)	7975(1)	24(1)
C(23)	2967(4)	2346(3)	7953(1)	30(2)
C(24)	3793(4)	2776(3)	8191(1)	27(1)

C(25)	5156(4)	2728(3)	8140(1)	30(1)
C(26)	5700(4)	2227(4)	7876(1)	33(1)
C(27)	4909(5)	1708(4)	7636(1)	31(1)
C(28)	5490(5)	1122(4)	7366(1)	39(1)
C(29)	4716(6)	608(4)	7136(1)	47(1)
C(30)	3379(6)	656(4)	7167(1)	42(1)
C(31)	2792(5)	1209(3)	7421(1)	36(1)
C(32)	3528(4)	1767(3)	7668(1)	27(1)
C(33)	2138(5)	2024(4)	9682(1)	37(1)
C(34)	2960(5)	2297(5)	9944(2)	53(1)
C(35)	3341(7)	1531(6)	10176(2)	69(2)
C(36)	2924(9)	518(6)	10156(2)	87(3)
C(37)	2123(11)	209(5)	9900(2)	98(3)
C(38)	1695(8)	963(4)	9660(2)	69(2)
C(39)	4054(4)	2832(3)	8814(1)	25(1)
C(40)	4566(4)	3543(3)	9060(1)	28(1)
C(41)	5247(5)	3150(4)	9328(1)	37(1)
C(42)	5461(5)	2060(4)	9365(1)	41(1)
C(43)	4970(5)	1352(4)	9130(1)	44(1)
C(44)	4286(5)	1723(4)	8850(1)	37(1)
C(45)	–81(4)	4659(3)	8833(1)	25(1)
C(46)	–919(4)	3779(4)	8875(1)	34(1)
C(47)	–2232(4)	3898(4)	8808(1)	41(1)
C(48)	–2717(5)	4874(4)	8705(1)	45(1)
C(49)	–1892(5)	5747(4)	8664(1)	45(1)
C(50)	–569(5)	5651(4)	8726(1)	33(1)
Cl(A)	7565(9)	10527(7)	8538(2)	195(3)
Cl(B)	6806(10)	8425(6)	8236(2)	194(4)
C(1S)	6470(30)	9778(15)	8270(7)	189(12)
C(2S)	2768(11)	9221(5)	8169(2)	98(3)
C(3S)	1262(14)	9026(9)	8114(4)	216(7)
C(4S)	3619(19)	8806(9)	7929(3)	223(7)
O(1S)	3055(7)	9596(4)	8402(2)	111(2)

Table A17–1. Crystal data and structure refinement for (*R*$_c$,*R*$_c$)-99.

Empirical formula	$C_{36}H_{41}AsCl_2N_2PdPt$	
Formula weight	937.01	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 13.0574(7) Å	α = 90°.
	b = 13.1029(6) Å	β = 90°.
	c = 19.9890(7) Å	γ = 90°.
Volume	3419.9(3) Å^3	
Z	4	
Density (calculated)	1.820 Mg/m^3	
Absorption coefficient	5.755 mm^{-1}	
F(000)	1824	
Crystal size	0.50 x 0.50 x 0.22 mm^3	
Theta range for data collection	1.86 to 27.50°.	
Index ranges	–16<=h<=13, –14<=k<=17, –21<=l<=25	
Reflections collected	23914	
Independent reflections	7773 [R(int) = 0.0290]	
Completeness to theta = 27.50°	100.0 %	
Absorption correction	None	
Max. and min. transmission	0.3641 and 0.1610	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	7773 / 0 / 386	
Goodness–of–fit on F^2	0.906	
Final R indices [I>2sigma(I)]	R_1= 0.0227, wR_2 = 0.0479	
R indices (all data)	R_1 = 0.0254, wR_2 = 0.0486	
Absolute structure parameter	0.006(3)	
Largest diff. peak and hole	1.129 and –0.542 e.Å^{-3}	

Table A17–2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for (R_c,R_c)-99. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pt(1)	6446(1)	6953(1)	6884(1)	29(1)
Pd(1)	8958(1)	7059(1)	7402(1)	34(1)
As(1)	6776(1)	7500(1)	7974(1)	28(1)
Cl(1)	7841(1)	5773(1)	7032(1)	43(1)
Cl(2)	9706(1)	7084(1)	6287(1)	71(1)
N(1)	6153(3)	6445(3)	5894(2)	41(1)
N(2)	10005(2)	8113(3)	7829(2)	45(1)
C(1)	4906(3)	7797(4)	6031(2)	48(1)
C(2)	5196(3)	7779(3)	6714(2)	34(1)
C(3)	4543(3)	8244(3)	7163(2)	42(1)
C(4)	3637(3)	8698(3)	6954(3)	54(1)
C(5)	3379(4)	8706(4)	6291(3)	70(2)
C(6)	4013(4)	8255(4)	5829(3)	66(2)
C(7)	5643(4)	7318(4)	5546(2)	54(1)
C(8)	6409(5)	8126(4)	5305(3)	79(2)
C(9)	7068(4)	6076(4)	5532(2)	61(1)
C(10)	5428(4)	5580(4)	5941(2)	57(1)
C(11)	8111(3)	6980(3)	8230(2)	30(1)
C(12)	8392(3)	6552(3)	8802(2)	32(1)
C(13)	7725(3)	6325(3)	9396(2)	39(1)
C(14)	11023(4)	7969(5)	7513(2)	71(2)
C(15)	9631(4)	9153(4)	7651(3)	64(1)
C(16)	10818(4)	8782(4)	8907(3)	66(2)
C(17)	10084(3)	8010(4)	8581(2)	45(1)
C(18)	10298(3)	6910(4)	8773(2)	42(1)
C(19)	11299(4)	6560(4)	8868(3)	62(1)
C(20)	11484(4)	5567(5)	9041(3)	66(1)
C(21)	10711(4)	4885(4)	9125(2)	54(1)
C(22)	9710(3)	5221(3)	9052(2)	42(1)
C(23)	9501(3)	6213(3)	8867(2)	34(1)
C(24)	5693(3)	7083(3)	8588(2)	33(1)

