Asymmetric Ligand Transformation Reactions Promoted by Cyclometallated Complexes

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Summary

Complex bis(μ-chloro)-bis{(*R*)-1-(dimethylamino)ethyl] naphtyl-C^2,*N*} palladium (II) (*Rc*)-**10** was found to successfully undergo insertion reactions at the palladium-carbon bond with the diphenylarsinoprop-1-yne ligand at room temperature which led to the formation of a new 7-membered metallacyce in the inserted product (*Rc,Rc*)-**67**. This reaction was also carried out on the platinum (II) metal template containing the naphythylamine moiety which gave complex (*Rc,Rc*)-**69**. The absolute stereochemistry of both complexes were confirmed by single crystal X-ray diffraction analysis. It was found that metal activated arsine substituted alkynes can undergo an intermolecular insertion reaction with the C-Pd bond of the naphthylamine cyclometallated complex to yield two homo and hetero bimetallic insertion products. The monoarsine precursor complexes (*Rc*)-**70** has shown to undergo a C-H bond activation followed by a C-C bond coupling at room temperature. This reaction can only be initiated with the presence of a platinum (II) metal. The reaction gave the coupling product (*Rc*)-**71** and was characterised by using the single-crystal X-ray diffraction analysis.

The chiral organopalladium template (*Rc*)-**10** was used to promote asymmetric hydroarsination reaction between diphenylarsine and various functionalised alkenyl phosphines with hydroxy, methoxy, dimethylamino, ester and ketone as functional groups. The addition of diphenylarsine is regiospecific, wherein the phosphorus atom occupies the coordination site *trans* to nitrogen exclusively. All the reactions showed good selectivity and the enantiomerically pure complexes were characterised by means of single crystal X-ray diffraction analysis. In the asymmetric hydroarsination reaction of alkenyl phosphines with hydroxy, methoxy and dimethylamino as functional groups, an unexpected elimination product (*Rc*)-**80** was observed.

Generally, the bidentate ligands can be easily liberated through two-step decomplexation by treatment with concentrated HCl followed by aqueous KCN solution. The free ligands can be recoordinated back with the palladium (II) complex without loss of optical purity.

The asymmetric Diels-Alder reaction promoted by chiral platinum (II) metal template (*Rc*)-**49** between DMPP and phenyldi[(*Z*)]prop-1-enyl]phosphine oxide showed poor stereoselectivity with two isomers (1:1) being formed. The diastereomeric mixture cannot be separated via column chromatography or fractional crystallisation. In order to confirm the identities of the two diastereomers, the chiral napthylamine auxiliary in the complexes was removed chemoselectively to give the corresponding neutral dichloro complex. However, the X-ray structural analysis of dichloro complex revealed the presence of both enantiomers in the unit cell. The cycloaddition reaction between DMPP and phenyldi[(*Z*)]prop-1-enyl]phosphine sulphide similarly showed poor selectivity. The diastereomeric mixture (1:1) cannot be separated by column chromatography or fractional crystallisation. They were coverted to the corresponding dichloro complex and could be separated via fractional crystallisation. The molecular structure and absolute configurations of the recrystallised (*Sp,Sp*)-**113** were established by single crystal X-ray crystallographic analysis. The optically active ligand (*Rp,Sp*)-**114** can be stereospecifically liberated from complex (*Sp,Sp*)-**113** by treatment of the dichloro complex with aquoues potassium cynanide at room temperature.

Nomenclature

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

X-ray Stuctural Data

The single crystal X-ray analyses were kindly performed by Dr. Li Yongxin at the Nanyang Technological University (Division of Chemistry and Biological Chemistry). Full structural data (listings of crystal and refinement data, bond distances and angles and thermal parameters) are available from Prof. Leung Pak-Hing upon request.

ABBREVIATION AND SYMBOLS

Ar	aryl group
br	broad
calcd	calculated
conc. HCl	concentrated hydrochloric acid
$CDCl_3$	chloroform-d_1
CD_2Cl_2	dichloromethane-D2
$CHCl_3$	chloroform
CH_2Cl_2	dichloromethane
d	doublet (in NMR assignments)

dd	doublet of doublet (in NMR assignments)
decomp.	decomposed
DMPP	3,4-dimethyl-1-phenylphosphole
DMSO	dimethyl sulphoxide
ee	enantiomeric excess
equiv.	equivalent
et.al.	and others
g	grams
h	hour(s)
Hz	hertz
KCN	potassium cyanide
m	multiplets (in NMR assignments)
Me	methyl
mg	milligram(s)
min	minute(s)
mL	mililiter
mmol	millimole(s)
M.p	melting point
NMR	Nuclear Magnetic Resonance

Ph	Phenyl
^{31}P NMR	$^{31}P\{^{1}H\}$ NMR
ppm	parts per million
q	quartet (in NMR assignments)
R	rectus (Latin: right absolute configuration)
rt	room temperature
S	sinister (Latin: left absolute configuration)
s	singlet (in NMR assignment)
t	triplet (in NMR assignment)
δ	NMR chemical shift in ppm
°	degree of angles
Å	angstrom(s)
°C	degree Celcius
$^{n}J_{AB}$	n-bond coupling constant between nuclei A and nuclei B
$[\alpha]_D$	specific rotation measure at sodium D line (589nm)

CHAPTER 1

Introduction

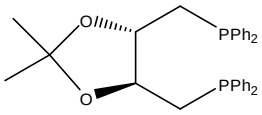
1.1 Chirality and its Significance

Chirality is a basic symmetry property of three-dimensional objects and a molecule is defined to be chiral if it cannot be superimposed upon its mirror image. The nature around us itself is chiral and most importantly the fundamental building blocks which make up the biological molecules of living things do so in one enantiomeric form only [L-form]. Thus, chirality has a very important part in our daily life.

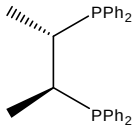
Chiral ligand design has become one important exercise in synthetic chemistry.[1] This is due to subtle control that ligands exert on the metal centre to which they are coordinated. Chiral ligands are especially important in asymmetric transition metal catalysis and synthesis.[2] These chiral ligands can form an asymmetric environment in close proximity to the metal centre thus they have been considered as useful auxiliary in metal-catalysed asymmetric reactions.

One of the more popular types of ligands that have attracted a lot of attention is enantiometrically pure mono phosphines and di-phosphines. This interest can be attributed to the fact that Knowles[3] and Horner[4] first reported the effectiveness of optically active P-chiral phosphorus ligands for chiral metal catalysts (Wilkinson's catalyst) on asymmetric hydrogenation reactions albeit with poor selectivity. Later, Kagan reported application of diphosphines with chiral carbon centres in the backbone such as DIOP **1** for Rh catalysed asymmetric hydrogenation.[5] This result suggested that chelating di-phosphine could give an enhanced selectivity compared to monodentate phosphines. Knowles made this significant discovery when he reported the efficiency of a C_2-symmetric chelating bisphosphine ligand, DIPAMP **2**.[6] In

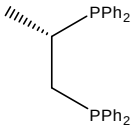
addition to that, Bosnich reported that P-chiral phosphine ligands were not necessary for attaining high selectivity and ligands with chiral backbones such as CHIRAPHOS **3** and PROPHOS **4** could also give excellent results in asymmetric reactions.[7] In view of this powerful utility of chiral phosphine ligands, Noyori reported the application of BINAP **5**, a ligand which possesses only an axial element of chirality to be effective in asymmetric hydrogenation reaction (up to 100 % ee).[8] Even until now, chiral phosphine ligands still remain a popular choice in asymmetric synthesis. An overview will be presented that will include synthetic methods and also their application in various asymmetric reactions.



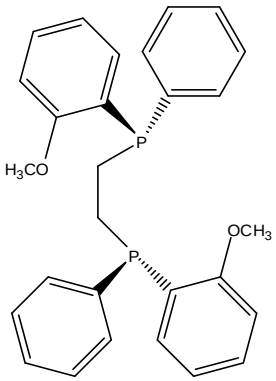
(*S*,*S*)-DIOP
1



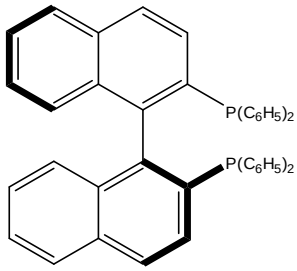
(*S*,*S*)-CHIRAPHOS
3



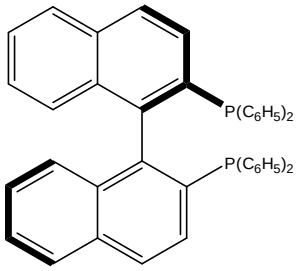
(*S*)-PROPHOS
4



(*S*,*S*)-DIPAMP
2



(*S*)-BINAP
5



(*R*)-BINAP
5

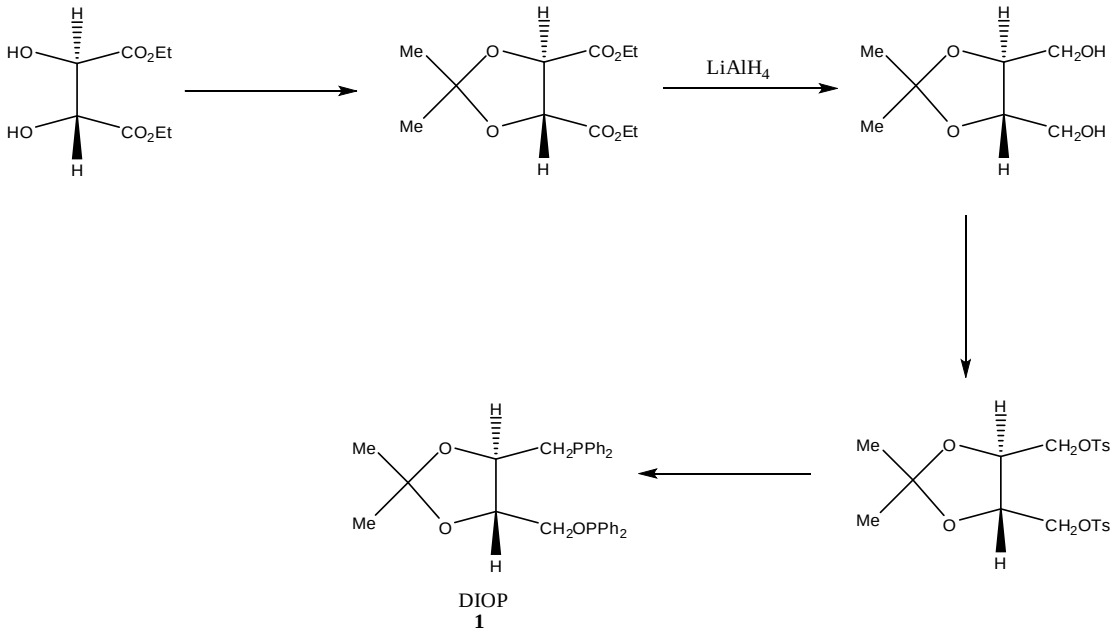
Figure 1.1

1.2 Chiral Phosphorus Ligands: An Overview

Although P-stereogenic ligands have been proven to be effective, few methods have been reported because they are difficult to synthesise. Three general synthetic methods have been reported:

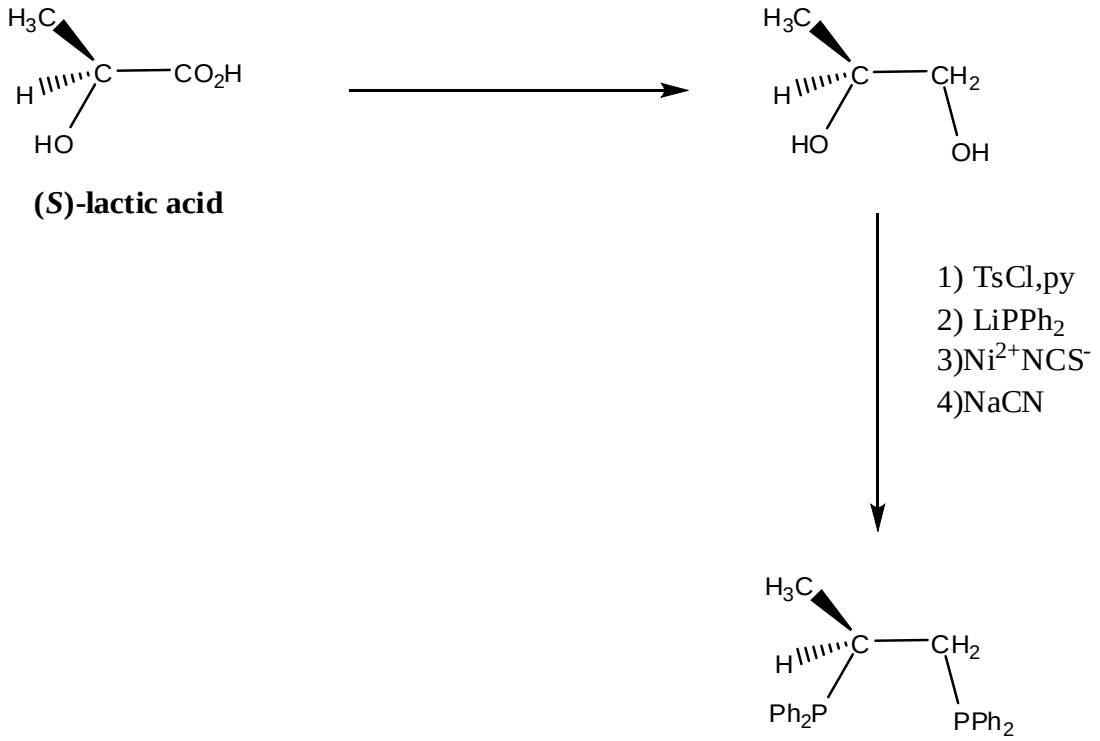
1.2.1 Preparation from naturally occurring chiral starting materials

This method involves transformation of readily accessible and naturally occurring chiral compounds such as amino acid, tartaric and lactic acids, carbohydrates, terpenes or alkaloids. Kagan's DIOP **1** was prepared from naturally occurring tartaric acid (Scheme 1.1).[9] The diphosphine is a solid which is easily purified by crystallisation and is quite air stable toward air oxidation.



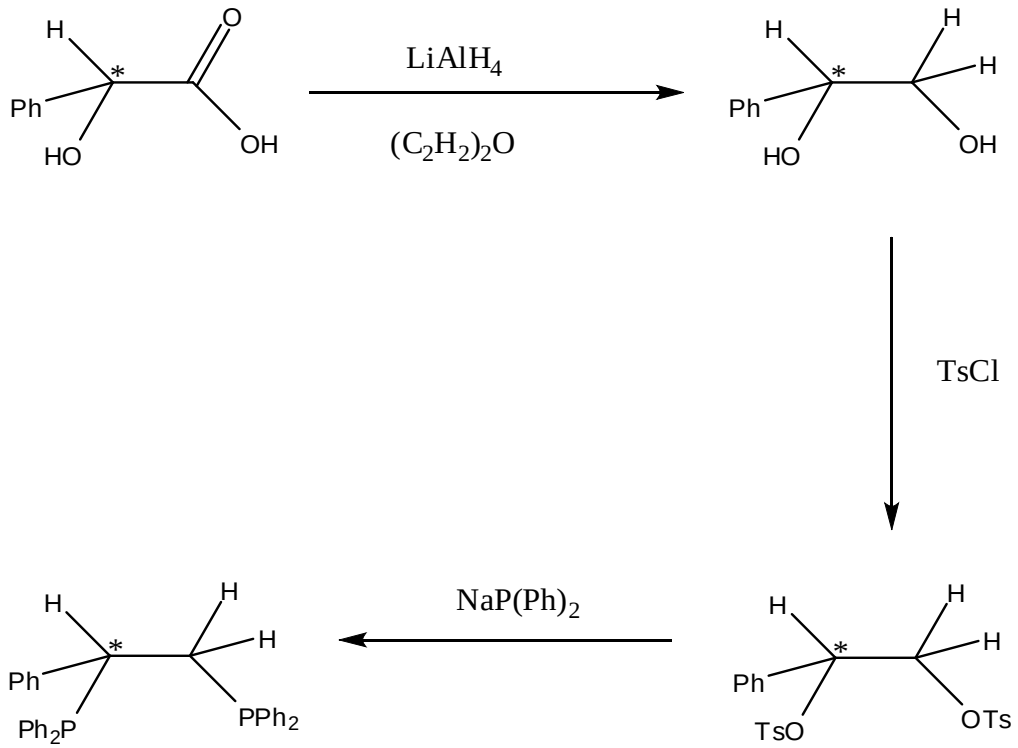
Scheme 1.1

(*R*)-prophos **4** a chiral diphosphine ligand was prepared from (*S*)-lactic acid by the route outlined in Scheme 1.2.[10] First the ditosylate derivative was easily crystallised to optical purity and secondly the diphosphine ligand was readily separated from its reaction mixture as the crystalline nickel complex. The optically pure diphosphine can be displaced from its metal centre with cyanide.



Scheme 1.2

PhenPhos **6** was prepared from the corresponding enantiomers of the readily available mandelic acid (Scheme 1.3).[11] The ligand is more readily isolated in the pure state than its methyl analogue PROPHOS **4,** apparently because of its higher melting point.



PhenPhos

6

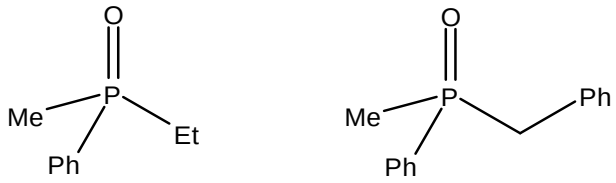
Scheme 1.3

1.2.2 Resolution by using chiral resolving agents

The key point about resolution is bringing together two stereogenic centres together to form a mixture of diastereomers. The original inseparable enantiomers could now be separated by means of fractional crystallisation or chromatography due to the different physical properties of diastereomers.

The first known optically active organophosphorus compound ethylmethylphenylphosphine oxide **7** was obtained by direct resolution of the racemate using (+)-bromocamphorsulfonic acid for the formation of separable diasteromers salts.[12] The two diastereomeric salts were isolated in the pure forms by fractional crystallisation from EtOAc and EtOAc/ether in good optical purity. In the

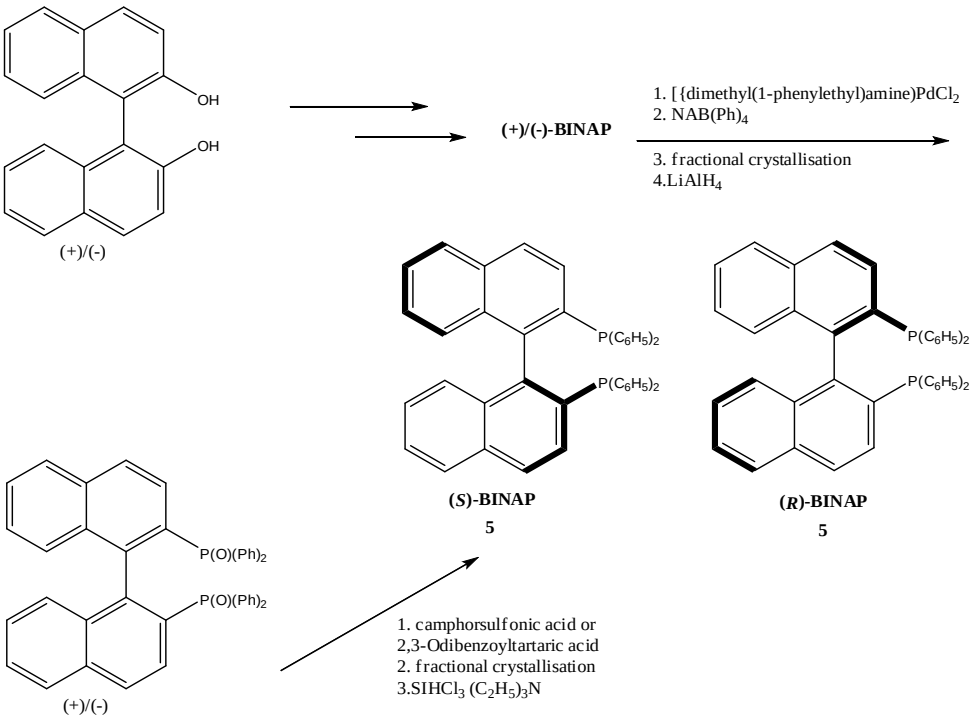
same lab, benzylmethylphenylphosphine oxide **8** was similarly resolved with camphorsulfonic acid as the resolving agent.



(+) and (-)-7 **(+) and (-)-8**

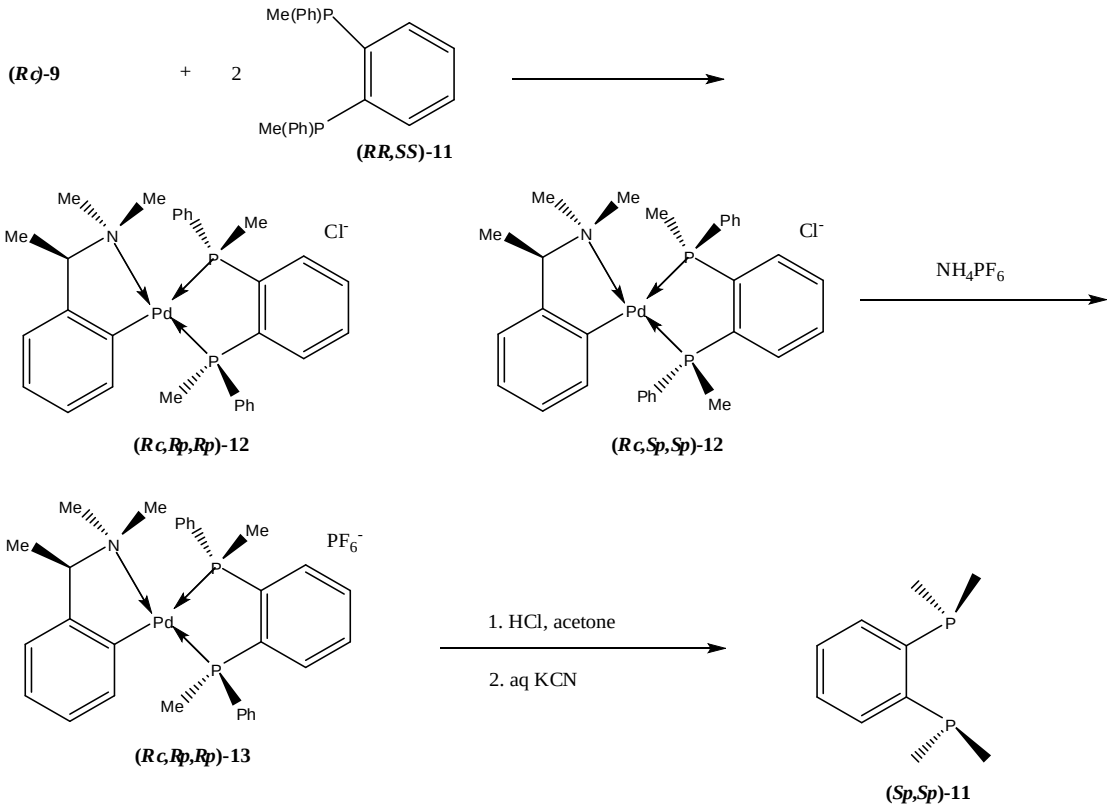
Figure 1.2

The improved methods for preparation of Noyori's BINAP **5** was through resolution of racemic BINAP **5** with an optically active dimethyl(1-phenylehtyl)aminopalladium (II) chloride complex. Later Noyori also reported that the racemic mixture can be resolved by fractional crystallisation with camphorsulfonic acid or 2,3-di-O-benzoyltartaric acid into its enantiometrically pure forms (Scheme 1.4). [8c]

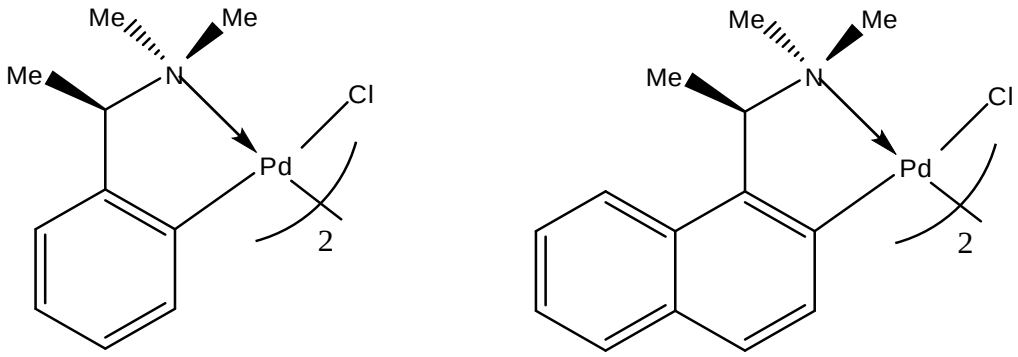


Scheme 1.4

Wild *et.al*. have found that chloro-bridged palladium (II) complexes containing orthometallated N,N-dimethyl(α-methylbenzyl)amines (*Rc*)-**9** and related napthyamines (*Rc*)-**10** are very useful resolving agents for bidendate phosphines (Figure 1.3).[13] The results are quite remarkable for resolution of o-phenylenebis(methylphenylphosphine) **11** as outlined in Scheme 1.5. Complex (*Rc,Rp,Rp*)- **13** can be precipitated out followed by two-step decomplexation allowed the isolation of the optically pure (*Sp,Sp*)-**11**. Meanwhile, (*Rp,Rp*)-**11** can be recovered from mother liquors in 90% yield.



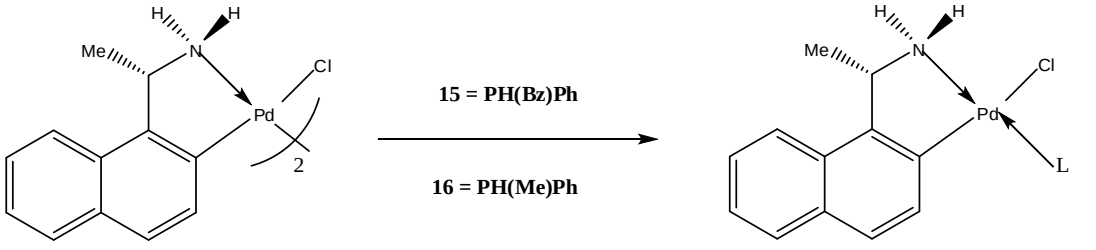
Scheme 1.5



(*Rc*)-9 **(*Rc*)-10**

Figure 1.3

The versatility of ortho-palladated derivatives containing 1-1(napthyl)ethylamine (*Rc*)-**14** as resolving agents have been further convincingly demonstrated.[14] Reaction of this dimeric complex with (+/-)-benzylphenylphosphine **15** and (+/-)-methylphenylphosphine **16** afforded the mononuclear complexes as a 1:1 mixture of the diastereomers (*Sc,Rp*)-**17**, (*Sc,Sp*)-**17,** (*Sc,Rp*)-**18**, (*Sc,Sp*)-**18** (Scheme 1.6). These diasteromers could be separated efficiently in a SiO_2 column with a *de* higher than 95% in both cases.



***(Rc)*-14** **(*Sc,Rp*)-17, (*Sc,Sp*)-17 , L= PH(Bz)Ph**

(*Sc,Rp*)-18, (*Sc,Sp*)-18 , L= PH(Me)Ph

Scheme 1.6

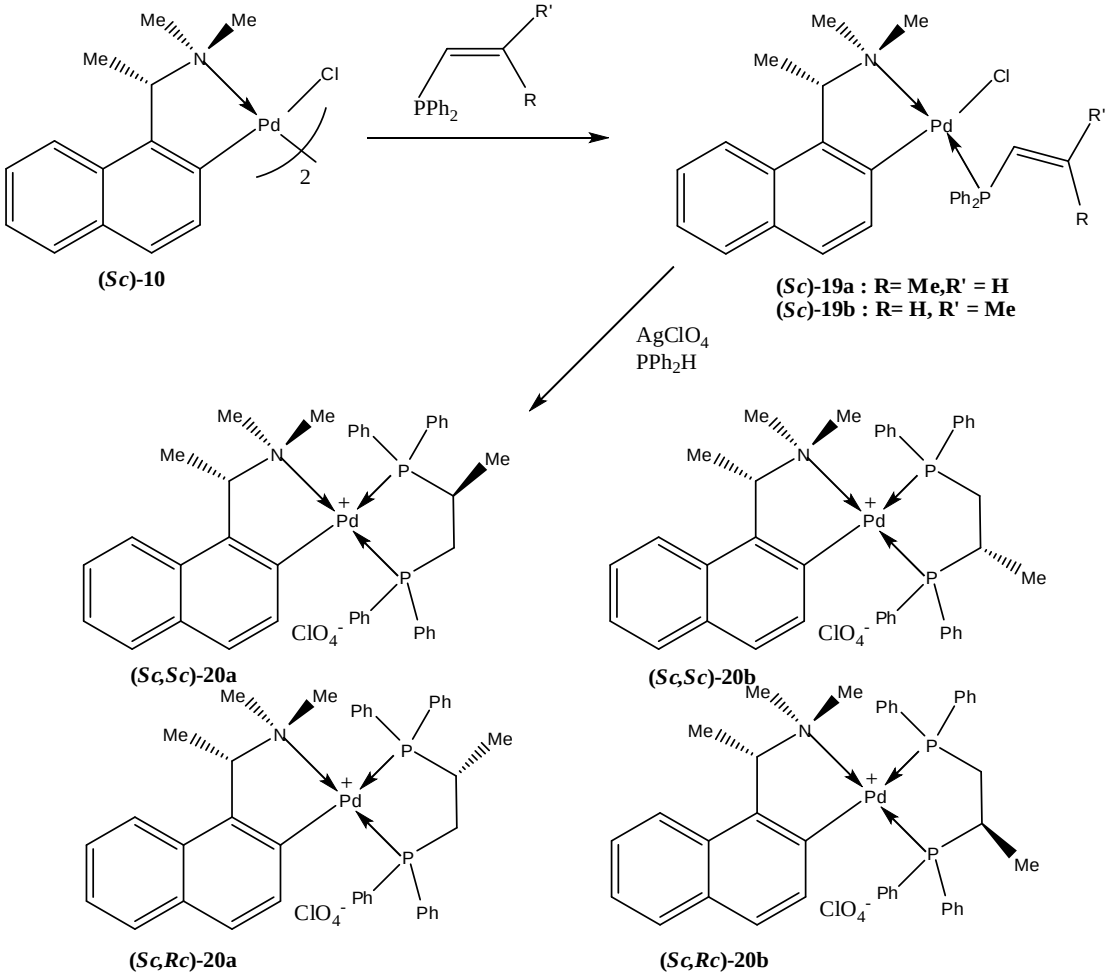
1.2.3 Asymmetric synthesis

An interesting approach to make useful chiral phoshine ligands from non-chiral staring materials as opposed to the limited pool of natural chirons is via asymmetric synthesis.

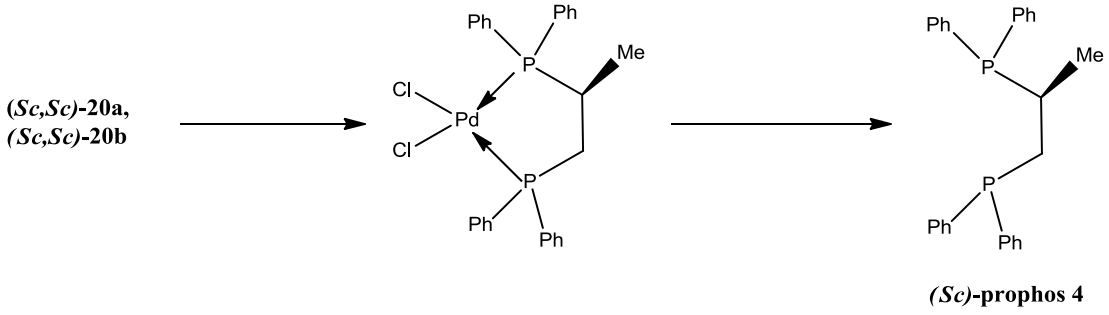
Hydrophosphination reaction, an addition of phosphorus-hydrogen atoms to carbon-carbon multiple bonds is one of the many ways to synthesise chiral phospine ligand. In recent years Leung *et.al*. has reported various functionalised preparation of chiral biphosphine ligands with different functional groups between diphenylphosphine and alkenyl phosphines.

An organopalladium complex containing ortho-metalated (*S*)-(1-(dimethylamino)ethyl)naphthalene (*Sc*)-**10** as the chiral auxiliary has been used to promote the asymmetric hydrophosphination reactions between diphenylphosphine and (*E*) or (*Z*)- diphenyl-1-propenylphosohine in high regio- and stereoselectivities (Scheme 1.7).[15] In two-step decomplexation , the optically active di-phosphine (*R*)- and (*S*)-prophos **4** can be liberated in high yields (Scheme 1.8).

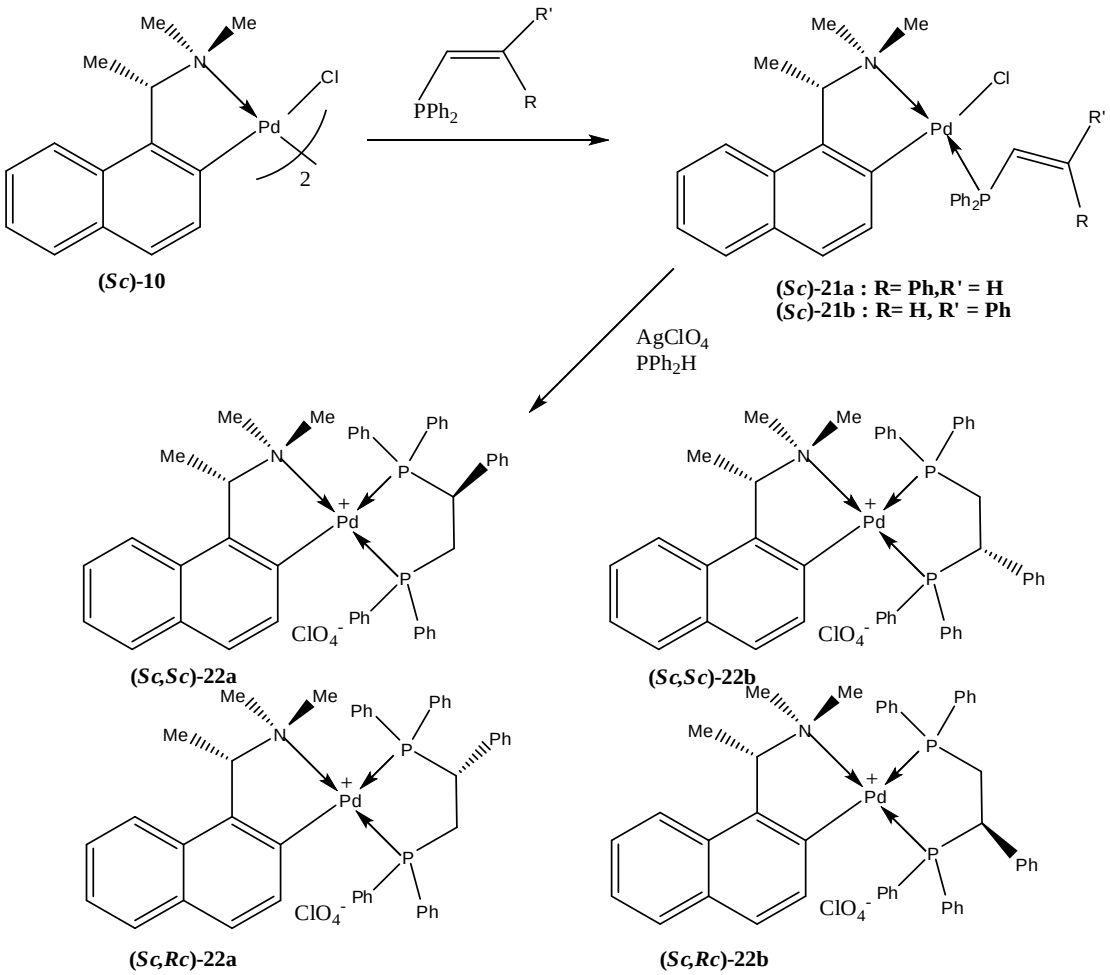
Leung *et.al*. has also reported a facile preparation of phenphos **6** via a chiral metal-template promoted asymmetric hydrophosphination reaction between diphenylphosphine and (*E*) or (*Z*)-diphenylphosphinostyrene with triethylamine as external base.[16] The reaction proceeded with high stereoselectivities under mild conditions. The newly formed chiral di-phosphine phenphos **6,** can be obtained as free ligand by a two-step transformation (Scheme 1.9).



Scheme 1.7



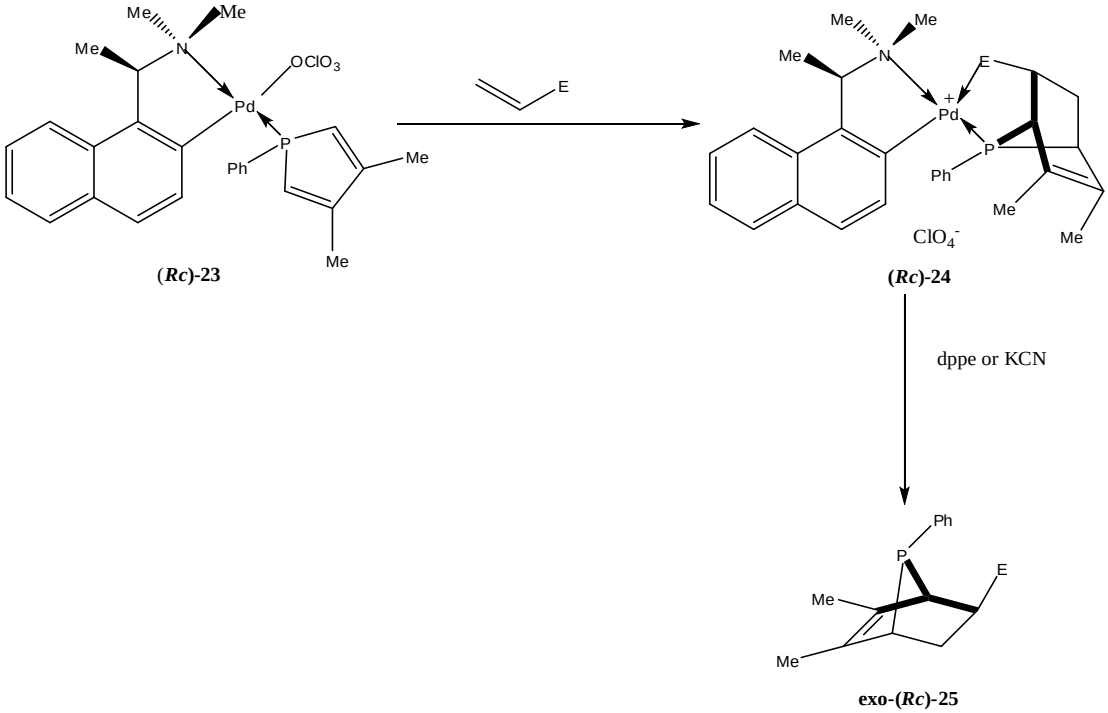
Scheme 1.8



Scheme 1.9

Leung *et.al.* has also worked extensively to prepare functionalised P-stereogenic phosphines by means of the same chiral naphthylamine template-promoted [4+2] cycloaddition reactions.[17] In several cases, up to six stereogenic centres could be generated. Another key conceptual feature of this methodology is the activation of the five-membered heterocycle 3,4-dimethyl-1-phenylphosphole (DMPP). DMPP itself is not a reactive cyclic diene but becomes reactive when it is coordinated onto a transition metal ion. Due to the steric and electronic features, *exo*-cycloadducts are always formed with high stereoselectivity when (*Rc*)-**23** is used as the reaction template (Scheme 1.10). The enantiomerically pure exo-phosphanorbornenes *exo*-

(*Rc*)-**25** could be liberated from the corresponding template complexes by displacement method with either KCN or dppe.

