ASYMMETRIC LIGAND TRANSFORMATION REACTIONS

PULLARKAT APPUKUTTAN SUMOD

(*BSc*, *MSc*, *MPhil*.)

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Summary

The [4+2] Diels-Alder reactions involving 3,4-dimethyl-1-phenylphosphole **44** and three sulfonated phosphine functionalized dienophiles viz. 3,4-dimethyl-1-phenylphosphole-1-sulfide **45**, diphenylvinylphosphine sulfide **53** and divinylphenylphosphine sulfide **56** were carried out by employing palladium complexes containing the ortho metalated (*R*)-(1-(dimethylamino)ethyl)naphthalene (R_c)-**36** as the chiral template. Appreciable selectivity and successful separation of the diastereomers formed in the cycloaddition reaction could be achieved only in the case of the reaction involving 3,4-dimethyl-1-phenylphosphole-1-sulfide. It was observed that 3,4-dimethyl-1-phenylphosphole functions as the cyclic diene whilst the sulfonated analogue 3,4-dimetyl-1-phenylphosphole-1-sulfide assumes the role of dienophile in the course of the cycloaddition. The absolute stereochemistry of the formed P^P(S) ligand was established by means of single crystal X-ray diffraction analysis of the formed cycloadduct (R_c,S_p,R_p)-**48**. In the case of the cycloaddition reactions involving **53** and **56**, separation of the diastereomers formed was not successful owing to the poor selectivity of the cycloaddition. These P^P(S) ligands were characterized by means of single crystal X-ray analysis of their dichloro complexes which crystallized out as racemic mixtures.

The cycloaddition reaction between 3,4-dimethyl-1-phenylphosphole-1-sulfide **45** and divinylphenylphosphine **58** resulted in the formation of four isomers in unequal amounts (17: 3: 1: 1). The major isomer (R_p,R_p,S_p)-**61b** was subsequently isolated as its dichloro complex (R_p,S_p)-**62b** and its solid state structure characterized by means of

single crystal X-ray diffraction analysis. The single crystal X-ray diffraction analysis confirmed the formation of a enantiomerically pure P^P(S) ligand with 5 chiral centers. Similar reactions involving **45** and arsine functionalized dienophiles *viz*., diphenylvinylarsine **65** and divinylphenylarsine **69** were carried out using the bis(acetonitrile) complex (R_c)-**51** as the reaction promoter. These reactions resulted in the formation of ligands of the type As^P(S) wherein the ligands coordinated to the palladium metal centre through sulfur and arsine. The selectivity in these cycloadditions was poor and the formed diastereomers could not be separated by either column chromatography or fractional crystallization.

Enantiomerically pure diphosphine ligands carrying one phosphorous and three carbon stereogenic centers were generated from the Diels-Alder reaction between phosphine functionalized terminal alkenols [i.e. (a) 3-diphenylphosphanyl-but-3-en-1-ol **72** (b) 2-diphenylphosphanyl-prop-2-en-1-ol **73**] and 3,4-dimethyl-1-phenylphosphole **44**, with platinum complex (R_c)-**43** as the chiral inductor. Both cycloaddition reactions showed good selectivity with only one enantiomer being formed. The products formed *viz*., (R_c,S_p)-**76** and (R_c,S_p)-**81** were isolated in high yield and were characterized by means of single crystal X-ray diffraction analysis. Their structures in solution were ascertained by means of 2D ^{1}H-^{1}H ROESY NMR spectroscopy. Subsequent decomplexation and re-preparation of the products proved the optical purity of the chiral diphosphines formed.

The chiral organopalladium template (R_c)-**36** was used to promote asymmetric hydrophosphination of phosphine functionalized alkenols. The reaction showed appreciable regio-stereoselectivity in the case of 3-diphenylphosphanyl-but-3-en-1-ol

ligand with the hydrophosphination products being formed in the ratio 4:1:18:2. The major isomer (R_c,R_c)-**87a** was subsequently isolated in appreciable yield (78%) in its optically pure form. The similar reaction involving 2-diphenylphosphanyl-prop-2-en-1-ol however did not exhibit appreciable selectivity.

Nomenclature

The nomenclature used throughout the thesis confirms to the format adopted by Chemical Abstract (Chemical Abstracts, 13th Collective Index, Index Guide, 1992-1996; Vol. 116-125, p 102).

X-ray Structural Data

The X-ray structural analyses were kindly carried out by Assoc. Prof.Jagadese J.Vittal, Ms. Tan Geok-Kheng and Prof. Lip Lin Koh at the National University of Singapore. 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
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
br	broad
bp	boiling point
ca.	about (Latin *circa*)
calcd.	calculated
$CDCl_3$	chloroform-d_1
CD_2Cl_2	dichloromethane-d_2
CD_3CN	acetonitrile-d_3
CHIRAPHOS	2,3-bis(diphenylphosphino)butane
d	doublet (in NMR assignments)

dec.	decomposition
DIOP	2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane
DIPAMP	1,2-bis[(o-methoxyphenyl)phenylphosphino]ethane
dm	decimeter
DMPP	3,4-dimentylphenylphosphole
DMPPS	3,4-dimethylphenylphosphole sulfide
dq	doublet of a quartet (in NMR assignments)
E	*entgegen* (German: *opposite*)
ee	enantiomeric excess
eq	equatorial
Et	ethyl
et al.	and others (Latin *et alii*)
g	gram(s)
HOMO	high energy occupied molecular orbital
HPLC	High Performance Liquid Chromatography
hr	hour(s)
Hz	Hz
i	iso
ie.	that is (Latin *id est*)
IR	infrared
LDA	lithium diisopropylamide

LUMO	lowest energy unoccupied molecular orbital
m	multiplet (in NMR assignments)
Me	methyl
mg	milligrams
MHz	megahertz
min	minutes
mp	melting point
NMR	Nuclear Magnetic Resonance
NOE	Nuclear Overhauser Effect
o	ortho
Ph	Phenyl
PLE	pig liver esterase
ppm	parts per million
Pr	propyl
q	quartet (in NMR assignments)
qn	quintet (in NMR assignments)
R	rectus (Latin: absolute configuration)
S	sinister (Latin: absolute configuration)
s	singlet (in NMR assignments)
T	temperature
THF	tetrahydrofuran
Z	*zusammen* (German: together)
Å	angstrom(s)

$^{n}J_{A\text{-}B}$	n-bond coupling constant between nuclei A and B
Δ	reflux
δ	NMR chemical shift in ppm
$[\alpha]_D$	specific rotation measured at sodium D line (589nm)

CHAPTER I

General Introduction

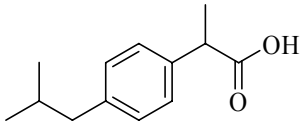
General Introduction

1.1 Chirality and its Significance

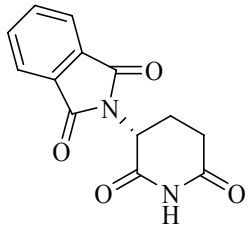
The concept of "chirality" has been known since the 18th century. In simple terms, chirality is "handedness", that is, the existence of left/right opposition. The term Chiral is derived from the Greek name *cheir* meaning "hand" and apparently was coined by Lord Kelvin in 1904, in his Baltimore Lectures on Molecular Dynamics and the Wave Theory of Light in which he stated ...*"I call any geometrical figure, or group of points, chiral, and say it has chirality, if its image in a plane mirror, ideally realized, cannot be brought to coincide with itself"*.[1a] Since Louis Pasteur discovered the existence of distinct chiral isomers in his laboratory,[1b] attempts have been made to understand and utilize this critical molecular property at the synthetic level.

The inherent chirality of living systems dictates extraordinary specificity in the recognition of chiral molecules, so that a molecule and its mirror image, whether it is a pharmaceutical, an insecticide, a herbicide, a flavor or a fragrance, will almost always elicit different biological effects. This specificity presents a challenge for the industrial synthesis of these compounds since chemists must control the three-dimensional spatial arrangements adopted by their products so that only the required enantiomer is produced. The importance of chirality of drugs has been increasingly recognized, and the consequences of using them as racemates or as enantiomers have been frequently discussed.

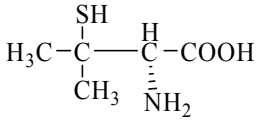
While there are examples where both enantiomers have similar therapeutic properties, for instance the drug ibuprofen, there are numerous cases where one of the isomers causes serious side-effects (Figure 1.1).



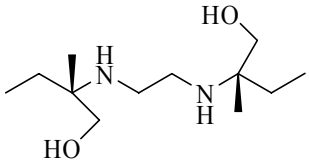
Ibuprofen-anti-inflamatory drug
(administered in racemic form)



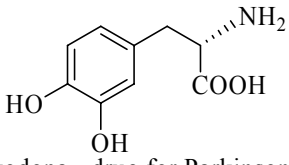
(*R*)-thalidomide-sedative
(*S*) form teratogenic



(*S*)-pencillamine -anti-arthritic
(*R*)-form toxic



(*S*,*S*)-(+)-ethambutol - anti-tubercular drug
(*R*,*R*)-form causes optical neuritis leading to blindness



(*S*)-levodopa - drug for Parkinson`s disease
(*R*)-form causes granulocytopenia

Figure 1.1

Therefore one of the most active areas of chemical research is centered on how to synthesize handed (chiral) compounds in a selective manner, rather than as mixtures of mirror-image forms (enantiomers) with different three-dimensional structures

(stereochemistries). Nature points the way in this endeavor: different enantiomers of a given biomolecule can exhibit dramatically different biological activities, and enzymes have therefore evolved to catalyze reactions with exquisite selectivity for the formation of one enantiomeric form over the other.

1.3 Methodologies in Synthesis of Compounds with Desired Chirality

Various well established strategies have been developed to achieve single enantiomer synthesis; they will be briefly discussed in this section. The main routes to single enantiomers can be classified as chiral pool method, chiral resolution, biological asymmetric methods and chemical asymmetric methods.

1.2.1 Synthesis from Chiral Pools

This method takes advantage of the inexpensive, readily available enantiomerically pure natural products such as lactic acid, carbohydrates, amino acids and their derivatives.[2] These can be manipulated into forming desired target molecules with retention or inversion of configuration or chirality.[3,4,5] Though chiral pool methodology produce least chiral impurities the obvious limitation is the limited diversity of chiral pools.

1.2.2 Chiral Resolution

Chiral resolution makes use of the fact that enantiomers differ in their interactions with chiral materials and constitutes the main method for the industrial synthesis of pure enantiomers. The racemic substrate is derivatised by reaction with a enantiomerically pure compound and the resulting diastereomeric product is separated by crystallization and also by means of chromatography.[6,7,8] The desired enantiomer is then regenerated by chemical manipulations. Another protocol followed involves kinetic resolution wherein the fact that enantiomers react at different rates towards chiral reagents is utilized. [9,10,11] The chiral entity may be a biocatalyst (enzyme or microorganism) or a chemocatalyst (chiral acid ,base or metal complex). In ideal case, one enantiomer is converted to the product while the other remains unchanged.

1.2.3 Asymmetric Synthesis

Asymmetric synthesis can be defined as any chemical reaction that affects the structural symmetry in the molecules of a compound, converting the compound into unequal proportions of compounds that differ in the dissymmetry of their structures at the affected centre.

A ‘normal’ reaction which gives enantiomeric products is required to produce each in equal amounts because of the enantiomeric relationship between the two transition states. If a component of the transition state other than the substrate is chiral, and present as a single enantiomer itself, then the enantiomeric products need not be

formed in equal amounts. One of the enantiomers should be formed in excess. This is the basis of asymmetric synthesis.[12] Despite success achieved using resolution and chiral pools, there has been increasing interest in asymmetric synthesis.

Asymmetric synthesis can be broadly classified into two categories; biological asymmetric methods (involving enzymes, whole organisms or catalytic antibodies)[13] and chemical asymmetric methods. The reagents affecting chemical asymmetric synthesis are used either stoichiometrically [14] or catalytically [15]. The discovery by Wilkinson and co-workers [16] that chlorotris(triphenylphosphine)rhodium, [$RhCl(PPh_3)_3$], can be used as an efficient catalyst for the hydrogenation of unhindered olefins, sparked a tremendous interest in asymmetric catalysis. The methodology involving replacement of the triphenylphosphine in the catalyst with chiral phosphines has resulted in the generation of a plethora of powerful homogeneous catalysts which in turn has led to the preparation of many chiral compounds in high enantiomeric purity.

1.3 Transition Metal Complexes in Asymmetric Synthesis

Among the various methods employed , enantioselective synthesis employing chiral transition metal complexes provides one of the most general and flexible methods in asymmetric synthesis The utilization of chiral catalysts, in particular transition metal complexes incorporating chiral ligands, has become an important approach to achieve enatioselectivity in homogeneous organic synthesis. Transition metals are often employed in the design of asymmetric catalysts because of their manifestations of variable oxidation states (useful in reactions involving redox processes) and coordination number

as well as their ability to coordinate with a wide range of ligands, either through σ or π-bonding and thus stabilize them. The incorporation of chiral ligands (chiral auxiliaries) serves to effect aymmetric induction. The chirality is transmitted to the site of reaction to discriminate the binding substrate, usually in terms of steric preference. Following the discovery of Wilkinson's catalysts, many examples of catalysis involving transition metal complexes have been reported.[17] These metallic species offer enormous possibilities and opportunities due to their diverse catalytic activity and also because they provide virtually unlimited per mutability by virtue of their organic ancillaries. Transition metal catalysis offers the possibility of achieving complex organic synthetic transformations that combine complete efficiency (100% yield) with complete chemical and stereochemical control (one product only) while minimizing or even eliminating reagents, waste products and solvents. This chemical utopia is achievable but will require an ever more sophisticated understanding of the interactions of transition metal species and their substrates, investigations of which will continue well into, if not throughout, the 21st century.

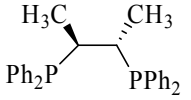
1.4 Transition Metal Complexes with Phosphine based Ligands in Asymmetric Catalysis

In 1968 Horner and Knowles showed that asymmetric hydrogenation is possible with Wilkinsons complex $RhCl(P(C_6H_5)_3$ modified with chiral ligands.[18,19,20] The discovery that diphosphines containing metal complexes are efficient catalysts was made by Kagan *et.al*.[21,22] They developed (-)-DIOP **3** whose successful application refuted a long held belief that it was necessary to have the chirality of the ligand centered at the

phosphorous atom.[23,24] Today transition metal species with phosphorous containing ancillary ligands are extensively used in catalysis, often providing dramatic or subtle selectivity in the conversion of substrates to desirable end products.

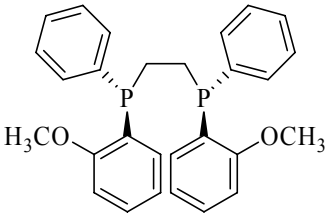
1.4.1 Asymmetric Hydrogenation

Attempts at hydrogenation of prochiral olefins using the Wilkinson complex resulted in low optical yields. Important progress was made by Bosnich, Kagan, Knowles and Sabacky when they prepared chiral bidentate phosphines and introduced them into the synthesis of Schrock/Osborn type[25] square planar 16 electron rhodium complexes.[26] Figure 1.2 shows examples of commonly used chiral bidentate phosphines.



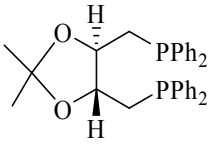
CHIRAPHOS

(1)



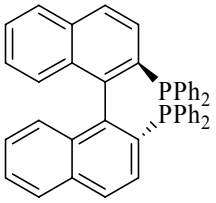
DIPAMP

(2)



DIOP

(3)



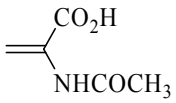
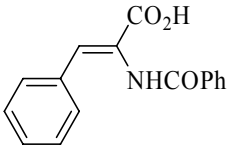
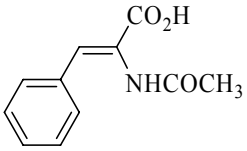
BINAP

(4)

Figure 1.2

Different kinds of substrates has been hydrogenated using these catalysts including amino acid precursors,[27] enamides,[28] carboxylic acid derivatives,[29,30] aldehydes,[31,32] ketones[33] and alcohols.[34,35,36] Table 1.1 gives an overview about the results for hydrogenation of amino acid precursors.[27]

Table 1.1 Chiral diphosphines, optical purity (%)

Substrates	DIPAMP	DIOP	CHIRAPHOS	BINAP
	94	73	91	67
	96	64	99	96
	95	81	89	84

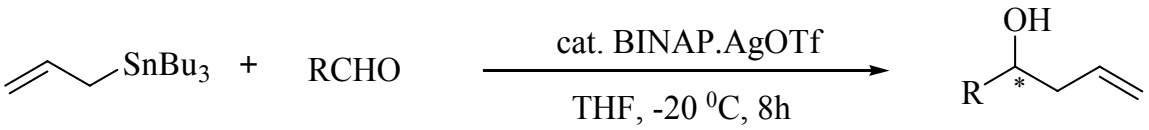
Summarizing literature data about asymmetric hydrogenations using chiral phosphine ligands., they should fulfill the following requirements:[37]

1. bidentate (1,2-diphosphine) ligands,
2. formation of five membered chelate rings,

3. rigid carbon backbone on the phosphine ligand,
4. aryl substituents at the phosphorous atom,
5. cheap chiral starting material and a short high yield synthesis.

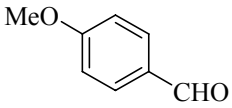
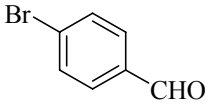
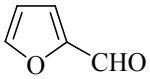
1.4.2 Allylation

Allylation reactions are an attractive route for the formation of carbon-carbon bonds because the allylated products can be transformed into organic molecules possessing a variety of functional groups.[38,39,40] Among selective allylation reactions, addition of an allyl group to carbonyl compounds to provide optically active secondary homoallylic alcohols is a valuable synthetic method because the products are readily transformed into β-hydroxycarbonyl compounds and various other chiral compounds.[41] There are a few methods available for a catalytic process including a chiral(acyloxy)borane complex [42,43] and a binaphthol-derived chiral titanium complex. [44,45,46] Yamamoto *et.al* have devised an alternative method involving BINAP•Ag(I) complex for asymmetric allylation of aldehydes (Scheme 1.1, Table 1.2). [47]



Scheme 1.1

Table 1.2 Asymmetric allylation of aldehydes catalysed by (*S*)-BINAP•AgOTf

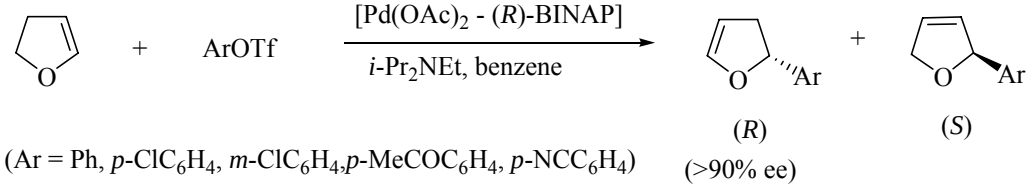
Substrate	Yield (%)	% ee
PhCHO	88	96
	59	97
	95	96
	94	93
(*E*)-PhCH=CHCHO	83	88
PhCH2CH2CHO	47	88

Various other chiral phosphine•Ag(I) complexes involving CHIRAPHOS **1**, DIPAMP **2** and DIOP **3** are known to promote the allylation of various substrates. [48]

1.4.3 Asymmetric Heck Reactions

Transition metal catalysed carbon-carbon bond formation reactions have become an invaluable tool for synthetic chemists. Among the most successful and widely applied of such transformations is the Heck reaction, which has been known since the late 1960s. Hayashi reported the first example of an intermolecular asymmetric Heck reaction in 1991 involving the phenylation of 2,3-dihydrofuran with phenyl triflate catalysed by a

$Pd(OAc)_2$/(*R*)-BINAP **4** combination which involves a aryl-palladium triflate BINAP intermediate.[49]



(Ar = Ph, *p*-ClC_6H_4, *m*-ClC_6H_4,*p*-$MeCOC_6H_4$, *p*-NCC_6H_4) (*R*) (>90% ee) (*S*)

Scheme 1.2

Chiral phosphine ligands have since been extensively used in asymmetric Heck reactions on varied substrates.[50] More recently, other novel planar chiral phosphines based on the (arene)tricarbonylchromium (0) unit have been employed for asymmetric Heck reaction involving phenylation of 2,3-dihydrofuran substrate.[51]

1.4.4 Other Reactions Involving Transition Metal Complexes with Phosphine Based Ligands

Asymmetric coupling reactions with Grignard reagents were found to be catalyzed by nickel-phosphine complexes.[52,53] Recently chiral (β-aminoalkyl)phosphine ligand containing palladium complexes have also been employed successfully for Grignard cross coupling reactions.[54,55,56] Asymmetric catalytic hydroformylation has been successfully carried out by employing rhodium(I) complexes containing chelating chiral diphosphines such as BINAP **4** and CHIRAPHOS **1** with moderate to high enantiomeric purity.[57,58,59] Recent developments have been centered on chiral phosphine-phosphite

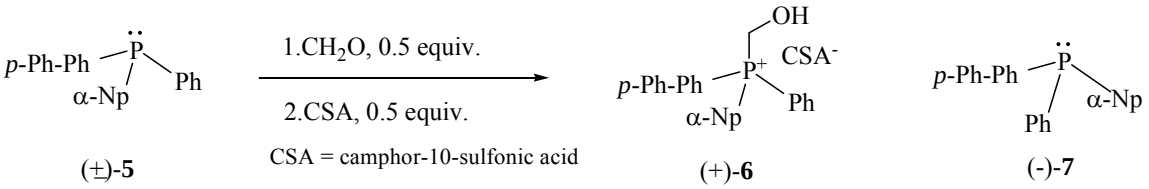
ligand containing rhodium(I) complexes.[60] More recently *P*-chiral diphosphines bearing methoxy groups have been investigated as ligands in rhodium-catalyzed asymmetric hydroformylation involving styrene derivatives as substrates.[61] Asymmetric hydrocarboxylation of styrene and its derivatives have also been carried out using Pd(II) complexes containing DIOP **3**.[62,63,64] Chiral phosphine complexes have also been used for asymmetric synthetic protocols like cycloaddition,[65] hydrovinylation,[66] hydroboration,[67] Suzuki coupling[68] and epoxidation[69] among others.

1.5 Methods for Preparation of P-Chiral Phosphines and Their Derivatives[70,71]

The driving force for the preparation of *P*-chiral systems stems from the rapidly growing utility of such compounds in not only asymmetric catalysis (Section 1.4) but also in fields like chemotherapy,[72] pest control,[73] bioorganic chemistry[74] and asymmetric synthesis.[75] The fact that *P*-chiral organophosphorous compounds could not be found in the natural pool of chirality has stimulated the research in the synthesis of such compounds in their enantiomerically pure forms.[76]

1.5.1 Kinetic Resolutions

The first kinetic resolution of a phosphine is due to Wittig and co-workers who succeeded in partially resolving *p*-biphenylyl-1-naphthylphenylphosphine by means of its quaternization with half-molar amounts of paraformaldehyde and (+)-camphor-10-sulfonic acid (Scheme 1.2).[77]



Scheme 1.2

The unreacted half of the phosphine was found to be enriched in the (-)-enantiomer while the other half, which was recovered from the hydroxymethylphosphonium salt **6** by treatment with Et_3N contained accordingly the (+)-enantiomer in excess.

Attempts to kinetically resolve phosphines through their partial oxidation with chiral peracids and amine oxides met with very little success.[78] The reverse approach, relying on reduction of racemic phosphines oxides with chiral reducing agents, led to more promising results. The reduction of oxides **8**, **9** and **10** by chiral alanes (Figure 1.3) derived from AlH_3 and (-)-1-phenylethylamine[79] or $LiAlH_4$ and (*S*)-2-(aniinomethyl)pyrrolidine[80] yielded more promising results.

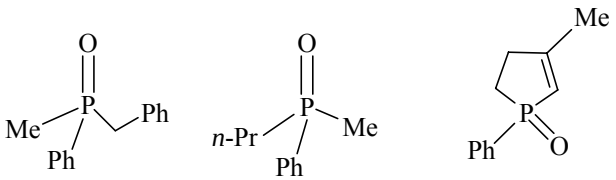
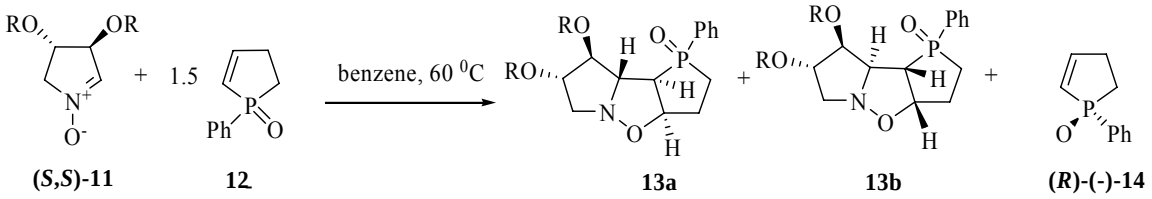


Figure 1.3

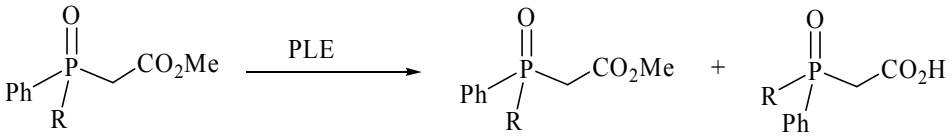
An efficient kinetic resolution of 1-phenyl-2-phospholene 1-oxide **12** by means of its 1,3-dipolar cycloadditions with chiral scalemic nitrones was developed by Brandi and co-workers.[81] Crucial to this development were previous observations that **12** is approached by nitrones exclusively in the *exo* mode[82] and only from the side bearing the P=O entity.[83] The resolution process is shown in Scheme 1.3.



Scheme 1.3

In the experiment involving the nitrone **11** possesing sterically demanding alkoxy groups (R= *t*-Bu), the unreacted (-)-*R*-**14** was isolated in 27% yield (to be compared with 33.3% theoretical yield after virtually complete conversion of the nitrone) and was determined to be of high enantiomeric purity (96%). The process proved similarly effective in resolution of phospholene sulfide and is likely to become of more general utility.

Enzymatic kinetic resolution of *P*-chiral phosphines derivatives has also been accomplished. A short series of simple phosphinylacetates (e.g., R= Me, Et, CH_2Ph, $CH{=}CH_2$) was successfully resolved *via* PLE-catalyzed hydrolysis which afforded unreacted esters and acids of up to 98% enantiomeric purity.[84]

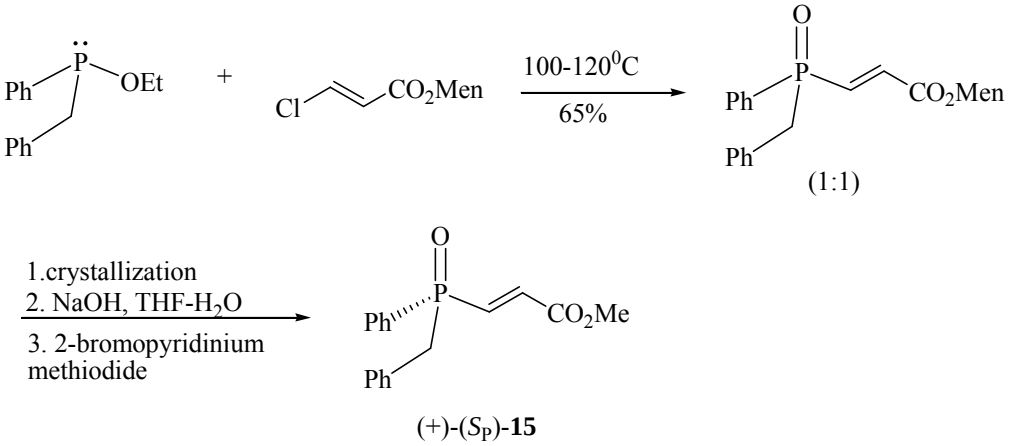


Scheme 1.4

Recent studies have shown that the enzyme bacterial phosphotriesterase catalyzes the stereoselective hydrolysis of phosphinate esters, affording facile kinetic resolution protocol.[85] Also lipase catalyzed kinetic resolution of P-chiral hydroxymethanephosphinates and hydroxymethylphosphine oxides have been reported in ionic liquids.[86]

1.5.2 Resolution *via* Covalent Diastereomers

This procedure have been employed for the first time in the preparation of the optically active phosphinyl acrylate **15** as shown in Scheme 1.5.[87]

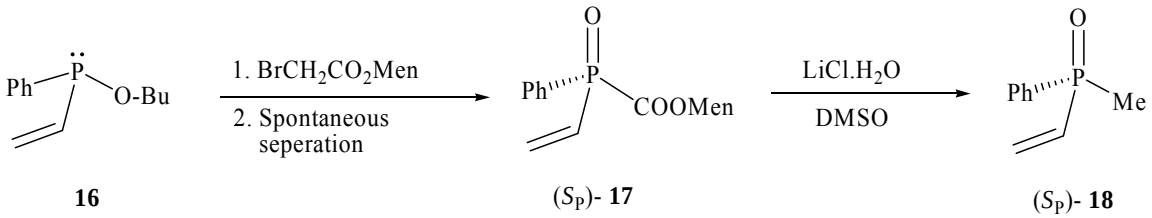


Scheme 1.5

Reaction of ethylbenzylphenylphosphinite with (-)-menthyl 2-chloroacrylate yielded a 1:1 mixture of *P*-epimeric menthyl *trans*-2-phosphinylacrylates of which one epimer could be isolated in pure form by a series of crystallization from acetone.

Subsequent transesterification afforded (+)-(S_p)-**15** in which phosphorous remained the sole stereogenic centre.

In a related Arbusov approach[88] butylphenylvinylphosphinite **16** was allowed to react with (-)-menthyl bromoacetate to afford equimolar mixture of menthyl (phenylvinylphosphinyl)acetates (R_P)/(S_P)-**17** from which one diastereomer spontaneously crystallized out from the crude reaction mixture upon cooling to room temperature. The product was then conveniently freed from the carbomenthoxy auxiliary by a one-step decarbalkoxylation yielding enantiomerically pure (S_P)-**18** (Scheme 1.6).



16 (S_P)- **17** (S_P)- **18**

Scheme 1.6

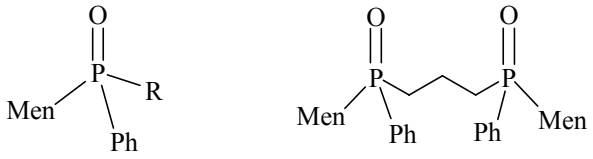
Other examples of the method being employed to separate *P*-chiral phosphines chalcogenides and aminoacids can also be found in literature.[90,91]

1.5.3 Self-Resolving Systems

This method is similar to that discussed in the previous section in that resolution was realized by means of a covalent bound auxiliary, but different in that the chiral, typically C-chiral, unit introduced to the phosphine structure for the purpose of resolution

is meant to be retained in the target structure. Preparation of chiral phosphines by this method requires that at least one of the three C-P bonds is formed under the circumstances that the C-chiral auxiliary subunit is already present in the organophosphorous precursor or in the reagent structure. Nevertheless, even in the most efficient cases, almost without exception, access to individual diastereomers of the desired C,P-chiral phosphines derivative had to rely ultimately on separation.

In 1975 Naylor and Walker reported that alkylation of sodium methylphenylphosphide with (+)-1-phenylethyl chloride followed by oxidation of the crude products by H_2O_2 led to the formation of a 63:37 mixture of oxides of which the major could be isolated by chromatography on silica gel.[92] Using similar methods diastereomers of novel oxides **19** and **20** and bis(oxide) **21** were also prepared, though except for (R_P,S_P)-**21**, they were not separated (Figure 1.4).



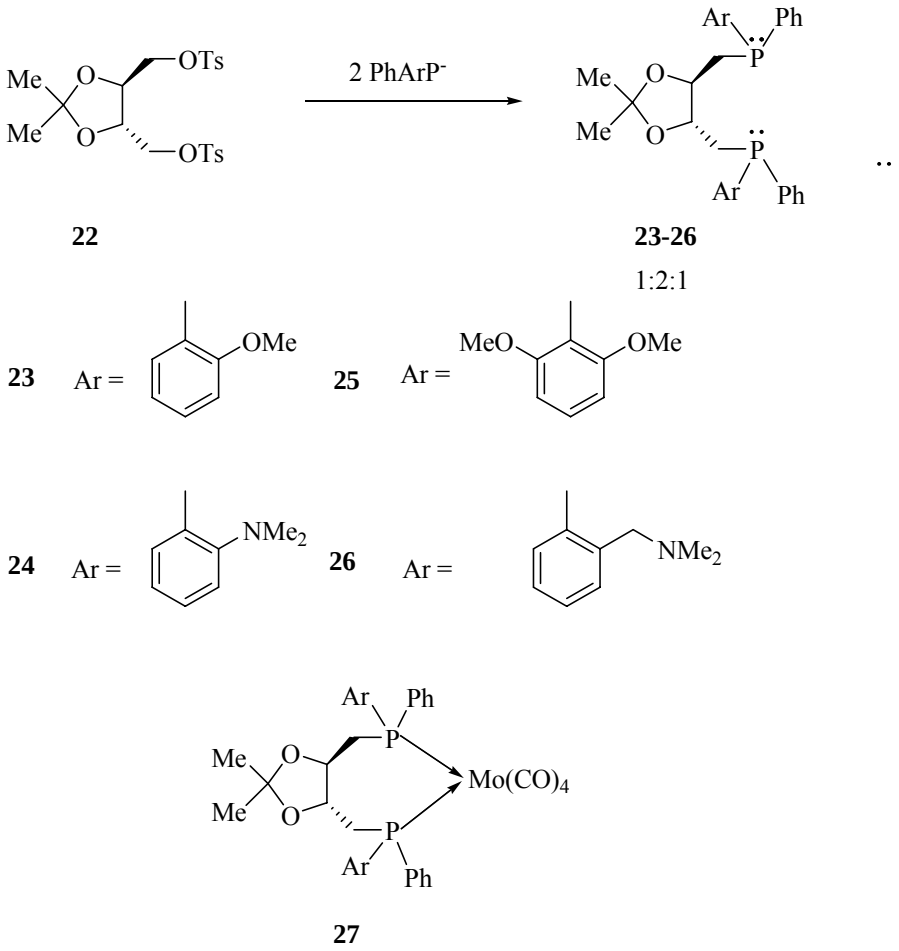
19 R= Et
20 R= *i*-Pr

21

Figure 1.4

Alkylations of phosphide anions with bifunctional racemic alkylating agent **22** derived from tartaric acid were studied by Burgess and co-workers[93] in the course of their work on P-chiral analogs of DIOP **3**. The systems studied are shown in Scheme 1.7. No carbon-to-phosphorous induction was observed in any of the alkylations studied and, by default, the 1:2:1 mixture of the three diastereomeric bis(phosphines) had to be dealt with

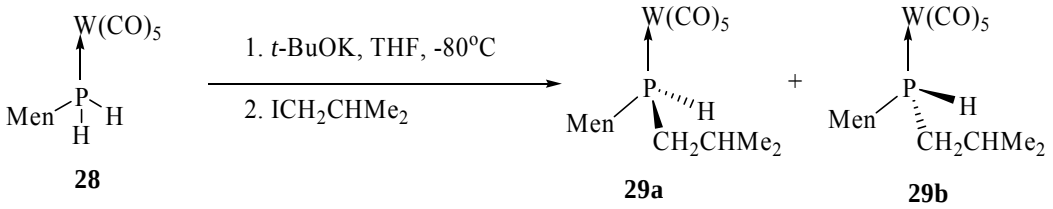
in each case. Even though careful crystallization yielded pure **23,** the other bis(phosphines) had to be converted into the corresponding mixture of their molybdenum tetra carbonyl complexes of the type **27** which proved eventually separable by flash chromatography.



Scheme 1.7

Mathey and co-workers have reported that raecmic primary and secondary phosphines coordinated to tungsten can be reacted with electrophiles in a highly stereoselective manner. As shown in Scheme 1.8 deprotonation and subsequent alkylation of (menthyphosphine)pentacarbonyltungsten **28** with *i*-BuI gives two diastereomeric

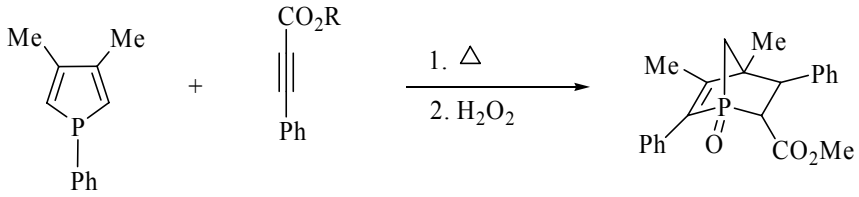
secondary phosphines complexes **29a** and **29b** as either 7:3 or 3:7 mixture depending on the reaction temperature.[94]



28 **29a** **29b**

Scheme 1.8

Cycloaddition reactions of an organophosphorous compound to a chiral auxiliary as a means of formation of self-resolving cycloadducts were employed by two groups. Mathey and co-workers[95] used a [4+2] cycloaddition of phosphole **30** to menthyl and bornylphenylpropiolates to obtain diastereomeric 1-phosphanorbornadienes of type **31** (Scheme 1.9). In the menthyl series the depicted oxidized major product was separated from its minor regioisomer on silica gel and was then resolved by HPLC into two individual *P*-epimeric oxides which were finally reduced back to phosphines by $SiHCl_3$-pyridine. The corresponding epimers in the bornyl series were not resolved.



30 R=menthyl/bornyl **31**

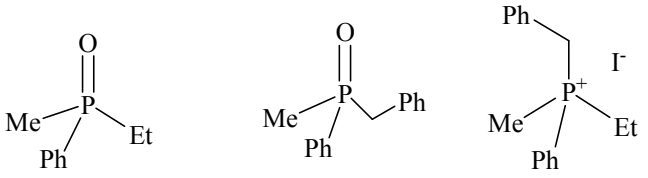
Scheme 1.9

1.5.4 Direct Resolutions

There are two main synthetic strategies adopted in direct resolution of chiral phosphines, one involving chromatography and the second by means of resolving agents.

a. *By Chromatography*: Since the advent of high performance chromatographic techniques and development of a range of chiral stationary phases (CSPs) resolution of rcemic mixtures by chromatographic methods has become a viable alternative to the existing classical methods of resolutions. Early analytical studies on chiral phosphines derivatives focused mainly on phosphine oxides[96] and typically required the prescience of π-basic[97], usually condensed aromatic[98], substituents in their structures since interactions based solely on the P=O dipole were considered not efficient enough. The number of successful, although not always complete, semi-preparative and preparative chromatographic resolutions of *P*-chiral phosphines and their derivatives is also continuously growing.[99]

b. By Resolving Agents: The first known optically active organophosphorous compound, ethylmethylphenylphosphine oxide **32**, was obtained by direct resolution of the racemate using (+)- bromocamphorsulfonic acid as the resolving agent for the separation of the diastereomeric salts by fractional crystallization. Subsequently the same technique was used to resolve benzymethylphenylphosphine oxide **33**.[100]

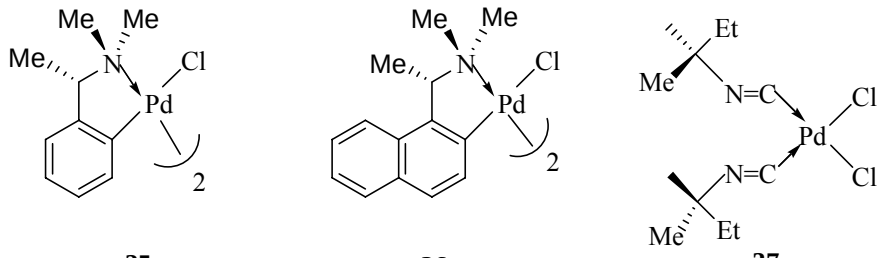


(+) and (-) - **32** (+) and (-) - **33** (+) and (-) -**34**

Figure 1.5

Resolution employing (-)-dibenzoyltartaric acid (DBTA) has been successful in difficult separation of diastereomeric *P*-chiral compounds[101,102] as well as for resolution of the backbone chiral diphosphorous systems such as NORPHOS[103] and BINAP **4**.[104] The first successful resolution of a simple P-chiral phosphonium salt was reported by McEwen and co-workers in 1959. They were able to resolve benzylethylmethylphenylphosphonium iodide **34** using silver hydrogen dibenzoyltartarate (Ag-DBHT) as the resolving agent and this methodology quickly gained more general use and importance.[105]

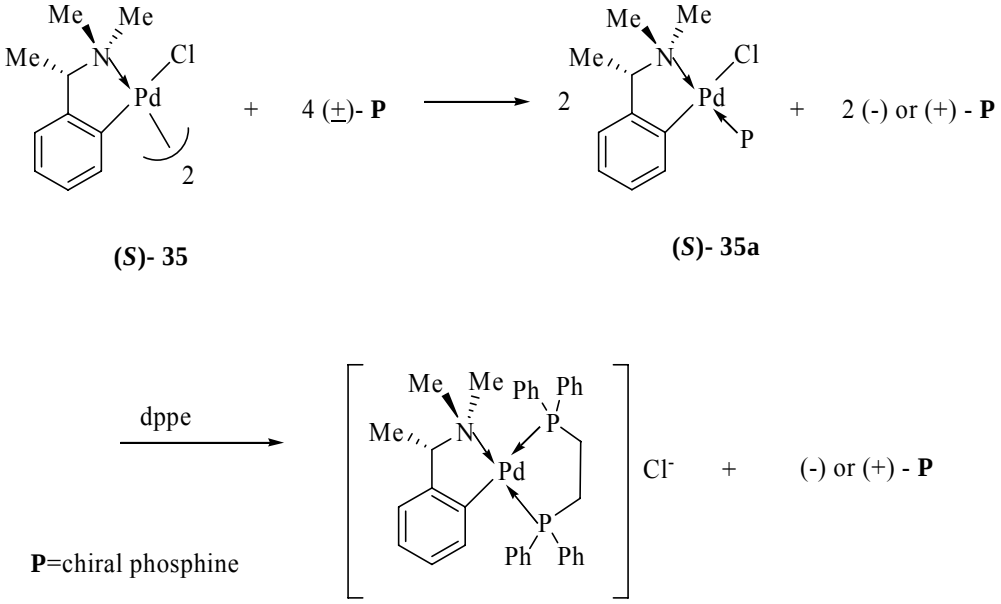
In the early 1970s, two groups developed general procedures for direct resolution of phosphines *via* their diastereomeric transition metal complexes. One of those procedures which was developed by Otsuka and co-workers[106] relies on chiral palladium (II) complexes **35** – **37** derived from enantiomeric 1-phenylethylamines, 1-napthylethylamines and *sec*-butylisonitrile as the resolving agents (Figure 1.6 ., only one isomer of each complex is shown).



35 **36** **37**

Figure 1.6

A general procedure of such resolution utilizing typically only 0.5 equiv of the resolving agent is given in Scheme 1.10.

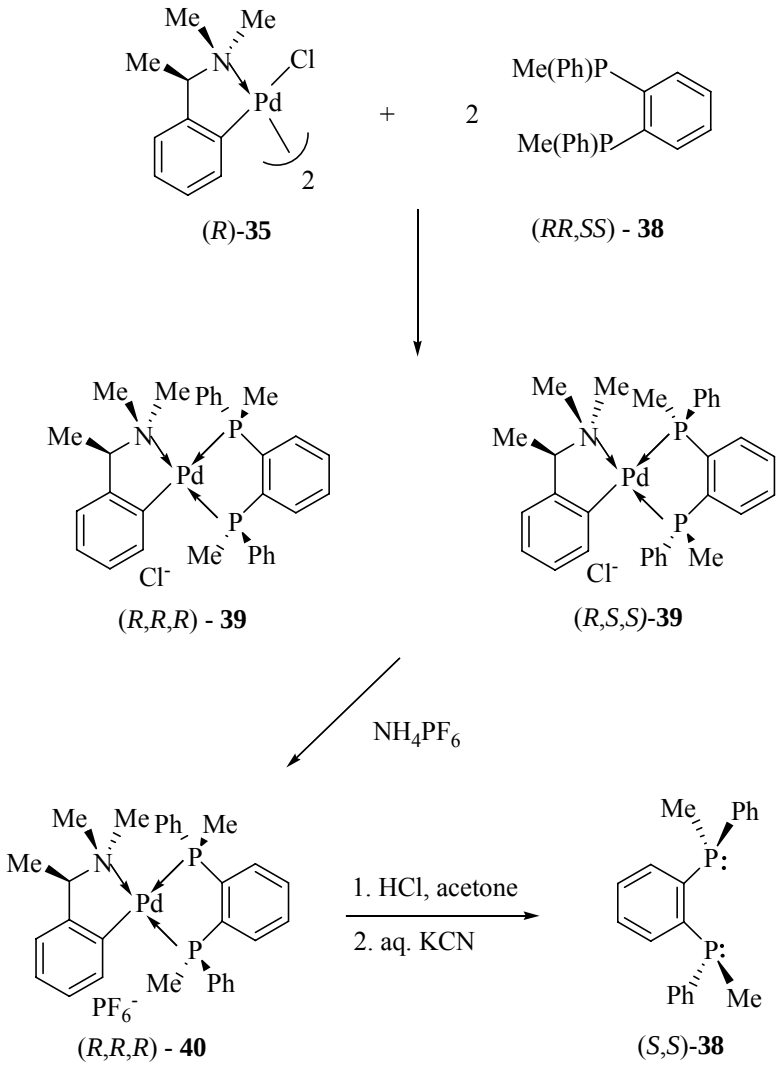


Scheme 1.10

Even though it was realized that matching of a suitable metal complex with the phosphines was a primary requirement, the method nevertheless proved efficient and reasonably general and thus provided access to phosphines in high enantiomeric purity. Typically, the unreacted excess phosphines remaining in the mother liquor provided one

enantiomer in highly enriched condition whereas the other enantiomer was usually recoverable from the precipitated crystalline complex of the type **35a**. It needs to be noted that, even though a preliminary analysis would infer that these resolutions come in the realm of classical kinetic resolution, they were driven by crystallization (or precipitation) of the less soluble of the two diastereomeric complexes equilibrating quickly in solution via ligand exchange rather than difference in complexation rates of the two phosphines enantiomers.

Complexes **35** and **36** were employed by Wild and co-workers[107-110] for the resolution of bidentate phosphines. Their remarkably efficient resolution of *o*-phenylenebis(methylphenylphosphine) **38** by the chloro-bridged dimmer (*R*)-**35** is shown in Scheme 1.11.[111] Nearly complete precipitation of the complex **40** followed by effective two step decomplexation resulted in the isolation of the optically pure (*S*,*S*)-**38** in 85% overall yield and subsequent recovery of the optically pure (*R*,*R*)-**38** from the mother liquor in high yield (90%) . The related bidentate ligands (*R*,*R*)- **41** and (*R*,*S*)- **42** (Figure 1.7) were also resolved using the same methodology although in the case of the "meso" – type (*R*,*S*)- **42** the complex **36** had to be used.



Scheme 1.11

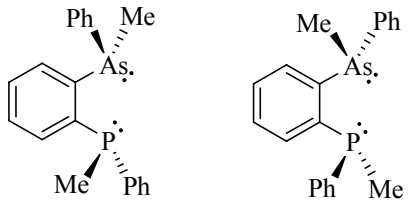
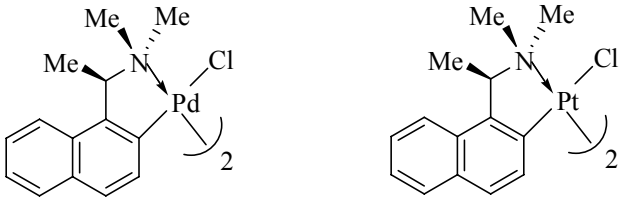


Figure 1.7

Complexes **35** and **36** were also used with success for resolution of some *P*-achiral axially dissymmetric phosphines [112,113,114] although they failed to resolve C_3-symmetric phosphines. The diastereomerism that ensued on interactions of such complexes with racemic phosphines could also be utilized for determination of the optical purity of the latter. [110,115] The versatility of this complex as resolving agent for several other asymmetric bidentate and monodentate ligands that contain tertiary phosphorous and arsine atoms has been demonstrated.[116-119]

1.6 The Two Important Chiral Templates used in the Project

The chiral templates chosen for the project are the organopalladium complex containing *ortho*-metalated (*R*)-(1-(dimethylamino)ethyl)naphthalene (*R*)-**36** and its platinum analog (*R*)-**43** (Figure 1.8).



(*R*)- 36 **(*R*)- 43**

Figure 1.8

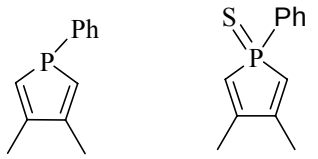
A unique stereochemical feature that makes this naphthalene ligand an ideal auxiliary for asymmetric ligand transformation reactions is that there is a strong internal steric repulsion between the methyl substituent on the stereogenic carbon and its neighboring napthylene proton.[120a] The crystallographic analysis and 2-dimensional solution NMR studies involving rotating Overhauser effect (ROESY) have confirmed

that the organometallic ring is locked into the static δ conformation, both in solid state and in solution.[121a] The prochiral NMe groups control the stereochemistry of the neighboring coordination sites by virtue of the fact that they are locked into non-equivalent axial and equatorial positions. Besides the steric based control, the auxiliary also influences an electronic control since the σ-donating nitrogen and the π-accepting naphthylene carbon of the organometallic ring control the regioselectivity of the incoming ligands. Ligands with soft donors (like phospholes) prefer to bind *trans* to the NMe_2 entity of the auxiliary.[121b]

1.7 Aims of the Present Project

This project is intended to contribute to the knowledge and development of synthetic methods involving *P*-chiral phosphines. To date the importance of chiral phosphines in asymmetric catalysis has been well established. This has led to the need for a variety of functionalized chiral phosphines with chirality residing either on the P or on the C-backbone or on both.

In the initial part of the project we seek to synthesize a series of chiral phosphines ligands of the type P^P(S) through [4+2] cycloaddition reactions involving 3,4-dimethyl-1-phenylphosphole (DMPP) **44** and its sulfonated analog (DMPPS) **45** as dienes. The ability of DMPPS **45** to act as diene and dienophile in asymmetric Diels-Alder reaction will be studied *via* an attempted metal template promoted cycloaddition between **44** and **45** .



44 **45**

Figure 1.9

The reaction of the phosphole **44** with various sulfonated phosphine functionalized dienophiles and that of the sulfonated phosphole **45** towards phosphine and arsine functionalized dienophiles will be studied in order to compare the effect of the sulfonation on reaction rates and selectivity in this class of metal template promoted cycloaddtions involving (*R*)-**36**. Notably, studies on chiral As^P(S) ligands are almost non-existent in literature. This study assumes added significance in view of the fact that mixed donor ligand systems have shown promising catalytic activity.[122,123,124]

In the second part of the project we wish to study the efficacy of the template (*R*)-**43** as chiral promoter in the asymmetric synthesis *via* Diels-Alder cycloaddition involving **44**, of chiral phosphanorbornene systems with hydroxyl functionality. The hydroxyl functionality of the synthesized chiral diphosphine has the potential to be converted to many other derivatives such as ether, ester or even nitride which therefore provides access to many other analogues. It needs to be noted that among other applications, chiral functionalized phosphines are efficient controllers for cytotoxicity of gold-based anti cancer drugs. [125,126] The drug activities and selectivities are critically controlled by the selected functionalities and their locations within a particular chiral phosphines skeleton. The synthesized chiral phosphines ligands therefore will have application in this study owing to the inherent potential of changing the hydroxyl entity in them to other selected functional groups.

The final part of the study involves asymmetric hydrophosphination reaction between diphenylphosphine and phosphine functionalized alkenols, employing the template **(*R*)-36**. The alkenols themselves are to be synthesized in a highly regiospecific manner by hydrophosphination of their alkynol precursors using diphenylphosphine. In fact, alkenylphosphines themselves are attracting interest as building blocks in organic synthesis and as useful ligand precursors for catalysis. The study will therefore involve a two-stage hydrophosphination of alkynols culminating in the synthesis of diphosphine ligands with chirality residing in the carbon backbone.

CHAPTER II

Palladium(II) Complex Promoted Cycloaddition reactions Involving Sulfonated - Phosphine Functionalized Dienophiles and Dienes.

2.1 Introduction

2.1.1 Classic and Inverse electron-demand Diels-Alder Reactions: Reactivity, Regio and Stereo-selectivity and Substituent Effects.

The asymmetric Diels-Alder reaction[127] (Nobel Prize 1950) is one of the most efficient and elegant methods for the construction of chiral six-membered rings. The formation of two carbon-carbon bonds leading to the creation of up to four concatenated stereogenic centers in a single step makes this reaction a versatile synthetic tool for constructing simple and complex molecules.[128,129,130] Reactivity studies on numerous Diels-Alder reactions involving various dienes and dienophiles have shown that the reactivity, regiochemistry and stereochemistry of the reaction depends on the HOMO-LUMO energy separation[131] of the components: the lower the energy difference, the lower is the transition state energy of the reaction.[132,133,134] Classic electron-demand Diels-Alder reactions are accelerated by electron-donating substituents in the diene and by electron-withdrawing substituents in the dienophile (Figure 2.1). On the other hand, inverse electron-demand Diels-Alder reactions are influenced by electronic effects of the substituents in the opposite way. The neutral electron-demand Diels-Alder reaction is HOMO-LUMO-diene controlled and is insensitive to substituent effects. The regiochemistry is determined by the overlap of the orbitals that have larger coefficients (larger lobes).

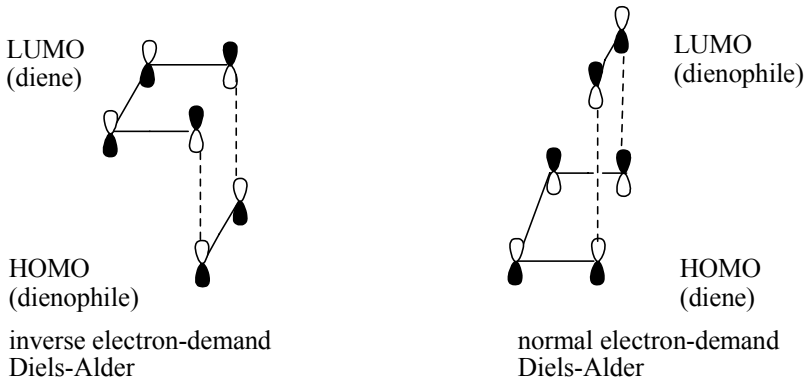


Figure 2.1

The greater the difference between the orbital coefficients of the two end atoms of the diene and the two atoms of the dienophile, which form the two bonds, the more regioselective the cycloaddition.

Cyclic dienes can give stereoisomeric products depending on whether the dienophile lies under or away from the diene in the transition state. When the diene and dienophile are aligned directly over each other the *endo* product is formed. Alternatively when the participating diene and dienophile are staggered with respect to each other the *exo* product is preferentially formed (Figure 2.2).