C(25)	5334(4)	7694(4)	9096(2)	53(1)
C(26)	4587(4)	7309(6)	9522(3)	80(2)
C(27)	4196(4)	6360(6)	9442(3)	80(2)
C(28)	4566(4)	5755(5)	8936(3)	68(2)
C(29)	5296(3)	6125(3)	3278(3)	56(2)
C(30)	–147(5)	5340(4)	8502(2)	46(1)
C(31)	7335(4)	9272(4)	8745(2)	53(1)
C(32)	7530(5)	10288(4)	8844(3)	76(2)
C(33)	7322(4)	10991(4)	8359(3)	72(2)
C(34)	6927(4)	10677(4)	7768(3)	63(1)
C(35)	6735(3)	9645(3)	7652(2)	46(1)

Table A18–1. Crystal data and structure refinement for (*R*$_c$,*S*$_c$)-100.

Empirical formula	$C_{36}H_{41}AsCl_2N_2PdPt$	
Formula weight	937.01	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2	
Unit cell dimensions	a = 22.5361(12) Å	α = 90°.
	b = 12.6788(6) Å	β = 90°.
	c = 13.2611(7) Å	γ = 90°.
Volume	3404.8(3) Å^3	
Z	4	
Density (calculated)	1.828 Mg/m^3	
Absorption coefficient	5.780 mm^{-1}	
F(000)	1824	
Crystal size	0.60 x 0.46 x 0.26 mm^3	
Theta range for data collection	1.71 to 27.49°.	
Index ranges	–23<=h<=29, –13<=k<=16, –17<=l<=16	
Reflections collected	11748	
Independent reflections	6933 [R(int) = 0.0256]	
Completeness to theta = 27.49°	99.9 %	
Absorption correction	Sadabs (Sheldrick, 2001)	
Max. and min. transmission	0.3149 and 0.1290	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	6933 / 1 / 386	
Goodness–of–fit on F^2	1.060	
Final R indices [I>2sigma(I)]	R_1= 0.0336, wR_2 = 0.0822	
R indices (all data)	R_1 = 0.0363, wR_2 = 0.0834	
Absolute structure parameter	0.007(6)	
Largest diff. peak and hole	3.006 and –1.905 e.Å^{-3}	

Table A18–2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for (R_c,S_c)-100. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pt(1)	8090(1)	10266(1)	6819(1)	32(1)
Pd(1)	7587(1)	10336(1)	8994(1)	27(1)
As(1)	6994(1)	9869(1)	6387(1)	26(1)
Cl(1)	8041(1)	11502(2)	8168(2)	42(1)
Cl(2)	8649(1)	10375(2)	10615(2)	56(1)
N(1)	9090(3)	10553(6)	7218(6)	50(2)
N(2)	7140(3)	9277(5)	9705(5)	37(1)
C(1)	8786(4)	9278(7)	5679(7)	46(2)
C(2)	8150(4)	9402(6)	5582(7)	43(2)
C(3)	7646(5)	9010(7)	4636(7)	51(2)
C(4)	7749(6)	8522(7)	3783(7)	56(2)
C(5)	8365(6)	8419(8)	3876(8)	62(2)
C(6)	8885(5)	8774(7)	4796(8)	56(2)
C(7)	9340(4)	9646(8)	6766(7)	51(2)
C(8)	9983(5)	9842(11)	6714(10)	84(4)
C(9)	9107(6)	11546(9)	6585(12)	79(3)
C(10)	9480(4)	10724(19)	8430(8)	135(10)
C(11)	6776(3)	10439(5)	7536(4)	26(1)
C(12)	6213(3)	10906(5)	7399(4)	27(1)
C(13)	5632(3)	11150(7)	6295(5)	38(2)
C(14)	7440(4)	9429(9)	10949(6)	62(3)
C(15)	7327(4)	8285(6)	9490(7)	51(2)
C(16)	6065(5)	8597(8)	9669(8)	57(2)
C(17)	6408(4)	9401(6)	9225(6)	38(2)
C(18)	6214(3)	10518(6)	9278(5)	37(2)
C(19)	6097(5)	10875(8)	10169(7)	52(2)
C(20)	5925(5)	11892(8)	10246(7)	60(2)
C(21)	5846(5)	12605(7)	9386(7)	50(2)
C(22)	5943(3)	12278(6)	8489(6)	40(2)
C(23)	6137(3)	11246(6)	8417(5)	31(1)
C(24)	6814(3)	8389(6)	6481(6)	37(2)

C(25)	6214(4)	8101(7)	6470(7)	51(2)
C(26)	6085(6)	7051(8)	6590(9)	70(3)
C(27)	6539(7)	6294(9)	6724(9)	82(4)
C(28)	7143(7)	6578(8)	6736(9)	71(3)
C(29)	7272(5)	7627(6)	6613(7)	49(2)
C(30)	6377(3)	10210(7)	4835(4)	31(1)
C(31)	5921(4)	9497(7)	4131(6)	48(2)
C(32)	5551(4)	9754(8)	3009(6)	54(2)
C(33)	5621(4)	10707(8)	2580(6)	50(2)
C(34)	6066(5)	11422(8)	3299(7)	54(2)
C(35)	6460(4)	11168(6)	4405(6)	42(2)

Table A 19–1. Crystal data and structure refinement for (*R*$_c$,*R*$_c$)-102.