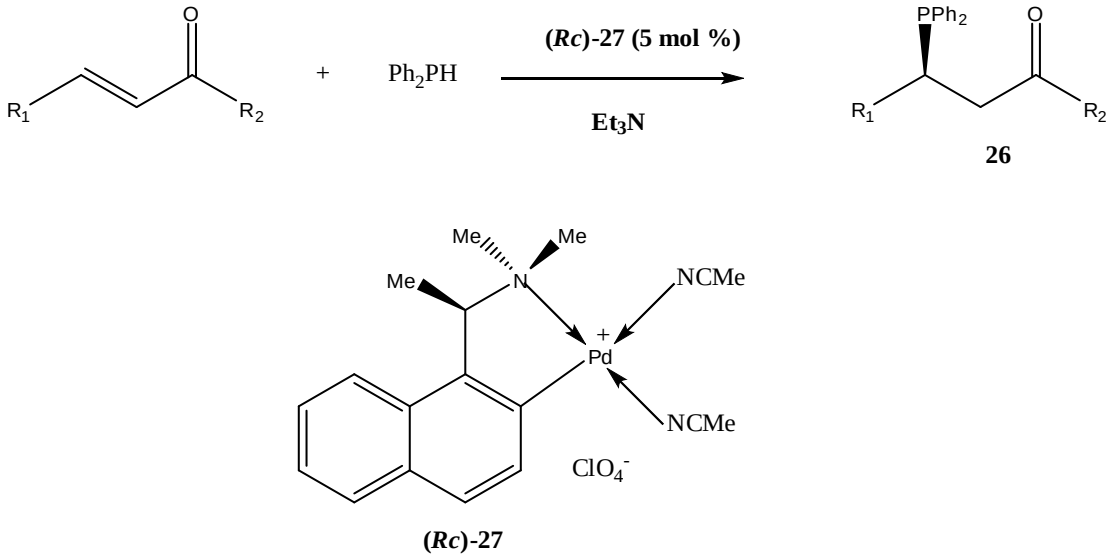


Scheme 1.10

Table 1.1 Synthesis of monophosphines via *exo*-cycloaddition reaction

	Substrate	**Temperature °**	**Time**
(*Rc*)-24a	E = -C(O)NMe_2	25	3d
(*Rc*)-24b	E = -C(O)-Et	25	9d
(*Rc*)-24c	E = -C(O)OMe	75	14d
(*Rc*)-24d	E = -C(S)NMe_2	25	6d
(*Rc*)-24e	E = -SPh	75	17d
(*Rc*)-24f	E = -S(O)CH=CH_2	75	4d

Scheme 1.11 illustrates the formation of chiral tertiary phosphines **26** via asymmetric hydrophosphination of aromatic enones catalysed by an organonopalladium complex (*Rc*)-**27** in high yields and stereoselectivity.[18] The procedure offers practical access to chiral tertiary mono-phosphines **26**. The results are presented in Table 1.2.



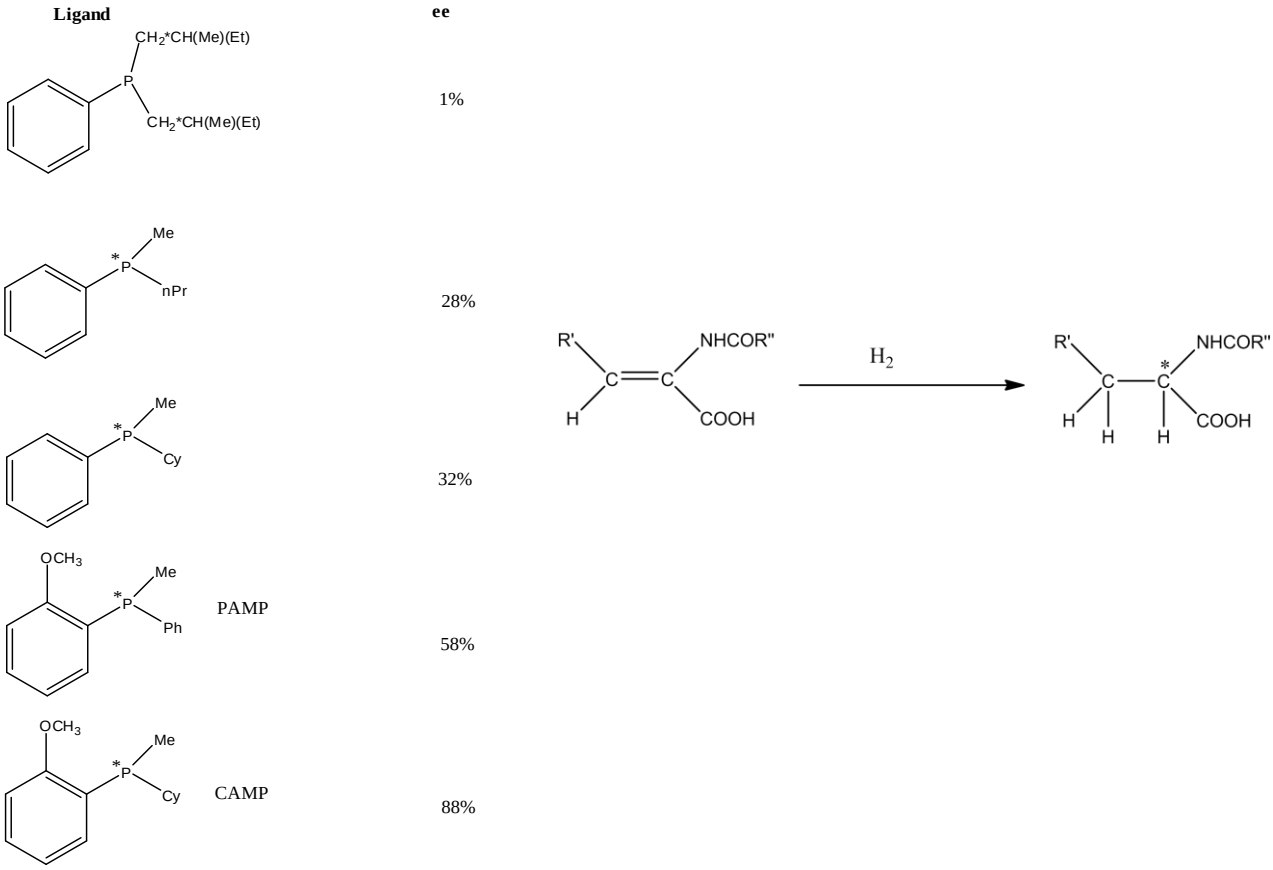
Scheme 1.11

Table 1.2 (*Rc*)-27 catalysed asymmetric hydrophosphination of various aromatic enones with Ph_2PH

Substrate	**R_1,R_2**	**Temp./°C**	**Time**	**ee(%)**
26-a	Ph,Ph	-80	23h	98
26-b	Ph, 2-Naph	-80	50h	94
26-c	2-Naph, 1-Naph	-80	6d	96
26-d	4-ClPh, Ph	-80	40h	98
26-e	4-NO_2Ph,Ph	-80	6d	88
26-f	3-NO_2Ph,Ph	-80	4d	85
26-g	4-OHPh,Ph	-80	7d	99

1.3 Applications of Chiral Phosphorus Ligands in Asymmetric Reactions

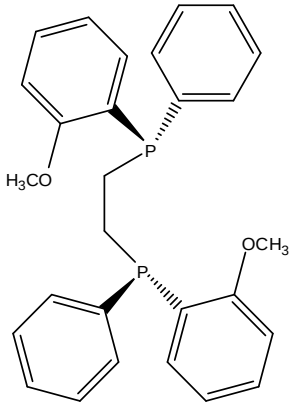
William S. Knowles discovered that the metal rhodium assisted by chiral phosphorus ligands DIPAMP **2** could be used in a chiral molecule to catalyse asymmetric hydrogenation reactions.[19] To get high ee values, Knowles's aim was to make a P-stereogenic ligand. Knowles soon developed an industrial synthesis of the amino acid L-DOPA which has been found to be useful in treatment of Parkinson's disease.[6b] This was the first industrial catalytic asymmetric reaction and has been followed by many other examples. Scheme 1.12 gave the summary of the application of various chiral phosphine ligands in asymmetric hydrogenation. DIPAMP **2** gave the best result at 95 % ee in the L-DOPA system (Table 3). Apart from that, DIPAMP **2** was easier to make than CAMP and can be obtained as air-stable solid.



Scheme 1.12

Table 1.3 Important amino acids produced by asymmetric catalysis using DIPAMP

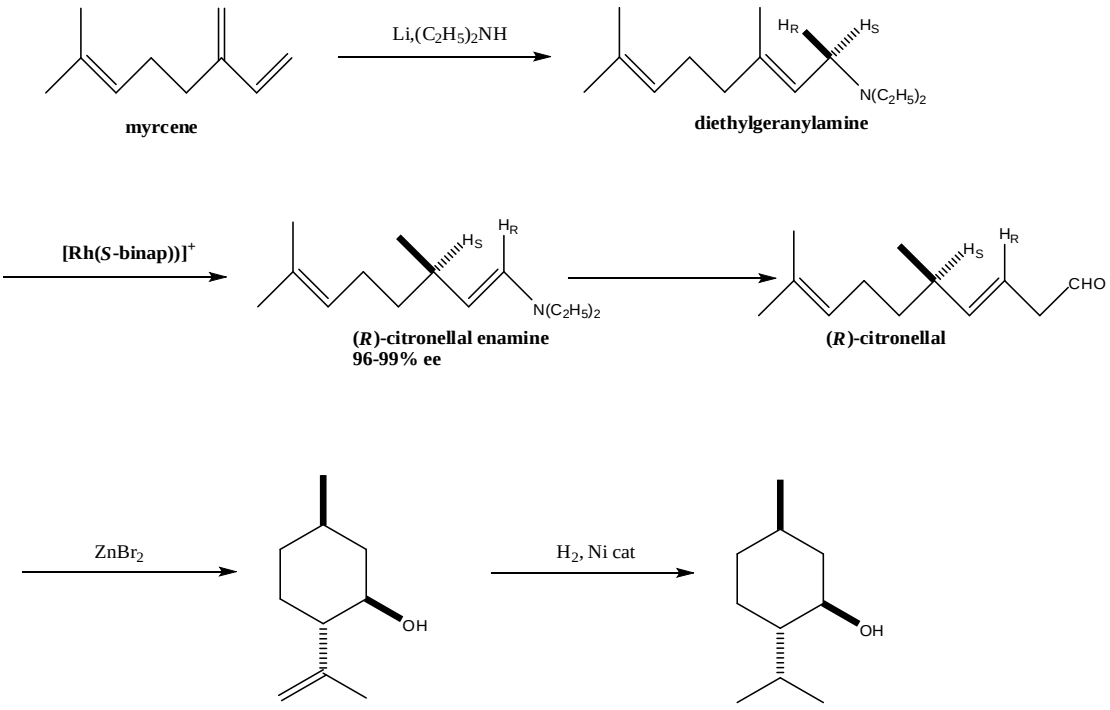
Product	ee value [%]
L-DOPA	94
L-phenylalanine	96
L-tryptophan	93
L-alanine	90
L-lysine	85



(*S*,*S*)-DIPAMP

2

The cationic BINAP-Rh complex developed by Noyori's group was best used in asymmetric isomerisation of allylic amines which realised an industrial synthesis of (-)-menthol from myrcene (Scheme 1.13). [20]



myrcene

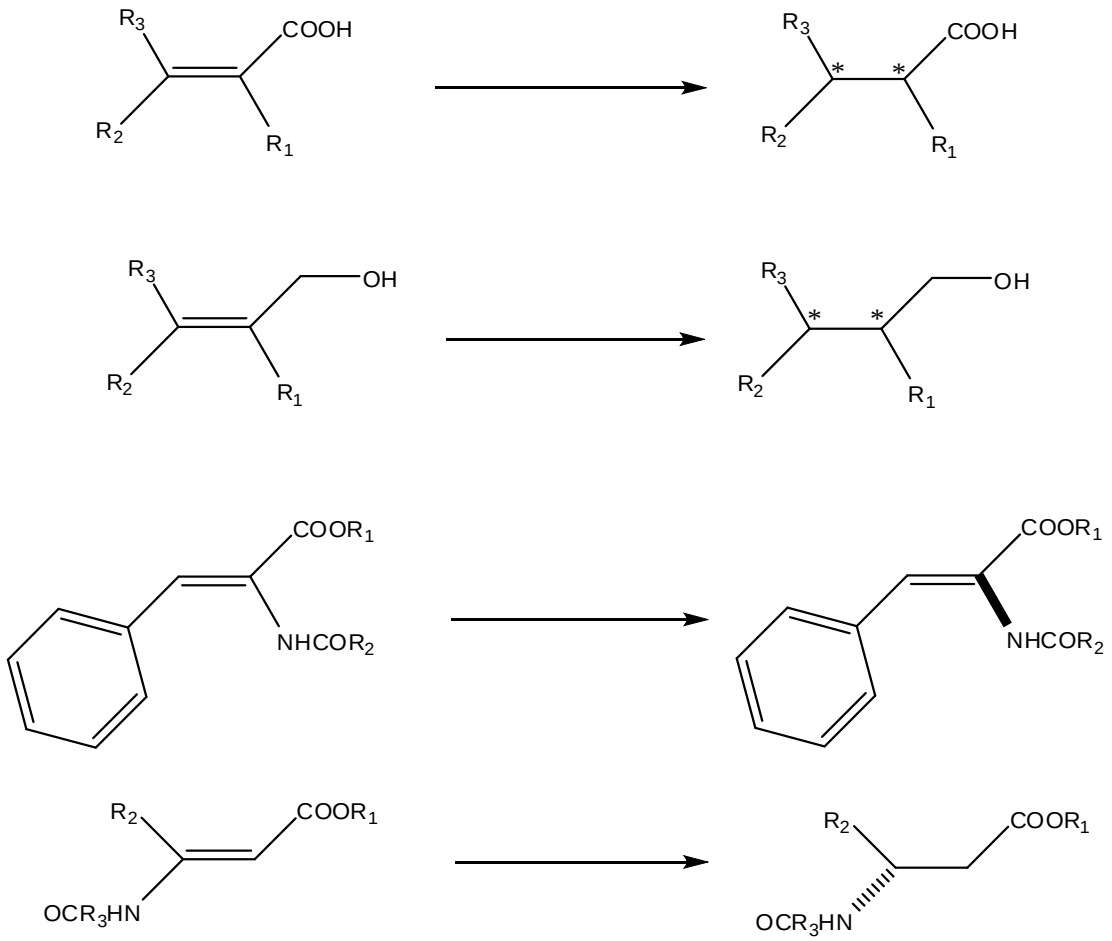
diethylgeranylamine

(*R*)-citronellal enamine
96-99% ee

(*R*)-citronellal

Scheme 1.13

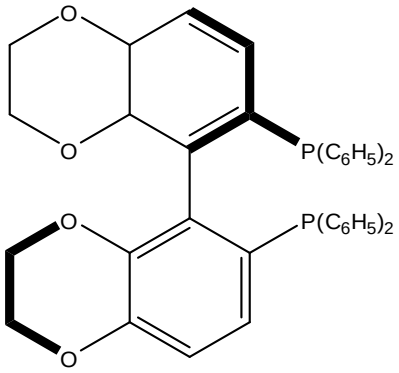
Apart from BINAP-Rh complex, BINAP ligand can also be used for other metals. Formation of BINAP-Ru^{II} dicarboxylate complexes was a breakthrough as these Ru complexes were found to give excellent results for asymmetric hydrogenation of various functionalised olefins as summarised in Scheme 1.14. [21]



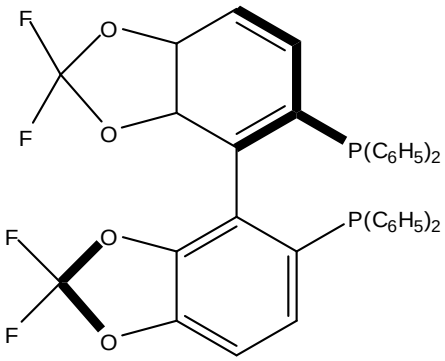
Scheme 1.14

Application of BINAP in asymmetric hydrogenation has resulted in expansion in the field of design and synthesis of similar biaryl diphosphines ligands. Two original chiral diphosphines, SYNPHOS **28** and DIFLUORPHOS **29** (Figure 1.2) have been

synthesised and have been screened in Ru^{II}-catalysed asymmetric hydrogenation of prochiral ketones.[22] The ligands were fully complementary with BINAP **5** in terms of enantioselectivity and the results are summarised in Table 1.4



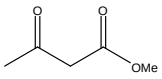
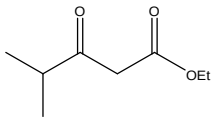
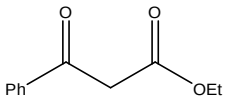
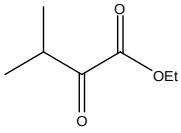
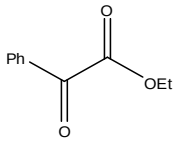
(*R*)-SYNPHOS



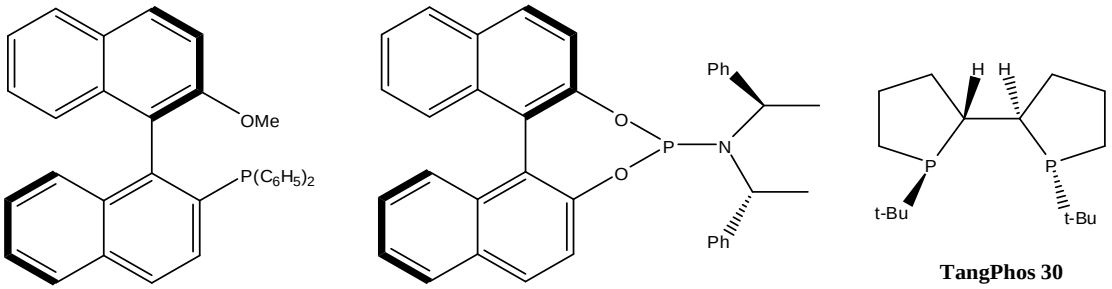
(*R*)-DIFLUORPHOS

Figure 1.2

Table 1.4 Screening of ligand in the asymmetric hydrogenation with 1 mol% $RuBr_2$[ligand] (% ee shown)

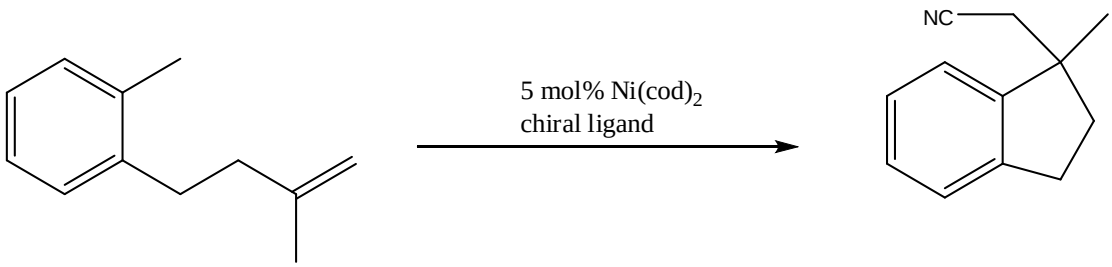
Substrate	BINAP 5	SYNPHOS 28	DIFLUORPHOS 29
	**99**	**99**	**99**
	**98**	**99**	**99**
	**88**	**97**	**92**
	**84**	**94**	**87**
	**72**	**92**	**67**

Apart from asymmetric hydrogenation reaction, P-stereogenic ligands have also been used for other asymmetric syntheses. In 2008, Watson and Jacobsen reported a nickel-catalysed intramolecular aryl-cyanation for which the P-stereogenic TangPhos **30** ligand gave the cyclised product with the highest level of enatioselectivity (Scheme 1.15). [23]



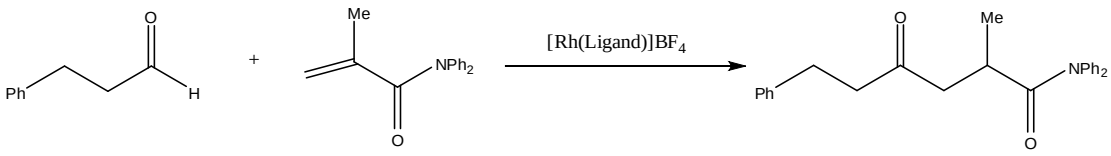
24% ee **34% ee** **TangPhos 30** **90%ee**

Figure 1.3



Scheme 1.15

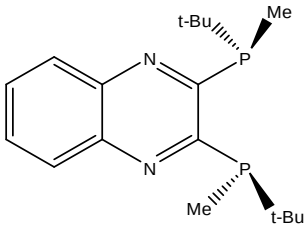
A rhodium-catalysed enantioselectve intermolecular hydroacylation of α,β-unsaturated amides using a chiral phosphine ligand has been reported by Shibata and Tanaka.[24] However, BINAP **5** and DIOP **1** gave very poor conversion rate and selectivity. The P-stereogenic ligand QuinoxP* **31** gave the highest yield and enantioselectivity (Scheme 1.16, Table 1.5).



Scheme 1.16

Table 1.5 Screening of chiral biphosphine ligands for asymmetric hydroacylation

Ligand	Conv (%)	Yield (%)	ee (%)
(*R*)-BINAP **5**	58	14	35
(*S*,*S*)-DIOP **1**	44	29	22
(*R*,*R*)-QuinoxP* **31**	90	74	99



(*R*,*R*)-QuinoxP* 31

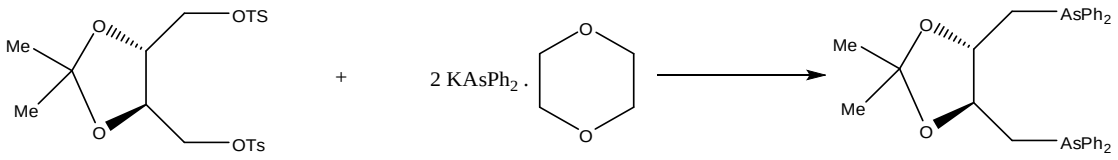
1.4 Chiral Arsine Ligands: An Overview

Very little work has been carried out on chemistry of arsines. The reason may be due to the lack of an NMR detectable spin-half nucleus. However, tertiary arsines have reduced air-sensitivity compared to analogous phosphines as well as increased configurational stability.[13] For example, mixed alkyl aryl substituted tertiary arsines themselves have much higher barriers to pyramidal inversion than similar tertiary phosphines.

Similar to phosphines chiral arsines can be prepared from synthesis from two different synthetic protocols.

1.4.1 Preparation from naturally occurring chiral starting materials

The chiral bidentate (*R*,*R*)-Diarsop **32** was synthesised by the reaction of 1,4-ditosyl-2,3-o-isoproplylidene-D-threitol with potassium diphenylarsenide dioxanate in THF and dioxane (Scheme 1.17).[25] The product was obtained as air-stable solid.

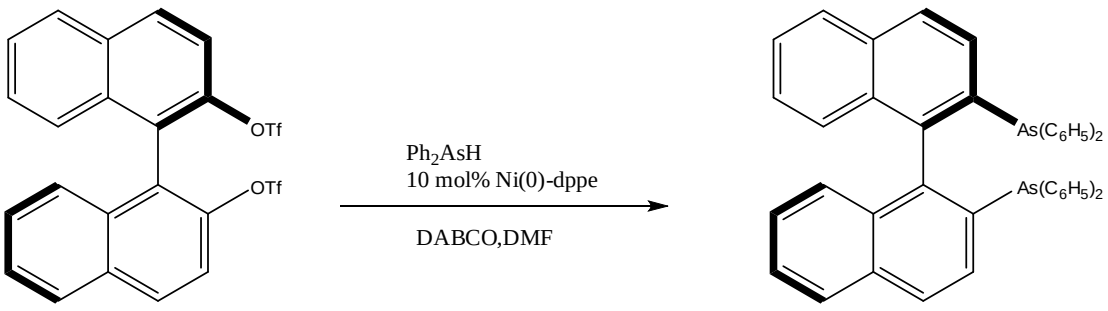


(*R,R*)-Diarsop 32

Scheme 1.17

(*R,R*)-Diarsop **32** is an analogue of the famous chiral diphosphine ligand, DIOP **1** which was prepared from the naturally occurring (+)-tartaric acid.

A new chiral arsine ligand, 2,2'-bis(diphenylarsino)-1,1'-binaphthyl (BINAs) **33**, the arsine analogue of BINAP **5** was prepared by heating a mixture of the chiral ditriflate of binaphthol, diphenylarsine and 1,4-diazabicyclo[2.2.2]octane (DABCO) with 10 mol and bis(1,5-cyclooctadine)nickel and 11 mol% bis(diphenylphosphino)ethane in DMF at 100 °C for 3 days (Scheme 1.18).[26] The optical purity of the formed material was more than 95 % ee.

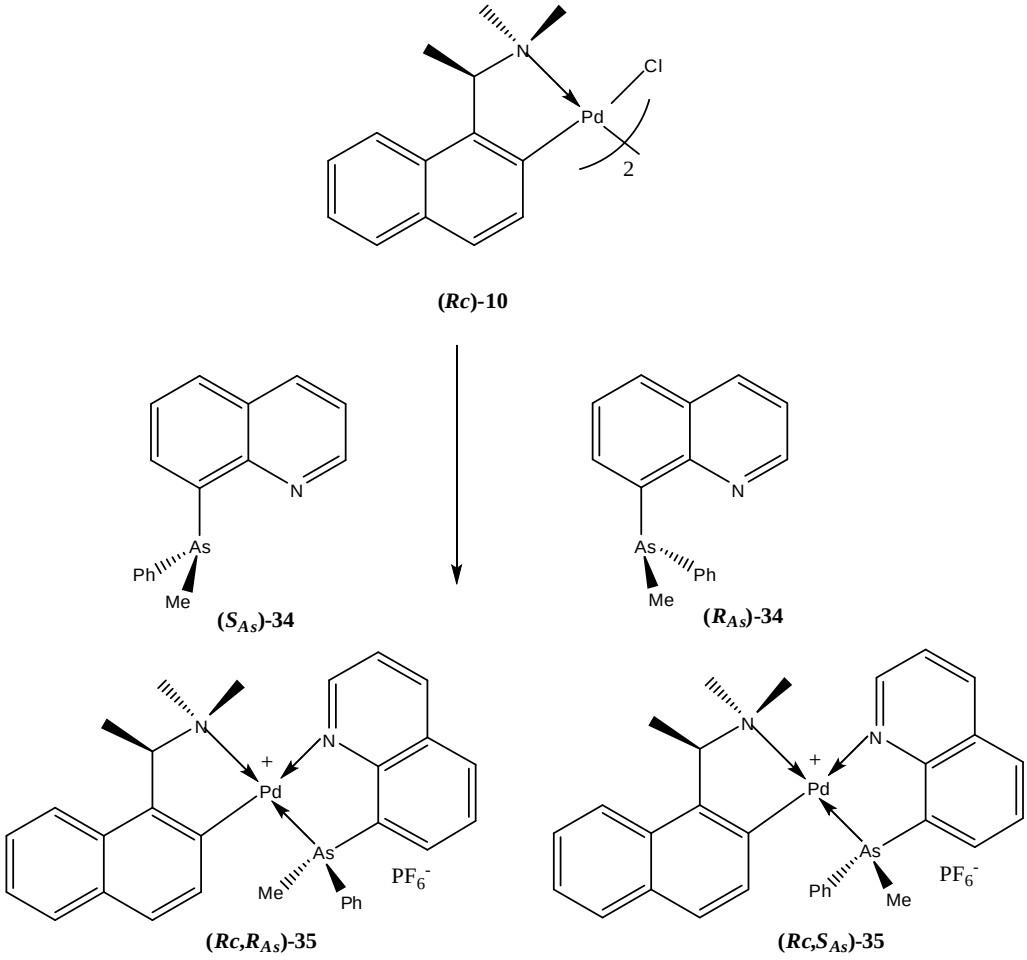


(*R*)-BINAP **(*R*)-BINAs 33**

Scheme 1.18

1.4.2 Resolution by using chiral resolving agents

The resolutions of (*R,S*)-methylphenyl(8-quinolyl)arsine **34** which was based upon the fractional cyrstallisation of a pair of diastereoisomeric palladium (II) complxes containing the bidentate ligand and an optically active ortho-metalated dimethyl(1-ethyl-α-naphthyl)amine (*Rc*)-**10** (Scheme 1.19).[27] The less soluble salt (R_c,R_{As}) -**35** was crystallised as fine white needles and repeated recrystallisation from mother liquors finally gave optically pure (R_c,S_{As}) -**35**.

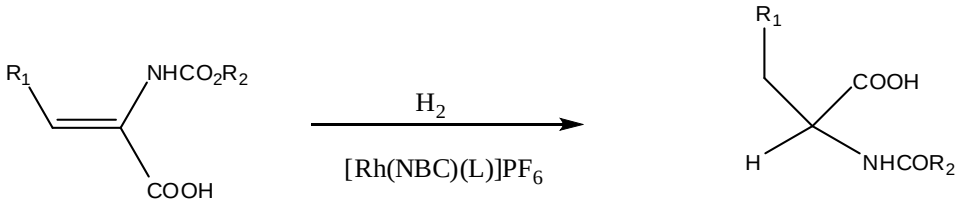


Scheme 1.19

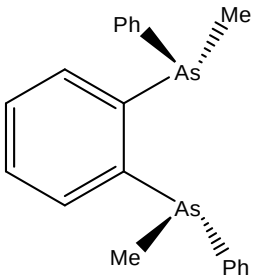
1.5 Applications of Chiral Arsine Ligands in Asymmetric Reactions

Although biphosphine ligands have been a very popular choice in asymmetric catalysis, bidentate arsine ligands can be superior in certain catalytic reactions.[28]

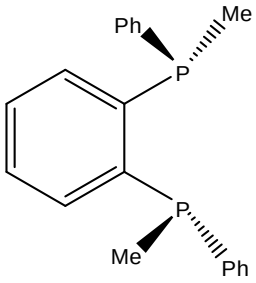
The rhodium (I) complex containing (*S,S*)-(-)1,2-phenylene-bis(methylphenylarsine), (*S,S*)-(-)-dias (*S,S*)-**36** was found to outperform its phosphorus analogue (*S,S*)-(-)diph (*S,S*) **-37** (Scheme 1.20).[29] The results were summarised in Table 1.6 where *ee* values could go as high as 90% in the asymmetric hydrogenation of the prochiral enamide.



a) R_1 = Ph, R_2 = Me
b) R_1 =R_2 = Ph
c) R_1 =i-Pr, R_2 = Me



$(S_{As}S_{As})$-**37**



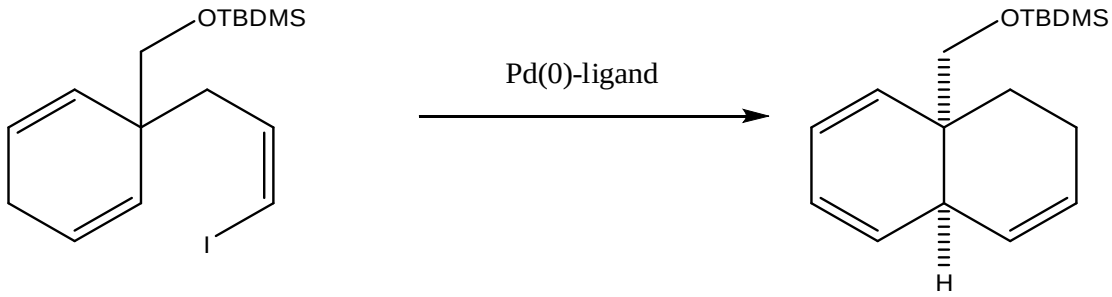
(S_P,S_P)-**37**

Scheme 1.20

Table 1.6 Enantiomeric excess of asymmetric hydrogenation products

Product	(S_{As},S_{As})-36	(S_P,S_P)-37
a	80%	79%
b	77%	64%
c	90%	94%

Evaluation of the effectiveness of BINAs **33** in asymmetric Heck reaction clearly showed an increased reaction rate comparing with what was seen using BINAP **5** (Table 1.7).[26] BINAs **33** also found to give a higher chemical yield and enantiomeric excess.



Scheme 1.21

Table 1.7

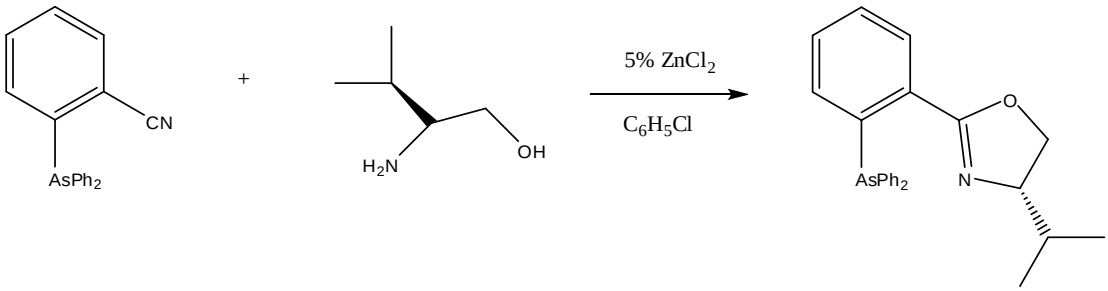
BINAs 33	**BINAP 5**
Yield = 90%, ee = 82 %	Yield = 55%, ee = 32%

1.6 Chiral Heterobidentate Ligands: An Overview

Ligands that are made up of hard and soft donors are called heterobidentate ligands. These types of ligands are also have been to be known catalytically active in a variety of asymmetric reactions including hydrogenation, carbonylation, hydroformylation of olefins and epoxides, allylation, and epoxidation.[30] Their catalytic utility is due to their hemilabile nature. One of the donor can vacate a coordination site thus allowing the incoming substrate to bind onto the metal centre and be activated for further reactions.[31]

1.6.1 Preparation from naturally occurring chiral starting materials

(*S*)-2-amino-3-methyl-1-butanol was treated with o-cyanoarsine ligand in the presence of $ZnCl_2$ resulting in a condensation reaction followed by cyclization to form the optically pure oxazoline functionalised As-N hetero-bidendate ligand (*Rc*)-**38**.[32]

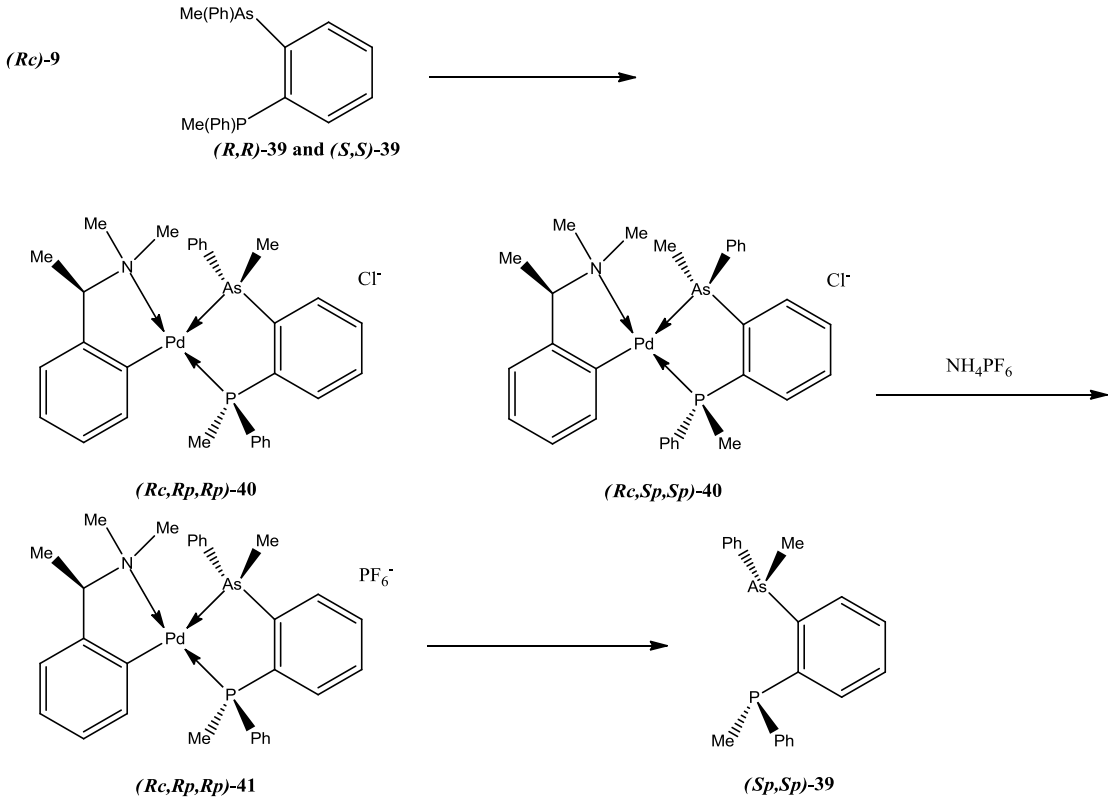


(*Rc*)-38

Scheme 1.22

1.6.2 Resolution by using chiral resolving agents

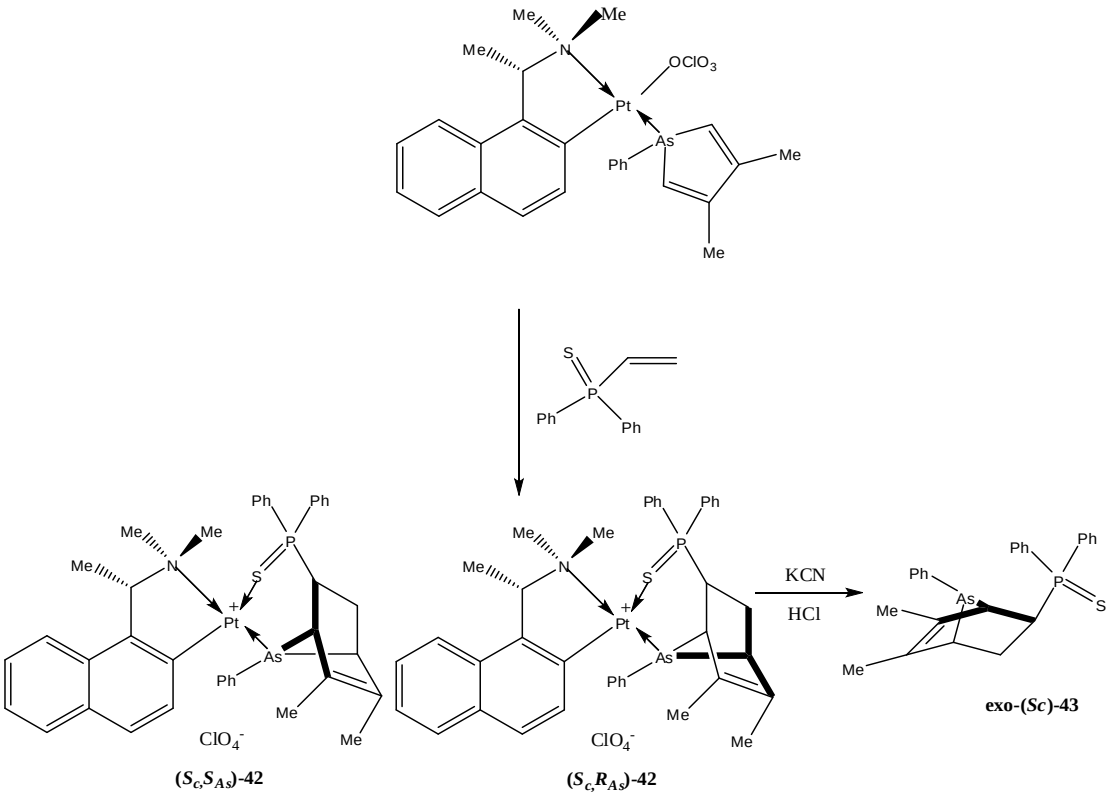
The resolution of the (*R*,*R*)-**39** and (*S*,*S*)-**39** diastereoisomers of the new asymmetric bidentate 1-(methylphenylarsino)-2-(methylphenylphosphino)benzene can be achieved by careful fractional crystallisation using hot methanol.[33] The enantiomers of (*R*,*R*)-**39** were then resolved using the chiral phenyl palladium complex (*Rc*)-**9**. The addition of excess aqueous NH_4PF_6 precipitated (*Rc*,R_{As},R_p)-**41** as colourless prisms. The ligands can be liberated by stereospecific displacements to give optically pure enantiomer as air-stable crystalline solids. This is the first resolution of an asymmetric bidentate containing dissimilar asymmetric donor atoms.



Scheme 1.23

1.6.3 Asymmetric reactions

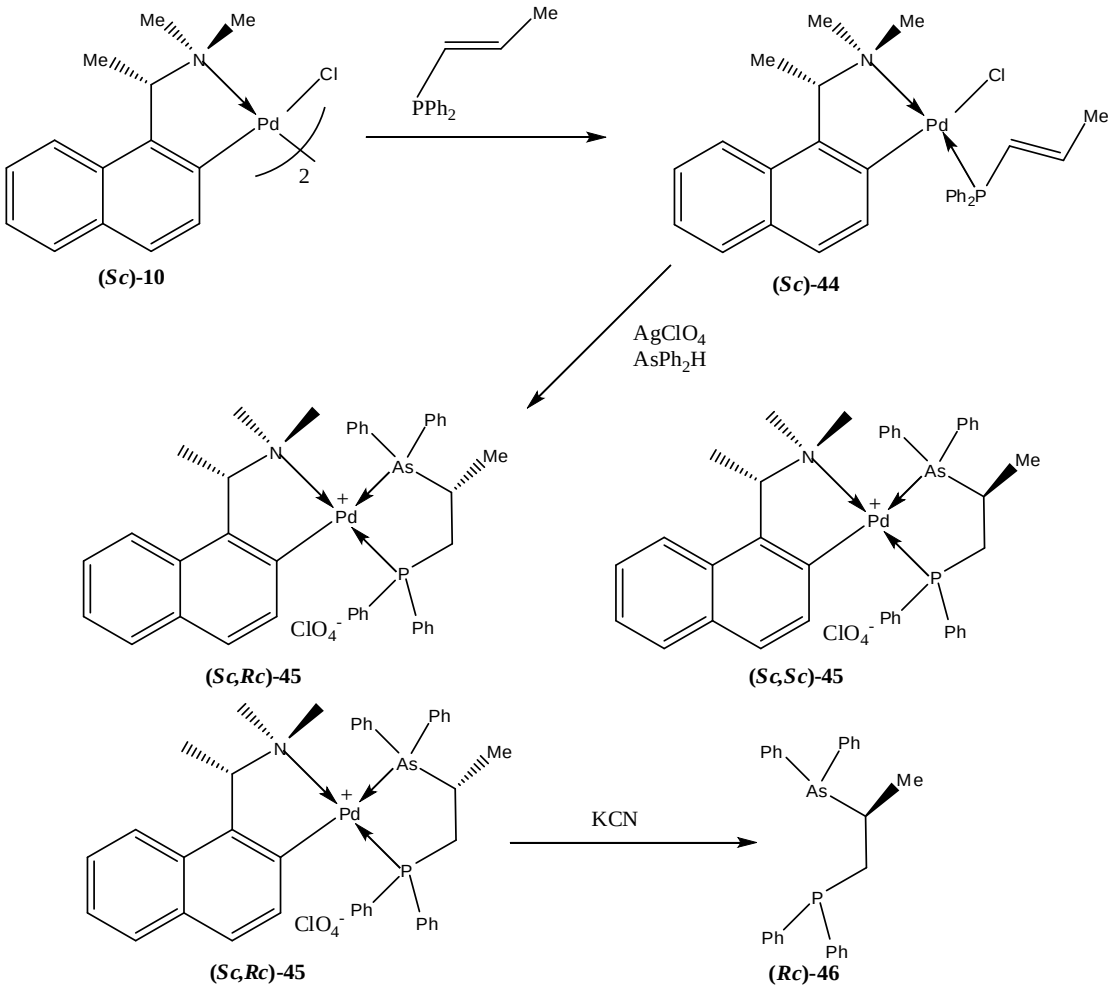
Leung *et.al.* has successfully reported a As/P=S heterobidentate ligands via asymmetric [4+2] Diels-Alder cycloaddition reaction between 3,4-dimethyl-1-phenylarsole (DMPA) and diphenylvinylphosphine sulfide promoted by a chiral platinum complex (Scheme 1.24).[34] Two diastereomers (S_c,S_{As})-**42** and (S_c,R_{As})-**42** were obtained in the ratio of 1:2. The diasteromers were converted to the neutral dichloro platinum complex and can be separated through fractional crystallisation with dichloromethane/diethyl ether. The optically pure ligand (S_{As})-**43** could be liberated by displacement reaction with aqueous KCN.