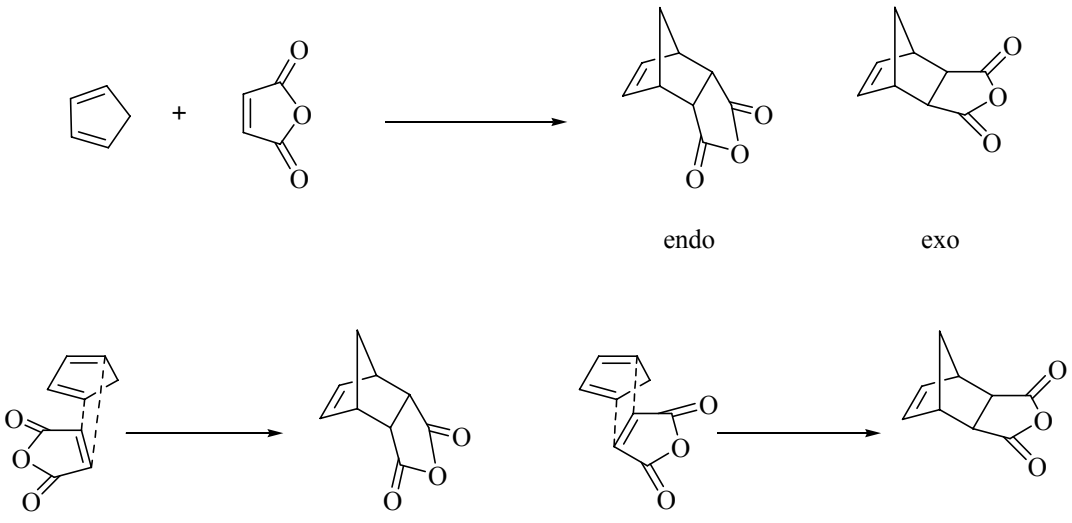


Figure 2.2

2.1.2 Importance of Chiral Mixed Donor Ligands

Chiral bidentate ligands have been used extensively to perform asymmetric transformations. The most commonly employed are bidentate phosphines, however, promising catalytic activity have been noticed for mixed donor ligands such as P-S ligands.[135] Ligands of the type P^P(S), where the ligand chelates through P and S atoms, are less studied. Particularly few reports exist on their complexes. The coordination chemistry of bis-phosphine monochalcogenides was first investigated by Grim and coworkers.[136] On the other hand P^P(S) ligands have been investigated to a much lesser extend.[137-140]

Phosphine sulfides were first synthesized by Strecker and Spitaler in 1926.[141] The synthesis involved direct addition of sulfur to triethyl phosphate at room temperature to form triethyl thionophosphate. It is also well documented that similar addition occurred with the trialkylphosphines, to form the trialkylphosphine sulfides.[142] From force-constant measurements by Siebert[143], the O=P bond order in $OPCl_3$ is determined to be 2.09 whereas the S=P bond order for $SPCl_3$ is 1.57, suggesting that both the P=O and P=S bonds have significant π character.[144]

Diphenylphosphine sulfide and divinylphenylphosphine sulfide are typical pentavalent phosphines. It was shown from previous works that the dienophile in these molecules is not the P=S bond, but rather the C=C counterpart. The reason probably lies in the fact that the P=S acts as an electron withdrawing group when attached to the vinylic group, thereby activating the double bond. Furthermore, the geometry at the pentavalent phosphorous does not allow proper alignment of the orbitals for a

cycloaddition. The presence of phenyl groups at the phosphine would cause steric hindrance and therefore not favor a cycloaddition to the P=S bond in these ligands.

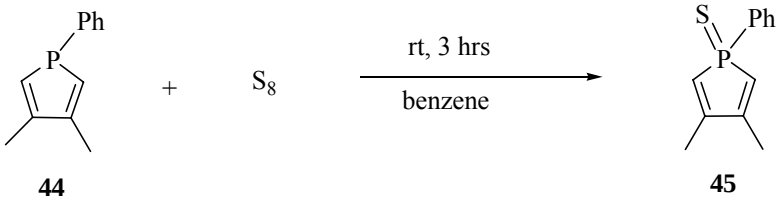
Phospholes exhibit great versatility as ligands in coordination chemistry. They can behave as two, four and six electron donors. Two electrons can be donated from the phosphorous lone pair, the diene system behaves as a four electron donor, and when both coordination modes operate simultaneously the ring acts as a six electron donor. This rich coordination chemistry prompted the study of their sulfonated analogues. The synthesis of 3,4-dimethyl-1-phenylphosphole 1-sulfide (DMPPS) **45** was first reported by Mathey *et. al* in 1970.[145] In the past thirty years the reactivity of phosphole sulfide towards various olefinic compounds in cycloaddition reactions have been intensively studied. Phosphole sulfide undergoes cycloaddition either as a cyclic diene or a dienophile *via* its C=C double bonds.[146] In behavior unlike that known for phosphole oxides, phosphole sulfides also act as dienophiles in reaction with dienes, thereby giving valuable cycloadducts[147,148] including a member of a rare class of phosphole heterocycles describable as phosphasteroids.[149] In contrast to the oxide analogue, DMPPS is a relatively stable ligand that does not undergo dimerization rapidly under mild conditions. For example, 3,4-dimethylphosphole sulfides are normally monomeric[150] whereas the corresponding oxides are dimeric.

As an analogue of phospholes, phosphole sulfides are precursors of phospholyl compounds. Phospholyl ligands are versatile ligands as they have the same number of π – electrons as the cyclopentadienyl ligand and they have the additional ability to coordinate a second metal *via* their phosphorous lone pair. This versatility has led to numerous studies on phospholyl ligands and their coordination chemistry.[151] Unlike phospholyl

ligands, phosphole sulfides have been less explored from the point of view of their coordination chemistry.

2.1.3 Preparation and Isolation of 3,4-Dimethyl-1-phenylphosphole 1-Sulfide (DMPPS) 45

DMPPS **45** can be prepared from 3,4-dimethyl-1-phenlphosphole **44** by treatment of the latter at room temperature with excess sulfur for 3 hours.[152] 3,4-dimethyl-1-phenylphosphole sulfide was obtained in 75% yield as pale yellow solid. The $^{31}P\{^{1}H\}$ NMR spectrum (121MHz, $CDCl_3$) exhibited a sharp singlet at δ 46.37 (Scheme 2.1).



44 **45**

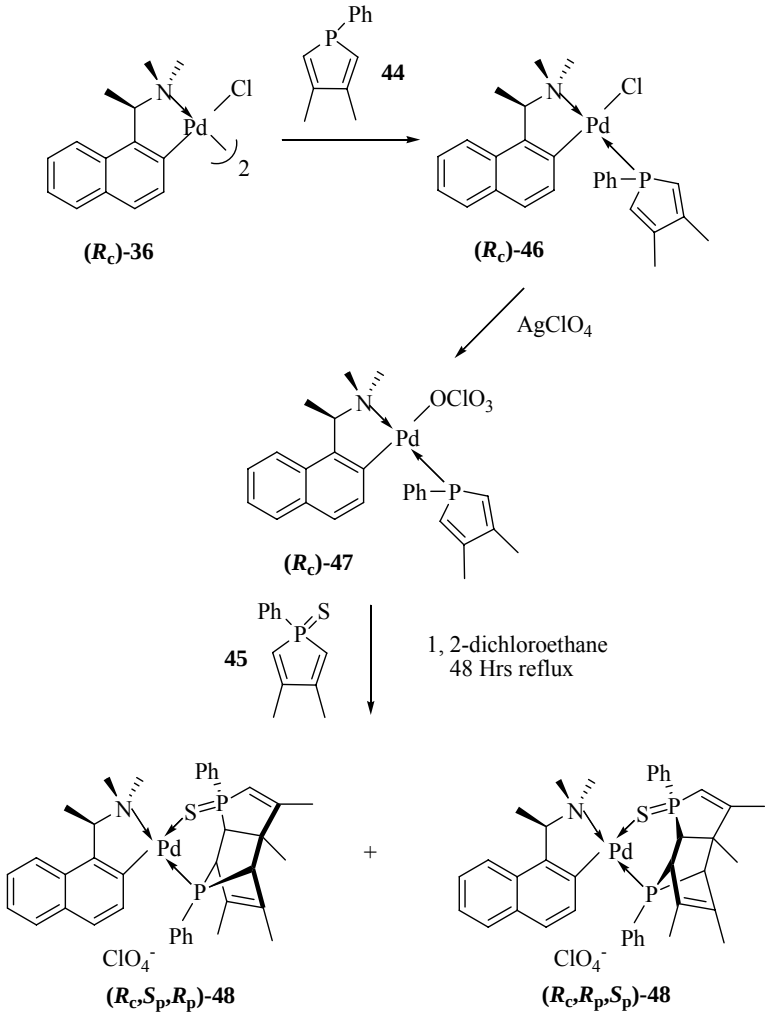
Scheme 2.1

The synthesis can also be achieved by the reaction of DMPP **44** with thiobenzophenone. The reaction rate is however considerably slower (5 days) and the yield, lower (71%).

2.2 Asymmetric Diels-Alder Reaction between DMPP and 3, 4- Dimethyl-1-phenylphosphole 1-Sulfide (DMPPS)

2.2.1 Preparation of *exo*-Products : (R_c,R_p,S_p)- 48 and (R_c,S_p,R_p)- 48

The reaction was initiated with (R_c)-**36** (Scheme 2.2). The neutral monomer (R_c)-**46** was obtained by coordinating DMPP regiospecifically to (R_c)-**36**.[153] Treatment of this chloro species in dichloromethane with aqueous silver perchlorate generated the corresponding perchlorate analogue (R_c)-**47** in quantitative yield.[154]



Scheme 2.2

A solution of (R_c)-**47** was subsequently refluxed with one equivalent of 3, 4-dimethyl-1- phenylphosphole 1-sulfide **45** in 1,2-dichloroethane. The reaction was monitored by means of $^{31}P\{^1H\}$ NMR spectroscopy (121 MHz) and was found to be complete in 48 hrs. Prior to isolation the $^{31}P\{^1H\}$ NMR spectrum of the crude product in CD_3CN exhibited two pairs of doublets indicative of a diastereomeric mixture (3:1). For the major diastereomer (R_c,S_p,R_p)-**48,** the doublets were observed at δ 61.30 (J_{P-P} = 11.4 Hz) and 115.27 (J_{P-P} = 11.4 Hz). For the minor isomer the doublets occurred at δ 61.96 (J_{P-P} = 11.4 Hz) and 114.80 (J_{P-P} = 11.4 Hz). The signals in the low field region at 115.3 and 114.8 of the NMR spectrum are typical for bridgehead phosphorous adopting the *exo-syn* stereochemistry.[155] The ^{31}P NMR analysis thus revealed that the two possible diastereomers were generated as a 3:1 mixture.

The first attempt to separate the two diastereomers by means of fractional crystallization from acetonitrile - diethyl ether yielded crystals which consisted of both diastereomers in almost equal ratio as evidenced by the $^{31}P\{^1H\}$ NMR spectrum. The mother liquor obtained from the first crystallization attempt was however found to be pure since only signals of the major isomer, (R_c,S_p,R_p)-**48**, was observed. The major isomer was subsequently purified by column chromatography on silica gel with an eluent system comprising of ethyl acetate/hexane (3:1). The complex was crystallized out from acetonitrile on slow diffusion of diethyl ether as pale yellow prisms. The single crystal X-ray diffraction analysis was employed to confirm the coordination chemistry of (R_c,S_p,R_p)-**48** .

2.2.2 Single Crystal X-ray Diffraction Analysis of (R_c,S_p,R_p)-48

The single crystal X-ray diffraction studies confirmed the coordination chemistry of the isolated major diastereomer **(R_c,S_p,R_p)-48** (Figure 2.3)**.** The formed cycloadduct coordinates to the palladium template as a bidentate chelate *via* phosphorous and sulfur atoms of the DMPP and the DMPP=S respectively.

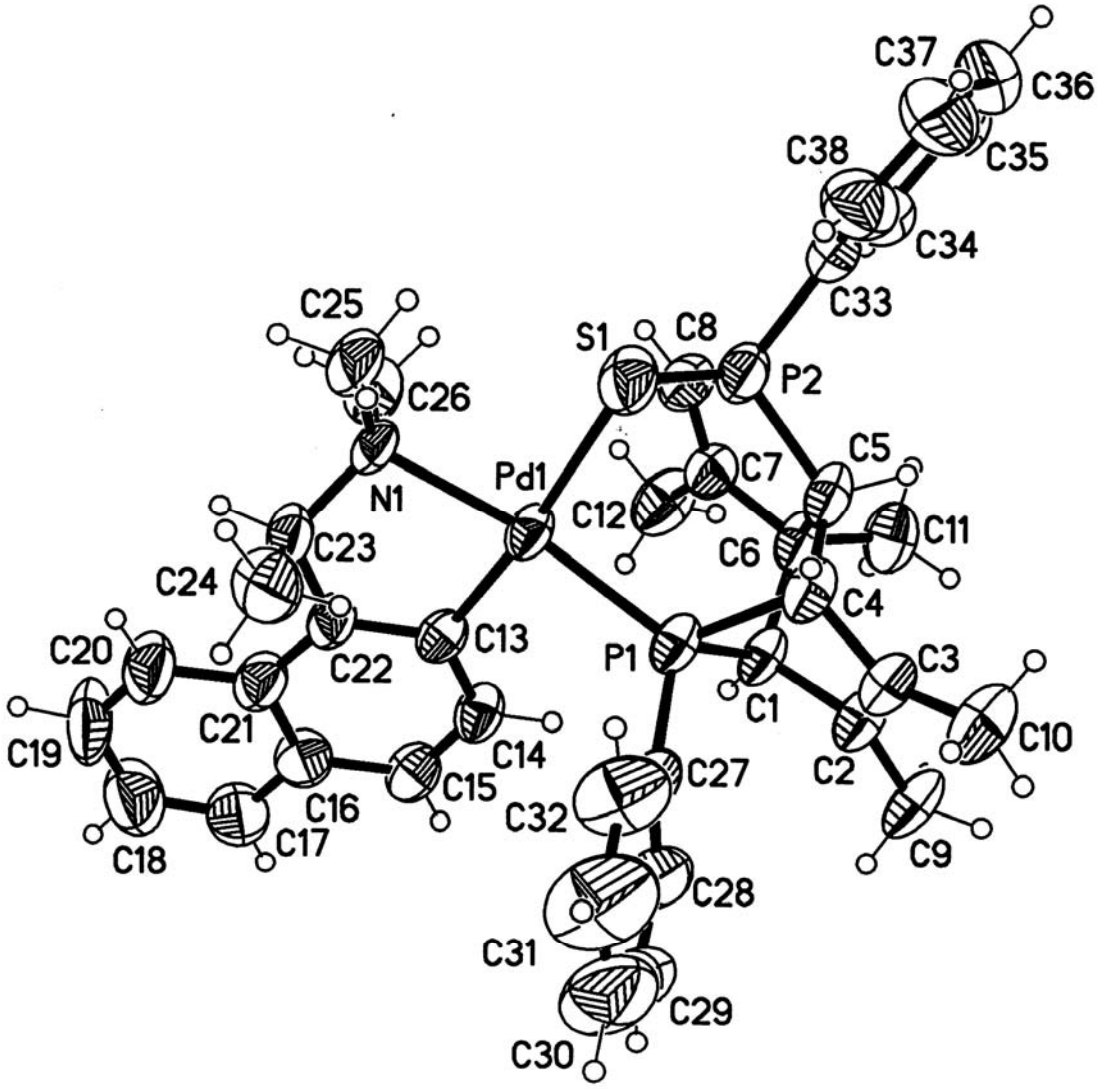


Figure 2.3 Molecular structure and absolute configuration of (R_c,S_p,R_p)-48

The sulfonated phosphole binds to the metal centre *trans* to the C of the metal template while the phosphorous of the DMPP occupies the position *trans* to the nitrogen of the template. This study also revealed that the absolute configurations at P(1), P(2), C(1), C(4), C(5) and C (6) in the complex were *S*, *R*, *R*, *S*, *R* and *R* respectively.

The geometry at the palladium centre is distorted square planar with angles at palladium in the range of 80.7(2) – 94.0(1) and 171.3(1) – 173.9(2)°. The bite angles formed by the two chelate rings are 80.7(2)° for the naphthylamine ring of the template and 94.01(6)° for the (S=P)-P chelate. Selected bond distances and angles are listed in Table 2.1.

Table 2.1 Selected bond lengths (Å) and angles (°) for (R_c,S_p,R_p)-48

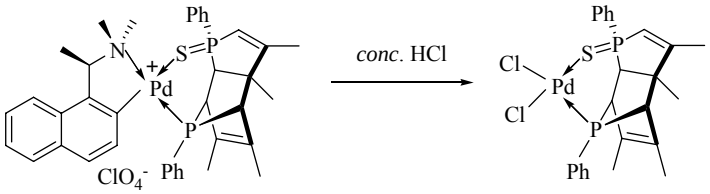
Pd(1)-C(13)	2.004(5)	Pd(1)-N(1)	2.146(4)
Pd(1)-P(1)	2.226(1)	Pd(1)-S(1)	2.481(1)
P(2)-S(1)	1.987(2)	P(2)-C(8)	1.768(6)
C(8)-C(7)	1.321(8)	C(6)-C(7)	1.535(8)
C(5)-C(6)	1.564(8)	P(2)-C(5)	1.832(6)
C(5)-C(4)	1.550(9)	C(1)-C(6)	1.544(8)
P(1)-C(4)	1.856(6)	P(1)-C(1)	1.874(5)
C(13)-Pd(1)-N(1)	80.7(2)	C(13)-Pd(1)-P(1)	92.0(1)
N(1)-Pd(1)-P(1)	171.3(1)	C(13)-Pd(1)-S(1)	173.9(2)
N(1)-Pd(1)-S(1)	93.4(1)	P(1)-Pd(1)-S(1)	94.0(1)
P(2)-S(1)-Pd(1)	92.4(1)	C(4)-P(1)-Pd(1)	116.7(2)

C(1)-P(1)-Pd(1)	123.9(2)	C(8)-P(2)-S(1)	113.0(2)

The bond angle at the bridgehead phosphorous, C(4)- P(1)- C(1) [80.4 (3) °], is in agreement with that observed for *exo* dimeric phosphole sulfides reported earlier[156] (*ca*. 80°) and is indicative of the elevated levels of strain at the bridge. This bridgehead angle was also the same as that observed for the cycloadduct obtained from the asymmetric dimerization of DMPP in the presence of the platinum(II) analogue of the same template.[157] The bridgehead C-P-C angle is also expectedly smaller than those seen in complexes obtained from the cycloaddition of diphenylvinylphosphine with DMPPS[158] (*ca*. 83°) and also for the *exo*-thioamide-substituted 7- phosphanorbornene P-S bidentate chelate.[159] The Pd-S and P=S distances were observed to be 2.481(1) and 1.987(2) A° respectively. It is noteworthy that in this cycloaddition DMPPS functions as a dienophile whereas DMPP functions as the cyclic diene.

2.2.3 Preparation of the Dichloro Complex (S_p,R_p)-49

The chiral naphthylamine auxiliary in complex (R_c,S_p,R_p)-**48** was removed chemoselectively by treatment with hydrochloric acid at room temperature. The dichloro complex (S_p,R_p)-**49** was obtained as yellow crystals from acetonitrile-diethyl ether. The $^{31}P\{^1H\}$ NMR spectrum of the complex in $CDCl_3$ showed signals at δ 60.54 (d, 1P, J_{PP} = 15.2 Hz), 106.63 (d, 1P, J_{PP} = 15.2 Hz).



(R_c,S_p,R_p)-48 **(S_p,R_p)-49**

Scheme 2.3

2.2.4 Single Crystal X-ray Structural Analysis of (S_p,R_p)-49

The molecular structure and the absolute configuration of the recrystallised (S_p,R_p)-**49** were established by single crystal X-ray crystallographic analysis (Figure 2.4). The absolute configurations of the stereogenic centers were found to be retained even after reaction under acidic conditions. Selected bond parameters are given in Table 2.2.

Table 2.2 Selected bond lengths (Å) and angles (°) for (S_p,R_p)-49

Pd(1)-P(1)	2.194(9)	Pd(1)-Cl(1)	2.318(1)
Pd(1)-S(1)	2.324(1)	Pd(1)-Cl(2)	2.381(1)
P(2)-S(1)	2.017(1)	C(5)-C(6)	1.559(5)
P(1)-Pd(1)-Cl(1)	83.0(4)	P(1)-Pd(1)-S(1)	91.5(4)
Cl(1)-Pd(1)-S(1)	171.8(4)	P(1)-Pd(1)-Cl(2)	174.4(3)
Cl(1)-Pd(1)-Cl(2)	94.9(4)	S(1)-Pd(1)-Cl(2)	91.1(4)
C(4)-P(1)-C(1)	81.1(2)	P(2)-S(1)-Pd(1)	93.1(5)

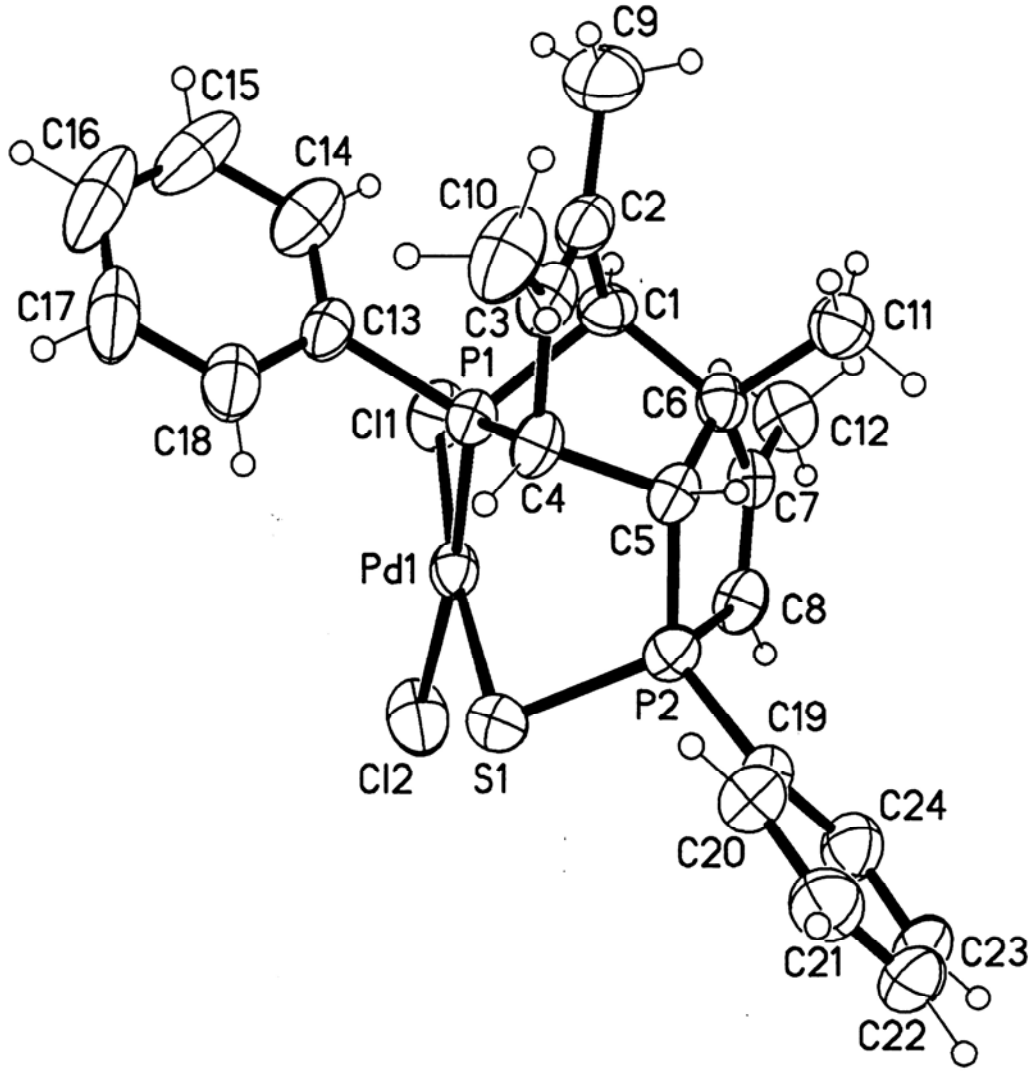
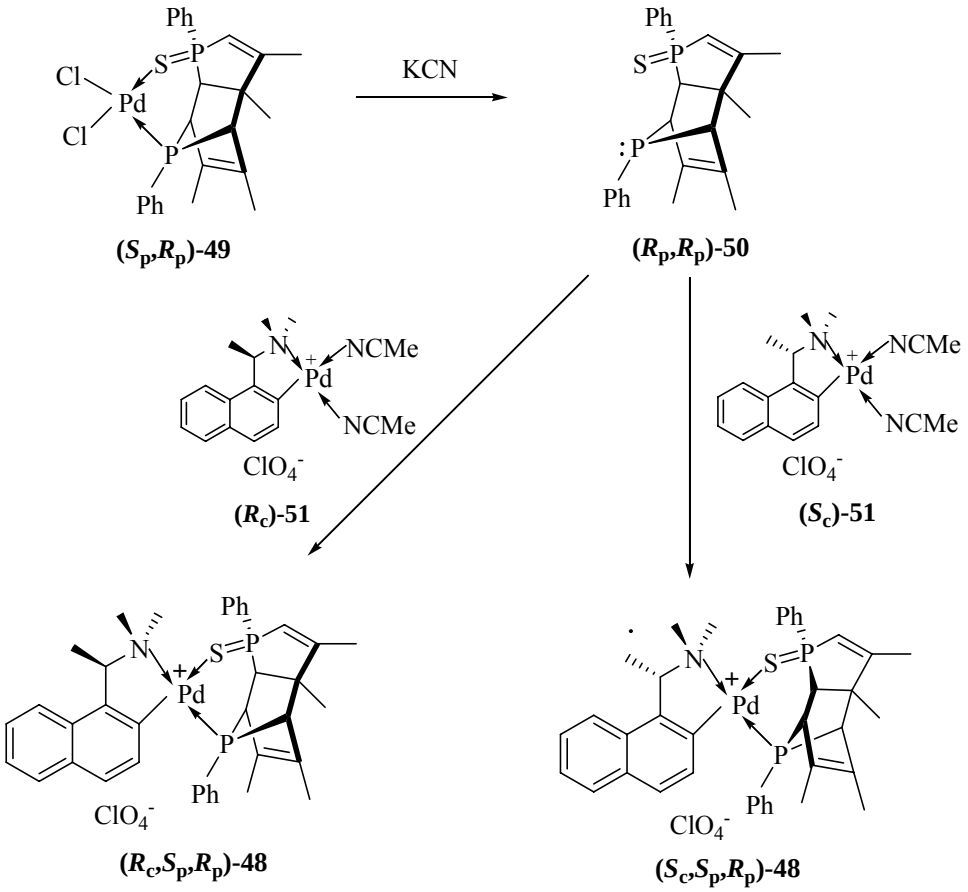


Figure 2.4 Molecular structure and absolute configuration of (S_p,R_p)-49

2.2.5 Decomplexation and the Optical Purity of (S_p,R_p)-49

The optically active ligand (R_p,R_p)-**50** can be stereospecifically cleaved off from the complex (S_p,R_p)-**49** by treatment of the dichloro complex with aqueous potassium cyanide at room temperature (Scheme2.4).



Scheme 2.4

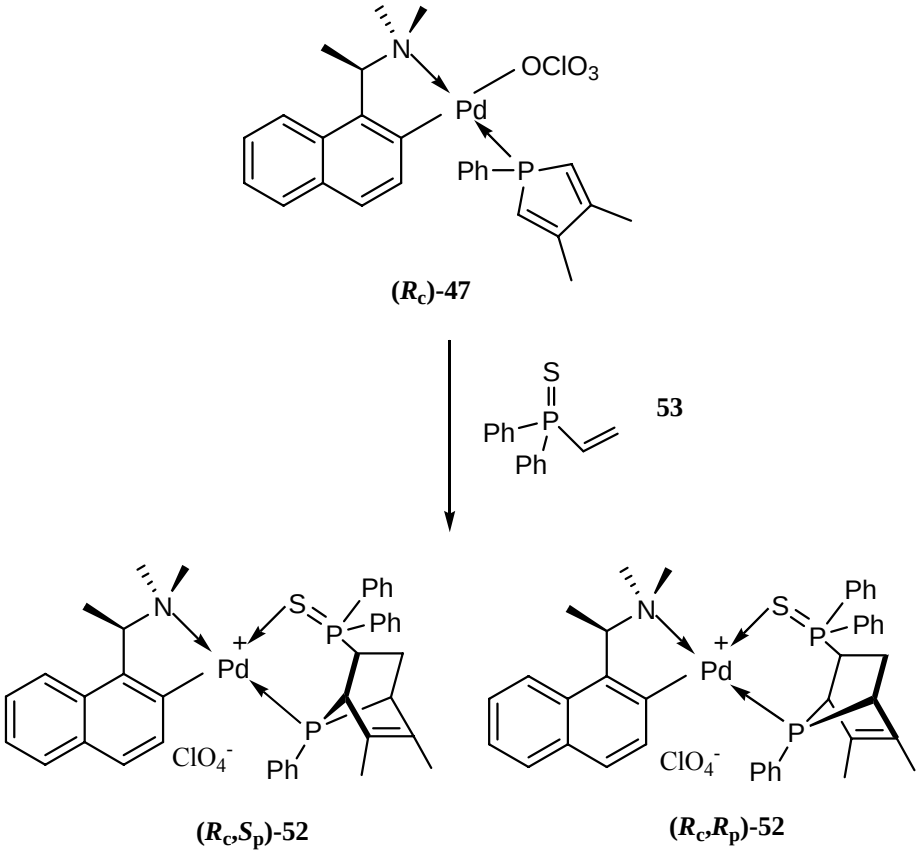
It is noteworthy that the apparent inversion of configuration that occurs at the tertiary phosphorous stereogenic center when the ligand is liberated from the metal is merely a consequence of the Cahn-Ingold-Prelog (CIP) sequence rule.[160] The liberated (R_p,R_p)-**50** was obtained as a colorless oil in 83% yield. The $^{31}P\{^{1}H\}$ NMR spectrum of the free ligand in $CDCl_3$ exhibited two doublets at δ 58.12 (d, 1P, $^{3}J_{PP}$ = 7.6Hz) and 106.50 (d, 1P, $^{3}J_{PP}$ = 7.6Hz), the low field resonance signal confirms the retention of the *exo-syn* stereochemistry.[155]

Owing to the susceptibility of the non coordinated bridgehead phosphorous to oxidation, the liberated (R_p,R_p)-**50** cannot be stored in its pure form. Hence the liberated ligand was re-complexed to selected metal ions to form stable metal complexes. Furthermore, in order to determine the optical purity of (R_p,R_p)-**50**, the liberated ligand was recoordinated to the bis(acetonitrile) complex (R_c)-**51** (Scheme 2.4). The recoordination procedure was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. In $CDCl_3$, the ^{31}P NMR spectrum of the crude recoordination product showed two doublets at δ 61.30 ($J_{P\text{-}P}$ = 11.4 Hz) and 115.27 ($J_{P\text{-}P}$ = 11.4 Hz). These NMR signals are identical with those recorded for the major diastereomer generated from the original cycloaddition reaction. No $^{31}P\{^1H\}$ signals could be detected at δ 61.96 and 114.80, thus conforming that liberated (R_p,R_p)-**50** is optically pure. In a further check, (R_p,R_p)-**50** was recoordinated regiospecifically to (S_c)-**51** to generate the diastereomeric complex (S_c,S_p,R_p)-**48**. The $^{31}P\{^1H\}$ NMR spectrum of the crude product in $CDCl_3$ showed two doublets at 61.96 and 114.80. No $^{31}P\{^1H\}$ NMR signals could be detected for the major diastereomer thus reaffirming that liberated (R_p,R_p)-**50** is stereochemically pure.

2.3 Asymmetric Diels-Alder Reaction between DMPP and diphenylvinylphosphine sulfide ligand.

2.3.1 Preparation of *exo*-Products : (R_c,R_p)- 52 and (R_c,S_p)- 52

The reaction of (R_c)-**47** with diphenylvinylphosphine sulfide **53**, proceeded smoothly under ambient conditions. The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy (121 MHz, $CDCl_3$) and was found to be completed in three days.



(R_c)-47

(R_c,S_p)-52 **(R_c,R_p)-52**

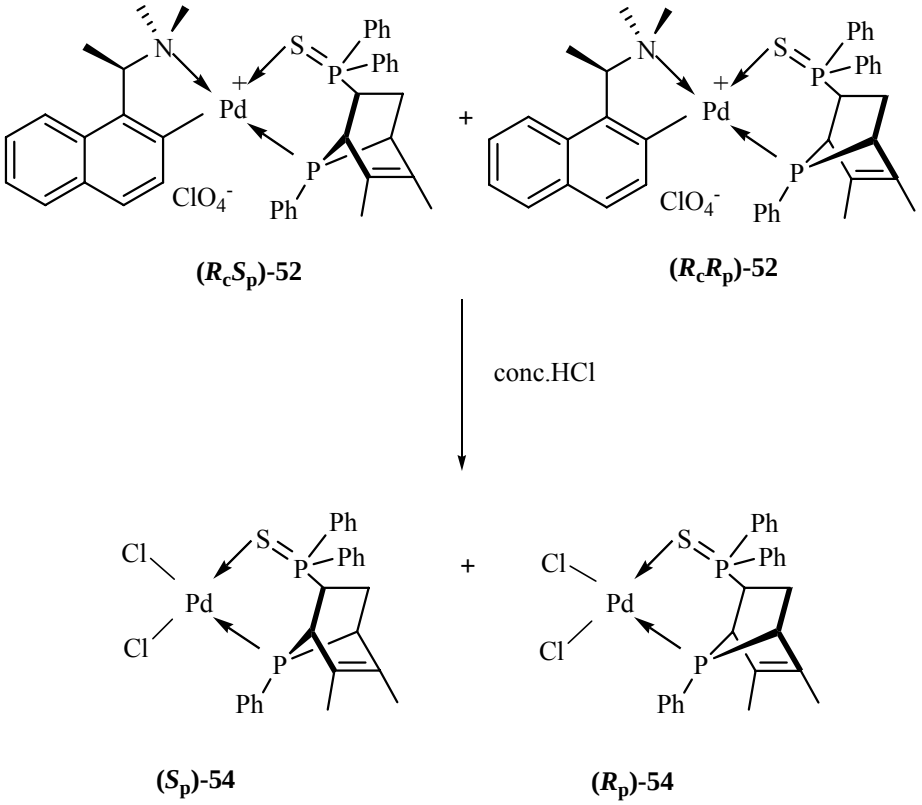
Scheme 2.5

On completion the ^{31}P NMR spectrum showed two pairs of singlets at δ 49.38, 113.28 (minor) and 52.06, 113.91 (major). The signals were attributed to a possible diastereomeric pair in a 2:1 ratio with the low field resonances indicative of bridgehead phosphorous with *exo*-*syn* stereochemistry.[155] The high field signals at δ 49.38 and 52.06 are attributed to the non-bridging phosphorous of the two diastereomeric cycloadducts (R_c,R_p)- **52** and (R_cS_p)- **52**. It needs to be noted that the non-observance of coupling between the two phosphorous centers is consistent with what has been observed in similar P^P(S) bidentate cycloadducts involving 7-phosphanorbornene systems on Pd(II).[158] Attempts to separate and isolate the two diastereomers *via* column chromatography and fractional crystallization, however, were not successful.

2.3.2 Preparation of the Dichloro Complex (S_p)-54 and (R_p)-54

To confirm the identity of the two diastereomers and with a view to possibly separate them *via* fractional crystallization, the chiral naphthylamine auxiliary in the 1:0.6 diastereomeric mixture was removed chemoselectively from palladium by stirring a dichloromethane solution of the complex mixture with concentrated hydrochloric acid at room temperature (Scheme 2.6) .

The $^{31}P\{^1H\}$ NMR spectrum (121 MHz) of the crude reaction mixture in $CDCl_3$ exhibited two singlets at δ 50.05 and 111.65. Fractional crystallization was attempted in a wide range of solvent systems. Yellow crystals suitable for single crystal X-ray diffraction analysis were finally obtained from acetonitrile-diethyl ether as yellow prisms in 76% yield.



(R_cS_p)-52 **(R_cR_p)-52**

(S_p)-54 **(R_p)-54**

Scheme 2.6

2.3.3 Single Crystal X-ray Diffraction Analysis of 54

The molecular structure of **54** was established by a single crystal X-ray structural determination. The single crystal X-ray diffraction analysis of **54**, however, reveals the presence of both enantiomers in the unit cell. The ORTEP for (R_p)-**54** is shown in Figure 2.5, and is taken as the representative molecule in order to study the coordination aspects for the cycloadducts which were formed as racemic mixture.

The phosphanorbornene skeleton coordinates to the palladium centre as bidentate chelate *via* P → Pd and P=S → Pd. The structural analysis revealed that the diphenylphosphinosulfide group is substituted at the *exo* position of the

phosphanorbornene skeleton. The geometry at the palladium is distorted square planar with angles at palladium in the range of 83.4(4) – 95.3(4) and 174.4(4)-178.7(4)°.

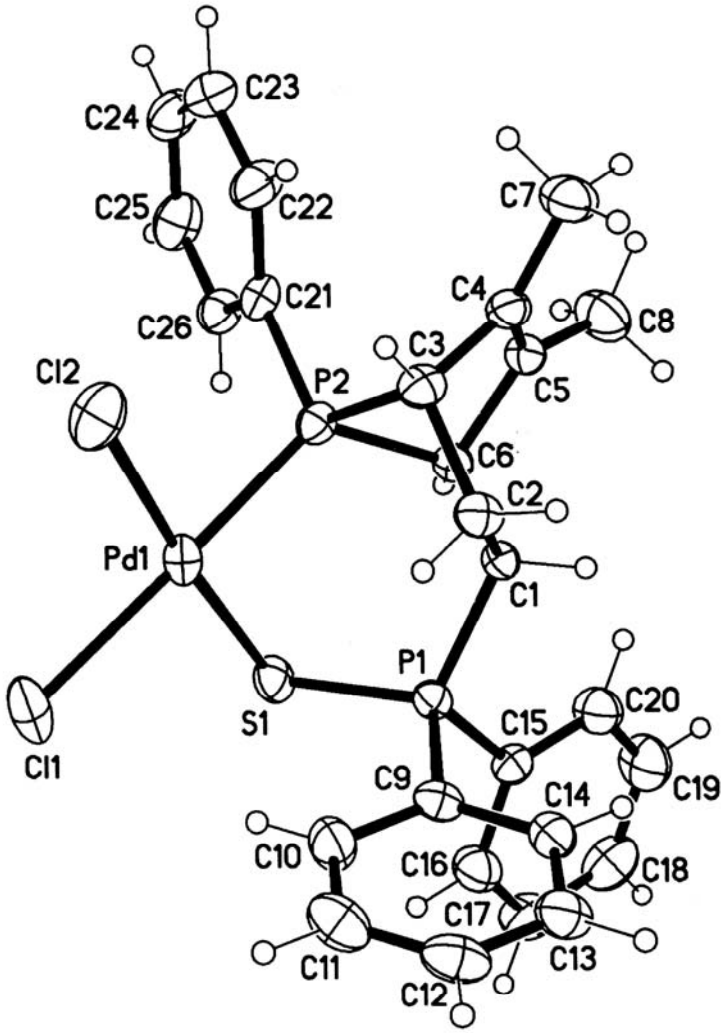


Figure 2.5 Molecular structure and absolute configuration of (R_p)-54

The bond angle at the bridgehead phosphorous, C(3)-P(2)-C(6) (81.47(15)°), is similar to those observed for (S_p,R_p)-**49** [81.06(16)°] indicative of similar levels of strain in the 7-phosphanorbornene P^P(S) ligand framework. It is also noted that the bridgehead

strain is much higher than that observed for the cycloadduct formed between DMPPS and diphenylvinylphosphine on a Pd(II) centre[158] [83.0(1)°], possibly due to the fact that in the latter the bridgehead P is less constrained by coordination requirements since the coordination is thru the S in the P=S bridgehead rather then directly through P. Selected bond distances and angles are listed in Table 2.3.

Table 2.3 Selected bond lengths (Å) and angles (°) for (R_p)-54

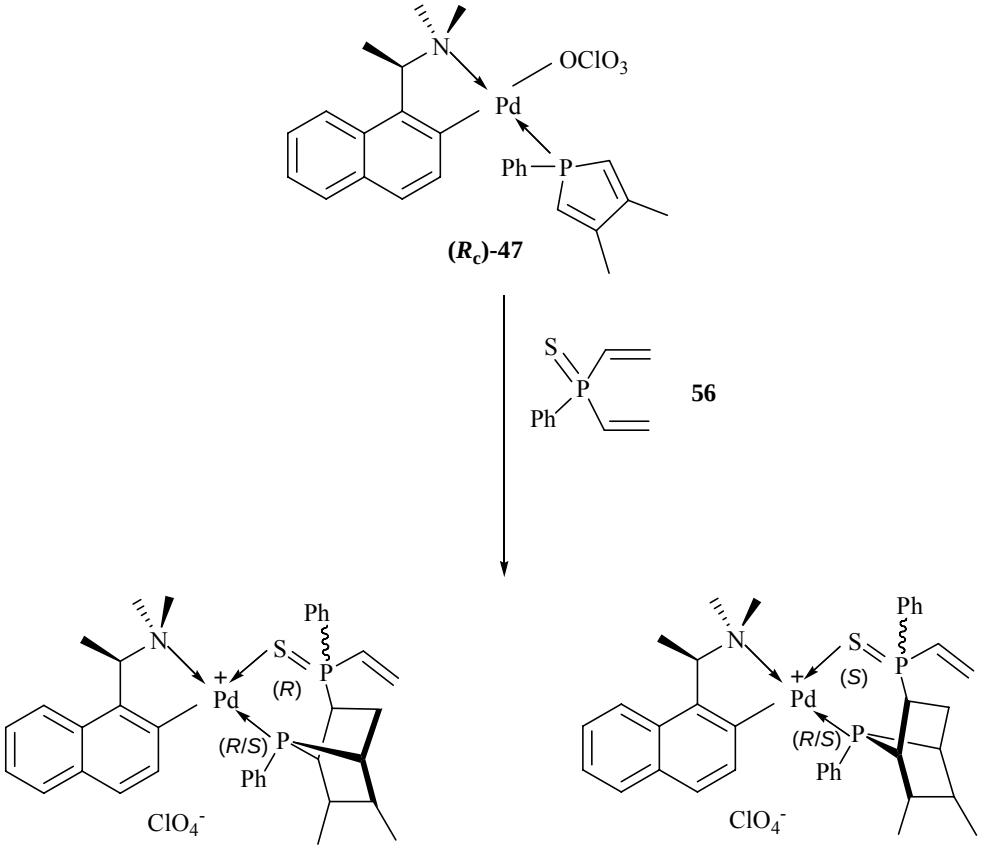
Pd(1)-P(2)	2.203(9)	Pd(1)-S(1)	2.299(9)
Pd(1)-Cl(2)	2.318(1)	Pd(1)-Cl(1)	2.401(9)
P(1)-C(15)	1.805(3)	P(1)- C(9)	1.805(3)
P(1)-C(1)	1.826(3)	P(1)-S(1)	2.012(1)
P(2)-C(3)	1.837(3)	P(2)-C(6)	1.849(3)
P(2)-Pd(1)-S(1)	90.9(3)	P(2)-Pd(1)-Cl(2)	83.4(4)
S(1)-Pd(1)-Cl(2)	174.3(4)	P(2)-Pd(1)-Cl(1)	178.6(4)
S(1)-Pd(1)-Cl(1)	90.3(3)	Cl(2)-Pd(1)-Cl(1)	95.2(4)
C(3)-P(2)-Pd(1)	116.4(1)	C(6)-P(2)-Pd(1)	120.2(1)
P(1)-S(1)-Pd(1)	101.1(4)		

It is noteworthy that the S → Pd bond in (R_p)-**54** is weaker than that in (S_p,R_p)-**49** [2.324(1)°] formed from cycloaddition of DMPP and DMPPS wherein the S belongs to the sulfonated phosphole acting as dienophile. The S → P bond although is of the same strength as that formed in the cycloadduct formed in the reaction between

DMPPS and diphenylvinylphosphine where the S belongs to the sulfonated phosphole acting as dienophile.

2.4 Metal Template Promoted Diels-Alder Reaction between DMPP and divinylphenylphosphine sulfide Ligand.

2.4.1 Preparation of *exo*-Products



(R_c,R_p,R_p) and **(R_c,S_p,R_p)-55** **(R_c,R_p,S_p)** and **(R_c,S_p,S_p)-55**

Scheme 2.7

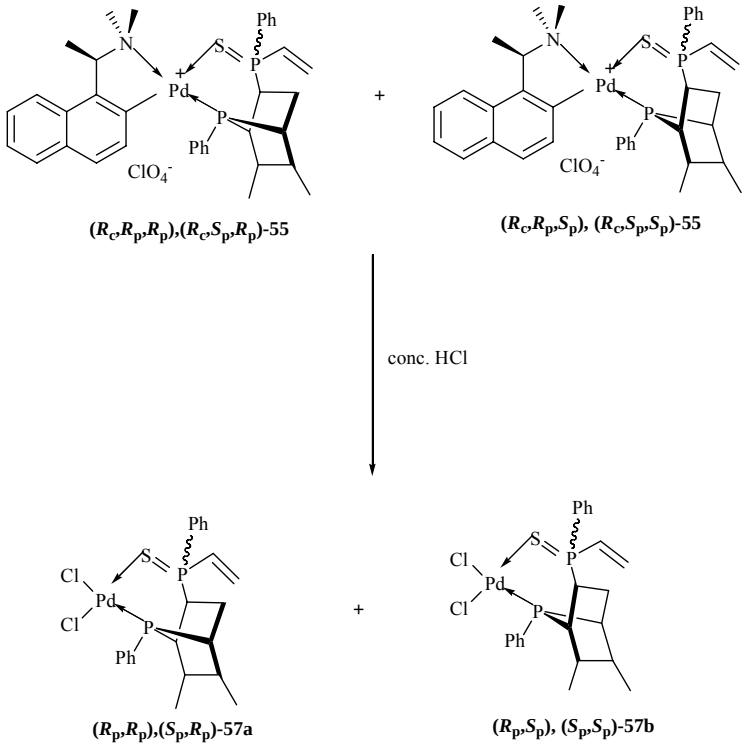
In order to further explore the reactions of sulfonated vinylphosphines towards DMPP and to understand the reason for the low selectivity observed in the case of the cycloaddition involving diphenylvinylphosphinesulfide and DMPP, a further reaction was carried out involving sulfonated divinylphenylphosphine and DMPP (Scheme 2.7).

The attempted Pd(II) template promoted cycloaddition reaction between (R_c)-**47** and sulfonated divinylphenylphosphine **56** proceeded at room temperature in dichloromethane and was monitored by $^{31}P\{^1H\}$ NMR spectroscopy (121MHz, $CDCl_3$). The reaction was found to be complete in 4 days. The crude reaction mixture showed the presence of 4 isomers in the ratio 3.14: 2.06: 1: 2.53. The set of resonance signals at the low field range between δ 113.22 and 114.54 was clearly indicative of the formation of the cycloadduct. Attempts to separate out the isomers by means of column chromatography and fractional crystallization proved futile.

2.4.2 Preparation of Dichloro Complexes of 55

In order to establish the structure of the cycloadduct formed and to possibly separate the isomers of **55** as neutral complexes, the dichloro complexes of the products were prepared by chemoselective removal of the *ortho*-metallated naphthylamine auxiliary as shown in Scheme 2.8.

Attempts to separate the isomers by means of column chromatography did not yield any results. Therefore attempt was made to separate the isomers by fractional crystallization.



$(R_c,R_p,R_p),(R_c,S_p,R_p)$-55 + (R_c,R_p,S_p), (R_c,S_p,S_p)-55

$(R_p,R_p),(S_p,R_p)$-57a + (R_p,S_p), (S_p,S_p)-57b

Scheme 2.8

2.4.3 Single Crystal X-ray Structural Analysis of 57

Single crystal X-ray diffraction analysis of the first crop of pale yellow prisms obtained from the reaction mixture containing the dichloro complexes revealed that both enantiomeric forms of one of the diastereomers has co-crystallized out (Figure 2.6). Subsequently another batch of crystals were obtained as yellow needles and analyzed by single crystal X-ray diffraction revealing the presence of the other diastereomer, also present as a enantiomeric mixture (Figure 2.7).

From the single crystal X-ray analysis**,** it was confirmed that the cycloadduct produced in the reaction between divinylphenylphosphine sulfide and DMPP coordinates

to the metal centre through S → Pd and P → Pd bonds. The geometry at the palladium is distorted square planar in both isomers. The angles at palladium are in the ranges 83.7(3) – 93.8(3)° and 175.5(4) – 176.7(4)° for (R_p,S_p) and (S_p,S_p)-**57b** and in the range 83.4(1) – 93.7(2)° and 174.8(1) – 176.2(2) for **(**R_p,R_p) and (S_p,R_p)-**57a.** The selected bond distances and angles for the two diastereomers are given in Table 2.4 and Table 2.5.

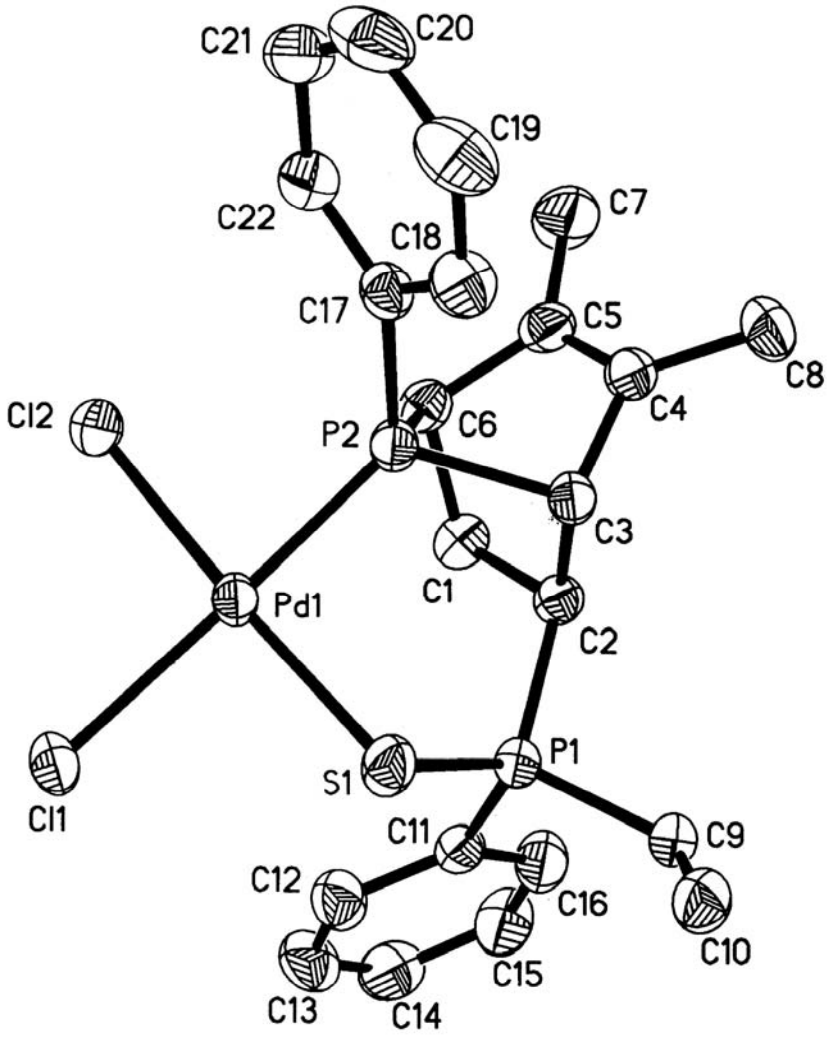


Figure 2.6 The molecular structure of enantiomeric complex (R_p,S_p) -57b (representative molecule from enantiomeric mixture)

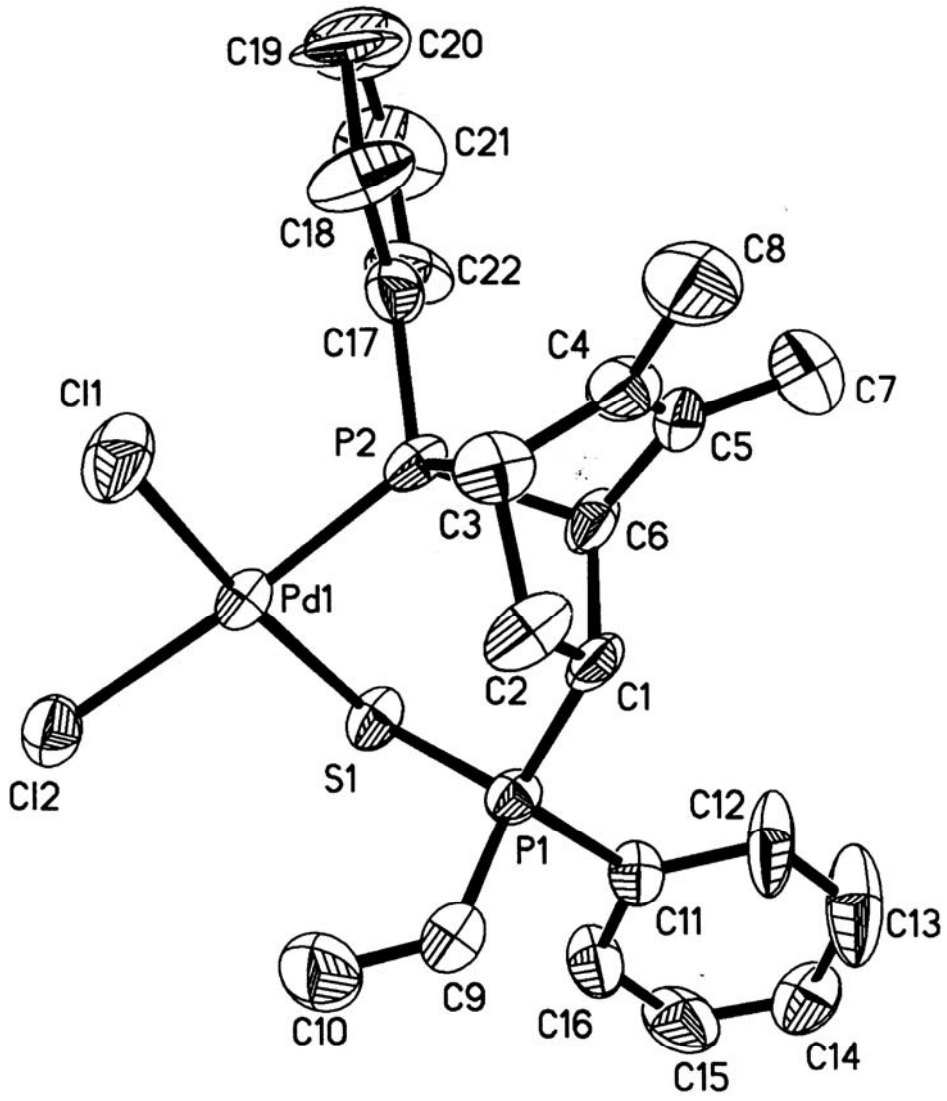


Figure 2.7 The molecular structure of the enantiomeric complex (S_p,R_p)-57a (representative molecule from enantiomeric mixture)

Table 2.4 Selected bond lengths (Å) and angles (°) for complex (R_p,S_p)- 57b

Pd(1)–P(2)	2.209(9)	Pd(1)–Cl(2)	2.314(9)
Pd(1)–S(1)	2.309(1)	Pd(1)–Cl(1)	2.397(1)
P(1)–C (9)	1.786(4)	P(1)–C(11)	1.796(4)
P(1)–C (2)	1.828(3)	P(1)–S(1)	2.006(1)

P(2)–C(6)	1.841(4)	P(2)–C(3)	1.845(3)
C(1)–C(6)	1.558(5)	C(1)–C(2)	1.564(5)
C(2)–C(3)	1.550(5)	C(3)–C(4)	1.523(5)
C(4)–C(5)	1.333(5)	C(5)–C(6)	1.513(5)
P(2)–Pd(1)–S(1)	92.6(3)	P(2)–Pd(1)-Cl(2)	83.7(3)
S(1)-Pd(1)-Cl(2)	175.5(4)	P(2)-Pd(1)-Cl(1)	176.6(4)
S(1)-Pd(1)-Cl(1)	89.9(3)	Cl(2)-Pd(1)-Cl(1)	93.8(3)
C(2)-P(1)-S(1)	113.6(1)	C(6)-P(2)-C(3)	81.7(2)
C(6)-P(2)-Pd(1)	113.9(1)	C(3)-P(2)-Pd(1)	119.6(1)
P(1)-S(1)-Pd(1)	102.5(5)		

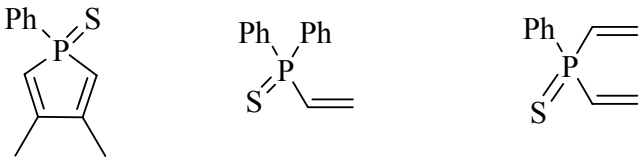
Table 2.5 Selected bond lengths (Å) and angles (°) for complex (S_p,R_p)-57a

Pd(1)-P(2)	2.191(4)	Pd(1)-S(1)	2.297(3)
Pd(1)-Cl(1)	2.316(4)	Pd(1)-Cl(2)	2.386(4)
P(1)-C(1)	1.834(13)	P(1)-S(1)	2.015(4)
P(2)-C(6)	1.866(12)	P(2)-C(3)	1.830(12)
C(1)-C(2)	1.517(19)	C(1)-C(6)	1.571(19)
C(2)-C(3)	1.529(19)	C(3)-C(4)	1.43(2)
C(4)-C(5)	1.32(2)		
P(2)-Pd(1)-S(1)	91.5(1)	P(2)-Pd(1)-Cl(1)	83.3(1)
S(1)-Pd(1)-Cl(1)	174.8(1)	P(2)-Pd(1)-Cl(2)	176.2(2)
S(1)-Pd(1)-Cl(2)	91.4(1)	Cl(1)-Pd(1)-Cl(2)	93.7(2)

C(1)-P(1)-S(1)	112.1(4)	C(3)-P(2)-Pd(1)	117.6(5)
C(6)-P(2)-Pd(1)	119.6(4)	P(1)-S(1)-Pd(1)	99.0(1)
C(2)-C(1)-P(1)	116.4(10)	C(3)-P(2)-C(6)	79.9(6)

2.5 Conclusion and Mechanistic Proposal for Asymmetric Diels-Alder Reactions involving DMPP and sulfonated dienophiles

Three sulfonated dienophiles were used in the attempted Palladium (II) metal template promoted asymmetric Diels-Alder reactions with 3,4-dimethyl-1-phenylphosphole (Figure 2.8).