Empirical formula	$C_{39.50}H_{44}AsCl_3N_2PdPt$	
Formula weight	1029.53	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	P4(3)2(1)2	
Unit cell dimensions	a = 13.3254(5) Å	α = 90°.
	b = 13.3254(5) Å	β = 90°.
	c = 43.827(3) Å	γ = 90°.
Volume	7782.3(7) Å^3	
Z	8	
Density (calculated)	1.757 Mg/m^3	
Absorption coefficient	5.133 mm^{-1}	
F(000)	4024	
Crystal size	0.30 x 0.28 x 0.10 mm^3	
Theta range for data collection	1.60to 27.50°.	
Index ranges	–17<=h<=17, –16<=k<=17, –38<=l<=56	
Reflections collected	55324	
Independent reflections	8953 [R(int) = 0.0697]	
Completeness to theta = 27.50°	100.0 %	
Absorption correction	Sadabs (Sheldrick, 2001)	
Max. and min. transmission	0.6278 and 0.3081	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	8953 / 19 / 449	
Goodness–of–fit on F^2	1.056	
Final R indices [I>2sigma(I)]	R_1= 0.0392, wR_2 = 0.0855	
R indices (all data)	R_1 = 0.0460, wR_2 = 0.0879	
Absolute structure parameter	0.001 (6)	
Largest diff. peak and hole	1.348 and –0.556 e.Å^{-3}	

Table A19–2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for (R_c,R_c)-102. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pt(1)	3164(1)	4039(1)	6468(1)	30(1)
Pd(1)	3335(1)	6427(1)	6262(1)	35(1)
As(1)	3862(1)	4345(1)	5987(1)	29(1)
Cl(1)	1973(1)	5334(2)	6346(1)	37(1)
Cl(2)	3980(5)	2851(4)	6585(2)	32(1)
N(1)	2571(4)	3802(4)	6907(1)	38(1)
N(2)	4477(5)	7459(4)	6138(1)	41(1)
C(1)	3940(5)	2634(5)	6893(2)	32(1)
C(2)	3980(5)	2851(4)	6585(2)	32(1)
C(3)	4480(5)	2171(5)	6387(2)	32(1)
C(4)	4938(5)	1330(5)	6502(2)	37(2)
C(5)	4898(5)	1083(5)	6814(2)	33(1)
C(6)	5323(5)	182(6)	6929(2)	42(2)
C(7)	5263(6)	–27(6)	7239(2)	52(2)
C(8)	4763(6)	642(6)	7435(2)	54(2)
C(9)	4355(5)	1506(6)	7330(2)	44(2)
C(10)	4391(5)	1748(5)	7019(1)	33(1)
C(11)	3445(5)	3392(5)	7097(2)	39(2)
C(12)	4176(6)	4202(6)	7192(2)	51(2)
C(13)	2132(6)	4697(6)	7055(2)	52(2)
C(14)	1779(6)	3029(6)	6890(2)	54(2)
C(15)	3449(5)	5691(5)	5872(1)	30(1)
C(16)	3149(5)	6036(5)	5600(1)	36(1)
C(17)	3148(7)	5463(6)	5299(2)	49(2)
C(18)	4324(7)	8415(6)	6312(2)	60(2)
C(19)	5454(6)	7015(6)	6234(2)	57(2)
C(20)	5241(6)	8431(7)	5690(2)	59(2)
C(21)	4472(6)	7676(6)	5801(2)	43(2)
C(22)	3412(5)	7882(5)	5688(2)	36(2)
C(23)	3044(6)	8866(6)	5680(2)	47(2)
C(24)	2076(6)	9060(6)	5583(2)	47(2)

C(25)	1474(6)	8274(6)	5481(2)	47(2)
C(26)	1832(6)	7325(6)	5481(3)	45(2)
C(27)	2810(5)	7099(5)	5587(2)	33(1)
C(28)	5311(5)	4419(5)	5958(2)	35(1)
C(29)	5901(5)	4174(5)	6209(2)	41(2)
C(30)	6941(6)	4273(6)	6190(2)	54(2)
C(31)	7368(6)	4636(6)	5932(2)	56(2)
C(32)	6783(6)	4877(6)	5680(2)	57(2)
C(33)	5765(6)	4778(6)	5698(2)	48(2)
C(34)	3453(5)	3321(5)	5698(1)	30(1)
C(35)	4094(6)	2862(5)	5496(2)	48(2)
C(36)	3766(7)	2077(6)	5311(2)	57(2)
C(37)	2777(7)	1769(6)	5332(2)	59(2)
C(38)	2117(7)	2227(7)	5533(2)	62(2)
C(39)	2466(6)	3008(6)	5717(2)	47(2)
C(1S)	6980(40)	7202(12)	5045(17)	176(17)
Cl(1A)	6631(9)	6014(10)	4934(2)	181(5)
Cl(2A)	6351(6)	8245(9)	4929(2)	161(4)

Table A20–1. Crystal data and structure refinement for (*R*$_c$,*R*$_c$)-105.