Scheme 1.24

The dissymmetrical chiral bidentate (*R*)-(+)-1-(diphenylphosphino)-2-(diphenylarsino)propane was also prepared by our group stereoselectively via the

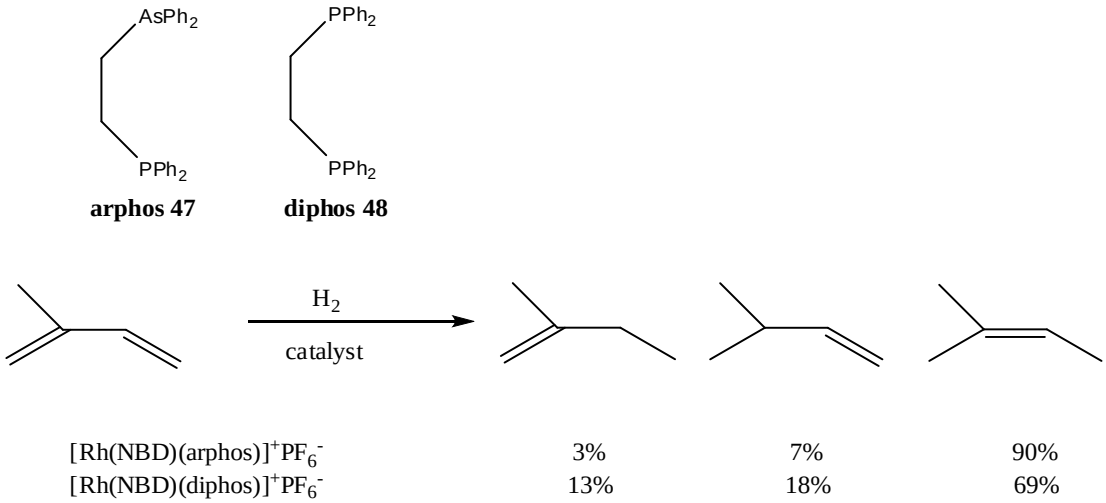
asymmetric hydroarsination reaction between diphenylarsine and diphenyl-1-propenyl-(*E*)-phosphine using the cyclometallated complex as the chiral reaction promoter (Scheme 1.25).[35] Only two diastereomeric complexes (S_c,R_c)-**45** and (S_c,S_c)-**45** were generated in the ratio of 8:1. The two diastereomeric products could be separated into their stereoisomerically pure products by fractional recrystallisation from dichloromethane-diethyl ether. Similarly the optically active ligand can be liberated via treatment with KCN (Scheme 1.25).



Scheme 1.25

1.7 Applications of Chiral Heterobidentate Ligands in Asymmetric Reactions

In hydrogenation of butadiene derivatives, arphos **47** had shown to be a better ligand auxiliary in comparison to diphos **48** (Scheme 1.26). [36]



Scheme 1.26

1.8 Two Important Chiral Templates Used in the Project

The chiral templates chosen for the project are the organopalladium complex containing ortho-metalated (R)-(1dimethylamino)ethyl)naphthalene (*Rc*)-**10** and its platinum analog (*Rc*)-**49** (Figure 1.4)

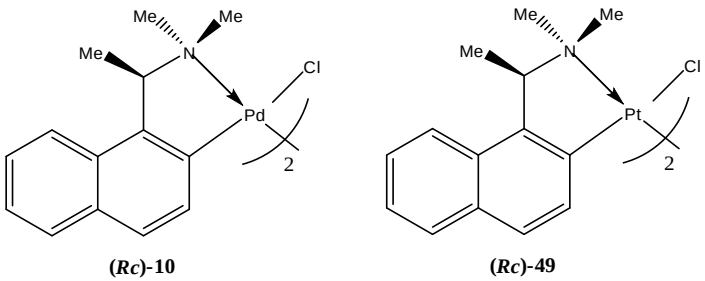


Figure 1.4

A unique stereochemical feature in the chiral napthylamine chelate ring in (*Rc*)-**10** is the internal repulsion between the methyl substituent on the stereogenic carbon and its

neighbouring naphthylene proton.[37] This particular interaction confines the methyl group in the axial position and hence the δ absolute conformation of the five-membered ring is fixed and not interconvertable in both the solid state and in solution.[38] Thus the prochiral NMe groups are fixed into the non-equivalent axial and equatorial positions. These NMe groups control the stereochemistry of the incoming substrates. Apart from that, the σ-donating nitrogen and π-accepting naphthylene carbon of the organometalic ring control the regioselectivity of the incoming ligands. Soft donors such as DMPP prefer to be coordinated to the position trans to the NMe_2 groups.[39]

Our group has successfully applied the chiral ortho metalated amine complexes in asymmetric [4+2] cycloaddition,[40] hydrophosphination,[41] hydroamination[42] and hydroarsination[35,43] reactions for the synthesis of a wide range of functionalised of P-chiral phosphines and phosphine ligands with chirality on the carbon backbones.

1.9 Aims of the Present Project

The project aims to enrich the chemistry of chiral arsines and is also part of ongoing efforts to understand the difference in phosphorus and arsenic reactivity. We aim to synthesise chiral bidentate P-stereogenic sulfonate and oxygenated phosphine ligands and P/As ligands with chirality residing on the carbon backbones carrying various functional groups.

Accordingly, this thesis is divided into four chapters. Chapter 2 deals with the studies of organo-palladium and organo-platinum complex activated insertion of C-C triple bond of an alkynylarsine into the C-Pd bond of naphthylamine complex. Apart from that we also look at the C-H bond activation of an alkynylarsine coordinated platinum (II) complex. Chapter 3 presents the asymmetric hydroarsination reaction to prepare

chiral hetero-bidentate ligand having chirality on carbon backbone with various functional groups. Lastly, chapter 4 involves the study of asymmetric [4+2] Diels-Alder cycloaddition reactions between oxygenated- and sulfonated- phosphine functionalised dienophiles and DMPP promoted by cycloplatinated (II) complex.

Chapter 2

Insertions of alkynylarsine into the Pd-C bond of cyclopalladated complex and Aromatic C-H bond activation of an alkynylarsine coordinated platinum (II) complex

2.1 Introduction

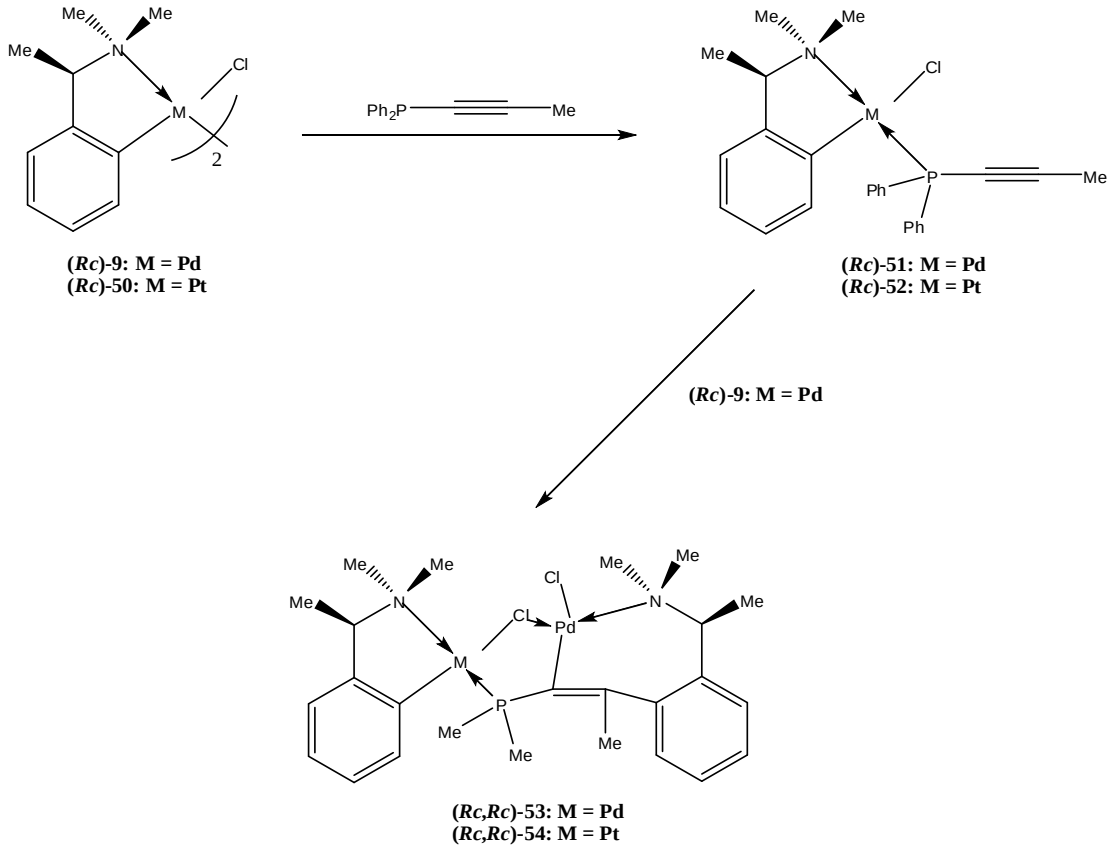
It is well known that palladium-carbon bond of orthopalladated complexes display a richness of high reactivities towards insertion reaction with a huge variety of unsaturated molecules such as carbon monoxide,[44] allenes,[45] alkenes,[46] alkynes,[47] isocynanides[48] and acyl halides[49]. Thus, the insertion reactions have a huge potential for the synthesis of a wide range of novel organic or organometallic compounds.

There are two factors governing the insertion reactions. Firstly, it depends on the electronic and steric effects of the alkyne substrate and secondly the coordination environment around the metal centre. Maitlis[50] and Clark[51] first reported insertion reactions of olefin an alkyne into the Pd-C bond of aryl or methyl palladium complexes in the 1970s. More recently, reports on monoinsertion into the Pd-C bond of the cyclopalladated complexes have been observed for a larger variety of alkynes.[52] Multiple insertions such as di- and tri-insertion of alkynes into the Pd-C bond of orthopalladated complexes could also take place resulting in the ring enlargement.[52]

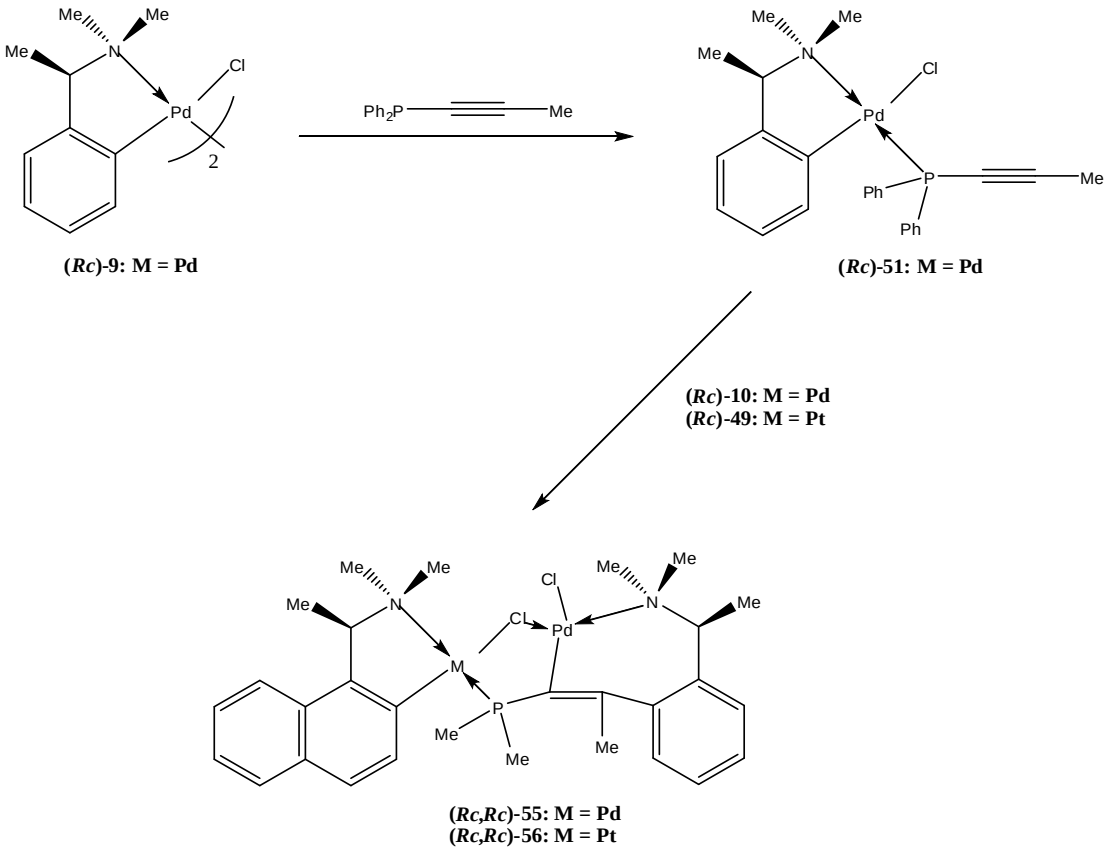
Alkynylphosphines are potentially bifunctional ligands which have been used in organometallic and coordination chemistry. In the case of bis(diphenylphosphino) acetylene (dppa), the lone pair electrons on P atom has been used to prepare numerous complexes or clusters in which dppa acts a bridging ligand.[53] The carbon-carbon triple bond moiety of alkynylphosphine is unreactive but can be activated upon coordination to a metal centre.[54] As a result of ligand coordination, the carbon-carbon triple bonds

are polarised with carbon attached to the phosphorus atom being negatively charged. This polarisation thus renders them susceptible to alkyne insertion reaction.

Leung *et. al.* has studied extensively insertion reaction of alkynyl phosphines in various cyclopalladated and cycloplatinated complexes.[55] The obtained results concluded that (a) only the ortho-palladated complex of benzylamine (*Rc*)-**9** was reactive towards alkynyl phosphines reaction (Scheme 2.1) (b) the ortho-palladated complex of napthylamine (*Rc*)-**10** was not reactive towards alkynyl phosphines insertions, and (c) the ortho-platinated complexes of phenyl (*Rc*)-**50** and napthylamine (*Rc*)-**49** were not reactive towards alknynyl phosphines insertions. These results tally with the many reports on insertion reaction of alkynes into the metal-carbon bond of orthopalladated complexes mostly those derived from benzylamines (mainly by Pfeffer *et.al.*). [47]

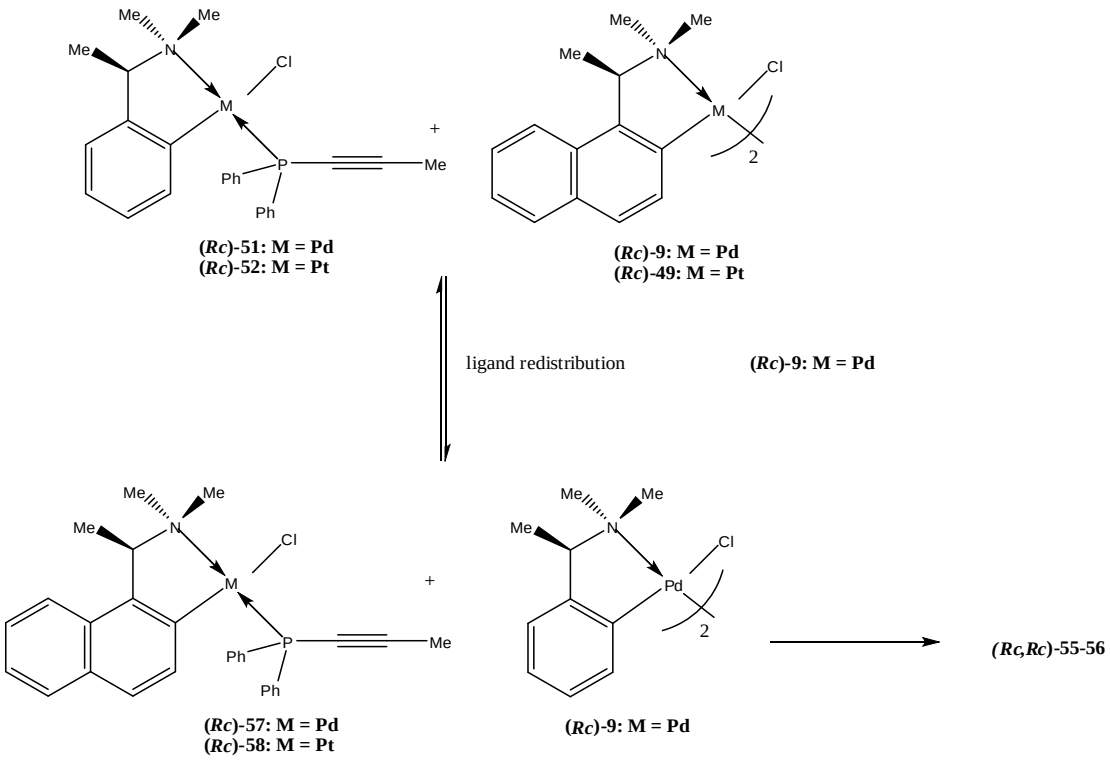


Scheme 2.1



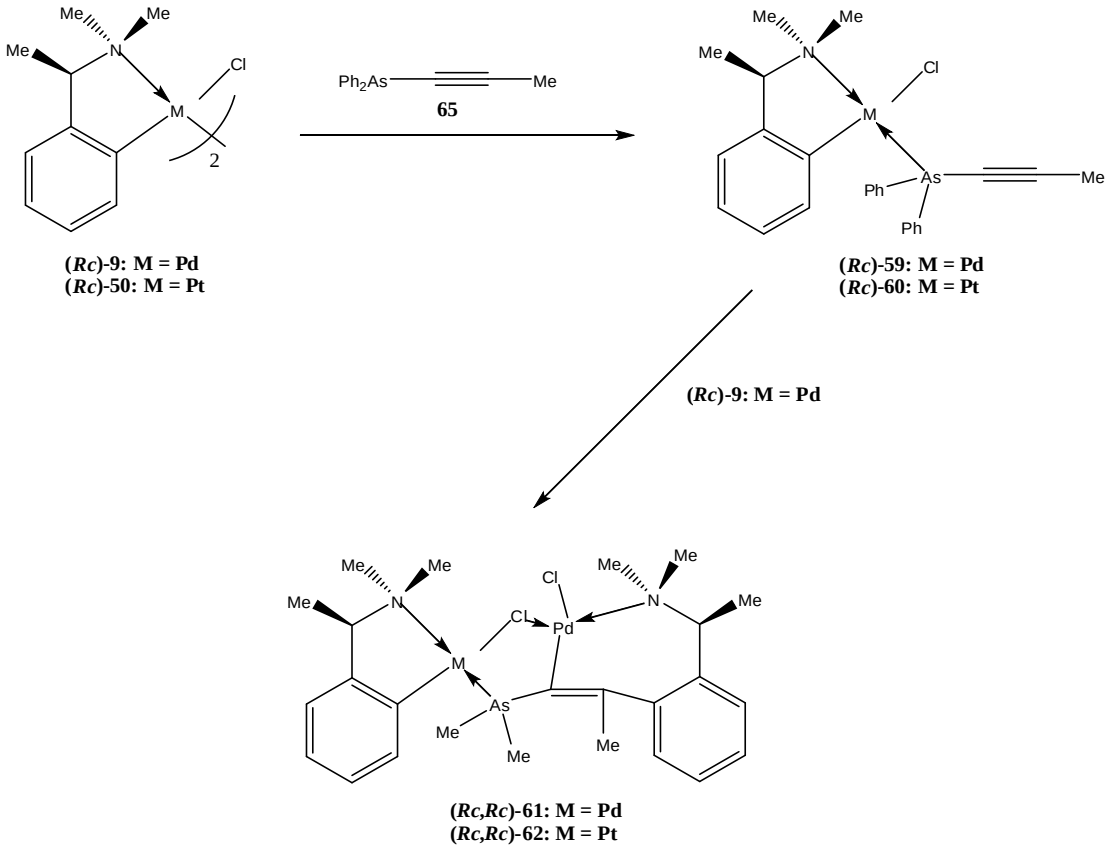
Scheme 2.2

The products of the reaction shown in Scheme 2.2 is indicative of the fact that the alkynyl phosphine had shifted from the ortho-palladated phenylamine (*Rc*)-**9** to the ortho-palladated naphthylamine (*Rc*)-**10** or ortho platinated complexes (*Rc*)-**49** resulting in the insertion of the C-C triple bond of the alkynyl phosphine into the C-Pd bond of the cyclo-palladated phenylamine complex to give (*Rc*,*Rc*)-**55-56.** We assumed that there was a ligand redistribution process prior to the insertion reaction. As illustrated in Scheme 2.3, the labile alkynykphosphine ligand was redistributed from the phenylamine template to to napthylamine template to form monomeric complex napthylamine complexes (*Rc*)-**57** and (*Rc*)-**58** which subsequently underwent insertion reaction to form (*Rc*,*Rc*)-**55-56**



Scheme 2.3

An analogous arsino alkyne insertion into the cyclopalladated complexes has also been reported by Leung *et.al.*[56] The C-C triple bond of the alkynylarsine is activated by the organoplatinum complex and can be inserted into the Pd-C bond of the achiral organopalladium (II) complex to give a hetero-bimetallic complex. Apart from the achiral organopalladium (II) complex, the chiral cyclopalladated and cycloplatinated complexes which incorporated the N,N-dimethylbenzylamine (*Rc*)-**9** and (*Rc*)-**50** motifs were successfully employed to promote a series of intermolecular mono insertion reaction of diphenyl-1-propynylarsine **65**, into the C-Pd bond of the chiral α-methyl N,N-dimethylbenzylamine palladacycle (*Rc*)-**9**. These insertion reactions showed high regioselectivity under mild conditions and a variety of homo- and hetero-bimetallic arsenic functionalised complexes (*Rc*,*Rc*)-**61-62** were formed.



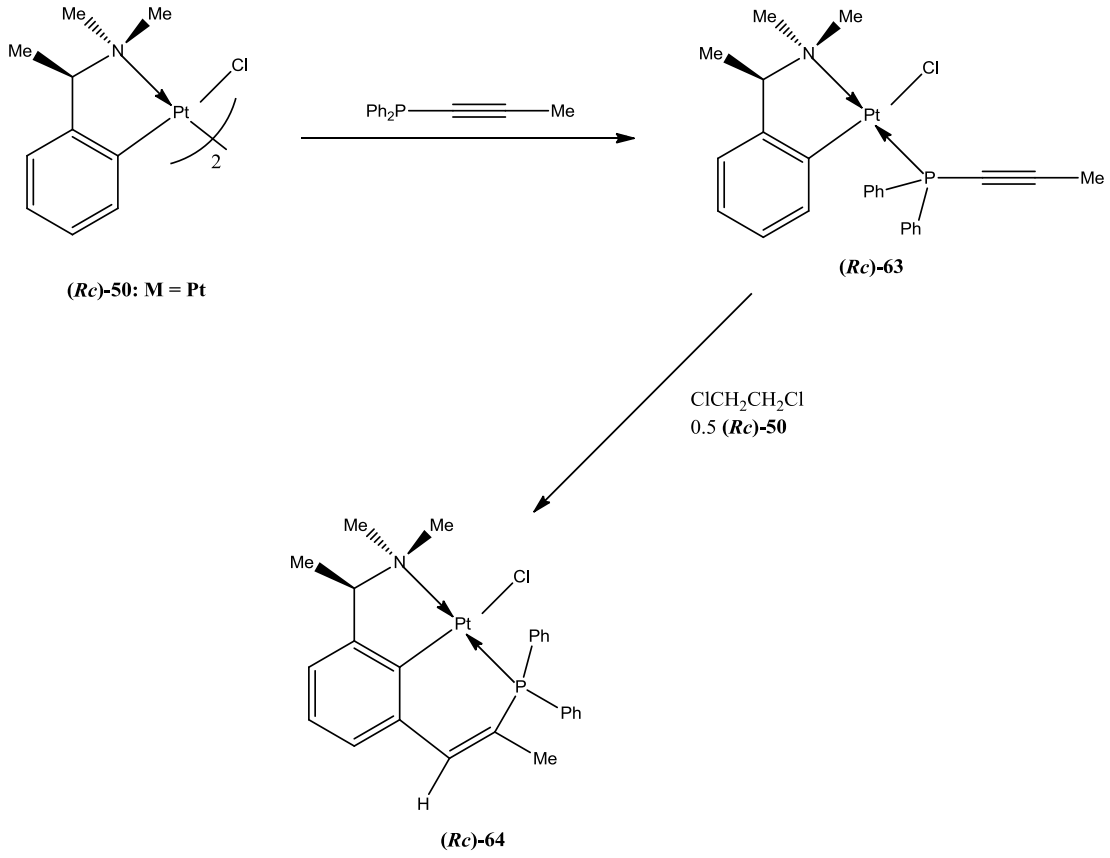
Scheme 2.4

In view of the relatively unexplored chemistry of arsines in insertion reactions, we aim to expand our work on the application of the cyclometallated-amine complexes for transformations that involve the insertion of alkynylarsines into the C-Pd bonds. The work that will be discussed in this chapter is about a series of intermolecular monoinsertion reactions of the palladium and platinum template coordinated alkynylarsine with the ortho-palladated napthylamine complex which eventually gave both homo- and hetero bimetallic complexes.

Transition-metal catalysed catalyzed C-H activation and coupling reactions of various organic substrates have become an interesting field.[57] These organometallic reagents undergo cross-coupling reactions. Most importantly C-H bond activation reactions can lead to C-C bond coupling. Leung *et.al*. has reported a C-H bond activation of an aromatic ring system which led to C-C coupling by of Pt (II) coordinated

alkynylphosphine.[55a] In the reports, the activated C-C triple unit of an alkynylphosphine can activate the aromatic C-H bond and promote C-C bond formation in an intramolecular manner. This process has led to the formation of a 6-membered metallacycle (Scheme 2.5).

The analogous arsino alkyne coupling reaction in coordinated platinum (II) complex has not been reported hitherto. The work that will be discussed in this chapter deals with the C-C coupling reactions under C-H activation of an alkynylarsine coordinated platinum (II) complexes.



Scheme 2.5

2.2 Results and Discussion

2.2.1 Insertion of alkynylarsine into C-Pd bond

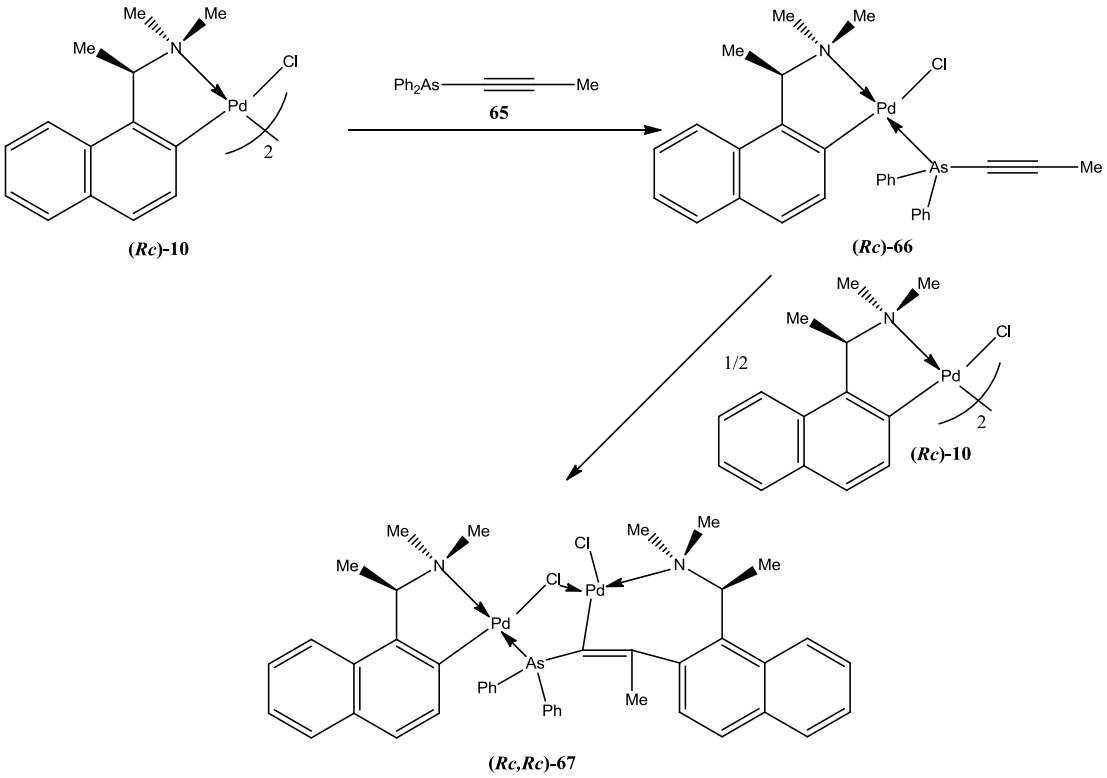
The monoalknylarsine coordinated precursor complex (*Rc*)-**66** was easily prepared by treatment of the dimeric palladium (II) complex with the diphenylarsinoprop-1-yne ligand **65** in dichloromethane for 2 h at room temperature. Electronically, the σ-donating nitrogen and the π-accepting naphthylene carbon of the organopalladium ring control the regioselectivity of the incoming ligands. Ligands with soft donors prefer to occupy the coordination site trans to the NMe_2 group.[39] Thus, the monodentate arsine ligand split the chloride bridge in (*Rc*)-**10** and regioselectively coordinated to the orthopalladated N,N-dimethyl naphthylamine complex in the position trans to naphthylamine-N donor atom to form the monomeric complex (*Rc*)-**66**. The monomeric complex (*Rc*)-**66** was then treated with 0.5 mole equivalent of the dimeric palladium (II) complex (*Rc*)-**10** at room temperature (Scheme 2.6). The reaction was monitored using TLC which showed that only one product was formed and left to stir for a week. The crude reaction mixture was then purified by silica gel chromatography and crystallised from acetone-hexane to give complex (*Rc,Rc*)-**67** as yellowish orange crystals: yield 0.19 g (45% yield), $[\alpha]_D$ -55 (c 0.6, CH_2Cl_2).

2.2.1.1 X-ray crystal Diffraction Analysis of (*Rc,Rc*)-67

The single crystal X-ray diffraction studies of the insertion product revealed that the desired insertion product has indeed been generated. As shown in Figure 2.1, the original carbon-carbon triple C(1)-C(2) bonds in the alkynylarsine has been inserted into the carbon-palladium bond C(4)-Pd(1) of the original cyclopalladated complex (*Rc*)-**10**, forming a new bond between C(2) and C(4). The C(1)-C(2) bond was consequently changed from C-C triple bond to C-C double bond. The ring expansion produced by the insertion of the triple bond into the carbon-palladium bond of the cyclopalladated complex (*Rc*)-**10** led to the formation of a new seven-membered ring.

In addition, the two palladium metal centres are connected by a μ-chloro ligand as well as the newly formed Pd(1)-C(1)-As(1)-Pd(2) linkage to give a 5-membered bimetallic heterocycle. As expected the absolute configurations of the two stereocentres at C(14) and C(40) remained unchanged.

The geometry at both the palladium centres are slightly distorted square planar. Bond angles at Pd(1) ranges from 84.8(1)-94.2(1)° and 170.7(1)-176.6(1)° while those at Pd(2) are in the range of 81.0(1)-99.9(1)° and 171.8(1)-176.4(1)°. Selected bond lengths and bond angles of the insertion product are given in Table 2.1.



Scheme 2.6

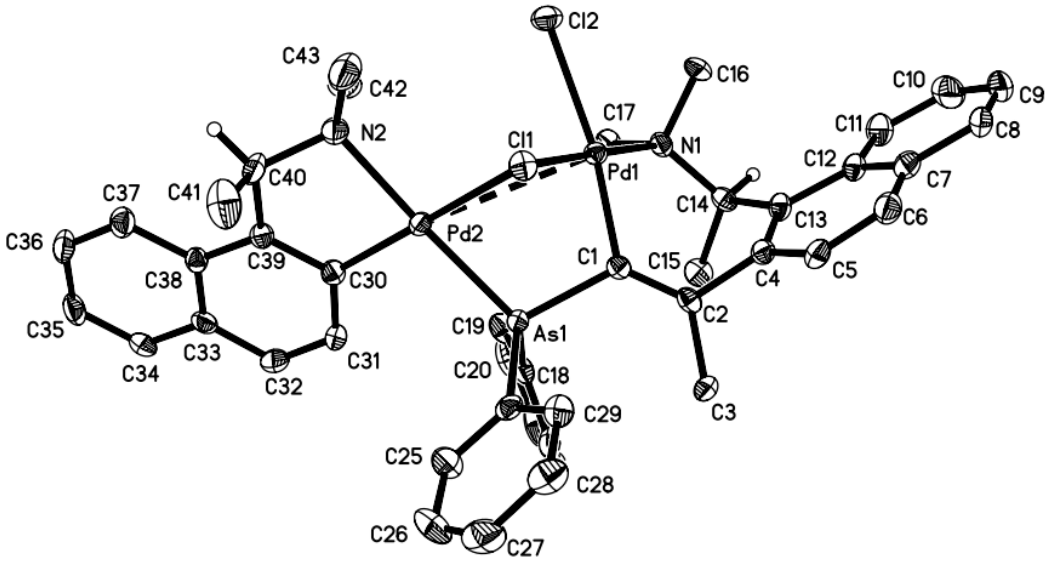


Figure 2.1 Molecular structure and absolute configuration of (*Rc,Rc*)-67

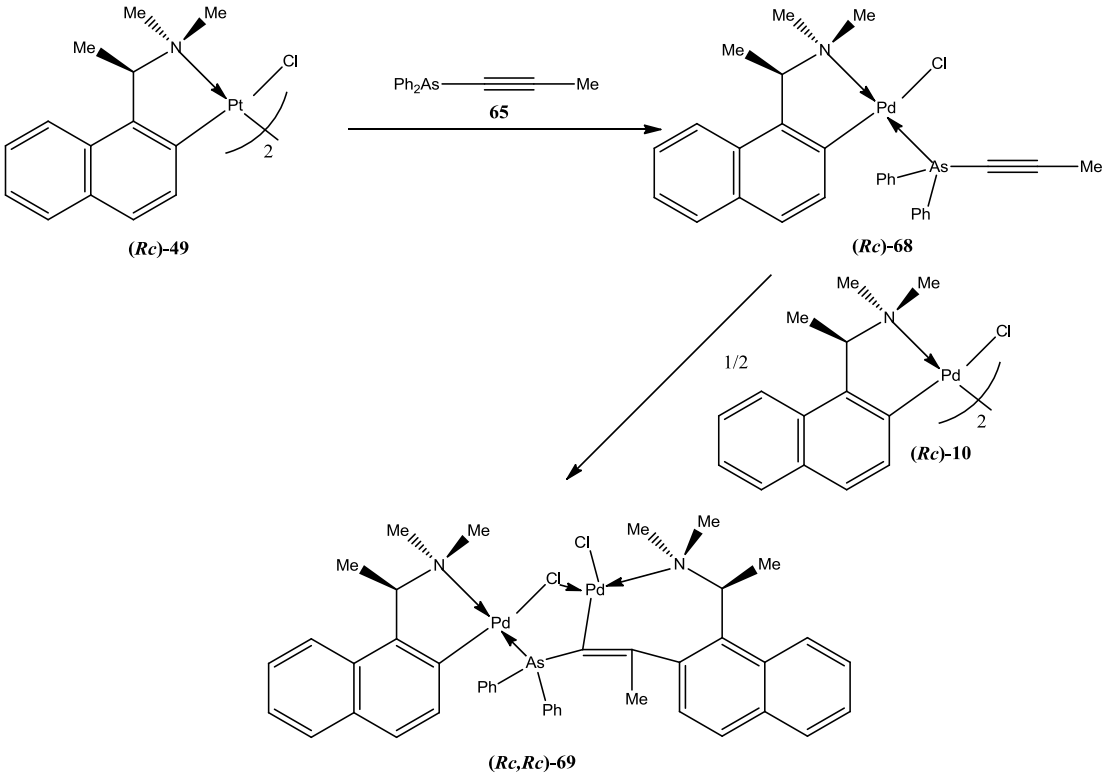
Table 2.1 Selected bond lengths (Å) and angles (°) for (*Rc,Rc*)-67

Pd(1)-C(1)	1.988(5)	C(1)-Pd(1)-N(1)	93.9(1)
Pd(1)-N(1)	2.219(4)	C(1)-Pd(1)-Cl(1)	84.8(1)
Pd(1)-Cl(1)	2.345(1)	N(1)-Pd(1)-Cl(1)	176.6(1)
Pd(1)-Cl(2)	2.455(1)	C(1)-Pd(1)-Cl(2)	170.7(1)
Pd(2)-C(30)	1.986(5)	N(1)-Pd(1)-Cl(2)	94.2(1)
Pd(2)-N(2)	2.114(4)	Cl(1)-Pd(1)-Cl(2)	87.4(1)
Pd(2)-As(1)	2.358(1)	C(30)-Pd(2)-N(2)	81.0 (1)
Pd(2)-Cl(1)	2.442(1)	C(30)-Pd(2)-As(1)	99.9(1)
C(1)-C(2)	1.319(7)	N(2)-Pd(2)-As(1)	176.4(1)
C(2)-C(3)	1.518(7)	C(30)-Pd(2)-Cl(1)	171.8(1)
C(2)-C(4)	1.491(7)	N(2)-Pd(2)-Cl(1)	97.1(1)
N(1)-C(14)	1.526(7)	As(1)-Pd(2)-Cl(2)	82.5(4)

C(13)-C(14)	1.518(7)	C(1)-C(2)-C(3)	125.5(5)

2.2.2 Studies Involving the Insertion Reaction on the Platinum (II) Analogue

In order to investigate the metal effect of palladium naphthylamine template (*Rc*)-**10**, similar reaction was conducted using the analogous platinum complex (*Rc*)-**49**. This reaction gives an insight into the subtle metal template effects arising from the presence of hetero metal centres toward the reactivity of the insertion of alkynykarsine into the carbon-palladium bond of the cyclopalladated N,N-dimethyl naphthylamine template.



Scheme 2.7

As illustrated in Scheme 2.7, the insertion reaction between complex **(*Rc*)-68** and 0.5 equiv of dimeric palladium (II) complex (*Rc*)-**10** was left to stir at room temperature for a week in dichloromethane and monitored by TLC which showed only one

product was formed. The crude reaction mixture was then purified by column chromatography in hexane-acetone. The product was crystallised out as yellow crystals from dichloromethane-hexane as (*Rc,Rc*)-**69**.

2.2.2.1 X-ray crystal Diffraction Analysis of (*Rc,Rc*)-69

The X-ray molecular structure of (*Rc,Rc*)-**69** is shown in Figure 2.2. As expected the original unsaturated C-C triple bond C(1)-C(2) has been inserted into the carbon-palladium bond C(4)-Pd(1). As a result of the insertion reaction, an enlarged seven-membered ring was formed. Apart from that, a new Pt(1)-Cl(1)-Pd(1)-C(1)-As(1) five- membered heterobimetallic ring connected by Cl in which the arsenic donor atom is coordinated regioselectively in the position trans to N donor of the naphthylamine auxiliary.