45 **53** **56**

Figure 2.8 Sulfonated dienophiles employed in conjunction with DMPP for the asymmetric Diels-Alder reactions

As can be seen from the results summarized in Table 2.6, appreciable selectivity and separation of the diastereomers formed in the cycloaddition could only be achieved in the case of the reaction wherein the sulfonated phosphole counterpart of DMPP acted as dienophile. A complete analysis of the reasons behind this observed selectivity is possible only by 2-dimensional NMR spectroscopic studies and single crystal X-ray analysis of the isolated pure diastereomers.

Table 2.6 Comparison of Stereoselectivity of ligands 45, 53 and 56 in Diels-Alder reactions involving DMPP

		45	**53**	**56**
Cycloaddition with (R_c)-**47**	Reaction conditions	Cycloaddition Reaction; rt; CH_2Cl_2; 2 days	Cycloaddition Reaction; rt; CH_2Cl_2; 3 days	Cycloaddition Reaction; rt; CH_2Cl_2; 4 days
	Selectivity	2 isomers 3.34:1	2 isomers 1.67:1	4 isomers 3.14: 2.06: 1: 2.53

Owing to the low selectivity in the case of cycloadditions involving **53** and **56**, resolution of the formed diastereomers by means of fractional crystallization or column chromatography did not yield desired results. A possible stereochemical explanation for the observed selectivity is therefore put forth based on model studies.

Due to the distinct electronic directing effect originating from the σ – donating nitrogen and π – accepting carbon atom of the *ortho*-metallated naphthylamine ring, it has been well established that when heterobidentate ligands are coordinated to the employed metal template, the softer of the two donors always takes up a position *trans* to NMe_2 group.[161,162] So the absence of regioisomers in all the three cycloadditions is expected in the case of these P^P(S) ligand systems.

For the cycloadditions involving **53** and **56** as dienophiles, the molecular model studies reveal that the steric repulsion in both approaching directions of the sulfonated dienophile to DMPP is small (Figure 2.9). The existence of sulfur atom between Pd and P extends the distance between the dienophilic centre and the metal allowing easy aligning of the dienophile to form both plausible diastereomers.

Furthermore the sterically bulky groups on the P are further away from the directing effects of NMe groups on the ortho-metallated naphthylamine template. This increase in distance from metal centre furthermore weakens the stereochemical control exerted by the naphthylamine auxiliary.

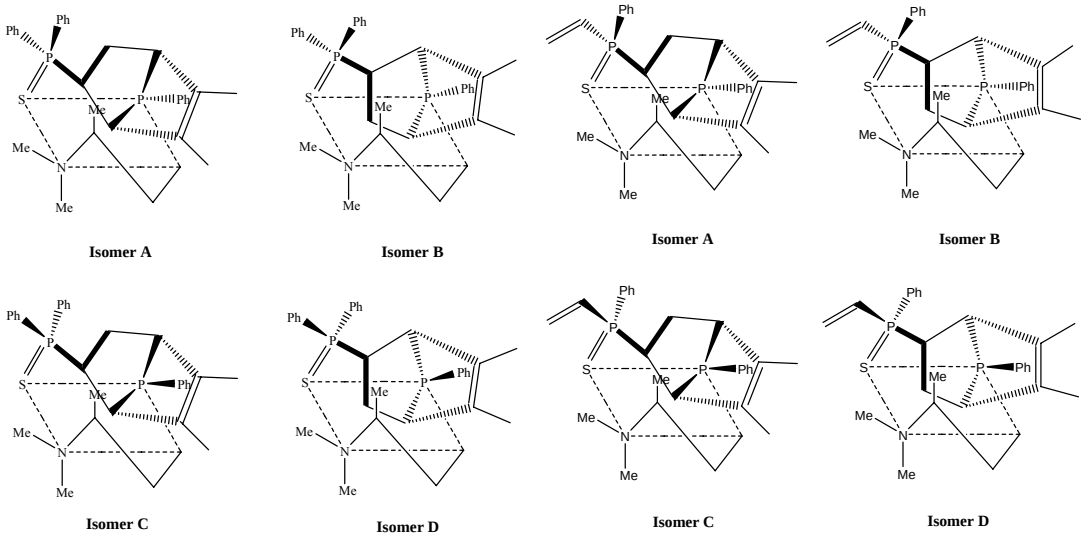


Figure 2.9 Possible diastereomers for the cycloaddition involving 53 and 56

In the case of the cycloaddition between DMPP and its sulfonated counterpart wherein the DMPPS acts as the dienophile it was observed that the selectivity between the two diastereomers were appreciable. It was also possible to isolate one of the

diastereomer and analyze it by means of single crystal X-ray diffraction. A Drieding model study based on the diffraction analysis is given in Figure 2.10.

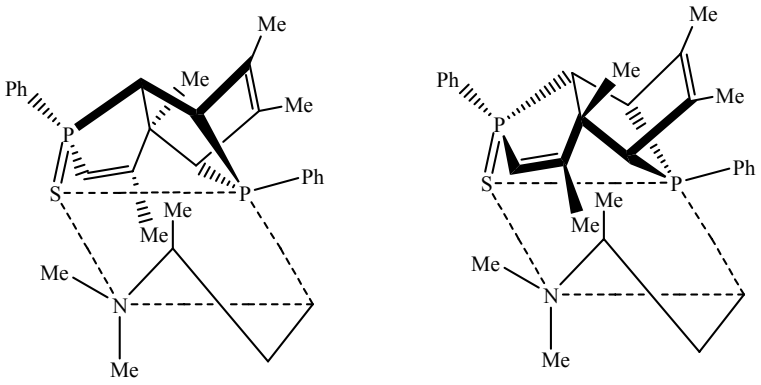


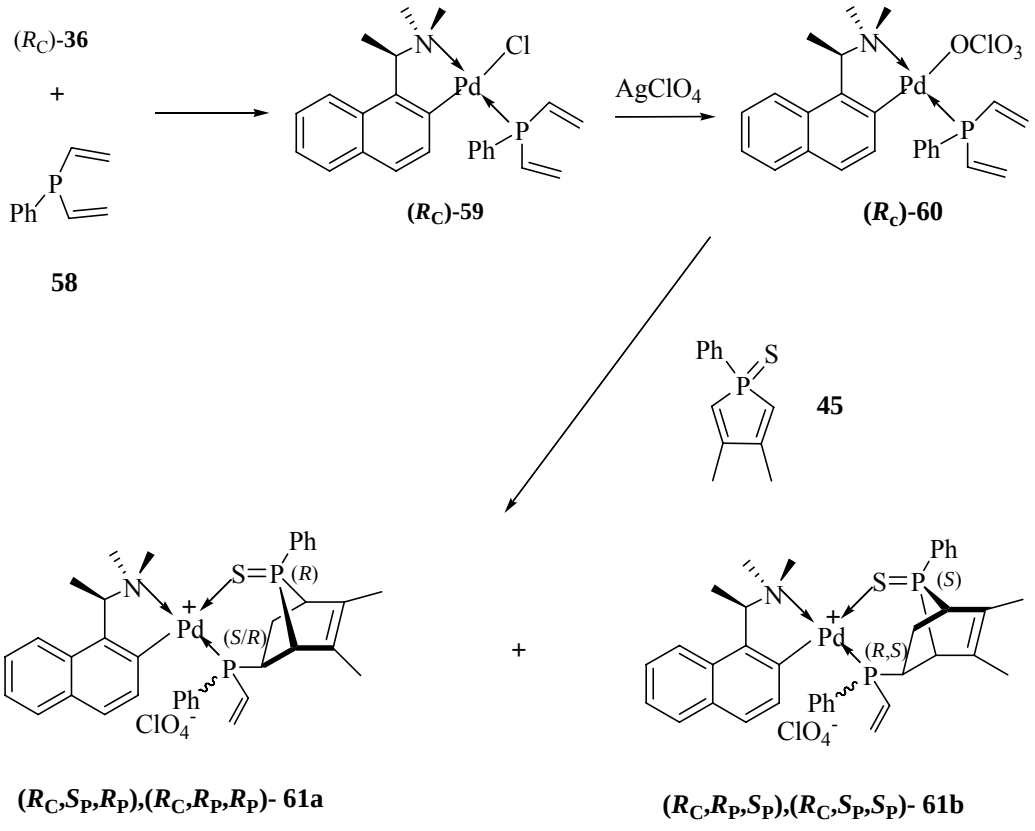
Figure 2.10 The two diastereomers formed in the cycloaddition of 45 and DMPP

It needs to be noted that the vinylic bond of the dienophile in the case of **45** is part of a phosphole 5-membered ring and therefore is much more restrained than the vinylic bonds in the case of **53** and **56** which are free to rotate along the P-C bond. It can be seen from the model studies that in the case of the less favored isomer B the phosphole ring projects into the metal coordination sphere. The methyl groups on the DMPPS entity therefore projects towards the cyclopalladated naphthylamine entity and therefore is sterically hindered by the methyl groups on both the chiral carbon centre of the naphthylamine ring and also the NMe groups as shown in Figure 2.8. Thus the fact that **45** is a dienophile wherein the vinylic entity is part of a substituted phosphole brings into consideration steric factors which are absent in the case of **53** and **56** and is believed to be the reason for the stereospecificity observed.

2.6 Asymmetric Diels-Alder Reaction Involving 3,4-Dimethyl-1-phenylphosphole-1-Sulfide and divinylphenylphosphine

2.6.1 Preparation of *exo*-Products:

A solution of the dimeric Pd complex (R_c)-**36** in dichloromethane was treated with two equivalents of diphenylvinylphosphine **58** for 6 hrs. (R_c)-**59** (Scheme 2.9).



(R_C,S_P,R_P),(R_C,R_P,R_P)- 61a + **(R_C,R_P,S_P),(R_C,S_P,S_P)- 61b**

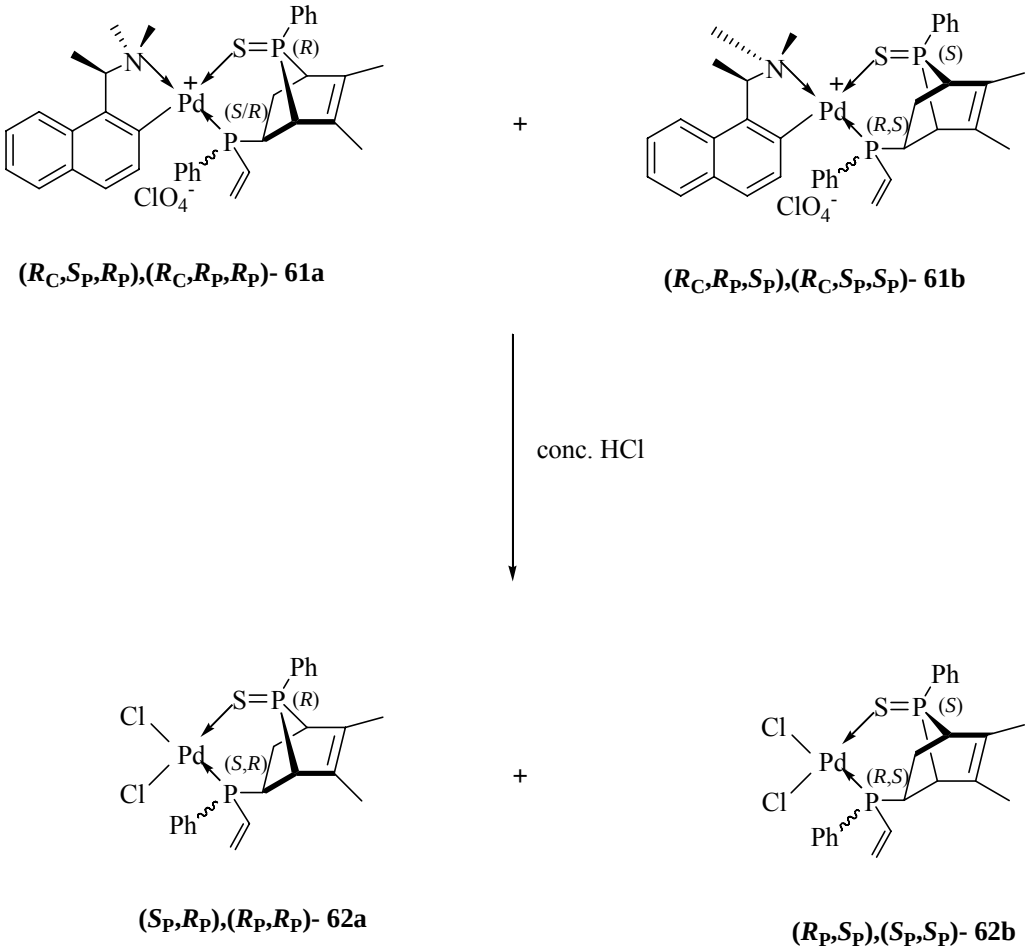
Scheme 2.9

The monomeric complex (R_c)-**59** was obtained in high yield (90%). The $^{31}P\{^{1}H\}$ NMR spectrum (121 MHz, $CDCl_3$) of (R_c)-**59** exhibited a singlet at δ 25.06 . The Cl ligand of the pure (R_c)-**59** was subsequently replaced by the ClO_4-group by treatment

with excess aqueous silver perchlorate solution in dichloromethane for 30 minutes. The percholorato complex (R_c)-**60** was obtained in quantitative yield (90%) upon work up. The 121 MHz $^{31}P\{^1H\}$ NMR spectrum of the complex in $CDCl_3$ exhibited a sharp singlet at δ 32.68.

The divinylphenylphosphine palladium complex (R_c)-**60** was reacted with an equivalent mole of DMPPS **45** to give a mixture of diastereomers as shown in Scheme 2.9. Prior to isolation, the 121MHz $^{31}P\{^1H\}$ NMR spectrum of the crude product in $CDCl_3$ exhibited eight singlets at δ 50.08, 54.51, 56.67, 59.18, 76.61, 77.14, 78.56 and 79.15. The high field signals at δ 76.61, 77.14, 78.56 and 79.15 are typical for bridgehead phosphorous adopting the *exo-syn* stereochemistry. The ^{31}P NMR spectrum thus revealed that the four isomers were generated as a 17: 3: 1: 1 mixture. Unfortunately, efforts to separate the isomers directly *via* column chromatography or fractional crystallization were unsuccessful.

To isolate the cycloadducts in their enantiomerically pure forms, the chiral naphthylamine auxiliary in the diastereomeric mixture was removed chemoselectively by stirring a dichloromethane solution of the diasteromeric complexes with concentrated hydrochloric acid at room temperature (Scheme 2.10). The major dichloro complex (R_p,S_p)-**62b** precipitated out of solution on adding *n*-hexanes to the crude reaction mixture in dichloromethane. Yellow prisms were obtained on recrystallisation from dichloromethane-diethyl ether. The 121 MHz $^{31}P\{^1H\}$ NMR spectrum of the complex in $CDCl_3$ exhibited two sharp singlets at δ 42.39 and 77.55. The other isomers could not be isolated from the mother liquor.



Scheme 2.10

2.6.2 Single Crystal X-ray Diffraction Analysis of (R_p,S_p)-62b

The molecular structure and absolute configuration of the recrystallised (R_p,S_p)-**62b** was established by single crystal X-ray crystallographic analysis (Figure 2.11). The cycloadduct coordinated to the palladium(II) centre *via* its phosphorous and sulfur donor atoms.

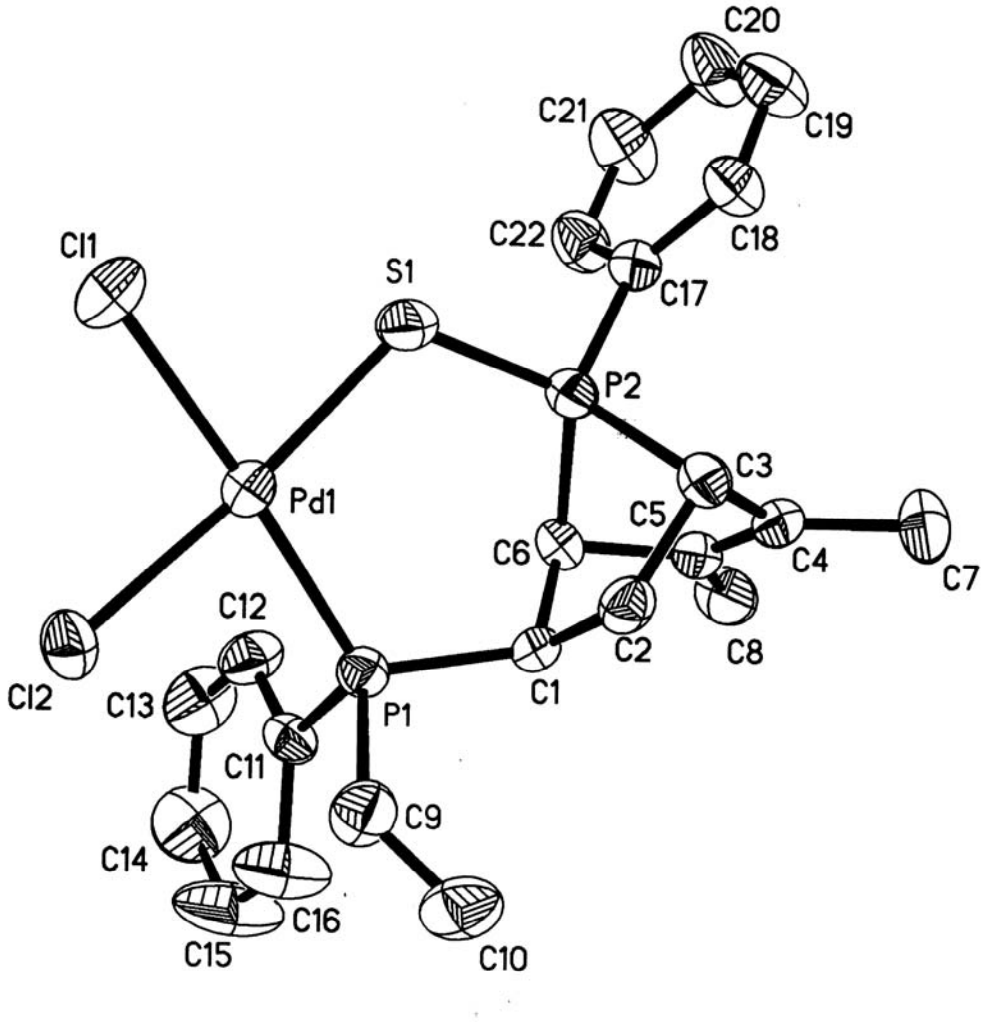


Figure 2.11 Molecular structure and absolute stereochemistry of (R_p,S_p)-62b

The geometry at the metal centre is distorted square planar with angles at palladium in the range of 82.7(5)-92.2(5)° and 100.7(5)-176.5(5)°. The absolute configurations of the newly formed stereogenic centers at P(1), C(1), C(3), C(6) and P(2) are *R*, *S*, *S*, *S* and *S* respectively. Selected bond lengths and bond angles are given in Table 2.7.

Table 2.7 Selected bond lengths (Å) and angles (°) of (R_p,S_p)-62b

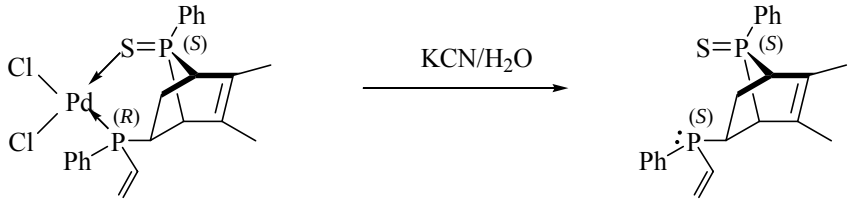
Pd(1)-P(1)	2.229(1)	Pd(1)-S(1)	2.289(1)
Pd(1)-Cl(2)	2.311(1)	Pd(1)-Cl(1)	2.374(1)
Pd(1)-C(9)	1.797(5)	P(1)-C(11)	1.813(5)
P(1)-C(1)	1.823(4)	P(2)-S(1)	2.008(1)
P(1)-Pd(1)-S(1)	100.7(5)	P(1)-Pd(1)-Cl(2)	84.4(5)
S(1)-Pd(1)-Cl(2)	174.8(5)	P(1)-Pd(1)-Cl(1)	176.5(5)
S(1)-Pd(1)-Cl(1)	82.7(5)	Cl(2)-Pd(1)-Cl(1)	92.1(5)
C(1)-P(1)-Pd(1)	117.0(2)	C(6)-P(2)-C(3)	83.7(2)
C(6)-P(2)-S(1)	117.7(2)	P(2)-S(1)-Pd(1)	115.1(7)
C(2)-C(1)-P(1)	111.3(3)	C(6)-C(1)-P(1)	115.8(3)
C(2)-C(3)-P(2)	100.1(3)		

The bond angles within the Pd-P-S ring are in the range of 100.7(5)-117.7(2)°. The bond angle at the bridgehead phosphorous C(6)-P(2)-C(3), (83.7(2)Å) is similar to that observed in related compounds containing the exo-cycloadduct formed from DMPPS and diphenylphenylphosphine[158] (83.0(1)Å) and also in the case of the *exo*-thioamide-substituted 7-phosphanorbornene P-S bidentate chelate.[159] The Pd(1)-P(1) bond distances in (R_p,S_p)-**62b** (2.229(1) Å) is similar to that in the complex involving diphenylvinylphosphine and DMPPS (2.242(1) Å), similarly the Pd(1)-S(1) bond length (2.289(1)Å) is almost the same as that found in the complex involving diphenylvinylphosphine as dienophile (2.299(1)Å). Apparently the P=S→Pd

coordination in (R_p,S_p)- **62b** is of similar strength as the coordination in the cycloadduct of DMPPS and diphenylvinylphosphine.

2.6.3 Decomplexation and the Optical Purity of the P-S Cycloadduct (R_p,S_p)-62b

The optically active diphosphine ligand (S_p,S_p)-**63** can be stereospecifically liberated from the complex (R_p,S_p)-**62b** by treatment with aqueous potassium cyanide at room temperature (Scheme 2.11).

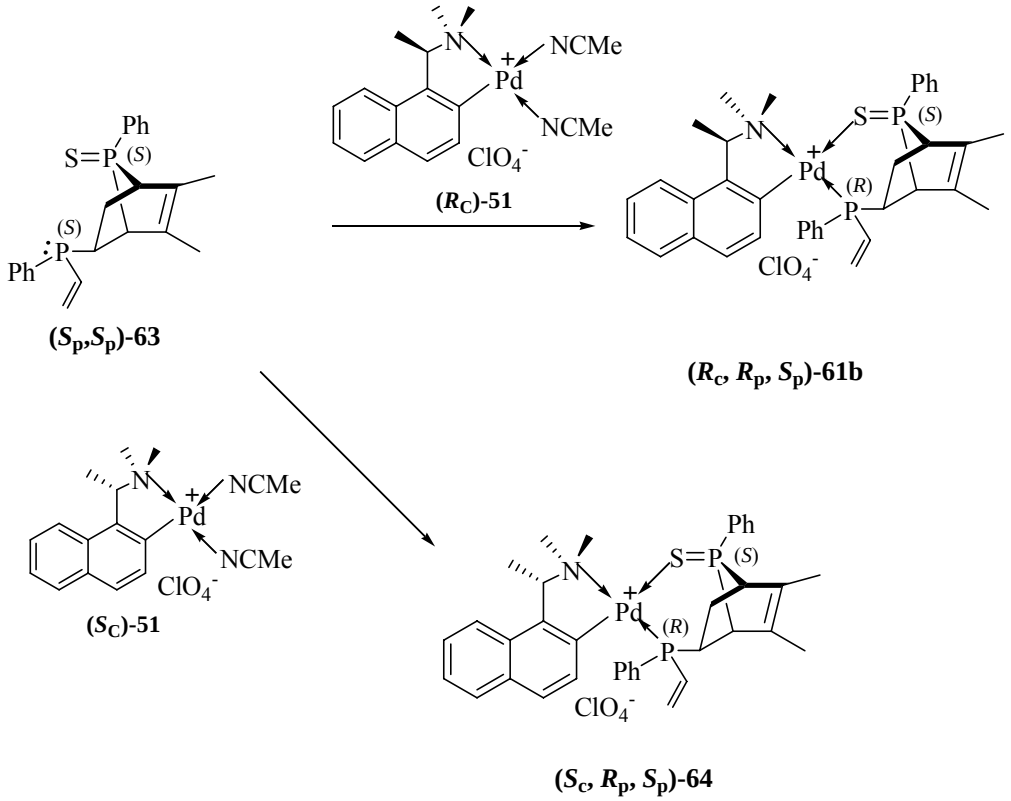


(R_p,S_p)-62b **(S_p,S_p)-63**

Scheme 2.11

Liberated (S_p,S_p)-**63** was obtained as colorless oil in 68 % yield. The $^{31}P\{1H\}$ NMR spectrum of the free ligand in $CDCl_3$ exhibited two singlets at δ 32.65 and 65.21. The low field resonance being a confirmation of the retention of the *exo-syn* stereochemistry.[155] Since the non-coordinated phosphorous atom is highly air-sensitive, the liberated ligand (S_p,S_p)-**63** cannot be stored in its pure form. Hence the liberated ligand was re-complexed to selected metal ions to form stable metal complexes. As there is a need to confirm the optical purity of complex (R_p,S_p)-**62b**, the liberated ligand was therefore coordinated to the bis(acetonitrile) complexes (R_c)-**51** and (S_c)-**51** as shown in Scheme 2.12. The recoordination to (R_c)-**51** generated the complex (R_c, R_p, S_p)- **61b .** The

121 MHz $^{31}P\{^{1}H\}$NMR spectrum in $CDCl_3$ for the complex formed after recoordination of the free ligand to (R_c)-**51** showed peaks at δ 50.08 and 76.60 which are identical to the resonance signals seen in the original cycloaddition reaction spectrum and are therefore assigned to (R_c, R_p, S_p)- **61b** in the original cycloaddition reaction spectrum . Similarly the $^{31}P\{^{1}H\}$ NMR spectrum for the product formed from coordination of the free ligand (S_p,S_p)-**63** to the bis(acetonitrile) complex (S_c)-**51** showed signals at δ 54.51 and 77.14 which match those seen in the original cycloaddition reaction and are attributed to the complex (S_c,R_p,S_p)- **64** which is the enantiomer of the original cycloaddition product (R_c,S_p ,R_p)-**61a** and therefore show similar chemical shifts.



Scheme 2.12

The re-coordination process therefore proves the optical purity of the released ligand and also helps to assign signals seen in the original cycloaddition reaction to the complexes (R_c, R_p, S_p)- **61b** and (R_c, S_p, R_p)-**61b.** The two remaining pairs of signals (δ 56.67, 59.18, 78.56 and 79.15) can be attributed to the complexes (R_c, R_p, S_p)-**61a** and (R_c, S_p, R_p)-**61a** though it is not possible to assign the observed signals to a particular isomer as in the case of (R_c, R_p, S_p)- **61b** and (R_c, S_p, R_p)-**61a**.

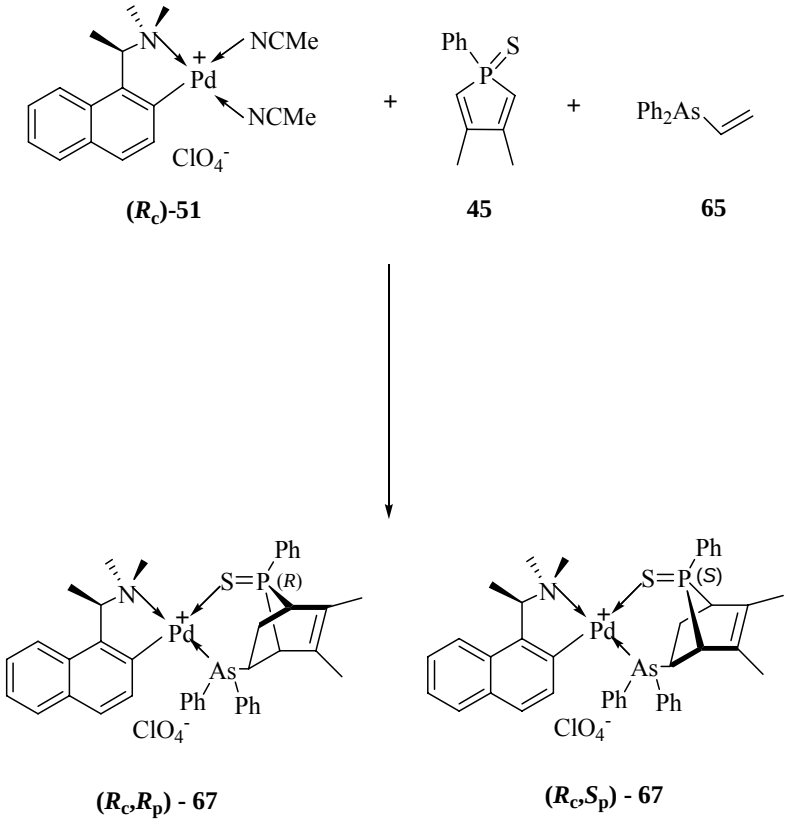
2.7 Cycloaddition Involving Metal Activated 3,4-Dimethyl-1-phenylphosphole-1-Sulfide and diphenylvinylarsine

2.7.1 Preparation of *exo*-Products:

The cycloaddition reaction was carried out by adding stoichiometric amounts of DMPPS **45** and diphenylvinylarsine **65** to a solution of the bis(acetonitrile) complex (R_c)-**51** in dichloromethane at room temperature (Scheme 2.13). The reaction was monitored using $^{31}P\{^1H\}$ NMR spectroscopy and was found to be complete in 3 days. Analysis of the $^{31}P\{^1H\}$ NMR spectrum (121MHz, $CDCl_3$) showed the formation of the diastereomeric products (R_c,R_p)-**67** and (R_c, S_p)-**67** as indicated by the resonance signals at δ 77.55 (s) and 79.69 (s). The signals were in the ratio 1:0.5 and therefore showed that the stereoselectivity of the cycloaddition is only moderate.

The regiochemistry of the formed cycloadduct is assigned based on comparison with cycloadducts formed in similar reactions involving DMPPS **45** and diphenylvinylphosphine[158] wherein the softer ligand (phosphine) takes up the position *trans* to the N of the chiral auxiliary and the sulfonated phosphole entity of the

cycloadduct binds trans to the aromatic C of the auxiliary. It needs to be noted that the high field signals are typical of P in the bridgehead position of the phosphanorbornene skeleton for this class of cycloadducts. This signal is also similar to the one observed for the cycloaddition reaction involving DMPP **44** and diphenylvinylphosphine **65**.[163]

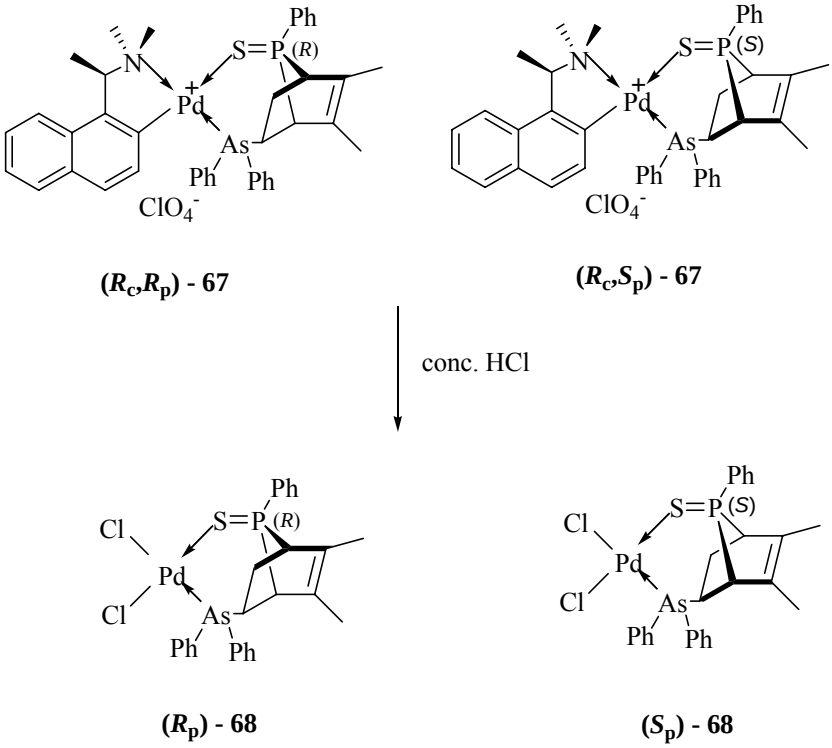


(R_c,R_p) - 67 **(R_c,S_p) - 67**

Scheme 2.13

Attempts to isolate the diastereomers by means of fractional crystallization and column chromatography did not succeed. With a view to isolating them as neutral complexes, the naphthylamine auxiliary was chemoselectively removed by treatment with concentrated hydrochloric acid (Scheme 2.14). After work-up, the $^{31}P\{^{1}H\}$ NMR spectrum in $CDCl_3$ showed a singlet at δ 77.99. The enantiomers formed on removal of

the chiral auxiliary ie., (R_p)- **68** and (S_p)- **68** is expected to show similar chemical shifts in the absence of chiral shift reagents.



(R_c,R_p) - 67 **(R_c,S_p) - 67**

(R_p) - 68 **(S_p) - 68**

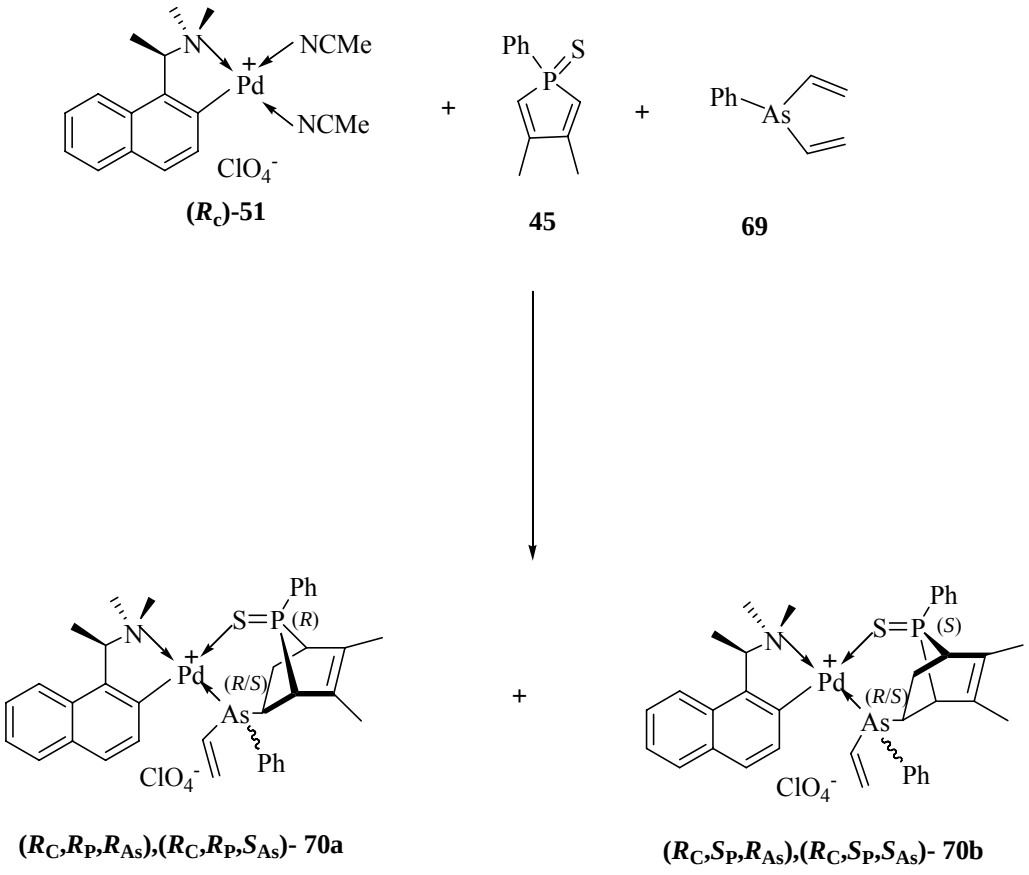
Scheme 2.14

The two enantiomers could not be separated by means of fractional crystallization or column chromatography. Suitable single crystals of the dichloro complex of the cycloadduct also could not be obtained for single crystal X-ray diffraction analysis. The structural integrity of the racemic cycloadduct was confirmed by cleaving of the ligand from the chiral metal template by treatment with aqueous KCN and subsequently re-coordinating it back to (R_c)-**51** whereby it regenerated the two diastereomers obtained in the original cycloaddition reaction.

2.8 Diels-Alder Reaction Involving the Metal Activated 3,4-Dimethyl-1-phenylphosphole 1-Sulfide and divinylphenylarsine

2.8.1 Preparation of *exo* products

The bis(acetonitrile)-complex (R_c)-**51** was allowed to react with 3,4-Dimethyl-1-phenylphosphole 1-Sulfide **45** and divinylphenylarsine **69** in dichloromethane at room temperature (Scheme 2.15).



(R_C,R_P,R_{As}),(R_C,R_P,S_{As})- 70a

(R_C,S_P,R_{As}),(R_C,S_P,S_{As})- 70b

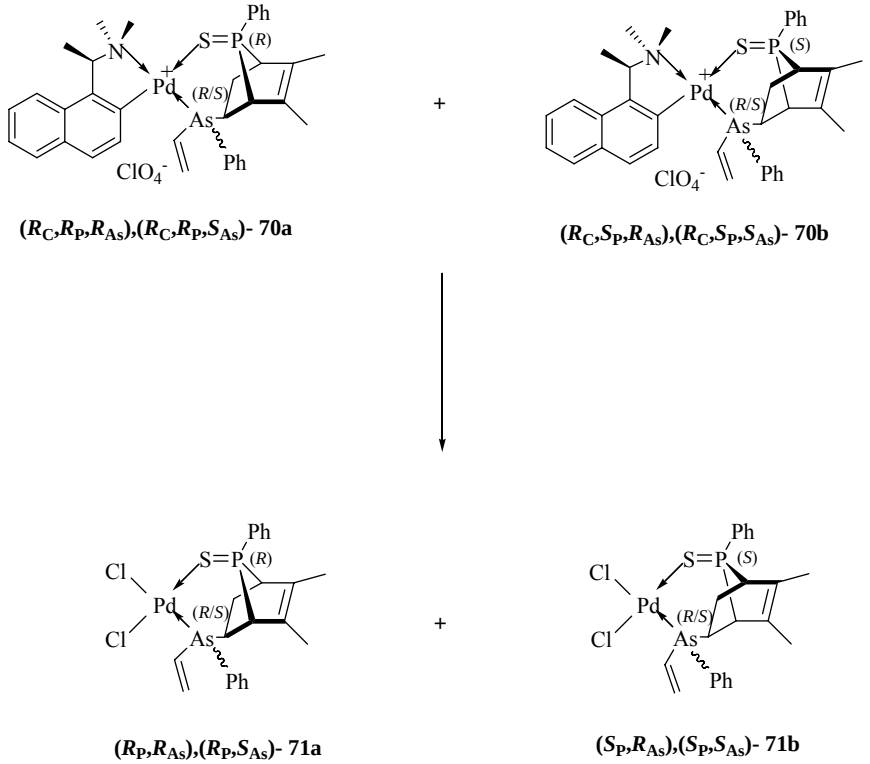
Scheme 2.15

The reaction was monitored by means of $^{31}P\{^1H\}$ spectroscopy and was found to be complete in 5 days. The 121 MHz $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture in $CDCl_3$ showed presence of 4 signals at δ 76.86, 77.27, 78.87 and

79.34. The signals were indicative of the bridgehead P in the formed cycloadduct and were in the same range as the DMPPS bridgehead P signal seen for the reactions involving diphenylvinylarsine discussed in Section 2.7.1. The NMR signals were indicative of the formation of four diastereomers in the ratio 4:1.7:1:1.3. Attempts at isolating the diastereomers by means of column chromatography and fractional crystallization techniques did not yield desirable results.

2.8.2 Preparation of chloro complexes for 70

The chiral naphthylamine auxiliary in the diastereomeric mixture was removed chemoselectively by stirring a solution of **70** in dichloromethane with concentrated hydrochloric acid at room temperature (Scheme 2.16).



(R_C,R_P,R_{As}),(R_C,R_P,S_{As})- 70a + **(R_C,S_P,R_{As}),(R_C,S_P,S_{As})- 70b**

(R_P,R_{As}),(R_P,S_{As})- 71a + **(S_P,R_{As}),(S_P,S_{As})- 71b**

Scheme 2.16

Attempted separation of the diastereomers using column chromatography and fractional crystallization did not succeed. Crystallization using dichloromethane- *n*-hexanes yielded pale yellow prisms suitable for single crystal X-ray diffraction analysis.

2.8.3 Single crystal X-ray diffraction analysis of 71

The molecular structure of the crystallized **71** was established by single crystal X-ray diffraction analysis. The analysis showed that both hand forms of the cycloadduct had co-crystallized out. The separation of the isomers by means of fractional crystallization was not successful. The X-ray crystallographic analysis confirmed the formation of the cycloadduct with coordination to metal centre via P=S sulfur and As donors. Selected bond lengths and angles for the representative isomer (S_p,R_{As})-**71b** are shown in Table 2.8.

The geometry at the palladium metal centre for (S_p,R_{As})-**71b** is distorted square planar with angles ranging from 84.3(4)-98.6(4) and 177.0(5)-173.5(4)°. The bond angle at the bridgehead phosphorous C(6)-P(1)-C(3) (83.3(2)Å) is larger than those observed for the analogous cycloadduct involving divinylphenylphosphine and DMPPS (79.9(6)Å) indicative of less strain at the bridgehead for the arsine analogue. The As→Pd bond in **(S_p,R_{As})- 71b**, (2.326(6)Å), is noticeably weaker than the P→Pd bond in the divinylphenylphosphine-DMPPS analogue (2.191(4)Å).

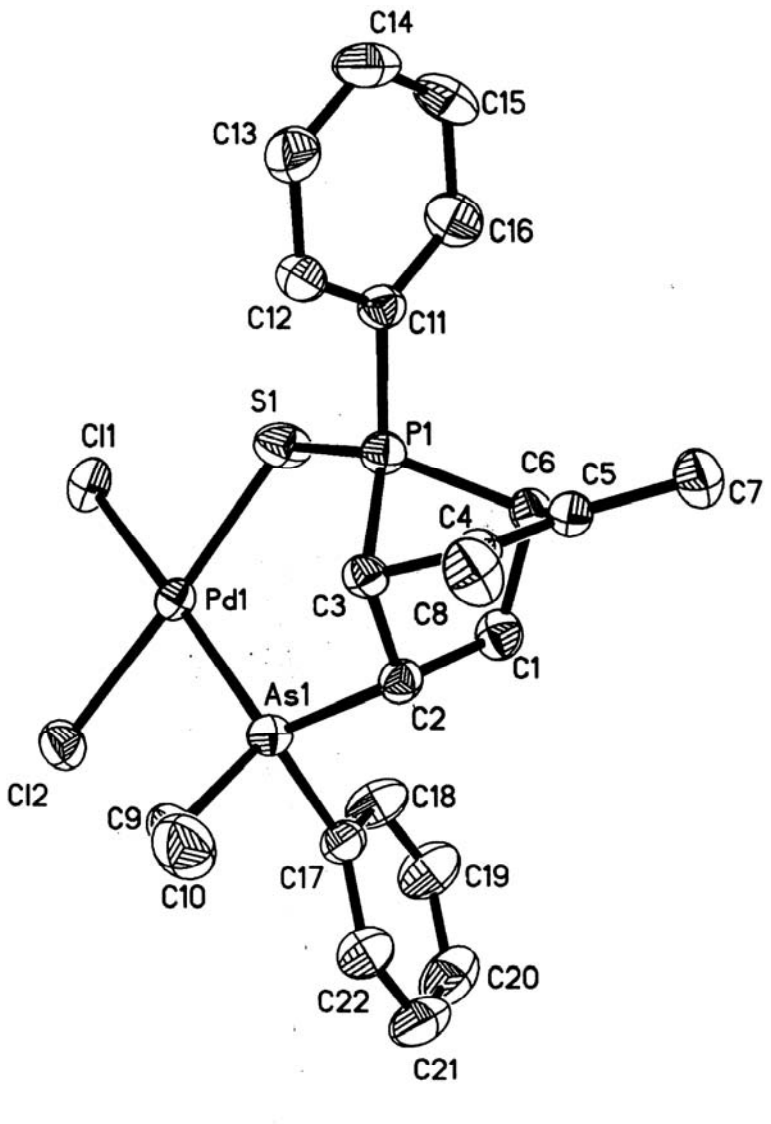


Figure 2.12 Molecular structure of 71

Table 2.8 Selected bond lengths (Å) and angles (°) for (S_p,R_{As})- 71b

Pd(1)-S(1)	2.301(1)	Pd(1)-Cl(2)	2.315(1)
Pd(1)-As(1)	2.326(6)	Pd(1)-Cl(1)	2.356(1)
As(1)-C(2)	1.957(5)	P(1)-C(6)	1.829(5)

P(1)-C(3)	1.831(5)	P(1)-S(1)	2.010(1)
C(1)-C(6)	1.548(7)	C(1)-C(2)	1.555(7)
C(2)-C(3)	1.546(6)		
S(1)-Pd(1)-Cl(2)	177.0(5)	S(1)-Pd(1)-As(1)	98.6(4)
Cl(2)-Pd(1)-As(1)	84.4(4)	S(1)-Pd(1)-Cl(1)	85.2(5)
Cl(2)-Pd(1)-Cl(1)	92.0(5)	As(1)-Pd(1)-Cl(1)	173.5(4)
C(6)-P(1)-C(3)	83.3(2)	P(1)-S(1)-Pd(1)	115.4(7)

2.9 Conclusions

The cycloaddition reaction involving DMPPS and divinylphenylphosphine showed appreciable selectivity (16.7:2.8:1:1). Furthermore the cycloaddition proceeded smoothly under mild conditions. In the documented cycloaddition reactions involving DMPPS, however, prolonged and strong heating conditions were generally required.[146d] In the case of the reactions involving DMPPS and the arsine functionalized dienophiles the selectivity was found to be poor with separation of isomers unsuccessful after repeated attempts using fractional crystallization and column chromatography. The rate of the reactions were similar to the one involving DMPP and diphenylvinylarsine[163] and much slower than the one involving DMPP **44** and diphenylvinylphosphine.[164] The most likely cause for the slower rate is the lower dienophilicity of diphenylvinylarsine. It is interesting to note that no Diels-Alder reaction is observed between free diphenylvinylarsine and DMPPS or involving divinylphenylarsine and DMPPS.

CHAPTER III

Platinum(II) complex promoted asymmetric Diels-Alder reaction in the synthesis of alcohol functionalized P-chiral diphosphines

3.1 Introduction

Enantiomerically pure diphosphines containing stereogenic phosphorous and carbon centers and selected functionalities have long been considered as powerful auxiliaries for metal based homogenous asymmetric catalysis.[165,166,167] These chiral ligands have also been extensively used in chemotherapy and asymmetric organic synthesis.[168,169] So far most of the reported *P*-stereogenic diphosphines have been synthesized utilizing their borane complexes or by optical resolution. To date complexes containing enantiomerically pure forms of orthometalated [1-(dimethylamino)ethyl]naphthalene are considered the most efficient resolving agents for certain types of chiral diphosphines with up to six stereogenic centers.[120b]

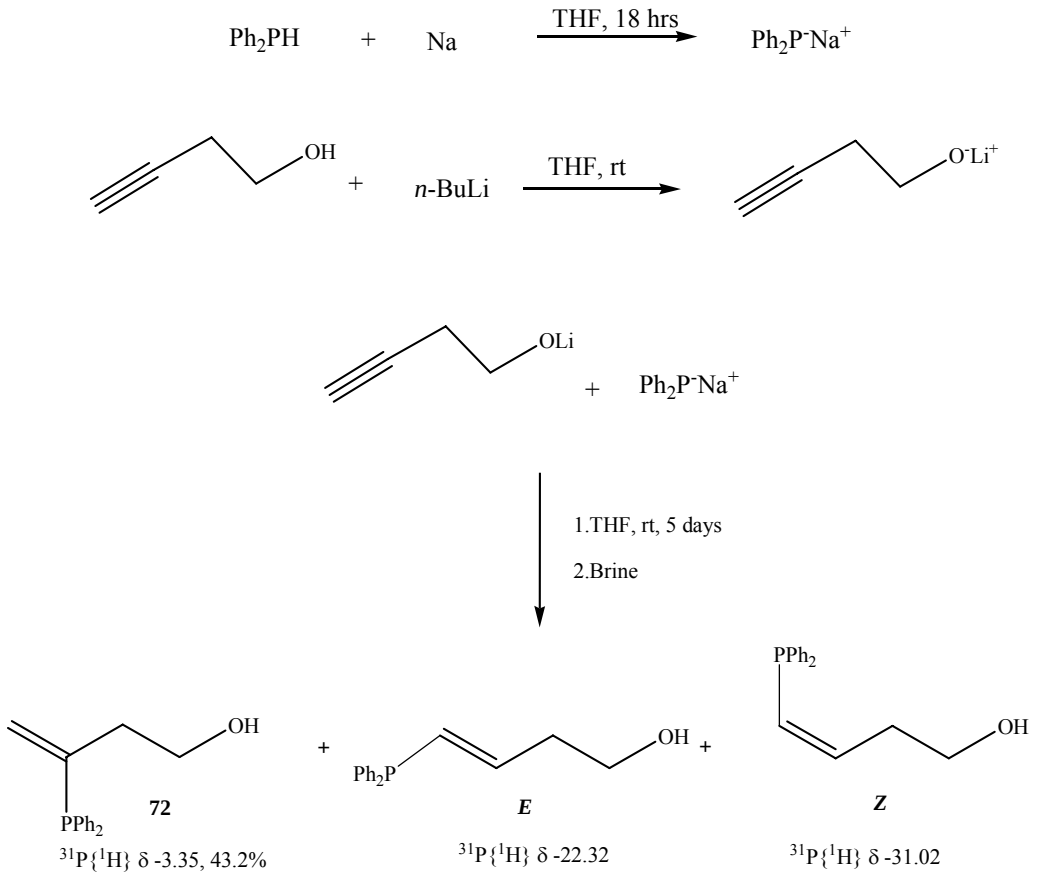
As an extension of the work discussed in chapter 2, wherein the palladium(II) complexes containing the enantiomerically pure forms of the orthometalated [1-(dimethylamino)ethyl]naphthalene **36** were employed to synthesize heterobidentate ligands of the type P^P(S) and As^P(S), we utilize the platinum analogue of the chiral auxiliary **43** to prepare enantiomerically pure alcohol functionalized 5-phosphino-7-phosphabicyclo[2.2.1]hept-2-ene ligands which contain one asymmetric phosphorous centre and three asymmetric carbon atoms in a highly stereoselective manner. It is of interest to note that the phosphine functionalized terminal alkynols employed in this cycloaddition reaction themselves will be synthesized in a highly regioselective manner *via* hydrophosphination of the respective terminal alkynol entity with diphenylphosphine. These ligands will subsequently be utilized as substrates for a second stage asymmetric

hydrophosphination employing the chiral auxiliary **36** (Chapter 4) to yield diphosphines with chirality residing in the C backbone.

3.2 Hydrophosphination of Terminal Alkynols with Dominant Markovnikov Regioselectivity

3.2.1 Synthesis of 3-Diphenylphosphanyl-but-3-en-1-ol, 72.

The synthetic protocol followed for the synthesis of 3-diphenylphosphanyl-but-3-en-1-ol is shown in Scheme 3.1.



Scheme 3.1

It is important to note that the hydroxyl group on the alkynol is susceptible to nucleophilic attack by the phosphide ion. Therefore it is necessary to protect the functional group which possesses an exchangeable proton that can quench the phosphide ion. Instead of using standard protecting groups such as silyl ether to mask the hydroxyl group, it was deprotonated so as to prevent it quenching the phosphide ion.