Empirical formula	$C_{35}H_{41}AsCl_2N_2Pd_2$	
Formula weight	848.32	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 13.0151(15) Å	α = 90°.
	b = 13.1345(15) Å	β = 90°.
	c = 19.995(2) Å	γ = 90°.
Volume	3418.1(3) Å^3	
Z	4	
Density (calculated)	1.648 Mg/m^3	
Absorption coefficient	2.196 mm^{-1}	
F(000)	1696	
Crystal size	0.60 x 0.46 x 0.26 mm^3	
Theta range for data collection	1.71 to 27.49°.	
Index ranges	–16<=h<=15, –17<=k<=17, –25<=l<=20	
Reflections collected	24278	
Independent reflections	7833 [R(int) = 0.0468]	
Completeness to theta = 27.50°	100.0 %	
Absorption correction	Sadabs (Sheldrick, 2001)	
Max. and min. transmission	0.8795 and 0.5053	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	7833 / 1 / 386	
Goodness–of–fit on F^2	1.001	
Final R indices [I>2sigma(I)]	R_1= 0.0365, wR_2 = 0.0686	
R indices (all data)	R_1 = 0.0447, wR_2 = 0.0711	
Absolute structure parameter	0.022(10)	
Largest diff. peak and hole	0.633 and –0.379 e.Å^{-3}	

Table A20–2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for (R_c,R_c)-105. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	3539(1)	3060(1)	6879(1)	30(1)
Pd(2)	1059(1)	2953(1)	7403(1)	35(1)
As(1)	3232(1)	2492(1)	7973(1)	30(1)
Cl(1)	2163(1)	4261(2)	7053(1)	44(1)
Cl(2)	324(1)	2923(1)	6285(2)	72(1)
N(1)	3829(3)	3569(3)	5889(2)	42(1)
N(2)	3(3)	1902(3)	7825(2)	47(1)
C(1)	5062(4)	2209(4)	6033(2)	49(1)
C(2)	4794(3)	2229(3)	6711(2)	34(1)
C(3)	5448(3)	1774(3)	7165(3)	44(1)
C(4)	6356(4)	1314(4)	6940(3)	54(1)
C(5)	6594(5)	1308(5)	6278(4)	74(2)
C(6)	5965(5)	1751(4)	5825(3)	66(2)
C(7)	4319(4)	2676(4)	5548(2)	56(1)
C(8)	3544(5)	1897(5)	5316(3)	82(2)
C(9)	2911(4)	3943(4)	5533(2)	62(2)
C(10)	4566(5)	4412(4)	5935(3)	61(2)
C(11)	1897(3)	3014(3)	8237(2)	31(1)
C(12)	1610(3)	3448(3)	8801(2)	33(1)
C(13)	2288(3)	3655(4)	9403(2)	42(1)
C(14)	–1014(4)	2047(5)	7501(3)	69(2)
C(15)	371(5)	854(4)	7641(3)	63(2)
C(16)	–829(5)	1238(4)	8899(3)	70(2)
C(17)	–86(4)	2003(4)	8573(2)	47(1)
C(18)	–298(3)	3096(4)	8771(2)	43(1)
C(19)	–1291(4)	3448(5)	8867(3)	62(2)
C(20)	–1487(5)	4440(5)	9031(3)	65(2)
C(21)	–699(4)	5109(4)	9127(3)	56(1)
C(22)	299(4)	4782(4)	9053(2)	43(1)
C(23)	518(3)	3779(4)	8870(2)	35(1)
C(24)	4308(3)	2914(4)	8588(2)	35(1)

C(25)	4693(4)	3874(4)	8506(2)	49(1)
C(26)	5429(5)	4262(5)	8929(3)	69(2)
C(27)	5788(5)	3671(6)	9432(3)	84(2)
C(28)	5432(5)	2720(6)	9520(3)	80(2)
C(29)	4684(4)	2315(4)	9093(2)	55(1)
C(30)	3062(3)	1057(3)	8147(2)	38(1)
C(31)	2676(4)	731(4)	8752(3)	55(1)
C(32)	2463(5)	–268(4)	8868(3)	73(2)
C(33)	2664(5)	–980(4)	8380(4)	75(2)
C(34)	3060(5)	–676(4)	7779(3)	68(2)
C(35)	3274(4)	352(3)	7660(3)	51(1)

Table A21–1. Crystal data and structure refinement for (*R*$_c$,*S*$_c$)-106.

Empirical formula	$C_{35}H_{41}AsCl_2N_2Pd_2$	
Formula weight	848.32	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2	
Unit cell dimensions	a = 22.3106(18) Å	α = 90°.
	b = 12.9235(10) Å	β = 115.438°.
	c = 13.0378(10) Å	γ = 90°.
Volume	3394.7(5) Å^3	
Z	4	
Density (calculated)	1.660 Mg/m^3	
Absorption coefficient	2.211 mm^{-1}	
F(000)	1696	
Crystal size	0.48 x 0.38 x 0.30 mm^3	
Theta range for data collection	1.73 to 27.50°.	
Index ranges	–27<=h<=28, –15<=k<=16, –14<=l<=16	
Reflections collected	12011	
Independent reflections	7549 [R(int) = 0.0337]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Sadabs (Sheldrick, 2001)	
Max. and min. transmission	0.5568 and 0.4176	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	7549 / 1 / 386	
Goodness–of–fit on F^2	0.989	
Final R indices [I>2sigma(I)]	R_1= 0.0415, wR_2 = 0.0917	
R indices (all data)	R_1 = 0.0475, wR_2 = 0.0949	
Absolute structure parameter	0.019(11)	
Largest diff. peak and hole	1.385 and –0.921 e.Å^{-3}	