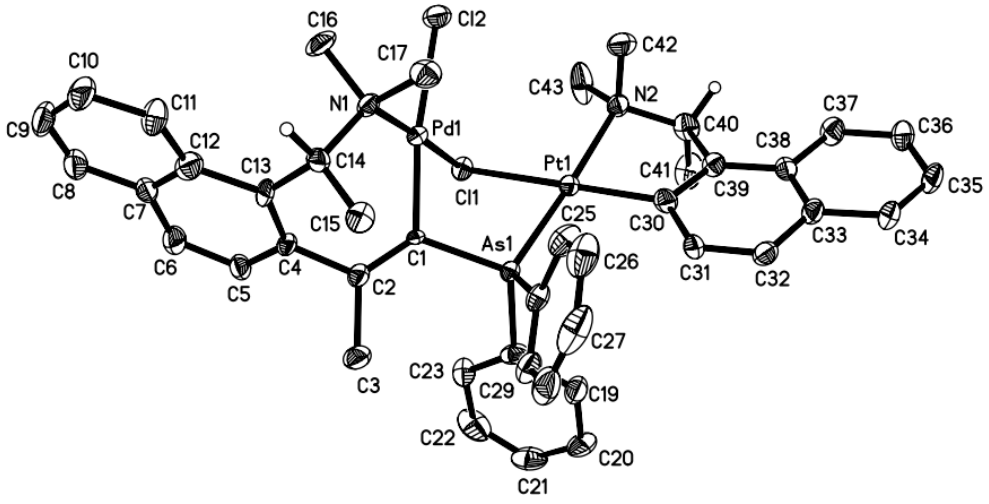


Figure 2.2 Molecular structure and absolute configuration of (*Rc,Rc*)-69

Similar to the insertion reaction reported earlier, insertion of the triple bond moiety into the carbon-palladium bond resulted in the formation of two new bonds namely

C(1)-Pd(1) and C(2)-C(4) bonds as shown in Figure 2.2. Both the C(14) and C(41) stereocentres of the complex adopts the *R* absolute configuration.

The geometry at both the palladium and platinum coordination sites are distorted square planar. Bond angles at the palladium centre ranges from 84.8(1) -94.5(1) ° and 160.6(1)-177.2(1)° while those at the platinum centre ranges from 81.1(1)-95.4(1)° and 172.7-176.1°. Selected bond lengths and bond angles of complex (*Rc,Rc*)-**69** are given in Table 2.2.

Table 2.2 Selected bond lengths (Å) and angles (˚) for (*Rc,Rc*)-69

Pt(1)-C(30)	1.981(5)	C(30)-Pt(1)-N(2)	81.1(1)
Pt(1)-N(2)	2.224(4)	C(30)-Pt(1)-As(1)	101.1(1)
Pt(1)-As(1)	2.343(1)	N(2)-Pt(1)-As(1)	176.1(1)
Pt(1)-Cl(2)	2.433(1)	C(30)-Pt(1)-Cl(1)	172.7(1)
Pd(1)-Cl(1)	2.350(1)	N(2)-Pt(1)-Cl(1)	95.4(1)
Pd(1)-Cl(2)	2.453(1)	As(1)-Pt(1)-Cl(1)	82.8(4)
Pd(1)-N(1)	2.141(1)	C(1)-Pd(1)-N(1)	93.9 (1)
Pd(1)-C(1)	1.979(6)	C(1)-Pd(1)-Cl(1)	84.8(1)
C(1)-C(2)	1.329(8)	N(1)-Pd(1)-Cl(1)	177.2(1)
C(2)-C(3)	1.519(9)	C(1)-Pd(1)-Cl(2)	170.6(1)
C(2)-C(4)	1.479(8)	N(1)-Pd(1)-Cl(2)	94.5(1)

N(2)-C(40)	1.496(5)	As(1)-C(2)-Pd(1)	107.1(3)
C(39)-C(40)	1.497(7)	C(1)-C(2)-C(3)	125.3(6)

2.2.3 Differences in Reactivity from its Alkynylphosphines Analogues

From our previous studies, it has been well established that chiral cyclopalladated and cycloplatinated complexes can promote a series of asymmetric insertion of coordinated 1-propnynldiphenylphosphine into the C-Pd bond of the orthopalladated N,N-dimethyl benzylamine.[55] It is important to note that the C-Pd bond of the phenylamine palladium (II) complex has been shown to undergo insertion reaction while its naphthylamine counterparts remained unreactive. Apparently the C-Pd bond of phenylamine complex is more reactive than the naphthylamine counterpart toward the insertion reaction (Scheme 2.1). Leung *et.al.* has also reported an analogous arsino alkyne insertion into C-Pd bond of ortho-palladated phenyl amine complex (Scheme 2.4).[56]

From the current studies on the reactivity of alkynylarsine in insertion reactions, the chemistry was found to be vastly different from that of alkynylphospines. We have observed that metal activated arsine substituted alkynes can undergo an intermolecular insertion reaction with the C-Pd bond of the naphthylamine cyclometallated complex to yield two homo and hetero bimetallic insertion products.

It has been generally accepted that the insertion reaction of alkynes involves the η^2-coordination of the alkyne to the metal centre followed by the migratory insertion of the C triple bond C unit into the metal-carbon bond of the palladacycle.[52h] The reactivity of the insertion reactions depend on various factors such as the electronic and steric properties of the alkyne, the other substituents on the palladium centre and

the reaction conditions (temperature, stoichiometry etc.).[52i] It is possible to rationalise the observed insertion reaction into carbon-palladium bond of the naphthylamine moiety on the basis of a simple model in which the HOMO of the alkyne overlaps with a LUMO located on the carbon atom of the C-Pd bond. [47f,g]

From the ^{1}H NMR spectrum of the product (Figure 2.3a), it is interesting to note that the number of the signals that are assigned to the methyl groups is doubled, which suggests the presence of two conformations due to instability of the seven membered ring within the complex in solution. At room temperature, two conformers existing in solutions can be detected by NMR. At higher temperature, the two conformers interconvert rapidly and thus only the average signals could be observed. VT NMR (Figure 2.3a-c) supports this to a certain extent, where the number of methyl signals is seven instead of fourteen at temperature above 35 ˚C. However at lower temperatures the signals could not be resolved probably due to poor solubility of the complexes.

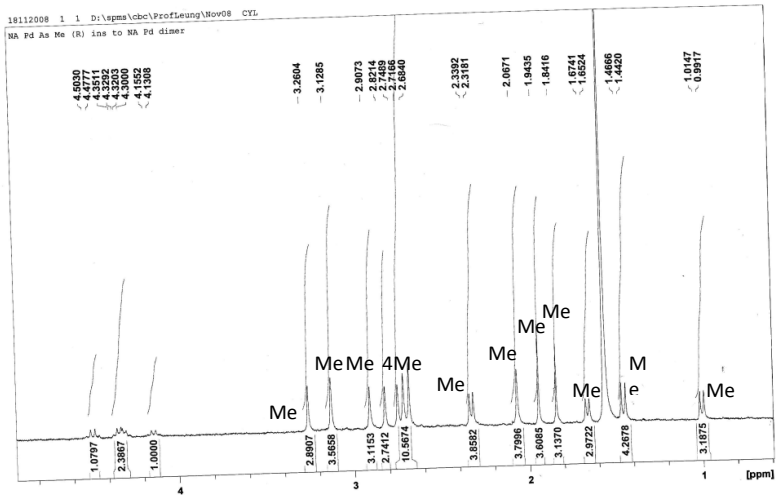


Figure 2.3a

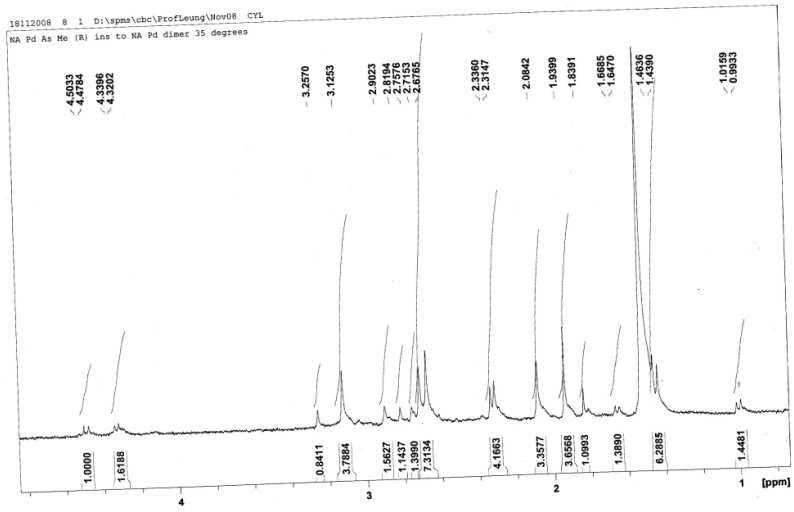


Figure 2.3b

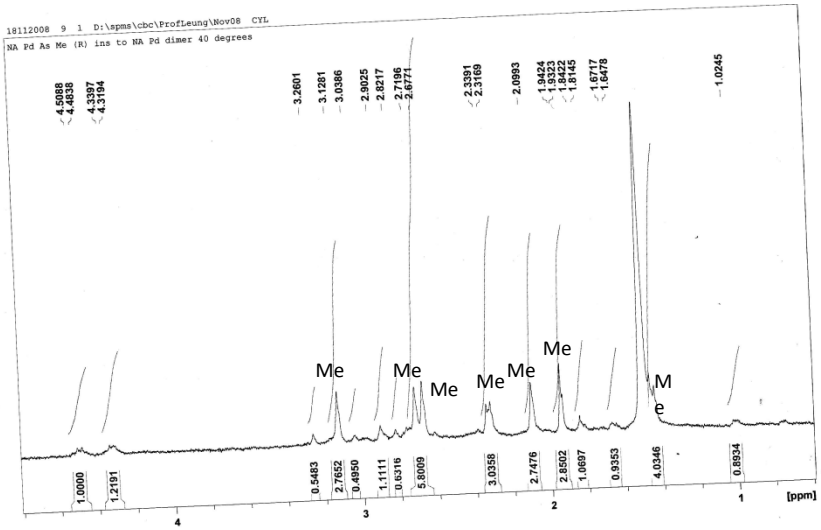


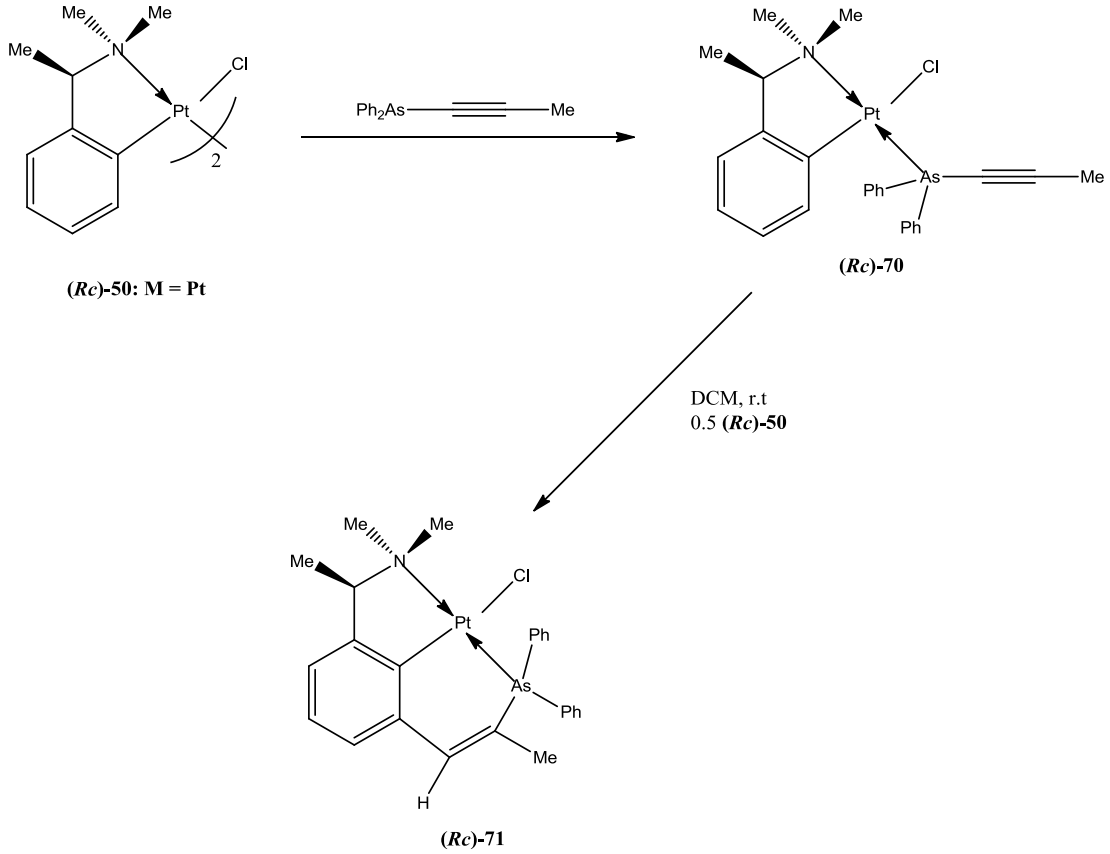
Figure 2.3c

Figure 2.3 VT NMR studies of complex (*Rc,Rc*)-67

a) r.t b) 35 ˚C c) 40 ˚C

2.2.4 Aromatic C-H bond activation of an alkynylarsine coordinated platinum (II) complex

As illustrated in Scheme 2.8, alkynyldiphenylarsine **65** was coordinated to (*Rc*)-**50** regioselectively to form the neutral complex (*Rc*)-**70**. The coupling reaction was conducted between precursor complex (*Rc*)-**70** and 0.5 mole equivalent of the dimeric complex (*Rc*)-**50**. The reaction was monitored using TLC and was left to stir at room temperature for a week. After purification by column chromatography, recrystallisation by slow addition of *n*-hexane to the combined fraction in acetone yielded complex (*Rc*)-**71** as bright yellow crystals. Yield 0.26 g (61% yield), $[\alpha]_D$ -21 (c 0.3, CH_2Cl_2).



Scheme 2.8

2.2.4.1 X-ray Crystal Diffraction Analysis of (*Rc*)-71

A crystallographic analysis revealed that the product isolated is the expected coupling product (Figure 2.4). A new C-C bond was formed between the C(11) carbon on the acetylenic moiety of the the alkynylarsine and C(2) carbon of the organometallic ring in the coupling product. Thus, the original C-C triple bond fragement has been reduced to a C-C double bond and a new 6 –membered metallacycle has been formed as a result. It is also important to note that the methyl group of the alkynylarsine has shifted from C(11) to its neighbouring C(12) carbon atom.

From previous studies on the coupling reaction of alkynylphosphines, it was reported that the methyl group also migrated.[55a] It was suggested that such migrations occur due to the steric repulsion between the methyl group and the δ-proton of the aromatic system. However details of the reaction mechanism have remained debatable and hence the proposed explanations were mainly deduction.[58] The migrations of the phenyl group of alkynylphosphines in the C-C coupling reactions were also observed.

The coordination geometry at the platinum coordination centre is distorted square planar with bond angles ranging from 82.8(1) -93.4(1) ° and 169.4(1)-173.2(1) ° respectively. Selected bond angles and bond lengths are given in Table 2.3.

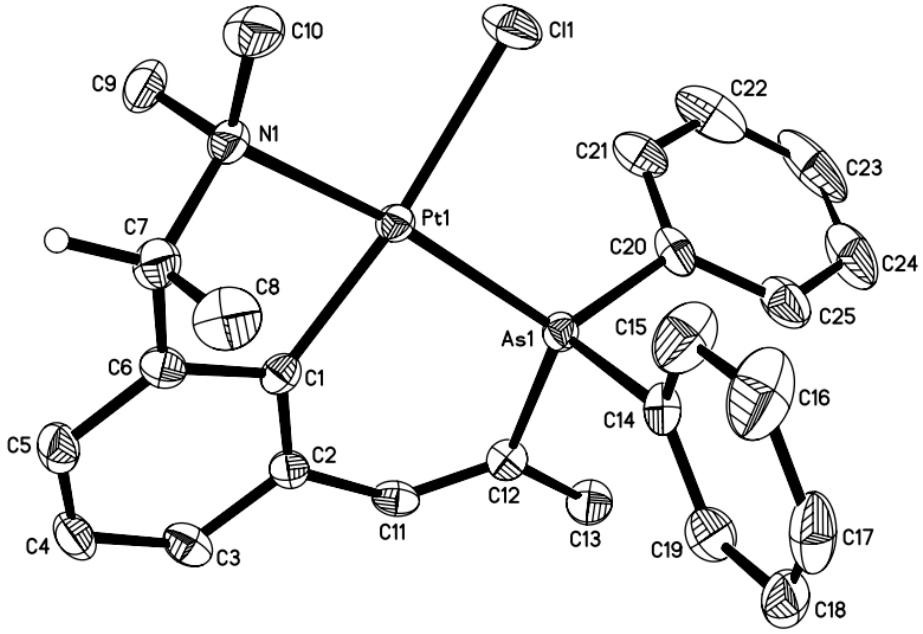


Figure 2.4 Molecular structure and absolute configuration of (*Rc*)-71

Table 2.3 Selected bond lengths (Å) and angles (˚) for (*Rc*)-71

Pt(1)-C(1)	2.006(5)	Pt(1)-As(1)	2.301(1)
Pt(1)-N(1)	2.134(3)	Pt(1)-Cl(1)	2.380(1)
As(1)-C(12)	1.923(5)	As(1)-C(14)	1.934(5)
As(1)-C(20)	1.935(5)	C(11)-C(12)	1.330(6)
C(2)-C(11)	1.479(6)	C(12)-C(13)	1.503(6)
C(1)-Pt(1)-N(1)	82.8(1)	C(1)-Pt(1)-As(1)	91.8(1)
N(1)-Pt(1)-As(1)	169.4(1)	C(1)-Pt(1)-Cl(1)	173.2(1)
N(1)-Pt(1)-Cl(1)	92.7(1)	As(1)-Pt(1)-Cl(1)	93.4(1)

2.3 Conclusions

In conclusion, a series of regioselective, intermolecular monoinsertion reaction of diphenyl-1-propynylarsine **65** unit into the C-Pd bonds of the chiral dimethyl-[1-(α-naphthyl)ethyl]-amine palladacycles were demonstrated under mild conditions in appreciable yields. In this study, cyclopalladated and cycloplatinated with the naphthylamine systems were found to be efficient reaction promoters for the insertion reactions. These reactions give new chiral homo- and hetero-bimetallic compounds.

The platinum metal coordinated alkynyldiphenylarsine ligand **65** has shown to undergo an intramolecular C-H activation and C-C coupling reaction in the presence of an external platinum ion just like its phosphine analogue. Furthermore, a methyl migration due to steric repulsion has occurred to form the final coupling product.

2.4 Experimental

All air-sensitve manipulations were carried out using Schlenk and cannula techniques under a positive pressure of purified nitrogen. All NMR spectra were recorded at 25 °C on Bruker Avance 300 and 500 spectrometer. Optical rotations were measured on the specified solution in a 0.1 dm cell at 20 °C with a Perkin-Elmer 341 polarimeter. Melting points were measured the SRS Optimelt Automated Melting Point System, SRS MPA100.

The dimeric naphthylamine palladium (II) (*Rc*)-**10,**[59] dimeric platinum (II) complex (*Rc*)-**49** [60] and **(***Rc***)-50** [55a] were prepared according to the standard methods. The diphenyl-1-propynylarsine **65** [61] was prepared by a revised literature method.

Synthesis of μ-chloro {{*R*-1-[1-(dimethylamino)ethyl]napthyl-C^2,N]}palladium (II) { *R*-1-[1-(dimethylamino)-2-(*E*)-1-(diphenylarsino)prop-1-en-2-yl)ethyl]napthyl-C^2,N] chloro palladium (II), (*Rc,Rc*)-67

diphenyl-1-propynylarsine **65** (0.24 g, 0.88 mmol) was dissolved in dichloromethane and into this (*Rc)*-**10** (0.3 g, 0.44 mmol) was added. The reaction mixture was stirred for 2 hours at room temperature to give complex (*Rc)*-**66**. The chiral palladium (II) complex (*Rc)*-**10** (0.3 g, 0.44 mmol) was then added into the solution. The insertion reaction was monitored by TLC. Upon completion of the reaction, the solvent was removed to give a brown residue, which was purified by column chromatography with hexane/acetone to give a yellowish orange solid. Crystallisation from acetone/hexane gave complex (*Rc,Rc*)-**67** as yellowish-orange crystals: 0.19 (45% yield) , 0.19 g (45% yield), $[\alpha]_D$ -55 (c 0.6, CH_2Cl_2). m.p 157-159 ˚C, $C_{43}H_{45}AsN_2Cl_2Pd_2$ (948.5) cacl: C 54.5, H 4.8, N 3.0; found C 54.1, H 4.3, N 3.2. ^{1}H NMR ($CDCl_3$, δ): 0.99 (d, J_{HH} = 6.9 Hz, 3H, CH*Me*), 1.47 (d, J_{HH} = 6.9 Hz, 3H, CH*Me*), 1.67 (d, J_{HH} = 6.9 Hz, 3H, CH*Me*), 1.84 (s, 3H, CH*Me*), 1.94 (s, 3H, CH*Me*), 2.07 (s, 3H, CH*Me*), 2.34 (d, J_{HH} = 6.9 Hz, 3H, CH*Me*), 2.68 (s, 3H, CH*Me*), 2.71 (s, 3H, CH*Me*), 2.74 (s, 3H, CH*Me*), 3.13 (s, 3H, CH*Me*), 3.26 (s, 3H, CH*Me*), 4.16 (q, 1H, C*H*Me), 4.30-4.35 (m, 2H, C*H*Me), 4.50 16 (q, 1H, C*H*Me), 6.75-8.47 (m, 45H, aromatics).

Synthesis of μ-chloro {{*R*-1-[1-(dimethylamino)ethyl]napthyl-C^2,N]}platinum (II) { *R*-1-[1-(dimethylamino)-2-(*E*)-1-(diphenylarsino)prop-1-en-2-yl)ethyl]napthyl-C^2,N] chloro palladium (II), (*Rc,Rc*)-69

diphenyl-1-propynylarsine **63** (0.16 g, 0.58 mmol) was dissolved in dichloromethane and into this (*Rc)*-**49** (0.25 g, 0.30 mmol) was added. The reaction mixture was

stirred for 2 hours at room temperature to give complex (*Rc)*-**68**. The chiral palladium (II) complex (*Rc)*-**10** (0.20 g, 0.30 mmol) was then added into the solution. The insertion reaction was monitored by TLC. Upon completion of the reaction, the solvent was removed to give a brown residue, which was purified by column chromatography with hexane/acetone to give a yellowish orange solid. Crystallisation from acetone/hexane gave complex (*Rc*,*Rc*)-**69** as yellowish-orange crystals: 0.12 (40% yield) , $[\alpha]_D$ -29 (c 0.2, CH_2Cl_2). m.p 168-170 ˚C , $C_{43}H_{45}AsN_2Cl_2PdPt$ (1037.2) cacl: C 49.8, H 4.4, N 2.7; found C 50.1, H 3.9, N 2.8. ^{1}H NMR ($CDCl_3$, δ): 0.99 (d, J_{HH} = 6.9 Hz, 3H, CH*Me*), 1.44 (d, J_{HH} = 6.9 Hz, 3H, CH*Me*), 1.65 (d, J_{HH} = 6.9 Hz, 3H, CH*Me*), 1.84 (s, 3H, CH*Me*), 1.94 (s, 3H, CH*Me*), 2.06 (s, 3H, CH*Me*), 2.33 (d, J_{HH} = 6.9 Hz, 3H, CH*Me*), 2.68 (s, 3H, CH*Me*), 2.71 (s, 3H, CH*Me*), 2.75 (s, 3H, CH*Me*), 2.82 (s, 3H, CH*Me*), 2.90 (s, 3H, CH*Me*), 3.13 (s, 3H, CH*Me*), 3.26 (s, 3H, CH*Me*), 4.16 (q, 1H, C*H*Me), 4.30-4.35 (m, 2H, C*H*Me), 4.50 16 (q, 1H, C*H*Me), 6.75-8.47 (m, 45H, aromatics).

Synthesis of chloro {R-1-[1(dimethylamino)ethyl][-3-((Z)-2-(diphenylarsino)prop-1-enyl]phenyl-C^2,N]} platinum (II), (*Rc*)-71

Complex **(***Rc***)-50** (0.50g, 0.66 mmol) was dissolved in dichloromethane (100 mL) and followed by addition of diphenylphosphinoprop-1-yne (0.35g, 1.32 mmol). The resulting solution was stirred at room temperature for 2 h. Removal of solvent followed drying under vacuo gave (*Rc***)-70**. Complex (*Rc***)-70** (0.40g, 0.62 mmol) was dissolved in dichloromethane followed by addition of 0.5 equivalent mole of complex**(***Rc***)-50** (0.23g, 0.31 mmol). The reaction mixture was stirred at room

temperature for a week. The crude reaction mixture was purified over a silica gel column chromatography using hexane:acetone as eluent. Recrystallisation from hexane/acetone gave **(*Rc*)-71** bright yellow crystals : (0.26 g (61%), $[\alpha]_D$ -21 (c 0.3, CH_2Cl_2). mp 212-214 ˚C Anal.Calcd for $C_{25}H_{27}NAsPtCl$: C 46.4, H 4.2, N 2.2. Found C 46.0, H 4.0, N 2.6. ^{1}H NMR ($CDCl_3$, δ): 1.57 (d, 3H, J_{HH} = 6.4 Hz, CH*Me*, 1.94 (d, 1H, J_{HH} = 1.3 Hz, =C*Me*), 2.92 (s, 3H, N*Me*), 2.96 (s, 3H, N*Me*), 3.89 (qn, 1H, J_{HH} = 6.4 Hz C*H*Me), 6.87 (d, 1H, J_{HH} = 1.3 Hz, =C*H*), 7.02-7.73 (m, 13H, aromatics)

CHAPTER 3

Asymmetric Hydroarsination Reactions

3.1 Introduction

P-stereogenic diphosphines or P- and C-stereogenic centres together with transition metals are excellent auxiliaries for asymmetric hydrogenation, hydroformylation, hydrosilyation, and carbon-carbon bond formation reactions with high selectivities.[1] The hydrophosphination reaction involving asymmetric addition reaction between a P-H moiety of a phosphine and a C-C double bond of an unsaturated compound is a

straightforward protocol for the synthesis of chiral phosphines. In recent years, Leung *et.al.* has prepared various functionalised chiral diphosphines with high selectivities by means of asymmetric hydrophosphination[41] and Diel-Alders[40] reactions promoted by chiral cyclometallated-amine complexes.

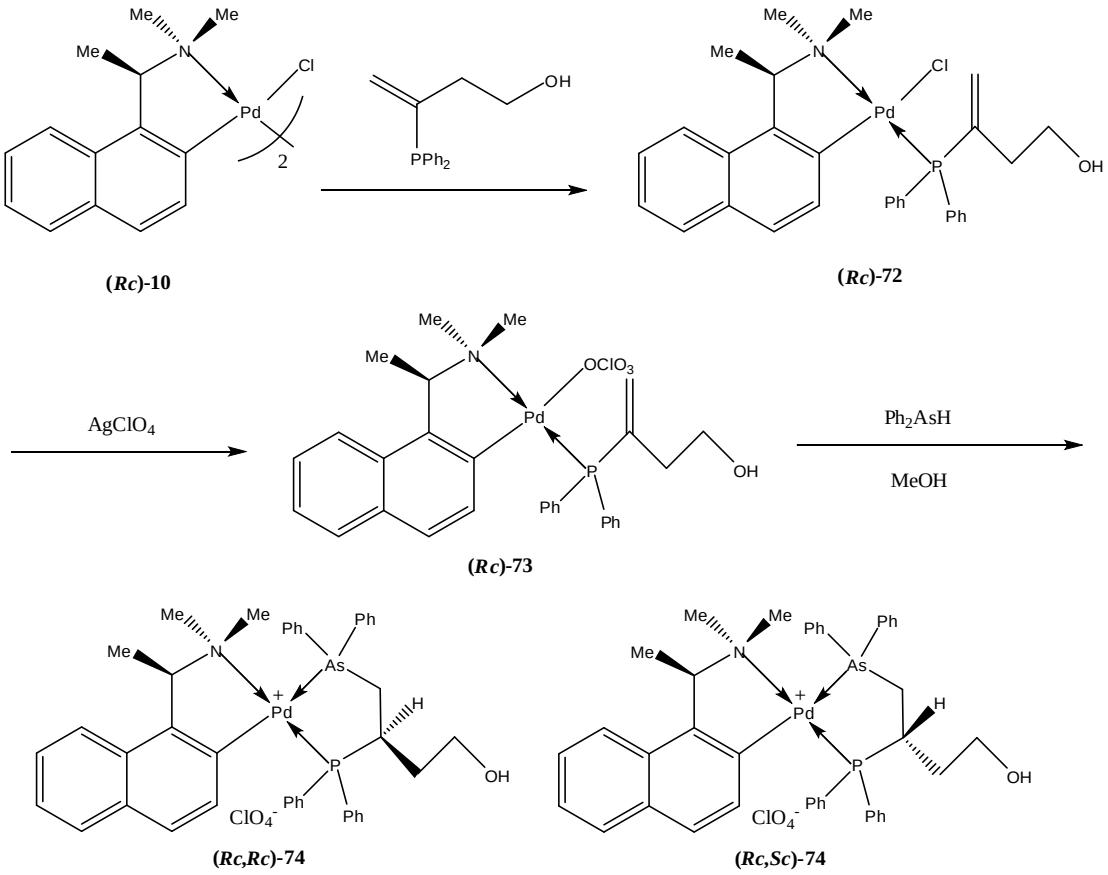
Like their organophosphine counterparts, organoarsenic compounds are found to be useful in various aspects of enantioselective catalysis. They have been found to be more effective than phosphines in catalysing a number of organic reactions.[28] However, available methods to prepare arsine ligands are limited and the number of reports on the addition of As-H moiety to a C-C double bond of an unsaturated compound is not vastly reported.[62] Applying chiral cyclometallated complexes as efficient chiral auxiliaries, Leung *et.al.* has recently published reports on the synthesis of an optically As-P heterobidentate ligand via Diels-Alder cycloaddition[40b-f] and asymmetric hydroarsination reaction.[35,43] To our knowledge, no other example of metal complex activated hydroarsination reactions involving diphenylarsine whereby a series of chiral bidentate As-P ligands bearing diphenylphosphino moiety with chirality residing on carbon backbone carrying various functional groups has been reported. In continuation of our exploration of chiral As-P chiral ligands, we herein report a facile protocol for the synthesis of As-P ligands promoted by chiral cyclometallated-amine complexes involving diphenylarsine and phoshine functionalised alkenes with hydroxy, methoxy, dimethylamino, ester and ketone as functional groups.

3.2 Results and Discussion

3.2.1 Asymmetric hydroarsination of 3-diphenylphosphino-but-3-en-1-ol

The monodentate 3-diphenylphosphino-but-3-en-1-ol was coordinated to the palladium complex (*Rc)*-**10** via a regiospecific bridge spiltting process (Scheme 3.1).[15] It is known that the chloro ligand in the template complex (*Rc*)-**72** is kinetically and thermodynamically stable and is not readily displaced by incoming monodentate arsine ligands.[63] Therefore to provide an empty coordination site for the incoming arsine ligand, complex (*Rc*)-**72** was treated with silver perchlorate.

The perchlorato complex (*Rc*)-**73** was then treated with diphenylarsine at -78°C and the reaction mixture was then left to stir for 24 h. The ^{31}P NMR spectrum showed a singlet at δ 77.6 indicating that only one diastereomer was generated out of the two possible diastereomers. Unlike the addition of the analogous secondary phosphine which resulted in cis-trans regioisomers of the products,[41] introduction of diphenylarsine in this reaction is regiospecific. The P atom occupies the coordination site trans to the N atom of the chiral auxilliary. Such high regioselectivity case has been previously observed for other P-As ligands.[33] The crude mixture was then purified by column chromatography and the product was obtained as a white solid in 55% isolated yield.



Scheme 3.1

3.2.1.1 X-ray crystal Diffraction Analysis of (*Rc*,*Rc*)-74

The single-crystal X-ray analysis of the crystallized pure product (*Rc*,*Rc*)-**74** showed that the expected five-membered P-As bidentate ligand has been formed (Figure 3.1). A new stereogenic centre at C(28) was generated which adopts the R absolute configuration while as expected the absolute configuration of the stereocentres at C(11) remained unchanged. The geometry at the Pd centre is distorted square planar with angles of 80.8(1) -100.2(1)° and 174.6(1) -178.6(1)°. The five-membered P-As chelate adopts the λ ring configuration with the CH_2CH_2OH substituent at C(28) occupying an equatorial position.[41a] The P and As donor atoms of the new heterobidentate are bonded regiospecifically to the metal centre with the softer P atom occupying the position trans to NMe_2 group. The larger N1-Pd1-As1 angle

[100.2(1)°] as compared with the smaller C1-Pd1-P1 angle [94.0(1)°] suggested a strong interchelate steric repulsion between NMe_2 and $AsPh_2$ groups.[35] Selected bond angles and bond lengths are given in Table 3.1

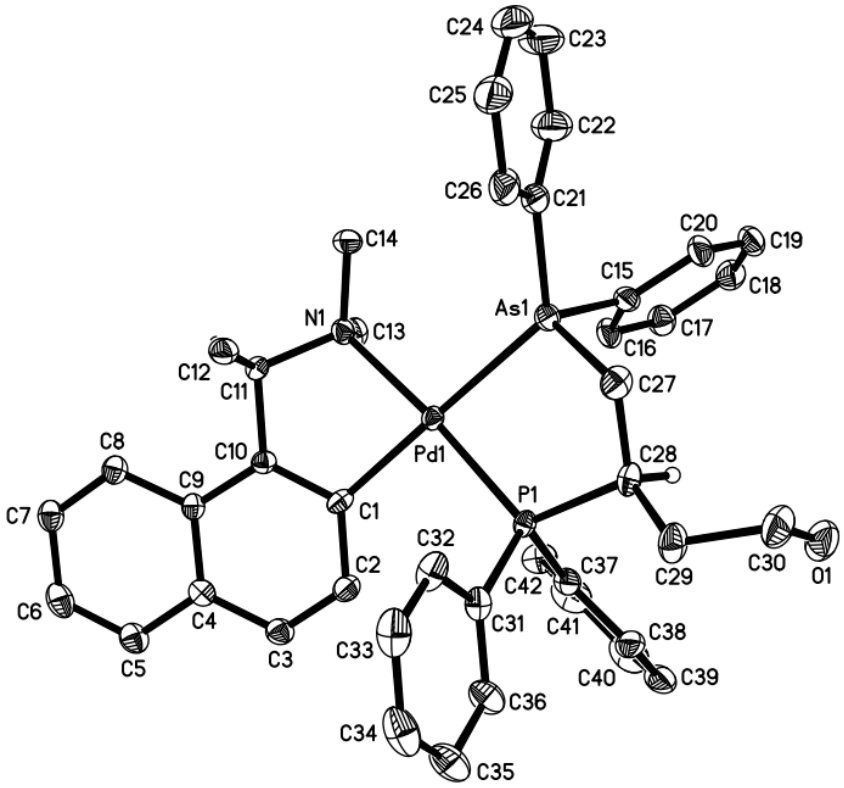


Figure 3.1 Molecular structure and absolute configuration of (*Rc*,*Rc*)-74

Table 3.1 Selected bond lengths (Å) and angles (°) for (*Rc*,*Rc*)-74

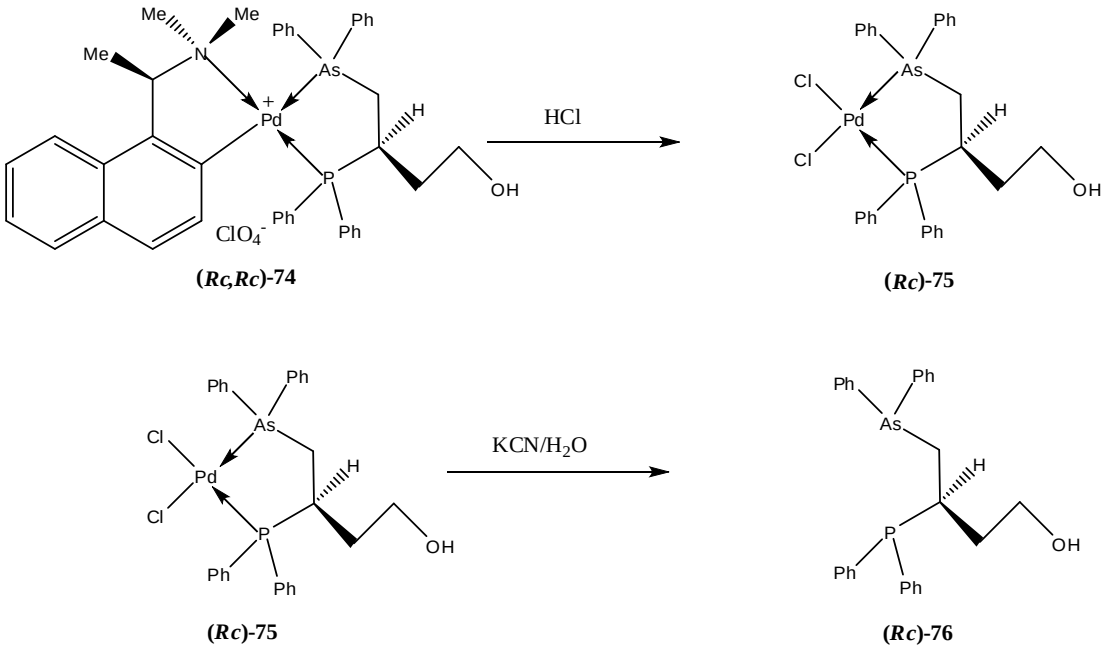
Pd(1)-C(1)	**2.043(3)**	**C(1)-Pd(1)-N(1)**	**80.8 (1)**
Pd(1)-N(1)	2.132(2)	C(1)-Pd(1)-P(1)	94.0(1)
Pd(1)-P(1)	2.261(1)	N(1)-Pd(1)-P(1)	174.6(1)

Pd(1)-As(1)	2.443(1)	C(1)-Pd(1)-As(1)	178.6(1)
As(1)-C(15)	1.922(3)	N(1)-Pd(1)-As(1)	100.2(1)
As(1)-C(21)	1.940(3)	P(1)-Pd(1)-As(1)	82.1(1)
As(1)-C(27)	1.947(3)	C(28)-P(1)-Pd(1)	112.4(1)
P(1)-C(28)	1.885 (3)	C(27)-As(1)-Pd(1)	102.4(1)
P(1)-C(31)	1.818(3)	C(29)-C(28)-C(27)	111.2(3)
P(1)-C(37)	1.821(3)	C(29)-C(28)-P(1)	113.4(2)
C(27)-C(28)	1.535(5)	C(28)-C(27)-As(1)	110.1(1)
C(28)-C(29)	1.532(4)	C(27)-C(28)-P(1)	111.7(2)

3.2.1.2. Liberation of the (C-chiral) P/As (*Rc*)-76

Treatment with strong acid is a standard method to remove the naphthylamine auxiliary. As shown in Scheme 3.2 the chiral naphthylamine in (*Rc*,*Rc*)-**74** can be removed chemoselectively from the palladium template by treatment with concentrated hydrochloric acid in dichloromethane. The resultant neutral dichloro complex (*Rc*)-**75** was obtained as yellow prisms in 83 % yield. The ^{31}P NMR spectum showed a singlet at δ 77.5.

The optically active P-As chiral bidentate (*Rc*)-**76** could be liberated from (*Rc*)-**75** $[\alpha]_D$ = -37.9 (c 0.5, CH_2Cl_2) by treatment of the dichloro complex with potassium cynanide at room temperature for ½ h. The liberated optically pure ligand (*Rc*)-**76** $[\alpha]_D$ = +62.3 (c 0.5, CH_2Cl_2) was obtained as white solid in 88% yield (Scheme 3.2). The ^{31}P NMR spectrum showed a singlet at δ -1.2 and the liberated ligand could be recoordinated back to the same metal template without loss of optical purity.