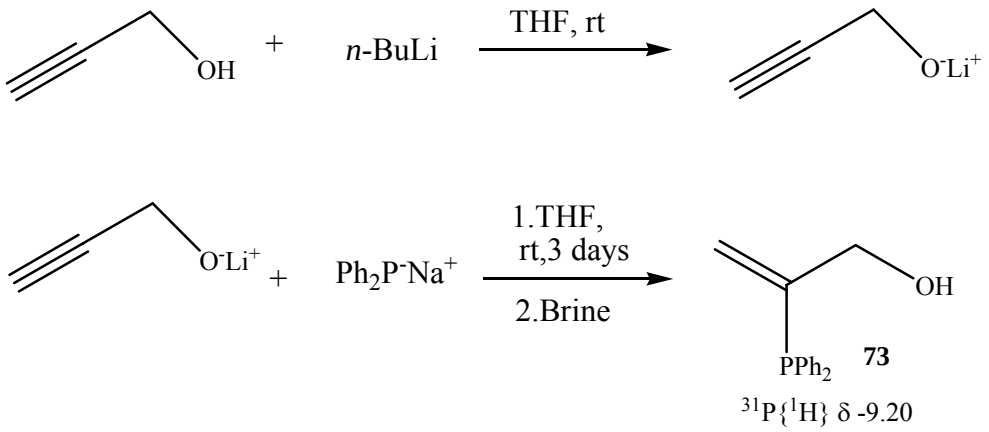
The $^{31}P\{^{1}H\}$ (121 MHz, $CDCl_3$) of the crude reaction product obtained after 'work-up' showed the presence of three products at δ -3.35, -22.32 and -31.02 in the ratio 5: 1: 1.2 . Isomer identification from $^{31}P\{^{1}H\}$ NMR spectroscopic data was carried out based on principles employed for similar reactions involving free radical addition of diphenylphosphine to alkynes.[170.171] Purification and separation of the isomers formed were achieved by means of silica gel chromatography which yielded the Markovnikov product as colorless oil in 43.2 % yield [$^{31}P\{^{1}H\}$ δ -3.35].

3.2.2 Synthesis of 2-Diphenylphosphanyl-prop-2-en-1-ol, 73.

The hydrophosphination of propargyl alcohol was carried out using the same method as that employed for 3-butyn-1-ol discussed in Section 3.2.1. The reaction was monitored by means of $^{31}P\{^{1}H\}$ NMR spectroscopy and was found to be complete in 3 days. Unlike in the case of 3-butyn-1-ol, only the Markovnikov product was selectively formed as a result of the hydrophosphination (Scheme 3.2).

The ^{31}P NMR (121 MHz, $CDCl_3$) spectrum of the crude reaction mixture after 'work-up' showed only one signal at δ -9.20 which was attributed to the Markovnikov

product. Purification of the product using silica gel column chromatography yielded pure **73** as colorless oil in 73.4% yield.



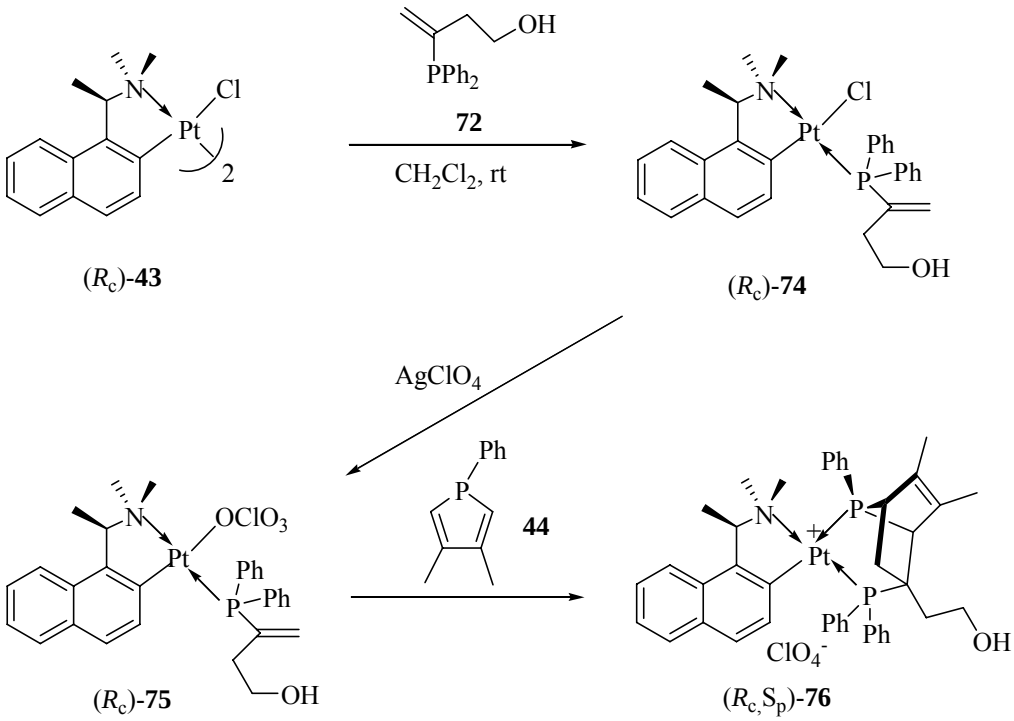
Scheme 3.2

3.3 Preparation and Isolation of butenol Substituted *exo*-cycloadduct: (R_c,S_p)-76

The 3-diphenylphosphanyl-but-3-en-1-ol ligand **72** was allowed to coordinate to the platinum complex (R_c)-**43** in dichloromethane yielding the complex (R_c)-**74** as dark yellow solid in 69.9 % yield (Scheme 3.3).

The $^{31}P\{^{1}H\}$ NMR spectrum of the complex ($CDCl_3$, 121 MHz) showed a signal at δ 22.14 (s, $^{1}J_{PtP}$ = 4182.8 Hz). The coordination shift and coupling constant is indicative of the formation of (R_c)-**74**. The Cl ligand of pure (R_c)-**74** was subsequently substituted by a ClO_4 ligand through treatment of the chloro complex with excess aqueous silver perchlorate in dichloromethane. The perchlorato complex (R_c)-**75** was obtained in 91.1% yield. When (R_c)-**75** was reacted with an equivalent of DMPP **44**, at room temperature in dichloromethane for 8 hrs. The cycloadduct (R_c,S_p)-**76** was obtained

as the sole product. The reaction was found to be highly selective with only one diastereomer formed exclusively as indicated by the $^{31}P\{^{1}H\}$ NMR spectrum.



Scheme 3.3

The $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 121 MHz) of the reaction product showed the following signals: δ 39.62 (d, 1P, $^{1}J_{Pt\text{-}P}$ = 3567.4 Hz, $^{3}J_{PP}$ = 22.8 Hz), 115.45 (d, 1P, $^{1}J_{Pt\text{-}P}$ = 1580.4 Hz, $^{3}J_{PP}$ = 22.8 Hz). The low field doublets are typical for bridgehead phosphorous adopting *exo-syn* stereochemistry.[155] It is noteworthy that the Pt-P (bridgehead) coupling in (R_c,S_p)-**76** is significantly smaller (1580.4 Hz) than that observed for the non-bridgehead P in the cycloadduct (3567.4 Hz). This is typical of P donor located *trans* to a strong π-accepting aromatic carbon atom.[172] The reaction

mixture was subsequently concentrated and layered with *n*-hexanes to yield yellow crystals of (R_c,S_p)-**76** in 79.7 % yield.

3.3.1 Single crystal X-ray diffraction analysis of (R_c,S_p)-76.

The molecular structure and absolute configurations of the recrystallised (R_c,S_p)-**76** were established by single crystal X-ray crystallographic analysis (Figure 3.1).

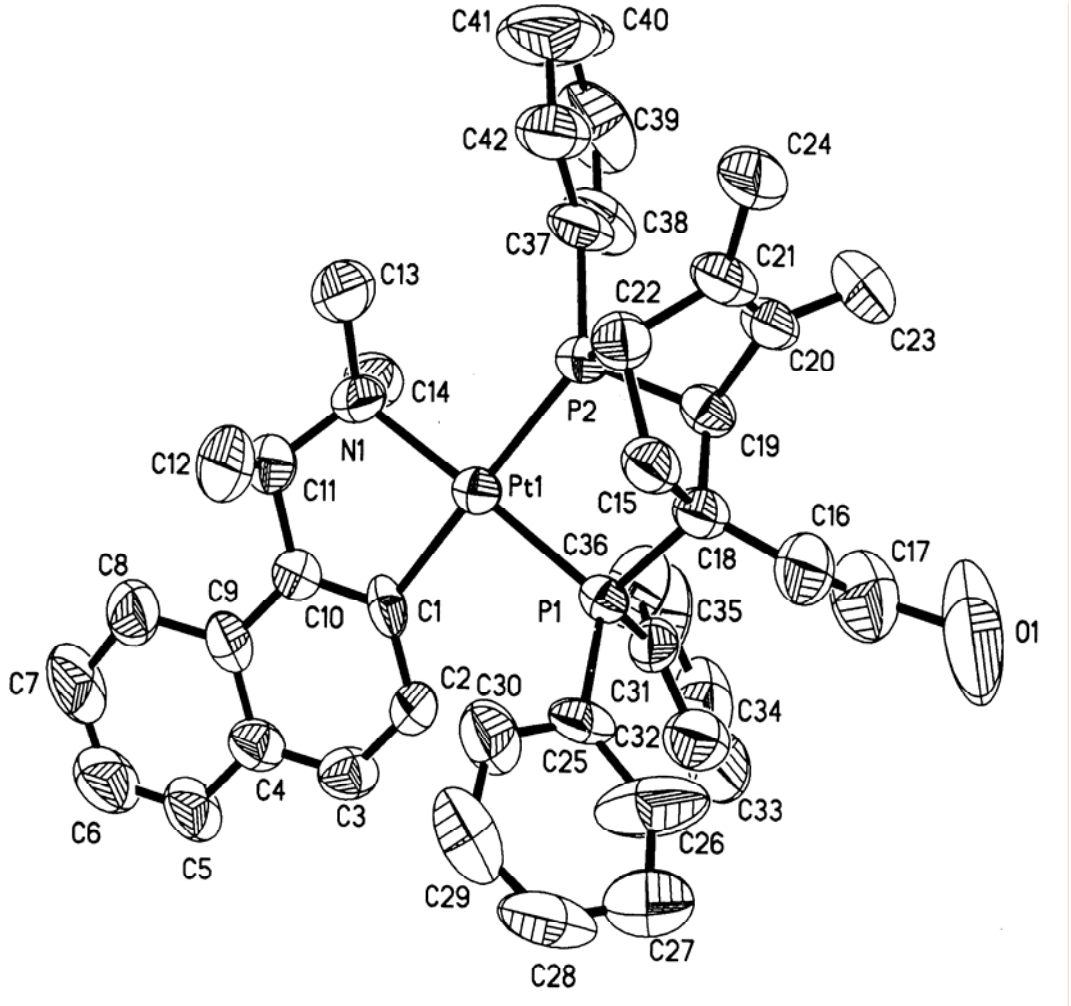


Figure 3.1 Molecular structure and absolute configuration of (R_c,S_p)-76.

The structural analysis revealed that the bridgehead P in the cycloadduct is substituted *trans* to the aromatic carbon of the naphthylamine chiral auxiliary. The cycloadduct is coordinated to the Platinum (II) centre as a bidentate chelate *via* its two P atoms.

Table 3.1 Selected bond lengths (Å) and angles (°) of (R_c,S_p)-76

Pt(1)-C(1)	2.069(9)	Pt(1)-N(1)	2.125(9)
Pt(1)-P(1)	2.252(3)	Pt(1)-P(2)	2.279(3)
O(1)-C(17)	1.54(2)	C(16)-C(17)	1.54(2)
C(16)-C(18)	1.54(2)	C(20)-C(21)	1.30(2)
C(1)-Pt(1)-N(1)	79.9(4)	C(1)-Pt(1)-P(1)	96.9(3)
N(1)-Pt(1)-P(1)	175.9(3)	C(1)-Pt(1)-P(2)	177.0(3)
N(1)-Pt(1)-P(2)	100.4(3)	P(1)-Pt(1)-P(2)	82.67(9)
C(18)-P(1)-Pt(1)	106.2(3)	C(19)-P(2)-C(22)	82.3(6)
C(19)-P(2)-Pt(1)	109.1(3)	C(22)-P(2)-Pt(1)	119.2(4)
C(22)-C(15)-C(18)	107.0(9)	C(19)-C(18)-C(15)	102.8(8)
C(19)-C(18)-P(1)	105.3(7)	C(15)-C(18)-P(1)	106.5(7)

The analysis confirms the absolute stereochemistry at the four newly generated chiral centers P(2), C(22), C(19) and C(18) to be *S*, *S*, *S* and *R* respectively. Selected bond lengths and bond angles for (R_c,S_p)-**76** are given in Table 3.1. The coordination geometry is distorted square planar with angles at platinum ranging between 79.9(4) –

100.4(3) and 175.9(3) to 177.0(3), with the bite angles of both the five membered chelate rings being acute. The angle around the bridgehead phosphorous is 82.3(6)Å, which is typical for this class of phosphanorbornene ligands.[121] The Pt(1)-P(1) and Pt(1)-P(2) distances are not significantly different [2.252(3)Å and 2.279(3)Å respectively].

3.3.2 Solution 2-D ^{1}H-^{1}H-ROESY NMR Spectroscopic Assignment of (R_c,S_p)-76

In order to confirm the structure of the cycloadduct formed in solution state, a 500 MHz solution 2-D ^{1}H-^{1}H ROESY NMR study of (R_c,S_p)-**76** was carried out in CD_2Cl_2. The 2-D ROESY NMR spectrum of (R_c,S_p)-**76** is shown in Figure 3.2. Figure 3.3 shows the numbering scheme adopted for the assignment. Strong NOE signals are observed for the interaction between H11 and all the three methyl groups *viz*. Me8, Me9 and Me10 (Signals F-H).

These NOE interactions are consistent with the staggered orientation of these substituents when the (*R*)-naphthylamine ring adopts the δ conformation.[121] Accordingly, Me10 shows interaction only with NMe(eq) (Signal C). The absence of a Me10-NMe(ax) NOE signal therefore indicates a δ conformation for the 5-membered (*R*)-metallated napthylamine ring. The interactions that provide the driving forces for Me10 to assume the axial position are also observed in the spectrum *viz*. H11-H19 (Signal I) and Me10-H19 (Signal N). The ROESY signals clearly reveal that as evidenced in the solid state, the (*R*)-naphthylamine organometallic ring adopts the δ conformation in solution. It was also observed that due to the rigid skew ring conformation and the strict planarity of the naphthylamine ring, the H13 aromatic proton projects towards the space below the PPh_2

group of the cycloadduct and exhibits NOE signals at characteristically low chemical shifts which are readily identified (Signals R and S). These signals also establish the regio-stereochemistry of the cycloadduct. The absence of any NOE signal between H4 and PPh indicates that the P-Phenyl group at the bridgehead adopts the *anti* position to the H4 group which is consistent with the *S* absolute configuration at the bridgehead phosphorous centre.

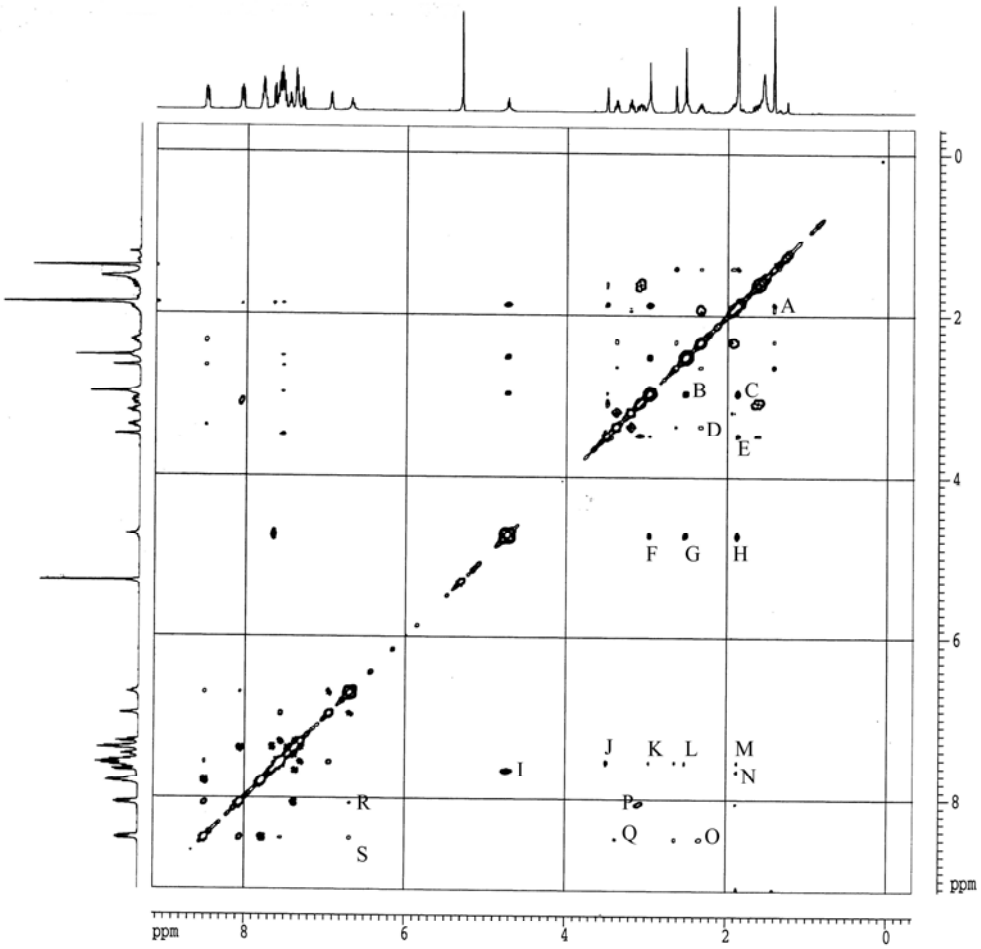


Figure 3.2 500MHz 2-D ROESY spectrum of (R_c,S_p)-76 in CD_2Cl_2. Selected NOE interactions: A: Me5-Me6; B: NMe(eq)-NMe(ax); C: Me10-NMe(eq); D: H3-H4; E: Me6-H7; F: NMe(ax)-H11; G: NMe(eq)-H11; H: Me10-H11; I: H11-H19; J: H7-PPh; K: NMe(ax)-PPh; L:

NMe(eq)-PPh; M: Me10-PPh; N: Me10-H19; O: H3-*o*-Ph; P: H7-*o*-Ph; Q: H7-o-Ph'; R: H13-*o*-Ph; S: H13-o-Ph'.

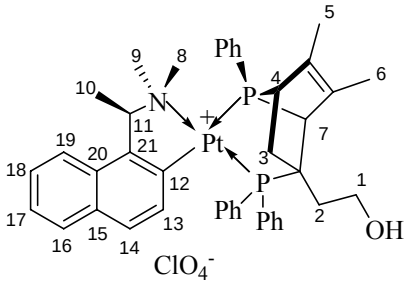
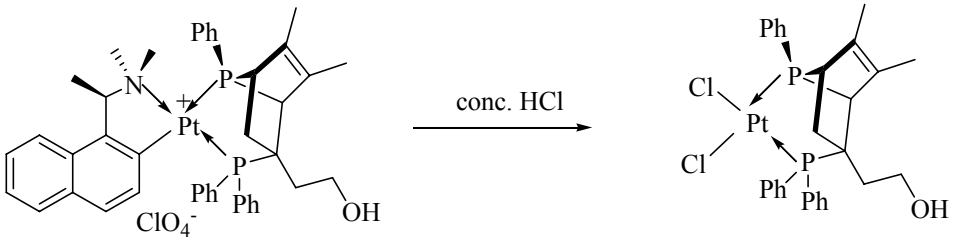


Figure 3.3 Numbering scheme used for (R_c,S_p)-76 in the 2-D ^{1}H-^{1}H-ROESY NMR studies.

3.3.3 Preparation and X-ray Structural Analysis of (S_p)-77

The chiral naphthylamine auxiliary in (R_c,S_p)-**76** was chemoselectively removed by stirring and dichloromethane solution of the complex with concentrated hydrochloric acid at room temperature (Scheme 3.4).



(R_c,S_p)-**76** (S_p)-**77**

Scheme 3.4

The dichloro complex (S_p)-**77** precipitated out as pale yellow microcrystals from dichloromethane-n-hexanes in 89.5 % yield. The ^{31}P{^{1}H} NMR spectrum of the complex in $CDCl_3$ showed the following signals : δ 35.59 (d, 1P, $^1J_{PtP}$ = 3435.2 Hz,

J_{PP} = 19.0 Hz), 94.96 (d, 1P, $^{1}J_{PtP}$ = 3191.9 Hz, J_{PP} = 19.0 Hz). In contrast to (R_c,S_p)-**76** , in (S_p)-**77** both non-equivalent phosphorous donor atoms are coordinated *trans* to Cl ligands and therefore the two P-Pt couplings are similar in magnitude. The molecular structure and absolute configuration of the complex (S_p)-**77** were established by single crystal X-ray crystallographic analysis (Figure 3.4).

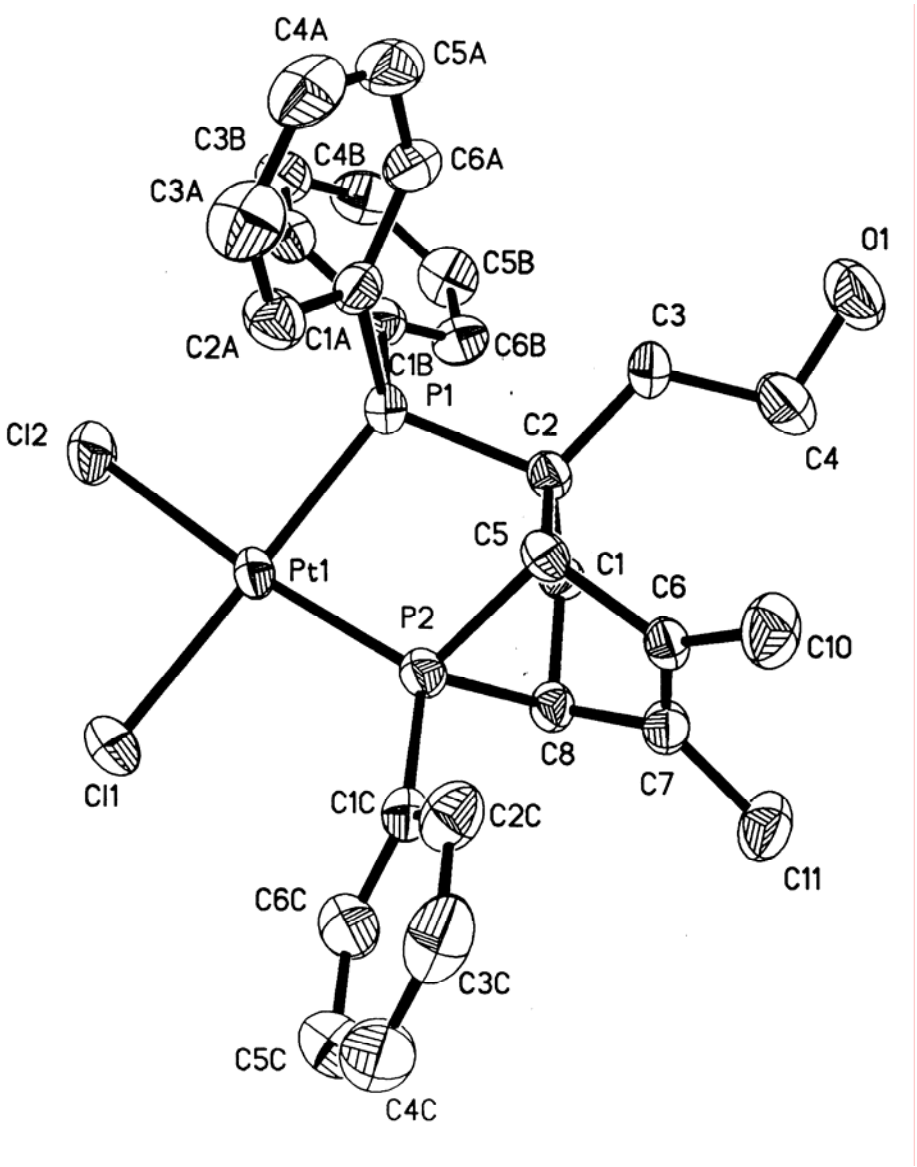


Figure 3.4 Molecular structure of (S_p)-77

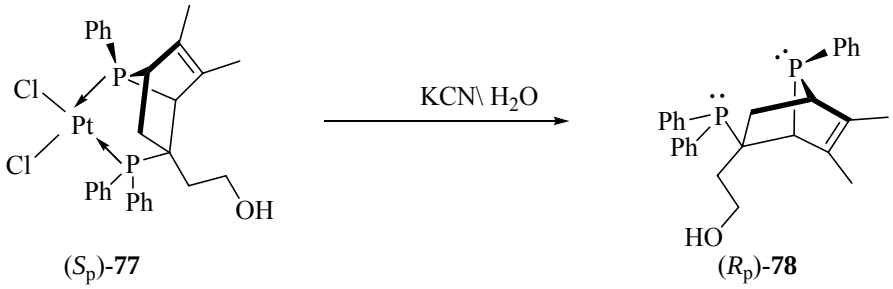
The structural analysis revealed that the phosphanorbornene skeleton has not undergone any change during the removal of the chiral naphthylamine auxiliary. The geometry at the platinum metal centre is distorted square planar with angles at platinum in the range of 83.11(5)- 97.04(6) and 174.48(6)- 179.17(6)°. The absolute configurations of the four stereogenic centers at P(2),C(1),C(8) and C(2) is *S*,*S*,*S* and *R*, respectively. Selected bond lengths and angles are given in Table 3.2.

Table 3.2 Selected bond lengths (Å) and angles (°) of (S_p)-77

Pt(1)-P(2)	2.213(1)	Pt(1)-P(1)	2.231(1)
Pt(1)-Cl(2)	2.350(1)	Pt(1)-Cl(1)	2.359(1)
P(1)-C(2)	1.876(5)	P(2)-C(8)	1.859(5)
P(2)-C(5)	1.847(5)		
P(2)-Pt(1)-P(1)	83.1(5)	P(2)-Pt(1)-Cl(2)	174.5(6)
P(1)-Pt(1)-Cl(2)	91.7(6)	P(2)-Pt(1)-Cl(1)	97.0(6)
P(1)-Pt(1)-Cl(1)	179.2(6)	Cl(2)-Pt(1)-Cl(1)	88.2(6)
C(5)-P(2)-C(8)	81.3(2)		

3.3.4 Decomplexation and Optical Purity of (S_p)-77

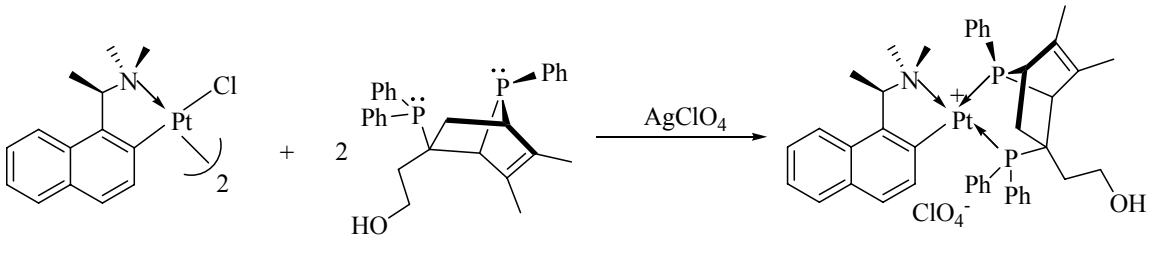
The optically active diphosphine ligand (R_p)-**78** can be chemoselectively liberated from the complex (S_p)-**77** by treatment of the dichloro complex with aqueous potassium cyanide at room temperature (Scheme 3.5).



(S_p)-**77** (R_p)-**78**

Scheme 3.5

The $^{31}P\{^{1}H\}$ NMR spectrum of the free ligand in $CDCl_3$ exhibited two doublets at δ 35.34 ($^{3}J_{PP}$ = 26.5 Hz) and 98.46 ($^{3}J_{PP}$ = 26.5 Hz). The low field resonance confirms that the *exo-syn* stereochemistry is retained.[155] Owing to the extreme air sensitivity of the released ligand attributed to the non-coordinated phosphorous atom, the liberated (R_p)-**78** cannot be stored in its pure form. Hence the liberated ligand was re-coordinated to the complex (R_p)-**43** (Scheme 3.6).



(R_c)-**43** (R_p)-**78** (R_c,S_p)-**76**

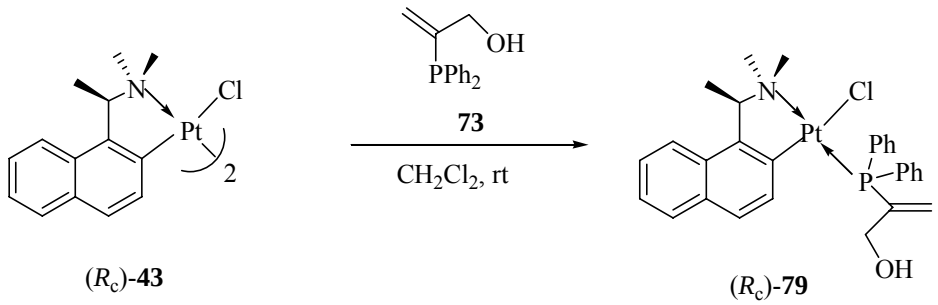
Scheme 3.6

This procedure also provides a means to confirm the optical purity of the released ligand. The recoordination procedure was monitored by $^{31}P\{^{1}H\}$ NMR spectroscopy. In $CDCl_3$, the $^{31}P\{^{1}H\}$ NMR spectrum of the crude reaction product showed only the signals originally observed for the sole diastereomer generated from the original cycloaddition reaction. The absence of any other signals indicated that (R_p)-**78** is enantiomerically pure.

3.4 Preparation and Isolation of the propenol substituted *exo*-cycloadduct: (R_c,S_p)-81

3.4.1 Preparation of chloro complex (R_c)-79.

The ligand 2-diphenylphosphanyl-prop-2-en-1-ol **73** in dichloromethane was added to a solution containing the dimeric complex (R_c)-**43** to yield the chloro complex (R_c)-**79** in 73.9% yield (Scheme 3.7).



(R_c)-**43** (R_c)-**79**

Scheme 3.7

The $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) spectrum of the complex (R_c)-**79** showed a singlet at δ 19.81 ($^{1}J_{Pt\text{-}P}$ = 4243.6 Hz). The reaction mixture was concentrated and layered with *n*-hexanes to yield pale yellow prisms of (R_c)-**79**.

3.4.2 Single crystal X-ray diffraction studies on (R_c)-79.

The single crystal X-ray diffraction analysis data showed that the ligand 2-diphenylphosphanyl-prop-2-en-1-ol **73** has coordinated *trans* to the NMe_2 group of the metal template (Figure 3.5). Selected bond lengths and bond angles are given in Table 3.3.

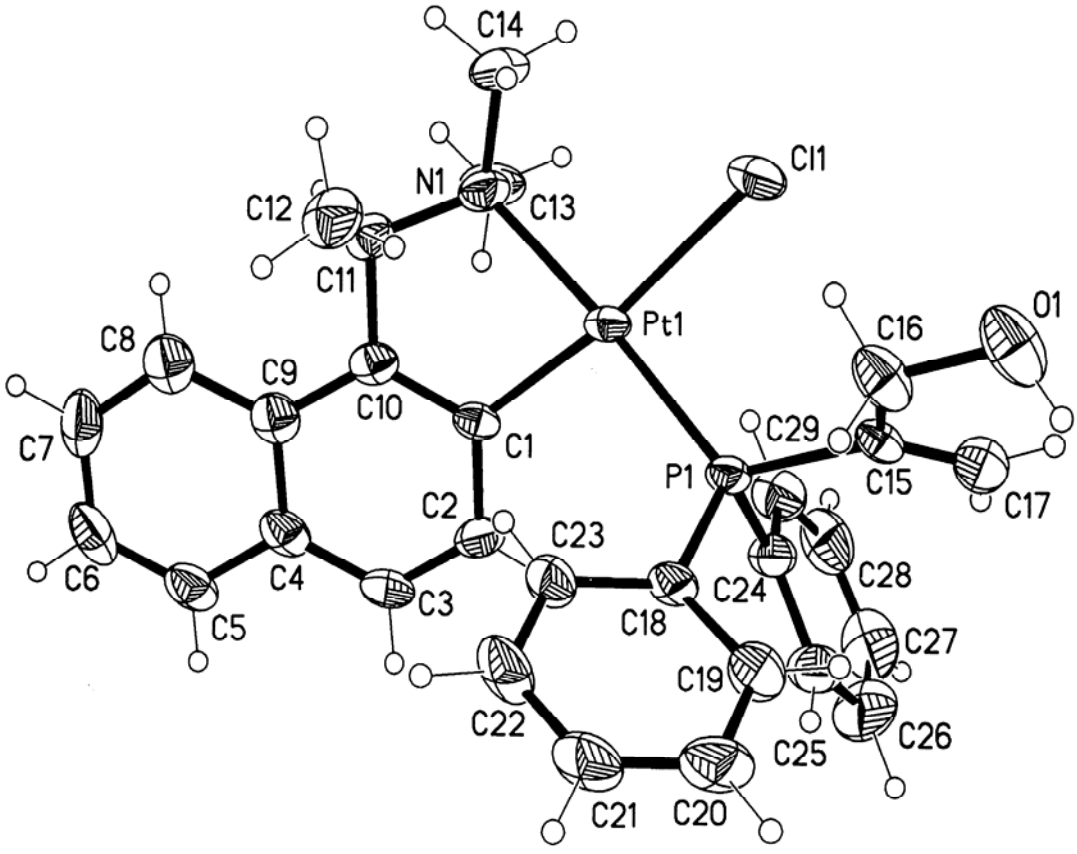


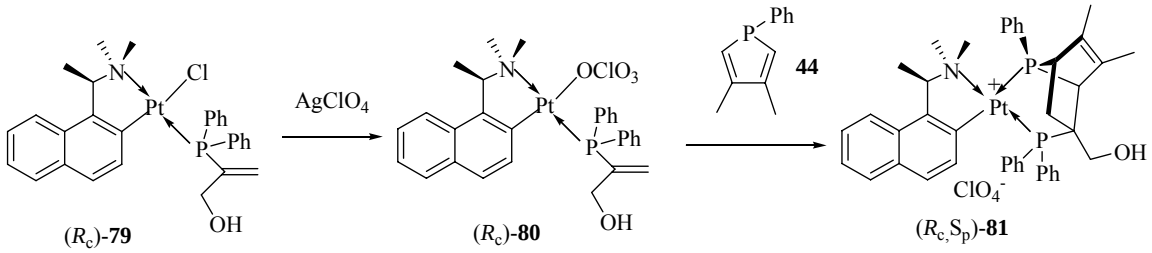
Figure 3.5 Molecular structure and absolute configuration of (R_c)-79

Table 3.3 Selected bond lengths (Å) and angles (°) for complex (R_c)-79

Pt(1)-C(1)	2.078(6)	Pt(1)-N(1)	2.181(5)
Pt(1)-P(1)	2.244(1)	Pt(1)-Cl(1)	2.423(1)
O(1)-C(16)	1.504(8)	C(15)-C(17)	1.311(8)
C(15)-C(16)	1.540(8)		
C(1)-Pt(1)-N(1)	74.00(1)	C(1)-Pt(1)-P(1)	102.1(2)
N(1)-Pt(1)-P(1)	175.6(1)	C(1)-Pt(1)-Cl(1)	171.2(1)
N(1)-Pt(1)-Cl(1)	98.0(1)	P(1)-Pt(1)-Cl(1)	86.1(5)

3.4.3 Asymmetric Diels-Alder reaction involving (R_c)-79 and DMPP 44

The complex (R_c)-**79** was treated with aqueous silver perchlorate to convert the Cl group to the more labile ClO_4 entity thus yielding complex (R_c)-**80** (Scheme 3.8).



Scheme 3.8

A solution of the perchlorato complex obtained (R_c)-**80** was then allowed to react with DMPP **44**. The mixture was allowed to stir at room temperature for 8 hrs to yield a

yellow solution of complex (R_c,S_p)-**81**. The $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture in $CDCl_3$ showed only two doublets at δ 42.04 (d, 1P, $^1J_{Pt\text{-}P}$ = 3591.9 Hz, J_{PP} = 22.8 Hz) and 117.82 (d, 1P, $^1J_{Pt\text{-}P}$ = 1586.1 Hz, J_{PP} = 19.0 Hz) . As in the case of the cycloaddition reaction involving 3-diphenylphosphanyl-but-3-en-1-ol and DMPP the $^{31}P\{^1H\}$ NMR spectrum was indicative of the formation of only one diastereomer. The low field doublets are typical of the bridgehead phosphorous of the formed cycloadduct adopting *exo-syn* stereochemistry.[155] The Pt-P coupling constants are also indicative of the regiochemistry of the cycloadduct. The lower value for the bridgehead P ($^1J_{Pt\text{-}P}$ = 1586.1 Hz) compared to the other P signal ($^1J_{Pt\text{-}P}$ = 1586.1 Hz) is typical of P positioned *trans* to strong π-accepting aromatic carbon atom.[172] Upon crystallization pale yellow needle like crystals were obtained using a crystallizing solvent system consisting of acetonitrile- diethyl ether in 81.2 % yield.

3.4.4 Single crystal X-ray Structural Analysis of (R_c,S_p)-81

The X-ray analysis of (R_c,S_p)-**81** reaffirms that, as desired, an enantiomerically pure complex has been formed (Figure 3.6). The analysis shows that the template directed synthesis of the platinum diphosphine adduct has proceeded with the desired regio- and stereoselectivity.

The structural analysis confirms the absolute stereochemistry at the newly generated four chiral centers P(2), C(21), C(18) and C(15) to be *S*, *S*, *S* and *S* respectively. The geometry at the platinum centre is distorted square planar with angles at platinum in the ranges of 80.9(3)- 100.5(2) and 174.9(2) – 175.1(2)°. The C-P-C angle within the

phosphorous-norbornene skeleton is acute (81.1(4) Å), the two associated P-C bonds being almost the same [1.851(8) and 1.852(8) Å for C(18) and C(21) respectively].

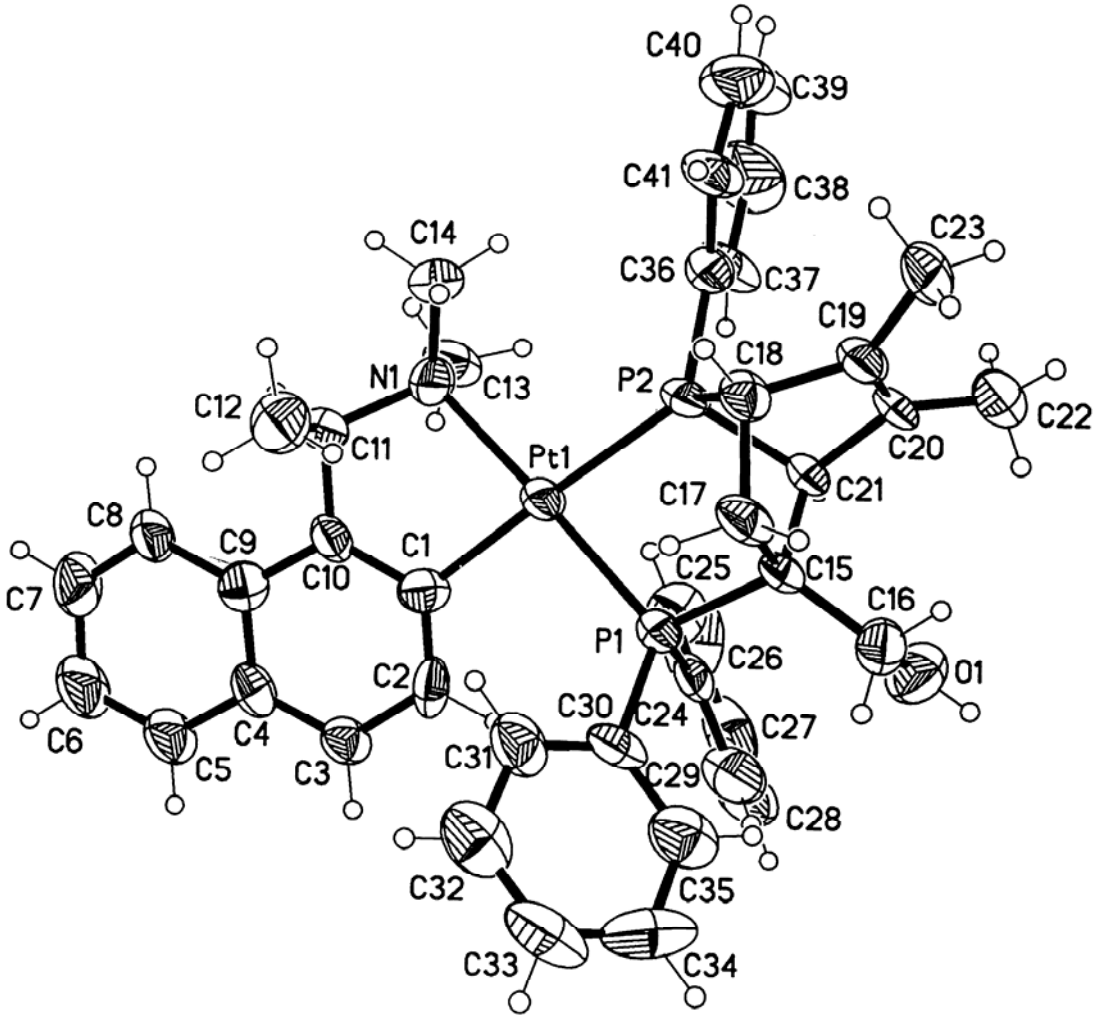


Figure 3.6 Molecular structure and absolute configuration of (R_c,S_p)-81

The two Pt-P bond distances are dissimilar, with the bond *trans* to the carbon of the naphthylamine auxiliary being longer by 0.027 Å. This indicates that the

phosphorous atoms have quite different donor abilities.[173] Selected bond lengths and bond angles are given in Table 3.4.

Table 3.4 Selected bond lengths (Å) and angles (°) of (R_c,S_p)-81

Pt(1)-C(1)	2.078(8)	Pt(1)-N(1)	2.157(6)
Pt(1)-P(1)	2.258(2)	Pt(1)-P(2)	2.285(2)
C(15)-C(16)	1.529(12)		
C(1)-Pt(1)-N(1)	80.9(3)	C(1)-Pt(1)-P(1)	95.8(2)
N(1)-Pt(1)-P(1)	175.1(2)	C(1)-Pt(1)-P(2)	174.9(2)
N(1)-Pt(1)-P(2)	100.5(2)	P(1)-Pt(1)-P(2)	82.5(7)
C(21)-P(2)-Pt(1)	109.1(2)	C(18)-P(2)-Pt(1)	119.8(3)
C(17)-C(18)-P(2)	99.7(5)	C(15)-C(21)-P(2)	96.0(5)
C(17)-C(15)-P(1)	106.4(5)	C(16)-C(15)-C(17)	112.0(7)
C(15)-P(1)-Pt(1)	106.4(3)		

3.4.5 Solution 2-D ^{1}H-^{1}H-ROESY NMR spectroscopic assignment of (R_c,S_p)-81

A 500MHz solution 2-D ^{1}H-^{1}H ROESY NMR study of (R_c,S_p)-**81** was carried out in CD_2Cl_2 in order to confirm the structure of the cycloadduct formed in solution state. The 2-D 1H ROESY NMR spectrum of (R_c,S_p)-**81** is shown in Figure 3.7**.** The numbering scheme adopted is shown in Figure 3.8. Strong NOE signals consistent with the staggered orientation of substituents when the (*R*)-naphthylamine ring adopts the δ

conformation are observed for the interaction between H10 and all the three methyl groups *viz*. Me7, Me8 and Me9 (Signals H-J).

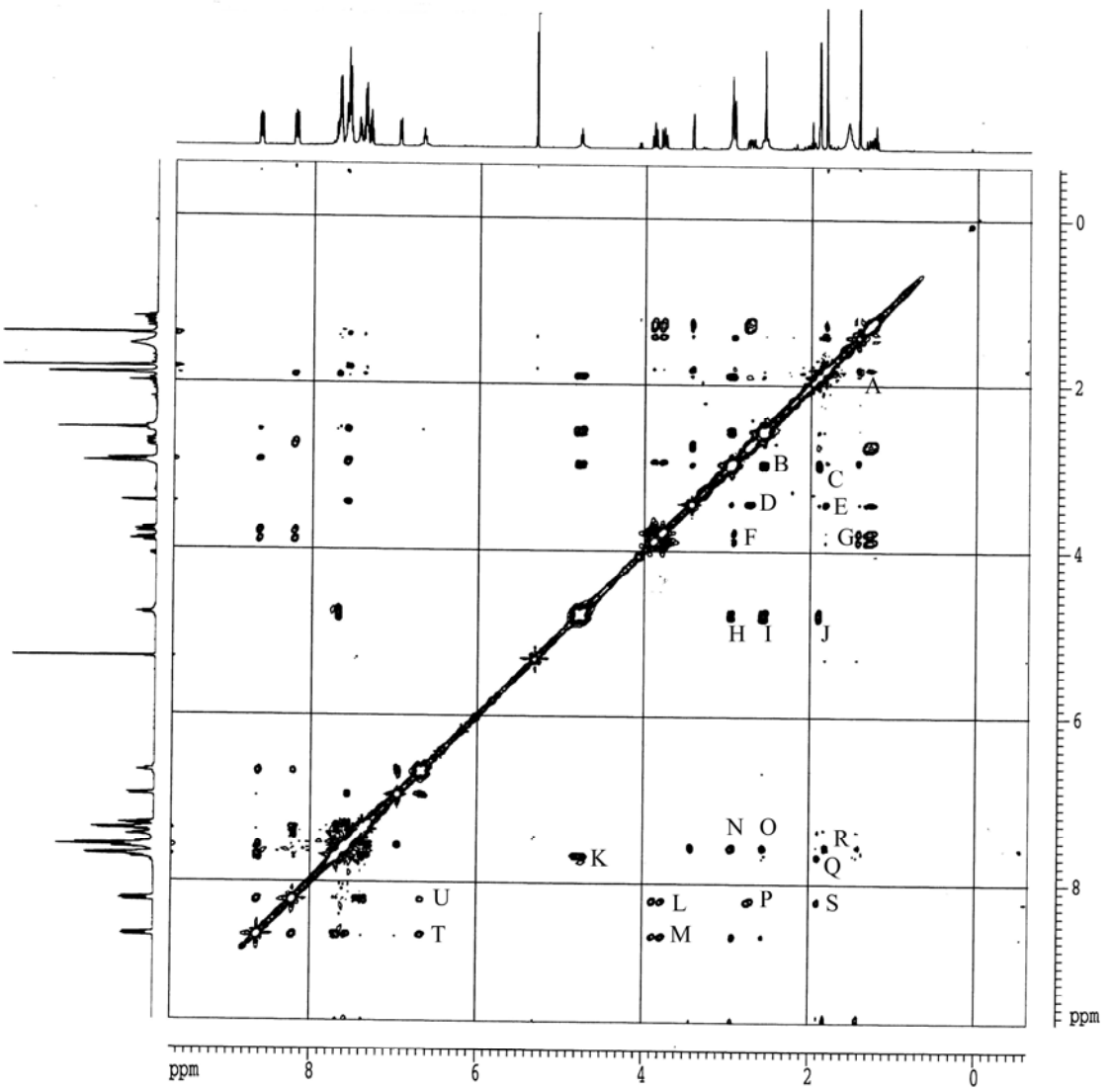


Figure 3.7 500MHz 2-D ROESY spectrum of (R_c,S_p)-81 in CD_2Cl_2. Selected NOE interactions: A: Me4-Me5; B: NMe(eq)-NMe(ax); C: Me9-NMe(eq); D: H2-H1; E: Me5-H1; F: Me(ax)-H3; G: Me4-H3; H: Me(ax)-H10; I: Me(eq)-H10; J: Me9-H10; K: H10-H18; L: H6-*o*-Ph; M: H6-*o*-Ph'; N: NMe(ax)-PPh; O: NMe(eq)-PPh; P: H2-*o*-Ph'; Q: Me9-PPh; R: Me5-PPh; S: Me9-*o*-Ph'; T: H12-*o*-Ph'; U: H12-*o*-Ph.

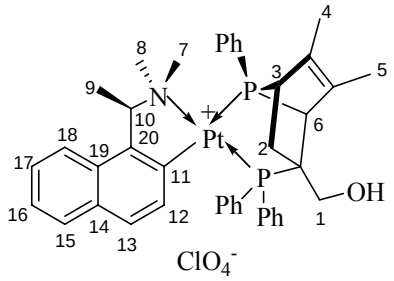
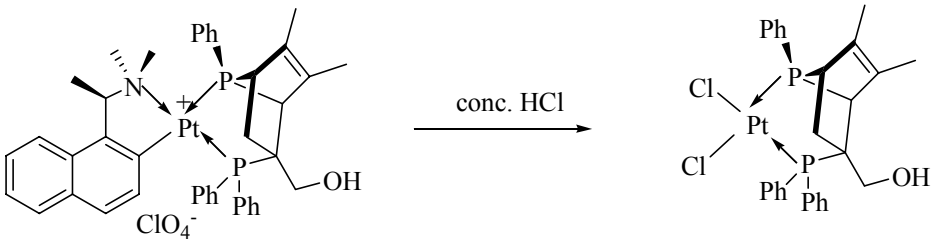


Figure 3.8 Numbering scheme used for (R_c,S_p)-81 in the 2-D ^{1}H-ROESY NMR studies.

As in the case of (R_c,S_p)-**76** discussed in Section 3.3.2, these NOE signals are consistent with the δ conformation of the (*R*)-naphthylamine ring.[121] As seen in the case of (R_c,S_p)-**76** , Me9 shows interaction only with NMe(eq) (Signal C) indicative of a δ conformation for the 5-membered (*R*)-metallated naphthylamine ring. It was also observed that the H13 aromatic proton projects towards the space below the PPh_2 group of the cycloadduct and exhibits NOE signals at characteristically low chemical shifts (Signals T and U). These signals also establish the regio-stereochemistry of the cycloadduct in solution.

3.4.6 Preparation and X-ray Structural Analysis of (S_p)-82

The chiral naphthylamine auxiliary in (R_c,S_p)-**81** was chemoselectively removed by stirring a dichloromethane solution of the complex with concentrated hydrochloric acid at room temperature (Scheme 3.9). Crystallization using dichloromethane *n*-hexanes yielded pale yellow prisms in 91.5 % yield.



(R_c,S_p)-**81** (S_p)-**82**

Scheme 3.9

The $^{31}P\{^1H\}$ NMR in $CDCl_3$ showed two doublets at δ 32.67 ($^1J_{PtP}$ = 3447.6, J_{PP} = 19.0 Hz) and 94.52 ($^1J_{PtP}$ = 3225.9, J_{PP} = 19.0 Hz). Since the two non-equivalent phosphorous donor atoms are coordinated *trans* to a chloro ligand, the two P-Pt couplings are of equal magnitude.

The molecular structure and the absolute stereochemistry of the dichloro complex were determined by single crystal X-ray structure analysis (Figure 3.9). Selected bond distances and angles are listed in Table 3.5. The study revealed that the absolute configurations have been retained from (R_c,S_p)-**81**. The absolute configurations at P(2), C(4), C(7) and C(1) are *S*, *S*, *S* and *S* respectively. The geometry at the Pt is distorted square planar with the angles of 84.0(4) – 93.2(4)° and 173.9(4)-176.7(4)°. The bond lengths of the two Pt-P bonds are 2.197(1) and 2.248(1)Å respectively. The diphosphine coordinates on the platinum as a bidentate ligand *via* the two phosphorous atoms. The angle formed around the bridgehead phosphorous is 81.9(2)°, which is typical for this class of phosphanorbornene ligands.

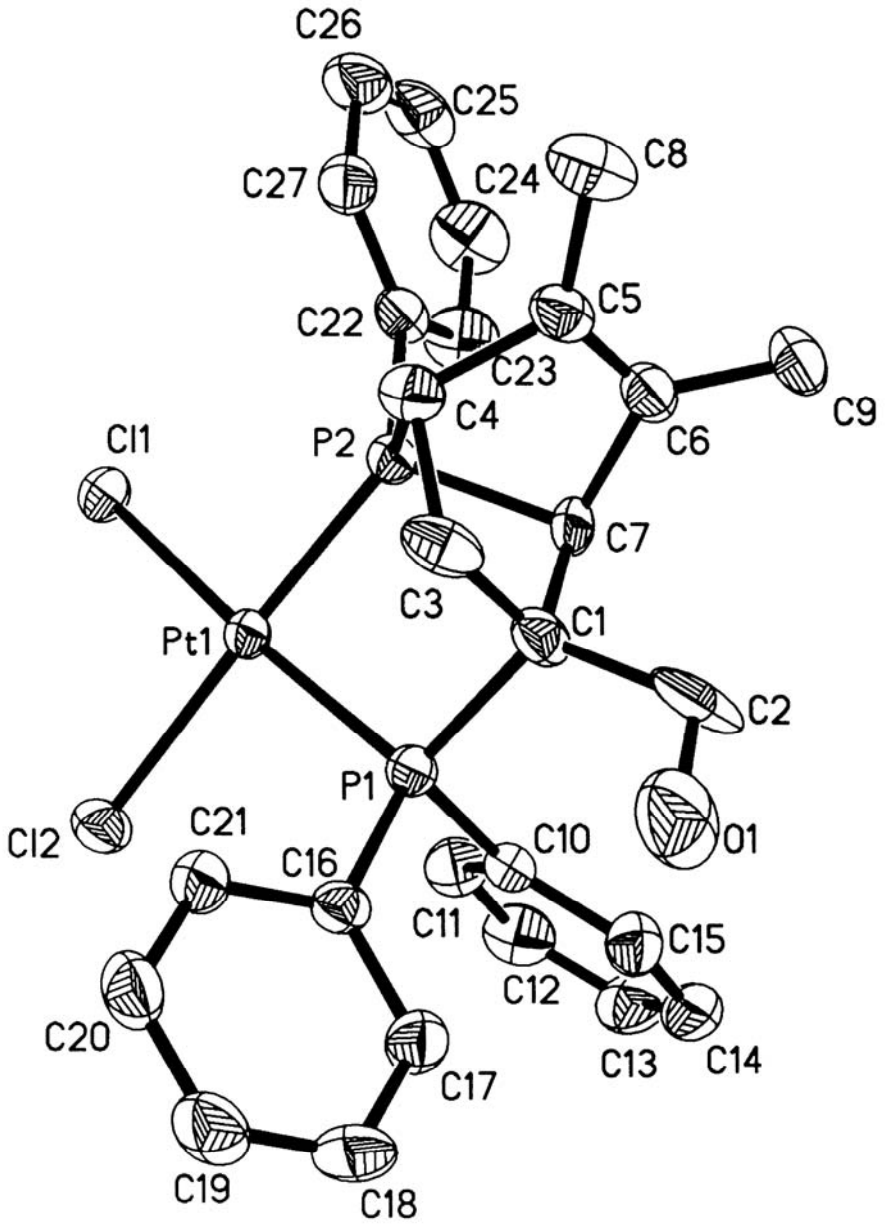


Figure 3.9 Molecular structure and absolute configuration of (S_p)-82

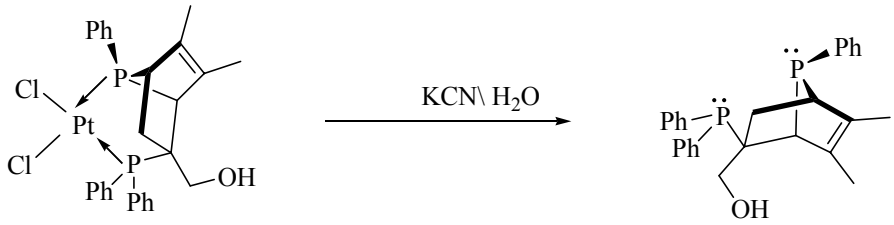
Table 3.5 Selected bond lengths (Å) and angles (°) for (S_p)-82

Pt(1)-P(2)	2.197(1)	Pt(1)-P(1)	2.248(1)
Pt(1)-Cl(2)	2.354(1)	Pt(1)-Cl(1)	2.367(1)

C(1)-C(2)	1.580(6)	O(1)-C(2)	1.378(6)
P(2)-Pt(1)-P(1)	84.0(4)	P(2)-Pt(1)-Cl(2)	176.7(4)
P(1)-Pt(1)-Cl(2)	93.0(4)	P(2)-Pt(1)-Cl(1)	93.2(4)
P(1)-Pt(1)-Cl(1)	173.9(4)	Cl(2)-Pt(1)-Cl(1)	89.9(4)
C(1)-P(1)-Pt(1)	104.9(1)	C(7)-P(2)-C(4)	81.9(2)
C(7)-C(1)-C(3)	104.6(3)	C(3)-C(1)-P(1)	104.9(3)
C(4)-C(3)-C(1)	106.2(3)	C(5)-C(4)-C(3)	107.2(4)
C(5)-C(6)-C(7)	111.2(4)	C(6)-C(7)-C(1)	109.7(3)

3.4.7 Decomplexation and Optical Purity of (S_p)-82.

Treatment of a dichloromethane solution of (S_p)-**82** with saturated aqueous potassium cyanide liberated the optically pure diphosphine (R_p)-**83** quantitatively as air sensitive oil (Scheme 3.10).