Table A21–2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for (R_c,S_c)-106. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	3117(1)	5040(1)	1886(1)	28(1)
Pd(2)	2590(1)	4962(1)	3981(1)	26(1)
As(1)	2025(1)	4465(1)	1382(1)	25(1)
Cl(1)	2947(1)	6266(1)	3121(1)	35(1)
Cl(2)	3678(1)	5007(2)	5579(1)	47(1)
N(1)	4121(3)	5504(4)	2375(5)	45(1)
N(2)	2173(2)	3876(4)	4721(4)	35(1)
C(1)	3392(4)	4110(5)	1102(7)	53(2)
C(2)	3297(3)	4156(5)	785(5)	39(2)
C(3)	2863(4)	3716(5)	–205(6)	45(2)
C(4)	3099(5)	3232(5)	–925(6)	64(3)
C(5)	3783(6)	3212(6)	–597(9)	78(3)
C(6)	4210(6)	3644(7)	380(9)	80(3)
C(7)	4441(4)	4568(6)	2205(7)	59(2)
C(8)	4579(5)	3823(7)	3204(8)	84(3)
C(9)	4459(4)	5958(6)	3543(6)	57(2)
C(10)	4126(4)	6326(6)	1588(6)	59(2)
C(11)	1768(2)	5012(5)	2527(4)	28(1)
C(12)	1203(3)	5453(4)	2394(4)	27(1)
C(13)	607(3)	5631(5)	1292(4)	35(1)
C(14)	2493(3)	4015(6)	5979(5)	47(2)
C(15)	2349(3)	2818(5)	4480(6)	45(2)
C(16)	1097(3)	3198(5)	4724(6)	44(2)
C(17)	1425(3)	3971(5)	4234(5)	33(1)
C(18)	1235(3)	5094(5)	4316(4)	30(1)
C(19)	1146(3)	5455(6)	5250(5)	44(2)
C(20)	995(4)	6458(5)	5343(5)	46(2)
C(21)	910(3)	7142(5)	4499(6)	44(2)
C(22)	970(3)	6811(4)	3531(5)	33(1)
C(23)	1139(3)	5781(4)	3438(4)	27(1)
C(24)	1859(3)	2994(4)	1462(2)	31(1)

C(25)	1267(3)	2688(5)	1437(5)	41(1)
C(26)	1152(4)	1648(5)	1555(6)	53(2)
C(27)	1640(4)	934(5)	1705(6)	58(2)
C(28)	2229(4)	1237(5)	1726(6)	54(2)
C(29)	2342(3)	2278(5)	1610(5)	40(1)
C(30)	1422(3)	4804(4)	–180(4)	29(1)
C(31)	989(3)	4085(5)	–918(5)	42(2)
C(32)	599(4)	4364(6)	–2041(5)	52(2)
C(33)	632(3)	5344(5)	–2416(5)	43(2)
C(34)	1045(3)	6046(5)	–1677(5)	42(2)
C(35)	1449(3)	5788(5)	–566(5)	38(1)

Table A22–1. Crystal data and structure refinement for (*R*$_p$)-111.

Empirical formula	$C_{22}H_{24}Cl_2P_2Pd$	
Formula weight	527.65	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 8.6866(12) Å	α = 90°.
	b = 14.7152(19) Å	β = 109.085°.
	c = 9.3560(12) Å	γ = 90°.
Volume	1130.2(3) Å^3	
Z	2	
Density (calculated)	1.551 Mg/m^3	
Absorption coefficient	1.204 mm^{-1}	
F(000)	532	
Crystal size	0.20 x 0.08 x 0.06 mm^3	
Theta range for data collection	2.30 to 27.50°.	
Index ranges	–11<=h<=11, –18<=k<=19, –7<=l<=12	
Reflections collected	8058	
Independent reflections	5110 [R(int) = 0.0392]	
Completeness to theta = 27.50°	100.0 %	
Absorption correction	Sadabs (Sheldrick, 2001)	
Max. and min. transmission	0.9313 and 0.7947	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	5110 / 1 / 245	
Goodness–of–fit on F^2	1.011	
Final R indices [I>2sigma(I)]	R_1= 0.0510, wR_2 = 0.0939	
R indices (all data)	R_1 = 0.0641, wR_2 = 0.0997	
Absolute structure parameter	0.07(4)	
Largest diff. peak and hole	1.296 and –0.527 e.Å^{-3}	

Table A22–2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for (R_p)-111. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	8435(1)	2575(1)	8354(1)	31(1)
P(1)	8547(2)	2233(1)	6059(2)	36(1)
P(2)	11135(2)	2420(1)	9151(2)	32(1)
Cl(1)	5586(2)	2660(2)	7314(1)	52(1)
Cl(2)	8464(2)	2909(1)	10826(2)	58(1)
C(1)	10679(8)	2304(4)	6148(7)	47(2)
C(2)	11744(8)	1910(4)	7630(7)	44(2)
C(3)	7366(8)	2897(4)	4431(6)	50(2)
C(4)	7816(12)	3891(5)	4559(9)	80(3)
C(5)	7990(8)	1059(4)	5633(6)	36(1)
C(6)	7869(9)	653(5)	4286(7)	49(2)
C(7)	7420(9)	–244(4)	4025(8)	54(2)
C(8)	7118(9)	–757(5)	5119(7)	52(2)
C(9)	7207(13)	–351(5)	6459(9)	75(3)
C(10)	7668(10)	549(4)	6735(7)	55(2)
C(11)	12058(7)	1726(4)	10818(6)	34(1)
C(12)	12252(9)	810(4)	10686(8)	48(2)
C(13)	13007(10)	299(5)	11988(9)	62(2)
C(14)	13488(9)	713(6)	13370(8)	58(2)
C(15)	13224(9)	1610(5)	13509(8)	56(2)
C(16)	12499(8)	2133(5)	12212(7)	48(2)
C(17)	12164(7)	3507(4)	9529(6)	34(1)
C(18)	13841(8)	3567(4)	10010(6)	41(2)
C(19)	14601(9)	4400(5)	10266(7)	51(2)
C(20)	13709(10)	5184(5)	10024(7)	55(2)
C(21)	12044(10)	5144(4)	9522(7)	49(2)
C(22)	11257(8)	4309(4)	9283(6)	40(2)

Table A 23–1. Crystal data and structure refinement for (*R*$_c$,*S*$_c$,*S*$_p$)-117.