(*Rc*,*Rc*)-74 **(*Rc*)-75** **(*Rc*)-75** **(*Rc*)-76**

Scheme 3.2

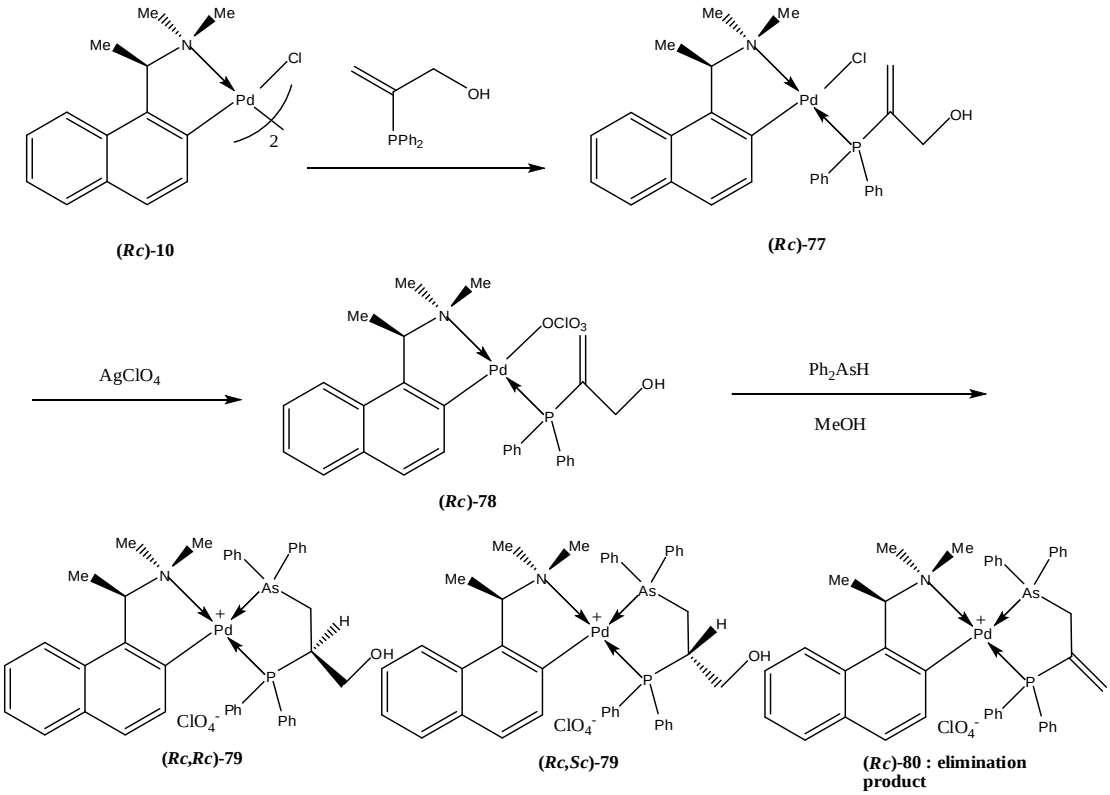
3.2.2 Asymmetric Hydroarsination of 2-diphenylphosphino-prop-2-en-1-ol

The 2-diphenylphosphino-prop-2-en-1-ol ligand which was obtained by hydrophosphination of propargyl alchohol [41a] was coordinated to the dimeric ortho-metalled palladium complex (*Rc*)-**10** as shown in Scheme 3.3. The chloro complex (*Rc*)-**77** was subsequently converted to the perchlorato complex by treatment with aqueous silver perchlorate. The perchlorato complex (*Rc*)-**78** was dissolved in methanol and reacted with diphenylarsine at -78°C. The ^{31}P NMR spectrum showed two singlets at δ 66.3 and 55.6 in the ratio of 2.6 to 1. After purification by silica gel chromatography the major product (*Rc,Rc*)-**79** was crystallised from acetonitrile-diethyl ether as air-stable white crystals.

3.2.2.1 X-ray crystal Diffraction Analysis of (*Rc*,*Rc*)-79

The single crystal X-ray diffraction analysis of the complex revealed that the expected five-membered P-As bidendate chelate has been formed (Figure 3.2). A new

stereogenic centre at C(28) was generated which adopts the R absolute configuration while the absolute configuration of the stereocentre at C(11) remained unchanged. The geometry at the palladium is distorted square planar with angles at palladium in the range 80.3(1) -103.0(1)° and 170.9(1) -174.6(1)°. Similar to diastereomeric complex (*Rc,Rc*)-**74** in the five-membered P-As bidentate chelate system the CH_2OH substituent at C(28) occupies an equatorial position.[41a,g]



Scheme 3.3

3.2.2.2 Liberation of the (C-chiral) P/As (*Rc*)-82

The treatment of complex (*Rc,Rc*)-**79** with concentrated hydrochloric acid generated (*Rc*) **-81** (Scheme 3.4). The dichloro complex was subsequently crystallized from dicholoromethane-dietyl-ether as yellow prisms in 88% yield, $[\alpha]_D$ = -120 (c 0.5, CH_2Cl_2). Further treatment of (*Rc*)-**81** with aqueous cyanide liberated the optically pure (*Rc*)-**82** in 79% yield, $[\alpha]_D$ = +30 (c 0.3, CH_2Cl_2) (Scheme 3.4). The

recoordination of the free ligand to the metal template employing the same protocol confirmed that (*Rc*)-**82** is optically pure.

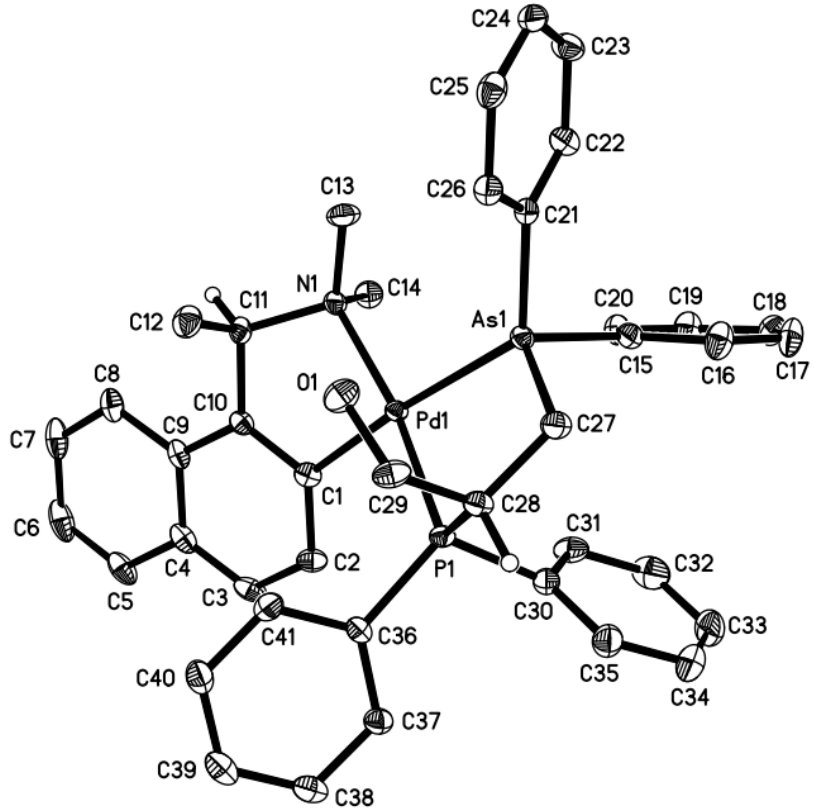
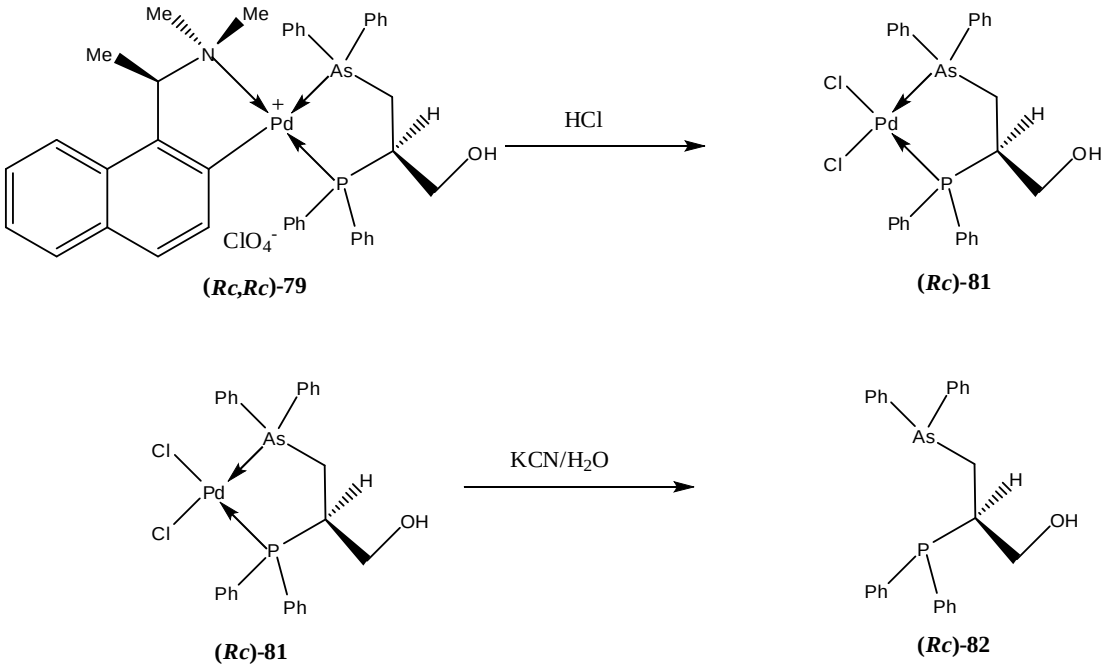


Figure 3.2 Molecular structure and absolute configuration of (*Rc*,*Rc*)-79

Table 3.2 Selected bond lengths (Å) and angles (˚) for (*Rc*,*Rc*)-79

Pd(1)-C(1)	**2.031(3)**	**C(1)-Pd(1)-N(1)**	**80.3 (1)**
Pd(1)-N(1)	2.138(2)	C(1)-Pd(1)-P(1)	94.9(1)
Pd(1)-P(1)	2.253(1)	N(1)-Pd(1)-P(1)	170.9(1)
Pd(1)-As(1)	2.463(1)	C(1)-Pd(1)-As(1)	174.6(1)

As(1)-C(15)	1.950(3)	N(1)-Pd(1)-As(1)	103.0(1)
As(1)-C(21)	1.954(3)	P(1)-Pd(1)-As(1)	82.4(1)
As(1)-C(27)	1.980(3)	C(28)-P(1)-Pd(1)	108.0(1)
P(1)-C(28)	1.863 (3)	C(27)-As(1)-Pd(1)	105.1(1)
P(1)-C(30)	1.815(3)	C(29)-C(28)-C(27)	113.2(2)
P(1)-C(36)	1.818(3)	C(29)-C(28)-P(1)	113.0(2)
C(27)-C(28)	1.541(4)	C(28)-C(27)-As(1)	111.2(1)
C(28)-C(29)	1.523(4)	C(27)-C(28)-P(1)	108.2(2)



(*Rc*,*Rc*)-79 **(*Rc*)-81** **(*Rc*)-81** **(*Rc*)-82**

Scheme 3.4

3.2.2.3 X-ray crystal Diffraction Analysis of (*Rc*)-80

The minor product isolated from silica gel chromatography was crystallised from dichloromethane-diethyl ether. The single-crystal X-ray diffraction revealed that it was (*Rc*)-**80** (Figure 3.3). The ^{31}P NMR spectrum showed a singlet at δ 55.6. The

single-crystal X-ray crystallographic analysis clearly established that the hydroxyl functional group has dissociated. The C28-C29 bond distance [1.35(1) Å] is consistent with a typical C-C double bond. A possible explanation to the presence of the elimination product could be found by analysing the structure of the coordination complex (*Rc*)-**77**. It was reported that upon coordination of the vinylic phosphine entity to the metal template, crystallographic data revealed that the oxygen atom of the –OH group was oriented in such a way that in was in close proximity to the Pd metal centre.[41a] This Pd-O interaction can activate the O-C bond which then underwent a cleavage assisted by the presence of uncoordinated diphenylarsine. From the previous analogous hydrophosphination reaction on 2-diphenylphosphinol-prop-2-en-1-ol ligand, the elimination product was not observed.[41a] This indicated the presence of uncoordinated diphenylphosphine couldn't assist the O-C cleavage.

Phosphines are softer than arsines and generally show higher affinity to bind to the platinum metal ions than arsines. The reason why loss of H_2O is not observed with phosphines is because in the intermediate, the exces phosphine will approach all possible coordination sites of the metal centre thus not allowing oxygen to be chelated to the metal. Hence, no C-O activation can occur. However for arsine which is a harder donor than phosphine, oxygen is allowed to bind to the metal centre and hence C-O activation can occur.

When the hydroarsination reaction was carried out on 3-diphenylphosphino-but-3-en-1-ol no elimination product was observed and only the expected hydroarsination product was present. This could be attributed to the longer chain length of CH_2CH_2OH moiety for 3-diphenylphosphanyl-but-3-en-1-ol which renders a weaker Pd-O interaction.

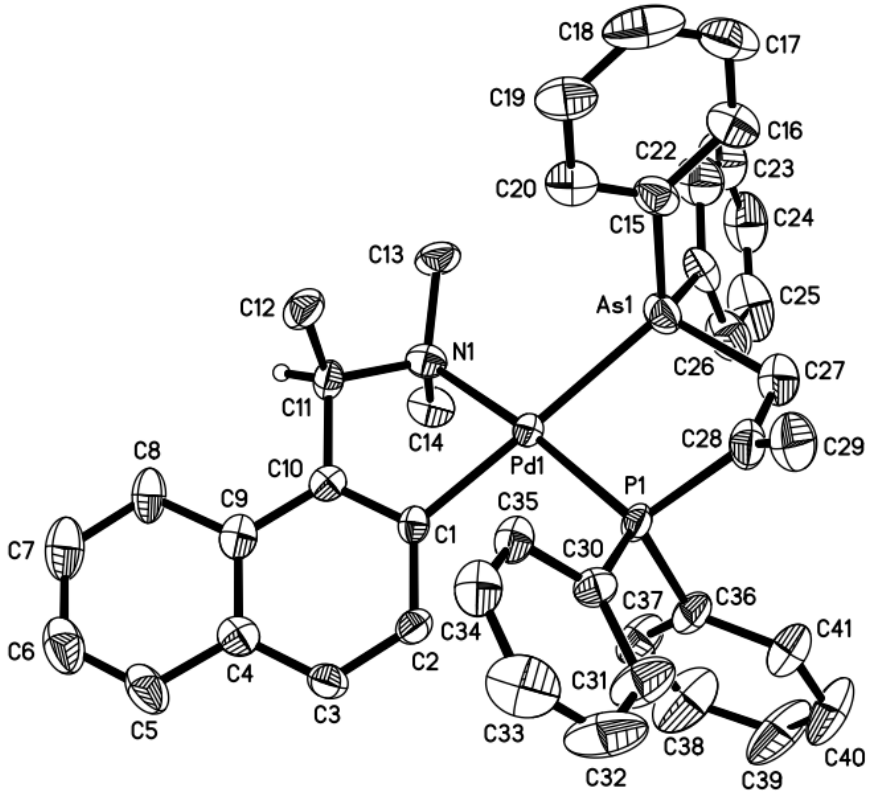


Figure 3.3 Molecular structure and absolute configuration of (*Rc*)-80

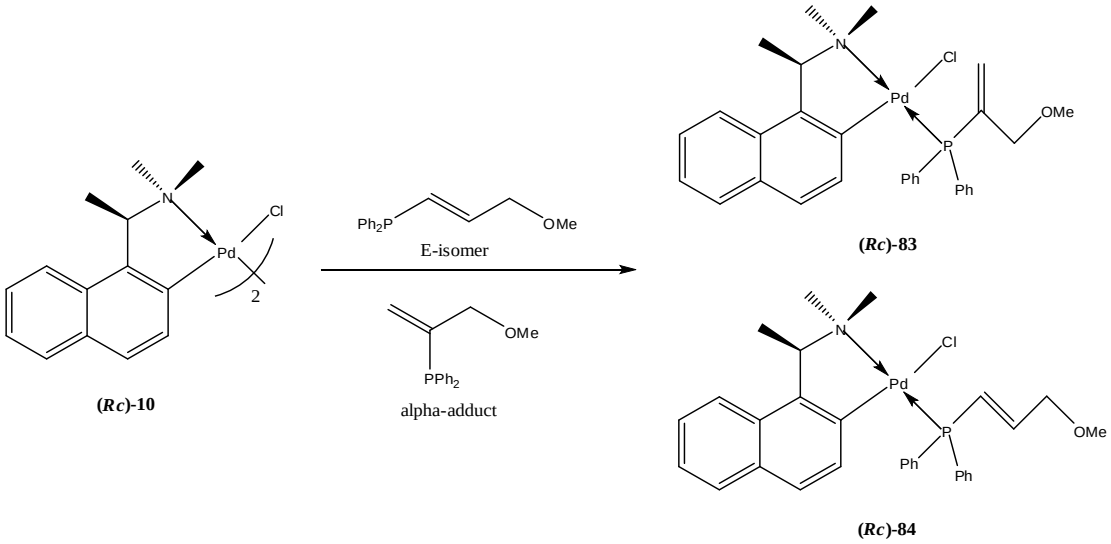
Table 3.3 Selected bond lengths (Å) and angles (°) for (*Rc*)-80

Pd(1)-C(1)	**2.046(6)**	**C(1)-Pd(1)-N(1)**	**80.3 (2)**
Pd(1)-N(1)	2.130(6)	C(1)-Pd(1)-P(1)	95.0(2)
Pd(1)-P(1)	2.247(1)	N(1)-Pd(1)-P(1)	174.3(2)
Pd(1)-As(1)	2.461(1)	C(1)-Pd(1)-As(1)	177.5(2)
As(1)-C(15)	1.940(8)	N(1)-Pd(1)-As(1)	99.9(1)
As(1)-C(21)	1.958(8)	P(1)-Pd(1)-As(1)	84.9(5)

As(1)-C(27)	1.940(8)	C(28)-P(1)-Pd(1)	109.5(3)
P(1)-C(28)	1.837 (8)	C(27)-As(1)-Pd(1)	104.6(2)
P(1)-C(30)	1.817(7)	C(29)-C(28)-C(27)	124.0(7)
P(1)-C(36)	1.825(7)	C(29)-C(28)-P(1)	122.8(6)
C(27)-C(28)	1.499(11)	C(28)-C(27)-As(1)	113.1(6)
C(28)-C(29)	1.347(12)	C(27)-C(28)-P(1)	104.6(2)

3.2.3 Asymmetric hydroarsination of 2-(diphenylphosphino) methyl prop-2-ene ether and 3-(*E*)- (diphenylphosphino) methyl prop-2-ene ether

The hydrophosphination reaction was first carried out between 3-methoxy-1-propyne and diphenylphosphine catalysed by $Ni(acac)_2$.[64] The ^{31}P NMR spectrum of the crude reaction product showed the presence of two singlets at δ – 7.0 and -13.3 in the ratio of 4:1 for the α-adduct and the *E*-isomers respectively. The structural assigment of the two isomeric products could be confirmed based on the spectroscopic data of other similar vinylic phosphines. The free phosphines ligands were not isolated and were allowed to coordinate to the palladium dimer (*Rc*)-**10** to generate the monomeric template complexes (*Rc*)-**83** and (*Rc*)-**84** (Scheme 3.5). However the two products cannot be separated efficiently by column chromatography. As in previous reactions, the terminal chloro ligand in (*Rc*)-**83** and (*Rc*)-**84** were replaced by a weakly coordinated perchlorato counterpart through treatment of these two complexes in dichloromethane with aqueous silver perchlorate.



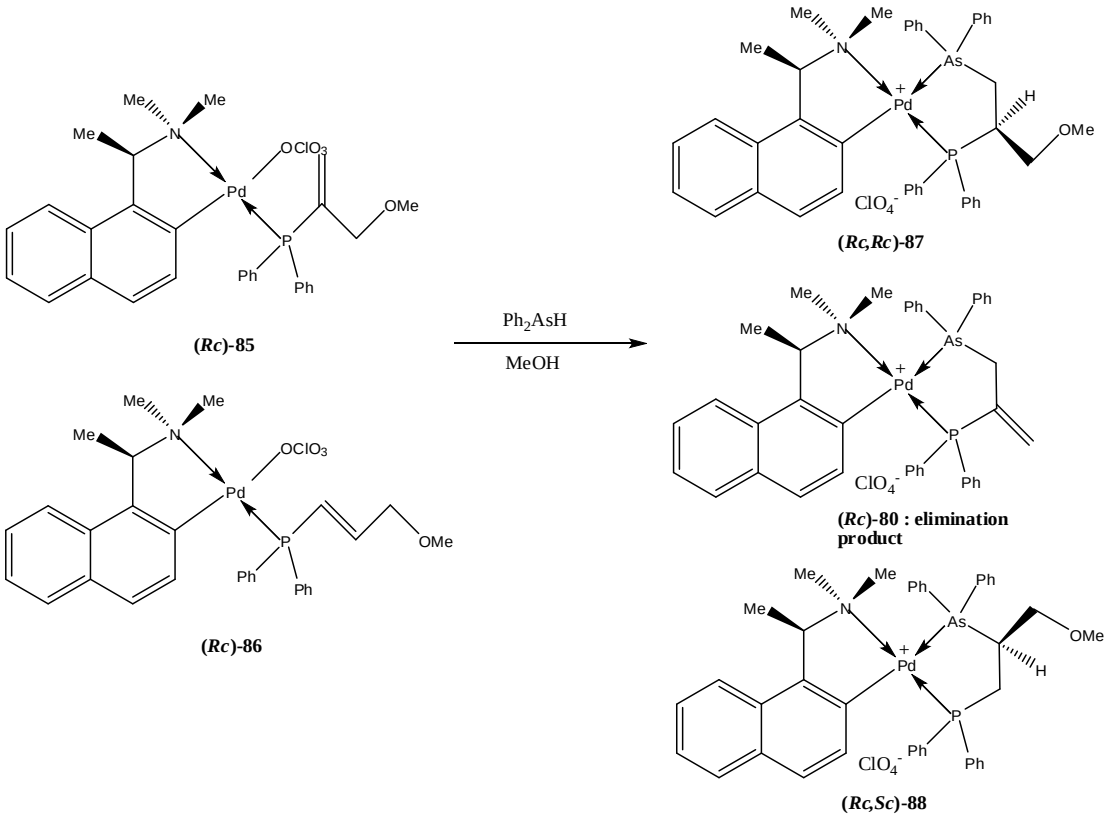
Scheme 3.5

The chemically reactive intermediate perchlorato complexes (*Rc*)-**85** and (*Rc*)-**86** were not isolated and were directly treated with 1 equivalent of diphenylarsine at -78°C (Scheme 3.6). The temperature was maintained at -78°C for 10 h and subsequently stirred at room temperature for 1 d. The ^{31}P NMR spectrum showed three singlets at δ 68.3, 55.6 and 53.1 with the intensity ratio 14.5:5:1 respectively. The major isomer (*Rc,Rc*)-**87** can be separated efficiently by column chromatography with dichloromethane/ diethyl ether as eluent.

3.2.3.1 X-ray crystal Diffraction Analysis of (*Rc,Rc*)-87

The single-crystal X-ray diffraction analysis of the isolated pure isomer of (*Rc,Rc*)-**87** verified that the expected five-membered P-As heterobidentate ligand was formed stereoselectively and regioselectively (Figure 3.4). The newly stereogenic centre at C(28) adopts the *R* absolute configuration. As shown in Figure 3.4, the phosphorus donor is coordinated regiospecifically to the metal centre in the position trans to σ-donating napthylamine-N atom, while the arsenic atom attaches to the position trans to the π-accepting aromatic carbon of the chiral auxiliary. The geometry at the Pd

centre is distorted square planar with angles of 80.0(4) -100.2(3) ° and 166.6(3) to 175.6(5) °. Selected bond lengths and angles are given in Table 3.4.



Scheme 3.6

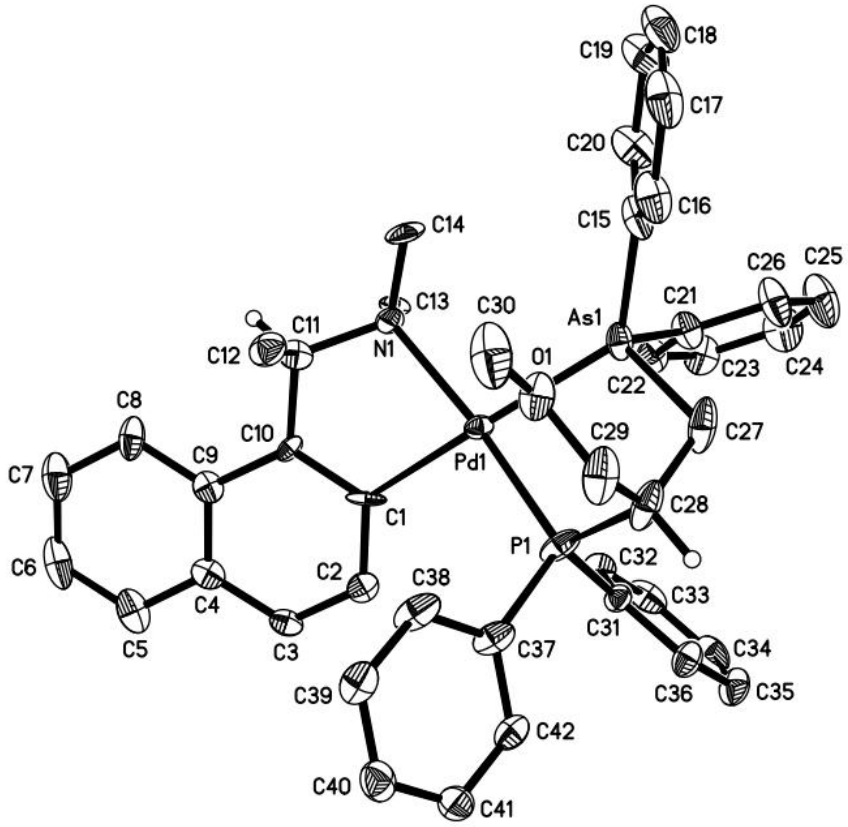


Figure 3.4 **Molecular structure and absolute configuration of (*Rc,Rc*)-87**

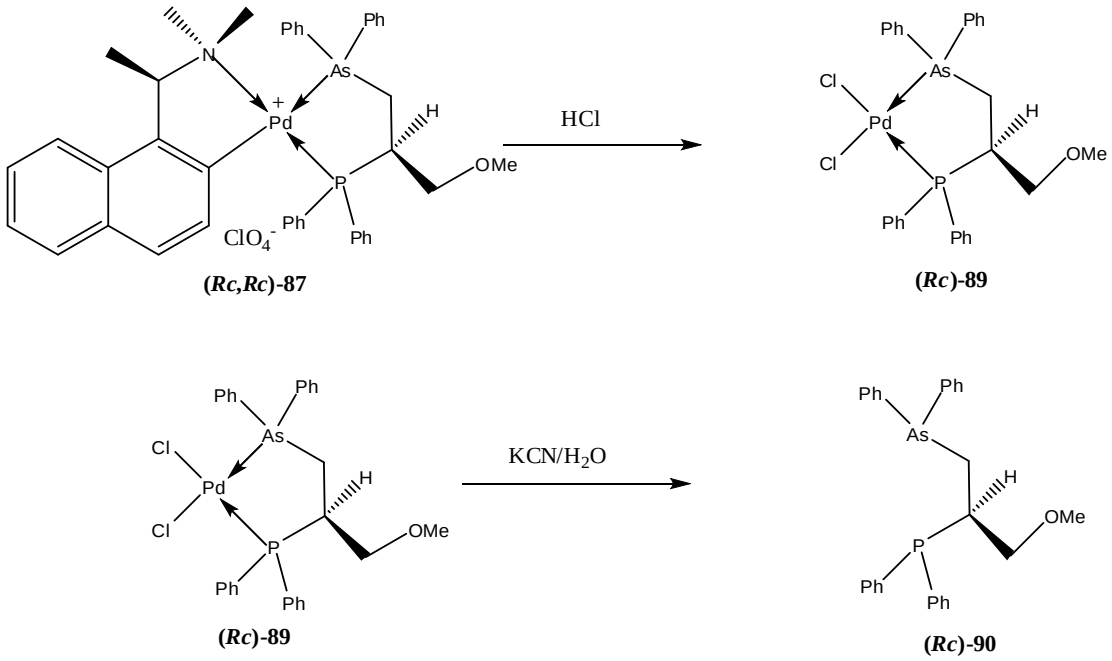
Table 3.4 **Selected bond lengths (Å) and angles (°) for (*Rc,Rc*)-87**

Pd(1)-C(1)	**2.079(8)**	**C(1)-Pd(1)-N(1)**	**80.0 (4)**
Pd(1)-N(1)	2.137(9)	C(1)-Pd(1)-P(1)	96.9(3)
Pd(1)-P(1)	2.242(1)	N(1)-Pd(1)-P(1)	169.3(4)
Pd(1)-As(1)	2.467(1)	C(1)-Pd(1)-As(1)	175.6(5)
As(1)-C(15)	1.948(3)	N(1)-Pd(1)-As(1)	100.2(3)
As(1)-C(21)	1.939(3)	P(1)-Pd(1)-As(1)	83.7(1)
As(1)-C(27)	1.974(3)	C(28)-P(1)-Pd(1)	108.5(1)
P(1)-C(28)	1.850 (4)	C(27)-As(1)-Pd(1)	104.5(1)

P(1)-C(31)	1.830(3)	C(27)-C(28)-C(29)	111.9(2)
P(1)-C(37)	1.815(3)	C(29)-C(28)-P(1)	113.0(2)
C(27)-C(28)	1.532(5)	C(28)-C(27)-As(1)	110.9(1)
C(28)-C(29)	1.533(4)	C(27)-C(28)-P(1)	109.0(2)

3.2.3.2 Liberation of the (C-chiral) P/As (*Rc*)-90

A solution of (*Rc*,*Rc*)-**87** in dichloromethane was then treated with concentrated hydrochloric acid to remove the napthylamine auxiliary chemoselectively to obtain the neutral dichloro complex (*Rc*)-**89**, $[\alpha]_D$ = -53.8 (c 0.1, CH_2Cl_2) (Scheme 3.7). The ^{31}P NMR spectrum of the isolated complex in $CDCl_3$ showed a singlet at δ 72.0. Treatment of (*Rc*)-**89** with aqueous potassium cyanide at room temperature for 30 min gave the optically pure ligand (*Rc*)-**90** as white solid in 89 % yield, $[\alpha]_D$ = -70.4 (c 0.3, CH_2Cl_2) (Scheme 3.7). The ^{31}P NMR spectrum showed a single at -7.6. The ^{31}P NMR spectrum of the recoordination product showed only one signal thus confirming that the liberated (*Rc*)-**90** is optically pure



(*Rc*,*Rc*)-87 **(*Rc*)-89**

(*Rc*)-89 **(*Rc*)-90**

Scheme 4.7

3.2.3.3 Identification of other minor products

From our previous reported hydroarsination reaction between diphenylarsine and 2-diphenylphosphino-prop-2-en-1-ol, an α-adduct which is quite similar to 2-(diphenylphosphino)methyl prop-2-ene ether we observed the presence of two products. As expected, we detected the P-As ligand (*Rc*)-**82** containing the hydroxy group at the chiral carbon centre. Other than that, an unexpected product was also observed where the hydroxyl functional group (*Rc*)-**80** had dissociated from the original alkenol phosphane and the vinlic double bond remained unreacted. The ^{31}P NMR spectrum of the substituted product showed a singlet at δ 55.6 which we also observed in the current hydroarsination reaction. From this observation we can affirm that when hydroarsintion reaction was carried out on (*Rc*)-**85**, apart from the expected formation of P-As ligands (*Rc*,*Rc*)-**87**, we also observe the formation of the unexpected elimination product (*Rc*)-**80**. Similarly, O-C activation can also happen to

the methoxy group which will then dissociate assisted by uncoordinated diphenylarsine.

The yield of the minor isomer that was formed in this hydroarsination reaction is relatively small and thus could not be isolated and crystallised effectively. However the structural assigment of the minor isomer could be confirmed based on the spectroscopic data of other analogous P-As ligand (*Rc*,*Sc*)-**98** with ^{31}P signal at δ 52.2. Thus the ^{31}P signal at δ 53.1 could be identified as (*Rc*,*Sc*)-**88**. The ^{1}H NMR spectrum of (*Rc*,*Sc*)-**88** is quite analogous to ^{1}H NMR spectrum of (*Rc*,*Sc*)-**98.**

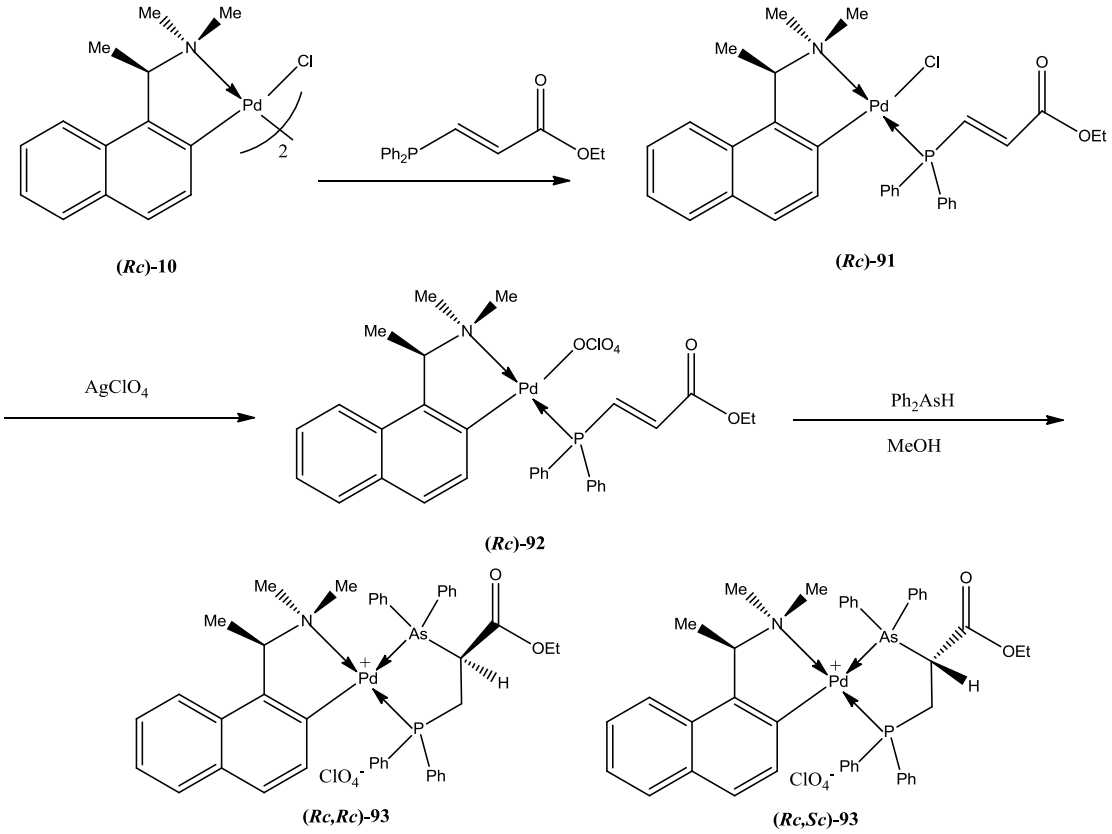
3.2.4 Asymmetric hydroarsination of 3-(diphenylphosphino)-(*E*)- ethyl prop-3-enoate

The 3-(diphenylphosphino)-(*E*)- ethyl prop-3-enoate ligand was allowed to coordinate to the palladium complex (*Rc*)-**10** in dichloromethane yielding the neutral complex monomeric complex (*Rc*)-**91** (Scheme 3.8). The inactive chloro ligand was subsequently removed by treatment with excess aqueous silver perchlorate.

The perchlorato complex (*Rc*)-**92** was not isolated and was then redissolved in methanol and reacted with one equivalent of diphenylarsine at -78°C to give the hydroarsination product as shown in Scheme 3.8. The reaction was monitored by ^{31}P NMR spectrum and was found to complete within 16 h. In $CDCl_3$, the ^{31}P NMR spectrum of the crude reaction mixture showed two singlets at δ 50.1 and 49.8 with the intensity ratio of 1: 8.2 respectively. The signals indicated the possible isomeric products (*Rc*,*Rc*)-**93** and (*Rc*,*Sc*)-**93** were generated during the hydroarsination reactions.

3.2.4.1 X-ray Crystal Diffraction Analysis of (*Rc,Rc*)-93

The major product (*Rc,Rc*)-**93** could be isolated efficiently by column choromatography in 67 % yield. The ^{31}P NMR spectrum ($CDCl_3$, 121 MHz) exhibited a singlet at δ 49.8 and its molecular structural and the absolute stereochemistry of the pure isomer were determined by X-ray crystallography (Figure 3.5). Selected bond lengths and angles of the complex are given in Table 3.5. The structural analysis established that the newly formed sterogenic centre at C(27) adopted the *R* absolute configuration while as expected the absolute configuration of the chiral carbon at C(11) remained unchanged. The X-ray analysis data also showed that this hydroarsination is very regioselective as the diphenylarsenido moiety was added preferentially to the β-carbon of the vinylphosphines to form the five-membered ring.



Scheme 3.8

The geometry at the Pd centre is distorted square planar with angles of 81.0(1)-98.7(1) ° and 175.4(1)-179.6(1) °. The P and As donor atoms of the heterobidentate ligand are also bonded regiospecifically to the metal centre with the softer P atom occupying the position trans to NMe_2 group. This was reflected by the Pd-P(1) and the Pd-As(1) bond distances which are 2.250(1) and 2.449(1) Å respectively with the bond trans to the carbon of the napthylamine ring being longer by 0.199 Å. This suggests that P and As have a very different donor abilities. In the five-membered heterobidentate metal chelate, the ester substituent at the chiral carbon centre C(27) is in the preferred equatorial position which is in agreement with our previous studies.

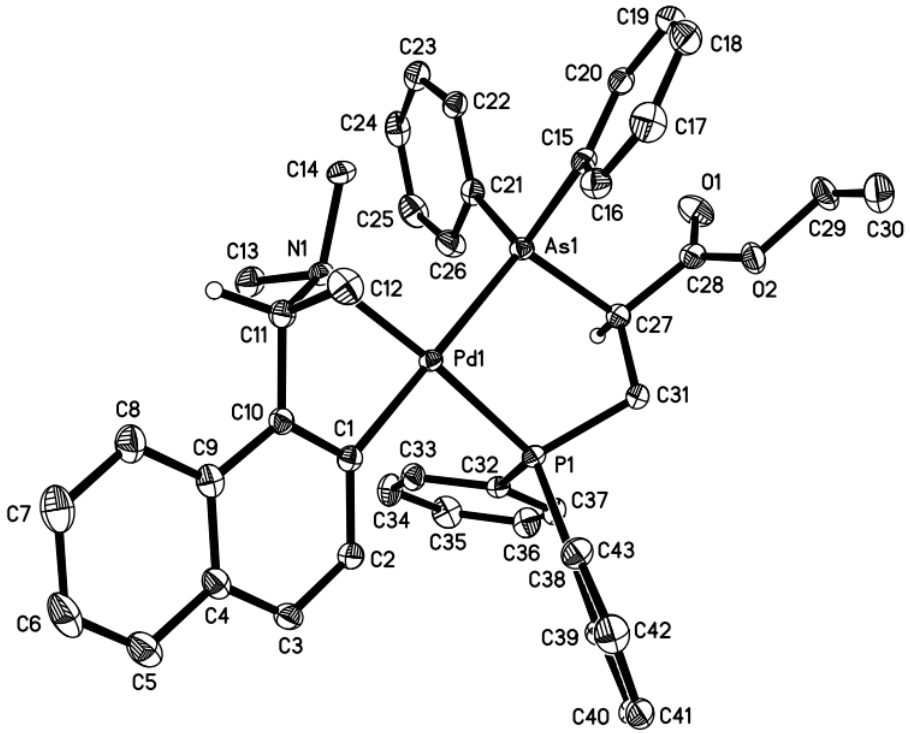


Figure 3.5 Molecular structure and absolute configuration of (*Rc,Rc*)-93

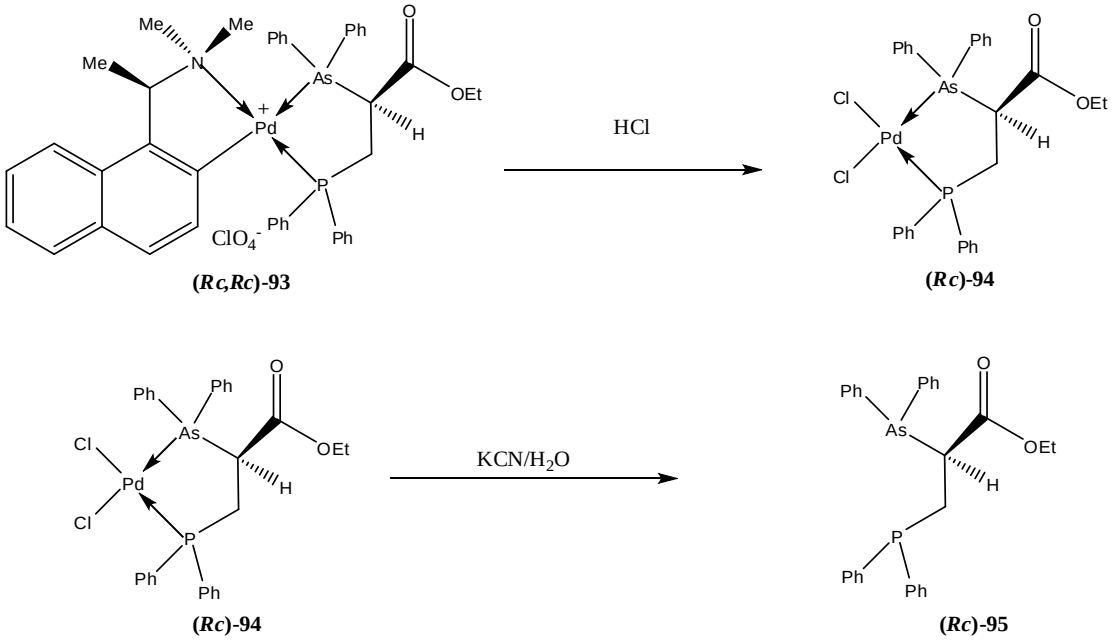
Table 3.5 Selected bond lengths (Å) and angles (°) for (*Rc,Rc*)-93

Pd(1)-C(1)	**2.040(1)**	**C(1)-Pd(1)-N(1)**	**81.0 (1)**
Pd(1)-N(1)	2.132(1)	C(1)-Pd(1)-P(1)	95.7(1)
Pd(1)-P(1)	2.250(1)	N(1)-Pd(1)-P(1)	175.4(1)
Pd(1)-As(1)	2.449(1)	C(1)-Pd(1)-As(1)	179.6(1)
As(1)-C(15)	1.935(1)	N(1)-Pd(1)-As(1)	98.7(1)
As(1)-C(21)	1.938(1)	P(1)-Pd(1)-As(1)	84.6(1)
As(1)-C(27)	1.997(1)	C(31)-P(1)-Pd(1)	109.4(1)
P(1)-C(31)	1.841 (1)	C(27)-As(1)-Pd(1)	105.0(1)
P(1)-C(32)	1.812(1)	C(28)-C(27)-C(31)	116.1(1)
P(1)-C(38)	1.814(1)	O(2)-C(29)- C(30)	106.0(1)
C(27)-C(28)	1.509(2)	C(31)-C(27)-As(1)	107.6(1)
C(28)-C(29)	1.523(2)	C(27)-C(31)-P(1)	110.5(1)

3.2.4.2 Liberation of the (C-chiral) P/As (*Rc*)-95

Removal of the napthylamine auxiliary by treatment with strong acid is a standard method that the leads to the formation of neutral dichloro palladium (II) complex (Scheme 3.9). The neutral dichloro complex (*Rc*)-**94** was obtained efficiently as yellow crystals in 83 % yield, $[\alpha]_D$ = +16.7 (c 0.3, CH_2Cl_2). The ^{31}P NMR spectrum of the dichloro complex (*Rc*)-5 in $CDCl_3$ showed a singlet at δ 55.4. Further treatment of complex (*Rc*)-**94** with aqueous potassium cyanide liberate the optically liberated the optically pure P-As ligand (*Rc*)-**95** as white solid in 81 % yield, $[\alpha]_D$ = -14.8 (c

0.3, CH_2Cl_2) (Scheme 3.9). The ^{31}P NMR spectrum of the liberated ligand in $CDCl_3$ exhibited a singlet at δ -17.1. In order to confirm the optical purity of the free ligand, the liberated optically pure ligand (*Rc*)-**95** was recoordinated to palladium template. The recoordination was monitored by ^{31}P NMR spectroscopy. In $CDCl_3$, the ^{31}P NMR spectrum of the crude recoordination product showed only one singlet at δ 49.8 thus confirming that the liberated (*Rc*)-**95** is optically pure.