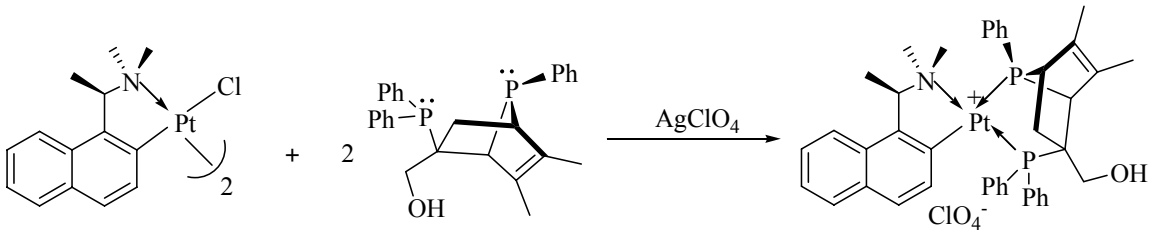
(S_p)-**82** (R_p)-**83**

Scheme 3.10

The $^{31}P\{^{1}H\}$ NMR spectrum of the free diphosphine in $CDCl_3$ exhibited a pair of doublets at δ 19.21 and 108.89. The low field ^{31}P resonance indicated that the *exo*-*syn*

stereochemistry remains. It is to be noted that the apparent inversion of configuration that takes place at the phosphorous stereogenic centre during the liberation process is merely a consequence of the Cahn-Ingold-Prelog (CIP) rules.[160]

The optical purity of (R_p)-**83** was confirmed by the re-preparation of (R_c,S_p)-**81** from the liberated ligand (R_p)-**83** and the dimeric complex (R_c)-**43** (Figure 3.11).



(R_c)-**43** (R_p)-**83** (R_c,S_p)-**81**

Scheme 3.11

The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed the same resonance signals that were obtained for the original cycloadduct (R_c,S_p)-**81** thus reaffirming that the liberated (R_p)-**83** is enantiomerically pure .

3.5 Conclusions

It is seen that the naphthylamine complex promotes the asymmetric Diels-Alder reaction between DMPP and phosphine functionalized terminal alkenols. The regio-stereoselectivity was found to be good with only one isomer being formed exclusively. It needs to be noted that the cheaper palladium analogue of the chiral promoter was the initial choice for synthesizing the diphosphine ligands containing stereogenic phosphorous centers, but was found to give poor selectivity. The formed alcohol

functionalized chiral diphosphines have the potential of being employed in the synthesis of gold-phosphine drugs though no biological studies were carried out as part of this project. The presence of the hydroxyl functionality provides access to other derivatives which can be used to study structure-functionality relationship in future biological studies.

CHAPTER IV

Palladium(II) complex promoted asymmetric hydrophosphination of phosphine functionalized alkenols

4.1 Introduction

One of the most promising processes for the construction of carbon-phosphorous bonds is the addition of phosphorous-hydrogen bonds to unsaturated carbon linkages. This synthetic protocol has immense potential in terms of synthetic value and atom economy. Compared to the addition of other heteroatom hydrogen bonds like hydrosilylation,[174] hydroboration,[175] hydrostannation[176] etc., hydrophosphination has been much less studied. With free phosphines, addition onto an unsaturated C-C bond has been achieved under basic,[177] radical[178,179] or thermal activation.[180] However due to the severe conditions involved, a mixture of products are often obtained, resulting in moderate yields. The *ortho*-metallated complex **36** has been previously used as chiral auxiliary to promote the asymmetric hydroamination of ethynyphosphines and aniline yielding *P*-chiral iminophosphines.[181]

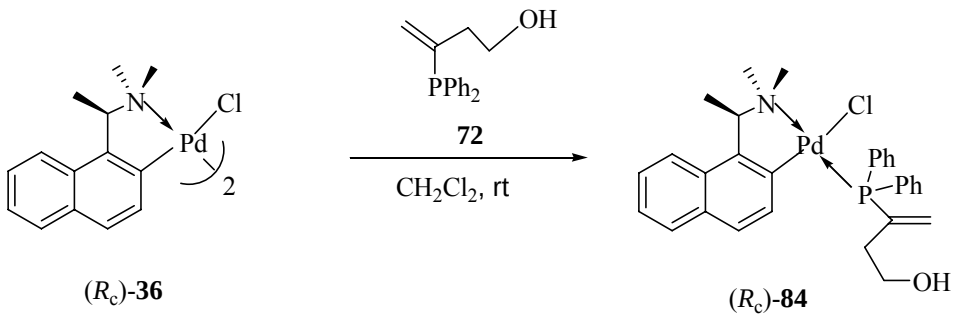
More recently hydrophosphination reactions between diphenylphosphine and (*E*)- and (*Z*)-diphenyl-1-propenylphosphine under mild conditions have also been achieved using the same complex.[182] In order to extend this protocol to the hydrophosphination of functionalized olefinic systems culminating in the synthesis of functionalized chiral diphosphines with chirality residing in the carbon backbone, the hydrophosphination of phosphine functionalized alkenols synthesized (Chapter 3, Section 3.2) is studied. It needs to be noted that this is a second stage hydrophosphination on the hydroxyl functionalised olefinic system since the compounds **72** and **73** themselves were prepared

by a regio- stereoselective hydrophosphination of the parent alkynols (*albeit* not involving the metal template complex).

4.2 Hydrophosphination of 3-Diphenylphosphanyl-but-3-en-1-ol

4.2.1 Synthesis of (R_c,R_c)-87a

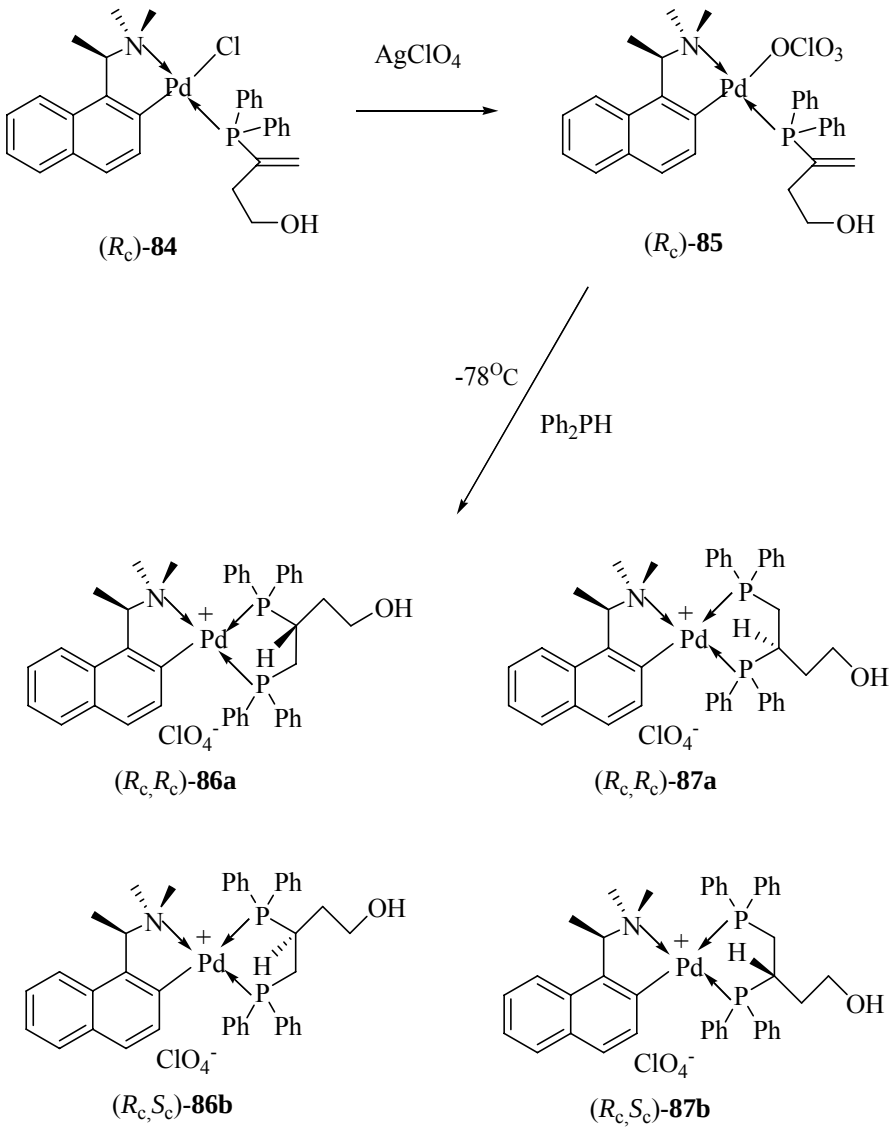
The 3-diphenylphosphanyl-but-3-en-1-ol ligand **72** was allowed to coordinate to the palladium complex (R_c)-**36** in dichloromethane yielding the complex (R_c)-**84** as yellow solid in 69.9 % yield (Scheme 4.1).



(R_c)-**36** (R_c)-**84**

Scheme 4.1

The $^{31}P\{^{1}H\}$ NMR spectrum of the complex ($CDCl_3$, 121MHz) showed a singlet signal at δ 40.59 . The coordination shift (Δ = 44.0 ppm) is indicative of the formation of (R_c)-**84**. The Cl-ligand in (R_c)-**84** was subsequently replaced by a ClO_4 counterpart through treatment of (R_c)-**84** with excess aqueous silver perchlorate in dichloromethane. The perchlorato complex (R_c)-**85** in dichloromethane was then reacted with an equivalent of diphenylphosphine at -78°C to yield the hydrophosphination products as shown in Scheme 4.2.



Scheme 4.2

The reaction temperature was maintained at -78°C for 10 hrs and subsequently stirred at room temperature for another 24 hrs to obtain a dark red solid product. The $^{31}P\{^{1}H\}$ NMR spectrum of the crude reaction mixture showed the presence of four pairs of doublets that are attributed to the isomers (R_c,R_c)-**86a**, (R_c,R_c)-**87a**, (R_c,S_c)-**86b** and (R_c,S_c)-**86b**. The $^{31}P\{^{1}H\}$ signals (121.5 MHz, $CDCl_3$) observed were as follows: δ 31.38

(d, J_{PP} = 34.2 Hz), 39.81 (d, J_{PP} = 22.7 Hz), 47.49 (d, J_{PP} = 34.2 Hz), 47.97 (d, J_{PP} = 30.4 Hz), 50.36 (d, J_{PP} = 30.4 Hz), 52.62 (d, J_{PP} = 30.4 Hz), 66.42 (d, J_{PP} = 34.2 Hz), 77.05 (d, J_{PP} = 22.7 Hz). The ratio of the isomers was found to be 4.0: 1.0: 18.5: 2.2. Subsequently the major isomer (R_c,R_c)-**87a** was separated by means of fractional crystallization as pale yellow crystals from dichloromethane- diethyl ether. The $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) of pure (R_c,R_c)-**87a** showed the following signals: δ 39.29 (d, 1P, J_{PP} = 26.6Hz), 76.06 (d, 1P, J_{PP} = 26.6 Hz).

4.2.2 Single Crystal X-ray Diffraction Analysis of (R_c,R_c)-87a

The single crystal X-ray diffraction analysis of the isolated pure isomer (R_c,R_c)-**87a** revealed that the expected five-membered diphosphine chelate has been formed (Figure 4.1). The newly formed stereogenic centre at C(16) adopts the *R* configuration as observed from Figure 4.1.

The geometry at the Pd centre is distorted square planar with angles of 80.4(2) – 101.5(1)° and 173.8(1) – 177.6(1)°. The five-membered diphosphine chelate adopts the λ ring configuration, with the CH2-CH2-OH substituent at C(16) occupying the axial position. The tetrahedral distortion is necessitated to reduce the unfavorable steric repulsions existing between the substituent on C(16) and the axial phenyl group on P(1). The same steric considerations are responsible for the staggered orientation of the phenyl groups on P(2) and the methyl groups on N(1). Selected bond lengths and angles are given in Table 4.1.

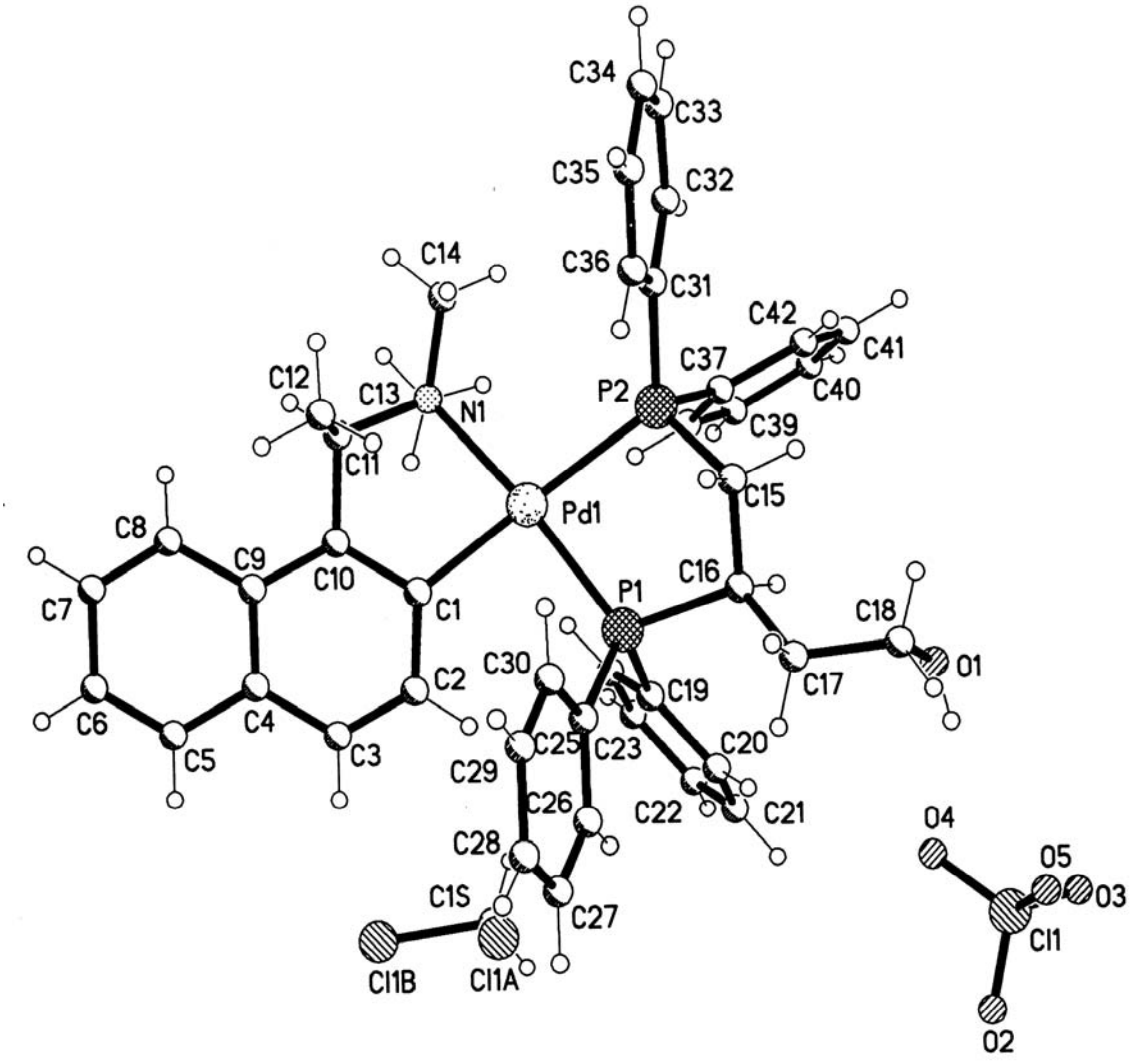


Figure 4.1 Molecular structure and absolute stereochemistry of (R_c,R_c)-87a

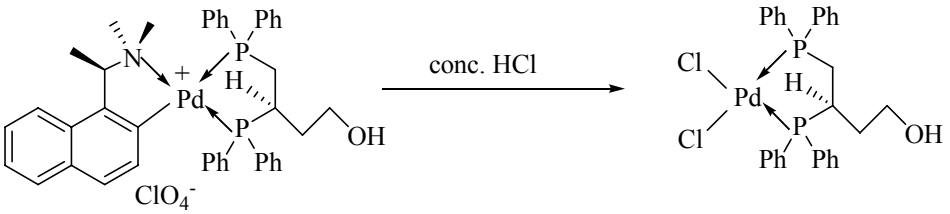
Table 4.1 Selected bond lengths (Å) and angles (°) for (R_c,R_c)-87a

Pd(1)-C(1)	2.053(4)	Pd(1)-N(1)	2.140(3)
Pd(1)-P(1)	2.250(1)	Pd(1)-P(2)	2.355(1)
P(1)-C(16)	1.862(5)	P(2)-C(15)	1.829(5)
O(1)-C(18)	1.434(10)	C(15)-C(16)	1.546(7)

C(16)-C(17)	1.536(6)	C(17)-C(18)	1.500(8)
C(1)-Pd(1)-N(1)	80.4(2)	C(1)-Pd(1)-P(1)	93.6(1)
N(1)-Pd(1)-P(1)	173.8(1)	C(1)-Pd(1)-P(2)	177.6(1)
N(1)-Pd(1)-P(2)	101.5(1)	P(1)-Pd(1)-P(2)	84.5(4)
C(16)-C(15)-P(2)	110.6(3)	C(17)-C(16)-C(15)	110.5(4)
C(17)-C(16)-P(1)	115.1(4)	C(15)-C(16)-P(1)	109.7(3)
C(18)-C(17)-C(16)	112.5(5)	O(1)-C(18)-C(17)	113.5(6)

4.2.3 Synthesis of the dichloro complex (R_c)-88

A solution of (R_c,R_c)-**87a** in dichloromethane was treated with concentrated hydrochloric acid to remove the naphthylamine auxiliary chemoselectively (Scheme 4.3).



(R_c,R_c)-**87a** (R_c)-**88**

Scheme 4.3

The $^{31}P\{^1H\}$ NMR spectrum of the dichloro complex (121 MHz, $CDCl_3$) showed signals at δ 51.05 (d, 1P, J_{PP} = 7.5 Hz) and 71.34 (d, 1P, J_{PP} = 7.5 Hz). The dichloro complex (R_c)-**88** crystallized from dichloromethane - *n*-hexanes as pale yellow prisms.

4.2.4 Single crystal X-ray diffraction analysis of (R_c)-88

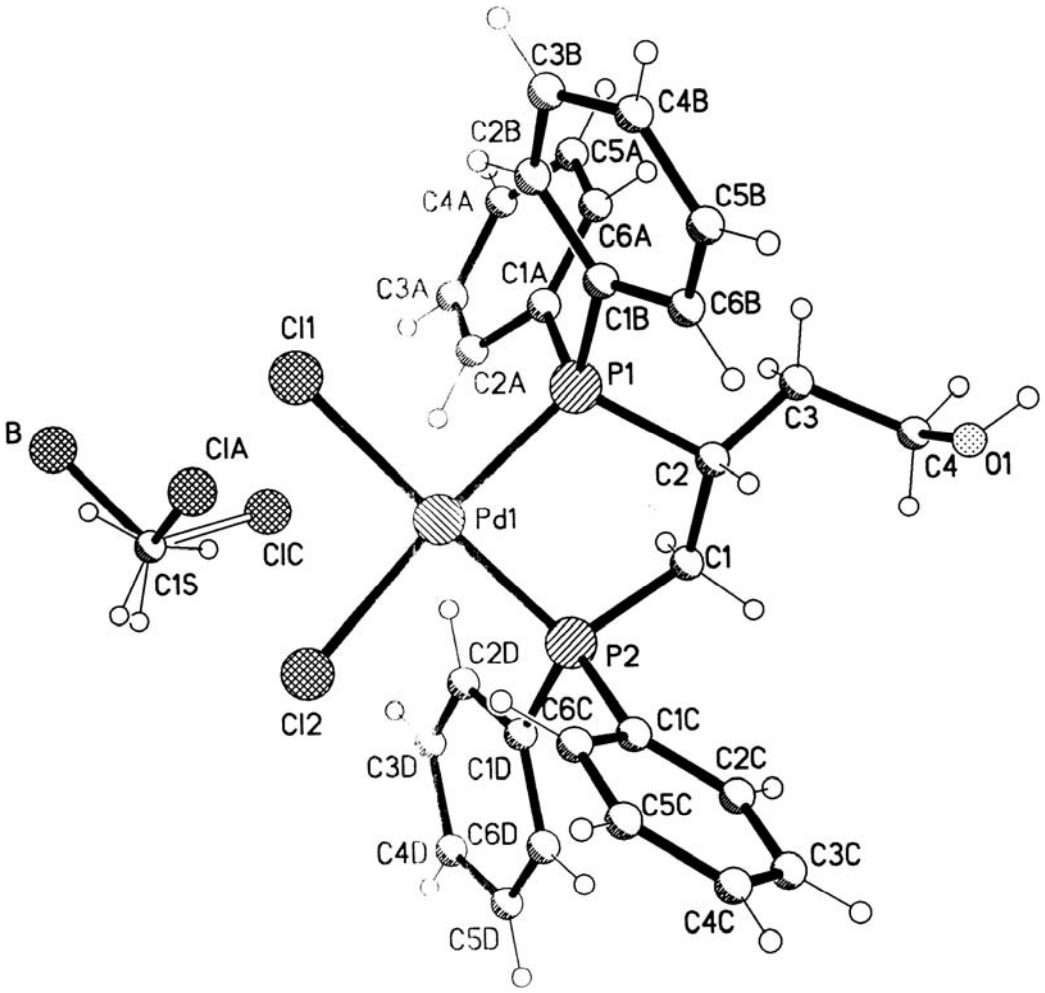


Figure 4.2 Molecular structure and absolute configuration of (R_c)-88

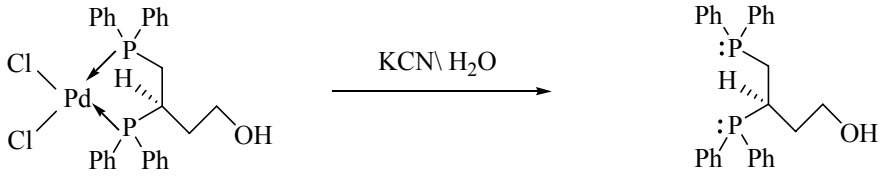
The single crystal X-ray diffraction analysis (Figure 4.2) confirmed that the naphthylamine auxiliary has been removed with no change to the diphosphine ligand structure and stereochemistry. Complex (R_c)-**88** adopts the original *R* absolute configuration at the chiral centre C(2). Selected bond lengths and angles for (R_c)-**88** are given in Table 4.2.

Table 4.2 Selected bond lengths (Å) and angles (°) for (R_c)-88

Pd(1)-P(2)	2.220(4)	Pd(1)-P(1)	2.233(4)
Pd(1)-Cl(2)	2.348(4)	Pd(1)-Cl(1)	2.368(4)
P(1)-C(2)	1.854(14)	P(2)-C(1)	1.839(14)
C(1)-C(2)	1.495(19)	C(2)-C(3)	1.529(19)
C(3)-C(4)	1.54(2)	C(4)-O(1)	1.43(2)
P(2)-Pd(1)-P(1)	86.0(1)	P(2)-Pd(1)-Cl(2)	89.3(1)
P(1)-Pd(1)-Cl(2)	174.8(2)	P(2)-Pd(1)-Cl(1)	176.3(1)
P(1)-Pd(1)-Cl(1)	92.1(1)	Cl(2)-Pd(1)-Cl(1)	92.7(1)
C(2)-P(1)-Pd(1)	108.9(5)	C(1)-P(2)-Pd(1)	108.5(5)
C(2)-C(1)-P(2)	109.9(1)	C(1)-C(2)-C(3)	114.0(1)
C(1)-C(2)-P(1)	108.7(1)	C(3)-C(2)-P(1)	113.0(9)
C(2)-C(3)-C(4)	112.9(1)	O(1)-C(4)-C(3)	109.4(1)

4.2.5 Decomplexation and Optical Purity of the (C-Chiral) diphosphine (R_c)-89

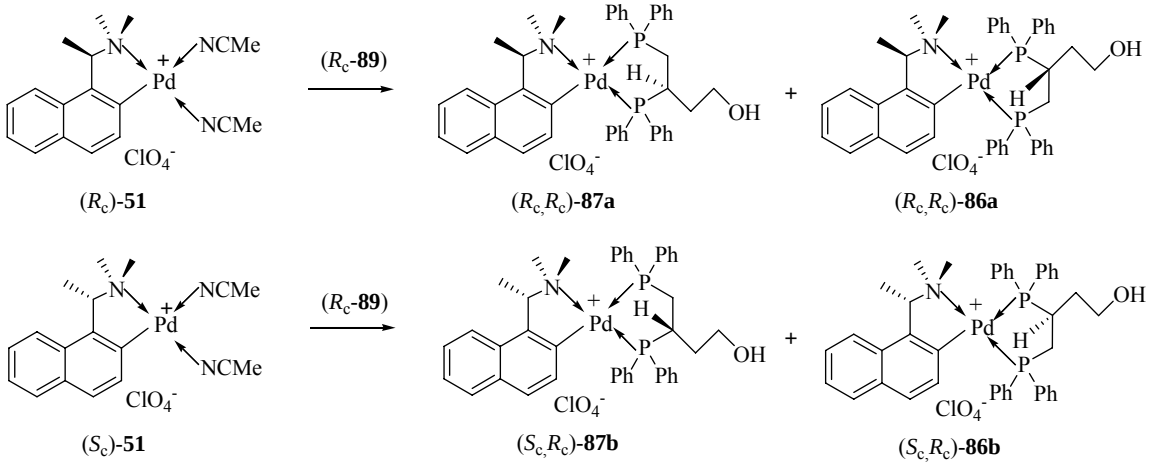
It is noteworthy that the optically active diphosphine ligand with chirality residing on the C atom (R_c)-**89** can be stereospecifically cleaved from (R_c)-**88** by treatment of the dichloro complex with aqueous potassium cyanide at room temperature for 2 hrs (Scheme 4.4).



(R_c)-**88** (R_c)-**89**

Scheme 4.4

The liberated ligand was obtained as pale yellow oil on removal of solvents under reduced pressure. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) spectra showed resonances at δ 19.31 (d, $^{3}J_{PP}$ = 19.0 Hz) and -0.17 (d, $^{3}J_{PP}$ = 19.0 Hz). Due to the extreme air sensitivity of the non-coordinated phosphorous atoms, the liberated (R_c)-**89** could not be stored in its pure form. Therefore the liberated ligand was re-complexed to the bis(acetonitrile) complex (R_c)-**51** (Scheme 4.5).



Scheme 4.5

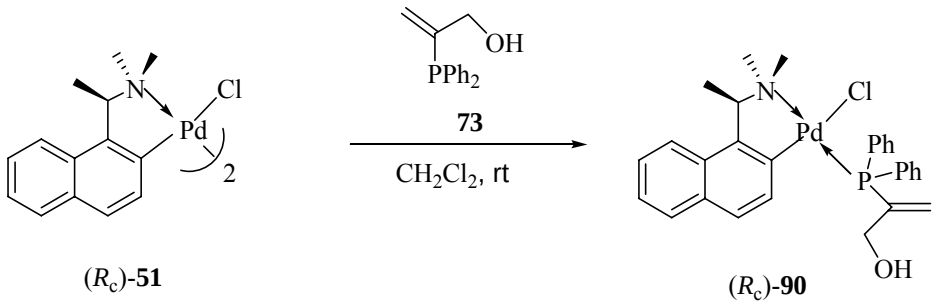
The recoordination process is also a means of verifying the optical purity of the released ligand. To establish the identity of the minor isomers that were generated in the original hydrophosphination reaction, (R_c)-**89** was re-complexed to the bis(acetonitrile)

complex (R_c)-**51**. The re-complexation of the released ligand (R_c)-**89** to the bis(acetonitrile) complex (R_c)-**51** was monitored by $^{31}P\{^1H\}$ NMR spectroscopy (121 MHz, $CDCl_3$) and gave signals at δ 39.65 (d, 1P, J_{PP} = 22.8 Hz), 47.91 (d, 1P, J_{PP} = 30.4 Hz), 50.23 (d, 1P, J_{PP} = 30.4 Hz) and 76.89 (d, 1P, J_{PP} = 22.8 Hz). The resonance signals at δ 39.65 and 76.89 are identical to those observed for the major product (R_c,R_c)-**87a** in the original hydrophosphination reaction. The signals at δ 47.91 and 50.23 matches signals seen in the original reaction mixture and are assigned to the regioisomeric product of (R_c,R_c)-**87a** viz. (R_c,R_c)-**86a.** Formation of regioisomers during the recoordination of liberated ligands to the naphthylamine auxiliary is well established. Previous studies on similar isomeric systems have shown that, for a pair of regioisomers such as (R_c,S_c)-**86a** and (R_c,S_c)-**87a** formed on the naphthylamine chiral auxiliary system, the separation in $^{31}P\{^1H\}$ resonance signals will be significantly larger than that observed for diastereomeric complexes such as (R_c,R_c)-**87a** and (R_c,S_c)-**87b**.[182,183]

The re-complexation reaction with (S_c)-**51** gave signals at δ 31.27 (d, 1P, J_{PP} = 30.4 Hz), 47.43 (d, 1P, J_{PP} = 34.2 Hz), 52.39 (d, 1P, J_{PP} = 34.2 Hz) and 66.37 (d, 1P, J_{PP} = 30.4 Hz). In order to assign these signals to (R_c,S_c)-**86b** and its regioisomer (R_c,S_c)-**87b** we need to draw an analogy with (R_c,R_c)-**86a** and (R_c,R_c)-**87a**. The coupling constants of the two pairs of signals are also a very good spectroscopic handle for pairing up the resonances of the minor isomers. Comparison of the signals to those of (R_c,R_c)-**86a** and (R_c,R_c)-**87a** clearly indicates that the signals at δ 31.27 (d, 1P, J_{PP} = 30.4 Hz) and 66.37 (d, 1P, J_{PP} = 30.4 Hz) are due to the diastereomer of (R_c,R_c)-**86a** viz., (R_c,S_c)-**86b**, and the signals at δ 47.43 (d, 1P, J_{PP} = 34.2 Hz), 52.39 (d, 1P, J_{PP} = 34.2 Hz) can be assigned to the regioisomer of (R_c,S_c)-**86b** viz., (R_c,S_c)-**87b**.

4.3 Hydrophosphination of 2-Diphenylphosphanyl-prop-2-en-1-ol

4.3.1 Synthesis of the Hydrophosphination products



(R_c)-**51** (R_c)-**90**

Scheme 4.6

The 2-diphenylphosphanyl-prop-2-en-1-ol ligand obtained by means of hydrophosphination of propargyl alcohol (Section 3.2.2) was coordinated to the dimeric orthometallated palladium complex (R_c-**36**) as shown in Scheme 4.6. The reaction was allowed to stir for 8 hrs at room temperature and then the solvent removed under reduced pressure to give a yellow solid. The 121 MHz $^{31}P\{^{1}H\}$ NMR spectrum of the complex showed a singlet signal at δ 40.59 in $CDCl_3$.

Crystallization using acetonitrile- diethyl ether gave yellow prisms of (R_c)-**90**. The monophosphine complex formed was characterized by means of single crystal X-ray diffraction analysis (Figure 4.3). Selected bond angles and bond lengths are given in Table 4.3. The coordination around the metal centre is distorted square planar with angles at palladium in the range of 80.6(2)-93.9(1) and 171.2(1)-173.4(1)°.

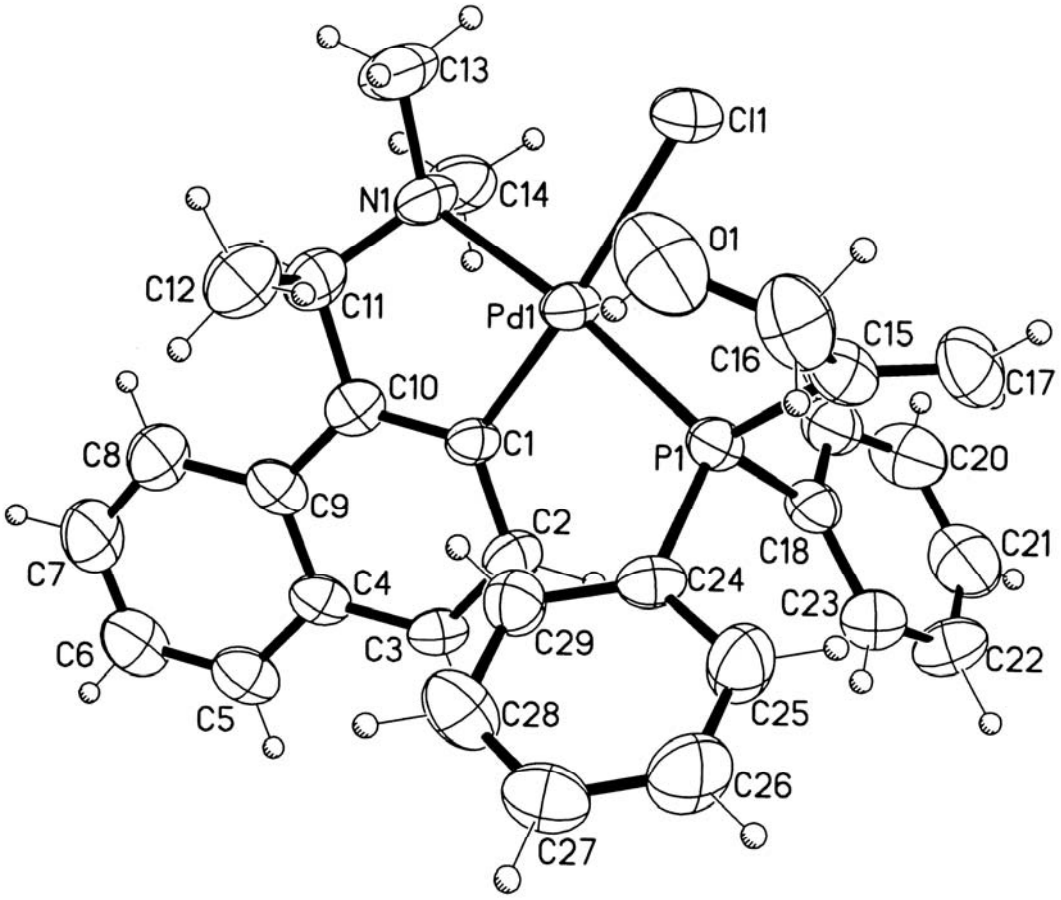


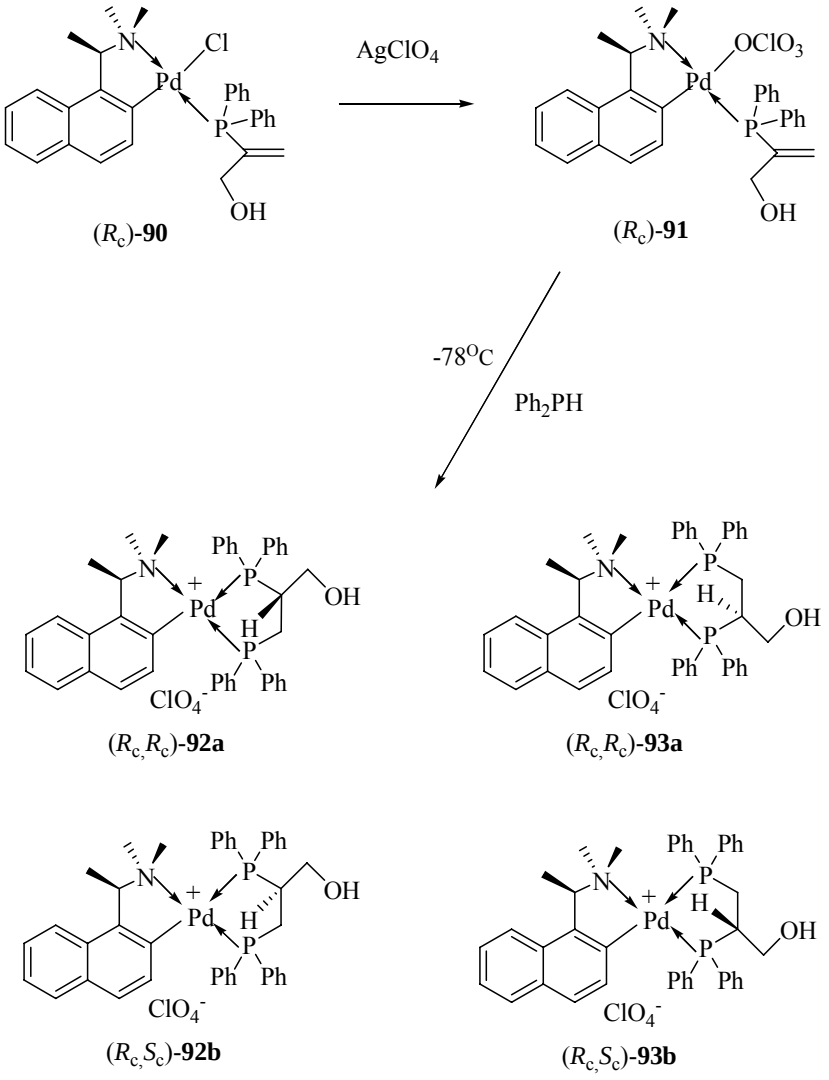
Figure 4.3 Molecular structure of (R_c)-90

Table 4.3 Selected bond lengths (Å) and bond angles (°) of (R_c)-90

Pd(1)-C(1)	2.005(4)	Pd(1)-N(1)	2.126(4)
Pd(1)-P(1)	2.251(1)	Pd(1)-Cl(1)	2.413(1)
O(1)-C(16)	1.380(7)	C(15)-C(17)	1.306(7)
C(15)-C(16)	1.490(8)		
C(1)-Pd(1)-N(1)	80.6(2)	C(1)-Pd(1)-P(1)	93.9(1)
N(1)-Pd(1)-P(1)	173.4(1)	C(1)-Pd(1)-Cl(1)	171.2(1)

N(1)-Pd(1)-Cl(1)	92.5(1)	P(1)-Pd(1)-Cl(1)	93.3(5)

The chloro complex (R_c)-**90** was subsequently converted to the perchlorato species by treatment with aqeous silver perchlorate as shown in Scheme 4.7.



Scheme 4.7

The perchlorato complex (R_c)-**91** was dissolved in dichloromethane and was allowed to react with diphenylphosphine at -78°C for 10 hrs and then stirred at room temperature for further 48 hrs to give a dark red solid upon removal of solvents under reduced pressure. The $^{31}P\{^1H\}$ spectrum ($CDCl_3$, 121 MHz) of the reaction mixture prior to attempted fractional crystallization showed the following signal pattern : δ 30.75 (d, 1P, J_{PP} = 30.4 Hz), 37.96 (d,1P, J_{PP} = 22.8 Hz), 41.88 (d, 1P, J_{PP} = 30.4 Hz), 41.94 (d, 1P, J_{PP} = 30.4 Hz), 49.42 (d, 1P, J_{PP} = 30.4 Hz), 51.30 (d, 1P, J_{PP} = 30.4 Hz), 60.85 (d, 1P, J_{PP} = 30.4 Hz) and 67.63 (d, 1P, J_{PP} = 22.8 Hz). The signals were indicative of the formation of isomers in the ratio 1: 2.4: 5.3: 7.8.

Attempted fractional crystallization using dichloromethane – *n*-hexanes gave yellow prisms suitable for single crystal X-ray diffraction analysis. Preliminary $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2) spectral studies on the crystals indicated the presence of two isomers since four doublet signals were observed at δ 41.55 (d, 1P, J_{PP} = 30.4 Hz), 41.97 (d, 1P, J_{PP} = 30.4 Hz), 50.01(d, 1P, J_{PP} = 30.4 Hz) and 51.46 (d, 1P, J_{PP} = 30.4 Hz).

4.3.2 Single crystal X-ray diffraction analysis of 92

Single crystal X-ray diffraction analysis of the yellow prisms obtained from the hydrophosphination reaction mixture confirmed that the two diastereomers (R_c,R_c)-**92a** and (R_c,S_c)-**92b** have co-crystallized out (Figure 4.4 and 4.5). Selected bond lengths and bond angles for the two diastereomers are given in Table 4.3.

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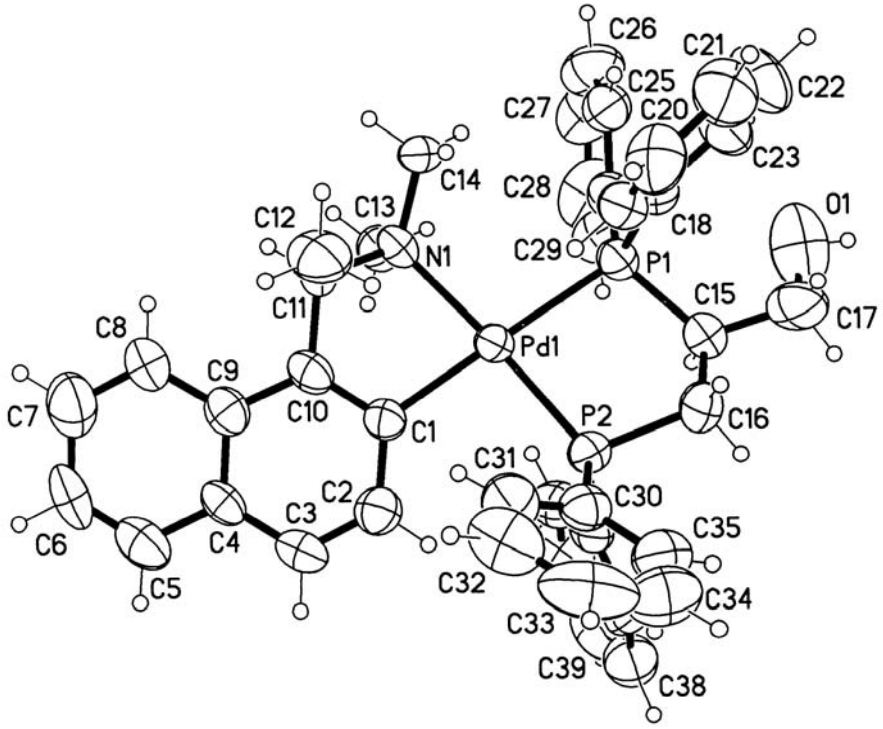


Figure 4.4 Molecular structure and absolute configuration of (R_c,R_c)-92a

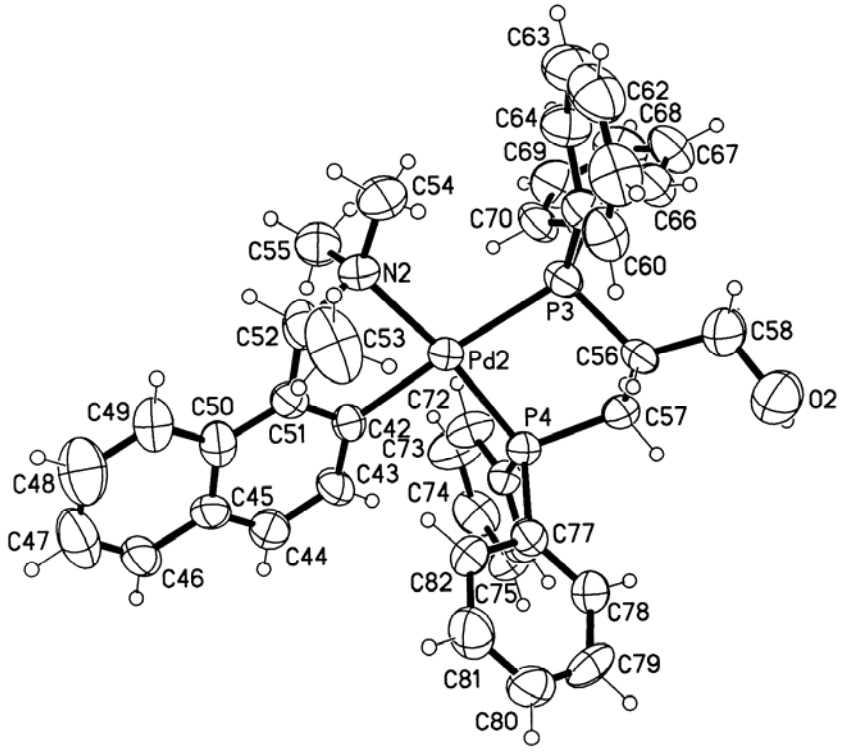


Figure 4.5 Molecular structure and absolute configuration of (R_c,S_c)-92b

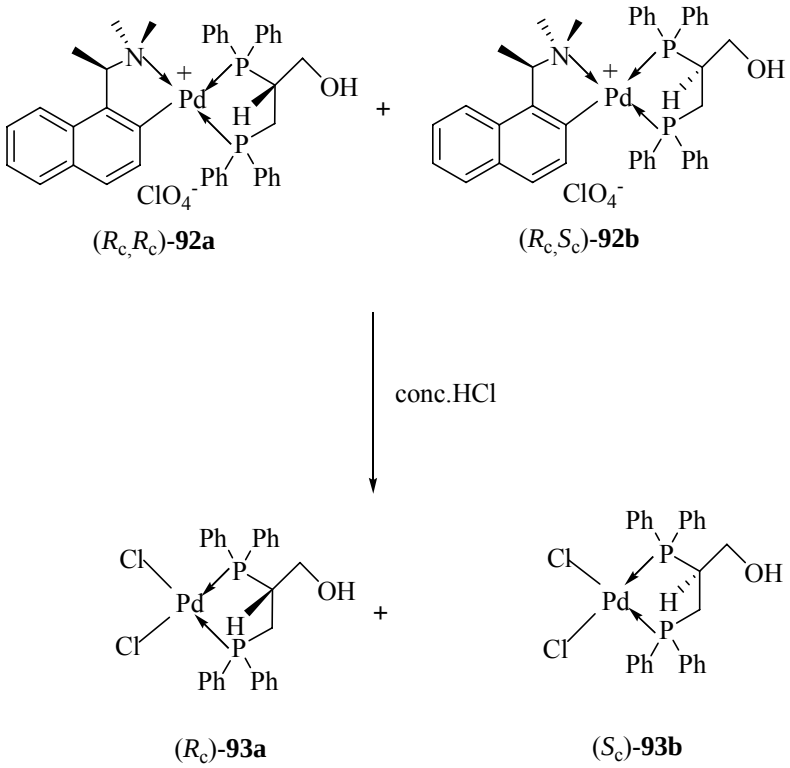
Table 4.3 Selected bond lengths (Å) and angles (°) of 92

	(R_c,R_c)-92a		(R_c,S_c)-92b
Pd(1)-C(1)	2.059(7)	Pd(2)-C(42)	2.059(7)
Pd(1)-N(1)	2.141(6)	Pd(2)-N(2)	2.140(6)
Pd(1)-P(2)	2.245(2)	Pd(2)-P(4)	2.257(1)
Pd(1)-P(1)	2.350(2)	Pd(2)-P(3)	2.394(1)
P(1)-C(15)	1.835(8)	P(3)-C(56)	1.853(8)
P(2)-C(16)	1.843(8)	P(4)-C(57)	1.828(8)
C(15)-C(16)	1.497(11)	C(56)-C(57)	1.537(11)
C(15)-C(17)	1.518(13)	C(56)-C(58)	1.491(12)
O(1)-C(17)	1.366(14)	O(2)-C(58)	1.447(12)
C(1)-Pd(1)-N(1)	80.4(3)	C(42)-Pd(2)-N(2)	79.8(3)
C(1)-Pd(1)-P(2)	95.7(2)	C(42)-Pd(2)-P(4)	93.3(2)
N(1)-Pd(1)-P(2)	175.1(2)	N(2)-Pd(2)-P(4)	172.8(2)
C(1)-Pd(1)-P(1)	174.0(2)	C(42)-Pd(2)-P(3)	175.6(2)
N(1)-Pd(1)-P(1)	99.4(2)	N(2)-Pd(2)-P(3)	101.7(2)
P(2)-Pd(1)-P(1)	84.8(7)	P(4)-Pd(2)-P(3)	85.1(7)

As can be seen from the single crystal X-ray diffraction data, the two diastereomers differ in the chirality at C(15) and C(56) respectively. For (R_c,S_c)-**92a** the chirality at C(15) is *S* whereas in the case of (R_c,R_c)-**92b** the chiral carbon C(56) adopts

the *R* configuration. Both diastereomers show similar coordination pattern with the geometry at the Pd metal centre being distorted square planar. The angles formed by the diphosphine chelate and the naphthylamine template at the Pd metal centre being in the range of 80.4(3)-99.4(2) and 174.0(2)-175.1(2)° for (R_c,R_c)-**92a** . The diastereomer (R_c,S_c)-**92b** showed slightly elevated strain with angles at the metal centre being in the range of 79.8(3)-101.7(2) and 172.9(2)-175.6(2)°.

The two diastereomers (R_c,R_c)-**92a** and (R_c,S_c)-**92b** which co-crystallized out were converted to their dichloro species (Scheme 4.8).



(R_c,R_c)-**92a** (R_c,S_c)-**92b**

(R_c)-**93a** (S_c)-**93b**

Scheme 4.8

The crude reaction mixture showed two doublets when monitored by $^{31}P\{^{1}H\}$ NMR spectroscopy (121 MHz, CD_2Cl_2) at δ 53.28 (d, 1P, J_{PP} = 7.6 Hz) and 66.15 (d, 1P, J_{PP} = 7.6 Hz). The reaction mixture was concentrated and diethyl ether added resulting in the formation of pale yellow crystals which were analyzed by means of single crystal X-ray diffraction analysis (Figure 4.7).

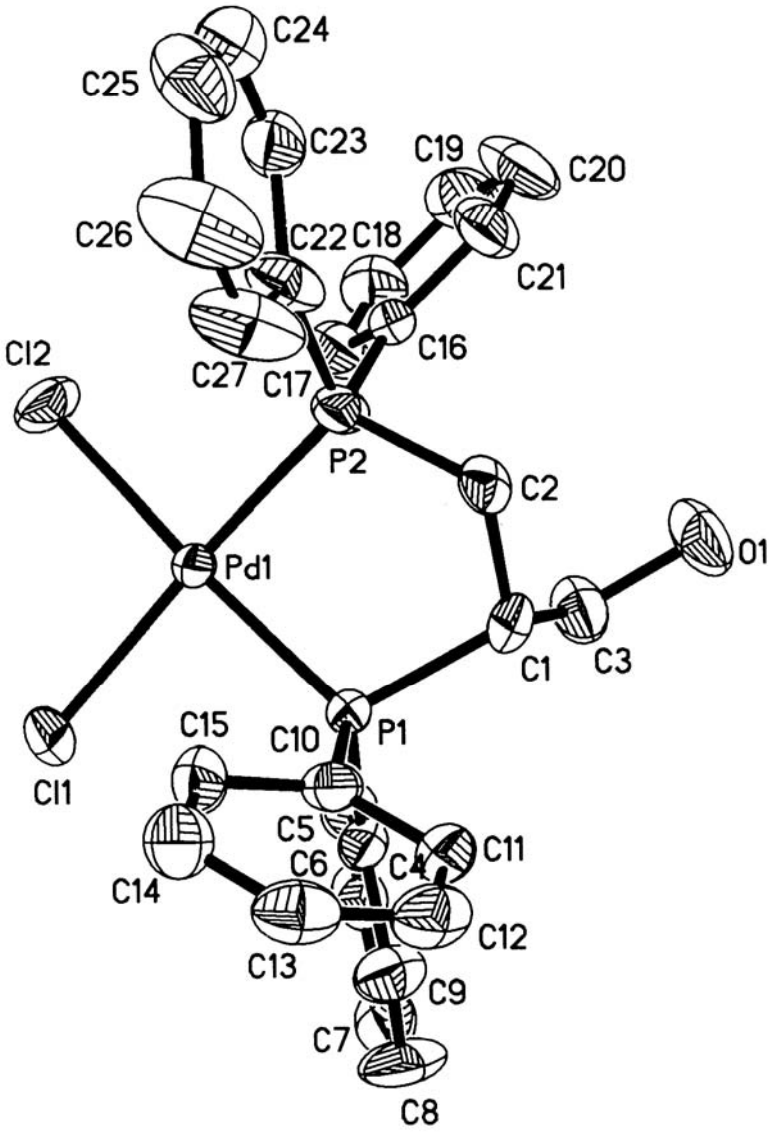


Figure 4.7 Molecular structure of 93

The single crystal X-ray diffraction analysis showed that as expected, the attempted separation of the neutral species did not succeed. The two enantiomers (R_c)-**93a** and (S_c)-**93b** co-crystallized out in the same unit cell.

4.4 Conclusions

The chiral organopalladium template promoted asymmetric hydrophosphination of phosphine functionalized alkenols has been demonstrated. The reaction showed appreciable regio-stereoselectivity in the case of 3-diphenylphosphanyl-but-3-en-1-ol ligand with the hydrophosphination products being formed in the ratio 4.0: 1.0: 18.5: 2.2. The major isomer (R_c,R_c)-**87a** was subsequently isolated in appreciable yield (78%) in its optically pure form.