Empirical formula	$C_{37}H_{42}ClNO_4P_2Pd$	
Formula weight	768.54	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 12.5387(8) Å	α = 90°.
	b = 16.3372(10) Å	β = 90°.
	c = 18.7069(11) Å	γ = 90°.
Volume	3832.1(4) Å^3	
Z	4	
Density (calculated)	1.479 Mg/m^3	
Absorption coefficient	0.817 mm^{-1}	
F(000)	1752	
Crystal size	0.20 x 0.18x 0.14 mm^3	
Theta range for data collection	1.65 to 27.50°.	
Index ranges	–16<=h<=16, –20<=k<=21, –24<=l<=20	
Reflections collected	30906	
Independent reflections	8806 [R(int) = 0.0458]	
Completeness to theta = 27.50°	100.0 %	
Absorption correction	Sadabs (Sheldrick, 2001)	
Max. and min. transmission	0.8942 and 0.8536	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	8806 / 62 / 494	
Goodness–of–fit on F^2	1.070	
Final R indices [I>2sigma(I)]	R_1= 0.0444, wR_2 = 0.0986	
R indices (all data)	R_1 = 0.0504, wR_2 = 0.1014	
Absolute structure parameter	–0.01(3)	
Largest diff. peak and hole	0.874 and –0.515 e.Å^{-3}	

Table A23–2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for (R_c,S_c,S_p)-117. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	7228(1)	4313(1)	4874(1)	26(1)
P(1)	6163(1)	3705(1)	4038(1)	29(1)
P(2)	5702(1)	4303(1)	5584(1)	28(1)
N(1)	8309(3)	4928(2)	5545(2)	33(1)
C(1)	9837(3)	4768(3)	4472(2)	33(1)
C(2)	8587(3)	4237(3)	4244(2)	33(1)
C(3)	8832(4)	3704(3)	3665(2)	40(1)
C(4)	9792(4)	3732(3)	3322(3)	43(1)
C(5)	10601(3)	4272(3)	3535(2)	40(1)
C(6)	11597(4)	4317(4)	3185(3)	52(1)
C(7)	12391(4)	4815(3)	3416(3)	60(2)
C(8)	12218(4)	5310(3)	4017(3)	55(1)
C(9)	11256(4)	5307(3)	4371(3)	47(1)
C(10)	10423(3)	4791(3)	4140(2)	38(1)
C(11)	9117(3)	5349(2)	5065(2)	36(1)
C(12)	8687(4)	6145(3)	4763(3)	47(1)
C(13)	7838(4)	5524(3)	6048(2)	48(1)
C(14)	8884(3)	4314(3)	5978(2)	43(1)
C(15)	6092(4)	4205(3)	3167(2)	43(1)
C(16)	5195(5)	5123(3)	3219(3)	52(1)
C(17)	4810(3)	3551(2)	5187(2)	31(1)
C(18)	4769(3)	3718(2)	4380(2)	32(1)
C(19)	4005(4)	3140(3)	3993(3)	42(1)
C(20)	6411(3)	2624(3)	3879(2)	34(1)
C(21)	6809(4)	2148(3)	4428(3)	41(1)
C(22)	6887(4)	1307(3)	4352(3)	51(1)
C(23)	6595(4)	944(3)	3721(4)	60(2)
C(24)	6217(4)	1410(3)	3166(3)	61(2)
C(25)	6105(4)	2247(3)	3243(3)	47(1)
C(26)	5990(3)	3964(2)	6485(2)	30(1)
C(27)	6455(3)	3197(3)	6568(2)	37(1)

C(28)	6835(4)	2945(3)	7225(2)	43(1)
C(29)	6738(4)	3456(3)	7809(2)	47(1)
C(30)	6272(4)	4213(3)	7740(2)	45(1)
C(31)	5900(4)	4473(3)	7075(2)	36(1)
C(32)	4898(3)	5219(2)	5621(2)	30(1)
C(33)	3991(3)	5262(2)	6055(2)	37(1)
C(34)	3337(4)	5936(3)	6035(3)	45(1)
C(35)	3567(4)	6571(3)	5576(3)	47(1)
C(36)	4448(4)	6540(3)	5140(3)	50(1)
C(37)	5118(4)	5862(3)	5169(3)	41(1)
Cl(1)	9401(1)	1997(1)	8493(1)	56(1)
O(1)	10506(3)	2159(3)	8469(3)	84(1)
O(2)	9141(14)	1316(10)	8089(8)	159(7)
O(3)	8915(14)	2664(9)	8244(12)	200(8)
O(4)	9104(9)	1844(9)	9187(3)	81(3)

Table A22–1. Crystal data and structure refinement for (*R*$_p$)-111.