(*Rc,Rc*)-93 **(*Rc*)-94** **(*Rc*)-94** **(*Rc*)-95**

Scheme 3.9

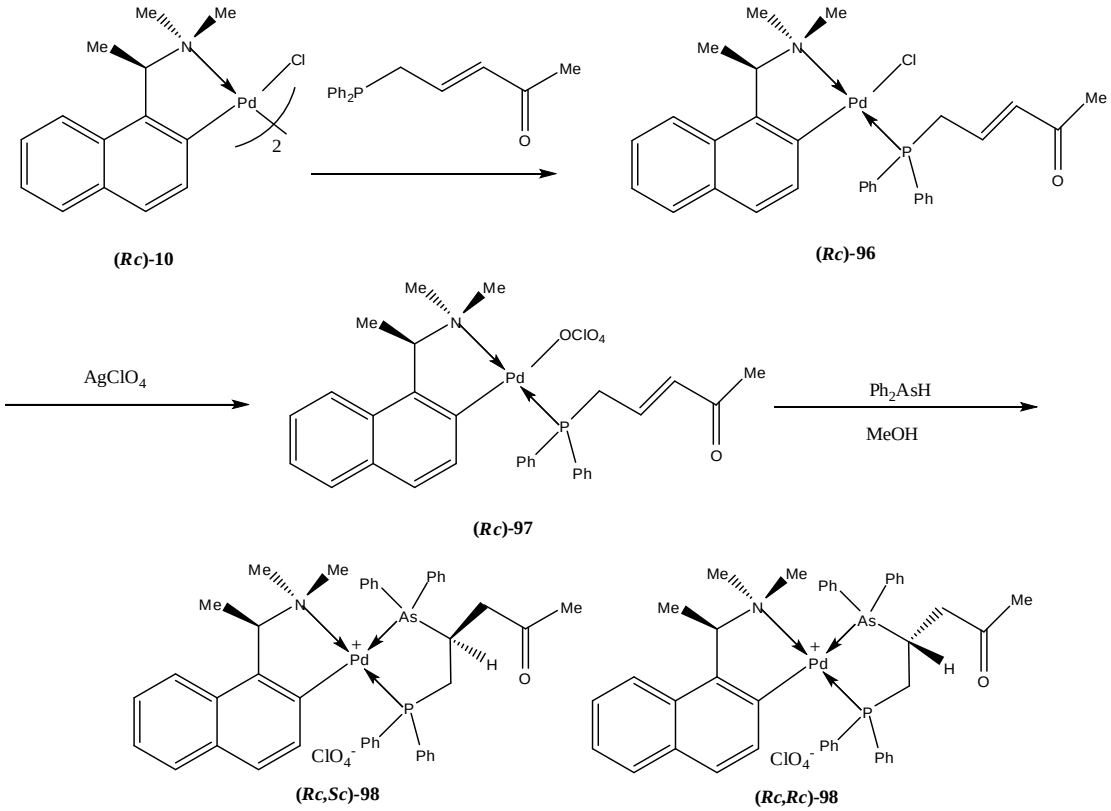
3.2.5 Asymmetric hydroarsination of 5-(diphenylphosphino) -(*E*)- pent-3-en-2-one

The analogous keto precursor complex containing 5-(diphenylphosphino)pent-3-en-2-one (*Rc*)-**96** was converted to the reactive perchlorato species by similar treatment with aqueous silver perchlorate. The intermediate was not isolated and was subsequently treated with 1 equivalent of diphenylarsine at -78°C to give two

possible diastereomeric products (*Rc*,*Sc*)-**98** and (*Rc*,*Rc*)-**98**. The temperature was kept at -78°C for 10 h and the reaction was found to complete in 5 d. Prior to purification, the ^{31}P NMR spectrum of the crude reaction mixture indicated two singlets at δ 52.2 and δ 51.2, with a diastereoselectivity of 6:1. After purification by silica gel column chromatography (dichloromethane/ethyl acetate), only the major product (*Rc*,*Sc*)-**98** was obtained. Complex (*Rc*,*Sc*)-**98** was crystallised from dichloromethane- hexane as yellow crystals in 35 % yield (Scheme 3.10). The ^{31}P NMR spectrum of the crystals exhibited a singlet at δ 52.1.

3.2.5.1 X-ray crystal Diffraction Analysis of (*Rc*,*Sc*)-98

The single-crystal X-ray diffraction of the complex (*Rc*,*Sc*)-**98** revealed that the expected five-membered P-As ligand had been formed (Figure 3.6). A new stereogenic centre were generated at C(27) which adopts the *S* absolute configuration while the absolute configuration of the stereocentre at C(12) remained unchanged. The keto functionality occupies the sterically favourably equatorial postion with is in agreement with our previous studies.



Scheme 3.10

The X-ray analysis also indicated that this hydroarsination reaction is highly regioselective as the diphenylarsino group was added to the β-carbon of the vinylphosphanes to form a five-membered chelate ring. However due to poor crystal quality, the bonds and angle parameters were not obtained.

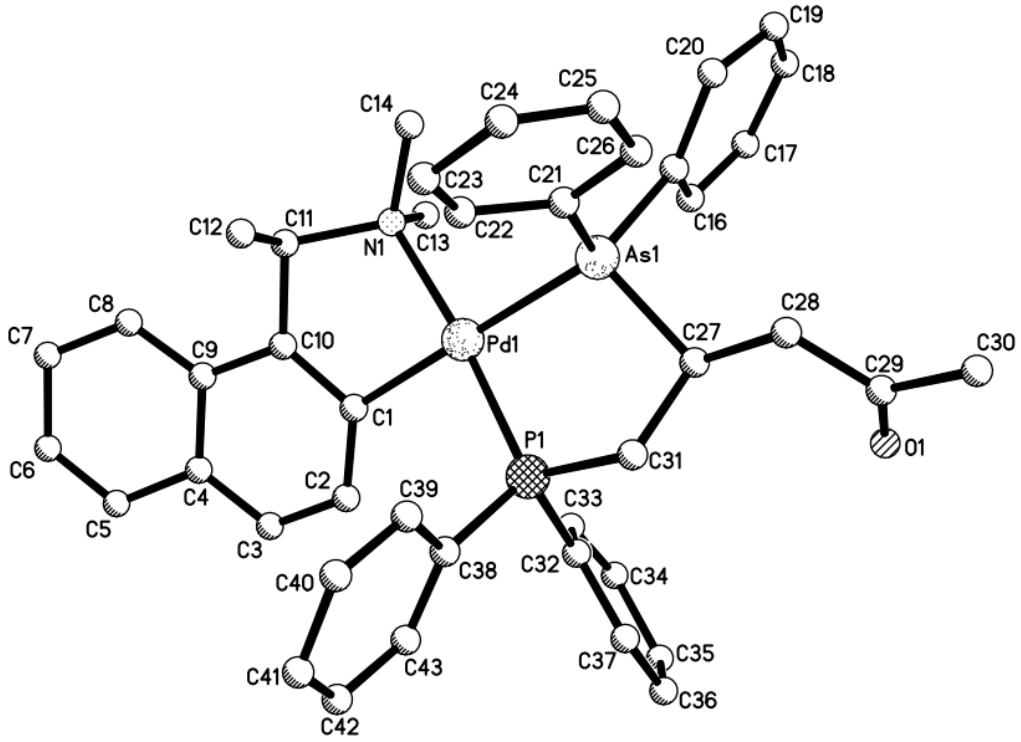


Figure 3.6 Molecular structure and absolute configuration of (*Rc,Sc*)-98

3.2.5.2 Liberation of the (C-chiral) P/As (*Sc*)-100

Upon subsequent treatment of complex (*Rc,Sc*)-**98** with concentrated hydrochloric acid (Scheme 3.11), the resultant neutral dichloro complex (*Sc*)-**99** was obtained as yellow crystals in 86 % yield, $[\alpha]_D$ = +42.9 (c 0.5, CH_2Cl_2). The ^{31}P NMR spectrum showed a singlet at δ 58.0. The chelating properties of the P-As ligand in complex (*Sc*)-**99** were studied by X-ray crystallography (Figure 3.7). Selected bond lengths and angles of the complex are given in Table 3.6. The structure analysis clearly confirmed that the newly formed stereogenic centre at C(13) adopted the *S* absolute configuration. The geometry at the metal centre is distorted square planar with angles of 86.9(1) -87.8(1) and 173.6(1)- 177.2(1) °. The C(13)-C(17) [1.535(6) Å] is consistent with a typical C-C single bond.

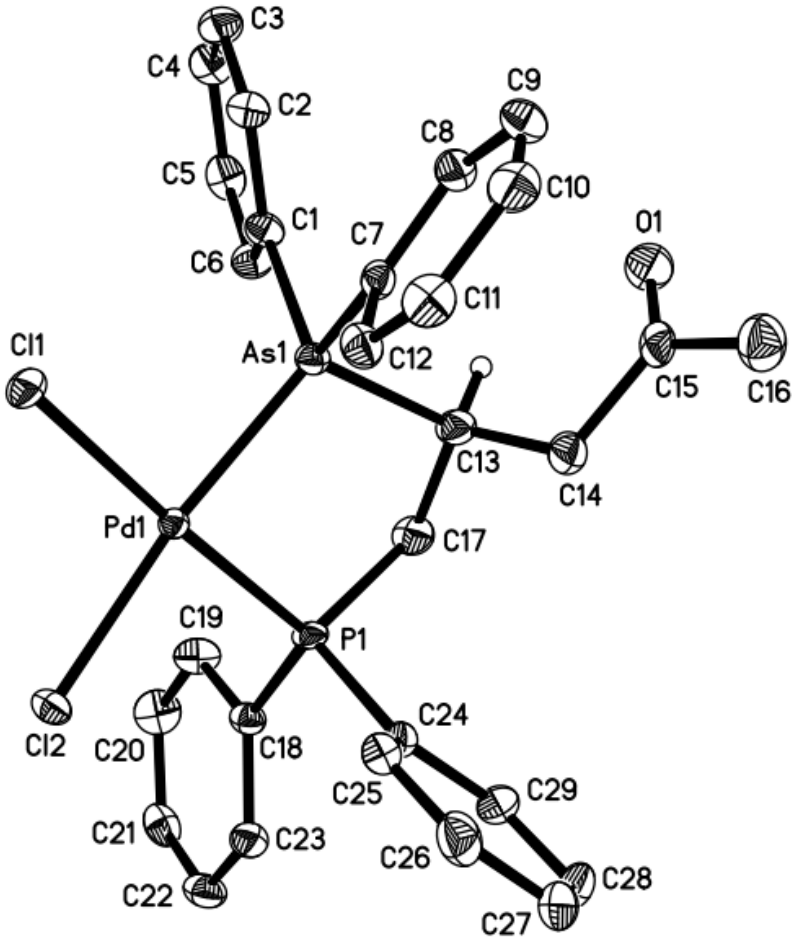


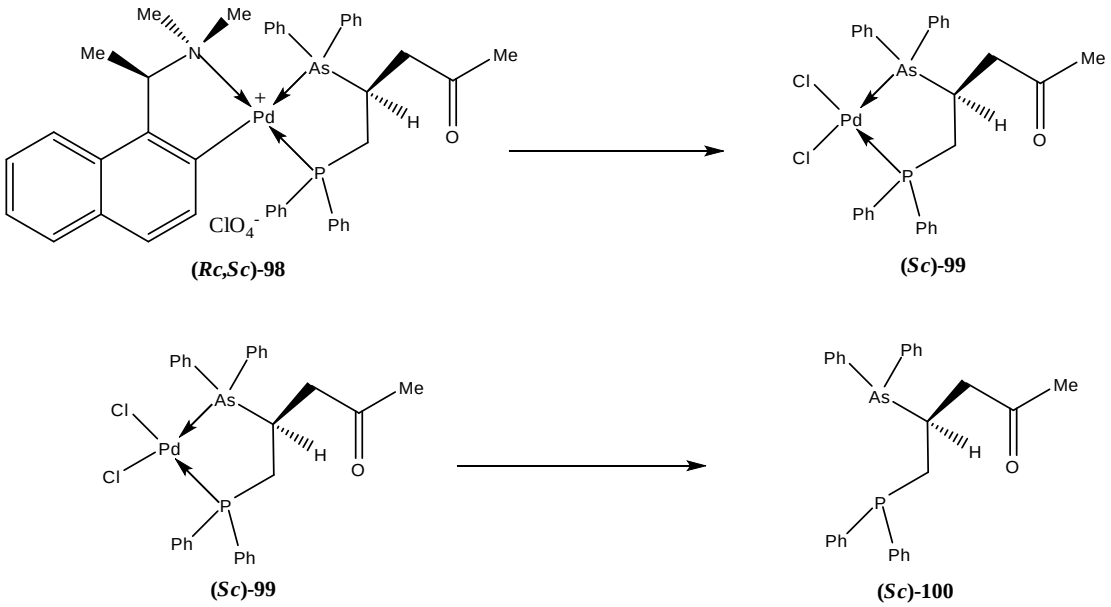
Figure 3.7 Molecular structure and absolute configuration of (*Sc*)-99

Table 3.6 Selected bond lengths (Å) and angles (°) for (*Sc*)-99

Pd(1)-Cl(1)	**2.358(1)**	**Cl(1)-Pd(1)-Cl(2)**	**95.0 (1)**
Pd(1)-Cl(2)	2.353(1)	Cl(2)-Pd(1)-P(1)	87.8(4)
Pd(1)-P(1)	2.228(1)	Cl(1)-Pd(1)-P(1)	177.2(1)

Pd(1)-As(1)	2. 345(1)	Cl(2)-Pd(1)-As(1)	173.6(1)
As(1)-C(7)	1.925(4)	Cl(1)-Pd(1)-As(1)	90.3(3)
As(1)-C(1)	1.934(4)	P(1)-Pd(1)-As(1)	86.9(1)
As(1)-C(13)	1.986(4)	C(17)-P(1)-Pd(1)	109.6(1)
P(1)-C(17)	1.851 (5)	C(13)-As(1)-Pd(1)	107.0(1)
P(1)-C(18)	1.822(4)	C(14)-C(13)-C(17)	113.8(4)
P(1)-C(37)	1.810(4)	C(13)-C(17)-P(1)	112.8(3)
C(13)-C(14)	1.546(6)	C(17)-C(13)-As(1)	107.6(3)
C(28)-C(29)	1.535(6)	C(14)-C(13)-As(1)	112.6(3)

Further treatment of (*Sc*)-**99** with aqueous potassium cyanide liberated the optically pure P-As ligand (*Sc*)-**100** as a white solid in 87 % yield, $[\alpha]_D$ = +16.7 (c 0.3, CH_2Cl_2) (Scheme 3.11). The ^{31}P NMR spectrum showed a singlet at δ -21.2. The optical purity of the chiral heterobidentate ligand (*Sc*)-**100** was confirmed by recoordination of the ligand to the same metal template. The recomplexation product gave a singlet at δ 52.1 which was identical to that originally recorded for complexes (*Rc*,*Sc*)-**98**.

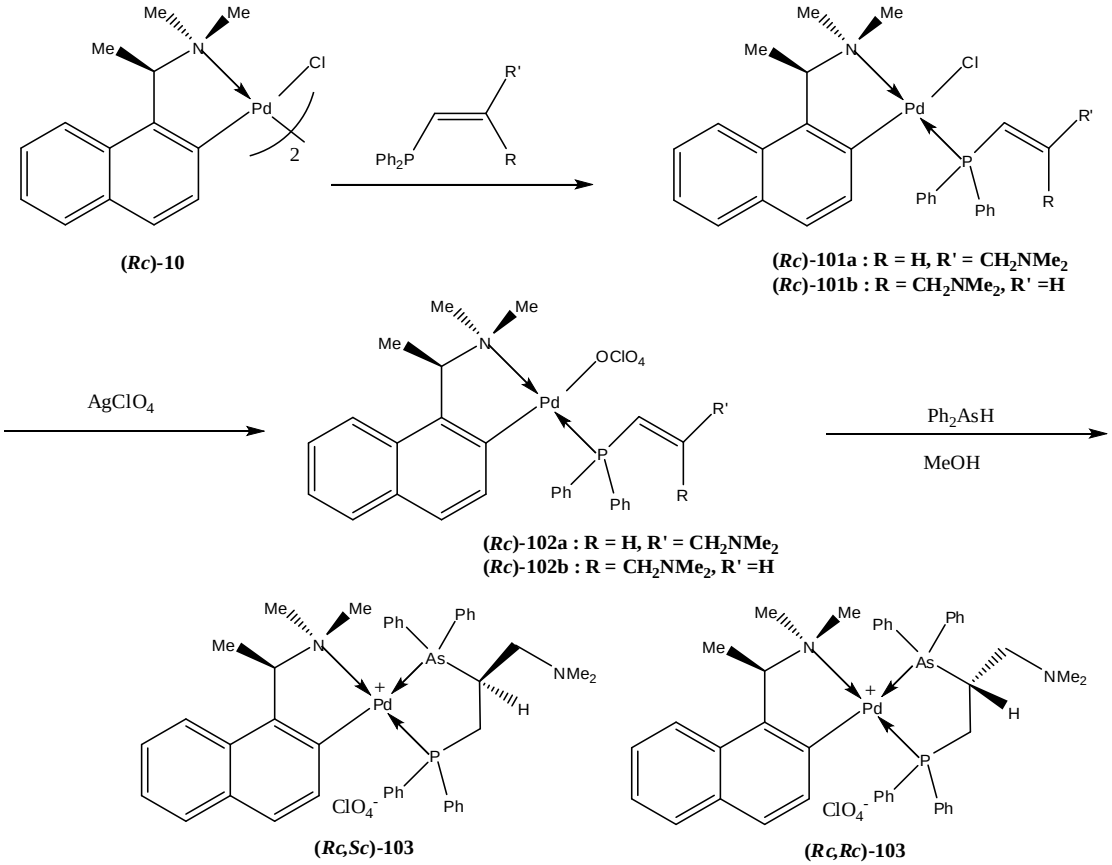


Scheme 3.11

3.2.6 Asymmetric Hydroarsination of (*E*)- and (*Z*)-3-diphenylphosphino N,N-dimethyl-2-propenylamine

(*E*)- and (*Z*)-3-diphenylphosphino N,N-dimethyl-2-propenylamine were obtained by hydrophosphination of N,N-dimethyl-2-propynylamine catalysed by AIBN in the ratio of 9:1.[65] The free vinyl phosphine ligands were not isolated and were allowed to coordinate to the palladium dimer (*Rc*)-**10** to generate the monomeric template complexes (*Rc*)-**101a** and (*Rc*)-**101b**. The ^{31}P NMR spectrum in $CDCl_3$ showed one single peak at δ 29.7 and 16.2 respectively for each coordination product. The isomers (*Rc*)-**101a** and (*Rc*)-**101b** could be separated efficiently in appreciable yield from column chromatography with dichloromethane and methanol as eluent. Complexes (*Rc*)-**101a** and (*Rc*)-**101b** were used for hydroarsination separately. Treatment of the chloro complex with aqueous silver perchlorate yielded the cationic perchlorato intermediate (*Rc*)-**100a** and (*Rc*)-**100b** in quantitative yield. These highly reactive species were not isolated and were subsequently reacted with one equivalent of

diphenylarsine at −78 ºC to yield the desired hyrdroarsination product (Scheme 3.12). The reaction was monitored by ^{31}P NMR spectroscopy and was found to be complete within 14 h. Prior to purification, ^{31}P NMR spectrum of the crude product in $CDCl_3$ showed one singlet at δ 51.5 which indicated the formation of one diastereomer out of the two possible diastereomers (*Rc,Rc*)-**103** and (*Rc,Sc*)-**103.** The hydroarsination reaction proceeded with high regiospecificity too. From our previous studies on similar types of ligands, the P atom always occupies the coordination site trans to the N of the chiral auxiliary while the As atom occupies the coordination site trans to the C of the chiral auxiliary. Other than that, the diphenyarsino groups were added to the the β-carbon of the (*E*)- and (*Z*)- 3-diphenylphino N,N-dimethyl-2-propenylamine to form five-membered chelate rings exclusively.



Scheme 3.12

3.2.6.1 X-ray crystal Diffraction Analysis of (*Rc,Rc*)-103

The molecular structure and the absolute stereochemistry of the sole product (*Rc*,*Rc*)-**103** were determined by single-crystal X-ray diffraction analysis (Figure 3.8). Selected bond lengths and angles are listed in Table 3.7. The coordination geometry around Pd atom is the expected distorted square planar. The angles around the palladium centre are in the ranges of 81.1(1) – 97.8(1) and 173.7(1) – 176.1(1)°. The Pd(1) – As(1) bond distance [2.460(1) Å] is significantly longer than Pd(1) P(1) [2.244(1) Å]. The C(27)-C(31) [1.527(4) Å] is consistent with a typical C-C single bond. A new chiral centre was generated at C(27) which adopts the *R* absolute configuration while as expected the absolute configuration of the stereocentre at C(11) remained unchanged. In the five-membered metal chelate, the amino group occupies a sterically favorable equatorial position in agreement with our previous studies.

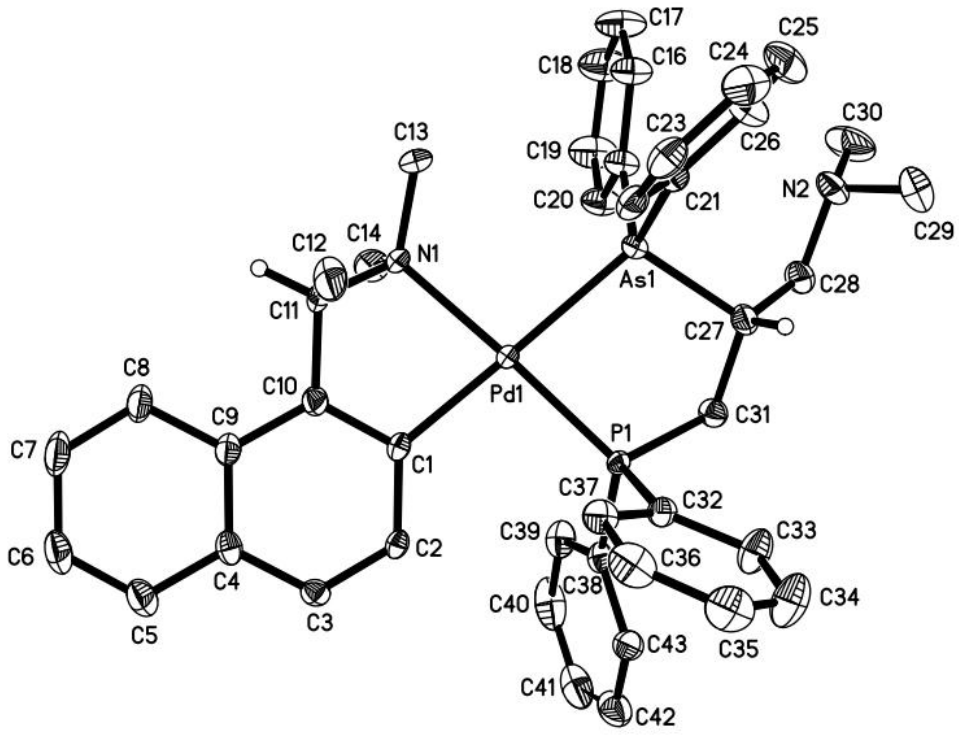


Figure 3.8 Molecular structure and absolute configuration of (*Rc,Rc*)-103

Table 3.7 Selected bond lengths (Å) and angles (°) for (*Rc,Rc*)-103

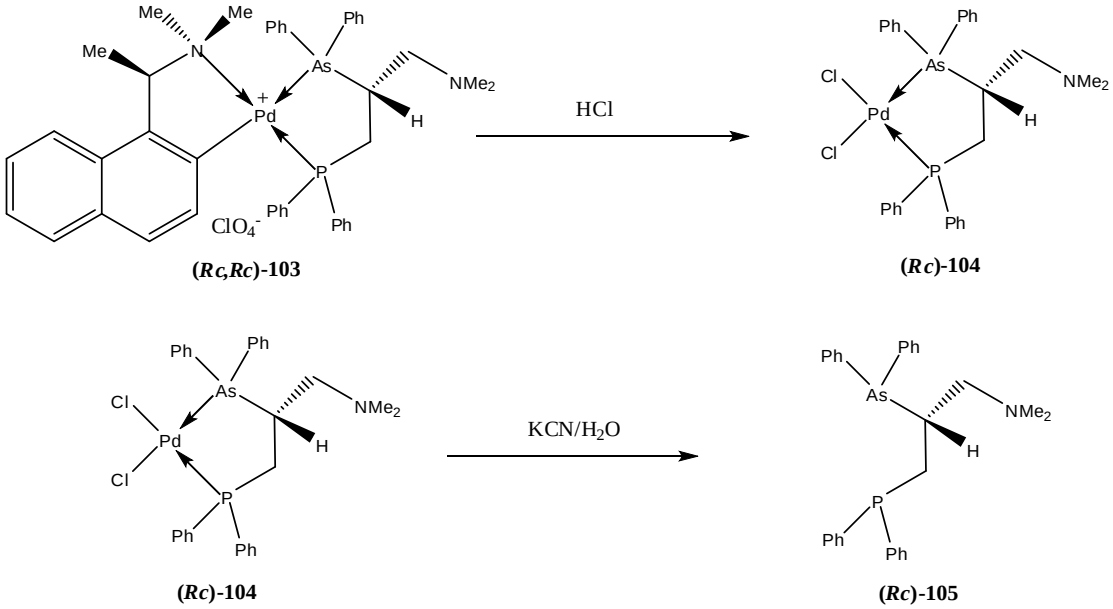
Pd(1)-C(1)	**2.056(3)**	**C(1)-Pd(1)-N(1)**	**81.3 (1)**
Pd(1)-N(1)	2.136(2)	C(1)-Pd(1)-P(1)	97.0(1)
Pd(1)-P(1)	2.244(1)	N(1)-Pd(1)-P(1)	173.7(1)
Pd(1)-As(1)	2.460(1)	C(1)-Pd(1)-As(1)	176.1(1)
As(1)-C(15)	1.942(3)	N(1)-Pd(1)-As(1)	97.8(1)
As(1)-C(21)	1.935(3)	P(1)-Pd(1)-As(1)	84.3(1)
As(1)-C(27)	1.988(3)	C(21)-As(1)-Pd(1)	116.0(1)
P(1)-C(31)	1.841 (1)	C(27)-As(1)-Pd(1)	106.6(1)
P(1)-C(32)	1.812(1)	C(28)-C(27)-C(31)	110.7(2)
P(1)-C(38)	1.814(1)	C(30)-N(2)- C(28)	111.8(3)
C(27)-C(28)	1.519(4)	C(30)-N(2)-C(29)	110.1(3)
C(27)-C(31)	1.527(4)	C(28)-C(27)-As(1)	113.8(1)

3.2.6.2 Liberation of the (C-chiral) P/As (*Rc*)-105

The chiral naphthylamine auxiliary on (*Rc,Rc*)-**103** could be chemoselectively removed by treatment of the isomers with concentrated hydrochloric acid (Scheme 3.13). Thus, the optically pure dichloro palladium complex (*Rc*)-**104** was obtained as a yellow solid in 84 % yield, $[\alpha]_D$ = - 27.3° (*c* 0.2, CH_2Cl_2). The ^{31}P NMR spectrum of product (*Rc*)-**104** exhibited a singlet at δ 57.6.

As indicated in Scheme 3.13, treatment of dichloro complex *(Rc*)-**104** with aqueous potassium cyanide conveniently gave the optically pure amino-functionalized

heterobidentate ligand (*Rc*)-**105** as a white solid in about 80% yield, $[\alpha]_D$ = – 15.0 (*c* 0.2, CH_2Cl_2). The ^{31}P NMR spectrum in $CDCl_3$ of the free chiral ligand showed a singlet at δ – 18.4. The liberated ligand could be recoordinated back to the same metal template without loss of optical purity.



(***Rc,Rc***)-**103** (***Rc***)-**104**

(***Rc***)-**104** (***Rc***)-**105**

Scheme 3.13

3.2.7 Asymmetric Hydroarsination of 2-diphenylphosphino N,N-dimethyl-2-propenylamine

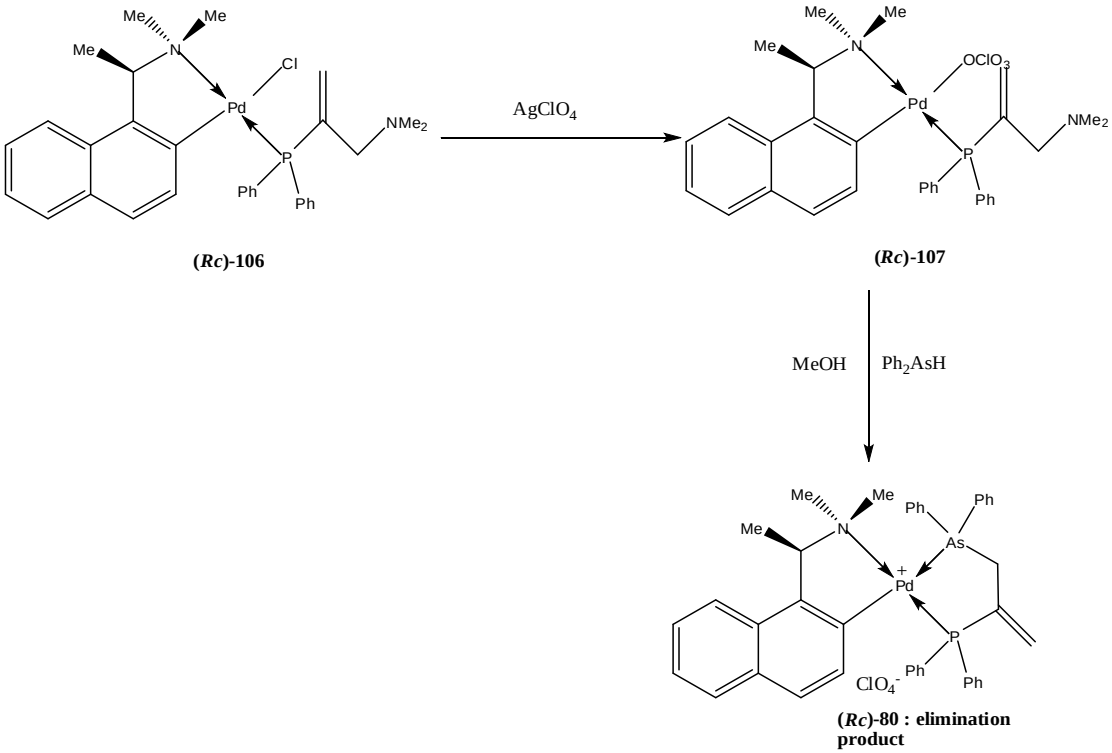
For comparison of the stereoselectivity, the Markovnikov form of another isomeric substrate 2-diphenylphosphino N,N-dimethyl-2-propenylamine was also employed for the asymmetric hydroarsination reaction. 2-diphenylphosphino N,N-dimethyl-2-propenylamine was prepared from hydrophoshination reaction of diphenlphosphido ions with propnylamine. After stirring the reaction mixture for 2d, the ^{31}P NMR spectrum of the crude products exhibited two singlets at δ -5.3 and -30.1 in the ratio of 3.5 to 1 for the Markovnikov and *Z*-isomers respectively. The free vinyl phosphine ligands were not isolated and were allowed to coordinate to the palladium dimer

(*Rc*)-**10** to generate the monomeric template complexes (*Rc*)-**106** and (*Rc*)-**101b**. The ^{31}P NMR spectrum in $CDCl_3$ showed one single peak at δ 42.3 and 16.2 respectively for each coordination product. The isomers (*Rc*)-**106** and (*Rc*)-**101b** could be separated efficiently in appreciable yield from column chromatography with dichloromethane and methanol as eluent. This provides the chance to study the selectivity of (*Rc*)-**106** for the subsequent hydroarsination reaction.

Similar to other monomeric complexes**,** (*Rc*)-**106** was converted to the reactive perchlorato complex by treatment with aqueous silver perchlorate (Scheme 3.14). Upon treatment of the perchlorate intermediate (*Rc*)-**107** with diphenylarsine under similar reaction conditions, the ^{31}P NMR spectrum of the crude products showed only a singlet at δ 55.6. From our previous hydroarsination reactions on similar analogous vinlyic phosphine with hydroxy and methoxy as functional groups, we observed a similar peak at δ 55.6. The product was identified as (*Rc*)-**80** an unexpected elimination product. From ^{1}H NMR spectrum, it was clearly evident that proton signals for dimethyl amino were absent and the vinylic protons at δ 5.06 (d, J_{PH} = 15.4 Hz) and 5.86 (d, J_{PH} = 32.6 Hz) were present. These observations clearly support that the dimethyl amino functional group has dissociated and the remaining double bond remained unreacted.

It is noteworthy that when hydroarsination reactions were attempted on two other analogous Markovnikov - type vinylic phosphines with hydroxy and methoxy as functional groups, apart from the substituted products, we also detected the formation of the expected heterobidentate As-P ligands. However with the current case for vinylic phosphines with dimethyl amino as functional group we did not observe any hydroarsination product at all as the ^{31}P NMR spectrum only showed a sharp singlet at δ 55.6 indicating the formation of a sole product. Like the previous hydroarsination

reaction in section 4.2.2, the N from the dimethylamino group can also be oriented in close proximity to the Pd metal centre. The Pd-N interaction can activate the N-C bond which then underwent N-C cleavage assisted by the presence of uncoordinated diphenylarsine.

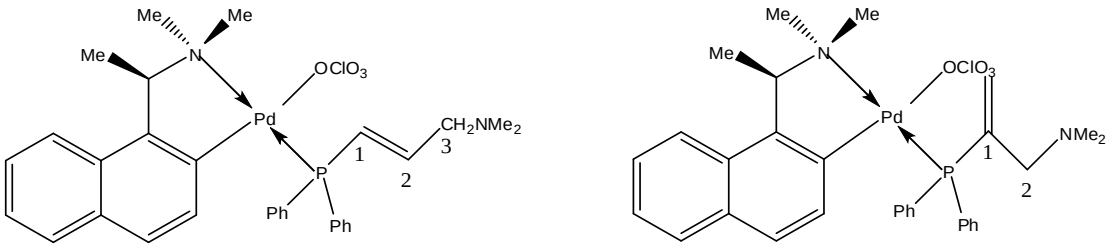


(*Rc*)-106 **(*Rc*)-107**

(*Rc*)-80 : elimination product

Scheme 3.14

Apart from that, when hydroarsination reactions were carried out on the *E*- and *Z*-isomers namely (*E*)- and (*Z*)-3-diphenylphosphanyl N,N-dimethyl-2-propenylamine, we observed only the presence of hydroarsination product (*Rc*,*Rc*)-**103** but no elimination product was detected. The differences could be attributed to the longer carbon chain length for the for (*E*)- and (*Z*)-3-diphenylphosphino N,N-dimethyl-2-propenylamine which renders a weaker Pd-N interaction (Scheme 3.15).



Scheme 3.15

3.3 Conclusions

In summary, we have demonstrated that transition metal complex-promoted asymmetric hydroarsination is a potential synthetic route for the preparation of heterobidentate chiral arsine ligands. The chiral napthyl palladium complex (*Rc*)-**10** has shown to be an excellent reaction promoter on the asymmetric hydroarsination between diphenylarsine and various alkenyl phosphines to generate enantiomerically pure As-P bidentate ligands. The reaction produced one new carbon chiral centre in very good stereoselectivity. The reaction is also regiospecific as the arsenic atom of the addition products remains in *cis* position relative to nitrogen while the phosphorus atom occupies the *trans* position relative to nitrogen.

An unexpected elimination product (*Rc*)-**80** was observed when the reaction was carried out on 2-diphenylphosphino-prop-2-en-1-ol, 2-diphenylphosphino- methyl prop-2-ene ether and 2-diphenylphosphino- N,N dimethyl -2-propenyl amine. This can be attributed to the Pd-O and Pd-N interactions which can activate the O-C and N-C bonds which then underwent cleavage assisted by uncoordinated diphenylarsine.

The chiral bidentate ligands can be easily liberated by treatment of the organic solution with aqueous potassium cyanide.

3.4 Experimental

All air-sensitve manipulations were carried out using Schlenk and cannula techniques under a positive pressure of purified nitrogen. All NMR spectra were recorded at 25 °C on Bruker Avance 300 and 500 spectrometer. Optical rotations were measure on the specified solution in a 0.1 dm cell at 20 °C with a Perkin-Elmer 341 polarimeter. Melting points were measured the SRS Optimelt Automated Melting Point System, SRS MPA100.

The dimeric naphthylamine palladium (II) **(*Rc*)-10,**[59] 3-diphenylphosphino-but-3-en-1-ol,[41a] 2-diphenylphosphino-prop-2-en-1-ol,[41a] 2-diphenylphosphino methyl prop-2-ene ether,[64] 3-(*E*)-diphenylphosphino- methyl prop-2-ene ether,[64] 3-diphenylphosphino-(*E*)- ethyl prop-3-enoate,[66] 5-diphenylphosphino -(*E*)- pent-3-en-2-one,[41e] (*E*)- and (*Z*)-3-diphenylphosphino N,N-dimethyl-2-propenylamine,[65] 2-diphenylphosphino N,N-dimethyl-2-propenylamine[41a] were prepared according to the standard methods.

Caution! *All perchlorate salts should be handled as potentially explosive compounds. Care should be taken in handling highly toxic arsane and cyanide compounds*.

Isolation of {(R)-1-[1-(dimethylamino)ethyl]-2napthyl-C,N][(R)-3-(diphenylphosphino)-4-(diphenylarsino)butan-1-ol]palladium(II) Perchlorate (*Rc*,*Rc*)-74. A solution of the complex (*Rc*)-**72** (0.5 g, 0.84 mmols) in dichloromethane was treated with aqueous silver perchlorate (0.4 g, 1.93 mmols) for 2 h. The white precipitate, silver chloride was filtered off using Celite. The solution was subsquently washed with water (3 x 30 ml), and then the organic layer was dried over magnesium sulphate. The solvent was removed and the yellow solid was redissolved

in methanol (100 ml). This solution was treated with diphenylarsine (0.19 g, 0.84 mmols) at -78°C. The crude product was monitored by ^{31}P NMR until no more starting material was present. Removal of solvent under reduced pressure gave the crude products as a yellow solid. The crude product mixture was then purified through a silica gel column with dichloromethane/ acetone as the eluent and then crystallised from dichloromethane / hexane to give complex (*Rc*,*Rc*)-**74** as white crystals; m.p. 210-211 °C (decomp.), $[\alpha]_D$ = +92.0 (c 0.7, CH_2Cl_2); 0.411g (55 % yield). $C_{42}H_{44}ClNO_5PAsPd$ (975.45) calcd: C 56.6, H 4.9, N 1.6. Found: C 56.4, H 4.8, N 1.5. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 77.6. ^{1}H NMR ($CDCl_3$, δ): 1.26 (m, 1H, $Ph_2AsCH'HCH$), 1.47 (m, 1H, $Ph_2AsCH'HCH$), 2.01(1H, m, $PCHCH_2$), 2.19 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CH*Me*), 2.54 (s, 3H, N*Me*), 2.86 (m, 2H, CH_2CH_2OH), 2.93 (m, 2H, CH_2CH_2OH) 2.95 (s, 3H, N*Me*), 3.70 (t, 1H, $^3J_{HH}$ = 6.7 Hz, OH), 4.62 (qn, 1H, $^3J_{HH}$ = 6.1 Hz, C*H*Me), 6.75-8.43 (m, 26H, aromatics).