The similar reaction involving 2-diphenylphosphanyl-prop-2-en-1-ol however did not exhibit appreciable selectivity. The major regio-isomer crystallized out as a racemic mixture. Subsequent attempts to separate them after conversion to the neutral dichloro species also did not succeed. It needs to be noted that in the case of 3-diphenylphosphanyl-but-3-en-1-ol the major product was the isomer wherein the phosphine functionalized alcoholic entity occupied a position *trans* to the NMe2 group of the chiral template whereas in the case of the major isomers (isolated as racemic mixture) of hydrophosphination involving 2-diphenylphosphanyl-prop-2-en-1-ol, the phosphine functionalized alcohol entity occupied a position *trans* to the C of the chiral template. This is believed to be due to the steric factor involved in the case of 3-diphenylphosphanyl-but-3-en-1-ol wherein the -CH2-CH2-OH entity on the chiral carbon

extends into the metal coordination sphere and is sterically hindered by the presence of the NMe2 group of the naphthylamine auxilliary. The shorter –CH2-OH group of the 2-diphenylphosphanyl-prop-2-en-1-ol meanwhile does not have an appreciable steric impact and therefore can afford to occupy the position *trans* to the C of the template.

Experimental Section

Experimental Section

All reactions and manipulations of air-sensitive compounds were carried out under a positive pressure of dry, oxygen-free nitrogen on a high-vacuum line, or on a standard Schlenk line. Solvents were dried and freshly distilled according to standard procedures and degassed prior to use when necessary. The 1-D ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra were measured on a Bruker ACF 300 spectrometer operating at 300.13 and 121.49 MHz respectively. The data is presented as follows: chemical shift, multiplicity, number of active nuclei and coupling constant(s) in Hertz (Hz). ^{1}H and $^{31}P\{^{1}H\}$ NMR chemical shifts are referenced relative to Me_4Si and H_3PO_4 respectively. Phase- sensitive ROESY spectra were obtained on a Bruker AMX 500 spectrometer and were acquired into 1024 X 512 matrix with a 250ms spin lock time and a spin lock field strength such that $\gamma B_1/2\pi$ = 5000 Hz and then transformed into 1024 X 1024 points using a sine bell weighting function in both dimensions. Optical rotations were measured on the specified solutions in a 1 cm cell at specified temperatures using a Perkin-Elmer model 341 polarimeter. Melting points were determined using a Büchi B-545 automatic melting point apparatus. Elemental analyses were performed by the Elemental Analysis laboratory of the Department of Chemistry at the National University of Singapore.

Materials

Both enantiomers of bis(acetonitrile)[1-[1-(dimethylamino) ethyl]-2-naphthalenyl-*C*,*N*] palladium(II) perchlorate (R_c)-**51** and (S_c)-**51**,[184] di-μ-chloro bis[1-

(dimethylamino)ethyl]-2-naphthalenyl-*C,N*]dipalladium(II) dichloromethane solvate (R_c)-**36**,[108] chloro[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*]3,4-dimethyl-1-phenylphosphole)palladium(II) (R_c)-**46**,[153] perchlorato(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*][3,4-dimethyl-1-phenylphosphole-*P*]palladium(II) (R_c)-**47**,[154] di-μ-chloro bis[(*R*)-1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*]diplatinum(II) dichloromethane solvate (R_c)-**43**,[185] 3,4-dimethyl-1-phenylphosphole **44**,[186] 3,4-dimethyl-1-phenylphosphole-1-sulfide **47**,[145] diphenylvinylphosphine,[187] diphenylvinylarsine **65**,[184] diphenylvinylphosphine sulfide[188] **53** were prepared as previously reported. Solvents were distilled, dried and degassed by standard procedures where necessary. Column chromatography was performed using silica gel 60 (0.040-0.063mm, Merck).

Caution! All perchlorate salts should be handled as potentially explosive compounds.

Synthesis of [(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*] [9-thio-9-phenylphosphino-2,3,6,7-tetramethyl-6-ethylene-10-phenyl-10-phosphabicyclo[2,2,1] hept-2-ene-P^9(*R*)P^{10}(*S*)]palladium (II)perchlorate, ($R_cS_pR_p$)-48

A solution of (R)$_c$-**47** (1.20g, 1.8 mmol) in 1,2-dichloroethane (50 mL) was treated with DMPPS **45** (0.40g, 1.8 mmol) and refluxed. The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy and was found to be complete in 2 days. Removal of solvent under reduced pressure gave a yellow solid (1.42 g, 97%). The ^{31}P NMR spectrum of the crude product in CD_3CN exhibited two pairs of doublets indicative of a diastereomeric mixture (1:0.3). For the major diastereomer (R_c,S_p,R_p)-**48,** the doublets were observed at

δ 61.3 ($J_{P\text{-}P}$ 11.4Hz) and 115.3 ($J_{P\text{-}P}$ 11.4Hz).For the minor isomer the doublets occurred at δ 62.0 ($J_{P\text{-}P}$ 11.4Hz) and 114.8_($J_{P\text{-}P}$ 11.4Hz). Attempted fractional crystallization yielded crystals which consist of both diastereomers but the mother liquor obtained showed presence of only the major isomer. The major isomer was subsequently purified by column chromatography on silica gel with ethyl acetate/hexane (3:1) and crystallized out from acetonitrile-ether as pale yellow prisms (0.55 g, 39%). $[\alpha]_D$ = -96.7° (*c* 0.3, CH_2Cl_2), mp: 238-240 º C. Anal. Calcd for $C_{38}H_{42}ClNO_4P_2PdS$: C, 56.2; H, 5.2; N, 1.7; S, 3.9. Found: C, 56.6; H, 5.6; N, 1.5; S, 3.6. $^{31}P\{^1H\}$ NMR ($CDCl_3$) : δ 61.34 (d, 1P, J_{PP} = 11.4Hz), 115.25 (d, 1P, J_{PP} = 11.4Hz) .^{1}H NMR ($CDCl_3$) : δ 1.57 (s, 3H, =C*Me*), 1.60 (s, 3H, =C*Me*), 1.62 (d, 3H, CH*Me,* $^3J_{HH}$ = 6.8 Hz), 2.04 (s, 3H, NMe_{axial}), 2.17 (s, 3H, C*Me*), 2.34 (s, 3H, =C*Me*), 2.65 (s , 3H, NMe_{equal}), 2.88 (d, 1H, $^3J_{HH}$ = 3Hz, H_1), 3.31 (m, 1H, H_4), 4.12 (dd, 1H, $^1J_{PH}$ = 14Hz, $^3J_{HH}$ = 7.23Hz, H_8), 4.23 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.02 Hz, H_{10}), 6.34 (d, 1H, $^2J_{PH}$ = 28Hz, H_7), 7.22-7.92 (m, 16H, *aromatics*).

Preparation of dichloro[9-thio-9-phenylphosphino-2,3,6,7-tetramethyl-6-ethylene-10-phenyl-10-phosphabicyclo[2,2,1]hept-2-ene-P^9(*R*)P^{10}(*S*)]palladium(II)perchlorate, (S_p,R_p)-49

The complex (R_c,S_p,R_p)-**48** (0.40g) was dissolved in dichloromethane (30 mL). To this solution, hydrochloric acid (4mL, 37%) was added and the resulting solution was stirred vigorously for 1 day. The reaction mixture was then washed with distilled water (3 X 10 mL) and dried with magnesium sulfate. Removal of all solvent left the crude product as yellow powder, 0.25g (87%). The dichloro complex (S_p,R_p)-**49** was then

further crystallized by slow diffusion of diethyl ether into a saturated solution of the compound in acetonitrile, as yellow crystals 0.18g. $[\alpha]_D$ = -175.57° (*c*0.1, CH_2Cl_2), mp: 254-256 º C. Anal. Calcd. for $C_{38}H_{42}ClNO_4PPdS$: C, 49.2; H, 4.4; S, 5.5. Found: C, 48.8; H, 4.5; S, 5.3. $^{31}P\{^1H\}$ NMR ($CDCl_3$) : δ 60.54 (d, 1P, J_{PP} = 15.2Hz), 106.63 (d, 1P, J_{PP} = 15.2Hz) . ^1H NMR (CD_2Cl_2) : δ 1.42 (s, 3H, =C*Me*), 1.45 (s, 3H, =C*Me*), 2.37 (s, 3H, =C*Me*), 2.59 (dd, 1H, $^3J_{HH}$ = 2.01Hz, H_1), 3.38 (m, 1H, H_4), 4.12 (dd, 1H, $^1J_{PH}$ = 14.25Hz, $^3J_{HH}$ = 7.23Hz, H_8), 6.79 (d, 1H, $^2J_{PH}$ = 28.5Hz, H_7), 7.4 1-7.83 (m, 16H, *aromatics*).

Decomplexation of 9-thio-9-phenylphosphino-2,3,6,7-tetramethyl-6-ethylene-10-phenyl-10-phosphabicyclo[2,2,1]hept-2-ene-P^9(*R*)P^{10}(*S*)-biphosphole, (R_p,R_p)-50.

To the solution of dichloro complex (S_p,R_p)-**49** (0.08 g) in dichloromethane (10 mL), an aqueous solution of potassium cyanide (0.3 g) was added under a nitrogen atmosphere, and the resulting solution was stirred vigorously for 1 h. The aqueous phase was separated, and the organic layer was washed with water (3 X 5 mL) and dried over magnesium sulfate. Removal of the solvent under vacuum gave ligand (R_p,R_p)-**50** as an air-sensitive colorless oil in 83 % yield (0.05 g); $[\alpha]_D$= -165.13° (*c* 0.1, CH_2Cl_2) , $^{31}P\{^1H\}$ NMR ($CDCl_3$) : δ 58.12 (d, 1P, $^3J_{PP}$ = 7.6Hz), 106.50 (d, 1P, $^3J_{PP}$ = 7.6Hz) .

To determine the optical purity of (R_p,R_p)-**50** , the liberated ligand was recoordinated to the bis(acetonitrile) complex (R_c)-**51** to regenerate the diastereomeric complex ($R_cS_pR_p$)-**48**. In $CDCl_3$, the ^{31}P NMR spectrum of the crude recoordination product showed two doublets at δ 61.3 and 115.3. In a further check (R_p,R_p)-**50** , was recoordinated regiospecifically to (S_c)-**51** to generate the diastereomeric complex

($S_cS_pR_p$)-**48**. The ^{31}P NMR spectrum of the crude product in $CDCl_3$ showed two doublets at 61.9 and 114.8.

Synthesis of diphenylvinylphosphine sulphide, 53

To a solution of diphenylvinylphosphine (3,17g, 0.015 moles) in distilled benzene, sublimed sulfur (0.48g, 0.015 moles) was added with stirring. The temperature rose to 55° C in 1 min and then dropped rapidly. The reaction mixture was allowed to stir for 30 minutes. A few solid particles appeared which were subsequently removed by filtration. The crude oil obtained on removal of benzene was dissolved in dichloromethane and hexane added till turbidity appeared. Yellow fine needles obtained on keeping at + 4.0°C (2.10 g, 87.7%). $^{31}P\{^1H\}$NMR $CDCl_3$: δ 37.05 (s, 1P), ^1H NMR ($CDCl_3$) : δ 6.80 (ddd, 1H, $^3J_{HHtrans}$ = 18.1 Hz, $^3J_{HHcis}$ = 11.6 Hz, $^2J_{HP}$ = 24.3 Hz, PC*H*), δ 6.27 (ddd, 1H, $^2J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 13.2 Hz, $^3J_{HP}$ = 14.6 Hz, *cis*-PCC*H*), 6.39 (ddd, 1H, $^2J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 7.3 Hz, $^3J_{HP}$ = 17.7 Hz, *trans*-PCC*H*), 7.44-7.79 (m, 10H, *aromatics*).

Synthesis of exo-cycloaddition products [(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-*C,N*][7-thio-7-diphenylphosphino-2,3-dimethyl-5-phenyl-5-phosphabicyclo[2.2.1]hept-2-ene-P^7(*R*/*S*)]palladium(II)perchlorate, (R_c,S_p)-52 and (R_c,R_p)-52

To a solution of complex (R_c)-**47** in dichloromethane (0.91g, 0.001 moles), diphenylvinylphosphine sulphide **53** (0.33g, 0.001 moles) was added and stirred for 72hrs at room temperature. The solvent was removed under reduced pressure to give a dark

yellow solid. This compound was chromatographed on a silica gel column (dichloromethane:diethyl ether) giving complexes (R_c,S_p)-**52** and (R_c,R_p)-**52** as pale yellow solids . (0.71 g, 70.6%). Anal. Calcd for $C_{40}H_{42}ClNO_4P_2PdS$: C, 57.4; H, 5.0; N, 1.7; S, 3.8. Found: C, 56.9; H, 5.3; N, 1.9; S, 3.7. $^{31}P\{^1H\}$NMR $CDCl_3$: δ 49.38 (s), 52.05 (s), 113.28 (s), 113.91 (s).

Synthesis of dichloro][7-thio-7-diphenylphosphino-2,3-dimethyl-5-phenyl-5-phosphabicyclo[2.2.1]hept-2-ene-P^7(*R*/*S*)]palladium(II), (S_p)-54 and (R_p)-54

A solution of complexes (R_c,S_p)-**52** and (R_c,R_p)-**52** (0.51 g , 0.0006 moles) in dichloromethane (5mL) was treated with excess concentrated hydrochloric acid (0.80 mL) for 1 day. The reaction mixture was subsequently washed with distilled water (3 X 10 mL), dried with magnesium sulphate and subsequently crystallized out from acetonitrile-diethyl ether as yellow prisms. (0.28g, 76%). Anal. Calcd. for $C_{26}H_{25}Cl_2P_2PdS$: C, 51.3; H, 4.1 ; S, 5.3. Found: C, 51.2; H, 4.1; S, 5.2. ^{1}H NMR ($CDCl_3$): δ 1.55 (s, 3H, C=C*Me*), 1.65 (s, 3H, C=C*Me*), 3.34 (m, 2H, S=PC*H* + PhPC*H*), 3.49 (m, 2H, S=PCHCH_2), 3.54 (m, 1H, PhPC*H*) , 7.35-8.33 (m, 15H, *aromatics*).

Synthesis of divinylphenylphosphine sulphide, 56

To a solution of divinylphenylphosphine (1.62g, 0.01mols) in benzene, excess sublimed sulfur (0.52g) was added and the mixture stirred vigorously for 6hrs. The

solution was filtered to remove excess sulfur. The crude product was subsequently concentrated and purified by silica-gel column chromatography (dichloromethane: n-hexanes). Removal of solvents gave yellow solid (1.45g, 74.7 %) of the desired product. $^{31}P\{^{1}H\}$NMR $CDCl_3$: δ 32.53 (s, 1P), ^{1}H NMR ($CDCl_3$) : δ 6.56 (ddd, 1H, $^{3}J_{HHtrans}$ = 18.1 Hz, $^{3}J_{HHcis}$ = 11.6 Hz, $^{2}J_{PH}$ = 24.6 Hz, PC*H*), 6.22 (ddd, 1H, $^{2}J_{HH}$ = 1.6 Hz, $^{3}J_{HH}$ = $^{3}J_{PH}$ = 13.6 Hz, *cis*-PCC*H*), 6.39 (ddd, 1H, $^{2}J_{HH}$ = 1.6 Hz, $^{3}J_{HH}$ = 15.7 Hz, $^{3}J_{PH}$ = 21.0 Hz, *trans*-PCC*H*), 7.48-7.84 (m, 10H, *aromatics*).

Synthesis of *exo*-cycloaddition products [(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*][5-thio-5-(ethenylphenylphosphino)-2,3-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-2-ene]palladium(II)perchlorate, 55.

Divinylphenylphosphine sulfide **56** (0.6g, 0.003 mols) was added with stirring to a solution of (R_c)-**47** (2.0 g, 0.003 mols) in dichloromethane. The reaction was allowed to stir for 4 days at room temperature. The solvent was removed to yield the compound as dark yellow solid. The product was further purified by means of silica-gel column chromatography using ethyl acetate – *n*-hexanes to yield the *exo*-products as yellow solid upon removal of solvents. (1.7 g, 73.9 %). $^{31}P\{^{1}H\}$NMR $CDCl_3$: 47.03 (s), 47.13 (s), 47.38 (s), 49.29 (s), 113.22 (s), 114.19 (br s, overlap) , 114.53 (s).

Synthesis of dichloro[5-thio-5-(ethenylphenylphosphino)-2,3-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-2-ene]palladium(II), 57.

A solution of the *exo*-products (0.98 g, 0.001 mols) in dichloromethane was treated with excess concentrated hydrochloric acid (2 mL) and stirred vigorously for 1 day. The reaction mixture was washed with water (3 X 10 mL) and further dried using magnesium sulphate .Pale yellow prisms were obtained from dichloromethane – *n*-hexanes (0.22 g, 39.3 %), $^{31}P\{^{1}H\}$NMR CD_2Cl_2 : 47.18 (s, 1H), 111.01 (s, 1H). ^{1}H NMR ($CDCl_3$): δ 1.24 (s, 3H, C=C*Me*), 1.65 (s, 3H, C=C*Me*), 2.82 (m, 1H, S=PCH*CH*$_2$), 3.15 (m, 2H, S=PC*H* + PhPC*H*), 3.4 (m, 1H, PhPC*H*), 6.62 (ddd, 1H, $^{3}J_{HHtrans}$ = 18.0 Hz, $^{3}J_{HHcis}$ = 11.4 Hz, $^{2}J_{PH}$ = 25.5 Hz, S=PC*H* vinylic), 6.32 (ddd, 1H, $^{2}J_{HH}$ = 1.6 Hz, $^{3}J_{HH}$ = $^{3}J_{PH}$ = 17.7 Hz, *cis*-PCC*H*), 6.43 (ddd, 1H, $^{3}J_{HH}$ = 12.1 Hz, $^{3}J_{PH}$ = 34.1 Hz, *trans*-PCC*H*), 7.40-7.69 (m, 10H, *aromatics*). The mother liquor yielded dark yellow crystals from dichloromethane - n-hexanes (0.08g, 14.3 %). $^{31}P\{^{1}H\}$NMR CD_2Cl_2 : 47.50 (s, 1H), 110.39 (s, 1H). ^{1}H NMR (CD_2Cl_2): δ 1.40 (s, 3H, C=C*Me*), 1.68 (s, 3H, C=C*Me*), 2.82 (m, 1H, S=PCH*CH*$_2$), 3.19 (m, 2H, S=PC*H* + PhPC*H*), 3.61 (m, 1H, PhPC*H*), 6.65 (ddd, 1H, $^{2}J_{HH}$ = 1.6 Hz, $^{3}J_{HH}$ = $^{3}J_{PH}$ = 17.7 Hz, *cis*-PCC*H*), 6.75 (ddd, 1H, $^{3}J_{HH}$ = 12.0 Hz, $^{3}J_{PH}$ = 34.3 Hz, *trans*-PCC*H*), 6.87 (ddd, 1H, $^{3}J_{HHtrans}$ = 18.1 Hz, $^{3}J_{HHcis}$ = 11.4 Hz, $^{2}J_{PH}$ = 25.1 Hz, S=PC*H* vinylic),7.40-7.93 (m, 10H, *aromatics*).

Preparation of chloro[(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-*C,N*][di-1-ethynylphosphine]palladium(II), (R_c)-59.

A solution of divinylphenylphosphine (1.30 g , 0.008 moles) and (R_c)-**36** (2.73 g , 0.004 moles) in dichloromethane was stirred for 3hrs. The solvent was removed and the resultant yellow precipitate was purified by chromatography on a silica gel column (ethyl acetate: *n*-hexanes, 3:2) to yield pure compound (R_c)-**59** as yellow solid (1.78 g, 76.9 %). m.p:203°C (dec.). Anal. Calcd for $C_{29}H_{31}ClNPd$: C, 58.9; H, 5.9; N, 2.6. Found: C, 59.3; H, 6.0; N, 2.8. $[\alpha]_{D=}$ - 99.1° (*c* 1.1; CH_2Cl_2). $^{31}P\{^1H\}$NMR $CDCl_3$: δ 25.05 (s, 1P), ^1H NMR ($CDCl_3$) : δ 1.97 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CH*Me*), 2.73 (s, 3H, N*Me*), 2.95 (d, 3H, $^4J_{PH}$ = 3.6 Hz, N*Me*), 4.34 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.0 Hz, C*H*Me), 5.68 (ddd, 1H, $^3J_{HH}$ = 19.0, $^3J_{PH}$ = 18.2, $^2J_{HH}$ = 1.3 Hz, cis –PCC*H*), 5.95 (ddd, 1H, $^3J_{PH}$ = 40.1, $^3J_{HH}$ = 11.5, $^2J_{HH}$ = 1.3 Hz, trans –PCC*H*), 6.14 (ddd, 1H, $^3J_{PH}$ = 40.1, $^3J_{HH}$ = 11.9 , $^2J_{HH}$ = 1.3 Hz, trans- PCC*H*) , 6.48 (ddd, 1H, $^2J_{PH}$ = 20.6, $^3J_{HH}$ = 19.2, $^3J_{HH}$ = 11.5 Hz, PC*H*), 6.68 (ddd, 1H, $^2J_{PH}$ = 20.0, $^3J_{HH}$ = 19.3, $^3J_{HH}$ = 11.9 Hz, PC*H*), 6.81-7.32 (m, 11H, aromatics) .

Synthesis of exo-cycloaddition products [(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*][5-phenyl-1-ethenylphosphino-2,3-dimethyl-7-thio-7-phenyl-7-phosphabicyclo[2.2.1]hept-2-ene]palladium(II)perchlorate, 61.

To a solution of (R_c)-**60** (0.92 g, 0.001 moles) in dichloromethane, DMPPS **45** (0.30 g, 0.001 moles) was added and stirred at room temperature for 3 days. The

dichloromethane was removed to yield a dark yellow solid which was further purified by column chromatography using silica gel (4: 1, ethyl acetate: *n*-hexanes) to yield the products as yellow solid upon removal of eluents (0.42 g, 62.0 %). $^{31}P\{^{1}H\}$NMR $CDCl_3$: δ 50.08 (s, 1P) , 54.51(s, 1P), 56.67 (s, 1P), 59.18 (s, 1P) , 76.61 (s, 1P) , 77.14 (s, 1P), 78.56 (s, 1P), 79.15 (s, 1P).

Preparation of dichloro[5-phenyl-1-ethenylphosphino-2,3-dimethyl-7-thio-7-phenyl-7-phosphabicyclo[2.2.1]hept-2-ene P^5,P^7]palladium(II), (R_p,S_p)-62b.

A solution containing mixture of complexes **61** (0.38g, 0.0005 moles) in dichloromethane was stirred vigorously with excess hydrochloric acid for 24 hrs . The reaction mixture was then washed with water (3 X 10 mL) and dried using magnesium sulphate . A pale yellow solid was obtained on removal of solvents. Fractional crystallization using dichloromethane- diethyl ether yielded pale yellow prisms (0.19 g, 61.4 %). $[\alpha]_D$ = +53.26° (*c*0.4, CH_2Cl_2) m.p : 254°C (dec.), $^{31}P\{^{1}H\}$NMR $CDCl_3$: 42.39 (s, 1H), 77.55 (s, 1H). ^{1}H NMR ($CDCl_3$): δ 1.41 (s, 3H, C=C*Me*), 1.64 (s, 3H, C=C*Me*), 2.43 (m, 1H, PCH*CH*$_2$), 3.29 (m, 1H, PhPC*H*), 3.33 (m, 1H, S=PC*H*), 3.59 (m, 1H, S=PC*H*), 6.12 (ddd, 1H, $^{3}J_{HHtrans}$ = 19.6Hz, $^{3}J_{HHcis}$ = 12.4 Hz, $^{2}J_{PH}$ = 26.0 Hz, PhPC*H* vinylic), 6.28 (ddd, 1H, $^{2}J_{HH}$ = 1.5 Hz, $^{3}J_{HH}$ = $^{3}J_{PH}$ = 18.2 Hz, *cis*-PCC*H*), 6.39 (ddd, 1H, $^{3}J_{HH}$ = 12.4 Hz, $^{3}J_{PH}$ = 35.0 Hz, *trans*-PCC*H*), 7.38-8.12 (m, 10H, *aromatics*)

Decomplexation of [5-phenyl-1-ethenylphosphino-2,3-dimethyl-7-thio-7-phenyl-7-phosphabicyclo[2.2.1]hept-2-ene P^5,P^7], (S_p,S_p)-63.

To the solution of dichloro complex (R_p,S_p)-**62b** (0.06 g) in dichloromethane (10 mL), an aqueous solution of potassium cyanide (0.3 g) was added under a nitrogen atmosphere, and the resulting solution was stirred vigorously for 3 h. The aqueous phase was separated, and the organic layer was washed with water (3x 5 mL) and dried over magnesium sulfate. Removal of the solvent under vacuum gave ligand (S_p,S_p)-**63** as an air-sensitive colourless oil in 68 % yield (0.028 g); $[\alpha]_D$= -11.54 ° (*c* 0.1, CH_2Cl_2) , $^{31}P\{^1H\}$ NMR ($CDCl_3$) : δ 32.65 (s), 65.21 (s).

Synthesis of diphenylvinylarsine, 65.

Sodium diphenylarsenide was prepared by addition of Na metal (1.50 g, 65.0 mmoles) to a stirring solution of diphenylarsine (5.00 g, 22.0 mmoles) in dried THF (100 mL) for 1 d. The sodium diphenylarsenide salt was added drop wise (over 1 hr.) to the vinylbromide (2.60 g, 24.0 mmoles) solution in THF which was cooled to -96°C (acetone/dry ice bath). The reaction mixture was allowed to reach ambient temperature and further refluxed for 3 hr. and left to stir overnight. The excess THF was distilled off and hydrolyzed with saturated ammonium chloride and extracted with diethyl ether. The organic layer was separated and dried over magnesium sulphate. The solvent was removed completely and the pale yellow oil obtained was distilled under reduced pressure. The product was obtained as a colorless viscous oil : yield 4.26 g (77%), bp 118-130°C at 0.2 mmHg, ^1H NMR ($CDCl_3$) : δ 5.64 (dd, 1H, $^3J_{HH}$ = 18 Hz (trans), $^2J_{HH}$ = 1.7 Hz (vicinal) AsCH=C*H*$_2$ (cis to As)), 6.00 (dd, 1H, $^3J_{HH}$ = 11 Hz (cis), $^2J_{HH}$ = 1.6 Hz

(vicinal) AsCH=CH_2 (trans to As)), 6.73 (dd, 1H, $^3J_{HH}$ = 19 Hz (trans), $^3J_{HH}$ = 11 Hz (cis), AsC*H*=CH_2), 7.14 – 7.36 (m, 10H, aromatics).

Synthesis of exo-cycloadduction products [(*R*)-1-[1-(dimetylamino)ethyl]-2-naphthyl-*C,N*][5-diphenylarsino-2,3-dimethyl-7-phenyl-7-thio-7-phosphabicyclo[2.2.1]hept-2-ene]palladium(II)perchlorate, (R_c,R_p)-67 and (R_c,S_p)-67.

To a solution of (R_c)-**51** in dichloromethane (1.23 g, 0.003 moles) , DMPPS **45** (0.58 g, 0.003 moles) and diphenylvinylarsine **65** (0.67 g, 0.003 moles) was added and left to stir for 3 days. The solvent was removed under reduced pressure to give a yellow residue. Purification was carried out by silica-gel column chromatography with ethyl acetate – *n*-hexanes (3:1 v/v) as eluent to give the diastereomeric complexes of the product (1.7 g, 83.0 %). $^{31}P\{^1H\}$ NMR ($CDCl_3$) : δ 77.55 (s) , 79.69 (s).

Synthesis of dichloro[5-diphenylarsino-2,3-dimethyl-7-phenyl-7-thio-7-phosphabicyclo[2.2.1]hept-2-ene]palladium(II), (R_p)-68 and (S_p)-68.

A solution of the diastereomers, (R_c,R_p)-**67** and (R_c,S_p)-**67** (1.0 g, 0.002 moles) in dichloromethane was stirred vigorously with excess concentrated dichloromethane (5 mL) for 8 hrs at room temperature. The excess acid was washed off with water (3 X 10 mL) and the organic layer was dried using magnesium sulphate. After removal of solvents under reduced pressure a yellow solid was obtained (0.72 g, 85.6 %). Anal. Calcd for $C_{30}H_{36}Cl_2SPAs$: C, 49.5 ; H, 4.9; S, 4.8. Found: C, 49.6 ; H, 4.6; S, 4.5, $^{31}P\{^1H\}$ NMR ($CDCl_3$) : δ 77.99, ^1H NMR ($CDCl_3$) : δ 1.58 (s, 3H, C=C*Me*), 1.66 (s, 3H,

C=C*Me*), 2.55 (m, 1H, AsC*H*), 2.82 (m, 3H, AsCHCH_2 + S=PC*H*), 3.23 (m, 1H, S=PC*H*) , 7.47-8.03 (m, 15H, *aromatics*).

Synthesis of dichlorophenylarsine.
(slight modification of literature procedure).[189]

Phenylarsonic acid (10g) was dissolved in concentrated hydrochloric acid (17 mL), in a separating funnel. Few crystals of iodine (54 mg) were added and sulfur dioxide was bubbled through the solution until separation of the product ceased. The lower layer (dark red) was collected under nitrogen and dried using molecular sieves (4A) overnight. The crude (pale yellow oil) was distilled under vacuum to give the pure product as pale yellow solution. Yield 9.02 g (82 %), bp 82-90° C at 0.8 mm Hg. ^{1}H NMR ($CDCl_3$): 7.52-7.88 (m, 5H, aromatics).

Synthesis of divinylphenylarsine, 69.

Vinylbromide (5.0g, 47 moles) in THF (100 mL) was added drop wise to magnesium turnings (vacuum dried with dry stirring for 8 hrs)(2.0 g, 83 moles), in THF (20 mL). The grignard generated was stirred at room temperature for 1hr. Excess THF (100 mL) was added to the reaction mixture to prevent solidification of the generated grignard. The grignard was then filtered into a dropping funnel and added dropwise (over 1.5 hrs) to a cooled (- 78 ° C) solution of dichlorophenylarsine in THF (100mL). The reaction mixture was allowed to reach ambient temperature and stirred overnight. The solvent was completely removed and the residue (dark red oil) was distilled under reduced pressure. The product was obtained as colorless viscous oil :

Yield 2.89 g (77 %), bp 58-61° C at 0.2 mm Hg. ^{1}H NMR ($CDCl_3$) : 5.66 (dd, 2H, $^{3}J_{HH}$ =19Hz , trans, $^{2}J_{HH}$ =1.6 Hz (vicinal) As-CH=C*H*$_2$ *(cis* to As*), 5.93* (dd, 2H, $^{3}J_{HH}$ = 11Hz (*cis*), $^{2}J_{HH}$ = 1.6Hz (vicinal*)* As-CH=*CH*$_2$*(trans* to As) *, 6.57*(dd, 2H, $^{3}J_{HH}$ =19Hz (*trans*) $^{3}J_{HH}$ = 11Hz (*cis*) AsC*H*=CH2, 7.16-7.41(m, 5H, *aromatics*).

Synthesis of exo-cycloaddition products [(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*][5-phenyl-1-ethenylarsino-2,3-dimethyl-7-thio-7-phenyl-7-phosphabicyclo[2.2.1]hept-2-ene]palladium(II)perchlorate, 70.

To a solution of (R_c)-**51** in dichloromethane (1.80 g, 0.004 moles), DMPPS **45** (0.84 g, 0.004 moles) and divinylphenylarsine **69** (0.78 g, 0.78 moles) was added and reaction was left stirring for 5 days at room temperature. A dark red solution was obtained which yielded the mixture of products on removal of solvents as dark red solid. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 76.86 (s), 77.27 (s), 78.87 (s), 79.34 (s) .

Synthesis of dichloro[5-phenyl-1-ethenylarsino-2,3-dimethyl-7-thio-7-phenyl-7-phosphabicyclo[2.2.1]hept-2-ene]palladium(II), 71.

A solution of the *exo*-cycloadducts **70** in dichloromethane (0.99 g, 0.001 moles) was treated with excess concentrated hydrochloric acid (5 mL) and stirred vigorously for 8 hrs. The reaction mixture was then washed with water (3 X 10 mL) dried using magnesium sulphate and solvent removed to yield crude product as dark yellow solid. The material was crystallized from dichloromethane – *n*-hexanes as pale yellow prisms

(0.22 g, 27 %). Anal. Calcd for $C_{22}H_{24}AsCl_2PPdS$: C, 43.9 ; H, 4.0; S, 5.3. Found: C, 43.9; H, 4.2; S, 5.2. $^{31}P\{^1H\}$NMR CD_2Cl_2 : 77.64 (s, 1H) . ^1H NMR (acetone-d_6): δ 1.69 (s, 3H, C=C*Me*), 1.72 (s, 3H, C=C*Me*), 3.12 (m, 1H, AsCH*CH₂*), 3.52 (m, 2H, PhAsC*H* + S=PC*H*), 3.56 (m, 1H, S=PC*H*), 6.41 (d , 1H, $^3J_{HH}$ = 11.2 Hz, *trans* -AsCH=C*H*) , 6.46 (d , 1H, $^3J_{HH}$ = 18.5 Hz, *cis*-AsCH=C*H*), 6.98 (dd, 1H, $^3J_{HH}$ = 18.1 Hz, $^3J_{HH}$ = 11.4 Hz , AsC*H*=CH_2) 7.53-8.22 (m, 10H, *aromatics*).

Synthesis of 3-diphenylphosphanyl-but-3-en-1-ol, 72.

Diphenylphosphide ion was generated by addition of diphenylphosphine (2.79 g, 0.016 moles) with stirring to a schlenk flask containing sodium metal (0.37 g, 0.016 moles) in THF (100 mL). The mixture was left to stir overnight. A solution of n-butyllithium in hexane (15% in hexane, 10.11 mL, 0.0162 moles) was added to 3-butyn-1-ol (1.22 mL, 0.0162 moles) in THF with stirring. The diphenylphosphide solution generated previously was then added to this solution drop wise with vigorous stirring at 0° C. The reaction mixture was allowed to reach room temperature and stirred for 5 days. The solvent was then distilled off to leave a dark brown slurry to which brine (150 mL) was added. The mixture was subsequently extracted with dichloromethane (3 X 100 mL). The organic layer was then dried with magnesium sulphate and solvent removed by distillation to give a dark yellow oil. The crude product was purified by means of silica gel column chromatography using 20% ethyl acetate in hexane under purified nitrogen. The product was collected as the first fraction which gave a yellow oil on removal of eluents (1.78 g, 43.2 %). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -3.36 (s).

Preparation of chloro[(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-*C,N*][3-diphenylphosphanyl-but-3-en-1-ol] platinum(II), (R_c)-74.

A solution of 3-diphenylphosphanyl-but-3-yn-1-ol **72** (1.75 g, 0.007 moles) in dichloromethane was added drop wise with stirring to (R_c)-**43** (3.00g, 0.003 moles) in dichloromethane. The reaction mixture was allowed to stir for 6 hrs at room temperature. A dark yellow solid was obtained on removal of solvents under reduced pressure (3.35 g, 69.9 %). $[\alpha]_D$ = +28.9° (*c* 0.5, CH_2Cl_2). mp: 223-226°C, Anal. Calcd for $C_{31}H_{35}Cl_3NP1OPt$: C, 48.47 ; H, 4.6; N, 1.8 Found: C, 48.7; H, 4.7; N, 1.8. $^{31}P\{^1H\}$ NMR ($CDCl_3$) : δ 22.14 (s, $^1J_{PtP}$ = 4182.8 Hz), ^{1}H NMR ($CDCl_3$): δ 1.97 (d, 3H, $^2J_{HH}$ = 2.6 Hz, CH*Me*), 2.91 (d, 3H, $^3J_{PH}$ = 0.8 Hz , N*Me*), 3.01 (d, 3H, $^3J_{PH}$ = 1.3 Hz, N*Me*), 4.00 (m, 2H, CH_2CH$_2$OH), 4.48 (m, 2H, CH$_2$CH_2OH), 4.6(qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.4 Hz, C*H*Me),), 5.19 (d, $^3J_{PH}$ = 16.4 Hz , *cis*-PC=CH_2), 5.95 (d, $^3J_{PH}$ = 33.7 Hz, *trans*-PC=CH_2), 6.49 – 8.14 (m, 16 H, *aromatics*).

Synthesis of [(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-*C,N*][(4*R*,7*S*)-5,6-dimethyl-7-phenyl-2-(diphenylphosphino)-7-phosphabicyclo[2.2.1]hept-5-en-2-yl ethanol]palladium(II) perchlorate, (R_c,S_p)-76.

To a solution of (R_c)-**74** (3.00 g , 0.004 moles) in dichloromethane , silver perchlorate (1.04 g, 0.005 moles) in water (3 mL) was added and stirred vigorously for 30 mins to ensure through mixing. The reaction mixture was then washed with water (3 X 10 mLs) to remove the excess perchlorate and the extracted organic layer was dried using

magnesium sulphate. A yellow solid was obtained on removal of solvents (3.01 g, 91.1 %). A solution of DMPP **44** (0.79g, 0.004 moles) in dichloromethane was added dropwise to the percholato complex (R_c)-**75** (3.01 g, 0.004 moles) in dichloromethane and allowed to stir at room temperature for 8 hrs. The reaction mixture was subsequently concentrated and layered with n-hexanes to yield yellow crystals (2.98 g, 79.7 %). $[\alpha]_D$ = -147.05° (*c* 0.7, CH_2Cl_2).m.p: 236-238°C, Anal. Calcd for $C_{42}H_{46}ClNO_5P_2Pt$: C, 53.8 ; H, 4.9; N, 1.5 Found: C, 53.6; H, 4.9; N, 1.4. $^{31}P\{^1H\}$ NMR ($CDCl_3$) : δ 39.62 (d, 1P, $^1J_{Pt\text{-}P}$ = 3567.4 Hz, $^3J_{PP}$ = 22.8 Hz), 115.45 (d, 1P, $^1J_{Pt\text{-}P}$ = 1580.4 Hz, $^3J_{PP}$ = 22.8 Hz). ^1H NMR (CD_2Cl_2) : δ 1.41 (s, 3H, C=C*Me*), 1.86 (s, 3H, C=C*Me*), 1.87 (d, 3H, $^2J_{HH}$ = 6.0 Hz, CH*Me*), 2.51 (s, 3H, N*Me*), 2.65 (m, 2H, Ph_2PC*CH2*), 2.95 (s, 3H, N*Me*), 3.18 (m, 2H,CH_2CH$_2$OH), 3.37 (m, 2H, CH_2CH_2OH), 3.41 (m, 1H, PhPC*H*), 3.47 (m, 1H, PC*H*), 4.73 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.0 Hz, C*H*Me), 6.64 – 8.48 (m, 21H, *aromatics*).

Synthesis of dichloro[(4*R*,7*S*)-5,6-dimethyl-7-phenyl-2-(diphenylphosphino)-7-phosphabicyclo[2.2.1]hept-5-en-2-yl ethanol]palladium(II), (S_p)-77.

A solution of the complex (R_c,S_p)-**76** (2.53 g, 0.003mols) in dichloromethane was stirred vigorously with concentrated hydrochloric acid (3mL) for 8 hrs. The resultant mixture was then washed with water (3 X 20 mL) and the organic layer dried with magnesium sulphate. Upon removal of solvents a pale yellow solid was obtained which yielded pale yellow microcrystals from dichloromethane-*n*-hexanes (1.88 g, 89.5

%). $[\alpha]_D$ = -36.2° (*c* 0.4, CH_2Cl_2), m.p: 288°C (decomp.), Anal. Calcd for $C_{28}H_{30}Cl_2OP_2Pt$: C, 47.4 ; H, 4.3 Found: C, 47.6 ; H, 4.6. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 35.59 (d, 1P, $^1J_{PtP}$ = 3435.2 Hz, J_{PP} = 19.0 Hz), 94.96 (d, 1P, $^1J_{PtP}$ = 3191.9 Hz, J_{PP} = 19.0 Hz). ^1H NMR ($CDCl_3$): δ 1.27 (s, 3H, C=C*Me*), 1.71 (s, 3H, C=C*Me*), 2.89 (m, 2H, $Ph_2PCC\mathit{H}_2$), 3.13 (m, 2H, $C\mathit{H}_2CH_2OH$), 3.19 (m, 2H, $CH_2\mathit{H}_2OH$) 3.44 (m, 1H, PhPC*H*), 3.52 (m, 1H, PhPC*H*), 7.47 – 8.26 (m, 15H, *aromatics*).

Decomplexation of [(4*R*,7*S*)-5,6-dimethyl-7-phenyl-2-(diphenylphosphino)-7-phosphabicyclo[2.2.1]hept-5-en-2-yl ethanol], (R_p)-78.

A solution of potassium cyanide (0.45 g, 7.00 mmols) in water (2 mls) was added to a solution of the complex (S_p)-**77** (0.05 g, 0.07 mmols) in dichloromethane (20 mL) and stirred vigorously to ensure through mixing. The reaction was complete in 4 hrs. The organic layer was washed with water (3 X 5 mL) and then dried with magnesium sulphate. A pale yellow oil was obtained on complete removal of solvents (0.018 g, 57.6 %). [α]$_D$ = +38.5 (*c* 0.1, CH_2Cl_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) : 35.34 (d, $^3J_{PP}$ = 26.5 Hz), 98.46 (d, $^3J_{PP}$ = 26.5 Hz).

A solution of the freshly released ligand in dichloromethane (0.007 g, 0.02 mmols) was added with stirring to a solution of complex **43**(0.007 g, 0.008 mmols) in dichloromethane and silver perchlorate (1.86 g, 0.009 mmols) in water . The reaction mixture was stirred at room temperature for 30 mins and then washed with water (3 X 5 mL) , dried with magnesium sulphate and then the organic layer dried to obtain a yellow solid. $^{31}P\{^1H\}$ NMR was identical to (R_c,S_p)-**76**.

Synthesis of 2-diphenylphosphanyl-prop-2-en-1-ol , 73.

Sodium metal (0.37 g, 0.016 moles) was placed in a 250 mL schlenk flask containing THF (100 mL). This was followed by the addition of diphenylphosphine (2.79 g, 0.016 moles) with stirring. The mixture was left to stir overnight and was observed to turn to a deep-red color characteristic of the diphenylphosphide ion. Propargyl alcohol (0.94 mL, 0.016 moles) was then placed in a 500 mL Schlenk flask with THF (100 mL). To this solution, *n*-butyllithium (15 % solution in hexane) (0.01618, 9.86 mL) was added with stirring. Following this the sodium diphenylphosphide generated was then transferred drop wise into the shclenk flask with stirring at 0° C. The react mixture was allowed to reach room temperature and further stirred over three days. Most of the THF was then distilled off followed by addition of brine (150 mL) to the residue. The mixture was then extracted three times, each time with 100 mL of dichloromethane. The organic layer was subsequently extracted and dried with magnesium sulphate and solvent removed via distillation, leaving a highly viscous dark red oil. The crude product was purified via elution through a silica-gel column using 20% v/v ethyl acetate: n-hexanes as eluent, under an inert atmosphere. The recovered product was pale yellow oxygen sensitive oil (2.87 g, 73.4 %). ^{31}P NMR ($CDCl_3$): δ - 9.20.

Synthesis of chloro[(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-*C,N*][2-diphenylphosphanyl-prop-2-en-1-ol] platinum(II), (R_c)-79.

A solution of 2-diphenylphosphanyl-prop-2-en-1-ol (1.99 g, 0.008 moles) in dichloromethane (20 mL) was added drop wise with stirring to a solution of complex (R_c)-**43**(3.5 g, 0.004 moles) in dichloromethane. The reaction was allowed to stir for 6 hrs after which solvent was removed under reduced pressure to give the crude product as yellow solid. The crude product was purified *via* silica gel column chromatography using (dichloromethane: *n*-hexanes, 3:1 v/v followed by acetone: dichloromethane, 1:1 v/v). The pure product was crystallized from dichloromethane: diethyl ether as yellow prisms. (1.98 g, 73.9 %). $[\alpha]_D$ = +55.0° (*c* 0.2, CH_2Cl_2), m.p: 240-241°C, Anal. Calcd for $C_{29}H_{31}ClNOPPt$: C, 51.9; H, 4.6; N, 2.1 Found: C, 51.9; H, 4.7; N, 2.2. $^{31}P\{^1H\}$ NMR ($CDCl_3$) : δ 19.81 (s, 1P, $^1J_{Pt\text{-}P}$ = 4243.6 Hz). ^1H NMR ($CDCl_3$) : δ 1.95 (d, 3H, $^2J_{HH}$ = 6.4 Hz, CH*Me*) , 2.85 (d, 3H, $^3J_{PH}$ = 0.8 Hz, N*Me*), 3.18 (d, $^3J_{PH}$ = 1.3 Hz, N*Me*), 4.09 (m, 2H, CH_2OH), 4.61 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.4 Hz, C*H*Me), 5.19 (d, $^3J_{PH}$ = 17.7 Hz , *cis*-PC=CH_2), 6.08 (d, $^3J_{PH}$ = 36.1 Hz, *trans*-PC=CH_2), 6.68 – 8.26 (m, 16 H, *aromatics*).

Synthesis of [(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-*C,N*][(4*R*,7*S*)-5,6-dimethyl-7-phenyl-2-(diphenylphosphino)-7-phosphabicyclo[2.2.1]hept-5-en-2-yl methanol]palladium(II) perchlorate, (R_c,S_p)-81.

To complex (R_c)-**79** (1.50 g, 0.002 moles) in dichloromethane , silver perchlorate (0.62 g, 0.003 moles) in distilled water (2 mL) added and the reaction mixture was stirred vigorously at room temperature for 30 mins. The crude product was passed through celite to remove the AgCl precipitate formed and subsequently washed with water (3 X 50 mL) and dried using magnesium sulphate . Removal of solvents gave the perchlorato complex (R_c)-**80**, as yellow solid (1.38 g, 93.8 %). A solution of the perchlorato complex (1.35 g, 0.002 moles) in dichloromethane was treated with DMPP **44** (0.37 g, 0.002 moles). The mixture was allowed to stir at room temperature for 8 hrs to yield a yellow solution. Pale yellow needle like crystals were obtained using a crystallizing solvent system consisting of acetonitrile- diethyl ether (1.34 g, 81.2 %). $[\alpha]_D$ = +4.43° (*c* 0.3, CH_2Cl_2), m.p: 253-245°C, Anal. Calcd. for $C_{41}H_{44}ClNO_5P_2Pt$: C, 53.4 ; H, 4.8; N, 1.5 Found: C, 52.9; H, 4.6; N, 1.7. $^{31}P\{^1H\}$ NMR ($CDCl_3$) : δ 42.04 (d, 1P, $^1J_{Pt\text{-}P}$ = 3591.9 Hz, J_{PP} = 22.8 Hz), 117.82 (d, 1P, $^1J_{Pt\text{-}P}$ = 1586.1 Hz, J_{PP} = 19.0 Hz) . ^1H NMR ($CDCl_3$) : δ 1.42 (s, 3H, C=C*Me*), 1.81 (s, 3H, C=C*Me*), 1.94 (d, 3H, $^2J_{HH}$ = 6.0 Hz, CH*Me*), 2.55 (s, 3H, N*Me*), 2.83 (m, 2H, Ph_2PCCH2), 3.03 (s, 3H, N*Me*), 3.67 (m, 2H, CH_2OH), 3.78 (m, 1H, PC*H*), 3.95 (m, 1H, PC*H*), 4.73 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.4 Hz, C*H*Me), 6.66 – 8.78 (m, 21H, *aromatics*).

Synthesis of dichloro[(4*R*,7*S*)-5,6-dimethyl-7-phenyl-2-(diphenylphosphino)-7-phosphabicyclo[2.2.1]hept-5-en-2-yl methanol]palladium(II) perchlorate, (S_p)-82.

A solution of the complex (R_c,S_p)-**81** (1.02 g, 0.001 moles) in dichloromethane was treated with concentrated hydrochloric acid (5 mLs), and allowed to stir vigorously for 8 hrs at room temperature. The resultant solution was washed with water (3 X 20 mL) and the organic layer dried with magnesium sulphate. Upon filtration and subsequent removal of solvents a pale yellow solid was obtained. Crystallization using dichloromethane – *n*-hexanes yielded pale yellow prisms (0.7888 g, 91.5 %). $[\alpha]_D$ = -24.7° (*c* 0.3, CH_2Cl_2) , m.p: 230°C (decomp.), Anal. Calcd for $C_{27}H_{28}OCl_2P_2Pt$: C, 46.6 ; H, 4.0 Found: C, 46.8; H, 4.0. $^{31}P\{^1H\}$ NMR ($CDCl_3$) : δ 32.67 (d, 1P, $^1J_{PtP}$ = 3447.6, J_{PP} = 19.0 Hz), 94.52 (d, 1P, $^1J_{PtP}$ = 3225.9, J_{PP} = 19.0 Hz). 1H NMR (CD_2Cl_2): δ 1.51 (s, 3H, C=C*Me*), 1.69 (s, 3H, C=C*Me*), 2.91 (m, 2H, $Ph_2PCC\mathit{H}_2$), 3.13 (d, 2H, $C\mathit{H}_2OH$), 3.43 (m, 1H, PhPC*H*), 3.89 (m, 1H, PhPC*H*), 7.52 – 8.29 (m, 15H, *aromatics*).

Decomplexation of [(4*R*,7*S*)-5,6-dimethyl-7-phenyl-2-(diphenylphosphino)-7-phosphabicyclo[2.2.1]hept-5-en-2-yl methanol], (R_p)-83.

A solution of the complex (S_p)-**82** in dichloromethane (0.05 g, 0.075 mmols) in dichloromethane (10 mL) was thoroughly stirred for 3 hrs with an excess of potassium cyanide (0.24 g , 7.460 mmols) in water (1 mL) . The organic layer was separated, washed with water (3 X 10 mL) and dried over magnesium sulphate. Removal of the solvent left colorless air sensitive oil (0.018 g, 56.2 %). [α]$_D$ = -52.4 (*c* 0.1, CH_2Cl_2),

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$) : δ 19.21 (d, 1P, $^{3}J_{PP}$ = 113.9 Hz), 108.89 (d, 1P, $^{3}J_{PP}$ = 113.9 Hz).

A solution of the freshly released ligand (R_p)-**83** (0.005 g, 0.011 mmols) in dichloromethane was added to a solution of complex (R_c)-**43** (0.005 g, 0.006 mmols) in dichloromethane (10 mL) and silver perchlorate (0.004 g, 0.022 mmols) in water (2 mL) with vigorous stirring . The reaction mixture was left to stir for 30 mins and subsequently washed with water (3 X 10 mL) and the organic layer dried with magnesium sulphate to yield the product as yellow solid. $^{31}P\{^{1}H\}$NMR ($CDCl_3$) was identical to the complex (R_c,S_p)-**81**.

Synthesis of chloro[(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*][3-(diphenylphosphino)but-3-en-1-ol], (R_c)-84.

To a solution of complex (R_c)-**36** in dichloromethane (1.88 g, 0.003 mols), 3-diphenylphosphanyl-but-3-yn-1-ol (1.41 g, 0.005 mols) in dichloromethane was added drop wise with stirring. The reaction mixture was allowed to stir for 8 hrs and then the solvent removed under reduced pressure to give a yellow solid (1.95 g, 95.6 %) m.p: 220-223°C, Anal. Calcd for $C_{30}H_{33}NClPOPd$: C, 60.4; H, 5.5; N, 2.4 Found: C, 60.4, H, 5.9, N, 2.4. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) : δ 40.59 (s). ^{1}H NMR ($CDCl_3$) : δ 2.07 (d, 3H, $^{2}J_{HH}$ = 6.4 Hz, CH*Me*), 2.72 (s, 3H, N*Me*), 2.98 (s, 3H, N*Me*), 3.98 (m, 2H, C$H_2$$CH_2$OH), 4.09 (m, 2H, $CH_2$$CH_2$OH), 4.37 (qn, 1H, $^{3}J_{HH}$ = $^{4}J_{PH}$ = 6.0 Hz , C*H*Me), 5.39 (d, 1H, $^{3}J_{PH}$ = 17.2 Hz, *cis*-PC=CH_2), 5.91 (d, 1H, $^{3}J_{PH}$ = 35.3 Hz, *trans*-PC=CH_2), 6.54 – 8.17 (m, 16H, *aromatics*).

Synthesis of [(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*][(*R*)3,4-bis(diphenylphosphino)butan-1-ol]palladium(II)perchlorate, (R_c,R_c)-87a.

A solution of complex (R_c)-**84** (1.56 g, 0.002 mols) in dichloromethane was treated with aqueous silver perchlorate (0.63 g, 0.003 mols) for 30 mins. The reaction mixture was subsequently washed with water (3 X 20 mL) and the organic layer dried using magnesium sulphate. Upon removal of solvent, perchlorato complex (R_c)-**85** was obtained as yellow solid (1.39 g, 94.5%). To (R_c)-**85** (1.39 g, 0.002 moles) in dichloromethane, diphenylphosphine (0.35 g, 0.002 moles) was added with stirring at -78° C. The temperature was maintained for 10 hrs and subsequently stirred at room temperature for 24 hrs to obtain a dark red solid upon solvent removal. Pale yellow crystals were obtained on crystallization using dichloromethane- diethyl ether (1.32 g, 78.0 %). $[\alpha]_D$ = -8.9° (*c* 1.4, CH_2Cl_2), m.p: 229-231°C (decomp.), Anal. Calcd for $C_{43}H_{46}Cl_3NO_5P_2Pd$: C, 55.5 ; H, 4.9; N, 1.5 , Found: C, 55.7; H, 5.2; N, 1.4. , $^{31}P\{^1H\}$ NMR ($CDCl_3$): 39.29 (d, 1P, J_{PP} = 26.6Hz), 76.06 (d, 1P, J_{PP} = 26.6 Hz). ^1H NMR ($CDCl_3$): 1.15 (m, 1H, $Ph_2P^1CH'HCH$), 1.38 (m, 1H, $Ph_2P^1CH'HCH$), 2.09 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CH*Me*), 2.41 (s, 3H, N*Me*), 2.71 (s, 3H, N*Me*), 2.91 (m, 1H, P^2CHCH_2), 3.07 (ddd, 2H, $^3J_{HH}$ = 3.2 Hz, $^3J_{HH}$ = 11.05, $^3J_{PH}$ = 17.55), 3.53 (m, 2H, CH_2CH_2OH), 4.52 (qn, 1H, $^3J_{HH}$ = 4JPH = 6.0Hz, C*H*Me), 6.81 – 8.47 (m, 26H, *aromatics*).

Synthesis of dichloro[(*R*)3,4-bis(diphenylphosphino)butan-1-ol]palladium(II), (R_c)-88.

A solution of the complex (R_c,R_c)-**87a** (0.99 g, 0.001 mols) in dichloromethane was stirred with concentrated hydrochloric acid (5 mL) for 8 hrs. The excess acid was then removed by washing with water (3 X 20 mL) and the organic layer dried using magnesium sulphate. Upon removal of solvent a pale yellow solid was obtained. Crystallization from dichloromethane- *n*-hexanes yielded pale yellow prisms (0.62 g, 86.1%). $[\alpha]_D$ = +37.5° (*c* 0.2, CH_2Cl_2). m.p: 214-217°C. Anal. Calcd. for $C_{29}H_{30}Cl_4OP_2Pd$: C, 49.4 ; H, 4.3, Found: C, 49.9; H, 4.7. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 51.05 (d, 1P, J_{PP} = 7.5 Hz), 71.34 (d, 1P, J_{PP} = 7.5 Hz). ^1H NMR (CD_2Cl_2) : 0.86 (m, 1H, P^1CHH'), 0.94 (m, 1H, P^1CHH'), 2.87 (ddd, $^3J_{HH}$ = 4.8 Hz, $^3J_{HH}$ = 12.4 Hz, $^3J_{PH}$ = 14.7 Hz).