Empirical formula	$C_{22}H_{24}Cl_2P_2Pd$	
Formula weight	527.65	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 8.6866(12) Å	α = 90°.
	b = 14.7152(19) Å	β = 109.085°.
	c = 9.3560(12) Å	γ = 90°.
Volume	1130.2(3) Å^3	
Z	2	
Density (calculated)	1.551 Mg/m^3	
Absorption coefficient	1.204 mm^{-1}	
F(000)	532	
Crystal size	0.20 x 0.08 x 0.06 mm^3	
Theta range for data collection	2.30 to 27.50°.	
Index ranges	–11<=h<=11, –18<=k<=19, –7<=l<=12	
Reflections collected	8058	
Independent reflections	5110 [R(int) = 0.0392]	
Completeness to theta = 27.50°	100.0 %	
Absorption correction	Sadabs (Sheldrick, 2001)	
Max. and min. transmission	0.9313 and 0.7947	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	5110 / 1 / 245	
Goodness–of–fit on F^2	1.011	
Final R indices [I>2sigma(I)]	R_1= 0.0510, wR_2 = 0.0939	
R indices (all data)	R_1 = 0.0641, wR_2 = 0.0997	
Absolute structure parameter	0.07(4)	
Largest diff. peak and hole	1.296 and –0.527 e.Å^{-3}	

Table A22–2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ × 10^3) for (R_p)-111. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	8435(1)	2575(1)	8354(1)	31(1)
P(1)	8547(2)	2233(1)	6059(2)	36(1)
P(2)	11135(2)	2420(1)	9151(2)	32(1)
Cl(1)	5586(2)	2660(2)	7314(1)	52(1)
Cl(2)	8464(2)	2909(1)	10826(2)	58(1)
C(1)	10679(8)	2304(4)	6148(7)	47(2)
C(2)	11744(8)	1910(4)	7630(7)	44(2)
C(3)	7366(8)	2897(4)	4431(6)	50(2)
C(4)	7816(12)	3891(5)	4559(9)	80(3)
C(5)	7990(8)	1059(4)	5633(6)	36(1)
C(6)	7869(9)	653(5)	4286(7)	49(2)
C(7)	7420(9)	–244(4)	4025(8)	54(2)
C(8)	7118(9)	–757(5)	5119(7)	52(2)
C(9)	7207(13)	–351(5)	6459(9)	75(3)
C(10)	7668(10)	549(4)	6735(7)	55(2)
C(11)	12058(7)	1726(4)	10818(6)	34(1)
C(12)	12252(9)	810(4)	10686(8)	48(2)
C(13)	13007(10)	299(5)	11988(9)	62(2)
C(14)	13488(9)	713(6)	13370(8)	58(2)
C(15)	13224(9)	1610(5)	13509(8)	56(2)
C(16)	12499(8)	2133(5)	12212(7)	48(2)
C(17)	12164(7)	3507(4)	9529(6)	34(1)
C(18)	13841(8)	3567(4)	10010(6)	41(2)
C(19)	14601(9)	4400(5)	10266(7)	51(2)
C(20)	13709(10)	5184(5)	10024(7)	55(2)
C(21)	12044(10)	5144(4)	9522(7)	49(2)
C(22)	11257(8)	4309(4)	9283(6)	40(2)

Table A 23–1. Crystal data and structure refinement for (R_c,R_c,S_p)-126.

Empirical formula	$C_{37}H_{42}ClNO_4P_2Pd$	
Formula weight	768.54	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.5512(10) Å	α = 90°.
	b = 15.4223(16) Å	β = 90°.
	c = 23.297(2) Å	γ = 90°.
Volume	3791.0(7) $Å^3$	
Z	4	
Density (calculated)	1.418 Mg/m^3	
Absorption coefficient	0.686 mm^{-1}	
F(000)	1672	
Crystal size	0.20 x 0.06x 0.06 mm^3	
Theta range for data collection	1.58 to 27.50°.	
Index ranges	–13<=h<=13, –20<=k<=16, –30<=l<=30	
Reflections collected	26912	
Independent reflections	8706 [R(int) = 0.0549]	
Completeness to theta = 27.50°	100.0 %	
Absorption correction	Sadabs (Sheldrick, 2001)	
Max. and min. transmission	0.9600 and 0.8750	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	8706 / 0 / 448	
Goodness–of–fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R_1= 0.0497, wR_2 = 0.0928	
R indices (all data)	R_1 = 0.0650, wR_2 = 0.0981	
Absolute structure parameter	0.00(3)	
Largest diff. peak and hole	0.879 and –0.414 e.$Å^{-3}$	

Table A23–2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ × 10^3) for (R_c,R_c,S_P)-126. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	717(1)	5044(1)	5987(1)	29(1)
P(1)	1323(1)	5539(1)	5114(1)	30(1)
P(2)	− 1267(1)	5606(1)	5724(1)	30(1)
N(1)	415(3)	4692(2)	6865(2)	35(1)
C(1)	2690(4)	4552(3)	6770(2)	32(1)
C(2)	2439(4)	4502(3)	6186(2)	32(1)
C(3)	3343(4)	4087(3)	5833(2)	37(1)
C(4)	4450(4)	3773(3)	6045(2)	39(1)
C(5)	4760(4)	3862(3)	6636(2)	35(1)
C(6)	5960(4)	3594(3)	6852(2)	44(1)
C(7)	6246(5)	3728(4)	7419(2)	50(1)
C(8)	5382(4)	4124(3)	7787(2)	49(1)
C(9)	4213(4)	4372(3)	7591(2)	41(1)
C(10)	3876(4)	4260(3)	7006(2)	35(1)
C(11)	1667(3)	4935(3)	7143(2)	36(1)
C(12)	1836(5)	5914(3)	7198(2)	47(1)
C(13)	− 674(4)	5118(4)	7178(2)	50(1)
C(14)	221(5)	3745(3)	6924(2)	47(1)
C(15)	3659(5)	6218(4)	5497(2)	55(1)
C(16)	2461(4)	6426(3)	5164(2)	40(1)
C(17)	− 52(4)	6003(3)	4722(2)	32(1)
C(18)	336(4)	6642(3)	4247(2)	44(1)
C(19)	− 986(4)	6392(3)	5151(2)	32(1)
C(20)	1891(4)	4781(3)	4577(2)	31(1)
C(21)	2935(4)	4937(4)	4230(2)	40(1)
C(22)	3251(5)	4362(4)	3801(2)	49(1)
C(23)	2531(5)	3638(4)	3704(2)	53(1)
C(24)	1480(5)	3487(3)	4038(2)	54(1)
C(25)	1175(5)	4047(3)	4477(2)	44(1)
C(26)	− 2334(4)	6171(3)	6206(2)	32(1)
C(27)	− 1921(5)	6937(3)	6457(2)	42(1)