Dichloro[(R)-3-(diphenylphosphino)-4-(diphenylarsino)butan-1-ol]palladium(II) (*Rc*)-75. A solution of the complex (*Rc*,*Rc*)-**74** (0.2 g, 0.22 mmols) in dichloromethane was stirred with concentrated hydrochloric acid (5 mL) for 16h. The excess acid was then removed by washing with water (3 x 20 mL) and the organic layer was dried using magnesium sulphate. Upon removal of the solvent, a pale yellow solid was obtained (0.12 g, 83 % yield); m.p. 223-224 °C (decomp.), $[\alpha]_D$ = -37.9 (c 0.5, CH_2Cl_2). $C_{28}H_{28}Cl_2OPAsPd$:calcd. C 50.6, H 4.2. Found: 50.4, H 4.0. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 77.5. ^{1}H NMR ($CDCl_3$, δ): 1.21 (m, 1H, $Ph_2AsCH'HCH$), 1.56 (m, 1H, $Ph_2AsCH'HCH$), 1.76 (1H, m, $PCHCH_2$), 3.20 (m, 2H, CH_2CH_2OH), 3.50 (m, 2H, CH_2CH_2OH), 7.28-7.36 (20H, m, aromatics).

Decomplexation of [(R)-3-(diphenylphosphino)-4-(diphenylarsino)butan-1-ol, (*Rc*)-76. A solution of the complex (*Rc*)-**75** (0.10 g, 0.15 mmols) in dichloromethane

was stirred vigorously with aqueous potassium cyanide (0.3 g in 5 ml of water) for 30 min. The resulting colourless organic layer was separated, washed with water and dried ($MgSO_4$). Upon the removal of solvent, a white solid (*Rc*)-**6** was obtained, $[\alpha]_D$ = -37.9 (c 0.5, CH_2Cl_2); 0.065 g (88 % yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): -1.2. ^1H NMR ($CDCl_3$, δ): 1.28 (m, 1H, $Ph_2AsCH'HCH$), 1.88 (m, 1H, $Ph_2AsCH'HCH$), 1.92 (1H, m, $PCHCH_2$), 2.57 (m, 2H, CH_2CH_2OH), 3.70 (m, 2H, CH_2CH_2OH), 7.28-7.36 (20H, m, aromatics).

Isolation of {(R)-1-[1-(dimethylamino)ethyl]-2-napthyl-C,N][(R)-3-(diphenylphosphino)-4-(diphenylarsino)propan-1-ol]palladium(II) Perchlorate (*Rc,Rc*)-79 A solution of the complex (*Rc*)-**77** (0.53 g, 0.92 mmols) in dichloromethane was treated with aqueous silver perchlorate (0.57 g, 2.76 mmols) for 2 h. The white precipitate, silver chloride was filtered off using Celite. The solution was subsquently washed with water (3 x 30 ml), and then the organic layer was dried over magnesium sulphate. The solvent was removed and the yellow solid was redissolved in methanol (100 ml). This solution was treated with diphenylarsane (0.21 g, 0.00092 mols) at -78°C. The temperature was maintained for 10 h then stirred at room temperature for 24 h. The crude product was monitored by ^{31}P NMR until no more starting material was present. Two new signals were observed at δ 66.3 and 55.6 in the ratio of 2.6 to 1 respectively. Removal of solvent under reduced pressure gave the crude products as a yellow solid. The crude product mixture was then purified through a silica gel column with dichloromethane/ acetone as the eluent. The major isomer was then crystallised from acetonitrile- diethyl ether to give complex (*Rc,Rc*)-**79** as white crystals; (0.18 g, 25 % yield); m.p. 203-204 °C (decomp.), $[\alpha]_D$ = -116 (c 0.3, CH_2Cl_2). $C_{41}H_{42}ClNO_5PasPd$ (903.87) calcd: C 56.2, N 1.6 H 4.8. Found: 56.4, N 1.7, H 4.6. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 66.3. ^1H NMR ($CDCl_3$, δ): 2.12 (d, 3H, $^3J_{HH}$ =

6.2 Hz, CH*Me*), 2.85 (s, 3H, N*Me*), 2.95 (s, 3H, N*Me*), 3.05 (1H, m, $Ph_2PCHCH2$), 3.50 (m, 2H, CH_2OH), 3.69 (m, 1H, $Ph_2AsCH'HCH$), 3.91 (m, 1H, $Ph_2AsCH'HCH$), 4.46 (qn, 1H, $^3J_{HH}$ = 6.1 Hz, C*H*Me), 6.72-8.26 (m, 26H, aromatics).

Dichloro[(R)-3-(diphenylphosphino)-4-(diphenylarsino)propan-1-ol]palladium(II) (*Rc*)-81.

A solution of the complex (*Rc,Rc*)-**79** (0.1 g, 0.13 mmols) in dichloromethane was stirred with concentrated hydrochloric acid (5 mL) for 16h. The excess acid was then removed by washing with water (3 x 20 mL) and the organic layer was dried using magenesium sulphate. Upon removal of the solvent, a pale yellow solid was obtained (0.066 g, 79 % yield); m.p. 213-214 °C (decomp.), $[\alpha]_D$ = -120 (c 0.5, CH_2Cl_2). $C_{27}H_{26}Cl_2OPAsPd$:calcd. C 49.9, H 4.0. Found: 50.3, H 4.2. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 70.0. ^1H NMR ($CDCl_3$, δ): 2.40-2.78 (2H, m, Ph_2AsCH_2CH), 3.32 (m, 2H, CH_2OH), 3.63 (m, 1H, $Ph_2PCHCH2$), 7.30-7.56 (m, 20H, aromatics).

Decomplexation of [(R)-3-(diphenylphosphino)-4-(diphenylarsino)propan-1-ol, (*Rc*)-82. A solution of the complex (*Rc*)-**81** (0.05 g, 0.077 mmols) in dichloromethane was stirred vigorously with aqueous potassium cyanide (0.3 g) for 30 min. The resulting colourless organic layer was separated, washed with water and dried ($MgSO_4$). Upon the removal of solvent, a white solid (*Rc*)-**82** was obtained, $[\alpha]_D$ = +30 (c 0.3, CH_2Cl_2); 0.033 g (90 % yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): -9.0 ^1H NMR ($CDCl_3$, δ): 2.19 (d, 2H, $^3J_{HH}$ = 7.7 Hz, Ph_2AsCH_2CH), 2.61 (1H, m, $PCHCH_2$), 3.72-3.95 (m, 2H, CH_2OH), 7.28-7.38 (m, 20H, aromatics).

Isolation of {(R)-1-[1-(dimethylamino)ethyl]-2-napthyl-C,N][(R)-3-(diphenylphosphino)-4-(diphenylarsino)prop-1-ene]palladium(II) Perchlorate

(*Rc*)-80 Purification from silica column chromatography followed by crystallisation from dichloromethane-diethyl ether gave the minor product **(*Rc*)-80** as white crystals; (0.12 g, 15 % yield); m.p. 203-204 °C (decomp.), $C_{41}H_{40}ClNO_4PasPd$ (858.48)calcd: C 57.3, N 1.6 H 4.7. Found: 57.4, N 1.7, H 4.6. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 55.6. ^1H NMR ($CDCl_3$, δ): 1.97 (d, 3H, $^3J_{HH}$ = 6.1 Hz, CH*Me*), 2.84 (s, 6H, NMe_2), 3.25 (2H, m, AsCH_2C), 4.64 (qn, 1H, $^3J_{HH}$ = 6.1 Hz, C*H*Me), 5.07 (d, 1H, $^2J_{HH}$ = 2.1 Hz C=C*H'*H), 5.77 (1H, $^2J_{HH}$ = 2.1 Hz C=CH'*H*), 6.76-8.05 (m, 26H, aromatics).

Isolation of {(R)-1-[1-(dimethylamino)ethyl]-2-napthyl-C,N][(R)-2-(diphenylphosphino)-3-(diphenylarsino)methyl propyl ether]palladium(II) Perchlorate (*Rc,Rc*)-87 A solution of the complex (*Rc*)-**83** and (*Rc*)-**84** (0.42 g, 0.70 mmols) in dichloromethane was treated with aqueous silver perchlorate (0.43 g, 2.10 mmols) for 2 h. The white precipitate, silver chloride was filtered off using Celite. The solution was subsquently washed with water (3 x 30 ml), and then the organic layer was dried over magnesium sulphate. The solvent was removed and the yellow solid was redissolved in methanol (100 ml). This solution was treated with diphenylarsine (0.156 g, 0.70 mmols) at -78°C. The temperature was maintained for 10 h then stirred at room temperature for 1 d. The crude product was monitored by ^{31}P NMR until no more starting material was present. Three new signals were observed at δ 68.3, 55.6 and 53.1 in the ratio of 14.5:5:1 respectively. Removal of solvent under reduced pressure gave the crude products as a yellow solid. The crude product mixture was then purified through a silica gel column with dichloromethane/ diethyl ether as the eluent. The major isomer was then crystallised from dichloromethane-diethyl ether to give complex (*Rc,Rc*)-**87** as white crystals; (0.32 g, 73 % yield); m.p. 210-212 °C (decomp.), $[\alpha]_D$ = -70.4 (c 0.3, CH_2Cl_2). $C_{42}H_{44}ClNO_5PasPd$ (932.99) calcd: C 56.6, N 1.6 H 4.9. Found: 56.4, N 1.7, H 4.6. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ):

68.3. ^{1}H NMR ($CDCl_3$, δ): 2.17 ((d, 3H, J_{HH} = 6.2 Hz, CH*Me*), 2.25 (m, 1H, CH'*H*OMe), 2.66 (s, 3H, N*Me*), 2.90 (s, 3H, CH_2O*Me*), 2.95 (s, 3H, N*Me*), 3.03 (m, 1H, C*H'*HOMe), 3.36 (m, 2H, AsCH_2), 3.76 (1H, m, Ph_2PC*H*CH2), 4.55 (qn, 1H, $^{3}J_{HH}$ = 6.1 Hz, C*H*Me), 6.74-8.42 (m, 26H, aromatics).

Dichloro][(R)-2-(diphenylphosphino)-3-(diphenylarsino)methyl propyl ether]palladium(II) (*Rc*)-89. A solution of the complex (*Rc*,*Rc*)-**87** (0.1 g, 0.11 mmols) in dichloromethane was stirred with concentrated hydrochloric acid (5 mL) for 16h. The excess acid was then removed by washing with water (3 x 20 mL) and the organic layer was dried using magenesium sulphate. Upon removal of the solvent, a pale yellow solid was obtained (0.06 g, 83 % yield); m.p. 223-224 °C (decomp.), $[\alpha]_D$ = -53.8 (c 0.1, CH_2Cl_2). $C_{28}H_{28}Cl_2OPAsPd$:calcd. C 50.6, H 4.2. Found: 50.3, H 4.2. ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 72.0. ^{1}H NMR ($CDCl_3$, δ): 2.41 (m, 1H, CH'*H*OMe), 2.79 (s, 3H, CH_2O*Me*), 2.83 (m, 1H, C*H'*HOMe), 2.93 (m, 2H, AsCH_2), 3.15 (1H, m, Ph_2PC*H*CH2), 7.31-8.16 (m, 20H, aromatics).

Decomplexation of [(R)-2-(diphenylphosphino)-3-(diphenylarsino)methyl propyl ether, (*Rc*)-90. A solution of the complex (*Rc*)-**89** (0.10 g, 0.15 mmols) in dichloromethane was stirred vigorously with aqueous potassium cyanide (0.3 g) for 30 min. The resulting colourless organic layer was separated, washed with water and dried ($MgSO_4$). Upon the removal of solvent, a white solid (*Rc*)-**90** was obtained, $[\alpha]_D$ = -46.4 (c 0.3, CH_2Cl_2); 0.09 g (90 % yield). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): -7.6 ^{1}H NMR ($CDCl_3$, δ): 1.33 (m, 1H, CH'*H*OMe), 2.05-2.36 (m, 2H, AsCH_2), 2.62 (m, 1H, C*H'*HOMe), 3.15 (s, 3H, CH_2O*Me*), 3.31 (1H, m, Ph_2PC*H*CH2), 7.24-7.41 (m, 20H, aromatics).

Isolation of {(R)-1-[1-(dimethylamino)ethyl]-2-napthyl-C,N][(R)-3-(diphenylphosphino)-4-(diphenylarsino)prop-1-ene]palladium(II) Perchlorate

(*Rc*)-80 Purification from silica column chromatography followed by crystallisation from dichloromethane-diethyl ether gave the minor product **(*Rc*)-80** as white crystals; (0.12 g, 15 % yield); m.p. 203-204 °C (decomp.), $C_{41}H_{40}ClNO_4PAsPd$:calcd. C 57.3, N 1.6 H 4.7. Found: 57.4, N 1.7, H 4.6. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 55.6. ^1H NMR ($CDCl_3$, δ): 1.94 (d, 3H, $^3J_{HH}$ = 6.1 Hz, CH*Me*), 2.83 (s, 3H, N*Me*), 3.31 (s, 3H, N*Me*), 3.05 (1H, m, PC*H*CH_2), 3.50 (m, 2H, CH_2OH), 2.17 (d, 1H, $^2J_{HH}$ = 10.1 Hz Ph_2AsC*H'*HC), 2.46 (d, 1H, $^3J_{HH}$ = 10.1 Hz Ph_2AsCH'*H*C), 4.51 (qn, 1H, $^3J_{HH}$ = 6.1 Hz, C*H*Me), 5.11 (d, 1H, $^2J_{HH}$ = 2.1 Hz C=C*H'*H), 5.77 (1H, $^2J_{HH}$ = 2.1 Hz C=CH'*H*), 6.82-8.26 (m, 26H, aromatics)

Isolation of {(R)-1-[1-(dimethylamino)ethyl]-2-napthyl-C,N][(S)-3-(diphenylphosphino)-2-(diphenylarsino)methyl propyl ether]palladium(II) Perchlorate (*Rc,Sc*)-88

(0.05 g, 8 % yield); m.p. 210-212 °C (decomp.), $[\alpha]_D$ = -70.4 (c 0.3, CH_2Cl_2). $C_{42}H_{44}ClNO_5PAsPd$:calcd. C 56.6, N 1.6 H 4.9. Found: 56.4, N 1.7, H 4.6. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 53.1. ^1H NMR ($CDCl_3$, δ): 2.02 ((d, 3H, J_{HH} = 6.2 Hz, CH*Me*), 2.31 (m, 1H, CH'*H*OMe), 2.56 (m, 1H, C*H'*HOMe), 2.66 (s, 3H, N*Me*), 2.88 (s, 3H, CH_2O*Me*), 2.75 (s, 3H, N*Me*), 3.19 (m, 2H, AsCH_2), 3.46 (1H, m, Ph_2PC*H*CH2), 4.53 (qn, 1H, $^3J_{HH}$ = 6.1 Hz, C*H*Me), 6.79-8.16 (m, 26H, aromatics).

Isolation of {(R)-1-[1-(dimethylamino)ethyl]-2napthyl-C,N][(R)-3-(diphenylphosphino)-2-(diphenylarsino)ethyl propanoate]palladium(II) Perchlorate (*Rc,Rc*)-93. A solution of the complex (*Rc*)-**91** (0.42 g, 0.67 mmols) in dichloromethane was treated with aqueous silver perchlorate (0.4 g, 1.93 mmols) for 2 h. The white precipitate, silver chloride was filtered off using Celite. The solution was subsquently washed with water (3 x 30 ml), and then the organic layer was dried over magnesium sulphate. The solvent was removed and the yellow solid was redissolved

in methanol (100 ml). This solution was treated with diphenylarsine (0.15 g, 0.67 mmols) at -78°C. The temperature was maintained for 10 h then stirred at room temperature for 24 h. The crude product was monitored by ^{31}P NMR until no more starting material was present. Removal of solvent under reduced pressure gave the crude products as a yellow solid. The crude product mixture was then purified through a silica gel column with dichloromethane/ ether as the eluent and then crystallised from dichloromethane / hexane to give complex (*Rc*,*Rc*)-**93** as white crystals; m.p. 215-217 °C (decomp.), $[\alpha]_D$ = -44.0 (c 0.3, CH_2Cl_2); 0.35 g (57 % yield). $C_{43}H_{44}ClNO_6PasPd$ (1088.38) calcd: C 56.2, H 4.8, N 1.5. Found: C 56.4, H 4.8, N 1.5. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 49.8. ^{1}H NMR ($CDCl_3$, δ): 0.86 (t, 3H, $^3J_{HH}$ = 6.0 Hz, OCH_2CH_3), 2.01 (s, 3H, N*Me*), 2.74 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CH*Me*), 2.95 (s, 3H, N*Me*), 3.04-3.27 (2H, m, PCH_2CH), 3.12 (m, 1H, $Ph_2AsCH'HCH$), 3.69 (q, 2H, $^3J_{HH}$ = 6.0 Hz, OCH_2CH_3), 4.57 (qn, 1H, $^3J_{HH}$ = 6.1 Hz, C*H*Me), 6.79-8.20 (m, 26H, aromatics).

Dichloro][(R)-3-(diphenylphosphino)-2-(diphenylarsino)ethyl propanoate]palladium(II) (*Rc*)-94. A solution of the complex (*Rc*,*Rc*)-**93** (0.045 g, 0.05 mmols) in dichloromethane was stirred with concentrated hydrochloric acid (5 mL) for 16h. The excess acid was then removed by washing with water (3 x 20 mL) and the organic layer was dried using magenesium sulphate. Upon removal of the solvent, a pale yellow solid was obtained (0.028 g, 83 % yield); m.p. 230-232 °C (decomp.), $[\alpha]_D$ = +16.7 (c 0.3, CH_2Cl_2). C29H28Cl2O_2PAsPd:calcd. C 50.3, H 4.2. Found: 50.4, H 4.0. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 55.4. ^{1}H NMR ($CDCl_3$, δ): δ): 0.92 (t, 3H, $^3J_{HH}$ = 7.2 Hz, OCH_2CH_3), 2.72-3.13 (2H, m, PCH_2CH), 3.12 (m, 1H, $Ph_2AsCH'HCH$), 3.76 (q, 2H, $^3J_{HH}$ = 7.2 Hz, OCH_2CH_3), 7.42-8.06 (20H, m, aromatics).

Decomplexation of [(R)-3-(diphenylphosphino)-2-(diphenylarsino)ethyl propanoate], (*Rc*)-95. A solution of the complex (*Rc*)-**94** (0.045 g, 0.05 mmols) in dichloromethane was stirred vigorously with aqueous potassium cyanide (0.3 g) for 30 min. The resulting colourless organic layer was separated, washed with water and dried ($MgSO_4$). Upon the removal of solvent, a white solid (*Rc*)-**95** was obtained, $[\alpha]_D$ = -14.8 (c 0.3, CH_2Cl_2); 0.023 g (88 % yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): -17.1. ^1H NMR ($CDCl_3$, δ): 0.95 (t, 3H, $^3J_{HH}$ = 7.1 Hz, OCH_2CH_3), 2.68-3.28 (2H, m, PCH_2CH), 2.28 (m, 1H, $Ph_2AsCH'HCH$), 3.65 (q, 2H, $^3J_{HH}$ = 7.2 Hz, OCH_2CH_3), 7.28-7.38 (20H, m, aromatics).

Isolation of {(R)-1-[1-(dimethylamino)ethyl]-2-napthyl-C,N][(S)-5-(diphenylphosphino)-4-(diphenylarsino)pentan-2-one]palladium(II) Perchlorate (*Rc,Sc*)-98. A solution of the complex (*Rc*)-**96** (0.68 g, 1.11 mmols) in dichloromethane was treated with aqueous silver perchlorate (0.69 g, 3.33 mmols) for 2 h. The white precipitate, silver chloride was filtered off using Celite. The solution was subsquently washed with water (3 x 30 ml), and then the organic layer was dried over magnesium sulphate. The solvent was removed and the yellow solid was redissolved in methanol (100 ml). This solution was treated with diphenylarsane (0.24 g, 1.11 mmols) at -78°C. The temperature was maintained for 10 h then stirred at room temperature for 5 d. The crude product was monitored by ^{31}P NMR until no more starting material was present. Two new signals were observed at δ 52.2 and 51.2 in the ratio of 6 to 1 respectively. Removal of solvent under reduced pressure gave the crude products as a yellow solid. The crude product mixture was then purified through a silica gel column with dichloromethane/ ethyl acetate as the eluent. The major isomer was then crystallised from dichloromethane- hexane to give complex (*Rc,Sc*)-**98** as white crystals; (0.55 g, 52 % yield); m.p. 210-212 °C (decomp.), $[\alpha]_D$ =

-35.0 (c 0.3, CH_2Cl_2). $C_{43}H_{44}ClNO_5PAsPd$:calcd. C 57.2, N 1.6 H 4.9. Found: 57.4, N 1.7, H 4.6. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 52.2. ^1H NMR ($CDCl_3$, δ): 1.94 (m, 1H, CH'*H*COMe), 1.99 (d, 3H, J_{HH} = 6.2 Hz, CH*Me*), 2.03 (s, 3H, CO*Me*), 2.18 (m, 1H, C*H'*HCOMe), 2.59 (m, 2H, PCH_2), 2.66 (s, 3H, N*Me*), 2.85 (s, 3H, N*Me*), 4.13 (1H, m, Ph_2AsC*H*CH2), 4.51 (qn, 1H, $^3J_{HH}$ = 6.1 Hz, C*H*Me), 6.85-8.26 (m, 26H, aromatics).

Dichloro[(S)-5-(diphenylphosphino)-4-(diphenylarsino)pentan-2-one]palladium(II) (*Sc*)-99. A solution of the complex (*Rc,Sc*)-**98** (0.2 g, 0.22 mmols) in dichloromethane was stirred with concentrated hydrochloric acid (5 mL) for 16h. The excess acid was then removed by washing with water (3 x 20 mL) and the organic layer was dried using magenesium sulphate. Upon removal of the solvent, a pale yellow solid was obtained (0.12 g, 81 % yield); m.p. 213-214 °C (decomp.), $[\alpha]_D$ = +42.9 (c 0.5, CH_2Cl_2). $C_{29}H_{28}Cl_2OPAsPd$ (675.70) calcd. C 51.5, H 4.1. Found: 51.3, H 4.2. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 58.0. ^1H NMR ($CDCl_3$, δ): 1.83 (s, 3H, CO*Me*), 2.22 (m, 1H, CH'*H*COMe), 2.52 (m, 1H, C*H'*HCOMe), 2.93 (1H, m, Ph_2AsC*H*CH2), 3.33 (m, 2H, PCH_2), 7.46-8.01 (m, 20H, aromatics).

Decomplexation of [(S)-5-(diphenylphosphino)-4-(diphenylarsino)pentan-2-one, (*Sc*)-100. A solution of the complex (*Sc*)-**99** (0.10 g, 0.15 mmols) in dichloromethane was stirred vigorously with aqueous potassium cyanide (0.3 g) for 30 min. The resulting colourless organic layer was separated, washed with water and dried ($MgSO_4$). Upon the removal of solvent, a white solid (*Sc*)-**100** was obtained, $[\alpha]_D$ = -46.4 (c0.3, CH_2Cl_2); 0.09 g (90 % yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): -21.2 ^1H NMR ($CDCl_3$, δ): δ): 1.89 (s, 3H, CO*Me*), 1.96 (m, 1H, CH'*H*COMe), 2.29 (m, 1H, C*H'*HCOMe), 2.77 (m, 2H, PCH_2), 3.06 (1H, m, Ph_2AsC*H*CH2), 7.26-7.49 (m, 20H, aromatics).

Isolation of {(R)-1-[1-(dimethylamino)ethyl]-2napthyl-C,N][(R)-3-(diphenylphosphino)-2-(diphenylarsino) N,N,dimethyl propyl amine]palladium(II) Perchlorate (*Rc,Rc*)-103.

A solution of the complex (*Rc*)-**101a** (0.58 g, 0.95 mmols) in dichloromethane was treated with aqueous silver perchlorate (0.6 g, 2.85 mmols) for 2 h. The white precipitate, silver chloride was filtered off using Celite. The solution was subsquently washed with water (3 x 30 ml), and then the organic layer was dried over magnesium sulphate. The solvent was removed and the yellow solid was redissolved in methanol (100 ml). This solution was treated with diphenylarsane (0.21 g, 0.95 mmols) at -78°C. The temperature was maintained for 10 h then stirred at room temperature for 24 h. The crude product was monitored by ^{31}P NMR until no more starting material was present. Removal of solvent under reduced pressure gave the crude products as a yellow solid. The crude product mixture was then purified through a silica gel column with dichloromethane/ ether as the eluent and then crystallised from dichloromethane /diethyl ether to give complex (*Rc,Rc*)-**103** as white crystals; m.p. 218-220 °C (decomp.), $[\alpha]_D$ = -75.0 (c 0.2, CH_2Cl_2); 0.40 g (47 % yield). $C_{43}H_{47}ClN_2O_4PAsPd$ (903.57): calcd. C 57.1, H 5.2, N 3.1. Found: C 56.7, H 4.9, N 3.2. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): δ 51.5. ^{1}H NMR ($CDCl_3$, δ): 1.79 (s, 3H, N*Me*), 1.88 (s, 6H, N*Me*$_2$), 2.18 (m, 2H, $^3J_{HH}$ = 6.0 Hz, *CH*$_2$NMe$_2$), 2.46 (m, 2H, PC*H*$_2$CH), 2.65 (s, 3H, N*Me*), 2.92 (d, 3.12, $^3J_{HH}$ = 6.1 Hz, CH*Me*), 3.24 (m, 1H, Ph_2AsC*H*CH$_2$), 4.57 (qn, 1H, $^3J_{HH}$ = 6.1 Hz, C*H*Me), 6.61-7.92 (m, 26H, aromatics).

The same procedure was adopted for the hydroarsination of (*Rc*)-**101b**. The ^{31}P NMR spectrum of the crude product in $CDCl_3$ showed one singlet at δ 51.5 which is similar the product from hydroarsination of (*Rc*)-**101a.**

Dichloro][(R)-3-(diphenylphosphino)-2-(diphenylarsino) N,N,dimethyl propyl amine] palladium(II) (*Rc*)-104.

A solution of the complex (*Rc,Rc*)-**103** (0.10 g, 0.11 mmols) in dichloromethane was stirred with concentrated hydrochloric acid (5 mL) for 16h. The excess acid was then removed by washing with water (3 x 20 mL) and the organic layer was dried using magenesium sulphate. Upon removal of the solvent, a pale yellow solid was obtained (0.064 g, 85 % yield); m.p. 230-232 °C (decomp.), $[\alpha]_D$ = -27.2 (c 0.2, CH_2Cl_2). $C_{29}H_{31}Cl_2NPAsPd$:calcd. C 51.4, H 4.6. Found: 51.4, H 4.3. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 57.6. ^1H NMR ($CDCl_3$, δ): δ): 1.95 (s, 6H, N*Me*$_2$), 2.13 (d, 2H, $^3J_{HH}$ = 7.0 Hz, *CH*$_2$NMe$_2$), 2.48 (m, 2H, PC*H*$_2$CH), 2.96 (m, 1H, $Ph_2AsCHCH_2$), 7.47-7.97 (m, 20H, aromatics).

Decomplexation of [(R)-3-(diphenylphosphino)-2-(diphenylarsino) N,N,dimethyl propyl amine], (*Rc*)-105.

A solution of the complex **(*Rc*)-104** (0.05 g, 0.074 mmols) in dichloromethane was stirred vigorously with aqueous potassium cyanide (0.3 g) for 30 min. The resulting colourless organic layer was separated, washed with water and dried ($MgSO_4$). Upon the removal of solvent, a white solid (*Rc*)-**105** was obtained, $[\alpha]_D$ = -10.8 (c 0.2, CH_2Cl_2); 0.032 g (88 % yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): -18.4. ^1H NMR ($CDCl_3$, δ): 2.09 (s, 6H, N*Me*$_2$), 2.32 (d, 2H, $^3J_{HH}$ = 7.0 Hz, *CH*$_2$NMe$_2$), 2.43 (m, 2H, PC*H*$_2$CH), 2.64 (m, 1H, $Ph_2AsCHCH_2$), 7.23-7.42 (m, 20H, aromatics).

Isolation of {(R)-1-[1-(dimethylamino)ethyl]-2-napthyl-C,N][(R)-3-(diphenylphosphino)-4-(diphenylarsino)prop-1-ene]palladium(II) Perchlorate (*Rc*)-80

Sodium metal (0.15g, 6.45 mmols) was placed in a 250 mL Schlenk flask containing THF (100 mL). This was followed by the addition of diphenylphosphine (0.60g, 3.23 mmols) with stirring. The mixture was stirred overnight and was observed to turn to a deep red colour which was characteristic of the diphenylphosphide ion. N,N-dimethyl propargyl amine (0.35 ml, 3.23 mmols) then was placed in a 500 ml Schlenk flask with THF (100 ml). The sodium diphenylphoshide generated was then transferred dropwise into the Schlenl flask with stirring at 0 °C. The reaction was mixture was allowed to reach room temperature and continued to be stirred over 2 days. To the crude reaction mixture, palladium dimer (*Rc*)-**10** (1.09 g, 1.62 mmols) was added and stirred for another 2 hours. Upon removal of solvent, the residue was purified by column chromatography on silica gel (dichloromethane/methanol) to afford isomers (*Rc*)-**106** and (*Rc*)-**101b**. A solution of the complex (*Rc*)-**106** (0.51 g, 0.84 mmols) in dichloromethane was treated with aqueous silver perchlorate (0.52 g, 2.51 mmols) for 2 h. The white precipitate, silver chloride was filtered off using Celite. The solution was subsquently washed with water (3 x 30 ml), and then the organic layer was dried over magnesium sulphate. The solvent was removed and the yellow solid was redissolved in methanol (100 ml). This solution was treated with diphenylarsine (0.19 g, 0.84 mmols) at -78°C. The temperature was maintained for 10 h then stirred at room temperature for 24 h. The crude product was monitored by ^{31}P NMR until no more starting material was present. Removal of solvent under reduced pressure gave the crude products as a yellow solid. The crude product mixture was then purified through a silica gel column with dichloromethane/ ether as the eluent and then

crystallised from dichloromethane /diethyl ether to give complex (*Rc*)-**80** as white crystals; m.p. 203-04 °C (decomp.), 0.36 g (50 % yield). $C_{41}H_{40}ClNO_4PAsPd$: calcd. C 57.3, H 4.7, N 1.6. Found: C 57.7, H 4.9, N 1.5. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): *δ* 55.6. ^1H NMR ($CDCl_3$, δ): 1.97 (d, $^3J_{HH}$ = 6.1 Hz, CH*Me*), 2.80 (1H, m, Ph_2AsCHH'), 2.88 (s, 6H, NMe_2), 3.16 (1H, m, Ph_2AsCHH'), 4.63 (qn, 1H, $^3J_{HH}$ = 6.1 Hz, C*H*Me), 5.06 (d, J_{PH} = 15.4 Hz, $Ph_2PC{=}CHH'$), 5.86 (d, J_{PH} = 32.6 Hz, $Ph_2PC{=}CH\ H'$), 6.76-7.74 (m, 26H, aromatics).

CHAPTER 4

Platinum (II) Promoted Cycloaddition Reactions Involving Oxygenated- and Sulfonated- Phosphine Functionalised Dienophiles and Dienes.

4.1 Introduction

The asymmetric Diels-Alder reaction is the most efficient protocol for the synthesis of chiral six-membered rings. Leung *et.al.* has worked extensively to prepare a wide series of functionalised mono- and diphosphines by applying organopalladium complex containing the optically active forms of ortho-palladated (1-dimethylamino)ethyl)naphthalene as the chiral template to promote the asymmetric cycloaddtion reactions.[40] It is important to note that the aromaticity of the 5-membered heterocyclic ring, 3,4-dimethyl-1-phenylphosphole (DMPP) is a rather poor cyclic diene for the classic [4+2] cycloaddition reactions. However when it is coordinated to a metal ion, it can be activated as a typical cyclic diene.[67] Furthermore, we observed that it is possible to select either the exo or the endo cycloaddition adducts in these asymmetric reactions by controlling the number of coordination sites available on the chiral template.[40a]

A hybrid ligand or heteroditopic ligand is a type of ligand that combines hard and soft donors. Their catalytic abilities arise from the presence of labile donor function while the other donor group remain firmly bound to the metal centres, thus leading to novel and unprecedented properties for the resulting metal complexes.[68]

Recently, diphosphines containing one tertiary phosphorus donor atom and one phosphorus oxide function were found to play an important role in organic syntheses. Phosphorus-sulfur based ligands are also a popular class of heterobidentate ligands and have been successfully used in many asymmetric reactions.[69] Our group has previously reported the successful formation of a few heterobidendate ligands, namely As*/P=S,[34] P*/P=O[70] and P*/P*=S[71]. In this chapter, we report the synthesis of a new chiral P*/P*=S ligand via the asymmetric cycloaddition raction between 3,4-

dimethyl-1-phenylphosphole (DMPP) and phenyldi[(Z)]prop-1-enyl]phosphine sulphide promoted by a chiral platinum complex.

4.2 Results and Discussion

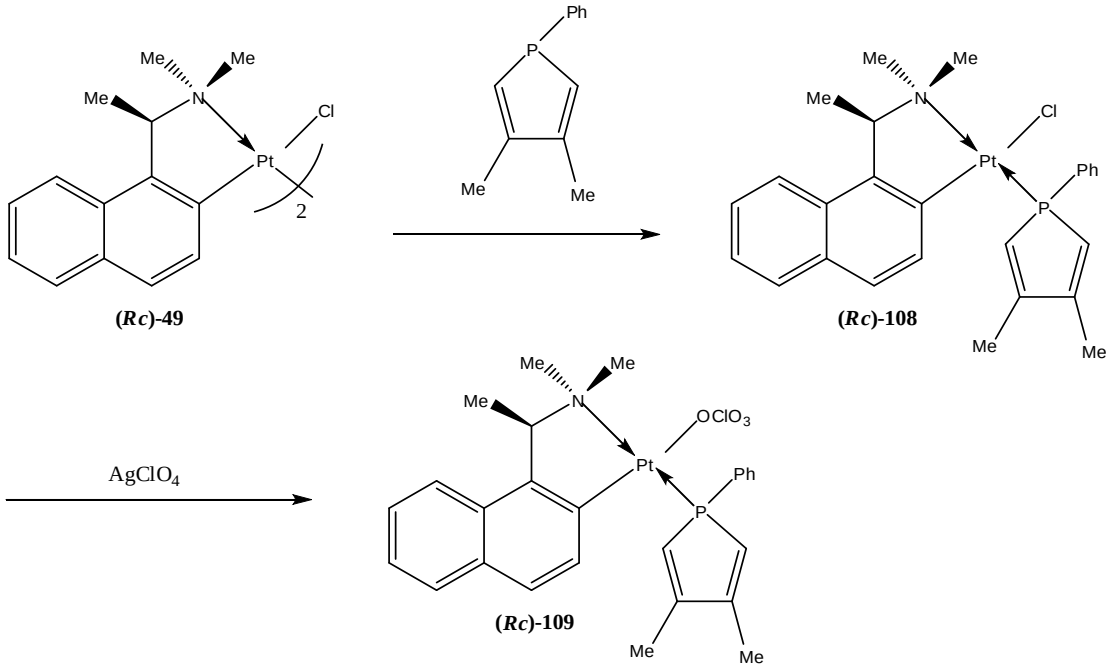
4.2.1 Asymmetric Diels-Alder Reaction between DMPP and phenyldi[(*Z*)]prop-1-enyl]phosphine oxide

As illustrated in Scheme 4.1, the coordinated DMPP in complex (*Rc*)-**108** can be activated toward cycloaddition reaction. Treatment of this chloro species in dichloromethane with aquous silver perchlorate yielded the perchlorato complex (*Rc*)-**109**. The conversion of (*Rc*)-**108** to (*Rc*)-**109** is quantitative and the complex can be used directly for further reaction. A solution of (*Rc*)-**109** was subsequently treated with one equivalent of phenyldi[(Z)]prop-1-enyl]phosphine oxide in 1,2-dichloroethane at 60 °C for 30 days (Scheme 4.2). The ^{31}P NMR spectrum of the crude reaction mixture in $CDCl_3$ showed two pair of singlets of similar intensities at δ 78.9 (J_{Pt-P} = 3805 Hz), 54.6 and δ 78.6 (J_{Pt-P} = 3813 Hz), 51.4 indicative of the formation of only two stereo chemically distinct cycloadducts. The signals in the low field region at δ 78.9 and 78.6 are typical for bridgehead phosphorus adopting the exo-syn stereochemistry. [72] The large Pt-P (bridgehead) coupling constant is typical of P donors located trans to σ-donor nitrogen atom. [40g]

4.2.1.1 X-ray crystal Diffraction Analysis of (*Sp,Rp*)-111

Attempts to isolate these diastereomic cationic complexes by fractional crystallisation or column chromatography were unsuccessful. In order to confirm the identities of the two diastereomers, the chiral napthylamine auxiliary in the complexes was removed

chemoselectively to give the corresponding neutral dichloro complex. The mixture was left to stir in dichloromethane with concentrated hydrochloric acid overnight (Scheme 4.3). The $^{31}P\{^{1}H\}$ NMR spectrum of the crude reaction mixture in $CDCl_3$ showed two singlets at δ 74.4 (J_{Pt-P} = 3800 Hz) and 26.1. Repeated fractional crystallisation from dichloromethane-diethyl ether gave light yellow crystals suitable for single crystal X-ray diffraction analysis. However, the X-ray structural analysis of dichloro complex revealed the presence of both enantiomers in the unit cell. The molecular structure of complex (*Sp*,*Rp*)-**111** is shown in Figure 4.1 and is taken as the representative molecule in order to study the coordination aspects of the products which were formed as a racemic mixture. The product is coordinated to the platinum metal centre as a bidentate ligand via phosphorus and oxygen donor atoms. Apart from that, the crystal analysis also confirmed that the desired cycloadduct had formed exclusively via the exo- cycloaddition reaction pathway. The coordination geometry is distorted square planar with angles at platinum ranging between 83.5(1)-95.4(1) ° and 174.3(1)-175.1(1) °. Selected bond lengths and angles are listed in Table 4.1.