Decomplexation of (*R*)-3,4-bis(diphenylphosphino)butan-1-ol, (R_c)-89.

A solution of the complex (R_c)-**88** (0.03 g, 0.05 mmol) in dichloromethane was stirred vigorously with aqueous potassium cyanide (0.16 g, 0.24 mmol) for 2 hrs. The organic layer was separated and washed with water (3 X 10 mL) and then dried with magnesium sulphate. A pale yellow oil was obtained on removal of solvents under reduced pressure (0.01 g, 57.2 %). $[\alpha]_D$ = +64.9 (*c* 0.2, CH_2Cl_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) : - 19.31 (d, $^3J_{PP}$ = 19.0 Hz), -0.172 (d, $^3J_{PP}$ = 19.0 Hz).

A solution of the freshly prepared free ligand (R_c)-**89** (0.1g, 0.02 mmol) in dichloromethane was added with stirring to a solution of complex (R_c)-**51** (0.01 g, 0.02 mmol) in dichloromethane. The reaction mixture was allowed to stir for 1hr at room temperature. The solvent was removed under reduced pressure to yield a yellow solid. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 39.65 (d, 1P, $^{3}J_{PP}$ = 22.8 Hz), 47.91 (d, 1P, $^{3}J_{PP}$ = 30.4 Hz), 50.23 (d, 1P, $^{3}J_{PP}$ = 30.4 Hz), 76.89 (d, 1P, $^{3}J_{PP}$ = 22.8 Hz).

Synthesis of chloro[(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*][2-(diphenylphosphino)prop-2-en-1-ol], (R_c)-90.

To a solution of complex (R_c)-**51** in dichloromethane (2.04 g, 0.003 mols), 2-dipenylphosphanyl-prop-2-en-1-ol (1.45 g, 0.006 mols) in dichloromethane was added drop wise with stirring. The reaction was allowed to stir for 8 hrs and then the solvent removed under reduced pressure to give a yellow solid. Crystallization using acetonitrile- diethyl ether gave yellow prisms (1.87 g, 93.0 %). $[\alpha]_D$ = -38.7° (*c* 0.3, CH_2Cl_2), m.p: 211-213°C, Anal. Calcd for $C_{29}H_{31}ClNOPPd$: C, 59.8 ; H, 5.3; N, 2.4 , Found: C, 60.0; H, 4.9; N, 2.5. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) : δ 38.65 (s). ^{1}H NMR ($CDCl_3$) : δ 2.02 (d, 3H, $^{2}J_{HH}$ = 6.4 Hz, CH*Me*), 2.80 (s, 3H, N*Me*), 2.98 (s, 3H, N*Me*), 4.12 (m, 2H, CH_2OH), 4.37 (qn, 1H, $^{3}J_{HH} = {}^{4}J_{PH}$ = 6.0 Hz , C*H*Me), 5.16 (d, 1H, 3JPH = 16.9 Hz, *cis*-PC=CH_2), 6.02 (d, 1H, 3JPH = 33.7 Hz, *trans*-PC=CH_2), 6.56 – 8.12 (m, 16H, *aromatics*).

Synthesis of [(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*][2,3-bis(diphenylphosphino)propan-1-ol]palladium(II)perchlorate, (R_c,R_c)-92a and (R_c,S_c)-92b.

To a solution of the complex (R_c)-**90** (1.57 g, 0.003 mols) in dichloromethane , silver perchlorate (0.83 g, 0.004 mols) in water (4 mL) was added and stirred for 30 mins at room temperature. The reaction mixture was then washed with water (3 X 20 mL) and dried with magnesium sulphate to yield the perchlorato complex (R_c)-**91** (1.82 g, 94.3 %). A solution of the perchlorato complex in dichloromethane (1.82 g, 0.003 mols) was cooled to -78 ° C and subsequently treated with diphenylphosphine (0.52 g, 0.003 mols) and the temperature was maintained for 10 hrs and then stirred at room temperature for further 48 hrs to give a dark red solid upon removal of solvents under reduced pressure. Crystallization employing dichloromethane-*n*-hexane gave yellow prisms (0.99 g, 39 %).Anal. Calcd for $C_{41}H_{42}ClNO_5P_2Pd$: C, 59.2 ; H, 5.0; N, 1.7 , Found: C, 58.9; H, 4.9; N, 1.7. $^{31}P\{^1H\}$NMR (CD_2Cl_2): δ 41.55 (d, 1P, $^3J_{PP}$ = 30.4 Hz), 41.97 (d, 1P, $^3J_{PP}$ = 30.4), 50.01 (d, 1P, $^3J_{PP}$ = 30.4), 51.46 (d, 1P, $^3J_{PP}$ = 30.4).

Synthesis of dichloro[2,3-bis(diphenylphosphino)propan-1-ol]palladium(II), (R_c)-93a and (R_c)-93b.

A mixture of complexes (R_c,R_c)-**92a** and (R_c,S_c)-**92b** (0.85 g, 0.001 mols) in dichloromethane was treated with concentrated hydrochloric acid (4 mL) and was left to stir for 8 hrs. The excess acid was then removed by means of washing with water (3 X 20

mL) and the organic layer was extracted and dried using magnesium sulphate. The reaction mixture was concentrated and *n*-hexanes added. Yellow prisms were obtained on standing (0.52 g, 84.5 %). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2) : δ 53.28 (d. 1P, J_{PP} = 7.6 Hz), 66.15 (d, 1P, J_{PP} = 7.6 Hz). 1H NMR (CD_2Cl_2): δ 2.29 – 2.47 (m, 2H, C*H*CH_2OH), 2.66 – 2.77 (m. 1H, PC*H*H'), 2.88 – 2.98 (m, 1H, PCH*H'*), 3.62 (dd, 2H, 3JPH = 10.4 Hz, 3JHH = 5.2 Hz , C*H*$_2$OH), 7.50 – 8.08 (m, 20H, *aromatics*).

References

1. a) Lord Kelvin. *Kelvin`s Baltimore Lectures and Modern Theoretical Physics*, Kagan, R.; Achinstein, P. (Eds.)., Bradford Books, USA, **1987**. b) Pasteur*, L. Ann. Phys.,***1848**, *24,* 442.

2. Morrison, J.D.; Scott, J.W. *Asymmetric Synthesis*, Academic Press, New York, **1984**, Vol 4, Chapter 1.

3. Bastien, N.; Bruno, S.; Alain, A.; Christiane, P. *Synthesis* , **2005**, *1*, 97-101.

4. Pierre, P.; Knauer, S.; Kranke, B.; Krause, L.; Kunz, H. *Curr. Org. Chem.*, **2004**, *8*, 1739-1761.

5. Nariyuki, Y.; Katsuya, A.; Kobayashi, T.; Fujimori, K. *Synthesis*, **2004**, *10*, 1554-1556.

6. Toga, Y.; Tachibana, K.; Ichida, A. *J. Liq. Chromatogr. Related Technol.*, **2003**, *26*, 3235-3248.

7. Maria, L.P.; Craig, T.W.; Alfonso, R.S.; John, R.; Keith, B; Georgina, H. *J. Chromatogr. A*, **2003**, *983*, 101-114.

8. Vivekanand, V.V.; Ravikumar, V.; Mohakhud, P.K.; Reddy, G. O. *J. Pharm. Biomed. Anal*., **2003**, *33*, 803-809.

9. Liu, J.; Zhang, Y.; Qiu, L; Yang, F.; Ye, L.; Xia, Y. *J. Ind. Microbiol. Biotechnol*., **2004**, *31*(11), 495-499 .

10. Santos, A.G.; Pereira, J.; Carlos, A. M.; Frenking, G. *Chem. Eur. J.*, **2004**, *11*(1), 330-343.

11. Martin, B.M.; Michaela, E.; Krisztian, B.; Baeckvall, J.E. *Angew. Chem., Int. Ed. Engl*., **2004**, 43(47), 6535-6539.

12. Procter, G. *Stereoselectivity in Organic Synthesis*, **1998**, Oxford university Press Inc., New York.

13 a) Stefan, L.; *Tetrahedron: Asymmetry* , **2004**, *15*(18), 2743-2748. b) Baker, G. C.; Ancliff, R.; Gouverneur, V., *Tetrahedron*, **2004**, *60*(35), 7607-7619. c) Kitazume, T.; Jiang, Z.; Kasai, K.; Mihara, Y.; Suzuki, M. *J. Fluorine Chem*., **2003**, *121*(2), 205-212. d) Shi, Z.D.; Yang, B.H.; Wu, Y.L.; Pan, Y.J.; Ji, Y.Y.; Yeh, M. *Bioorg. Med.l Chem. Lett.* , **2002**, 12(17), 2321-2324. e) Toker, J. D.; Wentworth, P.; Hu, Y.; Houk, K. N.; Janda, K. D. *J. Am. Chem. Soc*., **2000**, *122*(13), 3244-3245. f) Glieder, A.; Weis, R.; Skranc, W.; Poechlauer, P.; Dreveny, I.; Majer, S.; Wubbolts, M.; Schwab, H.; Gruber, K. *Angew. Chem. Intl. Ed*., **2003**, 42(39), 4815-4818. g) Barbas, C.F.; Rader, C.; Segal, D. J.; List, B.; Turner, J.M. *Adv. Protein Chem.*, **2001**, *55*, 317-366.

14. a) Radosevich, A.T.; Musich, C.; Toste, F.D. *J. Am. Chem. Soc*., **2005**, *127*(4), 1090-1091. b) Aggarwal, V.K.; Bae, I.; Lee, H.Y. Tetrahedron, 2004, *60*(43), 9725-9733. c) Pu, L. *Tetrahedron*, **2003**, *59*(50), 9873-9886. d) Uchida, T.; Tamura, Y.; Ohba, M.; Katsuki, T. *Tetrahedron Lett*., **2003**, *44*(43), 7965-7968. e) Massa, A.; Siniscalchi, F.R.; Bugatti, V.; Lattanzi, A.; Scettri, A. *Tetrahedron: Asymmetry*, **2002**, *13*(12), 1277-1283. f) Gomez, M.; Jansat, S.; Muller, G.; Maestro, M.A.; Saavedra, J. M.; Font-Bardia, M.; Solans, X. *J. Chem. Soc. Dalton Trans*., **2001**, *9*, 1432-1439. g) Magee, M. P.; Norton, J.R. *J. Am. Chem. Soc*., **2001**, *123*(8), 1778-1779. h) Yamashita, Y.; Odashima, K.; Koga, K. *Tetrahedron Lett*., **1999**, *40*(14), 2803-2806.

15. a) Ngo, H.L.; Hu, A.; Lin, W. *Tetrahedron Lett*., **2005**, *46*(4), 595-597. b) Gosselin, F.; O'Shea, P.D.; Roy, S.; Reamer, R.A.; Chen, C.Y.; Volante, R.P. *Org. Lett*., **2005**, *7*(2), 355-358. c) Anderson, C.E.; Donde, Y.; Douglas, C.J.; Overman, L.E., *J. Org. Chem*., **2005**, *70*(2), 648-657. d) Jeon, S.J.; Li, H.; Garcia, C.; LaRochelle, L.K.; Walsh, P.J. *J. Org. Chem*., **2005**, *70*(2), 448-455. e) Wang, M.C.; Liu, L.T.; Zhang, J.S.; Shi, Y.Y.; Wang, D.K. *Tetrahedron: Asymmetry*, **2004**, *15*(24), 3853-3859. f) Shintani, R.; Okamoto, K.; Otomaru, Y.; Ueyama, K.; Hayashi, T. *J. Am. Chem. Soc*., **2005**, 127(1), 54-55. g) Kang, S.H.; Kim, M.; Kang, S.Y. *Angew. Chem. Intl. Ed*., **2004**, *43*(45), 6177-6180. h) Ma, J.A.; Cahard, D. *Angew. Chem. Intl. Ed*., **2004**, *43*(35), 4566-4583. i) Valodkar, V. B.; Tembe, G. L.; Ram, R. N.; Rama, H. S. , *Catal. Lett*., **2003**, *90*(1-2), 91-94. j) Kiely, D.; Guiry, P.J. *Tetrahedron Lett*., **2003**, *44*(39), 7377-7380. k) Lurain, A.E.; Walsh, P.J. *J. Am. Chem. Soc*., **2003**, *125*(35), 10677-10683.

16. Osborn, J.A.; Jardine, F.H., Young, J.F.; Wilkinson, G. *J. Chem. Soc. A*., **1966**, 1711.

17. a) Matthias B.; Carsten, B, (Ed.), *Transition Metals for Organic Synthesis: Building Blocks and Fine Chemicals*, John Wiley & Sons, New York, **2004.** b) Collman, J.P.; Hegedus, L.S.; Norton, J.R., Finke, R. *Principles and Application of Organotransition Metal Chemistry*, Mill Valley, CA, University Science Books, **1987**. c) Heck, R.F., *Organotransitionmetal Chemistry*, New York, Academic press, **1974**, 110. d) Kochi, J.K., *Organometallic Mechanisms and Catalysis*, New York, Academic Press, **1978**.

18. Horner, L.; Siegel,H.; Buethe, H. *Angew.Chem*., **1968**, *80*, 168.

19. Horner, L.; Siegel, H.; Buethe, H. *Angew. Chem. Int. Ed. Engl*., **1968**, *7*, 942.

20. W.S.Knowles, W.S.; Sabacky, M.J. *J.Chem.Soc., Chem. Commun*., **1968**, 1445.

21 Dang, T.P.; Kagan, H.B. *J.Chem.Soc., Chem. Commun*., **1971**, 481.

22. H.B.Kagan, H.B, Dang, T.P. *J. Am. Chem. Soc*., **1972**, *94*, 6429).

23. Masamune, S.; Choy, W.; Peterson, J.S.; Sita, L.R. *Angew. Chem. Int. Ed. Engl*., **1985**, *24*, 1.

24. Burgess, K.; Ohlmeyer, M.J.; Whitmire, K.H. *Organomet*., **1992**, *11*, 3588.

25. Schrock, R.R.; Osborn, J.A. *J. Am. Chem. Soc*., **1971**, *93*, 2397.

26. Knowles, W.S. *Acc. Chem. Res*., **1983**, *16*, 106.

27. Koenig, K.E. *Asymmetric Synthesis*, Academic Press, Inc., **1985** ,Vol. 5, 71-79, and references therein.

28. Noyori, R.; Kitamura, M.; Takaya, H.; Kumobayashi, H.; Akutagawa, S. European Patent 0245960, 13.4.**1987**.

29. Ohta, T.; Takaya, H.; Kitamura, M.; Nagai, K.; Noyori, R. *J.Org. Chem*., **1987**, *52*, 3176.

30. Stoll, A.P.; Suess, R. *Helv. Chim. Acta*, **1974**, *57*, 2487.

31. Dang, T.P.; Aviron-Violet, P.; Colleuille, Y.; Varagnat, J. *J. Mol. Catal*., **1982**, *16*, 51.

32. Kitamura, M.; Ohkuma, T.; Takaya, H.; Noyori, R. Tetrahedron Lett., **1988**, *29*, 1555.

33. Chan, A.S.C.; Landis, C.R. *J.Mol.Catal*., **1989**, *49*, 165.

34. Takaya, H.; Ohta, T.; Sayo, N.; Komobuyashi, H.; Akutagava, A.; Inoue, S.I.; Kasahara, I.; Noyori, R. *J. Am. Chem. Soc*., **1987**, *109*, 1596.

35. Tsukahara, T.; Kawano, H.; Ishii, Y.; Takahashi, T.; Saburi, M.; Uchida, Y.; Akutagawa, S. *Chem. Lett*., **1988**, 2955.

36. Mashima, K.; Kusano, K.H.; Ohta, T.; Noyori, R.; Takaya, H. *J.Chem. Soc., Chem. Commun*., **1989**, 1208.

37. Brunner, H. *Angew. Chem*., **1983**, *95*, 425.

38. Roush, W.R. *Comprehensive Organic Synthesis*, Trost B.M, Fleming .I, Heathcock C.H (Eds), Oxford: Pergamon Press, Vol. II, **1991**, 1-53.

39. Yamamoto,Y.; Asao, N. *Chem. Rev*., **1993**, *93*, 2207-93.

40. Hoppe, D. *Methods of Organic Chemistry*, Helmchen, G.; Hoffmann, R.W.; Mulzer, J.; Schaumann, E. (Eds), Stuttgart, Georg Thieme Verlag, Vol.E 21b, **1995**, 1357-409.

41. Bach, T. *Angew. Chem. Int. Ed. Engl*., **1994**, *33*, 417.

42. Furuta, K.; Mouri, M.; Yamamoto, H. *Synlett*, **1991**, 561.

43. Ishihara, K.; Mouri, M.; Gao, Q. *J. Am.Chem.Soc*., **1993**, *115*, 11490.

44. Aoki,S.; Mikami, K.; Terada, M.; Nakai, T. *Tetrahedron*, **1993**, *49*, 1783.

45. Costa, A.L.; Piazza, M.G.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. *J. Am. Chem. Soc*., **1993**, *115*, 7001.

46. Keck, G.E.; Tarbet, K.H.; Geraci, L.S. *J. Am. Chem. Soc*., **1993**, *115*, 8467.

47. Yanagisawa, A.; Ishiba, A.; Nakashima, H.; Yamamoto, H. *Synlett*, **1997**, 88.

48. a) Trost, B.M.; Weber, L. *J. Am. Chem. Soc*., **1975**, *97*, 1611. b) Trost, N.M.; Verhoeven, T.R. *J. Am. Chem*. Soc., **1976**, *98*, 603. c) Trost, B.M.; Strege, P.E. *J.*

Am. Chem. Soc., **1977**, *99*, 1649. d) Trost, B.M.; Strege, P.E. *J. Am. Chem. Soc*., **1977**, 99, 1649. e) Consiglio,G.; Morandini, F.; Piccolo, O. *J.Am. Chem. Soc*., **1981**, *103*, 1846. f) Bosnich, B.; Mackenzie, P.B. *Pure and Appl. Chem*., **1982**, *54*, 189. g) Trost, B.M, Murphy, D.J. *Organometallics*, **1985**, *4*, 1143. h) Yanagisawa, A.; Nakashima, H.; Ishiba, A.; Yamamoto, H. *J.Am.Chem.Soc*., **1996**, *118*, 4723.

49. Osawa, F.; Kubo, A.; Hayashi, T. *J.Am. Chem. Soc*. **1991**, *113*, 1417.

50. a) Hou, X.L.; Dong, D.X.; Yuan, K. *Tetrahedron: Asymmetry*, **2004**, *15*(14), 2189-2191. b) Selvakumar, K.; Valentini, M.; Pregosin, P.S.; Albinati, A.; Eisentraeger, F. *Organometallics*, **2000**, *19*(7), 1299-1307. c) Loiseleur, O.; Hayashi, M.; Schmees, N.; Pfaltz, A. *Synthesis*, **1997**, *11*, 1338-1345. d) Trabesinger, G.; Albinati, A.; Feiken, N.; Kunz, R.W.; Pregosin, P.S.; Tschoerner, M. *J. Am. Chem. Soc.*, **1997**, *119*(27), 6315-6323. e) Sakuraba, S.; Awano, K.; Achiwa, K. *Synlett.*, **1994**, *4*, 291-2.

51. Gibson, S.E.; Ibrahim, H.; Pasquier, C.; Swamy, V.M. *Tetrahedron Asymmetry*, **2004**, *15*, 465-473.

52. Consiglio, G.; Bottegni, C. *Helv. Chim. Acta.*, **1973**, *56*, 460.

53. Kiso,Y.; Tamao,K.; Miyake,N.; Yamamoto,K.; Kumuda,M. *Tetrahedron Lett*., **1974**,3.

54. Hayashi, M.; Takaoki, K.; Hashimoto, Y.; Saigo, K. *Enantiomer*, **1997**, *2*(3-4), 293-296.

55. Wimmer, P.; Widhalm, M. *Monatsh. Chem*., **1996**, *127*(6/7), 669-681.

56. Hayashi, T.; Konishi, M.; Fukushima, M.; Kanehira, K.; Hioki, T.; Kumada, M. *J. Org. Chem.*, **1983**, *48*(13), 2195-202.

57. James, B.R.; Young, C.G. *J. Chem. Soc., Chem. Commun.*, **1983**, 1215.

58. Wu, X.M.; Funakoshi, K.; Sakai, K., *Tetrahedron Lett.*, **1992**, *33*, 6331.

59. Sakai, N.; Mano, S.; Nozaki, K.; Takaya, H. *J. Am. Chem. Soc.*, **1993**, *115*, 7033.

60. a) Nozaki, K.; Takaya, H.; Hiyama, T. *Top.Catal.*, **1998**, *4*(3,4), 175-185. b) Kockritz, A.; Sonnenschein, H.; Bischoff, S.; Theil, F.; Gloede, *J. Phosphorus, Sulfur Silicon Relat. Elem.*, **1998**, *132*, 15-19. c) Deerenberg, S.; Kamer, P.C. J.; Van Leeuwen, P.W.N.M. *Organometallics*, **2000**, *19*(11), 2065-2072. d) Horiuchi, T.; Ohta, T.; Shirakawa, E.; Nozaki, K.; Takaya, H. *Tetrahedron*, **1997**, *53*(23), 7795-7804. e) Horiuchi, T.; Ohta, T.; Shirakawa, E.; Nozaki, K.; Takaya, H. *J. Org. Chem.*, **1997**, *62*(13), 4285-4292. f) Horiuchi, T.; Shirakawa, E.; Nozaki, K.; Takaya, H. *Organometallics*, **1997**, *16*(13), 2981-2986.

61. Nettekoven, U.; Kamer, P.C.J.; Widhlam, M.; van Leeuwen, P.W.N.M., *Organometallics*, **2000**, *19*, 4596-4607.

62. Consiglio, G. *J. Organomet. Chem.*, **1977**, *132*, 26.

63. Hayashi, T.; Tanaka, M.;Ogata, I. *Tetrahedron Lett.*, **1978**, 3925.

64. Cometti, G.; Chiusoli, G.P., *J. Organomet. Chem.*, **1982**, *236*, C31.

65. a) Oderaotoshi, Y.; Cheng, W.; Fujitomi, S.; Kasano, Y.; Minakata, S.; Komatsu, M. *Org. Lett.*, **2003**, *5*(26), 5043-5046. b) Bernardinelli, G.H.; Kundig, E.P.; Meier, P.; Pfaltz, A.; Radkowski, K.; Zimmermann, N.; Neuburger-Zehnder, M. *Helv. Chim. Acta*, **2001**, *84*(10), 3233-3246. c) Wender, P.A.; Husfeld, C.O.;

Langkopf, E.; Love, J.A.; Pleuss, N. *Tetrahedron*, **1998**, *54*(25), 7203-7220. d) Larksarp, C.; Alper, H. *J. Am. Chem. Soc*., **1997**, *119*(16), 3709-3715.

66. a) Kumareswaran, R.; Nandi, M.; RajanBabu, T.V., *Org. Lett*., **2003**, *5*(23), 4345-4348. b) Englert, U.; Haerter, R.; Vasen, D.; Salzer, A.; Eggeling, E.B.; Vogt, D. *Organometallics*, **1999**, *18*(21), 4390-4398. c) Buono, G.; Siv, C.; Peiffer, G.; Triantaphylides, C.; Denis, P.; Mortreux, A.; Petit, F. *J. Org. Chem*., **1985**, *50*(10), 1781-2.

67. a) Demay, S.; Volant, F.; Knochel, P. *Angew. Chem. Intl. Ed*., **2001**, *40*(7), 1235-1238. b) Hayashi, T.; Matsumoto, Y.; Ito, Y. *Tetrahedron: Asymmetry*, **1991**, *2*(7), 601-12.

68. a) Jensen, J. F.; Johannsen, M. *Org. Lett*., **2003**, *5*(17), 3025-3028. b) Pickett, T.E.; Roca, F.X.; Richards, C.J. *J. Org.Chem*.,**2003**, *68*(7), 2592-2599.

69. a) Stoop, R.M.; Bachmann, S.; Valentini, M.; Mezzetti, A., Organometallics, **2000**, *19*(20), 4117-4126. b) Cross, R. J.; Newman, P.D.; Peacock, R.D.; Stirling, D. *J. Mol. Catal. A: Chem*., **1999**, *144*(2), 273-284.

70. Pietrusiewicz, K.M.; Zablocka, M., *Chem. Rev*. **1994**, *94*, 1375 .

71. Quin, L.D. *A Guide to Organophosphorous Chemistry*, Wiley Interscience, **2000**, 272-303.

72. a) Stec, W.J. *Organophosphorous Chem*., **1982**, *13*, 145. b) Zon, G., *Prog. Med. Chem*., **1982**, *19*, 205.

73. Fest, C.; Schmidt, K.J. *The Chemistry of Organophosphorous Pesticides*, Springer, Berlin, **1982**.

74. Stec, W.J. *Antisense Research and Applications*, Crooke,S.T.; Leblau,B.(Eds.), CRC Press, London, **1993**, 251.

75. Morrison, J.D. *Asymmetric Synthesis*, Academic Press, Inc., Orlando, FL, **1985**, Vol I-V.

76. Imamoto, T. *Handbook of Organophosphorous Chemistry*, Engel,R. (Eds)., Marcel Dekker, New York, **1992**, Chapter 1.

77. Wittig, G.; Cristau, H.J.; Braun, H. *Angew. Chem., Intl. Ed. Engl*., **1967**, 6, 700.

78. Okruszek, A.; *Dissertation, Center of Molecular and Macromolecular Studies*, Lodz, **1975**.

79. Cernia, E.; Giongo, G.M.; Marcati, F.; Marconi, W.; Palladino, N., *Inorg. Chim. Acta*., **1974**, *11*, 195.

80. Macpherson, A.J.; Smith, D.J.H. *J. Chem. Res*., **1984**, 32.

81. Brandi, A.; Cicchi, S.; Goti, A.; Koprowski, M.; Pietrusiewicz, K.M., *J. Org. Chem*., **1994**, *59*, 1315.

82. King, R.B.; Bakos, J.; Hoff, C.D.; Marko, L., *J. Org. Chem*., **1979**, *44*, 3095.

83. Pietrusiewicz, K.M.; Wieczorek, W.; Goti,A.; Brandi,A. *Phosphorous, Sulfur Silicon Relat. Elem*., **1992**, *70*, 131.

84. Kielbasinski, P.; Zurawinski, R.; Pietrusiewicz, K.M, Zablocka, M.; Mikolajczyk, M. *Tetrahedron Lett*., **1994**, *35*, 7081.

85. Li, Y.; Aubert, S.D.; Maes, E.G.; Raushel, F.M. *J. Am. Chem. Soc.* **2004**, *126*(29), 8888-8889.

86. Kielbasinski, P.; Albrycht, M.; Luczak, J.; Mikolajczyk, M. *Tetrahedron: Asymmetry* , **2002**, 13(7), 735-738.

87. Koszuk, J. *Dissertation, Technical University*, Lodz, **1981**.

88. a) Bodalski, R.; Rutkowska-Olma, E.; Pietrusiewicz, K.M. *Tetrahedron*, **1980**, *36*, 2353. b) Pietrusiewicz, K.M.; Zablocka, M.; Monkiewicz, J., *J. Org. Chem*., **1984**, *49*, 1522.

89. Okafo, G.N., *Capillary Electrophoresis (2nd Edition)*, **1998**, 183-247.

90. Pietrusiewicz, K.M. *Phosphorus, Sulfur Silicon Relat. Elem*., **1996**, 109-110.

91. Yoshioka, R.; Ohtsuki, O.; Da-Te, T.; Okamura, K.; Senuma, M. *Bull. Chem. Soc. Jpn*., **1994**, *67*(11), 3012-20.

92. Naylor, R.A.; Walker, B.J. *J. Chem. Soc., Chem. Commun*., **1975**, 45.

93. Burgess, K.; Ohlmeyer, M.J.; Whitmire, K.H., *Organometallics*, **1992**, *11*, 3588.

94. de Vaumas, R.; Marinetti, A.; Ricard, L.; Mathey, F., *J. Am. Chem. Soc*., **1992**, *114*, 261.

95. Breque, A.; Alcarez, J.; Richard, L.; Mathey, F.; Tambute, A.; Macaudiere, P., *New J. Chem*., **1989**, *13*, 369.

96. Okamoto, Y.; Honda, S.; Hatada, K.; Okamoto, I.; Toga, Y.; Kobayashi, S. *Bull. Chem. Soc. Jpn*., **1984**, *57*, 1681.

97. Pescher, P.; Caude, M.; Rosset, R.; Tambute, A., *J. Chromatogr*. **1986**, *371*, 159.

98. Macaudiere, P.; Caide, M.; Rosset, R.; Tambute, A. *J. Chromatogr*. , **1987**, *405*, 135.

99. a) Lammerhofer, M.; Hebenstreit, D.; Gavioli, E.; Lindner, W.; Mucha, A.; Kafarski, P.; Wieczorek, P. *Tetrahedron: Asymmetry* , **2003** , *14*(17), 2557-2565. b) Benincori, T.; Cirilli, R.; Ferretti, R.; La Torre, F.; Piccolo, O.; Zanitti, L., *Chromatographia.* **2002** , *55*(1/2). c) Ferretti, R.; Gallinella, B.; La Torre, F.;

Zanitti, L.; Bonifacio, F.; Piccolo, O. *Journal of Chromatography, A* , **1998** , *795*(2), 289-295. d) Brandi, A.; Cicchi, S.; Gasparrini, F.; Maggio, F.; Villani, C.; Koprowski, M.; Pietrusiewicz, K.M. *Tetrahedron: Asymmetry* , **1995** , *6*(8), 2017-22. e) Lecomte, L.; Sinou, D. *Journal of Chromatography* , **1990** , *514*(1), 91-6. , 25-31.

100. Meisenheimer, J.; Cooper, J.; Horing, M.; Lauter, W.; Lichtenstadt, L.; Samuel, W., *Justus Liebigs Ann. Chem*., **1926**, 449, 213.

101. Horner, L.; Simons, G., *Phosphorous,Sulfur Silicon Relat. Elem*., **1984**, *19*, 65.

102. Yamamoto,K.; Tomita,A.; Tsuji.J., *Chem. Lett*., **1978**, 3.

103. Brunner, H.; Pieronczyk, W., *Angew, Chem., Int. Ed. Engl*., **1979**, *18*, 620.

104. Takaya, H.; Akutagawa, S.; Noyori, R., *Org. Synth*., **1989**, *67*,20.

105. Kumli, K.F.; McEwen, W.E.; Vander Werf, C.A., *J. Am. Chem. Soc*., **1959**, *81*, 248.

106. a) Tani, K.; Brown, L.D.; Ahmed, J.; Ibers, J.A.; Yokota, M.; Nakamura, A.; Otsuka, S., *J. Am. Chem. Soc*., **1977**, *99*, 7876. b) Otsuka, S.; Nakamura, A.; Kano, T.; Tani, K., *J. Am. Chem. Soc*., **1971**, 4301.

107. Salem, G.; Wild, S.B., *Inorg. Chem*., **1983**, *22*, 4049.

108. Allen, D.G.; McLaughlin, G.M.; Robertson, G.B.; Steffen, W.L.; Salem, G.; Wild, S.B., *Inorg. Chem*., **1982**, *21*, 1007.

109. Martin, J.W.L.; Palmer, J.A.L.; Wild, S.B., *Inorg. Chem*., **1984** , *23*, 2664.

110. Leung, P.H.; Willis, A.C.; Wild, S.B., *Inorg. Chem*., **1992**, *31*, 1406.

111. Roberts, N.K.; Wild, S.B., *J. Am. Chem. Soc*., **1979**, *101*, 6254.

112. Alcock, N.H.; Brown, J.M.; Hulmes, D.I., *Tetrahedron: Asymmetry*, **1993**, *4*, 743.

113. Miyashita, A.; Yasuda, A.: Takaya,H.; Toriumi, K.; Ito, T.; Souchi, T.; Noyori, R. *J. Am. Chem. Soc*., **1980**, *102*, 7932.

114. Miyashita, A.; Takaya, H.; Souchi, T.; Noyori, R., *Tetrahedron*, **1984**, *40*, 1245.

115. Kyba, E.P.; Rines, S.P., *J. Org. Chem*., **1982**, *47*, 4800.

116. Leitch, J.; Salem, G.; Hockless, D.C.R. *J. Chem. Soc. Dalton Trans*., **1995**, 649.

117. Alcock, N.W.; Brown, J.M.; Pearson, M.; Woodward, S. *Tetrahedron: Asymmetry*., **1992**, *3*, 17.

118. Alcock, N.W.; Brown, J.M.; Hulmes, D.I. *Tetrahedron: Asymmetry*., **1993**, *4*, 743.

119. Ramsden, J.A.; Brown, J.B.; Hursthous, M.B.; Karalulov, A.I. *Tetrahedron: Asymmetry*., **1994**, *5*, 2033.

120. a) Chooi, S.; Tan, M.K.; Leung, P.H.; Mok, K.F., *Inorg. Chem*., **1994**, *33*, 3096-3103. b) Cheng, C.R.; Selvaratnam, S.; Mok, K.F.; Rees, N.H.; McFarlane, W.; Leung, P.H. *J. Chem. Soc., Chem. Commun*., **1997**, 751-752.

121. a) Aw, B.H.; Selvaratnam, S.; Leung, P.H.; Rees, N.H.; McFarlane, W., *Tetrahedron: Asymmetry*, 1996, *7*, 1753-1762. b) Leung, P.H. *Acc. Chem. Res*., **2004**, *37*(3), 169-177.

122. Dochnahl, M.; Doux, M.; Faillard, E.; Ricard, L.; Le Floch, P. *Eur. J. Inorg. Chem.* , **2005**, *1*, 125-134.

123. Zhang, W.; Shi, M. *Tetrahedron: Asymmetry* , **2004** , *15*(21), 3467-3476.

124. Zhang, W.; Shi, M. *Tetrahedron Lett.* , **2004**, *45*(48), 8921-8924.

125. Song, Y.; Vittal, J.J.; Srinivasan, N.; Chan, S.H.; Leung, P.H., *Tetrahedron: Asymmetry*, **1999**, *10*, 1433-1436.

126. Leung,P.H.; Chan, S.H.; Song, Y., *Gold Complexes. PCT Int. Appl*., **2001**, WO 0177121 A1.

127. a) Diels, O.; Alder, K. *Ann.,* **1928**, *460*, 98. b) Diels, O.; Alder, K.; Lubbert, W.; Naujokas, E.; Querberitz, F.; Rohl, K.; Segeberg, H. *Ann.,* **1929**, *470*, 62. c) Diels, O.; Alder, K. *Ber.,* **1929**, *62*, 2081, 2087.

128. Fringuelli, F.; Taticchi, A. *The Diels-Alder Reaction-Selected Practical Methods*, Wiley, New York, **2002**.

129. Fringuelli, F.; Taticchi, A., *Dienes in the Diels-Alder Reaction*, Wiley, New York, **1990**.

130. Paquette, L.A., *Comprehensive Organic Synthesis*, vol. 5, Pergamon Press, Oxford, **1991**.

131. a) Fleming, I., *Frontier Orbitals and Organic Chemical Reactions*, Wiley, New York, **1976**. b) Isaacs, N., *Physical Organic Chemistry,* 2nd edn, Longman, Harlow, **1995**. c) Fleming, I., *Pericyclic Reactions*, Oxford Science Publ., 67, Oxford University Press, **1999**.

132. Sauer, J.; Sustmann, R., *Angew Chem. Int. Ed. Engl*., **1980**, *19*, 779.

133. Houk, K.N., *J. Am. Chem. Soc*., **1973**, *95*, 4092.

134. Ginsburg, D. *Tetrahedron*, **1983**, *39*, 2095.

135. a) Gomez, A.R.; Mancheno, O.G.; Carretero, J.C. *Chem. Comm*., **2004** , *14*, 1654-1655. b) Mancheno, O.G.; Gomez, A.R.; Carretero, J.C. *J. Am. Chem. Soc.*, **2004**, *126*(2), 456-457. c) Gibson, V.C.; Long, N.J.; White, A.J.P.; Williams, C. K.; Williams, D.J.; Fontani, M.; Zanello, P. *J. Chem. Soc., Dalton Trans* , **2002**, *17*, 3280-3289. d) Gladiali, S.; Medici, S.; Pirri, G.; Pulacchini, S.; Fabbri, D.

Can. J. Chem. , **2001**, *79*(5/6), 670-678. e) Leung, P.H.; Loh, S-K.; Mok, K.F.; White, A.J.P.; Williams, D.J., *J. Chem. Soc., Dalton Trans*., **1996**, 4443-4448. f) Leung, P.H.; Willis, A.C.; Wild, S.B., *Inorg. Chem*., **1992**, *31*, 1406-1410.

136. a) Grim, S.O.; Satek, L.C., Tolman, C.A.; Jesson, J.P. *Inorg. Chem*., **1975**, *14*, 656. b) Grim, S.O.; Mitchell, J.D. *Synth. React. Inorg. Met. Org. Chem*., **1974**, *4*, 221. c) Grim, S.O.; Mitchell, J.D., *Inorg. Chem*., **1977**, *16*, 1762. d) Grim, S.O.; Smith, P.H.; Colquhoun, I.J.; McFarlane, W., *Inorg. Chem*., **1980**, *19*, 1395. e) Colquhoun, I.J.; Grim, S.O.; McFarlane, W., *Inorg. Chem*., **1981**, *20*, 2516. f) Grim, S.O, Walton, E.D., *Inorg. Chem*., **1980**, *19*, 1982.

137. Blagborough, T.C.; Davies, R.; Ivison, *J. Organomet. Chem*., **1994**, 85.

138. Suranna, G.P.; Mastrorilli, P.; Nobile, C.F.; Keim, W., *Inorg. Chim. Acta*., **2000**, *305*, 151-156.

139. Bond, A.M.; Colton, R, Pangiotidou, P., *Organometallics*, **1988**, *7*, 1767.

140. Uson, R., *J. Chem. Soc., Dalton Trans*., **1979**, 73.

141. Strecker and Spitaler, *Ber*., **1926**, *59*, 1772.

142. Kosolapoff, K. *Organophosphorous Compounds*, John Wiley, New York, **1950**, 235.

143. Siebert, Z. *Anorg. Chem*., **1954**, *275*, 210.

144. Van Wazer, J.R., *J. Am. Chem. Soc*., **1956**, *78*, 5709.

145. Mathey, F.; Faveliver, R.M. *Bull. Soc. Chim. Fr*., **1970**, 4433.

146. a) Deschamps, B.; Mathey, F., *Organometallics*, **1992**, *11*, 1411. b) Mathey, F., *Tetrahedron Lett*., **1973**, 3255. c) Mathey, F., *Tetrahedron*, **1976**, *32*, 2395. d) Kashman, Y.; Wagenstein, I.; Rudi, A., *Tetrahedron*, **1976**, *32*, 2427.

147. Kashman, Y.; Awerbouch, O. *Tetrahedron*, **1973**, *29*, 191-194.

148. Holand, S.; Ricard, L.; Mathey, F., *J. Org. Chem*., **1991**, *56*, 4031-4035.

149. Kashman, Y.; Awerbouch, O. *Tetrahedron Lett.*, **1973**, 3217.

150. Mathey, F.; Favelier, R.M. *Org. Magn. Reson*., **1972**, *4*, 171.

151. a) Nief, F.; Ricard, L.; Mathey, F. *Organometallics*, **1989**, *8*, 1473. b) Nief, F.; Mathey, F. *J. Chem. Soc. , Chem. Commun*., **1989**, 800.

152. Mathey, F.; Mankowski-Faveliver, R. *Bull. Soc. Chim. Fr*., **1970**, 4433.

153. Siah, S.Y.; Leung, P.H.; Mok, K.F. *J. Chem. Soc. Chem. Commun*., **1995**, 1747.

154. Loh, S.K.; Mok, K.F.; Leung, P.H, White, A.J.P.; Williams, D.J. *Tetrahedron: Asymmetry*, **1996**, *7*, 45.

155. Nelson, J.H. *Coord. Chem. Rev*., **1995**, *139*, 245.

156. Mercier, F.; Mathey, F.; Fischer, J.; Nelson, J.H. *J. Am. Chem. Soc*. **1984**, *106*, 425.

157. He, G.; Qin, Y.; Mok, K.F, Leung, P.H. *Chem. Commun*.., **2000**, 167-168.

158. Qin, Y.; White, A.J.P.; Williams, D.J.; Leung, P.H. *Organometallics*, **2002**, *21*, 5301 – 5306.

159. Qin, Y.; He, G.; Mok, K.F.; Vittal, J.J.; Leung, P.H. *J. Chem. Soc., Dalton Trans.* **2001**, 309.

160. Cahn, R.S.; Ingold, C.K.; Prelog, V. *Angew. Chem., Int. Ed. Engl*., **1966**, *5*, 385.

161. Chooi, S.Y.M, Hor, T.S.A, Leung, P.H, Mok, K.F. *Inorg. Chem*., **1992**, *31*, 1494.

162. Song, Y.C.; Mok, K.F.; Leung, P.H.; Chan, S.H. *Inorg. Chem*., **1998**, *36*, 6399.

163. Aw, B.H.; White, A.J.P.; Williams, D.J. *Organometallics*, **1996**, *15*, 3640-3643.

164. Selvaratnam, S.; White, A.J.P.; Williams D.J. *J. Organomet. Chem*., **1997**, 542, 61-65.

165. Bosnich, B. *Asymmetric Catalysis* , Martinus Nijhoff, Boston, MA, **1986**.

166. Kagan, H.B.; Sasaki, M. *The Chemistry of Organophosphorous Compounds*, Hartley, F.R., (Ed.), Wiley-Interscience, New York, **1990**, Vol.1, Chapt.3.

167. Sawamura, M.; Ito, Y., *Chem. Rev*., **1992**, *92*, 857-871.

168. Quin, L.D., *A Guide to Organophoaphorous Chemistry*, Wiley-Interscience, New York, **2000**, Chapter 11.

169. Evans, D.A.; Campos, K.R., Tedrow, J.S.; Michael, F.E.; Gagne, M.R. *J. Org. Chem*., **1999**, *64*, 2994-2995.

170. Grim, S.O.; Molenda, R.P.; Mitchell, J.D. *J. Org. Chem*., **1980**, *45*, 250.

171. Wagner, K.H.; Mitchell, T.N. *J. Organometallic Chem*., **1994**, *468*, 99-106.

172. Cross, R.J.; Dalgleish, I.G.; Smith, G.J.; Wardle, R. *J. Chem. Soc. , Dalton Trans*., **1972**, *8*, 992-996.

173. Imamoto, T.; Kusumoto, T.; Suzuki, N.; Sato, K. *J.Am. Chem.Soc*., **198**5, *107*, 5301.

174. Marciniec, B. *Comprehensive Handbook on Hydrosilylation*, Pergamon Press, Oxford, UK, **1992**.

175. Pelter, A.; Smith, K.; Brown, H.C. *Borane Reagents*, Academic Press, New York, **1988**.

176. Pereyre, M.; Quintard, J.P.; Rahm, A. *Tin in Organic Synthesis*, Butterworth & Co. Ltd., London, UK, **1987**.

177. a) Bookham, J.L.; Smithies, D.M. *J. Organomet. Chem*., **1999**, *577*, 305. b) King, R.B.; Kapoor, P.N. *J. Am. Chem. Soc*., **1969**, *91*, 5191. c) Schmidbaur, H.; Frazao, C.M.; Reber, G.; Muller, G. *Chem. Ber*., **1989**, *122*, 259. d) Markl, G.; Potthast, R. *Angew. Chem., Int. Ed. Engl*., **1967**, *6*, 86.

178. Mitchell, T.N.; Heesche-Wagner, K. *J. Organomet. Chem*., **1991**, *409*, 163.

179. Heesche-Wagner, K.; Mitchell, T.N. *J. Organomet. Chem*., **1994**, *468*, 99.

180. Hoffmann, H.; Diehr, H. *J. Chem. Ber*., **1965**, *98*, 363.

181. Liu, X.; Mok, K.F.; Leung, P.H. *Organometallics*, **2001**, *20*, 3918.

182. Yeo, W.C.; Tee, S.Y.; Tan, H.B.; Tan, G.K.; Koh, L.L.; Leung, P.H. *Inorg. Chem*, **2004**, *43*, 8102-8109.

183. Aw, B.H.; Hor, T.S.A.; Selvaratnam, S.; Mok, K.F.; White, A.J.P.; Williams, D.J.; Rees, N.H.; McFarlane, W.; Leung, P.H. *Inorg. Chem*., **1997**, *36*, 2138.

184. Chooi, S.Y.M.; Siah, S.Y.; Leung, P.H.; Mok, K.F. *Inorg. Chem*., **1993**, *32*, 4812.

185. Chooi, S.Y.M.; Ranford, J.D.; Leung, P.H.; Mok, K.F. *Tetrahedron: Asymmetry*, **1994**, *5*, 1805.

186. Breque, A.; Mathey, F.; Savignac, P. *Synthesis*, **1981**, 983.

187. King, R.B.; Kapoor, P.N. *J. Am. Chem. Soc*., **1971**, *93*, 4158.

188. Robert, R.; Joseph, P. *J. Org. Chem*., **1961**, *26*, 4623-6.

189. Baker, R.L.; Booth, E.; Jones, W.E.; Millidge, A.F.; Woodward, F.N. *J. Soc. Chem. Ind*., **1949**, *68*, 289.

Appendix

Appendix 1

X-ray Crystallographic Data for [(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*] [9-thio-9-phenylphosphino-2,3,6,7-tetramethyl-6-ethylene-10-phenyl-10-phosphabicyclo[2,2,1] hept-2-ene-P^9(*R*)P^{10}(*S*)]palladium (II)perchlorate, ($R_cS_pR_p$)-48. (Figure 2.3)

Table A.1.1 Crystal data and structure refinement for ($R_cS_pR_p$)-48

Empirical formula	C38 H42 Cl N O4 P2 Pd S.0.5{C4H10O}	
Formula weight	849.64	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 11.8816(16) Å	α = 90°.
	b = 15.681(2) Å	β = 101.760(3)°.
	c = 22.532(3) Å	γ = 90°.
Volume	4110.1(10) $Å^3$	
Z	4	
Density (calculated)	1.373 Mg/m^3	
Goodness-of-fit on F^2	0.996	
Final R indices [I>2sigma(I)]	R1 = 0.0568, wR2 = 0.1099	
R indices (all data)	R1 = 0.0888, wR2 = 0.1215	
Absolute structure parameter	-0.01(2)	

Table A.1.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for complex ($R_cS_pR_p$)-**48** . U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	7761(1)	2854(1)	6661(1)	45(1)
P(1)	9254(1)	2338(1)	6318(1)	46(1)
P(2)	9105(1)	1610(1)	7722(1)	53(1)
S(1)	7510(1)	1545(1)	7238(1)	63(1)
N(1)	6263(3)	3458(3)	6864(2)	50(1)
N(2)	7051(5)	1866(4)	-464(3)	72(2)
Cl(1)	7582(1)	9704(1)	3625(1)	70(1)
Cl(2)	8614(3)	4911(2)	8971(1)	123(1)
O(1)	7080(4)	9130(4)	3157(3)	100(2)
O(2)	8288(5)	10295(5)	3417(3)	124(2)
O(3)	8300(6)	9251(4)	4101(3)	122(2)
O(4)	6703(4)	10122(4)	3839(3)	114(2)
C(1)	10789(4)	2611(3)	6649(3)	46(1)
C(2)	11388(5)	1913(4)	6340(3)	54(1)
C(3)	10829(5)	1179(4)	6316(3)	57(2)
C(4)	9788(5)	1270(4)	6601(3)	51(2)
C(5)	10231(5)	1474(4)	7282(3)	54(2)
C(6)	10881(4)	2345(3)	7317(3)	48(1)
C(7)	10308(5)	2968(4)	7690(3)	51(1)
C(8)	9517(5)	2657(4)	7965(3)	55(2)
C(9)	12489(5)	2118(5)	6139(3)	73(2)
C(10)	11080(7)	344(5)	6058(4)	79(2)
C(11)	12156(5)	2257(4)	7645(3)	68(2)
C(12)	10668(6)	3874(4)	7736(3)	70(2)
C(13)	7846(4)	3972(3)	6240(2)	42(1)
C(14)	8806(4)	4350(4)	6072(3)	48(1)
C(15)	8748(5)	5136(4)	5801(3)	57(2)
C(16)	7707(5)	5611(4)	5699(3)	57(2)
C(17)	7644(6)	6441(5)	5442(3)	74(2)
C(18)	6647(7)	6896(6)	5372(4)	93(2)
C(19)	5688(6)	6551(5)	5560(4)	97(3)

C(20)	5722(6)	5756(5)	5782(4)	80(2)
C(21)	6738(5)	5263(4)	5880(3)	56(2)
C(22)	6832(4)	4434(4)	6146(3)	47(1)
C(23)	5804(5)	3995(4)	6319(3)	55(2)
C(24)	5155(5)	3484(5)	5800(3)	76(2)
C(25)	5374(5)	2864(5)	7004(3)	77(2)
C(26)	6682(6)	4014(5)	7402(3)	79(2)
C(27)	9046(5)	2320(4)	5504(3)	57(2)
C(28)	9721(5)	2780(5)	5176(3)	70(2)
C(29)	9468(7)	2741(7)	4558(4)	99(3)
C(30)	8590(10)	2243(9)	4257(4)	130(4)
C(31)	7932(9)	1797(9)	4566(5)	133(4)
C(32)	8149(7)	1847(6)	5175(4)	93(3)
C(33)	9350(6)	841(4)	8327(3)	58(2)
C(34)	10183(6)	983(5)	8820(3)	74(2)
C(35)	10423(7)	372(7)	9281(4)	94(3)
C(36)	9847(9)	-381(7)	9232(5)	103(3)
C(37)	9015(10)	-507(5)	8728(5)	100(3)
C(38)	8737(8)	81(5)	8274(4)	80(2)

Appendix 2

X-ray Crystallographic Data for dichloro[9-thio-9-phenylphosphino-2,3,6,7-tetramethyl-6-ethylene-10-phenyl-10-phosphabicyclo[2,2,1]hept-2-ene-$P^9(R)P^{10}(S)$]palladium(II)perchlorate (S_p,R_p)-49. . (Figure 2.4)

Table A.1.3 Crystal data and structure refinement for (S_pR_p)-49

Empirical formula	C24 H26 Cl2 P2 Pd S	
Formula weight	585.75	
Crystal system	Orthorhombic	
Space group	Pna2(1)	
Unit cell dimensions	a = 16.4405(8) Å	α = 90°.
	b = 9.4660(5) Å	β = 90°.
	c = 15.7152(8) Å	γ = 90°.
Volume	2445.7(2) $Å^3$	
Z	4	
Density (calculated)	1.591 Mg/m^3	
Goodness-of-fit on F^2	1.015	
Final R indices [I>2sigma(I)]	R1 = 0.0351, wR2 = 0.0561	
R indices (all data)	R1 = 0.0444, wR2 = 0.0576	
Absolute structure parameter	0.00(2)	

Table A 1.4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for complex (S_pR_p)-**49** . U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	6579(1)	3408(1)	4989(1)	36(1)
Cl(1)	7490(1)	3512(1)	3865(1)	52(1)
Cl(2)	7368(1)	4869(1)	5906(1)	66(1)
P(1)	5947(1)	1906(1)	4156(1)	33(1)
P(2)	4698(1)	4094(1)	5133(1)	37(1)
S(1)	5522(1)	3350(1)	5971(1)	48(1)
C(1)	5497(2)	2479(4)	3137(2)	37(1)
C(2)	5065(2)	1122(4)	2895(3)	45(1)
C(3)	4713(2)	544(4)	3566(3)	44(1)
C(4)	4880(2)	1412(3)	4361(2)	37(1)
C(5)	4471(2)	2878(3)	4264(2)	34(1)
C(6)	4830(2)	3573(3)	3446(2)	34(1)
C(7)	5183(2)	5005(3)	3673(2)	35(1)
C(8)	5099(2)	5435(3)	4477(2)	39(1)
C(9)	5080(3)	605(5)	1996(3)	70(1)
C(10)	4249(2)	-800(4)	3628(3)	64(1)
C(11)	4179(2)	3780(4)	2759(2)	48(1)
C(12)	5615(2)	5840(4)	3007(3)	51(1)
C(13)	6496(2)	268(3)	4026(2)	39(1)
C(14)	6953(3)	-27(4)	3311(3)	60(1)
C(15)	7347(3)	-1305(5)	3250(4)	80(2)
C(16)	7295(3)	-2267(5)	3885(5)	88(2)
C(17)	6844(3)	-1998(4)	4614(4)	71(2)
C(18)	6444(2)	-700(4)	4688(3)	54(1)
C(19)	3808(2)	4632(3)	5697(2)	36(1)
C(20)	3266(2)	3632(4)	5999(2)	46(1)
C(21)	2601(2)	4042(4)	6473(3)	54(1)
C(22)	2473(2)	5416(5)	6655(3)	57(1)
C(23)	3005(3)	6428(4)	6359(3)	58(1)
C(24)	3667(2)	6048(4)	5875(3)	49(1)

Appendix 3

X-ray Crystallographic Data for dichloro][7-thio-7-diphenylphosphino-2,3-dimethyl-5-phenyl-5-phosphabicyclo[2.2.1]hept-2-ene-P^7(*R*/*S*)]palladium(II), Complex 54. Figure 2.5.

Table A.1.5 Crystal data and structure refinement for complex 54

Empirical formula	C28 H29 Cl2 N P2 Pd S	
Formula weight	650.82	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.3423(6) Å	α = 90°.
	b = 18.4502(9) Å	β = 110.3160(10)°.
	c = 13.1919(7) Å	γ = 90°.
Volume	2817.2(2) Å^3	
Z	4	
Density (calculated)	1.534 Mg/m^3	
Goodness-of-fit on F^2	1.130	
Final R indices [I>2sigma(I)]	R1 = 0.0444, wR2 = 0.0983	
R indices (all data)	R1 = 0.0545, wR2 = 0.1020	

Table A 1.6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for complex **54**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	3035(1)	6973(1)	5480(1)	25(1)
Cl(1)	2892(1)	6117(1)	4067(1)	41(1)
Cl(2)	2092(1)	6250(1)	6350(1)	45(1)
P(1)	5487(1)	7898(1)	5970(1)	21(1)
P(2)	3136(1)	7743(1)	6786(1)	23(1)
S(1)	3979(1)	7775(1)	4741(1)	28(1)
C(1)	5302(3)	8102(2)	7254(2)	22(1)
C(2)	5240(3)	7422(2)	7938(3)	26(1)
C(3)	4081(3)	7486(2)	8152(3)	26(1)
C(4)	4088(3)	8182(2)	8757(3)	26(1)
C(5)	4144(3)	8760(2)	8163(3)	26(1)
C(6)	4148(3)	8518(2)	7061(2)	22(1)
C(7)	4109(3)	8173(2)	9898(3)	39(1)
C(8)	4253(4)	9538(2)	8466(3)	43(1)
C(9)	6422(3)	7119(2)	6179(3)	24(1)
C(10)	6031(3)	6471(2)	5643(3)	35(1)
C(11)	6756(4)	5870(2)	5887(3)	42(1)
C(12)	7850(3)	5921(2)	6629(3)	38(1)
C(13)	8244(3)	6567(2)	7146(3)	36(1)
C(14)	7533(3)	7166(2)	6927(3)	30(1)
C(15)	6191(3)	8652(2)	5584(3)	24(1)
C(16)	6455(3)	8570(2)	4651(3)	36(1)
C(17)	6950(3)	9128(2)	4269(3)	41(1)
C(18)	7178(3)	9776(2)	4816(3)	43(1)
C(19)	6907(4)	9867(2)	5737(4)	45(1)
C(20)	6414(3)	9307(2)	6127(3)	35(1)
C(21)	1755(3)	8077(2)	6745(3)	26(1)
C(22)	1303(3)	7908(2)	7551(3)	37(1)
C(23)	228(3)	8161(2)	7475(3)	41(1)
C(24)	-402(3)	8586(2)	6615(3)	41(1)
C(25)	43(3)	8760(2)	5818(3)	39(1)

C(26)	1113(3)	8501(2)	5876(3)	29(1)
N(1S)	5317(5)	5658(2)	8474(4)	88(2)
C(2S)	4898(5)	5372(2)	7683(4)	63(1)
C(1S)	4398(5)	5005(3)	6654(4)	74(2)

Appendix 4

X-ray Crystallographic Data for dichloro[5-thio-5-(ethenylphenylphosphino)-2,3-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-2-ene]palladium(II), (R_p,S_p)-57b.