C(28)	– 2662(5)	7371(3)	6843(2)	49(1)
C(29)	– 3824(5)	7049(4)	6999(2)	52(1)
C(30)	– 4254(5)	6291(3)	6756(2)	47(1)
C(31)	– 3512(4)	5851(3)	6367(2)	38(1)
C(32)	– 2146(4)	4734(3)	5383(2)	33(1)
C(33)	– 3175(4)	4883(4)	5023(2)	43(1)
C(34)	– 3736(5)	4208(4)	4732(2)	55(1)
C(35)	– 3308(5)	3373(4)	4797(2)	60(2)
C(36)	– 2297(5)	3211(3)	5156(2)	54(1)
C(37)	– 1722(4)	3887(3)	5451(3)	41(1)
Cl(1)	1114(1)	8509(1)	6217(1)	45(1)
O(1)	2251(5)	8929(5)	6159(2)	140(3)
O(2)	290(7)	9051(6)	6478(3)	175(4)
O(3)	1249(8)	7799(4)	6557(3)	178(4)
O(4)	588(5)	8312(3)	5676(2)	85(1)

Table A 24–1. Crystal data and structure refinement for (R_c,S_p)-131.

Empirical formula	$C_{30}H_{36}Cl_3N_2O_4PPd$	
Formula weight	732.33	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 9.8594(4) Å	α = 90°.
	b = 14.0726(6) Å	β = 90.2890(10)°.
	c = 11.7832(5) Å	γ = 90°.
Volume	1634.87(12) Å^3	
Z	2	
Density (calculated)	1.488 Mg/m^3	
Absorption coefficient	0.898 mm^{-1}	
F(000)	748	
Crystal size	0.60 x 0.34x 0.34 mm^3	
Theta range for data collection	1.73 to 27.50°.	
Index ranges	–12<=h<=12, –18<=k<=15, –15<=l<=11	
Reflections collected	11578	
Independent reflections	6980 [R(int) = 0.0166]	
Completeness to theta = 27.50°	99.8 %	
Absorption correction	Sadabs (Sheldrick, 2001)	
Max. and min. transmission	0.7499 and 0.6148	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	6980 / 4 / 374	
Goodness–of–fit on F^2	1.028	
Final R indices [I>2sigma(I)]	R_1= 0.0332, wR_2 = 0.0864	
R indices (all data)	R_1 = 0.0344, wR_2 = 0.0876	
Absolute structure parameter	0.02(2)	
Largest diff. peak and hole	0.715 and –0.332 e.Å^{-3}	

Table A24–2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for (*R*$_c$,*S*$_p$)-131. U(eq) is defined as one third of the trace of the

orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	3120(1)	3583(1)	6318(1)	34(1)
P(1)	4186(1)	3971(1)	4707(1)	40(1)
N(1)	2377(1)	2951(2)	7849(2)	37(1)
N(2)	3835(3)	4854(2)	7122(3)	44(1)
C(1)	2174(3)	1692(2)	6475(3)	34(1)
C(2)	2353(3)	2388(2)	5671(3)	36(1)
C(3)	1870(3)	2236(3)	4556(3)	43(1)
C(4)	1270(3)	1398(3)	4256(3)	50(1)
C(5)	1143(3)	637(3)	5049(3)	49(1)
C(6)	611(4)	–248(4)	4739(5)	69(1)
C(7)	528(4)	–969(4)	5465(5)	74(1)
C(8)	958(5)	–831(3)	6593(5)	71(1)
C(9)	1473(4)	24(3)	6951(4)	54(1)
C(10)	1598(4)	783(2)	6192(3)	40(1)
C(11)	2630(4)	1905(3)	7675(3)	40(1)
C(12)	4124(4)	1627(3)	7829(3)	52(1)
C(13)	3017(4)	3274(3)	8925(3)	53(1)
C(14)	869(3)	3106(3)	7964(3)	46(1)
C(15)	4944(4)	3012(3)	3884(3)	54(1)
C(16)	5892(5)	2384(3)	4597(5)	67(1)
C(17)	5652(4)	4690(3)	5119(3)	49(1)
C(18)	6083(4)	4548(3)	6376(3)	53(1)
C(19)	5170(4)	5078(3)	7148(3)	48(1)
C(20)	5635(5)	5808(4)	7822(4)	67(1)
C(21)	4768(6)	6330(4)	8473(4)	70(1)
C(22)	3402(5)	6137(3)	8418(4)	67(1)
C(23)	2962(5)	5390(3)	7733(4)	54(1)
C(24)	3247(4)	4668(3)	3676(3)	45(1)
C(25)	2565(4)	5457(3)	4070(4)	51(1)
C(26)	1857(4)	6042(3)	3318(5)	67(1)
C(27)	1791(5)	5824(4)	2204(5)	74(1)
C(28)	2439(7)	5042(6)	1819(4)	97(2)
C(29)	3159(6)	4453(4)	2536(4)	77(2)

Cl(1)	9398(1)	6335(1)	9105(1)	69(1)
O(1)	9639(4)	5571(3)	8362(3)	86(1)
O(2)	10404(6)	6817(7)	9582(7)	181(4)
O(3)	8524(12)	6078(6)	9934(7)	237(6)
O(4)	8485(8)	6988(6)	8574(7)	201(5)

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