Scheme 4.1

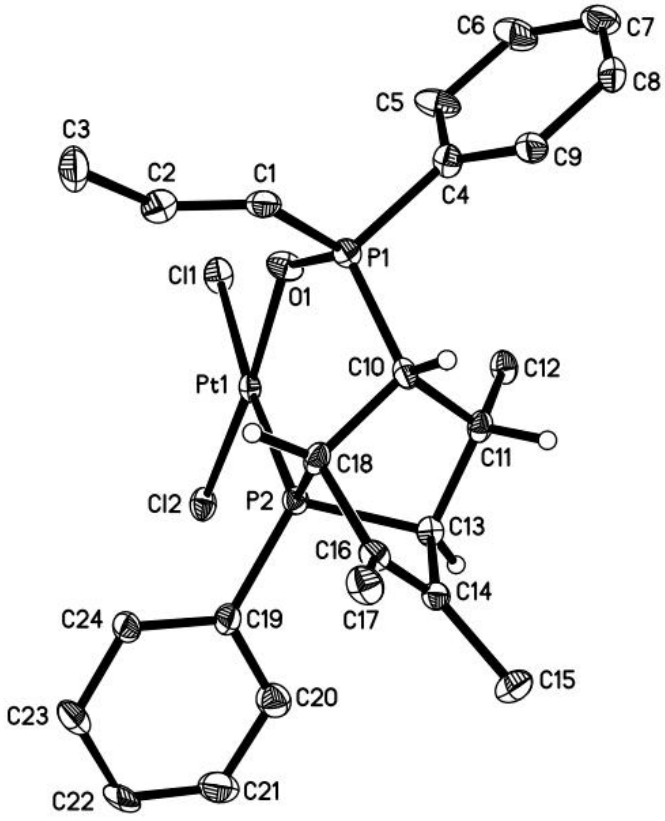
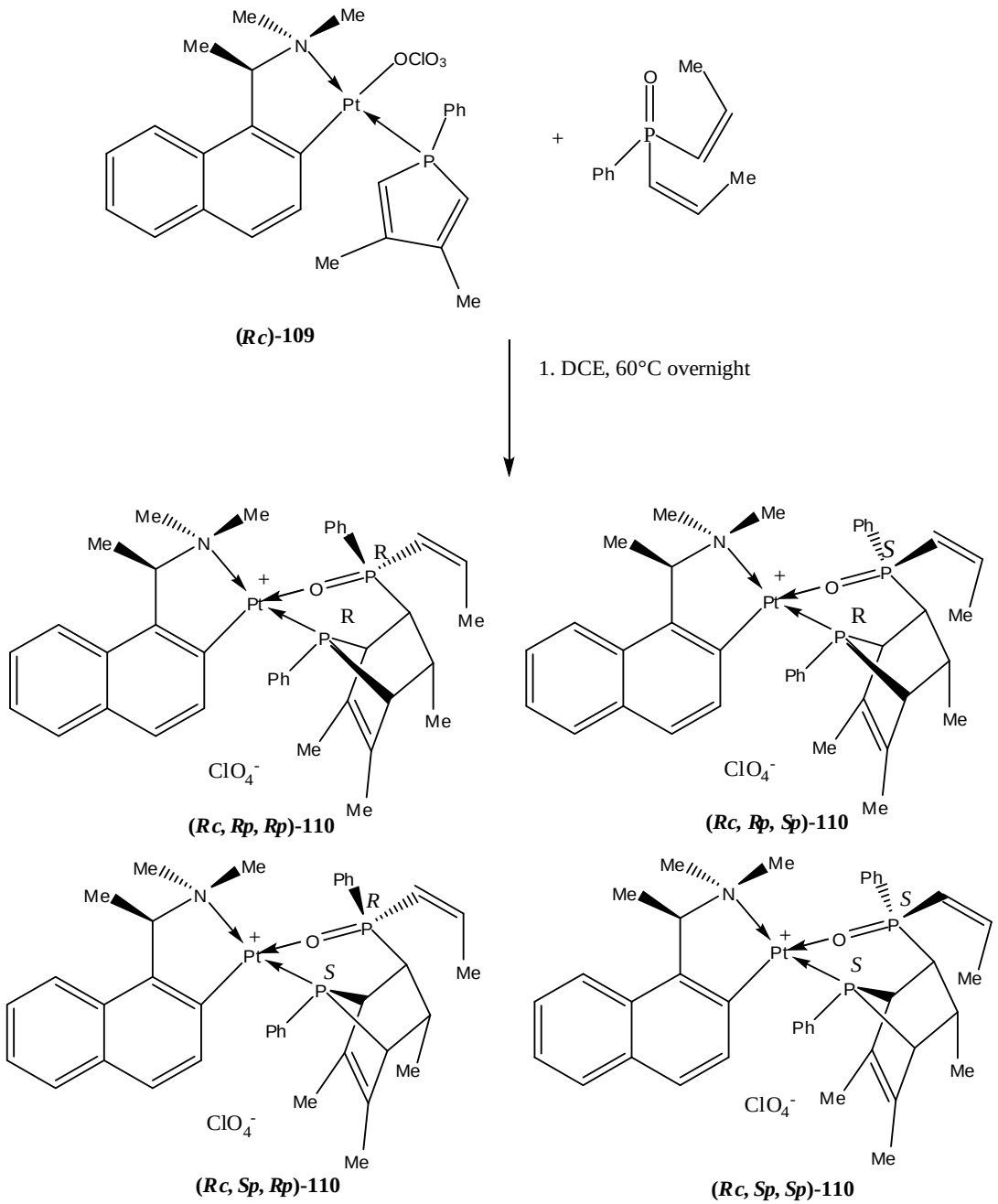


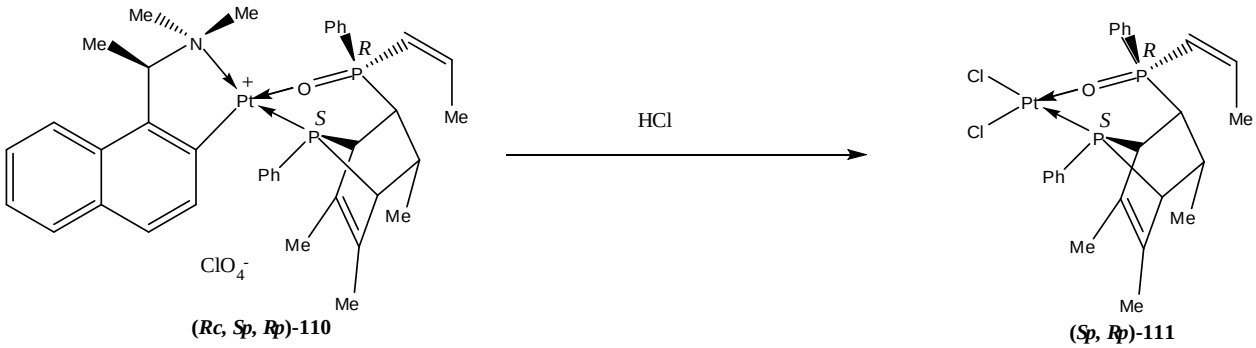
Figure 4.1 Molecular structure and absolute configuration of (*Sp,Rp*)-111


(Rc)-109
1. DCE, 60°C overnight
(Rc, Rp, Rp)-110
(Rc, Rp, Sp)-110
(Rc, Sp, Rp)-110
(Rc, Sp, Sp)-110

Scheme 4.2

Table 4.1 Selected bond lengths (Å) and angles (°) for (*Sp,Rp*)-111

Pt(1)-O(1)	2.051(5)	Pt(1)-P(2)	2.206(2)
Pt(1)-Cl(2)	2.273(1)	Pt(1)-Cl(1)	2.348(2)
C(1)-P(1)	1.775(7)	C(4)-P(1)	1.799(7)
O(1)-P(1)	1.520(6)	C(10)-P(1)	1.796(7)
C(13)-P(2)	1.840(7)	C(18)-P(2)	1.847(8)
C(19)-P(2)	1.820(8)	C(1)-C(2)	1.307(11)
O(1)-Pt(1)-P(2)	95.4(1)	O(1)-Pt(1)-Cl(2)	174.3(1)
P(2)-Pt(1)-Cl(2)	89.7(1)	O(1)-Pt(1)-Cl(1)	83.5(1)
P(2-Pt(1)-Cl(1)	175.1(1)	Cl(2)-Pt(1)-Cl(1)	91.6(1)
O(1)-P(1)-C(1)	109.1(4)	O(1)-P(1)-C(4)	110.4(3)
C(1)-P(1)-C(4)	108.2(3)	C(1)-P(1)-C(10)	107.7(4)
C(19)-P(2)-Pt(1)	117.0(3)	C(19)-P(2)-C(18)	110.3(4)
C(18)-P(2)-Pt(1)	116.8(2)	C(19)-P(2)-C(13)	106.9(3)



(*Rc, Sp, Rp*)-110 **(*Sp, Rp*)-111**

Scheme 4.3

4.2.2 Asymmetric Diels-Alder Reaction between DMPP and phenyldi[(*Z*)]prop-1-enyl]phosphine sulfide

Upon removal of the chloro ligand in (*Rc*)-**108** with $AgClO_4$, the resulting perchlorate complex (*Rc*)-**109** was treated with phenyldi[(*Z*)]prop-1-enyl]phosphine sulfide. The reaction mixture was heated at 60 °C in 1,2-dichloroethane for 30 days (Scheme 4.4). The $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture in $CDCl_3$ showed the presence of two pairs of singlets at δ 79.9 (J_{Pt-P} = 3631 Hz), 36.0 and 79.6 (J_{Pt-P} = 3654 Hz), 33.7 indicated the presence of two diastereomers. Unfortunately these cycloadducts could not be separated efficiently from either column chromatography or fractional crystallisation. Thus the mixture was then treated with concentrated hydrochloric acid to remove the chiral napthylamine complex. The mixture was recrystallised with dichloromethane/diethyl ether to produce the yellow crystals of the optically pure (*Sp*,*Sp*)-**113**.

4.2.2.1 X-ray crystal Diffraction Analysis of (*Sp*,*Sp*)-113

The $^{31}P\{^1H\}$ NMR spectrum of the crystals showed signals at δ 76.9 (J_{Pt-P} = 3631 Hz) and 33.7 The molecular structure and absolute configurations of the recrystallised (*Sp*,*Sp*)-**113** were established by single crystal X-ray crystallographic analysis (Figure 4.2). The analysis confirmed that the desired cycloadduct had formed via the exo-cycloaddition reaction. Coordination to the platinum metal centre is via the bridgehead phosphorus and the sulfur atoms of the PhP=S moiety. The stronger *trans* influence of the phosphorus atom versus the sulfur atom is evident in the difference of the Pt-Cl bond lengths. The Pt-Cl bond distance *trans* to the phosphorus atom (2.372(1) **Å** is longer than the Pt-Cl bond distances trans to the sulfur atom (2.327(1) **Å**. The geometry at the platinum centre is distorted square planar with angles at the

platinum in the range of 85.8(1) – 92.4(1) and 177.1(1)- 178.1(1) °. Selected bond lengths and angles are listed in Table 4.2.

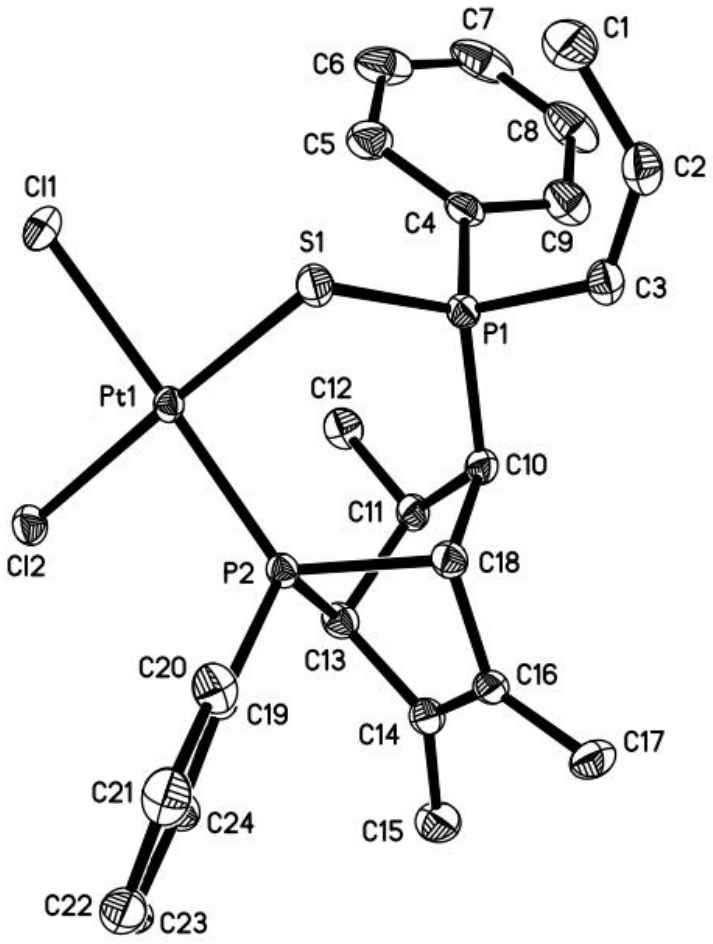


Figure 4.2 Molecular structure and absolute configuration of (*Sp,Sp*)-113

Table 4.2 Selected bond lengths (Å) and angles (˚) for (*Sp,Sp*)-113

Pt(1)-S(1)	2.289(1)	Pt(1)-P(2)	2.191(1)

Pt(1)-Cl(2)	2.327(1)	Pt(1)-Cl(1)	2.372(1)
C(3)-P(1)	1.786(3)	C(4)-P(1)	1.807(3)
S(1)-P(1)	2.024(1)	C(10)-P(1)	1.832(3)
C(13)-P(2)	1.841(3)	C(18)-P(2)	1.836(3)
C(19)-P(2)	1.800(3)	C(2)-C(3)	1.333(5)
S(1)-Pt(1)-P(2)	95.4(1)	S(1)-Pt(1)-Cl(2)	177.1(3)
P(2)-Pt(1)-Cl(2)	85.8(3)	S(1)-Pt(1)-Cl(1)	89.5(1)
P(2)-Pt(1)-Cl(1)	178.1(1)	Cl(2)-Pt(1)-Cl(1)	92.4(1)
S(1)-P(1)-C(3)	107.9(1)	S(1)-P(1)-C(4)	110.4(3)
C(1)-P(1)-C(4)	108.2(3)	C(1)-P(1)-C(10)	113.5(1)
C(19)-P(2)-Pt(1)	114.7(1)	C(19)-P(2)-C(18)	107.0(1)
C(18)-P(2)-Pt(1)	120.0(1)	C(19)-P(2)-C(13)	111.9(1)

4.2.2.2 Liberation of the (*Rp,Sp*)-114

The optically active ligand (*Rp,Sp*)-**114** can be stereospecifically liberated from complex (*Sp,Sp*)-**113** by treatment of the dichloro complex with aquoues potassium cynanide at room temperature. The liberated (*Rp,Sp*)-**114** was obtained as a colourless oil in 79% yield with [α] = 77 (c 0.1, DMSO). The $^{31}P\{^{1}H\}$ NMR spectrum of the free ligand in $CDCl_3$ exhibited two singlets at 74.9 and 32.3 with the low field chemical shift conforming the retention of the exo-syn stereochemistry. It is important to note that the apparent inversion of configuration that occurs at the tertiary phosphorus stereogenic centre when the ligand is liberated from the platinum metal is a consequence of the Cahn-Ingold-Prelog (CIP) sequence rule.[73] The optical purity of (*Rp,Sp*)-**114** was confirmed by the quantitative re-preparation of the free ligand and

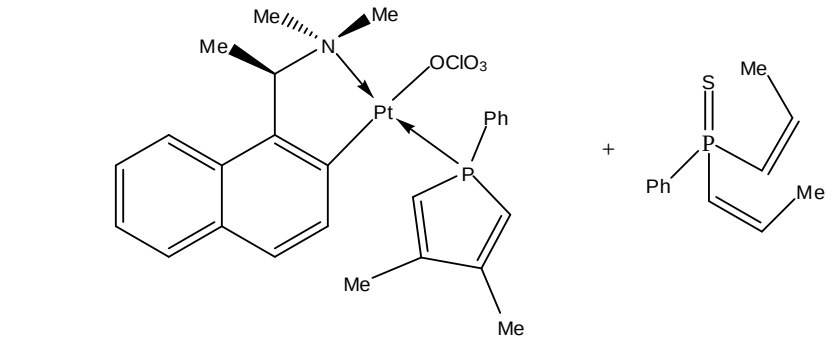
(*Rc*)-**49**, the 121 MHz ^{31}P NMR spectrum of the crude product showed signals at δ 79.9 (J_{Pt-P} = 3631 Hz), 36.0. These NMR signals are identical with those recorded from the cycloaddition reaction. In order to establish the identity of the other diastereomer, free ligand (*Rp,Sp*)-**114** was coordinated to the equally accessible (*Sc*)-**49** to form the diastereomic complex (*Sc,Sp,Sp*)-**112** (Scheme 4.5). The NMR signals were identical to those recorded for the enantiomeric counterpart, (*Rc,Rp,Rp*)-**112,** which was was generated originally from the Diels-Alder reaction.

4.3 Conclusions

The asymmetric Diels-Alder reaction between DMPP and phenyldi[(*Z*)]prop-1-enyl]phosphine oxide and phenyldi[(*Z*)]prop-1-enyl]phosphine sulphide showed poor stereoselectivity with two isomers being formed in almost equal yield. The rate of this reaction in comparison to phenyldi[(*Z*)]prop-1-enyl]phosphine is much slower.

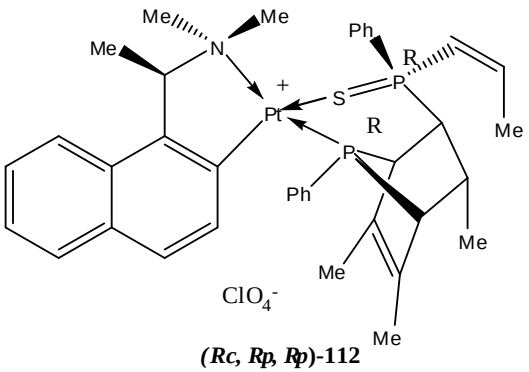
The cycloaddition reaction between DMPP and phenyldi[(*Z*)]prop-1-enyl]phosphine oxide formed two diastereomeric mixtures and these could not be separated via column chromatography or fractional crystallisation. The corresponding dichloro complexes were isolated in racemic forms.

The cycloaddition reaction between DMPP and phenyldi[(*Z*)]prop-1-enyl]phosphine sulphide also formed two diastereomeric mixtures and similarly could not be separated via column chromatography or fractional crystallisation. However, the corresponding dichloro complexes could be separated through fractional crystallisation to give (*Sp,Sp*)-**111.** The optically active ligand (*Rp,Sp*)-**112** can be stereospecifically liberated from complex (*Sp,Sp*)-**111** by treatment of the dichloro complex with aqueous potassium cyanide at room temperature.

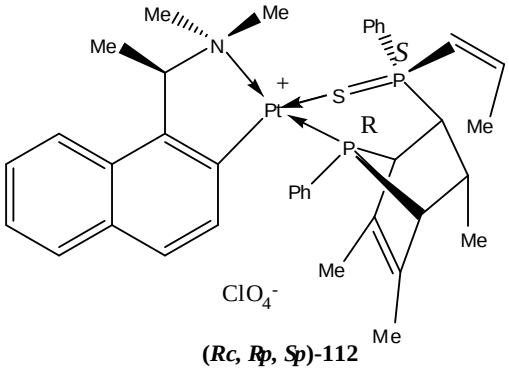


(*Rc*)-107

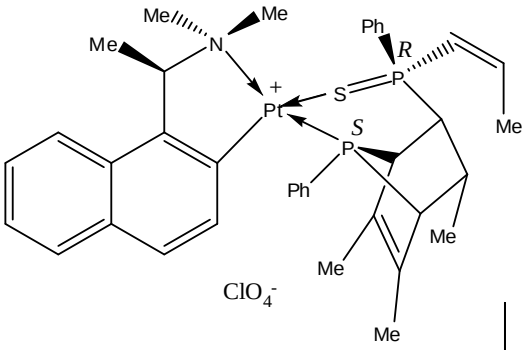
1. DCE, 60°C



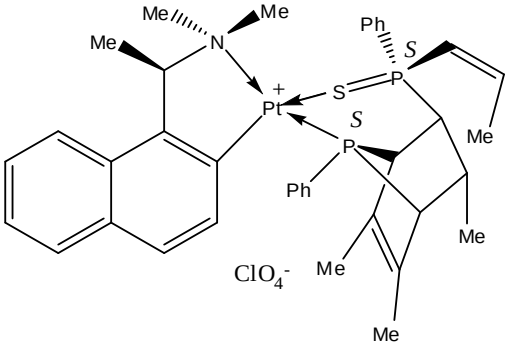
***(Rc, Rp, Rp)*-112**



(*Rc, Rp, Sp*)-112

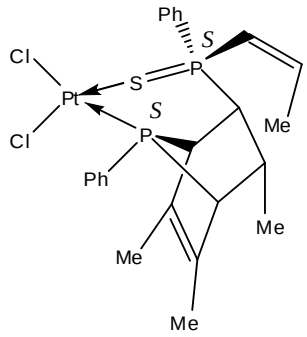


***(Rc, Sp, Rp)*-112**



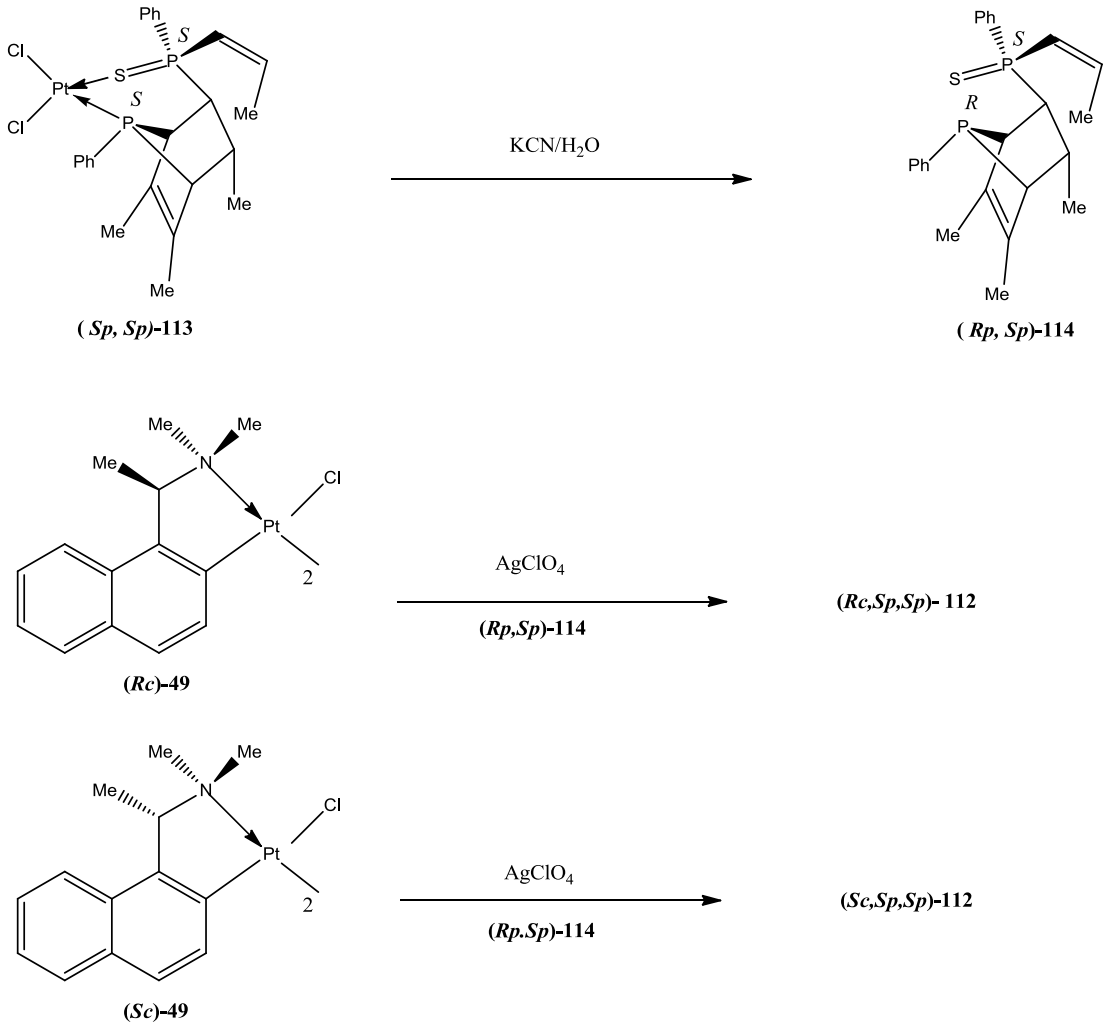
(*Rc, Sp, Sp*)-112

HCl



(*Sp, Sp*)-113

Scheme 4.4



Scheme 4.5

4.4 Experimental

General: the same to the chapter 4.4. (*Rc*)-**49**[60], phenyldi[(*Z*)]prop-1-enyl]phosphine oxide[74] and phenyldi[(*Z*)]prop-1-enyl]phosphine sulphide[74] were prepared following the literature procedures.

Synthesis of Dichloro[6-phenyl(*Z*)prop-1-enylphosphino oxide - 2,3,5-trimethyl -7- phenyl -7- phosphabicyclo[2.2.1]hept-5-ene] platinum (II) (*Sp,Rp*)-111

A solution of (*Rc*)-**108** (0.50g, 0.81 mmol) was stirred for 2 h in the presence of a solution of silver perchlorate 0.50g, 2.43 mmol) in water. The colourless organic layer after the removal of AgCl, and dried ($MgSO_4$) was treated with phenyldi[(*Z*)]prop-1-enyl]phosphine oxide (0.167 g, 0.83 mmol). The mixture was heated at 60 ˚C in dichloroethane for 30 d. Removal of solvent gave the mixture as white solid. The mixture was then redissolved in dichloromethane and was treated with hydrochloric acid overnight. The resultant mixture was then washed with water (3 X 50 ml), and the organic layer was dried with magnesium sulphate. Upon removal of the solvents a pale yellow solid was obtained. Recrystallisation from dichloromethane/diethyl ether afforded pale yellow crystals (0.14 g, 25 %). Mp 290 ˚C. $C_{24}H_{28}Cl_2OP_2Pt$ (660.39) calc C 43.6, H 4.2. found C 43.1, H 4.0 $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 74.4 (s, J_{Pt-P} = 3800 Hz, 1 P), 26.1 (s, 1 P). ^1H NMR (DMSO-d_6): 1.46 (s, 3H, C=C*Me*), 1.56 (s, 3H, C=C*Me*), 1.58 (d, 3H, *J* = 7.3 Hz CH*Me*), 1.88 (d, 3H, *J* = 6.5 Hz), 2.42 (m, 1H, PhPOC*H*), 2.69 (m, 1H, PhPOCHC*H*Me), 3.40 (m, 1H, PhPC*H*), 3.82 (m, 1H, PhPC*H*), 6.23 (m, 1H, PC*H*=CHMe), 6.54 (m, 1H, PCH=C*H*Me), 7.48-7.95 (m, 10H, aromatics).

Synthesis of Dichloro[6-phenyl(*Z*)prop-1-enylphosphino sulfide - 2,3,5-trimethyl -7- phenyl -7- phosphabicyclo[2.2.1]hept-5-ene] platinum (II) (*Sp,Sp*)-114

A solution of (*Rc*)-**108** (0.50g, 0.81 mmol) was stirred for 2 h in the presence of a solution of silver perchlorate 0.50g, 2.43 mmol) in water. The colourless organic layer after the removal of AgCl, and dried ($MgSO_4$) was treated with phenyldi[(*Z*)]prop-1-enyl]phosphine sulfide (0.184 g, 0.83 mmol). The mixture was heated at 60 ˚C in

dichloroethane for 30 d. Removal of solvent gave the mixture as white solid. The mixture was then redissolved in dichloromethane and was treated with hydrochloric acid overnight. The resultant mixture was then washed with water (3 X 50 ml), and the organic layer was dried with magnesium sulphate. Upon removal of the solvents a pale yellow solid was obtained. Recrystallisation from dichloromethane/diethyl ether afforded pale yellow crystals (0.15 g, 27 %). Mp 292 ˚C. $C_{24}H_{28}Cl_2SP_2Pt$ (676.10) calc C 42.6, H 4.1. found C 42.1, H 4.0 $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 79.9 (s, J_{Pt-P} = 3631Hz, 1 P), 33.7 (s, 1 P). ^1H NMR (DMSO-d_6): 1.42 (s, 3H, C=C*Me*), 1.53 (s, 3H, C=C*Me*), 1.58 (d, 3H, *J* = 7.3 Hz CH*Me*), 1.88 (d, 3H, *J* = 6.5 Hz), 2.38 (m, 1H, PhPSC*H*), 2.55 (m, 1H, PhPSCHC*H*Me), 3.40 (m, 1H, PhPC*H*), 3.82 (m, 1H, PhPC*H*), 6.20 (m, 1H, PC*H*=CHMe), 6.50 (m, 1H, PCH=C*H*Me), 7.48-7.95 (m, 10H, aromatics).

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Appendices

Table A1 Crystallographic data for (*Rc*,*Rc*)-67

Empirical formula	C44 H47 As Cl4 N2 Pd2
Formula weight	1033.36

Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P1
Unit cell dimensions	a = 12.5539(3) Å □= 108.4000(10)°. b = 12.9506(3) Å □=91.7450(10)°. c = 15.2541(3) Å □ = 115.0210(10)°.
Volume	2093.26(8) $Å^3$
Z	2
Density (calculated)	1.639 Mg/m^3
Absorption coefficient	1.933 mm^{-1}
F(000)	1036
Crystal size	0.30 x 0.22 x 0.20 mm^3
Theta range for data collection	1.43 to 26.50°.
Index ranges	-15<=h<=15, -16<=k<=15, -19<=l<=19
Reflections collected	44052
Independent reflections	16049 [R(int) = 0.0406]
Completeness to theta = 26.50°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6985 and 0.5948
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	16049 / 3 / 969
Goodness-of-fit on F^2	1.149
Final R indices [I>2sigma(I)]	R1 = 0.0259, wR2 = 0.0679
R indices (all data)	R1 = 0.0303, wR2 = 0.0917
Absolute structure parameter	0.018(8)
Largest diff. peak and hole	0.680 and -1.104 $e.Å^{-3}$

Table A2 Crystallographic data for (*Rc*,*Rc*)-69

Empirical formula	C44 H47 As Cl4 N2 Pd Pt
Formula weight	1122.05

Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P1
Unit cell dimensions	a = 12.5619(7) Å □= 108.385(3)°.
	b = 12.9392(7) Å □= 91.625(3)°.
	c = 15.2228(8) Å □ = 114.880(3)°.
Volume	2092.5(2) $Å^3$
Z	2
Density (calculated)	1.781 Mg/m^3
Absorption coefficient	4.843 mm^{-1}
F(000)	1100
Crystal size	0.32 x 0.14 x 0.08 mm^3
Theta range for data collection	1.82 to 35.44°.
Index ranges	-20<=h<=20, -21<=k<=20, -24<=l<=22
Reflections collected	97958
Independent reflections	34815 [R(int) = 0.0446]
Completeness to theta = 34.00°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6980 and 0.3064
Refinement method	Full-matrix-block least-squares on F^2
Data / restraints / parameters	34815 / 3 / 969
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0366, wR2 = 0.0808
R indices (all data)	R1 = 0.0573, wR2 = 0.1022
Absolute structure parameter	-0.005(3)
Largest diff. peak and hole	3.332 and -3.561 $e.Å^{-3}$

Table A3 Crystallographic data for (*Rc*,*Rc*)-71

Empirical formula	C35 H41 As Cl2 N2 Pd2	
Formula weight	848.32	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 13.0336(3) Å	□= 90°.
	b = 13.1559(3) Å	□= 90°.
	c = 20.0112(6) Å	□ = 90°.
Volume	3431.30(15) $Å^3$	
Z	4	
Density (calculated)	1.642 Mg/m^3	
Absorption coefficient	2.187 mm^{-1}	
F(000)	1696	
Crystal size	0.24 x 0.14 x 0.10 mm^3	
Theta range for data collection	1.85 to 30.53°.	
Index ranges	-15<=h<=18, -18<=k<=16, -27<=l<=28	
Reflections collected	61523	
Independent reflections	10421 [R(int) = 0.0431]	
Completeness to theta = 30.53°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8109 and 0.6218	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10421 / 0 / 386	
Goodness-of-fit on F^2	1.109	
Final R indices [I>2sigma(I)]	R1 = 0.0321, wR2 = 0.0684	
R indices (all data)	R1 = 0.0484, wR2 = 0.0819	
Absolute structure parameter	0.015(8)	
Largest diff. peak and hole	0.819 and -1.125 e.$Å^{-3}$	

Table A4 Crystallographic data for (*Rc*,*Rc*)-74

Empirical formula	C_{43} H_{45} As Cl_2 N_2 Pd_2, CH_2Cl_2
Formula weight	975.45
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 10.02820(10) Å □= 90°.
	b = 18.8206(3) Å □= 90°.
	c = 22.8781(4) Å □ = 90°.
Volume	4317.94(11) $Å^3$
Z	4
Density (calculated)	1.501 Mg/m^3
Absorption coefficient	1.457 mm^{-1}
F(000)	1984
Crystal size	0.40 x 0.30 x 0.10 mm^3
Theta range for data collection	1.78 to 34.09°.
Index ranges	-10<=h<=15, -29<=k<=29, -36<=l<=30
Reflections collected	56519
Independent reflections	17617 [R(int) = 0.0376]
Completeness to theta = 34.09°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8680 and 0.5933
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	17617 / 0 / 500
Goodness-of-fit on F^2	1.079
Final R indices [I>2sigma(I)]	R1 = 0.0427, wR2 = 0.1075
R indices (all data)	R1 = 0.0622, wR2 = 0.1234
Absolute structure parameter	0.032(8)
Largest diff. peak and hole	1.939 and -1.456 $e.Å^{-3}$

Table A5 Crystallographic data for (*Rc*,*Rc*)-79

Empirical formula	C42.33 H44 As Cl N1.67 O5 P Pd	
Formula weight	903.87	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 16.3768(4) Å	□= 90°.
	b = 21.2060(6) Å	□= 90°.
	c = 33.9413(8) Å	□ = 90°.
Volume	11787.4(5) $Å^3$	
Z	12	
Density (calculated)	1.528 Mg/m^3	
Absorption coefficient	1.464 mm^{-1}	
F(000)	5528	
Crystal size	0.40 x 0.24 x 0.20 mm^3	
Theta range for data collection	1.54 to 36.32°.	
Index ranges	-27<=h<=27, -35<=k<=35, -38<=l<=56	
Reflections collected	158839	
Independent reflections	56033 [R(int) = 0.0581]	
Completeness to theta = 36.32°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7584 and 0.5921	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	56033 / 0 / 1443	
Goodness-of-fit on F^2	1.014	
Final R indices [I>2sigma(I)]	R1 = 0.0441, wR2 = 0.0831	
R indices (all data)	R1 = 0.0740, wR2 = 0.1020	
Absolute structure parameter	0.002(4)	
Largest diff. peak and hole	0.747 and -1.475 $e.Å^{-3}$	

Table A6 Crystallographic data for (*Rc*)-80

Empirical formula	C41 H40 As Cl N O4 P Pd	
Formula weight	858.48	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 8.2780(4) Å	□= 90°.
	b = 12.7264(8) Å	□= 90°.
	c = 35.996(2) Å	□ = 90°.
Volume	3792.1(4) $Å^3$	
Z	4	
Density (calculated)	1.504 Mg/m^3	
Absorption coefficient	1.510 mm^{-1}	
F(000)	1744	
Crystal size	0.40 x 0.10 x 0.04 mm^3	
Theta range for data collection	1.70 to 26.35°.	
Index ranges	-6<=h<=10, -15<=k<=14, -43<=l<=44	
Reflections collected	22948	
Independent reflections	7611 [R(int) = 0.0571]	
Completeness to theta = 26.35°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9421 and 0.5834	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7611 / 214 / 494	
Goodness-of-fit on F^2	1.073	
Final R indices [I>2sigma(I)]	R1 = 0.0506, wR2 = 0.1168	
R indices (all data)	R1 = 0.0695, wR2 = 0.1410	
Absolute structure parameter	0.008(17)	
Largest diff. peak and hole	1.449 and -0.980 $e.Å^{-3}$	

Table A7 Crystallographic data for (*Rc*,*Rc*)-87

Empirical formula	C42.50 H45 As Cl2 N O5 P Pd
Formula weight	932.99
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2
Unit cell dimensions	a = 25.2257(9) Å □= 90°.
	b = 16.4446(5) Å □= 122.172(2)°.
	c = 23.2164(7) Å □ = 90°.
Volume	8152.0(5) Å^3
Z	8
Density (calculated)	1.520 Mg/m^3
Absorption coefficient	1.476 mm^{-1}
F(000)	3800
Crystal size	0.40 x 0.40 x 0.20 mm^3
Theta range for data collection	1.93 to 31.02°.
Index ranges	-36<=h<=36, -22<=k<=23, -33<=l<=33
Reflections collected	62654
Independent reflections	23026 [R(int) = 0.0311]
Completeness to theta = 31.02°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7567 and 0.5897
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	23026 / 956 / 1296
Goodness-of-fit on F^2	1.066
Final R indices [I>2sigma(I)]	R1 = 0.0325, wR2 = 0.0762
R indices (all data)	R1 = 0.0435, wR2 = 0.0857
Absolute structure parameter	0.001(5)
Largest diff. peak and hole	1.839 and -1.117 e.Å^{-3}

Table A8 Crystallographic data for (*Rc*,*Rc*)-93

Empirical formula	C45 H48 As Cl5 N O6 P Pd
Formula weight	1088.38
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 12.5299(4) Å □= 90°.
	b = 19.0521(7) Å □= 90°.
	c = 19.3619(6) Å □ = 90°.
Volume	4622.1(3) $Å^3$
Z	4
Density (calculated)	1.564 Mg/m^3
Absorption coefficient	1.483 mm^{-1}
F(000)	2208
Crystal size	0.40 x 0.30 x 0.30 mm^3
Theta range for data collection	2.36 to 31.08°.
Index ranges	-17<=h<=18, -27<=k<=26, -28<=l<=28
Reflections collected	76019
Independent reflections	14735 [R(int) = 0.0371]
Completeness to theta = 31.08°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6645 and 0.5883
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14735 / 0 / 545
Goodness-of-fit on F^2	1.007
Final R indices [I>2sigma(I)]	R1 = 0.0238, wR2 = 0.0481
R indices (all data)	R1 = 0.0282, wR2 = 0.0492
Absolute structure parameter	0.002(3)
Largest diff. peak and hole	0.429 and -0.422 $e.Å^{-3}$

Table A9 Crystallographic data for (*Sc*)-97

Empirical formula	C29 H28 As Cl2 O P Pd	
Formula weight	675.70	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.1448(5) Å	□= 90°.
	b = 14.3933(6) Å	□= 90°.
	c = 18.2105(8) Å	□ = 90°.
Volume	2659.0(2) $Å^3$	
Z	4	
Density (calculated)	1.688 Mg/m^3	
Absorption coefficient	2.216 mm^{-1}	
F(000)	1352	
Crystal size	0.30 x 0.16 x 0.08 mm^3	
Theta range for data collection	1.80 to 30.59°.	
Index ranges	-14<=h<=13, -20<=k<=16, -26<=l<=26	
Reflections collected	27325	
Independent reflections	8138 [R(int) = 0.0478]	
Completeness to theta = 30.59°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8427 and 0.5561	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8138 / 0 / 317	
Goodness-of-fit on F^2	1.099	
Final R indices [I>2sigma(I)]	R1 = 0.0346, wR2 = 0.0777	
R indices (all data)	R1 = 0.0437, wR2 = 0.0922	
Absolute structure parameter	0.031(10)	
Largest diff. peak and hole	1.691 and -1.146 $e.Å^{-3}$	

Table A10 Crystallographic data for (*Rc*,*Rc*)-103

Empirical formula	C43 H47 As Cl N2 O4 P Pd
Formula weight	903.57
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 9.4486(3) Å □= 90°.
	b = 19.1907(7) Å □= 90°.
	c = 22.5887(8) Å □ = 90°.
Volume	4095.9(2) $Å^3$
Z	4
Density (calculated)	1.465 Mg/m^3
Absorption coefficient	1.402 mm^{-1}
F(000)	1848
Crystal size	0.40 x 0.30 x 0.14 mm^3
Theta range for data collection	2.09 to 31.06°.
Index ranges	-13<=h<=13, -26<=k<=27, -32<=l<=32
Reflections collected	62216
Independent reflections	13065 [R(int) = 0.0571]
Completeness to theta = 31.06°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8278 and 0.6039
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13065 / 154 / 529
Goodness-of-fit on F^2	1.072
Final R indices [I>2sigma(I)]	R1 = 0.0338, wR2 = 0.0761
R indices (all data)	R1 = 0.0427, wR2 = 0.0877
Absolute structure parameter	-0.006(7)
Largest diff. peak and hole	0.727 and -0.898 $e.Å^{-3}$

Table A11 Crystallographic data for (*Sp,Rp*)-111

Empirical formula	C24 H28 Cl2 O P2 Pt
Formula weight	660.39
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)
Unit cell dimensions	a = 10.2697(3) Å □= 90°.
	b = 16.0568(5) Å □= 100.6530(10)°.
	c = 15.0084(4) Å □ = 90°.
Volume	2432.21(12) $Å^3$
Z	4
Density (calculated)	1.803 Mg/m^3
Absorption coefficient	6.135 mm^{-1}
F(000)	1288
Crystal size	0.32 x 0.18 x 0.16 mm^3
Theta range for data collection	1.87 to 31.09°.
Index ranges	-14<=h<=14, -22<=k<=23, -21<=l<=20
Reflections collected	29192
Independent reflections	13639 [R(int) = 0.0299]
Completeness to theta = 31.09°	98.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4402 and 0.2442
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13639 / 19 / 549
Goodness-of-fit on F^2	1.169
Final R indices [I>2sigma(I)]	R1 = 0.0343, wR2 = 0.0957
R indices (all data)	R1 = 0.0392, wR2 = 0.1080
Absolute structure parameter	0.016(6)
Largest diff. peak and hole	3.620 and -1.738 e.$Å^{-3}$

Table A12 Crystallographic data for (*Sp,Rp*)-113

Empirical formula	C25 H30 Cl4 P2 Pt S
Formula weight	761.38
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 9.15050(10) Å □= 90°.
	b = 19.0373(3) Å □= 107.9290(10)°.
	c = 17.7411(3) Å □ = 90°.
Volume	2940.43(8) $Å^3$
Z	4
Density (calculated)	1.720 Mg/m^3
Absorption coefficient	5.328 mm^{-1}
F(000)	1488
Crystal size	0.40 x 0.10 x 0.10 mm^3
Theta range for data collection	2.14 to 31.09°.
Index ranges	-13<=h<=12, -27<=k<=27, -25<=l<=25
Reflections collected	41786
Independent reflections	9437 [R(int) = 0.0406]
Completeness to theta = 31.09°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6178 and 0.2244
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9437 / 0 / 275
Goodness-of-fit on F^2	1.096
Final R indices [I>2sigma(I)]	R1 = 0.0277, wR2 = 0.0710
R indices (all data)	R1 = 0.0378, wR2 = 0.0740
Largest diff. peak and hole	1.590 and -1.278 $e.Å^{-3}$