Table A.1.7 Crystal data and structure refinement for complex (R_p,S_p)-57b

Empirical formula	C22 H24 Cl2 P2 Pd S	
Formula weight	559.71	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 12.724(3) Å	α = 90°.
	b = 20.666(4) Å	β = 114.095(4)°.
	c = 11.189(2) Å	γ = 90°.
Volume	2685.9(10) $Å^3$	
Z	4	
Density (calculated)	1.384 Mg/m^3	
Goodness-of-fit on F^2	1.066	
Final R indices [I>2sigma(I)]	R1 = 0.0748, wR2 = 0.1813	
R indices (all data)	R1 = 0.0919, wR2 = 0.1912	
Absolute structure parameter	-0.16(8)	

Table A 1.8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for complex (R_p,S_p)-**57b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	5045(1)	2263(1)	4289(1)	33(1)
Cl(1)	5697(4)	1617(2)	3041(4)	60(1)
Cl(2)	5012(3)	1395(2)	5679(4)	50(1)
P(1)	2904(3)	3250(2)	3893(3)	31(1)
P(2)	5181(3)	3035(2)	3016(3)	34(1)
S(1)	4373(3)	2977(2)	5389(3)	37(1)
C(1)	3151(10)	3513(6)	2464(12)	40(3)
C(2)	3059(11)	2987(8)	1451(12)	47(4)
C(3)	4193(11)	3007(8)	1285(11)	45(3)
C(4)	4335(12)	3627(8)	813(13)	51(4)
C(5)	4435(13)	4088(7)	1669(16)	56(4)
C(6)	4387(11)	3809(6)	2879(13)	40(3)
C(7)	4570(20)	4809(8)	1640(20)	88(6)
C(8)	4282(19)	3727(11)	-577(18)	86(6)
C(9)	1794(12)	2635(6)	3355(14)	45(3)
C(10)	1973(16)	2044(9)	3790(20)	72(5)
C(11)	2290(11)	3902(6)	4459(11)	34(3)
C(12)	1994(18)	4492(8)	3803(15)	76(6)
C(13)	1490(20)	4958(9)	4214(16)	87(7)
C(14)	1275(13)	4859(7)	5377(14)	52(4)
C(15)	1597(16)	4284(8)	5989(16)	61(4)
C(16)	2101(14)	3811(7)	5558(13)	49(4)
C(17)	6630(11)	3226(7)	3237(13)	45(3)
C(18)	7055(14)	3011(10)	2333(17)	68(5)
C(19)	8172(16)	3163(13)	2560(20)	98(8)
C(20)	8854(15)	3493(12)	3680(20)	92(7)
C(21)	8410(20)	3701(13)	4510(20)	97(7)
C(22)	7352(13)	3592(9)	4372(16)	66(5)

Appendix 5

X-ray Crystallographic Data for dichloro[5-thio-5-(ethenylphenylphosphino)-2,3-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-2-ene]palladium(II), (S_p,R_p)-57a. Figure 2.7.

Table A.1.9 Crystal data and structure refinement for complex (S_p,R_p)-57a

Empirical formula	C23 H26 Cl4 P2 Pd S	
Formula weight	644.64	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 8.9599(10) Å	α = 90°.
	b = 18.034(2) Å	β = 98.168(2)°.
	c = 16.6192(18) Å	γ = 90°.
Volume	2658.2(5) $Å^3$	
Z	4	
Density (calculated)	1.611 Mg/m^3	
Goodness-of-fit on F^2	1.090	
Final R indices [I>2sigma(I)]	R1 = 0.0441, wR2 = 0.1142	
R indices (all data)	R1 = 0.0511, wR2 = 0.1179	

Table A 1.10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for complex (S_p,R_p)-**57a** . U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	6659(1)	7065(1)	1698(1)	28(1)
Cl(1)	4605(1)	7733(1)	945(1)	47(1)
Cl(2)	6035(1)	5960(1)	1025(1)	38(1)
P(1)	7406(1)	7868(1)	3543(1)	28(1)
P(2)	8459(1)	6394(1)	2397(1)	27(1)
S(1)	7473(1)	8140(1)	2378(1)	36(1)
C(1)	6996(4)	6288(2)	3623(2)	34(1)
C(2)	8138(4)	6941(2)	3813(2)	29(1)
C(3)	9485(4)	6761(2)	3355(2)	28(1)
C(4)	10209(4)	6053(2)	3727(2)	33(1)
C(5)	9252(4)	5487(2)	3585(2)	35(1)
C(6)	7773(4)	5729(2)	3100(2)	32(1)
C(7)	9492(6)	4692(2)	3853(3)	54(1)
C(8)	11754(5)	6082(2)	4192(3)	47(1)
C(9)	8585(4)	8492(2)	4181(2)	32(1)
C(10)	9277(4)	9060(2)	3914(3)	41(1)
C(11)	5563(4)	7928(2)	3845(2)	34(1)
C(12)	4286(4)	8074(2)	3291(3)	42(1)
C(13)	2909(5)	8127(3)	3576(3)	49(1)
C(14)	2796(5)	8039(2)	4383(3)	51(1)
C(15)	4061(5)	7889(3)	4928(3)	50(1)
C(16)	5440(5)	7829(2)	4669(3)	45(1)
C(17)	9842(4)	5983(2)	1844(2)	31(1)
C(18)	11166(4)	6371(2)	1791(2)	40(1)
C(19)	12218(5)	6080(3)	1348(3)	50(1)
C(20)	11971(5)	5405(3)	968(3)	53(1)
C(21)	10675(5)	5015(2)	1020(2)	47(1)
C(22)	9597(4)	5303(2)	1466(2)	39(1)

Appendix 6

X-ray Crystallographic Data for dichloro[5-phenyl-1-ethenylphosphino-2,3-dimethyl-7-thio-7-phenyl-7-phosphabicyclo[2.2.1]hept-2-ene P^5,P^7]palladium(II), (R_p,S_p)-62b. Figure 2.11.

Table A.1.11 Crystal data and structure refinement for complex (R_p,S_p)-62b

Empirical formula	C22 H24 Cl2 P2 Pd S	
Formula weight	559.71	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 9.6477(4) Å	α = 90°.
	b = 15.0107(7) Å	β = 90°.
	c = 16.6936(8) Å	γ = 90°.
Volume	2417.55(19) $Å^3$	
Z	4	
Density (calculated)	1.538 Mg/m^3	
Goodness-of-fit on F^2	1.052	
Final R indices [I>2sigma(I)]	R1 = 0.0464, wR2 = 0.0873	
R indices (all data)	R1 = 0.0549, wR2 = 0.0903	
Absolute structure parameter	-0.04(3)	

Table A 1.12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (R_p,S_p)-**62b** . U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	4558(1)	1697(1)	3738(1)	29(1)
P(1)	4339(1)	2888(1)	2950(1)	29(1)
P(2)	4995(1)	3702(1)	4927(1)	30(1)
S(1)	5033(1)	2364(1)	4941(1)	40(1)
Cl(1)	4789(1)	374(1)	4507(1)	45(1)
Cl(2)	4068(1)	903(1)	2586(1)	41(1)
C(1)	4803(5)	3964(3)	3380(3)	28(1)
C(2)	6375(4)	3990(3)	3626(3)	33(1)
C(3)	6421(5)	4338(3)	4493(3)	38(1)
C(4)	5746(5)	5249(3)	4517(3)	34(1)
C(5)	4395(5)	5194(3)	4341(3)	33(1)
C(6)	3976(5)	4244(3)	4152(3)	31(1)
C(7)	6585(6)	6070(4)	4704(4)	52(2)
C(8)	3339(6)	5930(3)	4310(3)	47(1)
C(9)	5417(6)	2803(3)	2076(3)	42(1)
C(10)	6000(6)	3457(4)	1690(3)	51(2)
C(11)	2586(5)	3007(3)	2573(3)	31(1)
C(12)	1496(5)	2863(4)	3080(4)	43(1)
C(13)	143(6)	2932(4)	2819(4)	57(2)
C(14)	-101(6)	3181(5)	2038(4)	68(2)
C(15)	978(7)	3335(6)	1531(4)	87(3)
C(16)	2327(6)	3271(5)	1794(3)	65(2)
C(17)	4623(5)	4077(3)	5925(3)	33(1)
C(18)	5711(5)	4308(3)	6433(3)	39(1)
C(19)	5442(6)	4528(4)	7216(3)	52(2)
C(20)	4093(6)	4532(5)	7489(4)	59(2)
C(21)	3023(6)	4309(5)	6982(4)	58(2)
C(22)	3278(5)	4068(4)	6203(4)	43(1)

Appendix 7

X-ray Crystallographic Data for dichloro[5-phenyl-1-ethenylarsino-2,3-dimethyl-7-thio-7-phenyl-7-phosphabicyclo[2.2.1]hept-2-ene]palladium(II), Complex 71, Figure 2.12.

Table A 1.13 Crystal data and structure refinement for complex 71

Empirical formula	C22 H24 As Cl2 P Pd S	
Formula weight	603.66	
Temperature	273(2) K	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.5297(5) Å	α = 90°.
	b = 9.3137(4) Å	β = 97.4250(10)°.
	c = 20.1170(8) Å	γ = 90°.
Volume	2327.93(16) $Å^3$	
Z	4	
Density (calculated)	1.722 Mg/m^3	
Goodness-of-fit on F^2	1.189	
Final R indices [I>2sigma(I)]	R1 = 0.0585, wR2 = 0.1053	
R indices (all data)	R1 = 0.0770, wR2 = 0.1111	
Largest diff. peak and hole	0.851 and -0.689 $e.Å^{-3}$	

Table A 1.14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for complex **71**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	3433(1)	6698(1)	2338(1)	26(1)
As(1)	4176(1)	6555(1)	3457(1)	27(1)
Cl(1)	2840(1)	7026(1)	1187(1)	36(1)
Cl(2)	5131(1)	6010(2)	2123(1)	38(1)
P(1)	1302(1)	6962(1)	3408(1)	26(1)
S(1)	1713(1)	7361(2)	2492(1)	38(1)
C(1)	2771(4)	8424(5)	4116(3)	32(1)
C(2)	3195(4)	6853(5)	4126(2)	26(1)
C(3)	2188(4)	5881(5)	4007(2)	25(1)
C(4)	1590(4)	6093(5)	4611(2)	26(1)
C(5)	1227(4)	7443(5)	4640(2)	28(1)
C(6)	1530(4)	8330(5)	4063(3)	30(1)
C(7)	598(5)	8094(6)	5145(3)	42(1)
C(8)	1508(5)	4855(6)	5080(3)	42(1)
C(9)	4902(5)	4789(6)	3719(3)	40(1)
C(10)	4683(5)	3936(7)	4178(3)	54(2)
C(11)	-59(4)	6322(5)	3305(2)	28(1)
C(12)	-272(4)	4857(6)	3288(3)	33(1)
C(13)	-1322(4)	4386(7)	3153(3)	41(1)
C(14)	-2154(5)	5356(7)	3039(3)	44(2)
C(15)	-1953(4)	6799(7)	3069(3)	45(2)
C(16)	-904(4)	7301(6)	3206(3)	39(1)
C(17)	5241(4)	8024(6)	3689(3)	31(1)
C(18)	5128(5)	9319(6)	3356(3)	45(2)
C(19)	5844(5)	10433(7)	3522(3)	53(2)
C(20)	6694(6)	10223(8)	4028(3)	59(2)
C(21)	6819(5)	8947(8)	4368(3)	55(2)
C(22)	6081(5)	7845(7)	4197(3)	43(1)

Appendix 8

X-ray Crystallographic Data for [(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-*C*,*N*][(4*R*,7*S*)-5,6-dimethyl-7-phenyl-2-(diphenylphosphino)-7-phosphabicyclo[2.2.1]hept-5-en-2-yl ethanol]palladium(II) perchlorate, Complex (R_c,S_p)-76, Figure 3.1 .

Table A 1.15 Crystal data and structure refinement for complex (R_c,S_p)-76

Empirical formula	C42 H46 Cl N O5 P2 Pt	
Formula weight	937.28	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 9.3185(4) Å	α = 90°.
	b = 20.2115(9) Å	β = 90°.
	c = 21.4080(8) Å	γ = 90°.
Volume	4032.0(3) $Å^3$	
Z	4	
Density (calculated)	1.544 Mg/m^3	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0683, wR2 = 0.1477	
R indices (all data)	R1 = 0.0925, wR2 = 0.1589	
Absolute structure parameter	0.010(12)	
Largest diff. peak and hole	2.206 and -0.665 $e.Å^{-3}$	

Table A 1.16. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (R_c,S_p)-**76**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pt(1)	5286(1)	4041(1)	7200(1)	46(1)
P(1)	6958(3)	4832(1)	7058(1)	45(1)
P(2)	5684(3)	4274(2)	8228(1)	51(1)
O(1)	9490(30)	6764(9)	7958(8)	224(10)
N(1)	3629(11)	3325(5)	7280(4)	61(2)
C(1)	4854(13)	3873(5)	6265(4)	50(3)
C(2)	5219(13)	4291(5)	5761(4)	52(2)
C(3)	4835(12)	4117(6)	5163(5)	63(3)
C(4)	4063(13)	3553(7)	5028(5)	57(3)
C(5)	3681(15)	3375(8)	4423(6)	77(4)
C(6)	2940(20)	2825(10)	4309(7)	103(6)
C(7)	2475(17)	2423(10)	4778(8)	101(6)
C(8)	2793(15)	2558(8)	5388(7)	78(4)
C(9)	3616(11)	3148(6)	5535(5)	55(3)
C(10)	4061(13)	3326(6)	6153(5)	53(3)
C(11)	3737(14)	2890(7)	6718(5)	60(3)
C(12)	4906(19)	2358(6)	6789(6)	87(4)
C(13)	3605(15)	2913(7)	7871(6)	80(4)
C(14)	2211(12)	3679(7)	7258(6)	69(3)
C(15)	8429(13)	4325(6)	8085(5)	57(3)
C(16)	8893(14)	5551(7)	7888(7)	76(4)
C(17)	8320(20)	6257(9)	7791(10)	113(6)
C(18)	7753(11)	5002(6)	7850(5)	53(2)
C(19)	6447(12)	5095(6)	8293(4)	50(3)
C(20)	6961(14)	5103(7)	8962(5)	59(3)
C(21)	7427(14)	4523(8)	9132(5)	67(4)
C(22)	7390(12)	4038(7)	8581(4)	59(3)
C(23)	6745(18)	5702(8)	9361(6)	85(5)
C(24)	7952(18)	4268(8)	9746(5)	81(5)
C(25)	8456(12)	4638(7)	6543(4)	56(3)
C(26)	9450(20)	5091(10)	6351(9)	137(9)

C(27)	10610(20)	5009(11)	6007(8)	122(7)
C(28)	10642(18)	4376(13)	5750(6)	110(7)
C(29)	9739(19)	3864(8)	5919(7)	95(5)
C(30)	8620(13)	4023(9)	6312(6)	74(4)
C(31)	6094(13)	5586(6)	6766(5)	54(3)
C(32)	6667(19)	6051(8)	6371(6)	91(5)
C(33)	5830(30)	6581(8)	6123(8)	100(6)
C(34)	4470(30)	6653(10)	6288(9)	121(8)
C(35)	3830(20)	6194(9)	6666(11)	116(7)
C(36)	4680(20)	5671(8)	6892(8)	95(5)
C(37)	4312(14)	4194(8)	8839(5)	73(4)
C(38)	3139(16)	4591(10)	8821(7)	92(5)
C(39)	2060(19)	4530(13)	9277(9)	126(8)
C(40)	2330(40)	3990(20)	9739(10)	191(18)
C(41)	3520(30)	3594(19)	9742(11)	174(16)
C(42)	4406(18)	3702(9)	9295(6)	91(5)
Cl(1)	319(7)	7376(4)	6376(4)	209(4)
O(2)*	1410(20)	7526(13)	5890(8)	156(11)
O(3)*	960(20)	7444(12)	7009(7)	124(7)
O(4)*	-900(30)	7852(14)	6312(12)	300(20)
O(5)*	-220(30)	6690(10)	6290(12)	245(16)
O(2A)#	1770(20)	7530(20)	6118(17)	200
O(3A)#	430(40)	6786(13)	6789(15)	200
O(4A)#	-230(40)	7951(13)	6737(16)	200
O(5A)#	-690(30)	7230(20)	5850(13)	200

*sof=0.6 #sof=0.5

Appendix 9

X-ray Crystallographic Data for, Complex dichloro[(4*R*,7*S*)-5,6-dimethyl-7-phenyl-2-(diphenylphosphino)-7-phosphabicyclo[2.2.1]hept-5-en-2-yl ethanol]palladium(II), Complex (S_p)-77, Figure 3.4.

Table A 1.17 Crystal data and structure refinement for complex (S_p)-77

Empirical formula	C28 H30 Cl2 O P2 Pt	
Formula weight	710.45	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 11.1520(6) Å	α = 90°.
	b = 11.3003(5) Å	β = 90°.
	c = 21.2068(10) Å	γ = 90°.
Volume	2672.5(2) $Å^3$	
Z	4	
Density (calculated)	1.766 Mg/m^3	
Goodness-of-fit on F^2	0.978	
Final R indices [I>2sigma(I)]	R1 = 0.0355, wR2 = 0.0647	
R indices (all data)	R1 = 0.0403, wR2 = 0.0662	
Absolute structure parameter	-0.001(6)	

Table A 1.18. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for complex (S_p)-**77**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pt(1)	2124(1)	2974(1)	3039(1)	27(1)
P(1)	1741(1)	4573(1)	3623(1)	26(1)
P(2)	2706(1)	4305(1)	2336(1)	28(1)
Cl(1)	2555(2)	1281(1)	2429(1)	45(1)
Cl(2)	1526(2)	1705(1)	3859(1)	50(1)
O(1)	1089(5)	9050(4)	3471(2)	56(1)
C(1)	796(5)	5566(5)	2542(2)	27(1)
C(2)	1758(4)	5858(4)	3063(3)	26(1)
C(3)	1584(5)	7035(5)	3417(2)	34(1)
C(4)	1336(7)	8141(5)	3053(3)	53(2)
C(5)	3006(5)	5745(4)	2716(2)	26(1)
C(6)	3051(5)	6551(5)	2149(2)	27(1)
C(7)	2241(6)	6233(5)	1721(2)	32(1)
C(8)	1516(5)	5192(4)	1944(3)	28(1)
C(10)	3959(6)	7529(6)	2105(3)	47(2)
C(11)	1982(6)	6812(5)	1100(3)	47(2)
C(1A)	2915(6)	4837(5)	4206(2)	30(1)
C(2A)	3981(6)	4208(6)	4160(3)	40(2)
C(3A)	4884(6)	4389(7)	4591(3)	54(2)
C(4A)	4756(6)	5205(7)	5067(3)	49(2)
C(5A)	3704(7)	5813(6)	5115(3)	46(2)
C(6A)	2762(6)	5626(5)	4691(2)	39(1)
C(1B)	349(5)	4588(5)	4075(3)	31(1)
C(2B)	327(6)	3969(5)	4641(3)	37(1)
C(3B)	-689(7)	3929(6)	4995(3)	47(2)
C(4B)	-1719(6)	4502(6)	4800(3)	47(2)
C(5B)	-1716(6)	5093(6)	4242(3)	46(2)
C(6B)	-685(6)	5142(6)	3874(3)	39(2)
C(1C)	3835(5)	3957(5)	1761(3)	32(1)
C(2C)	4942(6)	4531(6)	1754(3)	42(2)
C(3C)	5769(6)	4260(7)	1300(4)	55(2)

C(4C)	5514(8)	3413(7)	855(4)	67(2)
C(5C)	4439(8)	2847(7)	859(4)	63(2)
C(6C)	3601(7)	3117(6)	1312(3)	47(2)

Appendix 10

X-ray Crystallographic Data for Complex chloro[(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-*C,N*][2-diphenylphosphanyl-prop-2-en-1-ol] platinum(II), Complex (R_c)-79, Figure 3.5.

Table A 1.19 Crystal data and structure refinement for complex (R_c)-79

Empirical formula	C29 H31 Cl N O P Pt	
Formula weight	671.06	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 12.3326(6) Å	α = 90°.
	b = 13.3464(7) Å	β= 90°.
	c = 16.1563(9) Å	γ = 90°.
Volume	2659.3(2) $Å^3$	
Z	4	
Density (calculated)	1.676 Mg/m^3	
Goodness-of-fit on F^2	1.010	
Final R indices [I>2sigma(I)]	R1 = 0.0346, wR2 = 0.0670	
R indices (all data)	R1 = 0.0408, wR2 = 0.0690	
Absolute structure parameter	0.006(7)	
Largest diff. peak and hole	1.802 and -0.534 $e.Å^{-3}$	

Table A 1.20. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (R_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)	1158(1)	1351(1)	8951(1)	26(1)
P(1)	1916(1)	349(1)	9905(1)	27(1)
Cl(1)	16(1)	-69(1)	8613(1)	40(1)
N(1)	535(4)	2391(4)	8024(3)	34(1)
O(1)	1593(4)	-2839(4)	9257(4)	55(2)
C(1)	1952(4)	2701(4)	9158(3)	26(1)
C(2)	2483(5)	3013(5)	9891(4)	35(1)
C(3)	3018(4)	3949(5)	9939(4)	35(2)
C(4)	3055(4)	4665(5)	9266(4)	36(2)
C(5)	3664(5)	5606(5)	9284(5)	43(2)
C(6)	3722(5)	6276(5)	8609(5)	50(2)
C(7)	3183(5)	6036(5)	7899(5)	50(2)
C(8)	2574(5)	5152(5)	7855(5)	43(2)
C(9)	2505(5)	4420(5)	8534(4)	34(1)
C(10)	1949(4)	3431(4)	8517(4)	29(1)
C(11)	1378(4)	3107(5)	7753(4)	32(1)
C(12)	2086(6)	2560(6)	7133(4)	48(2)
C(13)	-250(5)	3068(6)	8435(5)	48(2)
C(14)	66(6)	1842(6)	7316(4)	51(2)
C(15)	1606(4)	-1103(4)	9944(4)	31(1)
C(16)	1905(5)	-1752(5)	9190(4)	42(2)
C(17)	1146(5)	-1551(5)	10575(4)	44(2)
C(18)	3287(4)	262(4)	9815(4)	29(1)
C(19)	3800(5)	-540(5)	10239(4)	44(2)
C(20)	4840(5)	-646(6)	10166(5)	52(2)
C(21)	5345(5)	63(6)	9666(5)	48(2)
C(22)	4860(5)	846(5)	9236(5)	46(2)
C(23)	3813(5)	947(5)	9304(4)	34(1)
C(24)	1604(4)	759(4)	10948(4)	32(1)
C(25)	2198(6)	505(5)	11636(4)	45(2)
C(26)	1829(8)	640(7)	12418(5)	62(2)

C(27)	882(7)	1049(6)	12543(5)	61(2)
C(28)	303(6)	1332(6)	11879(5)	53(2)
C(29)	664(5)	1187(5)	11087(4)	42(2)

Appendix 11

X-ray Crystallographic Data for Complex [(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-*C,N*][(4*R*,7*S*)-5,6-dimethyl-7-phenyl-2-(diphenylphosphino)-7-phosphabicyclo[2.2.1]hept-5-en-2-yl methanol]palladium(II) perchlorate, Complex (R_c,S_p)-81, Figure 3.6.

Table A 1.21 Crystal data and structure refinement for complex (R_c,S_p)-81

Empirical formula	C43 H45 Cl N2 O5 P2 Pt	
Formula weight	962.29	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 9.419(2) Å	α = 90°.
	b = 20.225(5) Å	β = 90°.
	c = 21.293(6) Å	γ = 90°.
Volume	4056.3(18) $Å^3$	
Z	4	
Density (calculated)	1.576 Mg/m^3	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0529, wR2 = 0.1226	
R indices (all data)	R1 = 0.0629, wR2 = 0.1263	
Absolute structure parameter	0.025(10)	
Largest diff. peak and hole	3.937 and -1.773 $e.Å^{-3}$	

Table A 1.22. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for complex (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)	4770(1)	5960(1)	7198(1)	36(1)
P(1)	3093(2)	5176(1)	7058(1)	38(1)
P(2)	4457(2)	5690(1)	8231(1)	39(1)
O(1)*	1966(10)	3820(4)	7755(5)	66(2)
O(1A)#	10(20)	4607(16)	7614(9)	70(8)
N(1)	6480(7)	6665(3)	7274(4)	44(2)
C(1)	5142(9)	6125(4)	6249(4)	42(2)
C(2)	4679(10)	5763(4)	5780(4)	48(2)
C(3)	5033(8)	5919(4)	5135(4)	43(2)
C(4)	5913(10)	6461(4)	5002(4)	44(2)
C(5)	6267(11)	6653(5)	4395(4)	56(2)
C(6)	7137(13)	7183(7)	4268(5)	74(3)
C(7)	7693(13)	7539(6)	4788(5)	66(3)
C(8)	7366(11)	7390(5)	5377(5)	54(3)
C(9)	6439(9)	6858(4)	5509(4)	44(2)
C(10)	6012(9)	6671(4)	6136(4)	40(2)
C(11)	6389(10)	7107(5)	6689(4)	44(2)
C(12)	5318(14)	7648(4)	6777(5)	62(3)
C(13)	7804(9)	6278(5)	7250(5)	56(2)
C(14)	6463(13)	7082(5)	7839(5)	71(3)
C(15)	2356(9)	4985(4)	7857(4)	37(2)
C(16)	1288(10)	4418(4)	7900(5)	51(2)
C(17)	1717(10)	5663(5)	8121(4)	46(2)
C(18)	2761(9)	5889(4)	8627(4)	41(2)
C(19)	2763(10)	5389(5)	9156(4)	44(2)
C(20)	3240(10)	4807(4)	8962(3)	42(2)
C(21)	3710(9)	4844(4)	8283(3)	38(2)
C(22)	3423(12)	4171(5)	9314(5)	61(3)
C(23)	2275(13)	5577(6)	9816(4)	60(3)
C(24)	3976(11)	4434(4)	6743(4)	46(2)
C(25)	5416(13)	4375(6)	6825(5)	66(3)

C(26)	6189(16)	3856(6)	6595(8)	96(5)
C(27)	5507(19)	3365(6)	6251(6)	82(4)
C(28)	4125(18)	3414(6)	6157(5)	79(4)
C(29)	3290(14)	3922(5)	6404(5)	68(3)
C(30)	1574(9)	5384(5)	6553(4)	46(2)
C(31)	1457(10)	5996(6)	6320(4)	57(2)
C(32)	314(13)	6183(6)	5917(5)	71(3)
C(33)	-659(13)	5693(8)	5771(5)	80(4)
C(34)	-584(12)	5081(7)	6020(6)	84(4)
C(35)	546(11)	4929(6)	6425(5)	66(3)
C(36)	5850(11)	5717(5)	8819(4)	50(2)
C(37)	7007(12)	5277(6)	8773(4)	65(3)
C(38)	8042(16)	5280(8)	9230(7)	99(5)
C(39)	7981(14)	5700(9)	9734(6)	91(5)
C(40)	6896(14)	6113(7)	9788(6)	84(4)
C(41)	5813(11)	6146(6)	9332(4)	60(3)
Cl(1)	9016(5)	2875(3)	7424(3)	128(2)
O(2)	9541(16)	3230(6)	6908(6)	146(5)
O(3)	8067(17)	2401(6)	7248(8)	176(6)
O(4)	8230(19)	3424(8)	7715(7)	185(7)
O(5)	10120(16)	2713(9)	7849(8)	195(7)
C(1S)	10060(20)	7201(12)	9168(11)	192(11)
C(2S)	9150(20)	7492(9)	9624(8)	106(5)
N(1S)	8390(30)	7741(8)	10032(11)	170(8)

*sof=0.75 #sof=0.25

Appendix 12

X-ray Crystallographic Data for dichloro[(4*R*,7*S*)-5,6-dimethyl-7-phenyl-2-(diphenylphosphino)-7-phosphabicyclo[2.2.1]hept-5-en-2-yl methanol]palladium(II) perchlorate, Complex (S_p)-82, Figure 3.9.

Table A 1.23 Crystal data and structure refinement for complex (S_p)-82

Empirical formula	C28 H30 Cl4 O P2 Pt	
Formula weight	781.35	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 9.0762(10) Å	α = 90°.
	b = 17.7661(19) Å	β = 90°.
	c = 18.235(2) Å	γ = 90°.
Volume	2940.4(6) $Å^3$	
Z	4	
Density (calculated)	1.765 Mg/m^3	
Goodness-of-fit on F^2	0.988	
Final R indices [I>2sigma(I)]	R1 = 0.0260, wR2 = 0.0576	
R indices (all data)	R1 = 0.0296, wR2 = 0.0589	
Absolute structure parameter	0.004(5)	

Table A 1.24. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for complex (S_p)-**82**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pt(1)	6413(1)	2528(1)	2227(1)	23(1)
Cl(1)	7079(1)	1624(1)	1332(1)	33(1)
Cl(2)	7014(1)	1666(1)	3161(1)	36(1)
P(1)	5975(1)	3464(1)	3027(1)	24(1)
P(2)	5778(1)	3368(1)	1401(1)	25(1)
O(1)	4103(6)	4943(2)	3498(2)	72(1)
C(1)	5018(5)	4213(2)	2474(2)	32(1)
C(2)	4842(8)	5014(3)	2841(3)	66(2)
C(3)	3561(5)	3829(3)	2190(2)	37(1)
C(4)	3820(5)	3651(2)	1366(2)	33(1)
C(5)	3955(5)	4404(2)	966(2)	33(1)
C(6)	5133(6)	4777(2)	1205(2)	36(1)
C(7)	5982(5)	4317(2)	1773(2)	29(1)
C(8)	2796(6)	4636(3)	436(3)	49(1)
C(9)	5694(7)	5534(3)	983(3)	50(1)
C(10)	7701(5)	3846(2)	3372(2)	29(1)
C(11)	8983(5)	3447(3)	3242(2)	37(1)
C(12)	10325(5)	3699(3)	3508(3)	44(1)
C(13)	10406(6)	4341(3)	3897(3)	47(1)
C(14)	9146(6)	4746(3)	4044(3)	44(1)
C(15)	7803(5)	4510(2)	3784(3)	37(1)
C(16)	4853(5)	3207(2)	3816(2)	28(1)
C(17)	4921(5)	3592(2)	4480(2)	37(1)
C(18)	4044(5)	3368(3)	5064(2)	46(1)
C(19)	3104(6)	2767(3)	4994(3)	45(1)
C(20)	3045(6)	2375(3)	4345(3)	42(1)
C(21)	3931(4)	2590(2)	3760(2)	33(1)
C(22)	6539(5)	3348(2)	484(2)	31(1)
C(23)	7989(6)	3556(3)	386(3)	45(1)
C(24)	8587(6)	3552(3)	-312(3)	55(1)
C(25)	7777(7)	3332(3)	-900(3)	50(1)

C(26)	6336(7)	3112(3)	-806(3)	51(1)
C(27)	5686(6)	3125(3)	-107(2)	40(1)
C(1S)	184(7)	838(3)	2532(3)	66(2)
Cl(1A)	1212(2)	1611(1)	2806(1)	80(1)
Cl(1B)	78(2)	137(1)	3199(1)	94(1)

Appendix 13

X-ray Crystallographic Data for [(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*][(*R*)3,4-bis(diphenylphosphino)butan-1-ol]palladium(II)perchlorate, (R_c,R_c)-87a, Figure 4.1.

Table A 1.25 Crystal data and structure refinement for complex (R_c,R_c)-87a

Empirical formula	C43 H46 Cl3 N O5 P2 Pd	
Formula weight	931.50	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.0929(11) Å	α = 90°.
	b = 19.017(2) Å	β = 90°.
	c = 22.489(2) Å	γ = 90°.
Volume	4316.5(8) $Å^3$	
Z	4	
Density (calculated)	1.433 Mg/m^3	
Goodness-of-fit on F^2	1.077	
Final R indices [I>2sigma(I)]	R1 = 0.0487, wR2 = 0.1235	
R indices (all data)	R1 = 0.0537, wR2 = 0.1269	
Absolute structure parameter	-0.01(3)	

Table A 1.26. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (R_c,R_c)-**87a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	5174(1)	5680(1)	7369(1)	28(1)
P(1)	3453(1)	5077(1)	6989(1)	29(1)
P(2)	4523(1)	5170(1)	8278(1)	35(1)
N(1)	6875(3)	6275(2)	7634(2)	35(1)
O(1)	818(6)	3333(3)	7669(3)	96(2)
C(1)	5659(4)	6130(2)	6569(2)	29(1)
C(2)	5301(5)	5933(2)	5983(2)	36(1)
C(3)	5747(5)	6276(3)	5500(2)	39(1)
C(4)	6576(5)	6870(2)	5560(2)	36(1)
C(5)	7001(5)	7262(3)	5048(2)	47(1)
C(6)	7782(6)	7834(3)	5108(2)	51(1)
C(7)	8189(6)	8051(3)	5688(2)	47(1)
C(8)	7790(5)	7693(2)	6178(2)	38(1)
C(9)	6974(4)	7096(2)	6128(2)	34(1)
C(10)	6506(4)	6700(2)	6628(2)	31(1)
C(11)	6880(4)	6924(2)	7254(2)	34(1)
C(12)	5903(6)	7476(3)	7481(2)	46(1)
C(13)	8071(5)	5838(3)	7468(2)	47(1)
C(14)	6990(6)	6464(3)	8273(2)	48(1)
C(15)	2750(5)	5003(3)	8188(2)	42(1)
C(16)	2472(4)	4641(2)	7585(2)	37(1)
C(17)	974(5)	4600(3)	7470(3)	50(1)
C(18)	320(7)	4019(4)	7813(3)	82(2)
C(19)	3922(4)	4334(3)	6524(2)	36(1)
C(20)	2973(6)	3850(3)	6310(2)	48(1)
C(21)	3373(8)	3286(3)	5986(3)	61(2)
C(22)	4676(11)	3178(3)	5872(3)	87(3)
C(23)	5636(8)	3629(4)	6077(3)	74(2)
C(24)	5244(6)	4213(3)	6402(2)	50(1)
C(25)	2271(4)	5618(2)	6582(2)	34(1)
C(26)	1737(6)	5421(3)	6039(2)	48(1)

C(27)	796(6)	5853(3)	5765(3)	59(2)
C(28)	387(6)	6462(3)	6034(3)	58(2)
C(29)	924(6)	6648(3)	6578(3)	55(1)
C(30)	1857(5)	6241(3)	6848(3)	46(1)
C(31)	4622(6)	5625(3)	8994(2)	50(1)
C(32)	5521(8)	5440(4)	9422(2)	67(2)
C(33)	5577(10)	5819(5)	9949(3)	93(3)
C(34)	4769(11)	6341(4)	10063(3)	93(3)
C(35)	3846(9)	6538(4)	9649(4)	81(3)
C(36)	3784(7)	6186(3)	9102(3)	65(2)
C(37)	5267(5)	4323(3)	8415(2)	38(1)
C(38)	6218(5)	4062(3)	8029(2)	43(1)
C(39)	6793(6)	3410(3)	8139(3)	53(1)
C(40)	6426(6)	3030(3)	8628(3)	55(1)
C(41)	5455(6)	3275(3)	9013(3)	54(1)
C(42)	4861(6)	3913(3)	8907(2)	45(1)
C(1S)	5050(20)	4397(6)	4545(4)	234(12)
Cl(1A)	3606(3)	4923(2)	4773(1)	110(1)
Cl(1B)	5963(4)	5020(3)	4073(2)	176(2)
Cl(1)	-894(2)	2405(1)	6485(1)	91(1)
O(2)	-1416(12)	2423(5)	5932(3)	166(4)
O(3)	-786(10)	1731(5)	6687(4)	157(4)
O(4)	269(10)	2773(6)	6540(5)	175(4)
O(5)	-1783(15)	2696(9)	6843(7)	277(9)

Appendix 14

X-ray Crystallographic Data for dichloro[(*R*)3,4-bis(diphenylphosphino)butan-1-ol]palladium(II), (R_c)-88, Figure 4.1.

Table A 1.27 Crystal data and structure refinement for complex (R_c)-88

Empirical formula	C29 H30 Cl4 O P2 Pd	
Formula weight	704.67	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 9.193(2) Å	α = 90°.
	b = 9.091(2) Å	β = 99.492(6)°.
	c = 19.086(5) Å	γ = 90°.
Volume	1573.1(7) $Å^3$	
Z	2	
Density (calculated)	1.488 Mg/m^3	
Goodness-of-fit on F^2	1.140	
Final R indices [I>2sigma(I)]	R1 = 0.0970, wR2 = 0.2208	
R indices (all data)	R1 = 0.1087, wR2 = 0.2280	
Absolute structure parameter	0.01(9)	

Table A 1.28. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for complex(R_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)	5842(1)	2439(1)	7640(1)	14(1)
P(1)	7484(4)	1535(4)	8528(2)	16(1)
P(2)	5848(4)	215(4)	7160(2)	18(1)
Cl(1)	6003(4)	4821(4)	8150(2)	30(1)
Cl(2)	4041(4)	3172(5)	6685(2)	33(1)
C(1)	7430(15)	-816(16)	7635(7)	21(3)
C(2)	7621(14)	-483(15)	8412(7)	18(3)
C(3)	9016(14)	-1143(15)	8844(8)	23(3)
C(4)	8978(19)	-2831(19)	8873(9)	39(4)
O(1)	7872(15)	-3288(15)	9272(7)	52(3)
C(1A)	9316(4)	2271(5)	8505(2)	18(3)
C(2A)	9590(4)	2883(5)	7872(2)	35(4)
C(3A)	10989(5)	3410(6)	7822(3)	30(4)
C(4A)	12113(4)	3324(7)	8405(3)	35(4)
C(5A)	11839(4)	2712(6)	9038(3)	24(3)
C(6A)	10440(4)	2185(5)	9088(2)	26(3)
C(1B)	7072(4)	1854(5)	9419(2)	22(3)
C(2B)	7516(5)	3143(5)	9783(2)	22(3)
C(3B)	7105(5)	3414(7)	10440(2)	27(3)
C(4B)	6250(6)	2395(8)	10733(2)	39(3)
C(5B)	5806(5)	1105(7)	10368(2)	38(4)
C(6B)	6217(4)	835(6)	9711(2)	40(4)
C(1C)	4212(4)	-834(5)	7244(2)	14(3)
C(2C)	4162(5)	-2351(5)	7149(2)	26(3)
C(3C)	2890(5)	-3125(6)	7219(3)	38(4)
C(4C)	1669(5)	-2383(7)	7384(3)	47(4)
C(5C)	1718(4)	-867(7)	7479(3)	54(5)
C(6C)	2990(4)	-93(6)	7409(2)	29(3)
C(1D)	6043(5)	222(5)	6227(2)	29(3)
C(2D)	7136(5)	1126(6)	6039(2)	44(4)
C(3D)	7389(6)	1154(7)	5341(2)	64(6)

C(4D)	6549(7)	278(8)	4831(2)	48(5)
C(5D)	5455(6)	-626(7)	5018(2)	53(5)
C(6D)	5202(5)	-654(6)	5716(2)	38(4)
C(1S)	8290(30)	5867(15)	5630(20)	163(17)
ClA	7555(8)	5565(9)	6473(4)	92(2)
ClB*	9132(13)	7724(11)	5791(6)	83(3)
ClC#	9887(16)	4576(15)	5810(9)	75(5)

*sof =0.6 #sof=0.4

Appendix 15

X-ray Crystallographic Data for chloro[(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*][2-(diphenylphosphino)prop-2-en-1-ol], (R_c)-90, Figure 4.3.

Table A 1.29 Crystal data and structure refinement for complex (R_c)-90

Empirical formula	C29 H31 Cl N O P Pd	
Formula weight	582.37	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 12.2005(5) Å	α = 90°.
	b = 13.3602(6) Å	β = 90°.
	c = 16.7910(8) Å	γ = 90°.
Volume	2737.0(2) $Å^3$	
Z	4	
Density (calculated)	1.413 Mg/m^3	
Goodness-of-fit on F^2	0.928	
Final R indices [I>2sigma(I)]	R1 = 0.0523, wR2 = 0.0877	
R indices (all data)	R1 = 0.0674, wR2 = 0.0926	
Absolute structure parameter	0.03(3)	
Largest diff. peak and hole	1.519 and -0.538 $e.Å^{-3}$	

Table A 1.30. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for complex(R_c)-**90** . U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	1224(1)	1577(1)	8470(1)	37(1)
P(1)	2185(1)	805(1)	7504(1)	35(1)
Cl(1)	2679(1)	2748(1)	8756(1)	53(1)
N(1)	225(3)	2145(3)	9404(2)	44(1)
O(1)	3834(4)	738(4)	8852(3)	83(1)
C(1)	-141(4)	780(3)	8269(3)	32(1)
C(2)	-482(4)	292(4)	7564(3)	41(1)
C(3)	-1448(4)	-220(3)	7526(3)	38(1)
C(4)	-2145(4)	-290(3)	8191(3)	39(1)
C(5)	-3131(4)	-849(4)	8169(4)	52(2)
C(6)	-3776(5)	-921(4)	8833(4)	60(2)
C(7)	-3482(5)	-441(4)	9529(4)	66(2)
C(8)	-2538(4)	111(4)	9575(4)	53(2)
C(9)	-1846(4)	199(4)	8901(3)	41(1)
C(10)	-837(4)	739(4)	8920(3)	37(1)
C(11)	-465(4)	1287(4)	9658(3)	48(1)
C(12)	149(5)	551(5)	10204(3)	68(2)
C(13)	807(5)	2594(5)	10095(3)	68(2)
C(14)	-497(5)	2922(4)	9058(3)	61(2)
C(15)	3655(4)	1118(4)	7450(3)	46(1)
C(16)	4346(5)	747(5)	8119(4)	69(2)
C(17)	4085(4)	1594(4)	6846(3)	59(2)
C(18)	1706(4)	1187(3)	6522(4)	39(1)
C(19)	1322(4)	2161(4)	6459(3)	48(1)
C(20)	1067(5)	2572(4)	5740(4)	63(2)
C(21)	1152(6)	2010(5)	5075(4)	73(2)
C(22)	1509(6)	1031(5)	5112(4)	71(2)
C(23)	1787(5)	627(4)	5842(4)	56(2)
C(24)	2265(4)	-568(3)	7557(3)	38(1)
C(25)	3017(5)	-1068(5)	7091(4)	60(2)
C(26)	3136(6)	-2098(5)	7173(4)	67(2)

C(27)	2508(5)	-2619(4)	7706(4)	54(2)
C(28)	1779(5)	-2118(4)	8168(4)	60(2)
C(29)	1667(4)	-1088(4)	8104(3)	45(1)

Appendix 16

X-ray Crystallographic Data for [(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*][2,3-bis(diphenylphosphino)propan-1-ol]palladium(II)perchlorate, Complex-92, Figure 4.4 and 4.5.

Table A 1.31 Crystal data and structure refinement for complex 92

Empirical formula	C41.50 H43 Cl2 N O5 P2 Pd	
Formula weight	875.01	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 9.7268(4) Å	α = 105.5550(10)°.
	b = 10.9351(5) Å	β = 92.7950(10)°.
	c = 19.9748(9) Å	γ = 98.1280(10)°.
Volume	2017.83(15) $Å^3$	
Z	2	
Density (calculated)	1.440 Mg/m^3	
Goodness-of-fit on F^2	1.012	
Final R indices [I>2sigma(I)]	R1 = 0.0569, wR2 = 0.1238	
R indices (all data)	R1 = 0.0764, wR2 = 0.1340	
Absolute structure parameter	0.02(3)	
Largest diff. peak and hole	0.662 and -0.453 $e.Å^{-3}$	

Table A 1.32. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for complexe **92**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	9835(1)	9792(1)	9021(1)	43(1)
Pd(2)	8608(1)	9508(1)	3587(1)	41(1)
P(1)	9025(2)	7704(2)	8302(1)	49(1)
P(2)	8372(2)	10402(2)	8314(1)	48(1)
P(3)	9898(2)	11528(2)	3564(1)	46(1)
P(4)	10145(2)	8632(2)	2868(1)	41(1)
O(1)	8125(11)	5819(11)	6764(5)	147(4)
O(2)	14033(7)	11723(8)	3127(5)	103(2)
N(1)	11201(7)	9348(5)	9764(3)	55(2)
N(2)	7092(7)	10111(6)	4294(4)	55(2)
C(1)	10717(8)	11627(7)	9586(4)	45(2)
C(2)	10752(10)	12791(9)	9398(5)	57(2)
C(3)	11528(9)	13904(7)	9781(5)	57(2)
C(4)	12326(8)	13962(7)	10411(4)	50(2)
C(5)	13155(11)	15110(8)	10824(5)	71(3)
C(6)	13896(11)	15129(9)	11402(6)	82(3)
C(7)	13870(12)	13995(10)	11634(6)	89(3)
C(8)	13072(10)	12887(8)	11260(5)	70(2)
C(9)	12247(8)	12813(7)	10635(4)	53(2)
C(10)	11418(8)	11661(7)	10198(4)	49(2)
C(11)	11280(8)	10441(7)	10419(4)	49(2)
C(12)	10014(12)	10366(9)	10828(5)	85(3)
C(13)	12611(8)	9342(8)	9495(4)	58(2)
C(14)	10763(12)	8094(8)	9928(5)	75(3)
C(15)	8233(9)	7892(7)	7490(4)	57(2)
C(16)	7381(9)	8951(8)	7687(4)	61(2)
C(17)	7329(14)	6766(9)	6964(5)	93(4)
C(18)	7633(9)	6823(8)	8625(4)	54(2)
C(19)	6942(10)	7483(8)	9179(4)	61(2)
C(20)	5790(12)	6919(13)	9415(6)	83(3)
C(21)	5334(11)	5640(12)	9105(6)	94(3)

C(22)	5975(12)	4934(10)	8542(6)	93(3)
C(23)	7105(11)	5509(8)	8311(5)	75(3)
C(24)	10371(9)	6704(8)	8056(4)	58(2)
C(25)	10495(11)	5635(8)	8290(4)	71(3)
C(26)	11632(15)	5033(11)	8133(6)	99(4)
C(27)	12566(16)	5377(14)	7737(7)	110(4)
C(28)	12475(12)	6453(14)	7513(6)	103(4)
C(29)	11402(12)	7090(11)	7660(5)	83(3)
C(30)	7033(8)	11251(8)	8729(5)	55(2)
C(31)	7127(11)	11828(10)	9418(6)	72(3)
C(32)	6067(14)	12376(10)	9752(6)	85(4)
C(33)	4847(15)	12340(13)	9345(10)	107(5)
C(34)	4736(12)	11804(11)	8674(7)	89(3)
C(35)	5794(10)	11270(9)	8347(5)	72(2)
C(36)	9242(9)	11231(7)	7735(4)	50(2)
C(37)	8616(10)	11911(9)	7372(4)	68(2)
C(38)	9344(14)	12461(10)	6914(5)	87(3)
C(39)	10650(15)	12254(11)	6823(6)	94(4)
C(40)	11348(13)	11572(11)	7167(6)	91(3)
C(41)	10619(10)	11081(9)	7634(5)	69(2)
C(42)	7629(7)	7751(6)	3650(4)	40(2)
C(43)	7543(9)	6520(7)	3191(5)	49(2)
C(44)	6929(8)	5435(8)	3345(5)	58(2)
C(45)	6373(7)	5511(7)	3970(4)	49(2)
C(46)	5750(8)	4401(8)	4146(5)	61(2)
C(47)	5196(10)	4496(11)	4768(6)	83(3)
C(48)	5220(11)	5700(12)	5249(5)	87(3)
C(49)	5807(8)	6799(9)	5084(4)	62(2)
C(50)	6390(7)	6744(7)	4450(4)	49(2)
C(51)	7015(7)	7845(6)	4263(4)	42(2)
C(52)	7036(9)	9165(8)	4744(4)	58(2)
C(53)	8286(12)	9504(11)	5290(5)	97(4)
C(54)	7279(12)	11459(9)	4745(6)	93(4)
C(55)	5723(9)	9888(9)	3883(6)	83(3)
C(56)	11612(8)	11107(7)	3305(4)	47(2)
C(57)	11299(8)	9928(7)	2663(4)	53(2)

C(58)	12672(10)	12113(10)	3165(6)	75(3)
C(59)	10269(8)	12885(7)	4342(4)	50(2)
C(60)	11262(9)	12953(9)	4856(5)	66(2)
C(61)	11449(11)	13956(10)	5464(5)	74(3)
C(62)	10609(13)	14809(10)	5569(5)	85(3)
C(63)	9570(12)	14771(9)	5072(5)	81(3)
C(64)	9410(9)	13831(8)	4455(4)	61(2)
C(65)	9266(8)	12221(7)	2890(4)	52(2)
C(66)	9991(9)	13309(7)	2784(5)	59(2)
C(67)	9538(11)	13795(9)	2258(5)	77(3)
C(68)	8304(13)	13199(10)	1850(5)	79(3)
C(69)	7575(10)	12142(9)	1970(5)	77(3)
C(70)	8038(9)	11628(8)	2474(5)	60(2)
C(71)	9410(7)	7608(7)	2026(4)	44(2)
C(72)	8137(9)	7774(9)	1750(5)	64(2)
C(73)	7522(10)	7024(10)	1116(5)	78(3)
C(74)	8199(11)	6089(8)	721(4)	71(3)
C(75)	9450(9)	5915(9)	968(5)	59(2)
C(76)	10055(8)	6644(7)	1605(4)	49(2)
C(77)	11287(8)	7769(7)	3243(4)	41(2)
C(78)	12533(8)	7479(8)	2954(5)	53(2)
C(79)	13314(9)	6733(9)	3234(5)	58(3)
C(80)	12932(9)	6292(8)	3785(5)	64(2)
C(81)	11771(9)	6570(9)	4063(5)	70(2)
C(82)	10915(8)	7315(8)	3807(4)	51(2)
Cl(1)	5073(3)	2847(3)	6402(2)	91(1)
O(3)	4528(17)	3998(12)	6561(7)	224(7)
O(4)	6402(8)	3312(11)	6269(6)	160(4)
O(5)	4931(14)	2461(13)	6992(5)	201(6)
O(6)	4235(11)	2172(10)	5804(5)	153(4)
Cl(2)	4466(3)	9182(2)	1495(1)	73(1)
O(7)	5172(8)	8924(9)	2049(4)	111(3)
O(8)	5311(11)	9144(10)	969(4)	133(4)
O(9)	4103(9)	10418(6)	1695(4)	106(3)
O(10)	3204(8)	8341(8)	1290(5)	136(4)
C(1S)	2992(13)	9010(20)	5870(11)	206(10)

Cl(1A)	1335(7)	8484(6)	5932(3)	200(2)
Cl(1B)	4000(8)	8803(7)	6543(3)	225(3)

Appendix 17

X-ray Crystallographic Data for dichloro[2,3-bis(diphenylphosphino)propan-1-ol]palladium(II), Complex-93, Figure 4.7.

Table A 1.33 Crystal data and structure refinement for complex 93

Empirical formula	C28 H28 Cl4 O P2 Pd	
Formula weight	690.64	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 19.514(5) Å	α = 90°.
	b = 8.547(2) Å	β = 107.224(5)°.
	c = 17.987(4) Å	γ = 90°.
Volume	2865.3(12) $Å^3$	
Z	4	
Density (calculated)	1.601 Mg/m^3	
Goodness-of-fit on F^2	1.111	
Final R indices [I>2sigma(I)]	R1 = 0.0698, wR2 = 0.1387	
R indices (all data)	R1 = 0.0968, wR2 = 0.1492	
Largest diff. peak and hole	1.035 and -1.003 $e.Å^{-3}$	

Table A 1.34. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for complex **93**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	2404(1)	6578(1)	4400(1)	27(1)
P(1)	2716(1)	4249(2)	4950(1)	31(1)
P(2)	1560(1)	5306(2)	3493(1)	40(1)
Cl(1)	3342(1)	7757(2)	5361(1)	41(1)
Cl(2)	1984(1)	8980(2)	3780(1)	50(1)
O(1B)*	835(9)	770(18)	4051(10)	55(4)
C(1B)*	1884(13)	2980(30)	4741(9)	29(6)
C(2B)*	1525(9)	3268(13)	3865(10)	29(5)
C(3B)*	815(10)	2358(19)	3733(12)	45(5)
O(1)#	864(4)	1588(9)	4420(4)	59(2)
C(1)#	2007(4)	2811(10)	4472(5)	30(2)
C(2)#	1744(5)	3189(7)	3603(4)	31(2)
C(3)#	1400(5)	2724(11)	4839(5)	44(2)
C(4)	2888(3)	4241(7)	5992(3)	34(1)
C(5)	2450(3)	5141(8)	6298(4)	44(2)
C(6)	2539(4)	5188(9)	7082(4)	50(2)
C(7)	3078(4)	4301(9)	7577(4)	53(2)
C(8)	3513(5)	3387(10)	7290(4)	65(2)
C(9)	3427(4)	3366(8)	6485(4)	49(2)
C(10)	3469(3)	3379(7)	4724(3)	34(1)
C(11)	3612(3)	1778(7)	4797(4)	40(2)
C(12)	4189(4)	1161(8)	4612(4)	47(2)
C(13)	4634(4)	2099(8)	4358(4)	46(2)
C(14)	4511(4)	3691(8)	4276(4)	45(2)
C(15)	3933(3)	4338(7)	4458(4)	40(1)
C(16)	652(3)	5779(7)	3484(3)	39(2)
C(17)	531(4)	6896(8)	3980(4)	50(2)
C(18)	-157(4)	7276(9)	3975(5)	62(2)
C(19)	-732(4)	6530(11)	3464(5)	65(2)
C(20)	-619(4)	5400(12)	2985(4)	70(3)
C(21)	67(4)	5027(9)	2988(4)	57(2)

C(22)	1616(4)	5550(8)	2506(4)	48(2)
C(23)	1071(4)	6192(8)	1924(4)	47(2)
C(24)	1148(4)	6337(9)	1189(4)	56(2)
C(25)	1755(4)	5865(10)	1032(5)	66(2)
C(26)	2308(5)	5265(12)	1604(5)	83(3)
C(27)	2242(4)	5108(11)	2337(5)	79(3)
C(1S)	4145(5)	7671(11)	7439(5)	84(3)
Cl(1A)	4495(2)	7251(3)	8419(1)	93(1)
Cl(1B)	4441(1)	9466(3)	7200(1)	77(1)

*sof=0.3 #sof=0.7